

Electronic Supplementary Information

**Synthesis and reactivity of thiolate-bridged multi-iron complexes
supported by cyclic (alkyl)(amino)carbene**

**Yanpeng Zhang,^a Tao Mei,^a Dawei Yang,^{*,a} Yixin Zhang,^a Baomin Wang^a and
Jingping Qu^{*,a,b}**

*^aState Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116024,
P. R. China*

*^bKey Laboratory for Advanced Materials, East China University of Science and Technology,
Shanghai 200237, P. R. China*

*E-mail: qujp@dlut.edu.cn
yangdw@dlut.edu.cn

Contents:

<i>Table S1.</i> Crystallographic data for 1 and 2	S3
<i>Table S2.</i> Crystallographic data for 3 •2CH ₂ Cl ₂ and 4	S4
<i>Table S3.</i> Crystallographic data for 5 and 6	S5
<i>Figure S1.</i> ORTEP diagram of 1	S6
<i>Table S4.</i> Selected bond distances (Å) and bond angles (°) for 1	S6
<i>Figure S2.</i> ORTEP diagram of 2	S7
<i>Table S5.</i> Selected bond distances (Å) and bond angles (°) for 2	S7
<i>Figure S3.</i> ORTEP diagram of 3 •2CH ₂ Cl ₂	S8
<i>Table S6.</i> Selected bond distances (Å) and bond angles (°) for 3 •2CH ₂ Cl ₂	S8
<i>Figure S4.</i> ORTEP diagram of 4	S9
<i>Table S7.</i> Selected bond distances (Å) and bond angles (°) for 4	S9
<i>Figure S5.</i> ORTEP diagram of 5	S10
<i>Table S8.</i> Selected bond distances (Å) and bond angles (°) for 5	S10
<i>Figure S6.</i> ORTEP diagram of 6	S11
<i>Table S9.</i> Selected bond distances (Å) and bond angles (°) for 6	S11
<i>Figure S7.</i> The ¹ H NMR spectrum of 1 in THF-d ₈	S12
<i>Figure S8.</i> The ¹ H NMR spectrum of 2 in THF-d ₈	S12
<i>Figure S9.</i> The ¹ H NMR spectrum of 3 in THF-d ₈	S13
<i>Figure S10.</i> The ¹ H NMR spectrum of 4 in THF-d ₈	S13
<i>Figure S11.</i> The ¹ H NMR spectrum of 5 in CD ₂ Cl ₂	S14
<i>Figure S12.</i> The ¹ H NMR spectrum of 6 in THF-d ₈	S14
<i>Figure S13.</i> The ¹ H NMR spectrum of 7 in THF-d ₈	S15
<i>Figure S14.</i> The IR (KBr) spectrum of 1	S15
<i>Figure S15.</i> The IR (KBr) spectrum of 2	S16
<i>Figure S16.</i> The IR (KBr) spectrum of 3	S16
<i>Figure S17.</i> The IR (KBr) spectrum of 4	S17
<i>Figure S18.</i> The IR (KBr) spectrum of 5	S17
<i>Figure S19.</i> The IR (KBr) spectrum of 6	S18
<i>Figure S20.</i> The IR (KBr) spectrum of 7	S18

Table S1. Crystallographic data for **1** and **2**

	1	2
Formula	C ₄₀ H ₆₂ Br ₄ Fe ₂ N ₂	C ₄₀ H ₆₂ Cl ₄ Fe ₂ N ₂
Formula weight	1002.26	824.42
Crystal dimensions (mm ³)	0.32 × 0.31 × 0.22	0.31 × 0.27 × 0.22
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/n	P2(1)/n
a (Å)	9.2767(2)	9.1376(11)
b (Å)	14.5310(4)	14.5702(17)
c (Å)	15.8281(4)	15.7911(18)
α (°)	90.00	90.00
β (°)	90.4710(10)	90.838(3)
γ (°)	90.00	90.00
Volume (Å ³)	2133.55(9)	2102.1(4)
Z	2	2
T (K)	173(2)	301(2)
D _{calcd} (g cm ⁻³)	1.560	1.302
μ (mm ⁻¹)	4.454	0.973
F (000)	1016	872
No. of rflns. collected	26713	12173
No. of indep. rflns. /R _{int}	3741 / 0.0275	3693 / 0.0606
No. of obsd. rflns. [I ₀ > 2σ(I ₀)]	3385	2271
Data / restraints / parameters	3741 / 0 / 217	3693 / 0 / 217
R ₁ / wR ₂ [I ₀ > 2σ(I ₀)]	0.0323 / 0.0917	0.0570 / 0.1539
R ₁ / wR ₂ (all data)	0.0363 / 0.0936	0.1048 / 0.1674
GOF (on F ²)	1.021	1.049
Largest diff. peak and hole (e Å ⁻³)	1.406 / -0.836	0.411 / -0.630
CCDC	1570137	1544295

Table S2. Crystallographic data for **3•2CH₂Cl₂** and **4**

	3•2CH₂Cl₂	4
Formula	C ₄₄ H ₇₂ Br ₂ Cl ₄ Fe ₂ N ₂ S ₂	C ₄₄ H ₇₂ Br ₂ Fe ₂ N ₂ S ₂
Formula weight	1106.48	964.68
Crystal dimensions (mm ³)	0.33 × 0.25 × 0.21	0.34 × 0.32 × 0.28
Crystal system	Orthorhombic	Triclinic
Space group	Pbca	P-1
a (Å)	10.487(4)	9.2020(7)
b (Å)	18.279(6)	10.7924(10)
c (Å)	28.035(10)	12.6760(10)
α (°)	90.00	85.581(4)
β (°)	90.00	72.995(4)
γ (°)	90.00	78.723(4)
Volume (Å ³)	5374(3)	1180.33(17)
Z	4	1
T (K)	300(2)	233(2)
D _{calcd} (g cm ⁻³)	1.367	1.357
μ (mm ⁻¹)	2.333	2.426
F (000)	2288	504
No. of rflns. collected	73129	24257
No. of indep. rflns. /R _{int}	4726 / 0.1075	4142 / 0.0575
No. of obsd. rflns. [I ₀ > 2σ(I ₀)]	3058	3017
Data / restraints / parameters	4726 / 0 / 253	4142 / 0 / 235
R ₁ / wR ₂ [I ₀ > 2σ(I ₀)]	0.0704 / 0.1950	0.0420 / 0.0900
R ₁ / wR ₂ (all data)	0.1171 / 0.2143	0.0725 / 0.0972
GOF (on F ²)	1.047	1.016
Largest diff. peak and hole (e Å ⁻³)	1.259 / -0.861	0.677 / -0.339
CCDC	1570135	1544296

Table S3. Crystallographic data for **5** and **6**

	5	6
Formula	C ₄₀ H ₆₃ Br ₃ Fe ₄ N ₂ S ₄	C ₄₂ H ₆₈ Fe ₂ N ₈ S ₂
Formula weight	1163.29	860.86
Crystal dimensions (mm ³)	0.33 × 0.26 × 0.21	0.29 × 0.26 × 0.21
Crystal system	Monoclinic	Triclinic
Space group	P2(1)	P-1
a (Å)	10.0062(10)	9.1221(7)
b (Å)	16.5247(16)	9.6527(8)
c (Å)	15.3223(15)	14.2111(11)
α (°)	90.00	91.2950(10)
β (°)	100.251(3)	104.5310(10)
γ (°)	90.00	110.9850(10)
Volume (Å ³)	2493.1(4)	1122.17(15)
Z	2	1
T (K)	304(2)	220(2)
D _{calcd} (g cm ⁻³)	1.550	1.274
μ (mm ⁻¹)	3.740	0.778
F (000)	1180	460
No. of rflns. collected	26133	19905
No. of indep. rflns. /R _{int}	8713 / 0.0457	4588 / 0.0402
No. of obsd. rflns. [I ₀ > 2σ(I ₀)]	7476	4104
Data / restraints / parameters	8713 / 1 / 479	4588 / 89 / 290
R ₁ / wR ₂ [I ₀ > 2σ(I ₀)]	0.0337 / 0.0766	0.0650 / 0.1594
R ₁ / wR ₂ (all data)	0.0442 / 0.0797	0.0712 / 0.1641
GOF (on F ²)	0.997	1.039
Largest diff. peak and hole (e Å ⁻³)	0.600 / -0.562	1.741 / -1.134
Flack parameter	0.127(7)	—
CCDC	1570210	1570141

Figure S1. ORTEP diagram of **1**

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

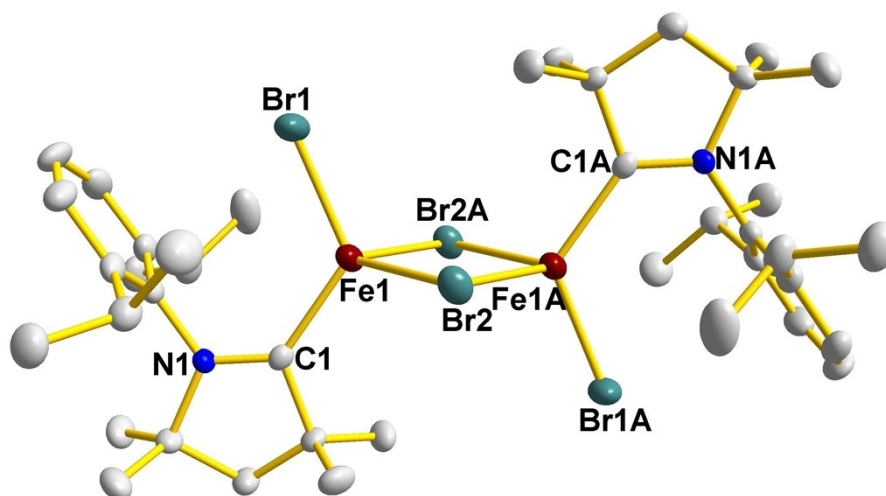


Table S4. Selected bond distances (Å) and bond angles (°) for **1**

Distances (Å)			
Fe1···Fe1A	3.432(8)	Fe1–C1	2.080(3)
Fe1–Br1	2.379(6)	Fe1–Br2	2.535(6)
Fe1–Br2A	2.526(7)	C1–N1	1.308(4)
Angles (°)			
Fe1–Br2–Fe1A	85.4(2)	Br2–Fe1–Br2A	94.6(2)
C1–Fe1–Br1	122.3(8)	N1–C1–Fe1	127.3(2)
Torsion angles (°)			
Fe1–Br2Br2A–Fe1A	0.0(2)	Br2–Fe1Fe1A–Br2A	0.0(2)
C1–Fe1Br1–Fe1A	0.4(6)		
Dihedral angle (°)			
C1Br1Fe1–Fe1Br2Br2A	88.5(4)		

Figure S2. ORTEP diagram of **2**

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

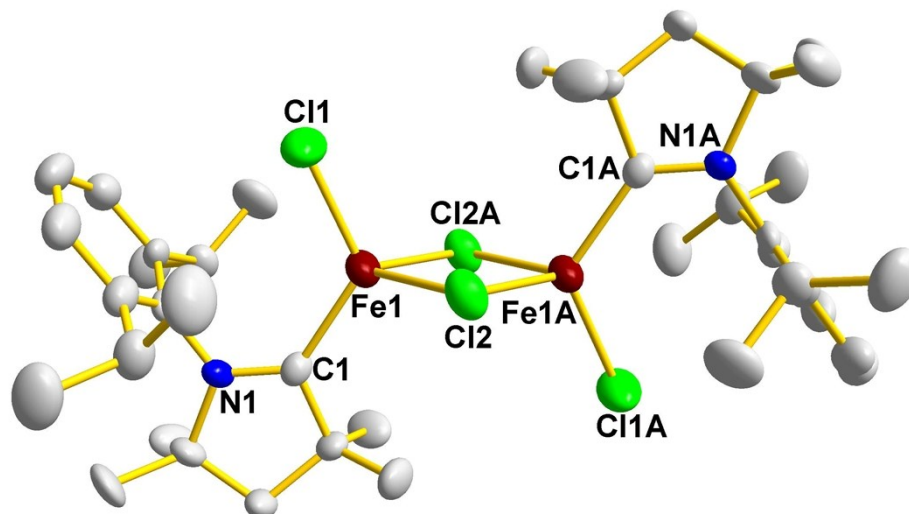


Table S5. Selected bond distances (Å) and bond angles (°) for **2**

Distances (Å)			
Fe1···Fe1A	3.355(3)	Fe1–Cl1	2.083(4)
Fe1–Cl1	2.224(2)	Fe1–Cl2	2.381(1)
Fe1–Cl2A	2.414(3)	C1–N1	1.321(5)
Angles (°)			
Fe1–Cl2–Fe1A	88.8(4)	Cl2–Fe1–Cl2A	91.2(4)
C1–Fe1–Cl1	121.8(1)	N1–C1–Fe1	127.3(3)
Torsion angles (°)			
Fe1–Cl2Cl2A–Fe1A	0.0(0)	Cl2–Fe1Fe1A–Cl2A	0.0(0)
C1–Fe1Cl1–Fe1A	3.0(7)		
Dihedral angle (°)			
C1Cl1Fe1–Fe1Cl2Cl2A	88.3(7)		

Figure S3. ORTEP diagram of **3**•2CH₂Cl₂

Two CH₂Cl₂ molecules and all hydrogen atoms are omitted for clarity (thermal ellipsoids shown at 50% probability).

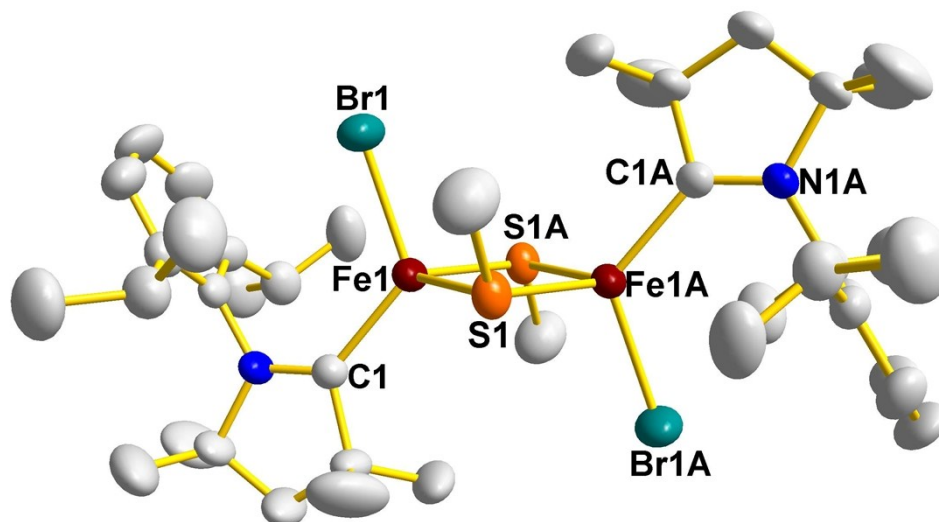


Table S6. Selected bond distances (Å) and bond angles (°) for **3**•2CH₂Cl₂

Distances (Å)			
Fe1···Fe1A	3.166(2)	Fe1–C1	2.067(6)
Fe1–Br1	2.400(1)	Fe1–S1	2.407(2)
Fe1–S1A	2.388(2)	C1–N1	1.305(8)
Angles (°)			
Fe1–S1–Fe1A	82.6(7)	S1–Fe1–S1A	97.4(7)
C1–Fe1–Br1	120.3(2)	N1–C1–Fe1	129.1(4)
Torsion angles (°)			
Fe1–S1S1A–Fe1A	0.0(0)	S1–Fe1Fe1A–S1A	0.0(0)
C1–Fe1Br1–Fe1A	3.8(2)		
Dihedral angle (°)			
C1Br1Fe1–Fe1S1S1A	84.5(8)		

Figure S4. ORTEP diagram of **4**

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

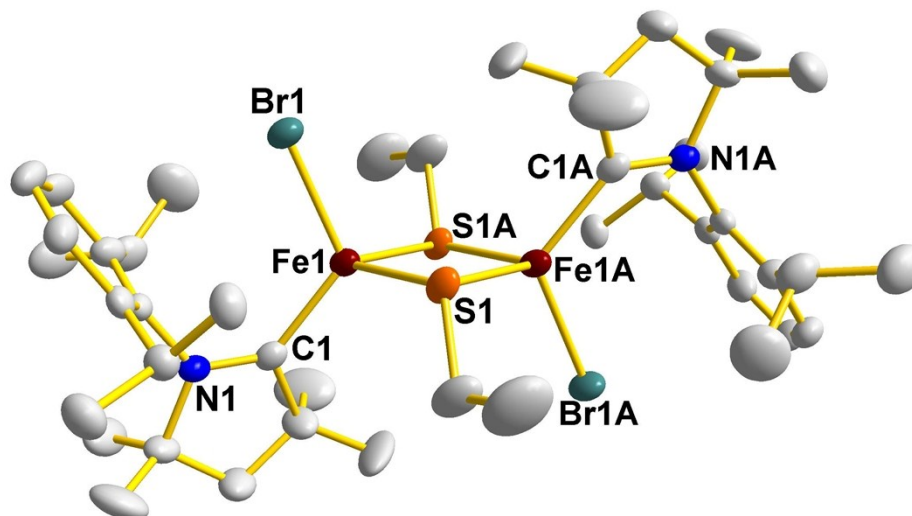


Table S7. Selected bond distances (Å) and bond angles (°) for **4**

Distances (Å)			
Fe1···Fe1A	3.215(7)	Fe1–C1	2.064(4)
Fe1–Br1	2.396(6)	Fe1–S1	2.410(5)
Fe1–S1A	2.383(9)	C1–N1	1.317(5)
Angles (°)			
Fe1–S1–Fe1A	84.2(4)	S1–Fe1–S1A	95.8(4)
C1–Fe1–Br1	118.5(0)	N1–C1–Fe1	130.7(3)
Torsion angles (°)			
Fe1–S1S1A–Fe1A	0.0(0)	S1–Fe1Fe1A–S1A	0.0(0)
C1–Fe1Br1–Fe1A	3.9(3)		
Dihedral angle (°)			
C1Br1Fe1–Fe1S1S1A	86.8(1)		

Figure S5. ORTEP diagram of **5**

Hydrogen atoms and Me₂-cAACH⁺ cation are omitted for clarity (thermal ellipsoids shown at 50% probability).

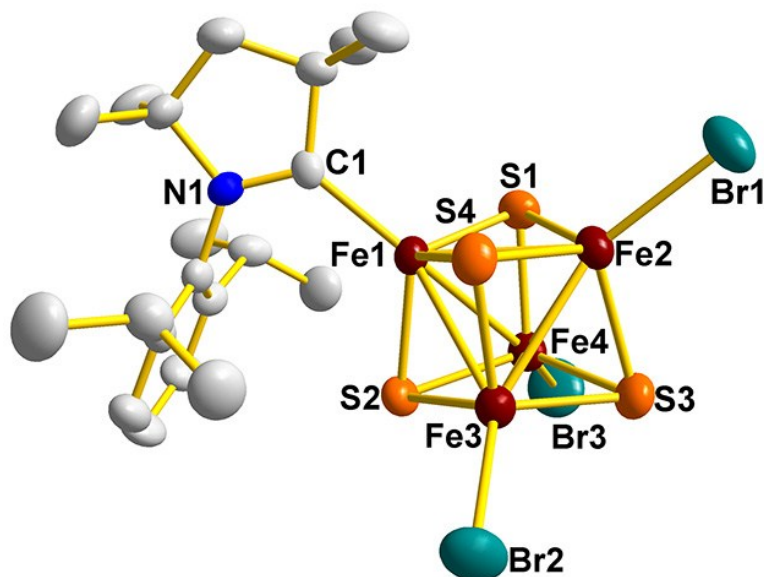


Table S8. Selected bond distances (Å) and bond angles (°) for **5**

Distances (Å)			
Fe1–Fe2	2.751(3)	Fe1–Fe3	2.763(8)
Fe1–Fe4	2.754(3)	Fe2–Fe3	2.742(9)
Fe2–Fe4	2.744(6)	Fe3–Fe4	2.736(5)
Fe1–C1	2.064(4)	C1–N1	1.304(5)
Fe1–S1	2.262(4)	Fe1–S2	2.279(7)
Fe1–S4	2.270(8)	Fe2–S1	2.281(2)
Fe2–S3	2.289(2)	Fe2–S4	2.268(4)
Fe3–S2	2.277(6)	Fe3–S3	2.257(8)
Fe3–S4	2.277(7)	Fe4–S1	2.289(0)
Fe4–S2	2.276(5)	Fe4–S3	2.288(1)
Fe2–Br1	2.352(9)	Fe3–Br2	2.342(5)
Fe4–Br3	2.331(8)		
Angles (°)			
Fe1–S1–Fe2	74.5(3)	Fe1–S1–Fe4	74.4(8)
Fe1–S2–Fe3	74.6(7)	Fe1–S2–Fe4	74.3(9)
Fe1–S4–Fe2	74.6(2)	Fe1–S4–Fe3	74.8(4)
S1–Fe1–S2	103.9(4)	S1–Fe1–S4	103.7(0)
S2–Fe1–S4	103.3(0)	S1–Fe1–C1	113.0(4)
S2–Fe1–C1	124.1(7)	S4–Fe1–C1	106.6(3)

Figure S6. ORTEP diagram of **6**

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

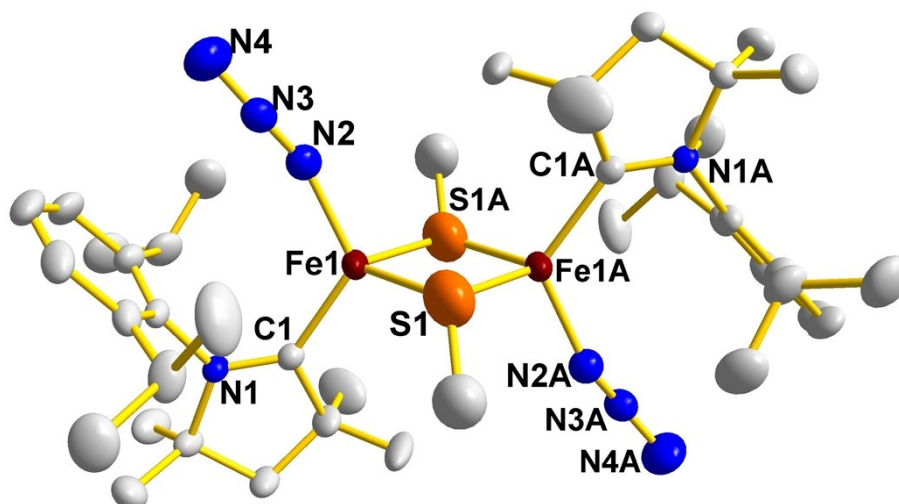


Table S9. Selected bond distances (Å) and bond angles (°) for **6**

Distances (Å)			
Fe1···Fe1A	3.109(7)	Fe1–C1	2.037(3)
C1–N1	1.300(4)	Fe1–S1	2.381(7)
Fe1–S1A	2.411(4)	Fe1–N2	1.934(7)
N2–N3	1.134(10)	N3–N4	1.206(11)
Angles (°)			
Fe1–S1–Fe1A	83.5(3)	Fe1–S1A–Fe1A	83.5(3)
S1–Fe1–S1A	96.5(3)	S1–Fe1A–S1A	96.5(3)
Fe1–N2–N3	155.1(7)	N2–N3–N4	161.8(10)

Figure S7. The ^1H NMR spectrum of **1** in THF-d_8

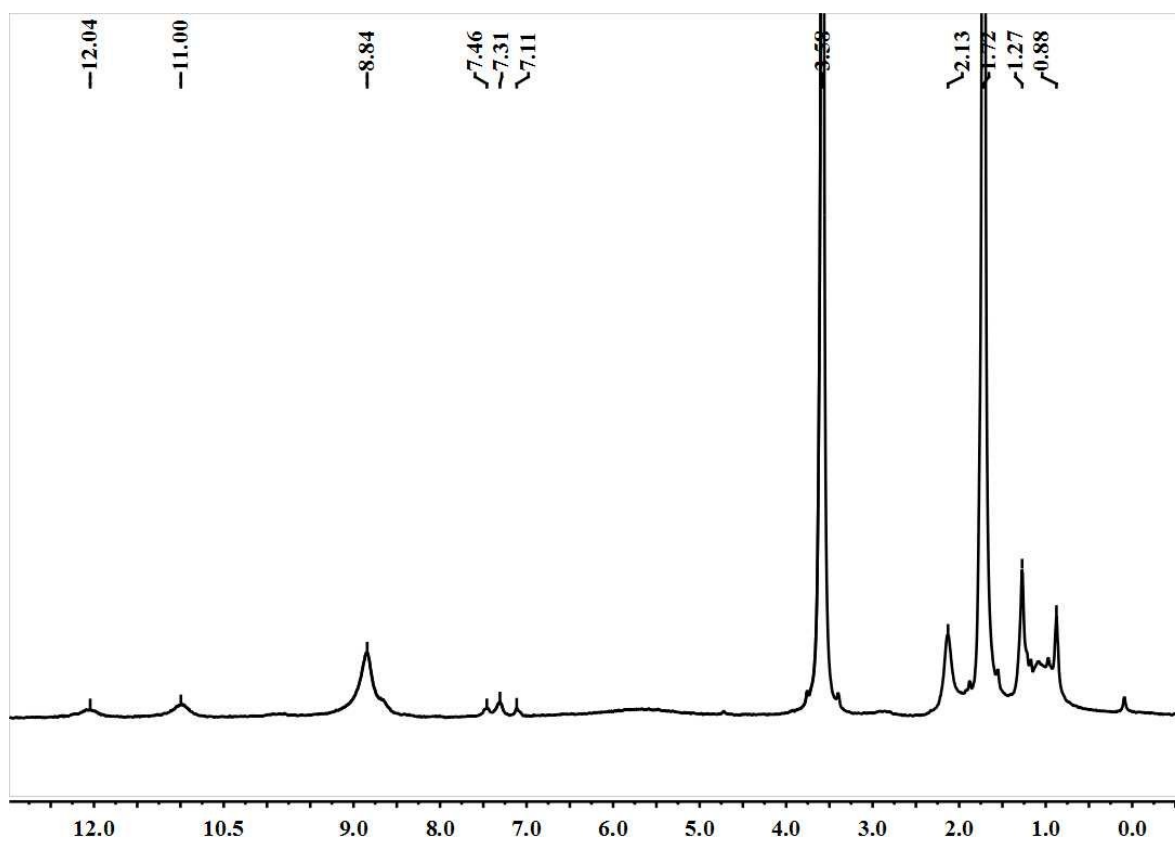


Figure S8. The ^1H NMR spectrum of **2** in THF-d_8

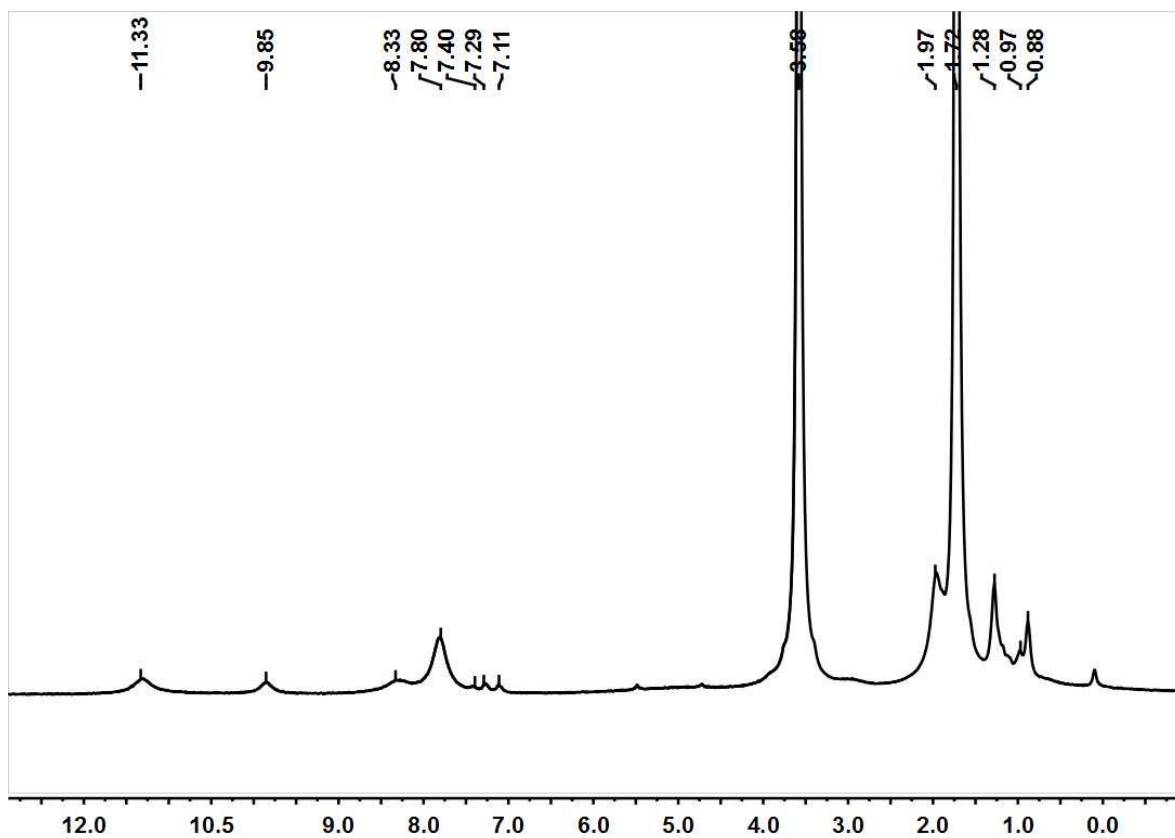


Figure S9. The ^1H NMR spectrum of **3** in THF-d_8

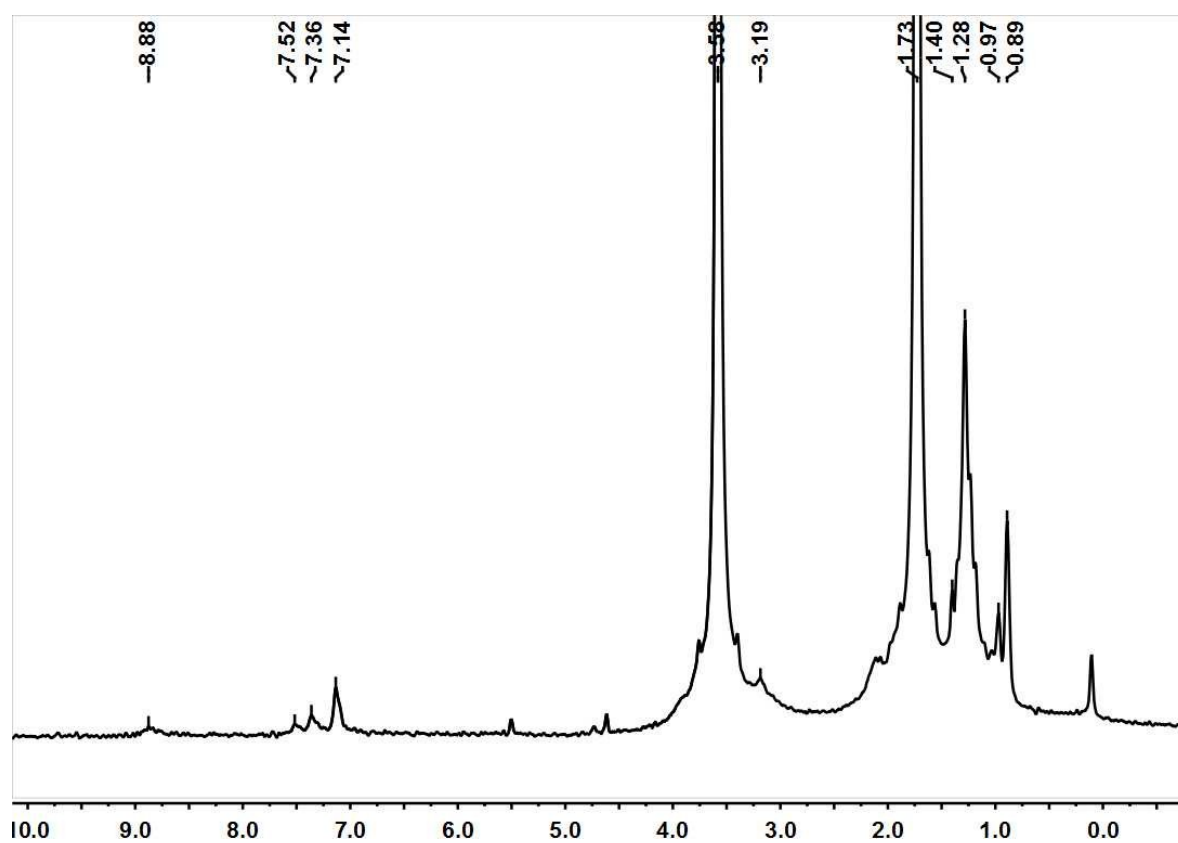


Figure S10. The ^1H NMR spectrum of **4** in THF-d_8

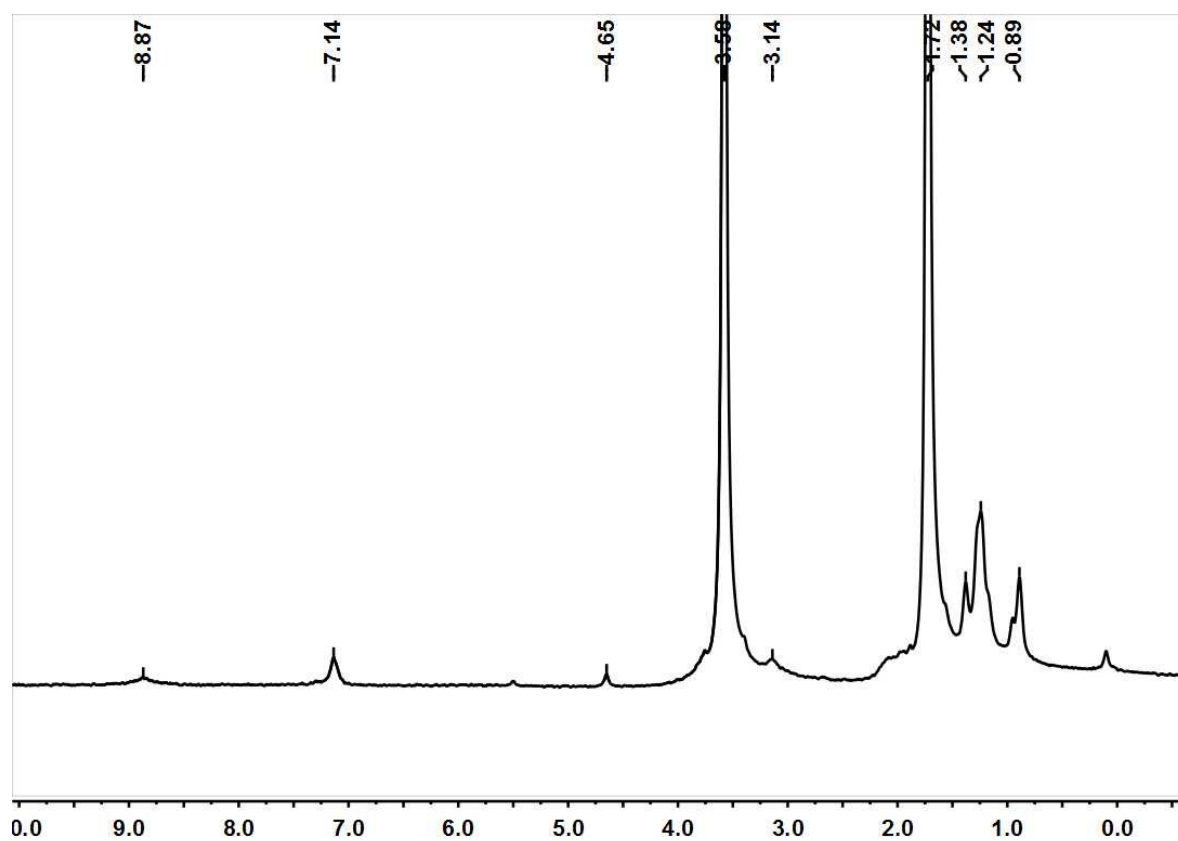


Figure S11. The ^1H NMR spectrum of **5** in CD_2Cl_2

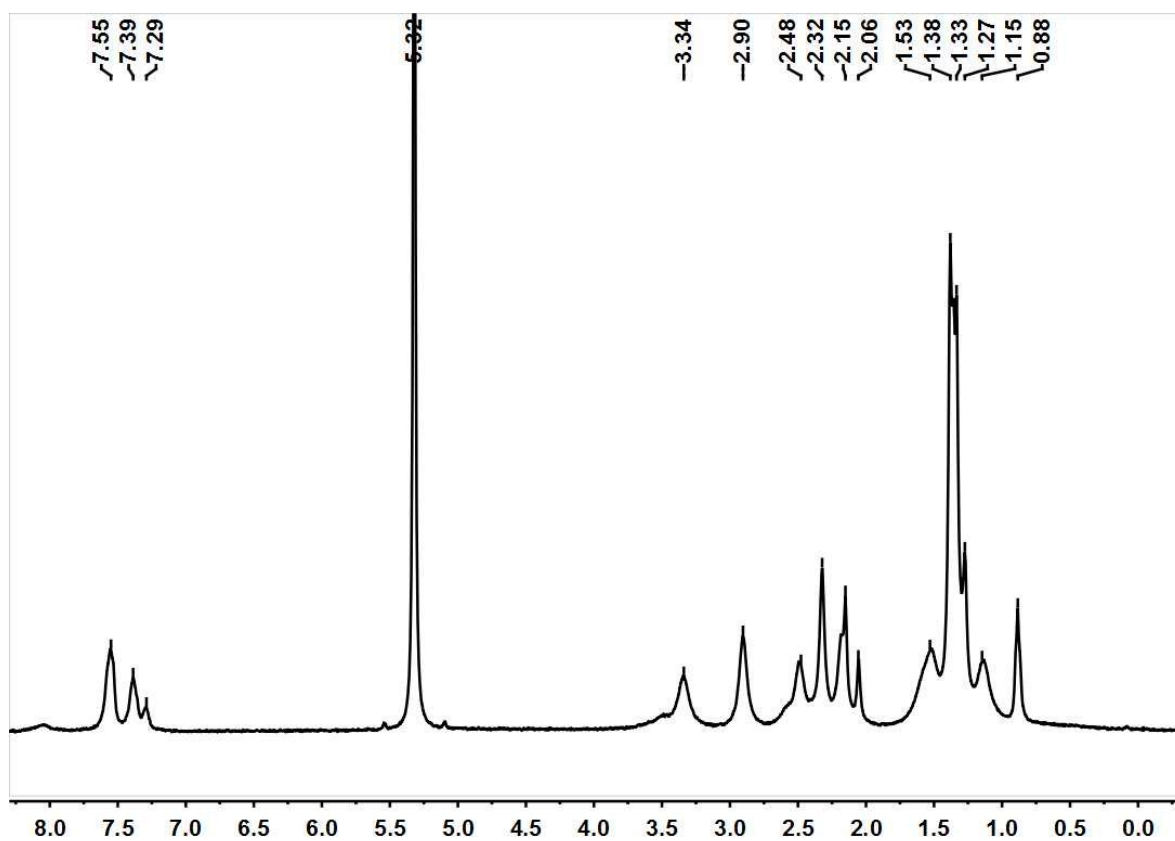


Figure S12. The ^1H NMR spectrum of **6** in THF-d_8

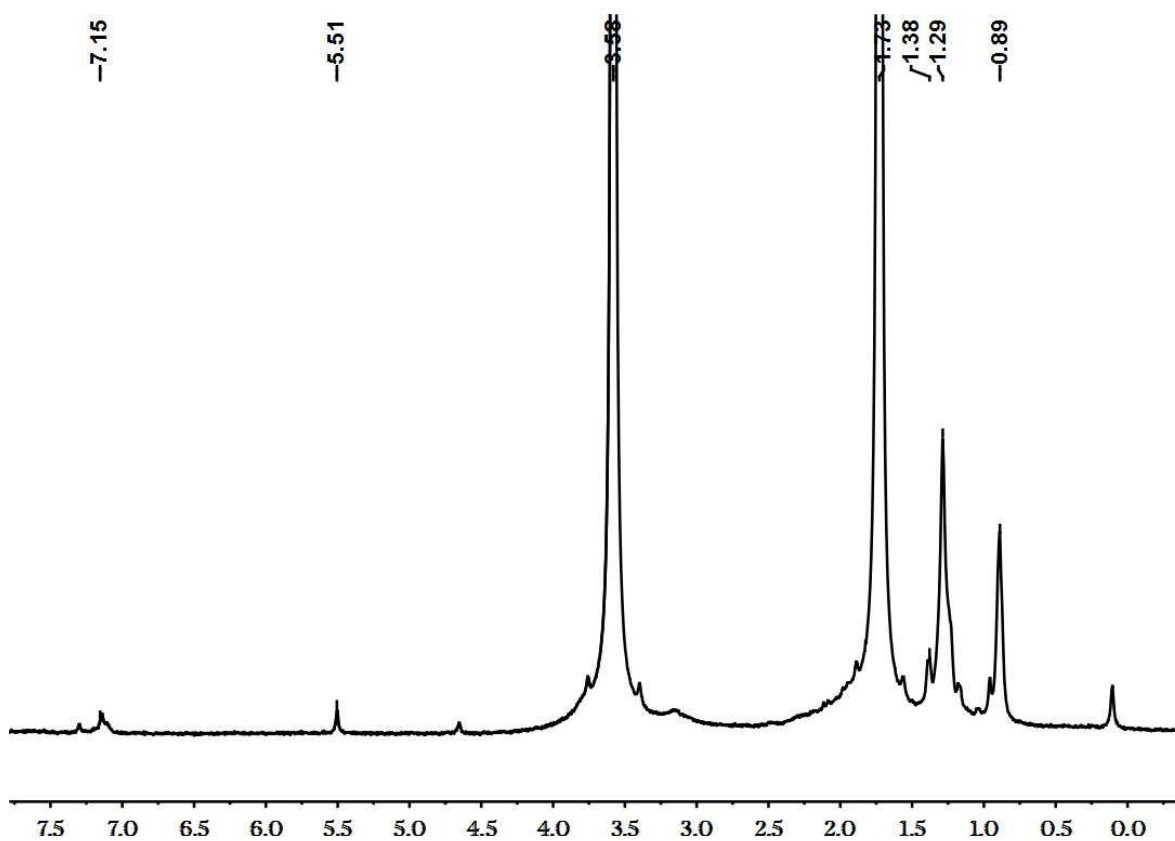


Figure S13. The ^1H NMR spectrum of **7** in THF-d_8

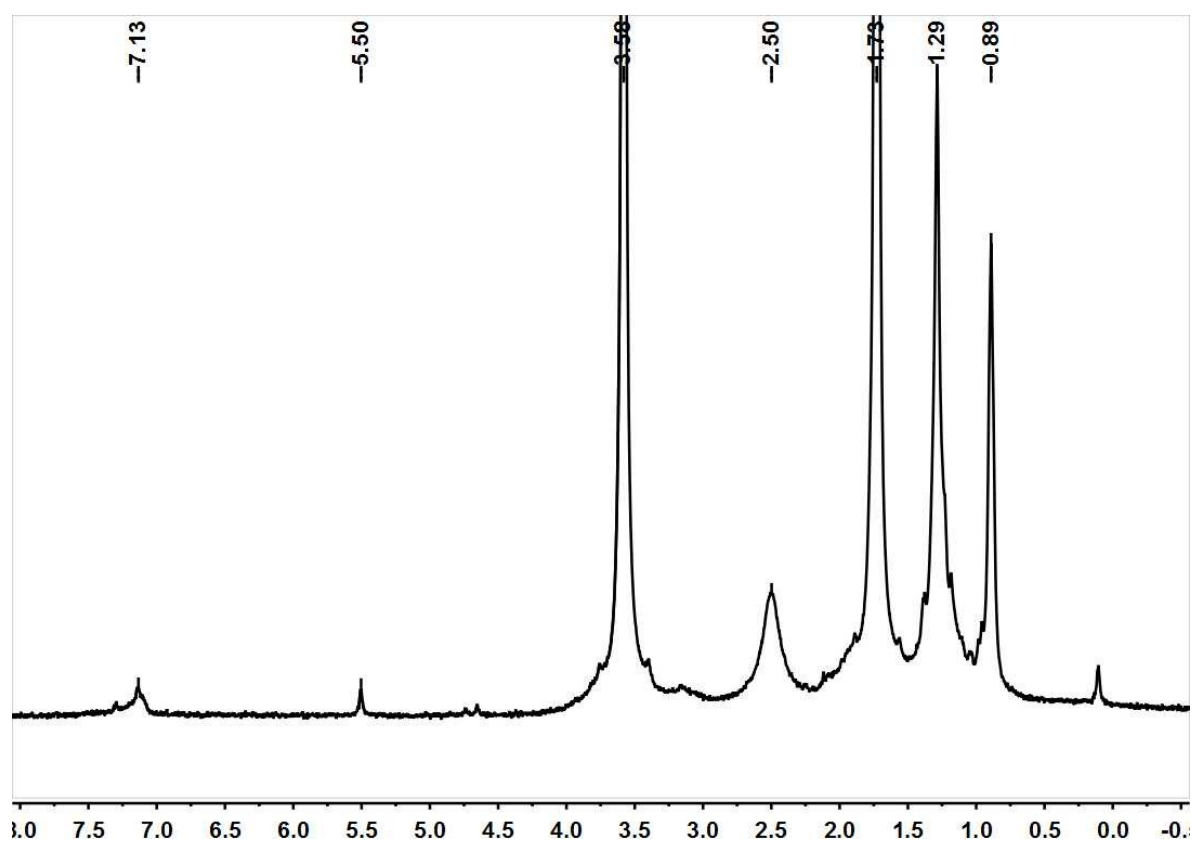


Figure S14. The IR (KBr) spectrum of **1**

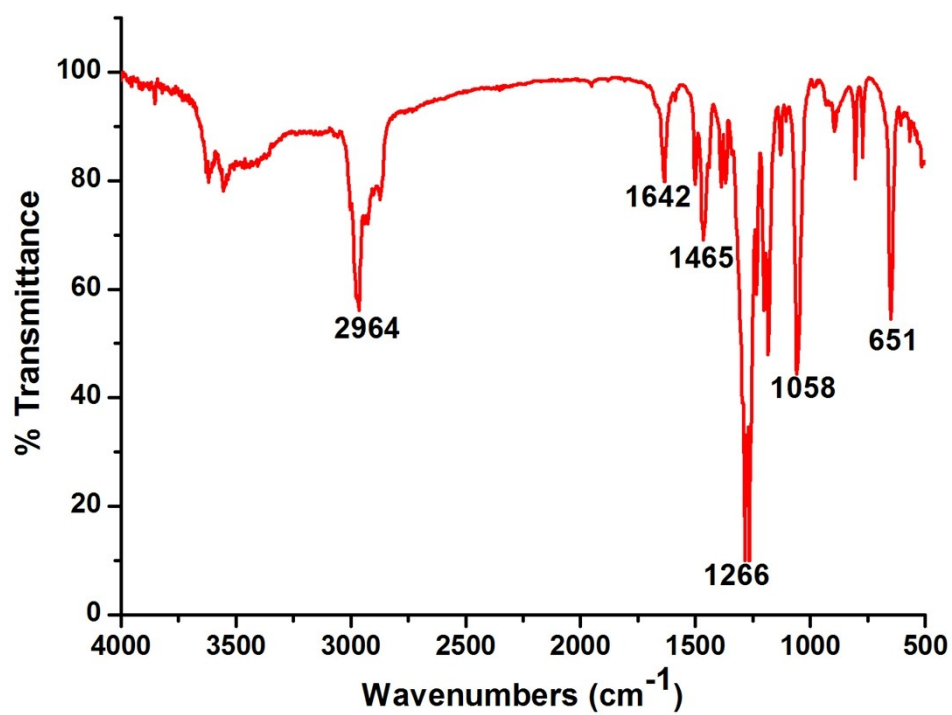


Figure S15. The IR (KBr) spectrum of **2**

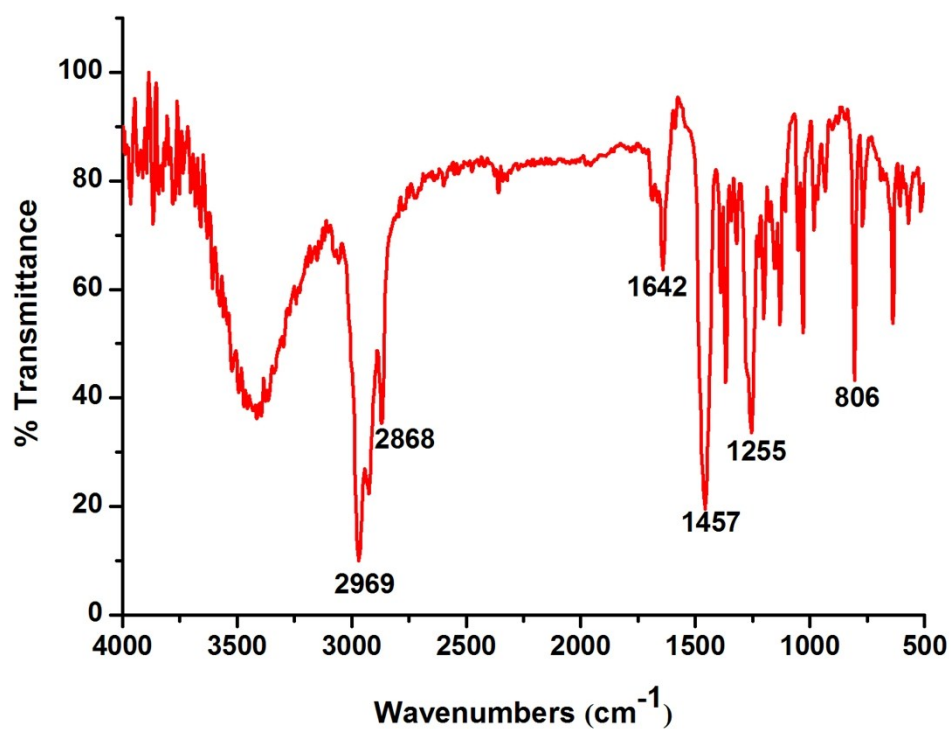


Figure S16. The IR (KBr) spectrum of **3**

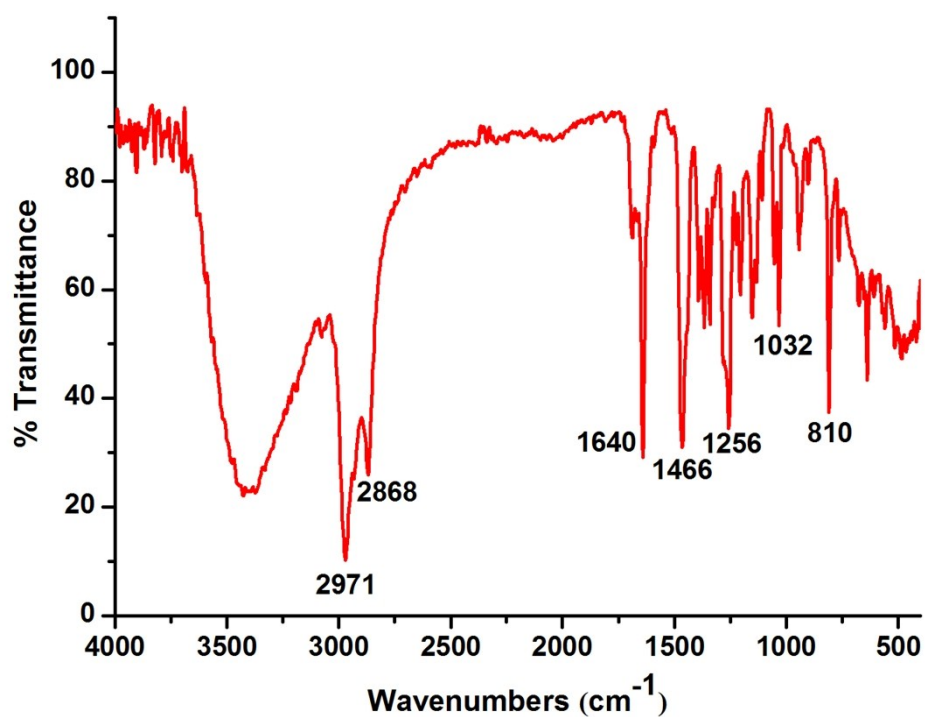


Figure S17. The IR (KBr) spectrum of **4**

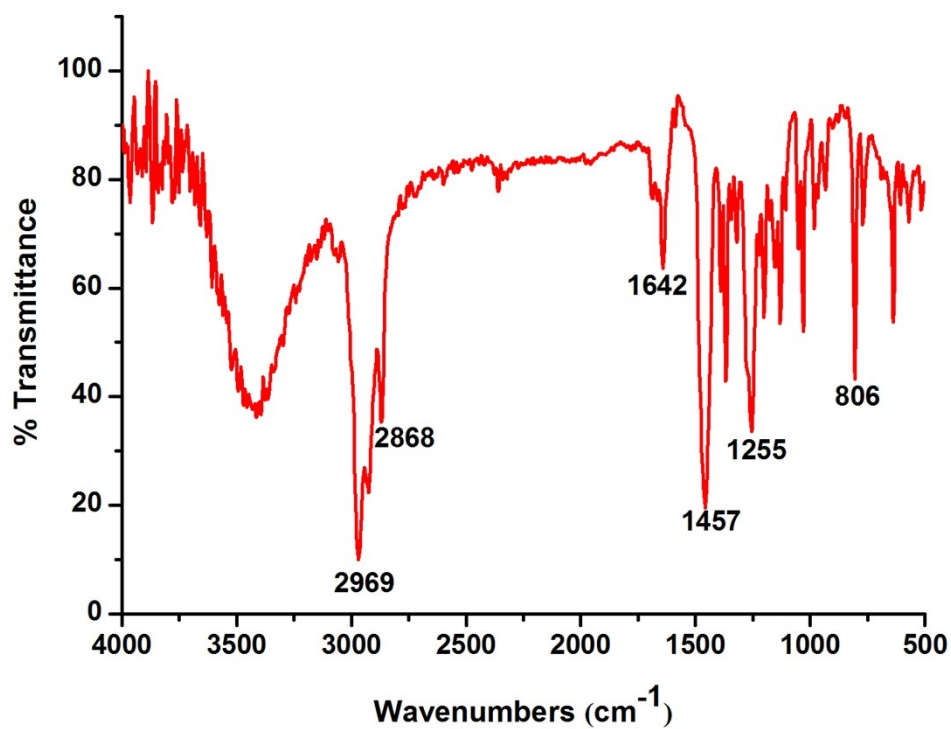


Figure S18. The IR (KBr) spectrum of **5**

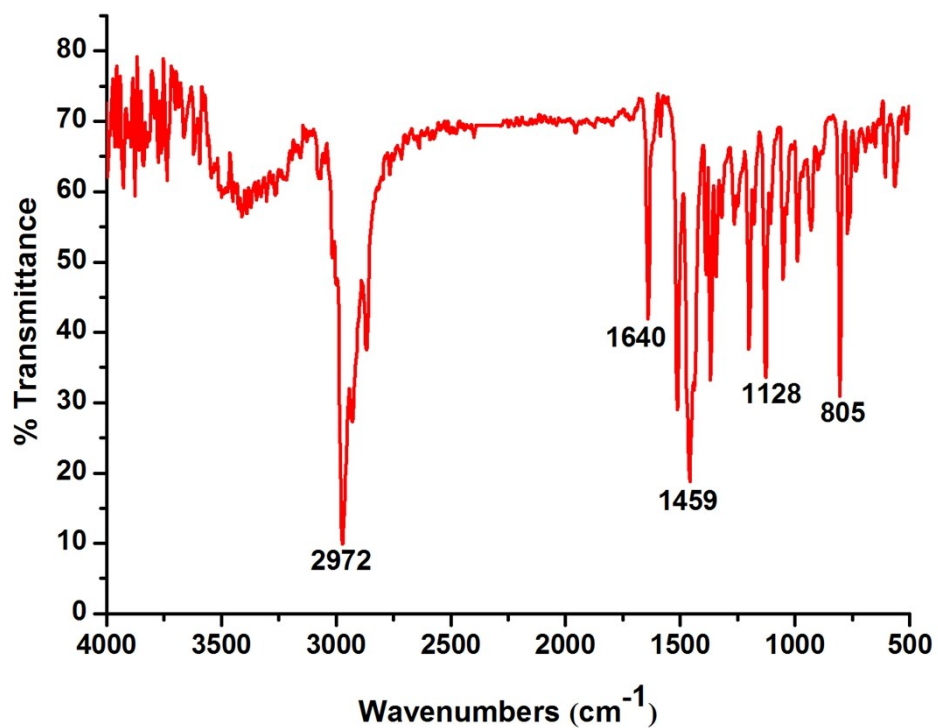


Figure S19. The IR (KBr) spectrum of **6**

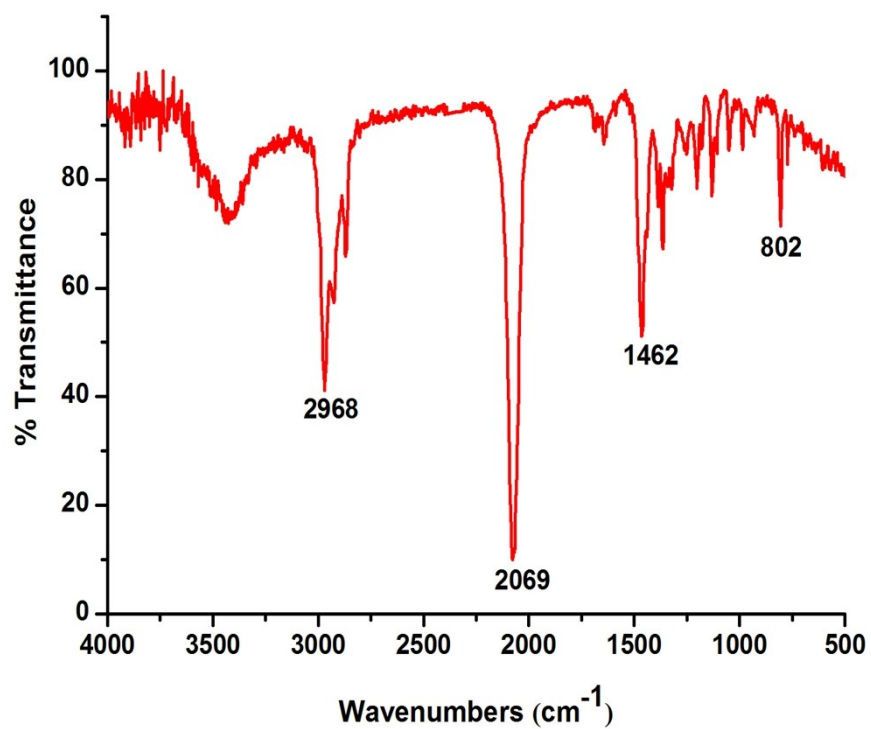


Figure S20. The IR (KBr) spectrum of **7**

