Electronic Supplementary Information

Low-valence Oxo-centered Triruthenium Complexes by Bridging Ligand Substitution with a Pyrazolydiazine or Pyridinyltetrazine Ligand

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Table S1. ^{1}H NMR Chemical Shifts (δ) for Compounds **3**—**8**.[a]

Compound	**3**	**4**	**5**	**6**			**7**	**8**
δ(acetate)	1.58 (3H)	1.30 (3H)	1.64 (6H)	1.30 (3H)		δ(acetate)	1.63 (6H)	2.14 (3H)
	1.99 (3H)	1.59 (3H),	1.90 (3H)	1.67 (6H)			1.99 (3H),	5.48 (12H)
	2.02 (3H)	2.05 (6H)	2.37 (6H)	2.31 (6H)			2.55 (6H)	
	2.05 (3H)	2.39 (3H)					3.12 (3H)	
	2.41 (3H)							
δ(pyrazole)	9.03 (1H, H-3)	2.81 (3H, Me)	8.99 (2H, H-3)	2.89 (6H, Me)		δ(pyridinyl)	8.82 (2H, H-3)	2.14 (2H, H-3)
	7.24 (1H, H-4)	2.98 (3H, Me)	7.22 (2H, H-4)	2.96 (6H, Me)			8.48 (2H, H-4)	1.30 (4H, H-4,5)
	8.41 (1H, H-5)	6.80 (1H, H-4)	8.51 (2H, H-5)	6.74 (2H, H-4)			8.05 (2H, H-5)	0.91 (2H, H-6)
δ(pyridazine)	8.01 (1H, H-4)	7.93 (1H, H-4)	8.03 (2H)	7.86 (2H)			9.11 (2H, H-6)	
	7.34 (1H, H-5)	7.21 (1H, H-5)						
δ(py)	9.24 (2H, o)	9.21 (2H, o)	9.25 (2H, o)	9.13 (2H, o)		δ(py)	9.26 (2H, o)	
	7.81 (2H, m)	7.80 (2H, m)	8.13 (2H, m)	8.10 (2H, m)			8.22 (2H, m)	
	8.22 (1H, p)	8.22 (1H, p)	8.34 (1H, p)	8.30 (1H, p)			8.36 (1H, p)	
δ(py')	9.24 (2H, o')	9.21 (2H, o')						
	8.12 (2H, m')	8.12 (2H, m')						
	8.34 (1H, p')	8.33 (1H, p')						

[a] ^{1}H NMR spectra (400 MHz) were recorded in CD_3CN at 298 K

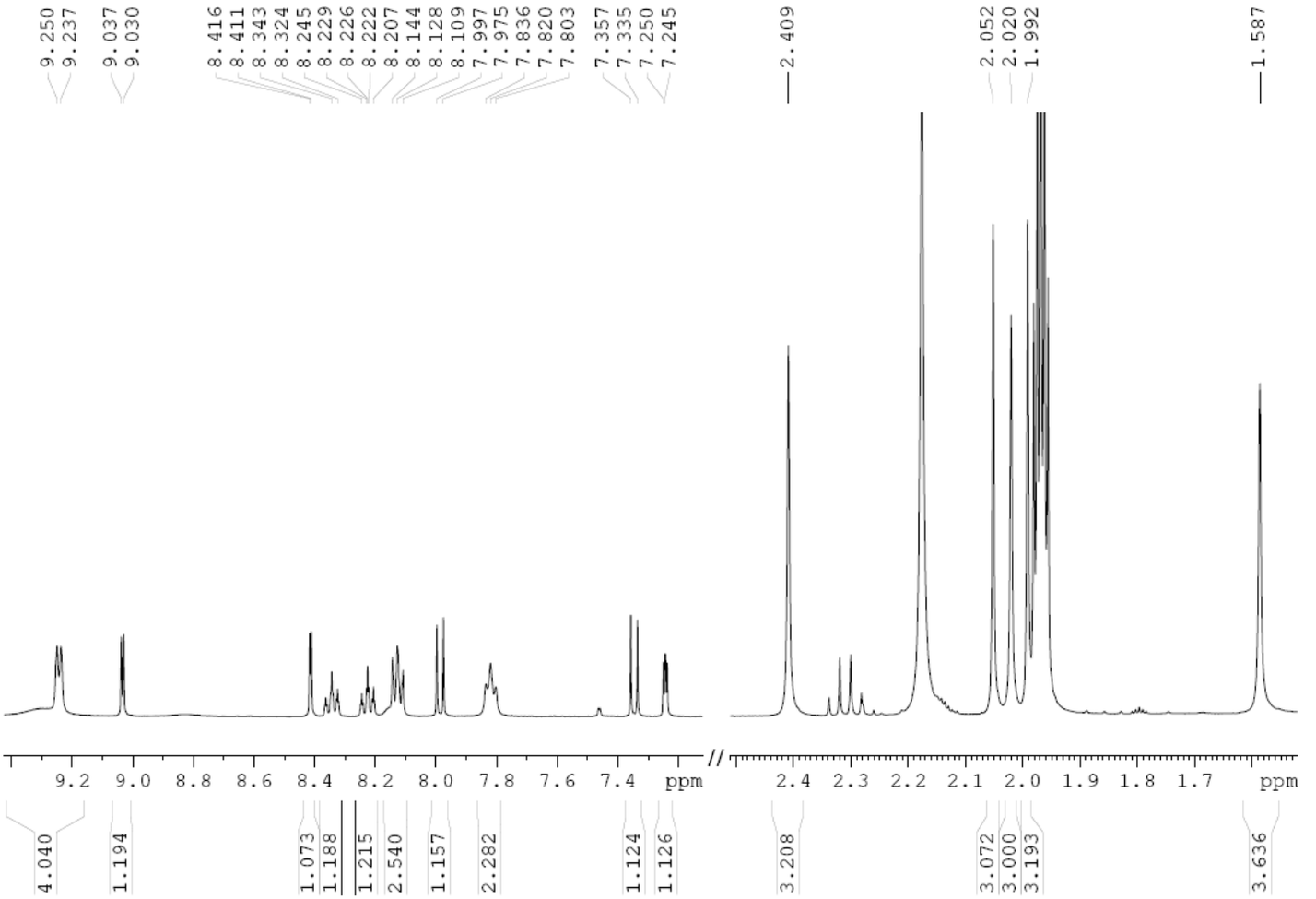

Fig. S1. ^{1}H NMR (400 MHz) spectrum of compound **3** in CD_3CN.

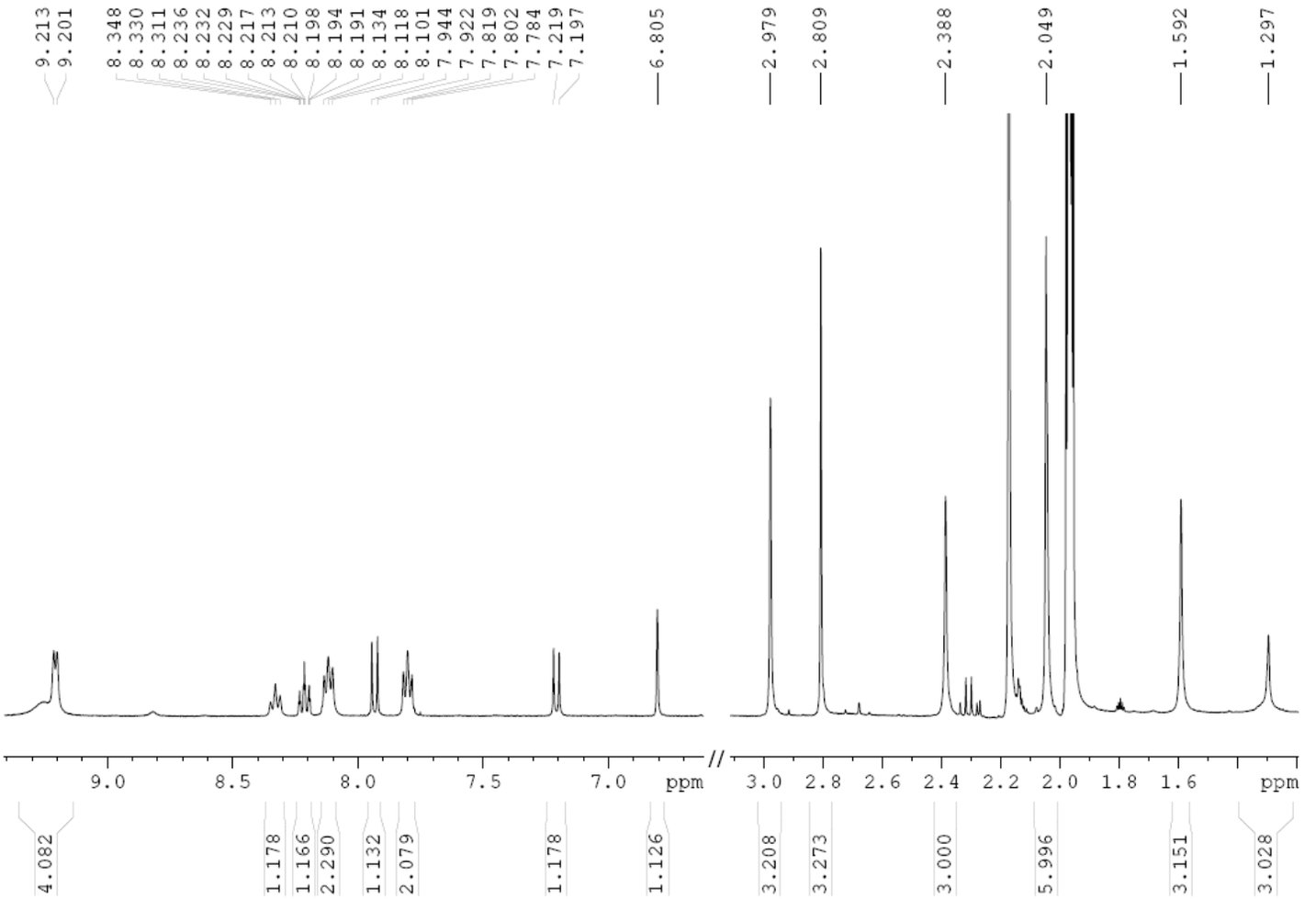

Fig. S2. ^{1}H NMR (400 MHz) spectrum of compound **4** in CD_3CN.

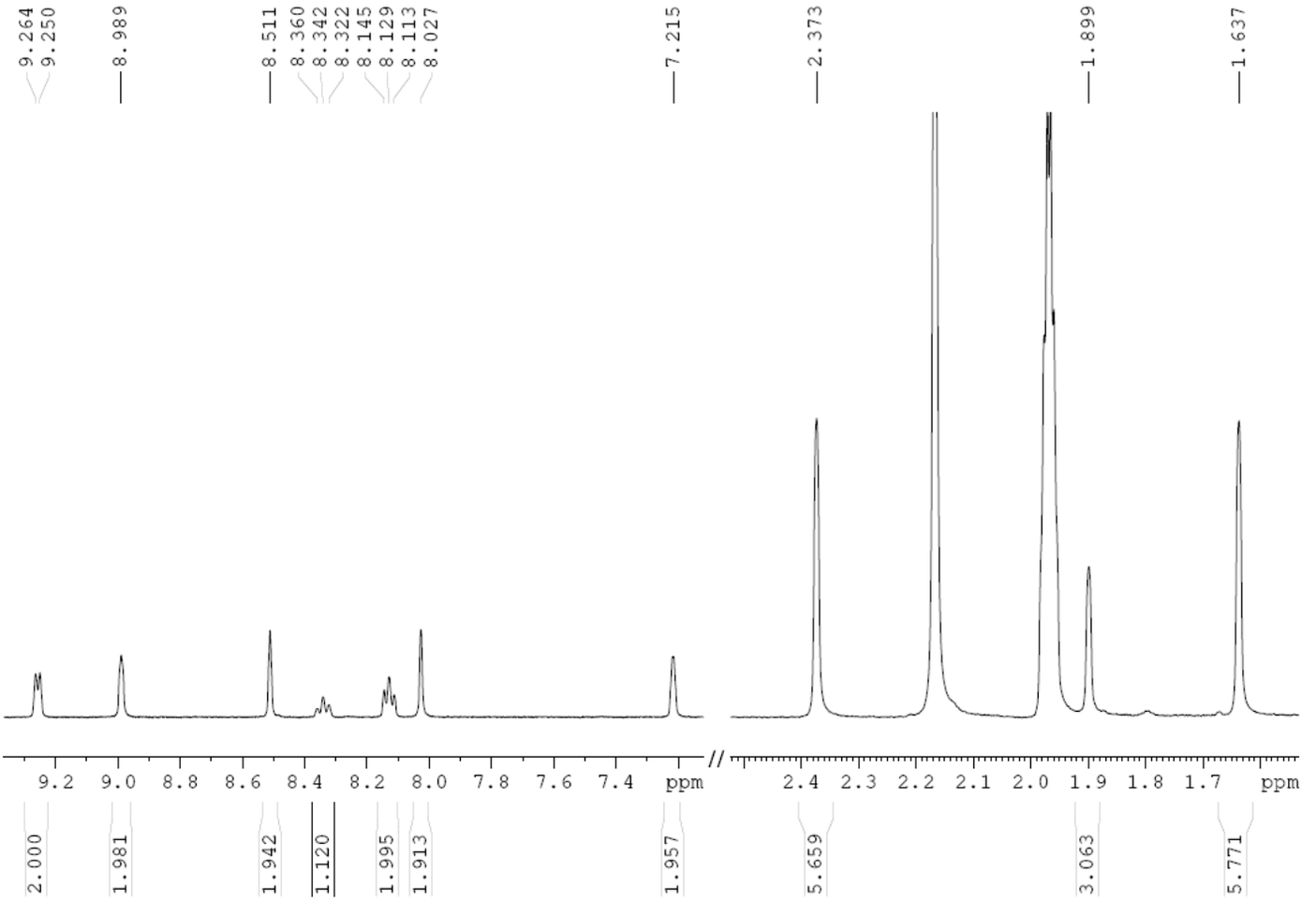

Fig. S3. ^{1}H NMR (400 MHz) spectrum of compound **5** in CD_3CN.

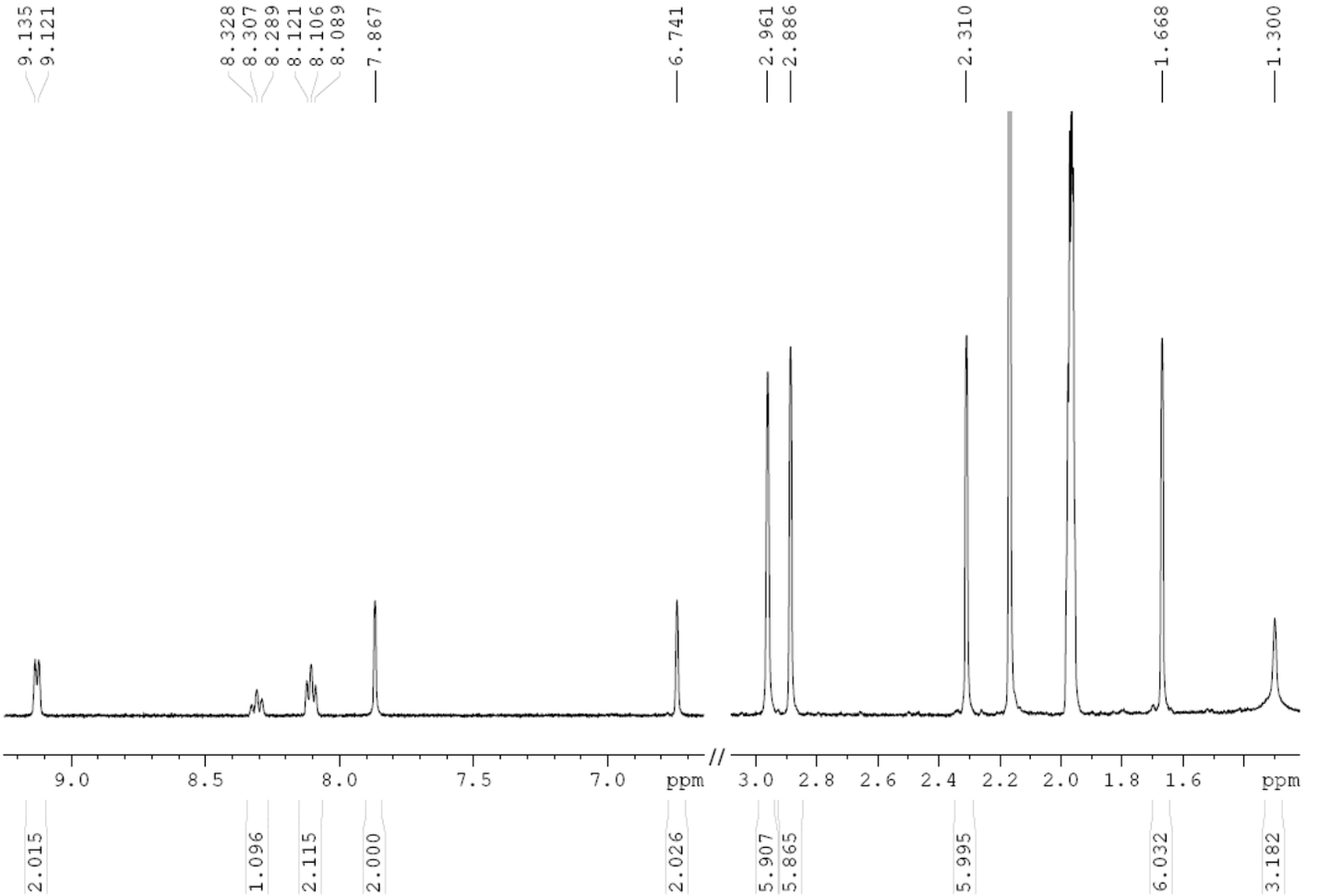

Fig. S4. ^{1}H NMR (400 MHz) spectrum of compound **6** in CD_3CN.

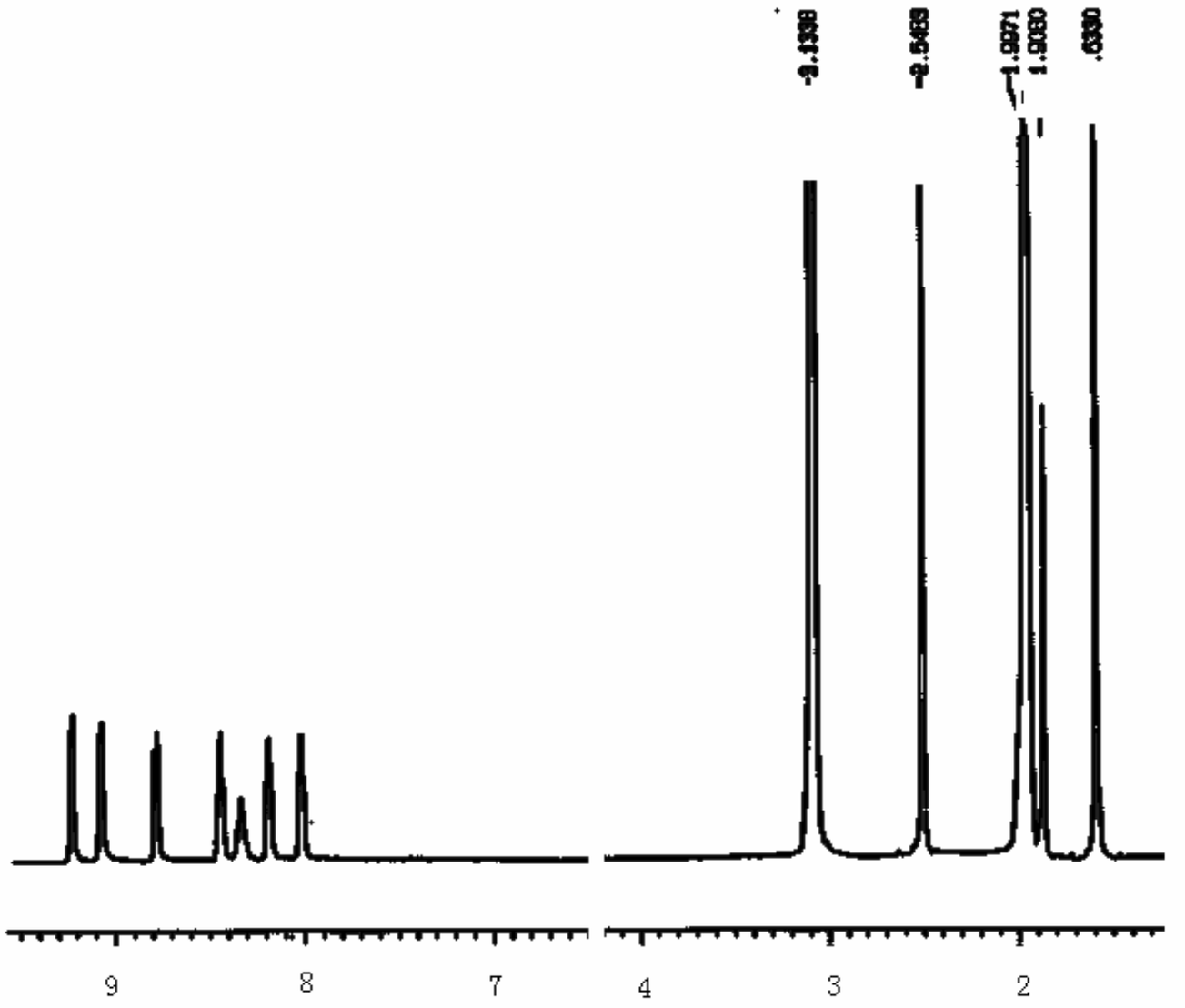

Fig. S5. ^{1}H NMR (400 MHz) spectrum of compound **7** in CD_3CN.

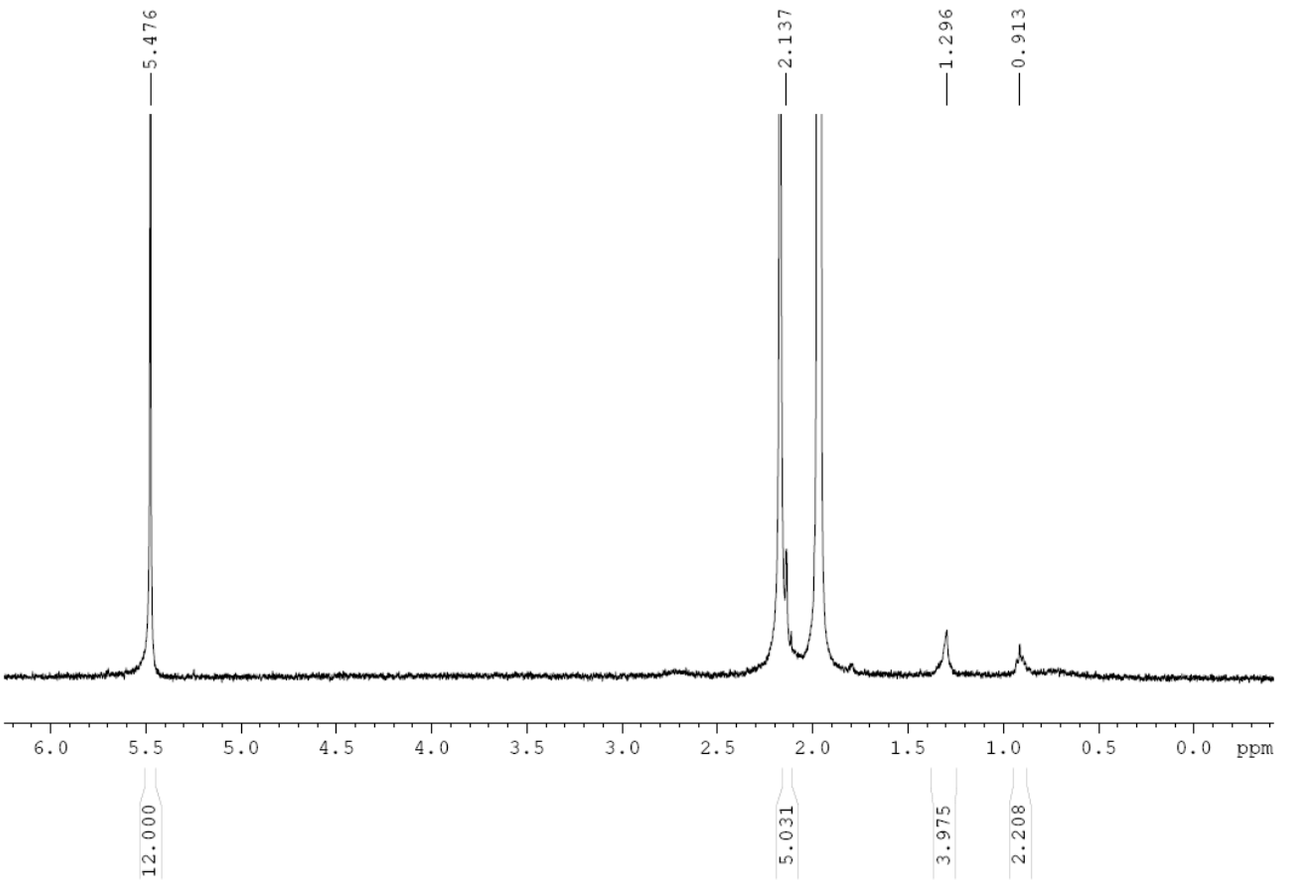

Fig. S6. ^{1}H NMR (400 MHz) spectrum of compound **8** in CD_3CN.

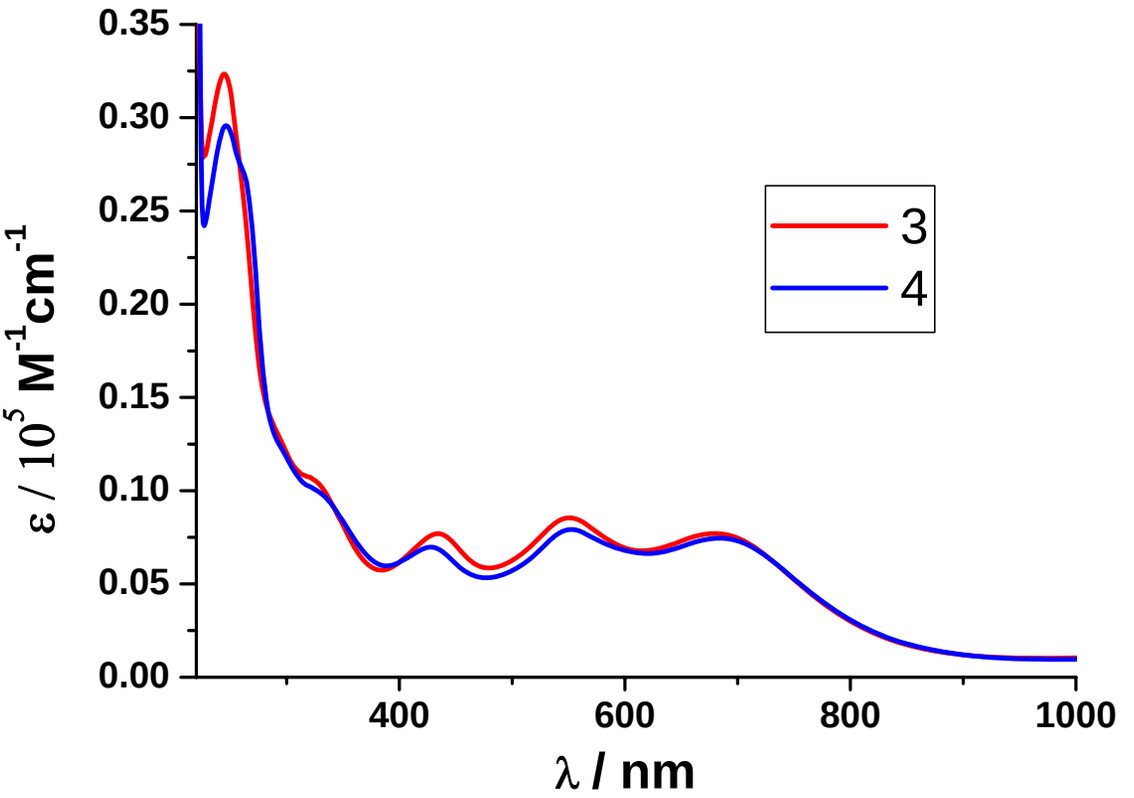

Fig. S7. Electronic absorption spectra of compound **3** (red line) and **4** (blue line) in dichloromethane.

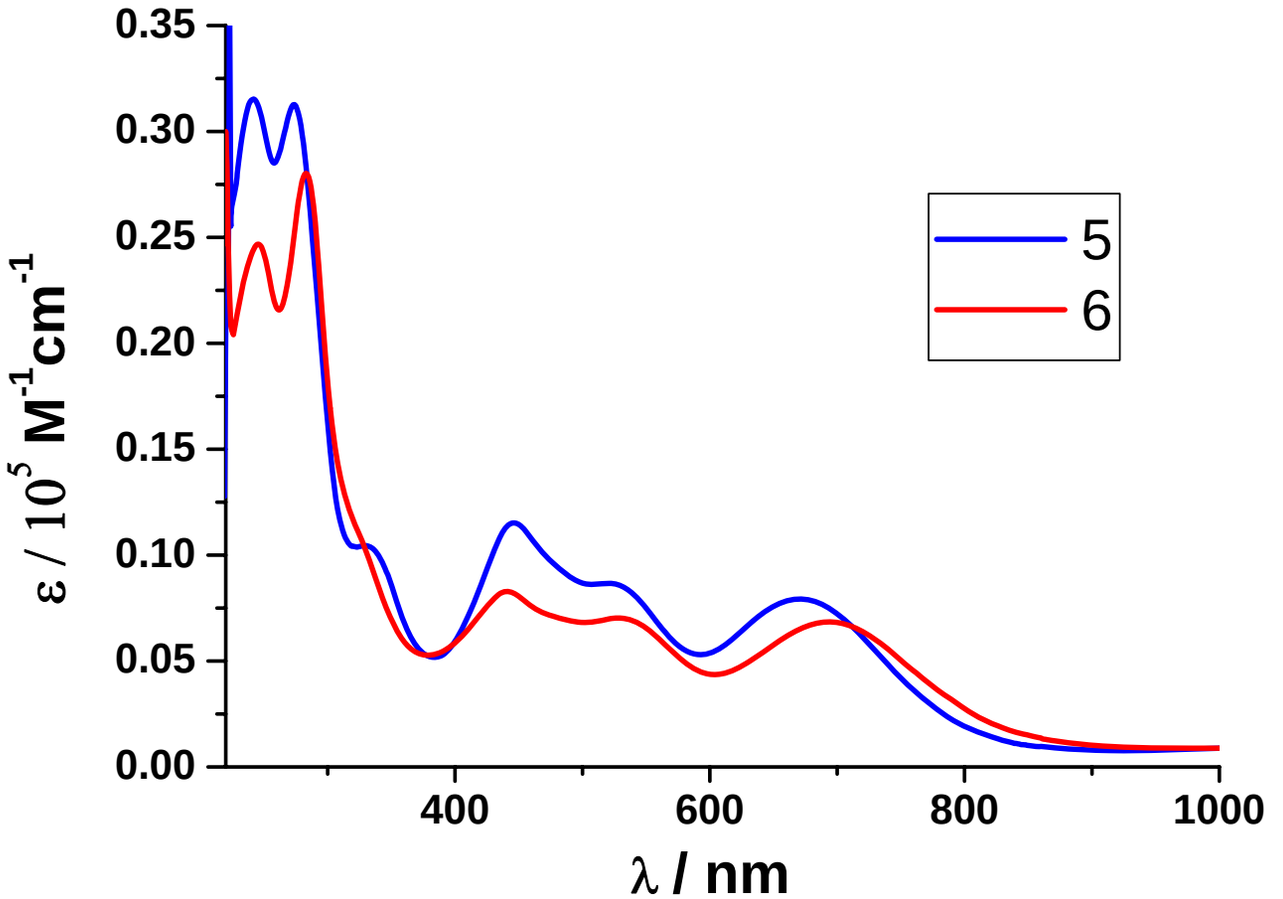

Fig. S8. Electronic absorption spectra of compound **5** (blue line) and **6** (red line) in dichloromethane.

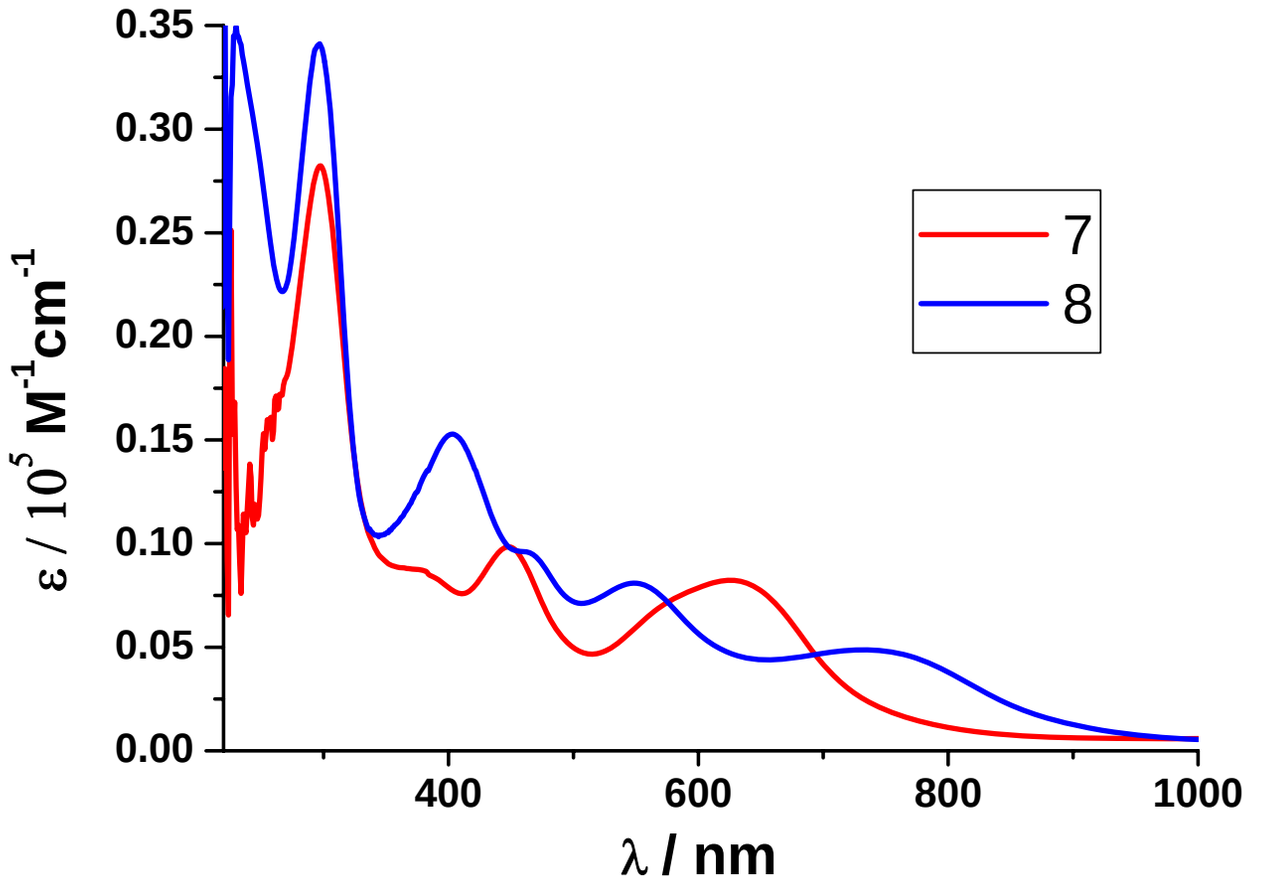

Fig. S9. Electronic absorption spectra of compound **7** (red line) and **8** (blue line) in dichloromethane.

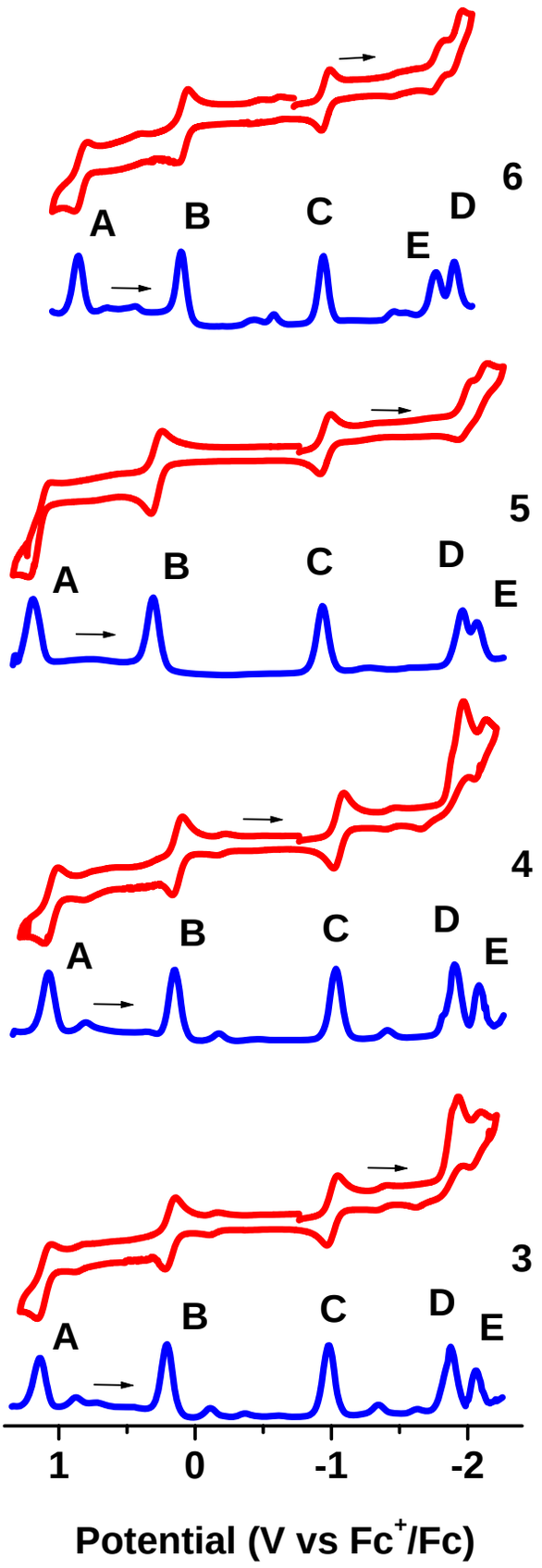

Fig. S10 Plots of cyclic and differential pulse voltammograms for compound **3**-**6** in 0.1 M acetonitrile solution of (Bu4N)(PF6). The scan rates are 100 mV s-1 for CV and 20 mV s-1 for DPV.

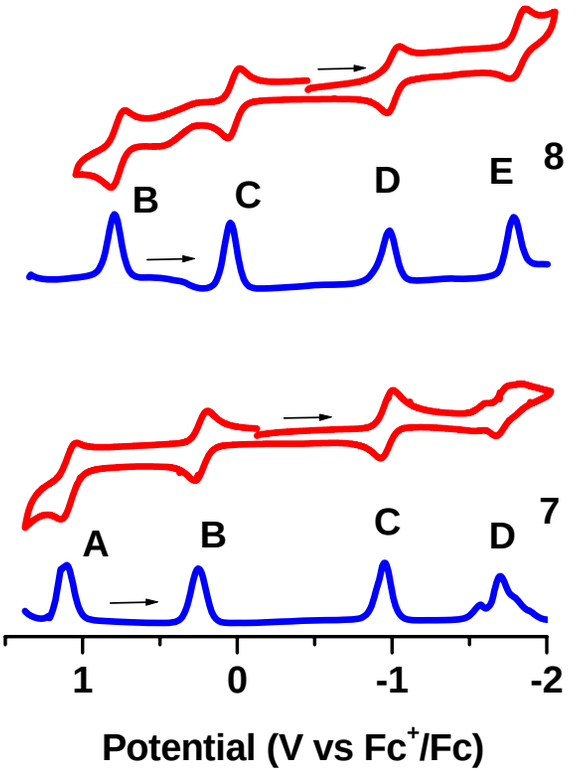

Fig. S11. Plots of cyclic and differential pulse voltammograms for compoundS **7** and **8** in 0.1 M acetonitrile solution of $(Bu_4N)(PF_6)$. The scan rates are 100 mV s^{-1} for CV and 20 mV s^{-1} for DPV.