Charge Transfer Properties of Benzo[*b*]thiophene Ferrocenyl Complexes

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Supporting Information

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Crystal packing analysis of 3-ferrocenylbenzo[*b*]thiophene (B). Within the asymmetric unit, a C-H…π edge-to-face interaction is observed between the C15–H15 group of the distal Cp ring of molecule **B1** with the benzo[*b*]thiophene of molecule **B2**, the closest contacts being with the C23 and C24 atoms (Figure S1). Specifically, the distances C15….C23 and H15…C23 and the angle C15-H15…C23 are 3.601(4) Å, 2.77 Å and 150°, respectively, whereas the distances C15….C24 and H15…C24 and the angle C15-H15…C24 are 3.744(4) Å, 2.81 Å and 176°, respectively. An additional C-H…π interaction is found between the C14-H14 group (distal Cp of molecule **B1**) and the proximal Cp ring of molecule **B2**, for which the distances C14….C33 and H14…C33 and the angle C14-H14…C33 are 3.677(5) Å, 2.50 Å and 153°, respectively.

In the packing mode, a sulfur – aromatic interaction[1] takes place between S2 (molecule **B2**) and the proximal Cp ring of a (x, 1+y, z) symmetry equivalent of molecule **B1**, the S2…C9 and S2…C13 intermolecular distances being 3.495(3) Å and 3.358(4) Å, respectively (Figure S2). Conversely, the S1 atom of molecule **B1** is not involved in any intermolecular contact with aromatic carbons shorter than 3.85 Å. The closest intermolecular contact [3.350(4) Å] between molecules of the same kind (**B2** – **B2**) is found between the (benzo[*b*]thiophene) C27 atom and the (x-1, y, z) symmetry equivalent of the (proximal Cp) C30 atom.

1 Meyer, E. A.; Castellano, R. K.; Diederich, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 1210–1250.

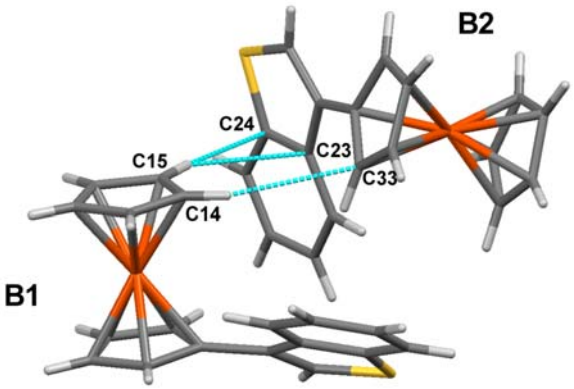


Figure S1. Intermolecular contacts between the independent molecules **B1** and **B2** in the asymmetric unit of (**B**). The atoms participating in C-H…π interactions (indicated by dashed lines) are labelled.

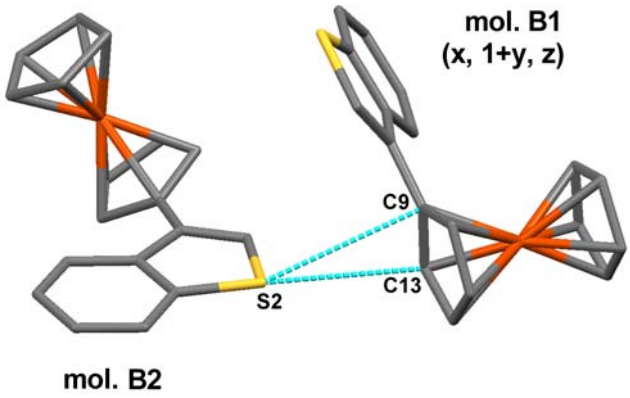


Figure S2. The intermolecular sulfur–aromatic interaction occurring between S2 (molecule **B2**) and the proximal Cp ring of the (x, 1+y, z) symmetry equivalent of molecule **B1** in the packing mode of (**B**). H-atoms have been omitted for clarity.

NMR and ESI spectra of the products.

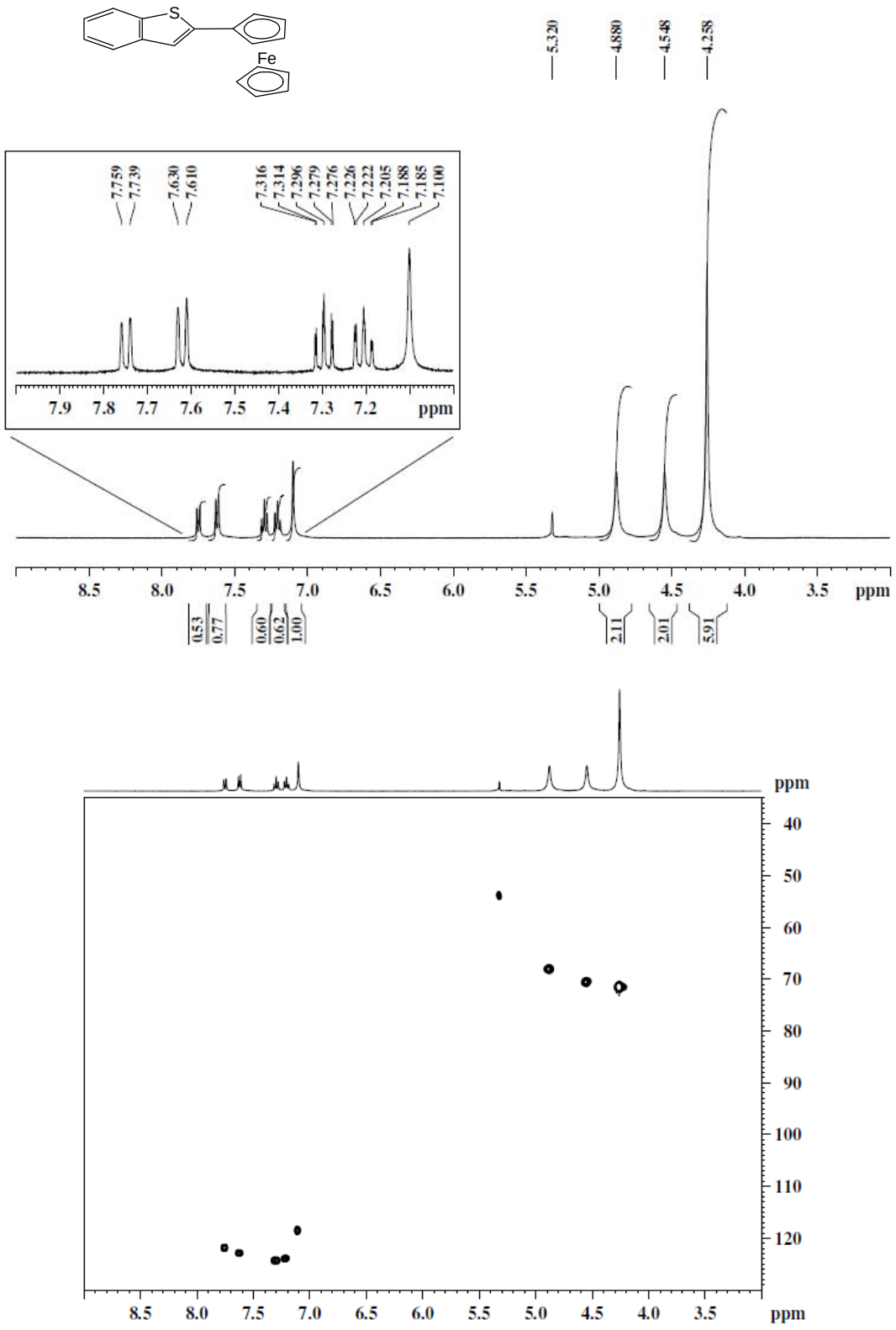


Figure S3. ^{1}H-NMR and 2D-heterocorrelated HMQC spectra of 2-ferrocenylbenzo[*b*]thiophene **(A).**

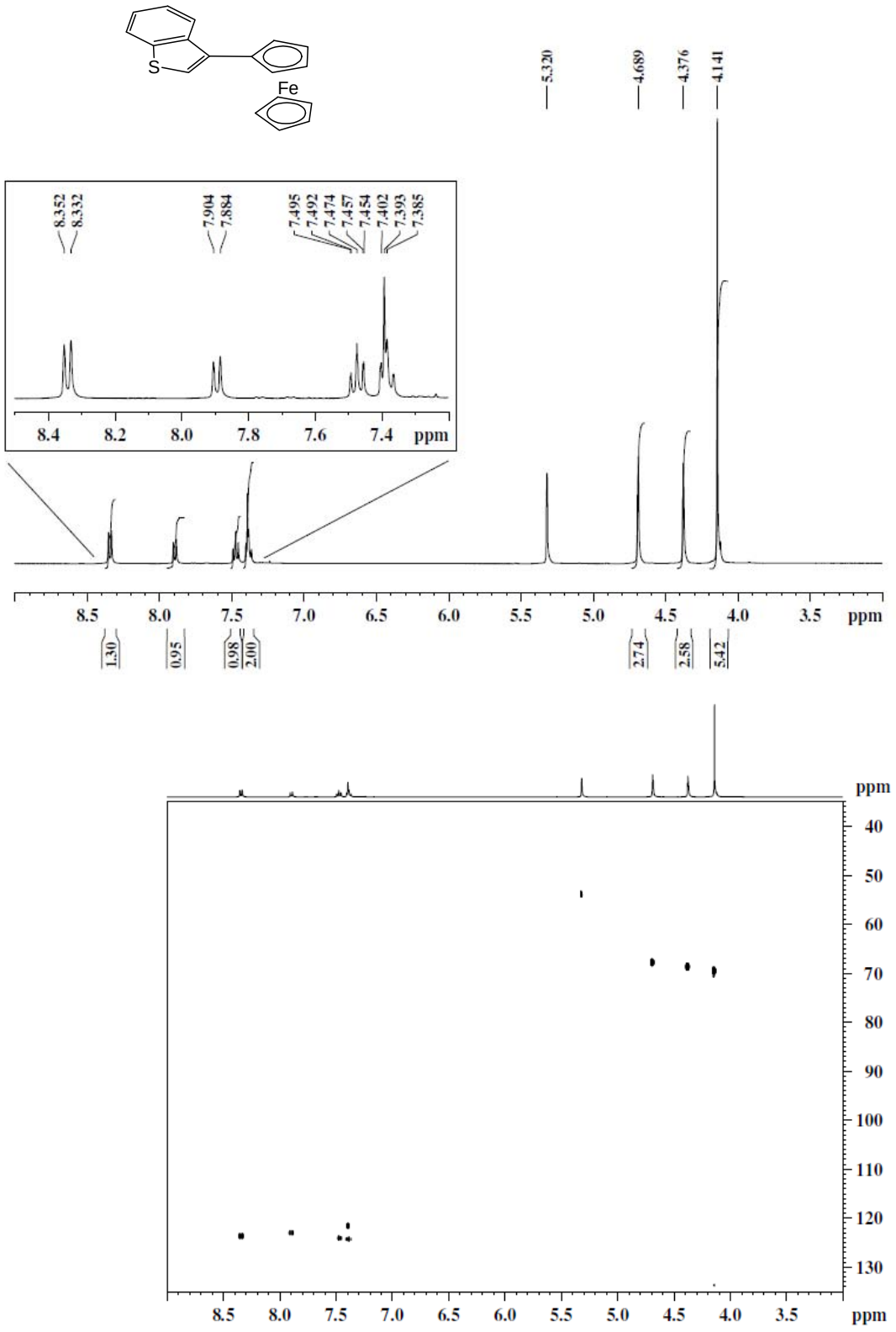


Figure S4. ^{1}H-NMR and 2D-heterocorrelated HMQC spectra of 3-ferrocenylbenzo[*b*]thiophene **(B).**

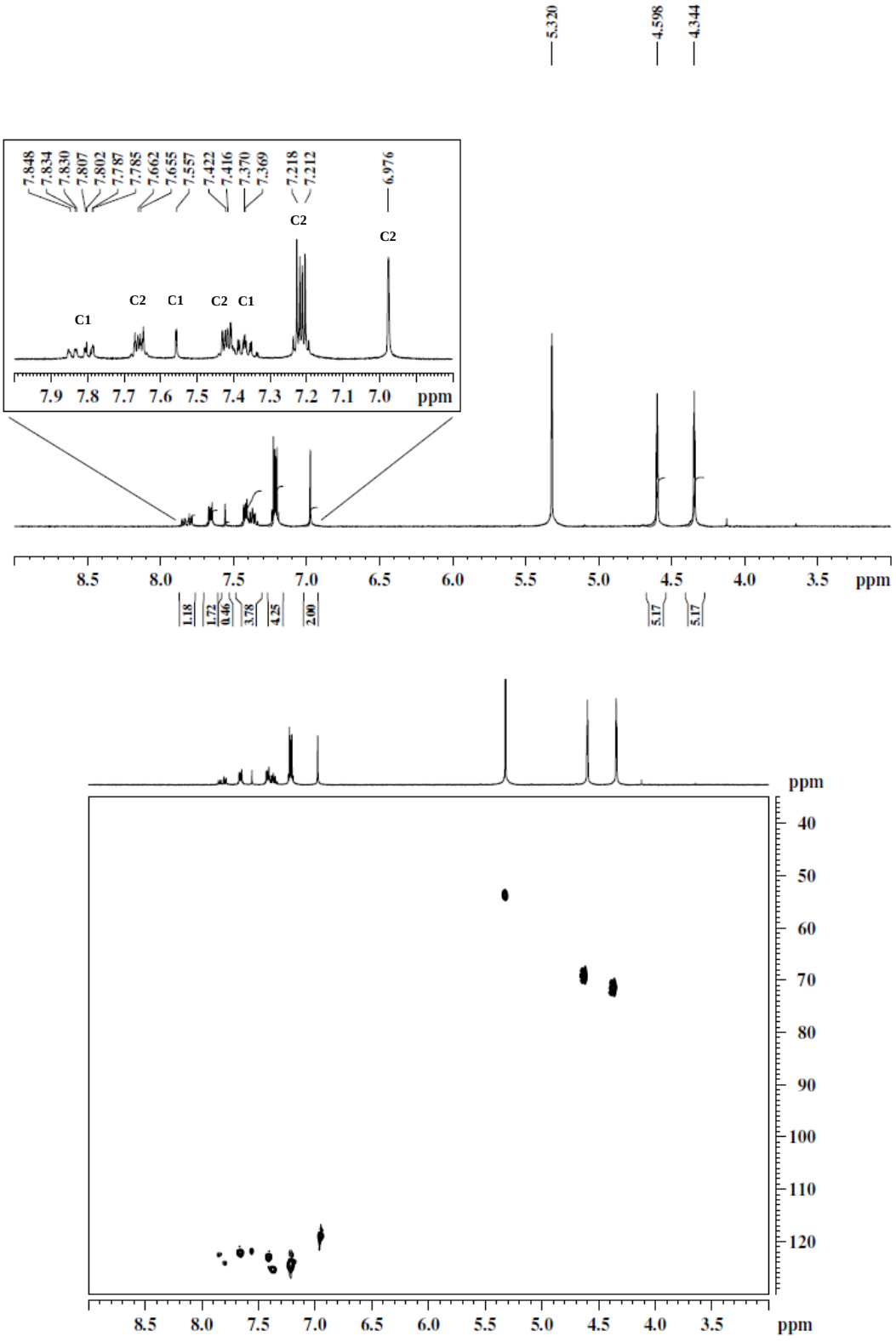


Figure S5. ^{1}H-NMR and 2D-heterocorrelated HMQC spectra of 1,1'-bis(2-benzo[*b*]thiophene)ferrocenes **(C1 + C2).**

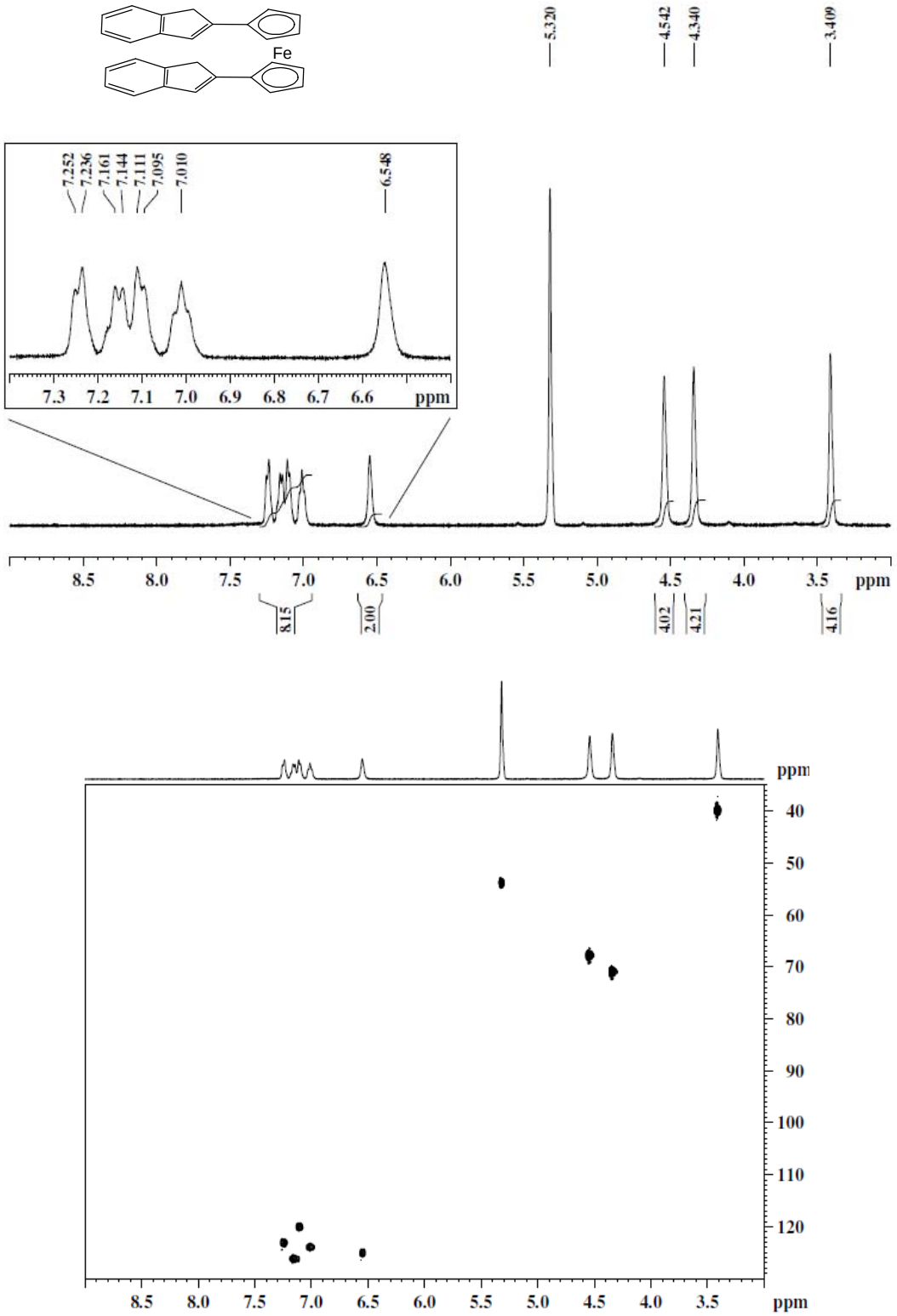


Figure S6 ^{1}H-NMR and 2D-heterocorrelated HMQC spectra of 1,1'-bis(2-indene)ferrocene **(D).**

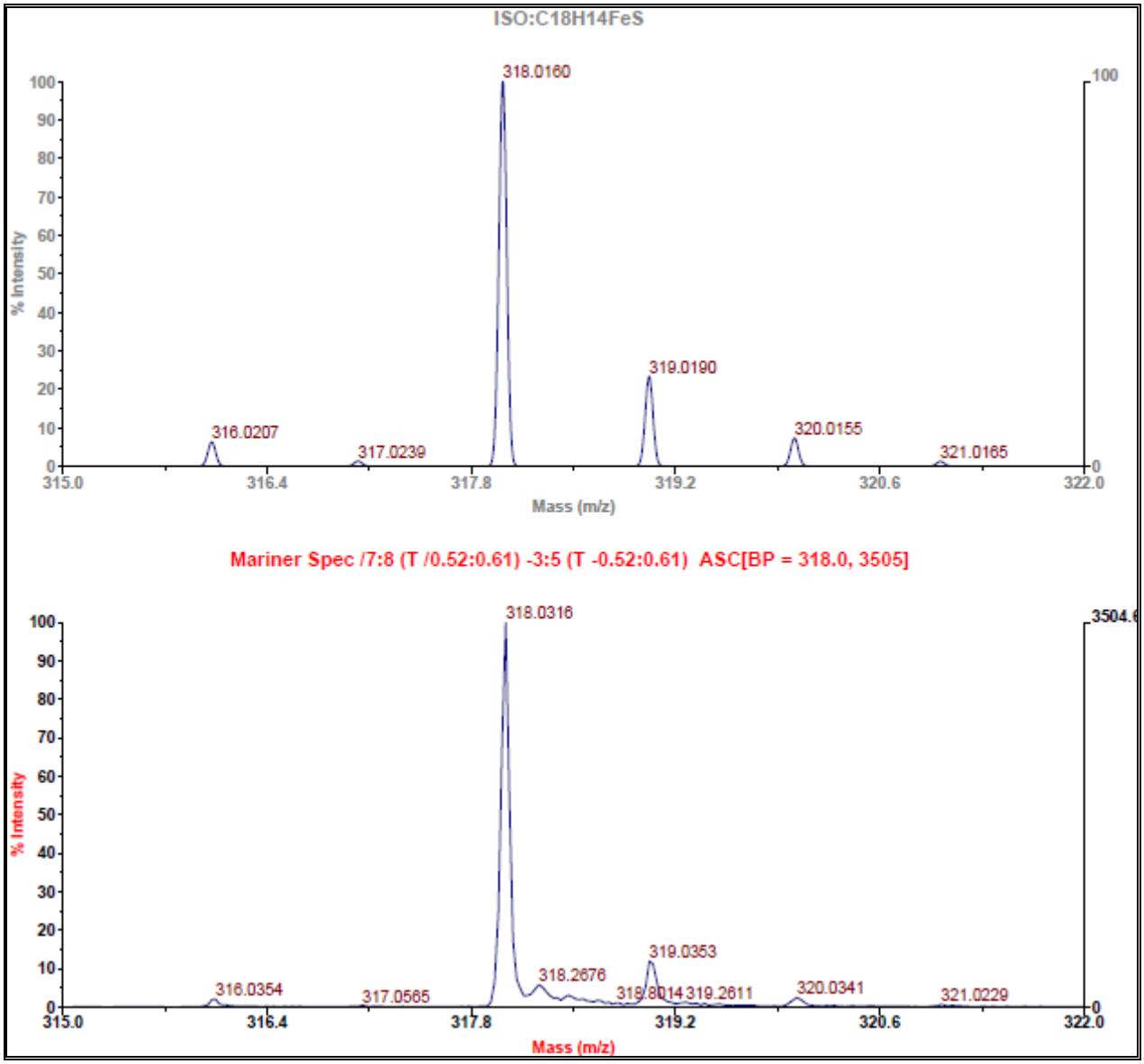


Figure S7. Experimental (bottom) and simulated (top) ESI mass spectra of 2-ferrocenylbenzo[*b*]thiophene **(A).**

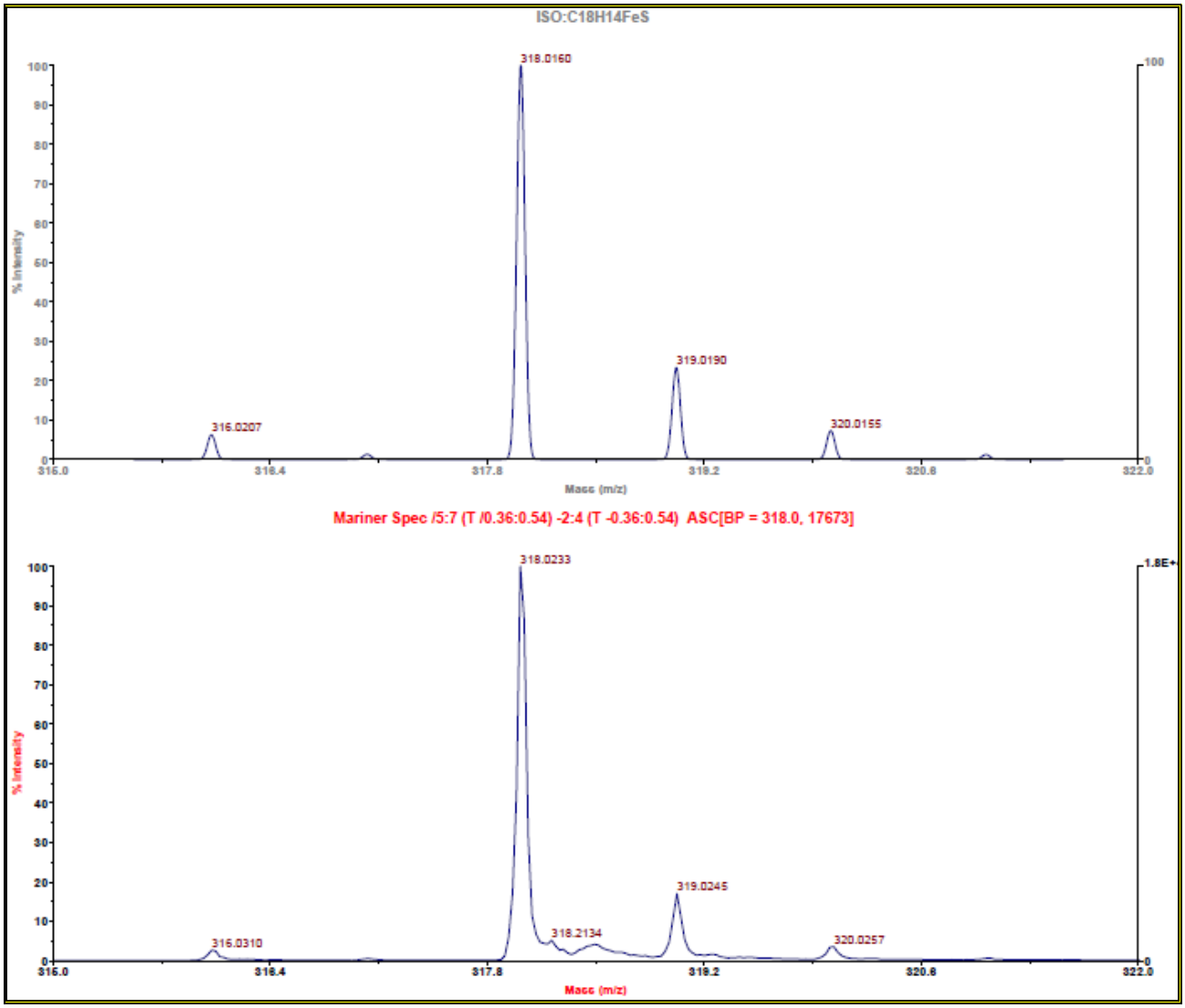


Figure S8. Experimental (bottom) and simulated (top) ESI mass spectra of 3-ferrocenylbenzo[*b*]thiophene **(B).**

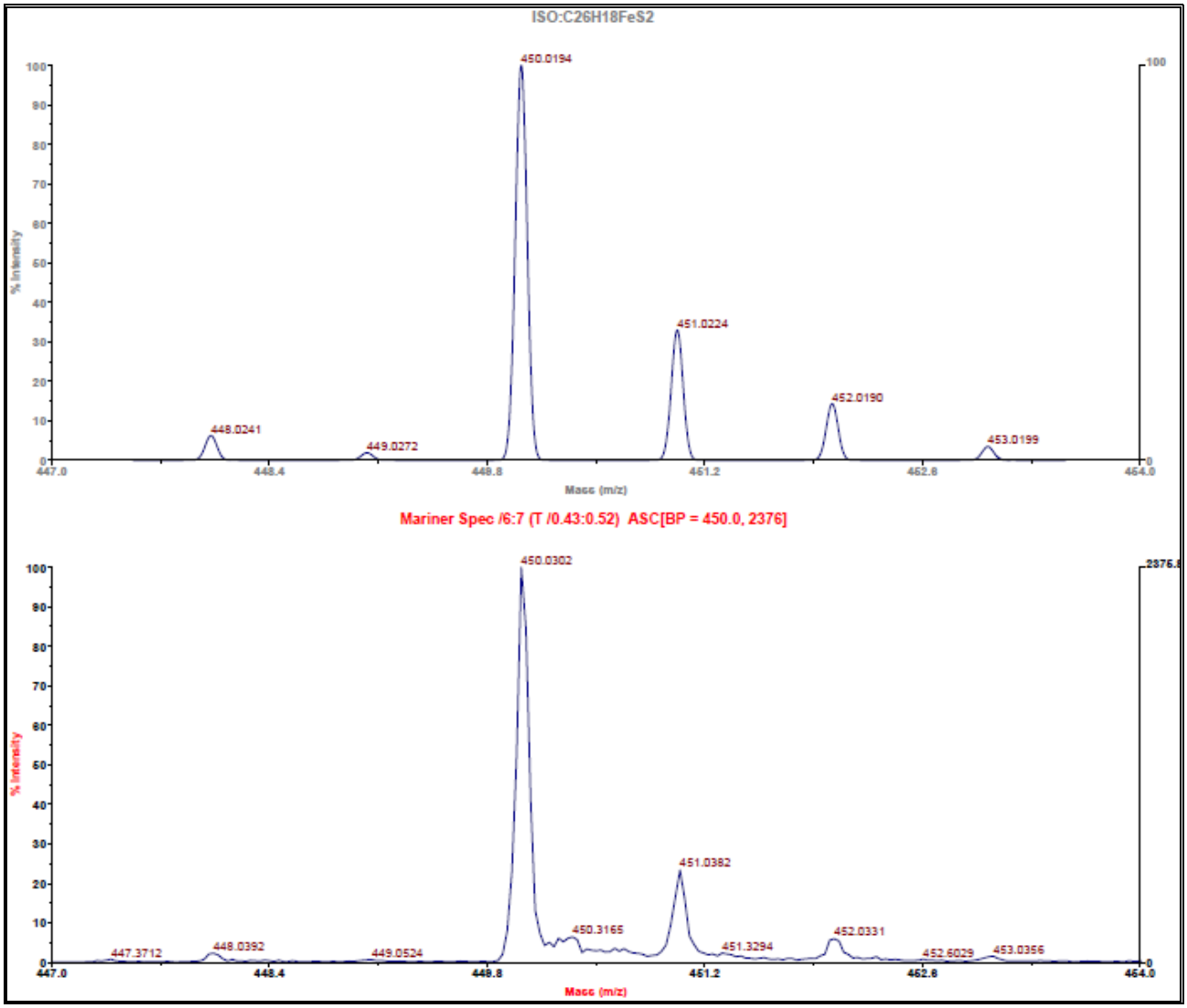


Figure S9. Experimental (bottom) and simulated (top) ESI mass spectra of 1,1'-bis(2-benzo[*b*]thiophene)ferrocenes **(C1 + C2).**

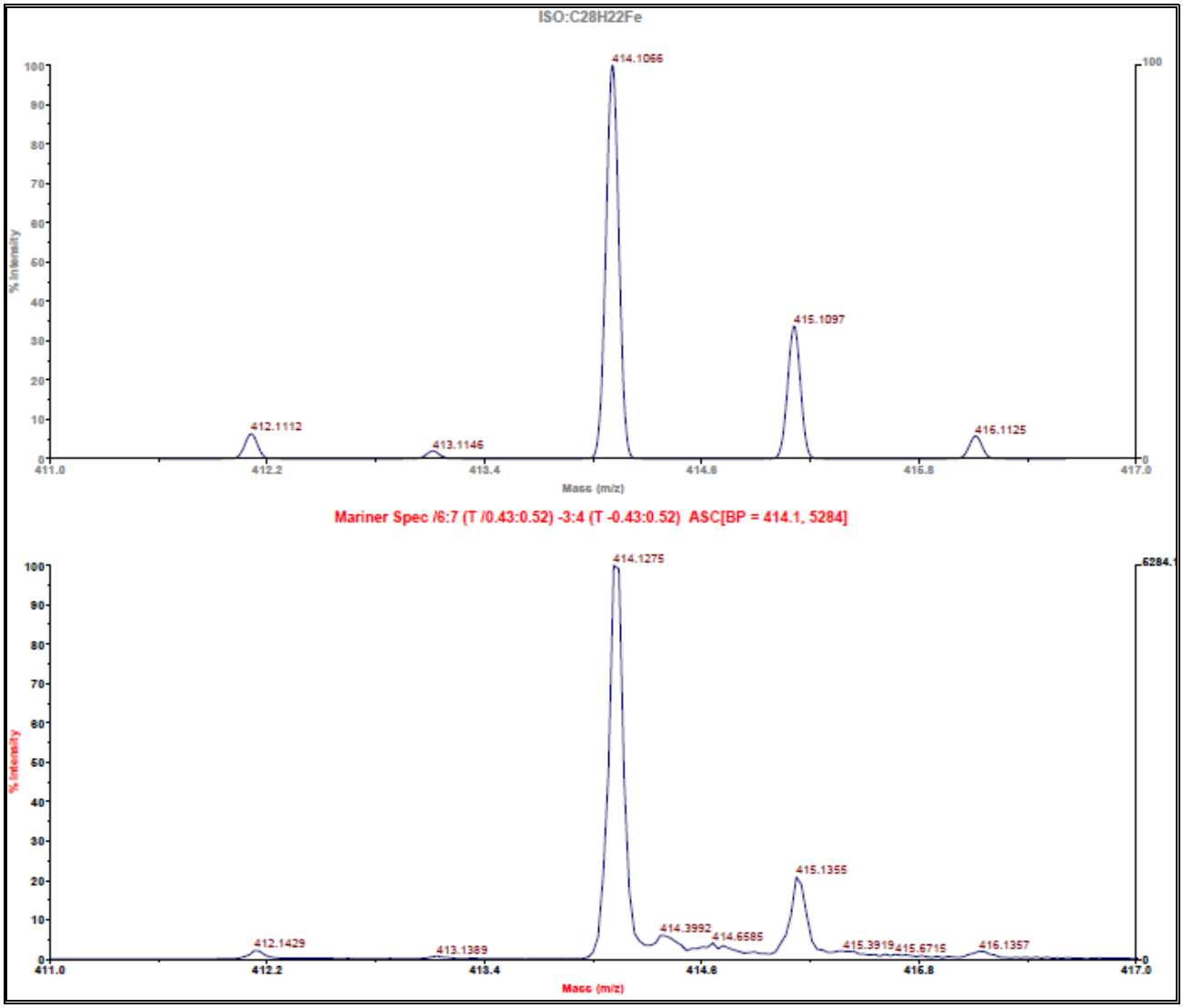


Figure S10. Experimental (bottom) and simulated (top) ESI mass spectra of 1,1'-bis(2-indene)ferrocene **(D).**

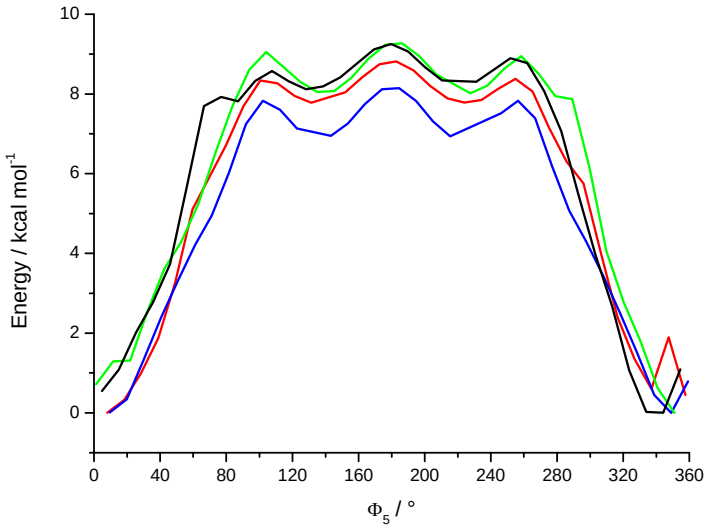


Figure S11. Energy profile along the dihedral Φ_5 of **C1** (red), **C2** (black), **D1** (blue) and **D2** (green); energies are relative to the energy of the initial structure which corresponds to the global minimum. The level of theory is BP86+D3BJ/TZP small core.

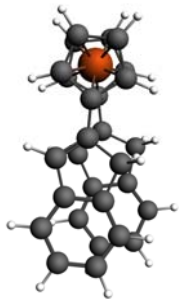
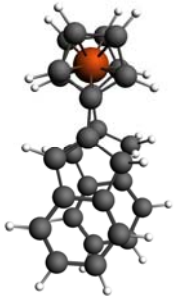
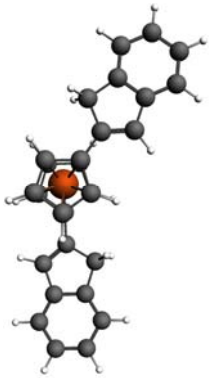
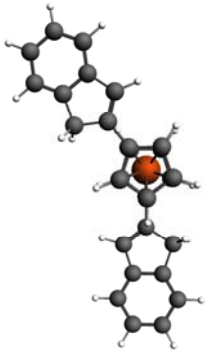
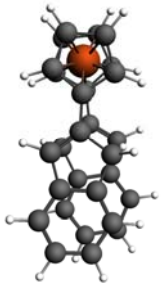
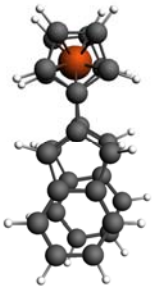
			
D1	**D1$^+$**	**D1’**	**D1’’**
			
D2	**D2$^+$**	**D2’**	**D2’’**

Figure S12. Fully optimized conformers of **D1** and **D2**; level of theory: BP86+D3/TZ2P small core.

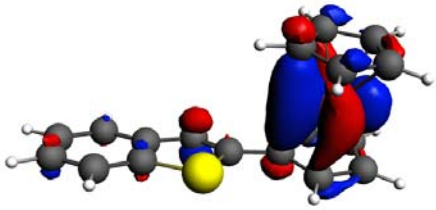
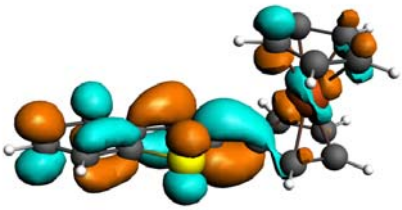
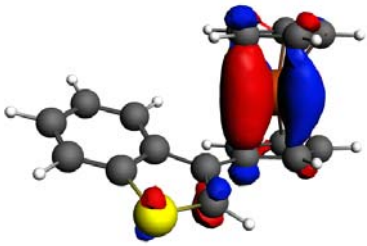
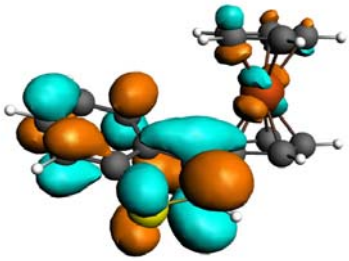
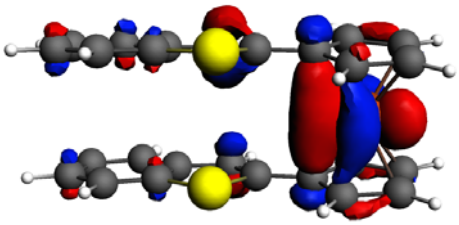
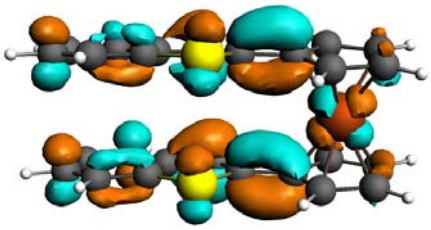
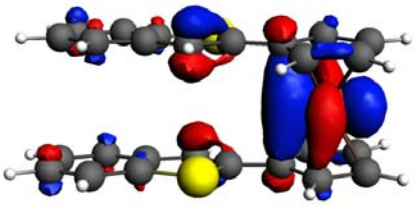
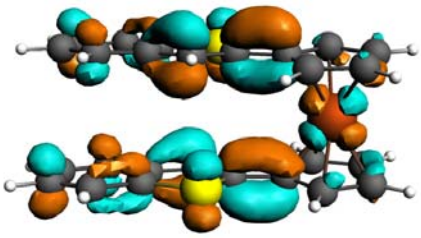
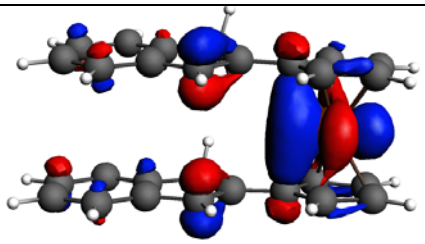
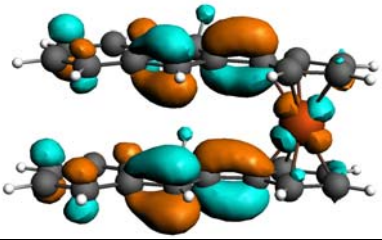
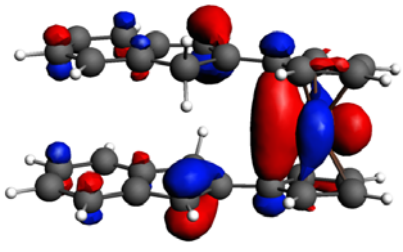
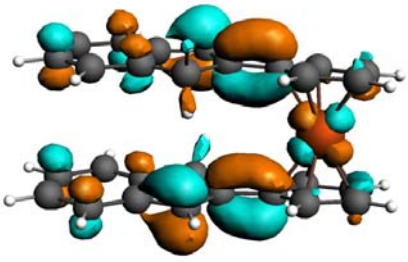
	
A: HOMO	**A: LUMO**
	
B: HOMO	**B: LUMO**
	
C1: HOMO	**C1: LUMO**
	
C2: HOMO	**C2: LUMO**
	
D1: HOMO	**D1: LUMO**
	
D2: HOMO	**D2: LUMO**

Figure S13. HOMO and LUMO of neutral complexes; level of theory: BP86/TZ2P small core (**A** and **B**) and BP86+D3/TZ2P small core (**C1**, **C2**, **D1** and **D2**).