

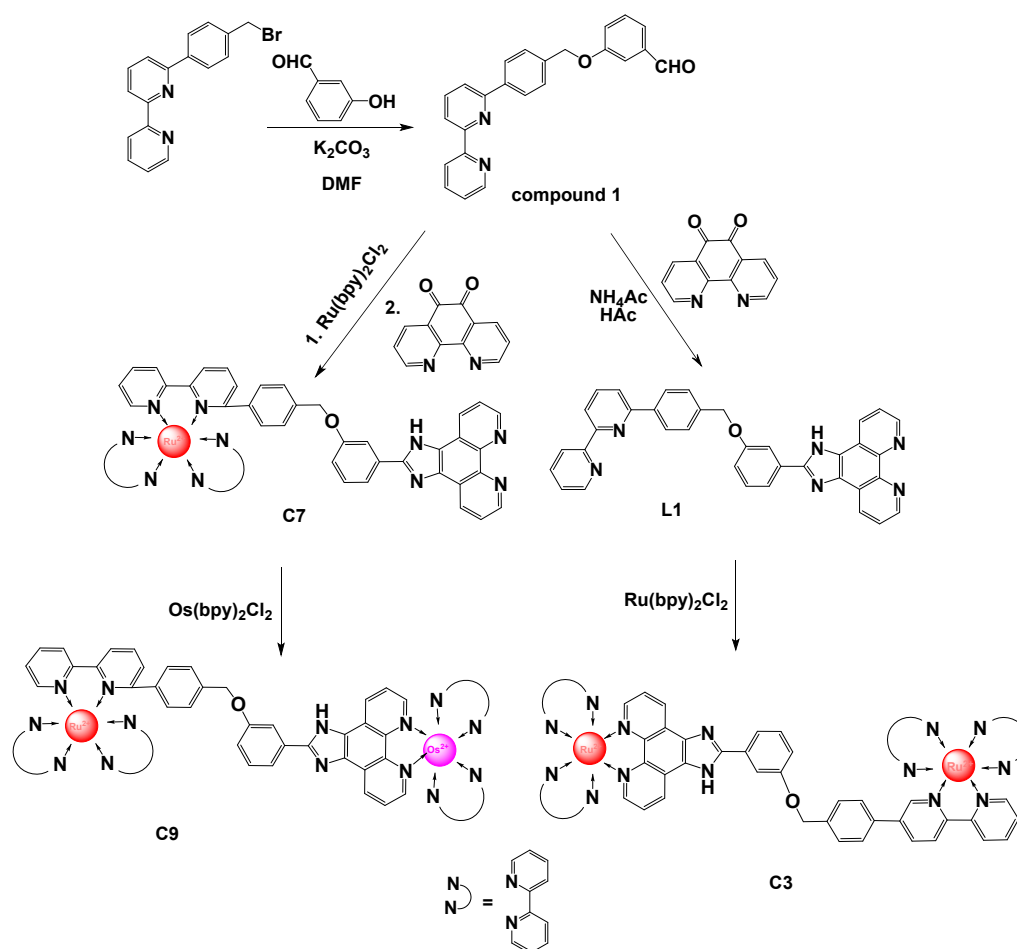
Energy transfer in metal-exchange binuclear complexes covalently linked by asymmetric ligands

Weijun Dai, Shiwen Yu, Wen Xu, Ci Kong, Zining Liu, Hongju Yin, Chixian He, Jian-Jun Liu*,

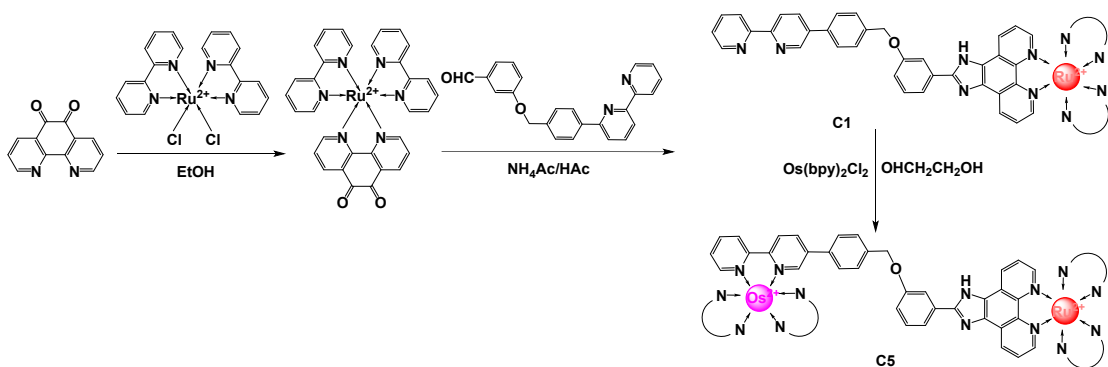
Feixiang Cheng*

College of Chemistry and Environmental Science, Qujing Normal University, Qujing 655011

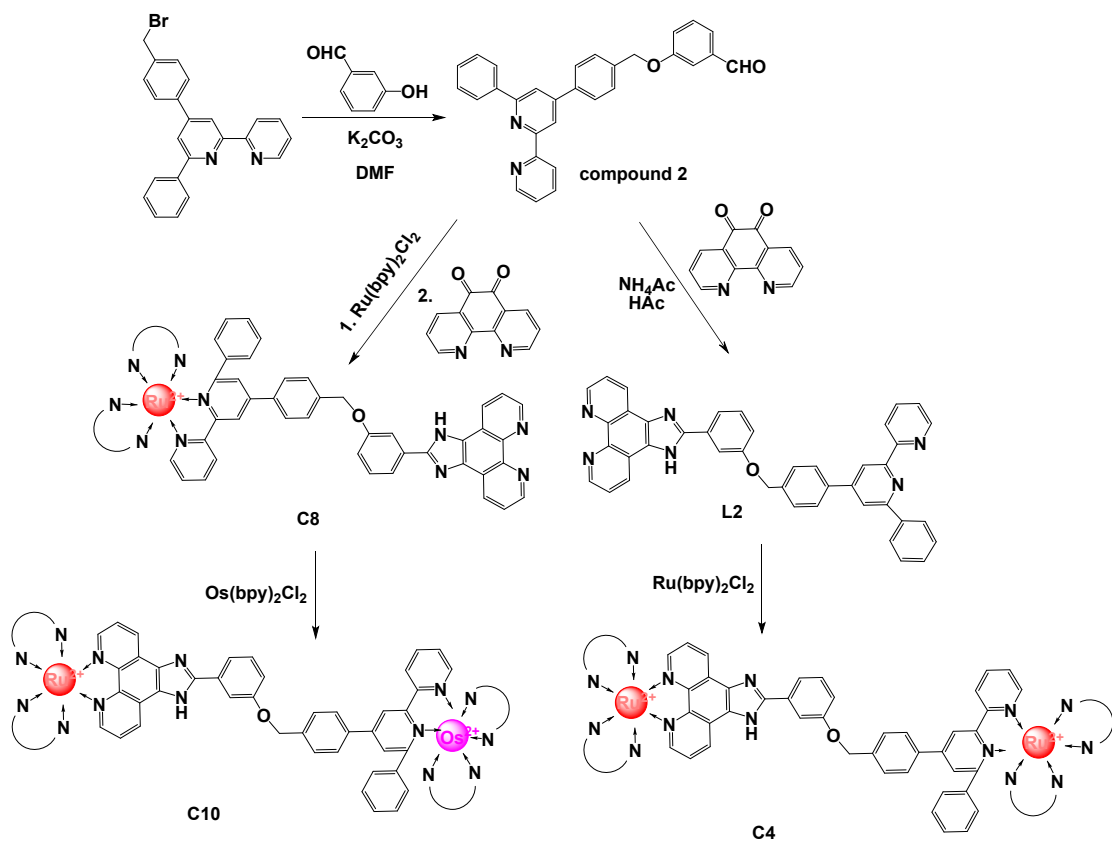
E-mail: jjliu302@163.com; chengfx2019@163.com



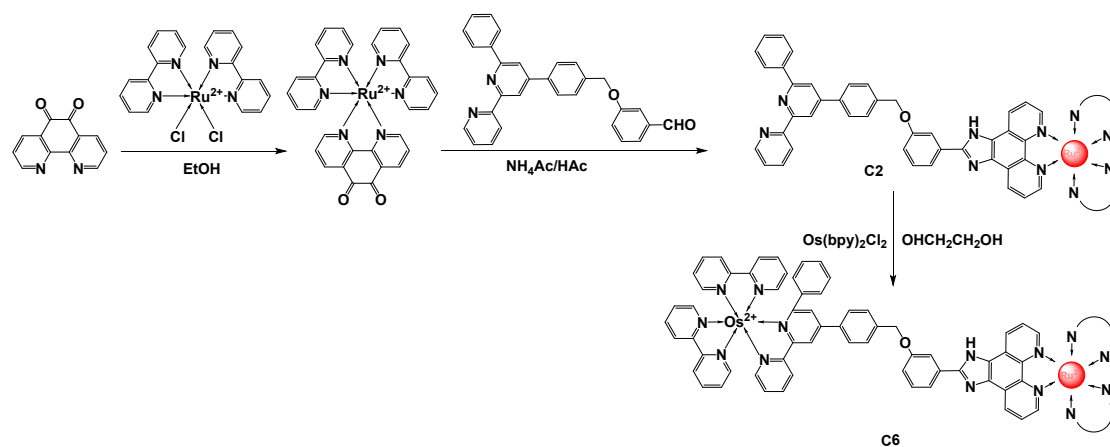
Scheme S1. Chemical structures of the target monometallic **C7**, homometallic **C3**, heterometallic **C9** complexes and corresponding bridging ligand **L1**. (The counter ions are omitted for clarity. The same below).



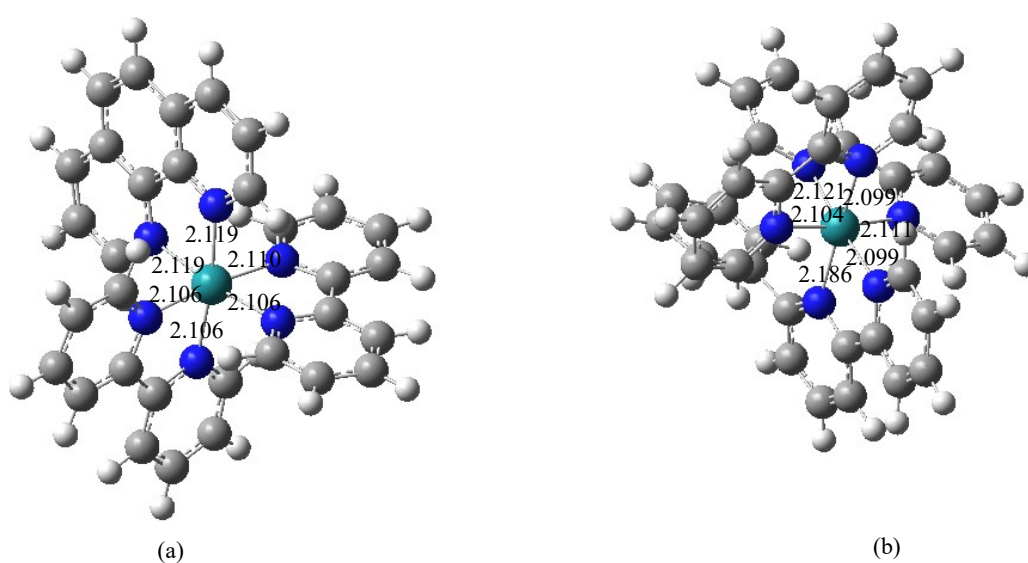
Scheme S2. Chemical structures of the target monometallic **C1**, homometallic **C5** complexes.



Scheme S3. Chemical structures of the target monometallic complex **C8**, homometallic complexes **C4**, **C10** bridged by ligand **L2**.



Scheme S4. Chemical structures of the target monometallic complex C2, heterometallic complex C6.



Scheme S5. The Ru-N bond lengths of octahedral Ru(bpy)₂(1,10-phenanthroline) moieties of complex C4, C8 and C10 presented in (a) and Ru-N bond lengths of the octahedral Ru(bpy)₂(6-phenyl-2,2'-bipyridine) of complexes C2, C4 and C6 presented in (b).

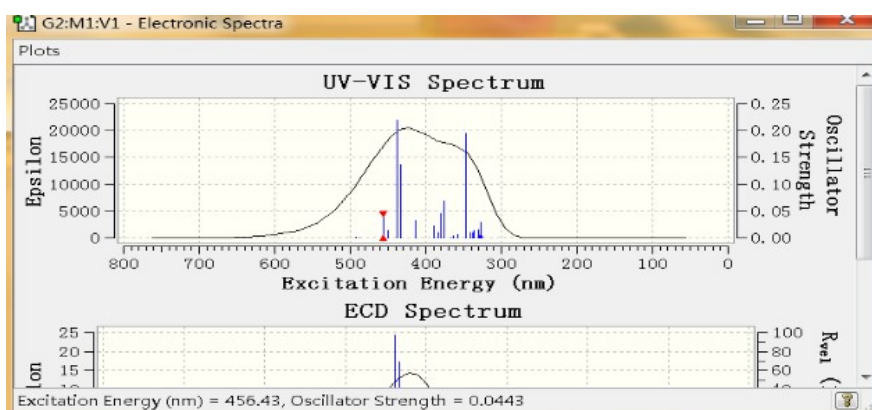


Figure S1. The UV-Vis spectrum of TD-DFT calculation of C1.

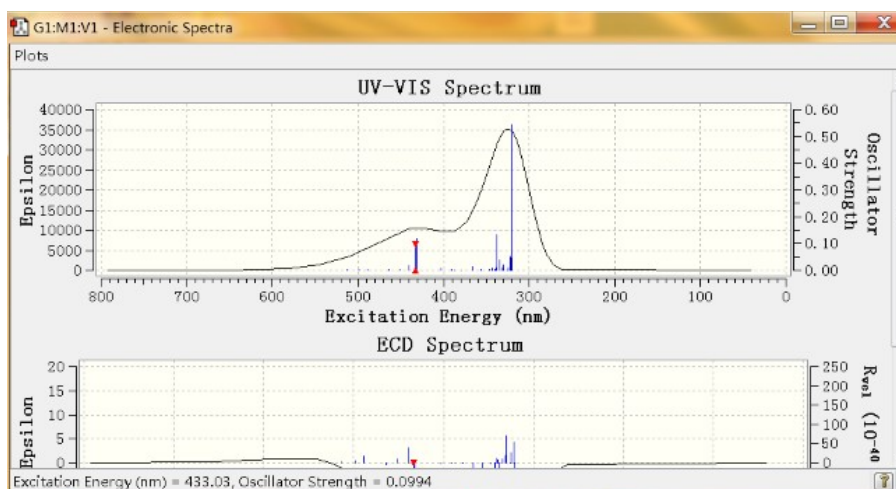


Figure S2. The UV-Vis spectrum of TD-DFT calculation of C7.

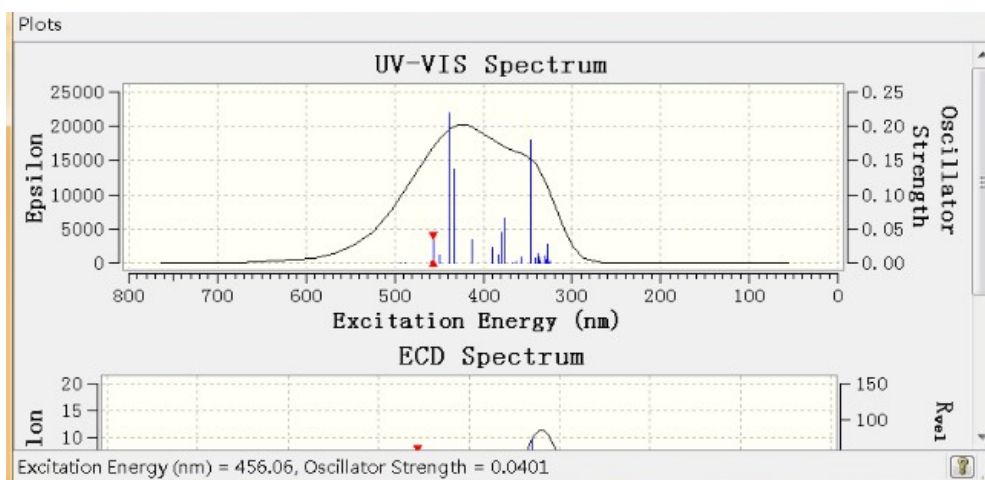


Figure S3. The UV-Vis spectrum of TD-DFT calculation of C2.

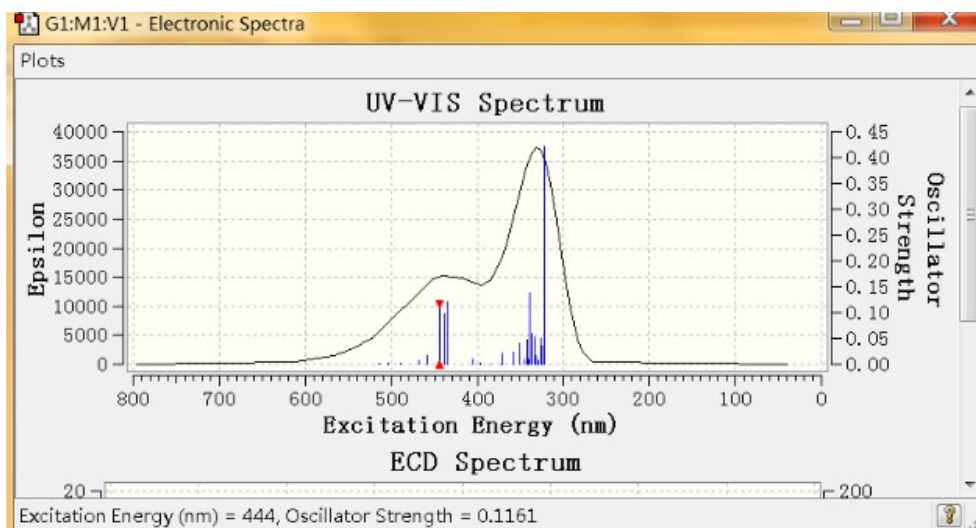


Figure S4. The UV-Vis spectrum of TD-DFT calculation of C8.

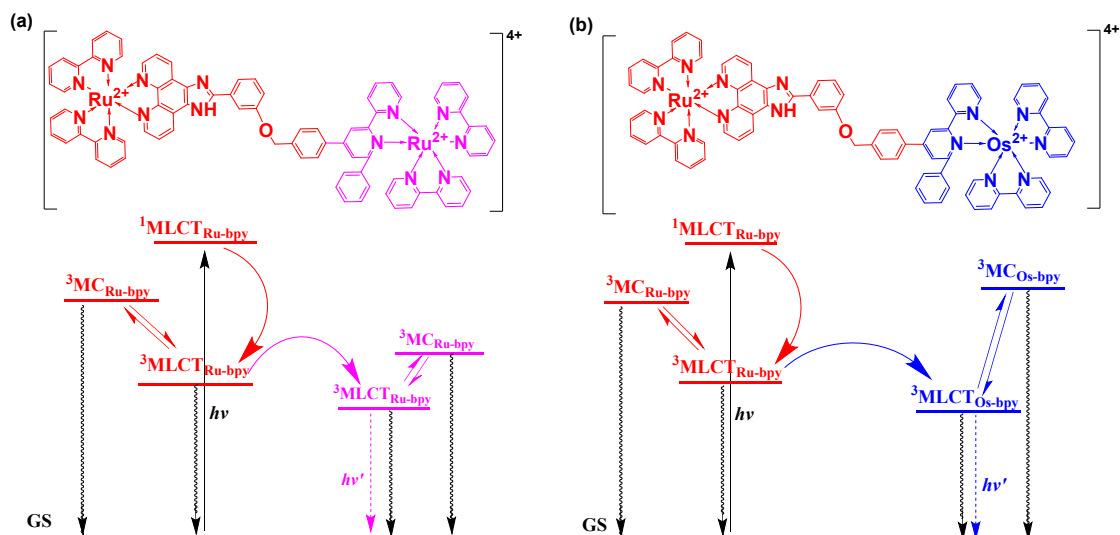


Figure S5. Energy level mechanism of the emissive state of multinuclear complexes C4 (a), C6 (b), where the straight line represents excitation; the dotted line represents luminescence, and the wavy line represents radiationless decay.

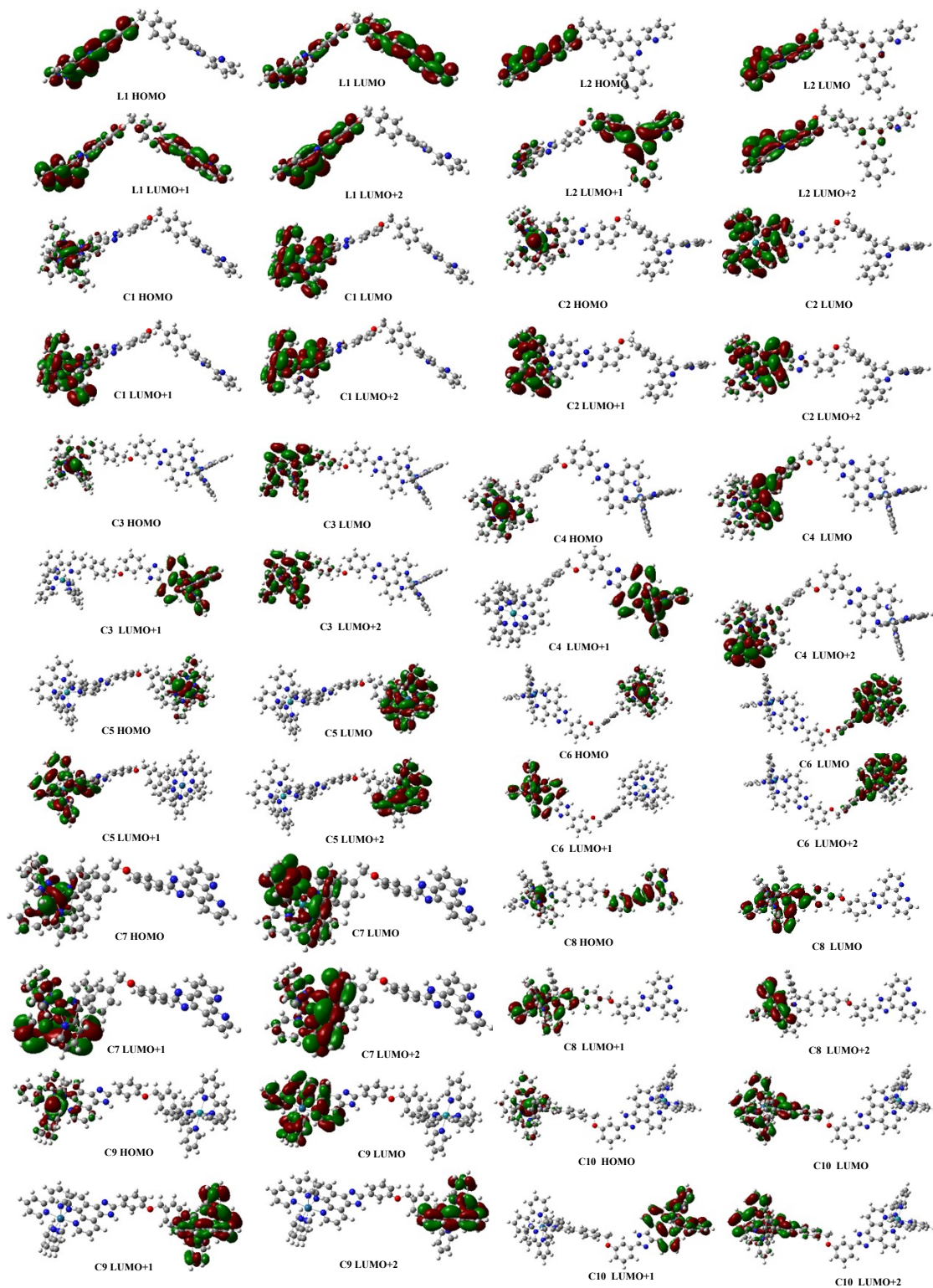


Figure S6. The HOMO and the LUMOs of all complexes.

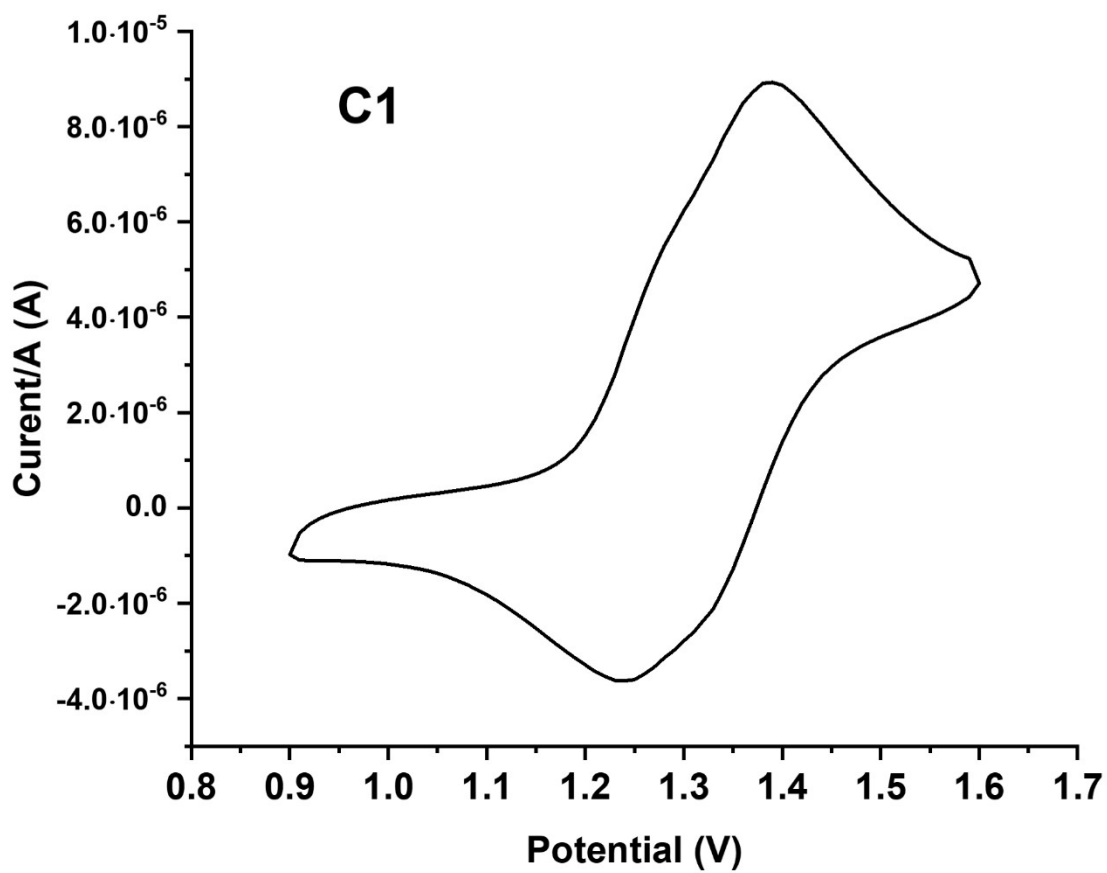


Figure S7. Oxidation cyclic voltammetry of complex C1.

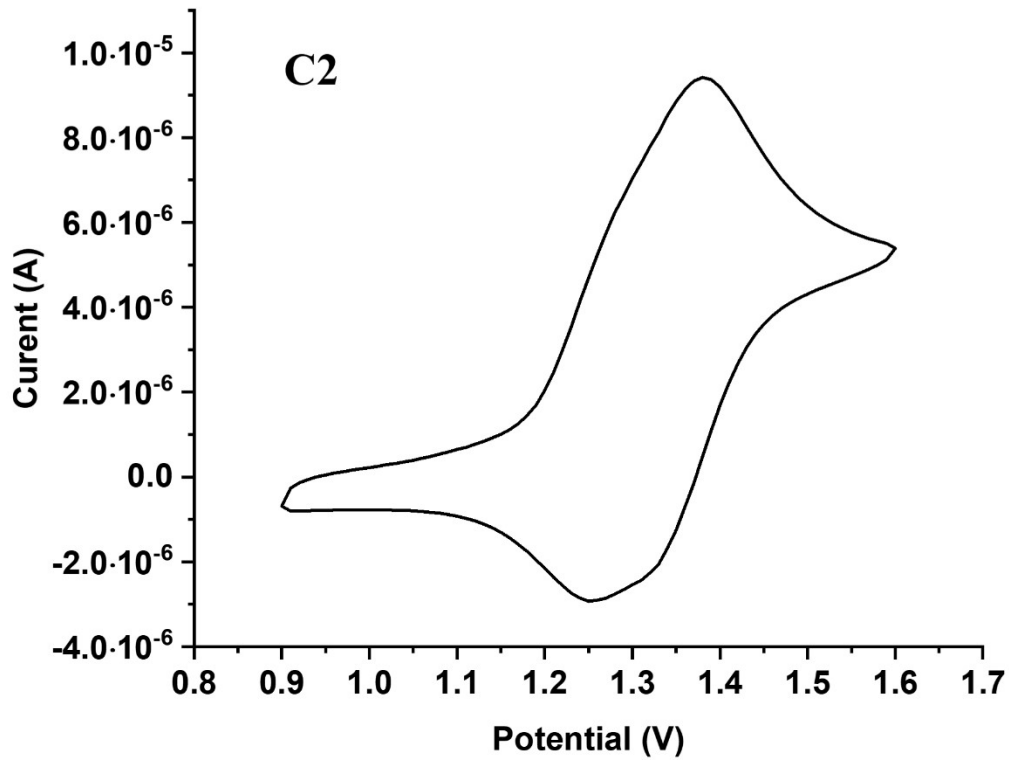


Figure S8. Oxidation cyclic voltammetry of complex C2.

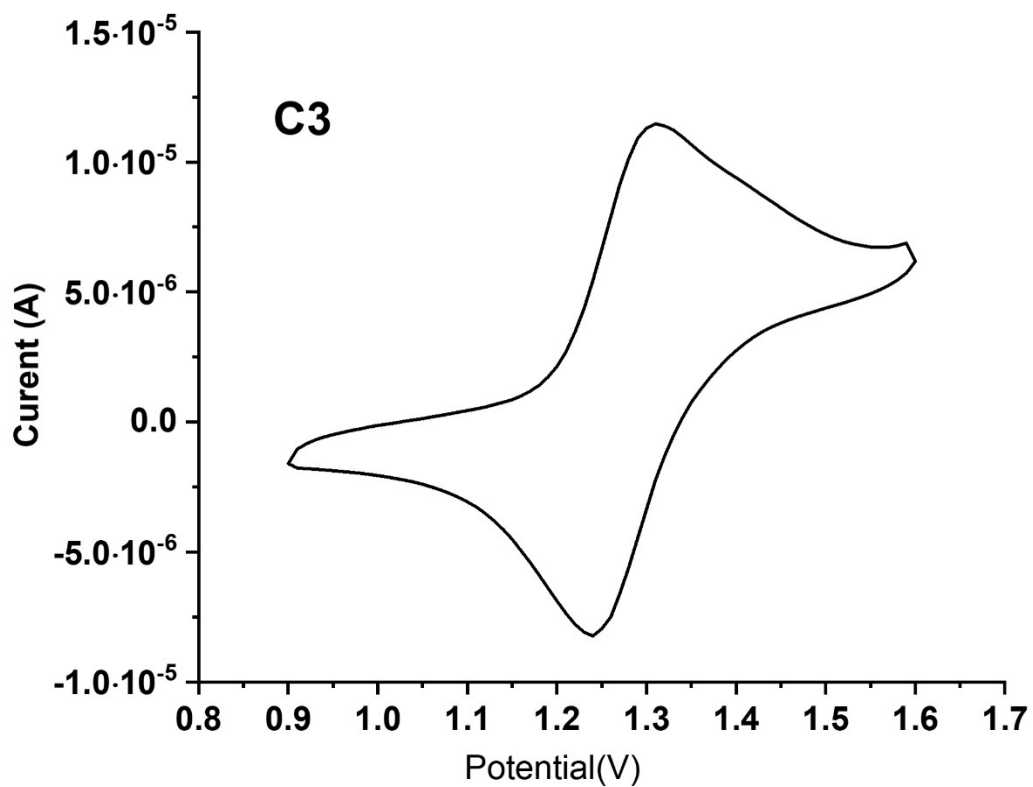


Figure S9. Oxidation cyclic voltammetry of complex C3.

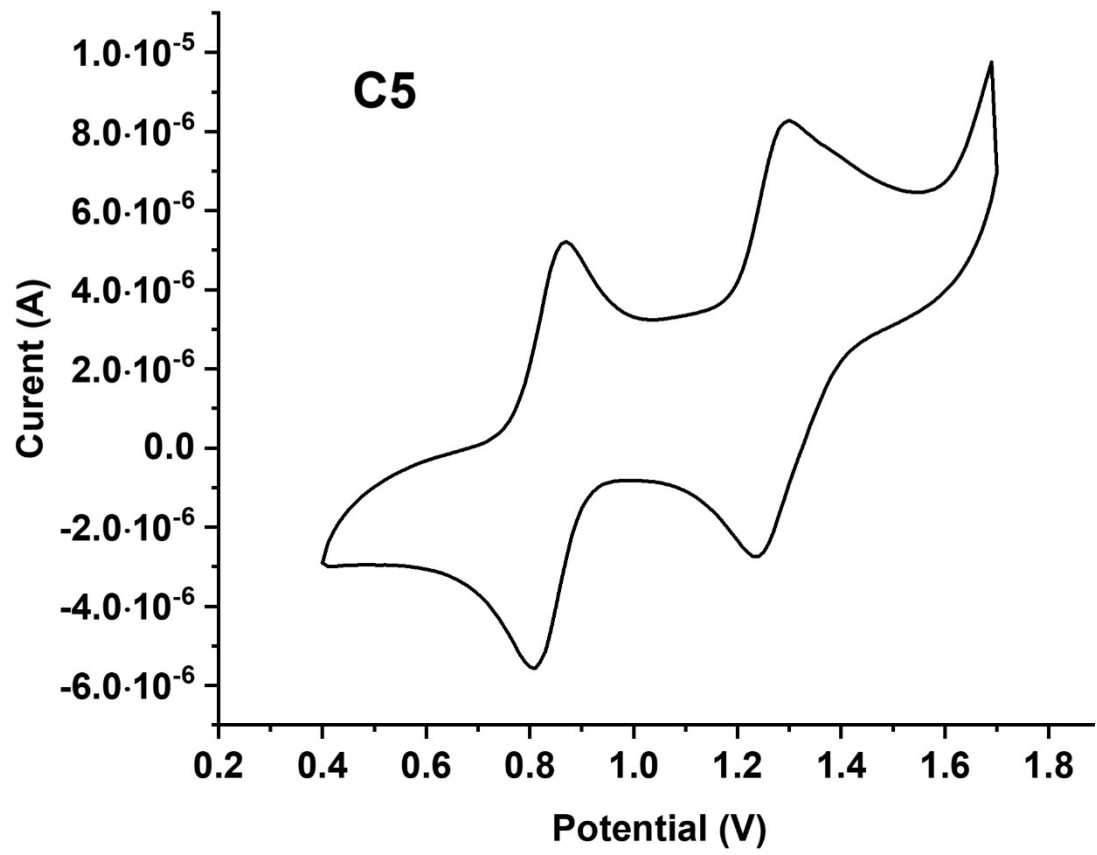


Figure S10. Oxidation cyclic voltammetry of complex C5.

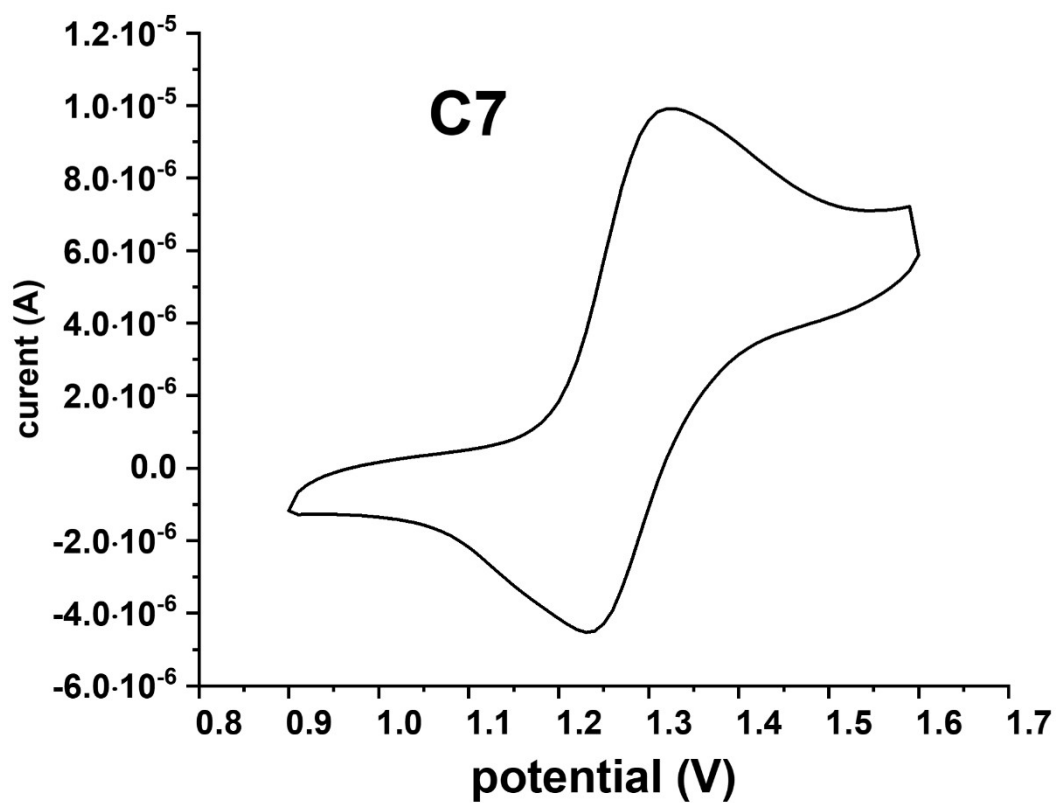


Figure S11. Oxidation cyclic voltammetry of complex C7.

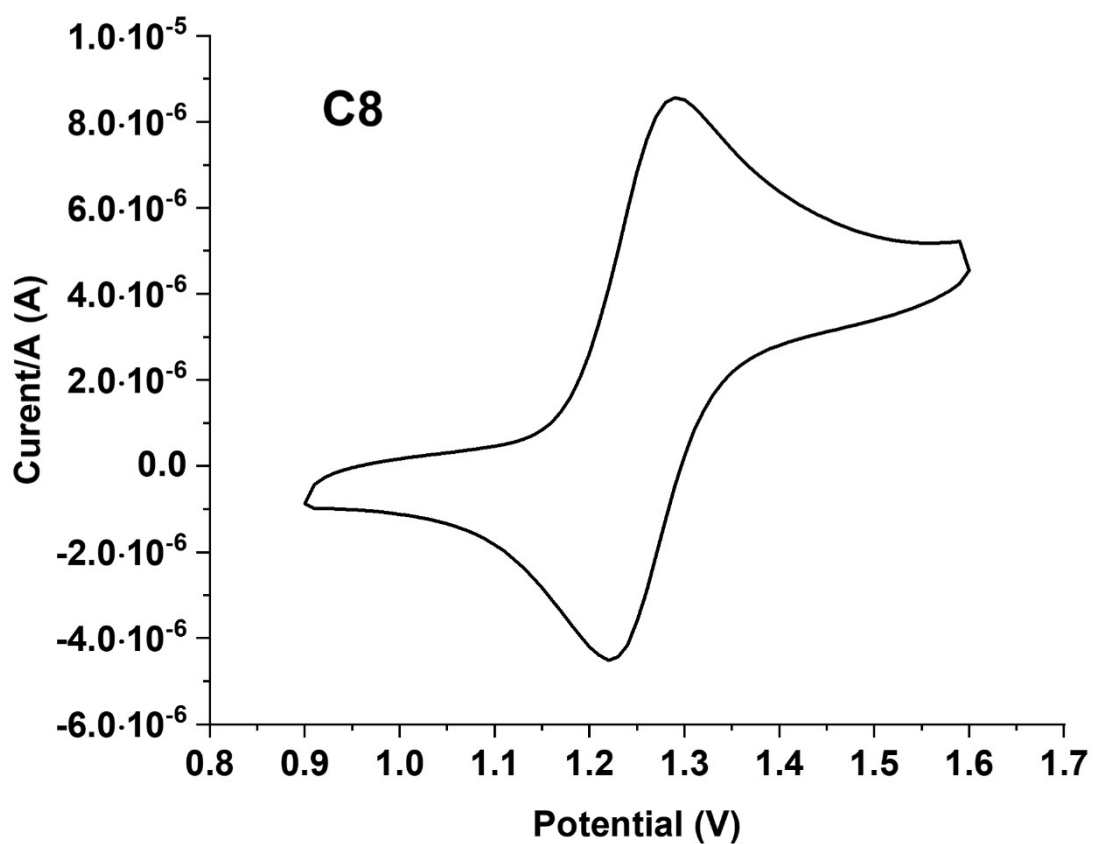


Figure S12. Oxidation cyclic voltammetry of complex C8.

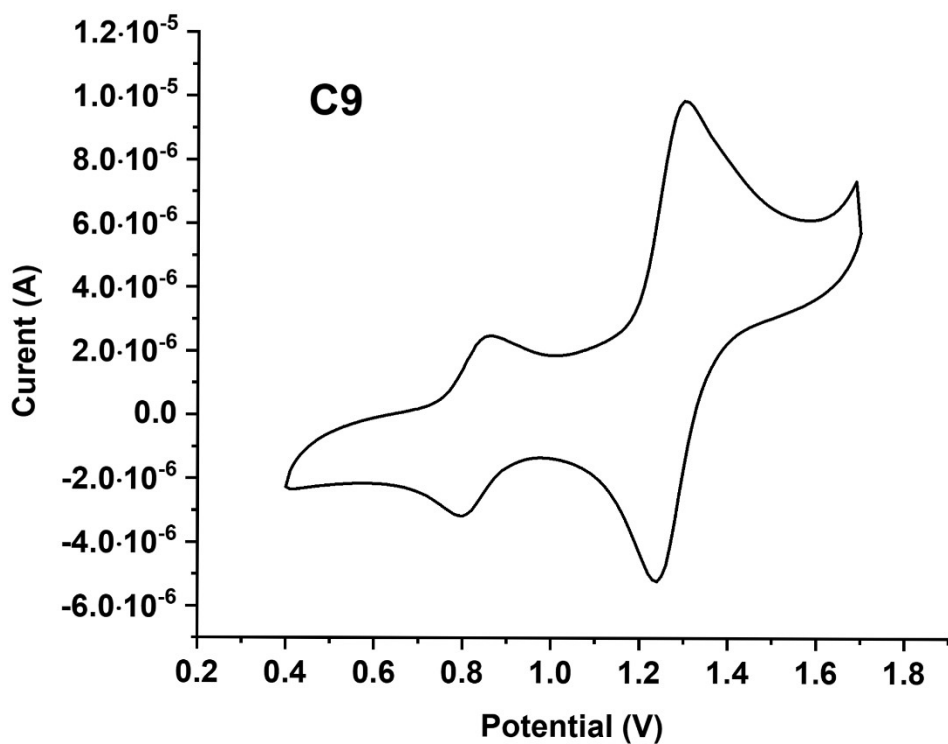


Figure S13. Oxidation cyclic voltammetry of complex C9.

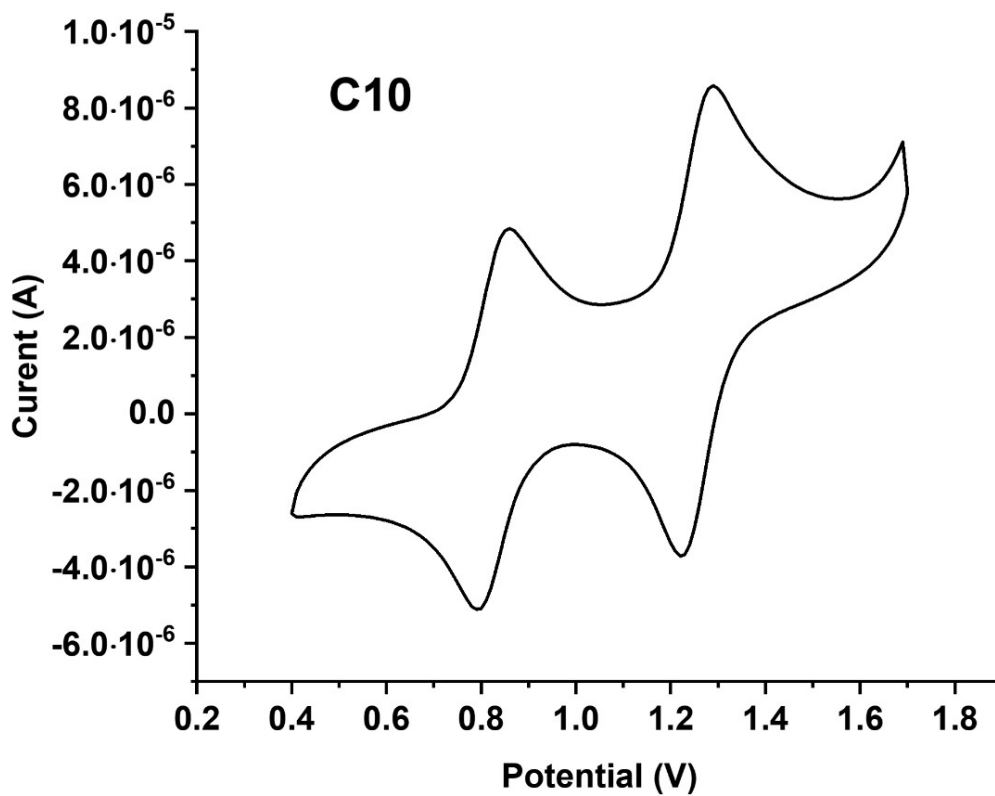


Figure S14. Reduction cyclic voltammetry of complex C10.

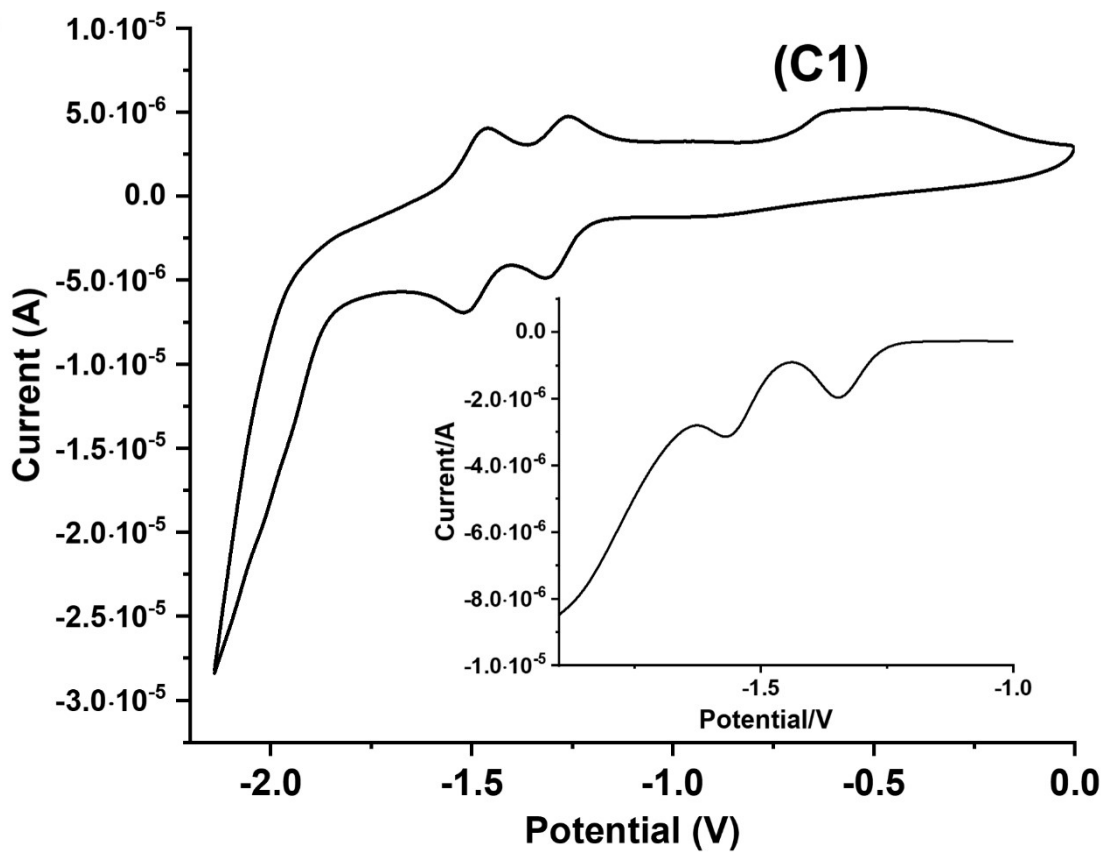


Figure S15. Reduction cyclic voltammetry of complex C1.

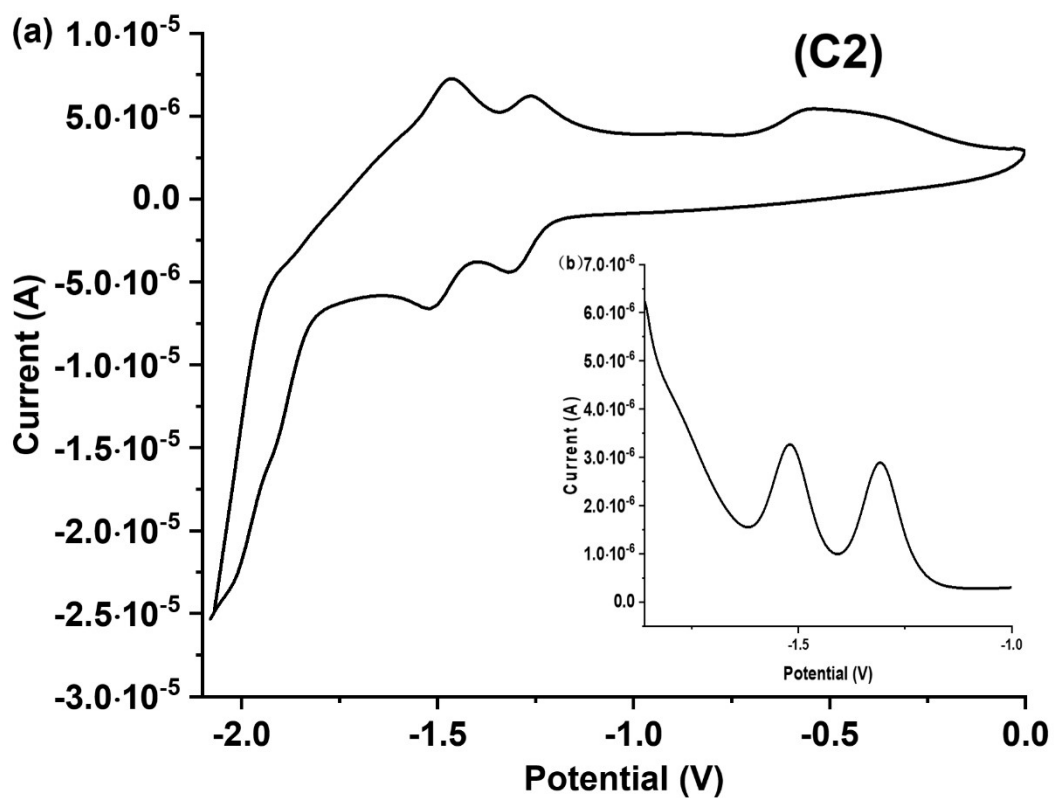


Figure S16. Reduction cyclic voltammetry of complex C2.

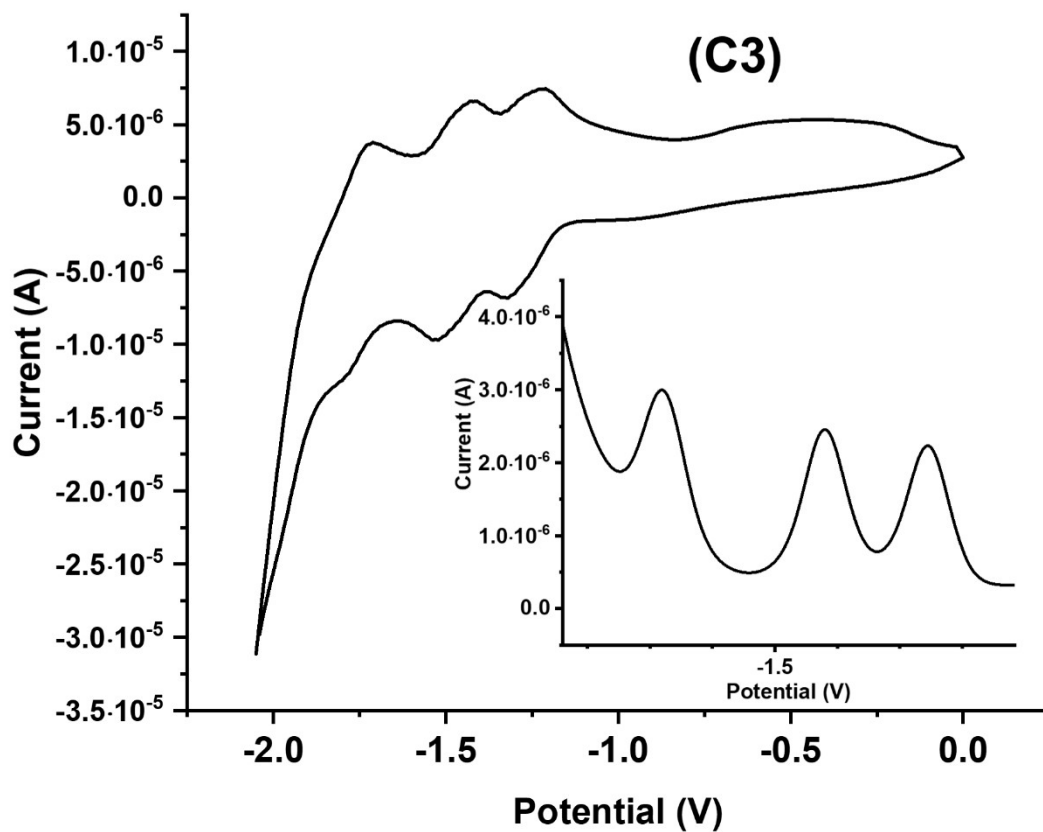


Figure S17. Reduction cyclic voltammetry of complex C3.

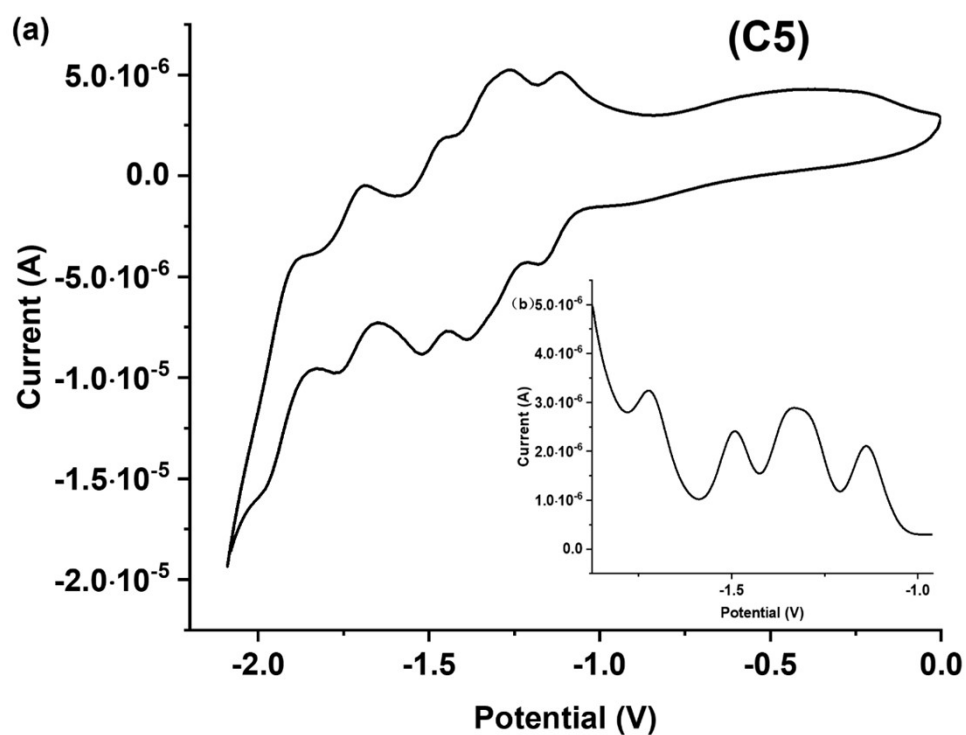


Figure S18. Reduction cyclic voltammetry of complex C5.

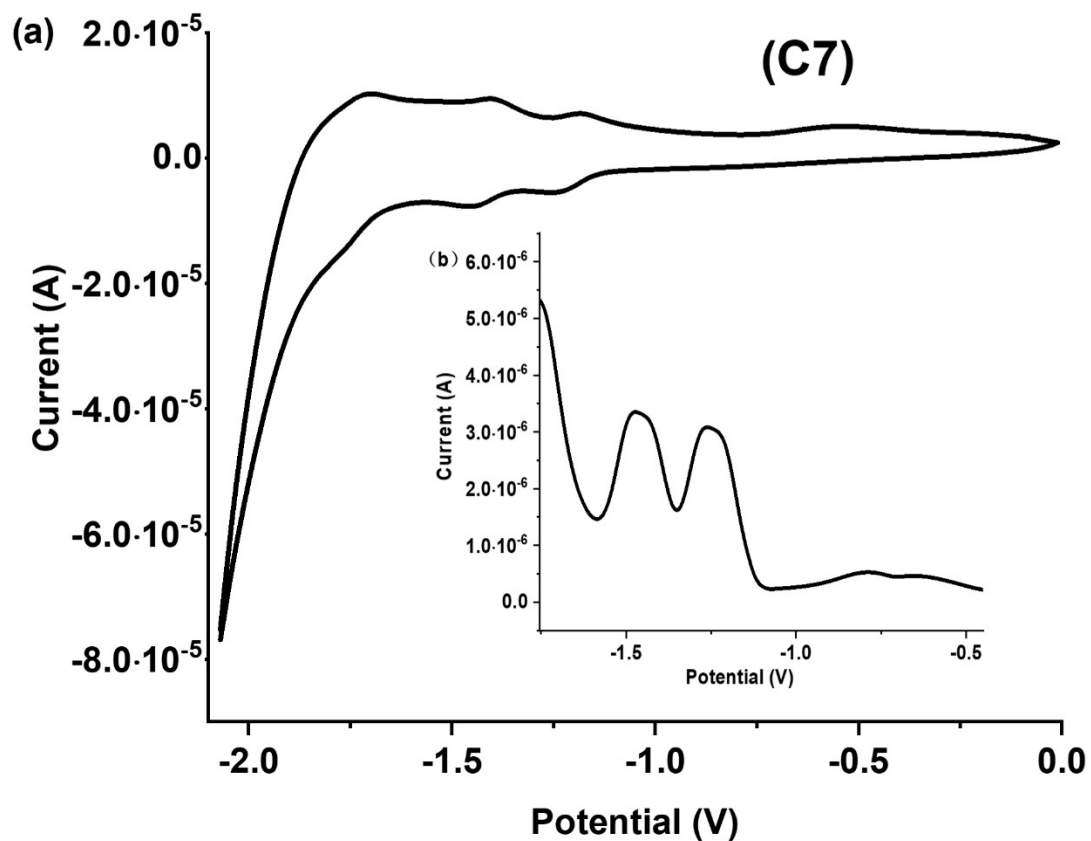


Figure S19. Reduction cyclic voltammetry of complex C7.

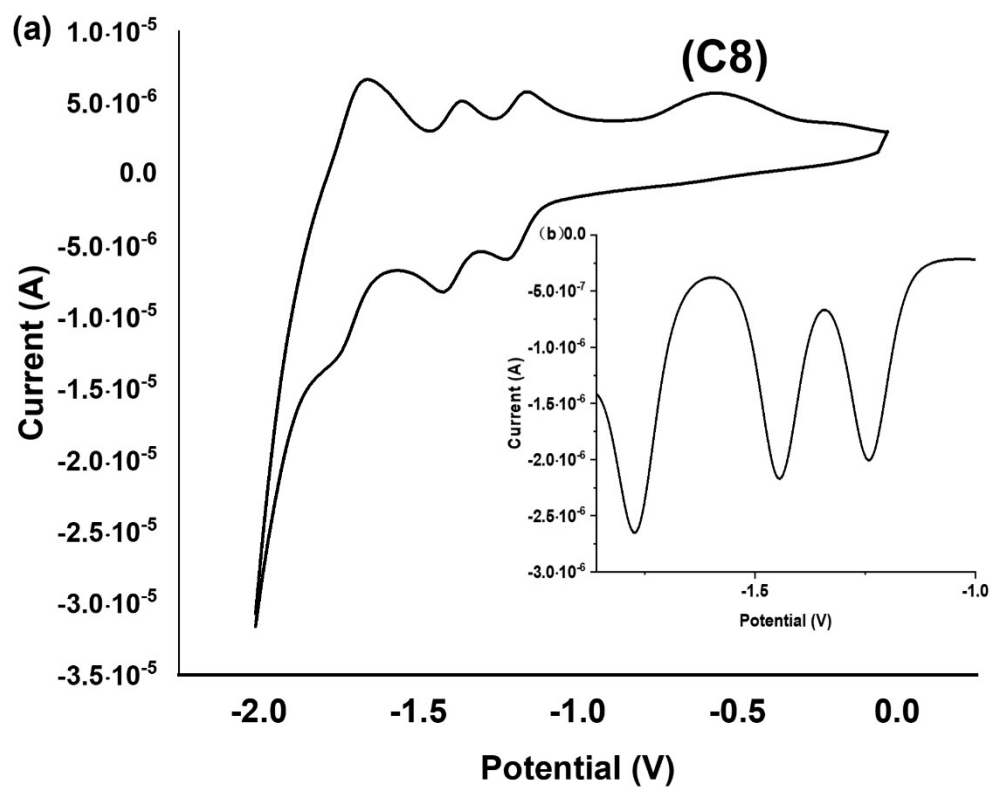


Figure S20. Reduction cyclic voltammetry of complex C8.

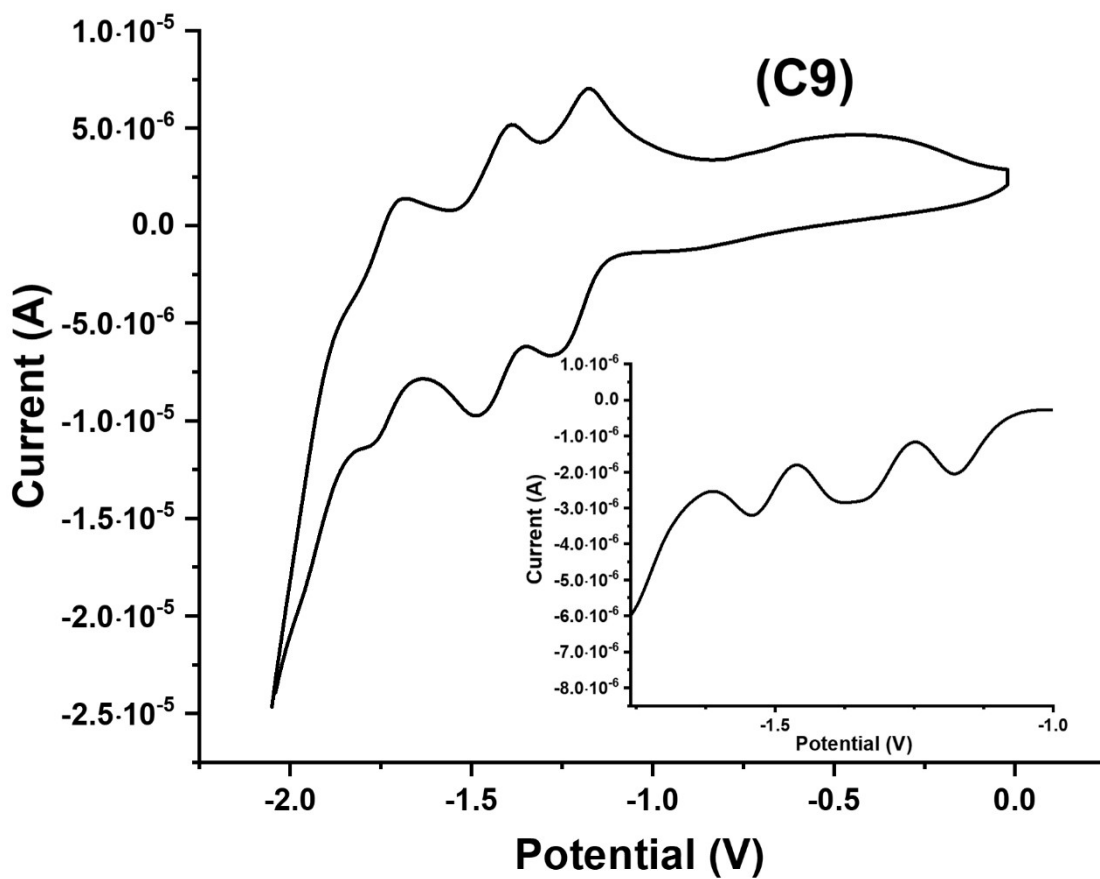


Figure S21. Reduction cyclic voltammetry of complex C9.

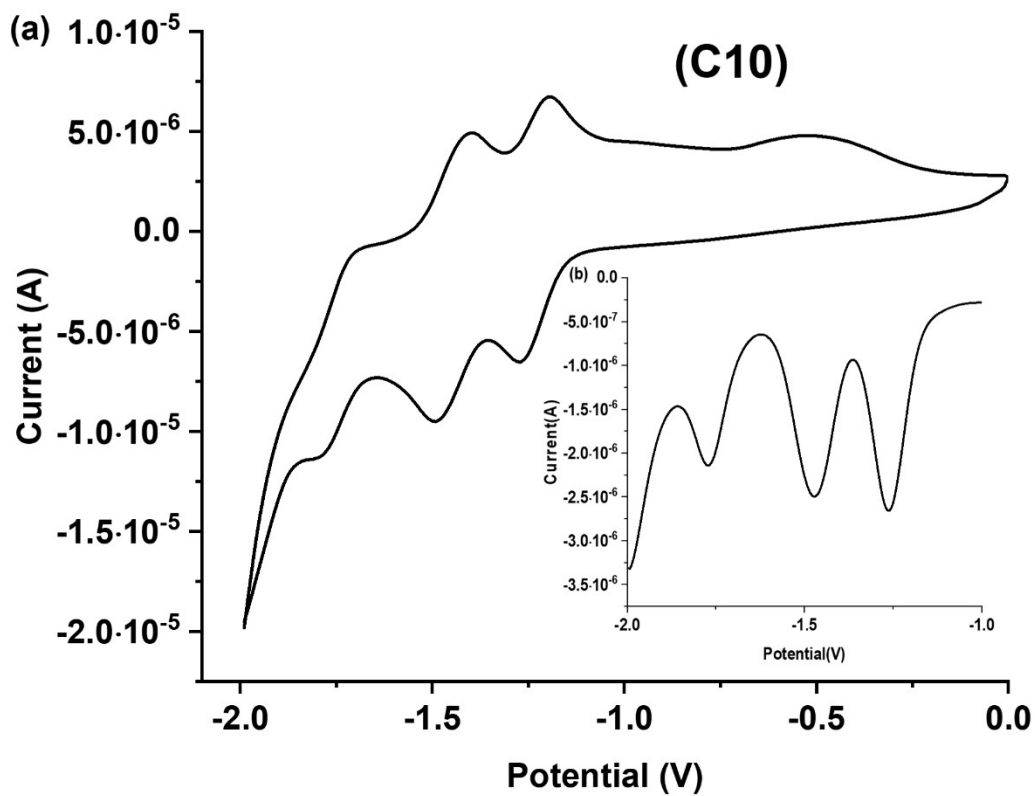


Figure S22. Reduction cyclic voltammetry of complex C10.

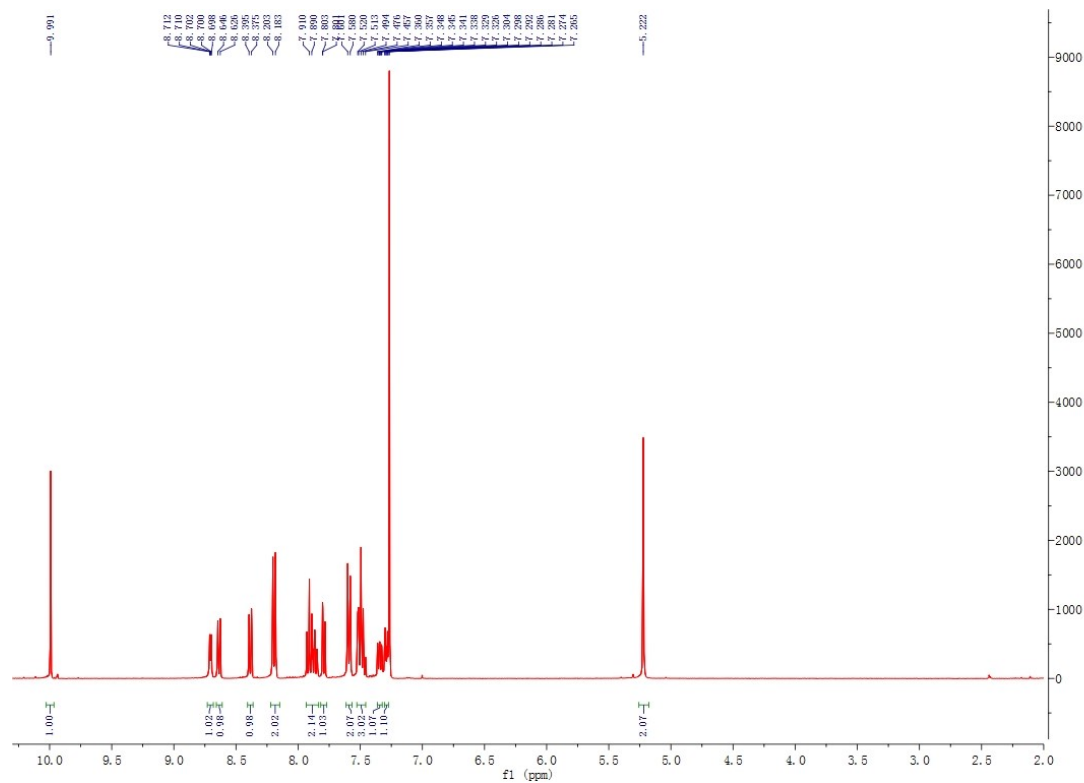


Figure S23. ^1H NMR (400 MHz, CDCl_3) spectrum of compound 1.

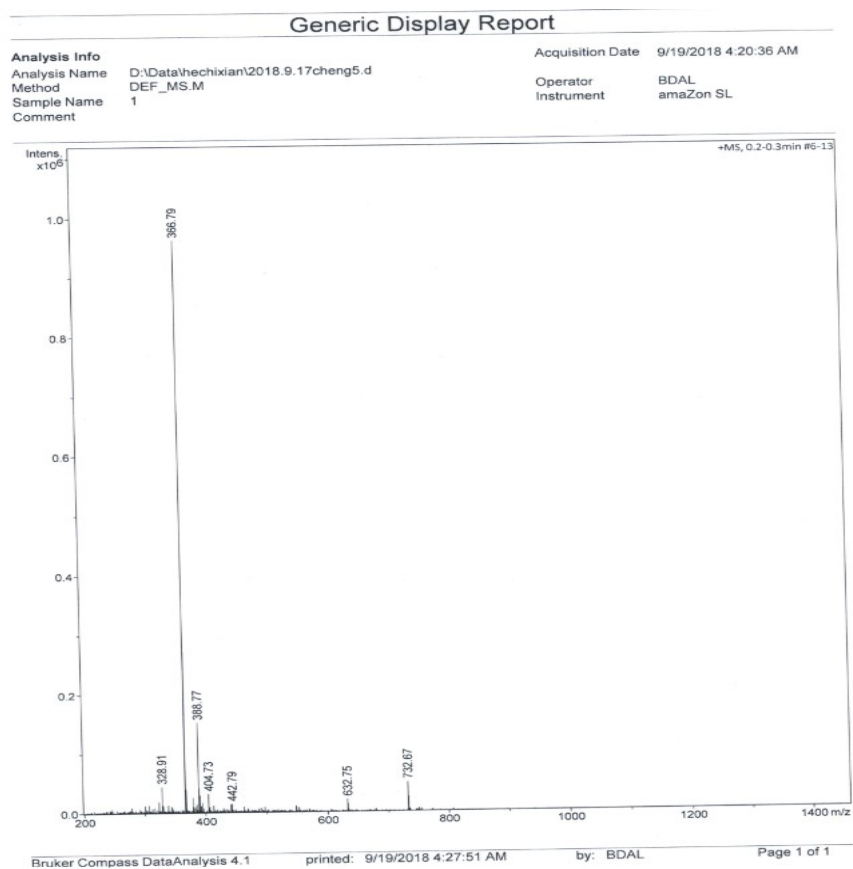


Figure S24. ESI-MS of compound 1.

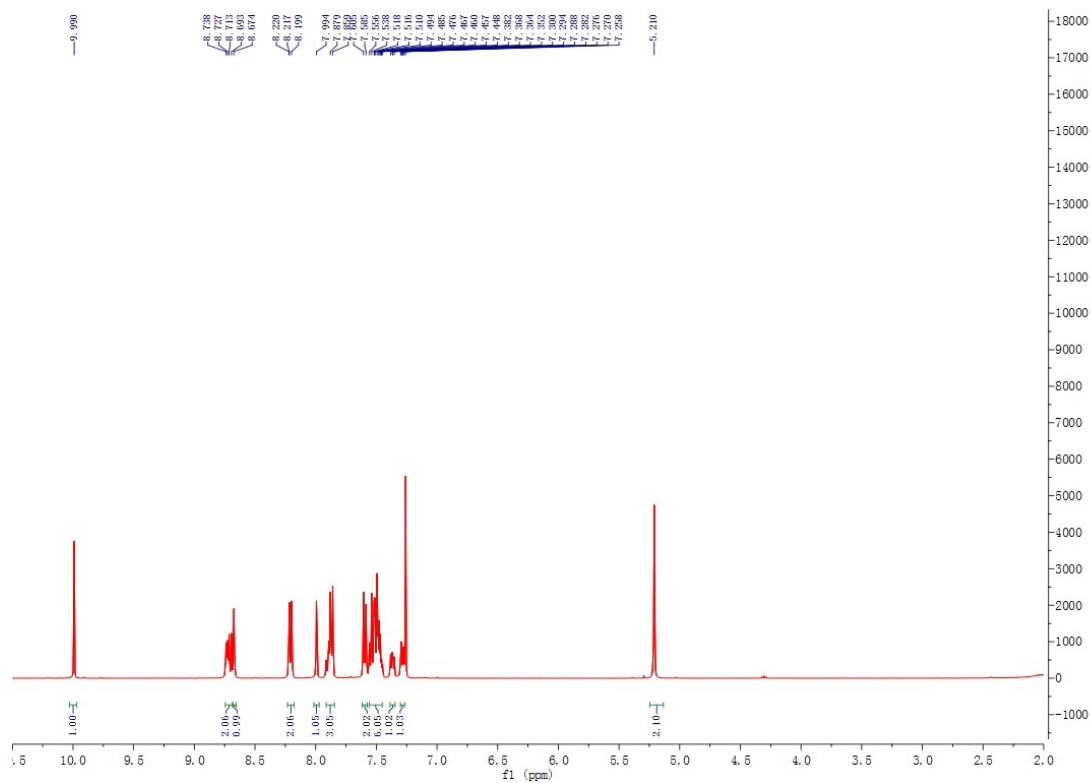


Figure S25. ^1H NMR (400 MHz, CDCl_3) spectrum of compound 2.

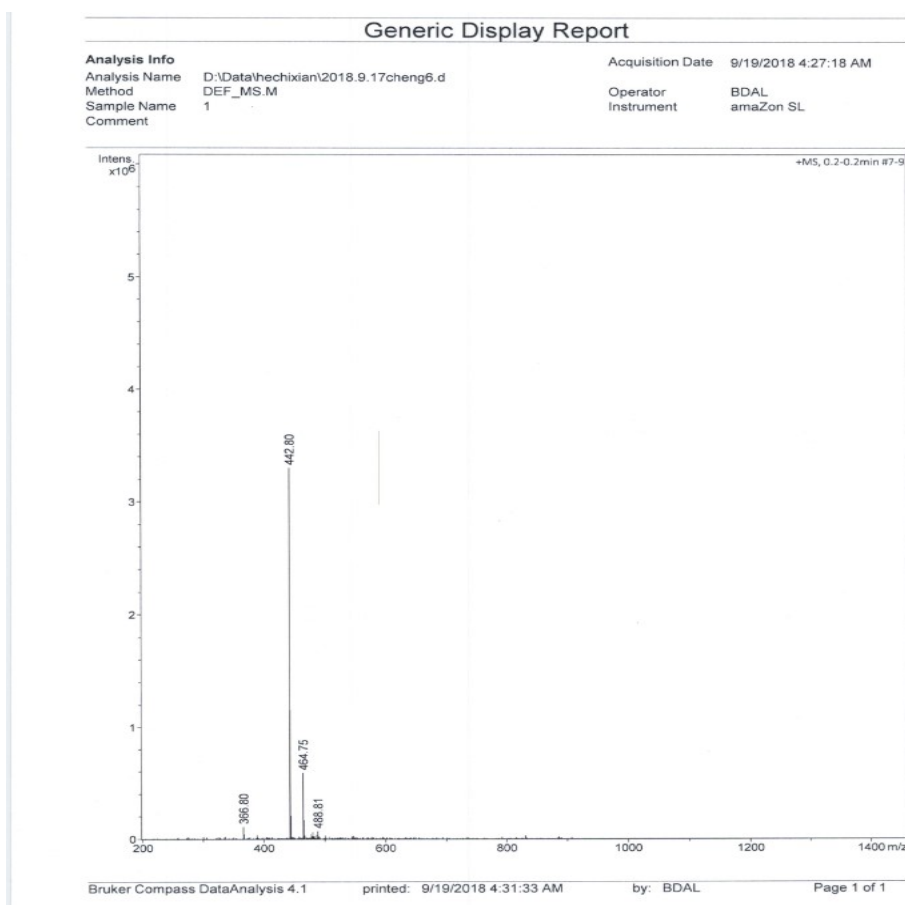


Figure S26. ESI-MS of compound 2.

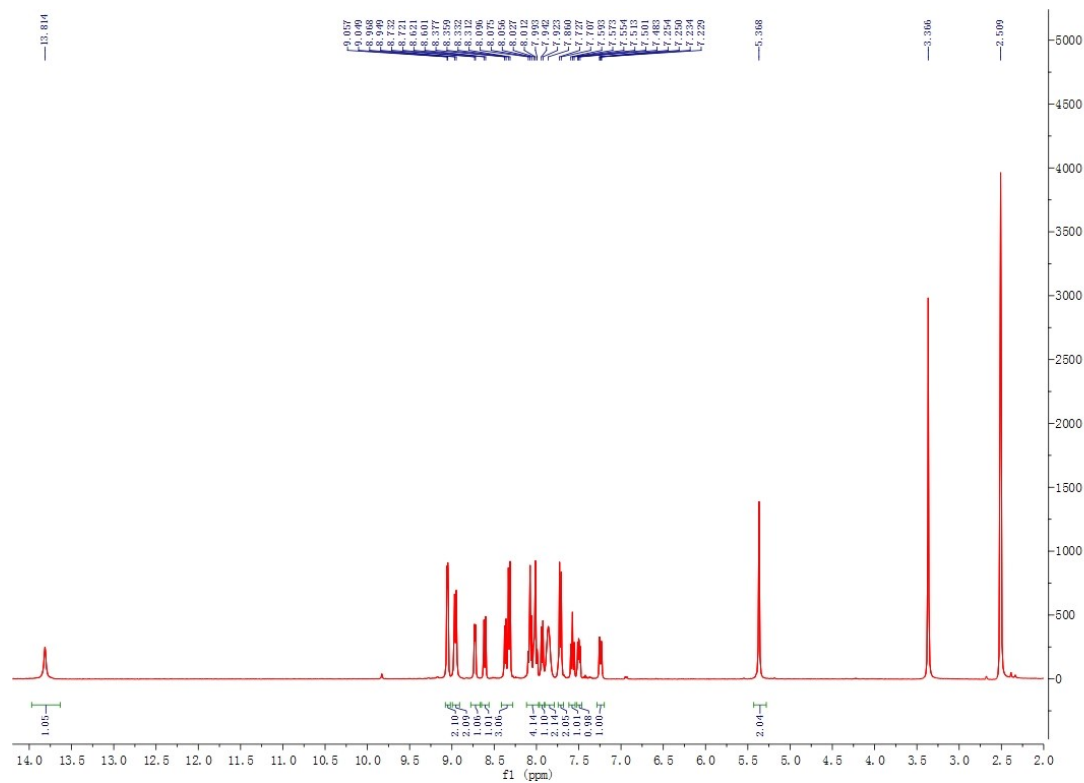


Figure S27. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) spectrum of ligand L1.

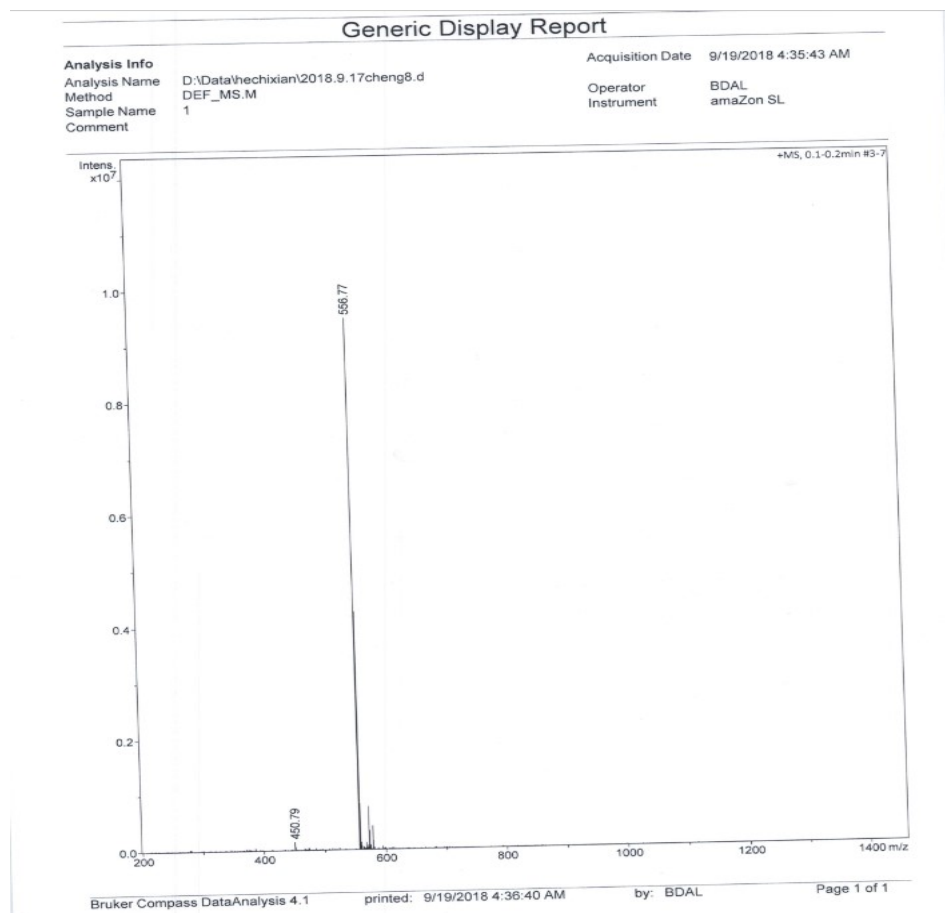


Figure S28. ESI-MS of ligand L1.

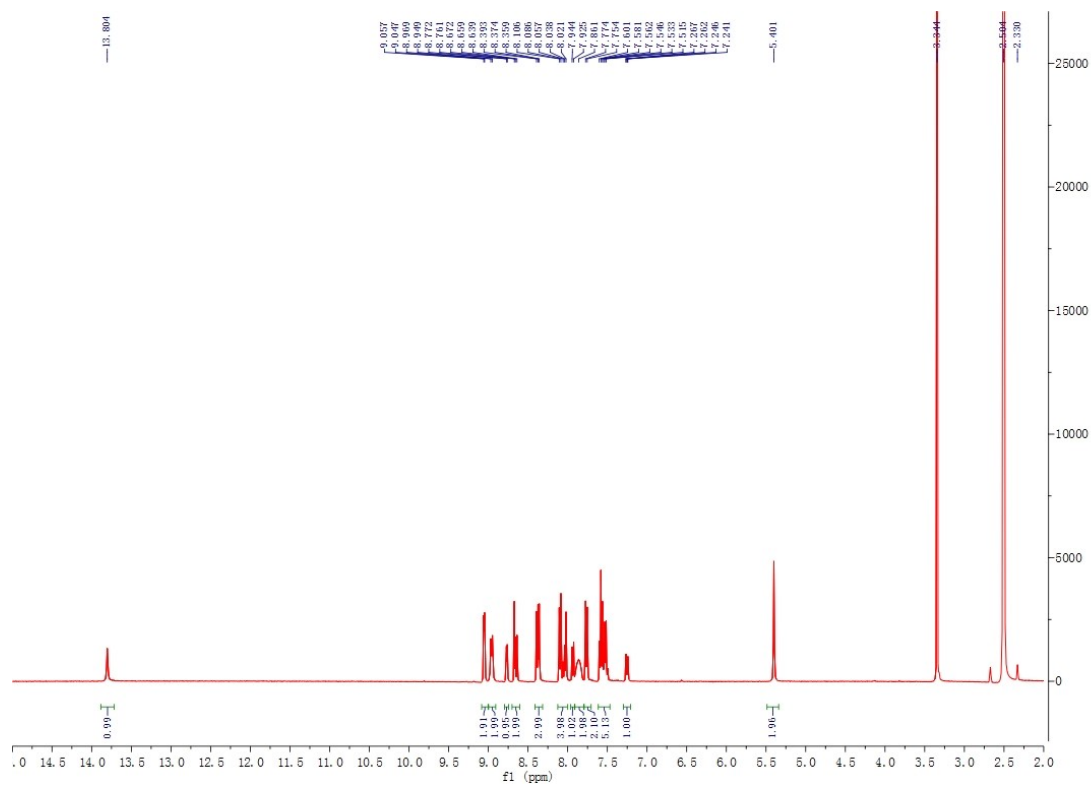


Figure S29. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) spectrum of ligand **L2**.

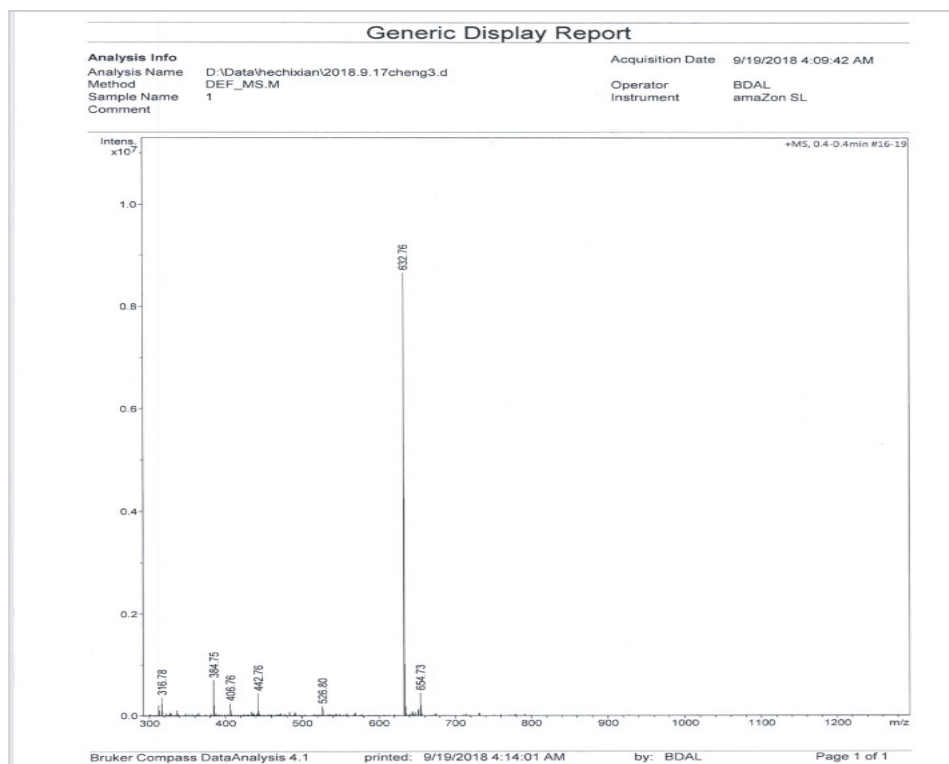


Figure S30. ESI-MS of ligand **L2**.

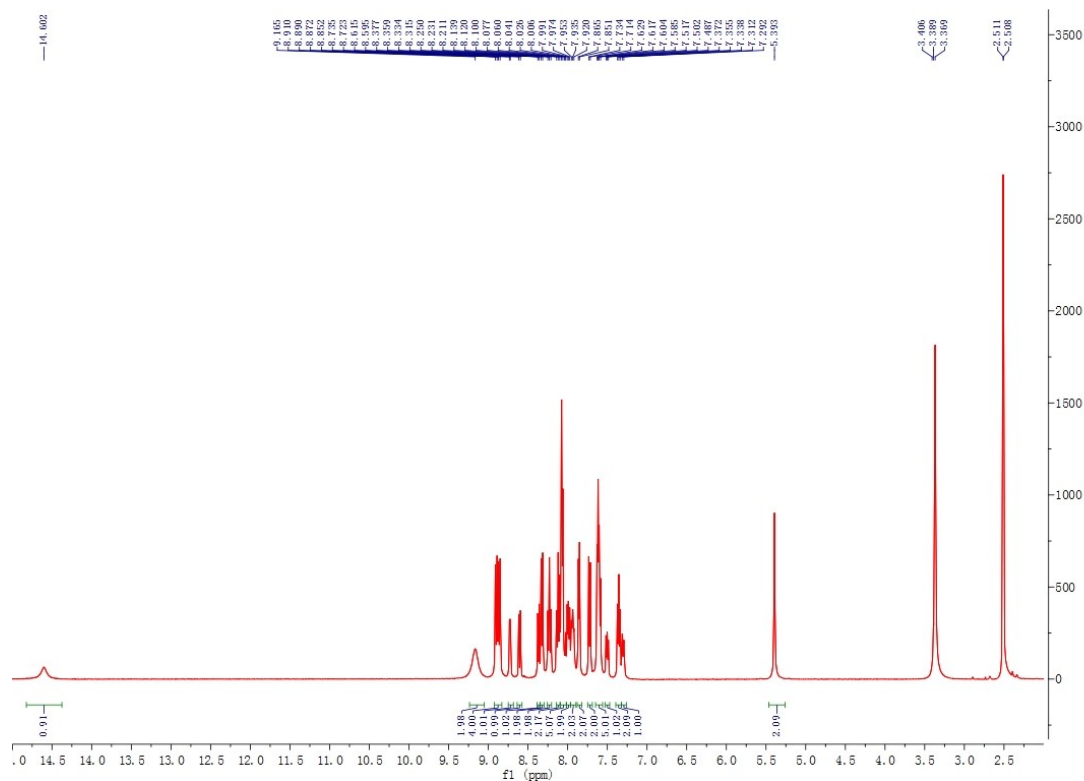


Figure S31. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) spectrum of complex C1.

F:\Users\lyman_3_180330163223

4/22/2018 10:43:07 AM

yuman_3_180330163223; #5 RT: 0.03 AV: 1 NL: 2.01E7
T: FIMS+pESI Full ms [150.00,2000.00]

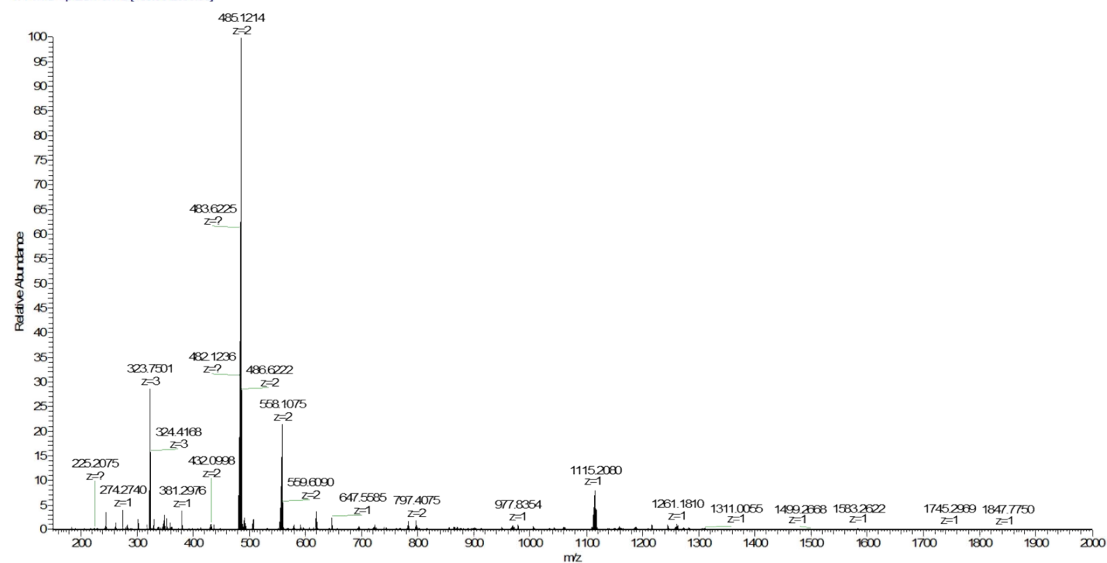


Figure S32. ESI-MS/MS of complex C1.

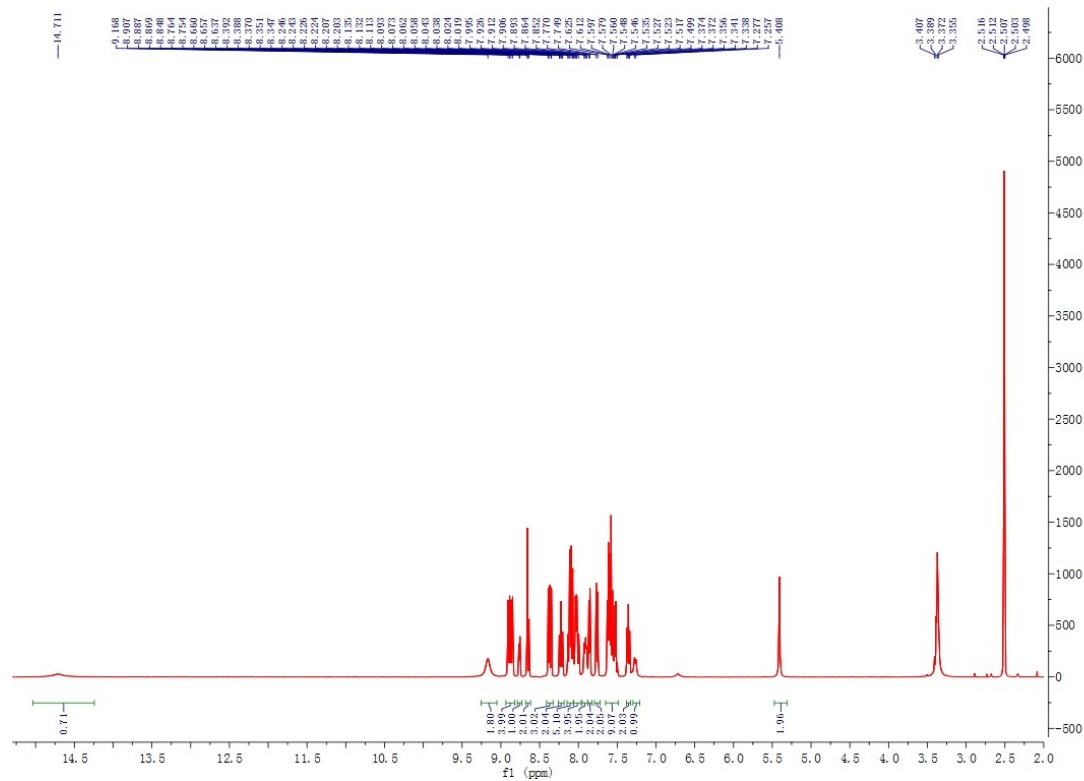


Figure S33. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) spectrum of complex C2.

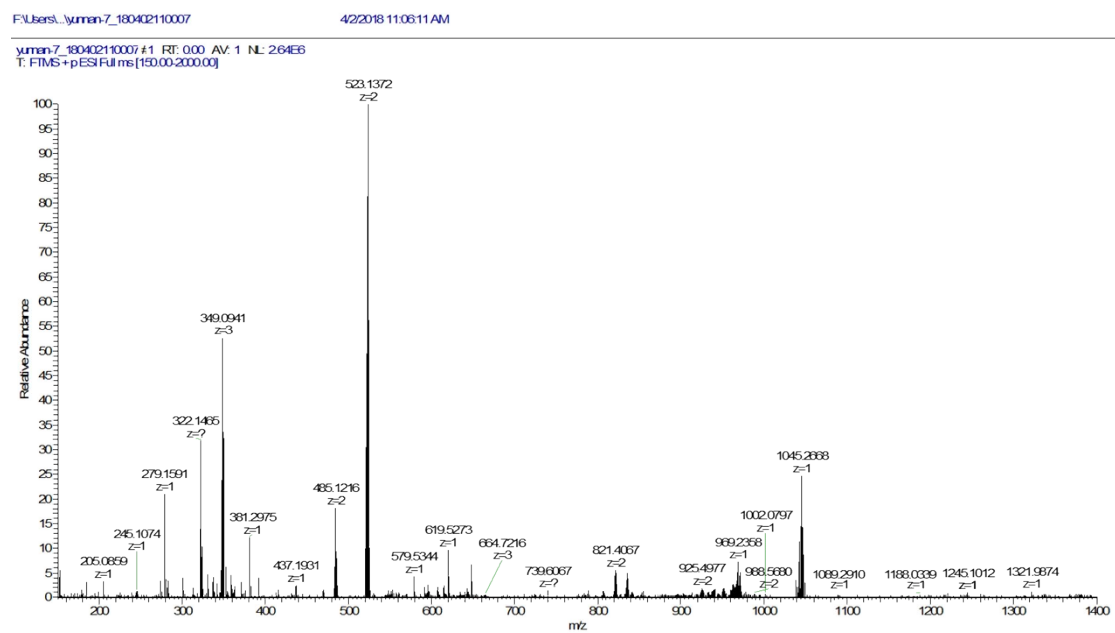


Figure S34. ESI-HRMS of complex C2.

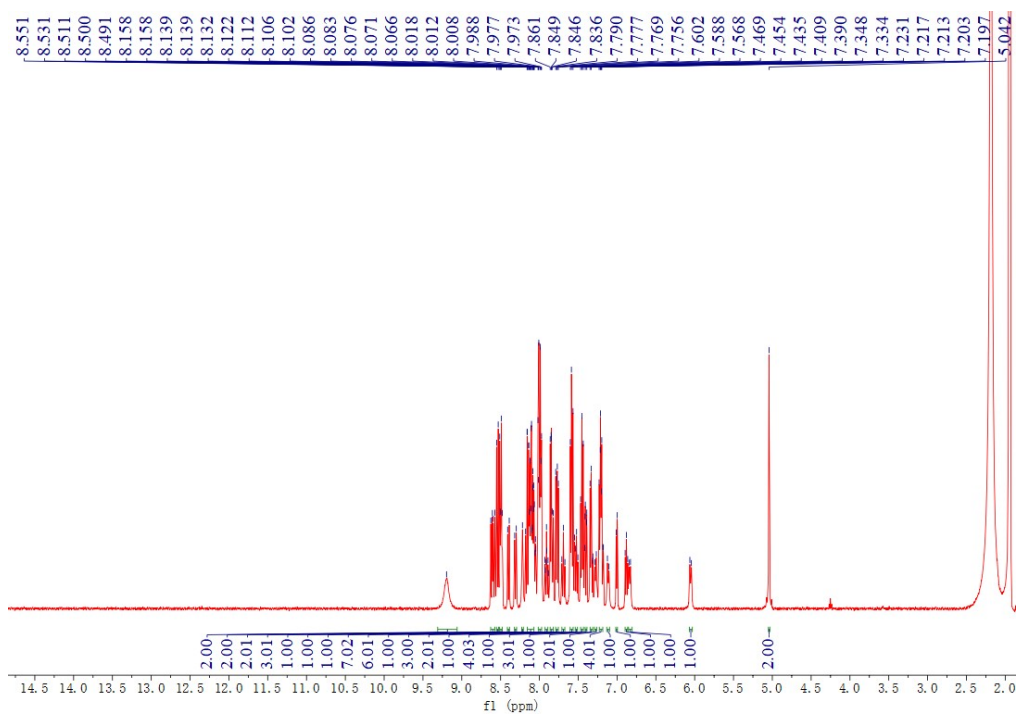


Figure S35. ^1H NMR (400 MHz, $\text{MeCN-}d_3$) spectrum of complex **C3**.

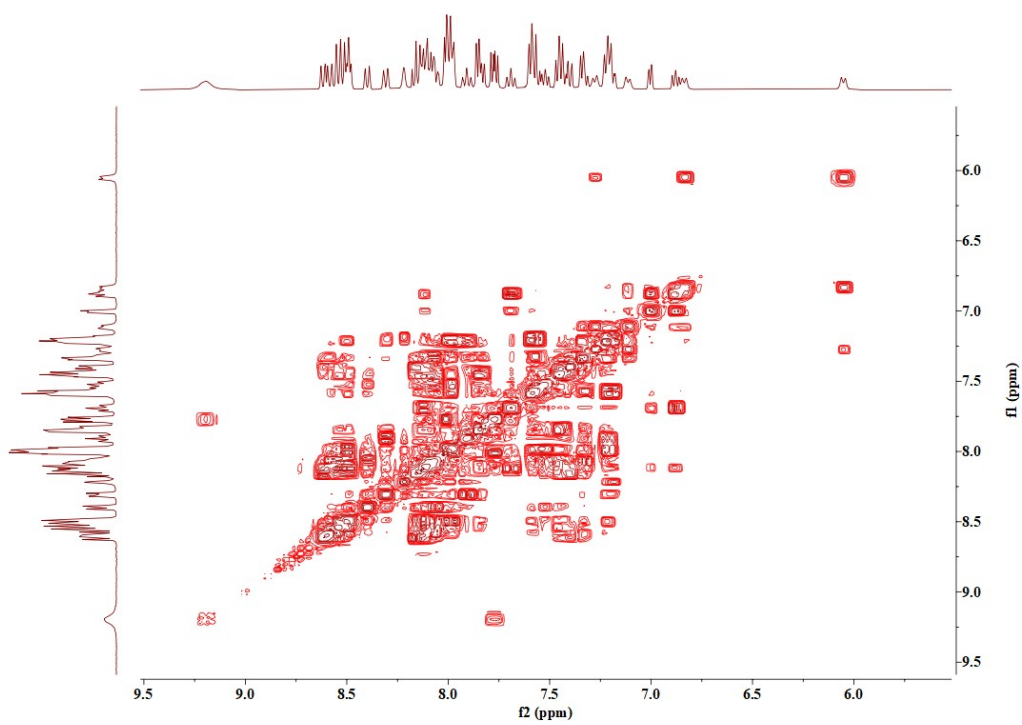


Figure S36. $^1\text{H-}^1\text{H}$ COSY (400 MHz, $\text{MeCN-}d_3$) spectrum of complex **C3**.

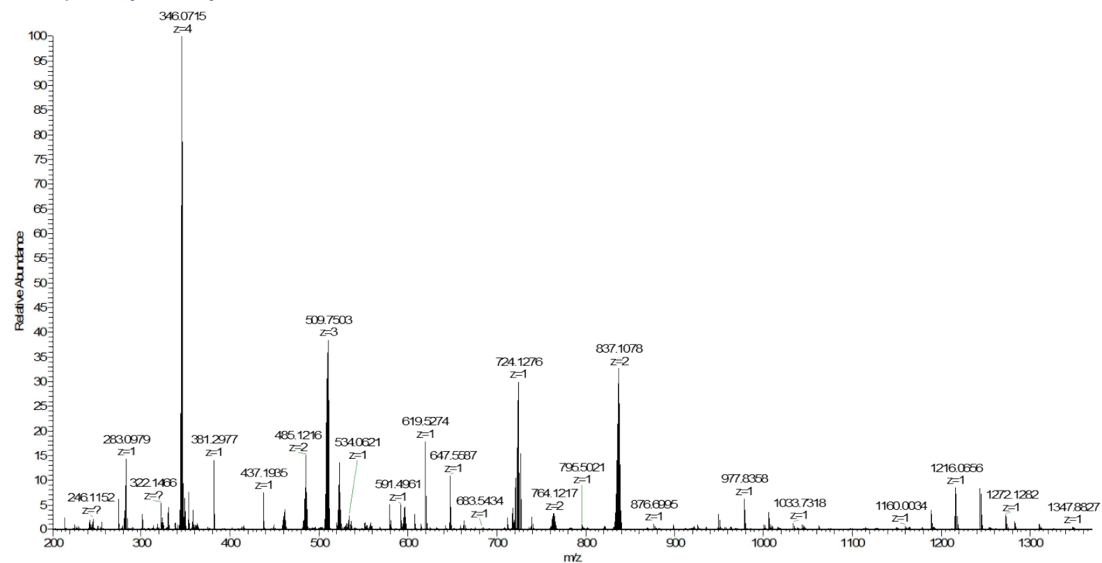
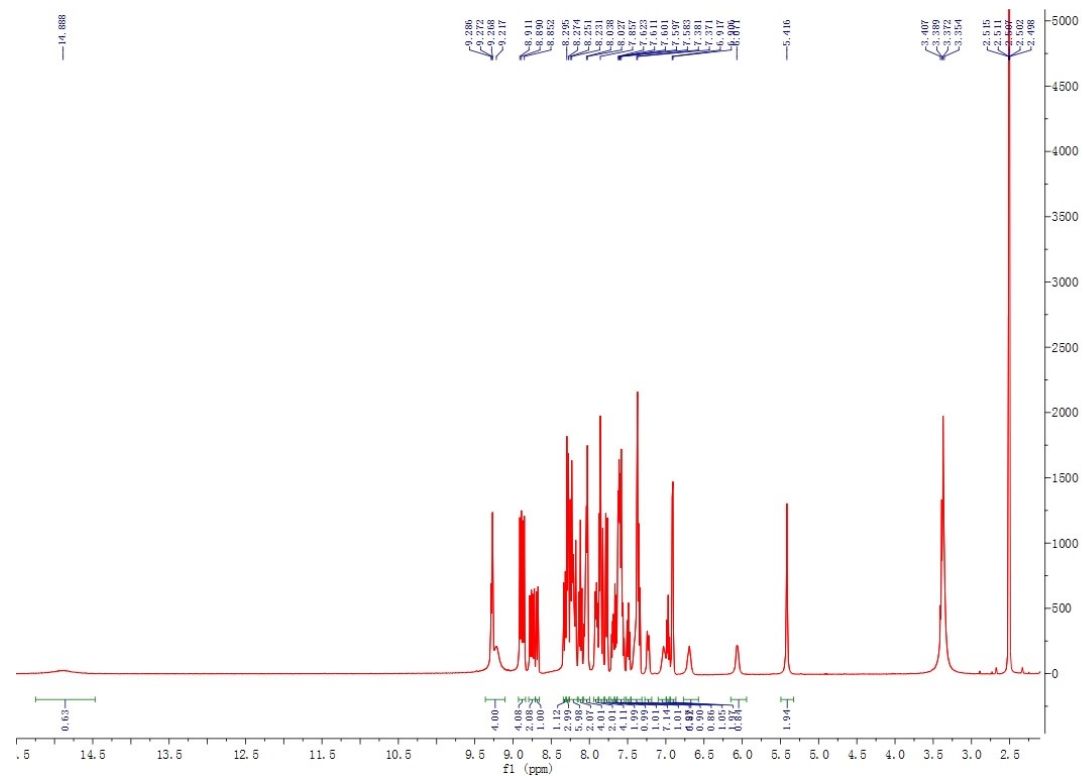
yuman-10_180402112308 A20 RT: 0.15 AV: 1 NL: 129E7
T: FIMS+pESI Full ms [200.00,2500.00]

Figure S37. ESI-HRMS of complex C3.

Figure S38. ¹H NMR (400 MHz, DMSO-*d*₆) spectrum of complex C4.

yuman-12_180402112308.f1 RT: 0.01 AV: 1 NL: 4.67EB
T: FTMS+pESI Full ms [200.00-2500.00]

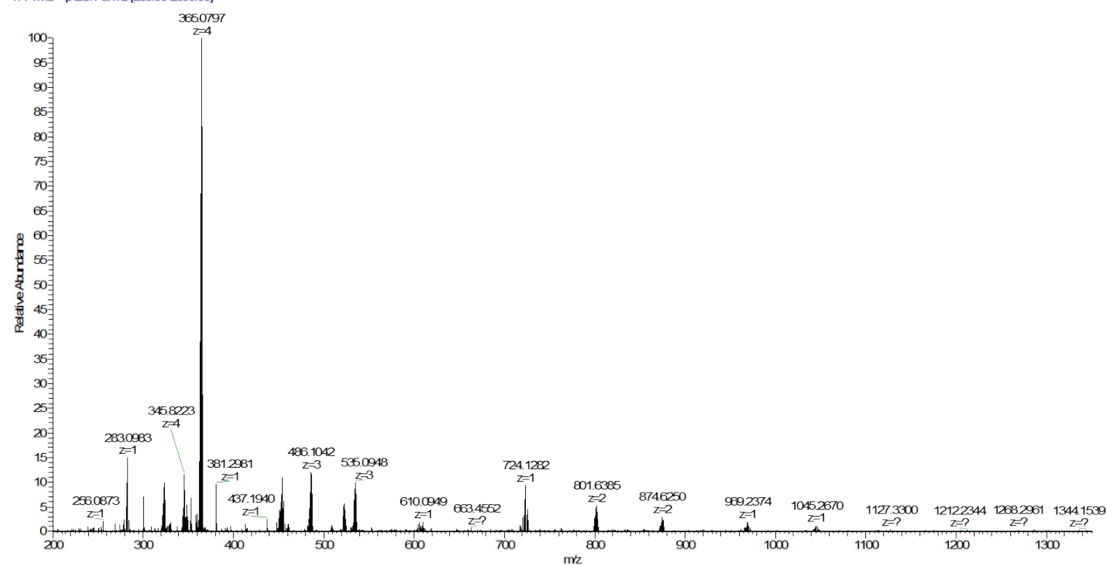


Figure S39. ESI-HRMS of complex C4.

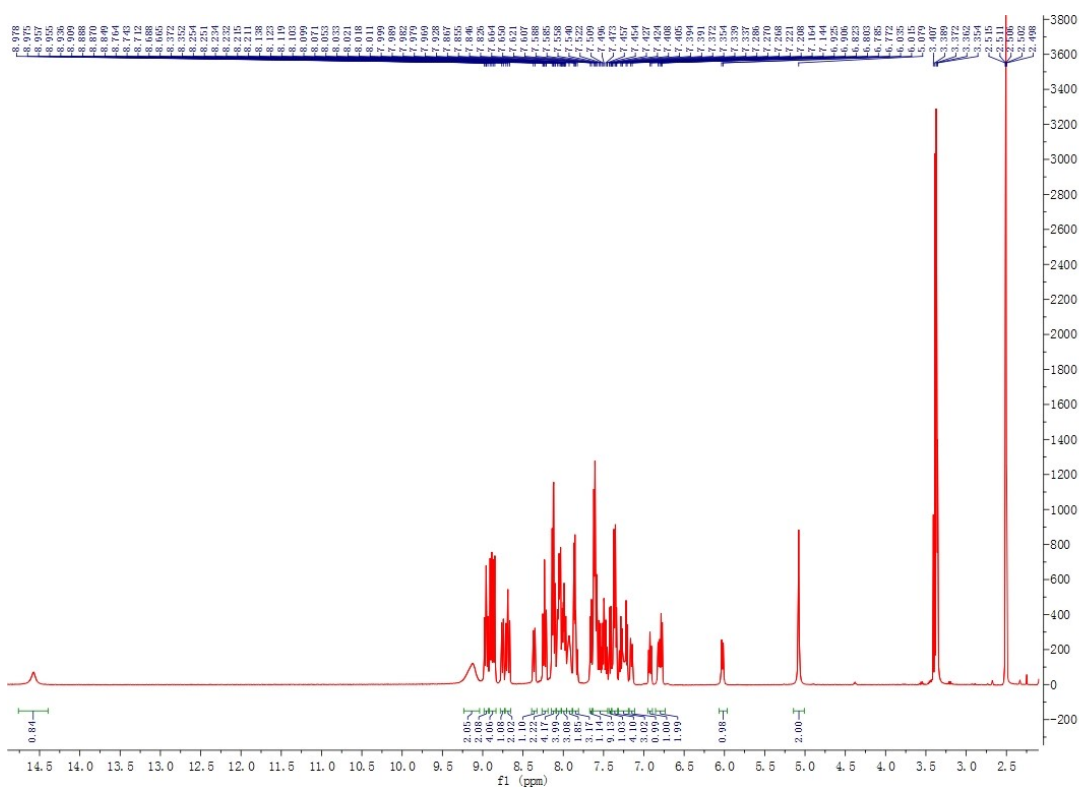


Figure S40. ¹H NMR (400 MHz, DMSO-d₆) spectrum of complex C5.

yuman-15_18040215030114 RT: 0.11 AV: 1 NL: 6.88E6
T: FIMS+pESIFull.ms [200.00,2500.00]

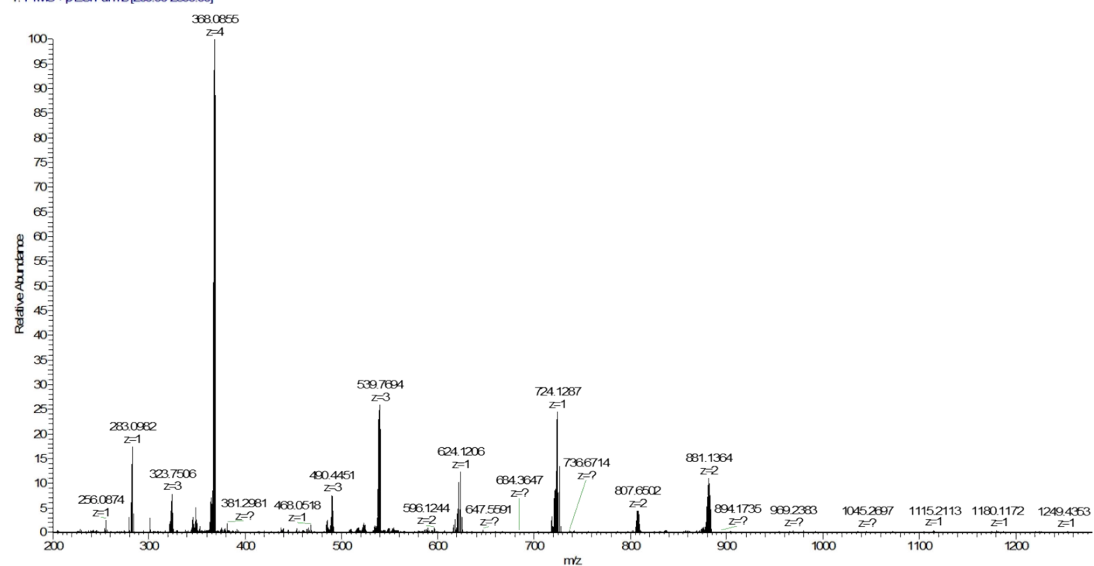


Figure S41. ESI-HRMS of complex C5.

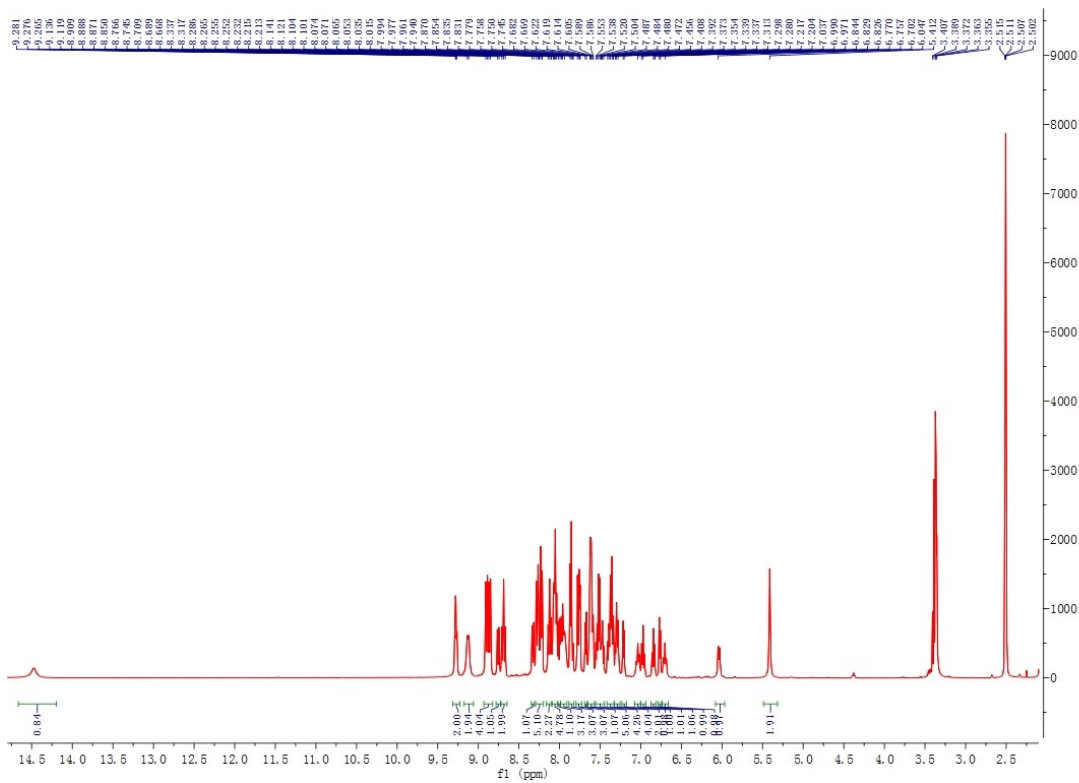


Figure S42. ¹H NMR (400 MHz, DMSO-d₆) spectrum of complex C6.

yuman_19_18040215030144.FI: 0.02 AV: 1 NL: 5.78EB
T: FIMS+pESI Full.ms [200.00,2800.00]

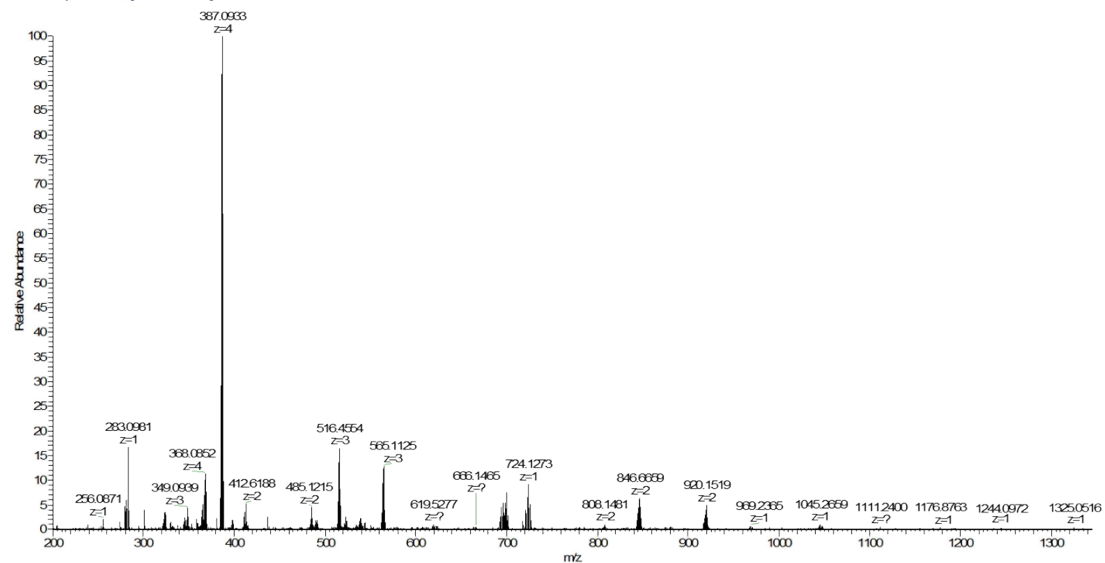


Figure S43. ESI-HRMS of complex C6.

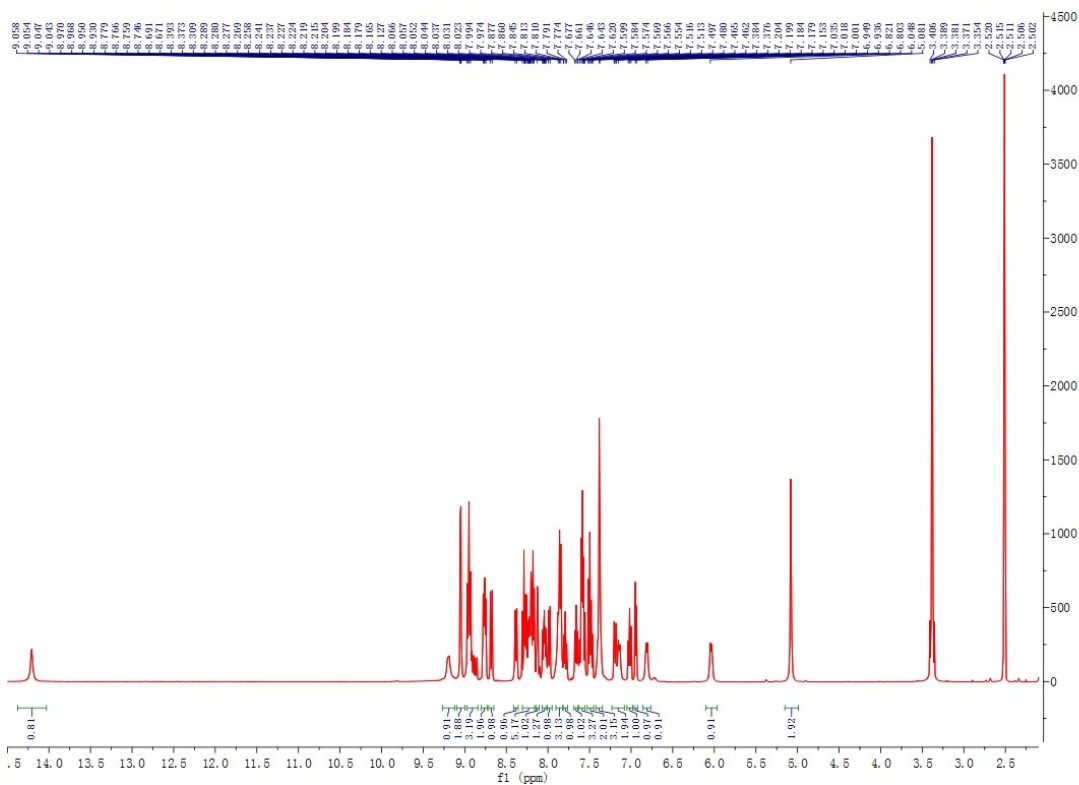


Figure S44. ¹H NMR (400 MHz, DMSO-d₆) spectrum of complex C7.

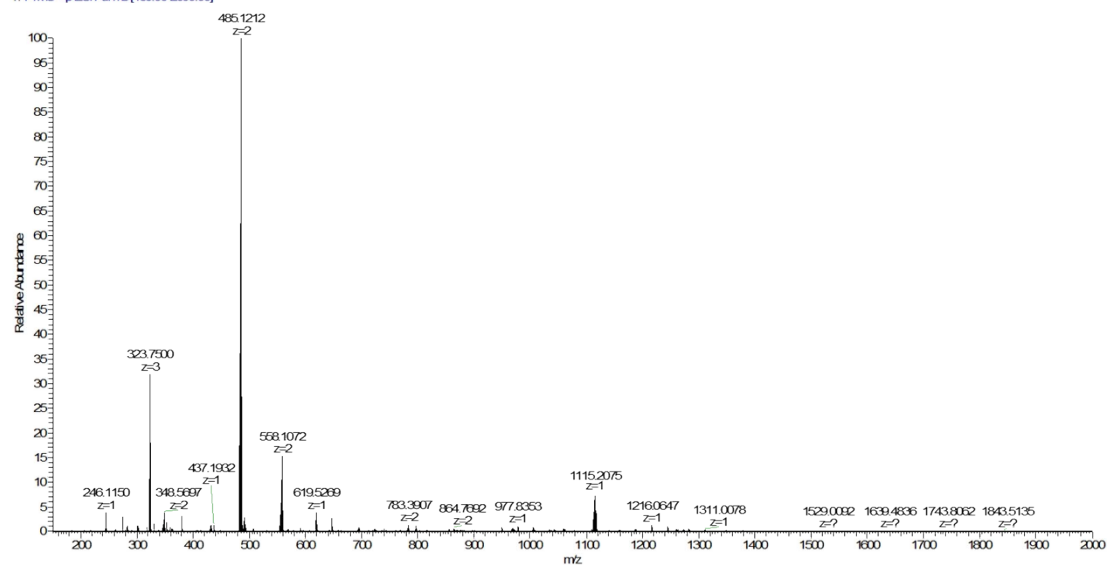
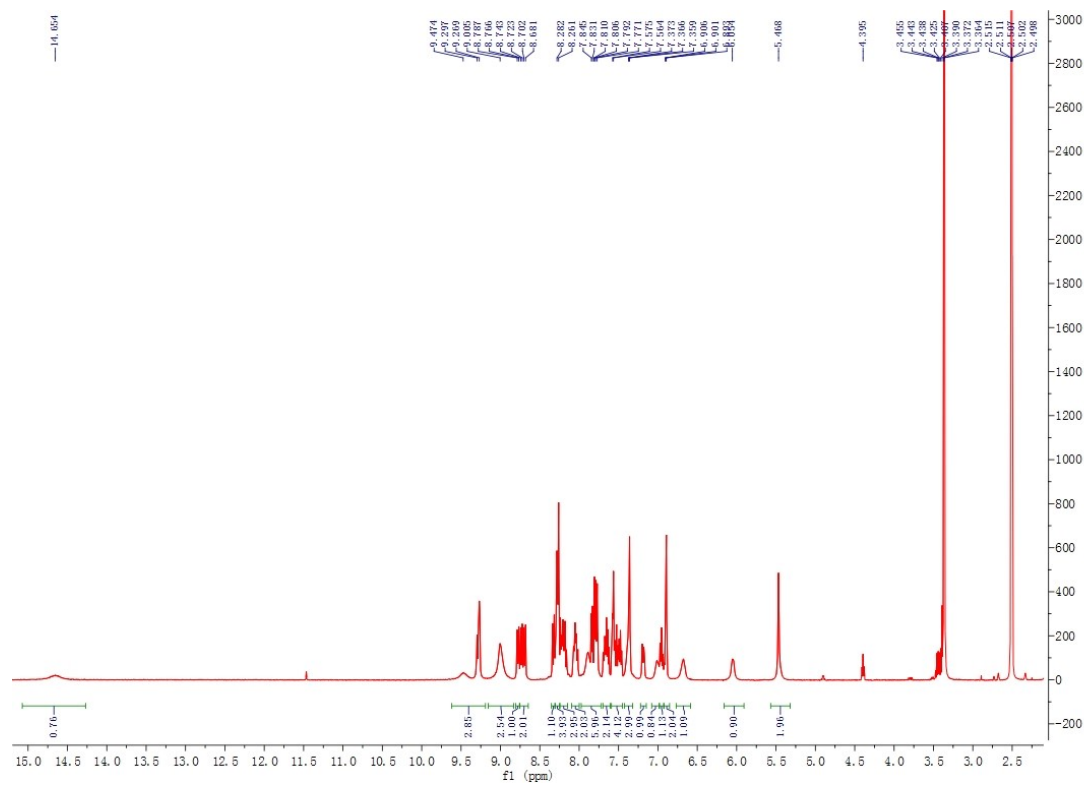
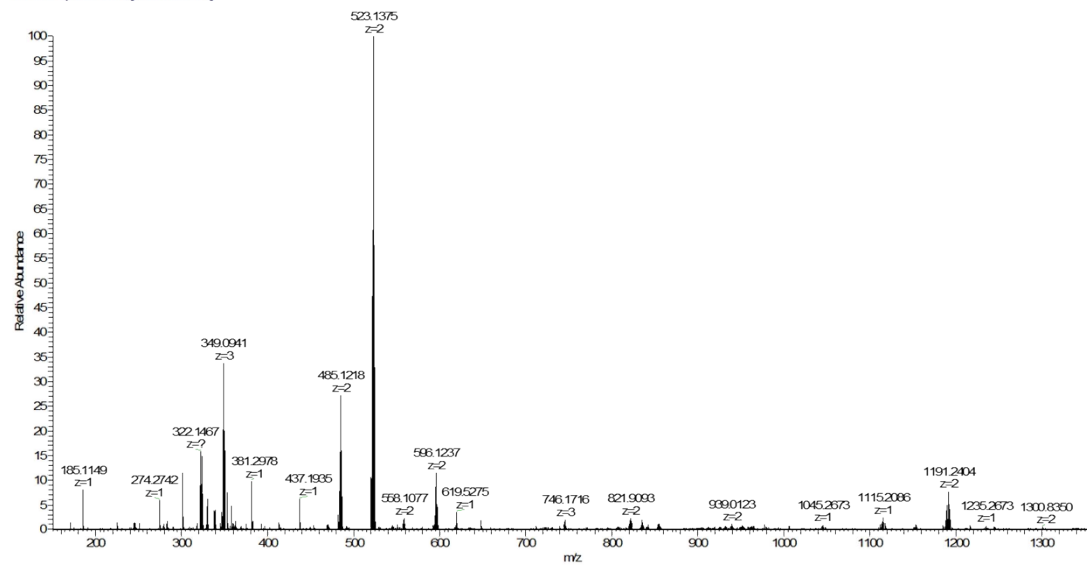
yuman_4_180330163223: #1 RT: 0.00 AV: 1 NL: 3.88E7
T: FTMS+pESI Fullms [150.00-2000.00]

Figure S45. ESI-HRMS of complex C7.

Figure S46. ¹H NMR (400 MHz, DMSO-d₆) spectrum of complex C8.

yuman_8_18040210007#1 RT: 0.00 AV: 1 NL: 728E6
T: FIMS+pESI Full ms [150.00-2000.00]



yuman_16_180402150301#4 RT: 0.02 AV: 1 NL: 566E6
T: FIMS+pESI Full ms [200.00-2500.00]

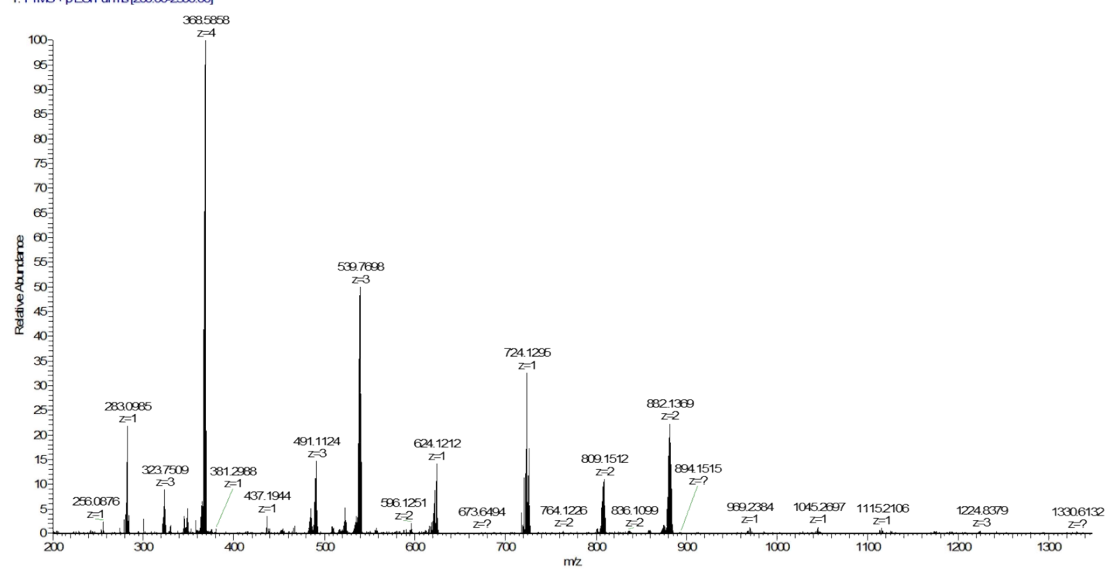


Figure S50. ESI-HRMS of complex C9.

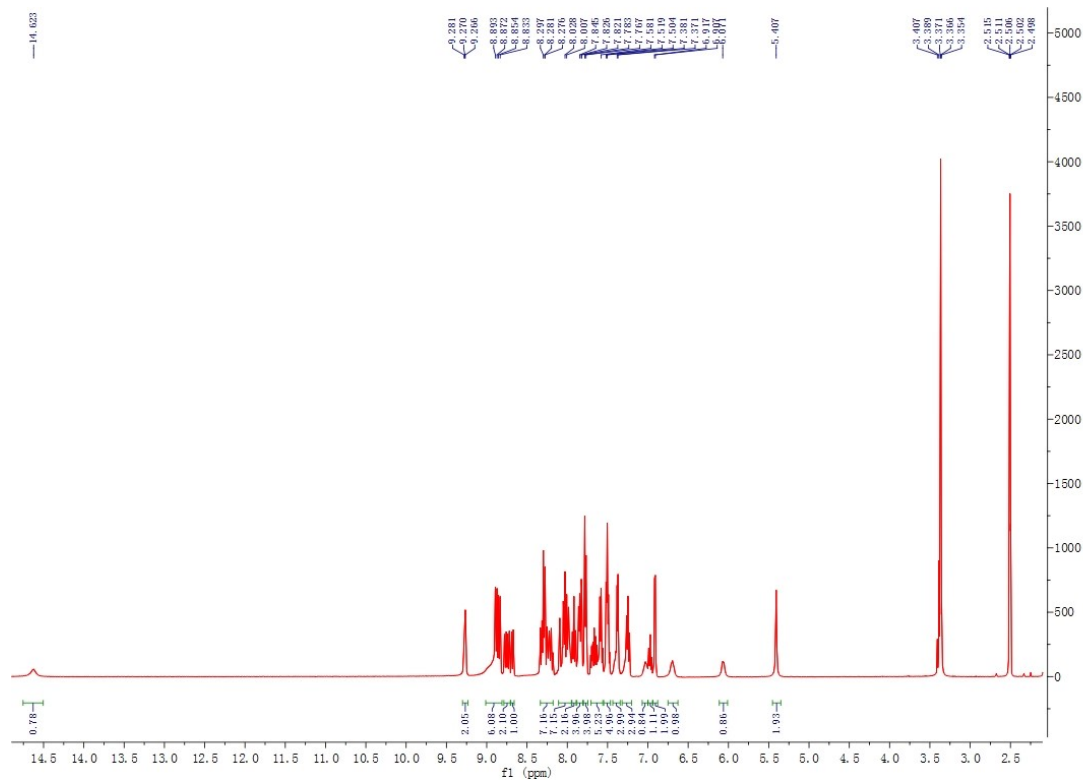


Figure S51. ^1H NMR (400 MHz, DMSO-d_6) spectrum of complex **C10**.

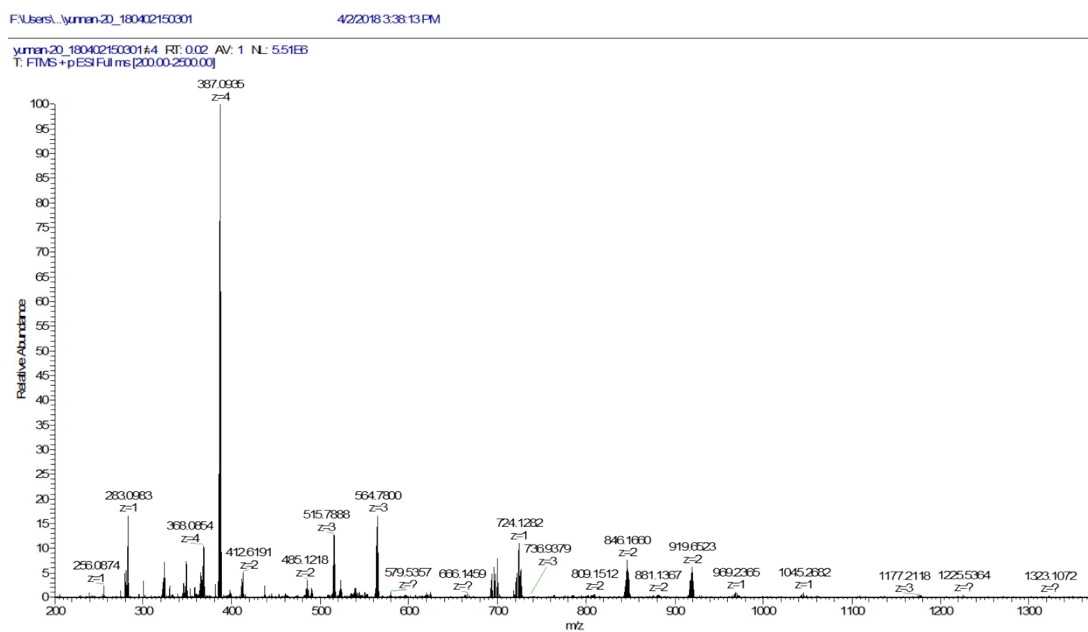


Figure S52. ESI-HRMS of complex **C10**.