10.1071/CH18192_AC

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Supplementary Material

Visible Light-Induced CO-Release Reactivity of a Series of Zn^{II}-Flavonolate Complexes

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Photoinduced dioxygenase-type reactivity of 1-4: Isolation of [(L)Zn(*O*-bs)] ClO_4(15-18)(L = 6-MeTPA, 6-Me_2TPA, BPQA, BQPA), (bs = *O*benzoylsalicylate).

[(6-MeTPA)Zn(O-bs)]ClO_4(15). ESI-MS： m/z ([(6-MeTPA)Zn(O-bs)]$^+$) Calcd: 609.1480; Found: 609.1467. FTIR (KBr, cm^{-1}): 1733 ($\nu_{C=O}$), 1093 (ν_{ClO4}), 619 (ν_{ClO4});

[(6-Me_2TPA)Zn(O-bs)]ClO_4(16). ESI-MS： m/z ([(6-Me_2TPA)Zn(O-bs)]$^+$) Calcd: 623.1637; Found: 623.1637. FTIR (KBr, cm^{-1}): 1728 ($\nu_{C=O}$), 1088 (ν_{ClO4}), 624 (ν_{ClO4});

[(BPQA)Zn(O-bs)]ClO_4(17). ESI-MS： m/z ([(BPQA)Zn(O-bs)]$^+$) Calcd: 645.1618; Found: 645.1619. FTIR (KBr, cm^{-1}):1730 ($\nu_{C=O}$), 1088 (ν_{ClO4}), 619 (ν_{ClO4});

[(BQPA)Zn(O-bs)]ClO_4(18). ESI-MS： m/z ([(BQPA)Zn(O-bs)]$^+$) Calcd: 695.1637; Found: 695.1630. FTIR (KBr, cm^{-1}): 1733 ($\nu_{C=O}$), 1093 (ν_{ClO4}), 619 (ν_{ClO4});

Photoinduced dioxygenase-type reactivity of 5-9: Isolation of [(L)Zn((O-4-MeObs))]ClO_4(19-23) (L = TPA, 6-MeTPA, 6-Me_2TPA, BPQA, BQPA), (bs = *O*benzoylsalicylate).

[(TPA)Zn(O-4-MeObs)]ClO_4(19). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.80 (d, 3H), 8.22 (dd, 1H), 7.98 (d, 2H), 7.92 (t, 3H), 7.57 (dd, 3H), 7.40 (m, 4H), 6.73 (d, 2H), 4.29 (s, 6H), 3.78 (s, 3H); ESI-MS：m/z ([(TPA)Zn(O-4-MeObs)]$^+$) Calcd: 625.1429; Found: 625.1432. FTIR (KBr, cm^{-1}): 1726 ($\nu_{C=O}$), 1092 (ν_{ClO4}), 624 (ν_{ClO4}).

[(6-MeTPA)Zn(O-4-MeObs)]ClO_4(20). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.81 (d, 2H), 8.14 (d, 1H), 7.89 (m, 4H), 7.77 (t, 1H), 7.57 (t, 1H), 7.52 (d, 2H), 7.38 (m, 3H), 7.32 (d, 1H), 7.22 (m, 2H), 6.71 (d, 2H), 4.28 (s, 2H), 4.22 (s, 4H), 3.80 (s, 3H); ESI-MS：m/z ([(6-MeTPA)Zn(O-4-MeObs)]$^+$) Calcd: 639.1586; Found: 639.1595. FTIR (KBr, cm^{-1}): 1722 ($\nu_{C=O}$), 1089 (ν_{ClO4}), 624 (ν_{ClO4}).

[(6-Me_2TPA)Zn(O-4-MeObs)]ClO_4(21).^{1}H NMR ($CDCl_3$, 400 MHz): δ8.42(s, 1H), 8.01(d, 1H), 7.95(d, 2H), 7.74(t, 1H), 7.65(t, 2H), 7.50(d, 1H), 7.36(d, 1H), 7.25(m, 2H), 7.22(d, 2H), 7.13(d, 2H), 6.92(d, 2H), 4.45(s, 4H), 4.33(s, 2H), 3.93(s, 3H); ESI-MS：m/z ([(6-Me_2TPA)Zn(O-4-MeObs)]$^+$) Calcd: 653.1742; Found: 653.1726. FTIR (KBr, cm^{-1}) ：1730 ($\nu_{C=O}$), 1092 (ν_{ClO4}), 622 (ν_{ClO4}).

[(BPQA)Zn(O-4-MeObs)]ClO_4(22). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.78 (d, 1H), 8.69 (d, 1H), 8.35 (d, 1H), 8.05 (d, 1H), 7.89 (dd, 4H), 7.77 (t, 1H), 7.56 (m, 6H), 7.33 (d, 2H), 7.22 (d, 2H), 6.74 (d, 2H), 4.52 (s, 2H), 4.33 (s, 4H), 3.81 (s, 3H); ESI-MS：m/z ([(BPQA)Zn(O-4-MeObs)]$^+$) Calcd: 675.1586; Found: 675.1591. FTIR (KBr, cm^{-1}): 1724 ($\nu_{C=O}$), 1089 (ν_{ClO4}), 624 (ν_{ClO4}).

[(BQPA)Zn(O-4-MeObs)]ClO_4(23). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.81 (d, 2H), 8.53 (d, 1H), 8.31 (d, 2H), 8.01 (d, 1H), 7.92 (d, 2H), 7.79 (d, 2H), 7.74 (t, 3H), 7.55 (t, 2H), 7.48 (t, 3H), 7.38 (d, 1H), 7.21 (t, 1H), 7.14 (d, 1H), 6.88 (d, 2H), 4.74 (s, 4H), 4.53 (s, 2H), 3.89 (s, 3H); ESI-MS：m/z ([(BQPA)Zn(O-4-MeObs)]$^+$) Calcd: 725.1742; Found: 725.1744. FTIR (KBr, cm^{-1}): 1726 ($\nu_{C=O}$), 1092 (ν_{ClO4}), 622 (ν_{ClO4}).

Photoinduced dioxygenase-type reactivity of 10-14: Isolation of [(L)Zn((O-4-MeObs))] ClO_4(24-28) (L = TPA, 6-MeTPA, 6-Me_2TPA, BPQA, BQPA), (bs = *O*benzoylsalicylate).

[(TPA)Zn(O-4-MeObs)]ClO_4(24). ESI-MS：m/z ([(TPA)Zn(O-4-MeObs)]$^+$) Calcd. 641.1201；Found: 641.1202. FTIR (KBr, cm^{-1}) ： 1726 ($\nu_{C=O}$), 1092 (ν_{ClO4}), 622 (ν_{ClO4}).

[(6-MeTPA)Zn(O-4-MeObs)]ClO_4(25).ESI-MS：m/z ([(6-MeTPA)Zn(O-4-MeObs)]$^+$) Calcd: 655.1357; Found: 655.1353. FTIR (KBr, cm^{-1}) ： 1726 ($\nu_{C=O}$), 1089 (ν_{ClO4}), 620 (ν_{ClO4}).

[(6-Me_2TPA)Zn(O-4-MeObs)]ClO_4(26). ESI-MS ： m/z ([(6-Me_2TPA)Zn(O-4-MeObs)]$^+$) Calcd: 669.1514; Found: 669.1495. FTIR (KBr, cm^{-1}) ： 1724 ($\nu_{C=O}$), 1092 (ν_{ClO4}), 622 (ν_{ClO4}).

[(BPQA)Zn(O-4-MeObs)]ClO_4(27). ESI-MS ： m/z ([(BPQA)Zn(O-4-MeObs)]$^+$) Calcd: 691.1367; Found: 691.1369. FTIR (KBr, cm^{-1}) ： 1726 ($\nu_{C=O}$), 1092 (ν_{ClO4}), 620 (ν_{ClO4}).

[(BQPA)Zn(O-4-MeObs)]ClO_4(28). ESI-MS ： m/z ([(BQPA)Zn(O-4-MeObs)]$^+$) Calcd: 741.1514; Found: 741.1549. FTIR (KBr, cm^{-1}) ： 1726 ($\nu_{C=O}$), 1089 (ν_{ClO4}), 622 (ν_{ClO4}).

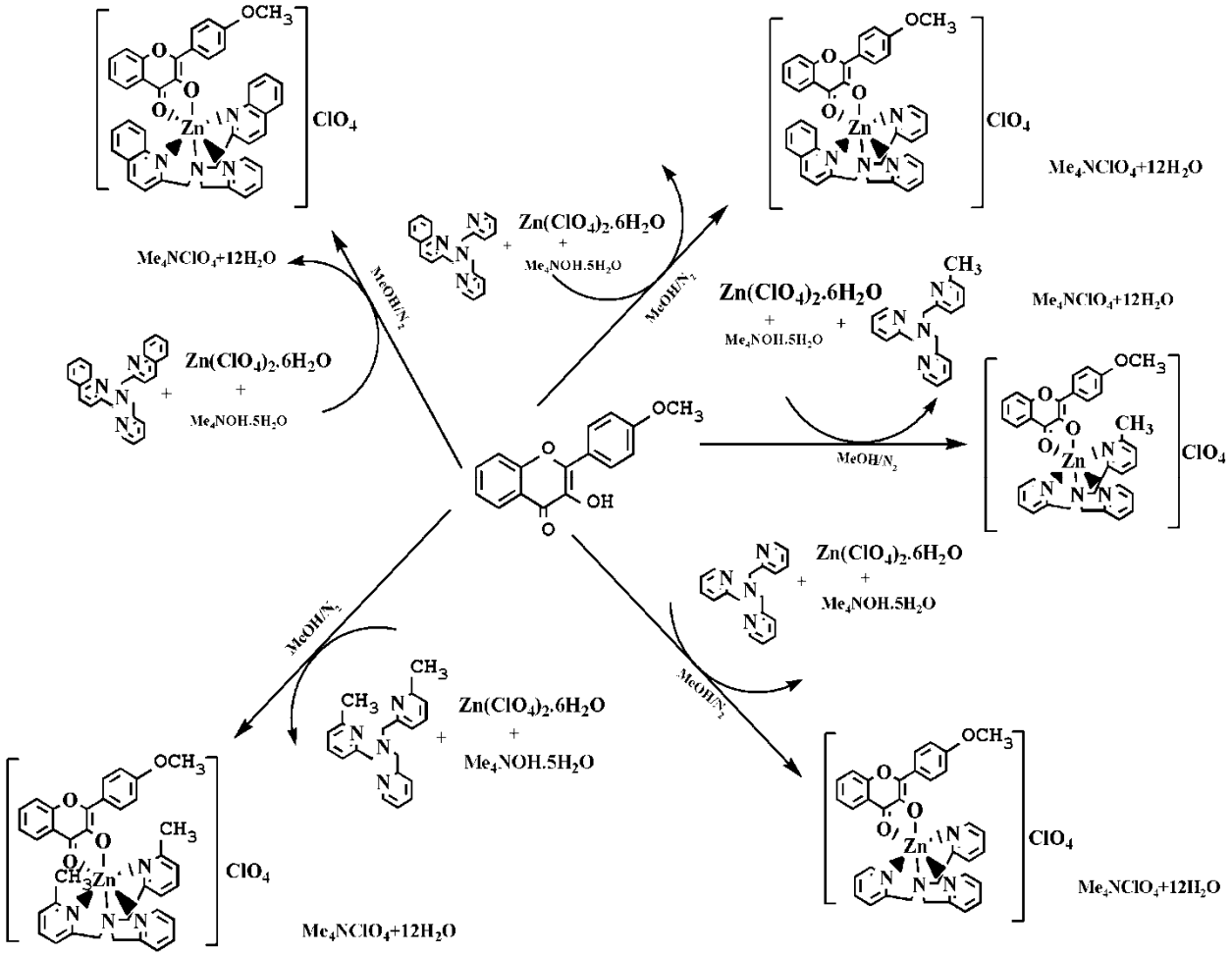
Stable experiments for complexes 1-14. All solid complexes were placed in dry air at room temperature for 30 days, by observing their colors and UV-Vis spectroscopy to evaluate the stability of the complexes. The results show that there are no changes in the spectral data of the complexes. Solution of each complex in CD_3CN (6×10^{-5} $mol\cdot L^{-1}$) was placed at room temperature for 72 h in air, the results show that there are no changes in colors and UV-Vis spectroscopy, suggesting the good stability of the complexes.

Dark control reactions for complexes 1-14. Solution of each complex in CD_3CN (6×10^{-5} $mol\cdot L^{-1}$) was prepared and placed in a 50 mL round-bottom flask in air. Each round-bottom flask was then covered with foil and illuminated with respective maximum absorption wavelength for 72 h. For all, assessment of the solution by ^1H NMR showed that no reaction occurred.

Anaerobic control reactions for 1-14. Solution of each complex in CD_3CN (6×10^{-5} $mol\cdot L^{-1}$) was prepared under N_2 and placed in a 50 mL round-bottom flask. Each round-bottom flask was illuminated with respective maximum absorption wavelength

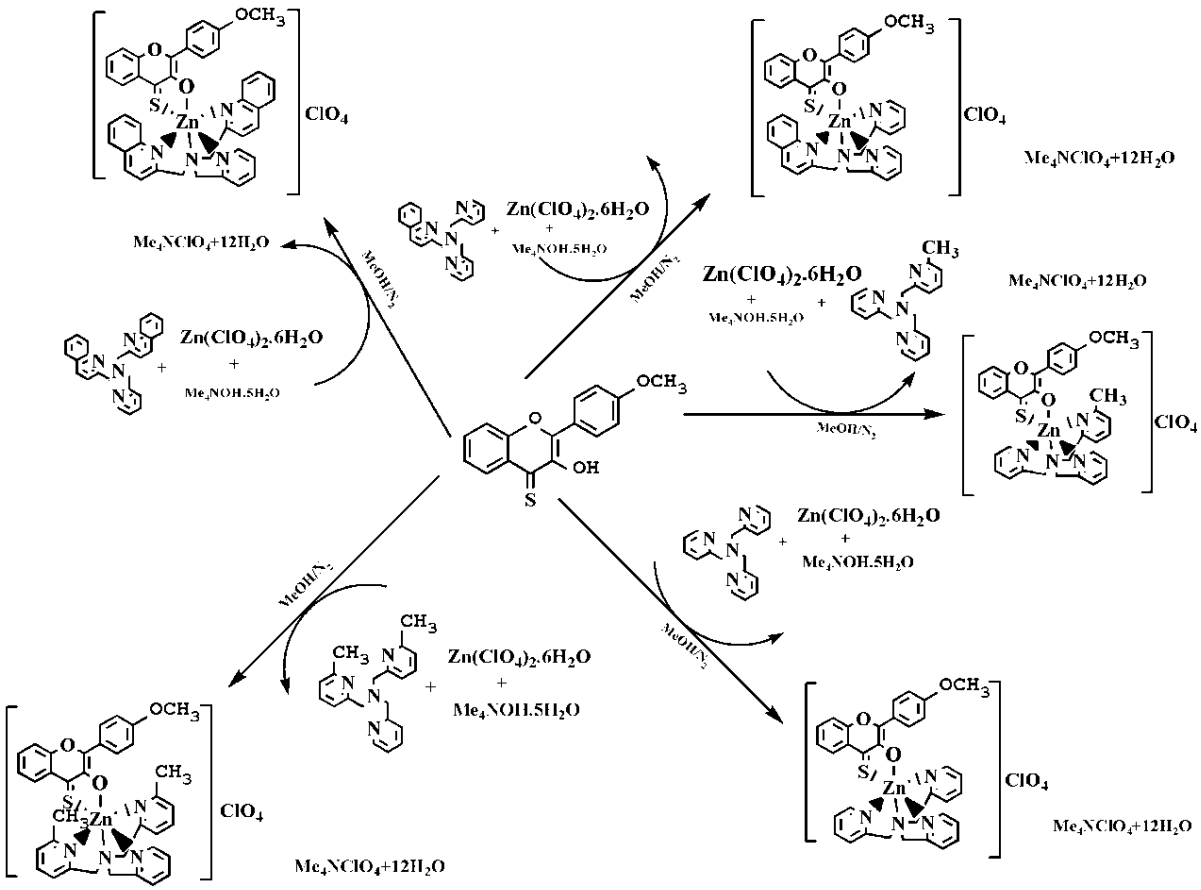
for 72 h. For all, assessment of the solution by ^{1}H NMR showed that no reaction occurred.

Cytotoxicity test: The frozen HeLa cells which are commercially available were unfreezed in 37□ water bath in 1 minute and were incubated 24 h into 96-well plates at 37□, in the presence of 5% CO_2. And the edge wells were filled with PBS buffer solution to avoid edge effect. Six complex including three different CO releasing units (**2**, **7**, **12**) and four different chelating ligands (**1**, **2**, **3**, **4**)which of concentration is from 1-50 μM were added above plates with 0.2 mL per well, and so did the blank groups and solvent groups as comparing groups. Sucking out samples and adding 0.02 mL MTT per well and cultivating 4 h after the plates were placed in incubator 24 h. Then, 0.2 mL DMSO was added into per well and obtaining absorbance values with microplate reader.



Scheme S1: Synthesis of complexes [(L)Zn(4-MeOFLH)]ClO_4

(L = TPA, 6-MeTPA, 6-Me_2TPA, BPQA, BQPA)



Scheme S2: Synthesis of complexes [(L)Zn(4-MeOFLTH)]ClO_4
(L = TPA, 6-MeTPA, 6-Me_2TPA, BPQA, BQPA)

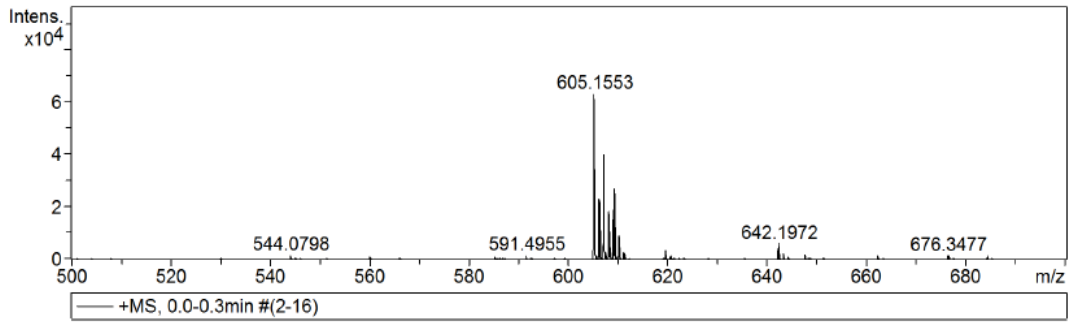


Figure S1 Mass spectrometry data of complex 1

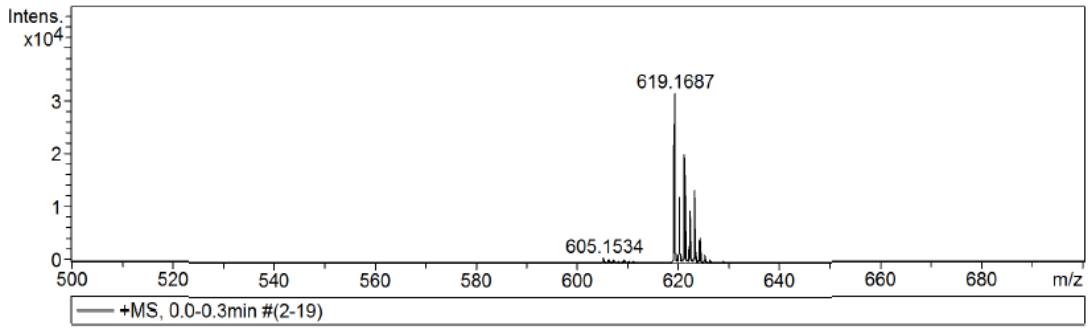


Figure S2 Mass spectrometry data of complex 2

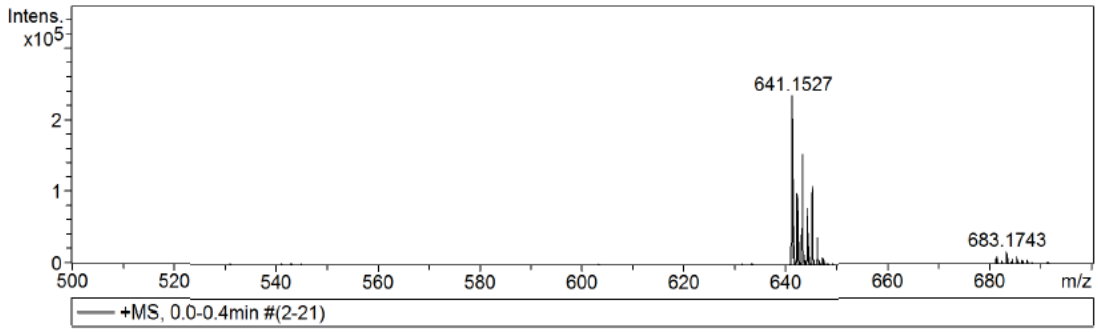


Figure S3 Mass spectrometry data of complex 3

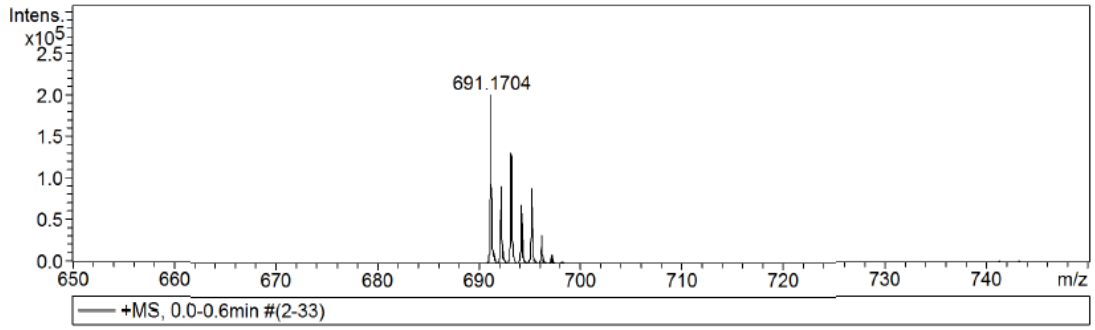


Figure S4 Mass spectrometry data of complex 4

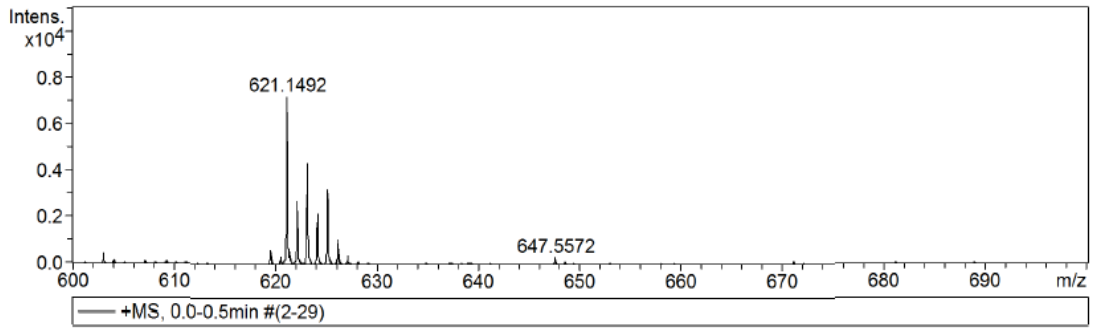


Figure S5 Mass spectrometry data of complex 5

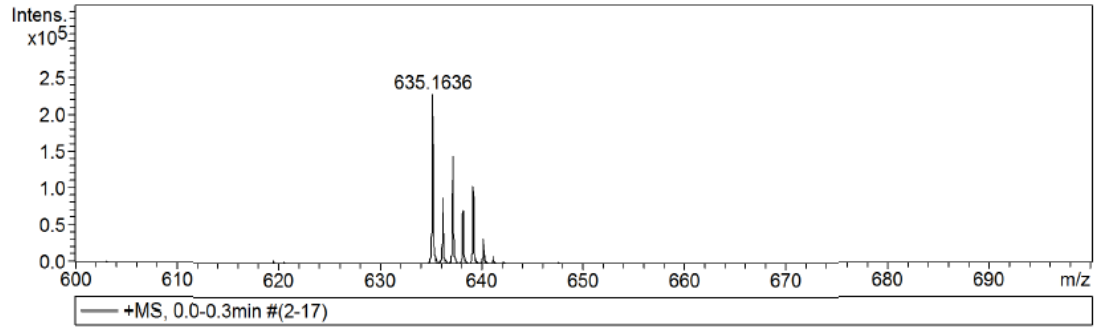


Figure S6 Mass spectrometry data of complex 6

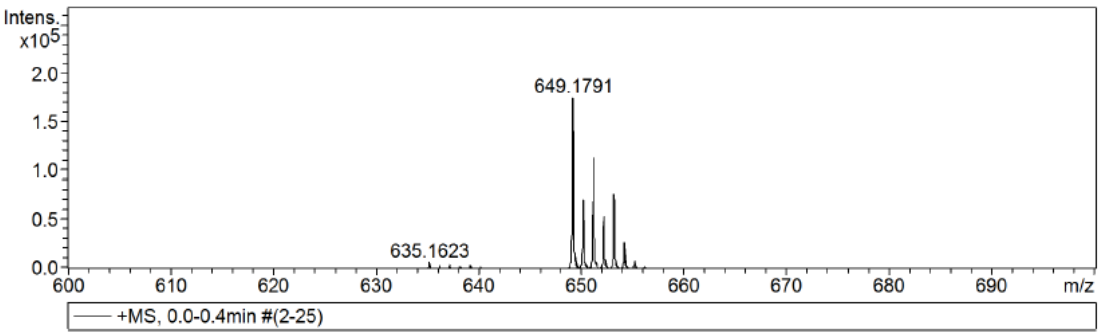


Figure S7 Mass spectrometry data of complex 7

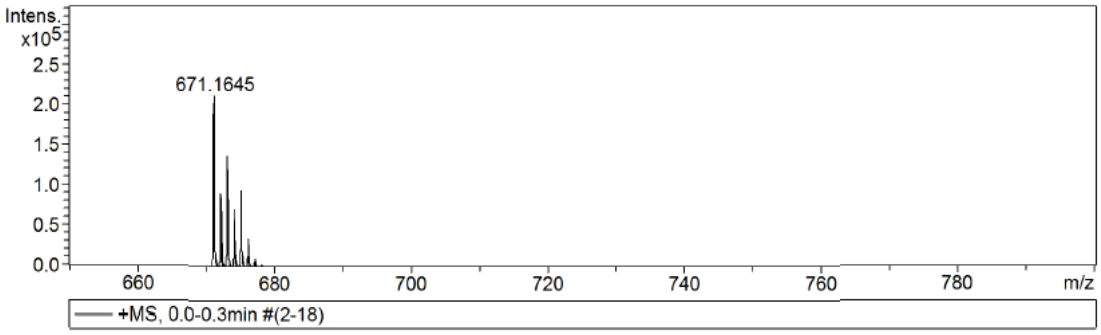


Figure S8 Mass spectrometry data of complex 8

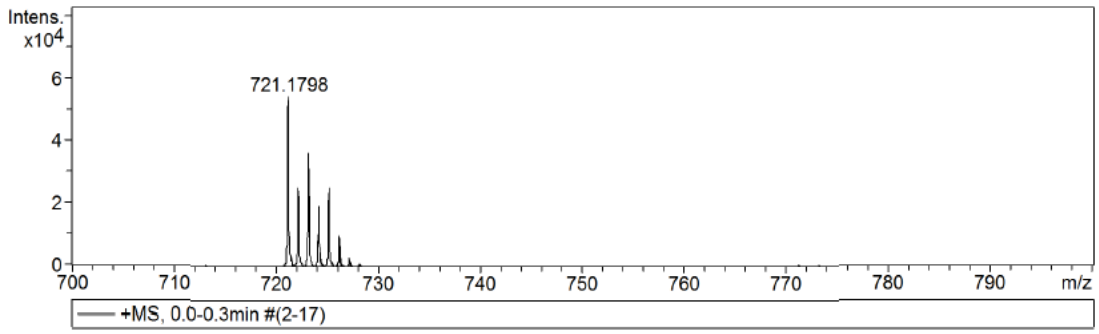


Figure S9 Mass spectrometry data of complex 9

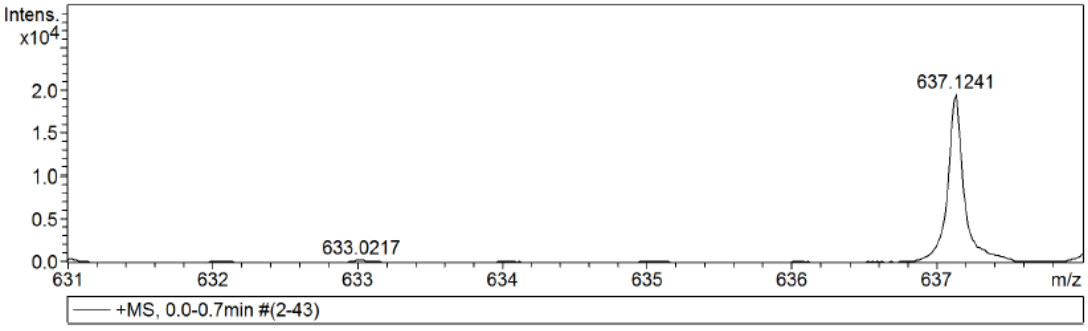


Figure S10 Mass spectrometry data of complex 10

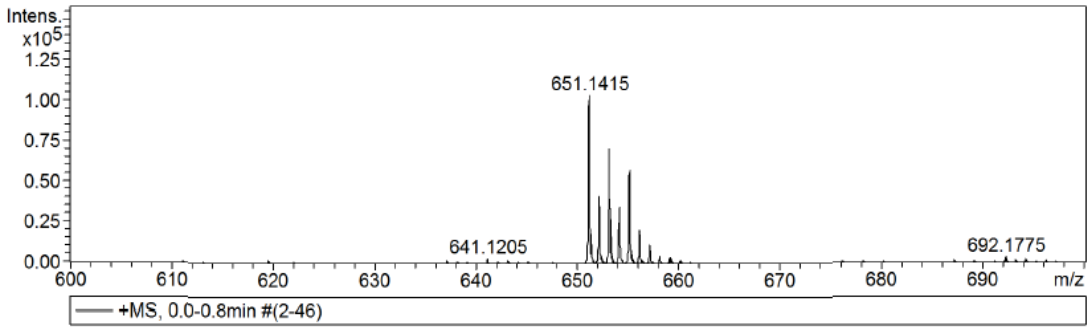


Figure S11 Mass spectrometry data of complex 11

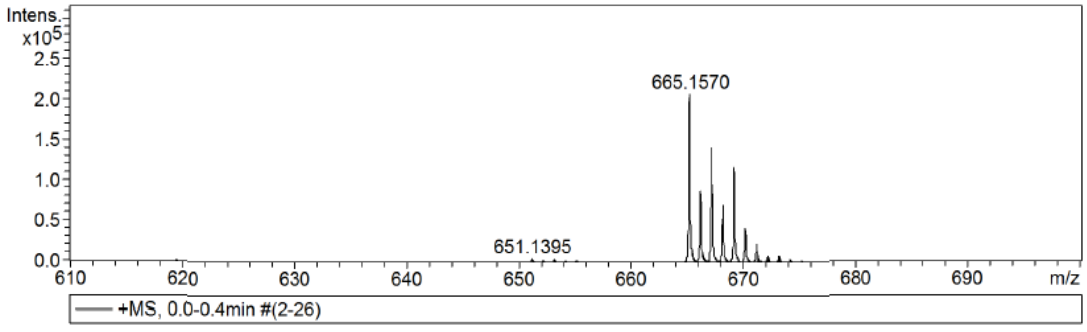


Figure S12 Mass spectrometry data of complex 12

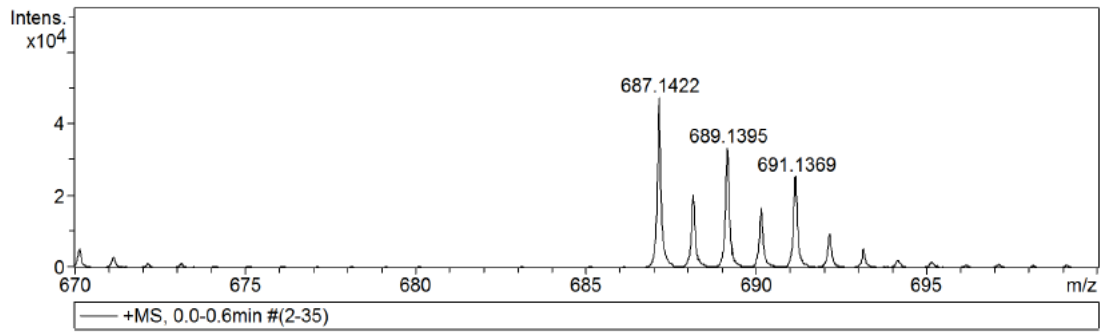


Figure S13 Mass spectrometry data of complex 13

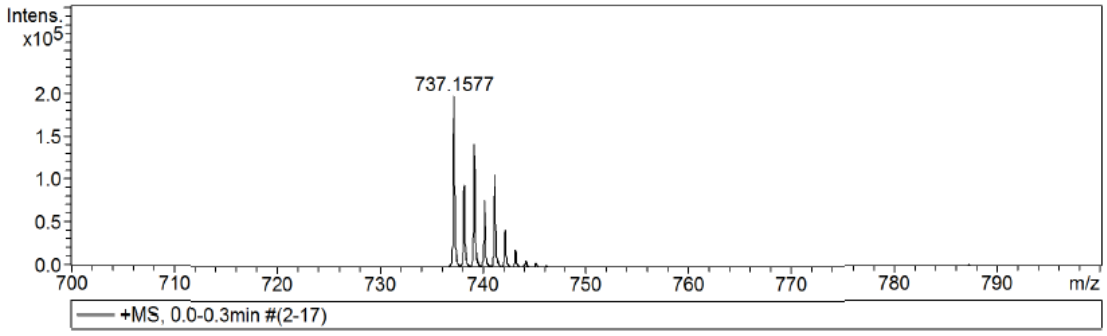


Figure S14 Mass spectrometry data of complex 14

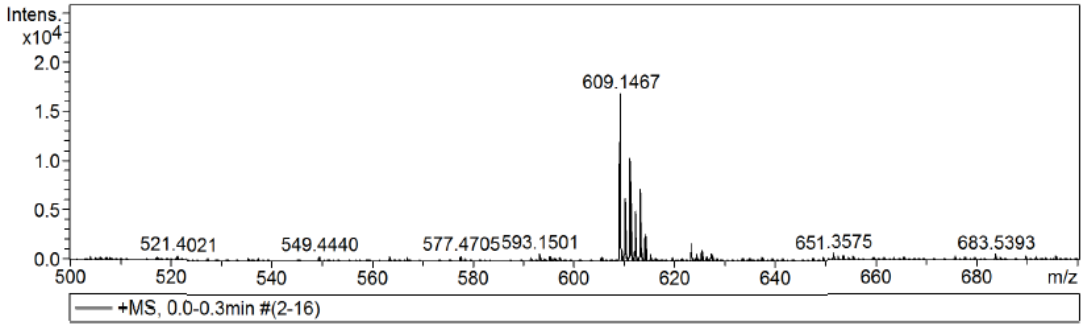


Figure S15 Mass spectrometry data of complex 15

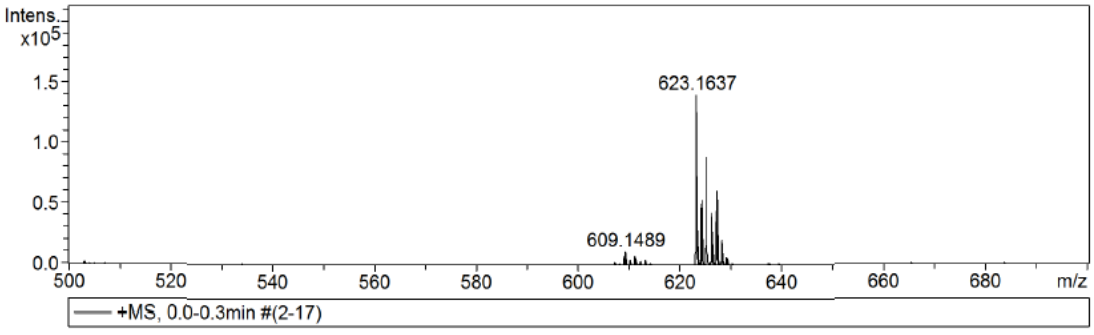


Figure S16 Mass spectrometry data of complex 16

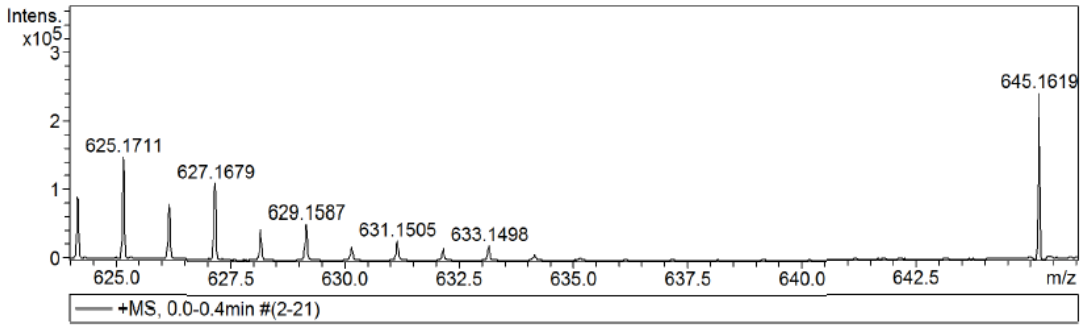


Figure S17 Mass spectrometry data of complex 17

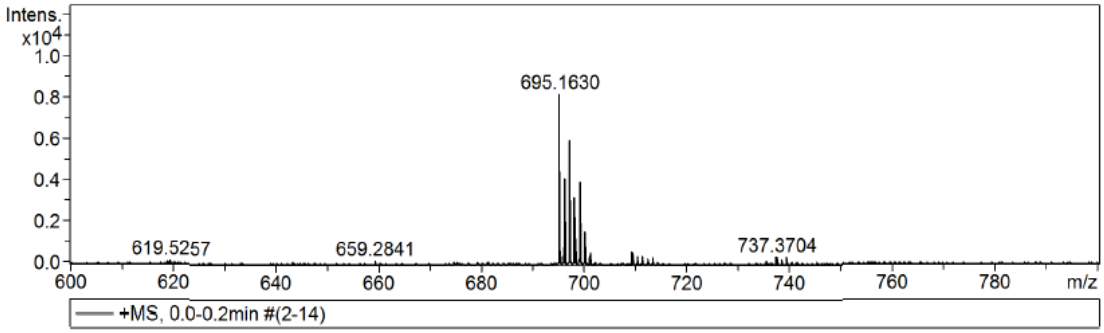


Figure S18 Mass spectrometry data of complex 18

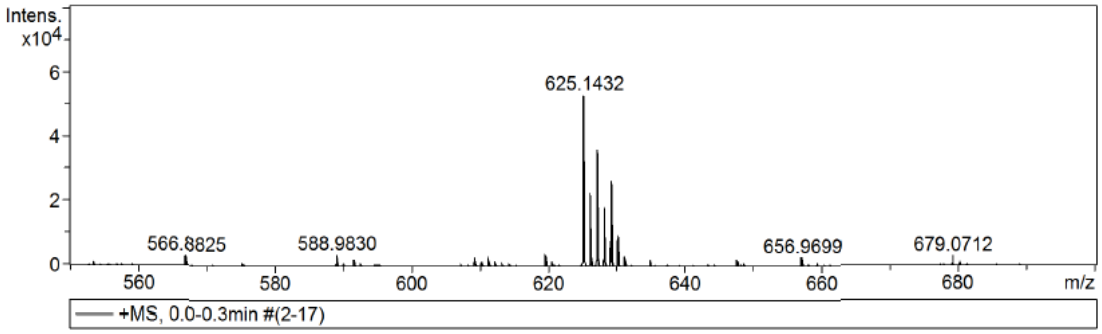


Figure S19 Mass spectrometry data of complex 19

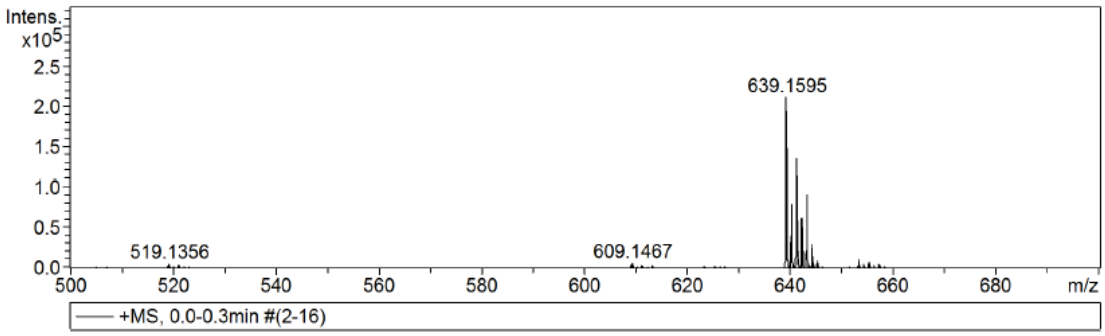


Figure S20 Mass spectrometry data of complex 20

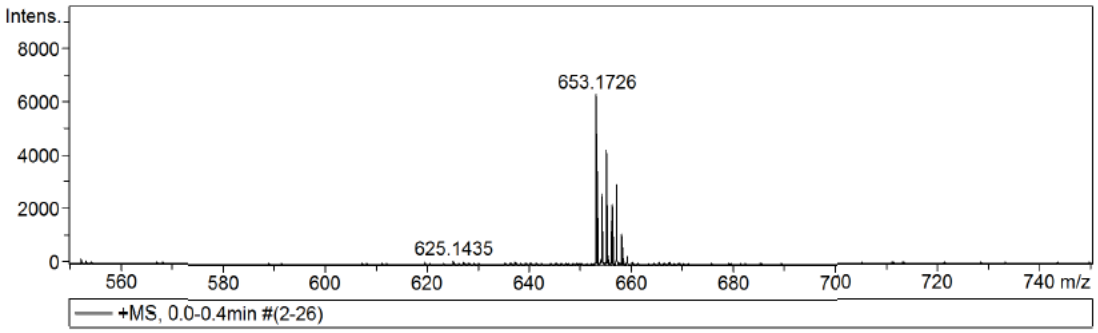


Figure S21 Mass spectrometry data of complex 21

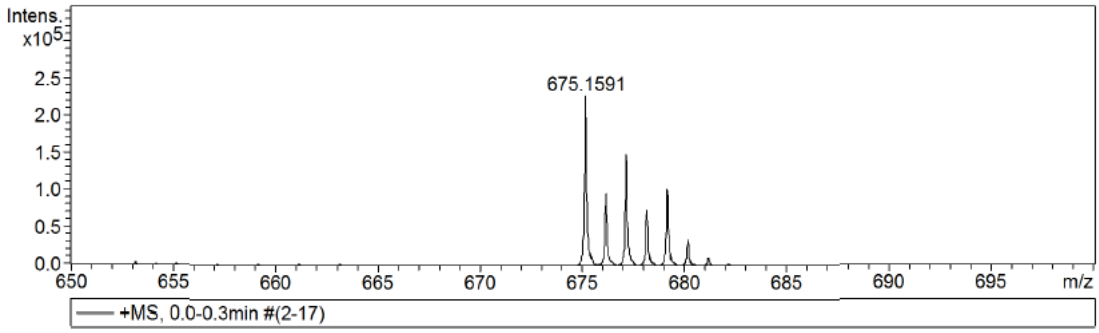


Figure S22 Mass spectrometry data of complex 22

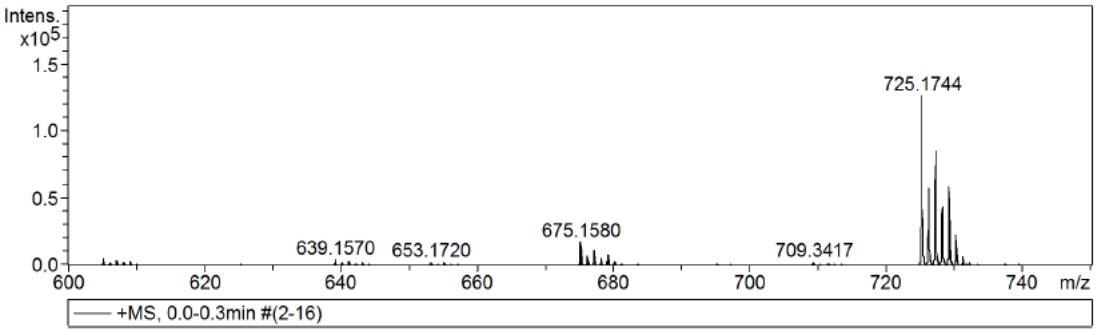


Figure S23 Mass spectrometry data of complex 23

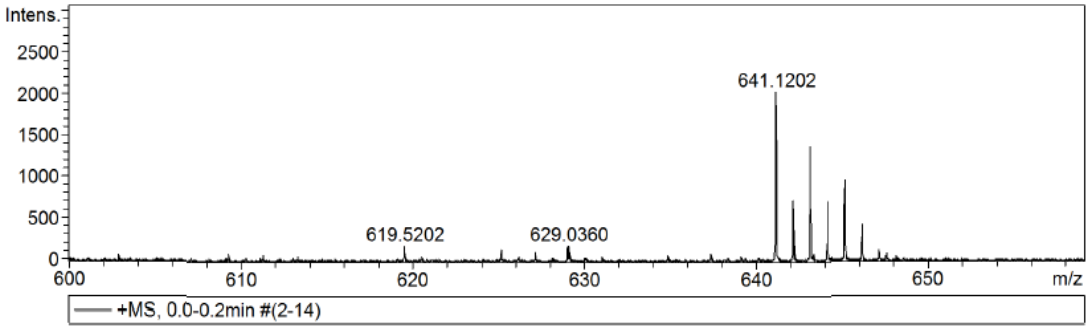


Figure S24 Mass spectrometry data of complex 24

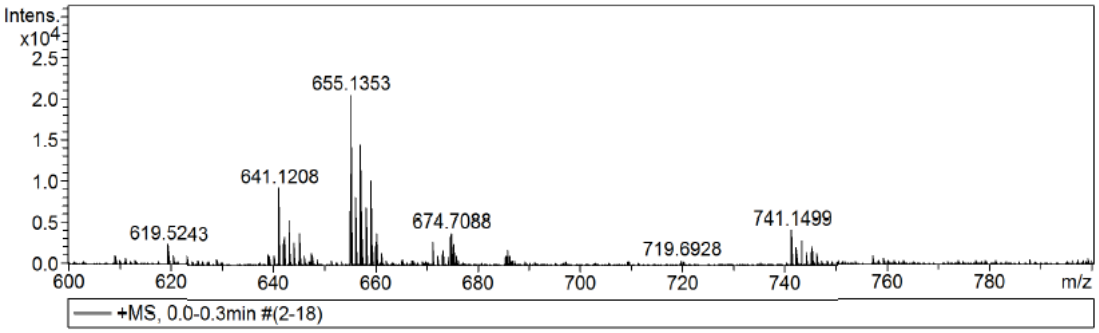


Figure S25 Mass spectrometry data of complex 25

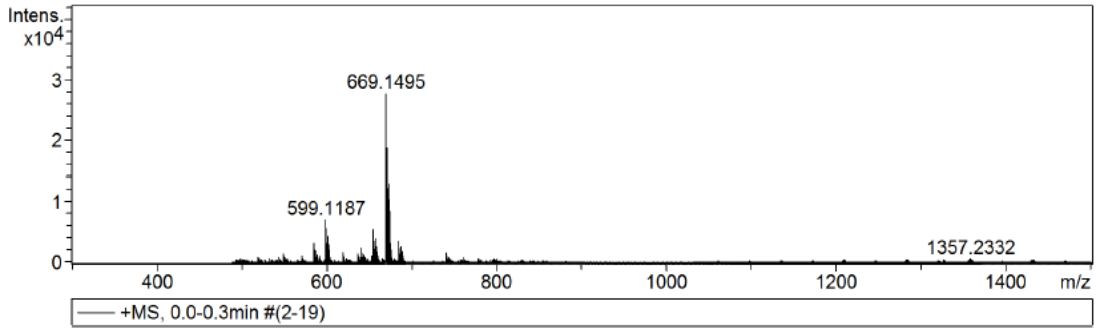


Figure S26 Mass spectrometry data of complex 26

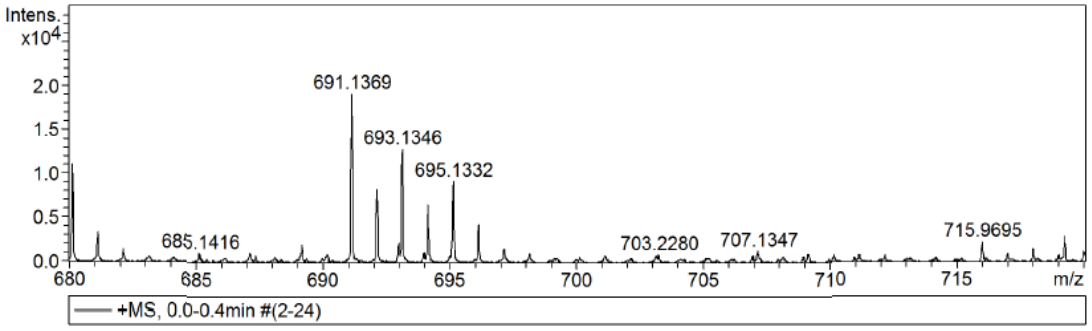


Figure S27 Mass spectrometry data of complex 27

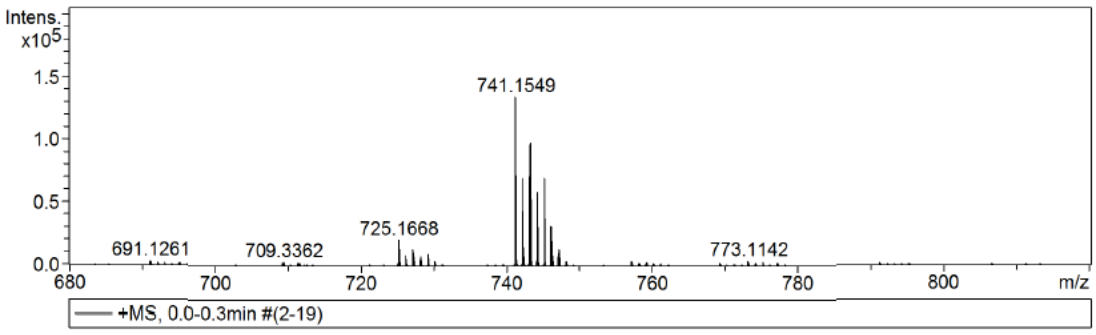


Figure S28 Mass spectrometry data of complex 28

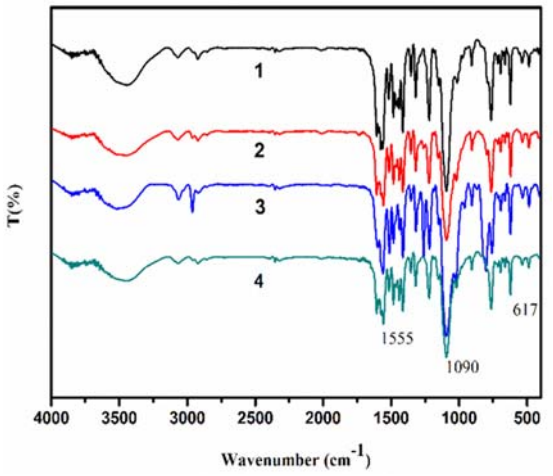


Figure S29 Infrared data of complexes 1-4

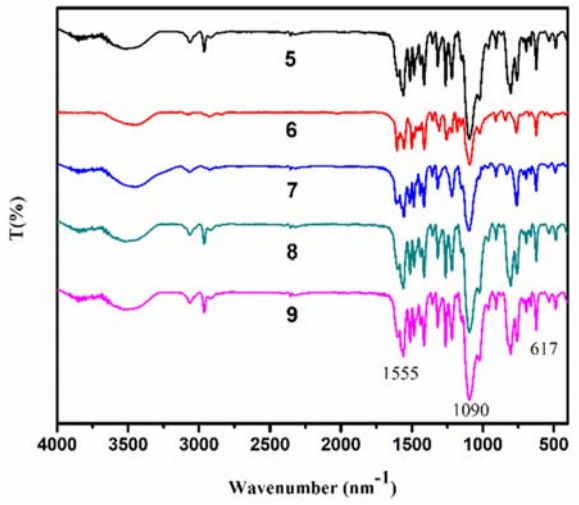


Figure S30 Infrared data of complexes 5-9

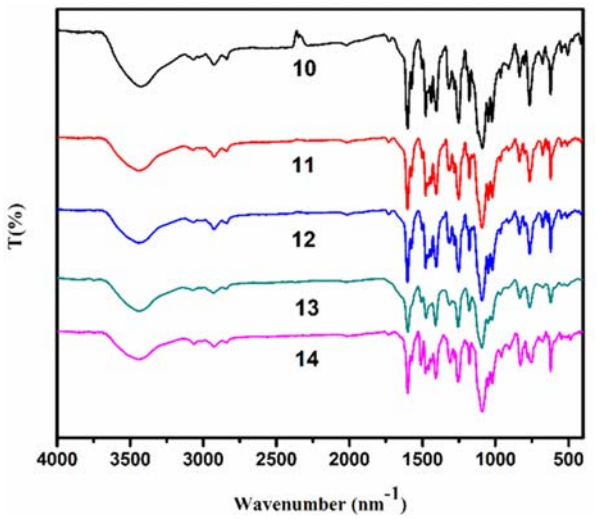


Figure S31 Infrared data of complexes 10-14

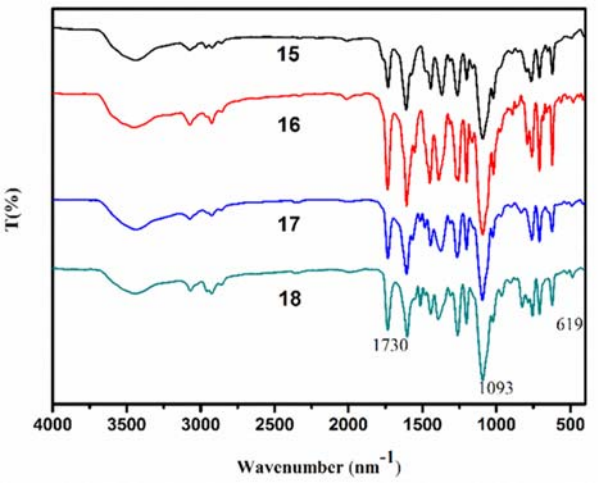


Figure S32 Infrared data of complexes 15-18

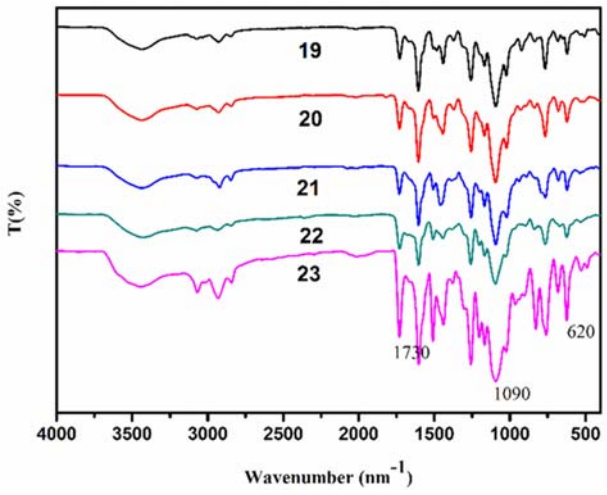


Figure S33 Infrared data of complexes 19-23

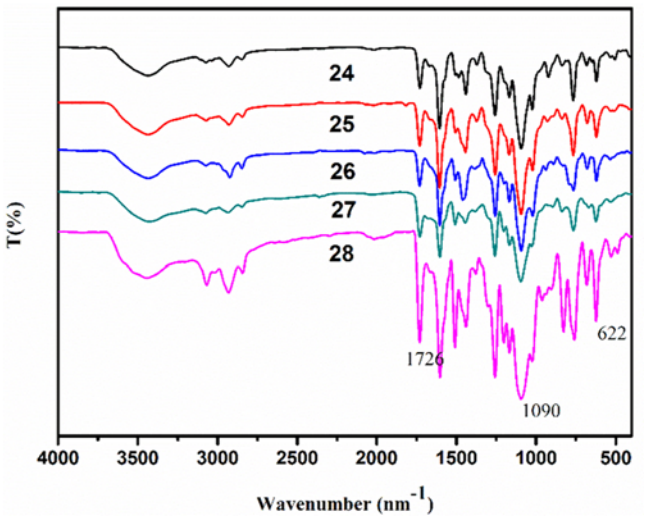


Figure S34 Infrared data of complexes 24-28

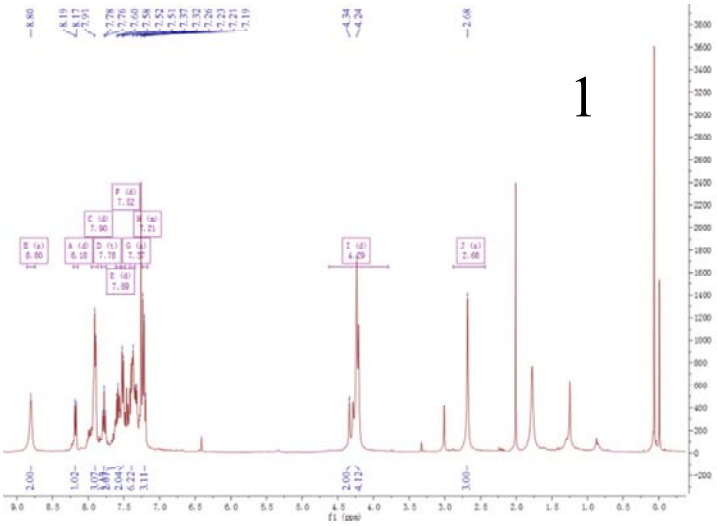


Figure S35 ^{1}H NMR of complex **1**

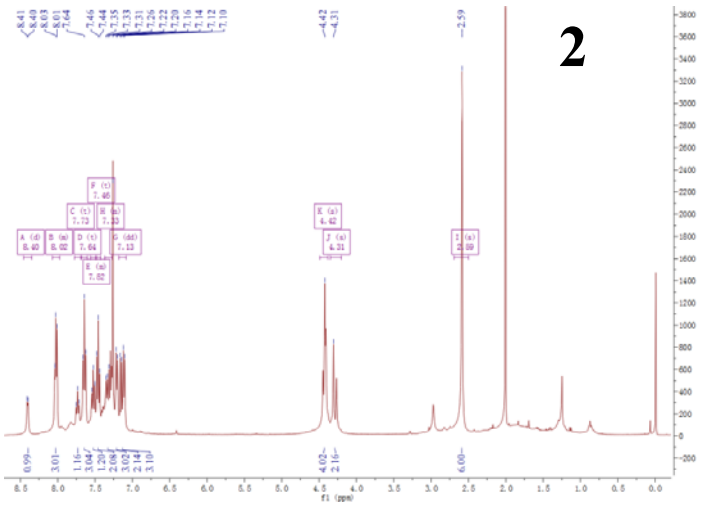


Figure S36 ^{1}H NMR of complex **2**

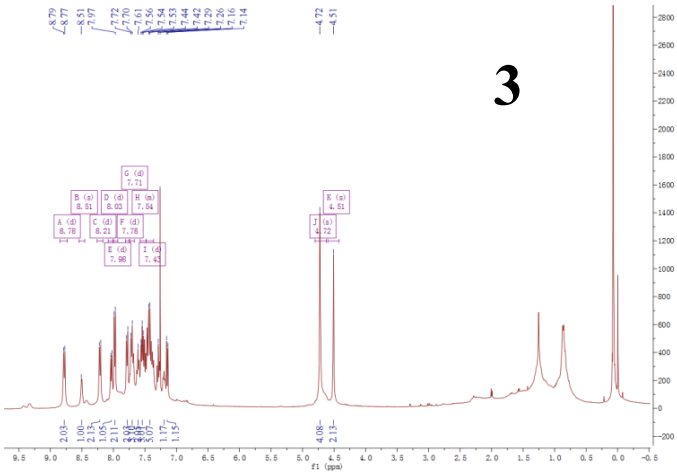


Figure S37 ^{1}H NMR of complex **3**

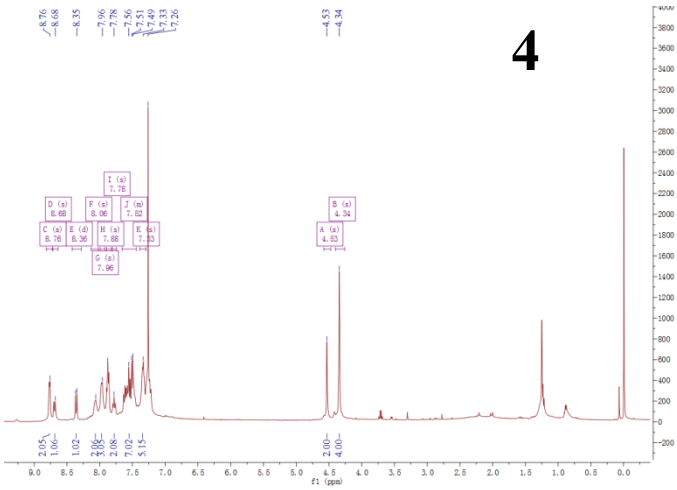


Figure S38 ^{1}H NMR of complex **4**

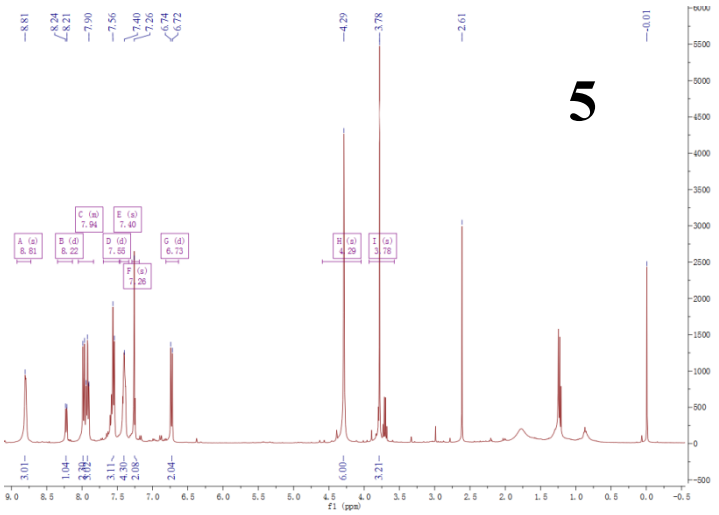


Figure S39 ^{1}H NMR of complex **5**

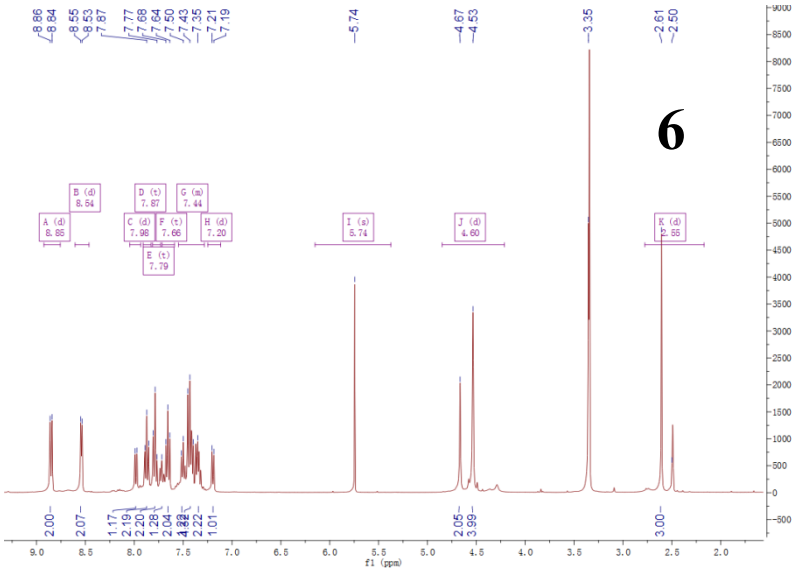


Figure S40 ^{1}H NMR of complex **6**

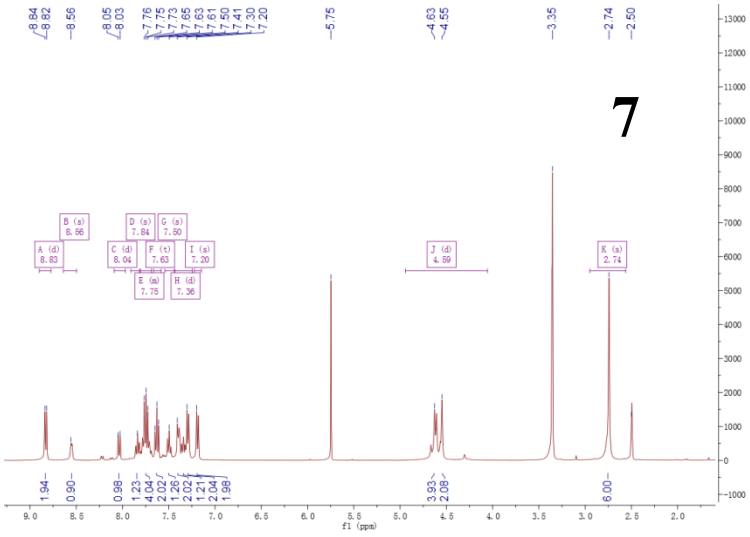


Figure S41 ^{1}H NMR of complex **7**

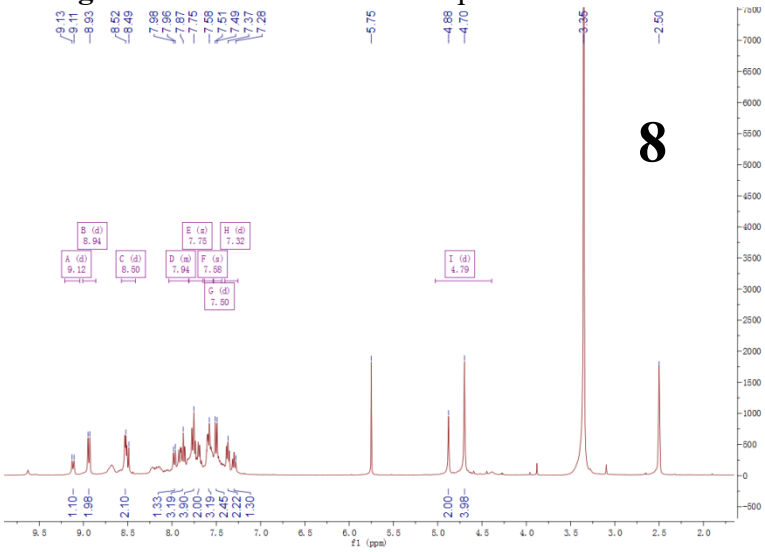


Figure S42 ^{1}H NMR of complex **8**

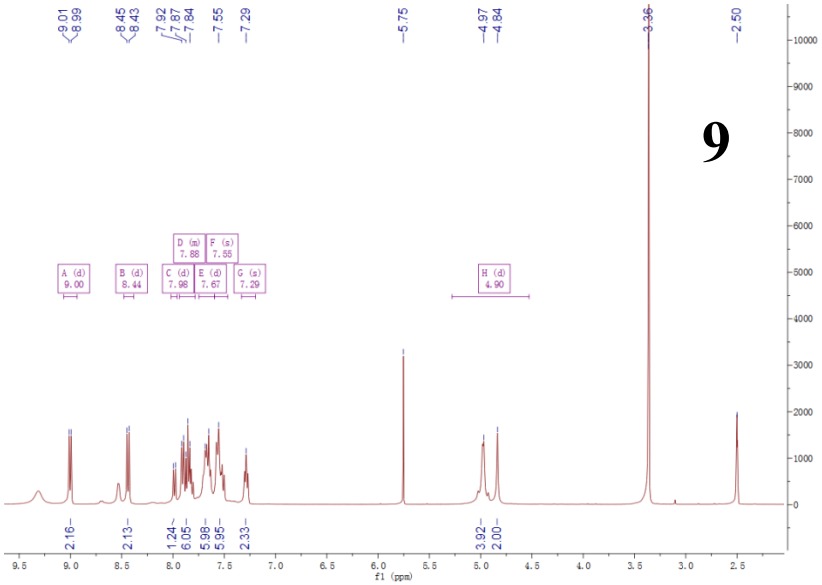


Figure S43 ^{1}H NMR of complex **9**

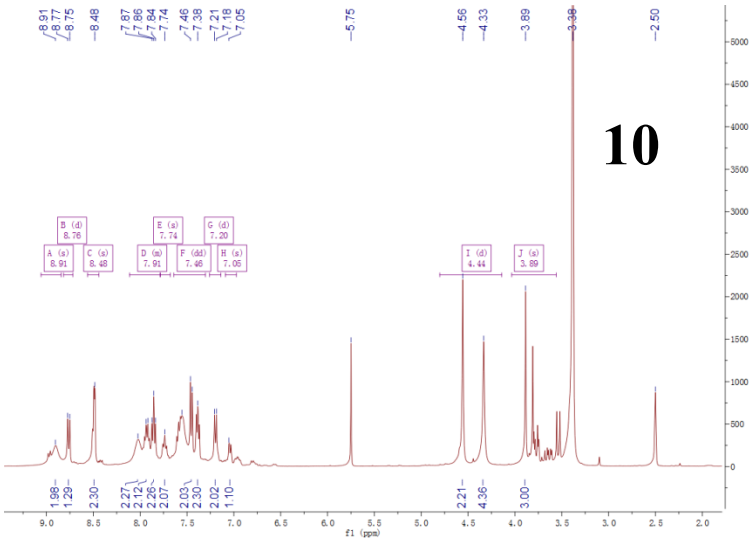


Figure S44 ^{1}H NMR of complex **10**

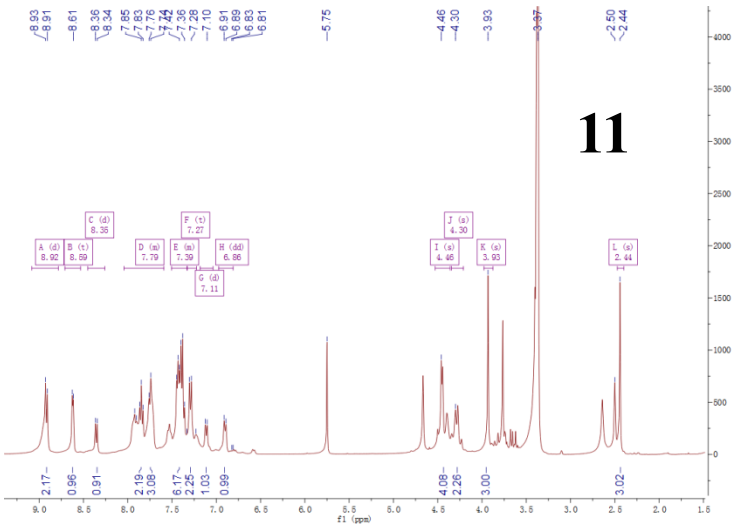


Figure S45 ^{1}H NMR of complex **11**

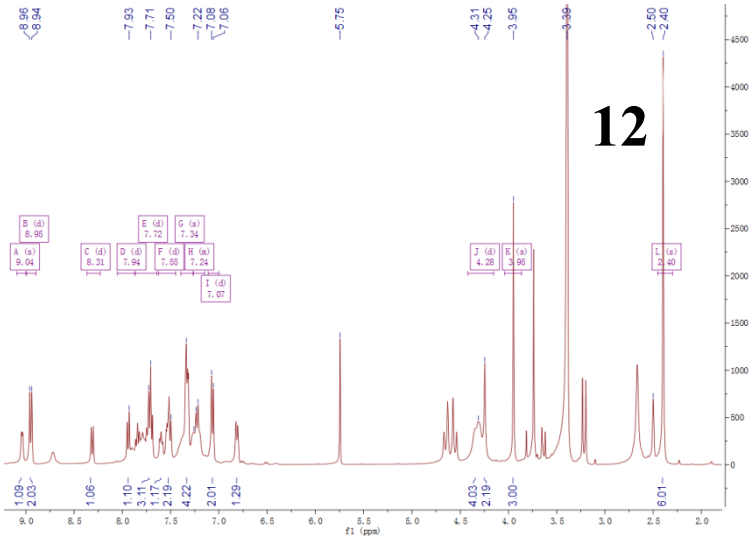


Figure S46 ^{1}H NMR of complex **12**

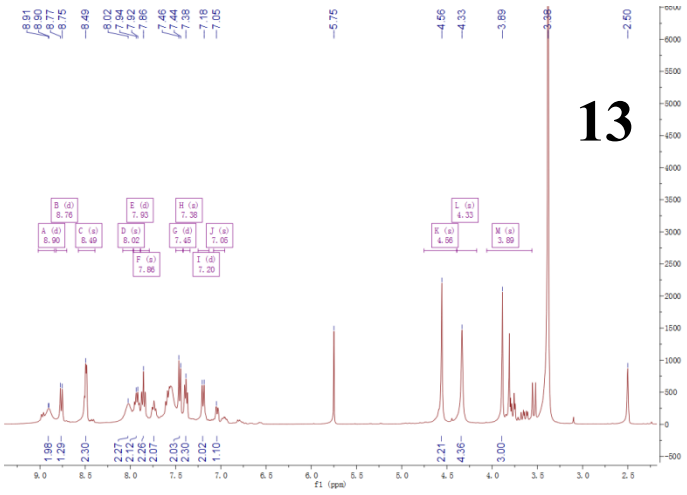


Figure S47 ^{1}H NMR of complex **13**

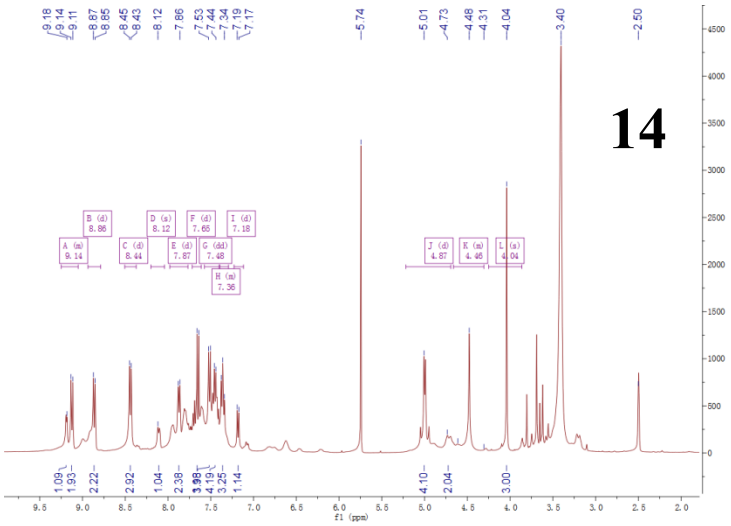


Figure S48 ^{1}H NMR of complex **14**