Synthesis and antibacterial activity study of ruthenium-based metallodrugs with membrane-disruptive mechanism against *Staphylococcus aureus*

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Supplementary Materials

Ligands L1–L3: The synthesis of L1, L2 and L3 were identical with the procedure as described previously[1,2,3].

L4: A mixture of terphenyl-4-formaldehyde(0.12mmol), 1,10-phenanthroline-5,6-dione (0.12 mmol), ammonium acetate (2.38 mmol) and glacial acetic acid (4.5 mL) were refluxed at 130 ℃ for 3 h under argon. After the mixture was cooled to room temperature, the solution was neutralized with aqueous ammonia solution. The resulting solid was filtered and washed with ethanol. The residue was collected and further purified through column chromatography on silica gel using ethanol/dichloromethane (2:1, v/v) as an eluent. Yield: 29.6 mg, 55 %. ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.83 (s, 1H), 9.12-8.93 (m, 3H), 8.42 (d, J = 8.2 Hz, 2H), 8.13-7.67 (m, 11H), 7.58–7.45 (m, 2H), 7.44-7.35 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.9 (s), 166.3 (s), 152.6 (s), 150.5 (s), 148.82(s), 147.7 (s), 145.6 (s), 141.7 (s), 139.1 (s), 138.1 (s), 136.6 (s), 130.7 (s), 129.4 (s), 129.0 (s), 128.5 (s), 128.0 (s), 127.4 (s), 127.4-126.9 (m), 126.6 (d, J = 18.2 Hz), 125.1 (s), 25.5 (s), 24.4 (s). HRMS (ESI) *m/z*: calcd for $C_{31}H_{20}N_4$ $[M+H]^+$, 449.1766; found 449.1767.

Complex Ru1, **Ru2, Ru3, Ru7, Ru8, Ru9, Ru13 and Ru14**: A mixture of **L3** (0.826 mmol) and corresponding reagent (0.826 mmol, $[Ru(bpy)_2Cl_2]\cdot 2H_2O$ for **Ru1**[4], $[Ru(phen)_2Cl_2]\cdot 2H_2O$ for **Ru2**, $[Ru(dmp)_2Cl_2]\cdot 2H_2O$ for **Ru3**, $[Ru(dmb)_2Cl_2]\cdot 2H_2O$ for **Ru7**[4], $[Ru(dtb)_2Cl_2]\cdot 2H_2O$ for **Ru8**, $[Ru(btp)_2Cl_2]\cdot 2H_2O$ for **Ru9**,

$[Ru(ncp)_2Cl_2]\cdot 2H_2O$ for **Ru13** and $[Ru(tmp)_2Cl_2]\cdot 2H_2O$ for **Ru14**) in ethylene glycol (15 mL) were heated at 150 ℃ for 8 h under argon. After the resulting red solution cooled to room temperature, saturated KPF_6 aqueous solution (10 mL) were added to obtain a red precipitate. The crude product was collected, dried and purified by column chromatography (neutral alumina, acetonitrile/xylene = 5:1, v/v). **Ru1**: yield: 65.0 %. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.07 (dd, J = 9.1, 0.9 Hz, 2H), 8.86 (dd, J = 15.1, 8.1 Hz, 4H), 8.44 (d, J = 8.1 Hz, 2H), 8.22 (t, J = 7.9 Hz, 2H), 8.11 (t, J = 7.7 Hz, 2H), 8.03-7.74 (m, 10H), 7.69-7.49 (m, 6H), 7.48 – 7.28 (m, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 156.7 (d, J = 20.9 Hz), 151.4 (s), 148.6 (s), 144.5 (s), 140.7 (s), 139.5 (s), 137.8 (d, J = 16.2 Hz), 130.2 (s), 129.0 (s), 127.8 (d, J = 11.5 Hz), 127.1 (d, J = 3.1 Hz), 126. (s), 125.8 (s), 124.4 (d, J = 6.3 Hz). HRMS (ESI) *m/z*: calcd for $C_{45}H_{32}N_8Ru$ $[M\text{-}2PF_6\text{-}H]^+$, 785.1727; found 785.1718. **Ru2**: yield: 74.0%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.04-8.97 (m, 2H), 8.72 (d, J = 17.8 Hz, 4H), 8.44 (d, J = 8.2 Hz, 2H), 7.97-7.75 (m, 8H), 7.68 (d, J = 5.5 Hz, 2H), 7.52 (t, J = 7.7 Hz, 2H), 7.40 (t, J = 6.7 Hz, 5H), 7.17 (d, J = 5.9 Hz, 2H), 2.55 (s, 6H), 2.45 (s, 6H). ^{13}C NMR(101 MHz, DMSO-d_6) δ 156.3 (d, J = 14.9 Hz), 151.9-151.6 (m), 151.9-151.3 (m), 151.9-147.1 (m), 144.8 (s), 140.2 (d, J = 141.4 Hz), 137.7-136.7 (m), 129.9 (s), 129.8-1295 (m), 128.4 (dd, J = 67.9, 55.0 Hz), 127.7-127.3 (m), 126.9 (d, J = 45.5 Hz), 126.5-126.4 (m), 126.4-124.8 (m), 124.2 (s), 124.2 (s), 20.7 (d, J = 9.2

Hz). HRMS (ESI) *m/z*: calcd for $C_{49}H_{40}N_8Ru$ $[M\text{-}2PF_6\text{-}H]^+$, 841.2354; found 841.2345. **Ru3**: yield: 54.5%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.11 (d, J = 8.0 Hz, 2H), 8.87 (d, J = 12.9 Hz, 4H), 8.45-8.39 (m, 2H), 8.05-7.92 (m, 6H), 7.84-7.79 (m, 2H), 7.69-7.65 (m, 2H), 7.64-7.59 (m, 2H), 7.58-7.51 (m, 2H), 7.50 – 7.42 (m, 3H), 7.36 – 7.30 (m, 2H), 1.43 (d, J = 2.8 Hz, 18H), 1.34 (d, J = 2.6 Hz, 18H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.8 (d, J = 17.7 Hz), 156.5 (d, J = 17.0 Hz), 152.5 (s), 150.8 (d, J = 13.8 Hz), 149.6 (s), 145.3 (s), 141.9 (s), 139.2 (s), 130.2 (s), 129.1 (s), 128.3 (d, J = 39.7 Hz), 128.0 – 127.5 (m), 127.3 (d, J = 23.4 Hz), 126.7 (s), 126.3 (s), 124.8 (s), 124.5 (s), 121.7 (s), 35.4 (d, J = 13.3 Hz), 30.0 (d, J = 10.9 Hz). HRMS (ESI) *m/z*: calcd for $C_{61}H_{64}N_8Ru$ $[M\text{-}2PF_6\text{-}H]^+$, 1009.4236; found 1009.4236. **Ru7**: yield: 52.0%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.02 (d, J = 8.0 Hz, 2H), 8.77 (d, J = 8.2 Hz, 4H), 8.46 – 8.37 (m, 6H), 8.13 (d, J = 5.2 Hz, 4H), 7.88 (d, J = 8.2 Hz, 4H), 7.77 (dd, J = 7.8, 5.2 Hz, 6H), 7.74-7.68 (m, 2H), 7.52 (t, J = 7.5 Hz, 2H), 7.41 (t, J = 7.3 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 152.6 (s), 148.9 (s), 147.2 (d, J = 9.9 Hz), 144.8 (s), 140.5 (s), 139.4 (s), 136.6 (s), 130.4 (s), 130.1 (s), 128.9 (s), 127.8 (d, J = 30.9 Hz), 126.9 (s), 126.5 (s), 126.4 (d, J = 27.1 Hz), 125.5 (s). HRMS (ESI) *m/z:* calcd for $C_{49}H_{32}N_8Ru$ $[M\text{-}2PF_6\text{-}H]^+$, 833.1728; found 833.1714. **Ru8**: yield: 74.8%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.91 (dd, J = 23.7, 8.2 Hz, 4H), 8.45 (dd, J = 10.8, 8.9 Hz, 4H), 8.34 (d, J = 8.2 Hz, 2H), 8.25 (d, J = 8.8 Hz, 2H), 7.99 (d, J =

8.4 Hz, 2H), 7.92 (d, *J* = 8.1 Hz, 2H), 7.78 (d, *J* = 7.4 Hz, 2H), 7.51 (dd, *J* = 15.6, 8.0 Hz, 4H), 7.46-7.31 (m, 5H), 1.94 (s, 6H), 1.72 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.9 (s), 166.3 (s), 152.6 (s), 150.5 (s), 148.8 (s), 147.7 (s), 145.6 (s), 141.7 (s), 139.1 (s), 138.0 (s), 136.6 (s), 130.7 (s), 129.4 (s), 129.0 (s), 128.5 (s), 128.0 (s), 127.4 (s), 127.4-126.9 (m), 126. 6 (d, *J* = 18.2 Hz), 125.1 (s), 25.5 (s), 24.4 (s). HRMS (ESI) *m/z*: calcd for $C_{53}H_{40}N_8Ru$ $[M\text{-}2PF_6\text{-}H]^+$, 889.2355; found 889.2350. **Ru9**: yield: 49.0%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.16 (d, *J* = 8.2 Hz, 2H), 8.44 (d, *J* = 8.4 Hz, 2H), 8.35 (d, *J* = 5.6 Hz, 2H), 8.31-8.16 (m, 7H), 7.99 (d, *J* = 8.3 Hz, 2H), 7.92 (s, 2H), 7.86-7.50 (m, 28H), 7.45 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 152.2 (d, *J* = 21.9 Hz), 152.1-151.8 (m), 147.9 (d, *J* = 13.3 Hz), 135.3 (d, *J* = 4.0 Hz), 130.5 (s), 130.9-129.5 (m), 129.0 (s), 129.0-128.6 (m), 128.6-127.7 (m), 127.2 (d, *J* = 22.7 Hz), 127.1-127.0 (m), 127.1-127.0 (m), 126.7 (s), 126.2 (dd, *J* = 43.0, 5.4 Hz). HRMS (ESI) *m/z*: calcd for $C_{73}H_{48}N_8Ru$ $[M\text{-}2PF_6\text{-}H]^+$,1137.2987; found 1137.2974. **Ru13**: yield: 58.0%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.99 (d, *J* = 7.9 Hz, 2H), 8.46 (d, *J* = 3.4 Hz, 4H), 8.43 (s, 1H), 7.96 – 7.91 (m, 4H), 7.87 (d, *J* = 7.3 Hz, 3H), 7.78 (d, *J* = 7.8 Hz, 3H), 7.70 (s, 2H), 7.59 (d, *J* = 5.2 Hz, 4H), 7.52 (t, *J* = 7.4 Hz, 3H), 7.41 (t, *J* = 6.9 Hz, 1H), 2.89 (d, *J* = 3.3 Hz, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.9 (s), 166.3 (s), 152.6 (s), 150.5 (s), 148.8 (s), 147.7 (s), 145.6 (s), 141.7 (s), 139.1 (s), 138.0 (s), 136.6 (s), 130.7 (s), 129.4 (s), 129.0 (s), 128.5 (s),

128.0 (s), 127.4 (s), 127.4-126.9 (m), 126.6 (d, *J* = 18.2 Hz), 125.1 (s), 25.5 (s), 24.4 (s). HRMS (ESI) *m/z*: calcd for $C_{53}H_{40}N_8Ru$ [M-2PF_6-H]$^+$,889.2355; found 889.2339. **Ru14**: yield: 60.0%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 14.41 (s, 1H), 9.10-9.00 (m, 2H), 8.51 (d, *J* = 17.8 Hz, 3H), 8.40 (t, *J* = 8.1 Hz, 2H), 8.08-7.65 (m, 13H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 2.91-2.62 (m, 12H), 2.23 (d, *J* = 20.3 Hz, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) *δ* 167.9 (s), 166.3 (s), 152.6 (s), 150.5 (s), 148.8 (s), 147.7 (s), 145.6 (s), 141.7 (s), 139.0 (s), 138.0 (s), 136.6 (s), 130.7 (s), 129.4 (s), 129.0 (s), 128.5 (s), 128.0 (s), 127.4 (s), 127.4-126.9 (m), 126.6 (d, *J* = 18.2 Hz), 125.1 (s), 25.5 (s), 24.4 (s). HRMS (ESI) *m/z*: calcd for $C_{57}H_{48}N_8Ru$ [M-2PF_6-H]$^+$,945.2983; found 945.2986.

Complex Ru4 and Ru10: These complexes were synthesized in an identical manner to that described for complex **Ru1** with **L1** in place of **L3. Ru4**: yield: 61.2%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.98 (d, *J* = 8.1 Hz, 2H), 8.78-8.66 (m, 4H), 8.05 (d, *J* = 4.9 Hz, 2H), 7.89 (dd, *J* = 8.3, 5.3 Hz, 2H), 7.65 (d, *J* = 5.8 Hz, 2H), 7.39 (dd, *J* = 11.7, 5.8 Hz, 3H), 7.16-7.02 (m, 3H), 7.00-6.91 (m, 1H), 2.53 (d, *J* = 13.7 Hz, 6H), 2.44 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) *δ* 156.2 (d, *J* = 16.2 Hz), 150.5 (d, *J* = 17.7 Hz), 150.3-150.1 (m), 150.1-149.2 (m), 145.3 (s), 142.8 (s), 130.0 (s), 128.4 (d, *J* = 14.5 Hz), 126.3 (s), 125.0 (d, *J* = 7.6 Hz), 20.7 (d, *J* = 9.7 Hz). HRMS (ESI) *m/z*: calcd for $C_{37}H_{32}N_8Ru$ [M-2PF_6-H]$^+$, 689.1725; found 689.1725. **Ru10**[5]: yield: 53.0%. ^{1}H NMR (500 MHz, DMSO-d_6) δ

14.17 (s, 1H), 8.91 (d, J = 8.3 Hz, 2H), 8.78 (d, J = 7.7 Hz, 2H), 8.65 (s, 1H), 8.43 (t, J = 8.5 Hz, 4H), 8.24 (d, J = 8.7 Hz, 2H), 7.98 (d, J = 8.3 Hz, 2H), 7.54-7.46 (m, 2H), 7.36 (d, J = 7.7 Hz, 4H), 1.92 (s, 6H), 1.67 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.9 (s), 166.3 (s), 152.6 (s), 150.5 (s), 148.8 (s), 147.7 (s), 145.6 (s), 141.7 (s), 139.1 (s), 138.0 (s), 136.6 (s), 130.7 (s), 129.4 (s), 129.0 (s), 128.5 (s), 128.0 (s), 127.4 (s), 127.4-126.9 (m), 126.6 (d, J = 18.2 Hz), 125.1 (s), 25.47 (s), 24.4 (s). HRMS (ESI) *m/z*: calcd for $C_{41}H_{32}N_8Ru$ $[M\text{-}2PF_6\text{-}H]^+$,737.1726; found 737.1721.

Complex Ru5 and Ru11: These complexes were synthesized in an identical manner to that described for complex **Ru1** with **L2** in place of **L3**. **Ru5**[6]: yield: 60.5%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.05 (d, J = 8.3 Hz, 2H), 8.77 – 8.69 (m, 4H), 8.33 (d, J = 7.5 Hz, 2H), 8.01 (s, 2H), 7.88 (s, 2H), 7.62 (dd, J = 31.0, 20.3 Hz, 5H), 7.44 – 7.35 (m, 4H), 7.16 (d, J = 5.9 Hz, 2H), 2.55 (s, 6H), 2.45 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 156.3 (d, J = 14.0 Hz), 154.1 (s), 150.4 (d, J = 11.0 Hz), 149.8-149.1 (m), 149.1-148.7 (m), 145.0 (s), 130.7 (s), 129.8 (d, J = 20.4 Hz), 129.3 (s), 129.0 (s), 128.4 (d, J = 14.1 Hz), 126.6 (s), 125.9 (s), 124.9 (d, J = 5.9 Hz), 123.9 (s), 20.7 (d, J = 9.7 Hz). HRMS (ESI) *m/z*: calcd for $C_{43}H_{36}N_8Ru$ $[M\text{-}2PF_6\text{-}H]^+$, 765.2040; found 765.2051. **Ru11**: yield: 52.0%. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.92 (d, J = 8.3 Hz, 2H), 8.85 (d, J = 8.1 Hz, 2H), 8.44 (t, J = 9.2 Hz, 4H), 8.25 (d, J = 8.5 Hz, 4H),

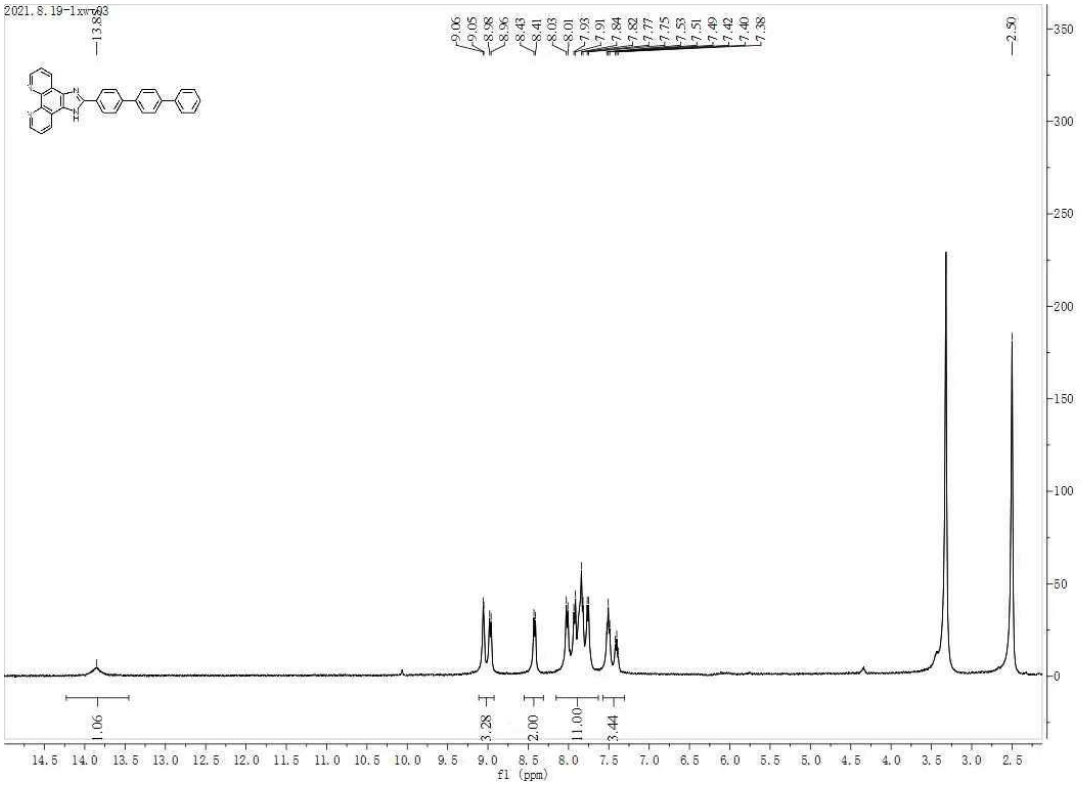
7.98 (d, J = 8.3 Hz, 2H), 7.58 (t, J = 7.2 Hz, 2H), 7.54 – 7.44 (m, 3H), 7.38 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 3.5 Hz, 2H), 1.94 (s, 6H), 1.70 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.7 (s), 166.1 (s), 148.9 (s), 148.5 (s), 147.9 (s), 138.9 (d, J = 53.1 Hz), 137.8 (s), 136.5 (s), 130.1 (s), 129.4 (d, J = 4.7 Hz), 128.9 (s), 127.3 (s), 127.1-126.7 (m), 126.5 (t, J = 12.3 Hz), 124.2 (d, J = 16.0 Hz), 25.3 (s), 24.4 (s). HRMS (ESI) *m/z*: calcd for $C_{47}H_{36}N_8Ru$ $[M\text{-}2PF_6\text{-}H]^+$,813.2040; found 813.2032.

Complex Ru6 and Ru12: These complexes were synthesized in an identical manner to that described for complex **Ru1** with **L4** in place of **L3**. **Ru6**: yield: 59.0%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.04 (d, J = 7.8 Hz, 2H), 8.72 (d, J = 17.3 Hz, 4H), 8.47 (d, J = 8.2 Hz, 2H), 7.96 (d, J = 7.3 Hz, 4H), 7.90 (d, J = 8.2 Hz, 2H), 7.83 (d, J = 8.1 Hz, 4H), 7.76 (d, J = 7.6 Hz, 2H), 7.68 (d, J = 5.6 Hz, 2H), 7.51 (t, J = 7.6 Hz, 2H), 7.44 – 7.38 (m, 5H), 7.17 (d, J = 5.6 Hz, 2H), 2.56 (s, 6H), 2.46 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 156.3 (d, J = 15.1 Hz), 150.4 (s), 149.4 (d, J = 14.9 Hz), 148.3 (s), 144.6 (s), 140.5-138.9 (m), 138.5 (s), 129.8 (s), 129.0 (s), 128.4 (d, J = 11.5 Hz), 127.7-126.5 (m), 126.5-125.9 (m), 126.5 – 125.9 (m), 125.6 (s), 124.9 (s), 20.7 (d, J = 8.8 Hz). HRMS (ESI) *m/z*: calcd for $C_{55}H_{44}N_8Ru$ $[M\text{-}2PF_6\text{-}H]^+$,917.2669; found 917.2667. **Ru12**: yield: 50.1%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.91 (d, J = 8.3 Hz, 2H), 8.77 (d, J = 7.5 Hz, 2H), 8.50-8.35 (m, 6H), 8.24 (d, J = 8.8 Hz, 2H), 7.97 (d, J = 8.4 Hz, 2H), 7.90-7.69 (m, 8H), 7.50 (t, J = 7.5 Hz, 2H), 7.44-7.28

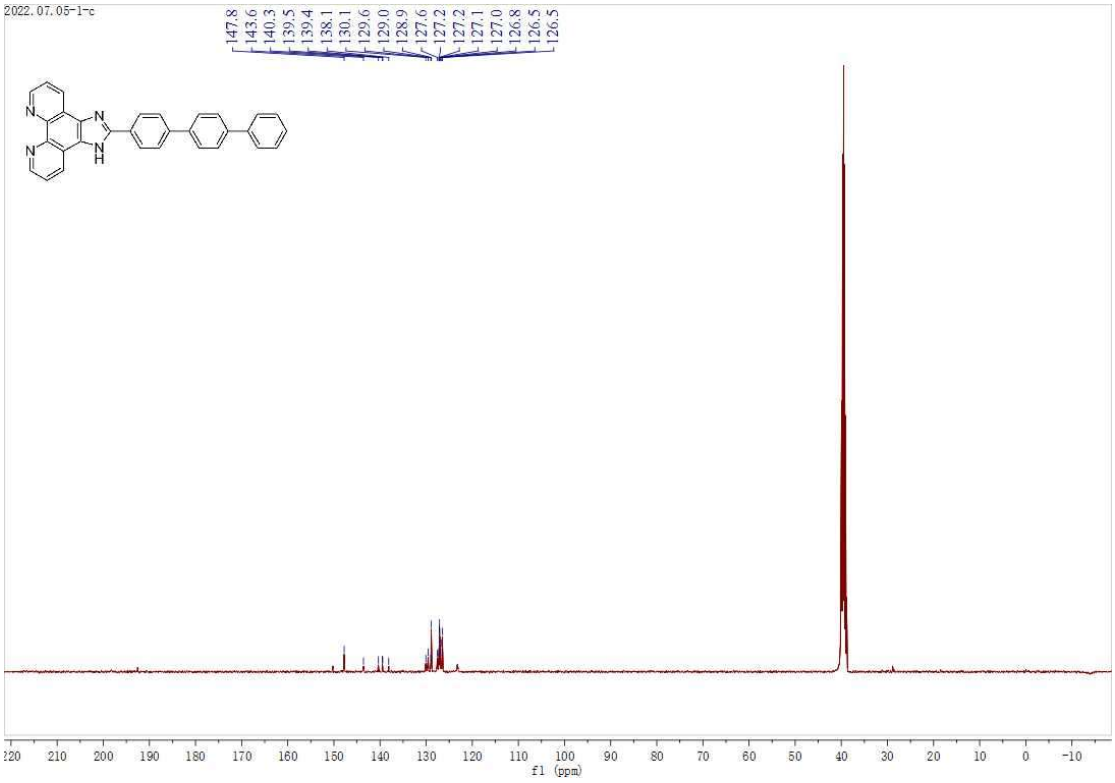
(m, 5H), 7.15 (s, 2H), 1.95 (s, 6H), 1.72 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.9 (s), 150.3 (s), 148.8 (s), 147.8 (s), 145.5 (s), 138.0 (s), 136.6 (s), 130.6 (s), 130.6-129.7 (m), 129.4 (s), 129.0 (s), 127.4 (d, J = 13.2 Hz), 127.0 (s), 126.5 (s), 125.0 (s), 25.4 (s), 24.4 (s). HRMS (ESI) *m/z*: calcd for $C_{59}H_{44}N_8Ru$ $[M\text{-}2PF_6\text{-}H]^+$,965.2670; found 965.2663.

Spectra of Ligands and Complexes

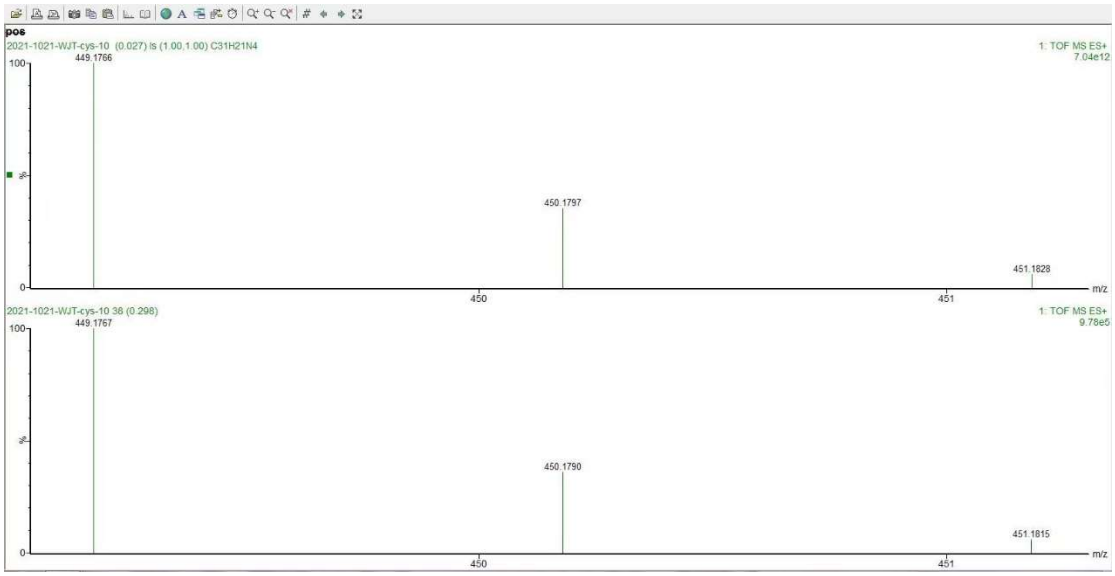
^{1}H NMR of L4



^{13}C NMR of L4



HRMS of L4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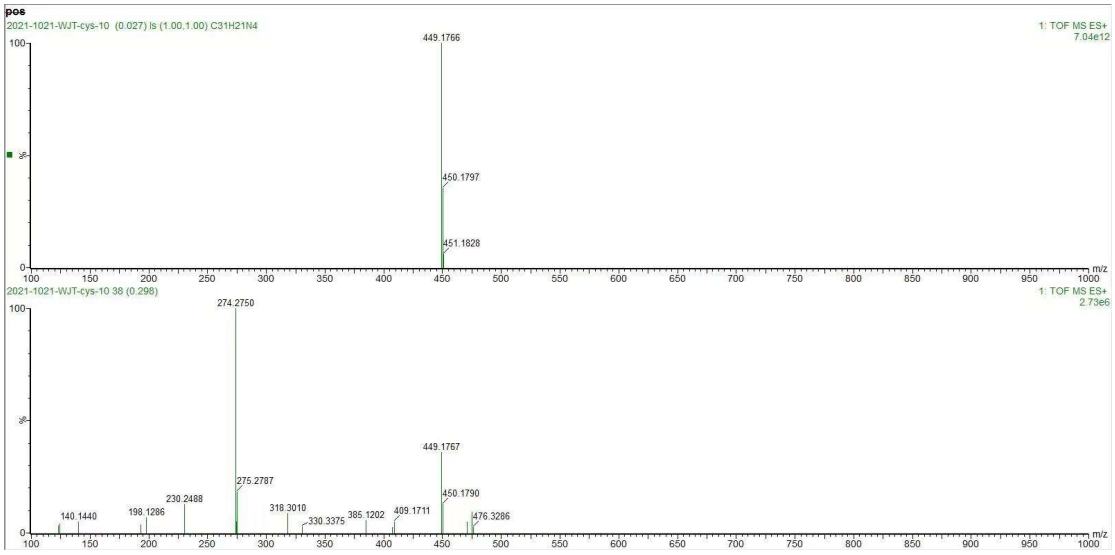
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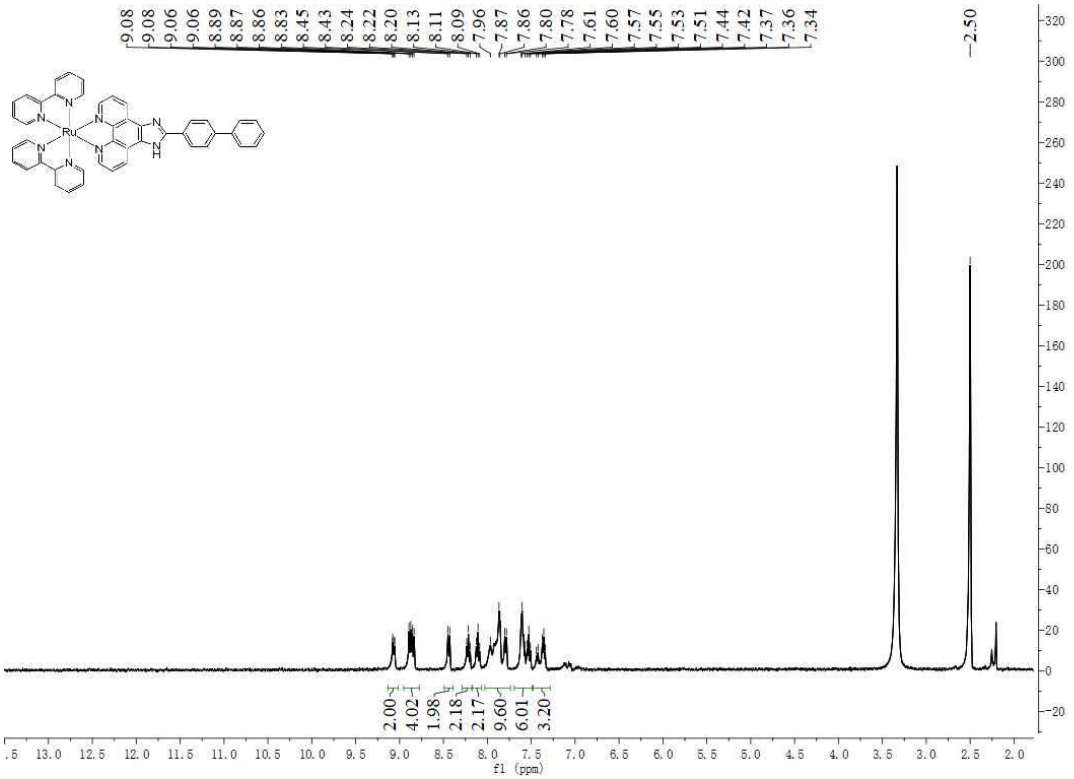
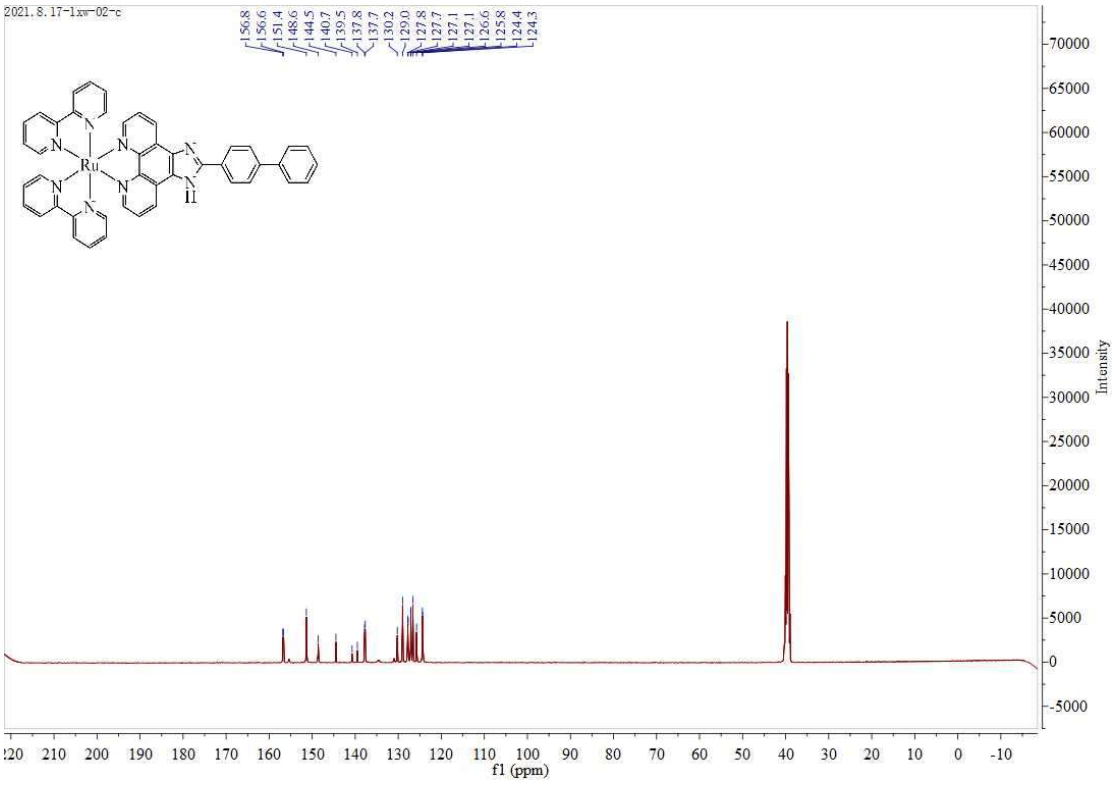
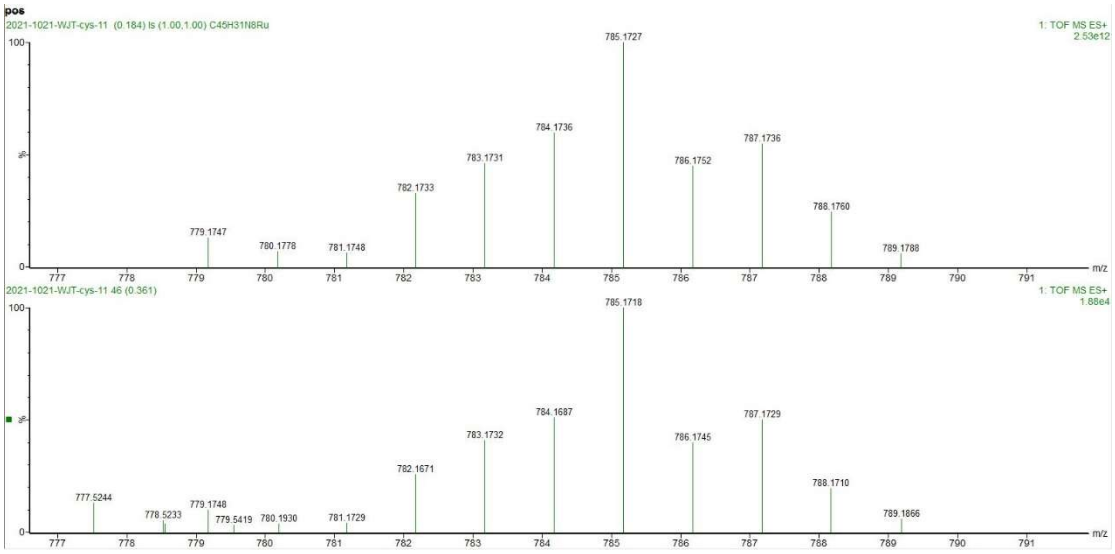
^{1}H NMR of Ru1



^{13}C NMR of Ru1



HRMS of Ru1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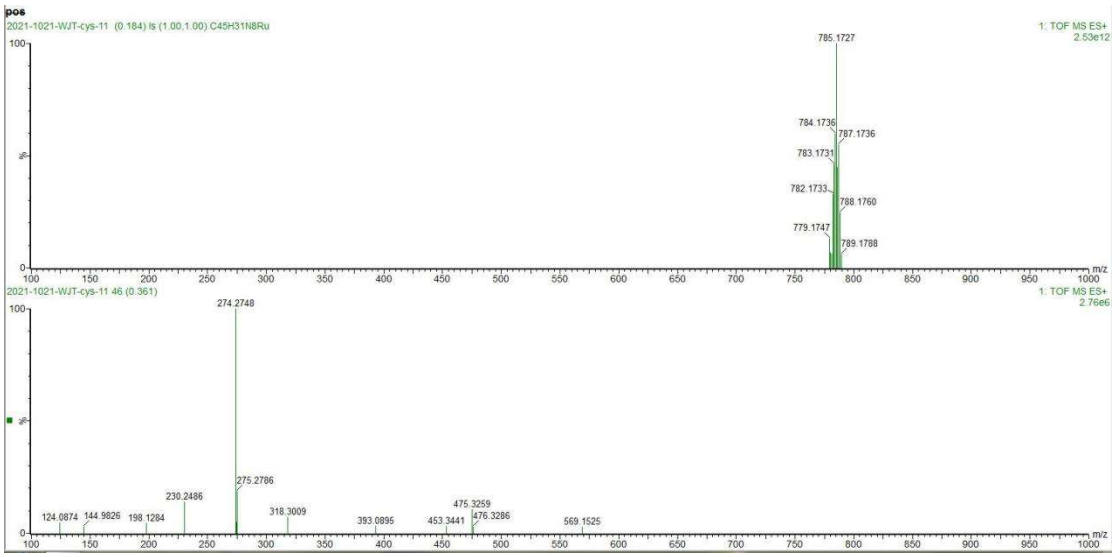
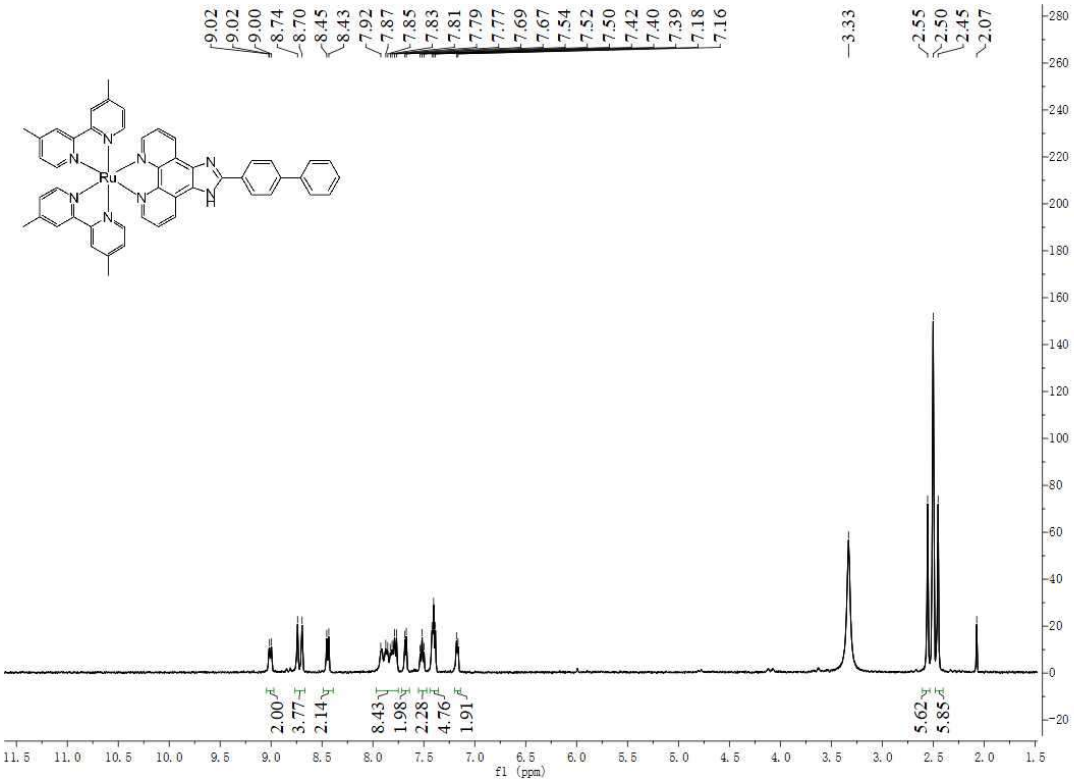
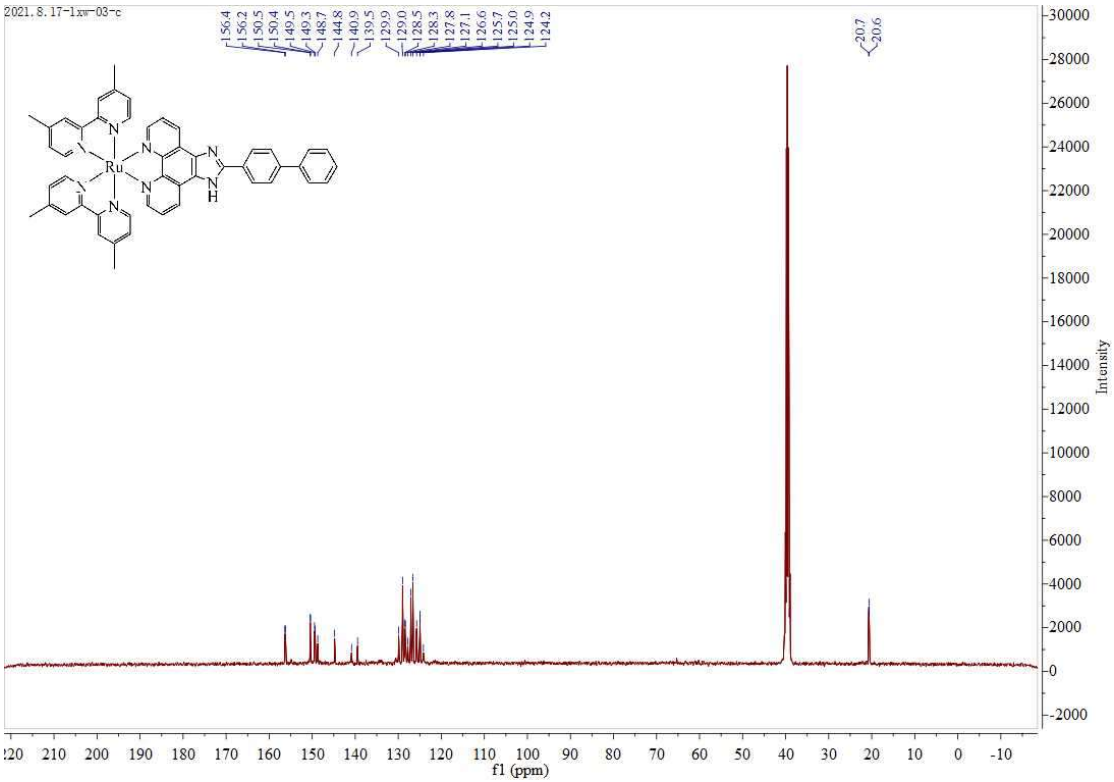
782.1671
788.1710
777.5244
778.5233
779.1748
779.5419
780.1930
781.1729
789.1866
m/z


pos
2021-1021-WJT-cys-11 (0.184) Is (1.00,1.00) C45H31N8Ru
1: TOF MS ES+
2.53e12
785.1727
784.1736
787.1736
783.1731
782.1733
788.1760
779.1747
789.1788
m/z
2021-1021-WJT-cys-11 46 (0.361)
1: TOF MS ES+
2.76e6
274.2748
275.2786
230.2486
318.3009
124.0874
144.9826
198.1284
393.0895
475.3259
453.3441
476.3286
569.1525
m/z

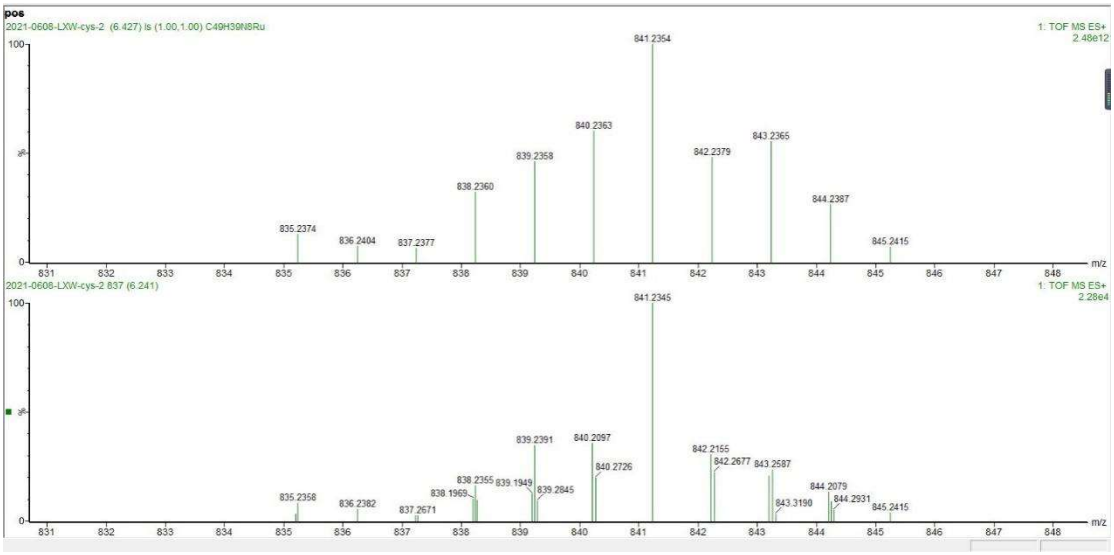
^{1}H NMR of Ru2

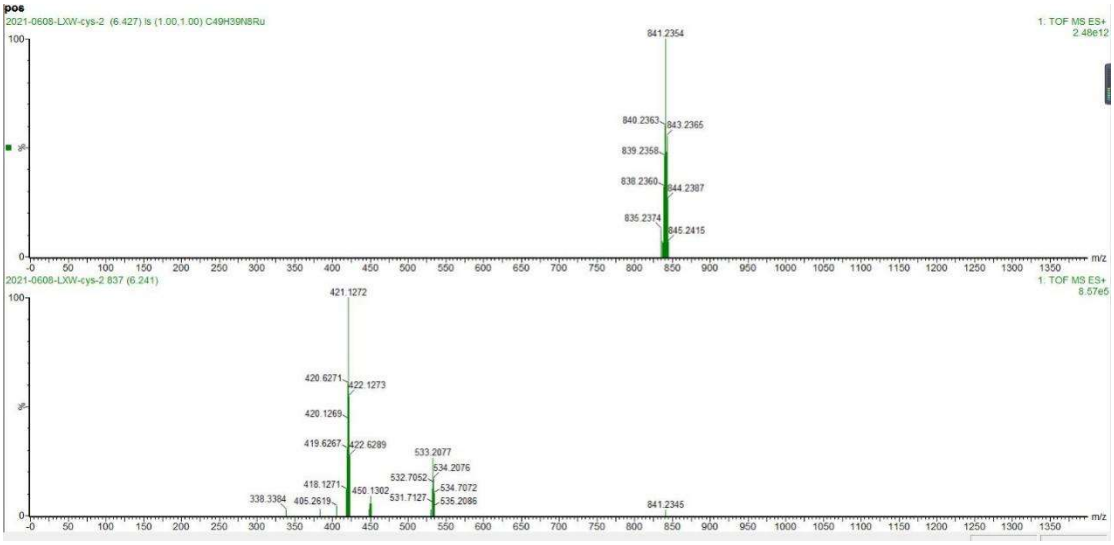


^{13}C NMR of Ru2

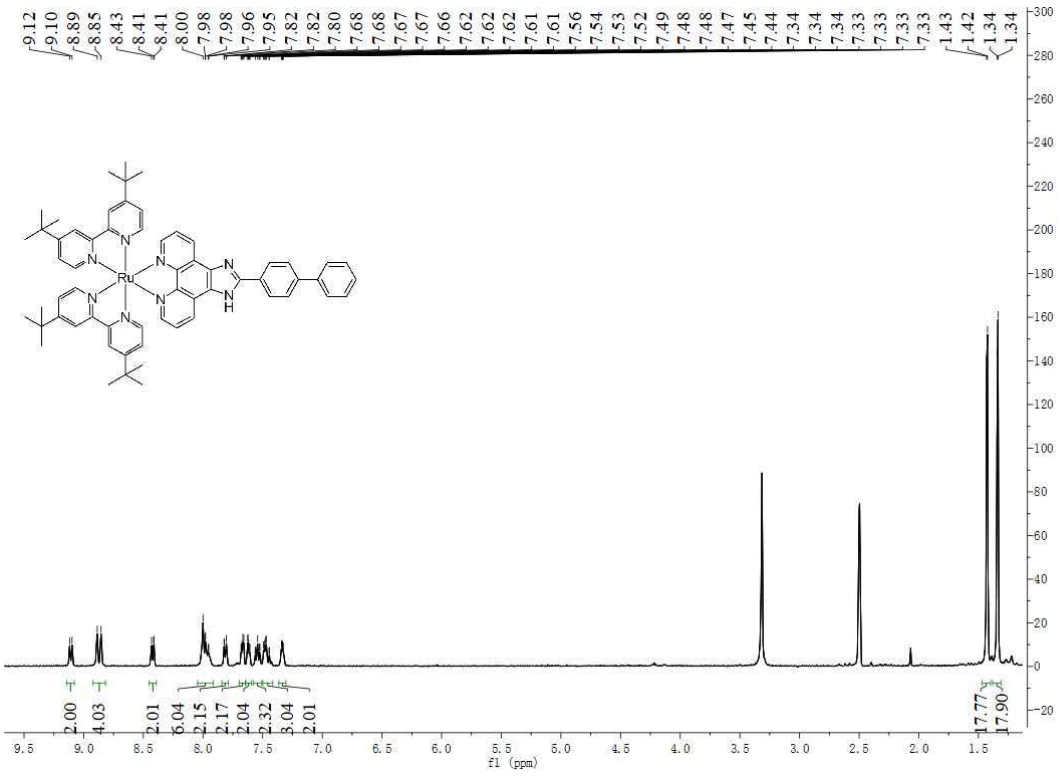


HRMS of Ru2

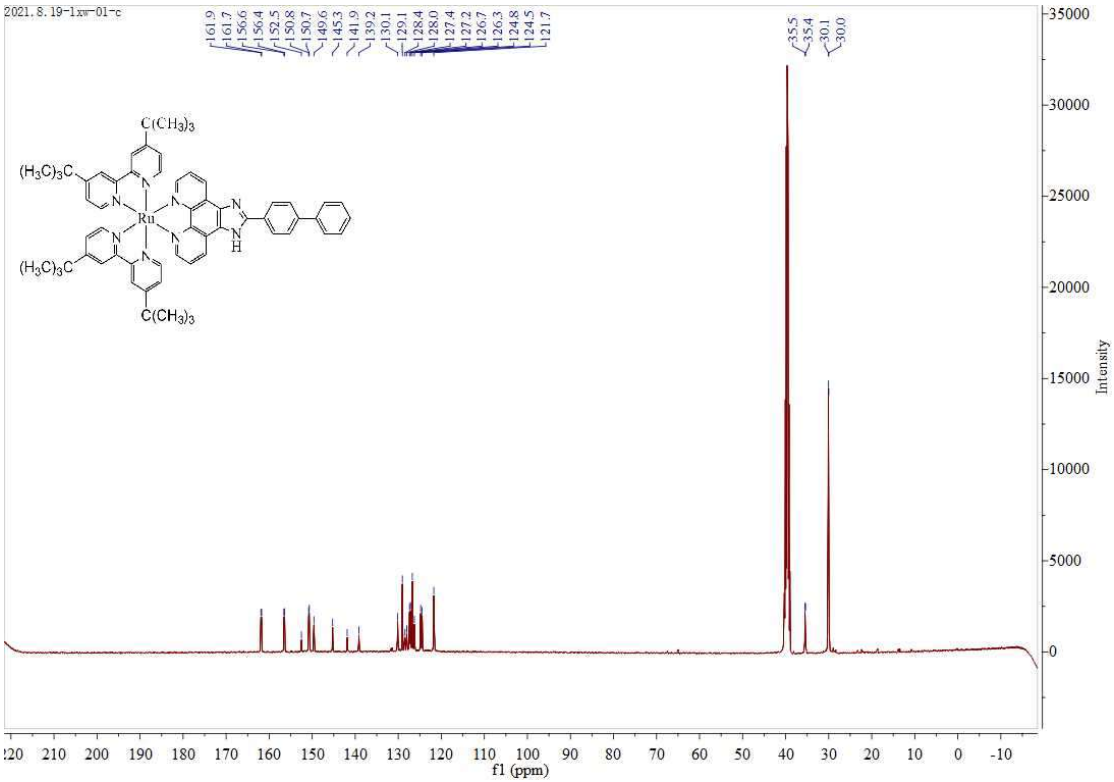

pos
2021-0608-LXW-cys-2 (6.427) Is (1.00,1.00) C49H39N8Ru
1: TOF MS ES+
2.48e12
841.2354
840.2363
839.2358
838.2360
843.2365
842.2379
844.2387
835.2374
836.2404
837.2377
845.2415
2021-0608-LXW-cys-2 837 (6.241)
1: TOF MS ES+
2.28e4
841.2345
839.2391
840.2097
842.2155
842.2677
843.2587
840.2726
838.2355
839.1949
838.1969
839.2845
844.2079
844.2931
843.3190
835.2358
836.2382
837.2671
845.2415
m/z


pos
2021-0608-LXW-cys-2 (6.427) Is (1.00,1.00) C49H39N8Ru
1: TOF MS ES+
2.48e12
841.2354
840.2363
843.2365
839.2358
838.2360
844.2387
835.2374
845.2415
2021-0608-LXW-cys-2 837 (6.241)
1: TOF MS ES+
8.57e6
421.1272
420.6271
422.1273
420.1269
419.6267
422.6289
533.2077
534.2076
532.7052
534.7072
418.1271
450.1302
531.7127
535.2086
338.3384
405.2619
841.2345
m/z

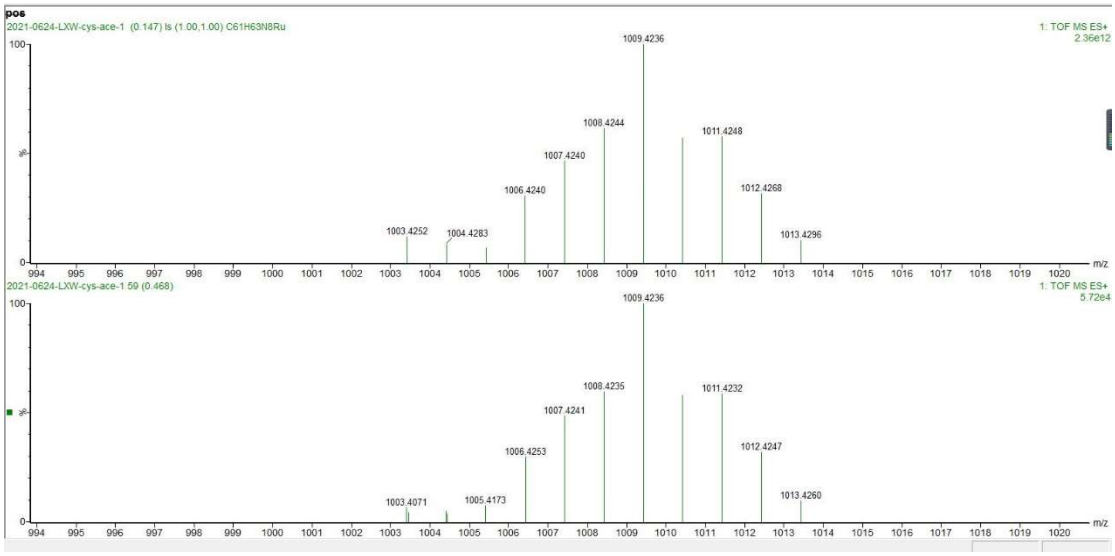
^{1}H NMR of Ru3

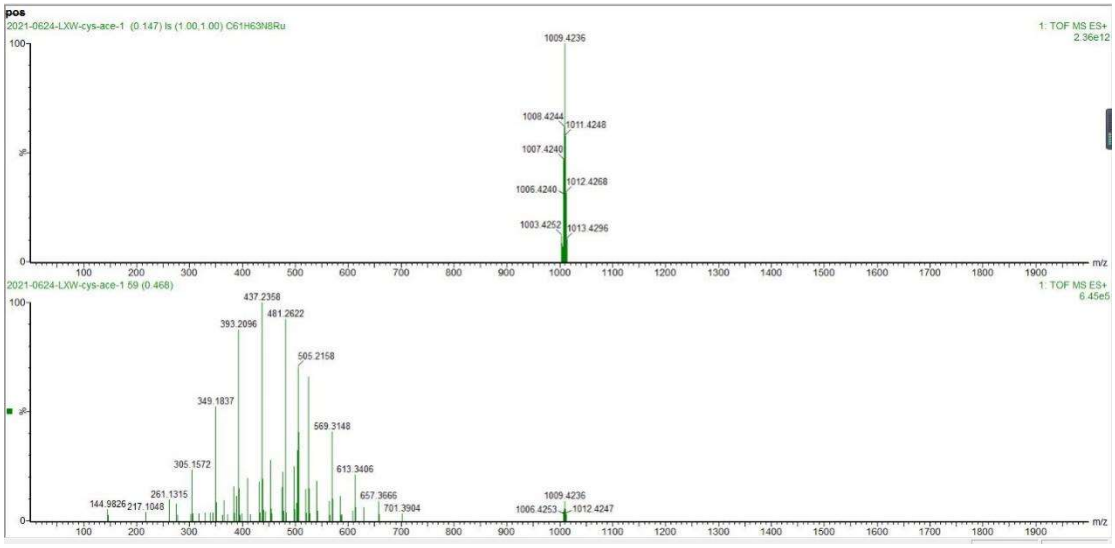


^{13}C NMR of Ru3

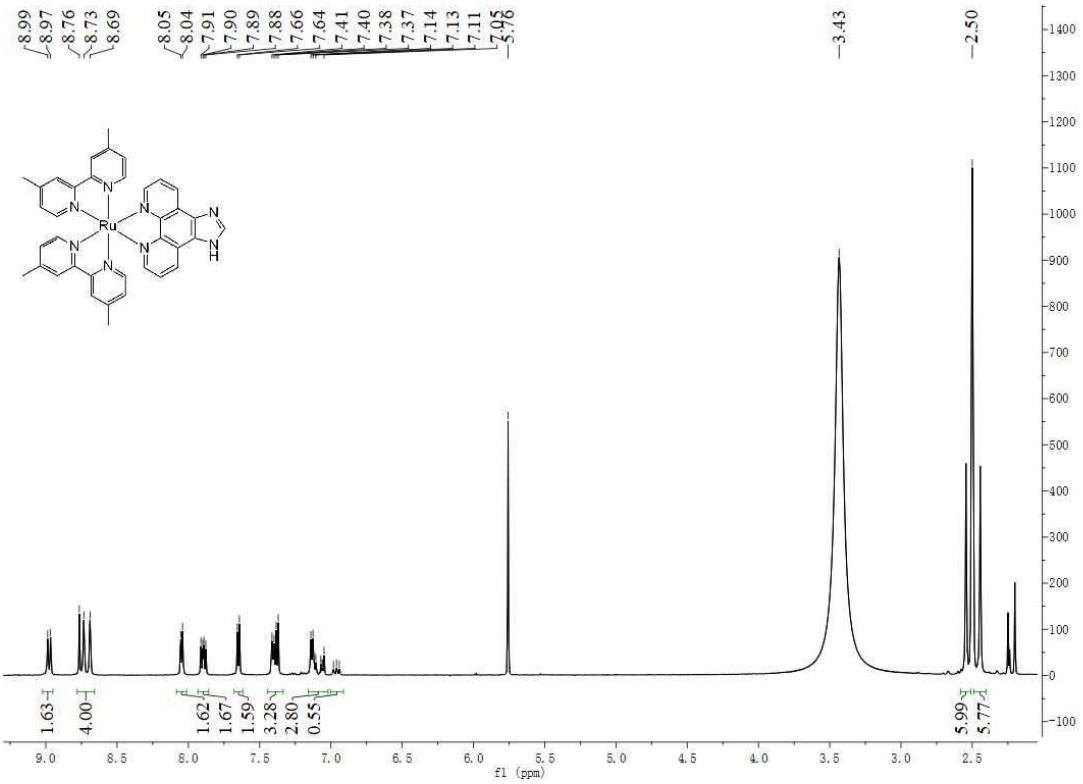


HRMS of Ru3

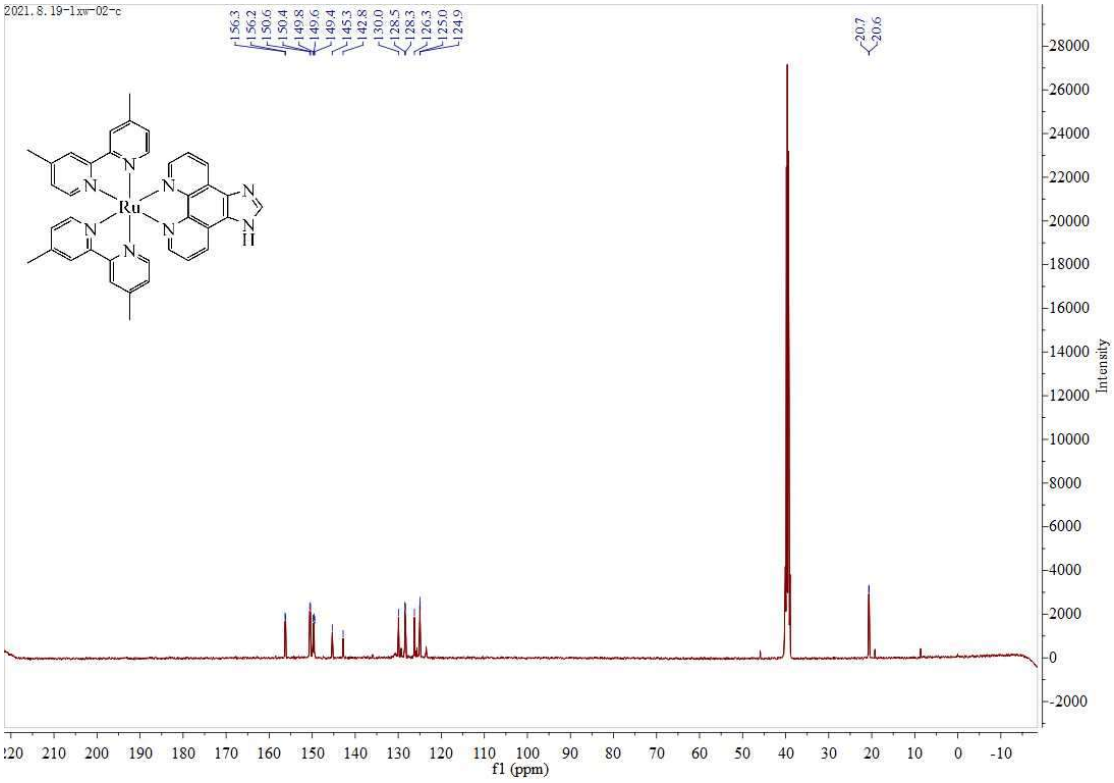

pos
2021-0624-LXW-cys-ace-1 (0.147) Is (1.00,1.00) C61H63N8Ru
1: TOF MS ES+
2.36e12
1009.4236
1008.4244
1011.4248
1007.4240
1006.4240
1012.4268
1003.4252
1004.4283
1013.4296
m/z
2021-0624-LXW-cys-ace-1.59 (0.468)
1: TOF MS ES+
5.72e4
1009.4236
1008.4235
1011.4232
1007.4241
1006.4253
1012.4247
1003.4071
1005.4173
1013.4260
m/z


pos
2021-0624-LXW-cys-ace-1 (0.147) Is (1.00,1.00) C61H63N8Ru
1: TOF MS ES+
2.36e12
1009.4236
1008.4244
1011.4248
1007.4240
1006.4240
1012.4268
1003.4252
1013.4296
m/z
2021-0624-LXW-cys-ace-1.59 (0.468)
1: TOF MS ES+
6.45e5
437.2358
481.2622
393.2096
505.2158
349.1837
569.3148
305.1572
613.3406
261.1315
657.3666
144.9826
217.1048
701.3904
1009.4236
1006.4253
1012.4247
m/z

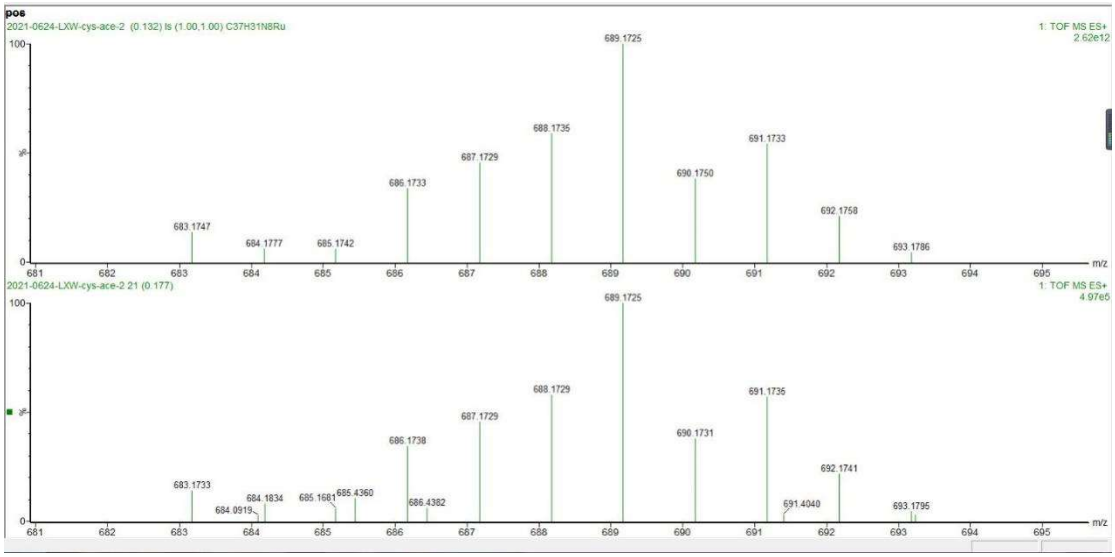
^{1}H NMR of Ru4

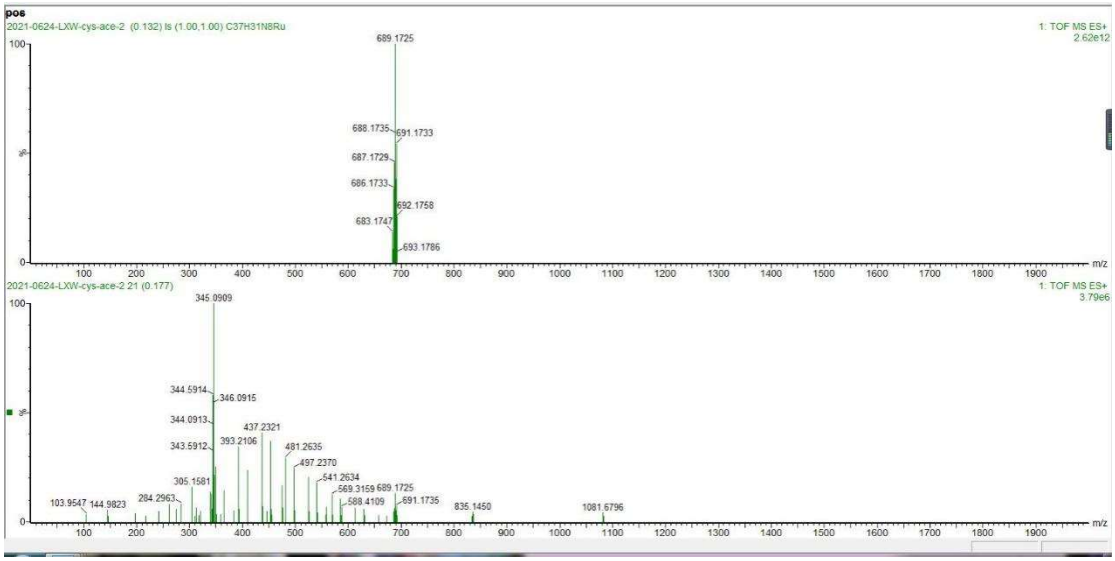


^{13}C NMR of Ru4

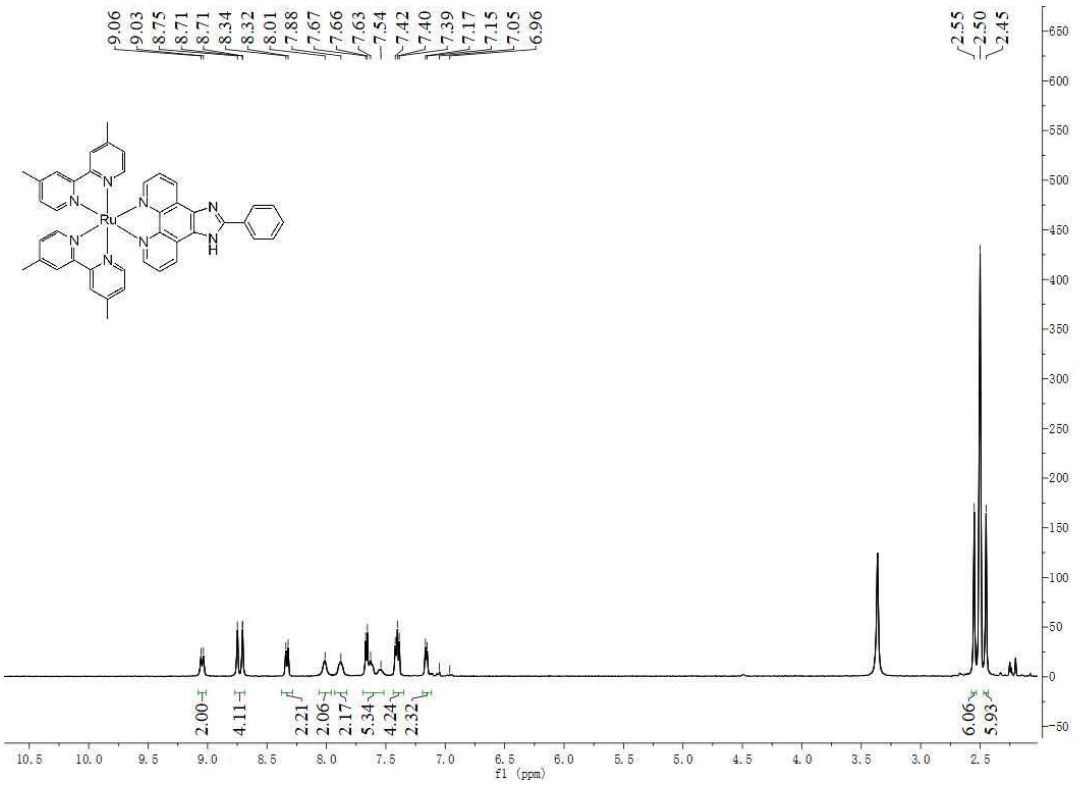


HRMS of Ru4

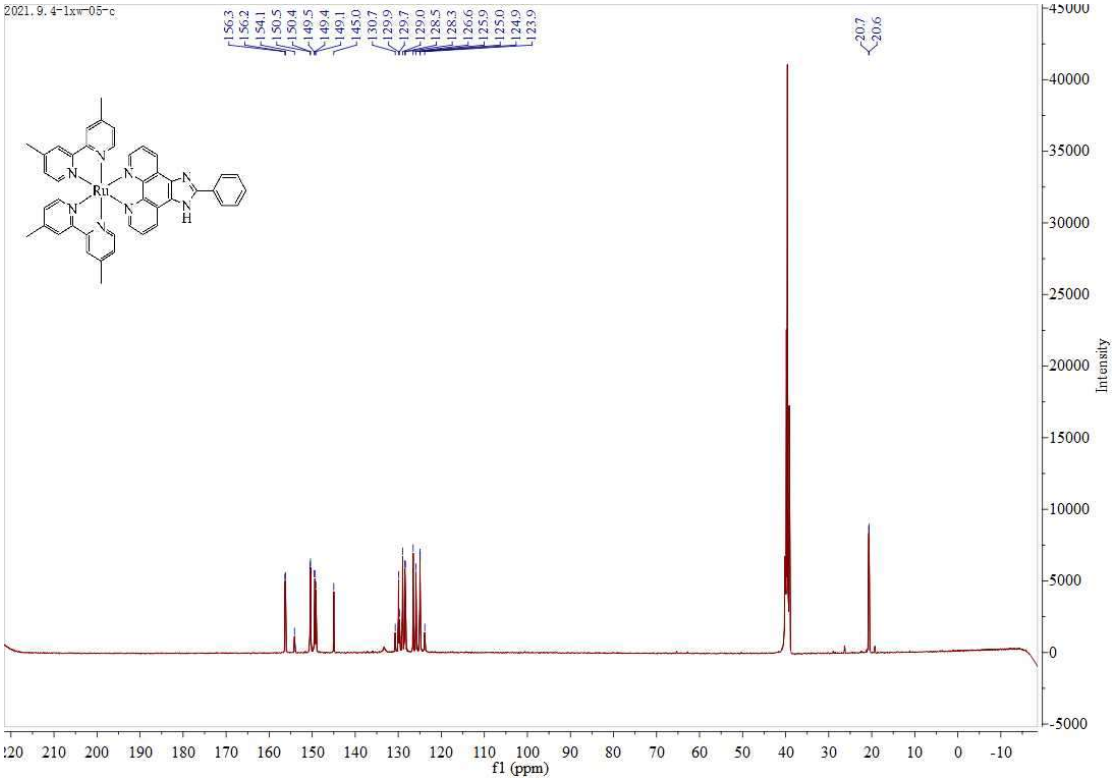

pos
2021-0624-LXW-cys-ace-2 (0.132) Is (1.00,1.00) C37H31N8Ru
1: TOF MS ES+
2.62e12
689.1725
688.1735
691.1733
687.1729
690.1750
686.1733
692.1758
683.1747
684.1777
685.1742
693.1786
2021-0624-LXW-cys-ace-2 21 (0.177)
1: TOF MS ES+
4.97e5
689.1725
688.1729
691.1736
687.1729
690.1731
686.1738
692.1741
683.1733
684.1834
685.1681
685.4360
686.4382
684.0919
691.4040
693.1795


pos
2021-0624-LXW-cys-ace-2 (0.132) Is (1.00,1.00) C37H31N8Ru
1: TOF MS ES+
2.62e12
689.1725
688.1735
691.1733
687.1729
686.1733
692.1758
683.1747
693.1786
2021-0624-LXW-cys-ace-2 21 (0.177)
1: TOF MS ES+
3.79e6
345.0909
344.5914
346.0915
344.0913
437.2321
343.5912
393.2106
481.2635
497.2370
541.2634
305.1581
569.3159
689.1725
103.9547
144.9823
284.2963
588.4109
691.1735
835.1450
1081.6796

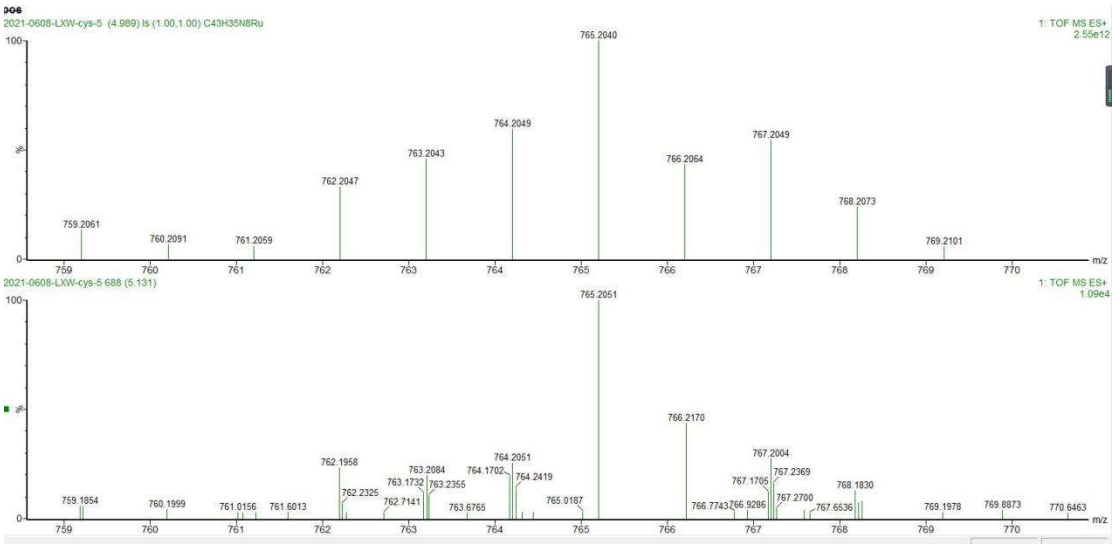
^{1}H NMR of Ru5

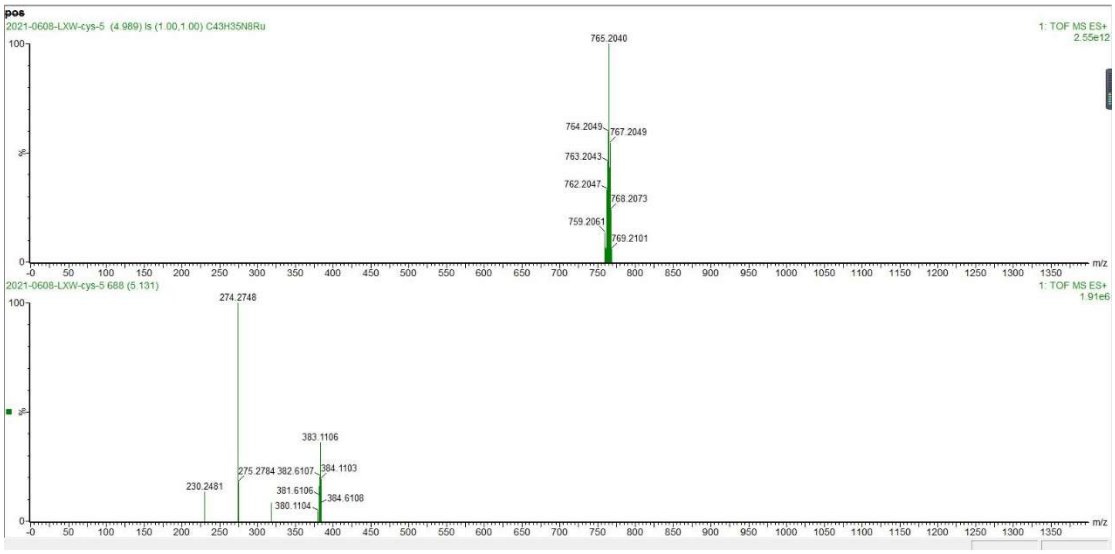


^{13}C NMR of Ru5

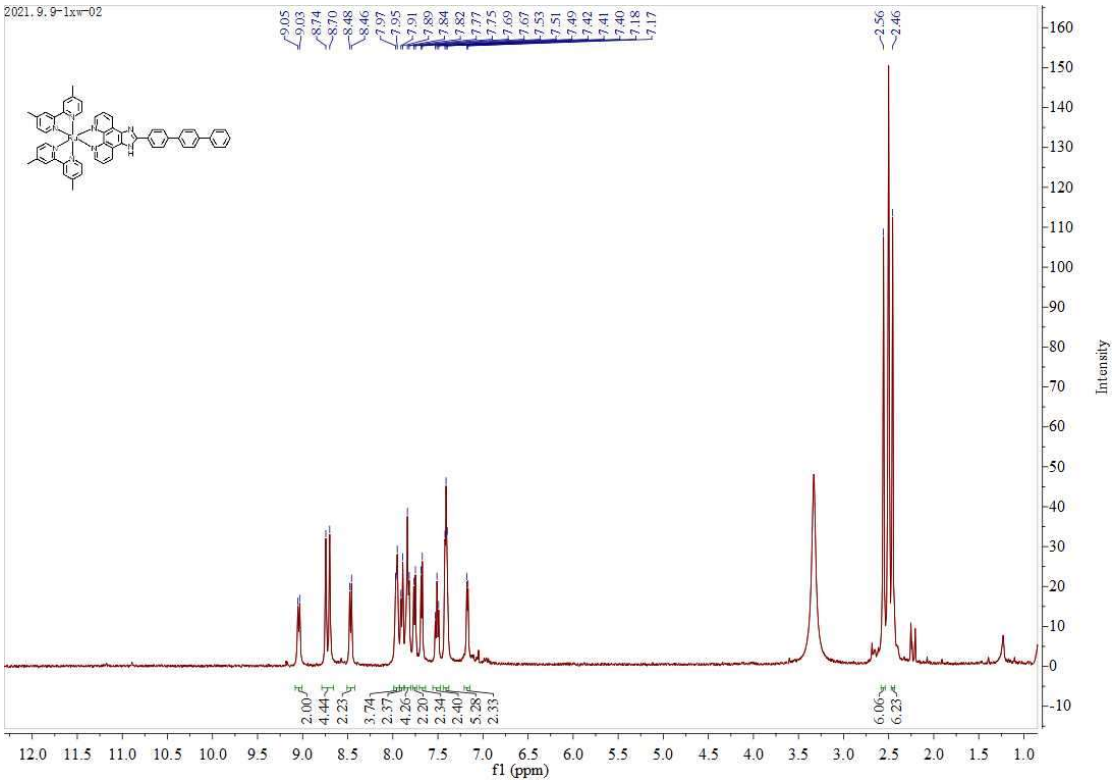


HRMS of Ru5

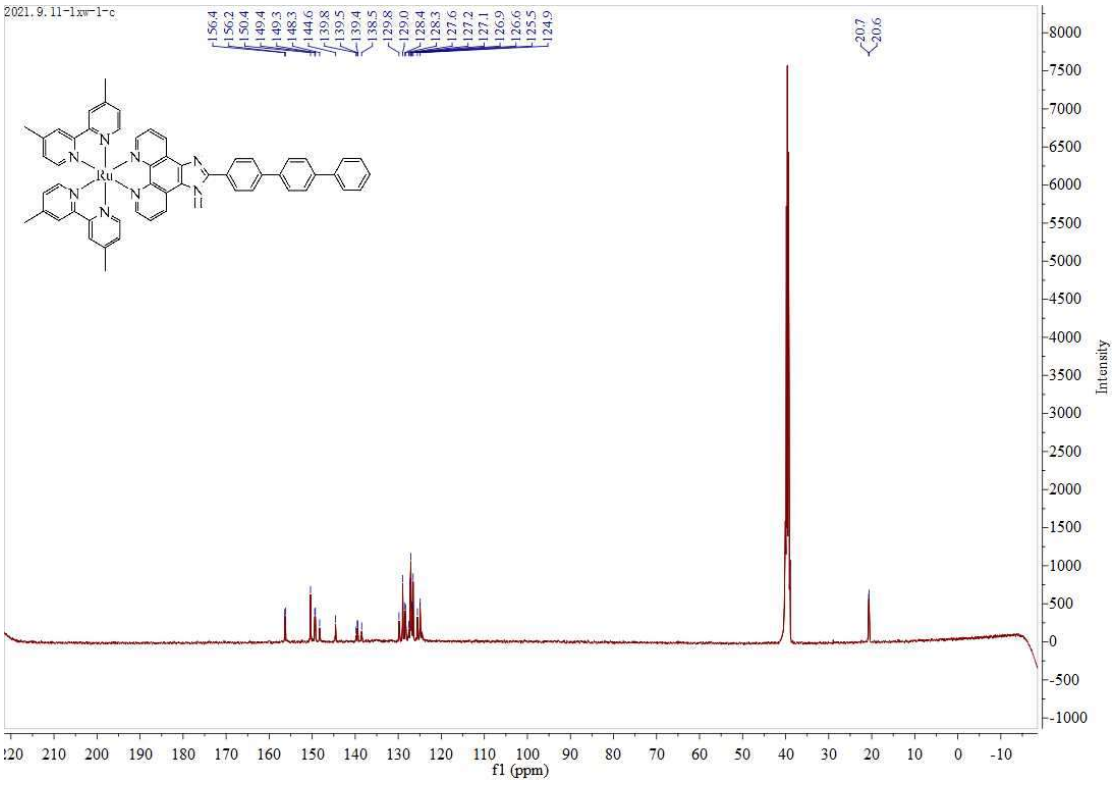

pos
2021-0608-LXW-cys-5 (4.989) Is (1.00,1.00) C43H35N8Ru
1: TOF MS ES+
2.55e12
765.2040
764.2049
763.2043
767.2049
766.2064
762.2047
768.2073
759.2061
760.2091
761.2059
769.2101
m/z
2021-0608-LXW-cys-5 688 (5.131)
1: TOF MS ES+
1.09e4
765.2051
766.2170
762.1958
767.2004
764.2051
763.2084
764.1702
763.1732
763.2355
764.2419
767.1705
767.2369
768.1830
759.1854
762.2325
762.7141
765.0187
767.2700
760.1999
761.0156
761.6013
763.6765
766.7743
766.9286
767.6536
769.1978
769.8873
770.6463


pos
2021-0608-LXW-cys-5 (4.989) Is (1.00,1.00) C43H35N8Ru
1: TOF MS ES+
2.55e12
765.2040
764.2049
767.2049
763.2043
762.2047
768.2073
759.2061
769.2101
m/z
2021-0608-LXW-cys-5 688 (5.131)
1: TOF MS ES+
1.91e6
274.2748
383.1106
275.2784
382.6107
384.1103
230.2481
381.6106
384.6108
380.1104
m/z

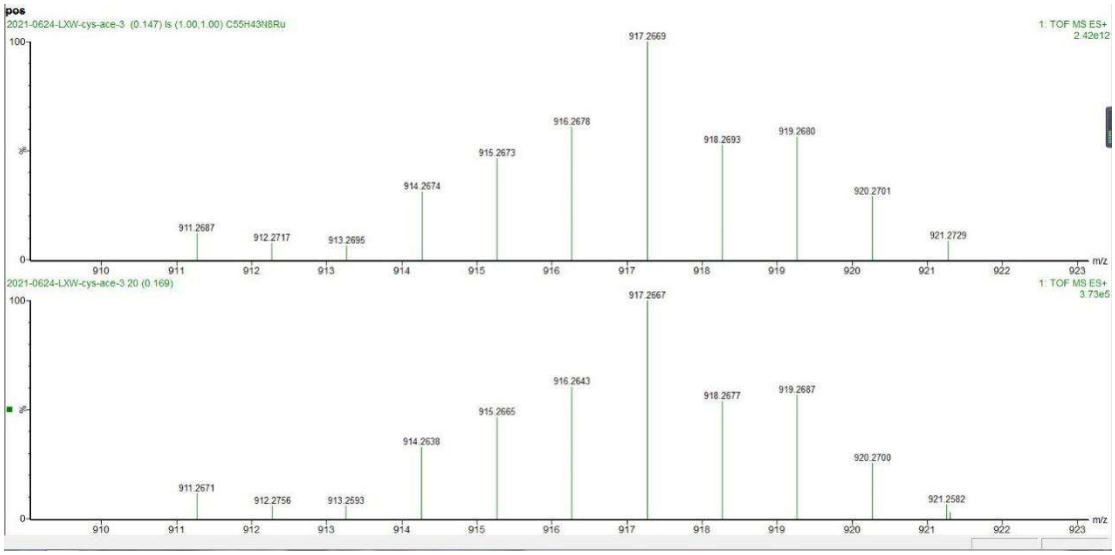
^{1}H NMR of Ru6

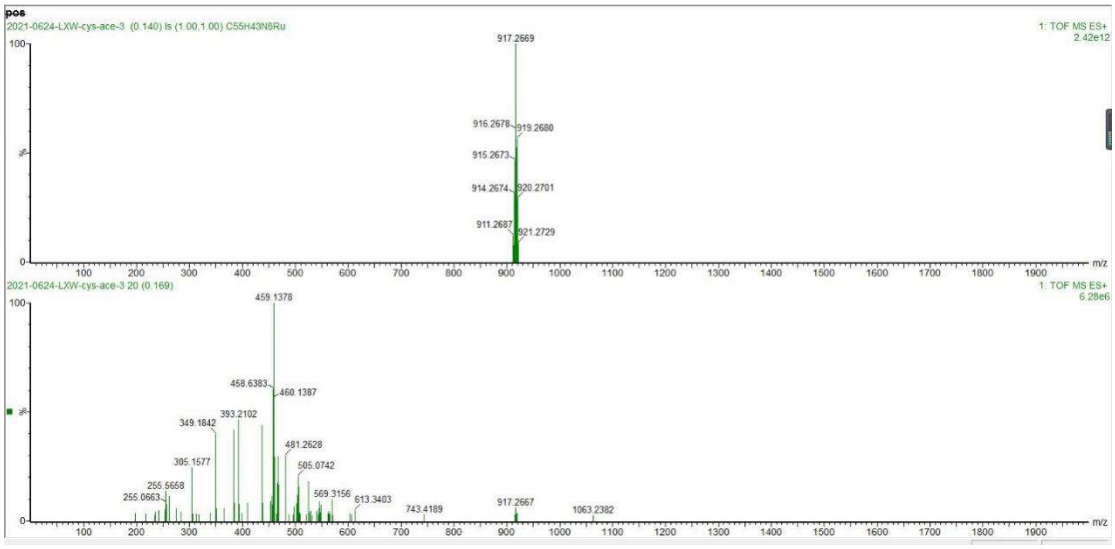


^{13}C NMR of Ru6

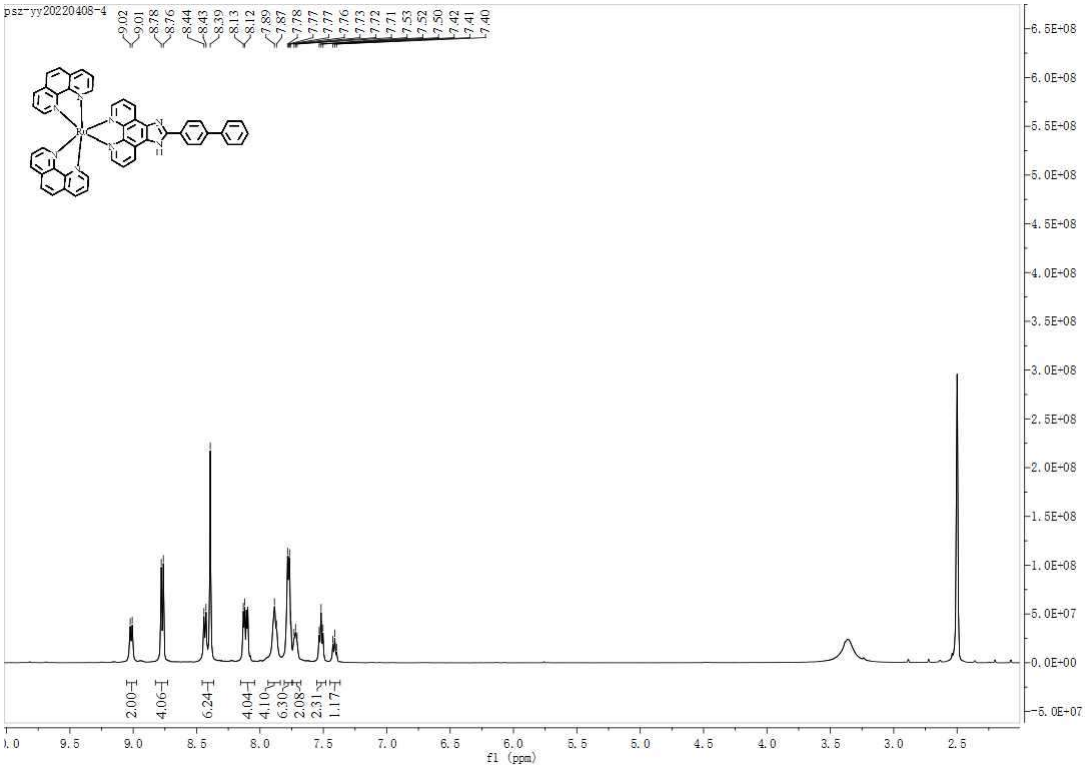


HRMS of Ru6

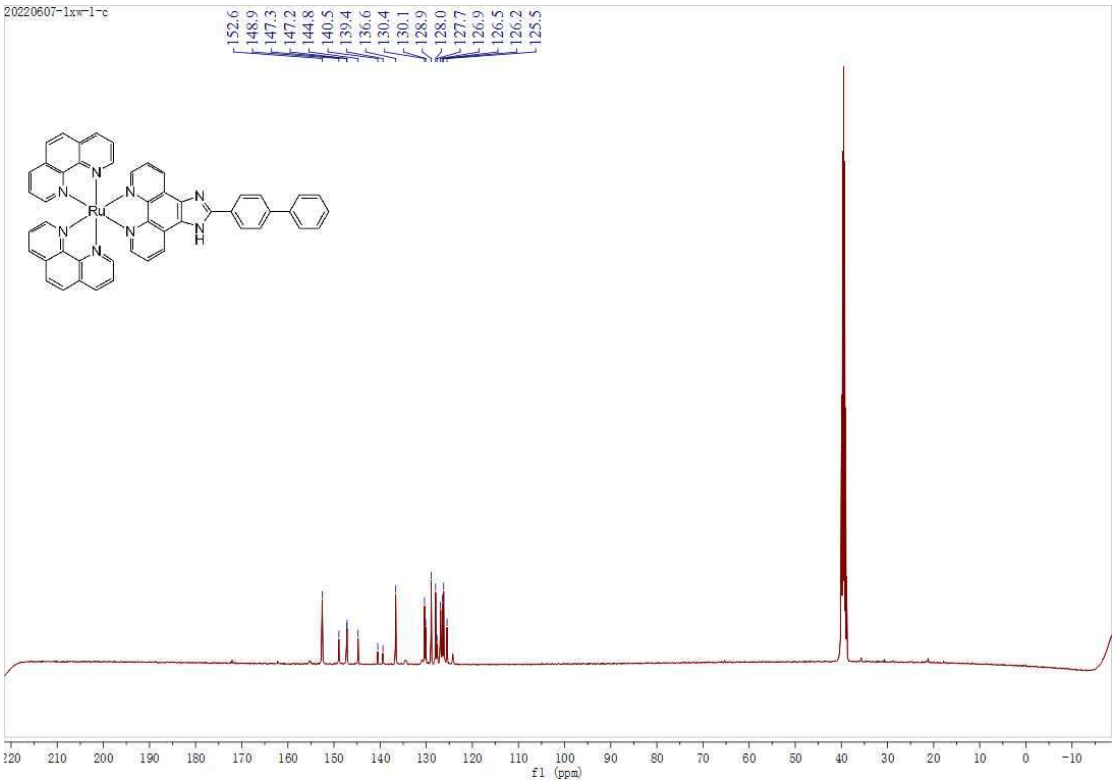

pos
2021-0624-LXW-cys-ace-3 (0.147) Is (1.00,1.00) C55H43N8Ru
1: TOF MS ES+
2.42e12
917.2669
916.2678
919.2680
918.2693
915.2673
914.2674
920.2701
911.2687
912.2717
913.2695
921.2729
m/z
2021-0624-LXW-cys-ace-3 20 (0.169)
1: TOF MS ES+
3.73e5
917.2667
916.2643
918.2677
919.2687
915.2665
914.2638
920.2700
911.2671
912.2756
913.2593
921.2582
m/z


pos
2021-0624-LXW-cys-ace-3 (0.140) Is (1.00,1.00) C55H43N8Ru
1: TOF MS ES+
2.42e12
917.2669
916.2678
919.2680
915.2673
914.2674
920.2701
911.2687
921.2729
m/z
2021-0624-LXW-cys-ace-3 20 (0.169)
1: TOF MS ES+
6.28e6
459.1378
458.6383
460.1387
393.2102
349.1842
481.2628
505.0742
305.1577
255.5658
255.0663
569.3156
613.3403
743.4189
917.2667
1063.2382
m/z

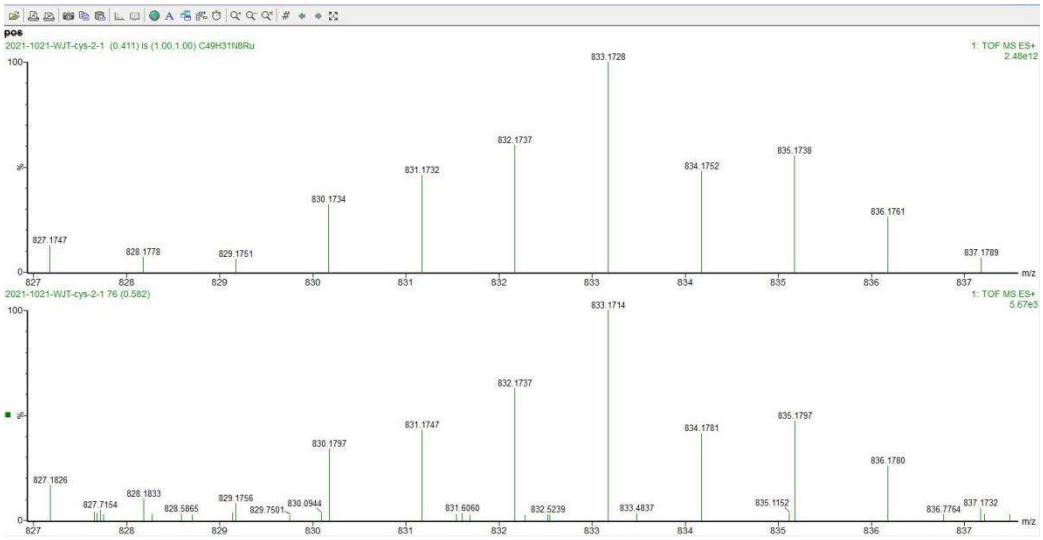
^{1}H NMR of Ru7

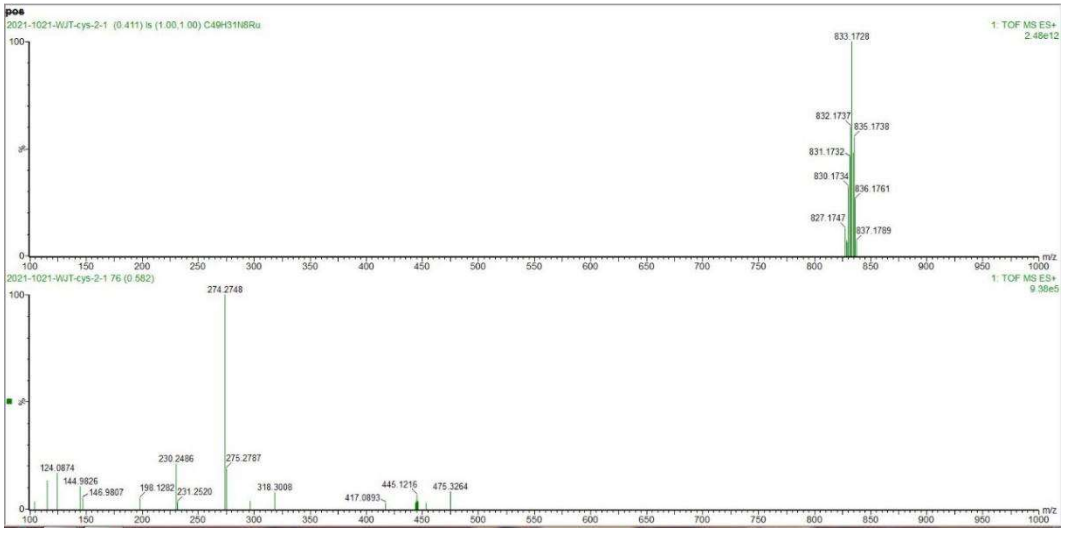


^{13}C NMR of Ru7

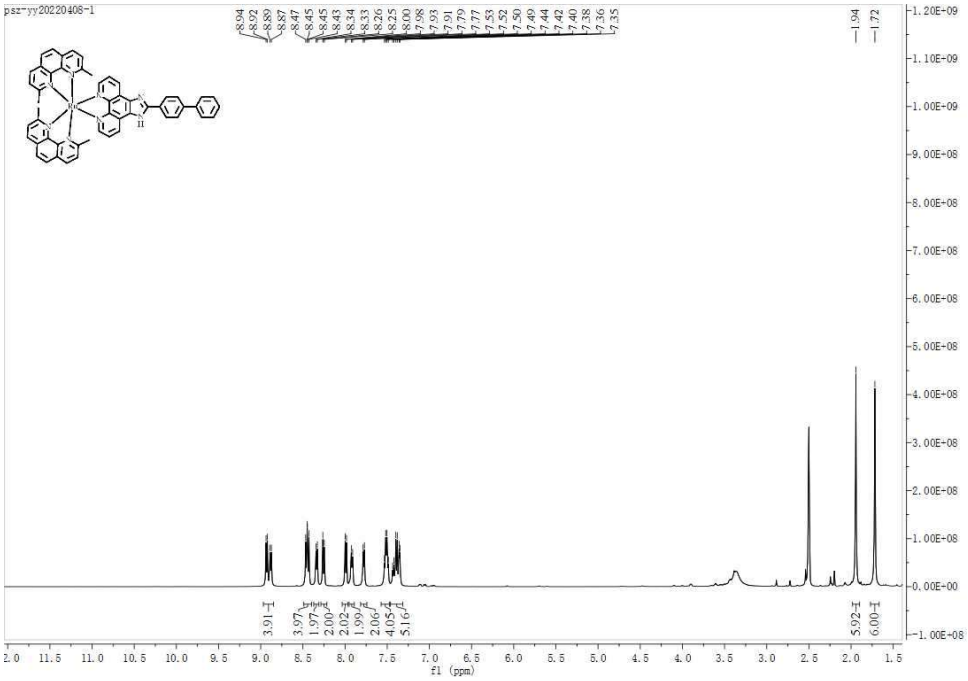


HRMS of Ru7

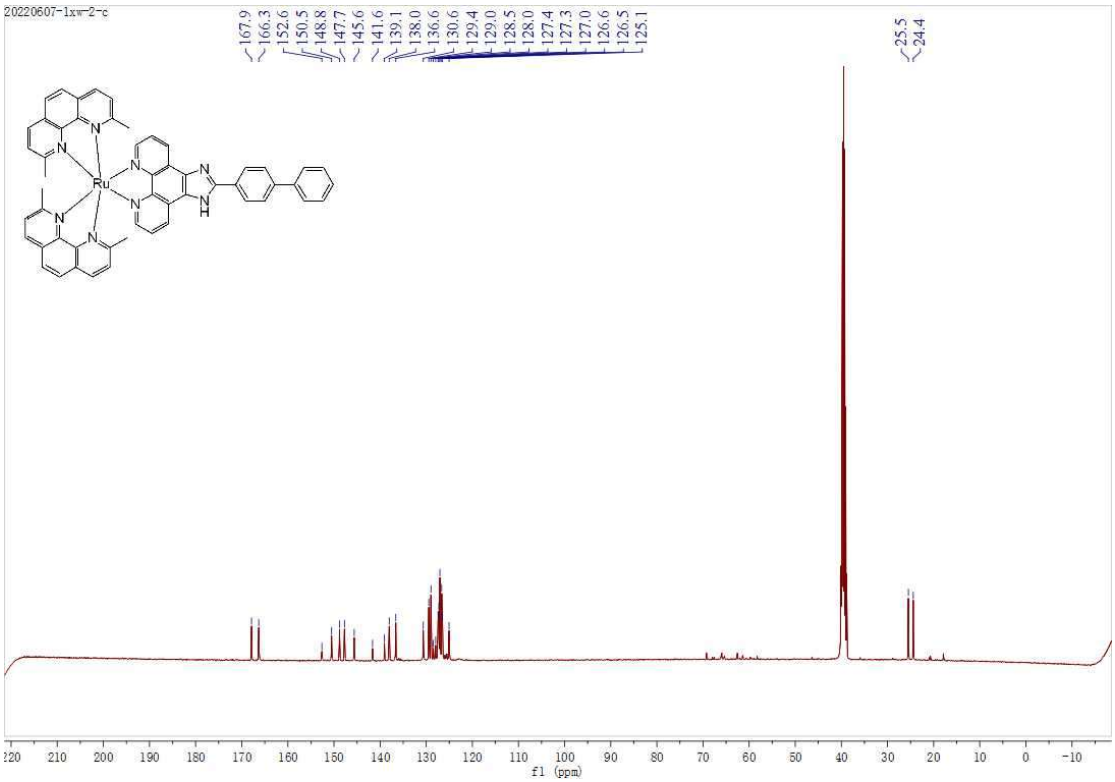

pos
2021-1021-WJT-cys-2-1 (0.411) Is (1.00,1.00) C49H31N8Ru
1: TOF MS ES+
2.48e12
833.1728
832.1737
831.1732
835.1738
834.1752
830.1734
836.1761
827.1747
828.1778
829.1751
837.1789
m/z
2021-1021-WJT-cys-2-1 76 (0.582)
1: TOF MS ES+
5.67e3
833.1714
832.1737
831.1747
835.1797
834.1781
830.1797
836.1780
827.1826
828.1833
827.7154
828.5865
829.1756
829.7501
830.0944
831.6060
832.5239
833.4837
835.1152
836.7764
837.1732
m/z


pos
2021-1021-WJT-cys-2-1 (0.411) Is (1.00,1.00) C49H31N8Ru
1: TOF MS ES+
2.48e12
833.1728
832.1737
835.1738
831.1732
830.1734
836.1761
827.1747
837.1789
m/z
2021-1021-WJT-cys-2-1 76 (0.582)
1: TOF MS ES+
9.38e5
274.2748
124.0874
144.9826
146.9807
230.2486
198.1282
231.2520
275.2787
318.3008
417.0893
445.1216
475.3264
m/z

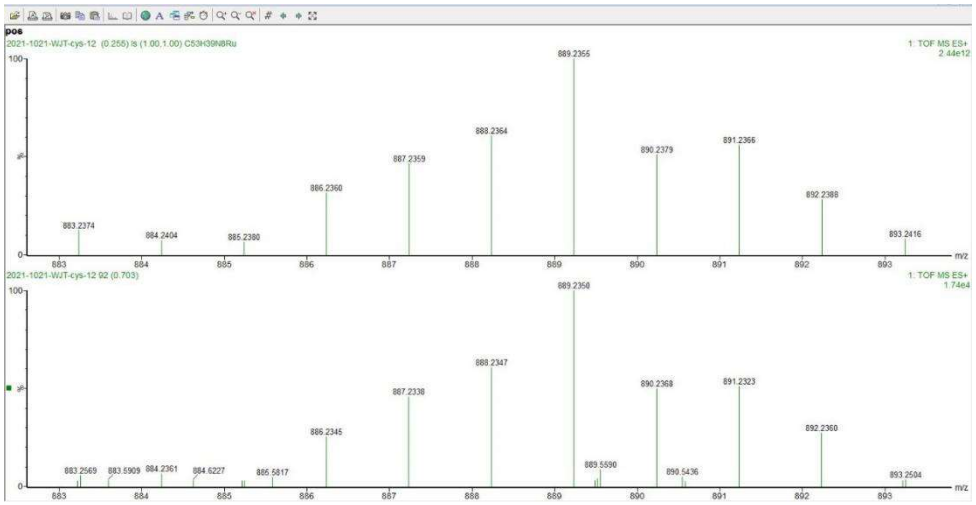
^{1}H NMR of Ru8

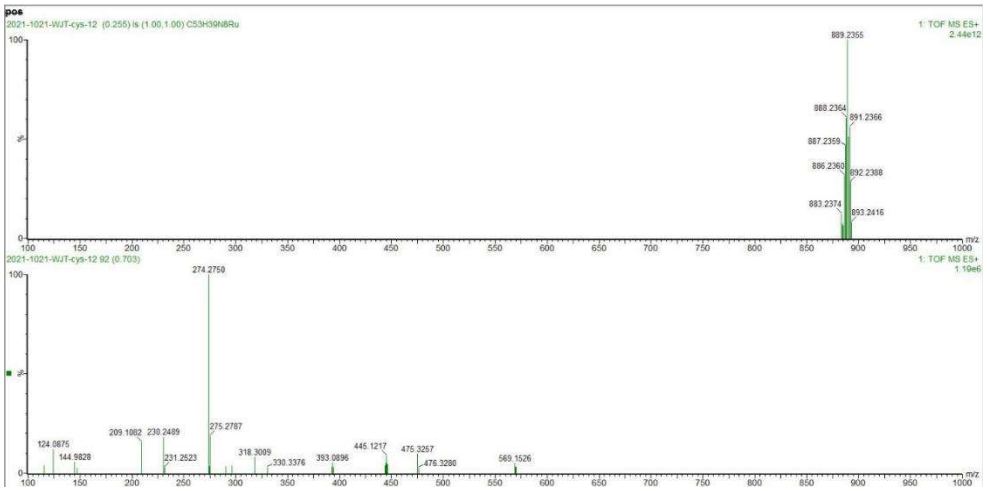


^{13}C NMR of Ru8

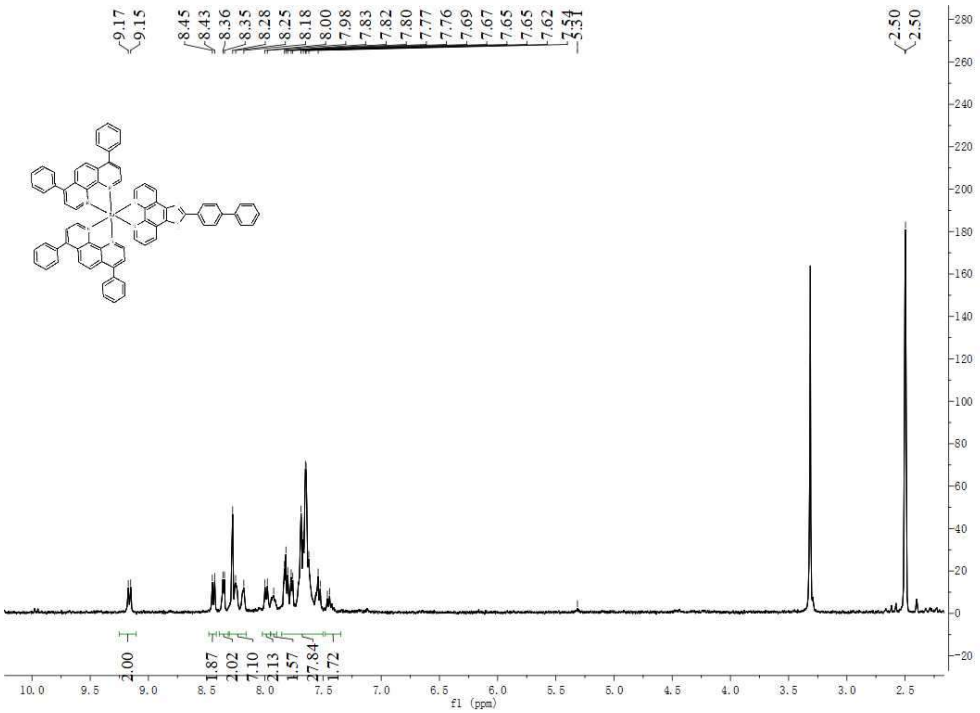


HRMS of Ru8

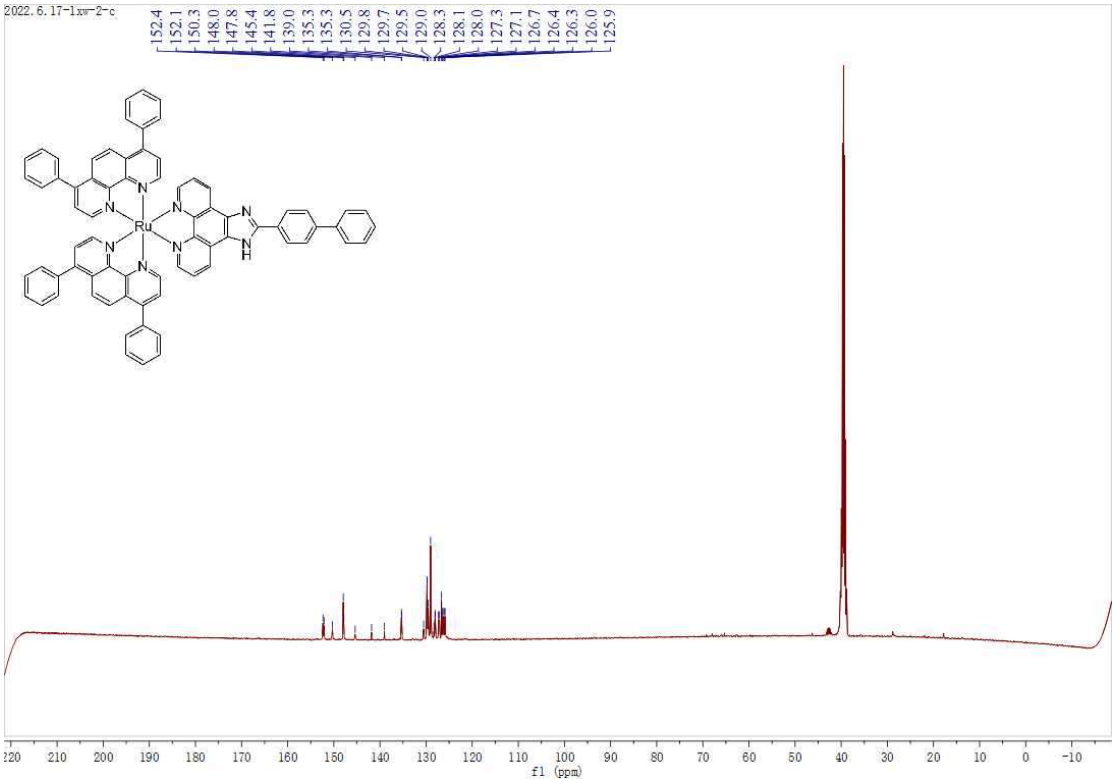

pos
2021-1021-WJT-cys-12 (0.255) is (1.00,1.00) C53H39N8Ru
1: TOF MS ES+
2.44e12
889.2355
888.2364
891.2366
890.2379
887.2359
886.2360
892.2388
883.2374
884.2404
885.2380
893.2416
mz
2021-1021-WJT-cys-12 92 (0.703)
1: TOF MS ES+
1.74e4
889.2350
888.2347
890.2368
891.2323
887.2338
886.2345
892.2360
883.2569
883.5909
884.2361
884.6227
885.5817
889.5590
890.5436
893.2504
mz


pos
2021-1021-WJT-cys-12 (0.255) is (1.00,1.00) C53H39N8Ru
1: TOF MS ES+
2.44e12
889.2355
888.2364
891.2366
887.2359
886.2360
892.2388
883.2374
893.2416
mz
2021-1021-WJT-cys-12 92 (0.703)
1: TOF MS ES+
1.19e6
274.2750
275.2787
209.1082
230.2489
124.0875
144.9828
231.2523
318.3009
330.3376
393.0896
445.1217
475.3257
476.3280
569.1526
mz

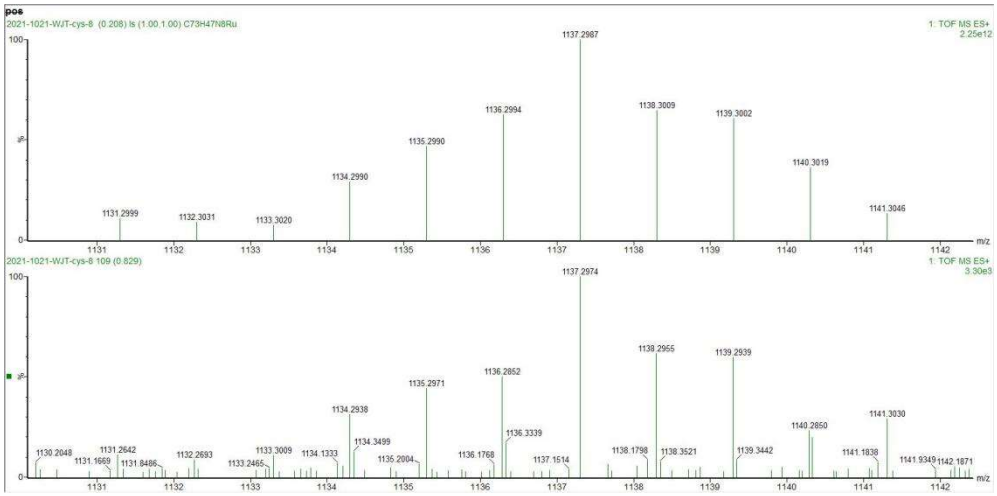
^{1}H NMR of Ru9



^{13}C NMR of Ru9



HRMS of Ru9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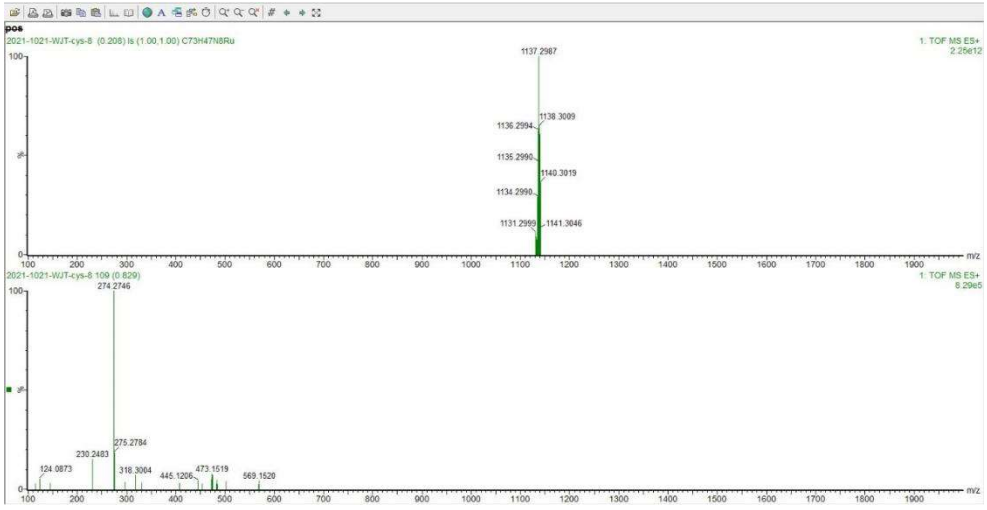
2021-1021-WJT-cys-8 (0.208) Is (1.00,1.00) C73H47N8Ru
1: TOF MS ES+
2.25e12
1137.2987
1136.2994
1138.3009
1139.3002
1135.2990
1140.3019
1134.2990
1131.2999
1141.3046
1132.3031
1133.3020
2021-1021-WJT-cys-8 109 (0.829)
1: TOF MS ES+
3.30e3
1137.2974
1138.2955
1139.2939
1136.2852
1135.2971
1134.2938
1140.2850
1141.3030
1136.3339
1134.3499
1130.2048
1131.2642
1131.1669
1131.8486
1132.2693
1133.3009
1134.1333
1133.2465
1135.2004
1136.1768
1137.1514
1138.1798
1138.3521
1139.3442
1141.1838
1141.9349
1142.1871


pos
2021-1021-WJT-cys-8 (0.208) Is (1.00,1.00) C73H47N8Ru
1: TOF MS ES+
2.25e12
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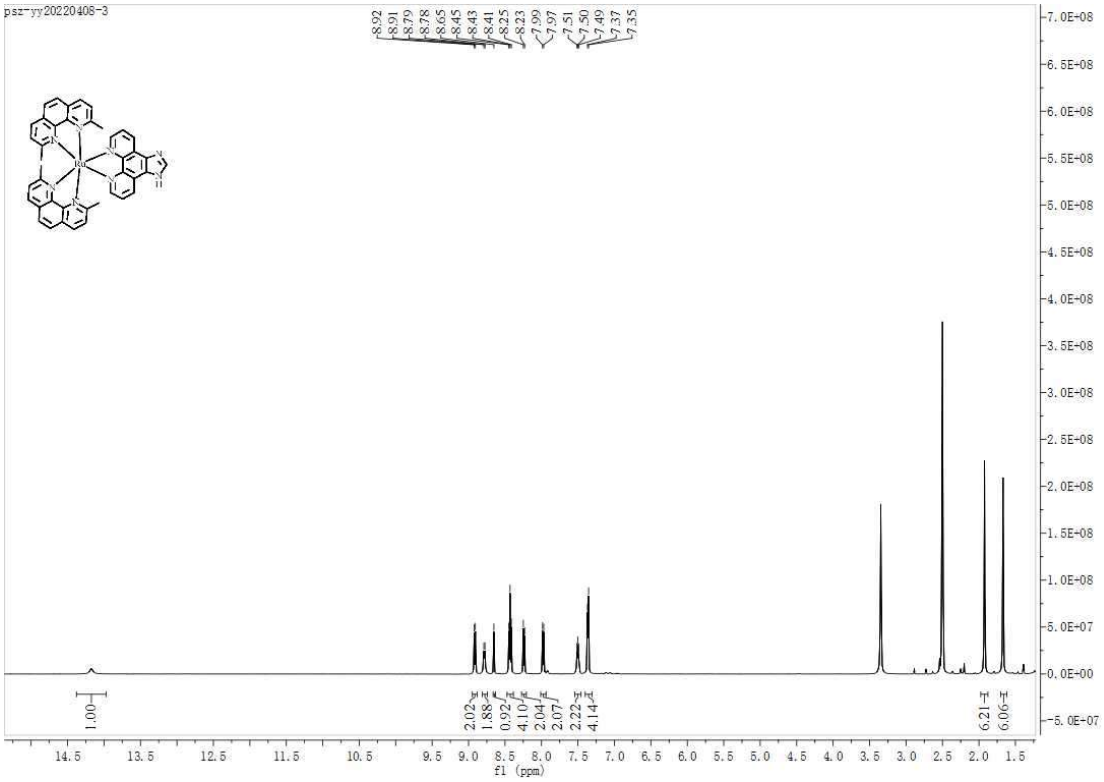
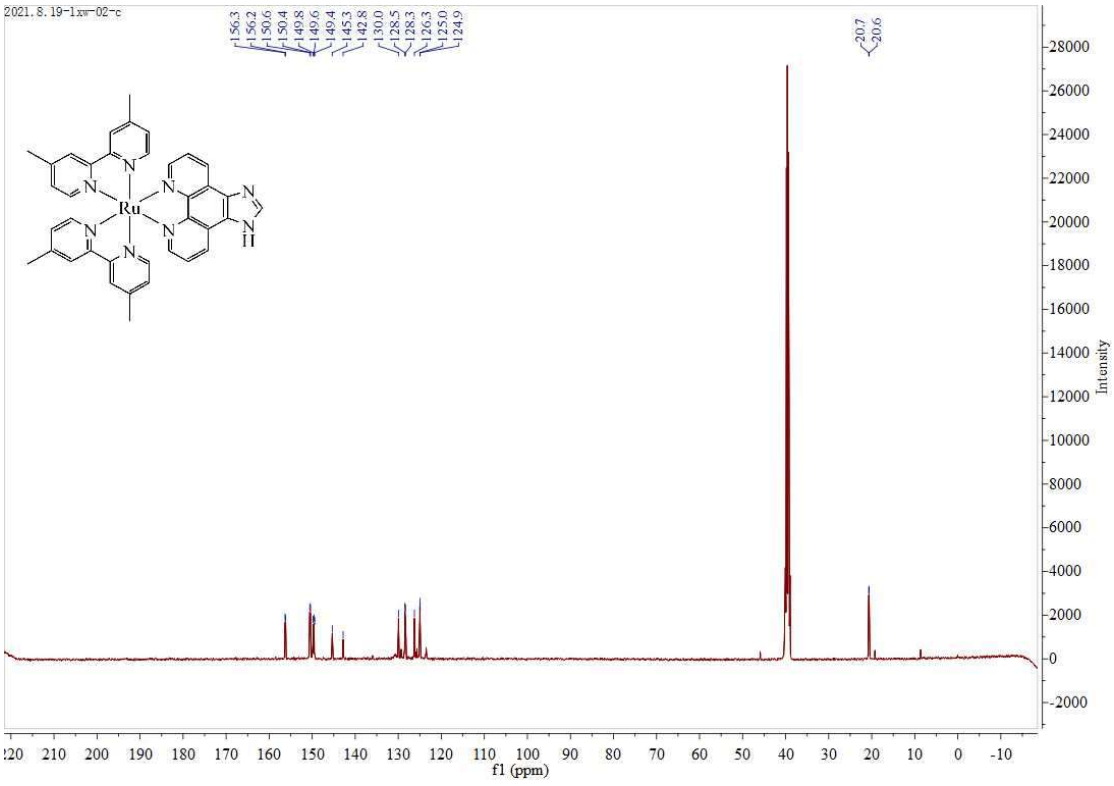
1138.3009
1136.2994
1135.2990
1140.3019
1134.2990
1131.2999
1141.3046
2021-1021-WJT-cys-8 109 (0.829)
1: TOF MS ES+
6.29e5
274.2746
275.2784
230.2483
124.0873
318.3064
445.1206
473.1519
569.1520

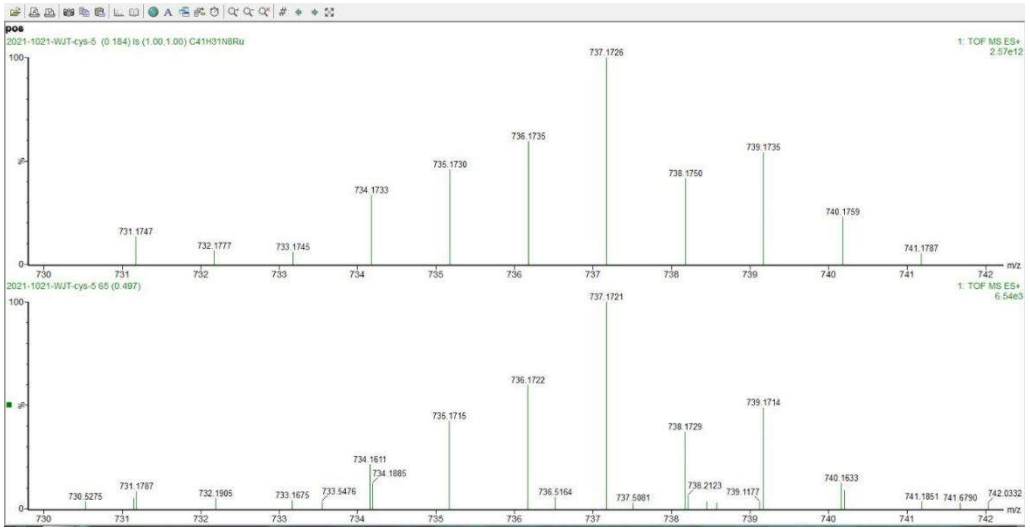
^{1}H NMR of Ru10



^{13}C NMR of Ru10



HRMS of Ru10


pos
2021-1021-WJT-cys-5 (0.184) is (1.00,1.00) C41H31N8Ru
1: TOF MS ES+
2.57e12
737.1726
736.1735
739.1735
735.1730
738.1750
734.1733
740.1759
731.1747
732.1777
733.1745
741.1787
2021-1021-WJT-cys-5 65 (0.497)
1: TOF MS ES+
6.54e3
737.1721
736.1722
739.1714
735.1715
738.1729
734.1611
734.1885
730.5275
731.1787
732.1905
733.1675
733.5476
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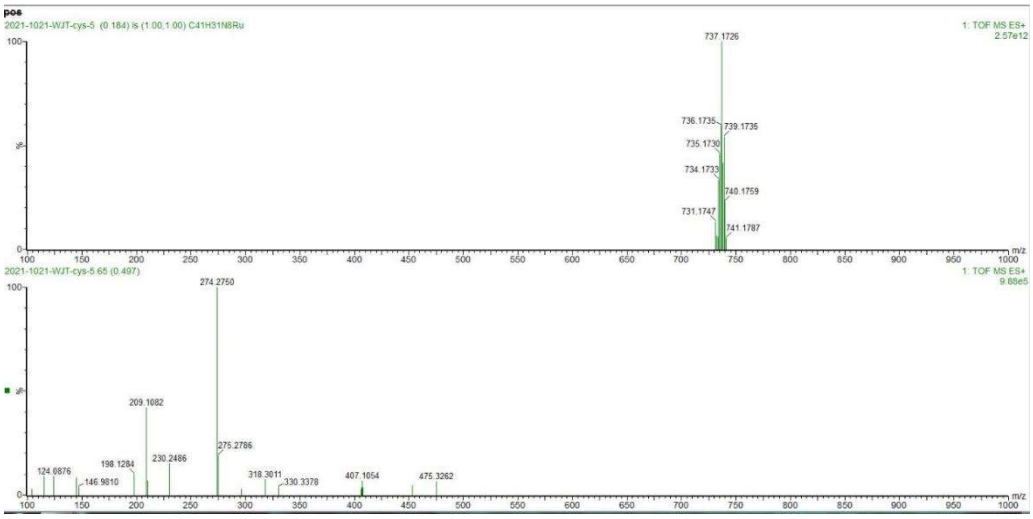
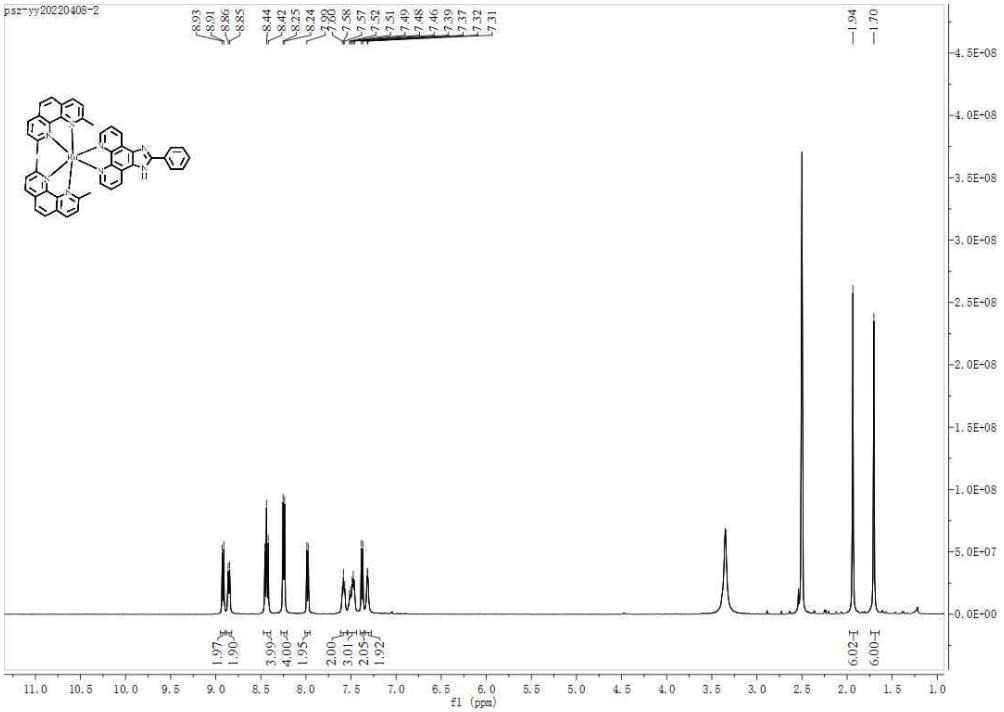
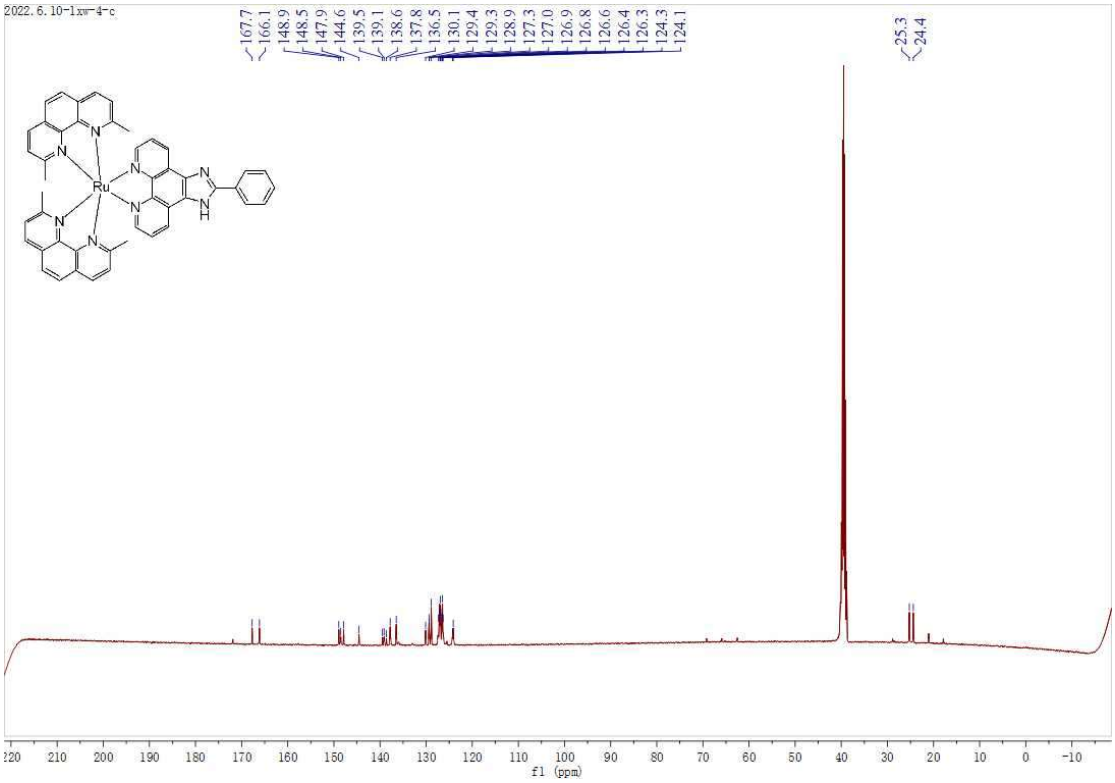
738.2123
739.1177
740.1633
741.1851
741.6790
742.0332
mz


pos
2021-1021-WJT-cys-5 (0.184) is (1.00,1.00) C41H31N8Ru
1: TOF MS ES+
2.57e12
737.1726
736.1735
739.1735
735.1730
734.1733
740.1759
731.1747
741.1787
2021-1021-WJT-cys-5 65 (0.497)
1: TOF MS ES+
9.68e5
274.2750
209.1682
275.2786
230.2486
198.1284
124.0876
146.9810
318.3011
330.3378
407.1054
475.3262
mz

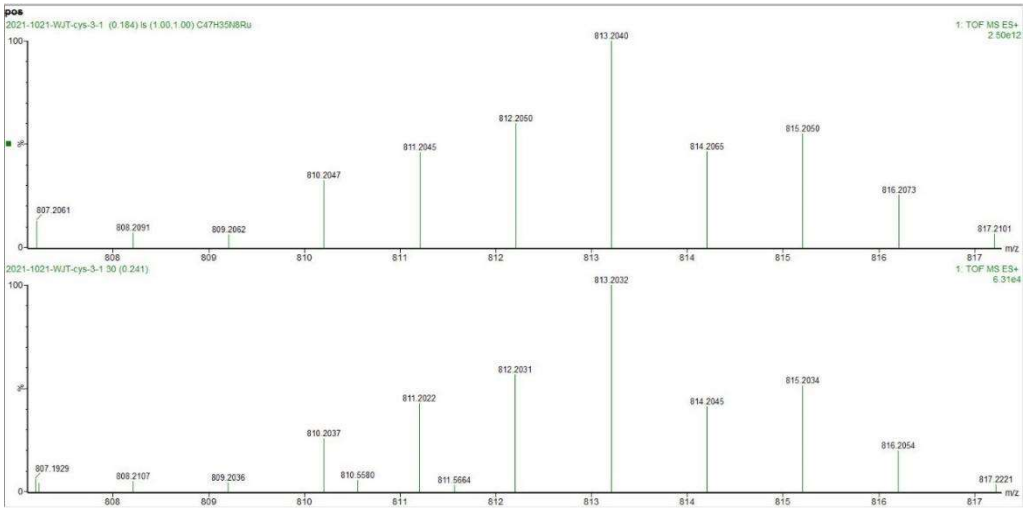
^{1}H NMR of Ru11



^{13}C NMR of Ru11



HRMS of Ru11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813.2040
812.2050
815.2050
811.2045
814.2065
810.2047
816.2073
807.2061
808.2091
809.2062
817.2101
2021-1021-WJT-cys-3-1 30 (0.241)
1: TOF MS ES+
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813.2032
812.2031
815.2034
811.2022
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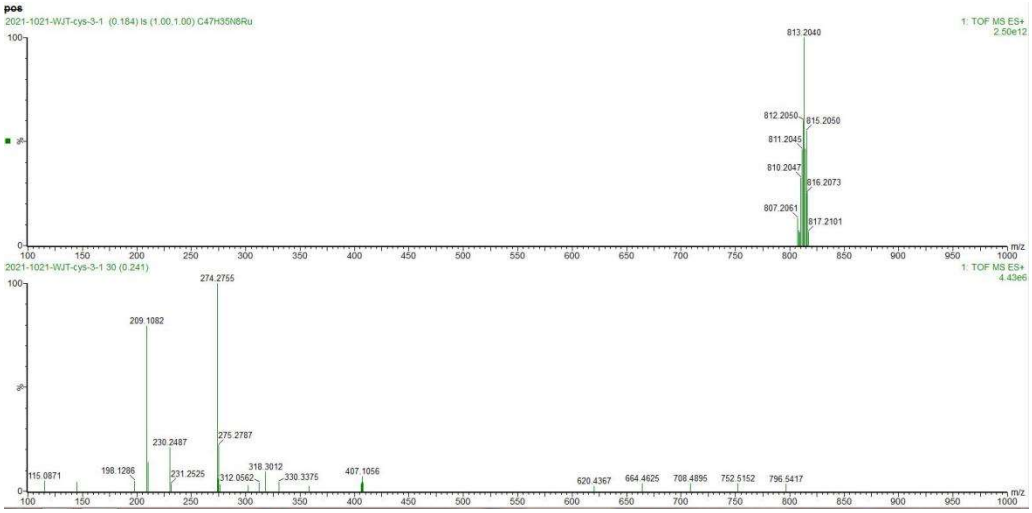
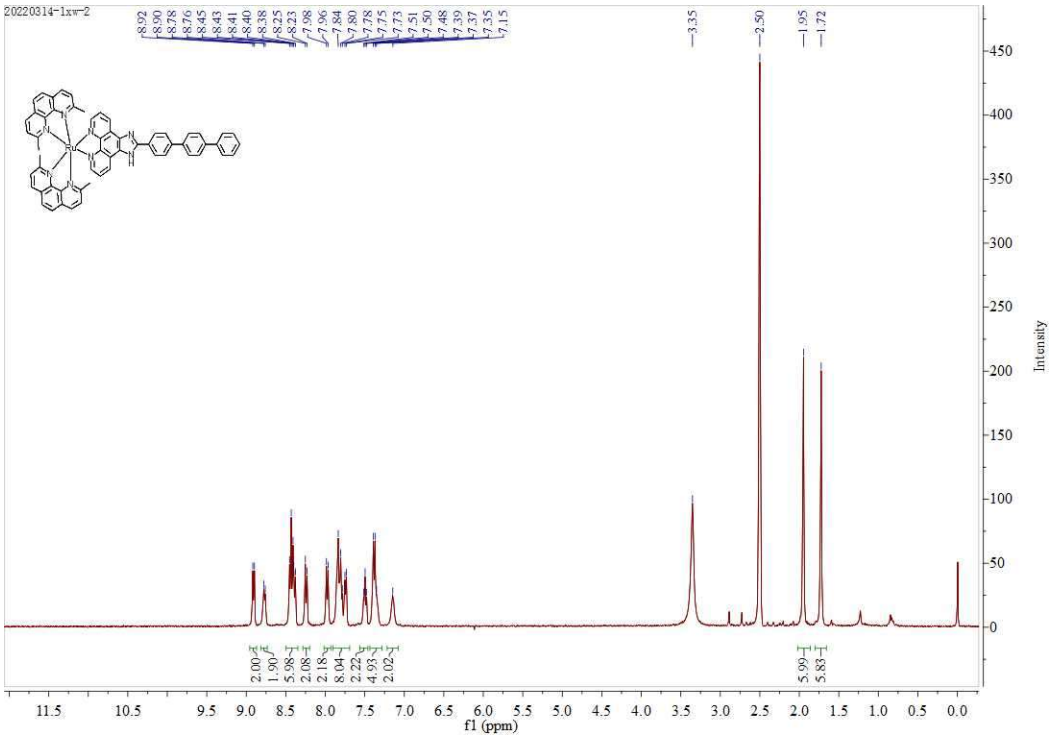
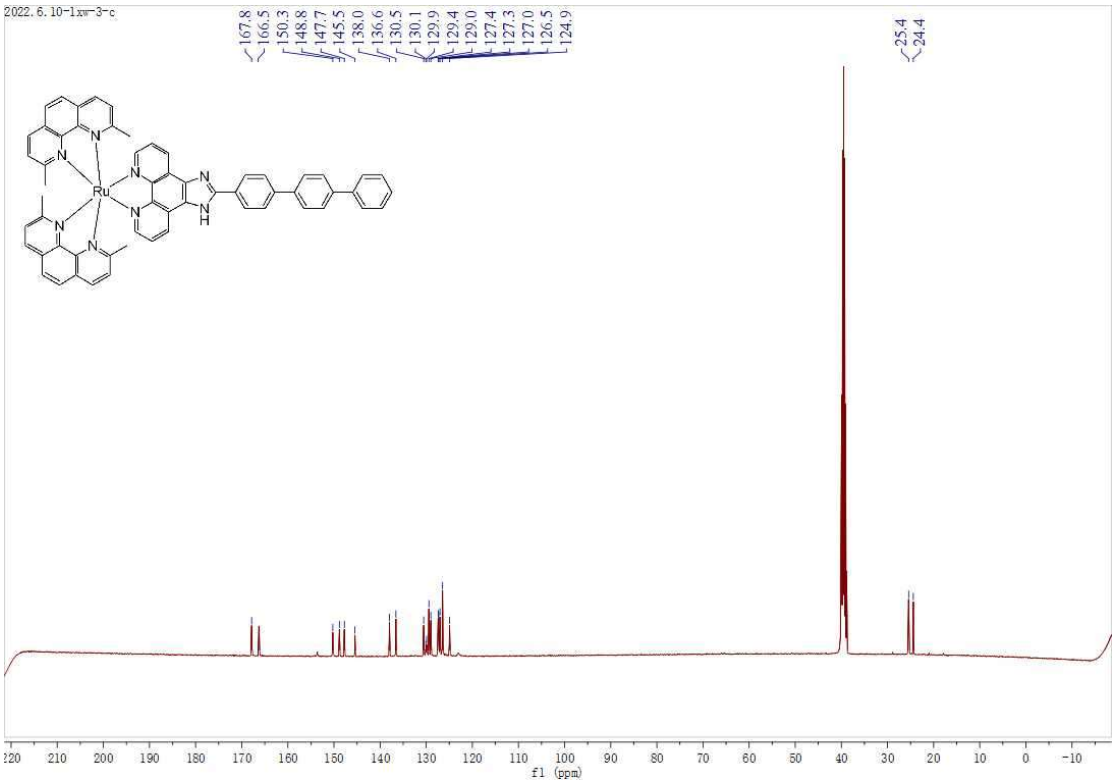
810.2037
816.2054
807.1929
808.2107
809.2036
810.5580
811.5664
817.2221


pos
2021-1021-WJT-cys-3-1 (0.184) Is (1.00,1.00) C47H35N8Ru
1: TOF MS ES+
2.50e12
813.2040
812.2050
815.2050
811.2045
810.2047
816.2073
807.2061
817.2101
2021-1021-WJT-cys-3-1 30 (0.241)
1: TOF MS ES+
4.43e6
274.2755
209.1082
230.2487
275.2787
198.1286
231.2525
318.3012
312.0562
330.3375
407.1056
115.0871
620.4367
664.4625
708.4895
752.5152
796.5417

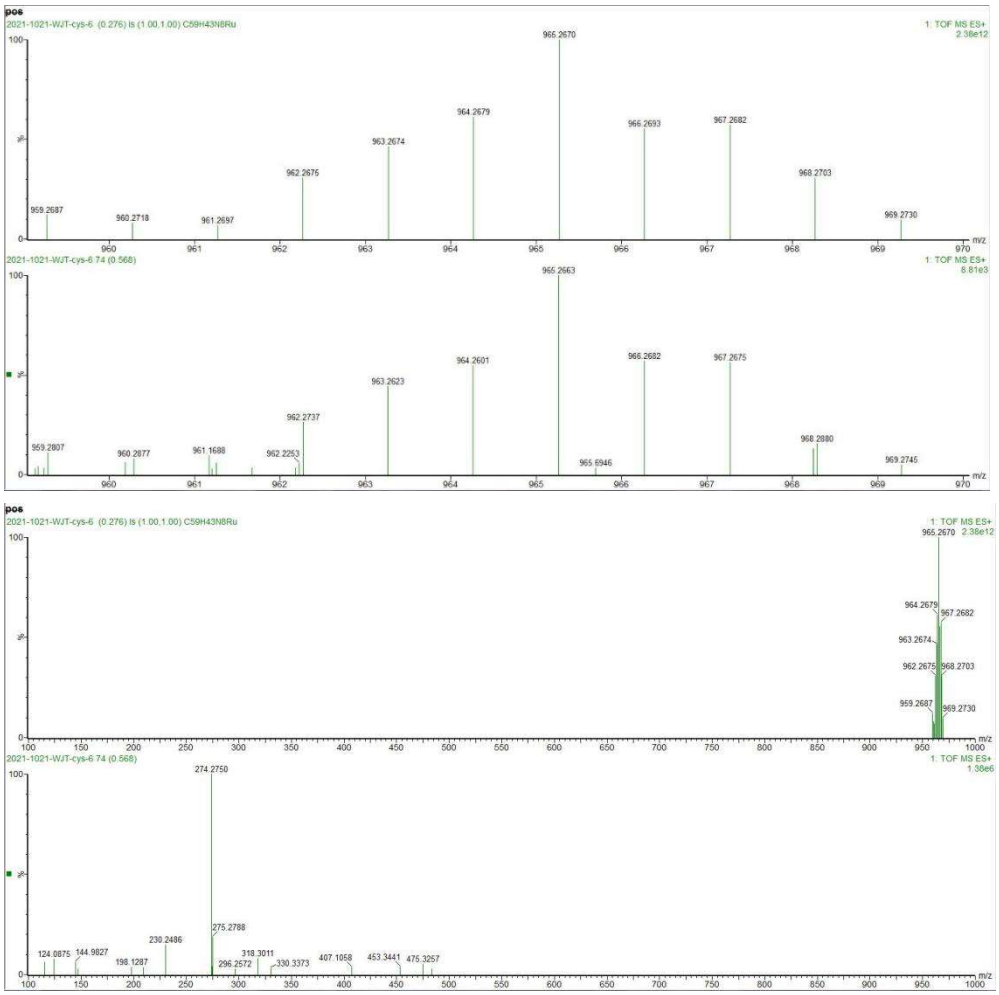
^{1}H NMR of Ru12



^{13}C NMR of Ru12



HRMS of Ru12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2.38e12
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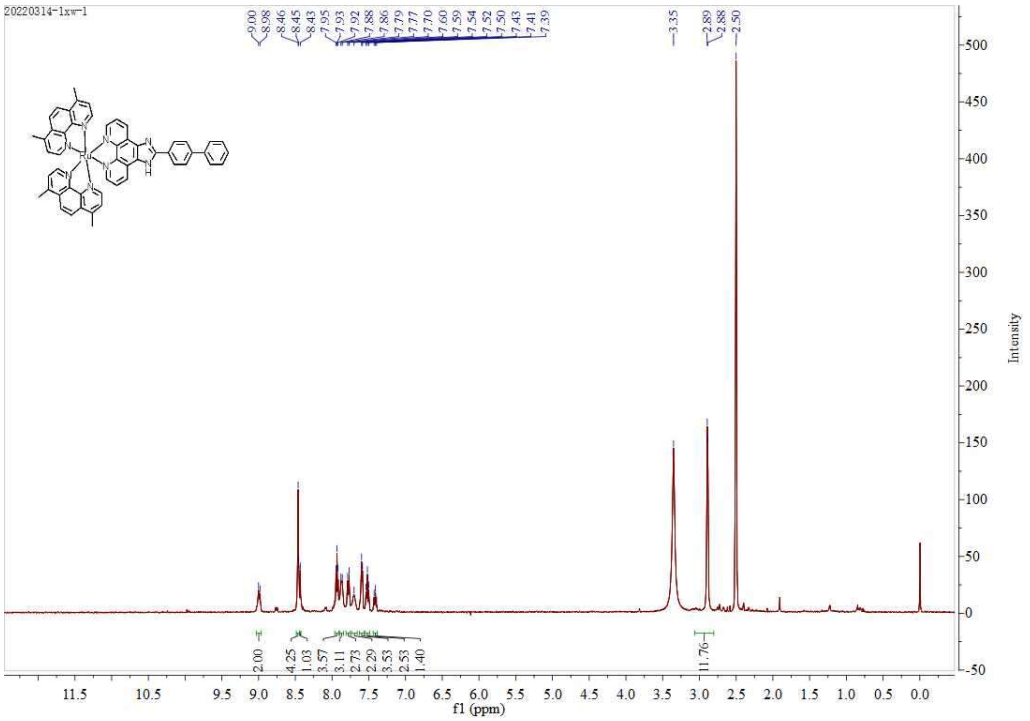
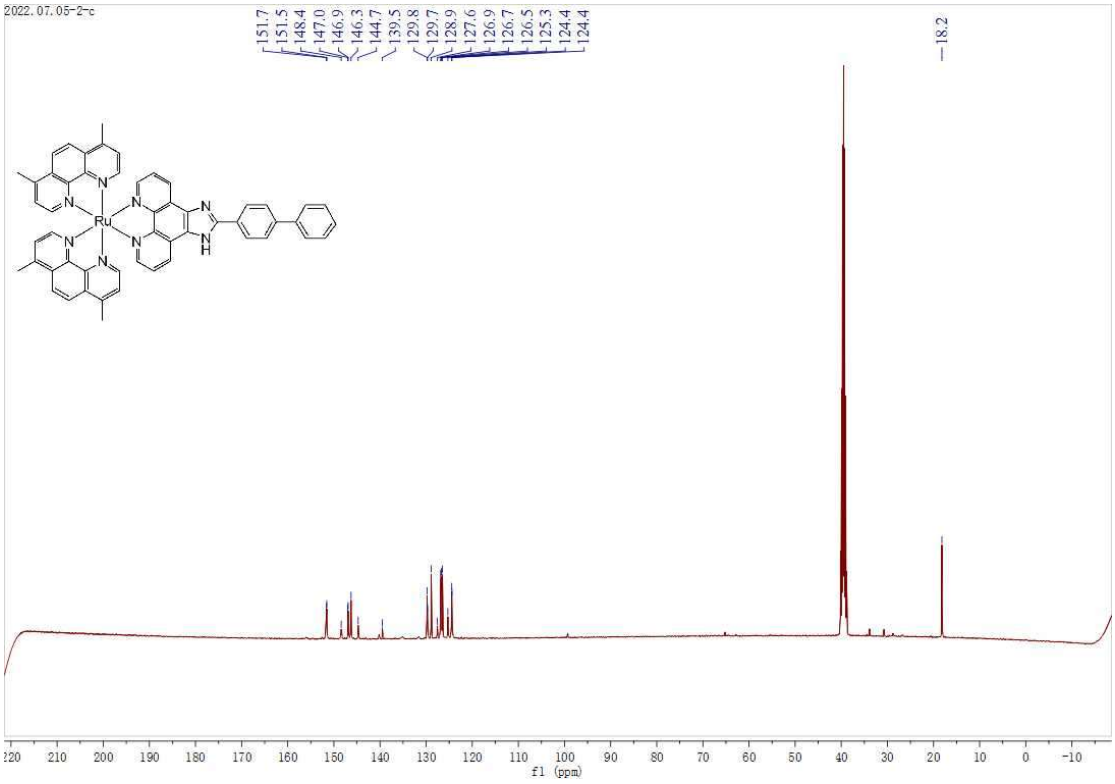
964.2679
966.2693
967.2682
963.2674
962.2675
968.2703
959.2687
960.2718
961.2697
969.2730
m/z
2021-1021-WJT-cys-6 74 (0.568)
1: TOF MS ES+
6.81e3
965.2663
964.2601
966.2682
967.2675
963.2623
962.2737
959.2807
960.2877
961.1688
962.2253
965.6946
968.2880
969.2745
m/z

pos
2021-1021-WJT-cys-6 (0.276) Is (1.00,1.00) C59H43N8Ru
1: TOF MS ES+
965.2670 2.38e12
964.2679
967.2682
963.2674
962.2675
968.2703
959.2687
969.2730
m/z
2021-1021-WJT-cys-6 74 (0.568)
1: TOF MS ES+
1.35e6
274.2750
275.2788
230.2486
124.0875
144.9827
198.1287
318.3011
296.2572
330.3373
407.1058
453.3441
475.3257
m/z

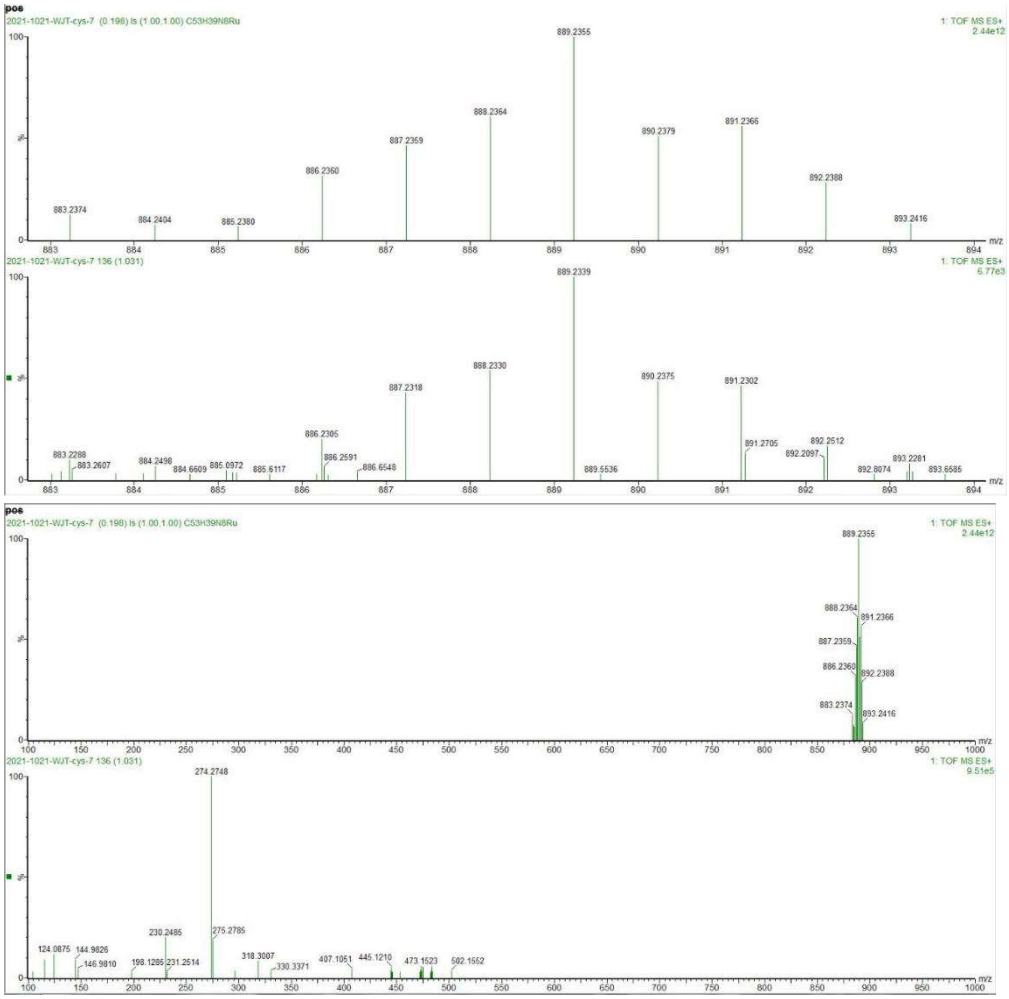
^{1}H NMR of Ru13



^{13}C NMR of Ru13



HRMS of Ru13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888.2364
887.2359
890.2379
891.2366
886.2360
892.2388
883.2374
884.2404
885.2380
893.2416
2021-1021-WJT-cys-7 136 (1.031)
1: TOF MS ES+
6.77e3
889.2339
888.2330
887.2318
890.2375
891.2302
886.2305
891.2705
892.2512
892.2097
883.2288
883.2607
884.2498
884.6609
885.0972
885.6117
886.2591
886.6548
889.5536
893.2261
892.8674
893.6585
pos
2021-1021-WJT-cys-7 (0.198) Is (1.00,1.00) C53H39N8Ru
1: TOF MS ES+
2.44e12
889.2355
888.2364
891.2366
887.2359
886.2360
892.2388
883.2374
893.2416
2021-1021-WJT-cys-7 136 (1.031)
1: TOF MS ES+
9.51e5
274.2748
230.2485
275.2785
124.0875
144.9826
146.9810
198.1285
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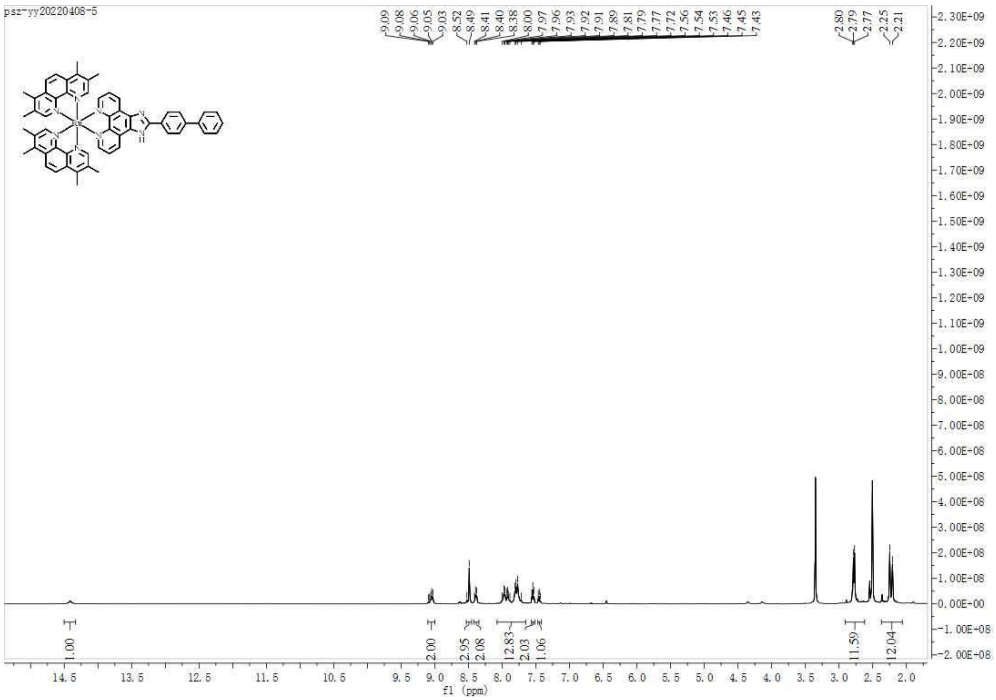
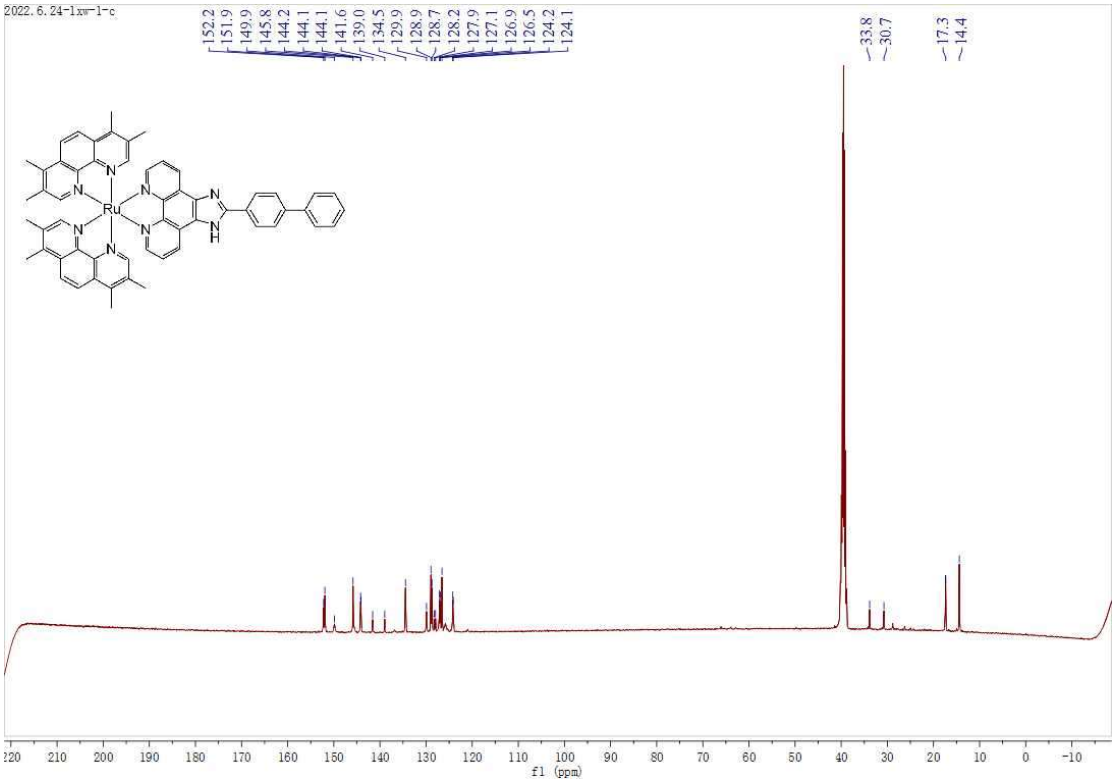
318.3007
330.3371
407.1051
445.1210
473.1523
582.1552

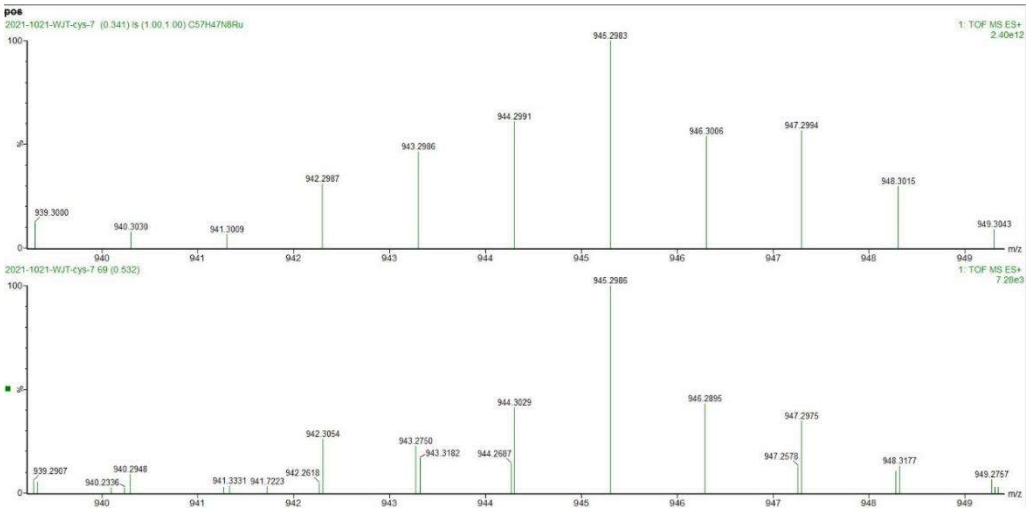
^{1}H NMR of Ru14



^{13}C NMR of Ru14



HRMS of Ru14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944.2991
946.3006
947.2994
943.2986
942.2987
948.3015
939.3000
940.3039
941.3009
949.3043
m/z
2021-1021-WJT-cys-7 69 (0.532)
1: TOF MS ES+
7.28e3
945.2986
944.3029
946.2895
942.3054
947.2975
943.2750
943.3182
944.2687
947.2578
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941.7223
942.2618
949.2757
m/z

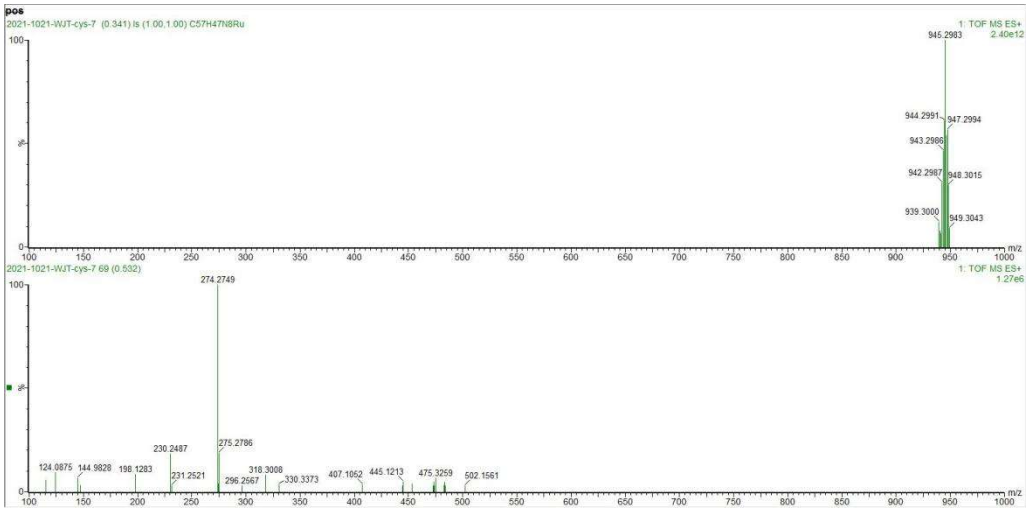
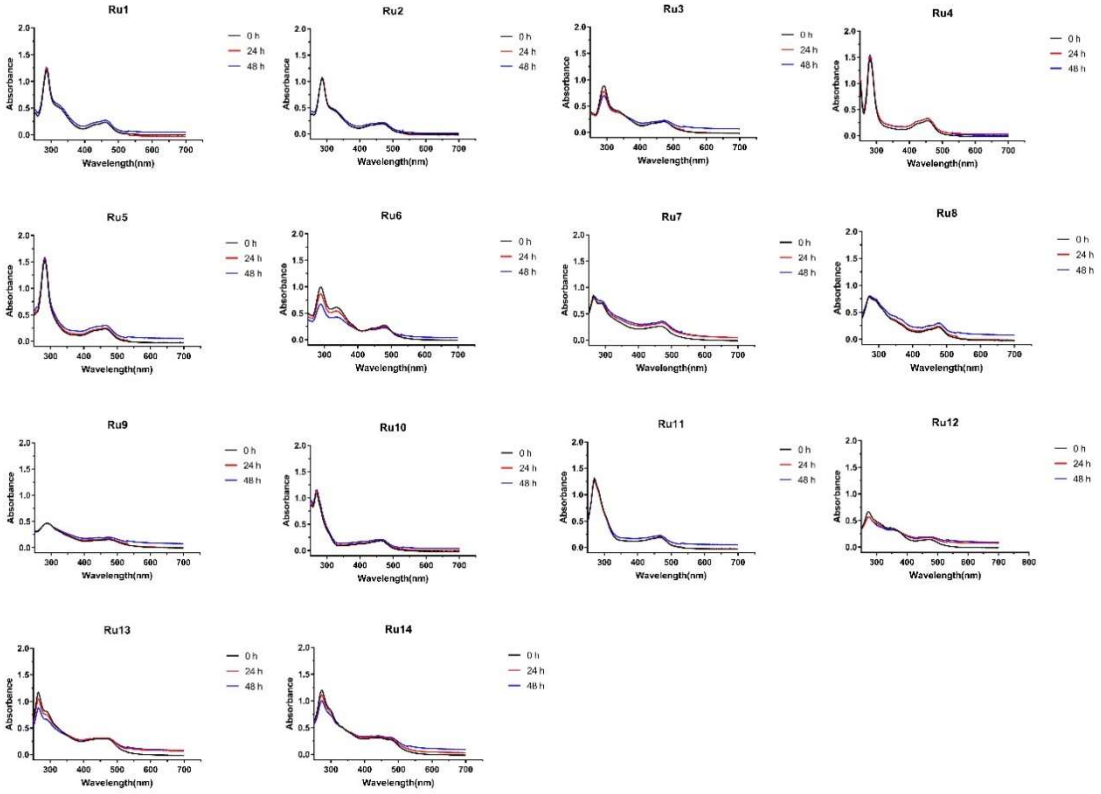
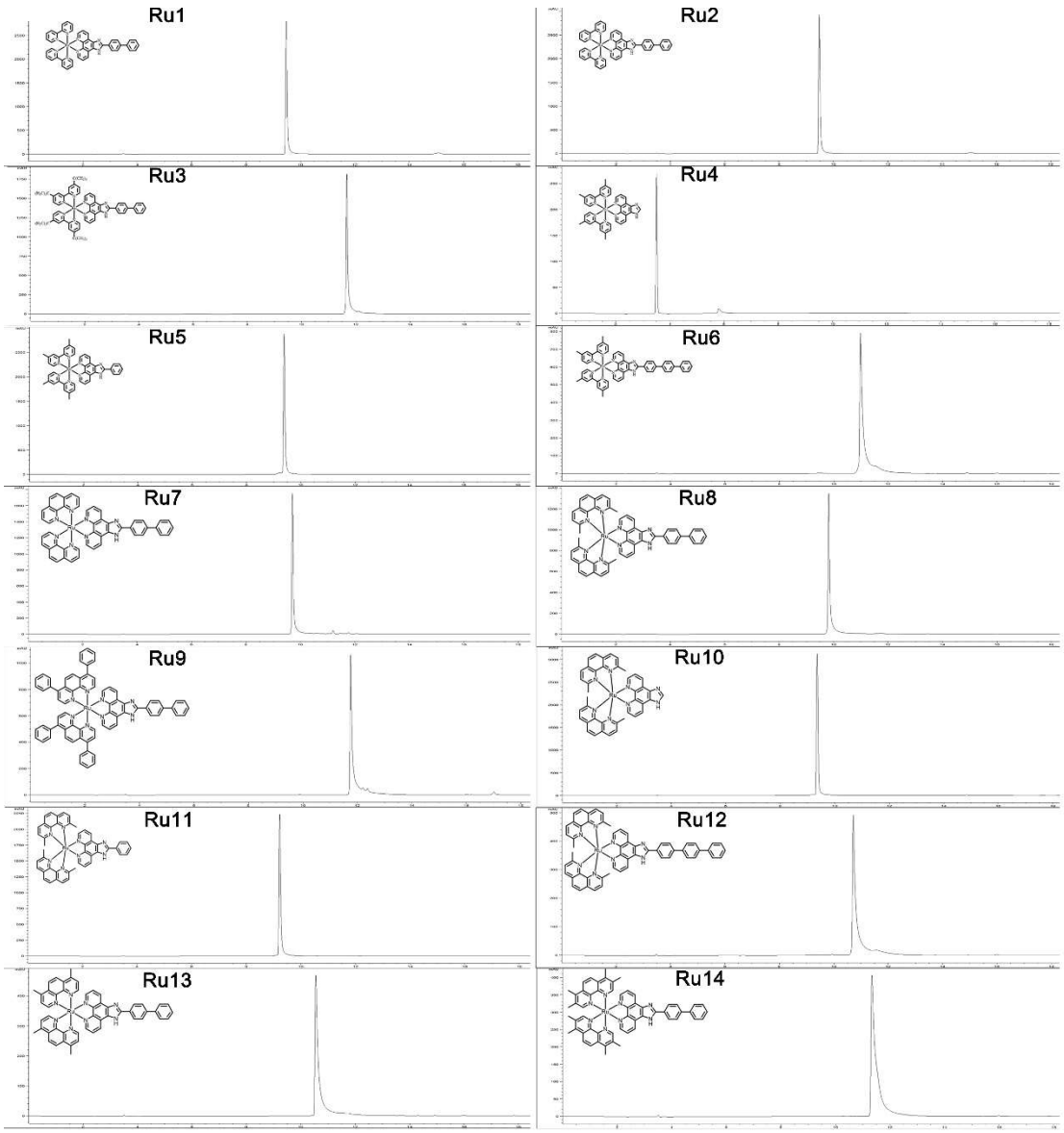

pos
2021-1021-WJT-cys-7 (0.341) Is (1.00,1.00) C57H47N8Ru
1: TOF MS ES+
2.40e12
945.2983
944.2991
947.2994
943.2986
942.2987
948.3015
939.3000
949.3043
m/z
2021-1021-WJT-cys-7 69 (0.532)
1: TOF MS ES+
1.27e6
274.2749
275.2786
230.2487
124.0875
144.9828
198.1283
231.2521
296.2567
318.3008
330.3373
407.1062
445.1213
475.3259
502.1561
m/z

Table S1 Crystal data and structure refinement for Ru2

Identification code	1_0m
Empirical formula	$C_{50}H_{44}F_{12}N_8OP_2Ru$
Formula weight	1163.94
Temperature/K	170.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.2796(14)
b/Å	23.099(3)
c/Å	18.796(3)
α/°	90
β/°	95.087(4)
γ/°	90
Volume/Å^3	4878.0(11)
Z	4
ρ_{calc}g/cm^3	1.585
μ/mm^{-1}	0.481
F(000)	2360.0
Crystal size/mm^3	0.25 × 0.15 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.032 to 50.052
Index ranges	$-13 \leq h \leq 12$, $-27 \leq k \leq 27$, $-22 \leq l \leq 20$
Reflections collected	32959
Independent reflections	8617 [R_{int} = 0.1129, R_{sigma} = 0.0959]
Data/restraints/parameters	8617/0/673
Goodness-of-fit on F^2	1.022
Final R indexes [I>=2σ (I)]	R_1 = 0.0782, wR_2 = 0.1933
Final R indexes [all data]	R_1 = 0.1175, wR_2 = 0.2290
Largest diff. peak/hole / e Å^{-3}	1.30/-1.40



Supplementary Figure 1: Stability of fourteen complexes in the PBS solution.



Supplementary Figure 2: The purity of fourteen complexes was investigated through HPLC

Reference

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