

## Supporting information for New Journal of Chemistry

### Electrochromic behavior of *fac*-tricarbonyl rhenium complexes

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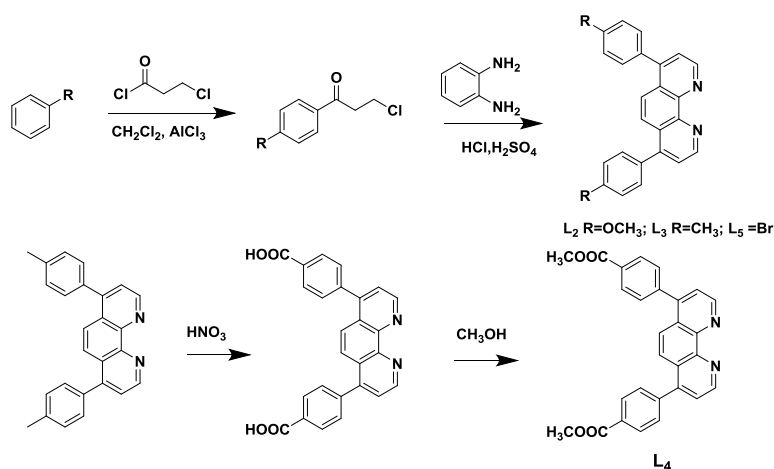
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## 1. Materials and methods

3-Chloropropionyl chloride (analytical reagent, 96%) was purchased from Shanghai Macklin Biochemical Co., Shanghai, China. Anisole (analytical reagent) was purchased from Aladdin Co., Shanghai, China. Anhydrous aluminum trichloride was purchased from Damao Chemical Reagent Factory, Tianjin, China. Toluene was purchased from Chongqing Chuandong Chemical (Group) Co., Chongqing, China. *o*-Phenylenediamine was purchased from Chengdu Kelong Chemical Reagent Company, Chengdu, China.  $\text{Re}(\text{CO})_5\text{Cl}$  (95%) was purchased from Bide Pharmatech Ltd., Shanghai, China. 4,7-Diphenylphenanthroline ( $\text{L}_1$ ) was purchased from Shanghai DiBai Chemical Reagent Company. Toluene and dichloromethane were redistilled before use.

$^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectra were obtained on a Bruker 600 MHz spectrometer. High-resolution mass spectra were recorded on a Bruker Impact II instrument (Germany). Infrared spectra were performed by a Spectrum-GX infrared spectrometer (Perkin-Elmer, USA) using KBr pellets. Cyclic voltammetry was determined on a CHI650B electrochemical workstation with  $\text{Ag}/\text{Ag}^+$  reference electrode, platinum disk ( $0.02\text{ cm}^2$ ) working electrode, and platinum wire counter electrodes, respectively. The spectroelectrochemistry was investigated using an UV-vis spectrophotometer UV-2700 (Shimadzu Instrument Co., Ltd, Japan). The color change of the ECD was presented by measuring the CIE (International Commission on Illumination)  $L^*a^*b^*$  color space coordinates with a color reader CR-10 plus (Konica Minolta, Inc., Japan). The single crystal structure was verified by an Agilent SuperNova EosS2 single crystal diffractometer (United States) using a graphite monochromatic  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ) source. The crystal was kept at  $287.64(16)\text{ K}$  during data collection. Using Olex2, the structure was solved with the Superflip structure solution program using Charge Flipping and refined with the ShelXL refinement package using Least Squares minimisation.

## 2. Synthesis of Ligands L<sub>2</sub>-L<sub>5</sub>



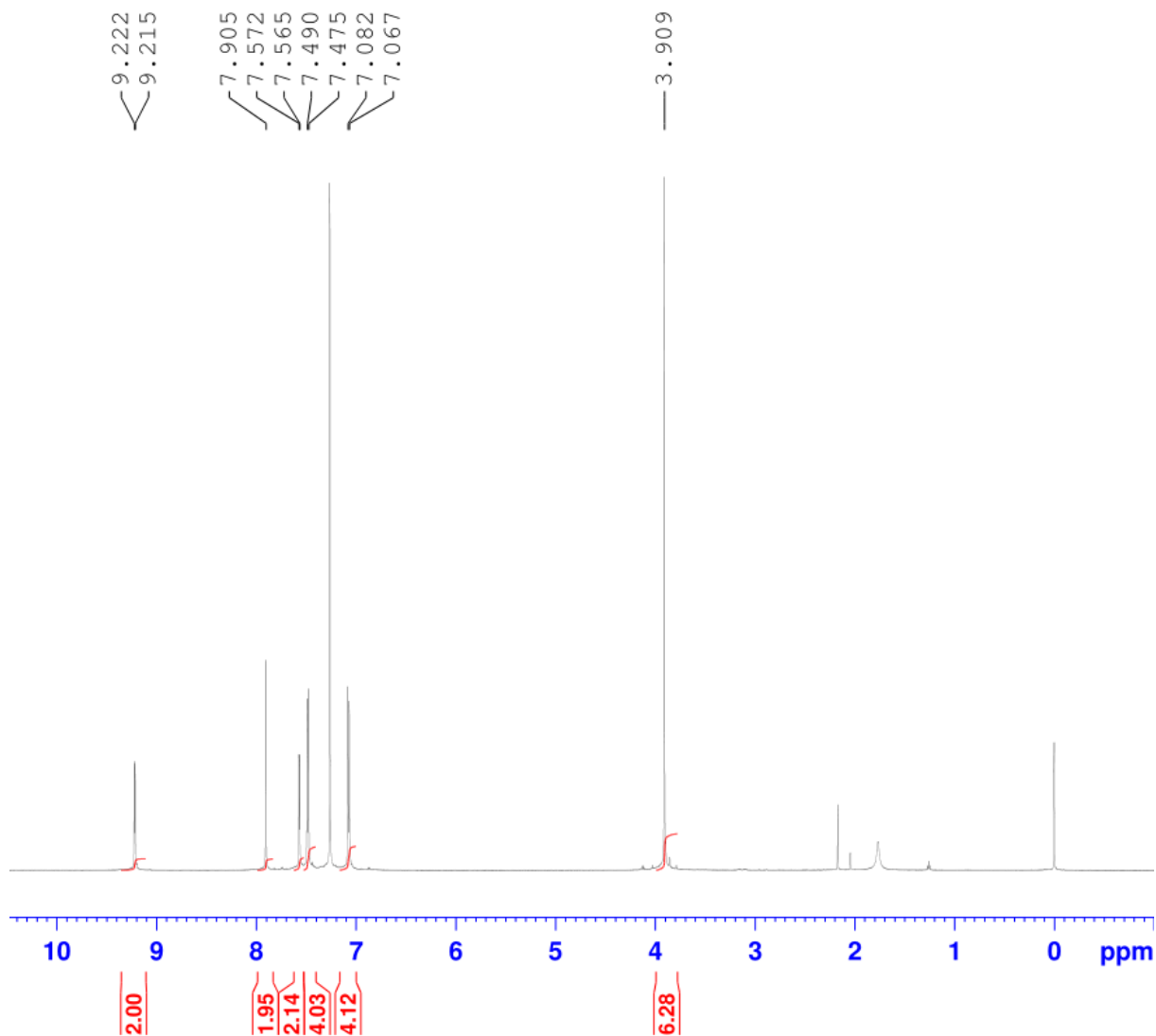
**Scheme S1.** Synthetic route of ligands L<sub>2</sub>-L<sub>5</sub>.

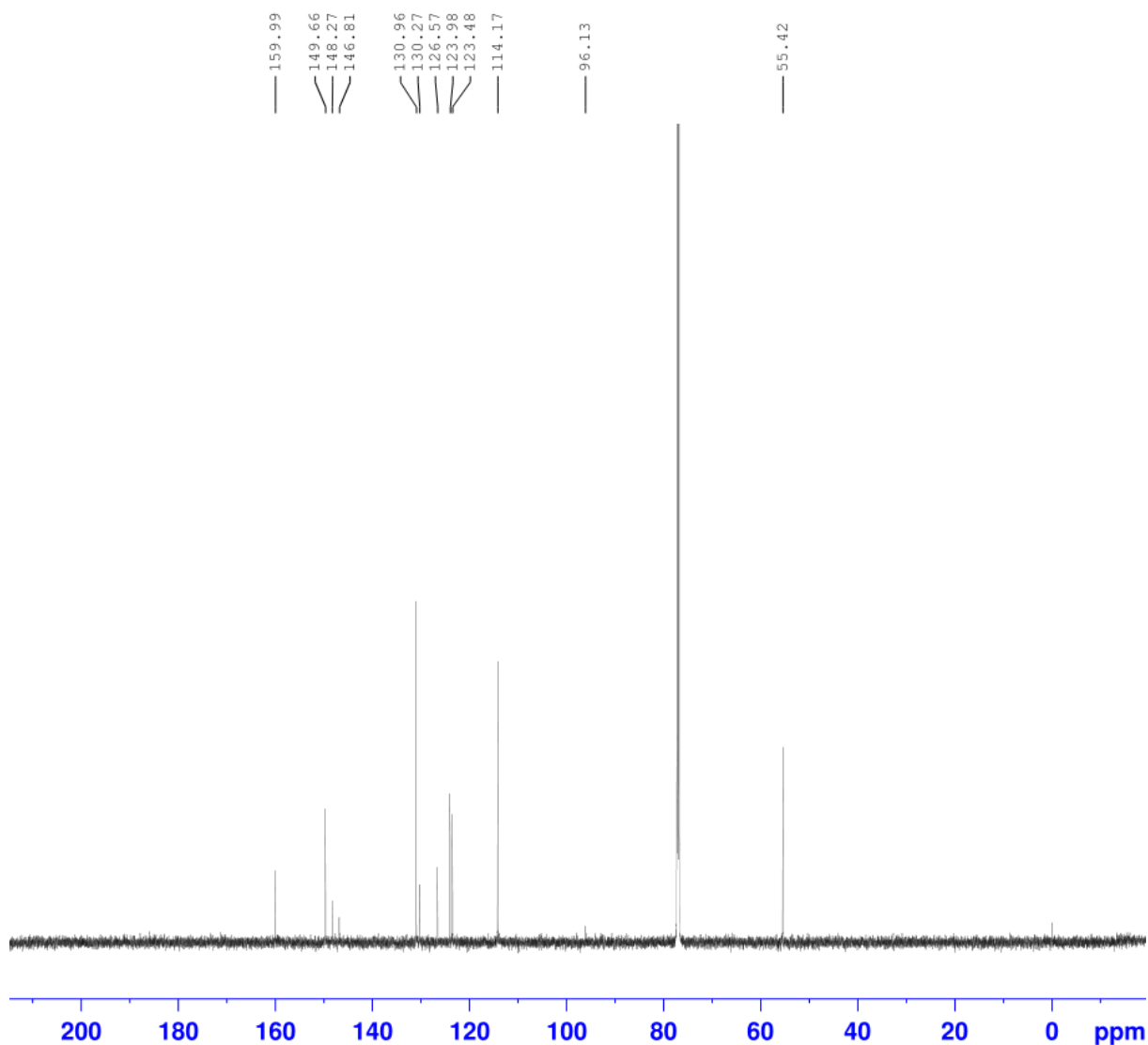
### 2.1. Synthesis of L<sub>2</sub>

A solution of anisole (3.20 mL, 30 mmol), 3-chloropropionyl chloride (3.20 mL, 33 mmol) and anhydrous aluminum trichloride (8.40 g, 63 mmol) in redistilled dichloromethane (40 mL) was stirred at 0 °C for 20 h, and then saturated ammonium chloride was added. The mixture was neutralized with 10wt.% NaOH solution, and extracted with dichloromethane (3 × 50 mL). All organic layers were combined, washed with saturated brine, dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated to dryness. The residue was purified by column chromatography on silica gel using ethyl acetate/petroleum ether 1:100 (v/v) as eluents, and 3-chloro-1-(4-methoxyphenyl)propan-1-one was obtained as a white solid (2.80 g, yielded 47%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ(ppm) = 7.938 (d, *J* = 4.8 Hz, 2H), 6.948 (d, *J* = 4.8 Hz, 2H), 3.910 (t, *J* = 2.4-5.4 Hz, 2H), 3.872 (s, 3H), 3.399 (t, *J* = 1.8-4.8 Hz, 2H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ(ppm): 195.16, 163.87, 130.35, 129.60, 113.90, 55.49, 40.93, 38.95.

Under nitrogen atmosphere, o-phenylenediamine (1.08 g, 10 mmol) was added in concentrated hydrochloric acid (24 mL), the mixture was stirred at 60 °C for 2-3 h, and then heated to 90 °C. 3-Chloro-1-(4-methoxyphenyl)propan-1-one (4.97 g, 25 mmol) was added in batches. After reacted for 2 h, concentrated sulfuric acid (6 mL) was added into reaction system, and reaction continued for 2 h. The mixture was adjusted to pH=9 with ammonia, extracted with chloroform (3 × 50 mL). All organic layers were combined, washed with saturated brine, dried over anhydrous MgSO<sub>4</sub>, filtered and

concentrated to dryness. The residue was purified by column chromatography on silica gel using ethyl acetate/petroleum ether 5:1 (v/v), and 4,7-bis(4-methoxyphenyl)-1,10-phenanthroline ( $L_2$ ) was obtained as a light yellow solid (0.50 g, yielded 14%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 9.219$  (d,  $J = 4.2$  Hz, 2H), 7.905 (s, 2H), 7.569 (d,  $J = 4.2$  Hz, 2H), 7.483 (d,  $J = 9.0$  Hz, 4H), 7.075 (d,  $J = 9.0$  Hz, 4H), 3.909 (s, 6H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm})$ : 159.99, 149.66, 148.27, 146.81, 130.96, 130.27, 126.57, 123.98, 123.48, 114.17, 55.42.





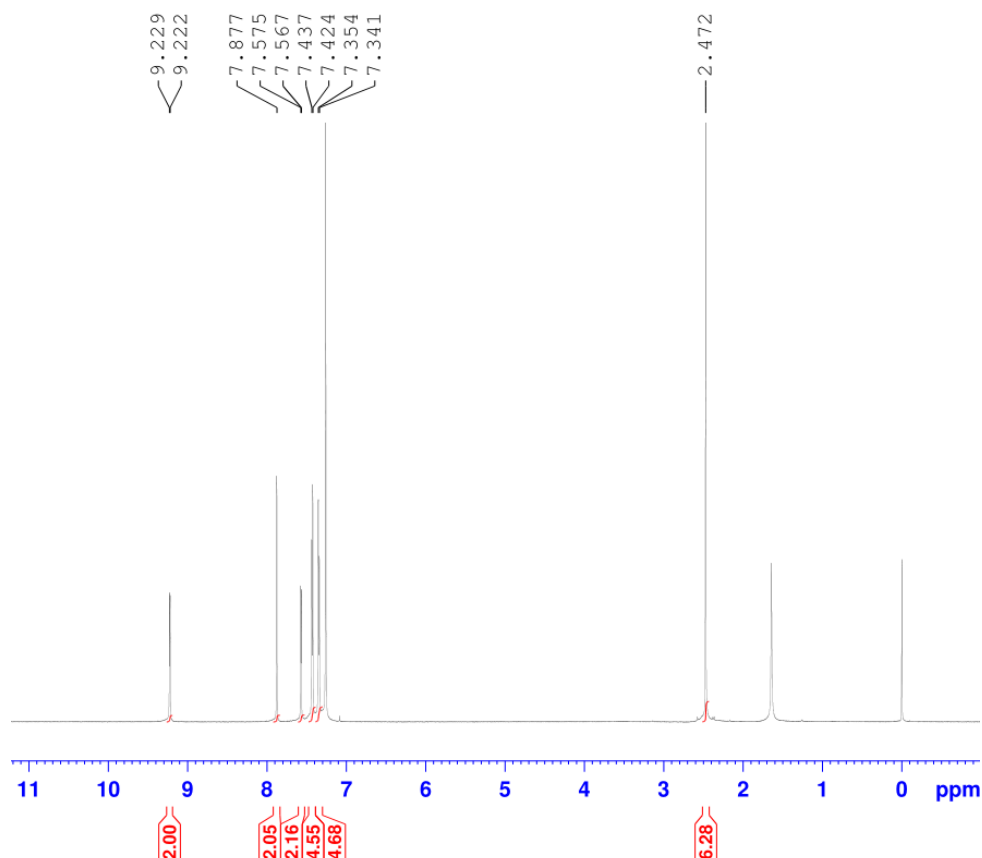
**Fig. S1.**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of  $L_2$  in  $\text{CDCl}_3$ .

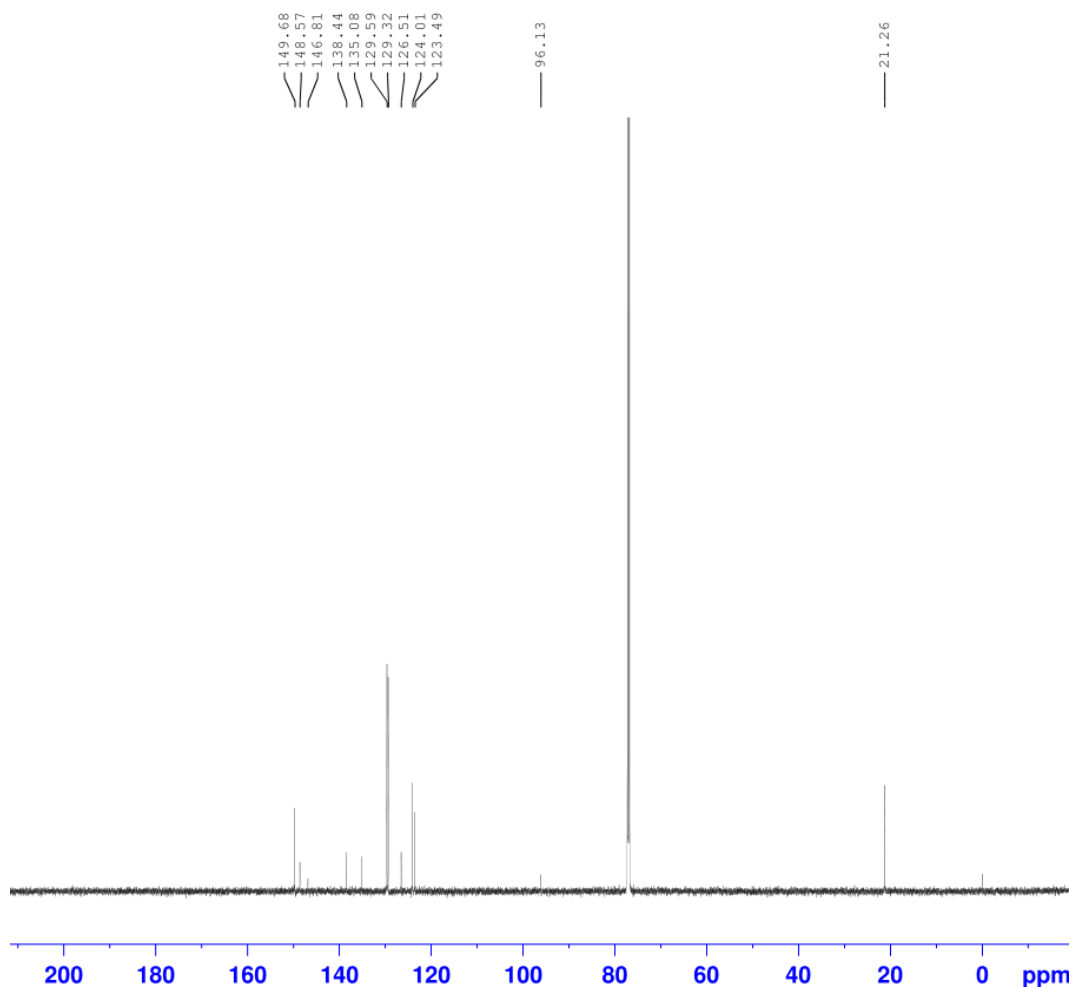
## 2.2. Synthesis of $L_3$

A solution of toluene (5.20 mL, 50 mmol), 3-chloropropionyl chloride (5.55 mL, 55 mmol) and anhydrous aluminum trichloride (14.00 g, 105 mmol) in redistilled dichloromethane (60 mL) was stirred at  $0\text{ }^\circ\text{C}$  for 20 h, and then saturated ammonium chloride was added. The mixture was neutralized with 10wt.% NaOH solution, and extracted with dichloromethane ( $3 \times 50\text{ mL}$ ). All organic layers were combined, washed with saturated brine, dried over anhydrous  $\text{MgSO}_4$ , filtered and concentrated to dryness. The residue was purified by column chromatography on silica gel using ethyl acetate/petroleum ether 1:100 (v/v) as eluents, and 3-chloro-1-(p-tolyl) propan-1-one was obtained as a white solid (6.44 g, yielded 70.5%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 7.858$  (d,  $J = 7.8\text{ Hz}$ ,

2H), 7.278 (d,  $J = 7.8$  Hz, 2H), 3.918 (t,  $J = 6.6-13.8$  Hz, 2H), 3.432 (t,  $J = 6.6-13.2$  Hz, 2H), 2.432 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm})$ : 196.29, 144.40, 134.04, 129.40, 128.17, 41.20, 38.80, 21.62.

Under nitrogen atmosphere, *o*-phenylenediamine (1.08 g, 10 mmol) was added in concentrated hydrochloric acid (24 mL), the mixture was stirred at 60 °C for 2-3 h, and then heated to 90 °C. 3-Chloro-1-(*p*-tolyl) propan-1-one (4.57 g, 25 mmol) was added in batches. After reacted for 2 h, concentrated sulfuric acid (6 mL) was added into reaction system, and reaction continued for 2 h. The mixture was adjusted to pH=9 with ammonia, extracted with chloroform (3  $\times$  50 mL). All organic layers were combined, washed with saturated brine, dried over anhydrous  $\text{MgSO}_4$ , filtered and concentrated to dryness. The residue was purified by column chromatography on silica gel using ethyl acetate/petroleum ether 2:1 (v/v), and 4,7-bis(4-Methylphenyl)-1,10-phenanthroline ( $\text{L}_3$ ) was obtained as a white solid (0.59 g, yielded 16%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 9.223$  (d,  $J = 4.2$  Hz, 2H), 7.877 (s, 2H), 7.571 (d,  $J = 4.8$  Hz, 2H), 7.431 (d,  $J = 7.8$  Hz, 4H), 7.348 (d,  $J = 7.8$  Hz, 4H), 2.472 (s, 6H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm})$ : 149.68, 148.57, 146.81, 138.44, 135.08, 129.59, 129.32, 126.51, 124.01, 123.49, 21.26.



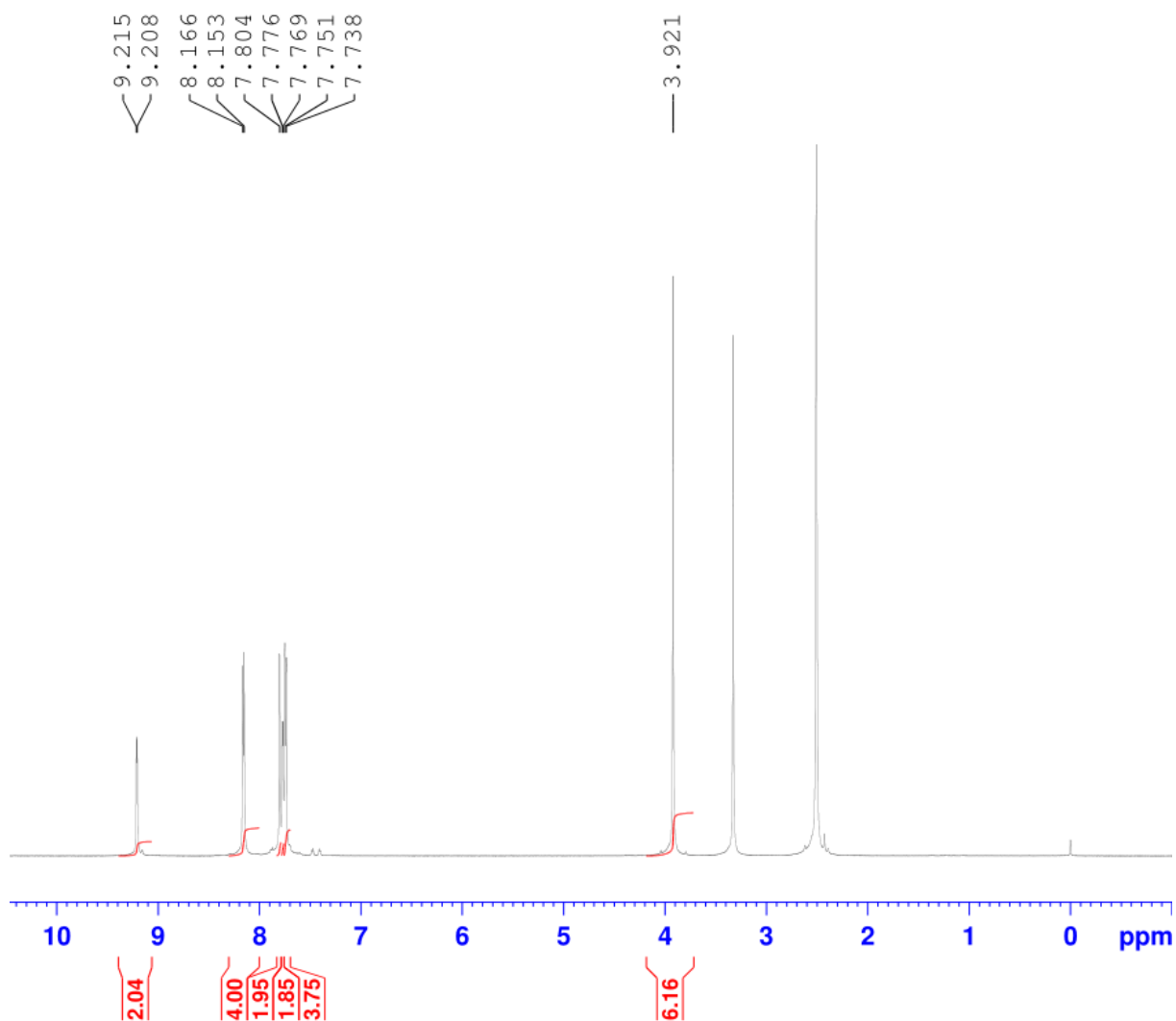


**Fig. S2.**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of  $\text{L}_3$  in  $\text{CDCl}_3$ .

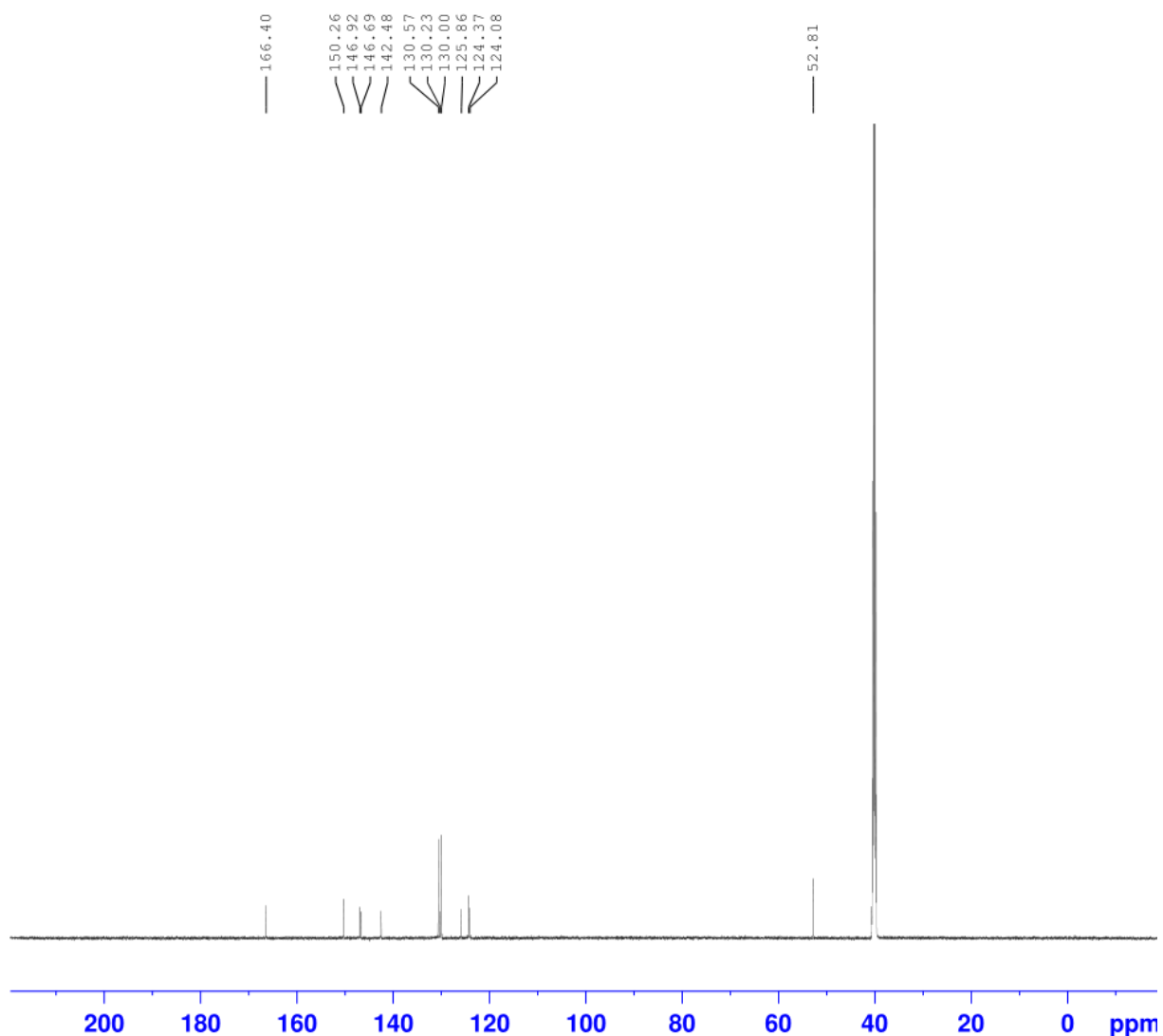
### 2.3. Synthesis of $\text{L}_4$

$\text{L}_4$  was synthesized via oxidation and esterification using  $\text{L}_3$  as the raw material.  $\text{L}_3$  (1.00 g), concentrated nitric acid (1 mL) and water (4 mL) were added into a reactor. After ultrasonic oscillation for 10 minutes, the mixture was stirred at  $180\text{ }^\circ\text{C}$  for 24 h, poured into 100 mL water, and filtered. The obtained solid was added into methanol, heated to reflux, concentrated and dried to obtain 4,4'-(1,10-phenanthroline-4,7-diyl) dibenzoic acid. Concentrated sulfuric acid (0.20 mL) and 4,4'-(1,10-phenanthroline-4,7-diyl) dibenzoic acid (0.42 g, 1 mmol) were added in methanol (15 mL), the mixture was refluxed for 72 h. The solution was adjusted  $\text{pH}=8$  using sodium carbonate, extracted with chloroform ( $3 \times 50\text{ mL}$ ), combined all organic layers, washed with saturated brine, dried over anhydrous  $\text{MgSO}_4$ , filtered and concentrated to dryness. The residue was purified by column chromatography on silica gel using ethyl acetate/petroleum ether 5:1 (v/v) to obtain 4,7-bis(4-carbomethoxyphenyl)-1,10-phenanthroline ( $\text{L}_4$ ) as a light white solid (0.50 g, yielded 59%).  $^1\text{H}$  NMR

(600 MHz, CDCl<sub>3</sub>)  $\delta$ (ppm) = 9.212 (d,  $J$  = 4.2 Hz, 2H), 8.160 (d,  $J$  = 7.8 Hz, 4H), 7.804 (s, 2H), 7.773 (d,  $J$  = 4.2 Hz, 2H), 7.745 (d,  $J$  = 7.8 Hz, 4H), 3.921 (s, 6H). <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>):  $\delta$ (ppm): 166.30, 150.26, 146.92, 146.69, 142.48, 130.57, 130.23, 130.00, 125.86, 124.37, 124.08, 52.81.







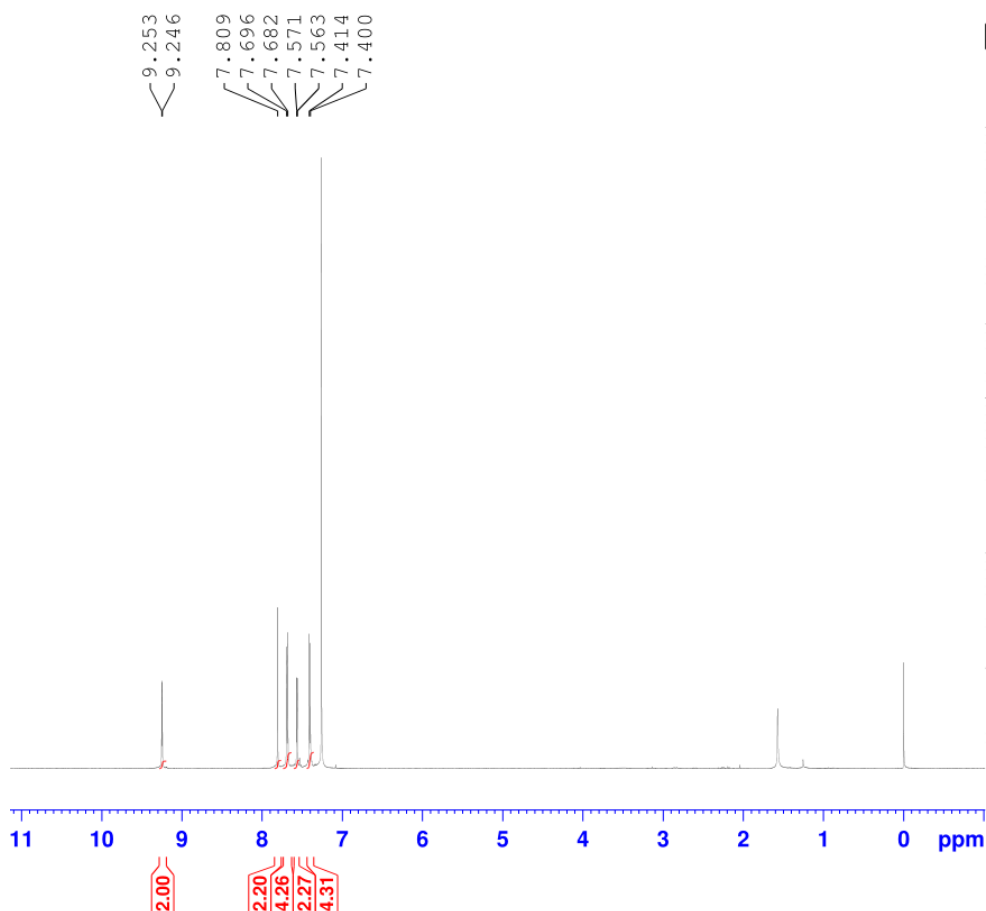
**Fig. S3.** <sup>1</sup>H NMR and <sup>13</sup>C NMR of L<sub>4</sub> in CDCl<sub>3</sub>.

#### 2.4. Synthesis of L<sub>5</sub>

A solution of bromobenzene (5.23 mL, 50 mmol), 3-chloropropionyl chloride (5.55 mL, 55 mmol) and anhydrous aluminum trichloride (14.00 g, 105 mmol) in redistilled dichloromethane (60 mL) was stirred at 0 °C for 20 h, and then saturated ammonium chloride was added. The mixture was neutralized with 10wt.% NaOH solution, and extracted with dichloromethane (3 × 50 mL). All organic layers were combined, washed with saturated brine, dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated to dryness. The precipitate was recrystallized in ethyl acetate and petroleum ether to give 3-chloro-1-(bromo) propan-1-one as a white solid (7.26 g, yielded 59%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ(ppm): 7.817 (t, *J* = 7.1-8.4 Hz, 2H), 7.626 (t, *J* = 6.6-8.4 Hz, 2H), 3.911 (t, *J* = 6.6-13.2 Hz, 4H),

3.420 (t,  $J = 6.6$ - $13.2$  Hz, 2H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 195.65, 135.16, 132.10, 129.54, 128.81, 41.23, 38.42.

Under nitrogen atmosphere, *o*-phenylenediamine (1.08 g, 10 mmol) was added in concentrated hydrochloric acid (24 mL), the mixture was stirred at 60 °C for 2-3 h, and then heated to 90 °C. 3-Chloro-1-(bromo) propan-1-one (6.19 g, 25 mmol) was added in batches. After reacted for 2 h, concentrated sulfuric acid (6 mL) was added into reaction system, and reaction continued for 2 h. The mixture was adjusted to pH=9 with ammonia, extracted with chloroform ( $3 \times 50$  mL). All organic layers were combined, washed with saturated brine, dried over anhydrous  $\text{MgSO}_4$ , filtered and concentrated to dryness. The residue was purified by column chromatography on silica gel using ethyl acetate/petroleum ether 5:1 (v/v), and 4,7-bis(4-bromophenyl)-1,10-phenanthroline ( $\text{L}_5$ ) was obtained as a white solid (0.95 g, yielded 19%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$ (ppm) = 9.249 (d,  $J = 4.2$  Hz, 2H), 7.809 (s, 2H), 7.689 (d,  $J = 8.4$  Hz, 4H), 7.567 (d,  $J = 4.8$  Hz, 2H), 7.407 (d,  $J = 8.4$  Hz, 4H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 149.93, 147.23, 146.89, 136.77, 131.93, 131.22, 126.16, 123.91, 123.42, 123.06.



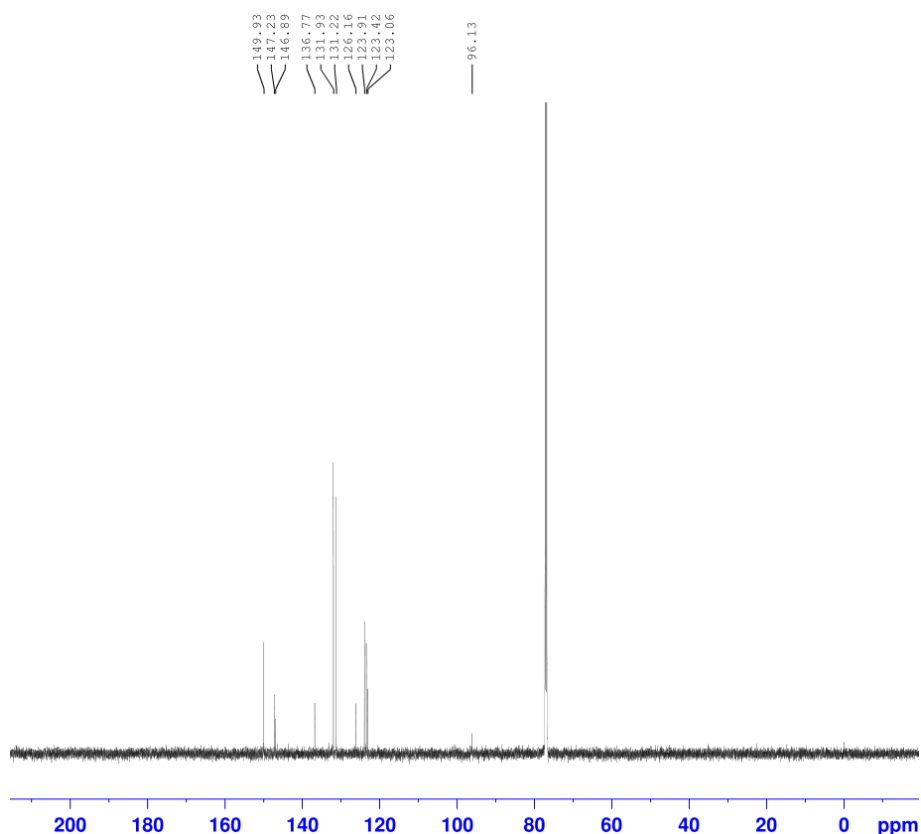
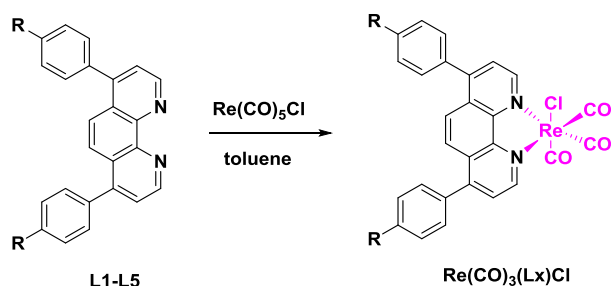


Fig. S4.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of  $\text{L}_5$  in  $\text{CDCl}_3$ .

### 3. Synthesis of rhenium(I) complexes $\text{fac-Re}(\text{CO})_3(\text{L}_x)\text{Cl}$ ( $x=1-5$ )

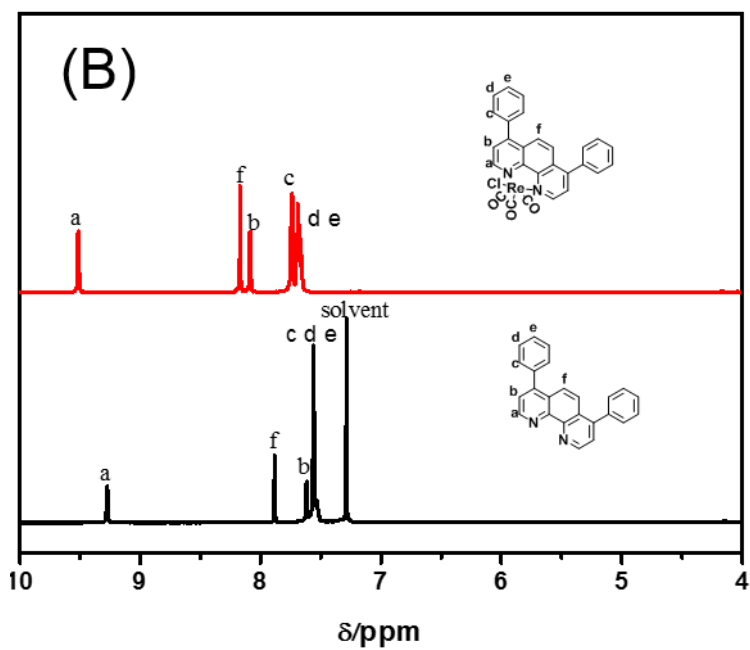
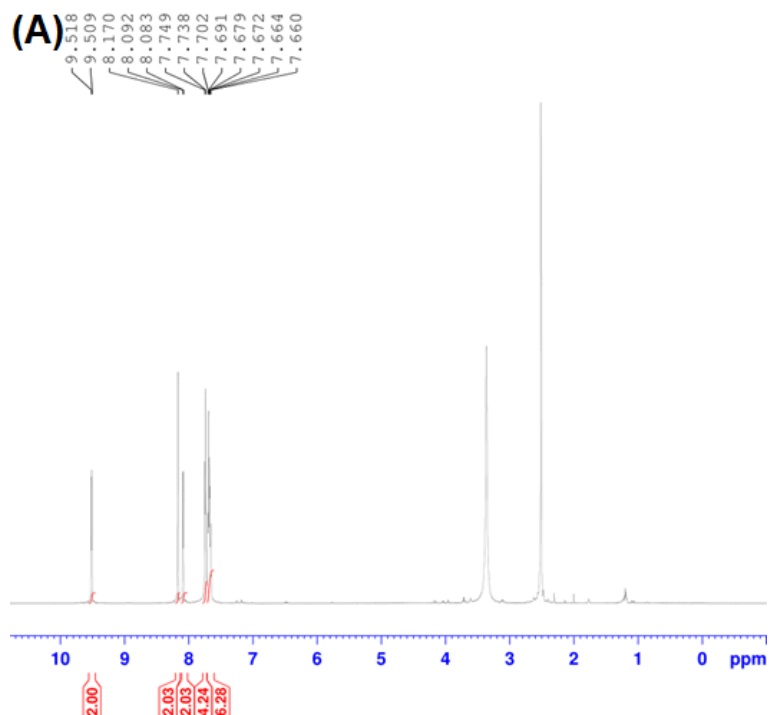


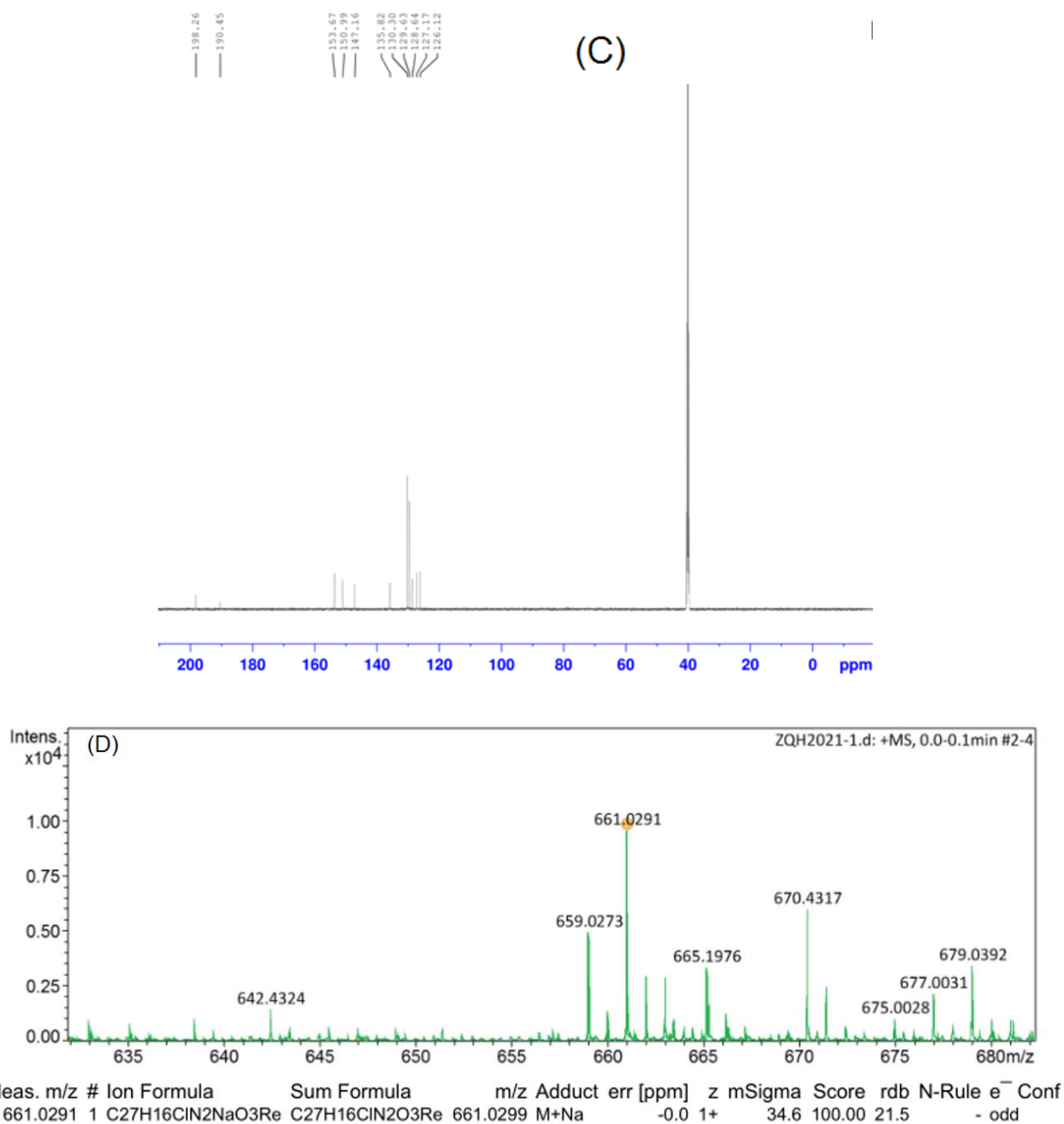
Scheme S2. Synthesis of Re(I) complexes  $\text{fac-Re}(\text{CO})_3(\text{L}_x)\text{Cl}$  ( $x=1-5$ ).

A mixture of ligand and  $\text{Re}(\text{CO})_5\text{Cl}$  (1:1 equiv.) in redistilled toluene was stirred for 20 h at  $110\text{ }^\circ\text{C}$  under nitrogen atmosphere, and then cooled to room temperature. The solution was concentrated and diethyl ether was added to precipitate. The precipitate was purified by chromatography on silica gel using different proportions of ethyl acetate/petroleum ether as eluent to afford target product.

**Fac-Re(CO) $_3$ (L $_1$ )Cl.** L1 (166 mg, 0.5 mmol) reacted with  $\text{Re}(\text{CO})_5\text{Cl}$  (188 mg, 0.5 mmol) to afford  $\text{Re}(\text{CO})_3(\text{L}_1)\text{Cl}$  as a yellow solid (221 mg, yielded 69%). M.P.:  $284.0\text{-}284.3\text{ }^\circ\text{C}$ . IR(KBr):  $\nu_{\text{C}=\text{O}} = 2016, 1913, 1879\text{ cm}^{-1}$ .  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6$ )  $\delta(\text{ppm}) = 9.518$  (d,  $J = 5.4\text{ Hz}$ , 2H), 8.170 (s, 2H),

8.022 (d,  $J = 5.4$  Hz, 2H), 7.749 (d,  $J = 6.6$  Hz, 4H), 7.660-7.702 (m, 6H).  $^{13}\text{C}$  NMR (150 MHz, DMSO- $d_6$ ):  $\delta(\text{ppm})$ : 198.26, 190.45, 153.67, 150.99, 147.16, 135.82, 130.30, 129.63, 128.64, 127.17, 126.12. HRMS(ESI) ( $\text{CHCl}_3$ , positive mode)  $m/z$  for  $\text{C}_{27}\text{H}_{16}\text{ClN}_2\text{O}_3\text{Re}$   $[\text{M}+\text{Na}]^+$ : calculated 661.0299, found 661.0291.

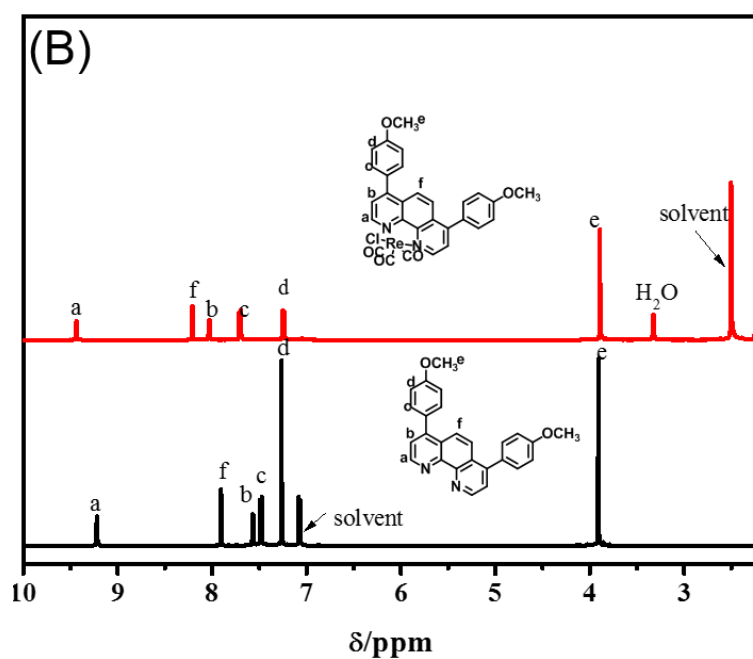
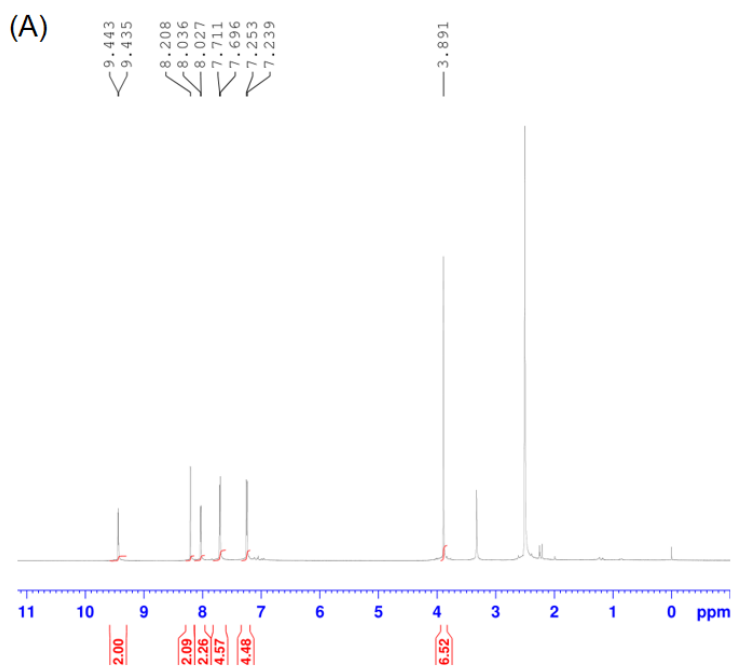


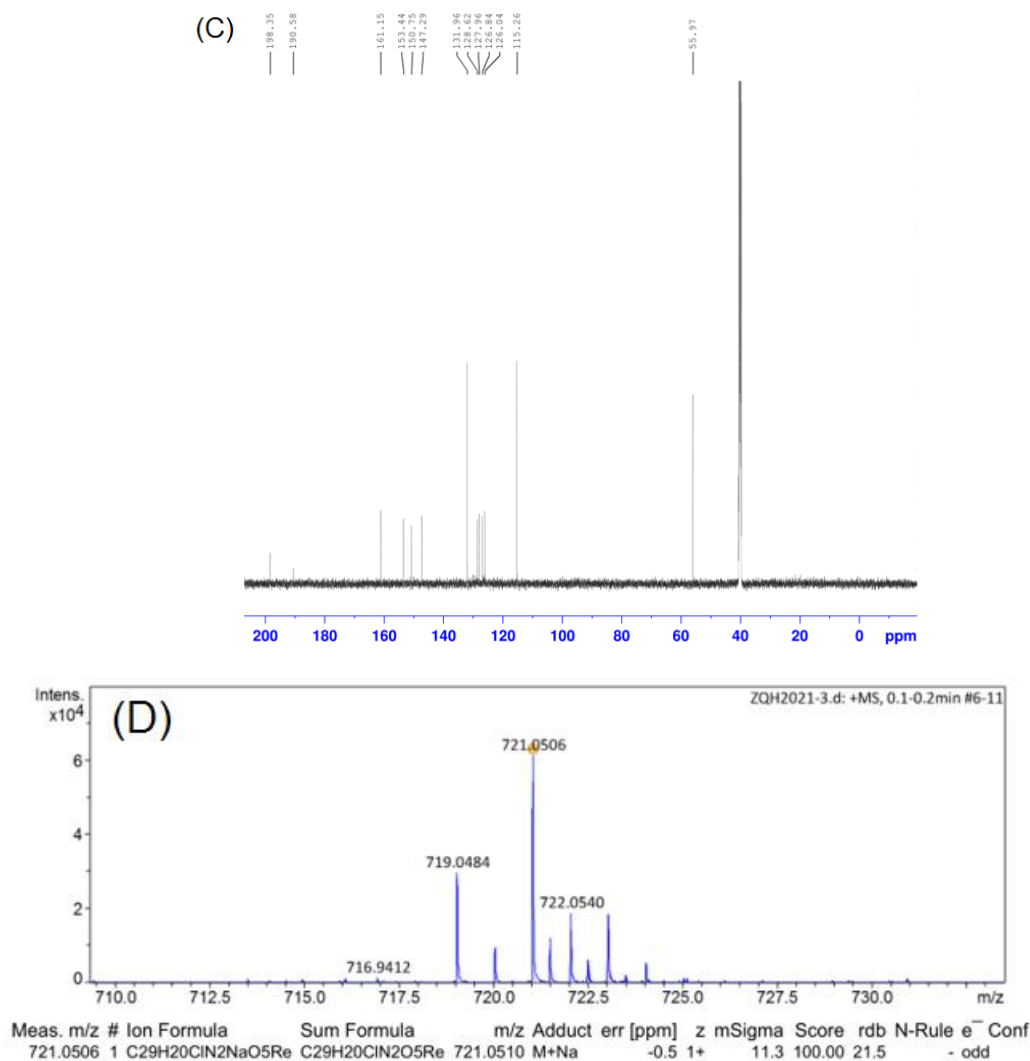


**Fig. S5.** <sup>1</sup>H NMR of Re(CO)<sub>3</sub>(L<sub>1</sub>)Cl (A), <sup>1</sup>H NMR comparison of L<sub>1</sub> in CDCl<sub>3</sub> and Re(CO)<sub>3</sub>(L<sub>1</sub>)Cl in DMSO-*d*<sub>6</sub> (C), <sup>13</sup>C NMR (C) and HRMS (D) of Re(CO)<sub>3</sub>(L<sub>1</sub>)Cl.

**Fac-Re(CO)<sub>3</sub>(L<sub>2</sub>)Cl.** L<sub>2</sub> (235 mg, 0.6 mmol) reacted with Re(CO)<sub>5</sub>Cl (217 mg, 0.6 mmol) to afford Re(CO)<sub>3</sub>(L<sub>2</sub>)Cl as a yellow solid (399 mg, yielded 95%). M.P.: 166-166.5 °C. IR(KBr): ν<sub>C=O</sub> = 2018, 1883 cm<sup>-1</sup>. <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) δ(ppm) = 9.439 (d, *J* = 4.80 Hz, 2H), 8.208 (s, 2H), 8.032 (d, *J* = 5.4 Hz, 2H), 7.704 (d, *J* = 9.0 Hz, 4H), 7.246 (d, *J* = 8.4 Hz, 4H), 3.891 (s, 6H). <sup>13</sup>C NMR (150

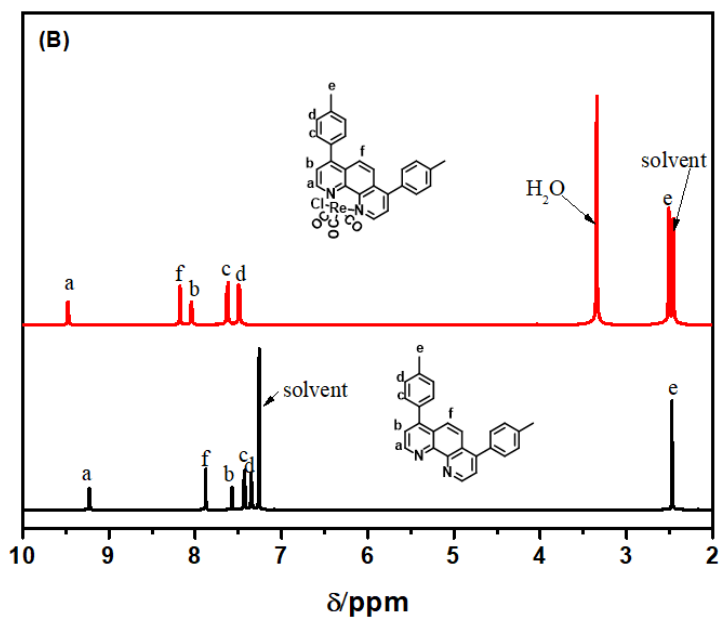
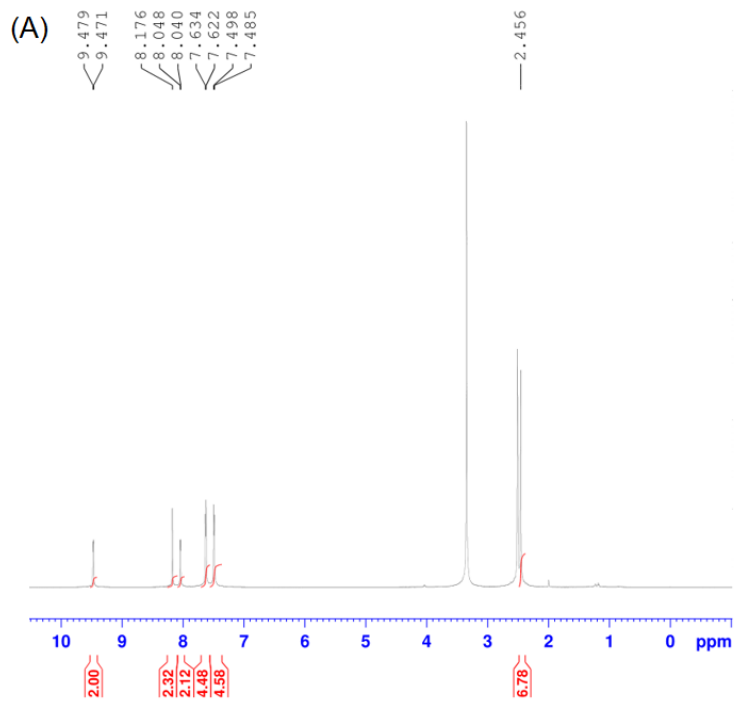
MHz, DMSO-*d*<sub>6</sub>) δ(ppm): 198.35, 190.58, 161.15, 153.44, 150.75, 147.29, 131.96, 128.62, 127.96, 126.84, 126.04, 115.26, 55.97. HRMS(ESI) (CHCl<sub>3</sub>, positive mode) *m/z* for C<sub>29</sub>H<sub>20</sub>ClN<sub>2</sub>O<sub>5</sub>Re [M+Na]<sup>+</sup>: calculated 721.0510, found 721.0506.



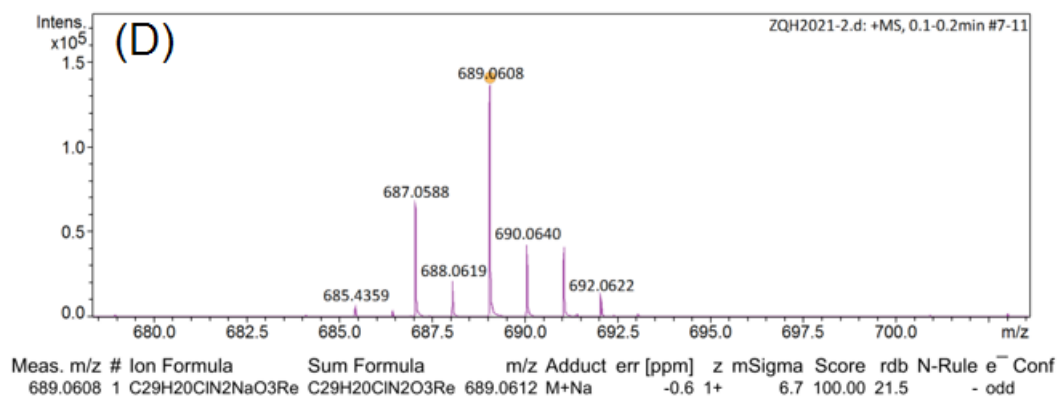
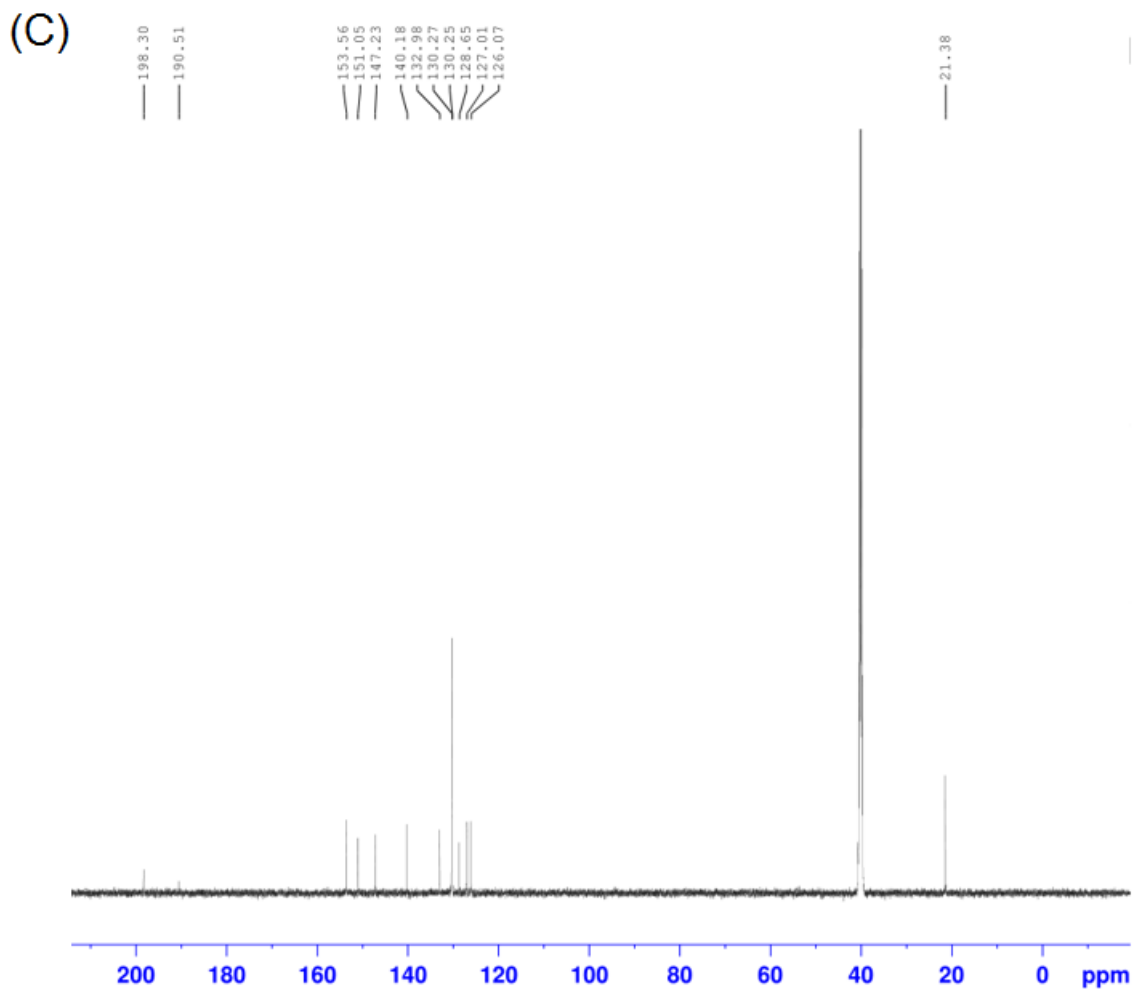


**Fig. S6.** <sup>1</sup>H NMR of Re(CO)<sub>3</sub>(L<sub>2</sub>)Cl (A), <sup>1</sup>H NMR comparison of L<sub>2</sub> in CDCl<sub>3</sub> and Re(CO)<sub>3</sub>(L<sub>2</sub>)Cl in DMSO-*d*<sub>6</sub> (C), <sup>13</sup>C NMR (C) and HRMS (D) of Re(CO)<sub>3</sub>(L<sub>2</sub>)Cl.

***Fac*-Re(CO)<sub>3</sub>(L<sub>3</sub>)Cl.** L<sub>3</sub> (180 mg, 0.5 mmol) reacted with Re(CO)<sub>5</sub>Cl (188 mg, 0.5 mmol) to afford Re(CO)<sub>3</sub>(L<sub>3</sub>)Cl as a yellow solid (243 mg, yielded 73%). M.P: 262.5-262.8 °C. IR(KBr): ν<sub>C=O</sub>= 2020, 1887 cm<sup>-1</sup>. <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) δ(ppm): 9.475 (d, *J* = 4.80 Hz, 2H), 8.176 (s, 2H), 8.044 (d, *J* = 4.80 Hz, 2H), 7.628 (d, *J* = 7.20 Hz, 4H), 7.492 (d, *J* = 7.80 Hz, 4H), 2.456 (s, 6H). <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>) δ(ppm): 198.30, 190.51, 153.56, 151.05, 147.23, 140.18, 132.98, 130.27, 130.25, 128.65, 127.01, 126.07, 21.38. HRMS(ESI) (CHCl<sub>3</sub>, positive mode) m/z for C<sub>29</sub>H<sub>20</sub>ClN<sub>2</sub>O<sub>3</sub>Re[M+Na]<sup>+</sup>: calculated 689.0612, found 689.0608.

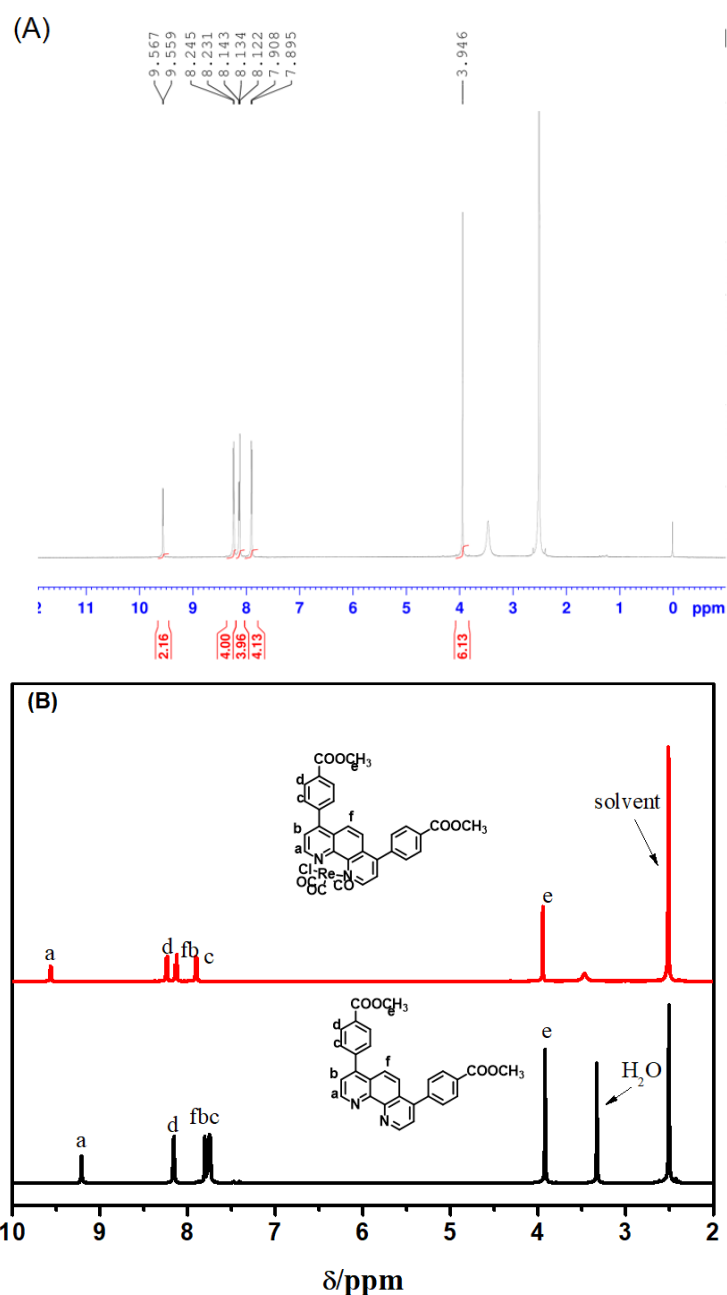


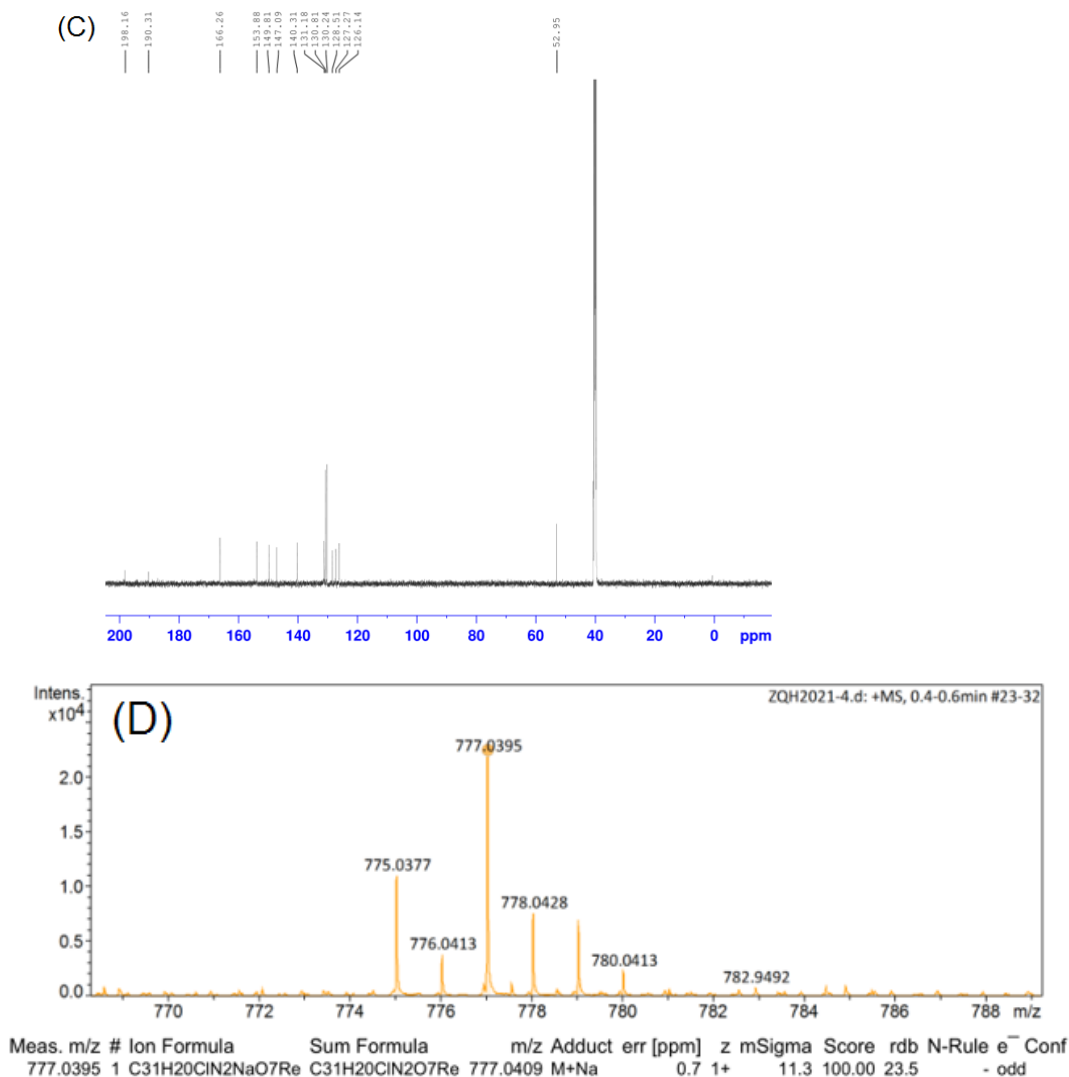




**Fig. S7.** <sup>1</sup>H NMR of *fac*-Re(CO)<sub>3</sub>(L<sub>3</sub>)Cl in DMSO-*d*<sub>6</sub> (A), <sup>1</sup>H NMR comparison of L<sub>3</sub> in CDCl<sub>3</sub> and *fac*-Re(CO)<sub>3</sub>(L<sub>3</sub>)Cl in DMSO-*d*<sub>6</sub> (B), <sup>13</sup>C NMR (C) and HRMS (D) of *fac*-Re(CO)<sub>3</sub>(L<sub>3</sub>)Cl.

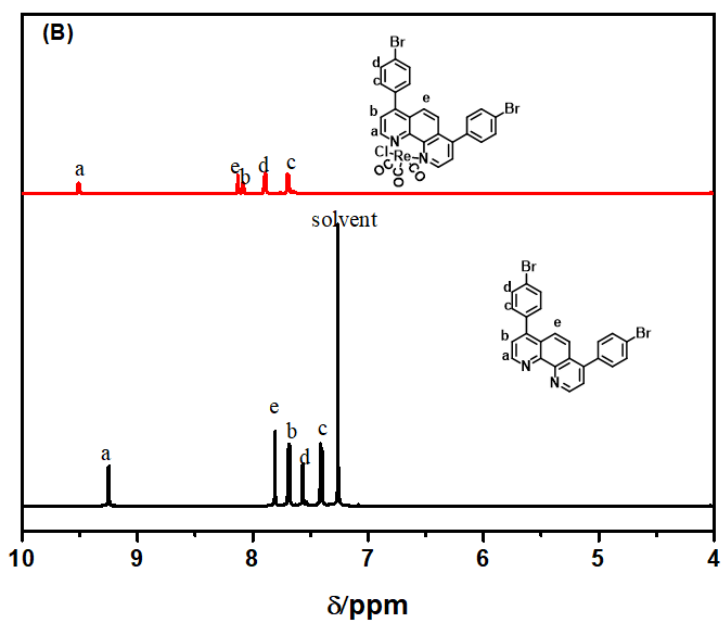
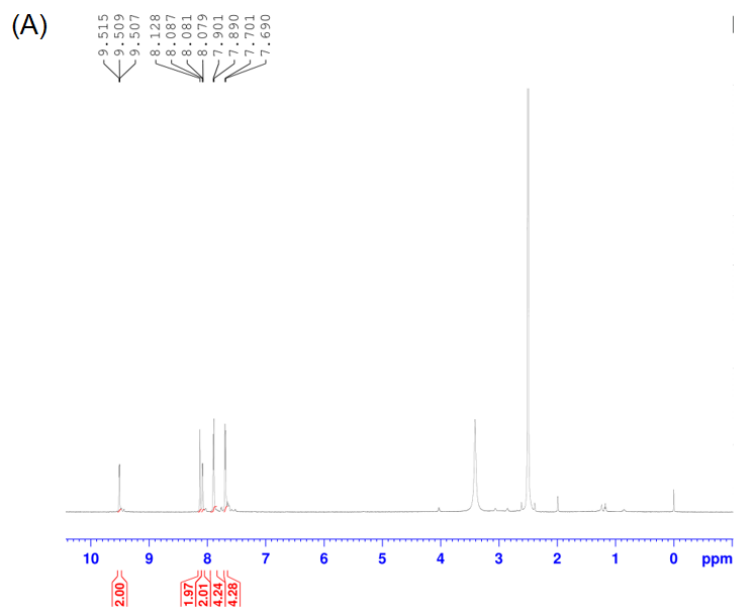
**Fac-Re(CO)<sub>3</sub>(L<sub>4</sub>)Cl.** L<sub>4</sub> (135 mg, 0.3 mmol) reacted with Re(CO)<sub>5</sub>Cl (108 mg, 0.3 mmol) to afford *fac*-Re(CO)<sub>3</sub>(L<sub>4</sub>)Cl as a yellow solid (293 mg, yielded 67%). M.P: 285.3-285.5 °C. IR(KBr):  $\nu_{C=O}$ : 2021, 1926, 1894 cm<sup>-1</sup>. <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>)  $\delta$ (ppm): 9.563 (d, *J* = 4.80 Hz, 2H), 8.238 (d, *J* = 8.40 Hz, 4H), 8.133 (t, *J* = 5.4-12.6 Hz, 4H), 7.902 (d, *J* = 7.80 Hz, 4H), 3.946 (s, 6H). <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>)  $\delta$ (ppm): 198.16, 190.31, 166.26, 153.88, 149.81, 147.09, 140.31, 131.18, 130.81, 130.24, 128.51, 127.27, 126.14, 52.95. HRMS(ESI) (CHCl<sub>3</sub>, positive mode) *m/z* for C<sub>31</sub>H<sub>20</sub>ClN<sub>2</sub>O<sub>7</sub>Re[M+Na]<sup>+</sup>: calculated 777.0409, found 777.0395.

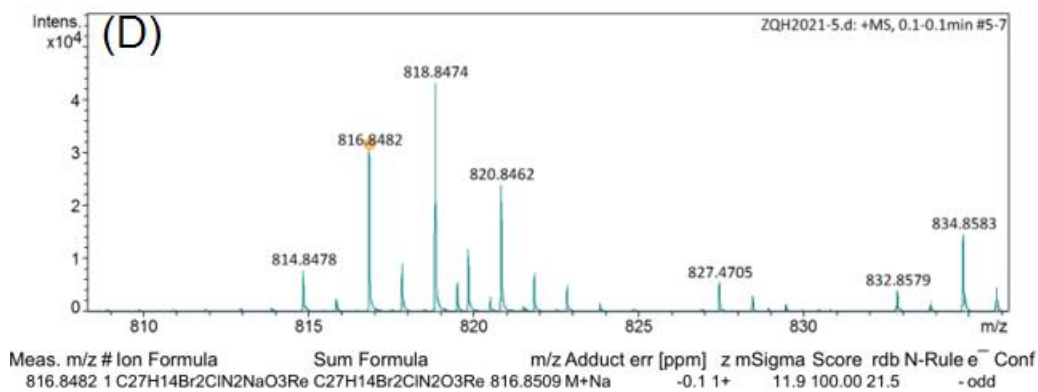
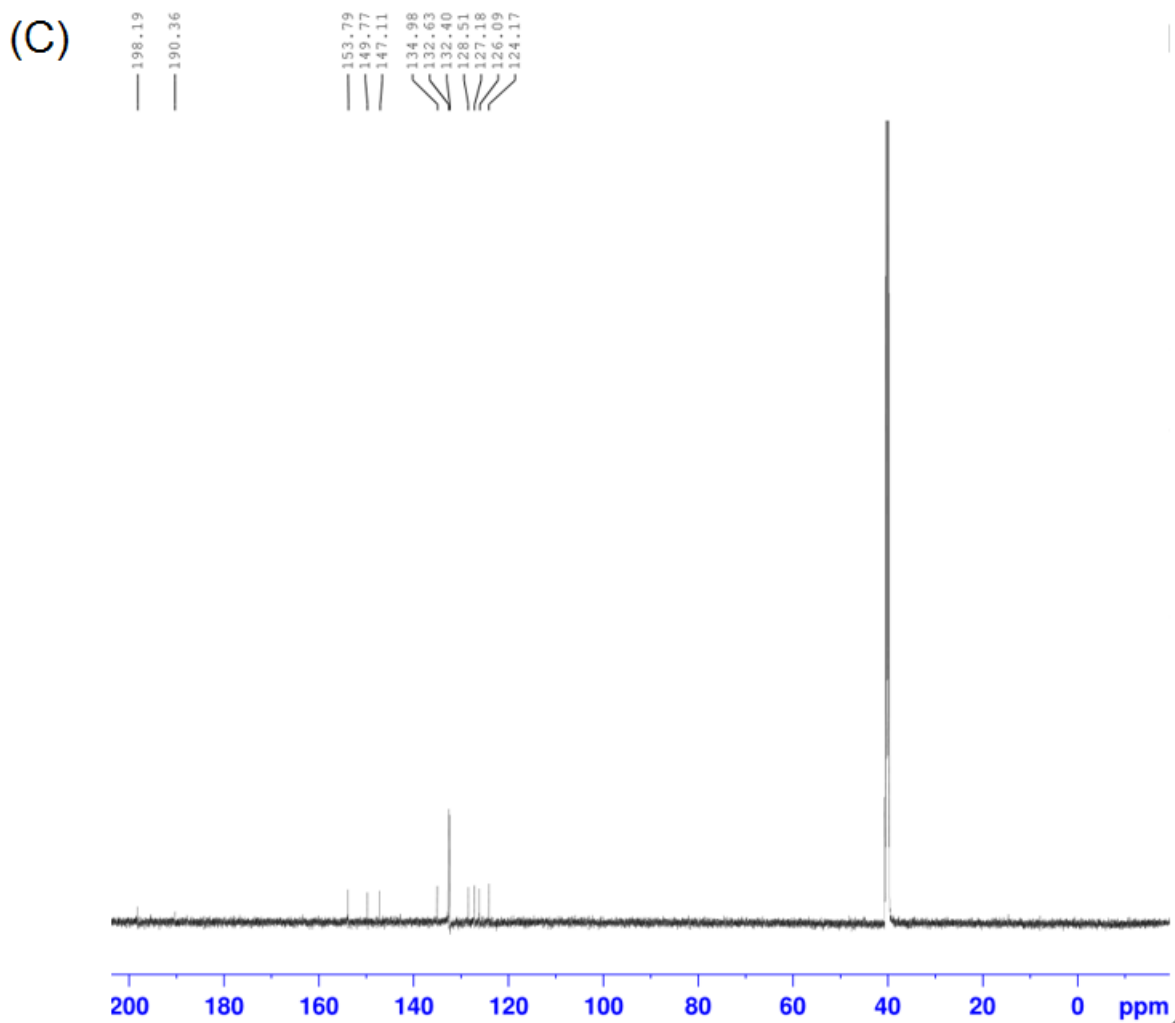




**Fig. S8.**  $^1\text{H}$  NMR of *fac*- $\text{Re}(\text{CO})_3(\text{L}_4)\text{Cl}$  in  $\text{DMSO}-d_6$  (A),  $^1\text{H}$  NMR comparison of  $\text{L}_4$  in  $\text{CDCl}_3$  and *fac*- $\text{Re}(\text{CO})_3(\text{L}_4)\text{Cl}$  in  $\text{DMSO}-d_6$  (B),  $^{13}\text{C}$  NMR (C) and HRMS (D) of *fac*- $\text{Re}(\text{CO})_3(\text{L}_4)\text{Cl}$ .

***Fac-Re(CO)<sub>3</sub>(L<sub>5</sub>)Cl.***  $\text{L}_5$  (294 mg, 0.6 mmol) reacted with  $\text{Re}(\text{CO})_5\text{Cl}$  (217 mg, 0.6 mmol) to give  $\text{Re}(\text{CO})_3(\text{L}_5)\text{Cl}$  as a yellow solid (420 mg, yielded 88%). M.P.:  $> 320$  °C. IR(KBr):  $\nu_{\text{C}=\text{O}}$  = 2017, 1920, 1882  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR(600 MHz,  $\text{DMSO}-d_6$ )  $\delta$ (ppm): 9.510 (t,  $J$  = 3.60 Hz, 2H); 8.128 (s, 2H); 8.082 (t,  $J$  = 1.20 Hz, 2H); 7.896 (d,  $J$  = 6.60 Hz, 4H); 7.696 (d,  $J$  = 6.60 Hz, 4H).  $^{13}\text{C}$  NMR (150MHz,  $\text{DMSO}-d_6$ )  $\delta$ (ppm): 198.19, 190.36, 153.79, 149.77, 147.11, 134.98, 132.63, 132.40, 128.51, 127.18, 126.09, 124.17. HRMS(ESI)( $\text{CHCl}_3$ , positive mode) m/z for  $\text{C}_{27}\text{H}_{14}\text{Br}_2\text{ClN}_2\text{O}_3\text{Re}$   $[\text{M}+\text{Na}]^+$ : calculated 816.8509, found 816.8482.





**Fig. S9.**  $^1\text{H}$  NMR of *fac*- $\text{Re}(\text{CO})_3(\text{L}_5)\text{Cl}$  in  $\text{DMSO}-d_6$  (A),  $^1\text{H}$  NMR comparison of  $\text{L}_5$  in  $\text{CDCl}_3$  and *fac*- $\text{Re}(\text{CO})_3(\text{L}_5)\text{Cl}$  in  $\text{DMSO}-d_6$  (B),  $^{13}\text{C}$  NMR (C) and HRMS (D) of *fac*- $\text{Re}(\text{CO})_3(\text{L}_5)\text{Cl}$ .

## 4. Crystal data and structure refinement

**Table S1** Crystal data and structure refinement for *fac*-Re(CO)<sub>3</sub>(L<sub>4</sub>)Cl

Compound	<i>fac</i> -Re(CO) <sub>3</sub> (L <sub>4</sub> )Cl
Formula	C <sub>31</sub> H <sub>20</sub> ClN <sub>2</sub> O <sub>7</sub> Re
Formula weight	754.14
Temperature/K	287.64(16)
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /m
a/Å	9.5221(4)
b/Å	20.0965(7)
c/Å	16.7407(5)
α/°	90
β/°	105.965(4)
γ/°	90
Volume/Å <sup>3</sup>	3080.0(2)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.626
μ/mm <sup>-1</sup>	4.080
F (000)	1472.0
Crystal size/mm <sup>3</sup>	0.2 × 0.2 × 0.02
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	6.99 to 58.322
Index ranges	-12 ≤ h ≤ 10, -26 ≤ k ≤ 25, -12 ≤ l ≤ 22
Reflections collected	18864
Independent reflections	7336 [R <sub>int</sub> = 0.0316, R <sub>sigma</sub> = 0.0471]
Data/restraints/parameters	7336/1/400
Goodness-of-fit on F <sup>2</sup>	1.026
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0440, wR <sub>2</sub> = 0.0949
Final R indexes [all data]	R <sub>1</sub> = 0.0696, wR <sub>2</sub> = 0.1039
Largest diff. peak/hole / e Å <sup>-3</sup>	1.22/-0.96
CCDC	2092640

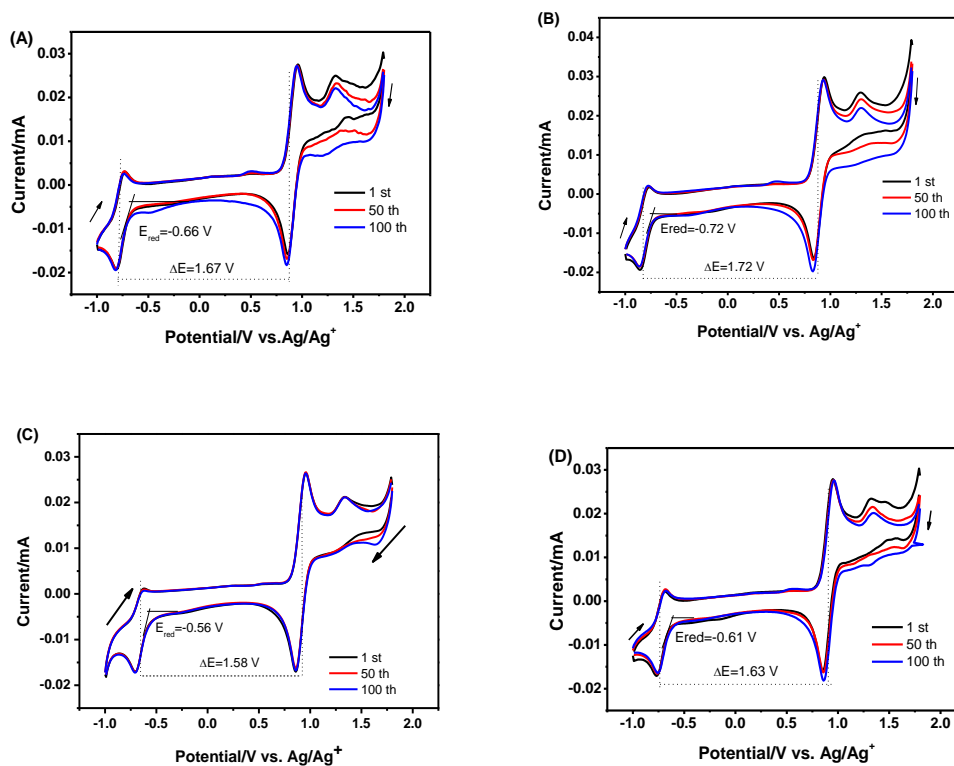
**Table S2** Selected length (Å) for *fac*-Re(CO)<sub>3</sub>(L<sub>4</sub>)Cl of the asymmetric unit. The atoms were numbered like on the molecular views.

Atoms	Length/Å
Re1-Cl1	2.464(2)
Re1-N1	2.179(4)
Re1-C1	1.884(9)
Re1-C2	1.936(6)
O1-C1	1.112(6)
O2-C2	1.113(6)
O3-C15	1.218(7)
O4-C15	1.328(8)
O4-C16	1.453(7)
N1-C3	1.350(6)
N1-C8	1.315(6)

**Table S3** Selected Angles (°) for *fac*-Re(CO)<sub>3</sub>(L<sub>4</sub>)Cl of the asymmetric unit. The atoms were numbered like on the molecular views.

Atoms	Angles(°)
N1-Re1-Cl1	82.41(11)
N1-Re1-N1	75.1(2)
C1-Re1-Cl1	174.5(3)
C1-Re1-N1	93.3(3)
C2-Re1-Cl	94.20(19)
C2-Re1-N1	172.9(2)
C2-Re1-N1 <sup>1</sup>	98.3(2)
C2-Re1-C2 <sup>1</sup>	88.2(4)
C3-N1-Re1	115.3(3)
C8-N1-Re1	126.4(3)
O1-C1-Re1	178.6(11)
O2-C2-Re1	178.7(6)

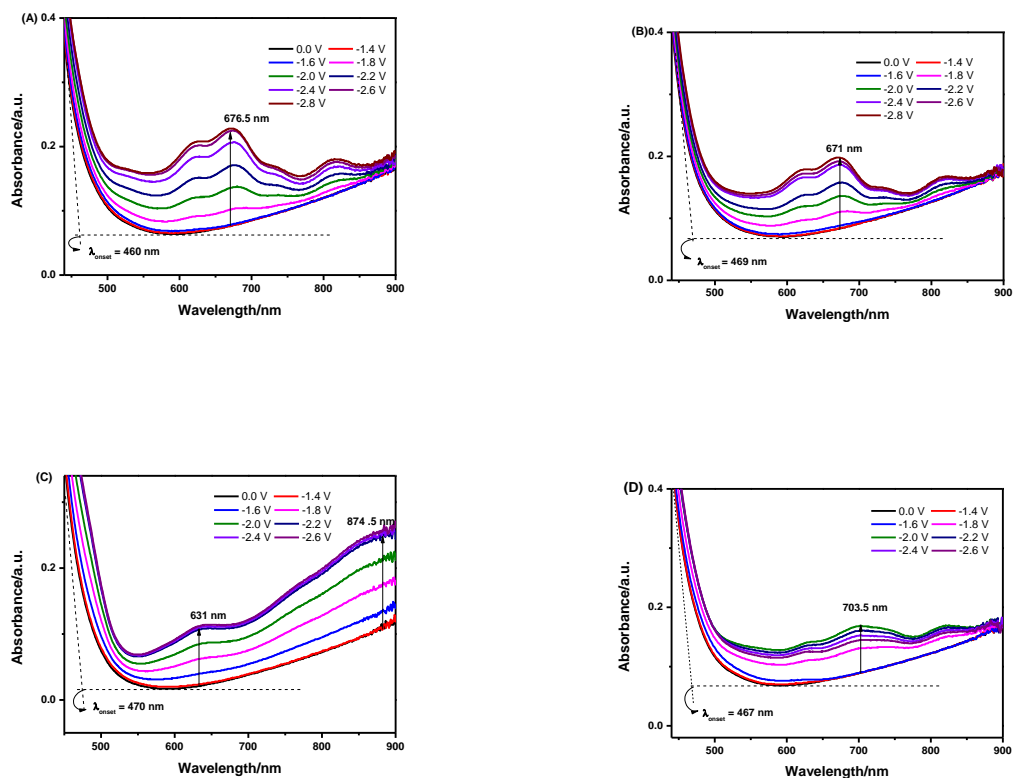
## 5. Cyclic voltammetry



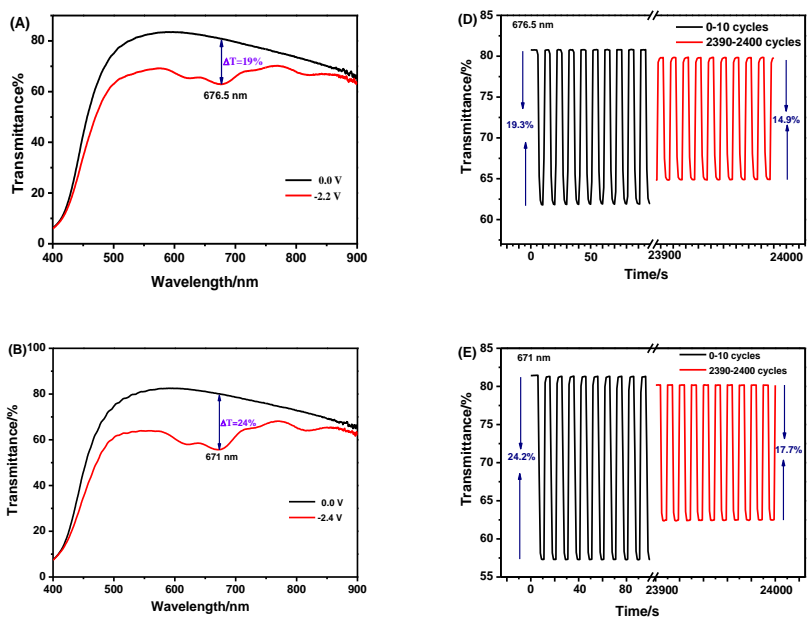
**Fig. S10.** Cyclic voltammograms of rhenium(I) complexes (0.5 mmol/L) in NMP under a nitrogen atmosphere at a scanning rate of 100 mV/s after 100 successive cycles for *fac*-Re(CO)<sub>3</sub>(L<sub>1</sub>)Cl (A), *fac*-Re(CO)<sub>3</sub>(L<sub>3</sub>)Cl (B), *fac*-Re(CO)<sub>3</sub>(L<sub>4</sub>)Cl (C) and *fac*-Re(CO)<sub>3</sub>(L<sub>5</sub>)Cl (D).

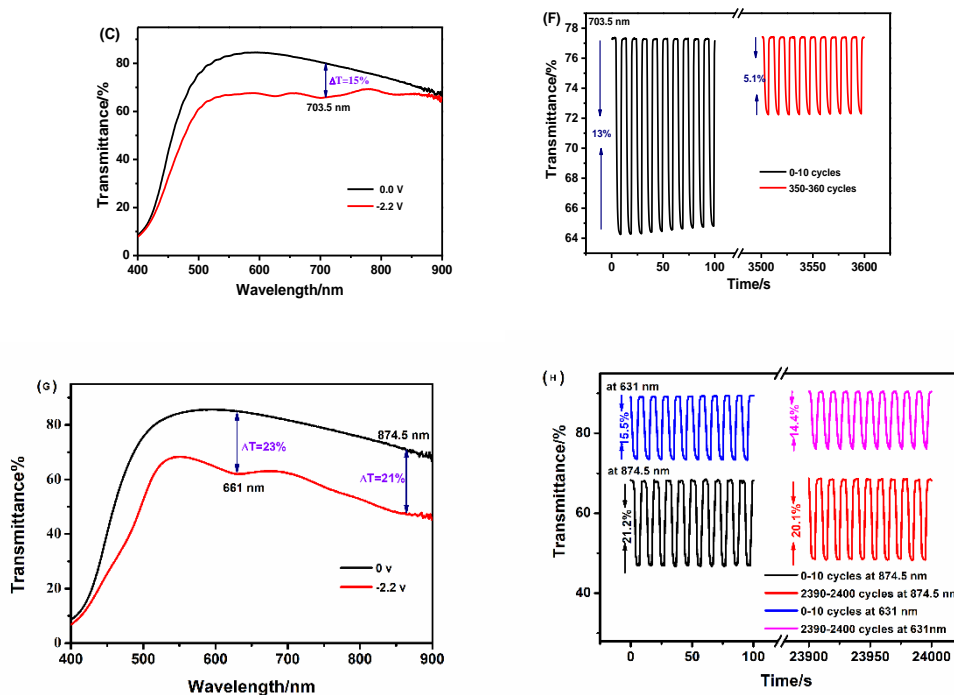


## 6. Electrochromic investigation

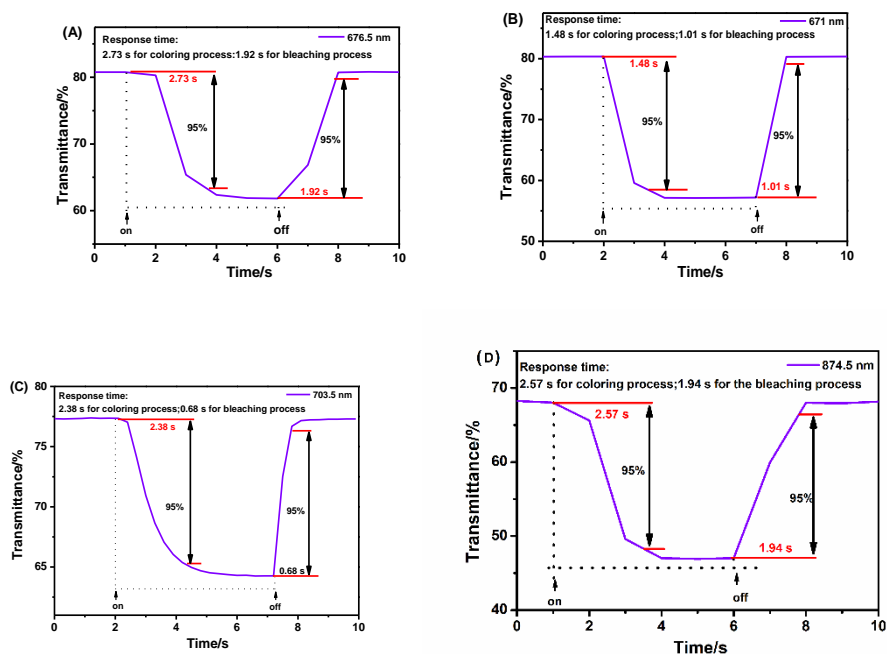


**Fig. S11.** UV-vis absorption spectra of ECDs based on  $fac\text{-Re}(\text{CO})_3(\text{L}_1)\text{Cl}$  (A), and  $fac\text{-Re}(\text{CO})_3(\text{L}_3)\text{Cl}$  (B) and  $fac\text{-Re}(\text{CO})_3(\text{L}_4)\text{Cl}$  (C) and  $fac\text{-Re}(\text{CO})_3(\text{L}_5)\text{Cl}$  (D) with concentration of 25 mmol/L at different applied potentials.

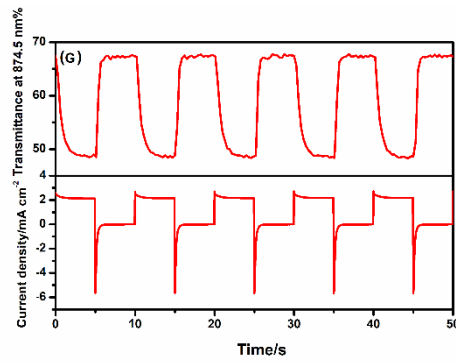
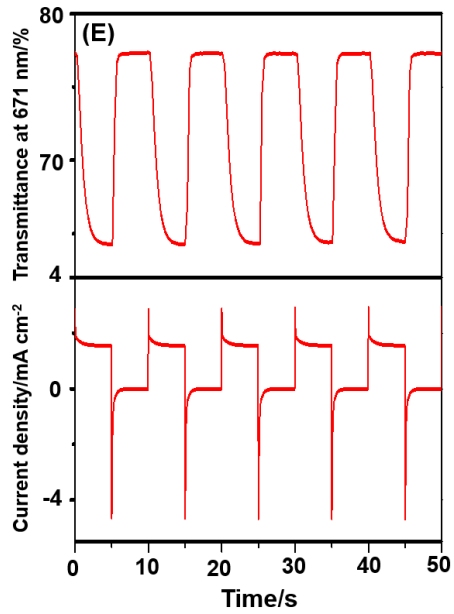
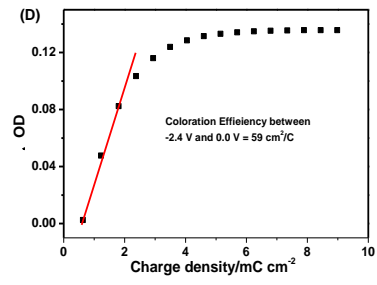
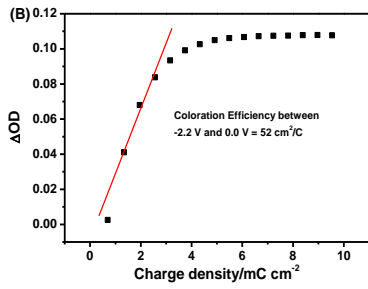
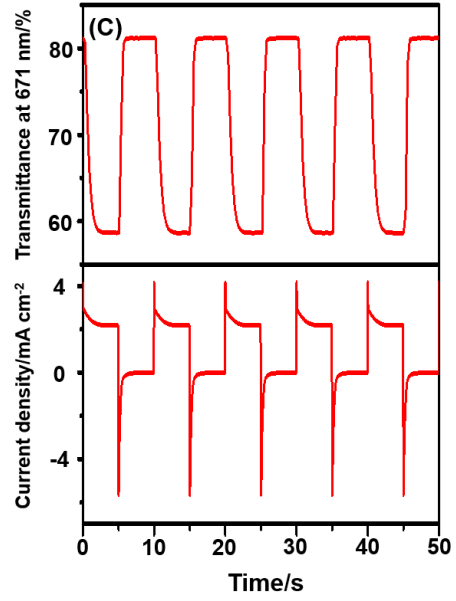
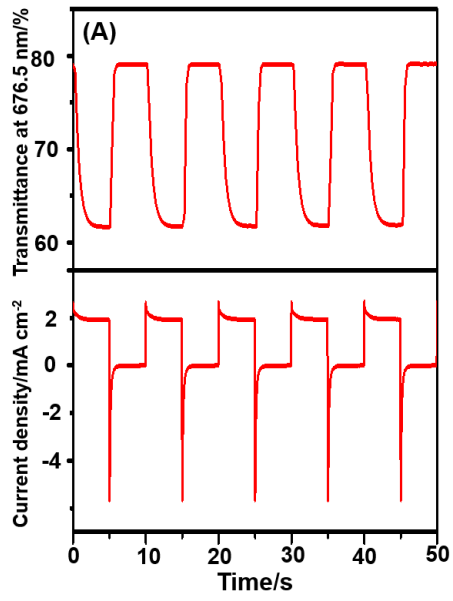


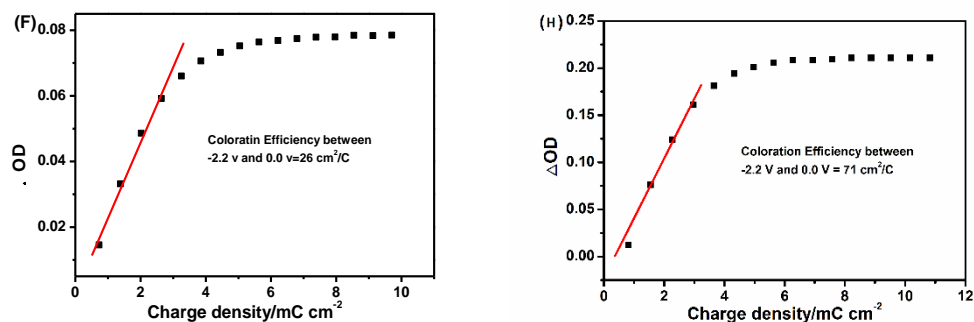


**Fig. S12.** Transmittance spectra of the ECDs based on *fac*-Re(CO)<sub>3</sub>(L<sub>1</sub>)Cl (A), *fac*-Re(CO)<sub>3</sub>(L<sub>3</sub>)Cl (B), *fac*-Re(CO)<sub>3</sub>(L<sub>5</sub>)Cl (C) and *fac*-Re(CO)<sub>3</sub>(L<sub>4</sub>)Cl (G) and in bleached state (black) and colored state (red). Electrochromic switching of the ECDs monitored at 676.5 nm for *fac*-Re(CO)<sub>3</sub>(L<sub>1</sub>)Cl (D), at 671 nm for *fac*-Re(CO)<sub>3</sub>(L<sub>3</sub>)Cl (E), at 703.5 nm for *fac*-Re(CO)<sub>3</sub>(L<sub>5</sub>)Cl (F), and at 663 nm and 874.5 nm between 0.0 and -2.2 V (H).



**Fig. S13.** Response time of ECDs based on *fac*-Re(CO)<sub>3</sub>(L<sub>1</sub>)Cl monitored at 676.5 nm between 0.0 and -2.2 V (A), *fac*-Re(CO)<sub>3</sub>(L<sub>3</sub>)Cl monitored at 671 nm between 0.0 and -2.4 V (B), *fac*-Re(CO)<sub>3</sub>(L<sub>5</sub>)Cl monitored at 703.5 nm between 0.0 and -2.2 V (C), and *fac*-Re(CO)<sub>3</sub>(L<sub>4</sub>)Cl monitored at 874.5 nm between 0.0 and -2.2 V (D).





**Fig. S14.** Chronoamperometry curves and the corresponding in-situ transmittance curves and optical density versus charge density of the ECDs based on *fac*-Re(CO)<sub>3</sub>(L<sub>1</sub>)Cl monitored at 676.5 nm between 0.0 and -2.2 V (A and B), *fac*-Re(CO)<sub>3</sub>(L<sub>3</sub>)Cl monitored at 671 nm between 0.0 and -2.4 V (B and D), *fac*-Re(CO)<sub>3</sub>(L<sub>5</sub>)Cl monitored at 703.5 nm between 0.0 and -2.2 V (E and F), and *fac*-Re(CO)<sub>3</sub>(L<sub>4</sub>)Cl monitored at 874.5 nm between 0.0 and -2.2 V (G and H).

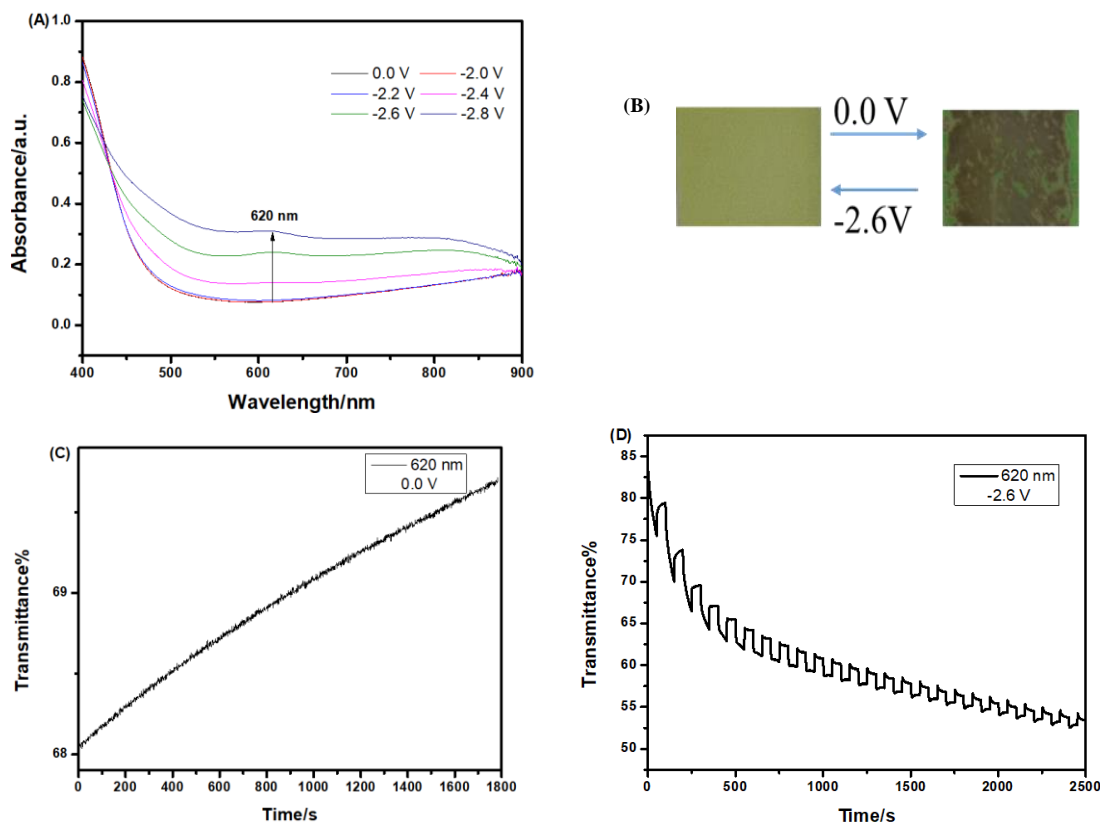
## 7. CIE L\*a\*b\* coordinate values

**Table S4** CIE L\*a\*b\* coordinate values for the ECDs based on *fac*-Re(CO)<sub>3</sub>(L<sub>x</sub>)Cl.

Complexes	L*a*b* (Bleached state)	L*a*b* (Bleached state)
<i>fac</i> -Re(CO) <sub>3</sub> (L <sub>1</sub> )Cl	46.4*8.4* 4.5*	37.2* -8.8* -2.6*
<i>fac</i> -Re(CO) <sub>3</sub> (L <sub>2</sub> )Cl	45.9*9.1* 2.2*	31.2* -9.5* -0.6*
<i>fac</i> -Re(CO) <sub>3</sub> (L <sub>3</sub> )Cl	46.8*8.8* 4.6*	34.4* -9.8* -2.4*
<i>fac</i> -Re(CO) <sub>3</sub> (L <sub>4</sub> )Cl	43.3*9.0* 4.7*	35.5* -7.9* 1.3*
<i>fac</i> -Re(CO) <sub>3</sub> (L <sub>5</sub> )Cl	46.9*9.2* 2.7*	37.2* -8.3* 1.5*

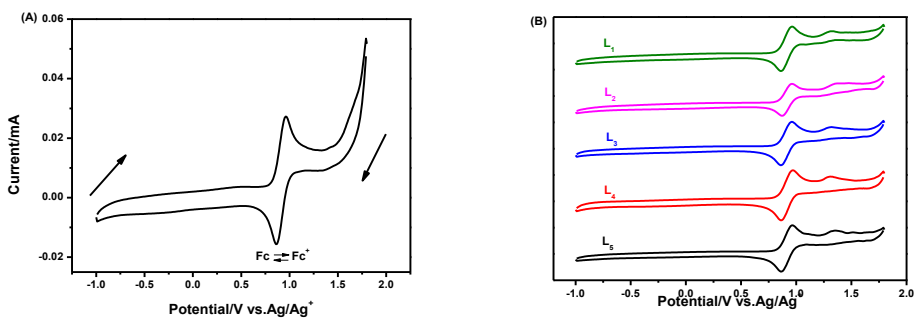
## 8. Solid-state electrochromic devices

Fabrication all-solid-state electrochromic devices: A transparent gel electrolyte was obtained by mixing polymethyl methacrylate (PMMA, M<sub>w</sub>: 120,000, 0.7 g), TBAP (0.8 g) and propylene carbonate (PC, 3.0 g) in dry acetonitrile (2 mL). *Fac*-Re(CO)<sub>3</sub>(L<sub>4</sub>)Cl(50 mmol/L) is added into mixture. The mixture was stirred rapidly at 50 °C until a gelation occurred. The mixture was coated on a new ITO-coated glass by a pulling method. Put another ITO, then the above two ITO glasses were bonded together and dried in a vacuum oven at 80 °C for 12 h to obtain all-solid-state electrochromic device.

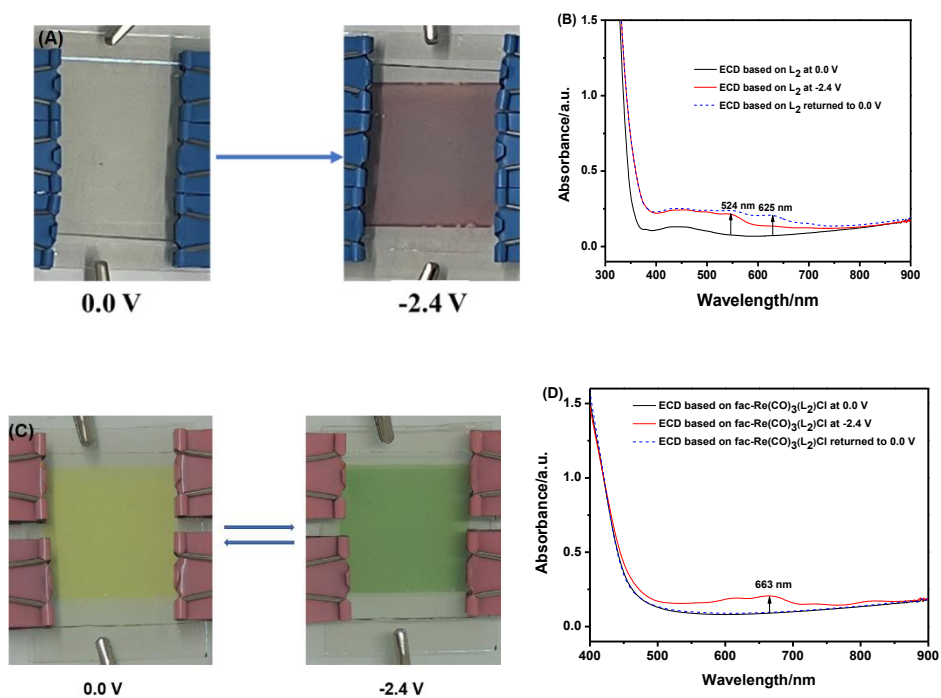


**Fig. S15.** UV-vis absorption spectra of solid-state-ECDs based on  $fac\text{-Re}(\text{CO})_3(\text{L}_4)\text{Cl}$  (A) at different applied potentials. (B) Photographs of solid-state-ECDs containing  $fac\text{-Re}(\text{CO})_3(\text{L}_4)\text{Cl}$  in its bleached and colored states. (C) Transmittance vs. time curve when no applied voltage is applied after the solid-state-ECDs is colored. And electrochromic switching of the ECDs based on  $fac\text{-Re}(\text{CO})_3(\text{L}_4)\text{Cl}$  monitored at 620 nm between 0.0 and -2.6 V (D)

## 9. Cyclic voltammetry and UV-vis absorption spectra



**Fig. S16.** Cyclic voltammograms of  $\text{Re}(\text{CO})_5\text{Cl}$  (A) and ligand  $\text{L}_1\text{-L}_5$  (B) (0.5 mmol/L) in NMP under a nitrogen atmosphere at a scanning rate of 100 mV/s.



**Fig. S17.** Photograph of the ECD based on  $L_2$  (A) and  $fac-Re(CO)_3(L_2)Cl$  (C) at an applied potential of 0.0 V, -2.4 V and returned to 0.0 V (C). UV-Vis absorption spectra of  $L_2$  (B) and  $fac-Re(CO)_3(L_2)Cl$  (D) at an applied potential of 0.0 V, -2.4 V and returned to 0.0 V.