

Supporting Information

Catalytic Copolymerization of Carbon Dioxide and Cyclohexene Oxide by a Trinuclear Cyclohexane-bridged Tetradentate Schiff Base Chromium Complex

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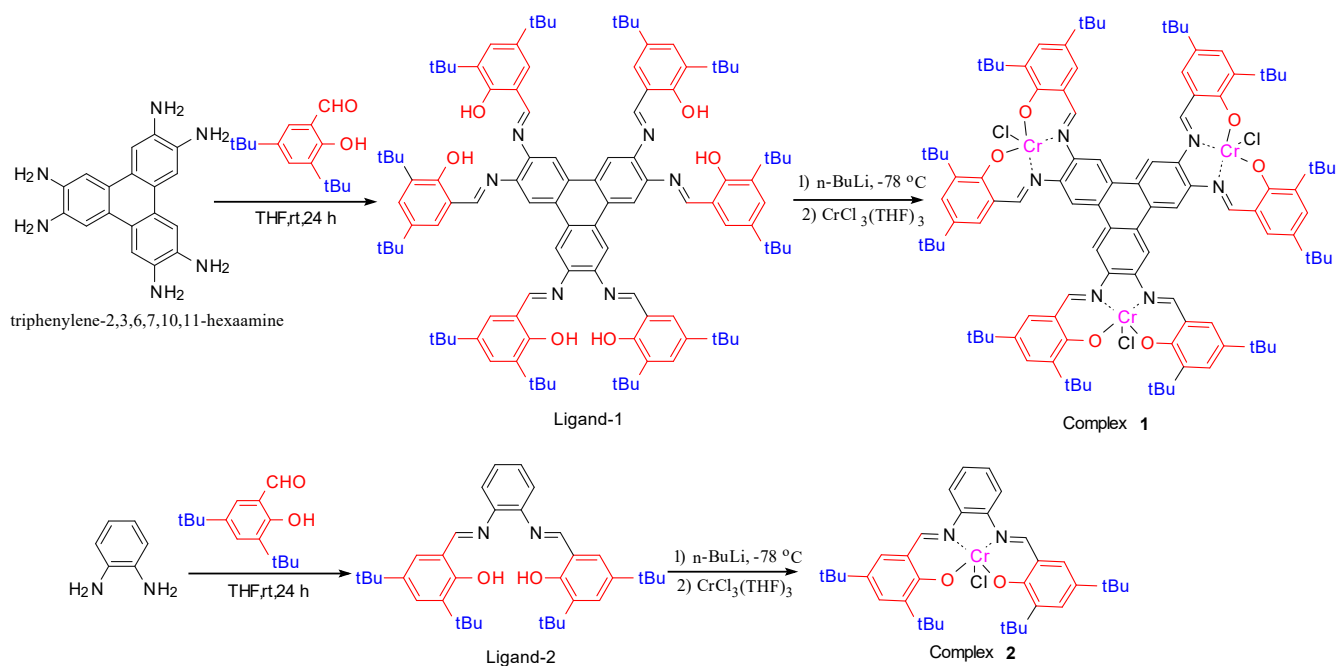
1. General Materials

All operations involving air- and moisture-sensitive compounds were performed under an argon atmosphere using standard Schlenk and vacuum line techniques. Chromium chloride tetrahydrofuran adduct ($\text{CrCl}_3 \cdot 3\text{THF}$) (AR) was purchased from Beijing Bailingwei Technology Co., Ltd. o-Phenylenediamine (AR) was obtained from Tianjin Kermel Chemical Reagent Co., Ltd. Triphenyl-2,3,6,7,10,11-hexylamine (AR) was sourced from Beijing Bailingwei Technology Co., Ltd. 3,5-Di-tert-butyl-2-hydroxybenzaldehyde (AR) was acquired from Shanghai Haichu Chemical. Bis(triphenylphosphine)iminium chloride (PPNCl) (99%) was purified three times by dissolving in acetone and precipitating with excess diethyl ether, followed by vacuum drying (Tianjin Heowns Biochemical Technology Co., Ltd.). Tetrabutylammonium chloride (TBACl) was recrystallized from ethanol before use. Calcium hydride (98%) was purchased from Sinopharm Chemical Reagent Co., Ltd. Epoxides were refluxed over calcium hydride and distilled under a nitrogen atmosphere. Toluene and tetrahydrofuran (THF) were refluxed and distilled from sodium/benzophenone under dry nitrogen. Triethylamine was distilled over calcium hydride (CaH_2). n-Butyllithium (n-BuLi) (2.5M in hexane) was obtained from Beijing Bailingwei Technology Co., Ltd. Anhydrous sodium sulfate was sourced from Beijing Yanfeng Chemical Co., Ltd. Carbon dioxide (99.99%) was supplied by Tianjin Sizhida Gas Co., Ltd.

2. Characterization

^1H and ^{13}C NMR spectra were recorded on a Bruker-300 spectrometer at frequencies of 300 MHz (^1H) and 100 MHz (^{13}C), respectively. All chemical shifts are reported in parts per million (ppm) using tetramethylsilane (TMS) as an internal reference at ambient temperature. Infrared spectra were obtained on a Bruker Vector 22 spectrometer at a resolution of 4 cm^{-1} , with 16 scans collected. High-pressure reaction kinetics were measured using an ASI React IR 1000 system, which features a stainless steel Parr high-pressure reactor modified with a permanently installed ATR crystal (SiComp) at the bottom of the reactor. UV-visible spectra were recorded in CH_2Cl_2 on a UV-CARY300 spectrometer. Molecular weight determinations were performed using a PL-GPC 220 instrument equipped with a refractive index detector. The column used was a MIXED-B 300×7.5 mm, maintained at 35°C , with THF as the eluent at a flow rate of 1.0 mL/min. ESI-MS was conducted in ESI mode on a Thermo Finnigan LCQ Advantage spectrometer, with a spray voltage of 4.8 kV, a spray current of $0.24\ \mu\text{A}$, and a capillary temperature of 230°C .

3. Synthesis of complex 1 and complex 2



Scheme S1 Synthetic routes to the complex **1** and complex **2**

The synthetic pathways for complex **1** and complex **2** are illustrated in Scheme S1. Under a nitrogen (N_2) atmosphere, 5 mmol of triphenyl-2,3,6,7,10,11-hexylamine was added to a three-necked flask containing 100 mL of anhydrous ethanol. The mixture was heated and refluxed for several minutes until the triphenyl-2,3,6,7,10,11-hexylamine was completely dissolved. Then, 33 mmol of 3,5-ditert-butyl-2-hydroxybenzaldehyde in anhydrous ethanol was added dropwise to the three-necked flask, and the mixture was heated and stirred under reflux for 12 hours. After the reaction was complete, heating was stopped, and the solution was cooled to room temperature. The reaction mixture was then transferred to a large beaker and allowed to stand. A large amount of yellow solid precipitated and was then filtered and washed three times with anhydrous ethanol. The product was vacuum dried at 60°C for 12 hours, yielding yellow solid of Ligand-1 with a yield of 70%. EA (%) $C_{108}H_{138}N_6O_6$: calc. N 5.20, H 8.61, C 80.26; found N 5.21, H 8.66, C 80.29. ^1H NMR (300 MHz, CDCl_3) δ (ppm): 8.73 (s, 6H, NCH), 7.52 - 8.63 (m, 6H, ArH), 7.43 - 7.51 (m, 6H, ArH), 7.55 - 7.41 (m, 6H, ArH), 0.97 - 1.58 (m, 108H, $\text{C}(\text{CH}_3)_3$). ^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 165.08 (s, $\text{C}=\text{N}$), 158.15 (s, Ar-C), 142.01 (s, C-N), 141.02 (s, COH), 138.05 (s, Ar-C), 129.01 (s, CH), 128.32 (s, CH), 127.08 (s, CH), 119.73 (s, CH), 119.09 (s, Ar-C), 36.14 (s, $\text{C}(\text{CH}_3)_3$), 35.18 (s, CH_3), 31.49 (s, CH_3), 29.35 (s, $\text{C}(\text{CH}_3)_3$). ESI-MS (m/z): $[\text{M}+\text{H}]^+$: 1616.07,

Found: 1616.2341.

Under a nitrogen (N₂) atmosphere, 2 mmol of Ligand-1 was added. After three argon purges, 40 mL of dry tetrahydrofuran (THF) was added. The system was cooled to -78°C using an acetone-liquid nitrogen bath, turning the solution from yellow to colorless. Then, 12.6 mmol of n-butyllithium in hexane was added dropwise. After the addition was complete, the system was warmed to 25°C and stirred for 30 minutes. In a glove box, 6.6 mmol of CrCl₃(THF)₃ was measured into another three-necked flask, and 40 mL of dry THF was added and stirred. The ligand solution was then added dropwise to the metal THF suspension, turning the solution from purple to dark green. Stirring was continued for 24 hours. The solvent was removed under vacuum, and the residual solid was dissolved in dry dichloromethane. After filtering out the insoluble material, the filtrate was evaporated to dryness, yielding a dark green solid of complex **1** with a yield of 85%. EA (%) C₁₀₈H₁₃₂Cl₃Cr₃N₆O₆: calc. N, 4.49; H, 7.11; C, 69.27; found N 4.47, H 7.19, C 69.38. ESI-MS (m/z): [M+H]⁺: 1870.75, Found: 1870.8321.

The synthesis of Ligand-2 was performed according to the reported procedure ^[19]. The synthesis of Ligand-2 is similar to that of Ligand-1, with triphenyl-2,3,6,7,10,11-hexylamine being replaced by o-phenylenediamine, yielding an orange solid of Ligand-2 with a yield of 75%. EA (%) C₃₆H₄₈N₂O₂: calc. N, 5.18; H, 8.95; C, 79.96; found N 5.21, H 8.97, C 79.98. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 8.67 (s, 2H), 7.45 (d, 2H), 7.31 (s, 4H), 7.21-7.25 (m, 2H), 1.45 (s, 18H), 1.33 (s, 18H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm): 165.63 (s, C=N), 158.37 (s, COH), 143.37 (s, Ar-C), 141.88 (s, Ar-C), 140.40 (d, CH), 139.23 (s, Ar-C), 137.21 (s, Ar-C), 126.82 (d, CH), 125.56 (s, CH), 120.17 (s, Ar-C), 119.25–117.95 (m, CH), 77.26–76.62 (t, CDCl₃), 35.08 (s, C(CH₃)₃), 34.13 (s, CH₃), 31.41 (s, CH₃), 29.39 (s, C(CH₃)₃). ESI-MS (m/z): [M+H]⁺: 541.37, Found: 542.1627.

The synthesis of complex **2** is similar to that of complex **1**, with ligand-1 being replaced by ligand-2, yielding a blackish-green solid of complex **2** with a yield of 90%. EA (%) C₃₆H₄₆ClCrN₂O₂: calc. N, 4.47; H, 7.40; C, 69.05; found N 4.49, H 7.42, C 69.16. ESI-MS (m/z): [M+H]⁺: 626.27, Found: 626.3815.

4. Copolymerization of Cyclohexene Oxide and Carbon Dioxide

The copolymerization reaction was conducted in a 100 mL stainless steel high-pressure reactor equipped with a magnetic stirrer, which had been vacuum-dried at 60°C for 2 hours.

Typically, the reactor was loaded with an appropriate amount of catalyst and epoxide, then pressurized with CO₂ to the desired pressure. The mixture was heated to the target temperature and stirred at approximately 200 rpm for the specified duration. After the reaction, the autoclave was cooled to room temperature, and the pressure was gradually released. The crude product was dissolved in CH₂Cl₂ and stirred to obtain a homogeneous solution. A small sample of this solution was analyzed using infrared spectroscopy to determine the selectivity of PCHC and CHC [1]. The remaining mixture was concentrated by rotary evaporation, then treated with methanol. The resulting precipitate was filtered and further purified twice by CH₂Cl₂/methanol treatment. The final isolated solid was vacuum-dried at 45°C overnight. The polymer was analyzed by NMR spectroscopy [2].

References

- [1] R. Mundil, Z. Host'alek, I. Sedenkova, J. Merna, *Macromol. Res.* 2015, 23, 161.
- [2] K. Bester, A. Bukowska, B. Mysliwiec, K. Hus, D. Tomczyk, P. Urbaniak, W. Bukowski, *Polym. Chem.* 2018, 9, 2147.

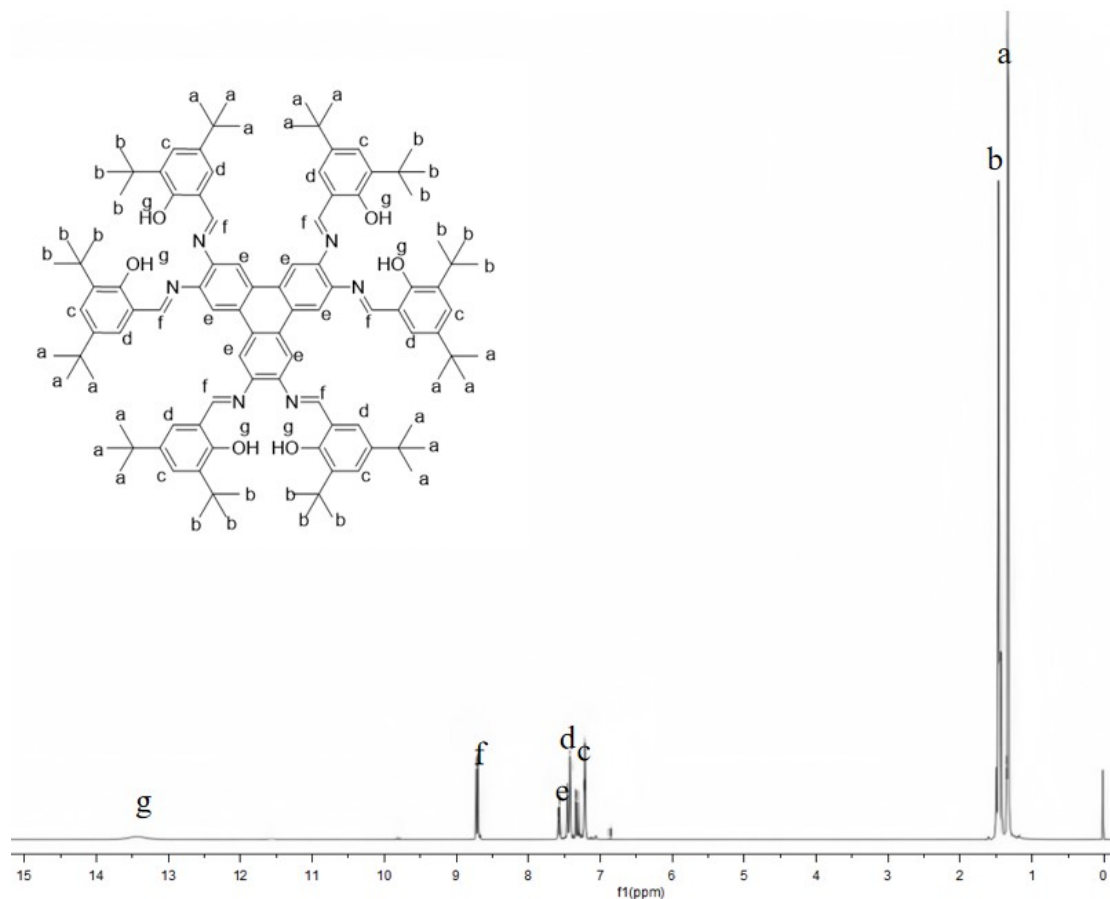


Figure S1 ¹H NMR Spectrum of Ligand-1

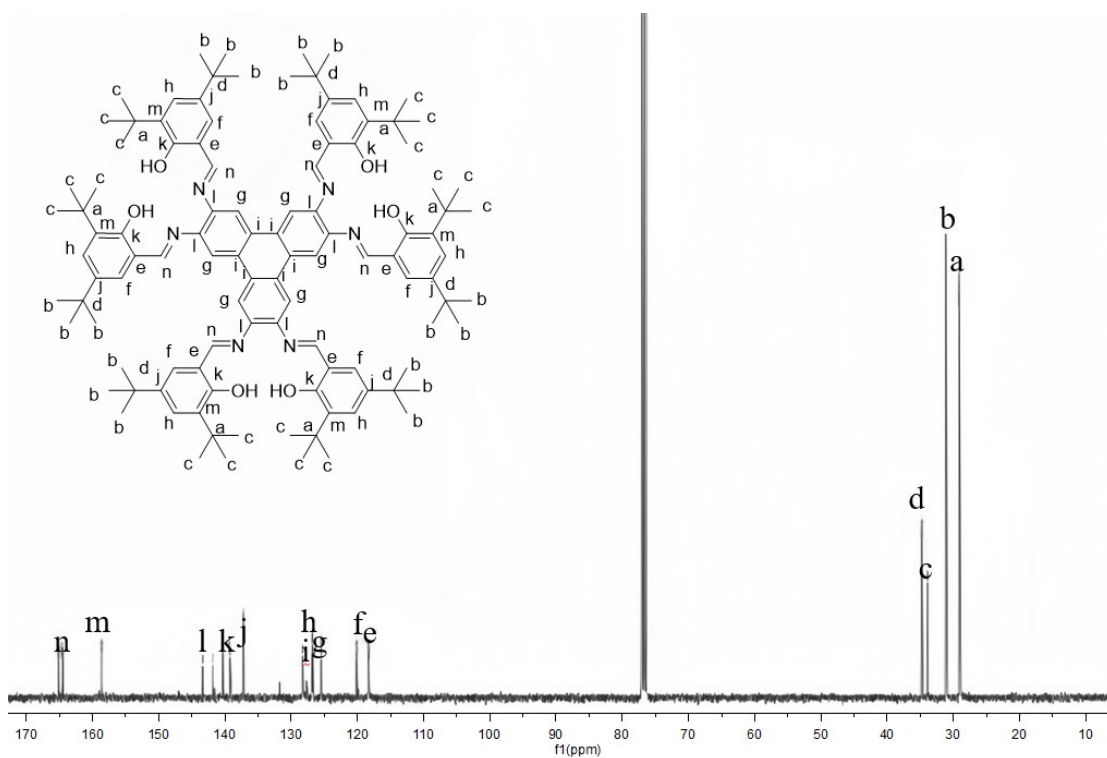


Figure S2 ¹³C NMR Spectrum of Ligand-1

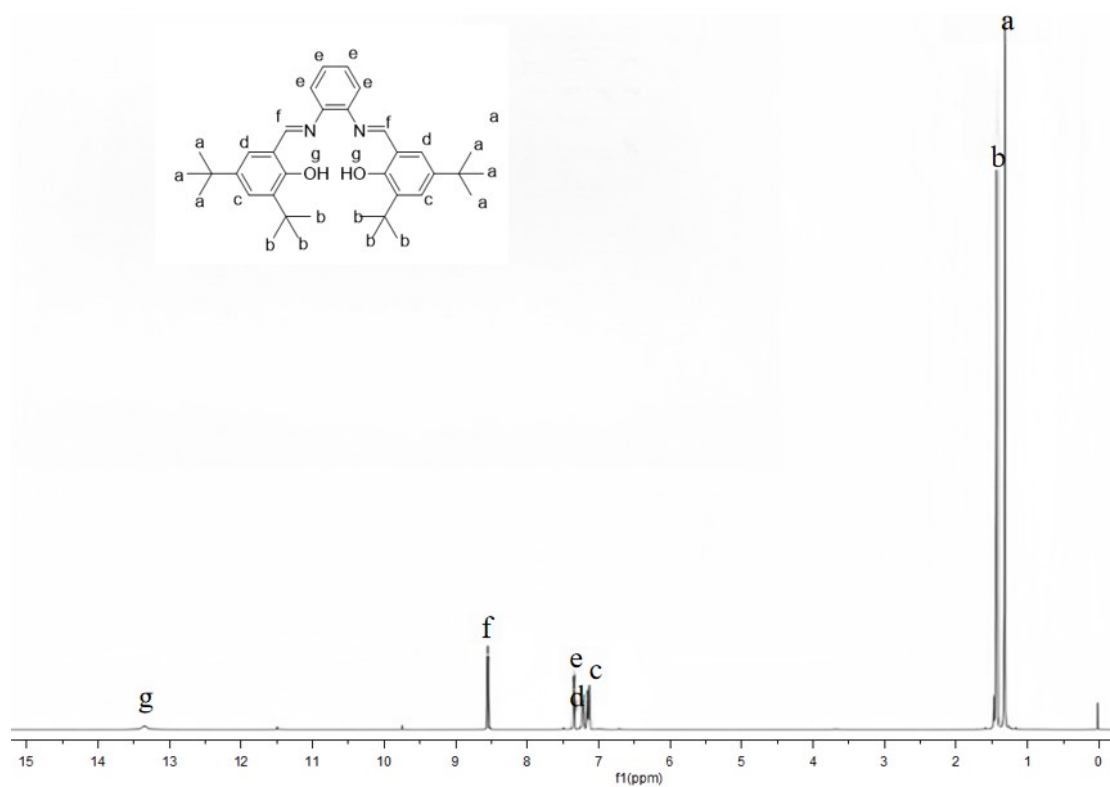


Figure S3 ¹H NMR Spectrum of Ligand-2

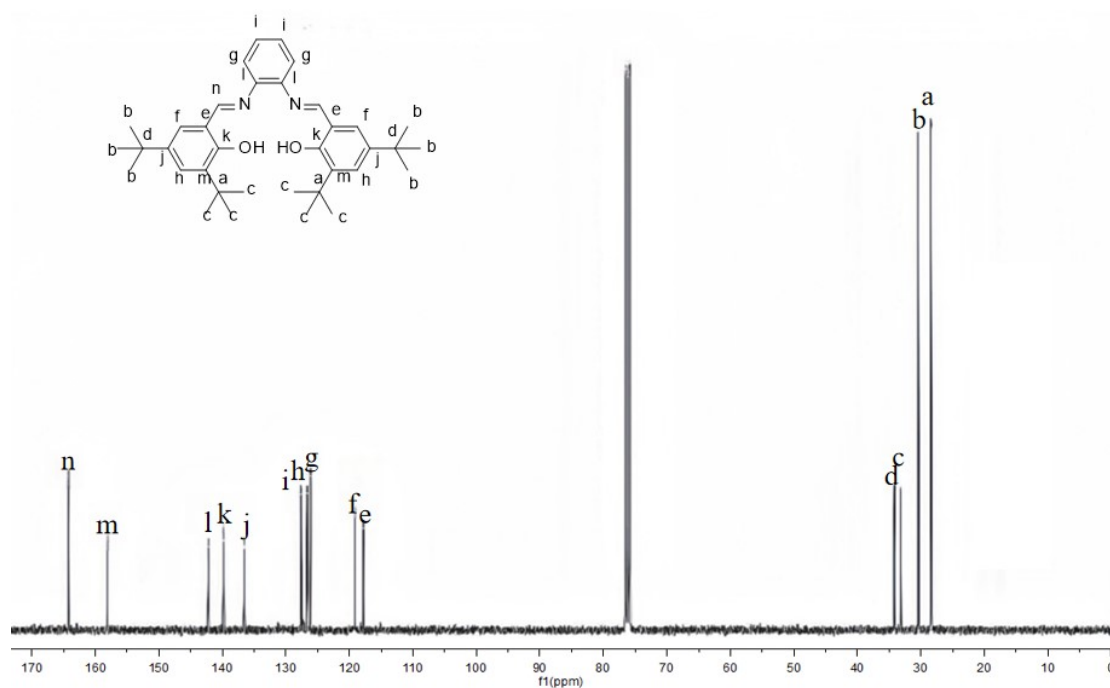


Figure S4 ¹³C NMR Spectrum of Ligand-2

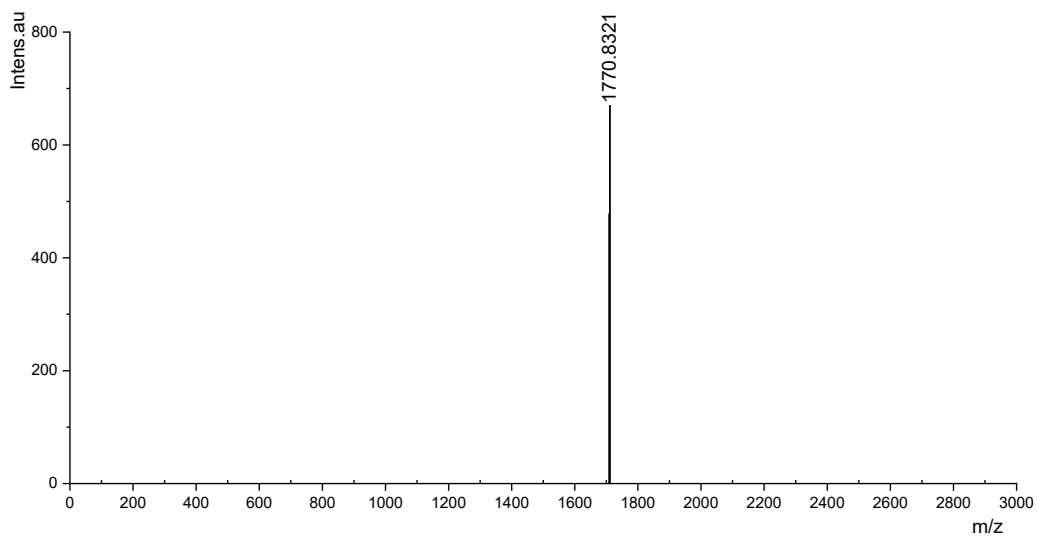


Figure S5 ESI-MS spectrum of complex 1

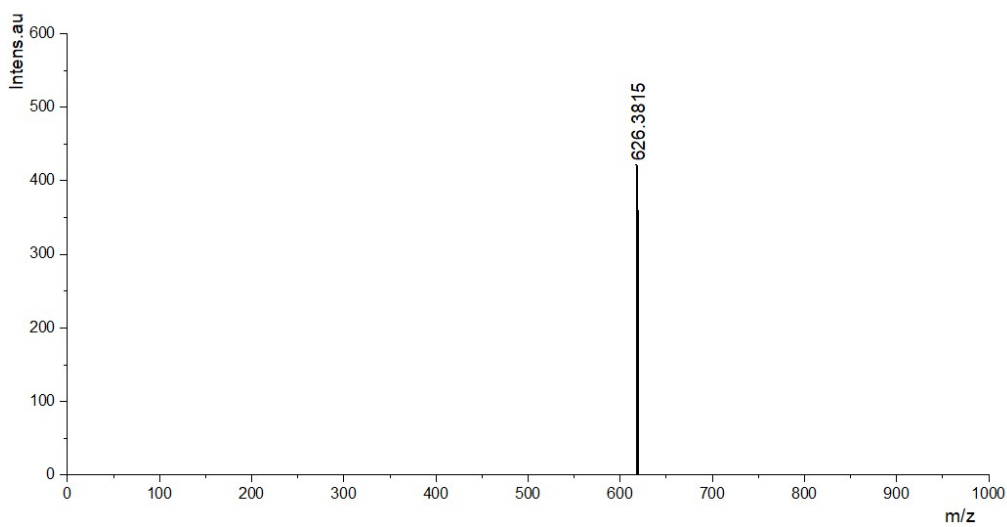
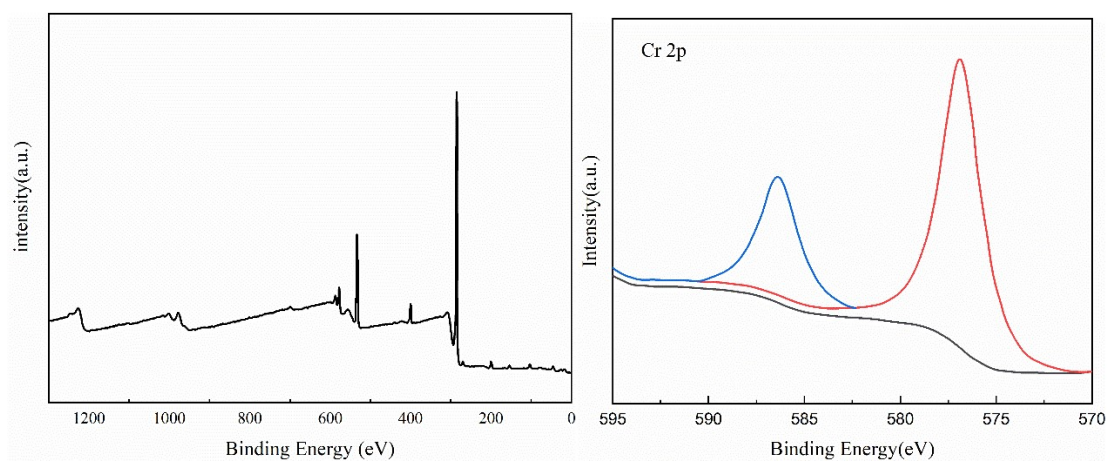


Figure S6 ESI-MS spectrum of complex 2



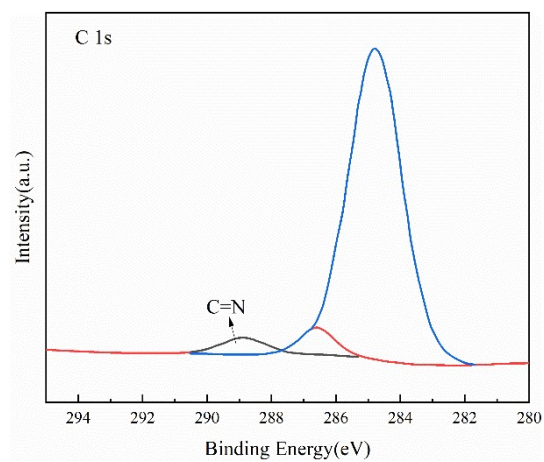


Figure S7 XPS spectrum of complex 1

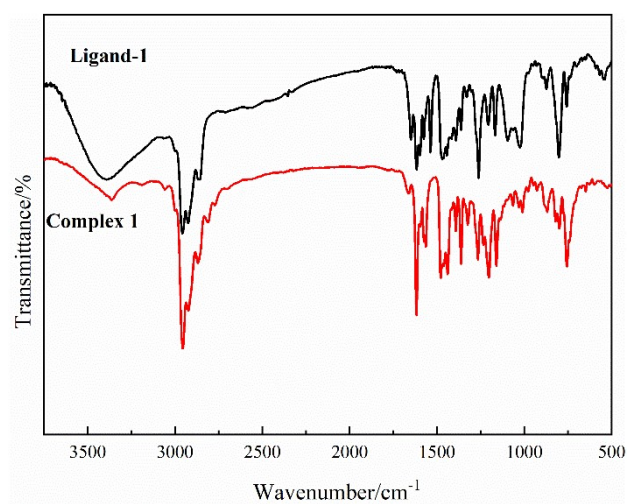


Figure S8 IR spectrum of complex 1

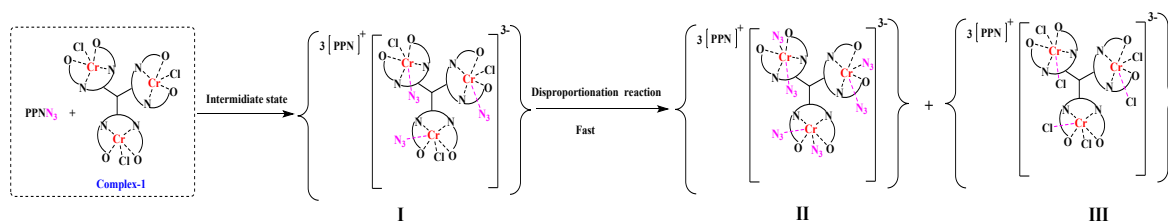


Figure S9 Proposed mechanism of interaction of complex 1/PPNN₃

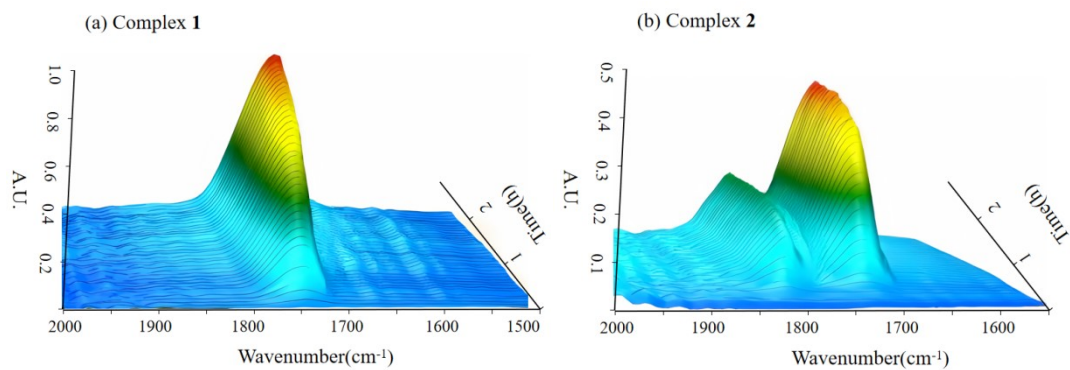


Figure S10 In-situ infrared spectra of the copolymerization reaction of CO₂ and CHO catalyzed by different metal complexes(a) complex 1, (b) complex 2

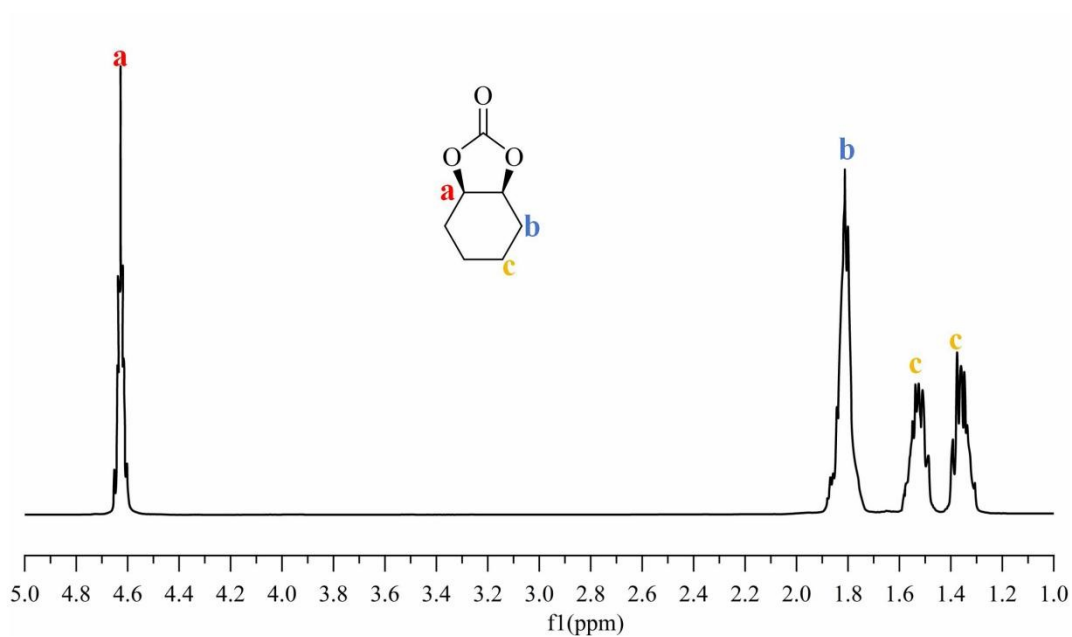
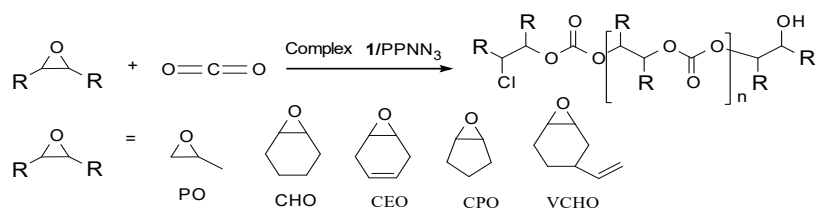


Figure S11 ¹H NMR spectrum of *cis*-cyclic cyclohexene carbonate (CHC) produced using complex 1 and PPNN₃ (entry 2 of table 1)

Table S1 Alternating copolymerization of various epoxides and CO₂ using complex **1** /PPNN₃^a

Entry	Epoxide	Conv(%) ^b	TOF(h ⁻¹) ^c	Selectivity(%) ^d	M _n ^e (g/mol)	D ^e
1	VCHO	70	525	88	14500	1.15
2	PO	96	720	0	-	-
3	CEO	46	345	75	7800	1.22
4	CPO	50	375	80	9200	1.38

^a Copolymerization conditions: 100 mmol epoxide, 80°C, 3MPa CO₂, 6 h, epoxide/cat/cocat= 4500/1/3 (Molar

ratio); ^c Turn over frequency (TOF) = the number of moles of epoxide converted to polycarbonate and cyclic carbonate per mole of complex per hour; ^d Polymer selectivity refers to the proportion of polycarbonate formed; ^e

Determined by GPC.