Electronic Supplementary Information

Synthesis, Structure and DFT Calculation of Bi- and Tridentate Ketiminate Ligands Assisted Aluminum Complexes: Potential Catalyst for Styrene Oxide-CO_2 Cycloaddition Reaction

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(a) (b)

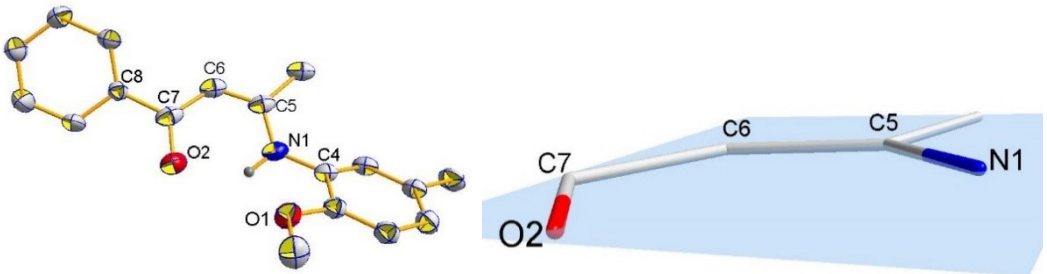

Figure S1. (a) The molecular geometry of ligand **L²H**. Thermal ellipsoids are drawn at 30% probability level. All the hydrogen atoms except the one on N(1) are omitted for clarity. (b) The ketiminate backbone showing the plane as O2-C7-C6-C5-N1

(a) (b)

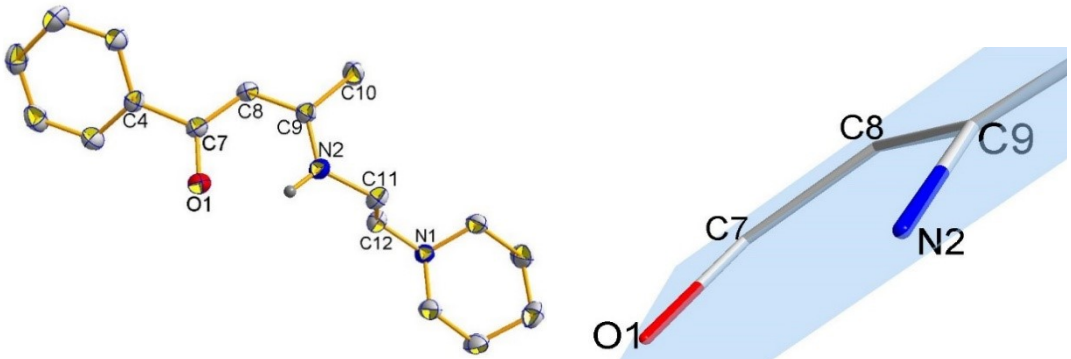

Figure S2. (a) The molecular geometry of ligand **L⁴H**. Thermal ellipsoids are drawn at 30% probability level. (b) The ketiminate backbone showing the plane as O1-C7-C8-C9-N2

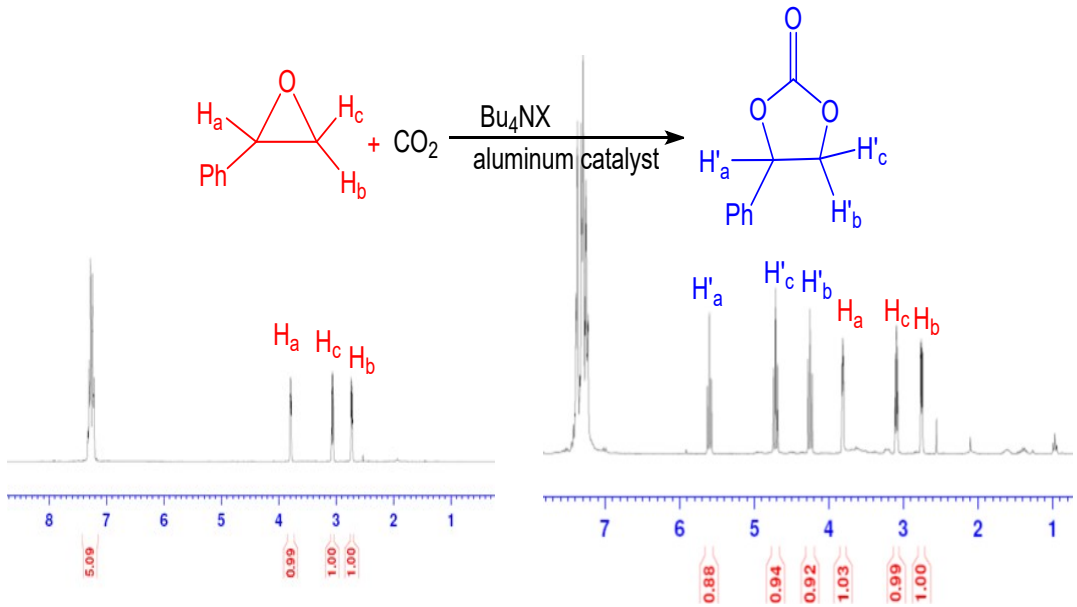

Figure S3. Corresponded ^{1}H NMR spectra of CO_2-styrene oxide cycloaddition reactions

Physical experiments & reagents

All the reactions were performed using stan cycles and dried over 4Å molecular sieves. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer. Chemical shifts for ^{1}H and $^{13}C\{1H\}$ spectra were recorded in ppm relative to the residual protons and $^{13}C\{1H\}$ of $CDCl_3$ (δ 7.24, 77.0 ppm) and C_6D_6 (δ 7.15, 128.0 ppm). Elemental analyses were performed on a Heraeus CHN-OS Rapid Elemental Analyzer at the Instrument Center, NCHU. Due to high moisture sensitivity and rapid decomposition, the elemental analyses of some metal complexes could not be performed well.

CO_2 cycloaddition reactions with styrene oxide. The general procedure for the cycloaddition reaction is presented in main text. A Schlenk flask was charged with 0.1 mmol of catalyst and 50 equiv. of styrene oxide. TBAI (tetra-n-butylammonium iodide) or TBAB (Tetra-n-butylammonium bromide, 1 equiv) and CO_2 balloon were used. The conversion was determined by ^{1}H NMR spectra.

DFT computation

The molecular structures of the four compounds were initially constructed and

optimized using Avogadro version1.2.0. The input geometries were then saved in appropriate formats compatible with quantum chemical calculations. All electronic structure calculations were performed using B3LYP hybrid functional in ORCA6.1.0.[1] The calculations included geometry optimization followed by single-point energy calculations to obtain orbital energies. Additional settings were included to ensure proper generation of molecular orbital information, including the HOMO and LUMO energies. Post-processing and visualization of molecular orbitals, including HOMO–LUMO surfaces and orbital energy inspection, were carried out using Chemcraft, a graphical program for quantum chemistry data analysis. Chemcraft enabled detailed examination of orbital shapes and energy levels based on the output generated from ORCA.

MTT assay

The MTT [3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazoliumbromide] (Sigma Chemical Co., St. Louis, MO, USA) assay was performed according to the previous method.[2] After 24 h, culture medium was replaced by 200 μL (0–250 μM) of complexes (1-5, 5a), and the cells were incubated for 48 h. The final concentration of solvent was less than 0.1% in cell culture medium. Culture medium was removed and replaced by 90 μL fresh culture medium. Ten

microliters of sterile filtered MTT solution (5 mg/mL) in phosphate buffered saline (PBS, pH 7.4) was added to each well, thereby reaching a final concentration of 0.5 mg MTT/mL. After 5 h, unreacted dye was removed, and the insoluble formazan crystals were dissolved in 200 μL/well DMSO and measured spectrophotometrically in a VersaMax tunable microplate reader (Molecular Devices, Sunnyvale, CA, USA) at 570 nm. The relative cell viability (%) related to control wells containing cell culture medium without samples was calculated by A_{570nm} [sample]/A_{570nm} [control] × 100. The IC_{50} value was calculated as the concentration of the compound at which cell growth was inhibited by 50% compared to untreated controls.

Complex	**Cell line**	**IC_{50} (μM)**
1	A2780	3.4±0.04
2	A2780	3.2±0.1
3	A2780	3.4±0.1
4	A2780	3.4±0.2
5	A2780	2.2±0.3
5a	A2780	3.2±0.1

Figure S4. IC_{50} values for complexes **1-5, 5a** in the human cancer cell line, A2780

Cell culture

Human cancer derived cell lines, A2780 (ovarian carcinoma) were handled as recommended by the suppliers and as previously described.[3] Briefly, A2780 cell lines was purchased from Merck (Darmstadt, Germany) and cultivated in DMEM (Dulbecco's modified Eagle's medium) supplemented with 10% (*v*/v) foetal bovine serum, 100 U/mL penicillin and 100 mg/mL streptavidin (all from Thermo Fischer Scientific, Waltham, MA, USA). A2780 was cultivated in RPMI (Roswell Park Memorial Institute) supplemented as DMEM and with MEM (Minimum essential medium) non-essential aminoacids (Thermo Fischer Scientific). Cultures were grown at 37 °C in a humidified atmosphere with 5% CO_2.

Reference

1 H. D. Snyder, T. G. Kucukkal, *J. Chem. Edn*., 2021, **98**, 1335-1341.

2 T. Mosmann, *J. Immunol. Methods*, 1983, **65**, 55-81.

3 A. Maron, K. Czerwinska, B. Machura, L. Raposo, C. Roma-Rodrigues, A. R. Fernandes, J. G. Malecki, A. Szlapa-Kula, S. Kula, S. Krompiec, *Dalton Trans*., 2018, **47**, 6444-6463.