Supporting Information

High-efficient green catalytic conversion for waste CS_2 by non-noble metal cage-based MOFs: an access to high-valued thiazolidine-2-thione

Wenyu Ding,‡ Xinyu Tang,‡ Sheng Jin, Zhao Li, Dongwei Xu, Xiaomin Kang* and Zhiliang Liu*

Inner Mongolia Key Laboratory of Chemistry and Physics of Rare Earth Materials, College of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot, 010021, PR China.

E-mail: kangxm@imu.edu.cn, cezlliu@imu.edu.cn

‡ These authors contributed equally to this work.

Table of Contents

Figure S16. The three-dimensional size of 1-isobutyl-2-phenylaziridine is 11.0 × 8.1 × 6.0 $Å^3$, and the three-dimensional size of 3-isobutyl-5-phenylthiazolidine-2-thione is 14.2 × 7.3 × 6.1 $Å^3$.

Figure S17. The three-dimensional size of 1-butyl-2-phenylaziridine is 11.4 × 8.6 × 6.4 $Å^3$, and the three-dimensional size of 3-butyl-5-phenylthiazolidine-2-thione is 15.4 × 7.2 × 6.0 $Å^3$.

Figure S18. The three-dimensional size of 1-methoxyethyl-2-phenylaziridine is 11.2 × 8.5 × 6.4 $Å^3$, and the three-dimensional size of 3-methoxyethyl-5-phenylthiazolidine-2-thione is 15.2 × 7.1 × 6.0 $Å^3$.

Figure S19. The three-dimensional size of 1-ethyl-2-(4-fluorophenyl)-aziridine is 10.8 × 7.2 × 6.16 $Å^3$, and the three-dimensional size of 3-ethyl-5-(4-fluorophenyl)-thiazolidine-2-thione is 13.4 × 7.1 × 5.9 $Å^3$.

Figure S20. The three-dimensional size of 1-ethyl-2-(4-chlorophenyl)-aziridine is 11.5 × 7.3 × 6.2 $Å^3$, and the three-dimensional size of 3-ethyl-5-(4-chlorophenyl)-thiazolidine-2-thione is 14.7 × 7.1 × 5.8 $Å^3$.

Figure S21. The three-dimensional size of 1-ethyl-2-(4-methyl)-aziridine is 11.3 × 7.2 × 6.2 $Å^3$, and the three-dimensional size of 3-ethyl-5-p-tolylthiazolidine-2-thione is 12.8 × 7.1 × 5.9 $Å^3$.

Figure S22. SEM images of compound **1** after 10 cycles of reaction.

Figure S23. The PXRD patterns of compound **1** after recycling.

Table S3. The ICP result of **1** after catalytic recycling (filter liquor).

Figure S24. The XPS analysis of compound **1** as a catalyst for the cycloaddition reaction of CO_2 with 1-ethyl-2-phenylaziridine after ten catalysis recycling.

Figure S25. The FT-IR spectra of compound **1** and ten-times-reused **1**.

Figure S26. ^1H NMR spectroscopy of digested compound **1** in the presence or absence of CS_2 (H_2O/DMSO = 0.1/0.55 mL).

Figure S27. PXRD pattern of compound Co(II/III).

Table S4. Comparison of yields of two isomeric [Co_3] cluster-based MOFs under optimized reaction conditions.

Table S1. Crystal data and structure refinement for compound **1**.

	1
Empirical formula	$C_{61}H_{74}Co_3N_8O_{22}$
Formula weight	1448.04
Temperature (K)	296.15
Crystal system	Hexagonal
Space group	$P6_3/mmc$
a (Å)	17.0841(8)
b (Å)	17.0841(8)
c (Å)	14.9800(9)
α (°)	90
β (°)	90
γ (°)	120
Volume (Å^3)	3786.4(4)
Z	2
ρ_{calc} (g/m^3)	1.270
μ (mm^{-1})	0.721
F (000)	1506.0
R_{int}	0.0977
GOF on F^2	1.023
Final R indexes [$I >= 2\sigma(I)$]	$R_1 = 0.0379$, $wR_2 = 0.1001$
Final R indexes [all data]	$R_1 = 0.0493$, $wR_2 = 0.1062$
Largest diff. peak and hole (e Å^{-3})	0.59/-0.41

Table S2. Bond lengths (Å) and bond angles (°) for compound **1**.

Bond distances			
Co1-O1	2.0330(4)	C7-C8[4]	1.375(3)
Co1-O2[1]	2.0723(13)	C7-C8	1.375(3)
Co1-O2[2]	2.0723(13)	C3-C2	1.490(5)
Co1-O2	2.0722(13)	C3-C4[2]	1.369(4)
Co1-O2[3]	2.0722(13)	C3-C4	1.369(4)
Co1-N1	2.163(3)	C1-C2[5]	1.367(3)
O2-C6	1.2347(18)	C1-C2	1.367(3)
N1-C5[2]	1.328(4)	C8-C8[6]	1.381(4)
N1-C5	1.328(4)	C5-C4	1.393(4)
C6-C7	1.507(3)		

Symmetry transformations used to generate equivalent atoms:

[1]-1+Y-X,+Y,-1/2-Z; [2]-1+Y-X,+Y,+Z; [3]+X,+Y,-1/2-Z; [4]-Y,-X,+Z; [5]1-Y,2+X-Y,+Z; [6]-1+Y,1+X,-1-Z

Bond Angles			
O1-Co1-O2[1]	92.43(4)	C5-N1-Co1	122.09(18)
O1-Co1-O2	92.43(4)	C5[3]-N1-Co1	122.09(18)
O1-Co1-O2[2]	92.43(4)	C5[3]-N1-C5	115.8(4)
O1-Co1-O2[3]	92.43(4)	O2-C6-O2[6]	126.4(2)
O1-Co1-N1	180.00	O2-C6-C7	116.79(12)
O2-Co1-O2[2]	175.14(8)	O2[6]-C6-C7	116.79(12)
O2-Co1-O2[3]	90.30(11)	C8[6]-C7-C6	120.98(13)
O2[1] -Co1-O2[2]	90.30(11)	C8-C7-C6	120.98(13)
O2[1] -Co1-O2[3]	175.14(8)	C8[6]-C7-C8	118.0(3)
O2[1]-Co1-O2	89.50(11)	C4-C3-C2	121.43(19)
O2[2]-Co1-O2[3]	89.50(11)	C4[3]-C3-C2	121.43(19)
O2-Co1-N1	87.57(4)	C4[3]-C3-C4	117.1(4)
O2[3] -Co1-N1	87.57(4)	C2-C1-C2[7]	119.9(4)
O2[2] -Co1-N1	87.57(4)	C1[8]-C2-C3	119.9(4)
O2[1] -Co1-N1	87.57(4)	C1-C2-C3	119.9(4)
Co1[4]-O1-Co1	120.0	C1-C2-C1[8]	120.1(4)
Co1-O1-Co1[5]	120.0	C7-C8-C8[9]	120.97(13)
Co1[4]-O1-Co1[5]	120.0	N1-C5-C4	123.9(3)

C6-O2-Co1	135.06(14)	C3-C4-C5	119.6(3)

Symmetry transformations used to generate equivalent atoms:

[1]+X,+Y,-1/2-Z; [2]-1+Y-X,+Y,-1/2-Z; [3]-1+Y-X,+Y,+Z; [4]-1+Y-X,-X,-1/2-Z; [5]-Y,1+X-Y,+Z; [6]-Y,-X,+Z; [7]1-Y,2+X-Y,+Z; [8]-1+Y-X,1-X,-1/2-Z; [9]-1+Y,1+X,-1-Z

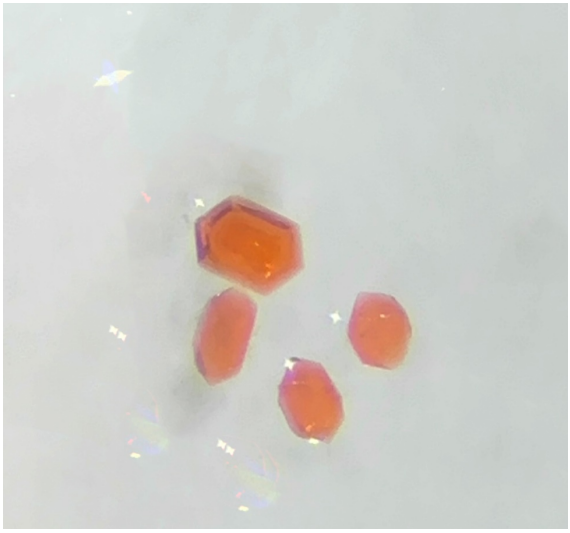

Figure S1. Image of as-synthesized compound **1**.

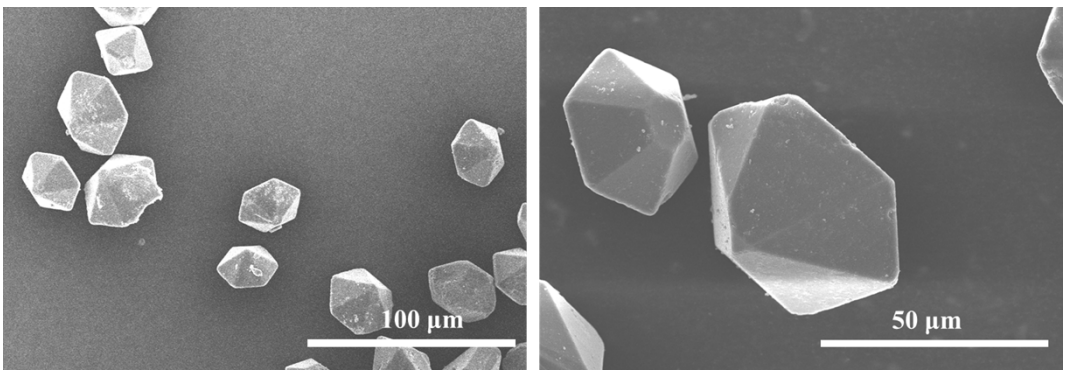

Figure S2. SEM images of compound **1**.

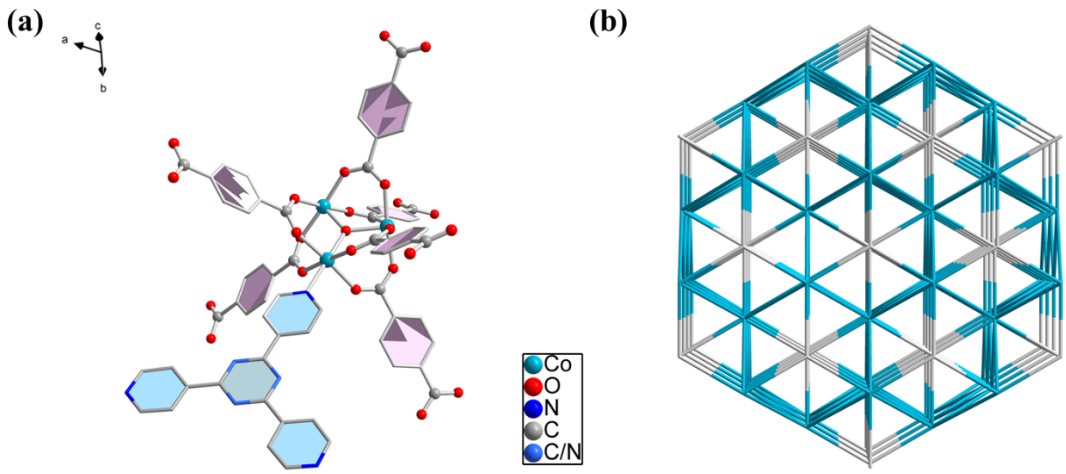

Figure S3. (a)The coordination environment of compound **1**; (b) The **pacs** topology of compound **1**.

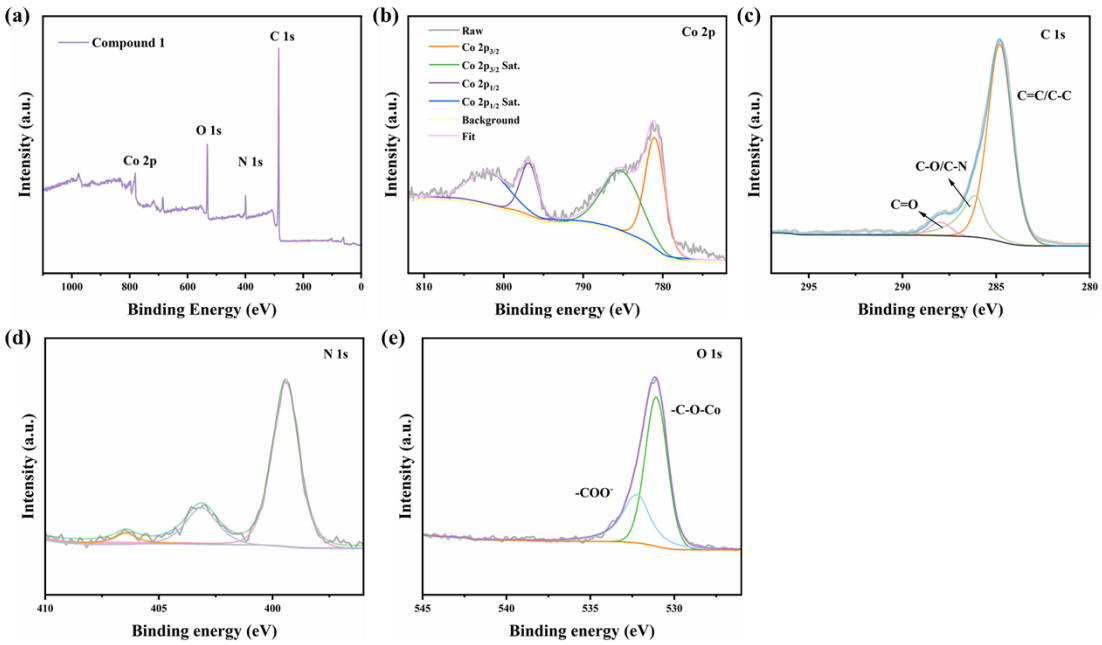

Figure S4. XPS spectra of **1**: a) XPS survey spectrum; b) Co 2p; c) C 1s; d) N 1s; e) O 1s.

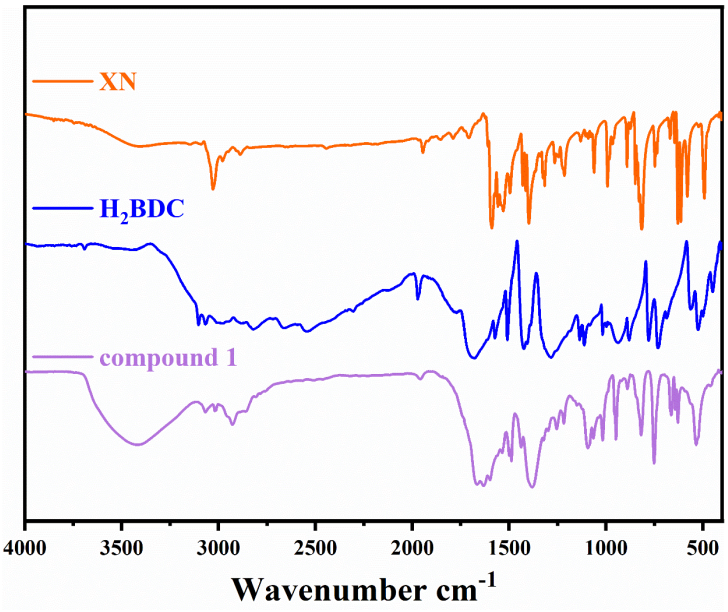

Figure S5. FT-IR spectra of compound **1** and ligands.

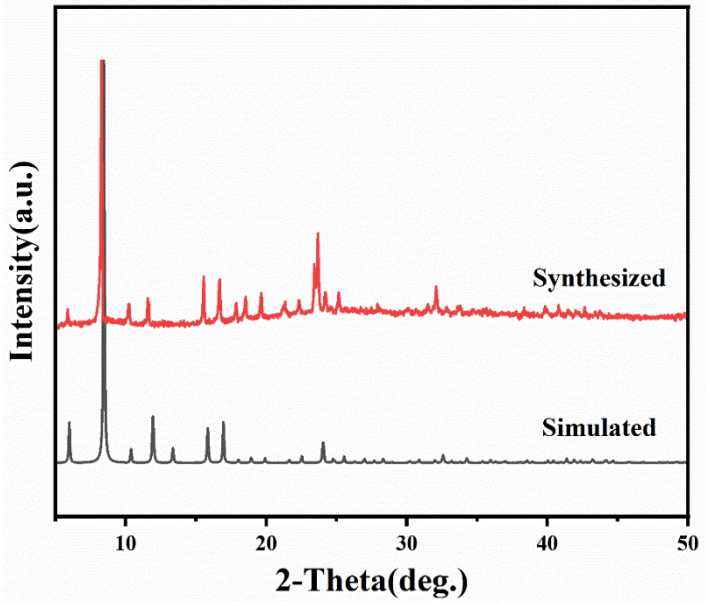

Figure S6. PXRD pattern of compound **1**.

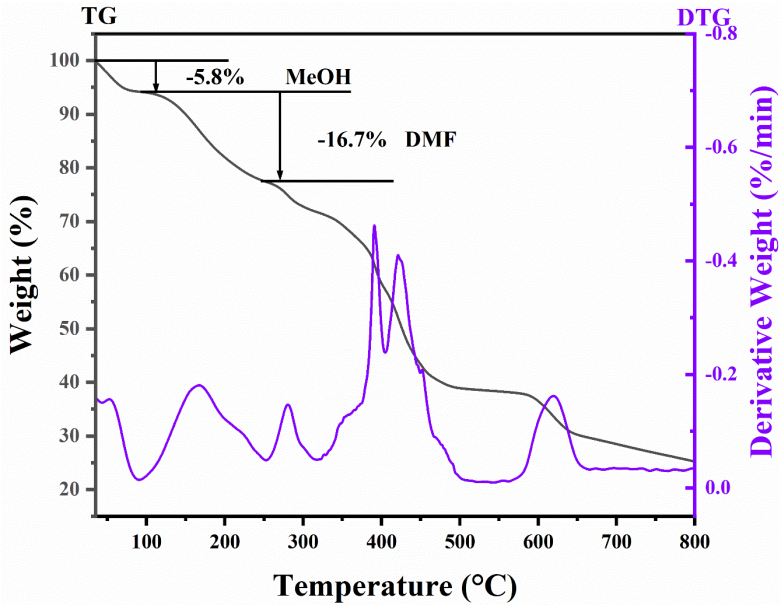

Figure S7. Thermogravimetric analysis of compound **1**.

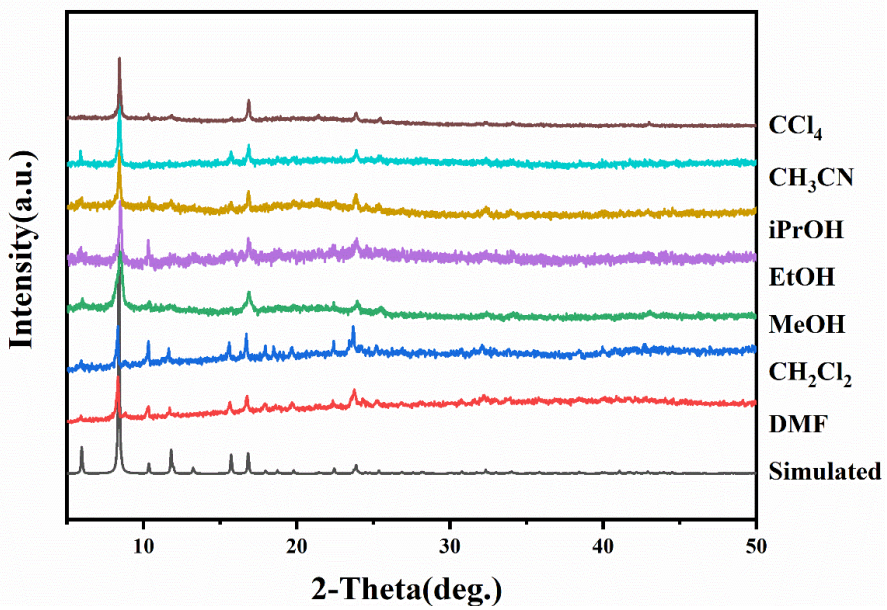

Figure S8. The PXRD patterns of the compound **1** after immersing in various organic solvents.

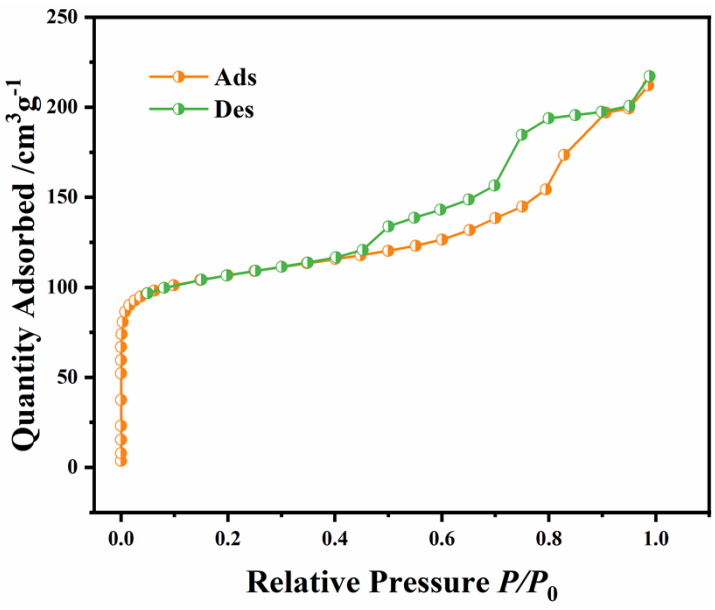

Figure S9. The N_2 adsorption of compound **1** (77 K).

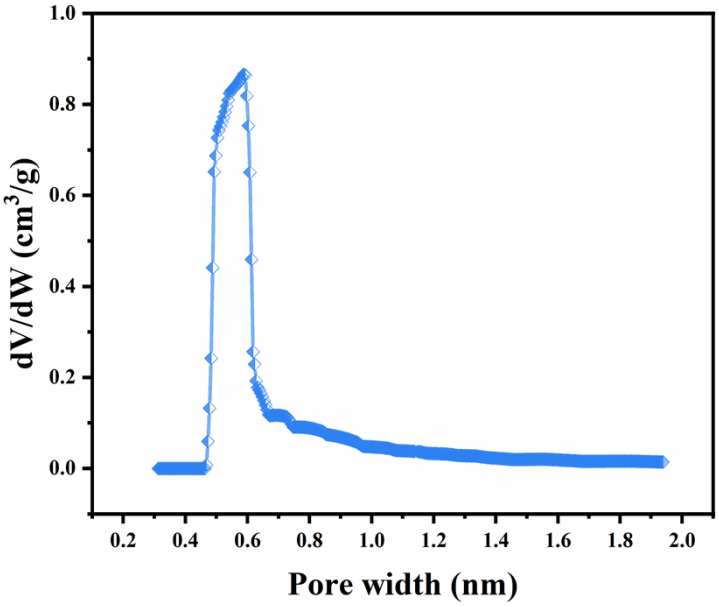

Figure S10. The adsorption average pore diameter of compound **1**.

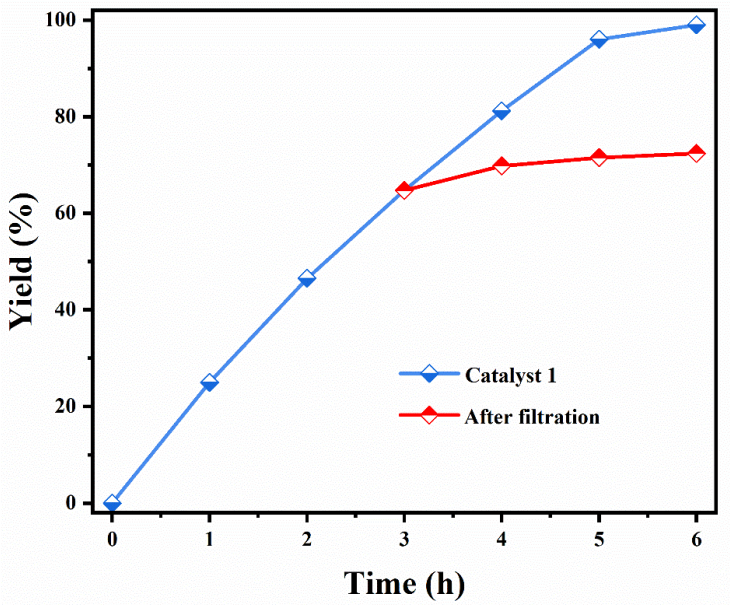

Figure S11. Catalyst filtration test for the cycloaddition of aziridines and CS_2.

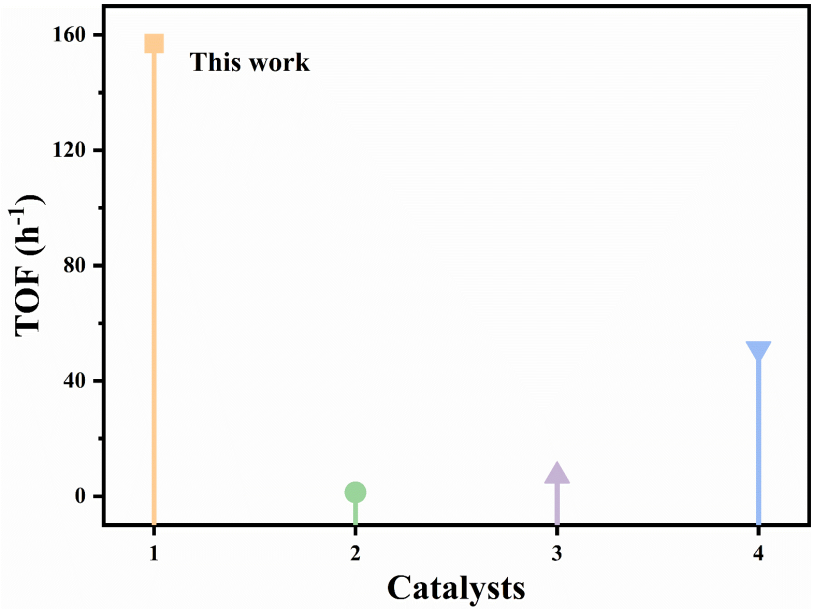

Figure S12. TOF values of different catalysts for the cycloaddition of CS_2 with 1-ethyl-2-phenylaziridine (1: compound **1** in this work; 2: $\{tBuC_6H_4CONC_6H_3(iPr)_2Eu[N(SiMe_3)_2]THF\}_2$; 3: ion-exchange resin D301R; 4: Dy_{24}-MOF).

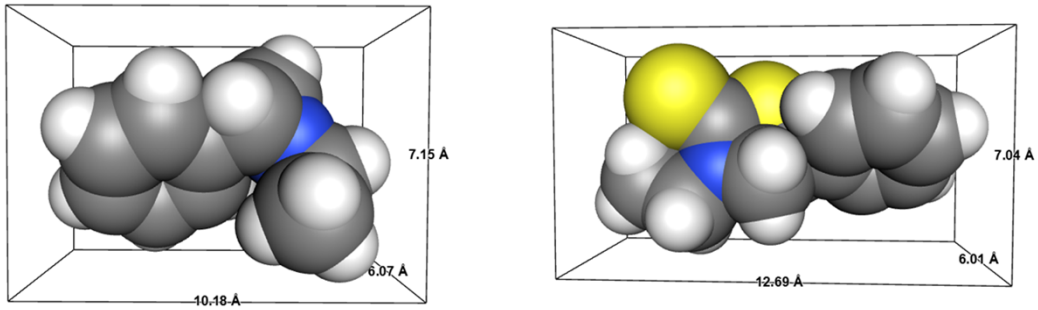

Figure S13. The three-dimensional size of 1-ethyl-2-phenylaziridine is 10.2 × 7.2 × 6.1 Å^3, and the three-dimensional size of 3-ethyl-5-phenylthiazolidine-2-thione is 12.7 × 7.0 × 6.0 Å^3.

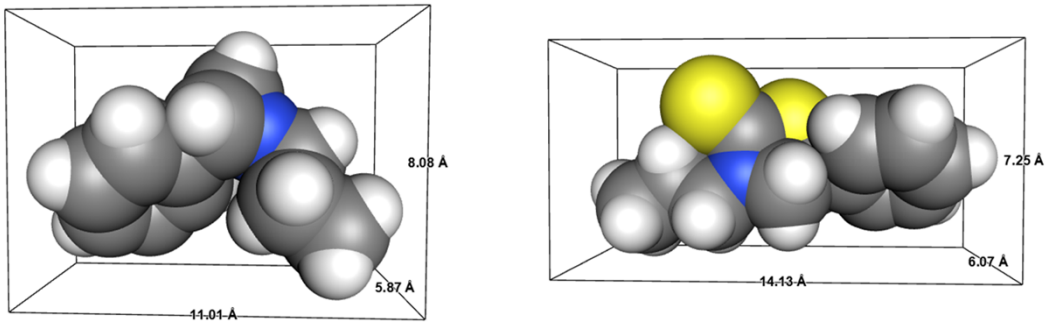

Figure S14. The three-dimensional size of 1-propyl-2-phenylaziridine is 11.0 × 8.1 × 5.9 Å^3, and the three-dimensional size of 3-propyl-5-phenylthiazolidine-2-thione is 14.1 × 7.3 × 6.1 Å^3.

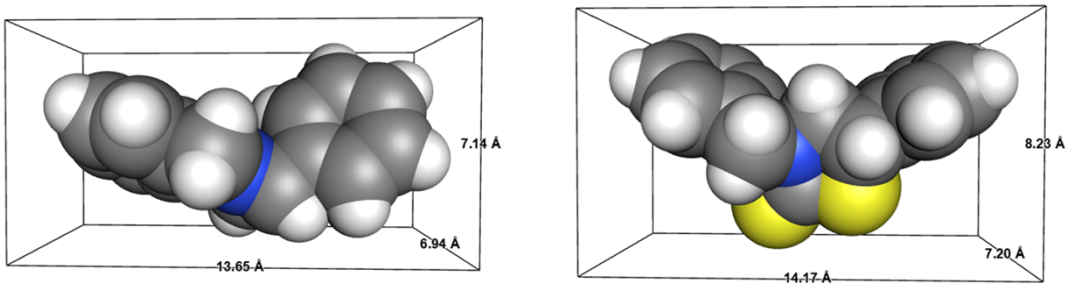

Figure S15. The three-dimensional size of 1-benzyl-2-phenylaziridine is 13.7 × 7.1 × 7.0 Å^3, and the three-dimensional size of 3-benzyl-5-phenylthiazolidine-2-thione is 14.2 × 8.2 × 7.2 Å^3.

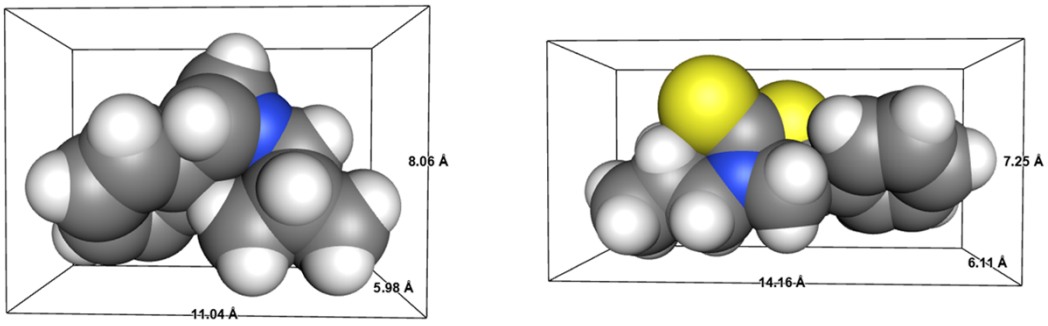

Figure S16. The three-dimensional size of 1-isobutyl-2-phenylaziridine is 11.0 × 8.1 × 6.0 Å^3, and the three-dimensional size of 3-isobutyl-5-phenylthiazolidine-2-thione is 14.2 × 7.3 × 6.1 Å^3.

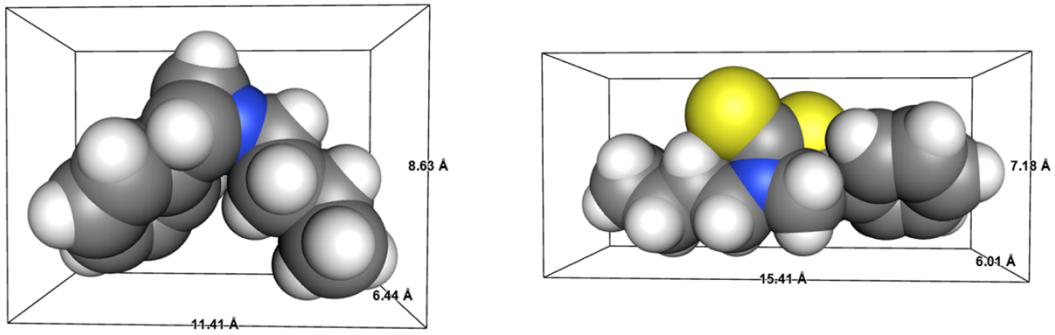

Figure S17. The three-dimensional size of 1-butyl-2-phenylaziridine is 11.4 × 8.6 × 6.4 Å^3, and the three-dimensional size of 3-butyl-5-phenylthiazolidine-2-thione is 15.4 × 7.2 × 6.0 Å^3.

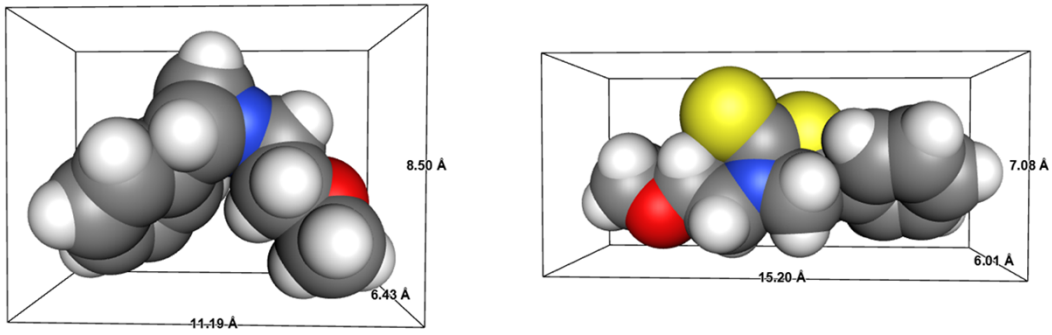

Figure S18. The three-dimensional size of 1-methoxyethyl-2-phenylaziridine is 11.2 × 8.5 × 6.4 Å^3, and the three-dimensional size of 3-methoxyethyl-5-phenylthiazolidine-2-thione is 15.2 × 7.1 × 6.0 Å^3.

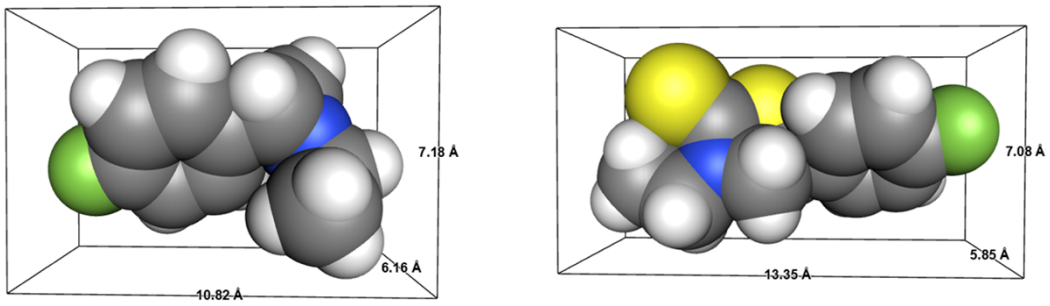

Figure S19. The three-dimensional size of 1-ethyl-2-(4-fluorophenyl)-aziridine is 10.8 × 7.2 × 6.16 Å^3, and the three-dimensional size of 3-ethyl-5-(4-fluorophenyl)-thiazolidine-2-thione is 13.4 × 7.1 × 5.9 Å^3.

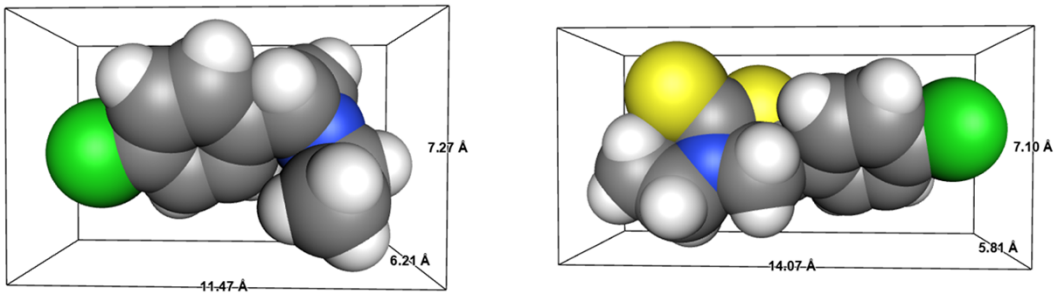

Figure S20. The three-dimensional size of 1-ethyl-2-(4-chlorophenyl)-aziridine is 11.5 × 7.3 × 6.2 Å^3, and the three-dimensional size of 3-ethyl-5-(4-chlorophenyl)-thiazolidine-2-thione is 14.7 × 7.1 × 5.8 Å^3.

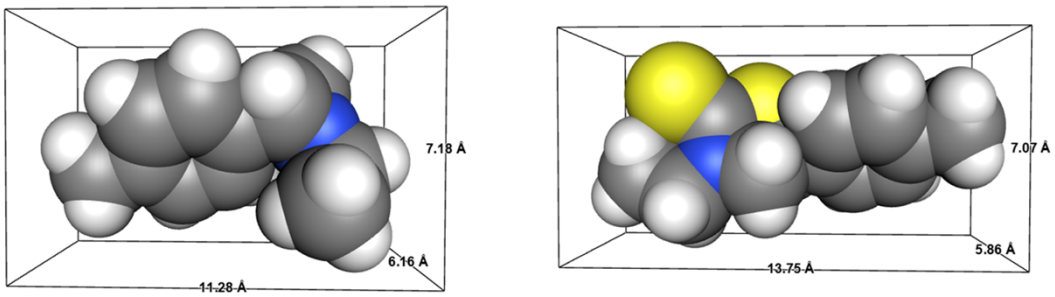

Figure S21. The three-dimensional size of 1-ethyl-2-(4-methyl)-aziridine is 11.3 × 7.2 × 6.2 Å^3, and the three-dimensional size of 3-ethyl-5-p-tolylthiazolidine-2-thione is 12.8 × 7.1 × 5.9 Å^3.

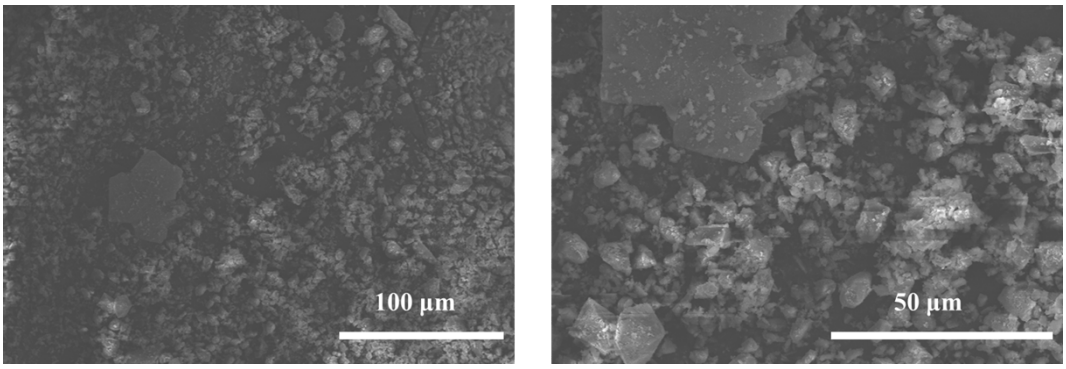

Figure S22. SEM images of compound **1** after 10 cycles of reaction.

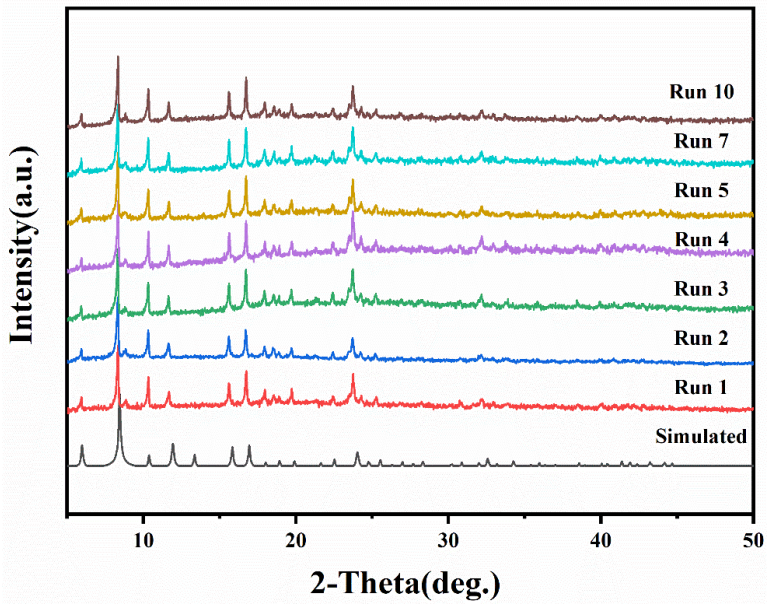

Figure S23. The PXRD patterns of compound **1** after recycling.

Table S3. The ICP result of **1** after catalytic recycling (filter liquor).

Recycle Times	Run 10
Co^{2+} (%)	0.16

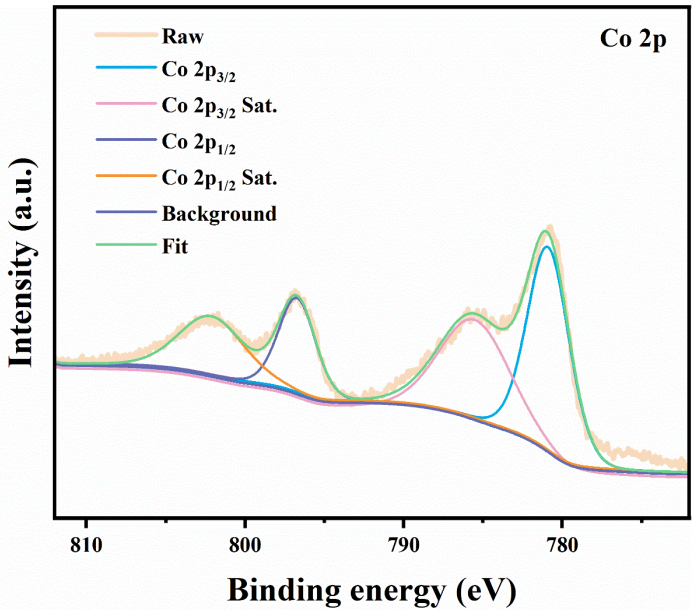

Figure S24. The XPS analysis of compound **1** as a catalyst for the cycloaddition reaction of CO_2 with 1-ethyl-2-phenylaziridine after ten catalysis recycling.

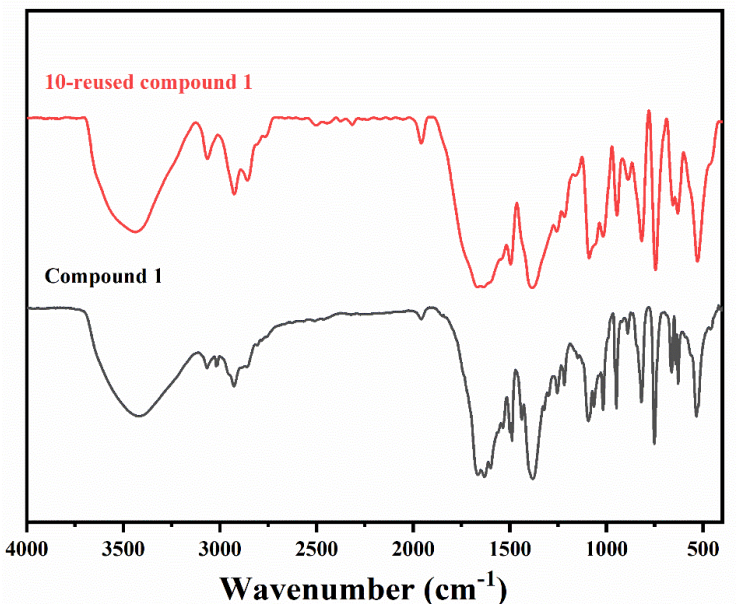

Figure S25. The FT-IR spectra of compound **1** and ten-times-reused **1**.

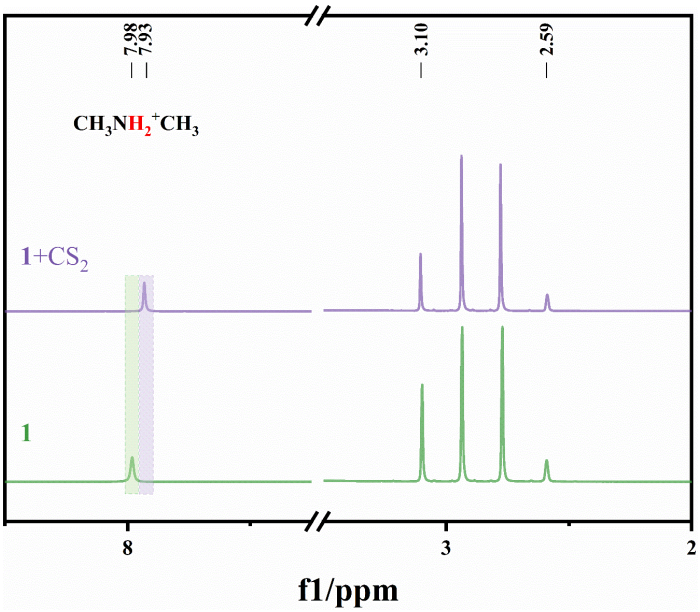

Figure S26. ^{1}H NMR spectroscopy of digested compound **1** in the presence or absence of CS_2 (H_2O/DMSO = 0.1/0.55 mL).

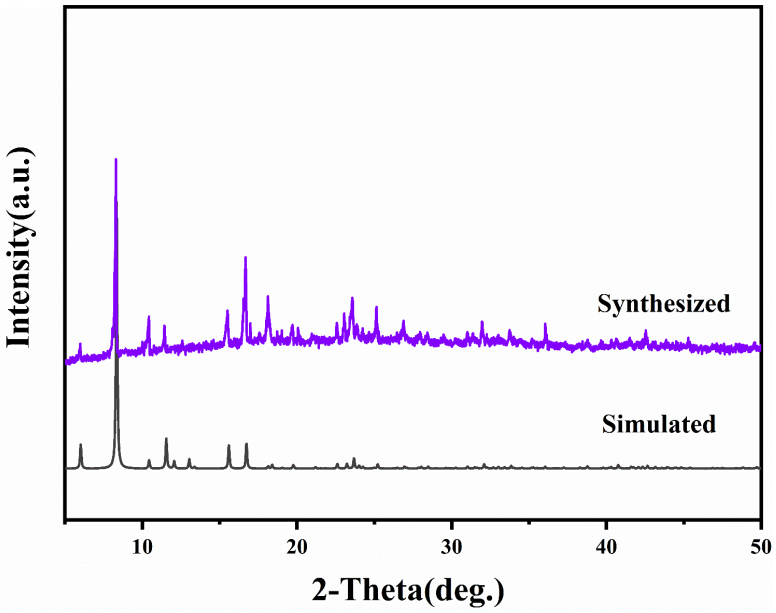

Figure S27. PXRD pattern of compound Co(II/III).

Table S4. Comparison of yields of two isomeric [Co_3] cluster-based MOFs under optimized reaction conditions.

Entry	Yield
Co(II/III)	81%
compound **1**	99%

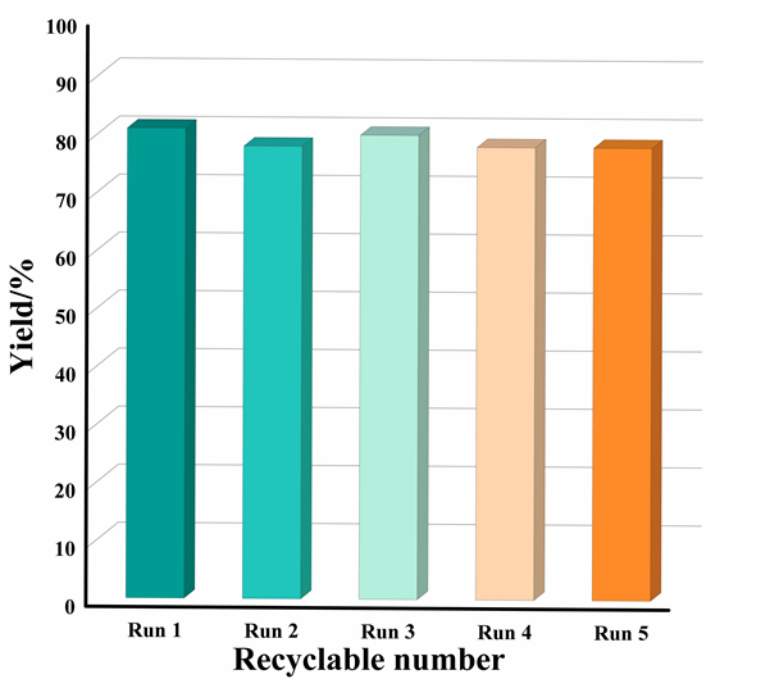

Figure S28. Recycling test of catalyst Co(II/III) in the CS_2 cycloaddition with 1-ethyl-2-phenylaziridine.

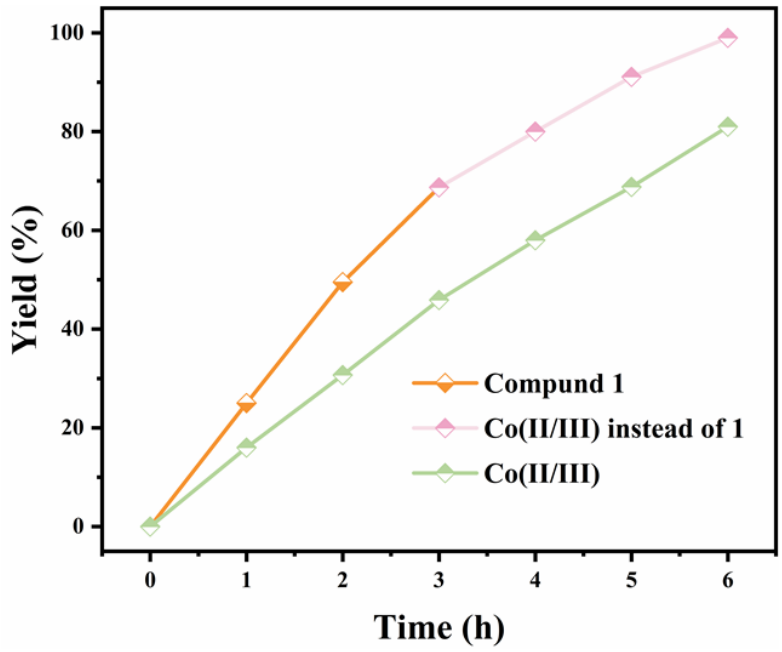

Figure S29. Catalyst filtration experiments of compound **1** and Co (II/III).

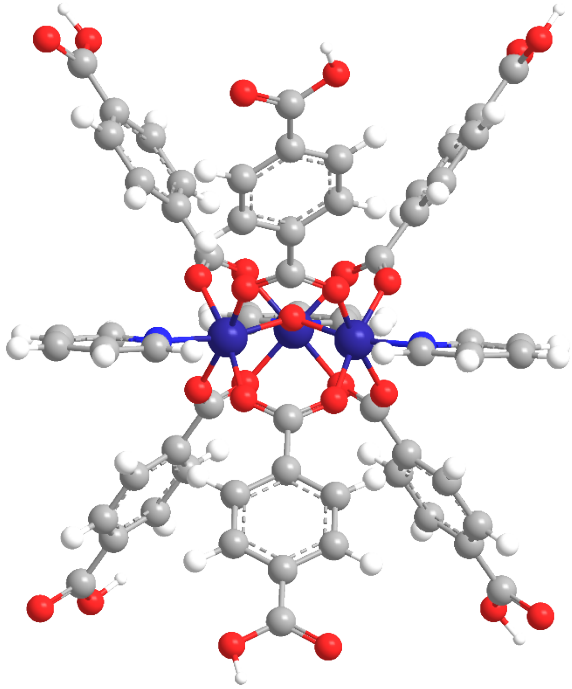

Figure S30. The DFT full optimized geometry of compound **1**. Color codes for atoms: bluish violet, Co; gray, C; red, O; blue, N; white, H.