

Supporting informations

**Solvent-polarity-controlled assembly of polynuclear titanium-calixarene complexes: constructing isolated  $\{\text{Ti}_7\}$ ,  $\{\text{Ti}_{13}\}$ ,  $\{\text{Ti}_{24}\}$  and  $\{\text{Tb}_2\text{Ti}_{13}\}$  clusters**

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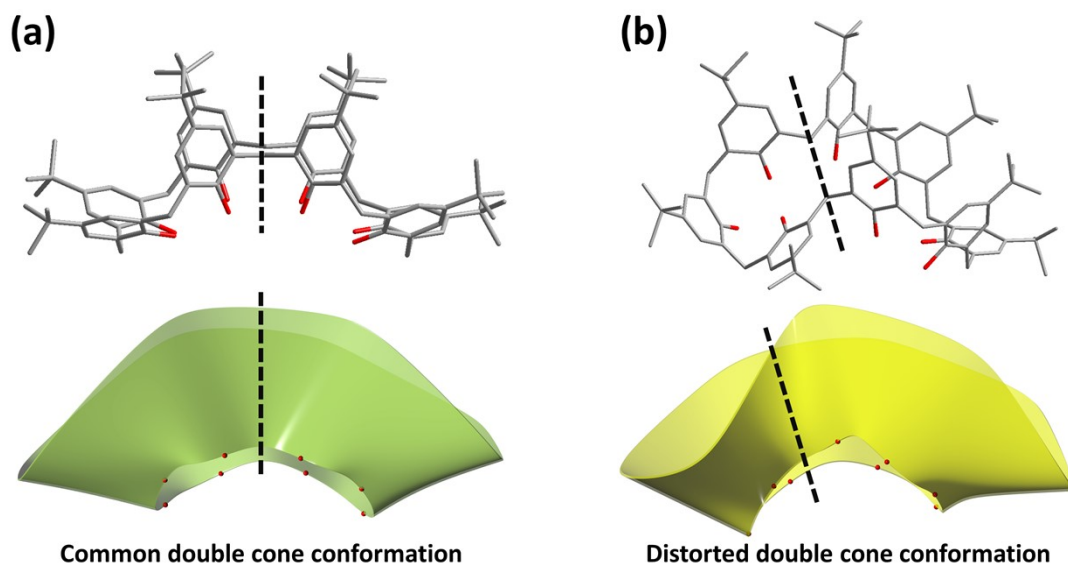
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**Table S1** Crystal data and structure refinement for compounds **CIAC-262--265**.

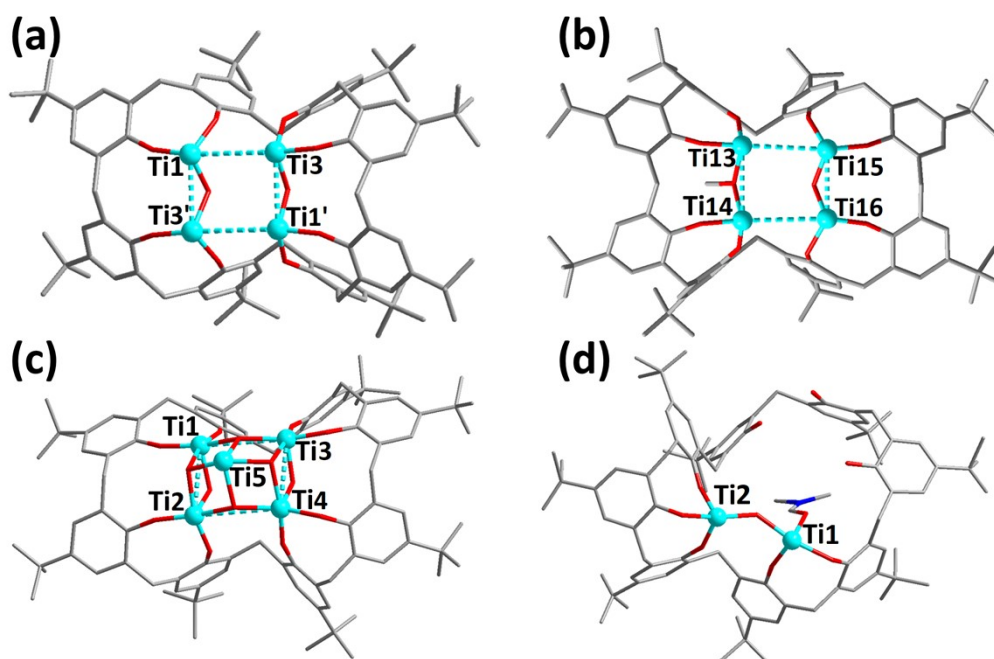
	<b>CIAC-262</b>	<b>CIAC-263</b>	<b>CIAC-264</b>	<b>CIAC-265</b>
Formula	C <sub>96</sub> H <sub>128</sub> O <sub>24</sub> Ti <sub>7</sub>	C <sub>185</sub> H <sub>235</sub> O <sub>42</sub> Ti <sub>13</sub>	C <sub>358</sub> H <sub>430</sub> N <sub>2</sub> O <sub>72</sub> Ti <sub>24</sub>	C <sub>279</sub> H <sub>346</sub> N <sub>4</sub> O <sub>54</sub> Tb <sub>2</sub> Ti <sub>13</sub>
Formula wt	2001.28	3753.42	7062.61	5560.12
Cryst. syst.	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	<i>C 2/c</i>	<i>C 2/c</i>	<i>P -1</i>	<i>P -1</i>
<i>a</i> (Å)	30.91	59.77	22.92	22.76
<i>b</i> (Å)	13.86	25.69	23.19	26.34
<i>c</i> (Å)	29.94	37.75	25.31	31.62
$\alpha$ (°)	90	90.00	111.59	94.27
$\beta$ (°)	114.26	112.77	108.55	93.77
$\gamma$ (°)	90	90.00	96.60	90.14
<i>V</i> (Å <sup>3</sup> )	11697.20(7)	53438.00(2)	11440.40(5)	18861.40(11)
<i>Z</i>	4	8	1	2
<i>T</i> (K)	293	180	180	190
<i>D</i> /g cm <sup>-3</sup>	1.136	0.933	1.025	0.979
$\mu$ / mm <sup>-1</sup>	4.354	3.537	3.814	4.438
<i>F</i> (000)	4200	15736	3696	5792
Total data	34572	148796	225026	230042
Unique data	6744	24515	28358	31751
<i>R</i> <sub>int</sub>	0.1043	0.1486	0.0489	0.0573
GOF	1.094	1.117	1.094	1.042
<i>R</i> <sub>I</sub> <sup>a</sup> [I > 2σ(I)]	0.0690	0.0897	0.0809	0.0894
<i>wR</i> <sub>2</sub> <sup>b</sup> (all data)	0.2142	0.2885	0.2461	0.2565

$$^aR_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|; ^b wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$$

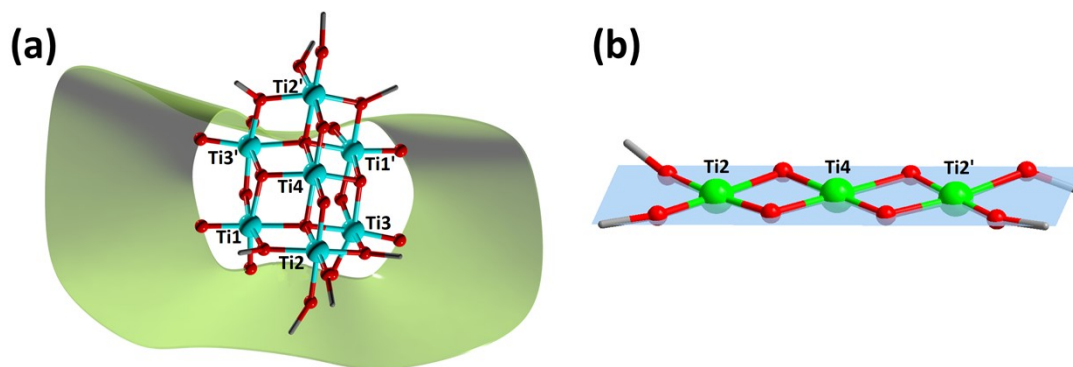
\*The formula is based on the contents without the unidentified disordered solvent molecules and counter ions.



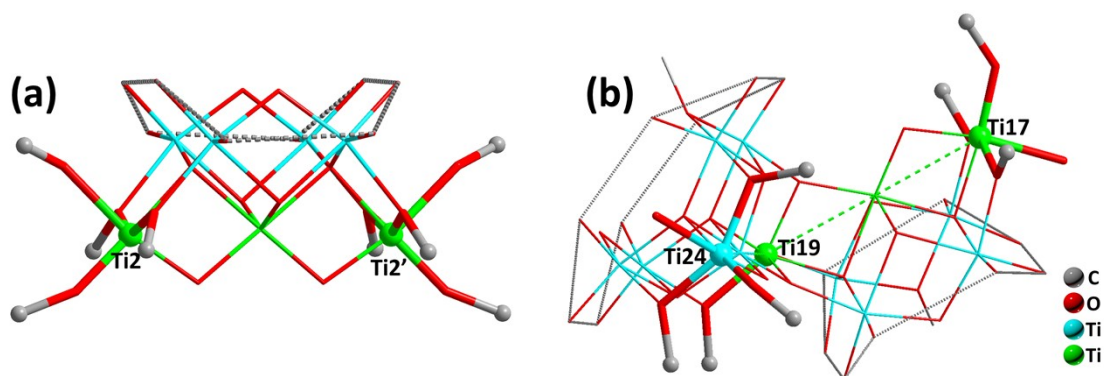
**Figure S1.** *p-tert*-Butylcalix[8]arene molecule adopting double cone conformation (a) or distorted double cone conformation (b).



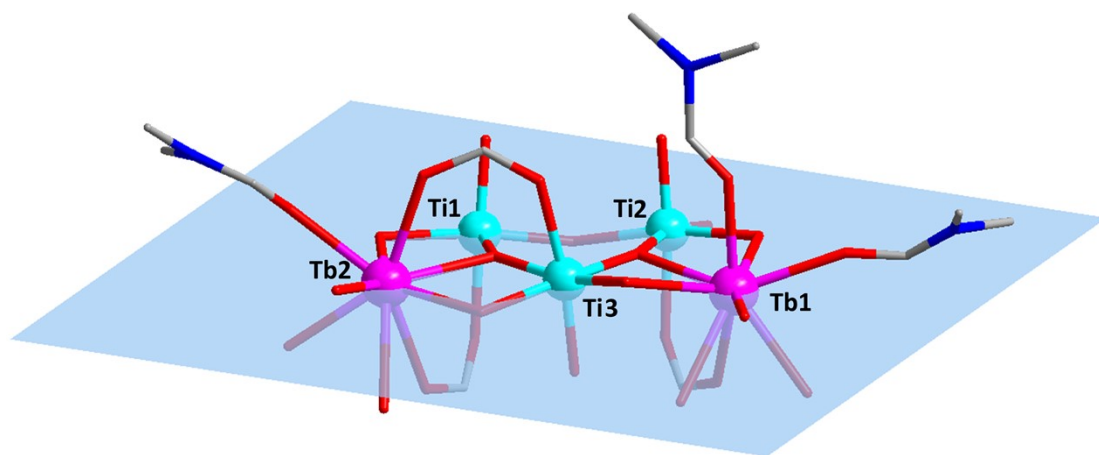
**Figure S2.** Top views of  $Ti_4$ -C8A units in **CIAC-262** (a) and **CIAC-263** (b),  $Ti_5$ -C8A unit in **CIAC-264** and **CIAC-265** (c), and  $Ti_2$ -C8A unit in **CIAC-265** (d). Atom color code: cyan, Ti; red, O; blue, N; gray, C.



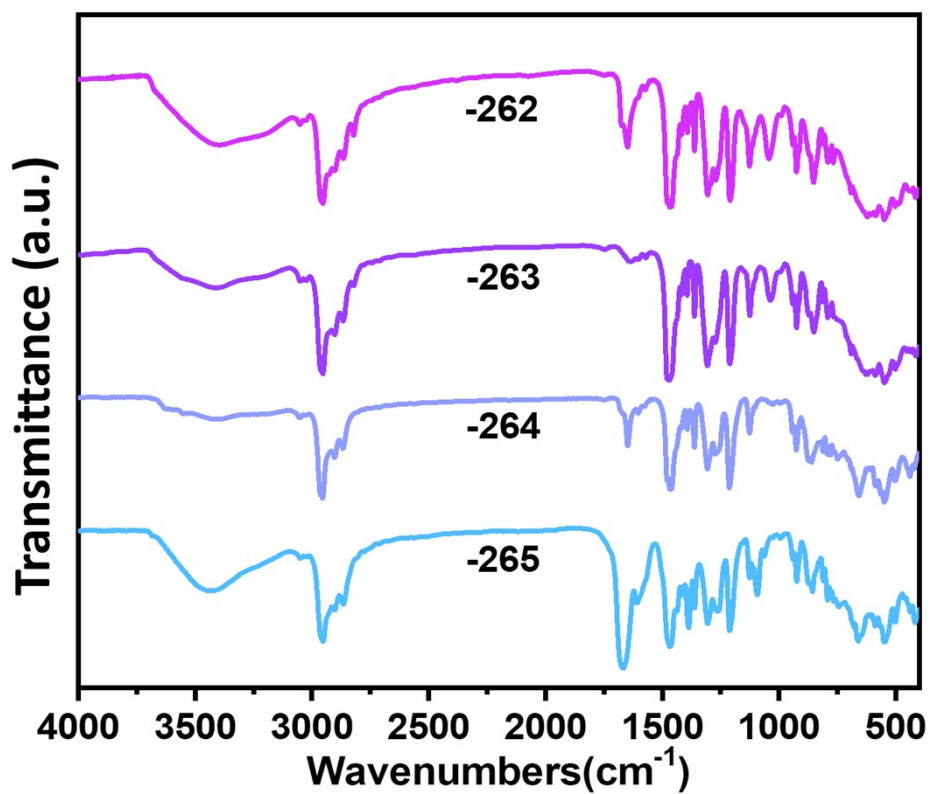
**Figure S3.** The molecular structure of **CIAC-262** and the scheme of the linear  $Ti_3$  unit bonded to a  $Ti_4$ -C8A unit. The green cone represents *p-tert*-butylcalix[8]arene. Atom color code: cyan, Ti; red, O; gray, C. Symmetry code: ('), 1-x, y, 1.5-z.



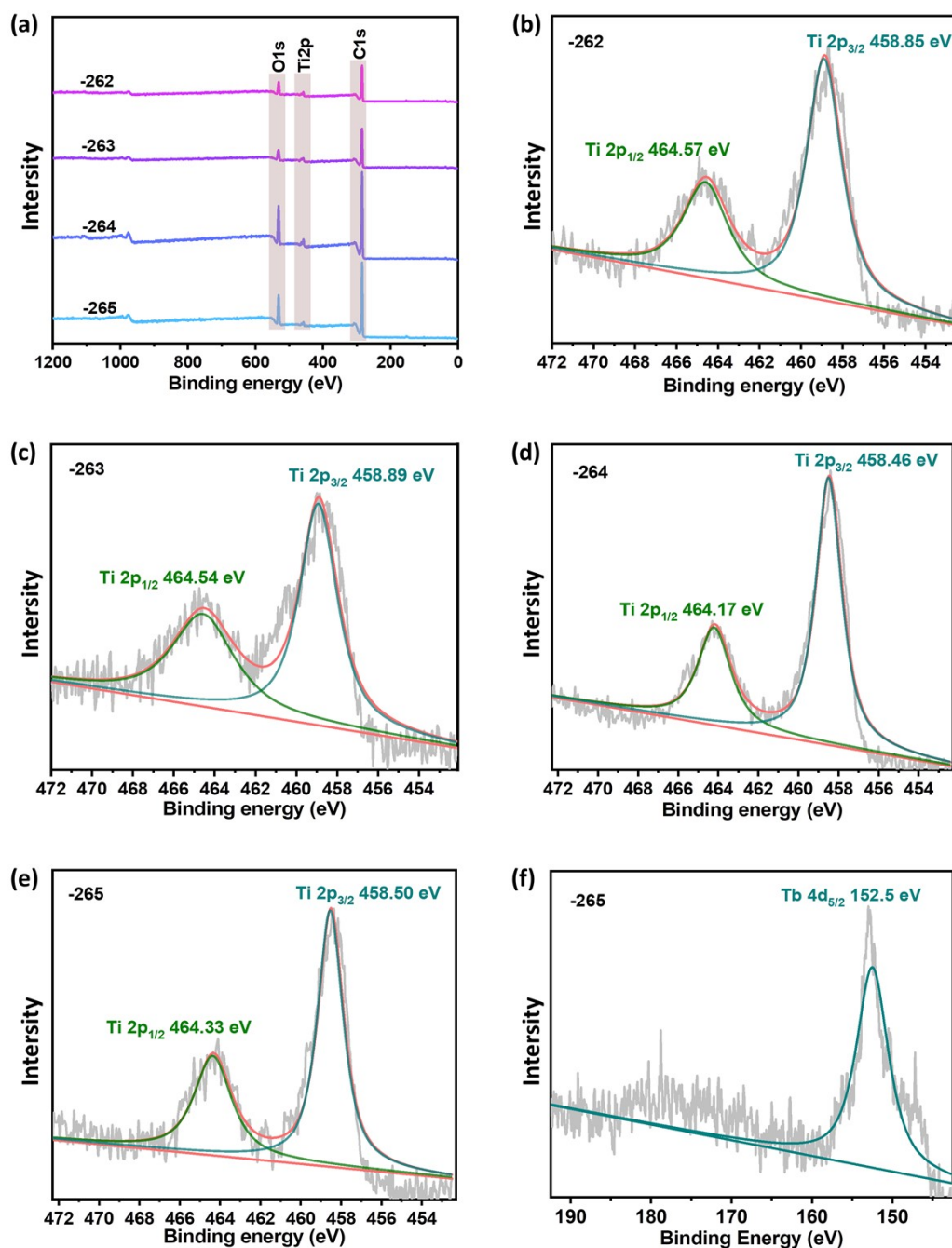
**Figure S4.** The coordinated methanol molecules in **CIAC-262** (a) and **-263** (b). The gray dotted lines represent *p-tert*-butylcalix[8]arene.



**Figure S5.** Five metal atoms located in a same plane in compound **CIAC-265**. Atom color code: cyan Ti; magenta, Tb; red, O; blue, N; gray, C.



**Figure S6.** FTIR spectra of compounds **CIAC-262 - -265**.



**Figure S7.** XPS spectra of compounds **CIAC-262** - **-265** (a), Ti 2p bands (b-e), the Tb 4d band of **CIAC-265** (f).

In addition to bond valence sum calculation (BVS), the XPS studied was also applied to further confirm the valence of the metal ions in compounds **CIAC-262** - **-265**, as

shown in Figure S7. The Ti 2p spectra of CIAC-262 - 265 are deconvoluted into the peaks that are centered at 464.57 and 458.85 eV, 464.54 and 458.89 eV, 464.17 and 458.46 eV, 464.33 and 458.50 eV, respectively, which indicated that all the Ti ions in the compounds CIAC-262 - 265 are tetravalent (Figure S7b-e). The Tb 4d spectrum reveals that Tb ions in compound CIAC-265 are trivalent (Figure S7f).

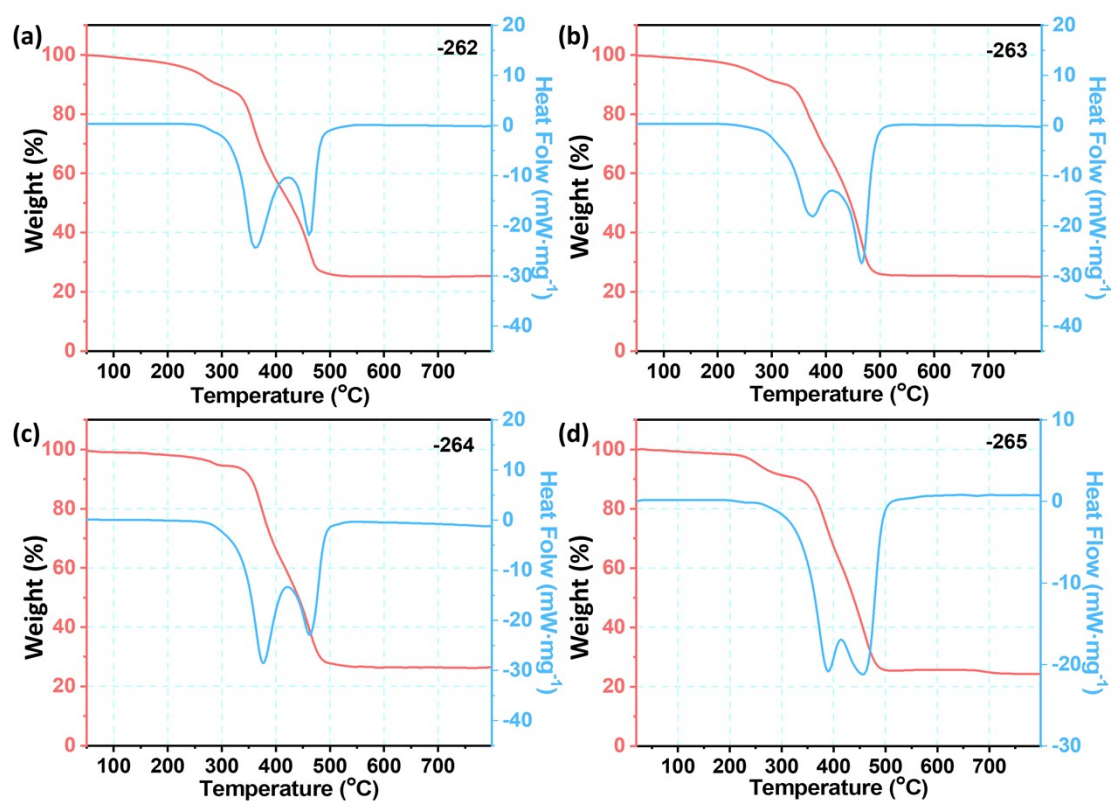
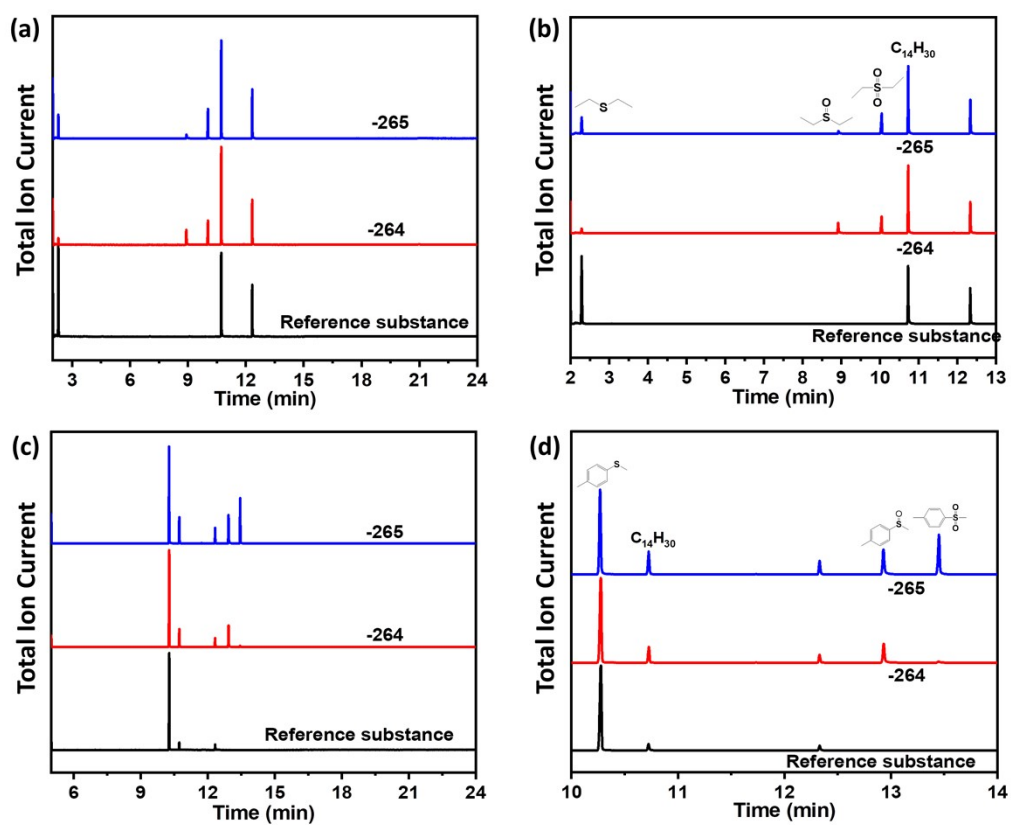
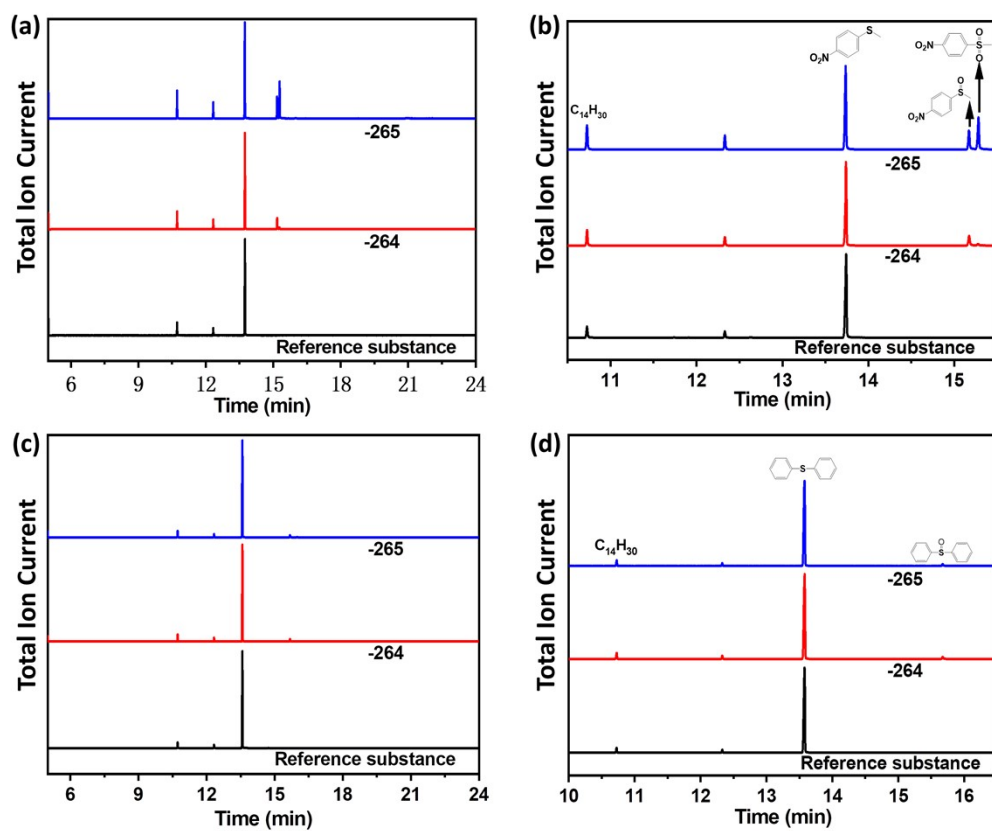


Figure S8. TGA-DSC curves for CIAC-262 - 265.

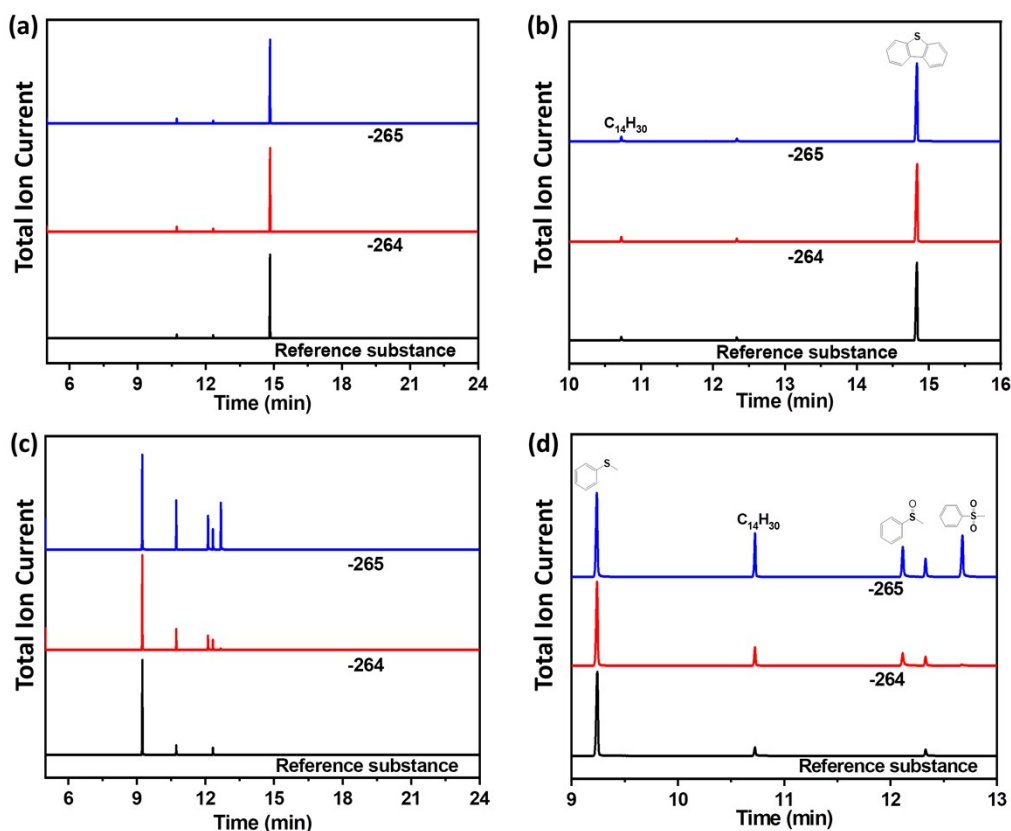


**Figure S9.** The GC-MS analysis of catalytic sulfoxidation of diethyl sulfide (a, b) and methyl *p*-tolyl sulfide (c, d) to corresponding sulfoxide and sulfone in the presence of CIAC-264 or -265.



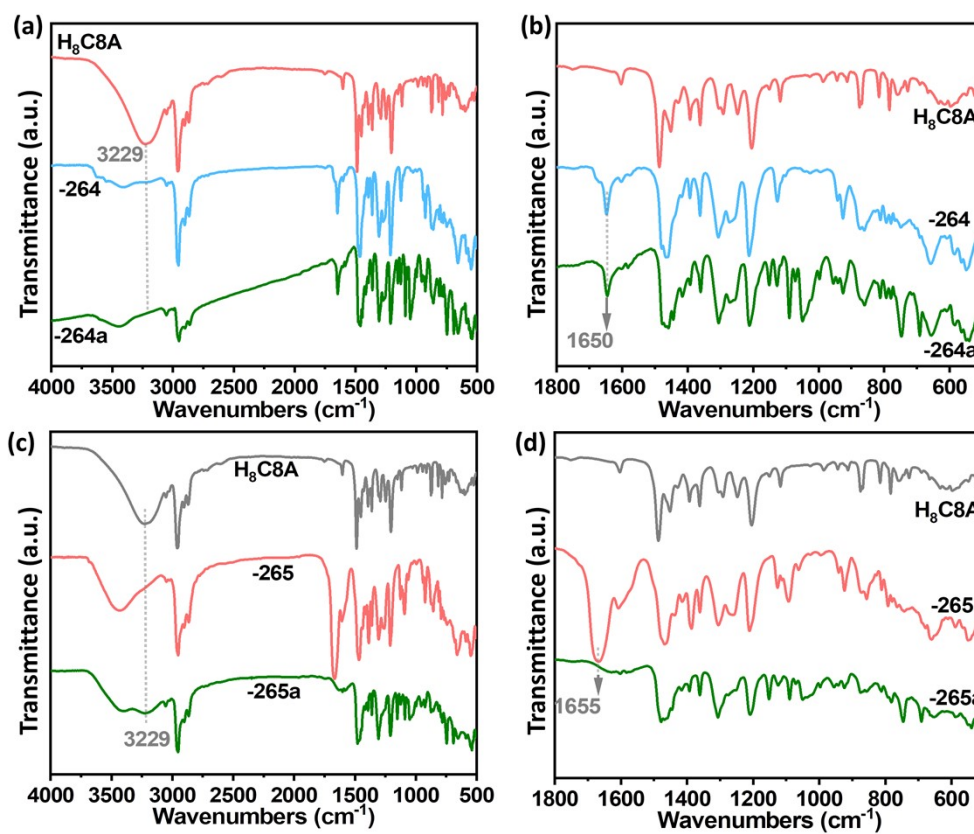


**Figure S10.** The GC-MS analysis of catalytic sulfoxidation of 4-nitrothioanisole (a, b) and diphenyl sulfide (c, d) to corresponding sulfoxide and sulfone in the presence of CIAC-264 or -265.

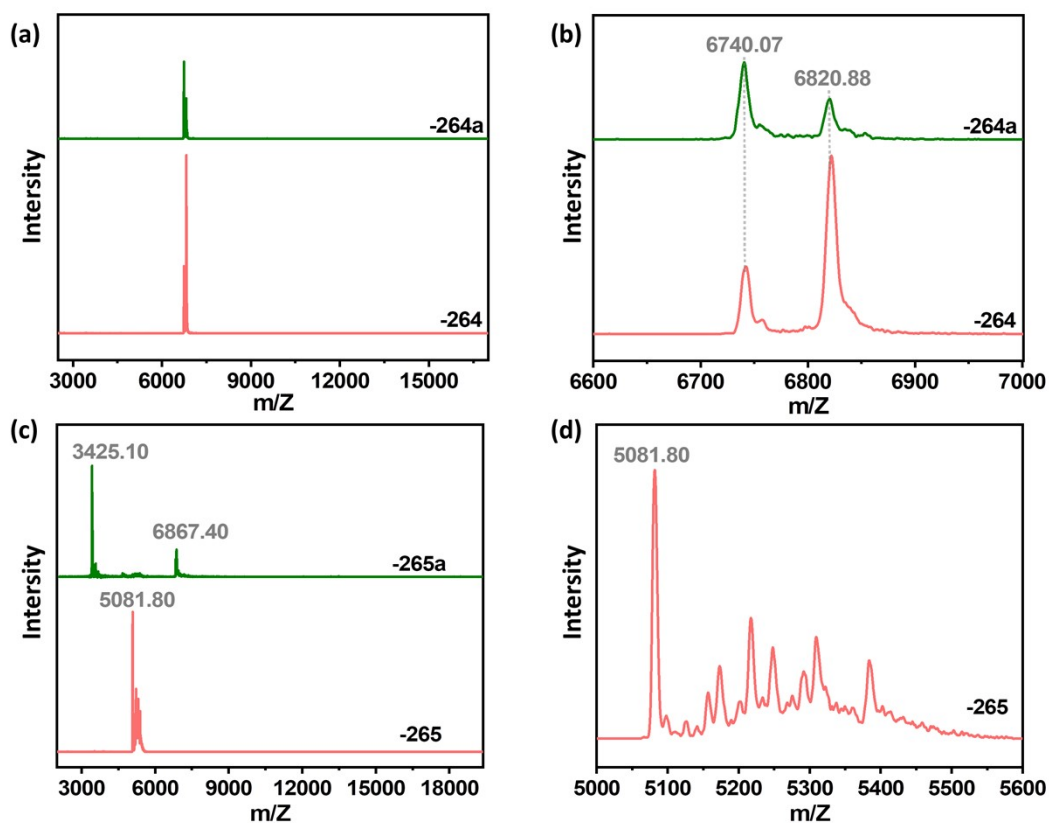


**Figure S11.** The GC-MS analysis of catalytic sulfoxidation of dibenzothiophene (a, b) and methyl phenyl sulfide (c, d) to corresponding sulfoxide and sulfone in the presence of **CIAC-264** or **-265**.

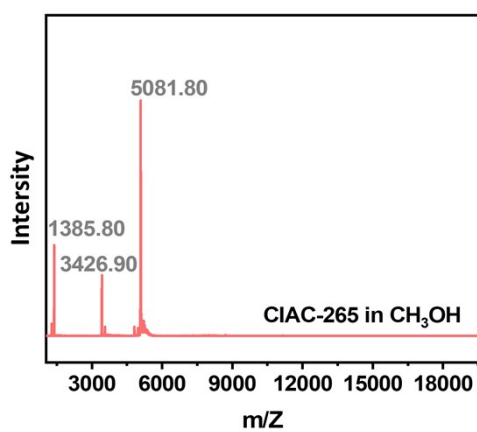
Prior to the quantitative analysis of the reaction mixture by gas chromatography (GC), qualitative analysis of the reaction mixture by gas chromatography mass spectrometry (GC-MS) is performed, as shown in [Figure S9-S11](#). The results of GC-MS demonstrated that both **CIAC-264** and **-265** efficiently catalyze the sulfides to the corresponding sulfoxides or sulfone without by-products.



**Figure S12.** FT-IR spectra of CIAC-264 (a, b) and -265 (c, d) before and after catalytic reaction.



**Figure S13.** The MALDI-TOF MS spectra of CIAC-264 (a, b) and -265 (c, d) before and after catalytic reaction.



**Figure S14.** The MALDI-TOF MS spectra of CIAC-265 in CH<sub>3</sub>OH.

**Table S2** The conversion of MPS with compound **CIAC-262** in different reaction time and reaction temperature.

Cat	Solvent	Time (h)	Temperature (K)	Oxidant	Conv. (%)	Sel. <sup>a</sup> (%)
<b>CIAC-262</b>	Methanol	1	313	H <sub>2</sub> O <sub>2</sub>	32.40	96.85
<b>CIAC-262</b>	Methanol	2	313	H <sub>2</sub> O <sub>2</sub>	48.60	97.88
<b>CIAC-262</b>	Methanol	3	313	H <sub>2</sub> O <sub>2</sub>	48.60	98.07
<b>CIAC-262</b>	Methanol	1	298	H <sub>2</sub> O <sub>2</sub>	7.54	95.98
<b>CIAC-262</b>	Methanol	1	313	H <sub>2</sub> O <sub>2</sub>	26.60	96.17
<b>CIAC-262</b>	Methanol	1	333	H <sub>2</sub> O <sub>2</sub>	65.40	98.32

Experiment condition: 0.5 mmol of methyl phenyl sulfide, 0.5 mmol of 30% H<sub>2</sub>O<sub>2</sub>, 0.001 mmol of compound **CIAC-262**, in methanol (2 mL). Products were quantified by GC analysis. <sup>a</sup> Selectivity to sulfoxide = (sulfoxide/(sulfoxide + sulfone)) × 100.

**Table S3** The conversion of MPS with compound **CIAC-263** in different reaction time and reaction temperature.

Cat	Solvent	Time (h)	Temperature (K)	Oxidant	Conv. (%)	Sel. <sup>a</sup> (%)
<b>CIAC-263</b>	Methanol	1	313	H <sub>2</sub> O <sub>2</sub>	60.00	96.00
<b>CIAC-263</b>	Methanol	2	313	H <sub>2</sub> O <sub>2</sub>	66.40	95.46
<b>CIAC-263</b>	Methanol	3	313	H <sub>2</sub> O <sub>2</sub>	66.20	95.79
<b>CIAC-263</b>	Methanol	1	298	H <sub>2</sub> O <sub>2</sub>	25.60	95.65
<b>CIAC-263</b>	Methanol	1	313	H <sub>2</sub> O <sub>2</sub>	60.00	96.01
<b>CIAC-263</b>	Methanol	1	333	H <sub>2</sub> O <sub>2</sub>	74.20	95.51

Experiment condition: 0.5 mmol of methyl phenyl sulfide, 0.5 mmol of 30% H<sub>2</sub>O<sub>2</sub>, 0.001 mmol of compound **CIAC-263**, in methanol (2 mL). Products were quantified by GC analysis. <sup>a</sup> Selectivity to sulfoxide = (sulfoxide/(sulfoxide + sulfone)) × 100.

**Table S4** The conversion of MPS with compound **CIAC-264** in different reaction time, reaction temperature, oxidant, and solvent.

Cat	Solvent	Time (h)	Temperature (K)	Oxidant	Conv. (%)	Sel. <sup>a</sup> (%)
<b>CIAC-264</b>	Methanol	1	313	H <sub>2</sub> O <sub>2</sub>	88.20	97.74
<b>CIAC-264</b>	Methanol	2	313	H <sub>2</sub> O <sub>2</sub>	91.20	96.51
<b>CIAC-264</b>	Methanol	3	313	H <sub>2</sub> O <sub>2</sub>	93.20	97.26
<b>CIAC-264</b>	Methanol	1	298	H <sub>2</sub> O <sub>2</sub>	96.00	98.28
<b>CIAC-264</b>	Methanol	1	313	H <sub>2</sub> O <sub>2</sub>	91.06	96.90
<b>CIAC-264</b>	Methanol	1	333	H <sub>2</sub> O <sub>2</sub>	36.00	98.85
<b>CIAC-264</b>	Methanol	1	298	H <sub>2</sub> O <sub>2</sub>	96.29	98.03
<b>CIAC-264</b>	Ethanol	1	298	H <sub>2</sub> O <sub>2</sub>	91.08	94.26
<b>CIAC-264</b>	Tetrahydrofuran	1	298	H <sub>2</sub> O <sub>2</sub>	73.28	70.88
<b>CIAC-264</b>	Acetonitrile	1	298	H <sub>2</sub> O <sub>2</sub>	72.61	81.32
<b>CIAC-264</b>	Octane	1	298	H <sub>2</sub> O <sub>2</sub>	0	--
<b>CIAC-264</b>	Methanol	1	298	--	0	--
<b>CIAC-264</b>	Methanol	1	298	TBHP	19.61	100

Experiment condition: 0.5 mmol of methyl phenyl sulfide, 0.5 mmol of oxidant (TBHP or 30% H<sub>2</sub>O<sub>2</sub>), 0.001 mmol of compound **CIAC-264**, in solvent (2 mL).

Products were quantified by GC analysis. <sup>a</sup> Selectivity to sulfoxide = (sulfoxide/(sulfoxide + sulfone)) × 100.

**Table S5** The conversion of MPS with compound **CIAC-265** in different reaction time, reaction temperature, oxidant, and solvent.



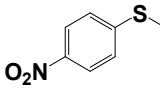
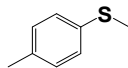
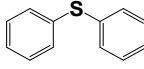
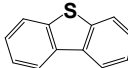
Cat	Solvent	Time (h)	Temperature (K)	Oxidant	Conv. (%)	Sel. <sup>a</sup> (%)
<b>CIAC-265</b>	Methanol	1	313	H <sub>2</sub> O <sub>2</sub>	89.80	85.71
<b>CIAC-265</b>	Methanol	2	313	H <sub>2</sub> O <sub>2</sub>	89.60	84.96
<b>CIAC-265</b>	Methanol	3	313	H <sub>2</sub> O <sub>2</sub>	87.56	85.23
<b>CIAC-265</b>	Methanol	1	298	H <sub>2</sub> O <sub>2</sub>	86.20	86.91
<b>CIAC-265</b>	Methanol	1	313	H <sub>2</sub> O <sub>2</sub>	86.20	84.92
<b>CIAC-265</b>	Methanol	1	333	H <sub>2</sub> O <sub>2</sub>	87.40	86.73
<b>CIAC-265</b>	Methanol	1	298	H <sub>2</sub> O <sub>2</sub>	85.71	87.52
<b>CIAC-265</b>	Ethanol	1	298	H <sub>2</sub> O <sub>2</sub>	77.82	75.88
<b>CIAC-265</b>	Tetrahydrofuran	1	298	H <sub>2</sub> O <sub>2</sub>	58.18	44.67
<b>CIAC-265</b>	Acetonitrile	1	298	H <sub>2</sub> O <sub>2</sub>	43.51	50.64
<b>CIAC-265</b>	Octane	1	298	H <sub>2</sub> O <sub>2</sub>	0	--
<b>CIAC-265</b>	Methanol	1	298	--	0	--
<b>CIAC-265</b>	Methanol	1	298	TBHP	19.90	100
--	Methanol	1	313	H <sub>2</sub> O <sub>2</sub>	2.60	100

Experiment condition: 0.5 mmol of methyl phenyl sulfide, 0.5 mmol of oxidant (TBHP or 30% H<sub>2</sub>O<sub>2</sub>), 0.001 mmol of compound **CIAC-265**, in solvent (2 mL).

Products were quantified by GC analysis. <sup>a</sup> Selectivity to sulfoxide = (sulfoxide/(sulfoxide + sulfone)) × 100.



**Table S6** The compounds **CIAC-264** and **-265** catalyzed oxidation of organic sulfides with 30% H<sub>2</sub>O<sub>2</sub> in THF.

Substrate		Conv. (%)	
		<b>-264</b>	<b>-265</b>
Methyl phenyl sulfide (MPS)		73.28	58.18
Diethyl sulfide (DES)		72.84	60.97
4-Nitrothioanisole (4-NMPS)		70.88	63.59
Methyl <i>p</i> -tolyl sulfide (4-MMPS)		56.10	57.15
Diphenyl sulfide (PPS)		22.09	54.49
Dibenzothiophene (DBT)		6.45	7.05

Reaction conditions: 0.5 mmol of organic sulfide, 0.5 mmol of 30% H<sub>2</sub>O<sub>2</sub>, 0.001 mmol of catalyst, 0.1 mmol of tetradecane in THF (2 mL). Products were quantified by GC analysis with respect to internal standard.