

Supplementary Data

Assembly of polyoxometalate-thiacalix[4]arene-based inorganic-organic hybrids as efficient catalytic oxidation desulfurization catalysts

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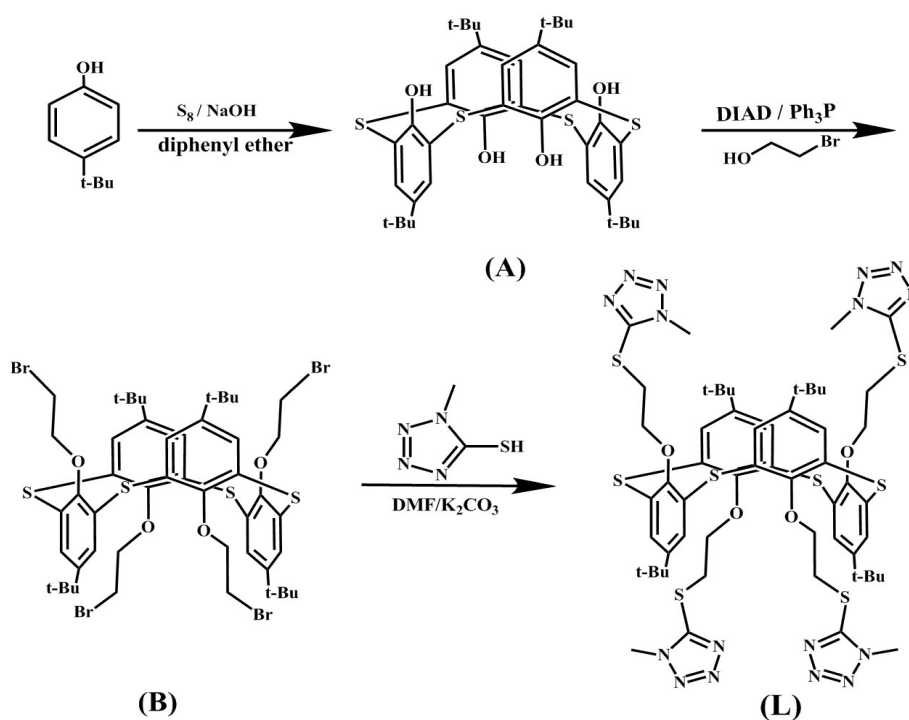
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Materials and instrumentation. Chemicals are purchased commercially. FT-IR spectra were measured on a Mattson Alpha-Centauri spectrometer. C, H and N contents were carried out on a Euro vector EA3000 elemental analyzer. Thermogravimetric curves were measured on a PerkinElmer TG-7 analyzer under nitrogen gas. ¹H NMR data were recorded in CDCl₃ on a Bruker 500 MHz and 600 MHz. Rigaku Dmx 2000 X-ray diffractometer with graphite monochromatized Cu K α radiation ($\lambda = 0.154 \text{ \AA}$) was used to measure powder X-ray diffraction (PXRD) patterns. ICP measurements were conducted on a Leeman Laboratories Prodigy inductively coupled plasma-optical atomic emission spectrometer (ICP-AES). HPLC and GC equipments were used to record the conversions of the substrates.

X-ray crystallography. Single crystal X-ray diffraction data of **1-3** were measured on an Oxford Diffraction Gemini R CCD diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Their crystal structures were solved by direct methods and refined on F² by full-matrix least-squares with SHELXL-2018/3.¹ Non-hydrogen atoms were located from difference Fourier maps

and refined anisotropically. Selected bond distances and angles were given in Table S2.

Synthesis of L. The intermediate A and B were synthesized according to previously reported method.^{2,3} A mixture of B (4.59 g, 4 mmol), K₂CO₃ (5.53 g, 40 mmol), DMF (250 mL) and 5-mercapto-1-methyltetrazole (2.36 g, 20 mmol) were heated for 10 h under nitrogen protection at 90°C. Then, cooled the solution and removed the solvent. The resulting mixture was stirred in water (150 mL) for 30 minutes. L ligand was obtained by filtration and washed with water for several times (yield: 67%). The characterization of L ligand was performed by ¹H NMR and IR (Figures S10a and S1a). ¹H NMR spectrum of L (600 MHz, CDCl₃): δ 7.49 (s, 8H), 4.28 (m, 8H), 3.90 (s, 12H), 2.87 (dd, 8H), 1.18 (s, 36H). IR (KBr, cm⁻¹): 3430 (w), 2962 (s), 2911 (m), 2874 (m), 1574 (w), 1542 (w), 1473 (s), 1440 (s), 1418 (m), 1383 (s), 1266 (s), 1240 (s), 1165 (s), 1089 (s), 1000 (s), 933 (w), 874 (m), 836 (m), 798 (w), 770 (w), 749 (w), 701 (m), 642 (w), 604 (w), 534 (w), 490 (w).



Scheme S1. Synthetic route for the L ligand.

References

1 D. Kratzert, J. J. Holstein and I. Krossing, *J. Appl. Crystallogr.*, 2015, **48**, 933-938.

2 N. Kon, N. Iki and S. Miyano, *Tetrahedron Lett.*, 2002, **43**, 2231-2234.

3 A. S. Ovsyannikov, M. H. Noamane, R. Abidi, S. Ferlay, S. E. Solovieva, I. S. Antipin, A. I. Konovalov, N. Kyritsakas and M. W. Hosseini, *CrystEngComm*, 2016, **18**, 691-703.

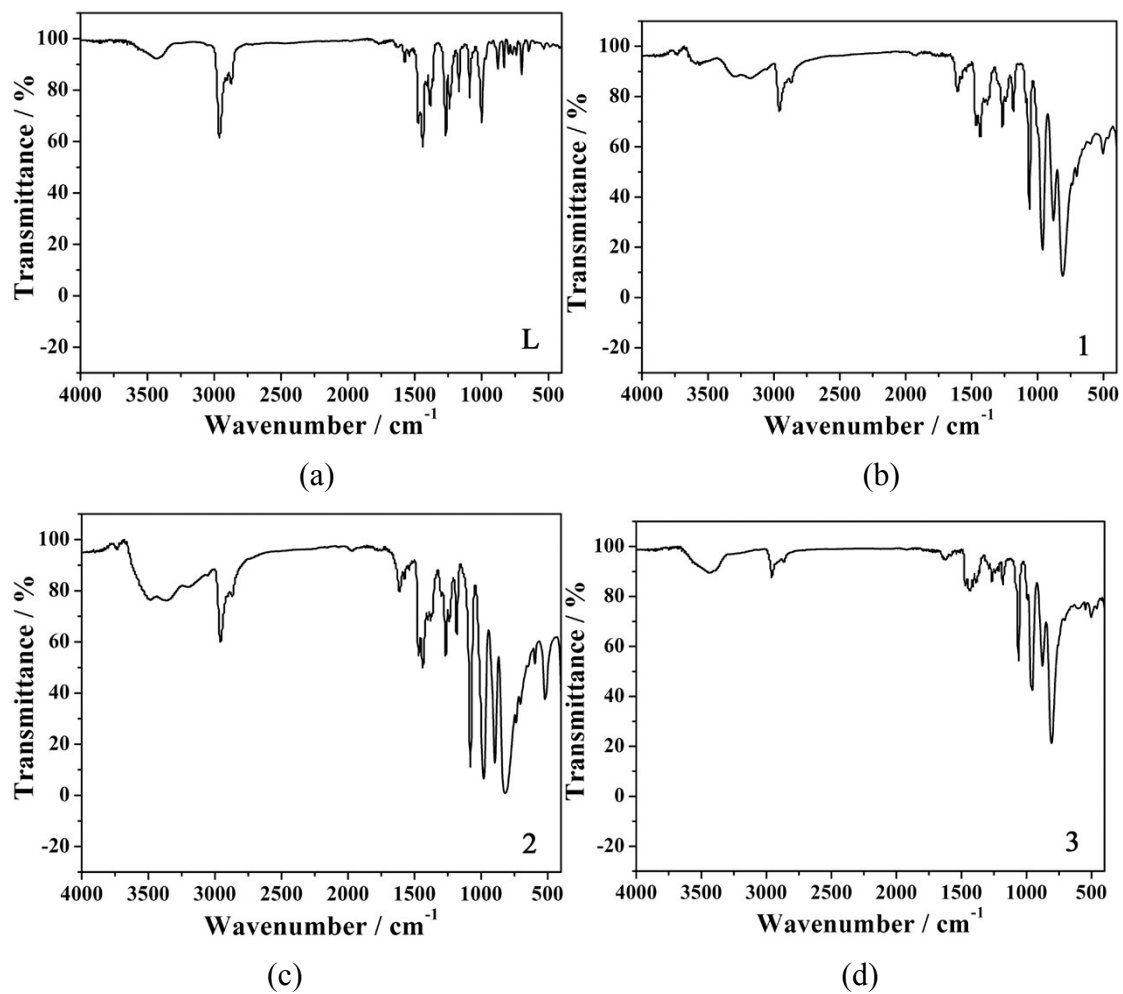


Fig. S1 IR spectra of L (a), 1 (b), 2 (c) and 3 (d).

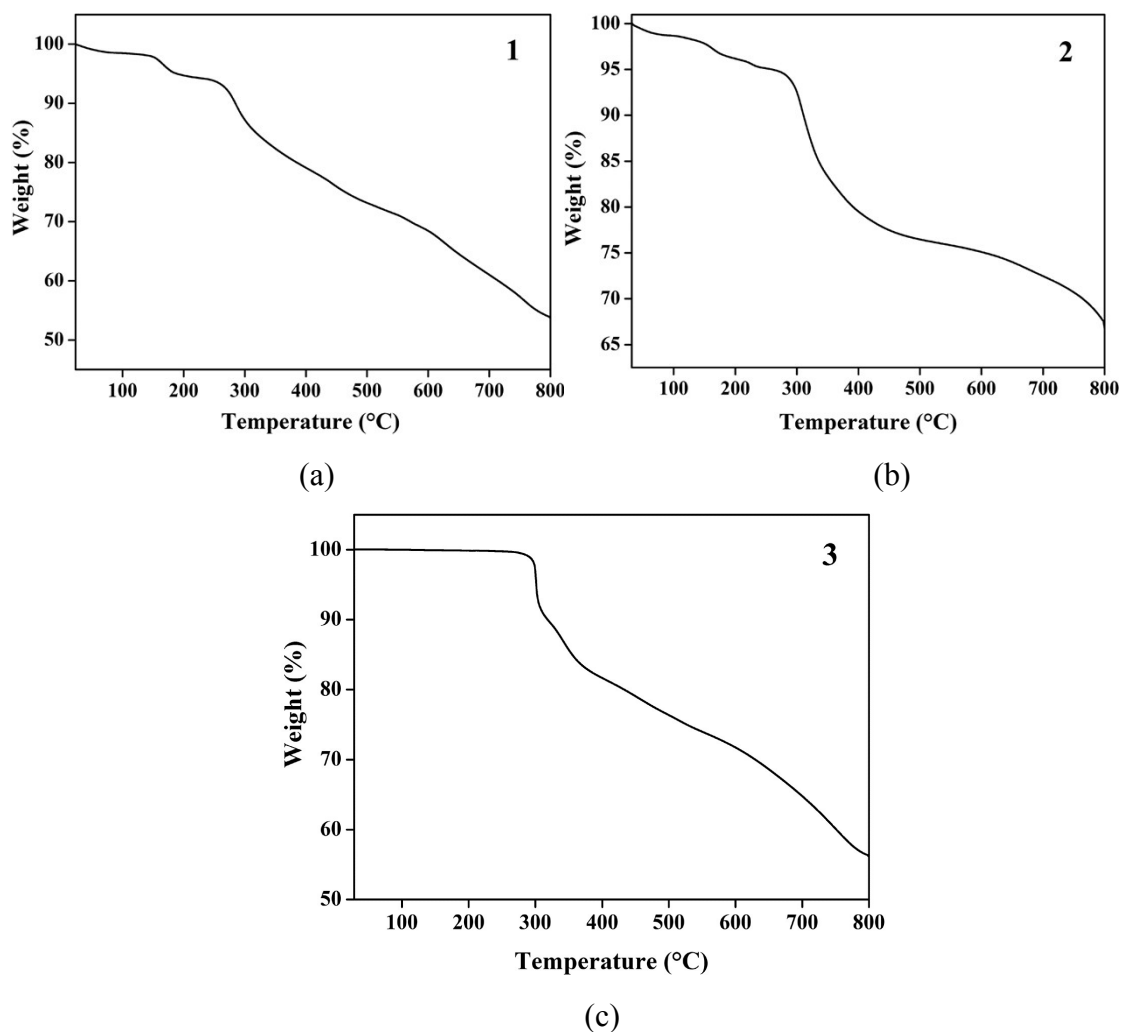


Fig. S2 Thermogravimetric curves: (a) The weight of loss corresponds to the water molecules and CH_3OH molecules before 218 °C for **1** (found: 5.80%, calcd: 5.77%). (b) The weight of loss corresponds to the water molecules and CH_3OH molecules before 227 °C for **2** (found: 4.43%, calcd: 4.45%). (c) The weight of loss for **3**.

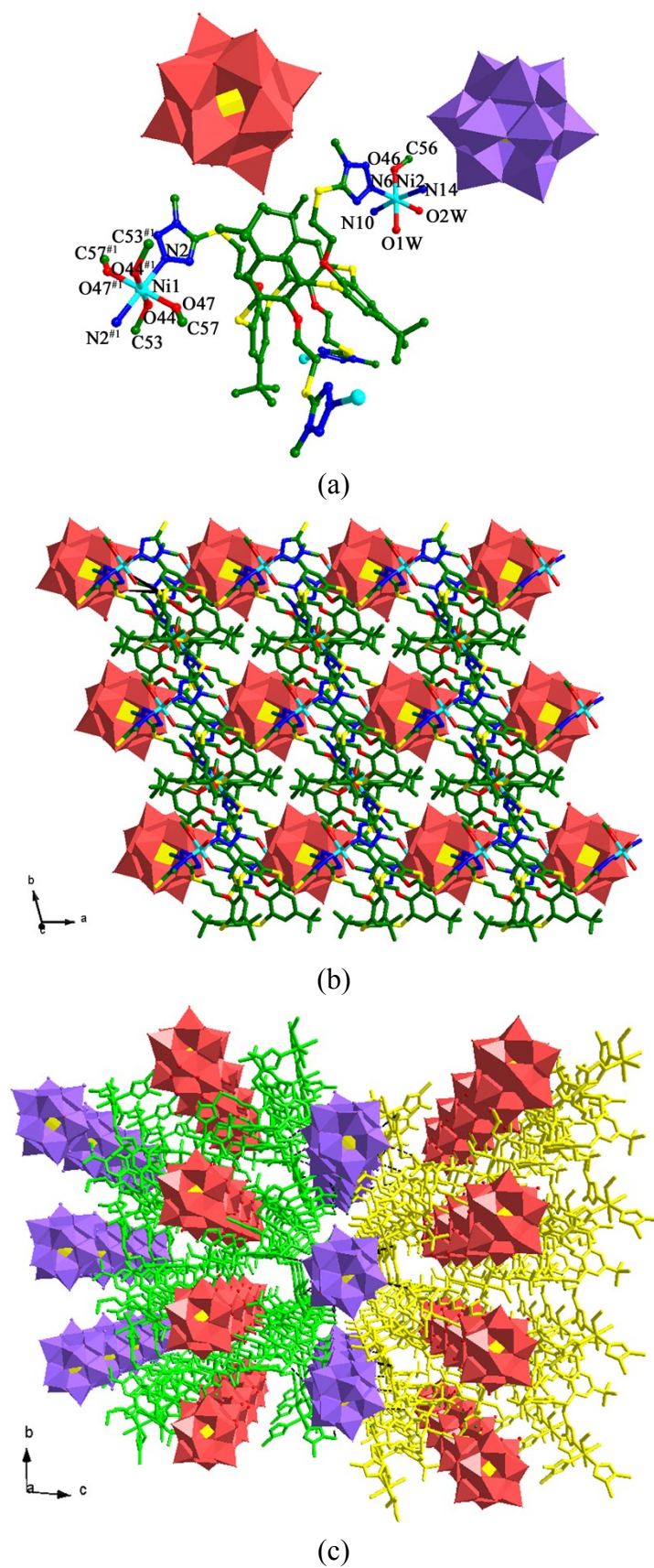


Fig. S3 (a) Coordination spheres of Ni(II) cations in **2**. (b) 2D layered architecture. (c) The 3D supramolecular architecture formed by hydrogen bonds.

Table S1 Hydrogen Bonds for **1** and **2** (Å and °)

	D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
1	C18-H18B···O45	0.961	2.628	3.17(4)	116.43
	C31-H31B···O32 ^{#3}	0.959	2.467	3.11(8)	125.00
	C45-H45B···O11 ^{#4}	0.960	2.464	3.11(5)	124.95
	C57-H57C···O36	0.960	2.546	3.30(2)	135.71
	C59-H59A···O16 ^{#5}	0.960	2.159	3.11(3)	172.30

Symmetry code for **2**: ^{#3} x+1, y, z; ^{#4} -x, -y+2, -z; ^{#5} -x, -y-1, -z.

	D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
2	C3-H3C···O23	0.965	2.464	3.39(4)	161.85
	C14-H14B···O31 ^{#3}	0.960	2.569	3.21(9)	125.19
	C39-H39B···O29	0.959	2.504	3.12(6)	122.55
	C54-H54C···O9	0.959	2.664	3.40(5)	133.54
	C58-H58B···O17 ^{#2}	0.960	2.527	3.20(4)	127.56

Symmetry code for **2**: ^{#2} x+1, y, z; ^{#3} -x+2, -y-2, -z.**Table S2** Selected Bond Distances (Å) and Angles (deg) for **1-3**

	Ni(1)-O(47)	2.017(8)	Ni(2)-O(1W)	2.059(7)
	Ni(1)-O(44)	2.057(7)	Ni(2)-N(10) ^{#2}	2.082(8)
	Ni(1)-N(2)	2.069(9)	Ni(2)-N(6)	2.092(9)
	Ni(2)-O(46)	2.043(8)	Ni(2)-N(14)	2.075(8)
1	Ni(2)-O(2W)	2.091(7)	O(47) ^{#1} -Ni(1)-N(2)	87.7(3)
	O(47)-Ni(1)-O(44)	93.1(3)	O(47)-Ni(1)-O(44) ^{#1}	86.9(3)
	O(44) ^{#1} -Ni(1)-N(2)	91.9(3)	O(44)-Ni(1)-N(2)	88.1(3)
	O(47)-Ni(1)-N(2)	92.3(3)	O(46)-Ni(2)-N(14)	92.5(4)
	O(46)-Ni(2)-O(1W)	177.1(3)	O(46)-Ni(2)-N(10) ^{#2}	87.3(3)

O(1W)-Ni(2)-N(14)	88.5(3)	N(14)-Ni(2)-N(10) ^{#2}	93.8(3)
O(1W)-Ni(2)-N(10) ^{#2}	89.9(3)	O(2W)-Ni(2)-N(6)	83.1(3)
O(46)-Ni(2)-O(2W)	93.5(4)	O(1W)-Ni(2)-O(2W)	89.3(3)
N(14)-Ni(2)-O(2W)	88.9(3)	N(10) ^{#2} -Ni(2)-O(2W)	177.2(3)
O(46)-Ni(2)-N(6)	90.0(4)	O(1W)-Ni(2)-N(6)	89.4(3)
N(14)-Ni(2)-N(6)	171.7(3)	N(10) ^{#2} -Ni(2)-N(6)	94.2(3)

Symmetry codes for **1**: ^{#1} -x+1, -y+1, -z; ^{#2} x, y-1, z.

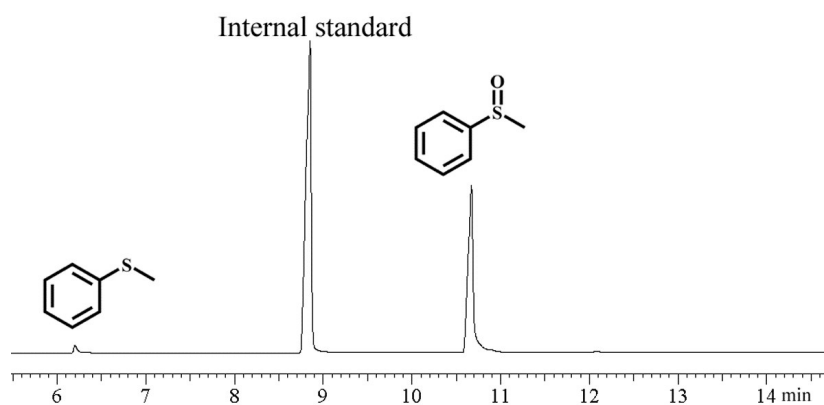
Ni(1)-O(44)	2.064(15)	Ni(2)-O(46)	2.040(11)
Ni(1)-O(47)	2.078(10)	Ni(2)-N(6)	2.098(12)
Ni(1)-N(2)	2.084(12)	Ni(2)-N(10)	2.099(14)
Ni(2)-O(1W)	2.040(10)	Ni(2)-N(14)	2.100(11)
Ni(2)-O(2W)	2.074(10)	O(44) ^{#1} -Ni(1)-O(47)	92.3(5)
O(44)-Ni(1)-N(2) ^{#1}	92.0(5)	O(44)-Ni(1)-O(47)	87.7(5)
O(47)-Ni(1)-N(2)	89.0(5)	O(44)-Ni(1)-N(2)	88.0(5)
2 O(46)-Ni(2)-O(2W)	92.8(5)	O(47)-Ni(1)-N(2) ^{#1}	91.0(5)
O(46)-Ni(2)-N(6)	87.4(5)	O(46)-Ni(2)-O(1W)	177.4(4)
O(2W)-Ni(2)-N(6)	177.6(5)	O(1W)-Ni(2)-O(2W)	89.4(4)
O(1W)-Ni(2)-N(14)	87.6(5)	O(1W)-Ni(2)-N(6)	90.3(4)
N(6)-Ni(2)-N(14)	92.9(5)	O(46)-Ni(2)-N(14)	93.8(5)
O(1W)-Ni(2)-N(10)	88.9(5)	O(2W)-Ni(2)-N(14)	89.4(4)
N(14)-Ni(2)-N(10)	172.5(5)	O(46)-Ni(2)-N(10)	90.0(5)
N(6)-Ni(2)-N(10)	93.6(5)	O(2W)-Ni(2)-N(10)	84.0(4)

Symmetry code for **2**: ^{#1} -x+3, -y-3, -z.

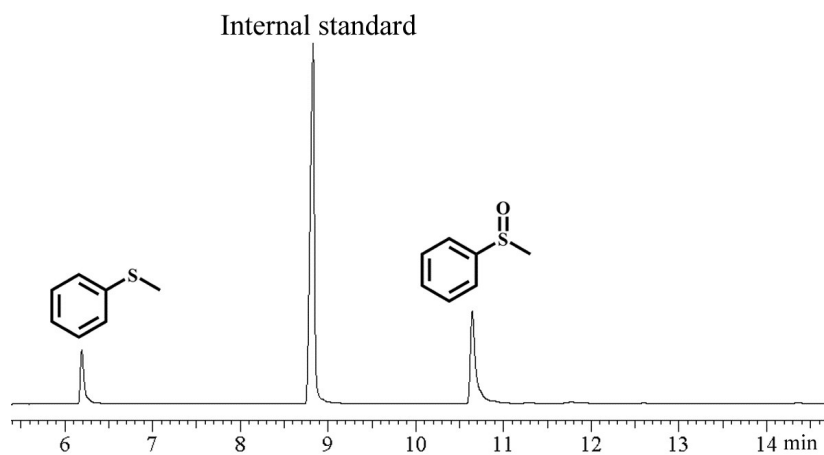
3 Ag(1)-N(1)	2.199(11)	Ag(1)-S(1)	2.505(3)
Ag(1)-N(6)	2.294(11)	Ag(1)-O(3)	2.7272(1)

Ag(2)-Ag(2) ^{#1}	2.679(8)	Ag(2)-N(2)	2.277(14)
Ag(2)-O(18)	2.8963(1)	N(1)-Ag(1)-N(6)	127.3(4)
N(1)-Ag(1)-S(1)	143.7(3)	N(1)-Ag(1)-O(3)	88.120(2)
N(6)-Ag(1)-S(1)	88.9(3)	N(6)-Ag(1)-O(3)	105.849(1)
S(1)-Ag(1)-O(3)	78.032(1)	N(2)-Ag(2)-Ag(2) ^{#1}	165.5(4)
N(2)-Ag(2)-O(18)	84.912(1)	O(18)-Ag(2)-Ag(2) ^{#1}	92.105(1)

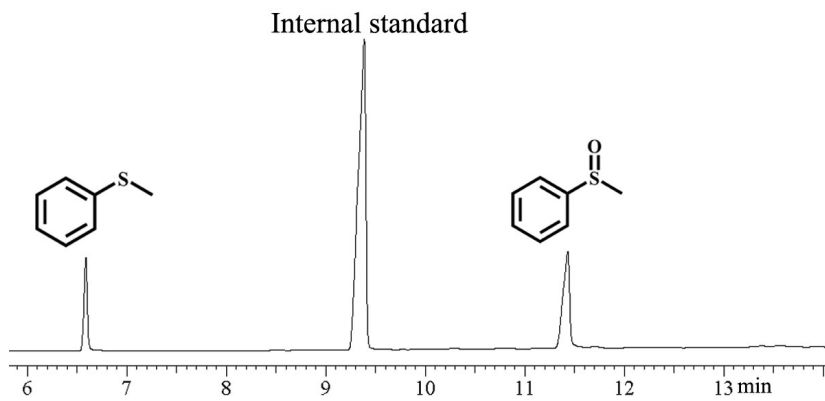
Symmetry code for **3**: ^{#1} $-x+1/2, -y+3/2, -z$.



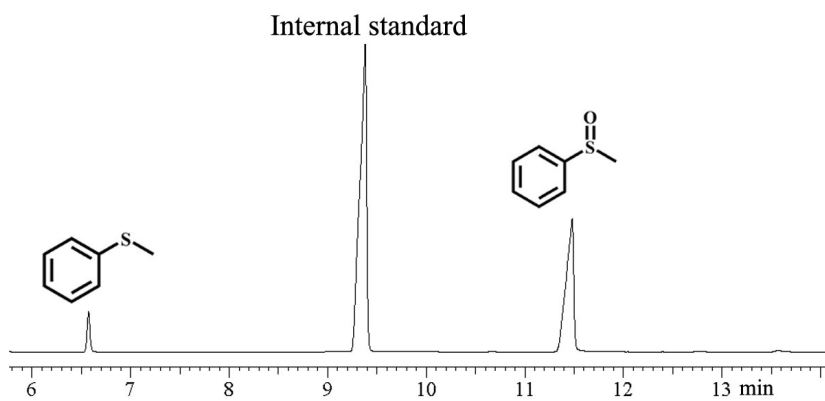
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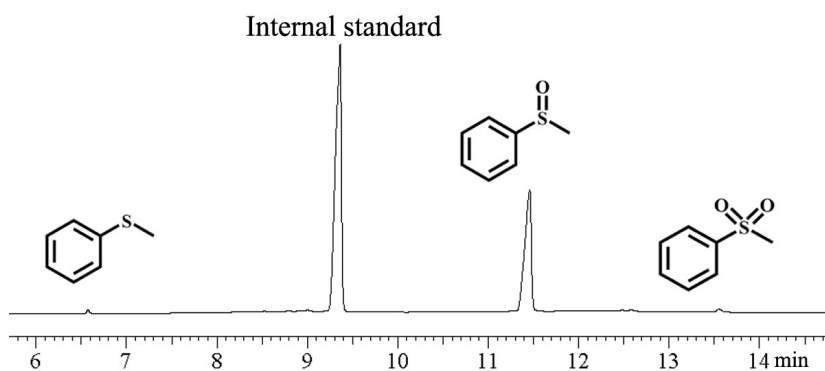
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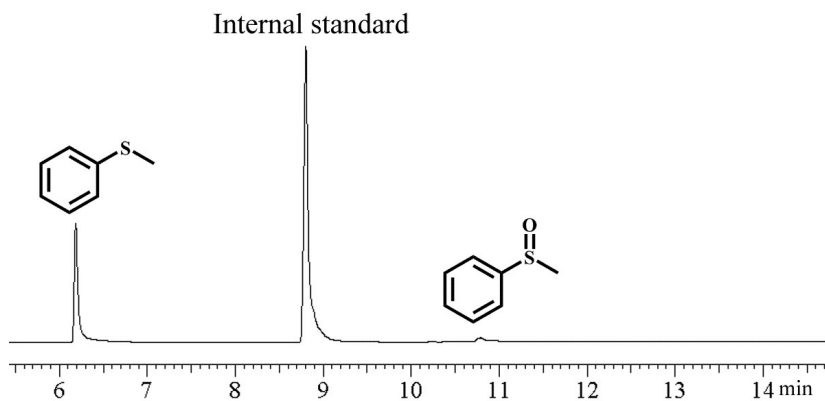
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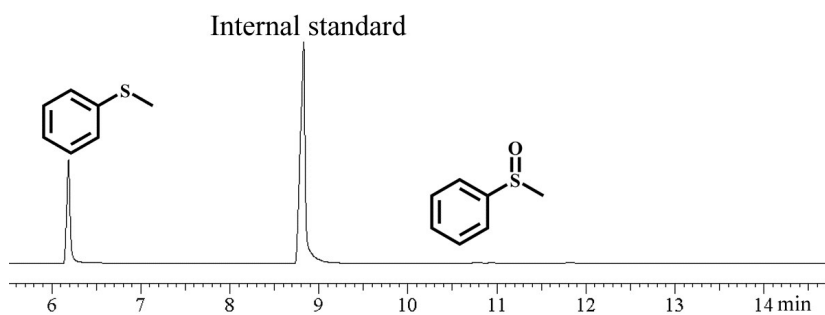
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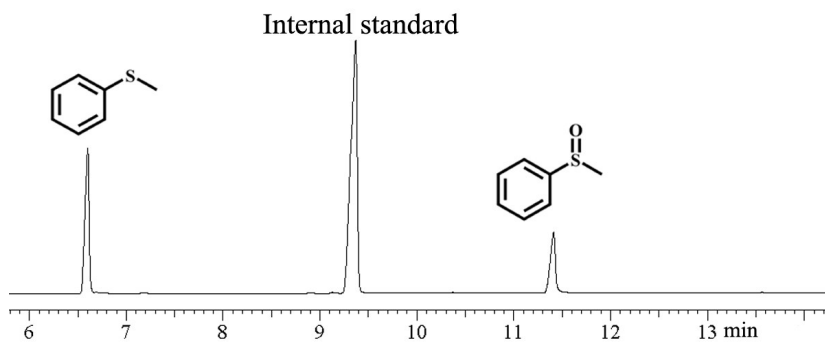
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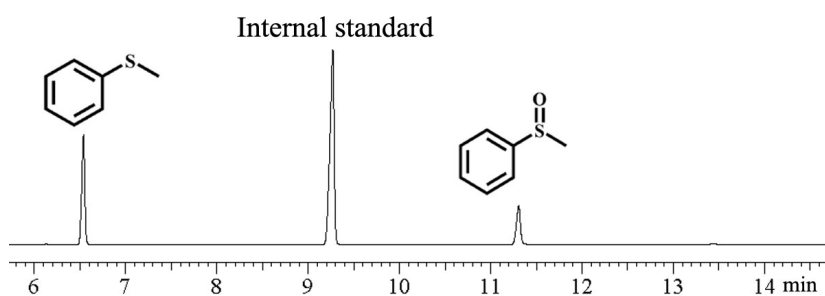
(f)



(g)



(h)



(i)

Fig. S4 GC of the oxidative desulfurization using MBT as the substrate at 25 °C in CH_2Cl_2 . (a) $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ as catalyst and TBHP as oxidant for 3 h. (b) $\text{H}_3\text{PW}_{12}\text{O}_{40}$ as catalyst and TBHP as oxidant for 3 h. (c) **1** as catalyst and TBHP as oxidant for 1 h. (d) **1** as catalyst and TBHP as oxidant for 2 h. (e) **1** as catalyst and TBHP as oxidant for 3 h. (f) $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ as catalyst and TBHP as oxidant for 3 h. (g) **L** as catalyst and TBHP as oxidant for 3 h. (h) TBHP as oxidant for 3 h. (i) **1** as catalyst and H_2O_2 as oxidant for 3 h.

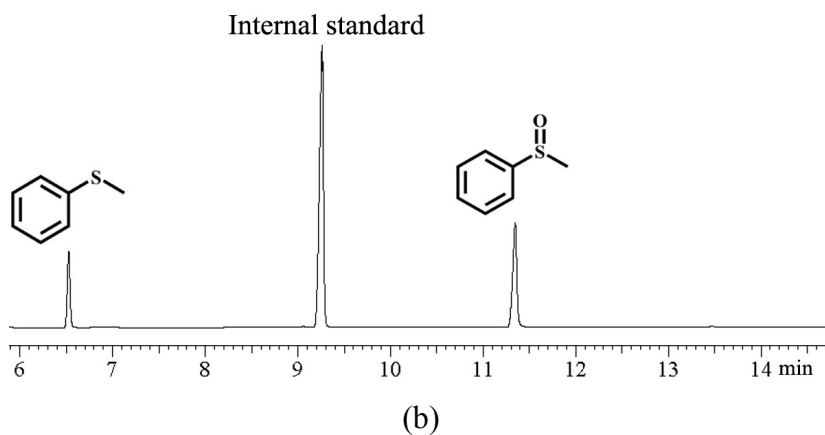
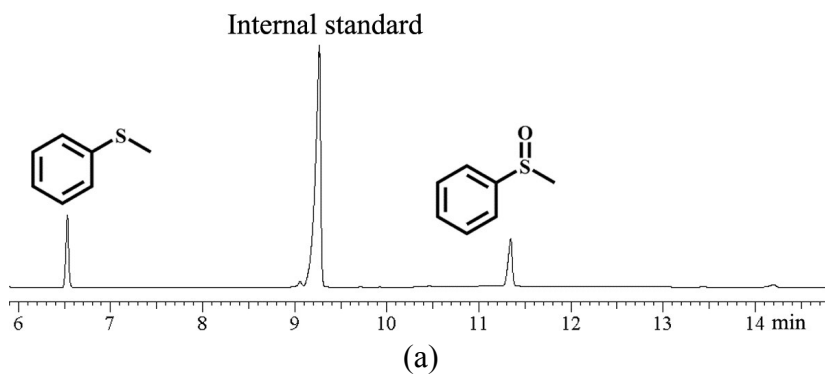
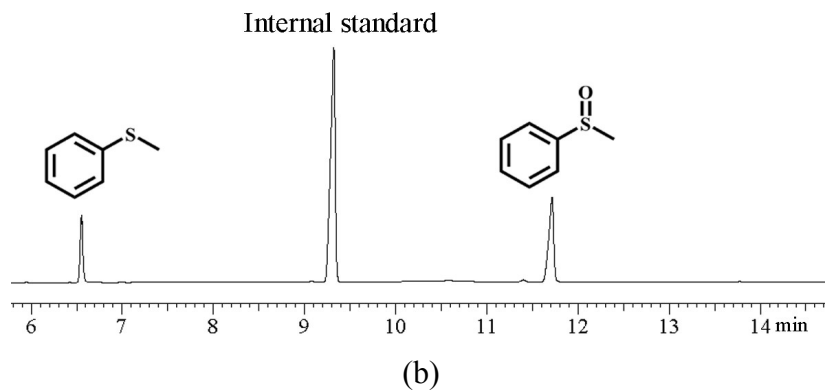
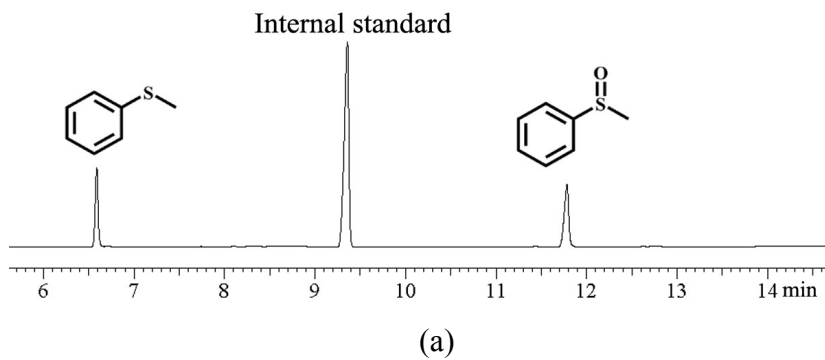


Fig. S5 GC of the oxidative desulfurization using MBT as the substrate, **1** as catalyst and TBHP as oxidant at 25 °C for 3 h. (a) in methanol. (b) in ethanol.



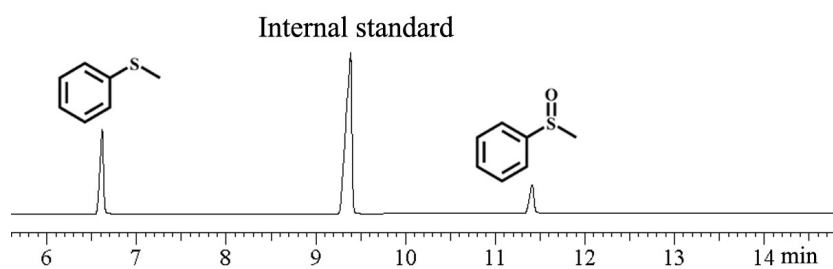
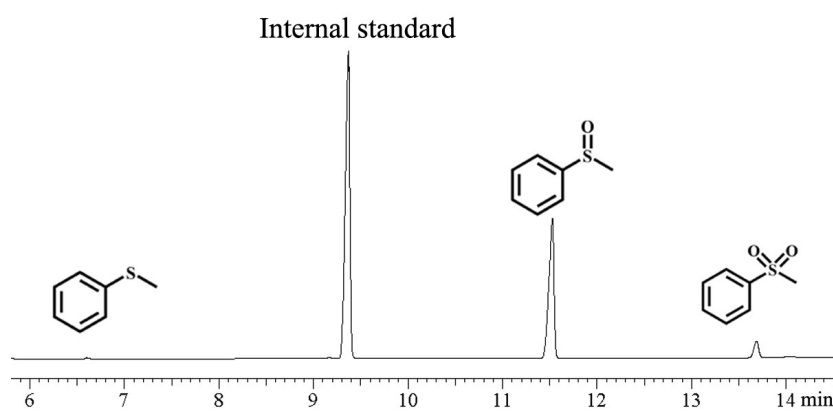
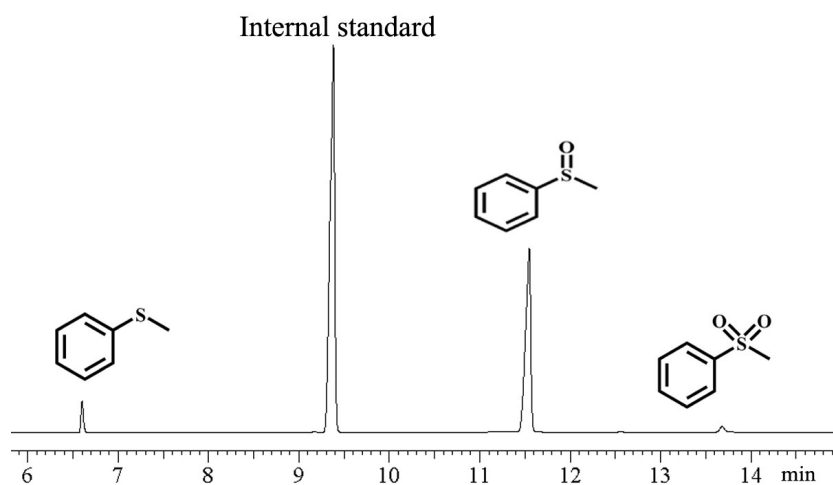
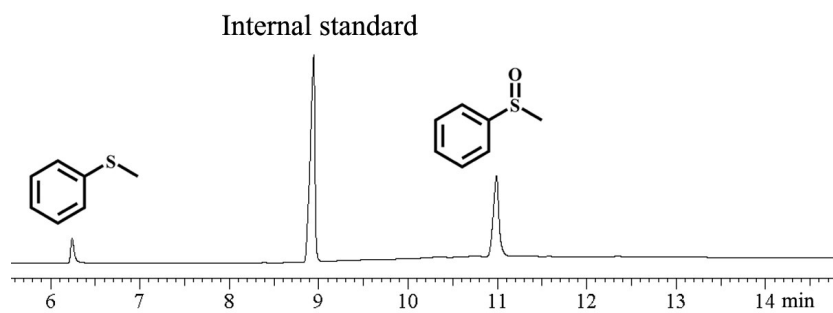


Fig. S6 GC of the oxidative desulfurization using MBT as the substrate in CH_2Cl_2 . (a)

3 as catalyst and TBHP as oxidant at 25 °C for 3 h. (b) **3** as catalyst and TBHP as oxidant at 40 °C for 2 h. (c) **3** as catalyst and TBHP as oxidant at 40 °C for 3 h. (d) **3** as catalyst and TBHP as oxidant at 50 °C for 1 h. (e) **3** as catalyst and TBHP as oxidant at 50 °C for 2 h. (f) TBHP as oxidant for at 50 °C 2 h.

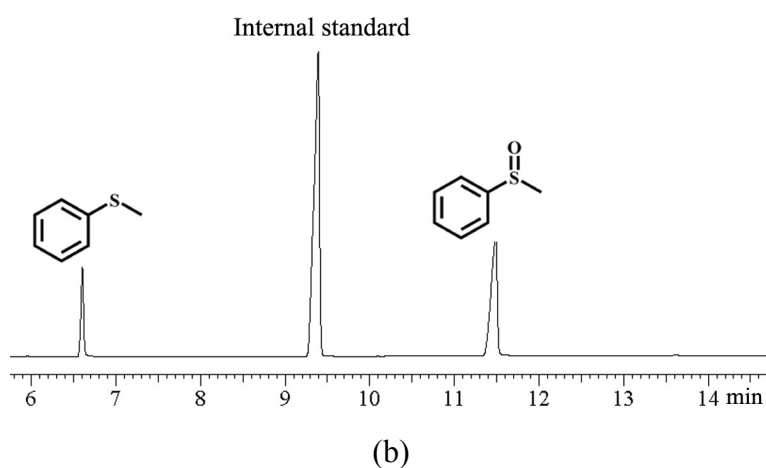
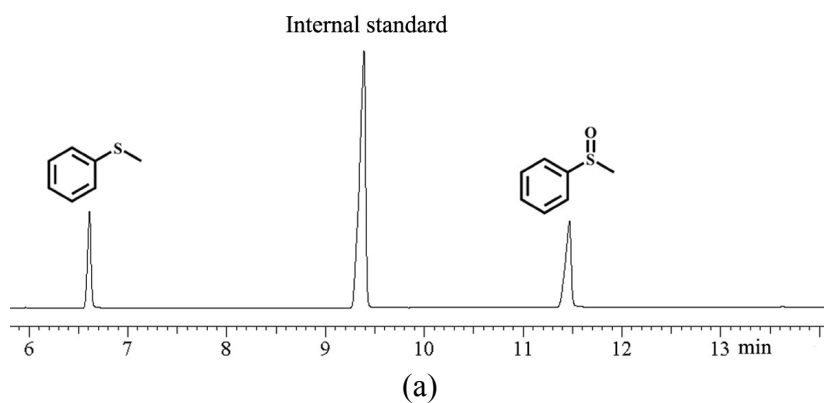
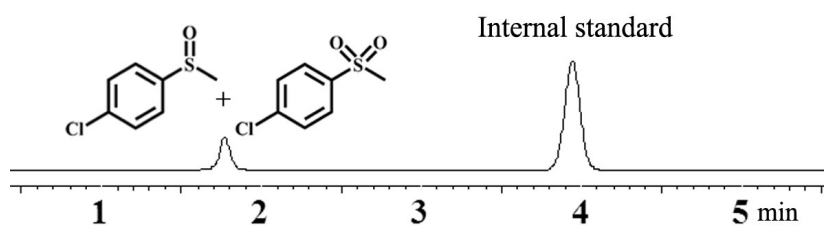
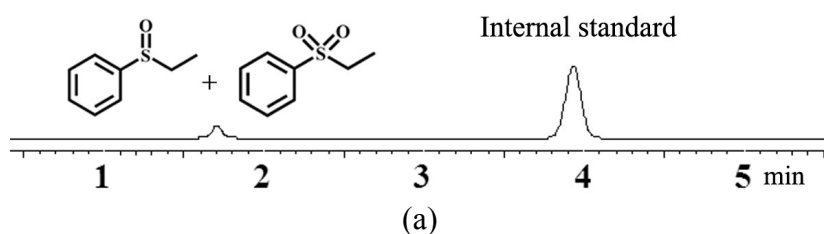
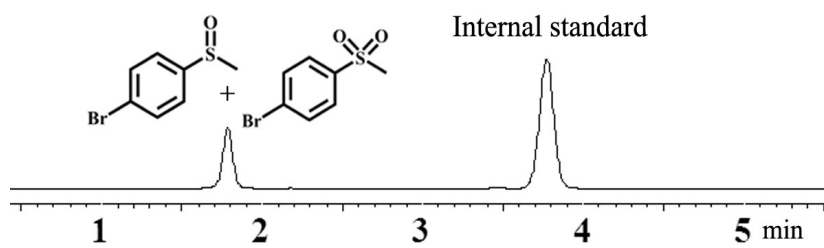


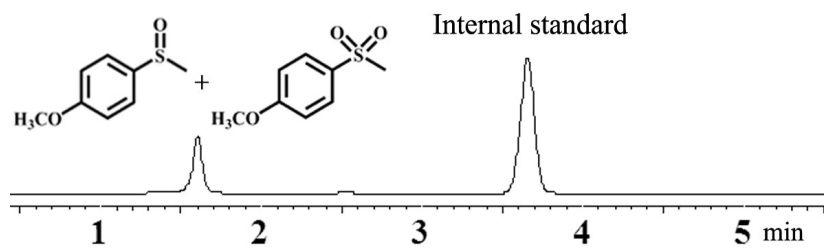
Fig. S7 GC of the oxidative desulfurization using MBT as the substrate, **3** as catalyst and TBHP as oxidant at 50 °C for 2 h. (a) in methanol. (b) in ethanol.



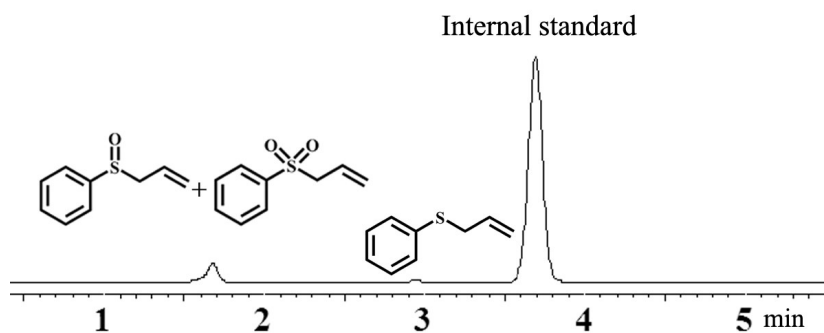
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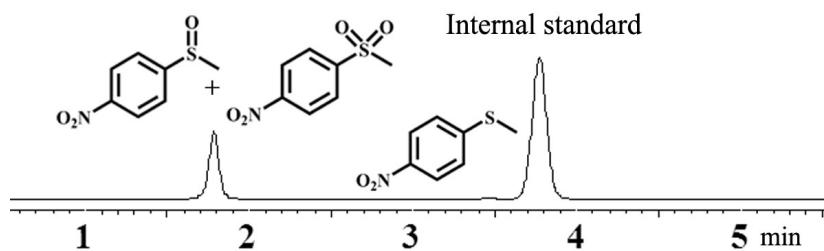
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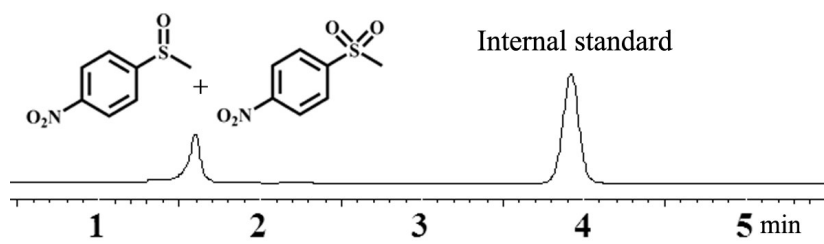
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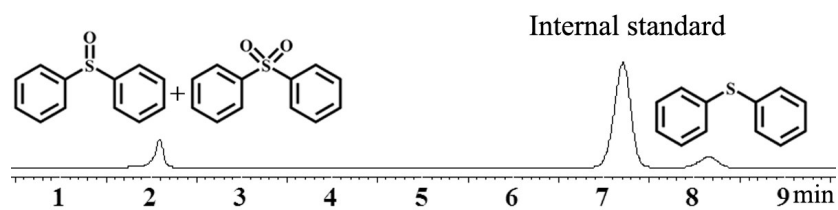
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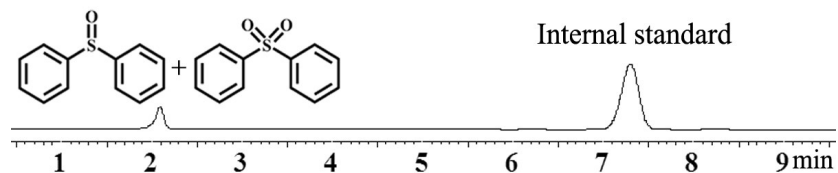
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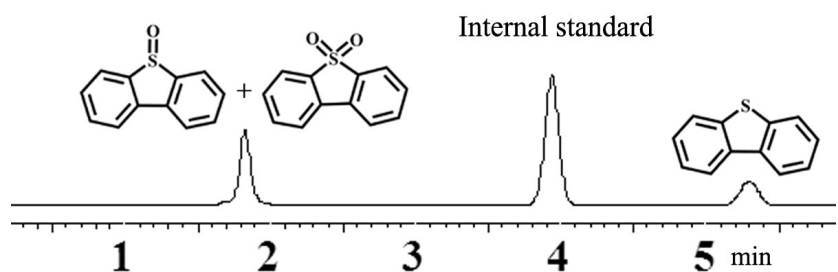
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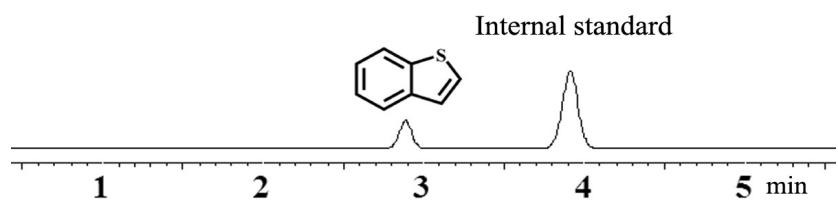
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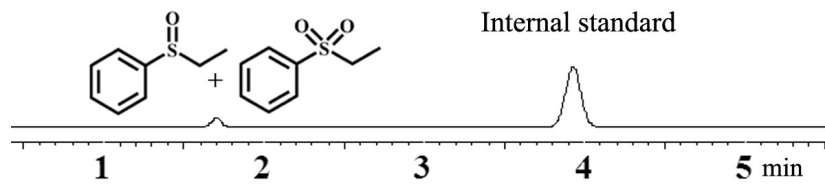


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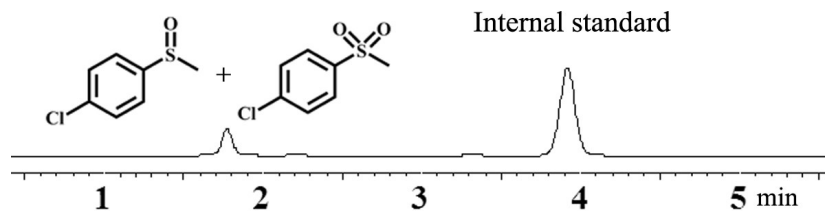


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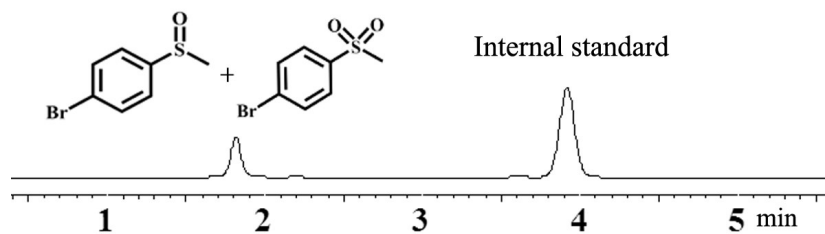
Fig. S8 HPLC data for catalysis of different sulfide-based substrates with **1** as catalyst and TBHP as oxidant in CH_2Cl_2 at 25 °C. (a) with ethylphenylsulfide for 3 h. (b) with 4-chlorothioanisole for 3 h. (c) with 4-bromothioanisole for 3 h. (d) with 4-methoxythioanisole for 3 h. (e) with allylphenylsulfide for 3 h. (f) with 4-nitrothioanisole for 3 h. (g) with 4-nitrothioanisole for 4 h. (h) with diphenylsulfide for 3 h. (i) with diphenylsulfide for 4 h. (j) with dibenzothiophene for 12 h. (k) with benzothiophene for 12 h.



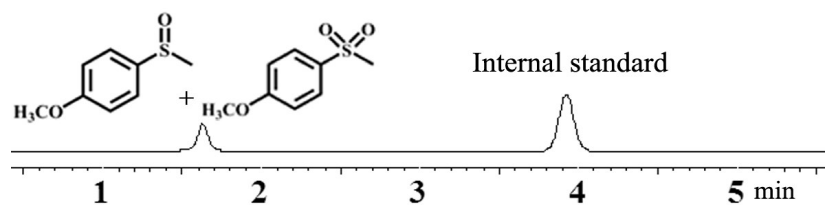
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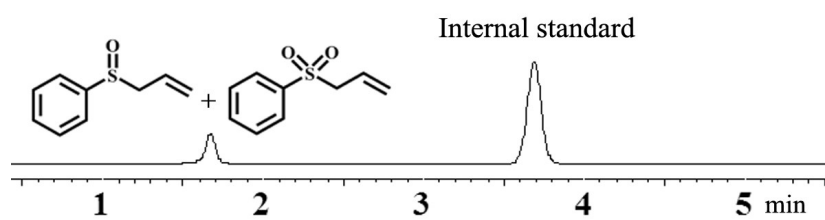
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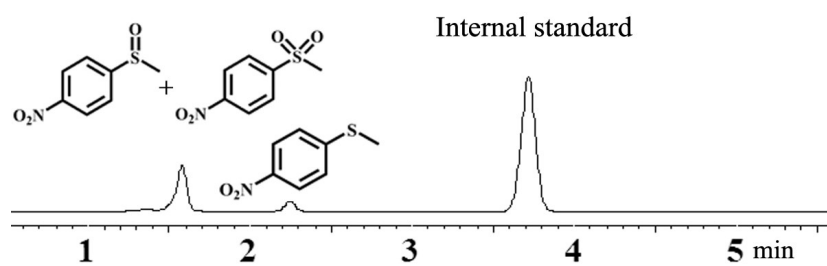
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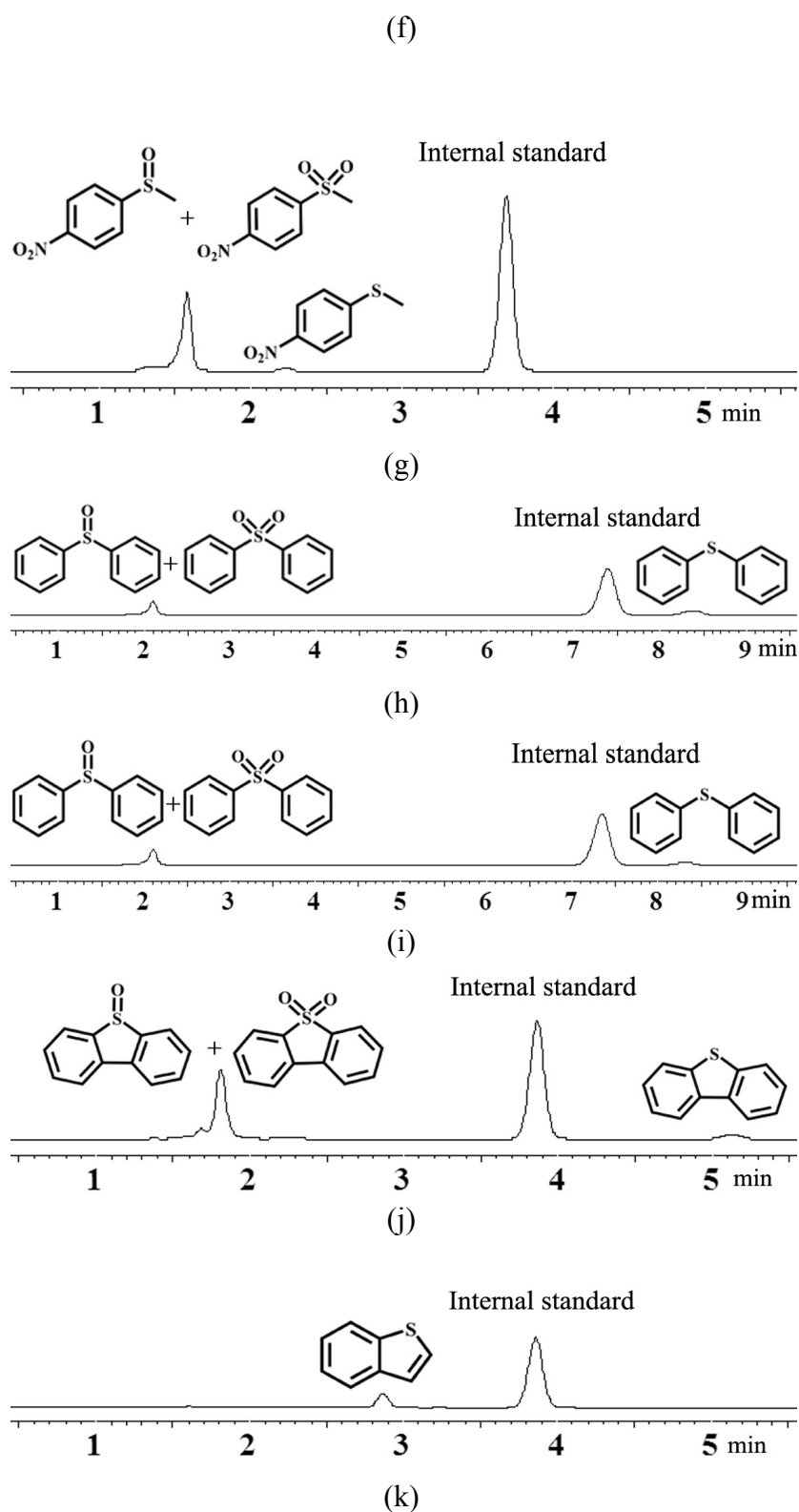
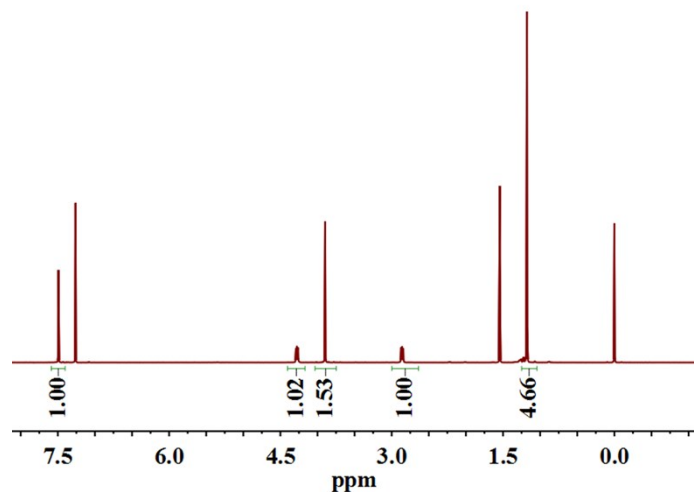
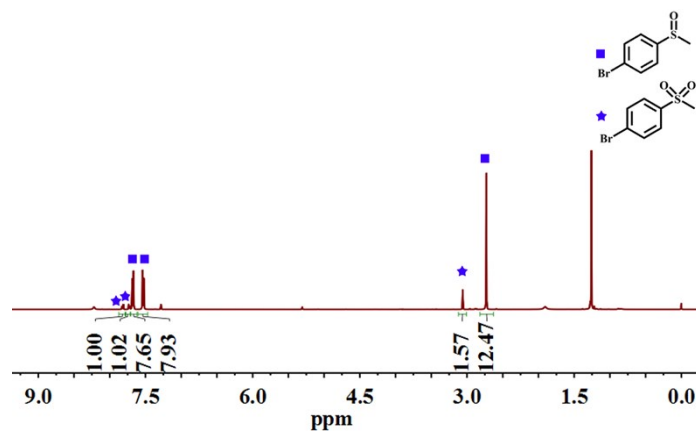


Fig. S9 HPLC data for catalysis of different sulfide-based substrates with **3** as catalyst and TBHP as oxidant in CH_2Cl_2 at 50°C . (a) with ethylphenylsulfide for 2 h. (b) with 4-chlorothiobenzene sulfone for 2 h. (c) 4-bromothiobenzene sulfone for 2 h. (d) with 4-methoxythiobenzene sulfone for 2 h. (e) with allylphenylsulfide for 2 h. (f) with 4-

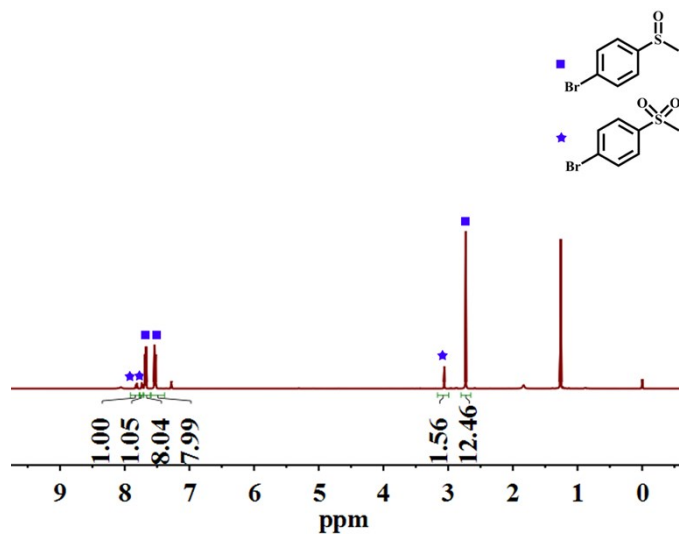
nitrothioanisole for 2 h. (g) with 4-nitrothioanisole for 7 h. (h) with diphenylsulfide for 2 h. (i) with diphenylsulfide for 3 h. (j) with dibenzothiophene for 12 h. (k) with benzothiophene for 12 h.



(a)

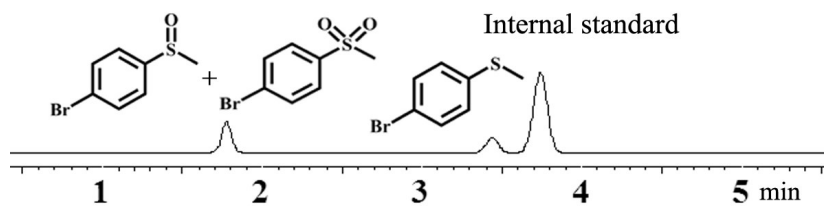


(b)

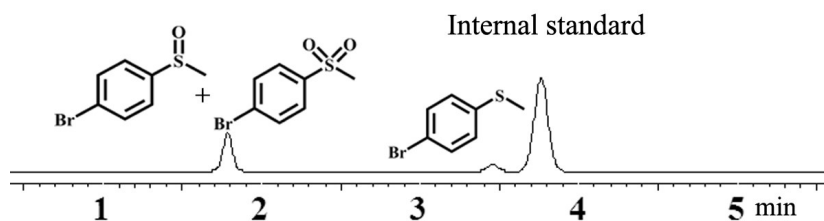


(c)

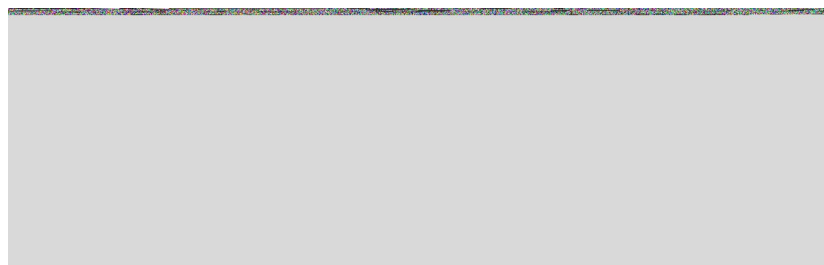
Fig. S10 (a) ^1H NMR spectrum of L (600 MHz, CDCl_3): δ 7.49 (s, 8H), 4.26-4.29 (m, 8H), 3.90 (s, 12H), 2.85-2.87 (dd, 8H), 1.18 (s, 36H). (b) 4-bromothioanisole (500 MHz, CDCl_3) catalyzed by **1**: δ 7.80-7.84 (m, 2H), 7.71-7.75 (m, 2H), 7.66-7.69 (m, 2H), 7.49-7.57 (m, 2H), 3.06 (s, 3H), 2.73 (s, 3H). (c) 4-bromothioanisole (500 MHz, CDCl_3) catalyzed by **3**: δ 7.79-7.85 (m, 2H), 7.70-7.75 (m, 2H), 7.65-7.69 (m, 2H), 7.50-7.56 (m, 2H), 3.06 (s, 3H), 2.73 (s, 3H).



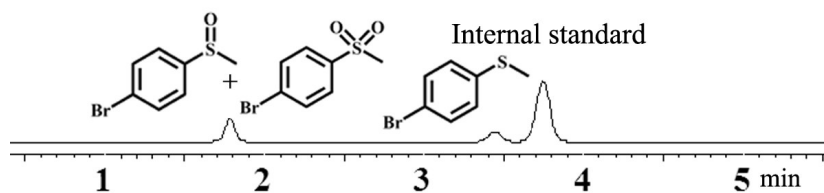
(a)



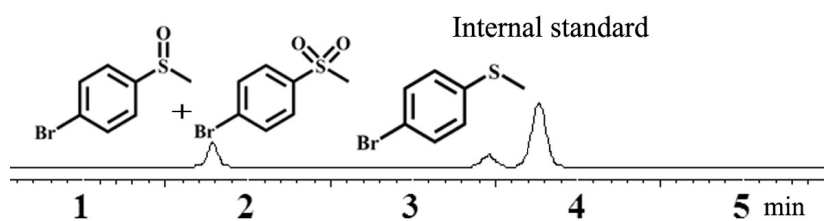
(b)



(c)

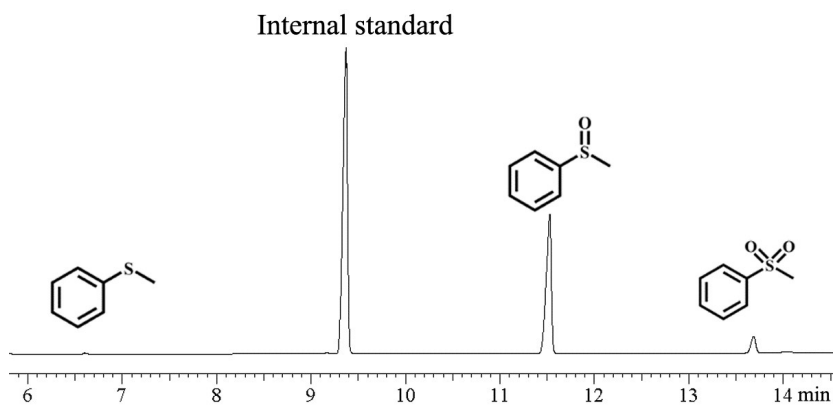
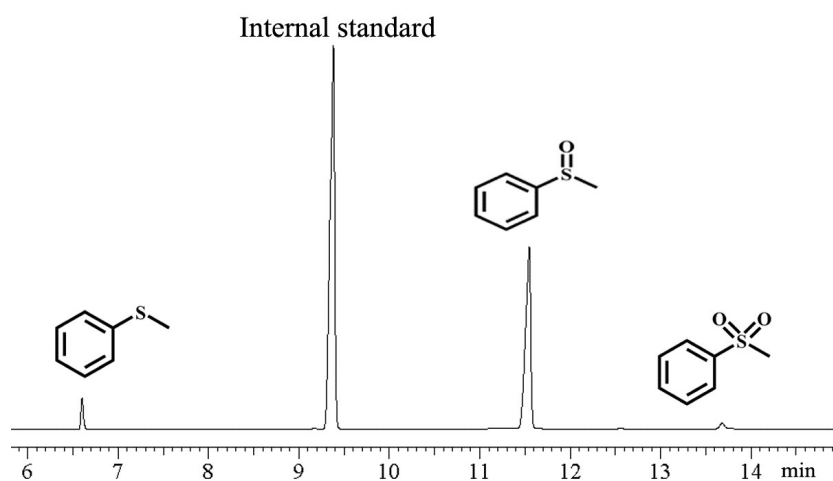
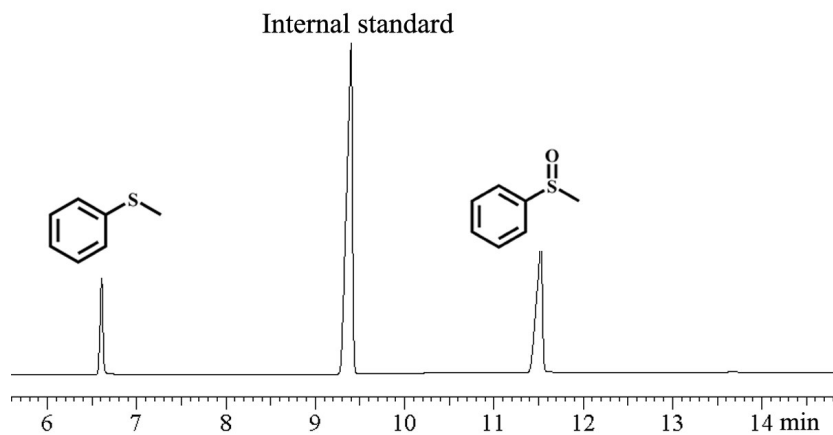


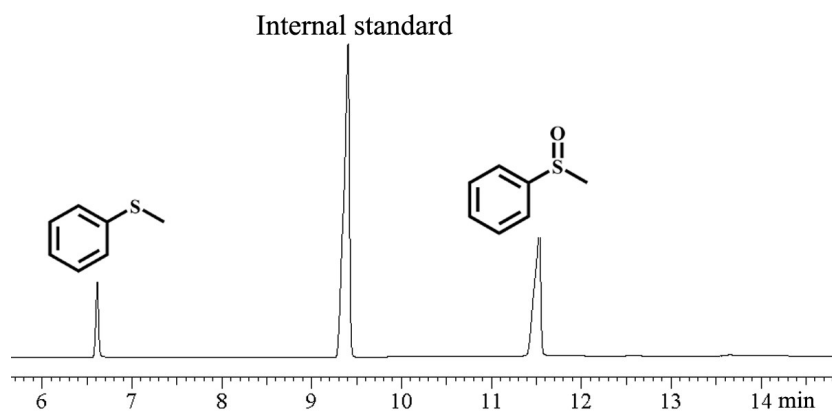
(d)



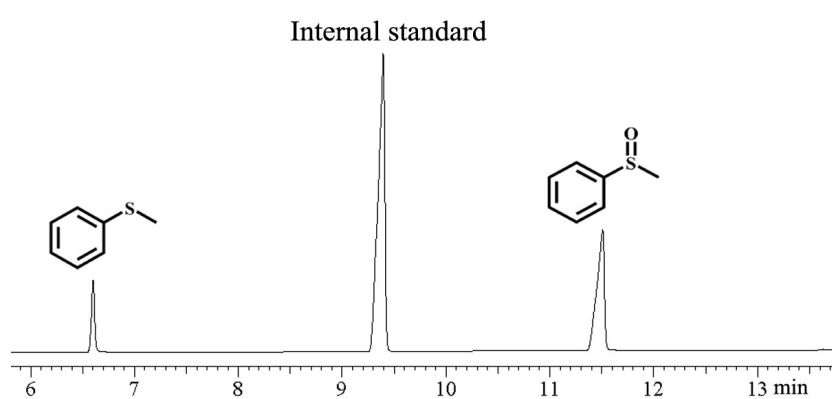
(e)

Fig. S11 HPLC of the oxidative desulfurization using 4-bromothioanisole as the substrate, **1** as catalyst and TBHP as oxidant at 25 °C in CH₂Cl₂. (a) 1 h. (b) 2 h. (c) 3 h. (d) 1 h, the filtrate after removing **1** after 1 h of the reaction. (e) 2 h, the filtrate after removing **1** after 1 h of the reaction.



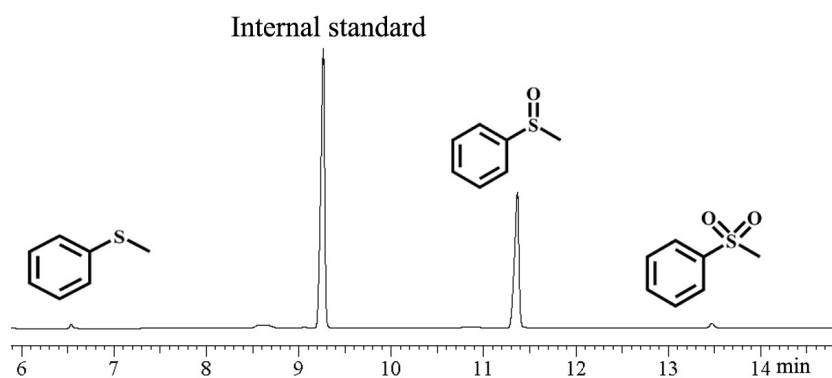


(d)

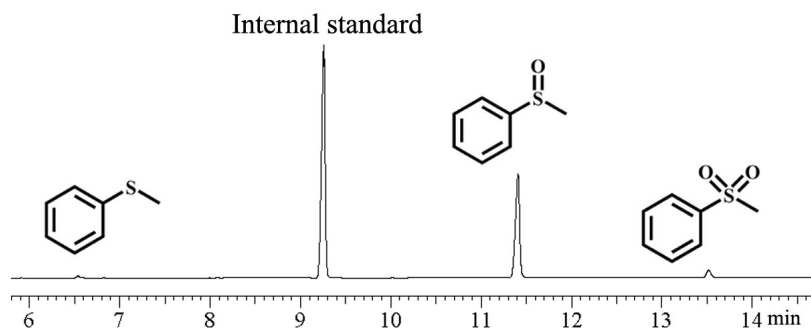


(e)

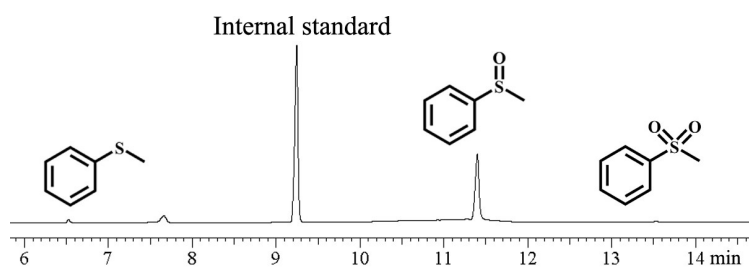
Fig. S12 GC of the oxidative desulfurization using MBT as the substrate, **3** as catalyst and TBHP as oxidant at 50 °C in CH₂Cl₂. (a) 0.5 h. (b) 1 h. (c) 2 h. (d) 0.5 h, the filtrate after removing **3** after 0.5 h of the reaction. (e) 1.5 h, the filtrate after removing **3** after 0.5 h of the reaction.



(a)

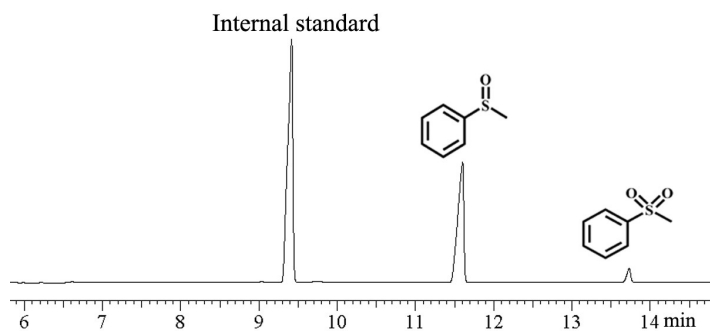


(b)

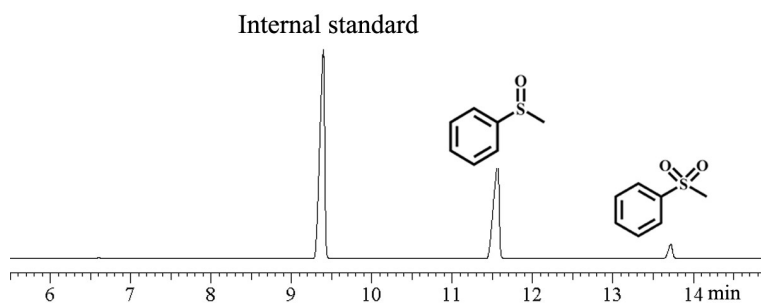


(c)

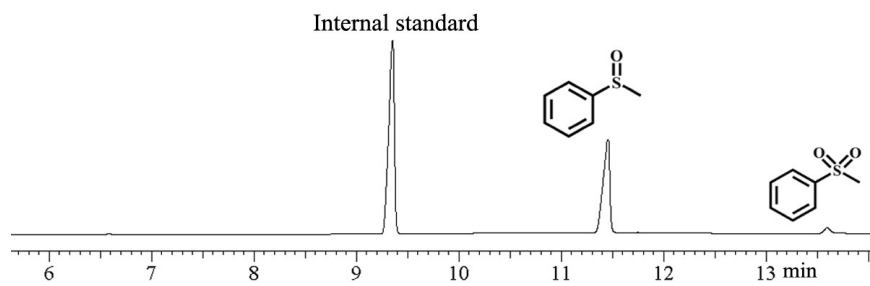
Fig. S13 GC of the oxidative desulfurization using MBT as the substrate and **1** as catalyst in the optimal conditions for different circles. (a) the second circle. (b) the third circle. (c) the fourth circle.



(a)



(b)



(c)

Fig. S14 GC of the oxidative desulfurization using MBT as the substrate and **3** as catalyst in the optimal conditions for different circles. (a) the second circle. (b) the third circle. (c) the fourth circle.