Supporting Information for

Cd(II)-MOF-IM: post-synthesis functionalization of Cd(II)-MOF for triphase transfer catalyst

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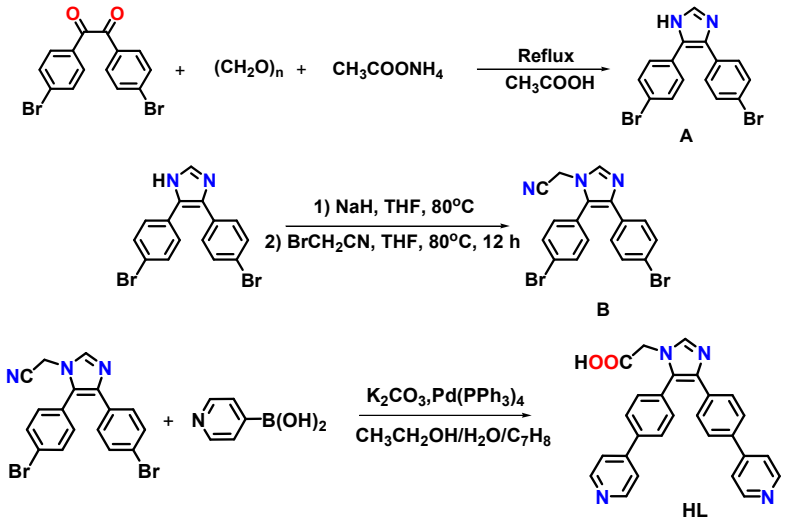
Content

1. Materials and measurements

All the chemicals were obtained from commercial sources and used without further purification. Dibromoimidazole (**A**, Scheme 1) was synthesized according to literature method.[1] Infrared (IR) spectrums were obtained in the 400-4000 cm^{-1} range using a Bruker ALPHA FT-IR Spectrometer. Elemental analyses were performed on a Perkin-Elmer model 2400 analyzer. ^1H NMR data were collected on an AM-300 and Varian Advance 600 spectrometer. Chemical shifts are reported in δ relative to TMS. All crystal data were obtained by Agilent SuperNova X-Ray single crystal diffractometer. GC-MS analysis data were performed on a J&K S011525-300 gas chromatographic (Agilent 6890GC-5973MS). The separation data were obtained by Agilent 1260 Infinity HPLC system equipped with an Agilent C18 reverse phase column (150 × 4.6 mm, 5 μm). Thermogravimetric analyses were carried out on a TA Instrument Q5 simultaneous TGA under flowing nitrogen at a heating rate of 10°C/min. XRPD patterns was obtained on D8 Advance X-ray powder diffractometer with Cu Kα radiation (λ = 1.5405 Å).

2. Synthesis of HL and 1



Scheme S1. Synthesis of **HL**.

(a) Synthesis of B

An anhydrous THF solution (50 mL) of **A** (10.58 mmol, 4.00 g), NaH (11.64 mmol, 0.28 g) was heated at 80°C for 1h, and then $BrCH_2CH_2CN$ (11.64 mmol, 1.40 g) was added to above system. The mixture was further stirred at 80°C (monitored by TLC). Once the reaction was finished, the reaction system was extracted by ethyl acetate and dried with $MgSO_4$. The crude product was purified by chromatography on silica gel using ethyl acetate as the eluent. Yield, 66%. IR (KBr pellet cm^{-1}): 3116 (m), 2965(m), 2320(m), 1913(vw), 1662(m), 1498(vs), 1390(s), 1328(m), 1246(s), 1073(s), 1010(s), 950(s), 913(m), 838(s), 728(m), 576(m). ^{1}H NMR (300 MHz, DMSO-*d*^{6}, 25°C, TMS, ppm): δ = 8.03 (s, 1H, $-C_3HN_2$), 7.79 (d, *J* = 6.0Hz, 2H, $-C_6H_4$), 7.49 (d, *J* = 6.0Hz, 2H, $-C_6H_4$), 7.41 (d, *J*= 6.0Hz, 2H, $-C_6H_4$), 7.33 (d, *J*= 6.0Hz, 2H, $-C_6H_4$), 5.23 (s, 2H, $-CH_2CN$). Elemental Analysis(%): calcd for $C_{17}H_{11}N_3Br_2$: C 48.95, H 2.66, N 10.07, Br 38.31; found: C 48.89, H 2.59, N 10.12, Br 38.40.

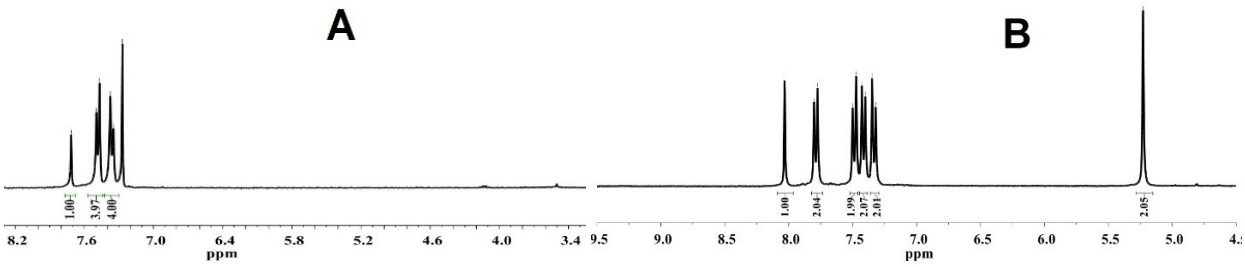


Fig. S1 ^{1}H NMR spectra of **A** and **B**.

(b) Synthesis of HL

A mixture of **B** (5.00 mmol, 2.03 g), pyridine-4-boronic acid (12.00 mmol, 1.48 g), K_2CO_3 (40.00 mmol, 5.53 g),

tetrakis(triphenylphosphine)palladium (0.50 mmol, 0.57 g) in a mixed solvent system (EtOH : H_2O : toluene = 3 : 2 : 3) was stirred at reflux for 48 h. Ligand **HL** was obtained as yellow crystalline solids (1.75 g, 81 %) after chromatography purification. IR (KBr pellet cm^{-1}): 3369(s), 3183(s), 3115(s), 3026(ms), 2329(vw), 1684(s), 1598 (vs), 1538(m), 1497(s), 1396(s), 1299(ms), 1249(ms), 1109(w), 955(w), 818(s), 733(w), 657(ms), 510(w). ^{1}H NMR (300 MHz, DMSO-d^6, 25℃, TMS, ppm): δ = 8.67 (d, J = 6.0Hz, 2H, -C_5H_4N), 8.56 (d, J = 6.0Hz, 2H, -C_5H_4N), 7.98 (d, J = 6.0Hz, 2H, - C_5H_4N), 7.90 (s, 1H, -C_3HN_2), 7.81 (d, J = 6.0 Hz, 2H, - C_5H_4N), 7.68 (m, 4H, -C_6H_4) , 7.52 (m, 4H, -C_6H_4) , 4.70 (s, 2H, -CH_2CN). Elemental Analysis(%): calcd for $C_{27}H_{20}N_4$: C 74.98, H 4.66, N 12.96; found: C 74.89, H 4.72, N 12.92.

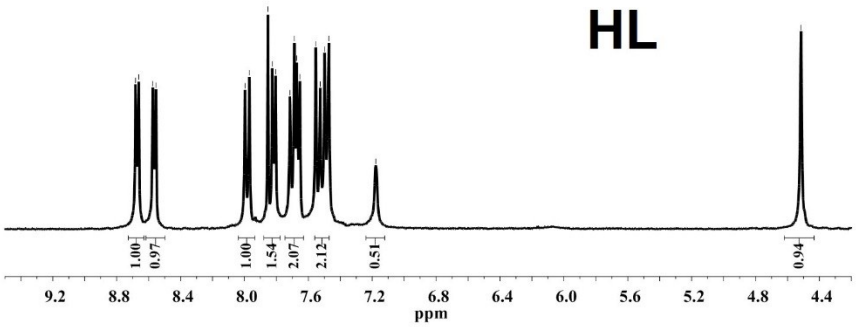
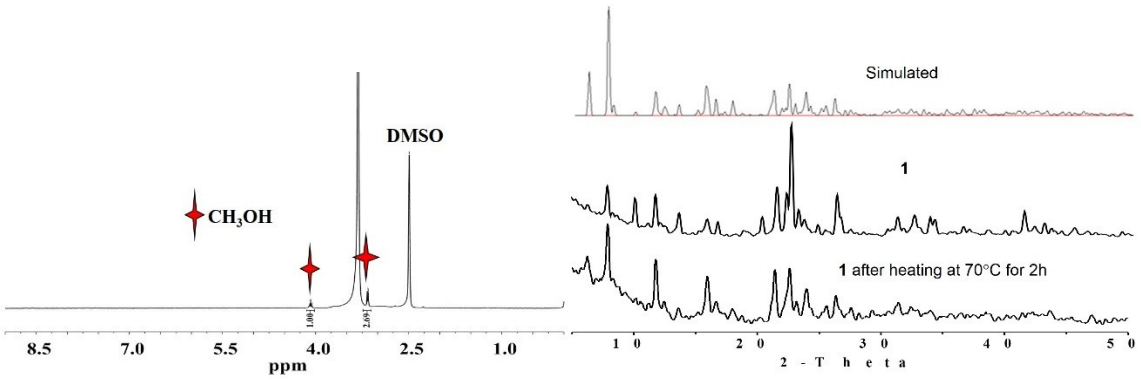


Fig. S2 ^{1}H NMR spectrum of **HL**.

(c) Synthesis of 1

A mixture of **HL** (8.64 mg, 0.02 mmol), $Cd(OAc)_2$ (0.01 mmol, 2.32 mg) and MeOH (2 mL) was sealed in a glass tube and then heated at 120˚C for 72 hours. After the mixture was allowed to cool to room temperature (50 hours), colorless crystals of **1** were isolated. Yield, 78 %. IR (KBr pellet cm^{-1}): IR (KBr pellet cm^{-1})： 3386(ms), 3097(ms), 2320(w), 1680(ms), 1607(vs), 1538(w), 1497(ms), 1392 (s), 1302 (w), 1107(vw), 1007(w), 821(ms), 702(vw), 654(vw). The H_2O and MeOH guest molecules cannot be stabilized in **1**, so the elemental analysis was performed on the desolvated sample. Elemental analysis (%): calcd for $C_{54}H_{50}CdN_8O_{10}$ ($CdL_2 \cdot 6H_2O$): C 59.87, H 4.64, N 10.35; found: C 59.82, H 4.67, N 10.51.



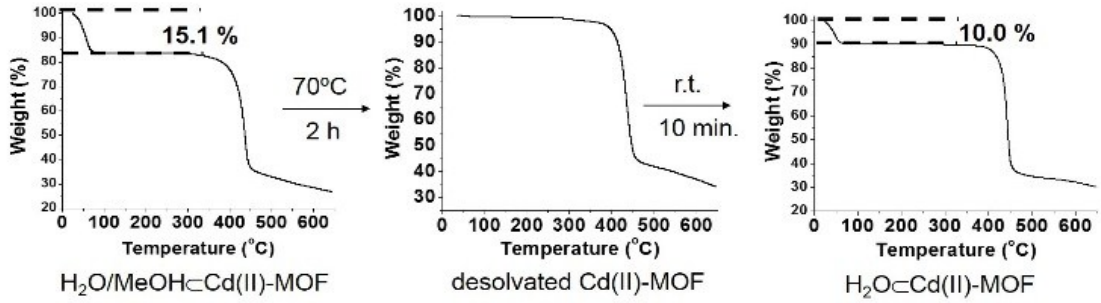


Fig. S3 Top: ^{1}HNMR of DMSO-d^6 extract and the XRPD patterns of the simulated, measured and desolvated **1**. Compared to simulated XRPD pattern, some peaks in the XRPD patterns for the as-synthesized sample of **1** and it was heated at 70°C for 2h are missing, which is caused by the unstable encapsulated guest molecules. Such phenomenon was observed for some other reported guest-encapsulated MOFs.[2] As shown in their TGA traces, the encapsulated molecules in the framework are not stable and they are mobile under ambient temperature. Bottom: TGA traces of **1**, desolvated **1** and it was allowed to stand at room temperature for ca. 10 min (calculated guest weight loss based on Cd**L**$_2$·6H$_2$O is 10.0 %).

3. X-ray structure determination[3]

All single-crystal X-ray intensity data were measured at 100 K on a Agilent SuperNova CCD-based diffractometer (Cu Kα radiation, λ = 1.54184 Å). After determination of crystal quality and initial tetragonal unit cell parameters, a hemi sphere of frame data was collected. The raw data frames were integrated with CrysAlisPro, Agilent Technologies, Version 1.171.36.32 (release 02-08-2013 CrysAlis171. NET) (compiled Aug 2 2013, 16:46:58). Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. Analysis of the data showed negligible crystal decay during data collection. The structure was solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least-squares against F^2, using the SHELXTL software package. The species in this region were too severely disordered to be modeled, and were treated with SQUEEZE/PLATON. These species include some CH_3OH and H_2O molecules. The contribution of the disordered species was removed from the structure factor calculations. The tabulated F(000), MW and density reflect known cell contents only. Eventually, all non-hydrogen atoms of the framework were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms.

CCDC 1447185 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_requeat/cif.

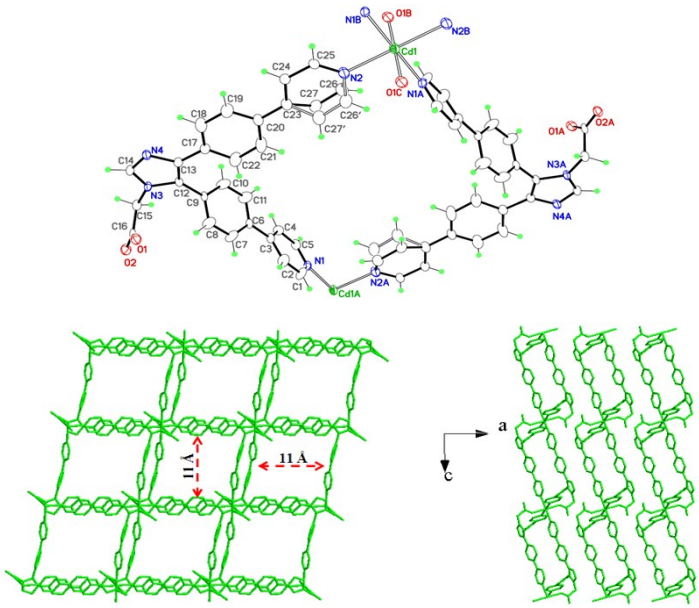


Fig. S4 Top: ORTEP figure of **1**. Bottom: single layer and layers stacking style of **1**.

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

Identification code	**1**	
Empirical formula	$C_{54}H_{38}CdN_8O_4$	
Formula weight	975.32	
Temperature	100.03(10) K	
Wavelength	1.54184 Å	
Crystal system, space group	Triclinic, *P -1*	
Unit cell dimensions	a = 8.8932(10) Å	alpha = 72.926(4) deg.
	b = 11.8369(5) Å	beta = 88.754(6) deg.
	c = 15.1942(8) Å	gamma = 88.696(6) deg.
Volume	1528.4(2) $Å^3$	
Z, Calculated density	1, 1.060 Mg/m^3	
Absorption coefficient	3.205 mm^{-1}	
F(000)	498	
Crystal size	0.3300 x 0.1200 x 0.0100 mm	
Theta range for data collection	3.91 to 67.06 deg.	
Limiting indices	-10<=h<=10, -10<=k<=14, -18<=l<=18	
Reflections collected / unique	9989 / 5457 [R(int) = 0.0679]	
Completeness to theta = 67.06	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.85798	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5457 / 0 / 323	
Goodness-of-fit on F^2	0.986	
Final R indices [I>2sigma(I)]	R1 = 0.0733, wR2 = 0.1886	
R indices (all data)	R1 = 0.0895, wR2 = 0.2008	
Largest diff. peak and hole	1.136 and -1.132 e. $Å^{-3}$	

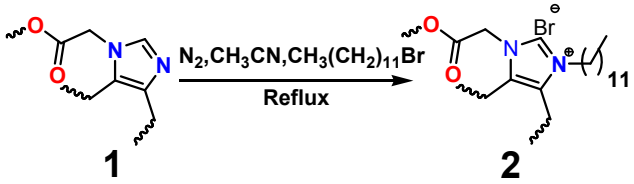
[a] $R1 = \Sigma \, ||F_o| - |F_c|| \, / \, \Sigma \, |F_o|$, $wR2 = \{\Sigma \, [w(F_o^2 - F_c^2)^2] \, / \, \Sigma \, [w(F_o^2)^2] \}^{1/2}$

Table S2. Selected bond lengths [A] and angles [deg] for **1**

Cd(1)-O(1)#1	2.285(4)	Cd(1)-O(1)#2	2.285(4)
Cd(1)-N(1)#3	2.361(4)	Cd(1)-N(1)#4	2.361(4)
Cd(1)-N(2)	2.363(5)	Cd(1)-N(2)#5	2.363(5)
N(1)-Cd(1)#6	2.361(4)	O(1)-Cd(1)#7	2.285(4)
O(1)#1-Cd(1)-O(1)#2	180.000(1)	O(1)#1-Cd(1)-N(1)#3	84.43(15)
O(1)#2-Cd(1)-N(1)#3	95.57(15)	O(1)#1-Cd(1)-N(1)#4	95.57(15)
O(1)#2-Cd(1)-N(1)#4	84.43(15)	N(1)#3-Cd(1)-N(1)#4	180.000(1)
O(1)#1-Cd(1)-N(2)	85.30(17)	O(1)#2-Cd(1)-N(2)	94.70(17)
N(1)#3-Cd(1)-N(2)	90.38(15)	N(1)#4-Cd(1)-N(2)	89.62(15)
O(1)#1-Cd(1)-N(2)#5	94.70(17)	O(1)#2-Cd(1)-N(2)#5	85.30(17)
N(1)#3-Cd(1)-N(2)#5	89.62(15)	N(1)#4-Cd(1)-N(2)#5	90.38(15)
N(2)-Cd(1)-N(2)#5	180.000(1)		

4. Post-synthesis functionalization of Cd(II)-MOF (1)

(a) Synthesis of 2 (reaction of 1 with $CH_3(CH_2)_{11}Br$)



Scheme S2. Synthesis of **2**.

The reaction was carried out in N_2 atmosphere. A CH_3CN (10 mL) suspension solution of **1** (0.4 mmol, 0.17g) and 1-bromododecane (0.25 mmol, 0.064 g) was heated at 80°C for 48 h. The product was collected by centrifugation washed with CH_3CN (10 mL × 2), MeOH (10 mL × 2), Et_2O (10 mL × 2) to generate **2** as light yellow crystalline solids. IR (KBr pellet cm^{-1}): 3366(s), 2966(ms), 1607 (vs), 1497(ms), 1390(s), 1225(vw), 1073(vw), 1009(ms), 959(vw), 822(s), 700(w), 652(w). Cd content in **2** is 9.78 % (based on ion-chromatography) and Br^- content is 64.4% (based on ICP).

Table S3. ICP measurement result of **2**.

element	Cd226.502	Cd228.802	Cd361.051
concentration	mg/mL	mg/mL	mg/mL
average	0.01631	0.01636	0.01639
standard deviation	0.00001	0.00002	0.00003

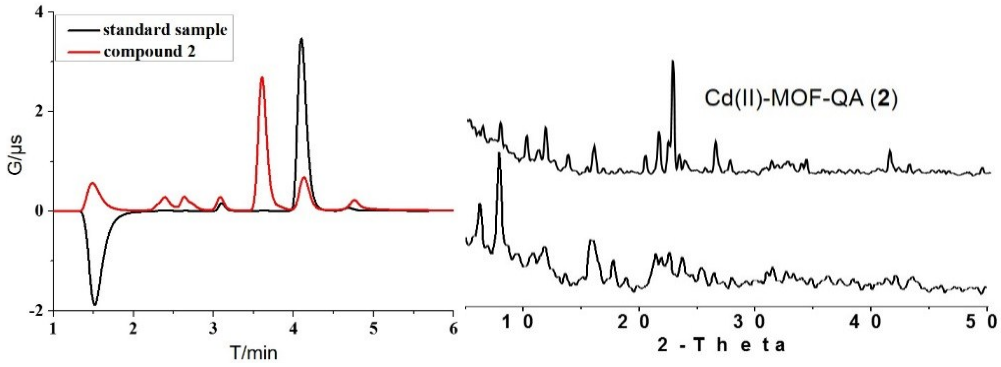
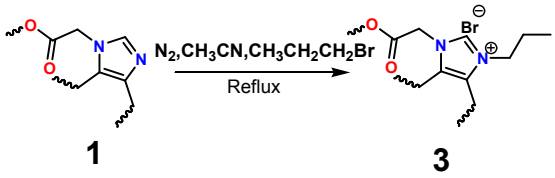


Fig. S5 Left: ion-chromatography and ICP measurement of **2**. Right: the XRPD patterns of **2** and it was heated at 200°C.

(b) Synthesis of 3 (reaction of 1 with $CH_3(CH_2)_2Br$)



Scheme S3. Synthesis of **3**.

The reaction was carried out in N_2 atmosphere. A CH_3CN (10 mL) suspension solution of **1** (0.1 mmol, 0.064 g) and 1-bromopropane (0.25 mmol, 0.031 g) was heated at 80°C for 48 h. The product was collected by centrifugation and washed with CH_3CN (10 mL × 2), MeOH (10 mL × 2), Et_2O (10 mL × 2) to generate **3** as light yellow crystalline solids. IR (KBr pellet cm^{-1}): IR (KBr pellet cm^{-1}): 3371(s), 2968(ms), 1607 (vs), 1496(ms), 1388(s), 1225(w), 1073(vw), 1008(vw), 958(vw), 821(s), 700(w), 652(w). Cd content in **2** is 10.00 % (based on ion-chromatography) and Br^- content is 70.1 % (based on ICP).

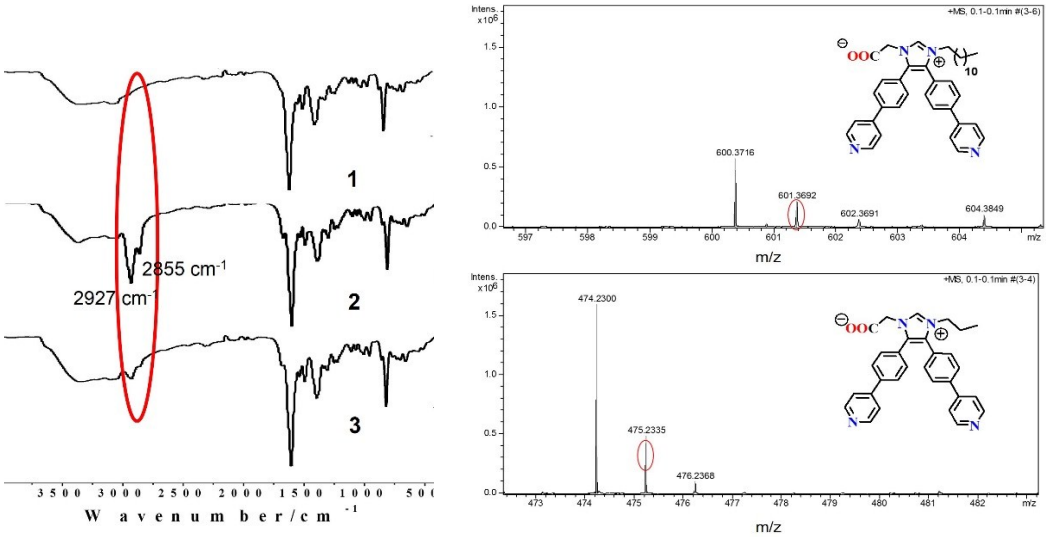


Fig. S6 Left: IR spectra of **1-3**. Compared to **1**, the alkyl chains decorated **2** (with $-(CH_2)_{11}CH_3$) and **3** (with $-CH_2CH_2CH_3$) show the clear C-H vibrations at 2927, 2855 cm^{-1}. Right: MS spectra of **HL** decorated with $-(CH_2)_{11}CH_3$ and $-CH_2CH_2CH_3$ groups.

Table S4. ICP measurement result of **3**.

element	Cd226.502	Cd228.802	Cd361.051
concentration	mg/mL	mg/mL	mg/mL
average	0.01637	0.01639	0.01647
standard deviation	0.00002	0.00000	0.00001

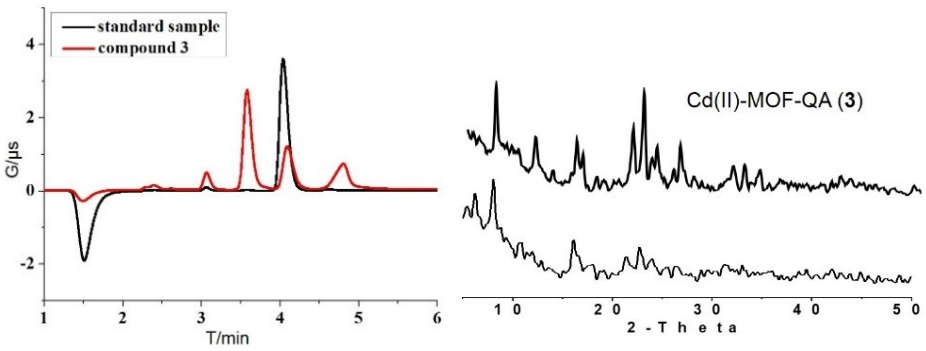
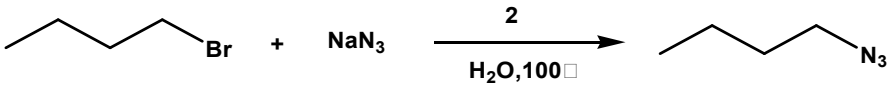


Fig. S7 Left: ion-chromatography and ICP measurement of **3**. Right: the XRPD patterns of **3** and it was heated at 200°C.

5. Azidation of 1-bromobutane catalyzed by 2 and 3 and leaching test

(a) Azidation of 1-bromobutane catalyzed by 2



Scheme S4. Azidation of 1-bromobutane catalyzed by **2**.

1-Bromobutane (1 equiv) was added to a suspension aqueous solution (4.5 mL) of NaN_3 (7.7 equiv) and **2** (2.6 mol %). The mixture was heated at 100°C and monitored by GC. The reaction system was extracted by CH_2Cl_2 and characterized by GC-MS once the reaction was finished. **2** was collected by centrifugation and reused for the next catalytic cycle.

(b) Leaching test for catalytic azidation based on 2

The solid catalyst of **2** was separated from the hot solution right after reaction for 3 h. The reaction was continued with the filtrate in the absence of **2** for additional 3 h. No further increase in either the conversion or selectivity of the azidated product was detected, which confirms that the catalytically active sites for this azidation reaction located on **2**.

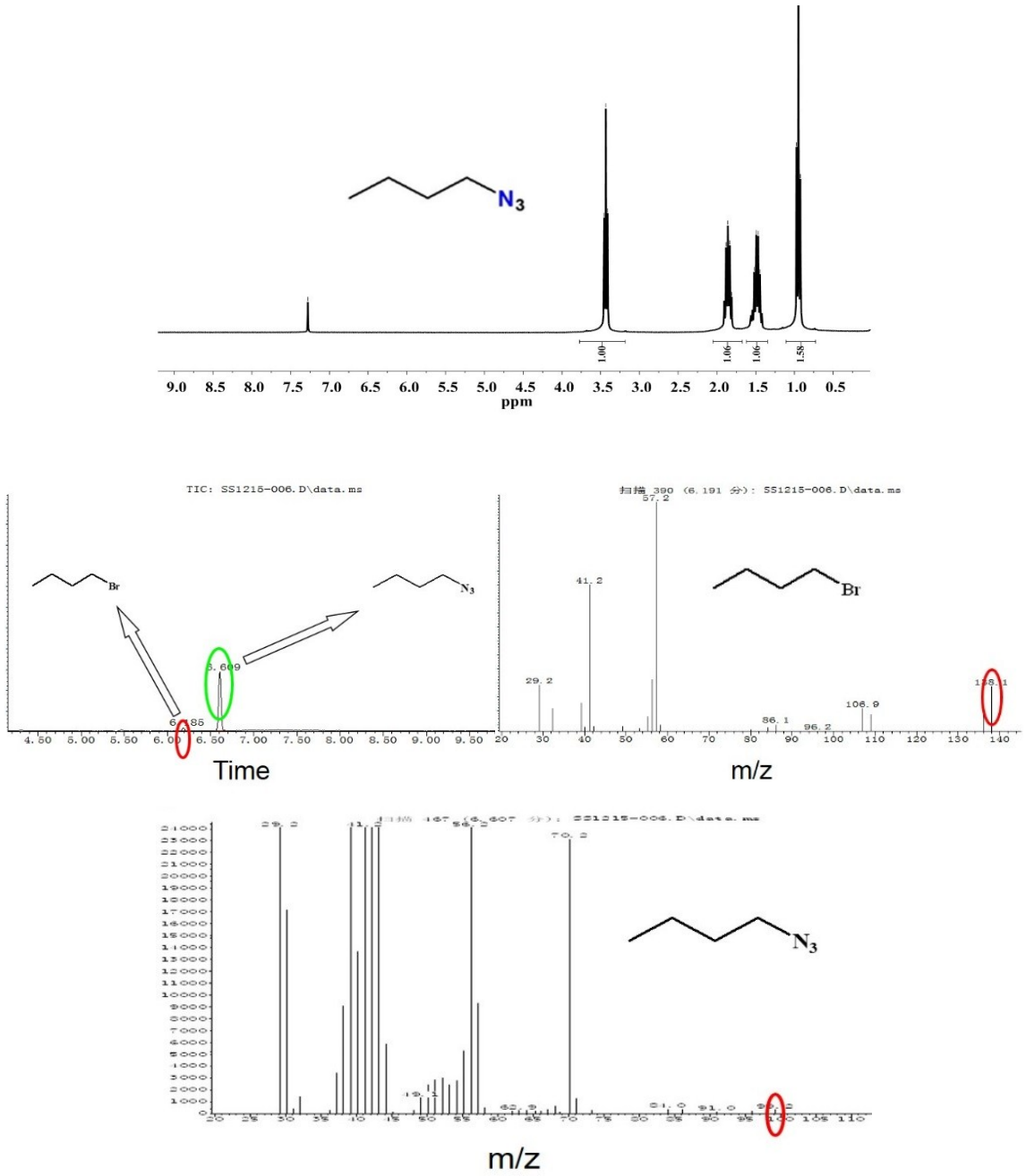
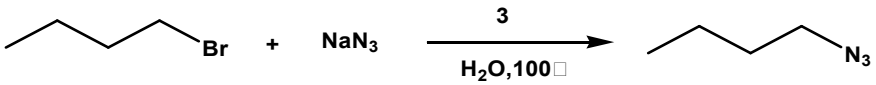


Fig. S8 ^{1}H NMR spectrum of n-butyl azide (top) and GC-MS spectra (bottom) of the azidation of 1-bromobutane catalyzed by **2.**

(c) Azidation of 1-bromobutane catalyzed by 3



Scheme S5. Azidation of 1-bromobutane catalyzed by **3**.

The reaction was carried out under the same reaction conditions as that for **2** but used **3** instead of **2** as the catalyst.

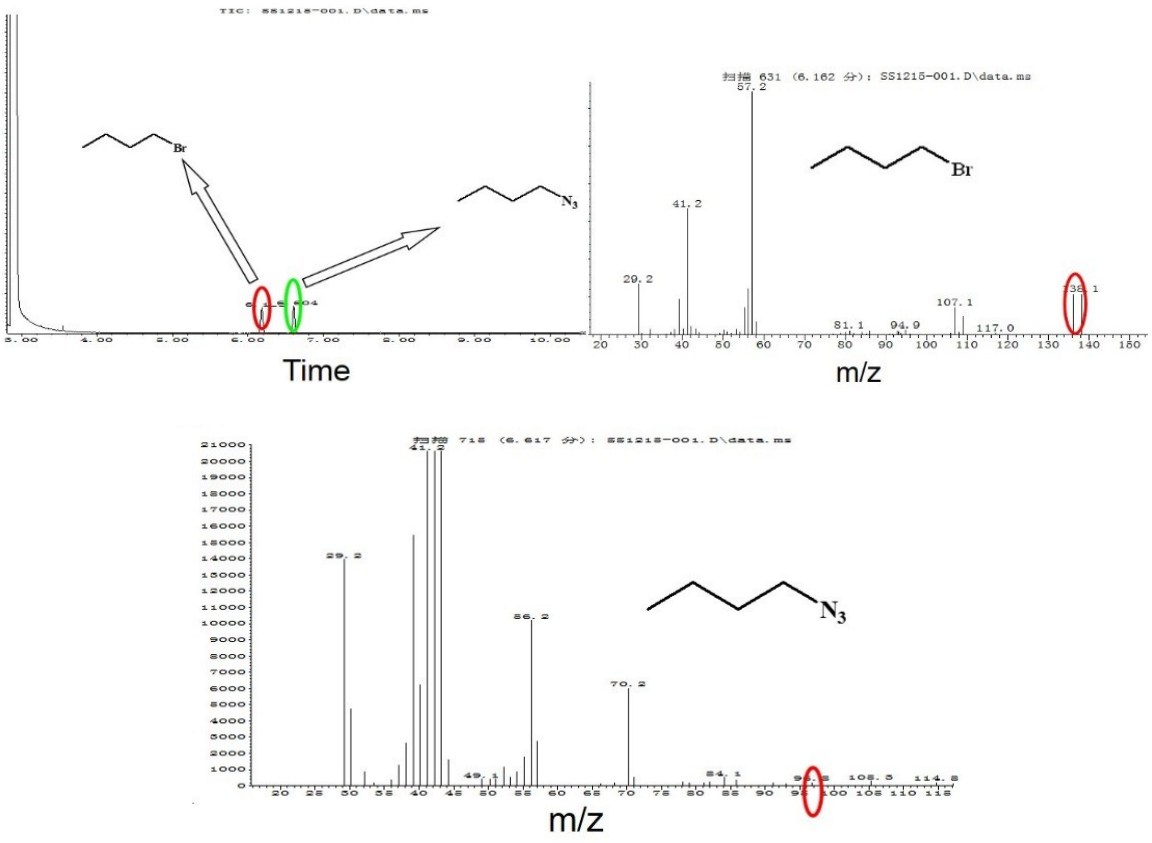


Fig. S9 GC-MS spectra of the azidation of 1-bromobutane catalyzed by **3.**

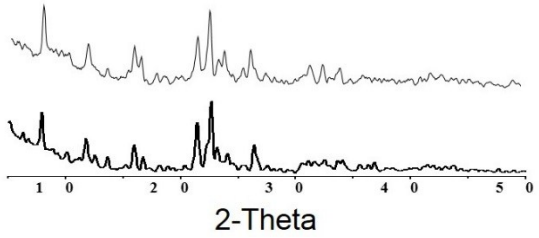
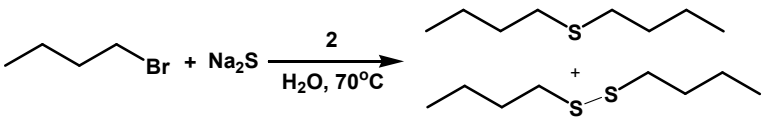


Fig. S10 XRPD patterns of **3** (top) and after the last catalytic cycle (bottom).

6. Thiolation of 1-bromobutane catalyzed by 2 and 3 and leaching test

(a) Thiolation of 1-bromobutane catalyzed by 2



Scheme S6. Thiolation of 1-bromobutane catalyzed by **2**.

1- Bromobutane (1 equiv) was added to a suspension aqueous solution (4.5 mL) of Na_2S (6.4 equiv) and **2** (2.6 mol %). The mixture was heated at 70°C and monitored by GC. The reaction system was extracted by CH_2Cl_2 and characterized by GC-MS once the reaction was finished. **2** was collected by centrifugation and reused for the next catalytic cycle.

(b) Leaching test for catalytic thioetherfication based on 2

The solid catalyst of **2** was separated from the hot solution right after reaction for 2 h. The reaction was continued with the filtrate in the absence of **2** for additional 1.5 h. No further increase in either the conversion or selectivity of the product was detected, which confirms that the catalytically active sites for this thioetherfication reaction located on **2** (Fig. S12).

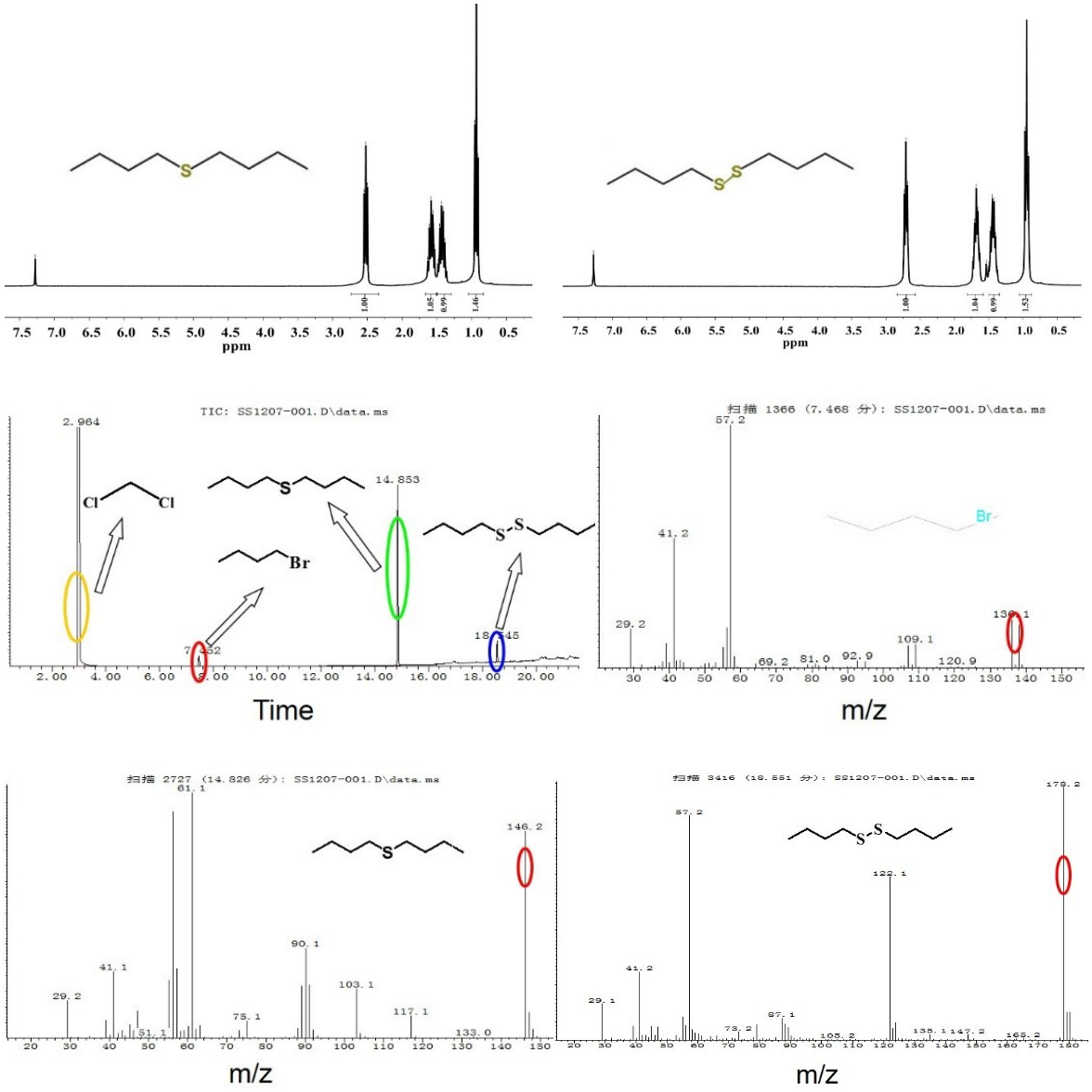


Fig. S11 ^{1}H NMR spectra of 1, 2-dibutyldisulfane and dibutyldisulfane (top), and GC-MS spectra (bottom) of the thiolation of 1-bromobutane catalyzed by **2.**

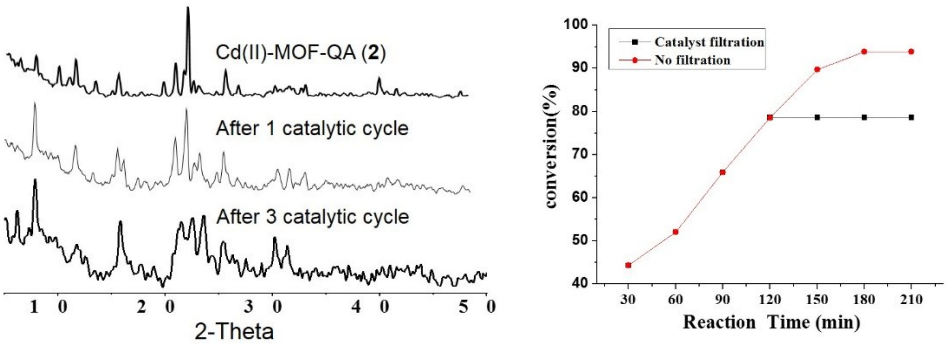


Fig. S12 Left: XRPD patterns of **2** and after the first and last catalytic cycle. Right: leaching test for catalytic thioetherfication based on **2**.

If the thiolation of 1-bromobutane catalyzed by **2** was carried out in N_2, the selectivity toward dibutylsulfane was largely enhanced (up to 97 %) and only tiny amount of dibutyldisulfane was detected based on GC-MS analysis (Figure S13).

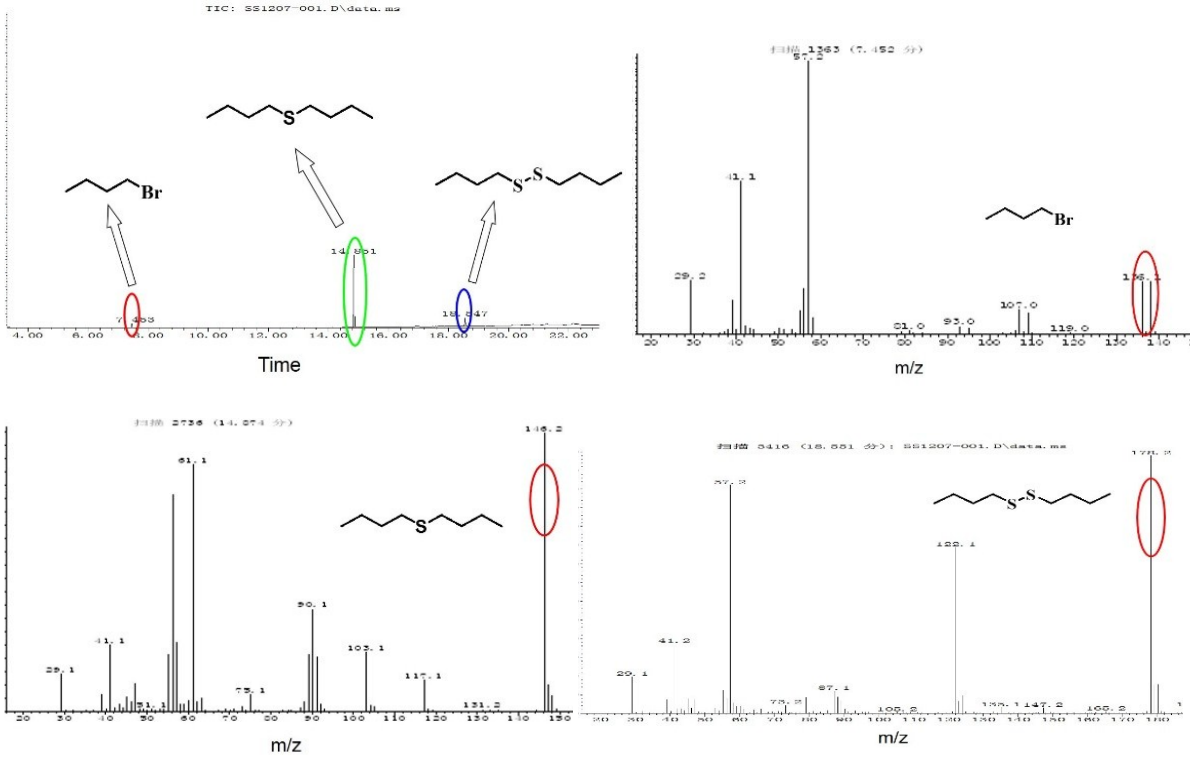
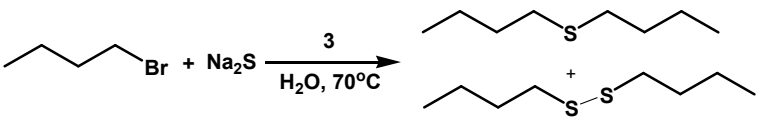


Fig. S13 GC-MS spectra of the thiolation of 1-bromobutane catalyzed by **2** in N_2.

(c) Thiolation of 1-bromobutane catalyzed by 3



Scheme S7. Thiolation of 1-bromobutane catalyzed by **3**.

The reaction was carried out under the same reaction conditions as that for **2** but used **3** instead of **2** as the catalyst.

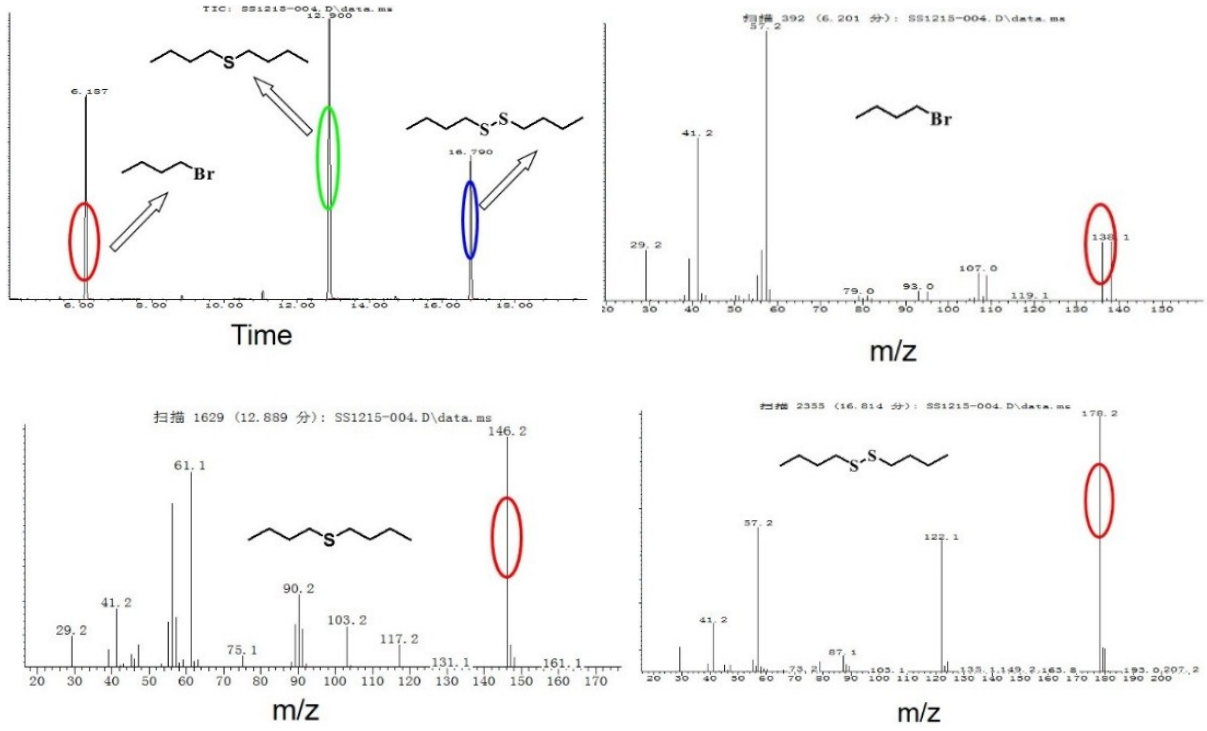


Fig. S14 GC-MS spectra of the thiolation of 1-bromobutane catalyzed by **3.**

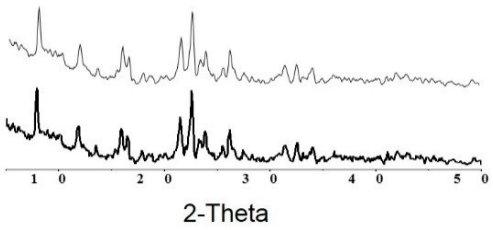


Fig. S15 XRPD patterns of **3** (top) and recollected of **3** after catalytic cycle (bottom).

7. Reference

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