Supplementary Information

A Cu(II) mediated new desulfurization pathway involving elimination of ethylene sulfide.

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Experimental section

General Remarks

All solvents were purified by standard methods and distilled before use. The ligand, 2,2'-thiodiacetic acid (H_2tda) purchased from Sigma Aldrich was used as received. All the reactions were carried out at room temperature under ambient conditions.

IR spectra (KBr pellet) were recorded using a Varian-3100 FTIR instrument and electronic absorption spectra were recorded on Shimazdu UV-1700 PhermaSpec Spectrophotometer. GC-MS data were collected on a Perkin Elmer CLARUS 680 instrument (at the Chemistry Department, Jadavpur University. Kolkata). ESI-MS analyses were performed using Bruker-amaZon SL instrument (at the Center of Genetic Disorders, Faculty of Science, Banaras Hindu University, Varanasi).   .

Syntheses

Synthesis of {[Cu(TMEDA)(tda)].(H_2TMEDA)$(NO_3)_2H_2O$} 1

To a well stirred mixture of $Cu(NO_3)_2.3H_2O$ (0.242g, 1 mmol) and TMEDA (300 μL, 2 mmol) in MeOH (5mL), was added a methanolic solution of triethylammonium salt of thiodiacetic acid (prepared *in situ* by mixing of H_2tda (0.150g, 1 mmol) and triethylamine (278 μL, 2 mmol) in 5 mL of methanol). After overnight stirring, the solvent was removed under reduced pressure and the blue product obtained was re-dissolved in methanol which on standing afforded blue, rectangular crystals of **2**. Yield: 0.340g (73%). Anal calc. for

$C_{16}H_{40}CuN_6O_{11}S$: C, 32.67, H, 6.86, N, 14.29. Found: C, 31.43, H, 6.90, N, 14.33. IR spectra (KBr, cm^{-1}): 1622 *v*(CO), 701 *v*(CS), 2930 *v*(NH).

Synthesis of {$[Cu_2(TMEDA)_2(\mu\text{-ox})(H_2O)_2].(NO_3)_2.2CH_3CN$} 2

Methanolic solution of triethylammonium salt of thiodiacetic acid (prepared *in situ* by mixing of H_2tda (0.076g, 0.5 mmol) and triethylamine (140 µL, 1 mmol) in 5 mL of methanol) was added to a well stirred mixture of $Cu(NO_3)_2.3H_2O$ (0.242g, 1 mmol) and TMEDA (151 µL, 1mmol) in methanol (5mL) followed by overnight stirring. The product obtained after removal of solvent was re-dissolved in methanol. Small quantity of a black residue was separated out by filtration. The crystals obtained after slow evaporation of the solvent from the filtrate were of poor quality. Diffraction quality crystals of **2** were obtained by recrystallization from acetonitrile. However, the crystals thus obtained effloresce rapidly. Yield: 0.117g (34%). Anal calc. for $C_{18}H_{42}Cu_2N_8O_{12}$: C, 31.35, H, 6.14, N, 16.25. Found: C, 31.86, H, 6.35, N, 17.10. IR spectra (KBr, cm^{-1}): 1644 *v*(CO).

Characterization

The IR spectra of complex **1** shows a band at 1622 cm^{-1} for the *v*(CO) and a weak band obtained at 2930 cm^{-1} for the *v*(NH) of TMEDA. The IR spectrum of complex **2** exhibits a strong peak at 1644 cm^{-1} which is characteristic of v_{asym}(COO) vibrations confirming its *bis*-bidentate bridging mode.[1] The band at 3430 cm^{-1} can be assigned to the coordinated water molecule.[2]

The electronic absorption spectra of complexes were recorded in methanol solution (2×10^{-4} M). Absorption spectrum of complex **1** is shown in **Figure S1**. It shows a band at ~ 291 nm with a shoulder at ~ 341 nm and a broad band around 590 nm. Complex **2** displays two absorbance maxima at ~ 275 and ~ 632 nm (**Figure S2**). Square pyramidal Cu^{2+} complexes generally show absorption at ca. 580-670 nm.[3] Higher energy band is possibly due to inter- or intra-ligand charge transfer transitions whereas lower energy bands are due to *d-d* transitions. The reaction of complex **1** with one equivalent of $Cu(NO_3)_2.3H_2O$ and TMEDA was monitored by UV-Vis spectral changes over a period of 1 hour (**Figure S3**). Initially, complex **1** shows a peak at ~ 283 nm with a marked shoulder at ~ 348 nm and a broad band around 600 nm. When $Cu(NO_3)_2.3H_2O$ and TMEDA was added the shoulder disappears completely. This was accompanied by a decrease in intensity and a blue shift from ~ 283 nm to 279 nm. The band maximum around 600 nm also shifts to lower energy side (from 600 nm to 632 nm).

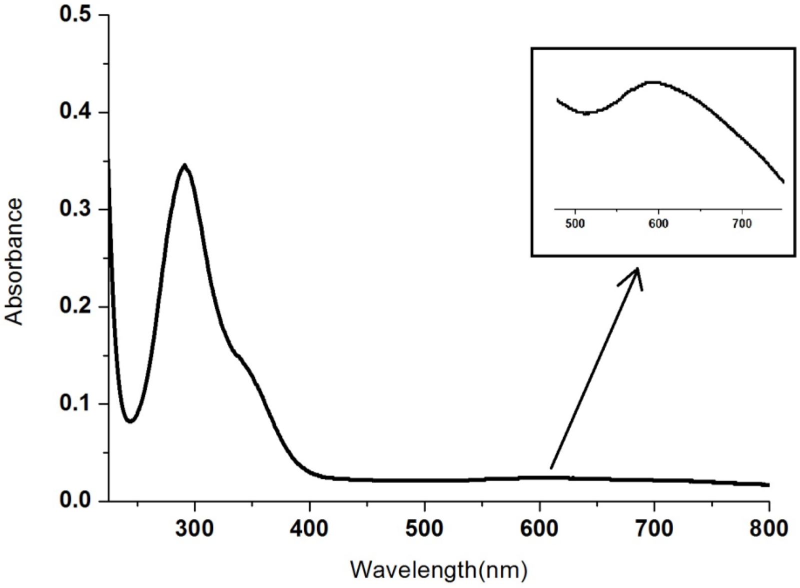

Figure S1 UV-Vis Spectrum of complex **1**

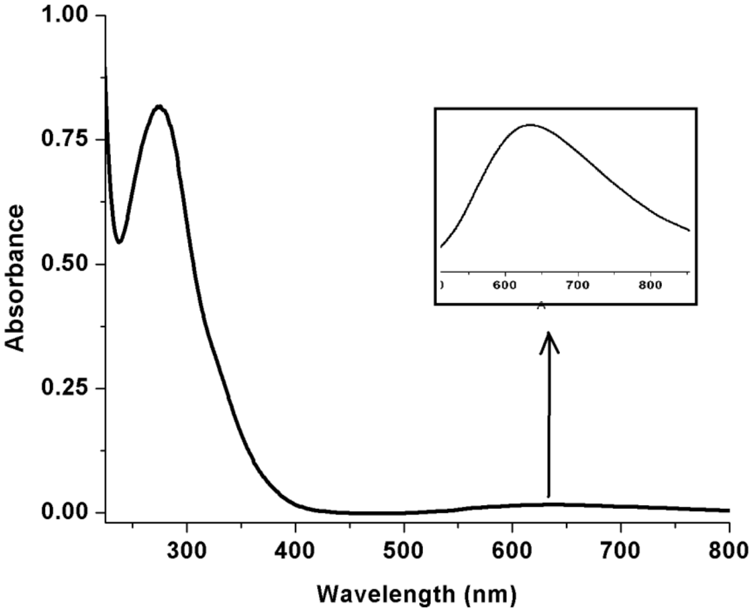

Figure S2 UV-Vis Spectrum of complex **2**

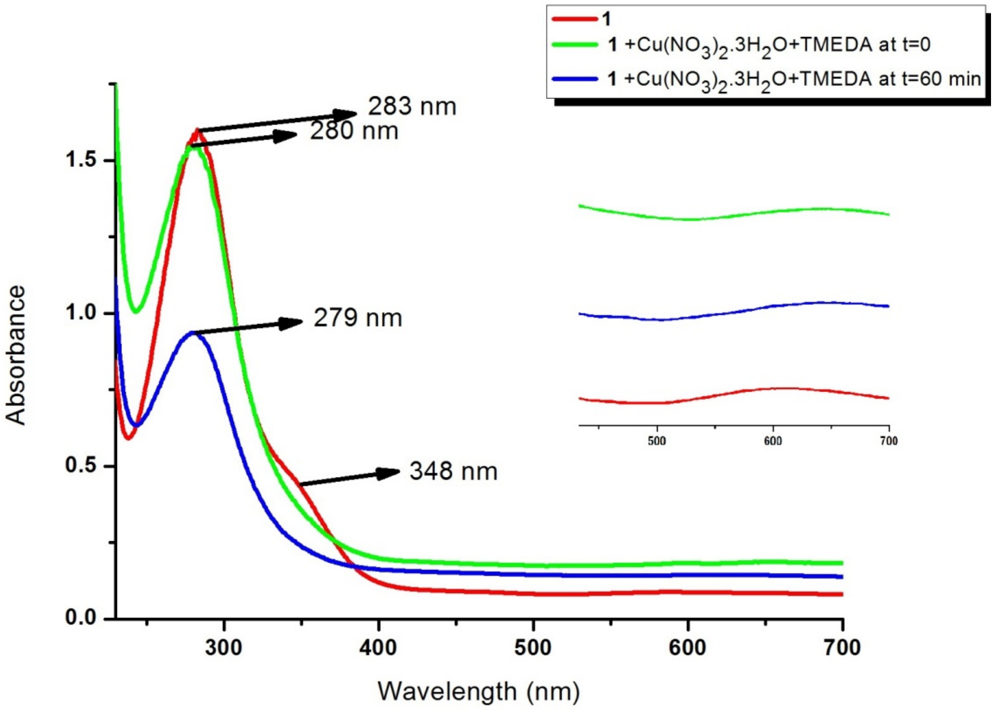

Figure S3 Electronic spectral changes during reaction of complex **1** with $Cu(NO_3)_2.3H_2O$ and TMEDA in methanol

Similarly, spectral changes could also be monitored when the reaction was carried out in aqueous medium. **Figure S4** shows the spectrum of **1**, those of **1** immediately after addition of $Cu(NO_3)_2.3H_2O$ and TMEDA solutions and the same solution after 2 hr.

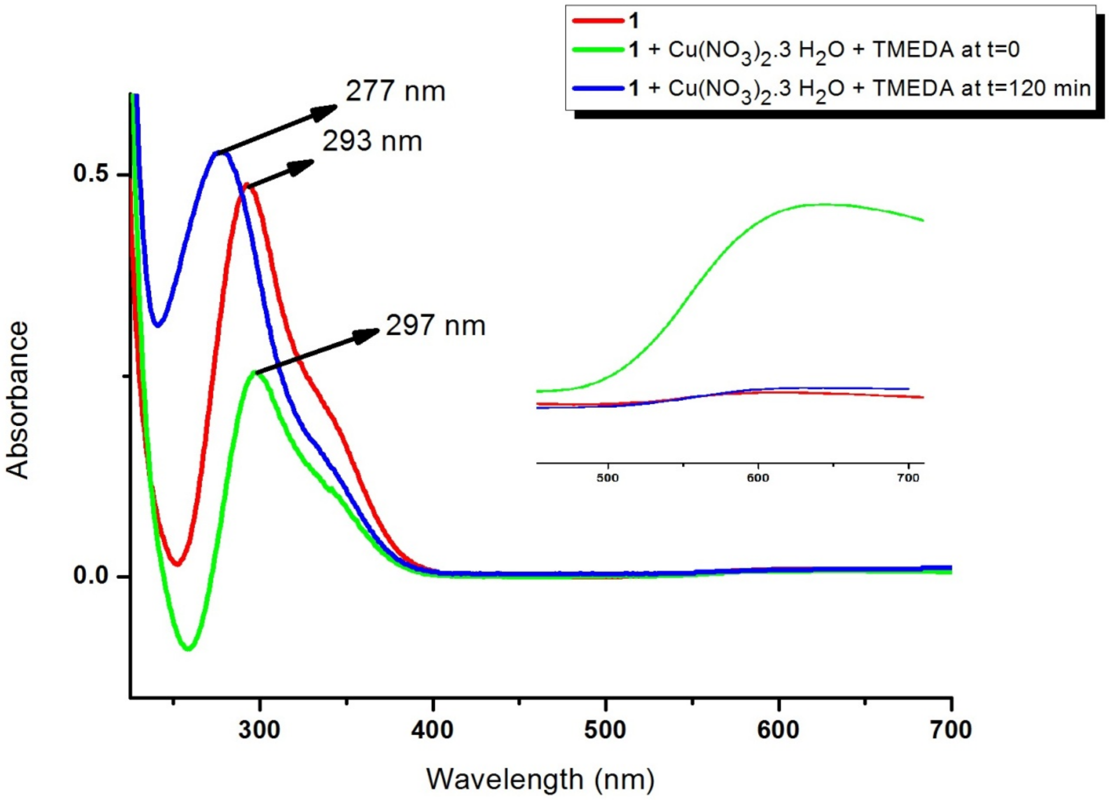

Figure S4 Electronic spectral changes during reaction of complex **1** with $Cu(NO_3)_2.3H_2O$ and TMEDA in water

The spectral features indicate the formation of **2** in both the above cases.

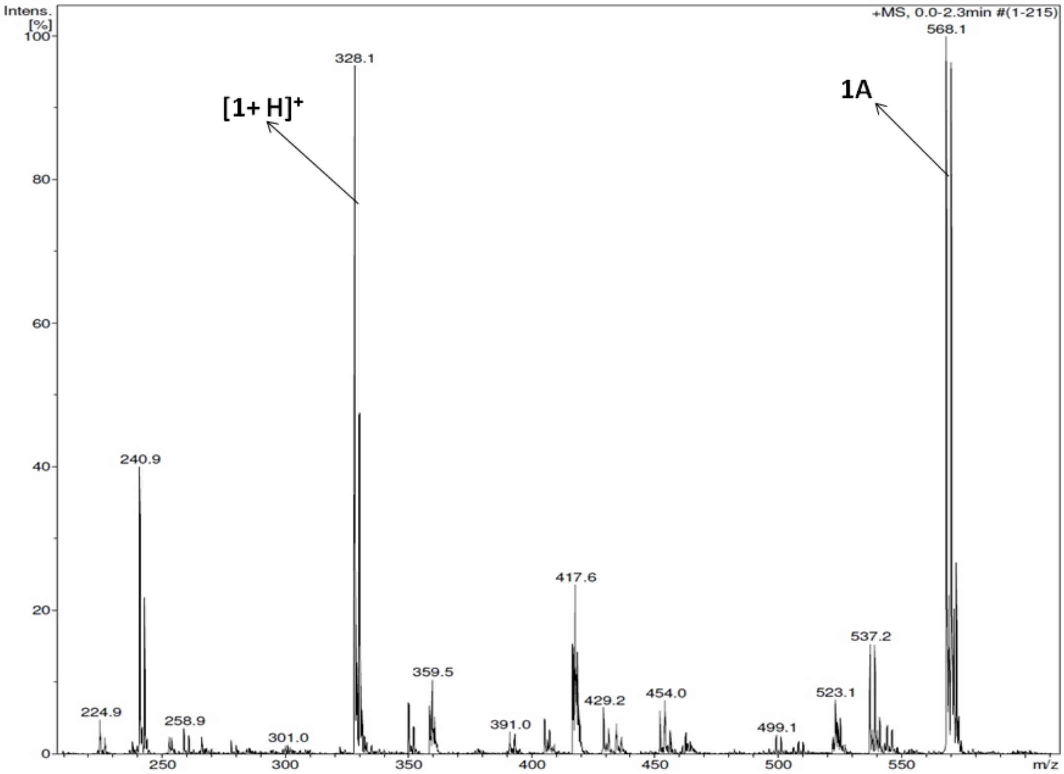

Figure S5 ESI-MS spectrum of reaction mixture at t=0 (m/z 200-600)

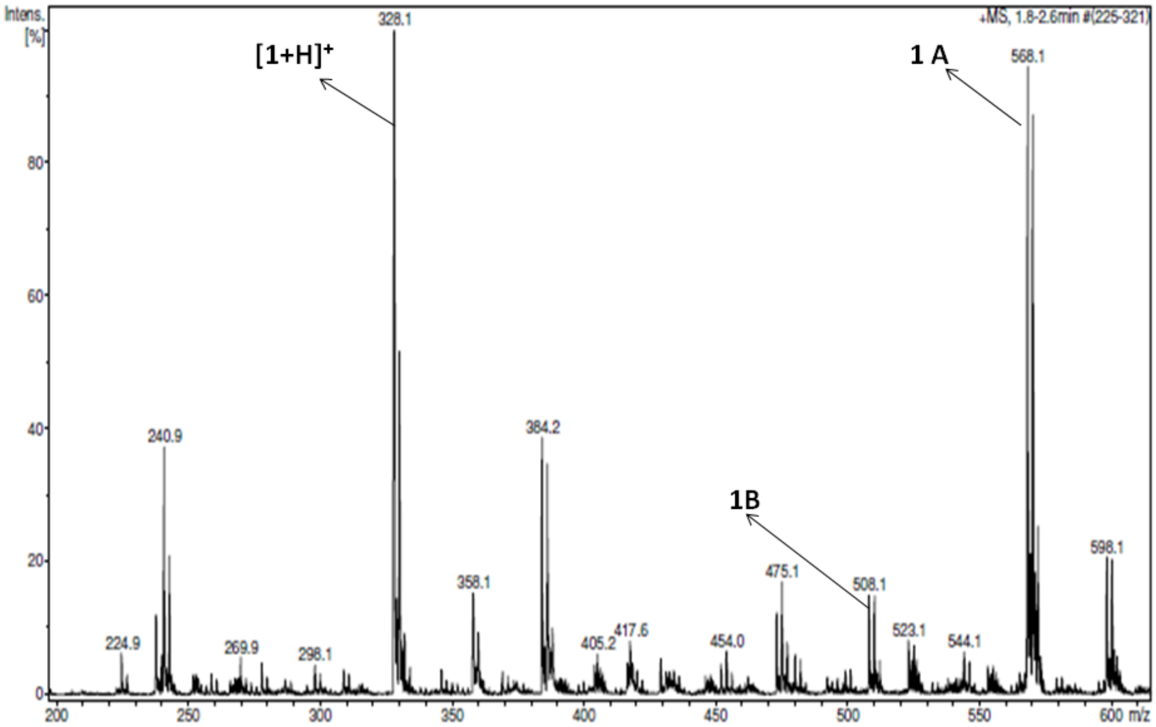

Figure S6 ESI-MS Spectrum of Reaction mixture at t=120 min (m/z 200-600)

The ESI-MS scans of the reaction mixture are depicted in **Figure S5** and **Figure S6**. At t=0, the peaks with the maximum intensity at m/z 328 and m/z 568.1 can be assigned to $[\mathbf{1}+\mathrm{H}]^+$ and one of the intermediates, **1A** respectively. The subsequent appearance of a new peak at m/z 508.1 gives weight to the pathway shown in **Scheme 3**. Base peak in the ESI-MS spectrum of complex **2** also appears at m/z=508.1(**Figure S7**) which further confirms the presence of complex **2** in the reaction mixture at t=120 min. As anticipated, the loss in mass of 60 must be due to elimination of thiirane.

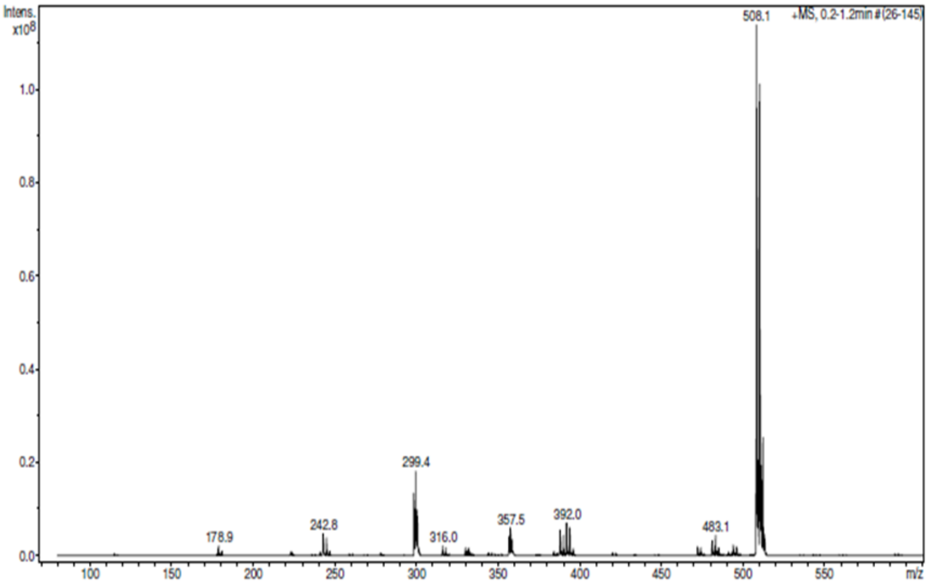

Figure S7 ESI-MS spectrum of complex **2**

GC-MS study

$Cu(NO_3)_2.3H_2O$ (0.159g, 0.66 mmol), TMEDA (0.1mL, 0.66mmol), triethylamine (0.1mL, 0.66 mmol) and thiodiacetic acid (0.050g, 0.33mmol) were stirred together in methanol. After 90 min. the metal complexes were precipitated out by adding excess of diethyl ether. A 0.5μL aliquot was withdrawn (out of 75.0 mL solution) and subjected to GC-MS study.

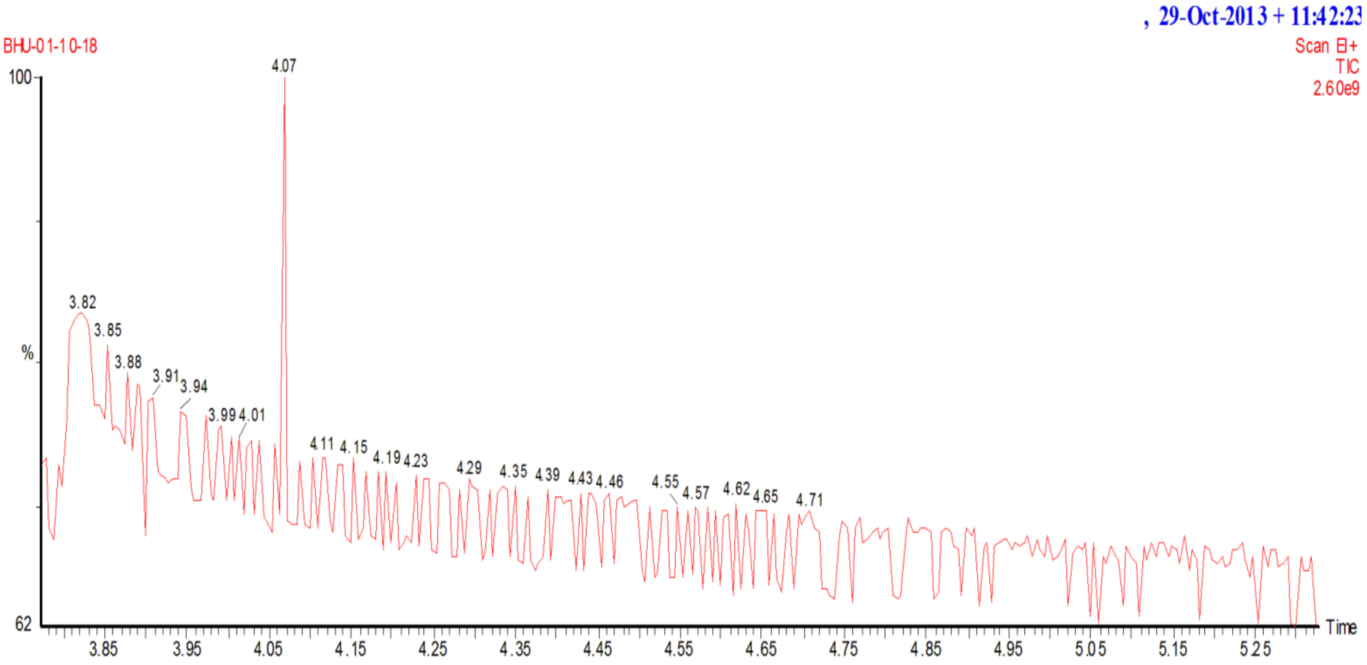

Figure S8 Gas chromatogram of GC-MS measurement of reaction mixture after 90 minutes

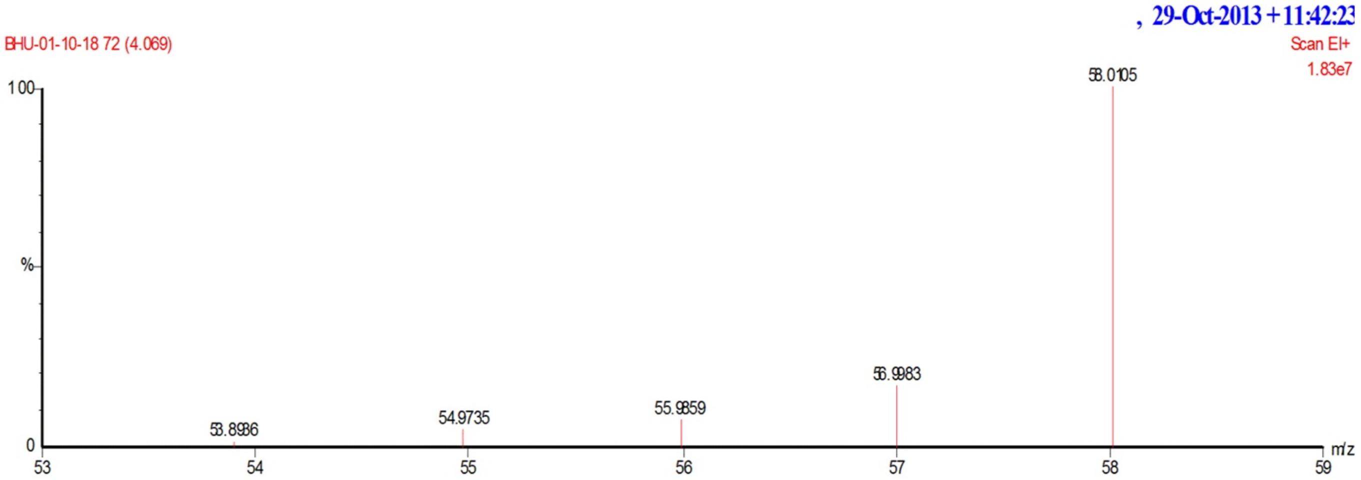

Figure S9 GC-MS graph for the corresponding chromatogram

Preparation of standard thiirane solution: A 10.0 mL acetonitrile solution containing 1.9 mg of thiirane was used as standard stock solution.

	Injection volume (μL)	Retention time (min.)	Area (a.u.)	A_2/ A_1
Standard thiirane solution	0.5	4.09	1435488(A_1)	0.989656
Organic fraction of reaction mixture	0.5	4.07	1420639(A_2)	

Total volume of organic fraction of the reaction mixture was 75.0 mL. Thus the quantity of thiirane in the reaction mixture was 14.1 mg.

References

1. K. Köhler, J. Eichhorn, F. Meyer, *Organometallics*, 2003, **22**, 4426-4432.
2. See ref 15 in manuscript
3. Z.D. Georgousis, P. C. Christidis, D. Hadjipavlou-Litina C. A. Bolos, *J. Mol. Struct.*, 2007, **837**, 30–37; F. A. Mautner, R. Vicente, S. S. Massoud, *Polyhedron*, 2006, **25**, 1673–1680.