

Tetra-(tetraalkylammonium)octamolybdate catalysts for selective oxidation of sulfides to sulfoxides with hydrogen peroxide

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Supplementary Information

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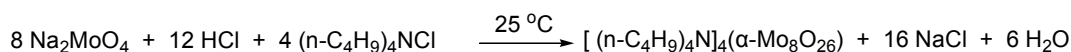
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1. General Methods

Melting points were determined in open capillaries on a Büchi melting point B-545 instrument and were uncorrected. NMR spectra were recorded with tetramethylsilane as the internal standard. Column chromatography was performed on silica gel (200-300 mesh) eluting with ethyl acetate and hexane or ethyl acetate and methanol. TLC was performed on glass-backed silica plates. Conversion, yield and selectivity were determined by GC analysis on HP-5 and DB-FFAP columns or ^1H NMR analysis in the presence of dimethyl maleate or bromobenzene as internal standard compounds. Purity of omeprazole was determined by HPLC analysis on C18 column. FT-IR spectra of catalysts were taken by the KBr disc method. All solvents were purchased from commercial sources and used without further purification. Catalysts besides tetra-(tetraalkylammonium)octamolybdate were available from commercial sources. All catalytic reactions and manipulations were performed open to air.

2. Synthetic procedure and characterization data of tetra-(tetraalkylammonium)octamolybdate catalysts

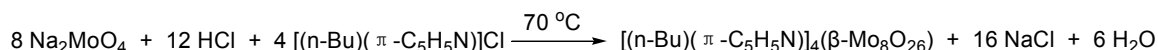
Dihydrate sodium molybdate (12.220 g, 0.05 mol) was dissolved into 30 mL of water and acidified with 6 mol/L of aqueous HCl to bring the solution to pH 4.5, and stirred for 1h. Then tetrabutylammonium chloride (8.0 g, 0.0282 mol) was added and stirred for 4 h. The precipitate was filtered off and thoroughly washed successively with water, absolute ethanol, acetone and diethyl ether, and the white solid was dried in vacuum at room temperature to give $[(\text{n-C}_4\text{H}_9)_4\text{N}]_4(\alpha\text{-Mo}_8\text{O}_{26})$ (10.2g) in 76% yield.¹



2a

$[(\text{n-C}_4\text{H}_9)_4\text{N}]_4(\alpha\text{-Mo}_8\text{O}_{26})$ (**2a**): white solid. ^1H NMR ($\text{d}^6\text{-DMSO}$, 300 MHz), δ (ppm) 0.94 (t, $J = 7.5$ Hz, $3\text{H} \times 4$), 1.26-1.38 (m, $2\text{H} \times 4$), 1.52-1.62 (m, $2\text{H} \times 4$), 3.17 (t, $J = 8.6$ Hz, $2\text{H} \times 4$); IR spectrum (KBr, cm^{-1}): 2961, 2938, 2872, 1633, 1481, 1460, 1379, 1345, 1149, 1104, 1053, 1025, 934, 921, 910, 872, 848, 807, 730, 712, 662, 555, 521, 409, 370, 311; Anal. Calcd. for $[(\text{n-C}_4\text{H}_9)_4\text{N}]_4(\alpha\text{-Mo}_8\text{O}_{26})$: C, 35.69%; H, 6.75%; N, 2.60%. Found: C, 35.47%; H, 6.78%; N, 2.60%.

A mixture of 12% dilute hydrogen chloride (9.5 mL, 0.038 mol) and aqueous solution of dihydrate sodium molybdate (6.11 g, 0.025 mol) was added dropwise into a 50 mL of aqueous solution of n-butylpyridinium chloride (8.233 g, 0.047 mol) under stirring at 70°C . After continuously stirring for 25 minutes, the resulted white precipitate was filtered, washed successively with water and diethyl ether, and dried in vacuum at room temperature to give $[(\text{n-C}_4\text{H}_9)(\pi\text{-C}_5\text{H}_5\text{N})]_4(\beta\text{-Mo}_8\text{O}_{26})$ (2.559 g) in 47% yield.²



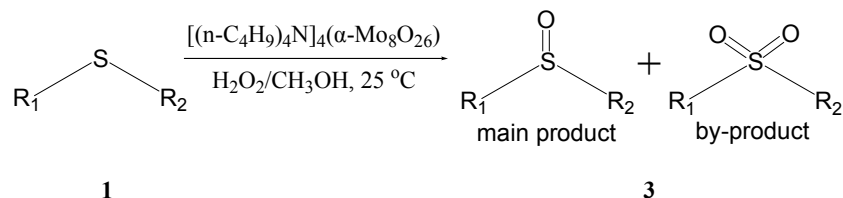
2b

$[(\text{n-C}_4\text{H}_9)(\pi\text{-C}_5\text{H}_5\text{N})]_4(\beta\text{-Mo}_8\text{O}_{26})$ (**2b**): white solid. ^1H NMR ($\text{d}^6\text{-DMSO}$, 300 MHz), δ (ppm) 0.91 (t, $J = 7.6$ Hz, 3H), 1.26-1.33 (m, 2H), 1.85-1.95 (m, 2H), 4.62 (t, $J = 7.5$ Hz, 2H), 8.16 (t, $J = 7.3$ Hz, 2H), 8.61 (t, $J = 7.9$ Hz, 1H), 9.11 (d, $J = 5.6$ Hz, 2H); IR spectrum (KBr, cm^{-1}): 3127, 3079, 3061, 2956, 2931, 2868, 1631, 1579, 1496, 1484, 1462, 1435, 1376, 1321, 1215, 1174, 941, 935, 912, 897, 837,

766, 713, 683, 664, 644, 573, 554, 520, 473, 449, 408, 366, 290; Anal. Calcd. for $[(n-C_4H_9)(\pi-C_5H_5N)]_4(\beta-Mo_8O_{26})$: C, 25.02%; H, 3.27%; N, 3.24%. Found: C, 24.85%; H, 3.31%; N, 3.36%.

3. Catalytic oxidation of different sulfides and characterization data of the corresponding products

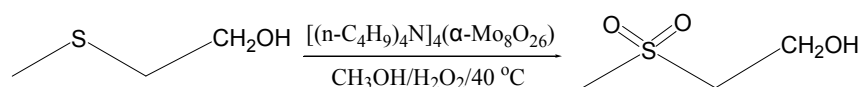
Procedure for oxidation of different sulfides to the corresponding sulfoxides:



The oxidation reaction was carried out in a 15 cm-height and 2.5 cm-diameter round tube with magnetic stirrer at room temperature. 0.0025 mmol $[(n-C_4H_9)_4N]_4(\alpha-Mo_8O_{26})$ and 2.5 mmol of sulfide (**1**) were added into the reactor, and then 4 mL methanol was added. After the reaction solution was stirred for 2 minutes, 30% aqueous hydrogen peroxide (2.5 mmol) was dropwise added into the solution under stirring. During the reaction process, the portion of catalyst dissolved in the organic substrate and product. The color of the reaction mixture changed from colorless to yellow, and then changed to pale yellow after H_2O_2 was used up. After completion of reaction, small amount of sodium thiosulfate was introduced into the reaction solution in order to eliminate the unreactive H_2O_2 . Then 10 mL ethyl acetate was added to self-precipitate the catalyst, and the catalyst was separated by filtration via a thin layer of alkaline Al_2O_3 . The solvents were removed under reduced pressure and the crude products were analyzed by gas chromatography or 1H NMR with dimethyl maleate or bromobenzene as internal standard. The further purification of sulfoxides was performed by flash chromatography (ethyl acetate/hexane or ethyl acetate/methanol) on silica gel.

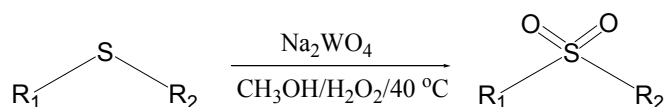
Procedure for oxidation of different sulfides to the corresponding sulfones:

Method A:

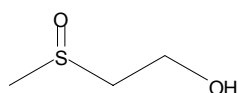


The oxidation reaction was carried out in a 15 cm-height and 2.5 cm-diameter round tube with magnetic stirrer at 40 °C. 0.0025 mmol $[(n-C_4H_9)_4N]_4(\alpha-Mo_8O_{26})$ and 2.5 mmol 2-(methylthio)ethanol were added into the reactor, and then 4 mL of methanol was added. After the reaction solution was stirred for 2 minutes, 30% aqueous hydrogen peroxide (0.55 mmol, 2 equivalents) was added dropwise into the solution under stirring. During the reaction process, the portion of catalyst dissolved in the organic substrate and product. The color of the reaction mixture changed from colorless to yellow. After completion of reaction, 10 mL of ethyl acetate was added to self-precipitate the catalyst, and the catalyst was separated by filtration via a thin layer of alkaline Al_2O_3 . The solvents were removed under reduced pressure to give methyl hydroxyethyl sulfone (100% yield). The product was analyzed by 1H NMR.

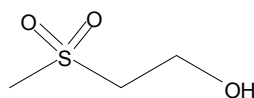
Method B:



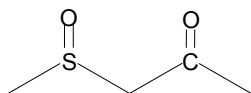
The oxidation reaction was carried out in a 15 cm-height and 2.5 cm-diameter round tube with magnetic stirrer at 40 °C. 0.05 mmol $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and 2.5 mmol sulfide were added into the reactor, then 4 mL of methanol was added. After the reaction solution was stirred for 2 minutes, 30% aqueous hydrogen peroxide (0.55 mmol, 2 equivalents) was added dropwise into the solution under stirring. During the reaction process, the portion of catalyst dissolved in the organic substrate and product. The color of the reaction mixture changed from colorless to yellow. After completion of reaction, 10 mL of ethyl acetate was added to self-precipitate the catalyst, and the catalyst was separated by filtration via a thin layer of alkaline Al_2O_3 . The solvents were removed under reduced pressure to give the product sulfone (100% yield). The products were analyzed by gas chromatography and ^1H NMR.



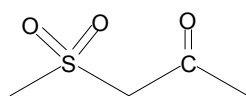
(3a) Colorless oil; ^1H NMR (d^6 -DMSO, 300 MHz), δ (ppm) 2.55 (s, 3H), 2.71-2.79 (m, 1H), 2.84-2.93 (m, 1H), 3.73-3.77 (m, 2H), 4.97 (s, 1H); ^{13}C NMR (d^6 -DMSO, 75 MHz), δ (ppm) 38.5, 54.1, 56.8.



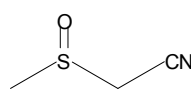
(3b) Colorless oil; ^1H NMR (d^6 -DMSO, 300 MHz), δ (ppm) 2.97 (s, 3H), 3.20 (t, J = 5.9 Hz, 2H), 3.76-3.81 (m, 2H), 5.11 (t, J = 5.1 Hz, 1H); ^{13}C NMR (d^6 -DMSO, 75 MHz), δ (ppm) 42.4, 55.2, 56.6.



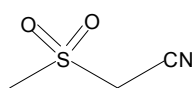
(3c) Pale yellow oil; ^1H NMR (d^6 -DMSO, 300 MHz), δ (ppm) 2.22 (s, 3H), 2.60 (s, 3H), 3.88 (d, J = 14.4 Hz, 1H), 4.08 (d, J = 14.4 Hz, 1H); ^{13}C NMR (d^6 -DMSO, 75 MHz), δ (ppm) 31.5, 38.3, 64.8, 201.8.



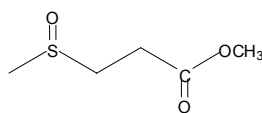
(3d) Colourless oil; ^1H NMR (d^6 -DMSO, 300 MHz), δ (ppm) 2.26 (s, 3H), 3.05 (3H, s), 4.47 (s, 2H); ^{13}C NMR (d^6 -DMSO, 75 MHz), δ (ppm) 31.5, 41.7, 64.6, 198.5.



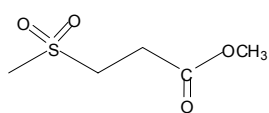
(3e) Colourless oil; ^1H NMR (d^6 -DMSO, 300 MHz), δ (ppm) 2.72 (s, 3H), 4.12 (d, J = 16.3 Hz, 1H), 4.37 (d, J = 16.3 Hz, 1H); ^{13}C NMR (d^6 -DMSO, 75 MHz), δ (ppm) 38.3, 40.4, 113.7.



(3f) White solid; Mp: 82-83 °C; ^1H NMR (d^6 -DMSO, 300 MHz), δ (ppm) 3.22 (s, 3H), 4.93 (s, 2H); ^{13}C NMR (d^6 -DMSO, 75 MHz), δ (ppm) 41.0, 43.2, 112.3.

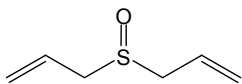


(3g) Colourless oil; ^1H NMR (d^6 -DMSO, 300 MHz), δ (ppm) 2.54 (s, 3H), 2.69-2.74 (m, 2H), 2.80-2.88 (m, 1H), 3.01-3.07 (m, 1H), 3.63 (s, 3H); ^{13}C NMR (d^6 -DMSO, 75 MHz), δ (ppm) 26.1, 37.9, 47.6, 51.7, 171.7.



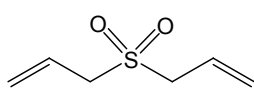
(3h) White solid; Mp: 93-95 °C; ^1H NMR ($\text{d}^6\text{-DMSO}$, 300 MHz), δ (ppm) 2.77 (t, $J = 7.5$ Hz, 2H), 3.00 (s, 3H), 3.38 (t, $J = 7.5$ Hz, 2H), 3.64 (s, 3H); ^{13}C NMR ($\text{d}^6\text{-DMSO}$, 75 MHz), δ (ppm) 25.9, 40.4, 49.2, 51.9,

170.8.

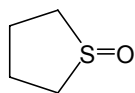


(3i) Colourless oil; ^1H NMR (CDCl_3 , 300 MHz), δ (ppm) 3.36 (dd, $J = 7.6, 13.3$ Hz, 2H), 3.49 (dd, $J = 7.3, 13.0$ Hz, 2H), 5.33-5.44 (m, 4H), 5.79-5.93 (m, 2H); ^{13}C NMR (CDCl_3 , 75 MHz), δ (ppm) 54.1, 123.5,

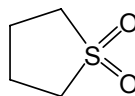
125.6.



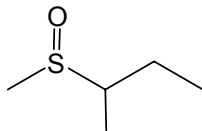
(3j) Colourless oil; ^1H NMR (300 MHz; CDCl_3) δ (ppm) 3.69 (d, $J = 7.3$ Hz, 4H), 5.38-5.50 (m, 4H), 5.82-5.96 (m, 2H); ^{13}C NMR (75 MHz; CDCl_3) δ (ppm) 55.9, 124.7, 124.8.



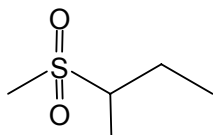
(3k) Colourless oil; ^1H NMR (CDCl_3 , 300 MHz), δ (ppm) 1.90-1.98 (m, 2H), 2.32-2.37 (m, 2H), 2.72-2.78 (m, 4H); ^{13}C NMR (CDCl_3 , 75 MHz), δ (ppm) 25.2, 54.2.



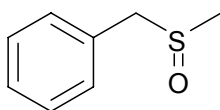
(3l) Colourless oil; ^1H NMR (CDCl_3 , 300 MHz), δ (ppm) 2.15-2.26 (m, 4H), 2.99-3.04 (m, 4H); ^{13}C NMR (CDCl_3 , 75 MHz), δ (ppm) 22.7, 51.1.



(3m) A mixture of two diastereomers (about 1:1 ratio), colourless oil; ^1H NMR ($\text{d}^6\text{-Acetone}$, 300 MHz), δ (ppm) 0.98-1.04 (m, 3H $\times$ 2), 1.14-1.19 (m, 3H $\times$ 2), 1.42-1.46 (m, 1H $\times$ 2), 1.77-1.82 (m, 1H $\times$ 2), 2.41 (s, 3H $\times$ 2), 2.41-2.47 (m, 1H, one isomer), 2.58 (brs, 1H, other isomer); ^{13}C NMR ($\text{d}^6\text{-Acetone}$, 75 MHz), δ (ppm) 10.3, 11.1, 11.5, 11.6, 23.1, 24.3, 34.7, 35.2, 57.6, 58.8.

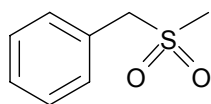


(3n) Colourless oil; ^1H NMR (CDCl_3 , 300 MHz), δ (ppm) 1.01-1.06 (m, 3H), 1.37 (t, $J = 3.5$ Hz, 3H); 1.49-1.54 (m, 1H), 2.04-2.08 (m, 1H), 2.78 (s, 3H), 2.80-2.84 (m, 1H); ^{13}C NMR (CDCl_3 , 75 MHz), δ (ppm) 11.1, 12.6, 22.4, 37.1, 60.4.

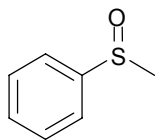


(3o) White solid; Mp: 55-57 °C; ^1H NMR (CDCl_3 , 300 MHz), δ (ppm) 2.44 (s, 3H), 3.91 (d, $J = 12.8$ Hz, 1H), 4.05 (d, $J = 12.8$ Hz, 1H), 7.26-7.29 (m, 2H), 7.34-7.40 (m, 3H); ^{13}C NMR (CDCl_3 , 75 MHz), δ (ppm)

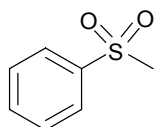
37.1, 60.0, 128.2, 128.7, 129.5, 129.8.



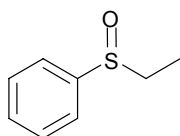
(3p) White solid; Mp: 124-126 °C; ^1H NMR ($\text{d}^6\text{-DMSO}$, 300 MHz), δ (ppm) 2.89 (s, 3H), 4.47 (s, 2H), 7.39-7.42 (m, 5H); ^{13}C NMR ($\text{d}^6\text{-DMSO}$, 75 MHz), δ (ppm) 39.4, 59.4, 128.3, 128.5, 129.1, 130.9.



(3q) Colourless oil; ^1H NMR (CDCl_3 , 300 MHz), δ (ppm) 2.61 (s, 3H), 7.36-7.45 (m, 3H), 7.52-7.56 (m, 2H); ^{13}C NMR (CDCl_3 , 75 MHz), δ (ppm) 43.7, 123.3, 129.2, 130.9, 145.4.

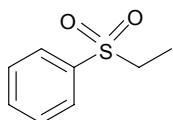


(3r) White solid; Mp: 85-87 °C; ^1H NMR (CDCl_3 , 300 MHz), δ (ppm) 3.05 (s, 3H), 7.55-7.60 (m, 2H), 7.63-7.66 (m, 1H), 7.93-7.97 (m, 2H); ^{13}C NMR (CDCl_3 , 75 MHz), δ (ppm) 44.4, 127.3, 129.3, 133.6, 140.5.



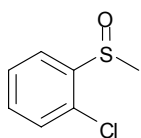
(3s) Colourless oil; ^1H NMR (CDCl_3 , 300 MHz), δ (ppm) 1.19 (t, $J = 7.4$ Hz, 3H), 2.70-2.80 (m, 1H), 2.81-2.96 (m, 1H), 7.47-7.54 (m, 3H), 7.59-7.62 (m, 2H); ^{13}C NMR (CDCl_3 , 75 MHz), δ (ppm) 5.7, 50.0, 123.9, 128.9, 130.7,

143.0.

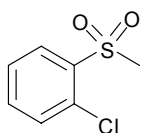


(3t) White solid; Mp: 39-41 °C; ^1H NMR ($\text{d}^6\text{-DMSO}$, 300 MHz), δ (ppm) 1.25 (t, $J = 7.5$ Hz, 3H), 3.10 (q, $J = 7.5$ Hz, 2H), 7.52-7.57 (m, 2H), 7.61-7.64 (m, 1H), 7.87-7.90 (m, 2H); ^{13}C NMR (CDCl_3 , 75 MHz), δ (ppm) 7.3, 50.4,

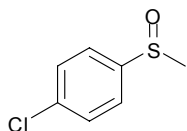
128.0, 129.1, 133.6, 138.4.



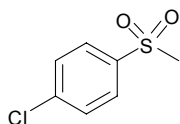
(3u) Colourless oil; ^1H NMR (CDCl_3 , 300 MHz), δ (ppm) 2.81 (s, 3H), 7.39-7.44 (m, 2H), 7.50-7.53 (m, 1H), 7.93-7.96 (m, 1H); ^{13}C NMR ($\text{d}^6\text{-DMSO}$, 75 MHz), δ (ppm) 41.4, 125.1, 128.5, 128.9, 129.8, 132.5, 143.8.



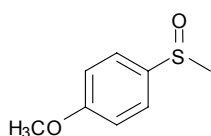
(3v) White solid; Mp: 84-86 °C; ^1H NMR (CDCl_3 , 300 MHz), δ (ppm) 3.27 (s, 3H), 7.48-7.51 (m, 1H), 7.56-7.59 (m, 2H), 8.14-8.17 (m, 1H); ^{13}C NMR (CDCl_3 , 75 MHz), δ (ppm) 42.7, 127.5, 130.8, 131.9, 132.5, 134.8, 138.0.



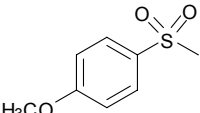
(3w) Colourless oil; ^1H NMR (CDCl_3 , 300 MHz), δ (ppm) 2.71 (s, 3H), 7.49 (d, $J = 8.6$ Hz, 2H), 7.58 (dd, $J = 1.9$, 6.9 Hz, 2H); ^{13}C NMR (CDCl_3 , 75 MHz), δ (ppm) 43.8, 124.8, 129.4, 137.0, 144.0.

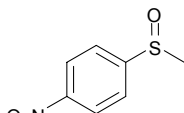


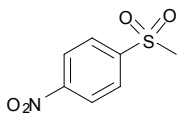
(3x) White solid; Mp: 96-98 °C; ^1H NMR (CDCl_3 , 300 MHz), δ (ppm) 3.05 (s, 3H), 7.55 (d, $J = 8.6$ Hz, 2H), 7.88 (d, $J = 8.6$ Hz, 2H); ^{13}C NMR (CDCl_3 , 75 MHz), δ (ppm) 44.5, 128.9, 129.7, 139.1, 140.5.

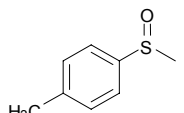


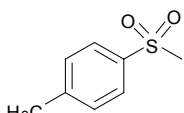
(3y) Colourless sticky oil; ^1H NMR (CDCl_3 , 300 MHz), δ (ppm) 2.65 (s, 3H), 3.81 (s, 3H), 6.96-7.01 (m, 2H), 7.53-7.58 (m, 2H); ^{13}C NMR (CDCl_3 , 75 MHz), δ (ppm) 43.8, 55.3, 114.7, 125.2, 136.4, 161.8.

 **(3z)** White solid; Mp: 118-120 °C; ¹H NMR (CDCl₃, 300 MHz), δ (ppm) 3.03 (s, 3H), 3.89 (s, 3H), 7.02 (d, J = 8.8 Hz, 2H), 7.87 (d, J = 8.8 Hz, 2H); ¹³C NMR (CDCl₃, 75 MHz), δ (ppm) 44.8, 55.7, 114.5, 129.6, 132.4, 163.7.

 **(3A)** Pale yellow solid; Mp: 150-152 °C; ¹H NMR (CDCl₃, 300 MHz), δ (ppm) 2.78 (s, 3H), 7.82 (d, J = 8.7 Hz, 2H), 8.36 (d, J = 8.7 Hz, 2H); ¹³C NMR (CDCl₃, 75 MHz), δ (ppm) 43.8, 124.4, 124.6, 149.4, 153.2.

 **(3B)** Pale yellow solid; Mp: 139-141 °C; ¹H NMR (CDCl₃, 300 MHz), δ (ppm) 3.12 (s, 3H), 8.16 (d, J = 8.8 Hz, 2H), 8.43 (d, J = 8.8 Hz, 2H); ¹³C NMR (CDCl₃, 75 MHz), δ (ppm) 44.3, 124.6, 128.9, 146.0, 150.9.

 **(3C)** white solid; Mp: 39-41 °C; ¹H NMR (CDCl₃, 300 MHz), δ (ppm) 2.40 (s, 3H), 2.69 (s, 3H), 7.31 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 8.2 Hz, 2H); ¹³C NMR (CDCl₃, 75 MHz), δ (ppm) 21.3, 43.9, 123.5, 130.0, 141.4, 142.5.

 **(3D)** white solid; Mp: 82-85 °C; ¹H NMR (CDCl₃, 300 MHz), δ (ppm) 2.45 (s, 3H), 3.03 (s, 3H), 7.36 (d, J = 8.0 Hz, 2H), 7.82 (d, J = 8.3 Hz, 2H); ¹³C NMR (CDCl₃, 75 MHz), δ (ppm) 21.6, 44.6, 127.4, 129.9, 137.8, 144.6.

4. Influence of the amount of oxidant in oxidation of thioanisole to sulfoxide

The influence of the amount of hydrogen peroxide was investigated with [(n-C₄H₉)₄N]₄(α -Mo₈O₂₆) as catalyst and thioanisole as substrate at room temperature and the results were summarized in table 1 and figure 1.

Table 1 Influence of the molar ratio of H₂O₂ to PhSMe^a

Entry	H ₂ O ₂ /PhSMe	Time (min)	Conversion (%) ^b	Yield (%) ^{b,c}	Selectivity (%) ^{b,c}
1	250/500	15	55.2	55.0	99.8
2	450/500	15	91.7	90.9	99.0
3	475/500	15	94.1	93.0	98.8
4	500/500	15	98.6	96.8	98.2
5	550/500	15	99.7	97.1	97.4
6	600/500	15	100	89.6	89.6
7	750/500	15	100	64.6	64.6

^aReaction conditions: thioanisole/[(n-C₄H₉)₄N]₄(α -Mo₈O₂₆) (mol/mol) = 500/1; 0.005 mmol [(n-C₄H₉)₄N]₄(α -Mo₈O₂₆); solvent: 4 mL of methanol; reaction temperature: 25 °C. ^bDetermined by GC on the crude reaction mixture. ^cYield = moles of SO/moles of substrate; selectivity = SO/(SO+SO₂).

Influence of the amount of H₂O₂ was vital to the performance of the oxidation reaction, especially to yield, but an excess of H₂O₂ decreased the reaction selectivity (Figure 1). While the ratio of H₂O₂/PhSMe was 1:1 to 1.1:1, the reaction conversion reached 99% in very short time (15 min) and the best result was obtained with 1:1 ratio of H₂O₂/PhSMe in both yield and selectivity (Table 1, entry 4).

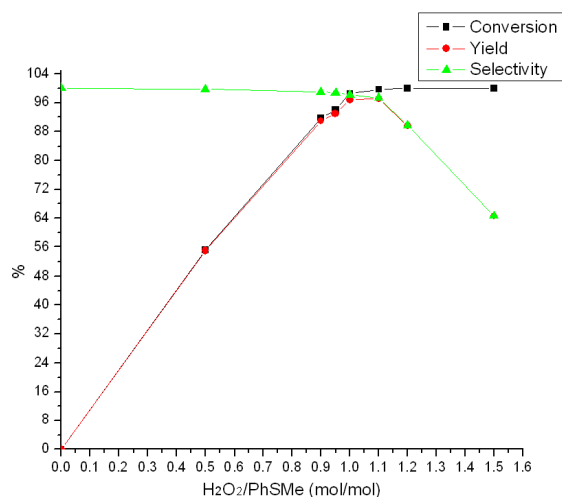


Figure 1 Influence of the molar ratio of H₂O₂ to PhSMe.

5. Influence of the reaction time in oxidation of thioanisole to sulfoxide

The influence of the reaction time was investigated with [(n-C₄H₉)₄N]₄(α -Mo₈O₂₆) as catalyst and thioanisole as substrate at room temperature and the results were summarized in table 2 and figure 2.

Table 2 Influence of the reaction time^a

Entry	H ₂ O ₂ /Catalyst/PhSMe	Time (min)	Conversion (%) ^b	Yield (%) ^{b,c}	Selectivity (%) ^{b,c}
1	500/1/500	5	97.5	95.7	98.5
2	500/1/500	10	99.0	96.9	98.3
3	500/1/500	15	99.7	96.6	97.2
4	500/1/500	30	99.8	96.2	96.8
5	500/1/500	60	99.9	95.9	96.4

^aReaction conditions: 2.5 mmol of thioanisole; 2.5 mmol H₂O₂; 0.005 mmol [(n-C₄H₉)₄N]₄(α -Mo₈O₂₆); solvent: 4 mL of methanol; reaction temperature: 25 °C. ^bDetermined by GC on the crude reaction mixture. ^cYield = moles of SO/moles of substrate; selectivity = SO/(SO+SO₂).

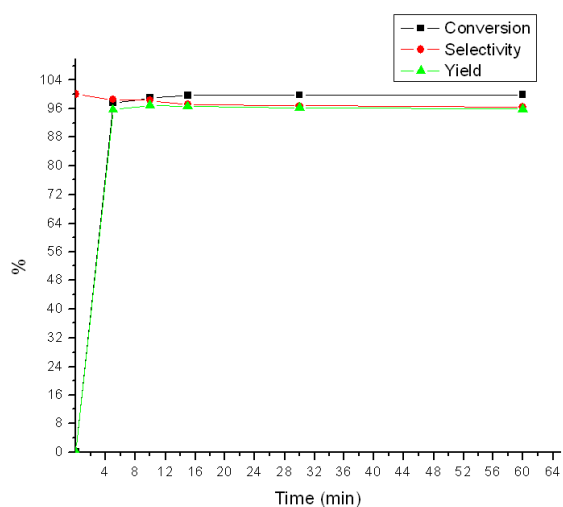


Figure 2 Influence of the reaction time.

The oxidation reaction was fast before 5 min and completed in 15 min (Figure 2). When the oxidation reaction was progressed for 10 minutes, the yield was the best but the selectivity fell slightly compared with the result obtained in 5 min (Table 2, entry 1 vs. entry2). The selectivity will decrease while prolonged the reaction time (Table 2, entry 2 vs. entries 3-5). So the best reaction time was 10 min based on both yield and selectivity.

6. Recycling of the catalyst

Procedure for recycling of catalyst: 0.025 mmol $[(n-C_4H_9)_4N]_4(\alpha-Mo_8O_{26})$ and 12.5 mmol thioanisole were added into a 15 cm-height and 2.5 cm-diameter round tube, then 4 mL of methanol was added. After the reaction solution was stirred for 2 minutes at room temperature, 30% aqueous hydrogen peroxide (12.5 mmol) was added dropwise into the solution under stirring. During the reaction process, the portion of catalyst dissolved in the organic substrate and product. The color of the reaction mixture changed from colorless to yellow, after H_2O_2 was used up, then it changed to pale yellow. After completion of reaction, 20 mL of ethyl acetate was added into the reaction solution in order to precipitate the catalyst. The catalyst was separated by filtration, washed with ethyl acetate, and dried in vacuum with 72.2% recovery yield. The solvents were removed under reduced pressure and the products were obtained.

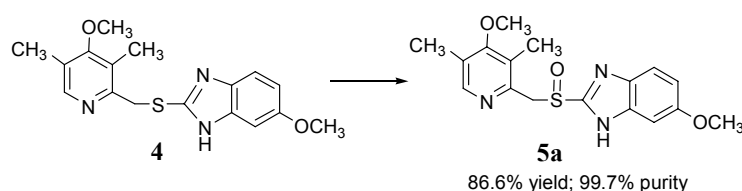
In the second cycle, 2.9 mL of methanol and 9.1 mmol thioanisole were added to the tube containing the recovered catalyst. After the reaction solution was stirred for 2 minutes, 30% aqueous hydrogen peroxide (9.1 mmol) was added dropwise into the solution under stirring. After completion of reaction, 20 mL of ethyl acetate was added into the reaction solution in order to precipitate the catalyst. The catalyst was separated by filtration, washed with ethyl acetate, and dried in vacuum with 84.6% recovery yield. The solvent were removed under reduced pressure and the products were obtained.

In the third cycle, the catalyst was recovered by filtration with 75.8% yield.

In the fourth cycle experiment, although only 0.0116 mmol catalyst was conducted in the reaction, 98% conversion was obtained in 20 min. the catalyst was recovered by filtration with 80.0% yield.

7. Preparation of omeprazole and characterization data

Scheme 1



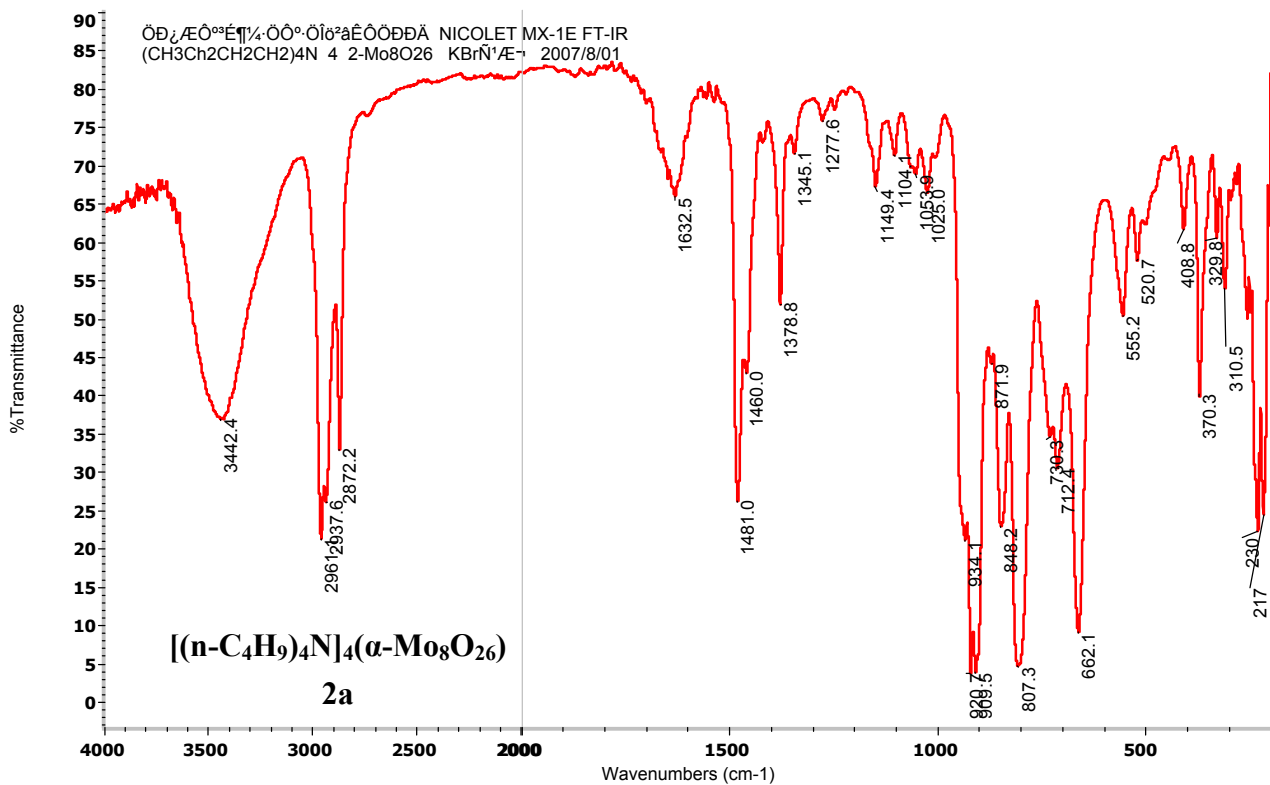
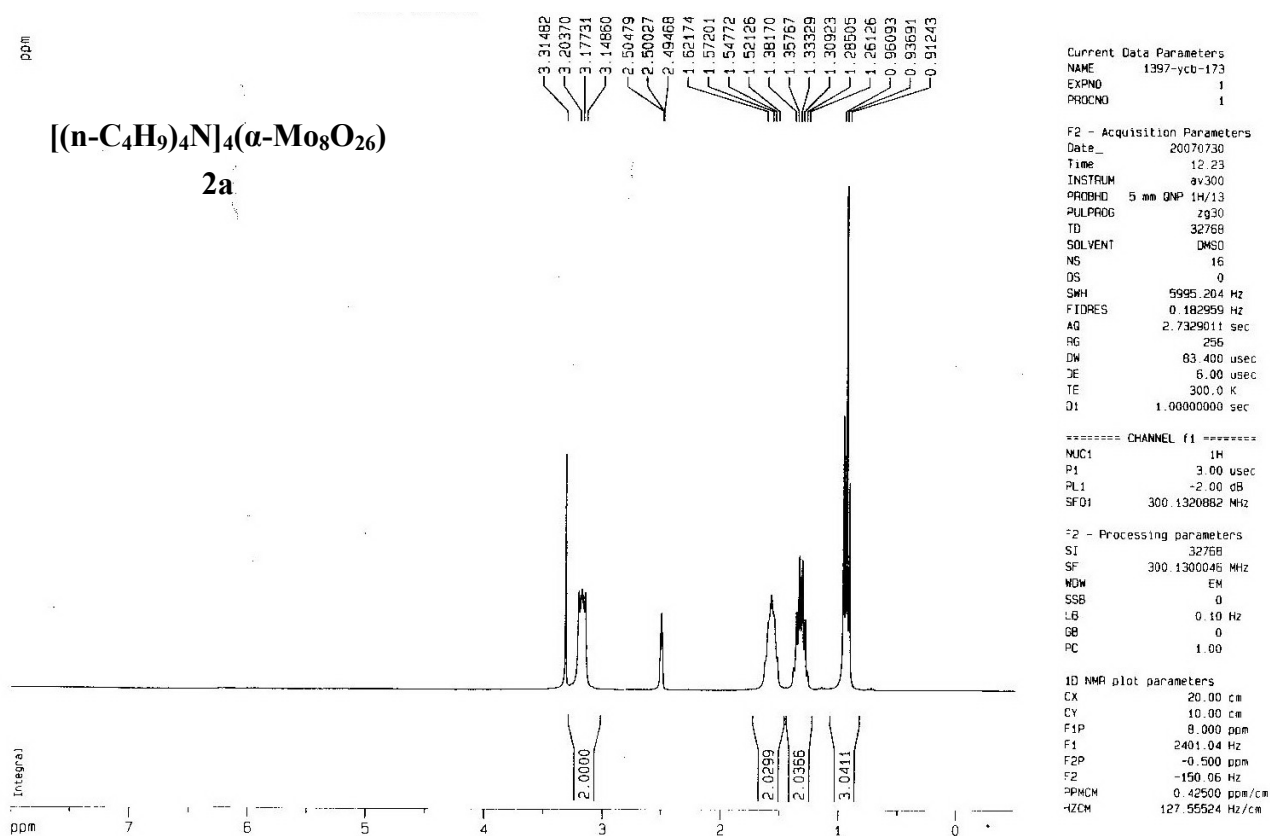
Procedure for preparation of omeprazole: 0.0984 g (0.0456 mmol) $[(n-C_4H_9)_4N]_4(\alpha-Mo_8O_{26})$ and 6.0g (18.24 mmol) 5-Methoxy-2-[(3,5-dimethyl-4-methoxy-2-pyridinyl)-methylthio]-1H-benzimidazole were added into a 250 mL three-necked flask, then 150 mL of isopropanol and 252.8 μ L of triethylamine (1.82 mmol) were added. When the temperature of reaction solution descended to 0

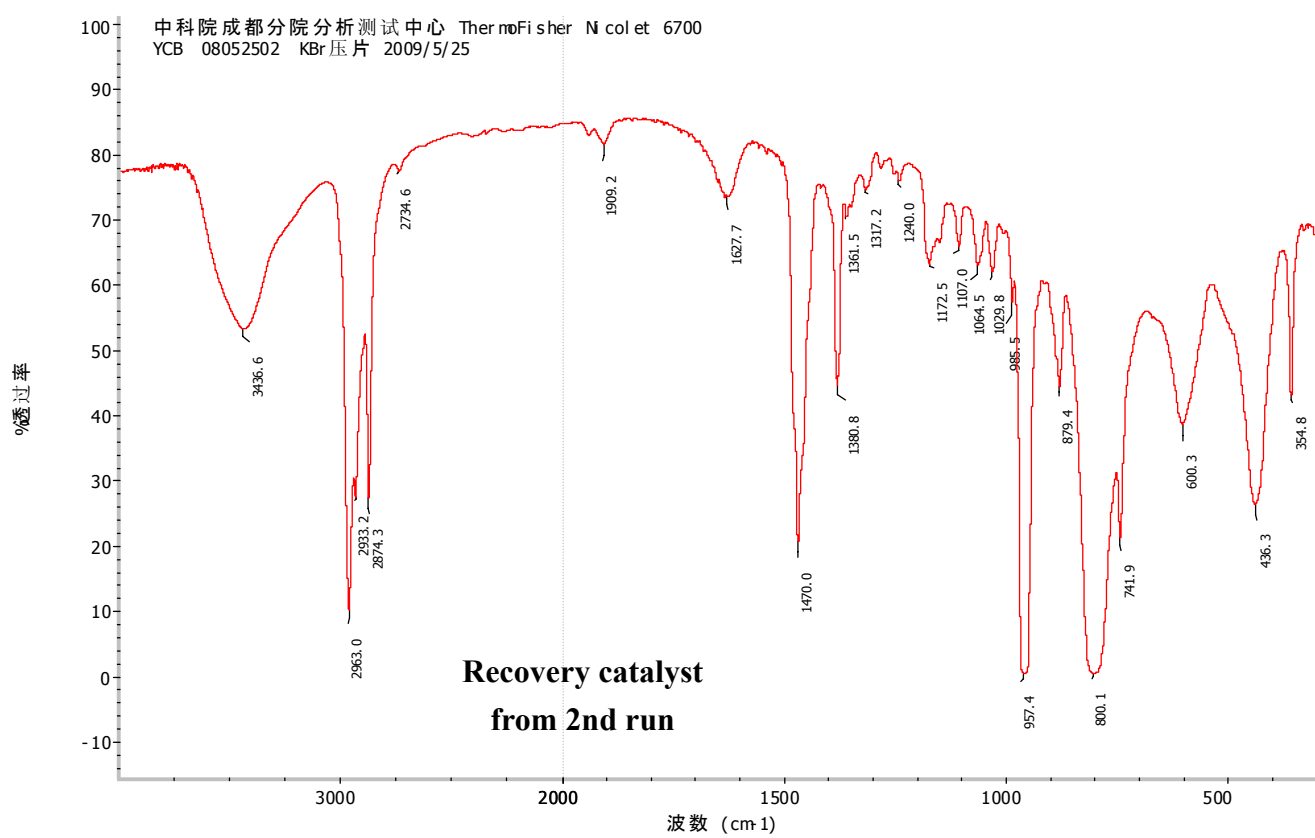
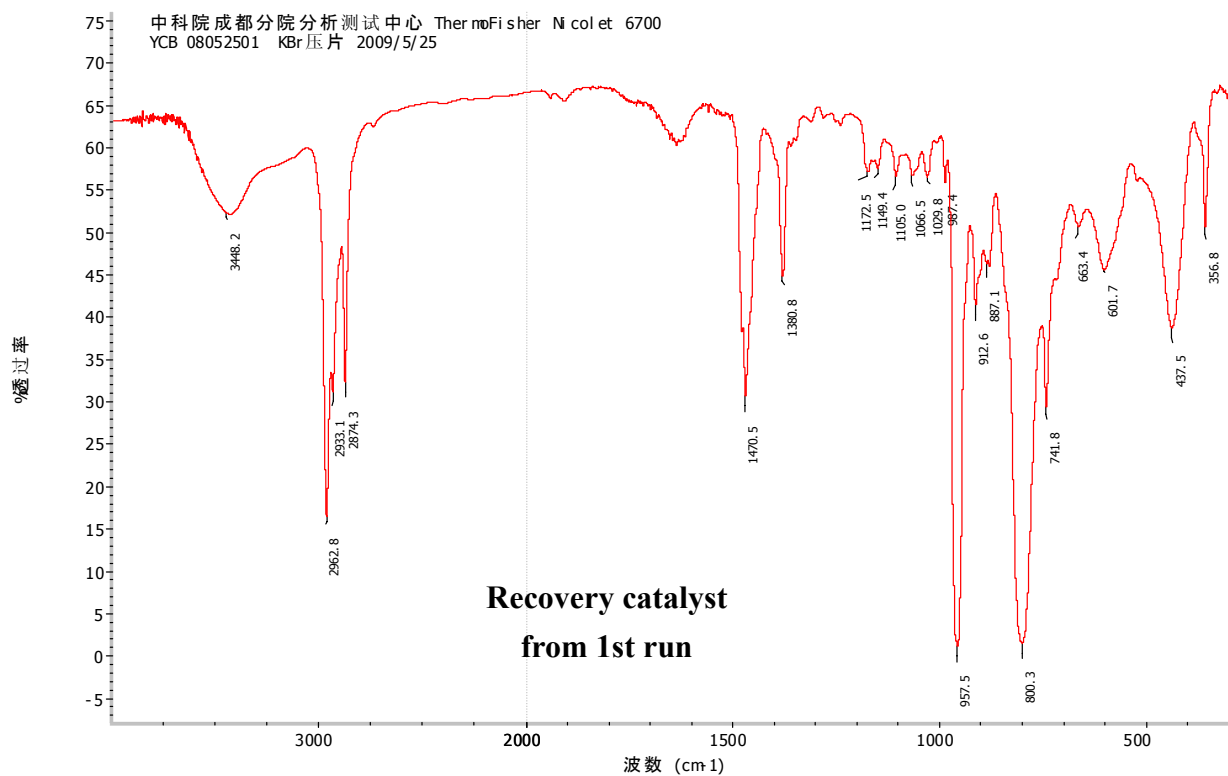
°C, 1.956 mL of 30% aqueous hydrogen peroxide (19.14 mmol) was dropwise added into the solution under stirring. The reaction was conducted under 0 °C. After completion of reaction (monitored by TLC), the reaction solution was transferred to a 1000 mL one-necked flask and 720 mL of cooled water was added under stirring at 0 °C. The white solid was filtered. Then 15 mL of 2-butanone and the resulted white solid were added to a flask, stirred for 2 hours under avoiding lights at 0 °C and filtered. The solid was washed with 200 mL of water and 30 mL of cooled ethanol-water (v/v, 1:1) and dried in vacuum to give omeprazole (**5a**) as a white solid (5.453 g) in 86.6% yield. The product was analyzed by HPLC, and the purity of omeprazole was 99.7% with 0.19% sulfone. Mp: 155-157°C; ¹H NMR (d⁶-DMSO, 300 MHz), δ (ppm) 2.16 (s, 3H), 2.19 (s, 3H), 3.68 (s, 3H), 3.80 (s, 3H), 4.68 (d, J = 13.5 Hz, 1H), 4.77 (d, J = 13.5 Hz, 1H), 6.92 (d, J = 7.2 Hz, 1H), 7.05 (brs, 1H), 7.55 (brs, 1H), 8.18 (s, 1H), 13.43 (s, 1H); ¹³C NMR (d⁶-DMSO+NaOH+D₂O, 75 MHz), δ (ppm) 11.7, 13.4, 56.0, 59.7, 60.4, 99.0, 112.3, 118.3, 126.3, 127.5, 138.4, 143.2, 149.6, 150.8, 155.9, 157.4, 164.3. The purity was determined by HPLC on C18 column, water/methanol/phosphoric acid/triethylamine (130:270:0.5:2), 0.7 mL/min, UV 254 nm, t_{major} = 6.78 min, t_{minor} = 9.67 min.

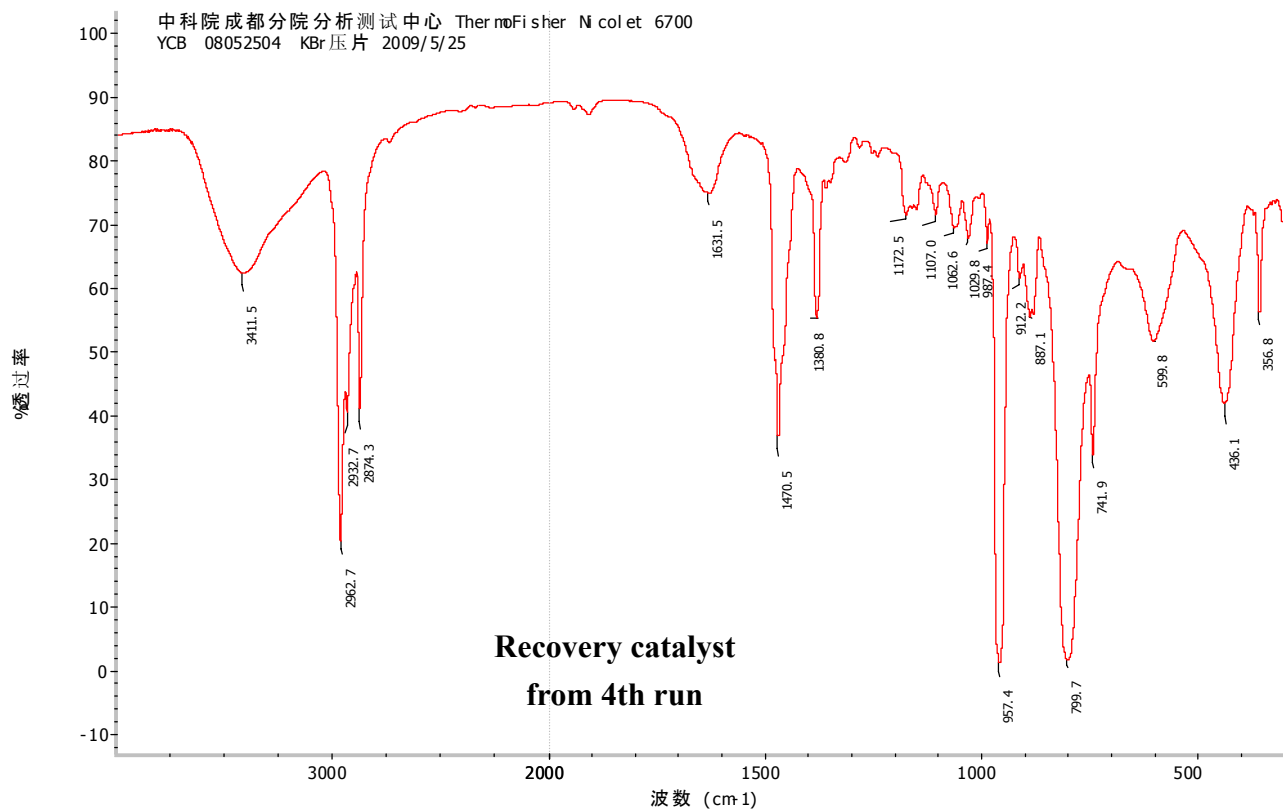
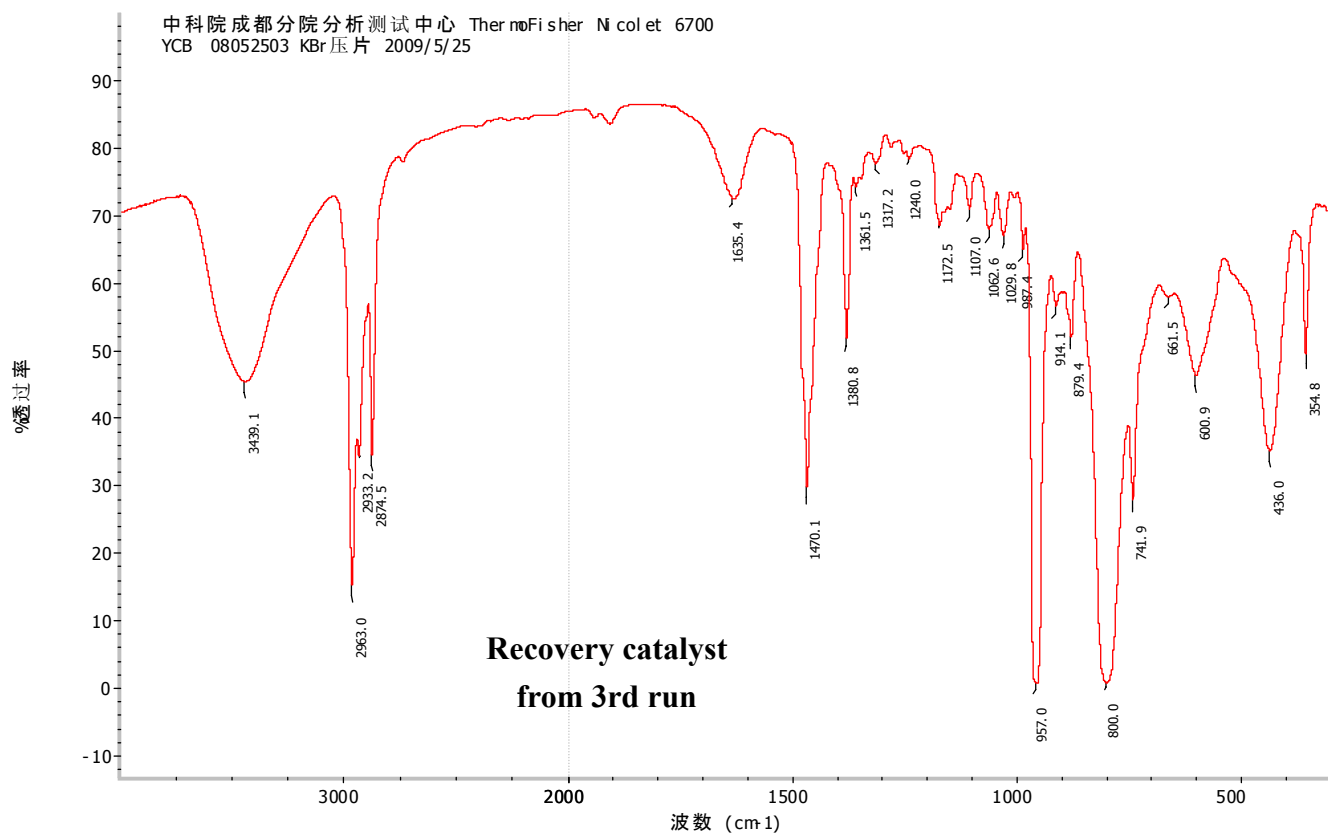
8. References

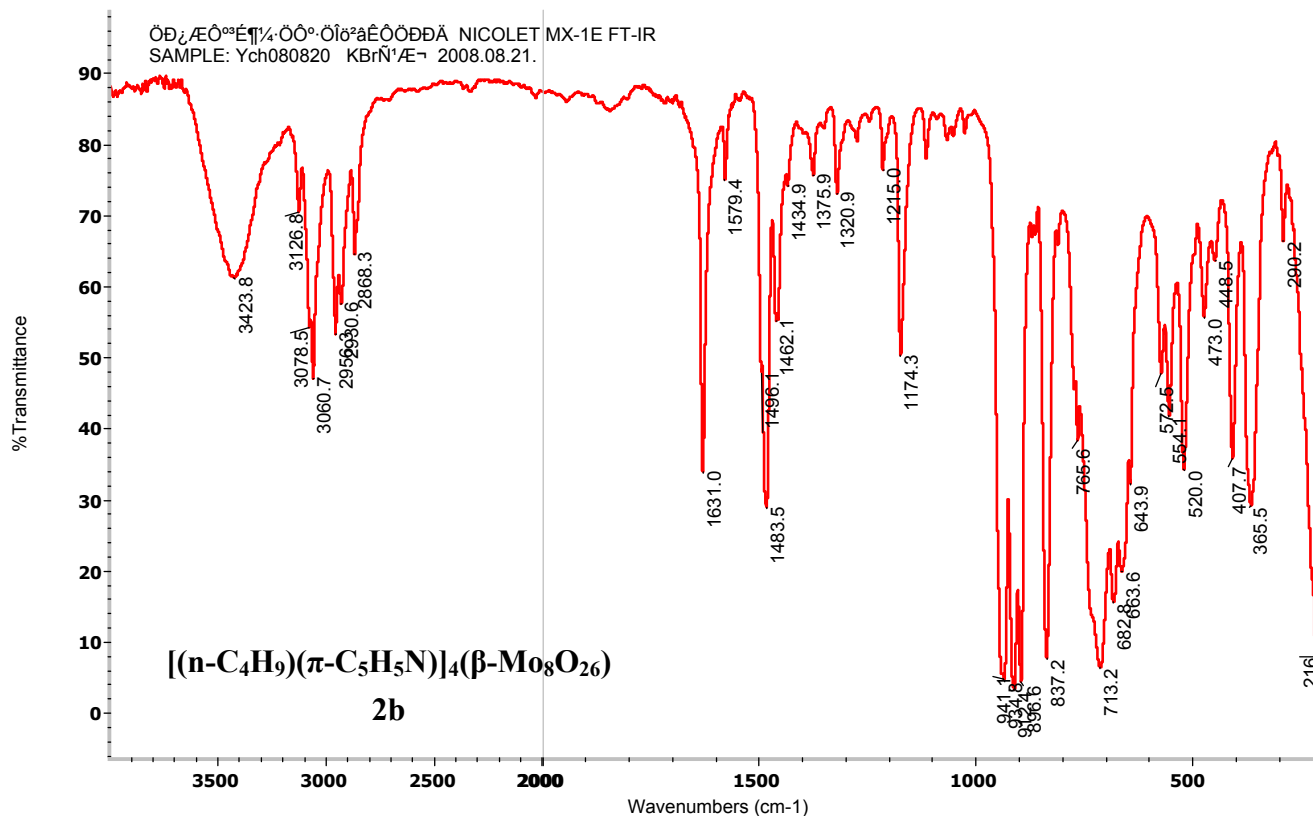
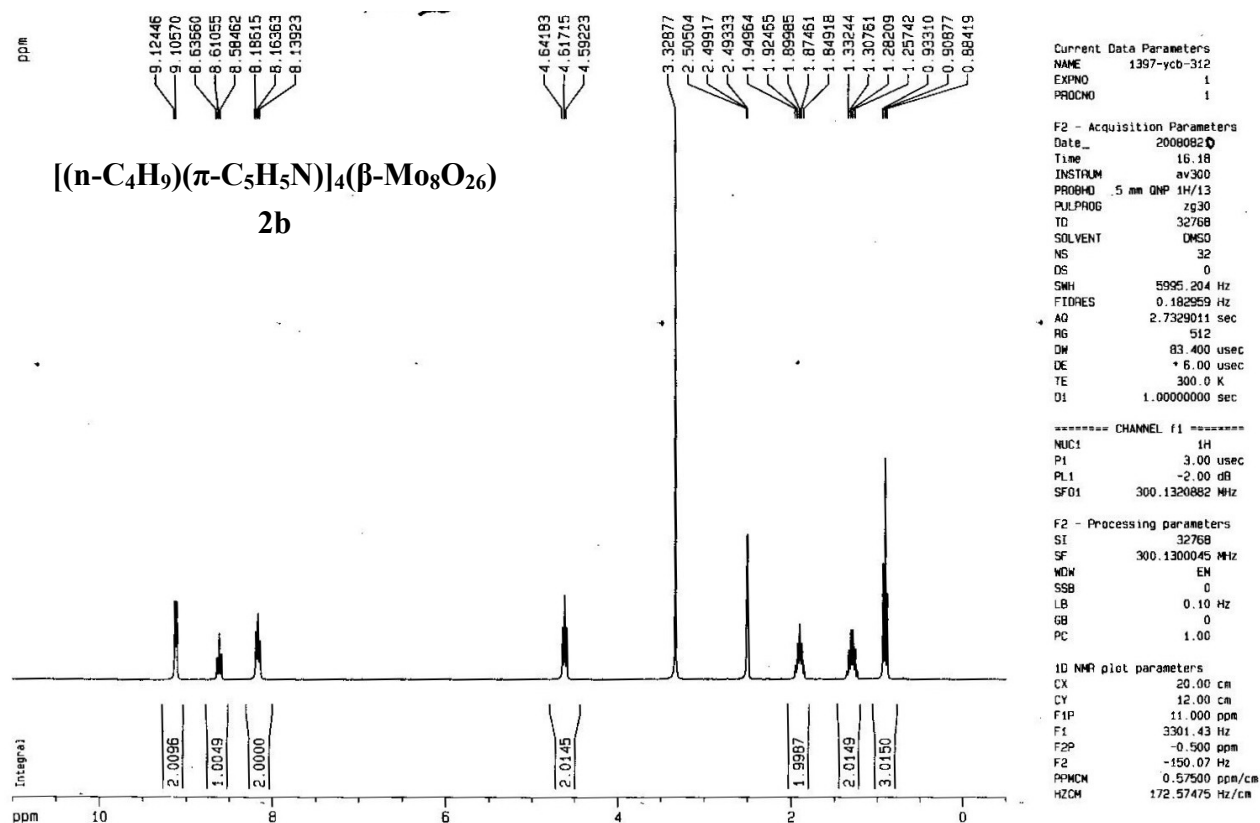
- 1 (a) M. Filowitz, R. K. C. Ho, W. G. Klemperer and W. Shum. *Inorg. Chem.*, 1979, **18**, 93; (b) W. G. Klemperer and W. Shum, *J. Am. Chem. Soc.*, 1976, **98**, 8291.
- 2 M. L. Guo and H. Z. Li, *Green Chem.*, 2007, **9**, 421.

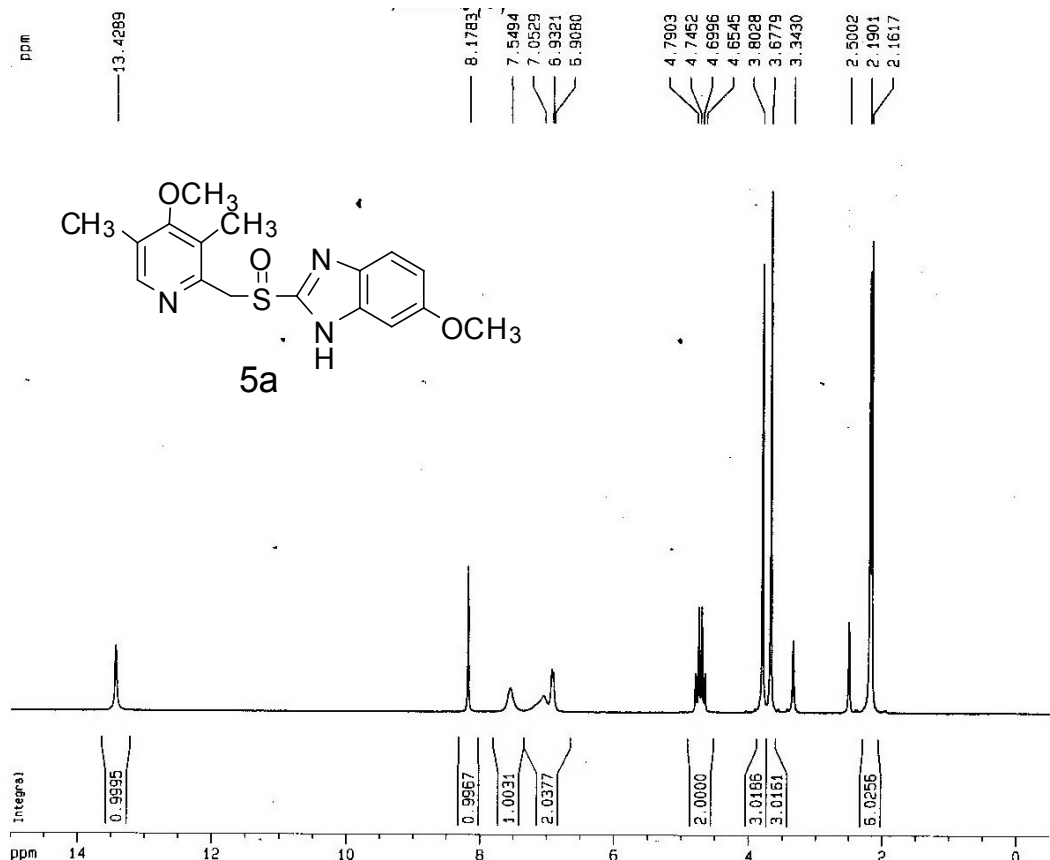
9. NMR and FT-IR spectra of tetra-(tetraalkylammonium)octamolybdate and recovery catalysts, and omeprazole











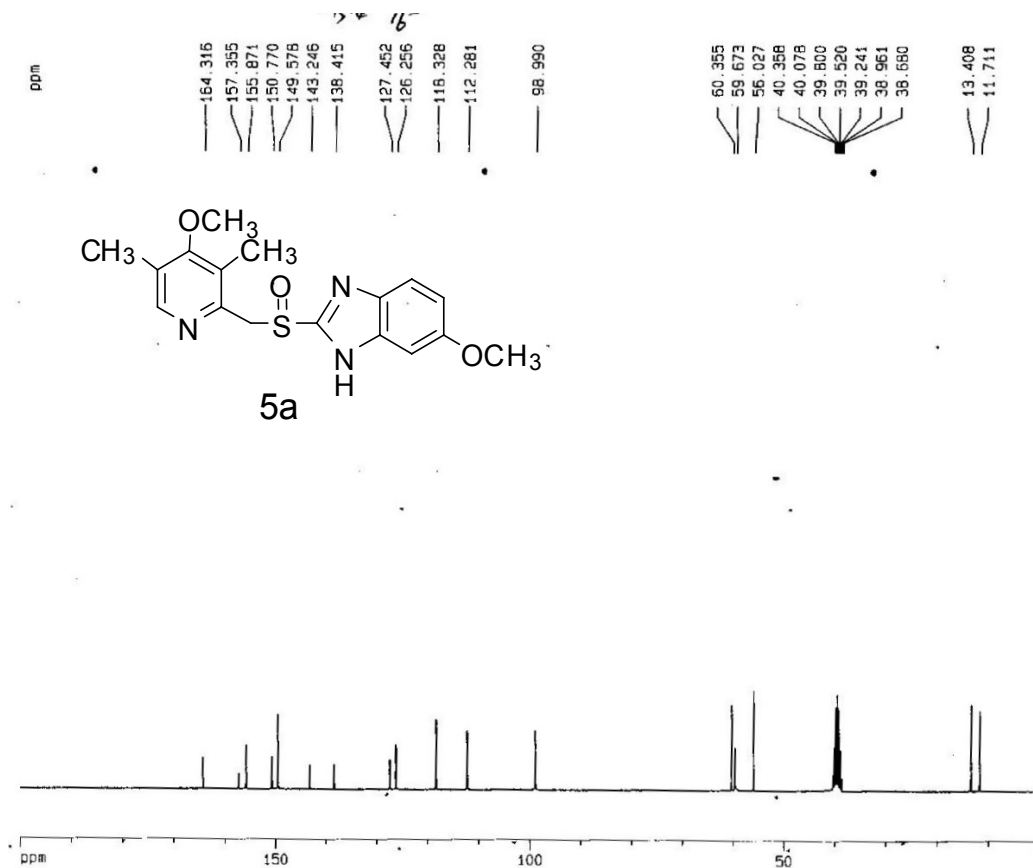
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