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SUPPORTING INFORMATION

Enhanced catalytic activity and stability of oxodiperoxo molybdenum modified mesoporous organosilicas in selective epoxidation reactions

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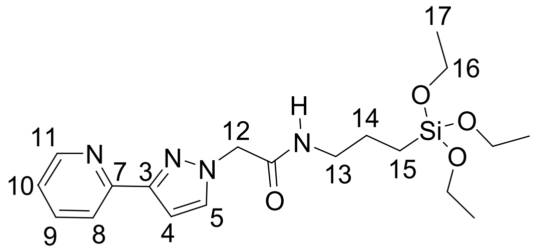
Experimental Procedures

General Remarks: Unless otherwise stated, all manipulations were carried out under an inert atmosphere of nitrogen and the solvents were dried by standard methods. Reagents were purchased from Aldrich chemicals and were used without further purification.

(a) (3-Triethoxysilylpropyl)[3-(2-pyridyl)-1-pyrazolyl]acetamide (1). 0.93 g (4.02 mmol) of [3-(2-pyridyl)-1-pyrazolyl]aceticacid ethylester were mixed with 0.89 g (4.02 mmol) of 3-triethoxysilylpropylamine and heated to 150 °C for 2 h. All volatiles were then removed in vacuum, resulting an oily residue in quantitative yield.



Scheme 1.

Numbering of the NMR resonances as given in Scheme 1.

^{1}H NMR (250.13 MHz, 25 °C, $CDCl_3$): δ 8.49 (d, *J* 5.0 Hz, H^{11}), 7.80 (d, *J* 7.9 Hz, H^8), 7.57 (dt, *J* 7.9 Hz, *J* 1.8 Hz, H^9), 7.47 (d, *J* 2.4 Hz, H^5), 7.09 (m, H^{10}), 6.82 (d, H^4), 6.65 (br, NH), 4.78 (s, H^{12}), 3.62 (q, *J* 7.0 Hz, H^{16}), 3.13 (q, *J* 6.2 Hz, H^{13}), 1.45 (m, H^{14}), 1.04 (t, H^{17}), 0.38 (m, H^{15}).

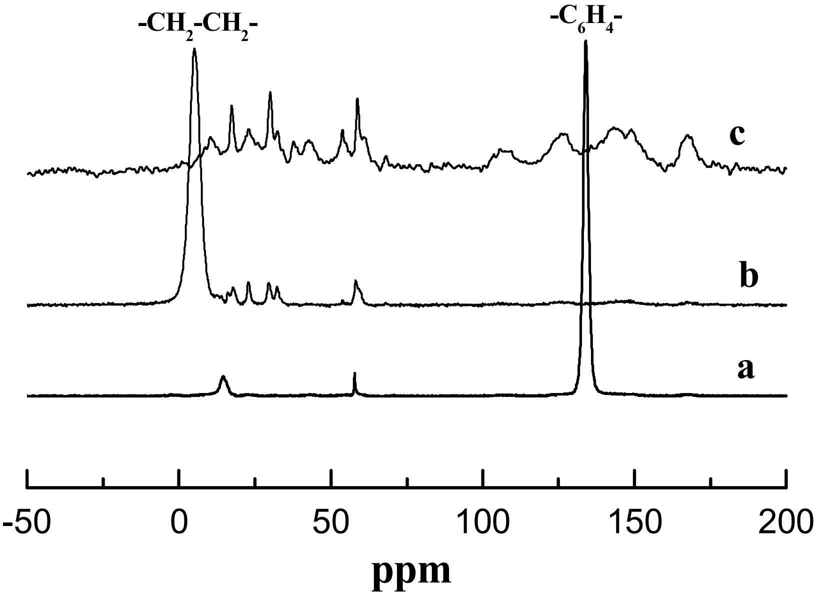
$^{13}C\{^1H\}$ NMR (62.89 MHz, 25 °C, $CDCl_3$): δ 166.7 (C=O), 152.7 (C^7), 151.2 (C^3), 148.9 (C^{11}), 136.1 (C^9), 132.2 (C^5), 122.2 (C^{10}), 119.7 (C^8), 104.9 (C^4), 57.7 (C^{16}), 54.8 (C^{12}), 41.3 (C^{13}), 23.3 (C^{14}), 17.8 (C^{17}), 7.0 (C^{15}).

(b) Oxodiperoxo{(3-triethoxysilylpropyl)[3-(2-pyridyl)pyrazol-1-yl]acetamide}molybdenum (2). 0.61 g (1.50 mmol) of **1** and 0.48 g (1.50 mmol) of $MoO(O_2)_2.(DMF)_2$ were dissolved in 30 mL of dry $CHCl_3$ and stirred for 4 h at room temperature. The solvent was removed in vacuum, the resulting yellow solid was washed with diethyl ether and dried in a vacuum.

Numbering of the NMR resonances as given in Scheme 1.

^{1}H NMR (250.13 MHz, 25 °C, $CDCl_3$): δ 9.32 (d, *J* 5.0 Hz, H^{11}), 8.28 (t, *J* 7.8 Hz, H^9), 7.97 (d,H^8), 7.71 (t, *J* 7.8 Hz, H^{10}), 7.57 (d, *J* 2.6 Hz, H^5), 6.91 (br,NH), 6.74 (d, H^4), 4.75 (s, H^{12}), 3.77 (q, *J* 7.0 Hz, H^{16}), 3.17 (q, *J* 6.0 Hz, H^{13}), 1.60 (m, H^{14}), 1.18 (t, H^{17}), 0.57 (m, H^{15}).
^{13}C-{^{1}H} NMR (62.89 MHz, 25 °C, CD_3CN): δ 165.9 (C=O), 155.4 (C^{11}), 151.4 (C^7), 150.2 (C^3), 144.8 (C^9), 136.4 (C^5), 127.1 (C^{10}), 124.8 (C^8), 105.9 (C^4), 59.0 (C^{16}), 54.8 (C^{12}), 42.8 (C^{13}), 23.6 (C^{14}), 18.7 (C^{17}), 8.1 (C^{15}).

(c) Synthesis of Oxodiperoxo{(3-triethoxysilylpropyl)[3-(2-pyridyl)pyrazol-1-yl]acetamide}molybdenum modified mesoporous materials BMo, EMo and MMo. A portion of 0.03 g of **2** dissolved in 5 mL of dry chloroform was added to a suspension of 0.30 g of the appropriate mesoporous support **B**, **E** or **M** in 30 mL of dry toluene. The mixture was stirred under an atmosphere of nitrogen for 12 h at 90 °C. The solid was filtered off, washed with $CHCl_3$ and dried under vacuum to obtain the mesoporous supported hybrid materials (contains ~3.3 wt.% of Mo).



Supporting Figure 1. ^{13}C CP-MAS NMR spectra of molybdenum modified mesoporous materials, (a) **BMo**, (b) **EMo** and (c) **MMo**.

Supporting Table 1. Textural properties of molybdenum containing mesoporous organosilicas and silicas before and after grafting reactions

Sample	BET surface area (m^2g^{-1})	BJH pore diameter (nm)
Benzene-silica (**B**)	765	2.7
BMo	613	2.5
Ethane-silica (**E**)	712	2.6
EMo	595	2.4
MCM-41 (**M**)	795	2.6
MMo	634	2.4

Supporting Table 2. Effect of different solvents on the epoxidation reaction of *cis*-cyclooctene [a]

Entry	Solvent	Yield of epoxide (%) [b]
1	Chloroform	96
2	Toluene	62
3	Acetonitrile	45

[a] Reaction conditions: 1 mmol of alkene, 1.2 mmol of ^{t}BuOOH (70% in H_2O), 1 mol% of **BMo**, 5 mL of solvent, 6 h, reflux.

[b] Yields were determined by GC-MS (Varian 3900) with respect to an internal standard (*n*-decane).