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FULL PAPER

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Synthesis, spectroscopic characterization and catalytic activity of *cis*-dioxidomolybdenum (VI) complexes with chiral tetradentate Schiff bases

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New chiral mononuclear *cis*-dioxidomolybdenum (VI) complexes, **MoO_2L^1–MoO_2L^{10}**, with tetradentate Schiff bases derived from various substituted salicylaldehydes and *1S*,*2S*-(+)-2-amino-1-(4-nitrophenyl)-1,3-propanediol were synthesized. All complexes were characterized by elemental analysis, circular dichroism, electronic and IR spectroscopy. ^{1}H NMR and also two-dimensional (COSY, NOESY and gHSQC) NMR measurements made for **MoO_2L^1–MoO_2L^{10}** complexes show that Schiff bases are coordinated to the MoO_2^{2+} cation, creating facial (*fac*) and meridional (*mer*) types of geometrical isomers. Moreover, catalytic activity studies were also performed for all complexes in asymmetric sulfoxidation of thioanisole and epoxidation of styrene, cyclohexene and two monoterpenes, i.e. *S*(−)-limonene and (−)-*α*-pinene, using aqueous 30% H_2O_2 or *tert*-butyl hydroperoxide as the oxygen source.

KEYWORDS

dioxidomolybdenum(VI), epoxidation, Schiff base, sulfoxidation

1 | INTRODUCTION

Transition metal complexes with Schiff base ligands as synthetic catalysts possess excellent activity in many various chemical reactions. They are considered as "privileged ligands"[1] in modern asymmetric catalysis. Schiff base ligands are able to stabilize many different metals in various oxidation states, controlling their performance in a large variety of useful catalytic transformations. Especially useful are chiral *N*-salicyl-*β*-amino alcohol Schiff base ligands,[2] which are very attractive owing to their simple synthesis from naturally available chiral amino acids[3] and whose structural and electronic properties can be fine-tuned. Such chiral Schiff bases are a group of ligands that are widely employed in various reactions, also asymmetric transformations with transition metals, i.e. sulfoxidation of organic sulfides,[4,5] enantioselective trimethylsilylcyanations,[6] asymmetric alkynylation of aldehydes,[5] epoxidation of cyclooctene,[7] oxidation of bromide[8] and stereoselective synthesis of cyclic ethers.[8,9] Moreover, after immobilization on a solid support, Schiff base complexes are still efficient catalysts using different oxidants, e.g. in oxidation of styrene or cyclohexene.[10]

Among the biologically important transition metals, the coordination chemistry of molybdenum has gained substantial attention as it was found to be an important biometal which has the ability to form complexes with versatile organic ligands, but can also promote facile electron-transfer pathways. Although different molybdenum complexes have been widely studied as catalysts, the chiral ones that especially useful in catalytic enantioselective oxidation reactions remain very limited.[11] Nevertheless, *cis*-dioxidomolybdenum (VI) complexes with tridentate and tetradentate Schiff bases have been successfully employed as catalysts in

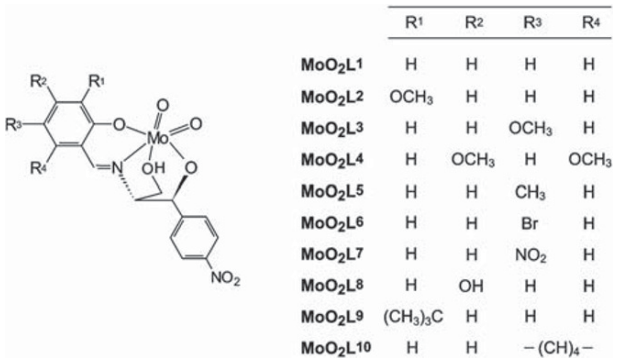
very efficient epoxidation of olefins (including styrene and cyclohexene)[12–15] and oxidation of sulfides to sulfoxides.[16–18] Lately, particular attention has been drawn to monocyclic and bicyclic monoterpenes, such as limonene and pinene, which are abundant natural products, but also inexpensive by-products, e.g. from the citrus fruit juice industry[19] and technical forestry resin or wood pulp by-produced in the manufacture of cellulose.[20]

We have an ongoing interest in the chemistry of dioxidomolybdenum (VI) complexes using different ONO tridentate donor ligands.[21,22] In this paper we describe 10 new *cis*-dioxidomolybdenum (VI) complexes with tetradentate ONOO Schiff base ligands, products of a single condensation of *1S*,*2S*-(+)-2-amino-1-(4-nitrophenyl)-1,3-propanediol with salicylaldehyde and its derivatives, presented in Figure 1. Very detailed investigation of their spectroscopic properties using IR, UV–vis, circular dichroism and one- and two-dimensional NMR techniques has been also performed. Moreover, their catalytic abilities in enantioselective sulfoxidation of thioanisole and epoxidation of alkenes, i.e. styrene and cyclohexene, and monoterpenes, i.e. *S*(−)-limonene and (−)-α-pinene, in the presence of aqueous 30% H_2O_2 or *tert*-butyl hydroperoxide as the terminal oxidant, have been studied.

2 | EXPERIMENTAL

2.1 | Measurements

All chemicals and reagents were obtained from commercial sources and used without further purification. Elemental analyses were performed with a Carlo Erba MOD 1106 instrument. Electronic spectra were measured on a Perkin-Elmer LAMBDA 18 spectrophotometer. CD spectra were recorded on a Jasco J-815 spectropolarimeter. IR spectra of solid samples (KBr pellets) were run on a Bruker IFS 66. NMR spectra were obtained in DMSO-d_6 solutions with a Bruker Avance III 700 MHz spectrometer using tetramethylsilane as a reference. A Shimadzu GC-2025 gas chromatograph with a Zebron ZB-5 capillary column (30 m × 0.25 mm × 0.25 mm) and Flame Ionization Detector detector were used to during catalytic studies. The identities of the oxidation products were confirmed by GC–MS model Shimadzu GCMS-QP2010 SE.



	R1	R2	R3	R4
MoO_2L^1	H	H	H	H
MoO_2L^2	OCH_3	H	H	H
MoO_2L^3	H	H	OCH_3	H
MoO_2L^4	H	OCH_3	H	OCH_3
MoO_2L^5	H	H	CH_3	H
MoO_2L^6	H	H	Br	H
MoO_2L^7	H	H	NO_2	H
MoO_2L^8	H	OH	H	H
MoO_2L^9	$(CH_3)_3C$	H	H	H
MoO_2L^{10}	H	H	$-(CH)_4-$	

FIGURE 1 Structural formulae of dioxidomolybdenum (VI) complexes

2.2 | Synthesis of dioxidomolybdenum (VI) complexes

A similar procedure was employed for synthesis of all complexes. To a solution of 1 mmol of *1S*,*2S*-(+)-2-amino-1-(4-nitrophenyl)-1,3-propanediol in MeOH (10 ml), 1 mmol of one of following aromatic *o*-hydroxyaldehydes was added: salicylaldehyde, 3-methoxysalicylaldehyde, 5-methoxysalicylaldehyde 4,6-dimethoxysalicylaldehyde, 5-methylsalicylaldehyde, 5-bromosalicylaldehyde, 5-nitrosalicylaldehyde, 4-hydroxysalicylaldehyde, 3-*tert*-butylsalicylaldehyde or 2-hydroxy-1-naphthaldehyde in 10 ml of MeOH. The reaction mixture was heated with stirring under reflux for 1 h. Then, *bis*(acetylacetonato) dioxidomolybdenum (VI) (1 mmol) in MeOH (10 ml) was added and stirred at under reflux for 2 h. After cooling, precipitates were separated as yellow solids, filtered off and washed with MeOH.

2.2.1 | MoO_2L^1

Yield 85%. Anal. calc for $C_{16}H_{14}N_2O_7Mo$: C, 43.5; H, 3.2; N, 6.3. Found: C, 43.3; H, 3.3; N, 6.3%. IR (KBr, cm^{-1}): 3417 (ν_{O-H}); 1631 ($\nu_{C=N}$); 1600, 1472 ($\nu_{C=C}$); 1510, 1348 (ν_{NO2}); 1294 (ν_{C-O}); 907, 882 ($\nu_{Mo=O}$). UV–vis spectrum in DMSO [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 274 (11220), 347 (1900). CD spectrum in DMSO [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 282 (7.18), 351 (6.97). ^{1}H NMR (DMSO-d_6, ppm) *mer*-isomer (65%): 8.73 (1H, s) (azomethine); 8.28 (2H, d, ^3J = 8.6 Hz), 7.77 (2H, t, ^3J = 8.6 Hz), 7.59 (1H, dd, ^3J = 7.7 Hz, ^4J = 1.6 Hz), 7.50 (1H, t, ^3J = 7.7 Hz), 6.95 (1H, ov), 6.88 (1H, d, ^3J = 8.9 Hz) (aromatic); 5.28 (1H, ov) (hydroxyl); 5.45 (1H, d, ^3J = 7.0 Hz), 3.93 (1H, m) (methine); 4.07 (1H, ov), 3.66 (1H, dt, ^3J = 12.3 Hz, ^4J = 5.6 Hz) (methylene); *fac*-isomer (35%): 8.79 (1H, s) (azomethine); 8.30 (2H, d, ^3J = 8.6 Hz), 7.70 (2H, t, ^3J = 8.6 Hz), 7.62 (1H, dd, ^3J = 7.8 Hz, ^4J = 1.6 Hz), 7.53 (1H, ov), 6.96 (1H, ov), 6.90 (1H, d, ^3J = 8.9 Hz) (aromatic); 5.97 (1H, d, ^3J = 4.7 Hz) (hydroxyl); 4.17 (1H, dd, ^3J = 9.1 Hz, ^4J = 4.1 Hz), 4.07 (1H, ov) (methine); 4.90 (1H, dd, ^3J = 9.3 Hz, ^4J = 4.6 Hz), 4.05 (1H, ov) (methylene).

2.2.2 | MoO_2L^2

Yield 87%. Anal. calc for $C_{17}H_{16}N_2O_8Mo$: C, 43.2; H, 3.4; N, 5.9. Found: C, 43.0; H, 3.4; N, 6.0%. IR (KBr, cm^{-1}): 3428 (ν_{O-H}); 1630 ($\nu_{C=N}$); 1599, 1470 ($\nu_{C=C}$); 1516, 1350 (ν_{NO2}); 1258 (ν_{C-O}); 929, 902 ($\nu_{Mo=O}$). UV–vis spectrum in DMSO [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 287 (13310), 360 (1720). CD spectrum in DMSO [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 293 (9.61), 374 (4.28). ^{1}H NMR (DMSO-d_6, ppm) *mer*-isomer (65%): 8.71 (1H, s) (azomethine); 8.26 (2H, d, ^3J = 8.7 Hz), 7.74 (2H, d, ^3J = 8.7 Hz), 7.21 (1H, ov), 7.20 (1H, ov), 6.93 (1H, t, ^3J = 7.9 Hz) (aromatic); 5.25 (1H, t, ^3J = 5.2 Hz) (hydroxyl); 5.43 (1H, d, ^3J = 6.9 Hz), 3.90 (1H, m) (methine); 4.04 (1H, ov), 3.63 (1H, dt, ^3J = 12.4 Hz, ^4J = 5.6 Hz) (methylene); 3.81 (3H, s) (methoxy); *fac*-isomer (35%): 8.78 (1H, s) (azomethine); 8.29 (2H, d, ^3J = 8.7 Hz), 7.66 (2H, d, ^3J = 8.7 Hz), 7.24 (1H, dd, ^3J = 7.9 Hz, ^4J = 1.2 Hz), 7.20 (1H, ov), 6.94 (1H, t, ^3J = 7.9 Hz) (aromatic); 5.95 (1H, d, ^3J = 4.7 Hz) (hydroxyl); 4.14 (1H, dd, ^3J = 9.1 Hz, ^4J = 4.1 Hz), 4.04 (1H, ov) (methine); 4.88 (1H, dd, ^3J = 9.3 Hz, ^4J = 4.7 Hz), 4.00 (1H, ov) (methylene); 3.82 (3H, s) (methoxy).

2.2.3 | MoO_2L^3

Yield 83%. Anal. calc for $C_{17}H_{16}N_2O_8Mo$: C, 43.2; H, 3.4; N, 5.9. Found: C, 43.3; H, 3.5; N, 5.9%. IR (KBr, cm^{-1}): 3425 (ν_{O-H}); 1631 ($\nu_{C=N}$); 1608, 1479 ($\nu_{C=C}$); 1516, 1348 (ν_{NO2}); 1238 (ν_{C-O}); 927, 896 ($\nu_{Mo=O}$). UV–vis spectrum in DMSO [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 277 (10210), 370 (1630). CD spectrum in DMSO [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 282 (5.94), 307 (−1.48), 386 (4.28). ^{1}H NMR (DMSO-d_6, ppm) *mer*-isomer (65%): 8.71 (1H, s) (azomethine); 8.27 (2H, d, ^3J = 8.6 Hz), 7.74 (2H, d, ^3J = 8.6 Hz), 7.21 (1H, d, ^3J = 3.1 Hz), 7.16 (1H, t, ^3J = 3.1 Hz), 6.91 (1H, d, ^3J = 9.0 Hz) (aromatic); 5.25 (1H, t, ^3J = 5.2 Hz) (hydroxyl); 5.41 (1H, d, ^3J = 6.9 Hz), 3.87 (1H, m) (methine); 4.03 (1H, ov), 3.63 (1H, dt, ^3J = 12.4 Hz, ^4J = 5.6 Hz) (methylene); 3.76 (3H, s) (methoxy); *fac*-isomer (35%): 8.78 (1H, s) (azomethine); 8.29 (2H, d, ^3J = 8.6 Hz), 7.65 (2H, d, ^3J = 8.6 Hz), 7.26 (1H, d, ^3J = 3.1 Hz), 7.14 (1H, t, ^3J = 3.1 Hz), 6.89 (1H, d, ^3J = 9.0 Hz) (aromatic); 5.99 (1H, d, ^3J = 4.7 Hz) (hydroxyl); 4.10 (1H, dd, ^3J = 9.1 Hz, ^4J = 4.1 Hz), 4.04 (1H, ov) (methine); 4.89 (1H, dd, ^3J = 9.3 Hz, ^4J = 4.6 Hz), 4.00 (1H, t, ^3J = 4.6 Hz) (methylene); 3.78 (3H, s) (methoxy).

2.2.4 | MoO_2L^4

Yield 79%. Anal. calc for $C_{18}H_{18}N_2O_9Mo$: C, 43.0; H, 3.6; N, 5.6. Found: C, 43.1; H, 3.7; N, 5.6%. IR (KBr, cm^{-1}): 3395 (ν_{O-H}); 1621 ($\nu_{C=N}$); 1601, 1478 ($\nu_{C=C}$); 1519, 1348 (ν_{NO2}); 1218 (ν_{C-O}); 936, 905 ($\nu_{Mo=O}$). UV–vis spectrum in DMSO [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 297 (22090). CD spectrum in DMSO [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 278 (−6.78), 338 (9.22). ^{1}H NMR (DMSO-d_6, ppm) *mer*-isomer (65%): 8.69 (1H, s) (azomethine); 8.24 (2H, d, ^3J = 8.7 Hz), 7.71 (2H, d, ^3J = 8.7 Hz), 6.44 (1H, d, ^3J = 2.7 Hz), 6.35 (1H, d, ^3J = 2.7 Hz) (aromatic); 5.23 (1H, t, ^3J = 5.2 Hz) (hydroxyl); 5.42 (1H, d, ^3J = 6.9 Hz), 3.88 (1H, m) (methine); 4.02 (1H, ov), 3.61 (1H, dt, ^3J = 12.4 Hz, ^4J = 5.6 Hz) (methylene); 3.88 (3H, s), 3.84 (3H, s) (methoxy); *fac*-isomer (35%): 8.27 (2H, d, ^3J = 8.7 Hz), 7.73 (2H, d, ^3J = 8.7 Hz), 6.46 (1H, d, ^3J = 2.7 Hz), 6.38 (1H, d, ^3J = 2.7 Hz) (aromatic); 5.93 (1H, d, ^3J = 4.7 Hz) (hydroxyl); 4.12 (1H, dd, ^3J = 9.1 Hz, ^4J = 4.1 Hz), 4.02 (1H, ov) (methine); 4.86 (1H, dd, ^3J = 9.3 Hz, ^4J = 4.7 Hz), 3.99 (1H, ov) (methylene); 3.89 (3H, s), 3.85 (3H, s) (methoxy).

2.2.5 | MoO_2L^5

Yield 82%. Anal. calc for $C_{17}H_{16}N_2O_7Mo$: C, 44.8; H, 3.5; N, 6.1. Found: C, 44.9; H, 3.4; N, 6.1%. IR (KBr, cm^{-1}): 3436 (ν_{O-H}); 1626 ($\nu_{C=N}$); 1603, 1478 ($\nu_{C=C}$); 1515, 1347 (ν_{NO2}); 1228 (ν_{C-O}); 931, 902 ($\nu_{Mo=O}$). UV–vis spectrum in DMSO [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 277 (10460), 353 (1620). CD spectrum in DMSO [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 282 (5.11), 305 (−1.40), 364 (4.94). ^{1}H NMR (DMSO-d_6, ppm) *mer*-isomer (65%): 8.67 (1H, s) (azomethine); 8.23 (2H, d, ^3J = 8.7 Hz), 7.71 (2H, d, ^3J = 8.7 Hz), 7.38 (1H, dd, ^3J = 8.2 Hz, ^4J = 2.1 Hz), 7.27 (1H, 1H, t, ^3J = 9.1 Hz), 6.83 (1H, d, ^3J = 8.2 Hz) (aromatic); 5.23 (1H, t, ^3J = 5.2 Hz) (hydroxyl); 5.41 (1H, d, ^3J = 6.9 Hz), 3.88 (1H, m) (methine); 4.03 (1H, ov), 3.61 (1H, dt, ^3J = 12.4 Hz, ^4J = 5.6 Hz) (methylene); 2.34 (3H, s) (methyl); *fac*-isomer (35%): 8.74 (1H, s) (azomethine); 8.26 (2H, d, ^3J = 8.7 Hz), 7.63 (2H, d, ^3J = 8.7 Hz), 7.41 (1H, dd, ^3J = 8.2 Hz, ^4J = 2.1 Hz), 7.29 (1H, 1H, t, ^3J = 9.1 Hz), 6.85 (1H, d, ^3J = 8.2 Hz) (aromatic); 5.94 (1H, d, ^3J = 4.7 Hz) (hydroxyl); 4.12 (1H, dd, ^3J = 9.1 Hz, ^4J = 4.1 Hz), 4.03 (1H, ov) (methine); 4.86 (1H, dd, ^3J = 9.3 Hz, ^4J = 4.7 Hz), 4.00 (1H, ov) (methylene); 2.36 (3H, s) (methyl).

2.2.6 | MoO_2L^6

Yield 84%. Anal. calc for $BrC_{16}H_{13}N_2O_7Mo$: C, 36.9; H, 2.5; N, 5.4. Found: C, 36.7; H, 2.4; N, 5.5%. IR (KBr, cm^{-1}): 3446 (ν_{O-H}); 1624 ($\nu_{C=N}$); 1607, 1548 ($\nu_{C=C}$); 1514, 1348 (ν_{NO2}); 1286 (ν_{C-O}); 934, 902 ($\nu_{Mo=O}$). UV–vis spectrum in DMSO [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 273 (12970), 349 (1990). CD spectrum in DMSO [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 278 (5.31), 302 (−2.15), 362 (5.76). ^{1}H NMR

(DMSO-d_6, ppm) *mer*-isomer (65%): 8.70 (1H, s) (azomethine); 8.24 (2H, d, ^3J = 8.7 Hz), 7.81 (1H, t, ^3J = 2.6 Hz), 7.73 (2H, d, ^3J = 8.7 Hz), 7.58 (1H, t, ^3J = 2.6 Hz), 6.87 (1H, d, ^3J = 8.8 Hz) (aromatic); 5.25 (1H, t, ^3J = 5.2 Hz) (hydroxyl); 5.42 (1H, d, ^3J = 6.9 Hz), 3.89 (1H, m) (methine); 4.03 (1H, ov), 3.62 (1H, dt, ^3J = 12.4 Hz, ^4J = 5.6 Hz) (methylene); *fac*-isomer (35%): 8.77 (1H, s) (azomethine); 8.27 (2H, d, ^3J = 8.7 Hz), 7.85 (1H, t, ^3J = 2.6 Hz), 7.65 (2H, d, ^3J = 8.7 Hz), 7.60 (1H, t, ^3J = 2.6 Hz), 6.89 (1H, d, ^3J = 8.8 Hz) (aromatic); 5.95 (1H, d, ^3J = 4.7 Hz) (hydroxyl); 4.13 (1H, dd, ^3J = 9.1 Hz, ^4J = 4.1 Hz), 4.03 (1H, ov) (methine); 4.87 (1H, dd, ^3J = 9.3 Hz, ^4J = 4.7 Hz), 4.00 (1H, ov) (methylene).

2.2.7 | MoO_2L^7

Yield 86%. Anal. calc for $C_{16}H_{13}N_3O_9Mo$: C, 39.4; H, 2.7; N, 8.6. Found: C, 39.5; H, 2.6; N, 8.6%. IR (KBr, cm^{-1}): 3440 (ν_{O-H}); 1642 ($\nu_{C=N}$); 1609, 1465 ($\nu_{C=C}$); 1518, 1348 (ν_{NO2}); 1287 (ν_{C-O}); 949, 916 ($\nu_{Mo=O}$). UV–vis spectrum in DMSO [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 275 (11400), 339 (7620). CD spectrum in DMSO [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 281 (3.78), 331 (3.30). ^{1}H NMR (DMSO-d_6, ppm) *mer*-isomer (65%): 9.02 (1H, s) (azomethine); 8.69 (1H, t, ^3J = 2.6 Hz), 8.28 (2H, d, ^3J = 8.7 Hz), 7.77 (2H, d, ^3J = 8.7 Hz), 7.61 (1H, t, ^3J = 2.6 Hz), 7.14 (1H, d, ^3J = 8.7 Hz) (aromatic); 5.23 (1H, t, ^3J = 5.2 Hz) (hydroxyl); 5.40 (1H, d, ^3J = 6.9 Hz), 3.87 (1H, m) (methine); 4.02 (1H, ov), 3.61 (1H, dt, ^3J = 12.4 Hz, ^4J = 5.6 Hz) (methylene); *fac*-isomer (35%): 9.09 (1H, s) (azomethine); 8.72 (1H, t, ^3J = 2.6 Hz), 8.31 (2H, d, ^3J = 8.7 Hz), 7.69 (2H, d, ^3J = 8.7 Hz), 7.63 (1H, t, ^3J = 2.6 Hz), 7.16 (1H, d, ^3J = 8.7 Hz) (aromatic); 5.93 (1H, d, ^3J = 4.7 Hz) (hydroxyl); 4.12 (1H, dd, ^3J = 9.1 Hz, ^4J = 4.1 Hz), 4.02 (1H, ov) (methine); 4.86 (1H, dd, ^3J = 9.3 Hz, ^4J = 4.7 Hz), 3.99 (1H, ov) (methylene).

2.2.8 | MoO_2L^8

Yield 82%. Anal. calc for $C_{16}H_{14}N_2O_8Mo$: C, 41.9; H, 3.1; N, 6.1. Found: C, 41.8; H, 3.0; N, 6.2%. IR (KBr, cm^{-1}): 3414 (ν_{O-H}); 1631 ($\nu_{C=N}$); 1608, 1491 ($\nu_{C=C}$); 1522, 1350 (ν_{NO2}); 1232 (ν_{C-O}); 931, 902 ($\nu_{Mo=O}$). UV–vis spectrum in DMSO [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 288 (11290), 339 (3410). CD spectrum in DMSO [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 276 (−3.91), 347 (8.63). ^{1}H NMR (DMSO-d_6, ppm) *mer*-isomer (65%): 10.24 (1H, s) (hydroxyl); 8.57 (1H, s) (azomethine); 8.24 (2H, d, ^3J = 8.7 Hz), 7.72 (2H, d, ^3J = 8.7 Hz), 7.27 (1H, t, ^3J = 7.4 Hz), 6.43 (1H, d, ^3J = 8.2 Hz), 6.25 (1H, s) (aromatic); 5.27 (1H, t, ^3J = 5.2 Hz) (hydroxyl); 5.45 (1H, d, ^3J = 6.9 Hz), 3.92 (1H, m) (methine); 4.06 (1H, ov), 3.65 (1H, dt, ^3J = 12.4 Hz, ^4J = 5.6 Hz) (methylene); *fac*-isomer (35%): 10.27 (1H, s) (hydroxyl); 8.59 (1H, s) (azomethine); 8.26 (2H, d, ^3J = 8.7 Hz), 7.64 (2H, d, ^3J = 8.7 Hz), 7.29 (1H, t, ^3J = 7.4 Hz), 6.46 (1H, d, ^3J = 8.2 Hz), 6.27 (1H, s) (aromatic); 5.98 (1H, d, ^3J = 4.7 Hz) (hydroxyl); 4.16 (1H, dd, ^3J = 9.1 Hz, ^4J = 4.1 Hz), 4.06 (1H, ov) (methine); 4.90 (1H, dd, ^3J = 9.3 Hz, ^4J = 4.7 Hz), 4.03 (1H, ov) (methylene).

2.2.9 | MoO_2L^9

Yield 78%. Anal. calc for $C_{20}H_{22}N_2O_7Mo$: C, 48.2; H, 4.5; N, 5.6. Found: C, 48.3; H, 4.6; N, 5.5%. IR (KBr, cm^{-1}): 3393 (ν_{O-H}); 1633 ($\nu_{C=N}$); 1587, 1482 ($\nu_{C=C}$); 1528, 1347 (ν_{NO2}); 1237 (ν_{C-O}); 930, 902 ($\nu_{Mo=O}$). UV–vis spectrum in DMSO [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 280 (10850), 352 (1680). CD spectrum in DMSO [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 286 (5.86), 309 (−0.78), 360 (5.12). ^{1}H NMR (DMSO-d_6, ppm) *mer*-isomer (65%): 8.68 (1H, s) (azomethine); 8.22 (2H, d, ^3J = 8.7 Hz), 7.70 (2H, d, ^3J = 8.7 Hz), 7.12 (1H, d, ^3J = 7.5 Hz), 7.06 (1H, d, ^3J = 7.5 Hz), 6.89 (1H, t, ^3J = 7.5 Hz) (aromatic); 5.23 (1H, t, ^3J = 5.2 Hz) (hydroxyl); 5.41 (1H, d, ^3J = 6.9 Hz), 3.89 (1H, m) (methine); 4.02 (1H, ov), 3.61 (1H, dt, ^3J = 12.4 Hz, ^4J = 5.6 Hz) (methylene); 1.38 (9H, s) (*tert*-butyl); *fac*-isomer (35%): 8.75 (1H, s) (azomethine); 8.25 (2H, d, ^3J = 8.7 Hz), 7.62 (2H, d, ^3J = 8.7 Hz), 7.14 (1H, d, ^3J = 7.5 Hz), 7.08 (1H, d, ^3J = 7.5 Hz), 6.91 (1H, t, ^3J = 7.5 Hz) (aromatic); 5.92 (1H, d, ^3J = 4.7 Hz) (hydroxyl); 4.12 (1H, dd, ^3J = 9.1 Hz, ^4J = 4.1 Hz), 4.02 (1H, ov) (methine); 4.86 (1H, dd, ^3J = 9.3 Hz, ^4J = 4.7 Hz), 3.99 (1H, ov) (methylene); 1.40 (9H, s) (*tert*-butyl).

2.2.10 | MoO_2L^{10}

Yield 81%. Anal. calc for $C_{20}H_{16}N_2O_7Mo$: C, 48.8; H, 3.3; N, 5.7. Found: C, 48.7; H, 3.5; N, 5.8%. IR (KBr, cm^{-1}): 3329 (ν_{O-H}); 1621 ($\nu_{C=N}$); 1606, 1456 ($\nu_{C=C}$); 1517, 1339 (ν_{NO2}); 1251 (ν_{C-O}); 929, 898 ($\nu_{Mo=O}$). UV–vis spectrum in DMSO [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 271 (11720), 302 (9740), 380 (2840). CD spectrum in DMSO [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 316 (−6.14), 383 (7.51). ^{1}H NMR (DMSO-d_6, ppm) *mer*-isomer (65%): 9.53 (1H, s) (azomethine); 8.44 (1H, d, ^3J = 8.5 Hz), 8.28 (2H, d, ^3J = 8.7 Hz), 8.05 (1H, d, ^3J = 8.8 Hz), 7.89 (1H, d, ^3J = 8.0 Hz), 7.76 (2H, d, ^3J = 8.7 Hz), 7.61 (1H, t, ^3J = 7.3 Hz), 7.42 (1H, t, ^3J = 7.3 Hz), 7.14 (1H, d, ^3J = 8.9 Hz) (aromatic); 5.28 (1H, t, ^3J = 5.2 Hz) (hydroxyl); 5.45 (1H, d, ^3J = 6.9 Hz), 3.92 (1H, m) (methine); 4.07 (1H, ov), 3.65 (1H, dt, ^3J = 12.4 Hz, ^4J = 5.6 Hz) (methylene); *fac*-isomer (35%): 9.55 (1H, s) (azomethine); 8.46 (1H, d, ^3J = 8.5 Hz), 8.30 (2H, d, ^3J = 8.7 Hz), 8.07 (1H, d, ^3J = 8.8

Hz), 7.91 (1H, d, ^3J = 8.0 Hz), 7.78 (2H, d, ^3J = 8.7 Hz), 7.63 (1H, t, ^3J = 7.3 Hz), 7.44 (1H, t, ^3J = 7.3 Hz), 7.16 (1H, d, ^3J = 8.9 Hz) (aromatic); 5.97 (1H, d, ^3J = 4.7 Hz) (hydroxyl); 4.16 (1H, dd, ^3J = 9.1 Hz, ^4J = 4.1 Hz), 4.06 (1H, ov) (methine); 4.90 (1H, dd, ^3J = 9.3 Hz, ^4J = 4.7 Hz), 4.03 (1H, ov) (methylene).

2.3 | Catalytic activity

2.3.1 | Sulfoxidation reactions

All dioxidomolybdenum (VI) complexes were tested as catalysts for sulfoxidation of thioanisole in the presence of aqueous 30% H_2O_2 or 5.5 M decane solution of *tert*-butyl hydroperoxide (TBHP) as the terminal oxidant. The catalyst, thioanisole and oxidant amounts were 0.01, 1 and 1.1 mmol, respectively. The reactions were run in CH_2Cl_2 and MeOH (7:3) solution for a better mixing of the aqueous oxidant with the halogenated solvent[23] and enhancing the yield and selectivity of sulfoxide by protic solvent.[24] After the appropriate reaction time, the solution was quenched with 3 ml of sodium sulfite solution (0.1 M), extracted with ethyl acetate and organic layers were evaporated to dryness. The yield and reaction rates were estimated on the basis of the integrated intensities of substrate and product signals in $CDCl_3$ using ^{1}H NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal standard. After addition of chiral shift reagent, Eu(hfc)$_3$,[25] the enantiomeric excesses of methyl phenyl sulfoxide were calculated.

2.3.2 | Epoxidation reactions

The catalytic abilities of all complexes were studied for epoxidation of alkenes, i.e. styrene and cyclohexene, and monoterpenes, i.e. *S*(−)-limonene and (−)-α-pinene, using aqueous 30% H_2O_2 or 5.5 M decane solution of *tert*-butyl hydroperoxide. Different amounts of catalysts and oxidants were also tested to optimize reaction conditions. All reactions were run in 1,2-dichloroethane at 80°C and monitored by GC using 1:100:200 molar ratio of catalyst, substrate and oxidant, respectively. The yields were recorded as GC yield based on the starting substrate. The identity of oxidation products were confirmed by GC–MS.

3 | RESULTS AND DISCUSSION

3.1 | IR spectra

The IR spectra for **MoO_2L^1**–**MoO_2L^{10}** complexes (Figure S1) exhibit medium bands centered at 3329–3446 cm^{-1} and are assigned to ν(O–H) vibrations of coordinated hydroxyl group. The characteristic imine C=N band, which exists at 1621–1642 cm^{-1}, indicates the presence of azomethine nitrogen atom of all Schiff base ligands coordinated to the molybdenum ion.[26,27] Asymmetric and symmetric N–O stretches have been found at 1505–1528 and 1339–1360 cm^{-1}, respectively, for all complexes and especially **MoO_2L^7** with additional nitro substituent attached to aromatic ring of salicylaldehyde moiety. Moreover, the appearance of ν(C–O) bands at 1218–1294 cm^{-1} also suggests the coordination alkoxide ions and OH groups. Finally, a pairs of sharp and strong bands at 907–949 and 882–916 cm^{-1} owing to the stretching ν_{asym}(O = Mo = O) and ν_{sym}(O = Mo = O) modes, respectively, clearly confirm the presence of a *cis*-[$Mo^{VI}O_2$] structure.[28]

3.2 | Electronic and circular dichroism spectra

Electronic absorption and circular dichroism spectra of *cis*-dioxidomolybdenum (VI) complexes were recorded in spectroscopic grade DMSO. The UV–vis spectra display intraligand π–π^* transitions in 271–288 nm region. The low-energy transitions appearing between 339–380 nm are assigned to a ligand-to-metal charge transfer transition arising from the phenolate oxygen p_π orbital to an empty d orbital of molybdenum atom.[29] The **MoO_2L^4** compound is an exception to this rule and exhibits only one strong broad band at 297 nm (ε_{max} = 22,090) and the spectrum of **MoO_2L^{10}** with naphthyl ring displays an additional band at 302 nm (ε_{max} = 9740). The circular dichroism spectra revealed the same bands in 276–293 nm with very strong positive sign of the Cotton effect, but with exceptions of **MoO_2L^4** and **MoO_2L^8**, which show a negative sign, and also bands in 338–386 nm region of the same origin as electronic spectra also with strong positive sign of the Cotton effect. Moreover, additional bands with negative sign of the Cotton effect appeared in the 302–316 region in the case of **MoO_2L^3**, **MoO_2L^5**, **MoO_2L^6**, **MoO_2L^9** and **MoO_2L^{10}** complexes.

3.3 | NMR measurements

The one- (^{1}H) and two-dimensional (COSY, NOESY, gHSQC) NMR spectra of *cis*-dioxidomolybdenum (VI) Schiff base complexes were recorded in DMSO-d_6. The ^{1}H NMR spectra of all complexes showed the presence of azomethine proton signals, proving a condensation reaction between all salicylaldehyde derivatives

and *1S,2S*-(+)-2-amino-1-(4-nitrophenyl)-1,3-propanediol. Complete assignments and identification of all proton signals and establishing a connection and proximity between all protons and their attachment to carbon atoms was achieved using two-dimensional NMR experiments and are listed in the Experimental section.

We reported earlier that *cis*-dioxidomolybdenum (VI), but also oxidovanadium(V) and *cis*-dioxidovanadium(V) complexes with unsymmetrical tridentate Schiff base ligands, products of monocondensation reaction of salicylaldehyde and its derivatives with amino alcohols and diamines, have been proven to possess a rigid and nearly planar backbone composed of three donor centers established by the Schiff base linkage, which prefer only a meridional coordination mode.[22,30] Moreover, such complexes with similar high-density ligands, i.e. pentadentate Schiff bases, also revealed only meridional arrangement of coordination sites.[31] It was possible to observe in solution a second isomer in the facial coordination arrangement but after reduction of imine functionality obtaining a flexible amine ligand system.[32] In the case of **MoO_2L^1-MoO_2L^{10}** complexes their Schiff bases are coordinated to the MoO_2^{2+} cation creating meridional (*mer*) and facial (*fac*) types of geometrical isomers, respectively (Figure 2). The ^{1}H NMR spectra show that all protons of both isomers are chemically different, giving rise to two sets of signals in a 65:35 ratio and the resonances of the *mer*-isomers are generally observed at lower frequencies (Figure S2). The chemical shift differences between the two methine protons of the amino alcohol chelate rings of the *fac*-isomers are rather very small, whereas for the *mer*-isomers a distinct separation between the two resonances is observed (over 1.5 ppm). On the other hand, the separations between the methylene protons are for the *fac*-isomers *ca.* 0.5 ppm bigger and, moreover, the signal of the proton of coordinated hydroxyl group is a doublet. Furthermore, taking **MoO_2L^3** as an example, the COSY spectrum shows a cross-peak between the coordinated hydroxyl proton doublet at 5.99 pm only with one of the methylene protons at 4.89 ppm, but the hydroxyl proton triplet of *mer*-isomer (5.25 ppm) reveals cross-peaks with both methylene protons at 4.03 and 3.63 ppm. In the case of both isomers the methylene protons show unambiguous connection with methine proton (at 3.87 for *mer*-isomer and 4.10 for *fac*-isomer) neighboring with azomethine nitrogen. Additionally, the NOESY spectrum reveals spacial proximity to the azomethine proton with signal at 8.73 ppm in the case of *mer*-isomer and one of the aromatic proton doublets (signal at 7.21 ppm), the methine proton (at 3.87 ppm) and one of the methylene protons (at 4.03 ppm), whereas the latter cross-peak is not present for the *fac*-isomer.

3.4 | Catalytic activity studies

3.4.1 | Enantioselective sulfoxidation of thioanisole

All *cis*-dioxidomolybdenum (VI) complexes **MoO_2L^1–MoO_2L^{10}** were tested for their catalytic activities for sulfoxidation of thioanisole with a slight excess (1.1 equiv.) of TBHP or aqueous 30% H_2O_2 as the terminal oxidant (Figure 3). The reactions were run in $CDCl_3$ at different temperatures (25 and −20°C) with optimized amounts of the catalysts (1 mol%) and under these conditions no overoxidation to the corresponding sulfone was detected**.** In control experiments carried out without any molybdenum (VI) Schiff base catalysts present or in the presence of $MoO_2(acac)_2$, no significant amounts of reactions products were detected. All studied complexes presented practically similar overall catalytic ability, suggesting that they may involve the same catalytic species.

The overall conversion of thioanisole to methyl phenyl sulfoxide in the presence of all molybdenum (VI) catalysts was slightly higher using 30% H_2O_2 as the oxidant, in comparison with TBHP (Table 1). In all cases the *R*-configured sulfoxides were obtained with enantiomeric excesses from 12 to 24% using 30% H_2O_2 (entries 1–13) and 10–19% when TBHP was employed as the

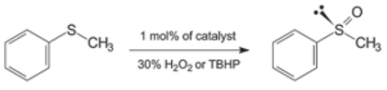


FIGURE 3 Sulfoxidation of thioanisole catalyzed by *cis*-dioxidomolybdenum (VI) complexes

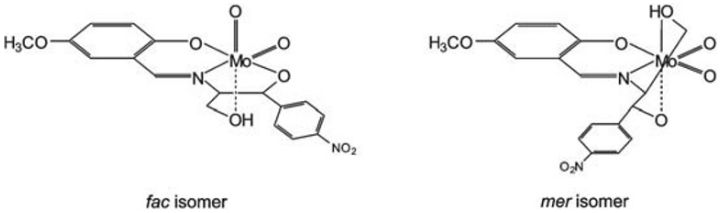


FIGURE 2 Facial (*fac*) and meridional (*mer*) geometrical isomers of **MoO_2L^3** complex

TABLE 1 Asymmetric sulfoxidation of thioanisole in the presence of molybdenum (VI) Schiff base complexes as catalysts

Entry	Catalyst	Oxidant	Temperature (°C)[a]	Yield (%)	*ee* (%)[b]
1	MoO_2L^1	H_2O_2	25	81	17
2	MoO_2L^2	H_2O_2	25	83	18
3	MoO_2L^2	H_2O_2	−20	86	22
4	MoO_2L^3	H_2O_2	25	82	20
5	MoO_2L^3	H_2O_2	−20	85	24
6	MoO_2L^4	H_2O_2	25	80	16
7	MoO_2L^5	H_2O_2	25	82	14
8	MoO_2L^6	H_2O_2	25	81	12
9	MoO_2L^7	H_2O_2	25	82	13
10	MoO_2L^7	H_2O_2	−20	85	18
11	MoO_2L^8	H_2O_2	25	79	13
12	MoO_2L^9	H_2O_2	25	81	14
13	MoO_2L^{10}	H_2O_2	25	78	16
14	MoO_2L^1	TBHP	25	75	13
15	MoO_2L^2	TBHP	25	80	14
16	MoO_2L^2	TBHP	−20	82	19
17	MoO_2L^3	TBHP	25	81	15
18	MoO_2L^3	TBHP	−20	84	18
19	MoO_2L^4	TBHP	25	79	11
20	MoO_2L^5	TBHP	25	83	13
21	MoO_2L^6	TBHP	25	82	12
22	MoO_2L^7	TBHP	25	81	10
23	MoO_2L^7	TBHP	−20	85	14
24	MoO_2L^8	TBHP	25	78	12
25	MoO_2L^9	TBHP	25	81	13
26	MoO_2L^{10}	TBHP	25	83	12

[a]Optimized reaction times were 1.5 h at 25°C and 5 h at −20°C.
[b]In all cases enantiomeric excess of methyl phenyl sulfoxide was found to be in *R* configuration.
TBHP, *tert*-butyl hydroperoxide.

terminal oxidant (entries 14–26). These results clearly show that the catalytic activities of all complexes in sulfoxidation of thioanisole are lower with TBHP than in the analogous reactions involving aqueous 30% H_2O_2. The reaction temperature seemed to have some effect on the observed enantioselectivity and a slight increase in the enantiomeric excess with lower reaction temperature was noticed. For example in the cases of MoO_2L^2, MoO_2L^3 and MoO_2L^7, the decrease in the reaction temperature was accompanied by longer reaction time but also a slight increase in enantioselectivity and without additional sulfone production (entries 3, 5, 10, 16, 18 and 23). In comparison with the other chiral but tridentate *cis*-dioxidomolybdenum (VI) Schiff base complexes, derived from amino alcohols, the conversions to thioanisole were similar,[21,22,33] but much higher amounts of catalysts (5 mol%) were needed to achieve them. Nevertheless, it seems that pathway for the formation of sulfoxide is very similar.[33]

It is noteworthy to mention that, in the case of the studied molybdenum (VI) complexes, the best enantioselectivities were achieved with catalysts possessing high electron-donating substituents where a higher electron density on the phenolate oxygen in salicylaldimine moiety helps to improve attainment of sufficient nucleophilicity by the metal centre. Mimoun *et al.* reported[34] that sufficient nucleophilic centers in d^0 metal catalysts have significant importance for a number of types of organic substrates used in catalytic oxidation processes.

3.4.2 | Epoxidation of alkenes and monoterpenes

Chiral *cis*-dioxidomolybdenum (VI) complexes with tetradentate Schiff bases, $\mathbf{MoO_2L^1}$–$\mathbf{MoO_2L^{10}}$ were studied as catalysts in the epoxidation of alkenes, such as styrene and cyclohexene, but also monoterpenes, which are naturally occurring cyclohexene derivatives, i.e. *S*(−)-limonene and (−)-*α*-pinene (Figure 4). As the terminal oxidants 30% aqueous H_2O_2 or TBHP were used and 1,2-dichloroethane was found to be the most efficient solvent with regards to other solvents like toluene, acetonitrile, ethanol, methanol, $CHCl_3$ and CH_2Cl_2. The poorer yields obtained especially with the latter may be caused by the lower reaction temperature for their reflux conditions. Considering our observations in conversion and selectivity, a higher reaction temperature, i.e. 80°C, has an overall benefit to achieve the best yields for all epoxidation reactions, which required 1 h to reach completion. Similar conclusions that higher reactions temperature can be responsible for obtaining better yields and reaction rates have been also drawn previously, and also the mechanisms suggested for alkene epoxidation seems to be similar.[35] In order to achieve suitable reaction conditions for a maximum oxidative conversion the influence of different reaction parameters was taken into account, i.e. the amount of catalyst (0.5, 1, 2 and 3 mol% loadings) and oxidant molar ratios to substrate (1:1, 2:1, 3:1 and 4:1). It was observed that using 1 mol% of each catalyst with 2:1 molar ratio of both oxidants to all substrates was sufficient to run the epoxidations and an increase in these ratios did not noticeably affect the reaction rates. Moreover, the selectivities toward epoxide in 1:1 ratio of oxidants to substrates were significantly smaller and when the amounts of 30% H_2O_2 or TBHP were increased to 3:1 or 4:1 ratios the amounts of epoxides were only slightly better.

As we have previously reported,[21,22] the oxidation of styrene with catalytic amounts of molybdenum (VI) Schiff base complexes using aqueous 30% H_2O_2 or TBHP as the terminal oxidants generally can result in five oxidation products, i.e. styrene oxide, benzaldehyde, benzoic acid, phenylacetaldehyde and 1-phenylethane-1,2-diol. Styrene oxide can be formed in the first step, but further reaction, via nucleophilic attack of the oxidant to styrene oxide followed by the cleavage of the intermediate hydroperoxystyrene, is very fast, converting the product into benzaldehyde,[36] which can also be further oxidized to benzoic acid. Moreover, the direct formation of benzaldehyde can also be facilitated via a radical mechanism by direct oxidative cleavage of the styrene side-chain double bond. The presence of water, in the case of aqueous 30% H_2O_2, can be blamed for the decomposition of the catalyst and thus the very low conversion of styrene. Moreover, it can be also responsible for the formation of 1-phenylethane-1,2-diol by the hydrolysis of styrene oxide and finally, styrene oxide isomerization can lead to the formation of phenylacetaldehyde.

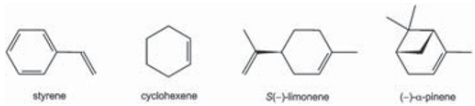


FIGURE 4 Substrates used for catalytic epoxidation studies

During our studies it was observed that the epoxidation of styrene by aqueous 30% H_2O_2 gave as expected low conversions (12–17%), but when TBHP was added to reaction mixtures in a non-aqueous environment, the conversions of styrene increased significantly to 64–76%. These reactions carried out with both oxidants led to the formation of styrene oxide as a major product along with only small amounts of benzaldehyde and without any additional by-products (Table 2, entries 1–13). Similar conversion (71–75%) and excellent epoxide selectivity were obtained by Judmaier *et al.*[37] with 0.5 mol% of molybdenum (VI) Schiff base catalysts loading in 5 h of reaction time, but in chloroform at 50°C.

The epoxidation of cyclohexene with catalytic amounts of *cis*-dioxidomolybdenum (VI) Schiff base complexes generally results in epoxidation products, i.e. cyclohexene oxide, and, after its eventual hydrolysis, cyclohexene-1,2-diol, but the formation of allylic oxidation products is also possible, i.e. 2-cyclohexen-1-ol and 2-cyclohexen-1-one (Figure 5). Mono- and bicyclic monoterpenes used in this study and possessing a cyclohexene ring, i.e. *S*(−)-limonene and (−)-*α*-pinene, gave analogous oxidation reaction products.

Generally, cyclohexene and (−)-*α*-pinene were converted to their corresponding epoxides with roughly the same yields as in the case of styrene, but selectivities to their epoxides are clearly much higher, especially in the case of cyclohexene (Table 2, entries 14–26) with excellent formation, up to 99%, of cyclohexene oxide. In the case of (−)-*α*-pinene and when TBHP was used, the main product was (−)-*α*-pinene oxide (up to 85%), but with aqueous 30% H_2O_2 lower conversions were achieved and even >30% of verbenol, an allylic oxidation product, was formed (Table 3, entries 14–26).

Suprisingly, *S*(−)-limonene was oxidized selectively to its epoxide with excellent conversion, especially with TBHP (Table 3, entries 4–13), compared with all of the other substrates, i.e. styrene, cyclohexene and (−)-*α*-pinene. When TBHP was used as the terminal oxidant,

TABLE 2 Epoxidation of styrene and cyclohexene in the presence of molybdenum (VI) Schiff base complexes as catalysts

Entry	Catalyst	Substrate	Yield (%)	Oxidant	Epoxide (%)
1	MoO_2L^2	Styrene	14	H_2O_2	80
2	MoO_2L^3	Styrene	17	H_2O_2	84
3	MoO_2L^7	Styrene	12	H_2O_2	82
4	MoO_2L^1	Styrene	69	TBHP	84
5	MoO_2L^2	Styrene	74	TBHP	86
6	MoO_2L^3	Styrene	76	TBHP	89
7	MoO_2L^4	Styrene	71	TBHP	85
8	MoO_2L^5	Styrene	72	TBHP	84
9	MoO_2L^6	Styrene	68	TBHP	88
10	MoO_2L^7	Styrene	74	TBHP	87
11	MoO_2L^8	Styrene	67	TBHP	83
12	MoO_2L^9	Styrene	64	TBHP	81
13	MoO_2L^{10}	Styrene	67	TBHP	84
14	MoO_2L^2	Cyclohexene	16	H_2O_2	96
15	MoO_2L^3	Cyclohexene	19	H_2O_2	97
16	MoO_2L^7	Cyclohexene	14	H_2O_2	97
17	MoO_2L^1	Cyclohexene	67	TBHP	98
18	MoO_2L^2	Cyclohexene	70	TBHP	99
19	MoO_2L^3	Cyclohexene	72	TBHP	98
20	MoO_2L^4	Cyclohexene	69	TBHP	98
21	MoO_2L^5	Cyclohexene	66	TBHP	99
22	MoO_2L^6	Cyclohexene	69	TBHP	99
23	MoO_2L^7	Cyclohexene	63	TBHP	98
24	MoO_2L^8	Cyclohexene	66	TBHP	99
25	MoO_2L^9	Cyclohexene	62	TBHP	97
26	MoO_2L^{10}	Cyclohexene	64	TBHP	98

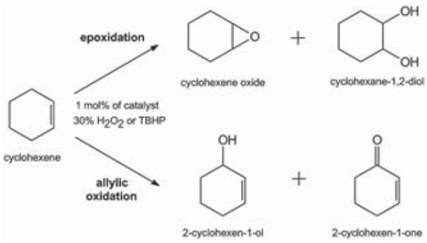


FIGURE 5 Possible epoxidation and allylic oxidation products of cyclohexene

cis- and *trans*-1,2-limonene oxide formed almost in equal proportions, providing epoxide practically quantitatively and only small amounts of diepoxide, owing to the presence of additional exocyclic isopropenyl moiety, were obtained as a by-product. On the other hand, epoxidation using aqueous 30% H_2O_2 resulted only in epoxide formation (Table 3, entries 1–3) but with a high excess of *trans*-1,2-limonene oxide.

Under the same reaction conditions, but at very low 0.05% loadings of two dioxidomolybdenum (VI) complexes equipped with naphtholate-oxazoline ligands as catalysts, the oxidation of *R*(+)-limonene resulted in *ca.* 60% conversion and up to 64% selectivity towards epoxide.[38] On the other hand, Judmaier *et al.*[39] reported catalytic activity of dimeric μ-oxido bridged dioxidomolybdenum (VI) complex with reduced Schiff base, which in chloroform at 50°C showed excellent epoxide yield and selectivity in the epoxidation of cyclohexene, but when *R*(+)-limonene was used as a substrate the reaction yielded almost equal amounts of epoxide and diepoxide.

TABLE 3 Epoxidation of monoterpenes with catalytic amounts of molybdenum (VI) Schiff base complexes as catalysts

Entry	Catalyst	Substrate	Yield (%)	Oxidant	Epoxide (%)
1	MoO_2L^2	*S*(−)-Limonene	22	H_2O_2	82
2	MoO_2L^3	*S*(−)-Limonene	25	H_2O_2	87
3	MoO_2L^7	*S*(−)-Limonene	28	H_2O_2	86
4	MoO_2L^1	*S*(−)-Limonene	95	TBHP	87
5	MoO_2L^2	*S*(−)-Limonene	99	TBHP	90
6	MoO_2L^3	*S*(−)-Limonene	99	TBHP	92
7	MoO_2L^4	*S*(−)-Limonene	96	TBHP	88
8	MoO_2L^5	*S*(−)-Limonene	98	TBHP	83
9	MoO_2L^6	*S*(−)-Limonene	97	TBHP	87
10	MoO_2L^7	*S*(−)-Limonene	99	TBHP	88
11	MoO_2L^8	*S*(−)-Limonene	96	TBHP	87
12	MoO_2L^9	*S*(−)-Limonene	98	TBHP	83
13	MoO_2L^{10}	*S*(−)-Limonene	96	TBHP	91
14	MoO_2L^2	(−)-*α*-Pinene	12	H_2O_2	67
15	MoO_2L^3	(−)-*α*-Pinene	15	H_2O_2	74
16	MoO_2L^7	(−)-*α*-Pinene	14	H_2O_2	69
17	MoO_2L^1	(−)-*α*-Pinene	61	TBHP	78
18	MoO_2L^2	(−)-*α*-Pinene	68	TBHP	82
19	MoO_2L^3	(−)-*α*-Pinene	64	TBHP	85
20	MoO_2L^4	(−)-*α*-Pinene	65	TBHP	79
21	MoO_2L^5	(−)-*α*-Pinene	66	TBHP	82
22	MoO_2L^6	(−)-*α*-Pinene	63	TBHP	77
23	MoO_2L^7	(−)-*α*-Pinene	57	TBHP	81
24	MoO_2L^8	(−)-*α*-Pinene	62	TBHP	73
25	MoO_2L^9	(−)-*α*-Pinene	64	TBHP	80
26	MoO_2L^{10}	(−)-*α*-Pinene	62	TBHP	75

4 | CONCLUSION

Within this paper we present the synthesis of 10 new chiral *cis*-dioxidomolybdenum (VI) complexes derived from tetradentate Schiff bases, products of a single condensation of salicylaldehyde and its derivatives with 1*S*,2*S*-(+)-2-Amino-1-(4-nitrophenyl)-1,3-propanediol, which have been characterized spectroscopically by UV–vis, CD, IR and NMR techniques.

All of these complexes have proved to show catalytic activity in the asymmetric sulfoxidation of thioanisole by aqueous 30% H_2O_2 and TBHP, resulting in better yields and enantioselectivities when reactions were carried out at much lower temperatures. Furthermore, catalytic abilities of MoO_2L^1–MoO_2L^{10} complexes have been tested in the epoxidation of model olefinic substrates, i.e. styrene and cyclohexene, and two monoterpenes, i.e. *S*(−)-limonene and (−)-*α*-pinene, using the same terminal oxidants. These complexes are able to catalyze their oxidative conversion to corresponding epoxides with excellent yields and selectivities. Under optimized reaction conditions, the best results have been achieved for *S*(−)-limonene, which was oxidized selectively to its epoxide with excellent conversion using TBHP as the terminal oxidant.

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AUTHOR CONTRIBUTIONS

Marta Karman: Investigation; methodology. **Grzegorz Romanowski:** Conceptualization; visualization.

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