

Bis(oxazoline)-based coordination polymers: A recoverable system for enantioselective Henry reactions

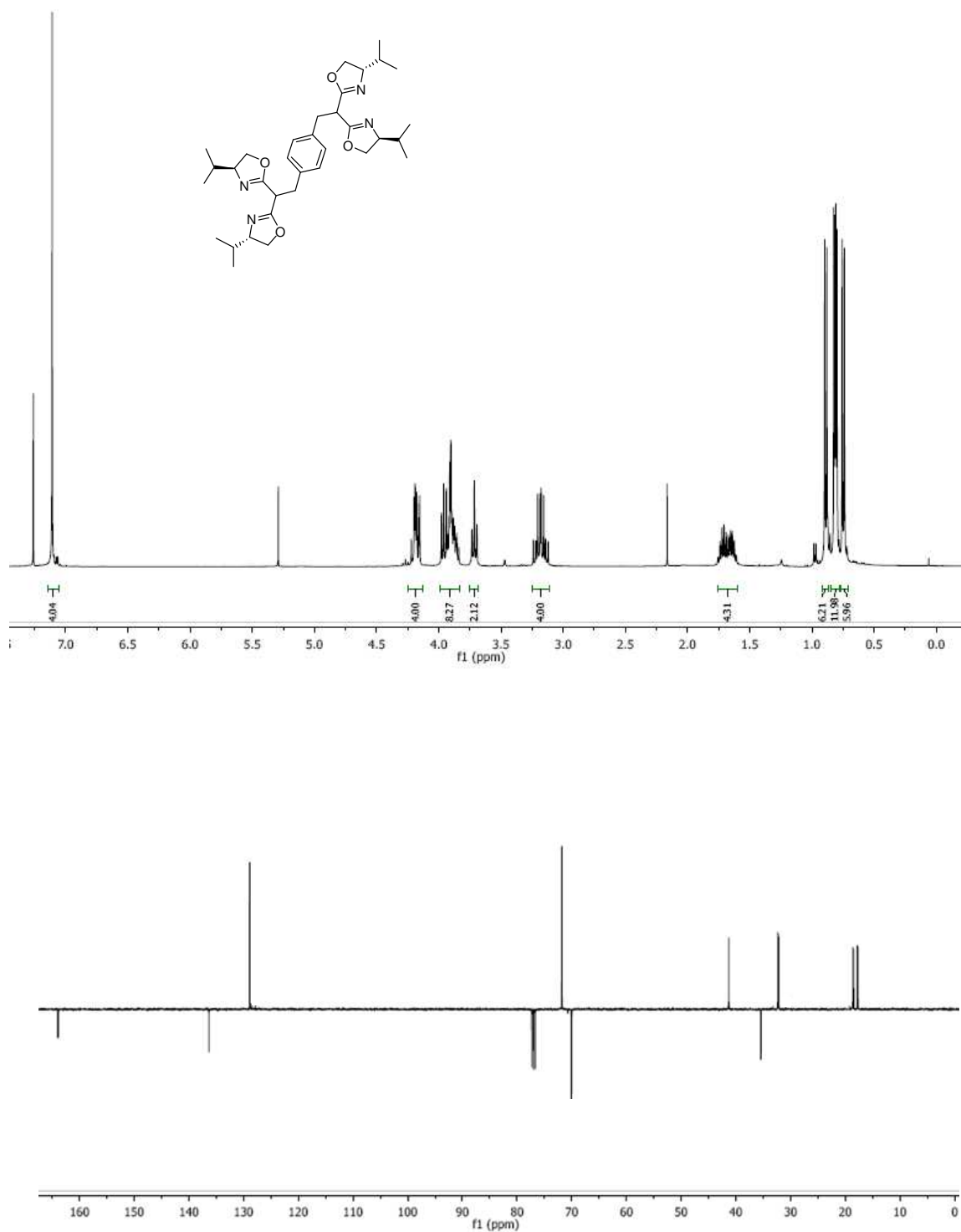
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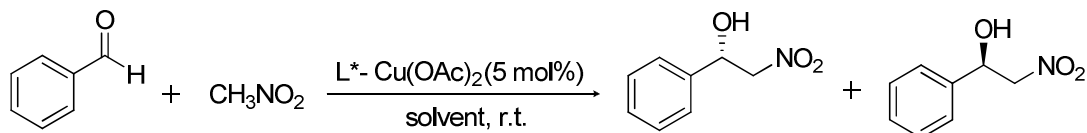
1. NMR spectra of the 1,4-bis(2,2-bis((S)-4-isopropyl-4,5-dihydrooxazol-2-yl)ethyl)benzene ligand (*i*-PrDiBox) (2).



2. Typical HPLC conditions and chromatograms from the Henry reactions

Enantioselectivities were determined by HPLC on a Waters Alliance Chromatograph with a PDA detector. The absolute configurations were established by comparison with literature data.¹

a) Reaction between benzaldehyde and nitromethane



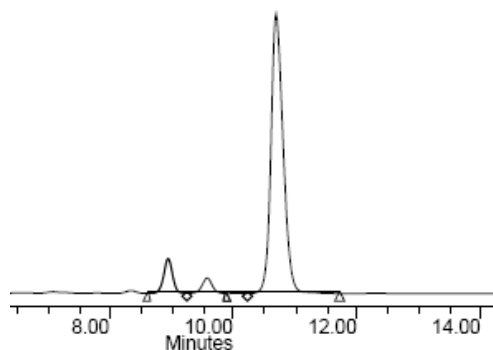
Conditions: *CHIRALCEL* OD-H column. *n*-hexane/isopropyl alcohol (85:15) at 0.8 mL·min⁻¹.

Retention times:

(2-nitrovinyl)benzene: 8.9 min

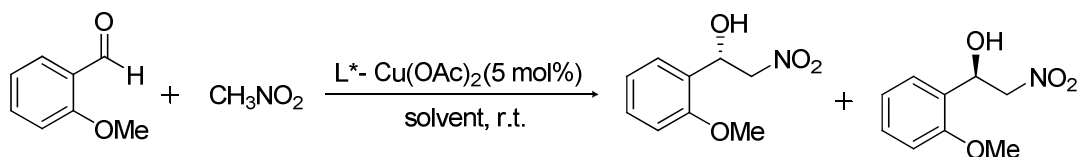
(*R*)-2-nitro-1-phenylethanol: 9.5 min

(*S*)-2-nitro-1-phenylethanol: 10.7 min



b) Reaction between *o*-anisaldehyde and nitromethane

¹ a) Evans, D. A.; Seidel, D.; Rueping, M.; Lam, H. W.; Shaw, J. T.; Downey, C. W. *J. Am. Chem. Soc.* **2003**, *125*, 12692; b) Purkarthofer, T.; Gruber, K.; Gruber-Khadjawi, M.; Waich, K.; Skranc, W.; Mink, D.; Griengl, H. *Angew. Chem. Int. Ed.* **2006**, *45*, 3454; c) Ginotra, S. K.; Singh, V. K. *Org. Biomol. Chem.* **2007**, *5*, 3932; d) Selvakumar, S.; Sivasankaran, D.; Singh, V. K. *Org. Biomol. Chem.* **2009**, *7*, 3156; e) Lang, K.; Park, J.; Hong, S. *J. Org. Chem.* **2010**, *75*, 6424; f) Cheng, L.; Dong, J.; You, J.; Gao, G.; Lan, J. *Chem. Eur. J.* **2010**, *16*, 6761.



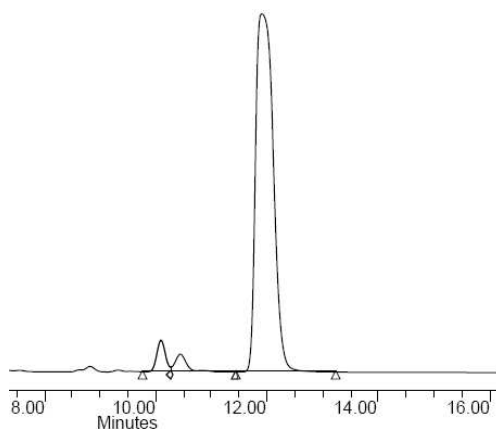
Conditions: CHIRALCEL OD-H column. *n*-hexane/isopropyl alcohol (85:15) at $0.8 \text{ mL} \cdot \text{min}^{-1}$.

Retention times:

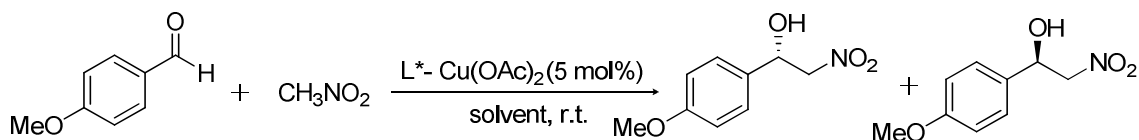
1-methoxy-2-(2-nitrovinyl)benzene: 10.6 min

(*R*)-1-(2-methoxyphenyl)-2-nitroethanol: 11.3 min

(*S*)-1-(2-methoxyphenyl)-2-nitroethanol: 13.0 min



c) Reaction between *p*-anisaldehyde and nitromethane



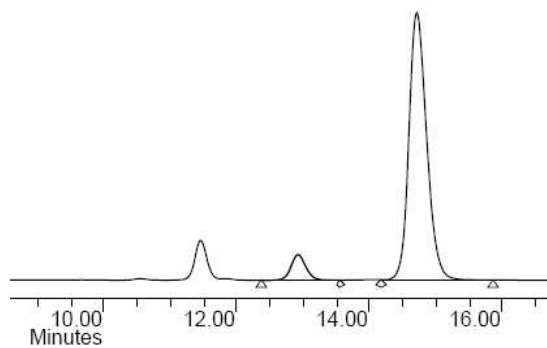
Conditions: CHIRALPAK IB column. *n*-hexane/isopropyl alcohol (85:15) at $0.8 \text{ mL} \cdot \text{min}^{-1}$.

Retention times:

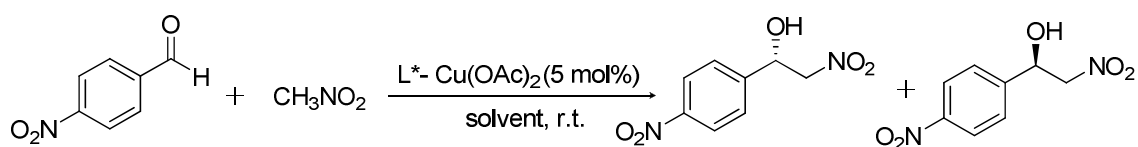
1-methoxy-4-(2-nitrovinyl)benzene: 11.4 min

(*R*)-1-(4-methoxyphenyl)-2-nitroethanol: 12.9 min

(*S*)-1-(4-methoxyphenyl)-2-nitroethanol: 14.7 min



d) Reaction between 4-nitrobenzaldehyde and nitromethane

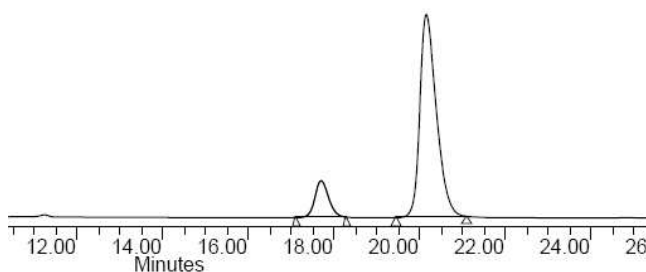


Conditions: *CHIRALPAK* IB column. *n*-hexane/isopropyl alcohol (85:15) at 0.8 mL·min⁻¹.

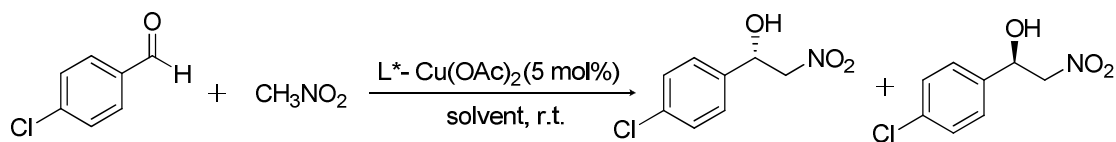
Retention times:

(*R*)-2-nitro-1-(4-nitrophenyl)ethanol: 17.6 min

(*S*)-2-nitro-1-(4-nitrophenyl)ethanol: 20.1 min



e) Reaction between 4-chlorobenzaldehyde and nitromethane

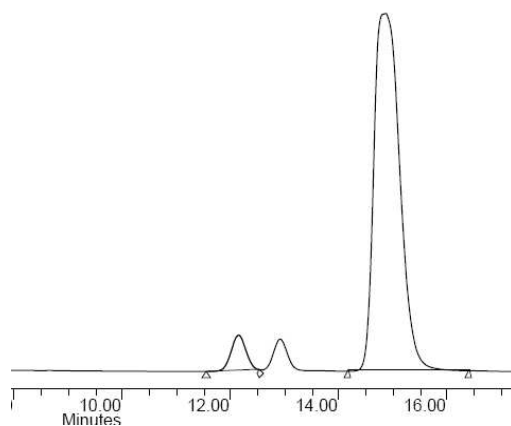


Conditions: *CHIRALCEL* OD-H column. *n*-hexane/isopropyl alcohol (85:15) at 0.8 mL·min⁻¹.
Retention times:

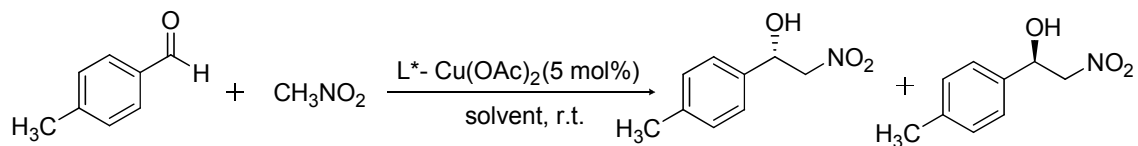
(*R*)-1-(4-chlorophenyl)-2-nitroethanol: 12.1 min

1-chloro-4-(2-nitrovinyl)benzene: 12.9 min

(*S*)-1-(4-chlorophenyl)-2-nitroethanol: 14.8 min



f) Reaction between 4-methylbenzaldehyde and nitromethane

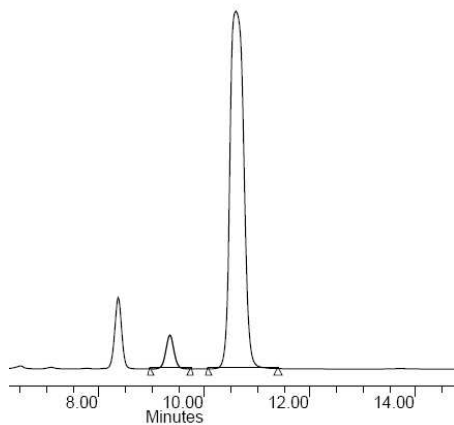


Conditions: *CHIRALPAK* IB column. *n*-hexane/isopropyl alcohol (85:15) at 0.8 mL·min⁻¹.
Retention times:

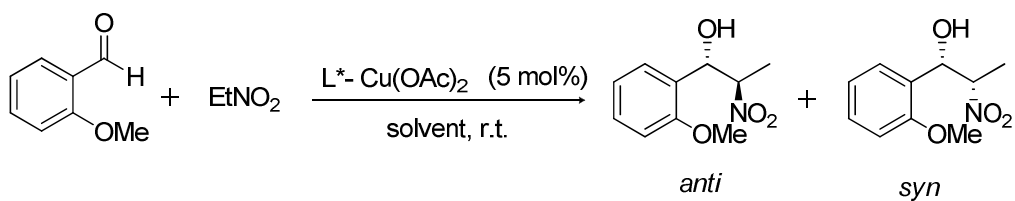
1-methoxy-2-(2-nitrovinyl)benzene: 8.3 min

(*R*)-2-nitro-1-*p*-tolylethanol: 9.3 min

(*S*)-2-nitro-1-*p*-tolylethanol: 10.6 min



g) Reaction between *o*-anisaldehyde and nitroethane



Conditions: *CHIRALPAK* AD-H column. *n*-hexane/isopropyl alcohol (95:5) at $1 \text{ mL} \cdot \text{min}^{-1}$.

Retention times:

(1*S*,2*R*)-1-(2-methoxyphenyl)-2-nitropropan-1-ol: 15.2 min

(1*R*,2*S*)-1-(2-methoxyphenyl)-2-nitropropan-1-ol: 20.4 min

(1*S*,2*S*)-1-(2-methoxyphenyl)-2-nitropropan-1-ol: 28.9 min

(1*R*,2*R*)-1-(2-methoxyphenyl)-2-nitropropan-1-ol: 30.0 min

