Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

SUPPORTING INFORMATION

Title: Polytopic bis(oxazoline)-based ligands for recoverable catalytic systems applied to the enantioselective Henry reaction

Author(s): Beatriz Angulo, José I. García,* Clara I. Herrerías, José A. Mayoral and Ana C. Miñana

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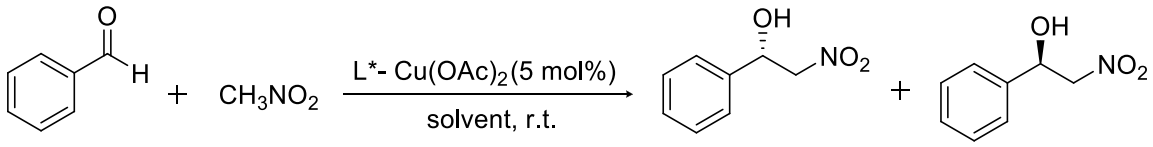
1. Typical HPLC conditions and chromatograms from the Henry reactions

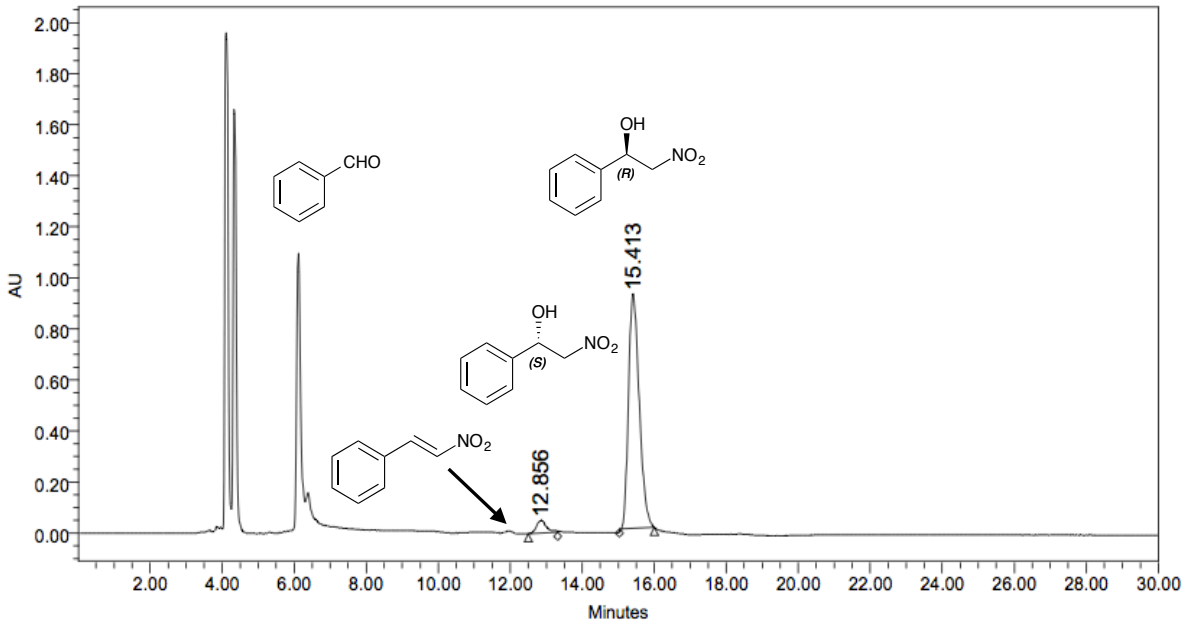
Enantioselectivities were determined by HPLC on a Waters Alliance Chromatograph with a PDA detector. Absolute configurations were established by comparison with literature data.[1]

1.1. Reaction between benzaldehyde and nitromethane

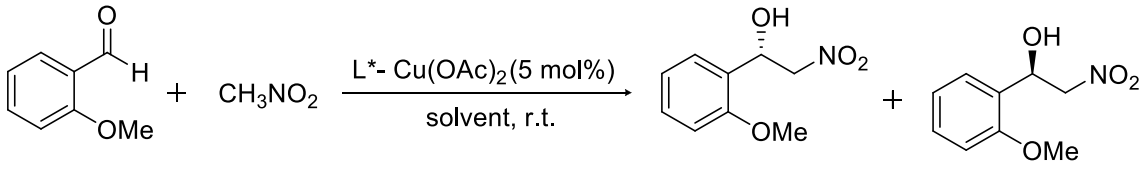


Conditions: *CHIRALCEL* OD-H column. *n*-hexane/isopropyl alcohol (85:15) at 0.8 mL·min^{-1}. Retention times:

Benzaldehyde: 6.2 min
(*R*)-2-nitro-1-phenylethanol: 12.9 min
(*S*)-2-nitro-1-phenylethanol: 15.4 min

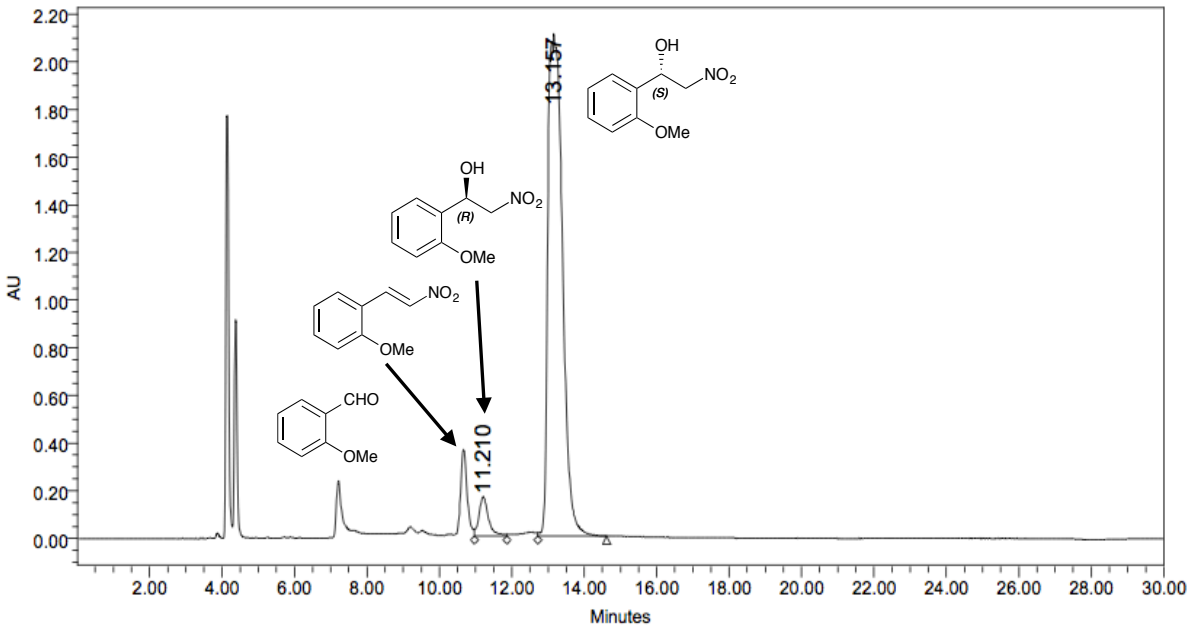


1.2. Reaction between *o*-anisaldehyde and nitromethane

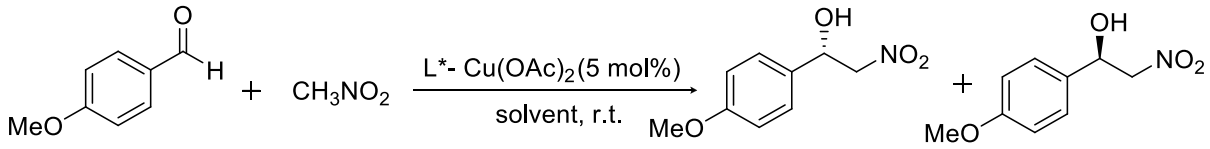


Conditions: *CHIRALCEL* OD-H column. *n*-hexane/isopropyl alcohol (85:15) at 0.8 $mL \cdot min^{-1}$. Retention times:

o-anisaldehyde: 7.3 min
1-methoxy-2-(2-nitrovinyl)benzene: 10.5 min
(*R*)-1-(2-methoxyphenyl)-2-nitroethanol: 11.2 min
(*S*)-1-(2-methoxyphenyl)-2-nitroethanol: 13.2 min

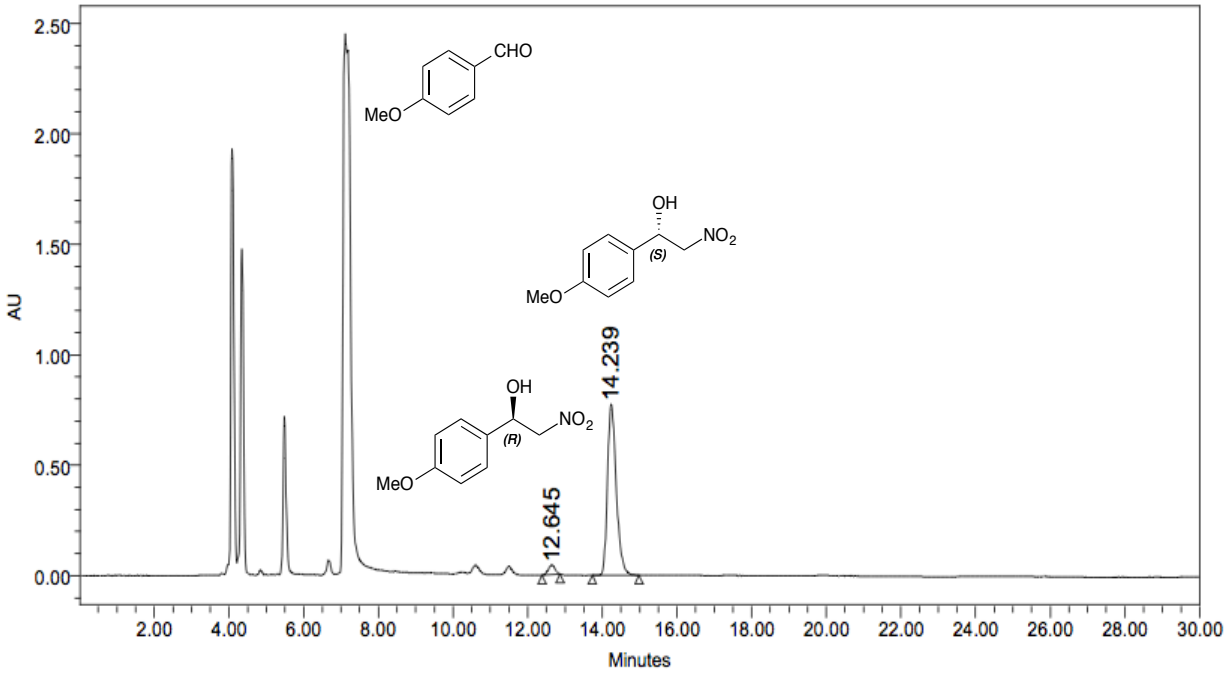


1.3. Reaction between *p*-anisaldehyde and nitromethane

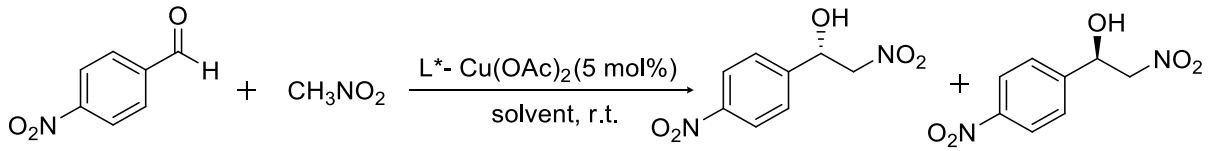


Conditions: *CHIRALPAK* IB column. *n*-hexane/isopropyl alcohol (85:15) at 0.8 mL·min^{-1}. Retention times:

p-anisaldehyde: 7.3 min
(*R*)-1-(4-methoxyphenyl)-2-nitroethanol: 12.6 min
(*S*)-1-(4-methoxyphenyl)-2-nitroethanol: 14.2 min

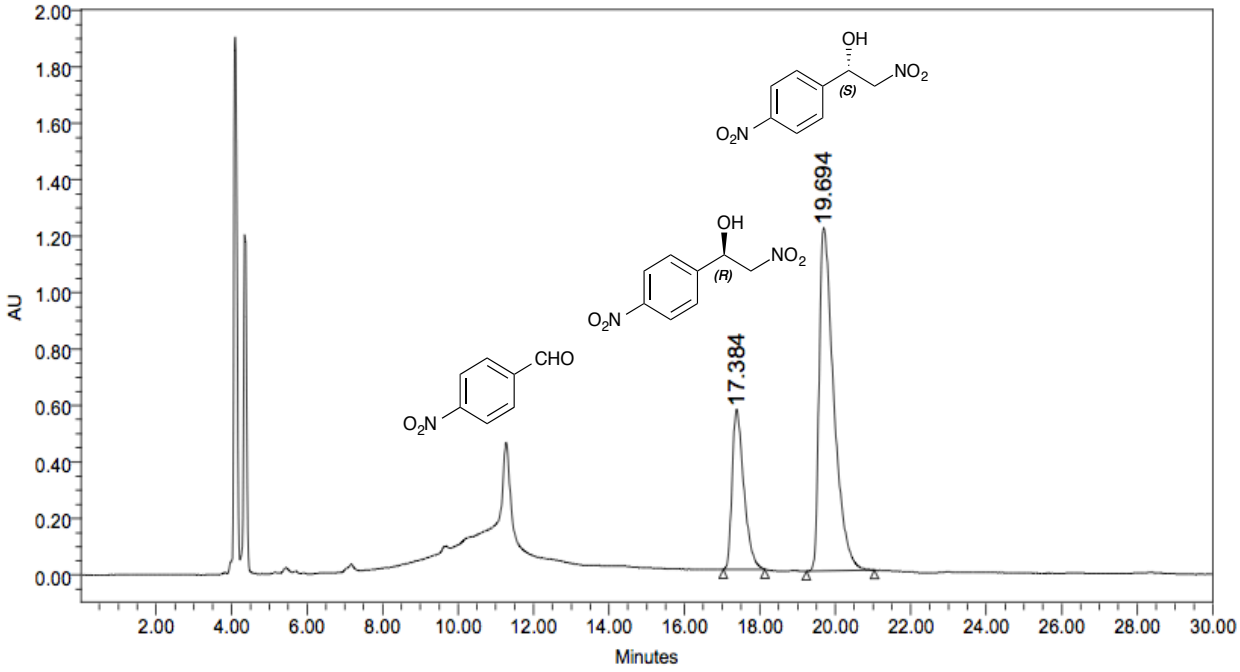


1.4. Reaction between 4-nitrobenzaldehyde and nitromethane

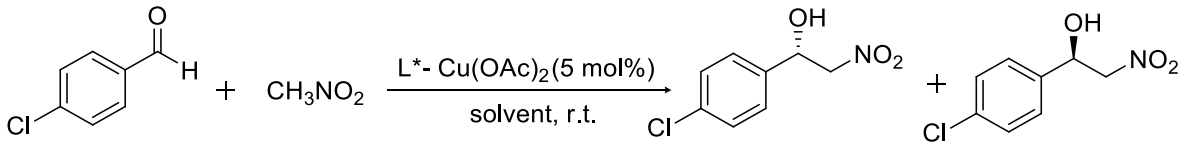


Conditions: *CHIRALPAK* IB column. *n*-hexane/isopropyl alcohol (85:15) at 0.8 mL·min^{-1}. Retention times:

4-nitrobenzaldehyde: 11.3 min
(*R*)-2-nitro-1-(4-nitrophenyl)ethanol: 17.4 min
(*S*)-2-nitro-1-(4-nitrophenyl)ethanol: 19.7 min

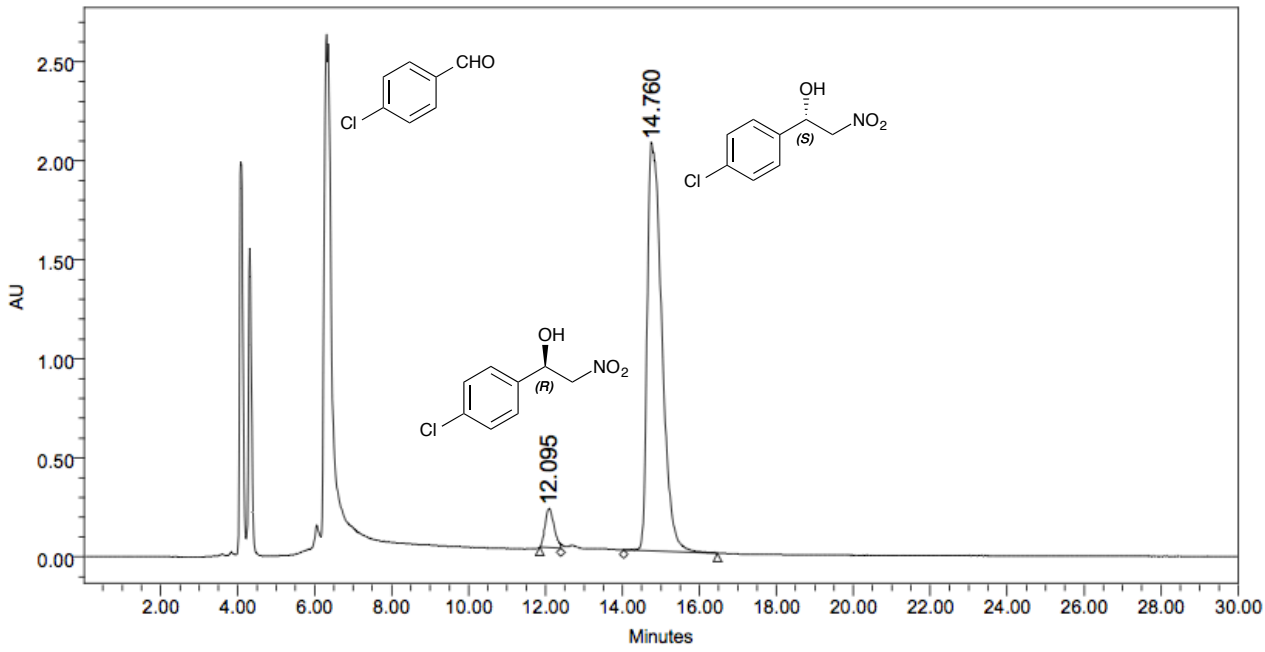


1.5. Reaction between 4-chlorobenzaldehyde and nitromethane

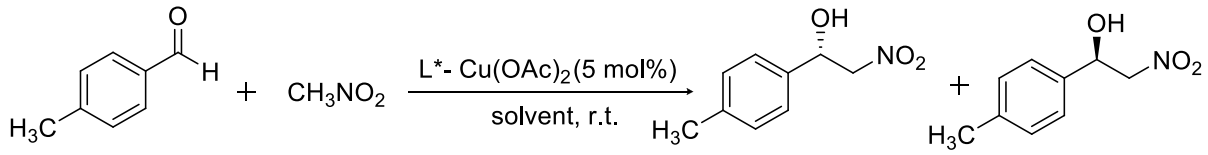


Conditions: *CHIRALCEL* OD-H column. *n*-hexane/isopropyl alcohol (85:15) at 0.8 $mL \cdot min^{-1}$. Retention times:

4-chlorobenzaldehyde: 6.5 min
1-chloro-4-(2-nitrovinyl)benzene: 12.1 min
(*S*)-1-(4-chlorophenyl)-2-nitroethanol: 14.8 min

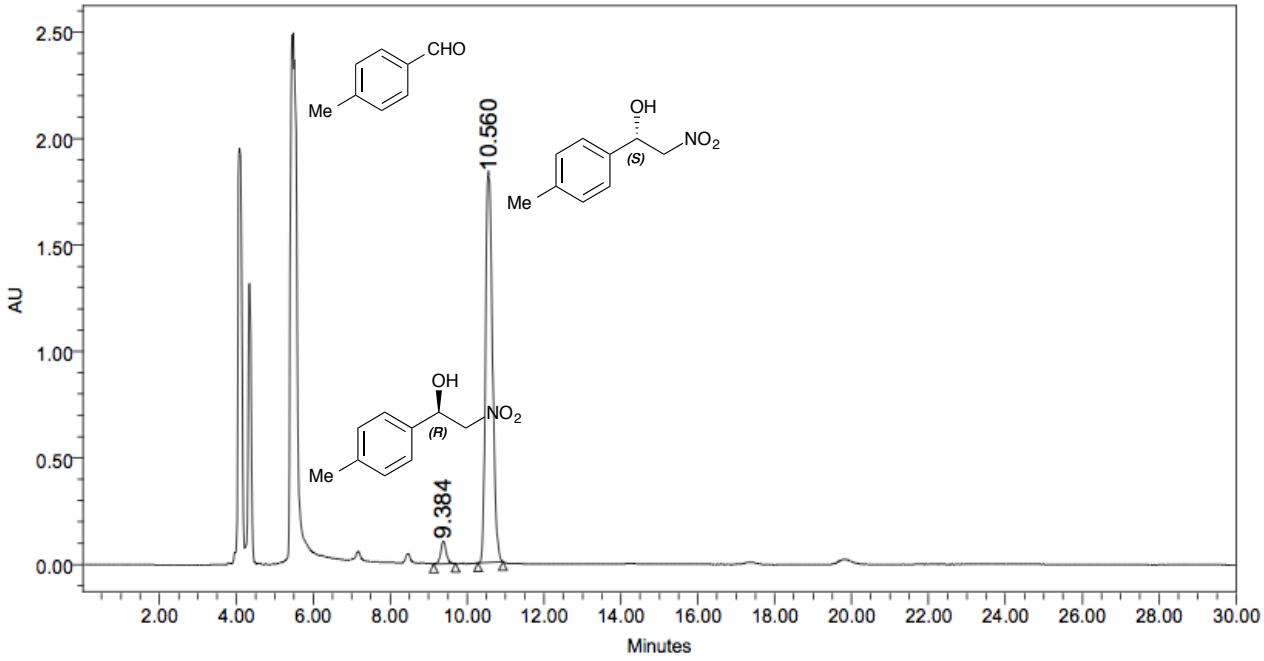


1.6. Reaction between 4-methylbenzaldehyde and nitromethane

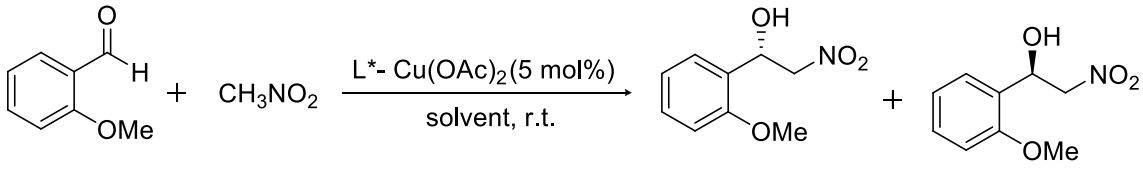


Conditions: *CHIRALPAK* IB column. *n*-hexane/isopropyl alcohol (85:15) at 0.8 mL·min^{-1}. Retention times:

4-methylbenzaldehyde: 5.1 min
(*R*)-2-nitro-1-*p*-tolylethanol: 9.4 min
(S)-2-nitro-1-*p*-tolylethanol: 10.6 min

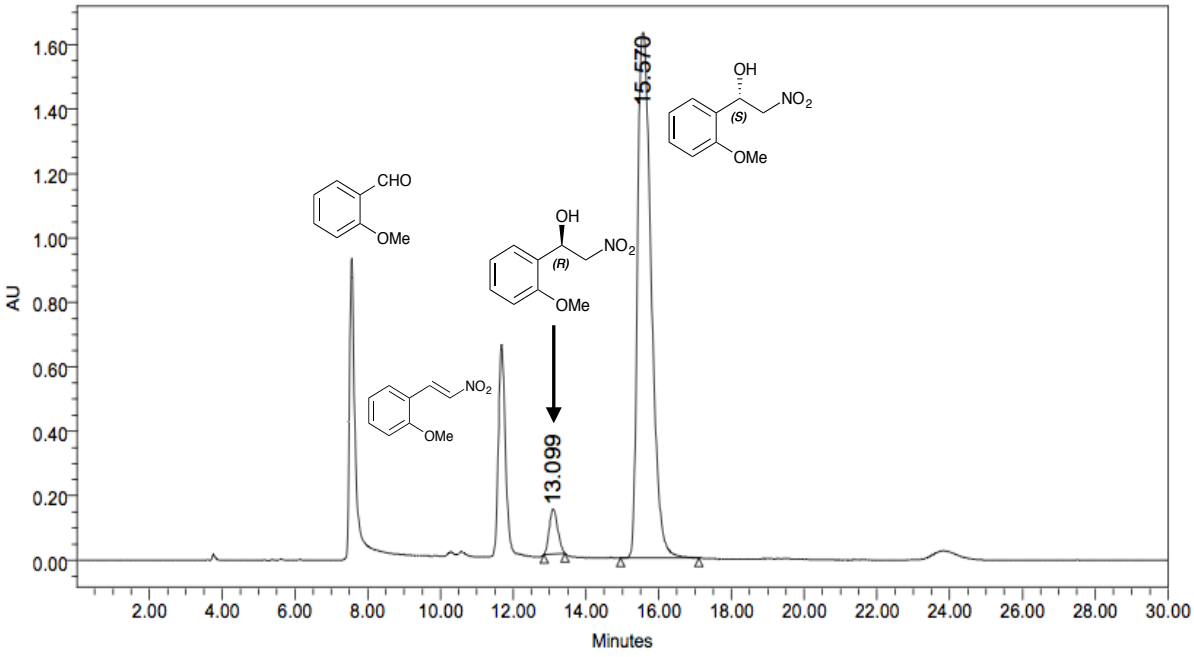


1.7. Reaction between *o*-anisaldehyde and nitromethane, catalysed by the TAX(iPr)Cu(OAc)$_2$ complex

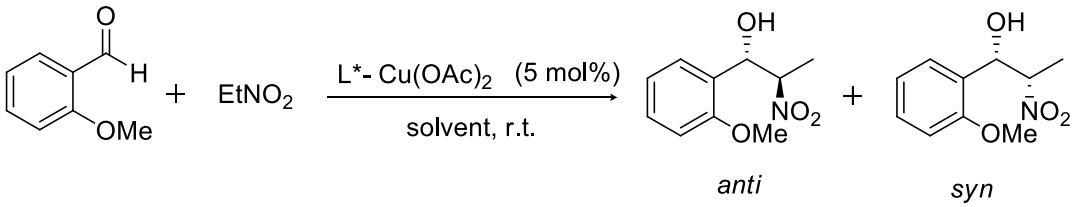


Conditions: *CHIRALCEL* OD-H column. *n*-hexane/isopropyl alcohol (85:15) at 0.8 mL·min^{-1}. Retention times:

o-anisaldehyde: 7.6 min
1-methoxy-2-(2-nitrovinyl)benzene: 11.8 min
(*R*)-1-(2-methoxyphenyl)-2-nitroethanol: 13.1 min
(*S*)-1-(2-methoxyphenyl)-2-nitroethanol: 15.6 min

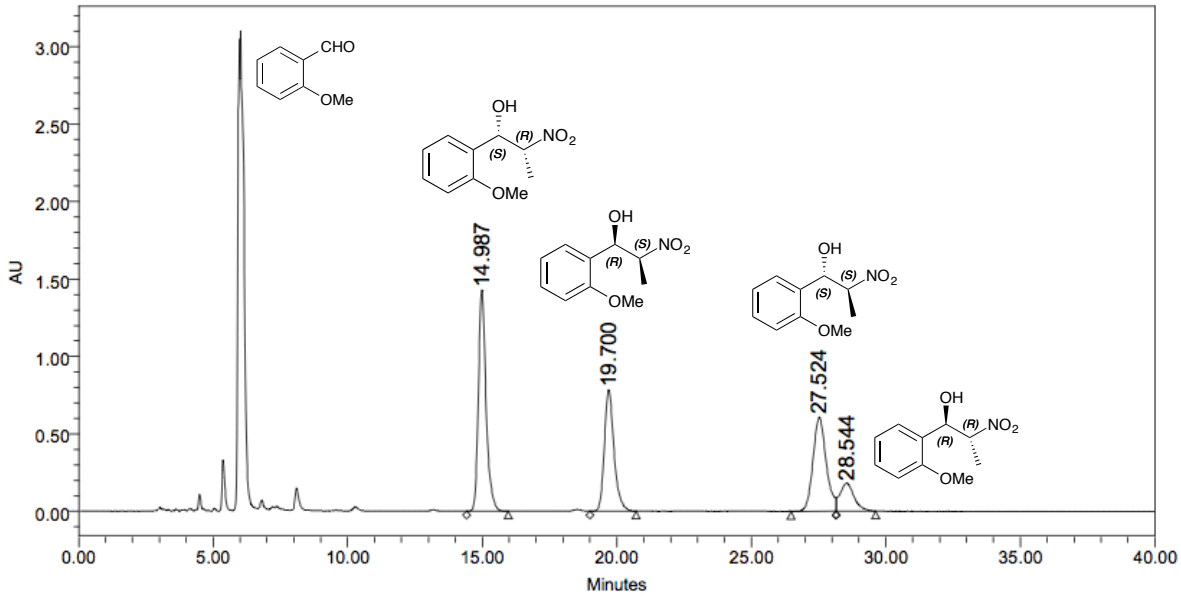


1.8. Reaction between *o*-anisaldehyde and nitroethane, catalysed by the TAX(iPr)Cu(OAc)$_2$ complex

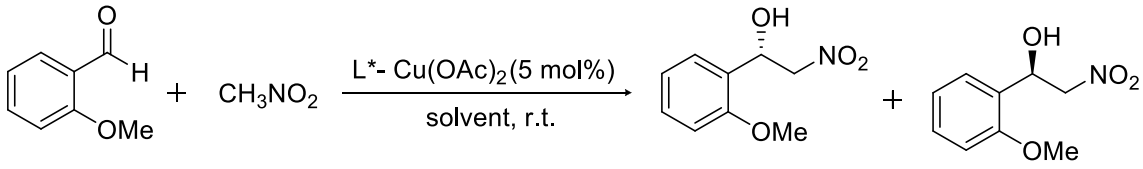


Conditions: *CHIRALPAK* AD-H column. *n*-hexane/isopropyl alcohol (95:5) at 1 mL·min^{-1}. Retention times:

o-anisaldehyde: 5.6 min
(1*S,2R*)-1-(2-methoxyphenyl)-2-nitropropan-1-ol: 15.0 min
(1*R,2S*)-1-(2-methoxyphenyl)-2-nitropropan-1-ol: 19.7 min
(1*S,2S)*-1-(2-methoxyphenyl)-2-nitropropan-1-ol: 27.5 min
(1*R,2R)*-1-(2-methoxyphenyl)-2-nitropropan-1-ol: 28.5 min

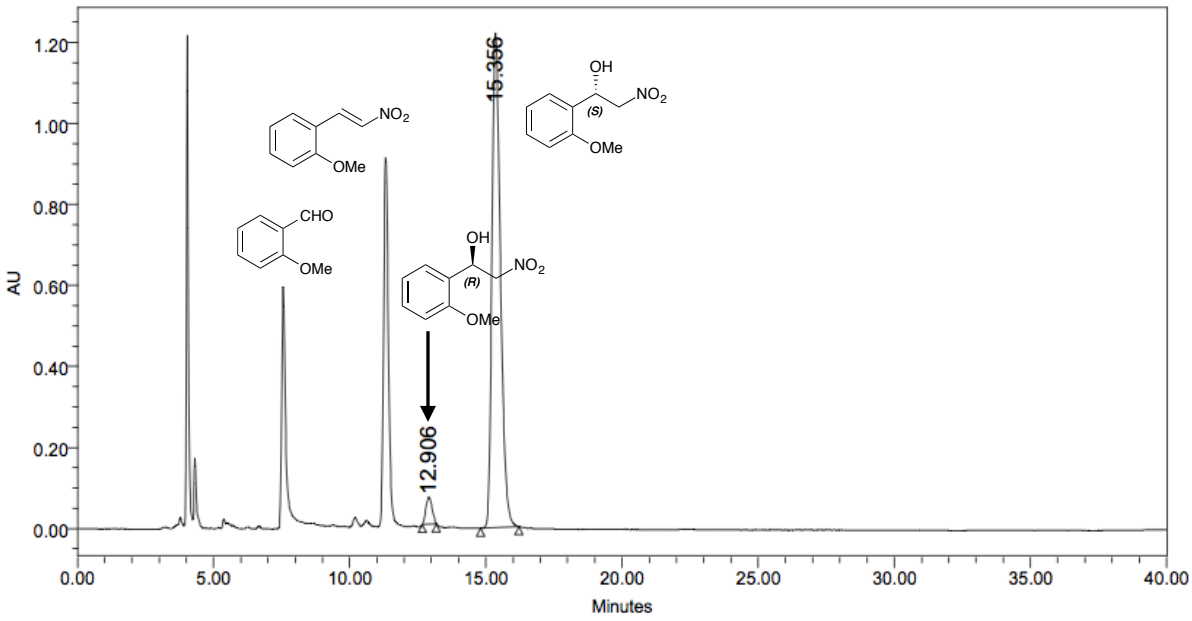


1.9. Reaction between *o*-anisaldehyde and nitromethane, catalysed by the QAX(iPr)Cu(OAc)$_2$ complex



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

o-anisaldehyde: 6.4 min
1-methoxy-2-(2-nitrovinyl)benzene: 10.7 min
(*R*)-1-(2-methoxyphenyl)-2-nitroethanol: 12.9 min
(*S*)-1-(2-methoxyphenyl)-2-nitroethanol: 15.4 min



2. References

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.