

Supporting Information

Concise methods for the synthesis of chiral polyoxazolines and their application in asymmetric hydrosilylation

Wei Jie Li^{*1}, Zun Le Xu² and Sheng Xiang Qiu¹

Address: ¹Program for Natural Product Chemical Biology & Drug Discovery, South China Botanical Garden, Chinese Academy of Sciences, 723 Xingke Road, Tianhe District, Guangzhou 510650, China and ²Department of Applied Chemistry, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, 135 Xingang West Road, Haizhou District, Guangzhou 510275, China

Email: Wei Jie Li - weijieli1688@yahoo.com.cn

* Corresponding author

Data for the hydrosilylation products of aromatic ketones (**8a–8h**)

(S)-1-Phenylethanol: 84% yield; HPLC analysis (Daicel Chiralcel OJ-H, 5% *i*-PrOH/hexane, 0.5 mL/min; t_r (major) = 22.5, t_r (minor) = 25.4) gave the isomeric composition of the product: 97% ee; $[\alpha]_D^{20}$ -49.8 (*c* 1.0, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃): δ 1.35 (d, *J* = 6.79 Hz, 3H), 3.08 (br s, 1H), 4.71 (q, *J* = 6.04, 6.79 Hz, 1H), 7.15–7.23 (m, 5H) ppm; ESI-MS, *m/z* (%): 123 ([M+H]⁺, 100); Anal. Calcd for C₈H₁₀O: C, 78.65; H, 8.25. Found: C, 78.32; H, 8.45.

(R)-1-Phenylethanol: 86% yield; HPLC analysis (Daicel Chiralcel OJ-H, 2% *i*-PrOH/hexane, 1.0 mL/min; t_r (major) = 10.6, t_r (minor) = 13.2) gave the isomeric composition of the product: 89% ee; $[\alpha]_D^{20}$ +43.6 (*c* 1.0, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃): δ 1.37 (d, *J* = 6.79 Hz, 3H), 3.05 (br s, 1H), 4.76 (q, *J* = 6.04, 6.79 Hz, 1H), 7.18–7.40 (m, 5H) ppm; ESI-MS, *m/z* (%): 123 ([M+H]⁺, 100); Anal. Calcd for C₈H₁₀O: C, 78.65; H, 8.25. Found: C, 78.15; H, 8.52.

(S)-1-(2-Naphthyl)ethanol: 85% yield; HPLC analysis (Daicel Chiralcel OD-H, 2% *i*-PrOH/hexane, 1.0 mL/min; t_r (major) = 21.7, t_r (minor) = 23.6) gave the isomeric composition of the product: 94% ee; $[\alpha]_D^{20}$ -41.7 (*c* 1.0, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ 1.54 (d, *J* = 6.79 Hz, 3H), 2.16 (br s, 1H), 5.03 (q, *J* = 6.04, 6.79 Hz, 1H), 7.41–7.48 (m, 3H), 7.76–7.83 (m, 4H) ppm; ESI-MS, *m/z* (%): 173 ([M+H]⁺, 100); Anal. Calcd for C₁₂H₁₂O: C, 83.69; H, 7.02. Found: C, 83.31; H, 7.24.

(S)-1-Phenylpropanol: 86% yield; HPLC analysis (Daicel Chiralcel OD-H, 4% *i*-PrOH/hexane, 0.5 mL/min; t_r (minor) = 17.4, t_r (major) = 20.4) gave the isomeric composition of the product: 94% ee; $[\alpha]_D^{20}$ -37.0 (*c* 0.50, CHCl₃); ¹H NMR (300

MHz, CDCl₃): δ 0.88 (t, J = 7.55 Hz, 3H), 1.65–1.81 (m, 2H), 1.96 (br s, 1H), 4.53 (t, J = 6.79 Hz, 1H), 7.21–7.30 (m, 5H) ppm; ESI-MS, m/z (%): 137 ([M+H]⁺, 100); Anal. Calcd for C₉H₁₂O: C, 79.37; H, 8.88. Found: C, 79.12; H, 8.97.

(S)-1-(2-Methylphenyl)ethanol: 89% yield; HPLC analysis (Daicel Chiralcel OB-H, 3% *i*-PrOH/hexane, 0.5 mL/min; t_r (major) = 14.6, t_r (minor) = 22.2) gave the isomeric composition of the product: 93% ee; $[\alpha]_D^{20}$ -50.8 (c 0.05, C₂H₅OH); ¹H NMR (300 MHz, CDCl₃): δ 1.43 (d, J = 6.04 Hz, 3H), 1.85 (br s, 1H), 2.32 (s, 3H), 5.10 (q, J = 6.04, 6.79 Hz, 1H), 7.09–7.23 (m, 3H), 7.48 (d, J = 7.55 Hz, 1H) ppm; ESI-MS, m/z (%): 137 ([M+H]⁺, 100); Anal. Calcd for C₉H₁₂O: C, 79.37; H, 8.88. Found: C, 79.05; H, 9.11.

(S)-1-(4-Methylphenyl)ethanol: 81% yield; HPLC analysis (Daicel Chiralcel OJ-H, 5% *i*-PrOH/hexane, 0.7 mL/min; t_r (major) = 10.9, t_r (minor) = 12.4) gave the isomeric composition of the product: 96% ee; $[\alpha]_D^{20}$ -54.1 (c 0.05, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ 1.45 (d, J = 6.79 Hz, 3H), 2.18 (br s, 1H), 2.36 (s, 3H), 4.82 (q, J = 6.04, 6.79 Hz, 1H), 7.15 (d, J = 8.30 Hz, 2H), 7.24 (d, J = 8.30 Hz, 2H) ppm; ESI-MS, m/z (%): 137 ([M+H]⁺, 100); Anal. Calcd for C₉H₁₂O: C, 79.37; H, 8.88. Found: C, 79.21; H, 8.92.

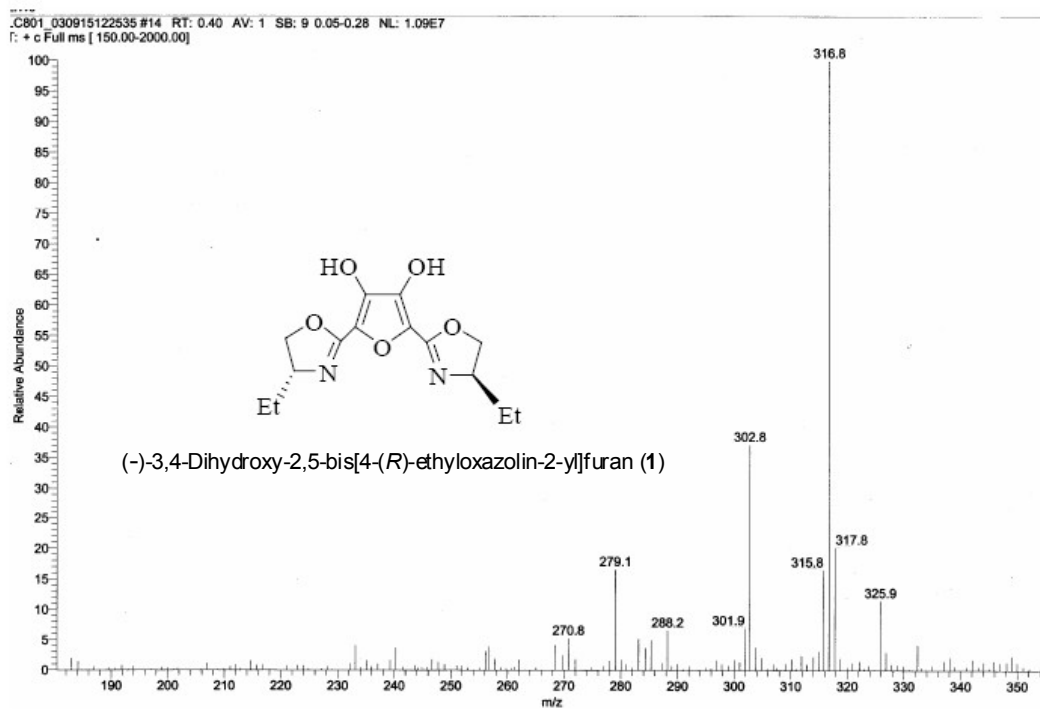
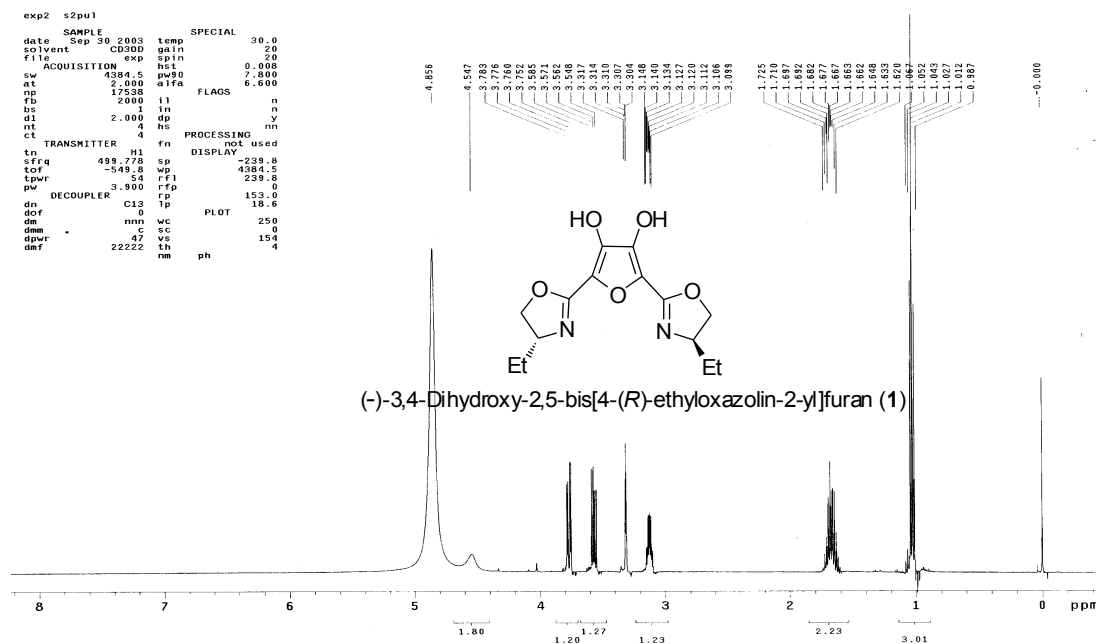
(S)-1-(2-Chlorophenyl)ethanol: 71% yield; HPLC analysis (Daicel Chiralcel OD-H, 2% *i*-PrOH/hexane, 0.8 mL/min; t_r (minor) = 16.6, t_r (major) = 17.8) gave the isomeric composition of the product: 90% ee; $[\alpha]_D^{20}$ -57.2 (c 0.05, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ 1.38 (d, J = 6.79 Hz, 3H), 3.57 (br s, 1H), 5.18 (q, J = 6.04, 6.79 Hz), 7.10–7.25 (m, 3H), 7.49 (d, J = 7.55 Hz, 1H) ppm; ESI-MS, m/z (%): 157

([M+H]⁺, 100); Anal. Calcd for C₈H₉ClO: C, 61.35; H, 5.79. Found: C, 61.14; H, 5.95.

(S)-1-(4-Chlorophenyl)ethanol: 76% yield; HPLC analysis (Daicel Chiralcel OJ-H, 5% *i*-PrOH/hexane, 0.5 mL/min; t_r (major) = 22.3, t_r (minor) = 26.0) gave the isomeric composition of the product: 94% ee; [α]_D²⁰ -48.8 (*c* 0.06, C₂H₅OC₂H₅); ¹H NMR (300 MHz, CDCl₃): δ 1.44 (d, *J* = 6.79 Hz, 3H), 2.42 (br s, 1H), 4.81 (q, *J* = 6.04, 6.79 Hz, 1H), 7.25–7.28 (m, 4H) ppm; ESI-MS, *m/z* (%): 157 ([M+H]⁺, 100); Anal. Calcd for C₈H₉ClO: C, 61.35; H, 5.79. Found: C, 61.23; H, 5.88.

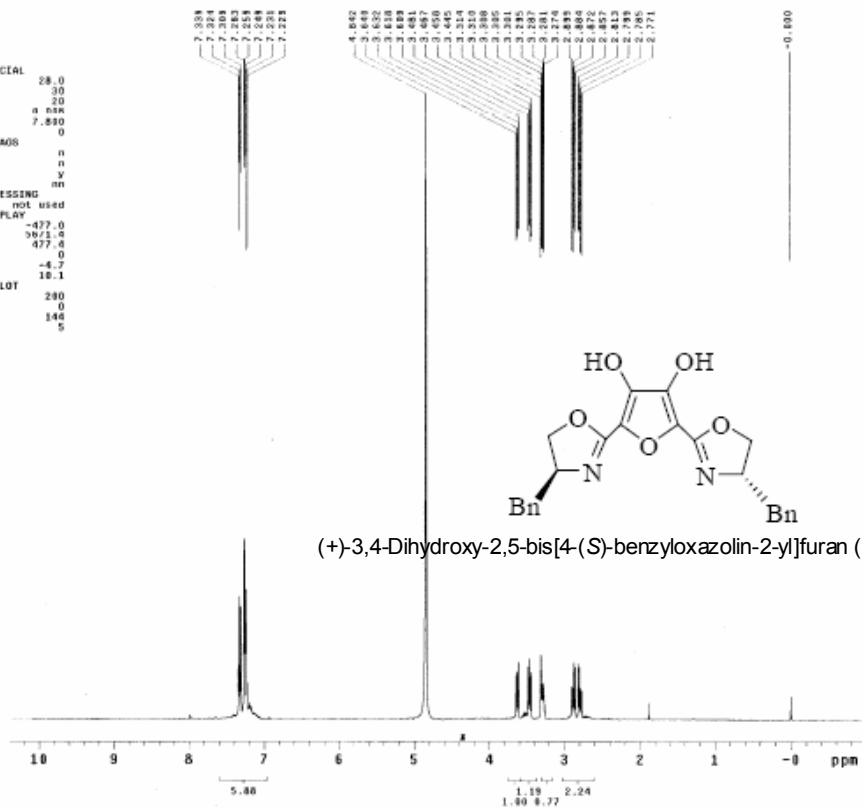
(S)-1-(4-Bromophenyl)ethanol: 79% yield; HPLC analysis (Daicel Chiralcel OJ-H, 5% *i*-PrOH/hexane, 0.5 mL/min; t_r (major) = 22.2, t_r (minor) = 24.1) gave the isomeric composition of the product: 96% ee; [α]_D²⁰ -37.6 (*c* 0.06, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ 1.38 (d, *J* = 6.04 Hz, 3H), 2.73 (br s, 1H), 4.77 (q, *J* = 6.04, 6.79 Hz, 1H), 7.15 (d, *J* = 8.30 Hz, 2H), 7.42 (d, *J* = 9.06 Hz, 2H) ppm; ESI-MS, *m/z* (%): 202 ([M+H]⁺, 100); Anal. Calcd for C₈H₉BrO: C, 47.79; H, 4.51. Found: C, 47.35; H, 4.63.

Copies of ¹H NMR and MS spectra for ligands (1-7)

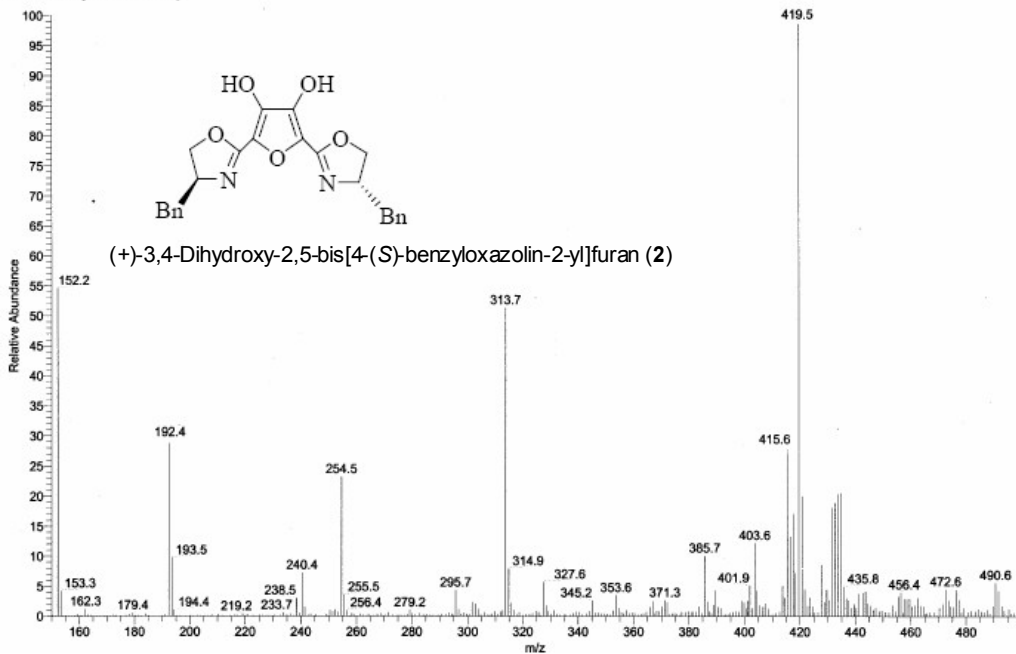


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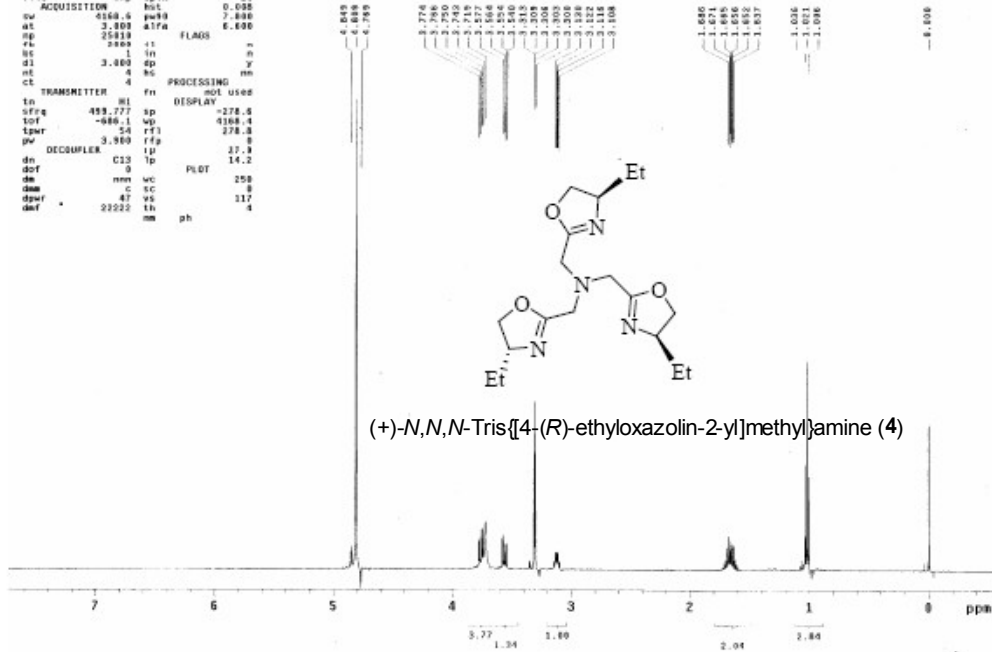
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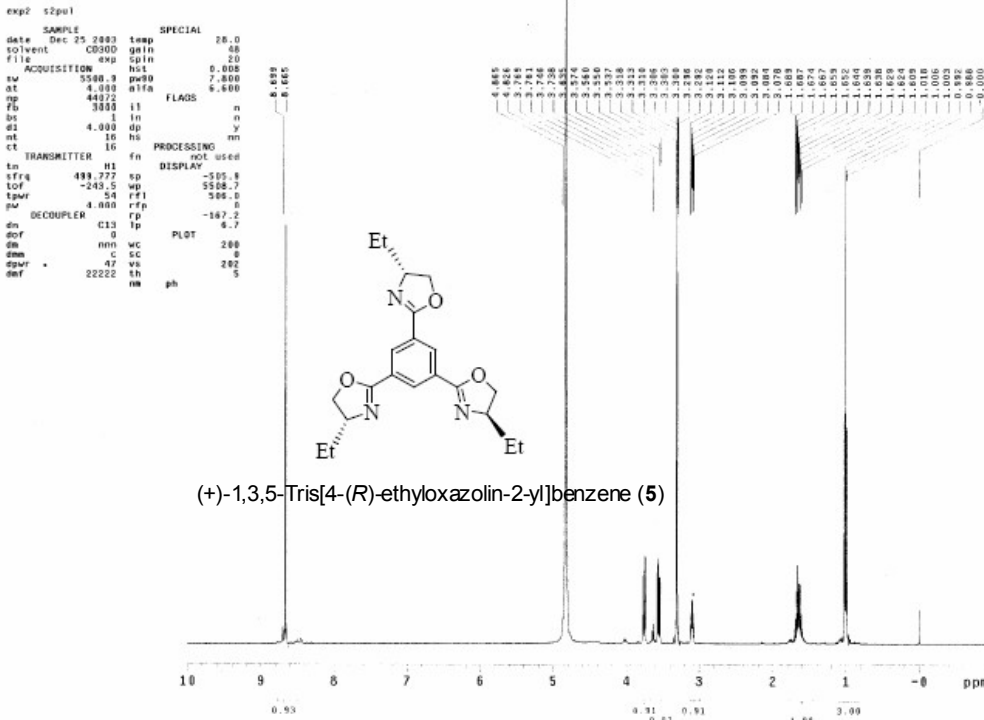
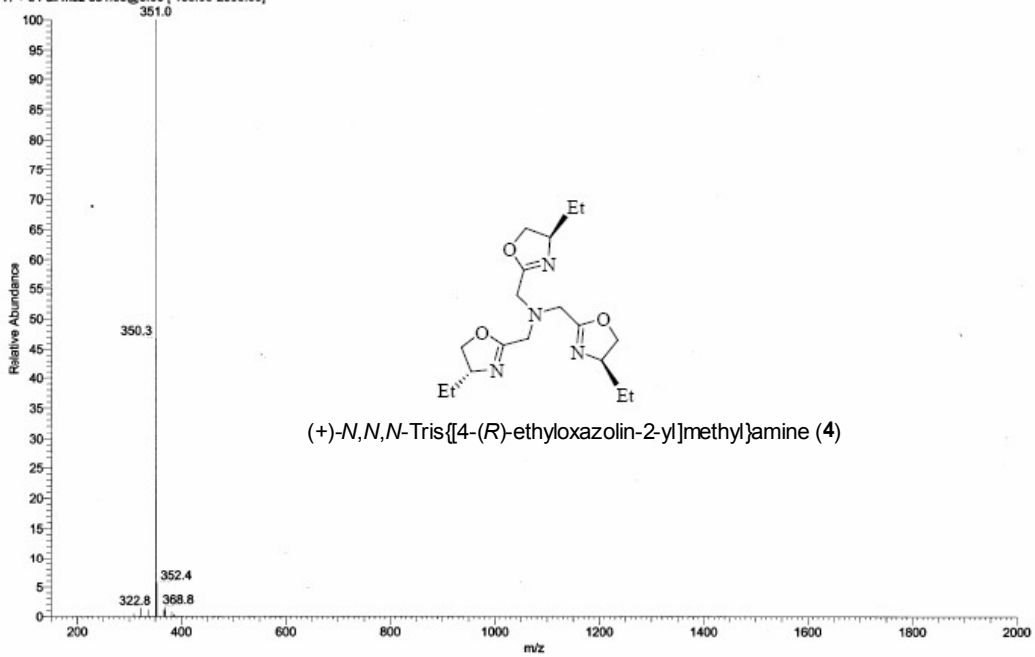

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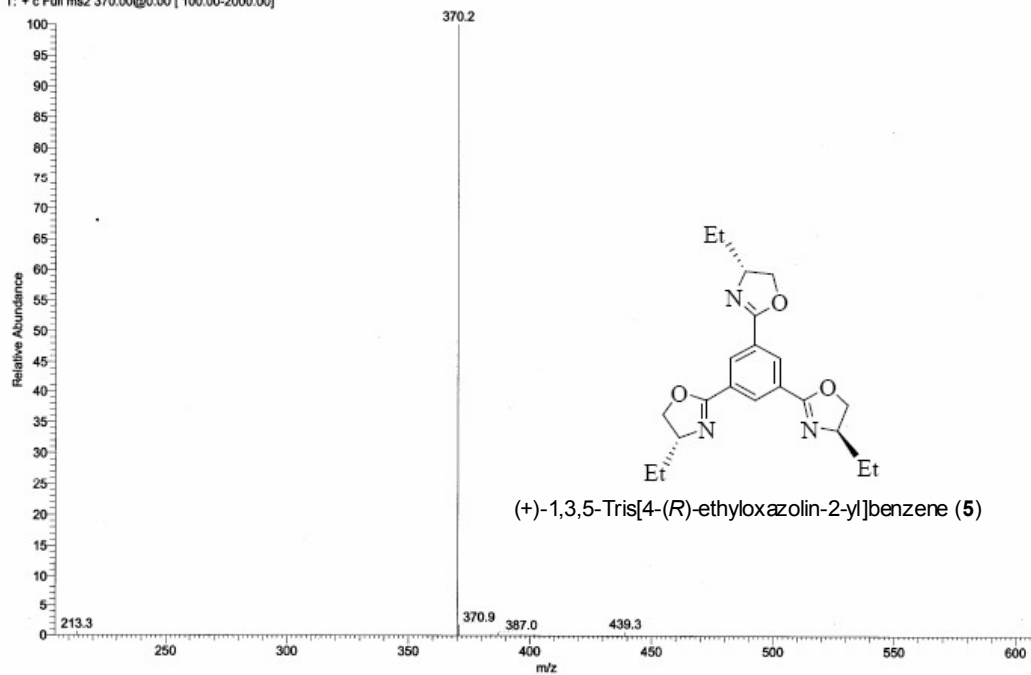
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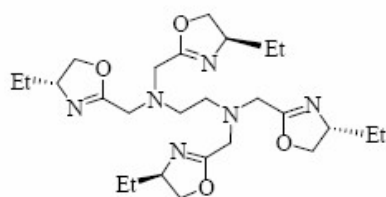
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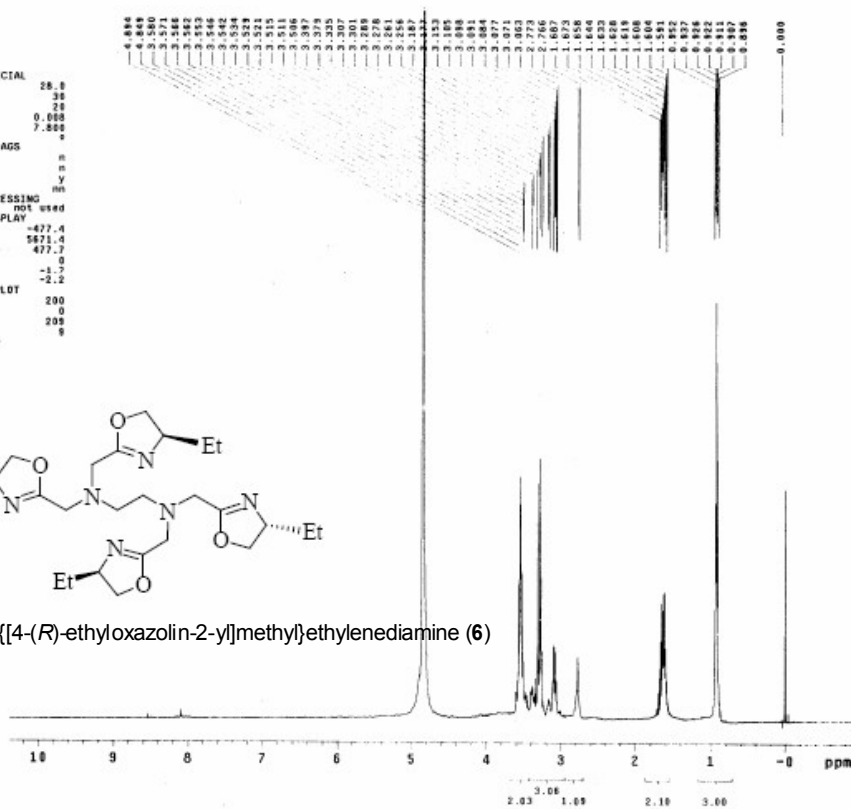
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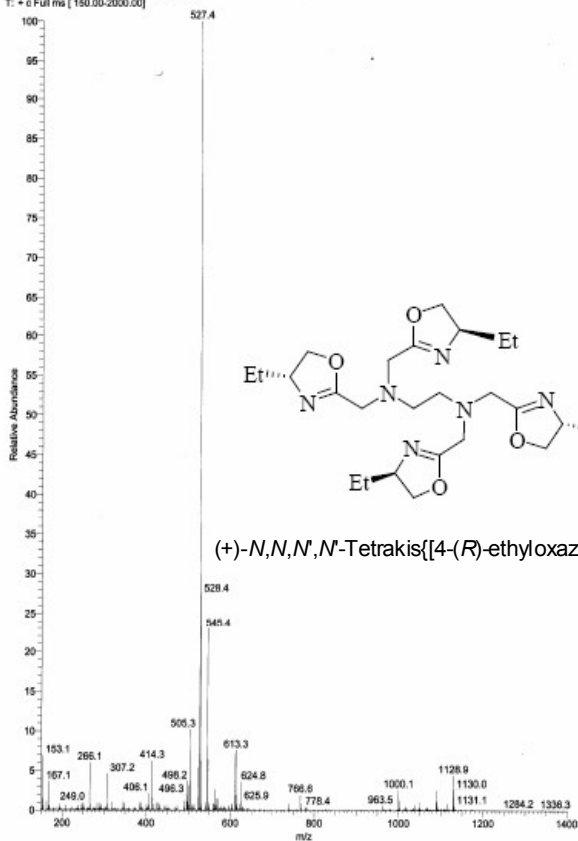
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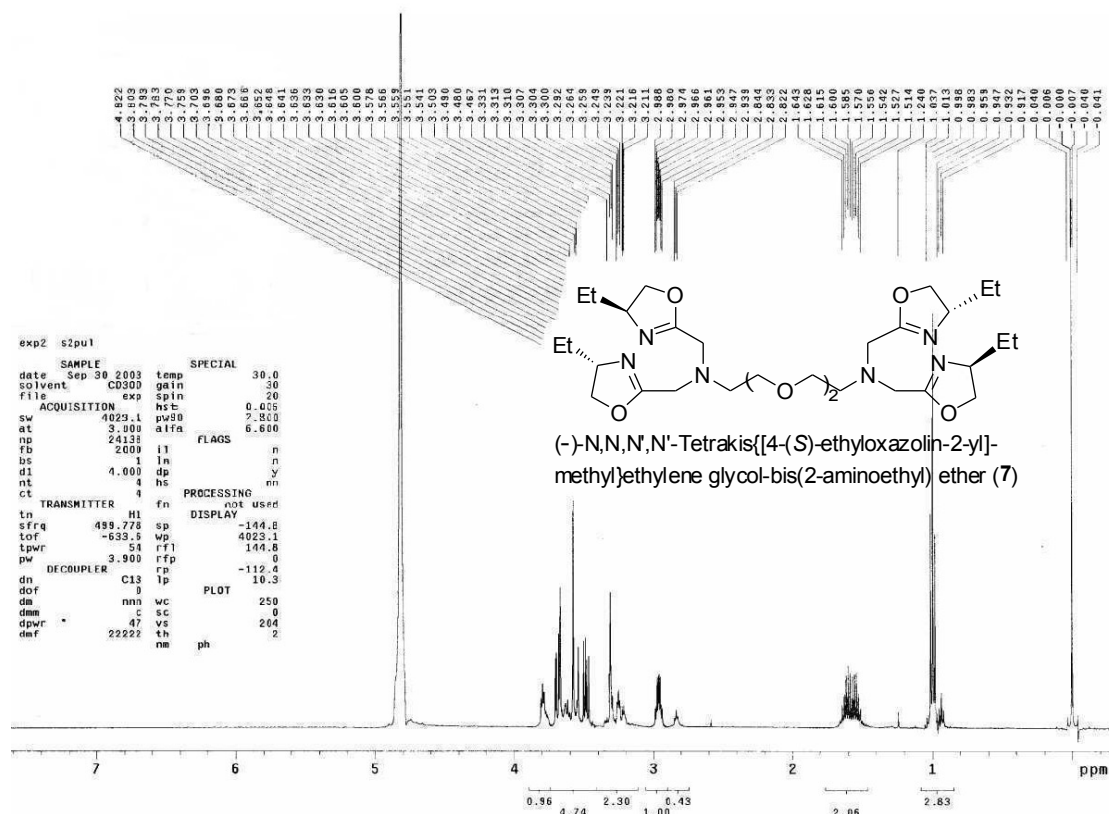
(+)-*N,N,N',N'*-Tetrakis[4-(*R*)-ethyloxazolin-2-yl]methyl]ethylenediamine (**6**)



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(+)-*N,N,N',N'*-Tetrakis[4-(*R*)-ethyloxazolin-2-yl]methyl]ethylenediamine (**6**)



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