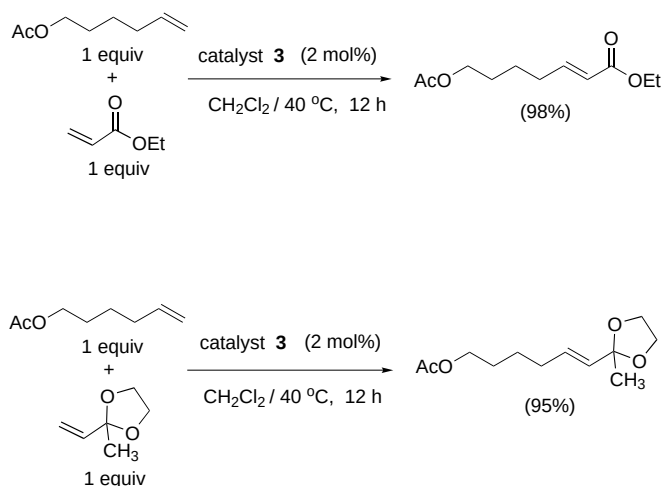




Scheme 6. Olefin CM with equal stoichiometry of substrates.

Experimental Section

General procedure (Scheme 6): 5-Hexenyl-1-acetate (200 μ L, 1.20 mmol, 1.0 equiv) and ethyl acrylate (130 μ L, 1.20 mmol, 1.0 equiv) were added simultaneously by using a syringe to a stirred solution of **3** (20 mg, 0.024 mmol, 2.0 mol %) in CH_2Cl_2 (2.5 mL, 0.5 N in acrylate) under a nitrogen atmosphere. The flask was fitted with a condenser and heated at reflux under nitrogen for 12 hours. The reaction mixture was then concentrated in vacuo, and the residue was purified directly on a silica-gel column (2×10 cm), eluting with hexane/ethyl acetate (9:1) to provide the CM product as a clear colorless oil (253 mg, 1.18 mmol, 98 %).

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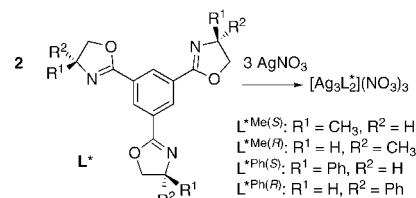
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An Enantiomerically Pure Propeller-Shaped Supramolecular Capsule Based on the Stereospecific Self-Assembly of Two Chiral Tris(oxazoline) Ligands around Three Ag^{I} Ions**

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The self-assembly of supramolecular structures by simply mixing ligands and labile metal ions has attracted considerable attention.^[1] Among the self-assembled supramolecular capsules,^[2] a few propeller-shaped structures have been described.^[3] In most cases racemates were obtained; however, recently chiral ligands have been reported to induce enantiomerically pure supramolecular capsules and helical superstructures.^[4] Herein we describe the completely stereospecific self-assembly of a propeller-shaped supramolecular capsule induced by a rigid chiral tris(oxazoline) unit acting as a tris-monodentate ligand and Ag^{I} metal ions having tetrahedral coordination geometry. The stereochemistry arises from the self-recognition of the ligand chirality^[5] during the self-assembly of the supramolecular capsule.

Chiral tris(oxazoline) ligands (L^*) were used to induce a predetermined chiral helicity because it is easy to introduce chirality and rigidity within the self-assembled superstructure from simple chiral amino alcohols.^[6] Simple mixing of Ag^{I} ions and L^* in a 3:2 ratio generated a single set of ^1H NMR resonances, which implies the formation of only one self-assembled structure (Scheme 1). The stoichiometry of the complex was identified by electrospray ionization (ESI) mass spectrometry. In particular, examination of the isotope distribution of the peak at m/z 1101.0, attributable to either $\{[\text{Ag}_3\text{L}_2^*](\text{NO}_3)_2\}^+$ or $\{[\text{Ag}_6\text{L}_4^*](\text{NO}_3)_4\}^{2+}$, showed a peak spacing of one mass unit typical of a +1 charged species; this



Scheme 1. Self-assembly of L^* and Ag^{I} ions into a trinuclear complex.

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confirms the presence of the former trinuclear complex. Evidence for the formation of a chiral helical superstructure comes from the CD spectra of the enantiomeric complexes $[\text{Ag}_3\text{L}_2^{*\text{Me}(S)}](\text{NO}_3)_3$ and $[\text{Ag}_3\text{L}_2^{*\text{Me}(R)}](\text{NO}_3)_3$. The CD signs are nearly opposite for the two complexes: $\Delta\epsilon(\lambda_{\text{max}}) = -8.1\text{ M}^{-1}\text{ cm}^{-1}(235\text{ nm})$ for the complex with the *S* ligand ($\text{L}^{*\text{Me}(S)}$) and $7.2\text{ M}^{-1}\text{ cm}^{-1}(235\text{ nm})$ for that with the *R* ligand ($\text{L}^{*\text{Me}(R)}$).

X-ray diffraction analysis of crystals of $[\text{Ag}_3\text{L}_2^{*\text{Me}(S)}](\text{NO}_3)_3$, which were obtained by slow diffusion of ether into an acetonitrile solution in a dark room, shows the presence of a D_3 -symmetric, dimeric, trinuclear, propeller-shaped supramolecular capsule with *M* helicity (Figure 1), in which $\text{L}^{*\text{Me}}$ acts as a tris-monodentate ligand.^[7] The complex consists of

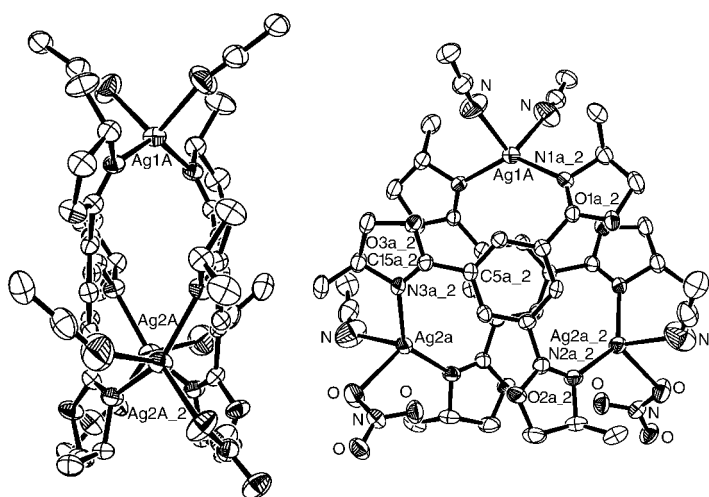


Figure 1. Structure of $(M)-[\text{Ag}_3\text{L}_2^{*\text{Me}(S)}](\text{CH}_3\text{CN})_4(\text{NO}_3)_2]^+$ in the solid state (ORTEP representations). Side view (left) and top view along pseudo- C_3 symmetric helical axis (right). All hydrogen atoms are omitted for clarity, only the heteroatoms of the upper $\text{L}^{*\text{Me}}$ ligand, the nitrate, and the acetonitrile ligands are indicated in the top view. Selected torsional angles $[\circ]$ (bond lengths $[\text{\AA}]$; bond angles $[\circ]$) for C5a_2, C15a_2, N3a_2, Ag2a: -7.9 (1.480, 1.263, 2.243; 126.99, 131.69).

an equilateral triangle of silver ions (av Ag–Ag distance $7.195\text{ \AA}$). Each silver ion binds to one oxazoline unit of $\text{L}^{*\text{Me}}$ above the plane of the silver atoms and to a second oxazoline unit of $\text{L}^{*\text{Me}}$ below the plane. Thus, the structure may be considered as a supramolecular helical capsule or triply bridged metallocyclophane, in which the silver ions constitute a triangle, with the ligands wrapping around the sides of the triangle.

It is noticeable that the two central phenyl rings lie nearly parallel to each other (interplanar distance $3.585\text{ \AA}$), which results in an aromatic stacking interaction.^[8] This stacking interaction seems to induce formation of the dimeric structure by the coordination of each silver ion to two oxazoline N atoms each linked to one phenyl ring. The silver ions are almost tetrahedrally coordinated by two oxazoline N atoms, CH_3CN , and NO_3^- because of a favorable stacking interaction (av N–Ag–N bond angle 133.68°). The helical chirality of $[\text{Ag}_3\text{L}_2^{*\text{Me}(S)}]^{3+}$ is determined by the configuration of the methyloxazoline moiety of the ligands.

To investigate the origin of the helical chirality in the complex, a model structure of the complex with the *R* ligand,

$(M)-[\text{Ag}_3\text{L}_2^{*\text{Me}(R)}]^{3+}$, was compared with the X-ray structure of $(M)-[\text{Ag}_3\text{L}_2^{*\text{Me}(S)}]^{3+}$ (Figure 2).^[9] Methyl substituents on the oxazoline rings are away from the coordinating Ag^I ions between the two aromatic planes in the crystal structure of $(M)-[\text{Ag}_3\text{L}_2^{*\text{Me}(S)}]^{3+}$. The average distance between the me-

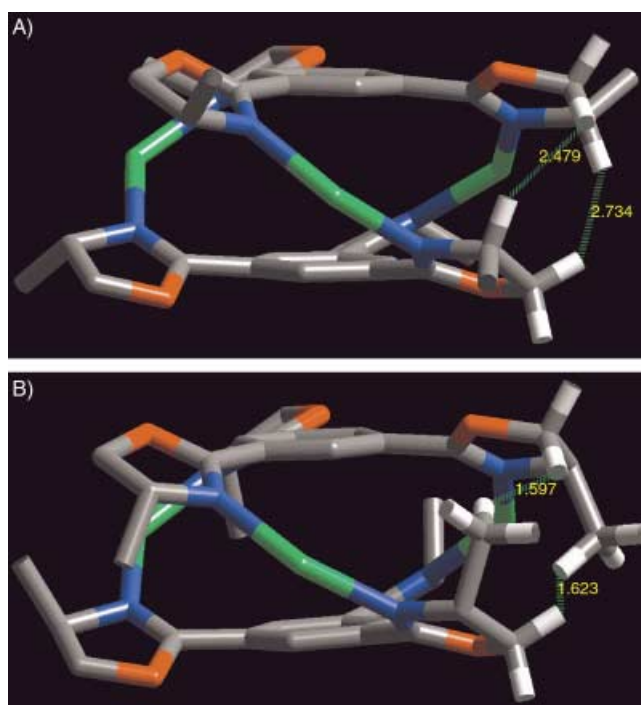


Figure 2. A) Crystal structure of $(M)-[\text{Ag}_3\text{L}_2^{*\text{Me}(S)}]^{3+}$ and B) model structure of $(M)-[\text{Ag}_3\text{L}_2^{*\text{Me}(R)}]^{3+}$. All hydrogen atoms except those at interacting sites are omitted for clarity. Atom color code: C (gray), O (red), N (blue), Ag (green), H (white). Both views were generated with the Cerius2 program.

thine hydrogen of the upper oxazoline ring and the methylene hydrogen of the lower oxazoline ring in $(M)-[\text{Ag}_3\text{L}_2^{*\text{Me}(S)}]^{3+}$ is $2.6\text{ \AA}$ —enough to relax the steric repulsions in the π - π stack of the crystal structure. In contrast the average distance between the methylene hydrogen of the upper oxazoline and the methyl hydrogen of the lower oxazoline ring in the model structure $(M)-[\text{Ag}_3\text{L}_2^{*\text{Me}(R)}]^{3+}$ is $1.6\text{ \AA}$ —far too short for the structure to exist. The resulting van der Waals repulsions at six points prohibit the formation of the complex $(M)-[\text{Ag}_3\text{L}_2^{*\text{Me}(R)}]^{3+}$, instead causing the exclusive formation of $(P)-[\text{Ag}_3\text{L}_2^{*\text{Me}(R)}]^{3+}$ with different helicity.

In addition to the completely stereospecific induction of helicity in the dimeric superstructure, the chirality recognition between ligands within the supramolecular helical box is of interest. Two approaches to ligand recognition are possible: ligand self- and hetero-recognition. An equimolar mixture of $\text{L}^{*\text{Me}(S)}$ and $\text{L}^{*\text{Me}(R)}$ in the presence of three equivalents of AgNO_3 was tested because one enantiopure ligand could specifically perceive its enantiomer to generate a *meso* complex, $[\text{Ag}_3\text{L}_2^{*\text{Me}(S)}\text{L}^{*\text{Me}(R)}]^{3+}$ (hetero-recognition), and/or each enantiomeric ligand could selectively recognize itself to give the homochiral complexes $(M)-[\text{Ag}_3\text{L}_2^{*\text{Me}(S)}]^{3+}$ and $(P)-[\text{Ag}_3\text{L}_2^{*\text{Me}(S)}]^{3+}$ (self-recognition). A mixture of $\text{L}^{*\text{Me}(S)}$, $\text{L}^{*\text{Me}(R)}$, and AgNO_3 in a 1:1:3 ratio generated a highly symmetric

single set of ^1H NMR resonances, which suggests that either exclusively self-recognition or exclusively hetero-recognition between the chiral ligands takes place. However, it is more likely that the *R* form of the ligand in the dimer recognizes the *R* form and that the *S* form recognizes the *S* form stereospecifically because of the triple steric repulsions between the methylene hydrogens of the upper oxazoline, $\text{L}^{*\text{Me}(\text{S})}$, and the methyl hydrogens of the lower oxazoline, $\text{L}^{*\text{Me}(\text{R})}$ of mesocate, $[\text{Ag}_3\text{L}^{*\text{Me}(\text{S})}\text{L}^{*\text{Me}(\text{R})}]^{3+}$ (vide supra). This high homoleptic diastereoselectivity was also observed in $[\text{Ag}_3\text{L}_2^{*\text{Ph}}]^{3+}$.

Crucial evidence for ligand self-recognition comes from the X-ray structure determination of the colorless crystals obtained from the racemic ligand $\text{L}^{*\text{Me}}$ with three equivalents of Ag^{I} ions. A racemic mixture of the homochiral complexes (*M*)- $[\text{Ag}_3\text{L}_2^{*\text{Me}(\text{S})}(\text{CH}_3\text{CN})_2(\text{NO}_3)_3]$ and (*P*)- $[\text{Ag}_3\text{L}_2^{*\text{Me}(\text{R})}(\text{CH}_3\text{CN})_2(\text{NO}_3)_3]$ is evident in the unit cell, similar to the structure of the pure enantiomer (*M*)- $[\text{Ag}_3\text{L}_2^{*\text{Me}(\text{S})}(\text{CH}_3\text{CN})_3(\text{NO}_3)_3]$ except for the composition of the counteranions and solvents (Figure 3).^[10]

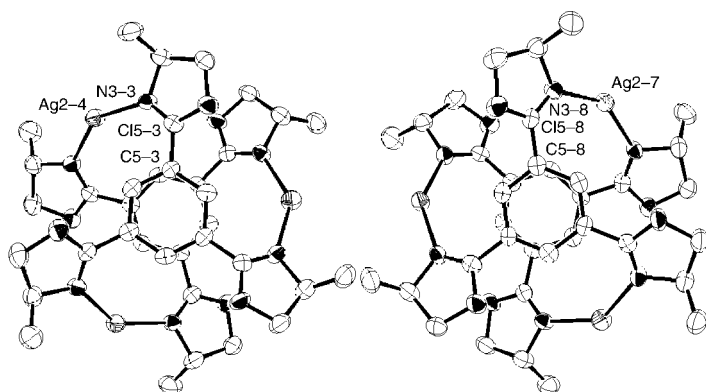


Figure 3. ORTEP representation of the racemic mixture of the homochiral complexes (*M*)- $[\text{Ag}_3\text{L}_2^{*\text{Me}(\text{S})}(\text{CH}_3\text{CN})_2(\text{NO}_3)_3]$ (left) and (*P*)- $[\text{Ag}_3\text{L}_2^{*\text{Me}(\text{R})}(\text{CH}_3\text{CN})_2(\text{NO}_3)_3]$ (right) in the unit cell. Selected torsional angles $[\circ]$ (bond lengths $[\text{\AA}]$; bond angles $[\circ]$) for C5-3, C15-3, N3-3, Ag2-4 of the *M* form: -10.3 (1.475, 1.264, 2.222; 126.50, 132.22); for C5-8, C15-8, N3-8, Ag2-7 of the *P* form: $+10.3$ (1.475, 1.264, 2.222; 126.50, 132.22).

Next, more evidence for the self-recognition of ligand chirality comes from an equimolar mixture of $\text{L}^{*\text{Me}(\text{S})}$ and $\text{L}^{*\text{Ph}(\text{R})}$ in the presence of three equivalents of Ag^{I} ions. Only two sets of ^1H NMR resonances were observed instead of the plausible three sets of peaks, which would be expected from consideration of all the possible ligand combinations (Figure 4). However, three sets of ^1H NMR resonances appeared when $\text{L}^{*\text{Me}(\text{S})}$ and $\text{L}^{*\text{Ph}(\text{S})}$ were mixed with Ag^{I} ions due to the presence of the heterodimer, $[\text{Ag}_3\text{L}^{*\text{Me}(\text{S})}\text{L}^{*\text{Ph}(\text{S})}]^{3+}$ in addition to the homodimers $[\text{Ag}_3\text{L}_2^{*\text{Me}(\text{S})}]^{3+}$ and $[\text{Ag}_3\text{L}_2^{*\text{Ph}(\text{S})}]^{3+}$ in the ^1H NMR spectra (Figure 4). Further evidence for the heterodimerization of different ligands with the same chirality appeared from ESI mass data of a 1:1:3 mixture of $\text{L}^{*\text{Ph}(\text{S})}$, $\text{L}^{*\text{Me}(\text{S})}$, and AgNO_3 : the peaks from the heterodimer complex $[\text{Ag}_3\text{L}^{*\text{Ph}(\text{S})}\text{L}^{*\text{Me}(\text{S})}](\text{NO}_3)_3$ were observed in addition to those of the homodimers $[\text{Ag}_3\text{L}_2^{*\text{Me}(\text{S})}](\text{NO}_3)_3$ and $[\text{Ag}_3\text{L}_2^{*\text{Ph}(\text{R})}](\text{NO}_3)_3$.^[11]

This study shows a rare example of the formation of enantiomerically pure, propeller-shaped supramolecular cap-

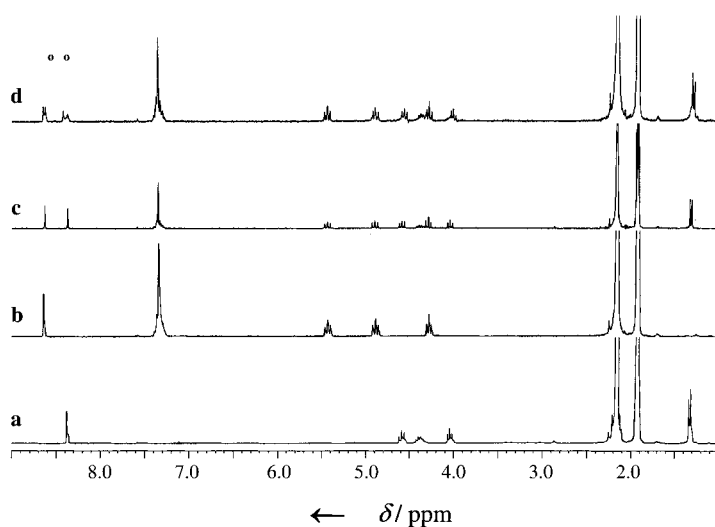


Figure 4. ^1H NMR spectra of chiral complexes (1.0 mM) in $[\text{D}_3]\text{acetonitrile}$. a) $[\text{Ag}_3\text{L}_2^{*\text{Me}(\text{S})}](\text{NO}_3)_3$; b) $[\text{Ag}_3\text{L}_2^{*\text{Ph}(\text{S})}](\text{NO}_3)_3$; c) $[\text{Ag}_3\text{L}_2^{*\text{Me}(\text{S})}](\text{NO}_3)_3$ + $[\text{Ag}_3\text{L}_2^{*\text{Ph}(\text{R})}](\text{NO}_3)_3$; d) $[\text{Ag}_3\text{L}_2^{*\text{Me}(\text{S})}](\text{NO}_3)_3$ + $[\text{Ag}_3\text{L}_2^{*\text{Ph}(\text{S})}](\text{NO}_3)_3$ + $[\text{Ag}_3\text{L}^{*\text{Ph}(\text{S})}\text{L}^{*\text{Me}(\text{S})}](\text{NO}_3)_3$ (open circles).

sules by the stereospecific recognition of enantiopure polynucleating ligands in the presence of metal ions. This is the first systematic study of the self-recognition phenomena of chiral ligands in the self-assembly of supramolecular helical boxes, as was unambiguously proven by both NMR spectroscopy and X-ray diffraction analysis. In an extension of this study modified tris(oxazoline) ligands and Ag^{I} ions could be used to generate a dimeric chiral capsule, which could function as a chiral catalyst.

Experimental Section

$[\text{Ag}_3\text{L}_2^{*\text{Me}}](\text{NO}_3)_3$: During all the reactions involving silver complexes, the reaction flask was wrapped with aluminum foil to shield the visible light. To a solution of $\text{L}^{*\text{Me}}$ (20 mg, 61 μmol) in degassed MeOH (1 mL) was added a solution of 1.5 equiv AgNO_3 in degassed water (1 mL). Stirring for 30 min resulted in a white suspension. The reaction mixture was concentrated to dryness, dissolved in a minimum amount of degassed acetonitrile, filtered through glass wool, and recrystallized in a refrigerator by slow evaporation of ether to give the desired silver complex as a colorless crystalline solid.

^1H NMR (300 MHz, $[\text{D}_3]\text{acetonitrile}$): δ = 8.48 (s, 6H of aromatic H), 4.68 (dd, $^3J(\text{H,H})$ = 9.0 Hz, 8.0 Hz, 6H of CH_2O), 4.46 (m, 6H of chiral C*H), 4.13 (dd, $^3J(\text{H,H})$ = 9.0 Hz, 8.0 Hz, 6H of CH_2O), 1.39 ppm (d, $^3J(\text{H,H})$ = 6.6 Hz, 18H of CH_3); ^{13}C NMR (75 MHz, $[\text{D}_3]\text{acetonitrile}$): δ = 163.8 (oxazoline), 130.3, 127.9 (aromatic), 75.6 (CH_2O), 63.0 (C*HN), 20.9 ppm (CH_3); MS (ESI $^+$, CH_3CN): m/z : 1101.0 ($[[\text{Ag}_3\text{L}_2^{*\text{Me}}](\text{NO}_3)_2]^+$), 930.1 ($[[\text{Ag}_3\text{L}_2^{*\text{Me}}](\text{NO}_3)]^+$), 761.2 ($[\text{AgL}_2^{*\text{Me}}]^+$), 434.1 ($[\text{AgL}^{*\text{Me}}]^+$); $[\alpha]_D^{24}$ = -50.8 for $[\text{Ag}_3\text{L}_2^{*\text{Me}(\text{S})}](\text{NO}_3)_3$, +48.5 for $[\text{Ag}_3\text{L}_2^{*\text{Me}(\text{R})}](\text{NO}_3)_3$ (c = 1.0, acetonitrile).

$[\text{Ag}_3\text{L}_2^{*\text{Ph}}](\text{BF}_4)_3$: Similar procedure as above; ^1H NMR (300 MHz, $[\text{D}_6]\text{acetone}$): δ = 8.96 (s, 6H of aromatic H), 7.44 and 7.34 (m, 30H of Ph-H), 5.69 (dd, $^3J(\text{H,H})$ = 9.2 Hz, 8.9 Hz, 6H of CH_2O), 5.30 (dd, $^3J(\text{H,H})$ = 9.2 Hz, 8.9 Hz, 6H of CH_2O), 4.54 ppm (t, $^3J(\text{H,H})$ = 8.9 Hz, 6H of chiral C*H); ^{13}C NMR (75 MHz, $[\text{D}_6]\text{acetone}$): δ = 166.8 (oxazoline), 140.9, 131.5, 129.3, 128.8, 128.3, 127.6 (aromatic), 77.9 (CH_2O), 70.5 ppm (C*HN); $[\alpha]_D^{24}$ = -28.5 for $[\text{Ag}_3\text{L}_2^{*\text{Ph}(\text{S})}](\text{BF}_4)_3$, +32.2 for $[\text{Ag}_3\text{L}_2^{*\text{Ph}(\text{R})}](\text{BF}_4)_3$ (c = 1.0, dichloromethane); $\Delta\epsilon$ (λ_{max}) = $-21.4\text{ M}^{-1}\text{ cm}^{-1}$ (241 nm) of $[\text{Ag}_3\text{L}_2^{*\text{Ph}(\text{S})}](\text{BF}_4)_3$ and $16.7\text{ M}^{-1}\text{ cm}^{-1}$ (240 nm) of $[\text{Ag}_3\text{L}_2^{*\text{Ph}(\text{R})}](\text{BF}_4)_3$ (c = 40 μM , CH_2Cl_2 + CH_3CN , 10:1, v/v).

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Deracemization of α -Methylbenzylamine Using an Enzyme Obtained by In Vitro Evolution**

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Enantiomerically pure chiral amines are valuable synthetic intermediates, particularly for the preparation of pharmaceutical compounds. Traditionally, chiral amines have been obtained by resolution-based procedures, for example, by kinetic resolution of a racemate using an enzyme^[1,2] or crystallization of a diastereomer using a chiral acid to form a salt.^[3] Increasingly, there is a desire to develop asymmetric approaches, or their equivalents, which can in principal deliver the product in 100 % yield and 100 % *ee*. For example, transaminases have been utilized for the conversion of

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