New chiral Cu^{II} complexes and their catalytic activity in enantioselective Henry reaction

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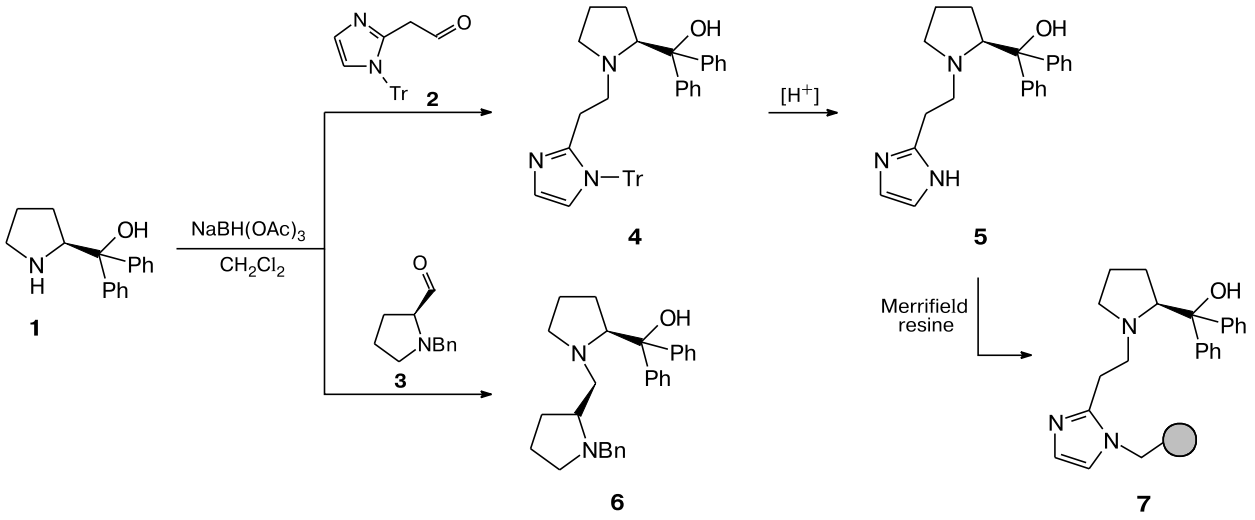
New chiral polydentante ligands capable of complexation of Cu^{2+} ions were synthesized using readily available derivatives of (*S*)-proline, D-glyceraldehyde, and imidazole as the starting materials. The synthesized complexes are efficient catalysts for enantioselective nitroaldol condensation (the Henry reaction).

Key words: Cu^{II} chiral complexes, enantioselective synthesis, nitroaldol condensation.

Design of novel catalytic systems based on the copper complexes with the various chiral ligands is one of the actual trends in the development of modern homogeneous enantioselective catalysis. This is due to the capability of such copper complexes to catalyze aldol condensation, the Michael addition, cycloadditions, and carbonyl-ene reactions (see, for example, Ref. 1) widely used in the synthesis of natural compounds. Earlier,[2] starting from (*S*)-1,1-diphenylprolinol **1** we have synthesized two chiral ligands, whose complexes with Cu^{II} was found to efficiently catalyze nitroaldol condensation (the Henry reaction). We report herein new results from our ongoing studies. In the present work, amino alcohol **1** was used as a chiral component in the reductive amination involving the known aldehydes **2** and **3** (Scheme 1). The studied reaction affords hitherto unknown compounds **4**—**6** bearing additional nucleophilic centers. It should be emphasized that due to the presence of a free amino group in imidazole **5**, we succeeded in immobilization of this polydentate ligand on a surface of the modified polystyrene to obtain modified resin **7**.

Isopropylidene derivative of D-glyceraldehyde **8** was chosen as an alternative source of primary chirality. Condensation of **8** with lithium derivative of 2-methylimidazole **9** stereoselectively affords a mixture of stereoisomers **10** (**10a** : **10b** ≈ 7 : 2), which can be easily resolved by chromatography (Scheme 2). Acidic protolysis of the major isomer **10a** results in triol **11** possessing, apparently, enhanced chelating ability due to the presence of three hydroxy groups in addition to the imidazole moiety.

Scheme 1



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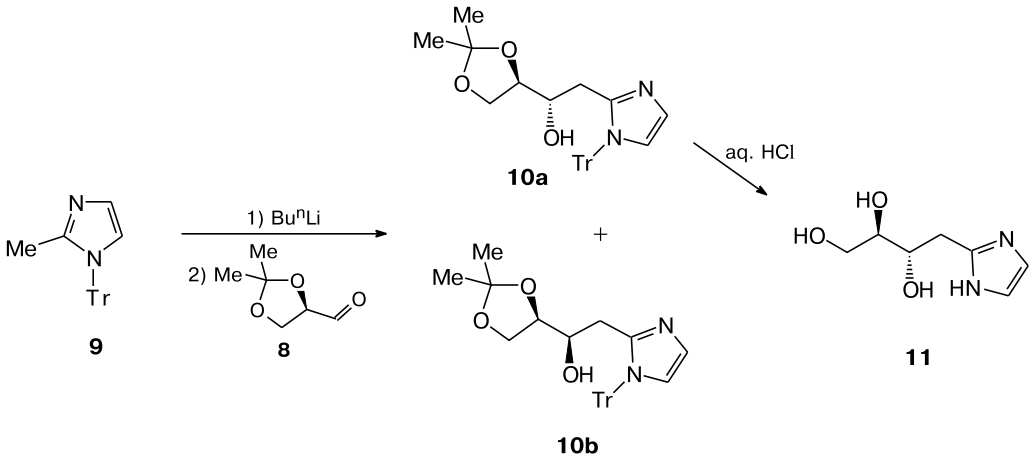
Scheme 2



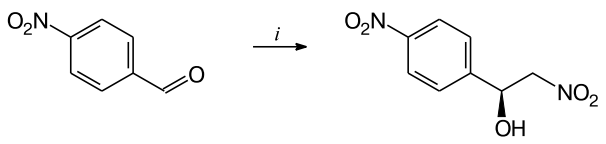
Structures of compounds **4—7**, **10**, and **11** were confirmed by spectral data and elemental analysis. The relative (absolute) configurations of stereoisomers **10** were determined by X-ray diffraction analysis (Table 1). Taking into account the crystallographic data and the known (*R*)-configuration of the isopropylidene moiety, the configuration of secondary hydroxy group of diastereomer **10a** and its product of proteolytic deprotection **11** was assigned as (*S*) (Fig. 1). Consequently, the same center of the minor isomer **10b** has (*R*)-configuration.

Table 1. Crystallographic characteristics, X-ray data collection, and structure refinement statistics R-0458F7 for compound **10a**

Parameter	Value
Molecular formula	$C_{29}H_{30}N_2O_3$
Molecular weight	379.48
T/K	110
Crystal system	Triclinic
Space group	$P\bar{1}$
Z (Z')	4 (2)
a/Å	10.5470(11)
b/Å	11.0226(12)
c/Å	12.1351(13)
α/deg	114.678(2)
β/deg	106.106(2)
γ/deg	92.025(2)
V/Å^3	1213.0(2)
d_{calc}/g cm^{-3}	1.269
μ/cm^{-3}	0.83
F(000)	808
$2\theta_{max}$/deg	58
Number of reflections	
measured	13869
independent (R_{int})	11984 (0.0459)
with $I > 2\sigma(I)$	10703
Number of refined parameters	634
R_1	0.0532
wR_2	0.1232
GOOF	1.048
Residual electron density, e Å^{-3} (d_{max}/d_{min})	0.339/−0.508

The ability of compounds **4—6** and **10—11** to bind the Cu^{2+} is indicated by the formation of dark blue solutions after short sonication (10 min) of these substances with a small excess of $Cu(OAc)_2 \cdot 2H_2O$ in anhydrous Pr^{i}OH. During this treatment, $Cu(OAc)_2 \cdot 2H_2O$ completely dissolves.* When modified polystyrene **7** is used, crystals of copper acetate dissolve and the polymer particles change their color to blue. Adding 4-nitrobenzaldehyde **12** (~10 mmol equiv.) and nitromethane (~100 mmol equiv.) into these solutions (or suspension in the case of polymer **7**) would induce nitroaldol condensation of the component to give non-racemic nitroalcohol **13** (Scheme 3). The yields and enantiomeric excesses of the reaction products are summarized in Table 2.

Scheme 3



i. **4—6**, **10**, **11**, $Cu(OAc)_2 \cdot 2H_2O$, $MeNO_2$, Pr^{i}OH, ~20 °C.

In summary, the obtained results (see Table 2) indicate that the more bulky chiral diphenylprolinol residue (L, **4—6**) exerts greater pronounced stereodifferentiation effect than the more conformationally mobile chiral moieties of ligands **10** and **11**. The size of the substituents more remote from the chiral centers affects the enanti-

* In the absence of compounds **4—6**, **10** and **11**, $Cu(OAc)_2 \cdot 2H_2O$ is virtually insoluble in Pr^{i}OH.

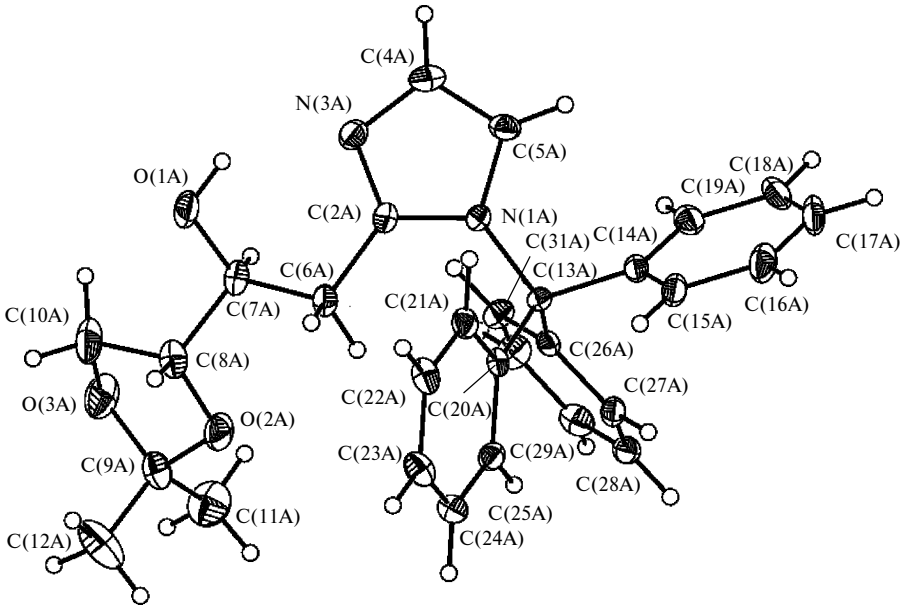


Fig. 1. Geometry of one of the independent molecules of compound **10a**. Nonhydrogen atoms are depicted at the 50% probability level.

Table 2. A comparison of nitroaldol condensation of nitromethane and 4-nitrobenzaldehyde in the presence of complexes $Cu^{II} \cdot L$

Entry	L[a]	τ/h[b]	Y_{13} (%)[c]	*ee* (%)[d]
1	**4**	8	91	72 (*R*)
2	**5**	24	90	64 (*R*)
3	**6**	20	87	57 (*R*)
4	**7**	8	99	29 (*R*)
5	**10a**	90	70	4 (*R*)
6	**10b**	90	71	~0
7	**11**	60	85	2 (*S*)

[a] L is ligand.
[b] τ is the reaction time.
[c] *Y* is the yield of nitro alcohol **13**.
[d] Enantiomeric excess; the configuration of the major isomer is given in the parenthesis.

oselectivity of the reaction in lesser extent (*cf.* entries *1* and *2*).

Experimental

Melting points were measured on a Kofler apparatus. IR spectra were recorded with a Bruker ALPHA-T spectrophotometer. ^1H and ^{13}C NMR spectra were run on Bruker AC-200 and Bruker AM-300 instruments at 298 K in $CDCl_3$ (if not indicated otherwise); the chemical shifts are given in the δ scale relative to the residual solvent signal (δ_H 7.27 and δ_C 77.0). High resolution electrospray ionization (ESI) mass spectra were recorded with a Bruker micrOTOF II mass spectrometer at capillary voltage of 4.5 kV using direct inlet (*via* a syringe pump) with MeOH as a solvent (a flow rate of 3 μL min^{-1}) operating on a positive ion mode (the mass range 500—3000 Da), rate of the nebulizer gas (nitrogen) flow was 4 L min^{-1} (180 °C). Optical rotation was measured on a Jasco DIP polarimeter. X-ray diffraction study of compound **10a** were performed with a Bruker SMART APEX2 diffractometer (Mo-Kα irradiation, graphite monochromator, ω scan mode). The structure was solved by direct method and refined anisotropically by full matrix least squares on F^2_{hkl}. Hydrogen atoms of the hydroxy groups and solvate water molecule were localized by a difference Fourier synthesis, all other hydrogen atoms were placed in calculated positions and refined using a riding model. Main crystallographic data and refinement parameters are given in Table 1. All calculations were performed with a SHELXTL PLUS program package[3].

Column chromatography was performed on Silica gel 60 (40—60 μm, Fluka) if not stated otherwise. The R_f values were measured using the precoated plates Silufol (Chemapol) and Kieselgel F254 (Fluka). Products of nitroaldol condensation were analyzed by HPLC (UV detection at 250 nm, elution with 10 vol.% of Pr^iOH in hexane, flow rate of 1 mL min^{-1}) with Kromasil 3 CelluCoat chiral stationary phase (a 4.6×150 mm column). The retention times for (*R*)-**13** and (*S*)-**13** are ~12 and ~15 min, respectively (*cf.* Ref. 2). Sonication was performed with an ultrasonic bath UZV-1/100-TN. The solvents including petroleum ether (b.p. 40—70 °C) were purified and dried following the standard procedures.

Commercially available (Acros Organics) 95% $NaBH(OAc)_3$, 2-methylimidazole, and Merrifield resin (1.0—1.1 (mmol of Cl) g^{-1}, 200—400 mesh) were used. (*S*)-1,1-Diphenylprolinol **1** (see Ref. 4), (1-trityl-1*H*-imidazol-2-yl)acetaldehyde **2** (see Ref. 5), (2*S*)-1-benzylpirrolidine-2-carbaldehyde **3** (see Ref. 6), and (4*R*)-2,2-dimethyl-1,3-dioxolane-4-carbaldehyde **8** (see Ref. 7) were synthesized by the known procedures. 2-Methyl-1-trityl-1*H*-imidazole **9** was synthesized similarly to 4-methyl derivative following the earlier described procedure.[8]

Diphenyl{(2*S*)-1-[2-(1-trityl-1*H*-imidazol-2-yl)-ethyl]pyrrolidin-2-yl}methanol (4). To a stirred solution of amino alcohol **1** (1.1 g, 4.34 mmol) and aldehyde **2** (1.8 g, 5.11 mmol) in $ClCH_2CH_2Cl$ (20 mL), 95% $NaBH(OAc)_3$ (1.5 g, 6.72 mmol) was added at 20 °C under argon. The reaction mixture was stirred at 20 °C for 5 h, treated with 1 *M* NaOH (30 mL), and extracted with Bu^{t}OMe. The organic layer was washed with brine, dried with Na_2SO_4, and solvent was removed *in vacuo*. Recrystallization from MeOH afforded compound **4** in the yield of 1.87 g (73%), coloress crystals, m.p. 183—185 °C, $[\alpha]_D^{25}$ +2.4 (*c* 1.00, CH_2Cl_2). Found (%): C, 83.45; H, 6.67; N, 7.28. $C_{41}H_{39}N_3O$. Calculated (%): C, 83.50; H, 6.67; N, 7.12. IR ($CHCl_3$), ν/cm^{-1}: 667, 703, 782, 1002, 1034, 1128, 1209, 1448, 1493, 2807, 2874, 2967, 3011, 3063, 3190, 3602, 3672. ^{1}H NMR (300.13 MHz), δ: 1.12—1.86 (m, 6 H, 3 CH_2); 1.94, 2.31, 2.59, 2.76 (all m, 1 H each, 2 CH_2N); 3.71 (m, 1 H, HCN); 6.87 (br.s, 1 H, OH); 6.70, 6.96 (both br.s, 1 H each, HC=); 7.03—7.60 (m, 25 H, H_{Ar}).

{(2*S*)-1-[2-(1*H*-Imidazol-2-yl)ethyl]pyrrolidin-2-yl}-(diphenyl)methanol (5). A solution of compound **4** (200 mg, 0.34 mmol) in 1 *M* HCl (5 mL) was heated at 80 °C for 4 h. The precipitate (80 mg) was filtered off and washed with water. The filtrate was concentrated *in vacuo* (2 Torr, 45 °C). The residue was dried under vacuum (40 °C, 2 Torr) for 1 h and dissolved in MeOH (3 mL). The solution was treated with K_2CO_3 (200 mg, 1.45 mmol) and the mixture was stirred for 2 h. The reaction mixture was diluted with AcOEt (5 mL), filtered through a short SiO_2 layer, and the SiO_2 pad was washed with AcOEt—MeOH, 1 : 1. Removal of the solvent afforded compound **5** in the yield of 95 mg (81%), colorless crystals, m.p. 204—205 °C (AcOEt—MeOH), R_f 0.68 (AcOEt—MeOH, 2 : 1), $[\alpha]_D^{22}$ +100.5 (*c* 1.00, MeOH). MS (ESI), *m/z*: found 348.2072 and 370.1887. Calculated for $C_{29}H_{34}N_2O$, $[M + H]^+$, 348.2070; $[M + Na]^+$ 370.1890. IR (KBr), ν/cm^{-1}: 703, 752, 767, 873, 1032, 1130, 1164, 1303, 1360, 1447, 1589, 2681, 2812, 2894, 2961, 3030, 3061, 3377, 3443. ^{1}H NMR (300.13 MHz), δ: 1.59—2.02 (m, 4 H, 2 CH_2); 2.28—2.80, 3.26 (m, 6 H, 2 CH_2N, CH_2C=); 3.94 (dd, 1 H, HCN, *J* = 9.0 Hz, *J* = 4.1 Hz); 5.34 (br.s, 1 H, OH); 6.87 (br.s, 2 H, 2 HC=); 7.07—7.81 (m, 15 H, H_{Ar}).

((2*S*)-1-{[(2*S*)-1-Benzylpyrrolidin-2-yl]methyl}pyrrolidin-2-yl)(diphenyl)methanol (6). To a stirred solution of amino alcohol **1** (253 mg, 1.03 mmol) and aldehyde **3** (230 mg, 1.22 mmol) in $ClCH_2CH_2Cl$ (4 mL), 95% $NaBH(OAc)_3$ (0.35 g, 1.57 mmol) was added at 20 °C under argon. The reaction mixture was stirred at 20 °C for 3 h, poured into 1 *M* NaOH (10 mL), and extracted with Bu^{t}OMe. The organic layer was separated, washed with brine, dried with Na_2SO_4, and the solvent was removed *in vacuo*. Column chromatography on Al_2O_3 (5/40 μm, L, neutral, from CHEMAPOL) using elution with petroleum ether—Bu^{t}OMe (9 : 1) afforded compound **6** in the yield of 290 mg (68%), oil, R_f 0.75 (petroleum ether—Bu^{t}OMe 2 : 1, Aluminumoxide 60 Typ E, Merck), $[\alpha]_D^{25}$ –92.1 (*c* 1.00, CH_2Cl_2). MS (ESI), *m/z*: found 427.2742. Calculated for $C_{29}H_{34}N_2O$, $[M + H]^+$, 427.2744. IR (KBr), ν/cm^{-1}: 699, 704, 746, 1032, 1117, 1372, 1450, 1493, 1598, 2800, 2871, 2921, 2963, 3027, 3060, 3330. ^{1}H NMR (300.13 MHz), δ: 1.18—1.91 (m, 8 H, 4 CH_2); 2.00, 2.13 (both m, 1 H each, CH_2N); 2.30 (m, 4 H, 2 CH_2N); 2.52, 2.70 (both m, 1 H each, CH_2N); 3.19 (m, 1 H, HCN); 3.37 (d, 1 H, H´CPh, *J* = = 13.1 Hz); 3.77 (d, 1 H, HCPh, *J* = 13.1 Hz); 3.88 (dd, 1 H, NCH—CO, *J* = 8.7 Hz, *J* = 4.2 Hz); 4.88 (br.s, 1 H, OH); 7.15, 7.26, 7.54, 7.56 (all m, 15 H, H_{Ar}). ^{13}C NMR (75.03 MHz), δ: 22.8, 24.5, 28.9, 29.3 (4 CH_2); 54.3, 55.9, 59.5, 61.8 (4 CH_2N); 62.5, 62.6 (2 CHN); 71.8 (CHO); 125.4, 125.9, 126.0, 126.2, 126.8, 127.9, 128.1, 128.9, 147.99 (C_{Ar}).

Modified polymer (7). A suspension of Merrifield resin (1.02 g, 1.02 equiv.), compound **5** (63 mg, 1.8 mmoL), and NaI (10 mg, 0.07 mmol) in MeCN (6 mL) was stirred at 80 °C for 60 h under argon. The resin was collected by filtration and successively washed with MeCN (10 mL), MeCN—Et_3N (9 : 1, 2×10 mL), EtOH—Et_3N (9 : 1, 2×10 mL), EtOH (2×10 mL), and CH_2Cl_2 (2×10 mL). Drying the resin at 80 °C under vacuum (2 Torr) afforded polymer **7** in the yield of 1.32 g (96%). Found (%): N, 3.71. Calculated (%): 4.20. IR (KBr), ν/cm^{-1}: 744, 906, 1027, 1066, 1154, 1180, 1267, 1363, 1448, 1491, 1601, 2852, 2922, 3024, 3082, 3423.

(1*S*)-1-[(4*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl]-2-(1-trityl-1*H*-imidazol-2-yl)ethanol (10a) and (1*R*)-1-[(4*R*)-2,2-dimethyl-1,3-dioxolan-4-yl]-2-(1-trityl-1*H*-imidazol-2-yl)ethanol (10b). To a stirred solution of 2-methylimidazole derivative **9** (5.3 g, 13.3 mmol) in THF (100 mL) chilled to –65 °C, 1.75 *M* BuLi in hexane (10 mL, 17.5 mmol) was added dropwise over 10 min under argon. The brown solution was stirred at –65 °C for 30 min, when a solution of aldehyde **8** (2.4 g, 18.3 mmol) in THF (10 mL) was added within 5 min. After warming up to –30 °C, the reaction mixture was neutralized by adding 5% aqueous citric acid (50 mL). The aqueous layer was separated, extracted with Bu^{t}OMe, the organic phase was washed with brine, dried with Na_2SO_4, and the solvent was removed *in vacuo*. After column chromatography on SiO_2 (70 g) using gradient elution from petroleum ether to EtOAc, the following compounds were isolated, in order of elution: isomer **10a** (2.12 g, 35%) and isomer **10b** (0.6 g, 10%).

Alcohol **10a**. R_f 0.89 (EtOAc), colorless crystals, m.p. 133—135 °C (diethyl ether—hexane), $[\alpha]_D^{25}$ +4.34 (*c* 1.00, CH_2Cl_2). MS (ESI), *m/z*: found 477.2145. Calculated for $C_{29}H_{30}N_2O_3$, $[M + Na]^+$, 477.2149. IR (KBr), ν/cm^{-1}: 640, 703, 747, 758, 858, 1059, 1134, 1171, 1209, 1267, 1367, 1406, 1447, 1492, 2820, 2873, 2901, 2934, 2983, 3056, 3205, 3301, 3321, 3503. ^{1}H NMR (200.13 MHz), δ: 1.14, 1.22 (both s, 3 H each, 2 Me); 1.96 (dd, 1 H, HCC=, *J* = 16.4 Hz, *J* = 9.2 Hz); 2.19 (dd, 1 H, HCC=, *J* = = 16.4 Hz, *J* = 2.5 Hz); 3.45 (ddd, 1 H, HCOH, *J* = 9.2 Hz, *J* = = 6.5 Hz, *J* = 2.5 Hz); 3.67 (dd, 1 H, HCCO, *J* = 7.8 Hz, *J* = 5.1 Hz); 3.79 (m, 1 H, HCO); 3.80 (dd, 1 H, H´CCO, *J* = 7.8 Hz, *J* = 6.1 Hz); 6.75 (d, 1 H, HC=, *J* = 1.5 Hz); 6.93 (d, 1 H, HC=, *J* = 1.5 Hz); 7.13 (m, 5 H, H_{Ar}); 7.34 (m, 10 H, H_{Ar}).

Alcohol **10b**. R_f 0.73 (EtOAc), colorless crystals, m.p. 177—179 °C (diethyl ether—hexane), $[\alpha]_D^{25}$ –2.96 (*c* 1.00, CH_2Cl_2). MS (ESI), *m/z*: found 477.2150. Calculated for $C_{29}H_{30}N_2O_3$, $[M + H]^+$, 477.2145. IR (KBr), ν/cm^{-1}: 640, 704, 752, 859, 880, 1074, 1133, 1231, 1378, 1458, 1492, 2871, 2907, 2934, 3058, 3280. ^{1}H NMR (200.13 MHz), δ: 1.19, 1.25 (both s, 3 H each, 2 Me); 1.95 (m, 2 H, H_2CC=); 3.22 (dd, 1 H, HCO, *J* = 8.0 Hz, *J* = 7.0 Hz); 3.48 (dd, 1 H, HCCO, *J* = 12.2 Hz, *J* = 6.0 Hz); 3.60 (m, 1 H, HCO); 3.82 (dd, 1 H, H´CCO, *J* = 12.2 Hz, *J* = = 6.1 Hz); 4.97 (br.s, 1 H, OH); 6.75 (d, 1 H, HC=, *J* = 1.3 Hz); 6.95 (d, 1 H, H´C=, *J* = 1.3 Hz); 7.13 (m, 5 H, H_{Ar}); 7.35 (m, 10 H, H_{Ar}).

(2*R*,3*S*)-4-(1*H*-Imidazol-2-yl)butane-1,2,3-triol (11). A solution of compound **10a** (2.78 g, 6.14 mmol) in 1 *M* HCl (50 mL) was heated at 80 °C for 4 h. After cooling to 20 °C, the precipitate was filtered off and washed with water. The filtrate was concentrated *in vacuo* (2 Torr, 50 °C). The residue was dried *in vacuo* (2 Torr, 40 °C, 1 h), dissolved in MeOH (30 mL) fol-

lowed by addition of K_2CO_3 (2.49 g, 18 mmol). The reaction mixture was stirred at 20 °C for 1 h, diluted with AcOEt (30 mL), and filtered through a short SiO_2 layer (elution with AcOEt—MeOH (1 : 1)). Removal of the solvent *in vacuo* and silica gel column chromatography of the residue (gradient elution from $CHCl_3$—EtOH (1 : 1) to EtOH) afforded triol **11** in the yield of 0.7 g (66%), resinous substance, R_f 0.68 (EtOAc—MeOH, 2 : 1), $[\alpha]_D^{22}$ –23.65 (c 1.00, MeOH). MS (ESI), *m/z*: found 173.0923, calculated for $C_7H_{12}N_2O_3$, $[M + H]^+$, 173.0921. ^{1}H NMR (200.13 MHz), δ: 2.65 (dd, 1 H, HCC=, J = 15.0 Hz, J = 8.6 Hz); 2.95 (dd, 1 H, H´CC=, J = 15.0 Hz, J = 3.5 Hz); 3.24—3.81 (m, 4 H, HCO); 6.39 (br.s, 1 H, OH); 6.90 (br.d, 2 H, HC=, J = 1.5 Hz).

Nitroaldol condensation. ***A.*** A mixture of a ligand (0.10 mmol), $Cu(OAc)_2 \cdot 2H_2O$ (21 mg, 0.11 mmol), and anhydrous Pr^iOH (1.5 mL) was sonicated for 10 min to give dark blue solution. Then 4-nitrobenzaldehyde **12** (152 mg, 1.0 mmol) and $MeNO_2$ (610 mg, 10 mmol) were added. The reaction mixture was maintained at 20 °C for the time specified in Table 2 until complete consumption of aldehyde **12** (TLC monitoring), then the solvent was removed *in vacuo*. Silica gel column chromatography of the residue (elution with $CHCl_3$) afforded compound **13**.

B. A mixture of polymer **7** (129 mg, ~0.1 equiv., ~10 mol.%), $Cu(OAc)_2 \cdot 2H_2O$ (22 mg, 0.11 mmol), and Pr^iOH (1.5 mL) was sonicated for 10 min and the resulting colored suspension was treated with $MeNO_2$ (610 mg, 10 mmol, 0.54 mL) and 4-nitrobenzaldehyde (151 mg, 1 mmol). The reaction mixture was stirred for 8 h until complete consumption of the starting aldehyde (TLC monitoring). The resin was filtered off, washed with $CHCl_3$, and the solvent was removed *in vacuo*. Silica gel column chromatography of the residue (elution with $CHCl_3$) afforded nitroalcohol **13** in the yield of 210 mg (85%).

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