E. BENEDETTI, N. DUCHEMIN, L. BETHGE, S. VONHOFF, S. KLUSSMANN, J.-J. VASSEUR, J. COSSY, M. SMIETANA,* S. ARSENIYADIS* (NOXXON PHARMA AG, BERLIN, GERMANY UNIVERSITÉS MONTPELLIER AND PSL RESEARCH UNIVERSITY, PARIS, FRANCE) DNA-Cellulose: An Economical, Fully Recyclable and Highly Effective Chiral Biomaterial for Asymmetric Catalysis Chem. Commun. 2015, 51, 6076-6079.

A Cellulose-Supported DNA-Based Ligand for **Asymmetric Catalysis**

$$R^{1} \xrightarrow{\mathsf{N}} + R^{3} \xrightarrow{\mathsf{N}} + R^{2} \xrightarrow{\mathsf{N}} \times \mathbb{R}^{2}$$

$$R^{2} \xrightarrow{\mathsf{N}} \times \mathbb{R}^{2}$$

$$CS\text{-}ct\text{-}DNA \\ \mathsf{MOPS} (\mathsf{pH} 6.5) \\ \mathsf{MeCN} \\ \mathsf{5} \, {}^{\circ}\mathsf{C}, \mathsf{3} \, \mathsf{d}$$

$$R^{2} \xrightarrow{\mathsf{N}} \times \mathbb{R}^{2}$$

$$R^{3} \xrightarrow{\mathsf{N}} \times \mathbb{R}^{2}$$

$$R^{3} \xrightarrow{\mathsf{N}} \times \mathbb{R}^{2}$$

$$R^{4} \xrightarrow{\mathsf{N}} \times \mathbb{R}^{2}$$

$$R^{3} \xrightarrow{\mathsf{N}} \times \mathbb{R}^{2}$$

 $R^1 = Me, R^3 = OMe > 99\%$ conversion, 81% ee (A)

 $R^1 = Me, R^3 = CI > 99\%$ conversion, 73% ee

 R^1 = Me, R^3 = Br 96% conversion, 66% ee

 $R^1 = n$ -Pr, $R^3 = OMe > 99\%$ conversion, 83% ee

 $R^1 = n$ -Pent, $R^3 = OMe > 99\%$ conversion, 73% ee

X = H >99% conversion, 62% ee X = OMe 80% conversion, 54% ee

X = CI >99% conversion, 50% ee

R¹ = Me 34% conversion, 78% ee $R^1 = C_6H_5 > 99\%$ conversion, 76% ee $R^1 = 2-BrC_6H_4$ 25% conversion, 65% ee

89% ee

92% conversion 14% conversion 97% ee

>99% conversion 81% ee

96% ee

68% conversion 28% conversion 93% ee

Significance: Copper-catalyzed asymmetric Friedel-Crafts alkylations (eq. 1) and Michael additions (eq. 2) proceeded in the presence of cellulose-supported calf thymus DNA and 4,4'-dimethyl-2,2'-bipyridine (dmbpy) to give the corresponding alkylation products with up to >99% conversion and up to 97% ee.

 $\textbf{SYNFACTS Contributors:} \ Yasuhiro \ Uozumi, \ Kotaro \ Yamamura$ Synfacts 2015, 11(7), 0773 Published online: 17.06.2015 DOI: 10.1055/s-0034-1380997; Reg-No.: Y06715SF

Comment: In the formation of compound A, the catalyst was recovered and reused nine times without adding any copper or dmbpy. Compound A was also prepared in 96% conversion and up to 80% ee by a continuous-flow process using the DNA-based catalyst packed in a medium-pressure liquid chromatography cartridge (residence time: 38 min, room temperature).

Category

Polymer-Supported Synthesis

Key words

DNA

asymmetric catalysis

Friedel-Crafts alkylation

Michael addition

copper

