



Palladium-catalyzed Hydroarylation of Bicyclic Alkenes: A Polymer-supported Approach II

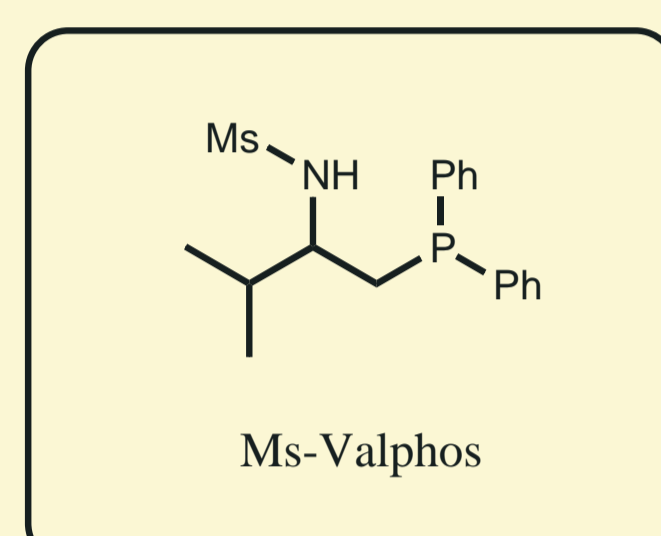
Carmine Raffa and Dieter E. Kaufmann*

Institut für Organische Chemie, Technische Universität Clausthal, D-38678 Clausthal-Zellerfeld, Germany

Introduction

An important challenge in contemporary organic chemistry is the design of new ligands for different transition metal-supported C-C-coupling reactions^[1]. Especially the design of new P-N-ligands for the palladium-catalyzed hydroarylation of bicyclic alkenes, leading to *Epibatidine*-like alkaloids, is still of great interest^[2]. *Ms-Valphos*, introduced by *Achiwa* in 1992, is one of the most powerful P-N-ligand in this field^[3]. As we have recently shown, it can be successfully used with several bicyclic substrates, leading to excellent chemical yields and enantioselectivities^[4].

Nevertheless, these soluble Pd complexes show many disadvantages concerning cost and reuse and in addition to the separation problems, deactivation of the homogenous catalysts by formation of less active species. To overcome these problems, we have chosen to prepare a system where the chiral (*L*)-*Valphos* ligand is attached via a structurally stable linker to a polystyrene support^[5].

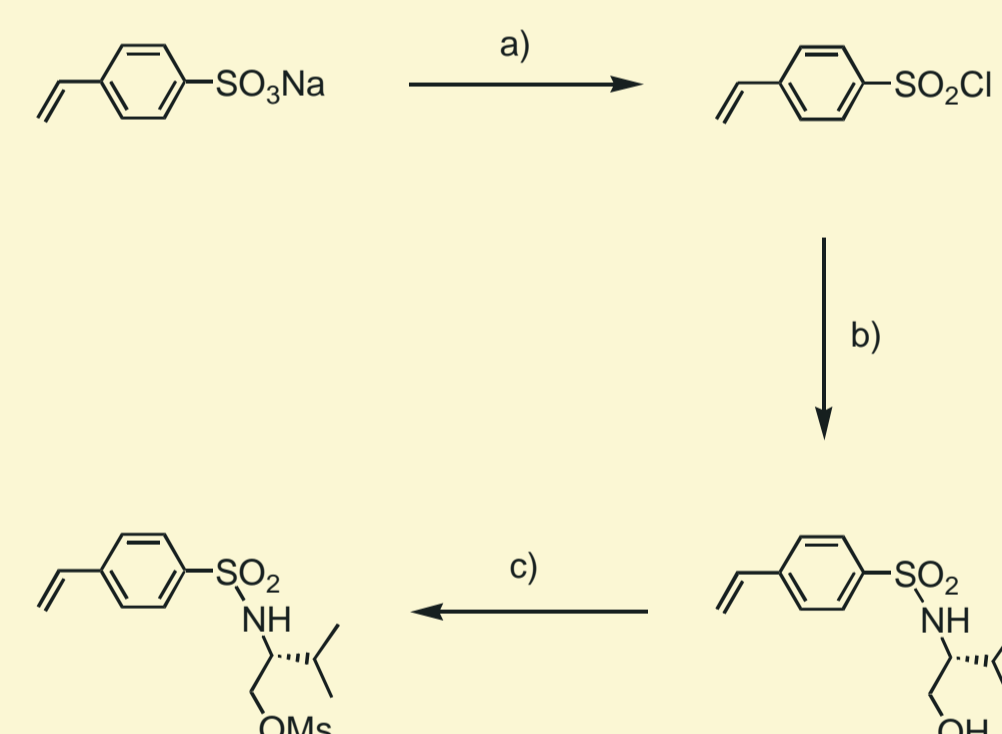


Approach

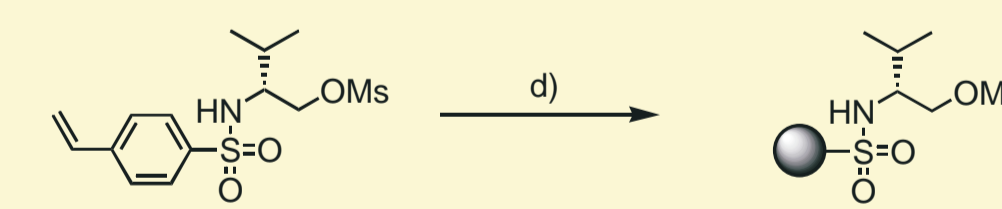
In order to find a simple and effective route to design a polymer-supported (*L*)-*Valphos*-analogue structure we have chosen the present synthetic approach, consisting of four main steps.

1. Synthesis of the monomer:

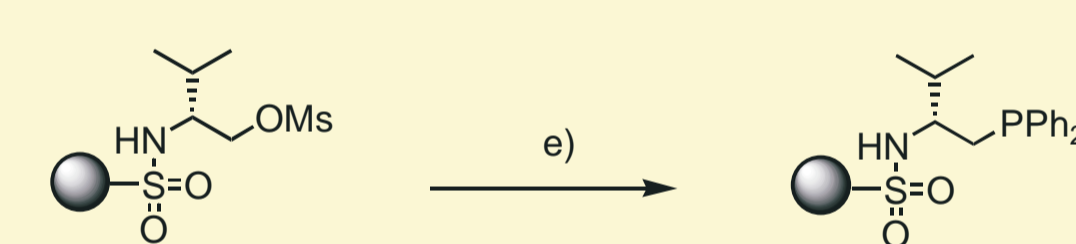
The synthesis of the required monomer follows the strongly modified route of *Ituno* and *Nakahama*.



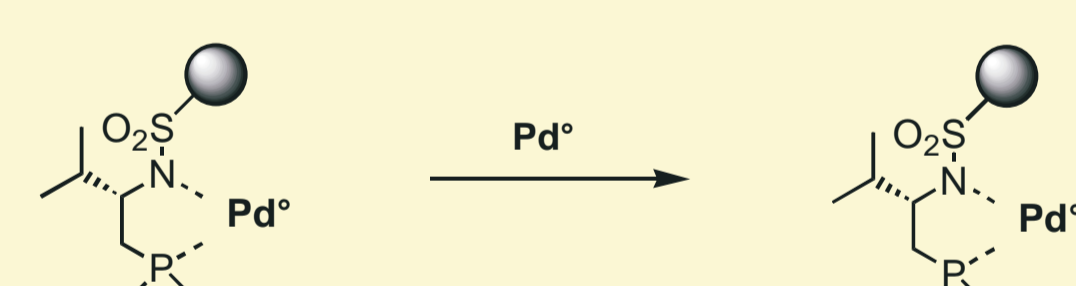
2. Polymerisation reaction:



3. Deprotection and phosphination:

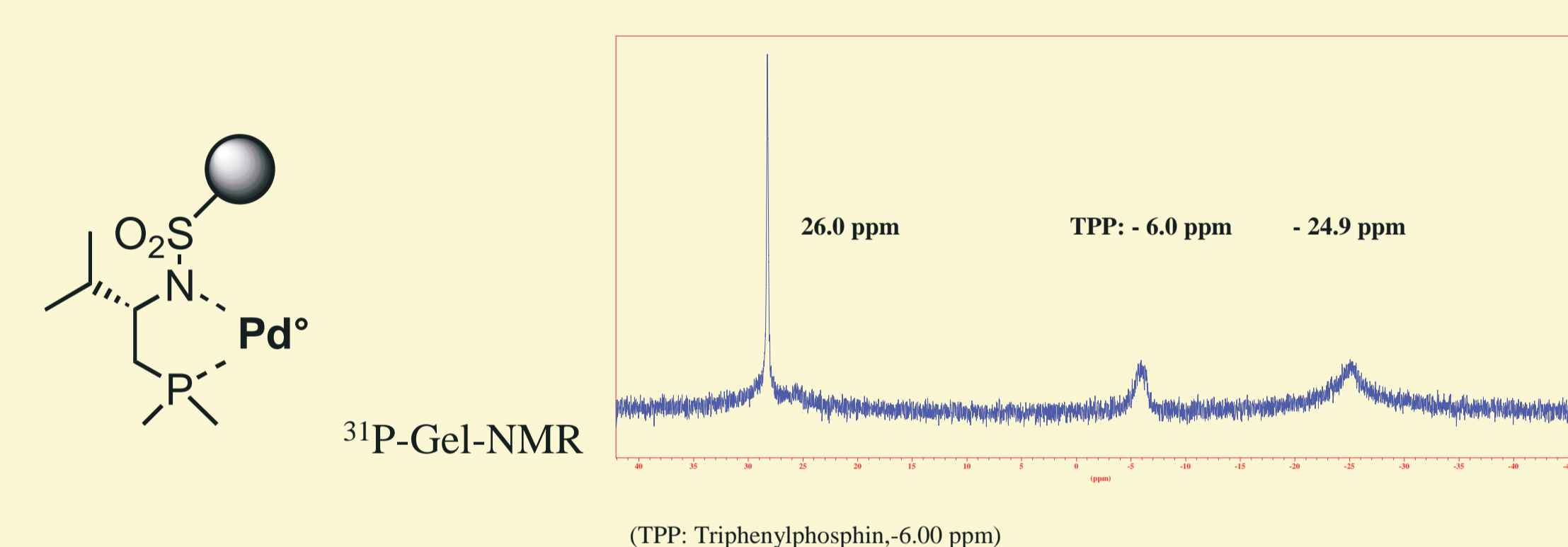
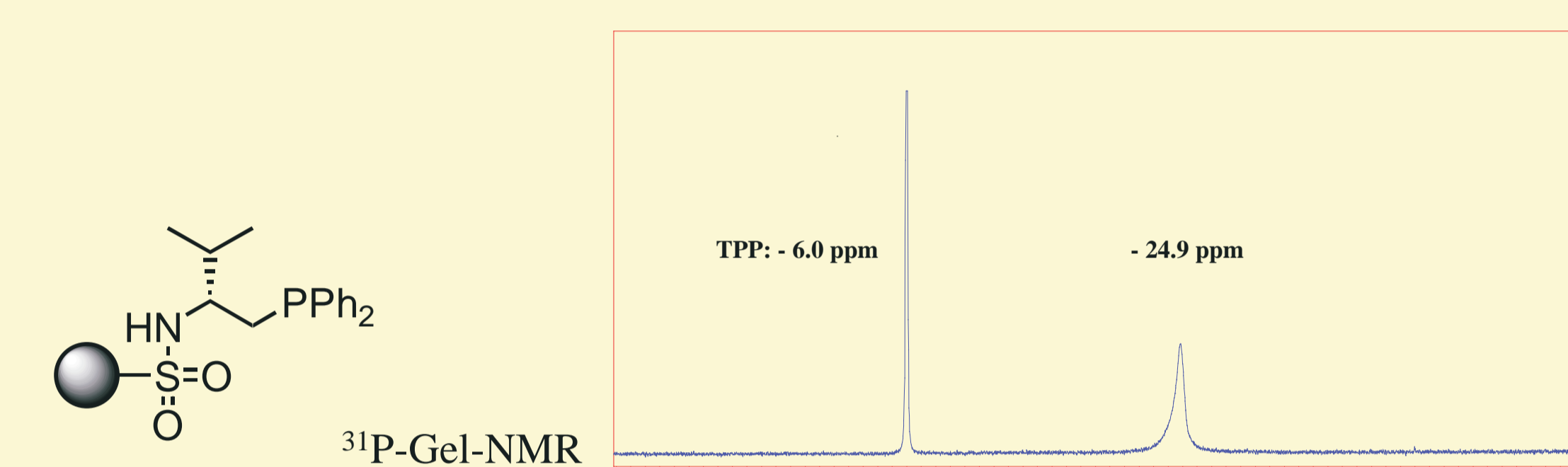
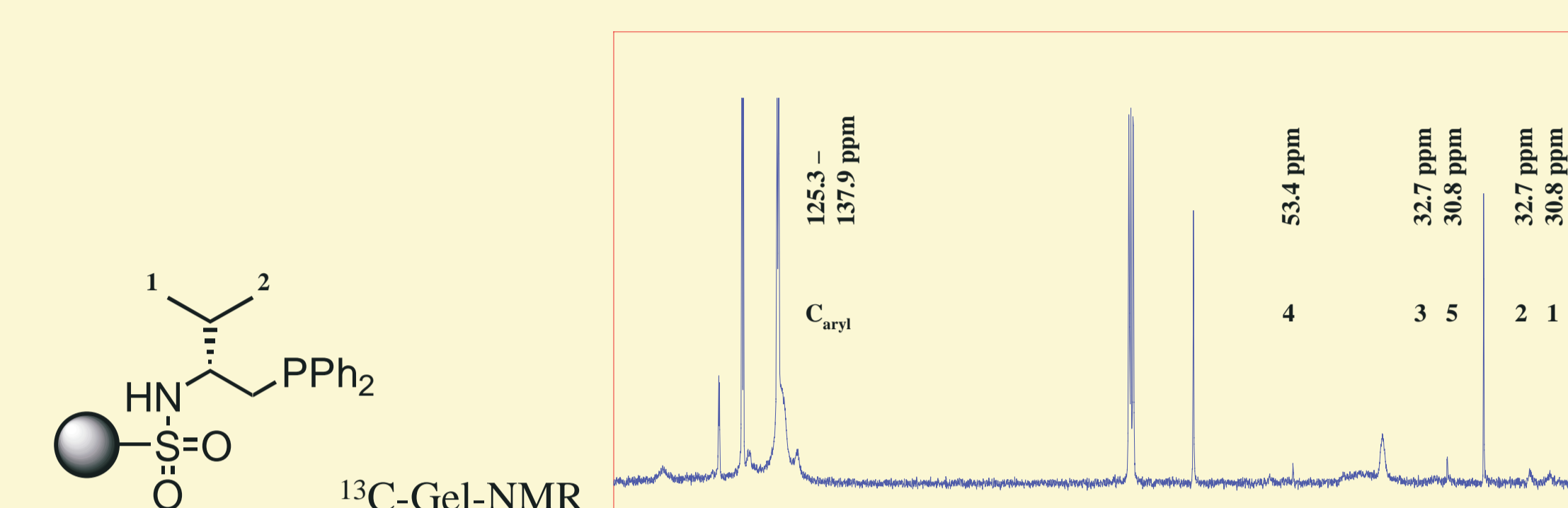


4. Complexation with Pd⁰:

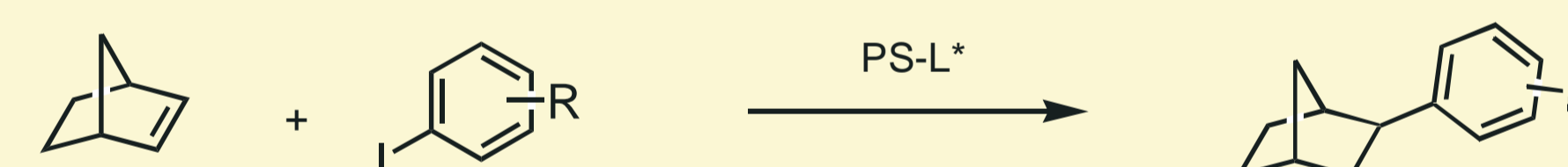


NMR-Data

The structure of the resulting polymer and the progress of complexation with Pd⁰ was verified by ¹³C- and ³¹P-gel-NMR.

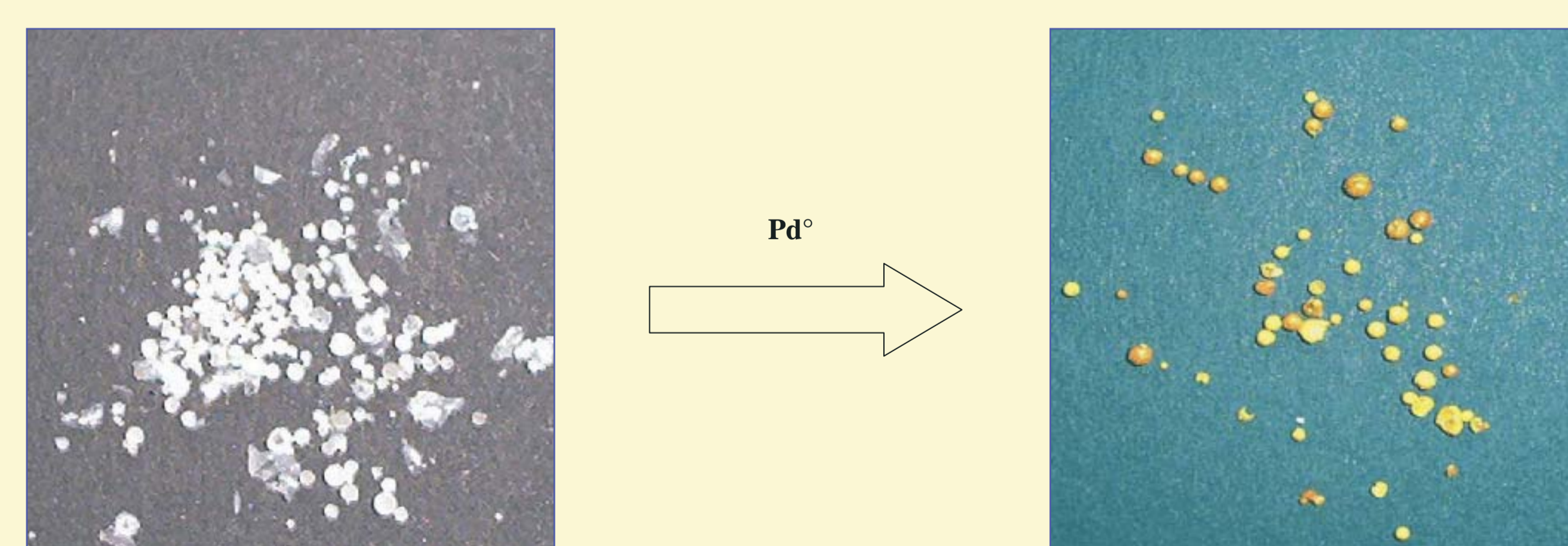


Results



	ArI	Solvent	T (°C)	Yield	ee (%)
1	iodobenzene	DMF	65	55	46
2	iodobenzene	DMF	55	47	46
3	iodobenzene	DMSO	65	45	25
4	iodobenzene	CH ₂ Cl ₂	60	n. r.	-
5	4-iodo-toluene	DMF	65	44	39
6	iodo-m-xylene	DMF	65	45	46
7	4-iodo-anisole	DMF	65	35	49
8	2-chloro-5-iodopyridine	DMF	65	34	51

Color change of polymer during complexation with Pd⁰:



Conclusion:

In the present approach we have prepared a polymer supported *Ms-Valphos* derivative, using an efficient and inexpensive for-step synthetic route. Extensive ¹³C- and ³¹P-Gel-NMR verified the resulting polymer-attached structure. Compared with soluble *Ms-Valphos*, the immobilised ligand leads only to moderate yield in the hydroarylation of *norborene*. Although the reasons for this finding are not clear yet, the color change of polymer during complexation might indicate the parallel formation of other heterogenous achiral structures on the surface of the solid support. Further investigations have to light this fact.

Literature:

- 1) A. Ashimori, L. Overmann, *J. Org. Chem.* **1992**, *57*, 4571-4572; R. C. Larock, P. L. Johnson, *J. Chem. Soc., Chem. Commun.* **1989**, 1368-1370.
- 2) H. Brunner, K. Kramler, *Synthesis* **1991**, 1121-1124; A. Miyashita, H. Takaya, K. Toriumi, T. Ito, R. Noyori, *J. Am. Chem. Soc.* **1980**, *102*, 7932.
- 3) K. Awano, K. Achiwa, *Synlett* **1994**, 291-292; S. Sakuraba, T. Okada, T. Morimoto, K. Achiwa, *Chem. Pharm. Bull.* **1995**, *43*, 927-934.
- 4) A. Otten, J. C. Namyslo, M. Stoermer, D. E. Kaufmann, *Eur. J. Org. Chem.* **1998**, 1997-200; J. C. Namyslo, D. E. Kaufmann, *Synlett* **1999**, 114-116.
- 5) K. Kamahori, S. Tada, K. Ito, S. Ituno, *Tetrahedron Asymmetry*, **1995**, 2547-2555; T. Ishizone, S. Nakahama, *Macromolecules* **1992**, 4480-4847.