

## Repetitive Application of a Fluorous Chiral BINAP–Ru Complex in the Asymmetric Hydrogenation of Olefins

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A trisperfluoroalkylsilyl-modified (S)-BINAP ligand has been prepared and its pertinent Ru complex applied to the asymmetric hydrogenation of olefins. Efficient separation of the Ru catalyst by filtration and its reuse was achieved. Relative

to the untagged complex with a Ru-leaching of 300 ppm, leaching into the product was low (1.6–4.9 ppm).

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### Introduction

The development of improved strategies for the recovery and reuse of catalysts has gained growing attention in recent years and remains an important topic. Many promising approaches are based on biphasic systems in which the catalytic entity is retained in one phase and the substrates and products are preferentially solubilised in the other phase.<sup>[1]</sup> Examples include aqueous–organic biphasic processes,<sup>[2]</sup> catalysis in ionic liquid–organic biphasic systems,<sup>[3]</sup> use of fluorous–organic biphasic systems (FBS)<sup>[4]</sup> and catalytic reactions in supercritical carbon dioxide.<sup>[5]</sup>

In the FBS concept, the catalyst is dissolved in a fluorous solvent and used in combination with an organic solvent containing the substrates. After the reaction, the two phases can be separated; the fluorous layer containing the catalyst can be reused. Perfluoro modifications of the ligands allow solvation of the catalyst in the fluorous phase. Common perfluoro modifications include trisperfluoroalkylsilyl tags, which were introduced by Curran and used extensively in earlier works of Deelman and van Koten.<sup>[6,7]</sup> In recent years, more sophisticated FBS were developed where the fluorous solvent was substituted by fluorous silica gel (FSG); this substitution allows the noncovalent immobilisation of fluorous compounds.<sup>[8,9]</sup>

Chiral BINAP is among the most popular ligands used in catalytic asymmetric reactions, and hence, it finds widespread application in catalytic processes like hydrogenations and C–C and C–N coupling reactions.<sup>[10]</sup> In recent years, a plethora of modified BINAP ligands has been synthesised and evaluated to explore the potential recovery and reuse of this important yet expensive compound in biphasic sys-

tems.<sup>[11]</sup> The paoply of modifications include the introduction of sulfonated phenyl groups as well as phosphonic acid groups into the ligand, rendering the ligand water-soluble and allowing its utilisation in aqueous–organic biphasic systems.<sup>[12]</sup> Phosphonic acid derivatives of BINAP were used for reactions in ionic liquids, as well.<sup>[13]</sup> The appendage of amino functions to the BINAP core was used to tether the ligand covalently to polymeric supports.<sup>[14]</sup> A second application of amino-modified BINAP dealt with the formation of ammonium salts, which could be applied in aqueous systems.<sup>[15]</sup> Amongst the variety of examples for modified BINAP were reports of BINAP ligands bearing perfluoroalkyl tails, which allowed their employment in FBS as well as their use in supercritical carbon dioxide as a reaction medium.<sup>[7,16–18]</sup> However, to the best of our knowledge, there exists no example for the successful recovery and reuse of a perfluorinated BINAP–metal complex. Hope et al.<sup>[18]</sup> have reported the application of a lightly perfluorinated BINAP in the ruthenium-catalysed asymmetric hydrogenation of ketones, where an attempt was made to recover the catalytic entity by filtration through FSG. However, instead of an active Ru complex, only partially oxidised BINAP was recovered, which was used for subsequent runs after the addition of new Ru<sup>II</sup> and formation of the complex.

All perfluoroalkyl-modified BINAP ligands reported to date have displayed a significant sensitivity towards oxidation. The prevention of catalyst degradation, either in liquid–liquid biphasic systems or in systems where the perfluorinated catalyst was filtered through fluorous silica gel, could not be achieved. Thus, in all published examples recovery of the perfluoro-modified compound led, at least partially, to the formation of inactive catalyst.

Herein, we report the use of Ru<sup>II</sup>/perfluorinated BINAP **1** in the asymmetric ruthenium-catalysed hydrogenation of olefins and its successful reuse by means of noncovalent immobilisation on FSG.<sup>[19]</sup> We originally intended to use this methodology to avoid the use of perfluorous solvents,

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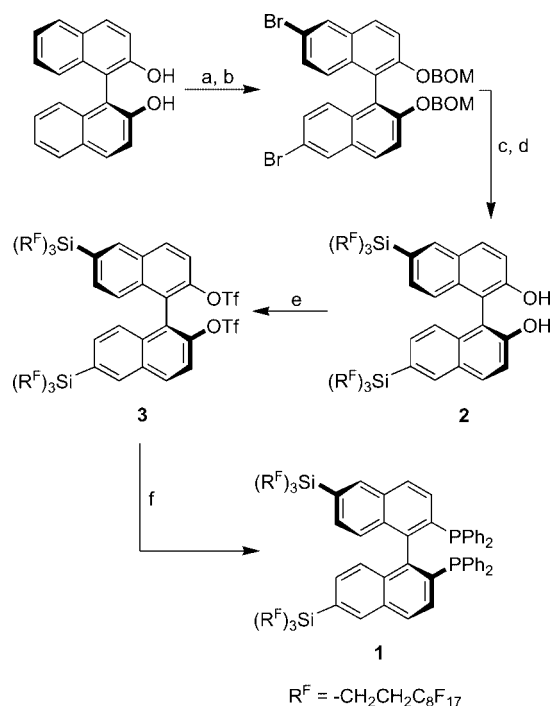
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which are expensive and not benign as far as environmental aspects are concerned. The supported catalyst can be used in organic solvents or water and the filtration of the crude reaction mixture allows its removal and potential reutilisation. This approach was successfully applied in Pd-catalysed C–C coupling reactions as well as metathesis reactions by using a perfluoroalkyl-modified Hoveyda catalyst.<sup>[9,20,21]</sup> A related strategy, where teflon was used as a solid support for the immobilisation of fluoros catalysts was reported by Gladysz.<sup>[22]</sup>

Our current method is performed under a hydrogen atmosphere, and the filtration step under an argon atmosphere, which prevents oxidation of the ligand and allows easy reuse of the Ru/I complex.

## Results and Discussion

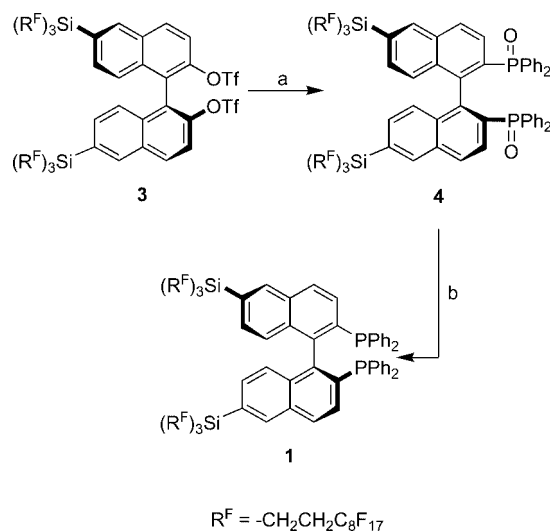
The synthesis of perfluoroalkyl-tagged chiral (*S*)-BINAP **1** was reported previously and is depicted in Scheme 1.<sup>[23]</sup>



Scheme 1. Synthesis of perfluoro-modified BINAP.<sup>[23]</sup> a)  $Br_2$ ,  $CH_2Cl_2$ ,  $-78^\circ C$ , 90–95%. b) NaH, BOM-Cl,  $0^\circ C$ , 99%. c) *t*BuLi, THF,  $-78^\circ C$ ;  $(C_8F_{17}CH_2CH_2)_3SiBr$ , 51–61%. d) HCl, THF,  $\Delta$ , 80–83%. e)  $Tf_2O$ , pyridine, BTF/ $CH_2Cl_2$ , 99%. f) 10%  $[NiCl_2(dppe)]$ ,  $HPPh_2$ , DABCO, BTF/DMF,  $100^\circ C$ , 29–59%.

The synthesis commenced with the bromination and protection of commercially available (*S*)-BINOL, which was followed by attachment of the perfluorosilyl group by bromo–lithium exchange on the BINOL core and reaction with  $(C_8F_{17}CH_2CH_2)_3SiBr$ . Instead of the more commonly applied  $C_6F_{13}$  chain, the trisperfluoroalkyl tag was chosen because of the enhanced fluoros–fluoros interactions that are observed with this tag.<sup>[23]</sup> Subsequent cleavage of the BOM group gave rise to perfluoro-modified BINOL **2**. The hydroxy functions were then transformed into bistriflate

groups, resulting in compound **3**, which was converted into **1** by the nickel-catalysed coupling of **3** with diphenylphosphane in moderate yield. The work up of the last step was rather difficult owing to similar  $R_f$  (retention factor) values of product **1** and  $HPPh_2$ . Hence, we alternatively investigated the synthesis of perfluoro-modified BINAP **1** via BINAP oxide **4**, similar to the route Nakamura chose for the synthesis of his perfluoro-modified BINAP (Scheme 2).<sup>[7,17]</sup>

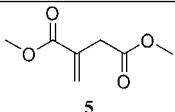
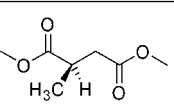
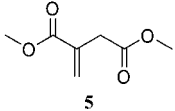
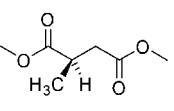
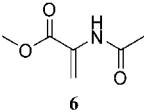
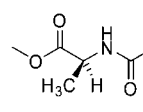
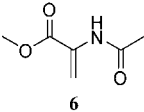
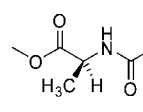
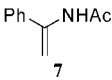
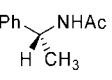
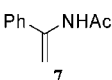
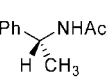


Scheme 2. Alternative route for the synthesis of BINAP **1** via BINAP oxide **4**. a) 10 mol-%  $[NiCl_2(dppe)]$ ,  $HPPh_2$ , DABCO, BTF/DMF,  $100^\circ C$ ; 10 mol-%  $H_2O_2$  69%. b) MeOTf,  $LiAlH_4$ , DME/BTF, 85%.

The purification of BINAP oxide **4** was significantly easier with the use of this strategy relative to that of the original procedure and gave rise to isolated **4** in 69% yield. The reduction was carried out by following the procedure of Imamoto in good yield by using trifluoromethanesulfonic acid methyl ester and  $LiAlH_4$ .<sup>[24]</sup> Interestingly, as also reported by Nakamura et al., the commonly practised reduction method with trichlorosilane did not work.<sup>[7,17]</sup> The overall yield for both transformations from triflate **3** to BINAP **1** was 59%. Despite the lengthening of the synthesis by one reduction step, we favour the latter alternative synthesis because of the easier purification process and ease of handling.

Heavily fluorinated BINAP **1**, which possesses a fluorine content of about 58%, was used in the asymmetric ruthenium-catalysed hydrogenation of olefins and the results were compared with those of the untagged (*S*)-BINAP to evaluate the influence of the perfluoroalkyl groups on the reaction and to investigate the potential reuse of the perfluorinated catalyst (Table 1). For this purpose, we utilised a mixture of  $[RuCl_2(benzene)]_2$  and BINAP **1** as an in situ prepared catalyst. Because we wanted to avoid the use of perfluorinated solvents, we suspended the FSG (prepared from silica gel with a 500 Å pore-size and bearing  $-CH_2CH_2C_6F_{13}$  tails)<sup>[19]</sup> in a mixture of methanol and BTF (1:1) containing the in situ formed catalyst as well as the substrate prior to the reaction. Upon completion of the re-

Table 1. Comparison of the hydrogenations with (*S*)-BINAP and perfluoro (*S*)-BINAP **1**.

Entry <sup>[a]</sup>	Substrate	Product	Ligand	S/C <sup>[c]</sup>	<i>t</i> [h]	Run	Conv. <sup>[d]</sup> [%]	<i>ee</i> [%]
1			( <i>S</i> )-BINAP	1000	2.5	–	95	93
2			<b>1</b>	1000	6	1 2 3 4 5	95 98 97 80 54	95 95 94 90 60
3			( <i>S</i> )-BINAP	1000	2	–	98	76
4			<b>1</b>	1000	6	1 2 3 4 5	96 96 96 85 44	90 89 88 84 78
5 <sup>[b]</sup>			( <i>S</i> )-BINAP	500	8	–	94	30
6 <sup>[b]</sup>			<b>1</b>	500	8	1 2 3 4 5	64 65 60 27 4	44 43 41 n.d. n.d.

[a] Conditions for reactions with (*S*)-BINAP: 2.6 μmol [RuCl<sub>2</sub>(benzene)]<sub>2</sub>, 5.2 μmol (*S*)-BINAP, 5 mL MeOH, 10 bar H<sub>2</sub>, 60 °C; conditions for reactions with perfluoro BINAP **1**: 2.6 μmol [RuCl<sub>2</sub>(benzene)]<sub>2</sub>, 5.2 μmol **1**, 500 mg FSG, 2.5 mL MeOH, 2.5 mL BTF, 10 bar H<sub>2</sub>, 60 °C. [b] With 30 bar H<sub>2</sub>. [c] Ratio: substrate/catalyst. [d] Average of two experiments as determined by <sup>1</sup>H NMR spectroscopy.

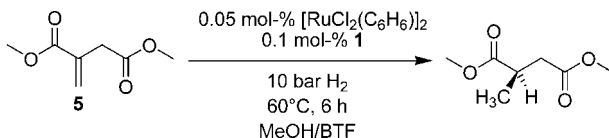
action, the solvent was carefully removed. This is in contrast to our earlier applications of this technique where on fluorosilica gel immobilised Pd<sup>II</sup>-phosphane or Ru-metathesis precatalysts, which are both air-stable, were suspended in the reaction mixture. The new procedure prevents air contact of the sensitive Ru-**1** catalyst and hence its oxidation.

Washing the residue with MeOH/H<sub>2</sub>O (80:20) allowed isolation of the products, whereas the fluorosilica catalyst was retained on the FSG and could be used in subsequent experiments.

As can be deduced from Table 1, ligand **1** shows a lower activity than conventional (*S*)-BINAP, but at the same time exhibits a slightly higher enantiomeric induction. More importantly, the perfluorinated catalyst could be reused several times. Table 1, Entries 2 and 4 illustrate that the activity of the catalyst could be maintained for three runs, but the activity decreases during subsequent runs. A common problem in the application of Ru complexes as catalysts is the leaching of ruthenium into the product. In our experiments, the leaching, which was determined by ruthenium elemental analysis for the hydrogenation of **5**, was very low (run 1: 4.9 ppm, run 2: 2.0 ppm, run 3: 1.6 ppm). For the first run, this corresponds to a 1.5% leaching of the total amount of ruthenium. A ruthenium content of more than 300 ppm for

reactions with unmodified BINAP and without FSG or silica underlines the strong retention of the ruthenium complex on FSG. Hence, the eventual decline of activity can be attributed to catalyst degradation and not to a loss of ruthenium. In contrast to reports by Hope where filtration of a perfluorinated catalyst over FSG led to destruction of the complex and isolation of at least partially oxidised ligand, this could be largely prevented by employing our methodology in which the whole complex was reisolated.<sup>[16]</sup> This was evident from the high *ee* values obtained for the second and third runs. We also performed the hydrogenation of **5** with the Ru-**1** catalyst under noninert conditions during the washing procedure. This led to a dramatic decrease in the activity of the catalyst as well as a significant drop in *ee* (12%) in the second run, which can be due to oxidation of the air-sensitive catalyst.

The addition of *α,α,α*-trifluorotoluene (BTF), usually used as a mediator to support the solubility of fluorosilica compounds in organic media, was necessary to obtain maximum enantiomeric excess. For the hydrogenation of itaconic acid dimethyl ester (**5**), a reproducible steady increase in the enantiomeric excess with concomitant increase in the BTF content was discovered (Table 2). At the same time, the catalytic activity did not change with increasing BTF content.

Table 2. Dependency of the enantiomeric excess on the BTF content in the hydrogenation of **5**.


Entry	BTF-content [%]	ee [%]
1	0	85
2	20	91
3	50	93
4	75	93

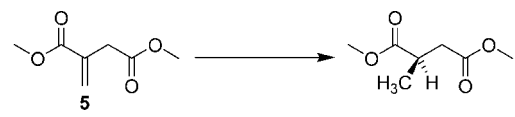
An identical dependency of the stereoselectivity of the catalyst, but not its activity, on the BTF content of the reaction was observed in experiments where FSG was present by applying the same reaction conditions as depicted in Table 2. If BTF was added to the reference experiment with unmodified BINAP (Table 1, Entry 1), the *ee* as well as the activity remained independent of the BTF content. These findings indicate a significant influence of BTF on the stereoselectivity of the Ru-**1** catalyst, whereas the catalyst without fluororous tags remained uninfluenced.

In all experiments, even without BTF, the intense brownish colour of the reaction mixture indicated a solvated Ru-species. The fact that the activity of the Ru-**1** complex decreased upon removal of FSG (74% within six hours, see below) points to an adsorbed species, which at least partially participated in the reaction as well. This is in accordance with our previous results obtained for fluororous Pd catalysts on FSG in Suzuki reactions.<sup>[20]</sup>

The test reaction, the hydrogenation of **5**, was also used to explore whether silica gel without fluororous modifications was suited as an alternative solid support by using identical conditions as in Table 1, Entry 2. As expected, a more rapid decline in the activity of the catalyst relative to the same reaction with FSG was observed, which suggested the presence of fluororous–fluororous interactions to be at least partially responsible for the strong retention of the catalyst on FSG during the washing step (Table 3).

Leaching of ruthenium was determined to be 23.5 ppm for the first run, which indicates a much lower retention of the catalyst on the unmodified surface of the silica gel that was used.

Substitution of C<sub>6</sub>F<sub>13</sub>-modified silica gel, which was used in the reactions of Table 1, by C<sub>8</sub>F<sub>17</sub>-modified material of

Table 3. Hydrogenation of **5** with perfluoro BINAP **1** and unmodified silica gel.<sup>[a]</sup>


Entry	Conversion [%]	ee [%]
1	96	93
2	88	90
3	70	83
4	32	73
5	16	n.d.

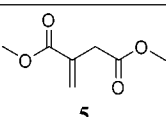
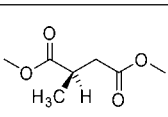
[a] 0.05[RuCl<sub>2</sub>(benzene)]<sub>2</sub>, 0.1 mol-% **1**, 5.0 mmol **5**, 500 mg unmodified silica gel (500 Å pore size), 2.5 mL MeOH, 2.5 mL BTF, 10 bar H<sub>2</sub>, 60 °C, 6 h.

the same type in the hydrogenation of **5**, did not lead to improved recycling properties of the catalyst. Despite the longer fluororous chains of the FSG which were expected to cause stronger fluororous–fluororous interactions, the activities in the different runs closely resembled Entry 2 in Table 1, which also shows a decline in the catalytic activity after the third cycle (data not shown).

Interestingly, the application of the Ru-modified BINAP **1** complex to the hydrogenation of itaconic acid dimethyl ester (**5**) without any silica gel led to a significant decrease in the activity and gave just 74% conversion after six hours, whereas the same reaction with fluororous silica gel (Table 1, Entry 2) or unmodified silica gel (Table 3) gave 95–96% conversion within the same timeframe. The same acceleration in the reaction was observed if FSG was added to the reference experiment (Table 1, Entry 1) with unmodified BINAP. Instead of 46% conversion, 64% was observed after one hour. Interestingly, the same turnover (64% within one hour) was reached when FSG was substituted by non-modified silica gel with 500-Å pore size. The same effect of this commercially available silica gel occurred when used in the hydrogenation of **5** with the fluororous Ru-**1** catalyst, where 96% conversion within six hours was observed.

To the best of our knowledge, there exists no precedent in the literature where a similar effect of silica gel was observed. The only examples where an influence of the silica gel on the hydrogenation reactions was reported were published by Thomas, who investigated an enhancement of enantioselectivity in rhodium- and palladium-catalysed hydrogenations of olefins with silica gel of small pore sizes (38–250 Å).<sup>[25]</sup>

Table 4. Influence of silica gels with different pore sizes on the hydrogenation of **5**.<sup>[a]</sup>

Entry	Substrate	Product	S/C <sup>[b]</sup>	Silica gel	<i>t</i> [h]	Conv. <sup>[c]</sup> [%]	ee [%]
1			1000	none	1	46	92
2			60 Å	1	13	92	
3			200 Å	1	16	91	
4			500 Å	1	64	93	
5			1000 Å	1	18	92	

[a] Reaction conditions: 2.6 μmol [RuCl<sub>2</sub>(benzene)]<sub>2</sub>, 5.2 μmol (*S*)-BINAP, 5 mL MeOH, 10 bar H<sub>2</sub>, 60 °C; 500 mg of respective silica gel.

[b] Ratio: substrate/catalyst. [c] Average of two experiments.

To gain more insight into this unexpected accelerating effect, a series of experiments with unmodified (*S*)-BINAP and unmodified silica gels with different pore sizes was conducted. To visualise possible accelerating effects more clearly, the reactions were stopped after one hour at a point of moderate conversion.

As can be seen in Table 4, the presence of silica gel with a pore size of 500 Å during the hydrogenation of **5** led to a distinct acceleration of 40% without loss of enantioselectivity, whereas other silica gels with smaller pore sizes gave less conversion. Even more significant accelerations were observed with substrates **7** and **8** in combination with 1000-Å pore-size silica gel (Table 5).

Table 5. Hydrogenations of **7** and **8**.<sup>[a]</sup>

Entry	Substrate	Product	S/C <sup>[b]</sup>	Silica gel	<i>t</i> [h]	Conv. <sup>[c]</sup> [%]	<i>ee</i> [%]
1 <sup>[c]</sup>			500	none	4	11	30
2 <sup>[c]</sup>			500	1000 Å <sup>[d]</sup>	4	95	30
3 <sup>[f]</sup>			500	none	42	12	66
4 <sup>[f]</sup>			500	1000 Å <sup>[d]</sup>	42	88	67

[a] Reaction conditions: 2.6 μmol [RuCl<sub>2</sub>(benzene)]<sub>2</sub>, 5.2 μmol (*S*)-BINAP, 5 mL MeOH, 60 °C. [b] Ratio: substrate/catalyst. [c] Average of two experiments. [d] 500 mg of silica gel. [e] With 30 bar H<sub>2</sub>. [f] With 35 bar H<sub>2</sub>.

Styrene derivative **7** showed more than a sevenfold increase in the conversion when 1000-Å silica gel was used. Cinnamic acid derivative **8** showed a conversion of 88% after 42 h, which corresponds to a sixfold increase in the reaction rate, also in the presence of 1000-Å silica gel. The reason for the rate enhancement that is observed upon the addition of silica gel of defined pore size to the reaction mixture remains unclear.

## Conclusions

In conclusion, we were able to use the perfluorous BINAP ligand 1/Ru complex in the asymmetric hydrogenations of olefins. By means of noncovalent immobilisation on FSG, which was suspended in the reaction mixture, the catalyst could be easily isolated and reused several times. This methodology avoided the use of perfluorinated solvents. However, the addition of BTF was essential for optimal stereoselectivity. This is the first example of a perfluorous BINAP catalyst that can retain its catalytic activity

over several reaction cycles. Furthermore, the ruthenium content in the product was very low, which confirms the strong retention of the ruthenium catalyst on the surface of the fluorinated silica. Ru impurities of the product ranged between 1.6 and 4.5 ppm, which is in significant contrast to the reactions with the pertinent untagged complex where more than 300 ppm of ruthenium was observed. This corresponds to a maximum leaching of 1.5% of the total amount of ruthenium per run. As a result of these advantages, the described strategy is recommended for the application of oxidation-sensitive perfluorinated catalysts.

Finally, an accelerating effect of unmodified porous silica (500 and 1000 Å pore size) was observed which was in one case responsible for an up to sevenfold increase in the reaction rate without concomitant loss of enantioselectivity.

## Experimental Section

**Supporting Information** (see footnote on the first page of this article): Procedures and analytical data for the asymmetric hydrogenation reactions.

## Acknowledgments

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- [1] C. C. Tzschucke, C. Markert, W. Bannwarth, S. Roller, A. Hebel, R. Haag, *Angew. Chem. Int. Ed.* **2002**, *41*, 3965–4000.
- [2] W. A. Hermann, C. W. Kohlpaintner, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1524–1544.
- [3] D. E. Kaufmann, M. Nouroozian, H. Henze, *Synlett* **1996**, 1091–1092; A. L. Monteiro, F. K. Zinn, R. F. de Souza, J. Dupont, *Tetrahedron: Asymmetry* **1997**, *8*, 177–179.
- [4] I. T. Horváth, J. Rábai, *Science* **1994**, *266*, 72–75; D. W. Zhu, *Synthesis* **1993**, 953–954; I. T. Horváth, *Acc. Chem. Res.* **1998**, *31*, 641–650; J. A. Gladysz, *Science* **1994**, *266*, 55–56; A. Studer, S. Hadida, R. Ferritto, S.-Y. Kim, P. Jeger, P. Wipf, D. P. Curran, *Science* **1997**, *275*, 823–826; B. Cornils, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2057–2059; J. A. Gladysz, D. P. Curran, I. T. Horváth (Eds.) *Handbook of Fluorous Chemistry*, Wiley-VCH, Weinheim, **2004**.
- [5] S. Kainz, D. Koch, W. Baumann, W. Leitner, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1628–1630.
- [6] B. Linclau, A. K. Singh, D. P. Curran, *J. Org. Chem.* **1999**, *64*, 2835–2842; B. Richter, B.-J. Deelman, G. van Koten, *J. Mol. Catal. A* **1999**, *145*, 317–321; B. Richter, A. L. Spek, G. van Koten, B.-J. Deelman, *J. Am. Chem. Soc.* **2000**, *122*, 3945–3951; B. Richter, E. de Wolf, G. van Koten, B.-J. Deelman, *J. Org. Chem.* **2000**, *65*, 3885–3893; E. de Wolf, B. Richter, B.-J. Deelman, G. van Koten, *J. Org. Chem.* **2000**, *65*, 5424–5427.
- [7] Y. Nakamura, S. Takeuchi, Y. Ohgo, *J. Fluor. Chem.* **2003**, *120*, 121–129.
- [8] D. P. Curran, S. Hadida, M. He, *J. Org. Chem.* **1997**, *62*, 6714–6715; D. P. Curran, Z. Zuo, *J. Am. Chem. Soc.* **1999**, *121*, 9069–9072.
- [9] C. C. Tzschucke, C. Markert, H. Glatz, W. Bannwarth, *Angew. Chem. Int. Ed.* **2002**, *41*, 4500–4503.
- [10] R. Noyori, *Asymmetric Catalysis In Organic Synthesis*, John Wiley & Sons, Inc., New York, **1994**; I. Ojima (Ed.), *Catalytic Asymmetric Synthesis*, Wiley-VCH, New York, **2000**.

- [11] M. Berthod, G. Mignani, G. Woodward, M. Lemaire, *Chem. Rev.* **2005**, *105*, 1801–1836.
- [12] M. F. Lalonde (Hoffmann-La Roche AG), *European Patent Appl. EP0667350*, **1995**; H. Ding, J. Kang, B. E. Hanson, C. W. Kohlpaintner, *J. Mol. Catal. A* **1997**, *124*, 21–28; A. Köckritz, S. Bischoff, M. Kant, R. Siefken, *J. Mol. Catal. A* **2001**, *174*, 119–126; M. Kant, S. Bischoff, R. Siefken, E. Grundemann, A. Köckritz, *Eur. J. Org. Chem.* **2001**, 477–481.
- [13] H. L. Ngo, A. Hu, W. Lin, *Chem. Commun.* **2003**, 1912–1913.
- [14] Q. H. Fan, G. J. Deng, X. M. Chen, W. C. Xie, D. Z. Jiang, D. S. Liu, A. S. C. Chan, *J. Mol. Catal. A* **2000**, *159*, 37–43; Q. H. Fan, G. J. Deng, C. C. Lin, A. S. C. Chan, *Tetrahedron: Asymmetry* **2001**, *12*, 1241–1247.
- [15] J. P. Genêt, C. Pinel, V. Ratovelomanana-Vidal, S. Mallart, X. Pfister, C. Cano de Andrade, J. A. Lafitte, *Tetrahedron: Asymmetry* **1994**, *5*, 665–674; T. Lamouille, C. Saluzzo, R. Ter Halle, F. Le Guyader, M. Lemaire, *Tetrahedron Lett.* **2001**, *42*, 663–664.
- [16] D. J. Birdsall, E. G. Hope, A. M. Stuart, W. Chen, Y. Hu, J. Xiao, *Tetrahedron Lett.* **2001**, *42*, 8551–8553; J. Bayardon, M. Cavazzini, D. Maillard, G. Pozzi, S. Quici, D. Sinou, *Tetrahedron: Asymmetry* **2003**, *14*, 2215–2224; M. Berthod, G. Mignani, M. Lemaire, *Tetrahedron: Asymmetry* **2004**, *15*, 1121–1126.
- [17] Y. Nakamura, S. Takeuchi, S. Zhang, K. Okumura, Y. Ohgo, *Tetrahedron Lett.* **2002**, *43*, 3053–3056.
- [18] E. G. Hope, A. M. Stuart, A. J. West, *Green Chem.* **2004**, *6*, 345–350.
- [19] D. Schwinn, H. Glatz, W. Bannwarth, *Helv. Chim. Acta* **2003**, *86*, 188–195.
- [20] C. C. Tzschucke, W. Bannwarth, *Helv. Chim. Acta* **2004**, *87*, 2882–2889.
- [21] C. C. Tzschucke, V. Andrushko, W. Bannwarth, *Eur. J. Org. Chem.* **2005**, 5248–5261; F. Michalek, W. Bannwarth, *Helv. Chim. Acta* **2006**, *89*, 1030–1037.
- [22] M. Wende, J. A. Gladysz, *J. Am. Chem. Soc.* **2003**, *125*, 5861–5872; L. V. Dinh, J. A. Gladysz, *Angew. Chem.* **2005**, *117*, 4164–4167.
- [23] V. Andrushko, D. Schwinn, C. C. Tzschucke, F. Michalek, J. Horn, C. Mößner, W. Bannwarth, *Helv. Chim. Acta* **2005**, *88*, 936–949.
- [24] T. Imamoto, S.-i. Kikuchi, T. Miura, Y. Wada, *Org. Lett.* **2001**, *3*, 87–90.
- [25] R. Raja, J. M. Thomas, M. D. Jones, B. F. G. Johnson, D. E. W. Vaughan, *J. Am. Chem. Soc.* **2003**, *125*, 14982–14983; M. D. Jones, R. Raja, J. M. Thomas, B. F. G. Johnson, D. W. Lewis, J. Rouzaud, K. D. M. Harris, *Angew. Chem. Int. Ed.* **2003**, *42*, 4326–4331.

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