Tris(perfluoroalkyl)silyl Entities as Unexpectedly Potent Tags for the Noncovalent Immobilization of Catalysts by Fluorous–Fluorous Interactions: Application to the Synthesis of Several Perfluoro-Tagged Ligands

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Unexpectedly high retention times were obtained in HPLC investigations for compounds equipped with $(C_8F_{17}CH_2CH_2)_3Si$ tags on C_8F_{17}-modified silica gel (*Fig. 4*). Hence, these tags have a high potential for the noncovalent immobilization of catalysts to be applied in organic solvents, allowing for an easy separation and re-use of the catalyst by filtration and reapplication. The tris(perfluoroalkyl)silyl tag could be incorporated in a straightforward manner into ligands as demonstrated by the synthesis of several prominent classes of ligands (*Schemes* 4–*6*).

1. Introduction. – Fluorous biphasic systems (FBS) allow for straightforward extraction of perfluoro-tagged compounds out of organic phases with fluorous solvents, which can be used for rapid workup of organic reactions, thereby circumventing column chromatographies [1]. This strategy has been demonstrated in a number of cases for the separation, recovery, and re-use of catalysts as well as for simplified product isolation [2]. Drawbacks of the approach are on the one side the high costs of perfluorinated solvents and on the other side their environmental persistence. Furthermore, high F-content (*ca.* 60%) is required for successfully applied biphasic systems.

As a consequence, solid-phase extraction on fluorous silica gel (FSG)[1]) was developed as an alternative method to separate perfluoro-tagged molecules from untagged ones [3]. This approach is possible with much lower F-content in the tags and was therefore dubbed as 'light fluorous technology' which allowed a simple purification by solid-phase extractions (SPE) on perfluorinated silica gel [4].

Similarly, the strong interactions between perfluoro-tagged compounds and perfluorinated stationary phases can also be applied to HPLC. In a series of seminal papers published more than twenty years ago, *Galan*, *Samain* and co-workers demonstrated that interactions between perfluorinated alkyl groups are unique and distinguishable from the lipophilic interactions of linear alkyl chains [5][6]. It was also demonstrated that the intensity of the fluorous–fluorous interaction between perfluorinated compounds and the perfluorinated stationary phase was dependent on the chain length of the tags. Furthermore, it was stressed that compounds with more than one tag displayed a significantly enhanced retention time. In addition, it was

[1]) Since fluorous–fluorous interactions of perfluoro entities are distinct from lipophilic interactions of alkyl chains, we have replaced our previously used term fluorous reversed-phase silica gel (FRPSG) by fluorous silica gel (FSG).

shown that perfluorinated aromatic systems lack completely the ability to form strong interactions with perfluorinated alkyl chains and that lipophilic compounds were not retained as intensively as they were on *C-18* reversed-phase stationary phases. The only disadvantage of the work was that the data were based on a limited number of examples.

Recently, we and others have demonstrated that fluorous–fluorous interactions can be applied to support perfluoro-tagged catalysts in a noncovalent fashion on perfluorinated silica gel [7][8]. Perfluoro-tagged Pd-catalysts supported on fluorous silica gel (FSG) were successfully applied for *Suzuki* and *Sonogashira* couplings in organic solvents (1,2-dimethoxyethane (= glyme)) and in H_2O [9] omitting perfluorinated solvents. The supported catalyst was separated after reaction by filtration and could be re-used in several consecutive runs without loss in efficiency. Depending on the FSG applied, the leaching of the Pd into the product was as low as 1.9% in glyme and 0.8% in H_2O, corresponding to 5.4 ppm Pd and 2.2 ppm Pd in the product. In all these examples, perfluoro-tagged phosphines were used for the immobilization [10].

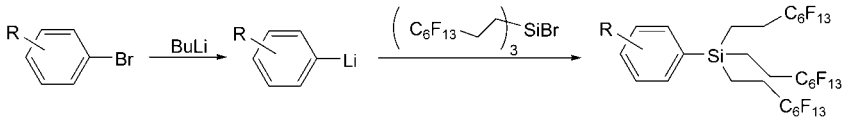
2. Results and Discussion. – 2.1. *Perfluoro-Tagged Compounds* **1**–**8** *and Their Behavior on FSGs* **9** and **10**. To extend the scope of applicability of FSG-supported catalysts, the work presented here was devoted to the identification of highly efficient perfluoro tags which can be used on a wide range of different ligands or their corresponding catalysts. The second requirement was calling for an easy introduction into the corresponding ligands.

In a recent publication, we have evaluated and compared the retention times of a number of mono(perfluoro)tagged and untagged molecules on C_6F_{13}- and C_8F_{17}-modified HPLC silica gels as stationary phases [11]. As mobile phase, MeCN/H_2O mixtures had been applied. The retention times obtained in this investigation are an indication of the intensity of the fluorous–fluorous interactions of the perfluoro tags and the perfluorinated stationary matrix. It became obvious that fluorous–fluorous interactions were clearly prevalent with C_8F_{17}-tagged compounds on C_8F_{17}-functionalized silica gel. Shorter perfluoro tags either on the compounds or as functionalization on the silica gel revealed much weaker interactions, sometimes close to those obtained on *C-18* reversed-phase material. In the said study, we had also included two compounds with two perfluoroalkyl chains each, which resulted in a significant increase in retention time. This is in accordance with previous work of *Samain* and co-workers [6] and later work of *Curran* and co-workers [12] [13], who investigated the retention times of phosphines carrying one, two, or three perfluoro tags on C_6F_{13}-modified stationary phases.

We reasoned that tris(perfluoroalkyl)silyl tags could fulfill all our requirements. On the one hand, they allow the insertion of multiple-tag entities during a single reaction step as illustrated in *Scheme 1*, and on the other hand, they can be introduced efficiently into phenyl rings which are rampant in many ligands of catalysts. This insertion has already been demonstrated for the introduction of the $(C_6F_{13}CH_2CH_2)_3Si$ group into aromatic systems for applications in fluorous biphasic systems [14–16].

To test the cooperativity of silyl tags, we used (2-methoxyethoxy)methyl(MEM)-protected and unprotected benzyl alcohol carrying either one or three C_6F_{13} or C_8F_{17} chains (*Fig. 1*, compounds **1**–**8**). Their retention times were investigated on

Scheme 1. *General Procedure for the Introduction of the Tris(perfluoroalkyl)silyl Tags into Aromatic Systems*



perfluorinated HPLC silica gels **9** and **10** as stationary phases (*Fig. 2*) and employing pure MeCN as well as mixtures of MeCN/H_2O (97:3 and 95:5) as the mobile phase.

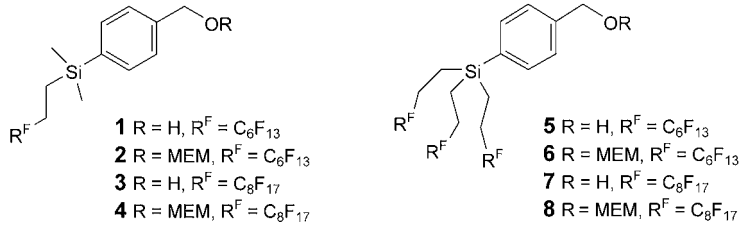


Fig. 1. *MEM-Protected and -unprotected perfluoro-tagged benzyl alcohols used in the study*

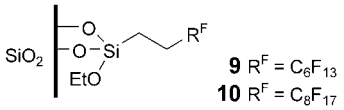


Fig. 2. *Fluorous silica gel* (FSG)

The results of these investigations are depicted in *Figs. 3* and *4*. The retention times of compounds **1**–**8** were evaluated by measuring their *k*-values. The *k*-value of a substance is defined as $k = (t_R - t_m)/t_m$, where t_R is the retention time of the substance and t_m the retention time of an unretarded marker substance like uracil. From these data, the following conclusions can be drawn: compounds **1**–**4** carrying one perfluoro tag displayed a very low retention time on FSG **9** and **10** as stationary phases, indicating the limited value of mono tags for immobilization of catalysts on FSG. The protection of the OH function of the benzyl alcohol with the MEM group had only a negligible effect on the retention time, which is evidence for the dominating effect of the perfluoro tags. For this reason, only the data obtained for the compounds **5**–**8** will be discussed in the following section.

For the $(C_6F_{13}CH_2CH_2)_3Si$ tag on compound **5**, in MeCN as eluent, a marked increase in retention time compared to compounds **1**–**4** was observed on FSG **9** (13.8 min, $k = 8.08$) and on FSG **10** (29.8 min, $k = 20.3$), which might be interpreted as the cooperative effect of the tags. Completely unexpected high retention times were obtained with the $(C_8F_{17}CH_2CH_2)_3Si$-modified benzyl alcohol **7** on FSG **9** (89.0 min, $k = 57.6$) and especially on **10** (287.0 min, $k = 204.0$). Compared to the retention times

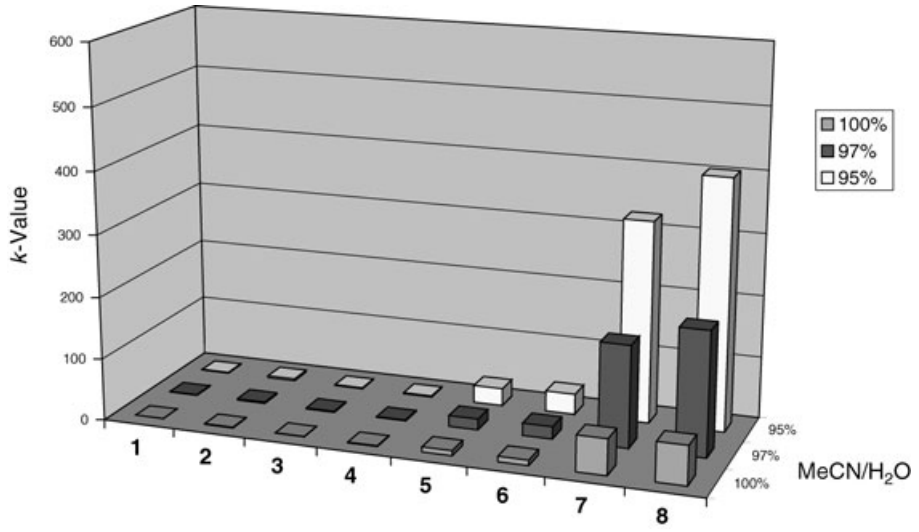


Fig. 3. *Comparison of the retention factors* (*k* values) *of* **1**–**8** *on* C_6F_{13}*-silica gel* **9**

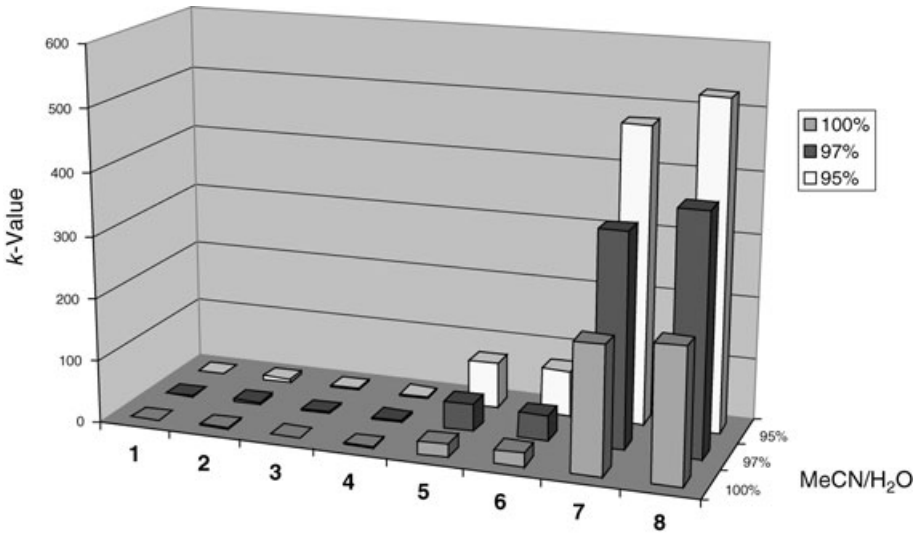


Fig. 4. *Comparison of the retention factors* (*k* values) *of* **1**–**8** *on* C_8F_{17}*-silica gel* **10**

of compound **5** equipped with the $(C_6F_{13}CH_2CH_2)_3Si$ tag, the retention time is higher by a factor of about ten although the number of F-atoms was only increased from 39 to 51. A similar relationship was observed for the pertinent MEM-protected derivatives **6** and **8**. From these results, it can be concluded that the $(C_8F_{17}CH_2CH_2)_3Si$ tag is especially suited for noncovalent immobilizations on C_8F_{17}-modified matrices like **10**. Further-

more, the retention times could be drastically increased by switching from MeCN as mobile phase to mixtures containing small amounts of H_2O, which is an indication of the pronounced hydrophobic effect of the tags in the presence of H_2O [17].

2.2. *Synthesis of Different Ligands Carrying Tris(perfluoroalkyl)silyl Tags.* 2.2.1. *Preamble.* For applications of complexes equipped with $(C_8F_{17}CH_2CH_2)_3Si$ tags in catalysis, one can envision two different possibilities. They can be employed in a permanent noncovalent immobilization of catalysts on FSG, which would be especially suitable in polar solvents, or in addition, they can be used in a 'catch and release' approach. This approach was demonstrated by a multi-step synthesis of quinazoline-2,4-diones starting from $(C_8F_{17}CH_2CH_2)_3Si$-tagged benzyl alcohol on perfluorinated silica gel [18]. Using the latter approach, the reaction is performed in a nonpolar reaction medium, causing a release of the catalyst from the support, allowing for conditions similar to homogeneous reaction conditions. After the reaction, the catalyst is relocated on the support due to a solvent switch toward more-polar media. Both approaches allow for an easy removal of the catalyst after reactions and recycling of the catalyst is possible as well. In the following, we demonstrate the versatility of the insertion of the highly effective $(C_8F_{17}CH_2CH_2)_3Si$ tags into three classes of prominent ligands.

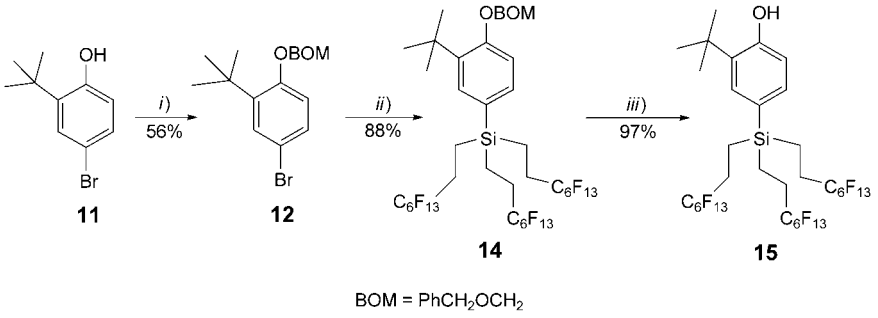
2.2.2. *Perfluorosilyl-Tagged Salen Ligands.* Chiral salen ligands have been used as their complexes with different metals for a whole array of different stereoselective reactions. The specific type of reaction depends on the nature of the coordinated metal ion. Hence, the envisaged perfluoro-tagged salen ligands **20** and **21**, once prepared, could be employed in many different ways [19–22].

For the synthesis of ligands **20** and **21**, the perfluoro-tagged salicylaldehyde derivatives **18** and **19** were needed, which represent versatile key intermediates themselves. Thus, first 2-(*tert*-butyl)phenol was brominated with *N*-bromosuccinimide (NBS) in MeCN (→**11**) [23]. For the subsequent introduction of the (perfluoroalkyl)silyl tag, we pursued two slightly different routes. In the first approach (*Scheme 2*), the OH functionality of **11** was protected as (benzyloxy)methyl (BOM) ether to yield **12**. Compound **12** was then subjected to a halogen/lithium exchange by *tert*-butyllithium, followed by treatment with the bromotris(perfluoroalkyl)silane **13**. From the obtained intermediate **14**, the BOM group was removed by hydrogenolysis to give the perfluoro-tagged phenol **15**. Initial protection of **11** as (2-methoxyethyl)methyl (MEM) ether required for its removal acidic hydrolysis under forcing conditions, leading finally to lower yields.

In a further experiment, we established that the introduction of the tris(perfluoro)-silyl tag was possible without protection of the phenolic OH function. Thus, phenol **11** was deprotonated and lithiated by addition of 3 equiv. of *tert*-butyllithium (*Scheme 3*). Subsequent direct reaction with the corresponding bromosilane **13** or **17** resulted in formation of the perfluoro-tagged phenols **15** and **16**, respectively. The success of this reaction might be owed to a slow nucleophilic attack of the sterically encumbered oxy anion, its reactivity being further attenuated by the strong coordination to the Li-atom, and hence, a comparably faster reaction of the C-nucleophile.

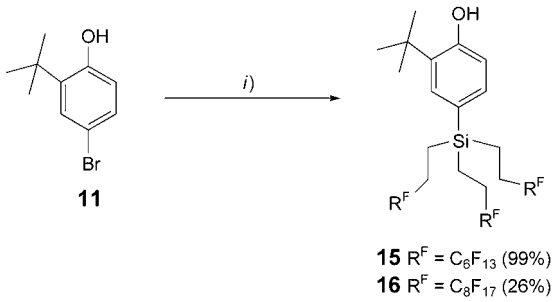
The perfluoro-tagged phenols **15** and **16** were then *o*-formylated by paraformaldehyde in the presence of anhydrous $MgCl_2$ and Et_3N [24]. The desired salicylaldehyde derivatives **18** and **19** were obtained in good yields. Reaction of aldehyde **18** with

Scheme 2. *Synthesis of* **15** *by Using the (Benzyloxy)methyl (BOM) Protecting Group*



i) NaH, BOM–Cl. *ii*) 2 equiv. *t*-BuLi, $(C_6F_{13}CH_2CH_2)_3SiBr$ (**13**). *iii*) H_2, Pd/C.

Scheme 3. *Synthesis of* **15** *and* **16** *without Protecting Groups*



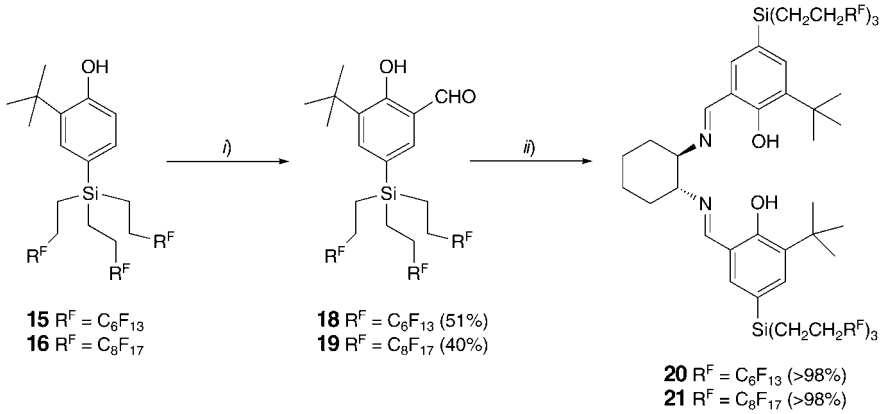
i) 3 equiv. *t*-BuLi; $(C_6F_{13}CH_2CH_2)_3SiBr$ (**13**) or $(C_8F_{17}CH_2CH_2)_3SiBr$ (**17**).

enantiomerically pure *trans*-cyclohexane-1,2-diamine liberated *in situ* from the tartrate gave the desired tetradentate *Schiff*-base ligand **20** in almost quantitative yield as yellow oil (*Scheme 4*). The same route was followed for the synthesis of ligand **21** comprising larger perfluoro entities, albeit sometimes lower yields due to decreased solubility of the intermediates were achieved (*Scheme 4*).

2.2.3. *Perfluorosilyl-Tagged [1,1′-Binaphthalene]-2,2′-diylbis[diphenylphosphine] Ligand.* Another versatile ligand in vogue these days is [1,1′-binaphthalene]-2,2′-diylbis[diphenylphosphine] (binap). This ligand became popular after *Noyori* had it applied to asymmetric hydrogenations of C=C and C=O bonds [25–29]. Among the most-popular reactions involving binap were the synthesis of naproxen and citronellol. Another milestone was the industrial synthesis of (–)-menthol where binap enabled one of the key steps, namely the allylamine–enamine tautomerization reaction [30][31]. Further application of this prominent ligand comprises C–C and C–N coupling reactions [32–34]. Hence, a binap ligand equipped with tris(perfluoroalkyl)silyl tags could have widespread applications in FSG-supported synthesis.

The synthesis of the (*S*)-binap ligand **28** (*Scheme 5*) equipped with $(C_8F_{17}CH_2CH_2)_3Si$ tags was carried out with some modifications by the route reported

Scheme 4. *Synthesis of the Perfluoro-Tagged Salen Ligands* **20** *and* **21**



15 $R^F = C_6F_{13}$
16 $R^F = C_8F_{17}$

18 $R^F = C_6F_{13}$ (51%)
19 $R^F = C_8F_{17}$ (40%)

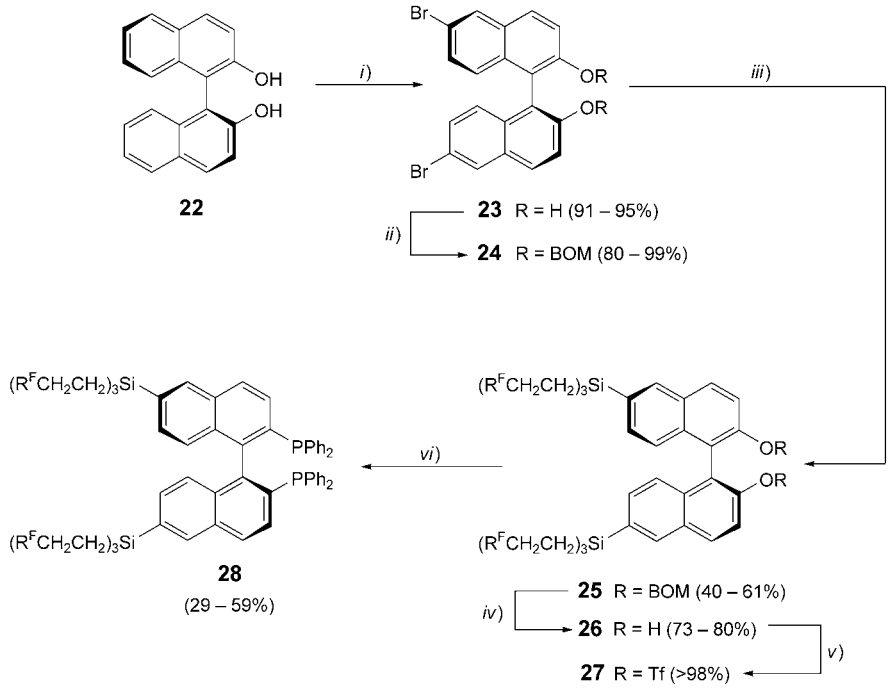
20 $R^F = C_6F_{13}$ (>98%)
21 $R^F = C_8F_{17}$ (>98%)

i) $(CH_2O)_n$, Et_3N, $MgCl_2$, THF. *ii*) (1*R*,2*R*)-Cyclohexane-1,2-diamine-L-tartrate, K_2CO_3, THF.

by *Nakamura* and co-workers for the introduction of $(C_6F_{13}CH_2CH_2)_3Si$ tags [35][36]. They had applied their ligand for reactions in fluorous-biphasic systems. Thus, commercially available (*S*)-binol **22** was brominated to yield the 6,6′-dibromo-[1,1′-binaphthalene]-2,2′-diol (**23**) in high yields (91–95%). The envisaged protection of the OH functions was as (benzyloxy)methyl ether (BOM). The BOM group would allow for an easy removal of the protecting group *via* hydrogenolysis. This is in contrast to *Nakamura*'s synthesis in which the MOM group was used. The protecting step proceeded with high yield to give **24** (80–99%), and Br/Li exchange followed by reaction with bromosilane **17** gave the desired perfluoro-tagged derivative **25** (40–61%; $R^F = C_8F_{17}$). Attempts to remove the BOM group by hydrogenation failed due to solubility problems even in the presence of (trifluoromethyl)benzene (BTF). Alternative cleavage under acidic conditions yielded the perfluoro-tagged binol **26** ($R^F = C_8F_{17}$) in decent yield (73–80%). Subsequent treatment with triflic acid anhydride (Tf_2O) and pyridine as base generated the bis-triflate **27** ($R^F = C_8F_{17}$), which was then subjected to the reaction conditions of *Cai* and co-workers [37]. To increase the solubility of **27** in DMF, addition of BTF was necessary. After a reaction time of three days at 100°, the desired bis-$(C_8F_{17}CH_2CH_2)_3Si$-tagged binap **28** ($R^F = C_8F_{17}$) was obtained in yields of 29–59%.

2.2.4. Hoveyda *Metathesis Ligand.* Within the last decade, olefin metathesis using *Grubbs*' Ru-complexes has become a very valuable reaction within synthetic organic chemistry [38–42]. Since the *Hoveyda* variant of the catalyst is fairly stable and easy to handle, our aim was to synthesize this specific complex carrying a $(C_8F_{17}CH_2CH_2)_3Si$ tag to allow for easy separation and recycling, especially in the FSG-supported form. The actual synthesis of our $(C_8F_{17}CH_2CH_2)_3Si$-tagged ligand is outlined in *Scheme 6*. The synthesis started off with cheap and readily available 5-bromo-2-hydroxybenzaldehyde (**29**), which was alkylated with isopropyl iodide in the presence of K_2CO_3 and Cs_2CO_3 [43]. The product **30** could be isolated in pure form after extractive workup in a yield of 96%. *Wittig* reaction of the aldehyde function of **30** led to the styrene derivative **31** (91%). Finally, the perfluoro tag was introduced after Br/Li exchange and

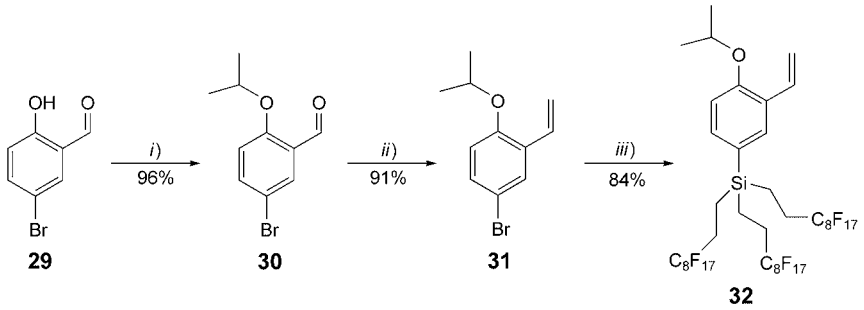
Scheme 5. *Synthesis of Perfluoro-Tagged (S)-binap*



BOM = $PhCH_2OCH_2$, Tf = CF_3SO_2, R^F = C_8F_{17}

i) Br_2, CH_2Cl_2, $-78°$. *ii*) NaH, BOM–Cl, THF, 0°. *iii*) *t*-BuLi, THF; $(C_8F_{17}CH_2CH_2)_3SiBr$ (**17**). *iv*) Conc. HCl, THF, reflux. *v*) Tf_2O, pyridine, (trifluoromethyl)benzene (BTF), CH_2Cl_2, 0°. *vi*) $PHPh_2$, cat. $[Ni(dppe)(Cl)_2]$ (dppe = ethane-1,2-diylbis[diphenylphosphine]), 1,4-diazabicyclo[2.2.2]octane (DABCO), DMF, BTF, 100°.

Scheme 6. *Synthesis of the Perfluoro-Tagged Styrene* **32**



i) i-PrI, K_2CO_3, Cs_2CO_3, DMF, r.t., 24 h. *ii*) $Ph_3P(Me)Br$, BuLi, THF, 0° to r.t., 24 h. *iii*) BuLi, THF, $(C_8F_{17}CH_2CH_2)_3SiBr$ (**17**).

reaction with bromosilane **17**. The pure desired perfluoro-tagged ligand **32** was obtained after short column chromatography in a yield of 84%.

Conclusions. – We have demonstrated that compounds equipped with $(C_8F_{17}CH_2CH_2)_3Si$ tags show unexpectedly high retention times in HPLC by using C_8F_{17}-modified silica gel as stationary phase, indicating exceptionally strong fluorous–fluorous interactions originating from optimal chain length and cooperativity of the individual $C_8F_{17}CH_2CH_2$ entities of the $(C_8F_{17}CH_2CH_2)_3Si$ tag.

In addition, we were able to show that these perfluorinated silyl tags can be inserted in a straightforward way into ligands of prominent classes of catalysts. Further work will now be focused on the formation of the pertinent perfluorinated catalysts and their application as FSG-supported entities for different kinds of catalytic reactions.

Generous financial support from *Fluka*, Buchs (Switzerland), is gratefully acknowledged. Also we would like to thank Dr. *M. Keller*, Mrs. *M. Schonhard*, and Mr. *F. Reinbold* for recording NMR spectra, Mr. *C. Warth* and Dr. *J. Wörth* for recording mass spectra, and Mr. *Hickl* for performing elemental analyses.

Experimental Part

General. All reagents were obtained from *Aldrich* or *Fluka* and were of highest purity available. THF was dried over Na/benzophenone and freshly distilled before use. CH_2Cl_2 and (trifluoromethyl)benzene (BTF) were dried over 4 Å molecular sieves. Et_2O was dried over KOH. Perfluorohexane (FC-72) was dried by filtration over anh. Al_2O_3 (*ICN Alumna N-Super I*). The preparation of **13** was described in [16]. Synthesis of **17** was performed in the same way. Column chromatography (CC): *MN* silica gel *60* (0.063–0.2 mm/70–230 mesh) ASTM for CC from *Baker*. M.p.: Electrothermal digital melting device *IA 9200*; uncorrected. NMR Spectra: at 250, 300, 400, and 500 MHz (^{1}H), 100.6 and 125.7 MHz (^{13}C), and 300 MHz (^{31}P); chemical shifts δ in ppm rel. to Me_4Si (= 0 ppm) for ^{1}H and rel. to $CHCl_3$ (= 77.0 ppm) for ^{13}C, resp., *J* in Hz. MS: *Finnigan-MAT8200* (EI), *MAT312* (Cl), or *TSQ-7000* (ESI) mass spectrometer; MALDI-TOFs (calibration limit 1047-3147 D) with a *Reflex III* in the reflector mode by using the dry-droplet method and the α-cyano-4-hydroxycinnamate matrix.

{4-{[(2-Methoxyethoxy)methoxy]methyl}phenyl}dimethyl(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silane (**2**). To a soln. of 1-bromo-4-{[(2-methoxyethoxy)methoxy]methyl}benzene (1.8 g, 6.5 mmol) in anh. THF (30 ml) at −78° was added 1.6M BuLi in hexane (4.9 ml, 7.8 mmol). After stirring for 10 min at −78°, chlorodimethyl(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silane was added. Within 1.5 h, the mixture was allowed to reach r.t. A sat. aq. NH_4Cl soln. (20 ml) was added and the org. solvent evaporated and the two remaining phases were separated. The crude product was purified by filtration over FSG (MeCN): **2** (2.4 g, 69%). Yellowish oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.25 (*s*, Me_2Si); 0.86–0.95 (*m*, CH_2Si); 1.79–2.04 (*m*, CH_2CF_2); 3.33 (*s*, MeO); 3.52 (*m*, OCH_2CH_2); 3.68 (*m*, OCH_2CH_2); 4.56 (*s*, OCH_2O); 4.75 (*s*, $ArCH_2$); 7.31 (*d*, *J* = 7.9, 2 arom. H); 7.42 (*d*, *J* = 7.9, 2 arom. H).

4-[Dimethyl(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silyl]benzenemethanol (**1**). To a soln. of **2** (2.0 g, 3.3 mmol) in THF (20 ml) was added conc. HCl soln. (1.0 ml). The mixture was heated under reflux for 3 h. Following evaporation, CH_2Cl_2 (20 ml) was added and the resulting mixture extracted with perfluorohexane (5 × 10 ml). After drying (Na_2SO_4), the fluorous solvent was evaporated and the residue purified by CC (cyclohexane/AcOEt 4:1): **1** (520 mg, 31%). Pale yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.26 (*s*, Me_2Si); 0.86–0.96 (*m*, CH_2Si); 1.81–2.04 (*m*, CH_2CF_2); 4.64 (*s*, $ArCH_2$); 7.32 (*d*, *J* = 7.7, 2 arom. H); 7.43 (*d*, *J* = 7.6, 2 arom. H). ^{13}C-NMR (125.7 MHz, $CDCl_3$): −3.4; 5.3; 26.1 (*t*); 65.3; 126.6; 133.9; 136.7; 142.2. CI-MS (isobutane): 530 (15), 512 (13, M^+), 511 (9, $[M-H^+]$), 496 (21), 495 (100, $[M-OH]^+$), 69 (8), 67 (8).

(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl){4-{[(2-methoxyethoxy)methoxy]methyl}phenyl}-dimethylsilane (**4**). As described for **2**, with 1-bromo-4-{[(2-methoxyethoxy)methoxy]methyl}benzene (1.0 g, 3.6 mmol), anh. THF (40 ml), 1.6M BuLi in hexane (2.3 ml, 3.6 mmol) (stirring for 20 min), and chloro(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)dimethylsilane. The crude product was purified by CC (cyclohexane/AcOEt 4:1): **4** (1.0 g, 41%). Yellowish oil. ^{1}H-NMR (250 MHz, $CDCl_3$): 0.30 (*s*, MeSi); 0.91–1.00 (*m*, CH_2Si); 1.89–2.00 (*m*, CH_2CF_2); 3.41 (*s*, MeO); 3.58 (*m*, OCH_2CH_2); 3.76 (*m*, OCH_2CH_2); 4.61 (*s*, OCH_2O); 4.80 (*s*, $ArCH_2$); 7.40 (*d*, *J* = 7.9, 2 arom. H); 7.51 (*d*, *J* = 7.9, 2 arom. H). CI-MS (NH_3): 718 (100, $[M^+H+NH_3]^+$), 671 (10), 612 (10), 595 (6).

4-[(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)dimethylsilyl]benzenemethanol (**3**). As described for **1**, with **4** (0.5 g, 0.7 mmol), THF (40 ml), and conc. HCl soln. (0.5 ml): **3** (210 mg, 48%). Pale

yellow oil. ^{1}H-NMR (250 MHz, $CDCl_3$): 0.33 (*s*, Me_2Si); 0.95–1.02 (*m*, CH_2Si); 1.92–2.03 (*m*, CH_2CF_2); 4.71 (*s*, $ArCH_2$); 7.39 (*d*, $J = 7.7$, 2 arom. H); 7.50 (*d*, $J = 7.6$, 2 arom. H). EI-MS: 612 (2, M^+), 499 (3), 169 (14), 165 (100).

Tris(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl){4-{[(2-methoxyethoxy)methoxy]methyl}phenyl}silane (**8**). To a stirred soln. of 1-bromo-4-{[(2-methoxy}ethoxymethoxy]methyl}benzene (1.0 g, 3.6 mmol) in dry THF (100 ml) at −78°, 1.6M BuLi in hexane (2.3 ml, 3.7 mmol) was added dropwise within 20 min. The soln. was stirred at −78° for 0.5 h. Then a soln. of **17** (4.32 g, 2.98 mmol) in dry THF (20 ml) was added dropwise within 30 min, and the mixture was allowed to warm to r.t. within 1.5 h. A sat. aq. NH_4Cl soln. was added, and the mixture was evaporated. After addition of CH_2Cl_2 (20 ml), the cloudy biphasic mixture was extracted with perfluorohexane (5 × 10 ml), the combined fluorous layer washed with CH_2Cl_2 (2 × 5 ml), and evaporated and the product purified by CC (cyclohexane/AcOEt 10:1, R_f 0.75): 3.56 g (76%) of **8**. Colorless viscous oil. ^{1}H-NMR (400 MHz, C_6F_{14}, C_6D_6 capillary): 1.35–1.42 (*m*, 3 CH_2Si); 2.21–2.37 (*m*, 3 CH_2CF_2); 3.41 (*s*, MeO); 3.63 (*m*, CH_2); 3.82 (*m*, CH_2); 4.72 (*s*, OCH_2O); 4.84 (*s*, $PhCH_2O$); 7.58 (*m*, 4 arom. H). ^{13}C-NMR (125.7 MHz, C_6D_6/C_6F_6 1:1 (*v*/*v*)): 1.97 (*s*); 25.6 (*m*); 58.5 (*s*); 67.7 (*s*); 69.2 (*s*); 72.6 (*s*); 95.7 (*s*); 107.0 (*m*); 109.8 (*m*); 112.0 (*m*); 114.2 (*m*); 117.2 (*m*); 119.3 (*m*); 121.2 (*m*); 131.0 (*s*); 134.4 (*s*); 137.9 (*m*); 139.9 (*m*); 142.1 (*s*). EI-MS: 1475 (69, $[M - MEM]^+$), 1459 (37, $[M - OMEM]^+$), 537 (16), 499 (8), 409 (23), 363 (14), 345 (27), 339 (50), 295 (18), 175 (27), 169 (14), 131 (25), 119 (48), 109 (19), 100 (11), 95 (15), 89 (100), 77 (48), 69 (53), 59 (67), 57 (12), 51 (37), 45 (23), CI-MS (isobutane): 1459 (24, $[M - OMEM]^+$), 499 (7), 409 (20), 89 (100). CI-MS (NH_3): 1583 (40, $[M + NH_3 + H]^+$), 1582 (100, $[M + NH_3]^+$), 1482 (9), 426 (11), 339 (10), 192 (16), 175 (11).

4-[Tris(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)silyl]benzenemethanol (**7**). To a mixture of **8** (200 mg 0.128 mmol) in anh. THF (20 ml) and iPrOH (2 ml), freshly sublimed CBr_4 (43 mg, 0.13 mmol) was added. The mixture was refluxed for 5 h at 70°. After the reaction was complete, the soln. was cooled to r.t. and evaporated. The crude product was extracted with perfluorohexane (5 × 10 ml), the combined fluorous layer washed with CH_2Cl_2 (2 × 5 ml) and evaporated, and the crude product purified by CC (cyclohexane/AcOEt 4:1, R_f 0.12): 120 mg of **7** (64%). M.p. 46°. ^{1}H-NMR (400 MHz, C_6F_{14}, C_6D_6 capillary): 1.22–1.36 (*m*, 3 CH_2Si); 2.11–2.31 (*m*, 3 CH_2CF_2); 3.31 (br., CH_2OH); 4.57 (*s*, CH_2OH); 7.44 (*d*, $J = 7.9$, 2 arom. H); 7.55 (*d*, $J = 7.9$, 2 arom. H). ^{13}C-NMR (125.7 MHz, C_6D_6/C_6F_6 1:1 (*v*/*v*)): 1.9 (*s*); 26.2 (*m*); 64.8 (s); 107.3 (*m*); 109.8 (*m*); 112.1 (*m*); 114.2 (*m*); 117.2 (*m*); 119.3 (*m*); 121.2 (*m*); 130.7 (*s*); 134.4 (*s*); 137.8 (*m*); 139.9 (*m*); 144.8 (*s*). EI-MS: 1475 (62, $[M - H]^+$), 1459 (41, $[M - OH]^+$), 499 (67), 363 (25), 339 (76), 345 (43), 295 (30), 175 (55), 131 (39), 119 (48), 95 (26), 89 (46), 77 (83), 69 (100), 58 (57), 51 (51). CI-MS (isobutane): 1459 (100, $[M - OH]^+$), 571 (8), 500 (12), 499 (66), 409 (40), 339 (13), 181 (19). CI-MS (NH_3): 1582 (31), 1493 (72, $[M + NH_3]^+$), 516 (58), 499 (100), 425 (45), 406 (19), 339 (33), 192 (35), 175 (22).

*1-[(Benzyloxy)methoxy]-4-bromo-2-(*tert*-butyl)benzene* (**12**). At 0° 4-bromo-2-(*tert*-butyl)phenol (1.01 mg, 4.40 mmol) was added to a suspension of 60% NaH in mineral oil (322 mg, 8.05 mmol) in THF (20 ml). To this soln., (benzyloxy)methyl chloride (BOM-Cl; 920 µl, 6.62 mmol) was added, and the mixture was stirred overnight at r.t. The solvent was evaporated, the residue taken up in Et_2O (50 ml), and the soln. washed with H_2O (150, 100 ml) and brine (100 ml) and evaporated. CC (cyclohexane/AcOEt 25:1) gave **12** (857 mg, 56%). Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.38 (*s*, *t*-Bu); 4.72 (*s*, $PhCH_2O$); 5.31 (*s*, OCH_2O); 7.09 (*d*, $J = 8.8$, H–C(6)); 7.25 (*dd*, $J = 8.6$, 2.4, H–C(5)); 7.29–7.36 (*m*, Ph); 7.38 (*d*, $J = 2.6$, H–C(3)). ^{13}C-NMR (100 MHz, $CDCl_3$): 28.4; 33.9; 68.9; 90.9; 112.9; 115.0; 126.7; 126.8; 127.2; 128.5; 128.6; 135.8; 139.5; 154.1. EI-MS: 350 (8, M^+), 348 (8, M^+), 320 (20, $[M - CH_2O]^+$), 318 (20, $[M - CH_2O]^+$); 91 (100, Bn^+).

*{4-[(Benzyloxy)methoxy]-3-(*tert*-butyl)phenyl}tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silane* (**14**). To a soln. of **12** (447 mg, 1.28 mmol) in dry THF (10 ml) under Ar was added 1.7M *t*-BuLi in pentane (1.5 ml, 2.6 mmol) at −78°. After 30 min, a soln. of **13** (1.04 mmol) in perfluorohexane (4 ml) and Et_2O (2 ml) was added. After stirring at r.t. overnight, the mixture was diluted with H_2O (200 ml) and extracted with perfluorohexane (3 × 5 ml). The combined extracts were washed with H_2O (100 ml), brine (100 ml), and MeCN (15 ml), dried (Na_2SO_4), and evaporated: **14** (1.23 mg, 88%). Slightly yellow clear oil. ^{1}H-NMR (400 MHz, C_6F_{14}, C_6D_6 capillary): 1.30–1.36 (*m*, 3 CH_2Si); 1.60 (*s*, *t*-Bu); 2.20–2.36 (*m*, 3 CH_2CF_2); 4.85 (*s*, $PhCH_2$); 5.45 (*s*, OCH_2O); 7.32–7.43 (*m*, 6 arom. H); 7.51 (*d*, $J = 8.1$, 1 arom. H); 7.65 (*d*, $J = 1.5$, 1 arom. H).

*2-(*tert*-Butyl)-4-[tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silyl]phenol* (**15**). *From* **14**: Under Ar, 10% Pd/C (10 mg, 0.009 mmol) was suspended in a soln. of **14** (200 mg, 0.15 mmol) in Et_2O (2 ml), AcOEt (4 ml), and AcOH (2 ml). The mixture was shaken at r.t. under H_2 for 40 h. The suspension was filtered through diatomaceous earth and diluted with Et_2O (30 ml). The soln. was washed with 1M Na_2CO (2 × 50 ml) and brine (50 ml), dried ($MgSO_4$), and evaporated: **15** (177 mg, 97%). Colorless oil.

*From 4-Bromo-2-(*tert*-butyl)phenol* (**11**): To a soln. of **11** (1.65 g, 7.2 mmol) in THF (30 ml) under Ar at −78°, 1.7M *t*-BuLi in pentane (12.7 ml, 21.6 mmol) was slowly added. After 30 min, a soln. of **13** (4.73 mmol) in

FC-72 (10 ml) was added. The mixture was stirred for 2 h at $-78°$ and 15 h at r.t. The mixture was diluted with sat. aq. NH_4Cl soln. (10 ml) and H_2O (250 ml). The fluorous/org. layer was separated, the aq. layer extracted with perfluorohexane (5 ml), and the combined fluorous phase washed with MeCN (20 ml) and evaporated. The resulting oil still contained some THF as evidenced by ^{1}H-NMR. Corrected for the THF content, 5.8 g of **15** (> 98%) was obtained. ^{1}H-NMR (400 MHz, C_6F_{14}, C_6D_6 capillary): 1.31–1.36 (*m*, 3 CH_2Si); 1.60 (*s*, *t*-Bu); 2.21–2.36 (*m*, 3 CH_2CF_2); 5.98 (br., OH); 6.87 (*d*, *J* = 7.7, HC(6)); 7.33 (*dd*, *J* = 7.7, 1.5, H–C(5)); 7.64 (*d*, *J* = 1.5, H–C(3)). CI-MS (isobutane): 1260 (14, $[M+C_3H_6]^+$), 1218 (55, M^+), 1213 (13, $[M-CH_3)^+]$), 72 (100). EI-MS: 1218 (39, M^+), 1203 (20, $[M-CH_3)^+$), 1175 (6, $[M-C_3H_7]^+$), 547 (7), 214 (25), 57 (100, $C_4H_9^+$). HR-MS: 1218.107 ($C_{34}H_{25}F_{39}OSi^+$; calc. 1218.105).

*2-(*tert*-Butyl)-4-[tris(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)silyl]phenol* (**16**). To a soln. of 4-bromo-2-(*tert*-butyl)phenol (1.29 g, 5.64 mmol) in THF (40 ml) and Et_2O (20 ml) under Ar at $-78°$, 2.2M *t*-BuLi in heptane (7.7 ml, 17 mmol) was slowly added. After 30 min, the mixture was warmed to $-25°$, and a soln. of **17** (3.71 mmol) in Et_2O (10 ml) was added. The mixture was stirred at 0° for 2 h and at r.t. for 15 h. After dilution with H_2O (10 ml) and Et_2O (50 ml), the mixture was extracted with H_2O (2 × 200 ml) and brine (100 ml), the org. phase evaporated, and the residue taken up in MeCN (15 ml) and extracted with perfluoroheptane (3 × 5 ml). The combined fluorous extract was filtered through diatomaceous earth and evaporated. CC (cyclohexane/AcOEt 20:1 → 10:1) resulted in a 1:1 mixture of **16** and disiloxane (2393 mg, 21%), which was used as such for the *ortho*-formylation. ^{1}H-NMR (300 MHz, $CDCl_3$, C_6F_6): 1.17–1.23 (*m*, 3 CH_2Si); 1.43 (*s*, *t*-Bu); 2.05–2.23 (*m*, 3 CH_2CF_2); 6.80 (*d*, *J* = 7.8, H–C(6)); 7.24 (*dd*, *J* = 7.8, 1.5, H–C(5)); 7.42 (*d*, *J* = 1.3, H–C(3)). ^{13}C-NMR (75.5 MHz, $CDCl_3$, C_6F_6): 4.4; 25.1 (*t*, *J*(CF) = 23.5); 29.2; 117.4; 122.2; 132.9; 133.3; 157.0.

*3-(*tert*-Butyl)-2-hydroxy-5-[tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silyl]benzaldehyde* (**18**). To a suspension of paraformaldehyde (327 mg, 10.89 mmol), anh. $MgCl_2$ (208 mg, 2.18 mmol), and Et_3N (760 µl, 5.47 mmol) in dry MeCN (25 ml), a soln. of **15** (1.38 g, 1.14 mmol) in THF (13 ml) was added, and the mixture was heated to reflux for 19 h. The mixture was diluted with 1N HCl (150 ml) and extracted with Et_2O (40, 30 ml), the combined extract washed with half-sat. NaCl soln. (200 ml), dried (Na_2SO_4), and evaporated, and the crude product purified by CC (silica gel, cyclohexane → cyclohexane/AcOEt 10:1; then FSG, 80-ml portions of MeCN/Et_2O 1:0, 10:1, 5:1, 3:1, 2:1, 1:1, 0:1). Evaporation of the fraction eluted with MeCN/Et_2O 2:1 yielded **18** (718 mg, 51%). Clear, slightly yellow oil. ^{1}H-NMR (400 MHz, C_6F_{14}, C_6D_6 capillary): 1.37–1.43 (*m*, 3 CH_2Si); 1.63 (*s*, *t*-Bu); 2.24–2.39 (*m*, 3 CH_2CF_2); 7.64 (*d*, *J* = 1.5, 1 arom. H); 7.86 (*d*, *J* = 1.5, 1 arom. H); 9.98 (*s*, OH); 12.37 (*s*, CHO). CI-MS (isobutane): 1247 (100, $[M+H]^+$). EI-MS: 1246 (33, M^+), 1231 (50, $[M-CH_3]^+$), 1203 (5, $[M-C_3H_7]^+$), 899 (2, $[M-C_8H_4F_{13}]^+$), 575 (10), 571 (8), 391 (10), 309 (64), 289 (41), 262 (27), 57 (100, $C_4H_9^+$). HR-MS: 1246.098 ($C_{35}H_{25}F_{39}O_2Si^+$; calc. 1246.100), 1231.075 ($C_{34}H_{22}F_{39}O_2Si^+$; cal. 1231.077).

*3-(*tert*-Butyl)-2-hydroxy-5-[tris(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)silyl]benzaldehyde* (**19**). To a suspension of paraformaldehyde (267 mg, 9.19 mmol), anh. $MgCl_2$ (175 mg, 1.84 mmol), and Et_3N (640 µl, 4.60 mmol) in dry MeCN (5 ml), a soln. of **19** (1.8 g, 50% purity, 0.61 mmol) in THF (10 ml) was added, and the mixture was heated to reflux for 49 h. The mixture was diluted with Et_2O (200 ml) and washed with 0.5N HCl (200 ml), H_2O (200 ml), and brine (100 ml), the Et_2O layer dried (Na_2SO_4) and evaporated, and the residue subjected to CC (petroleum ether 30–50, then cyclohexane/AcOEt 50:1 → 20:1): **19** (432 mg, 0.29 mmol, 46%) besides unreacted **16** (304 mg, 0.20 mmol). ^{1}H-NMR (300 MHz, $CDCl_3$, C_6F_6): 1.27–1.33 (*m*, 3 CH_2Si); 1.46 (*s*, *t*-Bu); 2.10–2.27 (*m*, 3 CH_2CF_2); 7.61 (*s*, 1 arom. H); 7.70 (*s*, 1 arom. H); 9.98 (*s*, CHO); 12.02 (*s*, OH). CI-MS (NH_3): 1546 (100, M^+).

*2,2′-{[(1*R*,2*R*)-Cyclohexane-1,2-diyl]bis[(*E*)-nitrilomethylidyne]}bis[6-(*tert*-butyl)-4-[tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorodecyl)silyl]phenol]* (**20**). To (1*R*,2*R*)-cyclohexane-1,2-diamine-L-tartrate (141 mg, 0.53 mmol) and K_2CO_3 (78 mg, 0.56 mmol) under Ar, a soln. of **18** (1.34 g, 1.07 mmol) in THF (20 ml) was added. To the suspension, H_2O (1 ml) was added. The resulting yellow soln. was stirred at r.t. for 24 h. The mixture was diluted with H_2O (200 ml) and extracted with Et_2O (3 × 30 ml). The combined extracts were washed with brine (50 ml), dried (Na_2SO_4), and evaporated: **20** (1.4 mg, > 98%). Yellow oil. ^{1}H-NMR (400 MHz, C_6F_{14}, C_6D_6 capillary): 1.30–1.36 (*m*, 6 CH_2Si); 1.44–1.52 (*m*, 2 H, alkyl); 1.59 (*s*, 2 *t*-Bu); 1.67–1.75 (*m*, 2 H, alkyl); 1.92–2.05 (*m*, 4 H, alkyl); 2.21–2.36 (*m*, 6 CH_2CF_2); 3.27 (*m*, 2 CH–N); 7.38 (*s*, 2 arom. H); 7.62 (*s*, 2 arom. H); 8.49 (*s*, 2 CH=N); 13.9 (br., 2 OH). ESI-MS (MeCN): 1343 (100, $C_{41}H_{38}F_{39}N_2OSi^+$). ESI-MS (neg.; MeCN): 2285 (61), 2207 (95), 2171 (41), 1199 (100). ESI-MS (neg.; CH_2Cl_2): 2606 (3, $[M+Cl]^-$), 2570 (5, $[M-H]^-$), 2267 (1, $[M-C_6F_{14}+Cl]^-$), 2231 (2, $[M-C_6F_{14}-H]^-$); 2189 (4), 1859 (4), 1529 (10), 1245 (39), 1121 (100).

*2,2′-{[(1*R*,2*R*)-Cyclohexane-1,2-diyl]bis[(*E*)-nitrilomethylidyne]}bis[6-(*tert*-butyl)-4-[tris(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)silyl]phenol]* (**21**). As described for **20**, with (1*R*,2*R*)-cyclohexane-1,2-diamine-L-tartrate (29 mg, 0.11 mmol), K_2CO_3 (30 mg, 0.22 mmol), **19** (345 mg, 0.22 mmol), THF (10 ml), and H_2O (0.5 ml). After dilution with H_2O (100 ml), workup yielded **21** (380 mg, >98%). Yellow oil. ^{1}H-NMR (400 MHz, C_7F_{16}, C_6D_6 capillary): 1.06–1.10 (*m*, 2 H, alkyl); 1.23–1.27 (*m*, 12 H, CH_2Si); 1.52 (*s*, 2 *t*-Bu); 1.67–1.71 (*m*, 2 H, alkyl); 1.93–2.02 (*m*, 4 H, alkyl); 2.15–2.27 (*m*, 6 CH_2CF_2); 3.24–3.26 (*m*, 2 CH–N); 7.27 (*s*, 2 arom. H); 7.54 (*s*, 2 arom. H); 8.40 (*s*, 2 CH=N).

(S$_a$)-6,6′-Dibromo-[1,1′-binaphthalene]-2,2′-diol (**23**). To a suspension of (*S*$_a$)-binol (**22**; 7.2 g, 25 mmol) in CH_2Cl_2 (250 ml) under Ar, a soln. of Br_2 (3.9 ml, 76 mmol) in CH_2Cl_2 (40 ml) was added at −78° within 15 min. The red soln. was stirred at −78° for 30 min, and stirring was continued for a further 3 h at r.t. To remove the excess of Br_2, a sat. Na_2SO_3 soln. (50 ml) was added. The aq. phase was extracted with AcOEt (3 × 50 ml) and the org. phase dried (Na_2SO_4) and evaporated. Recrystallization of the residue from cyclohexane/AcOEt gave **23** (10.6 g, 95%). Colorless crystals. M.p. 204°. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.01 (*s*, 2 OH); 6.96 (*d*, *J* = 9.2, 2 arom. H); 7.38 (*dd*, *J* = 8.9, 2.1, 2 arom. H); 7.40 (*d*, *J* = 9.2, 2 arom. H); 7.90 (*d*, *J* = 8.9, 2 arom. H); 8.06 (*d*, *J* = 2.1, 2 arom. H). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 110.8; 118.1; 119.1; 126.0; 130.5; 130.6; 130.7; 131.0; 132.0; 153.1. EI-MS: 444 (100, M^+), 284 (18, $[M-Br_2]^+$), 256 (31), 226 (26). Anal. calc. for $C_{20}H_{12}Br_2O_2$: C 54.09, H 2.72; found: C 54.32, H 2.88.

(S$_a$)-2,2′-Bis[(benzyloxy)methoxy]-6,6′-dibromo-1,1′-binaphthalene (**24**). To a 60% suspension of NaH in hexane (210 mg, 5.20 mmol) in anh. THF (3 ml) under Ar was added a soln. of **23** (0.8 g, 1.7 mmol) in anh. THF (6 ml) at 0° within 10 min (→ yellow). At 0°, benzyl chloromethyl ether (840 µl, 6.10 mmol) was added dropwise. After stirring for an additional 3 h at 0°, the mixture was quenched with H_2O (10 ml). The aq. phase was extracted with CH_2Cl_2 (3 × 12 ml), the org. phase dried ($MgSO_4$) and evaporated, and the residue subjected to CC (cyclohexane/AcOEt 10:1): **24** (1.2 g, 99%). Colorless crystals which can be recrystallized from cyclohexane/AcOEt. M.p. 114°. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.31 (‘*d*’, *J* = 11.7, 2 H, H_A of PhCH_2O); 4.37 (‘*d*’, *J* = 11.8, 2 H, H_B of PhCH_2O); 5.09 (‘*d*’, *J* = 6.9, 2 H, H_A of OCH_2O); 5.18 (‘*d*’, *J* = 7.0, 2 H, H_B of OCH_2O); 6.99 (*d*, *J* = 9.1, 2 arom. H); 7.03–7.07 (*m*, 2 arom. H); 7.21–7.27 (*m*, 4 arom. H); 7.66 (*d*, *J* = 9.1, 2 arom. H); 7.88 (*d*, *J* = 9.1, 2 arom. H); 8.04 (*d*, *J* = 2.1, 2 arom. H). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 69.9; 92.8; 118.1; 120.8; 127.3; 127.8; 128.4; 128.8; 129.9; 130.0; 131.0; 132.5; 137.1; 153.0. EI-MS: 683 (4, M^+), 654 (4), 624 (12). Anal. calc. for $C_{36}H_{28}Br_2O_4$: C 63.18, H 4.12; found: C 62.88, H 4.25.

(S$_a$)-2,2′-Bis[(benzyloxy)methoxy]-6,6′-bis[tris(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)silyl]-1,1″-binaphthalene (**25**; $R^F = C_8F_{17}$). A soln. of **24** (6.2 g, 9.1 mmol) in anh. THF (80 ml) under Ar was cooled to −78°, and 1.6M *t*-BuLi in hexane (22.0 ml, 37.3 mmol) was added within 30 min. After additional stirring of the orange soln. at −78° for 1.5 h, a soln. of **17** (26.4 g, 18.2 mmol) in dry perfluorohexane (60 ml) was added. Stirring at −78° was continued for 2 h. Then the dry-ice/acetone bath was removed and vigorous stirring continued until r.t. was reached. A sat. aq. NH_4Cl soln. (80 ml) was added, the THF evaporated, CH_2Cl_2 (100 ml) added, and the mixture extracted with perfluorohexane (6 × 25 ml). After evaporation of the fluorous solvent, the crude product was adsorbed on silica gel (25 g) with Et_2O (50 ml) and subjected to CC (cyclohexane/AcOEt 20:1): **25** (18.0 g, 61%). Colorless viscous oil. TLC (cyclohexane/AcOEt 10:1): R_f 0.25. ^{1}H-NMR (400 MHz, C_6F_{14}, C_6D_6 capillary): 1.12–1.19 (*m*, 6 CH_2Si); 2.33 (*m*, 6 CH_2CF_2); 4.31 (‘*d*’, *J* = 12.0, 2 H, H_A of PhCH_2); 4.36 (‘*d*’, *J* = 12.0, 2 H, H_B of PhCH_2); 5.04 (‘*d*’, *J* = 6.9, 2 H, H_A of OCH_2O); 5.16 (‘*d*’, *J* = 6.9, 2 H, H_B of OCH_2O); 7.02 (*m*, 4 arom. H); 7.17–7.28 (*m*, 6 arom. H); 7.44 (*d*, *J* = 8.6, 2 arom. H); 7.76 (*d*, *J* = 9.0, 2 arom. H); 8.05 (*d*, *J* = 9.5, 2 arom. H); 8.20 (*s*, 2 arom. H). CI-MS: 3263 (2, M^+), 2816 (7), 1387 (16), 1350 (19), 1017 (100), 979 (86), 940 (13).

(S$_a$)-6,6′-Bis[tris-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)silyl][1,1′-binaphthalene]-2,2′-diol (**26**; $R^F = C_8F_{17}$). To a soln. of **25** ($R^F = C_8F_{17}$; 1.9 g, 0.6 mmol) in THF (180 ml) at r.t. was added conc. HCl soln. (15 ml). After stirring under reflux for 6 h, H_2O (80 ml) was added and the org. solvent evaporated. AcOEt (90 ml) was added, the mixture extracted with perfluorohexane (6 × 30 ml), the fluorous solvent evaporated, and the crude product adsorbed on silica gel (4 g) with Et_2O (20 ml) and subjected to CC (cyclohexane/AcOEt 10:1 → 4:1): **26** (1.45 g, 80%). Colorless solid. TLC (cyclohexane/AcOEt 4:1): R_f 0.25. ^{1}H-NMR (400 MHz, C_6F_{14}, C_6D_6 capillary): 1.31–1.45 (*m*, 6 CH_2Si); 2.20–2.37 (*m*, 6 CH_2CF_2); 7.24 (*m*, 4 arom. H); 7.51 (*d*, *J* = 9.0, 2 arom. H); 8.11 (*d*, *J* = 9.0, 2 arom. H); 8.22 (*s*, 2 arom. H). MALDI-TOF-MS: 3022 (M^+), 1710, 1271, 1082, 1066.

(S$_a$)-6,6′-Bis[tris(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)silyl][1,1′-binaphthalene]-2,2′-diyl Bis(trifluoromethylsulfonate (**27**; $R^F = C_8F_{17}$). To a soln. of **26** ($R^F = C_8F_{17}$; 1.6 g, 0.53 mmol) in a mixture of CH_2Cl_2 (20 ml) and BTF (12 ml) was added pyridine (150 µl, 1.86 mmol). After cooling to 0°, Tf_2O (218 µl, 1.32 mmol) was added. The mixture was stirred at 0° for an additional 4 h. After evaporation, H_2O (30 ml) and CH_2Cl_2 (30 ml) were added, and the mixture was extracted with perfluorohexane (4 × 15 ml). The fluorous

phase was evaporated to give **27** (1.7 g, 99%). Yellowish oil. ^{1}H-NMR (400 MHz, C_6F_{14}, C_6D_6 capillary): 1.41–1.54 (*m*, 6 CH_2Si); 2.25–2.38 (*m*, 6 CH_2CF_2); 7.64 (*s*, 4 arom. H); 7.84 (*d*, *J* = 9.0, 2 arom. H); 8.26 (*d*, *J* = 9.5, 2 arom. H); 8.35 (*s*, 2 arom. H). MALDI-TOF-MS: 3265, 3221, 2685, 2108, 1500, 1238, 1066.

(S$_a$)-6,6′-Bis[tris(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)silyl][1,1′-binaphthalene]-2,2′-diyl}bis[diphenylphosphine] (**28**; $R^F = C_8F_{17}$). A soln. of [Ni(dppe)Cl_2] (30.0 mg, 57.0 μmol; dppe = ethane-1,2-diylbis[diphenylphosphine) and $PHPh_2$ (90%; 61.0 μl, 353 μmol) in degassed anh. DMF (6 ml) under Ar was heated up to 100° and stirred for 30 min. Then DABCO (258 mg, 2.30 mmol) and **27** (1.90 g, 574 μmol) were added to the mixture which was kept at 100°. Three additional portions of $PHPh_2$ (3 × 61 μl) were added after 1, 3, and 17 h. After 3 d at 100°, the mixture was allowed to cool to r.t., adsorbed on silica gel with degassed BTF (10 ml), and subjected to CC (degassed silica gel, degassed cyclohexane/AcOEt 10:1): **28** (1.1 g, 59%). Reddish viscous oil. TLC (cyclohexane/AcOEt 4:1): R_f 0.70. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.09–1.19 (*m*, 6 CH_2Si); 1.89–2.17 (*m*, 6 CH_2CF_2); 6.77–6.82 (*m*, 4 arom. H); 7.02–7.24 (*m*, 20 arom. H); 7.49–7.53 (*m*, 2 arom. H); 7.90–8.03 (*m*, 4 arom. H). ^{31}P-NMR (300 MHz, $CDCl_3$): −13.7. MALDI-TOF-MS: 3389 ([*M* + 2 O]$^+$), 3374 ([*M* + O]$^+$), 3359 (*M*$^+$), 3173 ([*M* − PPh_2]$^+$), 3082.

5-Bromo-2-isopropoxybenzaldehyde (**30**). To a soln. of 5-bromo-2-hydroxy-benzaldehyde (**29**; 10.22 g, 50.84 mmol) in DMF (150 ml) was added potassium carbonate (13.88 g, 100.4 mmol) and cesium carbonate (3.27 g, 10.0 mmol). Then, isopropyl iodide (15.0 ml, 25.5 g, 150 mmol) was added dropwise to the yellow suspension. The mixture was stirred for 24 h at r.t. and then poured into H_2O (500 ml). The aq. phase was extracted with Et_2O (4 × 100 ml) and the collected org. phase washed with H_2O (5 × 200 ml), dried ($MgSO_4$), and evaporated: pure **30** (11.87 g, 96%). Yellow solid. M.p. 31–33°. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.40 (*d*, *J* = 6.0, *Me*$_2$CH); 4.65 (*sept.*, *J* = 6.0, *Me*$_2$C*H*); 6.89 (*d*, *J* = 9.0, 1 arom. H); 7.59 (*dd*, *J* = 8.9, 2.6, 1 arom. H); 7.91 (*d*, *J* = 2.6, 1 arom. H); 10.39 (*s*, CHO). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 22.0; 71.8; 113.3; 116.1; 127.2; 131.1; 138.2; 159.5; 188.7. EI-MS: 244 (12), 242 (12, *M*$^+$), 202 (85), 201 (64), 200 (100), 199 (64), 184 (14), 182 (11), 145 (13), 143 (13), 63 (20), 43 (17). Anal. calc. for $C_{10}H_{11}BrO_2$: C 49.41, H 4.56; found: C 49.23, H 4.63.

4-Bromo-1-isopropoxy-2-vinylbenzene (**31**). A suspension of Ph_3P(Me)Br (10.0 g, 28.0 mmol) in anh. THF (250 ml) was cooled to 0°. Then 1.6M BuLi in hexane (17.5 ml, 28.0 mmol) was added slowly dropwise. The mixture was stirred for further 30 min at 0°. Meanwhile, a separate flask was charged with a soln. of **30** (5.7 g, 23 mmol) in anh. THF (50 ml), which was also cooled to 0°. After 30 min, the *Wittig* reagent was transferred under Ar to **30**, and then the mixture was warmed to r.t. After 24 h, the solvent was evaporated and the residue suspended in Et_2O (350 ml). After filtration, the filtrate was washed with brine (300 ml), dried (Na_2SO_4), and evaporated and the residue purified by CC (cyclohexane/AcOEt 20:1): **31** (5.1 g, 91%). Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.33 (*d*, *J* = 6.2, *Me*$_2$CH); 4.49 (*sept.*, *J* = 6.1, Me$_2$C*H*); 5.26 (*dd*, *J* = 11.1, 1.2, 1 H, CH=C*H*$_2$); 5.71 (*dd*, *J* = 17.8, 1.2, 1 H, CH=C*H*$_2$); 6.74 (*d*, *J* = 8.8, 1 arom. H); 6.96 (*dd*, *J* = 17.7, 11.3, C*H*=CH$_2$); 7.27 (*dd*, *J* = 8.8, 2.6, 1 arom. H); 7.57 (*d*, *J* = 2.5, 1 arom. H). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 22.1; 71.4; 113.1; 115.2; 116.0; 129.3; 130.1; 130.9; 131.2; 154.2. CI-MS (NH_3): 243 (96), 242 (57), 241 (100), 240 (45, *M*$^+$), 200 (61), 198 (55). Anal. calc. for $C_{11}H_{13}BrO$: C 54.79, H 5.43; found: C 55.02, H 5.44.

(4-Isopropoxy-3-vinylphenyl)tris(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)silane (**32**). To a soln. of **31** (171 mg, 0.710 mmol) in anh. THF (5 ml) at −78°, 1.6M BuLi in hexane (0.45 ml, 46 mg, 0.72 mmol) was added slowly dropwise, and the resulting yellow soln. was stirred for another 10 min. Then, a soln. of **17** (754 mg, 0.520 mmol) in anh. FC-72 (5 ml) was added. The mixture was allowed to warm to r.t. overnight. A sat. NH_4Cl soln. (6 ml) was added, and the nonaq. solvents were evaporated. After addition of CH_2Cl_2 (3 ml), the biphasic mixture was extracted with FC-72 (5 × 2 ml) and the extract evaporated. The crude product was purified by CC (cyclohexane): **32** (667 mg, 84%). White solid. M.p. 55–56°. ^{1}H-NMR (400 MHz, C_6F_{14}, C_6D_6 capillary): 1.38 (*m*, 3 CH_2Si); 1.57 (*d*, *J* = 6.3, *Me*$_2$CH); 2.32 (*m*, 3 CH_2CF_2); 4.77 (*sept.*, *J* = 6.1, Me$_2$C*H*); 5.38 (*dd*, *J* = 11.4, 1.5, 1 H, CH=C*H*$_2$); 5.89 (*dd*, *J* = 17.8, 1.3, 1 H, CH=C*H*$_2$); 7.10 (*d*, *J* = 8.1, 1 arom. H); 7.26 (*dd*, *J* = 18.0, 11.4, 1 H, C*H*=CH$_2$); 7.47 (*dd*, *J* = 8.1, 1.5, 1 arom. H); 7.82 (*d*, *J* = 1.5, 1 arom. H). ^{13}C-NMR (100.6 MHz, C_6F_6, C_6D_6 capillary): 157.0; 134.2; 131.9; 130.6; 127.6; 122.3; 113.3; 112.6; 70.6; 20.3; 19.8; 1.2. EI-MS: 1531 (2, [*M* + H]$^+$), 1530 (5, *M*$^+$), 491 (18), 409 (100), 389 (35), 345 (41), 339 (92), 309 (17), 295 (49), 289 (12), 245 (13), 239 (15), 169 (12), 133 (18), 127 (22), 119 (12), 109 (18), 77 (30), 69 (28), 59 (17), 51 (31). Anal. calc. for $C_{41}H_{25}F_{51}OSi$: C 32.17, H 1.65; found: C 32.33, H 1.54.

REFERENCES

[1] A. Studer, S. Hodida, R. Ferritto, S.-Y. Kim, P. Jeger, P. Wipf, D. P. Curran, *Science* (*Washington, D.C.*) **1997**, *275*, 823.
[2] I. T. Horváth, J. Rábai, *Science* (*Washington, D.C.*) **1994**, *266*, 72.
[3] D. P. Curran, *Synlett* **2001**, *9*, 1488.
[4] D. P. Curran, Z. Luo, *J. Am. Chem. Soc*. **1999**, *121*, 9069.
[5] G. E. Berendsen, K. A. Pikaart, L. de Galan, C. Olieman, *Anal. Chem*. **1980**, *52*, 1990.
[6] I. de Miguel, S. Exbrayat, D. Samain, *Chromatographia* **1987**, *24*, 849.
[7] C. C. Tzschucke, C. Markert, H. Glatz, W. Bannwarth, *Angew. Chem*. **2002**, *114*, 4678; *Angew. Chem., Int. Ed*. **2002**, *41*, 4500.
[8] A. Biffis, M. Zecca, M. Basato, *Green Chem.* **2003**, *5*, 170.
[9] C. C. Tzschucke, W. Bannwarth, *Helv. Chim. Acta* **2004**, *87*, 2882.
[10] S. Schneider, W. Bannwarth, *Angew. Chem*. **2000**, *112*, 4293; *Angew. Chem., Int. Ed.* **2000**, *39*, 4142.
[11] H. Glatz, C. Blay, H. Engelhardt, W. Bannwarth, *Chromatographia* **2004**, *59*, 567.
[12] Q. Zhang, Z. Luo, D. P. Curran, *J. Org. Chem*. **2000**, *65*, 8866.
[13] D. P. Curran, R. Ferritto, Y. Hua, *Tetrahedron Lett*. **1998**, *39*, 4937.
[14] Y. Nakamura, S. Takeuchi, Y. Ohgo, D. P. Curran, *Tetrahedron Lett*. **2000**, *41*, 57.
[15] B. Richter, E. de Wolf, G. van Koten, B.-J. Deelman, *J. Org. Chem*. **2000**, *65*, 3885.
[16] D. Schwinn, W. Bannwarth, *Helv. Chim. Acta* **2002**, *85*, 255.
[17] C. Beller, W. Bannwarth, *Helv. Chim. Acta* **2005**, *88*, 171.
[18] D. Schwinn, H. Glatz, W. Bannwarth, *Helv. Chim. Acta* **2003**, *86*, 188.
[19] L. Canali, D. C. Sherrington, *Chem. Soc. Rev.* **1999**, *28*, 85.
[20] E. N. Jacobsen, *Acc. Chem. Res.* **2000**, *33*, 421.
[21] J. M. Keith, J. F. Larrow, E. N. Jacobsen, *Adv. Synth. Catal.* **2001**, *343*, 5.
[22] T. Katsuki *Adv. Synth. Catal.* **2002**, *344*, 131.
[23] T. Oberhauser, *J. Org. Chem*. **1997**, *62*, 4504.
[24] N. U. Hofslokken, L. Skattebol, *Acta Chim. Scand.* **1999**, *277*, 157.
[25] R. Noyori, T. Ohkuma. M. Kitamura, H. Takaya, N. Syao, H. Kumobayashi, S. Akutagawa, *J. Am. Chem. Soc*. **1987**, *109*, 5856.
[26] R. Noyori, T. Ohkuma. M. Kitamura, H. Takaya, N. Syao, H. Kumobayashi, S. Akutagawa, *J. Am. Chem. Soc*. **1988**, *110*, 629.
[27] M. Kitamura, M. Tokunaga, T. Ohkuma, R. Noyori, *Org. Synth.* **1992**, *71*, 1.
[28] T. Ohta, H. Takaya, M. Kitamura, K. Nagai, R. Noyori, *J. Org. Chem*. **1987**, *52*, 3174.
[29] H, Takaya, T. Ohta, N. Sayo, H. Kumobayashi, S. Akutagawa, S. Inoue, I. Kasahara, R. Noyori, *J. Am. Chem. Soc*. **1987**, *109*, 1596.
[30] K. Tani, T. Yamagata, S. Otsuka, S. Akutagawa, H. Kumobayashi, T. Taketomi, A. Miyashita, R. Noyori, *Chem. Commun*. **1982**, 600.
[31] S. Inoue, H. Takaya, K. Tani, S. Ohtsuka, T. Sato, R. Noyori, *J. Am. Chem. Soc*. **1990**, *112*, 4897.
[32] F. Ozawa, A. Kubo, T. Hayashi, *J. Am. Chem. Soc*. **1991**, *113*, 1417.
[33] J. P. Wolfe, S. L. Buchwald, *J. Org. Chem*. **2000**, *65*, 1144.
[34] J. P. Wolfe, H. Tomori, J. P. Sadighi, J. Yin, S. L. Buchwald, *J. Org. Chem*. **2000**, *65*, 1158.
[35] Y. Nakamura, S. Takeuchi, Y. Ohgo, D. P. Curran, *Tetrahedron Lett*. **2000**, *41*, 57.
[36] Y. Nakamura, S. Takeuchi, S. Zhang, K. Okumura, Y. Ohgo, *Tetrahedron Lett*. **2002**, *43*, 3053.
[37] D. Cai, J. F. Payack, D . Bender, D. L. Hughes, T. R. Verhoeven, P. J. Reider, *J. Org. Chem*. **1994**, *59*, 7180.
[38] S. K. Armstrong, *J. Chem. Soc., Perkin Trans. 1* **1998**, 371.
[39] A. Fürstner, *Angew. Chem.* **2000**, *112*, 3140.
[40] T. M. Trnka, R. H. Grubbs, *Acc. Chem. Res.* **2001**, *34*, 18.
[41] S. J. Connon, S. Blechert, *Angew. Chem.* **2003**, *115*, 1944.
[42] A. H. Hoveyda, D. G. Gillingham, J. J. Van Veldhuizen, O. Kataoka, S. B. Garber, J. S. Kingsbury, J. P. A. Harrity, *Org. Biomol. Chem.* **2004**, *2*, 8.
[43] Q. Yao, *Angew. Chem.* **2000**, *112*, 4060; *Angew. Chem., Int. Ed.* **2000**, *41*, 3896.

Received December 13, 2004