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Straightforward Synthesis of Poly(dimethylsiloxane) Phases with Immobilized (1*R*)-3-(Perfluoroalkanoyl)camphorate Metal Complexes and Their Application in Enantioselective Complexation Gas Chromatography

Markus J. Spallek,[a] Golo Storch,[a] and Oliver Trapp*[a]

Dedicated to Professor Volker Schurig[‡]

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A straightforward synthesis of novel chiral polysiloxane-based metal stationary phases immobilized through a propylenoxy linker (Chirasil-Metal-OC_3) to the polymeric backbone is presented. Synthesis was accomplished in six steps with high overall yields starting from commercially available, enantiopure (+)-(1*S*)-camphorsulfonic acid. Two different approaches towards Chirasil-Metal phases featuring either a propylenoxy or propylenthio linker used for immobilization through hydrosilylation are presented. Furthermore, a new protocol for the fluoroacylation, which is one of the key steps in the synthesis of (1*R*)-3-(perfluoroalkanoyl)camphorate metal complexes, was developed to improve the isolation and overall yield. The immobilization of (1*R*,4*S*)-10-(allyloxy)-3-(heptafluorobutanoyl)camphor – 10-(allyloxy)-hfbc – onto polysiloxanes as well as the incorporation of nickel(II), oxovanadium(IV), europium(III), and lanthanum(III) was characterized by FT ATR IR and NMR spectroscopy. Overall, seven different Chirasil-Metal-OC_3 polymers with different separation properties were prepared by metal incorporation and variation of the amount of immobilized (1*R*,4*S*)-10-(allyloxy)-3-(heptafluorobutanoyl)camphor (10-allyloxy-hfbc: 3.5, 10.2, and 20.0 %). Their performance in enantioselective complexation gas chromatography was systematically studied and excellent enantioselectivity was found for Chirasil-Nickel-OC_3. Separation of 29 small-sized compounds, encompassing, among others, epoxides, substituted alkenes and alkynes as well as alcohols and amides, was achieved with high separation factors *a*. The synthetic strategy, enantiomer separations and thermal stability (up to 160 °C) demonstrates the versatility of the newly derived Chirasil-Metal-OC_3 phases.

Introduction

For 40 years, chiral metal-chelates, a privileged class of highly versatile chiral selectors, have successfully been employed in enantioselective complexation gas chromatography (GC).[1–4] While recent developments in enantioselective GC mainly focused on cyclodextrin-based chiral stationary phases (CSP),[5–11] chiral transition-metal and rare-earth metal complexes, such as metal (1*R*)-3-(trifluoroacetyl)camphorates,[12,13] were utilized as CSP because of their extraordinarily high ability to separate enantiomers of chiral compounds,[1] for example substituted oxiranes,[14] or to study the stereodynamics of stereolabile compounds, for example the stereotopic nitrogen in aziridines.[15,16] Rhodium(I) camphorates were the first examples of highly enantioselective compounds that were successfully employed as CSP in gas chromatographic separations of small olefins.[17] Later, manganese(II),[18] cobalt(II),[19] and nickel(II)[20,21] were successfully introduced.

These chiral complexes are also highly versatile chiral shift reagents in NMR spectroscopy.[22–26] Furthermore, these complexes can be applied as chiral Lewis acids (CLAs) in catalytic asymmetric transformations such as hetero-Diels–Alder reactions using oxovanadium(IV)[27–29] or europium(III),[29–32] or asymmetric cyclopropanations using copper(II) complexes.[33]

The versatility of alkanoyl-camphorate metal complexes as chiral selectors in enantioselective chromatography, as chiral shift reagents in NMR spectroscopy, and as catalysts in asymmetric syntheses[34] emphasizes the importance of making these diketonate ligands easily accessible and improving their chemical properties, for example, decreasing their high volatility, which typically limits the applicable temperature range in enantioselective complexation GC.[35] Higher temperatures lead to leaching of the chiral selector, which decreases the separation efficiency and limits the overall life-time. To improve the thermal stability and, in

[a] Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg,
Im Neuenheimer Feld 270, 69120 Heidelberg, Germany
Fax: +49-6221-544904
E-mail: trapp@oci.uni-heidelberg.de

[‡] On the occasion of 40 years of complexation gas chromatography

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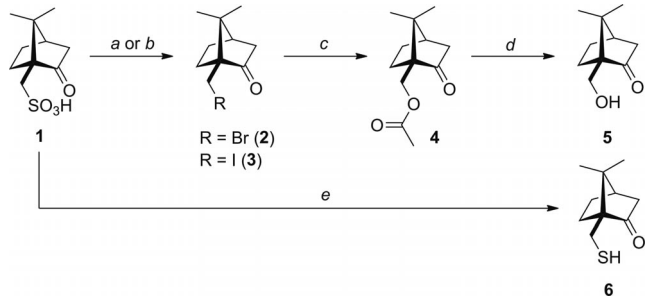
particular, to decrease leaching, the chiral metal-containing selector can be bonded to a polymeric backbone, a strategy commonly used to immobilize catalysts;[36–38] this was first achieved by Schurig et al.[39] by bonding selectors to hydridodimethylpolysiloxane (HMPS) by Pt-catalyzed hydrosilylation. This results in stationary phases with improved thermal stabilities and decreased column bleeding, which is of importance for mass spectrometric detection. The pivotal step of the immobilization strategy used by Schurig et al.[39] was the synthesis of 10-methylenecamphor, which required equimolar amounts of diazomethane[40] and thus limited large-scale synthesis of chiral stationary phases for preparative separations. In addition, the very short linker used decreased the conformational flexibility, which reduces the accessibility of the immobilized chiral selector. Furthermore, the fluoroacylation step in ligand synthesis remained the bottleneck for all camphor and monoterpene related CSPs and chiral shift reagents, because the reaction is accompanied by side reactions and tedious multistep workup procedures, diminishing the yields. Taking these limitations into account, we focused in the present work on the development of an extended, chemically bonded, chiral camphor-derived stationary metal phase with improved thermal stability, separation efficiency, and straightforward accessibility. Using high molecular-weight polysiloxanes ($M_w \approx 3000$ g/mol) guarantees thermal and chemical stability of both the polymeric backbone and the selector. Similar to related systems,[37,41,42] the development of a selector-to-support spacer of a well-defined length proved to be a key to enhanced efficiency and enantioselectivity. In the current study, we also present an exceptional improvement of the fluoroacylation reaction protocol. In subsequent applications, we demonstrate the capabilities and the potential of metal-coordinated CSPs. Furthermore, we demonstrate the versatility of these immobilized perfluoroalkanoyl-camphorate metal complexes as excellent selectors in enantioselective complexation GC.

Results and Discussion

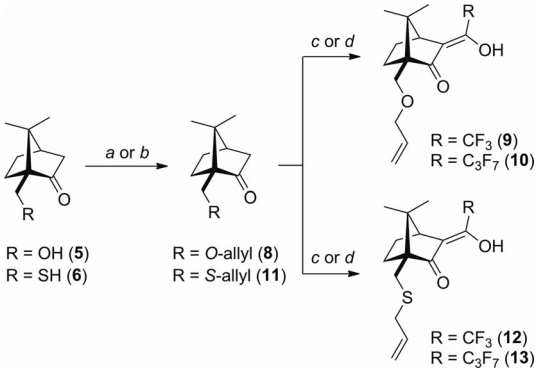
Synthesis

Overall, two different routes to the chiral, fluorinated compounds prior to immobilization were developed, taking the following design criteria into account: (i) The spacer length between polysiloxane (PS) and the bornyl moiety of the perfluoroalkanoyl-camphorate metal complex should be between 6–8 Å, because a shorter linker decreases the conformational flexibility and a longer linker causes folding and decreased selector accessibility; (ii) the linker must not show any competitive selectivity, which is realized by the use of alkyl or alkoxy chains; (iii) the linker must not exhibit any conformational restraints, and (iv) should be easily introduced in a modular way. All of these design criteria can be realized in 10-(allyloxy)- or 10-(allylthio)camphor. Starting from commercially available, enantiomerically pure (+)-(1*S*)-camphorsulfonic acid, these strategies furnished either fluoroacylated 10-(allyloxy)camphor (**8**) or 10-(allylthio)camphor (**11**), both of which were then subjected to immobilization on the polysiloxane support (cf. Schemes 1 and 2). For the preparation of **8**, (1*S*)-(+)-camphorsulfonic acid (**1**) was first converted into its potassium salt, which was then converted into the acid bromide derivative by reaction with phosphorus pentabromide, generated from phosphorus tribromide and bromine in carbon disulfide (Scheme 1). Elimination of sulfur dioxide in *o*-xylene with catalytic amounts of calcium dichloride yielded (1*S*,4*R*)-10-bromocamphor (**2**) in 35% yield. Reaction with excess potassium acetate and acetic acid under molten conditions (> 175 °C) resulted in formation of the corresponding 10-acetoxycamphor derivative **4** in quantitative yields (> 97%). (1*R*,4*R*)-10-Hydroxycamphor (**5**) was prepared from the acetate in good yields (92%) by reaction in 10 wt.-% methanolic solution of potassium hydroxide heated to reflux. Ether synthesis to yield (1*R*,4*R*)-10-(allyloxy)camphor (**8**) was performed by using **5** and allyl bromide under Williamson's ether synthesis conditions using sodium hydride in tetrahydrofuran (84% yield; Scheme 2). In an alternative route, we prepared (1*S*,4*R*)-10-iodocamphor (**3**) directly from **1** in quantitative yields (> 98%; Scheme 1). Although purification of **3** by column chromatography was recommended in previous reports,[43–46] due to the involvement of triphenylphosphane and triphenylphosphane oxide, we found that purification by sublimation was superior because large amounts of pure (1*S*,4*R*)-10-iodocamphor could be readily obtained in a short time. Following the previously described procedures, we were able to shorten the synthetic pathway from six to four steps, and (1*R*,4*R*)-10-(allyloxy)camphor (**8**) was obtained in a very good overall yield of 73%.



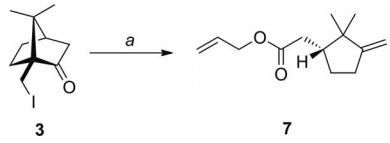
Scheme 1. Routes to 10-hydroxy- (**5**) and 10-thiocamphor (**6**). *Reagents and conditions*: (a) KOH, H_2O, room temp., quant.; PBr_5, Et_2O, 35 °C, 48 h, 35%; (b) I_2, PPh_3, toluene, 111 °C, 16 h, 98%. (c) KOAc, HOAc, 175 °C, 12 h, 93% for **2**, 97% for **3**; (d) KOH, MeOH, 65 °C, 6 h, 92%; (e) $SOCl_2$, 80 °C, 4 h; PPh_3, H_2O, dioxane, 4 h, 100 °C, 94%.

Additionally, we were able to prepare the 10-hydroxycamphor analogue (1*S*,4*R*)-10-thiocamphor (**6**) in a similar one-step reaction from (1*S*)-(+)-camphorsulfonic acid **1** in 94% yield, by using thionyl chloride and triphenylphosphane (Scheme 1). Applying the same strategy for ether synthesis, (1*S*,4*R*)-10-(allylthio)camphor (**11**) was obtained in 94% yield (Scheme 2). By this short, two-step approach, allylthio-camphor **11** was prepared in an excellent overall yield of 76%.



Scheme 2. Allyl/allylthio ether formation and fluoroacylation steps. *Reagents and conditions*: (a) NaH, C_3H_5Br, THF, 0–50 °C, 2 h, 84% for **8**, 94% for **11**. (b) LiH, CF_3CO_2Me, THF, 0–67 °C, 14 h, 94% for **9**, 94% for **12**. (c) LiH, $C_3F_7CO_2Et$, THF, 0–67 °C, 14 h, 75% for **10**, 77% for **13**.

In an effort to improve the overall yield of (1*R*,4*R*)-(10-allyloxy)camphor (**8**) by reducing the number of necessary steps, we tried to perform a Williamson's ether synthesis with 10-iodocamphor **3** and allyl alkoxide (Scheme 3). However, instead of the desired product, we obtained enantiopure (*R*)-allyl 2-(2,2-dimethyl-3-methylenecyclopentyl)acetate (**7**) in 54% yield. Early literature precedents[47,48] account for a transformation by invoking consecutive regioselective rearrangements initiated under basic conditions followed by in situ esterification. The observed one-step reaction might be of valuable interest for natural product synthesis.

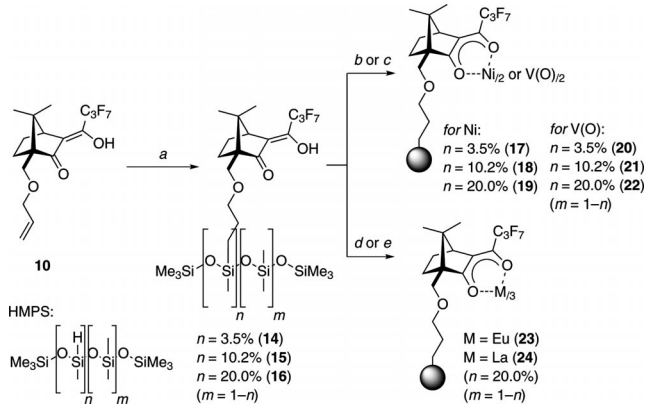


Scheme 3. Regioselective, base-induced camphor cleavage to methylenecyclopentyl ester **7**. *Reagents and conditions*: (a) NaH, C_3H_5OH, DMF, 80 °C, 24 h, 54%.

The key step in the synthesis – the introduction of a fluorinated substituent at the selector – is a necessary prerequisite for enhanced enantiomer recognition. The general procedure involves deprotonation of camphor or related monoterpene derivatives at the α-carbonyl position by lithium diisopropyl amide at low temperatures (–70 °C) to furnish the enolate and suppress side-reactions. Even though low temperatures can be applied, the reaction is generally accompanied by side-reactions such as *O*-acylation, decomposition, or incomplete conversion, which require cumbersome purification steps to isolate the product.[49] We therefore tested different bases for enolate formation. Sodium hydride in tetrahydrofuran showed only moderate conversions over four days at reflux temperature, but no *O*-acylation and only minor amounts of side products were detected (including methyl ethers as anomalous sodium hydride reduction products). Encouraged by this result, we applied potassium hydride and lithium hydride for enolate formation. Whereas use of the former base gave almost no conversion, we were pleased to find lithium hydride was the base of choice. Deprotonation of either 10-(allyloxy)- or 10-(allylthio)camphor was achieved under reflux conditions in 8 to 24 h. Addition of the fluorinated alkyl esters, instead of acyl chlorides, gave the desired *C*-fluoroacylation in very good yield and purity. Due to the different melting points of the fluorinated alkyl ester starting materials and the absence of side products, purification in the case of trifluoroacetylation could be achieved by evaporation of excess trifluoromethyl ester (b.p. 43 °C) to yield the analytically pure product. For the introduction of a hexafluorobutyl moiety, ethyl heptafluorobutyrate (b.p. 95–98 °C) was chosen. The pure product could be distilled at elevated temperatures (120 °C) under reduced pressure. Following this procedure (1*R*,4*S*)-10-(allyloxy)-3-(trifluoromethanoyl)-camphor (**9**, 94%), (1*R*,4*S*)-10-(allyloxy)-3-(heptafluorobutanoyl)camphor (**10**, 75%), (1*S*,4*S*)-10-(allylthio)-3-(heptafluorobutanoyl)camphor (**12**, 94%), and (1*S*,4*S*)-10-(allylthio)-3-(heptafluorobutanoyl)camphor (**13**, 77%) were obtained in very good to excellent isolated yields as colorless, viscous oils (Scheme 2). The lower yields achieved in the case of heptafluoroacylation was due to losses that occurred during the purification by distillation of only small amounts of product.

To investigate the potential of the newly derived, highly fluorinated (1*R*,4*S*)-10-(allyloxy)-3-(heptafluorobutanoyl)-camphor chiral ligands **10**, we chose polysiloxanes as a suitable support material because of its high thermal and chemical stability. First, hydridodimethylpolysiloxanes (HMPS, $M_w \approx 3000$ g/mol) with varying content of free silane groups were synthesized, characterized, and the silane content determined by NMR spectroscopic measurements (SiH content 3.5, 10.2 and 20.0%).[50] Immobilization was achieved by Pt-catalyzed hydrosilylation reaction of 10-(allyloxy)-camphor and HMPS using Karstedt's catalyst (Pt-divinyltetramethyldisiloxane) in anhydrous toluene under ultrasonification for 10 h at elevated temperatures (Scheme 4). Purification resulted in chemically-bonded CSPs with selector content of approximately 3.5 (**14**; 88% yield), 10.2 (**15**; 73% yield), and 20.0% (**16**; 73% yield) in good yields. Immobilization of (1*S*,4*S*)-10-(allylthio)-3-(heptafluorobutanoyl)camphor (**12**) failed with both the Karstedt's catalyst and Speier's catalyst (hexachloroplatinic acid; H_2PtCl_6).[51] This result is in line with the observation that the stereoelectronic properties of substituents on the reactants[52] (also at silicon)[53] strongly influence the reactivity of the carbon–carbon double bond and account for the generally more challenging hydrosilylation of allylthioethers. However, appropriate selection of the catalyst generally allows successful hydrosilylation.[54–58] Metal incorporation was accomplished by using a modification of the procedure developed by Schurig and co-workers[59] in which a two-phase liquid–liquid reaction between metal precursor and chiral polysiloxanes (Chirasil) was used. For the preparation of Chirasil-Nickel-OC_3, nickel(II) acetate tetrahydrate dissolved in methanol, and polysiloxanes **14**–**16** dissolved in *n*-heptane, were transformed in a two-phase mixture. This mixture becomes miscible at elevated temperatures and sep-

arates upon cooling and purification, resulting in nickel(II) bis[(1*R*,4*S*)-3-(heptafluorobutanoyl)-10-(propylenoxy)camphorates] immobilized on polysiloxane as pale-green to green oils [**17**: 3.5% Ni(hfpc)$_2$@PS, 92% yield; **18**: 10.2% Ni(hfpc)$_2$@PS, 89% yield; **19**: 20.0% Ni(hfpc)$_2$@PS, 85% yield]. Incorporation of oxovanadium(IV) was achieved by using oxovanadium(IV) sulfate pentahydrate and triethylamine to yield the Chirasil-Vanadyl-OC$_3$ polysiloxanes [**20**: 3.5% V(O)(hfpc)$_2$@PS, 79% yield; **21**: 10.2% V(O)(hfpc)$_2$@PS, 70% yield; **22**: 20.0% V(O)(hfpc)$_2$@PS, 74% yield] as purple oils. Using this procedure, europium(III) acetate and lanthanum(III) acetate hydrate furnished Chirasil-Europium-OC$_3$ [**23**; 20.0% Eu(hfpc)$_3$@PS, 80% yield] as a yellow oil, and Chirasil-Lanthanum-OC$_3$ [**24**; 20.0% La(hfpc)$_3$@PS, 86% yield] as an orange oil (Scheme 4).



Scheme 4. Synthesis of immobilized camphor ligands **14**–**16** and Chirasil-Metal-OC$_3$ [M = Ni, V(O), Eu, La] preparation. *Reagents and conditions*: (a) HMPS, Karstedt's cat., toluene, sonication, room temp. to 110 °C, 10 h, 88% for **14**, 73% for **15**, 73% for **16**. (b) Ni(OAc)$_2$·4H$_2$O, H$_2$O/heptane (2:3), 100 °C, 2 h, 92% for **17**, 89% for **18**, 85% for **19**. (c) V(O)SO$_4$·5H$_2$O, NEt$_3$, H$_2$O/heptane (2:3), 100 °C, 5 h, 79% for **20**, 70% for **21**, 74% for **22**. (d) Eu(OAc)$_3$·H$_2$O, NEt$_3$, H$_2$O/heptane (2:3), 100 °C, 5 h, 80% for **23**. (e) La(OAc)$_3$·H$_2$O, NEt$_3$, H$_2$O/heptane (2:3), 100 °C, 5 h, 86% for **24**.

The degree of immobilization of (1*R*,4*S*)-10-(allyloxy)-3-(heptafluorobutanoyl)camphor (**10**) onto polysiloxanes and the extent of metal incorporation were monitored by IR and NMR spectroscopic analyses.

Ligand Immobilization and Metal Incorporation Monitored by IR Spectroscopy

Chemical-bonding of the (1*R*,4*S*)-10-(allyloxy)-3-(heptafluorobutanoyl)camphor (**10**) on polysiloxanes can be detected by IR spectroscopy and was considered to be more than 99% complete by fading of the silane band at $\nu_{(Si-H)}$ = 2160 cm^{-1} and detection of two sets of bands resulting from symmetric $\nu_{(C=C)}$ and $\nu_{(C=O)}$ stretching frequencies and asymmetric $\delta_{(-OH)}$ deformations of the camphor-diketone ligand (Figure 1). By comparison of polysiloxanes of different silane content and their hydrosilylated (CB)CSPs **14**–**16**, a characteristic increase in the signal intensities along with a higher degree of SiH content (degree of ligand immobilization) was observed for the silane as well as for the carbonyl, carbon–carbon stretching, and carbon–hydroxyl deformation frequencies. Finally, metal incorporation of nickel(II) and oxovanadium(IV) was monitored. A pronounced change towards lower frequencies was observed for nickel(II) bis[(1*R*,4*S*)-3-(heptafluorobutanoyl)-10-(propylenoxy)camphorate] on polysiloxanes [**17**–**19**, Ni(hfpc)$_2$@PS$_{3.5–20.0\%}$, Chirasil-Nickel-OC$_3$] considering the $\nu_{(C=C)}$, $\nu_{(C=O)}$, and $\nu_{(O-Rh)}$ frequencies. Disappearance of the bands at 1701 and 1642 cm^{-1} of the diketone ligand

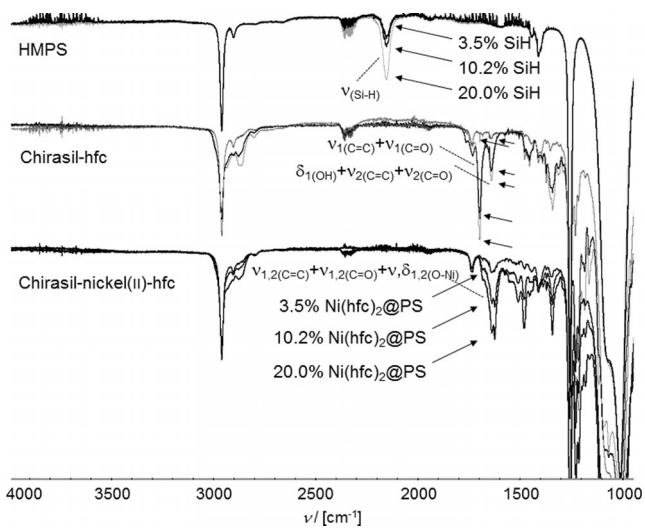


Figure 1. Immobilization of camphor diketone ligand **10** on polysiloxanes (SiH content: 3.5, 10.2, and 20.0%) and nickel(II) incorporation monitored by IR spectroscopic measurements (overlay of nine spectra, characteristic absorption bands marked with arrows): Chirasil-Nickel-OC$_3$.

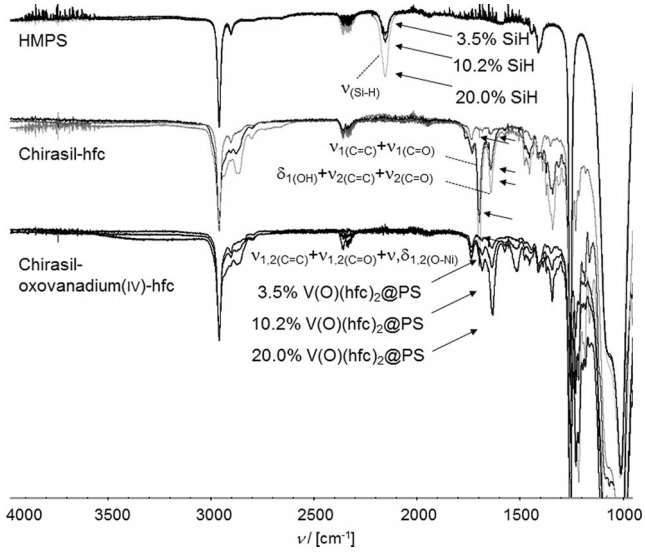


Figure 2. Immobilization of camphor diketone ligand **10** on polysiloxanes (SiH content: 3.5, 10.2, and 20.0%) and oxovanadium(VI) incorporation monitored by IR spectroscopic measurements (overlay of nine spectra, characteristic absorption bands marked with arrows): Chirasil-Vanadyl-OC$_3$.

and occurrence of two new bands at 1641 and 1627 cm^{-1} show successful nickel incorporation (Figure 1). Although less pronounced, this change was also observed for the incorporation of oxovanadium(IV), with bands at 1686 and 1635 cm^{-1}. Intensities differed in respect to the ligand content in Chirasil-Vanadyl-OC_3 materials **20**–**22** (Figure 2). For the IR spectra of Chirasil-Europium-OC_3 (**23**) and Chirasil-Lanthanum-OC_3 (**24**), see the Supporting Information.

Ligand Immobilization and Metal Incorporation Monitored by ^{1}H NMR Spectroscopy

The immobilization process was also monitored and verified by NMR spectroscopic measurements. Figure 3 shows the ^{1}H NMR spectra of starting materials and Chirasil-Metal-OC_3 phases. Due to detection limits, only the spectra for high silane ligand and metal camphorate content (20.0%) are displayed. In Figure 3 (A), the signal for the silane protons at δ = 4.68 ppm and methyl moieties of HMPS at δ = 0.2 to –0.3 ppm can be easily detected. In part B of Figure 3, (1*R*,4*S*)-10-(allyloxy)-3-(heptafluorobutanoyl)camphor (**10**) prior to immobilization is shown and can be identified by its allylic protons at δ = 5.93–5.86 (m, 1 H), 5.28 (dd, 1 H, methyleneCH_{2trans}), and 5.18 (dd, 1 H, methyleneCH_{2cis}) ppm, and by its characteristic singlets for the two *C*7-*exo*-methyl groups at δ = 1.07 and 0.96 ppm. In Figure 3 (C), immobilization onto the polysiloxane and complete conversion (> 99%) was confirmed by the reduced signals of all the allylic ligand-proton signals in the range between δ = 6.00 and 5.00 ppm as well as by the disappearance of the silane signal at δ = 4.68 ppm. The lack of signals in this region is noteworthy, because ether cleavage of the ligand and side reactions during hydrosilylation are possible, which would render purification as well as any further application of these polymers difficult (e.g., remaining SiH functionalities as a source for metal-reduction or free complex species altering polymer performance/selectivity/separation capabilities). Whereas these signals disappeared, the characteristic *C*7-methyl groups of the camphor moiety at δ = 1.07 and 0.96 ppm and the broad signal at δ = 11.69 ppm for the hydroxyl group of the β-diketonate are still present, confirming that successful immobilization onto the polymer had occurred. Furthermore, we were able to identify a triplet signal at δ = 0.91 ppm for the newly formed ligand-to-polymer silano-methyl bond (t, 2 H, -Si-CH_2-linker) and a multiplet at δ = 0.56–0.46 ppm for the silane methyl groups attached to the silicon atom opposite to the site of immobilization. Finally, metal incorporation was further confirmed by the disappearance of the hydroxyl signal at δ = 11.69 ppm as well as by a characteristic shift of the camphor-methylene signals between δ = 3.1 and 3.9 ppm for Chirasil-Europium-OC_3 (Figure 3, D) and Chirasil-Lanthanum-OC_3 (Figure 3, E). For validation by ^{13}C NMR spectroscopic studies and details of immobilized hfpc-ligand **16**, see the Supporting Information.

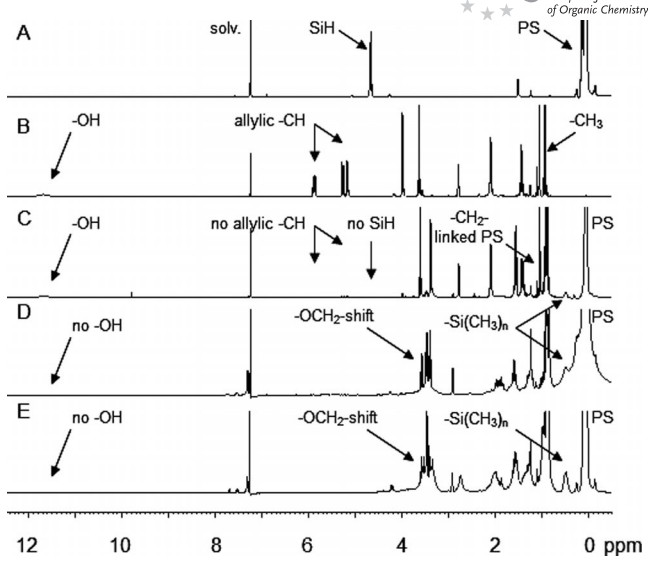


Figure 3. Immobilization of camphor-diketone ligand **10** on polysiloxane (SiH-content: 20%) and incorporation of europium(III) and lanthanum(III) monitored by ^{1}H NMR spectroscopy: Chirasil-Europium/Lanthanum-OC_3 (characteristic signals highlighted with arrows); ^{1}H NMR spectra: (a) HMPS; (b) free ligand [(1*R*,4*S*)-10-(allyloxy)-3-(heptafluorobutanoyl)camphor, **10**]; (c) hfpc@PS **16** (immobilization step); (d) Eu(hfpc)$_3$@PS (metal incorporation step); (e) La(hfpc)$_3$@PS (metal incorporation step).

Complexation Gas Chromatography – Selector Concentration

After characterization of the newly derived (CB)CSPs, their application in enantiomer separation by complexation gas chromatography was investigated. To this end, (CB) CSPs **12**–**19** and **20**–**22**, with a range of hfpc-metal content (3.5, 10.2, and 20.0%), where coated onto the inner surface of fused-silica capillaries (0.25 mm i.d.) using the static method described by Grob,[60] resulting in defined polymer film thickness' of 250 nm (for conditioning of columns, see the Supporting Information). To test the potential of Chirasil-Nickel-OC_3, we used the smallest classes of chiral compounds, namely alkyl- and halo-substituted oxiranes on Chirasil-Nickel-OC_3 as test substances. Chlorohydrin, methyl-oxirane, *n*-butyloxirane, and even *n*-octyloxirane were successfully baseline-separated. To investigate the influence of the amount of selector present at the polysiloxanes on the quality of enantioseparation, all separations were conducted with capillaries of the same film thickness under equal chromatographic conditions, but with varying hfpc-content. The results are shown in Figure 4. On (CB) CSP with 10.2% selector only the smallest selectand (methyloxirane) was partially separated. Chlorohydrin was baseline separated with a selector content of 20.0%. Complete enantioseparation of methyloxirane, *n*-butyloxirane, and *n*-octyloxirane was observed on CSPs containing 10.2 and 20.0% selector. Retention times increased and the quality of enantioseparation was enhanced with higher selector concentrations. The results are in accordance with literature reports, correlating prolonged chemical retention of enantiomers with an increase of selector concentration. Re-

markably, operation at 160 °C over a period of two weeks was possible without loss of retention, thus demonstrating the enhanced thermal stability of these novel (CB)CSPs.

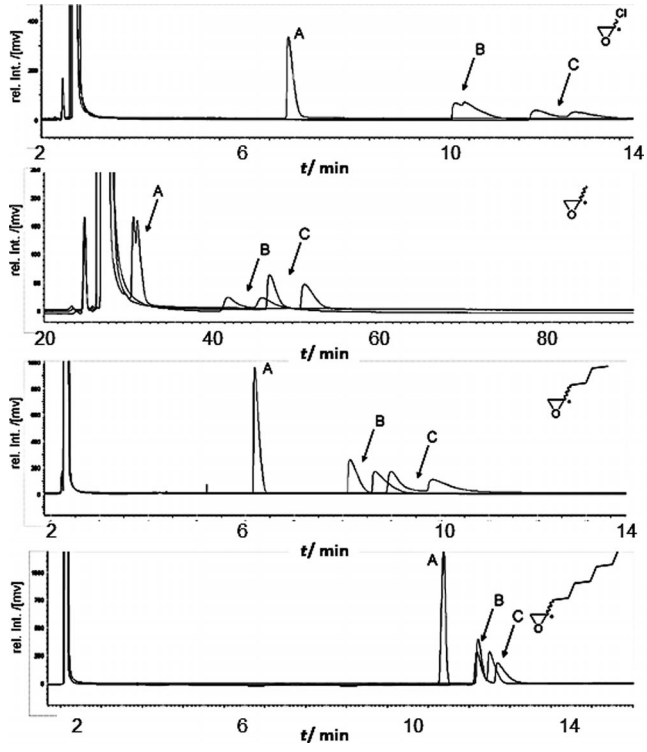


Figure 4. Enantiomer separation of oxiranes using Chirasil-Nickel-OC_3 stationary phases with varying selector concentration (a) 3.5% (**17**), (b) 10.2% (**18**), and (c) 20.0% (**19**); enantiomeric pairs highlighted with arrows. Separations were performed using Chirasil-Metal-OC_3 coated fused-silica capillaries, 250 nm film thickness; carrier gas: helium; conditions (top to bottom: 50 °C, 85 kPa; 40 °C, 85 kPa; 100 °C, 85 kPa and 110 °C, 120 kPa).

Chirasil-Nickel/Europium/Lanthanum-OC_3

Because enantiomer recognition in complexation GC relies on metal–organic coordination, the coordinating metal, the functional group of the selectand employed, and even immobilization[61] all have significant influence on the enantioselectivity. Yet, there is no general relationship between the nature of the molecular complexation of selectands and the separation factor of the enantiomers, as revealed for related Chirasil-Nickel stationary phases.[62] Chirasil-Europium-OC_3 (**23**) and Chirasil-Lanthanum-OC_3 (**24**) were prepared with 20.0% selector concentration. Racemic 2-[(prop-2-yn-1-yloxy)methyl]oxirane was chosen as a model substrate to test the enantiomer separation capability. Separation occurred on all (CB)CSPs, and prolonged retention times were observed with both Chirasil-Lanthanum-OC_3 and Chirasil-Europium-OC_3 without improvement of separation (Figure 5). For the europium-containing (CB)CSP, the retention time was almost doubled compared to lanthanum, and extensive peak broadening was observed. The results obtained indicate that rare-earth metals combined with (CB)CSP exhibit stronger complexation capabilities, but no increase in the separation factor α was observed. Therefore, the application of the corresponding Chirasil-nickel-OC_3 CSP in complexation GC was most effective (Figure 5).

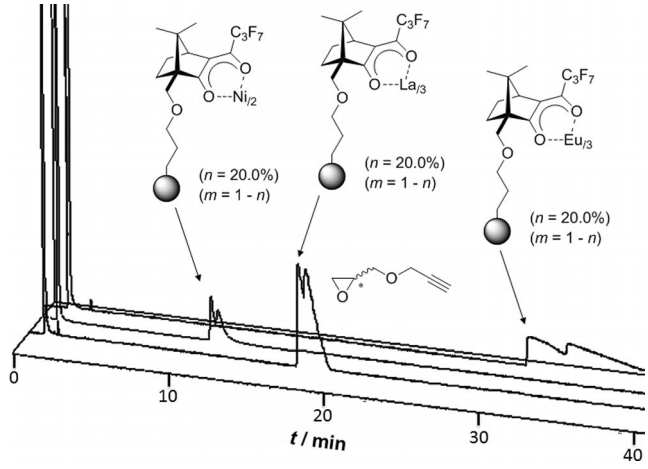


Figure 5. Influence of metal-chelate on the enantioseparation using $Ni(hfpc)_2$@PS (19), $Eu(hfpc)_3$@PS (23), and $La(hfpc)_3$@PS (24); Conditions: 25 m × 0.25 mm i.d., 250 nm film thickness; 80 °C, 85 kPa helium as carrier gas.

Extending the Scope of Separations with Chirasil-Nickel-OC_3

As shown in Figure 4, oxiranes were successfully baseline-separated on Chirasil-Nickel-OC_3 (**19**) with a selector concentration of 20.0% and a film thickness of 250 nm. To further extend the scope of separations, the film thickness was increased to 500 nm while keeping the selector concentration at 20.0%. In addition, a mixed phase consisting of 125 nm polydimethylsiloxane (GE SE 30) and 125 nm Chirasil-Nickel-OC_3 (20% selector) was prepared. Screening of various racemic compounds containing a range of functional groups resulted in enantioseparation of a broad range of compounds with generally high separation factors α. Separated compounds included halogen-, alkyl-, and aryl-substituted oxiranes, primary, secondary, and tertiary alcohols, substituted internal and terminal alkenes, alkynes, cyclic ethers, ketones, and allenes. Both oxiranes and alcohols (Table 1, entries **8**, **15a**–**17a**, and **28**) were successfully separated with α-values between 1.10 and 1.12 using the standard 25 m × 250 nm Chirasil-Nickel-OC_3 column.

Excellent enantioseparations were observed for methyloxirane (Table 1, entry **1c**, α = 1.32) on the mixed phase. The highest separation factor (α = 1.66) was observed for the enantiomer separation of a TMS-alkylbenzyl alcohol (Table 1, entry **18**) after only 6 min on an 8 m × 0.25 mm i.d. column (250 nm film thickness). Moreover, an extremely fast separation (47 seconds) was obtained for methyloxirane using a 5 m (500 nm) Chirasil-Nickel-OC_3 column (Table 1, entry **1b**; α = 1.21; 30 seconds adjusted retention time). (+/–)-Menthol was baseline separated in less than 1 min (α = 1.10) at 140 °C using the same column (Figure 6).

Table 1. Summarized data for the separation of enantiomers of racemic compounds using Chirasil-Nickel-OC_3 (**19**) as chiral stationary phase.[a]

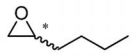
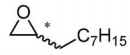
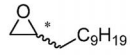
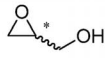
	Compound		T [K]	p [kPa]	t_R^A [min]	t_R^B [min]	t'^A_R [min]	t'^B_R [min]	k'(A)	k'(B)'	N_{eff}^A	N_{eff}^B	α	R_S
1a			313	85	3.7	4.1	1.5	1.9	0.69	0.87	300	400	1.27	1.13
1b		[f]	313	85	0.7	0.8	0.4	0.5	1.46	1.76	200	200	1.21	0.64
1c		[g]	303	85	4.1	4.7	2.0	2.6	0.97	1.28	500	300	1.32	1.38
2a			363	85	13.9	15.7	11.9	13.6	5.76	6.61	2900	1100	1.15	1.40
2b		[g]	353	85	4.8	5.3	2.9	3.4	1.53	1.77	3300	1100	1.15	1.47
3a			383	120	11.6	12.1	10.1	10.6	6.80	7.14	21100	8800	1.05	1.40
3b		[e]	393	120	12.9	13.6	11.5	12.2	8.23	8.68	14700	7000	1.06	1.35
3c		[g]	373	120	15.1	15.9	13.6	14.5	9.45	10.06	11900	3400	1.06	1.20
4a			373	120	36.6	38.4	35.1	36.9	23.67	24.92	24300	11400	1.06	1.65
4b		[f]	373	120	11.0	11.5	10.8	11.3	56.73	59.69	7000	2200	1.05	0.77
4c		[g]	383	120	29.9	31.5	28.5	30.0	19.63	20.72	23200	6000	1.06	1.40
5		[b]	318	100	14.3	15.6	10.8	12.1	3.11	3.50	1000	400	1.12	0.74
6			313	85	11.5	12.3	9.3	10.1	4.27	4.64	1200	800	1.09	0.66
7a			318	45	33.0	36.7	29.1	32.8	7.57	8.53	11800	5200	1.13	2.60
8		[e]	393	85	10.1	11.0	8.1	8.9	3.93	4.34	600	400	1.10	0.52
9a			363	100	14.4	14.9	12.7	13.2	7.40	7.68	31700	16600	1.04	1.43
9b		[e]	383	100	11.2	11.6	9.6	10.0	5.95	6.18	41100	33600	1.04	1.90
9c		[f]	343	100	7.4	7.8	7.2	7.6	32.91	34.69	7500	3100	1.05	0.90

Table 1. (*Continued*)

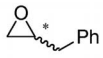
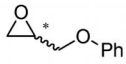
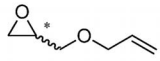
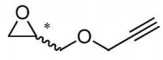
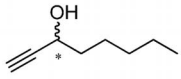
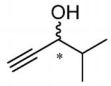
Compound		T [K]	p [kPa]	t_R^A [min]	t_R^B [min]	t'^A_R [min]	t'^B_R [min]	k'(A)	k'(B)'	N_{eff}^A	N_{eff}^B	α	R_S
9d	[g]	363	100	12.9	13.3	11.3	11.6	6.78	6.96	32800	15100	1.03	1.00
10	 [b]	373	120	5.0	5.2	4.2	4.4	5.06	5.31	11500	4500	1.05	1.00
11	 [c]	373	120	10.3	10.8	9.6	10.1	14.13	14.91	11700	4800	1.06	1.15
12a		318	120	21.5	25.5	20.0	24.0	13.65	16.41	800	300	1.20	1.03
12b	[g]	318	120	17.5	20.3	15.8	18.5	8.90	10.46	300	1400	1.17	1.03
13a		353	120	8.7	9.1	7.2	7.7	5.05	5.36	4500	3100	1.06	0.92
13b	[e]	373	120	6.8	7.1	5.4	5.6	3.84	4.05	9800	5900	1.06	1.18
13c	[f]	323	120	7.6	8.6	7.4	8.4	35.05	39.42	600	700	1.12	0.76
14a		353	85	11.3	11.7	9.3	9.7	4.65	4.86	3400	1600	1.04	0.51
14b	[e]	373	85	8.3	8.6	6.4	6.7	3.46	3.62	7400	5100	1.05	0.91
14c	[f]	323	120	6.9	7.4	6.7	7.2	31.46	34.05	1000	400	1.08	0.50
15a		393	120	5.2	5.6	3.7	4.2	2.55	2.85	5700	4900	1.11	2.00
15b	[e]	413	120	4.0	4.2	2.6	2.8	1.83	1.95	14800	11600	1.07	1.83
15c	[f]	383	120	1.5	1.7	1.4	1.5	7.33	8.25	2000	1400	1.13	1.22
16a		383	120	2.0	2.1	0.5	0.6	0.37	0.43	1000	1100	1.18	1.34
16b	[e]	403	120	2.1	2.1	0.7	0.7	0.50	0.56	2200	2300	1.13	1.47
16c	[g]	403	85	7.0	7.6	5.1	5.6	2.64	2.91	25700	13800	1.11	3.42

Table 1. (*Continued*)

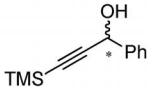
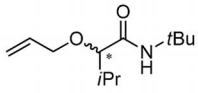
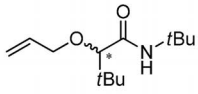
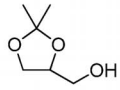
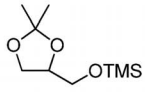
	Compound	T [K]	p [kPa]	t_R^A [min]	t_R^B [min]	t'^A_R [min]	t'^B_R [min]	k'(A)	k'(B)'	N_{eff}^A	N_{eff}^B	α	R_S
17a		373	120	13.4	14.8	11.9	13.4	8.32	9.35	2400	3100	1.12	1.55
18a [d]		416	120	3.4	5.5	3.1	5.3	11.94	19.83	2800	100	1.66	2.16
19a		383	120	14.3	15.2	12.9	13.7	8.88	9.49	6200	7000	1.07	1.37
19b [f]		368	120	5.0	5.5	4.8	5.3	25.43	28.10	1600	1400	1.11	0.99
20a		363	240	20.9	22.6	20.1	21.8	25.87	28.05	3800	3600	1.08	1.25
21a		413	100	10.9	11.0	9.1	9.3	5.10	5.19	28600	21600	1.02	0.69
21b [e]		413	85	22.9	23.2	21.0	21.3	11.32	11.50	47600	31000	1.02	0.78
22a		393	85	17.2	17.5	15.1	15.4	7.37	7.53	29100	26100	1.02	0.94
22b [e]		413	85	16.4	16.6	14.5	14.8	7.82	7.97	42800	35400	1.02	0.96
23a [b]		403	120	19.0	22.2	16.1	19.3	5.59	6.70	4000	3400	1.20	2.78
24a [b]		383	100	10.6	10.9	7.3	7.6	2.20	2.30	46200	44500	1.04	2.28
25a	(2*R*,5*R*)-, (2*S*,5*S*)-chalcogran	373	85	8.1	10.5	6.0	8.4	2.95	4.11	23200	32400	1.39	15.40
25b [f]		323	85	10.8	15.7	10.6	15.4	40.65	59.19	8000	4400	1.46	7.70
26a	(2*R*,5*S*)-, (2*S*,5*R*)-chalcogran	373	85	7.9	10.0	5.9	7.9	2.85	3.85	24700	31700	1.35	13.99
26b [f]		323	85	10.3	13.9	10.1	13.7	38.69	52.50	9000	5200	1.36	6.80
27a	(+/–)-camphor	353	120	29.7	31.3	28.2	29.9	19.91	21.06	5300	3900	1.06	0.96
27b [g]		343	120	42.5	44.5	41.0	43.1	28.29	29.69	6500	5400	1.05	0.95
28a	(+/–)-menthol	413	85	5.8	6.3	3.7	4.2	1.78	1.99	15000	9900	1.12	3.05

Table 1. (*Continued*)

Compound		T [K]	p [kPa]	t_R^A [min]	t_R^B [min]	t'^A_R [min]	t'^B_R [min]	k'(A)	k'(B)'	N_{eff}^A	N_{eff}^B	α	R_S
28b	[e]	423	120	5.2	5.5	3.7	4.0	2.58	2.80	18100	12000	1.08	2.4
28c	[f]	413	85	0.9	1.0	0.7	0.8	3.09	3.40	3800	3200	1.10	1.40
29a	EtO_2C C CO_2Et [e]	393	120	5.9	7.6	5.3	7.0	9.81	12.89	900	13600	1.31	3.50

[a] Separations were carried out using a 25 m Chirasil-Nickel-OC_3 (**19**) column (20% selector, 250 nm) unless otherwise indicated with helium as carrier gas. [b] 40 m × 0.25 mm i.d., 250 nm Chirasil-Nickel-OC_3 (**19**) column (20% selector, 250 nm). [c] 15 m × 0.25 mm i.d., 250 nm Chirasil-Nickel-OC_3 (**19**) column (20% selector, 250 nm). [d] 8 m × 0.25 mm i.d., 250 nm Chirasil-Nickel-OC_3 (**19**) column (20% selector, 250 nm). [e] 25 m × 0.25 mm i.d., 500 nm Chirasil-Nickel-OC_3 (**19**) column (20% selector, 500 nm). [f] 5 m × 0.25 mm i.d., 500 nm Chirasil-Nickel-OC_3 (**19**) column (20% selector, 500 nm). [g] 25 m × 0.25 mm i.d., 250 nm mixed Chirasil-Nickel-OC_3 (**19**) phase (50% **19**, 20% selector and 50% GE-SE 30).

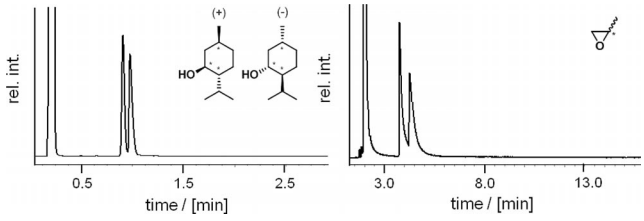


Figure 6. Separation of the enantiomers of (+/–)-menthol and methyloxirane using the novel Chirasil-Nickel-OC_3 CSPs (left: 5 m × 0.25 mm i.d., 500 nm Chirasil-Nickel-OC_3, 140 °C, 85 kPa; right: 250 nm mixed phase 50% Chirasil-Nickel-OC_3 in GE SE 30, 60 °C, 85 kPa).

For diethyl 1,3-allenedicarboxylates (Table 1, entry **29**) a separation factor of α = 1.33 was obtained. Comparison of the enantioseparation of monoalkylated oxiranes on a standard 25 m × 0.25 mm i.d. and a 25 m × 0.25 mm i.d. mixed Chirasil-Nickel-OC_3/GE SE 30 phase (Table 1, entries **1a/1c**; **2a/2b**; **3a/3c**, and **4a/4c**) showed that the separation factors α on the corresponding columns decreased with increasing length of the oxirane-homologues. Furthermore, all four stereoisomers of chlacogran, the principal component of the aggregation pheromone of the bark beetle (*Pityogenes chalcographus*), consisting of a set of two interconverting epimeric pairs (2*R*,5*R*-, 2*S*,5*S*-, 2*S*,5*R*- and 2*R*,5*S*-, Table 1, entries **25a**,**b** and **26a**,**b**) were also baseline separated. The measured and calculated values of each enantiomeric pair (a and b), the net retention time (t_0), the corrected retention times [t_R(a/b)′], separation factor (α), resolution (R_s), and effective plate-numbers [N_{eff}(a/b)] are listed in Table 1 for all tested columns. The observation of consistently good enantioseparation, combined with the broad versatility of this novel Chirasil-Nickel-OC_3 phase underlines the applicability of these new chiral stationary phases.

Conclusions

We have presented the complete synthesis of extended, chemically-bonded Chirasil-Metal-OC_3 stationary phases derived from enantiomerically pure (1*S*)-camphorsulfonic acid. Four different metals [Ni^{2+}, $V(O)^{2+}$, Eu^{3+}, La^{3+}] were incorporated and their different enantiomer separation capabilities were investigated by complexation GC. In addition to a drastic improvement of the fluoroacylation step, which represented the major bottleneck in the preparation of Chirasil-Metal in the past, we also reported a detailed NMR and IR spectroscopic study of the immobilization and metal-incorporation process. This allowed us to monitor and validate the extent of immobilization and confirmed conversions of more than 99% into the desired Chirasil phases. The preparation of immobilized Chirasil-Metal-OC_3 phases was performed with varying selector concentrations (3.5, 10.2, and 20.0%) and incorporation of different metals. This allowed an investigation of the influence of the selector concentration and the nature of the metal on the enantiomer separation. It was shown that a higher degree of selector concentration, up to 20%, is beneficial for enantioselectivity and resolution. Thus, Chirasil-Nickel-OC_3, with a selector concentration of 20.0% showed the best results. An enhanced thermal stability up to 160 °C was achieved with the novel Chirasil-Nickel-OC_3 CSP. To extend the scope of complexation GC to different substitution patterns and group functionalities, we investigated the enantiomer separation of 29 racemic compounds. All compounds could be baseline separated, and generally high sep-

aration factors of up to α = 1.66 were obtained. The new columns for complexation GC presented here are a valuable extension to the currently available choices of CSPs. With the new synthetic procedure, reliable columns with good temperature stability and a long life-time can be prepared. Due to the bonded nature of the selector, these phases can be also used in supercritical fluid chromatography.[63,64]

Experimental Section

General: All reagents and solvents were obtained from Acros, ABCR, Alfa Aesar, Sigma–Aldrich, or VWR and were used without further purification unless otherwise noted. THF was freshly distilled from sodium under an argon atmosphere. Deuterated solvents were purchased from Euriso-Top. NMR spectra were recorded with Bruker Avance 500, Bruker Avance 300, or Bruker ARX-250 spectrometers at room temp. Chemical shifts (ppm) were referenced to residual solvent protons.[65] GC and GC–MS measurements were performed with a Thermo PolarisQ Trace GC–MS, equipped with split injector (250 °C), FID (250 °C), and a quadrupole ion-trap MS (Thermo, San Jose, CA). Fused-silica capillaries (0.25 mm i.d.), obtained from Microquartz (München, Germany) were coated with polysiloxanes (GE SE 30, GE SE 52) and modified with Chirasil-Metal phases and combinations thereof by applying the static method described by Grob.[60] MS spectra were recorded with a Finnigan MAT TSQ 700 or a JEOL JMS-700 spectrometer. IR spectra were recorded with a Bruker Vector 22 FTIR. Elemental analyses were performed by the analytical laboratories of the Chemical Institute of the University of Heidelberg (Germany). Melting points were determined with a Büchi melting point apparatus.

Phosphorus Pentabromide: A dilute solution of phosphorus tribromide (499.5 g, 1.85 mol, 173.4 mL) in CS_2 (220 mL) was placed in a three-necked flask equipped with a mechanical stirrer, and bromine (294.7 g, 1.84 mol, 94.5 mL) was added slowly by using a dropping funnel at 0 °C under an argon atmosphere under vigorous stirring. The solvent was distilled off under reduced pressure after 3 h. After 48 h under high vacuum, phosphorus pentabromide (796.3 g, 1.84 mol, quant.) was obtained as a bright-yellow solid. The product was stored under an argon atmosphere.

(1*S*,4*R*)-10-Bromocamphor (2): (1*S*)-Camphorsulfonic acid (**1**; 350.0 g, 1.51 mol) was suspended in H_2O (150 mL) and neutralized by slow addition of a solution of potassium hydroxide (84.5 g, 1.51 mol) in H_2O (200 mL) at 0 °C. The solvent was removed under reduced pressure, followed by high vacuum. The product was powdered and dried two times over phosphorus pentoxide for 48 h to yield potassium (1*S*)-camphor-10-sulfonate (395 g, 1.46 mol, 97%) as a white salt; m.p. 320–328 °C. IR (KBr): $\tilde{\nu}$ = 3454, 2954, 2232, 2082, 1740, 1728, 1469, 1414, 1374, 1284, 1217, 1186, 1166, 1103, 1040, 973, 934, 936, 851, 780, 710 cm^{-1}. The compound was prepared according to literature.[66]

Potassium (1*S*)-camphor-10-sulfonate (200.0 g, 0.74 mol) was suspended in anhydrous Et_2O (1.1 L) in a three-necked flask equipped with a mechanical stirrer under an argon atmosphere. Phosphorus pentabromide (326.4 g, 0.76 mol) was added rapidly under vigorous stirring at 0 °C. The red solution was warmed to room temperature and stirring was continued for 30 min, followed by 30 min at 30 °C. For safety reasons, only one third of the reaction mixture was submitted to the work-up procedure at once. Therefore, one third of the solution was poured onto 1 kg ice and was immediately extracted with Et_2O (3 × 250 mL), to minimize decomposition to (1*S*)-camphorsulfonic acid. Finally, the organic layers were combined, washed with H_2O (100 mL) and dried with magnesium sulfate. Evaporation of the solvent and drying under high vacuum yielded (1*S*,4*R*)-camphorsulfonic acid bromide (90.9 g, 0.31 mol, 41%) as a microcrystalline, brown powder. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.93 (s, 3 H, CH_3), 1.14 (s, 3 H, CH_3), 1.43–1.52 (m, 1 H), 1.74–1.83 (m, 1 H), 1.99 (d, J = 18.3 Hz, 1 H), 2.04–2.16 (m, 2 H), 2.39–2.53 (m, 2 H), 3.90 (d, J = 14.7 Hz, 1 H, CH_2SO_2Br), 4.50 (d, J = 14.7 Hz, 1 H, CH_2SO_2Br) ppm. ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 19.7, 19.6, 25.4, 26.8, 42.2, 42.7, 48.0, 60.5, 69.1, 212.4 ppm. MS (EI): m/z (%) = 41 (41), 81 (80), 109 (82), 151 (100) $[M – (SO_2Br)]^+$, 187 (7), 229 (10). IR (KBr): $\tilde{\nu}$ = 2954, 2891, 1739, 1456, 1414, 1392, 1376, 1279, 1182, 1127, 1094, 1038, 967, 933, 853, 794, 764, 710 cm^{-1}.

The preparation of (1*S*,4*R*)-10-bromocamphor (**2**) was continued according to literature.[66] (1*S*)-10-Camphorsulfonyl bromide (45.0 g, 0.152 mol) was dissolved in freshly distilled, anhydrous *o*-xylol (1.2 L) in a three-necked flash equipped with an open, oil-filled valve for the extrusion of gas. A small amount of calcium chloride was added and the mixture was stirred for 48 h under the exclusion of light. Calcium chloride was then filtered off and the filtrate was heated to 144 °C under an argon atmosphere and the temperature was maintained until the generation of SO_2 ceased. The solvent was removed by rotary evaporation, resulting in a dark-brown oil, which was submitted to steam distillation (oil bath temperature 150 °C) over a period of four days to yield **2** (12.30 g, 0.053 mol, 35%) as colorless, needle-shaped crystals; m.p. 66–69 °C. ^{1}H NMR (300.51 MHz, $CDCl_3$): δ = 3.61 (d, J = 11.2 Hz, 1 H, CH_2Br), 3.40 (d, J = 11.2 Hz, 1 H, CH_2Br), 2.45–2.36 (m, 1 H), 2.17–1.97 (m, 3 H), 1.90 (d, J = 18.3 Hz, 1 H), 1.59–1.51 (m, 1 H), 1.44–1.36 (m, 1 H), 1.10 (s, 3 H, CH_3), 0.94 (s, 3 H, CH_3) ppm. ^{13}C NMR (75.56 MHz, $CDCl_3$): δ = 20.3, 20.4, 26.7, 27.7, 29.3, 43.0, 43.9, 48.2, 60.3, 215.5 ppm. MS (EI): m/z (%) = 41 (37), 53 (18), 67 (41), 81 (72), 93 (20), 109 (74), 123 (38), 133 (7), 151 (100) $[M – Br]^+$, 173 (1), 230 (7) $[M]^+$. IR (KBr): $\tilde{\nu}$ = 2967, 2935, 2884, 1744, 1465, 1451, 1421, 1382, 1328, 1287, 1234, 1215, 1195, 1167, 1071, 1043, 1018, 961, 934, 910, 873, 851, 809, 775, 745, 708 cm^{-1}.

(1*S*,4*R*)-10-Iodocamphor (3):[45,46] Synthesis of this compound was accomplished according to a procedure developed by Mulholland et al.[43] Instead of column chromatography, purification by sublimation proved to be the method of choice. To a suspension of (1*S*)-10-camphorsulfonic acid (65.0 g, 0.280 mol) in toluene (500 mL) was added iodine (142.0 g, 0.560 mol) and triphenylphosphane (293.5 g, 1.120 mmol) and the mixture was heated at reflux for 16 h. The solvent was removed under reduced pressure and EtOAc (500 mL) was added. The mixture was washed with saturated sodium thiosulfate solution (3 × 100 mL), H_2O (3 × 50 mL), and brine (2 × 50 mL). The solvent was removed and the residue was dried under high vacuum. Successive sublimation of small amounts of crude product yielded pure (1*S*,4*R*)-10-iodocamphor (76.3 g, 0.274 mol, 98%) as colorless crystals; m.p. 79–82 °C. ^{1}H NMR (300.51 MHz, $CDCl_3$): δ = 3.29 (d, J = 10.6 Hz, 1 H, CH_2I), 3.10 (d, J = 10.6 Hz, 1 H, CH_2I), 2.43–2.34 (m, 1 H), 2.16–2.13 (m, 1 H), 2.05–1.94 (m, 2 H), 1.89 (d, J = 18.3 Hz, 1 H), 1.63–1.56 (m, 1 H), 1.41–1.35 (m, 1 H), 1.06 (s, 3 H, CH_3), 0.89 (s, 3 H, CH_3) ppm. ^{13}C NMR (75.56 MHz, $CDCl_3$): δ = 0.7, 20.1, 20.3, 26.7, 30.5, 42.9, 44.0, 28.3, 59.0, 215.0 ppm. IR (KBr): $\tilde{\nu}$ = 2962, 2931, 1744, 1454, 1417, 1391, 1375, 1324, 1298, 1290, 1273, 1214, 1190, 1164, 1064, 1038, 766 cm^{-1}. $C_{10}H_{15}IO$ (278.13): calcd. C 43.18, H 5.44; found C 43.19, H 5.47.

(1*R*,4*R*)-10-Acetoxycamphor (4). Method A:[66] A mixture of (1*S*,4*R*)-10-bromocamphor (12.0 g, 0.052 mol), potassium acetate

(35.7 g, 0.363 mol), and acetic acid (20.3 g, 0.338 mol, 19.3 mL) were stirred at reflux temperature (175 °C) for 12 h. The crude mixture was allowed to cool (10 min) and then dissolved in H_2O (20 mL), while still hot. The solution was carefully neutralized with sodium carbonate and extracted with Et_2O (4 × 50 mL). The organic layers were combined, washed with brine (50 mL), and dried with magnesium sulfate. Evaporation of the solvent under reduced pressure followed by high vacuum, yielded (1*R*,4*R*)-10-acetoxycamphor (10.2 g, 0.048 mol, 93%) as a viscous, colorless oil.

Method B:[67] (1*S*,4*R*)-10-Iodocamphor (20.0 g, 0.072 mol) was used instead of (1*S*,4*R*)-10-bromocamphor. Reaction conditions and workup procedure were similar to those described in method A. Pure (1*R*,4*R*)-10-acetoxycamphor (14.7 g, 0.070 mol) was obtained in 97% yield. ^{1}H NMR (500.13 MHz, $CDCl_3$): δ = 0.98 (s, 3 H, CH_3), 1.05 (s, 3 H, CH_3), 1.37–1.41 (m, 2 H), 1.88 (d, J = 18.4 Hz, 2 H), 1.94 (dd, J = 2.9, J = 12.8 Hz, 1 H, -CH_2-CH_2-), 1.98–2.02 (m, 1 H), 2.04 (s, 1 H, OCH_3), 2.07–2.09 (m, 1 H), 2.40–2.45 (m, 1 H), 4.23 (d, ^2J = 12.4 Hz, 1 H, CH_2OCOH), 4.27 (d, ^2J = 12.4 Hz, 1 H, CH_2OCOH) ppm. ^{13}C NMR (125.76 MHz, $CDCl_3$): δ = 19.8, 20.7, 20.9, 25.5, 26.6, 43.3, 43.9, 47.0, 60.1, 60.5, 170.9, 216.1 ppm. MS (EI): *m*/*z* (%) = 43 (100), 55 (14), 67 (18), 79 (43), 95 (49), 107 (55), 122 (16), 135 (11), 150 (78) [M – (CO_2CH_3)]$^+$, 167 (5) [M – ($COCH_3$)]$^+$, 192 (8), 210 (10) [M]$^+$. IR (KBr): $\tilde{\nu}$ = 2964, 2887, 1746, 1454, 1417, 1392, 1366, 1322, 1242, 1200, 1034, 961, 857, 605 cm^{-1}.

(1*R*,4*R*)-10-Hydroxycamphor (5): This is a known compound.[66,67] (1*R*,4*R*)-10-Acetoxycamphor (10.2 g, 0.048 mol) was dissolved in a methanolic solution of potassium hydroxide (175 mL, 10 wt.-%) and heated at reflux temperature for 6 h. The solution was allowed to cool to room temperature and H_2O (200 mL) was added. The solution was extracted with Et_2O (3 × 100 mL), and the organic layers were combined, washed with brine (50 mL), dried with magnesium sulfate, and the solvent was evaporated under reduced pressure. Recrystallization from pentane yielded **5** (7.55 g, 0.045, 92%) as colorless crystals; m.p. 216–218 °C. ^{1}H NMR (300.51 MHz, $CDCl_3$): δ = 3.87 (d, J = 11.8 Hz, 1 H, CH_2OH), 3.63 (d, J = 11.8 Hz, 1 H, CH_2OH), 2.54 (br. s, 1 H, OH), 2.08–2.05 (m, 1 H), 2.04–1.93 (m, 1 H), 1.89–1.78 (m, 2 H), 1.64–1.55 (m, 1 H), 1.42–1.32 (m, 1 H), 1.00 (s, 3 H, CH_3), 0.97 (s, 3 H, CH_3) ppm. ^{13}C NMR (75.56 MHz, $CDCl_3$): δ = 19.3, 20.8, 26.0, 26.6, 43.4, 43.9, 46.7, 60.6, 61.6, 221.0 ppm. MS (EI): *m*/*z* (%) = 29 (20), 41 (48), 55 (28), 67 (33), 81 (40), 95 (95), 108 (100), 125 (13), 137(8) [M – (CH_3O)]$^+$, 153 (39) [M–(CH_3)]$^+$, 168 (18) [M]$^+$. IR (KBr): $\tilde{\nu}$ = 2955, 2876, 1729, 1610, 1457, 1417, 1390, 1370, 1323, 1300, 1288, 1272, 1217, 1201, 1178, 1162, 1143, 1107, 1060, 1028, 1009, 997, 950, 930, 919, 871, 852, 808, 769, 753, 710 cm^{-1}.

(1*R*,4*R*)-10-(Allyloxy)camphor (8): To a suspension of sodium hydride (1.20 g, 50 mmol) in anhydrous THF (150 mL), a solution of 10-hydroxycamphor (**5**; 8.00 g, 48 mmol) in anhydrous THF (30 mL) was slowly added at 0 °C. After 30 min, the mixture was warmed to room temperature and heated to reflux temperature for 30 min. The reddish mixture was then cooled to 0 °C and allyl bromide (6.04 g, 50 mmol, 4.32 mL) dissolved in anhydrous THF (30 mL) was added dropwise. The reaction mixture was stirred for 30 min at room temperature and then heated to 50 °C and maintained at this temperature for 2 h. The mixture was cooled to 0 °C, quenched with small amounts of EtOH (10 mL), and H_2O (200 mL) was added. The solution was extracted with pentane (4 × 50 mL) and the organic layers were combined, washed with H_2O (2 × 20 mL) and brine (2 × 20 mL) and dried with sodium sulfate. Evaporation of the solvent under reduced pressure, followed by high vacuum, yielded analytical pure **8** (8.31 g, 40 mmol, 84%) as a colorless oil. ^{1}H NMR (500.13 MHz, $CDCl_3$): δ = 5.92–5.85 (m, 1 H, -OCH_2CH-), 5.26 (dd, J = 17.4, ^2J = 1.6 Hz, 1 H, methylene-CH_{2trans}), 5.14 (dd, J = 10.3, ^2J = 1.6 Hz, 1 H, methylene-CH_{2cis}), 3.98 (d, J = 5.3 Hz, 2 H, -OCH_2CH-), 3.60 (d, ^2J = 10.6 Hz, 1 H, -CCH_2O-), 3.56 (d, ^2J = 10.6 Hz, 1 H, -CCH_2O-), 2.60–2.64 [m, 1 H, CHC(CH_3)$_2$], 2.07 (d, J = 18.0 Hz, 1 H), 2.42–2.37 (m, 1 H), 2.12–1.96 (m, 3 H), 1.84 (d, J = 18.3 Hz, 1 H), 1.38–1.34 (m, 2 H), 1.07 (s, 3 H, CH_3), 0.96 (s, 3 H, CH_3) ppm.^{13}C NMR (125.76 MHz, $CDCl_3$): δ = 20.3, 20.7, 25.2, 26.7, 43.5, 43.8, 47.0, 61.3, 66.4, 72.5, 116.3, 135.0, 217.6 ppm. MS (EI): *m*/*z* (%) = 41 (52), 55 (17), 67 (24), 81 (25), 95 (38), 109 (100), 123 (20), 151 (52) [M – (C_3H_5O)]$^+$, 167 (6) [M – (C_3H_5)]$^+$, 208 (13) [M]$^+$. HRMS (EI): *m*/*z* calcd. for $C_{13}H_{20}O_2$ [M]$^+$ 208.1463; found 208.1451. ATR-FTIR: $\tilde{\nu}$ = 2959, 2879, 1732, 1647, 1454, 1417, 1389, 1362, 1348, 1274, 1234, 1193, 1169, 1134, 1093, 1046, 1016, 988, 917, 857, 769, 723 cm^{-1}. $C_{13}H_{20}O_2$ (208.30): calcd. C 74.96, H 9.68; found C 75.10, H 9.74.

Allyl (*R*)-2-(1,2,2-Trimethyl-3-methylenecyclopentyl)acetate (7): Sodium hydride (2.88 g, 120 mmol) was suspended in anhydrous dimethylformamide (20 mL) in a three-necked flask under argon equipped with a reflux condenser, and allylic alcohol (10.22 g, 176 mmol, 12.0 mL), dissolved in anhydrous dimethylformamide (20 mL), was added dropwise. The mixture was stirred at room temperature for 2 h. To this mixture, (1*S*,4*R*)-10-iodocamphor (**3**) (33.38 g, 120 mmol) dissolved in anhydrous dimethylformamide (60 mL) was added dropwise and the mixture was stirred at 80 °C for 24 h. H_2O (100 mL) was added and the mixture was extracted with Et_2O (3 × 100 mL). The organic layers were combined, dried with magnesium sulfate, and the solvent carefully evaporated under reduced pressure (avoid high vacuum) to yield the title compound as a colorless oil (14.4 g, 65 mmol, 54%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 6.01–5.88 (m, 1 H, -OCH_2CH-), 5.34 (dt, J = 17.3, ^2J = 1.5 Hz, 1 H, methylene-CH_{2trans}), 5.26 (dt, J = 10.3, ^2J = 1.3 Hz, 1 H, methylene-CH_{2cis}), 3.80 [dt, J = 6.4, ^2J = 2.1 Hz, 2 H, -CH_2CC(CH_3)-], 4.60 (dt, J = 5.8, J = 1.3 Hz, 2 H, -CH_2O-), 2.53–2.39 (m, 4 H, -CH_2CHCH_2-), 2.21–2.12 (m, 1 H, -CH_2CHCH_2-), 2.08–1.98 [m, 1 H, -(CO)CH_2CHCH_2-], 1.44–1.34 [m, 1 H, -(CO)CH_2CHCH_2-], 1.09 (s, 3 H, CH_3), 0.86 (s, 3 H, CH_3) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 23.4, 26.5, 28.3, 30.4, 35.2, 43.8, 46.5, 65.0, 103.6, 118.2, 132.2, 161.2, 173.3 ppm. MS (EI): *m*/*z* (%) = 41 (35), 55 (9), 67 (17), 79 (12), 93 (30), 108 (100), 121 (20), 133 (4), 150 (7), 167 (32) [M – (C_3H_5)]$^+$, 193 (10) [M – (CH_3)]$^+$, 208 (4) [M]$^+$. HRMS (EI): *m*/*z* calcd. for $C_{13}H_{20}O_2$ [M]$^+$ 208.1463; found 208.1462.

(1*R*,4*S*)-10-(Allyloxy)-3-(trifluoromethanoyl)camphor (9): To a suspension of lithium hydride (160 mg, 20.1 mmol) in anhydrous THF (50 mL) in a three-necked flask under argon equipped with a reflux condenser, was added dropwise a solution of **8** (2.000 g, 9.6 mmol) in anhydrous THF (30 mL) at 0 °C. The mixture was stirred for 15 min at this temperature, then allowed to warm to room temperature and stirred for a further 15 min. The mixture was then heated at reflux temperature for 8 h until the solution became pale-orange. The mixture was cooled to room temperature and trifluoromethyl ester (2.828 g, 22.1 mmol, 2.22 mL) dissolved in anhydrous THF (40 mL) was added dropwise over a period of 30 min. After stirring for 20 min, the mixture was heated at reflux temperature for 12–14 h. Progress of the reaction was monitored by GC analysis of pH neutral samples and, if necessary, additional trifluoromethyl ester (b.p. 316 K) was added. Upon completion of the reaction, concd. hydrochloric acid (10 mL) was added, followed by addition of H_2O (500 mL) while stirring. The mixture was extracted with Et_2O (3 × 100 mL) and the organic layers were combined, washed with H_2O (2 × 200 mL) and brine (2 × 200 mL). The organic phase was

dried with sodium sulfate and the solvent was evaporated under reduced pressure. Drying in vacuo at elevated temperatures over a period of three days yielded analytically pure **9** (2.75 g, 9.0 mmol, 94%) as a colorless, viscous oil. ^{1}H NMR (500.13 MHz, $CDCl_3$): δ = 11.4 (br. s, 1 H, OH), 5.93–5.86 (m, 1 H, -OCH$_2$C*H*-), 5.28 (dd, J = 17.4, ^2J = 1.6 Hz, 1 H, methylene-CH$_{2trans}$), 5.18 (dd, J = 10.5, ^2J = 1.5 Hz, 1 H, methylene-CH$_{2cis}$), 4.00 (d, J = 5.4 Hz, 2 H, -OC*H*$_2$CH-), 3.65 (d, ^2J = 10.4 Hz, 1 H, -CC*H*$_2$O-), 3.63 (d, ^2J = 10.5 Hz, 1 H, -CC*H*$_2$O-), 2.85–2.82 [m, 1 H, C*H*C(CH$_3$)$_2$], 2.16–2.08 (m, 2 H), 1.50–1.39 (m, 2 H), 1.07 (s, 3 H, CH$_3$), 0.97 (s, 3 H, CH$_3$) ppm. ^{13}C NMR (125.76 MHz, $CDCl_3$): δ = 19.4, 21.5, 25.7, 26.5, 47.9, 49.2, 61.6, 65.4, 72.6, 116.1, 116.7, 117.8 (q, J = 2.5 Hz, *C*CCF$_3$), 119.4 (q, J = 276.6 Hz, CF$_3$), 134.7, 148.5 (q, J = 37.2 Hz, *C*CF$_3$), 212.2 ppm. ^{19}F NMR (282.76 MHz, $CDCl_3$): δ = –70.2 ppm. MS (EI): m/z (%) = 177 (21), 191 (17), 205 (17), 233 (100) [M – (C$_4$H$_7$O)]$^+$, 247 (15) [M – (C$_3$H$_5$O)]$^+$, 263 (6) [M – (C$_3$H$_5$)]$^+$, 304 (7) [M]$^+$. HRMS (EI): m/z = calcd. for C$_{15}$H$_{19}$F$_3$O$_3$ [M]$^+$ 304.1286; found 301.1288. ATR-FTIR: $\tilde{\nu}$ = 2963, 2874, 1702, 1648, 1703, 1648, 1507, 1476, 1454, 1419, 1393, 1374, 1363, 1348, 1313, 1293, 1266, 1222, 1188, 1140, 1067, 1004, 989, 924, 891, 854, 816, 809, 753, 717 cm^{-1}. C$_{15}$H$_{19}$F$_3$O$_3$ (304.31): calcd. C 59.20, H 6.29; found C 59.24, H 6.44.

(1*R*,4*S*)-10-(Allyloxy)-3-(heptafluorobutanoyl)camphor (10): To a suspension of lithium hydride (160 mg, 20.1 mmol) in anhydrous THF (50 mL) in a three-necked flask under argon equipped with a reflux condenser, was added dropwise a solution of **8** (2.000 g, 9.6 mmol) in anhydrous THF (30 mL) at 0 °C. The mixture was stirred for 15 min at this temperature, then allowed to warm to room temperature and stirred for a further 15 min. The mixture was then heated at reflux temperature for 10 h until the the solution became pale-orange. The mixture was cooled to room temperature and ethyl heptafluorobutyrate (5.346 g, 22.1 mmol, 3.83 mL) dissolved in anhydrous THF (40 mL) was added dropwise over a period of 30 min. After stirring for 20 min, the mixture was heated at reflux temperature for 14–18 h. Progress of the reaction was monitored by GC analysis of pH neutral samples. After completion of the reaction, concd. hydrochloric acid (10 mL) was added, followed by addition of H$_2$O (500 mL) while stirring. The mixture was extracted with Et$_2$O (3 × 100 mL) and the organic layers were combined, washed with H$_2$O (2 × 200 mL) and brine (2 × 200 mL). The organic phase was dried with sodium sulfate and the solvent was evaporated under reduced pressure. Drying in vacuo at elevated temperatures over a period of three days, followed by distillation at 120 °C under high vacuum (small-sized distillation apparatus equipped with a short connecting tube) yielded pure **10** (2.898 g, 7.2 mmol, 75%) as a colorless, viscous oil. ^{1}H NMR (500.13 MHz, $CDCl_3$): δ = 11.69 (br. s, 1 H, OH), 5.93–5.86 (m, 1 H, OCH$_2$C*H*), 5.28 (dd, J = 17.3, ^2J = 1.5 Hz, 1 H, methylene-CH$_{2trans}$), 5.18 (dd, J = 10.5, ^2J = 1.5 Hz, 1 H, methylene-CH$_{2cis}$), 4.00 (d, J = 5.2 Hz, 2 H, OC*H*$_2$CH), 3.66 (d, ^2J = 10.7 Hz, 1 H, -CC*H*$_2$O-), 3.63 (d, ^2J = 10.7 Hz, 1 H, -CC*H*$_2$O-), 2.82–2.79 [m, 1 H, C*H*C(CH$_3$)$_2$], 2.15–2.09 (m, 2 H), 1.49–1.42 (m, 2 H), 1.07 (s, 3 H, CH$_3$), 0.96 (s, 3 H, CH$_3$) ppm. ^{13}C NMR (125.76 MHz, $CDCl_3$): δ = 19.4, 21.4, 25.6, 26.4, 48.2, 49.3, 61.5, 65.4, 72.6, 116.7, 120.6, 134.7, 148.7 (dd, J = 29.5, J = 29.7 Hz, *C*CF$_2$CF$_2$CF$_3$), 212.0 ppm. ^{19}F NMR (282.76 MHz, $CDCl_3$): δ = –127.3 to –127.4 (m, C*F*$_2$CF$_2$CF$_3$), –119.4 (qdd, J = 8.8, 2.0, 283.4 Hz, CF$_2$C*F*$_2$CF$_3$), –117.9 (qd, J = 8.8, 283.4 Hz, CF$_2$C*F*$_2$CF$_3$), –119.4 (t, J = 8.8 Hz, CF$_2$CF$_2$C*F*$_3$) ppm. MS (EI): m/z (%) = 177 (7), 235 (5), 291 (9), 305 (10), 333 (100) [M – (C$_4$H$_7$O)]$^+$, 347 (14) [M – (C$_3$H$_5$O)]$^+$, 363 (4) [M – (C$_3$H$_5$)]$^+$, 404 (16) [M]$^+$. HRMS (EI): m/z calcd. for C$_{17}$H$_{19}$F$_7$O$_3$ [M]$^+$ 404.1222; found 404.1212. ATR-FTIR: $\tilde{\nu}$ = 2963, 2874, 1699, 1642, 1479, 1454, 1422, 1393, 1374, 1345, 1315, 1292, 1215, 1185, 1165, 1118, 1097, 1067, 1023, 958, 920, 897, 886, 855, 813, 780, 743, 724 cm^{-1}. C$_{17}$H$_{19}$F$_7$O$_3$ (404.32): calcd. C 50.50, H 4.74; found C 51.05 H 5.01.

(1*S*,4*R*)-10-Thiocamphor (6): (1*S*)-10-Camphorsulfonic acid (50.0 g, 0.215 mol) and thionyl chloride (51.21 g, 0.430 mol, 31.3 mL) were placed in a three-necked flask equipped with a condenser under an argon atmosphere, and an exhaust line for direct gas discharge into the fume hood. The reaction mixture was heated at 80 °C for 4–5 h until the evolution of hydrochloric acid and sulfur dioxide ceased. Thionyl chloride was then removed under reduced pressure in vacuo at elevated temperature. To the crude 10-camphorsulfonic acid was added triphenylphosphane (169.2 g, 0.645 mol) together with a 1:4 mixture of H$_2$O and dioxane (1500 mL) and the suspension was stirred at reflux temperature for 4 h. The suspension was allowed to cool to room temperature, H$_2$O (600 mL) was added, and the mixture was extracted with pentane (4 × 100 mL). The organic layers were combined, washed with H$_2$O (8 × 100 mL), followed by brine (2 × 25 mL) and dried with sodium sulfate. Evaporation of the solvent under reduced pressure and high vacuum yielded pure **6** (42.1 g, 0.228, 94%) as colorless crystals; m.p. 55–57 °C. ^{1}H NMR (300.51 MHz, $CDCl_3$): δ = 2.88 (d, J = 6.8 Hz, 1 H, C*H*$_2$SH), 2.83 (d, J = 6.8 Hz, 1 H, C*H*$_2$SH), 2.39–2.30 (m, 2 H), 2.08–2.05 (m, 1 H), 2.03–1.83 (m, 4 H), 1.72–1.65 (m, 1 H), 1.41–1.35 (m, 1 H), 1.01 (s, 3 H, CH$_3$), 0.90 (s, 3 H, CH$_3$) ppm. ^{13}C NMR (75.56 MHz, $CDCl_3$): δ = 19.8, 20.3, 21.4, 26.6, 27.0, 43.2, 43.6, 47.8, 60.6, 217.8 ppm. MS (EI): m/z (%) = 55 (18), 67 (30), 81 (47), 95 (42), 109 (50), 123 (37), 141 (34), 151(23) [M – (SH)]$^+$, 169 (5) [M – (CH$_3$)]$^+$, 184 (100) [M]$^+$. C$_{10}$H$_{16}$OS (184.30): calcd. C 65.17, H 8.75; found C 65.40, H 8.76.

(1*S*,4*R*)-10-(Allylthio)camphor (11): To a suspension of sodium hydride (2.74 g, 114 mmol) in anhydrous THF (250 mL) was slowly added a solution of **6** (20.00 g, 109 mol) in anhydrous THF (50 mL) at 0 °C. After 30 min, the mixture was allowed to warm to room temperature and then heated at reflux temperature for 30 min. The reddish mixture was then cooled to 0 °C and allyl bromide (13.39 g, 111 mmol, 9.58 mL), dissolved in anhydrous THF (50 mL), was added dropwise. The reaction mixture was stirred for 30 min at room temperature and then heated to 50 °C and maintained at this temperature for 2 h. The mixture was cooled to 0 °C, quenched with small amounts of EtOH (15 mL), and H$_2$O (400 mL) was added. The solution was extracted with pentane (4 × 100 mL) and the organic layers were combined, washed with H$_2$O (2 × 50 mL) and brine (2 × 50 mL), and dried with sodium sulfate. Evaporation of the solvent under reduced pressure, followed by high vacuum, yielded analytically pure (1*R*,4*R*)-10-(allyloxy)camphor (19.74 g, 88 mmol, 81%) as a colorless oil. ^{1}H NMR (500.13 MHz, $CDCl_3$): δ = 5.84–5.75 (m, 1 H, -SCH$_2$C*H*-), 5.15–5.09 (m, 2 H, methylene-CH$_2$), 3.20–3.12 (m, 2 H), 2.74 (d, ^2J = 13.1 Hz, 1 H, -CC*H*$_2$S-), 2.47 (d, ^2J = 13.0 Hz, 1 H, -CC*H*$_2$S-), 2.39–2.34 (m, 1 H), 2.08–1.96 (m, 3 H), 1.86 (d, J = 18.4 Hz, 1 H), 1.53–1.48 (m, 1 H), 1.39–1.35 (m, 1 H), 1.04 (s, 3 H, CH$_3$), 0.90 (s, 3 H, CH$_3$) ppm. ^{13}C NMR (125.76 MHz, $CDCl_3$): δ = 20.20, 20.2, 26.8, 26.9, 27.7, 37.0, 43.1, 43.5, 47.8, 60.9, 117.1, 134.4, 217.5 ppm. MS (EI): m/z (%) = 55 (28), 67 (30), 81 (39), 95 (14), 109 (39), 123 (20), 151 (16) [M – (C$_3$H$_5$S)]$^+$, 168 (13), 183 (62) [M – (C$_3$H$_5$)]$^+$, 224 (100) [M]$^+$. HRMS (EI): m/z = calcd. for C$_{13}$H$_{20}$OS [M]$^+$ 224.1325; found 224.1237. ATR-FTIR: $\tilde{\nu}$ = 3080, 2958, 2887, 1725, 1634, 1469, 1453, 1416, 1389, 1372, 1317, 1298, 1281, 1227, 1197, 1159, 1128, 1101, 1062, 1049, 1026, 989, 964, 914, 866, 851, 754 cm^{-1}. C$_{13}$H$_{20}$OS (224.36): calcd. C 69.59, H 8.97; found C 69.54, H 8.97.

(1*S*,4*S*)-10-(Allylthio)-3-(heptafluorobutanoyl)camphor (12): Lithium hydride (149 mg, 18.7 mmol) in anhydrous THF (60 mL) was

placed in a three-necked flask under argon equipped with a reflux condenser, and a solution of **11** (2.000 g, 8.9 mmol) in anhydrous THF (40 mL) was added dropwise at 0 °C. After stirring for 15 min, the suspension was allowed to warm to room temperature and stirred for a further 15 min. The mixture was then heated at reflux temperature for 24 h until the solution became pale-orange. The mixture was cooled to room temperature and trifluoromethyl ester (2.630 g, 20.5 mmol, 2.07 mL) dissolved in anhydrous THF (30 mL) was added dropwise over a period of 30 min. After stirring for 20 min, the mixture was heated at reflux temperature for 12–14 h. Progress of the reaction was monitored by GC analysis of pH neutral samples and, if necessary, additional trifluoromethyl ester (b.p. 316 K) was added. Upon completion of the reaction, concd. hydrochloric acid (10 mL) was added, followed by addition of H_2O (500 mL) while stirring. The mixture was extracted with Et_2O (3 × 100 mL) and the organic layers were combined, washed with H_2O (2 × 200 mL) and brine (2 × 200 mL). The organic phase was dried with sodium sulfate and the solvent was evaporated under reduced pressure. Drying in vacuo at elevated temperatures over a period of three days yielded analytically pure **12** (2.693 g, 8.4 mmol, 94%) as a colorless, viscous oil. ^{1}H NMR (300.08 MHz, $CDCl_3$): δ = 11.43 (br. s, 1 H, OH), 5.87–5.74 (m, 1 H, -SCH$_2$C*H*-), 5.17–5.11 (m, 2 H, methylene-CH$_2$), 3.26–3.13 (m, 2 H), 2.87–2.83 (m, 1 H), 2.80 (d, ^2J = 13.3 Hz, 1 H, -CC*H*$_2$S-), 2.51 (d, ^2J = 13.2 Hz, 1 H, -CC*H*$_2$S-), 2.17–2.03 (m, 2 H), 1.67–1.58 (m, 1 H), 1.50–1.44 (m, 1 H), 1.04 (s, 3 H, CH$_3$), 0.91 (s, 3 H, CH$_3$) ppm. ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 19.3, 20.9, 26.5, 26.8, 27.4, 36.9, 47.6, 50.1, 61.3, 117.4, 121.1 (CF$_3$), 134.2, 148.4 (m, J = 37.0 Hz, *C*CF$_3$), 212.4 ppm. ^{19}F NMR (282.76 MHz, $CDCl_3$): δ = –70.1 ppm. MS (EI): *m*/*z* (%) = 191 (15), 219 (21), 233 (24) [M – (C_4H_7S)]$^+$, 247 (34) [M – (C_3H_5S)]$^+$, 261 (27), 279 (56) [M – (C_3H_5)]$^+$, 320 (100) [M]$^+$. HRMS (EI): *m*/*z* = calcd. for $C_{15}H_{19}F_3O_2S$ [M]$^+$ 320.1058; found 320.1068. ATR-FTIR: $\tilde{\nu}$ = 2962, 2915, 1702, 1652, 1479, 1453, 1428, 1405, 1393, 1975, 1316, 1267, 1224, 1187, 1123, 1112, 1055, 1021, 1004, 990, 973, 952, 916, 869, 888, 748, 710 cm^{-1}. $C_{15}H_{19}F_3O_2S$ (320.37): calcd. C 56.24, H 5.98; found C 56.28, H 6.09.

(1*S*,4*S*)-10-(Allylthio)-3-(heptafluorobutanoyl)camphor (13): Lithium hydride (149 mg, 18.7 mmol) in anhydrous THF (50 mL) was placed in a three-necked flask under argon equipped with a reflux condenser, and a solution of **11** (2.000 g, 8.9 mmol) in anhydrous THF (40 mL) was added dropwise at 0 °C. After stirring for 15 min, the suspension was allowed to warm to room temperature and stirred for a further 15 min. The mixture was heated at reflux temperature for 24 h until the solution became pale-orange. The mixture was cooled to room temperature and ethyl heptafluorobutyrate (4.963 g, 20.5 mmol, 3.56 mL) dissolved in anhydrous THF (30 mL) was added dropwise over a period of 30 min. After stirring for 20 min, the mixture was heated at reflux temperature for 14–18 h. Reaction progress was monitored by GC analysis of pH neutral samples. Upon completion of the reaction, concd. hydrochloric acid (10 mL) was added, followed by addition of H_2O (500 mL) while stirring. The mixture was extracted with Et_2O (3 × 100 mL) and the organic layers were combined, washed with H_2O (2 × 200 mL) and brine (2 × 200 mL). The organic phase was dried with sodium sulfate and the solvent was evaporated under reduced pressure. Drying in vacuo at elevated temperatures over a period of three days, followed by distillation at 120 °C under high vacuum (small-sized distillation apparatus equipped with a short connecting tube) yielded pure **13** (2.893 g, 6.9 mmol, 77%) as a colorless, viscous oil. ^{1}H NMR (500.13 MHz, $CDCl_3$): δ = 11.68 (br. s, 1 H, OH), 5.84–5.76 (m, 1 H, -SCH$_2$C*H*-), 5.16–5.12 (m, 2 H, methylene-CH$_2$), 3.24–3.16 (m, 2 H), 2.83–2.81 (m, 1 H), 2.80 (d, ^2J = 13.2 Hz, 1 H, -CC*H*$_2$S-), 2.51 (d, ^2J = 13.2 Hz, 1 H, -CC*H*$_2$S-), 2.14–2.06 (m, 2 H), 1.65–1.60 (m, 1 H), 1.49–1.46 (m, 1 H), 1.04 (s, 3 H, CH$_3$), 0.89 (s, 3 H, CH$_3$) ppm. ^{13}C NMR (125.76 MHz, $CDCl_3$): δ = 19.3, 20.8, 26.5, 26.8, 27.4, 37.0, 43.3 (d, J = 47.7 Hz), 47.9, 50.1, 61.2, 117.4, 120.1 (CF$_3$), 134.2, 148.8 (dd, J = 29.4, 29.5 Hz, *C*CF$_2$CF$_2$CF$_3$), 212.2 ppm. ^{19}F NMR (282.46 MHz, $CDCl_3$): δ = –127.4 (s, -C*F*$_2$CF$_2$CF$_3$), –119.4 (qd, J = 9.0, 283.1 Hz, -CF$_2$C*F*$_2$CF$_3$), –117.9 (qd, J = 9.0, 283.5 Hz, CF$_2$C*F*$_2$CF$_3$), –80.6 (t, J = 8.8 Hz, CF$_2$CF$_2$C*F*$_3$) ppm. MS (EI): *m*/*z* (%) = 251 (7), 291 (12), 305 (9), 319 (16), 333 (19) [M – (C_4H_7S)]$^+$, 347 (32) [M – (C_3H_5S)]$^+$, 379 (53) [M – (C_3H_5)]$^+$, 420 (100) [M]$^+$. HRMS (EI): *m*/*z* calcd. for $C_{17}H_{19}F_7O_2S$ [M]$^+$ 420.0994; found 420.0999. ATR-FTIR: $\tilde{\nu}$ = 2963, 2916, 1743, 1700, 1639, 1479, 1454, 1429, 1405, 1394, 1375, 1338, 1312, 1292, 1258, 1215, 1183, 1162, 1110, 1099, 1058, 1025, 1007, 991, 973, 946, 918, 881, 813, 742, 729 cm^{-1}. $C_{17}H_{19}F_7O_2S$ (420.38): calcd. C 48.57, H 4.56; found C 48.81, H 4.86.

General Procedure for the Hydrosilylation of (1*R*,4*S*)-10-(Allyloxy)-3-(heptafluorobutanoyl)camphor on Polysiloxanes: Hydrido-methylpolysiloxane (0.17–0.36 mmol polymer; 3.5, 10.2, or 20.0% SiH content) was dissolved in anhydrous toluene (40 mL) under an argon atmosphere. To the solution was added **10** (for exact amounts, see experimental details of each compound) and five drops approx. 50 mg, 0.1 mg of "Pt", 5.1 × 10^{-4} mmol "Pt", 0.05 mol-%) of platinum-1,1,3,3-tetramethyl-1,3-divinyldisoloxane (Karstedt's catalyst, 2 wt.-% "Pt" in toluene). The solution was stirred for 5 h at room temperature under ultrasonication (control of temperature!) followed by 36 h starting at room temperature reaching 70 °C after 10 h under ultrasonication. Progress of the reaction was monitored by ^{1}H NMR spectroscopic analysis and additional (1*R*,4*S*)-10-(allyloxy)-3-(heptafluorobutanoyl)camphor (**10**) or hydrido-methylpolysiloxane was added until all SiH and all allylic proton signals disappeared, indicating full conversion of the starting materials. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the crude product was dissolved in CH_2Cl_2 (25 mL), filtered (pore size, diameter: 0.45 μm) and MeOH (5 mL) and active charcoal were added. The mixture was stirred for 24 h at reflux temperature, filtered (pore size, diameter: 0.45 μm) and the solvents were evaporated under reduced pressure. Column chromatography (silica; length: 19.0 cm, diameter: 1.5 cm; CH_2Cl_2/EtOH, 98:2) of the crude polymer yielded the analytically pure (1*R*,4*S*)-10-(allyloxy)-3-(heptafluorobutanoyl)camphor immobilized on polysiloxane. For ease of reproduction, the following amounts of starting materials proved to be necessary for complete immobilization and full consumption of starting material [23, 49, and 92 mg **10** per 100 mg of hydrido-methylpolysiloxane (3.5, 10.2, and 20.0% SiH content)].

[(1*R*,4*S*)-3-(Heptafluorobutanoyl)-10-(propylenoxy)camphor]$_{20.0\%}$-polysiloxane (16): Prepared according to the general procedure for immobilization of **10** on polysiloxane. Hydridomethylpolysiloxane (523 mg, 0.174 mmol polymer, 20.0% SiH content) and **10** (480 mg, 0.129 mmol) were reacted and purified by the described procedure to give **16** (735 mg, 73%) as a colorless, viscous oil. ^{1}H NMR (500.13 MHz, $CDCl_3$): δ = 11.70 (br. s, 1 H, OH), 3.63 (d, J = 10.5 Hz, 1 H, -CCH$_2$O-), 3.61 (d, J = 10.5 Hz, 1 H, -CCH$_2$O-), 3.40 (dt, J = 1.8, J = 6.6 Hz, 2 H, -OC*H*$_2$CH$_2$-), 2.82–2.78 [m, 1 H, C*H*C(CH$_3$)$_2$], 2.15–2.08 (m, 2 H, -OCH$_2$C*H*$_2$-), 1.61–1.54 (m, 2 H, -CHC*H*$_2$-), 1.47–1.39 (m, 2 H, -CHCH$_2$C*H*$_2$-), 1.06 (s, 3 H, CH$_3$), 0.95 (s, 3 H, CH$_3$), 0.91 (t, J = 7.4 Hz, 2 H, -SiCH$_2$-), 0.56–0.46 [m, 0.4 H, -Si(C*H*$_3$)$_{[1-n]}$-], 0.12–0.04 [m, 19 H, -O(C*H*$_3$)$_{(1-n)}$-Si(C*H*$_3$)$_{(1-n)}$ (CH$_3$)$_{[n]}$(hfpc)$_{[n]}$-] ppm. ^{13}C NMR (125.76 MHz, $CDCl_3$): δ = 0.8, 1.0, 1.8, 1.6, 19.4, 21.4, 22.8, 25.5, 26.4, 48.2, 49.3, 61.6, 65.9, 73.5, 111.0 (dd, J = 32.0, 29.8 Hz, CF$_2$*C*F$_2$CF$_3$), 116.6

(d, J = 32.0 Hz, $CF_2CF_2CF_3$), 118.6 (d, J = 32.0 Hz, $CF_2CF_2CF_3$), 120.7, 148.6 (dd, J = 26.1, 26.2 Hz, $CCF_2CF_2CF_3$), 212.0 ppm. ATR-FTIR: $\tilde{\nu}$ = 2963, 2867, 1735, 1701, 1642, 1507, 1580, 1457, 1392, 1378, 1344, 1315, 1259, 1229, 1216, 1186, 1164, 1068, 1091, 1015, 979, 957, 920, 896, 886, 841, 795, 744, 723, 707 cm^{-1}.

[(1*R*,4*S*)-3-(Heptafluorobutanoyl)-10-(propylenoxy)camphor]$_{10.2\%}$-polysiloxane (15): Prepared according to the general procedure for immobilization of **10** on polysiloxane. Hydridomethylpolysiloxane (1092 mg, 0.364 mmol polymer, 10.2% SiH content) and **10** (532 mg, 1.316 mmol) were reacted and purified by the described procedure to give **15** (605 mg, 73%) as a colorless oil. Analytical data were in agreement with polymer-bound [(1*R*,4*S*)-3-(heptafluorobutanoyl)-10-(propylenoxy)camphor] on polysiloxane (hfpc content 20.0%). ATR-FTIR: $\tilde{\nu}$ = 2962, 2879, 1734, 1700, 1654, 1643, 1457, 1393, 1374, 1344, 1315, 1258, 1231, 1218, 1185, 1164, 1067, 1011, 959, 921, 897, 793, 744, 724, 704 cm^{-1}.

[(1*R*,4*S*)-3-(Heptafluorobutanoyl)-10-(propylenoxy)camphor]$_{3.5\%}$-polysiloxane (14): Prepared according to the general procedure for immobilization of **10** on polysiloxane. Hydridomethylpolysiloxane (560 mg, 0.187 mmol polymer, 3.5% SiH content) and **10** (131 mg, 0.324 mmol) were reacted and purified by the described procedure to give **14** (605 mg, 88%) as a colorless oil. Analytical data were in agreement with polymer-bound [(1*R*,4*S*)-3-(heptafluorobutanoyl)-10-(propylenoxy)camphor] on polysiloxane (hfpc content 20.0%). ATR-FTIR: $\tilde{\nu}$ = 2962, 2905, 1735, 1700, 1415, 1353, 1257, 1231, 1216, 1011, 833, 788, 699 cm^{-1}.

General Procedure for the Preparation of Nickel(II) Bis[(1*R*,4*S*)-3-(heptafluorobutanoyl)-10-(propylenoxy)camphorate]$_{20.0\%}$-polysiloxane (Chirasil-Nickel-OC$_3$): Metal incorporation was accomplished by using a modified procedure of Fluck.[59] A two-phase solution of ligand polymer [100–390 mg, 3.5, 10.2, or 20.0% (1*R*,4*S*)-3-(heptafluorobutanoyl)-10-(propylenoxy)camphor content] in a mixture of anhydrous *n*-heptane/MeOH (3:2, 100 mL) was stirred for 1 h at room temperature and an additional 1 h at reflux temperature, upon which the solvents became miscible. The ligand polymer dissolved and cooling back to room temperature resulted in separation of the two phases (this step is recommended to achieve complete polymer dissolvation and polymer-purification prior to metal incorporation). To the solution was added nickel(II) acetate tetrahydrate (for exact amounts, see the experimental details of each compound) and the mixture was stirred at room temperature for 1 h and an additional 1 h at reflux temperature. The solution was allowed to cool to room temperature, resulting in phase reseparation. Metal incorporation can be monitored by the color change of the polymer-containing *n*-heptane phase from colorless to green, as well as by decolorization of the nickel-salt-containing MeOH phase. The *n*-heptane phase was decanted off and the MeOH layer was extracted once with *n*-heptane (30 mL). The organic layers were combined, the solvent was evaporated under reduced pressure, and the residue was dissolved in *n*-pentane (50 mL). The organic phase was washed with H_2O (5 × 100 mL) and dried with small amounts of magnesium sulfate. Evaporation of the solvent and drying in vacuo for three days yielded nickel(II) bis[(1*R*,4*S*)-3-(heptafluorobutanoyl)-10-(propylenoxy)camphorate]polysiloxanes (Chirasil-Nickel-OC$_3$) as green, viscous oils.

Nickel(II) Bis[(1*R*,4*S*)-3-(Heptafluorobutanoyl)-10-(propylenoxy)-camphorate]$_{3.5\%}$-polysiloxane (Chirasil-Nickel-OC$_{3\ 3.5\%}$; 17): Prepared according to the general procedure for the preparation of Chirasil-Nickel-OC$_3$. Thus, ligand polymer (298 mg) and nickel(II) acetate tetrahydrate (15 mg, 0.060 mmol) were reacted and purified by the described procedure to give nickel(II) bis[(1*R*,4*S*)-3-(heptafluorobutanoyl)-10-(propylenoxy)camphorate]$_{3.5\%}$-polysiloxane (277 mg, 92%) as a pale-green oil. ATR-FTIR: $\tilde{\nu}$ = 2962, 2905, 1737, 1654, 1637, 1481, 1447, 1413, 1344, 1257, 1231, 1216, 1182, 1010, 835, 788, 700 cm^{-1}.

Nickel(II) Bis[(1*R*,4*S*)-3-(heptafluorobutanoyl)-10-(propylenoxy)-camphorate]$_{10.2\%}$-polysiloxane (Chirasil-Nickel-OC$_{3\ 10.2\%}$; 18): Prepared according to the general procedure for the preparation of Chirasil-Nickel-OC$_3$. Thus, ligand polymer (390 mg) and nickel(II) acetate tetrahydrate (56 mg, 0.225 mmol) were reacted and purified by the described procedure to give nickel(II) bis[(1*R*,4*S*)-3-(heptafluorobutanoyl)-10-(propylenoxy)camphorate]$_{10.2\%}$-polysiloxane (360 mg, 89%) as a pale-green oil. ATR-FTIR: $\tilde{\nu}$ = 2962, 2906, 1739, 1640, 1627, 1576, 1512, 1481, 1445, 1412, 1373, 1345, 1258, 1230, 1216, 1183, 1075, 1010, 828, 788, 751, 702 cm^{-1}.

Nickel(II) Bis[(1*R*,4*S*)-3-(heptafluorobutanoyl)-10-(propylenoxy)-camphorate]$_{20.0\%}$-polysiloxane (Chirasil-Nickel-OC$_{3\ 20.0\%}$; 19): Prepared according to the general procedure for the preparation of Chirasil Nickel-OC$_3$. Thus, ligand polymer (190 mg) and nickel(II) acetate tetrahydrate (53 mg, 0.060 mmol) were reacted and purified by the described procedure to give nickel(II) bis[(1*R*,4*S*)-3-(heptafluorobutanoyl)-10-(propylenoxy)camphorate]$_{20.0\%}$-polysiloxane- (173 mg, 85%) as a green oil. ATR-FTIR: $\tilde{\nu}$ = 2962, 2878, 1739, 1641, 1627, 1481, 1457, 1413, 1388, 1373, 1344, 1258, 1229, 1215, 1183, 1163, 1075, 1015, 918, 833, 789, 750, 703 cm^{-1}.

Lanthanum(III) Tris[(1*R*,4*S*)-3-(heptafluorobutanoyl)-10-(propylenoxy)camphorate]$_{20.0\%}$-polysiloxane (Chirasil-Lanthanum-OC$_{3\ 20.0\%}$; 24): Incorporation of lanthanum was accomplished by following the standard procedure for Chirasil-Vanadyl-OC$_3$. Vanadyl(IV) sulfate pentahydrate was replaced by lanthanum(III) acetate hydrate (87.6 mg, 0.226 mmol), ligand polymer (200 mg), and anhydrous, distilled triethylamine (0.50 mL, 685 mg, 6.772 mmol). Incorporation of lanthanum was indicated by a color change of the *n*-heptane phase from colorless to orange-red. Workup and purification, including column chromatography as described for Chirasil-Vanadyl-OC$_3$, gave lanthanum(III) tris[(1*R*,4*S*)-3-(heptafluorobutanoyl)-10-(propylenoxy)camphorate]$_{20.0\%}$-polysiloxane (199 mg, 86%) as an orange to red viscous oil. ATR-FTIR: $\tilde{\nu}$ = 2962, 2879, 1687, 1684, 1645, 1525, 1480, 1455, 1413, 1387, 1372, 1344, 1258, 1229, 1214, 1197, 1184, 1161, 1074, 1014, 918, 838, 791, 748 cm^{-1}.

Europium(III) Tris[(1*R*,4*S*)-3-(heptafluorobutanoyl)-10-propylenoxycamphorate]$_{20.0\%}$-polysiloxane (Chirasil-Europium-OC$_{3\ 20.0\%}$; 23): Europium was incorporated by following the standard procedure used for Chirasil Vanadyl-OC$_3$. Vanadyl(IV) sulfate pentahydrate was replaced by europium(III) acetate hydrate (78.8 mg, 0.196 mmol), ligand polymer (212 mg), and anhydrous, distilled triethylamine (0.50 mL, 685 mg, 6.772 mmol). Incorporation of lanthanum was indicated by a change in color of the *n*-heptane phase from colorless to yellow. Workup and purification, including column chromatography as described for Chirasil-Vanadyl-OC$_3$, gave lanthanum(III) tris[(1*R*,4*S*)-3-(heptafluorobutanoyl)-10-(propylenoxy)camphorate]$_{20.0\%}$-polysiloxane (193 mg, 80%) as an orange to yellow to pale-orange viscous oil. ATR-FTIR: $\tilde{\nu}$ = 2962, 2877, 1738, 1702, 1685, 16447, 1577, 1575, 1530, 1479, 1457, 1413, 1389, 1372, 1345, 1258, 1229, 1214, 1198, 1182, 1161, 1075, 7014, 917, 833, 791, 745, 703 cm^{-1}.

General Procedure for the Preparation of Oxovanadium(IV) Bis[(1*R*,4*S*)-3-(heptafluorobutanoyl)-10-(propylenoxy)camphorate]$_{20.0\%}$-polysiloxane (Chirasil-Vanadyl-OC$_3$): Incorporation of oxovanadium was accomplished by using a modified procedure of Fluck.[59] Ligand polymer [200–450 mg, 3.5, 10.2 or 20.0% (1*R*,4*S*)-3-(heptafluorobutanoyl)-10-(propylenoxy)camphor content] was dissolved in a mixture of anhydrous *n*-heptane/MeOH (3:2, 100 mL) and stirred for 1 h at room temperature and 1 h at

reflux temperature, upon which the solvents became miscible (this step is recommended to furnish clean polymer dissolvation and polymer-purification prior to metal incorporation). Excess oxovanadium(IV) sulfate pentahydrate was added at room temperature and the mixture was stirred for 1 h (for exact amounts, see experimental details of each compound). The solution was then heated at reflux temperature, anhydrous, distilled triethyl-amine was added and the solution was stirred for 3–4 h at this temperature. Reaction progress was monitored by following a color change of the *n*-heptane phase from colorless to purple, as well as by decolorization of the vanadyl-sulfate-containing MeOH phase. Purification was accomplished by following the workup procedure, including column chromatography, as described for the preparation of Chirasil-Nickel-OC_3. The oxovanadium(IV) bis[(1*R*,4*S*)-3-(heptafluorobutanoyl)-10-(propylenoxy)camphorate]polysiloxanes (Chirasil-Vanadyl-OC_3) were obtained as reddish-purple, viscous oils.

Oxovanadium(IV) Bis[(1*R*,4*S*)-3-(heptafluorobutanoyl)-10-(propylenoxy)camphorate]$_{3.5\%}$-polysiloxane (Chirasil-Vanadyl-$OC_{3\ 3.5\%}$; 20): Prepared according to the general procedure used for the preparation of Chirasil-Vanadyl-OC_3. Thus, ligand polymer (200 mg), vanadyl(IV) sulfate pentahydrate (270 mg, 1.067 mmol, excess), and triethylamine (0.10 mL, 138 mg, 1.364 mmol) were reacted and purified by using the described procedure to give oxovanadium(IV) bis[(1*R*,4*R*)-3-(heptafluorobutanoyl)-10-(propylenoxy)camphorate]$_{3.5\%}$-polysiloxane (157 mg, 79%; corresponding to polymer starting material) as a pale reddish-purple oil. ATR-FTIR: $\tilde{\nu}$ = 2962, 2905, 1739, 1639, 1446, 1412, 1352, 1257, 1231, 1216, 1182, 1011, 834, 789, 701 cm^{-1}.

Oxovanadium(IV) Bis[(1*R*,4*S*)-3-(heptafluorobutanoyl)-10-(propylenoxy)camphorate]$_{10.2\%}$-polysiloxane (Chirasil-Vanadyl-$OC_{3\ 10.2\%}$; 21): Prepared according to the general procedure used for the preparation of Chirasil-Vanadyl-OC_3. Thus, ligand polymer (450 mg), vanadyl(IV) sulfate pentahydrate (1.750 g, 6.917 mmol, excess), and triethylamine (0.33 mL, 455 mg, 4.504 mmol) were reacted and purified by the described procedure to give oxovanadium(IV) bis[(1*R*,4*S*)-3-(heptafluorobutanoyl)-10-(propylenoxy)camphorate]$_{10.2\%}$-polysiloxane (314 mg, 70%; corresponding to polymer starting material) as a reddish-purple oil. ATR-FTIR: $\tilde{\nu}$ = 2962, 2905, 1739, 1685, 1638, 1576, 1560, 1517, 1446, 1413, 1373, 1346, 1258, 1231, 1217, 1184, 1197, 1011, 828, 789, 701 cm^{-1}.

Oxovanadium(IV) Bis[(1*R*,4*S*)-3-(heptafluorobutanoyl)-10-(propylenoxy)camphorate]$_{20.0\%}$-polysiloxane (Chirasil-Vanadyl-$OC_{320.0\%}$; 22): Prepared according to the general procedure used for the preparation of Chirasil-Vanadyl-OC_3. Thus, ligand polymer (230 mg), vanadyl(IV) sulfate pentahydrate (1.760 g, 6.957 mmol, excess), and triethylamine (0.33 mL, 455 mg, 4.504 mmol) were reacted and purified by the described procedure to give oxovanadium(IV) bis[(1*R*,4*S*)-3-(heptafluorobutanoyl)-10-(propylenoxy)camphorate]$_{10.2\%}$-polysiloxane (170 mg, 74%; corresponding to polymer starting material) as a reddish-purple, viscous oil. ATR-FTIR: $\tilde{\nu}$ = 2962, 2875, 1737, 1702, 1700, 1686, 1635, 1521, 1479, 1457, 1414, 1389, 1373, 1346, 1258, 1230, 1217, 1197, 1185, 1165, 1013, 917, 829, 792 cm^{-1}.

Supporting Information (see footnote on the first page of this article): ^1H, ^{13}C, ^{19}F NMR spectra and IR data for ligand **10**, hydridopolysiloxane and immobilized polymeric compounds **14**–**24**.

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[1] V. Schurig, *Inorg. Chem.* **1972**, *11*, 736.
[2] V. Schurig, F. Betschinger, *Chem. Rev.* **1992**, *92*, 873.
[3] V. Schurig, *J. Chromatogr. A* **2001**, *906*, 275.
[4] V. Schurig, *J. Chromatogr. A* **2002**, *965*, 315.
[5] V. Schurig, *Angew. Chem.* **1984**, *96*, 733; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 747; V. Schurig, *Angew. Chem.* **1984**, *96*, 733.
[6] V. Schurig, H.-P. Nowotny, *Angew. Chem.* **1990**, *102*, 969; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 939; V. Schurig, H.-P. Nowotny, *Angew. Chem.* **1990**, *102*, 969.
[7] V. Schurig, D. Schmalzing, U. Mühleck, M. Jung, M. Schleimer, P. Mussche, C. Duvekot, J. C. Buyten, *J. High Resolut. Chromatogr.* **1990**, *13*, 713.
[8] W. A. König, *J. High Resolut. Chromatogr.* **1993**, *16*, 338.
[9] H. Cousin, O. Trapp, V. Peulon-Agasse, X. Pannecoucke, L. Banspach, G. Trapp, Z. Jiang, J. C. Combret, V. Schurig, *Eur. J. Org. Chem.* **2003**, *17*, 3273.
[10] G. Sicoli, Z. Jiang, L. Jicsinsky, V. Schurig, *Angew. Chem.* **2005**, *117*, 4161; *Angew. Chem. Int. Ed.* **2005**, *44*, 4092; G. Sicoli, Z. Jiang, L. Jicsinsky, V. Schurig, *Angew. Chem.* **2005**, *117*, 4161.
[11] G. Sicoli, L. Tomoyuki, L. Jicsinszky, V. Schurig, *Eur. J. Org. Chem.* **2008**, 4241.
[12] R. R. Fraser, M. A. Petit, J. K. Saunders, *J. Chem. Soc., Chem. Commun.* **1971**, 1450.
[13] B. Freibush, M. F. Richardson, R. E. Sievers, C. S. J. Springer, *J. Am. Chem. Soc.* **1972**, *94*, 6717.
[14] V. Schurig, D. Wistuba, *Angew. Chem.* **1984**, *96*, 808.
[15] V. Schurig, W. Bürkle, A. Zlatkis, C. F. Poole, *Naturwissenschaften* **1979**, *66*, 423.
[16] S. Reich, O. Trapp, V. Schurig, *J. Chromatogr. A* **2000**, *892*, 487.
[17] V. Schurig, *Angew. Chem.* **1977**, *89*, 113; *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 110; V. Schurig, *Angew. Chem.* **1977**, *89*, 113.
[18] V. Schurig, R. Weber, *J. Chromatogr.* **1981**, *217*, 51.
[19] V. Schurig, W. Bürkle, *J. Am. Chem. Soc.* **1982**, *104*, 7573.
[20] V. Schurig, W. Bürkle, *Angew. Chem.* **1978**, *90*, 132; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 132; V. Schurig, W. Bürkle, *Angew. Chem.* **1978**, *90*, 132.
[21] V. Schurig, D. Wistuba, *Tetrahedron Lett.* **1984**, *25*, 5633.
[22] G. M. Whitesides, D. W. Lewis, *J. Am. Chem. Soc.* **1970**, *92*, 6979.
[23] V. Schurig, *Tetrahedron Lett.* **1972**, *13*, 3291.
[24] M. D. McCreary, D. W. Lewis, D. L. Wernick, G. M. Whitesides, *J. Am. Chem. Soc.* **1974**, *96*, 1038.
[25] D. Parker, *Chem. Rev.* **1991**, *91*, 1441.
[26] T. J. Wenzel, B. T. Wenzel, *Chirality* **2009**, *21*, 6.
[27] A. Togni, *Organometallics* **1990**, *9*, 3106.
[28] A. Togni, G. Rist, G. Rihs, A. Schweiger, *J. Am. Chem. Soc.* **1993**, *115*, 1908.
[29] F. Keller, H. Weinmann, V. Schurig, *Chem. Ber./Recueil* **1997**, *130*, 879.
[30] M. Bednarski, S. Danishefsky, *J. Am. Chem. Soc.* **1983**, *105*, 6968.
[31] M. Bednarski, C. Maring, S. Danishefsky, *Tetrahedron Lett.* **1983**, *24*, 3451.
[32] M. Quimpére, K. Jankowski, *J. Chem. Soc., Chem. Commun.* **1984**, 676.
[33] S. A. Matlin, W. J. Lough, L. Chan, D. M. H. Abram, Z. Zhou, *J. Chem. Soc., Chem. Commun.* **1984**, 1038.
[34] V. Schurig, E. Bayer, *CHEMTECH*, March **1976**, 212.
[35] V. Schurig, *J. Chromatogr. A* **1988**, *441*, 135.
[36] D. E. De Vos, I. F. J. Vankelecom, P. A. Jacobs, *Chiral Catalyst Immobilization and Recycling*, Wiley-VCH, Weinheim, Germany, **2000**.
[37] M. Felder, G. Giffels, C. Wandrey, *Tetrahedron: Asymmetry* **1997**, *8*, 1975.
[38] S. Sandel, S. K. Weber, O. Trapp, *Chem. Eng. Sci.* **2012**, in press.

[39] V. Schurig, D. Schmalzing, M. Schleimer, *Angew. Chem.* **1991**, *103*, 994; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 987; V. Schurig, D. Schmalzing, M. Schleimer, *Angew. Chem.* **1991**, *103*, 994.
[40] G. Opitz, N. Fischer, *Angew. Chem.* **1965**, *77*, 41; *Angew. Chem. Int. Ed. Engl.* **1965**, *4*, 70; G. Opitz, N. Fischer, *Angew. Chem.* **1965**, *77*, 41.
[41] C. Lang, U. Gärtner, O. Trapp, *Chem. Commun.* **2011**, *47*, 391.
[42] S. Sandel, S. K. Weber, O. Trapp, *Electrophoresis* **2012**, *33*, 1060–1067.
[43] J. E. H. Buston, I. Coldham, K. R. Mulholland, *J. Chem. Soc. Perkin Trans. 1* **1999**, 2327.
[44] G. Chelucci, *Chem. Soc. Rev.* **2006**, *35*, 1230.
[45] K. Bica, G. Gmeiner, C. Reichel, B. Lendl, P. Gaertner, *Synthesis* **2007**, 1333.
[46] F. W. Lewis, G. Egron, D. H. Grayson, *Tetrahedron: Asymmetry* **2009**, *20*, 1531.
[47] D. S. Tarbell, F. C. Loveless, *J. Am. Chem. Soc.* **1958**, *80*, 1963.
[48] J. H. Hutchinson, T. Money, S. E. Piper, *Can. J. Chem.* **1986**, *64*, 854.
[49] J. S. McConaghy, J. J. Bloomfield, *J. Org. Chem.* **1968**, *33*, 3425.
[50] O. Trapp, S. K. Weber, S. Bauch, *Angew. Chem.* **2007**, *119*, 7447; *Angew. Chem. Int. Ed.* **2007**, *46*, 7307; O. Trapp, S. K. Weber, S. Bauch, *Angew. Chem.* **2007**, *119*, 7447.
[51] J. L. Speier, *Adv. Organomet. Chem.* **1979**, *17*, 407.
[52] J. B. Perales, D. L. Van Vranken, *J. Org. Chem.* **2001**, *66*, 7270.
[53] C. Pietraszuk, S. Rogalski, M. Majchrzak, B. Marciniec, *J. Org. Chem.* **2006**, *691*, 5476.
[54] M. G. Voronkov, N. N. Vlasova, S. A. Bolshakova, S. V. Kirpichenko, *J. Organomet. Chem.* **1980**, *190*, 335.
[55] P. Strohriegl, *Makromol. Chem. Rapid Commun.* **1987**, *7*, 771.
[56] P. Strohriegl, M. Lux, H. Höcker, *Makromol. Chem. Rapid Commun.* **1987**, *188*, 811.
[57] L. N. Lewis, J. Stein, Y. Gao, R. E. Colborn, G. Hutchins, *Platinum Met. Rev.* **1997**, *41*, 66.
[58] Markó, S. Stérin, O. Buisine, G. Magnani, P. Branlard, B. Tinant, J. P. Declercq, *Science* **2002**, *298*, 204.
[59] M. Fluck, *Enantiomerenanalytik durch GC und SFC an Chirasil-Metall und Simulation von Elutionsprofilen aus der dynamischen Chromatographie*, Ph.D. Thesis, University of Tübingen, **1996**.
[60] K. Grob, *Making and manipulating capillary columns for gas chromatography*, Huethig Jehle Rehm, Heidelberg, Germany, **1986**.
[61] Z. Jiang, V. Schurig, *J. Chromatogr. A* **2008**, *1186*, 262.
[62] V. Schurig, W. Bürkle, K. Hintzer, R. Weber, *J. Chromatogr.* **1989**, *475*, 23.
[63] M. Schleimer, M. Fluck, V. Schurig, *Anal. Chem.* **1994**, *66*, 2893.
[64] V. Schurig, M. Fluck, *J. Biochem. Biophys. Methods* **2000**, *43*, 223.
[65] H. E. Gottlieb, V. Kotlyar, A. Nudelmann, *J. Org. Chem.* **1997**, *62*, 7512.
[66] F. Dallacker, J. Alroggen, H. Krings, B. Lauris, M. Lipp, *Justus Liebigs Ann. Chem.* **1961**, *647*, 26.
[67] G. Chelucci, S. Baldino, *Tetrahedron: Asymmetry* **2006**, *17*, 1529.

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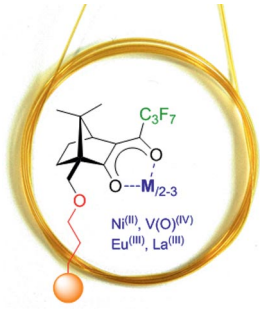
Gas Chromatography

A novel synthetic approach to camphor-based chemically bonded Chirasil-Metal-OC_3 [Ni, Eu, La, V(O)] stationary phases and thir application in enantioselective complexation GC is presented. Immobilization and metal incorporation was studied with a range of selector concentrations using NMR and IR spectroscopy. Overall, 29 compounds with different functionalities were separated with α-values up to 1.66.



Keywords: Chiral resolution / Chirality / Gas chromatography / Rare earths

