# Perfluorinated Bis(dihydrooxazole) Complexes Immobilized on Fluorous Reversed-Phase Silica Gel as Recyclable Catalysts for Enantioselective *Diels–Alder* Reactions

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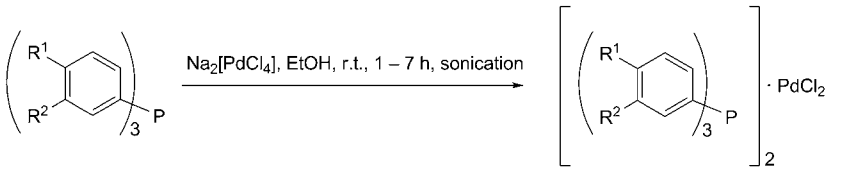
Dedicated to Prof. *Dieter Seebach* on the occasion of his 75th birthday

The three different perfluoroalkyl-tagged bis(dihydrooxazole)copper complexes **19**–**21** were synthesized and immobilized noncovalently on fluorous reversed-phase silica gel (FRPSG) by fluorous–fluorous interactions (*Schemes 2* and *3*). These supported catalysts were successfully applied to asymmetric *Diels–Alder* reactions in $H_2O$ and in $CH_2Cl_2$ (*Scheme 4*). Besides high conversion of the dienophile, we observed enantiomer excesses of up to 88% in $H_2O$ and 97% in $CH_2Cl_2$, and we were able to recover and re-use these catalytic systems several times. Despite the relatively high catalyst loading, the leaching of copper was remarkably low ranging from 2.4 to 5.9 ppm.

**Introduction.** – Fluorous biphasic systems (FBS), originally published in a seminal paper by *Horváth* and *Rábai* in 1994, allow for a simple catalyst recovery after catalytic processes. This is achieved by applying a biphasic system consisting of a fluorous and an organic solvent. Due to the perfluorinated ligands, the catalyst is located in the fluorous phase, while the substrate and reagents are dissolved in the organic phase [1]. This concept has been applied to numerous catalytic reactions, *e.g.*, hydroboration of alkenes [2a][2b], oxidation of aldehydes [2c], *Wacker* oxidation of alkenes [2d], and Pd-catalyzed allylic nucleophilic substitution [2e]. Our research group has applied this concept to C–C coupling reactions using perfluoro-tagged Pd-complexes (*Scheme 1*)

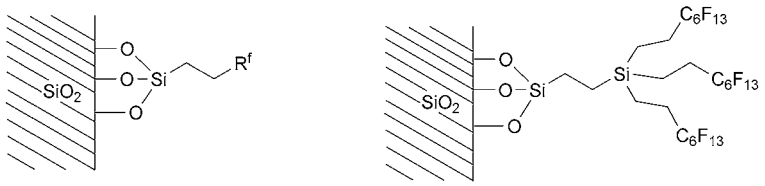
Scheme 1. *Perfluoro-Tagged Phosphine Ligands and the Corresponding Pd-Complexes*




| | $R^1$ | $R^2$ |
|---|---|---|
| **1a** | $C_8F_{17}$ | H |
| **1b** | H | $C_8F_{17}$ |
| **1c** | $C_8F_{17}CH_2CH_2$ | H |
| **1d** | H | $C_8F_{17}CH_2CH_2$ |
| **1e** | $C_7F_{15}CH_2O$ | H |

[3]. In two of these Pd-complexes, *i.e.*, in **1a** and **1b**, the perfluoro entities were directly linked to the benzene rings of the ligands, whereas in complexes **1c** – **1e**, the electron-withdrawing effect of the perfluoro-tag was reduced by a $CH_2CH_2$ or an $OCH_2$ spacer, respectively. These Pd-complexes were successfully applied in *Stille* coupling reactions and could be re-used several times without significant loss in activity [3]. Furthermore, the application was extended to *Suzuki* [4] and *Sonogashira* [5] couplings.

A disadvantage of the technology was the use of the perfluorinated solvents, which are expensive and environmentally persistent. To circumvent the use of perfluorinated solvents and still make use of fluorous–fluorous interactions, we have implemented some time ago the concept of FRPSG-supported catalysis (FRPSG = fluorous reversed-phase silicia gel; *Fig. 1*). In this technology, the perfluoro-tagged catalyst is noncovalently bound to the FRPSG by fluorous–fluorous interactions and directly applied in an organic solvent. After the reaction, the catalyst is removed by filtration and can be re-used. A similar strategy but with *Teflon* as solid support was pulished by *Gladysz* and co-workers [6].




**2** $R^f = C_6F_{13}$
**3** $R^f = C_8F_{17}$

**4**

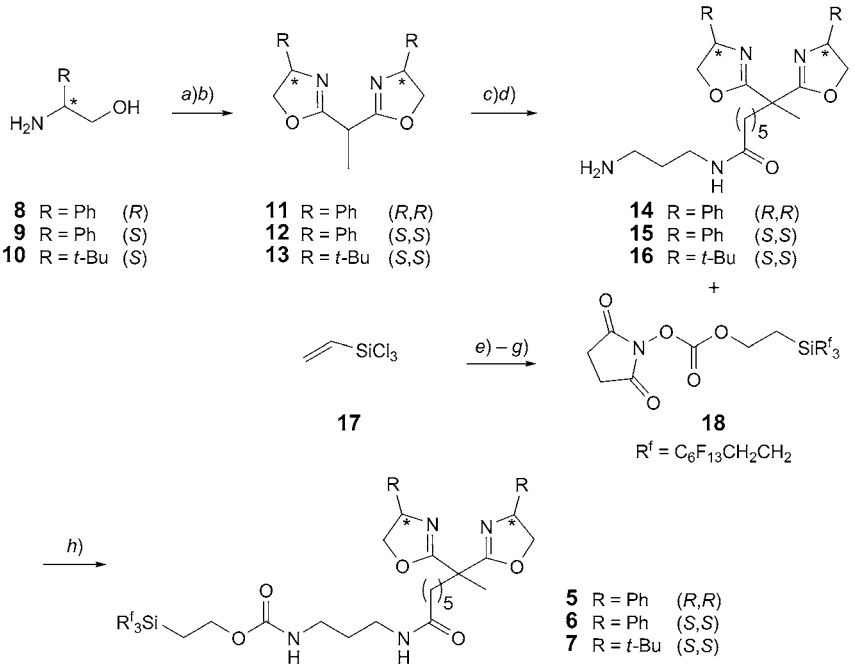
Fig. 1. *Fluorous reversed-phase $SiO_2$* (FRPSG)

In our previous work, we had established different perfluorinated silica gel-derived solid supports (see **2** – **4**) and had applied them successfully to a number of catalytic processes such as *Suzuki* and *Sonogashira* reactions [7][8], ring-closing-metathesis (RCM) reactions [9], and asymmetric hydrogenations [10].

Herein, we report on the application of the FRPSG-supported catalysis concept to *Diels–Alder* reactions in $H_2O$ and $CH_2Cl_2$ employing perfluorinated bis(dihydrooxazole) (box) ligands. To the best of our knowledge, only one example of a FRPSG-supported *Lewis* acid as recyclable catalyst for *Diels–Alder* reactions has been reported so far by *Nishikido* and co-workers, *i.e.*, $Sc[C(SO_2C_4F_9)_3]_3$ [11].

**Results and Discussion.** – The perfluoro-tagged ligands **5** – **7** employed in this study were synthesized according to *Scheme 2*, starting from the enantiomerically pure starting materials **8** – **10**, which had been obtained by reduction of the corresponding amino acids as reported [12]. Reaction of the 2-aminoethanols **8** – **10** with diethyl methylmalonate followed by ring closure with *p*-toluenesulfonyl chloride (TsCl) in the presence of *N*,*N*-dimethylpyridin-4-amine (DMAP) resulted in the corresponding bis(dihydrooxazole) **11** – **13** in moderate to good yields [13][14]. Alkylation of these [15] with 6-bromohexanoic acid methyl ester [16] and subsequent amide formation with propane-1,3-diamine yielded the desired amides **14** – **16** in 47 – 79% [17]. The synthesis of the activated *N*-succinimide-derived ester **18** started with the reaction of

Scheme 2. *Synthesis of the Perfluoro-Tagged box Ligands* **5**–**7**



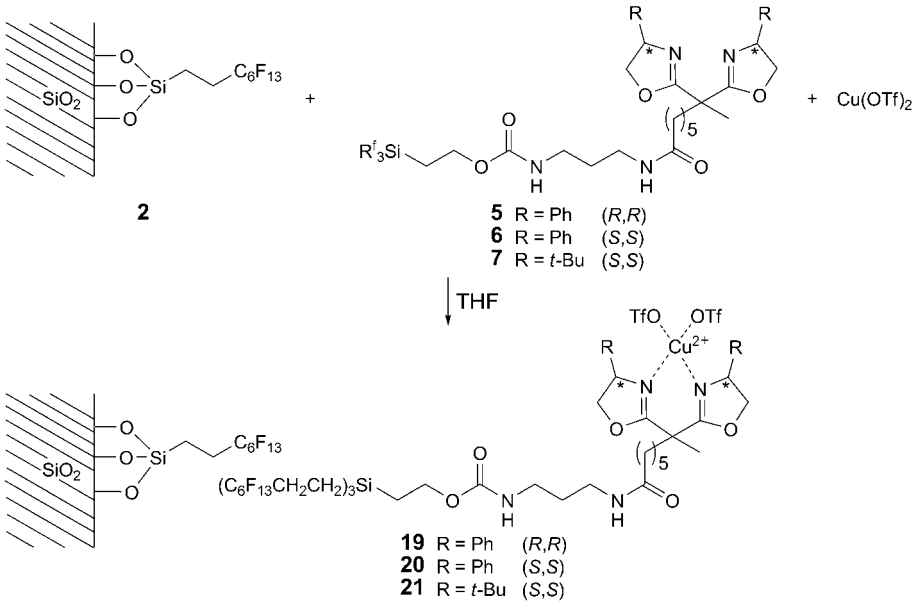

*a*) Diethyl methylmalonate, 110°, 3 d; R = Ph (*R*,*R*), 55–99%; R = Ph (*S*,*S*), 46%; R = *t*-Bu (*S*,*S*), 78%. *b*) DMAP, $Et_3N$, TsCl, $CH_2Cl_2$, r.t., 2 d; **11**, 57–68%; **12**, 58%; **13**, 33–78%. *c*) BuLi, THF, −78°, → 0°, 6-bromohexanoic acid methyl ester, → r.t., 2 h, reflux, 4 h; R = Ph (*R*,*R*), 57–60%; R = Ph (*S*,*S*), 66%; R = *t*-Bu (*S*,*S*), 43%. *d*) Propane-1,3-diamine, r.t., 2 d; **14**, 75–77%; **15**, 78%; **16**, 69%. *e*) $C_6F_{13}CH_2CH_2I$, $Et_2O$, −78°, *t*-BuLi, → 0°, 30 min, → −78°, **17**, r.t., 24 h; 71–91%. *f*) 9-Borabicyclo[3.3.1]nonane (9-BBN; 0.5M in THF), r.t., 20 h, 3M aq. NaOH, 35% aq. $H_2O_2$, r.t., 2 h; 65–90%. *g*) Disuccinimidyl carbonate, $Et_3N$, MeCN, r.t., 20 h; 31–48%. *h*) **18**, THF, $(i\text{-}Pr)_2EtN$, r.t., 1 h; **5**, 59–83%; **6**, 91%; **7**, 70–75%.

trichloro(ethenyl)silane (**17**) and $C_6F_{13}CH_2CH_2I$ [18]. A hydroboration/oxidation/hydrolyses sequence delivered the corresponding perfluorinated hydroxysilane (not shown in *Scheme 2*) [19], which was converted into the *N*-hydroxysuccinimide-derived carbonate **18** by a treatment with disuccinimidyl carbonate and $Et_3N$ [20]. Finally, the desired perfluoro-tagged ligands **5**–**7** were obtained in decent yields (59–91%) *via* coupling of the activated **18** and the amides **14**–**16** in the presence of *Hünig*'s base [21].

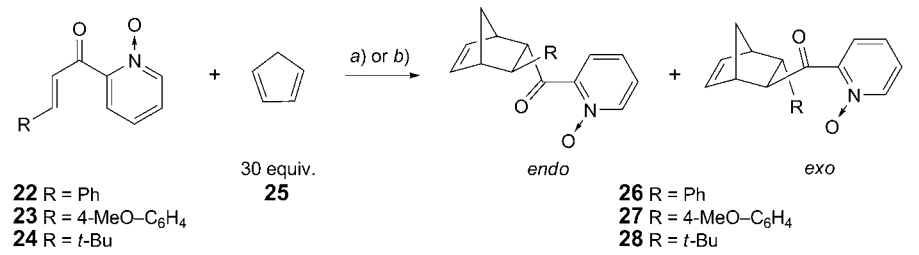
The noncovalent immobilization of the perfluorinated box ligands **5**–**7** on the FRPSG **2** is outlined in *Scheme 3*. For the immobilization process, the perfluoro-tagged ligands **5**–**7** were dissolved in THF, and $Cu(OTf)_2$ was added which was followed by FRPSG **2**. Evaporation of the solvent yielded the desired immobilized air-stable catalytic systems **19**–**21**.

The envisaged *Diels–Alder* reaction of the dienophiles **22**–**24** with cyclopenta-1,3-diene (**25**) for the evaluation the FRPSG-supported way of proceeding is outlined in *Scheme 4*. We focused on the *N*-oxides and not the parent pyridinyl compounds since

Scheme 3. *Noncovalent Immobilization of the Ligands* **5**–**7** *on the Solid Support*




Scheme 4. *Enantioselective* Diels–Alder *Reactions with* N-*Oxides* **22**–**24**




*a*) 5 or 10 mol-% of **19**–**21**, $H_2O$, 5°, 1 d. *b*) 10 mol-% of **19**–**21**, $CH_2Cl_2$, 5°, 45 min for **22**, 4.5 h for **23**, and 6 h for **24**.

the latter were reported to yield rather low ee values [22]. Initial experiments had indicated that the *exo*-product was only obtained in minute amounts, hence, the estimation of the ee values was carried out with respect to the *endo*-product. Since fluorous–fluorous interactions are increasing with the polarity of the solvent, we tested the reactions first in $H_2O$. This would guarantee for a strong noncovalent interaction between the support and the catalyst.

In earlier work on asymmetric hydrogenations, we had observed that silica gel or perfluorinated silica gel had an influence on the outcome of the reactions [10]. To rule this out for the present investigation, we performed the cycloaddition of all three dienophiles with cyclopentadiene **25** in the presence of silica gel and perfluorinated

silica gel **2** but without catalyst. The results (*Table 1*) indicated that for yet unknown reasons, the presence of silica gel led to higher conversion rates compared to the reactions without additive. Fortunately, this effect was not observed for the reactions in the presence of perfluorinated silica gel **2**. Hence the influence of the FRPSG **2** on the envisaged reactions could be neglected.

Table 1. *Influence of Silica Gel and Perfluorinated Silica Gel* **2** *on the* Diels–Alder *Reaction of* **22**–**24** *with* **25** (control experiments) *in* $H_2O$

| | Additive | Additive [mol-%] | Conversion [%][a]) | *endo*/*exo* Ratio[a]) |
|---|---|---|---|---|
| **22** | – | – | 44 | 94 : 6 |
| | $SiO_2$[b]) | 10 | 93 | 95 : 5 |
| | $SiO_2$[b]) | 5 | 93 | 96 : 4 |
| | **2** | 10 | 44 | 94 : 6 |
| | **2** | 5 | 43 | 94 : 6 |
| **23** | – | – | 10 | 95 : 5 |
| | $SiO_2$[b]) | 10 | 51 | 96 : 4 |
| | $SiO_2$[b]) | 5 | 57 | 96 : 4 |
| | **2** | 10 | 14 | 95 : 5 |
| | **2** | 5 | 14 | 95 : 5 |
| **24** | – | – | 3 | 76 : 24 |
| | $SiO_2$[b]) | 10 | 23 | 87 : 13 |
| | $SiO_2$[b]) | 5 | 19 | 86 : 14 |
| | **2** | 10 | 3 | 79 : 21 |
| | **2** | 5 | 3 | 77 : 23 |

[a]) Conversions and *endo*/*exo* ratios were determined by HPLC; they are the average of three independent experiments. [b]) 500 Å, 100–300 μm, 80 $m^2$/g.

For the enantioselective *Diels–Alder* reactions of the *N*-oxides **22**–**24** with cyclopentadiene **25** in $H_2O$ in the presence of 5 and 10 mol-% of the immobilized chiral catalysts **19**–**21**, the perfluoro-tagged ligands **5**–**7** were dissolved in THF, $Cu(OTf)_2$ and the FRPSG **2** were added, and the solvent evaporated (*Scheme 3*). The reaction itself was carried out in $H_2O$ at 5° for 1 d, and after each run, the solid support was filtered off, washed with MeCN, and re-used again. The results are summarized in *Table 2*. For the Ph-substituted bis(dihydrooxazole) catalysts **19** and **20**, high conversions up to 99% and enantiomer excesses (ee) up to 88% were obtained in the first run for all dienophiles. Surprisingly, with the *t*-Bu-substituted catalyst **21**, lower conversions and poor ee values were achieved. This might be an indication for the involvement of stacking interactions in the transition state. The re-use of the immobilized Cu-complexes was not only dependent on the catalyst but also on the dienophile employed and was generally entailed with significantly reduced conversions and lower ee values. The reason for this is yet unknown but might have its basis in the limited stability of the copper complex in $H_2O$. Being aware that the relatively high catalyst loading might lead to a substantial leaching, we performed a reaction between *N*-oxide **22** and cyclopentadiene **25** with 10 mol-% of all three FRPSG-supported catalysts **19**–**21**. Estimation of the copper values resulted in only 2.4–5.9 ppm of Cu in the aqueous phase.

Table 2. Diels–Alder *Reactions of* N-*Oxides* **22**–**24** *with* **25** *in the Presence of Catalysts* **19**, **20**, *or* **21** *in* $H_2O$

| | Catalyst | Catalyst [mol-%] | Conversion [%][a][b] | $ee_{endo}$ [%][a][b] | *endo*/*exo* Ratio[a] |
|---|---|---|---|---|---|
| **22** | **19** | 10 | > 99 (53) | – 83 (– 40) | 96 : 4 (95 : 5) |
| | **19** | 5 | 99 (50) | – 84 (– 30) | 97 : 3 (94 : 6) |
| | **20** | 10 | > 99 (72) | 74 (43) | 97 : 3 (95 : 5) |
| | **20** | 5 | 96 (60) | 73 (32) | 97 : 3 (95 : 5) |
| | **21** | 10 | 52 | – 14 | 94 : 6 |
| | **21** | 5 | 47 | – 14 | 94 : 6 |
| **23** | **19** | 10 | 99 (19) | – 75 (– 28) | 97 : 3 (96 : 4) |
| | **19** | 5 | 90 (12) | – 72 (– 13) | 97 : 3 (94 : 6) |
| | **20** | 10 | 93 (25) | 77 (49) | 97 : 3 (96 : 4) |
| | **20** | 5 | 76 (18) | 75 (34) | 97 : 3 (94 : 6) |
| | **21** | 10 | 24 | – 10 | 96 : 4 |
| | **21** | 5 | 18 | – 7 | 95 : 5 |
| **24** | **19** | 10 | 89 (18) | – 86 (– 83) | 75 : 25 (72 : 28) |
| | **19** | 5 | 69 (8) | – 88 (– 69) | 75 : 25 (74 : 26) |
| | **20** | 10 | 77 (27) | 87 (84) | 75 : 25 (71 : 29) |
| | **20** | 5 | 62 (14) | 88 (75) | 74 : 26 (71 : 29) |
| | **21** | 10 | 5 | – 5 | 79 : 21 |
| | **21** | 5 | 3 | – 4 | 80 : 20 |

[a]) The values in parentheses are for the second runs with the same catalyst. [b]) Conversions, $ee_{endo}$, and *endo*/*exo* ratios were determined by chiral HPLC, they are the average of three independent experiments.

Since the recycling experiments in $H_2O$ were not really convincing, we decided to switch from $H_2O$ to $CH_2Cl_2$ as reaction medium. We expected the fluorous–fluorous interactions to be still high enough as to allow for a decent binding of the perfluoro-tagged catalyst on the FRPSG. Control experiments with unmodified $SiO_2$ and FRPSG **2** as additives to the reaction in $CH_2Cl_2$ had led to negligible conversions in the range of 2–5%. *Fig. 2* shows the recycling properties of the chiral catalysts **19**–**21** in the *Diels–Alder* reactions of **22**–**24** with **25**. The obtained ee values are given in the legend of the figure, and those in parentheses are for the second, third, fourth, and fifth runs with the same catalyst. Overall, concerning recyclability and ee values, the results looked much more promising than in $H_2O$. Furthermore, the reactions were also significantly faster in $CH_2Cl_2$ (45 min for **22**, 4.5 h for **23**, and 6 h for **24**) compared to $H_2O$ as reaction medium. High conversions and ee values were achieved for all three *N*-oxides when Ph-substituted catalysts **19** and **20** were used, while the *t*-Bu-substituted box complex **21** resulted again in poor enantiomer excesses. In addition, the re-usability of **19** and **20** was found to be much better than for **21**, and high ee values were obtained even in the fifth run. Nevertheless, a decrease of conversion was observed during the recycling experiments, and decent conversions were observed over three runs.

To shed more light on the nature of the catalytic process itself, we performed filtration experiments of ongoing reactions in $CH_2Cl_2$. After filtration, the reaction continued and led to the same conversion and enantiomer excess as in the reaction without filtration. This was a clear indication that the reaction proceeded at least

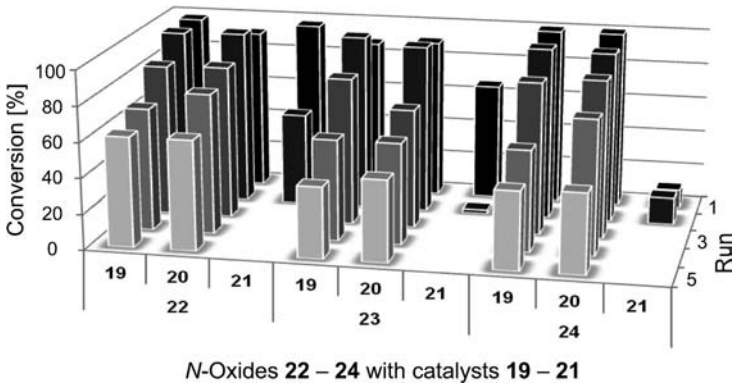



Fig. 2. Diels–Alder *reactions of* N-*oxides* **22**–**24** *with* **25** *in the presence of catalysts* **19**, **20**, *or* **21** *in* $CH_2Cl_2$. The ee values given below in parentheses are for the second, third, fourth, and fifth runs with the same catalyst. N-*Oxide* **22**: $ee_{endo}$ [%] with **19**, −97 (−95, −97, −96, −96); with **20**, 91 (90, 92, 87, 89); with **21**, −21 (−28). N-*Oxide* **23**: $ee_{endo}$ [%] with **19**, −91 (−92, −86, −90, −78); with **20**, 91 (91, 93, 84, 91); with **21**, −5 (−9). N-*Oxide* **24**: $ee_{endo}$ [%] with **19**, −94 (−93, −91, −92, −91); with **20**, 91 (91, 90, 89, 89); with **21**, −4 (−2).

partially in a homogeneous fashion which is in accordance with the results obtained in *Suzuki* reactions with FRPSG-supported Pd-complexes [8].

Assessment of the leaching using the same reaction as outlined above resulted in 3.3–5.0 ppm copper in the $CH_2Cl_2$ phase.

**Conclusions.** – We demonstrated that the principle of FRPSG-supported catalysts could be extended to asymmetric bis(dihydrooxazol)copper complexes. The phenyl-substituted FRPSG-supported perfluoro-tagged copper complexes **19** and **20** turned out to be useful catalysts for enantioselective *Diels–Alder* reactions in $H_2O$ as well as in $CH_2Cl_2$. Concerning recyclability, ee values, and reaction times, $CH_2Cl_2$ was superior as reaction media and allowed for three runs with decent yields. In both solvent systems, the leaching of copper was below 5.9 ppm.

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## Experimental Part

1. *General.* All reagents and solvents were of the highest purity available and were used without further purification. CC = Column chromatography. HPLC: *Agilent-1050* system with binary pump, sample changer, and diode-array detector; $t_R$ in min. Optical rotation: *Perkin-Elmer-341-MC* polarimeter; at 589 nm and 20°, calculated according to the *Drude* equation $[\alpha]_D = (\alpha^{exp} \cdot 100)/(c \cdot d)$. NMR Spectra: *Bruker* spectrometer; at 400.1 ($^1$H), 100.6 ($^{13}$C), and 235.4 MHz ($^{19}$F); $\delta$ in ppm rel. to $Me_4Si$ (= 0 ppm) for $^1$H and rel. to $CHCl_3$ (= 77.0 ppm) for $^{13}$C, resp., $FCCl_3$ as internal standard for $^{19}$F, *J* in Hz.

MS: *Thermo TSQ 700* or *MAT 95XL* (CI, HR-MS-CI) and *TSQ 7000* (ESI, APCI, HR-MS-APCI); in *m/z* (rel. %). Microanalysis (CHN): *Vario-EL* system from *Elementaranalysesysteme GmbH*.

2. *(4*R*,4′*R*)-2,2′-Ethylidenebis[4,5-dihydro-4-phenyloxazole]* (**11**; R = Ph (*R*,*R*)), *(4*S*,4′*S*)-2,2′-Ethylidenebis[4,5-dihydro-4-phenyloxazole]* (**12**; R = Ph (*S*,*S*)), *and (4*S*,4′*S*)-2,2′-Ethylidenebis[4-(1,1-dimethylethyl)-4,5-dihydrooxazole]* (**13**; R = *t*-Bu (*S*,*S*)). Diethyl methylmalonate and (2*R*)-phenylglycinol (= (*βR*)-*β*-aminobenzeneethanol), (2*S*)-phenylglycinol (= (*β*S)-*β*-aminobenzeneethanol), or (2*S*)-*tert*-leucinol (= (2*S*)-2-amino-3,3-dimethylbutan-1-ol; 2.0 equiv.) were heated for 3 d to 110°. Recrystallization from $CHCl_3$ gave the desired diols with R = Ph (*R*,*R*) (55–99%), R = Ph (*S*,*S*) (46%), and R = *t*-Bu (*S*,*S*) (78%), resp. White solid.

Each diol and DMAP (0.10 equiv.) were dissolved in $CH_2Cl_2$ (0.3M), and $Et_3N$ (8.25 equiv.) was added dropwise. Then a soln. of TsCl (2.2 equiv.) in $CH_2Cl_2$ (1.0M) was added, and the soln. was stirred at r.t. After 2 d, the addition of 0.025M aq. HCl was followed by the extraction of the aq. phase with AcOEt (3×). The combined org. phase was washed with aq. sat. $Na_2CO_3$ soln. and aq. sat. NaCl soln., dried ($Na_2SO_4$), and concentrated and the residue subjected to CC ($SiO_2$, AcOEt/EtOH 50:1): **11** (57–68%), **12** (58%), and **13** (33–78%), resp. Slightly yellow oils.

*Data of* **11** *and* **12**: $[\alpha]_{589}^{20} = +101.5$ (**11**, 3.5M, $CHCl_3$); $[\alpha]_{589}^{20} = -83.1$ (**12**, 5.3M, $CHCl_3$). $^1$H-NMR ($CDCl_3/CHCl_3$): 1.65 (*d*, $^3J$ = 7.2, *Me*CH); 3.77 (*q*, $^3J$ = 7.2, MeC*H*)); 4.17 and 4.18 ($\delta_A$) 4.68 and 4.69 ($\delta_B$; 2 *AB* patterns, *J*(*A*,*B*) = 8.4, *J*(*A*,4) = 7.8, *J*(*B*,4) = 10.1, 4 H, $CH_2$(5,5′)); 5.24 and 5.25 (*dd*, *J*(4,*B*) = 10.0, *J*(4,*A*) = 7.9, 2 H, H–C(4,4′); 7.26–7.35 (*m*, 10 arom. H). $^{13}$C-NMR ($CDCl_3/CDCl_3$): 15.46 (*Me*CH); 34.20 (Me*C*H)); 69.63, 69.67 (C(5,5′)); 75.40, 75.42 (C(4,4′)); 126.72, and 126.76 (2 $C_o$); 127.66 ($C_p$); 128.79 (2 $C_m$); 142.29, 142.31 ($C_{ipso}$); 167.06, 167.27 (C(2,2′)). CI-MS ($NH_3$): 337.1 (32), 322.1 (24), 321.1 (100, $[M+1]^+$), 320.1 (23), 319.1 (15), 243.1 (11), 201.0 (27), 191.0 (14), 190.0 (15), 175.0 (41), 120.0 (17), 104.0 (50), 91.0 (12). Anal. calc. for $C_{20}H_{20}N_2O_2$ (320.38): C 74.98, H: 6.29, N 8.74; found: C 74.69, H 6.31, N 8.46.

*Data of* **13**: $[\alpha]_{589}^{20} = -99.3$ (4.6M, $CHCl_3$). $^1$H-NMR ($CDCl_3/CHCl_3$): 0.87, 0.88 (*s*, 18 H, *t*-Bu); 1.48 (*d*, $^3J$ = 7.2, *Me*CH); 3.55 (*q*, $^3J$ = 7.2, MeC*H*); 3.83–3.86 (*m*, 2 H, H–C(4,4′)); 4.07 and 4.08 ($\delta_A$) 4.17 and 4.18 ($\delta_B$; 2 *AB* patterns, *J*(A,B) = 8.7, *J*(*A*,4) = 7.5, *J*(*B*,4) = 10.0, $CH_2$(5,5′)). $^{13}$C-NMR ($CDCl_3/CDCl_3$): 15.36 (*Me*CH); 25.74, 25.79 (*Me*$_3$C); 33.81, 33.85 (Me$_3$*C*); 34.12 (Me*C*H); 69.04, 69.05 (C(5,5′)); 75.57 (C(4,4′)); 165.42, 165.63 (C(2,2′)). APCI-MS (pos.): 282 (17), 281 (100, $[M+1]^+$). Anal. calc. for $C_{16}H_{28}N_2O_2$ (280.41): C 68.53, H 10.06, N 9.99; found: C 68.12, H 10.22, N 9.58.

3. N-*(3-Aminopropyl)-7,7-bis[(4*R*)-4,5-dihydro-4-phenyloxazol-2-yl]octanamide* (**14**; R = Ph (*R*,*R*)), N-*(3-Aminopropyl)-7,7-bis[(4S)-4,5-dihydro-4-phenyloxazol-2-yl)octanamide* (**15**; R = Ph (*S*,*S*)), *and* N-*(3-Aminopropyl)-7,7-bis[(4*S*)-4-(1,1-dimethylethyl)-4,5-dihydrooxazol-2-yl)octanamide* (**16**; R = *t*-Bu (*S*,*S*)). The bis(dihydrooxazole) **11**, **12**, or **13** was dissolved in dry THF (0.14M), and the mixture was cooled to −78°. After the dropwise addition of BuLi (1.1 equiv.), the soln. was stirred for 15 min at −78°. Then the mixture was warmed to 0° and stirred for an additional 15 min at −78°. Afterwards, a soln. of 6-bromohexanoic acid methyl ester (1.1 equiv.) in dry THF (0.31M) was added dropwise at 0°. After stirring for 2 h at r.t., the mixture was heated to reflux for further 4 h. After cooling to r.t., sat. aq. $NH_4Cl$ soln. and $CH_2Cl_2$ were added, and the org. phase was washed with $H_2O$ (2×). The combined aq. phase was extracted with $CH_2Cl_2$ (3×), the $CH_2Cl_2$ phase dried ($Na_2SO_4$) and concentrated, and the crude product purified by CC ($CH_2Cl_2$/AcOEt 4:1 + 0.5% $Et_3N$): methyl esters with R = Ph (*R*,*R*) (57–60%); R = Ph (*S*,*S*) (66%), and R = *t*-Bu (*S*,*S*) (43%), resp. Slightly yellow oils.

Each, methyl ester and propane-1,3-diamine (12.5 equiv.) were stirred for 2 d at r.t., and then the remaining propane-1,3-diamine was removed by bulb-to-bulb distillation. Sat. aq. NaCl soln. was added to the residue, and the aq. phase was extracted with $CHCl_3$/i-PrOH 8:2 (3×). The combined org. phase was washed with sat. aq. NaCl soln., dried ($Na_2SO_4$), and concentrated, and the crude product was purified by CC (MeOH/aq. $NH_3$ soln. 98:2): **14** (75–77%), **15** (78%), and **16** (69%); resp. Yellow oils.

*Data of* **14** *and* **15**: $[\alpha]_{589}^{20} = +102.6$ (**14**, 4.0M, $CHCl_3$); $[\alpha]_{589}^{20} = -106.4$ (**15**, 4.6M, $CHCl_3$). $^1$H-NMR ($CDCl_3/CHCl_3$): 1.35–1.46 (*m*, $CH_2$(4), $CH_2$(5)); 1.63 (*s*, Me(8)); 1.59–1.68 (*m*, $CH_2$(3), $CH_2$(6)); 1.98–2.09 (*m*, $CH_2$(2″)); 2.13 (*t*, *J*(2,3) = 7.6, $CH_2$(2)); 2.78 (*t*, *J*(3″,2″) = 6.4, $CH_2$(3″)); 3.26 (*dt*, *J*(1″,NH) = 6.1, *J*(1″,2″) = 6.3, $CH_2$(1″)); 3.26 (br. *s*, $NH_2$); 4.13 and 4.14 ($\delta_A$) 4.65 and 4.66 ($\delta_B$; 2 *AB* patterns *J*(A,B) = 8.4, *J*(*A*,4′) = 8.1, *J*(*B*,4′) = 10.0, 4 H, $CH_2$(5′), 5.22, 5.23 (*dd*, *J*(4′,*B*) = 10.2, *J*(4′,*A*) = 7.7, 2 H, H–C(4′)); 6.71 (*t*, *J*(NH,1″) = 6.2, NH); 7.24–7.35 (*m*, 10 arom. H). $^{13}$C-NMR ($CDCl_3/CDCl_3$): 21.55 (C(8)); 24.06

(C(6)); 25.51 (C(5)); 29.32 (C(3)); 30.65 (C(4)); 36.44 (C(2′)); 36.46 (C(2′)); 37.22 (C(1″)); 39.07 (C(3″)); 42.63 (C(7)); 69.44, 69.56 (C(5′)); 75.27, 75.36 (C(4′)); 126.71 (2 $C_o$); 127.62 ($C_p$); 128.72, 128.74 (2 $C_m$); 142.35, 142.37 ($C_{ipso}$); 169.73, 169.85 (C(2′)); 173.58 (C(1)). ESI-MS (pos.); 492 (30), 491 (100, $[M+1]^+$). HR-APCI-MS (MeOH): 491.30270 ($[M+H]^+$, $C_{29}H_{39}N_4O_3^+$; calc. 491.30222).

*Data of* **16**: $^1$H-NMR ($CDCl_3$/$CHCl_3$): 0.87 (*s*, 18 H, *t*-Bu); 1.32–1.33 (*m*, $CH_2$(4) $CH_2$(5)); 1.47 (*s*, Me(8)); 1.63 (*tt*, *J*(3,2) = 7.6, *J*(3,4) = 7.4, $C_2$(3)); 1.68 (*tt*, *J*(2″,3″) = 6.5, *J*(2″,1″) = 6.4, $CH_2$(2″)); 1.79–1.87, 1.95–2.01 (*m*, $CH_2$(6); 2.15 (*t*, *J*(2,3) = 7.6, $CH_2$(2)); 2.51 (br. *s*, $NH_2$); 2.83 (*t*, *J*(3″,2″) = 6.4, $CH_2$(3″)); 3.36 (*dt*, *J*(1″,NH) = 6.1, *J*(1″,2″) = 6.2, $CH_2$(1″)); 3.84, 3.85 (*dd*, *J*(4′,*B*) = 10.1, *J*(4′,*A*) = 7.2, 2 H, H–C(4′)); 4.03 and 4.06 ($\delta_A$), 4.12 and 4.13 $\delta_B$; 2 *AB* patterns, *J*(*A*,*B*) = 8.7, *J*(*A*,4′) = 7.3, *J*(*B*,4′) = 10.0, 4 H, $CH_2$(5′); 6.43 (*t*, *J*(NH,1″) = 5.6, NH). $^{13}$C-NMR ($CDCl_3$/$CDCl_3$): 21.48 (C(8)); 24.10 (C(6)); 25.69 (C(5)); 25.79, 25.87 ($Me_3C$); 29.56 (C(3)); 31.65 (C(4)); 33.90, 34.01 ($Me_3C$); 36.35 (C(2″)); 36.81 (C(2)); 37.67 (C(1″)); 39.71 (C(3″)); 42.40 (C(7)); 68.81, 68.84 (C(5′)); 75.35, 75.56 (C(4′)); 168.04, 168.19 (C(2′)); 173.47 (C(1)). APCI-MS (pos.): 559 (14), 464 (16), 463 (59), 452 (27), 451 (100, $[M+1]^+$).

4. *2,5-Dioxopyrrolidin-1-yl 2-[Tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silyl]ethyl Carbonate* (**18**). $C_6F_{13}CH_2CH_2I$ (4.0 equiv.) was dissolved in dry $Et_2O$ (0.085M) and cooled to −78°. After the dropwise addition of *t*-BuLi (8.0 equiv.), the soln. was warmed to 0°. After 30 min at 0°, the mixture was again cooled to −78°, and **17** was added. After stirring for 24 h at r.t., $H_2O$ was added, the org. phase washed with sat. aq. $NaHCO_3$ soln., dried ($Na_2SO_4$), and concentrated, and the crude product purified by CC ($SiO_2$; pure cyclohexane): perfluorinated silane (71–91%). Waxy solid.

The perfluorinated silane was dissolved in dry $Et_2O$ (0.25M), and 9-BBN (3.0 equiv.) was added. After stirring for 20 h at r.t., 3M aq. NaOH and 35% aq. $H_2O_2$ soln. were added, and the soln. was stirred for further 2 h at r.t. before $H_2O$ was added. The aq. phase was extracted with $Et_2O$ (3×), the combined org. phase washed with 10% aq. $Na_2S_2O_3$ soln. and sat. aq. NaCl soln., dried ($Na_2SO_4$), and concentrated, and the crude product purified by CC (cyclohexane → cyclohexane/AcOEt 4:1): hydroxysilane (65–90%). Waxy solid.

The hydroxysilane and $Et_3N$ (3.0 equiv.) were suspended in dry MeCN (0.18M), and disuccinimidyl carbonate (1.9 equiv.) was added as a solid. After stirring for 20 h at r.t., the solvent was evaporated, the residue dissolved in $CH_2Cl_2$, the org. phase washed with sat. aq. $NaHCO_3$ soln. (2×), dried ($Na_2SO_4$), and concentrated, and the crude product purified by CC (cyclohexane/AcOEt 4:1): **18** (31–48%). White solid.

$^1$H-NMR ($CDCl_3$/$CHCl_3$): 0.95–0.99 (*m*, 3 $CH_2C_6F_{13}CH_2CH_2$); 1.31 (*t*, *J*(2,1) = 8.1, $CH_2$(2)); 2.02–2.15 (*m*, 3 $C_6F_{13}CH_2CH_2$); 2.84 (*s*, $CH_2$(3′), $CH_2$(4′); 4.46 (*t*, *J*(1,2) = 8.0, $CH_2$(1)). $^{13}$C-NMR ($CDCl_3$/$CDCl_3$): 1.65 ($C_6F_{13}CH_2CH_2$); 12.66 (C(2)); 25.35 ($C_6F_{13}CH_2CH_2$); 25.56 (C(3′), C(4′)); 67.95 (C(1)); 151.53 (OC(O)O); 168.51 (C2′),C(5′)). $^{19}$F-NMR ($CDCl_3$/$CDCl_3$): −126.29 to −126.12 (6 F); −123.28 to −123.22 (6 F); −122.92 (6 F); −121.95 (6 F); −116.19 to −115.91 (6 F); −80.88 to −80.78 (9 F). CI-MS ($NH_3$): 1275 (11), 1274 (38), 1273 (100, $[M+NH_4]^+$), 836 (16), 197 (17), 180 (30).

5. *2-[Tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silyl]ethyl* N-*{3-{[7,7-Bis[(4*R*)-4,5-dihydro-4-phenyloxazol-2-yl]-1-oxooctylamino}propyl}carbamate* (**5**; R = Ph (*R,R*)), *2-[Tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silyl]ethyl* N-*{3-{[7,7-Bis[(4*S*)-4,5-dihydro-4-phenyloxazol-2-yl]1-oxooctylamino}-propyl}carbamate* (**6**; R = Ph (*S,S*)), *and 2-[Tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silyl]ethyl* N-*{3-{[7,7-Bis[(4*S*)-4-(1,1-dimethylethyl)-4,5-dihydrooxazol-2-yl]-1-oxooctylamino}propyl}carbamate* (**7**; R = *t*-Bu (*S,S*)). To a soln. of **18** (1.0 equiv.) in dry THF (0.01M), either **14**, **15**, or **16** was added. After the addition of (i-Pr)$_2$EtN (10.0 equiv.), the mixture was stirred for 1 h at r.t., and then sat. aq. $NaHCO_3$ soln. was added. The aq. phase was extracted with $Et_2O$ (3×), dried ($Na_2SO_4$), and concentrated and the crude product purified by CC (AcOEt/EtOH 40:1): **5** (59–83%), **6** (91%), and **7** (70–75%), resp. Colorless highly viscous oils.

*Data of* **5** *and* **6**: $[\alpha]_{365}^{20} = +119.8$ (**5**, 2.5M, $CHCl_3$); $[\alpha]_{365}^{20} = -120.7$ (**6**, 1.7M, $CHCl_3$). $^1$H-NMR ($CDCl_3$/$CHCl_3$): 0.90–0.95 (*m*, 3 $C_6F_{13}CH_2CH_2$); 1.14 (*t*, *J*(2‴,1‴) = 8.0, $CH_2$(2‴)); 1.35–1.48 (*m*, $CH_2$(4′), $CH_2$(5′)); 1.56 (*tt*, *J*(3′,2′) = 6.2, *J*(3′,4′) = 6.2, $CH_2$(3′)); 1.62–1.69 (*m*, $CH_2$(6′)); 1.64 (*s*, Me(8′)); 2.01–2.17 (*m*, $CH_2$(2), $CH_2$(2′), 3 $C_6F_{13}CH_2CH_2$); 3.15 (*dt*, *J*(1,NH) = 6.3, *J*(1,2) = 6.3, $CH_2$(1)); 3.16–3.23 (*m*, $CH_2$(3)); 4.18 (*t*, *J*(1‴,2‴) = 8.1, $CH_2$(1‴)); 4.14 and 4.15 ($\delta_A$), 4.66 and 4.67 ($\delta_B$, 2 *AB* patterns, *J*(*A*,*B*) = 8.4, *J*(*A*,4″) = 7.7, *J*(*B*,4″) = 10.2, 4 H, $CH_2$(5″)); 5.22, 5.24 (*dd*, *J*(4″,*B*) = 10.1, *J*(4″,*A*) = 7.8, 2 H, H–C(4″)); 5.39 (*t*, *J*(NH,3) = 6.8, NH); 5.88 (*t*, *J*(NH,1) = 6.3, NH); 7.23–7.35 (*m*, 10 arom. H).

$^{13}$C-NMR ($CDCl_3$/$CDCl_3$): 1.64 ($C_6F_{13}CH_2\mathit{C}H_2$); 12.72 (C(2‴)); 21.64 (C(8′)); 23.94 (C(4′)); 25.4 ($C_6F_{13}CH_2\mathit{C}H_2$); 25.46 (C(6′)); 29.19 (C(5′)); 30.15 (C(3′)); 35.73 (C(3)); 36.43 (C(2)); 36.53 (C(2′)); 37.37 (C(1)); 42.73 (C(7′)); 61.02 (C(1‴)), 69.57, 69.66 (C(5″)); 75.34, 75.40 (C(4″)); 115.84, 118.02, 118.71 (*C*F); 126.78 (2 $C_o$); 127.67 ($C_p$); 128.79 (2 $C_m$); 142.47 ($C_{ipso}$); 156.69 (NC(O)O); 169.81, 169.90 (C(2′)); 173.79 (C(1′)). $^{19}$F-NMR ($CDCl_3$/$CDCl_3$): −126.27 to −126.11 (6 F); −123.27 to −122.92 (6 F); −121.96 (6 F); −116.20 to −115.95 (6 F); −80.88 to −80.79 (9 F). ESI-MS (pos.): 1633 (19), 1632 (49), 1631 (100, $[M+1]^+$). HR-APCI-MS (MeOH): 1631.32580 ($[M+H]^+$, $C_{56}H_{54}F_{39}N_4O_5Si^+$; calc.1631.32408).

*Data of* **7**: $[\alpha]_{20}^{365} = -66.4$ (1.8M, $CHCl_3$). $^1$H-NMR ($CDCl_3$/$CHCl_3$): 0.87 (*s*, 18 H, *t*-Bu); 0.91–0.96 (*m*, 3 $C_6F_{13}CH_2C\mathit{H}_2$); 1.15 (*t*, *J*(2‴,1‴) = 7.8, H–$CH_2$(2‴)); 1.30–1.35 (*m*, $CH_2$(4′), $CH_2$(5′)); 1.46 (*s*, Me(8′)); 1.59–1.66 (*m*, $CH_2$(3′), $CH_2$(6′)); 2.00–2.09 (*m*, $CH_2$(2), 3 $C_6F_{13}C\mathit{H}_2CH_2$); 2.16 (*t*, *J*(2′,3′) = 7.6, $CH_2$(2′)); 3.18 (*dt*, *J*(1,NH) = 6.3, *J*(1,2) = 6.1, $CH_2$(1)); 3.29 (*dt*, *J*(3,NH) = 6.2, *J*(3,2) = 6.2, $CH_2$(3)); 3.84, 3.85 (*dd*, *J*(4″,*B*) = 10.3, *J*(4″,*A*) = 7.0, 2 H, H–C(4″)); 4.03 and 4.06 $\delta_A$, 4.12 and 4.13 $\delta_B$; 2 *AB* patterns, *J*(*A*,*B*) = 8.7, *J*(*A*,4″) = 7.2, *J*(*B*,4″) = 10.1, 4 H, $CH_2$(5″)); 4.19 (*t*, *J*(1‴,2‴) = 7.6, $CH_2$(1‴)); 5.37 (*t*, *J*(NH,1) = 6.8, NH); 5.88 (*t*, *J*(NH,3) = 6.5, NH). $^{13}$C-NMR ($CDCl_3$/$CDCl_3$): 1.65 ($C_6F_{13}CH_2\mathit{C}H_2$); 12.72 (C(2‴)); 21.46 (C(8′)); 24.07 (C(4′)); 25.17 ($CH_2\mathit{C}H_2C_6F_{13}\mathit{C}H_2CH_2$); 25.41 (C(6′)); 25.77, 25.83 ($\mathit{Me}_3$C); 29.52 (C(5′)); 30.20 (C(3′)); 33.89, 34.00 ($Me_3\mathit{C}$); 35.76 (C(3)); 36.36 (C(2)), 36.72 (C(2′)); 37.39 (C(1)); 42.41 (C(7′)); 61.04 (C(1‴)); 68.81, 68.84 (C(5″)); 75.38, 75.57 (C(4″)); 115.84, 118.01 (*C*F); 156.71 (NC(O)O); 168.03, 168.21 (C(2″)); 173.82 (C(1′)). $^{19}$F-NMR ($CDCl_3$/$CDCl_3$): −126.33 to −126.06 (6 F); −123.27 to −122.92 (6 F); −121.96 to −121.92 (6 F); −116.21 to −115.94 (6 F); −80.88 to −80.79 (9 F). ESI-MS (pos.): 1593 (17), 1592 (41), 1591 (100, $M^+$). HR-APCI-MS (MeOH): 1591.38620 ($[M+H]^+$, $C_{52}H_{62}N_4O_5F_{39}Si^+$; calc. 1591.38668).

6. *Noncovalent Immobilization of the Perfluoro-Tagged Ligands* **5**, **6**, *and* **7** *on FRPSG* **2***: General Procedure.* The perfluorinated ligands **5**, **6**, or **7** (10 μmol) were dissolved in THF (200 ml), and a soln. of $Cu(OTf)_2$ (10 μmol) in THF was added followed by FRPSG **2**. The solvent was evaporatated, and THF (2 × 200 ml) was added again. Concentration of the mixture yielded the immobilized catalysts **19**, **20**, and **21**, resp., with a loading of 10 μmol/g.

7. *Control Experiments in $H_2O$: General Procedure.* Unmodified $SiO_2$ or FRPSG **2** (25.0 mg, 10 μmol/g, 10 mol-%, and 12.5 mg, 10 μmol/g, 5 mol-%, resp.) was taken up in $H_2O$ (495 μl), and a soln. of the dienophile **22**, **23**, or **24** (0.5M in MeCN, 5.0 μl) was added. The mixture was cooled to 5° before cyclopenta-1,3-diene (**25**; 6.20 μl, 4.96 mg, 75.0 μmol, 30.0 equiv.) was added. After shaking the mixture for 24 h at 5°, the $SiO_2$ or FRPSG was filtered off and washed with MeCN (4 × 0.5 ml), and the solvent was evaporated. The residues were dissolved in heptane/i-PrOH 85 : 15 (500 μl) for adducts **26**, heptane/EtOH 80 : 20 (500 μl) for adducts **27**, or heptane/i-PrOH 98 : 2 (500 μl) for adducts **28**, and the conversions were determined by chiral HPLC.

8. Diels–Alder *Reactions with Immobilized Catalyst* **19**, **20**, *and* **21** *in $H_2O$: General Procedure.* The catalyst **19**, **20**, or **21** (25.0 mg, 10 μmol/g, 10 mol-%, and 12.5 mg, 10 μmol/g, 5 mol-%, resp.) was taken up in $H_2O$ (495 μl) in an *Eppendorf* reaction tube. A soln. of the dienophile **22**, **23**, or **24** (0.5M in MeCN, 5.0 μl) was added, and the mixture was cooled to 5° before cyclopenta-1,3-diene (**25**; 6.20 μl, 4.96 mg, 75.0 μmol, 30.0 equiv.) was added. After shaking the mixture for 24 h at 5°, the catalyst on FRPSG was filtered off and washed with MeCN (4 × 0.5 ml), and the solvent was evaporated. The residues of the adducts **26**, **27**, and **28**, resp., were dissolved and analyzed by chiral HPLC as described in *Exper. 7*. The recycled immobilized catalysts **19**, **20**, and **21** were re-used without further purification.

9. *Control Experiments in $CH_2Cl_2$: General Procedure.* As described in *Exper. 7*, with $CH_2Cl_2$ (450 μl) instead of $H_2O$, unmodified $SiO_2$ or FRPSG **2** (25.0 mg, 10 μmol/g, 10 mol-%), dienophile **22**, **23**, or **24** (0.05M in $CH_2Cl_2$, 50.0 μl), and cyclopenta-1,3-diene (**25**; 6.20 μl, 4.96 mg, 75.0 μmol, 30.0 equiv.). The mixture was shaken for 45 min with **22**, for 4.5 h with **23**, and for 6 h with **24** at 5°. Then, the reaction soln. was taken off *via* a syringe and concentrated. The residues of the adducts **26**, **27**, and **28**, resp., were dissolved and analyzed by chiral HPLC as described in *Exper. 7*.

10. Diels–Alder *Reactions with Immobilized Catalyst* **19**, **20**, *and* **21** *in $CH_2Cl_2$. General Procedure.* As described in *Exper. 8*, with $CH_2Cl_2$ (450 μl) instead of $H_2O$, catalyst **19**, **20**, or **21** (25.0 mg, 10 μmol/g, 10 mol-%), dienophile **22**, **23**, or **24** (0.05M in $CH_2Cl_2$, 50.0 μl), and cyclopenta-1,3-diene (**25**) (6.20 μl, 4.96 mg, 75.0 μmol, 30.0 equiv.). The mixture was shaken for 45 min with **22**, for 4.5 h with **23**, and for 6 h

with **24** at 5°. Then, the reaction soln. was taken off *via* a syringe and concentrated. The residues of adducts **26**, **27**, and **28**, resp., were dissolved and analyzed by chiral HPLC as described in *Exper. 7*. The recycled immobilized catalysts were re-used in the subsequent run without further purification.

11. *(1-Oxidopyridin-2-yl)[(1*R,*2*S,*3*S,*4*S*)-3-phenylbicyclo[2.2.1]hept-5-en-2-yl]methanone* (*endo*-**26**) *and (1-Oxidopyridin-2-yl)[(1*S,*2*S,*3*S,*4*R*)-3-phenylbicyclo[2.2.1]hept-5-en-2-yl]methanone* (*exo*-**26**). HPLC (*Chiralpak AD-H* (0.46 cm × 25 cm), heptane/i-PrOH 85:15, 1.0 ml/min, 30 min; $\lambda$ 230 nm): $t_R$ 11.6 + 13.5 (*exo*-products), 14.1 + 15.0 (*endo*-products), and 23.1 (starting material). $[\alpha]_{589}^{20} = +171.2$ (3.2M, $CHCl_3$); $ee_{endo}$ 93%. $^1$H-NMR ($CDCl_3/CHCl_3$): *endo*-**26**: 1.56 ($\delta_A$), 1.89 ($\delta_B$, *AB* pattern, $J(A,B) =$ 8.6, $J(A,4'') = 3.6$, $^4J(A,3'') = 1.8$, $J(B,4'') = J(B,1'') = 1.5$, $CH_2(7'')$); 3.09 (*m*, H–C(3″)); 3.35 (*m*, H–C(4″)); 3.39 (*m*, H–C(1″)); 4.50 (*dd*, $J(2'',3'') = 5.1$, $J(2'',1'') = 3.5$, H–C(2″)); 5.87 (*dd*, $J(6'',5'') =$ 5.7, $J(6'',1'') = 2.8$, H–C(6″)); 6.46 (*dd*, $J(5'',6'') = 5.6$, $J(5'',4'') = 3.2$, H–C(5″)); 7.17–7.21 (*m*, $H_p$); 7.27–7.36 (*m*, 2 $H_o$, 2 $H_m$, H–C(4), H–C(5)); 7.43 (*ddd*, $J(3,4) = 7.2$, $^4J(3,5) = 2.7$, $^5J(3,6) = 0.8$, H–C(3)); 8.17 (*ddd*, $J(6,5) = 6.2$, $^4J(6,4) = 1.6$, $^5J(6,3) = 0.7$, H–C(6)); *exo*-**26**: 1.51 (*ddd*, $J(A,B) = 8.6$, $J(A,4'') = 3.6$, $J(A,1'') = 1.8$, $H_A$–C(7″)); 1.85–1.87 (*m*, $H_B$–C(7″)); 3.21 (*m*, H–C(4″)); 3.24 (*m*, H–C(1″)); 6.06 (*dd*, $J(6'',5'') = 5.7$, $J(6'',1'') = 2.8$, H–C(6″)); 6.41 (*dd*, $J(5'',6'') = 5.6$, $J(5'',4'') = 3.2$, H–C(5″)); 7.54 (*ddd*, $J(3,4) = 7.2$, $^4J(3,5) = 2.7$, $^5J(3,6) = 0.8$, H–C(3)). $^{13}$C-NMR ($CDCl_3/CDCl_3$): *endo*-**26**: 46.44 (C(4″)); 46.52 (C(1″)); 47.66 (C(7″)); 49.20 (C(3″)); 58.28 (C(2″)); 125.74 (C(4)); 126.04 ($C_p$); 126.37 (C(5)); 127.47 (C(3)); 127.69 (2 $C_m$); 128.49 (2 $C_o$); 133.13 (C(6″)); 139.95 (C(5″), C(6)); 140.43 ($C_{ipso}$); 143.97 (C(2)); 198.58 (C(1′)); *exo*-**26**: 46.99 (C(4″)); 48.12 (C(1″)); 48.56 (C(7″)); 49.01 (C(3″)); 56.80 (C(2″)); 125.60 (C(4)); 126.12 ($C_p$); 126.64 (C(5)); 127.57 (C(3)); 127.98 (2 $C_m$); 128.06 (2 $C_o$); 131.08 (C(6″)); 136.28 (C(5″)); 137.14 (C(6)); 147.56 (C(2)). CI-MS ($NH_3$): 293 (10), 292 (41, $[M+1]^+$), 276 (20, $[M+1-O]^+$), 227 (15), 226 (100, $[M+1-C_5H_6]^+$), 210 (35, $[M+1-O-C_5H_6)^+]$, 209 (11), 185 (7). HR-CI-MS ($NH_3$): 292.13360 ($[M+H]^+$, $C_{19}H_{18}NO_2^+$; calc. 292.13375).

*[(1*R,*2*S,*3*S,*4*S*)-3-(4-Methoxyphenyl)bicyclo[2.2.1]hept-5-en-2-yl](1-oxidopyridin-2-yl)methanone* (*endo*-**27**) *and [(1*S,*2*S,*3*S,*4*R*)-3-(4-Methoxyphenyl)bicyclo[2.2.1]hept-5-en-2-yl](1-oxidopyridin-2-yl)-methanone* (*exo*-**27**). HPLC (*Chiralpak AD-H* (0.46 cm × 25 cm), *A* = heptane/i-PrOH 80:20 and *B* = heptane/EtOH 80:20, eluent *A*/*B* 1:3, 1.25 ml/min, 60 min; $\lambda$ 230 nm): $t_R$ 17.7 + 28.8 (*exo*-products), 18.9 + 22.9 (*endo*-products), 45.4 (starting material). $[\alpha]_{589}^{20} = +154.4$ (3.7M, $CHCl_3$); $ee_{endo}$ 93%. $^1$H-NMR ($CDCl_3/CHCl_3$): *endo*-**27**: 1.55 ($\delta_A$), 1.87 ($\delta_B$; *AB* pattern, $J(A,B) = 8.6$, $J(A,4'') = 3.6$, $J(A,3'') = 1.8$, $J(B,4'') = J(B,1'') = 1.5$, $CH_2(7'')$; 3.03 (*m*, H–C(4″)); 3.27 (*m*, H–C(1″)); 3.36 (*m*, H–C(3″)); 3.78 (*s*, MeO); 4.45 (*dd*, $J(2'',3'') = 5.1$, $J(2'',1'') = 3.4$, H–C(2″)); 5.87 (*dd*, $J(6'',5'') = 5.6$, $J(6'',1'') = 2.7$, H–C(6″)); 6.45 (*dd*, $J(5'',6'') = 5.6$, $J(5'',4'') = 3.2$, H–C(5″)); 6.84 (*d*, $^3J = 8.7$, 2 $H_o$); 7.23–7.35 (*m*, 2 $H_m$, H–C(4), H–C(5)); 7.41 (*ddd*, $J(3,4) = 7.3$, $^4J(3,5) = 2.7$, $^5J(3,6) = 0.8$, H–C(3)); 8.16 (*ddd*, $J(6,5) = 6.2$, $^4J(6,4) = 1.5$, $^5J(6,3) = 0.8$, H–C(6)); *exo*-**27**: 1.84–1.85 (*m*, $H_B$–C(7″)); 3.15 (*m*, H–C(1″)); 3.22 (*m*, H–C(3″)); 3.74 (*s*, MeO); 6.06 (*dd*, $J(6'',5'') = 5.6$, $J(6'',1'') = 2.7$, H–C(6″)); 6.41 (*dd*, $J(5'',6'') =$ 5.6, $J(5'',4'') = 3.2$, H–C(5″)); 6.75 (*d*, $^3J = 8.8$, 2 $H_o$); 7.10 (*d*, $^3J = 9.0$, 2 $H_m$); 7.52 (*ddd*, $J(3,4) = 7.3$, $^4J(3,5) = 2.7$, $^5J(3,6) = 0.8$, H–C(3)); 8.14 (*ddd*, $J(6,5) = 6.2$, $^4J(6,4) = 1.4$, $^5J(6,3) = 0.8$, H–C(6)). $^{13}$C-NMR ($CDCl_3/CDCl_3$): *endo*-**27**: 45.85 (C(4″)); 46.39 (C(1″)); 47.59 (C(7″)); 49.45 (C(3″)); 55.32 (MeO); 58.31 (C(2″)); 113.88 (2 $C_o$); 125.71 (C(4)); 126.25 (C(3)); 127.41 (C(5)); 128.58 (2 $C_m$); 133.01 (C(6″)); 136.01 ($C_{ipso}$); 139.92 (C(5″)); 140.38 (C(6)); 147.53 ($C_p$); 157.89 (C(2)); 198.74 (C(1′)); *exo*-**27**: 47.04 (C(4″)); 47.44 (C(1″)); 48.48 (C(7″)); 49.12 (C(3″)); 55.27 (MeO); 56.99 (C(2″)); 113.46 (2 $C_o$); 125.52 (C(4)); 126.55 (C(3)); 127.51 (C(5)), 128.87 (2 $C_m$); 136.37 (C(5″)); 137.11 (C(6″)); 158.00 (C(2)). CI-MS ($NH_3$): 322 (19, $[M+1]^+$), 306 (18, $[M+1-O]^+$), 257 (15), 256 (100, $[M+1-C_5H_6]^+$), 241 (11), 240 (73, $[M+1-O-C_5H_6]^+$), 239 (26), 210 (5), 185 (8). HR-CI-MS ($NH_3$): 322.14500 ($[M+H]^+$, $C_{20}H_{20}NO_3^+$; calc. 322.14432).

*[(1*R,*2*S,*3*S,*4*S*)-3-(1,1-Dimethylethyl)bicyclo[2.2.1]hept-5-en-2-yl-(1-oxidopyridin-2-yl)methanone* (*endo*-**28**) *and [(1*S,*2*S,*3*S,*4*R*)-3-(1,1-Dimethylethyl)bicyclo[2.2.1]hept-5-en-2-yl](1-oxidopyridin-2-yl)-methanone* (exo-**28**). HPLC: *Chiralpak AD-H* (0.46 cm × 25 cm, heptane/i-PrOH 98:2, 1.0 ml/min, 60 min; $\lambda$ 230 nm): $t_R$ 23.2 + 27.3 (*exo*-products), 31.1 + 35.2 (*endo*-products), 48.8 (starting material). $[\alpha]_{589}^{20} = +173.7$ (2.4M, $CHCl_3$); $ee_{endo}$ 93%. $^1$H-NMR ($CDCl_3/CHCl_3$): *endo*-**28**: 0.95 (*s*, *t*-Bu); 1.35 ($\delta_A$), 1.67 ($\delta_B$); *AB* pattern $J(A,B) = 8.5$, $J(A,4'') = 3.5$, $^4J(A,3'') = 1.7$, $J(B,4'') = J(B,1'') = 1.5$, $CH_2(7'')$); 1.88 (*dd*, $J(3'',2'') = 6.1$, $^4J(3'',A) = 1.8$, H–C(3″)); 2.77 (*ddd*, $J(4'',5'') = J(4'',A) = 3.1$, $J(4'',B) = 1.5$, H–C(4″)); 3.17 (*m*, H–C(1″)); 4.14 (*dd*, $J(2'',3'') = 5.9$, $J(2'',1'') = 3.2$, H–C(2″)); 5.76 (*dd*, $J(6'',5'') = 5.6$, $J(6'',1'') =$

2.7, H–C(6″)); 6.43 (*dd*, $J(5'',6'')=5.6$, $J(5'',4'')=3.3$, H–C(5″)); 7.31 (*ddd*, $J(4,3)=J(4,5)=7.5$, $^4J(4,6)=$ 1.4, H–C(4)); 7.32–7.36 (*m*, H–C(5)); 7.38 (*ddd*, $J(3,4)=7.5$, $^4J(3,5)=2.5$, $^5J(3,6)=0.8$, H–C(3)); 8.20 (*ddd*, $J(6,5)=6.1$, $^4J(6,4)=1.4$, $^5J(6,3_)=0.6$, H–C(6)); *exo*-**28**: 0.80 (*s*, *t*-Bu); 1.34–1.35 (*m*, $H_A$–C(7″)); 1.73 (*ddd*, $J(B,A)=8.3$, $J(B,4'')=J(B,1'')=1.5$, $H_B$–C(7″)); 2.64 (*dd*, $J(2'',3'')=6.3$, $^4J(2'',1'')=3.0$, H–C(2″)); 2.98 ($m_c$, H–C(4″)); 3.02 ($m_c$, H–C(1″)); 3.40 (*dd*, $J(3'',2'')=6.3$, $J(3'',A)=1.3$, H–C(3″)); 6.16 (*dd*, $J(6'',5'')=5.4$, $J(6'',1'')=2.8$, H–C(6″)); 6.19 (*dd*, $J(5'',6'')=5.5$, $J(5'',4'')=3.1$, H–C(5″)); 7.50–7.53 (*m*, H–C(3)). $^{13}$C-NMR ($CDCl_3$/$CDCl_3$): *endo*-**28**: 29.03 ($Me_3C$); 32.63 ($Me_3C$); 44.72 (C(4″)); 46.85 (C(1″)); 47.93 (C(7″)); 51.79 (C(2″)); 53.46 (C(3″)); 125.76 (C(4)); 126.38 (C(5)); 127.27 (C(3)); 131.53 (C(6″)); 140.47 (C(6)); 141.50 (C(5″)); 147.81 (C(2)); 199.64 (C(1′)); *exo*-**28**: 29.41 ($Me_3C$); 32.69 ($Me_3C$); 45.42 (C(4″)); 48.4 (C(7″)); 49.12 (C(1″)); 52.03 (C(3″)); 55.36 (C(2″)); 126.89 (C(3)); 135.05 (C(5″)); 137.04 (C(6″)); 140.47 (C(6)); 201.11 (C(1′)). CI-MS ($NH_3$): 273 (17), 272 (99, $[M+1]^+$), 207 (12), 206 (100, $[M+1-C_5H_6]^+$), 148 (7). HR-CI-MS ($NH_3$): 272.16440 ($[M+H]^+$, $C_{17}H_{22}NO_2^+$; calc. 272.16505).

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