

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

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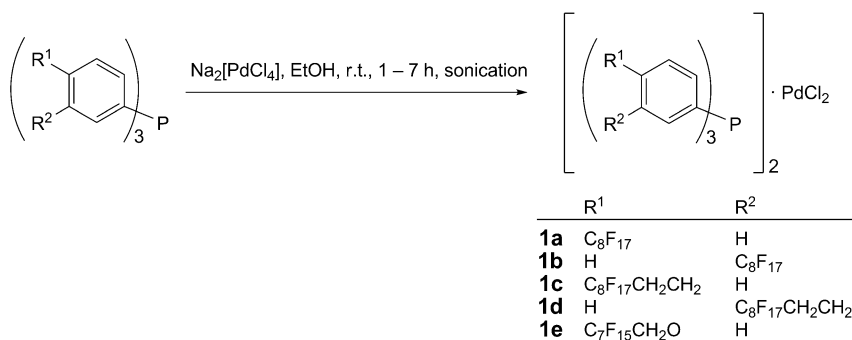
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Dedicated to Prof. Dieter Seebach on the occasion of his 75th birthday

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 H₂O and in CH₂Cl₂ (*Scheme 4*). Besides high conversion of the dienophile, we observed enantiomer excesses of up to 88% in H₂O and 97% in CH₂Cl₂, 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



[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 CH₂CH₂ or an OCH₂ 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 fluorine–fluorine interactions, we have implemented some time ago the concept of FRPSG-supported catalysis (FRPSG = fluorine reversed-phase silica gel; *Fig. 1*). In this technology, the perfluoro-tagged catalyst is noncovalently bound to the FRPSG by fluorine–fluorine 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 published by *Gladysz* and co-workers [6].

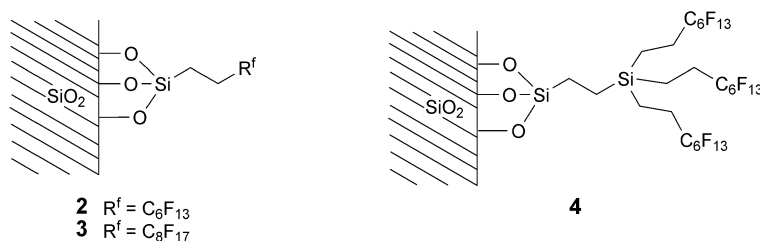
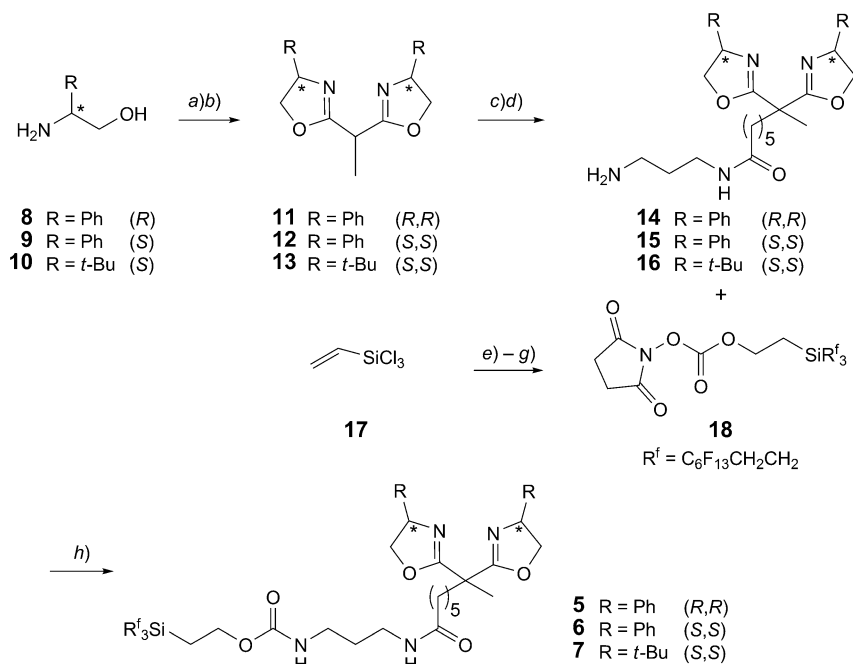


Fig. 1. Fluorine reversed-phase SiO₂ (FRPSG)

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 H₂O and CH₂Cl₂ 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(SO₂C₄F₉)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

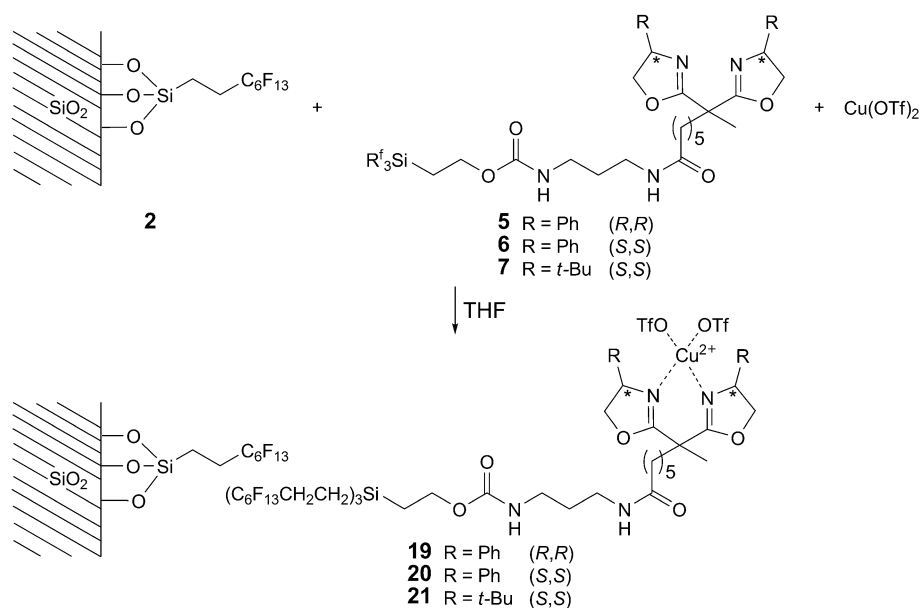
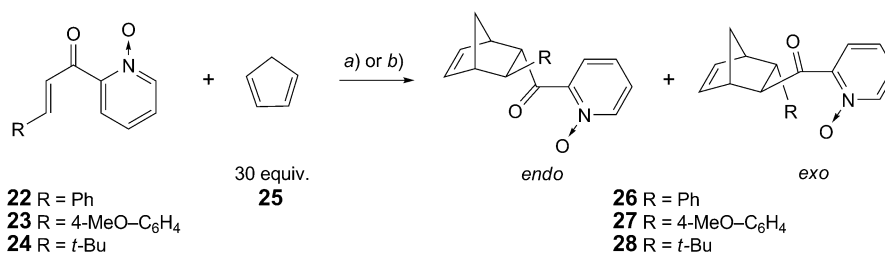
Scheme 2. Synthesis of the Perfluoro-Tagged box Ligands **5–7**

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, Et₃N, TsCl, CH₂Cl₂, 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) C₆F₁₃CH₂CH₂I, Et₂O, –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. H₂O₂, r.t., 2 h; 65–90%. g) Disuccinimidyl carbonate, Et₃N, MeCN, r.t., 20 h; 31–48%. h) **18**, THF, (i-Pr)₂EtN, r.t., 1 h; **5**, 59–83%; **6**, 91%; **7**, 70–75%.

trichloro(ethenyl)silane (**17**) and C₆F₁₃CH₂CH₂I [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 Et₃N [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 SupportScheme 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 fluorine–fluorine 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)}	<i>endo/exo</i> 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 m²/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 H₂O

	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 H₂O were not really convincing, we decided to switch from H₂O to CH₂Cl₂ as reaction medium. We expected the fluororous–fluororous 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 SiO₂ and FRPSG **2** as additives to the reaction in CH₂Cl₂ 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 H₂O. Furthermore, the reactions were also significantly faster in CH₂Cl₂ (45 min for **22**, 4.5 h for **23**, and 6 h for **24**) compared to H₂O 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 CH₂Cl₂. 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

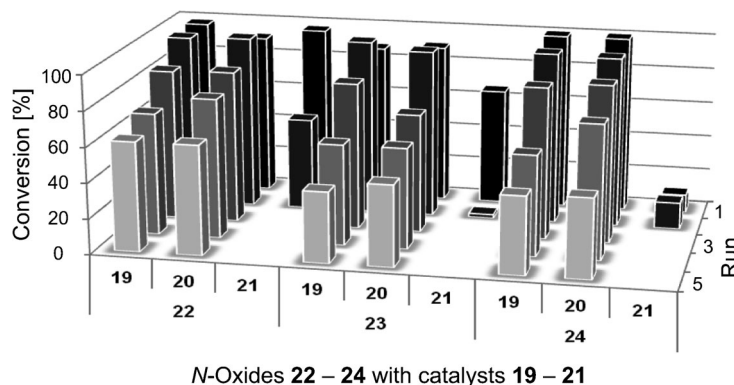


Fig. 2. Diels–Alder reactions of N-oxides **22**–**24** with **25** in the presence of catalysts **19**, **20**, or **21** in CH_2Cl_2 . The ee values given below in parentheses are for the second, third, fourth, and fifth runs with the same catalyst. N-Oxide **22**: ee_{endo} [%] with **19**, –97 (–95, –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 $[\alpha]_D = (\alpha^{\text{exp}} \cdot 100)/(c \cdot d)$. NMR Spectra: *Bruker* spectrometer; at 400.1 (^1H), 100.6 (^{13}C), and 235.4 MHz (^{19}F); δ in ppm rel. to Me_4Si (=0 ppm) for ^1H 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 (= (β *R*)- 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 CHCl₃ 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 CH₂Cl₂ (0.3M), and Et₃N (8.25 equiv.) was added dropwise. Then a soln. of TsCl (2.2 equiv.) in CH₂Cl₂ (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. Na₂CO₃ soln. and aq. sat. NaCl soln., dried (Na₂SO₄), and concentrated and the residue subjected to CC (SiO₂, AcOEt/EtOH 50:1): **11** (57–68%), **12** (58%), and **13** (33–78%), resp. Slightly yellow oils.

Data of **11** and **12**: [α]_D²⁰ = +101.5 (**11**, 3.5M, CHCl₃); [α]_D²⁰ = –83.1 (**12**, 5.3M, CHCl₃). ¹H-NMR (CDCl₃/CHCl₃): 1.65 (*d*, ³*J* = 7.2, MeCH); 3.77 (*q*, ³*J* = 7.2, MeCH); 4.17 and 4.18 (δ_A) 4.68 and 4.69 (δ_B ; 2 *AB* patterns, *J*(*A,B*) = 8.4, *J*(*A,4*) = 7.8, *J*(*B,4*) = 10.1, 4 H, CH₂(5,5')); 5.24 and 5.25 (*dd*, *J*(*A,B*) = 10.0, *J*(*4,A*) = 7.9, 2 H, H–C(4,4')); 7.26–7.35 (*m*, 10 arom. H). ¹³C-NMR (CDCl₃/CDCl₃): 15.46 (MeCH); 34.20 (MeCH); 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 (NH₃): 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 C₂₀H₂₀N₂O₂ (320.38): C 74.98, H: 6.29, N 8.74; found: C 74.69, H 6.31, N 8.46.

Data of **13**: [α]_D²⁰ = –99.3 (4.6M, CHCl₃). ¹H-NMR (CDCl₃/CHCl₃): 0.87, 0.88 (*s*, 18 H, *t*-Bu); 1.48 (*d*, ³*J* = 7.2, MeCH); 3.55 (*q*, ³*J* = 7.2, MeCH); 3.83–3.86 (*m*, 2 H, H–C(4,4')); 4.07 and 4.08 (δ_A) 4.17 and 4.18 (δ_B ; 2 *AB* patterns, *J*(*A,B*) = 8.7, *J*(*A,4*) = 7.5, *J*(*B,4*) = 10.0, CH₂(5,5')). ¹³C-NMR (CDCl₃/CDCl₃): 15.36 (MeCH); 25.74, 25.79 (Me₃C); 33.81, 33.85 (Me₃C); 34.12 (MeCH); 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 C₁₆H₂₈N₂O₂ (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[(4*S*)-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. NH₄Cl soln. and CH₂Cl₂ were added, and the org. phase was washed with H₂O (2 ×). The combined aq. phase was extracted with CH₂Cl₂ (3 ×), the CH₂Cl₂ phase dried (Na₂SO₄) and concentrated, and the crude product purified by CC (CH₂Cl₂/AcOEt 4:1 + 0.5% Et₃N): 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 CHCl₃/i-PrOH 8:2 (3 ×). The combined org. phase was washed with sat. aq. NaCl soln., dried (Na₂SO₄), and concentrated, and the crude product was purified by CC (MeOH/aq. NH₃ soln. 98:2): **14** (75–77%), **15** (78%), and **16** (69%); resp. Yellow oils.

Data of **14** and **15**: [α]_D²⁰ = +102.6 (**14**, 4.0M, CHCl₃); [α]_D²⁰ = –106.4 (**15**, 4.6M, CHCl₃). ¹H-NMR (CDCl₃/CHCl₃): 1.35–1.46 (*m*, CH₂(4), CH₂(5)); 1.63 (*s*, Me(8)); 1.59–1.68 (*m*, CH₂(3), CH₂(6)); 1.98–2.09 (*m*, CH₂(2')); 2.13 (*t*, *J*(2,3) = 7.6, CH₂(2)); 2.78 (*t*, *J*(3'',2'') = 6.4, CH₂(3'')); 3.26 (*dt*, *J*(1'',NH) = 6.1, *J*(1'',2'') = 6.3, CH₂(1'')); 3.26 (*br s*, NH₂); 4.13 and 4.14 (δ_A) 4.65 and 4.66 (δ_B ; 2 *AB* patterns *J*(*A,B*) = 8.4, *J*(*A,4*) = 8.1, *J*(*B,4*) = 10.0, 4 H, CH₂(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). ¹³C-NMR (CDCl₃/CDCl₃): 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]⁺, C₂₉H₃₉N₄O₃⁺; calc. 491.30222).

Data of 16: ¹H-NMR (CDCl₃/CHCl₃): 0.87 (s, 18 H, *t*-Bu); 1.32–1.33 (m, CH₂(4) CH₂(5)); 1.47 (s, Me(8)); 1.63 (tt, *J*(3,2) = 7.6, *J*(3,4) = 7.4, C₂(3)); 1.68 (tt, *J*(2'',3'') = 6.5, *J*(2'',1'') = 6.4, CH₂(2'')); 1.79–1.87, 1.95–2.01 (m, CH₂(6)); 2.15 (t, *J*(2,3) = 7.6, CH₂(2)); 2.51 (br. s, NH₂); 2.83 (t, *J*(3'',2'') = 6.4, CH₂(3'')); 3.36 (dt, *J*(1'',NH) = 6.1, *J*(1'',2'') = 6.2, CH₂(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 (δ_A), 4.12 and 4.13 δ_B; 2 AB patterns, *J*(A,B) = 8.7, *J*(A,4') = 7.3, *J*(B,4') = 10.0, 4 H, CH₂(5'); 6.43 (t, *J*(NH,1'') = 5.6, NH). ¹³C-NMR (CDCl₃/CDCl₃): 21.48 (C(8)); 24.10 (C(6)); 25.69 (C(5)); 25.79, 25.87 (Me₃C); 29.56 (C(3)); 31.65 (C(4)); 33.90, 34.01 (Me₃C); 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**). C₆F₁₃CH₂CH₂I (4.0 equiv.) was dissolved in dry Et₂O (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., H₂O was added, the org. phase washed with sat. aq. NaHCO₃ soln., dried (Na₂SO₄), and concentrated, and the crude product purified by CC (SiO₂; pure cyclohexane): perfluorinated silane (71–91%). Waxy solid.

The perfluorinated silane was dissolved in dry Et₂O (0.25M), and 9-BBN (3.0 equiv.) was added. After stirring for 20 h at r.t., 3M aq. NaOH and 35% aq. H₂O₂ soln. were added, and the soln. was stirred for further 2 h at r.t. before H₂O was added. The aq. phase was extracted with Et₂O (3 ×), the combined org. phase washed with 10% aq. Na₂S₂O₃ soln. and sat. aq. NaCl soln., dried (Na₂SO₄), and concentrated, and the crude product purified by CC (cyclohexane → cyclohexane/AcOEt 4 : 1): hydroxysilane (65–90%). Waxy solid.

The hydroxysilane and Et₃N (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 CH₂Cl₂, the org. phase washed with sat. aq. NaHCO₃ soln. (2 ×), dried (Na₂SO₄), and concentrated, and the crude product purified by CC (cyclohexane/AcOEt 4 : 1): **18** (31–48%). White solid.

¹H-NMR (CDCl₃/CHCl₃): 0.95–0.99 (m, 3 CH₂C₆F₁₃CH₂CH₂); 1.31 (t, *J*(2,1) = 8.1, CH₂(2)); 2.02–2.15 (m, 3 C₆F₁₃CH₂CH₂); 2.84 (s, CH₂(3'), CH₂(4')); 4.46 (t, *J*(1,2) = 8.0, CH₂(1)). ¹³C-NMR (CDCl₃/CDCl₃): 1.65 (C₆F₁₃CH₂CH₂); 12.66 (C(2)); 25.35 (C₆F₁₃CH₂CH₂); 25.56 (C(3'), C(4')); 67.95 (C(1)); 151.53 (OC(O)O); 168.51 (C(2'), C(5')). ¹⁹F-NMR (CDCl₃/CDCl₃): –126.29 to –126.12 (6 F); –123.28 to –122.22 (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 (NH₃): 1275 (11), 1274 (38), 1273 (100, [M + NH₄]⁺), 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(4R)-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(4S)-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(4S)-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)₂EtN (10.0 equiv.), the mixture was stirred for 1 h at r.t., and then sat. aq. NaHCO₃ soln. was added. The aq. phase was extracted with Et₂O (3 ×), dried (Na₂SO₄), 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: [α]₃₆₅²⁰ = +119.8 (**5**, 2.5M, CHCl₃); [α]₃₆₅²⁰ = –120.7 (**6**, 1.7M, CHCl₃). ¹H-NMR (CDCl₃/CHCl₃): 0.90–0.95 (m, 3 C₆F₁₃CH₂CH₂); 1.14 (t, *J*(2''',1''') = 8.0, CH₂(2''')); 1.35–1.48 (m, CH₂(4'), CH₂(5')); 1.56 (tt, *J*(3',2') = 6.2, *J*(3',4') = 6.2, CH₂(3')); 1.62–1.69 (m, CH₂(6')); 1.64 (s, Me(8')); 2.01–2.17 (m, CH₂(2), CH₂(2'), 3 C₆F₁₃CH₂CH₂); 3.15 (dt, *J*(1,NH) = 6.3, *J*(1,2) = 6.3, CH₂(1)); 3.16–3.23 (m, CH₂(3)); 4.18 (t, *J*(1''',2''') = 8.1, CH₂(1''')); 4.14 and 4.15 (δ_A), 4.66 and 4.67 (δ_B), 2 AB patterns, *J*(A,B) = 8.4, *J*(A,4'') = 7.7, *J*(B,4'') = 10.2, 4 H, CH₂(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 ($\text{CDCl}_3/\text{CDCl}_3$): 1.64 ($\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2$); 12.72 ($\text{C}(2'')$); 21.64 ($\text{C}(8')$); 23.94 ($\text{C}(4')$); 25.4 ($\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2$); 25.46 ($\text{C}(6')$); 29.19 ($\text{C}(5')$); 30.15 ($\text{C}(3')$); 35.73 ($\text{C}(3)$); 36.43 ($\text{C}(2)$); 36.53 ($\text{C}(2')$); 37.37 ($\text{C}(1)$); 42.73 ($\text{C}(7')$); 61.02 ($\text{C}(1''')$); 69.57, 69.66 ($\text{C}(5'')$); 75.34, 75.40 ($\text{C}(4'')$); 115.84, 118.02, 118.71 (CF); 126.78 (2 C_o); 127.67 (C_p); 128.79 (2 C_m); 142.47 (C_{ipso}); 156.69 ($\text{NC}(\text{O})\text{O}$); 169.81, 169.90 ($\text{C}(2'')$); 173.79 ($\text{C}(1')$). ^{19}F -NMR ($\text{CDCl}_3/\text{CDCl}_3$): –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 ($[M+H]^+$, $\text{C}_{56}\text{H}_{54}\text{F}_{39}\text{N}_4\text{O}_5\text{Si}^+$; calc. 1631.32408).

Data of 7: $[\alpha]_{20}^{365} = -66.4$ (1.8M, CHCl_3). ^1H -NMR ($\text{CDCl}_3/\text{CHCl}_3$): 0.87 (s, 18 H, *t*-Bu); 0.91–0.96 (*m*, 3 $\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2$); 1.15 (*t*, $J(2''',1'') = 7.8$, $\text{H}-\text{CH}_2(2''')$); 1.30–1.35 (*m*, $\text{CH}_2(4')$, $\text{CH}_2(5'')$); 1.46 (s, Me($8'$)); 1.59–1.66 (*m*, $\text{CH}_2(3')$, $\text{CH}_2(6')$); 2.00–2.09 (*m*, $\text{CH}_2(2)$, 3 $\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2$); 2.16 (*t*, $J(2',3') = 7.6$, $\text{CH}_2(2')$); 3.18 (*dt*, $J(1,\text{NH}) = 6.3$, $J(1,2) = 6.1$, $\text{CH}_2(1)$); 3.29 (*dt*, $J(3,\text{NH}) = 6.2$, $J(3,2) = 6.2$, $\text{CH}_2(3)$); 3.84, 3.85 (*dd*, $J(4'',B) = 10.3$, $J(4'',A) = 7.0$, 2 H, $\text{H}-\text{C}(4'')$); 4.03 and 4.06 δ_A , 4.12 and 4.13 δ_B ; 2 *AB* patterns, $J(A,B) = 8.7$, $J(A,4'') = 7.2$, $J(B,4'') = 10.1$, 4 H, $\text{CH}_2(5'')$); 4.19 (*t*, $J(1''',2'') = 7.6$, $\text{CH}_2(1''')$); 5.37 (*t*, $J(\text{NH},1) = 6.8$, NH); 5.88 (*t*, $J(\text{NH},3) = 6.5$, NH). ^{13}C -NMR ($\text{CDCl}_3/\text{CDCl}_3$): 1.65 ($\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2$); 12.72 ($\text{C}(2''')$); 21.46 ($\text{C}(8')$); 24.07 ($\text{C}(4')$); 25.17 ($\text{CH}_2\text{CH}_2\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2$); 25.41 ($\text{C}(6')$); 25.77, 25.83 (Me_3C); 29.52 ($\text{C}(5')$); 30.20 ($\text{C}(3')$); 33.89, 34.00 (Me_3C); 35.76 ($\text{C}(3)$); 36.36 ($\text{C}(2)$); 36.72 ($\text{C}(2')$); 37.39 ($\text{C}(1)$); 42.41 ($\text{C}(7')$); 61.04 ($\text{C}(1''')$); 68.81, 68.84 ($\text{C}(5'')$); 75.38, 75.57 ($\text{C}(4'')$); 115.84, 118.01 (CF); 156.71 ($\text{NC}(\text{O})\text{O}$); 168.03, 168.21 ($\text{C}(2'')$); 173.82 ($\text{C}(1')$). ^{19}F -NMR ($\text{CDCl}_3/\text{CDCl}_3$): –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 ($[M+H]^+$, $\text{C}_{52}\text{H}_{62}\text{N}_4\text{O}_5\text{F}_{39}\text{Si}^+$; 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 $\text{Cu}(\text{OTf})_2$ (10 μmol) in THF was added followed by FRPSG **2**. The solvent was evaporated, and THF (2 $\times$ 200 ml) was added again. Concentration of the mixture yielded the immobilized catalysts **19**, **20**, and **21**, resp., with a loading of 10 $\mu\text{mol/g}$.

7. *Control Experiments in H_2O : General Procedure.* Unmodified SiO_2 or FRPSG **2** (25.0 mg, 10 $\mu\text{mol/g}$, 10 mol-%, and 12.5 mg, 10 $\mu\text{mol/g}$, 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 $\times$ 0.5 ml), and the solvent was evaporated. The residues were dissolved in heptane/*i*-PrOH 85:15 (500 μl) for adducts **26**, heptane/*i*-PrOH 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 $\mu\text{mol/g}$, 10 mol-%, and 12.5 mg, 10 $\mu\text{mol/g}$, 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 $\times$ 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 $\mu\text{mol/g}$, 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 $\mu\text{mol/g}$, 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)[(1R,2S,3S,4S)-3-phenylbicyclo[2.2.1]hept-5-en-2-yl]methanone* (**endo-26**) and *(1-Oxidopyridin-2-yl)[(1S,2S,3S,4R)-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; λ 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, CHCl₃); ee_{endo} 93%. ¹H-NMR (CDCl₃/CHCl₃): **endo-26**: 1.56 (δ_A), 1.89 (δ_B , *AB* pattern, $J(A,B) = 8.6$, $J(A,4'') = 3.6$, $^4J(A,3'') = 1.8$, $J(B,4'') = J(B,1'') = 1.5$, CH₂(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)); 8.17 (*ddd*, $J(6,5) = 6.2$, $^4J(6,4) = 1.6$, $^5J(6,3) = 0.7$, H–C(6)); **exo-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 (NH₃): 293 (10), 292 (41, [M + 1]⁺), 276 (20, [M + 1 – O]⁺), 227 (15), 226 (100, [M + 1 – C₅H₆]⁺), 210 (35, [M + 1 – O – C₅H₆]⁺), 209 (11), 185 (7). HR-CI-MS (NH₃): 292.13360 ([M + H]⁺, C₁₉H₁₈NO₂⁺; calc. 292.13375).

[(1R,2S,3S,4S)-3-(4-Methoxyphenyl)bicyclo[2.2.1]hept-5-en-2-yl](1-oxidopyridin-2-yl)methanone (**endo-27**) and *[(1S,2S,3S,4R)-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; λ 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, CHCl₃); ee_{endo} 93%. ¹H-NMR (CDCl₃/CHCl₃): **endo-27**: 1.55 (δ_A), 1.87 (δ_B , *AB* pattern, $J(A,B) = 8.6$, $J(A,4'') = 3.6$, $J(A,3'') = 1.8$, $J(B,4'') = J(B,1'') = 1.5$, CH₂(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)). ¹³C-NMR (CDCl₃/CDCl₃): **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 (NH₃): 322 (19, [M + 1]⁺), 306 (18, [M + 1 – O]⁺), 257 (15), 256 (100, [M + 1 – C₅H₆]⁺), 241 (11), 240 (73, [M + 1 – O – C₅H₆]⁺), 239 (26), 210 (5), 185 (8). HR-CI-MS (NH₃): 322.14500 ([M + H]⁺, C₂₀H₂₀NO₂⁺; calc. 322.14432).

[(1R,2S,3S,4S)-3-(1,1-Dimethylethyl)bicyclo[2.2.1]hept-5-en-2-yl](1-oxidopyridin-2-yl)methanone (**endo-28**) and *[(1S,2S,3S,4R)-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; λ 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, CHCl₃); ee_{endo} 93%. ¹H-NMR (CDCl₃/CHCl₃): **endo-28**: 0.95 (*s*, *t*-Bu); 1.35 (δ_A), 1.67 (δ_B); *AB* pattern $J(A,B) = 8.5$, $J(A,4'') = 3.5$, $^4J(A,3'') = 1.7$, $J(B,4'') = J(B,1'') = 1.5$, CH₂(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)). ¹³C-NMR (CDCl₃/CDCl₃): *endo*-**28**: 29.03 (*Me₃C*); 32.63 (*Me₃C*); 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 (*Me₃C*); 32.69 (*Me₃C*); 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 (NH₃): 273 (17), 272 (99, [M+1]⁺), 207 (12), 206 (100, [M+1–C₅H₆]⁺), 148 (7). HR-CI-MS (NH₃): 272.16440 ([M+H]⁺, C₁₇H₂₂NO₂⁺; calc. 272.16505).

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