Carbenoid Pathways in Copper-Catalyzed Intramolecular Cyclopropanations of Phenyliodonium Ylides

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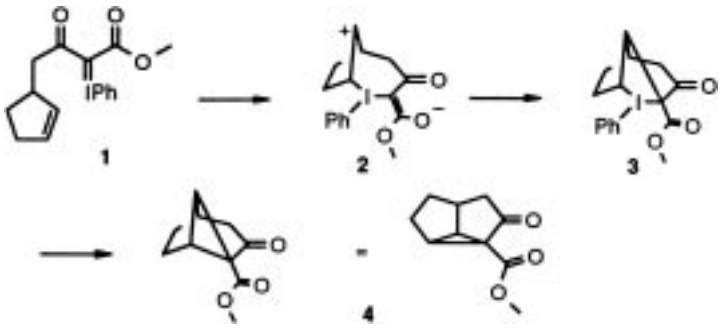
The enantioselectivity of the copper-catalyzed intramolecular cyclopropanation of allyl diazomalonates and the corresponding phenyliodonium ylides was investigated with a series of chiral, non-racemic ligands. The reaction of **6b** in the presence of the bis[dihydrooxazole] ligand **Xa** in refluxing 1,2-dichloroethane proceeded to **8b** with an enantiomer excess (ee) of up to 72% under optimized conditions. In contrast, **8b** resulting from reaction of ylide **7b** with the same ligand, but in CH_2Cl_2 at 0°, had an ee of only 30%. With other ligands, diazomalonate **6b** reacted with a lower enantioselectivity than ylide **7b**, however. The intramolecular cyclopropanation of the acetoacetate-derived phenyliodonium ylide **15b** afforded **16b** with 68% ee with ligand **Xa**, but the corresponding diazo compound was unreactive when exposed to chiral copper catalysts. The observation of asymmetric induction in the Cu-catalyzed reactions of the ylides **7** and **15** is consistent with a carbenoid mechanism; however, the discrepancy of the enantioselectivities observed between diazomalonate **6b** and ylide **7b** suggests a competing unselective pathway for cyclopropanation outside of the coordination sphere of copper.

Introduction. – The photochemical [1], thermal [2], or transition-metal-catalyzed [1][3][4] decomposition of phenyliodonium ylides [5] affords products typical for carbene or metal carbenoid intermediates. The mechanism of these reactions is, however, controversial. Carbene or carbenoid pathways have often been proposed or assumed, but experimental evidence in support of these hypotheses is scarce. Some years ago, we have investigated the decomposition of some diazo compounds and the corresponding phenyliodonium ylides in the presence of [Rh^{II}(carboxylato)] catalysts. Both precursors afforded the same selectivities in the intermolecular cyclopropanation of substituted styrenes and in the intramolecular competition for cyclopropanation *vs.* CH insertion. In addition, identical enantioselectivities resulted when the intramolecular CH insertion of a diazoacetoacetate and the corresponding phenyliodonium ylide was carried out in the presence of *Ikegami*'s chiral [Rh^{II}(carboxylato)] catalyst [6]. These results are consistent with a carbenoid mechanism.

However, the majority of the synthetically useful reactions with phenyliodonium ylides have been carried out under Cu-catalysis, and for Cu-catalysts the mechanism is not established. *Moriarty et al.* investigated the intramolecular cyclopropanation of ylide **1** to the tricyclic ketone **4** in the presence of [CuCl] (*Scheme 1*) [7]: the reaction proceeded in yields of 76 to 90%; surprisingly, it also occurred in the absence of catalyst, albeit in lower yield. The authors proposed a mechanism in which the electrophilic iodonium center attacks the C=C bond to afford a carbenium ion **2**, which, subsequently, undergoes transannular alkylation to yield **3**. Reductive elimination of PhI from **3** finally produces the cyclopropane **4**. The catalytic effect of Cu^{I}, in turn, was ascribed to electron transfer. A carbene mechanism was specifically ruled out.

Scheme 1



According to the mechanism of *Moriarty et al.*, the reaction does not take place in the coordination sphere of the metal, and, therefore, no asymmetric induction is to be expected if the decomposition of the iodonium ylide is effected by a chiral catalyst. Indeed, no enantioselective reactions of such ylides in conjunction with chiral, non-racemic Cu-catalysts have yet been reported in the literature. In this communication, we present the first observation of enantioselective intramolecular cyclopropanations with phenyliodonium ylides under Cu-catalysis. Some of the results have been published in preliminary form [8].

Results and Discussion. – Two known types of Cu-catalyzed intramolecular cyclopropanations were selected from the literature for this investigation, starting from diazomalonates and diazoacetoacetates, and/or the corresponding phenyliodonium ylides, respectively, as precursors. Our approach consisted in optimizing first the enantioselectivity of the diazo decomposition by screening a large number of Cu-catalysts and varying the reaction conditions. Subsequently, the corresponding phenyliodonium ylides were to be reacted under the same conditions. The observation of enantioselectivity upon reaction of the ylides would rule out the mechanism of *Moriarty et al.* Since the carbenoid nature of the Cu-catalyzed diazo decomposition is well-established [9], identical enantioselectivities for cyclopropanations, starting from the diazo compounds and from the corresponding ylides, respectively, under identical conditions, was expected to provide strong evidence in favor of a carbenoid pathway in Cu-catalyzed cyclopropanations of phenyliodonium ylides.

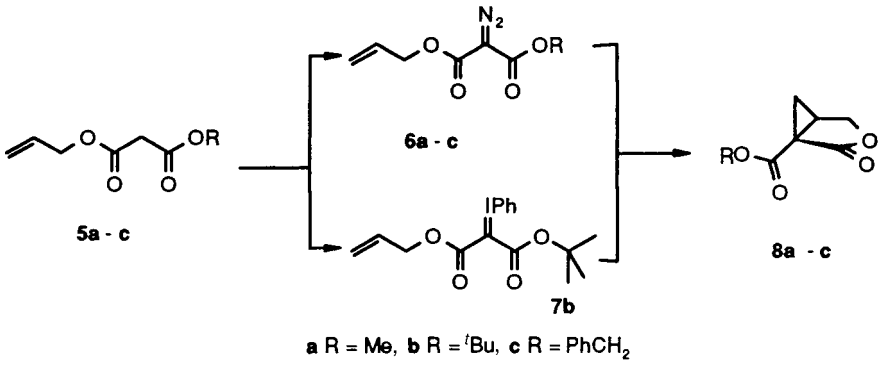
Cu-Catalyzed Decomposition of Allyl tert*-Butyl 2-(phenyliodonio)malonate* (**7b**). The Cu-catalyzed cyclopropanation of the allyl diazomalonates **6a**,**b** has been investigated by *Koskinen et al.* [10] with the objective to synthesize optically pure aminocyclopropane-1-carboxylic acids. The cyclopropanation of **6b** with [CuI-{$P(OEt)_3$}] required heating to $>105°$ overnight and provided **8b** in 76% yield. The reaction of **6a**,**b** with [CuOTf] (Tf = (trifluoromethyl)sulfonyl), and the chiral bis[dihydrooxazole] ligand **VI** occurred in 1,2-dichloroethane $(CH_2Cl)_2$ already at 65° and afforded **8a**,**b** in 72–73% yield. Enantioselectivities of 11 and 32% ee were obtained with the methyl ester **6a** and with the *tert*-butyl ester **6b**, respectively. No diazo decomposition took place at lower temperatures, however. The low reactivity of

diazomalonates in the presence of Cu-catalysts (and [Rh^{II}(carboxamidato)] catalysts is notorious [11].

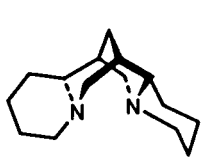
We have prepared **6b**,**c** by diazo transfer from *tert*-butyl allyl malonate (**5b**) and benzyl allyl malonate (**5c**), respectively according to the procedure of *Koskinen et al.* A selection of chiral ligands (see **I**–**III** and **V**–**XV** in the *Fig.*) in conjunction with 2% (with respect to the diazo compound) of [$Cu(OTf)_2$] in $(CH_2Cl)_2$ was then examined at 65°. The ligands **I** and **II** are commercially available. Most of the other ligands and catalyst **XVI** were synthesized according to literature procedures (see *Exper. Part*), except **III**, **IV**, **VIIc**, **IX**, **Xb**, **XI**, **XIIc**, and **XVb**–**d**, which were designed and synthesized specifically for this investigation (see below). The results of the Cu-catalyzed cyclopropanation in their presence are summarized in *Table 1*. All of the ligands tested were sufficiently reactive to effect diazo decomposition at 65°, although the yields of cyclopropanation products were quite variable. Even tertiary amines such as sparteine (**I**) or the piperidine derivative **II**, which are not generally applied in diazo decompositions, were found effective. The enantioselectivities produced by the catalysts varied enormously and in an unpredictable manner. For example, in the bis[dihydrooxazole] series **V**–**VII**, increasing the bulk of the substituents from isopropyl to *tert*-butyl resulted in an increase in enantioselectivity from 28 to 40% with **6b**, but with the Ph-substituted bis[dihydrooxazole] **VI**, the ee decreased to 12%. In general, the enantioselectivity in the decomposition of *tert*-butyl malonate **6b** was higher than that of the benzyl malonate **6c**, although there were exceptions (*i.e.* with **II**). In addition, the decomposition of **6c** required a slightly higher temperature than the 80° required for **6b**. The highest enantioselectivity (74% ee) was produced by the binaphthalene-derived bis[dihydrooxazole] **Xa**. This enantioselectivity compares favorably with the 32% ee reported by *Koskinen et al.* [10] with ligand **V**.

Further improvement of yield and enantioselectivity was attempted by optimization of the reaction conditions with **6b** and the most efficient ligand **Xa** (*Table 2*). Slow addition of **6b** within 16 h to the catalyst rather than at once had a detrimental effect on the enantioselectivity of the reaction, which decreased from 74 to 29% ee, while the yield increased from 21 to 52%. This is probably due to partial decomposition of the catalyst owing to the high reaction temperature [12]. In agreement with this hypothesis, the ee increased slightly to 74% when **6b** was added at once to the solution containing

Scheme 2



a R = Me, **b** R = ^{t}Bu, **c** R = $PhCH_2$



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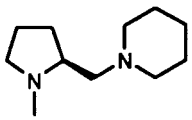

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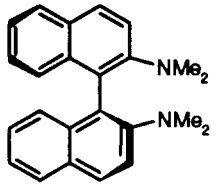

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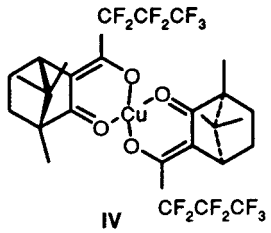

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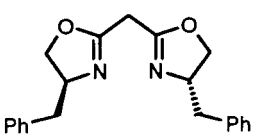

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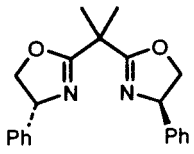

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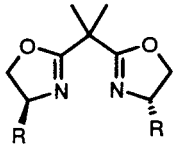
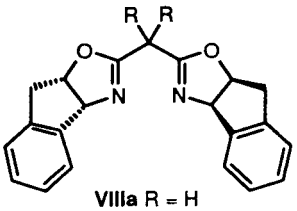
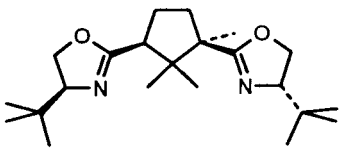


I **a** R = *i*Pr
VII **b** R = *t*Bu
c R = $C_6H_{11}CH_2$



VIIIa R = H
b R,R = CH_2



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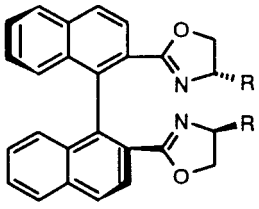
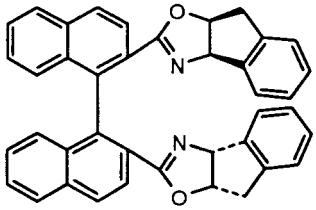
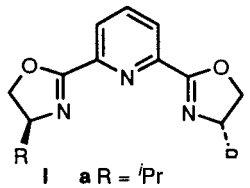


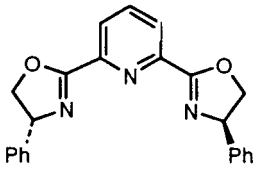
Xa R = *t*Bu
b R = $C_6H_{11}CH_2$



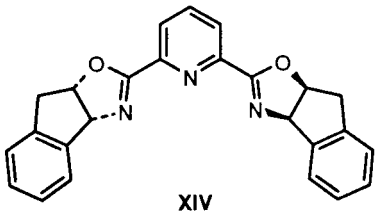
XI



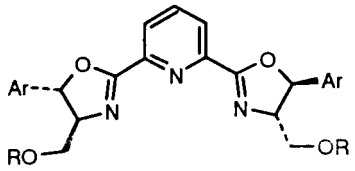
I **a** R = *i*Pr
XII **b** R = *t*Bu
c R = $C_6H_{11}CH_2$



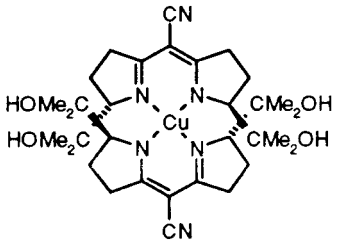
XIII



XIV



XV a Ar = *p*-$NO_2C_6H_4$, R = H
b Ar = *p*-$NO_2C_6H_4$, R = *t*$BuMe_2Si$
c Ar = *p*-$NO_2C_6H_4$, R = *t*$BuPh_2Si$
d Ar = *p*-$NO_2C_6H_4$, R = *i*Pr_3Si



XVI

Figure. *Catalysts and ligands*

Table 1. *Cu-Catalyzed Intramolecular Cyclopropanation of Diazomalonates* **6a**–**c**

Diazo compound	R	Ligand (mol-%)	Solvent, Temp. [°]	Product	Yield [%]	ee [%]	Ref., abs. configuration
6a	Me	**V** (5)	$(CH_2Cl)_2$, 65	**8a**	72	11	[10], (1*R*,5*S*)
6b	^{t}Bu	[CuI/P(OEt)$_3$]	MeC_6H_5, 105	**8b**	76	–	[10]
6b	^{t}Bu	**I** (2)	$(CH_2Cl)_2$, 65	**8b**	55	22	
6b	^{t}Bu	**II** (5)	$(CH_2Cl)_2$, 65	**8b**	48	11	
6b	^{t}Bu	**III** (2)	$(CH_2Cl)_2$, 65	**8b**	54	00	
6b	^{t}Bu	**IV** (5)	$(CH_2Cl)_2$, 65	**8b**	71	00	
6b	^{t}Bu	**V** (5)	$(CH_2Cl)_2$, 65	**8b**	73	32	[10] (1*S*,5*S*)
6b	^{t}Bu	**V** (5)	$(CH_2Cl)_2$, 85	**8b**	–	15	[10]
6b	^{t}Bu	**VI** (2)	$(CH_2Cl)_2$, 65	**8b**	78	12	(1*S*,5*S*)
6b	^{t}Bu	**VIIa** (2)	$(CH_2Cl)_2$, 65	**8b**	73	28	(1*S*,5*S*)
6b	^{t}Bu	**VIIb** (5)	$(CH_2Cl)_2$, 65	**8b**	53	40	(1*S*,5*S*)
6b	^{t}Bu	**VIIc** (2)	$(CH_2Cl)_2$, 65	**8b**	81	35	(1*S*,5*S*)
6b	^{t}Bu	**VIIIa** (2)	$(CH_2Cl)_2$, 65	**8b**	52	38	(1*R*,5*R*)
6b	^{t}Bu	**IX** (2)	$(CH_2Cl)_2$, 65	**8b**	48	05	(1*S*,5*S*)
6b	^{t}Bu	**Xa** (2)	$(CH_2Cl)_2$, 65	**8b**	21	74	(1*S*,5*S*)
6b	^{t}Bu	**Xb** (2)	$(CH_2Cl)_2$, 65	**8b**	44	22	(1*S*,5*S*)
6b	^{t}Bu	**XI** (2)	$(CH_2Cl)_2$, 65	**8b**	41	22	(1*R*,5*R*)
6b	^{t}Bu	**XIIc** (2)	$(CH_2Cl)_2$, 65	**8b**	52	02	(1*S*,5*S*)
6b	^{t}Bu	**XVI** (2)	$(CH_2Cl)_2$, 65	**8b**	50	25	(1*S*,5*S*)
6c	CH_2Ph	**I** (5)	$(CH_2Cl)_2$, 65	**8c**	35	04	
6c	CH_2Ph	**II** (5)	$(CH_2Cl)_2$, 80	**8c**	33	15	
6c	CH_2Ph	**VI** (5)	$(CH_2Cl)_2$, 80	**8c**	50	13	
6c	CH_2Ph	**VIIa** (5)	$(CH_2Cl)_2$, 80	**8c**	52	15	
6c	CH_2Ph	**VIIb** (5)	$(CH_2Cl)_2$, 80	**8c**	51	12	
6c	CH_2Ph	**VIIc** (5)	$(CH_2Cl)_2$, 80	**8c**	52	10	
6c	CH_2Ph	**IX** (5)	$(CH_2Cl)_2$, 80	**8c**	41	00	
6c	CH_2Ph	**Xa** (5)	$(CH_2Cl)_2$, 80	**8c**	57	04	
6c	CH_2Ph	**Xb** (5)	$(CH_2Cl)_2$, 80	**8c**	63	13	
6c	CH_2Ph	**XIIc** (5)	$(CH_2Cl)_2$, 80	**8c**	48	01	
6c	CH_2Ph	**XVI** (5)	$(CH_2Cl)_2$, 80	**8c**	51	42	

Table 2. *Optimization of the Cyclopropanation with* **6b** *and ligand* **Xa**[a])

Entry	Solvent[a])	Temp. [°]	Yield [%] of **8b**	ee [%]	Comment
1	$(CH_2Cl)_2$	65	21	74	Addition of **6b** at once
2	$(CH_2Cl)_2$	65	52	29	Addition of **6b** within 16 h
3	$(CH_2Cl)_2$	65	24	83	Simultaneous addition of **6b** and **Xa**, 16 h
4	TFT[b])	65	19	77	Addition of **6b** at once
5	TFT[b])	100	51	72	Addition of **6b** at once
6	Toluene	100	38	11	Addition of **6b** at once

[a]) 2 mol-% of catalyst. [b]) TFT = trifluorotoluene = (trifluoromethyl)benzene.

the catalyst, and it reached 83% when **6b** and the catalyst were added simultaneously within 16 h to the reaction mixture. A change of solvent from $(CH_2Cl)_2$ to trifluorotoluene (TFT) had no significant effect, while a temperature increase from 65 to 100° in TFT resulted in a significant increase in yield and only moderate loss of enantioselectivity. Several Rh^{II} catalysts were also investigated for the purpose of

comparison. Although the chemical yields of these reactions were satisfactory, the enantioselectivities never exceeded 10% [13].

In the light of the disappointing enantioselectivities resulting from the diazo decomposition of the benzyl ester **6c**, work with this group was discontinued, and the subsequent reactions were carried out only with the *tert*-butyl derivative. The phenyliodonium ylide **7b** was prepared by reaction of **5b** with $PhI(OAc)_2$ in MeOH in the presence of KOH [5]. This reaction proved to be very delicate. The ylide was unstable, and its formation was accompanied by substantial quantities of formal carbene dimers, the structures of which were not further investigated. In addition, transesterification of **5b** to *tert*-butyl methyl malonate occurred under the conditions of the reaction owing to ester exchange with the solvent. This secondary reaction could be suppressed by replacing MeOH with MeCN as solvent. With this modified procedure, the ylide **7b** was obtained as a yellow oil in yields varying from 55 to 80%.

The cyclopropanation of **7b** was effected with a selection of the catalysts used for the diazo decomposition (*Table 3*). Reactions were carried out routinely in CH_2Cl_2 at 0°, and some variations in the reaction conditions were studied with ligand **VIIc**. For reasons of the instability of **7b**, the cyclopropanations could not be carried out under the conditions required for diazo decomposition, so that the enantioselectivities for **6b** and **7b** with the same ligands are not directly comparable. Since the reactions with **7b** were effected at lower temperature than those of **6b**, the enantioselectivities are expected to be higher with **7b**. This is true in some cases (*i.e.* with ligands **VI** and **VIIc**), but in others (*i.e.* **VIIa**, **VIIb**, and **Xa**), the reverse trend results. The observation of enantioselectivity (up to 45% ee in the cyclopropanation of **7b**) indicates a reaction mechanism occurring in close proximity to the chiral catalyst. However, the irregular trends in the enantioselectivities upon reaction of diazomalonates and ylides show that some other pathway for cyclopropanation of the ylide must be available.

Table 3. *Cu-Catalyzed Intramolecular Cyclopropanation with Phenyliodonium Ylide* **7b**

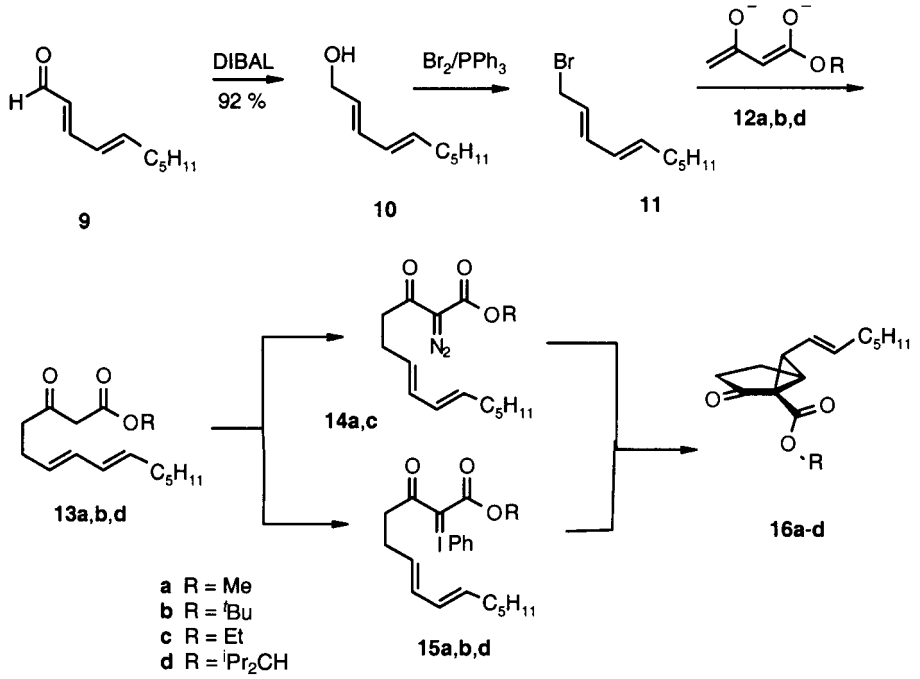
Ligand	(mol-%)	Solvent	Temp [°]	Yield [%] of **8b**	ee [%]
VI	(2)	CH_2Cl_2	0	48	31
VIIa	(2)	CH_2Cl_2	0	40	22
VIIb	(2)	CH_2Cl_2	0	18	11
VIIc	(2)	CH_2Cl_2	0	46	42
VIIc	(4)	CH_2Cl_2	0	47	40
VIIc	(2.4)	CH_2Cl_2	−20	45	42
VIIc	(2.4)	CH_2Cl_2	−50	43	45
VIIc	(2.4)	CH_2Cl_2	−78	41	34
VIIc	(2.4)	TFT[a])	0	47	25
Xa	(2)	CH_2Cl_2	0	34	30

[a]) TFT = trifluorotoluene.

Intramolecular Cyclopropanation of Phenyliodonium Ylide **15a**,**b**,**d**. In view of the instability of ylide **7b**, we turned our attention to the prostaglandin precursor **16**, which has been synthesized in the past by intramolecular cyclopropanation of the diazoacetoacetates **14a** [14] and **14c** [15] and from the phenyliodonium ylide **15a** [16] (*Scheme 3*). The keto esters **13a**,**b**,**d** were synthesized from (2*E*,4*E*)-deca-2,4-dienal (**9**)

according to established procedures with some minor modifications. DIBAL Reduction of aldehyde **9** afforded the known alcohol **10** [17][18], which was converted to the labile bromide **11** with Br_2/PPh_3 [17]. Alkylation of **11** with the dianions of acetoacetates **12a**,**b**,**d** [19] afforded the keto esters **13a**,**b**,**d**. Methyl ester **13a** was subjected to diazo transfer [20] to yield the diazoacetoacetate **14a**. Reaction of **13a**,**b**,**d** with $PhI(OAc)_2$ and KOH in MeOH, as described by *Moriarty et al.* [16], gave the phenyliodonium ylides **15a**,**b**,**d**. This latter transformation was much less problematic than that of the malonate-derived ylide **7b**. The ylides were isolated as yellow oils in 85–87% crude yield and were used without further purification.

Scheme 3



The diazoesters **14a**,**c** have been thermolyzed in refluxing benzene in the presence of $[Cu(acac)_2]$ for 24 h [14] or in refluxing toluene (2 h) in the presence of copper bronze [15] to give **16a** and **16c** in 63 and 50% yield, respectively (*Table 4*). We found **14a** unreactive towards decomposition with the conventionally used [Cu-(bis[dihydrooxazole] catalysts. The camphor-derived Cu-catalyst **IV** [21] was more reactive owing to the electron-attracting fluorinated side chain; **IV** effected diazo decomposition of **14a** in refluxing benzene to afford **16a** in 45% yield. However, the product was racemic. In contrast, ylide **15a** reacted in CH_2Cl_2 at 0° with all of the catalysts to give **16a** in yields of 22–63%. A selection of chiral ligands was screened; enantioselectivity was modest and culminated at 42% ee. With the more hindered *tert*-butyl ester **15b**, the ee increased to 68%. However, with the still more crowded 2-methyl-1-(1-methylethyl)-propyl ester **15d**, the enantioselectivity deteriorated, except with ligand **VIIIa**, which

Table 4. *Intramolecular Cyclopropanation of* **14** *and* **15**

Diazo compound or ylide	R	Catalyst or ligand (mol-%)	Solvent, T [°]	Product	Yield [%]	ee [%]	Ref.
14a	Me	[$Cu(acac)_2$]	C_6H_6, 80	**16a**	63	–	[14]
14a	Me	**IV** (5)	C_6H_6, 80	**16a**	45	0	
14c	Et	Cu-bronze	toluene, 110	**16c**	50	–	[15]
15a	Me	[CuCl]	CH_2Cl_2, 0	**16a**	75	–	[16]
15a	Me	**III** (2)	CH_2Cl_2, 0	**16a**	45	03	
15a	Me	**IV** (5)	CH_2Cl_2, 0	**16a**	56	10	
15a	Me	**Xa** (5)	CH_2Cl_2, 0	**16a**	22	25	
15a	Me	**Xb** (5)	CH_2Cl_2, 0	**16a**	52	38	
15a	Me	**XIIa** (2)	CH_2Cl_2, 0	**16a**	54	11	
15a	Me	**XIIb** (2)	CH_2Cl_2, 0	**16a**	55	32	
15a	Me	**XIIc** (2)	CH_2Cl_2, 0	**16a**	63	21	
15a	Me	**XIII** (2)	CH_2Cl_2, 0	**16a**	61	18	
15a	Me	**XIV** (2)	CH_2Cl_2, 0	**16a**	59	42	
15a	Me	**IX** (5)	CH_2Cl_2, 0	**16a**	57	07	
15a	Me	**XVb** (2)	CH_2Cl_2, 0	**16a**	36	34	
15a	Me	**XVc** (2)	CH_2Cl_2, 0	**16a**	50	33	
15a	Me	**XVd** (2)	CH_2Cl_2, 0	**16a**	42	39	
15b	^{t}Bu	**VIIIa** (2)	CH_2Cl_2, 0	**16c**	53	62	
15b	^{t}Bu	**VIIIb** (2)	CH_2Cl_2, 0	**16c**	45	16	
15b	^{t}Bu	**Xa** (2)	CH_2Cl_2, 0	**16c**	48	68	
15b	^{t}Bu	**Xb** (2)	CH_2Cl_2, 0	**16c**	51	22	
15b	^{t}Bu	**XI** (2)	CH_2Cl_2, 0	**16c**	54	26	
15b	^{t}Bu	**XIIb** (2)	CH_2Cl_2, 0	**16c**	52	07	
15b	^{t}Bu	**XIV** (2)	CH_2Cl_2, 0	**16c**	53	40	
15b	^{t}Bu	**XVd** (2)	CH_2Cl_2, 0	**16c**	55	14	
15d	^{i}Pr$_2$CH	[$Rh_2(OAc)_4$]	CH_2Cl_2, 0	**16d**	76	–	
15d	^{i}Pr$_2$CH	**VIIIa** (2)	CH_2Cl_2, 0	**16d**	79	52	
15d	^{i}Pr$_2$CH	**Xa** (2)	CH_2Cl_2, 0	**16d**	65	02	
15d	^{i}Pr$_2$CH	**Xb** (2)	CH_2Cl_2, 0	**16d**	63	12	
15d	^{i}Pr$_2$CH	**XI** (2)	CH_2Cl_2, 0	**16d**	65	07	
15d	^{i}Pr$_2$CH	**XIIv** (2)	CH_2Cl_2, 0	**16d**	52	08	
15d	^{i}Pr$_2$CH	**XIV** (2)	CH_2Cl_2, 0	**16d**	54	10	
15d	^{i}Pr$_2$CH	**XVb** (2)	CH_2Cl_2, 0	**16d**	54	10	

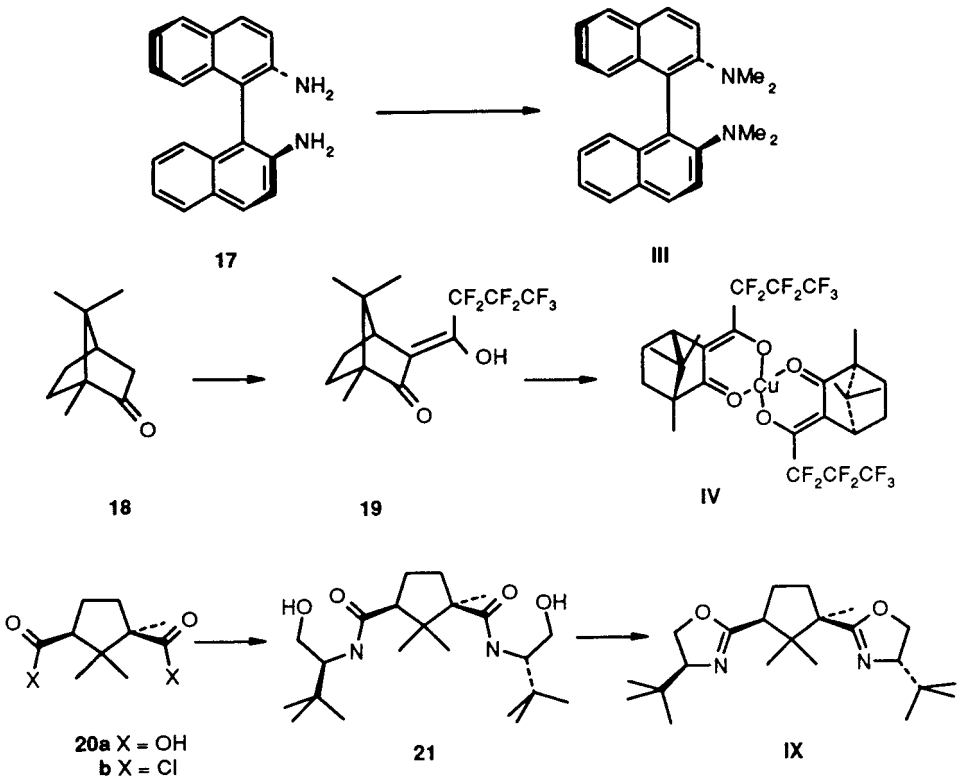
yielded 52% ee. The ylides reacted also with Rh^{II} catalysts; however, the enantioselectivities in these latter reactions were unsatisfactory with all of the catalysts tried [13].

The observation of up to 68% ee in intramolecular cyclopropanations with phenyliodonium ylides indicates that the mechanism proposed by *Moriarty et al.* cannot be the main pathway of the reaction. Unfortunately, the lack of reactivity of diazo compound **14a** does not allow comparison with the enantioselectivities achieved with the ylides, and it is not clear whether the less than 100% enantioselectivity must be attributed to an inadequate choice of catalysts or to competing, unselective cyclopropanation pathways. Although we have not observed spontaneous cyclopropanations of ylides in the absence of catalysts in the present investigation, such reactions have been reported in the past not only by *Moriarty et al.* [7], but also by ourselves [6], and for these reactions the mechanism outlined in *Scheme 1*, or a radical version thereof, is plausible. The present results lend some support for a metal carbenoid intermediate in the main pathway of the Cu-catalyzed ylide decomposition. However, this mechanistic

hypothesis needs to be backed up with more experimental evidence. From the synthetic point of view, the fact that enantioselective cyclopropanations with phenyliodonium ylides are possible should open up new possibilities and a larger choice of catalysts for metal carbenoid reactions.

Preparation of Ligands. Appropriate references for the synthesis of the known ligands used in this work are given in the experimental part. (*S*)-*N*,*N*,*N*′,*N*′-Tetramethyl-[1,1′-binaphthalene]-2,2′-diamine (**III**) was prepared by methylation of the commercially available diamine **17** (*Scheme 4*). Alkylation of (+)-camphor (**18**) with heptafluorobutanoyl chloride afforded **19**, which reacted with $[Cu(NO_3)_2]$ to give complex **IV**. The bis[dihydrooxazole] **IX**, in turn, was prepared from (+)-camphoric acid (**20a**), which was converted to the dichloride **20b** with PCl_5 [22]. Condensation of **20b** with L-*tert*-leucinol (=(2*S*)-2-amino-3,3-dimethylbutan-1-ol) in the presence of Et_3N afforded diamide **21**, which was converted to **IX** with TsCl in the presence of Et_3N and *N*,*N*-dimethylpyridin-4-amine (DMAP) [23].

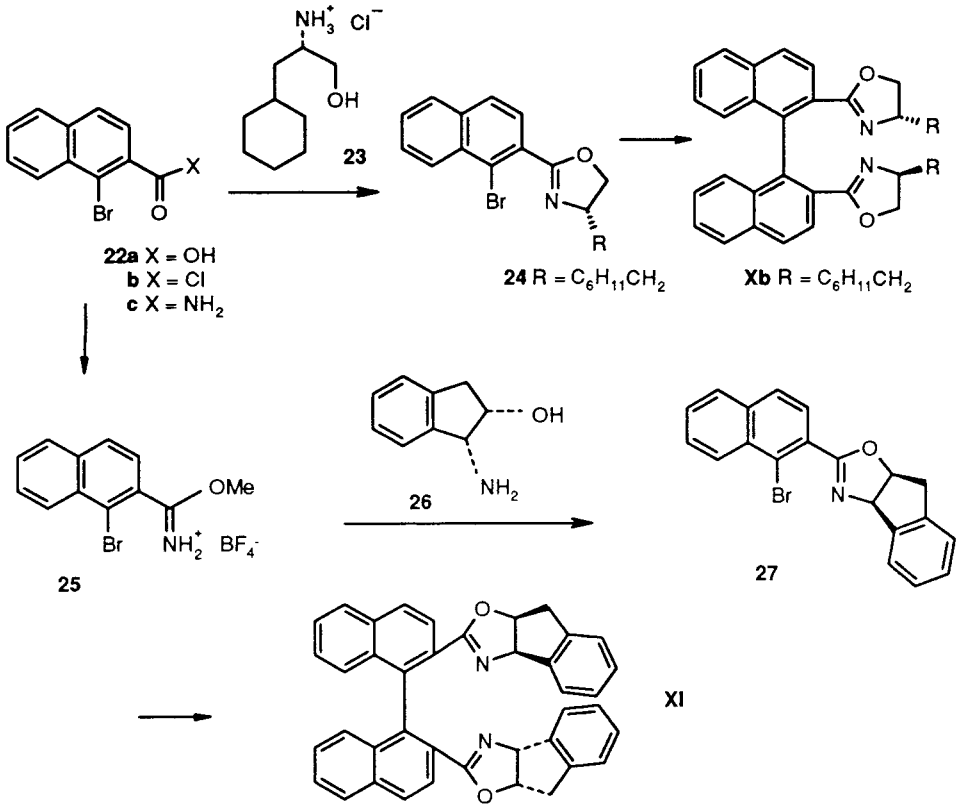
Scheme 4



The dihydrooxazol-substituted binaphthalene **Xb** was synthesized according to the method used for the *tert*-butyl analog **Xa** [24]: 1-bromo naphthalene-2-carboxylic acid (**22a**) was converted to the acid chloride **22b** with oxalyl chloride in the presence of a catalytic quantity of DMF (*Scheme 5*). Reaction of **22b** with (2*S*)-2-amino-3-cyclo-

hexylpropan-1-ol hydrochloride (**23**) in the presence of Et_3N afforded the amide, which was converted without isolation to the dihydrooxazol **24** by means of the *Burgess* reagent [25]. *Ullmann* coupling [26] of **24** with Cu in pyridine led to the binaphthalene derivative **Xb** as a mixture of stereoisomers of 70% de. This contrasts with the synthesis of the *tert*-butyl analogue **Xa**, which is fully diastereoselective. The de of **Xb** could be slightly improved by HPLC separation; however, since this operation had practically no effect on the enantioselectivity of the cyclopropanations, which was only marginal, the separation of the diastereoisomers was not completed, and the absolute configuration of the binaphthalene moiety was not determined. Bromo acid **22a** was also the starting material for **XI**: reaction with *Meerwein*'s salt afforded the imidate **25**, which was converted to the dihydrooxazole derivative **27** with (1*R*,2*S*)-1-aminoindan-2-ol (**26**). *Ullmann* coupling resulted in the formation of **XI** with only 66% de. Attempted separation of the diastereoisomers of **XI** was not successful.

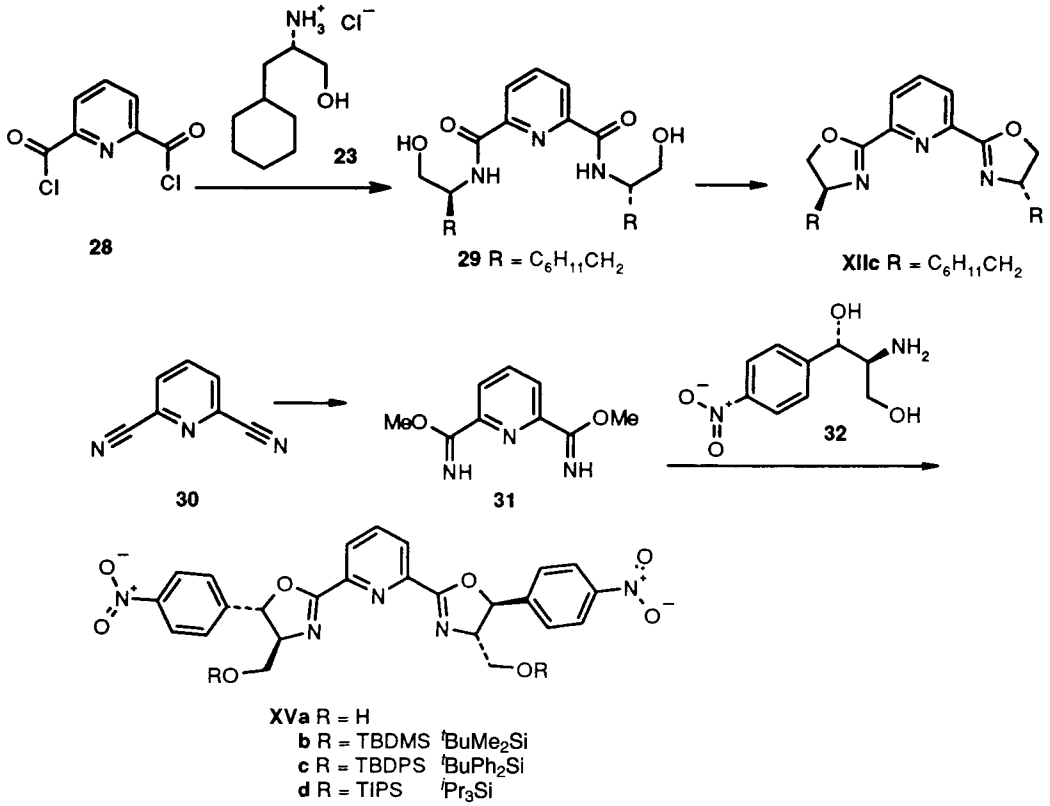
Scheme 5



The pybox ligand **XIIc** was synthesized from pyridine-2,6-dicarbonyl dichloride (**28**) and amino alcohol **23** *via* diamide **29** [27] (*Scheme 6*). Extension of known methods [28] towards the preparation of 4′,4″,5′,5″-tetrasubstituted pybox ligands **XV** failed. However, pyridine-2,6-dicarbonitrile (**30**) could be converted to the diimidate

31 with NaOMe in MeOH, as described for pyridine-2-carbonitrile [29]. Condensation of **31** with amino alcohol **32** in $(CH_2Cl)_2$ afforded the bis[dihydrooxazole] **XVa** in 78% yield, and silylation of **XVa** with several trialkylsilyl chlorides gave the derivatized ligands **XVb**–**d**.

Scheme 6



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Experimental Part

General. See [30]. FC = flash chromatography. GC: t_R in min.

1. *Allyl Diazomalonates* **6** *and Ylides* **7** *and Their Intramolecular Cyclopropanation*. *Allyl* tert-*Butyl 2-Diazomalonate* (**6b**). See [10].

Allyl Benzyl 2-Diazomalonate (**6c**). To monobenzyl malonate [31] (6.07 g, 31 mmol), allyl alcohol (3.63 g, 63 mmol), and *N*,*N*-dimethylpyridin-4-amine (DMAP; 382 mg, 3.12 mmol) in CH_2Cl_2 (30 ml), dicyclohexylcarbodiimide (DCC; 12.9 g, 63 mmol) was added at 0°. A white suspension precipitated while the mixture was stirred at r.t. overnight. After filtration, the filtrate was extracted with 0.5N HCl (2 × 30 ml). The org. layer was dried ($MgSO_4$) and evaporated, and the residue purified by bulb-to-bulb distillation: **5c** (6.36 g, 87%). Colorless oil. IR (NaCl): 2950*w*, 1734*s*, 1329*s*, 1271*m*, 1146*s*, 993*m*, 749*m*, 698*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 3.50

(*s*, 2 H); 4.66 (*dt*, *J* = 1.3, 6.0, 2 H); 5.22 (*s*, 2 H); 5.25–5.29 (*m*, 1 H); 5.32–5.38 (*m*, 1 H); 5.91 (*ddt*, *J* = 6.0, 10.7, 11.6, 1 H); 7.35–7.43 (*m*, 5 H, CH). ^{13}C-NMR (125 MHz, $CDCl_3$): 41.5 (*t*); 66.1 (*t*); 67.2 (*t*); 118.8 (*t*); 128.3 (*d*); 128.4 (*d*); 128.6 (*d*); 131.4 (*d*); 135.2 (*s*); 166.0 (*s*); 166.2 (*s*). MS: 234 (5, M^+), 108 (19), 107 (100), 100 (8), 92 (7), 91 (70), 90 (7), 87 (14), 79 (12), 77 (7), 65 (8). HR-MS: 234.08920 ($C_{13}H_{14}O_4^+$; calc. 234.08920).

To **5c** (1.33 g, 5.68 mmol) in MeCN (5.0 ml), TsN_3 [32] (1.12 g, 5.68 mmol) and K_2CO_3 (784 mg, 5.68 mmol) in MeCN (10.0 ml) were added at r.t. The mixture was stirred overnight. After evaporation, the yellow residue was dissolved in Et_2O (50 ml), the org. layer washed with 10% aq. K_2CO_3 soln. (2 × 50 ml), dried ($MgSO_4$), and evaporated to afford a yellow product, which was taken up in Et_2O/hexane 1:5. After filtration and evaporation of the filtrate, the residue was purified by FC (pentane/AcOEt 9:1): **6c** (1.23 g, 83%). Yellow oil. IR (NaCl): 3035*m*, 2141*s*, 1758*s*, 1732*s*, 1638*s*, 1643*m*, 1450*m*, 1392*m*, 1321*s*, 1303*s*, 1089*m*, 910*s*, 748*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.76 (*dt*, *J* = 1.3 and 5.7, 2 H); 5.28–5.32 (*m*, 1 H); 5.31 (*s*, 2 H); 5.35–5.41 (*m*, 1 H); 5.95 (*ddt*, *J* = 5.6, 10.4, 11.3, 1 H); 7.34–7.43 (*m*, 5 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 66.0 (*t*); 67.0 (*t*); 118.9 (*t*); 128.2 (*d*); 128.4 (*d*); 128.6 (*d*); 131.4 (*d*); 135.3 (*s*); 160.6 (*s*); 160.8 (*s*). ESI-MS: 283.0 ($[M + Na]^+$, $C_{13}H_{12}N_2NaO_4^+$; calc. 283.1).

*1-(Allyloxy)-2-(*tert*-butoxy)-1,3-dioxo-2-(phenyliodonio)propan-2-ide* (**7b**). To powdered KOH (261 mg, 4.00 mmol) in MeCN (3.0 ml), **5b** [9] (200 mg, 1.0 mmol) in MeCN (2.0 ml) and diacetoxyiodobenzene (322 mg, 1.00 mmol) were added at −10° in small portions. After stirring at −10° for 45 min, the solvent was evaporated and the residue dissolved in CH_2Cl_2 (5.0 ml). The soln. was poured on ice-water (5.0 ml) and the aq. phase extracted with CH_2Cl_2 (3 × 5 ml). The combined org. layer was dried ($MgSO_4$) and evaporated: **7b** as semi-solid oil in yields varying between 55 and 80%. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.45 (*s*, 9 H); 4.61–4.68 (*m*, 2 H); 5.05–5.43 (*m*, 2 H); 5.78–6.04 (*m*, 1 H); 7.35–7.62 (*m*, 3 H); 7.66–7.73 (*m*, 2 H).

Intramolecular Cyclopropanation with Diazomalonates **6b**,**c**: *Typical Procedure*. A soln. of $[Cu(OTf)_2]$ (3.2 mg, 8.9 µmol, 0.02 equiv.) and bis[dihydrooxazole] **Xa** (4.9 mg, 9.7 µmol, 0.022 equiv.) was stirred in $(CH_2Cl)_2$ (5.0 ml) at r.t. for 1 h. The temp. was raised to 65°, and **6b** (100 mg, 0.44 mmol) in $(CH_2Cl)_2$ (5.0 ml) was added at once. The mixture was stirred at 65° for 16 h. After evaporation, the residue was purified by FC (SiO_2, pentane/AcOEt 80:20): **8b** (18 mg, 21%) of 74% ee.

Intramolecular Cyclopropanation with Ylide **7b**: *Typical Procedure*. A soln. of $[Cu(OTf)_2]$ (6.4 mg, 18 µmol, 0.02 equiv.) and bis[dihydrooxazole] **VIIc** (7.3 mg, 19 µmol, 0.022 equiv.) was stirred in CH_2Cl_2 (10.0 ml) at r.t. for 1 h. The mixture was cooled to 0°, **7b** (362 mg, 0.90 mmol) in CH_2Cl_2 (10.0 ml) added in one portion, and the mixture then stirred at 0° for 4 h. After evaporation, the residue was purified by FC (SiO_2, pentane/AcOEt 80:20): **8b** (82 mg, 46%) of 42% ee. Colorless solid.

tert-*Butyl 2-Oxo-3-oxabicyclo[3.1.0]hexane-1-carboxylate* (**8b**): GC (*Lipodex E*, 110°): t_R 29.8 (1*R*,5*R*), 32.8 (1*S*,5*S*). M.p. 74° ([9]: m.p. 73–74°). $[\alpha]_D^{20} = 89.0$ (*c* = 0.50, $CHCl_3$) for 74% ee ([33]: $[\alpha]_D = 105.5$ (*c* = 1.3, CH_2Cl_2)). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.28–1.33 (*m*, 1 H); 1.50 (*s*, 9 H); 2.00 (*dd*, *J* = 4.9, 7.9, 1 H); 2.63–2.68 (*m*, 1 H); 4.16 (*d*, *J* = 9.4, 1 H); 4.35 (*dd*, *J* = 4.9, 0.4, 1 H). ^{13}C-NMR (100 MHz): 20.3 (*t*); 27.5 (*d*); 27.9 (*q*); 29.9 (*s*); 66.8 (*t*); 82.8 (*s*); 165.5 (*s*); 170.6 (*s*).

Benzyl 2-Oxo-3-oxabicyclo[3.1.0]hexane-1-carboxylate (**8c**): GC (*Lipodex E*, 130°): t_R 34.6, 51.0. $[\alpha]_D^{20} = -36.2$ (*c* = 0.81, $CHCl_3$) for 42% ee. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.33 (*dd*, *J* = 5.1, 5.3, 1 H); 2.03 (*dd*, *J* = 4.7, 8.2, 1 H); 2.64–2.71 (*m*, 1 H); 4.11 (*d*, *J* = 9.4, 1 H); 4.28 (*dd*, *J* = 4.7, 9.4, 1 H); 5.15 (*d*, *J* = 12.3, 1 H); 5.19 (*d*, *J* = 12.6, 1 H, CH_2); 7.23–7.35 (*m*, 5 H, CH). ^{13}C-NMR (125 MHz, $CDCl_3$): 20.8 (*t*); 28.0 (*d*); 29.4 (*s*); 67.0 (*t*); 67.4 (*t*); 128.1 (*d*); 128.4 (*d*); 128.6 (*d*); 135.1 (*s*); 166.5 (*s*); 170.2 (*s*). MS: 232 (9, M^+), 126 (71), 125 (10), 108 (59), 107 (75), 98 (39), 91 (100), 90 (13), 83 (15), 82 (13), 80 (33), 79 (17), 77 (12), 69 (14), 65 (22), 53 (20), 51 (14). HR-MS: 232.07403 ($C_{13}H_{12}O_4^+$; calc. 232.07356).

2. *Diazo Keto Ester* **14a** *and Ylides* **15a**,**b**,**d** *and Their Intramolecular Cyclopropanation*. *(2*E*,4*E*)-Deca-2,4-dien-1-ol* (**10**) [18]. (2*E*,4*E*)-Deca-2,4-dienal (**9**; tech., 90%) was purified by FC (pentane/AcOEt 98:2). Then **9** (3.25 g, 21.3 mmol) was reduced in Et_2O (60 ml) with 1M DIBAL in THF (38 ml, 21.3 mmol) at 0°. After 1 h, the reaction was quenched with H_2O (5 ml) and the mixture stirred until a gel was formed. After addition of solid $MgSO_4$, the gel precipitated and was removed by filtration. Evaporation of the filtrate afforded **10** (3.24 g, 98%) as a colorless oil, which was used without further purification. IR (NaCl): 3330*s* (br.), 2955*s*, 2924*s*, 2855*s*, 1461*w*, 1087*m*, 987*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.92 (*t*, *J* = 7.0, 3 H); 1.26–1.38 (*m*, 4 H); 1.39–1.47 (*m*, 2 H); 1.64–1.70 (br. *s*, 1 H); 2.07–2.14 (*m*, 2 H); 4.18 (*d*, *J* = 6.0, 2 H); 5.70–5.79 (*m*, 2 H); 6.07 (*dd*, *J* = 10.7, 15.1, 1 H); 6.24 (*dd*, *J* = 10.7, 15.5, 1 H). ^{13}C-NMR (125 MHz): 14.0 (*q*); 22.5 (*t*); 28.9 (*t*); 31.4 (*t*); 32.6 (*t*); 63.5 (*t*); 129.3 (*d*); 132.1 (*d*); 135.8 (*d*). MS: 154 (18, M^+), 110 (15), 98 (14), 97 (18), 95 (10), 84 (74), 83 (84), 82 (15), 81 (33), 80 (16), 79 (35), 77 (15), 71 (10), 70 (53), 69 (42), 68 (26), 67 (61), 66 (10), 57 (31), 56 (35), 55 (100), 54 (34), 53 (17), 51 (6). HR-MS: 154.1356 ($C_{10}H_{18}O^+$; calc. 154.1358).

*(2*E*,4*E*)-1-Bromodeca-2,4-diene* (**11**) [18]. To Ph_3P (5.30 g, 20.2 mmol) in MeCN (60 ml) at 0°, Br_2 (1.04 ml, 20.2 mmol) was added until the color of Br_2 faded. A small amount of Ph_3P was then added to remove unreacted

Br_2. The temp. was raised to r.t., and **10** (2.97 g, 19.2 mmol) in MeCN (25 ml) was added. After 10 min, the mixture was poured into petroleum ether. The layers were separated, and the MeCN was repeatedly extracted with petroleum ether (4 × 100 ml). Evaporation gave a crude oil which was purified by bulb-to-bulb distillation (0.2 mbar/100°): 3.55 g (85%) of **11**. Colorless oil, which was used without further treatment. IR (NaCl): 2957*s*, 2926*s*, 2856*m*, 1652*w*, 1466*w*, 1200*m*, 986*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.82 (*t*, *J* = 7.0, 3 H); 1.16–1.28 (*m*, 4 H); 1.29–1.37 (*m*, 2 H); 1.99–2.05 (*m*, 2 H); 3.96 (*d*, *J* = 8.2, 2 H); 5.65–5.74 (*m*, 2 H); 5.96 (*dd*, *J* = 11.0, 15.1, 1 H); 6.19 (*dd*, *J* = 11.0, 14.8, 1 H). ^{13}C-NMR (125 MHz): 14.0 (*q*); 22.5 (*t*); 28.7 (*t*); 31.4 (*t*); 32.6 (*t*); 33.9 (*t*); 126.1 (*d*); 128.7 (*d*); 135.4 (*d*); 137.9 (*d*). MS: 218 (5, M^+), 216 (5, M^+), 137 (36), 95 (23), 81 (33), 80 (21), 67 (100), 55 (12). HR-MS: 216.0487 ($C_{10}H_{17}$ $^{79}Br^+$; calc. 216.0514).

*Alkyl (6*E,*8*E*)-3-Oxotetradeca-6,8-dienoates* **13a**,**b**,**d**: *General Procedure* [19]. To NaH (656 mg, 16.4 mmol) in THF (30 ml) at 0°, 2-methyl-1-(1-methylethyl)propyl 3-oxobutanoate [34] (**12d**; 3.29 g, 16.4 mmol) was added slowly. After stirring for 10 min at 0°, 1.6M BuLi in hexane (16.4 ml, 16.4 mmol) was added slowly, and the orange soln. was stirred for 10 additional min. Crude **11** (3.24 g, 14.9 mmol) in THF (5 ml) was added to the dianion. The mixture was stirred for 30 min, whereupon it became colorless. It was decomposed with conc. HCl soln. (5.0 ml in 13 ml of H_2O) and Et_2O (40 ml) and extracted with Et_2O (2 × 25 ml). The combined org. layer was washed (H_2O) until neutrality, dried ($MgSO_4$), and evaporated, and the residue purified by FC (pentane/AcOEt 95:5): **13d** (3.97 g, 79%). Colorless oil.

*Methyl (6*E,*8*E*)-3-Oxotetradeca-6,8-dienoate* (**13a**) [14][16]. Yield 76%. ^{1}H-NMR (200 MHz, $CDCl_3$): 0.83–0.92 (*m*, 3 H); 1.18–1.45 (*m*, 6 H); 2.03 (*q*, *J* = 6.9, 2 H); 2.25–2.42 (*m*, 2 H); 2.63 (*t*, *J* = 7.3, 3 H); 3.44 (*s*, 2 H); 3.73 (*s*, 3 H); 5.45–5.70 (*m*, 2 H); 5.85–6.12 (*m*, 2 H).

tert-*Butyl (6*E,*8*E*)-3-Oxotetradeca-6,8-dienoate* (**13b**). From **11** and **12b**. Yield 71%. IR (NaCl): 2958*m*, 2927*s*, 1736*s*, 1719*s*, 1368*m*, 1250*m*, 1150*s*, 988*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.89 (*t*, *J* = 6.9, 3 H); 1.22–1.33 (*m*, 4 H); 1.35–1.41 (*m*, 2 H); 1.47 (*s*, 9 H); 2.02–2.08 (*m*, 2 H); 2.32–2.39 (*m*, 2 H); 2.63 (*t*, *J* = 7.2, 2 H); 3.35 (*s*, 2 H); 5.48–5.64 (*m*, 2 H); 5.93–6.07 (*m*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 14.0 (*q*); 22.6 (*t*); 26.4 (*t*); 28.0 (*q*); 29.0 (*t*); 31.4 (*t*); 32.6 (*t*); 42.5 (*t*); 50.7 (*t*); 82.0 (*s*); 129.4 (*d*); 129.8 (*d*); 131.5 (*d*); 133.6 (*d*); 166.4 (*s*); 202.6 (*s*). MS: 294 (1, M^+), 238 (21), 150 (10), 149 (10), 137 (13), 136 (48), 121 (16), 109 (12), 107 (10), 95 (14), 93 (12), 81 (20), 79 (39), 69 (12), 67 (31), 59 (15), 57 (100), 55 (17). HR-MS: 294.2223 ($C_{18}H_{30}O_3^+$; calc. 294.2195).

*2-Methyl-1-(1-methylethyl)propyl (6*E,*8*E*)-3-Oxotetradeca-6,8-dienoate* (**13d**). From **11** and **12d**. Yield 79%. IR (NaCl): 2982*s*, 2928*s*, 2874*m*, 1738*s*, 1714*s*, 1643*m*, 1465*w*, 1237*m*, 987*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.90 (*d*, *J* = 6.6, 6 H); 0.92 (*t*, *J* = 7.0, 3 H); 0.93 (*d*, *J* = 6.6, 6 H); 1.26–1.36 (*m*, 4 H); 1.37–1.44 (*m*, 2 H); 1.89–1.99 (*m*, 2 H); 2.04–2.11 (*m*, 2 H); 2.36–2.43 (*m*, 2 H); 2.69 (*t*, *J* = 7.2, 2 H); 3.50 (*s*, 2 H); 4.67 (*t*, *J* = 6.0, 1 H); 5.52–5.67 (*m*, 2 H); 5.96–6.11 (*m*, 2 H). ^{13}C-NMR (125 MHz): 14.0 (*q*); 17.2 (*q*); 19.5 (*q*); 22.5 (*t*); 26.4 (*t*); 29.0 (*t*); 29.4 (*d*); 31.4 (*t*); 32.5 (*t*); 42.9 (*t*); 49.4 (*t*); 84.1 (*d*); 129.3 (*d*); 129.8 (*d*); 131.6 (*d*); 133.7 (*d*); 167.1 (*s*); 202.1 (*s*). MS: 336 (1, M^+), 238 (12), 221 (11), 137 (11), 136 (28), 109 (10), 81 (10), 79 (14), 67 (20), 57 (100), 55 (11). HR-MS: 336.2622 ($C_{21}H_{36}O_3^+$; calc. 336.2664).

*Methyl (6*E,*8*E*)-2-Diazo-3-oxotetradeca-6,8-dienoate* (**14a**). See [14][15].

Phenyliodonium Ylides **15a**,**b**,**d**: *Typical Procedure*. To KOH (116 mg, 1.78 mmol) in MeOH (2.0 ml) at 0°, **13d** (150 mg, 0.44 mmol) in MeOH (2.0 ml) was added slowly. (Diacetoxy)iodobenzene (144 mg, 0.44 mmol) was added in portions, and the mixture was stirred for 10 min. The yellow soln. was then poured on ice-water (5 ml), which was extracted with CH_2Cl_2 (3 × 5 ml). The org. layer was dried ($MgSO_4$) and evaporated: **15d** (211 mg, 89%). Yellow oil.

1-Methoxy-1,3-dioxo-2-(phenyliodonio)tetradeca-6,8-dien-2-ide (**15a**) [16]. Yield 86%. ^{1}H-NMR ($CDCl_3$): 0.82–0.91 (*m*, 3 H); 1.19–1.43 (*m*, 6 H); 2.03 (*q*, *J* = 7.0, 2 H); 2.24–2.40 (*m*, 2 H); 2.60 (*t*, *J* = 7.1, 2 H); 3.71 (*s*, 3 H); 5.45–5.70 (*m*, 2 H); 5.85–6.12 (*m*, 2 H); 7.30–7.55 (*m*, 3 H); 7.68–7.75 (*m*, 2 H).

*1-(*tert-*Butoxy)-1,3-dioxo-2-(phenyliodonio)tetradeca-6,8-dien-2-ide* (**15b**). Yield 87%. Oil. ^{1}H-NMR (200 MHz, $CDCl_3$): 0.87 (*t*, *J* = 7.0, 3 H); 1.20–1.40 (*m*, 6 H); 1.43 (*s*, 9 H); 1.95–2.10 (*m*, 2 H); 2.35–2.48 (*m*, 2 H); 3.00–3.10 (*m*, 1 H); 3.40–3.50 (*m*, 1 H); 5.40–5.75 (*m*, 1 H); 5.85–6.10 (*m*, 1 H); 7.30–7.56 (*m*, 3 H); 7.68–7.76 (*m*, 2 H).

1-[2-Methyl-1-(1-methylethyl)propoxy]-1,3-dioxo-2-(phenyliodonio)tetradeca-6,8-dien-2-ide (**15d**). Yield 89%. ^{1}H-NMR (200 MHz, $CDCl_3$): 0.79 (*d*, *J* = 6.7, 6 H); 0.84 (*d*, *J* = 6.8, 6 H); 0.87 (*t*, *J* = 6.4, 3 H); 1.11–1.46 (*m*, 6 H); 1.72–2.09 (*m*, 4 H); 2.31–2.49 (*m*, 2 H); 3.15 (*t*, *J* = 2 H); 4.58 (*t*, *J* = 6.2, 1 H); 5.43–5.73 (*m*, 2 H); 5.88–6.11 (*m*, 2 H); 7.28–7.42 (*m*, 2 H); 7.44–7.54 (*m*, 1 H); 7.65–7.78 (*m*, 2 H).

Intramolecular Cyclopropanation by Diazo Decomposition of **14a**. The diazo decomposition of **14a** was carried out according to the procedure used for **6** with **IV** (5 mol-%) as catalyst in $(CH_2Cl)_2$ at 65° to afford racemic **16a** (45%). For data of **16a**, see below.

Intramolecular Cyclopropanation of Phenyliodonium Ylides **15a**,**b**,**d**: *Typical Procedure.* The appropriate ligand (11.2 μmol) and [Cu(OTf)$_2$] (3.4 mg, 10 μmol) were stirred in CH_2Cl_2 (6.0 ml) for 1 h. Ylide **15d** (252 mg, 0.47 mmol) in CH_2Cl_2 (6.0 ml) was added at 0°, and the mixture was stirred overnight at 0°. After evaporation, the residue was purified by FC (pentane/AcOEt 95:5) to give **16d**. For yields and enantioselectivity, see *Table 4*.

Methyl 'exo'-*6-[(1*E*)-Hept-1-enyl)-2-oxobicyclo[3.1.0]hexane-1-carboxylate* (**16a**) [14][16]. For yields and enantioselectivities, see *Table 4*. GC (*Lipodex E*, 130°): t_R 79.5, 89.7. $[\alpha]_D = +34.4$ ($c = 0.53$, $CHCl_3$) for 42% ee. ^{1}H-NMR (200 MHz, $CDCl_3$): 0.83–0.92 (*m*, 3 H); 1.08–1.53 (*m*, 6 H); 1.80–2.56 (*m*, 8 H); 3.64 (*s*, 3 H); 5.12 (*dd*, $J = 8.1$, 15.1, 1 H); 5.63 (*dt*, $J = 7.5$, 15.2, 1 H).

tert-*Butyl* 'exo'-*6-[(1*E*)-Hept-1-enyl]-2-oxobicyclo[3.1.0]hexane-1-carboxylate* (**16b**). Colorless oil. HPLC (*OJ*, hexane/^{i}PrOH 99:1, 0.5 ml/min). t_R 13.3, 14.7. $[\alpha]_D^{20} = -47.9$ ($c = 0.64$, $CHCl_3$) for 68% ee. IR (NaCl): 2957*m*, 2927*s*, 2872*m*, 1732*s*, 1715*s*, 1366*m*, 1249*m*, 1156*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.87 (*t*, $J = 7.0$, 3 H); 1.20–1.38 (*m*, 6 H); 1.47 (*s*, 9 H); 1.95–2.06 (*m*, 3 H); 2.11–2.24 (*m*, 3 H); 2.26 (*dd*, $J = 5.4$, 8.9, 1 H); 2.55–2.60 (*m*, 1 H); 5.23 (*ddt*, $J = 1.3$, 9.1, 15.4, 1 H); 5.73 (*dt*, $J = 6.9$, 15.4, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 14.0 (*q*); 20.7 (*t*); 22.4 (*t*); 28.1 (*q*); 28.8 (*t*); 31.3 (*t*); 32.5 (*t*); 33.5 (*t*); 33.8 (*d*), 37.4 (*d*); 46.1 (*s*); 81.6 (*s*); 123.4 (*d*); 135.7 (*d*); 165.0 (*s*); 206.3 (*s*). MS: 292 (0.5, M^+), 194 (18), 162 (10), 161 (18), 149 (14), 148 (53), 140 (33), 135 (11), 127 (11), 124 (15), 123 (18), 122 (10), 110 (13), 109 (17), 96 (12), 93 (13), 91 (18), 82 (11), 79 (26), 77 (15), 67 (11), 59 (10), 57 (100), 56 (16), 55 (36), 53 (11).

2-Methyl-1-(1-methylethyl)propyl 'exo'-*6-[(1*E*)-Hept-1-enyl]-2-oxobicyclo[3.1.0]hexane-1-carboxylate* (**16d**). HPLC (*AD*, hexane/^{i}PrOH 99:1, 0.5 ml/min): t_R 11.8, 14.0. $[\alpha]_D^{20} = +36.4$ ($c = 0.98$, $CHCl_3$) for 52% ee. IR (NaCl): 2961*s*, 2931*s*, 2874*s*, 1732*s*, 1714*s*, 1464*m*, 1372*m*, 1198*m*, 985*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.88 (*d*, $J = 6.9$, 3 H); 0.90 (*d*, $J = 6.9$, 3 H); 0.91 (*t*, $J = 7.0$, 3 H); 0.94 (*d*, $J = 7.0$, 3 H); 1.01 (*d*, $J = 6.6$, 3 H); 1.22–1.40 (*m*, 6 H); 1.90–2.03 (*m*, 4 H); 2.04–2.10 (*m*, 1 H); 2.17–2.31 (*m*, 3 H); 2.37 (*dd*, $J = 9.1$, 5.3, 1 H); 2.66 (*m*, 1 H); 4.71 (*dd*, $J = 6.6$, 5.3, 1 H); 5.25 (*dd*, $J = 15.4$, 9.1, 1 H); 5.77 (*dt*, $J = 13.6$, 6.6, 1 H). ^{13}C-NMR (125 MHz): 14.0 (*q*); 16.8 (*q*); 17.9 (*q*); 19.4 (*q*); 19.7 (*q*); 20.8 (*t*); 22.5 (*t*); 28.7 (*t*); 29.3 (*d*); 29.4 (*d*); 31.4 (*t*); 32.6 (*t*); 33.6 (*t*); 33.9 (*d*); 37.8 (*d*); 45.8 (*s*); 84.2 (*s*); 123.9 (*d*); 135.7 (*d*); 166.3 (*s*); 205.7 (*s*). MS: 334 (1, M^+), 237 (15), 236 (17), 219 (47), 218 (17), 194 (37), 162 (13), 161 (16), 149 (15), 148 (63), 140 (60), 137 (10), 135 (10), 127 (13), 124 (14), 123 (16), 110 (10), 109 (14), 98 (13), 97 (17), 91 (16), 83 (16), 79 (18), 77 (12), 57 (100), 55 (37). HR-MS: 334.2514 ($C_{21}H_{34}O_3^+$; calc. 334.2508).

3. *Ligands and Catalysts.* The known ligands and catalysts used in this work were either purchased (**I** and **II**) or were synthesized according to published procedures in the case of **V** [35], **VI** and **VIIa**,**b** [23][36], **VIIIa** [37], **VIIIb** [38], **Xa** [26], **XIIa,b** and **XIII** [27], **XIII** [39], and **XVI** [40].

*(*S*)-*N,N,N′,N′*-Tetramethyl-[1,1′-binaphthalene]-2,2′-diamine* (**III**). To 20% H_2SO_4 soln. (1.00 ml) and 40% aq. formaldehyde (554 μl, 7.40 mmol) in THF (1.0 ml), (*S*)-[1,1′-binaphthalene]-2,2′-diamine (**17**; 150 mg, 0.53 mmol) in THF (10 ml) and $NaBH_4$ (291 mg, 7.40 mmol) were added simultaneously. The mixture was stirred for 15 min at r.t. and was then poured on 2% aq. KOH soln. (50 ml). The soln. was extracted with AcOEt (3×20 ml), the combined org. layer dried ($MgSO_4$) and evaporated, and the crude product purified by recrystallization (benzene/EtOH 1:1): colorless crystals (152 mg, 85%). M.p. 255 ([41]: m.p. 252–256°). $[\alpha]_D^{20} = +184$ ($c = 1.05$, C_6H_6) ([41]: $[\alpha]_D^{20}$ (*ent*-**III**) $= -50$ ($c = 0.05$, dioxane)). IR ($CHCl_3$): 3014*m*, 1618*w*, 1595*w*, 1356*w*, 1224*m*, 746*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 2.49 (*s*, 12 H); 7.15–7.21 (*m*, 4 H); 7.26–7.32 (*m*, 2 H); 7.49 (*d*, $J = 9.1$, 2 H); 7.82 (*d*, $J = 7.9$, 2 H); 7.89 (*d*, $J = 8.8$, 2 H). ^{13}C-NMR (125 MHz): 43.4 (*q*); 120.6 (*d*); 123.3 (*d*); 125.9 (*d*); 126.1 (*d*); 126.3 (*s*); 127.7 (*d*); 128.4 (*d*); 129.7 (*s*); 134.7 (*s*); 149.7 (*s*). MS: 340 (13, M^+), 294 (15), 185 (14), 184 (100), 183 (6), 170 (6), 78 (7). HR-MS: 340.1940 ($C_{24}H_{24}N_2^+$; calc. 340.1939).

*Bis{3-[2,2,3,3,4,4,4-Heptafluoro-(1-oxo-*κ*O)butyl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-onato-*κ*O}copper* (**IV**). *3-(2,2,3,3,4,4,4-Heptafluoro-1-hydroxybutylidene)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one* (**19**). A soln. of 1.5M ^{t}BuLi (53.3 ml, 80.0 mmol) in pentane was added to (+)-camphor (**18**; 12.2 g, 80.0 mmol) in THF (60 ml) at −78°. After 15 min, heptafluorobutanoyl chloride [42] (9.30 g, 40.0 mmol) was added slowly. The temp. was raised to 25°, and the mixture was stirred overnight. After addition of aq. AcOH soln. (80 ml) and pentane (40 ml), the org. phase was evaporated, and the residue was dissolved in MeOH (60 ml). A suspension of [Cu(OAc)$_2$] (14.5 g, 80 mmol) in H_2O (140 ml) was added, and the resulting Cu-chelate was extracted with hexane (3×200 ml). A deep-green solid was obtained after evaporation of the solvent. Residual camphor was removed by sublimation at 140°/2 Torr. The free ligand **19** was liberated by dissolution of the product in Et_2O (400 ml) and washing with 10% H_2SO_4 soln. (2×100 ml). The combined org. layer was washed with sat. $NaHCO_3$ soln. (100 ml) and evaporated, and the residue distilled at 71°/1 Torr: pure **19** (10.2 g, 74%). $[\alpha]_D^{20} = +132.9$ ($c = 1.41$, $CHCl_3$) ([43]: $[\alpha]_D^{20} = +123$ ($c = 2.6$, $CHCl_3$)). IR (NaCl): 2965*m*, 1700*s*, 1643*m*, 1340*m*, 1219*s*, 1120*s*, 1043*m*, 955*m*, 744*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.83 (*s*, 3 H); 0.97 (*s*, 3 H); 1.02 (*s*, 3 H); 1.41–1.53 (*m*, 2 H); 1.73–1.83 (*m*, 1 H); 2.04–2.15 (*m*, 1 H); 2.84–2.88 (*m*, 1 H); 11.65–11.90 (br. *s*, 1 H). ^{13}C-NMR

(100 MHz): 8.5 (*q*); 18.2 (*q*); 20.3 (*q*); 26.7 (*t*); 30.1 (*t*); 47.5 (*d*); 49.0 (*s*); 58.0 (*s*); 120.6 (*s*); 148.4 (*s*); 214.0 (*s*). ^{19}F-NMR (376 MHz, $CDCl_3$): 36.1 – 36.3 (*m*, 2 F); 43.8 – 46.1 (*m*, 2 F); 82.9 – 83.1 (*m*, 3 F). MS: 348 (100, M^+), 333 (34), 320 (46), 305 (33), 179 (10), 151 (40), 123 (22), 119 (15), 109 (10), 108 (16), 95 (21), 83 (10), 55 (16). HR-MS: 348.0974 ($C_{14}H_{15}F_7O_2^+$; calc. 348.0960).

Copper Complex **IV**. To a soln. of $[Cu(NO_3)_2 \cdot 3\,H_2O]$ (2.78 g, 11.5 mmol) in H_2O (28 ml) and aq. NH_3 soln. (4.20 ml), ligand **19** (2.00 g, 5.76 mmol) was slowly added. The aq. layer was extracted with Et_2O (3×40 ml), the org. layer dried ($MgSO_4$) and evaporated, and the residue recrystallized from EtOH: pure **IV** (2.13 g, 97%). Green crystals. M.p. 134°. $[\alpha]_D^{20} = -21.9$ ($c = 0.04$, $CHCl_3$). IR ($CHCl_3$): 2967*m*, 1681*s*, 1522*s*, 1344*m*, 1260*m*, 1232*s*, 1198*m*, 1178*m*, 1119*m*, 1082*w*, 1046*w*, 956*w*, 901*w*, 788*m*, 720*s*. ESI-MS: 779.9 ($C_{28}{}^{62}CuF_{14}H_{28}O_4Na^+$; calc. 780.1); 781.7 ($C_{28}{}^{64}CuF_{14}H_{28}O_4Na^+$; calc. 782.1).

*2,2′-[(1*R*,3*S*)-2,2-Dimethylcyclopentane-1,3-diyl]bis[(4*S*)-4-(*tert*-butyl)-4,5-dihydrooxazole]* (**IX**). *(1*R*,3*S*)-1,2,2-Trimethylcyclopentane-1,3-dicarbonyl Dichloride* (**20b**) [26]. To a suspension of PCl_5 (10.4 g, 50 mmol) in hexane (20 ml) at 0°, (+)-camphoric acid (**20a**; 5.00 g, 25 mmol) was added in small portions. The mixture was stirred for 1 h at 0° and for 1 h at r.t. After evaporation, the yellow residue was distilled at 70°/0.1 Torr: **20b** (5.05 g, 85%). Yellow oil. $[\alpha]_D^{20} = +34.7$ ($c = 2.78$, $CHCl_3$). IR (neat): 2979*m*, 1786*s*, 1458*w*, 1382*w*, 1040*w*, 930*m*, 800*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.08 (*s*, 3 H); 1.38 (*s*, 3 H); 1.47 (*s*, 3 H); 1.62 – 1.79 (*m*, 1 H); 1.95 – 2.33 (*m*, 2 H); 2.52 – 2.70 (*m*, 1 H); 3.23 – 3.34 (*m*, 1 H). ^{13}C-NMR (50 MHz): 20.6 (*q*); 21.9 (*q*); 22.8 (*q*); 23.8 (*t*); 33.6 (*t*); 47.7 (*s*); 64.5 (*d*); 65.5 (*s*); 174.5 (*s*); 176.8 (*s*). MS: 201 (3, $[M - Cl]^+$), 175 (5), 173 (19), 172 (8), 165 (8), 164 (8), 138 (18), 137 (100), 136 (89), 131 (7), 129 (10), 118 (5), 110 (11), 109 (97), 108 (38), 96 (39), 95 (28), 93 (10), 91 (9), 89 (7), 83 (55), 82 (40), 81 (9), 79 (10), 77 (16), 69 (59), 68 (51), 67 (33), 65 (6), 55 (60), 53 (23). HR-MS: 201.07000 ($C_{10}H_{14}O_2Cl^+$; calc. 201.0682).

*(1*R*,3*S*)-*N,N′*-Bis[(1*R*)-1-(hydroxymethyl)-2,2-dimethylpropyl]-1,2,2-trimethylcyclopentan-1,3-diamide* (**21**). To L-*tert*-leucinol (=(2*S*)-2-amino-3,3-dimethylbutan-1-ol; 178 mg, 1.52 mmol) in CH_2Cl_2 (2.0 ml) at 0°, Et_3N (529 µl, 3.80 mmol, 5 equiv.) and **20b** (180 mg, 0.76 mmol) were added slowly. The mixture was stirred at 25° for 1 h. After evaporation, the crude product was purified by FC (CH_2Cl_2/MeOH 95 : 5): **21** (273 mg, 90%). Colorless solid. M.p. 175°. $[\alpha]_D^{20} = -53.5$ ($c = 2.09$, $CHCl_3$). IR (KBr): 3308*s*, 2960*s*, 1630*s*, 1534*s*, 1475*m*, 1367*m*, 1053*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.91 (*s*, 3 H); 0.95 (*s*, 9 H); 0.96 (*s*, 9 H); 1.08 (*s*, 3 H); 1.21 (*s*, 3 H); 1.66 – 1.77 (*m*, 1 H); 1.86 – 1.97 (*m*, 1 H); 2.08 – 2.18 (*m*, 1 H); 2.23 – 2.37 (*m*, 1 H); 2.96 – 3.04 (*m*, 1 H); 3.34 – 3.44 (*m*, 1 H); 3.45 – 3.63 (*m*, 3 H); 3.75 – 3.92 (*m*, 4 H); 5.84 (*d*, $J = 8.4$, 1 H); 5.98 (*d*, $J = 8.9$, 1 H). ^{13}C-NMR (100 MHz): 19.7 (*q*); 20.8 (*q*); 25.1 (*q*); 25.4 (*t*); 27.0 (*q*); 27.1 (*q*); 33.2 (*s*); 33.4 (*s*); 34.7 (*t*); 47.1 (*s*); 55.8 (*d*); 56.6 (*s*); 59.6 (*d*); 59.7 (*d*); 63.2 (*t*); 63.5 (*t*); 174.6 (*s*); 178.8 (*s*). MS: 398 (3, M^+), 367 (13), 283 (10), 282 (55), 264 (22), 255 (16), 254 (100), 236 (32), 213 (57), 195 (30), 186 (37), 168 (24), 144 (11), 137 (14), 118 (13), 111 (12), 109 (34), 95 (16), 86 (48), 83 (27), 69 (34), 60 (11), 57 (23), 55 (25), 45 (11). HR-MS: 398.3187 ($C_{22}H_{42}N_2O_4^+$; calc. 398.1444).

Ligand **IX**. To TsCl (299 mg, 1.6 mmol, 2.5 equiv.) in CH_2Cl_2 (2.0 ml), **21** (250 mg, 0.63 mmol), *N,N*-dimethylpyridin-4-amine (8 mg), and Et_3N (386 µl, 4.4 equiv.) in CH_2Cl_2 (3.0 ml) were added. The mixture was stirred for 2 d, then diluted with CH_2Cl_2 (5.0 ml), and washed with sat. NH_4Cl soln. (10 ml). After the usual workup, the crude product was purified by FC (hexane/AcOEt 80 : 20): **IX** (195 mg, 85%). Colorless solid. $[\alpha]_D^{20} = -123$ ($c = 1.39$, $CHCl_3$). IR (KBr): 2960*s*, 1643*s*, 1478*s*, 1381*s*, 1361*s*, 1292*m*, 1262*s*, 1211*m*, 1191*s*, 1169*s*, 1100*s*, 1043*m*, 989*s*, 920*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.88 (*s*, 12 H); 0.90 (*s*, 9 H); 1.03 (*s*, 3 H); 1.20 (*s*, 3 H); 1.62 – 1.73 (*m*, 1 H); 1.99 – 2.11 (*m*, 1 H); 2.12 – 2.25 (*m*, 2 H); 2.96 – 3.04 (*m*, 1 H); 3.76 – 3.88 (*m*, 2 H); 3.94 – 4.02 (*m*, 2 H); 4.09 – 4.19 (*m*, 2 H). ^{13}C-NMR (50 MHz): 20.4 (*q*); 25.0 (*q*); 25.6 (*t*); 26.0 (*q*); 26.1 (*q*); 33.5 (*s*); 33.8 (*s*); 35.3 (*t*); 46.8 (*s*); 48.1 (*d*); 50.7 (*s*); 68.1 (*t*); 75.1 (*d*); 75.4 (*d*); 168.8 (*s*); 172.0 (*s*). MS: 362 (6, M^+), 347 (14), 306 (22), 305 (100), 205 (20), 196 (10), 195 (50), 182 (10), 181 (28), 169 (13), 168 (90), 57 (11), 55 (10). HR-MS: 362.2927 ($C_{22}H_{38}N_2O_2^+$; calc. 362.2933).

*2,2′-([1,1′-Binaphthalene]-2,2′-diyl)bis[(4*S*)-4-(cyclohexylmethyl)-4,5-dihydrooxazole]* (**Xb**). *(4*S*)-2-(1-Bromonaphthalen-2-yl)-4-(cyclohexylmethyl)-4,5-dihydrooxazole* (**24**). To 1-bromonaphthalene-2-carboxylic acid (**22a**; 600 mg, 2.39 mmol) in CH_2Cl_2 (15 ml), oxalyl chloride (809 µl, 9.56 mmol) was added slowly, followed by 3 drops of DMF. The mixture became transparent and was allowed to stand at r.t. overnight. The solvent was evaporated and the residue dried *in vacuo*. The crude chloride **22b** was dissolved in CH_2Cl_2 (30 ml) and added at −10° to a soln. of (2*S*)-2-amino-3-cyclohexylpropan-1-ol hydrochloride (**23**; 509 mg, 2.63 mmol) and Et_3N (677 µl, 6.69 mmol). The mixture was stirred at r.t. overnight. After evaporation, the residue was treated with sat. NaCl soln. (15 ml) and extracted with CH_2Cl_2 (3×30 ml). The combined org. layer was dried ($MgSO_4$) and evaporated. The resulting solid was dissolved in THF (15 ml), and *Burgess* reagent [25] ([(methoxycarbonyl)sulfamoyl]triethylammonium hydroxide; 568 mg, 2.38 mmol) was added. After 24 h stirring, the solvent was evaporated and the remaining yellow oil purified by FC (hexane/AcOEt 95 : 5): **24** (756 mg, 85%). Slightly

yellow solid. M.p. 70°. $[\alpha]_D^{20} = 54.4$ ($c = 3.01$, CH_2Cl_2). IR ($CHCl_3$): 3014*m*, 2925*s*, 2360*s*, 1668*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.95–1.10 (*m*, 2 H); 1.14–1.39 (*m*, 3 H); 1.44–1.53 (*m*, 1 H); 1.54–1.65 (*m*, 1 H); 1.66–1.93 (*m*, 6 H); 4.11 (*dd*, *J* = 7.8, 7.8, 1 H); 4.44–4.54 (*m*, 1 H); 4.61 (*dd*, *J* = 8.1, 9.4, 1 H); 7.55–7.70 (*m*, 3 H); 7.81–7.90 (*m*, 2 H); 8.43 (*d*, *J* = 8.6, 1 H). ^{13}C-NMR (100 MHz): 26.1 (*t*); 26.2 (*t*); 26.5 (*t*); 33.4 (*t*); 33.5 (*t*); 34.8 (*d*); 44.2 (*t*); 65.0 (*d*); 73.5 (*t*); 123.1 (*s*); 126.7 (*d*); 127.5 (*d*); 127.6 (*d*); 127.8 (*d*); 128.1 (*d*); 128.2 (*d*); 128.6 (*s*); 132.2 (*s*); 134.8 (*s*); 163.6 (*s*). MS: 373 (10, M^+), 371 (10, M^+), 292 (24), 291 (16), 289 (19), 276 (32), 274 (32), 252 (16), 250 (18), 236 (11), 235 (92), 234 (17), 233 (100), 210 (31), 196 (30), 167 (30), 153 (14), 152 (11), 126 (24), 55 (15). HR-MS: 371.0912 ($C_{20}H_{22}{}^{79}BrNO^+$; calc. 371.0885), 373.0858 ($C_{20}H_{22}{}^{81}BrNO^+$; calc. 373.0864).

*2,2′-([1,1′-Binaphthalene]-2,2′diyl)bis[(4*S*)-4-(cyclohexylmethyl)-4,5-dihydrooxazole]* (**Xb**). Bromide **24** (740 mg, 1.99 mmol) was dried by azeotropic distillation with benzene (3 × 15 ml). Activated Cu powder (3.16 g, 49.7 mmol) and freshly distilled pyridine (20 ml) were added, and the mixture was heated to reflux for 24 h. The solvent was evaporated, the residue dissolved in CH_2Cl_2, and the remaining Cu removed by filtration through *Celite*. The org. phase was extracted with 20% NH_4OH soln. (50 ml) and washed repeatedly with sat. NH_4Cl, until the blue color of the soln. faded. The org. layer was dried ($MgSO_4$) and evaporated and the residue purified by FC (SiO_2, pentane/AcOEt 98:2): **Xb** (367 mg, 63%). Colorless foam, containing two stereoisomers in a 85:15 ratio. $[\alpha]_D^{20} = -120.1$ ($c = 1.02$, $CHCl_3$). IR ($CHCl_3$): 2925*s*, 2359*w*, 2852*m*, 1646*m*, 1448*m*, 750*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.69–0.81 (*m*, 2 H); 0.88–1.15 (*m*, 14 H); 1.32–1.39 (*m*, 2 H); 1.43–1.57 (*m*, 8 H); 3.38 (*dd*, *J* = 7.5, 7.6, 2 H); 3.70 (*dd*, *J* = 8.2, 9.1, 2 H); 3.82–3.90 (*m*, 2 H); 7.15–7.22 (*m*, 4 H); 7.36–7.41 (*m*, 2 H); 7.80–7.89 (*m*, 4 H); 7.97 (*d*, *J* = 8.5, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 26.1 (*t*); 26.5 (*t*); 33.1 (*t*); 33.3 (*t*); 34.3 (*d*); 43.7 (*t*); 64.1 (*d*); 72.8 (*t*); 126.0 (*s*); 126.1 (*d*); 126.3 (*d*); 126.7 (*d*); 127.0 (*d*); 127.5 (*d*); 127.8 (*d*); 132.9 (*s*); 134.2 (*s*); 137.8 (*s*); 163.6 (*s*). MS: 584 (38, M^+), 487 (23), 445 (10), 419 (35), 418 (100), 347 (19), 307 (11), 306 (43), 281 (14), 81 (15), 55 (21). HR-MS: 584.3387 ($C_{40}H_{44}N_2O_2^+$; calc. 584.3403).

*2,2′-([1,1′-Binaphthalene]-2,2′-diyl)bis[(3a*R*,8a*S*)-8,8a-dihydro-3a*H*-indeno[1,2-*d*]oxazole]* (**XI**). *1-Bromonaphthalene-2-carboxamide* (**22c**). 1-Bromonaphthalenecarboxylic acid (**22a**; 1.00 g, 3.98 mol) and $SOCl_2$ (2.90 ml, 40 mmol) were refluxed for 3 h, after which the excess of $SOCl_2$ was distilled off. The residue (1.05 g) was dried *in vacuo*, then dissolved in Et_2O, and gaseous NH_3 was passed through the soln. for 30 min. The precipitate was filtered, washed with H_2O, and recrystallized in EtOH to afford **22c**. Colorless crystals (946 mg, 95%). M.p. 204°. IR ($CHCl_3$): 3019*s*, 1677*s*, 1218*m*, 770*s*, 720*s*. ^{1}H-NMR (400 MHz, CD_3OD): 7.46 (*d*, *J* = 8.3, 1 H); 7.57–7.62 (*m*, 1 H); 7.63–7.68 (*m*, 1 H); 7.88–7.94 (*m*, 2 H); 8.33 (*d*, *J* = 8.8, 1 H). ^{13}C-NMR (100 MHz): 118.6 (*s*); 124.2 (*d*); 127.0 (*d*); 127.2 (*d*); 127.8 (*d*); 127.9 (*d*); 128.0 (*d*); 131.7 (*s*); 134.4 (*s*); 136.7 (*s*); 172.5 (*s*). MS: 251 (65, M^+), 250 (37), 249 (69, M^+), 248 (29), 234 (13), 233 (97), 232 (14), 231 (100), 205 (29), 203 (28), 126 (13), 125 (16), 124 (76), 74 (12), 73 (14), 72 (13), 61 (41), 48 (10). HR-MS: 248.9797 ($C_{11}H_8{}^{79}BrNO^+$; calc. 248.9789), 250.9776 ($C_{11}H_8{}^{81}BrNO^+$; calc. 250.9769).

*(3a*R*,8a*S*)-2-(1-Bromonaphthalen-2-yl)-8,8a-dihydro-3a*H*-indeno[1,2-*d*]oxazole* (**27**). To amide **22c** (617 mg, 2.47 mol) in $(CH_2Cl)_2$ (20 ml) was added, in portions, dry $(Me_3O)BF_4$ (469 mg, 2.47 mmol). The soln. was stirred overnight at r.t., whereupon (1*R*,2*S*)-1-amino-2,3-dihydro-1*H*-inden-2-ol (**26**; 405 mg, 2.71 mmol) was added, and the mixture was refluxed overnight. After cooling, it was poured on 5% aq. $NaHCO_3$ soln. (10 ml) and extracted with CH_2Cl_2 (3 × 20 ml). The combined org. layer was dried ($MgSO_4$) and evaporated. FC (SiO_2, pentane/AcOEt 90:10) of the residue afforded **27** (459 mg, 51%). Colorless solid. $[\alpha]_D^{20} = +167.0$ ($c = 0.50$, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$): 3.51 (*dd*, *J* = 17.9, 1.9, 1 H); 3.57 (*dd*, *J* = 17.9, 6.3, 1 H); 5.61–5.66 (*m*, 1 H); 5.86 (*d*, *J* = 8.2, 1 H); 7.29–7.35 (*m*, 3 H); 7.55–7.66 (*m*, 4 H); 7.80 (*d*, *J* = 8.5, 1 H); 7.83 (*d*, *J* = 7.9, 1 H); 8.39 (*d*, *J* = 8.8, 1 H). ^{13}C-NMR (125 MHz): 39.7 (*t*); 76.9 (*d*); 84.0 (*d*); 123.4 (*s*); 125.3 (*d*); 125.8 (*d*); 126.9 (*d*); 127.5 (*d*); 127.7 (*d*); 127.8 (*d*); 127.9 (*d*); 128.1 (*d*); 128.2 (*d*); 128.6 (*d*); 132.2 (*s*); 135.0 (*s*); 139.7 (*s*); 141.5 (*s*); 164.6 (*s*). MS: 365 (18, M^+), 363 (18, M^+), 132 (18), 131 (10), 105 (11), 104 (100), 103 (13), 77 (10). HR-MS: 363.0243 ($C_{20}H_{14}{}^{79}BrNO^+$; calc. 363.0259), 365.0198 ($C_{20}H_{14}{}^{81}BrNO^+$; calc. 365.0238).

Ligand **XI**. As described for **Xb**, with **27** (400 mg, 1.10 mmol). The crude product was purified by FC (SiO_2, pentane/AcOEt 95:5): **XI** (810 mg, 74%) as a mixture of two diastereoisomers in a 83:17 ratio. The de of a small sample could be increased to >98% after HPLC. M.p. 22°. $[\alpha]_D^{20} = +235.2$ ($c = 1.02$, $CHCl_3$). IR ($CHCl_3$): 3014*s*, 2968*m*, 1630*s*, 1360*w*, 1224*s*, 1099*m*, 998*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 2.39 (*d*, *J* = 17.7, 2 H); 2.89 (*dd*, *J* = 17.7, 7.0, 2 H); 4.63–4.68 (*m*, 2 H); 5.27 (*d*, *J* = 7.9, 2 H); 7.01–7.19 (*m*, 6 H); 7.40–7.45 (*m*, 2 H); 7.87 (*d*, *J* = 8.2, 2 H); 7.92 (*d*, *J* = 8.8, 2 H); 8.00 (*d*, *J* = 8.8, 2 H). ^{13}C-NMR (125 MHz): 39.0 (*t*); 76.3 (*d*); 82.6 (*d*); 124.9 (*s*); 125.3 (*d*); 125.8 (*d*); 126.0 (*d*); 126.3 (*d*); 126.8 (*d*); 127.0 (*d*); 127.1 (*d*); 127.6 (*d*); 127.7 (*d*); 127.8 (*d*); 133.0 (*s*); 134.0 (*s*); 137.5 (*s*); 139.7 (*s*); 141.7 (*s*); 164.5 (*s*). MS: 569 (20), 568 (47, M^+), 411 (35), 410 (100), 307 (15), 306 (63), 294 (11), 278 (15), 277 (16), 116 (16), 115 (38), 104 (16), 103 (13), 55 (21). HR-MS: 568.2145 ($C_{40}H_{28}N_2O_2^+$; calc. 568.2151).

2,6-Bis[(4S)-4-(cyclohexylmethyl)-4,5-dihydrooxazol-2-yl]pyridine (**XIIc**). To **23** (338 mg, 1.74 mmol) and Et_3N (664 µl, 4.8 mmol) in CH_2Cl_2 (5.0 ml) at 0°, pyridine-2,6-dicarbonyl dichloride (**28**; 162 mg, 0.79 mmol) in CH_2Cl_2 was slowly added. The mixture was allowed to stand at r.t. overnight. $SOCl_2$ (578 µl, 7.94 mmol) was added, and the mixture was heated to reflux for 2 h and then slowly poured on ice. The org. layer was washed with sat. NaCl soln. and 0.1M K_2CO_3, the org. layer dried (Na_2SO_4) and evaporated, and the residue purified by FC (SiO_2, CH_2Cl_2/MeOH 95:5): crude **29** as a solid. MeOH (5.5 ml), H_2O (2.5 ml), and NaOH (191 mg, 4.76 mmol) were added, and the mixture was heated to reflux for 2 h. After repeated extraction with CH_2Cl_2, the org. layer was dried (Na_2SO_4) and evaporated and the residue recrystallized from hexane/AcOEt: **XIIc** (224 mg, 69%). M.p. 208–210°. $[\alpha]_D^{20} = -134.2$ ($c = 1.05$, $CHCl_3$). IR ($CHCl_3$): 3020*s*, 2925*s*, 2853*s*, 1644*s*, 1572*m*, 1476*m*, 1449*m*, 1208*s*, 1046*s*, 975*s*, 715*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.89–1.02 (*m*, 4 H); 1.09–1.34 (*m*, 6 H); 1.35–1.43 (*m*, 2 H); 1.44–1.57 (*m*, 2 H); 1.59–1.83 (*m*, 12 H); 4.05–4.11 (*m*, 2 H); 4.36–4.46 (*m*, 2 H); 4.59 (*dd*, J = 8.3, 9.4, 2 H); 7.85 (*t*, J = 7.8, 1 H); 8.16 (*d*, J = 7.8, 2 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 26.1 (*t*); 26.4 (*t*); 33.3 (*t*); 33.4 (*t*); 34.8 (*d*); 44.1 (*t*); 64.7 (*d*); 73.8 (*t*); 125.5 (*d*); 137.1 (*d*); 146.9 (*s*); 162.0 (*s*). MS: 409 (100, M^+), 408 (16), 367 (13), 313 (32), 312 (61), 286 (11), 285 (43), 284 (32), 283 (21), 272 (13), 271 (14), 270 (27), 269 (13), 259 (11), 258 (51), 257 (13), 256 (55), 245 (10), 244 (45), 243 (25), 242 (64), 228 (14), 214 (20), 174 (13), 162 (10), 161 (10), 160 (18), 148 (12), 147 (20), 146 (24), 145 (35), 138 (30), 136 (11), 131 (17), 130 (13), 124 (18), 122 (10), 121 (18), 119 (11), 118 (17), 117 (28), 106 (16), 105 (16), 104 (15), 103 (23), 95 (13), 93 (15), 91 (10), 90 (13), 81 (39), 79 (21), 78 (14), 77 (14), 67 (33), 56 (17), 55 (94), 54 (11), 53 (13). HR-MS: 409.2692 ($C_{25}H_{35}N_3O_2^+$; calc. 409.2729).

2,6-Bis[(4S,5S)-4,5-dihydro-5-(4-nitrophenyl)-4-[[(trialkylsilyl)oxy]methyl}oxazol-2-yl]pyridine (**XVb–d**). *Dimethyl Pyridine-2,6-dicarboximidate* (**31**). Pyridine-2,6-dicarbonitrile (**30**; 1.00 g, 7.74 mmol) and Na (18 mg, 0.77 mmol) dissolved in MeOH were stirred at r.t. for 36 h. AcOH (44 µl) was added, and the solvent was evaporated. The solid colorless powder was dried *in vacuo:* crude **31** (1.48 g, 99%), which was used without further purification.

2,2′-(Pyridine-2,6-diyl)bis[(4S,5S)-4,5-dihydro-5-(4-nitrophenyl)oxazole-2,4-methanol] (**XVa**). A suspension of **31** (1.48 g, 7.66 mmol) and (1*S*,2*S*)-2-amino-1-(4-nitrophenyl)propane-1,3-diol (**32**; 3.58 g, 16.8 mmol, *Aldrich*) in $(CH_2Cl)_2$ (30 ml) was stirred under reflux during 2 d. After evaporation, MeOH (30 ml) was added to the residue and the precipitate recovered, washed, and dried: **XVa** (3.10 g, 78%). Grey amorphous solid. M.p. 251°. $[\alpha]_D^{20} = +296.1$ ($c = 0.31$, DMSO). ^{1}H-NMR (500 MHz, (D_6)DMSO): 3.62–3.69 (*m*, 2 H); 3.76–3.83 (*m*, 2 H); 4.14–4.19 (*m*, 2 H); 5.17 (*t*, J = 5.7, 2 H); 5.78 (*d*, J = 6.6, 2 H); 7.63 (*d*, J = 8.5, 4 H); 8.14 (*dd*, J = 7.2, 8.2, 1 H); 8.23–8.30 (*m*, 6 H). ^{13}C-NMR (125 MHz,(D_6)DMSO): 62.7 (*t*); 77.1 (*d*); 81.9 (*d*); 124.0 (*d*); 126.4 (*d*); 126.7 (*d*); 138.4 (*d*); 146.0 (*s*); 147.2 (*s*); 148.4 (*s*); 161.4 (*s*). MS: 489 (1, M^+), 342 (12), 312 (14), 311 (29), 193 (13), 191 (37), 190 (24), 167 (16), 164 (17), 151 (79), 150 (99), 149 (27), 148 (14), 147 (18), 146 (22), 145 (23), 137 (10), 136 (13), 131 (17), 122 (64), 121 (76), 120 (27), 118 (32), 117 (16), 106 (35), 105 (64), 104 (58), 103 (38), 94 (10), 93 (11), 92 (27), 91 (18), 90 (29), 89 (17), 79 (15), 78 (63), 77 (100), 76 (44), 75 (24), 74 (18), 73 (16), 65 (47), 64 (10), 63 (19), 60 (17), 57 (13), 55 (22), 52 (15), 51 (80), 50 (47). HR-MS: 489.1615 ($C_{25}H_{23}N_5O_6^+$; calc. 489.1648).

Ligands **XVb–d**: *General Procedure.* A suspension of **XVa** (300 mg, 0.58 mmol), *tert*-butylchlorodimethylsilane (191 mg, 1.27 mmol) and 1*H*-imidazole (208 mg, 3.06 mmol) in DMF (4.0 ml) was stirred overnight at r.t. The solvent was then evaporated, H_2O (10 ml) added, and the mixture extracted with CH_2Cl_2 (3 × 30 ml). The combined org. phase was dried (Na_2SO_4) and evaporated and the residue purified by FC (SiO_2, pentane/AcOEt 7:3, containing 2% of Et_3N): **XVb** (338 mg, 78%). Colorless foam.

*2,6-Bis[(4S,5S)-4-{[[(*tert*-butyl)dimethylsilyl]oxy}methyl]-4,5-dihydro-5-(4-nitrophenyl)-oxazol-2-yl]pyridine* (**XVb**): $[\alpha]_D^{20} = +194.2$ ($c = 1.09$, $CHCl_3$). IR ($CHCl_3$): 3020*s*, 2954*m*, 2360*m*, 1525*s*, 1348*s*, 1258*m*, 1222*s*, 1110*m*, 840*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.10 (*s*, 6 H); 0.11 (*s*, 6 H); 0.91 (*s*, 18 H); 3.75 (*dd*, J = 8.2, 10.1, 2 H); 4.14 (*dd*, J = 4.1, 10.1, 2 H); 4.29–4.35 (*m*, 2 H); 5.78 (*d*, J = 6.7, 2 H); 7.56 (*d*, J = 8.5, 4 H); 7.99 (*t*, J = 7.9, 1 H); 8.21 (*d*, J = 4.1, 4 H); 8.22 (*d*, J = 7.0, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): −5.4 (*q*); −5.3 (*q*); 18.3 (*s*); 25.8 (*q*); 65.1 (*t*); 77.1 (*d*); 83.8 (*d*); 123.9 (*d*); 126.3 (*d*); 137.6 (*d*); 146.6 (*s*); 147.6 (*s*); 148.0 (*s*); 162.5 (*s*). MS: 748 (1, M^+), 691 (23), 690 (40), 115 (18), 89 (62), 75 (43), 74 (13), 73 (100), 59 (15), 57 (10), 56 (10). HR-MS: 747.3153 ($C_{37}H_{49}N_5O_8Si_2^+$; calc. 747.3120).

*2,6-Bis[(4S,5S)-4-{[[(*tert*-butyl)diphenylsilyl]oxy}methyl]-4,5-dihydro-5-(4-nitrophenyl)-oxazol-2-yl]pyridine* (**XVc**). As described above, with (*tert*-butyl)chlorodiphenylsilane. Yield 84%. $[\alpha]_D^{20} = +112.1$ ($c = 1.00$, $CHCl_3$). IR ($CHCl_3$): 3019*s*, 2932*w*, 1525*s*, 1349*s*, 1113*s*, 772*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.08 (*s*, 18 H); 3.86 (*dd*, J = 7.6, 10.4, 2 H); 4.13 (*dd*, J = 3.8, 10.4, 2 H); 4.32–4.39 (*m*, 2 H); 5.81 (*d*, J = 6.3, 2 H); 7.36–7.41 (*m*, 8 H); 7.42–7.47 (*m*, 4 H); 7.51 (*d*, J = 8.8, 4 H); 7.64–7.69 (*m*, 8 H); 7.95 (*t*, J = 7.6, 1 H); 8.19 (*d*, J = 8.5, 4 H); 8.23 (*d*, J = 7.9, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 19.3 (*s*); 26.9 (*q*); 65.6 (*t*); 77.1 (*d*); 83.6 (*d*); 123.9 (*d*);

126.3 (*d*); 126.4 (*d*); 127.8 (*d*); 127.9 (*d*); 129.9 (*d*); 130.0 (*d*); 132.8 (*s*); 132.9 (*s*); 135.5 (*d*); 135.6 (*d*); 137.5 (*d*); 146.6 (*s*); 147.7 (*s*); 147.9 (*s*); 162.6 (*s*). MS: 996 (1, M^+), 938 (11), 227 (15), 202 (11), 201 (40), 200 (14), 199 (100), 197 (15), 135 (45), 78 (13), 77 (20). ESI-MS (pos. mode): 996.4 ($[M+H]^+$, $C_{57}H_{58}N_5O_8Si_2^+$; calc. 996.4). HR-MS: 995.3713 ($C_{57}H_{57}N_5O_8Si_2^+$; calc. 995.3746).

*2,6-Bis{(4*S*,5*S*)-4,5-Dihydro-5-(4-nitrophenyl)-4-{[(triisopropylsilyl)oxy]methyl}oxazol-2-yl}pyridine* (**XVd**). As described above, with chlorotriisopropylsilane. Yield 79%. $[\alpha]_D^{20} = +160.0$ ($c = 1.00$, $CHCl_3$). IR ($CHCl_3$): 3020*s*, 2945*m*, 2867*m*, 1525*s*, 1348*s*, 1110*m*, 754*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.07 (*d*, $J = 7.2$, 18 H); 1.08 (*d*, $J = 7.0$, 18 H); 1.12–1.20 (*m*, 6 H); 3.82 (*dd*, $J = 8.9$, 9.5, 2 H); 4.24 (*dd*, $J = 4.1$, 10.1, 2 H); 4.32–4.39 (*m*, 2 H); 5.84 (*d*, $J = 6.3$, 2 H); 7.58 (*d*, $J = 8.5$, 4 H); 7.99 (*t*, $J = 7.9$, 1 H); 8.22 (*d*, $J = 8.5$, 4 H); 8.26 (*d*, $J = 7.9$, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 11.9 (*q*); 18.0 (*q*); 65.6 (*t*); 77.3 (*d*); 83.9 (*d*); 123.9 (*d*); 126.4 (*d*); 137.6 (*d*); 146.7 (*s*); 147.6 (*s*); 148.0 (*s*); 162.6 (*s*). MS: 832 (1, M^+), 292 (25), 276 (26), 274 (25), 235 (85), 233 (100), 210 (43), 196 (46), 167 (64), 153 (34), 127 (21), 126 (58), 67 (21), 57 (31), 55 (73). ESI-MS (pos. mode): 832.4 ($[M+H]^+$, $C_{43}H_{62}N_5O_8Si_2^+$, calc. 832.4). HR-MS: 832.4088 ($C_{43}H_{61}N_5O_8Si_2^+$; calc. 831.4059).

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