Highly Enantio- and Regioselective Allylic Alkylations Catalyzed by Chiral [Bis(dihydrooxazole)]molybdenum Complexes

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In memory of *Luigi M. Venanzi*

A series of chiral C_2-symmetric bis[dihydrooxazoles] with a *trans*-1,2-diaminocyclohexane backbone was synthesized. In view of the promising results obtained by *Trost et al.* with related bis[pyridine] ligands, we tested these new ligands in the enantioselective molybdenum-catalyzed allylic alkylation of 1- and 3-monosubstituted allylic substrates. Enantiomer excesses of up to 98% and branched/linear ratios of up to 11 : 1 were obtained with (*E*)-3-(alkyl)allyl carbonates. (*E*)-3-Phenoxyallyl acetate gave a branched/linear ratio of > 20 : 1 and an ee of 98%. Crystal structures of the free ligand **7a** and of its tricarbonylmolybdenum(0) complex **28** are reported.

Introduction. – Transition-metal-catalyzed allylic substitution is one of the most efficient and most versatile methods for enantioselective C–C and C–heteroatom bond formation [1]. A number of chiral catalysts are available which afford high enantiomer excesses (ee) with many prochiral or racemic substrates. However, there are still classes of substrates which give unsatisfactory results with the known catalysts and, therefore, the search for new chiral ligands and catalyst systems continues.

Unsymmetrically substituted allyl derivatives are particularly demanding substrates, because, in addition to the requirement of enantiocontrol, the problem of regioselectivity has to be addressed. With most Pd-catalysts, monosubstituted allyl systems such as 1- or 3-arylallyl derivatives react with C-nucleophiles preferentially at the unsubstituted terminus, giving rise to a linear, achiral product. It is only recently that catalysts have been discovered which allow the preparation of branched, chiral regioisomers from 1- or 3-arylallyl esters, with good enantio- and regioselectivity. Such a reversal of regioselectivity has been achieved by means of Pd complexes with certain chiral ligands such as **1** [2], W [3] and Ir [4] complexes derived from phosphinodihydrooxazoles **2**, an Ir catalyst containing the phosphoramidite **3** [5] and, most recently, with a Mo complex [6] derived from the bis[pyridine] **4** [7]. In terms of regio- and enantioselectivity, the latter of these, developed by *Trost et al.* [6a,b], is the most selective catalyst available today, giving a branched/linear ratio of 49 : 1 and an ee of 99% in the reaction of methyl (*E*)-1-phenylallyl carbonate with dimethyl malonate.

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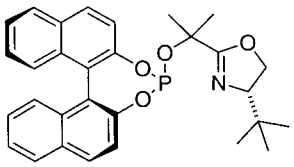
[1]) Laboratory for Chemical Crystallography (head: Prof. *M. Neuburger-Zehnder*).



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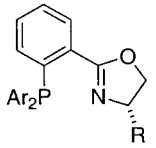

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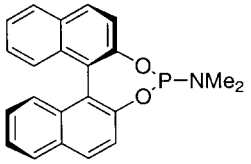

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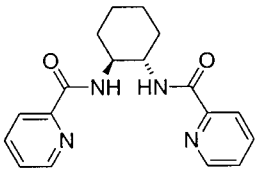

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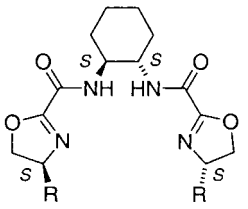
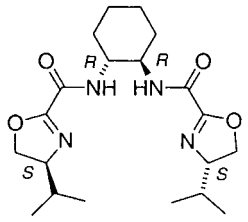
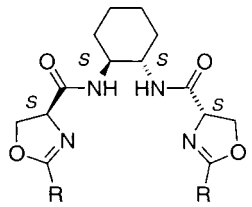
In the course of our work on chiral dihydrooxazole ligands [8], we prepared a series of bis[dihydrooxazoles] with a *trans*-1,2-diaminocyclohexane backbone. Although these ligands were originally designed for other applications [9], the promising results of *Trost et al.* [6a,b] with ligand **4** prompted us to test the bis[dihydrooxazoles] **5**–**7** in the Mo-catalyzed allylic alkylation of monosubstituted allyl derivatives (for a preliminary communication, see [10]).



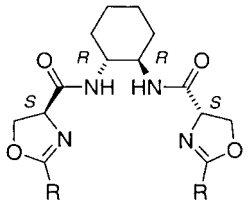
5a R = ^{i}Pr
b R = ^{t}Bu



5c



6a R = Ph
b R = Pr
c R = ^{i}Pr

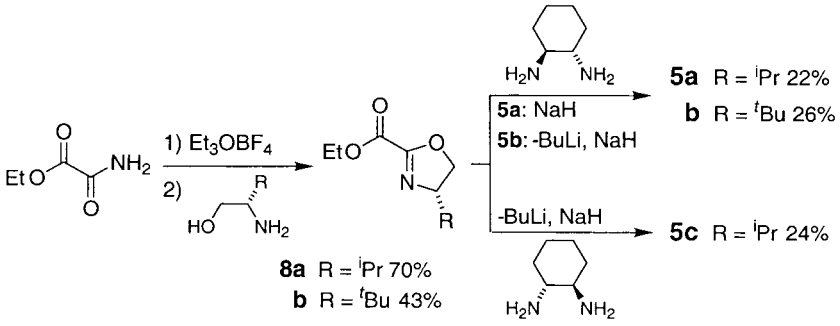


7a R = Ph
b R = Pr
c R = ^{i}Pr
d R = ^{t}Bu

Ligand Synthesis. – Ligands **5**–**7** can be readily prepared from chiral amino-alcohols and *trans*-cyclohexane-1,2-diamine as commercially available enantiomerically pure components.

The ligands **5** were obtained in just two steps from ethyl oxamate (*Scheme 1*). In the first step, ethyl oxamate was activated by treatment with triethyloxonium tetrafluoroborate and subsequently reacted with (*S*)-valinol or (*S*)-*tert*-leucinol to afford the dihydrooxazolecarboxylates **8**. However, initial attempts to convert this intermediate to the ligands **5a**–**c** failed; neither direct coupling with *trans*-cyclohexane-1,2-diamine without additional base nor hydrolysis to the corresponding carboxylic acid (which would have allowed amide formation in the presence of suitable coupling reagents) was successful. Finally, the synthesis of ligand **5a** was accomplished by reaction of ester **8** with *trans*-cyclohexane-1,2-diamine and NaH in DMSO at 40°. For the synthesis of ligands **5b** and **5c**, a different procedure was used. *trans*-Cyclohexane-1,2-diamine was first deprotonated with BuLi in THF and then combined with ester **8**. Subsequent addition of NaH and DMF and heating to 60° led to the desired bis[carboxamides] **5b** and **5c**. Although the yields of these reactions were low, the procedure is attractive because it is simple and avoids additional steps for the activation of the carboxy group of **8**.

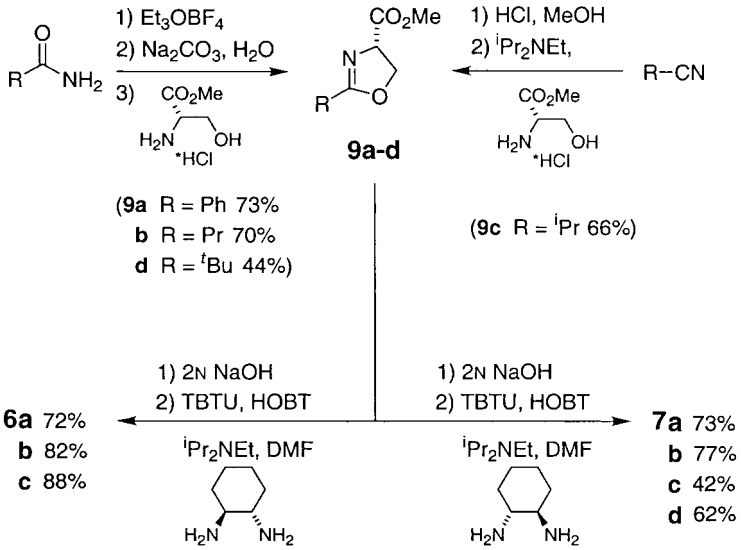
Scheme 1



The two series of diastereoisomeric ligands **6** and **7** were prepared from the corresponding amides or nitriles as shown in *Scheme 2*. In the synthesis of ligand **6a**, the imidate derived from benzamide was coupled with L-serine methyl ester hydrochloride to give the dihydrooxazolecarboxylate **9a** in 73% overall yield. The corresponding carboxylic acid was obtained in 76% yield by careful hydrolysis with 2N aq. NaOH at room temperature. Finally, coupling with *trans*-cyclohexane-1,2-diamine by means of standard procedures, gave the desired bis[dihydrooxazole] ligand **6a** in 95% yield. In the last two steps, no epimerization at the stereogenic center of the dihydrooxazole took place as can be judged by ^{13}C-NMR analysis and HPLC of the ligands.

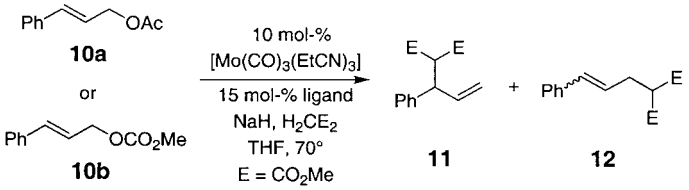
Molybdenum-Catalyzed Allylic Alkylation. – Initially, the Ph-substituted substrates **10a** and **10b** were used as test substrates to compare the performance of the bis[dihydrooxazole] ligands with ligand **4** (see *Table 1*). Generally, the catalyst was prepared by heating a degassed solution of $[Mo(CO)_3(EtCN)_3]$ and the ligand in THF at 70° for 1 h. The reactivity of acetate **10a** was found to be insufficient with reaction

Scheme 2



times of five days in THF at 70° (incomplete reaction) and of three days in toluene at 110°. With the more reactive carbonate **10b**, the bis[dihydrooxazoles] **5a** and **6b** induced similar levels of enantioselectivity as the bis[pyridine] ligand **4**; however, the branched/linear ratios were lower and the reactions somewhat slower. Furthermore, in line with observations by *Trost et al.* [6a,b], the corresponding branched substrate reacted with significantly lower ee (**6b**: 84 *vs.* 98%; *Scheme 3*).

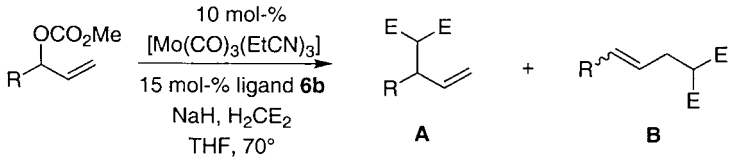
Table 1. *Enantioselective Mo-Catalyzed Allylic Alkylation of Substrates* **10a** *and* **10b**



Entry	Substrate	Ligand	Time	Yield [%][a])	**11**/**12**	ee of **11** [%][b])
1[c])	**10b**	**4**	3 h	70	49 : 1	99 (*R*)
2	**10a**	**5a**	5 d	38	9 : 1	98 (*R*)
3[d])	**10a**	**5a**	3 d	84	10 : 1	97 (*R*)
4	**10b**	**5a**	0.5 d	86	14 : 1	99 (*R*)
5	**10b**	**6b**	1 d	83	6 : 1	98 (*R*)

[a]) Combined yields of **11** and **12**. [b]) Determined by HPLC (*Daicel Chiralcel OJ*). [c]) *Entry* taken from [6a,b] (reaction at r.t.). [d]) Reaction in toluene at 110°.

Scheme 3



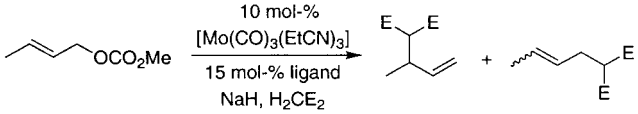
R = Ph: 1 day, 83%, **A**/**B** 6 : 1, 84% ee (*R*)

R = Me: 1 day, 83%, **A**/**B** 5 : 1, 80% ee (*R*)

Next we turned our attention towards the analogous alkyl-substituted substrates. Recently, achiral Ir [11] and Rh [12] catalysts have been shown to give high branched/linear ratios with such alkylallyl systems. However, highly enantioselective allylic substitutions with C-nucleophiles have not been achieved so far with this class of substrates[2]).

Our results for (*E*)-but-2-enyl methyl carbonate are summarized in *Table 2*. As expected, this substrate was less reactive than the corresponding 3-phenylallyl derivative and required reaction times of one day or more at 70°. Using ligand **4**, we obtained a 5 : 1 mixture **14**/**15** in 85% yield and 94% ee after one day at 70°. Practically the same yield and ee, albeit with lower regioselectivity of 1.5 : 1 was obtained with ligand **5a**. Reducing the amount of $[Mo(CO)_3(EtCN)_3]$ to 2.5% decreased the rate, but

Table 2. *Enantioselective Mo-Catalyzed Allylic Alkylation of Carbonate* **13**



13 **14** **15**

Entry	Ligand	Time [d]	Yield [%][a])	**14**/**15**	ee of **14** [%][b])
1	**4**	1	85	5 : 1	94 (*R*)
2	**5a**	1	88	1.5 : 1	94 (*R*)
3[c])	**5a**	5	80	1.5 : 1	93 (*R*)
4	**5b**	1.5	79	2.2 : 1	80 (*R*)
5	**5c**	5	53	0.6 : 1	26 (*S*)
6	**6a**	5	73	5 : 1	74 (*R*)
7	**7a**	3	76	7 : 1	85 (*S*)
8	**6b**	1	81	9 : 1	97 (*R*)
9	**7b**	2	80	11 : 1	96 (*S*)
10	**6c**	1.5	81	9 : 1	95 (*R*)
11	**7c**	1	86	7 : 1	92 (*S*)
12	**7d**	2	85	1.5 : 1	0

[a]) Combined yields of **14** and **15**. [b]) Determined by GC (*Chiraldex γ-CD-TA*). [c]) The reaction was performed with 2.5 mol-% of $[Mo(CO)_3(EtCN)_3]$ and 3.8 mol-% of **5a**.

[2]) Very recently, a promising Ir catalyst was reported by *Bartels* and *Helmchen* [5], which gave 86% ee and excellent regioselectivity with a homobenzyl-substituted allyl acetate.

left the regio- and enantioselectivity virtually unchanged (*Entry 3*). The *tert*-butyl-substituted ligand **5b** gave somewhat better regioselectivity, but lower ee. Finally, ligand **5c**, which is diastereoisomeric to ligand **5a**, reacted much slower and favored the formation of the linear product (*Entry 5*).

The Ph-substituted ligands **6a** and **7a** gave higher branched/linear ratios than **5a**, although with lower enantioselectivities (*Entries 6* and *7*). The best results were obtained with the propyl-substituted derivatives **6b** and **7b**, comparing favorably with the bis[pyridine] ligand **4**. Specifically, by employing ligand **6b**, a 9:1 mixture **14**/**15** was obtained in 81% yield with an ee of 97% (*Entry 8*), whereas ligand **7b** gave an 11:1 mixture **14**/**15** in 80% yield and 96% ee (*Entry 9*). The isopropyl-substituted ligands **6c** and **7c** gave slightly lower selectivities (*Entries 10* and *11*) and the *tert*-butyl-substituted ligand **7d** afforded only racemic product with a low branched/linear ratio. Again, the corresponding branched substrate reacted with considerably lower enantioselectivity (80 *vs.* 97% ee with ligand **6b**; *Scheme 3*).

The results show that the ee is determined predominantly by the chiral 1,2-diaminocyclohexane linker, while the two chiral dihydrooxazole units have a minor, although still significant influence. However, by systematic variation of the substituents at the dihydrooxazole ring, the regio- as well as the enantioselectivity can be optimized.

In addition to the bis[dihydrooxazole] ligands, we tested several other chiral N-ligands, but the selectivities were disappointingly low. For example, the ^{i}Pr-substituted pybox ligand [13] gave a 1.5:1 mixture of regioisomers in a 69% yield after two days; the branched product **14** was found to be racemic.

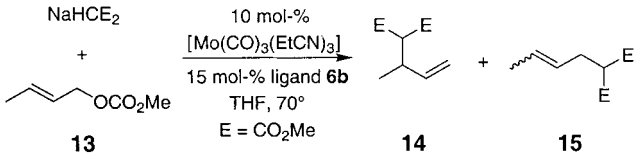
In the W-catalyzed allylic substitution with P,N-ligands, a strong influence of the addition order of malonate and the allyl substrate was found [3]. Good results were only obtained when the W catalyst was treated first with an excess of the sodium salt of dimethyl malonate, followed by addition of the allyl substrate. When the allyl ester was added first, a W-allyl complex was formed which did not react further.

The analogous Mo-catalyzed process behaves differently. Here, the performance of the Mo catalysts was virtually indifferent to the addition order (*Table 3*). Three different protocols, *i.e., a*) concurrent addition of carbonate **13** and deprotonated dimethyl malonate to the catalyst solution (*Entry 1*), *b*) catalyst pretreatment with malonate before addition of **13** (*Entry 2*), and *c*) catalyst pretreatment with **13** before addition of the malonate (*Entry 3*) were employed, all giving essentially the same results.

(*E*)-Hex-2-enyl methyl carbonate (**16**) also reacted with high regio- and enantioselectivity (*Table 4*). Ligands **4**, **7b**, and **7c** all gave an 8:1 ratio of **17**/**18** with 97–98% ee (*Entries 1*, *3*, and *5*). The corresponding diastereoisomers **6b** and **6c**, which are derived from the opposite enantiomer of *trans*-cyclohexane-1,2-diamine, gave lower branched/linear ratios and, in the case of **6c**, a distinctly lower ee (*Entries 2* and *4*). Ligands **6b**,**c** also induced the opposite absolute configuration to **7b**,**c**, implying that the enantioselectivity is largely controlled by the *trans*-1,2-diaminocyclohexane unit.

Allyl carbonates **19**–**22** all gave disappointing results. Substrates **19** and **20** reacted very sluggishly, whereas methyl geranyl carbonate **21** yielded predominantly the linear product. Substrate **22** was converted to the five-membered ring product **23**, however, with a very low ee of *ca.* 5%.

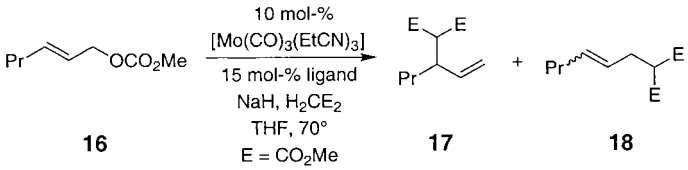
Table 3. *Influence of the Addition Order of Na[CH(CO$_2$Me)$_2$]* (**Nu**) *and* (E)*-But-2-enyl Methyl Carbonate* (**13**)



Entry	Addition order	Time [d]	Yield [%][a])	**14**/**15**	ee of **14** [%][b])
1	1) Cat. 2) (**Nu** + **13**)[c])	1	81	9 : 1	97 (*R*)
2	1) Cat. 2) **Nu** 3) **13**[d])	1	79	8 : 1	95 (*R*)
3	1) Cat. 2) **13** 3) **Nu**[e])	1	83	9 : 1	97 (*R*)

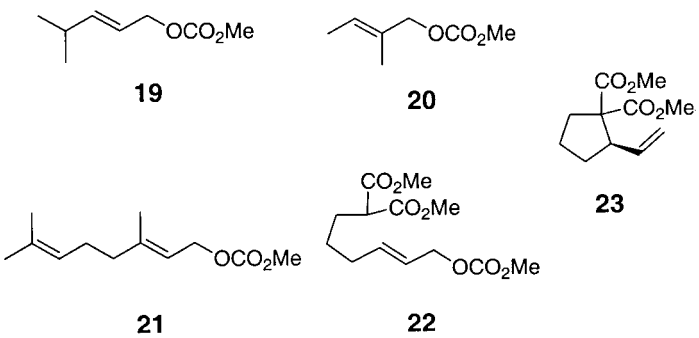
[a]) Combined yields of **14** and **15**. [b]) Determined by GC (*Chiraldex γ-CD-TA*). [c]) To the preformed catalyst solution ([Mo(CO)$_3$(EtCN)$_3$] and ligand **6b**; 1 h, 70°) were concurrently added carbonate **13** and the deprotonated malonate. The solution was degassed and the reaction started by heating the solution to 70°. [d]) The deprotonated malonate was added to the catalyst solution. The resulting solution was stirred at r.t. for 30 min and then heated to 70° for another 30 min. Finally, the carbonate **13** was added at r.t. and the solution heated to 70°. [e]) The carbonate **13** was added to the catalyst solution, and the resulting solution was stirred at r.t. for 30 min and then heated to 70° for another 30 min. Finally, the deprotonated malonate was added at r.t. and the solution heated to 70°.

Table 4. *Enantioselective Mo-Catalyzed Allylic Alkylation of Carbonate* **16**



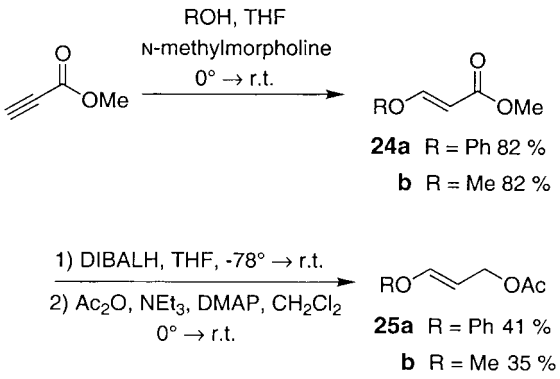
Entry	Ligand	Time [d]	Yield [%][a])	**17**/**18**	ee of **17** [%][b])
1	**4**	1.5	80	8 : 1	98 (+)
2	**6b**	2	69	2 : 1	96 (+)
3	**7b**	1.5	84	8 : 1	98 (−)
4	**6c**	2.5	54	2 : 1	86 (+)
5	**7c**	1.5	83	8 : 1	97 (−)

[a]) Combined yields of **17** and **18**. [b]) Determined by GC (*Chiraldex γ-CD-TA*).



Finally, the reactions of PhO- and MeO-substituted allyl acetates **25a** and **25b** were studied. These substrates were synthesized by *N*-methylmorpholine-catalyzed 1,4-addition of the corresponding alcohols to methyl propiolate (= methyl propynoate) [14], followed by reduction of the resulting **24a**,**b** with diisobutylaluminium hydride (DIBALH) and acetylation, in overall yields of *ca.* 30% [15] (*Scheme 4*)

Scheme 4



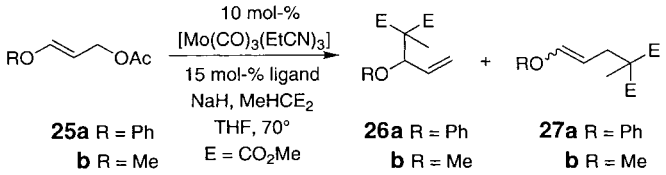
The $[Pd(PPh_3)_4]$-catalyzed reaction of **25b** with diethyl methylmalonate has been reported by *Cazes* and co-workers to yield only the branched product [16]. Consistent with *Cazes*' results, the related phenoxy derivative **25a** gave branched/linear ratios of $>20:1$ in all cases (*Table 5*). The best enantioselectivity (98% ee) was achieved with ligand **6b**, whereas the other ligands afforded 93–96% ee. The methoxy derivative **25b** reacted with distinctly lower regio- and enantioselectivity. In contrast to the analogous Pd-catalyzed reaction, the linear product **27b** was formed in varying amounts. High branched/linear ratios of 13:1 to $>20:1$ could be obtained with ligands **4** and **7c**, although the ee's were only moderate (74–76%; *Entries 6* and *10*).

Crystal Structures of Ligand 7a and the Corresponding Molybdenum Complex 28. – To obtain crystals suitable for X-ray analysis, the free ligand **7a** was heated together with an equimolar amount of $[Mo(CO)_3(EtCN)_3]$ in THF/toluene at 70° under Ar. After cooling to room temperature, approximately one third of the solvent was evaporated under a continuous stream of Ar. The resulting solution was left to stand for several days affording red-brown crystals which were suitable for X-ray analysis. The unit-cell of these crystals was found to contain one molecule of the free ligand **7a** (*Fig. 1*) and two Mo complexes **28** with essentially identical structures (*Scheme 5*).

The crystal structure of complex **28** (*Fig. 2*) reveals that the ligand **7a** binds to the Mo-atom with the two dihydrooxazole rings and one of the amide carbonyl groups. The other three coordination sites of the distorted octahedral complex are occupied by CO ligands. The two Mo–N bonds are of similar length (2.347(5) and 2.331(5) Å), while the Mo–O bond (2.268(5) Å) is slightly shorter. Obviously, the C_2-symmetry of ligand **7a** is lost when it binds to the $Mo(CO)_3$ fragment.

Not much is known about the structure of the actual catalyst. *Kocovsky* and co-workers [6c] suggested for an analogous bis[pyridine] complex that a tridentate

Table 5. *Enantioselective Mo-Catalyzed Allylic Alkylation of Acetates* **25a** *and* **25b**



Entry	Substrate	Ligand	Time [d]	Yield [%][a])	**26**/**27**	ee of **26** [%][b])
1	**25a**	**4**	2	79	>20:1	93 (−)
2	**25a**	**6b**	2	79	>20:1	98 (−)
3	**25a**	**7b**	1.5	81	>20:1	93 (+)
4	**25a**	**6c**	2	78	>20:1	95 (−)
5	**25a**	**7c**	2	75	>20:1	96 (+)
6	**25b**	**4**	1	60	>20:1	74 (+)
7	**25b**	**6b**	1	52	6:1	62 (+)
8	**25b**	**7b**	1	38	5:1	63 (−)
9	**25b**	**6c**	1	72	5:1	66 (+)
10	**25b**	**7c**	1	54	13:1	76 (−)
11	**25b**	**7d**	1	35	3:1	21 (−)

[a]) Combined yields of **26** and **27**. [b]) Determined by HPLC (*Daicel Chiralcel OJ*) and GC (*Chiraldex γ-CD-TA*).

Scheme 5

coordination of the Mo-center is required to generate an active catalyst. Based on the crystal structure shown in *Fig. 2*, it is tempting to speculate that the catalytic cycle involves an (allyl)dicarbonylmolybdenum intermediate, resembling complex **28**, with one CO replaced by an allyl ligand. This would imply that the two N-atoms of the chiral ligand are located *cis* to each other. *Trost et al.* [6a,b], on the other hand, have postulated a *trans*-arrangement of the two pyridine N-atoms for the related catalyst derived from the bis[pyridine] ligand **4**. *Curtis* and *Eisenstein* [17] have found that in (allyl)dicarbonylmolybdenum complexes, the allyl system and two CO ligands coordinate to the Mo-atom preferentially in a *facial* arrangement, with the two allyl termini oriented in the same direction as the two CO ligands (structure **29**). Calculations indicated that this geometry is 6–15 kcal/mol more stable than alternative geometries resulting from rotation of the allyl system by 90 or 180°. This could be an important factor contributing to the regio- and enantioselectivity of the catalytic process. Unfortunately, attempts to prepare and characterize (allyl)dicarbonylmolybdenum complexes derived from ligands **6** or **7** have not been successful so far. Thus,

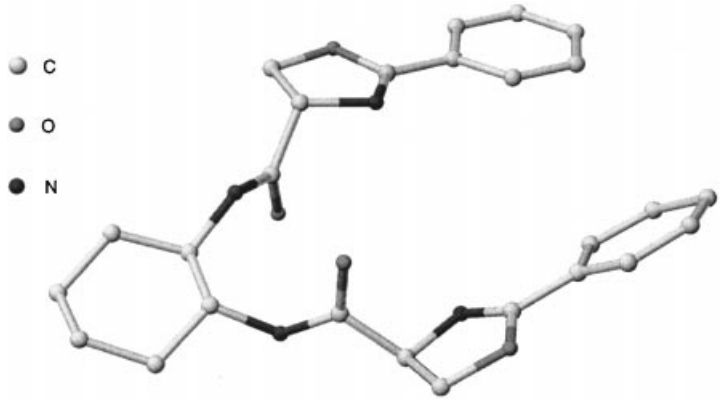


Fig. 1. *Crystal structure of ligand* **7a**. H-Atoms are omitted for clarity.

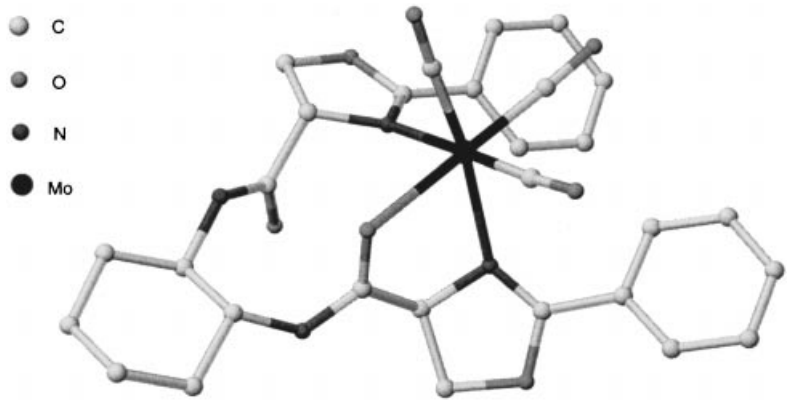
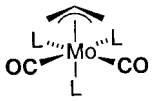


Fig. 2. *Crystal structure of complex* **28**. H-Atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo–O 2.268(5), Mo–N(1) 2.347(5), Mo–N(2) 2.331(5), Mo–C(1)O 1.935(6), Mo–C(2)O 1.934(7), Mo–C(3)O 1.914(6); O–Mo–N(1) 82.0(2), O–Mo–N(2) 71.6(2), O–Mo–C(2)O 97.6(3), O–Mo–C(3)O 98.1(2), N(1)–Mo–C(1)O 96.9(3), C(1)O–Mo–C(2)O 83.5(3).

additional studies will be necessary before a meaningful mechanistic model can be proposed.



29

Conclusion. – In summary, we have shown that high enantio- and regioselectivities can be obtained in Mo-catalyzed allylic substitutions with monosubstituted 3-alkyl- and 3-phenoxyallyl esters, in the presence of the bis[pyridine] ligand **4** or analogous chiral bis[dihydrooxazoles] **6** or **7**. In general, ligand **4**, which is structurally simpler, is the

ligand of choice. However, with certain substrates, ligands **6** or **7** give improved regio- and enantioselectivity. An attractive feature of the bis[dihydrooxazole] ligands is the option to finetune their structure by variation of the substituents at the dihydrooxazole rings.

Experimental Part

1. *General*. All reactions were carried out under Ar in pre-dried glassware with *Schlenk* techniques. The solvents were dried by destillation over the following drying agents and transferred under Ar: CH_2Cl_2 (CaH_2), Et_2O, THF (Na/benzophenone), toluene (Na/K alloy). All commercially available reagents were used as received. GC: *Restek Rtx-1701* or *Chiraldex γ-CD TFA* column (30 m × 0.25 mm each); injection temp. 180°, detection temp. 200°; FID detector; t_R in min. HPLC: *Chiracel OJ* column (25 cm) from *Daicel*; t_R in min. Flash chromatography (FC): *Merck* silica gel *60* (230–400 mesh). TLC: *Macherey-Nagel Polygram SIL G/UV$_{254}$*; detection by UV (254 nm) light or by dipping into a phosphomolybdic acid soln. or into a basic soln. of $KMnO_4$. Optical rotations: *Perkin-Elmer 141* polarimeter; *c* in g/100 ml. IR Spectra: *Nicolet FT-7199*; in cm^{-1}. NMR Spectra: *Bruker AC-200* (^1H, 200 MHz; ^{13}C, 50 MHz), *AMX-300* (^1H, 300 MHz; ^{13}C, 75 MHz), or *DRX-500* (^1H, 500 MHz; ^{13}C, 125 MHz); chemical shifts δ in ppm downfield from $SiMe_4$ (=0.0) as internal standard, *J* values in Hz; unless otherwise stated, $CDCl_3$ solns. MS: *Finnigan MAT-8200* (70 eV, EI), *Finnegan MAT-95* (ESI-HR-MS); in *m*/*z* (% of base peak).

2. *Ligand Synthesis.* N,N′-*[(1S,2S)-Cyclohexane-1,2-diyl]bis[(4S)-4,5-dihydro-4-(1-methylethyl)oxazole-2-carboxamide]* (**5a**). (1*S*,2*S*)-Cyclohexane-1,2-diamine (0.45 g, 4.0 mmol) and **8a** (1.5 g, 8.1 mmol) were dissolved in DMSO (20 ml). NaH (0.24 g, 9.9 mmol) was added, and the mixture was warmed to 40° and stirred for 1 d. The soln. was diluted with CH_2Cl_2 (150 ml) and quenched with ice-cold H_2O (50 ml). The mixture was neutralized by the addition of sat. aq. NH_4Cl soln. and extracted with CH_2Cl_2 (3 × 50 ml). The combined org. phase was dried (Na_2SO_4) and evaporated, and the residue purified by FC (silica gel; hexane/AcOEt 1:1): **5a** (0.34 g, 22%). Off-white solid. R_f (hexane/AcOEt = 1:2) 0.30. $[\alpha]_D^{20} = -7.7$ (*c* = 0.19, $CHCl_3$). IR (KBr): 3216 (br.), 3036*w*, 2958*m*, 2935*m*, 2872*m*, 1684*s*, 1638*s*, 1533*m*, 1471*m*, 1376*m*, 1367*m*, 1245*m*, 1191*m*, 977*m*, 895*w*, 841*w*, 605*w*. ^{1}H-NMR (300 MHz): 7.39 (br. *s*, 2 NH); 4.43 (*dd*, *J* = 9.5, 8.4, 2 H, dihydrooxazole); 4.16–4.01 (*m*, 4 H, dihydrooxazole); 3.85–3.75 (*m*, 2 C*H*NH); 2.12–2.05 (*m*, 2 H, CH_2); 2.05–1.71 (*m*, 4 H, CH_2, Me_2CH); 1.43–1.23 (*m*, 4 H, CH_2); 0.97 (*d*, *J* = 6.7, *Me*$_2$CH); 0.88 (*d*, *J* = 6.7, *Me*$_2$CH). ^{13}C-NMR (75 MHz): 157.7, 157.0 (C=O, C=N); 72.8 (N*C*HCH$_2$O); 71.6 (CH_2O); 53.2 (CHNH); 32.5 (Me_2CH); 32.2 (CH_2CH_2CH); 24.6 (CH_2CH_2CH); 18.9 (*Me*$_2$CH); 18.3 (*Me*$_2$CH). EI-MS: 392 (77, M^+), 364 (11), 349 (31), 321 (5), 280 (13), 252 (26), 236 (100), 209 (33), 193 (7), 181 (20), 157 (27), 139 (10), 114 (23), 96 (55). HR-MS: 392.2410 ($C_{20}H_{32}N_4O_4^+$; calc. 392.2423).

N,N′-*[(1S,2S)-Cyclohexane-1,2-diyl]bis[(4S)-4-(1,1-dimethylethyl)-4,5-dihydrooxazole-2-carboxamide]* (**5b**). To a soln. of (1*S*,2*S*)-cyclohexane-1,2-diamine (0.31 g, 2.7 mmol) in THF (20 ml), BuLi in hexane (3.5 ml, 5.6 mmol) was added dropwise at 0°. After stirring at r.t. for 20 min, a soln. of **8b** (1.2 g, 6.0 mmol) in THF (4 ml) was added dropwise. DMF (4 ml) was added and the soln. stirred for 1 h. Thereafter, NaH (177 mg, 7.4 mmol) was added and the soln. stirred at r.t. overnight and finally for 2 h at 60°. The soln. was diluted with CH_2Cl_2 (50 ml), and ice-cold H_2O (10 ml) was added. The mixture was neutralized with sat. aq. NH_4Cl soln. and extracted wtih CH_2Cl_2 (3 × 50 ml), the combined org. phase dried (Na_2SO_4) and evaporated, and the residue purified by FC (silica gel, hexane/AcOEt 1:2): **5b** (0.29 g, 26%). Off-white solid. R_f (hexane/AcOEt = 1:3) 0.42. $[\alpha]_D^{20} = -19.7$ (*c* = 0.80, $CHCl_3$). IR (KBr): 3242*m*, 3031*w*, 2953*m*, 2869*m*, 1681*s*, 1638*s*, 1530*m*, 1479*m*, 1396*w*, 1365*m*, 1260*m*, 1246*m*, 1186*m*, 979*m*, 931*w*, 840*w*, 597*m*, 581*m*. ^{1}H-NMR (300 MHz): 7.25–7.20 (*m*, 2 NH); 4.35 (*dd*, *J* = 10.4, 8.9, 2 H, dihydrooxazole); 4.21 (*t*, *J* = 8.9, 2 H, dihydrooxazole); 4.00 (*dd*, *J* = 10.4, 8.8, 2 H, dihydrooxazole); 3.87–3.83 (*m*, 2 C*H*NH); 2.13–2.07 (*m*, 2 H, CH_2); 1.82–1.77 (*m*, 2 H, CH_2); 1.37–1.33 (*m*, 4 H, CH_2); 0.90 (*s*, 2 *t*Bu). ^{13}C-NMR (75 MHz): 157.5, 157.1 (C=O, C=N); 76.2 (N*C*HCH$_2$O); 70.1 (CH_2O); 53.1 (CHNH); 33.7 (Me_3C); 32.2 (CH_2CH_2CH); 25.8 (*Me*$_3$C); 24.6 (CH_2CH_2CH). EI-MS: 420 (100, M^+), 405 (23), 392 (8), 363 (53), 335 (5), 322 (5), 295 (36), 266 (22), 250 (82), 223 (23), 195 (14), 182 (11), 171 (37), 167 (8), 141 (35), 128 (23), 96 (39), 81 (15), 69 (17), 57 (21). HR-MS: 420.2726 ($C_{22}H_{36}N_4O_4^+$; calc. 420.2736).

N,N′-*[(1R,2R)-Cyclohexane-1,2-diyl]bis[(4S)-4,5-dihydro-4-(1-methylethyl)oxazole-2-carboxamide]* (**5c**). As described for **5b** from (1*R*,2*R*)-cyclohexane-1,2-diamine (0.28 g, 2.5 mmol) and **8a** (1.0 g, 5.4 mmol). After 1 d, **5c** (0.24 g, 24%) was obtained as a colorless solid. R_f (hexane/AcOEt 1:2) 0.32. $[\alpha]_D^{20} = -108$ (*c* = 0.95, $CHCl_3$). IR (KBr): 3348 (br.), 3046*w*, 2958*m*, 2934*m*, 2872*m*, 1695*s*, 1643*s*, 1531*m*, 1479*m*, 1385*m*, 1362*m*,

1246*m*, 1190*m*, 975*m*, 953*m*, 932*m*. ^{1}H-NMR (300 MHz): 7.21 (br. *d*, *J* = 7.5, 2 NH); 4.42 (*dd*, *J* = 9.2, 8.0, 2 H, dihydrooxazole); 4.14–3.99 (*m*, 4 H, dihydrooxazole); 3.88–3.80 (*m*, 2 C*H*NH); 2.13–2.05 (*m*, 2 H, CH_2); 1.84–1.72 (*m*, 4 H, CH_2, Me_2CH); 1.37–1.33 (*m*, 4 H, CH_2); 0.95 (*d*, *J* = 6.8, Me_2CH); 0.88 (*d*, *J* = 6.8, Me_2CH). ^{13}C-NMR (75 MHz): 157.6, 157.0 (C=O, C=N); 72.6 (N*C*HCH$_2$O); 71.6 (CH_2O); 53.3 (CHNH); 32.5 (Me_2CH); 32.1 (CH_2CH_2CH); 24.6 (CH_2CH_2CH); 18.5 (Me_2CH); 18.2 (Me_2CH). EI-MS: 392 (64, M^+), 364 (12), 349 (27), 321 (6), 280 (12), 252 (25), 236 (89), 208 (36), 181 (23), 166 (12), 157 (36), 139 (15), 114 (37), 96 (100), 69 (60). Anal. calc. for $C_{20}H_{32}N_4O_4$: C 61.20, H 8.21, N 14.27; found: C 61.09, H 8.25, N 14.34.

N,N′-*[(1*S*,2*S*)-Cyclohexane-1,2-diyl]bis[(4*S*)-4,5-dihydro-2-phenyloxazole-4-carboxamide]* (**6a**). Sodium (4*S*)-4,5-dihydro-2-phenyloxazole-4-carboxylate (0.54 g, 2.5 mmol) and (1*S*,2*S*)-cyclohexane-1,2-diamine (0.14 g, 1.2 mmol) were dissolved in DMF (15 ml). *N*,*N*-Diisopropylethylamine (^{i}Pr$_2$NEt; 1.25 ml, 7.2 mmol), 1-hydroxy-1*H*-benzotriazole hydrate (HOBt; 0.40 g, 2.7 mmol) and *O*-(1*H*-benzotriazol-1-yl)-*N*,*N*,*N*′,*N*′-tetramethyluronium tetrafluoroborate (TBTU; 0.81 g, 2.5 mmol) were subsequently added, and the resulting soln. was stirred at r.t. for 5 h. The mixture was quenched with sat. aq. NH_4Cl soln. (40 ml) and extracted with AcOEt (3 × 100 ml), the org. phase dried (Na_2SO_4) and evaporated, and the residue purified by FC (silica gel, hexane/AcOEt 1:4): 0.55 g (95%) of **6a**. R_f (hexane/AcOEt 1:3) 0.27. HPLC (achiral; *Nucleosil 5-100-C$_{18}$/A*, 12.5 cm; MeOH/H_2O 60:40, 0.8 ml/min; 35°; 254 nm): t_R 18.05 (> 99.5%). $[\alpha]_D^{20} = +165$ (*c* = 0.79, DMF). IR (KBr): 3261*m*, 3088*m*, 2932*m*, 2895*w*, 2855*m*, 1646*s*, 1604*w*, 1557*m*, 1496*m*, 1450*m*, 1357*m*, 1299*m*, 1249*m*, 1233*m*, 1082*m*, 1068*m*, 1027*m*, 972*m*, 779*m*, 691*m*. ^{1}H-NMR (200 MHz): 8.04–7.98 (*m*, 4 arom. H); 7.54–7.39 (*m*, 6 arom. H); 6.97–6.92 (br. *d*, *J* = 7.3, 2 NH); 4.85 (*dd*, *J* = 10.2, 8.8, 2 H, dihydrooxazole); 4.73–4.56 (*m*, 4 H, dihydrooxazole); 3.76–3.72 (*m*, 2 C*H*NH); 2.06–1.96 (*m*, 2 H, CH_2); 1.75–1.69 (*m*, 2 H, CH_2); 1.35–1.24 (*m*, 4 H, CH_2). ^{13}C-NMR (50 MHz): 171.9, 165.6 (C=O, C=N); 131.6, 128.2, 128.1 (arom. CH); 126.7 (arom. C); 70.1 (CH_2O); 68.6 (N*C*HCH$_2$O); 52.7 (CHNH); 31.9 (CH_2CH_2CH), 24.3 (CH_2CH_2CH). EI-MS: 460 (16, M^+), 314 (100), 270 (5), 174 (5), 146 (35), 118 (16), 105 (62), 97 (5), 91 (27), 77 (16). HR-MS: 460.2112 ($C_{26}H_{28}N_4O_4^+$; calc. 460.2110).

N,N′-*[(1*S*,2*S*)-Cyclohexane-1,2-diyl]bis[(4*S*)-4,5-dihydro-2-propyloxazole-4-carboxamide]* (**6b**). As described for **6a**, from sodium (4*S*)-4,5-dihydro-2-propyloxazole-4-carboxylate (350 mg, 1.96 mmol). After 1 d, **6b** (305 mg, 87%) was obtained as a yellow solid. R_f (AcOEt) 0.31. $[\alpha]_D^{20} = +57.0$ (*c* = 0.89, $CHCl_3$). IR (KBr): 3266*s*, 3087*m*, 2966*m*, 2936*m*, 1669*s*, 1646*s*, 1559*m*, 1457*m*, 1384*m*, 1252*m*, 1181*m*, 1106*w*, 985*m*, 938*w*, 886*w*. ^{1}H-NMR (300 MHz): 6.79 (br. *d*, *J* = 6.7, 2 NH); 4.61–4.37 (*m*, 6 H, dihydrooxazole); 3.73–3.67 (*m*, 2 C*H*NH); 2.30 (*t*, *J* = 7.4, 2 $MeCH_2CH_2$); 2.04–1.95 (*m*, 2 H, CH_2); 1.75–1.60 (*m*, 6 H, $MeCH_2CH_2$, CH_2); 1.34–1.25 (*m*, 4 H, CH_2); 0.97 (*t*, *J* = 7.3, 2 $MeCH_2CH_2$). ^{13}C-NMR (75 MHz): 172.2, 170.8 (C=O, C=N); 70.1 (CH_2O); 68.4 (N*C*HCH$_2$O); 52.9 (CHNH); 32.3 (CH_2CH_2CH); 29.9 ($MeCH_2CH_2$); 24.6 (CH_2CH_2CH); 19.4 ($MeCH_2CH_2$); 13.7 (Me). EI-MS: 392 (8, M^+), 349 (2), 280 (100), 236 (7), 210 (12), 141 (8), 112 (14), 97 (6). HR-MS: 392.2415 ($C_{20}H_{32}N_4O_4^+$; calc. 392.2423).

N,N′-*[(1*S*,2*S*)-Cyclohexane-1,2-diyl]bis[(4*S*)-4,5-dihydro-2-(1-methylethyl)oxazole-4-carboxamide]* (**6c**). As described for **6a**, from sodium (4*S*)-4,5-dihydro-2-(1-methylethyl)oxazole-4-carboxylate (600 mg, 3.35 mmol). After 3 h, **6c** (585 mg, 93%) was obtained as a yellow solid. R_f (AcOEt) 0.35. $[\alpha]_D^{20} = +46.8$ (*c* = 1.04, $CHCl_3$). IR (KBr): 3267*m*, 2972*m*, 2936*m*, 2856*w*, 1664*s*, 1647*s*, 1559*m*, 1471*m*, 1387*m*, 1360*w*, 1332*w*, 1254*m*, 1235*m*, 1201*m*, 1150*m*, 1108*m*, 987*m*, 889*w*. ^{1}H-NMR (300 MHz): 6.77 (br. *d*, *J* = 6.9, 2 NH); 4.59–4.38 (*m*, 6 H, dihydrooxazole); 3.76–3.65 (*m*, 2 C*H*NH); 2.61 (*sept.*, *J* = 6.8, 2 Me_2CH); 2.05–1.97 (*m*, 2 H, CH_2); 1.77–1.72 (*m*, 2 H, CH_2); 1.33–1.17 (*m*, 16 H, Me_2CH, CH_2). ^{13}C-NMR (75 MHz): 174.7, 172.4 (C=O, C=N); 70.2 (CH_2O); 68.4 (N*C*HCH$_2$O); 52.9 (CHNH); 32.3 (CH_2CH_2CH); 28.3 (Me_2CH); 24.6 (CH_2CH_2CH), 19.7 (Me_2CH); 19.6 (Me_2CH). EI-MS: 392 (8, M^+), 349 (5), 280 (100), 236 (7), 210 (18), 141 (16), 112 (17), 97 (7), 84 (10), 71 (9). HR-MS: 392.2417 ($C_{20}H_{32}N_4O_4^+$; calc. 392.2423).

N,N′-*[(1*R*,2*R*)-Cyclohexane-1,2-diyl]bis[(4*S*)-4,5-dihydro-2-phenyloxazole-4-carboxamide]* (**7a**). As described for **6a**, from sodium (4*S*)-4,5-dihydro-2-phenyloxazole-4-carboxylate (1.2 g, 5.6 mmol). After 3 h, **7a** (1.13 g, 96%) was obtained as a colorless solid. R_f (hexane/AcOEt 1:3) 0.26. $[\alpha]_D^{20} = -40.9$ (*c* = 1.03, DMF). HPLC (achiral; *Nucleosil 5-100-C$_{18}$/A*, 12.5 cm, MeOH/H_2O 60:40, 0.8 ml/min, 35°, 254 nm): t_R 11.90 (> 99.5%). IR (KBr): 3371*m*, 3281*s*, 3074*m*, 2934*m*, 2863*m*, 1669*s*, 1654*s*, 1603*w*, 1580*m*, 1548*s*, 1515*s*, 1497*m*, 1451*m*, 1357*m*, 1304*m*, 1288*m*, 1250*m*, 1230*m*, 1084*m*, 1067*m*, 1026*m*, 970*m*, 959*m*, 780*m*, 693*s*. ^{1}H-NMR (500 MHz): 7.99–7.96 (*m*, 4 arom. H); 7.55–7.52 (*m*, 2 arom. H); 7.47–7.44 (*m*, 4 arom. H); 6.82 (br. *d*, *J* = 7.0, 2 NH); 4.68 (*dd*, *J* = 11.1, 8.3, 2 H, dihydrooxazole); 4.31 (*dd*, *J* = 11.1, 8.9, 2 H, dihydrooxazole); 4.05 (*t*, *J* = 8.6, 2 H, dihydrooxazole); 3.72–3.67 (*m*, 2 C*H*NH); 2.10–2.06 (*m*, 2 H, CH_2);1.79–1.76 (*m*, 2 H, CH_2); 1.34–1.29 (*m*, 4 H, CH_2). ^{13}C-NMR (75 MHz): 171.9, 166.2 (C=O, C=N); 132.1, 128.6, 128.4 (arom. CH); 126.8 (arom. C); 70.3 (CH_2O); 68.8 (N*C*HCH$_2$O); 52.9 (CHNH); 32.3 (CH_2CH_2CH); 24.7 (CH_2CH_2CH). EI-MS: 460 (10, M^+),

314 (100), 174 (4), 146 (26), 118 (11), 105 (49), 97 (6), 91 (16), 77 (10). HR-MS: 460.2104 ($C_{26}H_{28}N_4O_4^+$; calc. 460.2110).

N,N′-*[(1*R,2R*)-Cyclohexane-1,2-diyl]bis[(4*S*)-4,5-dihydro-2-propyloxazole-4-carboxamide]* (**7b**). As described for **6a**, from sodium (4*S*)-4,5-dihydro-2-propyloxazole-4-carboxylate (1.5 g, 8.4 mmol). After 1 d, **7b** (1.23 g, 82%) was obtained as a yellow solid. R_f (AcOEt) 0.30. $[\alpha]_D^{20} = +64.9$ ($c = 0.50$, $CHCl_3$). IR (film): 3310*m*, 3070*w*, 2963*m*, 2935*m*, 2873*m*, 2873*m*, 1661*s*, 1532*s*, 1456*m*, 1368*m*, 1267*m*, 1187*m*, 1147*m*, 1019*w*, 981*m*. ^{1}H-NMR (300 MHz): 6.63 (br. *d*, $J = 7.3$, 2 NH); 4.56 (*dd*, $J = 11.0$, 7.4, 2 H, dihydrooxazole); 4.41 (*dd*, $J = 11.0$, 8.6, 2 H, dihydrooxazole); 4.22 (*dd*, $J = 8.6$, 7.4, 2 H, dihydrooxazole); 3.72–3.56 (*m*, 2 C*H*NH); 2.35–2.28 (*m*, 2 $MeCH_2CH_2$); 2.04–1.96 (*m*, 2 H, CH_2); 1.76–1.66 (*m*, 6 H, $MeCH_2CH_2$, CH_2); 1.34–1.28 (*m*, 4 H, CH_2); 0.99 (*t*, $J = 7.4$, 2 Me). ^{13}C-NMR (75 MHz): 172.0, 171.2 (C=O, C=N); 70.3 (CH_2O); 68.5 (N*C*HCH_2O); 52.7 (*C*HNH); 32.1 (CH_2CH_2CH); 30.1 ($MeCH_2CH_2$); 24.7 (CH_2CH_2CH); 19.3 ($MeCH_2CH_2$); 13.7 (Me). EI-MS: 392 (3, M^+), 349 (2), 280 (100), 236 (5), 210 (5), 141 (4), 112 (17), 97 (8), 81 (6). HR-MS: 392.2418 ($C_{20}H_{32}N_4O_4^+$; calc. 392.2423).

N,N′-*[(1*R,2R*)-Cyclohexane-1,2-diyl]bis[(4*S*)-4,5-dihydro-2-(1-methylethyl)oxazole-4-carboxamide]* (**7c**). As described for **6a**, from sodium (4*S*)-4,5-dihydro-2-(1-methylethyl)oxazole-4-carboxylate (1.1 g, 6.3 mmol). After 1 d, **7c** (0.52 g, 44%) was obtained as a yellowish solid. R_f (AcOEt) 0.35. $[\alpha]_D^{20} = +63.3$ ($c = 0.96$, $CHCl_3$). IR (KBr): 3358*m*, 2979*m*, 2938*m*, 2860*w*, 1669*s*, 1530*s*, 1456*m*, 1387*m*, 1363*m*, 1324*w*, 1271*m*, 1200*m*, 1149*m*, 1118*m*, 1101*m*, 1064*w*, 1015*m*, 970*m*, 940*m*, 728*w*, 611*m*. ^{1}H-NMR (300 MHz): 6.59 (br. *d*, $J = 7.6$, 2 NH); 4.56 (*dd*, $J = 11.2$, 7.6, 2 H, dihydrooxazole); 4.42 (*dd*, $J = 11.2$, 8.5, 2 H, dihydrooxazole); 4.18 (*t*, $J = 8.4$, 2 H, dihydrooxazole); 3.71–3.66 (*m*, 2 C*H*NH); 2.63 (*sept.*, $J = 7.0$, 2 Me_2CH); 2.00–1.98 (*m*, 2 H, CH_2); 1.78–1.75 (*m*, 2 H, CH_2); 1.33–1.17 (*m*, 16 H, Me_2CH, CH_2). ^{13}C-NMR (75 MHz): 175.3, 172.0 (C=O, C=N); 70.5 (CH_2O); 68.4 (N*C*HCH_2O); 52.6 (CHNH); 32.4 (CH_2CH_2CH); 28.4 (Me_2CH); 24.7 (CH_2CH_2CH); 19.6 (Me_2CH). EI-MS: 392 (3, M^+), 349 (2), 280 (100), 236 (5), 210 (14), 141 (13), 112 (16), 97 (8), 84 (9), 71 (8). HR-MS: 392.2426 ($C_{20}H_{32}N_4O_4^+$; calc. 392.2423).

N,N′-*[(1*R,2R*)-Cyclohexane-1,2-diyl]bis[(4*S*)-2-(1,1-dimethylethyl)-4,5-dihydrooxazole-4-carboxamide]* (**7d**). As described for **6a**, from sodium (4*S*)-2-(1,1-dimethylethyl)-4,5-dihydrooxazole-4-carboxylate (600 mg, 3.11 mmol). After 1 d, **7d** (435 mg, 70%) was obtained as a yellowish solid. R_f (hexane/AcOEt 1:3) 0.39. $[\alpha]_D^{20} = +66.4$ ($c = 0.82$, $CHCl_3$). IR (KBr): 3369*m*, 2976*m*, 2957*m*, 2937*m*, 2862*m*, 1673*s*, 1649*m*, 1529*s*, 1481*m*, 1396*w*, 1365*w*, 1307*w*, 1232*w*, 1155*m*, 1145*m*, 1017*m*, 970*m*, 736*w*. ^{1}H-NMR (300 MHz): 6.57 (br. *s*, 2 NH); 4.58 (*dd*, $J = 11.2$, 7.8, 2 H, dihydrooxazole); 4.45 (*dd*, $J = 11.2$, 8.6, 2 H, dihydrooxazole); 4.17 (*t*, $J = 8.2$, 2 H, dihydrooxazole); 3.75–3.66 (*m*, 2 C*H*NH); 2.02–1.95 (*m*, 2 H, CH_2); 1.79–1.74 (*m*, 2 H, CH_2); 1.34–1.27 (*m*, 22 H, CH_2, Me). ^{13}C-NMR (75 MHz): 171.6, 171.8 (C=O, C=N); 70.8 (CH_2O); 68.4 (N*C*HCH_2O); 52.4 (CHNH); 33.5 (C); 32.4 (CH_2CH_2CH); 27.7 (Me); 24.7 (CH_2CH_2CH). EI-MS: 420 (2, M^+), 405 (1), 363 (3), 294 (100), 250 (5), 127 (13), 97 (6), 70 (8). HR-MS: 420.2729 ($C_{22}H_{36}N_4O_4^+$; calc. 420.2736).

*Ethyl (4*S*)-4,5-Dihydro-4-(1-methylethyl)oxazole-2-carboxylate* (**8a**). Triethyloxonium tetrafluoroborate (7.5 g, 39 mmol) was dissolved in 1,2-dichloroethane (200 ml) and ethyl oxamate (=ethyl aminooxoacetate) (4.6 g, 39 mmol) added. After stirring at r.t. for 1 d, (*S*)-valinol (4.5 g, 44 mmol) was added and the resulting mixture stirred at reflux for 1 d. The soln. was cooled to r.t., diluted with CH_2Cl_2 (200 ml), and poured into an ice-cold aq. NH_4Cl soln. (50 ml). The org. phase was washed with sat. aq. NH_4Cl soln. (25 ml), sat. aq. $NaHCO_3$ soln. (25 ml), and brine (25 ml), dried ($MgSO_4$), and evaporated and the crude product purified by FC (silica gel, hexane/AcOEt 1:1): **8a** (5.1 g, 70%). Colorless oil. R_f (pentane/ether 1:1) 0.32. $[\alpha]_D^{26} = -89.3$ ($c = 1.22$, $CHCl_3$). IR (film): 2963*m*, 2908*m*, 2876*m*, 1749*s*, 1650*s*, 1469*m*, 1376*m*, 1310*m*, 1258*m*, 1151*s*, 1016*m*, 965*m*, 932*m*, 862*w*, 790*w*, 774*w*. ^{1}H-NMR (300 MHz): 4.47–4.35 (*m*, 3 H, $MeCH_2O$, $CHCH_2$); 4.20–4.12 (*m*, 2 H, $CHCH_2$, $CHCH_2$); 1.92–1.83 (*m*, Me_2CH); 1.39 (*t*, $J = 7.0$, $MeCH_2O$); 1.01 (*d*, $J = 6.8$, *Me*CH); 0.92 (*d*, $J = 6.8$, *Me*CH). ^{13}C-NMR (75 MHz): 157.7, 155.6 (C=O, C=N), 73.1 ($CHCH_2$); 71.1 (CH_2CH); 62.9 ($MeCH_2O$); 32.3 (Me_2CH); 18.9 (Me_2CH); 18.1 (Me_2CH); 14.0 ($MeCH_2O$). EI-MS: 186 (2, $[M+H]^+$), 143 (43), 112 (13), 97 (13), 83 (5), 70 (100), 56 (27), 43 (56). Anal. calc. for $C_9H_{15}NO_3$: C 58.36, H 8.16, N 7.56; found: C 58.24, H 8.25, N 7.38.

*Ethyl (4*S*)-4-(1,1-Dimethylethyl)-4,5-dihydrooxazole-2-carboxylate* (**8b**). As described for **8a**, from ethyl oxamate (1.8 g, 15.1 mmol) and L-*tert*-leucinol (2.0 g, 17.1 mmol). After 1 d, **8b** (1.31 g, 43%) was obtained as a colorless solid. R_f (pentane/^{t}BuOMe 1:1) 0.58. $[\alpha]_D^{20} = -74.0$ ($c = 0.91$, $CHCl_3$). IR (film): 2960*s*, 2908*m*, 2872*m*, 1750*s*, 1651*s*, 1479*m*, 1397*m*, 1376*m*, 1338*m*, 1313*s*, 1265*s*, 1209*m*, 1149*s*, 1021*m*, 967*m*, 927*m*, 862*m*, 827*w*, 792*w*, 773*w*, 589*w*. ^{1}H-NMR (200 MHz): 4.44–4.04 (*m*, $MeCH_2O$, $CHCH_2$); 1.39 (*t*, $J = 7.1$, $MeCH_2O$); 0.95 (*s*, ^{t}Bu). ^{13}C-NMR (50 MHz): 157.6, 155.4 (C=O, C=N); 76.5 ($CHCH_2$); 69.6 (CH_2CH), 62.7 ($MeCH_2O$); 33.6 (Me_3C); 25.7 (Me_3C); 13.7 ($MeCH_2O$). EI-MS: 199 (0.4, M^+), 184 (1), 143 (100), 70 (57), 57 (35), 41 (29).

Methyl (4S)-4,5-Dihydro-2-phenyloxazole-4-carboxylate (**9a**) [18]. Triethyloxonium tetrafluoroborate (7.5 g, 39.5 mmol) was dissolved in 1,2-dichloroethane (300 ml). Benzamide (4.8 g, 39.5 mmol) was added and the soln. stirred at r.t. for 2 d resulting in precipitation of a white solid. The mixture was filtered and the residue washed with cold Et_2O and dissolved in 0.1M aq. Na_2CO_3 soln. (300 ml). The resulting soln. was extracted with CH_2Cl_2 (3×100 ml) and the combined org. phase dried (Na_2SO_4) and evaporated. The residue was dissolved in 1,2-dichloroethane (100 ml), and L-serine methyl ester hydrochloride (5.0 g, 32.3 mmol) was added. After heating under reflux for 20 h, the soln. was filtered and evaporated. The residue was purified by FC (silica gel, hexane/AcOEt 6:1): **9a** (5.95 g, 73%). Colorless oil. R_f (hexane/AcOEt 1:1) 0.56. IR (film): 3063*w*, 3002*w*, 2954*m*, 2908*w*, 2848*w*, 1743*s*, 1643*s*, 1603*w*, 1580*m*, 1496*m*, 1451*m*, 1437*m*, 1362*s*, 1297*m*, 1211*s*, 1179*m*, 1090*m*, 1070*m*, 1026*m*, 972*m*, 945*m*, 903*w*, 779*m*, 697*s*. ^{1}H-NMR (300 MHz): 8.00–7.96 (*m*, 2 arom. H); 7.52–7.37 (*m*, 3 arom. H); 4.95 (*dd*, $J = 10.6$, 8.0, 1 H, dihydrooxazole); 4.69 (*t*, $J = 8.3$, 1 H, dihydrooxazole); 4.59 (*dd*, $J = 10.6$, 8.7, 1 H, dihydrooxazole); 3.81 (*s*, MeO). ^{13}C-NMR (75 MHz): 171.6, 166.3 (C=O, C=N); 131.9, 128.6, 128.4 (arom. CH); 127.0 (arom. C); 69.6 (CH_2O); 68.7 (CHN); 52.7 (MeO). EI-MS: 205 (7, M^+), 146 (100), 118 (22), 105 (18), 91 (39), 77 (22), 51 (10).

Methyl (4S)-4,5-Dihydro-2-propyloxazole-4-carboxylate (**9b**). Butanamide (3.5 g, 40.0 mmol) was added to a soln. of triethyloxonium tetrafluoroborate (7.6 g, 40.0 mmol) in CH_2Cl_2 (100 ml) and stirred for 1 d. ^{i}Pr$_2$NEt (8.6 ml, 50.0 mmol) and L-serine methyl ester hydrochloride (6.2 g, 40.0 mmol) were added subsequently at 0°. The soln. was stirred at r.t. for 2 d and finally filtered. The remaining residue was extracted with CH_2Cl_2 (200 ml), the combined org. phase washed with sat. aq. NH_4Cl soln. (50 ml), dried (Na_2SO_4), and evaporated, and the residue purified by FC (silica gel, pentane/Et_2O 1:2): **9b** (4.80 g, 70%). Colorless oil. R_f (hexane/AcOEt 1:1) 0.46. $[\alpha]_D^{20} = +156$ ($c = 1.60$, $CHCl_3$). IR (film): 2966*m*, 2937*m*, 2877*m*, 1745*s*, 1662*s*, 1459*m*, 1438*m*, 1368*m*, 1338*m*, 1272*m*, 1204*s*, 1186*s*, 1062*m*, 1039*m*, 985*m*, 958*m*, 923*m*. ^{1}H-NMR (300 MHz): 4.73 (*dd*, $J = 10.5$, 7.7, 1 H, dihydrooxazole); 4.51–4.36 (*m*, 2 H, 4,5-dihydrooxazole); 3.79 (*s*, MeO); 2.31 (*t*, $J = 7.4$, $MeCH_2CH_2$); 1.68 (*sext.*, $J = 7.4$, $MeCH_2CH_2$); 0.97 (*t*, $J = 7.4$, $MeCH_2CH_2$). ^{13}C-NMR (75 MHz): 171.8, 170.8 (C=O, C=N); 69.2 (CH_2O); 68.1 (CHN); 52.6 (MeO); 29.8 ($MeCH_2CH_2$); 19.4 ($MeCH_2CH_2$); 13.7 ($MeCH_2CH_2$). EI-MS: 171 (1, M^+), 156 (3), 143 (32), 112 (100), 84 (19), 55 (8), 42 (36). Anal. calc. for $C_8H_{13}NO_3$: C 56.12, H 7.65, N 8.18; found: C 56.05, H 7.61, N 8.12.

Methyl 2-Methylpropanimidate Hydrochloride. To a soln. of the 2-methylpropanenitrile (7.3 ml, 80.0 mmol) in Et_2O (40 ml), MeOH (3.24 ml, 80.0 mmol) was added. HCl Gas was bubbled through this soln. for 3 h at 4° and the resulting soln. stirred for 24 h at r.t. The solvent was evaporated and the residue washed with pentane (20 ml) and Et_2O (2×15 ml): methyl 2-methylpropanimidate hydrochloride (9.82 g, 89%). Colorless solid. IR (KBr): 3075*s*, 3034*s*, 2976*s*, 2930*s*, 2874*s*, 2654*m*, 1653*s*, 1565*m*, 1486*s*, 1458*m*, 1408*s*, 1377*m*, 1339*w*, 1307*m*, 1216*m*, 1163*w*, 1113*s*, 949*m*, 903*m*, 879*m*, 811*m*, 795*s*, 599*m*. ^{1}H-NMR (300 MHz): 12.45 (br. *s*, 1 H, NH_2); 11.59 (br. *s*, 1 H, NH_2); 4.31 (*s*, MeO); 3.26 (*sept.*, $J = 6.9$, Me_2CH); 1.31 (*d*, $J = 6.9$, Me_2CH). ^{13}C-NMR (75 MHz): 183.8 (C=N); 60.8 (MeO); 33.2 (Me_2CH); 19.0 (Me_2CH). EI-MS: 100 (16), 86 (100), 73 (14), 70 (21), 68 (5), 58 (84), 54 (18), 43 (37), 39 (16), 36 (31). Anal. calc. for $C_5H_{12}ClNO$: C 43.64, H 8.78, N 10.17; found: C 43.51, H 8.71, N 10.10.

Methyl (4S)-4,5-Dihydro-2-(1-methylethyl)oxazole-4-carboxylate (**9c**). Methyl 2-methylpropanimidate hydrochloride (6.9 g, 50.0 mmol) and L-serine methyl ester hydrochloride (7.8 g, 50.0 mmol) were dissolved in CH_2Cl_2 (100 ml) and ^{i}Pr$_2$NEt (10.8 ml, 62.5 mmol) was added at 4°. After 1 h at 4°, the soln. was allowed to come to r.t. and was stirred for 2 d, during which a colorless solid formed. The mixture was filtered and the solid washed with CH_2Cl_2 (150 ml). The combined org. phase was washed with sat. aq. NH_4Cl soln. (30 ml), dried (Na_2SO_4), and evaporated, and the residue purified by FC (silica gel, ^{t}BuOMe 1:1): **9c** (6.30 g, 74%). Colorless oil. R_f (hexane/AcOEt 1:1) 0.43. $[\alpha]_D^{20} = +157$ ($c = 1.66$, $CHCl_3$). IR (film): 2976*m*, 2910*w*, 2879*w*, 1744*s*, 1658*s*, 1472*m*, 1438*m*, 1388*w*, 1363*m*, 1328*m*, 1278*m*, 1204*s*, 1150*m*, 1098*m*, 1060*m*, 1037*m*, 982*m*, 954*m*, 921*m*. ^{1}H-NMR (300 MHz): 4.75–4.69 (*m*, 1 H, dihydrooxazole); 4.50–4.36 (*m*, 2 H, dihydrooxazole); 3.79 (*s*, MeO); 2.64 (*sept. d*, $J = 7.0$, 0.7, Me_2CH); 1.22 (*d*, $J = 7.0$, 3 H, Me_2CH); 1.21 (*d*, $J = 7.0$, 3 H, Me_2CH). ^{13}C-NMR (75 MHz): 174.8, 171.9 (C=O, C=N); 69.3 (CH_2O); 68.0 (CHN); 52.6 (MeO); 28.2 (Me_2CH); 19.7 (Me_2CH); 19.6 (Me_2CH). EI-MS: 171 (4, M^+), 156 (1), 112 (100), 84 (39), 70 (14), 55 (10), 43 (25). HR-MS: 171.0890 ($C_6H_{13}NO_3^+$; calc. 171.0895).

Methyl (4S)-2-(1,1-Dimethylethyl)-4,5-dihydrooxazole-4-carboxylate (**9d**). As described for **9b**, from 2,2-dimethylpropanamide (4.0 g, 40.0 mmol). After 4 d, **9d** (3.25 g, 44%) was obtained as a yellowish solid. R_f (hexane/AcOEt 1:1) 0.40. $[\alpha]_D^{20} = +139$ ($c = 1.25$, $CHCl_3$). IR (film): 2975*s*, 2909*m*, 2874*m*, 1745*s*, 1650*s*, 1483*m*, 1461*m*, 1438*w*, 1396*m*, 1364*m*, 1301*m*, 1211*s*, 1180*m*, 1147*s*, 1061*m*, 1027*m*, 981*m*, 954*m*, 917*m*. ^{1}H-NMR (300 MHz): 4.71 (*dd*, $J = 10.5$, 7.7, 1 H, dihydrooxazole); 4.49–4.38 (*m*, 2 H, dihydrooxazole); 3.78 (*s*, MeO); 1.24 (*s*, ^{t}Bu). ^{13}C-NMR (75 MHz): 176.9, 172.0 (C=O, C=N); 69.5 (CH_2O); 68.2 (CHN); 52.5 (MeO); 33.4 (C);

27.7 (Me_3C). EI-MS: 185 (8, M^+), 170 (6), 126 (100), 110 (5), 70 (43), 57 (61). Anal. calc. for $C_9H_{15}NO_3$: C 58.36, H 8.16, N 7.56; found: C 68.12, H 8.11, N 7.62.

General Procedure (*G.P.*): *Sodium (4*S*)-4,5-Dihydro-2-phenyloxazole-4-carboxylate* [19]. A mixture of 2N aq. NaOH (3.8 ml, 7.6 mmol) and **9a** (1.65 g, 8.1 mmol) was stirred for 1 h at r.t. H_2O (15 ml) and acetone (150 ml) were added, and the soln. was cooled to 0°. The product crystallized and was filtered and dried *in vacuo:* corresponding sodium carboxylate (1.31 g, 76%). White solid. IR (KBr): 3061*w*, 2983*w*, 2910*w*, 1644*s*, 1601*s*, 1497*w*, 1478*w*, 1450*m*, 1410*s*, 1358*m*, 1325*m*, 1278*m*, 1247*w*, 1095*m*, 1062*w*, 1026*m*, 963*m*, 778*m*, 748*m*, 693*m*. ^{1}H-NMR (300 MHz, D_2O): 7.82 (*d*, *J* = 7.4, 2 arom. H); 7.51 (*t*, *J* = 7.3, 1 arom. H); 7.41 (*t*, *J* = 7.5, 2 arom. H); 4.67–4.56 (*m*, 2 H, dihydrooxazole); 4.45–4.33 (*m*, 1 H, dihydrooxazole). ^{13}C-NMR (75 MHz, D_2O): 179.6 (C=O); 166.9 (C=N); 132.7, 129.1, 128.6 (arom. CH); 126.8 (arom. C); 72.1 (CH_2O); 70.1 (CHN). EI-MS: 121 (44), 105 (100), 77 (91), 51 (32). ESI-MS (H_2O): 662 (84, $[3\,M + Na]^+$), 449 (46, $[2\,M + Na]^+$), 236 (100, $[M + Na]^+$), 214 (44, $[M + H]^+$).

*Sodium (4*S*)-4,5-Dihydro-2-propyloxazole-4-carboxylate.* According to the *G.P.* (0.5 h), from **9b** (4.2 g, 24.3 mmol): corresponding sodium carboxylate (4.10 g, 94%). Colorless solid. IR (KBr): 2966*m*, 2935*m*, 2876*m*, 1668*s*, 1605*s*, 1411*s*, 1363*m*, 1313*m*, 1264*m*, 1189*m*, 1068*m*, 1028*m*, 978*s*, 937*m*, 870*m*, 795*m*, 749*m*. ^{1}H-NMR (300 MHz, CD_3OD): 4.55–4.42 (*m*, 2 H, dihydrooxazole); 4.33 (*t*, *J* = 7.3, 1 H, dihydrooxazole); 2.31 (*t*, *J* = 7.4, $MeCH_2CH_2$); 1.67 (*sext.*, *J* = 7.4, $MeCH_2CH_2$); 0.98 (*t*, *J* = 7.4, $MeCH_2CH_2$). ^{13}C-NMR (75 MHz, CD_3OD): 179.5 (C=O); 171.7 (C=N); 72.8 (CH_2O); 71.7 (CH); 31.2 ($MeCH_2CH_2$); 20.6 ($MeCH_2CH_2$); 14.5 ($MeCH_2CH$). EI-MS: 157 (1), 87 (7), 72 (23), 59 (100), 44 (72). ESI-MS (MeOH): 381 (37, $[2\,M + Na]^+$), 202 (100, $[M + Na]^+$).

*Sodium (4*S*)-4,5-Dihydro-2-(1-methylethyl)-1,3-oxazole-4-carboxylate.* According to the *G.P.* (1 h), from **9c** (5.0 g, 29.2 mmol): corresponding sodium carboxylate (5.04 g, 95%). Colorless solid. IR (Nujol): 3299*w*, 3188*w*, 2724*w*, 1661*s*, 1603*s*, 1377*s*, 1302*m*, 1269*m*, 1203*m*, 1151*m*, 1100*m*, 1071*m*, 1031*m*, 972*m*, 934*m*, 871*w*, 795*m*. ^{1}H-NMR (300 MHz, D_2O): 4.50 (br. *s*, 2 H, dihydrooxazole); 4.32–4.25 (*m*, 1 H, dihydrooxazole); 2.69–2.60 (*m*, Me_2CH); 1.18 (br. *s*, Me_2CH). ^{13}C-NMR (75 MHz, D_2O): 179.8, 176.0 (C=O, C=N); 71.8 (CH_2O); 69.5 (CHN); 28.2 (Me_2CH); 19.2 (Me_2CH). EI-MS: 157 (1), 87 (26), 72 (41), 59 (32), 44 (100), 41 (40). ESI-MS (Aceton): 335 (12, $[2\,M - Na]^-$), 156 (100, $[M - Na]^-$).

*Sodium (4*S*)-2-(1,1-Dimethylethyl)-4,5-dihydrooxazole-4-carboxylate.* According to the *G.P.* (1 h), from **9d** (2.0 g, 10.8 mmol): corresponding sodium carboxylate (1.86 g, 89%). Colorless solid. IR (KBr): 3206*m*, 2981*m*, 2968*m*, 2933*m*, 2909*m*, 2872*w*, 1661*s*, 1604*s*, 1482*m*, 1410*s*, 1346*m*, 1315*m*, 1247*m*, 1226*w*, 1206*w*, 1141*s*, 1063*w*, 1004*m*, 966*m*, 933*m*, 791*m*, 741*m*. ^{1}H-NMR (300 MHz, D_2O): 4.54–4.46 (*m*, 2 H, dihydrooxazole); 4.26 (*t*, *J* = 13.7, 1 H, dihydrooxazole); 1.21 (*s*, ^{t}Bu). ^{13}C-NMR (75 MHz, D_2O): 179.8, 178.0 (C=O, C=N); 71.8 (CH_2O); 69.7 (CHN); 33.3 (C); 27.3 (Me_3C). EI-MS: 170 (0.2), 101 (14), 86 (9), 57 (100), 41 (70). ESI-MS (MeOH): 363 (8, $[2\,M - Na]^-$), 170 (100, $[M - Na]^-$).

3. *Synthesis of Substrates.* Allyl carbonates used in this work were synthesiszed according to published procedures [20].

*Methyl (*E*)-3-Phenoxyprop-2-enoate* (**24a**). To a soln. of methyl propiolate (= methyl propynoate; 4.9 g, 58.0 mmol) in THF (90 ml) were added slowly PhOH (11.5 g, 122.5 mmol) and *N*-methylmorpholine (4.9 g, 48.0 mmol) at 0°. The resulting soln. was stirred at r.t. for 1.5 h. The soln. was carefully acidified with 2N HCl (50 ml) and extracted with ^{t}BuOMe (3 × 150 ml), the combined org. phase washed with 1N NaOH (3 × 50 ml), dried (Na_2SO_4), and evaporated, and the residue purified by FC (silica gel, pentane/^{t}BuOMe 50:1): **24a** (8.45 g, 82%). Colorless oil. R_f (pentane/^{t}BuOMe 20:1) 0.36. IR (film): 3078*w*, 2951*m*, 2845*w*, 1717*s*, 1650*s*, 1630*m*, 1590*m*, 1490*m*, 1437*m*, 1325*m*, 1287*m*, 1226*s*, 1196*m*, 1169*m*, 1123*s*, 1046*m*, 952*m*, 843*m*, 759*m*, 692*m*. ^{1}H-NMR (300 MHz): 7.81 (*d*, *J* = 12.2, CH); 7.40–7.35 (*m*, 2 arom. H); 7.21–7.16 (*m*, 1 arom. H); 7.08–7.05 (*m*, 2 arom. H); 5.57 (*d*, *J* = 12.2, CH); 3.73 (*s*, MeO). ^{13}C-NMR (75 MHz): 167.7 (C=O); 159.2 (CHO); 155.9 (arom. C); 130.0, 125.0, 118.0 (arom. CH); 101.8 (COCH); 51.1 (MeO). EI-MS: 178 (60, M^+), 147 (100), 119 (19), 108 (18), 105 (10), 94 (10), 91 (35), 85 (6), 77 (61), 74 (9), 69 (7), 65 (18), 51 (29), 39 (19).

*Methyl (*E*)-3-Methoxypropenoate* (**24b**) [15]. As described for **24a**, from methyl propiolate (5.0 g, 59.5 mmol) and MeOH (8.0 g, 0.25 mol). After 18 h, **24b** (5.77 g, 82%) was obtained as a colorless oil. R_f (pentane/^{t}BuOMe 9:1) 0.52. IR (film): 3098*w*, 2952*m*, 2845*w*, 1714*s*, 1649*m*, 1630*s*, 1440*m*, 1334*m*, 1291*m*, 1246*m*, 1224*s*, 1196*m*, 1138*s*, 1049*m*, 973*w*, 919*m*, 824*m*, 747*m*, 565*w*, 541*w*. ^{1}H-NMR (300 MHz): 7.63 (*d*, *J* = 12.6, CH); 5.20 (*d*, *J* = 12.6, CH); 3.71, 3.70 (2*s*, 2 MeO). ^{13}C-NMR (75 MHz): 168.1 (C=O); 163.3 (CHO); 95.7 (CHCO); 57.3, 51.1 (2 MeO). EI-MS: 116 (8, M^+), 85 (100), 69 (6), 59 (7), 42 (8).

*(*E*)-3-Phenoxyprop-2-enyl Acetate* (**25a**). To a soln. of **24a** (8.4 g, 47.0 mmol) in THF (60 ml) was added dropwise a soln. of DIBALH (15.1 g, 106 mmol) in THF (100 ml) at −78°. The soln. was slowly warmed to r.t. and stirred overnight. Under vigorous stirring, H_2O (2 ml), 4N NaOH (2 ml), and H_2O (6 ml) were added subsequently at 0°. After further stirring for 20 min, the resulting solid was filtered and washed with Et_2O

(150 ml). The solvent was evaporated affording 3-phenoxyprop-2-en-1-ol (6.1 g, 86%; sensitive!) as a colorless oil.

To a soln. of 3-phenoxyprop-2-en-1-ol (6.1 g, 40.6 mmol), Et_3N (6.2 g, 60.9 mmol), and *N*,*N*-dimethylpyridin-4-amine (DMAP; 5 mg) in CH_2Cl_2 (80 ml) was added dropwise Ac_2O (6.2 g, 60.9 mmol) at 0°. After 2.5 d, sat. aq. $NaHCO_3$ soln. (55 ml) was added and the soln. extracted with ^{t}BuOMe (3 × 100 ml). The combined org. phase was dried (Na_2SO_4) and evaporated and the residue purified by FC (silica gel, pentane/^{t}BuOMe 20:1): **25a** (3.70 g, 41% over two steps). Colorless oil. R_f (pentane/Et_2O 20:1) 0.26. IR (film): 3066*w*, 3043*w*, 2954*w*, 2891*w*, 1739*s*, 1674*m*, 1592*m*, 1491*s*, 1383*m*, 1364*m*, 1222*s*, 1169*m*, 1137*m*, 1023*m*, 936*m*, 894*w*, 757*m*, 693*m*. ^{1}H-NMR (300 MHz): 7.34–7.29 (*m*, 2 arom. CH); 7.11–7.06 (*m*, 1 arom. CH); 7.01–6.98 (*m*, 2 arom. CH); 6.78 (*dt*, *J* = 12.1, 0.9, CH); 5.44 (*dt*, *J* = 12.1, 7.8, CH); 4.57 (*dd*, *J* = 7.8, 0.9, CH_2); 2.06 (*s*, Me). ^{13}C-NMR (75 MHz): 170.9 (C=O); 156.6 (arom. C); 148.2 (CHO); 129.7, 123.5, 117.1 (arom. CH); 105.6 (*C*HCH$_2$); 61.5 (CH_2O); 21.1 (Me). EI-MS: 192 (30, M^+), 149 (46), 133 (40), 121 (19), 105 (48), 94 (89), 77 (87), 51 (33), 43 (87). Anal. calc. for $C_{11}H_{12}O_3$: C 68.73, H 6.29; found: C 68.65, H 6.38.

*(*E*)-3-Methoxyprop-2-enyl Acetate* (**25b**) [16]. As described for **25a**, from **24b** (5.1 g, 44.4 mmol). After 5 h, 3-methoxy-prop-2-en-1-ol (2.8 g, 71%; sensitive!) was obtained as a colorless oil which was transformed (1 d) to **25b** (2.01 g, 35% over both steps). Colorless oil. R_f (pentane/Et_2O 1:1) 0.78. IR (film): 3072*w*, 3009*w*, 2957*m*, 2838*w*, 1739*s*, 1657*s*, 1453*m*, 1384*m*, 1365*m*, 1237*s*, 1217*s*, 1176*m*, 1022*m*, 946*m*. ^{1}H-NMR (300 MHz): 6.63 (*d*, *J* = 12.6, CH); 4.93 (*dt*, *J* = 12.6, 7.8, CH); 4.50 (*dd*, *J* = 7.8, 0.5, CH_2); 3.58 (*s*, MeO); 2.05 (*s*, Me). ^{13}C-NMR (75 MHz): 171.1 (C=O); 153.3 (CHO); 96.9 (*C*HCH$_2$); 62.6 (CH_2O); 56.1 (MeO); 21.0 (Me). EI-MS: 130 (12, M^+), 87 (77), 71 (92), 59 (19), 55 (17), 43 (100).

4. *Mo-Catalyzed Allylic Alkylation.* – 4.1. *Dimethyl 2-[(*R*)-1-Phenylprop-2-enyl]propanedioate* (**11**) [6]. As described in *Exper. 4.2*, from **10b** (32.7 mg, 0.17 mmol) and **5a** (10.0 mg, 0.025 mmol) (12 h): 14:1 mixture (36.3 mg, 86%) of **11** (99% ee (*R*)) and **12** as a colorless oil. R_f (hexane/AcOEt 4:1) 0.41. GC (*Restek Rtx-1701*, 30 m; 50–250°, 10°/min, 60 kPa H_2); t_R 17.1 (**11**), 19.7 ((*E*)-**12**). GC (*Hewlett-Packard hp-5ms*, 30 m; 50–250°, 10°/min; 60 kPa He): t_R 13.7 (**11**), 16.0 ((*E*)-**12**). HPLC (*Daicel, Chiralcel OJ*, 25 cm; heptane/EtOH 93:7; 220 nm): t_R 30.1 ((*S*)-**11**), 35.2 ((*R*)-**11**).

Data of **11**: $[\alpha]_D^{22} = +34.5$ (*c* = 1.03, $CHCl_3$; 99% ee). IR (film): 3031*w*, 2954*m*, 1760*s*, 1740*s*, 1639*w*, 1602*w*, 1494*w*, 1435*m*, 1263*m*, 1198*m*, 1163*m*, 1027*w*, 992*w*, 925*w*, 765*w*, 702*m*. ^{1}H-NMR (300 MHz): 7.32–7.19 (*m*, 5 arom. H); 5.99 (*ddd*, *J* = 17.0, 10.2, 8.1, CH); 5.15–5.06 (*m*, CH_2); 4.14–4.08 (*m*, C*H*CHCH$_2$); 3.87 (*d*, *J* = 11.0, CHCO); 3.74, 3.49 (2 *s*, 2 MeO). ^{13}C-NMR (75 MHz): 168.2, 167.8 (2 C=O); 139.9 (arom. C); 137.8 (CH); 128.7, 127.9, 127.1 (arom. CH); 116.6 (CH_2); 57.4 (*C*HCO); 52.6, 52.4 (2 MeO); 49.7 (*C*HCHCH$_2$). EI-MS: 248 (2, M^+), 217 (2), 189 (100), 156 (19), 129 (43), 117 (100), 91 (19).

*Data of Dimethyl 2-[(*E*)-3-Phenylprop-2-enyl]propanedioate* ((*E*)-**12**) [20c]: IR (film): 2955*w*, 2845*w*, 1730*s*, 1495*m*, 1435*m*, 1335*m*, 1260*s*, 1160*s*, 1025*m*, 965*s*, 865*m*. ^{1}H-NMR (300 MHz): 7.34–7.17 (*m*, 5 arom. CH); 6.47 (*d*, *J* = 15.8, CH); 6.13 (*dt*, *J* = 15.8, 7.2, CH); 3.73 (*s*, 2 MeO); 3.53 (*t*, *J* = 7.2, CHCO); 2.80 (*dt*, *J* = 7.2, 0.6, CH_2). ^{13}C-NMR (75 MHz): 169.0 (C=O); 136.8 (arom. C); 132.8 (CH); 128.3 (CH); 127.3 (CH); 126.0 (CH); 125.2 (CH); 52.5, 51.7 (CH, Me); 32.2 (CH_2). EI-MS: 248 (23, M^+), 188 (38), 157 (16), 129 (100), 117 (63), 91 (17).

4.2. *Dimethyl 2-[(*R*)-1-Methylprop-2-enyl]propanedioate* (**14**). A soln. of ligand **6b** (9.8 mg, 0.025 mmol) and $[Mo(CO)_3(EtCN)_3]$ (5.9 mg, 0.017 mmol) in freshly distilled THF (0.7 ml) was degassed and then stirred at 70° in an ampoule with *Young* valve under Ar for 1 h. A soln. of dimethyl malonate sodium salt (prepared from dimethyl malonate (40 mg, 0.3 mmol) and NaH (5.3 mg, 0.22 mmol) in THF (1.0 ml) at r.t.) and (*E*)-but-2-enyl methyl carbonate (**13**; 22.1 mg, 0.17 mmol) were added. The soln. was again degassed and then stirred at 70° for 24 h. After cooling to r.t., H_2O (3 ml) was added. The mixture was extracted with Et_2O (3 × 15 ml), the combined extract washed with brine (5 ml), dried ($MgSO_4$), and evaporated, and the resulting oil purified by FC (silica gel, pentane/^{t}BuOMe 10:1): **14**/**15** 9:1 (25.7 mg, 81% as a colorless oil. R_f (hexane/AcOEt 4:1) 0.35. GC (*Restek Trx-1701*, 30 m; 60–120°, 2°/min; 60 kPa H_2): t_R 23.2 (**14**), 27.4 ((*E*)-**15**), 28.1 ((*Z*)-**15**). GC (chiral; *Chiraldex γ-CD-TA*, 30 m; 50–100°, 1°/min; 90 kPa H_2): t_R 33.4 ((+)-(*R*)-**14**), 34.7 ((−)-(*S*)-**14**), 41.7 ((*E*)-**15**), 44.2 ((*Z*)-**15**).

Data of **14**: The ee (97%) of **14** and the regioselectivity were determined by GC. $[\alpha]_D^{20} = +19.4$ (*c* = 0.76, $CHCl_3$; 93% ee). IR (film): 3082*w*, 2956*m*, 2852*w*, 1739*s*, 1643*w*, 1436*m*, 1268*m*, 1200*m*, 1153*m*, 1022*m*, 921*m*, 802*w*. ^{1}H-NMR (300 MHz): 5.77 (*ddd*, *J* = 17.1, 10.2, 8.0, CH); 5.13–5.00 (*m*, CH_2); 3.74, 3.71 (2*s*, 2 MeO); 3.32 (*d*, *J* = 9.0, CHCO); 2.97–2.94 (*m*, MeC*H*); 1.10 (*d*, *J* = 6.8, Me). ^{13}C-NMR (75 MHz): 168.7, 168.7 (2 C=O); 139.7 (CH); 115.6 (CH_2); 57.6 (*C*HCO); 52.4, 52.3 (2 MeO); 38.1 (Me*C*H); 18.0 (Me). EI-MS: 187 (0.5, $[M+H]^+$), 155 (6), 127 (100), 111 (32), 101 (28), 95 (42). Anal. calc. for $C_9H_{14}O_4$: C 57.97, H 7.63; found: C 58.05, H 7.57.

*Data of Dimethyl 2-[(*E*)-But-2-enyl]propanedioate* (**15**) [20a]: IR (film): 2955*m*, 1736*s*, 1437*m*, 1268*m*, 1231*m*, 1154*m*, 1023*m*, 968*m*. ^{1}H-NMR (300 MHz): 5.61–5.49 (*m*, CH); 5.42–5.31 (*m*, CH); 3.73 (*s*, 2 MeO); 3.41 (*t*, *J* = 7.5, CH); 2.57 (*m*, CH_2); 1.64 (*dd*, *J* = 6.1, 1.0, Me). ^{13}C-NMR (75 MHz): 169.2 (C=O); 128.4 (CH); 126.2 (CH); 52.4 (MeO); 51.9 (CH); 31.9 (CH_2); 17.8 (Me). EI-MS: 186 (10, M^+), 154 (8), 132 (43), 126 (55), 123 (57), 111 (100), 101 (25), 95 (31).

4.3 *(–)-Dimethyl 2-(1-Propylprop-2-enyl]propanedioate* (**17**) [20b]. As described in *Exper. 4.2*, from (*E*)-hex-2-enyl methyl carbonate (**16**; 26.9 mg, 0.17 mmol) and **7b** (10.0 mg, 0.025 mmol) (1.5 d): 8:1 mixture (30.4 mg, 83.5%) of **17** (98% ee (–)) and **18** as a colorless oil. GC (*Restek Rtx-1701*, 30 m; iso 50° for 3 min, 50 → 250°, 10°/min; 60 kPa H_2): t_R 15.4 (**17**), 16.5 ((*Z*)-**18**), 16.6 ((*E*)-**18**). *GC (Hewlett-Packard hp-5ms*, 30 m; iso 50° for 3 min, 50 → 250°,10°/min; 60 kPa He): t_R 12.7 (**17**), 13.6 ((*Z*)-**18**), 13.8 ((*E*)-**18**). GC (chiral; *Chiraldex γ-CD-TA*, 30 m; 70–110°, 0.5°/min, 90 kPa H_2): t_R 35.7 ((+)-**17**), 36.3 ((–)-**17**), 55.5 ((*Z*)-**18**), 57.3 ((*E*)-**18**).

Data of **17**: R_f 0.49 (hexane/AcOEt 6:1). $[\alpha]_D^{20} = -4.5$ (*c* = 0.62, $CHCl_3$; 98% ee). IR (film): 3080*w*, 2957*m*, 2874*w*, 1740*s*, 1642*w*, 1436*m*, 1256*m*, 1235*m*. ^{1}H-NMR (300 MHz): 5.63 (*ddd*, *J* = 17.1, 10.2, 9.4, CH); 5.12–5.05 (*m*, CH_2); 3.74, 3.69 (2*s*, 2 MeO); 3.38 (*d*, *J* = 8.9, CHCO); 2.78 (*m*, C*H*CHCH_2); 1.43–1.24 (*m*, MeCH_2CH_2); 0.88 (*t*, *J* = 6.4, *Me*CH_2CH_2). ^{13}C-NMR (75 MHz): 168.8, 168.6 (2 C=O); 138.1 (CH); 117.4 (CH_2); 57.0 (CHCO); 52.4, 52.2 (2 MeO); 44.1 (*C*HCHCH_2); 34.5 (MeCH_2CH_2); 20.2 (MeCH_2CH_2); 13.8 (*Me*CH_2CH_2). EI-MS: 215 (0.2, $[M+H]^+$), 183 (7), 171 (48), 155 (100), 139 (84), 132 (55), 126 (33), 113 (48), 100 (41), 81 (44), 55 (74).

*Data of Dimethyl 2-[(*E*)-Hex-2-enyl]propanedioate* (**18**) [20b]: R_f (hexane/AcOEt 4:1) 0.41. IR (film): 2960*s*, 2930*m*, 2850*m*, 1760*s*, 1435*s*, 1340*m*, 1275*s*, 1160*s*, 1040*m*, 970*m*, 860*w*. ^{1}H-NMR (300 MHz): 5.47 (*m*, CH); 5.40–5.30 (*m*, CH); 3.72 (*s*, 2 MeO); 3.42 (*t*, *J* = 7.5, CH); 2.58 (*dt*, *J* = 7.5, 1.0, 2 H, CH_2); 1.95 (*dq*, *J* = 7.4, 1.0, 2 H, CH_2); 1.35 (*sext.*, *J* = 7.4, 2 H, CH_2); 0.86 (*t*, *J* = 7.3, Me). ^{13}C-NMR (75 MHz): 169.1 (C=O); 133.7 (CH); 125.1 (CH); 52.3 (MeO); 51.9 (CH), 34.2 (CH_2); 31.9 (CH_2); 22.4 (CH_2); 13.5 (Me). EI-MS: 214 (1, M^+), 182 (3), 165 (2), 151 (39), 132 (89), 111 (100), 100 (34), 95 (48), 82 (30), 67 (41), 55 (51).

4.4. *(–)-Dimethyl 2-Methyl-2-(1-phenoxyprop-2-enyl)propanedioate* (**26a**). As described in *Exper. 4.2*, from 3-phenoxyallyl acetate (**25a**; 32.7 mg, 0.17 mmol) and **6b** (9.8 mg, 0.025 mmol) (2 d): >95:5 mixture (37.5 mg, 79%) of **26a** (98% ee (–)) and **27a** as a colorless oil. R_f (hexane/AcOEt 6:1) 0.55. GC (*Hewlett-Packard hp-5ms*, 30 m; iso 60° for 3 min, 60–250°, 10°/min; 60 kPa He): t_R 16.9 (**26a**), 18.8 (**27a**).

Data of **26a**: HPLC (*Daicel, Chiralcel OJ*, 25 cm; heptane/EtOH 93:7; 220 nm); t_R 23.6 ((+)-**26a**), 57.1 ((–)-**26a**). $[\alpha]_D^{20} = -17.7$ (*c* = 1.89, $CHCl_3$; 98% ee). IR (film): 3002*w*, 2954*w*, 2845*w*, 1739*s*, 1597*m*, 1494*m*, 1455*m*, 1435*m*, 1265*m*, 1230*s*, 1115*m*, 1096*m*, 988*m*, 888*w*, 755*m*, 692*m*. ^{1}H-NMR (300 MHz): 7.26–7.21 (*m*, 2 arom. H); 6.96–6.89 (*m*, 3 arom. H); 5.95 (*dq*, *J* = 17.3, 5.4, CH); 5.40–5.31 (*m*, CH, CH_2); 3.74, 3.63 (2*s*, 2 MeO); 1.55 (*s*, Me). ^{13}C-NMR (75 MHz): 170.2, 170.0 (2 C=O); 158.0 (arom. C); 132.9 (CH); 129.3, 121.4 (arom. CH); 119.7 (CH_2); 116.2 (arom. CH); 80.1 (CH); 58.6 (C); 52.7, 52.7 (2 MeO); 15.0 (Me). EI-MS: 278 (12, M^+), 185 (34), 159 (8), 146 (10), 133 (19), 125 (7), 71 (100). HR-MS: 278.1153 ($C_{15}H_{18}O_5^+$; calc. 278.1152).

*Data of Dimethyl 2-Methyl-2-[(*E*)-3-phenoxyprop-2-enyl]propanedioate* (**27a**). ^{1}H-NMR (300 MHz): 7.36–7.26 (*m*, 2 arom. CH); 7.12–6.95 (*m*, 3 arom. CH); 6.47 (*dt*, *J* = 12.1, 1.1, CH); 5.29–5.19 (*m*, CH); 3.73 (*s*, 2 MeO); 2.59 (*dd*, *J* = 8.1, 1.1, CH_2); 1.45 (*s*, Me). ^{13}C-NMR (75 MHz): 172.2 (C=O); 157.0 (arom. C); 144.8 (CH); 129.6, 122.8, 116.5 (arom. CH); 106.6 (CH); 54.1 (C); 52.5 (MeO); 34.0 (CH_2); 19.8 (Me). EI-MS: 278 (23, M^+), 185 (10), 133 (100), 125 (69), 77 (42).

4.5. *(+)-Dimethyl 2-(1-Methoxyprop-2-enyl]-2-methylpropanedioate* (**26b**). As described in *Exper. 4.2*, from 3-methoxyallyl acetate (**25b**; 22.1 mg, 0.17 mmol) and **4** (8.1 mg, 0.025 mmol) (1 d): >95:5 mixture (22.0 mg, 60%) of **26b** (74% ee (+)) and **27b** as a colorless oil. R_f (pentane/Et_2O 7:1) 0.46. GC (*Hewlett-Packard hp-5ms*, 30 m; iso 60° for 3 min, 60–250°, 10°/min; 60 kPa He); t_R 10.9 (**26b**), 12.4 (**27b**). GC (chiral; *Chiraldex γ-CD-TA*, 30 m; 50–110°, 1°/min; 75 kPa H_2): t_R 42.5 ((–)-**26b**), 34.7 ((+)-**26b**), 55.8 (**27b**).

Data of **26b**: $[\alpha]_D^{20} = +1.5$ (*c* = 0.71, $CHCl_3$; 74% ee). IR (film): 2994*w*, 2954*m*, 1740*s*, 1642*w*, 1457*m*, 1436*m*, 1264*m*, 1235*m*, 1113*m*, 1096*m*, 998*w*, 941*w*. ^{1}H-NMR (300 MHz): 5.74 (*ddd*, *J* = 17.5, 10.0, 7.2, CH); 5.37–5.31 (*m*, CH_2); 4.26 (*d*, *J* = 7.2, CH); 3.74 (*s*, CO_2Me); 3.68 (*s*, CO_2Me); 3.29 (*s*, MeO); 1.41 (*s*, MeC). ^{13}C-NMR (75 MHz): 170.6, 170.4 (2 C=O); 133.1 (CH); 120.0 (CH_2); 83.8 (CH); 58.7 (C); 57.3 (MeO); 52.6 (2 CO_2*Me*); 15.2 (Me). EI-MS: 216 (0.1, M^+), 185 (1), 157 (3), 125 (3), 71 (100), 59 (4), 41 (23). Anal. calc. for $C_{10}H_{16}O_5$: C 55.54, H 7.45; found: C 55.42, H 7.54.

*Data of Dimethyl 2-[(*E*)-3-Methoxyprop-2-enyl]-2-methylpropanedioate* (**27b**): ^{1}H-NMR (300 MHz): 6.32 (*d*, *J* = 12.6, CH); 4.58 (*m*, CH); 3.72 (*s*, 2 CO_2Me); 3.50 (*s*, MeO); 2.48 (*dd*, *J* = 7.9, 1.1, CH_2); 1.39 (*s*, Me). ^{13}C-NMR (75 MHz): 172.4 (C=O); 150.0 (CH); 96.1 ($CHCH_2$); 55.8 (MeO); 54.2 (C); 52.4 (CO_2*Me*); 34.3 (CH_2); 19.6 (Me). EI-MS: 216 (7, M^+), 185 (1), 169 (1), 156 (11), 125 (11), 71 (100).

5. *Preparation and X-Ray Analysis of Complex* **28**. (O-*6-33)-Tricarbonyl[*N,N′-*[(1*R,2*R*)*-cyclohexane-1,2-diyl]bis[(4*S*)*-4,5-dihydro-2-phenyloxazole-4-carboxamide-*κN[1],κO[4]]molybdenum*(0) (**28**). A soln. of ligand **7a** (140.0 mg, 0.30 mmol) and $[Mo(CO)_3(EtCN)_3]$ (99.7 mg, 0.29 mmol) in freshly distilled THF (15 ml) and toluene (15 ml) was degassed and then stirred at 70° in an ampoule with *Young* valve under Ar for 1 h. After cooling to r.t., the soln. was filtered, and the amount of solvent was reduced to 2/3 by evaporation under a stream of Ar. Storage at r.t. under Ar for several days afforded a mixture of **7a** and **28** as red-brown crystals which were suitable for X-ray analysis. The crystals proved to be extremely air-sensitive. ^{1}H-NMR (500 MHz, (D_6)acetone): 8.52 (br. *s*, 4 H_o); 8.33 (br. *s*, 2 NH); 7.65 (*t*, $J = 7.4$, 2 H_p); 7.53 (*t*, $J = 7.6$, 4 H_m); 5.49 (br. *s*, 2 NC*H*CH_2O); 5.21 (*t*, $J = 9.3$, 2 H, CH_2O); 4.73 (*t*, $J = 9.7$, 2 H, CH_2O); 3.96 (*m*, 2 NHC*H*); 2.01 (*m*, 2 H, CH_2CH_2CH); 1.75 (*m*, 2 H, CH_2CH_2CH); 1.54 (*m*, 2 H, CH_2CH_2CH); 1.34 (*m*, 2 H, CH_2CH_2CH). ^{13}C-NMR (125 MHz, (D_6)acetone): 229.3 (CO); 175.4, 168.9 (C=O, C=N); 132.9 (C_p); 129.8 (C_o); 128.2 (C_m); 125.6 (C_{ipso}); 70.7 ($NCHCH_2O$); 69.2 (CH_2O); 54.2 (CHNH); 31.1 (CH_2CH_2CH); 24.2 (CH_2CH_2CH).

X-Ray Structure Analysis of 2 (**28**)·**7a**·*0.63(THF)*. Formula, 2 $(C_{26}H_{26}MoN_4O_4 \cdot 3\,CO) \cdot C_{26}H_{26}N_4O_4 \cdot 0.63\,(C_4H_8O_1)$. Redbrown crystal (needle), $0.10 \times 0.12 \times 0.40$ mm; $a = 14.8060(5)$, $b = 24.5701(5)$, $c = 26.3578(8)$ Å; $V = 9588.75(7)$ Å^3, $\rho_{calc} = 1.23$ g cm^{-3}, $\mu = 0.32$ cm^{-1}, no absorption correction applied, $Z = 4$, orthorhombic, space group $P2_12_12_1$ (No. 19), $\lambda = 0.71073$ Å, $T = 193$ K, diffraction measurement method CCD, 15298 reflections collected, $(\pm h, \pm k, \pm l)$, $(\sin\theta)/\lambda = 0.57$ Å, 11457 observed reflections ($I \geq 2\sigma(I)$), 1079 refined parameters, $R = 0.0780$, $R_w = 0.0722$, max. residual electron density 1.77 (−1.06), H-atoms calculated and refined as riding atoms. Dataset was collected with an *Enraf-Nonius KappaCCD* diffractometer. Programs used: computing cell refinement, HKL Scalepack (*Otwinowski & Minor*, 1997); computing data reduction, HKL Denzo and Scalepack (*Otwinowski & Minor*, 1997); structure solution, SIR92 [21]; structure refinement, CRYSTALS [22]. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication no CCDC 146225. Copies of the data can be obtained, free of charge, on application to the director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. Code +44(12233)36-033; e-mail: deposit@ccdc.cam.ac.uk).

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