Screening of Various Catalysts for the Asymmetric Cyclopropanation of Structurally Typical Silyl Enol Ethers—Scope and Limitations of Evans's Bisoxazoline Copper Catalyst**

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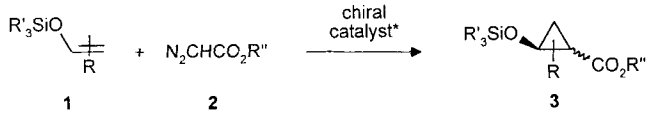
Abstract: The scope and limitations of asymmetric syntheses of 2-siloxycyclopropanecarboxylates **3** were examined by combination of structurally typical silyl enol ethers and methyl diazoacetate with various chiral catalysts. It was found that the Schiff base complex **5**·$Cu(OAc)_2$ and the bisoxazoline complex **6**·CuOTf gave the highest stereoselectivities (e.g., 72% *ee* for *cis*-**3d** with **5**·$Cu(OAc)_2$ as catalyst or 76% and 73% *ee* for *cis*- and *trans*-**3a**, respectively, with **6**·CuOTf as catalyst). High enantioselectivities or diastereoselectivities were obtained. Other catalysts based on copper, rhodium or ruthenium complexes afforded significantly lower values. In further investigations, Evans's bisoxazoline complex **6**·CuOTf proved to be limited to 1,1-disubstituted silyl enol ethers (e.g. **1a** and **1e**) for high enantiomeric excesses (up to >95%, poor diastereoselectivities) and to 1,2-substituted enol ethers (e.g. **1c**) for high diastereoselectivities (*cis*:*trans* < 3:97, ee_{trans} = 49%).

Keywords
asymmetric catalysis · cycloadditions · cyclopropanecarboxylates · diazoacetates · silyl enol ethers

Introduction

During the past decade donor–acceptor-substituted cyclopropanes have proved to be readily available and versatile building blocks for the synthesis of natural products and compounds of interest for pharmaceutical purposes.[3] The strong demand for enantiomerically pure products motivated us to investigate asymmetric additions of carbenoid species generated from diazo compounds to silyl enol ethers catalysed by chiral metal complexes (Scheme 1), which is probably the most elegant route to enantiomerically enriched functionalized cyclopropanes.[4]

In earlier studies, the scope of Pfaltz's semicorrin complexes[5] and of Schiff base copper complexes developed by Aratani et al.[6] [**4**·$Cu(OAc)_2$ and **5**·$Cu(OAc)_2$, respectively] has been demonstrated.[7, 8] Here, we present results using several catalytic systems recently described.



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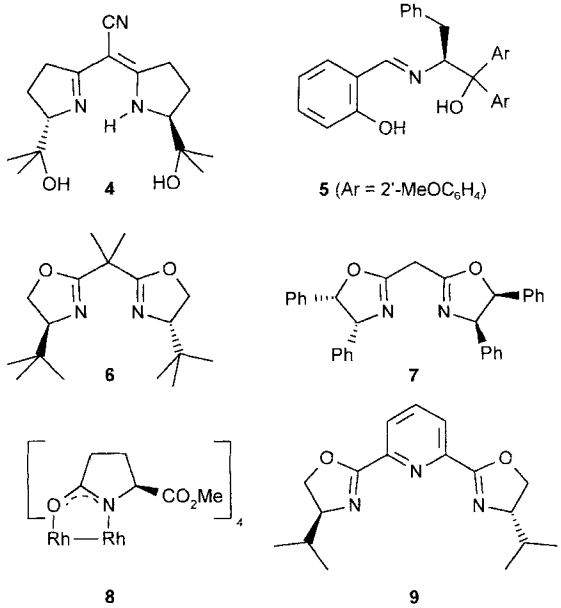
Scheme 1. Cyclopropanation of silyl enol ethers.

Selection of the catalysts: From the large number of chiral catalysts for stereoselective cyclopropanation of olefins, we selected the most effective systems introduced by Evans,[9] Masamune,[10] Doyle[11] and Nishiyama[12] [**6**·CuOTf, **7**·CuOTf, **8** and **9**·$Ru^{II}Cl_2$, respectively]. Three of these ligands are based on



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[**] Synthesis of Optically Active 2-Siloxycyclopropanecarboxylates by Asymmetric Catalysis, Part 3 (based on dissertations by R. Schumacher[1] and F. Dammast[2]). For Part 2 see ref. [7].

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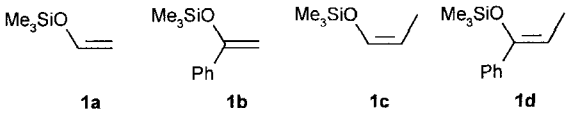
C_2-symmetric bisoxazoline structures (**6**, **7** and **9**), while Doyle's system **8** consists of a dinuclear rhodium complex. Nishiyama's catalyst **9** is the first example of a chiral ruthenium complex used for cyclopropanation reactions.[8] Bisoxazoline catalysts **6**·CuOTf, **7**·CuOTf and **9**·$Ru^{II}Cl_2$ induced excellent stereoselectivities in intermolecular cyclopropanation reactions with olefins of low functionality like styrene or 2,4-dimethyl-2,4-hexadiene. Doyle's $Rh_2\{(5S)\text{-MEPY}\}_4$ catalyst (**8**) gave excellent results, especially in intramolecular reactions. However, the scope and limitations of these catalysts are so far unknown, since functionalized olefins, in particular electron-rich alkenes, have not been studied.

Selection of the silyl enol ethers: Silyl enol ethers **1a–d** used in this study were selected for various reasons. Olefin **1a**, bearing only a siloxy substituent, is the simplest derivative. 1-Phenyl-1-trimethylsiloxyethene (**1b**) contains an additional phenyl group,



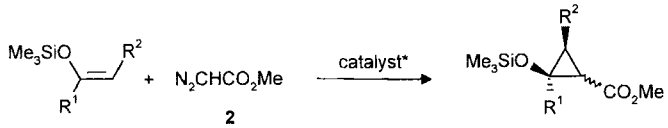
1a **1b** **1c** **1d**

which seems to be important for the chiral induction with some catalysts.[7] The other silyl enol ethers—**1c** and **1d**—were selected for similar reasons, but should lead to the corresponding 3-methyl-2-siloxycyclopropanecarboxylates. The stereochemical information at the methyl-substituted position is retained during ring opening reactions of donor–acceptor-substituted cyclopropanes.[8]

Results

Cyclopropanation reactions (Scheme 2) were carried out under conditions typical for each of the catalytic systems. Generally, the optimized temperature, reaction time, and the ratio of catalysts and diazoacetate reported in the literature were applied or adapted to the reactivity of the corresponding silyl enol ether.

With the simplest enol ether **1a**, the stereochemical outcome of the cyclopropanation was complex (see Table 1). The optical yields were low to moderate, exceeding 70% only in the case of bisoxazoline complex **6**·CuOTf. On the other hand, Masamune's catalyst **7**·CuOTf furnished only *trans*-cyclopropane **3a**; the *cis* isomer could not be detected by ^{1}H NMR spectroscopy, but the *ee* of *trans*-**3a** was disappointingly low. High



1a	R^1 = H	R^2 = H	**3a**
1b	R^1 = Ph	R^2 = H	**3b**
1c	R^1 = H	R^2 = Me	**3c**
1d	R^1 = Ph	R^2 = Me	**3d**

Scheme 2. Screening of various catalysts in the cyclopropanation of silyl enol ethers.

Table 1. Synthesis of **3a** by reaction of silyl enol ether **1a** with **2** in the presence of various catalysts (the best values are given in bold).

	4·$Cu(OAc)_2$ [a]	**5**·$Cu(OAc)_2$ [a,b]	**6**·CuOTf	**7**·CuOTf	**8**	**9**·Ru^{II}
yield/%	43	**53**	**55**	**50**	35	44
cis:*trans*	25:75	28:72	34:66	**<3:97**	57:43	28:72
ee_{cis}/%	12	30	**76**	–	24	13
ee_{trans}/%	33	30	**73**	11	<5	41

[a] Taken from ref. [8a]. [b] In this case, ligand **5** contained phenyl instead of *ortho*-anisyl groups.

enantiomeric excesses *and* good diastereomeric ratios were not obtained in any of these examples.

Phenyl-substituted silyl enol ether **1b** gave more consistent results (Table 2).[13] With Aratani's or Evans's catalysts (**5**·$Cu(OAc)_2$ and **6**·CuOTf, respectively), the enantiomeric excesses were the same within the experimental error (±2.5%). In both cases, the diastereoselection was low. The other catalysts employed gave inferior optical yields combined with low *cis*/*trans* ratios. Masamune's catalytic system (**7**·CuOTf) proved to be too reactive for the starting material or the products. All attempts to obtain the cyclopropane derivative **3b** with this catalyst led only to polymeric products.

Table 2. Synthesis of **3b** by reaction of silyl enol ether **1b** with **2** in the presence of various catalysts (the best values are given in bold).

	4·$Cu(OAc)_2$ [a]	**5**·$Cu(OAc)_2$	**6**·CuOTf	**7**·CuOTf	**8**	**9**·Ru^{II}
yield/%	53	**58**	**69**	0 [b]	50	**75**
cis:*trans*	45:55	**59:41**	**41:59**		60:40	64:36
ee_{cis}/%	40	**75**	**77**		23	43
ee_{trans}/%	48	**55**	**56**		7	53

[a] Taken from ref. [8a]. [b] Only polymeric products were obtained.

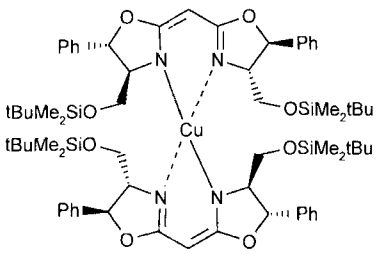
Olefin **1c** is the synthetically most interesting silyl enol ether used in this study, leading to 3-methyl-2-trimethylsiloxycyclopropanecarboxylates. We were therefore particularly anxious to achieve high stereoselectivities in its cyclopropanation giving **3c**. High diastereomeric selection was observed (Table 3), particularly with **6**·CuOTf and **7**·CuOTf as catalysts. However, the best enantiomeric excess was only 49%, obtained with **6**·CuOTf. The catalysts **4**·$Cu(OAc)_2$ and **5**·$Cu(OAc)_2$ gave only slightly lower selectivities. It is worth noting that in this and in the following case Nishiyama's ruthenium complex completely failed to catalyse the cyclopropanation reaction, but furnished fumaric and maleic esters only, the dimerization products of methyl diazoacetate.

In previous studies, silyl enol ether **1d** was used as the standard olefin.[7, 8] The reaction with methyl diazoacetate catalysed

Table 3. Synthesis of **3c** by reaction of silyl enol ether **1c** with **2** in the presence of various catalysts (the best values are given in bold and the preferred configuration at C-1 in parentheses).

	4·$Cu(OAc)_2$ [a]	**5**·$Cu(OAc)_2$ [a]	**6**·CuOTf	**7**·CuOTf	**8**	**9**·Ru^{II}
yield/%	40	48	39	**64**	27	0 [b]
cis:*trans*	15:85	25:75	**<3:97**	**<3:97**	42:58	
ee_{cis}/%	15 (*R*)	25 (*S*?)	–	–	16	
ee_{trans}/%	40 (*S*)	46 (*R*)	**49 (*R*)**	28 (*S*)	<5	

[a] Taken from ref. [8a]. [b] No conversion of **1c** was observed.



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by Schiff base complex **5**·Cu(OAc)$_2$ gave good enantioselectivities combined with low diastereoselection. However, these results could not be fully reproduced under our standard conditions; the optical yield was approximately 10% lower than reported. The diastereomeric ratio using Evans's catalyst **6**·CuOTf was high, while the enantiomeric excess did not exceed 30%. In contrast, Aratani's system **5**·Cu(OAc)$_2$ led to better enantioselectivities combined with a poor *cis*/*trans* ratio. Another variant of Masamune's system, bisoxazoline complex **10**, induced stereoselectivities in between the two preceding results, whereas with catalyst **7**·CuOTf only low values were obtained. Disappointingly, neither Doyle's rhodium complex **8** nor Nishiyama's ruthenium catalyst **9**·RuCl$_2$ provided the desired cyclopropane derivative **3d** (Table 4).

Table 4. Synthesis of **3d** by reaction of silyl enol ether **1d** with **2** in the presence of various catalysts (the best values are given in bold and the preferred configuration at C-1 in parentheses).

	4·Cu(OAc)$_2$	**5**·Cu(OAc)$_2$	**6**·CuOTf	**7**·CuOTf	**10**	**8**	**9**·Ru^{II}
yield/%	18	**51**	**59**	41	42	0 [a]	0 [b]
cis:*trans*	35:65	42:58	**13:87**	37:63	26:74		
ee_{cis}/%	5 (?)	**72 (*R*)**	30 (*R*)	25 (*R*)	17 (*S*)		
ee_{trans}/%	68 (*S*)	**66 (*R*)**	22 (*R*)	23 (*S*)	62 (*R*)		

[a] Only traces of **3d** were found. [b] No conversion of **1d** was observed.

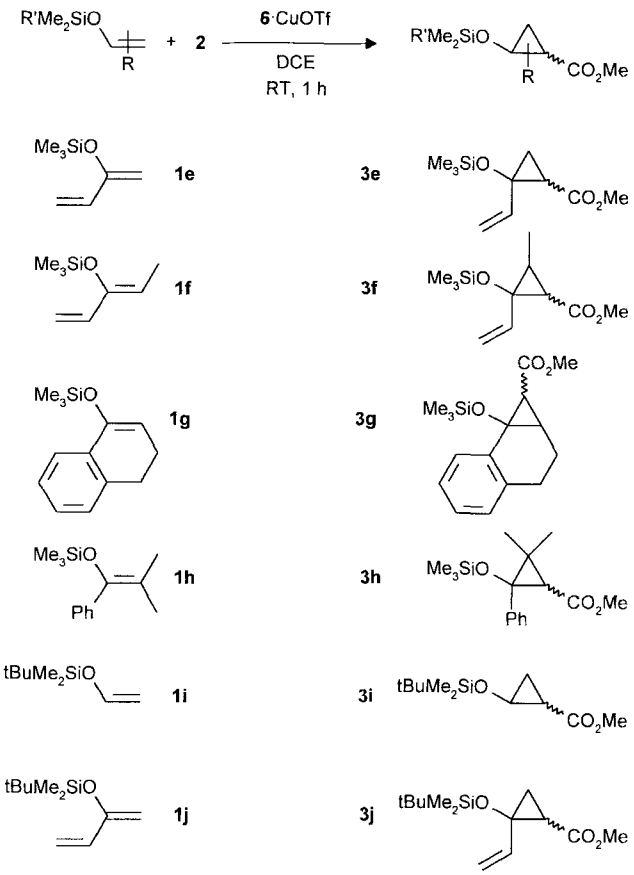
Scope and limitations of Evans's bisoxazoline catalyst: From these results it can be seen that, between them, Aratani's and Evans's catalyst are most effective for the enantioselective cyclopropanation reaction of silyl enol ethers. Since the influence of the silyl enol ether structure has been studied in detail only in the first case,[7] more experiments were carried out with complex **6**·CuOTf and varying the olefin or diazo components.

First, different silyl enol ethers were tested in the reaction (Scheme 3). They varied in the substitution pattern at the double bond, and in two cases the trimethylsiloxy group was replaced by the sterically more demanding *tert*-butyldimethylsiloxy group. The data collected in Table 5 show that there is a high dependence of the asymmetric induction on the structure of

Table 5. Synthesis of **3e**–**j** by reaction of silyl enol ethers **1e**–**j** with **2** in the presence of catalyst **6**·CuOTf.

SM	Prod.	Yield/%	*cis*:*trans*	ee_{cis}/%	ee_{trans}/%
1e	**3e**	72	45:55	>95	74
1f	**3f**	28 [a]	<10:90	–	64
1f [b]	**3f**	35	36:64	72	72
1g	**3g**	42	85:15	26	–
1h	**3h**	0 [c]	-	-	–
1i	**3i**	66	32:68	80	75
1j	**3j**	50	38:62	>95	69

[a] Product was not obtained in pure form. [b] Catalyst: **5**·Cu(OAc)$_2$. [c] Only **1h** was reisolated.



Scheme 3. Cyclopropanation of further silyl enol ethers in the presence of catalyst **6**·CuOTf (DCE = 1,2-dichloroethane).

silyl enol ethers **1**. Like the 1,1-disubstituted (**1b**) and 1-monosubstituted (**1a**) olefins described above, **1e** gave high enantioselectivities (56 to >95% *ee* for **1a**,**b**,**e**), but unfortunately low diastereoselection. Nevertheless, the *ee* of at least 95% for *cis*-**3e** is the best value recorded so far for a silyl enol ether. A switch from Me$_3$SiO to *t*BuMe$_2$SiO groups (**1a**→**1i**; **1e**→**1j**) had no significant influence on the results. On the other hand, trisubstituted olefins, such as **1f** and **1g**, only furnished good *cis*:*trans* ratios, whereas the enantiomeric excesses in these cases were moderate (**1f**) to low (**1g**). For comparison, olefin **1f** was also converted into **3f** by use of catalyst **5**·Cu(OAc)$_2$. The selectivities resemble those obtained from the reaction of **1d** in the presence of Schiff base complex **5**·Cu(OAc)$_2$, giving good enantioselectivities together with low diastereoselection (see Table 4 and refs. [7,8]). Tetrasubstituted olefin **1h** did not react at all under the reaction conditions. In contrast, in intramolecular cyclopropanations, even tetrasubstituted double bonds reacted with good enantioselectivities.[14]

It is known from many examples in literature[9a, 10] that bulky ester groups in the diazo component generally increase the stereoselectivity of the cyclopropanation reaction. Therefore, we replaced the methyl group in methyl diazoacetate with *tert*-butyl and (−)-menthyl groups for the reaction of olefin **1d** using **6**·CuOTf as catalyst (Scheme 4). Surprisingly, both the diastereoselectivities and the enantioselectivities of the major diastereomers [*trans*-(men)-**3d**] *decreased* with increasing size of the substituent (Table 6), whereas the minor diastereomers were formed with considerably higher *ee*.

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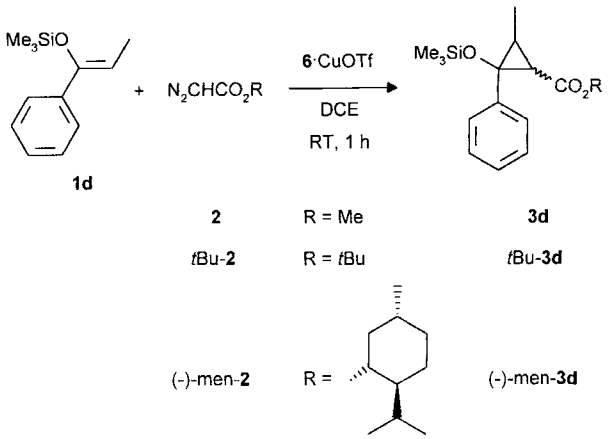


Scheme 4. Effect of ester group in the diazo component on the stereoselectivity of cyclopropanation.

Table 6. Synthesis of **3d** by reaction of silyl enol ether **1d** with diazoacetates **2** in the presence of catalyst **6**·CuOTf.

Diazoacetate	Product	Yield/%	*cis*:*trans*	ee_{cis}/%	ee_{trans}/%
2	**3d**	59	13:87	30	22
*t*Bu-**2**	*t*Bu-**3d**	30	21:79	51	19
(−)-men-**2**	(−)-men-**3d**	69 [a]	22:78	62 [b]	9 [b]

[a] Product contained ca. 10% dimers (^{13}C NMR, fumaric and maleic diesters). [b] *de*.

Discussion

This study shows that the objective of obtaining high diastereomeric *and* enantiomeric excesses in the cyclopropanation of silyl enol ethers has so far not be reached, although the catalysts used are very powerful for the cyclopropanation of standard olefins (e.g. styrene). Especially the complexes described by Masamune and Doyle gave only disappointing results. The reasons for the large differences in chiral induction between silyl enol ethers and styrene as substrates are not clear at the moment. However, our experiments allow predictions to be made regarding the best catalysts for obtaining high selectivities for a given substitution pattern in the silyl enol ether. Di- and trisubstituted silyl enol ethers containing a phenyl group are most efficiently converted into cyclopropanes in the presence of Aratani's Schiff base copper complex, whereas Evans's bisoxazoline catalysts give good to excellent enantioselectivities for 1,1-disubstituted double bonds. In spite of the high *cis*/*trans* selectivities obtained with some catalysts, the synthetically most interesting silyl enol ether **1c** did not afford cyclopropane **3c** with preparatively useful enantiomeric excesses.

For all bisoxazoline complexes employed in this study, the sense of chiral induction is uniform and consistent with the results reported for previous reactions with, for example, styrene. Thus, the knowledge of the absolute configuration of the siloxycyclopropanes and the degree of enantiomeric excesses should allow a mechanistic interpretation of the carbene addition, which we will present elsewhere, together with the determination of configuration.[15]

Experimental Section

All reactions were performed under argon in a flame-dried reaction flask. The solutions of starting materials **2** and **1** were added by a syringe pump "Precidor" (INFORS AG, Basel). All solvents were dried by standard methods. A Büchi kugelrohr apparatus was used for distillation of small quantities. ^{1}H NMR: Bruker AC200 spectrometer, 200 MHz. Internal standard: benzene ($\delta = 7.26$). Polarimetry: Perkin-Elmer 241 at the Na_D line and 25 °C. The enantiomeric excesses were determined by ^{1}H NMR shift measurements in the presence of ca. 0.15 equiv of Eu(hfc)$_3$ as chiral shift reagent (estimated error 2.5%). Starting materials were prepared following known procedures: **2**,[16] **1a**,[17] **1b**,[17] **1c**,[18] **1d**,[17] **1e**,[19] **1f**,[20] **1g**,[17] **1h**,[21] **1i**,[22] **1j**,[23] **5**,[8b] **6**[24] and **10**.[25] The ligands/catalysts **7**, **8** and **9** were purchased from Aldrich.

General Procedures A–E for the Cyclopropanation of Silyl Enol Ethers (all reactions are collected in Tables 7 and 8); for spectroscopical and analytical data see references: **3a**, **3b**, **3c**, **3d** *t*Bu-**3d**, **3e**;[26] **3g**;[7] **3j**.[27]

Procedure A—Aratani/Pfaltz catalyst: A few drops of a solution of silyl enol ether **1** (10.0 mmol) and **2** (0.667 g, 6.67 mmol) in 1,2-dichloroethane (8 mL) were added to a solution of Cu(OAc)$_2$ (0.067 g, 0.33 mmol) and **5** (0.171 g, 0.367 mmol) in 1,2-dichloroethane (2 mL) [Pfaltz's catalyst: **4**·Cu(OAc)$_2$ (0.10 mmol)] at 80 °C until the reaction started (evolution of N_2 and change of colour of the mixture). Then, the mixture was cooled to 50 °C, and the remaining solution of the olefin was added by a syringe pump over a period of 5 h. The reaction mixture was allowed to cool to RT, and the solvent was evaporated. The residue was dissolved in pentane and rapidly filtered through a short column of alumina (neutral, activity III). The crude product obtained by evaporation of pentane was further purified by bulb-to-bulb distillation to give the pure cyclopropanecarboxylates **3**.

Procedure B—Evans catalyst (**6**·CuOTf): A mixture of CuOTf·0.5C$_6$H$_6$ (0.083 g, 0.33 mmol) and **6** (0.107 g, 0.363 mmol) in 1,2-dichloroethane (2 mL) was stirred at RT for 30 min to give a clear, dark-green solution of the catalyst. Then, a solution of silyl enol ether **1** (10.0 mmol) and **2** (0.667 g, 6.67 mmol) in 1,2-dichloroethane (8 mL) was added at RT over a period of 1 h. After additional stirring for 30 min, the reaction mixture was worked up

Table 7. Synthesis of **3a–d** by reaction of silyl enol ethers **1a–d** with **2** in the presence of various catalysts.

1 (mmol)	Proc.	Yield/g	Yield/%	*cis*:*trans*	$[\alpha]_D^{20}$ [a]	*c* [g 100 mL^{-1}]	ee_{cis}/%	ee_{trans}/%
a (15.0)	[b,c]	0.810	43	25:75	+26.1	5.12	12	33
a (15.0)	[b,d]	0.998	53	28:72	−29.4	1.76	30	30
a (10.0)	B	0.695	55	34:66	−58.4	1.78	76	73
a (5.00)	C	0.315	50	<3:97	+7.7	2.06		11
a (1.00)	D	0.139	35	57:43	+3.4	1.72	24	<5
a (5.00)	E	0.277	44	28:72	−19.8	2.13	13	41
b (7.00)	[b,c]	0.981	53	45:55	+54.7	5.98	40	48
b (10.0)	A [d]	1.03	58	59:41	−106.1	2.81	75	55
b (10.0)	B	1.21	69	41:59	−75.3	2.12	77	56
b (5.00)	C	–	0	–			–	–
b (1.00)	D	0.131	50	60:40	+29.9	1.79	23	7
b (5.00)	E	0.658	75	64:36	−64.6	1.99	43	53
c (18.0)	[b,c]	0.720	40	15:85	+8.7	6.58	15	40
c (12.0)	[b,d]	0.765	48	25:75	−3.3	4.40	25	46
c (10.0)	B	0.523	39	<3:97	−10.8	2.06	–	49
c (5.00)	C	0.429	64	<3:97	+7.1	2.50	–	28
c (1.00)	D	0.092	27	42:58	+2.9	0.62	16	<5
c (5.00)	E	–	0	–	–		–	–
d (15.0)	A [c]	0.550	18	35:65	+16.6	2.16	5	68
d (7.50)	A [e]	0.580	42	26:74	−20.1	2.40	17	62
d (10.0)	A [d]	0.949	51	42:58	−64.1	1.98	72	66
d (10.0)	B	1.09	59	13:87	−15.5	1.92	30	22
d (5.00)	C	0.382	41	37:63	−4.9	2.02	25	23
d (1.00)	D	–	0				–	–
d (5.00)	E	–	0	–	–		–	–

[a] In $CHCl_3$ (mixture of diastereomers). [b] Taken from ref. [8a]. [c] Catalyst: **4**·0.5Cu^{II}. [d] Catalyst: **5**·Cu(OAc)$_2$. [e] Catalyst: **10**.

Table 8. Synthesis of **3e–j** by reaction of silyl enol ethers **1e–j** with diazoacetate **2** and of **3d** by reaction of **1d** with diazoacetates *t*Bu-**2** and (−)-men-**2**, following procedure B.

1 (mmol)	**3**	Yield/g	Yield/%	*cis*:*trans*	$[\alpha]_D^{20}$ [a]	*c* [g 100 mL^{-1}]	ee_{cis}/%	ee_{trans}/%
e (10.0)	**e**	1.03	72	45:55	−134.8	2.11	>95	74
f (4.00)	**f**	0.177 [b]	28	10:90	–		–	64
f (2.00) [c]	**f**	0.107	35	36:64	−77.6	1.91	72	72
g (10.0)	**g**	0.805	42	85:15	−20.8	2.11	26	–
h (10.0)	**h**	0 [d]	0	–	–		–	–
i (10.0)	**i**	1.02	66	32:68	−54.3	2.25	80	75
j (5.00)	**j**	0.424	50	38:62	−113.0	2.74	>95	69
d (5.00) [e]	*t*Bu-**d**	0.333	30	21:79	−5.5	2.42	51	19
d (5.00) [f]	(−)-men-**d**	0.927 [g]	59	22:78	−55.2	1.95	62 [h]	9 [h]

[a] In $CHCl_3$ (mixture of diastereomers). [b] Product was not obtained in pure form. [c] Catalyst: **5**·$Cu(OAc)_2$; procedure A. [d] Olefin **1h** was reisolated. [e] Reaction with *t*Bu-**2**. [f] Reaction with (−)-men-**2**. [g] Sample contained approximately 10% of maleic and fumaric diesters. [h] *de*.

as described in procedure A. In some experiments, the reaction scale was proportionally reduced.

Procedure C—Masamune catalyst (**7**·CuOTf): A mixture of CuOTf·0.5C_6H_6 (0.008 g, 0.033 mmol) and **7** (0.017 g, 0.036 mmol) in 1,2-dichloroethane (1 mL) was stirred at RT for 30 min to give a clear solution of the catalyst. Then, a solution of silyl enol ether **1** (5.00 mmol) and **2** (0.333 g, 3.33 mmol) in 1,2-dichloromethane (4 mL) was added at RT over a period of 3 h. After additional stirring for 30 min, the reaction mixture was worked up as described in procedure A.

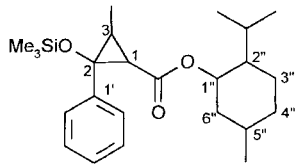
Procedure D—Doyle catalyst (Rh_2\{(5*S*)-MEPY\}$_4$): A solution of **2** (0.500 g, 5.00 mmol) in 1,2-dichloroethane (2 mL) was added over a period of 5 h to a solution of silyl enol ether **1** (1.00 mmol) and of Rh_2\{(5*S*)-MEPY\}$_4$ (7.7 mg, 0.010 mmol) in 1,2-dichloroethane (1 mL) at 70–80 °C. After additional stirring for 1 h and cooling to RT, the reaction mixture was worked up following procedure A.

Procedure E—Nishiyama catalyst (**9**·Ru^{II}): A mixture of *para*-cymeneruthenium(II)dichloride dimer (0.020 g, 0.033 mmol) and **9** (0.040 g, 0.132 mmol) in 1,2-dichloroethane (1 mL) was stirred at RT for 30 min. Then, a solution of silyl enol ether **1** (5.00 mmol) and of **2** (0.333 g, 3.33 mmol) in 1,2-dichloroethane (4 mL) was added over a period of 15–18 h. After additional stirring for 30 min, the mixture was worked up as described in procedure A.

Methyl *c/t*-3-Methyl-*t/c*-2-vinyl-*c/t*-2-trimethylsiloxy-*r*-1-cyclopropanecarboxylate (3f): b.p. 65 °C (0.1 mbar). ^{1}H NMR (C_6D_6, 200 MHz), *cis* isomer: δ = 0.34 (s, 9H, $SiMe_3$), 1.59 (d, J = 6.4 Hz, 3H, 3-Me), 1.84–1.94 (m, 2H, 1-H, 3-H), 3.47 (s, 3H, OMe), 4.91 (dd, J = 1.0, 10.6 Hz, 1H, 2′-H), 5.14 (dd, J = 1.0, 17.1 Hz, 1H, 2′-H), 5.81 (dd, J = 10.6, 17.1 Hz, 1H, 1′-H); *trans* isomer: δ = 0.27 (s, 9H, $SiMe_3$), 1.16 (d, J = 5.7 Hz, 3H, 3-Me), 1.84–1.94 (m, 2H, 1-H, 3-H), 3.45 (s, 3H, OMe), 5.25 (dd, J = 1.8, 10.6 Hz, 1H, 2′-H), 5.57 (dd, J = 1.8, 17.0 Hz, 1H, 2′-H), 6.40 (dd, J = 10.6, 17.0 Hz, 1H, 1′-H). ^{13}C NMR (C_6D_6, 50.3 MHz), *cis* isomer: δ = 1.8 (q, $SiMe_3$), 7.8 (q, 3-Me), 27.3 (d, C-3), 30.1 (d, C-1), 51.1 (q, CO_2*Me*), 66.4 (s, C-2), 112.7 (t, C-2′), 142.5 (d, C-1′), 169.2 (s, *C*O_2Me); *trans* isomer: δ = 1.4 (q, $SiMe_3$), 11.6 (q, 3-Me), 27.8 (d, C-3), 37.7 (d, C-1), 51.8 (q, CO_2*Me*), 68.1 (s, C-2), 113.9 (t, C-2′), 138.5 (d, C-1′), 171.3 (s, *C*O_2Me). IR (film): $\tilde{\nu}$ = 2960 cm^{-1} (C-H), 1740 (C=O). $C_{11}H_{20}O_3Si$ (228.4): calcd. C 57.86, H 8.83; found C 57.39, H 9.12.

Methyl 2-*tert*-Butyldimethylsiloxycyclopropanecarboxylate (3i): b.p. 65 °C (0.1 mbar). ^{1}H NMR (C_6D_6, 200 MHz), *cis* isomer: δ = 0.16, 0.18 (2s, 3H each, $SiMe_2$), 0.63 (ddd, J = 5.3, 6.4, 8.3 Hz, 1H, 3-H), 1.05 (s, 9H, *t*Bu), 1.53 (ddd, J = 6.7, 7.0, 8.3 Hz, 1H, 1-H), 1.63 (ddd, J = 4.8, 5.3, 6.7 Hz, 1H, 3-H), 3.34 (ddd, J = 4.8, 6.4, 7.0 Hz, 1H, 2-H), 3.53 (s, 3H, CO_2Me); *trans* isomer: δ = 0.11, 0.13 (2s, 3H each, $SiMe_2$), 0.98 (s, 9H, *t*Bu), 1.09 (ddd, J = 4.2, 5.3, 8.0 Hz, 1H, 3-H), 1.35 (ddd, J = 5.3, 6.0, 6.4 Hz, 1H, 3-H), 1.92 (ddd, J = 2.1, 6.0, 8.0 Hz, 1H, 1-H), 3.44 (s, 3H, CO_2Me), 3.95 (ddd, J = 2.1, 4.2, 6.4 Hz, 1H, 2-H). ^{13}C NMR (C_6D_6, 50.3 MHz), *cis* isomer: δ = −4.63, −4.54 (2q, $SiMe_2$), 14.6 (t, C-3), 18.7, 26.32 (q, s, *t*Bu), 21.9 (d, C-1), 51.6 (s, CO_2*Me*), 53.6 (d, C-2), 170.0 (s, *C*O_2Me); *trans* isomer: δ = −4.66, −4.60 (2q, $SiMe_2$), 17.6 (t, C-3), 18.6, 26.29 (q, s, *t*Bu), 23.2 (d, C-1), 51.7 (q, CO_2*Me*), 55.8 (d, C-2), 173.2 (s, *C*O_2Me). IR (film): $\tilde{\nu}$ = 2960, 2930, 2860 cm^{-1} (C-H), 1730 (C=O). $C_{11}H_{22}O_3Si$ (230.4): calcd. C 57.35, H 9.63; found C 57.46, H 9.90.

(−)-Menthyl *c/t*-3-Methyl-*t/c*-2-phenyl-*c/t*-2-trimethylsiloxy-*r*-1-cyclopropanecarboxylate [(−)-men-3d]: After evaporation of all volatile compounds [b.p. < 130 °C (0.001 mbar)], the sample contained approximately 10% (−)-menthyl maleate and (−)-menthyl fumarate (^{13}C NMR).



(-)-men-**3d**

^{1}H NMR (C_6D_6, 200 MHz), *cis* isomer: δ = 0.19, 0.20 (2s, 9H, *cis*-*A*-$SiMe_3$, *cis*-*B*-$SiMe_3$), 0.76–2.49 (m, 24H, 1-H, 3-H, 3-Me, menthyl), 5.03–5.13 (m, 1H, CO_2CH), 7.12–7.23, 7.29–7.59 (2m, 5H, Ar); *trans* isomer: δ = 0.059, 0.063 (2s, 9H, *trans*-*B*-$SiMe_3$, *trans*-*A*-$SiMe_3$), 0.76–2.49 (m, 24H, 1-H, 3-H, 3-Me, menthyl), 4.70–4.84 (m, 1H, CO_2CH), 7.12–7.23, 7.29–7.59 (2m, 5H, Ar). ^{13}C NMR: see Table 9. IR (film): $\tilde{\nu}$ = 3070, 3040 cm^{-1} (=C-H), 2960, 2930, 2870 (C-H), 1730 (C=O). $C_{24}H_{38}O_3Si$ (402.7): calcd. C 71.59, H 9.51; found C 71.76, H 9.70.

Table 9. ^{13}C NMR data of (−)-men-**3d**.

Signal	*trans*-A	*trans*-B	*cis*-A [a]	*cis*-B
$SiMe_3$ (q)	1.0	[e]		1.1
3-Me (q)	12.0	12.1		8.0
5″-Me (q) [d]	16.5	16.4		16.9
2″-CH*Me*$_2$ (2q) [d]	22.12, 21.04	22.09, 20.99		22.2, 21.1
C-4″ (t) [c]	23.7	23.4		23.8
C-3 (d)	24.2	24.7		25.4
C-5″ (d)	26.4	26.3		26.5
2″-*C*HMe$_2$ (d)	31.3	31.4		31.6
C-3″ (t) [c]	34.51	34.46		34.6
C-1 (d)	37.3	37.5		29.5
C-6″ (t)	41.5	41.1		41.8
C-2″ (d)	47.36	47.43		47.6
C-2 (s)	69.9	70.1		66.6
C-1″ (d)	73.9	73.7		73.5
C-2′ (d) [b]	130.1	129.9		
C-1′ (s)	139.4	139.6		143.7
*C*O$_2$Me (s)	169.5	169.4	168.2	168.1

[a] Missing signals of *cis*-A could not be unambiguously identified due to low intensity. [b] Missing signals are hidden by solvent signals (C_6D_6) and/or not unambiguously identifiable. [c] Signals are exchangeable. [d] Signals are exchangeable. [e] Chemical shift is identical with that of *trans*-A-$SiMe_3$.

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