Rhodium(II)-Catalyzed Inter- and Intramolecular Cyclopropanations with Diazo Compounds and Phenyliodonium Ylides: Synthesis and Chiral Analysis

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Dedicated to Professor *Paul Müller* on the occasion of his 65th birthday and retirement from the University of Geneva

Different classes of cyclopropanes derived from *Meldrum*'s acid (=2,2-dimethyl-1,3-dioxane-4,6-dione; **4**), dimethyl malonate (**5**), 2-diazo-3-(silyloxy)but-3-enoate **16**, 2-diazo-3,3,3-trifluoropropanoate **18**, diazo(triethylsilyl)acetate **24a**, and diazo(dimethylphenylsilyl)acetate **24b** were prepared *via* dirhodium(II)-catalyzed intermolecular cyclopropanation of a set of olefins **3** (*Schemes 1* and *4–6*). The reactions proceeded with either diazo-free phenyliodonium ylides or diazo compounds affording the desired cyclopropane derivatives in either racemic or enantiomer-enriched forms. The intramolecular cyclopropanation of allyl diazo(triethylsilyl)acetates **28**, **30**, and **33** were carried out in the presence of the chiral dirhodium(II) catalyst [Rh_2[(*S*)-nttl)$_4$]] (**9**) in toluene to afford the corresponding cyclopropane derivatives **29**, **31** and **34** with up to 37% ee (*Scheme 7*). An efficient enantioselective chiral separation method based on enantioselective GC and HPLC was developed. The method provides information about the chemical yields of the cyclopropane derivatives, enantioselectivity, substrate specifity, and catalytic activity of the chiral catalysts used in the inter- and intramolecular cyclopropanation reactions and avoids time-consuming workup procedures.

1. Introduction. – Due to its unusual bonding and large inherent ring strain, the cyclopropane moiety is unique among cyclic hydrocarbons in its properties, synthesis, and reactions. Naturally occurring and synthetic cyclopropanes bearing simple or complex functionalities are endowed with a large spectrum of biological properties ranging from enzyme inhibitions to insecticidal, antifungal, herbicidal, antimicrobial, antibiotic, antibacterial, antitumor, and antiviral activities [1]. Thus, they constitute a common structural motif in pyrethroids [2], the antidepressant tranylcyclopromine [3], papain and cystein protease inhibitors [4], potentially antipsychotic substances [5], anti-HIV agents [6], and marine lactones [7]. Accordingly, a great deal of effort has been developed over the last two decades to make the stereochemically controlled synthesis of substituted cyclopropanes more appealing to organic chemists [8]. Besides the resolution of their racemates [9], a number of synthetic methodologies, including the asymmetric *Simmons–Smith* reaction and metal-catalyzed reaction of diazo

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compounds with olefins, have been developed to access to the enantiomerically pure or enriched cyclopropanes [10].

The latter proceeds *via* an asymmetric carbene-transfer reaction. Thus, the transition-metal-catalyzed decomposition of the diazo precursor affords a metallocarbene (= metal-carbene complex; see *Fig. 1*) as reactive intermediate, which then transfers the carbene moiety to an appropriate substrate. The enantioselectivity of the reaction may be controlled by chiral ligands surrounding the metal. Recently, phenyliodonium ylides were used as potential substitutes to diazo compounds; the utility of the ylide approaches is directly related to the level of selectivity of the process, which is believed to proceed also *via* metallocarbenes as intermediates [11].

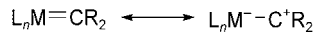
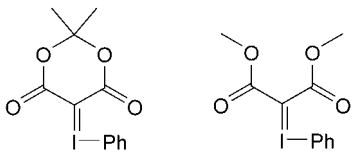


Fig. 1. *Metal–carbene complex*

The ways in which efficiency and practicality of these procedures are defined is depending on a large number of factors. Among these factors are suitable catalyst, scale, reagent costs, time allotted and required, and suitable equipments and reliable methods used in the determination of the enantiomer excess (ee) of the resulting cyclopropanes. The development of accurate non chiroptic methods for the determination of enantiomer purity has been critical for the development of enantioselective catalysis. Thus, a prerequisite in the metal-catalyzed asymmetric synthesis is a precise and reliable assessment of the enantiomer purity of the resulting products [12]. Among these methods are: polarimetric methods, gas-chromatographic methods, liquid-chromatographic methods, and NMR spectroscopy. The modern and most sensitive methods used in the determination of enantiomer purity of the outcome of metal-catalyzed reactions, allowing a detection as little as 0.1% of one enantiomer in the presence of another, are chiral-GC and -HPLC methods [13–17]. Here, we report on the synthesis of cyclopropane derivatives *via* inter- and intramolecular cyclopropanations and their chiral analysis on either *Chirasil-β-Dex* as chiral stationary phase in GC or *Chiralcel OD* (cellulose tris(3,5-dimethylphenylcarbamate)) coated on 10-μm silica gel as chiral stationary phase in HPLC.

2. Results and Discussion. – 2.1. *Intermolecular Cyclopropanation*. 2.1.1. *Diazo-Free One-Pot Procedure.* The conventional ylide approach used to prepare cyclopropanes consisted of the intermolecular cyclopropanation of olefins with isolated phenyliodonium ylides **1** or **2** (*cf. Fig. 2*). The efficiency of this method is depending on how convenient is the ylide to be handled and isolated in pure form.

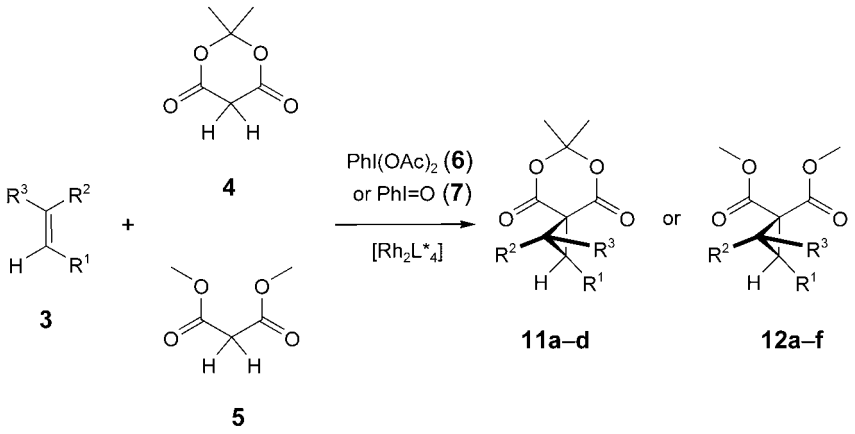


1 **2**

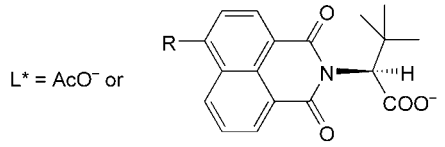
Fig. 2. *Phenyliodonium ylids* **1** *and* **2** *generated* in situ *from* Meldrum*'s acid* (**4**) *and dimethyl malonate* (**5**)

To avoid the difficulty in isolating sensitive ylides, a method was developed to generate the phenyliodonium ylides **1** and **2** *in situ*. Thus, a set of cyclopropanes derived from *Meldrum*'s acid (=2,2-dimethyl-1,3-dioxane-4,6-dione; **4**) and dimethyl malonate (=dimethyl propanedioate; **5**) were prepared by a user-friendly diazo-free one-pot procedure. The intermolecular cyclopropanation of olefins **3a**–**f**) was carried out with either **4** or **5** and bis(acetato-κO)phenyliodine (=diacetoxyiodobenzene; $PhI(OAc)_2$; **6**) or iodosylbenzene PhI=O; **7**) in the presence of 5 mol-% of rhodium(II) catalyst $[Rh_2(OAc)_4]$ (**8**) to afford the racemic cyclopropane derivates **11** and **12**, respectively, with high yield (up to 85%) (*Scheme 1*).

Scheme 1. *One-Pot Synthesis of Cyclopropane Derivatives* **11** *and* **12** *from* Meldrum*'s Acid* (**4**) *or Dimethyl Malonate* (**5**), *Respectively, and* $PhI(OAc)_2$ (**6**) *or* PhI=O (**7**), *in Presence of the Achiral Rhodium(II) Catalyst* **8** (L=AcO) *or the Chiral Rhodium(II) Catalyst* **9** (L=(*S*)-nttl) *or* **10** (L=4-Cl-(*S*)-nttl)



a R^1= Ph, R^2=R^3=H
b R^1= 4-MeC_6H_4, R^2=R^3=H
c R^1= Pr, R^2=R^3=H
d R^1= Me, R^2=H, R^3=Et
e R^1= 4-ClC_6H_4, R^2=R^3=H
f R^1= 4-BrC_6H_4, R^2=R^3=H



catalyst **8** = $[Rh_2(OAc)_4]$, L* = AcO^-
catalyst **9** = $[Rh_2\{(S)\text{-nttl}\}_4]$, L* = (*S*)-nttl, R = H
catalyst **10** = $[Rh_2\{4\text{-Cl-}(S)\text{-nttl}\}_4]$, L* = Cl-(*S*)-nttl, R = Cl

The ylides **1** and **2** were generated and decomposed by the appropriate rhodium catalyst *in situ* to afford the cyclopropanes upon reaction with olefins [11]. Attempts to use a chiral rhodium(II) catalyst, *i.e.*, $[Rh_2, \{(S)\text{-nttl}\}_4]$ (**9**; below, *Scheme 2*), instead of $[Rh_2(OAc)_4]$ (**8**) afforded the enantiomer-enriched cyclopropanes **11a**–**f** derived from *Meldrum*'s acid with 57, 51, 70, 33, and 30% ee, respectively. The cyclopropanation of styrene (**3a**) with dimethyl malonate (**5**) and iodosylbenzene (**7**) furnished the cyclopropane **12a** with only 37% ee, while **12b**–**f** were obtained with low ee (<20%) (*cf. Figs. 3–6*).

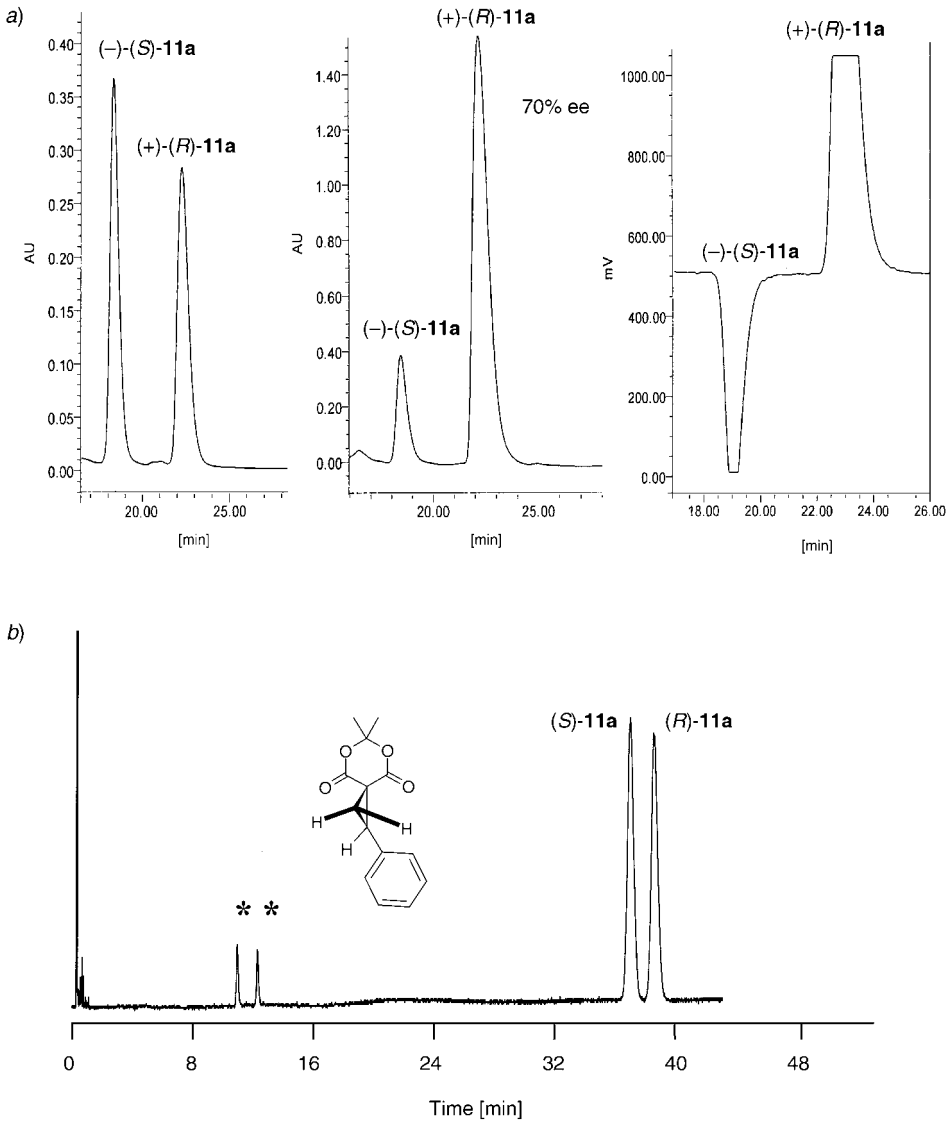


Fig. 3. *Analysis of* **11a**: a) *HPLC and* b) *GC*. Cyclopropanation conditions: **4** + **3a**, ylide precursor **6**, catalyst **10**. * = By-products (see *Chap. 2.3*).

The situation improved markedly when a Cl-substituent was introduced into the 4-position of the naphthalene ring of the catalyst ligand **9** to form [Rh_2{4-Cl-(*S*)-nttl}] (**10**). In the presence of **10**, the asymmetric cyclopropanation of styrene (**3a**) with *Meldrum*'s acid (**4**) and bis(acetato-κO)phenyliodine (**6**) in CH_2Cl_2 gave **11a** with 70% ee (81% yield) (*cf. Fig. 3*), while the cyclopropanation of styrene (**3a**) with dimethyl malonate (**5**) and iodosylbenzene (**7**) in CH_2Cl_2 afforded **12a** with 66% ee (77% yield). Similarly, cyclopropane derivative **12e** was obtained with 56% ee (*cf. Fig. 7*).

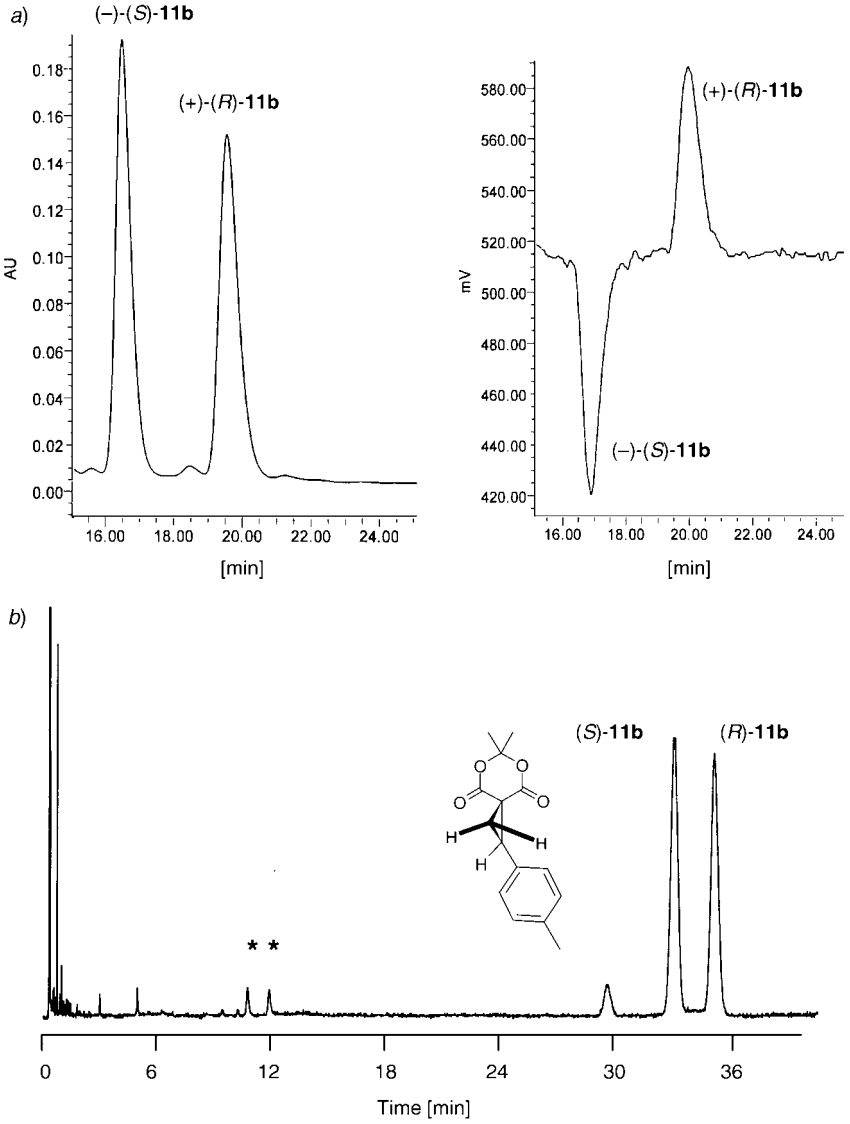


Fig. 4. *Analysis of* **11b**: a) *HPLC and* b) *GC.* * = By-products (see *Chapt. 2.3*).

The catalysts $[Rh_2\{(S)\text{-nttl}\}_4]$ (**9**) and $[Rh_2\{4\text{-Cl-}(S)\text{-nttl}\}]$ (**10**) were prepared *via* condensation of the appropriate 1,8-naphthalic anhydride **13a** or **13b** and the amino acid L-*tert*-leucine (=(2*S*)-2-amino-3,3-dimethylbutanoic acid; **14**) in DMF under reflux, which afforded the ligands **15a**,**b** easily and in high yield (*Scheme 2*). Ligand exchange was carried out by refluxing $[Rh_2(OAc)_4]$ (**8**) with a tenfold excess of ligand **15a** or **15b** in chlorobenzene (see *Exper. Part*), furnishing the desired chiral dirhodium(II) catalyst **9** or **10** in 80–90% chemical yield.

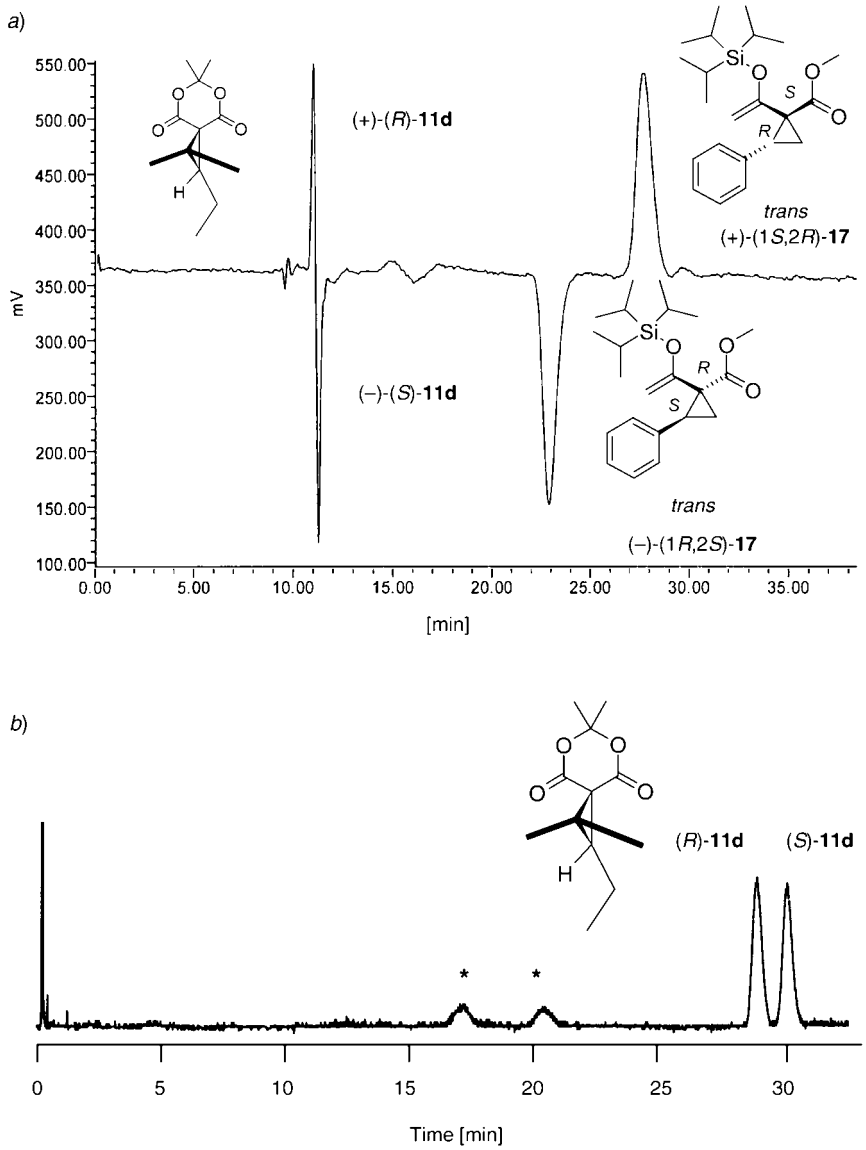


Fig. 5. *Analysis of* **11d**: a) *HPLC and* b) *GC.* * = By-products (see *Chapt. 2.3*).

2.1.2. *Cyclopropanation with Isolated Diazo Compounds.* The intermolecular cyclopropanations of styrene were carried out with either 2-diazo-3-(silyloxy)but-3-enoate **16** (*Scheme 3*) or 2-diazo-3,3,3-trifluoropropanoate **18** (*Scheme 4*) and achiral rhodium catalyst [$Rh_2(OAc)_4$] (**8**) affording *trans*-**17** and a mixture of *cis*- and *trans*-**19** in 60 and 70% yield, respectively. Reduction of *cis*/*trans*-**19** gave the alcohols *cis*/*trans*-**20**, while hydrolysis afforded the acids *cis*/*trans*-**21**. Esterification of *trans*-**20** with either 3,5-dinitrobenzoic acid or 4-nitrobenzoic acid yielded *trans*-**22** and -**23**, respectively (*cf. Fig. 8*).

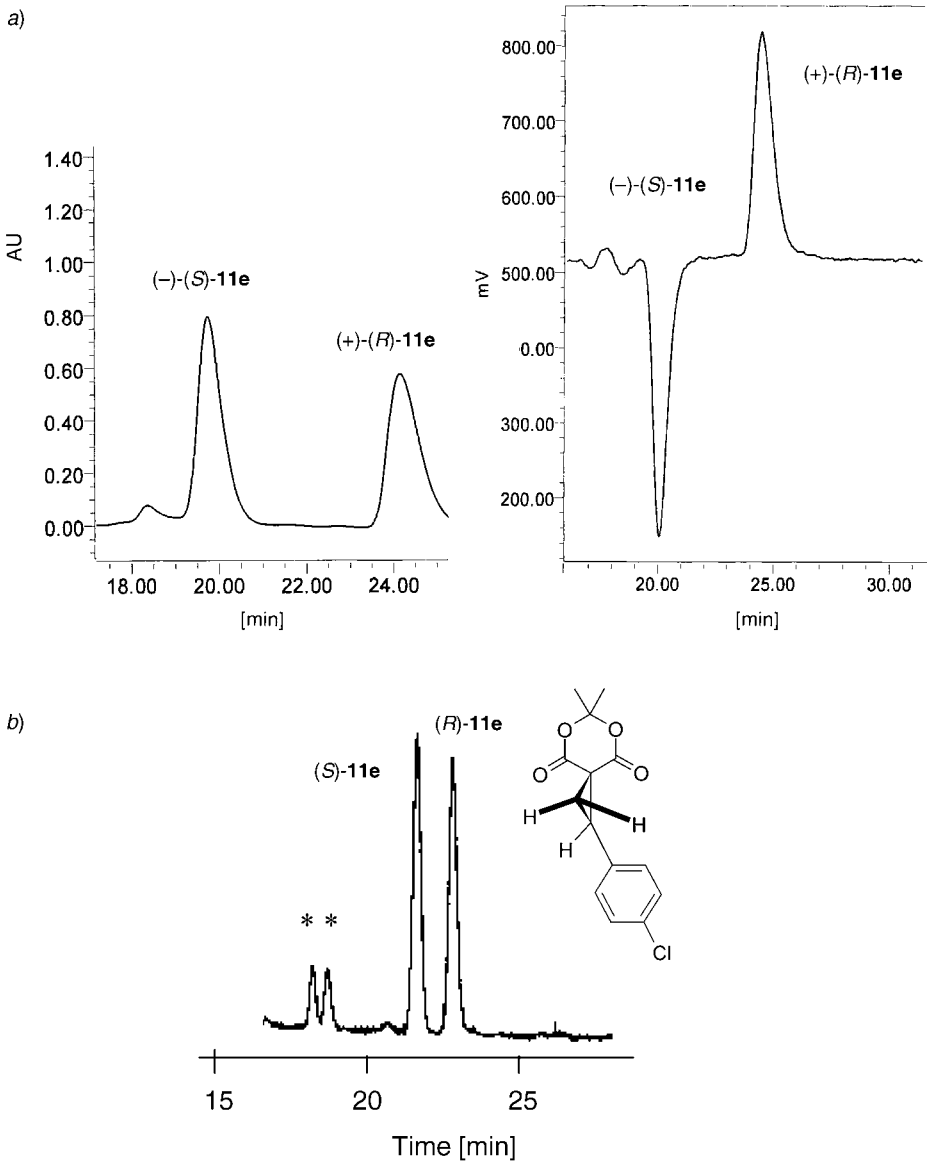


Fig. 6. *Analysis of* **11e**: a) *HPLC and* b) *GC*. * = By-products (see *Chapt. 2.3*).

In the presence of the chiral rhodium(II) catalyst $[Rh_2\{(S)\text{-pttl}\}_4]$ or $[Rh_2\{(S)\text{-bpttl}\}_4]$, and $[Rh_2\{(S)\text{-nttl}\}_4]$ in refluxing toluene, the intermolecular cyclopropanations of styrene with diazo(triethylsilyl)- and diazo(dimethylphenylsilyl)acetate **24a** and **24b** provided the silylated 2-phenylcyclopropane-1-carboxylates *cis*/*trans*-**25a** and *cis*/*trans*-**25b**, respectively, with similar diastereoisomer ratio (*trans*/*cis* 82:18) (*Scheme 5*; *cf.* below, *Fig. 9*,*a*).

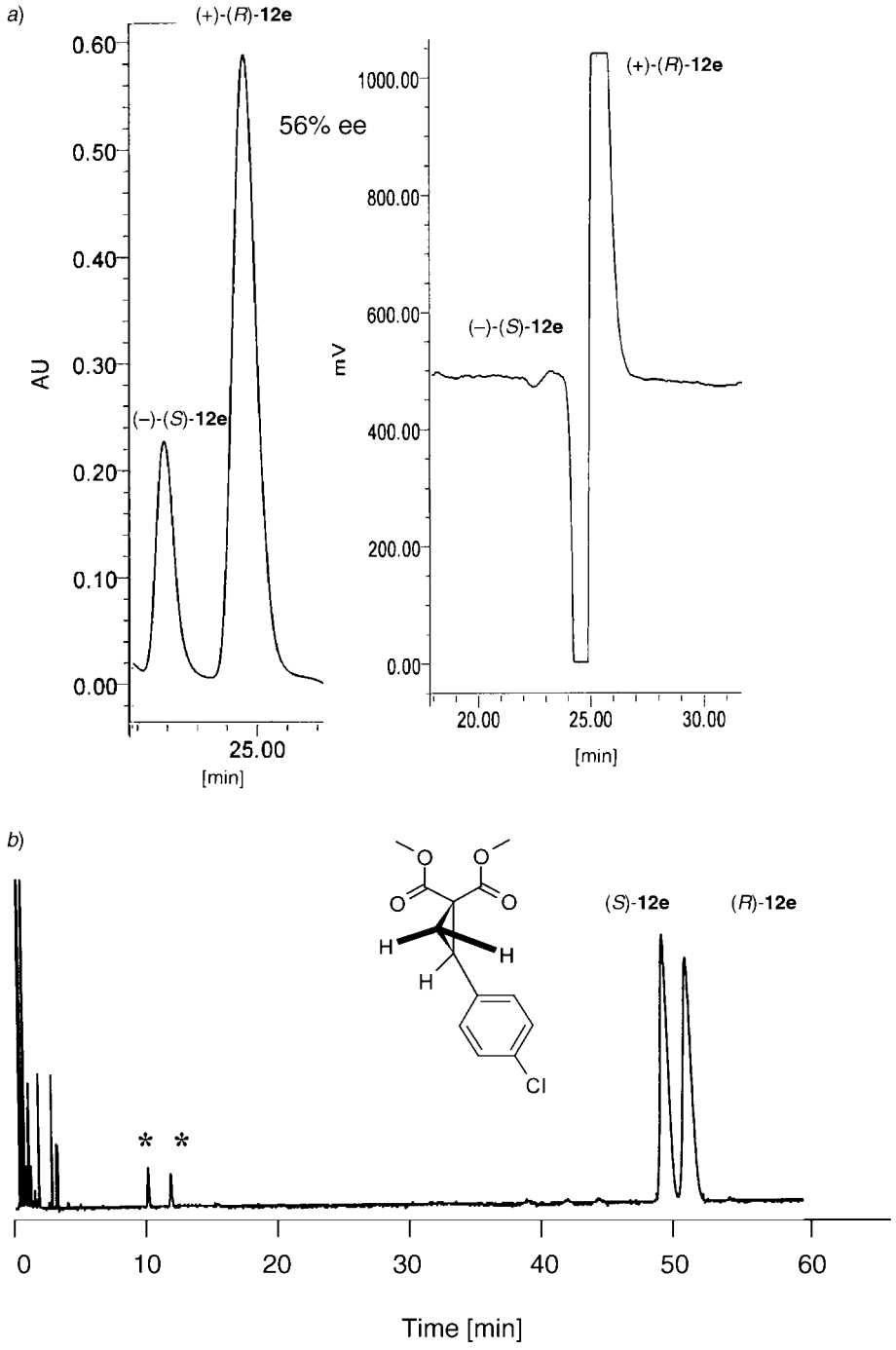
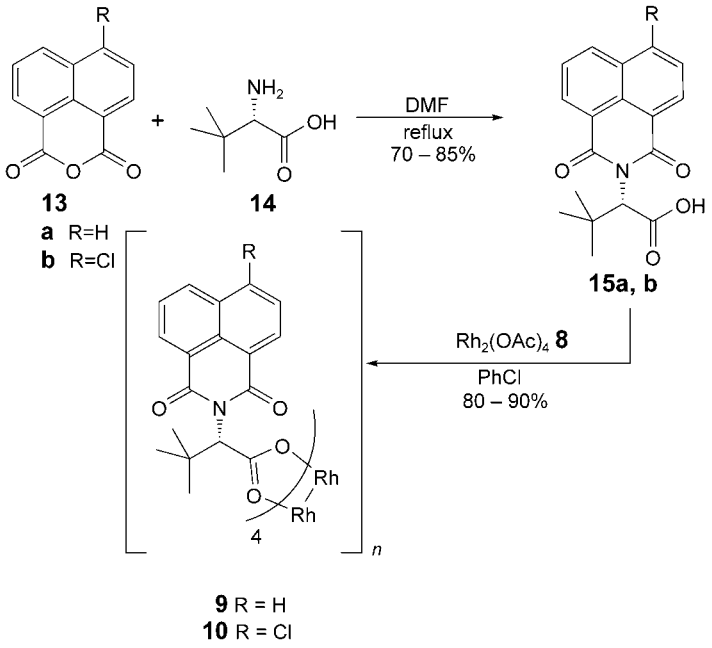
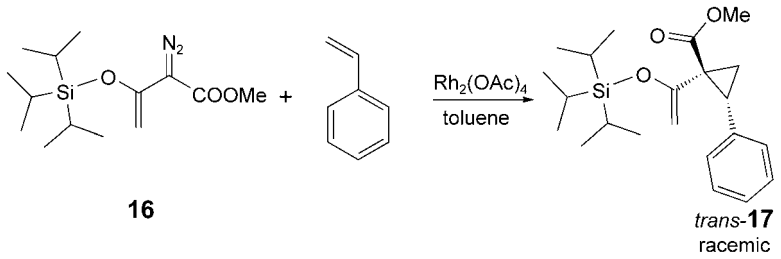


Fig. 7. *Analysis of* **12e**: a) *HPLC and* b) *GC*. Cyclopropanation conditions: **5** + **3e**, ylide precursor **7**, catalyst **10**. * = By-products (see *Chapt. 2.3*).

Scheme 2. *Synthesis of Chiral Rhodium(II) Catalysts*

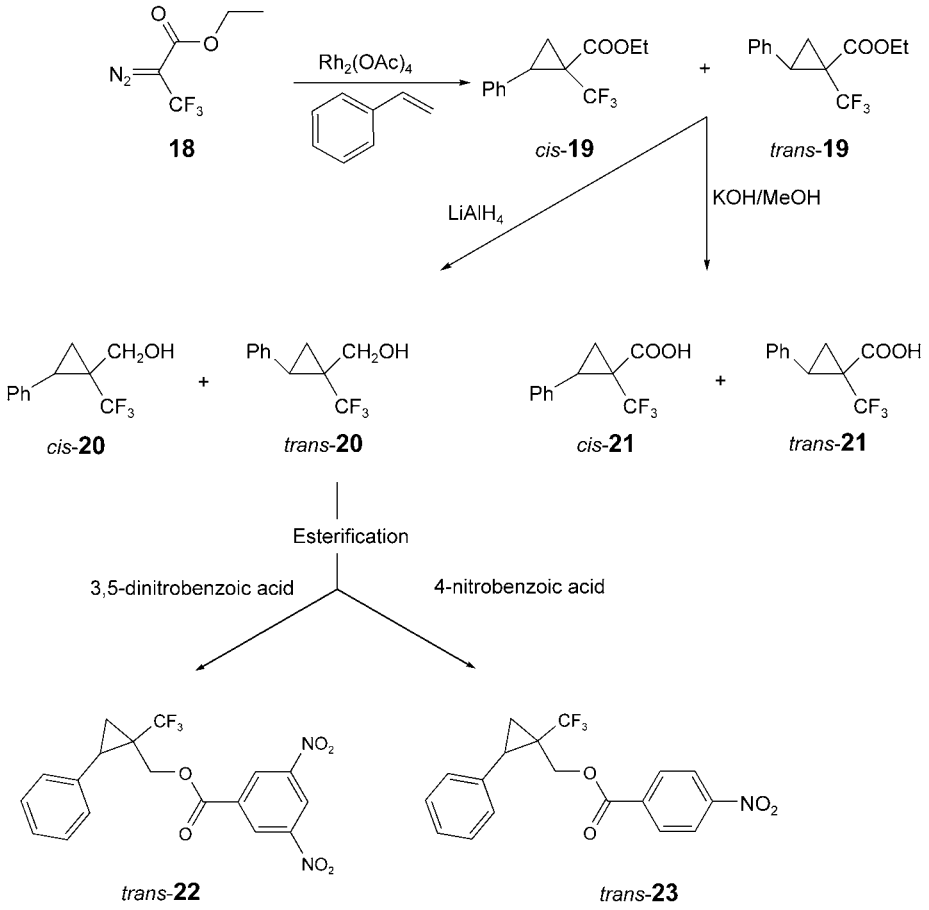


Scheme 3. *Intermolecular Cyclopropanation of Styrene with 2-Diazo-3-(silyloxy)but-3-enoate* **16**



The preference for the formation of *trans*-**25** where the phenyl and ethoxycarbonyl groups are *cis*-positioned (see *Scheme 5*) is of some interest since, in the cyclopropanation with ethyl diazoacetate, the *trans*-isomer usually predominates. However, upon protiodesilylation of *cis*/*trans*-**25a** 18 : 82 with Bu_4NF, epimerization occurred and the desilylated cyclopropanecarboxylates *cis*/*trans*-**26** were isolated in an equal entantiomer ratio of 48 : 48 (*cf. Scheme 6* and *Fig. 9*, *b* – *d*), even when the reaction was carried out at $-78°$. The enantioselective GC separation of the enantiomers of the silylated cyclopropanecarboxylates *cis*/*trans*-**25a** failed but could be achieved upon their reduction with $LiAlH_4$ to a diastereoisomer mixture *cis*/*trans*-**27**. The relative configurations of the diastereoisomeric alcohols *cis*/*trans*-**27** were verified by comparison of the NMR signals of the CH_2OH group with those reported for the trimethylsilyl

Scheme 4. *Intermolecular Cyclopropanation of Styrene with 2-Diazo-3,3,3-trifluoropropanoate* **18**



analogues [18]. The latter failed to undergo protiodesilylation upon exposure to Bu_4NF, even upon prolonged reaction times (*cf. Fig. 10*).

2.2. *Intramolecular Cyclopropanation.* The intramolecular cyclopropanation of allyl diazo(triethylsilyl)acetates **28**, **30**, and **33** were carried out in the presence of chiral rhodium(II) catalyst $[Rh_2\{(S)\text{-nttl}\}_4]$ (**9**) in toluene affording the corresponding cyclopropanes **29**, **31**, and **34** with 37, 8 and 32% ee, respectively (*Scheme 7* and *Fig. 11*). The diazo decomposition of **28** generated by-products whose structure could not be established. However, a β-lactone may be implicated (see below). The diazo decomposition of 2-methyl substituted diazoacetate **30**, in turn, proceeded to **31** in mediocre yield of *ca.* 20% with up to 8% ee, and was accompanied by the formation of the β-lactone **32** (15–18% yield). In contrast, the reaction proceeded well with the (2*Z*)-pent-2-enyl diazoester **33** resulting in yields of *ca.* 70% of cyclopropane **34** with 32% ee. The structure of **34** was confirmed *via* protiodesilylation with Bu_4NF in THF to

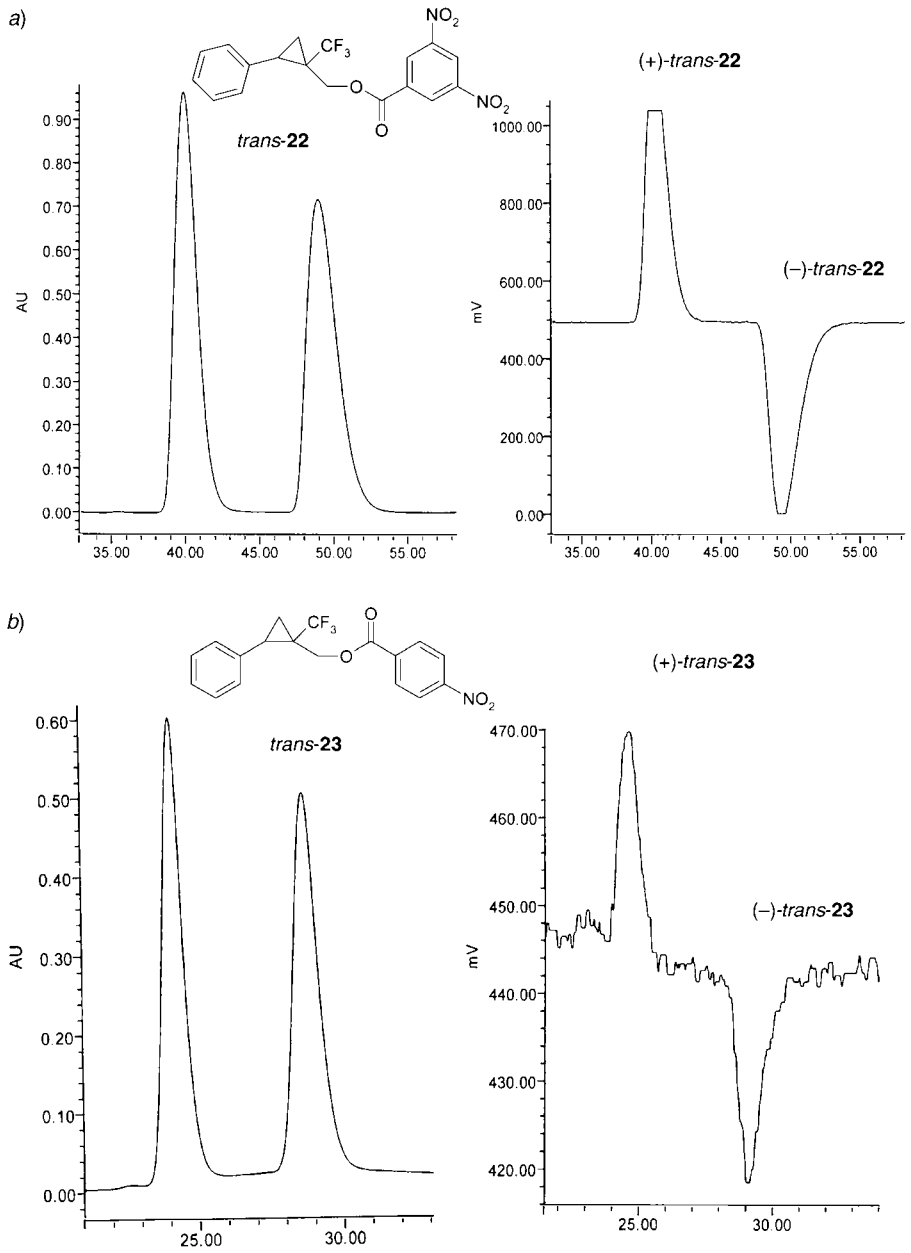
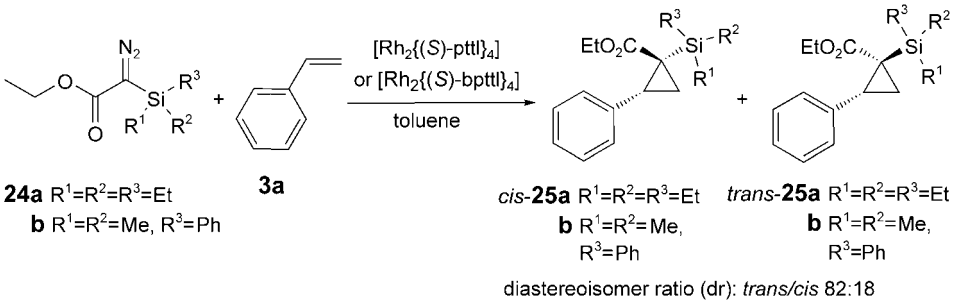
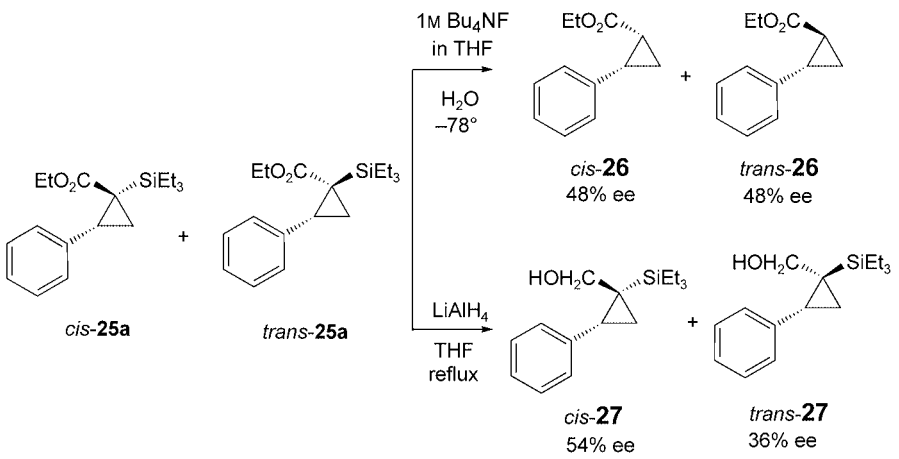


Fig. 8. *HPLC Analysis of esters* trans-**22** *and* trans-**23**, *obtained by cyclopropanation of styrene with diazopropanoate* **18** *and further transformations* (see *Scheme 4*)

Scheme 5. *Intermolecular Cyclopropanation of Styrene with Diazo(triethylsilyl)acetate* **24a** *and Diazo(dimethylphenylsilyl)acetate* **24b**



Scheme 6. *Desilylation and Reduction of* cis/trans-*2-Phenyl-1-(triethylsilyl)cyclopropanecarboxylates* cis/trans-**25a**



the known **35** with 22% ee, which was used for the determination of the ee. The absolute configuration of **34** was determined according to [18].

2.3. *Enantioselective Separation of Cyclopropane Derivatives: Enantioselective Analysis* (GC *vs.* HPLC). For efficient monitoring of the reaction progress, enantioselective gas chromatography (GC) was first used for the determination of the enantiomer excess of the resulting cyclopropane derivatives. The enantiomer separation of the cyclopropane derivatives is demonstrated by using *Chirasil-β-Dex* as a chiral stationary phase for enantioselective gas chromatography. The reactions were monitored qualitatively and quantitatively with GC/MS and dodecane as internal standard. Thus, after a simple filtration and a single GC run, information regarding the yield of the resulting cyclopropane derivatives and the selectivity of the catalyst is provided without further workup.

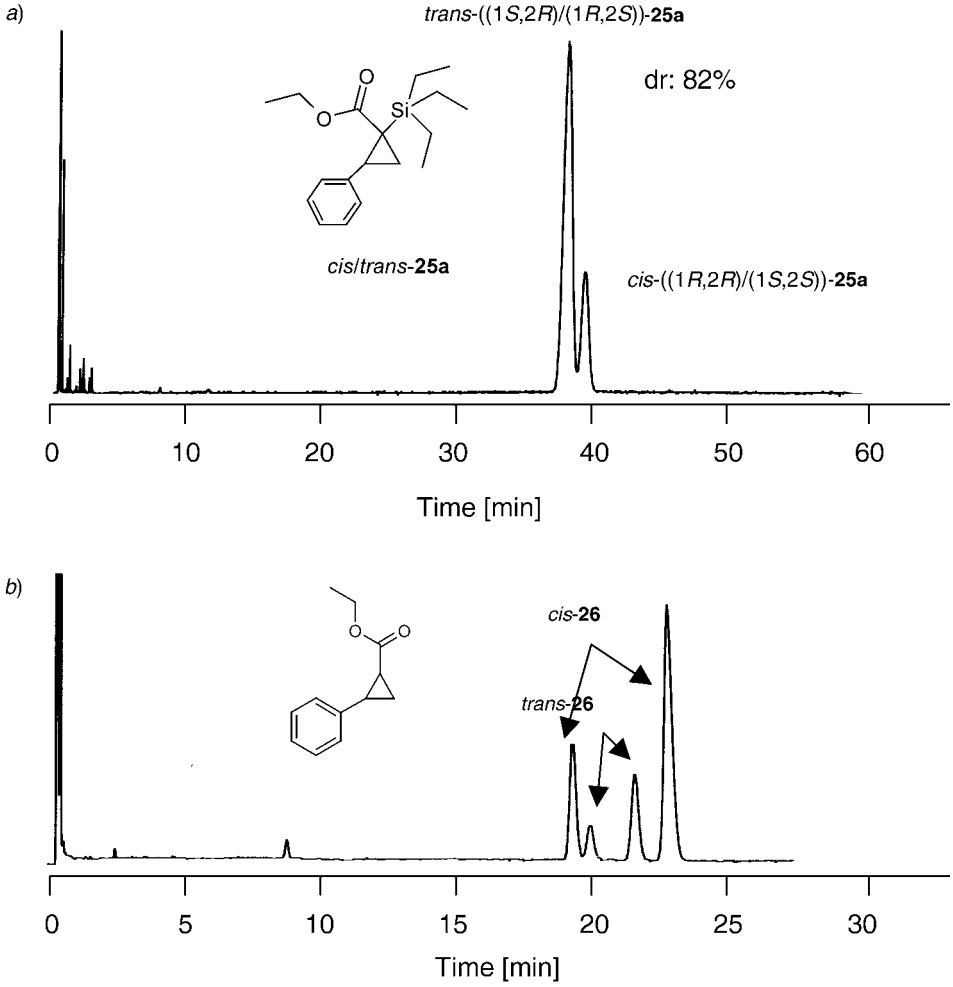


Fig. 9. *GC Separation* a) *of the diastereoisomers* cis/trans-**25b**, b) *of the diastereoisomers* cis/trans-**26**, c) *of the enantiomers of* cis-**26**, *and* d) *of the enantiomers of* trans-**26**. The silylated *cis*/*trans*-**25a** were obtained by cyclopropanation (see *Scheme 5*) and the desilylated *cis*- and *trans*-**26** by subsequent desilylation (*Scheme 6*). Note the effect of the silyl moiety on the separation: enantiomers of silylated *cis*/*trans*-**25a** were not separated, while those of *cis*- and *trans*-**26** were baseline-separated (*Fig. 9,b–d*).

Despite the baseline GC separation, some of the cyclopropane derivatives **11** and **12** from *Meldrum*'s acid (**4**) and dimethyl malonate (**5**) underwent a thermal decomposition on GC affording as by-products the cyclopropanedicarboxylic acid derivatives (*cf. Fig. 3–7*) in *ca.* 16% yield. The latter were identified qualitatively and quantitatively by GC/MS. The enantiomeric cyclopropanedicarboxylic acid derivatives resulting from the thermal decomposition on GC were baseline-separated in some cases (*e.g.*, by-products of **11a**, **b**, **d**, **e** and **12e**, **f**) while others were not (*cf. Fig. 3–7*).

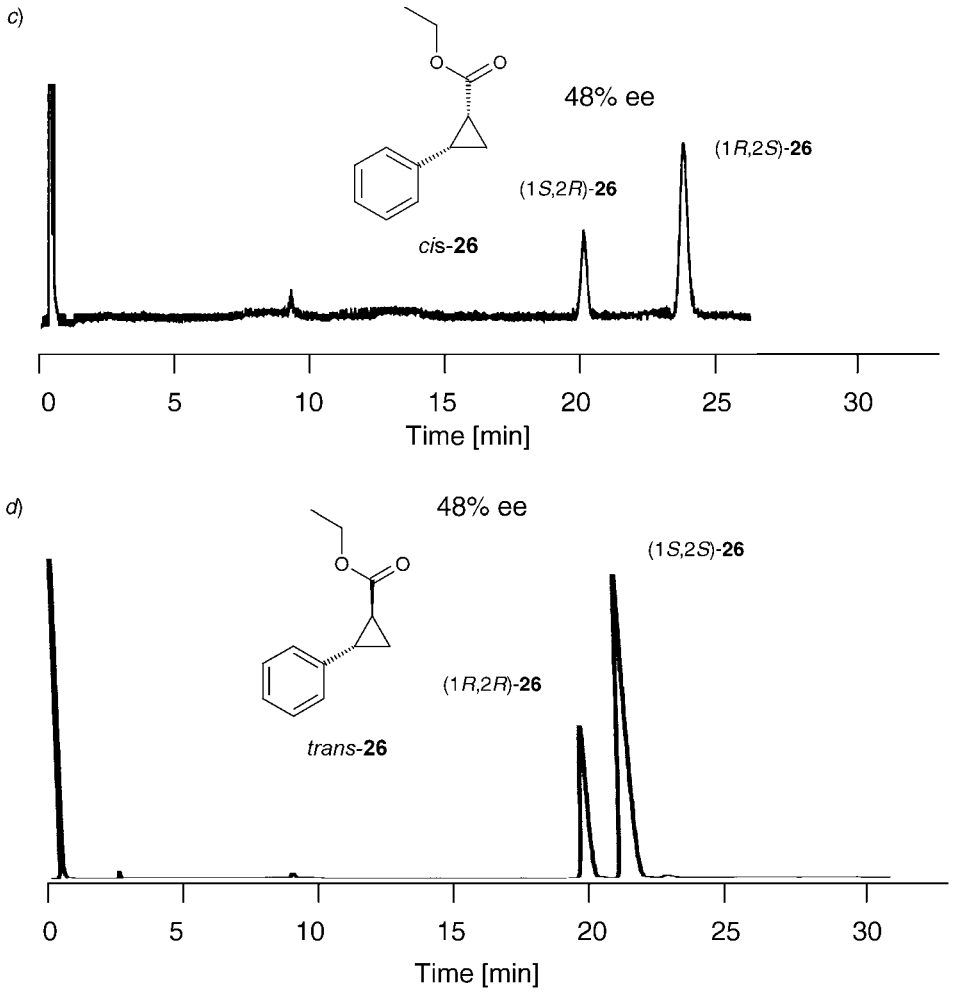


Fig. 9 (cont.)

In addition, some compounds, *i.e.*, *trans*-**22** and *trans*-**23**, were not separated at all by GC. The effect of the silyl moiety on the chiral separation was noticed in case of the silylated cyclopropane derivatives **25** and the corresponding desilylated **26** (*cf. Schemes 5* and *6* and *Fig. 9*). Only the silylated diastereomeric *cis*/*trans*-**25** could be separated but not their enantiomers (*Fig. 9*,*a*). The four enantiomers of the corresponding desilylated *cis*/*trans*-**26** were baseline separated (*cf. Fig. 9*,*b* – *d*). Other cyclopropane derivatives containing an alcohol moiety were successfully resolved with reasonable resolution and separation factor (*cf. Fig. 10*). Among the different classes of cyclopropane derivatives separated by GC, **12a**, **17**, and *trans*-**20** were the fastest eluted enantiomers with resolutions (R_s) of 4.29, 1.80, and 3.37 and separation factors (α) of 1.10, 1.04, and 1.08, respectively. The latter can be used in the high-throughput screening to discover the enantioselective catalyst in a combinatorial approach. The

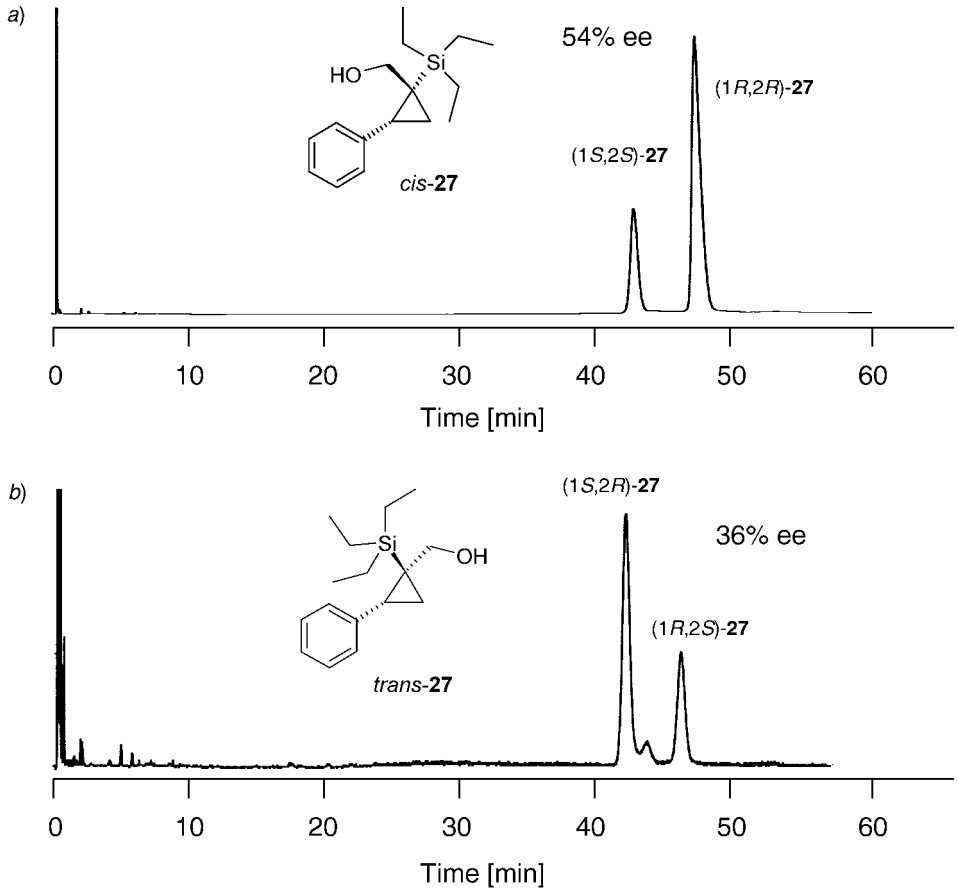


Fig. 10. *GC Separation*[a]) *of the enatiomers of* cis-**27** *and* [b]) *of the enantiomersof* trans-**27**. The silylated *cis*- and *trans*-**27** were obtained by cycloproparation (→ cis/trans-**25a**, *Scheme 5*) followed by reduction (*Scheme 6*).

chromatographic parameters including the separation factor (α) and the resolution (R_s) of the GC enantiomer separation of the prepared cyclopropane derivatives are summarized in *Table 1*.

To avoid the thermal decomposition by GC and to achieve a base-line separation of all cyclopropane derivatives concomitant with the determination of the sign of their optical rotations, we used a HPLC workstation equipped with a sensitive optical-rotation detector for the monitoring of the optical activity of racemic and enantiomer-enriched cyclopropane derivatives resulting from the Rh^{II}-catalyzed asymmetric carbene-transfer reactions. The polysaccharide chiral stationary phase was *Chiralcel-OD* (=cellulose tris(3,5-dimethylphenylcarbamate) and the mobile phase was hexane/^{i}PrOH 90:10 (*v*/*v*) for all **11** and **12** and 99:1 (*v*/*v*) for **17**, **22**, and **23** (see *Exper. Part*). The chromatographic parameters of the HPLC separation of cyclopropane derivatives are summarized in *Table 2*. The absolute configurations of **11**, **12**, and **17** were

Scheme 7. *Rhodium(II)-Catalyzed Intramolecular Cyclopropanation of Allyl Diazo(triethylsilyl)acetates*

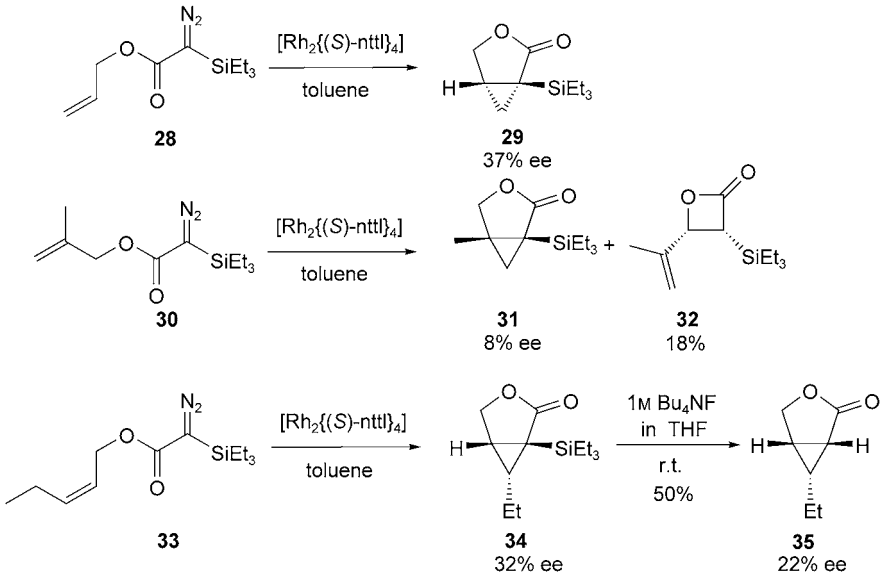


Table 1. *GC Separation of Racemic Cyclopropane Derivatives on* Chirasil-β-Dex: *Oven Temperature* (T), *Retentiom Time* (t_R), *Resolution* (R_s), *and Separation Factor* (α)

	T[a])	t_R (S)	t_R (R)	R_s	α
11a	130°	37.2	38.8	1.89	1.04
11b	140°	33.0	35.1	2.84	1.06
11c	100°	14.8	15.7	2.33	1.05
11d	85°	28.7	29.9	1.63	1.04
11e	130°	21.9	23.1	2.22	1.26
12a	130°	8.7	9.6	4.29	1.10
12b	120°	22.6	24.1	2.65	1.06
12c	80°	13.7	15.9	1.14	1.02
12d	75°	25.9	27.2	1.93	1.05
12e	115°	48.5	50.2	1.45	1.03
12f	140°	22.4	23.8	2.60	1.06
trans-**17**	130°	23.2	25.7	4.89	1.10
trans-**20**	120°	4.8	5.2	3.37	1.08
cis-**21**	150°	15.4	17.7	5.46	1.14
trans-**22**	n.s.[b])	n.s.[b])	n.s.[b])	n.s.[b])	n.s.[b])
trans-**23**	n.s.[b])	n.s.[b])	n.s.[b])	n.s.[b])	n.s.[b])
cis/*trans*-**25a**	125°	37.4 (*trans*)	38.6 (*cis*)	1.05	1.03
cis/*trans*-**25b**	150°	29.4 (*trans*)	30.7 (*cis*)	1.77	1.04
trans-**26**	100°	19.7	21.3	3.28	1.08
cis-**27**	130°	42.4	46.7	3.80	1.10
trans-**27**	130°	41.6	45.6	3.71	1.09

[a]) Head pressure 150 KPa, injector temperature 200°, and FID temperature 250°. [b]) n.s. = not separated by GC.

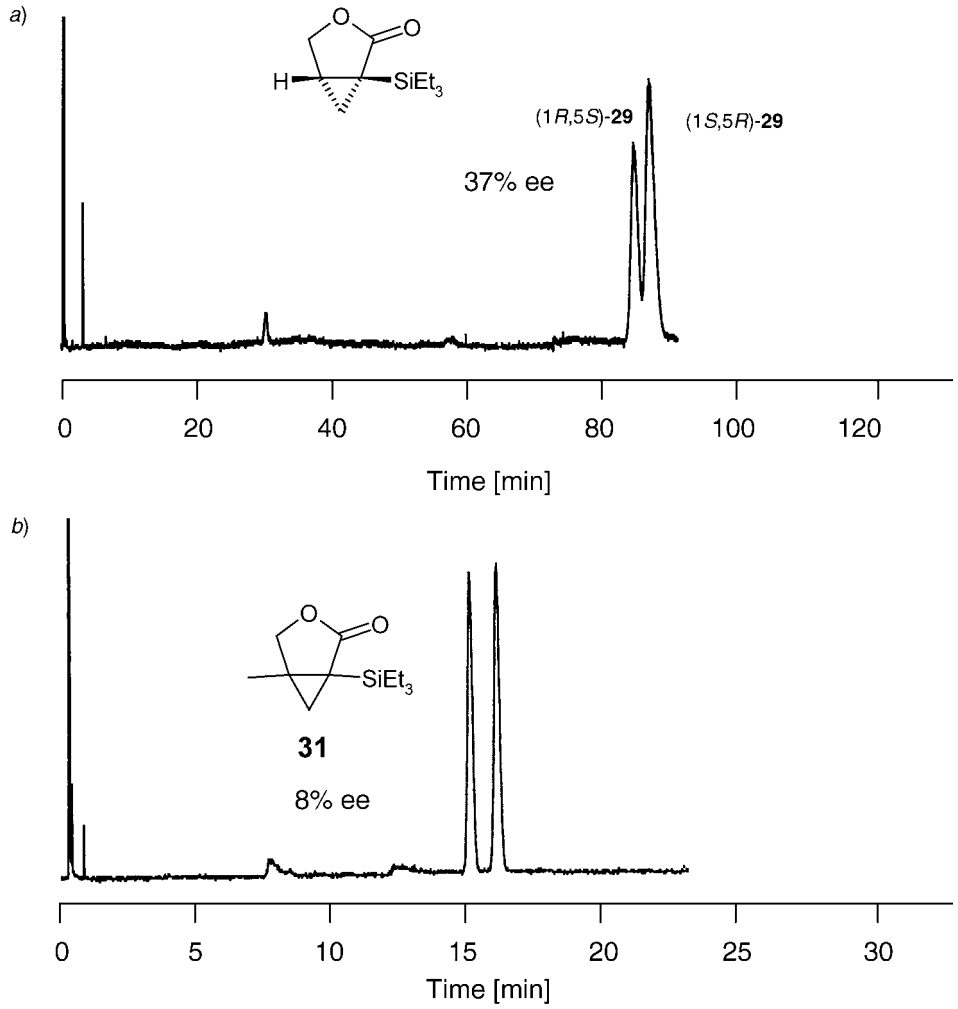


Fig. 11. *GC Separation of the enantiomers of* a) **29**, b) **31**, c) **34**, *and* d) **35**. The silylated **29**, **31**, and **34** were obtained by cyclopropanation and **35** by subsequent desilylation (*Scheme 7*). Note the effect of the silyl moiety on the separation *Fig. 11, c vs. d*.

determined by previously reported procedures; however, those of **22** and **23** are not yet known.

3. Conclusion. – A set of cyclopropane derivatives were prepared *via* inter- and intramolecular cyclopropanation catalyzed by achiral and chiral rhodium(II) catalysts. Both the diazo and ylide approach were utilized to access the cyclopropanes. The advantages of the liquid-chromatographic separation of cyclopropane enantiomers over the gas-chromatographic analysis of the same compounds were demonstrated. The results revealed that HPLC equipped with a chiralyzer might be a useful tool in the

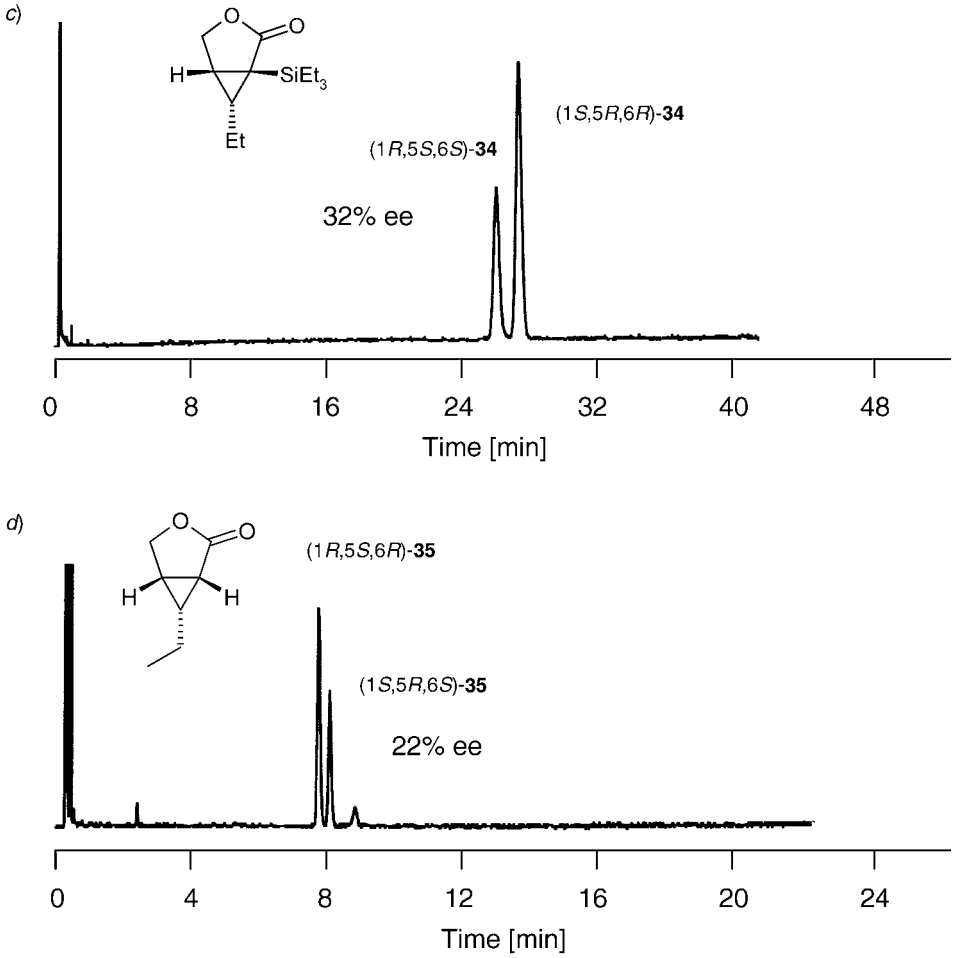


Fig. 11 (cont.)

determination of the enantiomer excess as well as in identifying the absolute configuration of cyclopropanes prepared *via* metal-catalyzed carbene-transfer reaction.

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Experimental Part

1. *General.* All olefins were commercially available and distilled prior to use. *Meldrum*'s acid (**4**), dimethyl malonoate (**5**), bis(acetato-κO)phenyliodine ([PhI(OAc)$_2$]; **6**), 1,8-naphthalic anhydride (=1*H*,3*H*-naphtho[1,8-*cd*]pyran-1,3-dione; **13a**) and its 4-Cl-substituted derivative **13b** were purchased from *Acros Organics* (Geel, Belgium). Iodosylbenzene (PhI=O; **7**), [Rh$_2${(*S*)-nttl}$_4$] (**9**) and [Rh$_2${4-Cl-(*S*)-nttl}$_4$] (**10**) were prepared as described below. [Rh$_2$(OAc)$_4$] (**8**) was purchased from *Pressure Chemical* (Pittsburgh, USA). Solvents were dried prior use. HPLC-Grade hexane and propan-2-ol were purchased from *Fluka* (Buchs,

Table 2. *HPLC Separation of Racemic Cyclopropane Derivatives on* Chiralcel OD *at Room Temperature: Retentiom Time* (t_R), *Resolution* (R_s) *and the Separation Factor* (α)[a])

	t_R (*S*)-(−)	t_R (*R*)-(+)	R_s	α
11a[b])	18.4	22.1	3.19	1.21
11b[b])	16.9	19.9	2.57	1.19
11c[b])	27.1	29.2	2.61	1.20
11d[b])	10.9	11.1	1.03	1.01
11e[b])	19.7	24.1	3.24	1.23
12a[b])	18.7	19.6	3.20	1.11
12b[b])	24.3	25.9	2.62	1.02
12c[b])	–	–	–	–
12d[b])	–	–	–	–
12e[b])	21.9	24.5	1.80	1.12
12f[b])	25.3	26.7	2.64	1.05
trans-**17**[c])	23.2 (1*R*,2*S*)	25.7 (1*S*,2*R*)	2.96	1.22
trans-**22**[c])	38.4 (n.d.)	46.8 (n.d.)	2.19	1.22
trans-**23**[c])	24.4 (n.d.)	29.1 (n.d.)	3.11	1.20

[a]) n.d. = Absolute configuration not determined. [b]) Mobile phase: ^{i}PrOH/hexane 10 : 90 (*v*/*v*), flow rate 0.3 ml/min. [c]) Mobile phase: hexane 1 : 99 (*v*/*v*), flow rate 0.3 ml/min.

Switzerland). Diazo compounds were synthesized as described below [18–20]. CC = column chromatography; FC = flash chromatography. IR Spectra: *Shimadzu FT-IR-9100* spectrometer. ^{1}H- and ^{13}C-NMR Spectra: *Bruker* (400 MHz) spectrometer; δ(H) in ppm rel. to the internal standard $SiMe_4$ (= 0 ppm), *J* in Hz. HPLC: *Waters* binary pump, model *1525* (Milford, MA, USA), equipped with a dual λ absorbance detector model *2487*, an autosampler model *717plus*, and an optical-rotation detector (*Chiralyzer*, *IBZ Messtechnik GmbH*, Hannover, Germany) operating at r.t.; UV detector set at 245 nm; *Chiralcel OD* column (4.6 × 250 mm coated on 10-μm silica gel) from *Daicel Chemical Industries Ltd.* (Tokyo, Japan), data collection with Breeze software from *Waters*; the mobile phase was filtered through a *Millipore* membrane filter (0.2 μm) from *Nihon Millipore* (Yonezawa, Japan) and degassed before use; the buffer was adjusted with a pH meter from *Orion Research* (model *611*; *Orion Research Inc.*, USA); flow 0.3 ml/min. GC: *Hewlett-Packard 580* (Waldbronn, Germany) equipped with a flame-ionization detector (FID); the chiral stationary phase, permethylated pent-5-enyl-β-cyclodextrin (20% (*w*/*w*)), was dissolved in dimethylpolysiloxane containing 5% Si–H groups (*Gelest*, *ABCR GmbH & Co.*, Karlsruhe, Germany) and coated on a 20 m × 0.25 mm fused-silica capillary column (0.25-μm film thickness) according to [12], injector temp. 200°, FID temp. 250°, oven temp. varying depending on the structure of the cyclopropane; H_2 as carrier gas (150 KPa column-head pressure).

2. *Catalyst [Rh$_2$[(*S*)-nttl]$_4$]* (**10**). *(αS)-6-Chloro-α-(1,1-dimethylethyl)-2,3-dihydro-1,3-dioxo-1*H-*naphtho[1,8-*cd*]pyridine-2-acetic Acid* (**15b**). A mixture of L-*tert*-leucine (**14**; 1.01 g, 7.72 mmol) and 4-chloro-1,8-naphthalic anhydride (2.0 g, 8.6 mmol; **13b**) in DMF (25 ml) was heated to reflux for 1.0 h under N_2. The DMF was removed by distillation, and the solid residue was purified by FC (SiO_2, AcOEt/MeOH 99 : 1): 2.56 g (86%) of **15b**. Colorless solid. M.p. 122°. $[\alpha]_D^{24} = -53$ (*c* = 0.1, $CHCl_3$). IR (KBr): 3088*w*, 2956*w*, 2912*w*, 2862*w*, 1736*m*, 1703*m*, 1660*s*, 1585*m*, 1569*m*, 1366*s*, 1341*s*, 1234*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.11 (*s*, 9 H); 5.48 (*s*, 1 H); 7.69 (*d*, *J* = 8, 1 H); 7.74 (*t*, *J* = 8, 1 H); 8.40–8.45, (*m*, 1 H); 8.44 (*d*, *J* = 8, 1 H); 8.55–8.65 (*m*, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 28.5 (*q*); 36.1 (*s*); 59.8 (*d*); 124.2 (*s*); 124.9 (*s*); 128.9 (*s*); 129.1 (*d*); 130.7 (*d*); 130.8 (*d*); 131.7 (*s*); 131.8 (d); 132.3 (*d*); 132.7 (*s*); 163.8 (*s*); 164.1 (*s*); 173.6 (*s*). MS: 345, 347 (0, M^+), 289 (26, $[M - C_4H_8]^+$), 273 (21), 272 (10), 271 (62), 245 (10), 241 (12), 216 (29), 214 (10), 190 (11), 188 (34), 160 (15), 126 (12), 73 (100), 57 (40). HR-MS: 289.0168 ($C_{14}H_8^{35}ClNO_4^+$; calc. 289.0142), 291.0139 ($C_{14}H_8^{35}ClNO_4^+$; calc. 291.0112).

*Tetrakis{μ-[αS)-6-chloro-α-(1,1-dimethylethyl)-2,3-dihydro-1*H-*naphtho[1,8-*cd*]pyridine-2-acetato-κO:κO′]dirhodium(Rh–Rh)* ([Rh_2{(*S*)-4-Cl-nttl}$_4$]; **10**). Dirhodium(II) acetate ([$Rh_2(OAc)_4$]; 110 mg, 0.25 mol), **15b** (0.82 g, 2.4 mmol), and chlorobenzene (40 ml) were heated under reflux and N_2 in a *Soxhlet* apparatus fitted with a thimble containing dried Na_2CO_3 and sand in a 1 : 1 ratio (removal of AcOH). After 24 h, the solvent was evaporated, and the gummy residue was purified by FC (basic alumina, MeOH): **10** (85%). Green solid. $[\alpha]_D^{24} = +166$ (*c* = 0.1, $CHCl_3$). IR (KBr): 2956*w*, 1709*s*, 1667*s*, 1608*m*, 1591*m*, 1575*m*, 1399*m*, 1366*m*, 1344*s*. ^{1}H-NMR

(400 MHz, $CDCl_3$): 1.31 (*s*, 9 H); 5.79 (*s*, 1 H); 8.28–8.30 (*m*, 2 H); 8.32 (*d*, *J* = 8, 1 H); 8.43 (*d*, *J* = 8, 1 H); 8.51–8.60 (*m*, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 28.8 (*q*); 29.4 (*q*); 29.7 (*q*), 36.2 (*s*); 62.1 (*d*); 121.8 (*s*), 123.2 (*s*); 123.3 (*s*); 127.4 (*d*); 127.8 (*d*); 128.4 (*d*); 128.9 (*s*); 131.8 (*d*); 132.2 (*d*); 138.5 (*s*); 162.4 (*s*); 162.7 (*s*); 186.8 (*s*). MALDI-MS: 1605.0680 ($C_{72}H_{60}^{35}Cl_4N_4NaO_{16}Rh_2^+$; calc. 1605.0768).

3. *Intermolecular Cyclopropanation of Olefins with* Meldrum's *Acid* (**4**): *General Procedure:* CH_2Cl_2 (10 ml) was added by syringe to a mixture of **4** (2.10 mmol, 1 equiv.), **6** (1.4 equiv.), $[Rh_2(OAc)_4]$ or $[Rh_2\{(S)\text{-nttl}\}_4]$ (5 mol-%), Al_2O_3 (2.3 equiv.), and 4-Å molecular sieves (250 mg), followed by the addition of the olefin (10 equiv.). The mixture was thermostatted in an oil bath to 30° and stirred under Ar. Then 100-µl samples were taken after several time intervals. The samples were filtered by using a syringe filter holder (0.2-µm pore size), and the org. phase was diluted with CH_2Cl_2 (100 µl) and analyzed by GC. The reaction progress was monitored qualitatively and quantitatively by GC/MS (dodecane as internal standard). When maximum conversion was reached, the reaction was terminated by filtration through *Celite*. The residue on the *Celite* was washed twice with CH_2Cl_2. Evaporation of the combined filtrates followed by CC (silica gel, pentane/AcOEt 2:1 afforded the desired cyclopropane derivatives **11a–d**.

Data of **11a–f**: In agreement with those reported in [**11**].

4. *Iodosylbenzene* (PhI=O; **7**). To finely powdered **6** (32.2 g, 0.10 mol) was added 3N NaOH (150 ml) within 5 min under vigorous stirring, and the lumps of solid which formed where crushed with a spatula. The mixture was stirred for 45 min and then diluted with H_2O (100 ml). The crude yellow solid was collected by filtration, washed with H_2O (3 × 100 ml), and dried under vacuum. It was suspended in $CHCl_3$ (75 ml), macerated, and separated by filtration. The crude **6** was air-dried and used without further purification.

5. *Intermolecular Cyclopropanation of Olefins with Dimethyl Malonate* (**5**): *General Procedure.* To a mixture of **7** (1.4 equiv.), olefin (10 equiv.), MgO (2.3 equiv.), rhodium(II) catalyst (5 mol-%), and 4-Å molecular sieves (250 mg) in CH_2Cl_2 (10 ml), **5** (0.01 mol) was added. The mixture was stirred under Ar for 24 h. Then, 100-µl samples were taken after several time intervals and analyzed as described in *Exper. 3*. Workup as described in *Exper. 3* and CC (silica gel, heptane/AcOEt 5:1) afforded the desired cyclopropane derivatives **12a–f**.

Dimethyl 2-Phenylcyclopropane-1,1-dicarboxylate (**12a**): ^{1}H-NMR (400 MHz, $CDCl_3$): 1.71 (*dd*, *J* = 4, 4, 1 H); 2.18 (*dd*, *J* = 4, 4, 1 H); 3.21 (*t*, *J* = 8, 1 H); 3.34 (*s*, 3 H); 3.76 (*s*, 3 H); 7.19–7.28 (*m*, 5 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 19.1 (*t*); 32.6 (*d*); 37.2 (*s*); 52.2 (*q*); 52.6 (*q*); 127.4 (*d*); 128.2 (*d*); 128.4 (*d*); 134.5 (s); 164.8 (*s*); 169.4(*s*). HR-MS: 234.0897 ($C_{13}H_{14}O_4^+$; calc. 234.0892).

Dimethyl 2-(4-Methylphenyl)cyclopropane-1,1-dicarboxylate (**12b**): ^{1}H-NMR (400 MHz, $CDCl_3$): 1.79 (*dd*, *J* = 4, 4, 1 H); 2.18 (*dd*, *J* = 8, 8, 1 H); 2.20 (*s*, 3 H); 3.21 (*t*, *J* = 12, 1 H); 3.42 (*s*, 3 H); 3.81 (*s*, 3 H); 7.15 (*s*, 4 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 19.0 (*t*); 20.9 (*q*); 32.3 (*d*); 37.0 (*s*); 52.0 (*q*); 52.6 (*q*); 128.1 (*d*); 128.7 (*d*); 131.3 (*s*); 136.9 (*s*); 166.9 (*s*); 170.1 (*s*). HR-MS: 248.10530 ($C_{14}H_{16}O_4^+$; calc. 248.10491). Anal. calc. for $C_{14}H_{16}O_4$ (248.28): C 67.73, H 6.50; found: C 67.50, H 6.58.

Dimethyl 2-Propylcyclopropane-1,1-dicarboxylate (**12c**): ^{1}H-NMR (400 MHz, $CDCl_3$): 0.90 (*t*, *J* = 7, 3 H); 1.09–1.19 (*m*, 1 H); 1.37–1.52 (*m*, 5 H); 3.34 (*s*, 3 H); 3.76 (*s*, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 13.7 (*q*); 21.5 (*t*); 22.2 (*t*); 28.2 (*d*); 30.6 (*t*); 33.9 (*s*); 52.2 (*q*); 52.4 (*q*); 168.8 (*s*); 171.4(*s*).

Data of **12d**: In agreement with those reported in [**10**].

Dimethyl 2-(4-Chlorophenyl)cyclopropane-1,1-dicarboxylate (**12e**): ^{1}H-NMR (400 MHz, $CDCl_3$): 1.72 (*dd*, *J* = 4, 4, 1 H); 2.13 (*dd*, *J* = 8, 1 H); 3.16 (*t*, *J* = 8, 1 H); 3.40 (*s*, 3 H); 3.79 (*s*, 3 H); 7.12 (*d*, *J* = 8, 2 H); 7.23 (*d*, *J* = 8, 2 H). ^{13}C-NMR (100 MHz, $CDCl_3$); 18.1 (*t*); 30.7 (*d*); 36.2 (*s*); 51.9 (*q*); 52.4 (*q*); 127.6 (*d*); 129.0 (*d*); 132.1 (*s*), 132.3 (*s*); 165.8 (*s*); 168.9 (*s*). HR-MS: 268.0492 ($C_{13}H_{13}^{35}ClO_4^+$; calc. 268.0502). Anal. calc. for $C_{13}H_{13}ClO_4$ (268.70): C 58.11, H 4.88; found: C 58.0, H 4.70.

Dimethyl 2-(4-Bromophenyl)cyclopropane-1,1-dicarboxylate (**12f**): ^{1}H-NMR (400 MHz, $CDCl_3$): 1.75 (*dd*, *J* = 4, 4, 1 H); 2.15 (*dd*, *J* = 8, 8, 1 H); 3.21 (*t*, *J* = 8, 1 H); 3.42 (*s*, 3 H); 3.81 (*s*, 3 H); 7.08 (*d*, *J* = 4, 2 H); 7.40 (*d*, *J* = 8, 2 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 19.1 (*t*); 32.6 (*d*); 37.2 (*s*); 52.2 (*q*); 52.6 (*q*); 120.4 (*s*); 129.1 (*d*); 129.9 (*d*); 132.6 (*s*); 165.8 (*s*); 168.9 (*s*). MS: 314 (14, M^+), 312 (14, M^+), 282 (82), 280 (28), 250 (20), 148 (19), 202 (19), 201 (100), 199 (69), 195 (26), 193 (26), 173 (20), 170 (27), 145 (27), 129 (13), 115 (62), 114 (23), 113 (10), 103 (12), 102 (10), 89 (16), 77 (14), 63 (17), 59 (45), 51 (10). HR-MS: 312.0010 ($C_{13}H_{13}^{79}BrO_4^+$; calc. 311.9997), 313.9998 ($C_{13}H_{13}^{81}BrO_4^+$; calc. 313.9977). Anal. calc. for $C_{13}H_{13}BrO4$ (311.9): C 50.86, H 4.16; found: C 50.64, H 4.10.

6. *Intermolecular Cyclopropanation of Styrene with Methyl 2-Diazo-3-[(triisopropylsilyl)oxy]but-3-enoate* (**16**): *Methyl 2-Phenyl-1-{1-[(triisopropylsilyl)oxy]ethenyl}cyclopropanecarboxylate* (*trans*-**17**). The rhodium catalyst (0.008 mmol) was activated by heating in *vacuo*, and dissolved in toluene (3 ml). After addition of styrene (730 mg, 7 mmol), the mixture was cooled to 0°, and **16** (208 mg, 0.70 mmol) in toluene (2 ml) was added

dropwise. After the addition, stirring was continued for 1 h. The solvent was evaporated and the residue purified by FC (SiO_2, Et_2O/pentane 5:95): *trans*-**17** (60%). IR (KBr): 2955*w*, 2868*w*, 1747*s*, 1608*s*, 1451*w*, 1475*w*, 1349*s*, 1266*s*, 1214*s*. 1188*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.84 (*d*, *J* = 7.2, 9 H); 0.94 (*d*, *J* = 7.2, 9 H); 0.96–1.04 (*m*, 3 H); 1.67 (*dd*, *J* = 4.9, 9.15, 1 H); 1.74 (*dd*, *J* = 5.1, 7.4, 1 H); 3.04 (*t*, *J* = 8.5, 1 H); 3.74 (*s*, 3 H); 4.25 (*s*, 1 H); 4.23 (*s*, 1 H); 7.51–7.60 (*m*, 5 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 12.8 (*d*); 17.8 (*q*); 17.9 (*q*); 19.7 (*t*), 31.5 (*d*); 38.6 (*s*); 52.1 (*q*); 93.6 (*t*); 127.3 (*s*); 127.7 (*d*); 128.8 (*d*); 136.4 (*s*); 154.9 (*s*); 173.8 (*s*). MS 359 (2, M^+), 332 (26), 331 (100), 141 (10), 117 (19), 115 (13), 103 (10), 91 (12), 89 (28), 75 (37), 61 (10), 59 (27). HR-MS: 359.2054 ($C_{21}H_{31}O_3Si^+$; calc. 359.2043). Data in agreement with those reported in [19].

7. *Rh^{II}-Catalyzed Carbene Transfer with Ethyl 2-Diazo-3,3,3-trifluoropropanoate* (**18**): *Ethyl* cis/trans-*2-Phenyl-1-(trifluoromethyl)cyclopropanecarboxylate* (*cis*/*trans*-**19**). At r.t., **18** (92 mg, 0.50 mmol) in CH_2Cl_2 (5 ml) was added within 8 h to the olefin (5 mmol) in CH_2Cl_2 (5 ml) containing the appropriate catalyst (5 mol-%). After completion of the reaction, the mixture was passed through a short plug of silica gel, which was subsequently washed with CH_2Cl_2 (20 ml). The solvent was evaporated and the crude product purified by FC: *cis*- and *trans*-**19**.

Data of cis-**19**. IR (film): 3034*w*, 2980*w*, 1725*s*, 1386*m*, 1298*s*, 1225*s*, 1158*s*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 1.32–1.34 (*t*, *J* = 7.3, 3 H); 1.90–1.98 (*m*, 2 H); 3.02–3.05 (*t*, *J* = 9, 1 H); 4.21–4.27 (*m*, 2 H); 7.16–7.32 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$, 100 MHz): 14 (*q*); 16.2 (*t*); 32.4 (*d*); 35 (*q*); 62.4 (*t*); 128.0 (*d*); 129.2 (*d*); 129.6 (*q*); 129.8 (*d*); 133.5 (*s*); 168.5 (*s*). MS: 258 (41), 238 (27), 213 (13), 210 (18), 193 (43), 192 (26), 190 (42), 185 (63), 184 (16), 183 (21), 181 (10), 173 (15), 170 (47), 166 (20), 165 (87), 164 (34), 147 (14), 146 (77), 145 (26), 135 (25), 134 (11), 133 (23), 116 (30), 115 (100), 107 (28), 105 (16), 104 (17), 91 (29), 89 (20), 79 (13), 78 (13), 77 (21), 65 (19), 63 (18), 51 (22). HR-MS: 258.0869 ($C_{13}H_{13}O_2F_3^+$; calc. 258.0868).

Data of trans-**19**. IR (film): 3014*w*, 2984*w*, 1735*s*, 1456*w*, 1386*m*, 1225*s*, 1149*s*, 1158*s*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.82–0.84 (*t*, *J* = 7.4, 3 H); 1.80–1.88 (*m*, 1 H); 2.03–2.06 (*m*, 1 H); 3.01–3.04 (*t*, *J* = 9, 1 H); 4.01–4.07 (*m*, 2 H); 7.12–7.32 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$, 100 MHz): 13.9 (*q*); 15.2 (*t*); 30.4 (*d*); 34 (*q*); 61.4 (*t*); 124.0 (*q*); 128.2 (*d*); 129.2 (*d*); 133.4 (*s*); 167.5 (*s*). MS: 258 (41), 238 (30), 213 (13), 210 (22), 193 (43), 210 (22), 193 (43), 192 (30), 190 (45), 186 (10), 185 (76), 184 (16), 183 (23), 181 (12), 173 (16), 171 (10), 170 (49), 166 (23), 165 (95), 164 (34), 147 (13), 146 (71), 145 (25), 135 (33), 134 (10), 133 (21), 127 (20), 123 (10), 116 (31), 115 (100), 107 (36), 105 (16), 104 (17), 91 (23), 89 (22), 79 (15), 78 (13), 77 (22), 65 (15), 63 (19), 51 (24). HR-MS: 258.0864 ($C_{13}H_{13}O_2F_3^+$; calc. 258.0868).

7. *Hydrolysis of* cis/trans-**19**: cis/trans-*2-Phenyl-1-(trifluoromethyl)cyclopropanecarboxylic Acid* (*cis*/*trans*-**21**). See [20]: *cis*- or *trans*-**19** (34 mg, 0.13 mmol) was hydrolyzed with KOH (15 mg, 0.27 mmol) in MeOH (1.5 ml) at r.t. overnight. The solvent was evaporated, and the residue was treated with 1N HCl and extracted twice with CH_2Cl_2. Recrystallization from CH_2Cl_2/pentane afforded *cis*- or *trans*-**21** in 65–75% yield.

Data of cis-**21**: IR (film): 3034*w*, 2880*w*, 1705*s*, 1440s, 1386*m*, 1298*s*, 1125*s*, 1155*s*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 2.04–2.06 (*m*, 2 H); 3.12–3.15 (*m*, 1 H); 7.36–7.38 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$, 100 MHz): 17 (*t*); 32.8 (*q*); 34 (*d*); 124.0 (*q*); 128.2 (*d*); 128.6 (*d*); 129.8 (*d*); 133.2 (*s*); 176.5 (*s*). MS: 230 (38, M^+), 210 (20), 190 (19), 185 (53), 176 (12), 173 (12), 170 (12), 166 (14), 165 (58), 164 (26), 147 (13), 146 (60), 145 (16), 117 (50), 116 (29), 115 (100), 114 (12), 107 (68), 105 (13), 91 (25), 90 (10), 89 (27), 79 (20), 78 (11), 77 (25), 75 (10), 65 (14), 63 (26), 51 (32). HR-MS: 230.0559 ($C_{11}H_9O_2F_3^+$; calc. 230.0555).

Data of trans-**21**: IR (film): 3036*w*, 2920*m*, 1705*s*, 1460*m*, 1436*m*, 1393*m*, 1318*s*, 1125*s*, 1145*s*, 1078*s*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 2.04–2.06 (*m*, 2 H); 3.12–3.15 (*m*, 1 H); 7.36–7.38 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$, 100 MHz): 16 (*t*); 30.8 (*d*); 34 (*q*); 124.0 (*q*); 127.2 (*d*); 128.4 (*d*); 129.3 (*d*); 132.2 (*s*); 169.5 (*s*). MS: 230 (37, M^+), 210 (21), 190 (19), 185 (53), 176 (12), 170 (11), 166 (13), 165 (58), 164 (26), 147 (14), 146 (61), 145 (16), 137 (10), 133 (17), 117 (14), 116 (29), 115 (100), 114 (13), 107 (78), 91 (24), 90 (12), 89 (28), 79 (25), 78 (13), 76 (10), 75 (11), 65 (18), 63 (32), 62 (11), 51 (41), 50 (16). HR-MS: 230.0557 ($C_{11}H_9O_2F_3^+$; calc. 230.0555).

8. *Reduction of* cis/trans-**19**: cis/trans-*2-Phenyl-1-(trifluoromethyl)cyclopropanemethanol* (*cis*/*trans*-**20**). See [20]: At 0°, *cis*- or *trans*-**19** (72 mg, 0.28 mmol) in THF (2 ml) was added within 30 min by syringe to $LiAlH_4$ (19 mg, 0.5 mmol) in THF. After the addition, the mixture was heated to reflux for 4 h. AcOEt was added to decompose the remaining $LiAlH_4$, followed by H_2O. After extraction with Et_2O, the org. layer was filtered through a plug of silica gel, which was washed with AcOEt (20 ml). The solvent was evaporated and the crude product purified by FC (SiO_2, CH_2Cl_2/pentane 60:40): *cis*- or *trans*-**20**.

Data of cis-**20**. IR (film): 3632*w*, 1387*w*, 1211*m*, 1215*m*, 1223*s*, 1138*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.23–1.35 (*m*, 1 H); 1.64–1.67 (*m*, 1 H); 2.58–2.59 (*t*, *J* = 7.7, 1 H); 3.75 (*d*, *J* = 13, 1 H); 4.02 (*d*, *J* = 13, 1 H); 7.23–7.25 (*m*, 5 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 11.5 (*t*); 26.4 (*d*); 31.4 (*q*); 64.5 (*t*); 125 (*q*); 126.4 (*d*); 129.1 (*d*); 134.6 (*s*). MS: 216 (14, M^+), 198 (22), 186 (18), 185 (16), 166 (16), 165 (25), 164 (11), 130 (11), 129 (100), 128

(16), 117 (21), 116 (10), 115 (24), 107 (15), 104 (14), 91 (26), 89 (10), 78 (13), 77 (14), 63 (10), 51 (15). HR-MS: 216.0784 ($C_{11}H_{11}OF_3^+$; calc. 216.0762).

Data of trans-**20**. IR (film): 3032*w*, 2923*w*, 1698*s*, 1432*m*, 1395*m*, 1311*s*, 1239*m*, 1223*m*, 1149*m*, 1135*s*, 1075*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.33–1.37 (*m*, 1 H); 1.47–1.52 (*m*, 1 H); 2.76–2.79 (*t*, *J* = 9.0, 1 H); 3.65 (*d*, *J* = 13, 1 H); 3.62 (*d*, *J* = 13, 1 H); 7.13–7.21 (*m*, 5 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 11.3 (*t*); 25.4 (*d*); 30.8 (*q*); 61.5 (*t*); 126 (*q*); 127.8 (*q*); 128.4 (*d*); 128.9 (*d*); 134.9 (*s*). MS: 216 (15, M^+), 198 (26), 186 (21), 185 (19), 166 (19), 165 (25), 164 (10), 130 (12), 129 (100), 128 (16), 117 (21), 116 (11), 115 (24), 107 (16), 104 (15), 91 (18), 89 (10), 78 (14), 77 (15), 63 (10), 51 (16). HR-MS: 216.0771 ($C_{11}H_{11}OF_3^+$; calc. 216.0762).

9. *Esterification of* trans-**20**: *General Procedure*. Under anhydrous conditions, a mixture of *trans*-**20** (0.1 mmol) and 3,5-dinitrobenzoic acid or 4-nitrobenzoic acid (0.12 mmol) in pyridine (10 ml) was slowly heated to reflux temp. and maintained under gentle reflux for 2 h and then cooled. H_2O was added, the mixture extracted with AcOEt, the org. layer washed with 1N HCl and H_2O, dried (Na_2SO_4), and evaporated, and the residue purified by FC (SiO_2, Et_2O/pentane 20:80).

*3,5-Dinitrobenzoic Acid [*trans-*2-Phenyl-1-(trifluoromethyl)cyclopropyl]methyl Ester* (*trans*-**22**): IR (film): 3052*w*, 2923*w*, 1708*s*, 1532*m*, 1498*m*, 1318*s*, 1249*m*, 1263*m*, 1169*m*, 1175*s*, 1085*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.15–1.23 (*m*, 1 H); 1.53–1.57 (*m*, 1 H); 2.38–2.39 (*t*, *J* = 7.7, 1 H); 4.07 (*s*, 2 H); 7.21–7.24 (*m*, 5 H); 9.12–9.16 (*m*, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 11.1 (*t*); 24.9 (*d*); 30.7 (*q*); 59.5 (*t*); 125.1 (*q*); 127.5 (*d*); 128.9 (*d*); 134.8 (*s*); 123 (*d*); 130.9 (*d*); 149.2 (*s*); 132.1 (*s*); 168.4 (*s*). HR-MS: 410.3029 ($C_{18}H_{13}F_3N_2O_6^+$; calc. 410.3027).

*4-Nitrobenzoic Acid [*trans-*2-Phenyl-1-(trifluoromethyl)cyclopropyl]methyl Ester* (*trans*-**23**): IR (film): 3152*w*, 2980*w*, 1710*s*, 1562*m*, 1488*m*, 1330*s*, 1260*m*, 1278*m*, 1178*m*, 1180*s*, 1095*s*. ^{1}H-MR (400 MHz, $CDCl_3$): 1.14–1.22 (*m*, 1 H); 1.53–1.57 (*m*, 1 H); 2.38–2.39 (*t*, *J* = 7.7, 1 H); 4.05 (*s*, 2 H); 7.23–7.25 (*m*, 5 H); 8.23–8.30 (*m*, 4 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 11.0 (*t*); 24.6 (*d*); 30.5 (*q*); 59.3 (*t*); 125.0 (*q*); 127.3 (*d*); 128.4 (*d*); 128.9 (*d*); 136.0 (*s*); 123 (*d*); 130.4 (*d*); 136.5 (*s*); 152.4 (*s*); 168.9 (*s*). HR-MS: 356.3049 ($C_{18}H_{14}F_3NO_4^+$; calc. 365.3056).

10. *Rh^{II}-Catalyzed Intermolecular Cyclopropanation of Styrene with Silylated Diazoacetate* **24a**,**b**: *General Procedure*. To the Rh^{II} catalyst (2 mol-%) was added styrene (920 µl, 8.0 mmol) under Ar and the silylated diazoacetate **24a** or **24b** (0.85 mmol). The mixture was heated until the decomposition of the diazoacetate was completed (*ca*. 2 h). The solvent was evaporated, and the crude product was purified by FC according to [18].

Ethyl cis/trans-*2-Phenyl-1-(triethylsilyl)cyclopropanecarboxylate* (*cis*/*trans*-**25a**): IR (film): 2958*w*, 2878*w*, 1714*s*, 1461*m*, 1208*m*, 1004*m*, 698*s*. MS: 304 (7, M^+), 275 (15), 231 (19), 135 (19), 131 (100), 115 (40), 87 (70), 75 (35), 59 (37). HR-MS : 304.1849 ($C_{18}H_{28}O_2Si^+$, calc. 304.1858). NMR Data were obtained from diastereoisomer mixtures. *trans*-**25a**: ^{1}H-NMR (300 MHz, $CDCl_3$): 0.68–0.76 (*m*, 6 H); 1.08 (*t*, *J* = 7.7, 9 H); 1.20–1.26 (*m*, 1 H); 1.36 (*t*, *J* = 7.0, 3 H); 1.96 (*dd*, *J* = 6.4, 4.9, 1 H); 2.46 (*t*, *J* = 7.2, 1 H); 3.80 (*dd*, *J* = 7.2, 0.8, 2 H); 7.20–7.32 (*m*, 5 H). ^{13}C-NMR (75 MHz, $CDCl_3$) : 2.8 (*t*); 7.6 (*q*); 13.5 (*t*); 13.9 (*q*); 27.5 (*d*); 60.1 (*t*); 126.4 (*d*); 126.9 (*d*); 128.5 (*d*); 137.5 (*s*); 172.3 (*s*). *cis*-**25a**: ^{1}H-NMR (300 MHz, $CDCl_3$): 0.25–0.48 (*m*, 6 H); 0.85 (*t*, *J* = 7.9, 9 H); 0.92 (*t*, *J* = 7.1, 3 H); 1.44–1.48 (*m*, 1 H); 1.80 (*dd*, *J* = 8.8, 4.0, 2 H); 2.76 (*dd*, *J* = 7.0, 8.8, 1 H); 4.22 (*qd*, *J* = 7.1, 0.8, 2 H); 7.20–7.32 (*m*, 5 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 3.8 (*t*); 7.7 (*q*); 14.3 (*q*); 16.0 (*t*); 31.6 (*d*); 60.7 (*t*); 127.9 (*d*); 128.0 (*d*); 130.0 (*d*); 138.3(*s*); 172.3 (*s*).

Ethyl cis/trans-*1-(Dimethylphenylsilyl)-2-phenylcyclopropane-1-carboxylate* (*cis*/*trans*-**25b**): IR (film): 2971*w*, 1716*s*, 1427*m*, 1275*s*, 1108*s*. MS: 324 (9, M^+), 246 (9), 144 (12), 136 (14), 135 (100), 107 (14), 103 (21), 75 (11). HR-MS: 324.1545 ($C_{20}H_{24}O_2Si^+$, calc. 324.1546). NMR Data were obtained from diastereoisomer mixtures. *trans*-**25b**: ^{1}H-NMR (300 MHz, $CDCl_3$): 0.52 (*s*, 3 H); 0.55 (*s*, 3 H); 0.89 (*t*, *J* = 7.17, 3 H); 1.15–1.20 (*m*, 1 H); 2.02 (*m*, 1 H); 2.45 (*t*, *J* = 8.3, 1 H); 3.77 (*dd*, *J* = 1.1, 7.17, 2 H); 7.20–7.30 (*m*, 5 H); 7.42–7.44 (*m*, 5 H); 7.64–7.67 (*m*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): −3.6 (*q*); −2.1 (*q*); 13.9 (*t*); 14.4 (*t*); 22.6 (*s*); 28.2 (*d*); 60.2 (*t*); 126.4 (*d*); 127.7 (*d*); 127.8 (*d*); 128.7 (*d*); 129.3 (*d*); 134.2 (*d*); 136.7 (*s*); 137.0 (*s*); 172.0 (*s*). *cis*-**25b**: ^{1}H-NMR (300 MHz, $CDCl_3$): 0.52 (*s*, 3 H); 0.55 (*s*, 3 H); 0.89 (*t*, *J* = 7.2, 3 H); 1.61 (*dd*, *J* = 4.0, 6.8, 1 H); 1.88 (*dd*, *J* = 4.0, 8.9, 1 H); 2.89 (*dd*, *J* = 6.8, 8.7, 1 H); 4.14 (*q*, *J* = 7.2, 2 H); 7.20–7.30 (*m*, 5 H); 7.42–7.44 (*m*, 5 H); 7.64–7.67 (*m*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): −2.6 (*q*); −2.1 (*q*); 13.9 (*t*); 16.1 (*t*); 19.8 (*s*); 32.5 (*d*); 60.2 (*t*); 126.8 (*d*); 127.3 (*d*); 127.9 (*d*); 128.5 (*d*); 130.0 (*d*); 133.9 (*d*); 136.7 (*s*); 137.0 (*s*); 172.0 (*s*).

11. *Desilylation of* cis/trans-**25a**: *Ethyl* cis/trans-*2-Phenylcyclopropanecarboxylate* (*cis*/*trans*-**26**). To *trans*-**25a** (48% ee)/*cis*-**25a** (30% ee) 82:18 (142 mg, 0.56 mmol) in THF (3.0 ml) was added 1M Bu_4NF (1.0 ml) in THF at −78°. The temp. was allowed to reach r.t. After stirring for 2–4 h, the mixture was quenched with H_2O (2 ml) and extracted with CH_2Cl_2. The org. layer was dried ($MgSO_4$) and evaporated, and the residue was purified by FC (SiO_2, pentane/AcOEt 97:3): *cis*/*trans*-**26** 70:30, (1*S*,2*S*)-*trans*-**26** (48% ee), and (1*R*,2*S*)-*cis*-**26** (48% ee) in 81% yield (*cf. Fig. 9*,*c* and *d*).

Similarily, starting from *trans*-**25a** (54% ee)/*cis*-**25a** (27% ee) 82:18, *trans*-**26** (51% ee)/*cis*-**26** (49% ee) were obtained.

The same procedure was applied to *trans*/*cis*-**25b** 88:12 (100.5 mg, 0.31 mmol; from reaction with [Rh_2{(*S*)-pptl}$_4$]), which afforded (1*S*,2*S*)-*trans*-**26** (31%; 15% ee) and (1*R*,2*S*)-*cis*-**26** (18%; 13% ee).

Data of trans-**26**: IR (film): 2982*w*, 1725*s*, 1185*s*, 755*m*, 698*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.26 (*t*, *J* = 7.2, 3 H); 1.56–1.68 (*m*, 1 H); 1.86–1.92 (*m*, 1 H); 2.48–2.54 (*m*, 1 H); 4.16 (*q*, *J* = 7.2, 2 H); 7.07–7.30 (*m*, 5 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.3 (*q*); 17.0 (*t*); 24.1 (*d*); 26.1 (*d*); 60.6 (*t*); 126.1 (*d*); 126.4 (*d*);128.4 (*d*); 140.1 (*s*); 173.4 (*s*). MS: 190 (33, M^+), 145 (23), 117 (100), 115 (50), 91 (21). HR-MS: 190.0981 ($C_{12}H_{14}O_2^+$; calc. 190.0994).

Data of cis-**26**: IR (film): 3009*w*, 1721*s*, 1186*s*, 1081*w*, 864*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.93 (*t*, *J* = 7.2, 3 H); 1.27–1.35 (*m*, 2 H); 1.70–1.76 (*m*, 1 H); 2.05–2.13 (*m*, 1 H); 2.59 (*m*, 1 H); 3.88 (*q*, *J* = 7.2, 2 H); 7.20–7.28 (*m*, 5 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 11.0 (*t*); 13.9 (*q*); 21.8 (*d*); 25.4 (*d*); 60.1 (*t*); 126.6 (*d*); 127.8 (*d*);129.3 (*d*); 136.6 (*s*); 170.9 (*s*). MS: 190 (32, M^+), 145 (20), 117 (100), 115 (53), 91 (23). HR-MS: 190.1003 ($C_{12}H_{14}O_2^+$; calc. 190.0994).

12. *Reduction of* cis/trans-**25a**: cis/trans-*2-Phenyl-1-(triethylsilyl)cyclopropanemethanol* (*cis*/*trans*-**27**). To $LiAlH_4$ (2 equiv.) in THF (2.0 ml) was added, under Ar, *cis*/*trans*-**25a** (0.80 mmol) in THF (4.0 ml). The mixture was stirred overnight at r.t. The excess of $LiAlH_4$ was decomposed by the addition of ethane-1,2-diamine (2 ml), followed by 8% NaOH soln. (2.0 ml) and H_2O. The crude product was extracted with Et_2O (10 ml), dried (Na_2SO_4), filtered, and evaporated. The diastereoisomers were separated by FC (SiO_2, CH_2Cl_2/pentane 80:20): *cis*- and *trans*-**27**.

Data of trans-**27a**: Yield 45%. Colorless oil. IR (film): 2945*m*, 2871*m*, 1458*w*, 1239*w*, 1003*s*, 726*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.68 (*q*, *J* = 7.9, 6 H); 0.87–0.99 (*m*, 2 H); 1.05 (*t*, *J* = 7.9, 9 H); 2.24 (*t*, *J* = 6.7, 1 H); 3.22 (*d*, *J* = 11.8, 1 H); 3.53 (*d*, *J* = 11.8, 1 H); 7.24–7.30 (*m*, 5 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 2.6 (*t*); 7.6 (*q*); 11.7 (*t*); 15.9 (*s*); 24.3 (*d*); 65.7 (*t*); 126.2 (*d*); 128.3 (*d*); 128.9 (*d*); 138.4 (*s*). MS: 233 (12, [$M - C_2H_5$]$^+$), 215 (27), 130 (36), 115 (43), 103 (100), 87 (65), 75 (80). HR-MS: 233.1386 ($C_{14}H_{21}OSi^+$; calc. 233.1362).

Data of cis-**27a**: Yield 13%. Colorless oil. IR (film): 2951*m*, 2874*m*, 1455*w*, 1238*w*, 1005*s*, 726*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.24–0.40 (*m*, 6 H); 0.85 (*t*, *J* = 7.7, 9 H); 1.20 (*t*, *J* = 5.6, 1 H); 1.47 (*s*, 1 H); 2.10–2.20 (*m*, 2 H); 3.27 (*d*, *J* = 11.0, 1 H); 3.87 (*d*, *J* = 11.0, 1 H); 7.20–7.30 (*m*, 5 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 3.3 (*t*); 7.6 (*q*); 12.0 (*t*); 17,6 (*s*); 27.0 (*d*); 71.5 (*t*); 126.2 (*d*); 127.9 (*d*); 129.7 (*d*); 139.7 (*s*). MS: 233 (8, [$M - C_2H_5$]$^+$), 215 (21), 171 (12), 130 (39), 115 (39), 103 (100), 87 (60), 75 (85). HR-MS: 233.1372 ($C_{14}H_{21}OSi^+$; calc. 233.1361).

13. *Intramolecular Cyclopropanation of Allyl Diazo(triethylsilyl)acetates* **28**, **30**, *and* **33**: *General Procedure.* To the Rh^{II} catalyst (2 mol-% with respect to the allyl diazo(triethylsilyl)acetates) was added the diazosilylacetate **28**, **30**, or **33** (0.40 mmol) under Ar within 5 min. The mixture was stirred for 2 h at r.t. The soln. was evaporated and the residue purified by FC to afford the desired cyclopropane derivatives according to [18].

(1S,5R)-1-(Triethylsilyl)-3-oxabicyclo[3.1.0]hexan-2-one (**29**): FC (SiO_2, pentane/AcOEt 97:3) afforded **29**. For yields, see *Table 2*. Colorless oil. $[\alpha]_D^{20} = +7.2$ (*c* = 1.00, EtOH; for 30% ee). IR (film): 2954*m*, 2876*m*, 1753*s*, 1248*m*, 994*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.59–0.67 (*m*, 6 H); 0.96 (*t*, *J* = 8.1, 9 H); 1.17 (*dd*, *J* = 7.0, 4.5, 1 H); 2.04–2.06 (*m*, 1 H); 4.24 (*m*, 2 H). ^{13}C-NMR (MHz, $CDCl_3$): 2.0 (*t*); 7.2 (*q*); 13.3 (*s*); 15.6 (*t*); 21.9 (*t*); 68.2 (*t*); 178.8 (*s*). MS: 183 (85, [$M - C_2H_5$]$^+$), 139 (30), 111 (100), 83 (42), 59 (27), 53 (36). HR-MS: 183.0850 ($C_9H_{15}O_2Si^+$; calc. 183.0841).

cis-*(1S,5R)-5-Methyl-1-(triethylsilyl)-3-oxabicyclo[3.1.0]hexan-2-one* (**31**): FC (SiO_2, pentane/AcOEt 97:3) afforded **31** (20%; with [Rh_2{(*S*)-nttl}$_4$]). Colorless oil. IR: 2954*m*, 2879*m*, 1750*s*, 1188*s*, 1056*s*, 1006*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.68–0.76 (*m*, 6 H); 0.99 (*t*, *J* = 7.5, 9 H); 1.09 (*d*, *J* = 4.2, 1 H); 1.16 (*d*, *J* = 3.9, 1 H); 1.36 (*s*, 3 H); 3.94 (*d*, *J* = 8.8, 1 H); 4.20 (*d*, *J* = 8.8, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 2.5 (*t*); 7.3 (*q*); 16.8 (*q*); 22.9 (*t*); 30.0 (*s*); 72.2 (*t*); 113.9 (*s*); 179.4 (*s*). MS: 197 (100, [$M - C_2H_5$]$^+$), 125 (92), 115 (36), 103 (24), 97 (54), 87 (52). HR-MS: 197.1004 ($C_{12}H_{22}O_2Si^+$; calc. 197.0998).

cis-*4-Isopropenyl-3-(triethylsilyl)oxetan-2-one* (**32**): FC (SiO_2, pentane/AcOEt 97:3) afforded **32** (18%; with [Rh_2{(*S*)-nttl}$_4$]). IR (film): 2956*m*, 2874*m*, 1807*s*, 1255*w*, 1111*s*, 1008*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.67–0.76 (*m*, 6 H); 0.98 (*t*, *J* = 8.1, 9 H); 1.79 (*s*, 3 H); 3.55 (*dd*, *J* = 6.4, 2.5, 1 H); 4.88 (*d*, *J* = 6.4, 1 H); 5.08 (*s*, 1 H); 5.26 (*s*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 3.5 (*t*); 7.2 (*q*); 19.1 (*d*); 44.6 (*q*); 73.3 (*d*); 113.0 (*t*); 140.2 (*s*); 170.0 (*s*). MS: 226 (3, M^+), 198 (17), 197 (100), 125 (54), 103 (38), 75 (54). HR-MS: 226.138750 ($C_{12}H_{22}O_2Si^+$; calc. 226.1389).

(1S,5R,6R)-6-Ethyl-1-(triethylsilyl)-3-oxabicyclo[3.1.0]hexan-2-one (**34**). FC (SiO_2, pentane/AcOEt 97:3) gave **34** (76%; [Rh_2{(*S*)-nttl}$_4$]; 38% ee as determined after desilylation to **35**). Colorless oil. IR (film): 2952*m*, 2873*m*, 1745*s*, 1197*w*, 1070*m*, 1000*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.64 (*q*, *J* = 7.7, 6 H); 0.96 (*t*, *J* = 7.7, 9 H); 1.04

(t, J = 7.2, 3 H); 1.26–1.55 (m, 3 H); 2.08 (t, J = 5.6, 1 H); 4.13 (d, J = 9.6, 1 H); 4.29 (dd, J = 9.6, J = 5.5, 1 H). ^{13}C-NMR (MHz, $CDCl_3$): 2.1 (t); 7.2 (q); 13.3 (q); 17.0 (t); 19.4 (s); 27.1 (d); 27.3 (d); 65.1 (t); 177.1 (s). MS: 211 (100 $[M-C_2H_5]^+$), 115 (16), 109 (15), 103 (69), 81 (25), 75 (46). HR-MS: 211.1158 ($C_{11}H_{19}O_2Si^+$; calc. 211.1154).

14. *Desilylation of* **34**: *(1*R*,5*S*,6*R*)-6-Ethyl-3-oxabicyclo[3.1.0]hexan-2-one* (**35**). At r.t., 1M Bu_4NF in THF (1 ml) was added dropwise to **34** (0.56 mmol). After stirring for 2–4 h, H_2O (2 ml) was added, and the mixture was extracted with CH_2Cl_2. The org. layer was dried ($MgSO_4$) and evaporated and the residue purified by FC (SiO_2, pentane/AcOEt 96:4): 12 mg (37%) of **35**. Colorless oil. $[\alpha]_D^{20} = 26.3$ (c = 0.24, EtOH; for 28% ee). IR (film): 2965*m*, 2876*w*, 1756*s*, 1173*w*, 1058*s*, 979*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.07 (t, J = 6.8, 3 H); 1.40–1.43 (m, 3 H); 2.18–2.29 (m, 2 H); 4.15 (d, J = 9.9, 1 H); 4.41 (dd, J = 9.8, 5.3, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 13.3 (q); 16.3 (t); 22.5 (d); 22.7 (d); 23.9 (d); 66.0 (t); 175.1 (s). MS: 126 (3, M^+), 111 (9), 97 (15), 85 (100), 67 (84), 55 (46). HR-MS: 126.0688 ($C_7H_{10}O_2^+$; calc. 126.0680).

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