Electronically Tuned Chiral Ruthenium Porphyrins: Extremely Stable and Selective Catalysts for Asymmetric Epoxidation and Cyclopropanation

Albrecht Berkessel,* Patrick Kaiser, and Johann Lex[a]

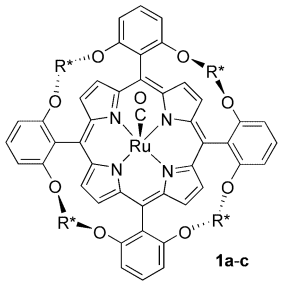
Dedicated to Prof. Dr. Drs. h.c. Helmut Schwarz on the occasion of his 60th birthday

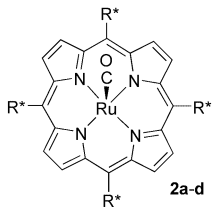
Abstract: We report the use of three enantiomerically pure and electronically tuned ruthenium carbonyl porphyrin catalysts for the asymmetric cyclopropanation and epoxidation of a variety of olefinic substrates. The D_4-symmetric ligands carry a methoxy, a methyl or a trifluoromethyl group at the 10-position of each of the 9-[*anti*-(1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracene)]-substituents at the *meso*-positions of the porphyrin. Introduction of a CF_3-substituent in this remote position resulted in greatly improved catalyst stability, and turnover numbers of up to 7500 were achieved for cyclopropanation, and up to 14200 for epoxidation, with *ee* values typically >90% and ≈80%, respectively. In one example, the axial CO ligand at the ruthenium was exchanged for PF_3, resulting in the first chiral ruthenium porphyrin with a PF_3 ligand reported to date. In cyclopropanations with ethyl diazoacetate, the latter catalyst performed exceedingly well, and gave a 95% *ee* in the case of 1,1-diphenylethylene as substrate.

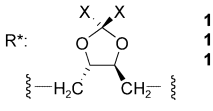
Keywords: asymmetric catalysis · cyclopropanation · epoxidation · porphyrins · ruthenium

Introduction

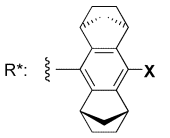
In organic synthesis, asymmetric epoxidation and cyclopropanation are very useful transformations of the C=C double bond, and a number of highly efficient and selective catalyst systems have been developed for both reaction types.[1–3] In recent years, the potential of ruthenium porphyrins in these fields has become evident: For example, in 1996 Gross et al. reported the first application of the chiral, tartaric acid-derived ruthenium porphyrin **1a** in asymmetric olefin epoxidation, 58% *ee* were achieved with styrene as substrate.[4, 5] This ruthenium porphyrin **1a** was also tested in the asymmetric cyclopropanation of styrene with ethyl diazoacetate by Simonneaux et al. in 1998, and *ee* values up to 52% were reported.[6, 7] Recently, further improvement resulted from using the phenyl- (**1b**) and in particular the 3-chlorophenyl-substituted catalyst **1c**: Enantiomeric excesses up to 83% were achieved in the epoxidation of 4-chlorostyrene, and total turnover numbers reached up to ≈500 (epoxidation of *trans*-β-methylstyrene).[8] In 1997, both we[9, 10] and the group of Che[11] reported the synthesis of the chiral ruthenium carbonyl porphyrin **2a**, starting from the corresponding D_4-symmetric porphyrin first described by Halterman et al.[12] The latter ruthenium porphyrin **2a** turned out to be an extremely active and selective catalyst for the asymmetric cyclopropanation of styrenes with ethyl diazoacetate: For example, in our hands, styrene (**3**) gave a quantitative yield of the corresponding cyclopropanes with a *trans*/*cis* ratio of 96:4, and with an *ee* of the *trans*-product **4a** of 91% (at 0 °C; 87% *ee* at 25 °C; Scheme 1).[10] More than 1000 catalyst turnovers could easily be achieved.[9, 10] In catalytic epoxidation, the ruthenium porphyrin **2a** allowed the conversion of for example 1,2-dihydronaphthalene (**5**) to its epoxide **6** in 77% *ee* (Scheme 1).[10] Again, catalyst loadings were in the range of 0.1 mol%.







1a: X = CH_3
1b: X = Ph
1c: X = 3-Cl-Ph



2a: X = H
2b: X = OCH_3
2c: X = CH_3
2d: X = CF_3

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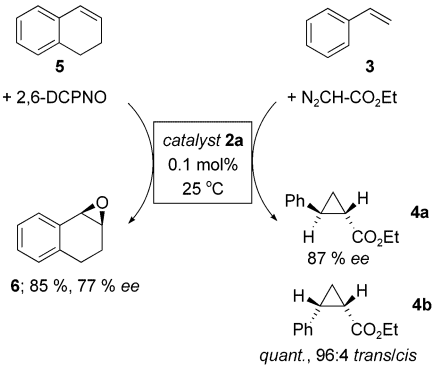
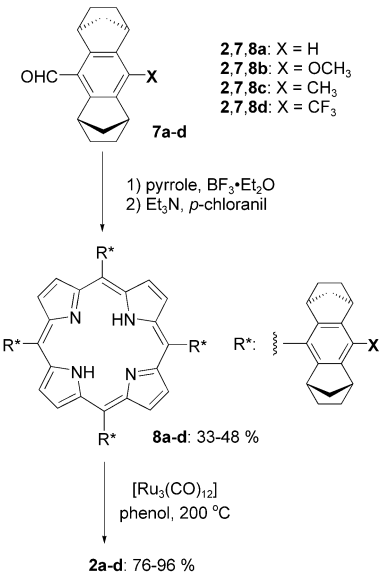
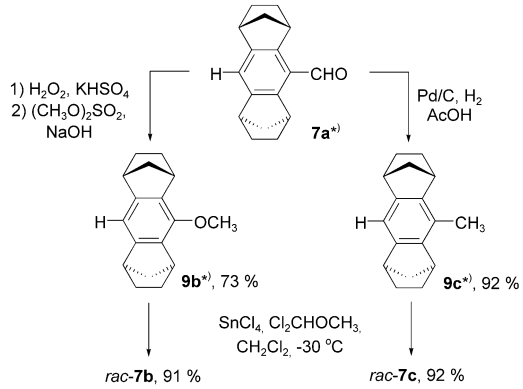
We reasoned that electronic fine-tuning of the porphyrin ligand of **2a** might allow a further increase in catalyst stability, that is total turnover numbers, and also in selectivity.[13] We herein report the synthesis of a new generation of chiral ruthenium porphyrins **2b–d** that carry either a methoxy, a methyl or a trifluoromethyl group in the 10-position of the 9-[*anti*-(1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracene)]-*meso*-substituents (X in **2b–d**), together with the catalytic performance of these materials. As it turned out, in particular the CF_3 substitution improved the catalyst stability tremendously, and total turnover numbers of up to 7500 were achieved for cyclopropanation, and up to 14200 for epoxidation, with *ee* values typically in the range $\geq 90\%$ and $\approx 80\%$, respectively. These catalyst stabilities are the best reported ever in homogeneous cyclopropanation, especially in epoxidation. Furthermore, the X-ray crystal structure and remarkable catalytic activity of the first chiral Ru–porphyrin carrying an axial PF_3-group instead of CO (**2e**) is also reported.



Scheme 1. Asymmetric epoxidation and cyclopropanation with the chiral ruthenium porphyrin **2a** as catalyst. DCPNO: 2,6-dichloropyridine-*N*-oxide.



Scheme 2. Preparation of the chiral ruthenium porphyrins **2a–d** from the aldehydes **7a–d**.



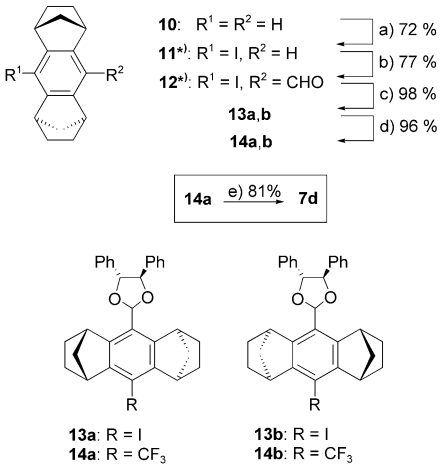
Scheme 3. Conversion of the unsubstituted aldehyde *rac*-**7a** to the methoxylated and methylated aldehydes *rac*-**7b** and *rac*-**7c**. *): racemic mixture.

Results and Discussion

Synthesis of the ruthenium porphyrin catalysts: As shown in Scheme 2, we prepared the chiral Ru–porphyrins **2a–d** by ruthenium insertion into the porphyrin ligands **8a–d** by using $[Ru_3(CO)_{12}]$ as the metal source and refluxing phenol as the solvent, a method described by us before.[9] The porphyrins **8a–d** were prepared from the aldehydes **7a–d** by the Lindsey method.[15]

Consequently, the synthetic approach as a whole hinges on the availability of the aldehydes **7a–d** in enantiomerically pure form. First, for the preparation of the methoxy- and methyl-substituted aldehydes **7b** and **7c** in racemic form, the benzaldehyde derivative *rac*-**7a** served as the starting material (Scheme 3).[12] Dakin oxidation/methylation or catalytic hydrogenation afforded the anisol and toluene derivatives *rac*-**9b** and *rac*-**9c**, respectively.[16] The formylation of the intermediates *rac*-**9b**,**c** was performed according to Rieche, using Cl_2CH-OCH_3 in the presence of $SnCl_4$.[17] For the separation of the enantiomers of *rac*-**7a–c**, acetalization with (*R*,*R*)-hydrobenzoin,[18] fractional crystallization and hydrolysis proved successful. By this method, aldehyde **7a** was obtained in 60% overall yield from the racemic mixture.[19, 20] Similarly, this method provided methoxy aldehyde *ent*-**7b** in 28% yield, methylated aldehyde **7c** (22%) and its enantiomer *ent*-**7c** (52%).[20] The enantiomeric purities of the aldehyde products were generally $\geq 99\%$ (GC, HPLC). Furthermore, the absolute configurations of aldehydes **7a**, *ent*-**7b**, *ent*-**7c** and **7d** were established unambiguously by X-ray structural analyses of the intermediate crystalline (*R*,*R*)-hydrobenzoin acetals.[16] In the case of trifluoromethylated aldehyde **7d**, a number of unsuccessful attempts were made to introduce the CF_3 substituent at the aldehyde stage, or to formylate a trifluoromethylated precursor. Finally, the sequence shown in Scheme 4 proved to be the most efficient one: First, the *meso*-precursor **10**[12] was iodinated to *rac*-**11**, followed by a Rieche formylation to afford the iodo aldehyde *rac*-**12** in 56% overall yield. When treated with (*R*,*R*)-hydrobenzoin in the presence of PPTS, this material afforded 98% of the diastereomeric acetals **13a** and **13b**. The copper-catalyzed

trifluoromethylation of **13a**,**b** with CF_3-TMS[21] proceeded smoothly and with an excellent yield of **14a**,**b** (96%). Finally, the separation of **14a** by crystallization and hydrolysis afforded the enantiomerically pure (≥99%) aldehyde **7d**. Again, the absolute configuration of the aldehyde **7d** was established by X-ray crystallography of the acetal **14a**.[16] As summarized in Scheme 2, both the porphyrin synthesis and the ruthenium insertion proceeded smoothly.



Scheme 4. Preparation of the trifluoromethylated aldehyde **7d** from the octahydro-bis-methano-anthracene **10**. *): racemic mixture; a) $PhI(OAc)_2$, I_2; b) $SnCl_4$, Cl_2CHOCH_3; c) (*R*,*R*)-hydrobenzoin, PPTS; d) CF_3-TMS, CuI, KF; e) aq. HCl, $(CH_2O)_n$.

The X-ray crystal structure of the enantiomerically pure tetrakis-trifluoromethylated ruthenium porphyrin **2d** is shown in Figure 1a. As expected from other crystal structures of Ru–porphyrins,[11] a CO molecule occupies one of the (homotopic) axial positions of the Ru–porphyrin, whereas a molecule of the solvent methanol is coordinated to the other. Furthermore, Figure 1a nicely demonstrates the "chiral rim" on both perimeters of the porphyrin, composed of the methano and ethano bridges of the *meso*-substituents.

For the generation of the ruthenium–PF_3–porphyrin **2e**, treatment of CO–porphyrin **2a** with PF_3 at atmospheric pressure resulted in quantitative conversion. The X-ray crystal structure of this novel chiral Ru–porphyrin is shown in Figure 1b. Again, one of the axial positions at the ruthenium ion is occupied by the PF_3 ligand, whereas the other one is occupied by a solvent molecule, in this case acetonitrile.

Catalytic asymmetric cyclopropanation: A screening of various types of olefins (i.e., terminal, *E*- and *Z*-di- and trisubstituted, etc.) revealed that terminal olefins are the substrates of choice for the ruthenium porphyrin catalysts presented here. Our results obtained in the asymmetric cyclopropanation of various terminal olefins with ethyl diazoacetate in the presence of the catalysts **2a**–**d** and **2e** are summarized in Table 1. Generally, 0.1 mol% of catalyst (relative to olefin) were employed, and a slight excess of the diazoacetate (1.1 equiv). We generally found that the *trans*-cyclopropanes are formed preferentially. With styrene (**3**) as

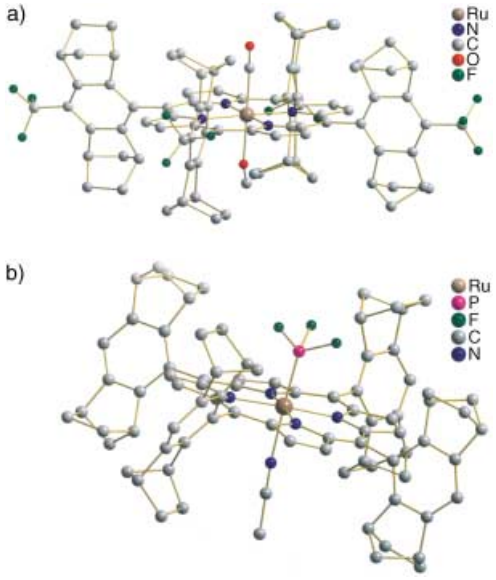


Figure 1. X-ray crystal structure of the ruthenium porphyrin a) **2d** and b) chiral ruthenium-PF_3-porphyrin **2e**. a) The upper axial coordination site is occupied by a CO molecule, whereas the lower one carries a methanol molecule. b) The upper axial coordination site is occupied by a PF_3 molecule, whereas the lower one carries an acetonitrile molecule.

substrate, *trans*/*cis* ratios are generally better than 95:5, and enantiomeric excesses of the *trans*-product reached up to 93%. The latter result (Table 1, entry 7) was achieved with the tetrakis-CF_3-substituted catalyst **2d** and represents the best *ee* value achieved so far in the Ru–porphyrin catalyzed asymmetric cyclopropanation of styrene.[8, 22] The determination of the total turnover numbers of the Ru–porphyrins *ent*-**2c** and **2d** revealed that these catalysts perform 5500 and 7200 cyclopropanation cycles, respectively. Overall, the tetrakis-CF_3-substituted Ru–porphyrin **2d** performs best (Table 1, entries 6,7).

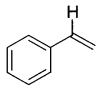
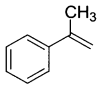
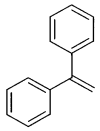
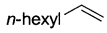
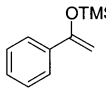
With α-methylstyrene as substrate, the *trans*-selectivity of the Ru–porphyrins **2a**–**e** is somewhat less pronounced. Nevertheless, enantiomeric excesses of the *trans*-products were generally ≥90%. Again, the tetrakis-CF_3-substituted Ru–porphyrin **2d** showed the best catalytic activity, with basically quantitative conversion of the substrate olefin within 5 h at 25 °C (Table 1, entry 12). As expected, a further increase in enantioselectivity (up to 94%) was achieved by lowering the reaction temperature (−18 °C; Table 1, entry 14).

In the case of styrene as substrate, the absolute configurations of the product cyclopropanes could readily be assigned based on literature data.[25] However, no such data appeared to be available for the cyclopropanation products of α-methylstyrene. We therefore analyzed the corresponding cyclopropane configurations as follows. First, the mixture of stereoisomers obtained from a $[Cu(acac)_2]$-catalyzed cyclopropanation of α-methylstyrene with ethyl diazoacetate was separated into the racemic mixtures of the *trans*- and *cis*-isomers by preparative HPLC on silica gel. The individual enantiomers were then obtained by preparative HPLC on Chiralpak AD, and all four stereoisomeric cyclopropane esters were converted to the (*S*)-phenethylamides. One of the

diastereomeric phenethylamides of both the *trans*-and the *cis*-cyclopropanes was analyzed by X-ray crystallography. By this procedure, two X-ray crystal structures allowed the assignment of all four of the cyclopropane absolute configurations (see Experimental Section).

Our results obtained with 1,1-diphenylethylene as substrate are summarized in entries 15–20 of Table 1. Among the carbonyl complexes **2a**–**d**, again the tetrakis-CF_3-substituted Ru–porphyrin **2d** performed best, both in terms of rate and enantioselectivity. However, it is interesting to note that the ruthenium–PF_3–porphyrin **2e** (Table 1, entries 19, 20) shows characteristics significantly different from its CO counterpart (Table 1, entry 15): Whereas the reaction rate of the PF_3-complex **2e** is about one half of that of the CO-complex **2a**, the enantioselectivity of the former catalyst is significantly higher (94 vs 77%: Table 1, entries 15, 19). In the case of the **2a**, we could show both by NMR- and in situ IR spectroscopy that addition of diazo acetate resulted in rapid loss of the CO ligand and formation of the carbene complex.[23] We therefore assume that in the case of **2e**, the phosphine ligand does not dissociate, and that a pseudo-octahedral ruthenium species acts as a carbene carrier (as opposed to a five-coordinated Ru complex in the case of **2a**).[10, 23] This assumption is in accord with the known higher stability of other (achiral) Ru–porphyrin complexes of PF_3 compared with their CO analogues.[24]

Table 1. Catalytic cyclopropanation of olefins with ethyl diazoacetate.[a]

	Olefin	Catalyst	T [°C]	Conversion of olefin [%][c]	*trans*/*cis* (% *de*)[c]	*ee trans* [%][c]	*ee cis* [%][c]
1		**2a**	25	80	96:4 (92)	87 (1*S*,2*S*)	14 (1*S*,2*R*)
2		*ent*-**2a**	0	[b]	95:5 (90)	91 (1*R*,2*R*)	27 (1*R*,2*S*)
3		*ent*-**2b**	25	81	96:4 (92)	90 (1*R*,2*R*)	31 (1*R*,2*S*)
4		*ent*-**2c**	25	83	96:4 (92)	89 (1*R*,2*R*)	11 (1*R*,2*S*)
5		*ent*-**2c**	0	72	98:2 (96)	92 (1*R*,2*R*)	19 (1*R*,2*S*)
6		**2d**	25	94	97:3 (94)	89 (1*S*,2*S*)	< 1
7		**2d**	0	70	96:4 (92)	93 (1*S*,2*S*)	7 (1*S*,2*R*)
8		**2e**	25	81	96:4 (92)	87 (1*S*,2*S*)	14 (1*S*,2*R*)
9		**2a**	25	79	66:34 (32)	90 (1*S*,2*S*)	38 (1*S*,2*R*)
10		*ent*-**2b**	25	76	68:32 (36)	91 (1*R*,2*R*)	43 (1*R*,2*S*)
11		*ent*-**2c**	25	81	67:33 (34)	91 (1*R*,2*R*)	46 (1*R*,2*S*)
12		**2d**	25	> 98	69:31 (38)	91 (1*S*,2*S*)	36 (1*S*,2*R*)
13		**2e**	25	78	66:34 (32)	90 (1*S*,2*S*)	38 (1*S*,2*R*)
14		**2e**	–18[d]	73	73:28 (45)	94 (1*S*,2*S*)	53 (1*S*,2*R*)
15		**2a**	25	91	–	77 (*S*)	
16		*ent*-**2b**	25	76	–	77 (*R*)	
17		**2c**	25	86	–	76 (*S*)	
18		**2d**	25	98	–	82 (*S*)	
19		**2e**	25	56	–	94 (*S*)	
20		**2e**	–18[d]	18	–	95 (*S*)	
21		**2a**	25	20	86:14 (72)	46 (1*S*,2*S*)	9[e]
22		*ent*-**2b**	25	15	85:15 (70)	40 (1*R*,2*R*)	< 2[e]
23		*ent*-**2c**	25	20	82:18 (64)	39 (1*R*,2*R*)	< 2[e]
24		**2d**	25	30	85:15 (70)	46 (1*S*,2*S*)	4[e]
25		**2e**	25	42	99.5:0.5 (99)	82 (1*S*,2*S*)	6[e]
26		**2e**	25	98	70:30 (40)	83[e]	43[e]
27		**2e**	–18[d]	85	62:38 (24)	76[e]	20[e]

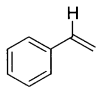
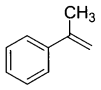
[a] Typical reaction conditions: substrate olefin/DAE/catalyst 1000:1100:1 in 1,2-dichloroethane; DAE was added over a period of 5 h by means of a syringe pump. [b] Styrene/DAE/catalyst 1000:660:1; DAE was added over a period of 2 h by means of a syringe pump; olefin conversion based on DAE consumed was quantitative. [c] Conversions and ratios of stereoisomers were determined by capillary GC as described in the Supplement. Relative and absolute configurations were determined as described in the text. [d] Catalyst loading was 0.2 mol% relative to olefin. [e] Absolute configuration not determined.

Entries 21–27 of Table 1 summarize our evaluation of the catalysts **2a**–**e** in the asymmetric cyclopropanation of non-conjugated terminal olefins (1-octene, entries 21–25) and enol ethers (α-trimethylsiloxystyrene, entries 6, 27). Whereas all CO-complexes (**2a**–**d**) afforded *trans*/*cis* ratios in the range of 85:15 and only moderate *ee* values (39–46%) in the case of 1-octene, almost perfect diastereoselectivity (*trans*/*cis* 99.5:0.5) resulted from the use of the PF_3–porphyrin **2e**, with an *ee* of the *trans*-cyclopronane of 82% (Table 1, entry 25). This result again indicates that the carbene carriers generated from the porphyrins **2a** (axial CO) and **2e** (axial PF_3) are not identical, that is the PF_3 ligand remains bound to the ruthenium ion. Finally, in the case of α-trimethylsiloxystyrene, the Ru–PF_3 catalyst afforded a *trans*/*cis*-ratio of about 2:1, and moderate *ee* values of $\approx$80% (Table 1, entries 26, 27). Please note that with this particular substrate, the diastereo- and enantioselectivities *decrease* when the reaction temperature is lowered from 25 to $-18\,^{\circ}C$.

Our results obtained with phenyl diazomethane as the carbene source and with styrene (entry 1) and α-methylstyrene (entry 2) as substrates are summarized in Table 2. Whereas the *trans*/*cis* selectivities are only moderately in favor of the *trans*-diastereomers in both cases, the *trans*-cyclopropane from α-methylstyrene was formed with excellent enantioselectivity (96% *ee*).

Finally, for the determination of the total turnover number (TTN), one equivalent of the ruthenium porphyrin catalysts *ent*-**2c** and **2d** was exposed to a mixture of 10000 equiv styrene and 16250 equiv ethyl diazoacetate in 1,2-dichloroethane at room temperature. Again, the CF_3-substituted catalyst **2d** proved best: After 72 h, 75.2% of the olefin were converted to cyclopropane(s), that is 7520 catalyst turnovers had occurred.

Table 2. Cyclopropanation of styrene and α-methylstyrene with phenyl diazomethane, using the ruthenium porphyrin **2e** as catalyst.[a]

	Olefin	Conversion of olefin [%][b]	*trans*/*cis* (% *de*)[b]	*ee trans* [%][b]	*ee cis* [%][b]
1		6	51:49 (2)	72 (1*R*,2*R*)	–
2		45	83:17 (66)	96 (n.d.)	34 (n.d.)

[a] Typical reaction conditions: substrate olefin/phenyl diazomethane/catalyst 500:800:1 in 1,2-dichloroethane at 25 °C. [b] See footnote [c] of Table 1.

exposed to a mixture of 30000 equiv styrene and 33000 equiv 2,6-DCPNO in benzene at room temperature. Again, the CF_3-substituted catalyst **2d** proved best: The epoxidation finally stalled at 47.3% conversion of olefin to epoxide, that is 14200 catalyst turnovers had occurred. We attribute the outstanding stability of the catalyst **2d** to the electron withdrawing effect of the four CF_3 substituents. In other words, the general competition of oxygen transfer versus oxidative destruction of the catalyst is shifted in favor of the former. By the same token, the higher electrophilicity of the oxygen donor (i.e., Ru-oxo species) results in higher turnover rates. With 1,2-dihydronaphthalene as substrate (Table 1, entries 4–8), up to 83% *ee* were observed. In the case of the non-conjugated olefin 1-octene (Table 1, entries 9–12), the turnover frequency became fairly low (ca. 2 h^{-1}), and the enantiomeric excesses of the product epoxides dropped to less than 40%. Obviously,

Catalytic asymmetric epoxidation: Our results obtained in epoxidation catalysis are summarized in Table 3. We employed the so-called Hirobe-conditions, that is 2,6-dichloropyridine *N*-oxide (2,6-DCPNO) as the oxygen donor (1.1 equiv relative to olefin) in benzene at room temperature.[26] Typically, catalyst loadings of 0.1 mol% (relative to olefin) were used. We were delighted to see that styrene (**3**) was epoxidized at a turnover rate of almost 400 h^{-1}, and with $\approx$80% enantiomeric excess. These results were achieved with the trifluoromethylated catalyst **2d** (Table 3, entry 3).

For the determination of the total turnover number (TTN), one equivalent of the ruthenium porphyrin catalyst **2d** was

Table 3. Catalytic asymmetric epoxidation of olefins using 2,6-dichloropyridine *N*-oxide (2,6-DCPNO) as oxygen donor.[a]

	Olefin	Catalyst	Reaction time [h]	Yield of epoxide [%][b]	Turnover frequency [h^{-1}]	*ee* of epoxide [%][c]
1		*ent*-**2b**	2.5	82[d]	328	76 (*R*)
2		*ent*-**2c**	2.5	78[d]	312	76 (*R*)
3		**2d**	2.5	97[d]	388	79 (*S*)
4		**2a**[e]	48	85	–	71 (1*R*,2*S*)
5		*ent*-**2b**	7.5	66[f]	88	80 (1*S*,2*R*)
6		**2c**	7.5	63[f]	85	77 (1*R*,2*S*)
7		*ent*-**2c**	7.5	70[f]	94	78 (1*S*,2*R*)
8		**2d**	7.5	89[f]	118	83 (1*R*,2*S*)
9	*n*-hexyl	**2a**	45	10	2	21 (*R*)
10		*ent*-**2b**	45	8	2	36 (*S*)
11		**2c**	45	9	2	22 (*R*)
12		**2d**	45	16	4	18 (*R*)

[a] Typical reaction conditions: substrate olefin/2,6-DCPNO/catalyst 1000:1100:1 in benzene, room temperature. [b] Yield of epoxide determined by capillary GC, using bromobenzene or 1,2-dibromobenzene as internal standard. [c] *ee* determined by capillary GC as described in the Experimental Section. [d] After 20 h, an epoxide yield = 98% was observed. [e] Chromatographically purified material. [f] After 70 h, an epoxide yield = 98% was observed.

electron-rich olefins are the substrates of choice for our ruthenium–porphyrin catalysts.

We routinely purified our ruthenium–porphyrins by recrystallization prior to use as catalysts. In one case (Table 3, entry 4), we employed the catalyst **2a** *without* recrystallisation, that is chromatographically pure material. As shown in Table 3, this catalyst required about six-fold longer reaction times. The time course of this reaction showed the typical lag phase, also reported by Groves et al. (data not shown).[27] It has been proposed that the lag phase is due to oxidative catalyst activation. On the other hand, our observation suggests that oxidative removal of some inhibitory impurity—which is no longer present in recrystallized material—may as well account for the induction period.

Conclusion

In summary, we have synthesized a new and electronically tuned generation of ruthenium porphyrin catalysts and have shown their outstanding performance in cyclopropanation and epoxidation. Clearly, fourfold introduction of the electron withdrawing CF_3 substituent provides the most reactive (i.e., electrophilic) catalyst. Besides impressive enantioselectivities, the latter ruthenium porphyrin **2d** is unmatched with respect to catalyst stability, that is total turnover numbers achieved.

Experimental Section

General: Optical rotations were measured at 589 nm using a Propol polarimeter (Dr. W. Kernchen) from Optik-Elektronik-Automation, or a Perkin–Elmer polarimeter 343plus. In HPLC analysis, the sense of optical rotation was determined using the Chiralizer instrument from IBZ Messtechnik GmbH. Analytic HPLC data were obtained using a Merck Hitachi L-6200A intelligent pump with Merck L-7000 interface, L-7250 autosampler, L-7300 column oven, L-7100 pump, L-4500 diode array detector and D7000 HSM software V3.1. The following columns have been used for analytical HPLC separation: LiChroSpher Si60 (Merck, 5 μm, 250 × 4 mm); Chiralpak AD (Daicel, 5 μm, 250 × 4.6 mm); Supersphere 60 RP-Select B (Merck, 5 μm, 125 × 4 mm); Chiralcel OJ-R (Daicel, 5 μm, 150 × 4.6 mm). Preparative HPLC separations were performed using a Merck NovaPrep 200 pump with L-7400 UV detector and TurboPrep software V2.41. The following columns have been used for preparative HPLC separation: LiChroSorb Si60 (Merck, 12 μm, 25 × 5 cm); Chiralpak AD (Daicel, 20 μm, 50 × 5 cm). Analytical and preparative HPLC separations were carried out at 25 °C. Capillary GC data were obtained using a Hewlett-Packard HP 6890 Series GC System with flame ionization detector and HP-ChemStation software revised version A.05.01. The following columns have been used for analytical GLC separation: HP-1, Hewlett-Packard, crosslinked methyl silicon gum, 25 m, nitrogen as carrier gas; β-CD1, Macherey-Nagel, heptakis-(2,6-di-*O*-methyl-3-*O*-pentyl)-β-cyclodextrin, 25 m, He as carrier gas; CB1, Chrompak, Chirasil-Dex CB, 25 m, He as carrier gas. GC analysis with a mass sensitive detector was performed using a Hewlett–Packard HP 6890 Series GC System with a HP 5973 detector, HP-ChemStation software G1701 AA V3.0 and a Hewlett Packard HP-5 crosslinked silicon gum column, 25 m, He as carrier gas. High resolution mass spectroscopy (HR-MS) was carried out on a Finnigan MAT 900S instrument with ES ion source and PEG as reference substances. Nuclear magnetic resonance spectra were recorded on Bruker AC250, AC300, DPX300 or DRX500 instruments. The chemical shift δ (ppm) is referenced against the solvent signal, the multiplicity is recorded as follows: br s (broad singlet), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), coupling constants in Hz. The assignment of the signals is based on 2-D experiments. Infrared spectra (IR) were obtained on a Perkin–Elmer 1600 Series FT-IR and a Perkin–Elmer 1000 Paragon FT-IR instrument with Spectrum V. 1.5 software, the intensity of the absorptions are reported as follows: w (weak), m (medium), s (strong). Elemental analysis was performed using an Elementar CHN-Analysator Vario EL instrument. X-ray structures were obtained using a Nonius Kappa CCD instrument with Denzo software. The structural calculations were performed with ShelXS86 and refined with ShelXL93 software. Melting points were obtained in open capillary tubes and are corrected.

Solvents and reagents for the catalytic studies were purchased from Fluka AG and used as received. Solvents for the analytical HPLC were purchased from Rathburn Chemicals or Acros Chemicals, and used as received. Solvents for flash chromatography or preparative HPLC were dried and distilled according to standard procedures. α-Trimethylsiloxystyrene[28] and phenyldiazomethane[29] were prepared according to the literature procedures.

General procedure a) for the catalytic cyclopropanation of olefins with ethyl diazoacetate and the ruthenium porphyrin catalysts 2a–e at 25 °C (0 °C): A 15 mL Schlenk tube was charged with the catalyst (315 nmol, 1 equiv, see Table 4), the olefin (315 μmol, 1000 equiv) and dry 1,2-dichloroethane (2 mL) under an argon atmosphere. A solution of ethyl diazoacetate (36 μL, 40 mg, 347 μmol, 1100 equiv) in dry 1,2-dichloroethane (2 mL) was added continuously while stirring at 25 °C (0 °C) within 5 h by means of a syringe pump. After the addition was complete, bromobenzene or 1,2-dibromobenzene (internal standard, 315 μmol, 1000 equiv) was added and a small sample of the crude product was analyzed by GC or HPLC.

Table 4. Catalyst loadings used for the cyclopropanation reactions.

Catalyst	**2a**	**2b**	**2c**	**2d**	**2e**
mass [μg] (315 nmol)	400	438	418	486	420

General procedure b) for the catalytic cyclopropanation of olefins with ethyl diazoacetate and the ruthenium porphyrin catalyst 2e at −18 °C: A 15 mL Schlenk tube was charged with the catalyst **2e** (840 μg, 630 nmol, 1 equiv), the olefin (315 μmol, 500 equiv) and dry 1,2-dichloroethane (2 mL) under an argon atmosphere. A solution of ethyl diazoacetate (36 μL, 40 mg, 347 μmol, 550 equiv) in dry 1,2-dichloroethane (2 mL) was added continuously while stirring at −18 °C within 5 h by means of a syringe pump. After the addition was complete, bromobenzene or 1,2-dibromobenzene (internal standard, 315 μmol, 500 equiv) was added and a small sample of the crude product was analyzed by GC or HPLC.

General procedure c) for the determination of the total turnover number of the catalytic cyclopropanation of styrene with ethyl diazoacetate and the ruthenium porphyrin catalysts: A 25 mL Schlenk flask was charged with the catalyst (666 nmol, 1 equiv), styrene (759 μL, 687 mg, 6.66 mmol, 10000 equiv) and dry 1,2-dichloroethane (5 mL) under an argon atmosphere. A solution of ethyl diazoacetate (1.138 mL, 1.235 g, 10.82 mmol, 16250 equiv) in dry 1,2-dichloroethane (15 mL) was added continuously while stirring at 25 °C within 3 d by means of a syringe pump. After the addition was complete, bromobenzene (internal standard, 300 μL, 447 mg, 2.85 mmol, 4278 equiv) was added and a small sample of the crude product was analyzed by GC.

General procedure d) for the catalytic cyclopropanation of olefins with phenyl diazomethane and catalyst 2e: A 15 mL Schlenk tube was charged with catalyst **2e** (0.82 mg, 630 nmol, 1 equiv), the olefin (315 μmol, 500 equiv) and dry 1,2-dichloroethane (2 mL) under an argon atmosphere. A solution of phenyl diazomethane (60 mg, 504 μmol, 800 equiv) in dry 1,2-dichloroethane (2 mL) was added continuously while stirring at 25 °C within 5 h by means of a syringe pump. After the addition was complete, dibromobenzene or dibenzyl ether (internal standard, 315 μmol, 500 equiv) was added and a small sample of the crude product was analyzed by GC.

General procedure e) for the catalytic cyclopropanation of olefins with [Cu(acac)$_2$] as catalyst: A Schlenk tube was charged with the olefin, [Cu(acac)$_2$] (5.2 mg per mmol olefin, 4 mol %) and dry 1,2-dichloroethane (1 mL per mmol olefin) under an argon atmosphere. A solution of the diazo compound (1.1 equiv) in dry 1,2-dichloroethane (5 mL) was added

continuously while stirring at 25 °C within 15 h by means of a syringe pump. After the addition was complete, the solvent was removed by rotary evaporation, and the crude products were purified by Kugelrohr distillation under reduced pressure.

General procedure f) for the amidation of the ethyl cyclopropanecarboxylates with (*S*)-(−)-1-phenylethylamine: A 50 mL Schlenk tube was charged with a solution of (*S*)-(−)-1-phenylethylamine (496 mg, 3.9 mmol, 5.0 equiv) in absolute *n*-hexane (10 mL) under an argon atmosphere. To the stirred solution, 1.6 N *n*-butyllithium (2.2 mL, 3.5 mmol, 4.5 equiv) in absolute *n*-hexane (5 mL) was added dropwise at −78 °C. After 30 min, a solution of the ethyl cyclopropanecarboxylate (0.78 mmol, 1.0 equiv) in dry *n*-hexane (10 mL) was added, and the stirred suspension was allowed to reach room temperature overnight. Saturated aqueous ammonium chloride solution (10 mL) was added. The organic layer was separated, and the aqueous layer was extracted with *n*-hexane (2 × 10 mL). The combined organic phases were washed with saturated sodium bicarbonate solution (2 × 10 mL), water (10 mL), and dried over Na_2SO_4. After filtration, the solution was concentrated to a volume of a few mL. The desired amides crystallized within a few days at 4 °C. The purity of the product was checked by analytical HPLC.

General procedure g) for the catalytic epoxidation of olefins with 2,6-dichloropyridine-*N*-oxide and the ruthenium porphyrin catalysts 2a–d: A 15 mL Schlenk flask was charged with the catalyst (315 nmol, 1 equiv, see Table 5), the olefin (315 μmol, 1000 equiv), 1,2-dibromobenzene (internal standard, 74 mg, 38 μL, 315 μmol, 1000 equiv) and dry benzene (2 mL) under an argon atmosphere. 2,6-Dichloropyridine-*N*-oxide (55 mg, 347 μmol, 1100 equiv) was added. The solution was stirred at 25 °C, until no further conversion of the olefin could be observed by GC analysis.

Table 5. Catalyst loadings used for the epoxidation reactions.

Catalyst	**2a**	**2b**	**2c**	**2d**
mass [μg] (315 nmol)	400	438	418	486

General procedure h) for the determination of the total turnover number of the catalytic epoxidation of styrene with 2,6-dichloropyridine-*N*-oxide and the ruthenium porphyrin catalysts: A 5 mL Schlenk flask was charged with the catalyst (314.4 nmol, 1 equiv), styrene (982 mg, 1.084 mL, 9.432 mmol, 30000 equiv), 1,2-dibromobenzene (internal standard, 743 mg, 380 μL, 3.151 mmol, 10022 equiv) and dry benzene (2 mL) under Ar. 2,6-Dichloropyridine-*N*-oxide (1.701 g, 10.375 mmol, 33000 equiv) was added. The mixture was stirred at 25 °C, until no further conversion of the olefin could be observed by GC analysis.

Asymmetric cyclopropanation, GC- and HPLC analysis

Cyclopropanation of styrene with ethyl diazoacetate: GC-column CB1, helium 1.2 mL min^{-1} (constant flow modus), injector 250 °C (pulsed split modus), detector (FI 250 °C, oven: 80 °C; 5 °C min^{-1} 114 °C (40 min), 5 °C min^{-1} 120 °C (1 min), 20 °C min^{-1} 160 °C (2 min):

styrene $\tau_R = 3.4$ min

1,2-dibromobenzene $\tau_R = 10.5$ min

(1*S*,2*R*)-ethyl 2-phenylcyclopropanecarboxylate $\tau_R = 35.3$ min

(1*R*,2*S*)-ethyl 2-phenylcyclopropanecarboxylate $\tau_R = 38.5$ min

(1*R*,2*R*)-ethyl 2-phenylcyclopropanecarboxylate $\tau_R = 39.7$ min

(1*S*,2*S*)-ethyl 2-phenylcyclopropanecarboxylate $\tau_R = 41.0$ min

Cyclopropanation of α-methylstyrene with ethyl diazoacetate: GC-column CB1, helium 1.3 mL min^{-1} (constant flow modus), injector 250 °C (pulsed split modus), detector (FID) 250 °C, oven: 80 °C; 5 °C min^{-1} 110 °C (30 min), 5 °C min^{-1} 120 °C (5 min), 20 °C min^{-1} 160 °C (2 min):

α-methylstyrene $\tau_R = 3.4$ min

1,2-dibromobenzene $\tau_R = 10.5$ min

(1*R*,2*S*)-ethyl 2-methyl-2-phenylcyclopropanecarboxylate $\tau_R = 29.2$ min

(1*S*,2*R*)-ethyl 2-methyl-2-phenylcyclopropanecarboxylate $\tau_R = 31.3$ min

(1*S*,2*S*)-ethyl 2-methyl-2-phenylcyclopropanecarboxylate $\tau_R = 36.6$ min

(1*R*,2*R*)-ethyl 2-methyl-2-phenylcyclopropanecarboxylate $\tau_R = 37.6$ min

Cyclopropanation of 1,1-diphenylethylene with ethyl diazoacetate: GC-column CB1, helium 1.2 mL min^{-1} (constant flow modus), injector 250 °C (pulsed split modus), detector (FID) 250 °C, oven: 80 °C; 5 °C min^{-1} 115 °C (10 min), 5 °C min^{-1} 125 °C (10 min), 20 °C min^{-1} 140 °C (5 min), 20 °C min^{-1} 160 °C (5 min):

1,2-dibromobenzene $\tau_R = 10.4$ min

1,1-diphenylethylene $\tau_R = 30.3$ min

(1*R*)/(1*S*)-ethyl 2,2-diphenylcyclopropanecarboxylate $\tau_R = 40.0$ min.

analytical HPLC-column Chiralcel OJ-R, isopropanol/acetonitrile/water 75:10:15 (0.4 mL min^{-1}), UV/Vis array detector and optical rotation detector (Chiralyser), t_R based on Chiralyser detection:

(−)-(1*R*)-ethyl 2,2-diphenylcyclopropanecarboxylate $\tau_R = 15.8$ min

(+)-(1*S*)-ethyl 2,2-diphenylcyclopropanecarboxylate $\tau_R = 24.6$ min

Cyclopropanation of 1-octene with ethyl diazoacetate: GC-column CB1, helium 1.2 mL min^{-1} (constant flow modus), injector 250 °C (pulsed split modus), detector (FID) 250 °C, oven: 80 °C, 5 °C min^{-1} 95 °C (55 min), 5 °C min^{-1} 120 °C (5 min), 20 °C min^{-1} 160 °C (2 min):

1-octene $\tau_R = 1.7$ min

1,2-dibromobenzene $\tau_R = 18.1$ min

cis-ethyl 2-(*n*-hexyl)-cyclopropanecarboxylate $\tau_R = 51.3$ min

(*cis* major enantiomer obtained in catalysis with (1*S*)-configurated Ru–porphyrins)

cis-ethyl 2-(*n*-hexyl)-cyclopropanecarboxylate $\tau_R = 54.0$ min

(*cis* major enantiomer obtained in catalysis with (1*R*)-configurated Ru–porphyrins)

(1*R*,2*R*) ethyl 2-(*n*-hexyl)-cyclopropanecarboxylate $\tau_R = 57.6$ min

(1*S*,2*S*) ethyl 2-(*n*-hexyl)-cyclopropanecarboxylate $\tau_R = 58.7$ min

Cyclopropanation of α-trimethylsiloxystyrene with ethyl diazoacetate: GC-column β-CD1, helium 100 kPa (constant pressure modus), injector 200 °C (split modus), detector (FID) 200 °C, oven: 76 °C:

α-trimethylsiloxystyrene $\tau_R = 11.3$ min

1,2-dibromobenzene $\tau_R = 17.7$ min

(−)-*cis*-ethyl 2-trimethylsiloxy-cyclopropanecarboxylate $\tau_R = 332.1$ min

(*cis* major enantiomer obtained in catalysis with (1*R*)-configurated Ru–porphyrins)

(+)-*cis*-ethyl 2-trimethylsiloxy-cyclopropanecarboxylate $\tau_R = 362.8$ min

(*cis* major enantiomer obtained in catalysis with (1*S*)-configurated Ru–porphyrins)

(−)-*trans*-ethyl 2-trimethylsiloxy-cyclopropanecarboxylate $\tau_R = 430.9$ min

(*trans* major enantiomer obtained in catalysis with (1*R*)-configurated Ru–porphyrins)

(+)-*trans*-ethyl 2-trimethylsiloxy-cyclopropanecarboxylate $\tau_R = 441.7$ min

(*trans* major enantiomer obtained in catalysis with (1*S*)-configurated Ru–porphyrins)

Cyclopropanation of styrene with phenyl diazomethane: GC-column CB1, helium 1.4 mL min^{-1} (constant flow modus), injector 250 °C (pulsed split modus), detector (FID) 250 °C, oven: 80 °C (3 min), 10 °C min^{-1} 123 °C (73 min), 10 °C min^{-1} 150 °C (5 min), 20 °C min^{-1} 200 °C (2 min):

styrene $\tau_R = 4.0$ min

cis-1,2-diphenylcyclopropane $\tau_R = 45.0$ min

dibenzyl ether $\tau_R = 60.6$ min

(1*S*,2*S*)-1,2-diphenylcyclopropane $\tau_R = 74.7$ min

(1*R*,2*R*)-1,2-diphenylcyclopropane $\tau_R = 75.9$ min

Analytical HPLC-column Chiralpak AD, UV/Vis-array-detector and optical rotation detector (Chiralyser); before each run, the column was flushed with *n*-hexane/isopropanol 9:1 (0.7 mL min^{-1}); 7 min before sample injection, the solvent was switched to pure *n*-hexane (0.7 mL min^{-1}), retention times are based on Chiralyser detection:

(+)-(1*R*,2*R*)-1,2-diphenylcyclopropane $\tau_R = 7.4$ min

(−)-(1*S*,2*S*)-1,2-diphenylcyclopropane $\tau_R = 9.8$ min

Cyclopropanation of α-methylstyrene with phenyl diazomethane: GC-column β-CD1, helium 100 kPa (constant pressure modus), injector 200 °C

(split modus), detector (FID) 200 °C, oven: 80 °C (5 min), 20 °C min^{-1} 108 °C

α-methylstyrene $\tau_R = 2.3$ min

1,2-dibromobenzene $\tau_R = 8.5$ min

(−)-*cis*-1-methyl-1,2-diphenylcyclopropane $\tau_R = 36.1$ min

(*cis* major enantiomer obtained in catalysis with (1*R*)-configurated Ru–porphyrins)

(+)-*cis*-1-methyl-1,2-diphenylcyclopropane $\tau_R = 40.4$ min

(*cis* major enantiomer obtained in catalysis with (1*S*)-configurated Ru–porphyrins)

(−)-*trans*-1-methyl-1,2-diphenylcyclopropane $\tau_R = 66.6$ min

(*trans* major enantiomer obtained in catalysis with (1*R*)-configurated Ru–porphyrins)

(+)-*trans*-1-methyl-1,2-diphenylcyclopropane $\tau_R = 67.2$ min

(*trans* major enantiomer obtained in catalysis with (1*S*)-configurated Ru-porphyrins)

Asymmetric epoxidation, GC-analysis

Epoxidation of styrene: GC-column CB1, helium 1.1 mL min^{-1} (constant flow modus), injector 200 °C (pulsed split modus), detector (FID) 250 °C, oven: 76 °C (33 min), 10 °C min^{-1} 115 °C (3 min), 20 °C min^{-1} 180 °C:

styrene $\tau_R = 6.3$ min

(*S*)-styrene oxide $\tau_R = 28.8$ min

(*R*)-styrene oxide $\tau_R = 31.2$ min

1,2-dibromobenzene $\tau_R = 37.8$ min

Epoxidation of 1,2-dihydronaphthalene: GC-column CB1, helium 1.4 mL min^{-1} (constant flow modus), injector 250 °C (pulsed split modus), detector (FID) 250 °C, oven: 110 °C (30 min), 20 °C min^{-1} 150 °C (5 min), 20 °C min^{-1} 200 °C (2 min):

1,2-dihydronaphthalene $\tau_R = 6.5$ min

1,2-dibromobenzene $\tau_R = 7.2$ min

(1*S*,2*R*)-1,2-epoxy-1,2,3,4-tetrahydronaphthalene $\tau_R = 21.3$ min

(1*R*,2*S*)-1,2-epoxy-1,2,3,4-tetrahydronaphthalene $\tau_R = 23.6$ min

Epoxidation of 1-octene: GC-column CB1, helium 1.5 mL min^{-1} (constant flow modus), injector 200 °C (pulsed split modus), detector (FID) 250 °C, oven: 68 °C (17 min), 10 °C min^{-1} 120 °C (4 min), 30 °C min^{-1} 200 °C:

1-octene $\tau_R = 2.7$ min

(*R*)-1,2-epoxyoctane $\tau_R = 14.8$ min

(*S*)-1,2-epoxyoctane $\tau_R = 15.1$ min

1,2-dibromobenzene $\tau_R = 23.3$ min

Determination of the relative and absolute configurations of the cyclopropanes obtained from the reaction of α-methylstyrene and ethyl diazoacetate

Cyclopropanation of α-methylstyrene with [Cu(acac)$_2$] and ethyl diazoacetate: α-Methylstyrene (7.4 g, 8.2 mL, 63.0 mmol) was cyclopropanated according to the GP d) with ethyl diazoacetate (7.9 g, 7.3 mL, 69.3 mmol, 1.1 equiv) and [Cu(acac)$_2$] (660 mg, 2.52 mmol, 0.04 equiv). After workup, the mixture of the stereoisomers was obtained as a colorless liquid (8.4 g, 41.0 mmol, 65 %). The diastereomers were separated via preparative HPLC on a LiChroSorb Si 60 column. The two pairs of enantiomers were then separated via preparative HPLC on a Chiralpak AD column. All four cyclopropanes could be obtained in pure form (GC).

Mixture of all four stereoisomers: b.p. 73 °C (0.4 mbar); GC-MS column HP-5, He 1.0 mL min^{-1} (constant flow modus), Injector 250 °C (split modus), oven: 100 °C (5 min), 20 °C min^{-1} 200 °C (15 min), 20 °C min^{-1} 280 °C (10 min), $\tau_R = 8.7$ min (*cis*, *m*/*z*: 204, 175, 159, 147, 131, 115, 103, 91, 77), $\tau_R = 9.1$ min (*trans*, *m*/*z*: 204, 175, 159, 147, 131, 115, 103, 91, 77); analytical HPLC LiChroSpher Si 60, *n*-hexane/dichloromethane 70:30 (0.5 mL min^{-1}), $\tau_R = 22.0$ min (*trans*), $\tau_R = 37.2$ min (*cis*); preparative HPLC LiChroSorb Si 60, *n*-hexane/dichloromethane 70:30 (60 mL min^{-1}), $\tau_R = 12.2$ min (*trans*), $\tau_R = 16.2$ min (*cis*); analytical HPLC Chiralpak AD, *n*-hexane (0.5 mL min^{-1}), $\tau_R = 12.2$ min [(+)-*trans*-(1*S*,2*S*)], $\tau_R = 14.2$ min [(−)-*trans*-(1*R*,2*R*)], $\tau_R = 27.3$ min [(+)-*cis*-(1*S*,2*R*)], $\tau_R = 29.2$ min [(−)-*cis*-(1*R*,2*S*)]; preparative HPLC Chiralpak AD, *n*-hexane (60 mL min^{-1}), $\tau_R = 19.2$ min [(+)-*cis*-(1*S*,2*R*)], $\tau_R = 27.5$ min [(−)-*trans*-(1*R*,2*R*)], $\tau_R = 30.7$ min [(+)-*cis*-(1*S*,2*R*)], $\tau_R = 33.1$ min [(−)-*cis*-(1*R*,2*S*)].

trans-Enantiomers: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.41-7.14$ (m, 5H, aryl-H), 4.24–4.11 (m, 2H, CH_2CH_3), 1.95 (dd, $^3J_{cis} = 8.3$ Hz, $^3J_{trans} = 6.1$ Hz, 1H, HC), 1.51 (s, 3H, q-C-CH_3), 1.44–1.38 (m, 2H, H_2C), 1.29 (t, $^3J = 7.1$ Hz, 3H, CH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 172.2$ (carboxyl-C), 145.9 (aryl-C), 128.4 (aryl-C), 127.3 (aryl-C), 126.4 (aryl-C), 60.5 (OCH_2), 30.6 (benzyl-C), 27.8 (CH), 20.8 (CH_2), 19.9 (q-C-CH_3), 14.4 (OCH_2-CH_3); (1*S*,2*S*)-isomer: elemental analysis calcd (%) for $C_{13}H_{16}O_2$ (204.26): C 76.44, H 7.90; found: C 76.16, H 7.83; (1*S*,2*S*)-isomer: $[\alpha]_D^{20} = +286°$ ($CHCl_3$, $c = 0.328$).

cis-Enantiomers: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.41-7.14$ (m, 5H, aryl-H), 3.88–3.63 (m, 2H, CH_2CH_3), 1.88 (dd, $^3J = 7.7$, $^3J = 5.4$ Hz, 1H, HC), 1.76 (dd, $^3J = 7.7$ Hz, $^2J = 4.6$ Hz, 1H, C*H*H′$_{cis}$), 1.45 (s, 3H, q-C-CH_3), 1.13 (dd, $^3J = 5.4$, $^2J = 4.6$ Hz, 1H, CH*H*′$_{trans}$), 0.92 (t, $^3J = 7.1$ Hz, 3H, CH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 171.2$ (carboxyl-C), 141.9 (aryl-C), 128.7 (aryl-C), 128.1 (aryl-C), 126.6 (aryl-C), 60.0 (OCH_2), 32.0 (benzyl-C), 28.5 (CH), 28.5 (q-C-CH_3), 19.4 (CH_2), 13.9 (CH_2-CH_3); (1*S*,2*R*)-isomer: elemental analysis calcd (%) for $C_{13}H_{16}O_2$ (204.26 g mol^{-1}): C 76.44, H 7.90; found: C 76.15, H 7.81; (1*S*,2*R*)-isomer: $[\alpha]_D^{20} = +61°$ ($c = 0.614$, $CHCl_3$); (1*R*,2*S*)-isomer: elemental analysis calcd (%) for $C_{13}H_{16}O_2$ (204.26 g mol^{-1}): C 76.44, H 7.90; found: C 76.16, H 7.84.

Preparation of *trans*-(1*S*,2*S*)-2-methyl-2-phenylcyclopropane-(1*S*′)-(1-phenylethyl)-carboxamide: (1*S*,2*S*)-Ethyl 2-methyl-2-phenylcyclopropanecarboxylate (80 mg, 392 μmol, 1 equiv) was amidated with (*S*)-(−)-1-phenylethylamine (237 mg, 252 μL, 1.96 mmol, 5 equiv) according to procedure e). The amide was obtained as colorless crystals (39 mg, 140 μmol, 36 %). M.p. 123 °C (*n*-hexane); analytical HPLC Supersphere 60 RP-Select B, methanol/water 70:30 (0.3 mL min^{-1}), $\tau_R = 13.7$ min; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.48-7.14$ (m; 10H, aryl-H), 5.89* (br s; 1H, NH), 5.25–5.10 (m; 1H, C*H*-NH), 1.67 (dd, $^3J_{cis} = 8.3$, $^3J_{trans} = 5.8$ Hz; 1H, C*H*-CONH), 1.53 (s; 3H, q-C-CH_3), 1.50 (d, $^3J = 7.0$ Hz; 3H, CH-CH_3), 1.49 (dd, $^3J = 5.8$, $^2J = 4.8$ Hz; 1H, C*H*H′$_{cis}$), 1.33 (dd, $^3J = 8.3$, $^2J = 4.8$ Hz; 1H, CH*H*′$_{trans}$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 169.4$ (s; amide-C), 146.2 (aryl-C), 143.3 (aryl-C), 128.6 (aryl-C), 128.4 (aryl-C), 127.3 (aryl-C), 126.5 (aryl-C), 126.2 (aryl-C), 126.2 (aryl-C), 49.1 (NH-C), 30.9 (CH-CO), 28.7 (q-*C*-CH_3), 22.0 (CH-CH_3), 19.6 (CH_2), 18.8 (q-C-CH_3); IR (neat): $\tilde{\nu} =$ = 3277 (m), 3056 (w), 3024 (w), 2971 (w), 2925 (w), 2869 (w), 1635 (s), 1600 (w), 1539 (s), 1493 (s), 1444 (m), 1433 (m), 1397 (m), 1375 (w), 1301 (w), 1232 (m), 1116 (w), 1083 (w), 1068 (w), 1027 (w), 970 (w), 950 (w), 920 (w), 903 (w), 843 (w), 761 (m), 696 cm^{-1} (s); HR-MS (ESI, $\Delta m = 0.005$): *m*/*z*: calcd for: 302.152; found: 302.152 [*M*+Na]$^+$. The chemical shift of the amide N-H resonance strongly depends on the water content of the $CDCl_3$. Due to the hindered rotation around the amide bond, more than one amide proton signal may be detected.

Preparation of *trans*-(1*R*,2*R*)-2-methyl-2-phenylcyclopropane-(1*S*′)-(1-phenylethyl)-carboxamide: (1*R*,2*R*)-Ethyl 2-methyl-2-phenylcyclopropanecarboxylate (160 mg, 783 μmol, 1 equiv) was amidated with (*S*)-(−)-1-phenylethylamine (474 mg, 504 μL, 3.92 mmol, 5 equiv) according to procedure e). The amide was obtained as colorless crystals (90 mg, 322 μmol, 41 %), the purity of the amide was confirmed by HPLC analysis. The relative configuration of the product was determined by X-ray analysis. M.p. 124 °C (*n*-hexane); analytical HPLC Supersphere 60 RP-Select B, methanol/water 70:30 (0.3 mL min^{-1}), $\tau_R = 13.3$ min; NMR and IR data are indistinguishable from the data of the *trans*-(1*S*,2*S*)-isomer; HR-MS (ESI, $\Delta m = 0.005$): *m*/*z*: calcd for: 302.152; found: 302.152 [*M*+Na]$^+$.

Preparation of *cis*-(1*S*,2*R*)-2-methyl-2-phenylcyclopropane-(1*S*′)-(1-phenylethyl)-carboxamide: (1*S*,2*R*)-Ethyl 2-methyl-2-phenylcyclopropanecarboxylate (50 mg, 245 μmol, 1 equiv) was amidated with (*S*)-(−)-1-phenylethylamine (148 mg, 158 μL, 1.22 mmol, 5 equiv) according to procedure e). The amide was obtained as colorless crystals (33 mg (118 μmol, 48 %). M.p. 149 °C (*n*-hexane); analytical HPLC Supersphere 60 RP-Select B, methanol/water 70:30 (0.25 mL min^{-1}), $\tau_R = 17.5$ min; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.39-7.18$ (m; 8H, aryl-H), 7.11–7.04 (m; 2H, aryl-H), 5.42* (br s; 1H, NH), 4.95–4.81 (m; 1H, C*H*-NH), 1.86 (dd, $^3J_{cis} = 8.2$, $^3J_{trans} = 5.6$ Hz; 1H, C*H*-CONH), 1.65 (dd, $^3J = 5.6$ Hz, $^2J = 5.0$ Hz; 1H, C*H*H′$_{cis}$), 1.44 (s; 3H, q-C-CH_3), 1.29 (d, $^3J = 6.8$ Hz; 3H, CH-CH_3), 1.33 (dd, $^3J = 8.2$ Hz, $^2J = 5.0$ Hz; 1H, CH*H*′$_{trans}$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 170.0$ (s; amide-C), 142.8.2 (aryl-C), 141.3 (aryl-C), 128.9 (aryl-C), 128.5 (aryl-C), 128.5 (aryl-C), 127.3 (aryl-C), 126.9 (aryl-C), 126.2 (aryl-C), 48.7 (NH-C), 31.2 (q-*C*-CH_3), 30.2 (CH-CO), 28.6 (q-C-*C*H_3), 20.8 (CH-*C*H_3), 18.9 (CH_2); IR (neat): $\tilde{\nu} = 3271$ (m), 3056 (w), 3024 (w), 2966 (w), 2922 (w), 2865 (w), 1640 (s), 1601 (w), 1539 (s), 1494 (s), 1444 (m), 1395 (w), 1376 (w), 1257

(m), 1212 (m), 1131 (w), 1114 (w), 1087 (w), 1068 (w), 1026 (w), 981 (w), 896 (w), 862 (w), 844 (w), 757 (m), 696 cm^{-1} (s); HR-MS (ESI, $\Delta m = 0.005$): m/z: calcd for 302.152; found: 302.152 $[M+Na]^+$. *) see previous paragraph.

Preparation of *cis*-(1*R*,2*S*)-2-methyl-2-phenylcyclopropane-(1*S*′)-(1-phenylethyl)-carboxamide: (1*R*,2*S*)-Ethyl 2-methyl-2-phenylcyclopropanecarboxylate (50 mg, 245 μmol, 1 equiv) was amidated with (*S*)-(−)-1-phenylethylamine (148 mg, 158 μL, 1.22 mmol, 5 equiv) according to (e). The amide was obtained as colorless crystals (24 mg, 86 μmol, 35 %), the purity of the amide was confirmed by HPLC analysis. The relative configuration of the product was determined by X-ray analysis. M.p. 192 °C (*n*-hexane); analytical HPLC Supersphere 60 RP-Select B, methanol/water 70:30 (0.25 mL min^{-1}), $\tau_R = 16.4$ min; NMR and IR data are undistinguishable from the data of the *cis*-(1*S*,2*R*)-isomer; HR-MS (ESI, $\Delta m = 0.005$): m/z: calcd for 302.152; found: 302.153 $[M+Na]^+$.

Determination of the relative configurations of the cyclopropanes obtained from the reaction of α-trimethylsiloxy styrene with ethyl diazoacetate

α-Trimethylsiloxy styrene (3.0 g, 15.6 mmol, 1.0 equiv) was cyclopropanated according to the general procedure d) with ethyl diazoacetate (2.0 g, 1.8 mL, 17.2 mmol, 1.1 equiv) and $[Cu(acac)_2]$ (164 mg, 624 μmol, 0.04 equiv). After workup, the mixture of the stereoisomers was obtained as a colorless liquid (1.4 g, 5.0 mmol, 32 %). The stereoisomers were separated or enriched, respectively, via preparative HPLC on a Chiralpak AD column. The amidation following GP e) afforded the ring opened γ-keto amide exclusively. An assignment of the absolute configuration of the cyclopropanes was thus not possible. The relative configuration was assigned by NMR experiments. GC-MS column HP-5, helium 1.0 mL min^{-1} (constant flow modus), Injector 250 °C (split modus), oven: 100 °C (5 min), 20 °C min^{-1} 200 °C (15 min), 20 °C min^{-1} 280 °C (10 min), $\tau_R = 10.4$ min (*trans*, m/z: 278, 249, 205, 159, 131, 105, 73), $\tau_R = 10.7$ min (*cis*, m/z: 278, 249, 205, 159, 131, 105, 73); analytical HPLC LiChroSpher Si 60, *n*-hexane/dichloromethane 70:30 (1.0 mL min^{-1}), $\tau_R = 29.8$ min (*trans*), $\tau_R = 33.2$ min (*cis*); analytical HPLC Chiralpak AD, *n*-hexane (0.6 mL min^{-1}), $\tau_R = 13.1$ min [(+)-*trans*], $\tau_R = 15.4$ min [(+)-*cis*], $\tau_R = 19.5$ min [(−)-*cis*], $\tau_R = 20.4$ min [(−)-*trans*]; preparative HPLC Chiralpak, *n*-hexane (60 mL min^{-1}), $\tau_R = 27.1$ min [(+)-*trans*], $\tau_R = 30.2$ min [(+)-*cis*], $\tau_R = 31.5$ min [(−)-*trans*], $\tau_R = 33.7$ min [(−)-*cis*].

trans-Enantiomers: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.46-7.19$ (m; 5H, aryl-H), 3.87–3.76 (m; 2H, CH_2CH_3); 2.25 (dd, $^3J_{cis} = 9.1$, $^3J_{trans} = 7.0$ Hz; 1H, CH), 1.94 (dd, $^3J_{trans} = 7.0$, $^2J = 5.9$ Hz; 1H, CHH'_{cis}), 1.48 (dd, $^3J_{cis} = 9.1$, $^2J = 5.9$ Hz; 1H, CHH'_{trans}), 0.93 (t, $^3J = 7.0$ Hz; 3H, CH_2CH_3), −0.08 (s; 9H, $Si(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 173.9$ (carboxyl-C), 136.6 (aryl-C), 129.0–125.0 (aryl-C; an assignment of the ^{13}C NMR signals of the aryl carbon atoms was not possible due to their low intensity; their approximate chemical shifts were obtained from 2D-experiments), 65.4 (benzyl-C), 60.2 (OCH_2), 30.4 (CH), 19.3 (CH_2), 14.2 (OCH_2-CH_3), 0.7 ($Si(CH_3)_3$).

cis-Enantiomers: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.51-7.20$ (m; 5H, aryl-H), 4.16 (q; $^3J = 7.2$ Hz; 2H, CH_2CH_3), 1.99–1.87 (m; 2H, CH, CHH'_{cis}), 1.64 (dd, $^3J_{cis} = 8.1$, $^2J = 5.3$ Hz; 1H, CHH'_{trans}), 1.23 (t, $^3J = 7.2$ Hz; 3H, CH_2CH_3), 0.04 (s; 9H, $Si(CH_3)_3$; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 169.1$ (carboxyl-C), 142.8 (aryl-C), 129.0–125.0 (aryl-C, an assignment of the ^{13}C NMR signals of the aryl carbon atoms was not possible due to their low intensity. Their approximate chemical shifts were obtained from 2D-experiments.), 63.5 (benzyl-C), 60.6 (OCH_2), 31.1 (CH), 20.2 (CH_2), 14.4 (OCH_2-CH_3), 0.8 ($Si(CH_3)_3$).

Cyclopropanation of 1,1-diphenylethylene with $[Cu(acac)_2]$ and ethyl diazoacetate: 1,1-Diphenylethylene (3.1 g, 3.0 mL, 17.0 mmol, 1.0 equiv) was cyclopropanated according to the general procedure (d) with ethyl diazoacetate (2.1 g, 2.0 mL, 18.7 mmol, 1.1 equiv) and $[Cu(acac)_2]$ (178 mg, 680 μmol, 0.04 equiv). After workup, the product was obtained as a colorless liquid (2.5 g, 9.3 mmol, 55 %). The enantiomers were separated via preparative HPLC on a Chiralpak AD column. Racemic mixture: b.p. 95 °C (0.4 mbar); GC-MS column HP-5, helium 1.0 mL min^{-1} (constant flow modus), Injector 250 °C (split modus), oven: 100 °C (5 min), 20 °C min^{-1} 200 °C (15 min), 20 °C min^{-1} 280 °C (10 min), $\tau_R = 14.7$ min (m/z: 266, 237, 192, 178, 165, 115, 91); analytical HPLC Chiralpak AD, *n*-hexane (0.5 mL min^{-1}), $\tau_R = 31.0$ min [(+)-*S*], $\tau_R = 32.6$ min [(−)-*R*]; preparative HPLC Chiralpak AD, *n*-hexane (70 mL min^{-1}), $\tau_R = 22.1$ min [(+)-*S*], $\tau_R = 29.4$ min [(−)-*R*]; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.40-7.15$ (m, 10H, aryl-H), 4.00–3.85 (m, 2H, CH_2CH_3), 2.54 (dd, $^3J_{cis} = 8.1$, $^3J_{trans} = 5.9$ Hz; 1H, CH), 2.17 (dd, $^3J_{trans} = 5.9$, $^2J = 4.9$ Hz; 1H, CHH'_{cis}), 1.58 (dd, $^3J_{cis} = 8.1$ Hz, $^2J = 4.9$ Hz; 1H, CHH'_{trans}), 1.00 (t, $^3J = 7.1$ Hz; 3H, CH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 170.6$ (carboxyl-C), 144.8 (aryl-C), 140.2 (aryl-C), 129.7 (aryl-C), 128.4 (aryl-C), 128.2 (aryl-C), 127.6 (aryl-C), 126.9 (aryl-C), 126.5 (aryl-C), 60.4 (CH_2CH_3), 39.8 (benzyl-C), 29.0 (CH), 20.1 (CH_2), 14.0 (CH_2CH_3); (1*S*)-enantiomer: elemental analysis calcd (%) for $C_{13}H_{16}O_2$ (266.13 g mol^{-1}): (1*S*)-enantiomer: C 81.17, H 6.81; found: C 80.81, H 6.72; (1*S*)-isomer: $[\alpha]_D^{20} = +180°$ ($c = 0.512$, $CHCl_3$).

Determination of the absolute configurations of the cyclopropanes obtained from the reaction of 1,1-diphenylethylene with ethyl diazoacetate

Preparation of (1*S*)-2,2-diphenylcyclopropane carboxylic acid: A 50 mL flask was charged with (1*S*)-ethyl 2,2-diphenylcyclopropanecarboxylate (220 mg, 827 μmol), potassium hydroxide (0.5 g, 10.6 mmol), water (5 mL) and methanol (35 mL). The mixture was stirred at room temperature for 12 h. Conc. HCl (2 mL) and water (10 mL) were added and the mixture was extracted three times with a total of 150 mL dichloromethane. The collected extracts were washed twice with water (20 mL) and dried over magnesium sulfate. Evaporation of the solvent afforded the free acid as a colorless solid (173 mg, 726 μmol, 88 %). The absolute configuration of the acid was determined by correlation of the optical rotation with literature data.[30] M.p. 141 °C (dichloromethane); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.35-7.12$ (m; 10H, aryl-H), 2.57 (dd, $^3J_{cis} = 8.0$, $^3J_{trans} = 5.9$ Hz; 1H, CH), 2.17 (dd, $^3J_{trans} = 5.9$, $^2J = 4.8$ Hz; 1H, CHH'_{cis}), 1.58 (dd, $^3J_{cis} = 8.0$, $^2J = 4.8$ Hz; 1H, CHH'_{trans}); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 176.5$ (carboxyl-C), 144.5 (aryl-C), 129.6 (aryl-C), 128.5 (aryl-C), 128.4 (aryl-C), 127.6 (aryl-C), 127.1 (aryl-C), 126.7 (aryl-C), 41.0 (benzyl-C), 28.5 (CH), 20.7 (CH_2); elemental analysis calcd (%) for $C_{16}H_{14}O_2$ (238.28 g mol^{-1}): C 80.65, H 5.92; C 80.15, H 6.01, $[\alpha]_D^{20} = +221°$ ($c = 0.329$, $CHCl_3$).

Determination of the relative and absolute configurations of the cyclopropanes obtained from the reaction of 1-octene with ethyl diazoacetate

Preparation of enantiomerically enriched (1*S*,2*S*)-2-(*n*-hexyl)-cyclopropane carboxylic acid: A catalytic cyclopropanation of 1-octene was carried out with catalyst **2e**, and the reaction product was purified by Kugelrohr distillation (b.p. 110 °C at 2 mbar) and chromatography on silica gel (*n*-hexane) [purity > 97 %, > 99 % *de*, 82 % *ee* (GC), sense of optical rotation (+)]. A 50 mL flask was charged with this enantiomerically enriched (1*S*,2*S*)-2-(*n*-hexyl)-diphenylcyclopropane carboxylic ethyl ester (50 mg, 252 μmol), potassium hydroxide (0.2 g, 4.25 mmol), water (5 mL) and methanol (15 mL). The mixture was stirred at room temperature for 12 h. Concentrated hydrochloric acid (1 mL) and water (20 mL) were added and the mixture was extracted three times with a total of 60 mL dichloromethane. The collected extracts were washed twice with water (10 mL) and dried over magnesium sulfate. Evaporation of the solvent afforded the free acid as a colorless oil (38 mg, 223 μmol, 89 %). The *trans*-configuration of the major product was assigned by NMR experiments, and correlation of the data with those of a pure sample of the *trans*-enantiomers, obtained by palladium catalyzed cyclopropanation of *trans*-ethyl non-2-enoate with CH_2N_2. The absolute configuration of the acid was determined by correlation of the sense of optical rotation with literature data.[31] ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.44-1.16$ (m; 13H, cyclopropyl-CHH'_{cis}, cyclopropyl-CH, *n*-alkyl-H), 0.90–0.82 (m; 3H, CH_3), 0.78–0.72 (m; 1H, cyclopropyl-CHH'_{trans}) [chemical shifts from 2D-data for the *trans*-acid: 1.42, 1.33, 1.32, 1.29, 1.28, 1.26, 1.21, 0.87, 0.76; for the *cis*-acid: 1.66, 1.55, 1.32, 1.30, 1.29, 1.28, 1.26, 1.06, 0.94, 0.87]; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 180.9$ (carboxyl-C), 33.0 (*n*-alkyl-CH_2), 31.8 (*n*-alkyl-CH_2); 29.0 (*n*-alkyl-CH_2), 28.9 (*n*-alkyl-CH_2), 24.1 (C_6H_{13}-*C*H), 22.6 (*n*-alkyl-CH_2), 20.0 (*C*H-COOH), 16.4 (cyclopropyl-CH_2), 14.1 (CH_3) [chemical shifts for the *cis*-acid: $\delta = 179.5$ (carboxyl-C), 33.0 (*n*-alkyl-CH_2), 31.8 (*n*-alkyl-CH_2); 29.5 (*n*-alkyl-CH_2), 26.9 (*n*-alkyl-CH_2), 23.2 (C_6H_{13}-*C*H), 22.6 (*n*-alkyl-CH_2), 18.0 (*C*H-COOH), 14.4 (cyclopropyl-CH_2), 14.1 (CH_3); (1*S*,2*S*)-isomer: $[\alpha]_D^{20} = +16°$ [$c = 0.369$, $CHCl_3$ (effective concentration of pure (1*S*,2*S*)-enantiomer, the real concentration of the enantiomeric mixture (82 % *ee*, > 99 % *de*) was 450 mg per 100 mL)].

Determination of the relative and absolute configurations of the cyclopropanes obtained from the reaction of styrene with phenyl diazomethane

Styrene (1.0 g, 1.1 mL, 9.6 mmol, 1.0 equiv) was cyclopropanated according to the GP d) with phenyl diazomethane (1.3 g, 10.6 mmol, 1.1 equiv) and $[Cu(acac)_2]$ (124 mg, 384 μmol, 0.04 equiv). After workup, the mixture of the stereoisomers was obtained as a colorless liquid (0.65 g, 3.4 mmol,

35%). The stereoisomers were then separated or enriched, respectively, via preparative HPLC on a Chiralpak AD column. The relative configurations of the cyclopropanes were assigned by NMR-experiments. The absolute configuration of the *trans*-products was assigned by correlation of the sense of optical rotation with literature data.[32] GC-MS column HP-5, helium 1.0 mL min^{-1} (constant flow modus), Injector 250 °C (split modus), oven: 100 °C (5 min), 20 °C min^{-1} 200 °C (15 min), 20 °C min^{-1} 280 °C (10 min), τ_R = 10.0 min (*cis*, *m*/*z*: 194, 179, 165, 115), τ_R = 10.8 min (*trans*, *m*/*z*: 194, 179, 165, 115), analytical HPLC Chiralpak AD, *n*-hexane (0.6 mL min^{-1}), τ_R = 14.2 min [(+)-(1*R*,2*R*)], τ_R = 14.5 min [(−)-(1*S*,2*S*)], τ_R = 18.7 min *cis-meso*; preparative HPLC Chiralpak AD, *n*-hexane (70 mL min^{-1}), τ_R = 16.8 min [(+)-(1*R*,2*R*)], τ_R = 19.2 min [(−)-(1*S*,2*S*)], τ_R = 24.5 min [*cis-meso*].

trans-Enantiomers: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39–7.29 (m; 4H, aryl-H), 7.29–7.17 (m; 6H, aryl-H), 2.23 (t, ^3J = 7.0 Hz; 2H, CH), 1.51 (t, ^3J = 7.0 Hz; 2H, CH_2; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.4 (aryl-C), 128.3 (aryl-C), 125.7 (aryl-C), 125.6 (aryl-C), 27.9 (CH), 18.1 (CH_2).

cis-Enantiomers: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.18–7.14 (m; 4H, aryl-H), 7.14–7.09 (m; 2H, aryl-H), 7.03–6.98 (m; 4H, aryl-H), 2.54 (dd, $^3J_{cis}$ = 8.5 Hz, $^3J_{trans}$ = 6.5 Hz; 2H, CH), 1.52–1.33 (m; 2H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.3 (aryl-C), 128.9 (aryl-C), 127.5 (aryl-C), 125.5 (aryl-C), 24.1 (CH), 11.3 (CH_2).

Determination of the relative configurations of the cyclopropanes obtained from the reaction of α-methylstyrene with phenyl diazomethane

α-Methylstyrene (10.0 g, 11.1 mL, 85.0 mmol, 1.0 equiv) was cyclopropanated according to the general procedure (d) with phenyl diazomethane (11.1 g, 93.5 mmol, 1.1 equiv) and [Cu(acac)$_2$] (898 mg, 3.4 mmol, 0.04 equiv). After workup, the mixture of the stereoisomers was obtained as a colorless liquid (4.7 g, 23 mmol, 27%). The relative configurations were assigned by NMR experiments. GC-MS column HP-5, helium 1.0 mL min^{-1} (constant flow modus), Injector 250 °C (split modus), oven: 100 °C (5 min), 20 °C min^{-1} 200 °C (15 min), 20 °C min^{-1} 280 °C (10 min), τ_R = 10.3 min (*cis*, *m*/*z*: 208, 193, 178, 130, 115, 91), τ_R = 11.2 min, (*trans*, *m*/*z*: 208, 193, 178, 130, 115, 91); analytical HPLC Chiralpak AD, *n*-hexane (0.3 mL min^{-1}), τ_R = 13.3 min [(−)-*cis*], τ_R = 13.9 min [(+)-*cis*], τ_R = 15.0 min [(−)-*trans*], τ_R = 16.1 min [(+)-*trans*].

trans-Enantiomers: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.18 (m; 10H, aryl-H), 2.40 (dd, $^3J_{cis}$ = 8.7, $^3J_{trans}$ = 6.2 Hz; 1H, CH), 1.44 (dd, $^3J_{cis}$ = 8.7, ^2J = 5.1 Hz; 1H, C*H*H′$_{cis}$), 1.23 (dd, $^3J_{trans}$ = 6.2, ^2J = 5.1 Hz; 1H, CH*H*′$_{trans}$), 1.11 (s; 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.8 (aryl-C), 139.1 (aryl-C), 129.1 (aryl-C), 128.3 (aryl-C), 128.1 (aryl-C), 126.9 (aryl-C), 126.0 (aryl-C), 125.7 (aryl-C), 31.4 (CH), 26.9 (q-cyclopropyl-C), 21.0 (CH_3), 18.6 (CH_2).

cis-Enantiomers: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.19–6.96 (m; 8H, aryl-H), 6.76–6.71 (m; 2H, aryl-H), 2.21 (dd, $^3J_{cis}$ = 8.6, $^3J_{trans}$ = 5.8 Hz; 1H, CH), 1.53 (s; 3H, CH_3), 1.49 (dd, $^3J_{trans}$ = 5.8, ^2J = 5.8 Hz; 1H, C*H*H′$_{cis}$), 1.25 (dd, $^3J_{cis}$ = 8.6, ^2J = 5.8 Hz; 1H, CH*H*′$_{trans}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.3 (aryl-C), 139.8 (aryl-C), 129.9 (aryl-C), 127.9 (aryl-C), 127.5 (aryl-C), 127.4 (aryl-C), 125.8 (aryl-C), 125.0 (aryl-C), 31.1 (q-cyclopropyl-C), 31.1 (CH), 29.6 (CH_3), 19.7 (CH_2).

Details of the X-ray crystal structure analyses

Crystal data for **2d**: $C_{89}H_{72}F_{12}N_4ORu \cdot CH_3OH \cdot 1.5\,H_2O$, M = 1601.64 g mol^{-1}, red crystals from chloroform/methanol, 0.25 × 0.20 × 0.10 mm, orthorhombic, a = 17.021(1), b = 28.006(1), c = 15.840(1) Å, V = 7550.8(7) Å^3, space group $P2_12_12$, Z = 4, ρ_{calcd} = 1.409 g cm^{-3}, μ = 0.293 mm^{-1}, θrange 1.29 to 25.00°, 13204 measured reflections, 13204 independent reflections, refinement method: full-matrix least-squares on F^2, 1000 parameter, goodness-of-fit on F^2 = 1.046, final residuals $R1$ = 0.0945 and $\omega R2$ = 0.2069 for 9792 observed reflections with $I > 2\sigma(I)$.

Crystal data for **2e**: $C_{84}H_{76}F_3N_4PRu \cdot CH_3CN \cdot C_6H_6$, M = 1449.69 g mol^{-1}, red crystals from benzene/acetonitrile, 0.20 × 0.15 × 0.15 mm, monoclinic, a = 9.727(1), b = 27.357(1), c = 14.753(1) Å, β = 107.057(10)°, V = 3753.1(5) Å^3, space group $P2_1$, Z = 2, ρ_{calcd} = 1.283 g cm^{-3}, μ = 0.288 mm^{-1}, θ range 1.44 to 25.00°, 230644 measured reflections, 12873 independent reflections, refinement method: full-matrix least-squares on F^2, 910 parameter, goodness-of-fit on F^2 = 1.021, final residuals $R1$ = 0.0667 and $\omega R2$ = 0.1590 for 9842 observed reflections with $I > 2\sigma(I)$.

Crystal data for *trans*-(1*R*,2*R*)-2-methyl-2-phenylcyclopropane-(1*S*′)-(1-phenylethyl)-carboxamide (**15**): $C_{19}H_{21}NO$, M = 279.38 g mol^{-1}, colorless needles from *n*-hexane, 0.20 × 0.15 × 0.15 mm, monoclinic, a = 10.782(1), b = 5.244(1), c = 14.916(1) Å, β = 109.45(1)°, V = 795.23(18) Å^3, space group $P2_1$, Z = 2, ρ_{calcd} = 1.167 g cm^{-3}, μ = 0.071 mm^{-1}, θ range 1.45 to 31.11°, 3568 measured reflections, 2088 independent reflections, refinement method: full-matrix least-squares on F^2, 275 parameter, goodness-of-fit on F^2 = 1.193, final residuals $R1$ = 0.0560 and $\omega R2$ = 0.1053 for 1319 observed reflections with $I > 2\sigma(I)$.

Crystal data for *cis*-(1*R*,2*S*)-2-methyl-2-phenylcyclopropane-(1*S*′)-(1-phenylethyl)-carboxamide (**16**): $C_{19}H_{21}NO$, M = 279.38 g mol^{-1}, colorless needles from *n*-hexane, 0.20 × 0.15 × 0.12 mm, tetragonal, a = 13.586(1), c = 18.236(1) Å, V = 3366.0(4) Å^3, space group $I4_1$, Z = 8, ρ_{calcd} = 1.103 g cm^{-3}, μ = 0.067 mm^{-1}, θ range 1.87 to 26.98°, 11662 measured reflections, 3223 independent reflections, refinement method: full-matrix least-squares on F^2, 276 parameter, goodness-of-fit on F^2 = 1.103, final residuals $R1$ = 0.0469 and $\omega R2$ = 0.0629 for 1794 observed reflections with $I > 2\sigma(I)$.

Crystal data for (1*S*)-diphenylcyclopropane carboxylic acid (**17**): $C_{16}H_{14}O_2$, M = 238.28 g mol^{-1}, colorless needles from dichloromethane, 0.20 × 0.15 × 0.15 mm, monoclinic, a = 11.959(1), b = 9.803(1), c = 11.931(1), β = 113.01(1)°, V = 1287.4(2) Å^3, space group $P2_1/c$, Z = 4, ρ_{calcd} = 1.229 g cm^{-3}, μ = 0.080 mm^{-1}, θ range 1.85 to 27.00°, 3073 measured reflections, 1626 independent reflections, refinement method: full-matrix least-squares on F^2, 219 parameter, goodness-of-fit on F^2 = 1.063, final residuals $R1$ = 0.0480 and $\omega R2$ = 0.1154 for 1182 observed reflections with $I > 2\sigma(I)$.

All data were collected on a Nonius KappaCCD diffractometer ($Mo_{K\alpha}$ radiation λ = 0.71073 Å at 293(2) K, graphite monochromator λ/ω scans). The structures were solved using direct methods (SHELXS-97, G. M. Sheldrick, Program for the Solution of Crystal Structures, University of Göttingen (Germany), **1997**), followed by full-matrix least squares refinement with anisotropic thermal parameters for Ru, Ph, F, C and O and isotropic parameters for H, (SHELXL-97, G. M. Sheldrick, Program for the Refinement of Crystal Structures, University of Göttingen (Germany), **1997**).

CCDC-210099 (**2d**), -210100 (**2e**), -210101 (*trans*-(1*R*,2*R*)-2-methyl-2-phenylcyclopropane-(1*S*′)-(1-phenylethyl)-carboxamide) (**15**), -210102 (*cis*-(1*R*,2*S*)-2-methyl-2-phenylcyclopropane-(1*S*′)-(1-phenyl-ethyl)-carboxamide) (**16**), -210103 ((1*S*)-diphenylcyclopropane carboxylic acid) (**17**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; (fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

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