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C11-Chirasil-Dex as chiral stationary phase in GC: enantioselective separation of cyclopropane derivatives

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Dedicated to Prof. Volker Schurig on the occasion of his 65th birthday.

Abstract

Chirasil-β-Dex containing an undecamethylene spacer (C11-Chirasil-Dex) was used as chiral stationary phase (CSP) in enantioselective gas chromatography (GC). The versatility of the new stationary phase in the simultaneous enantiomeric separation of a set of cyclopropane derivatives is demonstrated. The GC method provides information about the chemical yields of the cyclopropane products, enantioselectivity, substrate specifity, and catalytic activity of the chiral catalysts used in the intermolecular cyclopropanation of olefins and avoids time-consuming work-up procedures.

Keywords: Chirasil-β-Dex; Cyclopropanes; Enantiomeric excess; Gas chromatography; Rhodium complexes

1. Introduction

Substituted cyclopropanes have been characterized with a large spectrum of biological properties ranging from enzyme inhibitions to insecticidal, antifungal, herbicidal, antimicrobial, antibiotic, antibacterial, antitumor and antiviral activities [1]. They are used as chiral building blocks in the photodegradable and low mammalian-toxic insecticides namely pyrethroids [2], the antidepressant tranylcypromine [3], papain and cystein protease inhibitors [4], the potential anti-psychotic substances [5], anti-HIV agents [6], and marine lactones [7]. Accordingly, effort has been focused during last decades on the stereo-controlled synthesis of pure and enantioenriched substituted cyclopropanes [8]. Besides the resolution of their racemates [9], a number of synthetic methodologies including asymmetric Simmons–Smith reaction, metal-catalyzed reaction of diazo compounds with olefins, and asymmetric ylide cyclopropanation have been developed [10]. The utility of the ylide approaches is directly related to the level of selectivity of the process, which is believed to proceed in via metal carbenes as intermediates [11,12].

The ways in which efficiency and practicality of this procedure are defined is depending on a large number of factors such as suitable catalyst, scale, reagent costs, time allotted and required. Most importantly, the requirement of suitable equipments and reliable methods for the determination of the enantiomeric excesses (ee) of the resulting products arising from asymmetric catalysis. The development of accurate non-chiroptic methods for the determination of enantiomeric 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 enantiomeric purity of the resulting products [13]. 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 enantiomeric 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

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chiral GC and HPLC methods. For an efficient monitoring of the reaction progress, enantioselective gas chromatography (GC) was the method of choice for the simultaneous determination of the enantiomeric excesses of the cyclopropane products resulting from the cyclopropanation of olefins catalyzed by dirhodium(II) catalyst.

Although a large number of chiral stationary phases (CSPs) have been developed [14–18], the choice of an appropriate column is still difficult. Modified cyclodextrins (CDs) have been widely used as chiral stationary phases for GC separation of racemic chiral compounds. These CD derivatives are dissolved in polysiloxane phases and are used for preparing efficient capillary columns.

Chirasil-β-Dex, a polysiloxane-anchored permethylated β-cyclodextrin with 3, 5 and 8 spacer have been successfully used as CSP in GC [14]. In this contribution, we report on the investigation of Chirasil-β-Dex with a new 11-spacer as CSP for the gas chromatographic enantiomers separation of a set of cyclopropane derivatives prepared via metal-catalyzed carbene transfer reactions.

2. Experimental

2.1. Chemicals

Meldrum's acid (2,2-dimethyl-1,3-dioxane,4,6-dione) (**4**) and diacetoxyiodobenzene [PhI(OAc)$_2$] (**6**), 1,8-naphthalic anhydride (**12a**) and its 4-Cl-substitued **12b** were purchased from Acros Organics (Belgium). Iodosyl benzene [PhI = O] (**7**) was prepared as described below. $Rh_2(OAc)_4$ was purchased from Pressure Chemical (Pittsburgh, USA). $Rh_2\{(S)\text{-nttl}\}_4$ (**8**) and the ligand used in its preparation *N*-1,8-naphthoyl-(*S*)-*tert*-leucine (**14a**) were prepared as previously reported. Substituted [$Rh_2\{(S)\text{-nttl}\}_4$] catalysts were prepared according to literature procedure [12]. All olefins were commercially available and distilled prior to use.

2.2. Instruments

Infrared (IR) spectra were measured on a Shimadzu FT-IR-9100 spectrometer. ^{1}H and ^{13}C NMR and spectra were recorded on a Brucker (400 MHZ) spectrometere. Chemical shifts of ^{1}H NMR are expressed in ppm downfield relative to internal standard (tetramethysilane at 0 ppm). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad peak and for IR weak (w), medium (m) and strong (s).

2.3. Synthesis of mono-undec-10-enylated β-cyclodextrin [13]

In nitrogen atmosphere, 90 g (80 mmol) of anhydrous β-cyclodextrin (Fluka, Buchs, Switzerland), dried in vacuo at 80 °C over P_4O_{10} for 48 h, were placed into 4 l three-necked, round-bottomed flask equipped with a nitrogen inlet, dropping funnel and reflux condenser fitted with a mercury valve, and were dissolved in 2 l anhydrous DMSO. To the solution was added 10 g (0.25 mol) of dried powdered sodium hydroxide and stirring was continued for 1 h at room temperature. To the vigorously stirred solution, was added 45 ml (0.2 mol) 11-Bromo-undec-1-ene. Stirring was continued for 60 h at room temperature. The reaction mixture was separated from sodium bromide and from unreacted sodium hydroxide by filtration and subsequently concentrated almost to dryness in vacuo and 60 °C. The residue was diluted with methanol and the product was precipitated by adding 200 ml diethyl ether. Purification was performed using silica (ethanol/toluene 2:1).

2.4. Synthesis of permethyl-mono-undec-10-enyl β-cyclodextrin

In nitrogen atmosphere, 1.43 g (59.6 mmol) sodium hydride (55–60% in paraffin oil (Fluka, Buchs, Switzerland) was repeatedly washed with *n*-hexane to remove paraffin oil and then transferred into an ice-cooled three necked, round-bottomed flask equipped with a nitrogen inlet, a dropping funnels, and reflux condenser fitted with a mercury valve. A 1.35 g (1.08 mmol) of 11-undec-1-enylated β-cyclodextrin was dissolved in 30 ml DMF and added slowly via the dropping funnel to the sodium hydride in nitrogen atmosphere, whereupon the vigorous reaction with evolution of hydrogen (caution!) started. After the vigorous reaction has ceased half the amount of 5.25 ml (84.15 mmol) of methyl iodide was added slowly at a bath temperature of 20 °C. After stirring for 30 min, the second half of the reagent was added to the reaction mixture. After stirring for one hour, the reaction mixture was decanted from unreacted sodium hydride and was carefully poured into 200 ml water. The aqueous phase was extracted three times with 100 ml ether. The combined ether layers were washed three times with 20 ml water to remove residual DMF. The organic layer was subsequently dried over anhydrous sodium sulphate, then filtrated and washed with THF. The solid yellowish residue was dried, purified by silica yielding 0.47 g of pure product. MS (positive FAB, in methanol/H_2O 10:1) *m* (nominal mass)/*z* 1568.86 $[M+H]^+$, calcd: $M_r = 1567.81\ g\ mol^{-1}$. ^{1}H NMR ($CDCl_3$) δ 5.74 (m, 1H, olefinic CH-group), 5.11 (d, 1H, anomeric H), 5.02 (m, 2H, olefinic CH_2), 4.7 (t, 1H, H-2), 4.32 (m, 2H, H-6), 3.37 (t, 2H, CH_2), 3.81 (t, 1H, H-4), 3.61 (s, 3H, OCH_3), 3.47 (s, 3H, OCH_3), 3.34 (s, 3H, OCH_3), 1.99 (m, 2H, CH_2 in allylic position), 1.23 (br, 14H, 7^*CH_2). ^{13}C NMR ($CDCl_3$) δ 139.24 (olefinic CH-group), 114.12 (olefinic CH_2), 98.98 (C-1), 77.53 (C-4), 71.39 (C-3), 71.03 (C-2), 70.83 (C-5), 61.319 (C-6), 67.99 (CH_2), 61.39 (CH_3), 58.99 (CH_3), 58.57 (CH_3), 33.83 (CH_2), 30.11 (CH_2), 29.61 (CH_2), 29.53 (CH_2), 29.16 (CH_2), 28.96 (CH_2), 26.01 (CH_2), 25.64 (CH_2) [13].

2.5. Preparation of Chirasil-Dex by hydrosilylation

In nitrogen atmosphere, 0.56 g (approximately 0.19 mmol) dimethylpolysiloxane containing 9.3% CH_3–Si–H

groups and 0.37 g (0.23 mmol) of permethylated 11-undec-1-enyl β-cyclodextrin, dried in vacuo at 40 °C over P_4O_{10} for 72 h, and 100 ml of dry toluene were placed into 100 ml three-necked, round-bottomed flask equipped with a nitrogen inlet and reflux condenser fitted with a mercury valve. To the refluxing reaction mixture were added a few droplets of a semi-concentrated solution of the catalyst H_2PtCl_6 in anhydrous THF at intervals of 150 min each. After 48 h reflux at 115 °C, the solvent was evaporated in vacuo with rotary evaporator yielding 1.35 g product.

In ^{1}H NMR ($CDCl_3$), a new peak appears at 4.61 ppm assigned for the existence of Si–H group, which did not react. A large peak appeared at 0.07 ppm assigned for the methyl group in Si–CH_3.

2.6. Representative procedure for the synthesis of cyclopropanes 10

Dichloromethane (10 ml) was added through syringe into a 50 ml round bottom flask containing a mixture of Meldrum's acid (**4**, 10 mmol, 1 equiv.), $PhI(OAc)_2$ (**6**) (1.4 equiv.), $[Rh_2(OAc)_4]$, $[Rh_2\{(S)\text{-nttl}\}_4]$ [17], or $[Rh_2\{4\text{-Cl-}(S)\text{-nttl}\}_4]$ (5 mol%), Al_2O_3 (2.3 equiv.) and molecular sieves 4 Å (250 mg), followed by the addition of the olefin (10 equiv.). The reaction mixture was thermostatted in an oil bath to 30 °C and stirred under argon. 100 μl Samples were taken after several time intervals. The samples were filtered using a syringe filter holder (0.2 μm pore size) and the organic layer was diluted with 100 μl of dichloromethane and analysed

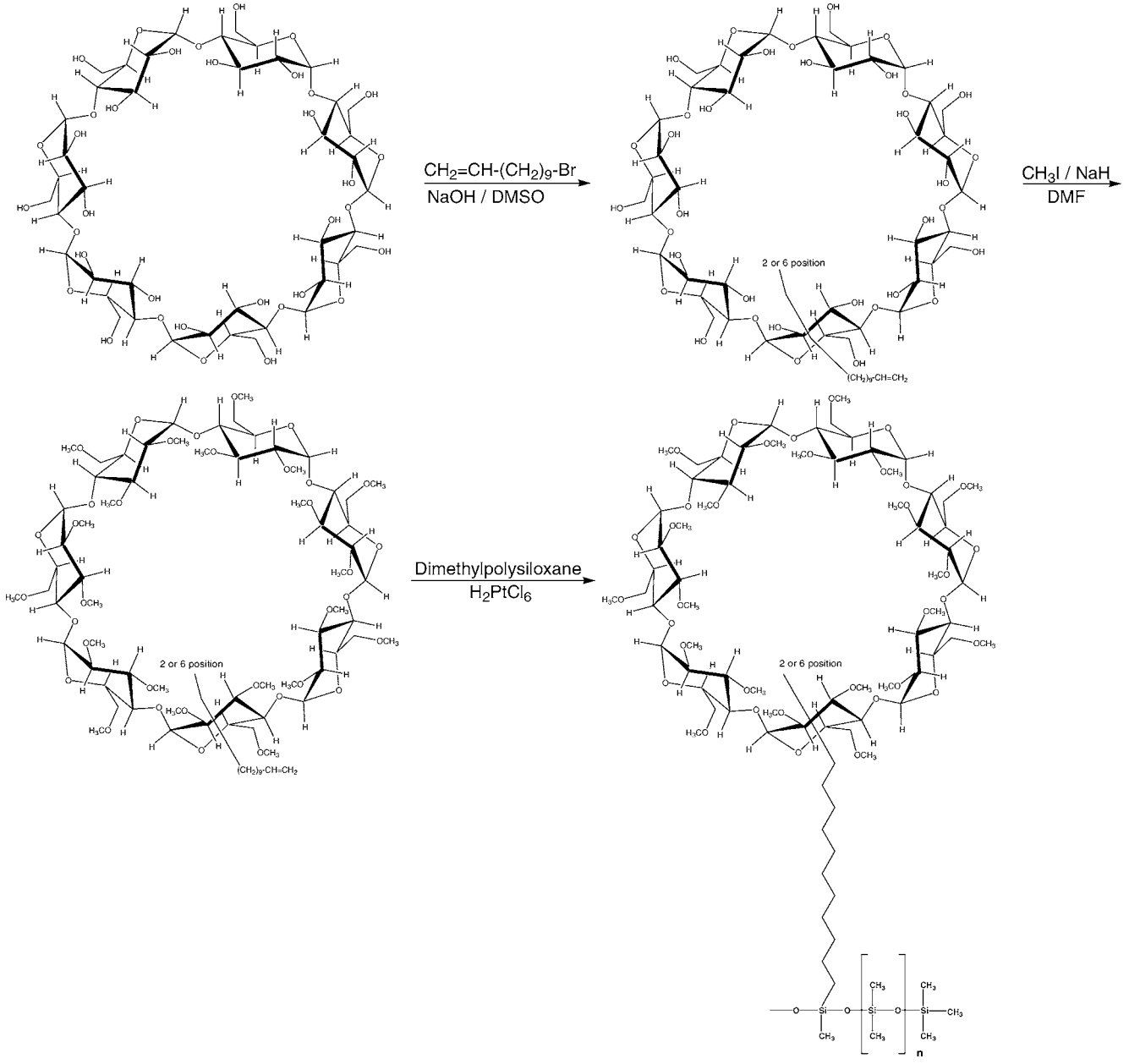

Fig. 1. The structure of the synthesized permethylated β-cyclodextrin with a new C11-spacer (C11-Chirasil-Dex) bonded to a polysiloxane backbone.

by GC. The reaction progress was monitored qualitatively and quantitatively by GC/MS using dodecane as an internal standard. When maximum conversion was reached (2 h), the reaction was terminated by filtration through celite. The residue on the celite was washed twice with dichloromethane. Evaporation of the combined filtrates under reduced pressure followed by chromatography on silica gel column with pentane/ethyl acetate (2:1 v/v) as eluent afforded the desired cyclopropane derivatives. The characterisations of the cyclopropanes **10** were in agreement to the previously reported data [19].

2.7. General procedure for the synthesis of cyclopropanes 11

Dimethyl malonate (**5**) (0.01 mol) is added to a mixture of iodosyl benzene (**7**) (1.4 equiv.), olefins **3** (10 equiv.), MgO (2.3 equiv.), rhodium(II) catalyst (5 mol%) and 250 mg molecular sieves 4 Å in dichloromethane (10 ml). The reaction mixture is stirred under argon for 24 h. A 100 μl samples were taken after several time intervals. The samples were filtered using a syringe filter holder (0.2 μm pore size) and the organic layer was diluted with 100 μl of dichloromethane for the GC analysis. The reaction progress was monitored qualitatively and quantitatively by GC/MS using dodecane as an internal standard. When maximum conversion was reached (3 h), the reaction was terminated by filtration through celite. The residue on the celite was washed twice with dichloromethane. Evaporation of the combined filtrates under reduced pressure followed by chromatography on silica gel column with heptane/ethyl acetate (5:1 v/v) as eluent afforded the desired cyclopropane derivatives.

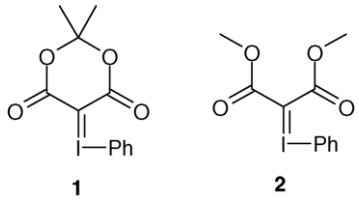

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Fig. 2. The phenyliodonium ylied derived from Meldrum's acid (**1**) and from dimethyl malonate **(2)**.

2.8. Enantioselective gas chromatographic analysis

A gas chromatograph (Hewlett Packard 580, Waldbronn, Germany) equipped with a flame ionization detector (FID) was used in chiral analysis of cyclopropane derivatives.

The chiral stationary phase chirasil-β-cyclodextrin with the new 11-spacer was coated on a non-deactivated coated on 19 m × 0.25 mm fused silica capillary column (0.25 μm film thickness) according to the literature procedure [13]. The analytical conditions were: injector temperature, 200 °C; FID temperature, 200 °C; oven temperature is varying according to the cyclopropanes. Hydrogen was used as the carrier gas (100 kPa column head pressure).

3. Results and discussion

Chirasil-β-Dex with a new 11-spacer (C11-Chirasil-Dex) was synthesized and characterized by ^{1}H, ^{13}C NMR and IR spectroscopy confirming the chemical link of the cyclodextrin moiety to the polysiloxane backbone [13]. However, the position of the 11 spacer (O6 versus O2) is still elusive (cf. Fig. 1).

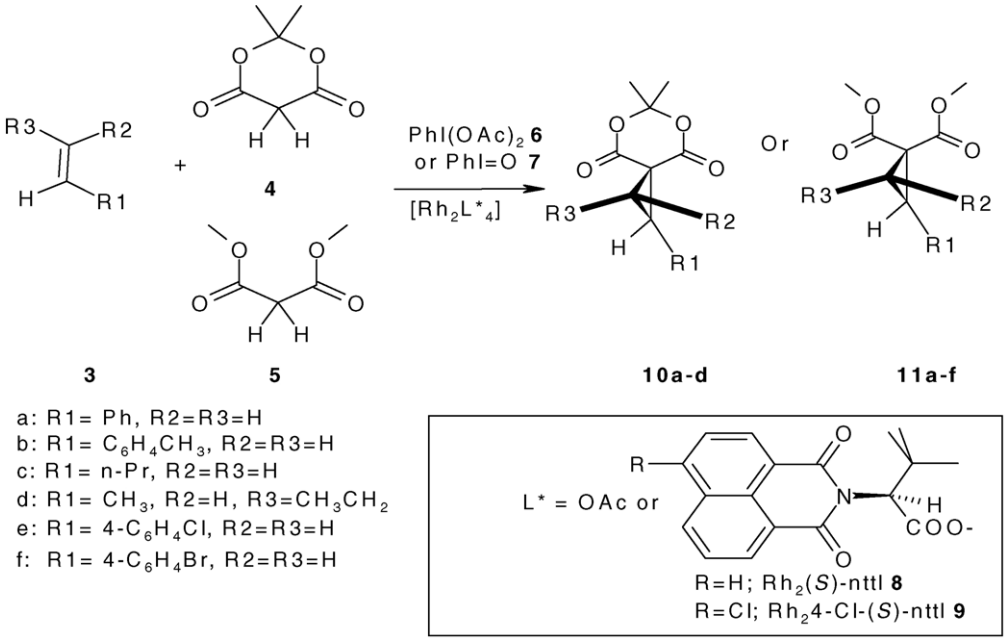

Fig. 3. One pot synthesis of cyclopropane derivatives **10** and **11** using either Meldrum's acid (**4**) or dimethyl malonate (**5**) and $PhI(OAc)_2$ (**6**) or PhI = O (**7**), respectively in presence of dirhodium(II) catalyst.

The new stationary phase was previously used in the determination of enantiomeric excesses of secondary alcohols and their corresponding esters resulting from the lipase-catalyzed enantioselective transesterification in organic solvents [13].

The application of the C11-Chirasil-Dex was extended to monitor the intermolecular cyclopropanation of olefins catalyzed by rhodium(II) catalyst. Thus, the cyclopropanation of the phenyliodonium ylide (**1**) or (**2**) (cf. Fig. 2) was adapted in such a way that the ylide (**1**) was generated from Meldrum's acid (**4**) and $PhI(OAc)_2$ (**6**) and that of **2** was generated from dimethyl malonate (**5**) and PhI = O (**7**). Both are generated in situ and decomposed by an appropriate Rh(II)-catalyst in the presence of an olefin to afford the corresponding cyclopropane derivatives **10** and **11**, respectively (cf. Fig. 3).

The reaction conditions were first optimized with styrene **3a** as substrate and with $[Rh_2(OAc)_4]$ in CH_2Cl_2. The amount of catalyst was maintained constant at 5 mol%. According to the previously reported results, a significant excess of olefin **3** (5- to 10-fold) is necessary, since otherwise the intermediate metallocarbene decomposes as has been observed for Rh(II)-catalyzed olefin cyclopropanations with the isolated phenyliodoniun ylide (**1**) [19]. A basic additive is required for the reaction, this is probably to facilitate the deprotonation of the active methylene and to scavenge either the acid released from using $PhI(OAc)_2$ (**6**) or the water when using PhI = O (**7**) as oxidant for the generation of the ylide (**1**) or (**2**), respectively. While addition of molecular sieves alone had only a minor effect on the yield of **10a** and **11a**, the combination of molecular sieves with a basic additive led to the highest yield of cyclopropane derivatives. The most satisfactory results were obtained when using Al_2O_3 in combination with molecular sieves as additives in case of $PhI(OAc)_2$ (**6**) to afford the cyclopropanes **10**, while MgO with molecular sieves were required when using PhI = O (**7**) to afford the cyclopropanes **11** in a satisfactory yield.

After optimization of the reaction conditions, the in situ approach was performed using a set of olefins **3a**–**f** and achiral rhodium acetate $[Rh_2(OAc)_4]$ as catalyst in CH_2Cl_2. Results are summarized in Table 1.

Satisfactory yields were obtained when using electron-rich olefins, this is probably, due to the electron deficient nature of the carbene reactions. The asymmetric version of the reaction was performed using chiral Rh(II) catalyst $\{Rh_2[(S)\text{-nttl}\}_4$ (**8**) and $\{Rh_2[4\text{-Cl-}(S)\text{-nttl}\}_4$ (**9**) where the protected amino acids [(*S*)-*N*-naphtholyl-*tert*-leucine] (**14a**)

Table 1
One pot synthesis of cyclopropane derivatives **10a** and **11a** using $[Rh_2(OAc)_4]$

Compound	R^1	R^2	R^3	Yield (%) **10**	Yield (%) **11**
3a	Ph	H	H	85	75
3b	$C_6H_4CH_3$	H	H	77	72
3c	*n*-Pr	H	H	75	67
3d	Me	H	Et	55	35
3e	4-C_6H_4Cl	H	H	70	68
3f	4-C_6H_4Br	H	H	65	3

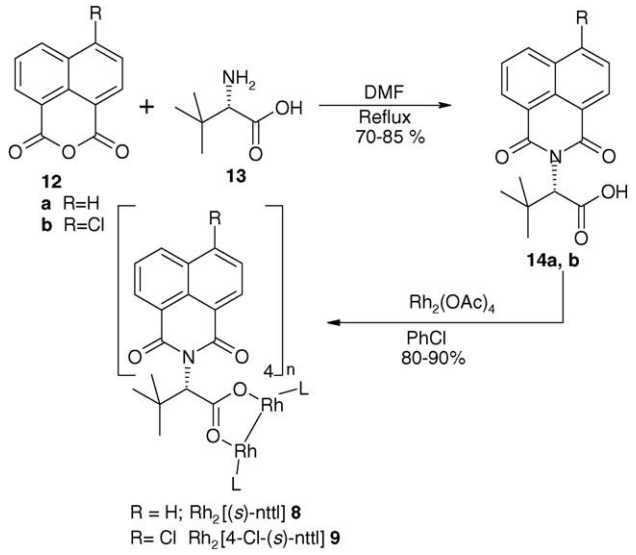

Fig. 4. Synthesis of chiral rhodium(II) catalyst **8** and **9**.

and its 4-chloro derivative **14b** were prepared via condensation of the anhydride (1,8-naphthalic anhydride (**12a**) and its corresponding 4-chloro derivative **12b** and the amino acid (*L-tert*-leucine) (**13**). Ligand exchange was carried out by refluxing $[Rh_2(OAc)_4]$ with a 10-fold-excess of either ligand in chlorobenzene for 24 h. The acetic acid released from $[Rh_2(OAc)_4]$ is absorbed in a soxhlet extractor containing anhydrous Na_2CO_3 and sand (1:1). The chiral rhodium catalyst was isolated in 85% chemical yield (cf. Fig. 4).

The optimized reaction conditions consisting of 10 mmol of **3**, 1.4 equiv. of $PhI(OAc)_2$ or PhI = O, 2.3 equiv. of Al_2O_3 or MgO and molecular sieves MS 4 Å (250 mg) in 10 ml CH_2Cl_2, were applied for the one pot asymmetric synthesis of cyclopropane derivatives **10** and **11a**–**f,** respectively using 5 mol% of $Rh_2\{(S)\text{-nttl}\}_4$ (**8**). The ees for **10** derived from Meldrum's acid (**4**) and $PhI(OAc)_2$ (**6**) were higher than those derived from dimethyl malonate (**5**) and PhI = O (**7**) (cf. Table 2).

Table 2
Asymmetric cyclopropanation of olefins (**3**) with Meldrum's acid (**4**) or dimethyl malonate (**5**) and diacetoxyiodobenzene (**6**) or iodosyl benzene (**7**) in presence of $Rh_2\{(S)\text{-nttl}\}_4$ (**8**) (5 mol%) in CH_2Cl_2

Olefins	Cyclopropane	Yield (%)	ee (%)
3a	**10a**	90	43
3a	**11a**	72	37
3b	**10b**	75	36
3b	**11b**	65	33
3c	**10c**	56	70
3c	**11c**	50	38
3d	**10d**	50	31
3d	**11d**	53	25
3e	**10e**	70	39
3e	**11e**	66	30
3f	**10f**	72	32
3f	**11f**	62	29

However, the situation improved markedly, when a chloro substituent was introduced into the 4-position of the naphthalene ring to form Rh_2[4-Cl-(*s*)-nttl] (**9**), and the enantiomeric excess reached 66% ee (77% yield) in the cyclopropanation of styrene **3a** with dimethyl malonate (**5**) and iodosyl benzene (**7**) in CH_2Cl_2 to afford **11a**, while **10a** resulted from the asymmetric cyclopropanation of styrene **3a** with Meldrum's acid (**4**) and diacetoxyiodobenezene (**6**) in CH_2Cl_2 was obtained with 60% ee (81% yield). The results revealed that the enantioselectivity of the chiral catalyst could be improved by an electronic effect on the chiral ligand. Attempts to introduce other substituents on the chiral ligand are still under investigations.

The reactions were monitored qualitatively and quantitatively using GC/MS with *n*-dodecane as internal standard on the C11-Chirasil-dex as a chiral stationary phase (CSP) for enantioselective gas chromatography. Thus, from a simple filtration and a single run, information regarding the yield of the resulting cyclopropane derivatives and the selectivety of the catalyst can be provided without further work up.

Although, a baseline gas chromatographic separation was achieved for all cyclopropanes prepared (cf. Figs. 5 and 6), some of them especially those derived from Meldrum's acid (**4**), the cyclopropane derivatives **10** decomposed in GC affording the corresponding cyclopropane dicarboxylic acid derivatives in approximately 16% yield. The latter has been identified qualitatively and quantitatively using GC/MS.

The GC parameters including oven temperature (*T*), retention time (t_R), resolution (R_s) and the separation factor (α) are recorded in Table 3.

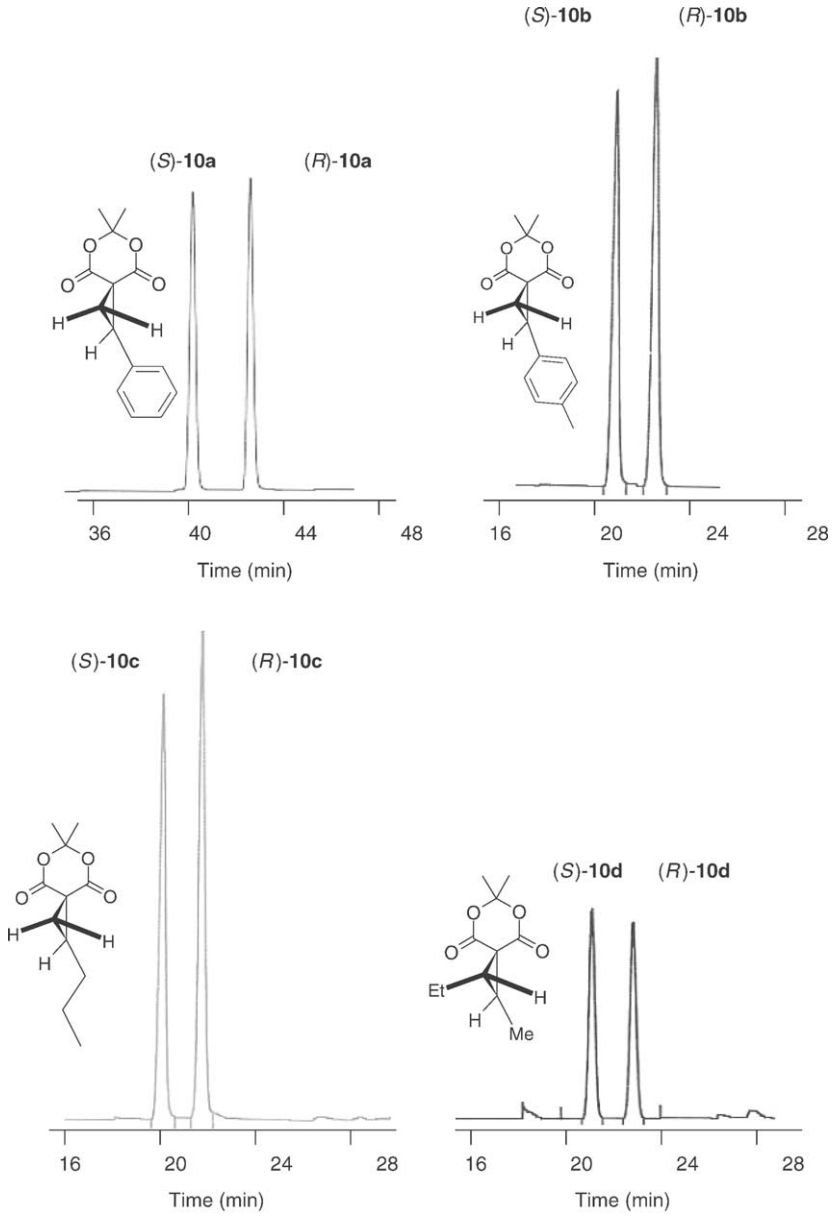

Fig. 5. Gas chromatographic enantiomers separation of cyclopropanes derived from Meldrum's acid.

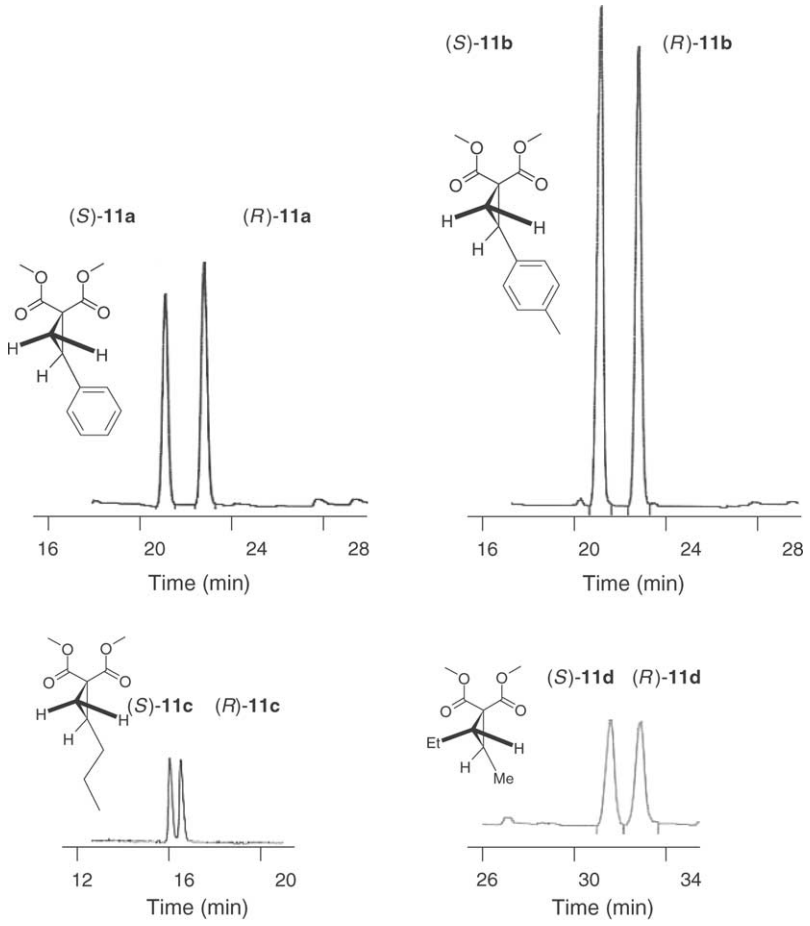

Fig. 6. Gas chromatographic enantiomers separation of cyclopropanes derived from dimethyl malonate.

Table 3
Oven temperature (T), retentiom time (t_R), resolution (R_s) and the separation factor (α) of the simultaneous baseline separation of racemic cyclopropane derivatives

Compounds	Oven temperature[a] (°C)	t_R (S)	t_R (R)	R_s	α
10a	100	40.4	42.8	4.96	1.06
10b	140	20.7	22.0	3.25	1.06
10c	100	20.9	22.1	2.96	1.05
10d	110	21.0	22.3	3.45	1.04
10e	130	21.9	23.1	2.22	1.26
10f	140	22.9	23.1	1.03	1.01
11a	130	20.8	22.20	3.36	1.06
11b	120	20.8	22.1	3.25	1.06
11c	100	15.7	16.2	1.50	1.02
11d	100	32.7	33.7	1.71	1.05
11e	115	49.0	49.7	0.81	1.01
11f	140	43.3	43.6	0.75	1.00

[a] The head pressure is 100 kPa, the injector temperature is 200 °C and the FID temperature is 250 °C.

4. Conclusion

The utility of polysiloxane-anchored permethylated β-cyclodextrins (Chirasil-β-Dex) as CSP in GC was demonstrated in the baseline separation of a set of cyclopropanes prepared in one pot. The GC method is useful for the reaction monitoring and provides chemical yields of the cyclopropane products, enantioselectivity, substrate specifity, and catalytic activity of the chiral catalysts used in the asymmetric cyclopropanation of olefins and avoids time-consuming work-up procedures.

Acknowledgments

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