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Synthesis of highly diastereo- and enantiomerically enriched tetracarbonyl(η^3-allyl)iron(1 +) complexes for allylic substitutions with silyl enol ethers and silyl ketene acetals

Dieter Enders *, Udo Frank, Peter Fey, Bernd Jandeleit, Braj Bhushan Lohray

Institut für Organische Chemie, Rheinisch-Westfälische Technische Hochschule, Professor Pirlet-Straße 1, D-52074 Aachen, Germany

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Abstract

The preparation of highly diastereo- and enantiomerically enriched alkoxycarbonyl-substituted tetracarbonyl(η^3-allyl)iron(1 +) complexes **2a–d** (**2a–c**: 20–53%, *de* > 90–≥ 95% or greater; **2d**: 31–40%, *ee* ≥ 99%) by means of an auxiliary controlled complexation (aux. = 8-phenylmenthyl) of diastereo- or of enantiopure (*E*)-configuration enoates **1** as starting materials is reported. The nucleophilic addition of various silyl enol ethers or silyl ketene acetals **3a–e** to the complexes **2a–d** followed by oxidative cleavage of the carbonyliron fragment offers an efficient access to 6-oxoenoates **4** in moderate to excellent yields (five steps, 5–72%) with diastereomeric or enantiomeric excesses ranging from *de* > 90–≥ 95% (**4a–f**) or *ee* ≥ 96–≥ 99% (**4g–k**) with retention of the (*E*)-double bond geometry. The reaction proceeds with virtually complete chirality transfer from C–O via C–Fe to C–C with retention (double inversion) of stereochemistry of the stereogenic centre with respect to the starting material **1**. It has been proven that a uniform configuration of the carbon atom bearing the leaving group in **1** is essential for controlling the absolute stereochemistry during the formation of complexes of type **2** with a definite absolute configuration at the allylic position.

Keywords: Iron; Tetracarbonyl(η^3-allyl)iron(1 +) complex; Planar chirality; Allylic substitution; a^4-Umpolung; 6-Oxoenoates; Asymmetric synthesis; Chirality transfer

1. Introduction

Cationic metal–π-complexes of odd and even numbered unsaturated polyenic ligands, which can be regarded as stabilized carbocation equivalents coordinated to a transition metal, are of increasing importance as useful synthetic equivalents in organic synthesis taking advantage of their enhanced reactivity towards a wide variety of soft nucleophiles [1,2]. Among the various carbon–carbon and carbon–heteroatom bond forming reactions promoted or catalysed by transition metals, allylic substitution via electrophilic π-allyl complexes has been one of the most intensively investigated [3–8]. Current knowledge about the stereochemical course of the formation and reactivity of cationic tetracarbonyl(π-allyl)iron complexes is limited. Studies devoted to the synthetic potential of alkyl- and aryl-substituted tetracarbonyl(η^3-allyl)iron(1 +) complexes have demonstrated that these species undergo regioselective nucleophilic attack by a multitude of soft carbon and heteroatom nucleophiles preferentially at the less substituted or at the *syn*-substituted allyl termini affording (*Z*)-configuration addition products [9]. Polar effects on the regioselectivity of nucleophilic addition reactions to tetracarbonyl(η^3-allyl)iron(1 +) complexes caused by electron withdrawing functionalities (e.g. CO_2R, $CONR_2$, COR, SO_2Ph, etc.) have been examined by our group [10] and likewise by Green and coworkers [11] and Speckamp and coworkers [12]. Acceptor substituted tetracarbonyl(η^3-allyl)iron(1 +) complexes in their diastereo- and enantiomerically pure form were shown to give allyl coupled addition products with complete stereo- and γ-regioselectivity after oxidative removal of the stabilizing $Fe(CO)_4$-fragment [10–12]. Highly diastereo- and enantiomerically enriched alkoxycarbonyl-substituted tetracarbonyl(η^3-allyl)iron complexes **A**, representing synthetic equivalents of a^4-synthons **D** which allow an umpolung [13] of classical d^4-chemistry, could be synthesized by control

* Corresponding author.

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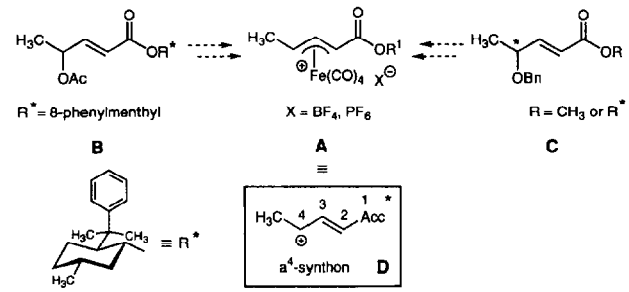


Fig. 1. Approaches to diastereo- and enantiomerically enriched (π-allyl)Fe(CO)$_4$(1 +) complexes from enoates.

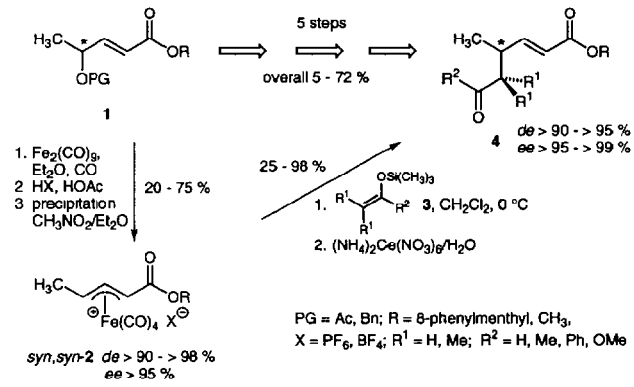
of an appropriate chiral auxiliary **B** or by employment of enantiopure starting materials **C** (Fig. 1).

2. Results and discussion

2.1. Synthesis of the ester-substituted tetracarbonyl(η^3-allyl)iron(1 +) complexes

We now wish to report the synthesis of highly diastereo- and enantiomerically enriched alkoxycarbonyl-functionalized tetracarbonyl(η^3-allyl)iron(1 +) complexes **2a** and **2b,c** via auxiliary controlled complexation of epimeric acetates (4*R*/*S*)-**1a** or, alternatively, the diastereomeric pure enoates (4*S*)-**1b** and (4*R*)-**1c**. Likewise, the antipodal enantiomerically pure methyl pentenoates (4*S*)-**1d** and (4*R*)-**1d** were transformed to similar complexes **2d** and *ent*-**2d**. The nucleophilic addition of various silyl enol ethers or silyl ketene acetals **3a–e** provides, after oxidative removal of the tetracarbonyliron fragment, an access to the stereocontrolled synthesis of 6-oxoenoates **4a–k** of high diastereomeric- and enantiomeric purities (Scheme 1).

In order to obtain more detailed information about the stereochemical course of formation, the stereochemistry and the synthetic potential of tetracarbonyl(η^3-allyl)iron(1 +) complexes, we have prepared a series of highly diastereo- and/or enantiomerically enriched alkoxycarbonyl-functionalized tetracarbonyl(π-allyl)-



Scheme 1.

iron(1 +) complexes. Starting from lactic acid derivatives, the epimeric acetate (4*R*/*S*)-**1a**, the diastereomeric pure enoates (4*S*)-**1b** and (4*R*)-**1c** and the enantiopure methyl pentenoates (4*S*)-**1d** and (4*R*)-**1d** were readily obtained in acceptable yields via the corresponding protected lactaldehydes after conventional olefination procedures (vide supra) ((4*R*/*S*)-**1a** (38%) from (*R*/*S*)-acetoxy propanal (three steps); (4*S*)-**1b** (19%), (4*R*)-**1c** (29%), (4*S*)-**1d** (40%) and (4*R*)-**1d** (31%) (each three steps) from (*S*)-ethyl lactate or (*R*)-isobutyl lactate respectively) (Fig. 2).

The enoates **1a–d** were transformed to the tetracarbonyl(η^3-allyl)iron(1 +) complexes **2** by initial complexation with nonacarbonyldiiron [$Fe_2(CO)_9$] to neutral tetracarbonyl(η^2-alkene)iron(0) species followed by subsequent protonation with anhydrous HPF_6 or HBF_4 in diethyl ether [14,15]. The complexes **2** were obtained in good yields (20–75%) as moderately air- and moisture-sensitive pale yellow powders in excellent diastereo- and enantiomeric purities (**2a–c**: *de* > 90–≥ 98%; **2d**/*ent*-**2d**: *de*, *ee* > 99%) (Scheme 1, Table 1).

The complexation of the epimeric mixture of the acetyl-protected 8-phenylmenthyl ester **1a** [16] with $Fe_2(CO)_9$ and protonation with anhydrous HPF_6 initially yielded the cationic (π-allyl)complex **2a** with a moderate diastereomeric excess (80%, *de* ≈ 40%). Repeated precipitation of **2a** from a solution in ni-

Table 1
Tetracarbonyl(η^3-allyl)iron(1 +)complexes **2a–d** prepared from the enoates **1a–d**

Enoates **1**	PG [a]	Complexes **2**	R	X	Yield (%) [b]	*de* (%) [c]
(4*R*/*S*)-**1a**	Ac	**2a**	8-phenylmenthyl	PF_6	(80) [d] 20	(40) [d] > 98
(4*S*)-**1b**	Bn	**2b** [e]	8-phenylmenthyl	PF_6	30	> 90
(4*R*)-**1c**	Bn	**2c**	8-phenylmenthyl	PF_6	53	> 90 [f]
(4*S*)-**1d**	Bn	**2d**	Me	BF_4	75	> 95
(4*R*)-**1d**	Bn	*ent*-**2d**	Me	BF_4	75	> 95

[a] PG = protecting group.
[b] Based on isolated material after (repeated) reprecipitation of **2** from a solution in nitromethane with cold diethyl ether. All complexes gave satisfactory spectroscopic and analytical data.
[c] Determined by ^{1}H NMR spectroscopy (300 MHz).
[d] In parentheses: values for the crude reaction product.
[e] Complex **2b** is identical with **2a** by NMR spectroscopy.
[f] Accuracy restricted by paramagnetic impurities.

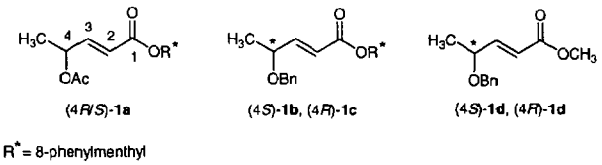


Fig. 2. 4-Oxygenated enoates and their numbering scheme.

tromethane with cold ether afforded the complex in virtually diastereomerically pure form (20%, $de \geq 98\%$) as could be easily determined by ^{1}H NMR spectroscopy ((major/minor diastereomer) **2a**: δ (α-CH) = 2.28 ppm/2.95 ppm). In addition, ^{1}H NMR spectroscopy showed that both the ester functionality and the methyl group of **2a** are placed in a *syn* relationship with respect to the β-hydrogen atom of the allylic subunit. The exact position of the $Fe(CO)_4$-fragment could not unambiguously be determined. Variations of the chiral auxiliary based on alternative chiral pool precursors (e.g. R = (−)-menthol, (−)-borneol, (−)-8-(*p*-anisidyl)menthol [17]) proved to be less diastereofacially discriminating during the complexation step ($de \approx 0\%$). Furthermore, no synthetically attractive enrichment could be observed by precipitation following the procedure described above. In this context, the influence of the configurative uniformity of the carbon atom bearing the leaving group on the trajectory of the incoming $Fe(CO)_4$-moiety was examined. Starting from the diastereomerically pure epimeric benzyl-protected enoates (4*S*)-**1b** and (4*R*)-**1c** the complexes **2b** and **2c** were obtained in high diastereomeric purity ($de > 90\%$) in acceptable to good yields (**2b**: (30%); **2c** (53%)] (Scheme 1, Table 1) as single *syn,syn*-configuration isomers following the precipitation procedure described above. ^{1}H NMR spectroscopy unambiguously demonstrated that the complex **2c** is, in contrast to **2b**, not identical with the diastereomer **2a** obtained from complexation of the epimeric acetates **1a** (2c: δ (α-CH) = 2.04 ppm). Although the absolute position of the $Fe(CO)_4$-group of the complexes **2b** (≡ **2a**) and **2c** could not unambiguously be determined, the occurrence of diastereomeric forms can be explained by complexation of opposite diastereotopic faces of the allylic plane by the $Fe(CO)_4$-fragment. From these results it seems reasonable that the trajectory of complexation by the $Fe(CO)_4$ is mainly determined by the uniformity of the configuration of the carbon atom bearing the OAc or OBn leaving group with less control shown by the chiral auxiliary. Furthermore, transformation of the enoates (4*S*)- and (4*R*)-**1d** to the planar chiral tetracarbonyl(η^3-allyl)iron(1 +) complexes **2d** and *ent*-**2d** (R = Me, 75%) yielded the electrophilic complexes as single *syn,syn* disubstituted diastereomers ($de \geq 95\%$) after precipitation (Scheme 1, Table 1). The reaction was best performed at 30 °C in diethyl ether with anhydrous HBF_4. Unfortunately, their enantiomeric purity could only be indirectly measured from the enantiomeric excesses of the products **4** obtained from nucleophilic addition reactions of various silyl enol ethers or silyl ketene acetals **3** (vide supra).

Table 2
6-Oxoenoates **4** via nucleophilic addition of silyl/enol ethers and silyl/ketene acetals **3** to the tetracarbonyl(η^3-allyl)iron(1 +) complexes **2**

Complexes **2**	6-Oxoenoates **4**	R^1	R^2	Yield (%) [a]	$[\alpha]_D^{RT}$ (*c*, $CHCl_3$)	*de*,*ee* (%)	Configuration
2a	**4a**	H	Ph	52	+10.3(1.08)	$de \geq 95$ [b]	(4*R*)
2a	**4b**	H	Me	71	−6.4(3.30)	$de \geq 95$ [b]	(4*R*)
2a	**4c**	H	OMe	80	−9.1(2.23)	$de \geq 95$ [b]	(4*R*)
2a	**4d**	Me	H	25 [c]	−16.5(0.93)	$de \geq 95$ [b]	(4*S*)
2a	**4e**	Me	OMe	90	−16.1(3.32)	$de \geq 95$ [b]	(4*S*)
2b	**4e**	Me	OMe	56	−15.1(2.15)	$de \geq 90$ [b]	(4*S*)
2c	**4f**	Me	OMe	75	+33.3(1.62)	$de > 93$ [b]	(4*R*)
2d	**4g**	Me	OMe	86	−48.1(2.58)	$ee \geq 96$ [d]	(4*S*)
2d	**4h**	H	OMe	73	−29.4(2.03)	$ee \geq 99$ [e]	(4*R*)
ent-**2d**	*ent*-**4h**	H	OMe	71	+29.1(2.14)	$ee \geq 99$ [e]	(4*S*)
ent-**2d**	**4i**	Me	H	98 [f]	+48.4(2.38)	– [g]	(4*R*)
2d	**4j**	H	Me	69	−33.3(2.12)	$ee > 99$ [c]	(4*R*)
ent-**2d**	*ent*-**4j**	H	Me	69	+35.2(2.77)	$ee > 99$ [c]	(4*S*)
ent-**2d**	**4k**	H	Ph	92	+5.4(2.82)	$ee \geq 96$ [d]	(4*S*)

[a] Based on isolated material after column chromatography (silica gel 60, diethyl ether–light petroleum = 1:2–1:4). All new products gave satisfactory analytical and spectroscopic data.
[b] *de*-value determined by ^{13}C NMR spectroscopy (75 MHz).
[c] Purified by column chromatography on neutral aluminium oxide, activity grade III (diethyl ether–light petroleum = 1:4).
[d] *ee*-value determined indirectely via ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectroscopy after ozonolysis and acetalization with (−)-(*R*,*R*)-butane-2,3-diol.
[e] *ee*-value determined by GLC_{CSP} on chiral peralkylated β-cyclodextrine phases and by correlation of optical rotations.
[f] Yield of the crude reaction product of sufficient purity.
[g] Enantiomeric purity could not be determined.

2.2. Nucleophilic addition reactions

The electrophilic tetracarbonyl(η^3-allyl)iron(1 +) complexes **2** thus obtained are subjected towards nucleophilic addition reactions by various achiral silyl enol ethers or silyl ketene acetals **3a–e** (Scheme 1, Table 2), which in turn are readily accessible from their corresponding carbonyl precursors according to established procedures [18]. In a typical example, the reaction was performed by the addition of an excess (2.0 equivalents) of the appropriate nucleophile **3** to a suspension of 1.0 equivalent of the complexes **2** in dichloromethane at 0 °C and subsequent warming of the reaction mixture to room temperature. 6-Oxoenoates **4** of excellent diastereo- and enantiomeric purity (**4a–f**: *de* > 90–≥ 95%; **4g–k**: *ee* ≥ 96–≥ 99%) were obtained in fair to excellent yields (52–98%, **4d**: 25%) after oxidative removal of the tetracarbonyliron moiety of the initially formed soluble neutral substituted tetracarbonyl(η^2-alkene)iron(0) complexes and careful purification of the crude reaction products **4** by flash column chromatography (silica gel, diethyl ether–light petroleum or *n*pentane, 1:2–1:4; exclusion of diastereomeric enrichment) as colourless or pale yellow oils (Scheme 1, Table 2).

The reaction proceeds with virtually complete induction of the newly generated stereogenic centres and with complete γ-regioselectivity with respect to the ester functionality retaining the (*E*) double bond geometry of the starting material **1**. The diastereomeric excesses of **4a–f** were easily determined by ^{13}C NMR spectroscopy (75 MHz) (*de* > 90–≥ 95%), while the determination of the enantiomeric purities of **4h**, *ent*-**4h**, **4j** and *ent*-**4j** (*ee* > 99%) was performed by GLC employing chiral stationary phases (permethylated or perpentylated β-cyclodextrines) and by comparison with the racemic material making use of the racemic complex *rac*-**2d**. In addition, ozonolysis of **4g** and **4k** followed by reductive work-up afforded the corresponding aldehydes which were subsequently converted to the 1,3-dioxolanes with (−)-(*R,R*)-butane-2,3-diol [19,20]. Analysis of the ^1H and ^{13}C NMR spectra of the resulting acetals showed diastereomeric excesses of *de* = *ee* ≥ 95% for **4g** and **4k**. However, all attempts (GLC_{CSP}, analytical HPLC, ^1H NMR shift experiments making use of LIS-reagents or Pirkle's alcohol as chiral cosolvent, as well as derivatization) to determine the enantiomeric purity of the 6-oxoenoate **4i** failed.

Ozonolysis of the addition products **4c** and *ent*-**4h** in dichloromethane at −78 °C yielded, after reductive work-up with dimethyl sulphide, the corresponding 3-methyl-4-oxo-methyl butanoate **5** and *ent*-**5** which unfortunately suffer from rapid partial racemisation under the reaction conditions (Fig. 3).

Comparison of the sign and the value of the optical rotation of the chiral aldehydes **5** thus obtained (from *ent*-**4h**: $[\alpha]_D^{20} = -10.8$ (*c* = 2.64, Et_2O); from *ent*-**4h**: $[\alpha]_D^{23} = +13.1$ (*c* = 0.50, Et_2O)) with those data given

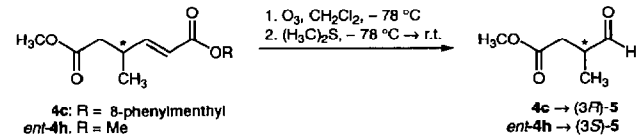


Fig. 3. Determination of the absolute configuration by derivatization of **4c** and *ent*-**4h** to 3-methyl-4-oxo-methyl butanoate **5**.

for (*S*)-**5** in the literature ($[\alpha]_D = -71.2$ (*c* = 1, Et_2O), *ee* = 93%) [21] allowed both the assignment of the absolute configurations of the 6-oxoenoates **4** (Table 2) and a proposal for a possible reaction mechanism (vide supra) for the complete reaction sequence starting from the enoates **1**. Owing to the shielding effect of the leaving group, complexation of the enoates **1** seems to be directed to the opposite side of the double bond in **1** with respect to the sterically demanding leaving group. Cleavage of the C–O bond of the OPG-leaving group proceeds with formation of a new carbon–iron bond. Owing to the relative *anti*-arrangement of the tetracarbonyliron moiety and the OPG-leaving group, the absolute configuration of the carbon atom which bore the OPG-subunit is inverted. Based on the assumption of a uniform reaction mechanism for the complexes **2** with the closely related nucleophiles of type **3a–e** the nucleophilic attack then occurs *anti* to the $Fe(CO)_4$-fragment of **2** [10], as has been described for numerous other transition-complexed carbocations [22].

In conclusion, the obtained results clearly demonstrate that the absolute configuration of the newly generated stereogenic centres is exclusively determined by the absolute position of the $Fe(CO)_4$-moiety with respect to the allylic plane and the overriding *anti*-directing effect of the $Fe(CO)_4$-group [23]. Repeated precipitation of **2a** resulted in a selective enrichment of that diastereomeric complex possessing the absolute configuration (4*R*) at the reaction centre. The complexes **2b** and **2c**, based on the epimeric enoates (4*S*)-**1b** and (4*R*)-**1c**, yield epimeric addition products (4*S*)-**4e** and (4*R*)-**4e** (Table 2), proving that **2b** and **2c** must possess opposite absolute configurations at the reaction centres in the 4-position due to complexing opposite diastereotopic faces, thus making them clearly distinguishable by NMR spectroscopy (vide infra). Therefore, the complexation, as well as the absolute stereochemistry of possible resulting nucleophilic addition products, is exclusively controlled by the configuration of the carbon atom bearing the leaving group. In addition, the enantiomeric relationship of **2d** and *ent*-**2d** was easily established by comparison of the sign and the value of the optical rotation of the 6-oxoenates **4h,j** and *ent*-**4h,j** (Table 2). Furthermore, the reaction sequence starting from the enantiopure methyl pentenoates (4*S*)- and (4*R*)-**1d** provides a general synthetic approach to functionalized 6-oxoenoates **4** of high enantiomeric purity by virtually complete chirality transfer (from C–O via C–Fe to C–C) with overall retention (double inver-

sion) with respect to the starting material (4*S*)-**1d** or (4*R*)-**1d** and without the need for a chiral auxiliary. In addition, these results also prove a chirality transfer process for the reaction sequence starting from the enoates (4*S*)-**1b** or (4*R*)-**1c** via their corresponding tetracarbonyl(π-allyl)iron(1 +) complexes to the 6-oxoenoates **4**. By the correct choice of the starting material (e.g. (*S*)- or (*R*)-lactic acid or other α-hydroxy carbonic acid derivatives [23]) not only both enantiomeric forms of an appropriate addition product are readily accessible via the enantiomeric complexes **2d** and *ent*-**2d**, but also variations in their substitution patterns should become possible.

3. Conclusion

In summary, we have shown that highly diastereo- and enantiomerically enriched alkoxycarbonyl-substituted tetracarbonyl(η^3-allyl)iron(1 +) complexes **2** can be prepared in moderate to good yields by means of an auxiliary controlled complexation (aux. = 8-phenylmenthyl) of diastereo- or of enantiopure enoates **1** as starting materials (**2a–c**: *de* > 90–≥ 95%, **2d**/*ent*-**2d**: *ee* ≥ 99%). It has been proven that a uniform configuration of the carbon atom bearing the leaving group in **1** is essential for the discrimination of the diastereotopic faces of the double bond and thus the control of its complexation by an attacking tetracarbonyliron moiety to stereochemically well-defined tetracarbonyl (η^3-allyl)iron(1 +) complexes via the corresponding neutral tetracarbonyl(η_2-alkene)iron(0) complexes. Nucleophilic addition of various silyl enol ethers and silyl ketene acetals **3a–e** to the complexes **2** followed by oxidative cleavage of the carbonyliron fragment offers an efficient access to 6-oxoenoates **4** in fair to excellent yields (five steps, 5–72%) with diastereomeric or enantiomeric excesses ranging from for **4a–f**: *de* > 90–≥ 95% and for **4g–k**: *ee* ≥ 96–≥ 99%). Further investigations are focused on synthetic applications by variation of the nucleophilic components and the substitution patterns of the iron complexes.

4. Experimental

4.1. General

All reactions were carried out under an atmosphere of dry carbon monoxide or dry argon using standard Schlenk or vacuum line techniques unless otherwise stated. Solvents were dried and purified by conventional methods prior to use. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were freshly distilled from sodium benzophenone ketyl, dichloromethane (CH_2Cl_2) from calcium hydride under argon. Light petroleum refers to the fraction with b.p. 40–80 °C. Reagents of commercial quality were obtained from commercial suppliers and were used from freshly opened containers without further purification unless otherwise stated.

Analytical precoated glass-backed TLC plates (silca gel 60 F_{254}) and silica gel 60 (230–400 mesh equivalent to particle size 0.040–0.063 mm) were purchased from Merck, Darmstadt. Neutral aluminium oxide activity grade III (7% water) was obtained from Woelm Pharma. Analytical GLC was performed on Siemens Sichromat 2 and 3 equipped with an SE-54-CB or an OV-1-CB column (both 25 m × 0.25 mm), carrier gas: nitrogen, FID. GLC_{CSP} analyses for the determination of enantiomeric purities were conducted on chiral permethylated or perpentylated β-cylodextrine phases (50 m), carrier gas: nitrogen. Optical rotations were measured using a Perkin–Elmer P 241 polarimeter and chloroform of Merck UVASOL quality. Melting points are uncorrected and were measured on a Dr. Tottoli apparatus or a Büchi SMR 20. ^1H NMR (500/300/90 MHz) and ^{13}C NMR (125/75/20 MHz) spectroscopy was conducted on a Varian Unity 500, a Varian VXR 300 and a Varian EM 390 using tetramethylsilane (TMS) as internal standard. IR spectra were recorded on a Perkin–Elmer FT-IR 1750 spectrophotometer. Mass spectroscopic analyses were obtained on a Varian MAT 212 (EI 70 eV). Microanalyses were obtained with a Heraeus CHN-O-RAPID or a Heraeus Mikro UD elemental analyser.

All silyl enol ethers and silyl ketene acetals **3** were prepared from their corresponding carbonyl precursors and trimethylchlorosilane according to literature procedures [18]. The nucleophiles **3** were handled and stored with exclusion of moisture and air. The 8-phenylmenthyloxycarbonyl-substituted diethylphosphonate has been prepared by transesterification of the methoxycarbonyl-functionalized precursor [24] with (−)-8-phenylmenthol in the presence of *p*-toluenesulphonic acid [25]. The methyl enoates (4*S*)-**1d** and (4*R*)-**1d** were prepared from (*S*)-ethyl lactate or (*R*)-isobutyl lactate following the protection–/reduction–/olefination-sequence as described for (4*S*)-**1b** and (4*R*)-**1c** in an overall yield of 40% and 31% respectively (vide supra) [26]. Alternatively, (4*S*)-**1d** can now be purchased from ACROS chimica, Belgium. Nonacarbonyldiiron was synthesized by photolysis of pentacarbonyliron in glacial acetic acid [27]. Anhydrous HPF_6 and HBF_4 were freshly prepared, as described in Section 4.2.

4.2. Synthesis of the enoates (4*R*/*S*)-**1a**, (4S)-**1b** and (4R)-**1c**

4.2.1. (*E*,4*R*/*S*,1′*R*,2′*S*,5′*R*)-4-Acetoxy-2′-(1″-methyl-1″-phenylethyl-5′methyl-cyclo-hexyl)pentenoate (4*R*/*S*)-**1a**

The acetoxy-protected enoate (4*R*/*S*)-**1a** was synthesized from (*R*/*S*)-acetoxy propanal via a *Knoeve-*

nagel condensation with malonic acid (53%) [28]. Transformation of the resulting α,β-unsaturated acid into the corresponding acid chloride with oxalyl chloride (80%) [29] and trapping of the acid chloride with lithiated (−)-8-phenylmenthol (90%) [16] gave (4*R*/*S*)-**1a** in 38% overall yield (three steps) from (*R*/*S*)-acetoxy propanal as a viscous colourless oil. $R_f \approx 0.36$ (both epimers, diethyl ether–light petroleum, 1:4). $[\alpha]_D^{21} = +1.5$ ($c = 1.09$, $CHCl_3$). ^1H NMR (90 MHz, $CDCl_3$, TMS(int), epimer 1/epimer 2, ppm): δ 7.3–6.9 (m, 5H, C_6H_5), 6.6–6.1 (m, 1H, CH=$CHCO_2$), 5.5–5.1 (m, 1H, CH=$CHCO_2$), 5.0–4.6 (m, 1H $CHCHO$), 4.3–4.0 (m, 1H, $CHCH_3$), 2.3–0.6 (m, 23H, cyclohexyl-CH_2, -$CHCH_3$, $CH(CH_3)_2$, $C(CH_3)_2Ph$). ^{13}C NMR (20 MHz, $CDCl_3$, TMS(int), epimer 1/epimer 2, ppm): δ 169.8 (CH=$CHCO_2$), 151.9/151.8 (*ipso*-C), 145.4/145.3 (CH=$CHCO_2$), 128.0/125.4/124.9 (aromatic-CH), 121.5/121.1 (CH=$CHCO_2$), 74.5 ($CHCHO$), 68.7 ($CHCH_3$), 50.5 ($CHCHO$), 41.7 (CH_2CHO), 39.5 [$C(CH_3)_2Ph$], 34.6 (CH_2), 31.3/31.2 (CH), 28.7/28.6 [$C(CH_3)_2Ph$], 26.5 (CH_2), 24.1/24.0 [$C(CH_3)_2Ph$], 21.8 ($CHCH_3$), 21.0 (CO_2CH_3), 19.5 (CH, CH_3). IR (film, cm^{-1}): 3090, 3060, 3030 (aromatic-CH, =C–H), 2960, 2930, 2880, 1740 (C=O), 1710 (C=O), 1665 (C=C), 1600, 770, 700. MS *m*/*z* (rel. intensity (%)): 372 (0.4, $M^+\cdot$), 214 (12), 120 (10), 119 (100, $C(CH_3)_2C_6H_5^+$), 118 (41), 105 (6, $C_8H_9^+$), 99 (18), 91 (19, $C_7H_7^+$), 43 (11, $C_2H_3O^+$). Anal. Found: C, 74.09; H, 8.66. $C_{23}H_{32}O_4$ ($M_r = 372.5$). Calc.: C, 74.16; H, 8.66%.

4.2.2. (−)-(E,4S,1′R,2′S,5R)-4-Benzyloxy-2′-(1″-methyl-1″-phenylethyl-5′-methyl-cyclohexyl)pentenoate (4S)-1b

The benzyloxy-protected enoate (4*S*)-**1b** was prepared in diastereomeric pure form from commercially available (*S*)-ethyl lactate. Benzylation of the hydroxy group of (*S*)-ethyl lactate was performed by a literature procedure of Knowles and coworkers (67%) [30] with Ag_2O–BnBr in diethyl ether. Reduction of the benzyl-protected esters with DIBAH in diethyl ether [31] yielded the corresponding benzyl-protected lactaldehyde (approximately quantitative) without significant racemisation. Subsequent Horner–Wadsworth–Emmons-olefination of the crude protected (*S*)-lactaldehyde derivative with the appropriate 8-phenylmenthyl ester-functionalized phosphonate was performed according to a literature procedure of Jäger and Wehner (29%) [32] and yielded the enoate (4*S*)-**1b** in 19% overall yield (three steps) starting from (*S*)-ethyl lactate as a colourless liquid after flash column chromatography (silica gel, diethyl ether–light petroleum 1:4). $R_f = 0.40$ (diethyl ether–light petroleum 1:4). $[\alpha]_D^{28} = -30.0$ ($c = 1.90$, $CHCl_3$). $de > 95\%$ (^{13}C NMR). ^1H NMR (300 MHz, $CDCl_3$, TMS(int), ppm): δ 7.37–7.18 (m, 5H, C_6H_5), 7.10–7.00 (m, 5H, $CH_2C_6H_5$), 6.42 (dd, $J(^1H–^1H) = 15.8/6.1$ Hz, 1H, CH=$CHCO_2$), 5.44 (dd, $J(^1H–^1H) = 15.8/1.0$ Hz, 1H, CH=$CHCO_2$), 4.86 (dt, $J(^1H–^1H) = 10.6/4.4$ Hz, 1H, $CHCHO$), 4.45 (m, 2H, $OCH_2C_6H_5$), 3.95 (m, 1H, $CHCH_3$), 2.12–0.90 (m, 8H, cyclohexyl-CH_2, -CH), 1.30 [s, 3H, $C(CH_3)_2Ph$], 1.24 (d, $J(^1H–^1H) = 6.4$ Hz, 3H, $CHCH_3$), 1.20 [s, 3H, $C(CH_3)_2Ph$], 0.87 (d, $J(^1H–^1H) = 6.4$ Hz, 3H, cyclohexyl-$CHCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$, TMS(int), ppm): δ 165.40 (CH=$CHCO_2$), 151.68 (*ipso*-C), 148.30 (CH=$CHCO_2$), 138.26 (OCH_2C), 128.37/127.90/127.58/127.51/125.36/124.88 (aromatic-CH), 121.54 (CH=$CHCO_2$), 74.37 ($CHCHO$), 73.82 ($CHCH_3$), 70.63 (OCH_2), 50.47 ($CHCHO$), 41.67/39.63/34.61 (C, CH_2), 31.28/28.14 (CH, CH_3), 26.56 (C, CH_2), 24.73/21.80/20.56 (CH, CH_3). IR (film, cm^{-1}): 3088, 3060, 3031 (aromatic-CH, =C–H), 2955, 2926, 2869, 1713 (C=O), 1658 (C=C), 1600, 1496 (aromatic-C=C), 1455, 1389, 1370 (*gem*.-CH_3), 1346, 1297, 1270, 1179, 1093 (C–O–C), 1051, 1030, 995, 981, 766, 736, 700. MS *m*/*z* (rel. intensity (%)): 420 (0.3, $M^+\cdot$), 214 (11), 120 (10), 119 (100, $C(CH_3)_2C_6H_5^+$), 118 (43), 105 (12, $C_8H_9^+$), 91 (74, $C_7H_7^+$), 77 (10, $C_6H_5^+$), 65 (5, $C_5H_5^+$), 41 (13), 28 (16). Anal. Found: C, 79.42; H, 8.53. $C_{28}H_{36}O_3$ ($M_r = 420.6$). Calc.: C, 79.96; H, 8.63%.

4.2.3. (+)-(E,4R,1′R,2′S,5′R)-4-Benzyloxy-2′-(1″-methyl-1″-phenylethyl-5′-methyl-cyclohexyl)pentenoate (4R)-1c

Starting from commercially accessible (*R*)-isobutyl lactate, the enoate (4*R*)-**1c** was synthesized in the same manner as described for the epimer (4*S*)-**1b** in an overall yield of 32% (three steps) as a colourless oil. $R_f = 0.79$ (diethyl ether–light petroleum 1:4). $[\alpha]_D^{29} = +47.6$ ($c = 1.73$, $CHCl_3$). $de > 95\%$ (^{13}C NMR). ^1H NMR (300 MHz, $CDCl_3$, TMS(int), ppm): δ 7.36–7.18 (m, 5H, C_6H_5), 7.10–7.00 (m, 5H, $OCH_2C_6H_5$), 6.56 (dd, $J(^1H–^1H) = 15.8/6.0$ Hz, 1H, CH=$CHCO_2$), 5.45 (dd, $J(^1H–^1H) = 15.8/1.0$ Hz, 1H, CH=$CHCO_2$), 4.87 (dt, $J(^1H–^1H) = 10.4/4.4$ Hz, 1H, $CHCHO$), 4.42 (m, 2H, $OCH_2C_6H_5$), 3.97 (m, 1H, $CHCH_3$), 2.10–0.90 (m, 8H, cyclohexyl-CH_2, -CH), 1.32 [s, 3H, $C(CH_3)_2Ph$], 1.27 (d, $J(^1H–^1H) = 6.4$ Hz, 3H, $CHCH_3$), 1.21 [s, 3H, $C(CH_3)_2Ph$], 0.87 (d, $J(^1H–^1H) = 6.7$ Hz, 3H, cyclohexyl-$CHCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$, TMS(int), ppm): δ 165.43 (CH=$CHCO_2$), 151.51 (*ipso*-C), 148.36 (CH=$CHCO_2$), 138.20 (OCH_2C), 128.35/127.88/127.55/−127.53/125.35/124.96 (aromatic-CH), 121.81 (CH=$CHCO_2$), 74.40 ($CHCHO$), 73.80 ($CHCH_3$), 70.61 (OCH_2), 50.50 ($CHCHO$), 41.71/39.67/34.58 (C, CH_2), 31.29/27.79 (CH, CH_3), 26.59 (C, CH_2), 25.12/21.79/20.53 (CH, CH_3). Anal. Found: C, 79.56; H, 8.90. $C_{28}H_{36}O_3$ ($M_r = 420.6$). Calc.: C, 79.96; H, 8.63%. All other spectroscopic data correspond with those given for the epimer (4*S*)-**1b**.

4.3. Synthesis of tetracarbonyl[(2-4-η^3)-(2-alkoxycarbonyl-4-methylallyl)iron(1 +) hexafluorophosphates **2a–c** and tetrafluoroborates **2d** (ent-**2d**)

According to literature procedures [14,15] 20 mmol of the corresponding enoates **1** and 25 mmol (9.09 g) diironnonacarbonyl [$Fe_2(CO)_9$] were placed under argon in a Schlenk flask and 200 ml anhydrous degassed diethyl ether was added. The suspension was saturated with carbon monoxide and the reaction mixture was stirred under an atmosphere of carbon monoxide with exclusion of light until the insoluble orange $Fe_2(CO)_9$ had been completely consumed (ca. 8 h). The resulting yellowish-brown mixture was filtered over sand/celite®. The residue was washed with diethyl ether until the filtrate was colourless. The clear yellow filtrate was diluted with additional diethyl ether to give a total volume of ca. 400 ml. A solution of 20 mmol anhydrous hexafluorophosphoric acid (HPF_6) (for **2a–c**) or alternatively tetrafluoroboric acid (HBF_4) (for **2d**/*ent*-**2d**) (freshly prepared by dehydration of 3.9 ml aqueous HPF_6 (60%) or 3.4 ml aqueous HBF_4 (48%) with 17 ml acetic anhydride at 0 °C) was added dropwise with rapid stirring at room temperature or at 30 °C. The tetracarbonyl(π-allyl)iron complexes **2** were obtained after precipitation, washing and drying in vacuo as colourless to pale yellow moderately air stable solids. Highly diastereo- and enantiomerically enriched pure *syn,syn* configuration complexes **2** (*de*, *ee* > 95%) were obtained by repeated fractional reprecipitation from a nitromethane solution of crude **2** with excess of cold diethyl ether.

4.3.1. syn,syn-Tetracarbonyl(2-4η^3)-(1'R,2'S,5'R)-{2-[2'-(1''-methyl-1''-phenyl-ethyl)-5'-methylcyclohexyloxycarbonyl)-4-methyl]allyl}iron(1 +) hexafluorophosphate **2a**

According to the general procedure (Section 4.3), 4.4 g (20 mmol) (4*R*/*S*)-**1a** were reacted with 9.1 g (25 mmol) nonacarbonyldiiron [$Fe_2(CO)_9$] and 25 mmol HPF_6 to yield 10.00 g (80%) of complex **2a** as a pale yellow powder. Diastereomeric pure **2a** was obtained by repeated precipitation from a solution in nitromethane with cold diethyl ether (2.5 g, 20%). Analytical data for **2a**. M.p. 146 °C (decomp.). *syn*-CH_3/*anti*-CH_3 = 100:0 (^{1}H NMR). *de* > 95% (^{13}C NMR). ^{1}H NMR (300 MHz, CD_3CN, TMS(int), ppm): δ 7.42–7.08 (m, 5H, C_6H_5), 6.00 (dd, $J(^1H-^1H)$ = 12.0/10.4 Hz, 1H, C*H*–$CHCO_2$), 4.90 (m, 1H, CHC*H*O), 4.53 (dq, $J(^1H-^1H)$ = 12.0/6.0 Hz, 1H, C*H*CH_3), 2.40–0.80 (m, 8H, cyclohexyl-CH, -CH_2), 2.28 (d, $J(^1H-^1H)$ = 10.4 Hz, 1H, CH–C*H*CO_2), 2.02 (d, $J(^1H-^1H)$ = 5.7 Hz, 3H, CHCH_3), 1.32 [s, 3H, $C(CH_3)_2Ph$], 1.22 [s, 3H, $C(CH_3)_2Ph$], 0.87 (d, $J(^1H-^1H)$ = 5.4 Hz, 3H, cyclohexyl-CHCH_3). ^{13}C NMR (75 MHz, CD_3CN, TMS(int), ppm): δ 198.71/197.74/196.44/195.86 (Fe–C≡O), 169.63 (CH–CH*C*O_2), 152.63 (*ipso*-C), 129.11/126.42/126.17 (aromatic-CH), 99.66 (*C*H–$CHCO_2$), 88.15 (*C*HCH_3), 77.47 (CH*C*HO), 52.94 (CH–*C*HCO_2), 51.11 (*C*HCHO), 42.07 (CH_2), 40.17 [*C*$(CH_3)_2Ph$], 34.94 (CH_2), 31.96 (cyclohexyl-*C*HCH_3), 29.97 (CH, CH_3), 26.88 (CH_2), 23.40/22.01/20.62 (CH_3). IR (KBr, cm^{-1}): 3061 (aromatic-CH), 2964, 2953, 2929, 2884, 2873, 2857, 2154, 2105, 2097, 2084 (Fe–C≡O), 1719 (C=O), 1600, 1580, 1541, 1497, 1401, 1379, 1272, 1221, 1177, 1129, 1094, 1097, 1050, 1033, 837, 769, 706, 608, 592, 559. MS *m*/*z* (rel. intensity (%)): 481 (4, $M^+ \cdot - PF_6^-$), 369 (3, $M^+ \cdot - PF_6^-$, −4CO), 231 (28), 168 [50, $Fe(CO)_4$], 119 (74, $C(CH_3)_2 - C_6H_5^+$), 69 (100, $C_4H_5O^+$). Anal. Found: C, 47.52; H, 4.70. $C_{25}H_{29}F_6FeO_6P$ (M_r = 626.3). Calc.: C, 47.94; H, 4.67%.

According to the general procedure (Section 4.3), 2.6 g (6.2 mmol) (4*S*)-**1b** were reacted with 3.0 g (8.0 mmol) nonacarbonyldiiron [$Fe_2(CO)_9$] and 8.0 mmol HPF_6 to yield 1.16 g (30%) of complex **2b** as a pale yellow powder. All spectroscopic data correspond with those given for **2a**. [*de* > 90% (^{13}C NMR)].

4.3.2. syn,syn-Tetracarbonyl-(2-4η^3)-(1'R,2'S,5'R)-{2-[2'-(1''-methyl-1''-phenyl-ethyl)-5'-methylcyclohexyloxycarbonyl)-4-methyl]allyl}iron(1 +) hexafluorophosphate **2c**

According to the general procedure (Section 4.3), 1.0 g (2.4 mmol) (4*R*)-**1c** was reacted with 1.1 g (3.0 mmol) nonacarbonyldiiron [$Fe_2(CO)_9$] and 3.0 mmol HPF_6 to yield 0.80 g (53%) of complex **2a** as a pale yellow powder. Analytical data for **2c**. M.p. 124 °C (decomp.). *syn*-CH_3/*anti*-CH_3 = 100:0 (^{1}H NMR). *de* > 90% (^{13}C NMR). ^{1}H NMR (300 MHz, CD_3NO_2, TMS(int), ppm, line broadening by paramagnetic impurities): δ 7.50–7.00 (m, 5H, C_6H_5), 5.96 (m, 1H, C*H*–$CHCO_2$), 4.98 (m, 1H, C*H*CH_3), 2.80 (d, $J(^1H-^1H)$ = 11.0 Hz, 1H, CH–C*H*CO_2), 2.40–0.95 (m, 8H, cyclohexyl-CH, -CH_2), 2.20 (m, 3H, CHCH_3), 1.36 [s, 3H, $C(CH_3)_2Ph$], 1.23 [s, 3H, $C(CH_3)_2Ph$], 0.92 (d, $J(^1H-^1H)$ = 5.4 Hz, 3H, cyclohexyl-CHCH_3). ^{13}C NMR (75 MHz, CD_3NO_2, TMS(int), ppm): δ 198.17/197.99/196.96/195.48 (Fe–C≡O), 169.49 (CH–CH*C*O_2), 153.78 (*ipso*-C), 129.58/126.96/126.15 (aromatic-CH), 96.42 (*C*H–$CHCO_2$), 90.52 (*C*HCH_3), 77.81 (CH*C*HO), 57.57 (*C*H–*C*HCO_2), 51.40 (*C*HCHO), 42.35 (CH_2), 40.29 [*C*$(CH_3)_2Ph$], 35.34 (CH_2), 31.96/31.27 (CH, CH_3), 26.91 (CH_2), 22.13/21.72/19.90 (CH, CH_3). All other spectroscopic and analytical data of **2c** correspond with those given for **2a** and **2b**.

4.3.3. syn,syn-Tetracarbonyl-(2-4η^3)-{2-methoxycarbonyl-4-methylallyl}iron(1 +) tetrafluoroborate **2d** [ent-**2d**]

According to the general procedure (Section 4.3), 4.40 g (20.0 mmol) (4*S*)-**1d** [(4*R*)-**1d**] were reacted with 9.10

g (25.0 mmol) nonacarbonyldiiron [$Fe_2(CO)_9$] and 25.0 mmol HBF_4 to yield 6.36 g (75%) of complex **2d** [*ent*-**2d**] as a pale yellow powder. Analytical data for **2d**. M.p. 95 °C (decomp.). *syn*-CH_3/*anti*-CH_3 = 100:0 (^{1}H NMR). *ee* > 99% (indirectly from the *ee*-values of the enoates **4h** and **4j**). ^{1}H NMR (500 MHz, CD_3NO_2, TMS(int), ppm): δ 6.35 (ddd, $J(^1H-^1H)$ = 12.5/10.7/0.9 Hz, 1H, C*H*–$CHCO_2$), 4.97 (dqd, $J(^1H-^1H)$ = 12.5/6.4/0.9 Hz, 1H, C*H*CH_3), 3.90 (s, 3H, OCH_3), 3.64 (d, $J(^1H-^1H)$ = 10.7 Hz, 1H, CH–C*H*CO_2), 2.19 (d, $J(^1H-^1H)$ = 6.4 Hz, 3H, CHC*H*$_3$). ^{13}C NMR (125 MHz, CD_3NO_2, TMS(int), ppm): δ 198.73/198.15/ – 196.92/196.27 (Fe–C≡O), 171.44 (CH–CH*C*O_2), 100.83 (*C*H–$CHCO_2$), 89.26 (*C*HCH_3), 54.53 (OCH_3), 53.38 (CH–*C*HCO_2), 21.11 (CH*C*H_3). IR (KBr, cm^{-1}): 3050 (=C–H), 2970, 2950, 2160, 2100, 2040, 2020, 1980 (Fe–C≡O), 1720 (C=O), 1630, 1610, 1530, 1520, 1440, 1395, 1325, 1270, 1170 (C–O), 1100–1030, 940, 890, 615, 600. MS *m*/*z* (rel. intensity (%)): 369 (0.2, M^+· + 1), 252 (11, M^+· – BF_4^-, –CO), 224 (24, M^+· – BF_4^-, –2CO), 196 (31, M^+· – BF_4^-, –3CO), 168 (47, M^+· – BF_4^-, –4CO), 138 (30), 110 (100), 109 (10), 108 (16), 83 (12), 57 (11), 56 (46, Fe^+), 53 (10), 49 (10). Anal. Found: C, 32.91; H, 2.80. $C_{10}H_9BF_4FeO_3$ (M_r = 367.8). Calc.: C, 32.65; H, 2.47%.

4.4. General procedure for the reaction of the tetracarbonyl(η^3-allyl)iron(1 +) complexes 2a–d with silyl enol ethers or silyl ketene acetals 3 to 6-oxoenoates 4

For the addition of the silyl enol ethers and silyl ketene acetals **3**, a Schlenk flask was charged under argon with 3.0 mmol of the appropriate complex **2**, and the complex was suspended in 10 ml of anhydrous dichloromethane at 0 °C. To the stirred yellow suspension was added a solution of 6.0 mmol of the appropriate silyl enol ether or silyl ketene acetal **3** in 6 ml of anhydrous dichloromethane and the reaction mixture was warmed to room temperature. Upon complete transformation of the insoluble suspended cationic complex **2** into the soluble neutral substituted tetracarbonyl(η^2-alkene)iron(0) complex (clear yellow solution), the reaction mixture was diluted with water (10–20 ml) and treated at 0 °C with an excess of solid $(NH_4)_2Ce(NO_3)_6$ (ca. 4 equivalents) until the evolution of carbon monoxide had stopped and the solution had turned yellowish-red (ca. 8 h). After repeated extraction with dichloromethane or diethyl ether and separation of the organic extracts, Fe^{III} ions were removed from the latter by successive washing with saturated aqueous NH_4F solution and finally with pH 7 buffer and/or water. The combined organic extracts were dried ($MgSO_4$), concentrated under reduced pressure, and the residue purified by flash column chromatography (silica gel 60, diethyl ether–light petroleum or pentane mixtures; **4d**: neutral aluminium oxide, activity grade III) to afford the 6-oxoenoates **4** in spectroscopically and analytically pure form.

4.4.1. (E,4R,1′R,2′S,5′R)-4-Methyl-6-oxo-6-phenyl-[2′-(1″-methyl-1″-phenylethyl)-5′-methyl)cyclohexyl]hexenoate 4a

According to the general procedure (Section 4.4), the reaction of 1.40 g (2.2 mmol) of the complex **2a** with 0.96 g (5.0 mmol) of the appropriate silyl enol ether **3a** yielded 0.48 g (52%) of the enoate **4a** as a red-brown oil. Analytical data for **4a**. R_f = 0.34 (diethyl ether–light petroleum 1:4). $[\alpha]_D^{24}$ = +10.3 (*c* = 1.08, $CHCl_3$). *de* ≥ 95% (^{13}C NMR). ^{1}H NMR (300 MHz, $CDCl_3$, TMS(int), ppm): δ 7.98–7.42 (m, 5H, COC_6H_5), 7.28–7.06 (m, 5H, C_6H_5), 6.64 (dd, $J(^1H-^1H)$ = 15.8/6.0 Hz, 1H, C*H*=$CHCO_2$), 5.21 (d, $J(^1H-^1H)$ = 15.8 Hz, 1H, C*H*=$CHCO_2$), 4.83 (dt, $J(^1H-^1H)$ = 10.8/4.4 Hz, 1H, CHC*H*O), 3.06–2.85 (m, 3H, CH_2C*H*CH_3), 2.10–0.80 (m, 8H, cyclohexyl-CH_2, -CH), 1.20 (s, 6H, C(CH_3)$_2$Ph), 1.06 (d, $J(^1H-^1H)$ = 6.0 Hz, 3H, CHCH_3), 0.86 (d, 3H, cyclohexyl-CHCH_3). ^{13}C NMR (75 MHz, $CDCl_3$, TMS(int), ppm): δ 197.99 (*C*OC_6H_5), 165.79 (CH=*C*HCO_2), 151.72 (*ipso*-C, *C*H=$CHCO_2$), 136.95/ 133.14/ 128.62/ 128.00/ 127.89/ – 125.39/124.83 (aromatic-CH), 120.35 (CH= *C*HCO_2), 74.16 (*C*HCHO), 50.51 (*C*HCHO), 44.01/41.68/39.62/34.61 (CH, CH_2), 31.70/31.27 (CH), 28.05 (CH, CH_3), 26.54 (C, CH_2), 24.75/21.78/18.94 (CH, CH_3). IR (film, cm^{-1}): 3090, 3060, 3020 (aromatic-CH, =C–H), 2960–2870, 1710 (C=O), 1690 (C=O), 1655 (C=C), 1600, 1580, 1495 (aromatic-C=C), 1450, 1390, 1365 (*gem*.-CH_3), 1270, 1180 (C–O), 1130, 1095, 1000, 980, 910, 765, 755, 735, 700, 690. MS *m*/*z* (rel. intensity (%)): 430 (0.4, M^+·), 313 (4, M^+· – $C(CH_3)_2C_6H_5$), 219 (10), 214 (17), 201 (21), 120 (10), 119 (100, $C(CH_3)_2C_6H_5^+$), 118 (62), 105 (42, $C_8H_9^+$), 91 (22, $C_7H_7^+$), 77 (13, $C_6H_5^+$), 41 (10). Anal. Found: C, 80.29; H, 8.30. $C_{29}H_{36}O_3$ (M_r = 432.6). Calc.: C, 80.52; H, 8.39%.

4.4.2. (E,4R,1′R,2′S,5′R)-4-Methyl-6-oxo-[2′-(1″-methyl-1″-phenylethyl)-5′-methyl)-cyclohexyl]heptenoate 4b

According to the general procedure (Section 4.4), the reaction of 1.40 g (2.2 mmol) of the complex **2a** with 0.65 g (5.0 mmol) of the appropriate silyl enol ether **3b** yielded 0.60 g (71%) of the enoate **4b** as a colourless oil. Analytical data for **4b**. R_f = 0.17 (diethyl ether–light petroleum 1:4). $[\alpha]_D^{23}$ = –6.4 (*c* = 3.30, $CHCl_3$). *de* ≥ 95% (^{13}C NMR). ^{1}H NMR (300 MHz, $CDCl_3$, TMS(int), ppm): δ 7.28–7.08 (m, 5H, C_6H_5), 6.54 (dd, $J(^1H-^1H)$ = 15.8/6.4 Hz, 1H, C*H*=$CHCO_2$), 5.15 (dd, $J(^1H-^1H)$ = 15.8/1.4 Hz, 1H, C*H*=$CHCO_2$), 4.83 (dt, $J(^1H-^1H)$ = 10.7/4.3 Hz, 1H, CHC*H*O), 2.52–2.30 (m, 2H, CHCH_2), 2.12 [s, 3H, C(=O)CH_3], 2.08–0.80 (m, 8H, cyclohexyl-CH_2, -CH), 1.30 [s, 3H,

$C(CH_3)_2Ph$], 1.20 (s, 3H, $C(CH_3)_2Ph$), 0.99 (d, 3H, $J(^1H-^1H) = 6.7$ Hz, $CHCH_3$), 0.86 (d, $J(^1H-^1H) = 6.4$ Hz, 3H, cyclohexyl-$CHCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$, TMS(int), ppm): δ 206.43 ($C(=O)CH_3$), 165.72 ($CH=CHCO_2$), 151.70 (*ipso*-C), 151.39 ($CH=CHCO_2$), 127.87/125.38/124.84 (aromatic-CH), 120.34 ($CH=CHCO_2$), 74.16 ($CHCHO$), 50.52 ($CHCHO$), 49.00/41.69/39.63/34.62 (C, CH_2), 31.34/31.28 (CH), 30.41/28.01 (CH, CH_3), 26.55 (C, CH_2), 24.80/21.80/18.80 (CH, CH_3). IR (film, cm^{-1}): 3090–3020 (=C–H), 2960–2870, 1715 (C=O), 1655 (C=C), 1600, 1585, 1495 (aromatic-C=C), 1460, 1445, 1390, 1365 (*gem.*-CH_3), 1270, 1180 (C–O), 1130, 1095, 1000, 985, 765, 700. MS *m/z* (rel. intensity (%)): 370 (1, $M^+\cdot$), 251 (3, $M^+\cdot - C(CH_3)_2C_6H_5$), 214 (17), 120 (10), 119 (100, $C(CH_3)_2C_6H_5^+$), 118 (57), 105 (9, $C_8H_9^+$), 95 (11), 91 (33, $C_7H_7^+$), 55 (10), 43 (58, $C_2H_3O^+$), 41 (22), 28 (13). Anal. Found: C, 78.20; H, 9.25. $C_{24}H_{34}O_3$ ($M_r = 370.5$). Calc.: C, 77.80; H, 9.25%.

4.4.3. *(E,4R,1'R,2'S,5'R)-4-Methyl-5-methoxycarbonyl-[2'-(1''-methyl-1''-phenyl-ethyl)-5'-methyl)cyclohexyl]pentenoate* **4c**

According to the general procedure (Section 4.4), the reaction of 1.66 g (2.65 mmol) of the complex **2a** with 0.88 g (6.0 mmol) of the appropriate silyl ketene acetal **3c** yielded 0.82 g (80%) of the enoate **4c** as a colourless oil. Analytical data for **4c**. $R_f = 0.36$ (diethyl ether–light petroleum 1:4). $[\alpha]_D^{28} = -9.1$ ($c = 2.23$, $CHCl_3$). *de* ≥ 95% (^{13}C NMR). ^1H NMR (300 MHz, $CDCl_3$, TMS(int), ppm): δ 7.28–7.08 (m, 5H, C_6H_5), 6.54 (dd, $J(^1H-^1H) = 15.8/6.7$ Hz, 1H, $CH=CHCO_2$), 5.19 (dd, $J(^1H-^1H) = 15.8/1.7$ Hz, 1H, $CH=CHCO_2$), 4.83 (dt, $J(^1H-^1H) = 10.8/4.4$ Hz, 1H, $CHCHO$), 3.66 (s, 3H, OCH_3), 2.72 (m, 1H, $CHCH_3$), 2.40–2.18 (m, 2H, $CHCH_2$), 2.08–0.80 (m, 8H, cyclohexyl-CH_2, -CH), 1.30 [s, 3H, $C(CH_3)_2Ph$], 1.20 [s, 3H, $C(CH_3)_2Ph$], 1.03 (d, 3H, $J(^1H-^1H) = 7.1$ Hz, $CHCH_3$), 0.86 (d, $J(^1H-^1H) = 6.4$ Hz, 3H, cyclohexyl-$CHCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$, TMS(int), ppm): δ 172.06 (CO_2CH_3), 165.62 ($CH=CHCO_2$), 151.60 (*ipso*-C), 150.79 ($CH=CHCO_2$), 127.89/125.41/124.91 (aromatic-CH), 120.59 ($CH=CHCO_2$), 74.15 ($CHCHO$), 51.52 (OCH_3), 50.50 ($CHCHO$), 41.67/39.89/–39.62/34.60 (C, CH_2), 32.59 ($CHCH_3$), 31.26/27.96 (CH, CH_3), 30.41/28.01 (CH, CH_3), 26.55 (C, CH_2), 24.86/21.78/18.80 (CH, CH_3). IR (film, cm^{-1}): 3089–3022 (=C–H), 2955–2872, 1741 (C=O), 1713 (C=O), 1654 (C=C), 1601, 1581, 1496 (aromatic-C=C), 1458, 1441, 1389, 1366 (*gem.*-CH_3), 1272, 1179 (C–O), 1133, 983, 734, 702. MS *m/z* (rel. intensity (%)): 386 (1, $M^+\cdot$), 267 (2, $M^+\cdot - C(CH_3)_2C_6H_5$), 214 (17), 155 (11), 119 (100, $C(CH_3)_2C_6H_5^+$), 118 (59), 105 (9, $C_8H_9^+$), 91 (18, $C_7H_7^+$), 41 (18). Anal. Found: C, 74.81; H, 9.02. $C_{24}H_{34}O_4$ ($M_r = 386.5$). Calc.: C, 74.58; H, 8.87%.

4.4.4. *(E,4S,1'R,2'S,5'R)-4,5,5-Trimethyl-6-oxo-[2'-(1''-methyl-1''-phenyl-ethyl)-5''-methyl)cyclohexyl]pentenoate* **4d**

According to the general procedure (Section 4.4), the reaction of 1.30 g (2.1 mmol) of the complex **2a** with 0.60 g (4.2 mmol) of the appropriate silyl enol ether **3d** yielded 0.20 g (25%) of the enoate **4d** as a colourless oil after purification by column chromatography on neutral aluminium oxide, activity grade III. Analytical data for **4c**. $R_f = 0.36$ (diethyl ether–light petroleum 1:4). $[\alpha]_D^{28} = -16.5$ ($c = 0.93$, $CHCl_3$). *de* ≥ 95% (^{13}C NMR). ^1H NMR (300 MHz, $CDCl_3$, TMS(int), ppm): δ 9.44 (s, 1H, CHO), 7.30–7.10 (m, 5H, C_6H_5), 6.60 (dd, $J(^1H-^1H) = 15.8/8.4$ Hz, 1H, $CH=CHCO_2$), 5.20 (dd, $J(^1H-^1H) = 15.8/1.4$ Hz, 1H, $CH=CHCO_2$), 4.84 [dt, $J(^1H-^1H) = 10.8/4.4$ Hz, 1H, $CHCHO$], 2.47 (m, 1H, $CHCH_3$), 2.20–1.00 (m, 8H, cyclohexyl-CH_2, -CH), 1.30 (s, 3H, $C(CH_3)_2Ph$), 1.21 (s, 3H, $C(CH_3)_2Ph$), 1.00 [s, 6H, $CCH(CH_3)_2$], 0.93 (d, $J(^1H-^1H) = 6.7$ Hz, 3H, $CHCH_3$), 0.87 (d, $J(^1H-^1H) = 6.7$ Hz, 3H, cyclohexyl-$CHCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$, TMS(int), ppm): δ 205.05 (CHO), 165.31 ($CH=CHCO_2$), 151.61 (*ipso*-C), 147.71 ($CH=CHCO_2$), 127.87/125.36/124.93 (aromatic-CH), 123.20 ($CH=CHCO_2$), 74.33 ($CHCHO$), 50.53 ($CHCHO$), 48.49 [$CHC(CH_3)_2$], 43.50 ($CHCH_3$), 41.70 (C, CH_2), 39.72/34.61 (C, CH_2), 31.29/27.93 (CH, CH_3), 26.58 (C, CH_2), 24.94/21.79/20.23/17.74/14.40 (CH, CH_3). IR (film, cm^{-1}): 3088, 3057, 3022 (aromatic-CH, =C–H), 2966, 2926, 2872, 2070 (HCO), 1713 (C=O), 1715 (C=O), 1652 (m, C=C), 1601, 1581 (aromatic-C=C), 1496, 1458, 1446, 1389, 1368 (*gem.*-CH_3), 1345, 1294, 1267, 1182 (C–O), 1132, 1110, 1094, 1048, 1032, 996, 953, 933, 767, 734, 702. MS *m/z* (rel. intensity (%)): 384 (0.4, $M^+\cdot$), 265 (2, $M^+\cdot - C(CH_3)_2C_6H_5$), 214 (11), 120 (10), 119 (100, $C(CH_3)_2C_6H_5^+$), 118 (48), 105 (10, $C_8H_9^+$), 91 (20, $C_7H_7^+$), 55 (13), 41 (14). Anal. Found: C, 78.33; H, 9.11. $C_{25}H_{36}O_3$ ($M_r = 384.5$). Calc.: C, 78.09; H, 9.44%.

4.4.5. *(E,4S,1'R,2'S,5'R)-4,5,-Dimethyl-5-methoxycarbonyl-[2'-(1''-methyl-1''-phenylethyl)-5'-methyl)cyclohexyl]hexenoate* **4e**

Data for the reaction of complex **2b** with the silyl ketene acetal **3e** are given in square brackets. According to the general procedure (Section 4.4), the reaction of 1.88 g (3.0 mmol) of the complex **2a** [**2b**: 0.70 g (1.1 mmol)] with 1.05 g (6.0 mmol) [**2b**: 0.40 g (2.3 mmol)]of the appropriate silyl ketene acetal **3e** yielded 1.10 g (90%) [**2b**: 0.37 g (56%)] of the enoate **4e** as a colourless oil. Analytical data for **4e**. $R_f = 0.43$ (diethyl ether–light petroleum 1:4). From **2a**: $[\alpha]_D^{22} = -16.1$

($c = 3.32$, $CHCl_3$); from **2b**: $[\alpha]_D^{24} = -15.1$ ($c = 2.15$, $CHCl_3$). From **2a**: $de \geq 95\%$; from **2b**: $de \geq 90\%$ (^{13}C NMR). ^1H NMR (300 MHz, $CDCl_3$, TMS(int), ppm): δ 7.28–7.08 (m, 5H, C_6H_5), 6.64 (dd, $J(^1H-^1H) = 15.7/8.4$ Hz, 1H, $CH{=}CHCO_2$), 5.25 (dd, $J(^1H-^1H) = 15.6/1.3$ Hz, 1H, $CH{=}CHCO_2$), 4.84 (dt, $J(^1H-^1H) = 10.4/4.4$ Hz, 1H, $CHCHO$), 3.66 (s, 3H, OCH_3), 2.56 (m, 1H, $CHCH_3$), 2.08–0.80 (m, 8H, cyclohexyl-CH_2, -CH), 1.30 (s, 3H, $C(CH_3)_2Ph$), 1.22 (s, 3H, $C(CH_3)_2Ph$), 1.10 [s, 3H, $CCH(CH_3)_2$], 1.08 [s, 3H, $CCH(CH_3)_2$], 0.91 (d, $J(^1H-^1H) = 7.1$ Hz, 3H, $CHCH_3$), 0.86 (d, $J(^1H-^1H) = 6.7$ Hz, 3H, cyclohexyl-$CHCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$, TMS(int), ppm): δ 177.27 (CO_2CH_3), 165.50 ($CH{=}CHCO_2$), 151.44 (*ipso*-C), 148.72 ($CH{=}CHCO_2$), 127.88/125.37/124.92 (aromatic-CH), 122.88 ($CH{=}CHCO_2$), 74.25 (CHCHO), 51.73 (OCH_3), 50.58 (CHCHO), 45.53 [$CHC(CH_3)_2$], 43.50 ($CHCH_3$), 41.72/−39.72/34.61 (C, CH_2), 31.29/27.40 (CH, CH_3), 26.66 (C, CH_2), 25.54/23.51/21.80/20.84/14.54 (CH, CH_3). IR (film, cm^{-1}): 3085, 3060, 3020 (aromatic-CH, =C–H), 2980, 2960, 2880, 1730 (C=O), 1715 (C=O), 1650 (m, C=C), 1600 (aromatic-C=C), 1500, 1460, 1445, 1390, 1370 (*gem.*-CH_3), 1350, 1295, 1270, 1250, 1240, 1180 (C–O), 1095, 1035, 990, 765, 700. MS *m/z* (rel. intensity (%)): 414 (3, $M^+\cdot$), 295 (6, $M^+ - C(CH_3)_2C_6H_5$), 214 (18), 155 (11), 123 (12), 120 (11), 119 (100, $C(CH_3)_2C_6H_5^+$), 118 (65), 105 (12, $C_8H_9^+$), 95 (11), 91 (24, $C_7H_7^+$), 41 (14), 32 (11), 28 (29). Anal. Found: C, 75.06; H, 9.10. $C_{26}H_{38}O_4$ (M_r = 414.6). Calc.: C, 75.33; H, 9.24%.

4.4.6. *(E,4R,1'R,2'S,5'R)-4,5,-Dimethyl-5-methoxycarbonyl-[2'-(1''-methyl-1''-phenylethyl)-5'-methyl)cyclohexyl]hexenoate 4e*

According to the general procedure (Section 4.4), the reaction of 0.62 g (1.0 mmol) of the complex **2c** with 0.35 g (6.0 mmol) of the appropriate silyl ketene acetal **3e** yielded 0.31 g (75%) of the enoate **4f** as a colourless oil. Analytical data for **4f**. $R_f = 0.36$ (diethyl ether–light petroleum 1:4). $[\alpha]_D^{24} = +33.3$ ($c = 1.62$, $CHCl_3$). *de* > 93% (^{13}C NMR). ^1H NMR (300 MHz, $CDCl_3$, TMS(int), ppm): δ 7.28–7.08 (m, 5H, C_6H_5), 6.64 (dd, $J(^1H-^1H) = 15.8/8.7$ Hz, 1H, $CH{=}CHCO_2$), 5.20 (d, $J(^1H-^1H) = 15.8$ Hz, 1H, $CH{=}CHCO_2$), 4.84 (dt, $J(^1H-^1H) = 10.8/4.8$ Hz, 1H, $CHCHO$), 3.65 (s, 3H, OCH_3), 2.54 (m, 1H, $CHCH_3$), 2.08–0.80 (m, 8H, cyclohexyl-CH_2, -CH), 1.30 (s, 3H, $C(CH_3)_2Ph$), 1.22 (s, 3H, $C(CH_3)_2Ph$), 1.10 [s, 3H, $CCH(CH_3)_2$], 1.08 [s, 3H, $CCH(CH_3)_2$], 0.95 (d, $J(^1H-^1H) = 6.7$ Hz, 3H, $CHCH_3$), 0.86 (d, $J(^1H-^1H) = 6.4$ Hz, 3H, cyclohexyl-$CHCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$, TMS(int), ppm): δ 177.27 (CO_2CH_3), 165.45 ($CH{=}CHCO_2$), 151.41 (*ipso*-C), 148.66 ($CH{=}CHCO_2$), 127.88/−125.36/124.90 (aromatic-CH), 122.85 ($CH{=}CHCO_2$), 74.14 (CHCHO), 51.74 (OCH_3), 50.58 (CHCHO), 45.49 [$CHC(CH_3)_2$], 43.47 ($CHCH_3$), 41.71/39.70/34.56 (C, CH_2), 31.27/27.39 (CH, CH_3), 26.60 (C, CH_2), 25.54/23.51/−21.80/20.84/14.54 (CH, CH_3). All other analytical and spectroscopic data correspond with those given for **4e**.

4.4.7. *(E,4S)-4,5,-Dimethyl-5-methoxycarbonyl-methyl hexenoate 4g*

According to the general procedure (Section 4.4), the reaction of 2.70 g (7.3 mmol) of the complex **2d** with 2.61 g (15.0 mmol) of the appropriate silyl ketene acetal **3e** yielded 1.35 g (86%) of the enoate **4g** as a colourless oil. Analytical data for **4g**. $R_f = 0.32$ (diethyl ether–light petroleum 1:4). $[a]_D^{24} = -48.1$ ($c = 2.38$, $CHCl_3$). *ee* ≥ 96% (^{13}C NMR, after ozonolysis of **4g** and acetalization of the resulting aldehyde with (−)-(2*R*,3*R*)-butanediol). ^1H NMR (300 MHz, $CDCl_3$, TMS(int), ppm): δ 6.88 (dd, $J(^1H-^1H) = 15.8/8.7$ Hz, 1H, $CH{=}CHCO_2$), 5.83 (dd, $J(^1H-^1H) = 15.8/1.0$ Hz, 1H, $CH{=}CHCO_2$), 3.73 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 2.65 (m, 1H, $CHCH_3$), 1.15 [s, 3H, $C(CH_3)_2$], 1.14 [s, 3H, $C(CH_3)_2$], 1.01 (d, $J(^1H-^1H) = 7.1$ Hz, 3H, $CHCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$, TMS(int), ppm): δ 177.27 ($C(CH_3)_2CO_2$), 166.79 ($CH{=}CHCO_2$), 149.99 ($CH{=}CHCO_2$), 121.99 ($CH{=}CHCO_2$), 51.82/51.47 (OCH_3), 45.57 [$C(CH_3)_2$], 43.81 ($CHCH_3$), 23.31/21.22 [$C(CH_3)_2$], 14.88 ($CHCH_3$). IR (film, cm^{-1}): 3000 (=C–H), 2960, 2900, 2860, 1730 (C=O), 1660 (m, C=C), 1465, 1440, 1385, 1373 (*gem.*-CH_3), 1345, 1305, 1275, 1200, 1180 (C–O), 1145, 1075, 1045, 1030, 995, 950, 910, 875, 855, 785, 775, 745, 720. MS *m/z* (rel. intensity (%)): 214 (2, $M^+\cdot$), 182 (31, $M^+\cdot - HOCH_3$), 155 (50, $M^+\cdot - C_2H_3O_2$), 154 (24), 123 (33), 114 (100, $M^+\cdot - C_5H_8O_2$), 113 (87, $M^+\cdot - C_5H_9O_2$), 102 (84), 95 (30), 87 (17), 82 (40), 81 (26), 73 (21), 70 (14), 59 (21), 55 (21), 53 (11), 43 (11), 41 (24). Anal. Found: C, 61.63; H, 8.58. $C_{11}H_{18}O_4$ ($M_r = 214.3$). Calc.: C, 61.66; H, 8.47%.

4.4.8. *(E,4R)-5-Methoxycarbonyl-methyl hexenoate 4h / (E,4S)-5-methoxycarbonyl-methyl hexenoate ent-4h*

Data for the reaction of complex *ent*-**2d** with the silyl ketene acetal **3e** are given in square brackets. According to the general procedure (Section 4.4), the reaction of 2.50 g (6.8 mmol) of the complex **2d** [*ent*-**2d**: 0.73 g (2.0 mmol)] with 2.0 g (13.7 mmol) of the appropriate silyl ketene acetal **3e** [*ent*-**2d**: 0.58 g (4.0 mmol)] yielded 0.92 g (73%) of the enoate **4g** [*ent*-**2d**: 0.26 g (71%)] as a pale yellow oil. Analytical data for **4h** and *ent*-**4h**. $R_f = 0.27$ (diethyl ether–light petroleum 1:2). For **4h**: $[\alpha]_D^{24} = -29.4$ ($c = 2.03$, $CHCl_3$); for *ent*-**4h**: $[\alpha]_D^{25} = +29.1$ ($c = 2.14$, $CHCl_3$). *ee* ≥ 99% (GLC_{CSP} on a chiral perpentylated β-cyclodextrine phase). ^1H NMR (300 MHz, $CDCl_3$,

TMS(int), ppm): δ 6.91 (dd, $J(^1H-^1H)$ = 15.8/7.1 Hz, 1H, C*H*=CHCO$_2$), 5.83 (dd, $J(^1H-^1H)$ = 15.8/1.3 Hz, 1H, CH=C*H*CO$_2$), 3.73 (s, 3H, OCH$_3$), 3.68 (s, 3H, OCH$_3$), 2.87 (m, 1H, C*H*CH$_3$), 2.40 (m, 2H, CHC*H*$_2$), 2.14 (s, 3H, C(=O)CH$_3$), 1.12 (d, $J(^1H-^1H)$ = 6.7 Hz, 3H, CHC*H*$_3$). ^{13}C NMR (75 MHz, CDCl$_3$, TMS(int), ppm): δ 172.08 (CH$_2$*C*O$_2$), 166.96 (CH=CH*C*O$_2$), 152.05 (*C*H=CHCO$_2$), 120.01 (CH=*C*HCO$_2$), 51.64/51.49 (OCH$_3$), 40.13 (CH*C*H$_2$), 33.02 (*C*HCH$_3$), 19.08 (CH*C*H$_3$). IR (film, cm^{-1}): 3060 (=C–H), 2955, 2940, 2880, 2840, 1730 (C=O), 1660 (C=C), 1440, 1360, 1320, 1280, 1260, 1200, 1175 (C–O), 1095, 1010, 985. MS *m/z* (rel. intensity (%)): 186 (0.1, M$^+$·), 155 (39, M$^+$· − OCH$_3$), 154 (100, M$^+$· − HOCH$_3$), 127 (25, M$^+$· − C$_2$H$_3$O$_2$), 126 (31), 125 (14), 123 (35), 122 (87), 113 (18), 111 (21), 95 (65), 94 (49), 85 (34), 81 (23), 68 (12), 67 (48), 59 (41, C$_2$H$_3$O$_2^+$), 55 (17), 53 (26), 43 (14), 41 (33), 39 (16). Anal. Found: C, 58.35; H, 7.66. C$_9$H$_{14}$O$_4$ (M_r = 186.2). Calc.: C, 58.05; H, 7.58%.

4.4.9. (E,4R)-4,5,5-Trimethyl-6-oxo-methyl hexenoate 4i

According to the general procedure (Section 4.4), the reaction of 3.70 g (10.0 mmol) of the complex *ent*-**2d** with 2.88 g (20.0 mmol) of the appropriate silyl enol ether **3d** yielded 1.80 g (98%) of the enoate **4i** as a pale yellow oil. Analytical data for **4i**. R_f = 0.25 (diethyl ether–light petroleum 1:4). $[\alpha]_D^{24}$ = +48.4 (c = 2.38, CHCl$_3$). Enantiomeric excess could not be determined. ^{1}H NMR (300 MHz, CDCl$_3$, TMS(int), ppm): δ 9.48 (s, 1H, CHO), 6.90 (dd, $J(^1H-^1H)$ = 15.8/8.7 Hz, 1H, C*H*=CHCO$_2$), 5.85 (dd, $J(^1H-^1H)$ = 15.8/1.3 Hz, 1H, CH=C*H*CO$_2$), 3.74 (s, 3H, OCH$_3$), 2.63 (m, 1H, C*H*CH$_3$), 1.14 (d, $J(^1H-^1H)$ = 6.7 Hz, 3H, CHC*H*$_3$), 1.03 [s, 3H, C(CH$_3$)$_2$], 1.02 [s, 3H, C(CH$_3$)$_2$]. ^{13}C NMR (75 MHz, CDCl$_3$, TMS(int), ppm): δ 205.16 (CHO), 166.70 (CH=CH*C*O$_2$), 149.15 (*C*H=CHCO$_2$), 122.32 (CH=*C*HCO$_2$), 51.56 (OCH$_3$), 48.51 [*C*(CH$_3$)$_2$], 41.29 (*C*HCH$_3$), 20.13/17.85 [C(*C*H$_3$)$_2$], 14.52 (CH*C*H$_3$). IR (film, cm^{-1}): 3060 (=C–H), 2980, 2940, 2880, 2840, 2710 (HCO), 1730 (C=O), 1660 (m, C=C), 1460, 1440, 1380, 1370 (*gem.*-CH$_3$), 1350, 1300, 1275, 1200, 1180 (C–O), 1140, 1100, 1080, 1040, 1015, 990. MS *m/z* (rel. intensity (%)): 184 (0.8, M$^+$·), 156 (12, M$^+$· − CO), 155 (13, M$^+$· − CHO), 113 (79, M$^+$· − C$_4$H$_7$O), 81 (60), 71 (22, C$_4$H$_7$O$^+$), 70 (55), 59 (40, C$_2$H$_3$O$_2^+$), 58 (32), 57 (35), 55 (69), 43 (100, C$_2$H$_3$O$^+$), 41 (55), 39 (34), 32 (23), 28 (63). Anal. Found: C, 64.99; H, 8.51. C$_{10}$H$_{16}$O$_3$ (M_r = 184.2). Calc.: C, 65.19; H, 8.75%.

4.4.10. (E,4R)-5-Methoxycarbonyl-methyl hexenoate 4j / (E,4S)-5-methoxycarbonyl-methyl hexenoate ent-4j

Data for the reaction of complex *ent*-**2d** with the silyl ketene acetal **3b** are given in square brackets. According to the general procedure (Section 4.4), the reaction of 3.70 g (10.0 mmol) of the complex **2d** [*ent*-**2d**: 1.85 g (5.0 mmol)] with 2.6 g (20.0 mmol) of the appropriate silyl ketene acetal **3b** [*ent*-**2d**: 1.30 g (10.0 mmol)] yielded 1.17 g (69%) of the enoate **4j** [*ent*-**2d**: 0.59 g (69%)] as a pale yellow oil. Analytical data for **4j** and *ent*-**4j**. R_f = 0.27 (diethyl ether–light petroleum 1:2). For **4j**: $[\alpha]_D^{26}$ = −33.3 (c = 2.12, CHCl$_3$); for *ent*-**4j**: $[\alpha]_D^{24}$ = +35.2 (c = 2.77, CHCl$_3$). *ee* > 99% (GLC$_{CSP}$ on a chiral permethylated β-cyclodextrine phase). ^{1}H NMR (300 MHz, CDCl$_3$, TMS(int), ppm): δ 6.89 (dd, $J(^1H-^1H)$ = 15.8/7.1 Hz, 1H, C*H*=CHCO$_2$), 5.81 (dd, $J(^1H-^1H)$ = 15.8/1.3 Hz, 1H, CH=C*H*CO$_2$), 3.72 (s, 3H, OCH$_3$), 2.91 (m, 1H, C*H*CH$_3$), 2.52 (m, 2H, CHC*H*$_2$), 2.14 (s, 3H, C(=O)CH$_3$), 1.08 (d, $J(^1H-^1H)$ = 6.7 Hz, 3H, CHC*H*$_3$). ^{13}C NMR (75 MHz, CDCl$_3$, TMS(int), ppm): δ 206.47 (*C*(=O)CH$_3$), 167.00 (CH=CH*C*O$_2$), 152.64 (*C*H=CHCO$_2$), 119.72 (CH=*C*HCO$_2$), 51.44 (OCH$_3$), 49.14 (CH*C*H$_2$), 31.67/30.44 (*C*HCH$_3$/C(=O)*C*H$_3$), 18.99 (CH*C*H$_3$). IR (film, cm^{-1}): 3060 (=C–H), 2960, 2940, 2880, 1720 (C=O), 1690 (C=O), 1660 (C=C), 1440, 1360, 1320, 1280, 1195, 1175 (C–O), 1015, 985. MS *m/z* (rel. intensity%): 170 (0.3, M$^+$·), 139 (20, M$^+$· − OCH$_3$), 138 (30, M$^+$· − HOCH$_3$), 127 (28, M$^+$· − C$_2$H$_3$O), 113 (11), 111 (13, M$^+$· − C$_2$H$_3$O$_2$), 96 (16), 95 (39), 81 (13), 67 (18), 43 (100, C$_2$H$_3$O$^+$), 41 (13). Anal. Found: C, 63.26; H, 8.51. C$_9$H$_{14}$O$_3$ (M_r = 170.2). Calc.: C, 63.51; H, 8.29%.

4.4.11. (E,4R)-4,5,5-Trimethyl-6-oxo-methyl hexenoate 4k

According to the general procedure (Section 4.4), the reaction of 2.95 g (8.0 mmol) of the complex *ent*-**2d** with 3.10 g (16.0 mmol) of the appropriate silyl enol ether **3a** yielded 1.71 g (92%) of the enoate **4k** as a yellow oil. Analytical data for **4k**. R_f = 0.21 (diethyl ether–light petroleum 1:4). $[\alpha]_D^{25}$ = +5.4 (c = 2.82, CHCl$_3$). *ee* ≥ 96% (^{13}C NMR, after ozonolysis of **4k** and acetalization of the resulting aldehyde with (−)-(2*R*,3*R*)-butanediol). ^{1}H NMR (300 MHz, CDCl$_3$, TMS(int), ppm): δ 8.00–7.90 (m, 2H, *ortho*-CH), 7.60–7.42 (m, 3H, *meta*-CH, *para*-CH), 6.99 (dd, $J(^1H-^1H)$ = 15.8/6.4 Hz, 1H, C*H*=CHCO$_2$), 5.86 (dd, $J(^1H-^1H)$ = 15.8/1.0 Hz, 1H, CH=C*H*CO$_2$), 3.71 (s, 3H, OCH$_3$), 3.15–2.93 (m, 3H, CHC*H*$_2$), 1.16 (d, $J(^1H-^1H)$ = 6.4 Hz, 3H, CHC*H*$_3$). ^{13}C NMR (75 MHz, CDCl$_3$, TMS(int), ppm): δ 197.90 (*C*OC$_6$H$_5$), 167.05 (CH=CH*C*O$_2$), 152.92 (*C*H=CHCO$_2$), 136.91 (*ipso*-C), 133.19 (*para*-C), 128.64, 128.01 (*ortho*-C, *meta*-C), 119.75 (CH=*C*HCO$_2$), 51.43 (OCH$_3$), 44.17 (CH*C*H$_2$), 31.95 (*C*HCH$_3$), 19.15 (CH*C*H$_3$). IR (film, cm^{-1}): 3090, 3060, 3030 (aromatic-CH, =C–H), 2970, 2960, 2900, 2880, 2845, 1725 (C=O), 1690 (C=O), 1660 C=C), 1600, 1580, 1450, 1440, 1370, 1320, 1275, 1210, 1180 (C–O), 1000, 985, 760, 690. MS *m/z* (rel. intensity (%)): 232 (0.4, M$^+$·), 158 (20), 127 (14,

$M^+ \cdot - COC_6H_5$), 105 (100, $COC_6H_5^+$), 95 (12), 77 (42, $C_6H_5^+$), 51 (10). Anal. Found: C, 72.42; H, 6.85. $C_{14}H_{16}O_3$ (M_r = 232.3). Calc.: C, 72.39; H, 6.94%.

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