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"Chirality transfer" in iron-mediated dienylic substitutions via highly enantiomerically enriched planar chiral 1-phenylsulfonyl-substituted tricarbonyl(η⁵-pentadienyl)iron(1+) complexes

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Abstract

The preparation of highly diastereo- and enantiomerically enriched planar chiral 1-phenylsulfonyl-substituted tricarbonyl(η⁵-pentadienyl)iron(1+) complexes **7** [*syn,syn*-(1*R*,5*R*)-**7** and *syn,syn*-(1*S*,5*S*)-**7** (*cisoid*- or *U*-forms); *de* > 99% ≡ 5-*syn*-CH_3/5-*anti*-CH_3 ≫ 100:1, *ee* > 99%; 87% quant. from resolved **6**] is described. Starting from the enantiopure diene (1*E*,3*E*,*S*)-**5** both enantiomers of the cationic complexes *syn,syn*-**7** become readily accessible via chromatographic resolution of the diastereomeric mixture of the corresponding neutral tricarbonyl(η⁴-diene)iron(0) complexes **6** [(1*R*,5*S*)-**6** ≡ Ψ-*endo*-**6** and (1*S*,5*S*)-**6** ≡ Ψ-*exo*-**6**; *de* > 99%, *ee* > 99%; 85% quant. prior to resolution]. The nucleophilic addition of hetero and carbon atom nucleophiles (morpholine, silyl enol ether **8** and silyl ketene acetal **9**) to the racemic complex *syn,syn*-(1*R*/*S*,5*R*/*S*)-**7** afforded the neutral tricarbonyl(η⁴-diene)iron(0) complexes *rac*-Ψ-*exo*-**10a–c** in moderate yields [43–68% from *syn,syn*-(1*R*/*S*,5*R*/*S*)-**7**] as single geometrical isomers [(*E,Z*) or (*E,E*); kinetic (*U*-form/strong nucleophile) or thermodynamic (*S*-form/less reactive nucleophile) control]. Likewise, nucleophilic addition to the stereochemically homogeneous complexes *syn,syn*-(1*R*,5*R*)-**7** or *syn,syn*-(1*S*,5*S*)-**7** followed by oxidative cleavage of the carbonyl-iron fragment offers an access to ε-substituted dienes **11a–c** in moderate to fair yields [45–65%, (*E,Z*)/(*E,E*) = > 85:1–1:3] with enantiomeric excesses ranging from > 99%/98.9% [(1*E*,3*Z*,*R*)-**11a**/(1*E*,3*Z*,*S*)-**11a**] to 93% [(6*E*,8*E*,*S*)-**11b**]. The stereochemistry of the formation and the stereochemical pathways of the nucleophilic addition reactions of the nonracemic complexes *syn,syn*-**7** leading to the dienes **11a–c** as well as spectroscopic and structural details are discussed. Furthermore, the reaction proceeds with virtually complete "chirality transfer" from C–O via C–Fe to C–N or C–C, respectively, with either retention or inversion of stereochemistry of the stereogenic centre with respect to the starting material (*S*)-**1** depending strongly on the reaction conditions. The observed ε-regioselectivity of the nucleophilic addition reaction displays the synthetic equivalence of the cationic complexes of type *syn,syn*-**7** with a planar chiral a⁶-synthon allowing an umpolung of the classical d⁶-chemistry.

Keywords: Iron; Tricarbonyl(η⁴-diene)iron(0) complex; Tricarbonyl(η⁵-pentadienyl)iron(1+) complex; Planar chirality; Dienylic substitution; 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 reagents in organic synthesis taking advantage of their enhanced reactivity towards a wide variety of soft nucleophiles [1–3] (for a general use of transition metals in organic synthesis see Ref. [1]; for the general chemistry of organo-iron compounds see Ref. [3]). Recently, acyclic tricarbonyl(η⁵-pentadienyl)iron(1+) complexes, although less stable (and more electrophilic) than their cyclic counterparts [4,5], have attracted a considerable interest in stoichiometric asymmetric synthesis, since they owe planar chirality when the coordinated ligand is unsymmetrically substituted and the metal fragment distinguishes between the two enantiotopic faces of the ligand [6]. Therefore, tricarbonyl(η⁵-pentadienyl)iron(1+) complexes represent valuable tools for organic synthesis (e.g. synthesis

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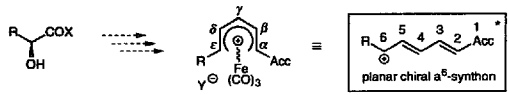


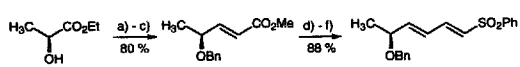
C A B

X = OH, OR, NR_2; R = alkyl, aryl; Y = BF_4^-, PF_6^- etc.
Acc = acceptor = CO_2R, SO_2Ph, $PO(OR)_2$ etc.

Fig. 1. Approaches to diastereo- and enantiomerically enriched (π-pentadienyl)$Fe(CO)_3(1+)$ complexes.

of polyunsaturated natural products or polyfunctionalized tricarbonyl(π-diene)iron complexes) [3,4]. Moreover, their synthetic potential and usefulness as planar chiral organometallic electrophilic agents towards a wide variety of carbon and heteroatom nucleophiles deeply relies on the accessibility of the corresponding tricarbonyl(η^4-diene)iron(0) complexes in enantiomerically pure form as their most likely precursors. Therefore, various methods have been developed to obtain highly diastereo- and/or enantiomerically enriched complexes of this type [4,7–10] (for separation of diastereomers see Ref. [7]; for enzymatic kinetic resolutions see Ref. [8]; for diastereoselective complexation of chirally modified diene ligands see Ref. [9]; for enantioselective complexation of prochiral 1,3-dienes by chirally modified tricarbonyl transfer reagents see Ref. [10]). Unfortunately, reactions of isolated (*cisoid*) cationic tricarbonyl(π-pentadienyl)iron complexes with nucleophiles often give rise to mixtures of regio- and/or stereoisomers due to kinetic or thermodynamic reaction control of the nucleophilic addition reaction which in turn depends on electronic and steric effects of substituents as well as the type of nucleophile employed [4,11,12] (for recent examples see Ref. [11]). In addition, the 'in situ method' allows regio- and stereocontrolled dienylic substitutions via *transoid* or *S*-shaped cationic tricarbonyl(η^5-pentadienyl)iron(1 +) complexes leading stereoselectively to (*E,E*)-configured tricarbonyl(η^4-diene)iron(0) complexes [4,13] (also, for recent examples see Ref. [14]). In all cases the incoming nucleophile invariably attacks the coordinated pentadienyl ligand *trans* with respect to the $Fe(CO)_3$ moiety [4]. However, progress has to be made in order to better understand the delicate balance of factors governing the regio- and stereoselectivities of such kinds of dienylic substitution giving this approach a quantitative and qualitative as well as predictive value. By analogy to our established regio- and stereocontrolled chirality transfer process in allylic substitution reactions via acceptor substituted tetracarbonyl(η^3-allyl)iron(1 +) complexes [15] (also, for application of this methodology in natural product synthesis see Ref. [16]), the corresponding acceptor-substituted tricarbonyl(η^5-pentadienyl)iron(1 +) complexes **A**, representing planar chiral synthetic equivalents of a^6-synthons **B** and allowing an umpolung of classical d^6-chemistry [17], should be readily accessible starting from enantiopure *chiral pool*-precursors **C** (Fig. 1).

We now wish to report on the synthesis of highly diastereo- and enantiomerically enriched phenylsulfonyl functionalized tricarbonyl(η^5-pentadienyl)iron(1 +) complexes *syn,syn*-**7** as a model system for our approach to complexes of type **A** (Fig. 1). Key steps are the chromatographic separation of diastereomeric tricarbonyl(η^4-diene)iron(0) complexes *Ψ-endo-/Ψ-exo*-**6** which in turn are based on the enantiopure precursor ethyl-(*S*)-lactate [(*S*)-**1**] and their stereoselective transformation to the enantiomeric cationic complexes *syn,syn*-**7**. The nucleophilic addition of nitrogen (morpholine) and carbon atom nucleophiles (silyl enol ether **8**, silyl ketene acetal **9**) provides access either to new ε-substituted tricarbonyl(η^4-diene)iron(0) complexes **10a–c** or, after oxidative removal of the tricarbonyliron fragment, to ε-functionalized phenylsulfonyl-substituted dienes **11a–c** of high diastereomeric and enantiomeric purity.



(*S*)-**1** (*E,S*)-**2** *ee* > 99 % (1*E*,3*E*,*S*)-**5** *ee* > 99 % (1*E*,3*E*)/(1*E*,3*Z*) >> 100:1

Scheme 1. (a) $Cl_3CC(=NH)OBn$ (2.0 equiv.), TfOH (0.1 equiv.), CH_2Cl_2–cyclohexane = 1:7, room temperature, 60 h, 95%; (b) DIBAH (1.4 equiv.), Et_2O, −78 °C, 1 h then excess 4 N HCl, 0–5 °C, 98%; (c) $MeO_2CCH_2P(=O)(OEt)_2$ (1.0 equiv.), Et_3N (1.1 equiv.), LiBr (1.2 equiv.), CH_3CN, 0 °C to room temp., 12 h, 86%; (d) DIBAH (2.0 equiv.), Et_2O, −78 °C, 1 h then 4 N HCl, 96%; (e) Swern-oxidation, 96%, → $H_3CCH(OBn)CH=CHCHO$ [(*E,S*)-**3**]; (f) $PhSO_2CH_2P(=O)(OEt)_2$ (**4**) (1.0 equiv.), Et_3N (1.1 equiv.), LiBr (1.2 equiv.), CH_3CN, 0 °C to room temp., 12 h, 96%.

2. Results and discussion

2.1. Synthesis of the phenylsulfonyl-substituted tricarbonyl(η^4-diene)iron(0) complexes 6

As outlined in Scheme 1, commercially available enantiopure ethyl-(*S*)-lactate [(*S*)-1], was converted in three steps to the methyl 4-phenylmethoxy-pent-2-enoate [(*E*,*S*)-2] (for a review see Ref. [18]) by protection of (*S*)-1 under acidic conditions with *O*-benzyl-2,2,2-trichloroacetimidate/TfOH in dichloromethane–cyclohexane = 1:7 (95%) [19], reduction of the protected ester with DIBAL-H (98%) (for reviews see Ref. [20]) and subsequent olefination of the corresponding protected lactaldehyde with methyl diethylphosphono acetate/LiBr/–Et_3N/MeCN following the protocol of Rathke et al. (86%; overall yield from (*S*)-1: 80%, *ee* > 99%) [21]. The DIBAL-H-reduction of the enoate (*E*,*S*)-2 furnished the corresponding allylic alcohol (96%) which was directly subjected to a *Swern* oxidation to yield the appropriate unsaturated aldehyde (*E*,*S*)-3 (96%). The reaction of the aldehyde with diethyl phosphono methylphenylsulfone 4 [prepared in three steps from thiophenol (overall yield: 59%)] [22] under the olefination conditions as described above yielded the enantio- and diastereomerically pure diene (1*E*,3*E*,*S*)-5 as an air- and moisture-stable colourless solid (96%, overall yield from (*E*,*S*)-2: 88%), *ee* > 99%, (1*E*,3*E*)/(1*E*,3*Z*) ≫ 100:1) (Scheme 1).

Conversion of diene (1*E*,3*E*,*S*)-5 to the corresponding tricarbonyl(η^4-diene)iron(0) complexes (1*R*,5*S*)-6 (Ψ-*endo*-6) and (Ψ-*exo*-6) was performed following the two general methods as depicted in Scheme 2 (for a preliminary assignment of the relative and the absolute configurations vide supra and Fig. 2). Either thermal complexation with nonacarbonyldiiron [$Fe_2(CO)_9$] in toluene (85%) (method a) [23] or photochemical complexation of (1*E*,3*E*,*S*)-5 with pentacarbonyliron [$Fe(CO)_5$] in toluene (96% to quant.) (method b) [24] initially yielded, after separation from pyrophoric iron containing side products, a mixture of the diastereomeric neutral tricarbonyl(η^4-diene)iron(0) complexes (1*R*,5*S*)-6 and (1*S*,5*S*)-6 as highly viscous yellow–orange-coloured oils (method a: *de* ≤ 4%, method b: *de* = 0%). Other established complexation methods like sonification of (1*E*,3*E*,*S*)-5 in the presence of nonacarbonyldiiron [$Fe_2(CO)_9$] in benzene [25] proved to be synthetically unattractive since in no case was complete conversion of (1*E*,3*E*,*S*)-5 observed. The complexes turned out to be very stable in pure form but they decomposed slowly in solution. The diastereomeric ratio of the pre-purified mixtures was easily determined by means of ^{1}H NMR spectroscopy (vide supra). Since there is no significant influence of the carbinol atom (C_e) bearing the benzyloxy group in diastereofacial discrimination of one of the diastereotopic faces of the diene system both diastereomers 6 are formed in almost equal amounts (*de* = 0–4%) regardless of the method employed or the reaction condition. Both diastereomers of 6 can be enriched by column chromatography (silica gel) due to their remarkable difference in their R_f values (diastereomer 1 = (1*R*,5*S*)-6: R_f = 0.22, diastereomer 2 = (1*S*,5*S*)-6: R_f = 0.16, in both cases light petroleum–ethyl ether = 2:1; *de* [(1*R*,5*S*)-6] > 99%; *de* [(1*S*,5*S*)-6] ≈ 70–80%) [26]. Fractional crystallization of (1*S*,5*S*)-6 from diethyl ether at 4 °C yields samples with a diastereomeric excess greater than 99% (^{1}H NMR spectroscopy, 500 MHz) (vide supra). Likewise, starting from the racemic diene (1*E*,3*E*,*R*/*S*)-5 the racemic mixture of diastereomeric complexes *rac*-Ψ-*endo*-6/*rac*-Ψ-*exo*-6 was prepared. By analogy to the notation of Clinton and Lillya [26] for similar substituted tricarbonyl(η^4-diene)iron(0) complexes [planar

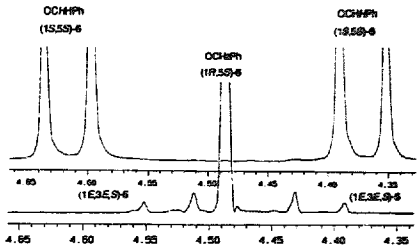
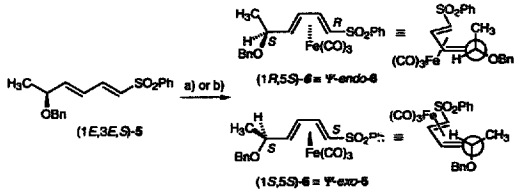


Fig. 2. $^3J(^1H–^1H)$ coupling constants (Hz) and n.O.e.-effects (%) of the cation *syn*,*syn*-(1*R*/*S*,5*R*/*S*)-7.



Scheme 2. (a) $Fe_2(CO)_9$ (2.0 equiv.), toluene, Δ, 48–60 h, 85% (both diastereomers, *de* ≤ 4%), then separation of diastereomers (*de* = *ee* > 99%); (b) $Fe(CO)_5$ (1.3 equiv.), toluene, *hν*, room temp., 12 h, 96% (both diastereomers, *de* = 0%) then separation of diastereomers (*de* = *ee* > 99%).

(η^4-diene)$Fe(CO)_3$ complexes with an additional stereogenic centre in α-position to the complexed diene unit] and numerous additional examples [27], it is generally accepted that the diastereomer possessing the higher R_f value (less polar, OBn-group directed *endo* relative to the $Fe(CO)_3$ moiety) is assigned to be the *Ψ-endo*-**6** isomer and that with the lower R_f value (more polar, OBn-group directed *exo* relative to the $Fe(CO)_3$ moiety) the *Ψ-exo*-**6** isomer (Scheme 2). Due to the known absolute configuration of the carbinol carbon atom (C_ε) bearing the OBn-group [(*S*)] the formation of only two diastereomeric complexes **6** becomes possible which in turn are each enantiomerically pure since it is known that complexes of this type are stable to racemization under the chosen reaction conditions [28]. Thus, assignment of the relative configuration of the carbinol carbon atom and the $Fe(CO)_3$-group (facial position) should allow the assignment of the absolute configuration of each diastereomer or enantiomer respectively. For that reason, complex *Ψ-endo*-**6** should be identical with (1*R*,5*S*)-**6** and *Ψ-exo*-**6** with (1*S*,5*S*)-**6**, considering the stereochemical aspects discussed above (for a numbering scheme of the dienylic carbon and hydrogen atoms see Fig. 1 and Fig. 2).

The diastereomeric complexes **6** gave only slightly differing infrared and mass spectra. In addition, both the ^1H NMR and ^{13}C NMR spectra of the complexes **6** displayed the characteristic high field shifts for complexed olefinic atoms (vide supra). The resonances of the internal protons H_β and H_γ of the complexed diene **5** can be observed in the 'olefinic region' at $\delta = 5.32–5.68$ ppm [12]. In particular, the strong high field shift of the resonances of the terminal protons H_α and H_δ ($\delta(H_\alpha) = 1.44–1.59$ ppm, $\delta(H_\delta) = 1.17–1.30$ ppm) is indicative for (*E*,*E*)-configured complexed dienes [12]. Furthermore, the single bond between the complexed double bonds must possess an *s-cis* conformation (n.O.e. ($H_\gamma \rightarrow H_\beta$) = 12.8%) and so the termini of the complexed ligand **5** in both complexes **6** must show *syn*,*syn*-substitution patterns (n.O.e. [$H_\gamma \rightarrow H_\varepsilon$ (*Ψ-exo*-**6**) = 4.6%]. All resonances of the 'olefinic' carbon atoms are found at $\delta = 66–85$ ppm. The signals for the Fe–CO groups appear with line broadening at $\delta = 205$, 207 and 212 ppm. In order to obtain more structural and stereochemical information both resolved complexes **6** were subjected to extensive n.O.e-^1H NMR experiments (vide infra). The results obtained strongly support the general structural features described above. Unfortunately, all n.O.e. effects of (1*R*,5*S*)-**6** and (1*S*,5*S*)-**6** are very similar and do not allow an unambiguous assignment of the relative and, therefore, of the absolute stereochemistry with respect to the facial position of the $Fe(CO)_3$ moiety relative to the plane through the complexed diene and the carbinol carbon atom bearing the stereogenic centre (C_ε) with known absolute (*S*)-configuration. All attempts to obtain crystals of the complex

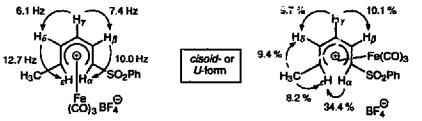


Fig. 3. Determination of the diastereomeric and enantiomeric purity of the complexes **6** by ^1H NMR spectroscopy (300 MHz, $CDCl_3$, *de* = *ee* for both diastereomers > 99%).

(1*S*,5*S*)-**6** (*Ψ-exo*-**6**) suitable for a doubtless determination of the absolute configuration by X-ray analysis turned out to be unsatisfactory.

The determination of the diastereomeric and, likewise, the enantiomeric purity of both complexes, (1*R*,5*S*)-**6** (*Ψ-endo*-**6**) and (1*S*,5*S*)-**6** (*Ψ-exo*-**6**), was easily accomplished by ^1H NMR spectroscopy in $CDCl_3$ (Fig. 3). Starting from the enantiopure diene ligand (1*E*,3*E*,*S*)-**5**, its complexation with an '$Fe(CO)_3$' moiety results in the introduction of a new element of chirality (planar chirality) and only the formation of two corresponding diastereomeric tricarbonyl(η^4-diene)iron(0) complexes (1*R*,5*S*)-**6** (*Ψ-endo*-**6**) and (1*S*,5*S*)-**6** (*Ψ-exo*-**6**) becomes possible which, of course, after their separation by means of column chromatography provides access to the enantiopure complexes **6** (*Ψ-endo*-**6** and *Ψ-exo*-**6**) (*de* = *ee* > 99%) (vide supra).

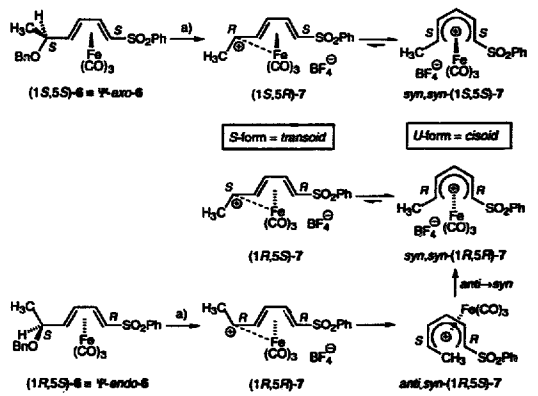
In particular, the methylene protons (H_a and H_b) of the benzyloxy group of both complexes **6** exhibit a significant difference in both chemical shift and splitting patterns. The resonances of diastereotopic methylene protons (H_a and H_b) of the benzyloxy group of the complex (1*S*,5*S*)-**6** (*Ψ-exo*-**6**) appear as a typical AB-spin system (two doublets at $\delta = 4.37$ and 4.61 ppm, $^2J(^1H_a - ^1H_b) = 11.6$ Hz). In contrast, the complex (1*R*,5*S*)-**6** (*Ψ-endo*-**6**) shows almost isochrone resonances for the methylene protons H_a and H_b, thus a singlet-type signal is observed for these protons ($\delta =$ 4.47 and 4.49 ppm, approx. A,A'-spin system). These results clearly demonstrate a remarkable different chemical environment for the methylene protons of the complex (1*R*,5*S*)-**6** (*Ψ-endo*-**6**) compared to (1*S*,5*S*)-**6** (*Ψ-exo*-**6**) which is probably caused by pointing of the OBn-group into the half-room of the shielding electron-rich tricarbonyl fragment. In general, the complex (1*S*,5*S*)-**6** (*Ψ-exo*-**6**) turns out to be more stable than the diastereomeric complex (1*R*,5*S*)-**6** (*Ψ-endo*-**6**) since in its NMR spectra the uncomplexed ligand (1*E*,3*E*,*S*)-**5** could be observed frequently. In addition, due to their analytically useful signal separation the ^1H NMR spectroscopic signals for the protons H_α, H_γ and H_ε as well as for the CH_3-groups can be used for the determination of the diastereomeric purity of the complexes (1*R*,5*S*)-**6** (*Ψ-endo*-**6**) and (1*S*,5*S*)-**6** (*Ψ-exo*-**6**). Fig. 3 shows the characteristic ^1H NMR spectroscopic signals of the methylene protons H_a and H_b of the resolved complexes **6**.

2.2. Synthesis of the phenylsulfonyl-substituted tricarbonyl(η^5-dienyl)iron(1 +)complexes 7

The synthesis of the cationic tricarbonyl(η^5-dienyl)iron(1 +) complexes **7** were performed by treatment of a solution of the resolved highly diastereo- and enantiomerically enriched complexes (1*R*,5*S*)-**6** and (1*S*,5*S*)-**6** (*de* = *ee* > 99%) in diethyl ether at ca. 30 °C with excess HBF_4 (54% in diethyl ether) [4] (also, for a representative example see Ref. [29]). Under these conditions the OBn-group of the complexes **6** is cleaved and the cations **7** are formed in good to excellent yields (87% quant.). To run the reaction to completion both the addition of *n*-pentane and extended precipitation periods at room temperature (12 h) were essential (Scheme 3). The cations **7** are obtained as moderately air- and moisture-stable pale yellow solids in spectroscopically and analytically pure forms after filtration and can be stored at 4 °C in a refrigerator under argon for several months. ^1H NMR and ^{13}C NMR spectroscopic analyses demonstrated that whether starting from (1*R*,5*S*)-**6**, from (1*S*,5*S*)-**6** or from *rac*-Ψ-*endo*-**6**/*rac*-Ψ-*exo*-**6** mixtures, the cationic complexes **7** thus obtained, gave identical proton- and carbon-NMR spectra (vide supra).

Based on both the observed results and on previous work of Mahler and coworkers [30], Sorensen and Jablonski [31], Lillya and coworkers [32] and very recently Salzer and coworkers [12] we propose the following reaction mechanisms and stereochemical pathways for the formation of the cations **7** as shown in Scheme 3.

Based on the assumption that the OBn-leaving group of (1*S*,5*S*)-**6** (Ψ-*exo*-**6**) is cleaved *exo* with respect to the metal fragment [Fe(CO)$_3$] [4] the initially generated *transoid* cation (1*S*,5*R*)-**7** (*S*-form) should be formed with inversion of the stereogenic centre at C_e due to the pre-positioning of the CH_3-group at C_e in (1*S*,5*S*)-**6** (Ψ-*exo*-**6**). This intermediate (1*S*,5*R*)-**7** should then rearrange to the *cisoid* cation *syn*,*syn*-(1*S*,5*S*)-**7** probably by rotation around the C_7–C_8 axis which again should result in an inversion of the absolute stereochemistry by changing the diastereotopic faces at C_e. In full accordance to previous results [12,30–32], starting from the diastereomerically pure complex (1*R*,5*S*)-**6** (Ψ-*endo*-**6**) the cation *anti*,*syn*-(1*R*,5*S*)-**7** (*U*-form) (double inversion at C_e) should be formed via the intermediate cation (1*R*,5*R*)-**7** (*S*-form). Since an (irreversible) *anti*-CH_3 → *syn*-CH_3 conversion from *anti*,*syn*-(1*R*,5*S*)-**7** to *syn*,*syn*-(1*R*,5*R*)-**7** (configurative lability, inversion at C_e) is easy and thermodynamically preferred due to steric interactions at temperatures above 0 °C, only a *syn*,*syn*-configured cation **7**, thus obtained, is detectable by means of NMR spectroscopy [32]. In addition, both *cisoid* complexes *syn*,*syn*-(1*S*,5*S*)-**7** and *syn*,*syn*-(1*R*,5*R*)-**7** (*U*-forms) are believed to be in an equilibrium with their thermodynamically unfavourable *transoid* counterparts (1*S*,5*R*)-**7** and (1*R*,5*S*)-**7** (*S*-forms) (conformative lability) (Scheme 3). Thus, under the reaction conditions (precipitation temperature: 30 °C) the complex Ψ-*exo*-**6** should have been converted diastereoselectively to the cation *syn*,*syn*-(1*S*,5*S*)-**7** and the complex Ψ-*endo*-**6** highly diastereoselectively to the cation *syn*,*syn*-(1*R*,5*R*)-**7** (for the determination of the stereochemical purity vide supra). The formation of only one observable *cisoid* cation *syn*,*syn*-(1*R*/*S*,5*R*/*S*)-**7** from the diasteromeric mixture *rac*-Ψ-*endo*-**6**/*rac*-Ψ-*exo*-**6** is easily explained by the pro-



Scheme 3. Proposed stereochemical pathway for the formation of the cationic tricarbonyl(η^5-dienyl)iron(1 +) complexes *syn*,*syn*-(1*R*,5*R*)-**7** and *syn*,*syn*-(1*S*,5*S*)-**7** from (1*R*,5*S*)-**6** (Ψ-*endo*-**6**) and (1*S*,5*S*)-**6** (Ψ-*exo*-**6**). (a) HBF_4, Et_2O–*n*-pentane, 30 °C to room temp., 12 h (87% quant.).

posed mechanism and strongly supports this working hypothesis.

From both the stereochemical proposals in Scheme 2 and Scheme 3 as well as from a similar very recent contribution of Salzer and coworkers [12], the following postulates concerning the stereochemistry of nucleophilic addition reactions to the complexes *syn,syn*-**7** can be proposed:

- Due to an (irreversible) *anti*-$CH_3 \rightarrow$ *syn*-CH_3 conversion from *anti,syn*-(1*R*,5*S*)-**7** to *syn,syn*-(1*R*,5*R*)-**7** (configurative lability, inversion at C_ε) the complexes (1*R*,5*S*)-**6** (*Ψ-endo*-**6**) and (1*S*,5*S*)-**6** (*Ψ-exo*-**6**) have to be resolved since otherwise starting from the optically active diene (1*E*,3*E*,*S*)-**5** the racemic *cisoid* cationic complex *syn,syn*-(1*R*/*S*,5*R*/*S*)-**7** would be obtained.
- Principally, both enantiomers of the complexes *syn,syn*-**7** should be accessible from (1*E*,3*E*,*S*)-**5** as a single stereochemically well-defined starting material.
- Nucleophilic additions at C_ε to *syn,syn*-(1*R*,5*R*)-**7** should yield addition products with overall retention (fourfold inversion), while nucleophilic additions to *syn,syn*-(1*S*,5*S*)-**7** should result in addition products with inversion (triple inversion) of stereochemistry with respect to the stereogenic centre of the starting material (1*E*,3*E*,*S*)-**5**.
- For a given cation **7** and depending on the nature of the nucleophile, the nucleophilic addition at C_ε of a *cisoid* cation should give rise to products with (*E,Z*)-double bond geometry while the nucleophilic addition to the corresponding *transoid* cation should give an access to (*E,E*)-configured products. In addition, the geometric isomers should possess the opposite absolute configuration of the newly generated stereogenic centre C_ε.

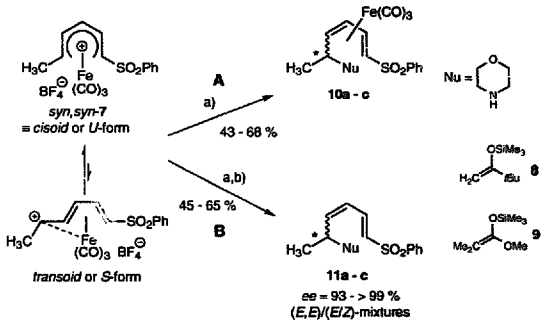
The expected *cisoid*-structure (*U*-form) and additional stereochemical properties (*syn,syn*-substitution patterns at the dienylic termini) of the complexes **7** were unambiguously established by means of numerous NMR spectroscopic experiments (Fig. 2). By analogy to the previously reported results, the doublet signal for the *syn*-CH_3-group in the proton-NMR spectrum of all complexes **7** is found shifted downfield at $\delta = 1.99$ ppm while typical resonances for *anti*-CH_3-groups generally are observed further upfield at $\delta \approx 1.4$ ppm [30–32]. The coupling constants $^3J(^1H_\alpha{-}^1H_\beta) = 10.0$ Hz and $^3J(^1H_\delta{-}^1H_\varepsilon) = 12.7$ Hz are typical for an *anti*-arrangement (equivalent to *syn*-substitution of the SO_2Ph and CH_3-group) of these protons while the coupling constants of the other protons of the complexed dienylic unit [$^3J(^1H_\beta{-}^1H_\gamma) = 7.4$ Hz and $^3J(^1H_\gamma{-}^1H_\delta) = 6.1$ Hz] are indicative for their *cis*-relationship. In particular, the observed n.O.e.-effects ($H_\alpha \rightarrow H_\varepsilon = 34.4\%$, $CH_3 \rightarrow H_\delta = 9.4\%$ and $CH_3 \rightarrow H_\varepsilon = 8.2\%$) as well as the other n.O.e.-effects strongly support the assignment of the *cisoid*-structure (*U*-form) with *syn,syn*-substitution patterns (relative to the '*meso*'-hydrogen atom on C_γ) at the dienylic termini (Fig. 2).

Compared to the neutral complexes **6** all proton and carbon resonances of the cations **7** show significant downfield shifts (δ(H) = 3.69–7.06 ppm vs. 1.17–5.69 ppm; δ (C) = 82–107 ppm vs. 66–85 ppm) due to the cationic nature of **7**. All spectroscopic investigations demonstrate clearly that either starting from enantiopure (1*R*,5*S*)-**6** (*Ψ-endo*-**6**) or from (1*S*,5*S*)-**6** (*Ψ-exo*-**6**) stereochemical uniform (but enantiomeric) cationic tricarbonyl(η^5-dienyl)iron(1 +) complexes *syn,syn*-(1*R*,5*R*)-**7** or *syn,syn*-(1*S*,5*S*)-**7** are readily accessible [*de* > 99% (≡ 5-*syn*-CH_3/5-*anti*-$CH_3 \gg$ 100:1)], *ee* > 99%). In addition, the enantiomeric relationship of *syn,syn*-(1*R*,5*R*)-**7** {$[\alpha]_D^{28} = +56.6$ (*c* = 0.98, acetone)} and *syn,syn*-(1*S*,5*S*)-**7** {$[\alpha]_D^{28} = -44.7$ (*c* = 1.02, acetone)} is unambiguously verified by both their opposite sign of optical rotation and their comparable magnitude. The slightly differing magnitude might be explained due to beginning decomposition of the dissolved complexes **7** during the determination of their optical rotation. In addition, these results clearly exclude an *anti* → *syn* isomerization via a (possible) π-σ-π-mechanism and are in excellent accordance with similar results observed in iron-mediated allylic substitution reactions making use of the corresponding tetracarbonyl(η^3-allyl)iron(1 +) complexes with equivalent substitution patterns at the allylic termini [15]. An *anti* → *syn* isomerization of the complex *anti,syn*-(1*R*,5*S*)-**7** following a π-σ-π-mechanism involving a mesomeric allylic species, which in turn is well established for the *anti* → *syn* interconversion of cationic (η^3-allyl)palladium complexes (for recent reviews see Ref. [33]), seems to be unlikely and would give rise to the complex *syn,syn*-(1*S*,5*S*)-**7** rather than *syn,syn*-(1*R*,5*R*)-**7** by changing both the configuration on C_ε and the diastereotopic faces of the complexed dienyl ligand (double inversion).

The enantiomeric excesses of the cations **7**, thus obtained, could not be determined directly but were established indirectly by the enantiomeric excesses of the addition products (vide supra). In addition, starting from the unresolved racemic mixture of the diastereomeric complexes *rac-Ψ-endo*-**6**/*Ψ-exo*-**6** gives rise to diastereomerically uniform (pure *syn,syn*-isomer) but racemic mixtures of complexes of the type *syn,syn*-(1*R*/*S*, 5*R*/*S*)-**7** [*de* > 99% (≡ 5-*syn*-CH_3/5-*anti*-$CH_3 \gg$ 100:1), *ee* = 0%].

2.3. Nucleophilic addition reactions to the tricarbonyl(η^5-dienyl)iron(1 +)complexes 7

In order to gain insight to the regio- and stereochemical outcome of the nucleophilic addition we investigated the nucleophilic addition of different types of hetero and carbon atom nucleophiles (morpholine, silyl enol ether



Scheme 4. Nucleophilic addition reactions to the cationic complexes *syn,syn*-**7**. (a) Nucleophile (3–5 equiv.), CH_2Cl_2, room temp., 10 min (43–68%). (b) as (a) then evaporation, $(NH_4)_2Ce(NO_3)_6$, CH_3CN–MeOH = 3:1, room temp., 12 h (45–65%).

8, silyl ketene acetal **9** [34]) to the racemic cationic complex *syn,syn*-(1*R*/*S*,5*R*/*S*)-**7** to form the corresponding neutral *ε*-substituted tricarbonyl(η^4-diene)iron(0) complexes **10** (Scheme 4, pathway A, Table 1). The reaction was performed by dropwise addition of a solution of an excess (3–5 equiv.) of the appropriate nucleophile in dichloromethane to a suspension of the complex *syn,syn*-(1*R*/*S*,5*R*/*S*)-**7** in dichloromethane at ambient temperature. The major isomers of the neutral soluble *ε*-substituted tricarbonyl(η^4-diene)iron(0) complexes **10** were obtained after chromatographic purification of the crude reaction mixture as pale yellow solids (43–68%), each in diastereomerically pure form with respect to the double bond geometry at C_γ–C_δ [(*E*,*Z*) or (*E*,*E*)] (Table 1).

In accordance with previous results [4,11,12] and depending on the nucleophilicity of the nucleophiles, the basic morpholine and the strongly nucleophilic silyl ketene acetal **9** reacted with *syn,syn*-(1*R*/*S*,5*R*/*S*)-**7** (*cisoid* or *U*-form) to give the (*E*,*Z*)-configured complexes **10a** and **10c** respectively. As expected, the less reactive silyl enol ether **8** (nucleophilicity: **9** > **8**) gave rise to an (*E*,*E*)-configured complex **10b** by nucleophilic addition to the more reactive *transoid* cation **7** (*S*-form) which in turn is permanently regenerated by the equilibrium between the *U*-form and the *S*-form of the cation **7** (Scheme 3). Due to the chromatographic purification it cannot be excluded that minor diastereomers derived from addition to the corresponding diastereomeric cation **7** have been separated. All nucleophilic additions to the complexed (η^5-pentadienyl)-ligand of **7** should result in the formation of only one diastereomer with respect to a possible *Ψ-endo*/*Ψ-exo*-isomerization since, in general, nucleophilic attack proceeds *exo* to the $Fe(CO)_3$ moiety giving rise to *Ψ-exo*-complexes (*rac*-*Ψ-exo*-**10**) [4,12].

The (*E*,*Z*)-geometry of **10a** and **10c** was confirmed by NMR spectroscopy since if one of the substituents at the complexed diene termini C_α or C_δ occupies an *anti*-position [equivalent to (*Z*)-configuration, *syn*-protons] both resonance signals of the protons at C_α or C_δ show a significant downfield-shift (δ = 1.98–2.59 ppm). In accordance with the NMR spectroscopic data for the (*E*,*E*)-configured complexes (1*R*,5*S*)- or (1*S*,5*S*)-**6** the corresponding resonances for the *anti*-protons H_α and

Table 1
Results of the nucleophilic addition reactions to the complexes *syn,syn*-(1*R*/*S*,5*R*/*S*)-**7** to yield the neutral *ε*-substituted complexes *rac*-*Ψ-exo*-**10**

Complex *syn,syn*-**7**	Nucleophile	Addition-products **10** [a]	Nu	Yield (%) [b]
(1*R*/*S*,5*R*/*S*)-**7**	morpholine	(1*E*,3*E*,1*R*/*S*,3*R*/*S*)-**10a**	$N[(CH_2)_2]_2O$	68 [c]
(1*R*/*S*,5*R*/*S*)-**7**	**8**	(6*E*,8*E*,5*R*/*S*,9*R*/*S*)-**10b**	CH_2CO^tBu	57 [c]
(1*R*/*S*,5*R*/*S*)-**7**	**9**	(4*Z*,6*E*,3*R*/*S*, 7*R*/*S*)-**11c**	CMe_2CO_2Me	43 [d]

[a] Based on isolated stereoisomeric pure material after column chromatography (silica gel 60, diethyl ether or ethyl acetate–light petroleum mixtures). All new products gave satisfactory analytical and spectroscopic data.
[b] Based on isolated material (both isomers) after column chromatography (silica gel 60, diethyl ether or ethyl acetate–light petroleum mixtures). All new products gave satisfactory analytical and spectroscopic data.
[c] Reaction course at room temp.
[d] Reaction course at −78 °C.

H_δ of the complex **10b** were found shifted upfield at $\delta = 1.48$ and 1.08 ppm (vide infra).

Likewise, the synthesis of the (*E,Z*)- or (*E,E*)-configured dienes **11a–c** was performed in the same manner as described above making use of the highly enantiomerically enriched cations *syn,syn*-(1*R*,5*R*)-**7** or *syn,syn*-(1*S*,5*S*)-**7** followed by oxidative decomplexation of the corresponding crude complexes of type **10** with ceric ammonium nitrate [CAN, $(NH_4)_2Ce(NO_3)_6$] under homogenous conditions in acetonitrile–methanol = 3:1 at room temperature [35] (Scheme 4, pathway **B**, Table 2). The dienes **11a–c** were obtained after chromatographic purification (silica gel, ethyl acetate or diethyl ether/light petroleum mixtures) as mixtures of geometric isomers in 45–65% yield. As expected, the geometric isomerism of the complexes **10** is reflected in the (*E,E*)/(*E,Z*)-ratio of the dienes **11a–c**, thus obtained, which was easily determined by NMR spectroscopy or by analytical HPLC on a chiral phase (Daicel OD) which also allowed the determination of the enantiomeric purity of the dienes **11a,b** (vide supra). Again, the reactive morpholine should have had reacted with the less reactive *U*-form to form the (*E/Z*)-configured aminodienes **11a** [(*E,E*)/(*E,Z*) = 1: > 57 to 1: > 87] while the silyl enol ether **8** selectively reacted with the corresponding *transoid* cation of **7** giving rise to the (*E/E*)-configured diene **11b** [(*E,E*)/(*E,Z*) = > 65:1]. The nucleophilic addition of the silyl ketene acetal **9** yields preferentially the (*E/Z*)-configured diene **11c** under standard reaction conditions [(*E,E*)/(*E,Z*) = 1:6.6]. Unfortunately the (*E,E*)-/(*E,Z*)-mixtures were neither separable by preparative column chromatography nor by preparative HPLC methods. Performing the nucleophilic addition reactions at lower temperatures (e.g. −30 °C/morpholine or −78 °C/**9**, Table 2) clearly demonstrated by change of the (*E,Z*)/(*E,E*)-ratio of the dienes **11a,c** that under these conditions

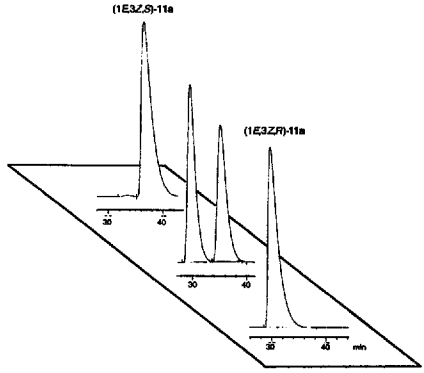


Fig. 4. Determination of the enantiomeric purities of the addition products **11a** by analytical HPLC performed on a Daicel OD stationary phase (UV-detection) [(1*E*,3*Z*,*R*)-**11a**: *ee* > 99%; (1*E*,3*Z*,*S*)-**11a**: *ee* = 98.9%].

even reactive nucleophiles were added increasingly to the more reactive *transoid* cation **7** (*S*-form) (Table 2). The observed *ε*-regioselectivity of the nucleophilic addition reaction of the test-nucleophiles clearly show the synthetic equivalence of the cationic complexes *syn,syn*-**7** with a planar chiral a^6-synthon allowing an umpolung of the classical d^6-chemistry [17] (Fig. 1).

The enantiomeric excesses of the dienes **11a,b** (**11a**: *ee* > 99%, *ee* = 98.9%, **11b**: *ee* = 93%) were determined by analytical HPLC on a chiral stationary phase (Daicel OD) and by comparison with the racemic material obtained from the racemic cation *syn,syn*-(1*R/S*,5*R/S*)-**7**. Fig. 4 shows the fully resolved HPLC-diagrams (Daicel OD, UV-detector) of the amin-

Table 2
Results of the nucleophilic addition reactions to the complexes *syn,syn*-(1*S*,5*S*)-**7**, *syn,syn*-(1*R*,5*R*)-**7** and *syn,syn*-(1*R/S*,5*R/S*)-**7** with oxidative decomplexation to the *ε*-substituted dienes **11**

Complex *syn,syn*-**7**	Nucleophile	Addition-products **11** [a]	Nu	Yield (%) [b]	(*E,E*)/(*Z,E*) [c]	*ee* (%) [d]
(1*R*,5*R*)-**7**	morpholine	(1*E*,3*Z*,*S*)-**11a**	$N[(CH_2)_2]_2O$	45 [e]	1: > 87	98.9
(1*S*,5*S*)-**7**	morpholine	(1*E*,3*Z*,*R*)-**11a**	$N[(CH_2)_2]_2O$	63 [e]	1: > 57	> 99
(1*R/S*,5*R/S*)-**7**	morpholine	(1*E*,3*Z*,*R/S*)-**11a**	$N[(CH_2)_2]_2O$	58 [f]	1:3.5	—
(1*S*,5*S*)-**7**	**8**	(6*E*,8*E*,*S*)-**11b**	CH_2CO_tBu	55 [e]	> 65:1	93.0
(1*R*,5*R*)-**7**	**9**	(4*Z*,6*E*,*S*)-**11c**	CMe_2CO_2Me	61 [e]	1:5	— [g]
(1*R/S*,5*R/S*)-**7**	**9**	(4*Z*,6*E*,*R/S*)-**11c**	CMe_2CO_2Me	65 [h]	1:6.6	—

[a] Major geometric isomer. The absolute configurations for the addition products **11** are based on the working hypothesis described in Scheme 3.
[b] Based on isolated material (both isomers) after column chromatography (silica gel 60, diethyl ether or ethyl acetate–light petroleum mixtures). All new products gave satisfactory analytical and spectroscopic data.
[c] Determination of the (*E,E*)/(*Z,E*) ratio by ^1H NMR spectroscopy (300 MHz) and by analytical HPLC (Daicel OD phase).
[d] Determination of the enantiomeric excesses (*ee*) by analytical HPLC (Daicel OD phase).
[e] Reaction course at room temp.
[f] Reaction course at −30 °C.
[g] *ee* value could not be determined.
[h] Reaction course at −78 °C.

odienes (1*E*,3*Z*,*R*)-**11a** [from *syn,syn*-(1*S*,5*S*)-**7**], (1*E*,3*Z*,*R*/*S*)-**11a** [from *syn,syn*-(1*R*/*S*,5*R*/*S*)-**7**] and (1*E*,3*Z*,*S*)-**11a** [from *syn,syn*-(1*R*,5*R*)-**7**]. Likewise, this is the experimental proof of the proposed relative stereochemical pathways of the formation of the cationic complexes **7** starting from resolved diastereo- and enantiomerically pure (η^4-diene)Fe(CO)$_3$-complexes **6** (Scheme 3). In addition, the enantiomeric relationship of (1*E*,3*Z*,*R*)-**11a** {$[\alpha]_D^{26} = +52.0$ ($c = 1.14$, $CHCl_3$)} and (1*E*,3*Z*,*S*)-**11a** {$[\alpha]_D^{26} = -36.5$ ($c = 1.05$, $CHCl_3$)} is unambiguously verified by both their opposite sign of optical rotation and their comparable magnitude. The slightly differing magnitude might be eventually explained due to the different diastereomeric purity of (1*E*,3*Z*,*R*)-**11a** [(*E*,*E*)/(*E*/*Z*) = 1: > 57] compared to (1*E*,3*Z*,*S*)-**11a** [(*E*,*E*)/(*E*/*Z*) = 1: > 87].

Unfortunately, all attempts to determine the enantiomeric purity of compounds **11c** by classical methods (NMR-shift experiments, GLC on chiral phases, analytical HPLC, derivatization, etc.) failed. The absolute configuration of the major diastereomer and enantiomer of the dienes **11** could not be determined by derivatization, degradation or modification nor by any absolute physical methods (e.g. X-ray analysis) and will be the subject of further investigations.

3. Conclusion

In summary, we have shown that complexation of the diastereo- and enantiomerically pure diene (1*E*,3*E*,*S*)-**5**, readily available from the (*S*)-lactic acid derivative (*S*)-**1**, yields initially a mixture of corresponding diastereomeric but enantiomerically pure neutral tricarbonyl(η^4-diene)iron(0) complexes **6** (*de* = 0–4% ≡ Ψ-*endo*-**6**/Ψ-*exo*-**6** ≈ 1:1; Ψ-*endo*-**6** and Ψ-*exo*-**6**: *ee* > 99%). Although the diastereoselectivity of the complexation reaction is very low and the uniform configuration of the carbon atom bearing the OBn-leaving group does not discriminate between the two diastereotopic faces of the diene ligand (as originally expected), the complexes **6** can be easily resolved by column chromatography on silica gel and/or fractional crystallization (Ψ-*endo*-**6** and Ψ-*exo*-**6**, *de* > 99%, *ee* > 99%) due to their remarkable difference in their R_f values. In the key step the diastereo- and enantiopure complexes **6** [(1*R*,5*S*)-**6** and (1*S*,5*S*)-**6**] are transformed stereoselectively to the corresponding highly diastereo- and enantiomerically enriched tricarbonyl(η^5-pentadienyl)iron(1 +) complexes **7** [*syn,syn*-(1*R*,5*R*)-**7** and *syn,syn*-(1*S*,5*S*)-**7**, *de* > 99% ≡ 5-*syn*-CH_3/5-*anti*-CH_3 ≫ 100:1; *ee* > 99%]. The nucleophilic addition of hetero and carbon atom nucleophiles (morpholine, silyl enol ether **8** and silyl ketene acetal **9**) to the racemic complex *syn,syn*-(1*R*/*S*,5*R*/*S*)-**7** afforded initially the new neutral ε-substituted tricarbonyl(η^4-diene)iron(0) complexes *rac*-Ψ-*exo*-**10a–c** in moderate yields [43–68% from *syn,syn*-(1*R*/*S*,5*R*/*S*)-**7**] which were isolated as single geometrical isomers [(*E*,*Z*) or (*E*,*E*)]. Likewise, nucleophilic addition to the highly diastereo- and enantiomerically enriched complexes *syn,syn*-(1*R*,5*R*)-**7** or *syn,syn*-(1*S*,5*S*)-**7** followed by oxidative cleavage of the carbonyliron fragment offers an access to ε-substituted phenylsulfonyl-substituted dienes **11a–c** in moderate to fair yields [45–65%, (*E*,*Z*)/(*E*,*E*) = > 85:1–1:3] with enantiomeric excesses ranging from > 99%/98.9% [(1*E*,3*Z*,*R*)-**11a**/(1*E*,3*Z*,*S*)-**11a**] to 93% [(6*E*,8*E*,*S*)-**11b**]. On this model system it has been shown that starting from a single and stereochemically well-defined diene [(1*E*,3*E*,*S*)-**5**] and without the need of an additional chiral auxiliary, both enantiomeric tricarbonyl(η^5-pentadienyl)iron(1 +) complexes **7** [*syn,syn*-(1*R*,5*R*)-**7** and *syn,syn*-(1*S*,5*S*)-**7**] become readily accessible possibly allowing a flexible integration of such key intermediates in complex synthetic schemes and providing a general synthetic approach to functionalized polyunsaturated target molecules of high enantiomeric purity. The ε-regioselectivity of the nucleophilic addition reaction of the test-nucleophiles proves the synthetic equivalence of the cationic complexes *syn,syn*-**7** with a planar chiral a^6-synthon allowing an umpolung of the classical d^6-chemistry [17]. As expected, the observed double bond geometry [(*E*,*Z*) or (*E*,*E*)] for the complexes *rac*-Ψ-*exo*-**10** as well as for the dienes **11a–c** clearly demonstrates the reactivity relationship of a given nucleophile (basicity or nucleophilicity)/electrophile (*U*- or *S*-form) combination. By proper choice of the starting materials (different α-hydroxy carbonic acid derivatives and/or acceptors) variations in the substitution patterns of the cationic complexes of type **7** should easily become possible. Further investigations are focused on the determination of the absolute configuration of the addition products to verify the overall stereochemical outcome of this "chirality transfer" process as well as on an extension to possible synthetic applications by variation of the nucleophilic components.

4. Experimental

4.1. General

All reactions were carried out under an atmosphere of dry argon using standard Schlenk or vacuum line techniques unless otherwise stated. Solvents were dried and purified by conventional methods prior to use. Diethyl ether (Et_2O) was freshly distilled from sodium benzophenone ketyl, ethanol-free dichloromethane (CH_2Cl_2), acetonitrile and *n*-pentane from calcium hydride under argon. Toluene was distilled from molten sodium under argon. Light petroleum refers to the fractions with b.p. 40–80 °C. Reagents of commercial qual-

ity were obtained from commercial suppliers and were used from freshly opened containers without further purification unless otherwise stated.

Analytical pre-coated glass-backed TLC plates (silca gel 60 F_{254}) and silica gel 60 (230–400 mesh, i.e. particle size 0.040–0.063 mm) were purchased from Merck, Darmstadt. Melting points are uncorrected and were measured on a Dr. Tottoli apparatus. 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. Optical rotations were measured using a Perkin–Elmer P 241 polarimeter and chloroform of Merck UVASOL quality. Analytical HPLC for the determination of enantiomeric purities was conducted on a Hewlett-Packard 1050 equipped with a chiral stationary phase (Daicel OD), UV-detector. Preparative HPLC was performed on a Gilson Abimed, Merck-LiCrosorb®-column (25 cm × 25 mm, silica 60, particle size 0.007 mm), UV-detector. ^{1}H NMR (500/300 MHz) and ^{13}C NMR (125/75 MHz) spectroscopy was conducted on a Varian Unity 500 and a Varian VXR 300 using tetramethylsilane (TMS) as internal standard. IR spectra (film, KBr) were recorded on a Perkin–Elmer FT/IR 1750 spectrophotometer. Mass spectroscopic analyses were obtained on a Varian MAT 212 (EI 70 eV, 1 mA). Microanalyses were obtained with a Heraeus CHN-O-RAPID elemental analyser. High resolution mass spectroscopic analyses were performed on a Finnigan MAT 95.

The methyl enoate (*E,S*)-**2** has been prepared starting from ethyl-(*S*)-lactate [(*S*)-**1**] by subsequent benzylation with *O*-benzyl trichloroacetimidate [19], reduction of the protected ester with DIBAL-H [20] and subsequent Horner–Wadsworth–Emmons olefination of the resulting OBn-lactaldehyde with methyl diethyl phosphonoacetate [21] in an overall yield of 80%. Alternatively, (*E,S*)-**2** is now commercially available from ACROS chimica, Belgium [18]. Diethyl phosphonomethylphenylsulfone (**4**) was prepared in 59% overall yield from thiophenol by successive chloromethylation with paraformaldehyde–hydrochloric acid, Michaelis–Arbuzov-rearrangement of the resulting thiophenyl chloro methylether to the corresponding phosphonate and its oxidation to the sulfone according to a procedure of Shahak and Almog [22]. Pentacarbonyliron was obtained from the BASF AG and used without further purification. Nonacarbonyldiiron has been synthesized by photolysis of pentacarbonyliron in glacial acetic acid [36]. Anhydrous HBF_4 (54% in diethyl ether) was purchased from Merck, Darmstadt. Morpholine was distilled from calcium hydride and handled under argon. The silyl enol ether **8** and silyl ketene acetal **9** were prepared from their corresponding carbonyl precursors and trimethylchlorosilane according to literature procedures [34]. The nucleophiles **8** and **9** were handled and stored with exclusion of moisture and air.

4.2. Safety note

Most reactions with compounds containing the iron-carbonyl moiety lead to variable amounts of iron carbonyls, especially pentacarbonyliron. These compounds are volatile and presumably toxic and must be handled with utmost care. They can be oxidatively decomposed either with $KOH–H_2O_2$, dil. HNO_3 or $Br_2–H_2O$ [37].

4.3. Materials

4.3.1. (E,S)-(−)-4-(Phenylmethoxy)pent-2-enal [(E,S)-3]

In a flame-dried Schlenk-flask equipped with a dropping funnel were placed 11.0 g (50.0 mmol) of the methyl enoate (*E,S*)-**2** in 150 ml abs. diethyl ether and reduced by dropwise addition of 120 ml (120 mmol) DIBAL-H (1.0 M in *n*-hexane) at −78 °C under argon. Upon complete conversion (t.l.c. control, ca. 1 h) and quenching (ice cold 4–6 M hydrochloric acid), work-up was performed by successive extraction (diethyl ether), washing (saturated aqueous NaCl solution), drying ($MgSO_4$) and evaporation. The remaining residue was purified by filtration (silica gel, light petroleum–diethyl ether = 1:1) to yield the allylic alcohol as a colourless liquid (9.21 g, 96%). $R_f = 0.29$ (diethyl ether–light petroleum = 1:1). $[\alpha]_D^{22} = -49.6$ ($c = 1.29$, $CHCl_3$).

According to Swern's procedure [38], 8.23 g (42.8 mmol) of the allylic alcohol were oxidized at −65 °C in 120 ml abs. dichloromethane under argon in the presence of 6.03 g (47.5 mmol, 4.1 ml) oxalylchloride and 7.42 g (49.2 mmol, 6.75 ml) dimethylsulfoxide. Upon complete conversion (t.l.c. control) and quenching (triethylamine 21.7 g (214.0 mmol, 29.7 ml), work-up was performed by successive dilution (H_2O), extraction (dichloromethane), successive washing (0.1 M HCl, saturated aqueous $NaHCO_3$ solution, saturated aqueous NaCl solution), drying ($MgSO_4$) and evaporation. The remaining residue was purified by filtration (silica gel, light petroleum–diethyl ether = 1:1) to yield (*E,S*)-**3** as a yellow liquid (7.74 g, 96%). $R_f = 0.59$ (diethyl ether–light petroleum = 1:1). $[\alpha]_D^{22} = -49.0$ ($c = 1.25$, $CHCl_3$). *ee* > 99%. ^{1}H NMR (300 MHz, $CDCl_3$, TMS(int), ppm): δ 9.57 (d, $J(^1H–^1H) = 7.8$ Hz, 1H, CHO), 7.38–7.24 (m, 5H, $OCH_2C_6H_5$), 6.75 (dd, $J(^1H–^1H) = 15.9/5.8$ Hz, 1H, C*H*=CHCHO), 6.27 (ddd, $J(^1H–^1H) = 15.6/7.8/1.4$ Hz, 1H, CH=C*H*CHO), 4.54 (d, $J(^1H–^1H) = 11.9$ Hz, 1H, $OCHHC_6H_5$), 4.47 (d, $J(^1H–^1H) = 11.9$ Hz, 1H, OC*H*HC_6H_5), 4.23 (qdd, $J(^1H–^1H) = 6.4/5.8/1.4$ Hz, 1H, C*H*CH_3), 1.38 (d, $J(^1H–^1H) = 6.4$ Hz, 3H, $CHCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$, TMS(int), ppm): δ 193.41 (CHO), 157.90 (β-C), 137.82 (*ipso*-CCH_2), 131.55 (α-C), 128.43, 127.76, 127.56 (aromatic-C), 73.75 (γ-C), 70.92 ($OCH_2C_6H_5$), 20.34 (CH_3). IR (film, cm^{-1}): 3090, 3065, 3030 (aromatic-CH, C=C–

H), 2980, 2930, 2865, 2820, 2730 (OC–H), 1695 (C=O), 1640, 1610, 1585, 1495 (aromatic-C=C, olefinic-C=C), 1455, 1370 (CH_3), 1340, 1310, 1290, 1205, 1125, 1100 (C–O–C), 1075, 1030, 1010, 980, 935, 820, 740, 700, 620. MS *m/z* (rel. intensity %): 190 (0.1, $M^{+\cdot}$), 160 (1.4, $M^{+\cdot} - CH_2O$), 146 (10), 131 (7), 117 (3), 107 (5), 99 (1.4, $M^{+\cdot} - C_6H_5CH_2$), 92 (23), 91 (100, $C_7H_7^+$), 84 (11), 83 (6), 79 (11), 77 (9, $C_6H_5^+$), 65 (12, $C_5H_5^+$), 55 (9), 51 (6, $C_4H_3^+$), 43 (5), 39 (8, $C_3H_3^+$). Anal. Found: C, 75.32; H, 7.76. $C_{12}H_{14}O_2$ (M_r = 192.2) calc.: C, 75.76; H, 7.42%.

4.3.2. *(1E,3E,5S)-(−)-5-Phenylmethoxy-1-phenylsulfonylhexa-1,3-diene [(1E,3E,S)-5]*

According to the olefination procedure of Rathke et al. [21], 1.55 g (17.8 mmol) of anhydrous LiBr [previously dried for 12 h at 120 °C in high vacuo], 4.33 g (14.8 mmol) of diethyl phosphono methylphenylsulfone (**4**) and 1.65 g (16.3 mmol) of triethylamine were dissolved under argon at room temperature in 15 ml of anhydrous acetonitrile and the resulting clear solution was cooled to 0 °C. To the reaction mixture were added dropwise 2.81 g (14.8 mmol) of the aldehyde (*E,S*)-**3** dissolved in 5 ml of anhydrous acetonitrile and stirring was continued after removal of the cooling bath. Upon complete consumption of the starting material (t.l.c. control, ca. 12 h), the reaction was quenched by addition of 5 ml 0.1 M hydrochloric acid. After addition of 20 ml of water the organic phase was diluted with diethyl ether (20 ml), the organic phase was separated and the aqueous phase was extracted with diethyl ether (3 × 20 ml). The combined organic extracts were washed with saturated NaCl solution (20 ml), dried ($MgSO_4$), filtered and the solvents evaporated under reduced pressure. Final purification and removal of traces of the undesired (*E,Z*)-isomer was achieved by preparative column chromatography (silica gel, diethyl ether–light petroleum = 1:2) to give a viscous yellow oil. Recrystallization from diethyl ether–light petroleum mixtures yielded 5.29 g (96%) of a colourless solid. Analytical data for (1*E*,3*E*)-**5**: m.p. = 55 °C. R_f = 0.18 (diethyl ether–light petroleum = 1:3). $[\alpha]_D^{23} = -60.8$ (c = 1.53, $CHCl_3$). *ee* > 99%. ^{1}H NMR (300 MHz, $CDCl_3$, TMS(int), ppm): δ 7.93–7.87 (m, 2H, *ortho*-CH), 7.65–7.51 (m, 3H, *para*-CH, *meta*-CH), 7.35–7.23 (m, superimposed, 6H, C*H*=CHSO$_2$, OCH$_2$C$_6$*H*$_5$), 6.37 (d, $J(^1H–^1H)$ = 14.6 Hz, 1H, CH=C*H*SO$_2$), 6.29 (dd, $J(^1H–^1H)$ = 15.3/10.2 Hz, 1H, CHCH=C*H*), 6.18 (dd, $J(^1H–^1H)$ = 15.3/6.1 Hz, 1H, CHC*H*=CH), 4.52 (d, $J(^1H–^1H)$ = 12.0 Hz, 1H, OCH*H*C$_6$H$_5$), 4.42 (d, $J(^1H–^1H)$ = 12.0 Hz, 1H, OC*H*HC$_6$H$_5$), 4.07 (quint., $J(^1H–^1H)$ = 6.4 Hz, 1H, C*H*CH=CH), 1.30 (d, $J(^1H–^1H)$ = 6.4 Hz, 1H, CHC*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$, TMS(int), ppm): δ 147.15 (δ-C), 141.44 (β-C), 140.42 (*ipso*-CSO$_2$), 138.10 (*ipso*-CCH$_2$), 133.29 (*para*-C), 129.93 (α-C), 129.24, 128.37, 127.61, 127.53, 127.51 (*meta*-C, *ortho*-C, aromatic-C), 125.82 (γ-C), 74.40 (ε-C), 70.58 (OCH$_2$C$_6$H$_5$), 20.87 (CH_3). IR (KBr, cm^{-1}): 3060, 3045, 3035 (aromatic-CH, =C–H), 2975, 2930, 2865, 1595, 1495 (aromatic-C=C, olefinic-C=C), 1450, 1370, 1320, 1310 (S=O), 1180, 1145 (S=O), 1085 (C–O–C), 1030, 830, 785, 720, 700, 595, 560. MS *m/z* (rel. intensity %): 328 (0.1, $M^{+\cdot}$), 270 (2), 222 (5), 187 (3, $M^{+\cdot} - SO_2C_6H_5$), 169 (6), 143 (3, $H_2SO_2C_6H_5^+$), 141 (1, $SO_2C_6H_5^+$), 129 (17), 91 (100, $C_7H_7^+$), 77 (11, $C_6H_5^+$), 65 (6, $C_5H_5^+$), 43 (13). Anal. Found: C, 69.48; H, 6.14. $C_{19}H_{20}O_4S$ (M_r = 328.4) calc.: C, 69.11; H, 6.10%.

4.3.3. *Tricarbonyl[(1-4η)-(1E,3E.1R,5S)-5-phenylmethoxy-1-(phenylsulfonyl)hexa-1,3-diene]iron(0) [(1R,5S)-6] (ψ-endo-6) and tricarbonyl[(1-4η)-(1E,3E,1S,5S)-5-phenylmethoxy-1-(phenylsulfonyl)hexa-1,3-diene]iron(0) [(1S,5S)-6] (ψ-exo-6)*

4.3.3.1. Method A: thermal complexation of (1E,3E,S)-5 with nonacarbonyldiiron in toluene. To a flame-dried Schlenk-flask equipped with a condenser, a bubbler and a magnetic stirring bar was added 21.5 g (59.0 mmol) of nonacarbonyldiiron [$Fe_2(CO)_9$] and the solid was suspended under argon in 160 ml of abs. degassed toluene. After addition of a solution of 9.7 g (29.5 mmol) of the diene (1*E*,3*E*,*S*)-**5** in a minimum amount of abs. degassed toluene, the reaction mixture was heated to reflux for 48 to 60 h (the colour of the reaction mixture changes from orange [suspended $Fe_2(CO)_9$] to dark green indicating the formation of $Fe_3(CO)_{12}$ while simultaneously a thin iron mirror was formed on the inner surface of the flask). Upon complete reaction (t.l.c. control, observation of carbon monoxide evolution), the solvent was partly removed (to ca. 2/3 of its original volume) under reduced pressure into a cooling trap and the concentrate was filtered over a short path of Celite®–sand by means of an inert gas frit under argon and the filtercake was washed with abs. dichloromethane until the filtrate was colourless. The combined bright yellow organic filtrates were evaporated under reduced pressure to an orange-brown residue which was further subjected to a pre-purification by column chromatography (silica gel, diethyl ether–light petroleum = 2:3, collection of all yellow bands) to yield a yellow-orange, very viscous, ^{1}H NMR spectroscopically pure oil (11.4 g, 85%, both diastereomers, *de* ≤ 4%). The resulting mixture of enantiopure but diastereomeric tricarbonyl(η^4-diene)iron(0) complexes [(1*R*,5*S*)-**6** (*Ψ-endo-6*) and (1*S*,5*S*)-**6** (*Ψ-exo-6*)] were diastereo- and enantiomerically enriched by column chromatography (silica gel, diethyl ether–light petroleum = 1:2, separate collection of the yellow bands) (*de*, *ee* > 99% for (1*R*,5*S*)-**6** (*Ψ-endo-6*), yellow-orange viscous oil) and fractional crystallization from concentrated enriched solutions of the fraction with the lower R_f value (*de* = 70–80% for

(1*S*,5*S*)-**6** (Ψ-*exo*-**6**) in diethyl ether–*n*-pentane mixtures at −25 °C (*de*, *ee* > 99% for (1*S*,5*S*)-**6** (Ψ-*exo*-**6**), yellow crystals).

4.3.3.2. Method B: photochemical complexation of (1E,3E,S)-5 with pentacarbonyliron in toluene. An aluminium-foil-wrapped Dema irradiation apparatus equipped with a mercury medium pressure lamp (Philips HPK 125 W or TQ 150 W) and connected to a bubbler was charged with 4.70 g (14.3 mmol) of the diene (1*E*,3*E*,*S*)-**5**, 3.62 g (18.5 mmol) of pentacarbonyliron [$Fe(CO)_5$] and 250 ml of abs. degassed toluene. The intensively stirred reaction mixture was irradiated for ca. 12 h at room temperature. Upon complete reaction (t.l.c. control, observation of carbon monoxide evolution), the solvent was partly condensed into a cooling trap and the supernatant solution of the product mixture decanted from insoluble residues after sedimentation. The residues were washed once with abs. degassed diethyl ether (ca. 50 ml) and the combined organic solutions were evaporated by means of a cooling trap. Further pre-purification was performed as described under method A (Section 4.3.3.1) to yield a yellow-orange, very viscous, ^{1}H NMR spectroscopically pure oil (6.25 g, 96%, both diastereomers, *de* = 0%). Both final purification and separation of the diastereomers were accomplished as described under method A (Section 4.3.3.1). A racemic mixture of the diastereomeric tricarbonyl(η^4-diene)iron(0) complexes (1*R*/*S*,5*R*/*S*)-**6** (*rac*-Ψ-*exo*-**6** and *rac*-Ψ-*exo*-**6**) has been synthesized from the racemic diene (1*E*,3*E*,*R*/*S*)-**5** mixture following the procedure described above. Analytical data for (1*R*,5*S*)-**6** (Ψ-*endo*-**6**); (1*S*,5*S*)-**6** (Ψ-*exo*-**6**): m.p. = 56 °C (decomp.) [(1*S*,5*S*)-**6** (Ψ-*exo*-**6**)]. R_f = 0.22 (diethyl ether–light petroleum = 1:2 [(1*R*,5*S*)-**6** (Ψ-*endo*-**6**)]; R_f = 0.16 (diethyl ether–light petroleum = 1:2 [(1*S*,5*S*)-**6** (Ψ-*exo*-**6**)]. $[\alpha]_D^{23} = -28.6$ (*c* = 1.15, $CHCl_3$) [(1*R*,5*S*)-**6** (Ψ-*endo*-**6**)]; $[\alpha]_D^{23} = -35.9$ (*c* = 1.85, $CHCl_3$) [(1*S*,5*S*)-**6** (Ψ-*exo*-**6**)]. *de* = 0–4% (prior to separation of diastereomers); *de* > 99% (after separation of diastereomers by column chromatography and/or recrystallization) (^{1}H NMR, 500 MHz). ^{1}H NMR (500 MHz, $CDCl_3$, TMS(int), (1*R*,5*S*)-**6** (Ψ-*endo*-**6**), ppm): δ 7.92–7.88 (m, 2H, *ortho*-CH), 7.63–7.56 (m, 1H, *para*-CH), 7.56–7.50 (m, 2H, *meta*-CH), 7.36–7.24 (m, 5H, $OCH_2C_6H_5$), 5.69 (ddd, $J(^1H-^1H)$ = 7.3/5.2/0.9 Hz, 1H, $CH{=}CHSO_2$), 5.32 (ddd, $J(^1H-^1H)$ = 8.9/5.2/0.9 Hz, 1H, $CHCH{=}CH$), 4.49 (d, $J(^1H-^1H)$ = 11.6 Hz, 1H, $OCHHC_6H_5$), 4.47 (d, $J(^1H-^1H)$ = 11.6 Hz, 1H, $OCHHC_6H_5$), 3.40 (dq, $J(^1H-^1H)$ = 7.5/6.1 Hz, 1H, $CHCH_3$), 1.59 (dd, $J(^1H-^1H)$ = 7.2/1.0 Hz, 1H, $CH{=}CHSO_2$), 1.38 (d, $J(^1H-^1H)$ = 6.2 Hz, 3H, $CHCH_3$), 1.17 (ddd, $J(^1H-^1H)$ = 8.7/7.6/1.1 Hz, 1H, $CHCH{=}CH$). ^{13}C NMR (125 MHz, $CDCl_3$, TMS(int), (1*R*,5*S*)-**6** (Ψ-*endo*-**6**), ppm): δ 212.38, 207.28, 205.70 (Fe–C=O, broad, identical with Ψ-*exo*-**6**), 141.70 (*ipso*-CSO_2), 138.08 (*ipso*-CCH_2), 133.26 (*para*-C), 129.40 (*meta*-C), 128.08, 127.77, 127.67 (aromatic-C), 127.08 (*ortho*-C), 85.53 (γ-C), 79.84 (β-C), 76.09 (ε-C), 70.37 ($OCH_2C_6H_5$), 67.55 (α-C), 66.10 (δ-C), 22.37 (CH_3). ^{1}H NMR (500 MHz, $CDCl_3$, TMS(int), (1*S*,5*S*)-**6** (Ψ-*exo*-**6**), ppm): δ 7.91–7.87 (m, 2H, *ortho*-CH), 7.61–7.57 (m, 1H, *para*-CH), 7.55–7.49 (m, 2H, *meta*-CH), 7.36–7.25 (m, 5H, $OCH_2C_6H_5$), 5.69 (ddd, $J(^1H-^1H)$ = 7.0/5.2/1.1 Hz, 1H, $CH{=}CHSO_2$), 5.36 (dd, $J(^1H-^1H)$ = 8.9/5.2 Hz, 1H, $CHCH{=}CH$), 4.61 (d, $J(^1H-^1H)$ = 11.6 Hz, 1H, $OCHHC_6H_5$), 4.37 (d, $J(^1H-^1H)$ = 11.6 Hz, 1H, $OCHHC_6H_5$), 3.65 (dq, $J(^1H-^1H)$ = 6.1/5.8 Hz, 1H, $CHCH_3$), 1.44 (dd, $J(^1H-^1H)$ = 7.1/1.0 Hz, 1H, $CH{=}CHSO_2$), 1.33 (d, $J(^1H-^1H)$ = 6.1 Hz, 3H, $CHCH_3$), 1.30 (ddd, $J(^1H-^1H)$ = 8.9/5.4/1.2 Hz, 1H, $CHCH{=}CH$). ^{13}C NMR (125 MHz, $CDCl_3$, TMS(int), (1*S*,5*S*)-**6** (Ψ-*exo*-**6**), ppm): δ 212.38, 207.28, 205.70 (Fe–C=O, broad, identical with Ψ-*exo*-**6**), 141.96 (*ipso*-CSO_2), 138.12 (*ipso*-CCH_2), 133.13 (*para*-C), 129.33 (*meta*-C), 128.41, 127.72, 127.61 (aromatic-C), 127.02 (*ortho*-C), 83.31 (γ-C), 78.61 (β-C), 74.33 (ε-C), 70.57 ($OCH_2C_6H_5$), 70.12 (δ-C), 66.76 (α-C), 22.19 (CH_3). IR [CH_2Cl_2, (1*S*,5*S*)-**6** and (1*R*,5*S*)-**6**, cm^{-1}]: 3062, 3034 (w, aromatic-CH, =CH), 2978, 2931, 2869, 2068, 2001 (Fe–C=O), 1814, 1605, 1586, 1497 (aromatic-C=C, complexed-C=C), 1479, 1448, 1424, 1377 (CH_3), 1317, 1307 (S=O), 1148 (S=O), 1086 (C–O–C), 1067, 1028, 908, 814, 690, 629, 612, 597, 568. MS *m*/*z* [(1*S*,5*S*)-**6** and (1*R*,5*S*)-**6**, rel. intensity %]: 469 (0.5, $M^{+\cdot}$ + 1), 440 (1.7, $M^{+\cdot}$ − CO), 412 (0.8, $M^{+\cdot}$ − 2CO), 386 (10), 385 (28), 384 (97, $M^{+\cdot}$ − 3CO), 293 (14, 384 − C_7H_7), 278 (43), 277 (17), 276 (100, $H_2C{=}CH{-}CH{=}CH{-}CH{=}CHSO_2C_6H_5Fe^+$), 239 (8), 224 (7), 212 (12), 199 (8), 198 (51), 186 (12), 184 (11), 180 (46), 161 (15), 152 (7), 151 (12), 148 (11), 143 (2, $H_2SO_2C_6H_5^+$), 141 (3, $SO_2C_6H_5^+$), 135 (12), 134 (32), 133 (41), 121 (8), 105 (5), 91 (42, $C_7H_7^+$), 81 (10), 79 (20, $C_6H_7^+$), 77 (22, $C_6H_5^+$), 65 (10), 56 (65, Fe^+), 55 (5), 51 (10), 41 (8), 39 (10). Anal. Found: C, 56.45; H, 4.36. $C_{22}H_{20}FeO_6S$ (M_r = 468.3) calc.: C, 56.42; H, 4.30%.

4.3.4. Tricarbonyl[(1-5η)-(1R,5R)-5-methyl-1-phenylsulfonyl)pentadienyl]iron(1 +)tetrafluoroborate [(1R,5R)-7] and tricarbonyl[(1-5η)-(1S,5S)-5-methyl-1-phenyl-sulfonyl)pentadienyl]iron(1 +)tetrafluoroborate [(1S,5S)-7]

According to the general procedures [29], the dropwise addition of 1.20 ml (8.8 mmol) of HBF_4 (54-proz. in diethyl ether) to a solution of 1.64 g (3.5 mmol) of the diastereo- and enantiopure tricarbonyl(η^4-diene)iron(0) complex (1*R*,5*S*)-**6** (Ψ-*endo*-**6**) in a mixture of 30 ml abs. degassed diethyl ether and 50 ml abs. degassed *n*-pentane under argon at room temperature resulted in the formation of a light brown precipitate accompanied

with a dark yellow oil. After stirring for 12 h at ambient temperature to transform the generated oil to the solid salt, an additional 50 ml of abs. *n*-pentane were added to complete the precipitation. After filtration by means of an inert gas frit under argon, the residue was washed with diethyl ether–*n*-pentane = 1:1 to 1:2 until the filtrate remained colourless. The complex was dried under reduced pressure (high vacuo) to yield 1.60 g (quant.) of a pale brown, ^{1}H NMR spectroscopically pure and homogeneous tricarbonyl(η^5-pentadienyl)iron(1 +) complex *syn,syn*-(1*R*,5*R*)-**7** (*de* > 99%). The complex can be used for the addition reactions without further work-up or purification and can be stored under argon at −25 °C and is only slightly air- and moisture-sensitive. By analogy, the reaction of 1.00 g (2.2 mmol) of the diastereo- and enantiopure tricarbonyl(η^4-diene)iron(0) complex (1*S*,5*S*)-**6** [Ψ-*exo*-**6**] with 0.45 ml (3.3 mmol) of HBF_4 (54-proz. in diethyl ether) in a mixture of 40 ml diethyl ether and 50 ml *n*-pentane under argon yielded 0.85 g (87%) of the pale-brown coloured tricarbonyl(η^5-pentadienyl)iron(1 +) complex *syn,syn*-(1*S*,5*S*)-**7**. The racemic complex *syn,syn*-(1*R/S*,5*R/S*)-**7** has been synthesized from a diastereomeric mixture of the racemic tricarbonyl(η^4-diene)iron(0) complexes (*rac*-Ψ-*endo*-**6** and *rac*-Ψ-*exo*-**6**) following the procedure described above. Analytical data for *syn,syn*-(1*R*,5*R*)-**7** and *syn,syn*-(1*S*,5*S*)-**7**: m.p. = 98 °C (decomp.). $[\alpha]_D^{28} = +56.6$ ($c = 0.98$, acetone, *syn,syn*-(1*R*,5*R*)-**7**); $[\alpha]_D^{28} = -44.7$ ($c = 1.02$, acetone, *syn,syn*-(1*S*,5*S*)-**7**). *de* > 99% ≡ 5-*syn*-CH_3/5-*anti*-CH_3 ≫ 100:1 [^{1}H NMR, 500 MHz, *syn,syn*-(1*R*,5*R*)-**7** and *syn,syn*-(1*S*,5*S*)-**7**]. *ee* > 99% [*syn,syn*-(1*R*,5*R*)-**7** and *syn,syn*-(1*S*,5*S*)-**7**]. ^{1}H NMR (500 MHz, CD_3NO_2, TMS(int), ppm): δ 8.04–8.01 (m, 2H, *ortho*-CH), 7.86–7.82 (m, 1H, *para*-CH), 7.74–7.70 (m, 2H, *meta*-CH), 7.06 (ddt, $J(^1H-^1H)$ = 7.1/6.1/0.9 Hz, 1H, C*H*–CH–$CHSO_2$), 6.71 (ddd, $J(^1H-^1H)$ = 10.0/7.4/0.7 Hz, 1H, CH–C*H*–$CHSO_2$), 6.18 (ddquint., $J(^1H-^1H)$ = 12.3/6.0/0.8 Hz, 1H, $H_3CCH-CH$), 3.85 (dqd, $J(^1H-^1H)$ = 12.7/6.1/0.8 Hz, 1H, C*H*CH_3), 3.69 (dd, $J(^1H-^1H)$ = 10.0/1.0 Hz, 1H, CH–CH–C*H*SO_2), 1.99 (dd, $J(^1H-^1H)$ = 6.1/0.9 Hz, 3H, CHC*H*$_3$). ^{13}C NMR (125 MHz, CD_3NO_2, TMS(int), ppm): δ 205.86, 197.59, 197.23 (Fe–C=O), 139.33 (*ipso*-C), 136.69 (*para*-C), 131.50 (*meta*-C), 129.58 (*ortho*-C), 106.76 (δ-CH), 103.48 (β-CH), 99.20 (ε-CH), 94.29 (α-CH), 87.71 (γ-CH), 21.65 (CH_3). IR (KBr, cm^{-1}): 3103, 3070 (aromatic-CH, –C–H), 2977, 2931, 2126, 2089, 2084, 2001 (Fe–C=O), 1631, 1584, 1530, 1479 (aromatic-C=C), 1448, 1385 (CH_3), 1320, 1308 (S=O), 1148 (S=O), 1085, 1038, 1070, 900, 761, 732, 689, 597, 555. MS *m/z* (rel. intensity %): 374 (0.4), 332 (0.4, $M^+ - HBF_4, -CO$), 304 (0.4, 332 − CO), 276 (3, 332 − 2CO), 198 (2), 180 (3), 141 (0.4, $SO_2C_6H_5^+$), 98 (9), 83 (20), 79 (5, $C_6H_7^+$), 77 (3, $C_6H_5^+$), 58 (20), 56 (5, Fe^+), 55 (19), 49 (19), 43 (100), 41 (7), 39 (9). Anal. Found: C, 39.97; H, 3.39. $C_{15}H_{13}BF_4FeO_5S$ (M_r = 448.0) calc.: C, 40.22; H, 2.93%.

4.4. General procedure for the reaction of the tricarbonyl(η^5-pentadienyl)iron(1 +) complexes 7 with nucleophiles to ε-substituted tricarbonyl(η^4-diene)iron(0) complexes 10 or ε-substituted 1-phenylsulfonyl-butadienes 11

For the addition of the nucleophiles, a Schlenk-flask was charged under argon with 1.0 mmol of the appropriate tricarbonyl(η^5-pentadienyl)iron(1 +) complex **7** and the complex was suspended in 10–15 ml of anhydrous dichloromethane at room temperature. To the stirred yellow suspension was added dropwise a solution of 3.0–5.0 mmol of the appropriate nucleophile in 1–5 ml of anhydrous dichloromethane and stirring of the reaction mixture was continued at room temperature. Upon complete transformation of the insoluble suspended cationic complex *syn,syn*-**7** into the soluble neutral substituted tricarbonyl(η^4-diene)iron(0) complexes **10a–c** (clear, intensive yellow solution, ca. 1 to 10 min), solvent and excess nucleophile were removed from the reaction mixture under reduced pressure (rotary evaporator and high vacuo). The crude reaction mixture was either subjected to column chromatography (silica gel, solvent mixtures as indicated) to yield substituted *exo*-tricarbonyl(η^4-diene)iron(0) complexes *rac*-Ψ-*exo*-**10** as stable yellow solids or, alternatively, oxidative decomplexation was accomplished by addition of 10.0 mmol CAN dissolved in 10–15 ml of a mixture of methanol–acetonitrile = 3:1 and stirring of the reaction mixture for 12 h at room temperature. After dilution with water (10–20 ml) and dichloromethane (10–20 ml), the organic phase was separated and the aqueous phase was extracted with dichloromethane (3 × 20 ml). Fe^{III} ions were removed from the combined organic extracts by successive washing with saturated aqueous NH_4F solution and finally with water. The organic phase was dried ($MgSO_4$), concentrated under reduced pressure, and the residue purified by flash column chromatography (silica gel 60, solvent mixtures as indicated) to afford the ε-substituted 1,3-butadienes **11** in spectroscopically and analytically pure form. Mixtures of (*E,E*)/(*E/Z*)-isomers could not be separated by either column chromatography or by preparative HPLC on LiChrosorb®.

4.4.1. Tricarbonyl[(1-4η)-(1E,3Z,1R / S,5R / S)-1-(phenylsulfonyl)-5-(morpholine-4-yl)hexa-1,3-diene]-iron(0) [(1E,3Z,1R / S,5R / S)-10a]

According to the general procedure (Section 4.4), the reaction of 0.150 g (0.33 mmol) of the racemic iron complex *syn,syn*-(1*R/S*,5*R/S*)-**7** with 0.144 g (1.67 mmol) morpholine in 5 ml of dichloromethane

yielded after purification by column chromatography (silica gel, diethyl ether–ethyl acetate = 1:1) 0.099 g (68%) of the substituted complex (1*E*,3*Z*,1*R*/*S*,5*R*/*S*)-**10a** as a yellow solid. Analytical data for (1*E*,3*Z*,1*R*/*S*,5*R*/*S*)-**10a**: m.p. = 117 °C. R_f = 0.31 (diethyl ether–ethyl acetate = 1:1). ^{1}H NMR (500 MHz, C_6D_6 TMS(int), ppm): δ 7.88–7.83 (m, 2H, *ortho*-CH), 7.00–6.95 (m, 3H, *meta*-CH, *para*-CH), 5.69 (ddd, $J(^1H-^1H)$ = 7.5/5.2/0.9 Hz, 1H, C*H*=CHSO$_2$), 4.57 (ddd, $J(^1H-^1H)$ = 7.0/5.2/0.9 Hz, 1H, CHCH=C*H*), 3.31–3.25 (m, 2H, OC*H*$_2$), 3.22–3.15 (m, 2H, OC*H*H), 2.59 (dd, $J(^1H-^1H)$ = 7.6/0.9 Hz, 1H, CH=C*H*SO$_2$), 1.99–1.90 (m, superimposed, 2H, C*H*CH$_3$, CHC*H*=CH), 1.88–1.82 (m, 2H, NCH*H*), 1.77–1.67 (m, 2H, NC*H*H), 0.90 (d, $J(^1H-^1H)$ = 6.1 Hz, 3H, CHC*H*$_3$). ^{13}C NMR (125 MHz, C_6D_6, TMS(int), ppm): δ signals of the Fe–C=O groups are not detectable, 143.01 (*ipso*-CSO$_2$), 132.90 (*para*-C), 129.40 (*meta*-C), 127.18 (*ortho*-C), 89.29 (β-C), 85.21 (γ-C), 69.39 (α-C), 67.07 (CH$_2$O), 62.44 (δ-C), 60.42 (ε-C), 48.19 (CH$_2$N), 18.46 (CH$_3$). IR ($CHCl_3$, cm^{-1}): 3026, 3020, 3015 (aromatic-CH, =C–H), 2966, 2070 (*apical*-Fe–C=O), 2011 (*basal*-Fe–C=O), 1585 (aromatic-C=C, complexed-C=C), 1448, 1307 (S=O), 1148 (S=O), 955, 792, 724, 689, 617, 592, 558. MS *m*/*z* (rel. intensity %): 447 (0.41, $M^{+\cdot}$), 419 (1.2, $M^{+\cdot}-CO$), 391 (4, $M^{+\cdot}-2CO$), 364 (17), 363 (75, $M^{+\cdot}-3CO$), 278 (21, 363 − C_4H_7NO), 276 (17, 363 − C_4H_9NO), 238 (19), 218 (29), 214 (12), 198 (14), 182 (16), 166 (32), 160 (11), 148 (18), 141 (3, $SO_2C_6H_5^+$), 135 (24), 134 (33), 133 (36), 114 (100, $C_6H_{12}NO^+$), 91 (9), 86 (11, $C_4H_8NO^+$), 84 (11), 81 (13), 79 (37), 77 (33, $C_6H_5^+$), 70 (12), 57 (15), 56 (91, Fe^+), 53 (11), 43 (8), 42 (21), 41 (16), 39 (11). Anal. Found: C, 51.00; H, 4.77; N, 3.09. $C_{19}H_{21}FeNO_6S$ (M_r = 447.3) calc.: C, 51.02; H, 4.73; N 3.13%. HRMS *m*/*z*: found 391.05438, calc. 391.05407 for $^{12}C_{17}^{1}H_{21}^{56}Fe^{14}N^{16}O_4^{32}S \equiv M^{+\cdot}-2CO$.

4.4.2. Tricarbonyl[(6-9η)-(6*E*,8*E*,1*R* / *S*,5*R* / *S*)-9-(phenylsulfonyl)-2,2,5-trimethylnona-6,8-dien-3-one]iron(0) [(6*E*,8*E*,1*R* / *S*,5*R* / *S*)-**10b**]

According to the general procedure (Section 4.4), the reaction of 0.150 g (0.33 mmol) of the racemic iron complex *syn*,*syn*-(1*R*/*S*,5*R*/*S*)-**7** with 0.172 g (1.00 mmol) of the silyl enol ether **8** in 5 ml of dichloromethane yielded after purification by column chromatography (silica gel 60, light petroleum–diethyl ether = 5:2) 0.088 g (57%) of the substituted complex (6*E*,8*E*,1*R*/*S*,5*R*/*S*)-**10b** as a very viscous yellow oil which solidified to a yellow solid. Analytical data for (6*E*,8*E*,1*R*/*S*,5*R*/*S*)-**10b**: m.p. = 56 °C (decomp.). R_f = 0.16 (light petroleum–diethyl ether = 3:1). ^{1}H NMR (300 MHz, $CDCl_3$, TMS(int), ppm): δ 7.92–7.86 (m, 2H, *ortho*-CH), 7.65–7.50 (m, 3H, *meta*-CH, *para*-CH), 5.67 (ddd, $J(^1H-^1H)$ = 6.6/5.0/≈ 1.0 Hz, 1H, C*H*=CHSO$_2$), 5.31 (ddd, $J(^1H-^1H)$ = 9.1/5.1/≈ 1.0 Hz, 1H, CHCH=C*H*), 2.57 (dd, $J(^1H-^1H)$ = 17.6/6.3 Hz, 1H, CHCH*H*CO), 2.50 (dd, $J(^1H-^1H)$ = 17.6/6.3 Hz, 1H, CHC*H*HCO), 2.06 (m, 1H, C*H*CH$_3$), 1.48 (d, $J(^1H-^1H)$ = 7.1 Hz, 1H, CH=C*H*SO$_2$), 1.08 (m, superimposed, 9H/3H/1H, C(CH$_3$)$_3$/CHC*H*$_3$/−CHC*H*=CH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS(int), ppm): δ signals of the Fe–CO groups are not detectable, 213.74 (C=O), 141.81 (*ipso*-CSO$_2$), 133.13 (*para*-C), 129.29 (*meta*-C), 127.06 (*ortho*-C), 86.07 (β-C), 78.69 (γ-C), 72.55 (α-C), 67.17 (δ-C), 45.91 (CH_2), 44.11 ($C(CH_3)_3$), 33.58 (ε-C), 26.19 ($C(CH_3)_3$), 23.05 (CH_3). IR (film, cm^{-1}): 3065 (aromatic-CH, =C–H), 2970, 2870, 2065 (vs, *apical*-Fe–CO), 1995 (*basal*-Fe–CO), 1700 (C=O), 1480 (aromatic-C=C, complexed-C=C), 1448, 1307 (S=O), 1139 (S=O), 1085, 760, 725, 690. MS *m*/*z* (rel. intensity %): 432 (1.1, $M^{+\cdot}-CO$), 404 (2, $M^{+\cdot}-2CO$), 378 (9), 377 (24), 376 (100, $M^{+\cdot}-3CO$), 320 (2), 312 (6), 276 (19), 251 (32), 228 (11), 227 (11), 198 (18), 180 (8), 151 (10), 149 (11), 148 (13), 143 (3, $H_2SO_2C_6H_5^+$), 141 (3, $SO_2C_6H_5^+$), 135 (19), 134 (23), 133 (23), 121 (10), 94 (9), 79 (18), 77 (17, $C_6H_5^+$), 57 (42, $C_4H_9^+$), 56 (17, Fe^+), 41 (19). Anal. Found: C, 55.23; H, 5.40; $C_{21}H_{24}FeO_6S$ (M_r = 460.3) calc.: C, 54.79; H, 5.25%. HRMS *m*/*z*: found 376.07915, calc. 376.07955 for $^{12}C_{18}^{1}H_{24}^{56}Fe^{16}O_3^{32}S \equiv M^{+\cdot}-3CO$.

4.4.3. Tricarbonyl[(4-7η)-(4*Z*,6*E*,3*R* / *S*,7*R* / *S*)-7-(phenylsulfonyl)-2,2,3-trimethylhepta-4,6-dienate]iron(0) [(4*Z*,6*E*,3*R* / *S*,7*R* / *S*)-**10c**]

According to the general procedure (Section 4.4), the reaction of 0.480 g (1.07 mmol) of the racemic iron complex *syn*,*syn*-(1*R*/*S*,5*R*/*S*)-**7** with 0.470 g (2.70 mmol) of the silyl ketene acetal **9** in 10 ml of dichloromethane yielded after purification by column chromatography (silica gel 60, light petroleum–diethyl ether = 2:1) 0.212 g (43%) of the substituted complex (4*Z*,6*E*,3*R*/*S*,7*R*/*S*)-**10c** as a very viscous yellow oil which solidified to a yellow solid. Analytical data for (4*Z*,6*E*,3*R*/*S*,7*R*/*S*)-**10c**: R_f = 0.32 (light petroleum–diethyl ether = 1:1). ^{1}H NMR (500 MHz, $CDCl_3$, TMS(int), ppm): δ 7.98–7.94 (m, 2H, *ortho*-CH), 7.65–7.55 (m, 3H, *meta*-CH, *para*-CH), 5.04 (dd, $J(^1H-^1H)$ = 8.2/0.9 Hz, 1H, CHCH=C*H*), 5.84 (ddd, $J(^1H-^1H)$ = 7.5/5.5/0.9 Hz, 1H, C*H*=CHSO$_2$), 3.14 (s, 3H, OCH$_3$), 2.58 (dd, $J(^1H-^1H)$ = 7.8/≈ 1.0 Hz, 1H, CH=C*H*SO$_2$), 2.51 (ddd, $J(^1H-^1H)$ = 11.2/8.2/≈ 1.0 Hz, 1H, CHC*H*=CH), 1.30 (dq, $J(^1H-^1H)$ = 11.5/6.7 Hz, 1H, C*H*CH$_3$), 1.06 (d, $J(^1H-^1H)$ = 6.7 Hz, 3H, CHC*H*$_3$), 1.00 (s, 3H, C(CH$_3$)(C*H*$_3$)), 0.98 (s, 3H, C(C*H*$_3$)(CH$_3$)). ^{13}C NMR (75 MHz, $CDCl_3$, TMS(int), ppm): δ 212.3, 207.9, 205.3 (Fe–C=O), 177.20 (C=O), 141.84 (*ipso*-CSO$_2$), 133.22 (*para*-C), 129.39 (*meta*-C), 127.10 (*ortho*-C), 88.93 (β-C), 84.52 (γ-C), 68.51 (α-C), 66.34 (δ-C),

51.07 (OCH_3), 48.30 ($C(CH_3)_2$), 40.41 (ε-C), 23.83 (CH_3), 19.13 ($C(CH_3)_2$), 17.17. IR (film, cm^{-1}): 3062 (aromatic-CH, =C–H), 2981, 2951, 2881, 2064 (*apical*-Fe–C=O), 2001 (*basal*-Fe–C=O), 1730 (C=O), 1636 (complexed-C=C), 1585 (aromatic-C=C), 1462, 1448, 1379 (gem. CH_3), 1368 (gem. CH_3), 1317, 1307 (S=O), 1260 (CO–O–C), 1190, 1147 (S=O), 1086, 1000, 915, 755, 724, 692, 618, 595, 558. MS *m/z* (rel. intensity %): 406 (7, $M^{+\cdot}-2CO$), 380 (9), 379 (22), 378 (100, $M^{+\cdot}-3CO$), 336 (5), 318 (27, $378-CH_3CO_2H$), 278 (19), 277 (13), 276 (47), 254 (11), 253 (16), 239 (10), 198 (24), 182 (10), 181 (14), 180 (23), 149 (9), 148 (10), 143 (10, $H_2SO_2C_6H_5^+$), 141 (4, $SO_2C_6H_5^+$), 135 (17), 134 (31), 133 (20), 125 (12, $SOC_6H_5^+$), 121 (18), 107 (10), 91 (15), 81 (12), 80 (15), 79 (33), 77 (28, $C_6H_5^+$), 70 (11), 57 (26), 56 (47, Fe^+), 55 (16), 51 (9), 43 (15), 41 (27), 39 (14). Anal. Found: C, 52.09; H, 4.83; $C_{20}H_{22}FeO_7S$ (M_r = 462.3) calc.: C, 51.96; H, 4.80%.

4.4.4. (1*E*,3*Z*,*R*)-5-(*N*-Morpholin-4-yl)-1-(phenylsulfonyl)hexa-1,3-diene [(1*E*,3*Z*,*R*)-11a] and (1*E*,3*Z*,*S*)-5-(*N*-morpholin-4-yl)-1-(phenylsulfonyl)hexa-1,3-diene [(1*E*,3*Z*,*S*)-11a]

According to the general procedure (Section 4.4), the reaction of 0.250 g (0.56 mmol) of the iron complex *syn,syn*-(1*S*,5*S*)-7 with 0.243 g (2.78 mmol) of morpholine in 10 ml dichloromethane yielded after oxidative cleavage with a solution of 3.05 g (5.56 mmol) CAN in 20 ml methanol–acetonitrile (3:1) and after purification by column chromatography (silica gel 60, light petroleum–ethyl acetate = 1:1) 0.107 g (63%) of the diene (1*E*,3*Z*,*R*)-**11a** as a pale yellow solid. By analogy, reaction of 0.300 g (0.67 mmol) of the iron complex *syn,syn*-(1*R*,5*R*)-7 with 0.260 g (3.00 mmol) of morpholine in 10 ml dichloromethane yielded after oxidative cleavage with a solution of 3.05 g (5.56 mmol) of CAN in 20 ml of methanol–acetonitrile (3:1) and after purification by column chromatography (silica gel 60, light petroleum–ethyl acetate = 1:1) 0.093 g (45%) of the diene (1*E*,3*Z*,*S*)-**11a**. Analytical data for (1*E*,3*Z*,*R*)-**11a** and (1*E*,3*Z*,*S*)-**11a**: m.p. = 111 °C (decomp.; (1*E*,3*Z*,*R*)-**11a**). R_f = 0.17 (light petroleum–ethyl acetate = 1:1). $[\alpha]_D^{26} = +52.0$ (c = 1.14, $CHCl_3$, (1*E*,3*Z*,*R*)-**11a**); $[\alpha]_D^{26} = -36.5$ (c = 1.05, $CHCl_3$, (1*E*,3*Z*,*S*)-**11a**). *de* > 96% ≡ (3*Z*)/(3*E*): > 57:1 [(1*E*,3*Z*,*R*)-**11a**, HPLC on Daicel OD, cyclohexane–*i*-PrOH = 99:1, flow: 0.7 ml min^{-1}]; *de* > 98% ≡ (3*Z*)/(3*E*): > 87:1 [(1*E*,3*Z*,*S*)-**11a**, conditions see above], R_t(1*E*,3*Z*,*R*)-**11a** = 29.5 min, R_t(1*E*,3*Z*,*S*)-**11a** = 35.1 min. *ee* > 99% [(1*E*,3*Z*,*R*)-**11a**, HPLC on Daicel OD, cyclohexane–*i*-PrOH = 99:1, flow: 1.0 ml min^{-1}]; *ee* = 98.9% [(1*E*,3*Z*,*R*)-**11a**, conditions see above]. ^1H NMR (300 MHz, $CDCl_3$, TMS(int), (1*E*,3*Z*,*R*)-**11a**, ppm): δ 7.93–7.88 (m, 2H, *ortho*-CH), 7.65–7.52 (m, 4H, C*H*=CHSO$_2$, *meta*-CH, *para*-CH), 6.39 (d, $J(^1H-^1H)$ = 14.8 Hz, 1H, CH=C*H*SO$_2$), 6.14 (t, $J(^1H-^1H)$ = 11.2 Hz, 1H, CHCH=C*H*), 5.90 (dd, br., $J(^1H-^1H)$ = 10.8/9.9 Hz, 1H, CHC*H*=CH), 3.74–3.68 (m, 4H, OCH_2), 3.15 (dq, br., $J(^1H-^1H)$ = 9.6/6.4 Hz, 1H, C*H*CH$_3$), 2.58–2.44 (m, 4H, NCH_2), 1.19 (d, $J(^1H-^1H)$ = 6.7 Hz, 3H, CHC*H*$_3$). ^1H NMR (300 MHz, $CDCl_3$, TMS(int), (1*E*,3*E*,*S*)-**11a**, significant signals, ppm): δ 7.26 (dd, $J(^1H-^1H)$ = 12.1/10.2 Hz, 1H, C*H*=CHSO$_2$), 6.34 (d, $J(^1H-^1H)$ = 12.3 Hz, 1H, CH=C*H*SO$_2$), 3.03 (m, br., 1H, C*H*CH$_3$), 1.18 (d, superimposed with (1*E*,3*Z*,*R*)-**11a**, $J(^1H-^1H)$ = 6.6 Hz, 3H,CHC*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$, TMS(int), (1*E*,3*Z*,*R*)-**11a**, ppm): δ 145.10 (δ-C), 140.56 (*ipso*-CSO_2), 136.34 (β-C), 133.45 (*para*-C), 131.25 (α-C), 129.35 (*meta*-C), 127.63 (*ortho*-C), 125.06 (γ-C), 67.04 (CH_2O), 57.56 (ε-C), 50.86 (CH_2N), 18.17 (CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, TMS(int), (1*E*,3*E*,*S*)-**11a**, ppm): δ 143.56 (δ-C), 141.68 (β-C), 140.74 (*ipso*-CSO_2), 133.32 (*para*-C), 129.44 (α-C), 129.28 (*meta*-C), 127.56 (*ortho*-C), 126.72 (γ-C), 67.08 (CH_2O), 62.20 (ε-C), 50.50 (CH_2N), 16.72 (CH_3). IR (KBr, cm^{-1}): 3031 (aromatic-CH, =C–H), 2952, 2938, 2891, 1641 (olefinic-C=C), 1584 (aromatic-C=C), 1449, 1364, 1308 (S=O), 1285, 1267, 1211, 1187, 1146 (S=O), 1114, 1086 (C–O–C), 1002, 968, 920, 883, 847, 759, 719, 690, 597, 552. MS *m/z* (rel. intensity %): 308 (1.5, $M^{+\cdot}+1$), 307 (6, $M^{+\cdot}$), 293 (15), 292 (84, $M^{+\cdot}-CH_3$), 167 (11), 166 (100, $M^{+\cdot}-SO_2C_6H_5$), 151 (12), 150 (64), 143 (2, $H_2SO_2C_6H_5^+$), 141 (2, $SO_2C_6H_5^+$), 126 (8), 125 (18, $SOC_6H_5^+$), 114 (20, $C_6H_{12}NO^+$), 86 (13, $C_4H_8NO^+$), 79 (16), 77 (27, $C_6H_5^+$), 56 (22), 42 (9), 41 (8). Anal. Found: C, 61.88; H, 6.80; N, 4.52. $C_{16}H_{21}NO_3S$ (M_r = 307.4) calc.: C, 62.51; H, 6.89; N, 4.56%. HRMS *m/z*: found 307.12416, calc. 307.12422 for $^{12}C_{16}^{1}H_{21}^{14}N^{16}O_3^{32}S \equiv M^{+\cdot}$.

4.4.5. (6*E*,8*E*,*S*)-9-(Phenylsulfonyl)-2,2,5-trimethylnona-6,8-dien-3-one [(6*E*,8*E*,*S*)-11b]

According to the general procedure (Section 4.4), the reaction of 0.250 g (0.56 mmol) of the iron complex *syn,syn*-(1*S*,5*S*)-7 with 0.285 g (1.67 mmol) of the silyl enol ether **8** in 10 ml dichloromethane yielded after oxidative cleavage with a solution of 3.05 g (5.56 mmol) of CAN in 20 ml methanol–acetonitrile (3:1) and after purification by column chromatography (silica gel 60, light petroleum–diethyl ether = 3:1) 0.098 g (55%, both isomers) of the diene (6*E*,8*E*,*S*)-**11b** as a pale yellow oil. Analytical data for (6*E*,8*E*,*R*)-**11b**: R_f = 0.25 (light petroleum–diethyl ether = 3:1). $[\alpha]_D^{26} = +15.2$ (c = 1.18, $CHCl_3$). *de* > 97% ≡ (6*E*)/(6*Z*): > 65:1, HPLC on Daicel OD, cyclohexane–*i*-PrOH = 99:1, flow: 0.7 ml min^{-1}, R_t(6*E*,8*E*,*R*/*S*)-**11b** = 49.1/50.4 min, R_t(6*Z*,8*E*,*S*/*R*)-**11b** = 24.1/26.8 min. *ee* = 93% [(6*E*,8*E*,*R*)-**11b**], *ee* ≈ 60% [(6*Z*,8*E*,*S*)-**11b**], (HPLC

on Daicel OD, conditions and retention times see above). ^{1}H NMR (300 MHz, $CDCl_3$, TMS(int), (6*E*,8*E*,*R*)-**11b**, ppm): δ 7.90–7.85 (m, 2H, *ortho*-CH), 7.64–7.49 (m, 3H, *meta*-CH, *para*-CH), 7.23 (dd, br., $J(^1H,^1H)$ = 15.1/9.1 Hz, 1H, C*H*=CHSO$_2$), 6.29 (d, $J(^1H,^1H)$ = 15.1 Hz, 1H, C*H*=CHSO$_2$), 6.16 (dd, $J(^1H,^1H)$ = 15.1/6.7 Hz, 1H, CHC*H*=CH), 6.10 (dd, $J(^1H,^1H)$ = 15.1/9.1 Hz, 1H, CHCH=C*H*), 2.91 (sept., $J(^1H,^1H)$ = 6.7 Hz, 1H, C*H*CH$_3$), 2.55 (dd, $J(^1H,^1H)$ = 17.5/6.7 Hz, 1H, CH*H*C(=O)), 2.50 (dd, $J(^1H,^1H)$ = 17.6/7.1 Hz, 1H, C*H*HC(=O)), 1.11 (s, 9H, C(CH$_3$)$_3$), 1.03 (d, $J(^1H,^1H)$ = 6.7 Hz, 3H, CHC*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$, TMS(int), (6*E*,8*E*,*R*)-**11b**, ppm): δ 213.68 (C=O), 151.29 (δ-C), 142.62 (β-C), 141.03 (*ipso*-CSO$_2$), 133.19 (*para*-C), 129.24 (*meta*-C), 128.36 (α-C-8), 127.49 (*ortho*-C), 124.74 (γ-C), 44.12 (*C*(CH$_3$)$_3$), 42.76 (CH$_2$), 32.26 (ε-C), 26.19 (C(*C*H$_3$)$_3$), 19.27 (CH$_3$). IR (film, cm^{-1}): 3022 (aromatic-CH, =C–H), 2968, 2934, 2873, 1704 (C=O), 1640 (C=C), 1592, 1479 (aromatic-C=C), 1463, 1447, 1367, 1317, 1307 (S=O), 1282, 1222, 1191, 1146 (S=O), 826, 719, 689, 668, 601, 555. MS *m*/*z* (rel. intensity %): 320 (16, M$^{+\cdot}$), 279 (17), 263 (3, M$^{+\cdot}$ − C(CH$_3$)$_3$), 237 (11), 236 (52), 235 (14), 195 (14), 179 (12, M$^{+\cdot}$ − SO$_2$C$_6$H$_5$), 143 (17, H$_2$SO$_2$C$_6$H$_5^+$), 141 (7, SO$_2$C$_6$H$_5^+$), 139 (9), 125 (43, SOC$_6$H$_5^+$), 121 (13), 109 (10, SC$_6$H$_5^+$), 95 (18), 94 (25), 93 (17), 91 (8), 85 (27), 79 (31), 77 (35, C$_6$H$_5^+$), 57 (100, C(CH$_3$)$_3^+$), 43 (14), 41 (31), 39 (10). Anal. Found: C, 65.83; H, 7.42. $C_{18}H_{24}O_3S$ (M_r = 320.5) calc.: C, 67.47; H, 7.55. HRMS *m*/*z*: found 320.14391, calc. 320.14462 for $^{12}C_{18}^{1}H_{24}^{16}O_3^{32}S \equiv M^{+\cdot}$.

4.4.6. *Methyl-(4Z,6E,S)-7-(phenylsulfonyl)-2,2,3-trimethyl-hepta-4,6-dienate [(4Z,6E,S)-11c]*

According to the general procedure (Section 4.4), the reaction of 0.358 g (0.80 mmol) of the iron complex *syn,syn*-(1*R*,5*R*)-**7** with 0.348 g (1.67 mmol) of the silyl ketene acetal **9** in 8 ml dichloromethane at −78 °C yielded after oxidative cleavage with a solution of 1.75 g (3.19 mmol) CAN in 20 ml methanol–acetonitrile (3:1) and after purification by column chromatography (silica gel 60, light petroleum–diethyl ether = 3:1) 0.157 g (61%, both isomers) of the diene (4*Z*,6*E*,*S*)-**11c** as a colourless solid. Analytical data for (4*Z*,6*E*,*S*)-**11c**: m.p. = 101 °C. R_f = 0.19 (light petroleum–diethyl ether = 2:1). $[\alpha]_D^{RT}$ not determined. *de* = 66% ≡ (4*Z*)/(4*E*) = 5:1 (^{1}H NMR, 300 MHz). *ee* not determined. ^{1}H NMR (300 MHz, $CDCl_3$, TMS(int), (4*Z*,6*E*,*S*)-**11c**, ppm): δ 7.94–7.88 (m, superimposed with (4*E*,6*E*,*R*)-**11c**, 2H, *ortho*-CH), 7.67–7.51 (m, superimposed with (4*E*,6*E*,*R*)-**11c**, 4H, C*H*=CHSO$_2$, *meta*-CH, *para*-CH), 6.38 (d, $J(^1H,^1H)$ = 14.3 Hz, 1H, CH=C*H*SO$_2$), 6.08 (t, $J(^1H,^1H)$ = 11.3 Hz, 1H, CHC*H*=CH), 5.84 (dd, br., $J(^1H,^1H)$ ≈ 11.5/10.8 Hz, 1H, CHCH=C*H*), 3.65 (s, 3H, OCH$_3$), 3.11 (dq, $J(^1H,^1H)$ = 11.1/6.6 Hz, 1H, C*H*CH$_3$), 1.17 (s, 3H, C(CH$_3$)(C*H*$_3$)), 1.13 (s, 3H, C(C*H*$_3$)(CH$_3$)), 0.99 (d, superimposed with (4*E*,6*E*,*R*)-**11c**, $J(^1H,^1H)$ = 6.6 Hz, 3H, CHC*H*$_3$). ^{1}H NMR (300 MHz, $CDCl_3$, TMS(int), (4*E*,6*E*,*R*)-**11c**, ppm): δ 7.94–7.88 (m, superimposed with (4*Z*,6*E*,*S*)-**11c**, 2H, *ortho*-CH), 7.67–7.51 (m, superimposed with (4*Z*,6*E*,*S*)-**11c**, 3H, *meta*-CH, *para*-CH), 7.24 (dd, $J(^1H,^1H)$ = 14.8/10.0 Hz, 1H, C*H*=CHSO$_2$), 6.31 (d, $J(^1H,^1H)$ = 14.4 Hz, 1H, CH=C*H*SO$_2$), 6.21–6.05 (m, superimposed with (4*Z*,6*E*,*S*)-**11c**, 2H, CHC*H*=C*H*), 3.66 (s, 3H, OCH$_3$), 2.61 (dq, $J(^1H,^1H)$ = 7.2/6.6 Hz, 1H, C*H*CH$_3$), 1.12 (s, 6H, C(CH$_3$)$_2$), 0.98 (d, superimposed with (4*Z*,6*E*,*S*)-**11c**, $J(^1H,^1H)$ = 6.8 Hz, 3H, CHC*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$, TMS(int), (4*Z*,6*E*,*S*)-**11c**, ppm): δ 177.12 (C=O), 144.86 (δ-C), 140.74 (β-C), 136.79 (*ipso*-CSO$_2$), 133.31 (*para*-C), 130.72 (α-C), 129.27 (*meta*-C), 127.54 (*ortho*-C), 124.61 (γ-C), 51.79 (OCH$_3$), 45.81 (*C*(CH$_3$)$_2$), 39.56 (ε-C), 22.18, 21.88 (C(*C*H$_3$)$_2$), 15.72 (CH$_3$). ^{13}C NMR (75 MHz, $CDCl_3$, TMS(int), (4*E*,6*E*,*R*)-**11c**, ppm): δ 177.32 (C=O), 148.08 (δ-C), 142.28 (β-C), 140.86 (*ipso*-CSO$_2$), 133.22 (*para*-C), 129.24 (*meta*-C), 128.60 (α-C), 127.54 (*ortho*-C), 126.86 (γ-C), 51.79 (OCH$_3$), 45.73 (*C*(CH$_3$)$_2$), 44.65 (ε-C), 23.16, 21.51 (C(*C*H$_3$)$_2$), 15.08 (CH$_3$). IR (KBr, cm^{-1}): 3092, 3068, 3043, 3029 (aromatic-CH, =C–H), 2995, 2980, 2969, 2953, 2877, 1728 (C=O), 1634 (olefinic-C=C), 1584 (aromatic-C=C), 1467, 1448, 1432, 1391 (gem. CH$_3$), 1372 (gem. CH$_3$), 1316, 1304 (S=O), 1285, 1267, 1191, 1148 (S=O), 1133, 1085, 1003, 967, 893, 847, 836, 760, 718, 691, 598, 555. MS *m*/*z* (rel. intensity %): 322 (3, M$^{+\cdot}$), 290 (4, M$^{+\cdot}$ − CH$_3$OH), 262 (12, M$^{+\cdot}$ − HCO$_2$CH$_3$), 222 (5), 181 (15, M$^{+\cdot}$ − SO$_2$C$_6$H$_5$), 149 (19), 143 (23, H$_2$SO$_2$C$_6$H$_5^+$), 125 (32, SOC$_6$H$_5^+$), 122 (12), 121 (100, (CH$_3$)$_2$C=C(CH$_3$)CH=CHCH=CH$^+$), 111 (5), 107 (9), 105 (11), 97 (7), 95 (5), 93 (10), 91 (11), 81 (12), 80 (24), 79 (55, CH$_2$=CHCH=CHCH=CH$^+$), 77 (38, C$_6$H$_5^+$), 73 (10), 65 (6, C$_5$H$_5^+$), 59 (6), 55 (6), 51 (11, C$_4$H$_3^+$), 43 (6), 41 (16), 39 (10). Anal. Found: C, 63.14; H, 6.86. $C_{17}H_{22}O_4S$ (M_r = 322.4) calc.: C, 63.33; H, 6.88%.

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