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Total Asymmetric Synthesis of Glycomimetics and Polypropionates of Biological Interest

Pierre Vogel*

Abstract: Using readily available chiral auxiliaries such as (+)- and (–)-camphanic acid, (*R*,*R*)- and (*S*,*S*)-tartaric acid derivatives (*e.g.* RADO(*R*)-COCl, SADO(*R*)-COCl) efficient diastereoselective syntheses of rare sugars and glycomimetics have been developed. They engage the 'naked sugar' (enantiomerically pure 7-oxanorbornene) methodologies in which the chiral auxiliaries are recovered at an early stage of the multistep syntheses. A new reaction cascade starting with the hetero-Diels-Alder addition of sulfur dioxide to 1-(1-phenylethoxy)-1,3-dienes derived from inexpensive (+)- and (–)-1-phenylethanol allows the one-pot, four-component synthesis of polyfunctional sulfones, sulfonamides and sulfonic esters containing up to three stereogenic centers. The method ensures a high molecular and stereochemical diversity. The reaction cascade can also produce polyketide and polypropionate fragments in one-pot operations. The latter contain up to three contiguous stereogenic centers and do not have to be modified (deprotection, activation) before using them as nucleophilic partners in diastereoselective cross-aldol reactions, thus permitting the quick access to complicated polypropionate antibiotics such as Baconipyrones, Ryfamicyn S and Apoptolidines.

Keywords: Chiral auxiliaries · Diastereoselective synthesis · 'Naked sugars' · New organic chemistry of sulfur dioxide · Polypropionate antibiotics

1. Introduction

More than 55% of the drugs currently in use are chiral compounds and near 90% of the latter are administrated as racemic mixtures.[1–4] This proportion is diminishing as safety and efficiency of single enantiomers are usually better than for racemates.[5–7] The pharmaceutical industry is thus confronted with the necessity to produce drugs that are enantiomerically pure, and also compounds that are more and more complicated with respect to their chemical multifunctionality and stereochemistry. Racemate resolution and chiral separation technologies[8] are sometimes economical. In some cases, deracemization can be a very economical option.[9] Asymmetric synthesis may represent a cost-effective alternative if the molecular complexity can be reached in a few synthetic steps.[10–12] Thus in the future medicinal chemistry will require more and more efficiency in access to both molecular complexity and enantiopurity. One of the most elegant approach is asymmetric induction by enantiomerically pure catalysts, provided the latter are non-toxic and inexpensive, or have high turnover numbers, and lead to high enantiomeric excesses. If not, enantiomeric enrichment might add too much to the cost of drug production.[11] Alternatively, diastereoselective synthesis[13] relying on inexpensive enantiomerically pure starting materials (chiral pool) or on chiral auxiliaries that can be recycled at an early stage of a multistep synthesis remains quite often the best method in terms of toxicity and respect toward the environment. With the 'naked sugars of the first[14,15] and second generation',[16,17] the 'aza-naked sugars',[18,19] and a new reaction cascade using Umpolung with sulfur dioxide[20] our group has presented a number of methodologies that permit the quick and efficient construction of a large variety of compounds of biological interest. They can be prepared pure in both their enantiomeric forms with the same ease. Examples of applications will be reviewed here.

2. 'Naked Sugars of the First Generation': Asymmetric Syntheses of Conduramines Inhibitors of Glycosidases

The 1-cyanovinyl (1'*S*)-camphanate (derived from (1*S*)-camphanic acid and pyruvonitrile) adds to furan in the presence of ZnI_2 as catalyst. After seven days at room temperature a mixture of four possible diastereomeric Diels-Alder adducts is formed (95%) from which adduct **1** can be isolated pure by crystallization. Unreacted furan is recovered and the diastereomer mixture left from the crystallization is heated to give furan and 1-cyanovinyl (1'*S*)-camphanate that can be recycled to prepare more of the diastereomerically pure adduct **1** (the reversibility of the furan Diels-Alder addi-

*Correspondence: Prof. Dr. P. Vogel
Laboratoire de glycochimie et de synthèse asymétrique (LGSA)
Ecole Polytechnique Fédérale de Lausanne (EPFL)
Batochime
CH-1015 Lausanne-Dorigny
Tel.: + 41 21 693 93 71
Fax: + 41 21 693 93 50
E-mail: pierre.vogel@epfl.ch

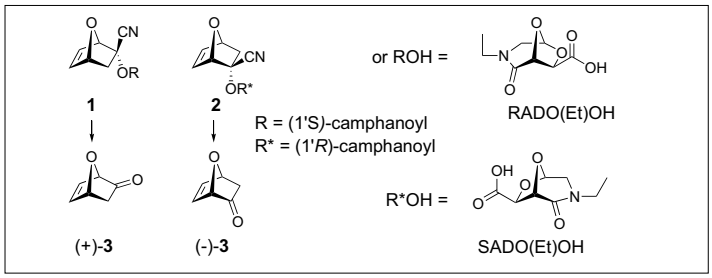


Fig.1.

tion is exploited here). Starting from (1*R*)-camphanic acid which is also commercially available, pure adduct **2** can be prepared in large quantities as readily. Camphanic acid auxiliaries can be replaced by the chiral auxiliaries (1*R*,5*S*,7*R*)-3-ethyl-2-oxo-3-aza-6,8-dioxabicyclo[3.2.1]octane-7-carboxylic acid (RADO(Et)OH) or (1*S*,5*R*,7*S*)-3-ethyl-2.oxo-3-aza-6,8-dioxabicyclo[3.2.1] octane-7-carboxylic acid (SADO(Et)OH) derived from (*R,R*)-tartaric acid and (*S,S*)-tartaric acid.[21]

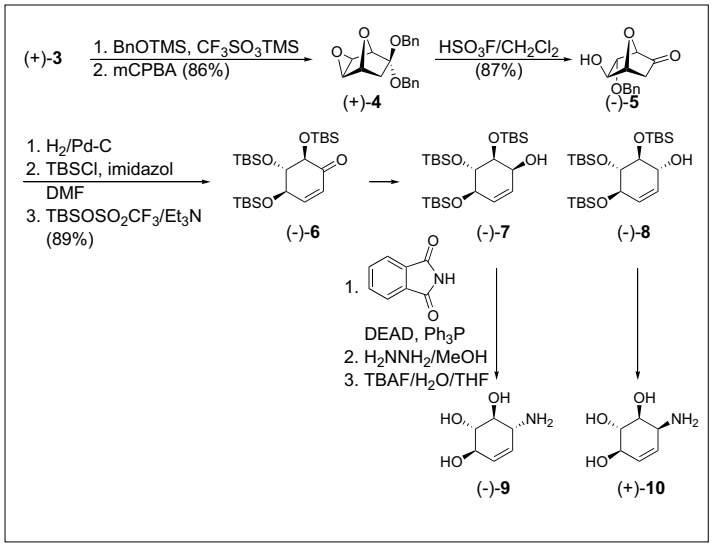
Enantiomerically pure 7-oxanorbornenyl derivatives **1** and **2** and their products of saponification (recovery of the chiral auxiliary in the aqueous phase), ketones (+)-**3** and (−)-**3** (Fig. 1), are coined 'naked sugars of the first generation' because they are chirons (= enantiomerically pure synthetic intermediates) like those derived from natural hexoses. They are enantiomerically pure like natural sugars, but with three unsubstituted (naked) carbon centers, the substitution of which follows highly stereoselective routes giving polysubstituted 7-oxabicyclo[2.2.1] heptane-2-ones that can be oxidized into the corresponding uronolactones.[22]

Benzyl acetal of (+)-**3** was epoxidized into (+)-**4**. Upon acidic treatment (+)-**4** was converted into (−)-**5**. After debenzylation, silylation and a treatment with (*t*-Bu)Me_2SiOTf/Et_3N, cyclohexenone (−)-**6** was obtained.[23] Reduction of (−)-**6** followed by Mitsunobu displacement furnished (−)-Conduramine B-1 ((−)-**8**) (Scheme 1). Its N-benzyl derivatives are selective and competitive inhibitors of β-glucosidases.[24] Enone (−)-**6** can also be converted into alcohol (−)-**9** which was then transformed into (+)-ent-Conduramine F-1 ((+)-**10**). N-benzyl derivatives of (+)-**10** are selective and competitive inhibitors of α-glucosidases.[25]

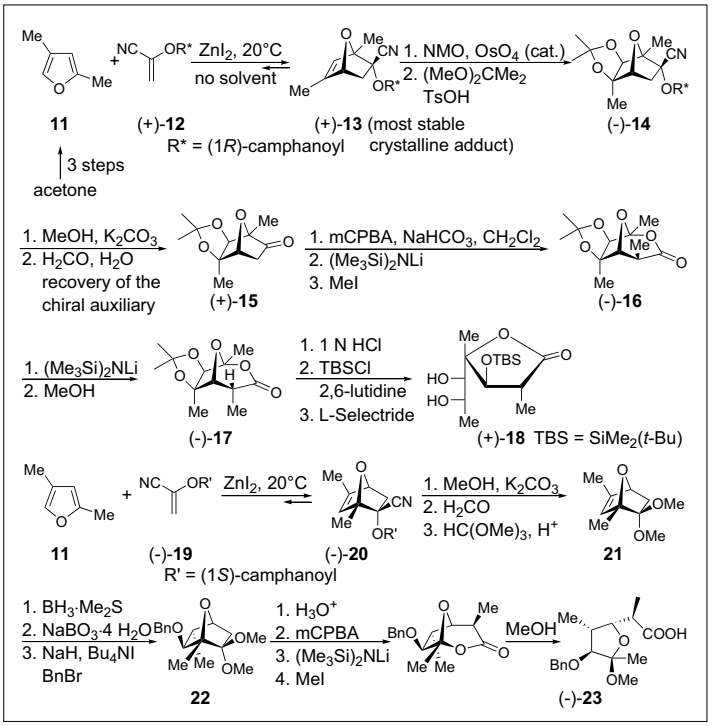
3. 'Naked Sugars of the Second Generation': Synthesis of Doubly Branched Chain Sugars and of Polypropionates

Doubly branched heptono-1,4-lactones as well as polypropionate fragments have been obtained from 2,4-dimethylfuran *via* its Diels-Alder addition to 1-cyanovinyl-(1'*R*)-camphante (+)-**12**.[16] Without solvent, the ZnI_2-catalyzed and reversible cycloaddition leads to a major crystalline diastereomeric adduct (+)-**13**. Double hydroxylation of the alkene moiety of (+)-**13**, followed by diol protection as an acetonide provides (−)-**14**. Methanolysis followed by treatment with formaline liberates ketones (+)-**15** and allows recovery of the chiral auxiliary (1*R*-camphanic acid). Baeyer-Villiger oxidation and subsequent α-methylation generates the *exo*-α-methyluronolactone (−)-**16**. Quenching of the lithium enolate of (−)-**16** with MeOH at −50 °C gives the *endo*-α-methyluronolactone (−)-**17**. Acidic hydrolysis of (−)-**17** and subsequent silylation and reduction forms (+)-**18** as major heptono-1,4-lactone (Scheme 2). Similarly, enantiomers of this doubly branched sugar can be prepared starting from adduct (−)-**20** obtained by addition of 2,4-dimethylfuran to 1-cyanovinyl (1'*S*)-camphanate (−)-**19**. After conversion of (−)-**20** into dimethyl acetal **21**, regio- and *exo*-face-selective hydroboration **19** and further transformations generate the doubly branched uronic acid.[16]

The method of thermodynamic diastereoselection (through diastereoselective crystallization of equilibrating adducts, see Scheme 2) has been applied to furan derivatives bearing chiral auxiliaries that can be recovered readily. For instance, the acetal of (2*S*,3*S*)-butane-2,3-diol and furfural is equilibrated in molten maleic anhydride with one major crystalline product.[26] In a similar way, (1*S*)-camphanate of furfuryl alcohol **24** undergoes Diels-Alder addition in molten maleic anhydride giving one major crystalline adduct (+)-**25**[27] that has been converted into doubly branched carbahexopyranoses and derivatives[28] and into



Scheme 1. Total asymmetric synthesis of (–)-conduramine B-1 ((–)-**9**) and (+)-ent-conduramine F-1 ((+)-**10**)



Scheme 2. Applications of the 'naked sugars of the second generation' to the total asymmetric synthesis of doubly branched-chain sugar derivatives and of polypionate fragments

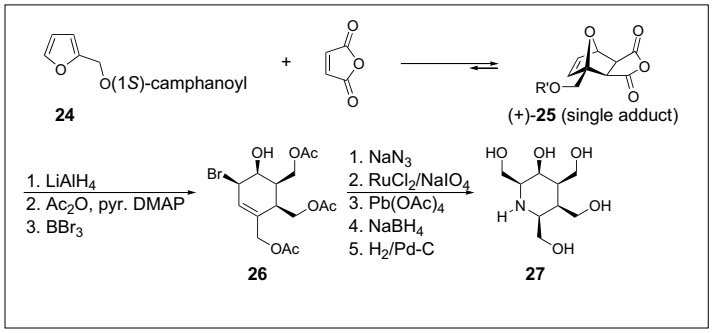
the new 2,6-dideoxy-2,6-iminoheptitol **27** (Scheme 3).[29]

4. A New Asymmetric C–C bond Forming Reaction: Umpolung with Sulfur Dioxide

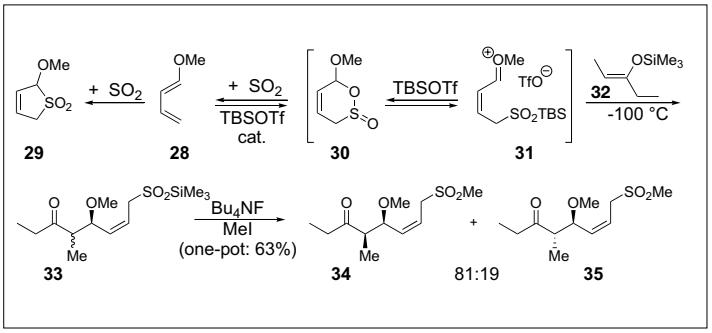
When (*E*)-1-methoxybutadiene (**28**) is reacted with a large excess of SO_2, in the absence or in the presence of a Lewis acid catalyst (*e.g.* TBSOTf) only sulfolene **29** is formed between −100 and −60 °C. At 0–20 °C quick polymerization occurs. However, when a mixture of **28** and enoxysilane **32** is reacted with SO_2 + TBSOTf at −100 °C, silyl sulfinate **33** forms. After solvent evaporation (recovery of SO_2) and treatment with Bu_4NF and MeI a 81:19 mixture of methyl sulfones **34** and **35** is obtained (100% (*Z*)-stereoselectivity).[30,31] The formation of **33** is explained by invoking the fast hetero-Diels-Alder **28** + SO_2 giving sultine **30** that is immediately heterolyzed into zwitterion **31**. In the absence of enoxysilane, it equilibrates back to **28** which finally undergoes the cheletropic addition with SO_2. In the presence of **32**, oxyallylation occurs producing **33**, and then **34** + **35** (Scheme 4). The reaction of enantiomerically enriched diene (+)-**36** (Greene's chiral auxiliary;[32] >99%) and enoxysilane **37** in SO_2 and $Yb(OTf)_3$ as catalyst, the same one-pot sequence of reaction generates (−)-**38** in 79% yield and 25:1 diastereoselectivity. Similarly, diene (−)-**39** and enoxysilane **40** (cat: $(CF_3SO_2)_2NH$), gives a 93% yield of a 14.1:1 mixture of (−)-**41** and **42** (Scheme 5).[33–35] The results (Scheme 5) are interpreted in terms of the formation of sultines **43** that are ionized into zwitterions **44** (Scheme 6). The least sterically hindered face of the diene undergoes suprafacial cycloaddition leading to unlike relative configuration between the β-alkoxy and ε-methyl group in (−)-**41** and **42**. The face of the zwitterionic intermediate *anti* with respect to the sulfinyl moiety (which is not allowed to rotate freely because of Coulombic interactions between it and the oxycarbenium moiety of **44**) adds to the enoxysilane preferentially on the face realizing minimal steric interaction with **44**. In these C–C bond forming reactions that condense two electron-rich unsaturated systems, sulfur dioxide realizes an Umpolung by converting the 1-oxy-1,3-dienes into 1-oxyallylic cationic intermediates that react with high regio- and face selectivity onto their C1 centers with nucleophilic alkenes. No direct experimental proof has been provided yet for the mechanism proposed in Scheme 6.

5. One-pot, Four-component Synthesis of Sulfones, Sulfonamides, and Sulfonic Esters

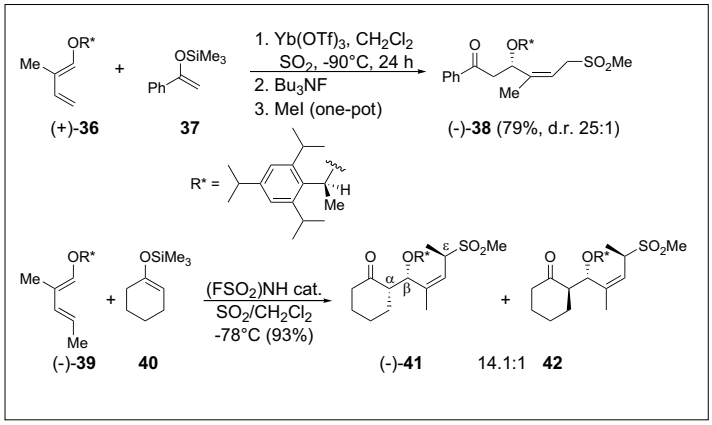
Organosulfones and sulfonamides are important compounds because of their chemical and biological properties. Other electrophiles, EX, apart from MeI (*e.g.* allyl, methallyl, arylmethyl bromides; $BrCH_2COOEt$;[36] alkyl iodides, 2,4-dinitrofluorobenzene) combine with a large variety of 1-alkoxy- or 1-trialkylsilyloxy-1,3-diene **48**, SO_2 and enoxysilanes or allylsilanes **47**, thus realizing a combinatorial, one-pot, four-component synthesis of polyfunctional sulfones **50**. If the crude silyl sulfinates **49** are oxidized with Cl_2 or N-chlorosucciminide (NCS), the corresponding sulfonyl chlorides **51** are formed that can be reacted *in situ* with primary or secondary amines to generate polyfunctional sulfonamides **52** or with alcohols, to give the corresponding sulfonic esters **53** (Scheme 7).[37,38] For the first time new medium-size heterocyclic systems such as (+)-**57** have been prepared (Scheme 8). The reaction of **54** with diene (−)-**55** (97% *ee*) in SO_2/toluene premixed with 0.3 equiv. of Tf_2NSiMe_3 at −78 °C gives a single silyl sulfinate **56**. Starting with (+)-**55** and **54** and by



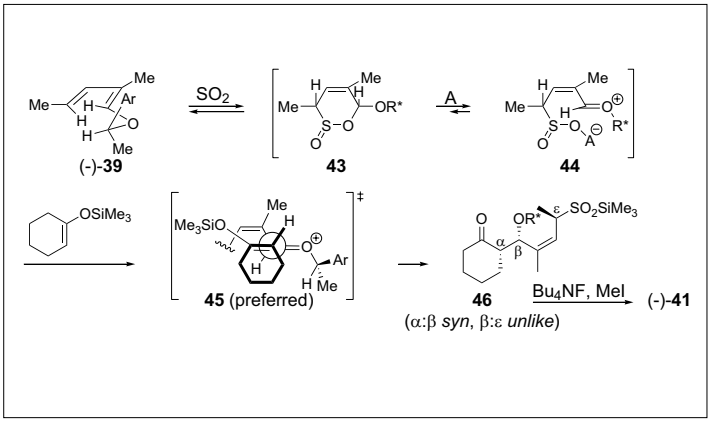
Scheme 3. Total asymmetric synthesis of a doubly-branched iminoalditol



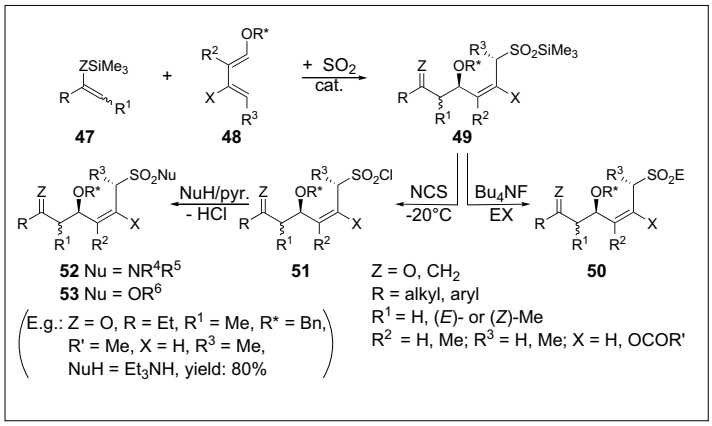
Scheme 4. Oxyallylation of enoxysilane



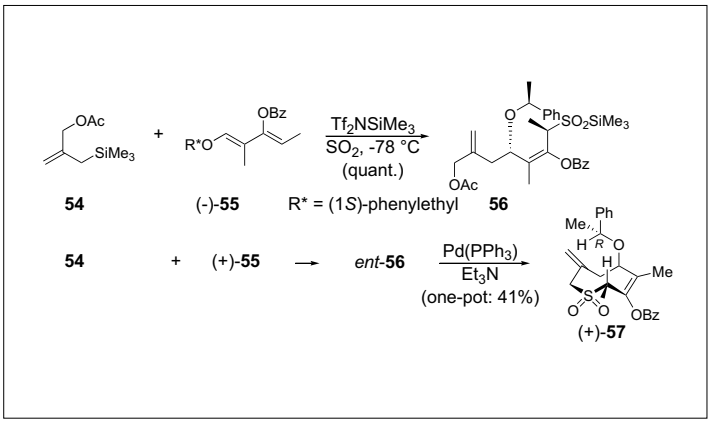
Scheme 5. Examples of one-pot, asymmetric and diastereoselective four-component synthesis of polyfunctional (*Z*)-alkenyl methyl sulfones containing up to three stereogenic centers



Scheme 6. Possible interpretation of the diastereoselectivity of the reaction cascade hetero-Diels-Alder addition, zwitterion formation and its quenching by enoxysilanes



Scheme 7. Combinatorial, one-pot, four component syntheses of sulfones, sulfonamides and sulfonic esters



Scheme 8. Syntheses of a tetrahydro-2H-thiocene derivative

treatment of the intermediate silyl sulfinate (*ent*-**56**) with $Pd(Ph_3P)$, the 2H-thiocene derivative (+)-**57** is obtained in 41% overall yield (Scheme 8).[38]

6. One-pot Synthesis of Polypropionate Stereotriads: Total Asymmetric Syntheses of Natural Polyketide Antibiotics

The thermal desulfinylation of α-substituted β,γ-unsaturated sulfinic acids is stereoselective.[39,40] This is also observed with **60** → **61** + SO_2 (Scheme 9).

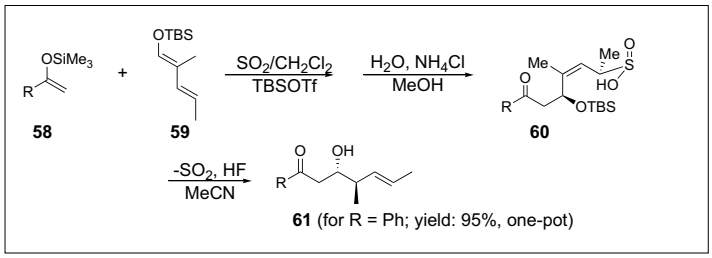
Because the desulfinylation of β,γ-unsaturated sulfinic acids requires acidic conditions (to form the sulfinic acids) it is often accompanied by elimination or/and retro-aldol reactions. Furthermore, sulfinic acids undergo disproportion.[39] We have found that the silyl sulfinate intermediates of type **49** (Scheme 7) can be desilylated by 1:1 $Pd(OAc)_2/PPh_3$ catalyst, liberating the corresponding β,γ-unsaturated sulfinic acids that undergo a palladium-catalyzed desulfinylation in the presence of K_2CO_3 and isopropanol with high yield and stereoselectivity.[41] The mechanism of the latter reaction is under investigation.

The usefulness of our one-pot polypropionate synthesis is demonstrated in the expeditious assemblies of the cyclohexanone unit **68** of baconipyrones A and B (Scheme 10),[42] and of a stereoheptad (−)-**73** corresponding to the C_{19}–C_{27}-ansa chain of Rifamycins (Scheme 11).[43]

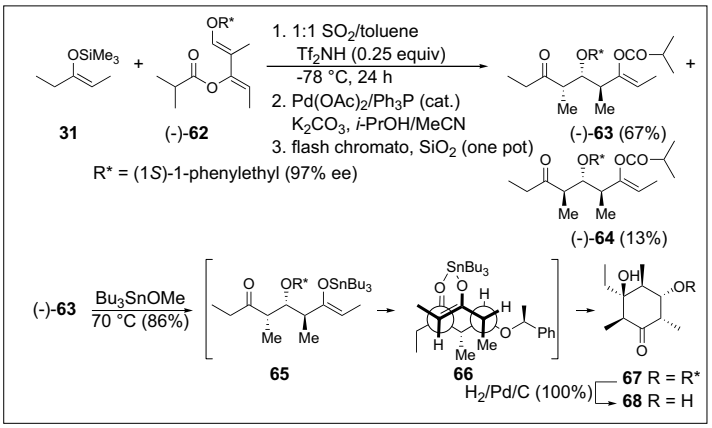
Reaction of **31** and (−)-**62** (97% *ee*) with SO_2 in toluene and Tf_2NH provides a silyl sulfinate. The residue is treated with $Pd(OAc)_2/Ph_3P$ catalyst in the presence of K_2CO_3, isopropanol and acetonitrile providing pure stereotriads (−)-**63** (67% yield) and (−)-**64** (13%). Treatment of (−)-**63** with Bu_3SnOMe at 70 °C promotes a highly stereoselective intramolecular aldol reaction giving **67**. Hydrogenolysis of **67** affords **68**. In this case, inexpensive (1*S*)-1-phenylethanol is used as chiral auxiliary to generate the starting diene (−)-**62**. The silyl (*Z*)-enol ether **69** derived from (−)-**63** reacts with 9-bromo-9-borabicyclo[3.3.1] nonane (Br-BBN) in CH_2Cl_2 (silyl/boron exchange) and then with aldehyde (+)-**70** to produce a 12.5:1 mixture of aldols (+)-**71** and 9-epimer in 81% yield. Pure (+)-**71** is reduced under Evans' conditions to give diol (−)-**72** (83%), a stereoheptad equivalent to Kishi's intermediate (−)-**73** of the asymmetric synthesis of Ryfamycin S. The latter was derived from (−)-**72** (does not have to be purified for the next step) as shown in Scheme 11. Thus, Kishi's advanced intermediate is obtained in 25% overall yield in eight steps starting from inexpensive diene (−)-**62**. The synthesis requires the isolation of only four synthetic intermediates.[43] Application of our reaction cascade to the asymmetric synthesis of the polypropionate fragment of Apoptolidin has also been successful[44] (Scheme 12).

7. Short Synthesis of the C_{16}–C_{28} Polyketide Fragment of Apoptolidin A Aglycone

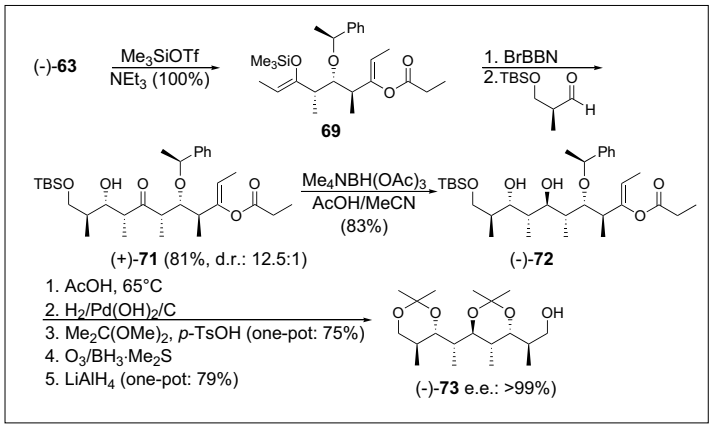
Apoptolidin A (**74**) (Fig. 2) isolated from *Nocardiopsis* sp. and natural analogues B (**75**) and C(**76**) are among the most interesting leads for cancer chemotherapy as they induce apoptosis selectively in cancer cells.[45] We have reported a very short synthesis of Nicolaou's intermediate C_1–C_{11} fragment of **71**,[46–52] applying our one-pot four-component synthesis of polyfunctional sulfones. A short synthesis of Koert's C_{16}–C_{28} fragment (**86**) of apoptolidinone A applying our new organic chemistry of sulfur dioxide is shown in Scheme 11. The enantiomerically enriched (97% *ee*) diene **77** (derived from inexpensive (*R*)-1-phenylethanol) and silyl ethers **78** (1:1 *E*/*Z* mixture) were added to a premixed solution of $(CF_3SO_2)_2NH$ in SO_2/CH_2Cl_2 (5:1) cooled to 78 °C. After stirring overnight at



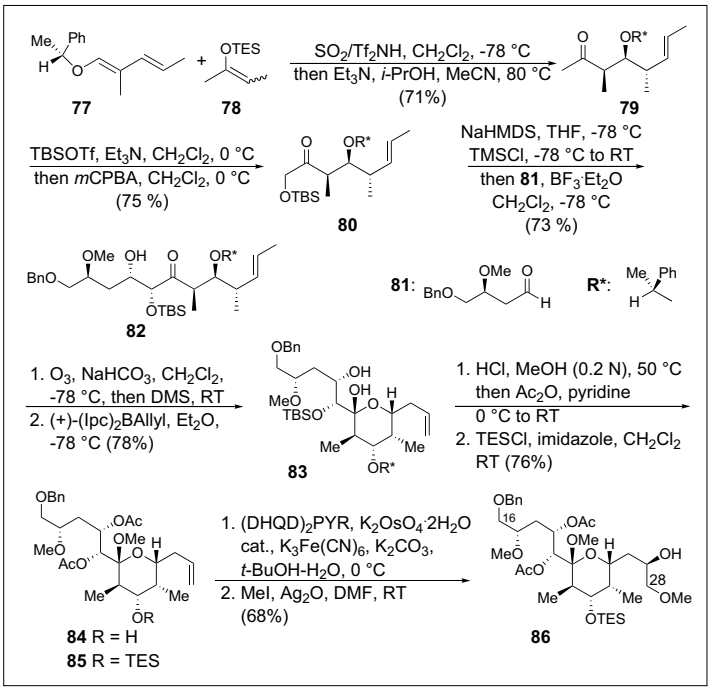
Scheme 9.



Scheme 10. Three-step synthesis of the cyclohexanone subunit of Baconipyrones A and B



Scheme 11. Expeditious asymmetric synthesis of C_{19}–C_{27}-ansa chain of Rifamycins: formal total synthesis of Rifamycin S



Scheme 12. Synthesis of Koert's C_{16}–C_{28} polyketide fragment of Apoptolidine A

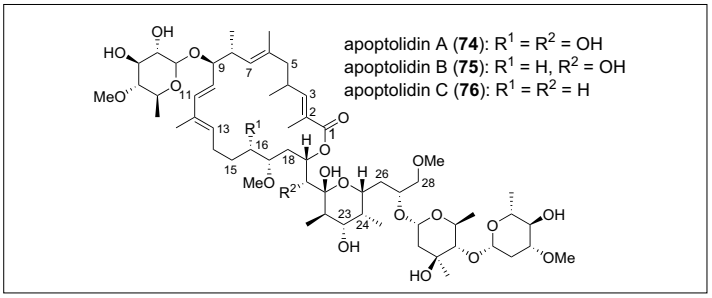


Fig. 2.

this temperature a β,γ-unsaturated silyl sulfinate formed. After recovery of the solvent (SO_2 and CH_2Cl_2) by evaporation at low temperature, *in situ* alcoholysis liberated a β,γ-unsaturated sulfinic acid that underwent stereoselective retro-ene elimination of SO_2 affording the stereotriad **79** (α,β,γ-*syn*,*anti*) and its *anti*/*anti* diastereoisomer as a 4:1 mixture. α-Hydroxylation of methyl ketone **79** (crude 4:1 mixture) was achieved by dimethyl(*tert*-butyl)silyl enol ether formation and subsequent Rubottom oxidation giving **80**. The latter underwent Mukaiyama aldol coupling with aldehyde **81** producing alkene **82** in 73% yield with 2,4,5-*anti*,*syn* relative configuration as expected by the Evans polar model.[53,54] Ozonolysis of alkene **82** provided the corresponding aldehyde which was treated under Brown's allylation conditions.[55] Acidic treatment of **83** led to desilylation, debenzylation and Fischer glycosidation giving the corresponding methyl pyranoside which was not isolated. Careful treatment of the resulting oil with Ac_2O-pyridine (0–20 °C) acetylated selectively the acyclic 1,2-diol moiety affording diacetate **84**. The cyclohexanol moiety was then silylated into silyl ether **85** under standard conditions. Sharpless asymmetric dihydroxylation[56] of the terminal akene moiety of **85** using $(DHQD)_2PYR$ ligand[57] furnished corresponding 1,2-diol. Selective monomethylation of the crude mixture using MeI-Ag_2O[58] afforded alcohol **86** (68%).

The rapid access of this advanced fragment of apoptolidin A is made possible by the utilization of our one-pot reaction cascade giving rise to functionally rich stereotriads. These quickly accessible intermediates contain both an alkyl ketone on one terminus, allowing for aldol couplings, and an alkene on the other which can readily be converted to other functionalities for chain expansion. Our synthesis of **86**, key intermediate used for the total synthesis of apoptolidin A, starts from inexpensive diene **77** and enoxysilane **78** and requires only nine steps, thus making the shortest synthesis of the C_{16}–C_{28} fragment reported to date. The method developed should enable us to prepare several analogues of biological interest.

8. Conclusion

Using readily available chiral auxiliaries such a (+)- or (–)-camphanic acid, our RADO(*R*)COCl and SADO(*R*)COCl derived from (*R,R*)- and (*S,S*)-tartaric acid, respectively, and (+)- and (–)-1-phenylethanol, efficient asymmetric synthesis of important compounds of biological have been developed. In many cases the chiral auxiliaries are recovered at an early stage of the multistep synthesis. The chemistry developed permits the attainment of high molecular complexity and diversity in terms of polyfunctionality and stereochemistry. Enantiomerically pure Diels-Alder adducts of furan and derivatives have been converted into all kinds of rare sugars and glycomimetics. A new reaction cascade starting with the hetero-Diels-Alder addition of sulfur dioxide to enantiomerically pure 1-(1(*S*)- or 1(*R*)-phenylethyloxy)-1,3-dienes generate sultines that are ionized into zwitterionic species that react at low temperature with electron-rich alkenes such as enoxysilanes producing silyl sulfinate intermediates. The latter can be converted either to enantiomerically pure, polyfunctional sulfones, sulfonamides, sulfonic esters or to polypropionate fragments containing up to three contiguous stereogenic centers in one-pot operations. The latter reaction cascade generates stereotriads that are ready for further C–C bond forming reactions including stereoselective cross-aldol condensations, thus permitting quick access to complicated polyketide and polypropionate antibiotics and analogues.

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