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Asymmetric oxidation of sulfenates to sulfinates as a new route to optically active *ortho*-phosphorylated phenyl sulfoxides

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Abstract—An asymmetric synthesis of benzenesulfinates bearing a phosphonate group at the *ortho*-position, based on the diastereoselective oxidation of the corresponding sulfenates, has been developed. For this purpose, a number of sulfenates were prepared in high yields by TFFA-promoted condensation of different chiral alcohols with a suitable sulfenyl chloride precursor. Diastereomeric excesses were determined by ^{31}P NMR spectroscopic data with the configuration of the newly created stereogenic centre being assigned through correlation and chemical studies. A practical synthesis of both enantiomers of diisopropyl (2-methylsulfinyl)phenylphosphonate **6** in enantiomeric excess close to 85% is also presented.

1. Introduction

Difunctionalized phosphorus and sulfur organic compounds have been recognized not only as useful synthetic intermediates,[1] but also as biologically relevant materials.[2] Due to their chelating features, they have been employed as ligands for transition metal complexes and in various catalytic processes.[3] Representative examples related to this work include the *ortho*-sulfanylphenylphosphonic acid **I** and its methyl sulfide derivative **II**. The former has been found active as a metallophosphatase inhibitor[4] while the latter has been involved in the preparation of a new class of platinum(II) complexes[5] designed for the treatment of solid tumours (Fig. 1). In a recent study by Natile et al., the α-sulfinylphosphonate ligand **III** was shown to act as an *O*,*S*-donor towards platinum.[6] On the other hand, Hiroi et al. demonstrated the usefulness of chiral aromatic sulfoxide ligands **IV** appended with a phosphano functionality in a Tsuji–Trost allylation reaction (ee up to 85%).[7]

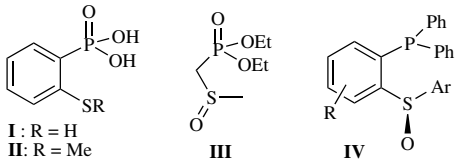

Figure 1.

Over the past few years, we have taken much interest in the design of aromatic chiral ligands possessing spatially proximate stereodefined P and/or -S atom centres. To this end, some of us developed an efficient method for the large scale preparation of (2-alkylsulfanyl)phenylphosphonic acid diesters and related P-stereogenic phenylphosphonamides. The synthesis is based on the *ortho*-lithiation of an aryl phosphorothioate or phosphorodiamidothioate, followed by migration of the phosphorylated moiety from sulfur to carbon.[8,9] To extend further the potential of this synthetic protocol and in view of the increasing importance of mixed P,S-containing compounds in coordination chemistry, we have recently focused special attention on the synthesis of optically active sulfoxide derivatives in both series. There are currently many methods for obtaining chiral

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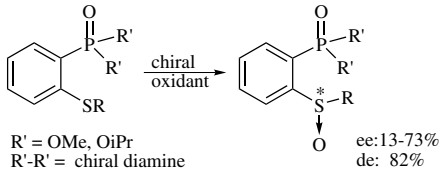
sulfoxides.[10] Among them, the resolution of a 2-sulfinylated phenylphosphonic acid monoester only gave us one enantiomerically pure sulfoxide.[11] As summarized in Scheme 1, the direct enantioselective oxidation of *o*-phosphonophenyl sulfides achieved under catalytic or stoichiometric conditions was found to occur with low to moderate selectivity. Moreover, studies on the diastereoselective oxidation of phenylsulfides which bear a defined chiral phosphonamido group[9,12] at the *ortho*-position (derived from *trans*-*N*,*N*′-dimethylcyclohexane-1,2-diamine), have shown that diastereoselection is variable, depending on the nature of the oxidizing reagent. In particular, the replacement of achiral oxidants by homochiral ones, such as Davis' oxaziridines, increases the diastereomeric excess from 15–26% up to 82%.



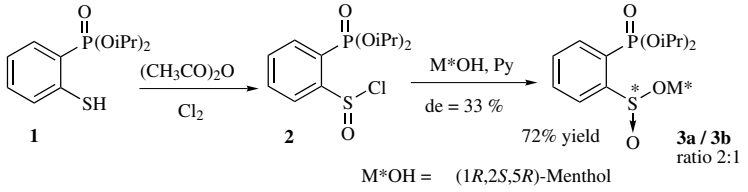
Scheme 1.

Taking into account these not fully satisfactory results we considered to study Andersen's approach, (the reaction of a chiral sulfinate and an organometallic reagent with inversion of the configuration at the sulfur atom),[13] for the preparation of optically active phenylsulfoxides bearing an *ortho*-phosphonate group. While several diastereoselective methods exist for the generation of sulfinate esters from sulfinyl chlorides and chiral alcohols,[14] the possibility of employing enantiopure sulfenates for their synthesis appealed to us as an alternative and interesting approach. To the best of our knowledge, there are only a few examples dealing with the oxidation of sulfenates. Kagan et al. reported that the modified Sharpless chiral titanium reagent was able to give optically active sulfinates with enantiomeric excesses up to 36%.[15] The self-photoinduced singlet oxygen and *m*-chloroperoxybenzoic acid oxidations of *sec*-alkyl 4-nitrobenzenesulfenates were each only slightly diastereoselective.[16] It is worth mentioning that extension of this stereoselective oxidation to sulfenamides, that is, *N*-sulfenyloxazolidinones, has been successfully used by Evans to produce chiral sulfoxides in high enantioselectivities.[17] Herein, we describe the diastereoselective oxidation of enantiopure *o*-(*O*-diisopropylphosphonyl)benzenesulfenates derived from various chiral alcohols and a suitable sulfur precursor.

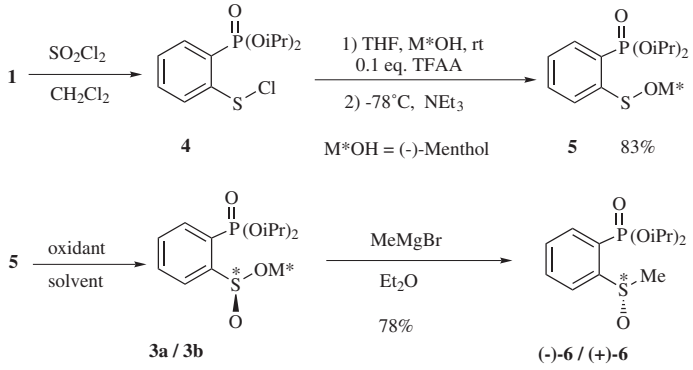
2. Results and discussion

At first, we investigated the formation of diastereomeric *O*-menthyl benzenesulfinates **3** (Scheme 2) in a Phillips-type synthesis.[13a,c,18] Accordingly, the *ortho*-mercapto phenyl-phosphonate **1** was initially converted into its sulfinyl chloride **2**, which could be further esterified without isolation by (−)-menthol using pyridine as base in ether to afford the desired sulfinate esters **3** in good yield but poor selectivity (33% de). Additionally, **3** are oils and attempts to separate both epimers failed.

Therefore, the objective herein was to prepare optically active *ortho*-phosphonylated benzenesulfenates derived from chiral alcohols and to work up oxidizing procedures through which the required diastereomeric sulfinates would be accessible with high diastereomeric excesses and chemical yields. (1*R*,2*S*,5*R*)-Menthyl benzenesulfenate **5** was chosen as the first candidate for these investigations (Scheme 3). Thus, chlorination of thiol **1**



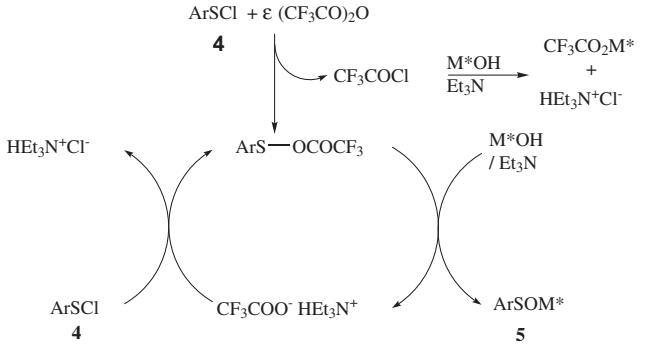
Scheme 2.



Scheme 3.

with sulfuryl chloride furnished **4**. Sulfenyl chloride **4** was condensed with (−)-menthol at 0 °C in the presence of Et_3N as previously described for the preparation of alkyl benzenesulfenates[19] to provide the desired sulfenate **5**, although, in only 20% yield.

In search of more efficient conditions, we found that the yield was dramatically improved when a catalytic amount (0.1 equiv) of trifluoroacetic anhydride (TFAA) was used as a chemical promoter. In agreement with this result, the overall nucleophilic substitution on sulfenyl chloride **4** can be confidently assumed to follow Scheme 4. According to this scheme, TFAA should give rise to a sulfenyl trifluoroacetate, a more reactive species for displacement by an alcohol. As outlined in the catalytic cycle, the generated triethylammonium trifluoroacetate salt can be viewed as being capable of acting also as a catalyst for the overall process. This hypothesis has been fully checked in separate experiments. On the other hand, it is noteworthy that the intermediate sulfenyl chloride **4** was easily generated and directly used without isolation and purification through the first reaction sequence outlined in Scheme 3.



Scheme 4.

We next examined the reaction of the enantiopure menthyl benzenesulfenate **5** with some achiral and chiral oxidizing agents. The main results of this diastereoselective oxidation leading to epimeric sulfinates **3a** and **3b** are collected in Table 1. The extent of asymmetric induction in the formation of sulfinate esters **3** was determined by analysis of the ^{31}P NMR spectra of the crude reaction mixture; the downfield diastereomeric peak represents isomer **3a**, while the upfield signal refers to **3b** (14.13 and 13.95 ppm, respectively).

The reaction of sulfenate **5** with *m*CPBA gave sulfinates **3** in 97% yield with a diastereomer ratio of only 56:44 (entry 1). The use of *N*-haloamides as oxidants, which is well established for the conversion of sulfides into sulfoxides,[20] provided higher des ranging from 40% to 76% (entries 2–5). Oxidations are nearly complete within 15 min and *N*-bromosuccinimide (NBS) is clearly the oxidant of choice in terms of selectivity. It should be pointed out that, compared to the peracid oxidation, these halogen-mediated oxidations carried out in aqueous media (THF or CH_3CN/H_2O) occurred with an opposite diastereoselectivity, **3b** being the major isomer. This stereochemical outcome can be rationalized by reference to a two-step mechanism. In agreement with the literature reports dealing with the hydrolysis of (acylamino) and (alkoxy)sulfonium salts,[21] we can reasonably speculate that the haloamide mediated oxidation of sulfenate **5** proceeds via the formation of an (alkoxy)halosulfonium cation, followed by mild deplacement of the S–X bond with a molecule of water, causing inversion of configuration at the sulfur.

The data presented in Table 1 also show that the two enantiomers of commercially available (8,8-dichlorocamphorylsulfonyl)oxaziridine, noted here (−)-Ox and (+)-Ox, afforded the 'matched' pair of diastereomers **3a** and **3b** (66% de) and the 'mismatched' pair (40% de), respectively. This effect is accompanied by an inversion of the configuration at sulfur, demonstrating that the asymmetric induction is due mainly to the incoming chiral oxaziridine and not to the menthyl group of a sulfenate. Obviously, it is reasonable to expect that the de values of sulfinates formed by oxidation of sulfenates depend on the bulkiness of the alkoxy moiety. Along this line, we briefly examined the reaction between the achiral *O*-methyl 2-(diisopropylphosphoryl)benzenesulfenate **7** and the (−)-Ox, which was found to give the corresponding sulfinate ester **8** but with only 20% ee. In addition, the oxidation with oxaziridines requires long completion times and the formation of a sulfonimine by-product makes the purification procedure less convenient. As already pointed out, oily *O*-menthyl benzenesulfinates **3a** and **3b** could not be separated as pure diastereomers by flash chromatography.

Table 1. Oxidation of (1*R*,2*S*,5*R*)-(−)-menthyl benzenesulfenate **5** into epimeric sulfinates **3**

Entry	Oxidant[a]	Solvent/temperature (°C)/time	Yield[b] (%)	Diastereomeric ratio[c] **3a/3b**	de (%)
1	*m*CPBA	CH_2Cl_2/−78 to 0/1 h	97	56/44	12
2	NCS	THF–H_2O/rt/15 min	95	30/70	40
3	NIS	MeCN–H_2O/rt/15 min	88	23/77	54
4	*N*-BPT	MeCN–H_2O/rt/15 min	92	17/83	66
5	NBS	MeCN–H_2O/rt/15 min	95	12/88	76
6	(−)-Ox	CCl_4/rt/4 days	65	17/83	66
7	(+)-Ox	CCl_4/rt/4 days	65	70/30	40

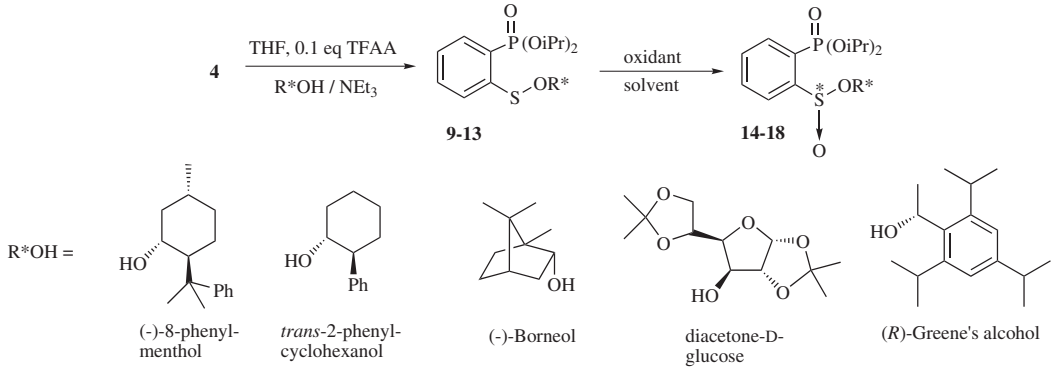
[a] *N*-Bromophthalimide (*N*-BPT). (8,8-Dichlorocamphorylsulfonyl)-oxaziridine noted (+) and (−)-Ox.
[b] Isolated yield of purified products for a complete reaction.
[c] Diastereomeric ratio based on ^{31}P NMR of the crude mixture, epimer **a** having the downfield signal.

In order to determine the configuration of the newly created stereogenic sulfinyl centre in menthyl sulfinate **3**, the diastereomerically enriched mixture with a 76% de and $\{[\alpha]_D = +10$ (c 1.0, $CHCl_3)\}$ (Table 1, entry 5) was treated with methylmagnesium bromide to afford, as expected, optically active methyl sulfoxides **6** with 76% ee (measured by HPLC analysis on a chiral column and ^1H NMR with (*R*)-(+)-*t*-butyl-phenylphosphinothioic acid[22]). Comparing the sign of the specific rotation of *o*-(*O*-diisopropylphosphonyl)phenyl methyl sulfoxide **6** $\{[\alpha]_D = -116$ (c 0.55, $CHCl_3)\}$ with the one provided in the literature for enantiopure (*R*)-(2-methylsulfinyl)phenylphosphonic dimethyl ester ($[\alpha]_D = +150.7$),[11] we were able to assign the (*S*)-absolute configuration to the sulfoxide enantiomer (−)-**6**. It follows that the major dextrorotatory diastereomer **3b** formed in the asymmetric oxidation of (−)-menthyl sulfenate **5** with NBS has an (*R*)-configuration at the sulfur. It should be pointed out that the epimer with the (*S*)-configuration at sulfur was found to predominate over the other epimer in the reaction of sulfinyl chloride **2** with (−)-menthol from an analysis of the ^{31}P NMR spectrum of a mixture **3a/3b** equals to 2:1 (Scheme 2).

Previous work on the asymmetric synthesis of menthyl sulfinates from sulfinyl chlorides and (−)-menthol under classical conditions has established that the (+)-diastereomer produced, invariably had an (*R*)-configuration at sulfur.[23]

The above results encouraged us to extend this new asymmetric oxidation of sulfenates by using chiral alcohol inductors other than (−)-menthol. They include: 8-phenylmenthol, (1*R*,2*S*)-(−)-*trans*-2-phenylcyclohexanol,[24] borneol,[25] diacetone-D-glucose[26] and (*R*)-1-(2,4,6-triisopropylphenyl)ethanol.[27] Most of them were chosen on the basis of established useful protocols for sulfinate syntheses starting from sulfinyl chlorides. By applying the TFAA-induced condensation of sulfenyl chloride **4** with these alcohols according to Scheme 3, enantiomerically pure benzenesulfenates **9**–**13** were routinely formed in yields ranging from 80% to 85% after purification. Their reactions with enantiopure oxaziridines as well as NBS or *m*CPBA were then examined. The chemical yields and diastereomeric excess values of the corresponding sulfinate esters **14**–**18**, together with other experimental data are collected in Table 2.

Table 2. Stoichiometric oxidation of chiral benzenesulfenates **9**–**13** into the corresponding epimeric sulfinates **14**–**18**



Sulfenates : **9** **10** **11** **12** **13**

Sulfinates : **14** **15** **16** **17** **18**

Entry	Chiral sulfenate[a]	Oxidant	Solvent[b]/T °C/time	Sulfinate epimers	Yield[c] (%)	Diastereomeric ratio[d] **a/b**	^{31}P NMR[e] **a/b**	de (%)
1	**9**	NBS	MeCN–H_2O/rt/10 min	**14**	70	17.5/82.5		65
2	**9**	(+)-Ox	CCl_4/rt/10 days	**14**	79	92.5/7.5	13.39/13.18	85
3	**9**	(−)-Ox	CCl_4/rt/10 days	**14**	85	9/91		82
4	**10**	NBS	MeCN–H_2O/rt/1 h	**15**	67	87/13	13.04/12.95	74
5	**10**	(+)-Ox	CCl_4/rt/4 days	**15**	76	42/58	12.54/12.51[b]	16
6	**11**	NBS	MeCN–H_2O/rt/10 min	**16**	92	62.5/37.5	13.06/12.99	25
7	**11**	(−)-Ox	CCl_4/rt/8 days	**16**	84	45/55		10
8	**12**	*m*CPBA	CH_2Cl_2/−78 to 0/1 h	**17**	94	22.5/77.5		55
9	**12**	NBS	MeCN/H_2O/rt/1 h	**17**	65	23/77	12.29/12.11	54
10	**12**	(+) or (−)-Ox	CCl_4/rt/12 days	**17**	74	27/73		46
11	**13**	*m*CPBA	THF/−78 to 0/1 h	**18**	95	69/31		38
12	**13**	(+)-Ox	CCl_4/rt/10 days	**18**	77	54.5/45.5	13.09/12.90	9
13	**13**	(−)-Ox	CCl_4/rt/7 days	**18**	85	7/93		86

[a] Substrate concentrations were about 0.05 M in all solvents. MeCN–H_2O (2:1 v/v).
[b] ^{31}P NMR spectrum taken in MeOD in entry 5.
[c] Isolated yield after purification.
[d] The diastereomeric ratio was determined by ^{31}P NMR spectral analysis at 400 MHz in $CDCl_3$ of the crude reaction products.
[e] In each case, epimer **a** has a downfield shift of the ^{31}P NMR resonance.

These compounds, easily characterized by ^{31}P NMR spectroscopy, usually absorb upfield from their dicoordinate sulfenates. As a general trend, the sulfenates, which were less stable than the sulfinates, can be stored under argon in a refrigerator for over one month with essentially no decomposition. Moreover, to reach completion for the oxidation, it took several days with oxaziridines while it took only a few minutes to 1 h with NBS or *m*CPBA.

The oxidation of chiral benzenesulfenates **9**–**13** produces a mixture of epimeric sulfinates **14**–**18** in good yields. The diastereomeric ratios of the sulfinate esters is found to be strongly dependent on the structure of substrates and again sensitive to the oxidizing reagent used. Thus, the NBS-mediated oxidation of (1*R*,2*S*,5*R*)-8-phenylmenthyl sulfenate **9** proceeded with significantly lower diastereoselectivity (Table 2, entry 1, 65% de) than the corresponding process with the parent menthyl compound **5** (Table 1, entry 5, 76% de). If we assume that the direction of the asymmetric oxidation is not really affected by the remote phenyl group on the chiral moiety, the major epimer **14b** formed should have the (*R*)-configuration at sulfur. Unexpectedly, the diastereoselectivity of the oxidation is reversed when using the sulfenate ester of (1*R*,2*S*)-*trans*-2-phenylcyclohexanol **10** with NBS providing preferentially the sulfinate epimer **15a** with 74% de (Table 2, entry 4). The sense of asymmetric induction is also inverted with (+)-Ox as seen in entry 5, compared to the result obtained in entry 2. We have no explanation at this time to account for the observed selectivity in the formation of **15**. More importantly, epimeric phenylmenthyl sulfinates **14a** and **14b** were produced with a good level of diastereocontrol using chiral oxaziridines (+)-Ox and (−)-Ox (entries 2 and 3, respectively). This suggests that the method developed herein is almost practically useful for the synthesis of phenylsulfoxide enantiomers appended with a 2-phosphonyl group. In contrast, the oxidation of bornyl sulfenate **11** by (−)-Ox occurred in an essentially stereorandom fashion (10% de, entry 7). Interesting results were obtained with the DAG benzenesulfenate ester **12**. Accordingly, **12** was converted into the corresponding sulfinates **17a** and **b** having nearly similar diastereomer ratio by reaction with either *m*CPBA, NBS or chiral oxaziridines (entries 8–10, 55–46% de), **17b** being the major diastereomer formed whatever the oxidant used. Although the diastereoselection was somewhat modest, we were pleased to isolate the major epimer as a white solid in a diastereomerically pure state by a single recrystallization from ether/pentane (1:2, v/v) with a recovery of 46%. Efforts to obtain suitable crystals of **17b** for X-ray analysis are currently in progress. The last two entries also show that the oxidation with (+)-Ox of sulfenate **13**, derived from the Greene's alcohol, proceeded in the mismatched manifold to afford a diastereomeric mixture of sulfinates **18a**,**b** in a 55/45 ratio. The reaction of (−)-Ox with **13**, which occurred in the matched manifold, gave sulfinate **18b** as a major epimer. Furthermore, since the reaction of this latter diastereomeric mixture with methylmagnesium bromide gave sulfoxide **6** with $[\alpha]_D = -145.2$ ($CHCl_3$), **18b** was concluded to have an (*R*)-configuration at sulfur.

3. Conclusion

We have reported that the oxidation of various phosphorus-based enantiopure benzenesulfenates with achiral and chiral reagents takes place under mild conditions to yield the corresponding sulfinates in high chemical yields. (−)-Menthol and *trans*-2-phenylcyclohexanol were found to be the most efficient auxiliaries using NBS as oxidant regarding diastereomeric excess (76% and 74%, respectively). The oxidation of 8-phenylmenthyl sulfenates with Davis' oxaziridines allows a practical synthesis of both enantiomers of diisopropyl 2-(methylsulfinyl)phenylphosphonate **6** in nearly 85% ee. DAG and Green's alcohol derivatives were similarly oxidized with variable diastereoselectivity. Efforts to optimize the procedure and extend the oxidation protocol to other types of derivatives are currently underway.

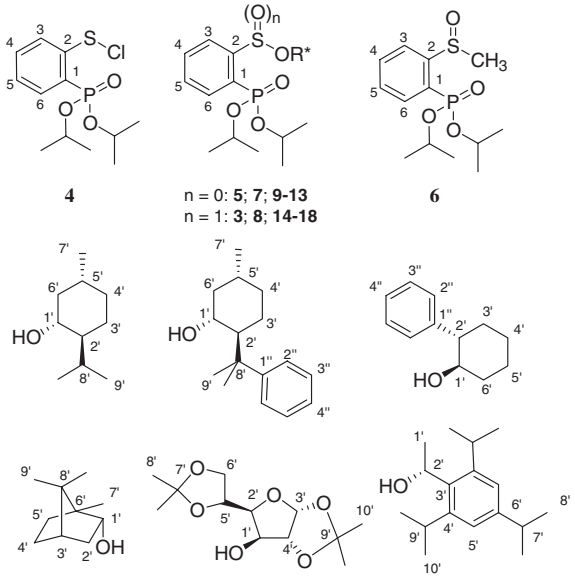
4. Experimental

4.1. General

Reactions were carried out under a nitrogen or argon atmosphere. THF was purified with a PURE-SOLV™ apparatus developed by Innovative Technology Inc. Et_3N was distilled over CaH_2. CCl_4 was distilled over P_2O_5 and stored over $CaCl_2$ under a nitrogen atmosphere. The synthesis of diisopropyl 2-(sulfanyl)phenylphosphonate **1** has been described previously.[11]

NMR spectra were recorded in $CDCl_3$, unless otherwise stated, on Brüker spectrometers at 250, 400 or 500 MHz. Chemical shifts δ were indicated in ppm using TMS as the internal standard or H_3PO_4 as the external standard for ^{31}P NMR spectra. Coupling constants *J* are given in hertz (Hz). ^{13}C $\{^1H\}$ NMR spectra were recorded at 62.9, 100.6 or 125.7 MHz and ^{31}P $\{^1H\}$ NMR spectra at 101.2, 161.9 or 202 MHz. Mass spectra were obtained on a GC/MS Saturn 2000 or on a Waters QTOF micro. Optical rotation values were measured on a Perkin–Elmer 241 automatic polarimeter. IR spectra were recorded with a Perkin–Elmer 16 PC FT-IR instrument. Satisfactory analytical data were obtained using a THERMOQUEST NA 2500 instrument. Thin layer chromatography (TLC) were performed on silica gel 60 F_{254}, with UV or 5% potassium permanganate solution detections. Flash chromatography was achieved on silica gel columns (40–63 μm) using nitrogen pressure. HPLC analysis of mixture of enantiomeric sulfoxides **6** was performed on a Column Daicel Chiralpak AD-H 250 mm × 4.6 mm × 5 μm. Flow: 1 mL/min. Column temperature: 20 °C. Eluent 80% *n*-heptane/20% propanol-2, PDA 207.0 nm, $t_0 =$ 3.34 min; $t_a = 5.53$ min; $t_b =$ 7.55 min.

Numeral identifications of carbon atoms for compounds listed above are arbitrary and given only for helping the description of NMR spectra.



4 n = 0: **5**; **7**; **9-13** n = 1: **3**; **8**; **14-18** 6

4.2. Typical procedure for the synthesis of sulfenates

To a stirred solution of diisopropyl 2-(sulfanyl)-phenylphosphonate **1** (2 g, 7.29 mmol) in dichloromethane (20 mL) was slowly added sulfuryl chloride (0.76 mL, 9.48 mmol) under nitrogen flow. The solution was stirred for 30 min at room temperature. After evacuation of the solvent and gases, THF (25 mL) was added followed by menthol (1.140 g, 7.29 mmol) and trifluoroacetic anhydride (103 μL, 0.73 mmol). After cooling to −78 °C, triethylamine (2.03 mL; 14.6 mmol) was added. The reaction mixture was allowed to reach room temperature, stirred for one another hour and then hydrolyzed with a 5% solution of H_2SO_4. The aqueous layer was extracted with diethyl ether. The combined extracts were washed successively with a 5% solution of K_2CO_3 and brine, dried over $MgSO_4$ and concentrated. The resulting oil was purified by silica gel chromatography with pentane–ethyl acetate as eluent to yield enantiopure menthyl sulfenate **5** in 83% yield.

This procedure was extended to the synthesis of sulfenate esters **9**–**13** with chemical yields ranging from 75% to 85%.

4.2.1. Diisopropyl 2-(chlorosulfinyl)phenylphosphonate 4. Conversion: 100%. Orange liquid. ^{1}H NMR (250 MHz): δ 1.16 (d, 6H, $^3J_{HH} = 6.2$); 1.31 (d, 6H, $^3J_{HH} = 6.2$); 4.68 (dsept, 2H, $^3J_{HH} = 6.2$, $^3J_{HP} = 8.8$); 7.21–7.31 (m, 1H); 7.46–7.57 (m, 1H); 7.57–7.82 (m, 2H). ^{31}P NMR (101 MHz): δ 17.4. ^{13}C NMR (62.9 MHz): δ 24.0 (d, $^3J = 5.0$, CH_3); 24.3 (d, $^3J = 3.8$, CH_3); 73.2 (d, $^2J = 5.7$, CH); 115.4 (d, $^1J = 286.2$, C_1); 126.9 (d, $^2J = 14.6$, C_6); 127.7 (d, $^3J = 6.3$, C_5); 133.7 (d, $^4J = 2.5$, C_4); 133.9 (d, $^3J = 8.8$, C_3); 141.8 (d, $^2J = 8.8$, C_2).

4.2.2. (−)-Menthyl 2-(diisopropylphosphoryl)benzenesulfenate 5. Yield 83%. Colourless oil. $[\alpha]_D = -105$ (*c* 1, $CHCl_3$). ^{1}H NMR (250 MHz): δ 0.82 (d, 3H, $^3J_{HH} = 6.9$); 0.88 (d, 3H, $^3J_{HH} = 7.0$); 0.96 (d, 3H, $^3J_{HH} = 6.5$); 1.23 (d, 6H, $^3J_{HH} = 6.1$); 1.39 (d, 6H, $^3J_{HH} = 6.1$); 0.80–1.08 (m, 2H); 1.20–1.47 (m, 3H); 1.61–1.70 (m, 2H); 2.33–2.45 (m, 2H); 3.48 (dt, 1H, $^3J_{HH} = 4.1$, $^3J_{HH} = 10.7$); 4.61–4.78 (m, 2H); 7.14 (ddt, 1H, $^3J_{HH} = 7.4$, $^4J_{HH} = 1.0$, $^4J_{HP} = 3.3$); 7.45–7.49 (m, 1H); 7.65–7.79 (m, 2H). ^{31}P NMR (101.2 MHz): δ 16.4. ^{13}C NMR (62.9 MHz): δ 16.6 (s, $C_{9'}$); 21.7 (s, $C_{9'}$); 22.7 (s, $C_{7'}$); 23.8 (s, $C_{3'}$); 24.3 (d, $^3J = 3.2$, CH_3); 24.7 (d, $^3J = 3.9$, CH_3); 26.0 (s, $C_{8'}$); 32.4 (s, $C_{4'}$); 34.8 (s, $C_{5'}$); 41.5 (s, $C_{6'}$); 49.6 (s, $C_{2'}$); 71.8 (d, $^2J = 5.0$, CH); 71.9 (d, $^2J = 4.8$, CH); 87.6 (s, $C_{1'}$); 122.2 (d, $^1J = 189.9$, C_1); 122.9 (d, $^3J = 13.2$, C_5); 125.5 (d, $^3J = 13.2$, C_3); 132.5 (d, $^4J = 3.1$, C_4); 134.0 (d, $^2J = 8.8$, C_6); 149.5 (d, $^2J = 10.1$, C_2). IR (NaCl) cm^{-1}: 2955; 2870; 1580; 1450; 1424; 1385; 1373; 1250 (νP=O); 1103; 980 (νP–O); 764 (νS–O). MS *m*/*z* (%): 429 (MH^+; 58); 290 (100); 273 (31); 249 (33); 206 (95); 189 (99); 136 (12). Analysis for $C_{22}H_{37}O_4PS$: calculated (C: 61.66; H: 8.70); found (C: 61.40; H: 9.04).

4.2.3. Methyl 2-(diisopropylphosphoryl)benzenesulfenate 7. Yield 87%. Colourless liquid. ^{1}H NMR (250 MHz): δ 1.23 (d, 6H, $^3J_{HH} = 6.2$); 1.38 (d, 6H, $^3J_{HH} = 6.2$); 3.78 (s, 3H); 4.67 (dsept, 2H, $^3J_{HH} = 6.2$, $^3J_{HP} = 7.8$); 7.14–7.21 (m, 1H); 7.49–7.59 (m, 2H); 7.70–7.78 (m, 1H). ^{31}P NMR (101 MHz): δ 16.6. ^{13}C NMR (62.9 MHz): δ 24.0 (d, $^3J = 4.8$, CH_3); 24.4 (d, $^3J = 3.9$, CH_3); 65.4 (s, CH_3–O); 71.7 (d, $^2J = 5.3$ Hz, CH); 120.6 (d, $^3J = 13.2$, C_5); 122.2 (d, $^1J = 189.3$, C_1); 124.5 (d, $^3J = 13.2$, C_3); 132.8 (d, $^4J = 2.5$, C_4); 134.0 (d, $^2J = 8.8$, C_6); 147.9 (d, $^2J = 10.7$, C_2). IR (NaCl) cm^{-1}: 2977; 2931; 1580; 1449; 1423; 1385; 1374; 1245 (νP=O); 1143; 1102; 987 (νP–O); 760 (νS–O). GC/MS *m*/*z* (%): 305 (MH^+; 48); 304 (M^+; 100); 274 (24); 273 (74); 206 (95); 190 (45); 189 (82). Analysis for $C_{13}H_{21}O_4PS$: calculated (C: 51.30; H: 6.95); found (C: 51.00; H: 6.82).

4.2.4. L-8-Phenylmenthyl 2-(diisopropylphosphoryl)benzenesulfenate 9. Yield 81%. White solid. Mp: 71 °C. $[\alpha]_D = +40.0$ (*c* 0.5, $CHCl_3$). ^{1}H NMR (400 MHz): δ 0.66–1.14 (m, 3H); 0.78 (d, 3H, $^3J_{HH} = 6.5$); 1.23 (d, 3H, $^3J_{HH} = 6.2$); 1.25 (d, 3H, $^3J_{HH} = 6.2$); 1.22–1.61 (m, 3H); 1.42 (d, 3H, $^3J_{HH} = 5.6$); 1.44 (d, 3H, $^3J_{HH} = 5.9$); 1.47 (s, 3H); 1.58 (s, 3H); 1.92–1.98 (m, 1H); 2.09–2.18 (m, 1H); 3.65 (dt, 1H, $^3J_{HH} = 10.4$, $^3J_{HH} = 6.8$); 4.70 (dsept, 2H, $^3J_{HP} = 6.0$, $^3J_{HH} = 6.2$); 7.10–7.21 (m, 2H); 7.27–7.40 (m, 4H); 7.46 (t, 1H, $^3J_{HH} = 7.4$); 7.56 (m, 1H, $^3J_{HH} = 7.8$); 7.72 (ddt, 1H, $^3J_{HH} = 7.2$, $^3J_{HP} = 13.4$, $^4J_{HH} = 1.3$). ^{31}P NMR (162 MHz): δ 15.8. ^{13}C NMR (100.6 MHz): δ 22.4 (s, $C_{7'}$); 24.1 (d, $^3J = 4.5$, CH_3); 24.2 (d, $^3J = 4.4$, CH_3); 24.5 (s, $C_{9'}$); 25.1 (s, $C_{9'}$); 28.0 (s, $C_{3'}$); 30.3 (s, $C_{5'}$); 32.2 (s, $C_{4'}$); 35.0 (s, $C_{6'}$); 40.9 (s, $C_{8'}$); 53.2 (s, $C_{2'}$); 71.6 (d, $^2J = 5.4$, CH); 71.7 (d, $^2J = 5.1$, CH); 89.5 (s, $C_{1'}$); 121.2 (d, $^1J = 189.2$, C_1); 122.8 (d, $^3J = 12.9$, C_5); 124.0 (d, $^3J = 13.7$, C_3); 125.6 (s, $C_{4''}$); 126.3 (s, $C_{2''}$); 128.3 (s, $C_{3''}$); 132.2 (d, $^4J = 2.4$, C_4); 133.5 (d, $^2J = 8.8$, C_6); 150.1 (d, $^2J = 10.3$, C_2); 151.2 (s, $C_{1''}$). IR (KBr) cm^{-1}: 2975; 1448; 1243; 981; 759. MS *m*/*z* (%): 527 (M+Na; 15); 313 (100); 271 (33); 229 (8). HRMS calculated for $C_{28}H_{41}O_4PSNa$ (M+Na): 527.2361; found 527.2371.

4.2.5. (1*R*,2*S*)-*trans*-2-Phenyl-1-cyclohexyl 2-(diisopropylphosphoryl)benzenesulfenate 10. Yield 79%. Colourless

oil. $[\alpha]_D = -149.5$ (c 1, $CHCl_3$). ^1H NMR (250 MHz): δ 1.18 (d, 6H, $^3J_{HH} = 6.2$); 1.35 (d, 6H, $^3J_{HH} = 6.2$); 1.25–1.70 (m, 4H); 1.72–1.80 (m, 1H); 1.86–1.98 (m, 2H); 2.51–2.79 (m, 2H); 3.51 (dt, 1H, $^3J_{HH} = 10.1$, $^3J_{HH} = 4.0$); 4.63 (dsept, 2H, $^3J_{HP} = 7.5$, $^3J_{HH} = 6.2$); 6.30 (tt, 1H, $^3J_{HH} = 5.5$, $^4J_{HH} = 0.9$); 6.90–6.99 (m, 2H); 7.25–7.39 (m, 5H); 7.63 (ddd, 1H, $^3J_{HH} = 6.5$, $^3J_{HP} = 14.0$, $^4J_{HH} = 2.1$). ^{31}P NMR (100.1 MHz): δ 16.5. ^{13}C NMR (62.9 MHz): δ 24.1 (d, $^3J = 5.0$, CH_3); 24.4 (d, $^3J = 3.8$, CH_3); 25.3 (s, $C_{5'}$); 26.2 (s, $C_{4'}$); 33.1 (s, $C_{6'}$); 33.7 (s, $C_{3'}$); 51.7 (s, $C_{2'}$); 71.4 (d, $^2J = 5.0$, CH); 71.6 (d, $^2J = 5.7$, CH); 89.6 (s, $C_{1'}$); 121.5 (d, $^1J = 189.3$, C_1); 122.2 (d, $^3J = 12.6$, C_5); 123.0 (s, $C_{4''}$); 123.9 (d, $^3J = 13.8$, C_3); 127.0 (s, $C_{2''}$); 128.7 (s, $C_{3''}$); 132.5 (d, $^4J = 2.5$, C_4); 133.6 (d, $^2J = 8.2$, C_6); 144.2 (s, $C_{1''}$); 148.2 (d, $^2J = 10.1$, C_2). IR (NaCl) cm^{-1}: 2976; 1447; 1245; 980. MS m/z (%): 449 (MH^+; 31); 407 (27); 365 (11); 291 (97); 273 (13); 249 (100); 231 (22); 207 (32); 159 (8). HRMS calculated for $C_{24}H_{34}O_4PS$ (M+H): 449.1915; found 449.1914.

4.2.6. (*S*)-Bornyl 2-(diisopropylphosphoryl)benzenesulfenate 11. Yield 81%. Colourless oil. $[\alpha]_D = -38.5$ (c 0.74, $CHCl_3$). ^1H NMR (250 MHz): δ 0.78 (s, 3H); 0.86 (s, 3H); 1.02 (s, 3H); 1.23 (d, 6H, $^3J_{HH} = 6.2$); 1.27–1.31 (m, 1H); 1.38 (d, 6H, $^3J_{HH} = 6.2$); 1.64–1.78 (m, 4H); 2.05–2.11 (m, 1H); 2.24–2.31 (m, 1H); 3.91–3.97 (m, 1H); 4.66 (dsept, 2H, $^3J_{HP} = 11.8$, $^3J_{HH} = 6.2$); 7.14 (ddt, 1H, $^4J_{HP} = 8.3$, $^3J_{HH} = 7.3$, $^4J_{HH} = 1.4$); 7.46–7.59 (m, 2H); 7.76 (ddd, 1H, $^3J_{HP} = 14.1$, $^3J_{HH} = 7.4$, $^4J_{HH} = 1.1$). ^{31}P NMR (101 MHz): δ 16.3. ^{13}C NMR (62.9 MHz): δ 14.4 (s, $C_{7'}$); 19.2 (s, $C_{9'}$); 20.2 (s, $C_{9'}$); 24.1 (d, $^3J = 5.0$, CH_3); 24.4 (d, $^3J = 3.8$, CH_3); 26.7 (s, $C_{4'}$); 28.5 (s, $C_{5'}$); 37.8 (s, $C_{2'}$); 45.3 (s, $C_{3'}$); 48.9 (s, $C_{8'}$); 50.7 (s, $C_{6'}$); 71.6 (d, $^2J = 10.0$, CH); 93.7 (s, $C_{1'}$); 121.5 (d, $^2J = 10.0$, C_6); 121.9 (d, $^1J = 189.3$, C_1); 124.2 (d, $^3J = 13.8$, C_3); 132.5 (d, $^4J = 3.1$, C_4); 134.1 (d, $^3J = 8.8$, C_5); 148.9 (d, $^2J = 10.1$, C_2). IR (NaCl) cm^{-1}: 1579; 1244; 980. MS m/z (%): 427 (MH^+; 67); 290 (100); 273 (23); 249 (32); 207 (83); 189 (64); 154 (9); 137 (40); 109 (8). HRMS calculated for $C_{22}H_{36}O_4PS$ (M+H): 427.2072; found 427.2072.

4.2.7. (Diacetone-D-glucosyl) 2-(diisopropylphosphoryl)-benzenesulfenate 12. Yield 81%. Colourless oil. $[\alpha]_D = -139.1$ (c 1, $CHCl_3$). ^1H NMR (500 MHz): δ 1.20 (d, 6H, $^3J_{HH} = 6.2$); 1.23 (d, 6H, $^3J_{HH} = 6.2$); 1.27 (s, 3H); 1.36–1.38 (m, 6H); 1.43 (s, 3H); 3.98–4.03 (m, 1H); 4.07–4.11 (m, 1H); 4.15–4.19 (m, 2H); 4.47–4.53 (m, 1H); 4.66 (dsept, 2H, $^3J_{HH} = 6.2$, $^3J_{HP} = 7.7$); 4.88 (d, 1H, $^3J_{HH} = 6.4$); 5.89 (d, 1H, $^3J_{HH} = 3.7$); 7.18 (dt, 1H, $^3J_{HH} = 7.2$, $^4J_{HP} = 2.9$); 7.47 (t, 1H, $^3J_{HH} = 7.3$); 7.70 (ddd, 1H, $^3J_{HH} = 7.4$, $^3J_{HP} = 13.7$, $^4J_{HH} = 1.1$); 7.86 (dd, 1H, $^3J_{HH} = 8.0$, $^4J_{HP} = 5.7$). ^{31}P NMR (202 MHz): δ 16.8. ^{13}C NMR (125 MHz): δ 23.6 (d, $^3J = 4.8$, CH_3); 24.0 (d, $^3J = 4.9$, CH_3); 25.5 (s, $C_{8'}$); 26.1 (s, $C_{8'}$); 26.6 (s, $C_{10'}$); 26.9 (s, $C_{10'}$); 67.8 (s, $C_{5'}$); 71.4 (d, $^2J = 5.0$, CH); 71.5 (d, $^2J = 5.4$, CH); 71.7 (s, $C_{5'}$); 81.4 (s, $C_{4'}$); 83.2 (s, $C_{1'}$); 86.1 (s, $C_{2'}$); 104.8 (s, $C_{3'}$); 109.3 (s, $C_{7'}$); 111.9 (s, $C_{9'}$); 121.8 (d, $^3J = 12.5$, C_3); 122.0 (d, $^1J = 189.3$, C_1); 124.5 (d, $^3J = 12.5$, C_5); 132.3 (s, C_4); 133.3 (d, $^2J = 8.4$, C_6); 146.3 (d, $^2J = 10.3$, C_2). IR (NaCl) cm^{-1}: 1217; 986. MS m/z (%): 532 (M^+; 28); 475 (11); 293 (73); 273 (75); 249 (16); 231 (32); 207 (35); 189 (100); 154 (12); 101 (14). Analysis for $C_{24}H_{37}O_{10}PS$: calculated (C: 54.12; H: 7.00); found: (C: 53.98; H: 7.49).

4.2.8. (2,4,6-Triisopropylphenyl)-2-(*R*)-ethyl 2-(diisopropylphosphoryl)benzenesulfenate 13. Yield 80%. Colourless oil. $[\alpha]_D = +54.7$ (c 0.85, $CHCl_3$). ^1H NMR (500 MHz): δ 1.16 (d, 6H, $^3J_{HH} = 6.2$); 1.20 (d, 6H, $^3J_{HH} = 6.3$); 1.25 (d, 6H, $^3J_{HH} = 7.0$); 1.28 (d, 6H, $^3J_{HH} = 6.1$); 1.33 (d, 6H, $^3J_{HH} = 6.2$); 1.76 (d, 3H, $^3J_{HH} = 6.8$); 2.86 (sept, 1H, $^3J_{HH} = 6.9$); 3.77–3.80 (m, 2H); 4.61 (dsept, 2H, $^3J_{HP} = 7.9$, $^3J_{HH} = 7.1$); 5.20 (qd, 1H, $^3J_{HH} = 6.9$); 7.00 (s, 2H); 7.12 (dt, 1H, $^3J_{HH} = 7.6$, $^4J_{HP} = 3.1$); 7.42 (t, 1H, $^3J_{HH} = 7.2$); 7.46–7.49 (m, 1H); 7.73 (ddd, 1H, $^3J_{HP} = 14.1$, $^3J_{HH} = 7.5$, $^4J_{HH} = 1.1$). ^{31}P NMR (202 MHz): δ 16.6. ^{13}C NMR (126 MHz): δ 22.9 (s, $C_{8'}$); 23.5 (d, $^3J = 4.7$, $CH_3(CH)$); 23.9 (d, $^3J = 4.8$, $CH_3(CH)$); 23.9 (s, $C_{10'}$); 24.0 (s, $C_{10'}$); 25.2 (s, $C_{9'}$); 29.2 (s, $C_{1'}$); 34.0 (s, $C_{7'}$); 71.1 (d, $^2J = 5.4$, CH); 71.3 (d, $^2J = 5.3$, CH); 82.0 (s, $C_{2'}$); 120.9 (d, $^3J = 12.9$, C_3); 121.3 (d, $^1J = 191.4$, C_1); 123.3 (s, $C_{5'}$); 123.7 (d, $^3J = 13.7$, C_5); 132.2 (s, $C_{3'}$); 133.1 (s, C_4); 133.7 (d, $^2J = 8.7$, C_6); 140.9 (s, $C_{6'}$); 148.0 (s, $C_{4'}$); 148.5 (d, $^2J = 10.6$, C_2). MS m/z (%): 521 (MH^+; 5); 291 (16); 231 (100); 189 (7); 147 (4). IR (NaCl) cm^{-1}: 1578; 1244; 986. HRMS calculated for $C_{29}H_{46}O_4PS$ (M+H): 521.2854; found 521.2846.

4.3. Typical oxidation procedures of chiral sulfenates with NBS in CH_3CN–H_2O

NBS (208 mg, 1.17 mmol) was added portionwise to a stirred solution of menthyl sulfenate **5** (500 mg, 1.17 mmol) in a mixture of acetonitrile and water 2/1. The concentration of sulfenate ester was ca. 5×10^{-2} M. After addition, stirring was continued for 5–60 min and the mixture was quenched by adding a 5% solution of H_2SO_4. The aqueous layer was extracted three times with dichloromethane. The organic phase was successively washed out with a 5% aqueous solution of potassium carbonate and 5% sodium thiosulfate in water. After drying and evaporation of the organic solvent, the crude extract, whose purity was usually satisfactory as shown by the NMR spectrum, was purified on a silica gel column with pentane–ethyl acetate as eluent to provide epimeric menthyl sulfinates **3a** and **3b** (493 mg).

With chiral Davis oxaziridines: A chiral oxaziridine (69 mg, 0.23 mmol) was added portionwise to a stirred solution of sulfenate ester **5** (100 mg, 0.23 mmol) in carbon tetrachloride (3–4 mL) under a nitrogen atmosphere. After complete conversion, the solvent was evaporated and the residue dissolved in pentane. The mixture was filtered and washed once with pentane. The sulfinate was further purified on silica gel chromatography if necessary.

With *m*CPBA: Sulfenate ester **5** (200 mg, 0.47 mmol) was oxidized by the addition of 108 mg (0.47 mmol, 75% purity) of *m*CPBA in CH_2Cl_2 or THF at −78 °C. The reaction was allowed to reach room temperature.

The solvent was evaporated and the crude sulfinate directly purified by silica gel chromatography.

4.3.1. (−)-Menthyl 2-(diisopropylphosphoryl)benzenesulfinate 3. Yield 95%. Colourless oil. $[\alpha]_D = +10.0$ (c 1, $CHCl_3$); dr: 12/88. NMR of the major diastereomer: ^1H (250 MHz): δ 0.71 (d, 3H, $^3J_{HH} = 6.9$); 0.82 (d, 3H, $^3J_{HH} = 7.0$); 0.90 (d, 3H, $^3J_{HH} = 6.3$); 1.23 (d, 3H, $^3J_{HH} = 6.0$); 1.26 (d, 3H, $^3J_{HH} = 6.0$); 1.39 (d, 3H, $^3J_{HH} = 6.2$); 1.42 (d, 3H, $^3J_{HH} = 6.2$); 0.80–1.43 (m, 4H); 1.61–1.67 (m, 2H); 1.90–2.10 (m, 3H); 4.22 (dt, 1H, $^3J_{HH} = 10.7$, $^3J_{HH} = 4.5$); 4.67–4.90 (m, 2H); 7.57 (ddt, 1H, $^3J_{HH} = 7.7$, $^4J_{HH} = 1.2$, $^4J_{HP} = 3.2$); 7.74 (tt, 1H, $^3J_{HH} = 7.7$); 7.92 (ddd, 1H, $^3J_{HH} = 7.7$, $^4J_{HH} = 1.2$, $^3J_{HP} = 13.6$); 8.24 (ddd, 1H, $^3J_{HH} = 7.7$, $^4J_{HH} = 1.2$, $^4J_{HP} = 4.9$). ^{31}P (101.2 MHz): δ 13.95. ^{13}C (62.9 MHz): δ 16.3 (s, $C_{9'}$); 21.3 (s, $C_{9'}$); 22.7 (s, $C_{9'}$); 23.7 (s, $C_{3'}$); 24.1 (d, $^3J = 4.9$, CH_3); 24.2 (d, $^3J = 4.9$, CH_3); 24.4 (d, $^3J = 3.9$, CH_3); 24.5 (d, $^3J = 3.9$, CH_3); 25.7 (s, $C_{8'}$); 32.2 (s, $C_{4'}$); 34.4 (s, $C_{5'}$); 43.4 (s, $C_{6'}$); 48.6 (s, $C_{2'}$); 72.0 (d, $^2J = 6.0$, CH); 72.2 (d, $^2J = 5.8$, CH); 80.4 (s, $C_{1'}$); 124.7 (d, $^3J = 11.9$, C_3); 128.0 (d, $^1J = 188.7$, C_1); 131.4 (d, $^3J = 13.2$, C_5); 133.3 (d, $^2J = 12.0$, C_6); 133.4 (d, $^4J = 3.1$, C_4); 149.5 (d, $^2J = 10.0$, C_2). Minor diastereomer: ^1H (250 MHz): δ 4.10–4.20 (m, 1H); 4.42–4.59 (m, 2H). ^{31}P (101.2 MHz): δ 14.13. ^{13}C (62.9 MHz): δ 79.5 (s, $C_{1'}$). IR (NaCl) cm^{-1}: 2954; 2869; 1582; 1454; 1386; 1374; 1255 (νP=O); 1178; 1128 (νS=O); 1103; 982 (νP–O); 757 (νS–O). MS m/z (%): 445 (MH^+; 31); 307 (21); 289 (12); 247 (20); 206 (20); 205 (100); 159 (10). HRMS calculated for $C_{22}H_{38}O_5PS$ (M+H): 445.2178 found: 445.2173.

4.3.2. Methyl 2-(diisopropylphosphoryl)benzenesulfinate 8. Yield 66%. Colourless liquid. ee: 20%. ^1H NMR (250 MHz): δ 1.25 (d, 3H, $^3J_{HH} = 6.2$); 1.26 (d, 3H, $^3J_{HH} = 6.2$); 1.40 (d, 3H, $^3J_{HH} = 6.0$); 1.42 (d, 3H, $^3J_{HH} = 6.0$); 3.73 (s, 3H); 4.73–4.80 (m, 2H); 7.62 (ddt, 1H, $^3J_{HH} = 7.5$, $^4J_{HH} = 1.3$, $^4J_{HP} = 3.0$); 7.76 (tt, 1H, $^3J_{HH} = 7.5$, $^4J_{HH} = {}^5J_{HP} = 1.5$); 7.95 (ddd, 1H, $^3J_{HH} = 7.5$, $^4J_{HH} = 1.5$, $^3J_{HP} = 13.7$); 8.22 (ddd, 1H, $^3J_{HH} = 7.5$, $^4J_{HH} = 1.3$, $^4J_{HP} = 4.8$). ^{31}P NMR (101.2 MHz): δ 13.8. ^{13}C NMR (62.9 MHz): δ 24.1 (d, $^3J = 4.8$, CH_3); 24.2 (d, $^3J = 4.8$, CH_3); 24.3 (d, $^3J = 4.0$, CH_3); 24.4 (d, $^3J = 4.2$, CH_3); 53.7(s, CH_3–O); 72.0 (d, $^2J = 5.7$, CH); 72.1 (d, $^2J = 5.7$, CH); 124.7 (d, $^3J = 12.3$, C_5); 128.8 (d, $^1J = 189.0$, C_1); 131.8 (d, $^3J = 13.1$, C_3); 132.9 (d, $^4J = 3.0$, C_4); 134.1 (d, $^2J = 8.3$, C_6); 147.9 (d, $^2J = 10.5$, C_2). IR (NaCl) cm^{-1}: 3480; 2979; 2936; 1582; 1454; 1428; 1386; 1375; 1255 (νP=O); 1178; 1130 (νS=O); 1103; 984 (νP–O); 769 (νS–O). GC/MS m/z (%): 321 (MH^+; 7); 289 (29); 219 (11); 206 (14); 205 (100); 188 (8); 139 (14). HRMS calculated for $C_{13}H_{22}O_5PS$ (M+H): 321.0926; found 321.0931.

4.3.3. L-(8-Phenyl)-menthyl 2-(diisopropylphosphoryl)-benzenesulfinate 14. Yield 70%. Colourless oil. $[\alpha]_D = -15.2$ (c 0.7, $CHCl_3$); dr: 17.5/82.5. NMR of the major diastereomer: ^1H (400 MHz): δ 0.72–1.05 (m, 2H); 0.89 (d, 3H, $^3J_{HH} = 5.8$); 1.11 (s, 3H); 1.19 (s, 3H); 1.20–1.56 (m, 4H); 1.27 (d, 6H, $^3J_{HH} = 6.4$); 1.29 (d, 6H, $^3J_{HH} = 6.4$); 1.91–1.98 (m, 1H); 1.91–1.98 (m, 1H); 2.35–2.41 (m, 1H); 4.49 (dt, 1H, $^3J_{HH} = 10.5$, $^3J_{HH} = 4.4$); 4.80 (dsept, 2H, $^3J_{HP} = 8.5$, $^3J_{HH} = 6.7$); 6.97 (tt, 1H, $^3J_{HH} = 7.0$, $^4J_{HH} = 1.4$); 7.04–7.13 (m, 2H); 7.22–7.31 (m, 2H); 7.52–7.58 (m, 1H); 7.60–7.67 (m, 2H); 7.87 (ddd, 1H, $^3J_{HH} = 7.6$, $^3J_{HP} = 3.7$, $^4J_{HH} = 1.3$); 8.00–8.04 (m, 1H). ^{31}P (162 MHz): δ 13.18. ^{13}C (100.6 MHz): δ 22.2 (s, $C_{7'}$); 24.1 (d, $^3J = 4.7$, CH_3); 24.4 (s, $C_{9'}$); 24.6 (d, $^3J = 4.3$, CH_3); 25.1 (s, $C_{9'}$); 27.6 (s, $C_{3'}$); 28.7 (s, $C_{5'}$); 32.2 (s, $C_{4'}$); 34.8 (s, $C_{6'}$); 40.5 (s, $C_{8'}$); 52.5 (s, $C_{2'}$); 72.0 (d, $^2J = 6.3$, CH); 72.3 (d, $^2J = 5.9$, CH); 83.3 (s, $C_{1'}$); 124.7 (s, $C_{2''}$); 125.2 (s, $C_{4''}$); 125.7 (s, $C_{3''}$); 126.1 (d, $^3J = 7.8$, C_3); 127.1 (d, $^1J = 197.0$, C_1); 128.4 (d, $^2J = 14.0$, C_6); 131.2 (d, $^2J = 14.1$, C_2); 132.9 (d, $^3J = 8.0$, C_5); 133.7 (d, $^4J = 3.0$, C_4); 151.6 (s, $C_{1''}$). Minor diastereomer: ^1H (400 MHz): δ 0.91 (d, 3H, $^3J_{HH} = 5.7$); 2.43–2.46 (m, 1H); 4.30–4.36 (m, 1H); 4.67–4.81 (m, 2H); 7.74–7.79 (m, 1H); 7.87–7.95 (m, 1H). ^{31}P (162 MHz): δ 13.39. ^{13}C (100.6 MHz): δ 22.3 (s, $C_{7'}$); 25.9 (s, $C_{9'}$); 27.7 (s, $C_{3'}$); 28.3 (s, $C_{5'}$); 30.0 (s, $C_{4'}$); 34.9 (s, $C_{6'}$); 40.6 (s, $C_{8'}$); 51.6 (s, $C_{2'}$); 80.1 (s, $C_{1'}$); 124.8 (s, $C_{2''}$); 125.3 (s, $C_{4''}$); 125.4 (s, $C_{3''}$); 127.8 (d, $^1J = 187.0$, C_1); 131.3 (d, $^2J = 13.1$, C_2); 133.4 (d, $^3J = 8.0$, C_5); 133.6 (d, $^4J = 3.0$, C_4); 150.5 (s, $C_{1''}$). IR (NaCl) cm^{-1}: 2975; 1454; 1247; 1121 (R–SO–OR′); 983; 732 (S–O st). MS m/z (%): 543 (M+Na; 31); 329 (100); 288 (28); 245 (8). HRMS calculated for $C_{28}H_{41}O_5NaPS$ (M+Na): 543.2310; found 543.2282.

4.3.4. ((1*R*,2*S*)-*trans*-2-Phenyl-1-cyclohexyl) 2-(diisopropylphosphoryl)benzenesulfinate 15. Yield 67%. Colourless oil. $[\alpha]_D = -56.9$ (c 2.9, $CHCl_3$); dr: 87/13. NMR of the major diastereomer (CD_3OD): ^1H (400 MHz): δ 1.22 (d, 3H, $^3J_{HH} = 6.2$); 1.23 (d, 3H, $^3J_{HH} = 6.1$); 1.34 (d, 3H, $^3J_{HH} = 6.2$); 1.35 (d, 3H, $^3J_{HH} = 6.4$); 1.30–1.89 (m, 7H); 2.20–2.25 (m, 1H); 2.69–2.74 (m, 1H); 4.48 (dt, 1H, $^3J_{HH} = 10.5$, $^3J_{HH} = 6.2$); 4.60–4.75 (m, 2H); 6.99–7.11 (m, 5H); 7.54–7.61 (m, 2H); 7.75–7.81 (m, 2H). ^{31}P (161 MHz): δ 13.04. ^{13}C (100.6 MHz): δ 23.1 (d, $^3J = 4.6$, CH_3); 23.2 (d, $^3J = 4.6$, CH_3); 23.3 (d, $^3J = 3.9$, CH_3); 23.4 (d, $^3J = 4.3$, CH_3); 24.9 (s, $C_{5'}$); 25.6 (s, $C_{4'}$); 34.1 (s, $C_{3'}$); 34.2 (s, $C_{6'}$); 51.1 (s, $C_{2'}$); 72.7 (d, $^2J = 6.1$, CH); 73.0 (d, $^2J = 5.8$, CH); 82.5 (s, $C_{1'}$); 124.4 (d, $^3J = 12.6$, C_3); 126.4 (s, $C_{4''}$); 127.1 (d, $^1J = 190.3$, C_1); 127.8 (s, $C_{3''}$); 128.2 (s, $C_{2''}$); 131.5 (d, $^3J = 13.4$, C_5); 132.8 (d, $^2J = 8.5$, C_6); 133.7 (d, $^4J = 2.9$, C_4); 143.0 (s, $C_{1''}$); 151.2 (d, $^2J = 10.5$, C_2). Minor diastereomer (CD_3OD): ^1H (400 MHz): δ 2.35–2.41 (m, 1H); 2.67–2.72 (m, 1H); 7.18–7.29 (m, 5H); 7.48–7.54 (m, 2H); 7.81–7.87 (m, 2H). ^{31}P (161 MHz): δ 12.95. ^{13}C (100.6 MHz): δ 24.8 (s, $C_{5'}$); 25.7 (s, $C_{4'}$); 33.4 (s, $C_{3'}$); 34.5 (s, $C_{6'}$); 80.5 (s, $C_{1'}$); 125.0 (d, $^3J = 12.4$, C_3); 128.0 (s, $C_{3''}$); 128.3 (s, $C_{2''}$); 131.7 (d, $^3J = 13.6$, C_5); 132.6 (d, $^2J = 9.3$, C_6); 133.7 (s, C_4); 143.3 (s, $C_{1''}$); 151.6 (d, $^2J = 10.4$, C_2). IR (NaCl) cm^{-1}: 2979; 2931; 1248 (P=O); 1124 (S=O); 988 (P–O–C). MS m/z (%): 487 (M+Na; 43); 445 (10); 329 (76); 313 (51); 287 (100); 271 (28); 245 (46); 227 (29). HRMS calculated for $C_{24}H_{34}O_5PS$ (M+H): 465.1865; found 465.1856.

4.3.5. (*S*)-Bornyl 2-(diisopropylphosphoryl)benzenesulfinate 16. Yield 92%. Colourless oil. $[\alpha]_D = +3.0$ (c 0.75, $CHCl_3$); dr: 62/38. NMR of the major diastereomer:

^{1}H (250 MHz): δ 0.76 (s, 3H); 0.78 (s, 3H); 0.78–0.81 (m, 3H); 0.93–1.00 (m, 1H); 1.15 (d, 6H, $^3J_{HH} = 6.2$); 1.20 (d, 6H, $^3J_{HH} = 6.2$); 1.26–1.20 (m, 1H); 1.33 (d, 6H, $^3J_{HH} = 6.2$); 1.34 (d, 6H, $^3J_{HH} = 6.0$); 1.64–1.78 (m, 4H); 2.20–2.31 (m, 1H); 4.51–4.83 (m, 3H); 7.51 (ddt, 1H, $^3J_{HH} = 7.4$, $^4J_{HP} = 3.1$, $^4J_{HH} = 1.1$); 7.63–7.71 (m, 1H); 7.90 (ddd, 1H, $^3J_{HP} = 13.4$, $^3J_{HH} = 7.5$, $^4J_{HH} = 1.2$); 8.14–8.24 (m, 1H). ^{31}P (162 MHz): δ 13.06. ^{13}C (62.9 MHz): δ 12.2 (s, $C_{7'}$); 17.8 (s, $C_{9'}$); 18.7 (s, $C_{9'}$); 22.7 (d, $^3J = 4.8$, CH_3); 23.0 (d, $^3J = 4.9$, CH_3); 25.7 (s, $C_{4'}$); 26.9 (s, $C_{5'}$); 35.4 (s, $C_{2'}$); 43.9 (s, $C_{3'}$); 46.6 (s, $C_{8'}$); 48.7 (s, $C_{6'}$); 70.8 (d, $^2J = 6.2$, CH); 81.2 (s, $C_{1'}$); 123.1 (d, $^2J = 12.5$, C_6); 127.1 (d, $^1J = 189.3$, C_1); 130.1 (d, $^3J_{CP} = 13.3$, C_3); 131.9 (s, C_4); 132.4 (d, $^3J = 9.4$, C_5); 149.4 (d, $^2J = 8.6$, C_2). Minor diastereomer: ^{1}H (250 MHz): δ 0.92–0.99 (m, 6H); 4.51–4.83 (m, 3H); 7.81–7.90 (m, 1H). ^{31}P (162 MHz): δ 12.99. ^{13}C (62.9 MHz): δ 12.0 (s, $C_{7'}$); 18.9 (s, $C_{9'}$); 35.9 (s, $C_{2'}$); 43.8 (s, $C_{3'}$); 47.2 (s, $C_{8'}$); 84.9 (s, $C_{1'}$); 123.3 (s, C_6); 132.2 (s, C_4); 149.6 (s, C_2). IR (NaCl) cm^{-1}: 2979; 1247; 1106 (S=O); 992; 909; 735. HRMS for $C_{22}H_{36}O_5PS$ (M+H): calculated 443.2013; found 443.2012.

4.3.6. (Diacetone-D-glucosyl) 2-(diisopropylphosphoryl)-benzenesulfinate 17. Yield 94%. Colourless oil. $[\alpha]_D = +13.6$ (c 1.88, $CHCl_3$); dr: 32/68. NMR of the major diastereomer: ^{1}H (400 MHz): δ 1.22–1.51 (m, 24H); 3.50 (dd, 1H, $^2J_{HH} = 8.5$, $^3J_{HH} = 6.6$); 3.82 (dd, 1H, $^2J_{HH} = 8.5$, $^3J_{HH} = 6.4$); 4.27–4.33 (m, 1H); 4.44 (d, 1H, $J_{HH} = 4.2$); 4.65 (d, 1H, $J_{HH} = 3.7$); 4.77–4.91 (m, 2H); 4.98 (d, 1H, $J_{HH} = 3.0$); 5.92 (d, 1H, $J_{HH} = 3.7$); 7.62–7.69 (m, 1H); 7.75–7.80 (m, 1H); 7.92 (dd, 1H, $^3J_{HP} = 13.7$, $^3J_{HH} = 7.5$); 8.24 (dd, 1H, $^3J_{HH} = 7.3$, $^4J_{HP} = 4.6$). ^{31}P (101 MHz): δ 12.05. ^{13}C (62.9 MHz): δ 22.7 (d, $^3J = 4.7$, CH_3); 22.8 (d, $^3J = 4.4$, CH_3); 23.0 (d, $^3J = 4.3$, CH_3); 23.1 (d, $^3J = 4.1$, CH_3); 24.3 (s, $C_{8'}$); 25.2 (s, $C_{8'}$); 25.4 (s, $C_{10'}$); 25.7 (s, $C_{10'}$); 64.3 (s, $C_{6'}$); 71.0 (d, $^2J = 6.1$, CH); 71.2 (d, $^2J = 6.0$, CH); 72.1 (s, $C_{5'}$); 79.2 (s, $C_{4'}$); 80.0 (s, $C_{1'}$); 82.5 (s, $C_{2'}$); 104.0 (s, $C_{3'}$); 107.3 (s, $C_{7'}$); 111.1 (s, $C_{9'}$); 122.7 (d, $^3J = 12.6$, C_3); 126.9 (d, $^1J = 189.3$, C_1); 130.9 (d, $^3J = 11.9$, C_5); 132.1 (s, C_4); 132.2 (d, $^2J = 6.9$, C_6); 148.6 (d, $^2J = 10.7$, C_2). Minor diastereomer: ^{1}H (400 MHz): δ 3.91–3.94 (m, 1H); 4.90 (d, 1H, $J_{HH} = 3.7$); 5.86 (d, 1H, $J_{HH} = 3.6$); 8.27–8.29 (m, 1H). ^{31}P (101 MHz): δ 12.23. ^{13}C (62.9 MHz): δ 24.1 (s, $C_{8'}$); 25.6 (s, $C_{8'}$); 25.8 (s, $C_{10'}$); 25.9 (s, $C_{10'}$); 65.7 (s, $C_{6'}$); 70.8 (d, $^2J = 5.7$, CH); 71.6 (s, $C_{5'}$); 78.7 (s, $C_{4'}$); 79.3 (s, $C_{1'}$); 82.2 (s, $C_{2'}$); 104.1 (s, $C_{3'}$); 107.8 (s, $C_{7'}$); 111.1 (s, $C_{9'}$); 122.7 (d, $^3J = 12.7$, C_3); 127.2 (d, $^1J = 188.7$, C_1); 130.6 (d, $^3J = 13.2$, C_5); 148.5 (d, $^2J = 10.7$, C_2). IR (NaCl) cm^{-1}: 2983; 2936; 2249; 1735; 1455; 1376; 1248; 1138; 989; 732. MS m/z (%): 571 (M+Na; 35); 529 (12); 313 (100); 271 (37); 269 (16); 227 (13). HRMS for $C_{29}H_{38}O_{10}PS$ (M+H): calculated 549.1923; found 549.1944.

The DAG-sulfinates **17** (94 mg) were recrystallized twice from a mixture of ether–pentane 2:1 to give diastereomerically pure **17b** (43 mg, 46%) according to ^{31}P NMR: δ_P 12.11 (100%). $[\alpha]_D = +102.3$ (c 0.3, $CHCl_3$).

4.3.7. (2,4,6-Triisopropylphenyl)-2-(*R*)-ethyl 2-(diisopropylphosphoryl)benzenesulfinate 18. Yield 85%. Colourless oil. $[\alpha]_D = +47.0$ (c 1.35, $CHCl_3$); dr: 7/93. NMR of the major diastereomer: ^{1}H (400 MHz): δ 0.89 (d, 3H, $^3J_{HH} = 6.2$); 0.96 (d, 3H, $^3J_{HH} = 6.1$); 1.10 (d, 3H, $^3J_{HH} = 6.2$); 1.15–1.25 (m, 21H); 1.80 (d, 3H, $^3J_{HH} = 6.9$); 2.80 (sept, 1H, $^3J_{HH} = 6.9$); 3.25–3.36 (m, 1H); 3.50–3.62 (m, 1H); 4.40 (dsept, 1H, $^3J_{HP} = 7.9$, $^3J_{HH} = 6.2$); 4.58 (dsept, 1H, $^3J_{HP} = 10.4$, $^3J_{HH} = 6.3$); 6.11 (qd, 1H, $^3J_{HH} = 6.8$); 6.93 (s, 2H); 7.46–7.49 (m, 1H); 7.75 (t, 1H, $^3J_{HH} = 6.5$); 7.87 (ddd, 1H, $^3J_{HP} = 14.8$, $^3J_{HH} = 7.5$, $^4J_{HH} = 1.2$); 8.31 (ddd, 1H, $^3J_{HH} = 7.9$, $^4J_{HP} = 4.8$, $^4J_{HH} = 1.0$). ^{31}P (161 MHz): δ 12.90. ^{13}C (62.9 MHz): δ 23.4 (d, $^3J = 4.9$, CH_3(CH)); 23.5 (d, $^3J = 4.9$, CH_3(CH)); 23.7 (d, $^3J = 4.0$, CH_3(CH)); 23.9 (d, $^3J = 4.1$, CH_3(CH)); 24.3 (s, $C_{8'}$); 24.4 (s, $C_{10'}$); 24.7 (s, $C_{9'}$); 29.3 (s, $C_{1'}$); 34.1 (s, $C_{7'}$); 71.5 (d, $^2J = 6.3$, CH); 71.6 (d, $^2J = 6.3$, CH); 74.8 (s, $C_{2'}$); 120.7 (s, $C_{5'}$); 123.2 (s, $C_{3'}$); 124.3 (d, $^3J = 11.9$, C_3); 127.7 (d, $^1J = 188.0$, C_1); 131.0 (d, $^3J = 13.2$, C_5); 132.9 (d, $^4J = 2.5$, C_4); 133.1 (d, $^2J = 7.5$, C_6); 145.1 (s, $C_{6'}$); 148.0 (s, $C_{4'}$); 151.1 (d, $^2J = 10.1$, C_2). Minor diastereomer: ^{1}H (400 MHz): δ 4.70–4.82 (m, 1H); 8.20–8.24 (m, 1H). ^{31}P (161 MHz): δ 13.09. IR (NaCl) cm^{-1}: 2963; 2871; 2239; 1460; 1378; 1249; 1125; 986. MS m/z (%): 559 (M+Na; 18); 330 (21); 329 (100); 287 (16). HRMS calculated for $C_{29}H_{46}O_5PS$ (M+H): 537.2804; found 537.2794.

4.4. The Grignard reaction leading to diisopropyl (2-methylsulfinyl)phenylphosphonate 6

Menthyl sulfinate ester **5** (500 mg, 1.12 mmol) was added dropwise at 0 °C to a solution of methylmagnesium bromide (3 M in Et_2O, 1.12 mL, 3.36 mmol) in diethyl ether. The mixture was stirred for 1 h at room temperature. A 5% aqueous solution of sulfuric acid (10 mL) was added and the aqueous layer extracted with diethyl ether. The organic extracts were washed successively with a 5% aqueous solution of potassium carbonate and brine, dried over $MgSO_4$, filtered and evaporated to afford a yellow oil, which was further purified on silica gel chromatography.

The reaction was extended to sulfinates derived from 8-phenylmenthol **14**, *trans*-2-phenylcyclohexanol **15** and Greene's alcohol **18** (Table 2, entries 2, 4 and 13, respectively). The 2-phosphorylated phenyl methyl sulfoxide (*R*)-(+)-**6** was formed in 85% and 74% ee in the two former cases, while the (*S*)-(−)-**6** isomer was produced in the latter with 86% ee.

Yield 78%. Colourless liquid. $[\alpha]_D = -145.2$ (c 1.3, $CHCl_3$). Ee = 86%. ^{1}H NMR (400 MHz): δ 1.27 (d, 3H, $^3J_{HH} = 7.1$); 1.29 (d, 3H, $^3J_{HH} = 6.6$); 1.37 (d, 3H, $^3J_{HH} = 6.2$); 1.43 (d, 3H, $^3J_{HH} = 6.2$); 2.87 (s, 3H); 4.77 (dsept, 2H, $^3J_{HH} = 6.2$, $^3J_{HP} = 7.9$); 7.57 (ddt, 1H, $^3J_{HH} = 7.3$, $^3J_{HP} = 3.0$, $^4J_{HH} = 0.8$); 7.79 (t, 1H, $^3J_{HH} = 7.7$); 7.86 (ddd, 1H, $^3J_{HH} = 7.5$, $^3J_{HP} = 13.5$, $^4J_{HH} = 0.8$); 8.29 (dd, 1H, $^3J_{HH} = 7.6$, $^4J_{HP} = 5.6$). ^{31}P NMR (162 MHz): δ 12.7. ^{13}C NMR (100 MHz): δ 24.2 (d, $^3J = 4.8$, CH); 24.3 (d, $^3J = 4.9$, CH); 24.4 (d, $^3J = 3.8$, CH); 24.5 (d, $^3J = 4.1$, CH); 45.2 (s, CH_3(SO)); 72.3 (d, $^2J = 6.0$, CH); 124.1 (d, $^3J = 12.5$, C_3); 127.4 (d, $^1J = 190.1$, C_1); 130.7 (d, $^2J = 13.1$, C_6); 133.3 (d,

$^3J = 8.1$, C_5); 133.8 (d, $^4J = 2.9$, C_4); 151.1 (d, $^2J = 10.9$, C_2). IR (NaCl) cm^{-1}: 2978; 2933; 1581; 1454; 1426; 1386; 1375; 1251 (νP=O); 1178; 1141; 1103; 1066 (νS=O); 984 (νP–O); 769 (νS–O). GC/MS m/z (%): 305 (MH^+; 5); 205 (100); 204 (18); 203 (19); 206 (95); 159 (17); 139 (13). Analysis for $C_{13}H_{21}O_4PS$: calculated (C: 51.31; H: 6.96; S: 10.53) found (C: 51.42; H: 7.05; S: 10.25).

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