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Graphical Abstract

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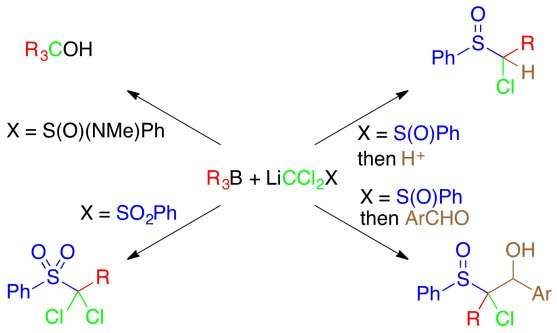

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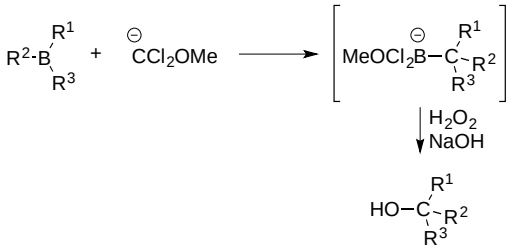
ABSTRACT

Known reagents that transfer three alkyl groups of a trialkylborane intramolecularly to a single carbon atom lack features to influence stereochemistry. We have investigated four reagents of type $LiCCl_2X$, where X might be amenable to variation. All behaved differently. With X = OR (R = cyclohexyl, menthyl), the reagent decomposed, leading to only low yields of triple migration products. With X = S(O)Ph, a single migration occurred, followed by isomerisation to boron enolate-like species that hydrolysed to α-chloroalkyl phenyl sulfoxides or reacted with aldehydes to aldol-like products. With X = SO_2Ph, the major product was the corresponding α,α-dichloroalkyl phenyl sulfone, apparently formed through a redox reaction. With X = S(O)(NMe)Ph, products of three intramolecular alkyl migrations were obtained with unhindered trialkylboranes. Attempts have been made to gain understanding of the sulfoxide process by investigating proportions of aldol-like products, using X-ray crystallography and *ab initio* calculations.

1. Introduction

Rearrangement reactions of organoboron species provide many well-established synthetic methods, several of which have no counterparts outside of organoboron chemistry. For example, several types of reaction, including carbonylation,[1] cyanidation[2] and the DCME (dichloromethyl methyl ether) reaction (**Scheme 1**),[3] allow transfer of all three alkyl groups from a trialkylborane to a single carbon atom to generate tertiary-alkylboron compounds, which can be oxidised to tertiary alcohols. Under different conditions the carbonylation reaction can be controlled to allow synthesis of products from just one or two alkyl group migrations,[4] and cyanidation can also be controlled to give products of two alkyl migrations,[5] but the DCME reaction proceeds so readily to give three migrations that it cannot be stopped at an intermediate stage except by using alternative substrates possessing fewer alkyl groups.



Scheme 1. Formation of tertiary alcohols by reaction of a trialkylborane with the anion of DCME

In principle, variants of the DCME reaction could have enormous synthetic potential, for example if one or more of the three leaving groups on carbon could be changed to render it less readily displaced (so that the reaction could be intercepted before all three groups had migrated) or incorporate a chiral moiety (leading to the possibility of asymmetric induction). However, only a few attempts at variation have been reported. Anions derived from haloforms behave in much the same manner as the anion from DCME, although the yields are somewhat poorer.[6] The reactions of trialkylboranes with the anion derived from tris(phenylthio)methane result in two spontaneous alkyl group migrations, allowing synthesis of ketones following oxidation, but the third migration can be induced by addition of mercuric chloride to the mixture.[7]

In the present study we have undertaken reactions of organoboranes with anions derived from an alternative alkoxydichloromethane, a dichloromethyl sulfoxide, a dichloromethyl sulfone and a dichloromethyl sulfoximine. The behaviour of each anion type turned out to be quite different from the others, revealing some new reaction types and indicating some novel reaction mechanisms.

2. Results and Discussion

Reaction with dichloro(menthyloxy)methane (1): The simplest analogues of DCME, which might nevertheless offer interesting new possibilities in reactions with trialkylboranes, would involve replacing the methoxy group of DCME by an alternative alkoxy group. We decided to investigate the reactions of dichloro(menthyloxy)methane (**1**), the anion of which (**2**) might complex to an unsymmetrical trialkylborane (*i.e.* one bearing three different alkyl groups) to give two different diastereoisomeric complexes (**3** and **4**), the stabilities of which would not be identical and the rearrangements of which might differ in terms of which diastereotopic chlorine would be displaced first and/or which alkyl groups were located appropriately to displace particular leaving groups (**Fig. 1**).[8] In principle, this could lead to the production of a significant excess of one enantiomer of the final tertiary alcohol over the other. Therefore, we decided to look at the reaction of the anion with such an unsymmetrical trialkylborane, and in order that the three alkyl groups should have significantly different characteristics and the tertiary alcohol product could be readily monitored by HPLC, we selected cyclopentyl(2-(4-methoxyphenyl)ethyl)thexylborane (**5**) as the substrate.

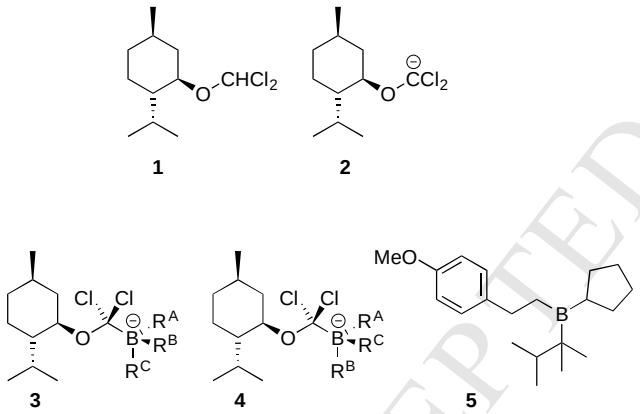


Fig. 1. Structures **1**-**5**

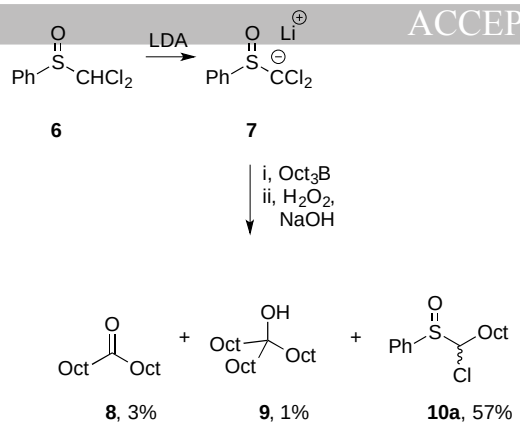
The first task was to prepare **1**. A literature procedure[9] was used to prepare the formate ester of (–)-menthol, the purity of which was confirmed by comparison of its reported ^{1}H NMR data[9] and its reported optical rotation[10] with those of the isolated product. Several different methods[11,12,13] were tried in order to convert the menthyl formate into **1**. In all cases there were problems with formation of menthyl chloride as a significant by-product, but a reasonably pure sample of **1** could be obtained by use of a mixture of PCl_5 and $POCl_3$ to introduce the chlorines, then removal of the $POCl_3$ under reduced pressure and extraction of the product into hexane, leaving the PCl_5 as a residue.

Unfortunately, when this product was subjected to a standard DCME-like reaction with **5**, no tertiary alcohol was formed. Even with the less hindered tri-*n*-octylborane and tricyclopentylborane only very low yields of tertiary alcohols were obtained (5% and 4%, respectively) and similarly generated cyclohexyloxydichloromethane also did not provide encouraging results. Although we did not rule out the possibility of finding an appropriate alkoxydichloromethane that might react in the desired manner, in view of the disappointing results with **1** we decided to look instead at alternative types of reagents.

Reaction with (dichloromethylsulfinyl)benzene (6): Compound **6** offers interesting possibilities as a reagent because of its chirality, resulting from the presence of a stereogenic sulfur atom. It was prepared by chlorination of methyl phenyl sulfoxide according to a literature procedure[14] and was obtained as a colourless oil in 73% yield after column chromatography. We presumed that the two chloride groups would be more readily displaced than the sulfoxide group but hoped that the third group might be susceptible to displacement under appropriate conditions.[15]

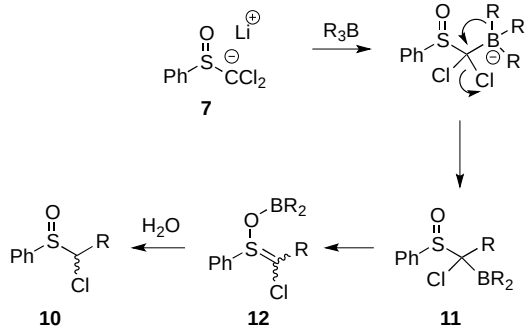
A solution of trioctylborane was prepared by hydroboration of 1-octene with borane dimethyl sulfide complex in THF. This was then added at –78 °C to a solution of anion **7**, prepared by deprotonation of **6** (1 equiv.) using lithium diisopropylamide (LDA, 1.1 equiv.). The solution was stirred at –78 °C for 1 h then the cooling bath was removed and the mixture stirred for a further 1 h before oxidation of the organoboron product with alkaline hydrogen peroxide. Work-up and separation of the products by column chromatography gave the products expected from two alkyl group migrations (dioctyl ketone, **8**, **Scheme 2**) and three alkyl group migrations (trioctylmethanol, **9**), but in low isolated yields, 3% and 1%, respectively; GC yields were 6% and 3% respectively. The major product (57% yield) was a diastereoisomeric mixture of 1-chlorononyl phenyl sulfoxides (**10a**), evidently formed *via* a single alkyl group migration followed by hydrolysis of the organoboron intermediate rather than oxidation. The rest of the material was octanol, resulting from the oxidation of residual octylboron moieties. All of the products contained small quantities of the 2-octyl isomers because of the formation of about 6% of 2-octyl groups during the hydroboration step.

To our knowledge there are no known reactions of substituted sulfoxides with organoboron compounds similar to that resulting in the formation of compound **10a**. Reactions of dimethylsulfoxonium ylides with trialkylboranes are known, but in those reactions dimethyl sulfoxide serves as a leaving group.[16] Reactions of α-chlorosulfoxides with alkyllithium reagents in the presence of alkylboronate esters result in thiophilic addition of the alkyllithium to the sulfoxide followed by elimination of sulfoxide with formation of an α-chloroalkyllithium species, which then goes on to bring about homologation of the boronate ester.[17] However, the formation of **10a** appears to be more akin in nature to the formation of homologated carbonyl compounds by reactions of trialkylboranes with diazocarbonyl compounds[18] or with anions derived from α-bromocarbonyl and related compounds.[19] In those reactions the isolable boron intermediates are boron enolates.[20] Similar base-induced reactions occur with α-bromosulfonyl compounds.[21] We assume the present reaction is similar and that the boron-containing product of the reaction with a generalised trialkylborane is **12**, formed by rearrangement of the initially formed intermediate **11** (**Scheme 3**).



6 **7** **8**, 3% **9**, 1% **10a**, 57%

Scheme 2. Initial reaction of the anion derived from **6** with trioctylborane



7 **10** **11** **12**

Scheme 3. Possible mechanism for the formation of 10

Compounds of type similar to **10a** have been prepared by alkylation of anions derived from aryl chloromethyl sulfoxides with alkyl halides[22] and are useful synthetic intermediates. Several interesting questions therefore arise.

1. Can a wider range of organic groups be introduced using the route of **Scheme 3** than is possible by nucleophilic substitution reactions of organic halides?
2. How do the proportions of diastereoisomers formed according to **Scheme 3** compare with those formed by alkylation of the anions derived from chloromethyl sulfoxides? Is the predominant isomer the same one?
3. Could the intermediates of type **12** provide other useful products by reaction with other electrophiles?

We have conducted some experiments to help answer such questions.

To address point 1, we optimised the reaction conditions, including replacing the oxidation step by a simple hydrolysis step with aqueous ammonium chloride solution, and then we carried out reactions with a range of organoboranes, including triethylborane, tributylborane, tricyclopentylborane, triphenylborane, the trialkylborane mixture formed by hydroboration of styrene, and 9-octyl-9-borabicyclo[3.3.1]nonane (9-Oct-9-BBN). The pure tri-*prim*-alkylboranes gave good yields of compounds **10**, but the yields from the impure cases (formed by hydroboration of 1-octene and styrene) were much lower, presumably because of lower proportions of tri-*prim*-alkylboranes present in the mixtures, while tricyclopentylborane and triphenylborane gave no comparable products (**Table 1**). 9-Oct-9-BBN gave 40% of **10a**. From these results it would seem that only relatively unhindered organoboranes take part in the reaction, presumably because the initial complexation of the anion with more hindered organoboranes is impeded. Also, no reaction took place with pinacol butylboronate, in this case presumably because of the lower electrophilicity of the boron reagent.

Table 1. Preparation of 1-chloroalkyl sulfoxides (**10**) according to **Scheme 3**

Product	R	Yield (%)[b]	Diastereoisomer ratio[a]
10a	Oct[c]	61	84:16
10a[d]	Oct[d]	40	82:18
10b	Et	92	78:22
10c	Bu	88	84:16
10d[e]	$PhCH_2CH_2$[e]	40	81:19
10e	Cyclopentyl	0	–
10f	Ph	0	–

[a] Determined from the ^{1}H NMR spectrum of the crude product prior to purification.

[b] Isolated yield for the mixture of diastereoisomers.

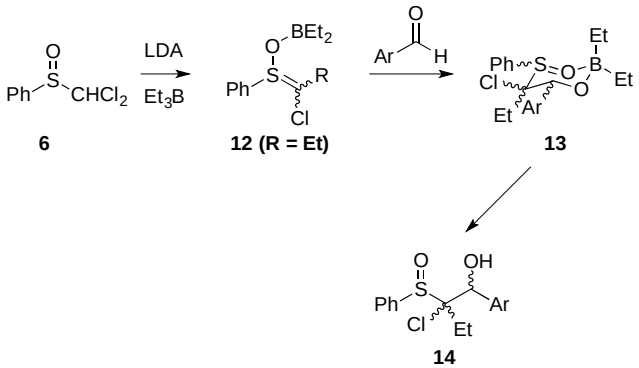
[c] Only around 82% of the R_3B molecules would be $(1\text{-Oct})_3B$ because the hydroboration gives *ca.* 6% of 2-octyl groups.

[d] 9-Oct-9-BBN was used in this case.

[e] Only around 40-50% of the R_3B molecules would be $(PhCH_2CH_2)_3B$ because the hydroboration gives *ca.* 20% of 1-phenylethyl groups.

In order to address point 2 we have compared the chemical shifts of the protons adjacent to Cl for the two diastereoisomers of **10a** with those reported for 1-chloroethyl phenyl sulfoxide ($PhS(O)CHClCH_3$, **10g, R = Me**) prepared by methylation of **7**. For **10a** the signals for the two isomers were at δ 4.46 (minor isomer, 22%) and 4.36 (major isomer, 78%) ppm. For **10g**, the situation is more confused; reported values are 4.70 (major isomer, 60%) and 4.50 (minor isomer, 40%) ppm in one report,[23] but the other way round, in unspecified proportions and lower yield, in another.[24] Clearly, the selectivity is low for this reaction, but somewhat better for the new reaction. Because of the contradictory data in the literature, we have repeated the literature reaction giving the higher yield and confirm that it gives the two diastereoisomers in around 60:40 proportions, with the predominant diastereoisomer being the one that is the minor one in the novel organoborane reaction.

Point 3 was addressed by carrying out reactions of **7** with triethylborane up to the point where intermediate **12** would be formed and then adding alternative electrophiles (D_2O, $Ph_2I^+TfO^-$, substituted benzaldehydes) before work-up. Use of D_2O gave the expected deuterio analogue of **10b**, while diphenyliodonium triflate did not react. The most interesting reactions involved the substituted benzaldehydes (**Scheme 4**).



6 **12 (R = Et)** **13** **14**

Scheme 4. Reactions of **6** with Et_3B and then benzaldehydes

All six substituted benzaldehydes tested gave aldol-like products **14** as mixtures of diastereoisomers, in combined yields of 45–58% (isolated, following column chromatography), sometimes along with small quantities of an impurity (**15**). In principle, four diastereomers of **14** are possible and in several examples all four were formed. If the transition state were to be a tight cyclohexane-like structure **13**, similar to that involved in reactions of boron enolates with aldehydes, then one might have expected the Ph and Ar groups to be pseudo-equatorial, leading to a *SR* or *RS* relationship for the configurations of the S atom and the carbon atom bearing the hydroxyl group, with the configuration of the double bond in **12** determining the configuration of the chlorine-bearing carbon atom in **14**. However, the pseudo-tetrahedral arrangement of groups around the sulfur atom in **12**, compared to the trigonal arrangement of groups around the corresponding carbon atom in boron enolates, would obviously have a significant effect. The presence of at least three diastereoisomers in all of the present cases and all four in some suggests that the stereo-control is much less than for the related aldol reactions of boron enolates.[25]

Nevertheless, it was of interest to identify which diastereoisomers were predominant, so the reaction with benzaldehyde (giving product **14a**) was investigated more closely. The structures of one enantiomer of each of the four possible diastereoisomers (all of which were inevitably racemic) are given in **Fig. 2**. The crude product **14a** was separated by chromatography (silica; 3% ethyl acetate/chloroform).

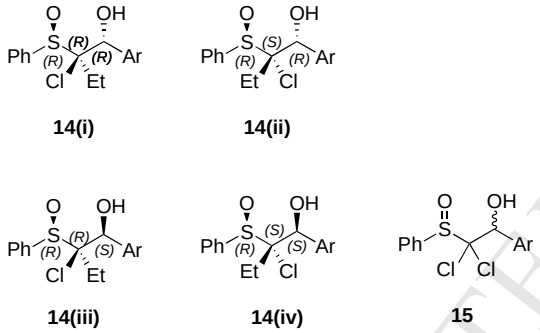


Fig. 2. Structures of the diastereoisomers of **14** and the impurity **15** formed alongside them

The first isomer eluted from the column (23% yield) was a solid with relative stereochemistry, as confirmed by X-ray crystallography, of *RRR/SSS*, confirming it as **14a(i)**. The second isomer to elute (referred to as **14a(ii)**, 2.5% yield) was contaminated with a single diastereoisomer of **15a** (2.5% yield), formed by direct reaction of anion **7** with benzaldehyde. This was confirmed by independent synthesis of a mixture of diastereoisomers of **15a** by deprotonation of **6** with LDA followed by addition of benzaldehyde. The sample of **14a(ii)** was contaminated with the less polar of the two isomers of **15a**, although the stereochemistry of this compound was not determined. The third and fourth isomers (**14a(iii)** and **14a(iv)**, total yield 32%; *ca.* 18% of one and 14% of the other isomer) co-eluted, so they were converted into their 4-nitrobenzoates by reaction with 4-nitrobenzoyl chloride in the presence of triethylamine. The 4-nitrobenzoate esters were separated by column chromatography and the individual isomers were then characterised by X-ray crystallography, confirming the least polar one to be derived from **14a(iii)** and the more polar one to be derived from **14a(iv)**. By a process of elimination, therefore, the structure of diastereoisomer **14a(ii)** must be as shown in **Fig. 2**.

Having conclusively established the identities of the four diastereoisomers of **14a**, we assigned the structures of the diastereoisomers of the other products of type **14** by reference to their NMR spectra, particularly noting the chemical shift of the C*H*OH proton and its coupling constant to the OH proton. **Table 2** shows the yields of the different diastereoisomers for the various products **14**.

Table 2. Yields of diastereoisomers of compounds **14** formed according to **Scheme 4**

Compound	Yield of specific diastereoisomer (%)[a]				Total product yield (%)[b]
	(i)	**(ii)**	**(iii)**	**(iv)**	
14a	23	2.5	14	18	57.5
14b	18	–	17	17	52
14c	18	–	17	10	45
14d	10	4	14	20	48
14e	22	8	11	9	50

[a] Amount of pure material isolated after chromatography or calculated by proportion of each component in a fraction after chromatography.

[b] By addition of yields of individual diastereoisomers; yields of crude product prior to chromatography were greater.

Assuming a chair transition state in which the phenyl group of the sulfoxide and the aryl group of the aldehyde are pseudo-equatorial, stereoisomers **(iii)** and **(iv**) might have been expected to predominate. Instead, three diastereoisomers were formed in broadly comparable yields (9-23%), while the other diastereoisomer **(ii)** was invariably formed in low yield (0-8%). It was not immediately clear why one isomer was formed in so much lower yield than the others, so these aspects were probed computationally.

Calculations were carried out using Spartan 10 at the B3LYP/6-31G(d) level of theory. Initially the geometry of the sulfoxide enolate was investigated. Two local minima were identified, corresponding to the structures shown in **Fig. 3**. In both cases, the phenyl ring can be considered to be either *pseudo E* or *pseudo Z* to the Et group, although there is significant deviation from planarity, with a Et-C-S-Ph dihedral angle of 163° for **12*E*** and 39° for **12*Z***. The isomer designated **12*E*** is calculated to be 5.3 kJmol^{-1} more stable than **12*Z***.

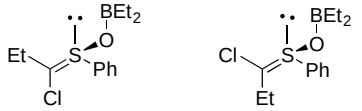


Fig. 3. Calculated structures (B3LYP/6-31G(d)) and energies of major and minor isomers of intermediate **12 (R = Et)**

After extensive conformational analysis based on cyclohexane-like structure **13**, four transition states were located at the B3LYP/6-31G(d) level of theory and the relative energies are summarised in **Table 3** and the corresponding structures are depicted in **Fig. 4**. The transition states TS3 and TS4, leading to **14a(iii)** and **14a(iv**) respectively, resemble twisted chairs in which both phenyl rings are pseudo-equatorial. Transition state TS2, leading to **14a(ii)**, also resembles a twisted chair in which the aldehyde phenyl is now pseudo-axial. This would explain why this transition state is considerably higher in energy. In

contrast, transition state TS1, leading to **14a(i)** resembles a twisted boat which now permits both phenyl rings to be pseudo-equatorial, despite the 1,3-anti arrangement of oxygen atoms in the product. Therefore, the calculations correctly predict the minor stereoisomer, and the relatively small difference in energy between the three lowest energy transition states means it would be difficult to predict which will be the major isomer with any level of confidence.

Table 3. Relative B3LYP/6-31G(d) Free Energies of TS1, TS2, TS3 and TS4 Transition States

Transition State	Diastereoisomer	G° (a.u.)	Δ*E* (KJ/mol)
TS1	**14a(i)** (RRR)	–1811.05655	6.7
TS2	**14a(ii)** (RSR)	–1811.03936	51.8
TS3	**14a(iii)** (RRS)	–1811.05909	0 (lowest)
TS4	**14a(iv)** (RSS)	–1811.05351	14.7

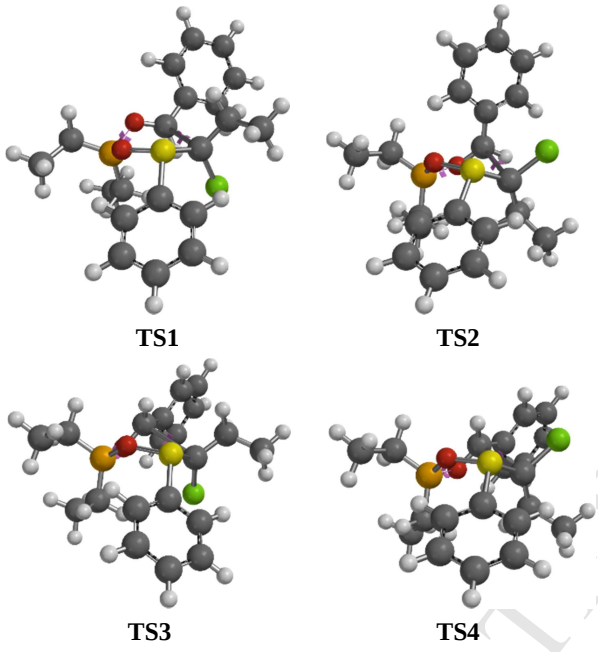
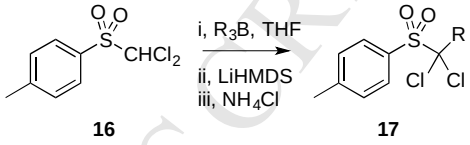


Fig. 4: Calculated B3LYP/6-31G(d) TS1 TS2, TS3 and TS4 Transition States

Compound **16** was prepared ***Reaction with dichloromethyl 4-tolyl sulfone (16)***: Although reactions of trialkylboranes with the anion **7** derived from (dichloromethylsulfinyl)benzene (**6**) had provided some interesting new reaction types, displacement of the sulfinyl group had not proved useful and the goal of generating a *tert*-alkylboron compound in good yield had not been realised. Therefore, it was decided to investigate the reaction of the anion derived from compound **16**, which contains, instead of a sulfinyl group, a sulfonyl group, which should be a better leaving group. It was recognised that this reagent would not benefit from the possibility of asymmetric induction offered by **6**, and also that there was precedent in the case of a monobromo-substituted sulfone for a reaction that resulted in replacement of the Br by an alkyl group from the organoborane in exactly the same way as seen with **6** (see above), but it was felt nevertheless to be worthy of investigation. In the event, the major product was of a completely different kind.

Compound **16** was prepared in 40% yield by a known route from sodium 4-toluenesulfinate, KOH and chloroform.[26] It was mixed with a trialkylborane (Et_3B or Bu_3B), the mixture was cooled to –78 °C and lithium bis(trimethylsilyl)amide (LiHMDS), which has previously been used for the deprotonation of **16**,[27] was added dropwise. The solution was stirred for 30 minutes at –78 °C and 90 minutes at room temperature and then worked up. The only product isolated following column chromatography was **17** (**Scheme 5**), in 46% yield for R = Et and 44% yield for R = *n*-Bu. The structure of **17a** was confirmed by X-ray crystallography.

The formation of compound **17** formally involves replacement of hydride by the alkyl group of the trialkylborane and is therefore an oxidation product; some other component of the reaction mixture must have been reduced. It is probably significant that the yield of **17** was in each case less than 50%, consistent with half of the original **16** having been reduced. At this stage it is not clear what process might be occurring or even whether the reaction is ionic or radical in nature, but it is an interesting reaction worthy of further investigation in the future.



16 **17**

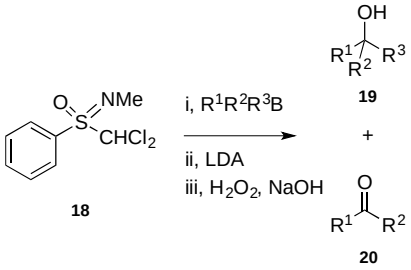
(a, R = Et, 46%; b, R = *n*-Bu, 44%)

Scheme 5. Reactions of the anion of **16** with trialkylboranes

Reaction with N-methyl-S-(dichloromethyl)-S-phenylsulfoximine (18): The final reagent investigated was compound **18**, which was prepared by chlorination of *N*,*S*-dimethyl-*S*-phenylsulfoximine with *t*-butyl hypochlorite according to a known procedure.[28] In the first experiment, an equimolar mixture of **18** and trioctylborane in THF at –78 °C was treated with LDA and the mixture allowed to warm up to room temperature and stirred for 1 hour before oxidation with alkaline hydrogen peroxide. Work up and gas chromatographic analysis revealed the presence of octanol (corresponding to 37% of original octyl groups), the product of two alkyl group migrations (dioctyl ketone, 13% yield) and that of three alkyl group migrations (trioctylmethanol, 39% yield). A few reactions were conducted to try to optimise production of the triple migration product. Use of dichloromethane as co-solvent, a 20% excess of **18** and an overnight reaction period gave a GC calculated yield of 81% of the tertiary alcohol **19** along with 11% of ketone **20** and octanol corresponding to 12% of original octyl groups (all figures inclusive of 2-octyl isomers). These conditions (except without any THF present in the cases of the mixed trialkylboranes) were adopted as standard and the procedure (**Scheme 6**) was applied to a range of organoboranes that were either purchased or generated *in situ* as described in the experimental section. The purpose of these experiments was to establish the limitations of the reaction and to determine whether the formation of the tertiary alcohol products (**19**) resulted from sequential intramolecular transfers of alkyl groups from boron to carbon. The results are given in **Table 4**.

As can be seen from **Table 4**, all of the reactions involving tri-*prim*-alkylboranes, *sec*-alkyl-di-*prim*-alkylboranes and phenyldi-*prim*-alkylboranes gave significant yields of the triple migration product. The modest yield from the reaction of triethylborane is primarily due to loss of product through evaporation and/or dissolution in water during the work-up procedure. The low yield in the case of 2-phenyl-2-hexanol reflects the poor synthesis of the mixed trialkylborane, which contained a substantial amount of phenyldibutylborane. However, additional experiments conducted with more hindered organoboranes such as

dioctylthexylborane, butyldicyclohexylborane, tricyclohexylborane and triphenylborane did not give the expected *tert*-alcohol products. The fact that the less hindered mixed trialkylboranes gave rise to the corresponding tertiary alcohols verified that the reactions involve three intramolecular organic group transfers, and this opens the way potentially to a process involving asymmetric induction if an appropriate enantiomerically enriched sulfoximine is used. This will be explored in future work.



Scheme 6. Reactions of anions of **18** with organoboranes

Table 4. Products formed in reactions according to **Scheme 6** (ratio $R^1R^2R^3B$:18:LDA = 1:1.2:1.2)

Alkyl groups of $R^1R^2R^3B$			Yields of products (%)[a]	
R^1	**R^2**	**R^3**	**19**	**20**
Et	Et	Et	47[b]	–
Bu	Bu	Bu	81	13
Oct	Oct	Oct	81(75)[c]	11[c]
Bu[d]	Bu[d]	*c*-Hex[d]	(73)	–
Bu[d]	Bu[d]	*c*-Pent[d]	(68)	–
Bu[e]	Bu[e]	Ph[e]	(51)	–
Me[f]	Bu[f]	Ph[f]	(30)[g]	–

[a] By GC estimation; figures in parentheses are of materials isolated by chromatography.

[b] A significant proportion of the product mixture may have been lost by evaporation during work-up.

[c] All compounds contained 2-octyl isomers as a result of the preparation of trioctylborane by hydroboration of 1-octene.

[d] The trialkylborane was prepared *in situ* from BCl_3, by sequential additions of an alkene, Et_3SiH and *n*-BuLi.

[e] The trialkylborane was prepared *in situ* from $PhBCl_2$ and 2 equiv. of *n*-BuLi.

[f] The trialkylborane was prepared *in situ* from $PhBCl_2$ then sequential addition of 1 equiv. of *n*-BuLi and 1-equiv. of MeLi; the product contained both PhBBuMe and $PhBBu_2$.

[g] $PhC(OH)Bu_2$ (30% yield) was also isolated.

3. Conclusion

Four different kinds of anionic reagents of the type Cl_2XC^- have been generated from the corresponding Cl_2CHX compounds and reacted *in situ* with trialkylboranes. Each of the four reagent types behaved differently. Alkoxydichloromethyl carbanions (*i.e.* X = OR, where R is menthyl or cyclohexyl) appear to decompose more quickly than they react with organoboranes, in contrast to the case of X = OMe, where the reagent undergoes a very useful reaction with organoboranes. This suggests that steric inhibition of complexation of the anion to the organoborane is an issue. Dichloro(phenylsulfinyl)methyl anion (X = SOPh) reacts to give the product of replacement of one of the chlorine atoms by an alkyl group from the organoborane, probably *via* a boron enolate-like intermediate that can also be trapped with aldehydes to give β-hydroxyalkyl sulfoxides. By contrast, a related sulfonyl-substituted anion (X = 4-$MeC_6H_4SO_2$) reacts to give the product of overall replacement of hydride by an alkyl group from the trialkylborane. Finally, the anion derived from *S*-dichloromethyl-*N*-methyl-*S*-phenylsulfoximine (X = PhSO(NMe)) reacts to give the product of displacement of all three leaving groups by alkyl groups from the trialkylborane, leading to tertiary alcohols on oxidation. These results illustrate several different pathways, some with unprecedented mechanistic implications.

4. Experimental section

Triethylborane and tributylborane were purchased as 1M solutions in THF and used directly. Other simple trialkylboranes and 9-alkyl-9-BBN were made by reaction of borane dimethyl sulfide or 9-BBN with the corresponding alkene according to well established procedures.[29] Other unsymmetrical trialkylboranes were prepared *in situ* by sequential additions of Et_3SiH and an alkene in the presence of BuLi to BCl_3 or $PhBCl_2$ according to a literature method.[30] The organoboranes prepared by the latter approach were generally mixtures of different trialkylboranes. NMR signal assignments are based on expected chemical shifts and coupling patterns and have not been rigorously confirmed. As far as possible, first order ^{1}H NMR coupling patterns are reported, even though some second order effects might complicate the appearance of the signals.

*4.1. Formation and reaction of dichloro(menthyloxy)methane (**1**)*

Two oven dried 100 mL round bottomed flasks (one equipped with a magnetic stirrer bar and septum – capped stopcock, and the other with a septum) joined by a sintered glass tube were assembled hot and cooled under a stream of N_2. The flask with the stirrer bar was transferred to a N_2 glove-bag, PCl_5 (1.5 g, 7.2 mmol) and $POCl_3$ (2.0 mL, excess) were added, the flask was removed from the glove-bag, reconnected to the sinter tube and immersed in an ice bath, and 1-menthyl formate (1.0 g, 5.4 mmol) was added drop-wise with vigorous stirring. The mixture was stirred at 0 °C for a further 6 h. Excess $POCl_3$ was removed under reduced pressure, dry hexane (25 mL) was introduced, and the solution was filtered through the sinter into the second flask. The hexane solution was transferred *via* cannula to a 50 mL flask already under N_2, and the hexane was evaporated under a fast N_2 stream to give the impure crude *title compound* (**1**) as an air-sensitive oil (80% conversion determined by ^{1}H NMR spectroscopy); ^{1}H (400 MHz; $CDCl_3$) δ 7.10 (1H, s, $CHCl_2$), 3.70 (1H, app dt, *J* = 10.6, 4.1 Hz, CHO), 0.65 – 2.30 (18H, m, CH, CH_2, CH_3); ^{13}C (101 MHz; $CDCl_3$) δ 97.7, 81.1, 47.4, 40.2, 33.6, 31.1, 24.8, 22.6, 21.9, 20.8 and 15.7; unable to get further data due to the compound's instability. The crude product was dissolved in anhydrous THF (10 mL) and transferred drop-wise *via* cannula to a solution of trioctylborane (5 mmol) in THF (15 mL) at 0 °C, to which a freshly prepared solution of lithium triethylcarboxide (15 mmol) in dry THF (10 mL) was added dropwise over 15 min. The cooling bath was removed, and the mixture was stirred for a further 1 h. A solution of ethylene glycol (0.90 mL, 16 mmol) in dry THF (5 mL) was added drop-wise, and the solution stirred overnight at room temperature. The flask was then immersed in an ice bath, and NaOH (1.20 g) in distilled water (5 mL) added drop-wise. Once the initial reaction subsided, a solution of hydrogen peroxide in water (30% by weight, 4.0 mL) and ethanol (5 mL) were added. The mixture was heated to 45-50 °C for a further 1 h, with additional ethanol added as needed to dissolve any boron salts that precipitated. The aqueous layer was saturated with K_2CO_3, and an aliquot from the

organic layer showed a 5% yield of tri-*n*-octylmethanol by GC analysis.

*4.2. Preparation of Dichloromethyl Phenyl Sulfoxide (**6**)*[14]

N-Chlorosuccinimide (1.95 g, 14.62 mmol, 2.05 equiv.) was added to a solution of methyl phenyl sulfoxide (1.00 g, 7.13 mmol) in THF (15 mL) at 0 °C. The solution was stirred at 0 °C overnight and filtered. The solvent was removed *in vacuo* and the residue purified by flash column chromatography (4:1 petroleum ether/diethyl ether) to afford the *title compound* (1.084 g, 73%) as a colourless oil, R_f = 0.26 (4:1 petroleum ether/diethyl ether); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.86 – 7.74 (2H, m, aromatic CH), 7.68 – 7.51 (3H, m, aromatic CH) and 6.17 (1H, s, CH); ^{13}C NMR (101 MHz; $CDCl_3$) δ 138.1, 133.2, 129.1, 126.7 and 83.1.

*4.3. Reaction of Dichloromethyl Phenyl Sulfoxide (**6**) with Trioctylborane*

Borane (100 µL, 10.0 M in dimethyl sulfide, 1.0 mmol, 1 equiv.) and THF (5 mL) were added to a septum-capped 25 mL flask containing a stirrer bar. The flask was immersed in an ice-bath and 1-octene (0.47 mL, 3.0 mmol, 3 equiv.) was added dropwise. The cooling bath was removed and the solution was left to stir at room temperature for 1 h. The solution was mixed with a solution of dichloromethyl phenyl sulfoxide (**6**) (209 mg, 1.0 mmol, 1 equiv.) in THF (5 mL) and cooled to –78 °C. LDA (1.1 mmol in 2.0 mL of THF, 1.1 equiv.) was added dropwise and the solution was stirred for 1 h at the same temperature. The cooling bath was removed, and the reaction stirred for a further 1 h. The solution was cooled to 0 °C and oxidised with aq. NaOH (3.0 M, 5 mL) followed by aq. H_2O_2 (30%, 3 mL). After the initial reaction subsided, the mixture was gently warmed (40 °C) and stirred overnight. The aqueous layer was saturated with NaCl and tetradecane (221.9 mg) was added. A sample from the organic layer was subjected to GC analysis. The results were: 1-octanol (55% of original octyl groups), dioctyl ketone (**8**) (6% yield) and trioctylmethanol (**9**) (3% yield).

The organic layer was separated, and the aqueous layer was extracted with dichloromethane (3 × 10 mL). The organic layers were combined, dried over magnesium sulfate and filtered. The volatile solvents were evaporated under reduced pressure and the crude product was purified by column chromatography on silica gel (5% EtOAc/petroleum ether) to yield **10a** (163 mg, 57%), 1-octanol (188 mg, 48% of original octyl groups), dioctyl ketone (**8**) (8 mg, 3% yield) and trioctylmethanol (**9**) (5 mg, 1% yield).

*4.4. General Procedure for Synthesis of 1-Chloroalkyl Phenyl Sulfoxides (**10**)*

n-BuLi (0.38 mL, 1.6 M in hexane, 0.60 mmol, 1.2 equiv.) was added dropwise to a cooled (–78 °C) solution of diisopropylamine (91 µL, 0.65 mmol, 1.3 equiv.) in dry THF (5 mL). The solution was warmed to 0 °C over a period of 20 min. The solution was cooled again to –78 °C. To this solution was added dichloromethyl phenyl sulfoxide (**6**) (105 mg, 0.50 mmol, 1.0 equiv.) and the mixture was stirred for 10 min. Trialkylborane (0.50 mmol, 1.0 equiv.) in THF (5 mL) was added and the mixture was stirred for 1 h, then the reaction was quenched by addition of saturated ammonium chloride solution (5 mL) before being warmed to room temperature. The organic layer was separated, the aqueous layer was extracted with dichloromethane (3 x 10 mL) and the organic layers were combined and dried over magnesium sulfate. The solvents were evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (the eluent is indicated in each case) to afford the corresponding sulfoxide (**10**).

*4.5. 1-Chlorononyl Phenyl Sulfoxide (**10a**)*

According to the general procedure, followed by flash column chromatography (4:1 petroleum ether/diethyl ether), the reaction of trioctylborane with the anion from **6** gave **10a** (88 mg, 61%) as a colourless oil as a 84:16 mixture of diastereoisomers; $\nu_{max.}$ (neat) 3063, 2955, 2924, 2854, 1464, 1444 and 1051 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.80 – 7.70 (2H of major isomer, m, aromatic CH), 7.69 – 7.63 (2H of minor isomer, m, aromatic CH), 7.60 – 7.49 (3H of both isomers, m, aromatic CH), 4.53 (1H of minor isomer, dd, *J* = 9.5, 4.0 Hz, C*H*Cl), 4.40 (1H of major isomer, dd, *J* = 9.8, 3.0 Hz, C*H*Cl), 2.32 – 2.15 (1H of minor isomer, m, one of CH_2), 2.24 (1H of major isomer, dddd, *J* = 14.3, 9.4, 5.8, 3.0 Hz, one of CH_2), 1.93 (1H of major isomer, app. dtd, *J* = 14.3, 9.8, 4.5 Hz, one of CH_2), 1.83 – 1.05 (12H of major isomer and 13H of minor isomer, m, CH_2 protons) and 0.87 (3H of both isomers, app. t, *J* = 6.9 Hz, CH_3); ^{13}C NMR (101 MHz; $CDCl_3$) (major isomer): δ 141.3 (quat C), 132.2 (CH), 129.1 (CH), 126.0 (CH), 77.4 (CH), 31.9 (CH_2), 31.3 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.0 (CH_2), 25.6 (CH_2), 22.8 (CH_2) and 14.2 (CH_3). Identifiable chemical shifts for the minor isomer: δ 131.9 (CH), 129.0 (CH), 125.8 (CH), 76.7 CH), 31.9 (CH_2), 31.2 (CH_2), 29.2 (CH_2), 28.9 (CH_2) and 26.3 (CH_2); EI-MS *m/z* (%) 286 (M^+, ^{35}Cl, l5%), 234 (20), 125 (100), 78 (100); HRMS: Found: M^+, 286.1159. $C_{15}H_{23}{}^{35}ClOS$ requires 286.1158.

*4.6. 1-Chlorononyl Phenyl Sulfoxide (**10a**) by Reaction with n-Octyl-9-BBN*

The *n*-octyl-9-BBN was prepared first. 9-BBN dimer (61 mg, 0.25 mmol) was placed in a 5 mL round bottom flask and flushed with nitrogen for 10 minutes. THF (2 mL) was added and the solution was cooled to 0°C. 1-Octene (79 mL, 0.5 mmol) was added dropwise and the solution was allowed to warm to r.t. and stirred for 2 h.

The general procedure was used for the reaction of 9-octyl-9-BBN, which was added to the sulfoxide anion. Working up and purifying the crude product afforded **10a** (57 mg, 40%, 82:18 mixture of diastereoisomers).

*4.7. 1-Chloropropyl Phenyl Sulfoxide (**10b**)*

According to the general procedure, followed by flash column chromatography (4:1 petroleum ether/diethyl ether), the reaction of triethylborane with **6** gave **10b** (92 mg, 92%) as a colourless oil as a 78:22 mixture of diastereoisomers; $\nu_{max.}$(neat) 3061, 2974, 2937, 2877, 1444, 1084 and 1049 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.78 – 7.69 (2H of major isomer, m, aromatic CH), 7.68 – 7.62 (2H of minor isomer, m, aromatic CH), 7.58 – 7.46 (3H of both isomers, m, aromatic CH), 4.46 (1H of minor isomer, dd, *J* = 9.7, 4.1 Hz, C*H*Cl), 4.36 (1H of major isomer dd, *J* = 9.0, 3.1 Hz, C*H*Cl), 2.23 (1H of each isomer, app. dqd, *J* = 14.6, 7.3, 3.1 Hz, one of CH_2), 1.96 (1H of major isomer, ddq, *J* = 14.6, 9.0, 7.3 Hz, one of CH_2), 1.59 (1H of minor isomer, ddq, *J* = 14.4, 9.7, 7.3 Hz, one of CH_2), 1.10 (3H of major isomer, t, *J* = 7.3 Hz, CH_3) and 1.06 (3H of minor isomer, t, *J* = 7.3 Hz, CH_3); ^{13}C NMR (101 MHz; $CDCl_3$) (major isomer): δ 141.2 (quat C), 132.2 (CH), 129.1 (CH), 126.0 (CH), 78.6 (CH), 24.9 (CH_2) and 10.0 (CH_3); (minor isomer): δ 139.3 (quat C), 132.0 (CH), 128.9 (CH), 125.6 (CH), 78.2 (CH), 24.8 (CH_2) and 11.0 (CH_3); MS ($APCl^+$) *m/z* 205 (MH^+, ^{37}Cl, 10%), 203 (MH^+, ^{35}Cl, 30), 244 (30), 150 (100) and 109 (62); HRMS: Found MH^+, 203.0292. $C_9H_{12}{}^{35}ClOS$ requires 203.0297.

*4.8. 1-Chloropentyl Phenyl Sulfoxide (**10c**)*

According to the general procedure, followed by flash column chromatography (30% diethyl ether/petroleum ether), the reaction

of tributylborane with **6** gave **10c** (101 mg, 88%) as a colourless oil as a 84:16 mixture of diastereoisomers; $\nu_{max.}$ (neat) 3057, 2957, 2931, 2862, 1444, 1084 and 1049 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 7.82 – 7.49 (5H of both isomers, m, aromatic CH), 4.53 (1H of minor isomer, dd, *J* = 9.5, 4.1 Hz, C*H*Cl), 4.40 (1H of major isomer, dd, *J* = 9.8, 3.0 Hz, C*H*Cl), 2.31 – 2.21 (1H of minor isomer, m, one of CH_2), 2.26 (1H of major isomer, dddd, *J* = 14.3, 8.6, 5.6, 3.0 Hz, one of CH_2), 1.94 (1H of major isomer, app. dtd, *J* = 14.3, 9.9, 4.6 Hz, one of CH_2), 1.78 – 1.22 (4H of major isomer and 5H of minor isomer, m) and 0.90 (3H of both isomers, app. t, *J* = 7.2 Hz, CH_3); ^{13}C NMR (101 MHz; $CDCl_3$) (major isomer): δ 141.3 (quat C), 132.2 (CH), 129.1 (CH), 126.0 (CH), 77.4 (CH), 31.1 (CH_2), 27.7 (CH_2), 22.2 (CH_2) and 13.9 (CH_3). Identifiable chemical shifts for the minor isomer: δ 129.0 (CH), 126.8 (CH), 125.8 (CH), 30.9 (CH_2), 28.4 (CH_2) and 22.1 (CH_2); MS ($APCl^+$) *m/z* 233 (MH^+, ^{37}Cl, 10%), 231 (MH^+, ^{35}Cl, 33%), 272 (40), 150 (100); HRMS: Found MH^+, 231.0619. $C_{11}H_{16}{}^{35}ClOS$ requires 231.0610.

*4.9. 1-Chloro-3-phenylpropyl Phenyl Sulfoxide (**10d**)*

According to the general procedure, followed by flash column chromatography (4:1 petroleum ether/diethyl ether), the reaction of tris(2-phenylethyl)borane (impure material from reaction of styrene with borane dimethyl sulfide) with **6** gave **10d** (56 mg, 40%) as a colourless oil as a 81:19 mixture of diastereoisomers; $\nu_{max.}$ (neat) 3061, 3026, 2955, 2930, 2856, 1444, 1085 and 1049 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 7.67 – 7.58 (2H of the major isomer, m, aromatic CH), 7.59 – 7.54 (2H of minor isomer, m, aromatic CH), 7.53 – 7.38 (3H of both isomers, m, aromatic CH), 7.27 – 7.04 (5H of both isomers, m, aromatic CH), 4.40 (1H of minor isomer, dd, *J* = 10.3, 3.7 Hz, C*H*Cl), 4.30 (1H of major isomer, dd, *J* = 10.2, 2.8 Hz, C*H*Cl), 2.95 (1H of major isomer, ddd, *J* = 13.9, 9.0, 4.7 Hz, one of CH_2), 2.90 (1H of minor isomer, ddd, *J* = 13.7, 8.3, 5.1 Hz, one of CH_2), 2.71 (1H of each isomer, app. dt, *J* = 13.9, 8.2 Hz, one of CH_2), 2.47 (1H of each isomer, app. dddd, *J* = 14.3, 9.0, 7.8, 2.8 Hz, one of CH_2), 2.15 (1H of major isomer, dddd, *J* = 14.3, 10.2, 8.8, 4.7 Hz, one of CH_2) and 1.84 (1H of minor isomer, dddd, *J* = 14.2, 10.3, 8.2, 5.2 Hz, one of CH_2); ^{13}C NMR (126 MHz; $CDCl_3$) (major isomer): δ 141.0 (quat C), 139.5 (quat C), 132.3 (CH), 129.2 (CH), 128.8 (CH), 128.6 (CH), 126.6 (CH), 125.9 (CH), 76.4 (CH), 32.8 (CH_2) and 31.8 (CH_2). (minor isomer): δ (quaternary C were not clear), 132.0 (CH), 129.0 (CH), 128.8 (CH), 128.7 (CH), 126.7 (CH), 125.8 (CH), 75.3 (CH), 32.5 (CH_2) and 32.0 (CH_2); MS (EI) *m/z* 278 (M^+, ^{35}Cl, 5%), 91 (90); HRMS: Found M^+, 278.0533. $C_{15}H_{15}{}^{35}ClOS$ requires 278.0532.

*4.10. Deuteration of the Sulfoxide Enolate (**d-10b**)*

The above general procedure was followed, but the reaction was quenched with D_2O (5 mL) and then worked up as for **10a** to yield two diastereomers of ***d*-10b** (93 mg, 93%, approx. 73:27 ratio) as a colourless oil; ^1H NMR (400 MHz; $CDCl_3$) δ 7.79 – 7.70 (2H of major isomer, m, aromatic CH), 7.69 – 7.62 (2H of minor isomer, m, aromatic CH), 7.59 – 7.47 (3H of both isomers, m, aromatic CH), 2.29 (1H of minor isomer, app. dq, *J* = 14.6, 7.3 Hz, one of CH_2), 2.28 (1H of major isomer, app. dq, *J* = 14.7, 7.3 Hz, one of CH_2), 2.01 (1H of major isomer, app. dq, *J* = 14.6, 7.3 Hz, one of CH_2), 1.56 (1H of minor isomer, app. dq, *J* = 14.6, 7.3 Hz, one of CH_2), 1.15 (3H of major isomer, app. t, *J* = 7.3 Hz, CH_3) and 1.12 (3H of minor isomer, app. t, *J* = 7.3 Hz, CH_3); ^{13}C NMR (101 MHz; $CDCl_3$) (major isomer): δ 141.3 (quat C), 132.2 (CH), 129.1 (CH), 126.0 (CH), 78.3 (1:1:1 t, *J* = 25.1 Hz, CD), 24.8 (CH_2) and 10.0 (CH_3); (minor isomer): δ 139.4 (quat C), 131.9 (CH), 129.0 (CH), 125.7 (CH), (CD signal not clear), 24.8 (CH_2) and 11.0 (CH_3).

*4.11. Reaction of Dichloromethyl Phenyl Sulfoxide (**6**) with Triethylborane and Aromatic Aldehydes – General Procedure*

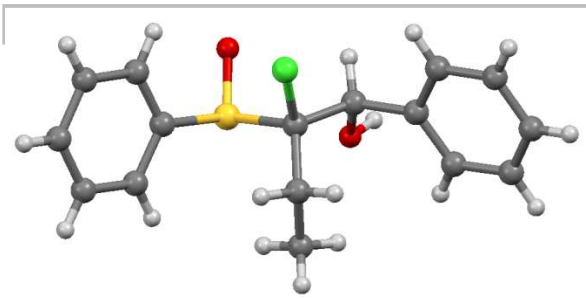
To a cooled (–78 °C) solution of diisopropylamine (183 μL, 1.3 mmol, 1.3 equiv.) in dry THF (5 mL), *n*-BuLi (0.75 mL, 1.6 M in hexane, 1.2 mmol, 1.2 equiv.) was added dropwise. The solution was warmed to 0 °C over a period of 20 min. then cooled to –78 °C. A solution of **6** (209 mg, 1.0 mmol, 1.0 equiv.) in THF (3 mL) was added and the mixture was stirred for 10 min. Triethylborane (1.0 mL, 1.0 M in THF, 1.0 mmol, 1.0 equiv.) was added and stirring was continued for 1 h. The appropriate aromatic aldehyde (1.0 mmol) was added and the mixture was stirred for a further 1 h. The mixture was allowed to warm to 0 °C over a period of 20 min and quenched by addition of sat. aq. ammonium chloride solution (10 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 × 15 mL); the organic layers were combined and dried over magnesium sulfate. The solvents were evaporated under reduced pressure and the crude material obtained was subjected to silica-gel column chromatography (eluted with a suitable ratio of ethyl acetate/chloroform) to afford the four pure diastereoisomers of the product (except for methoxy substituted products, where only three diastereoisomers were formed).

*4.12. Compound **14a***

The general procedure was followed. The reaction of triethylborane and benzaldehyde (102 μL, 1.0 mmol) with **6**, followed by flash column chromatography (3% ethyl acetate/chloroform) gave three fractions; the first fraction contained **14a(i)** (72 mg, 23%) as a colourless solid; the second fraction contained a mixture of **14a(ii)** and **15a** (16 mg, 5% of the mixture, 1:1 ratio) as a colourless oil; the third fraction contained diastereoisomers **14a(iii)** and **14a(iv)** (100 mg, 32%, 45:55 ratio) as a colourless oil.

Data for 14a(i): Colourless solid (72 mg, 23%), m.p. 181 – 182 °C; $\nu_{max.}$ (neat) 3201, 3065, 2968, 2937, 2879, 1442 and 1031 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 7.98 – 7.94 (2H, m, aromatic CH), 7.71 – 7.60 (3H, m, aromatic CH), 7.28 (5H, app. s), 5.66 (1H, app. s, OH), 4.96 (1H, app. s, C*H*OH), 3.00 (1H, dq, *J* = 15.3, 7.2 Hz, one of CH_2), 2.01 (1H, dq, *J* = 15.3, 7.4 Hz, one of CH_2) and 1.30 (3H, app. t, *J* = 7.3 Hz, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.3 (quat C), 136.3 (quat C), 132.8 (CH), 129.0 (CH), 128.8 (CH), 128.5 (CH), 128.1 (CH), 127.7 (CH), 83.7 (quat C), 78.6 (CH), 23.3 (CH_2) and 8.0 (CH_3); MS (ES^-) *m/z* (%), 347 ($(M+Cl)^-$, $^{37}Cl_2$, 13%), 345 ($(M+Cl)^-$, $^{37}Cl^{35}Cl$, 67%), 343 ($(M+Cl)^-$, $^{35}Cl_2$, 100%), 313 (74), 255 (65), 223 (82); HRMS: Found $(M+Cl)^-$, 343.0317. $C_{16}H_{17}{}^{35}Cl_2O_2S$ requires 343.0326.

Selected crystallographic data: $C_{16}H_{17}ClO_2S$, FW = 308.80, T = 296(2) K, λ = 1.54184 Å, Triclinic, P-1, a = 11.2998(3) Å, b = 11.4679(3) Å, c = 12.4272(3) Å, α= 96.840(2)°, β= 92.254(2)°, γ = 104.801(2)°, V = 1541.78(7) $Å^3$, Z = 4, $\rho_{calc.}$ = 1.330 Mg/m^3, crystal size = 0.322 x 0.272 x 0.190 mm^3, μ = 3.442 mm^{-1}, reflections collected = 25725, Independent reflections = 6107, R_{int} = 0.0223, parameters = 365, R_1 = 0.0332, wR_2 = 0.0847 for I>2σ(I) and R_1 = 0.0396, wR_2 = 0.0888 for all data. CCDC 1451735 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/structures



Data for mixture of 14a(ii) and 15a: Colourless oil (16 mg, 5%, *ca*. 1:1 mixture of **14a(ii)** and **15a**); $\nu_{max.}$ (neat) 3348, 3061, 3005, 2931, 2883, 1610, 1444 and 1047 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.88 – 7.83 (2H of **15a**, m, aromatic CH), 7.77 – 7.72 (2H of **14a(ii)**, m, aromatic CH), 7.68 - 7.36 (8H of each compound, m, aromatic CH), 5.50 (1H of **15a**, d, *J* = 2.7 Hz, C*H*OH), 5.20 (1H of **14a(ii)**, d, *J* = 8.7 Hz, C*H*OH), 4.92 (1H of **14a(ii)**, d, *J* = 8.7 Hz, OH), 4.15 (1H of **15a**, d, *J* = 2.7 Hz, OH), 2.39 (1H of **14a(ii)** dq, *J* = 14.7, 7.2 Hz, one of CH_2), 1.28 (1H of **14a(ii)**, dq, *J* = 14.7, 7.1 Hz, one of CH_2) and 1.07 (3H of **14a(ii)**, app. t, *J* = 7.2 Hz); MS ($APCl^+$) *m/z* (%) 374 ($(M+Na+CH_3CN)^+$, ^{37}Cl, 40%), 372 ($(M+Na+CH_3CN)^+$, ^{35}Cl, 100%), 333 ($(M+Na)^+$, ^{37}Cl, 11%), 331 ($(M+Na)^+$, ^{35}Cl, 53%), 228 (13) HRMS: Found $(M+Na)^+$, 331.0519. $C_{16}H_{17}{}^{35}ClNaO_2S$ requires 331.0535.

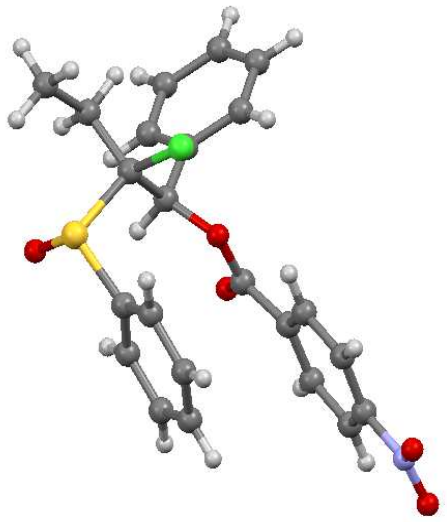
Data for mixture of 14a(iii) and 14a(iv): Colourless oil (100 mg, 32%, 45:55 mixture of diastereoisomers); $\nu_{max.}$ (neat) 3338, 3065, 2939, 2879, 1442 and 1020 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.88 – 7.84 (2H of **14a(iii)**, m, aromatic CH), 7.84 – 7.80 (2H of **14a(iv)**, m, aromatic CH), 7.65 – 7.32 (8H of each isomer, m, aromatic CH), 5.33 (1H of **14a(iv)**, d, *J* = 4.0 Hz, C*H*OH), 5.18 (1H of **14a(iii)**, d, *J* = 3.3 Hz, C*H*OH), 3.61 (1H of **14a(iii)**, d, *J* = 3.3 Hz, OH), 3.20 (1H of **14a(iv)**, d, *J* = 4.0 Hz, OH), 2.23 – 2.12 (2H of **14a(iii)**, m, CH_2), 1.88 (1H of **14a(iv)**, dq, *J* = 15.0, 7.4 Hz, one of CH_2), 1.50 (1H of **14a(iv)**, dq, *J* = 15.0, 7.3 Hz, one of CH_2), 0.95 (3H of **14a(iv)**, app. t, *J* = 7.4 Hz, CH_3) and 0.84 (3H of **14a(iii)**, app. t, *J* = 7.5 Hz, CH_3); ^{13}C NMR (101 MHz; $CDCl_3$) δ 138.8 (quat C), 138.5 (quat C), 138.0 (quat C), 137.8 (quat C), 132.5 (CH), 132.3 (CH), 129.0 (CH), 128.9 (CH), 128.9 (CH), 128.8 (CH), 128.7 (CH), 128.4 (CH), 128.3 (CH), 128.0 (CH), 127.4 (CH), 127.2 (CH), 93.6 (quat C), 89.5 (quat C), 78.1 (CH), 75.2 (CH), 27.7 (CH_2), 24.7 (CH_2), 10.1 (CH_3) and 9.3 (CH_3); MS (ES^+) *m/z* (%) 374 ($(M+Na+CH_3CN)^+$, ^{37}Cl, 13%), 372 ($(M+Na+CH_3CN)^+$, ^{35}Cl, 42%), 333 ($(M+Na)^+$, ^{37}Cl, 37%), 331 ($(M+Na)^+$, ^{35}Cl, 100%), 254 (20); HRMS: Found $(M+Na)^+$, 331.0550. $C_{16}H_{17}{}^{35}ClNaO_2S$ requires 331.0536.

*4.13. Synthesis of 4-Nitrobenzoate Derivatives of Compounds **14a(iii)** and **14a(iv)***

The mixture of two diastereoisomers **14a(iii)** and **14a(iv)** (94 mg, 0.3 mmol) was dissolved in THF (10 mL). Triethylamine (93 µL, 0.66 mmol, 2.2 equiv.) was added, followed by 4-dimethylaminopyridine (10 mg, catalytic amount) and 4-nitrobenzoyl chloride (112 mg, 2 equiv.). The solution was warmed up to room temperature and stirred for 24 h. The reaction was then quenched with sat. sodium bicarbonate. The organic layer was separated and the aqueous layer was extracted with chloroform (2 × 10 mL) and dried over magnesium sulfate. The solvents were removed to yield a mixture of two diastereoisomeric 4-nitrobenzoates (110 mg, 80%). The two diastereomers were separated by flash column chromatography on silica gel (1% EtOAc/$CHCl_3$).

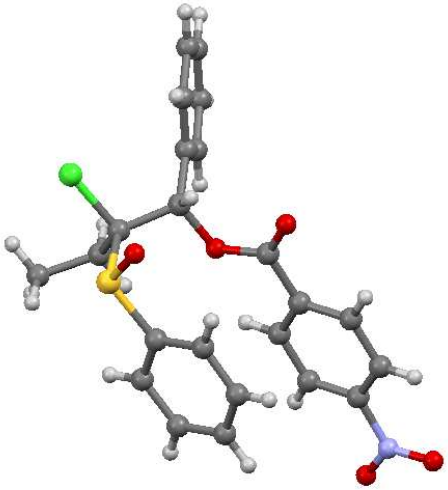
4-Nitrobenzoate of 14a(iii): R_f = 0.21 (1% EtOAc/$CHCl_3$), 60 mg (43%), colourless solid, m.p. 133 – 134 °C; $\nu_{max.}$ (neat) 1728, 1523, 1074 and 1047 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.31 (2H, d, *J* = 9.0 Hz, aromatic CH), 8.22 (2H, d, *J* = 9.0 Hz, aromatic CH), 7.78 – 7.68 (4H, m, aromatic CH), 7.54 – 7.46 (3H, m, aromatic CH), 7.44 – 7.38 (3H, m, aromatic CH), 6.55 (1H, s, CHO), 2.30 – 2.12 (2H, m, CH_2) and 1.13 (3H, app. t, *J* = 7.5 Hz, CH_3); ^{13}C NMR (101 MHz; $CDCl_3$) δ 162.6 (quat C), 151.0 (quat C), 138.2 (quat C), 134.8 (quat C), 134.3 (quat C), 132.4 (CH), 131.1 (CH), 129.6 (CH), 129.1 (CH), 128.8 (CH), 128.4 (CH), 127.5 (CH), 123.9 (CH), 88.6 (quat C), 77.6 (CH), 27.5 (CH_2) and 9.8 (CH_3); MS ($APCl^+$) *m/z* (%) 523 ($(M+Na+CH_3CN)^+$, ^{37}Cl, 25%), 521 ($(M+Na+CH_3CN)^+$, ^{35}Cl, 100%), 482 ($(M+Na)^+$, ^{35}Cl, 17%), 480 ($(M+Na)^+$, ^{35}Cl, 58%); HRMS: Found $(M+Na)^+$, 480.0657. $C_{23}H_{20}{}^{35}ClNaO_5S$ requires 480.0648.

Selected crystallographic data: $C_{23}H_{20}ClNO_5S$, FW = 457.91, T = 150(2) K, λ = 1.54184, Triclinic, P-1, a = 7.3284(2) Å, b = 12.4907(3) Å, c = 12.9031(4) Å, α= 110.993(2)°, β= 102.930(2)°, γ = 95.432(2)°, V = 1054.73(5) $Å^3$, Z = 2, $\rho_{calc.}$ = 1.442 Mg/m^3, crystal size = 0.261 x 0.235 x 0.155 mm^3, μ = 2.841 mm^{-1}, reflections collected = 16433, Independent reflections = 4150, R_{int} = 0.0187, parameters = 281, R_1 = 0.0303, wR_2 = 0.0819 for I>2σ(I) and R_1 =0.0311, wR_2 = 0.0824 for all data. CCDC 1451736 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/structures



4-Nitrobenzoate of 14a(iv): R_f = 0.19 (1% EtOAc/$CHCl_3$), 40 mg (29%) colourless solid, m.p. 127 – 129 °C; $\nu_{max.}$ (neat) 3053, 2978, 2922, 2854, 1732, 1608, 1442 and 1049 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.08 (2H, d, *J* = 9.0 Hz, aromatic CH), 7.79 (2H, dd, *J* = 8.4, 1.1 Hz, aromatic CH), 7.68 (2H, d, *J* = 9.0 Hz, aromatic CH), 7.49 - 7.45 (2H, m, aromatic CH), 7.35 – 7.31 (3H, m, aromatic CH), 7.16 (2H, app. t, *J* = 7.9 Hz, aromatic CH), 6.89 (1H, tt, *J* = 7.4, 1.1 Hz, aromatic CH), 6.44 (1H, s, CHO), 2.19 (1H, dq, *J* = 15.2, 7.0 Hz, one of CH_2), 1.42 (1H, dq, *J* =15.2, 7.3 Hz, one of CH_2) and 1.23 (3H, app. t, *J* = 7.2 Hz, CH_3); ^{13}C NMR (101 MHz; $CDCl_3$) δ 162.0 (quat C), 150.5 (quat C), 138.7 (quat C), 135.4 (quat C), 134.5 (quat C), 131.2 (CH), 130.6 (CH), 129.5 (CH), 128.8 (CH), 128.7 (CH), 128.4 (CH), 126.6 (CH), 123.1 (CH), 88.8 (quat C), 72.1 (CH), 30.0 (CH_2) and 8.4 (CH_3); MS ($APCl^+$) *m/z* 523 ($(M+Na+CH_3CN)^+$, ^{37}Cl, 10%), 521 ($(M+Na+CH_3CN)^+$, ^{35}Cl, 26%), 482 ($(M+Na)^+$, ^{37}Cl, 27%), 480 ($(M+Na)^+$, ^{35}Cl, 100%); HRMS: Found $(M+Na)^+$, 480.0627. $C_{23}H_{20}{}^{35}ClNaO_5S$ requires 480.0648.

Selected crystallographic data: $C_{23}H_{20}ClNO_5S$, FW = 457.91, T = 293(2) K, λ = 1.54184, Triclinic, P-1, a = 6.4998(2) Å, b = 7.7680(3) Å, c = 22.2674(8) Å, α= 91.378(3)°, β= 93.748(3)°, γ = 108.174(3)°, V = 1064.75(7) $Å^3$, Z = 2, $\rho_{calc.}$ = 1.428 Mg/m^3, crystal size = 0.457 x 0.135 x 0.065 mm^3, μ = 2.815 mm^{-1}, reflections collected = 16565, Independent reflections = 4198, R_{int} = 0.0475, parameters =282, R_1 = 0.0728, wR_2 = 0.2281 for I>2σ(I) and R_1 =0.0810, wR_2 = 0.2311 for all data. CCDC 1451737 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/structures



*4.14. Reduction of the 4-Nitrobenzoate Derivative of **14a(iii)***

The 4-nitrobenzoate derivative of **14a(iii)** (27 mg, 0.05 mmol) was dissolved in $CHCl_3$ (1 mL) and added dropwise with swirling to a solution of sodium borohydride (10 mg) in a mixture of ethanol and $CHCl_3$ (5 mL). The solution was swirled for 15 minutes further. Ice-cold water (5 mL) and 2M HCl (3 mL) were added. The mixture was extracted with chloroform (3 × 5 mL) and the chloroform extract was dried over magnesium sulfate. After removal of the solvents, the crude product was purified by flash column chromatography to yield **14a(iii)** (10 mg, 67%) as a colourless oil. While this compound was not analytically pure, it was sufficiently pure to allow the peaks for compound **14a(iii)** in the original mixture of **14a(iii)** and **14a(iv)** to be identified.

*4.15. Compounds **14b***

The general method, involving the reaction of triethylborane and 3-methoxybenzaldehyde (121 μL, 1.0 mmol) with **6** followed by flash column chromatography (3% ethyl acetate/chloroform), gave three fractions; the first contained diastereoisomer **14b(i)** (60 mg, 18%) as a colourless solid; the second contained diastereoisomer **14b(iii)** (56 mg, 17%) as a colourless oil; the third contained diastereoisomer **14b(iv)** (56 mg, 17%) as a colourless oil.

Data for 14b(i): Colourless solid (60 mg, 18%), m.p. 177 – 178 °C; $\nu_{max.}$ (neat) 3242, 2978, 2872 and 1041 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.95 (2H, dd, *J* = 8.1, 1.5 Hz, aromatic CH), 7.70 – 7.60 (3H, m, aromatic CH), 7.18 (1H, t, *J* = 8.1 Hz, aromatic CH), 6.88 – 6.79 (3H, m, aromatic CH), 5.66 (1H, s, OH), 4.93 (1H, s, C*H*OH), 3.77 (3H, s, OCH_3), 2.98 (dq, *J* = 15.5, 7.2 Hz, 1H, one of CH_2), 2.03 (dq, *J* = 15.5, 7.4 Hz, 1H, one of CH_2) and 1.30 (3H, app. t, *J* = 7.3 Hz, CH_3); ^{13}C NMR (101 MHz; $CDCl_3$) δ 159.1 (quat C), 138.9 (quat C), 136.3 (quat C), 132.8 (CH), 129.0 (CH), 128.6 (CH), 128.1 (CH), 121.3 (CH), 114.6 (CH), 113.7 (CH), 83.7 (quat C), 78.5 (CH), 55.4 (CH_3), 23.4 (CH_2) and 8.0 (CH_3); MS ($APCl^+$) *m/z* (%) 341 (MH^+, ^{37}Cl, 35), 339 (MH^+, ^{35}Cl, 100), 186 (20), 136 (17); HRMS: Found MH^+, 339.0819. $C_{17}H_{20}{}^{35}ClO_3S$ requires 339.0822.

Data for 14b(iii): Colourless oil (56 mg, 17%); $\nu_{max.}$ (neat) 3296, 3061, 2997, 2957, 2835, 1600, 1442 and 1020 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.85 (2H, dd, *J* = 8.2, 1.4 Hz, aromatic CH), 7.60 – 7.49 (3H, m, aromatic, CH), 7.28 (1H, t, *J* = 7.9 Hz, aromatic CH), 7.16 - 7.09 (2H, m, aromatic CH), 6.89 (1H, ddd, *J* = 8.2, 2.5, 0.7 Hz, aromatic CH), 5.13 (1H, s, C*H*OH), 3.81 (3H, s, OCH_3), 3.52 (1H, br., OH), 2.11 (2H, app. q, *J* = 7.5 Hz, CH_2) and 0.86 (3H, app. t, *J* = 7.5 Hz, CH_3); ^{13}C NMR (101 MHz; $CDCl_3$) δ 159.3 (quat C), 139.4 (quat C), 138.5 (quat C), 132.3 (CH), 129.0 (CH), 128.8 (CH), 127.5 (CH), 121.0 (CH), 114.4 (CH), 114.3 (CH), 89.5 (quat C), 77.9 (CH), 55.4 (CH_3), 24.9 (CH_2) and 10.1 (CH_3); MS ($APCl^+$) *m/z* (%) 363 ($(M+Na)^+$, ^{37}Cl, 13%), 361 ($(M+Na)^+$, ^{35}Cl, 36%), 341 (MH^+, ^{37}Cl, 20%), 339 (MH^+, ^{35}Cl, 56%), 195 (25), 154 (60); HRMS: Found: 361.0636. $C_{17}H_{19}{}^{35}ClNaO_3S$ requires 361.0641.

Data for 14b(iv): Colourless oil (56 mg, 17%); $\nu_{max.}$ (neat) 3356, 3061, 2937, 2883, 2837, 1599, 1442 and 1037 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.83 (2H, dd, *J* = 8.1, 1.5 Hz, aromatic CH), 7.62 – 7.52 (3H, m, aromatic CH), 7.25 (1H, t, *J* = 7.9 Hz, aromatic CH), 7.06 – 7.00 (2H, m, aromatic CH), 6.88 (1H, ddd, *J* = 8.3, 2.6, 0.9 Hz, aromatic CH), 5.31 (1H, d, *J* = 3.9 Hz, C*H*OH), 3.80 (3H, s, OCH_3), 3.14 (1H, d, *J* = 3.9 Hz, OH), 1.91 (1H, dq, *J* = 15.0, 7.4 Hz, one of CH_2), 1.51 (1H, dq, *J* = 15.0, 7.4 Hz, one of CH_2) and 0.98 (3H, app. t, *J* = 7.4 Hz, CH_3); ^{13}C NMR (101 MHz; $CDCl_3$) δ 159.6 (quat C), 139.5 (quat C), 138.8 (quat C), 132.5 (CH), 129.4 (CH), 128.9 (CH), 127.2 (CH), 120.7 (CH), 114.7 (CH), 113.7 (CH), 93.4 (quat C), 74.8 (CH), 55.4 (CH_3), 27.9 (CH_2) and 9.3 (CH_3); MS (ES^+) *m/z* (%) 404 ($(M+Na+CH_3CN)^+$, ^{37}Cl, 35%), 402 ($(M+Na+CH_3CN)^+$, ^{35}Cl, 100%), 363 ($(M+Na)^+$, ^{37}Cl, 33%), 361 ($(M+Na)^+$, ^{35}Cl, 75%), 341 (MH^+, ^{37}Cl, 12%), 339 (MH^+, ^{35}Cl, 32%), 258 (15), 177 (15); HRMS: Found MH^+, 339.0822. $C_{17}H_{20}{}^{35}ClO_3S$ requires 339.0822.

*4.16. Compound **14c***

The general procedure for reaction of triethylborane and 4-methoxybenzaldehyde (121 μL, 1.0 mmol) with **6**, followed by flash column chromatography (3% ethyl acetate/chloroform), gave three fractions; the first contained diastereoisomer **14c(i)** (60 mg, 18%) as a colourless solid; the second contained diastereoisomer **14c(iii)** (42 mg, 12%) as a colourless oil; the third contained a mixture of **14c(iii)** and **14c(iv)** (52 mg, 15%, 1:2 ratio) as a colourless oil.

Data for 14c(i): Colourless solid (60 mg, 18%), m.p. 136 – 138 °C; $\nu_{max.}$ (neat) 3327, 3060, 2972, 2935, 2835, 1610, 1442 and 1030 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.95 (2H, dd, *J* = 8.0, 1.5 Hz, aromatic CH), 7.69 – 7.60 (3H, m, aromatic CH), 7.20 (2H, d, *J* = 8.8, Hz, aromatic CH), 6.80 (2H, d, *J* = 8.8, aromatic CH), 5.61 (1H, s, OH), 4.91 (1H, s, C*H*OH), 3.77 (3H, s, OCH_3), 2.97 (1H, dq, *J* = 15.4, 7.2 Hz, one of CH_2), 2.00 (1H, dq, *J* = 15.4, 7.4 Hz, one of CH_2) and 1.29 (3H, app. t, *J* = 7.3 Hz, CH_3); ^{13}C NMR (101 MHz; $CDCl_3$) δ 159.7 (quat C), 136.4 (quat C), 132.7 (CH), 129.9 (CH), 129.4 (quat C), 129.0 (CH), 128.1 (CH), 113.1 (CH), 84.0 (quat C), 78.3 (CH), 55.3 (CH_3), 23.2 (CH_2) and 8.0 (CH_3); MS (ES^+) *m/z* (%) 404 ($(M+Na+CH_3CN)^+$, ^{37}Cl, 30%), 402 ($(M+Na+CH_3CN)^+$, ^{35}Cl, 100%), 363 ($(M+Na)^+$, ^{37}Cl, 16%), 361 ($(M+Na)^+$, ^{35}Cl, 50%),

254 (70), 185 (35); HRMS: Found $(M+Na)^+$, 361.0641. $C_{17}H_{19}{}^{35}ClNaO_3S$, requires 361.0641.

Data for 14c(iii): Slightly impure colourless oil (42 mg, 12%); $\nu_{max.}$ (neat) 3311, 3063, 2997, 2931, 2837, 1608, 1442 and 1030 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 7.87 – 7.83 (2H, m, aromatic, CH), 7.59 – 7.50 (3H, m, aromatic CH), 7.48 (2H, d, *J* = 8.8 Hz, aromatic CH), 6.90 (2H, d, *J* =8.8 Hz, aromatic CH), 5.17 (1H, s, C*H*OH), 3.82 (3H, s, OCH_3), 3.40 (1H, br., OH), 2.22 – 2.11 (2H, m, CH_2) and 0.84 (3H, app. t, *J* = 7.5 Hz, CH_3); ^{13}C NMR (101 MHz; $CDCl_3$) δ 160.0 (quat C), 138.5 (quat C), 132.2 (CH), 129.9 (CH), 129.8 (quat C), 128.8 (CH), 127.4 (CH), 113.4 (CH), 89.7 (quat C), 77.7 (CH), 55.4 (CH_3), 24.7 (CH_2) and 10.1 (CH_3); MS ($APCl^+$) *m/z* (%) 339 (MH^+, ^{35}Cl, 3%), 156 (100), 120 (63); HRMS: Found MH^+, 339.0826. $C_{17}H_{20}{}^{35}ClO_3S$ requires 339.0822.

Data for mixture of diastereoisomers 14c(iii) and **14c(iv)**: Colourless oil. (52 mg, 15%, isomers **14c(iii)** and **14c(iv)** in a 1:2 ratio); $\nu_{max.}$ (neat) 3267, 3063, 2970, 2841, 1606, 1440 and 1030 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 7.85 (2H of **14c(iii)**, dd, *J* = 8.2, 1.5 Hz, aromatic CH), 7.81 (2H of **14c(iv)**, dd, *J* = 8.1, 1.6 Hz, aromatic CH), 7.60 – 7.50 (3H of both isomers, m, aromatic CH), 7.48 (2H of **14c(iii)**, d, *J* = 8.8 Hz, aromatic CH), 7.39 (2H of **14c(iv)**, d, *J* = 8.7 Hz, aromatic CH), 6.92 – 6.84 (2H of both isomers, m, aromatic CH), 5.28 (1H of **14c(iv)**, s, C*H*OH), 5.13 (1H of **14c(iii)**, s, C*H*OH), 3.81 (3H of **14c(iii)**, s, OCH_3), 3.80 (3H of **14c(iv)**, s, OCH_3), 3.52 (1H of **14c(iii)**, s, OH), 3.23 (1H of **14c(iv)**, s, OH), 2.16 (2H of **14c(iii)**, app. q, *J* = 7.5 Hz, CH_2), 1.86 (1H of **14c(iv)**, dq, *J* = 15.0, 7.4 Hz, one of CH_2), 1.51 (1H of **14c(iv)**, dq, *J* = 15.0, 7.3 Hz, one of CH_2), 0.95 (3H of **14c(iv)**, app. t, *J* = 7.4 Hz, CH_3) and 0.86 (3H of **14c(iii)**, app. t, *J* = 7.5 Hz, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) isomer **14c(iii)**: δ 159.9 (quat C), 138.5 (quat C), 132.2 (CH), 130.2 (quat C), 129.9 (CH), 128.7 (CH), 127.4 (CH), 113.4 (CH), 89.9 (quat C), 77.6 (CH), 55.4 (CH_3), 24.8 (CH_2) and 10.1 (CH_3); isomer **14c(iv)**: δ 160.1 (quat C), 138.8 (quat C), 132.4 (CH), 130.2 (quat C), 129.5 (CH), 128.9 (CH), 127.2 (CH), 113.8 (CH), 93.8 (quat C), 75.0 (CH), 55.4 (CH_3), 27.6 (CH_2) and 9.3 (CH_3). Peaks for the OMe and one of the aromatic quaternary carbon atoms were not resolved for the two isomers; MS ($APCl^+$) *m/z* (%) 363 ($(M+Na)^+$, ^{37}Cl, 35%), 361 ($(M+Na)^+$, ^{35}Cl, 100%), 194 (100), 125 (100), 77 (100); HRMS: Found $(M+Na)^+$, 361.0641. $C_{17}H_{19}{}^{35}ClNaO_3S$ requires 361.0641.

*4.17. Compound **14d***

The general procedure for the reaction of triethylborane and 4-bromobenzaldehyde (185 mg, 1.0 mmol) with **6**, followed by flash column chromatography (1% ethyl acetate/chloroform), gave three fractions; the first contained diastereoisomer **14d(i)** (40 mg, 10%) as a colourless solid; the second contained a mixture of **14d(ii)** and **15d** (30 mg, 8% of the mixture, 1:1 ratio) as a colourless oil; the third fraction contained diastereoisomers **14d(iii)** and **14d(iv)** (130 mg, 34%, 40:60 ratio) as a colourless oil.

Data for 14d(i): Colourless solid (40 mg, 10%), m.p. 156 – 158 °C; $\nu_{max.}$ (neat) 3225, 3062, 2982, 2924, 2858, 1610, 1442 and 1030 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 7.95 (2H, dd, *J* = 8.0, 1.4 Hz, aromatic CH), 7.73 – 7.60 (3H, m, aromatic CH), 7.40 (2H, d, *J* = 8.5 Hz, aromatic CH), 7.16 (2H, d, *J* = 8.5 Hz, aromatic CH), 5.75 (1H, s, OH), 4.93 (1H, s, C*H*OH), 2.98 (1H, dq, *J* = 15.4, 7.2 Hz, one of CH_2), 1.92 (1H, dq, *J* = 15.4, 7.4 Hz, one of CH_2) and 1.29 (3H, app. t, *J* = 7.3 Hz, CH_3); ^{13}C NMR (101 MHz; $CDCl_3$) δ 136.3 (quat C), 136.1 (quat C), 132.9 (CH), 130.9 (CH), 130.4 (CH), 129.1 (CH), 128.0 (CH), 122.7 (quat C), 83.1 (quat C), 78.1 (CH), 23.2 (CH_2) and 7.9 (CH_3); MS (ES^-) *m/z* (%) 425 ($(M+Cl)^-$, $^{81}Br^{35}Cl^{37}Cl$ and $^{79}Br^{37}Cl_2$ combined, 49%), 423 ($(M+Cl)^-$, $^{81}Br^{35}Cl_2$ and $^{79}Br^{37}Cl^{35}Cl$ combined, 100%), 421 ($(M+Cl)^-$, $^{79}Br^{35}Cl_2$, 66%), 197 (27); HRMS: Found $(M+Cl)^-$, 420.9439. $C_{16}H_{16}{}^{79}Br^{35}Cl_2O_2S$ requires 420.9431.

Data for mixture of 14d(ii) and 15d: Colourless oil (30 mg, 8%, 1:1 ratio); $\nu_{max.}$ (neat) 3344, 3065, 2974, 2939, 2881, 1591, 1444, 1074 and 1010 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 7.87 – 7.46 (9H of each compound, m, aromatic CH), 5.49 (1H of **15d**, d, *J* = 2.5 Hz, C*H*OH), 5.15 (1H of **14d(ii)**, d, *J* = 8.8 Hz, C*H*OH), 5.03 (1H of **14d(ii)**, d, *J* = 8.8 Hz, OH), 4.32 (1H of **15d** , d, *J* = 2.5 Hz, OH), 2.39 (1H of **14d(ii)**, dq, *J* = 14.6, 7.2 Hz, one of CH_2), 1.31 – 1.20 (1H of **14d(ii)**, m, one of CH_2) and 1.08 (3H of **14d(ii)**, app. t, *J* = 7.2 Hz, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$) chemical shifts for both compounds: δ 137.3 (quat C), 137.3 (quat C), 136.6 (quat C), 134.7 (quat C), 133.6 (CH), 132.6 (CH), 131.4 (CH), 131.2 (CH), 130.8 (CH), 130.7 (CH), 129.1 (CH), 128.8 (CH), 128.2 (CH), 127.2 (CH), 122.9 (quat C), 121.6 (quat C), 93.8 (quat), 85.7 (quat C), 79.8 (CH), 77.6 (CH), 25.5 (CH_2) and 8.0 (CH_3); MS (ES) *m/z* (%) 425 ($(M+Cl)^-$, $^{81}Br^{35}Cl^{37}Cl$ and $^{79}Br^{37}Cl_2$ combined, 49%), 423 ($(M+Cl)^-$, $^{81}Br^{35}Cl_2$ and $^{79}Br^{37}Cl^{35}Cl$ combined, 100%), 421 ((M+Cl), $^{79}Br^{35}Cl_2$, 68%), 200 (16), 198 (30); HRMS: Found $(M+Cl)^-$, 420.9430. $C_{16}H_{16}{}^{79}Br^{35}Cl_2O_2S$ requires 420.9431.

Data for mixture of 14d(iii) and 14d(iv): Colourless oil (130 mg, 34%, 40:60 ratio); $\nu_{max.}$ (neat) 3306, 3065, 2941, 2883, 1591, 1442 and 1030 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 7.81 (2H of **14d(iii)**, dd, *J* = 8.3, 1.3 Hz, aromatic CH), 7.77 (2H of **14d(iv)**, dd, *J* = 8.2, 1.4 Hz, aromatic CH), 7.63 – 7.43 (5H of each isomer, m, aromatic CH), 7.40 (2H of **14d(iii)**, d, *J* = 8.5 Hz, aromatic CH), 7.33 (2H of **14d(iv)**, d, *J* = 8.4 Hz, aromatic CH), 5.28 (1H of **14d(iv)**, d, *J* = 3.6 Hz, C*H*OH), 5.08 (1H of **14d(iii)**, d, *J* = 3.3 Hz, C*H*OH), 4.09 (1H of **14d(iii)**, d, *J* = 3.3 Hz, OH), 3.47 (1H of **14d(iv)**, d, *J* = 3.6 Hz, OH), 2.11 (2H of **14d(iii)**, app. q, *J* = 7.5 Hz, CH_2), 1.81 (1H of **14d(iv)**, dq, *J* = 15.1, 7.4 Hz, one of CH_2), 1.48 (1H of **14d(iv)**, dq, *J* = 15.1, 7.3 Hz, one of CH_2), 0.96 (3H of **14d(iv)**, app. t, *J* = 7.4 Hz, CH_3) and 0.82 (3H of **14d(iii)**, app. t, *J* = 7.5 Hz, CH_3); ^{13}C NMR (101 MHz; $CDCl_3$) chemical shifts for both isomers: δ 138.4 (quat C), 138.1 (quat C), 137.0 (quat C), 137.0 (quat C), 132.6 (CH), 132.3 (CH), 131.5 (CH), 131.1 (CH), 130.4 (CH), 130.0 (CH), 129.0 (CH), 128.8 (CH), 127.4 (CH), 127.2 (CH), 123.1 (quat C), 122.9 (quat C), 93.0 (quat C), 89.4 (quat C), 77.3 (CH), 74.7 (CH), 27.8 (CH_2), 24.8 (CH_2), 10.0 (CH_3) and 9.3 (CH_3); MS (ES^-) *m/z* (%) 425 ($(M+Cl)^-$, $^{81}Br^{35}Cl^{37}Cl$ and $^{79}Br^{37}Cl_2$ combined, 13%), 423 ($(M+Cl)^-$, $^{81}Br^{35}Cl_2$ and $^{79}Br^{37}Cl^{35}Cl$ combined, 46%), 421 ($(M+Cl)^-$, $^{79}Br\ ^{35}Cl_2$, 26%), 299 (100), 255 (62); HRMS: Found $(M+Cl)^-$, 420.9423. $C_{16}H_{16}{}^{79}Br^{35}Cl_2O_2S$ requires 420.9431.

*4.18. Compound **14e***

The general procedure for reaction of triethylborane and 4-fluorobenzaldehyde (108 μL, 1.0 mmol) with **6**, followed by flash column chromatography (5% ethyl acetate/chloroform), gave three fractions; the first contained diastereoisomer **14e(i)** (70 mg, 22%) as a colourless solid; the second contained a mixture of compounds **14e(ii)** and **15e** (56 mg, 17%, 1:1 ratio) as a colourless oil; the third contained diastereoisomers **14e(iii)** and **14e(iv)** (64 mg, 20%, 54:46 ratio) as a colourless oil.

Data for 14e(i): Colourless solid (70 mg, 22%), m.p. 102 – 104 °C; $\nu_{max.}$ (neat) 3321, 3065, 2972, 2924, 2852, 1602, 1442 and 1053 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 7.95 (2H,dd, *J* = 8.1, 1.5 Hz,), 7.71 – 7.61 (3H, m, aromatic CH), 7.29 - 7.22 (2H, m, aromatic CH), 7.00 – 6.93 (2H, m, aromatic CH), 5.73 (1H, s, exchanged with D_2O, OH), 4.94 (1H, s, C*H*OH), 2.99 (1H, dq, *J* = 15.5, 7.2 Hz, one of CH_2), 1.95 (1H, dq, *J* = 15.5, 7.3 Hz, one

of CH_2) and 1.30 (3H, app. t, J = 7.3 Hz, CH_3); ^{13}C NMR (101 MHz; $CDCl_3$) δ 162.8 (d, J = 247 Hz, quat C), 136.2 (quat C), 133.0 (d, J = 3 Hz, quat C), 132.9 (CH), 130.4 (d, J = 8 Hz, CH), 129.1 (CH), 128.0 (CH), 114.7 (d, J = 22 Hz, CH), 83.4 (quat C), 78.1 (CH), 23.2 (CH_2) and 7.9 (CH_3); MS (APCl$^+$) *m/z* (%) 392 ((M+Na+CH_3CN)$^+$, ^{37}Cl, 33%), 390 (M+Na+CH_3CN)$^+$, ^{35}Cl, 100%), 329 (MH$^+$, ^{37}Cl, 8%), 327 (MH$^+$, ^{35}Cl, 23%), 165 (78), 150 (93); HRMS: Found MH$^+$, 327.0632. $C_{16}H_{17}{}^{35}ClFO_2S$ requires 327.0622.

Data for mixture of 14e(ii) and 15e: Colourless oil (56 mg, 17%, 1:1 ratio); $\nu_{max.}$ (neat) 3346, 3061, 3005, 2941, 1604, 1444 and 1047 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.84 (2H of either **14e(ii)** or **15e**, dd, J = 8.4, 1.2 Hz, aromatic CH), 7.74 (2H of either **14e(ii)** or **15e**, dd, J = 8.1, 1.4 Hz, aromatic CH), 7.68 – 7.52 (5H of each compound, m, aromatic CH), 7.14 – 7.06 (2H of each compound, m, aromatic CH), 5.51 (1H of **15e**, d, J = 2.5 Hz, C*H*OH), 5.18 (1H of **14e(ii)**, d, J = 8.6 Hz, C*H*OH), 5.00 (1H of **14e(ii)**, d, J = 8.6 Hz, OH), 4.30 (1H of **15e** , d, J = 2.5 Hz, OH), 2.36 (1H of **14e(ii)**, dq, J = 14.6, 7.2 Hz, one of CH_2), 1.26 (1H of **14e(ii)**, dq, J = 14.6, 7.1 Hz, one of CH_2) and 1.07 (3H of **14e(ii)**, app. t, J = 7.2 Hz, CH_3); ^{13}C NMR (101 MHz; $CDCl_3$) chemical shifts for both compounds: δ 163.5 (d, J = 249 Hz, quat C), 162.4 (d, J = 254 Hz, quat C), 137.2 (quat C), 136.8 (quat C), 133.5 (CH), 133.3 (d, J = 3 Hz, quat C), 132.5 (CH), 131.5 (d, J = 3 Hz, quat C), 131.0 (d, J = 8 Hz, CH), 130.71 (d, J = 8 Hz, CH), 129.1 (CH), 128.7 (CH), 128.1 (CH), 127.2 (CH), 115.2 (d, J = 22 Hz, CH), 115.0 (d, J = 22 Hz, CH), 86.0 (quat C), 83.6 (quat C), 79.6 (CH), 77.4 (CH), 25.5 (CH_2) and 8.1 (CH_3); MS (APCl$^+$) *m/z* (%) 392 (M+Na+CH_3CN)$^+$, ^{37}Cl, 33%), 390 ((M+Na+CH_3CN)$^+$, ^{35}Cl, 100%), 329 (MH$^+$, ^{37}Cl, 8%), 327 (MH$^+$, ^{35}Cl, 37%), 349 (35), 390 (100), 261 (25); HRMS: Found MH$^+$, 327.0638. $C_{16}H_{17}{}^{35}ClFO_2S$ requires 327.0622.

Data for mixture of 14e(iii) and 14e(iv): Colourless oil (64 mg, 20%, 54:46 ratio); $\nu_{max.}$ (neat) 3323, 3065, 2984, 2941, 2885, 1602, 1442 and 1030 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.84 (2H of **14e(iii)**, dd, J = 8.2, 1.4 Hz, aromatic CH), 7.80 (2H of **14e(iv)**, dd, J = 8.1,1.5 Hz, aromatic CH), 7.63 – 7.43 (5H of both isomers, m, aromatic CH), 7.08 – 7.00 (2H of both isomers, m, aromatic CH), 5.36 (1H of **14e(iv)**, d, J = 3.5 Hz, C*H*OH), 5.21 (1H of **14e(iii)**, d, J = 3.2 Hz, C*H*OH), 3.80 (1H of **14e(iii)**, d, J = 3.2 Hz, OH), 3.37 (1H of **14e(iv)**, d, J = 3.5 Hz, OH), 2.21 – 2.05 (2H of **14e(iii)**, m, CH_2), 1.83 (1H of **14e(iv)**, dq, J = 15.1, 7.4 Hz, one of CH_2), 1.50 (1H of **14e(iv)**, dq, J = 15.1, 7.3 Hz, one of CH_2), 0.96 (3H of **14e(iv)**, app. t, J = 7.4 Hz, CH_3) and 0.80 (3H of **14e(iii)**, app. t, J = 7.5 Hz, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1 (quat C, d, J = 248 Hz), 163.0 (quat C, d, J = 248 Hz), 138.6 (quat C), 138.2 (quat C), 133.9 (quat C, d, J = 3 Hz), 133.6 (quat C, d, J = 3 Hz), 132.6 (CH), 132.4 (CH), 130.5 (CH, d, J = 8 Hz), 130.1 (CH, d, J = 8 Hz), 129.0 (CH), 128.8 (CH), 127.4 (CH), 127.2 (CH), 115.4 (CH, d, J = 22 Hz), 114.9 (CH, d, J = 21 Hz), 93.2 (quat C), 89.2 (quat C), 77.4 (CH), 74.7 (CH), 27.9 (CH_2), 24.4 (CH_2), 10.0 (CH_3) and 9.3 (CH_3); MS (APCl$^+$) *m/z* (%) 392 ((M+Na+CH_3CN)$^+$, ^{37}Cl, 33%), 390 ((M+Na+CH_3CN)$^+$, ^{35}Cl, 100%), 351 ((M+Na)$^+$, ^{37}Cl, 20%), 349 ((M+Na)$^+$, ^{35}Cl, 55%); HRMS: Found (M+Na)$^+$, 349.0435. $C_{16}H_{17}{}^{35}ClFNaO_2S$ requires 349.0441.

*4.19. Synthesis of 2,2-Dichloro-1-phenyl-2-(phenylsulfinyl)-1-ethanol (**15a**)*

LDA (0.6 mmol) was prepared freshly in THF (5 mL) and cooled in a dry-ice bath. A solution of dichloromethyl phenyl sulfoxide (**6**) (105 mg, 0.5 mmol) in THF (1 mL) was added. After the solution was stirred for 10 minutes, benzaldehyde (51 μL, 0.5 mmol) was added and the solution stirred for 30 minutes further. The solution was extracted into 1:1 ether-toluene (3 × 20 mL) and the extract was dried over magnesium sulfate. The solvents were removed to afford the diastereoisomers of **15a** (126 mg, 80%) as a colourless solid. The diastereoisomers were separated by flash column chromatography (4% EtOAc/$CHCl_3$).

Data for the first diastereoisomer: Colourless solid (75 mg, 48%), m.p. 186 – 188 °C; R_f = 0.25 (4% EtOAc/$CHCl_3$); $\nu_{max.}$ (neat) 3342, 3061, 3011, 1444, 1080 and 1051 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.89 – 7.81 (2H, m, aromatic CH), 7.69 – 7.60 (3H, m, aromatic CH), 7.57 (2H, app. t, J = 7.6, aromatic CH), 7.44 – 7.39 (3H, m, aromatic CH), 5.49 (1H, d, J = 2.5 Hz, C*H*OH) and 4.14 (1H, d, J = 2.5 Hz, OH); ^{13}C NMR (101 MHz; $CDCl_3$) δ 137.4, 135.6, 133.4, 129.6, 129.1, 128.7, 128.2 (broad), 102.1 and 80.2; MS (APCl$^+$) *m/z* (%) 382 ((M+Na+CH_3CN)$^+$, $^{37}Cl_2$, 1%), 380 ((M+Na+CH_3CN)$^+$, ^{35}Cl^{37}Cl, 9%), 378 ((M+Na+CH_3CN)$^+$, $^{35}Cl_2$, 12%), 319 (MH$^+$, $^{37}Cl_2$, 3%), 317 (MH$^+$, ^{37}Cl^{35}Cl, 20%), 315 (MH$^+$, $^{35}Cl_2$, 29%), 198 (100), 157 (23); HRMS: Found MH$^+$, 315.0004. $C_{14}H_{13}{}^{35}Cl_2O_2S$ requires 315.0013.

Data for the second diastereoisomer: Colourless solid (66 mg, 32%), m.p 193 – 194 °C; R_f = 0.22 (4% EtOAc/$CHCl_3$); $\nu_{max.}$ (neat) 3244, 1442 and 1043 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.95 – 7.83 (2H, m, aromatic CH), 7.63 (1H, app. tt, J = 7.3, 1.4 Hz, aromatic CH), 7.60 – 7.53 (4H, m, aromatic CH), 7.45 – 7.33 (3H, m, aromatic CH), 5.48 (1H, d, J = 5.3 Hz, C*H*OH) and 4.08 (1H, d, J = 5.3 Hz, OH); ^{13}C NMR (101 MHz; $CDCl_3$) δ 137.5, 136.1, 133.1, 129.3, 129.2, 128.6, 128.3, 128.0, 102.3 and 76.5; MS (APCl$^+$) *m/z* (%) 382 ((M+Na+CH_3CN)$^+$, $^{37}Cl_2$, 5%), 380 ((M+Na+CH_3CN)$^+$, ^{35}Cl^{37}Cl, 20%), 378 ((M+Na+CH_3CN)$^+$, $^{35}Cl_2$, 31%), 319 (MH$^+$, $^{37}Cl_2$, 4%), 317 (MH$^+$, ^{35}Cl^{37}Cl, 17%), 315 (MH$^+$, $^{35}Cl_2$, 24%), 198 (100), 157 (29); HRMS: Found MH$^+$, 315.0016. $C_{14}H_{13}{}^{35}Cl_2O_2S$ requires 315.0013.

*4.20. Synthesis of Dichloromethyl 4-Tolyl Sulfone (**16**)*[26]

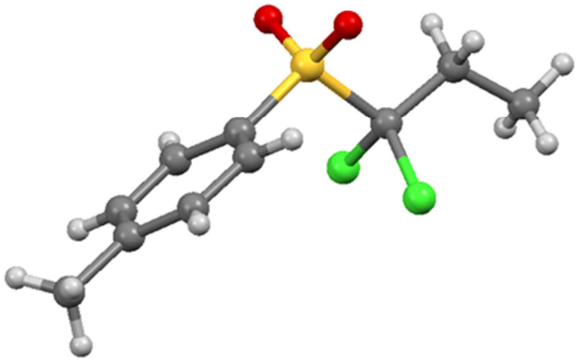
4-Toluenesulfinic acid sodium salt dihydrate (8.5 g, 40 mmol) was placed in a 100 mL flask, followed by chloroform (12 mL, 150 mmol), potassium hydroxide (2.8 g, 50 mmol) and water (40 mL). The mixture was stirred and heated to reflux for 12 h. The mixture was then extracted with dichloromethane (3 × 20 mL) and the organic extracts were combined and dried over magnesium sulfate. The solvents were removed to give the essentially pure *title compound* (3.81 g, 40%) as a colourless solid, m.p. 89 – 90 °C (lit.[26] 89.5 – 90 °C); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.91 (2H, d, J = 8.0 Hz, aromatic CH), 7.43 (2H, d, J = 8.0 Hz, aromatic CH), 6.23 (1H, s, $CHCl_2$) and 2.50 (3H, s, CH_3); ^{13}C NMR (101 MHz; $CDCl_3$) δ 147.2, 131.4, 130.1, 129.0, 80.0 and 22.0.

*4.21. General Procedure for the Reaction of Dichloromethyl 4-Tolyl Sulfone (**16**) with Trialkylboranes*

Dichloromethyl 4-tolyl sulfone (**16**) (120 mg, 0.50 mmol) was dissolved in THF (5 mL) and the trialkylborane (0.50 mmol) in THF (0.5 – 5 mL)[31] was added. The mixture was cooled to –78 °C and lithium bis(trimethylsilyl)amide (LiHMDS) (0.60 mL, 1.0 M in THF, 0.60 mmol) was added dropwise. The solution was stirred for 30 min at –78 °C and 90 min at room temperature. The solution was then quenched with sat. ammonium chloride (5 mL). The organic layer was separated and the aqueous layer was extracted with chloroform (3 × 10 mL). The solution was dried over magnesium sulfate. After the removal of volatile solvents under vacuum, the crude product was further purified by silica column chromatography (5% diethyl ether/petroleum ether) to give the product with yield and data as below.

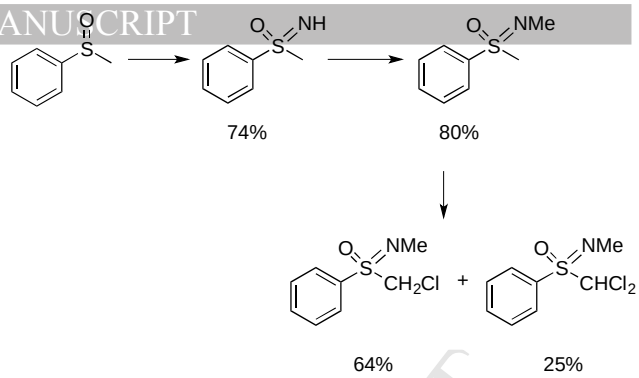
1-((1,1-Dichloropropyl)sulfonyl)-4-methylbenzene (17a): Colourless solid (62 mg, 46%), m.p. 52 – 54 °C; R_f = 0.28 (5% diethyl ether/petroleum ether); $\nu_{max.}$ (NaCl film) 3069, 2986, 2943, 2883, 1595, 1455, 1334, 1156 and 1076 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 7.96 (2H, d, *J* = 8.0 Hz, aromatic CH), 7.40 (2H, d, *J* = 8.0 Hz, aromatic CH), 2.54 (2H, q, *J* = 7.2 Hz, CH_2), 2.49 (3H, s, CH_3) and 1.32 (3H, t, *J* = 7.2 Hz, CH_3); ^{13}C NMR (126 MHz; $CDCl_3$) δ 146.6 (quat C), 132.5 (CH), 129.6 (CH), 129.2 (quat C), 102.0 (quat C), 33.6 (CH_2), 22.0 (CH_3) and 8.8 (CH_3); MS (APCl+) *m/z* (%) 288 ($(M+NH_4)^+$, $^{37}Cl_2$, 15%), 286 ($(M+NH_4)^+$, $^{37}Cl^{35}Cl$, 68%), 284 ($(M+NH_4)^+$, $^{35}Cl_2$, 100%), 250 (8), 214 (13), 119 (100); HRMS: Found $(M+NH_4)^+$, 284.0272. $C_{10}H_{16}{}^{35}Cl_2NO_2S$ requires 284.0273.

Selected crystallographic data: $C_{10}H_{12}Cl_2O_2S$, FW = 267.1, T = 296(2) K, λ = 1.54184, Monoclinic, P21/n, a = 10.8436(3) Å, b = 17.6380(3) Å, c = 13.1040(3) Å, α= 90°, β = 102.560(2)°, γ = 90°, V = 2446.29(10) $Å^3$, Z = 8, $\rho_{calc.}$ = 1.451 Mg/m^3, crystal size = 0.885 x 0.146 x 0.056 mm^3, μ = 6.202 mm^{-1}, reflections collected = 20117, independent reflections = 4902, R_{int} = 0.0289, parameters = 275, R_1 = 0.0339, wR_2 = 0.0920 for I>2σ(I) and R_1 =0.0418, wR_2 = 0.0994 for all data. CCDC 1451738 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/structures



1-((1,1-Dichloropentyl)sulfonyl)-4-methylbenzene (17b): Colourless solid (65 mg, 44%), m.p. 65 – 67 °C; R_f = 0.3 (5% diethyl ether/petroleum ether); $\nu_{max.}$ (neat) 3068, 2960, 2937, 2874, 1595, 1336, 1155 and 1084 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 7.96 (2H, d, *J* = 8.0 Hz, aromatic CH), 7.40 (2H, d, *J* = 8.0 Hz, aromatic CH), 2.52 – 2.46 (2H, m, CH_2), 2.49 (3H, s, CH_3), 1.80 – 1.71 (2H, m, CH_2), 1.44 (2H, app. quintet, *J* = 7.4 Hz, CH_2) and 0.96 (3H, t, *J* = 7.4 Hz, CH_3); ^{13}C NMR (101 MHz; $CDCl_3$) δ 146.5 (quat C), 132.4 (CH), 129.5 (CH), 128.9 (quat C), 100.9 (quat C), 39.1 (CH_2), 26.4 (CH_2), 22.1 (CH_2), 21.9 (CH_3) and 13.9 (CH_3); MS ($APCl^+$) *m/z* (%) 316 ($(M+NH_4)^+$, $^{37}Cl_2$, 15%), 314 ($(M+NH_4)^+$, $^{37}Cl^{35}Cl$, 64%), 312 ($(M+NH_4)^+$, $^{35}Cl_2$, 100%), 280 (70), 119 (100); HRMS: Found $(M+NH_4)^+$, 312.0583. $C_{12}H_{20}{}^{35}Cl_2NO_2S$ requires M, 312.0592.

*4.22. Synthesis of N-Methyl-S-(dichloromethyl)-S-phenylsulfoximine (**18**)*



4.23. Synthesis of S-Methyl-S-phenylsulfoximine[32]

Methyl phenyl sulfoxide (0.7 g, 5 mmol) was dissolved in chloroform (10 mL). Sodium azide (360 mg, 5.5 mmol) was added and the flask was immersed in an ice-bath. Sulfuric acid (1.25 mL) was added dropwise. The mixture was then warmed to 45 °C and left to stir overnight. Ice-water (10 mL) was added and the organic layer was separated. The aqueous layer was extracted with chloroform (10 mL). The aqueous layer was made slightly alkaline (pH ≈ 8.0) with 20% NaOH and extracted into chloroform (3 × 20 mL). The combined extracts were dried over magnesium sulfate and filtered. After removal of the solvent under reduced pressure, the *title compound* (0.571 g, 74%) was obtained as a pale yellow oil; ^1H NMR (400 MHz; $CDCl_3$) δ 8.02 – 7.98 (2H, m, aromatic CH), 7.61 (1H, app. tt, *J* = 7.3, 1.3 Hz, aromatic CH), 7.54 (2H, app. broad t, *J* = 7.4 Hz, aromatic CH), 3.09 (3H, s, CH_3) and 2.46 (1H, broad s, NH); ^{13}C NMR (101 MHz; $CDCl_3$) δ 143.6, 133.2, 129.4, 127.8 and 46.3.

4.24. Synthesis of N,S-Dimethyl-S-phenylsulfoximine[33]

A mixture of *S*-methyl-*S*-phenylsulfoximine (0.531 g, 3.42 mmol) and formaldehyde (8 mL, 37% in water) in 90% formic acid (30 mL) was heated at 100 °C for 48 h. Sulfuric acid (21 mL, 2.0 M) was added and the resulting solution was extracted with chloroform (3 × 20 mL). The organic layer was dried over magnesium sulfate and the solvent was removed to leave the *title compound* (0.462 g, 80%) as a colourless oil; ^1H NMR (400 MHz; $CDCl_3$) δ 7.88 (2H, d, *J* = 7.0 Hz, aromatic CH), 7.64 – 7.51 (3H, m, aromatic CH), 3.06 (3H, s, CH_3) and 2.62 (3H, s, CH_3); ^{13}C NMR (101 MHz; $CDCl_3$) δ 138.7, 133.1, 129.7, 128.9, 45.1 and 29.7.

4.25. Chlorination of N,S-Dimethyl-S-phenylsulfoximine[28]

A solution of *N,S*-dimethyl-*S*-phenylsulfoximine (169 mg, 1.0 mmol) in dichloromethane (10 mL) was placed in a 25 mL flask, followed by addition of potassium carbonate (207 mg, 1.5 mmol). The flask was wrapped in aluminium foil and immersed in an ice-bath. *t*-Butyl hypochlorite[34] (0.23 mL, 2 mmol) was added dropwise by syringe. The cooling bath was removed and the mixture was stirred for 1 h, then heated to reflux for 2 h, after which it was filtered. The solvents were removed from the filtrate under reduced pressure to give the crude product. After column chromatography on silica gel (20% diethyl ether/petroleum ether), two products were separated (mono and dichloromethyl products).

***N*-Methyl-*S*-(chloromethyl)-*S*-phenylsulfoximine**: Colourless oil (131 mg, 64%); R_f: 0.2 (5:1, petroleum ether/diethyl ether); ^1H NMR (400 MHz; $CDCl_3$) δ 7.98 – 7.92 (2H, m, aromatic CH), 7.66 (1H, app. tt, *J* = 7.4, 1.2 Hz, aromatic CH), 7.57 (2H, app. broad t, *J* = 7.5, aromatic CH), 4.66 (1H, d, *J* = 12.3 Hz, one of CH_2), 4.54 (1H, d, *J* = 12.3 Hz, one of CH_2)

and 2.85 (3H, s, CH_3); ^{13}C NMR (101 MHz; $CDCl_3$) δ 135.1, 133.9, 130.0, 129.4, 57.7 and 29.6.

***N*-Methyl-*S*-(dichloromethyl)-*S*-phenylsulfoximine (18)**: Colourless solid (59 mg, 25%), m.p. 33 – 35 °C; R_f: 0.3 (5:1, petroleum ether/diethyl ether); ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.08 – 8.04 (2H, m, aromatic CH), 7.70 (1H, app. tt, *J* = 7.5, 1.2 Hz, aromatic CH), 7.58 (2H, app. t, *J* = 7.7 Hz), 6.34 (1H, s, CH) and 3.09 (3H, s, CH_3); ^{13}C NMR (101 MHz; $CDCl_3$) δ 134.4 (CH), 132.9 (quat C), 130.7 (CH), 129.1 (CH), 80.8 (CH) and 29.9 (CH_3); MS (ES^+) *m/z* (%) 242 (MH^+, $^{37}Cl_2$, 7%), 240 (MH^+, $^{37}Cl^{35}Cl$, 32%), 238 (MH^+, $^{35}Cl_2$, 38%); HRMS: Found MH^+, 237.9851. $C_8H_{10}{}^{35}Cl_2NOS$ requires 237.9860.

*4.26. General Procedure for the Reaction of Compound **18** with Trialkylboranes*

4.26.1. Preparation of trialkylboranes

All trialkylboranes were prepared *in situ* and used directly. Trioctylborane and tricyclopentylborane were prepared by hydroboration of 1-octene and cyclopentene, respectively, by a well-established method,[29] according to the following procedure. To borane dimethyl sulfide complex (50 µL, 10.0 M, 0.50 mmol) in THF (2 mL) in a septum-capped 50 mL round bottom flask immersed in an ice bath was added 1-octene (0.24 mL, 1.50 mmol) or cyclopentene (132 µL, 1.50 mmol) dropwise. The cooling bath was removed and the mixture was left to stir at room temperature for 1 h to provide the solution used in the reaction.

Dibutylcyclohexylborane and dibutylcyclopentylborane were prepared by adaptation of a method of Soundarajan and Matteson,[30] followed by addition of *n*-BuLi, according to the following procedure. To a mixture of BCl_3 (0.50 mL, 1.0 M in hexane, 0.5 mmol) and cyclohexene (51 µL, 0.5 mmol) or cyclopentene (44 µL, 0.5 mmol) in hexane (2 mL) at -78 °C was added Et_3SiH (80 µL, 0.5 mmol) dropwise and the mixture was stirred for 15 min. The cooling bath was removed and the mixture was stirred for 30 min and then re-cooled to -78 °C. *n*-BuLi (0.63 mL, 1.6 M in hexane, 1.0 mmol) was added dropwise, then the cooling bath was removed and the mixture was allowed to stir for 1 h to provide the solution used in the reaction.

Dibutylphenylborane was prepared as follows. To a solution of $PhBCl_2$ (65 µL, 0.5 mmol) in dichloromethane (2 mL) at -78 °C was added *n*-BuLi (0.63 mL, 1.6 M in hexane, 1.0 mmol) dropwise. The cooling bath was removed and the mixture was allowed to stir for 1 h to provide the solution used in the reaction.

Butylmethylphenylborane was prepared as follows. To a solution of $PhBCl_2$ (65 µL, 0.5 mmol) in dichloromethane (5 mL) at -78 °C was added *n*-BuLi (0.31 mL, 1.6 M in hexane, 0.5 mmol), followed by MeLi (0.31 mL, 1.6 M in hexane, 0.5 mmol). The cooling bath was removed and the mixture was allowed to stir for 1 h to provide the solution used in the reaction. It was recognised that this procedure was not likely to provide the pure mixed trialkylborane, and indeed a substantial amount of dibutylphenylborane was present in the solution, but it could serve to establish whether the reaction would work in this case.

*4.26.2. Reactions of trialkylboranes with **18***

LDA was prepared by dropwise addition of *n*-BuLi (0.38 mL, 1.6 M in hexane, 0.61 mmol, 1.2 equiv.) to a cooled (–78 °C) solution of diisopropylamine (91 µL, 0.65 mmol, 1.3 equiv.) in dry THF (2 mL). The solution was allowed to warm to 0 °C over 20 min, then added dropwise to a solution of **18** (119 mg, 0.50 mmol) and a trialkylborane (0.50 mmol) in THF and/or dichloromethane (5 mL) at –78 °C. The solution was stirred for 1 h at –78 °C and overnight at room temperature, then oxidised by stirring overnight with NaOH (3.0 M, 3 mL) and aq. H_2O_2 (30%, 3 mL). The organic layer was separated, the aqueous layer was saturated with NaCl and extracted with dichloromethane (3 x 10 mL), and the organic layers were combined, dried ($MgSO_4$) and filtered. Evaporation under reduced pressure left a crude product that was purified by column chromatography (silica gel, 5% EtOAc/petroleum ether). GC yields were based on the crude product by reference to an added internal standard (tetradecane).

5-Butylnonan-5-ol:[35] A pure sample of the title compound for use in determining a GC response factor was obtained from reaction of *n*-BuLi with 5-nonanone. Colourless oil; ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.48 – 1.18 (18H, m, all CH_2 groups), 1.07 (1H, broad s, OH) and 0.84 (9H, t, *J* = 6.6 Hz, CH_3); ^{13}C NMR (101 MHz; $CDCl_3$) δ 74.7, 39.1, 25.8, 23.5 and 14.3. Use of the response factor thus obtained revealed a GC yield of 81% in the reaction of tributylborane with compound **18**.

9-Octylheptadecan-9-ol:[2a] Colourless oil (81% GC yield; 75% isolated yield); ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.50 – 1.03 (43H, m, all CH_2 and OH), and 0.88 (9H, t, *J* = 6.9 Hz, CH_3); ^{13}C NMR (126 MHz; $CDCl_3$) δ 74.6, 39.5, 32.0, 30.4, 29.7, 29.5, 23.6, 22.8 and 14.2.

5-Cyclohexylnonan-5-ol: Colourless oil (83 mg, 73%); $\nu_{max.}$ (neat) 3477, 2955, 2928, 2854 and 1450 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.84 – 1.66 (5H, m), 1.54 – 0.97 (19H, m) and 0.91 (6H, t, *J* = 7.0 Hz, CH_3); ^{13}C NMR (101 MHz; $CDCl_3$) δ 75.9 (quat C), 45.2 (CH), 36.2 (CH_2), 27.1 (CH_2), 26.9 (CH_2), 26.8 (CH_2), 25.6 (CH_2), 23.6 (CH_2) and 14.3 (CH_3); MS (EI-MS) *m/z* (%): molecular ion not seen; 208 ($M^+ - H_2O$, 17%), 151 (38), 109 (72), 69 (94); HRMS: Found ($M^+ - H_2O$), 208.2196. $C_{15}H_{28}$ requires M, 208.2191.

5-Cyclopentylnonan-5-ol: Colourless oil (72 mg, 68%); $\nu_{max.}$ (neat) 3485, 2953, 2931, 2864 and 1456 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 2.08 – 1.82 (1H, m, CH), 1.68 – 1.17 (20H, m, all CH_2), 1.02 (1H, br, OH) and 0.91 (6H, t, *J* = 7.1 Hz, CH_3); ^{13}C NMR (101 MHz; $CDCl_3$) δ 75.3 (quat C), 47.6 (CH), 37.5 (CH_2), 26.2 (CH_2), 26.0 (CH_2), 25.8 (CH_2), 23.6 (CH_2) and 14.3 (CH_3); MS (EI-MS) *m/z* (%): molecular ion not seen; 194 ($M^+ - H_2O$, 28%), 137 (35), 95 (76); HRMS: Found ($M^+ - H_2O$), 194.2035. $C_{14}H_{26}$ requires M, 194.2035.

5-Phenylnonan-5-ol:[36] Colourless oil (56 mg, 51%); $\nu_{max.}$ (neat) 3419, 2957, 2931, 2860, 1458 and 1078 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.43 – 7.29 (4H, m, *o*- and *m*-CH), 7.22 (1H, tt, *J* = 7.0, 1.5 Hz, *p*-CH), 1.88 – 1.69 (5H, m), 1.33 – 1.13 (6H, m), 1.10 – 0.95 (2H, m) and 0.84 (6H, t, *J* = 7.0 Hz, CH_3); ^{13}C NMR (101 MHz; $CDCl_3$) δ 146.6 (quat C), 128.1 (CH), 126.3 (CH), 125.4 (CH), 77.1 (quat C), 42.9 (CH_2), 25.7 (CH_2), 23.2 (CH_2) and 14.2 (CH_3); MS (EI-MS) m/z (%): molecular ion not seen; 203 (M^+ – OH, 35%), 160 (33), 138 (55), 115 (64); HRMS: Found (M^+ – OH), 203.1800. $C_{15}H_{23}$ requires M, 203.1800.

2-Phenylhexan-2-ol:[37] Colourless oil (27 mg, 30%); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.47 – 7.43 (2H, m, aromatic CH), 7.38 – 7.32 (2H, m, aromatic CH), 7.25 (1H, tt, *J* = 7.3, 1.3 Hz, *p*-CH), 1.90 (1H, s, OH), 1.87 – 1.75 (2H, m, CH_2), 1.57 (3H, s, CH_3), 1.32 – 1.20 (3H, m, CH_2 and one of CH_2), 1.19 – 1.08 (1H, m, one of CH_2) and 0.86 (3H, t, *J* = 7.1 Hz, CH_3); ^{13}C NMR (101 MHz; $CDCl_3$) δ 148.2 (quat C), 128.2 (CH), 126.5 (CH), 124.9 (CH), 74.8 (quat C), 44.0 (CH_2), 30.2 (CH_3), 26.2 (CH_2), 23.1 (CH_2) and 14.1 (CH_3).

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Supplementary Material

Computational details, atomic coordinates for calculated structures. Copies of ^{1}H and ^{13}C NMR spectra.