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Lithium–Titanium Exchange of Tertiary α-Sulfonyl Carbanions: Synthesis, Structure, Dynamics and Reactivity of Bis(1-sulfonylalkyl)titaniums

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Lithium–titanium exchange of tertiary α-sulfonyl carbanions with $ClTi(OiPr)_3$ and $Cl_2Ti(OiPr)_2$ in diethyl ether gave bis(1-sulfonylalkyl)titaniums and not the corresponding (1-sulfonylalkyl)titaniums. X-ray crystal structure analysis of di(isopropoxy)bis[1-(phenylsulfonyl)cyclobutyl]titanium and di(isopropoxy)bis[1-(phenylsulfonyl)isopropyl]titanium showed asymmetric distorted octahedral complexes, having hexacoordinate Ti atoms, two C–Ti bonds, four Ti–O bonds, and two four-membered Ti–O–S–C_α rings. According to ^1H NMR spectroscopy bis(1-sulfonylcycloalkyl)titaniums are non-fluxional at room temperature. This suggests that chiral bis(1-sulfonylalkyl)titaniums should be configurationally stable. The bis(1-sulfonylalkyl)titaniums are stable at room temperature towards β-H elimination. They selectively add to benzaldehyde in the presence of acetophenone but do not react with methyl iodide. The reaction of tertiary acyclic α-sulfonyl carbanions with $ClTi(OiPr)_3$ in tetrahydrofuran (THF) gives different titanium derivatives with unspecified structures, which not only selectively react with benzaldehyde in the presence of acetophenone but are also alkylated by methyl iodide.

Introduction

Lithium–titanium exchange of stabilised carbanions is a valuable technique that can be used to gain selectivity in reactions with electrophiles.[1] Some time ago, we and others studied the Li–Ti exchange of dilithium α-sulfonyl dicarbanions **1**[2–5] and lithium α-sulfonimidoyl carbanions **2**[6–10] (Figure 1). Titanation of **1** and **2** yields C_α–Ti bonded titanium complexes, which possess synthetically valuable reactivities and exhibit interesting fluxional behaviour. In a continuation of these studies, we became interested in the Li–Ti exchange of tertiary α-sulfonyl carbanions **3** (R^1, R^2 = alkyl, aryl). Chiral carbanions **3**, carrying two different alkyl groups or an alkyl and an aryl group at the C_α atom and a *tert*-butyl or trifluoromethyl group at the S atom, are accessible in enantiopure form through stereoselective deprotonation of the corresponding chiral sulfones.[11,12] Reactions of **3** with electrophiles are highly stereoselective. However, carbanions **3** are configurationally stable only at low temperatures. At elevated temperatures, they undergo fast racemisation through rotation around the C_α–S bond and C_α inversion. This precludes, for example, isolation of **3** in non-racemic form and their utilisation in reactions with electrophiles at elevated temperatures. The corresponding central chiral (sulfonylalkyl)titaniums **4** are expected to possess a higher configurational stability and chemoselectivity than **3** because of the C_α–Ti bond. Lithium α-sulfonyl carbanions are important intermediates in organic synthesis,[13] and the availability of the chiral titanium derivatives **4** could significantly add to their synthetic utility. In contrast to **1** and **2**, knowledge about the Li–Ti exchange of **3** and precise information about the structure and reactivity of (1-sulfonylalkyl)titaniums is scarce.[3,14–17] For example, titanation of the primary carbanion **3** (R^1 = R^2 = H, R^3 = Ph) with $ClTi(OiPr)_3$ gave, according to reactivity studies[14] and ^{13}C NMR spectroscopy,[3,15] a C_α–Ti bonded titanium derivative, the precise structure of which was, however, not established. X-ray crystal structure analysis and NMR spectroscopy had shown that the reaction of similar primary

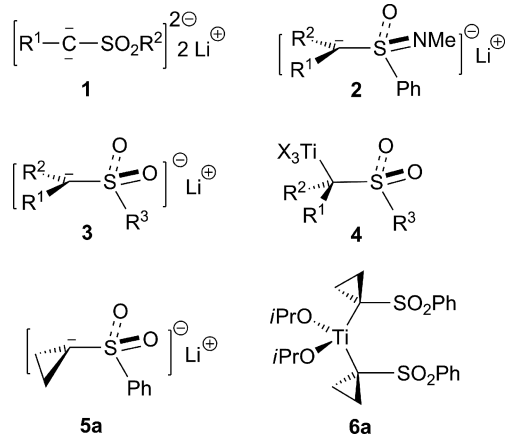

Figure 1. Lithium α-sulfonyl and α-sulfonimidoyl carbanions and titanium derivatives.

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carbanion **3** ($R^1 = R^2 = H$, R^3 = Tol), with Cl_2TiCp_2, furnishes the corresponding C_α–Ti bonded (1-sulfonylalkyl)-titanium.[17] A ^{13}C NMR spectroscopic investigation of the Li–Ti exchange of the secondary carbanion **3** ($R^1 = H$, $R^2 = SiMe_3$, R^3 = Ph) with $ClTi(OiPr)_3$ provided evidence for C-titanation. In contrast, a similar study of the Li–Ti exchange of the tertiary carbanion **3** (R^1 = Et, $R^2 = SiMe_3$, R^3 = Ph), revealed the absence of a C-titanation and pointed to O-titanation.[3,18] The only explicit information about the Li–Ti exchange of a tertiary α-sulfonyl carbanion concerns the cyclopropylsulfonyl anion **5a**. Titanation of **5a** with $ClTi(OiPr)_3$ afforded the bis(1-sulfonylcyclopropyl)-titanium **6a** and not, as expected, the corresponding (1-sulfonylcyclopropyl)titanium derivative.[15] The structure of **6a** was secured by X-ray crystal structure analysis and by NMR spectroscopy.

The reactivity of (1-sulfonylalkyl)titaniums has been less explored than the Li–Ti exchange of **3**. The titanium species derived from the primary carbanion **3** ($R^1 = R^2 = H$, R^3 = Ph), was found to selectively react with aldehydes in the presence of ketones,[14] and **6a** was observed to be inert towards methyl iodide.[15]

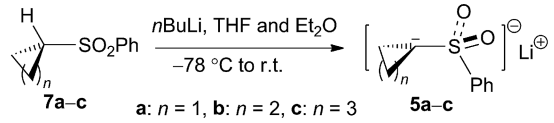
Given the paucity of information about (1-sulfonylalkyl)-titaniums, we chose to first study the Li–Ti exchange of racemic and achiral tertiary α-sulfonyl carbanions **3** and the chemistry of their titanium derivatives.

In this paper we describe the synthesis, structure, dynamics and reactivity of bis(1-sulfonylalkyl)titaniums.[19]

Results and Discussion

Synthesis of Bis(1-sulfonylalkyl)titaniums in Diethyl Ether

Three different groups of tertiary α-sulfonyl carbanions were selected for the investigation of the Li–Ti exchange, the cyclic *S*-phenyl carbanions **5a**–**c**, the acyclic *S*-phenyl carbanions **3a**–**e**, and the acyclic *S*-*tert*-butyl carbanions **3f**–**h** (Scheme 1). The *S*-*tert*-butyl-substituted carbanions were picked because of the envisioned synthesis of chiral, non-racemic (1-sulfonylalkyl)titaniums of type **4**, carrying a *tert*-butyl group at the S atom. The cyclic carbanions were chosen because of an investigation of the fluxional behaviour

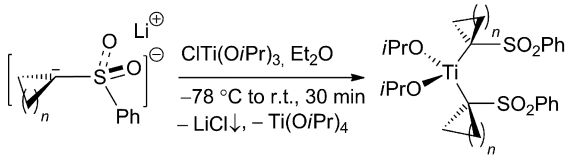


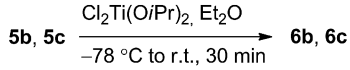
a: $R^1 = R^2$ = Me, R^3 = Ph; **b**: $R^1 = R^2$ = Et, R^3 = Ph; **c**: R^1 = Me, R^2 = Et, R^3 = Ph; **d**: R^1 = Me, R^2 = *i*Pr, R^3 = Ph; **e**: R^1 = Me, R^2 = *i*Bu, R^3 = Ph; **f**: $R^1 = R^2$ = Me, R^3 = *t*Bu; **g**: $R^1 = R^2$ = Et, R^3 = *t*Bu; **h**: R^1 = Me, R^2 = Et, R^3 = *t*Bu

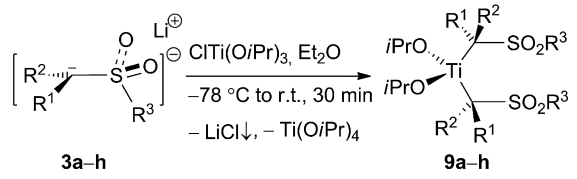
Scheme 1. Secondary sulfones and tertiary α-sulfonyl carbanions.

of the corresponding titanium derivatives by ^1H NMR spectroscopy. Finally, the *S*-phenyl carbanions were selected to study the influence of a sterically less demanding group at the S atom upon the Li–Ti exchange and to gain information about the scope and limitations of the process. All acyclic carbanions carried alkyl groups of different sizes at the anionic C atom to determine their influence upon the Li–Ti exchange. The lithium carbanions **3a**–**h** and **5a**–**c** were synthesised from the corresponding sulfones **8a**–**h** and **7a**–**c** upon treatment with *n*BuLi in tetrahydrofuran (THF) and diethyl ether.[11,20–23]

Titanation of the cyclobutyl anion **5b** with 1.1 equiv. $ClTi(OiPr)_3$ in diethyl ether at –50 °C to room temperature gave bis(1-sulfonylcyclobutyl)titanium **6b** (Scheme 2), which was isolated through crystallisation from *n*-hexane in 47% yield. Similar treatment of the cyclopentyl anion **5c** with $ClTi(OiPr)_3$ in diethyl ether afforded bis(1-sulfonylcyclopentyl)titanium **6c**, which was isolated in 59% yield through crystallisation from *n*-hexane. Bis(1-sulfonylcyclopropyl)titanium **6a** was prepared from **5a** and $ClTi(OiPr)_3$ in diethyl ether, as described previously, in 60% yield.[3,15] Titanation of **5b** and **5c** with 0.7 equiv. $Cl_2Ti(OiPr)_2$ in diethyl ether and crystallisation also furnished the corresponding bis(1-sulfonylcycloalkyl)titaniums **6b** and **6c** each in 66% yield.







a: $R^1 = R^2$ = Me, R^3 = Ph; **b**: $R^1 = R^2$ = Et, R^3 = Ph; **c**: R^1 = Me, R^2 = Et, R^3 = Ph; **d**: R^1 = Me, R^2 = *i*Pr, R^3 = Ph; **e**: R^1 = Me, R^2 = *i*Bu, R^3 = Ph; **f**: $R^1 = R^2$ = Me, R^3 = *t*Bu; **g**: $R^1 = R^2$ = Et, R^3 = *t*Bu; **h**: R^1 = Me, R^2 = Et, R^3 = *t*Bu

Scheme 2. Titanation of lithium α-sulfonyl carbanions with chlorotitanium reagents.

Titanation of the dimethyl-substituted carbanion **3a** and the diethyl-substituted carbanion **3b**, each with 1.1 equiv. $ClTi(OiPr)_3$ in diethyl ether at –50 °C to room temperature, provided, after crystallisation from diethyl ether, the corresponding bis(1-sulfonylalkyl)titaniums **9a** and **9b** in 53 and 50% yield, respectively.

According to ^1H NMR spectroscopic analysis of the crude reaction mixtures, the carbanions **3a**, **3b** and **5a**–**c** were quantitatively converted upon treatment with

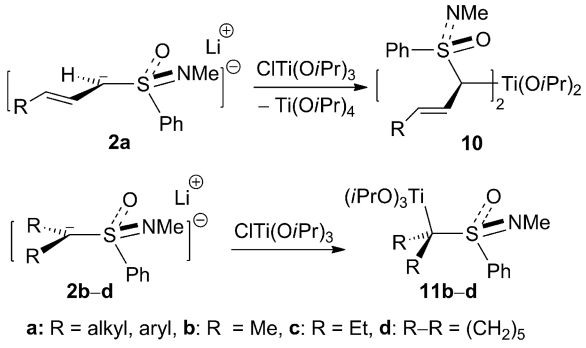
$ClTi(OiPr)_3$ in diethyl ether into 1:1 mixtures of the corresponding bis(1-sulfonylalkyl)titaniums and $Ti(OiPr)_4$. Formation of further (1-sulfonylalkyl)titaniums was not observed. In all cases, lithium chloride precipitated from the ethereal solutions of $Ti(OiPr)_4$ and the titanium derivatives. The mode of combination of the carbanions **3a**, **3b** and **5a**–**c** with the titanium reagents had no influence upon the formation of the corresponding bis(1-sulfonylalkyl)titaniums and $Ti(OiPr)_4$. Crystallisation gave the pure titanium derivatives in medium to good yields. A quantitative isolation of the titanium derivatives by crystallisation was not attempted because the mixtures with $Ti(OiPr)_4$ could be used in reactions with electrophiles (see below). Addition of water to **6a**–**c**, **9a** and **9b** caused rapid hydrolysis with formation of the corresponding sulfones. The bis(1-sulfonylalkyl)titaniums **6a**–**c**, **9a** and **9b** are stable at room temperature in benzene, THF, and *n*-hexane solutions and in the crystal, for a prolonged period of time, provided water and oxygen are excluded.

Generally, alkyltitaniums with β-H atoms can undergo β-hydride elimination.[1b,24,25] Interestingly, a β-H elimination of **6a**–**c**, **9a** and **9b** with formation of the corresponding α,β-unsaturated sulfones was not observed in the above solvents at room temperature or during crystallisation from *n*-hexane at elevated temperatures. Whereas the kinetic stability of **6a** and **6b** is perhaps not surprising because of the small rings both contain, that of **6c** and, in particular, of **9a** and **9b**, which carry four and six β-H atoms, respectively, is noteworthy. A direct comparison with the kinetic stability of $R_2Ti(OiPr)_2$ (R = cC_3H_5, cC_4H_7, cC_5H_9, $CHMe_2$, $CHEt_2$) is not possible, because isolation and structural characterisation of the parent dialkyltitaniums have not been described.[1b,24,26] It has been postulated that the synthesis of the Kulinkovich reagent from $Ti(OiPr)_4$ and *i*PrMgBr involves the formation of $(iPr)_2Ti(OiPr)_2$ as intermediate,[27] which apparently suffers β-H elimination already at low temperatures.[28]

The reactions of carbanions **3c**–**h** with $ClTi(OiPr)_3$ in diethyl ether also quantitatively furnished, according to negative test reactions with MeI (see below), the corresponding bis(1-sulfonylalkyl)titaniums **9c**–**h**, which were, however, not isolated. Considering the use of racemic carbanions, **9c**, **9d**, **9e** and **9h** were perhaps mixtures of the D,L- and *meso*-configured complexes.

The synthesis of bis(1-sulfonylalkyl)titaniums **6b**, **6c** and **9a**–**h** shows that the C-titanion of **5a** is no exemption. The titanation of tertiary α-sulfonyl carbanions in diethyl ether generally affords the corresponding bis(1-sulfonyalkyl)titaniums, irrespective of the size of the alkyl groups at the anionic C atom, the substituent at the S atom, and the ring size in case of the cyclic carbanions.

It seems interesting to compare the Li–Ti exchange of the α-sulfonyl carbanions **3** with that of α-sulfonimidoyl carbanions **2** (Scheme 3). Whereas the reaction of the allylic carbanions **2a** with $ClTi(OiPr)_3$ in diethyl ether (and THF) also afforded bis(1-sulfonimidoylalkenyl)titaniums **10**,[6] that of the alkyl-substituted carbanions **2b**–**d** gave the corresponding (1-sulfonimidoylalkyl)titaniums **11b**–**d**.[7]



Scheme 3. Li–Ti exchange of lithium α-sulfonimidoyl carbanions.

Structure and Dynamics of Bis(1-sulfonylalkyl)titaniums

X-ray crystal structure analyses of **6b** and **9a** provided proof for their structures as bis(1-sulfonylalkyl)titaniums, showing Ti–C distances of 2.174–2.251 Å and Ti–O*i*Pr distances of 1.745–1.789 Å (Figures 2 and 3, Tables 1 and 2).[29]

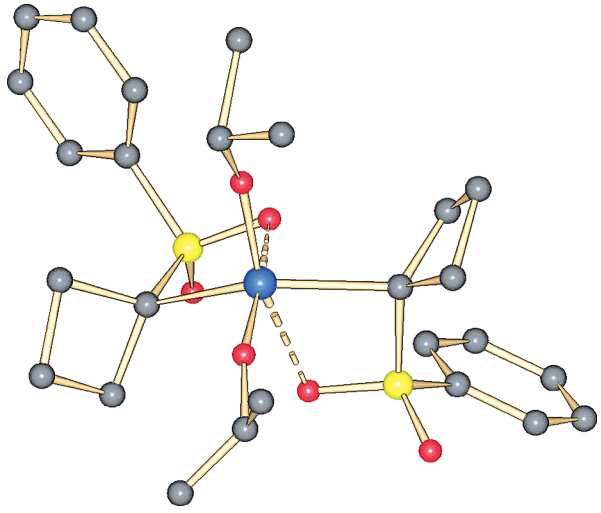


Figure 2. Structure of bis(1-sulfonylcyclobutyl)titanium **6b** in the crystal.

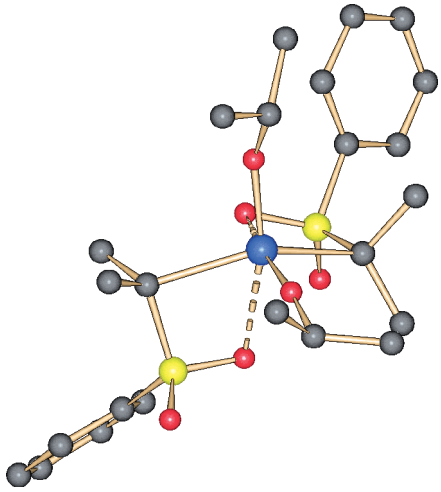


Figure 3. Structure of bis(1-sulfonylisopropyl)titanium **9a** in the crystal.

Table 1. Selected bond lengths [Å] of **6a**,[15] **6b** and **9a**.

	C_α–Ti	Ti–O*i*Pr	Ti-O	C_α–S
6a	2.181(3)	1.771(3)	2.315(3)	1.725(4)
	2.174(4)	1.745(2)	2.243(2)	1.719(4)
6b	2.205(3)	1.789(3)	2.242(2)	1.733(3)
	2.223(3)	1.751(2)	2.278(2)	1.737(3)
9a	2.234(6)	1.768(5)	2.204(4)	1.748(6)
	2.251(6)	1.763(4)	2.271(4)	1.742(7)

Table 2. Selected bond and dihedral angles [°] of **6a**,[15] **6b** and **9a**.

	C–Ti–C	O–Ti-O	Ti–C_α–S	C_α–S–O(Ti)	O-S-C_α–Ti
6a	139.8(1)	102.6(1)	95.8(1)	99.8(1)	–83.8(1)
6b	141.5(1)	103.7(1)	92.1(1)	101.5(1)	–2.5(1)
9a	143.4(2)	103.0(2)	90.7(2)	100.8(2)	5.5(4)

In the crystal, the Ti atoms of **6b** and **5a** are hexacoordinate and have distorted octahedral coordination geometries, because of an additional coordination by two O atoms of the sulfonyl groups. Evidence for the two O–Ti–C_α–S chelate rings is provided by the O–Ti distances, the C_α–Ti–O–S dihedral angles, the conformations around the C_α–S bonds, and the widening of the C_α–Ti–C_α bond angles. The coordination of the sulfonyl O atoms to the Ti atom makes the S atoms of **6b** and **9a** stereogenic, having opposite configurations, and both complexes are asymmetric. Bis(1-sulfonylcyclopropyl)titanium **6a** adopts a similar structure in the crystal.[15] It would have been interesting to compare the crystal structures of **6a**, **6b** and **9a** with those of the parent dialkyldialkoxytitaniums; however, crystal structures of dialkyldialkoxytitaniums carrying secondary alkyl groups at the Ti atom are not available.[30]

It is interesting to note that bis(1-sulfonimidoylpropenyl)titanium **10a** adopts a similar structure in the crystal (Figure 4) as bis(1-sulfonylalkyl)titaniums **6a**, **6b** and **9a**.[6] Whereas **10a** has the *cis*,*cis*,*cis*-configuration, **6a**, **6b** and **9a** have the *cis*,*cis*,*trans*-configuration.

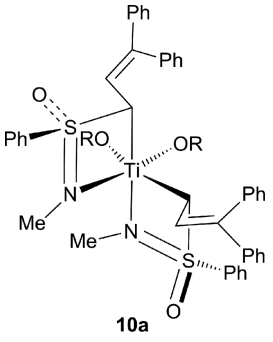


Figure 4. Structure of bis(1-sulfonimidoylpropenyl)titanium **10a**.

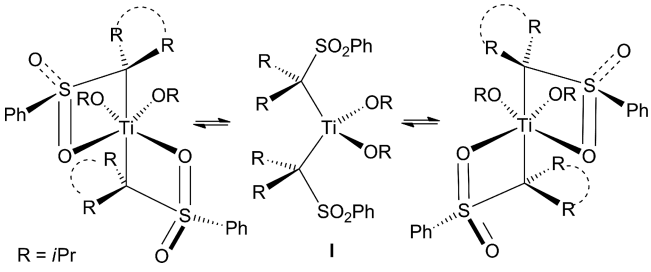
The C-titanation of α-sulfonyl carbanions **3** causes a downfield shift of the signal of the C_α atom in the ^{13}C NMR spectra of the titanium derivatives (Table 3).[3,15] This effect can be used as a probe for the *C*-titanation of α-sulfonyl carbanions in case of an in situ synthesis.

Table 3. Selected ^{13}C NMR spectroscopic data of lithium α-sulfonyl carbanions **3a**, **3b** and **5a**[a] and bis(1-sulfonylalkyl)titaniums **6a**–**c**, **9a** and **9b**.[b]

	δ ($^{13}C_\alpha$) [ppm]		δ ($^{13}C_\alpha$) [ppm]	δ [ppm]
5a	28.5	**6a**	52.4	23.9
5b	n.d.[c]	**6b**	69.5	n.d.[c]
5c	n.d.[c]	**6c**	76.7	n.d.[c]
3a	42.5	**9a**	64.5	22.0
3b	54.3	**9b**	75.8	21.5

[a] In [D_8]THF. [b] In [D_6]benzene. [c] n.d.: not determined.

The ^1H NMR spectra of **6a**–**c**, **9a** and **9b** in [D_6]benzene and [D_8]THF at room temperature showed only half the number of signals expected for asymmetric structures of the type found in the crystal. This means that the titanium derivatives in solution either undergo rapid enantiomerisation, leading to an exchange of the diastereotopic groups at the C_α atoms and of the diastereotopic isopropoxy groups, or adopt an achiral structure with a tetrahedral tetracoordinated Ti atom. Enantiomerisation can occur via an achiral tetracoordinated intermediate **I**, having no bonds between the sulfonyl O atoms and the Ti atom (Scheme 4), or by a twisting mechanism without rupturing any of the Ti–O and Ti–C bonds.[6,31] It is interesting to note that **10a** shows a dynamic phenomenon, which leads to intramolecular exchange of the diastereotopic groups at the Ti atom.[6]



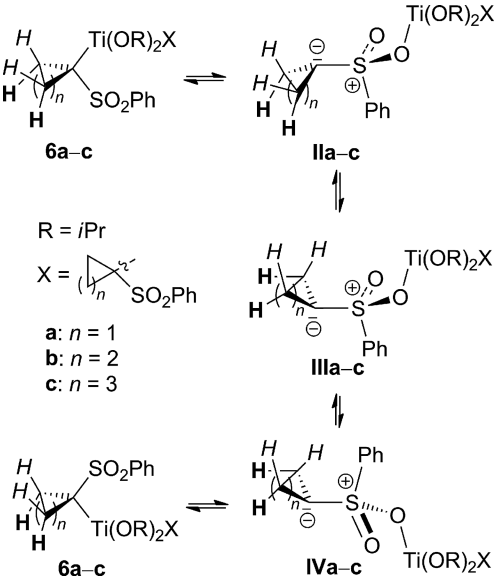
Scheme 4. Exchange of diastereotopic groups R and X of the octahedral bis(1-sulfonylalkyl)titaniums **6a**–**c**, **9a** and **9b**.

Fluxional Behaviour of Bis(1-sulfonylalkyl)titaniums

Crucial to the envisioned synthesis of chiral, non-racemic bis(1-sulfonylalkyl)titaniums of type **9** will be the configurational stability of the C_α atom. Therefore, bis(1-sulfonylcycloalkyl)titaniums **6a**–**c** were investigated by ^1H NMR spectroscopy to establish whether they are fluxional, resulting in a topomerisation of the titanyl group. The tris(isopropoxy)(1-sulfonimidoylalkyl)titaniums **11a** and **11b** were found to be non-fluxional at room temperature by ^1H NMR spectroscopic analysis.[7] Topomerisation of the titanyl group of **6a**–**c** should proceed via the intermediate formation of the O-titanated carbanions **IIa**–**c**, **IIIa**–**c** and **IVa**–**c**, including (1) a migration of the titanyl group to an O atom under cleavage of the C_α–Ti bond, (2) inversion of the C_α atom, (3) rotation around the C_α–S bond, (4) migration of the titanyl group to the C_α atom with formation of the C_α–Ti bond, and (5) ring inversion in the cases of **6b**

and **6c** (not shown). The topomerisation causes an exchange of environments of the *syn* and *anti* H atoms. The ^{1}H NMR spectra of **6a**–**c** in [D$_6$]benzene exhibited at room temperature different sharp signals for the H atoms in *syn* and *anti* positions to the titanyl group. In addition, the ^{1}H NMR spectra of **6a** in [D$_8$]toluene at room temperature and at 80 °C showed no differences. Thus, **6a**–**c** are non-fluxional and a topomerisation of the titanyl group either does not take place or is slow at these temperatures.

In principle, each step of the topomerisation of **6a**–**c** could be rate determining (Scheme 5). There is evidence, however, suggesting that cleavage of the C$_\alpha$–Ti bond should be the rate-determining step. The ^{1}H NMR spectra of the lithium sulfonyl carbanions **5a**–**c** in [D$_8$]THF, which are expected to form a C–Li contact ion pair (**5a**)[32] and O–Li bonded contact ion pairs (**5b**, **5c**),[23] show only single signals for the respective *syn* and *anti* H atoms at room temperature. This indicates that C$_\alpha$ inversion and C$_\alpha$–S bond rotation, which lead to an exchange of environments of the H atoms, are fast. Variable-temperature ^{1}H NMR spectroscopy of **5a** in [D$_8$]THF had given an estimated barrier of $\Delta G^{\neq}_{247} = 11.6 \pm 0.3$ kcal mol^{-1} for the exchange.[3]



Scheme 5. Topomerisation of the titanyl group of **6a**–**c**.

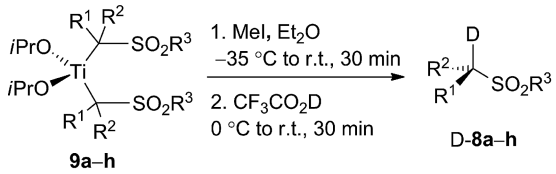
The lack of a fluxional behaviour of **6a**–**c** also excludes the possibility of the titanium derivatives undergoing a reversible β-titanium hydride elimination as observed in the case of the tris(diethylamino) analogue of **11c**.[7]

In summary, the above results strongly suggest that chiral bis(1-sulfonylalkyl)titaniums of type **9** should have configurationally stable C$_\alpha$ atoms, at least at room temperature.

Reactivity of Bis(1-sulfonylalkyl)titaniums

Reaction with Methyl Iodide

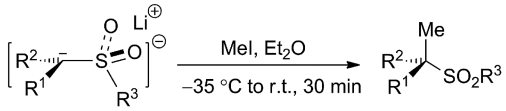
Bis(1-sulfonylcyclopropyl)titanium **6a** did not react with methyl iodide at room temperature, whereas the corresponding sulfonyl carbanion **5a** was rapidly methylated even at low temperatures.[15] To see whether the lack of a reaction of **6a** is typical for titanium derivatives of this type, bis(1-sulfonylalkyl)titaniums **9a**–**h** were studied. Treatment of the bis(1-sulfonylalkyl)titaniums, which were admixed with Ti(O*i*Pr)$_4$, with methyl iodide in diethyl ether at –35 °C to room temperature did not afford the corresponding methylated sulfones. Quenching of the reaction mixtures with CF_3CO_2D gave the corresponding deuterated sulfones D-**8a**–**h** (82% D to 98% D) in 91–97% yield (Scheme 6).



a: R^1 = R^2 = Me, R^3 = Ph
b: R^1 = R^2 = Et, R^3 = Ph
c: R^1 = Me, R^2 = Et, R^3 = Ph
d: R^1 = Me, R^2 = *i*Pr, R^3 = Ph
e: R^1 = Me, R^2 = *i*Bu, R^3 = Ph
f: R^1 = R^2 = Me, R^3 = *t*Bu
g: R^1 = R^2 = Et, R^3 = *t*Bu
h: R^1 = Me, R^2 = Et, R^3 = *t*Bu

Scheme 6. Attempted methylation of bis(1-sulfonylalkyl)titaniums.

For comparison, the tertiary carbanions **3a**–**h** were treated with methyl iodide under similar conditions, which afforded the corresponding methylated sulfones **12a**–**h** in 79–97% yield (Scheme 7).

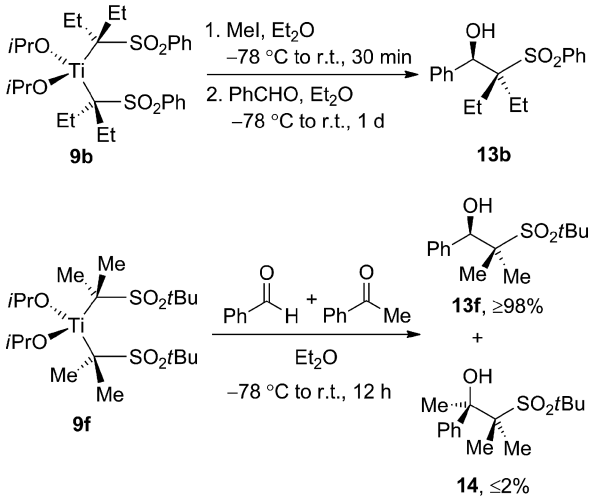


a: R^1 = R^2 = Me, R^3 = Ph
b: R^1 = R^2 = Et, R^3 = Ph
c: R^1 = Me, R^2 = Et, R^3 = Ph
d: R^1 = Me, R^2 = *i*Pr, R^3 = Ph
e: R^1 = Me, R^2 = *i*Bu, R^3 = Ph
f: R^1 = R^2 = Me, R^3 = *t*Bu
g: R^1 = R^2 = Et, R^3 = *t*Bu
h: R^1 = Me, R^2 = Et, R^3 = *t*Bu

Scheme 7. Methylation of lithium α-sulfonyl carbanions.

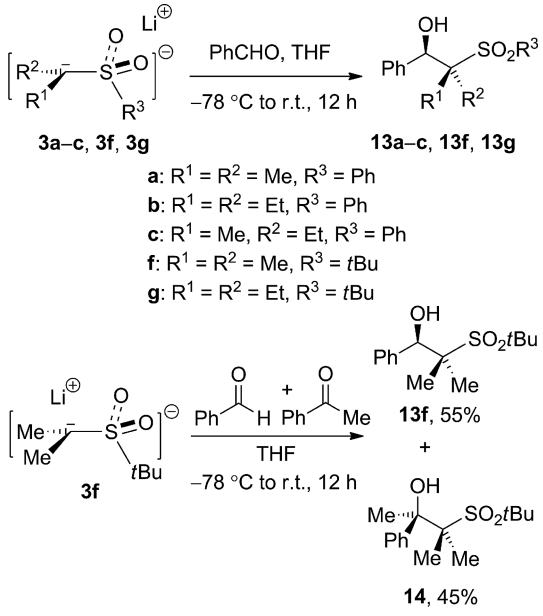
Reaction with Benzaldehyde and Acetophenone

The reactivity of bis(1-sulfonylalkyl)titaniums **9** towards aldehydes was then investigated. Treatment of a mixture of **9b** and Ti(O*i*Pr)$_4$, which was prepared from carbanion **3b** and ClTi(O*i*Pr)$_3$ in diethyl ether, first with methyl iodide and then with benzaldehyde gave β-hydroxy sulfone **13b** in 91% yield (Scheme 8). Formation of the methylated sulfone **12b** was not detected. Treatment of a mixture of **8f** and Ti(O*i*Pr)$_4$ with a 1:1 mixture of benzaldehyde and acetophenone only provided β-hydroxy sulfone **13f**, according to GC analysis. Formation of the β-hydroxy sulfone **14** could not be detected. Interestingly, both sulfonylalkyl groups of **9b** and **9f** were utilised in the reaction with the aldehyde. The C$_\alpha$–Ti bonded titanium derivative of **3** (R^1 = R^2 = H, R^3 = Ph) shows a similar aldehyde-ketone selectivity.[14]



Scheme 8. Reaction of bis(1-sulfonylalkyl)titaniums with carbonyl compounds.

Reaction of α-sulfonyl carbanions **3a**–**c**, **3f** and **3g** with benzaldehyde under similar conditions afforded the corresponding β-hydroxy sulfones **13a**–**c**, **13f** and **13g** in 82–88% yield (Scheme 9). The reaction of carbanion **3f** with a 1:1 mixture of benzaldehyde and acetophenone was, as expected,[11] unselective and gave, according to GC–MS analysis, a mixture of β-hydroxy sulfones **13f** and **14** in a ratio of 55:45.

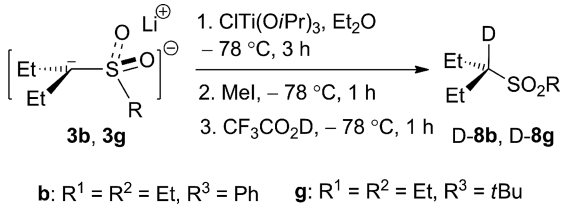


Scheme 9. Reaction of lithium α-sulfonyl carbanions with carbonyl compounds.

The bis(1-sulfonylalkyl)titaniums showed a lower reactivity towards benzaldehyde than the corresponding lithium carbanions.

Estimation of the Rate of the Lithium–Titanium Exchange in Diethyl Ether

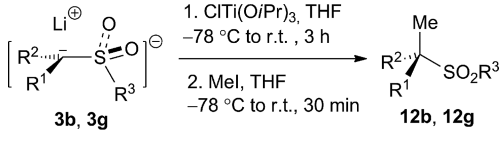
It was of interest to obtain information about the rates of titanation of **3** and formation of **9** in diethyl ether. The large difference in reactivity between **3** and **9** towards methyl iodide was used as a chemical probe for the formation of the latter. Whereas carbanions **3** already react at –78 °C with methyl iodide, titanium derivatives **9** are inert even at room temperature. Carbanions **3b** and **3g** were treated with $ClTi(OiPr)_3$ in diethyl ether at –78 °C. After the mixtures were kept for 3 h at low temperatures, methyl iodide was added at the same temperature. The reactions were quenched after 1 h with CF_3CO_2D at –78 °C. This sequence of steps gave the corresponding deuterated sulfones D-**8b** (95% D) and D-**8k** (95% D) in 91 and 97% yield, respectively (Scheme 10). Formation of the methylated sulfones **12b** and **12g** was not observed. These results show that formation of **9b** and **9g** from the corresponding carbanions **3b** and **3g** in diethyl ether already occurred at –78 °C. This observation is of significance for the envisioned synthesis of chiral, non-racemic derivatives of **9**, because of the limited configurational stability of **3**.



Scheme 10. Li–Ti exchange of α-sulfonyl carbanions at low temperatures.

Lithium–Titanium Exchange in Tetrahydrofuran

Titanation of the tertiary α-sulfonyl carbanions with $ClTi(OiPr)_3$ in THF was also investigated to establish whether (1-sulfonylalkyl)titaniums instead of bis(1-sulfonylalkyl)titaniums are obtained. Carbanions **3b** and **3g** were treated with 1.1 equiv. $ClTi(OiPr)_3$ in THF at –78 °C and then the mixtures were warmed to room temperature. Precipitation of lithium chloride, in contrast to the reactions in diethyl ether, did not occur. Subsequently, methyl iodide was added at –78 °C to the mixtures, which were subsequently warmed to room temperature. Surprisingly, the two-step sequences afforded the corresponding methyl sulfones **12b** and **12g** in 96 and 91% yield, respectively (Scheme 11). Formation of **12b** and **12g** occurred already at low temperatures.

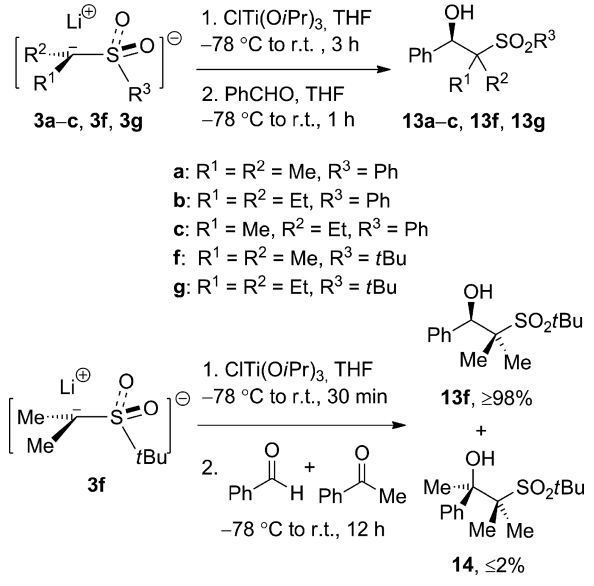


Scheme 11. Titanation of α-sulfonyl carbanions in THF and reactivity of the titanium derivatives towards methyl iodide.

A similar treatment of carbanions **3a**–**c**, **3f** and **3g** first with $ClTi(OiPr)_3$ in THF and then with benzaldehyde, furnished the corresponding β-hydroxy sulfones **13a**–**c**, **13f** and

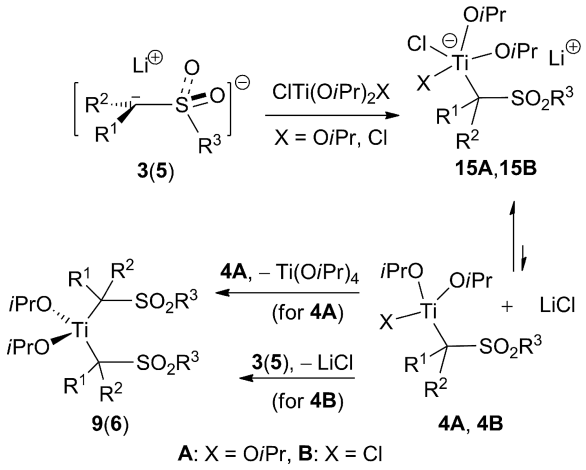
13g in 60–89% yield. The β-hydroxy sulfone **13c** was obtained as a 1:1 mixture of the diastereomers.

The results obtained in the experiments with methyl iodide implied that in THF either a C-titanation of the α-sulfonyl carbanions **3b** and **3g** had not occurred or titanium derivatives other than **9b** and **9g** had been formed. To distinguish between these possibilities, a competition experiment with benzaldehyde/acetophenone was conducted. Titanation of **3f** with $ClTi(OiPr)_3$ in THF under similar conditions followed by the addition of a 1:1 mixture of benzaldehyde and acetophenone only afforded β-hydroxy sulfone **13f**, according to GC–MS analysis (Scheme 12). Formation of **14** was not detected. These results clearly show that the reactions of **3b**, **3g** and **3f**, and most likely also those of **3a** and **3c**, with $ClTi(OiPr)_3$ in THF had not given the corresponding bis(1-sulfonylalkyl)titaniums. Instead, titanium derivatives of different structures had been formed that show a similar selectivity for benzaldehyde as bis(1-sulfonylalkyl)titaniums, but, in contrast to the latter, are also reactive towards methyl iodide.



Scheme 12. Titanation of α-sulfonyl carbanions in THF and reactivity of the titanium derivatives derived thereof towards carbonyl compounds.

The Li–Ti exchange of **3** and **5** gave two unexpected results. First, titanation of the carbanions in diethyl ether affords bis(1-sulfonylalkyl)titaniums instead of (1-sulfonylalkyl)titaniums. Second, titanation in THF furnished different titanium derivatives. According to the trapping experiments with methyl iodide (cf. Scheme 10), titanation of the carbanions and formation of the bis(1-sulfonylalkyl)-titaniums in diethyl ether are relatively fast processes at low temperatures. Carbanions **3**(**5**) are expected to react with $ClTi(OiPr)_3$ in both solvents under C-titanation and formation of the ate complexes **15A** (Scheme 13). The ate complexes are perhaps in equilibrium with the corresponding (1-sulfonylalkyl)titaniums **4A** and lithium chloride. Given the low solubility of lithium chloride in diethyl ether, equilibrium is shifted towards the 1-(sulfonylalkyl)titaniums **4A**, which suffer disproportionation and furnish the bis(1-sulfonylalkyl)titaniums **9**(**6**) and $Ti(OiPr)_4$. In THF the solubility of lithium chloride precludes a shift of the equilibrium towards **4A** and thus the ate complexes are the dominating species.



Scheme 13. Proposed course of the titanation of tertiary α-sulfonyl carbanions.

A key feature of Scheme 13 is the proposed Schlenk-type equilibrium of (1-sulfonylalkyl)titaniums **4A** shown in Equation (1).

$$2\ RTi(OiPr)_3 \rightleftharpoons R_2Ti(OiPr)_2 + Ti(OiPr)_4 \quad (1)$$

4A **9**(**6**)

Whereas the disproportionation of heteroatom-substituted titanium(IV) derivatives is well documented,[33] a Schlenk equilibrium of alkyl(aryl)titaniums has, to our knowledge, not been described. It had been postulated, however, that protonolysis of $(PhCH_2)_4Ti$ with one equivalent of EtOH affords $(PhCH_2)_3Ti(OEt)$, which suffers disproportionation, giving a mixture of $(PhCH_2)_2Ti(OEt)_2$ and $(PhCH_2)_4Ti$.[26b,34,35] Disproportionation of **4A** could occur within a dimer through a stepwise transfer first of an isopropoxy group and then of a sulfonylalkyl group.

Formation of bis(1-sulfonylalkyl)titaniums **6** from carbanions **5** upon titanation with $Cl_2Ti(OiPr)_2$ in diethyl ether has to follow a somewhat different course because of the application of only 0.7 equiv. of the titanium reagent. Reaction of the carbanions with the titanium reagent presumably gave the ate complexes **15B** together with unreacted **5**. Driven by the precipitation of lithium chloride, the ate complexes were perhaps converted into chloro(1-sulfonylalkyl)titaniums **4B**, which reacted with carbanions **5** at the Ti atom and afforded **6**.

Conclusions

The Li–Ti exchange of tertiary alkyl-substituted α-sulfonyl carbanions with chlorotitanium reagents takes place at the anionic C atom and yields bis(1-sulfonylalkyl)titaniums

in diethyl ether as solvent. The bis(1-sulfonylalkyl)titaniums adopt distorted octahedral structures in the crystal, because of additional coordination of sulfonyl O atoms to the Ti atom. The mechanism of the formation of the bis(1-sulfonylalkyl)titaniums is has not yet been elucidated. The topomerisation of the titanyl group of bis(1-sulfonylalkyl)titaniums, which has to involve cleavage of the C_α–Ti bond, is either slow or nonexistent at room temperature. This indicates that chiral bis(1-sulfonylalkyl)titaniums should be configurationally stable at room temperature. The bis(1-sulfonylalkyl)titaniums are inert towards methyl iodide and react selectively with benzaldehyde in the presence of acetophenone, whereby both sulfonylalkyl residues are transferred to the aldehyde. The reaction of the dialkyl-substituted α-sulfonyl carbanions with chlorotitanium reagents in THF takes a different course. Titanium derivatives of undefined structure are formed, which are methylated by methyl iodide but react selectively with benzaldehyde in the presence of acetophenone.

Experimental Section

General Comments and Materials: All reactions were carried out in anhydrous solvents under argon in oven-dried glassware by using Schlenk, cannula and syringe techniques. $ClTi(OiPr)_3$ was obtained from commercial sources and distilled under argon before use. $Cl_2Ti(OiPr)_2$ was obtained as colourless crystals from $Ti(OiPr)_4$ and $TiCl_4$ in *n*-hexane.[3,36] Diethyl ether (denoted as ether) and tetrahydrofuran (THF) were filtered through alumina and distilled from potassium/benzophenone under argon. *n*-Hexane was distilled from potassium/benzophenone under argon. Methyl iodide was distilled from CaH_2 under argon. [D_8]THF and [D_6]benzene were distilled from potassium in a micro solvent still under argon. Benzaldehyde and acetophenone were distilled from CaH_2. *n*BuLi was standardised by titration with diphenylacetic acid.[37] All other reagents were obtained from commercial sources and used without further purification. Sulfones **8a**–**c** and **8f**–**h** were prepared through oxidation of the corresponding sulfanes, which were obtained from the corresponding thiols and alkyl halides by following standard procedures. Sulfones **8d** and **8e** were synthesised through methylation of the corresponding parent sulfones, which were obtained starting from the corresponding thiols and alkyl halides via the corresponding sulfanes by following standard procedures. Analytical thin-layer chromatography (TLC) was performed on E. Merck pre-coated TLC plates (silica gel 60 F_{254}, layer thickness 0.2 mm). Flash chromatography (denoted as chromatography) was performed with E. Merck silica gel 60 (0.063–0.200 mm). Gas chromatography was done with a Chrompack CP-9000 instrument by using a DB 5 Carlo Erba CP-Sil-8 column: length 30 m, diameter 0.32 mm, film thickness 0.25 μm. ^1H and ^{13}C NMR spectra were recorded with Varian VXR 300 (300 MHz, 75 MHz), Varian Gemini 300 (300 MHz, 75 MHz) or Varian Unity 500 (500 MHz, 125 MHz) instruments. Chemical shifts are reported relative to $SiMe_4$ (δ = 0.00 ppm), $CHCl_3$ (δ = 7.24 ppm, 77.1 ppm) and [D_6]-benzene (δ = 7.16 ppm, 128.0 ppm) as internal standards. Splitting patterns in the ^1H NMR spectra are designated as s, singlet; d, doublet; dd, double doublet; t, triplet; q, quartet; quin, quintet; sept, septet; m, multiplet; br, broad; app, apparent, and combinations thereof. Peaks in the ^{13}C NMR spectra are denoted as "u" for carbons with zero or two attached protons and as "d" for carbons with one or three attached protons, as determined from the APT pulse sequence. Assignments in the ^1H NMR spectra were made by GMQCOSY, GNOE, HETCOR experiments and those in the ^{13}C NMR spectra were made by DEPT experiments. Solutions of titanium derivatives in [D_8]THF and [D_6]benzene for NMR spectroscopy were sealed in tubes. IR spectra were recorded with a Perkin–Elmer PE 1759 FT instrument. Only peaks of $\tilde{\nu} \geq 800\ cm^{-1}$ are listed, vs. = very strong, s = strong, m = medium, w = weak. Low-resolutions mass spectra were recorded with a Varian MAT 212 S instrument using electron impact ionisation (EI, 70 eV). Only peaks of $m/z \geq 80$ and an intensity of $\geq 10\%$, except decisive ones, are listed. Elemental analyses were performed by the Institute of Organic Chemistry (RWTH Aachen University) micro analytical laboratory with a Perkin–Elmer CHN-analyzer 240C and a Heraeus CHN-Rapid analyzer. Melting points were determined with a SMP 20 Büchi apparatus and are uncorrected.

Reaction of Lithium α-Sulfonyl Carbanions 3 with Methyl Iodide. General Procedure (GP1): To a solution of sulfone **8** (2.20 mmol) in diethyl ether (10 mL) was added at –78 °C, *n*BuLi (1.60 M in *n*-hexane, 1.62 mL, 2.59 mmol). The yellow mixture was stirred for 15 min at room temperature, then cooled to –35 °C and treated dropwise with MeI (4.10 mmol). The mixture was stirred for 30 min at room temperature, then cooled to 0 °C and treated with CF_3CO_2D (2.00 M in THF, 3.40 mL, 6.80 mmol). The mixture was treated with H_2O (20 mL) and 2 N aqueous HCl (5 mL) and extracted with diethyl ether (3 × 40 mL). The combined organic phases were washed with saturated aqueous $Na_2S_2O_3$ and H_2O (40 mL). The organic phase was dried ($MgSO_4$) and concentrated in vacuo. Purification by chromatography (*n*-hexane/EtOAc, 1:1) gave methylated sulfone **12**.

Treatment of Bis(1-sulfonylalkyl)titaniums 9 with Methyl Iodide. General Procedure (GP2): To a solution of sulfone **8** (2.20 mmol) in diethyl ether (10 mL) was added at –78 °C, *n*BuLi (1.60 M in *n*-hexane, 1.62 mL, 2.59 mmol). The yellow mixture was stirred for 15 min at room temperature, then cooled to –78 °C and treated dropwise with $ClTi(OiPr)_3$ (688 mg, 2.64 mmol). The orange mixture was stirred for 3 h at room temperature, then cooled to –35 °C and treated with MeI (594 mg, 4.18 mmol). The mixture was stirred for 30 min at room temperature, then CF_3CO_2D (2.00 M in THF, 3.40 mL, 6.80 mmol) was added at 0 °C. The mixture was stirred for 30 min at room temperature, treated with H_2O (20 mL) and 2 N aqueous HCl (5 mL) and extracted with diethyl ether (3 × 40 mL). The combined organic phases were washed with saturated aqueous $Na_2S_2O_3$ and H_2O (40 mL). The organic phase was dried ($MgSO_4$) and concentrated in vacuo. Purification by chromatography (*n*-hexane/EtOAc, 1:1) gave deuterated sulfone D-**8**.

Reaction of Putative Titanium Derivatives 15A with Methyl Iodide. General Procedure (GP3): To a solution of sulfone **8** (2.20 mmol) in THF (10 mL) was added at –78 °C, *n*BuLi (1.60 M in *n*-hexane, 1.62 mL, 2.59 mmol). The yellow mixture was stirred for 15 min at room temperature, then cooled to –78 °C and treated dropwise with $ClTi(OiPr)_3$ (688 mg, 2.64 mmol). The orange mixture was then stirred for 3 h at room temperature, cooled to –78 °C and treated with MeI (594 mg, 4.18 mmol). The mixture was stirred for 30 min at room temperature, then cooled to 0 °C and treated with CF_3CO_2D (2.00 M in THF, 3.40 mL, 6.80 mmol). The mixture was stirred for 30 min at room temperature, treated with H_2O (20 mL) and 2 N aqueous HCl (5 mL) and extracted with diethyl ether (3 × 40 mL). The combined organic phases were washed with saturated aqueous $Na_2S_2O_3$ and H_2O (40 mL). The organic phase was dried ($MgSO_4$) and concentrated in vacuo. Purification by chromatography (*n*-hexane/EtOAc, 1:1) gave methylated sulfone **12**.

Reaction of Lithium α-Sulfonyl Carbanions 3 with Benzaldehyde. General Procedure (GP4): To a solution of sulfone **8** (2.20 mmol) in THF (20 mL) was added at –78 °C, *n*BuLi (1.60 M in *n*-hexane, 1.62 mL, 2.59 mmol). The yellow mixture was stirred for 15 min at room temperature, then cooled to –78 °C and treated dropwise with PhCHO (466 mg, 4.39 mmol). The mixture was stirred for 15 min at room temperature, then cooled to 0 °C and treated with 2 N aqueous HCl (25 mL) and extracted with diethyl ether (3 × 70 mL). The combined organic phases were washed with saturated aqueous $NaHCO_3$ and H_2O (40 mL). The organic phase was dried ($MgSO_4$) and concentrated in vacuo. A layer of *n*-hexane (3 mL) was placed on the viscous oil and the mixture was stored at 2 °C. Crystallisation was complete after 24 h. The liquid phase was removed by using a syringe, and the solid alcohol **13** was washed with cold *n*-hexane (1 mL) and dried in vacuo.

Reaction of the Putative Titanium Derivatives 15A with Benzaldehyde. General Procedure (GP5): To a solution of sulfone **8** (2.20 mmol) in THF (20 mL) was added at –78 °C, *n*BuLi (1.60 M in *n*-hexane, 1.62 mL, 2.59 mmol). The yellow mixture was stirred for 15 min at room temperature, then cooled to –78 °C and treated dropwise with $ClTi(OiPr)_3$ (688 mg, 2.64 mmol). The orange mixture was stirred for 3 h at room temperature, cooled to –78 °C and treated with PhCHO (466 mg, 4.39 mmol). The mixture was stirred for 1 h at room temperature, then treated with 2 N aqueous HCl (25 mL) and extracted with diethyl ether (3 × 40 mL). Drying ($MgSO_4$) and concentration of the combined organic phases in vacuo gave alcohol **13**.

Bis[1-(phenylsulfonyl)cyclopropyl-*C*,*O*]bis(2-propanolato)titanium (6a): To a solution of sulfone **7a** (1.110 g, 6.09 mmol) in diethyl ether (20 mL) was added at –78 °C, *n*BuLi (1.52 M in *n*-hexane, 4.41 mL, 6.70 mmol). After the colourless suspension of the lithium carbanion **5a** was stirred for 15 min at room temperature, it was cooled to –50 °C and added dropwise by using a cannula at –50 °C to a solution of $ClTi(OiPr)_3$ (1.910 g, 7.33 mmol) in diethyl ether (15 mL). The mixture was then warmed to room temperature, whereby the suspension became a clear solution from which, after 10 min, LiCl precipitated. The suspension was stirred for 1 h at room temperature, then filtered under argon through a fritted glass covered with dry kieselguhr. Concentration in vacuo gave a yellow oil, which was dissolved in *n*-hexane (25 mL) at 60 °C. Cooling the mixture to 2 °C for 3 h produced colourless crystals. The mother liquor was removed by using a syringe and the crystals were washed with a small amount of cold *n*-hexane. Drying in vacuo gave bis(1-sulfonylcycloalkyl)titanium **6a** (965 mg, 60%) as colourless crystals. ^{1}H NMR (300 MHz, [D$_6$]benzene): δ = 1.24 (d, J = 6.04 Hz, 12 H, *i*Pr), 1.26 (m, 4 H, CH_2), 1.58 (m, 4 H, CH_2), 4.86 (sept, J = 6.04 Hz, 2 H, *i*Pr), 6.98 (m, 6 H, Ph), 8.25 (m, 4 H, Ph) ppm. ^{13}C NMR (75 MHz, [D$_6$]benzene): δ = 16.9 (u, CH_2), 26.1 (d, *i*Pr), 52.3 (u, CTi), 80.4 (d, *i*Pr), 128.6 (d, Ph), 128.7 (d, Ph), 132.7 (d, Ph), 140.4 (u, Ph) ppm. ^{1}H NMR (300 MHz, [D$_8$]toluene): δ = 1.13 (m, 4 H, CH_2), 1.19 (d, J = 6.04 Hz, 12 H, *i*Pr), 1.46 (m, 4 H, CH_2), 4.79 (sept, J = 6.04 Hz, 2 H, *i*Pr), 7.00 (m, 2 H, Ph), 7.08 (m, 4 H, Ph), 8.08 (m, 4 H, Ph) ppm. ^{13}C NMR (75 MHz, [D$_8$]toluene): δ = 16.8 (u, CH_2), 26.1 (d, *i*Pr), 52.3 (u, CTi), 80.3 (d, *i*Pr), 128.5 (d, Ph), 128.6 (d, Ph), 132.6 (d, Ph), 140.5 (u, Ph) ppm. $C_{24}H_{36}O_6S_2Ti$ (528.50): calcd. C 54.54, H 6.10; found C 54.26, H 6.16.

Bis[1-(phenylsulfonyl)cyclobutyl-*C*,*O*]bis(2-propanolato)titanium (6b): To a solution of sulfone **7b** (810 mg, 4.13 mmol) in diethyl ether (25 mL) was added at –78 °C, *n*BuLi (1.59 M in *n*-hexane, 2.84 mL, 4.54 mmol). The yellow suspension of the lithium carbanion **5b** was stirred at room temperature for 15 min, cooled to –50 °C and then added by using a cannula at –50 °C to a solution $ClTi(OiPr)_3$ (1.290 g, 4.95 mmol) in diethyl ether (15 mL). The mixture was then warmed to room temperature, whereby LiCl precipitated after 10 min. The orange mixture was stirred for 1.5 h at room temperature, then filtered under argon through a fritted glass covered with dry kieselguhr. Concentration in vacuo gave a yellow solid, which was dissolved in *n*-hexane (75 mL) at 50 °C. Cooling the mixture to 2 °C for 12 h produced yellow crystals. The mother liquor was removed by using a syringe and the crystals were washed with a small amount of cold *n*-hexane. Drying in vacuo gave bis(1-sulfonylcycloalkyl)alkyltitanium **6b** (655 mg, 57%) as yellow crystals. ^{1}H NMR (300 MHz, C_6D_6): δ = 1.43 (d, J = 6.3 Hz, 12 H, *i*Pr), 1.70 (m, 2 H, CH_2), 2.15 (m, 2 H, CH_2), 2.48 (m, 4 H, CH_2), 2.80 (m, 4 H, CH_2), 5.09 (sept, J = 6.1 Hz, 2 H, *i*Pr), 7.04 (m, 6 H, Ph), 8.24 (m, 4 H, Ph) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 18.2 (u, CH_2), 26.9 (d, *i*Pr), 32.9 (u, CH_2), 69.5 (u, CTi), 80.7 (d, *i*Pr), 129.6 (d, Ph), 129.3 (d, Ph), 133.3 (d, Ph), 139.5 (u, Ph) ppm. $C_{26}H_{36}O_6S_2Ti$ (556.56): calcd. C 56.11, H 6.52; found C 55.78, H 6.58.

Synthesis with $Cl_2Ti(OiPr)_2$: To a solution of sulfone **7b** (1.070 g, 5.44 mmol) in diethyl ether (30 mL) was added at –78 °C, *n*BuLi (1.50 M in *n*-hexane, 4.00 mL, 6.00 mmol). The yellow solution was then added by using a cannula to a solution of $Cl_2Ti(OiPr)_2$ (910 mg, 3.84 mmol) in diethyl ether (20 mL) at –78 °C whereby, after 30 min, LiCl precipitated. After the suspension was stirred for 3 h at room temperature, it was filtered under argon through a fritted glass covered with dry kieselguhr. Concentration of the filtrate in vacuo gave a brown sticky oil, which was dissolved in *n*-hexane (60 mL) at 60 °C. The solution was concentrated in vacuo to half of its original volume and kept for 3 h at 2 °C. Filtration and drying in vacuo gave **6b** (999 mg, 66%) as yellow crystals.

Bis[1-(phenylsulfonyl)cyclopentyl-*C*,*O*]bis(2-propanolato)titanium (6c): To a solution of *n*BuLi (1.52 M in *n*-hexane, 4.43 mL, 6.73 mmol) in diethyl ether (10 mL) was added at –78 °C a solution of sulfone **7c** (1.290 g, 6.13 mmol) in diethyl ether (30 mL) by using a cannula. The mixture was stirred at room temperature for 15 min then the solution of carbanion **5c** was cooled to –50 °C and added by using a cannula at –50 °C to a solution of $ClTi(OiPr)_3$ (1.920 g, 7.36 mmol) in diethyl ether (20 mL). The mixture was warmed to room temperature, whereby LiCl precipitated after 10 min. The yellow mixture was stirred for 2 h at room temperature, then filtered under argon through a fritted glass covered with dry kieselguhr. Concentration in vacuo gave a yellow oil, which was dissolved in *n*-hexane (25 mL) at 60 °C. Cooling the mixture to 2 °C for 12 h produced colourless crystals. The mother liquor was removed by using a syringe and the crystals were washed with a small amount of cold *n*-hexane. Drying in vacuo gave bis(1-sulfonylcycloalkyl)-titanium **6c** (1.057 g, 59%) as colourless crystals. ^{1}H NMR (300 MHz, [D$_6$]benzene): δ = 1.29 (m, 4 H, CH_2), 1.35 (d, J = 6.04 Hz, 12 H, *i*Pr), 1.50 (m, 4 H, CH_2), 2.43 (m, 4 H, CH_2), 2.55 (m, 4 H, CH_2), 4.99 (sept, J = 6.04 Hz, 2 H, *i*Pr), 7.00 (m, 6 H, Ph), 8.20 (m, 4 H, Ph) ppm. ^{13}C NMR (75 MHz, [D$_6$]benzene): δ = 26.3 (d, *i*Pr), 27.0 (u, CH_2), 35.2 (u, CH_2), 76.7 (u, CTi), 79.5 (d, *i*Pr), 129.0 (d, Ph), 129.2 (d, Ph), 132.6 (d, Ph), 140.3 (u, Ph) ppm.

Synthesis with $Cl_2Ti(OiPr)_2$: To a solution of sulfone **7c** (1.619 g, 7.70 mmol) in diethyl ether (30 mL) was added at –78 °C, *n*BuLi (1.50 M in *n*-hexane, 5.80 mL, 8.70 mmol). The solution of **5c** was stirred at room temperature for 15 min, then cooled to –78 °C and added by using a cannula at –78 °C to a solution of $Cl_2Ti(OiPr)_2$ (1.322 g, 5.58 mmol) in diethyl ether (20 mL). After 10 min, LiCl started to precipitate. The orange mixture was stirred for 3 h at room temperature, then filtered under argon through a fritted glass covered with dry kieselguhr. Concentration of the mixture in vacuo

gave a orange sticky oil, which was dissolved at 60 °C in *n*-hexane (60 mL). The warm solution was filtered under argon through a fritted glass covered with dry kieselguhr and concentrated in vacuo to half of its volume. Cooling the mixture to 2 °C for 12 h produced yellow crystals. The mother liquor was removed by using a syringe and the crystals were washed with a small amount of cold *n*-hexane. Drying in vacuo gave **6c** (1.485 g, 66%) as yellow crystals.

Bis[1-(phenylsulfonyl)isopropyl-*C*,*O*]bis(2-propanolato)titanium (9a): To a solution of sulfone **8a** (1.210 g, 6.57 mmol) in diethyl ether (20 mL) was added at –78 °C, *n*BuLi (1.52 M in *n*-hexane, 4.76 mL, 7.23 mmol). The yellow suspension of the lithium carbanion **3a** was stirred at room temperature for 15 min, cooled to –50 °C and then added by using a cannula at –50 °C to a solution $ClTi(OiPr)_3$ (2.053 g, 7.88 mmol) in diethyl ether (15 mL). The mixture was then warmed to room temperature, whereby LiCl precipitated after 10 min. The orange mixture was stirred for 1 h at room temperature, then filtered under argon through a fritted glass covered with dry kieselguhr. Concentration in vacuo gave a yellow solid, which was dissolved in *n*-hexane (25 mL) at 60 °C. Cooling the mixture to 2 °C for 72 h produced yellow crystals. The mother liquor was removed by using a syringe and the crystals were washed with a small amount of cold *n*-hexane. Drying in vacuo gave bis(1-sulfonylalkyl)titanium **9a** (927 mg, 53%) as yellow crystals. ^{1}H NMR (300 MHz, [D$_6$]benzene): δ = 1.34 (d, J = 6.05 Hz, 12 H, *i*Pr), 1.68 (s, 12 H, Me), 4.94 (sept, J = 6.05 Hz, 2 H, *i*Pr), 6.95–7.07 (m, 6 H, Ph), 8.08 (m, 4 H, Ph) ppm. ^{13}C NMR (75 MHz, [D$_6$]benzene): δ = 23.9 (d, Me), 26.1 (d, *i*Pr), 64.5 (u, CTi), 79.8 (u, *i*Pr), 128.6 (d, Ph), 128.8 (d, Ph), 132.5 (d, Ph), 139.9 (u, Ph) ppm.

Bis[3-(phenylsulfonyl)pentyl-*C*,*O*]bis(2-propanolato)titanium (9b): To a solution of *n*BuLi (1.50 M in *n*-hexane, 5.16 mL, 7.74 mmol) in diethyl ether (10 mL) was added at –78 °C a solution of sulfone **8b** (1.500 g, 7.06 mmol) in diethyl ether (20 mL) by using a cannula. The mixture was stirred at room temperature for 15 min, then the solution of carbanion **3b** was cooled to –50 °C and added by using a cannula at –50 °C to a solution of $ClTi(OiPr)_3$ (2.210 g, 8.48 mmol) in diethyl ether (15 mL). The mixture was warmed to room temperature, whereby LiCl precipitated after 10 min. The yellow mixture was stirred for 4 h at room temperature, then filtered under argon through a fritted glass covered with dry kieselguhr. The mixture was concentrated to half of its volume and cooled to 2 °C for 12 h, which produced yellow crystals. The mother liquor was removed by using a syringe and the crystals were washed with a small amount of cold *n*-hexane. Drying in vacuo gave bis(1-sulfonylalkyl)titanium **9b** (1.039 g, 50%) as yellow crystals. ^{1}H NMR (300 MHz, [D$_6$]benzene): δ = 1.05 (br. s, 12 H, CH_3CH$_2$), 1.38 (d, J = 6.05 Hz, 12 H, *i*Pr), 1.80–2.40 (br. s, 8 H, CH$_3$CH_2), 5.02 (sept, J = 6.05 Hz, 2 H, *i*Pr), 6.95–7.07 (m, 6 H, Ph), 8.16 (m, 4 H, Ph) ppm. ^{13}C NMR (75 MHz, [D$_6$]benzene): δ = 12.2 (d, *C*H$_3$CH$_2$), 21.1 (u, CH$_3$*C*H$_2$), 26.6 (d, *i*Pr), 75.8 (u, CTi), 80.5 (d, *i*Pr), 129.4 (d, Ph), 129.6 (d, Ph), 132.9 (d, Ph), 141.5 (u, Ph) ppm. ^{1}H NMR (300 MHz, [D$_8$]THF): δ = 0.95 (tr, J = 7.42 Hz, 12 H, *C*H$_3$CH$_2$), 1.40 (d, J = 6.04 Hz, 12 H, *i*Pr), 1.92–1.94 (br. s, 8 H, CH$_3$*C*H$_2$), 5.01 (sept, J = 6.04 Hz, 2 H, *i*Pr), 7.53–7.60 (m, 6 H, Ph), 7.97–8.01 (m, 4 H, Ph) ppm. ^{13}C NMR (75 MHz, [D$_8$]THF): δ = 11.7 (d, *C*H$_3$CH$_2$), 21.0 (u, CH$_3$*C*H$_2$), 26.3 (d, *i*Pr), 75.5 (u, CTi), 80.5 (d, *i*Pr), 129.5 (d, Ph), 129.6 (d, Ph), 133.3 (d, Ph), 141.4 (u, Ph) ppm. $C_{28}H_{44}O_6S_2Ti$ (588.64): calcd. C 57.13, H 7.53; found C 57.9, H 7.55.

(*tert*-Butylsulfonyl)benzene (12a): Treatment of sulfone **8a** (486 mg, 2.64 mmol) with *n*BuLi (1.50 M in *n*-hexane, 1.91 mL, 2.86 mmol) and MeI (260 μL, 4.10 mmol) in THF as described in GP1 gave sulfone **12a** (439 mg, 84%) after crystallisation from diethyl ether/*n*-hexane (1:3), as colourless crystals, m.p. 83 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.35 (s, 9 H, *t*Bu), 7.56 (m, 2 H, Ph), 7.66 (m, 1 H, Ph), 7.88 (m, 2 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.6 (d, *t*Bu), 59.8 (u, *t*Bu), 128.7 (d, Ph), 130.5 (d, Ph), 133.5 (d, Ph), 135.4 (u, Ph) ppm. IR (KBr): $\tilde{\nu}$ = 3435 (m), 3062 (m), 3029 (m), 2978 (s), 2937 (s), 2873 (m), 2208 (m), 2017 (m), 1931 (m), 1838 (m), 1718 (m), 1625 (m), 1584 (m), 1478 (s), 1452 (s), 1398 (m), 1366 (m), 1284 (vs), 1205 (s), 1135 (vs), 1078 (vs), 1022 (s), 997 (m), 942 (m), 804 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 198 (2) [M$^+$], 143 (5), 78 (7), 77 (6), 58 (5), 57 (100), 56 (5), 51 (5). $C_{10}H_{14}O_2S$ (198.28): calcd. C 60.57, H 7.12; found C 60.30, H 7.14.

Treatment of sulfone **8a** (486 mg, 2.64 mmol) with *n*BuLi (1.50 M in *n*-hexane, 1.91 mL, 2.86 mmol), $ClTi(OiPr)_3$ (745 mg, 2.86 mmol), MeI (260 μL, 4.10 mmol) and CH_3CO_2D (420 μL, 6.80 mmol) in ether as described in GP2 gave sulfone D-**8a** (466 mg, 96%) (88% D) as colourless crystals.

[(3-Methylpentane-3-yl)sulfonyl]benzene (12b): Treatment of sulfone **8b** (467 mg, 2.20 mmol) with *n*BuLi (1.50 M in *n*-hexane, 1.76 mL, 2.64 mmol) and MeI (260 μL, 4.10 mmol) in THF as described in GP1 gave sulfone **12b** (393 mg, 79%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.01 (t, J = 7.40 Hz, 6 H, CH_3CH$_2$), 1.21 (s, 3 H, Me), 1.66 (app. sext, J = 7.39 Hz, 2 H, CH$_3$CH_2), 1.88 (app. sext, J = 7.38 Hz, 2 H, CH$_3$CH_2), 7.55 (m, 2 H, Ph), 7.64 (m, 1 H, Ph), 7.87 (m, 2 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.5 (d, *C*H$_3$CH$_2$), 19.4 (d, Me), 25.6 (u, CH$_3$*C*H$_2$), 66.1 (u, CS), 128.7 (d, Ph), 130.3 (d, Ph), 133.4 (d, Ph), 136.5 (u, Ph) ppm. IR (KBr): $\tilde{\nu}$ = 3539 (w), 3335 (w), 3066 (m), 2973 (s), 2942 (s), 2884 (s), 2345 (w), 1754 (w), 1725 (w), 1585 (m), 1460 (vs), 1447 (vs), 1386 (s), 1337 (m), 1286 (vs), 1206 (m), 1163 (vs), 1128 (vs), 1079 (vs), 1012 (m), 1000 (m), 933 (w), 875 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 226 (0.1) [M$^+$], 143 (4), 86 (6), 85 (100), 84 (5), 77 (6), 69 (7.14), 57 (17), 55 (5), 51 (4). $C_{12}H_{18}O_2S$ (226.34): calcd. C 63.68, H 8.02; found C 63.57, H 8.04.

Treatment of sulfone **8b** (467 mg, 2.20 mmol) with *n*BuLi (1.50 M in *n*-hexane, 1.76 mL, 2.64 mmol), $ClTi(OiPr)_3$ (745 mg, 2.86 mmol), MeI (260 μL, 4.10 mmol) and CH_3CO_2D (420 μL, 6.80 mmol) in ether as described in GP2 gave sulfone D-**8b** (439 mg, 94%) (90% D).

Treatment of sulfone **8b** (467 mg, 2.20 mmol) with *n*BuLi (1.50 M in *n*-hexane, 1.76 mL, 2.64 mmol), $ClTi(OiPr)_3$ (687 mg, 2.64 mmol) and MeI (260 μL, 4.10 mmol) in THF as described in GP3 gave sulfone **12b** (478 mg, 96%) as a yellow oil.

(*tert*-Pentylsulfonyl)benzene (12c): Treatment of sulfone **8c** (436 mg, 2.20 mmol) with *n*BuLi (1.50 M in *n*-hexane, 1.76 mL, 2.64 mmol) and MeI (260 μL, 4.10 mmol) in THF as described in GP1 gave sulfone **12c** (411 mg, 88%) as a pale-yellow oil. R_f = 0.64 (EtOAc/*n*-hexane, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.95 (t, J = 7.56 Hz, 3 H, CH_3CH$_2$), 1.28 (s, 6 H, Me), 1.75 (q, J = 7.41 Hz, 2 H, CH$_3$CH_2), 7.55 (m, 2 H, Ph), 7.65 (m, 1 H, Ph), 7.88 (m, 2 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.2 (d, *C*H$_3$CH$_2$), 12.0 (d, Me), 27.8 (u, CH$_3$*C*H$_2$), 63.3 (u, CMe$_2$), 128.7 (d, Ph), 130. 6 (d, Ph), 133.5 (u, Ph) ppm. IR (KBr): $\tilde{\nu}$ = 3386 (w), 3065 (m), 2975 (s), 2941 (s), 2882 (m), 2370 (w), 2346 (w), 1795 (w), 1724 (w), 1585 (m), 1463 (vs), 1447 (vs), 1391 (s), 1366 (m), 1296 (vs), 1287 (vs), 1169 (s), 1130 (vs), 1078 (vs), 1060 (m), 1024 (m), 999 (m), 923 (w), 875 (m), 806 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 212 (0.3) [M$^+$], 143 (9), 85 (9), 77 (7), 71 (100), 70 (8), 55 (13), 51 (6). $C_{11}H_{16}O_2S$ (212.31): calcd. C 62.23, H 7.60; found C 62.11, H 7.71.

Treatment of sulfone **8c** (436 mg, 2.20 mmol) with *n*BuLi (1.50 M in *n*-hexane, 1.76 mL, 2.64 mmol), $ClTi(OiPr)_3$ (745 mg, 2.86 mmol), MeI (260 μL, 4.10 mmol) and CH_3CO_2D (420 μL,

6.80 mmol) in ether as described in GP2 gave sulfone D-**8c** (409 mg, 94%) (67% D).

[(2,3-Dimethylbutan-2-yl)sulfonyl]benzene (12d): Treatment of sulfone **8d** (467 mg, 2.20 mmol) with *n*BuLi (1.50 M in *n*-hexane, 1.76 mL, 2.64 mmol) and MeI (260 μL, 4.10 mmol) in THF as described in GP1 gave sulfone **12d** (473 mg, 95%) after crystallisation from diethyl ether/*n*-hexane (1:3), as colourless crystals, m.p. 78 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.08 (d, J = 6.87 Hz, 6 H, *i*Pr), 1.24 (s, 6 H, Me), 2.22 (sept, J = 6.86 Hz, 1 H, *i*Pr), 7.55 (m, 2 H, Ph), 7.64 (m, 1 H, Ph), 7.87 (m, 2 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.9 (d, *i*Pr), 19.4 (d, Me), 31.5 (d, *i*Pr), 66.45 (u, CS), 128.7 (d, Ph), 130.3 (d, Ph), 133.4 (d, Ph), 136.8 (u, Ph) ppm. IR (KBr): $\tilde{\nu}$ = 3078 (m), 2996 (s), 2965 (s), 2941 (s), 2877 (s), 2196 (w), 2014 (w), 1914 (w), 1827 (w), 1786 (w), 1706 (w), 1621 (w), 1583 (m), 1465 (vs), 1450 (vs), 1386 (s), 1371 (m), 1318 (s), 1288 (vs), 1218 (s), 1176 (s), 1150 (vs), 1124 (vs), 1074 (vs), 1025 (s), 997 (s), 936 (m), 883 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 226 (10) [M$^+$], 143 (27), 86 (12), 85 (100), 84 (42), 77 (46), 69 (23), 57 (30), 55 (15), 51 (43). $C_{12}H_{18}O_2S$ (226.34): calcd. C 63.68, H 8.02; found C 63.26, H 8.01.

Treatment of sulfone **8d** (467 mg, 2.20 mmol) with *n*BuLi (1.50 M in *n*-hexane, 1.76 mL, 2.64 mmol), $ClTi(OiPr)_3$ (745 mg, 2.86 mmol), MeI (260 μL, 4.10 mmol) and CH_3CO_2D (420 μL, 6.80 mmol) in ether as described in GP2 gave sulfone D-**8d** (434 mg, 93%) (88% D).

(2,4-Dimethylpentan-2-yl)sulfonylbenzene (12e): Treatment of sulfone **8e** (498 mg, 2.20 mmol) with *n*BuLi (1.50 M in *n*-hexane, 1.73 mL, 2.60 mmol) and MeI (260 μL, 4.10 mmol) in THF as described in GP1 gave sulfone **12e** (513 mg, 97%) after crystallisation from diethyl ether/*n*-hexane (1:3) as colourless crystals, m.p. 60 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.96 (d, J = 6.60 Hz, 6 H, *i*Pr), 1.34 (s, 6 H, Me), 1.66 (d, J = 5.50 Hz, 2 H, CH_2), 1.75 (m, J = 6.59 Hz, 1 H, *i*Pr), 7.55 (m, 2 H, Ph), 7.65 (m, 1 H, Ph), 7.87 (m, 2 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.0 (d, *i*Pr), 24.3 (d, *i*Pr), 25.1 (d, Me), 42.7 (u, CH_2), 63.9 (u, CS), 128.7 (d, Ph), 130.7 (d, Ph), 133.5 (d, Ph), 135.5 (u, Ph) ppm. IR (KBr): $\tilde{\nu}$ = 3426 (w), 3063 (w), 2969 (vs), 2935 (s), 2869 (s), 2199 (w), 1583 (m), 1467 (s), 1448 (s), 1388 (s), 1369 (m), 1353 (m), 1297 (vs), 1162 (vs), 1129 (vs), 1074 (vs), 1023 (s), 998 (m), 982 (m), 941 (m), 866 (w), 805 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 241 (0.5) [M$^+$], 99 (42), 83 (7), 78 (6), 77 (13), 57 (100), 55 (9), 51 (10). $C_{13}H_{20}O_2S$ (240.36): calcd. C 64.96, H 8.39; found C 64.93, H 8.33.

Treatment of sulfone **8e** (498 mg, 2.20 mmol) with *n*BuLi (1.50 M in *n*-hexane, 1.73 mL, 2.60 mmol), $ClTi(OiPr)_3$ (745 mg, 2.86 mmol), MeI (260 μL, 4.10 mmol) and CH_3CO_2D (420 μL, 6.80 mmol) in ether as described in GP2 gave sulfone D-**8e** (468 mg, 94%) (86% D).

(2-*tert*-Butylsulfonyl)-2-methylpropane (12f): Treatment of sulfone **8f** (361 mg, 2.20 mmol) with *n*BuLi (1.50 M in *n*-hexane, 1.76 mL, 2.64 mmol) and MeI (260 μL, 4.10 mmol) in THF as described in GP1 gave sulfone **12e** (329 mg, 84%) after crystallisation from diethyl ether/*n*-hexane (1:3) as colourless crystals, m.p. 127 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.51 (s, 18 H, *t*Bu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.1 (d, *t*Bu), 64.7 (u, *t*Bu) ppm. IR (KBr): $\tilde{\nu}$ = 3904 (w), 3855 (w), 3839 (w), 3736 (w), 3690 (w), 3677 (w), 3650 (w), 3630 (w), 3422 (m), 2989 (s), 2976 (s), 2939 (s), 2374 (w), 2346 (w), 2161 (w), 1687 (m), 1655 (m), 1561 (m), 1476 (vs), 1456 (s), 1394 (s), 1376 (s), 1364 (s), 1270 (vs), 1179 (s), 1088 (vs), 1013 (s), 965 (m), 946 (m), 934 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 71 (11), 58 (4), 57 (100), 56 (12), 55 (8). $C_8H_{18}O_2S$ (178.29): calcd. C 53.89, H 10.18; found C 53.79, H 10.25.

Treatment of sulfone **8f** (361 mg, 2.20 mmol) with *n*BuLi (1.50 M in *n*-hexane, 1.76 mL, 2.64 mmol), $ClTi(OiPr)_3$ (745 mg, 2.86 mmol), MeI (260 μL, 4.10 mmol) and CH_3CO_2D (420 μL, 6.80 mmol) in ether as described in GP2 gave sulfone D-**8f** (350 mg, 97%) (82% D).

(3-*tert*-Butylsulfonyl)-3-methylpentane (12g): Treatment of sulfone **8g** (423 mg, 2.20 mmol) with *n*BuLi (1.50 M in *n*-hexane, 1.76 mL, 2.64 mmol) and MeI (260 μL, 4.10 mmol) in THF as described in GP1 gave sulfone **12g** (400 mg, 88%) after crystallisation from diethyl ether/*n*-hexane (1:3) as pale-yellow crystals, m.p. 54 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.02 (t, J = 7.39 Hz, 6 H, CH_3CH_2), 1.43 (s, 3 H, Me), 1.50 (s, 9 H, *t*Bu), 1.85 (app. sext, J = 7.39 Hz, 2 H, CH_3CH_2), 2.05 (app. sext, J = 7.38 Hz, 2 H, CH_3CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.6 (d, CH_3CH_2), 21.0 (d, Me), 26.1 (d, *t*Bu), 27.5 (u, CH_3CH_2), 66.0 (u, *t*Bu), 72.2 (u, CS) ppm. IR (KBr): $\tilde{\nu}$ = 3485 (w), 2974 (vs), 2942 (s), 2882 (s), 1468 (s), 1385 (s), 1368 (s), 1337 (s), 1275 (vs), 1186 (s), 1148 (s), 1112 (vs), 1094 (vs), 1070 (s), 1017 (m), 946 (w), 804 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 207 (0.008) [M$^+$], 85 (17), 71 (8), 69 (5), 58 (5), 57 (100), 56 (22), 55 (11). $C_{10}H_{22}O_2S$ (206.35): calcd. C 58.21, H 10.75; found C 58.38, H 10.40.

Treatment of sulfone **8g** (423 mg, 2.20 mmol) with *n*BuLi (1.50 M in *n*-hexane, 1.76 mL, 2.64 mmol), $ClTi(OiPr)_3$ (745 mg, 2.86 mmol), MeI (260 μL, 4.10 mmol) and CH_3CO_2D (420 μL, 6.80 mmol) in ether as described in GP2 gave sulfone D-**8g** (392 mg, 88%) (86% D).

Treatment of sulfone **8g** (423 mg, 2.20 mmol) with *n*BuLi (1.50 M in *n*-hexane, 1.76 mL, 2.64 mmol), $ClTi(OiPr)_3$ (687 mg, 2.64 mmol) and MeI (260 μL, 4.10 mmol) in THF as described in GP3 gave sulfone **12g** (413 mg, 91%) after crystallisation from diethyl ether/*n*-hexane (1:3) as colourless crystals.

(2-*tert*-Butylsulfonyl)-2-methylbutane (12h): Treatment of sulfone **8h** (392 mg, 2.20 mmol) with *n*BuLi (1.50 M in *n*-hexane, 1.76 mL, 2.64 mmol) and MeI (260 μL, 4.10 mmol) in THF as described in GP1 gave sulfone **12h** (376 mg, 89%) after crystallisation from diethyl ether/*n*-hexane (1:3) as colourless crystals, m.p. 64 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.00 (t, J = 7.39 Hz, 3 H, CH_3CH_2), 1.45 (s, 6 H, Me), 1.51 (s, 9 H, *t*Bu), 1.96 (q, J = 7.38 Hz, 2 H, CH_3CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.4 (d, CH_3CH_2), 22.1 (d, Me), 26.2 (d, *t*Bu), 29.9 (u, CH_3CH_2), 65.3 (u, CS), 69.1 (u, CS) ppm. IR (KBr): $\tilde{\nu}$ = 3905 (w), 3855 (w), 3843 (w), 3752 (w), 3736 (w), 3690 (w), 3677 (w), 3657 (w), 3630 (m), 3414 (m), 2977 (vs), 2946 (s), 2886 (s), 2374 (w), 2346 (m), 2176 (w), 1720 (m), 1687 (m), 1656 (m), 1638 (m), 1562 (m), 1474 (vs), 1391 (s), 1368 (s), 1308 (s), 1267 (vs), 1185 (s), 1156 (s), 1089 (vs), 1040 (s), 1018 (s), 967 (w), 938 (m), 923 (w), 800 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 193 (0.2) [M$^+$], 72 (6), 71 (100), 70 (14), 57 (70), 56 (8), 55 (11).

Treatment of sulfone **8h** (392 mg, 2.20 mmol) with *n*BuLi (1.50 M in *n*-hexane, 1.76 mL, 2.64 mmol), $ClTi(OiPr)_3$ (745 mg, 2.86 mmol), MeI (260 μL, 4.10 mmol) and CH_3CO_2D (420 μL, 6.80 mmol) in ether as described in GP2 gave sulfone D-**8h** (358 mg, 91%) (99% D).

(±)-2-Methyl-1-phenyl-2-(phenylsulfonyl)propan-1-ol (13a). From 3a and PhCHO: Treatment of sulfone **8a** (750 mg, 4.07 mmol) with *n*BuLi (1.50 M in *n*-hexane, 2.98 mL, 4.48 mmol) and PhCHO (860 mg, 8.10 mmol) in THF as described in GP4 gave alcohol **13a** (976 mg, 84%) as colourless crystals.

From Putative 15Aa and PhCHO in THF: Treatment of sulfone **8a** (750 mg, 4.07 mmol) with *n*BuLi (1.50 M in *n*-hexane, 2.98 mL, 4.48 mmol), $ClTi(OiPr)_3$ (1.27 g, 4.88 mmol) and PhCHO (860 mg,

8.10 mmol) in THF as described in GP5 gave alcohol **13a** (1.005 g, 85%) as pale-yellow crystals, m.p. 174–176 °C, R_f = 0.53 (EtOAc/*n*-hexane, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.94 (s, 3 H, Me), 1.41 (s, 3 H, Me), 4.24 (s, 1 H, OH), 5.19 (s, 1 H, CHO), 7.30–7.96 (m, 10 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9 (d, Me), 21.6 (d, Me), 66.7 (u, CS), 74.7 (d, CO), 128.00 (d, Ph), 128.03 (d, Ph), 129.0 (d, Ph), 130.5 (d, Ph), 128.3 (d, Ph), 134.2 (d, Ph), 134.9 (d, Ph), 137.9 (u, Ph) ppm. IR (KBr): $\tilde{\nu}$ = 3905 (w), 3547 (vs), 3087 (m), 3052 (m), 3029 (m), 3000 (m), 2969 (m), 2937 (m), 2196 (w), 1967 (w), 1914 (w), 1831 (w), 1601 (m), 1581 (m), 1494 (m), 1450 (s), 1386 (s), 1368 (m), 1338 (m), 1284 (vs), 1189 (s), 1148 (vs), 1122 (vs), 1074 (vs), 1048 (vs), 1027 (s), 1002 (s), 948 (m), 921 (s), 851 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 290 (7) [M$^+$], 184 (100), 149 (71), 132 (17), 79 (35), 77 (62), 57 (52). $C_{16}H_{18}O_3S$ (290.38): calcd. C 66.18, H 6.25; found C 65.85, H 6.26.

(±)-2-Ethyl-1-phenyl-2-(phenylsulfonyl)butan-1-ol (13b). From 3b and PhCHO in THF: Treatment of sulfone **8b** (750 mg, 3.53 mmol) with *n*BuLi (1.50 M in *n*-hexane, 2.60 mL, 3.90 mmol) and PhCHO (750 mg, 7.07 mmol) in THF as described in GP4 gave alcohol **13b** (921 mg, 82%) as colourless crystals.

From Putative 15Ab and PhCHO in THF: Treatment of sulfone **8b** (750 mg, 3.53 mmol) with *n*BuLi (1.50 M in *n*-hexane, 2.60 mL, 3.90 mmol), $ClTi(OiPr)_3$ (1.100 g, 4.22 mmol) and PhCHO (750 mg, 7.07 mmol) in THF as described in GP5 gave alcohol **13b** (899 mg, 80%) as colourless crystals.

From 9b and PhCHO in Ether in the Presence of MeI: To a solution of sulfone **8b** (750 mg, 3.53 mmol) in diethyl ether (20 mL) was added at –78 °C, *n*BuLi (1.50 M in *n*-hexane, 2.60 mL, 3.98 mmol). The yellow mixture was stirred for 15 min at room temperature, then cooled to –78 °C and treated dropwise with $ClTi(OiPr)_3$ (1.100 g, 4.22 mmol). The orange mixture was stirred for 3 h at room temperature, cooled to –78 °C and treated with MeI (424 μL, 6.70 mmol). After the mixture was stirred for 30 min at room temperature, it was cooled to –78 °C and treated with PhCHO (116 mg, 10.9 mmol). The mixture was then stirred for 1 d at room temperature, treated with 2 N aqueous HCl (25 mL) and extracted with diethyl ether (3 × 40 mL). Drying ($MgSO_4$) and concentration of the combined organic phases gave alcohol **13b** (1.023 g, 91%) as colourless crystals, m.p. 114 °C, R_f = 0.63 (EtOAc/*n*-hexane, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.62 (dd, *J* = 7.4 Hz, 3 H, CH_3CH_2), 1.16 (dd, *J* = 7.6 Hz, 3 H, CH_3CH_2), 1.53 (dq, *J* = 7.4, 14.8 Hz, 1 H, CH_3CH_2), 1.76 (dq, *J* = 7.4, 14.8 Hz, 1 H, CH_3CH_2), 2.00 (dq, *J* = 7.6, 15.4 Hz, 1 H, CH_3CH_2), 2.25 (dq, *J* = 7.6, 15.1 Hz, 1 H, CH_3CH_2), 4.23 (s, 1 H, OH), 4.97 (s, 1 H, CHO), 7.28–7.95 (m, 10 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.4 (d, CH_3CH_2), 9.4 (d, CH_3CH_2), 19.3 (u, CH_3CH_2), 23.9 (u, CH_3CH_2), 73.9 (u, CS), 76.1 (d, CO), 128.1 (d), 128.3 (d), 128.9 (d), 130.1 (d, Ph), 128.3 (d), 133.8 (d, Ph), 137.3 (u), 138.9 (u, Ph) ppm. IR (KBr): $\tilde{\nu}$ = 3493 (vs), 3070 (m), 3031 (w), 2991 (m), 2945 (m), 2923 (m), 2884 (m), 2183 (w), 1627 (m), 1583 (m), 1494 (m), 1451 (s), 1386 (m), 1344 (m), 1279 (vs), 1179 (m), 1150 (s), 1133 (s), 1110 (s), 1092 (m), 1073 (s), 1056 (s), 1027 (m), 999 (m), 974 (w), 925 (m), 816 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 318 (6) [M$^+$], 212 (96), 197 (100), 177 (58), 143 (52), 107 (40), 91 (40), 77 (62), 57 (91). $C_{18}H_{22}O_3S$ (318.43): calcd. C 67.89, H 6.96; found C 67.70, H 6.88.

(±)-2-Methyl-1-phenyl-2-(phenylsulfonyl)butan-1-ol (13c). From 3c and PhCHO: Treatment of sulfone **8c** (750 mg, 3.78 mmol) with *n*BuLi (1.50 M in *n*-hexane, 2.80 mL, 4.20 mmol) and PhCHO (800 mg, 7.53 mmol) in THF as described in GP4 gave a mixture of diastereomeric alcohols **13c** (990 mg, 86%) in a ratio of 1:1 as colourless crystals.

From Putative 15Ac and PhCHO: Treatment of sulfone **8c** (750 mg, 3.78 mmol) with *n*BuLi (1.50 M in *n*-hexane, 2.80 mL, 4.20 mmol), $ClTi(OiPr)_3$ (1.183 g, 4.54 mmol) and PhCHO (864 mg, 8.14 mmol) in THF as described in GP5 gave a mixture of diastereomeric alcohols **13c** (862 mg, 75%) as colourless crystals, m.p. 130 °C, R_f = 0.62 (EtOAc/*n*-hexane, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.52 (dd, *J* = 7.4 Hz, 3 H_A, CH_3CH_2), 0.98 (dd, *J* = 7.6 Hz, 3 H_B, CH_3CH_2), 1.05 (s, 3 H_A, Me), 1.35 (dq, *J* = 7.5, 15.1 Hz, 1 H_A, CH_3CH_2), 1.46 (s, 3 H_B, Me), 1.49 (dq, *J* = 7.5, 15.1 Hz, 1 H_A, CH_3CH_2), 1.95 (dq, *J* = 7.6, 15.4 Hz, 1 H_B, CH_3CH_2), 2.29 (dq, *J* = 7.6, 15.4 Hz, 1 H_B, CH_3CH_2), 4.27 (d, *J* = 1.4 Hz, 1 H_A, OH), 4.30 (d, *J* = 1.7 Hz, 1 H_B, OH), 4.97 (d, *J* = 1.7 Hz, 1 H_B, CHO), 5.12 (d, *J* = 1.4 Hz, 1 H_A, CHO), 7.30–7.96 (m, 10 H_A, 10 H_B, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.2 (d, CH_3CH_{2A}), 9.3 (d, CH_3CH_{2B}), 11.1 (d, Me_A), 18.6 (d, Me_B), 20.6 (u, CH_3CH_{2A}), 26.2 (u, CH_3CH_{2B}), 69.5 (u, CS_A), 70. 6 (u, CS_B), 74.9 (d, CO_A), 76.0 (d, CO_B), 127.9–138.6 (16 signals, Ph) ppm. IR (KBr): $\tilde{\nu}$ = 3461 (vs), 3064 (m), 3028 (m), 3001 (m), 2979 (m), 2943 (m), 2202 (w), 957 (w), 1892 (w), 1583 (w), 1494 (m), 1451 (vs), 1391 (m), 1346 (m), 1285 (vs), 1195 (m), 1151 (vs), 1132 (vs), 1074 (vs), 1060 (vs), 1041 (s), 1026 (s), 907 (w), 859 (w), 809 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 304 (16) [M$^+$], 198 (100), 183 (92), 163 (76), 105 (43), 143 (48) (33), 79, 77 (81), 57 (39). $C_{17}H_{20}O_3S$ (304.40): calcd. C 67.08, H 6.62; found C 66.84, H 6.53.

(±)-2-(*tert*-Butylsulfonyl)-2-methyl-1-phenylpropan-1-ol (13f). From 3f and PhCHO: Treatment of sulfone **8f** (750 mg, 4.57 mmol) with *n*BuLi (1.50 M in *n*-hexane, 3.40 mL, 5.10 mmol) and PhCHO (970 mg, 9.14 mmol) in THF as described in GP4 gave alcohol **13f** (1.087 g, 88%) as colourless crystals.

From Putative 15Af and PhCHO in THF: Treatment of sulfone **8f** (750 mg, 4.57 mmol) with *n*BuLi (1.50 M in *n*-hexane, 3.40 mL, 5.10 mmol), $ClTi(OiPr)_3$ (1.430 g, 5.48 mmol) and PhCHO (970 mg, 9.13 mmol) in THF as described in GP5 gave alcohol **13f** (865 mg, 70%) as colourless crystals, m.p. 112–114 °C; R_f = 0.58 (EtOAc/*n*-hexane, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.18 (s, 3 H, Me), 1.54 (s, 3 H, Me), 1.60 (s, 9 H, *t*Bu), 4.2–4.4 (br. s, 1 H, OH), 5.41 (s, 1 H, CHO), 7.28–7.40 (m, 5 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.3 (d, Me), 22.9 (d, Me), 26.0 (d, *t*Bu), 67.3 (u, *t*Bu), 72.6 (u, CS), 75.7 (d, CO), 128.0 (d, Ph), 128.2 (d, Ph), 128.3 (d, Ph), 138.0 (u, Ph) ppm. IR (KBr): $\tilde{\nu}$ = 3415 (vs), 3086 (w), 3060 (m), 3032 (m), 2997 (m), 2937 (m), 2882 (m), 2161 (w), 1957 (w), 1889 (w), 1719 (w), 1602 (m), 1489 (s), 1470 (m), 1452 (s), 1397 (m), 1377 (m), 1365 (s), 1296 (s), 1259 (vs), 1190 (s), 1146 (m), 1131 (s), 1080 (vs), 1062 (vs), 1028 (m), 1004 (s), 962 (m), 946 (m), 919 (w), 854 (m), 801 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 270 (15) [M$^+$], 164 (40), 149 (100), 132 (30), 108 (60), 91 (48), 79 (27), 57 (98). $C_{14}H_{22}O_3S$ (270.39): calcd. C 62.19, H 8.20; found C 62.10, H 8.20.

(±)-2-(*tert*-Butylsulfonyl)-2-ethyl-1-phenylbutan-1-ol (13g). From 3g and PhCHO: Treatment of sulfone **8g** (750 mg, 3.90 mmol) with *n*BuLi (1.50 M in *n*-hexane, 2.90 mL, 4.35 mmol) and PhCHO (830 mg, 7.82 mmol) in THF as described in GP4 gave alcohol **13g** (1.013 g, 87%) as colourless crystals.

From Putative 15Ag and PhCHO in THF: Treatment of sulfone **8g** (750 mg, 3.90 mmol) with *n*BuLi (1.50 M in *n*-hexane, 2.90 mL, 4.35 mmol), $ClTi(OiPr)_3$ (1.220 g, 4.68 mmol) and PhCHO (830 mg, 7.82 mmol) in THF as described in GP5 gave alcohol **13g** (698 g, 60%) as colourless crystals, m.p. 117–118 °C; R_f = 0.62 (EtOAc/*n*-hexane, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.52 (dd, *J* = 7.4 Hz, 3 H, CH_3CH_2), 1.15 (dd, *J* = 7.4 Hz, 3 H, CH_3CH_2), 1.61 (s, 9 H, *t*Bu), 1.74 (dq, *J* = 7.4, 14.8 Hz, 1 H, CH_3CH_2), 2.01 (dq, *J* = 7.5, 15.1 Hz, 1 H, CH_3CH_2), 2.14 (dq, *J* = 7.5, 14.8 Hz, 1

H, CH_3CH_2), 2.31 (dq, J = 7.6, 15.4 Hz, 1 H, CH_3CH_2), 4.41 (s, 1 H, OH), 5.33 (s, 1 H, CHO), 7.33 (m, 2 H, Ph), 7.35 (m, 1 H, Ph), 7.43 (m, 2 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.8 (d, CH_3CH_2), 9.9 (d, CH_3CH_2), 20.4 (u, CH_3CH_2), 24.9 (u, CH_3CH_2), 26.1 (d, *t*Bu), 69.1 (u, CS), 76.5 (d, CO), 81.2 (u, *t*Bu), 128.2 (d, Ph), 128.4 (d, Ph), 128.4 (d, Ph), 139.2 (u, Ph) ppm. IR (KBr): $\tilde{\nu}$ = 3475 (vs), 2980 (s), 2946 (m), 2373 (w), 2345 (w), 2150 (w), 1655 (m), 1498 (m), 1482 (m), 1459 (s), 1408 (m), 1385 (m), 1372 (m), 1363 (m), 1338 (m), 1322 (m), 1267 (vs), 1243 (s), 1201 (s), 1175 (m), 1156 (m), 1117 (m), 1092 (s), 1077 (vs), 1046 (m), 1016 (m), 982 (w), 966 (w), 931 (m), 879 (w), 813 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 298 (6) [M$^+$], 192 (28), 177 (100), 136 (44), 119 (54), 107 (40), 91 (40), 77 (17), 57 (62). $C_{16}H_{26}O_3S$ (298.44): calcd. C 64.39, H 8.78; found C 64.26, H 8.85.

Reaction of Lithium α-Sulfonyl Carbanion 3f with Benzaldehyde and Acetophenone: (±)-2-(*tert*-Butylsulfonyl)-2-methyl-1-phenylpropan-1-ol (13f) and (±)-3-(*tert*-Butylsulfonyl)-3-methyl-2-phenylbutan-2-ol (14): To a solution of sulfone **8f** (820 mg, 5.00 mmol) in diethyl ether (20 mL) was added at –78 °C, *n*BuLi (1.38 M in *n*-hexane, 3.99 mL, 5.50 mmol). The solution of **3f** was stirred for 15 min at room temperature, cooled to –78 °C then added by using a cannula to a solution of PhCHO (530 mg, 5.00 mmol) and PhCOMe (600 mg, 5.00 mmol) in diethyl ether (20 mL) at –78 °C. After the mixture was warmed to room temperature within 4 h, it was stirred for 12 h. Then 2 N aqueous HCl was added and the mixture was extracted with diethyl ether (4× 25 mL). GC–MS analysis [R_t = 3.55 (PhCHO), 6.11 (PhCOMe), 13.49 (**13f**), 17.78 (**14**) min] revealed the formation of **13f** and **14** in a ratio of 55:45.

Treatment of Bis(1-sulfonylalkyl)titanium 9f with Benzaldehyde and Acetophenone: (±)-2-(*tert*-Butylsulfonyl)-2-methyl-1-phenylpropan-1-ol (13f): To a solution of sulfone **8f** (820 mg, 5.00 mmol) in diethyl ether (20 mL) was added at –78 °C, *n*BuLi (1.38 M in *n*-hexane, 3.99 mL, 5.50 mmol). The solution of **3f** was then stirred for 15 min at room temperature, cooled to –78 °C and $ClTi(OiPr)_3$ (1.560 g, 5.99 mmol) was added. The mixture was stirred at room temperature for 3 h then cooled to –78 °C and added by using a cannula to a solution of PhCHO (530 mg, 5.00 mmol) and PhCOMe (600 mg, 5.00 mmol) in diethyl ether (20 mL) at –78 °C. The mixture was warmed to room temperature over 4 h, stirred for 12 h, then 2 N aqueous HCl was added and the mixture was extracted with diethyl ether (4× 25 mL). GC analysis [R_t = 13.49 (**13f**) min] only showed the formation of **13f**.

Treatment of the Putative Titanium Derivative 15Af with Benzaldehyde and Acetophenone: (±)-2-(*tert*-Butylsulfonyl)-2-methyl-1-phenylpropan-1-ol (13f): To a solution of sulfone **8f** (820 mg, 5.00 mmol) in THF (20 mL) was added at –78 °C, *n*BuLi (1.38 M in *n*-hexane, 3.99 mL, 5.50 mmol). The solution of **3f** was then stirred for 15 min at room temperature, cooled to –78 °C and $ClTi(OiPr)_3$ (1.560 g, 5.99 mmol) was added. The mixture was stirred at room temperature for 3 h then cooled to –78 °C and added by using a cannula to a solution of PhCHO (530 mg, 5.00 mmol) and PhCOMe (600 mg, 5.00 mmol) in diethyl ether (20 mL) at –78 °C. The mixture was warmed to room temperature over 4 h, stirred for 12 h, then 2 N aqueous HCl was added and the mixture was extracted with diethyl ether (4× 25 mL). GC analysis [R_t = 13.49 (**13f**) min] only revealed the formation of **13f**.

Supporting Information (see footnote on the first page of this article): Analytical and spectroscopic data of sulfones **8a**–**h** and copies of the ^{1}H and ^{13}C NMR spectra of **6a**–**c**, **7a**–**c**, **8a**–**h**, **12a**–**h**, **13a**–**c**, **13f** and **13g**.

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