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Lithiated γ-*O*-functionalized propyl phenyl sulfides and sulfones of the type Li[CH(SO_xPh)CH_2CH_2OR] (x = 0, 2). [Li{CH(SPh)CH_2CH_2O*t*-Bu}(tmeda)] – A structurally characterized organolithium inner complex

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Dedicated to Professor Ingo-Peter Lorenz on the occasion of his 65th Birthday.

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ABSTRACT

Lithiation of *O*-functionalized alkyl phenyl sulfides PhSCH$_2$CH$_2$CH$_2$OR (R = Me, **1a**; *i*-Pr, **1b**; *t*-Bu, **1c**; CPh$_3$, **1d**) with *n*-BuLi/tmeda in *n*-pentane resulted in the formation of α- and *ortho*-lithiated compounds [Li{CH(SPh)CH_2CH_2OR}(tmeda)] (α-**2a**–**d**) and [Li{*o*-C_6H_4S$CH_2CH_2CH_2$OR)(tmeda)] (*o*-**2a**–**d**), respectively, which has been proved by subsequent reaction with *n*-Bu$_3$SnCl yielding the requisite stannylated γ-OR-functionalized propyl phenyl sulfides *n*-Bu$_3$SnCH(SPh)CH_2CH_2OR (α-**3a**–**d**) and *n*-Bu$_3$Sn(*o*-C_6H_4S$CH_2CH_2CH_2$OR) (*o*-**3a**–**d**). The α/*ortho* ratios were found to be dependent on the sterical demand of the substituent R. Stannylated alkyl phenyl sulfides α-**3a**–**c** were found to react with *n*-BuLi/tmeda and *n*-BuLi yielding the pure α-lithiated compounds α-**2a**–**c** and [Li{CH(SPh)CH_2CH_2OR}] (α-**4a**–**b**), respectively, as white to yellowish powders. Single-crystal X-ray diffraction analysis of [Li{CH(SPh)CH_2-CH_2O*t*-Bu}(tmeda)] (α-**2c**) exhibited a distorted tetrahedral coordination of lithium having a chelating tmeda ligand and a *C*,*O* coordinated organyl ligand. Thus, α-**2c** is a typical organolithium inner complex.

Lithiation of *O*-functionalized alkyl phenyl sulfones PhSO$_2$CH$_2$CH$_2$CH$_2$OR (R = Me, **5a**; *i*-Pr, **5b**; CPh$_3$, **5c**) with *n*-BuLi resulted in the exclusive formation of the α-lithiated products Li[CH(SO_2Ph)CH_2CH_2OR] (**6a**–**c**) that were found to react with *n*-Bu$_3$SnCl yielding the requisite α-stannylated compounds *n*-Bu$_3$SnCH(-SO_2Ph)CH_2CH_2OR (**7a**–**c**). The identities of all lithium and tin compounds have been unambiguously proved by NMR spectroscopy (^{1}H, ^{13}C, ^{119}Sn).

1. Introduction

Since the reports of Köbrich on the carbenoid properties of halogenmethyl lithium compounds ("Köbrich's carbenoids") [1], heteroatom-functionalized methyllithium compounds have been in the focus of many investigations [2,3]. Compounds of the types Li-CH_2YR_n (**I**) and Li$CH_2YO_xR_n$ (**II**) having Lewis-basic (YR_n = OR, SR, NR_2, PR_2, etc.; R = alkyl, aryl) and dipole stabilized [4] (YO_xR_n = POR_2; SOR, SO_2R, etc; R = alkyl, aryl) functionalizations, respectively, are of special interest. In the case of Köbrich's thermally highly unstable compounds, an intramolecular interaction between the halo substituents and lithium atoms play a crucial role for the carbenoid properties [5]. On the other hand, also intermolecular interactions between the Lewis-basic heteroatom with the lithium center may have a severe influence on the stability and reactivity of these compounds. Thus, in contrast to the dinuclear *S*-functionalized compounds [{LiCHR′SR}$_2$] (**Ia**; R = alkyl, aryl; R′ = H, alkyl, aryl) [6,7] only the monomeric derivative [Li(CH_2SPh)(pmdta)] (pmdta = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine) exhibited at elevated temperature a carbenoid reactivity [8]. Thus, the degree of aggregation seems to be decisive for the reactivity. In the case of the sulfonylmethyl lithium compounds [Li(CH_2SO_2R)L$_x$] (**IIa**, L = neutral *N* or *O* donor) the manner of the Li coordination (α-C vs. O) was found to be essential for their structures and reactivities [9–11].

Lithiation reactions of alkyl phenyl sulfides resulting in type **Ia** compounds (R′ = alkyl, R = Ph) were found to proceed with different regioselectivities (α- vs. *ortho*-lithiation) depending on R′ [12]. The introduction of a donor function in R′ in a position favorably for intramolecular coordination may give rise to the formation of organometallic inner complex formation. Thus, γ-NR_2-functionalized propyl phenyl sulfides PhSCH$_2$CH$_2$CH$_2$NR$_2$ were found to favor the α-lithiation yielding such inner complexes [13,14]. Here, we report on the regioselectivities in lithiation reactions of γ-OR-functionalized propyl phenyl sulfides PhSCH$_2$CH$_2$CH$_2$OR (**1a**–**d**) and on tin–lithium transmetallation reactions yielding sulfur-functionalized organolithium compounds of the type LiCH(SPh)CH_2-CH_2OR. Structural investigations gave proof that the *tert*-butoxy derivative (R = *t*-Bu, α-**1a**) is an organometallic inner complex in the solid state. Furthermore, we report on lithiation reactions of the requisite sulfone derivatives resulting in lithium compounds of the type Li[CH(SO_2Ph)CH_2CH_2OR] (**6a**–**c**).

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2. Results and discussion

2.1. Lithiation of $PhSCH_2CH_2CH_2OR$

The γ-OR-functionalized propyl phenyl sulfides, $PhS-CH_2-CH_2-CH_2OR$ (R = Me, **1a**; *i*-Pr, **1b**; *t*-Bu, **1c**; CPh_3, **1d**) have been obtained by conventional methods from $PhSCH_2CH_2CH_2Br$ and $PhSCH_2CH_2CH_2OH$, respectively (see Section 3). Compounds **1a–d** were found to react with *n*-BuLi/tmeda in *n*-pentane yielding the α- and *ortho*-lithiated compounds **2a–d** as revealed by the subsequent reaction with *n*-Bu_3SnCl yielding the requisite stannylated γ-OR-functionalized propyl phenyl sulfides **3a–d** (Scheme 1).

Both, lithiation and stannylation proceeded at room temperature with a high degree of conversion (>85%). The α/*ortho* ratios were found to be time dependent showing that the *ortho* derivatives are the kinetically controlled products whereas the α derivatives are under thermodynamic control (Table 1), as it has already been shown in lithiation reactions of PhSMe [15]. In accordance with that ^{13}C NMR spectroscopic investigations of the reaction mixture **1c**/*n*-BuLi/tmeda in deuterated benzene revealed after about 15 min a high portion of the *ortho*-lithiated product *o*-**3c** which was decreased in the course of reaction with concomitant increase of the portion of the α-lithiated product α-**3c**. Analogous results could be obtained in the lithiation reaction of **1b**.

The quantitative evaluation of the α/*ortho* ratios of the air-stable stannylated compounds α-**3**/*o*-**3** revealed a strong dependency on the sterical demand of the γ-OR substituent, see Table 1 (column 4): With the increasing bulkiness of the "parent" primary (Me), secondary (*i*-Pr) and tertiary (*t*-Bu) alkyl groups R, the portion of the α-product decreases from 100% to 66%. In accordance with that the sterically highly demanding CPh_3 derivative gave 42% *ortho* product. The α/*ortho* ratios (values taken from Ref. [14]) for the secondary and sterically highly demanding menthyl (Men) and borneyl (Bor) derivatives lie – as expected – between the sterically less demanding secondary isopropoxy (**3b**) and the tertiary *tert*-butoxy (**3c**) derivatives.

Fractional distillation under vacuum of the stannylated sulfides **3a–c** (α/*ortho* mixtures) resulted in the pure α-stannylated products α-**3a–c** that were obtained as colorless to pale yellow oils in (isolated) yields between 49% and 81%, whereas the distillation of α-**3d** failed due to its high boiling point. The identities of α-**3a–c** have been confirmed by microanalysis, ^1H, ^{13}C and ^{119}Sn NMR spectroscopy (Table 2). In tetraorgano tin compounds of the type *n*-$Bu_3Sn–R'$ the $^1J(^{119}Sn,^{13}C_{Bu})$ coupling constants reflect the electronic influence of the substituents R′ such that the higher the magnitude of the $^1J(^{119}Sn,^{13}C_{Bu})$ coupling constant the lower the electronic influence of R′ [16,17]. Inspection of Table 2 reveals that the electronic influence of the groups $R' = CH(SPh)CH_2CH_2OR$ is not significantly dependent on the substituent R (α-**3a–c**: 325.6–328.7 Hz). Furthermore, the electronic influence proved to be roughly the same as that of other α-S-functionalized groups such as $R' = CH_2SPh$ (321.2 Hz [18]) and R′ = CH(Me)SPh (323.0 Hz [12]) but smaller than that of R′ = CMe(Ph)SPh (310.9 Hz [14]). All these values are in-between those of the methyl (R′ = Me, 330.1 Hz [17]) and the ethyl group (R′ = Et, 319.0 Hz [19]).

Table 1
Degree of conversion (in %) and α/*ortho* ratios (given in parentheses) for the lithiation and subsequent stannylation of *O*-functionalized sulfides (**1a–d**) according to Scheme 1. For comparison (taken from Ref. [14]) the requisite values for the menthyl (Men) and borneyl (Bor) derivatives are also given.

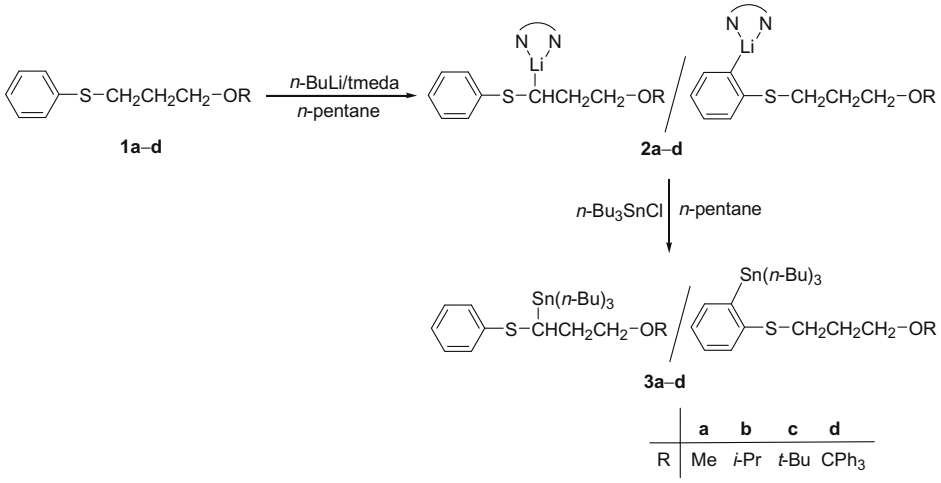
	R	$t = 1$[a]	$t = 24$[a]	$t = 72$[a]
3a	Me	72 (95:5)	92 (100:0)	94 (100:0)
3b	*i*-Pr	65 (65:35)	91 (81:19)	93 (92:8)
3c	*t*-Bu	76 (52:48)	86 (66:34)	91 (79:21)
3d	CPh_3		85 (58:42)	
	Men		90 (73:27)	
	Bor		90 (68:32)	

[a] t is the reaction time in h.

2.2. Tin–lithium transmetallion of $n\text{-}Bu_3SnCH(SPh)CH_2CH_2OR$

The α-stannylated sulfides α-**3a–c** were found to react smoothly in hydrocarbons (*n*-pentane) with *n*-BuLi/tmeda in a tin–lithium transmetallation reaction yielding the pure α-lithiated sulfides α-**2a–c** (Scheme 2). The organolithium compounds α-**2a–c** could be isolated as colorless to yellowish powders in (isolated) yields between 51% and 89%. In contrast to this, metallation of the sulfides **1b**/**c** with *n*-BuLi/tmeda according to Scheme 1 gave only mixtures of α- and *ortho*-lithiated products; experiments to isolate these lithium compounds resulted in the formation of oily products only. Although the requisite lithiation reaction starting from **1a** led to the exclusive formation of the α-product, the tin–lithium transmetallation reaction proved to be superior because a pure solid compound could be isolated.

The lithiated compounds α-**2a–c** were not only highly moisture sensitive but even pyrophoric. They were well soluble in THF. These solutions were found to be stable at −40 °C whereas at room temperature decomposition was observed within 1 day. Furthermore, there was found an increasing solubility (R = Me < *i*-Pr < *t*-



Scheme 1. Synthesis of lithiated (**2a–d**) and stannylated γ-OR functionalized sulfides (**3a–d**).

Table 2
Selected NMR spectroscopic data (δ in ppm, J in Hz) of α-stannylated sulfides *n*-$Bu_3SnCH(SPh)CH_2CH_2OR$ (α-**3a**–**c**).

	R	$\delta_{\alpha\text{-C}}$ ($^1J_{Sn,C}$)	$\delta_{\alpha\text{-C (Bu)}}$ ($^1J_{Sn,C}$)	$\delta(^{119}Sn)$
α-**3a**	Me	25.1 (250.8)	10.2 (328.7)	−10.7
α-**3b**	*i*-Pr	24.9 (249.2)	10.0 (325.9)	−9.7
α-**3c**	*t*-Bu	24.9 (247.5)	10.0 (325.6)	−9.5

Bu) in benzene and these solutions were stable for a longer period even at room temperature. When the tin–lithium transmetallations were performed in absence of tmeda (α-**3a**/**b** + *n*-BuLi), the lithiated products α-**4a**/**b** were also found to be solids. In contrast to the tmeda adducts, they were only soluble in coordinating solvents such as THF whereas these solutions were also not stable at room temperature. All these findings indicate that the tmeda-free products are of higher aggregation in the solid state. In contrast to that – at least the tmeda adduct α-**2c** – proved to be monomeric in the solid state (vide infra).

The identities of the lithiated compounds α-**2a**–**c** were confirmed by ^1H and ^{13}C NMR spectroscopy and in the case of *tert*-butoxy derivative (α-**2c**) also by single-crystal X-ray diffraction analysis. In that case also the inspection of the $^1J(\alpha\text{-}^{13}C,^1H)$ coupling constant revealed a decrease upon lithiation by 10 Hz (130 Hz in α-**2c** vs. 140 Hz in **1c**) being in accordance with an α-C–Li bond also in THF solution as expected [20]. Due to the high quadrupole moment of the most abundant lithium isotope ^7Li (I = 3/2, 92.6% abundance) the signals of the β- and γ-protons of the alkyl chains in α-**2a**–**c** appeared broad whereas, surprisingly, the α-proton signals remained to be sharp. The α-protons were found strongly highfield shifted (0.88–0.92 ppm) compared to the sulfides **1a**–**c** (2.99–3.00 ppm). The signals of all other protons also remained to be sharp and showed smaller shifts (up to 0.4 ppm) upon lithiation. In the ^{13}C NMR spectra the signals for the α-C atoms (15.5–15.8 ppm in α-**2a**–**c** vs. 30.4–30.5 ppm in **1a**–**c**) and for the *i*-C atoms of the phenyl substituents (152.1–152.4 ppm in α-**2a**–**c** vs. 136.6–136.8 ppm in **1a**–**c**) showed the most significant shifts.

Furthermore, the synthesis of lithiated sulfides via tin–lithium transmetallation opened up an alternative way to proof that *ortho*- and α-lithiation of the sulfides (see Table 1) are under kinetic and thermodynamic control, respectively. Thus, an *ortho*-stannylated enriched mixture of the methoxy functionalized derivatives *o*-**3a** and α-**3a** (80:20) was prepared by metallation of **1a** quenched with *n*-Bu_3SnCl after 30 min and subsequent chromatographic work-up (Scheme 3). The following transmetallation with *n*-BuLi/tmeda and the repeated reaction with *n*-Bu_3SnCl after 12 h led to the exclusive formation of the α-stannylated product α-**3a**.

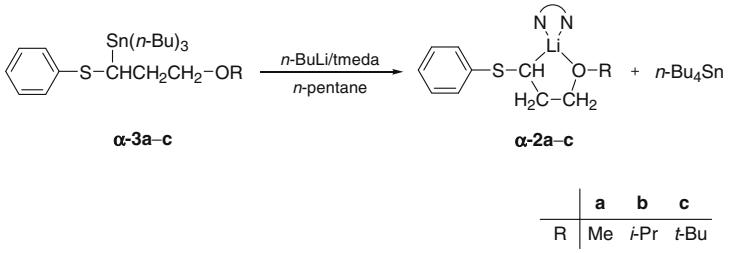
2.3. Molecular structure of [Li{CH(SPh)CH_2CH_2Ot-Bu}(tmeda)]

Crystals of [Li{CH(SPh)CH_2CH_2O*t*-Bu}(tmeda)] (α-**2c**) suitable for X-ray diffraction analysis were obtained from *n*-pentane at −10 °C. The compound crystallized in isolated monomeric molecules without unusual intermolecular interactions (shortest distance between non-hydrogen atoms: 3.492(7) Å, C2···C16′). The molecular structure is shown in Fig. 1, selected geometrical parameters are given in Table 3. The primary donor set of Li is built up by two N atoms of the tmeda ligand as well as by the α-C and the O atom of the organo ligand. Thus, α-**2c** is a typical organolithium inner complex having a distorted tetrahedral coordination of Li. The chelate bindings of the tmeda and the organo ligand give rise to relatively small angles N1–Li–N2 (87.2(3)°) and C7–Li–O (88.0(3)°) with concomitant enlargement of the angles N2–Li–O (131.6(4)°) and N2–Li–C7 (122.3(4)°). Both of the five-membered rings (C_2N_2Li) and (C_3LiO) exhibit an envelope conformation twisted on C17 and C9, respectively. The Li–C7 bond length (2.151(9) Å) is in the expected range [21]. The Li–O bond (1.984(7) Å) was also found to be in the expected range as the comparison with Li–O bonds in other complexes of tetrahedral coordinated lithium showed (median: 1.968 Å, lower/higher quartile: 1.938/2.004 Å; n = 131, n – number of observations [21]). The Li···S distance of 3.337(1) Å indicates that there are no interactions between these two atoms.

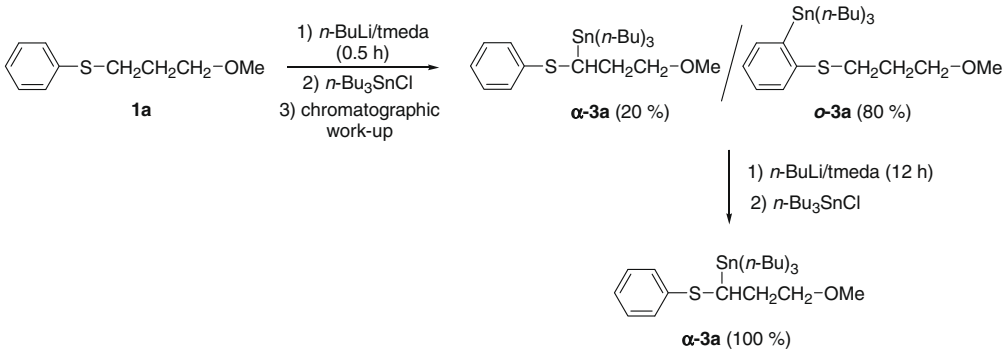
2.4. Lithiation of $PhSO_2CH_2CH_2CH_2OR$

The γ-OR-functionalized propyl phenyl sulfones, $PhSO_2CH_2CH_2CH_2OR$ (R = Me, **5a**; *i*-Pr, **5b**), have been obtained by oxidation of the respective sulfides $PhSCH_2CH_2CH_2OR$ **1a**, **b** with acetic acid/hydrogen peroxide whereas **5c** (R = CPh_3) was received by reaction of $PhSO_2CH_2CH_2CH_2OH$ with Ph_3CCl in presence of DBU (see Section 3). Compounds **5a**–**c** were found to react with *n*-BuLi in *n*-pentane (**5a**/**b**) or in toluene (**5c**) at room temperature yielding the α-lithiated compounds **6a**–**c** (Scheme 4). In contrast to the sulfides (**1a**–**c**) only α-lithiation and no *ortho*-metallation was observed which is due to the higher acidity of the α-protons in sulfones. For this reason, the metallation could also be performed with *n*-BuLi in absence of an *N*-donor co-ligand.

The lithiated sulfones **6a**–**c** were isolated in high yields as white to pale yellow powders. They proved to be moisture and air sensitive but less reactive than the analogous lithiated sulfides α-**2a**–**c**. All lithiated sulfones were unsoluble in non-coordinating solvents like *n*-pentane or toluene. They showed a decreasing solubility in THF and DMSO (R = Me > *i*-Pr > CPh_3). While the THF solutions could be handled at room temperature without decomposition, in the case of the DMSO solutions a color change from yellow to black within few hours gave proof of a decomposition at room temperature. The identities of the lithiated compounds **6a**–**c** have been confirmed by ^1H and ^{13}C NMR spectroscopy. In the case of the methoxy functionalized lithiated sulfone **6a** an increase of the $^1J(\alpha\text{-}^{13}C,^1H)$ coupling constant by 10 Hz (147 Hz in **6a** vs. 137 Hz in **5a**) indicates that the lithium atom is not coordinated to the α-C atom [20a,22] but to the O atoms of the sulfonyl group as usually found in lithiated sulfones [9,23–25]. A comparison of the ^1H NMR spectra of the lithiated sulfones **6a**–**c** to the requisite



Scheme 2. Synthesis of α-lithiated γ-OR functionalized sulfides (α-**2a**–**c**) by tin–lithium transmetallation.



Scheme 3. To the *ortho*/α isomerization of the lithiated γ-OMe functionalized sulfide *o*-**3a**.

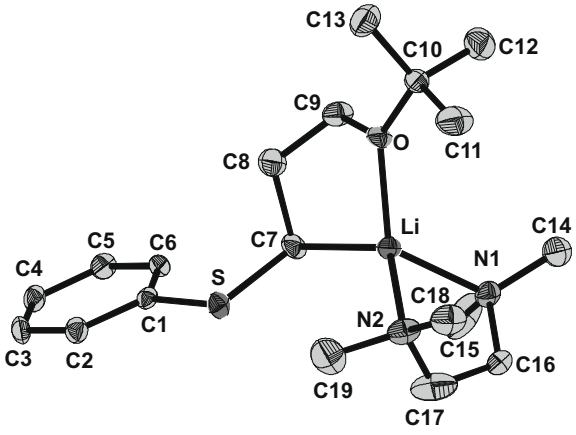


Fig. 1. Molecular structure of [Li{CH(SPh)CH_2CH_2O*t*-Bu}(tmeda)] in crystals of α-**2c**. The ellipsoides are shown with a probability of 50%. H atoms have been omitted for clarity.

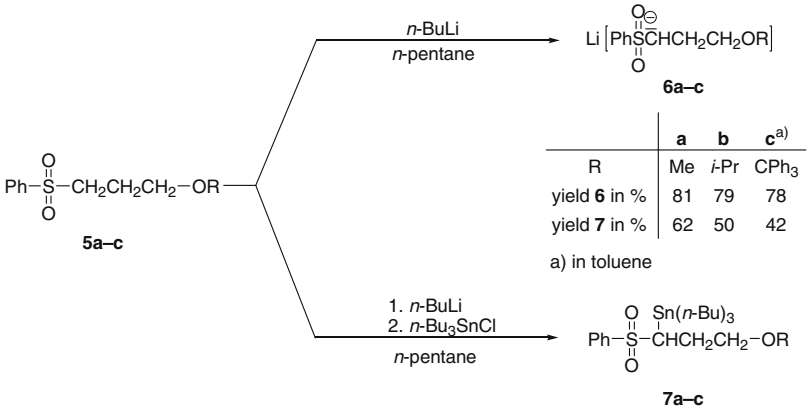
Table 3
Selected bond lengths (in Å) and angles (in °) of [Li{CH(SPh)CH_2CH_2O*t*-Bu}(tmeda)] (α-**2c**).

Li–C7	2.151 (9)	C7–Li–C8	99.5 (4)
Li–O	1.984 (7)	N1–Li–N2	87.2 (3)
Li–N1	2.191 (8)	N1–Li–O	118.6 (4)
Li–N2	2.111 (9)	N2–Li–O	131.6 (4)
C7–S	1.737 (5)	O–Li–C9	105.9 (3)
C7–C8	1.548 (6)	O–Li–C7	88.0 (3)
C8–C9	1.465 (7)	N1–Li–C7	110.6 (4)
C9–O	1.430 (6)	N2–Li–C7	122.3 (4)

sulfones **5a**–**c** revealed that the most significant highfield shifts were found for the α-protons (1.70–1.75 ppm in **6a**–**c** vs. 3.12–3.22 ppm in **5a**–**c**) while all other signals showed smaller differences. In the ^{13}C NMR spectra the most distinct shifts were observed for the signals of the α-C (42.2–45.2 ppm in **6a**–**c** vs. 53.6–53.9 ppm in **5a**–**c**) and *i*-C atoms (152.4–155.8 ppm in **6a**–**c** vs. 139.1–139.2 ppm in **5a**–**c**).

The synthesis of the γ-OR-functionalized stannylated sulfones **7a**–**c** was done by lithiation of the sulfones **5a**–**c** as described above followed by addition of *n*-Bu_3SnCl (Scheme 4). Chromatographic work-up of the reactions mixtures gave the pure α-stannylated products **7a**–**c** as colorless to pale yellow oils with (isolated) yields of 42–62%. Their identities have been confirmed by microanalysis and ^1H, ^{13}C and ^{119}Sn NMR spectroscopy (Table 4). The $^1J(^{119}Sn,^{13}C_{Bu})$ coupling constants (337.0–338.9 Hz) were found to be in a very narrow range being in accordance with the requisite couplings in other *n*-$Bu_3SnCH(SO_2Ph)CH_2CH_2OR$ derivatives (R = Men, 336.4 Hz [26]; Bor, 336.9 Hz [14]). As comparison to the structurally similar – but non-OR-functionalized – ligand $CH(Me)SO_2Ph$ (329.2 Hz [27]) and $CH(Bn)SO_2Ph$ (336.9 Hz [27]) revealed, the γ-OR substituent does not significantly affect the electronic influence. On the other hand, the substitution pattern of the α-C atom influences the electronic properties of α-sulfonyl ligands: the $^1J(^{119}Sn,^{13}C_{Bu})$ coupling constants of the compounds having secondary α-C atoms (329.2–338.9 Hz) lie in-between of those having tertiary (*n*-$Bu_3SnCMe(Et)SO_2Ph$, 325.6 Hz [25]) and primary (*n*-$Bu_3SnCH_2SO_2Ph$, 346.1 Hz [28]) α-C atoms, respectively.

In summary, the investigations gave proof that in lithiation reactions of alkyl phenyl sulfides bearing a Lewis-basic substituent in chelating favored position (γ-OR group) the regioselectivity (α/*ortho* ratio) can be understood in terms of an inner complex



	a	b	c[a]
R	Me	*i*-Pr	CPh_3
yield **6** in %	81	79	78
yield **7** in %	62	50	42

a) in toluene

Scheme 4. Lithiation and stannylation of *O*-functionalized sulfones.

Table 4
Selected NMR spectroscopic data (δ in ppm, J in Hz) of stannylated sulfones **7a**–**c**.

		$\delta_{\alpha\text{-C}}$ ($^1J_{Sn,C}$)	$\delta_{\alpha\text{-C (Bu)}}$ ($^1J_{Sn,C}$)	δ (^{119}Sn)
7a	Me	50.9 (129.3)	11.9 (338.9)	2.6
7b	*i*-Pr	50.9 (134.5)	11.7 (337.6)	3.7
7c	CPh_3	51.0 (126.4)	11.5 (337.0)	2.7

formation that depends on the sterical demand and the electronic properties of the alkoxy substitution. This inner complex formation gives rise to a stabilization of the α-lithiated derivatives over the *ortho*-lithiated ones. Thus, the formation of a proper substrate–alkyllithium complex en route to lithiation seems to be decisive both for *ortho*- and α-lithiation as known for other heteroatom substituted hydrocarbons [29]. In the requisite sulfones exclusively α-lithiated products were obtained due to the higher acidity of the α-protons.

3. Experimental section

3.1. General comments

Organolithium compounds were prepared and handled under purified argon using standard Schlenk techniques. *n*-Pentane, *n*-hexane, diethyl ether, THF, benzene, toluene, toluene-d_8, benzene-d_6 and THF-d_8 were distilled from sodium benzophenone ketyl. DMSO-d_6 was dried over molecular sieve 4A. NMR spectra were recorded on Varian Gemini 200, Gemini 2000, and Varian 500 spectrometers using the protio impurities and the ^{13}C resonances of the deuterated solvents as references for ^{1}H and ^{13}C NMR spectroscopy, respectively. $\delta(^{119}Sn)$ is relative to external $SnMe_4$ in C_6D_6. The preparative centrifugally accelerated thin layer chromatography was made by using a Chromatotron (Harrison Research). Reactions of $BrCH_2CH_2CH_2X$ (X = OH, Br) with KSPh in MeOH afforded $PhSCH_2CH_2CH_2X$.

3.2. Preparation of $PhSCH_2CH_2CH_2OR$ (**1a**–**d**)

R = Me (**1a**), *i*-Pr (**1b**). To the respective alcohol ROH (200 ml) sodium hydride (7.9 g, 0.28 mol) was added slowly. When no further H_2 was liberated, $PhSCH_2CH_2CH_2Br$ (57.8 g, 0.25 mol) was added and the reaction mixture was refluxed for 6 h and stirred at room temperature overnight. The reaction mixture was diluted with water (200 ml), extracted with diethyl ether (3 × 80 ml) and the combined organic extracts were dried (Na_2SO_4). After filtration and evaporation of the solvent under reduced pressure the residue was distilled in vacuo.

R = Me (**1a**). Yield: 37.3 g (82%). Bp: 115–118 °C (4 Torr). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.88 (m, 2H, $CH_2CH_2CH_2$), 2.99 (m, 2H, CH_2SPh), 3.30 (s, 3H, OCH_3), 3.46 (m, 2H, CH_2OMe), 7.13–7.17 (m, 1H, *p*-H, SPh), 7.24–7.28 (m, 2H, *m*-*H*, SPh), 7.31–7.34 (m, 2H, *o*-*H*, SPh). ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.5 (s, $CH_2CH_2CH_2$), 30.5 (s, CH_2SPh), 58.7 (s, OCH_3), 71.0 (s, CH_2OMe), 125.8 (s, *p*-*C*, SPh), 128.8 (s, *m*-*C*, SPh), 129.1 (s, *o*-*C*, SPh), 136.6 (s, *i*-*C*, SPh).

R = *i*-Pr (**1b**). Yield: 32.1 g (62%). Bp: 124 °C (5 Torr). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.13 (d, ^3J(H,H) = 6.23 Hz, 6H, CH_3), 1.86 (m, 2H, $CH_2CH_2CH_2$), 3.00 (m, 2H, CH_2SPh), 3.30–3.76 (m, 3H, $OCH\text{-}Me_2$ + CH_2O*i*-Pr), 7.12–7.16 (m, 1H, *p*-*H*, SPh), 7.22–7.29 (m, 2H, *m*-*H*, SPh), 7.30–7.35 (m, 2H, *o*-H, SPh). ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.1 (s, CH_3), 29.7 (s, $CH_2CH_2CH_2$), 30.4 (s, CH_2SPh), 66.2 (s, $OCH(Me)_2$), 71.5 (s, CH_2OCHMe_2), 125.7 (s, *p*-*C*, SPh), 128.8 (s, *m*-*C*, SPh), 129.0 (s, *o*-*C*, SPh), 136.7 (s, *i*-*C*, SPh).

R = *t*-Bu (**1c**). To a stirred mixture of *tert*-butanol (200 ml), phosphoric acid (40 ml, 85%) and sodium sulfate (30 g) at 60 °C $PhSCH_2CH_2CH_2OH$ (18.6 g, 0.1 mol) was added dropwise and then the reaction mixture was refluxed for 12 h. After cooling to room temperature the mixture was neutralized with aqueous ammonia and diluted with water (150 ml). The aqueous phase was extracted with diethyl ether (3 × 80 ml) and the combined organic extracts were dried (Na_2SO_4). After evaporation of the solvents the residue was purified by means of column chromatography (silica; *n*-pentane/diethyl ether 3:1). Yield: 14.0 g (63%). Bp: 73–75 °C (0.06 Torr).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.17 (s, 9H, $OC(CH_3)_3$), 1.84 (m, 2H, $CH_2CH_2CH_2$), 2.99 (m, 2H, CH_2SPh), 3.43 (m, 2H, CH_2OCCH_3), 7.11–7.16 (m, 1H, *p*-*H*, SPh), 7.22–7.27 (m, 2H, *m*-*H*, SPh), 7.30–7.33 (m, 2H, *o*-*H*, SPh). ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.6 (s, $OC(CH_3)_3$), 30.2 (s, $CH_2CH_2CH_2$), 30.5 (s, $^1J(^{13}C,^1H)$ = 140 Hz, CH_2SPh), 59.8 (s, $OC(CH_3)_3$), 72.7 (s, CH_2OCCH_3), 125.2 (s, *p*-*C*, SPh), 128.4 (s, *m*-*C*, SPh), 129.5 (s, *o*-C, SPh), 136.8 (s, *i*-*C*, SPh). (Here and in the following C—H coupling constants were obtained from H-coupled ^{13}C NMR spectra.)

R = CPh_3 (**1d**). To a stirred solution of $PhSCH_2CH_2CH_2OH$ (12.6 g, 0.08 mol) and chlorotriphenylmethane (25.1 g, 0.09 mol) in dichloromethane (150 ml), 1,8-diazabicyclo[5.4.0]undec-7-ene (5.3 g, 0.04 mol) was added dropwise. After stirring for 2 days the solution was diluted with water (300 ml). The aqueous phase was extracted with dichloromethane (3 × 150 ml) and the combined organic extracts were dried (Na_2SO_4). After filtration and evaporation of the solvent under reduced pressure the residue was purified by means of column chromatography (silica; *n*-pentane/diethyl ether 1:1). Yield: 7.6 g (30%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.88–1.94 (m, 2H, $CH_2CH_2CH_2$), 3.02 (m, 2H, CH_2SPh), 3.18 (m, 2H, CH_2OCPh_3), 7.12–7.42 (m, 12H, *p*-*H*, SPh + *p*-*H*, $OCPh_3$ + *m*-*H*, SPh + *m*-*H*, $OCPh_3$ + m, 8H, *o*-*H*, SPh + *o*-*H*, $OCPh_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.0 s, (s, $CH_2CH_2CH_2$), 30.7 (s, CH_2SPh), 62.2 (s, CH_2OCPh_3), 86.6 (s, Ph_3CO), 125.7 (s, *p*-*C*, SPh), 126.9 (s, *p*-*C*, Ph_3CO), 127.7 (s, *m*-*C*, SPh), 128.7 (s, *o*-*C*, SPh), 128.8 (s, *m*-*C*, Ph_3CO), 129.1 (s, *o*-*C*, Ph_3CO), 136.6 (s, *i*-*C*, SPh), 144.2 (s, *i*-*C*, Ph_3CO).

3.3. Preparation of $n\text{-}Bu_3SnCH(SPh)CH_2CH_2OR$ (R = Me, α-**3a**; *i*-Pr, α-**3b**; *t*-Bu, α-**3c**; CPh_3, α-**3d**)

At −78 °C to a stirred solution of *n*-BuLi (0.01 mol, 1.5 M in *n*-hexane) and tmeda (1.16 g, 0.01 mol) in *n*-pentane (20 ml) the respective compound **1a**–**d** (0.01 mol) was added slowly via a syringe. After stirring for 24 h at room temperature $n\text{-}Bu_3SnCl$ (3.2 g, 0.01 mol) was added dropwise. To the suspension obtained a saturated aqueous solution of NH_4Cl (15 ml) was added. The aqueous phase was extracted with diethyl ether (3 × 20 ml). After drying the combined organic extracts (Na_2SO_4), filtration, and evaporation of the solvents the α/*ortho* ratios in the residues were determined by integration of the requisite ^{119}Sn NMR signals. In the case of **3a**–**c** the α-products (α-**3a**–**c**) have been obtained in a pure state by vacuum distillation. Due to the high boiling point α-**3d** could not be obtained in this way.

R = Me (α-**3a**). Yield: 3.80 g (81%). Bp: 137–141 °C (0.05 Torr). Anal. Calc. $C_{22}H_{40}OSSn$ (471.33): C, 56.06; H, 8.55. Found: C, 56.67; H, 7.84%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (t, ^3J(H,H) = 7,47 Hz, 9H, δ-CH_3, Bu), 1.10–1.29 (m, 6H, α-CH_2, Bu), 1.32–1.42 (m, 6H, γ-CH_2, Bu), 1.54–1.70 (m, 6H, β-CH_2, Bu), 1.90–1.94 (m, 2H, CH_2CH_2CH), 2.98–3.05 (m + d, $^2J(^{119}Sn,H)$ = 52.8 Hz, 1H, Sn*CH*), 3.04 (s, 3H, OCH_3), 3.14–3.21 (m, 2H, CH_2OMe), 7.49–7.53 (m, 1H, *p*-*H*, SPh + m, 2H, *m*-*H*, SPh), 7.81–7.84 (m, 2H, *o*-*H*, SPh). ^{13}C NMR (125 MHz, $CDCl_3$): δ 10.2 (s + d + d, $^1J(^{117}Sn,C)$ = 313.8 Hz, $^1J(^{119}Sn,C)$ = 328.7 Hz, α-*C*, Bu), 13.7 (s, δ-*C*, Bu), 25.1 (s + d, $^1J(^{119}Sn,C)$ = 250.8 Hz, SnCH), 27.4 (s + d, $^3J(^{119}Sn,C)$ = 58.1 Hz, γ-*C*, Bu), 29.1 (s + d, $^2J(^{119}Sn,C)$ = 19.7 Hz, β-*C*, Bu), 33.4 (s, CH_2CH_2CH), 58.5 (s, OCH_3), 71.1 (s, CH_2OMe), 125.3 (s, *p*-C, SPh), 128.4 (s, *m*-C, SPh), 128.6 (s, *o*-C, SPh), 138.9 (s, *i*-C, SPh). ^{119}Sn NMR (186 MHz, THF-d_8): δ −10.7 (s).

R = *i*-Pr (α-**3b**). Yield: 3.45 g (69%). Bp: 158–161 °C (0.03 Torr). Anal. Calc. for $C_{24}H_{44}OSSn$ (499.38): C, 57.76; H, 8.82. Found: C,

57.78; H, 8.33%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, ^3J(H,H) = 7.48 Hz, 9H, δ-CH_3, Bu), 0.97–1.01 (m, 6H, α-CH_2, Bu), 1.09/1.10 (d/d, ^3J(H,H) = 6.10 Hz/^3J(H,H) = 6.10 Hz, 3H/3H, $CH_2OCH(CH_3)_2$), 1.29–1.37 (m, 6H, γ-CH_2, Bu), 1.49–1.57 (m, 6H, β-CH_2, Bu), 2.04–2.08 (m, 2H, CH_2CH_2CH), 3.06 (m + d, ^2J(^{119}Sn,H) = 52.0 Hz, 1H, SnC*H*), 3.41–3.48 (m, 1H + 2H, $CH_2OCH(CH_3)_2$ + CH_2Oi-Pr), 7.10–7.14 (m, 1H, *p-H*, SPh), 7.23–7.27 (m, 2H, *m*-H, SPh), 7.34–7.36 (m, 2H, *o-H*, SPh). ^{13}C NMR (125 MHz, $CDCl_3$): δ 10.0 (s + d + d, ^1J(^{117}Sn,C) = 311.2 Hz, ^1J(^{119}Sn,C) = 325.9 Hz, α-*C*, Bu), 13.7 (s, δ-*C*, Bu), 22.0/22.2 (s/s, $CH_2OCH(CH_3)_2$), 24.9 (s + d, ^1J(^{119}Sn,C) = 249.2 Hz, Sn*C*H), 27.4 (s + d, ^3J(^{119}Sn,C) = 58.8 Hz, γ-*C*, Bu), 29.1 (s + d, ^2J(^{119}Sn,C) = 19.7 Hz, β-*C*, Bu), 34.3 (s, CH_2CH_2CH), 66.9 (s + d, ^3J(^{119}Sn,C) = 20.7 Hz, *C*H_2OCH$(CH_3)_2$), 71.5 (s, $CH_2OCH(CH_3)_2$), 125.3 (s, *p-C*, SPh), 128.4 (s, *m-C*, SPh), 128.6 (s, *o-C*, SPh), 139.1 (s, *i-C*, SPh). ^{119}Sn NMR (186 MHz, $CDCl_3$): δ −9.7 (s).

R = *t*-Bu (α-**3c**). Yield: 2.58 g (49%). Bp: 176 °C (0.01 Torr). Anal. Calc. for $C_{25}H_{46}OSSn$ (513.05): C, 58.82; H, 9.30. Found: C, 58.52; H, 8.97%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.79 (t, ^3J(H,H) = 7.26 Hz, 9H, δ-CH_3, Bu), 0.86–0.90 (m, 6H, α-CH_2, Bu), 1.02 (s, 9H, $CH_2OC(CH_3)_3$), 1.18–1.27 (m, 6H, γ-CH_2, Bu), 1.39–1.47 (m, 6H, β-CH_2, Bu), 1.91–1.95 (m, 2H, CH_2CH_2CH), 2.95 (m + d, ^2J(^{119}Sn,H) = 52.3 Hz, 1H, Sn*C*H), 3.17–3.23/3.25–3.32 (m/m, 1H/1H, CH_2O*t*-Bu), 7.01–7.02 (m, 1H, *p-H*, SPh), 7.11–7.15 (m, 2H, *m-H*, SPh), 7.24–7.26 (m, 2H, *o-H*, SPh). ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.0 (s + d + d, ^1J(^{117}Sn,C) = 310.8 Hz, ^1J(^{119}Sn,C) = 325.6 Hz, α-*C*, Bu), 13.6 (s, δ-*C*, Bu), 24.9 (s + d, ^1J(^{119}Sn,C) = 247.5 Hz, Sn*C*H), 27.5 (s + d, ^3J(^{119}Sn,C) = 57.5 Hz, γ-*C*, Bu), 27.6 (s, $CH_2OC(CH_3)_3$), 29.0 (s + d, ^2J(^{119}Sn,C) = 20.6 Hz, β-*C*, Bu), 34.9 (s, CH_2CH_2CH), 60.8 (s, *C*H_2O*t*-Bu), 72.6 (s, $CH_2OC(CH_3)_3$), 125.3 (s, *p*-C, *SPh*), 128.4 (s, *m-C*, SPh), 128.5 (s, *o-C*, SPh), 139.1 (s, *i-C*, SPh). ^{119}Sn NMR (186 MHz, $CDCl_3$): δ −9.5 (s).

R = CPh_3. ^{119}Sn NMR (186 MHz, $CDCl_3$): α-**3d** δ –9.7 (s); *o*-**3d** δ –43.6 (s).

3.4. Ortho-stannylated and -lithiated sulfides

Ortho-stannylated enriched mixtures of *o*-**3a** (*o*:α = 60–80:40–20), *o*-**3b** (*o*:α = 50:50) and *o*-**3c** (*o*-**3c**:α-**3c**:**1c** = 3:1:10) were prepared by lithiation of **1a** (lithiation time: 30 min), **1b** and **1c** (lithiation times: 3 h), respectively, as described above followed by a subsequent chromatographic work-up using preparative centrifugally accelerated thin layer chromatography (eluent: *n*-pentane).

n-Bu_3Sn(*o*-$C_6H_4SCH_2CH_2CH_2OR$) (R = Me, *o*-**3a**; *i*-Pr, *o*-**3b**; *t*-Bu, *o*-**3c**).

R = Me, *o*-**3a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95 (t, ^3J(H,H) = 7,33 Hz, 9H, δ-CH_3, Bu), 0.99–1.23 (m, 6H, α-CH_2, Bu), 1.35–1.43 (m, 6H, γ-CH_2, Bu), 1.54–1.70 (m, 6H, β-CH_2, Bu), 1.86−1.96 (m, 2H, $CH_2CH_2CH_2$), 3.00 (m, 2H, PhSCH_2), 3.30 (s, 3H, OCH_3), 3.45 (m, 2H, CH_2OMe), 7.11–7.15 (m, 1H, *H4*, C_6H_4), 7.22–7.26 (m, 2H, *H5* + *H3*, C_6H_4), 7.35–7.39 (m, 1H, *H6*, C_6H_4). ^{13}C NMR (125 MHz, $CDCl_3$): δ 10.7 (s + d + d, ^1J(^{117}Sn,C) = 330.3 Hz, ^1J(^{119}Sn,C) = 345.7 Hz, α-*C*, Bu), 13.5 (s, δ-*C*, Bu), 27.2 (s + d, ^3J(^{119}Sn,C) = 60.5 Hz, γ-*C*, Bu), 28.9 (s + d, ^2J(^{119}Sn,C) = 19.5 Hz, β-*C*, Bu), 29.1 (s, $CH_2CH_2CH_2$), 30.0 (s, PhSCH_2), 58.2 (s, OCH_3), 70.6 (s, *C*H_2OMe), 125.5 (s, *C6*, C_6H_4), 128.6/128.7/136.5 (s/s/s, *C3*,*C4*,*C5*, C_6H_4), 144.4 (s + d, ^2J(^{119}Sn,C) = 23.0 Hz, *C2*–S, C_6H_4), 145.7 (s + d, ^1J(^{119}Sn,C) = 392.8 Hz, *C1*–Sn, C_6H_4). ^{119}Sn NMR (186 MHz, $CDCl_3$): δ −43.5 (s).

R = *i*-Pr, *o*-**3b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (t, ^3J(H,H) = 7.30 Hz, 9H, δ-CH_3, Bu), 0.92–0.96 (m, 6H, α-CH_2, Bu), 1.16 (d, ^3J(H,H) = 6.18 Hz, 6H, $CH_2OCH(CH_3)_2$), 1.34–1.39 (m, 6H, γ-CH_2, Bu), 1.54–1.62 (m, 6H, β-CH_2, Bu), 1.86–1.95 (m, 2H, $CH_2CH_2CH_2$), 3.02 (m, 2H, PhSCH_2), 3.49–3.57 (m, 1H + 2H, $CH_2OCH(CH_3)_2$ + CH_2Oi-Pr), 7.11–7.16 (m, 1H, *H4*, C_6H_4), 7.24–7.28 (m, 2H, *H5* + *H3*, C_6H_4), 7.37–7.39 (m, 1H, *H6*, C_6H_4). ^{13}C NMR (125 MHz, $CDCl_3$): δ 10.8 (s + d + d, ^1J(^{117}Sn,C) = 330.3 Hz, ^1J(^{119}Sn,C) = 345.8 Hz, α-*C*, Bu), 13.6 (s, δ-*C*, Bu), 22.0 (s, $CH_2OCH(CH_3)_2$), 27.3 (s + d, ^3J(^{119}Sn,C) = 60.7 Hz, γ-*C*, Bu), 29.0 (s + d, ^2J(^{119}Sn,C) = 19.6 Hz, β-*C*, Bu), 29.8 (s, $CH_2CH_2CH_2$), 32.3 (s, PhSCH_2), 66.3 (s, *C*H_2OCH$(CH_3)_2$), 71.3 (s, $CH_2OCH(CH_3)_2$), 125.4 (s, *C6*, C_6H_4), 128.6/128.7/136.5 (s, *C3*, C_6H_4) (s/s/s, *C3*,*C4*,*C5*, C_6H_4), 144.6 (s + d, ^2J(^{119}Sn,C) = 23.1 Hz, *C2*–S, C_6H_4), 145.8 (s + d, ^1J(^{119}Sn,C) = 391.3 Hz, *C1*–Sn, C_6H_4). ^{119}Sn NMR (186 MHz, $CDCl_3$): δ −43.4 (s).

R = *t*-Bu, *o*-**3c**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92 (t, ^3J(H,H) = 7.30 Hz, 9H, δ-CH_3, Bu), 0.92–0.96 (m, 6H, α-CH_2, Bu), 1.20 (s, 9H, $CH_2OC(CH_3)_3$), 1.34–1.39 (m, 6H, γ-CH_2, Bu), 1.54–1.62 (m, 6H, β-CH_2, Bu),1.84–1.91 (m, 2H, $CH_2CH_2CH_2$), 3.02 (m, 2H, PhSCH_2), 3.46 (m, 2H, CH_2O*t*-Bu), 7.11–7.17 (m, 1H, *H4*, C_6H_4), 7.23–7.28 (m, 2H, *H5* + *H3*, C_6H_4), 7.38–7.40 (m, 1H, *H6*, C_6H_4). ^{13}C NMR (125 MHz, $CDCl_3$): δ 10.8 (s + d + d, ^1J(^{117}Sn,C) = 330.4 Hz, ^1J(^{119}Sn,C) = 345.8 Hz, α-*C*, Bu), 13.6 (s, δ-*C*, Bu), 27.3 (s + d, ^3J(^{119}Sn,C) = 60.8 Hz, γ-*C*, Bu), 27.4 (s, $CH_2OC(CH_3)_3$), 29.1 (s + d, ^2J(^{119}Sn,C) = 19.6 Hz, β-*C*, Bu), 31.5 (s, $CH_2CH_2CH_2$), 32.3 (s, PhSCH_2), 59.9 (s, *C*H_2OC$(CH_3)_3$), 72.5 (s, $CH_2OC(CH_3)_3$), 125.3 (s, *C6*, C_6H_4), 128.68/128.75/136.5 (s/s/s, *C3*,*C4*,*C5*, C_6H_4), 144.8 (s + d, ^2J(^{119}Sn,C) = 23.2 Hz, *C2*–Sn, C_6H_4), 145.8 (s, *C1*–Sn, C_6H_4). ^{119}Sn NMR (186 MHz, $CDCl_3$): δ −43.6 (s).

3.4.1. NMR experiments

In a Schlenk tube the solvent of a solution of *n*-BuLi (ca 0.5 mmol) in *n*-hexane was removed in vacuo. To the residue a 1:1 mixture of the requisite sulfide **1b**/**1c** (0.5 mmol) and tmeda (0.5 mmol) in benzene-d_6 (ca 0.5 ml) was added via a syringe. Then the reaction mixture was transferred to a NMR tube which was sealed by melting.

[Li(*o*-$C_6H_4SCH_2CH_2CH_2OR$)(tmeda)] (R = *i*-Pr, *o*-**2b**; *t*-Bu, *o*-**2c**).

R = *i*-Pr (*o*-**2b**). ^{13}C NMR (50 MHz, benzene-d_6): δ 22.0 (s, $OCH(CH_3)_2$), 30.4 (s, $CH_2CH_2CH_2$), 34.0 (s, PhSCH_2), 46.1 (s, NCH_3, tmeda), 56.9 (s, *C*H_2N, tmeda), 66.9 (s, *C*H_2Oi-Pr), 71.4 (s, O$CH(CH_3)_2$), 121.6/122.3/125.5/141.8 (s/s/s/s, C_6H_4), 151.1 (s, *C*–S, C_6H_4), *C*–Li not found due to bad signal-to-noise ratio.

R = *t*-Bu (*o*-**2c**). ^{13}C NMR (50 MHz, benzene-d_6): δ 27.0 (s, $OC(CH_3)_3$), 30.9 (s, $CH_2CH_2CH_2$), 34.6 (s, PhSCH_2), 46.0 (s, NCH_3, tmeda), 57.4 (s, *C*H_2N, tmeda), 60.6 (s, *C*H_2O*t*-Bu), 73.4 (s, $OC(CH_3)_3$), 119.3/121.5/125.1/141.4 (s/s/s/s, C_6H_4), 152.0 (s, *C*–S, C_6H_4), 186.1 (s, *C*–Li, C_6H_4).

3.5. Preparation of [Li{CH(SPh)CH_2CH_2OR}(tmeda)] (R = Me, α-**2a**; i-Pr, α-**2b**; t-Bu, α-**2c**)

At −78 °C to a stirred solution of *n*-BuLi (0.01 mol, 1.5 M in *n*-hexane) and tmeda (1.16 g, 0.01 mol) in *n*-pentane (20 ml) the respective tin compound **3a**–**c** (0.01 mol) was added slowly via a syringe. The reaction mixture was stirred for 2 h at this temperature and then stirred overnight at room temperature. The yellowish precipitate was filtered off, washed with cold *n*-pentane (4 × 10 ml) and dried in vacuo.

R = Me (α-**2a**). Yield: 2.68 g (88%). ^{1}H NMR (400 MHz, THF-d_8): δ 0.88–0.92 (m, 1H, *CH*Li), 2.12 (s, br, 2H, CH_2CH_2 CHLi), 2.16 (s, 12H, $CH_2N(CH_3)_2$, tmeda), 2.31 (s, 4H, CH_2N$(CH_3)_2$, tmeda), 3.35 (s, 3H, CH_3O), 3.49 (s, br, 2H, CH_3OCH_2), 6.68–6.72 (m, 1H, *p-H*, SPh), 6.96–7.00 (m, 2H, *m-H*, SPh), 7.10–7.12 (m, 2H, *o-H*, SPh). ^{13}C NMR (100 MHz, THF-d_8): δ 15.5 (s, Li*C*H), 36.1 (s, $CHCH_2CH_2$), 46.2 (s, N$(CH_3)_2$ tmeda), 58.5 (s, CH_2OCH_3), 58.8 (s, *C*H_2N tmeda), 76.4 (s, *C*H_2OMe), 121.3 (s, *p-C*, SPh), 125.5 (s, *o-C*, SPh), 127.8 (s, *m-C*, SPh), 152.1 (s, *i-C*, SPh).

R = *i*-Pr (α-**2b**). Yield: 1.54 g (51%). ^{1}H NMR (400 MHz, THF-d_8): δ 0.88–0.92 (m, 1H, *CH*Li), 1.18 (d, ^3J(H,H) = 6.02 Hz, 6H, $OCH(CH_3)_2$), 2.14 (s, br, 2H, CH_2CH_2CHLi), 2.15 (s, 12H, NCH_3, tme-

da), 2.31 (s, 4H, CH_2N, tmeda), 3.57 (s, br, 2H, CH_2O*i*-Pr), 3.66 (quin, ^3J(H,H) = 6.02 Hz, 1H, OCH(CH$_3$)$_2$), 6.69–6.71 (m, 1H, *p*-*H*, SPh), 6.95–6.99 (m, 2H, *m*-*H*, SPh), 7.10–7.12 (m, 2H, *o*-*H*, SPh). ^{13}C NMR (100 MHz, THF-d_8): δ 15.8 (s, *C*HLi), 22.4 (s, OCH(*C*H$_3$)$_2$), 36.6 (s, CH$_2$*C*H$_2$CHLi), 46.2 (s, N*C*H$_3$, tmeda), 58.9 (s, *C*H$_2$N, tmeda), 71.5 (s, *C*H$_2$O*i*-Pr), 72.5 (s, O*C*H(CH$_3$)$_2$), 121.2 (s, *p*-*C*, SPh), 125.5 (s, *m*-*C*, SPh), 127.8 (s, *p*-*C*, SPh), 152.3 (s, *i*-*C*, SPh).

R = *t*-Bu (α-**2c**). Yield: 3.06 g (89%). ^{1}H NMR (500 MHz, THF-d_8): δ 0.89 (m, 1H, *CH*Li), 1.15 (s, 9H, (*CH*$_3$)$_3$CO), 2.15 (s, 12H, CH$_2$N(*CH*$_3$)$_2$, tmeda), 2.31 (s, 4H *CH*$_2$N(CH$_3$)$_2$, tmeda), 2.49 (s, br, 2H, CH$_2$*CH*$_2$CHLi), 3.51 (s, br, 2H, *CH*$_2$O*t*-Bu), 6.65–6.69 (m, 1H, *p*-*H*, SPh), 6.95–6.99 (m, 2H, *m*-*H*, SPh), 7.09–7.12 (m, 2H, *o*-*H*, SPh). ^{13}C NMR (100 MHz, benzene-d_6): δ 15.8 (s, ^1J(^{13}C,^{1}H) = 130 Hz, *C*HLi), 27.8 (s, (*C*H$_3$)$_3$CO), 36.9 (s, CH$_2$*C*H$_2$CHLi), 46.2 (s, CH$_2$N(*C*H$_3$)$_2$, tmeda), 58.9 (s, *C*H$_2$N(CH$_3$)$_2$, tmeda), 64.7 (s, (CH$_3$)$_3$*C*O), 74.1 (s, *C*H$_2$O*t*-Bu), 121.2 (s, *p*-*C*, SPh), 129.5 (s, *m*-*C*, SPh), 129.5 (s, *o*-*C*, SPh), 152.4 (s, *i*-*C*, SPh).

3.6. Preparation of [Li{CH(SPh)CH$_2$CH$_2$OR}] (R = Me, α-**4a**; i-Pr, α-**4b**)

At −78 °C to a stirred solution of *n*-BuLi (0.01 mol, 1.5 m in *n*-hexane) in *n*-pentane (20 ml) the respective tin compound **3a**–**b** (0.01 mol) was added slowly via a syringe. The reaction mixture was stirred for 2 h at this temperature and then stirred overnight at room temperature. The yellowish precipitate was filtered off, washed with *n*-pentane (4 × 10 ml) and dried in vacuo.

R = Me (α-**4a**). Yield: 1.69 g (90%). ^{1}H NMR (200 MHz, THF-d_8): δ 0.86–0.90 (m, br, *CH*Li), 2.08–2.15 (m, br, 2H, CH$_2$*CH*$_2$CHLi), 3.35 (s, 3H, C*H*$_3$O), 3.49 (s, br, 2H, C*H*$_2$OMe), 6.66–6.74 (m, 1H, *p*-*H*, SPh), 6.94–7.10 (m, 2H, *m*-*H*, SPh), 7.12–7.14 (m, 2H, *o*-*H*, SPh). ^{13}C NMR (50 MHz, THF-d_8): δ 15.35 (s, *C*HLi), 36.1 (s, CH$_2$*C*H$_2$CHLi), 58.5 (s, *C*H$_3$O), 76.3 (s, *C*H$_3$OMe), 121.3 (s, *p*-*C*, SPh), 125.5 (*o*-*C*, SPh), 127.8 (s, *m*-*C*, SPh), 152.1 (s, *i*-*C*, SPh).

R = *i*-Pr (α-**4b**). Yield: 1.90 g (90%). ^{1}H NMR (400 MHz, THF-d_8): δ 0.83–0.93 (m, 1H, *CH*Li), 1.17 (d, $^3J_{H,H}$ = 6.23 Hz, 6H, CH$_2$OCH(C*H*$_3$)$_2$), 2.13 (s, br, 2H, CH$_2$*CH*$_2$CHLi), 3.53 (s, br, 2H, C*H*$_2$O*i*-Pr), 3.61 (sept, $^3J_{H,H}$ = 6.02 Hz, 1H, CH$_2$OC*H*(CH$_3$)$_2$), 6.66–6.71 (m, 1H, *p*-*H*, SPh), 6.91–7.09 (m, 2H, *m*-*H*, SPh), 7.11–7.16 (m, 2H, *o*-*H*, SPh). ^{13}C NMR (100 MHz, THF-d_8): δ 15.7 (s, *C*HLi), 22.4/22.4 (s/s, CH$_2$OCH(*C*H$_3$)$_2$), 36.6 (s, CH$_2$CH$_2$CHLi), 71.4 (s, *C*H$_2$O*i*-Pr), 72.5 (s, CH$_2$O*C*H(CH$_3$)$_2$), 121.2 (s, *p*-*C*, SPh), 125.4 (s, *o*-*C*, SPh), 127.7 (s, *m*-*C*, SPh), 152.3 (s, *i*-*C*, SPh).

3.7. Preparation of PhSO$_2$CH$_2$CH$_2$CH$_2$OR (R = Me, **5a**; i-Pr, **5b**)

To a stirred mixture of the sulfide **1a** or **1b** (0.05 mol) in acetic acid (150 ml), H_2O_2 (40 ml, 30% in water) was added dropwise. After stirring for 4 h at room temperature and for 30 min at 90 °C, the reaction mixture was poured on ice (100 g). The aqueous phase was extracted with toluene (4 × 10 ml). The combined organic phases were dried (Na_2SO_4) and after filtration the solvents were evaporated under reduced pressure. The residues proved to be pure (>98%) and were used without further purification.

R = Me (**5a**). Yield: 9.9 g (93%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.96–1.98 (m, 2H, CH$_2$*CH*$_2$CH$_2$), 3.14–3.22 (m, 2H, *CH*$_2$SO$_2$Ph), 3.23 (s, 3H, OC*H*$_3$), 3.36–3.39 (m, 2H, *CH*$_2$OMe), 7.51–7.55 (m, 2H, *m*-*H*, SO$_2$Ph), 7.59–7.64 (m, 1H, *p*-*H*, SO$_2$Ph), 7.86–7.89 (m, 2H, *o*-*H*, SO$_2$Ph). ^{13}C NMR (100 MHz, CDCl$_3$): δ 23.3 (s, CH$_2$*C*H$_2$CH$_2$), 53.6 (s, ^1J(^{13}C,^{1}H) = 137 Hz, *C*H$_2$SO$_2$Ph), 58.6 (s, *C*H$_2$OMe), 70.2 (s,*C*H$_3$O), 128.0 (s, *o*-*C*, SO$_2$Ph), 129.2 (s, *m*-*C*, SO$_2$Ph), 133.6 (s, *p*-*C*, SO$_2$Ph), 139.2 (s, *i*-*C*, SO$_2$Ph).

R = *i*-Pr (**5b**). Yield: 9.1 g (88%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.05 (d, ^3J(H,H) = 6,10 Hz, 6H, CH$_2$OCH(C*H*$_3$)$_2$), 1.88–1.94 (m, 2H, CH$_2$*CH*$_2$CH$_2$), 3.15–3.18 (m, 2H, *CH*$_2$SO$_2$Ph), 3.37–3.41 (m, 2H, C*H*$_2$O*i*-Pr), 3.44 (qui, ^3J(H,H) = 6,10 Hz, 1H, CH$_2$OC*H*(CH$_3$)$_2$), 7.51–7.54 (m, 2H, *m*-*H*, SO$_2$Ph), 7.59–7.63 (m, 1H, *p*-*H*, SO$_2$Ph), 7.86–7.89 (m, 2H, *o*-*H*, SO$_2$Ph). ^{13}C NMR (125 MHz, CDCl$_3$): δ 21.9 (s, CH$_2$OCH(*C*H$_3$)$_2$), 23.6 (s, CH$_2$*C*H$_2$CH$_2$), 53.6 (s, *C*H$_2$SO$_2$Ph), 65.4 (s, *C*H$_2$O*i*-Pr), 71.6 (s, CH$_2$OCH(CH$_3$)$_2$), 128.0 (s, *o*-*C*, SO$_2$Ph), 129.2 (s, *o*-*C*, SO$_2$Ph), 133.6 (s, *p*-*C*, SO$_2$Ph), 139.2 (s, *i*-*C*, SO$_2$Ph).

3.8. Preparation of PhSO$_2$CH$_2$CH$_2$CH$_2$OCPh$_3$ (**5c**)

At room temperature to a stirred solution of PhSO$_2$CH$_2$CH$_2$-CH$_2$OH (5.0 g, 0.03 mol) and Ph$_3$CCl (8.4 g, 0.03 mol) in dichloromethane (150 ml), 1,8-diazabicyclo[5.4.0]undec-7-ene (5.3 g, 0.04 mol) was added dropwise. After stirring for 2 days at this temperature, the solution was diluted with water (300 ml). The aqueous phase was extracted with dichloromethane (3 × 150 ml) and the combined organic extracts were dried (Na_2SO_4). After filtration and evaporation of the solvent under reduced pressure the residue was purified by means of column chromatography (silica; *n*-pentane/diethyl ether 3:1). Yield: 5.1 g (46%).

^{1}H NMR (400 MHz, CDCl$_3$): δ 1.91–1.98 (m, 2H, CH$_2$*CH*$_2$CH$_2$), 3.12 (m, 2H, C*H*$_2$OCPh$_3$), 3.18–3.21 (m, 2H, C*H*$_2$SO$_2$Ph), 7.05–7.28 (m, 3H + 6H, *p*-*H* + *m*-*H*, CPh$_3$), 7.29–7.39 (m, 6H, *o*-*H*, CPh$_3$), 7.52–7.56 (m, 2H, *m*-*H*, SO$_2$Ph), 7.62–7.66 (m, 1H, *p*-*H*, SO$_2$Ph), 7.87–7.90 (m, 2H, *o*-*H*, SO$_2$Ph). ^{13}C NMR (100 MHz, CDCl$_3$): δ 23.8 (s, CH$_2$*C*H$_2$CH$_2$), 53.9 (s, *C*H$_2$SO$_2$Ph), 61.5 (s, *C*H$_2$OCPh$_3$), 86.8 (s, OCPh$_3$), 127.1 (s, *p*-*C*, CPh$_3$), 127.8 (s, *m*-*C*, CPh$_3$), 128.1 (s, *o*-*C*, SO$_2$Ph), 128.5 (s, *o*-*C*, CPh$_3$), 129.3 (s, *m*-*C*, SO$_2$Ph), 133.6 (s, *p*-*C*, SO$_2$Ph), 139.1 (s, *i*-*C*, SO$_2$Ph), 143.8 (s, *i*-*C*, CPh$_3$).

3.9. Preparation of Li[CH(SO$_2$Ph)CH$_2$CH$_2$OR] (R = Me, **6a**; i-Pr, **6b**; CPh$_3$, **6c**)

At room temperature to a stirred solution of *n*-BuLi (0.01 mol, 1.5 M in *n*-hexane) in *n*-pentane (20 ml) (or toluene in the case of **6c**) the respective sulfone **5a**–**c** (0.01 mol) was added slowly via a syringe. After stirring for 24 h the yellowish precipitate was filtered off, washed with *n*-pentane (3 × 10 ml) and dried in vacuo.

R = Me (**6a**). Yield: 1.78 g (81%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.74 (m, 1H, CH$_2$CH$_2$C*H*), 1.89 (m, 2H, CH$_2$*CH*$_2$CH), 2.98 (m, 2H, C*H*$_2$OMe), 3.07 (s, 3H, OC*H*$_3$), 7.04–7.09 (m, 1H, *p*-*H*, SO$_2$Ph), 7.17–7.20 (m, 2H, *m*-*H*, SO$_2$Ph), 7.49–7.50 (m, 2H, *o*-*H*, SO$_2$Ph). ^{13}C NMR (100 MHz, THF-d_8): δ 28.2 (s, CH$_2$*C*H$_2$CH), 42.8 (s, ^1J(^{13}C,^{1}H) = 147 Hz, CH$_2$CH$_2$CH), 58.6 (s, OCH$_3$), 76.3 (s, *C*H$_2$OMe), 125.9 (s, *o*-*C*, SO$_2$Ph), 127.1 (s, *m*-*C*, SO$_2$Ph), 128.5 (s, *p*-*C*, SO$_2$Ph), 152.4 (s, *i*-*C*, SO$_2$Ph).

R = *i*-Pr (**6b**). Yield: 1.96 g (79%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.95 (d, ^3J(H,H) = 6.02 Hz, 6H, OCH(C*H*$_3$)$_2$), 1.70 (s, br, 1H, CH$_2$CH$_2$C*H*), 1.87 (m, 2H, CH$_2$*CH*$_2$CH), 2.98 (m, 2H, C*H*$_2$O*i*-Pr), 3.34 (m, 1H, OC*H*(CH$_3$)$_2$), 7.05–7.09 (m, 2H, *m*-*H*, SO$_2$Ph), 7.17–7.19 (m, 2H + 1H, *o*-*H* + *pH*, SO$_2$Ph). ^{13}C NMR (100 MHz, DMSO-d_6): δ 22.0 (s, OCH(*C*H$_3$)$_2$), 28.5 (s, CH$_2$CH$_2$CH), 42.2 (s, CH$_2$CH$_2$CH), 69.6 (s, *C*H$_2$O*i*-Pr),71.1 (s, O*C*H(CH$_3$)$_2$), 125.8 (s, *o*-*C*, SO$_2$Ph), 127.2 (s, *m*-*C*, SO$_2$Ph), 129.2 (s, *p*-*C*, SO$_2$Ph), 155.4 (s, *i*-*C*, SO$_2$Ph).

R = CPh$_3$ (**6c**). Yield: 3.5 g (78%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.75 (s, br, 1H, CH$_2$CH$_2$C*H*), 2.11 (s, br, 2H, CH$_2$*CH*$_2$CH), 2.29 (s, br, 2H, C*H*$_2$OCPh$_3$) 7.05–7.30 (m, br, 5H + 15H, *p*-, *m*-, *o*-*H*, SO$_2$Ph + *p*-, *m*-, *o*-*H*, OCPh$_3$). ^{13}C NMR (100 MHz, DMSO-d_6): δ 21.0 (s, CH$_2$CH$_2$CH), 45.2 (s, CH$_2$CH$_2$CH), 67.0 (s, *C*H$_2$OCPh$_3$), 85.2 (s, OCPh$_3$), 125.1 (s, *p*-*C*, CPh$_3$), 127.5 (s, *m*-*C*, CPh$_3$), 128.0 (s, *m*-*C*, SO$_2$Ph), 128.1 (s, *o*-*C*, CPh$_3$), 128.7 (s, *o*-*C*, SO$_2$Ph), 137.2 (s, *p*-*C*, SO$_2$Ph), 144.5 (s, *i*-*C*, CPh$_3$), 155.8 (s, *i*-*C*, SO$_2$Ph).

3.10. Preparation of n-Bu$_3$SnCH(SO$_2$Ph)CH$_2$CH$_2$OR (R = Me, **7a**; i-Pr, **7b**; CPh$_3$, **7c**)

At room temperature to a stirred solution of *n*-BuLi (0.01 mol, 1.5 M in *n*-hexane) in *n*-pentane (20 ml) (or toluene in the case of **7c**) the respective sulfone **5a**–**c** (0.01 mol) was added. After

24 h *n*-Bu_3SnCl (3.2 g, 0.01 mol) was added slowly. To the suspension obtained water was added (15 ml) and the aqueous phase was extracted with diethyl ether (3 × 15 ml). After drying the combined organic extracts (Na_2SO_4) and filtration the solvent was evaporated. The residues were purified by preparative centrifugal thin layer chromatography (silica; *n*-pentane/diethyl ether 3:1).

R = Me (**7a**). Yield: 3.12 g (62%). Anal. Calc. for $C_{22}H_{40}O_3SSn$ (503.02): C, 52.47; H, 7.95. Found: C, 52.11; H, 7.53%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.91 (t, ^3J(H,H) = 7.33 Hz, 9H, δ-CH_3, Bu), 1.12–1.19 (m, 6H, α-CH_2, Bu), 1.33–1.39 (m, 6H, γ-CH_2, Bu), 1.53–1.62 (m, 6H, β-CH_2, Bu), 1.92–1.96 (m, 2H, CH_2CH_2CHSn), 3.03–3.06 (m + d, $^2J(^{119}$Sn,H) = 140.9 Hz, 1H, SnC*H*), 3.05 (s, 3H, CH_3O), 3.06–3.12 (m, 2H, CH_2OMe), 7.47–7.50 (m, 2H, *m*-*H*, SO_2Ph), 7.53–7.55 (m, 1H, *p*-*H*, SO_2Ph), 7.82–7.84 (m, 2H, *o*-*H*, SO_2Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.9 (s + d + d, $^1J(^{117}$Sn,C) = 323.9 Hz, $^1J(^{119}$Sn,C) = 338.9 Hz, α-*C*, Bu), 13.7 (s, δ-*C*, Bu), 27.3 (s + d, $^2J(^{119}$Sn,C) = 63.9 Hz, β-*C*, Bu), 27.9 (s, CH_2CH_2CHSn), 28.9 (s + d, $^3J(^{119}$Sn,C) = 19.4 Hz, γ-*C*, Bu), 50.9 (s + d, $^1J(^{119}$Sn,C) = 129.3 Hz, *C*HSn), 58.3 (s, *C*H_2OMe), 70.4 (s, OCH_3), 127.6 (s, *o*-*C*, SO_2Ph), 128.9 (s, *m*-*C*, SO_2Ph), 132.4 (s, *p*-*C*, SO_2Ph), 141.2 (s, *i*-*C*, SO_2Ph). ^{119}Sn NMR (186 MHz, $CDCl_3$): δ 2.6 (s).

R = *i*-Pr (**7b**). Yield: 2.49 g (50%). Anal. Calc. for $C_{24}H_{44}O_3SSn$ (531.04): C, 54.28; H, 8.29. Found: C, 53.95; H, 8.64%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.90 (t, ^3J(H,H) = 7,47 Hz, 9H, δ-CH_3, Bu), 0.93/0.97 (d/d, ^3J(H,H) = 6.23 Hz, 3H + 3H, OCH(CH_3)$_2$), 1.12–1.20 (m, 6H, α-CH_2, Bu), 1.21–1.39 (m, 6H, γ-CH_2, Bu), 1.49–1.64 (m, 6H, β-CH_2, Bu), 1.92–1.96 (m, 2H, CH_2CH_2CHSn), 2.97–3.10 (m, 2H + 1H, CH_2O*i*-Pr + C*H*Sn), 3.22 (quin, ^3J(H,H) = 6.02 Hz, 1H, OC*H*(CH_3)$_2$), 7.46–7.56 (m, 2H, *m*-*H*, SO_2Ph + m, 1H, *p*-*H*, SO_2Ph), 7.82–7.84 (m, 2H, *p*-*H*, SO_2Ph). ^{13}C NMR (125 MHz, $CDCl_3$): δ 11.7 (s + d + d, $^1J(^{117}$Sn,C) = 322.5 Hz, $^1J(^{119}$Sn,C) = 337.6 Hz, α-*C*, Bu), 13.7 (s, δ-*C*, Bu), 21.9/21.9 (s/s, OCH(CH_3)$_2$), 27.3 (s + d, $^2J(^{119}$Sn,C) = 65,9 Hz, β-*C*, Bu), 28.3 (s, CH_2CH_2CHSn), 28.8 (s + d, $^3J(^{119}$Sn,C) = 19.4 Hz, γ-*C*, Bu), 50.9 (s + d + d, $^1J(^{117}$Sn,C) = 128.6 Hz, $^1J(^{119}$Sn,C) = 134.5 Hz, *C*HSn), 65.9 (s + d, $^3J(^{119}$Sn,C) = 15.2 Hz, CH_2O*i*-Pr), 71.3 (s, OCH(CH_3)$_2$), 127.7 (s, *o*-*C*, SO_2Ph), 128.9 (s, *m*-*C*, SO_2Ph), 132.4 (s, *p*-*C*, SO_2Ph), 141.3 (s, *i*-*C*, SO_2Ph). ^{119}Sn NMR (186 MHz, $CDCl_3$): δ 3.7 (s).

R = CPh_3 (**7c**). Yield: 3.07 g (42%). Anal. Calc. for $C_{40}H_{52}O_3SSn$ (731.20): C, 65.70; H, 7.11. Found: C, 67.38; H, 7.10%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.90 (t, ^3J(H,H) = 7,33 Hz, 9H,, δ-CH_3, Bu), 1.02–1.17 (m, 6H, α-CH_2, Bu), 1.22–1.36 (m, 6H, γ-CH_2, Bu), 1.48–1.55 (m, 6H, β-CH_2, Bu), 2.02–2.11 (m, 2H, CH_2CH_2CHSn), 2.68–2.73/2.86–2.90 (m/m, 1H/1H, CH_2OCPh_3), 3.12 (m, 1H, C*H*Sn), 7.19–7.27 (m, 6H + 6H, *m*-*H* + *o*-*H*, $OCPh_3$), 7.28–7.32 (m, 3H, *p*-*H*, $OCPh_3$), 7.33–7.45 (m, 2H, *m*-*H*, SO_2Ph), 7.52–7.55 (m, 1H, *p*-*H*, SO_2Ph), 7.79–7.81 (m, 2H, *p*-*H*, SO_2Ph). ^{13}C NMR (125 MHz, $CDCl_3$): δ 11.5 (s + d + d, $^1J(^{117}$Sn,C) = 319.8 Hz, $^1J(^{119}$Sn,C) = 337,0 Hz, α-*C*, Bu), 13.6 (s, δ-*C*, Bu), 22.6 (s, CH_2CH_2CHSn), 27.2 (s + d, $^2J(^{119}$Sn,C) = 63.6 Hz, β-*C*, Bu), 28.8 (s + d, $^3J(^{119}$Sn,C) = 19.4 Hz, γ-*C*, Bu), 51.0 (s + d, $^1J(^{119}$Sn,C) = 126.4 Hz, *C*HSn), 62.1 (s, CH_2OCPh_3), 86.6 (s, $OCPh_3$), 127.0 (s, *p*-*C*, $OCPh_3$), 127.7 (s, *m*-*C*, $OCPh_3$), 127.9 (s, *o*-*C*, SO_2Ph), 128.4 (s, *o*-*C*, $OCPh_3$), 128.7 (s, *m*-*C*, SO_2Ph), 132.4 (s, *p*-*C*, SO_2Ph), 140.9 (s, *i*-*C*, SO_2Ph), 143.8 (s, *i*-*C*, $OCPh_3$). ^{119}Sn NMR (186 MHz, $CDCl_3$): δ 2.7 (s).

Table 5
Crystallographic data for of [Li{CH(SPh)CH_2CH_2O*t*-Bu}(tmeda)] (α-**2c**).

Empirical formula	$C_{19}H_{35}LiN_2OS$
M_r	346.49
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	14.578(5)
b (Å)	12.880(3)
c (Å)	13.397(4)
V (Å)	2138(1)
Z	4
D_{calc} (g cm^{-1})	1.076
μ (Mo Kα) (mm^{-1})	0.158
F(0 0 0)	760
Θ range (°)	3.05–26.37
Reflection collected	20 220
Reflection observed [$I > 2\sigma(I)$]	2570
Reflection independent	4376 (R_{int} = 0.076)
Data/restraints/parameters	4376/0/224
Goodness-of-fit on F^2	0.999
R_1, wR_2 [$I > 2\sigma(I)$]	0.0841, 0.2277
R_1, wR_2 (all data)	0.1320, 0.2502
Largest difference in peak and hole (e Å^{-3})	0.98/−0.36

3.11. X-ray crystallography

Data for X-ray diffraction analysis of single crystals of α-**2c**, obtained from *n*-pentane solution at −10 °C, were collected at 130(2) K on a CCD Oxford Xcalibur S (λ(Mo Kα) = 0.71073 Å) in ω and φ scans mode. A summary of the crystallographic data, the data collection parameters, and the refinement parameters is given in Table 5. Semi-empirical from equivalents absorption corrections were carried out with SCALE3 ABSPACK [30]. The structure was solved with direct methods [31]. Structure refinement was carried out using full-matrix least-square routines against F^2 with SHELXL-97 [32]. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were placed in calculated positions and refined with calculated isotropic displacement parameters.

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Appendix A. Supplementary material

CCDC 709946 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via <http://www.ccdc.cam.ac.uk/data_request/cif>.

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