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Divergent Reactivity of Alkyl Aryl Sulfones with Bases: Selective Functionalization of *ortho*-Aryl and α-Alkyl Units Enabled by a Unique Carbanion Transmetalation

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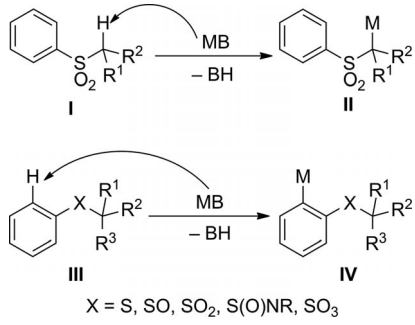
The electron-accepting sulfonyl group exhibits a strong acidifying influence on neighboring α-H atoms. The Julia and related olefinations are based on this effect. Here a surprising reversal in the metalation selectivity of branched alkyl aryl sulfones is described. Such sulfones were found to initially undergo directed *ortho*-metalation with good regioselectivity, despite having a more acidic α-H atom. The structure of the alkyl unit profoundly, but predictably, influences the regioselectivity of the attack of the base. In β- and γ-branched *ortho*-(alkylsulfonyl)aryllithiums a transmetalation to the α-carbanion proceeds only upon warming. Correspondingly generated *ortho*- or α-carbanions were then selectively applied thus permitting access to synthetically interesting compound classes.

Introduction

Carbanions, especially organolithium compounds, are central intermediates in organic chemistry.[1] They are crucial intermediates in a number of widely applied transformations, such as nucleophilic addition,[1,2] alkylation,[3] cross-coupling,[4] and rearrangement reactions,[5] as exemplified by [1,2]-[6] or [2,3]-Wittig rearrangements.[7] The facility and selectivity of carbanion generation is strongly dependent on the availability of exchangeable or activating groups. The electron-accepting sulfonyl group displays a strongly acidifying influence on neighboring α-H atoms in a fashion similar to that associated with carbonyl groups (**I** → **II**, Scheme 1).[8] The Julia olefination and related variants are based on this molecular feature.[9] In contrast, aryl sulfones, sulfonates, sulfonamides, sulfoximines, sulfoxides, sulfides and related compounds **III** bearing no α-H atoms undergo directed *ortho*-metalations (DOMs) at the aryl unit based on the complex-induced proximity effect (CIPE), a well-known strategy for activating protons kinetically.[10] Both processes are very effectively mediated by bases, such as *n*-, *sec*-, or *tert*-butyllithium as well as LDA.

These two basic metalation modes generally exclude each other because of the dominating acidity of α-H atoms. DOM was thus thought possible only if α-H atoms are absent (Scheme 1). So far only one strategy exists to reverse the selectivity of metalation; this consists of dianion generation by initial α-deprotonation and subsequent DOM, which reacts with electrophiles initially at the more nucleophilic *ortho*-position and only then at the α-position.[11] However, this procedure is compromised by low atom economy, since one equivalent of base is wasted, and the reaction displays low levels of selectivity with various electrophiles.



Scheme 1. Generally observed metalation modes for sulfones.

We recently discovered a surprising reversal in metalation selectivity with the special β,β-disilylated sulfone **V** (Scheme 2).[12] This species was found to initially undergo DOM with essentially complete regioselectivity, despite having an acidic α-H atom; the formed aryllithium **VI** subsequently rearranges completely to afford sulfonylalkyllithium **VII** upon warming. The site of initial deprotonation was unequivocally determined by deuteration studies. Moreover, it was demonstrated for a single example of a branched alkyl phenyl sulfone that DOM dominates.

Gais and co-workers subsequently reported that a number of conformationally constrained sulfoximines also

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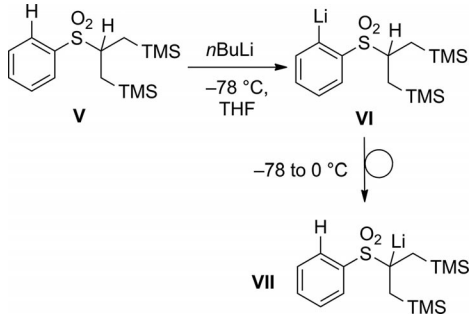


Scheme 2. Reversed metalation selectivity and transmetalation of sulfone **V**.

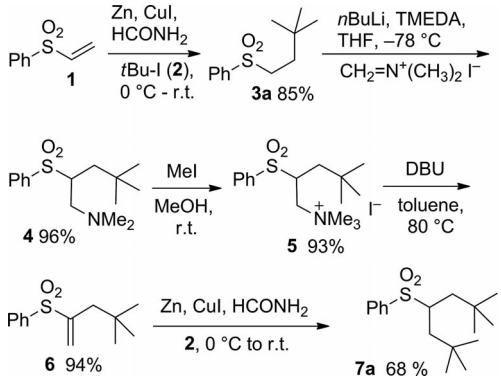
react by initial DOM followed by transmetalation to the corresponding α-carbanions.[13] A conceptually different γ→α-transmetalation of two similarly acidic positions initiated by deprotonation with LDA was very recently observed in alkynyl benzyl sulfones.[14]

Nothing is known about the scope of kinetic DOM over α-deprotonation for alkyl aryl sulfones with respect to sulfone structure and metalation conditions. We present herein a detailed reactivity study of branched alkyl phenyl sulfones toward bases. The factors, which are responsible for the regioselectivity of the deprotonation, will be outlined. In β- and γ-branched alkyl aryl sulfones DOM is favored over α-deprotonation and a subsequent transmetalation to the α-carbanion proceeds upon warming. Both carbanions can be selectively applied to give access to a variety of synthetically interesting compound classes.

Results

Preparation of Starting Materials

A previous alkylation approach to 2,2,6,6-tetramethylhept-4-yl phenyl sulfone (**7a**) proceeded in only 0.8% yield.[12] Radical addition conditions proved to be much more efficient in permitting access to **7a** (Scheme 3). Monoalkylated sulfone **3a** was synthesized by Zn/CuI-mediated reductive coupling of *tert*-butyl iodide (**2**) with phenyl vinyl sulfone (**1**) in formamide in good yield.[15] The

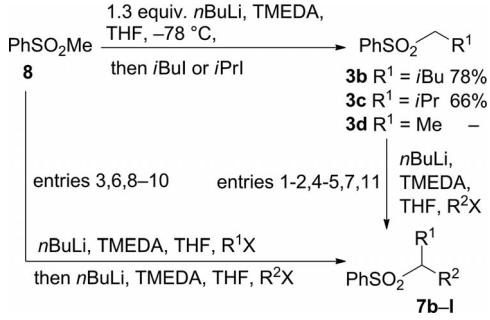


Scheme 3. Synthesis of 2,2,6,6-tetramethylhept-4-yl phenyl sulfone (**7a**).

resulting alkylated sulfone **3a** was subsequently deprotonated with *n*BuLi in the presence of TMEDA. Nucleophilic addition of the resulting α-anion to Eschenmoser's salt furnished amine **4** in excellent yield.

Subsequent elimination to vinyl sulfone **6** was achieved in two high-yielding steps by initial methylation of **4** with methyl iodide in methanol and subsequent treatment of the corresponding quarternary ammonium salt **5** with DBU. Repetition of the reductive *tert*-butyl radical addition provided sulfone **7a** in an overall 49% yield over the five steps.

Isopentyl phenyl sulfone (**3b**) and isobutyl phenyl sulfone (**3c**) were prepared from methyl phenyl sulfone (**8**) by deprotonation with *n*BuLi and subsequent alkylation using isobutyl or isopropyl iodide, respectively (Scheme 4). Monosubstituted sulfones **3a**–**c** and commercially available ethyl phenyl sulfone (**3d**) were used as starting materials for the synthesis of unsymmetrically branched sulfones **7b**,**c**,**e**,**f**,**h** (Table 1, Entries 1,2,4,5,7) and symmetrical **7l** (Table 1, Entry 11) by alkylation reactions in good to excellent yields. No overalkylation was observed except for **7l**, where 10% of *tert*-butyl phenyl sulfone was formed (not shown). Symmetrically branched alkyl sulfones **7d**, **g**,**i**–**k** ($R^1 = R^2$) were prepared by sequential alkylation of **8** with the same alkyl halide in the presence of TMEDA in good to excellent yield in a one-pot procedure (Table 1, Entries 3,6,8–10). When



Scheme 4. Preparation of α-substituted phenyl sulfones **7b**–**l**.

Table 1. α-Substituted phenyl sulfones **7b**–**l** by alkylation reactions.[a]

Entry	**3** or **8**	R^2X	Product	R^1	R^2	Yield [%][b]
1	**3a**	EtI	**7b**	CH_2tBu	Et	95
2	**3a**	MeI	**7c**	CH_2tBu	Me	94
3	**8**	*i*BuI	**7d**	*i*Bu	*i*Bu	81
4	**3b**	EtI	**7e**	*i*Bu	Et	89
5	**3b**	MeI	**7f**	*i*Bu	Me	85
6	**8**	*i*PrI	**7g**	*i*Pr	*i*Pr	54
7	**3c**	EtI	**7h**	*i*Pr	Et	80
8	**8**	BnBr	**7i**	Bn	Bn	70
9	**8**	*i*PentI[c]	**7j**	*i*Pent	*i*Pent	61
10	**8**	EtI	**7k**	Et	Et	72
11	**3d**[d]	MeI	**7l**	Me	Me	79[e]

[a] General conditions: 10 mmol sulfone, 13 mmol *n*BuLi, 20 mmol TMEDA, –78 °C, 10 min, then 13 mmol alkyl halide, –78 °C, 10 min, then warmed to room temp. until complete (see table entries 1,2,4,5,7). For symmetrically branched sulfones, the addition of reagents was repeated (see table entries 3,6,8–10). [b] Isolated. [c] *i*Pent = isopentyl. [d] Used from commercial supplier. [e] 10% of *tert*-butyl phenyl sulfone isolated.

2.6 equiv. of *n*BuLi and the alkyl halide were used, the reaction stopped after some time and mixtures of desired symmetrically branched products **7** and monoalkylated sulfones **3** were isolated in less than satisfactory yields.

The structures of the most and least sterically encumbered sulfones **7d**, **7g**, and **7k** were determined by X-ray crystallography to establish whether a correlation between their geometric features and deprotonation selectivity exists (see Figures 1, 2, and 3).[16] Significantly, the α-H atom of **7d** is in an almost synclinal arrangement to the C10 and C14 methyl groups, respectively, leading to significant steric shielding (Figure 1). In contrast, the α-H atom of **7g** displays a close contact to only one methyl group (Figure 2). Compounds **7d** and **7k** have an almost staggered conformation about the C7–S1 bond. Compound **7g** deviates more strongly from a staggered conformation having torsion angles from O1 to C8, C11 and H(C7) of –83.0, 49.9 and 162.9°, respectively, and from O2 to C8, C11 and H(C7) of 48.1, –179.5 and –66.1°, respectively. The torsion angles O1–S1–C1–C2 of **7d**, **7g** and **7k** vary to some extent and amount to 12.2(1), –8.3(2) and 11.1(3)°, respectively, whereas the O2–S1–C1–C6 torsion angle has a narrow range of –40.3(1), 40.2(2) and –38.9(3)°, respectively. The distances between O1 and H(C2) are similar, around 2.5 Å (2.53, 2.50, 2.52 Å), whereas the O2–H(C6) distance is around 2.77 Å (2.76, 2.79, 2.75 Å). The distance of the *gauche*-oriented O2 to H(C7) is within 2.80–2.83 Å (2.82, 2.83, 2.80 Å).

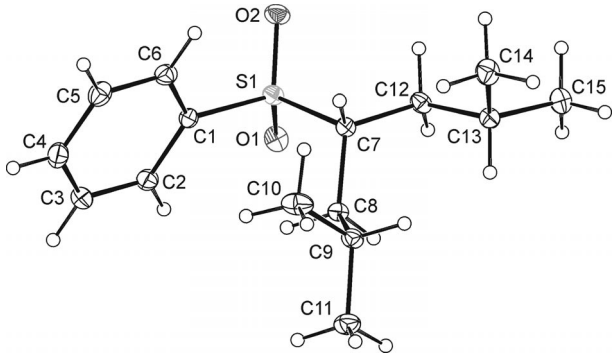


Figure 1. X-ray crystallographic view of 2,6-dimethylhept-4-yl phenyl sulfone (**7d**). Displacement ellipsoids are drawn at 30% probability level.

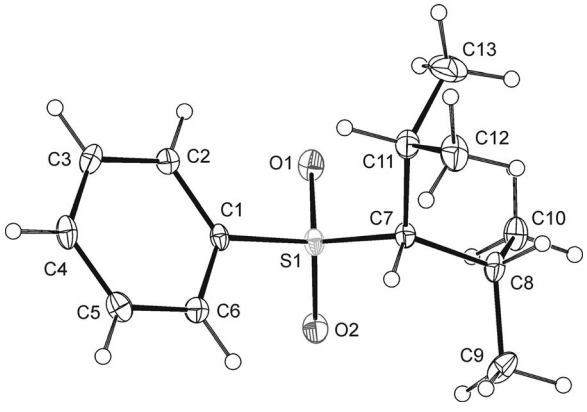


Figure 2. Crystal structure of 2,4-dimethylpent-3-yl phenyl sulfone (**7g**). Displacement ellipsoids are drawn at 30% probability level.

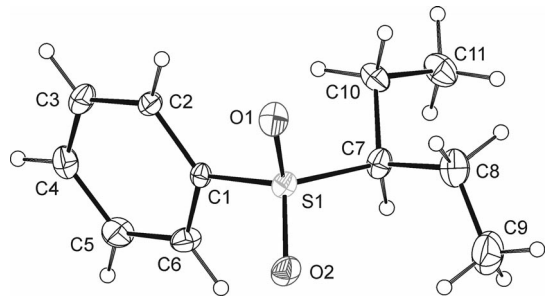


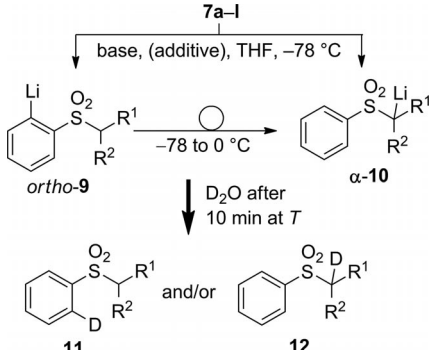
Figure 3. X-ray crystal structure of pent-3-yl phenyl sulfone (**7k**). Displacement ellipsoids are drawn at 30% probability level. (The molecule contains two independent units in the elementary cell.)

Determination of the Site of Initial Metalation and the Facility of the Subsequent Transmetalation Reactions of Diverse Sulfones 7

The deprotonation regioselectivity of sulfones **7** with diverse steric demands around the α-position and the potential of subsequent rearrangement was investigated by treating sulfones **7a**–**l** with *n*BuLi in the presence of different additives at –78 °C for a constant time of 10 min (Table 2). A defined amount of the solution was removed quickly by syringe and added to a vial containing deuterium oxide under inert conditions. Products **11** and/or **12** were then isolated and analyzed by ^{1}H NMR spectroscopy. The remainders of reaction mixtures were warmed at intervals of 20 degrees to 0 °C and aliquots were similarly analyzed. The mass balance for all reactions was quantitative and the observed ratio of **11**:**12** accounted for deprotonation and/or transmetalation intermediates *ortho*-**9**:α-**10**. Symmetrically substituted sulfones **7a** or **7d** bearing γ-branched alkyl groups were deprotonated with high selectivity at the *ortho*-position in the presence of TMEDA at –78 °C forming *ortho*-**9a**,**d** (Table 2, Entries 1,5). Their transmetalation to the α-carbanion α-**10a**,**d** occurred upon warming to 0 °C. When one of the branched groups was replaced by a linear alkyl chain as in unsymmetrical sulfones **7b**,**c** or **7e**,**f**, the regioselectivity of the initial deprotonation to *ortho*-**9** dropped (Table 2, Entries 1 vs. 2,3 and 5 vs. 9,10). The bulkier the γ-branching of one alkyl chain, the slower was the transmetalation of *ortho*-**9** to α-**10** (Table 2, Entries 2,3 vs. 9,10).

Additives had a significant impact on the course of deprotonation. For all studied substrates **7c**,**d**,**g**, HMPA triggered immediate α-deprotonation to α-**10c**,**d**,**g** (Table 2, Entries 4,8,12); even after very short deprotonation times, essentially no *ortho*-**9** was observed. Moreover, *ortho*-**9d** produced by deprotonation of **7d** in the presence of 2 equiv. TMEDA instantaneously rearranged to α-**10d** at –78 °C after adding 6 equiv. of HMPA (not shown). Lithium chloride, which leads to the modification of aggregates of organolithium compounds and acts as a catalyst in a

Table 2. Metalation selectivity of sulfones **7** and subsequent carbanion transmetalation.



Entry	7	R^1	R^2	Base	Additive	11/12[a]				
						–78 °C	–60 °C	–40 °C	–20 °C	0 °C
1	**7a**	CH_2tBu	CH_2tBu	*n*BuLi	TMEDA	23.7:1	12.2:1	1:1.4	1:6.4	1:9.4
2	**7b**	CH_2tBu	Et	*n*BuLi	TMEDA	8.3:1	7:1	2:1	0:100	0:100
3[b]	**7c**	CH_2tBu	Me	*n*BuLi	TMEDA	1.4:1	1.5:1	1:1.7	1:2.5	1:2.9
4	**7c**	CH_2tBu	Me	*n*BuLi	HMPA[c]	0:100	1:57	n.d.[d]	n.d.	n.d.
5	**7d**	*i*Bu	*i*Bu	*n*BuLi	TMEDA	31.3:1	22.8:1	2.7:1	1:46.5	1:46
6	**7d**	*i*Bu	*i*Bu	*n*BuLi	TMEDA/LiCl[e]	12:1	3.9:1	1:1.6	0:100	0:100
7	**7d**	*i*Bu	*i*Bu	LDA	–	16.5:1	2.3:1	1:2.3	1:6.1	1:75
8	**7d**	*i*Bu	*i*Bu	*n*BuLi	HMPA[c]	0:100	0:100	n.d.	n.d.	n.d.
9	**7e**	*i*Bu	Et	*n*BuLi	TMEDA	1:1.3	1:3.9	1:35	1:68	0:100
10	**7f**	*i*Bu	Me	*n*BuLi	TMEDA	1:3.3	1:2.8	n.d.	n.d.	n.d.
11[b]	**7g**	*i*Pr	*i*Pr	*n*BuLi	TMEDA	1.9:1	1:2.6	1:47	0:100	0:100
12	**7g**	*i*Pr	*i*Pr	*n*BuLi	HMPA[c]	1:99	1:99	n.d.	n.d.	n.d.
13	**7h**	*i*Pr	Et	*n*BuLi	TMEDA	1:3.6	1:6.8	0:100	0:100	0:100
14	**7i**	Bn	Bn	*n*BuLi	TMEDA	1:13.3	1:10.1	1:24	1:31	1:9.6
15	**7j**	*i*Pent[f]	*i*Pent	*n*BuLi	TMEDA	1:29.7	1:75	n.d.	n.d.	n.d.
16	**7k**	Et	Et	*n*BuLi	TMEDA	1:15.8	1:13.3	n.d.	n.d.	n.d.
17	**7l**	Me	Me	*n*BuLi	TMEDA	1:23.5	1:23:5	n.d.	n.d.	n.d.

[a] Initial conditions: 0.5 mmol sulfone, 0.55 mmol base, 1 mmol TMEDA, THF, –78 °C, ratio **11:12** determined by integration of the ^{1}H NMR spectra. [b] Reaction run in duplicate with very similar result. [c] 3 mmol HMPA. [d] n.d.: not determined since immediate α-deprotonation. [e] 2 mmol LiCl. [f] *i*Pent = isopentyl.

number of transformations,[17] did not influence the metalation regioselectivity of **7d** to a large extent, but accelerated the transmetalation of *ortho*-**9d** to α-**10d** (Table 2, Entry 6). LDA can also be used as a base with similar results (Table 2, Entry 7), whereas KHMDS was unreactive as a base under the conditions.[18]

The nature of branching and its distance from the sulfone group proved to be important factors dictating regioselectivity of the initial deprotonation. Surprisingly, only a low 1.9:1 deprotonation regioselectivity in favor of DOM intermediate *ortho*-**9g** was observed for **7g**, where the branching point is in the closer β-position (Table 2, Entry 11). An experiment run at –100 °C improved the initial *ortho*-**9g**/α-**10g** ratio to 6:1 (not shown). The selectivity switched, however, to preferred formation of α-**10h** for the less branched substrate **7h** (Table 2, Entry 13). Two-dimensional branching, as in diarylated sulfone **7i**, or a more distant branching at the δ-position as in **7j**, changed the regioselectivity to complete α-deprotonation generating α-**10i**,**j** (Table 2, Entries 14,15). Sulfones **7k** and **7l**, having chains without additional branching, were selectively deprotonated at the α-position regardless of deprotonation time (Table 2, Entries 16,17). It must be mentioned that withdrawing samples by syringe may introduce a small temperature error, which is inherent to all entries. However, the results, as such, are self-consistent since it can be expected that the same error applies to all entries.

Preparative Applications of Selected Sulfones 7

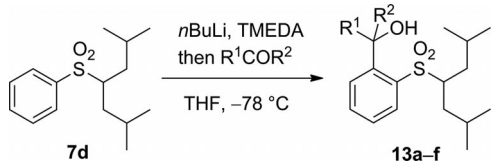
Both regioselective deprotonation of sulfones **7** and the rearrangement of derived carbanions *ortho*-**9** and α-**10** are synthetically valuable transformations. The aryllithium derived from **7d**, generated under standard conditions at –78 °C after short metalation time, underwent addition to aldehydes providing secondary benzylic alcohols **13a**–**f** in good to excellent yields (Table 3).

It is noteworthy that nucleophilic additions to enolizable and non-enolizable ketones giving tertiary benzylic alcohols also proceeded in very good yields (Table 3, Entries 5 and 6).

The α-carbanion generated from sulfone **7k** at –78 °C added smoothly to aldehydes affording α-(hydroxyalkyl)-phenyl sulfones **14a**–**e** in good yields (Table 4, Entries 1–5). However, its reaction with ketones failed to provide desired tertiary alcohols **14f**–**g** (Table 4, Entries 6,7).

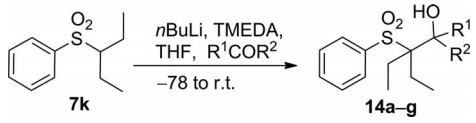
For sulfones, such as **7d**, initially subjected to DOM, conditions for selective reaction with aldehydes at the α-

Table 3. Deprotonation of **7d** and addition of ***ortho*-9d** to aldehydes and ketones.



Entry	Product	R^1	R^2	Yield [%]
1	**13a**	Ph	H	84
2	**13b**	*i*Pr	H	90
3	**13c**	EtCH=CH	H	79
4	**13d**	$PhCH_2CH_2$	H	93
5	**13e**	$–(CH_2)_5–$		85
6	**13f**	Ph	Ph	94

Table 4. Deprotonation of **7k** and addition of **α-10k** to aldehydes and ketones.



Entry	Product	R^1	R^2	Yield [%]
1	**14a**	Ph	H	80
2	**14b**	4-Br-C_6H_4	H	65
3	**14c**	*i*Pr	H	70
4	**14d**	EtCH=CH	H	64
5	**14e**	PhCH=CH	H	71
6	**14f**	$–(CH_2)_5–$		13[a]
7	**14g**	Ph	Ph	0[b]

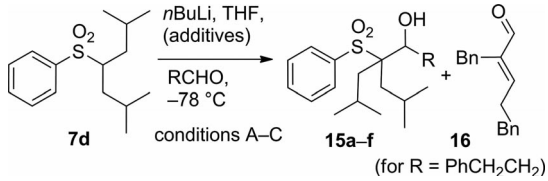
[a] Product **14f** was inseparable from **7k** (80% recovered). [b] 97% **7k** and 95% benzophenone recovered.

position, (i.e. the first step of the Julia olefination) had to be identified by varying deprotonation conditions (Table 5). Under condition A starting sulfone **7d** was deprotonated by *n*BuLi with TMEDA in THF at –78 °C and the reaction mixture was warmed to 0 °C over the course of one hour thus allowing transmetalation of *ortho*-**9d** to α-**10d**. Subsequently, structurally different aldehydes were added and found to afford α-(hydroxyalkyl) phenyl sulfones **15a**–**f** (recovery of starting **7d** 29–45%).

Under condition B, the deprotonation of **7d** with *n*BuLi in the presence of TMEDA was performed at –20 °C for 10 min and the aldehyde was added to the reaction mixture at –78 °C. Condition C involved deprotonation of **7d** with *n*BuLi and HMPA as an additive at –78 °C for 10 min followed by addition of the aldehyde. Benzaldehyde provided hydroxy sulfone **15a** in good yield under all conditions (Table 5, Entry 1), products **15b**–**c** resulting from reactions of **7d** with bromobenzaldehydes were obtained in moderate yield and were accompanied by unidentified byproducts and partial recovery of starting material (Table 5, Entries 2,3). Reaction with enolizable hydrocinnamic aldehyde was complicated by competing formation of self-aldol condensation product **16** (Table 5, Entry 4). Condition A proved ideal for the coupling, whereas the use of HMPA corresponded to a low yield of **15d**. Reactions with α,β-unsaturated aldehydes furnished hydroxy sulfones **15e** and **15f** in good to excellent yields (Table 5, Entries 5,6).

Because the Julia olefination remains the most important application of α-sulfonyl carbanions, it was investigated with substrates **7k** (Table 6, Entries 1–6) and **7d** (Table 6, Entries 7–12). For reactions using **7k** standard deprotonation conditions worked well for reaction with diverse aldehydes (cf. Table 2). For the reaction of aromatic and α,β-unsaturated aldehydes with **7d** the use of HMPA as an additive according to condition C (vide supra, Table 5) proved ideal (Table 6, Entries 7–9). Deprotonation of **7d** by *n*BuLi with TMEDA and subsequent transmetalation of *ortho*-**9d** to α-**10d** similar to conditions A (vide supra, Table 5) was most effective for enabling aliphatic aldehydes to avoid competitive deprotonation of the aldehyde (Table 6, Entries

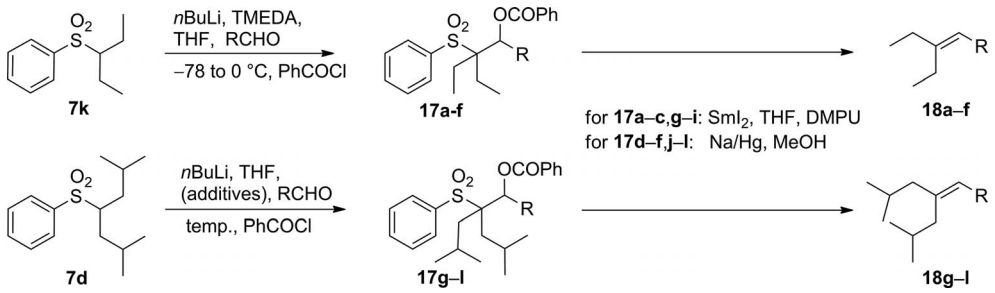
Table 5. *ortho*-Deprotonation/transmetalation of **7d** to **α-10d** and addition to structurally diverse aldehydes.



Entry	R	Product	Yield [%] condition A[a]	Yield [%] condition B[b]	Yield [%] condition C[c]
1	Ph	**15a**	78	82	75
2	4-BrC_6H_4	**15b**	42[d]	–[e]	48[f]
3	3-BrC_6H_4	**15c**	44[g]	–[e]	63[h]
4	$PhCH_2CH_2$	**15d**	61[i]	53[j]	25[k]
5	EtCH=CH	**15e**	50	–[e]	61
6	PhCH=CH	**15f**	70	96	98

[a] Condition A: Deprotonation at –78 °C in the presence of 2 equiv. TMEDA, then warmed to 0 °C during 1 h, addition of the aldehyde at –78 °C. [b] Condition B: Deprotonation at –20 °C in the presence of 2 equiv. TMEDA for 10 min, addition of the aldehyde at –78 °C. [c] Condition C: Deprotonation in the presence of 6 equiv. HMPA at –78 °C for 10 min, addition of the aldehyde at –78 °C. [d] 45% **7d** recovered. [e] Not performed. [f] 31% **7d** recovered. [g] 33% **7d** recovered. [h] 18% **7d** recovered. [i] Additionally, 29% **16** formed and 26% **7d** recovered. [j] Additionally, 31% **16** formed and 41% **7d** recovered. [k] Additionally, 63% **16** formed and 69% **7d** recovered.

Table 6. Scope of the Julia reaction with **7d** and **7k**.



Entry	R	Product	Yield [%]	Product	Yield [%]
1	Ph	**17a**	88[a]	**18a**	82[d]
2	4-BrC_6H_4	**17b**	87[a]	**18b**	78[d]
3	PhCH=CH	**17c**	88[a]	**18c**	68[d]
4	$PhCH_2CH_2$	**17d**	91[a]	**18d**	76[e]
5	C_5H_{11}	**17e**	66[a]	**18e**	64[e]
6	$C_{11}H_{23}$	**17f**	83[a]	**18f**	92[e]
7	Ph	**17g**	55[b]	**18g**	68[d]
8	4-BrC_6H_4	**17h**	61[b]	**18h**	71[d]
9	PhCH=CH	**17i**	80[b]	**18i**	82[d]
10	$PhCH_2CH_2$	**17j**	67[c]	**18j**	79[e]
11	C_5H_{11}	**17k**	78[c]	**18k**	89[e]
12	$C_{11}H_{23}$	**17l**	58[c]	**18l**	64[e]

[a] General conditions: 0.5 mmol sulfone, 0.6 mmol *n*BuLi, 1 mmol TMEDA, –78 °C, 10 min, then 0.6 mmol aldehyde, warmed to 0 °C until complete conversion, then 0.65 mmol benzoyl chloride, –78 °C, 20 min, then 0.75 mmol 3-(dimethylamino)propan-1-ol. [b] General conditions: 0.37 mmol sulfone, 0.43 mmol *n*BuLi, 2.22 mmol HMPA, –78 °C, 10 min, then 0.47 mmol aldehyde, –78 °C until complete conversion, then 0.49 mmol benzoyl chloride, 20 min, warmed to room temp., then 0.56 mmol 3-(dimethylamino)propan-1-ol. [c] General conditions: 0.74 mmol sulfone, 0.86 mmol *n*BuLi, 2 mmol TMEDA, –78 °C to –20 °C, 1 h, then 0.93 mmol aldehyde at –78 °C, then –20 °C until complete conversion, then 0.96 mmol benzoyl chloride, 20 min, warmed to room temp., then 1.11 mmol 3-(dimethylamino) propan-1-ol. [d] 0.16 mmol **17**, 6 mmol DMPU, 0.96 mmol SmI_2, 0 °C, 2 h. [e] 0.13 mmol **17**, 0.31 mmol Na/Hg, –20 °C, 3 h.

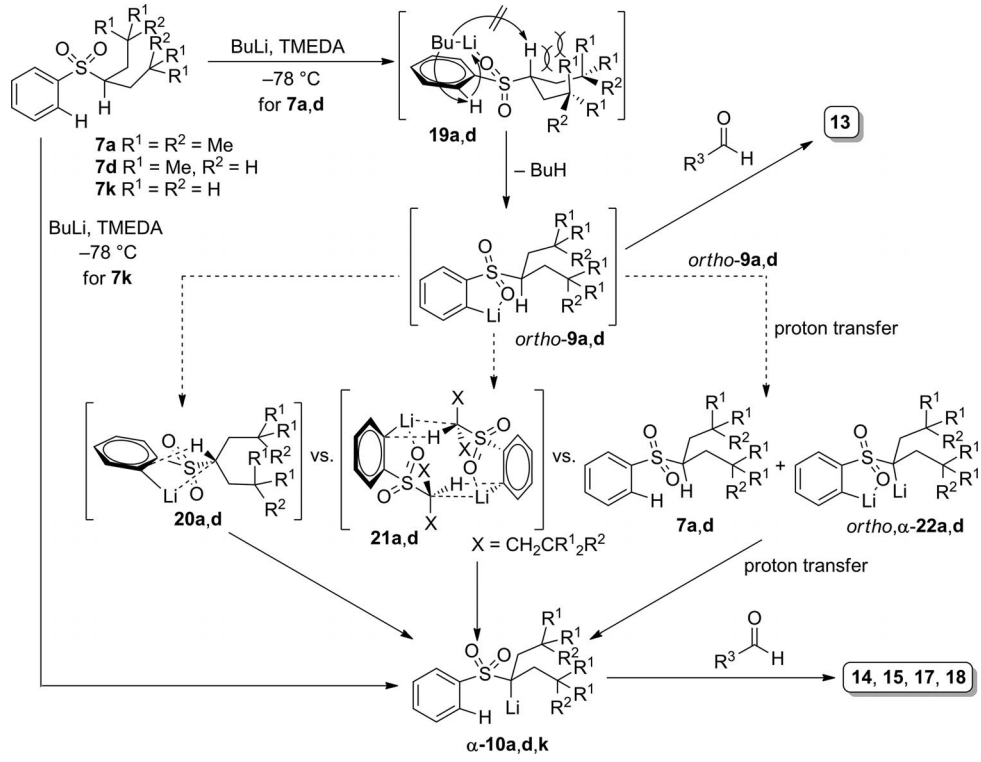
10–12). All resulting alkoxides were acylated in situ with benzoyl chloride affording β-benzoyloxy sulfones **17a**–**l** in good yields (Table 6, Entries 1–12). For the reductive elimination of **17a**–**c** and **17g**–**i** SmI_2 in THF/DMPU was used at –78 °C[19] providing the corresponding olefins **18a**–**c** and **18g**–**i** in good yields (Table 6, Entries 1–3 and 7–9).

However, saturated β-benzoyloxy sulfones **17d**–**f** and **17j**–**l** resulting from aliphatic aldehydes were completely inert to treatment with SmI_2 and even after prolonged reaction times the starting material was fully recovered. Conversely, classical deoxygenations with sodium amalgam in methanol at –20 °C afforded desired olefins **18d**–**f** and **18j**–**l** in good to excellent yields (Table 6, Entries 4–6 and 10–12). These results are in agreement with recent results obtained using different substrates.[20]

Discussion

Several aspects of this chemistry deserve comment. Alkyl aryl sulfones bearing H atoms in α-position and being branched in both γ-positions such as **7a** or **7d** (R^1 = Me, R^2 = Me, H) undergo, in contrast to the vast majority of known alkyl aryl sulfones bearing H atoms in the α-position, selective DOM to *ortho*-**9a**,**d** instead of α-deprotonation (Scheme 5). Steric hindrance seems to be responsible for the different metalation selectivity. The conformation around the α-H atom of **7a** and **7d** is very constrained (viz. Figure 1 vs. Figures 2, 3). Considering that butyllithium in THF will initially precomplex at one of the Lewis-basic sulfonyl oxygen atoms in **19a**,**d**, it is likely that the transition state for deprotonation of the at best *gauche*-oriented H atom in the α-position, which is shielded by the methyl groups of the chain (cf. Figure 1), has a considerable activation barrier. At the same time, the *ortho*-position of the arene unit in **19a**,**d**, despite being thermodynamically much less acidic, is accessible without steric constraints. Therefore deprotonation proceeds selectively at the *ortho*-position affording *ortho*-**9a**,**d**.

Several scenarios for the transmetalation from *ortho*-**9a**,**d** to α-**10a**,**d** may be envisaged. It may proceed by an intramolecular lithium-proton transfer through a four-membered transition state **20a**,**d**. Alternatively, a concerted lithium-proton exchange of two monomeric aryllithium units proceeding through transition state **21a**,**d** or from a similar dimeric aggregate may lead to α-**10a**,**d**. A third possibility involves possible stepwise transmetalation, in which one *ortho*-**9a**,**d** deprotonates another *ortho*-**9a**,**d** molecule. This would result in an *ortho*,α-sulfonyl dilithium intermediate *ortho*,α-**22a**,**d** and free **7a**,**d**. Such intermediates are indeed known, but have previously been generated by reverse sequential metalation reactions starting with α-deprotonation followed by a slower DOM.[11,13,21] A distinction of these three transmetalation pathways cannot be made at present.



Scheme 5. Mechanistic proposal for the initial lithiation of sufones **7a**, **d** and their *ortho*→α-transmetalation.

If only one γ-position is branched or the branching is flat as in the dibenzylic derivative **7i** the *ortho*-:α-lithiation selectivity drops in the order **7b** > **7c** > **7e** > **7i**, because α-deprotonation becomes increasingly more favorable with increasing degrees of conformational freedom. Sulfones with no additional branching, such as **7k** ($R^1 = R^2 = H$), (or more remote branching, such as **7j**), undergo regular α-deprotonation to α-**10k**, because the α-proton of the alkyl chain in flexible **7k** is freely exposed for deprotonation by precoordinated BuLi (cf. Figure 3).

Compound **7g**, despite having the branching points in the closer β-position, can occupy orientations in which only one face around the α-proton is shielded by an adjacent methyl group (cf. Figure 2). Therefore α-deprotonation competes with moderately favored *ortho*-metalation (Table 2, Entry 11).

However, if the available coordination sites at butyllithium are blocked by the much stronger Lewis base HMPA, a direct approach of the base proceeds to the most acidic α-proton for all studied substrates, regardless of their steric features via a much earlier transition state.

Conclusions

A surprising reversal of the deprotonation selectivity of alkyl phenyl sulfones has been discovered. If the alkyl unit is branched in the γ-position with respect to the sulfone unit, the initital deprotonation takes place at the less acidic *ortho*-position due to steric shielding of the H atom located in the α-position. The scope and limitations for this process were determined. The *ortho*-sulfonylphenyllithium intermediates transmetalate to the thermodynamically preferred α-sulfonyl carbanions on warming. Both carbanion types can be applied as nucleophiles; the former provide *ortho*-disubstituted aryl sulfones, whereas the latter can be used in Julia olefinations upon completion of the transmetalation process.

The metalation methodology described here has many implications for organic chemistry as such processes may also be observed and exploited in other compound classes, such as sulfides, sulfoxides or phosphine oxides. Such scenarios are currently under investigation in these laboratories and will be elaborated upon in due course.

Experimental Section

For general information see the Supporting information. Compounds **3a**,[15] **3b**,[22] **3c**,[23] **6**,[24] **7a**,[12] **7c**,[15] **7d**,[25] **7g**,[25] **7i**,[26] **7k**,[25] **7l**,[27] **18a**,[28] and **18b**[29] are literature-known and their analytical data agree to those reported in the cited references.

Monoalkylation of Methyl Phenyl Sulfone 8 (General Procedure): *n*BuLi (8.13 mL, 13 mmol, 1.6 M in hexane) was added dropwise to a stirred solution of **8** (1.56 g, 10 mmol) and TMEDA (3 mL, 19.5 mmol) in dry THF (50 mL) under a nitrogen atmosphere at –78 °C. After stirring for 15 min, the corresponding alkyl iodide (13 mmol) was added dropwise at –78 °C. The reaction mixture was stirred at this temperature for 10 min and at –60 °C until complete as indicated by TLC. The reaction mixture was quenched with saturated NH_4Cl solution. The layers were separated and the aqueous was extracted with diethyl ether (3× 50 mL). The combined organic extracts were washed with brine, dried with $MgSO_4$, filtered

and the solvents evaporated. Purification by column chromatography (EtOAc/hexane, 1:20, gradient to 1:10) gave sulfones **3b**,**c**.

***N*,*N*,4,4-Tetramethyl-2-(phenylsulfonyl)pentylamine (4):** *n*BuLi (0.316 mL, 0.51 mmol, 1.6 M in hexane) was added dropwise to a stirred solution of sulfone **3a** (100 mg, 0.44 mmol) and TMEDA (0.15 mL, 0.98 mmol) in dry THF (3 mL) under a nitrogen atmosphere at –78 °C. After stirring for 15 min, Eschenmoser's salt (244 mg, 1.32 mmol) was added as a solid at –78 °C. The reaction mixture was warmed to room temperature and stirred for 30 min until complete as indicated by TLC. The mixture was quenched with water, acidified with HCl (1 M) and the ammonium salt was extracted with water (2× 20 mL). The aqueous layer was treated with sodium hydroxide until the solution had pH 8–9. The desired product was extracted with diethyl ether (3× 20 mL). The combined organic extracts were washed with brine, dried with $MgSO_4$, filtered and the solvents evaporated. Purification by column chromatography (EtOAc/hexane, 1:20) gave 120 mg (96%) of amine **4** as colorless crystals, m.p. 89–91 °C. R_f (EtOAc/hexane, 1:5) = 0.28. IR: $\tilde{\nu}$ = 2952, 2867, 2770, 1467, 1449, 1368, 1287, 1262, 1139, 1084, 731, 690 cm^{-1}. MS (ESI^+): *m*/*z* (%) = 284 (100) [M + H^+]. $C_{15}H_{25}NO_2S$ (283.43): calcd. C 63.56, H 8.89, N 4.94, S 11.31; found C 63.53, H 8.87, N 4.84, S 11.03. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.85 (s, 9 H), 1.16 (dd, *J* = 6.3, 14.7 Hz, 1 H), 1.90 (s, 6 H), 2.12 (dd, *J* = 2.6, 14.7 Hz, 1 H), 2.28 (dd, *J* = 4.6, 13.6 Hz, 1 H), 2.72 (dd, *J* = 8.9, 13.6 Hz, 1 H), 3.07 (m, 1 H), 7.44 (m, 2 H), 7.53 (m, 1 H), 7.84 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.5 (q), 31.0 (s), 39.8 (t), 44.9 (q), 60.1 (d), 61.5 (t), 128.6 (d), 128.9 (d), 133.1 (d), 140.5 (s) ppm.

***N*,*N*,*N*,4,4-Pentamethyl-2-(phenylsulfonyl)pent-1-ylammonium Iodide (5):** Iodomethane (185 μL, 3 mmol) was added to a solution of amine **4** (100 mg, 0.35 mmol) in methanol (3 mL) at room temperature. After standing in the dark for 48 h, the mixture was concentrated and the residue was diluted with diethyl ether, filtered and washed with diethyl ether, giving 138 mg (93%) of ammonium salt **5** as a pale yellow solid, m.p. 147–149 °C. IR: $\tilde{\nu}$ = 3001, 2954, 1477, 1447, 1303, 1237, 1147, 1085, 968, 748, 727, 693, 599 cm^{-1}. MS (ESI^+): *m*/*z* (%) = 298 (100) [M – I^-], 156 (20) [M – $PhSO_2H$ – I^-]. HRMS (ESI^+): *m*/*z* [M – I^-] calcd. for $C_{16}H_{28}NO_2S^+$: 298.1835, found 298.1833. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.71 (s, 9 H), 1.51 (dd, *J* = 6.7, 15.7 Hz, 1 H), 1.66 (dd, *J* = 2.1, 15.7 Hz, 1 H), 3.74 (s, 9 H), 3.90 (m, 1 H), 3.97 (dd, *J* = 2.5, 15.4 Hz, 1 H), 4.20 (dd, *J* = 8.1, 15.4 Hz, 1 H), 7.62 (m, 2 H), 7.70 (m, 1 H), 7.82 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.6 (q), 31.6 (s), 43.7 (t), 56.6 (q), 57.8 (d), 68.1 (t), 129.8 (d), 130.4 (d), 135.1 (d), 135.8 (s) ppm.

4,4-Dimethyl-2-(phenylsulfonyl)-1-pentene (6): Ammonium salt **5** (688 mg, 1.62 mmol) and DBU (0.48 mL, 3.23 mmol) were stirred in dry toluene (50 mL) at 80 °C for 5 h. The reaction mixture was washed with HCl (1 M, 50 mL), water (50 mL), brine (50 mL) and dried with $MgSO_4$. After filtration and evaporation, the product was purified by column chromatography (EtOAc/hexane, 1:20) giving 360 mg (94%) of **6** as a colorless oil. The spectroscopic data are in agreement with those in the cited literature.[24]

Phenyl 2,2,6,6-Tetramethylhept-4-yl sulfone (7a): A mixture of zinc dust (153 mg, 2.52 mmol) and CuI (111 mg, 0.56 mmol) in formamide (10 mL) was stirred at 0–10 °C for 15 min. Vinyl sulfone **6** (340 mg, 1.4 mmol) was added followed by *tert*-butyl iodide (140 μL, 1.15 mmol). The mixture was aged at 0 °C for 1 h, warmed to room temperature and kept at this temperature for 5 h. Ethyl acetate (50 mL) was added, the precipitate was filtered off and rinsed with ethyl acetate. Heptane (50 mL) and HCl (1 M, 30 mL) were added to the filtrate. The layers were separated, the organic was dried with $MgSO_4$, filtered and the solvents evaporated. Purification by column chromatography (EtOAc/hexane, 1:10) gave 224 mg (68%) of sulfone **7a** as colorless crystals, m.p. 98–99 °C. The spectroscopic data are in agreement with those in the cited literature.[12] ***CAUTION:*** The Zn/CuI residue should not be dried completely as it may self-ignite in air, particularly on larger scale. It should be covered by water after filtration and rinsing with ethyl acetate.

Alkylation of Sulfones 3a–d (General Procedure): *n*BuLi (1.31 mL, 2.1 mmol, 1.6 M in hexane) was added dropwise to a stirred solution of sulfones **3a**–**d** (2 mmol) and TMEDA (0.6 mL, 4 mmol) in dry THF (10 mL) at –78 °C under a nitrogen atmosphere. After stirring for 15 min, the corresponding alkyl iodide (2.2 mmol) was added dropwise at –78 °C. After 10 min, the reaction mixture was stirred at temperature *T* until complete as indicated by TLC (Table 7). The reaction mixture was quenched with saturated NH_4Cl solution, the layers were separated and the aqueous was extracted with diethyl ether (3× 20 mL). The combined organic extracts were washed with brine, dried with $MgSO_4$, filtered and the solvents evaporated. Purification by column chromatography (EtOAc/hexane, 1:20) gave sulfones **7b**,**c**,**e**,**f**,**h**,**l**.

Table 7. Alkylation of sulfones **3a**–**d**.

Entry	Starting sulfone	Iodide	Product	*T* [°C]
1	**3a**	EtI	**7b**	–60
2	**3a**	MeI	**7c**	–60
3	**3b**	EtI	**7e**	–40
4	**3b**	MeI	**7f**	–40
5	**3c**	EtI	**7h**	–78
6	**3d**	MeI	**7l**	–[a]

[a] Quenched directly after 10 min of deprotonation.

2,2-Dimethylhex-4-yl Phenyl Sulfone (7b): Yield 483 mg (95%) as colorless crystals, m.p. 41–42 °C. R_f (EtOAc/hexane, 1:5) = 0.46. IR: $\tilde{\nu}$ = 2957, 2868, 1474, 1447, 1303, 1086, 727, 692 cm^{-1}. MS (ESI^+): *m*/*z* (%) = 277 (100) [M + Na^+], 239 (20), 185 (20). $C_{14}H_{22}O_2S$ (254.39): calcd. C 66.10, H 8.72, S 12.60; found C 66.25, H 8.75, S 12.49. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.81 (s, 9 H), 1.04 (t, *J* = 7.0 Hz, 3 H), 1.39 (dd, *J* = 7.0, 14.8 Hz, 1 H), 1.72 (m, 1 H), 1.92 (m, 2 H), 2.89 (m, 1 H), 7.56 (m, 2 H), 7.64 (m, 1 H), 7.90 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.7 (q), 24.2 (t), 29.3 (q), 30.8 (s), 40.6 (t), 62.9 (d), 129.0 (d), 129.1 (d), 133.6 (d), 138.4 (s) ppm.

2-Methylhex-4-yl Phenyl Sulfone (7e): Yield 428 mg (89%) as a colorless oil. R_f (EtOAc/hexane, 1:5) = 0.33. IR: $\tilde{\nu}$ = 2958, 2871, 1465, 1447, 1301, 1140, 1084, 762, 728, 692 cm^{-1}. MS (ESI^+): *m*/*z* (%) = 263 (100) [M + Na^+]. $C_{13}H_{20}O_2S$ (240.36): calcd. C 64.96, H 8.39, S 13.34; found C 65.13, H 8.45, S 13.47. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.78 (d, *J* = 6.2 Hz, 3 H), 0.88 (d, *J* = 6.4 Hz, 3 H), 0.98 (t, *J* = 7.5 Hz, 3 H), 1.43 (m, 1 H), 1.50–1.72 (m, 3 H), 1.85 (m, 1 H), 2.89 (m, 1 H), 7.54 (m, 2 H), 7.63 (m, 1 H), 7.86 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.4 (q), 21.95 (q), 22.02 (t), 23.1 (q), 26.0 (d), 36.7 (t), 64.0 (d), 129.1 (d), 129.3 (d), 133.7 (d), 138.5 (s) ppm.

4-Methylpent-2-yl Phenyl Sulfone (7f): Yield 385 mg (85%) as a colorless solid, m.p. 39–40 °C. R_f (EtOAc/hexane, 1:5) = 0.30. IR: $\tilde{\nu}$ = 2958, 2874, 1468, 1447, 1303, 1290, 1141, 1085, 766, 732, 692 cm^{-1}. MS (ESI^+): *m*/*z* (%) = 249 (100) [M + Na^+]. $C_{12}H_{18}O_2S$ (226.34): calcd. C 63.68, H 8.02, S 14.17; found C 63.91, H 8.00, S 14.43. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.75 (d, *J* = 6.4 Hz, 3 H), 0.86 (d, *J* = 6.4 Hz, 3 H), 1.22 (d, *J* = 6.9 Hz, 3 H), 1.35 (m, 1 H), 1.68 (m, 2 H), 3.02 (m, 1 H), 7.51 (m, 2 H), 7.59 (m, 1 H), 7.82 (m, 2

H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6 (q), 21.1 (q), 23.8 (q), 25.3 (d), 38.0 (t), 58.7 (d), 129.24 (d), 129.27 (d), 133.7 (d), 137.6 (s) ppm.

2-Methylpent-3-yl Phenyl Sulfone (7h): Yield 362 mg (80%) as colorless crystals, m.p. 54–55 °C. R_f (EtOAc/hexane, 1:5) = 0.27. IR: $\tilde{\nu}$ = 3065, 2966, 2938, 2879, 1585, 1467, 1447, 1392, 1303, 1288, 1178, 1142, 1080, 999 cm^{-1}. MS (ESI$^+$): *m*/*z* (%) = 249 (100) [M + Na$^+$]. $C_{12}H_{18}O_2S$ (226.34): calcd. C 63.68, H 8.02, S 14.17; found C 63.46, H 8.25, S 14.29. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.6 Hz, 3 H), 1.00 (d, *J* = 6.5 Hz, 3 H), 1.01 (d, *J* = 7.0 Hz, 3 H), 1.69 (m, 1 H), 1.88 (m, 1 H), 2.36 (m, 1 H), 2.78 (td, *J* = 2.4, 5.8 Hz, 1 H), 7.54 (m, 2 H), 7.62 (m, 1 H), 7.87 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8 (q), 17.2 (q), 17.4 (t), 21.8 (q), 27.0 (d), 71.4 (d), 128.4 (d), 129.1 (d), 133.4 (d), 139.5 (s) ppm.

Sequential Dialkylation of Methyl Phenyl Sulfone 8 (General Procedure): *n*BuLi (8.13 mL, 13 mmol, 1.6 M in hexane) was added dropwise to a stirred solution of **8** (1.56 g, 10 mmol) and TMEDA (3 mL, 19.5 mmol) in dry THF (50 mL) at –78 °C under a nitrogen atmosphere. After stirring for 15 min, the corresponding alkyl halide (13 mmol) was added dropwise at –78 °C. After stirring for 10 min, the reaction mixture was warmed to temperature T_1 and stirred for time *t* (Table 8). The reaction mixture was cooled to –78 °C, TMEDA (3 mL, 19.5 mmol) and *n*BuLi (8.13 mL, 13 mmol, 1.6 M in hexane) were added dropwise. After 10 min, the corresponding alkyl halide (13 mmol) was added, the solution was stirred at –78 °C for 5 min, warmed to temperature T_2 and stirred until complete as indicated by TLC. The reaction mixture was quenched with saturated NH_4Cl solution. The layers were separated and the aqueous was extracted with diethyl ether (3 × 50 mL). The combined organic extracts were washed with brine, dried with $MgSO_4$, filtered and the solvents evaporated. Purification by column chromatography (EtOAc/hexane, 1:40, gradient to 1:10) gave alkylated sulfones **7d**,**g**,**i**–**k**.

Table 8. Reaction temperatures and times for the preparation of **7d**, **g**,**i**–**k**.

Entry	Halide	Product	T_1 [°C]	*t* [h]	T_2 [°C]
1	*i*BuI	**7d**	room temp.	1	room temp.
2	*i*PrI	**7 g**	–60	4	room temp.
3	BnBr	**7i**	room temp.	1	–78
4	*i*AmI	**7j**	–78	2	–78
5	EtI	**7k**	0	1	room temp.

2,8-Dimethylnon-5-yl Phenyl Sulfone (7j): Yield 1.81 g (61%) as a colorless oil. R_f (EtOAc/hexane, 1:5) = 0.45. IR: $\tilde{\nu}$ = 2955, 2870, 1467, 1447, 1302, 1141, 1084, 757, 726, 691 cm^{-1}. MS (ESI$^+$): *m*/*z* (%) = 615 (10) [2M + Na$^+$], 319 (100) [M + Na$^+$]. $C_{17}H_{28}O_2S$ (296.47): calcd. C 68.87, H 9.52, S 10.82; found C 68.81, H 9.55, S 10.71. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.77 (2×d, *J* = 6.7 Hz, 12 H), 1.13 (m, 2 H), 1.24 (m, 2 H), 1.47 (m, 2 H), 1.52 (m, 2 H), 1.79 (m, 2 H), 2.86 (m, 1 H), 7.49 (m, 2 H), 7.59 (m, 1 H), 7.82 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.3 (q), 22.6 (q), 25.6 (t), 28.0 (d), 35.9 (t), 65.1 (d), 128.9 (d), 129.2 (d), 133.6 (d), 138.5 (s) ppm.

***ortho*- to α-Rearrangement of 7a–l and Deuteration:** The respective additive (TMEDA, HMPA) (1 mmol, 3 mmol) and base (0.55 mmol) were added to a stirred solution of sulfone **7a**–**l** (0.5 mmol) in THF (5 mL) at –78 °C. After 10 min at –78 °C 1 mL of the solution was taken by a syringe and added to a dry capped vial containing D_2O. The product was extracted with diethyl ether (2 mL). The organic extract was dried with $MgSO_4$, filtered and the solvents evaporated. The remaining reaction mixture was placed in a bath at –60 °C and kept for 10 min. Another sample (1 mL) was removed and deuterated as described above. The procedure was repeated at –40 °C, –20 °C and 0 °C. The mass balance was determined to be quantitative for each mixture and the products were analyzed by ^{1}H NMR spectroscopy.

2,6-Dimethylhept-4-yl 2-(1-Hydroxyalkyl)phenyl Sulfones 13a–f (General Procedure): *n*BuLi (0.72 mL, 1.15 mmol, 1.6 M in hexane) was added dropwise to a stirred solution of sulfone **7d** (268 mg, 1 mmol) and TMEDA (0.3 mL, 1.95 mmol) in dry THF (5 mL) at –78 °C under a nitrogen atmosphere. After stirring for 15 min, the aldehyde or ketone (1.2 mmol) in THF (2.5 mL) was added dropwise at –78 °C. The reaction mixture was stirred for 3 h until complete as indicated by TLC, quenched with water and warmed to room temperature. The layers were separated and the aqueous was extracted with diethyl ether (3 × 20 mL). The combined organic extracts were washed with brine, dried with $MgSO_4$, filtered and the solvents evaporated. Purification by column chromatography (EtOAc/hexane, 1:20) gave sulfones **13a**–**f**.

2,6-Dimethylhept-4-yl 2-(1-Hydroxybenzyl)phenyl Sulfone (13a): Yield 315 mg (84%) as colorless crystals, m.p. 99–100 °C. R_f (EtOAc/hexane, 1:5) = 0.45. IR: $\tilde{\nu}$ = 3435, 2950, 1468, 1441, 1388, 1371, 1296, 1278, 1141, 1114, 954, 765 cm^{-1}. MS (ESI$^+$): *m*/*z* (%) = 771 (40) [2M + Na$^+$], 397 (25) [M + Na$^+$], 392 (100) [M$^+$ + H_2O]. $C_{22}H_{30}O_3S$ (374.54): calcd. C 70.55, H 8.07, S 8.56; found C 70.53, H 8.10, S 8.69. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.70 (d, *J* = 6.5 Hz, 3 H), 0.78 (d, *J* = 6.5 Hz, 3 H), 0.83 (d, *J* = 6.5 Hz, 3 H), 0.87 (d, *J* = 6.5 Hz, 3 H), 1.41 (m, 2 H), 1.54 (m, 1 H), 1.69 (m, 2 H), 1.82 (m, 1 H), 3.21 (tt, *J* = 7.1, 5.1 Hz, 1 H), 3.35 (d, *J* = 4.6 Hz, 1 H), 6.71 (d, *J* = 4.6 Hz, 1 H), 7.35 (m, 7 H), 7.53 (dd, *J* = 7.6, 1.4 Hz, 1 H), 8.00 (dd, *J* = 7.9, 1.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.1 (q), 22.3 (q), 23.12 (q), 23.14 (q), 25.8 (d), 25.9 (d), 38.1 (t), 38.8 (t), 61.8 (d), 71.1 (d), 127.5 (d), 128.3 (d), 128.4 (d), 129.2 (d), 131.2 (d), 132.2 (d), 134.9 (d), 137.1 (s), 142.4 (s), 144.9 (s) ppm.

2,6-Dimethylhept-4-yl 2-(1-Hydroxyisobutyl)phenyl Sulfone (13b): Yield 306 mg (90%) as colorless crystals, m.p. 44–46 °C. R_f (EtOAc/hexane, 1:5) = 0.44. IR: $\tilde{\nu}$ = 3495, 2960, 1468, 1336, 1295, 1143, 1131, 1026, 744, 723 cm^{-1}. MS (ESI+): *m*/*z* (%) = 363 (100) [M + Na$^+$]. $C_{19}H_{32}O_3S$ (340.52): calcd. C 67.02, H 9.47, S 9.42; found C 67.27, H 9.43, S 9.54. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.71 (d, *J* = 6.3 Hz, 3 H), 0.77 (m, 6 H), 0.85 (2×d, *J* = 6.3 Hz, 6 H), 1.11 (d, *J* = 6.5 Hz, 3 H), 1.39 (m, 4 H), 1.68 (m, 2 H), 2.22 (m, 1 H), 2.66 (d, *J* = 4.9 Hz, 1 H), 3.16 (tt, *J* = 7.3, 4.9 Hz, 1 H), 5.01 (dd, *J* = 4.9, 8.4 Hz, 1 H), 7.45 (m, 1 H), 7.63 (m, 2 H), 7.95 (dd, *J* = 8.0, 1.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.0 (q), 20.1 (q), 22.1 (q), 22.2 (q), 23.0 (q), 23.1 (q), 25.8 (d), 25.9 (d), 33.8 (d), 38.3 (t), 38.7 (t), 61.7 (d), 75.2 (d), 127.8 (d), 128.7 (d), 131.4 (d), 134.0 (d), 136.7 (s), 144.3 (s) ppm.

(*E*)-2,6-Dimethylhept-4-yl 2-(1-Hydroxypent-2-enyl)phenyl Sulfone (13c): Yield 279 mg (79%) as a colorless oil. R_f (EtOAc/hexane, 1:5) = 0.25. IR: $\tilde{\nu}$ = 3496, 2957, 2931, 1468, 1379, 1289, 1136, 1113, 998, 762 cm^{-1}. MS (ESI+): *m*/*z* (%) = 375 (100) [M + Na$^+$]. $C_{20}H_{32}O_3S$ (352.53): calcd. C 68.14, H 9.15, S 9.10; found C 67.97, H 9.29, S 9.07. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.66 (d, *J* = 6.5 Hz, 3 H), 0.77 (d, *J* = 6.5 Hz, 3 H), 0.81 (d, *J* = 6.5 Hz, 3 H), 0.86 (d, *J* = 6.5 Hz, 3 H), 0.97 (t, *J* = 7.5 Hz, 3 H), 1.37 (m, 2 H), 1.50 (m, 1 H), 1.56–1.84 (m, 3 H), 2.07 (m, 2 H), 2.95 (br. s, 1 H), 3.21 (m, 1 H), 5.70 (dd, *J* = 5.9, 15.4 Hz, 1 H), 5.88 (dt, *J* = 6.2, 15.4 Hz, 1 H), 6.00 (m, 1 H), 7.41 (m, 1 H), 7.59 (m, 1 H), 7.67 (m, 1 H), 7.91 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.7 (q), 22.0 (q), 22.2 (q), 23.0 (q), 23.1 (q), 25.4 (t), 25.78 (d),

25.81 (d), 38.2 (t), 38.7 (t), 61.6 (d), 69.7 (d), 127.9 (d), 128.3 (d), 129.8 (d), 131.3 (d), 134.1 (d), 134.9 (d), 135.9 (s), 144.1 (s) ppm.

2,6-Dimethylhept-4-yl 2-(1-Hydroxy-3-phenylpropyl)phenyl Sulfone (13d): Yield 374 mg (93%) as a colorless oil. R_f (EtOAc/hexane, 1:5) = 0.35. IR: $\tilde{\nu}$ = 3498, 2957, 1468, 1454, 1331, 1295, 1140, 1115, 1058, 747, 725 cm^{-1}. MS (ESI+): *m*/*z* (%) = 425 (100) [M + Na$^+$]. $C_{24}H_{34}O_3S$ (402.59): calcd. C 71.60, H 8.51, S 7.96; found C 71.43, H 8.55, S 7.77. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.73 (d, *J* = 6.4 Hz, 3 H), 0.82 (d, *J* = 6.4 Hz, 3 H), 0.87 (d, *J* = 6.4 Hz, 3 H), 0.92 (d, *J* = 6.4 Hz, 3 H), 1.41 (m, 2 H), 1.57 (m, 1 H), 1.62–1.86 (m, 3 H), 2.13 (m, 1 H), 2.27 (m, 1 H), 2.75 (m, 1 H), 3.00 (m, 2 H), 3.15 (m, 1 H), 5.46 (m, 1 H), 7.25 (m, 5 H), 7.47 (m, 1 H), 7.65 (m, 1 H), 7.75 (m, 1 H), 7.99 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.9 (q), 22.1 (q), 22.8 (q), 22.9 (q), 25.5 (d), 25.6 (d), 32.8 (t), 38.2 (t), 38.5 (t), 39.4 (t), 61.5 (d), 69.2 (d), 126.0 (d), 128.1 (d), 128.5 (d), 128.7 (d, 2 C), 131.2 (d), 133.4 (d), 135.7 (s), 141.5 (s), 144.9 (s) ppm.

2,6-Dimethylhept-4-yl 2-(1-Hydroxycyclohexyl)phenyl Sulfone (13e): Yield 312 mg (85%) as a colorless oil. R_f (EtOAc/hexane, 1:5) = 0.44. IR: $\tilde{\nu}$ = 3495, 2955, 2930, 1468, 1386, 1288, 1267, 1133, 1112, 994, 768, 745 cm^{-1}. MS (ESI+): *m*/*z* (%) = 389 (30) [M + Na$^+$], 349 (100) [M – OH$^-$], 223 (20) [M + H$^+$ – OH – CH(*i*Bu)$_2$]. $C_{21}H_{34}O_3S$ (366.56): calcd. C 68.81, H 9.35, S 8.75; found C 68.87, H 9.23, S 8.97. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.70 (d, *J* = 6.2 Hz, 6 H), 0.78 (d, *J* = 6.2 Hz, 6 H), 1.32 (m, 2 H), 1.54 (m, 4 H), 1.65–1.89 (m, 10 H), 4.21 (m, 1 H), 4.53 (s, 1 H), 7.30 (ddd, *J* = 8.1, 6.7, 1.8 Hz, 1 H), 7.48 (m, 2 H), 8.07 (dd, *J* = 8.1, 1.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.9 (t), 22.3 (q), 23.0 (q), 25.7 (t), 25.9 (d, 2 C), 38.8 (t, 2 C), 40.1 (t), 61.9 (d), 75.3 (s), 126.7 (d), 129.2 (d), 133.1 (d), 133.2 (d), 136.7 (s), 152.2 (s) ppm.

2,6-Dimethylhept-4-yl 2-(1-Hydroxy-1-phenylbenzyl)phenyl Sulfone (13f): Yield 424 mg (94%) as colorless crystals, m.p. 112–113 °C. R_f (EtOAc/hexane, 1:5) = 0.59. IR: $\tilde{\nu}$ = 3403, 2955, 1467, 1441, 1383, 1291, 1167, 1113, 1072, 1043, 956, 765, 748 cm^{-1}. MS (ESI+): *m*/*z* (%) = 473 (100) [M + Na$^+$], 329 (40) [M + Na$^+$ – OH – CH(*i*Bu)$_2$], 307 (30) [M + H$^+$ – OH – CH(*i*Bu)$_2$]. HRMS (ESI+): *m*/*z* [M + Na$^+$] calcd. for $C_{28}H_{34}O_3SNa^+$: 473.2121, found 473.2120. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.74 (d, *J* = 6.6 Hz, 6 H), 0.87 (d, *J* = 6.6 Hz, 6 H), 1.35 (m, 2 H), 1.52 (m, 2 H), 1.74 (m, 2 H), 3.75 (m, 1 H), 6.30 (s, 1 H), 6.88 (dd, *J* = 7.9, 1.3 Hz, 1 H), 7.08 (m, 4 H), 7.23 (m, 6 H), 7.35 (td, *J* = 7.9, 1.5 Hz, 1 H), 7.41 (td, *J* = 7.9, 1.3 Hz, 1 H), 8.14 (dd, *J* = 7.9, 1.5 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.3 (q), 23.1 (q), 25.8 (d, 2 C), 38.4 (t), 38.5 (t), 62.6 (d), 83.4 (s), 127.6 (d), 127.7 (d), 128.1 (d), 128.2 (d), 132.4 (d), 133.7 (d), 134.0 (d), 137.2 (s), 147.4 (s), 148.2 (s) ppm.

(2-Hydroxyalkyl) Phenyl Sulfones 14a–e (General Procedure): *n*BuLi (0.41 mL, 0.65 mmol, 1.6 M in hexane) was added dropwise to a stirred solution of sulfone **7k** (106 mg, 0.5 mmol) and TMEDA (0.15 mL, 0.98 mmol) in dry THF (4 mL) at –78 °C under a nitrogen atmosphere. After stirring for 10 min, the aldehyde (0.7 mmol) in THF (2 mL) was added dropwise at –78 °C. The reaction mixture was warmed to 0 °C, stirred at this temperature for 1 h until complete as indicated by TLC and quenched with water. The layers were separated and the aqueous was extracted with diethyl ether (3 × 20 mL). The combined organic extracts were washed with brine, dried with $MgSO_4$, filtered and the solvents evaporated. Purification by column chromatography (EtOAc/hexane, 1:50) gave sulfones **14a**–**e**.

2-Ethyl-1-phenyl-2-(phenylsulfonyl)butan-1-ol (14a): Yield 127 mg (80%) as colorless crystals, m.p. 119–121 °C. R_f (EtOAc/hexane, 1:5) = 0.30. IR: $\tilde{\nu}$ = 3488, 2975, 2943, 1447, 1281, 1143, 1073, 722, 691 cm^{-1}. MS (ESI+): *m*/*z* (%) = 341 (100) [M + Na$^+$], 199 (20) [M + Na$^+$ – PhSO$_2$H], 165 (20) [PhSO$_2$H + Na$^+$]. $C_{18}H_{22}O_3S$ (318.43): calcd. C 67.89, H 6.96, S 10.07; found C 67.91, H 7.11, S 9.89. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.58 (t, *J* = 7.4 Hz, 3 H), 1.12 (t, *J* = 7.5 Hz, 3 H), 1.47 (dq, *J* = 7.5, 15.0 Hz, 1 H), 1.72 (dq, *J* = 7.4, 15.0 Hz, 1 H), 1.96 (dq, *J* = 7.5, 15.1 Hz, 1 H), 2.21 (dq, *J* = 7.5, 15.1 Hz, 1 H), 4.19 (d, *J* = 2.5 Hz, 1 H), 4.92 (d, *J* = 2.5 Hz, 1 H), 7.22 (m, 5 H), 7.54 (m, 2 H), 7.65 (m, 1 H), 7.90 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.5 (q), 9.4 (q), 19.5 (t), 24.0 (t), 74.1 (d), 76.1 (s), 128.1 (d), 128.38 (d), 128.41 (d), 129.0 (d), 130.2 (d), 133.9 (d), 137.5 (s), 139.1 (s) ppm.

1-(4-Bromophenyl)-2-ethyl-2-(phenylsulfonyl)butan-1-ol (14b): Yield 129 mg (65%) as colorless crystals, m.p. 119–121 °C. R_f (EtOAc/hexane, 1:5) = 0.22. IR: $\tilde{\nu}$ = 3487, 2981, 2940, 1485, 1446, 1281, 1144, 1073, 1010, 725, 690 cm^{-1}. MS (ESI+): *m*/*z* (%) = 419/417 (100/100) [M + Na$^+$], 165 (40) [PhSO$_2$H + Na$^+$]. $C_{18}H_{21}BrO_3S$ (396.33): calcd. C 54.41, H 5.33, S 8.07, Br 20.11; found C 54.41, H 5.33, S 7.98, Br 20.21. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.67 (t, *J* = 7.4 Hz, 3 H), 1.10 (t, *J* = 7.5 Hz, 3 H), 1.53 (dq, *J* = 7.4, 14.8 Hz, 1 H), 1.69 (dq, *J* = 7.4, 14.8 Hz, 1 H), 1.92 (dq, *J* = 7.5, 15.0 Hz, 1 H), 2.16 (dq, *J* = 7.5, 15.0 Hz, 1 H), 4.32 (d, *J* = 2.5 Hz, 1 H), 4.90 (d, *J* = 2.5 Hz, 1 H), 7.15 (m, 2 H), 7.39 (m, 2 H), 7.56 (m, 2 H), 7.67 (m, 1 H), 7.90 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.7 (q), 9.5 (q), 19.8 (t), 24.1 (t), 73.9 (d), 75.8 (s), 122.0 (s), 129.1 (d), 130.2 (d), 130.3 (d), 131.3 (d), 134.1 (d), 137.4 (s), 138.3 (s) ppm.

4-Ethyl-2-methyl-4-(phenylsulfonyl)hexan-3-ol (14c): Yield 100 mg (70%) as colorless crystals, m.p. 90–91 °C. R_f (EtOAc/hexane, 1:5) = 0.29. IR: $\tilde{\nu}$ = 3515, 2966, 2886, 1446, 1278, 1120, 1073, 1016, 758, 721, 690 cm^{-1}. MS (ESI+): *m*/*z* (%) = 307 (100) [M + Na$^+$], 165 (40) [PhSO$_2$H + Na$^+$]. $C_{15}H_{24}O_3S$ (284.41): calcd. C 63.34, H 8.51, S 11.27; found C 63.53, H 8.48, S 11.25. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (2×t, *J* = 7.5 Hz, 6 H), 1.04 (2×d, *J* = 6.6 Hz, 6 H), 1.54 (dq, *J* = 7.5, 14.8 Hz, 1 H), 1.83 (dq, *J* = 7.5, 15.1 Hz, 1 H), 2.03 (dq, *J* = 7.5, 14.8 Hz, 2 H), 2.21 (m, 1 H), 3.19 (d, *J* = 7.8 Hz, 1 H), 3.80 (dd, *J* = 3.0, 7.8 Hz, 1 H), 7.51 (m, 2 H), 7.61 (m, 1 H), 7.87 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.9 (q), 9.1 (q), 17.6 (q), 23.3 (t), 24.3 (q), 24.9 (t), 29.5 (d), 74.4 (s), 77.8 (d), 128.9 (d), 130.2 (d), 133.8 (d), 138.8 (s) ppm.

(*E*)-3-Ethyl-3-(phenylsulfonyl)oct-5-en-4-ol (14d): Yield 96 mg (64%) as colorless crystals, m.p. 65–66 °C. R_f (EtOAc/hexane, 1:5) = 0.32. IR: $\tilde{\nu}$ = 3493, 2969, 2939, 1446, 1281, 1131, 1075, 971, 721, 691, 604 cm^{-1}. MS (ESI+): *m*/*z* (%) = 319 (100) [M + Na$^+$], 165 (30) [PhSO$_2$H + Na$^+$]. $C_{16}H_{24}O_3S$ (296.42): calcd. C 64.83, H 8.16, S 10.82; found C 64.94, H 8.24, S 10.52. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.96 (m, 9 H), 1.61 (dq, *J* = 7.4, 14.8 Hz, 1 H), 1.80 (dq, *J* = 7.5, 15.1 Hz, 1 H), 1.94 (m, 4 H), 3.47 (d, *J* = 6.1 Hz, 1 H), 4.34 (t, *J* = 6.1 Hz, 1 H), 5.55 (ddt, *J* = 1.4, 6.2, 15.2 Hz, 1 H), 5.71 (dtd, *J* = 0.8, 7.1, 15.2 Hz, 1 H), 7.50 (m, 2 H), 7.60 (m, 1 H), 7.86 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.5 (q), 8.8 (q), 13.3 (q), 22.0 (t), 23.6 (t), 25.5 (t), 73.4 (s), 74.8 (d), 126.7 (d), 128.8 (d), 130.4 (d), 133.8 (d), 136.9 (d), 138.3 (s) ppm.

(*E*)-4-Ethyl-1-phenyl-4-(phenylsulfonyl)hex-1-en-3-ol (14e): Yield 122 mg (71%) as colorless crystals, m.p. 85–86 °C. R_f (EtOAc/hexane, 1:5) = 0.20. IR: $\tilde{\nu}$ = 3491, 2974, 2943, 2886, 1446, 1361, 1279, 1133, 1073, 969, 755, 721, 690, 604 cm^{-1}. MS (ESI+): *m*/*z* (%) = 367 (100) [M + Na$^+$], 327 (10) [M – OH$^-$]. $C_{20}H_{24}O_3S$ (344.15): calcd. C 69.73, H 7.02, S 9.31; found C 69.67, H 6.89, S 9.13. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.05 (m, 6 H), 1.77 (dq, *J* = 7.4, 15.0 Hz, 1 H), 1.88 (dq, *J* = 7.6, 15.1 Hz, 1 H), 2.04 (m, 2 H), 3.69 (d, *J* = 6.6 Hz, 1 H), 4.56 (td, *J* = 1.3, 6.6 Hz, 1 H), 6.28 (dd, *J* = 6.6, 15.8 Hz, 1 H), 6.64 (dd, *J* = 1.3, 15.8 Hz, 1 H), 7.27 (m, 5 H),

7.48 (m, 2 H), 7.61 (m, 1 H), 7.89 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.5 (q), 8.7 (q), 22.2 (t), 23.2 (t), 73.6 (s), 74.6 (d), 126.7 (d), 127.1 (d), 127.9 (d), 128.6 (d), 128.7 (d), 130.3 (d), 132.9 (d), 133.7 (d), 136.4 (s), 138.0 (s) ppm.

2-Hydroxyalkyl Phenyl Sulfones 15a–f (General Procedure). Condition A: *n*BuLi (0.27 mL, 0.43 mmol, 1.6 M in hexane) was added dropwise to a stirred solution of sulfone **7d** (100 mg, 0.37 mmol) and TMEDA (0.1 mL, 0.65 mmol) in dry THF (4 mL) at –78 °C under a nitrogen atmosphere. After stirring for 10 min, the reaction mixture was warmed to 0 °C during 1 h, followed by dropwise addition of the aldehyde (0.44 mmol) in THF (2 mL) at –78 °C. The reaction mixture was warmed to –20 °C, stirred at this temperature until complete as indicated by TLC, quenched with water and warmed to room temperature. The layers were separated and the aqueous was extracted with diethyl ether (3 × 20 mL). The combined organic extracts were washed with brine, dried with $MgSO_4$, filtered and the solvents evaporated. Purification by column chromatography (EtOAc/hexane, 1:20) gave sulfones **15a**–**f**.

Condition B: *n*BuLi (0.27 mL, 0.43 mmol, 1.6 M in hexane) was added dropwise to a stirred solution of sulfone **7d** (100 mg, 0.37 mmol) and TMEDA (0.1 mL, 0.65 mmol) in dry THF (4 mL) at –20 °C under a nitrogen atmosphere. After stirring for 10 min, the aldehyde (0.44 mmol) in THF (2 mL) was added dropwise at –78 °C. The reaction mixture was warmed to –20 °C, stirred at this temperature until complete as indicated by TLC, quenched with water and warmed to room temperature. The layers were separated and the aqueous was extracted with diethyl ether (3 × 20 mL). The combined organic extracts were washed with brine, dried with $MgSO_4$, filtered and the solvents evaporated. Purification by column chromatography (EtOAc/hexane, 1:20) gave sulfones **15a**,**d**,**f**.

Condition C: *n*BuLi (0.27 mL, 0.43 mmol, 1.6 M in hexane) was added dropwise to a stirred solution of sulfone **7d** (100 mg, 0.37 mmol) and HMPA (0.4 mL, 2.22 mmol) in dry THF (4 mL) at –78 °C under a nitrogen atmosphere. After stirring for 10 min, the aldehyde (0.44 mmol) in THF (2 mL) was added dropwise at –78 °C. The reaction mixture was stirred at this temperature until complete as indicated by TLC, quenched with water and warmed to room temperature. The layers were separated and the aqueous was extracted with diethyl ether (3 × 20 mL). The combined organic extracts were washed with brine, dried with $MgSO_4$, filtered and the solvents evaporated. Purification by column chromatography (EtOAc/hexane, 1:20) gave sulfones **15a–f**.

2-Isobutyl-4-methyl-1-phenyl-2-(phenylsulfonyl)pentan-1-ol (15a): Yield 104 mg (75%, condition C) as a colorless oil. R_f (EtOAc/hexane, 1:5) = 0.37. IR: $\tilde{\nu}$ = 3476, 2961, 2870, 1470, 1446, 1389, 1280, 1123, 1075, 751, 723, 690, 631 cm^{-1}. MS (ESI+): *m*/*z* (%) = 397 (100) [M + Na^+], 256 (60) [M – $PhSO_2$ + Na^+], 165 (20) [$PhSO_2H$ + Na^+]. $C_{22}H_{30}O_3S$ (374.54): calcd. C 70.55, H 8.07, S 8.56; found C 70.26, H 8.03, S 8.39. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.78 (d, *J* = 6.6 Hz, 3 H), 0.83 (d, *J* = 6.5 Hz, 3 H), 1.06 (2×d, *J* = 6.5 Hz, 6 H), 1.37 (dd, *J* = 4.2, 15.0 Hz, 1 H), 1.52 (dd, *J* = 6.0, 15.0 Hz, 1 H), 1.71 (m, 1 H), 1.88 (dd, *J* = 5.4, 15.4 Hz, 1 H), 1.96 (dd, *J* = 4.6, 15.4 Hz, 1 H), 2.43 (m, 1 H), 4.00 (d, *J* = 3.3 Hz, 1 H), 5.16 (d, *J* = 3.3 Hz, 1 H), 7.31 (m, 3 H), 7.36 (m, 2 H), 7.49 (t, *J* = 7.8 Hz, 2 H), 7.62 (m, 1 H), 7.83 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.60 (d), 23.63 (d), 25.5 (q), 25.9 (q), 26.1 (q), 26.1 (q), 38.7 (t), 41.8 (t), 76.2 (s), 76.8 (d), 128.2 (d), 128.6 (d), 128.7 (d), 129.2 (d), 130.5 (d), 133.7 (d), 138.7 (s), 139.4 (s) ppm.

1-(4-Bromophenyl)-2-isobutyl-4-methyl-2-(phenylsulfonyl)pentan-1-ol (15b): Yield 80 mg (48%, condition C) as a colorless solid, m.p. 109–110 °C. R_f (EtOAc/hexane, 1:5) = 0.30. IR: $\tilde{\nu}$ = 3478, 2961, 2931, 2870, 1488, 1472, 1446, 1282, 1125, 1075, 1011, 759, 730, 690 cm^{-1}. MS (ESI+): *m*/*z* (%) = 931/929/927 (15/30/15) [2M + Na^+], 477/475 (95/100) [M + Na^+], 165 (40) [$PhSO_2H$ + Na^+]. $C_{22}H_{29}BrO_3S$ (452.43): calcd. C 58.27, H 6.45, S 7.07, Br 17.62; found C 58.56, H 6.39, S 7.32, Br 17.84. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.81 (d, *J* = 6.6 Hz, 3 H), 0.87 (d, *J* = 6.5 Hz, 3 H), 1.05 (d, *J* = 6.5 Hz, 6 H), 1.36 (dd, *J* = 4.1, 15.0 Hz, 1 H), 1.51 (dd, *J* = 6.1, 15.0 Hz, 1 H), 1.67 (m, 1 H), 1.83 (dd, *J* = 5.4, 15.4 Hz, 1 H), 1.91 (dd, *J* = 4.6, 15.4 Hz, 1 H), 2.39 (m, 1 H), 4.14 (d, *J* = 3.3 Hz, 1 H), 5.09 (d, *J* = 3.3 Hz, 1 H), 7.24 (m, 2 H), 7.46 (m, 2 H), 7.54 (m, 2 H), 7.66 (m, 1 H), 7.85 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.8 (d), 24.0 (d), 25.5 (q), 25.9 (q), 26.1 (q), 26.2 (q), 38.9 (t), 41.8 (t), 75.9 (s), 76.5 (d), 122.7 (s), 128.9 (d), 129.1 (d), 130.5 (d), 131.0 (d), 133.9 (d), 138.5 (s), 138.6 (s) ppm.

1-(3-Bromophenyl)-2-isobutyl-4-methyl-2-(phenylsulfonyl)pentan-1-ol (15c): Yield 106 mg (63%, condition C) as a colorless solid, m.p. 81–82 °C. R_f (EtOAc/hexane, 1:5) = 0.39. IR: $\tilde{\nu}$ = 3488, 2961, 2871, 1668, 1473, 1457, 1447, 1389, 1282, 1129, 1075, 759, 728, 690 cm^{-1}. MS (ESI+): *m*/*z* (%) = 477/475 (100/98) [M + Na^+], 165 (40) [$PhSO_2H$ + Na^+]. $C_{22}H_{29}BrO_3S$ (452.43): calcd. C 58.27, H 6.45, S 7.07, Br 17.62; found C 58.44, H 6.47, S 6.96, Br 17.94. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85 (2×d, *J* = 6.6 Hz, 6 H), 1.07 (2×d, *J* = 6.6 Hz, 6 H), 1.39 (dd, *J* = 4.6, 15.0 Hz, 1 H), 1.47 (dd, *J* = 5.6, 15.0 Hz, 1 H), 1.66 (m, 1 H), 1.85 (dd, *J* = 5.4, 15.4 Hz, 1 H), 1.92 (dd, *J* = 4.6, 15.4 Hz, 1 H), 2.41 (m, 1 H), 4.20 (d, *J* = 3.0 Hz, 1 H), 5.08 (d, *J* = 3.0 Hz, 1 H), 7.19 (t, *J* = 7.8 Hz, 1 H), 7.33 (d, *J* = 7.9 Hz, 1 H), 7.44 (m, 1 H), 7.51 (t, *J* = 1.7 Hz, 1 H), 7.56 (t, *J* = 7.7 Hz, 2 H), 7.67 (m, 1 H), 7.89 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.5 (d), 23.8 (d), 25.3 (q), 25.6 (q), 25.9 (q), 26.0 (q), 38.5 (t), 41.7 (t), 75.5 (s), 76.3 (d), 122.7 (s), 127.6 (d), 128.7 (d), 129.5 (d), 130.3 (d), 131.5 (d), 132.1 (d), 133.8 (d), 138.2 (s), 141.5 (s) ppm.

4-Isobutyl-6-methyl-1-phenyl-4-(phenylsulfonyl)heptan-3-ol (15d): Yield 123 mg (61%, condition A) as a colorless oil. R_f (EtOAc/hexane, 1:5) = 0.46. IR: $\tilde{\nu}$ = 3509, 3085, 2960, 2925, 1603, 1584, 1496, 1469, 1446, 1388, 1279, 1123, 1075, 1000, 931, 755 cm^{-1}. MS (ESI+): *m*/*z* (%) = 425 (95) [M + Na^+], 283 (100) [M + Na^+ – $PhSO_2H$]. HRMS (ESI+): *m*/*z* [M + Na^+] calcd. for $C_{24}H_{34}O_3SNa^+$: 425.2121, found 425.2120. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.75 (d, *J* = 6.6 Hz, 3 H), 0.87 (d, *J* = 6.5 Hz, 3 H), 0.88 (d, *J* = 6.4 Hz, 3 H), 0.99 (d, *J* = 6.4 Hz, 3 H), 1.35 (dd, *J* = 5.6, 15.2 Hz, 1 H), 1.60 (dd, *J* = 6.1, 15.3 Hz, 1 H), 1.70 (dd, *J* = 3.9, 15.3 Hz, 1 H), 1.86 (m, 1 H), 1.89–2.09 (m, 4 H), 2.62 (m, 1 H), 2.97 (m, 1 H), 3.20 (d, *J* = 6.6 Hz, 1 H), 4.19 (m, 1 H), 7.17 (m, 3 H), 7.25 (m, 2 H), 7.49 (t, *J* = 7.7 Hz, 2 H), 7.58 (m, 1 H), 7.89 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.5 (d), 24.0 (d), 25.3 (q), 25.46 (q), 25.50 (q), 25.7 (q), 33.3 (t), 35.1 (t), 39.4 (t), 41.2 (t), 72.7 (d), 77.4 (s), 126.0 (d), 128.5 (d), 128.6 (d), 128.7 (d), 130.2 (d), 133.5 (d), 139.2 (s), 141.7 (s) ppm.

(*E*)-4-Isobutyl-2-methyl-4-(phenylsulfonyl)non-6-en-5-ol (15e): Yield 80 mg (61%, condition C) as a colorless oil. R_f (EtOAc/hexane, 1:5) = 0.30. IR: $\tilde{\nu}$ = 3489, 2960, 2928, 2871, 1447, 1335, 1284, 1127, 1077, 972, 758, 724, 690 cm^{-1}. MS (ESI+): *m*/*z* (%) = 375 (100) [M + Na^+], 233 (30) [M – $PhSO_2H$ + Na^+], 165 (30) [$PhSO_2H$ + Na^+]. HRMS (ESI+): *m*/*z* [M + Na^+] calcd. for $C_{20}H_{32}O_3SNa^+$: 375.1964, found 375.1964. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (3×d+t, *J* = 6.5 Hz, 12 H), 0.94 (d, *J* = 6.6 Hz, 3 H), 1.45 (dd, *J* = 4.5, 15.0 Hz, 1 H), 1.60 (dd, *J* = 5.6, 15.3 Hz, 1 H), 1.72 (dd, *J* = 4.5, 15.3 Hz, 1 H), 1.79 (dd, *J* = 5.7, 15.0 Hz, 1 H), 2.00 (m, 4 H), 2.90 (d, *J* = 5.0 Hz, 1 H), 4.51 (t, *J* = 4.9 Hz, 1 H), 5.56 (dd, *J* = 5.3, 15.3 Hz, 1 H), 5.72 (dt, *J* = 6.8, 15.3 Hz, 1 H), 7.44 (m, 2 H), 7.54 (m, 1 H), 7.84 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.4 (q), 23.7 (d), 23.9 (d), 25.4 (q), 25.6 (t), 25.7 (q),

25.9 (q), 26.0 (q), 39.1 (t), 40.9 (t), 74.7 (d), 75.9 (s), 127.0 (d), 128.7 (d), 130.7 (d), 133.6 (d), 137.4 (d), 139.3 (s) ppm.

(*E*)-4-Isobutyl-6-methyl-1-phenyl-4-(phenylsulfonyl)hept-1-en-3-ol (15f): Yield 145 mg (98%, condition C) as a colorless oil. R_f (EtOAc/hexane, 1:5) = 0.32. IR: $\tilde{\nu}$ = 3479, 2960, 2870, 1447, 1281, 1124, 1075, 972, 752, 724, 691 cm^{-1}. MS (ESI+): *m*/*z* (%) = 824 (20), 423 (100) [M + Na^+], 281 (40) [M – $PhSO_2H$ + Na^+], 165 (10) [$PhSO_2H$ + Na^+]. $C_{24}H_{32}O_3S$ (400.57): calcd. C 71.96, H 8.05, S 8.00; found C 71.74, H 7.77, S 8.27. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (2×d, *J* = 6.6 Hz, 6 H), 0.92 (d, *J* = 6.7 Hz, 3 H), 0.99 (d, *J* = 6.6 Hz, 3 H), 1.58 (dd, *J* = 4.6, 15.0 Hz, 1 H), 1.65 (dd, *J* = 5.6, 15.3 Hz, 1 H), 1.78 (dd, *J* = 4.5, 15.3 Hz, 1 H), 1.92 (dd, *J* = 5.7, 15.0 Hz, 1 H), 2.05 (m, 2 H), 3.18 (s, 1 H), 4.76 (d, *J* = 6.0 Hz, 1 H), 6.28 (dd, *J* = 6.3, 15.7 Hz, 1 H), 6.63 (dd, *J* = 1.3, 15.7 Hz, 1 H), 7.15–7.28 (m, 5 H), 7.40 (t, *J* = 7.8 Hz, 2 H), 7.53 (m, 1 H), 7.85 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.6 (d), 23.9 (d), 25.3 (q), 25.5 (q), 25.7 (q), 25.9 (q), 39.2 (t), 40.6 (t), 74.2 (d), 76.1 (s), 126.7 (d), 127.3 (d), 128.0 (d), 128.5 (d), 128.6 (d), 130.6 (d), 133.4 (d), 133.5 (d), 136.5 (s), 139.0 (s) ppm.

(*E*)-2-Benzyl-5-phenyl-2-pentenal (16): For yields see Table 5, colorless oil. R_f (EtOAc/hexane, 1:5) = 0.54. IR: $\tilde{\nu}$ = 3085, 3062, 3027, 1685, 1638, 1602, 1584, 1495, 1453, 1289, 1030, 1002, 698 cm^{-1}. MS (ESI+): *m*/*z* (%) = 525 (25), 273 (100) [M + Na^+]. HRMS (ESI+): *m*/*z* [M + Na^+] calcd. for $C_{18}H_{18}ONa^+$: 273.1250, found 273.1251. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.70 (m, 4 H), 3.54 (s, 2 H), 6.59 (m, 1 H), 7.10 (m, 5 H), 7.18 (m, 3 H), 7.26 (m, 2 H), 9.40 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.1 (t), 31.2 (t), 34.4 (t), 126.3 (d), 126.6 (d), 128.52 (d), 128.55 (d), 128.7 (d), 128.8 (d), 139.3 (s), 140.1 (s), 143.1 (s), 154.8 (d), 194.8 (d) ppm.

2-Benzoyloxy Sulfones 17a–f (General Procedure): *n*BuLi (0.37 mL, 0.6 mmol, 1.6 M in hexane) was added dropwise to a stirred solution of sulfone **7k** (106 mg, 0.5 mmol) and TMEDA (0.15 mL, 0.98 mmol) in dry THF (5 mL) at –78 °C under a nitrogen atmosphere. After stirring for 10 min, the aldehyde (0.6 mmol) in THF (2 mL) was added dropwise at –78 °C. The reaction mixture was slowly warmed to 0 °C and stirred until complete as indicated by TLC. Benzoyl chloride (75 μL, 0.65 mmol) was added at –78 °C. After 20 min, 3-(dimethylamino)propan-1-ol (88 μL, 0.75 mmol) was added. After 10 min, the reaction was quenched with water. The layers were separated and the aqueous was extracted with diethyl ether (3 × 20 mL). The combined organic extracts were washed successively with 1 M HCl, 5% $NaHCO_3$ and brine solutions, dried with $MgSO_4$, filtered and the solvents evaporated. Purification by column chromatography (EtOAc/hexane, 1:20) gave benzoyloxy sulfones **17a**–**f**.

2-Ethyl-1-phenyl-2-(phenylsulfonyl)but-1-yl Benzoate (17a): Yield 186 mg (88%) as a colorless solid, m.p. 120–121 °C. R_f (EtOAc/hexane, 1:5) = 0.21. IR: $\tilde{\nu}$ = 2981, 2946, 1724, 1450, 1294, 1264, 1145, 1107, 1089, 1073, 759, 715 cm^{-1}. MS (ESI): *m*/*z* (%) = 445 (100) [M + Na^+], 303 (70) [M – $PhSO_2H$ + Na^+]. HRMS (ESI+): *m*/*z* [M + Na^+] calcd. for $C_{25}H_{26}O_4SNa^+$: 445.1444, found 445.1443. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.5 Hz, 3 H), 1.26 (t, *J* = 7.5 Hz, 3 H), 1.95 (dq, *J* = 7.5, 15.1 Hz, 1 H), 1.98 (dq, *J* = 7.5, 15.1 Hz, 1 H), 2.16 (dq, *J* = 7.5, 15.2 Hz, 1 H), 2.38 (dq, *J* = 7.4, 15.2 Hz, 1 H), 6.51 (s, 1 H), 7.26 (m, 2 H), 7.27–7.30 (m, 3 H), 7.34 (m, 3 H), 7.38 (m, 2 H), 7.53 (m, 1 H), 7.73 (m, 2 H), 7.77 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.8 (q), 9.0 (q), 22.4 (t), 23.1 (t), 74.2 (s), 76.8 (d), 128.17 (d), 128.24 (d), 128.3 (d), 128.6 (d, 2 C), 129.58 (d), 129.63 (d), 129.72 (s), 133.0 (s), 133.1 (d), 136.8 (s), 138.8 (s), 164.4 (s) ppm.

1-(4-Bromophenyl)-2-ethyl-2-(phenylsulfonyl)butyl Benzoate (17b): Yield 218 mg (87%) as colorless crystals, m.p. 150–151 °C. R_f (EtOAc/hexane, 1:5) = 0.44. IR: $\tilde{\nu}$ = 2981, 1725, 1299, 1265, 1146, 1095, 723, 714 cm^{-1}. MS (ESI): *m*/*z* (%) = 638 (40), 525/523 (100/100) [M + Na^+], 383/381 (40/40) [M – $PhSO_2H$ + Na^+]. $C_{25}H_{25}BrO_4S$ (500.44): calcd. C 59.88, H 5.03, S 6.39, Br 15.94; found C 60.06, H 5.11, S 6.22, Br 15.92. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.5 Hz, 3 H), 1.17 (t, *J* = 7.5 Hz, 3 H), 1.93 (m, 3 H), 2.28 (dq, *J* = 7.5, 15.0 Hz, 1 H), 6.42 (s, 1 H), 7.21 (m, 4 H), 7.29 (m, 3 H), 7.36 (m, 2 H), 7.47 (m, 1 H), 7.65 (m, 2 H), 7.68 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.07 (q), 9.12 (q), 21.9 (t), 23.4 (t), 74.1 (s), 76.3 (d), 123.0 (s), 128.5 (d), 128.9 (d), 129.6 (s), 129.7 (d), 129.8 (d), 130.1 (d), 131.6 (d), 133.4 (d), 133.5 (d), 136.1 (s), 138.8 (s), 164.5 (s) ppm.

(*E*)-4-Ethyl-1-phenyl-4-(phenylsulfonyl)hex-1-en-3-yl Benzoate (17c): Yield 198 mg (88%) as colorless crystals, m.p. 140–142 °C. R_f (EtOAc/hexane, 1:5) = 0.26. IR: $\tilde{\nu}$ = 2980, 2888, 1720, 1449, 1299, 1286, 1263, 1144, 1095, 1070, 1025, 965, 756, 713, 691, 603 cm^{-1}. MS (ESI+): *m*/*z* (%) = 471 (100) [M + Na^+], 185 (30) [M – $PhSO_2H$ – $PhCOO^-$]. $C_{27}H_{28}O_4S$ (448.58): calcd. C 72.29, H 6.29, S 7.15; found C 72.58, H 6.39, S 7.34. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.26 (2×t, *J* = 7.5 Hz, 6 H), 2.14 (m, 3 H), 2.34 (dq, *J* = 7.5, 15.0 Hz, 1 H), 6.23 (d, *J* = 7.9 Hz, 1 H), 6.42 (dd, *J* = 7.9, 15.7 Hz, 1 H), 6.81 (d, *J* = 15.7 Hz, 1 H), 7.22–7.45 (m, 9 H), 7.52 (m, 2 H), 7.62 (m, 2 H), 7.94 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.6 (q), 8.8 (q), 22.9 (t), 23.5 (t), 73.4 (s), 75.6 (d), 122.8 (d), 126.9 (d), 128.1 (d), 128.3 (d), 128.6 (d), 128.8 (d), 129.57 (d), 129.64 (s), 130.2 (d), 133.1 (d), 133.2 (d), 135.9 (s), 136.1 (d), 139.2 (s), 164.9 (s) ppm.

4-Ethyl-1-phenyl-4-(phenylsulfonyl)hex-3-yl Benzoate (17d): Yield 205 mg (91%) as a colorless solid, m.p. 126–127 °C. R_f (EtOAc/hexane, 1:5) = 0.36. IR: $\tilde{\nu}$ = 2980, 2871, 1719, 1451, 1387, 1302, 1268, 1177, 1143, 1105, 1077, 1026, 758, 712, 693 cm^{-1}. MS (ESI+): *m*/*z* (%) = 473 (100) [M + Na^+], 331 (60) [M – $PhSO_2H$ + Na^+]. $C_{27}H_{30}O_4S$ (450.59): calcd. C 71.97, H 6.71, S 7.12; found C 71.93, H 6.92, S 6.83. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.08 (t, *J* = 7.5 Hz, 3 H), 1.14 (t, *J* = 7.5 Hz, 3 H), 1.87 (dq, *J* = 7.5, 15.0 Hz, 1 H), 2.10 (m, 3 H), 2.32 (m, 1 H), 2.53 (m, 1 H), 2.68 (m, 1 H), 2.72 (m, 1 H), 5.72 (dd, *J* = 1.7, 10.5 Hz, 1 H), 7.23 (m, 3 H), 7.32 (m, 2 H), 7.39 (t, *J* = 7.8 Hz, 2 H), 7.56 (m, 3 H), 7.66 (m, 3 H), 7.88 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.3 (q), 8.6 (q), 22.3 (t), 23.4 (t), 32.9 (t), 33.4 (t), 73.4 (s), 74.4 (d), 126.1 (d), 128.4 (d), 128.6 (d, 2 C), 128.7 (d), 129.4 (s), 129.7 (d), 130.4 (d), 133.2 (d), 133.4 (d), 138.9 (s), 141.1 (s), 166.0 (s) ppm.

3-Ethyl-3-(phenylsulfonyl)non-4-yl Benzoate (17e): Yield 138 mg (66%) as a colorless oil. R_f (EtOAc/hexane, 1:5) = 0.30. IR: $\tilde{\nu}$ = 2956, 2932, 2859, 1720, 1449, 1301, 1268, 1145, 1105, 1077, 1026, 757, 712, 692 cm^{-1}. MS (ESI+): *m*/*z* (%) = 855 (10) [2M + Na^+], 439 (100) [M + Na^+]. $C_{24}H_{32}O_4S$ (416.57): calcd. C 69.20, H 7.74, S 7.70; found C 69.47, H 7.71, S 8.00. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.82 (t, *J* = 6.8 Hz, 3 H), 1.10 (2×t, *J* = 7.5 Hz, 6 H), 1.16–1.35 (m, 6 H), 1.87 (m, 2 H), 2.01 (m, 3 H), 2.13 (m, 1 H), 5.60 (dd, *J* = 1.9, 10.6 Hz, 1 H), 7.30 (t, *J* = 7.5 Hz, 2 H), 7.49 (m, 3 H), 7.54 (m, 2 H), 7.60 (t, *J* = 7.5 Hz, 1 H), 7.89 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.6 (q), 8.7 (q), 14.2 (q), 22.7 (t), 22.8 (t), 22.9 (t), 26.7 (t), 31.6 (t), 31.8 (t), 73.8 (s), 75.1 (d), 128.4 (d), 129.1 (d), 129.76 (s), 129.82 (d), 130.3 (d), 133.2 (d), 133.5 (d), 139.4 (s), 166.1 (s) ppm.

3-Ethyl-3-(phenylsulfonyl)pentadec-4-yl Benzoate (17f): Yield 208 mg (83%) as a colorless oil. R_f (EtOAc/hexane, 1:5) = 0.40. IR: $\tilde{\nu}$ = 2925, 2854, 1720, 1449, 1302, 1267, 1146, 1077, 1070, 1026, 757, 711, 691 cm^{-1}. MS (ESI+): *m*/*z* (%) = 523 (100) [M + Na^+], 359 (20) [M^+ – $PhSO_2$]. $C_{30}H_{44}O_4S$ (500.73): calcd. C 71.96, H 8.86, S 6.40; found C 71.82, H 8.68, S 6.65. ^1H NMR (400 MHz,

$CDCl_3$): δ = 0.84 (t, J = 6.8 Hz, 3 H), 1.10 (2×t, J = 7.5 Hz, 6 H), 1.15–1.34 (m, 18 H), 1.87 (m, 2 H), 2.01 (m, 3 H), 2.13 (m, 1 H), 5.61 (dd, J = 1.9, 10.6 Hz, 1 H), 7.30 (t, J = 7.5 Hz, 2 H), 7.48 (m, 3 H), 7.54 (m, 2 H), 7.59 (t, J = 7.5 Hz, 1 H), 7.90 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.66 (q), 8.72 (q), 14.3 (q), 22.78 (t), 22.82 (t), 22.9 (t), 26.9 (t), 29.4 (t), 29.49 (t), 29.53 (t), 29.6 (t), 29.7 (t, 2 C), 31.5 (t), 32.0 (t), 73.6 (s), 74.9 (d), 128.3 (d), 129.0 (d), 129.7 (s), 129.8 (d), 130.2 (d), 133.1 (d), 133.4 (d), 139.3 (s), 165.9 (s) ppm.

2-Benzoyloxy Sulfones 17g–i (General Procedure): nBuLi (0.27 mL, 0.43 mmol, 1.6 M in hexane) was added dropwise to a stirred solution of sulfone **7d** (100 mg, 0.37 mmol) and HMPA (0.4 mL, 2.22 mmol) in dry THF (4 mL) at –78 °C under a nitrogen atmosphere. After stirring for 10 min, the aldehyde (0.47 mmol) in THF (1.5 mL) was added dropwise at –78 °C. The reaction mixture was stirred at this temperature until complete as indicated by TLC. Benzoyl chloride (57 μL, 0.49 mmol) was added. After 20 min, the reaction mixture was warmed to room temperature during 20 min and 3-(dimethylamino)propan-1-ol (65 μL, 0.56 mmol) was added. After 10 min, the reaction was quenched with water. The layers were separated and the aqueous was extracted with diethyl ether (3× 20 mL). The combined organic extracts were washed successively with 1 M HCl, 5% $NaHCO_3$ and brine solutions, dried with $MgSO_4$, filtered and the solvents evaporated. Purification by column chromatography (EtOAc/hexane, 1:20) gave compounds **17g–i**.

2-Isobutyl-4-methyl-1-phenyl-2-(phenylsulfonyl)pentyl Benzoate (17g): Yield 97 mg (55%) as colorless crystals, m.p. 176–177 °C. R_f (EtOAc/hexane, 1:5) = 0.38. IR: $\tilde{\nu}$ = 2963, 2871, 1725, 1449, 1314, 1298, 1142, 1126, 1105, 1094, 1077, 1069, 1002, 754, 724, 713, 692 cm^{-1}. MS (ESI+): m/z (%) = 501 (100) [M + Na$^+$], 359 (50) [M – $PhSO_2H$ + Na$^+$]. $C_{29}H_{34}O_4S$ (478.64): calcd. C 72.77, H 7.16, S 6.70; found C 72.98, H 6.85, S 6.42. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.83 (d, J = 6.7 Hz, 3 H), 1.03 (d, J = 6.7 Hz, 3 H), 1.10 (d, J = 6.6 Hz, 3 H), 1.12 (d, J = 6.5 Hz, 3 H), 1.59 (dd, J = 3.4, 15.2 Hz, 1 H), 2.03 (dd, J = 6.4, 15.2 Hz, 1 H), 2.18 (d, J = 5.0 Hz, 2 H), 2.30 (m, 1 H), 2.45 (m, 1 H), 6.71 (s, 1 H), 7.18 (t, J = 7.8 Hz, 2 H), 7.32 (m, 6 H), 7.51 (m, 3 H), 7.57 (dd, J = 1.2, 8.3 Hz, 2 H), 7.69 (dd, J = 1.1, 8.4 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.7 (d), 23.8 (d), 25.7 (q), 25.9 (q), 26.1 (q), 26.3 (q), 40.3 (t), 41.5 (t), 76.6 (s), 77.4 (d), 128.3 (d), 128.46 (d), 128.52 (d), 128.9 (d), 129.6 (d), 129.9 (d), 130.1 (s), 130.2 (d), 133.0 (d), 133.5 (d), 136.8 (s), 139.5 (s), 164.7 (s) ppm.

1-(4-Bromophenyl)-2-isobutyl-4-methyl-2-(phenylsulfonyl)pentyl Benzoate (17h): Yield 126 mg (61%) as colorless crystals, m.p. 209–210 °C. R_f (EtOAc/hexane, 1:5) = 0.50. IR: $\tilde{\nu}$ = 2964, 2872, 1726, 1451, 1389, 1301, 1264, 1143, 1126, 1093, 1076, 756, 713, 691 cm^{-1}. MS (ESI+): m/z (%) = 581/579 (60/60) [M + Na$^+$], 439/437 (100/95) [M – $PhSO_2H$ + Na$^+$], 295/293 (50/50) [M – $PhSO_2H$ – $PhCOO^-$], 214 (40) [M – $PhSO_2H$ – $PhCOO^-$ – Br]. $C_{29}H_{33}BrO_4S$ (557.54): calcd. C 62.47, H 5.97, S 5.75, Br 14.33; found C 62.18, H 5.59, S 5.92, Br 14.41. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (d, J = 6.6 Hz, 3 H), 1.01 (d, J = 6.6 Hz, 3 H), 1.07 (d, J = 6.6 Hz, 3 H), 1.12 (d, J = 6.4 Hz, 3 H), 1.58 (dd, J = 3.7, 15.2 Hz, 1 H), 2.02 (dd, J = 6.3, 15.2 Hz, 1 H), 2.08 (dd, J = 4.5, 15.2 Hz, 1 H), 2.16 (dd, J = 5.3, 15.2 Hz, 1 H), 2.30 (m, 1 H), 2.43 (m, 1 H), 6.63 (s, 1 H), 7.24 (m, 2 H), 7.36 (m, 4 H), 7.43 (m, 3 H), 7.53 (m, 1 H), 7.58 (m, 2 H), 7.69 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.75 (d), 23.84 (d), 25.7 (q), 25.8 (q), 26.1 (q), 26.3 (q), 40.4 (t), 41.5 (t), 76.4 (s), 76.8 (d), 123.2 (s), 128.58 (d), 128.64 (d, 2 C), 129.6 (d), 129.8 (s), 130.1 (d), 131.5 (d), 133.3 (d), 133.5 (d), 135.9 (s), 139.3 (s), 164.7 (s) ppm.

(*E*)-4-Isobutyl-6-methyl-1-phenyl-4-(phenylsulfonyl)hept-1-en-3-yl Benzoate (17i): Yield 149 mg (80%) as colorless crystals, m.p. 95–96 °C. R_f (EtOAc/hexane, 1:5) = 0.36. IR: $\tilde{\nu}$ = 3028, 2870, 1721, 1448, 1298, 1262, 1141, 1094, 1078, 752, 727, 712, 691 cm^{-1}. MS (ESI+): m/z (%) = 527 (100) [M + Na$^+$], 385 (30) [M – $PhSO_2H$ + Na$^+$], 241 (30) [M – $PhSO_2H$ – $PhCOO^-$], 185 (40) [M – $PhSO_2H$ – $PhCOO^-$ – CH_2=C(CH_3)$_2$]. $C_{31}H_{36}O_4S$ (504.68): calcd. C 73.78, H 7.19, S 6.35; found C 73.80, H 7.18, S 6.27. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.97 (m, 12 H), 1.83–2.03 (m, 3 H), 2.09 (dd, J = 4.9, 15.1 Hz, 1 H), 2.20 (m, 2 H), 6.15 (m, 2 H), 6.71 (d, J = 14.8 Hz, 1 H), 7.06–7.33 (m, 10 H), 7.38 (m, 3 H), 7.76 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.8 (d), 24.0 (d), 25.5 (q), 25.7 (q), 25.8 (q), 25.9 (q), 40.1 (t), 40.6 (t), 75.5 (s), 76.2 (d), 122.8 (d), 127.1 (d), 128.4 (d), 128.6 (d), 128.75 (d), 128.81 (d), 129.6 (d), 130.0 (s), 130.6 (d), 133.1 (d), 133.2 (d), 136.1 (s), 137.5 (d), 140.0 (s), 164.9 (s) ppm.

2-Benzoyloxy Sulfones 17j–l (General Procedure): nBuLi (0.54 mL, 0.86 mmol, 1.6 M in hexane) was added dropwise to a stirred solution of sulfone **7d** (200 mg, 0.74 mmol) and TMEDA (0.3 mL, 2 mmol) in dry THF (6 mL) at –78 °C under a nitrogen atmosphere. The reaction mixture was warmed to –20 °C during 1 h and the aldehyde (0.93 mmol) in THF (2 mL) was added dropwise. The reaction mixture was stirred at this temperature until complete as indicated by TLC. Benzoyl chloride (114 μL, 0.96 mmol) was added and the reaction mixture was warmed to room temperature after 20 min. 3-(Dimethylamino)propan-1-ol (130 μL, 1.11 mmol) was added and the reaction was quenched with water after 10 min. The layers were separated and the aqueous was extracted with diethyl ether (3× 20 mL). The combined organic extracts were washed successively with 1 M HCl, 5% $NaHCO_3$ and brine solutions, dried with $MgSO_4$, filtered and the solvents evaporated. Purification by column chromatography (EtOAc/hexane, 1:20) provided compounds **17j–l**.

4-Isobutyl-6-methyl-1-phenyl-4-(phenylsulfonyl)hept-3-yl Benzoate (17j): Yield 251 mg (67%) as colorless crystals, m.p. 78–79 °C. R_f (EtOAc/hexane, 1:5) = 0.39. IR: $\tilde{\nu}$ = 2961, 2870, 1720, 1602, 1470, 1266, 1230, 1141, 1105, 1070, 1026, 755, 711, 693 cm^{-1}. MS (ESI+): m/z (%) = 1035 (10) [2M + Na$^+$], 529 (100) [M + Na$^+$], 387 (30) [M – $PhSO_2H$ + Na$^+$]. $C_{31}H_{38}O_4S$ (506.70): calcd. C 73.48, H 7.56, S 6.33; found C 73.45, H 7.69, S 6.44. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.96 (2×d, J = 6.5 Hz, 6 H), 1.02 (2×d, J = 6.5 Hz, 6 H), 1.84 (dd, J = 4.3, 15.2 Hz, 1 H), 1.87 (dd, J = 4.3, 15.2 Hz, 1 H), 1.91–2.06 (m, 3 H), 2.11 (m, 1 H), 2.23 (m, 2 H), 2.57 (m, 1 H), 2.66 (m, 1 H), 5.89 (dd, J = 2.0, 9.9 Hz, 1 H), 7.09 (m, 2 H), 7.12 (m, 1 H), 7.21 (m, 2 H), 7.29 (m, 4 H), 7.41 (t, J = 7.8 Hz, 1 H), 7.48 (m, 1 H), 7.53 (m, 2 H), 7.79 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.9 (d), 24.0 (d), 25.7 (q), 26.1 (q), 33.5 (t), 34.9 (t), 39.6 (t), 40.4 (t), 75.3 (d), 76.1 (s), 126.1 (d), 128.45 (d), 128.54 (d), 128.7 (d), 128.9 (d), 129.7 (d), 129.8 (s), 130.4 (d), 133.2 (d), 133.3 (d), 139.9 (s), 141.3 (s), 166.0 (s) ppm.

4-Isobutyl-2-methyl-4-(phenylsulfonyl)dec-5-yl Benzoate (17k): Yield 273 mg (78%) as a colorless oil. R_f (EtOAc/hexane, 1:5) = 0.38. IR: $\tilde{\nu}$ = 3063, 2959, 2929, 2870, 1722, 1602, 1585, 1492, 1450, 1446, 1266, 1079, 1069, 935, 758, 726 cm^{-1}. MS (ESI+): m/z (%) = 495 (60) [M + Na$^+$], 353 (100) [M – $PhSO_2H$ + Na$^+$]. $C_{28}H_{40}O_4S$ (472.68): calcd. C 71.15, H 8.53, S 6.78; found C 71.38, H 8.53, S 6.65. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.79 (t, J = 6.9 Hz, 3 H), 0.97 (d, J = 6.6 Hz, 3 H), 1.00 (d, J = 6.6 Hz, 3 H), 1.03 (d, J = 6.6 Hz, 3 H), 1.05 (d, J = 6.5 Hz, 3 H), 1.10–1.37 (m, 6 H), 1.68 (m, 1 H), 1.82–1.99 (m, 4 H), 2.04 (dd, J = 4.1, 15.1 Hz, 1 H), 2.14 (m, 1 H), 2.22 (m, 1 H), 5.78 (dd, J = 2.0, 10.1 Hz, 1 H), 7.27 (t, J = 8.0 Hz, 2 H), 7.32 (t, J = 8.0 Hz, 2 H), 7.43 (m, 1 H), 7.46 (m,

1 H), 7.50 (m, 2 H), 7.81 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2 (q), 22.6 (t), 23.8 (d), 24.0 (d), 25.7 (q, 2 C), 25.8 (q), 26.1 (q), 26.8 (t), 32.1 (t), 32.6 (t), 39.6 (t), 40.4 (t), 75.6 (d), 76.6 (s), 128.4 (d), 128.9 (d), 129.7 (d), 130.1 (s), 130.4 (d), 133.1 (d, 2 C), 140.1 (s), 165.9 (s) ppm.

4-Isobutyl-2-methyl-4-(phenylsulfonyl)hexadec-5-yl Benzoate (17l): Yield 239 mg (58%) as a colorless oil. R_f (EtOAc/hexane, 1:5) = 0.49. IR: $\tilde{\nu}$ = 2931, 2923, 2854, 1721, 1450, 1302, 1268, 1175, 1078, 1026, 756, 711, 691 cm^{-1}. MS (ESI+): *m*/*z* (%) = 579 (100) [M + Na$^+$], 437 (40) [M – $PhSO_2H$ + Na$^+$]. $C_{34}H_{52}O_4S$ (556.84): calcd. C 73.34, H 9.41, S 5.76; found C 73.47, H 9.47, S 6.04. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.80 (t, *J* = 6.9 Hz, 3 H), 0.96 (2×d, *J* = 6.5 Hz, 6 H), 1.02 (2×d, *J* = 6.5 Hz, 6 H), 1.06–1.33 (m, 18 H), 1.66 (m, 1 H), 1.88 (m, 4 H), 2.02 (dd, *J* = 4.1, 15.1 Hz, 1 H), 2.10 (m, 1 H), 2.19 (m, 1 H), 5.74 (dd, *J* = 2.0, 10.1 Hz, 1 H), 7.21–7.32 (m, 4 H), 7.36–7.51 (m, 4 H), 7.79 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (q), 22.6 (t), 23.6 (d), 23.8 (d), 25.5 (q, 2 C), 25.6 (q), 25.9 (q), 26.9 (t), 29.30 (t), 29.33 (t), 29.5 (t), 29.6 (t, 2 C), 29.7 (t), 31.9 (t), 32.5 (t), 39.4 (t), 40.2 (t), 75.4 (d), 76.4 (s), 128.1 (d), 128.6 (d), 129.5 (d), 129.9 (s), 130.2 (d), 132.9 (d, 2 C), 140.0 (s), 165.6 (s) ppm.

Julia Olefination with Samarium Diiodide (General Procedure): Benzoylated compound **17a**–**c**, **g**–**i** (0.16 mmol) was dissolved in THF (1.5 mL) and DMPU (0.73 mL, 6 mmol). After degassing the mixture by three freeze-pump-thaw cycles, a solution of SmI_2 (9.6 mL, 0.96 mmol) was added at 0 °C. After 2 h at room temperature, the reaction mixture was diluted with diethyl ether and decanted from samarium salts, which were washed thoroughly with diethyl ether. The combined organic layers were washed with a saturated NH_4Cl solution and the aqueous was extracted with diethyl ether (3 × 20 mL). The combined organic extracts were dried with $MgSO_4$, filtered and the solvents evaporated. Purification by column chromatography (EtOAc/hexane, 1:10) afforded olefins **18a**–**c**, **g**–**i**.

(*E*)-(4-Ethylhexa-1,3-dien-1-yl)benzene (18c): Yield 20 mg (68%) as a colorless oil. R_f (EtOAc/hexane, 1:10) = 0.96. IR: $\tilde{\nu}$ = 3030, 2967, 2936, 2878, 1682, 1495, 1452, 1399, 1029, 962, 919, 748, 695 cm^{-1}. MS (EI): *m*/*z* (%) = 186 (100) [M$^+$], 157 (40), 145 (50). $C_{14}H_{18}$ (186.30): calcd. C 90.26, H 9.74; found C 89.91, H 9.77. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.98 (2×t, *J* = 7.5 Hz, 6 H), 2.08 (q, *J* = 7.5 Hz, 2 H), 2.22 (q, *J* = 7.5 Hz, 2 H), 5.90 (d, *J* = 11.0 Hz, 1 H), 6.39 (d, *J* = 15.5 Hz, 1 H), 6.96 (dd, *J* = 11.0, 15.5 Hz, 1 H), 7.11 (m, 1 H), 7.23 (m, 2 H), 7.33 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.7 (q), 13.7 (q), 24.2 (t), 29.7 (t), 123.2 (d), 125.5 (d), 126.1 (d), 126.9 (d), 128.5 (d), 130.0 (d), 138.2 (s), 148.1 (s) ppm.

(2-Isobutyl-4-methylpent-1-en-1-yl)benzene (18g): Yield 26 mg (68%) as a colorless oil. R_f (EtOAc/hexane, 1:10) = 0.85. IR: $\tilde{\nu}$ = 2980, 2956, 2926, 2868, 1462, 1383, 1365, 1164, 1076, 953, 737, 698, 669 cm^{-1}. MS (EI): *m*/*z* (%) = 216 (100) [M$^+$], 173 (50). HRMS (EI): *m*/*z* [M$^+$] calcd. for $C_{16}H_{24}^+$: 216.1878, found 216.1876. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.79 (d, *J* = 6.6 Hz, 6 H), 0.92 (d, *J* = 6.6 Hz, 6 H), 1.81 (m, 2 H), 1.99 (d, *J* = 7.4 Hz, 2 H), 2.09 (d, *J* = 7.4 Hz, 2 H), 6.30 (s, 1 H), 7.16 (m, 3 H), 7.27 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.77 (q), 22.80 (q), 26.6 (d), 26.7 (d), 39.1 (t), 47.1 (t), 125.9 (d), 127.5 (d), 128.1 (d), 129.2 (d), 139.1 (s), 141.7 (s) ppm.

4-Bromo-1-(2-isobutyl-4-methylpent-1-en-1-yl)benzene (18h): Yield 33 mg (71%) as a colorless oil. R_f (EtOAc/hexane, 1:10) = 0.89. IR: $\tilde{\nu}$ = 2980, 2955, 2926, 2868, 1486, 1463, 1384, 1366, 1260, 1164, 1097, 1072, 1011, 953, 824, 669 cm^{-1}. MS (EI): *m*/*z* (%) = 296/294 (30/30) [M$^+$], 172 (90) [M$^+$ – Br – *i*Pr], 129 (100) [M$^+$ – Br – 2 *i*Pr]. HRMS (EI): *m*/*z* [M$^+$] calcd. for $C_{16}H_{23}{}^{79}Br^+$: 294.0983, found 294.0980. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.80 (d, *J* = 6.6 Hz, 6 H), 0.92 (d, *J* = 6.6 Hz, 6 H), 1.81 (m, 2 H), 2.00 (d, *J* = 7.1 Hz, 2 H), 2.07 (d, *J* = 7.1 Hz, 2 H), 6.23 (s, 1 H), 7.04 (d, *J* = 8.4 Hz, 2 H), 7.40 (d, *J* = 8.4 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.75 (q), 22.78 (q), 26.61 (d), 26.63 (d), 39.1 (t), 47.1 (t), 119.7 (s), 126.3 (d), 130.9 (d), 131.2 (d), 138.0 (s), 142.7 (s) ppm.

(*E*)-1-(4-Isobutyl-6-methyl-1-phenyl)hepta-1,3-heptadiene (18i): Yield 32 mg (82%) as a colorless oil. R_f (EtOAc/hexane, 1:10) = 0.89. IR: $\tilde{\nu}$ = 2954, 2925, 2868, 1595, 1497, 1383, 1366, 962, 746, 691 cm^{-1}. MS (EI): *m*/*z* (%) = 242 (50) [M$^+$], 199 (30) [M$^+$ – *i*Pr], 143 (100) [M$^+$ – *i*Pr – CH_2=C(CH_3)$_2$]. $C_{18}H_{26}$ (242.40): calcd. C 89.19, H 10.81; found C 89.16, H 10.88. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85 (d, *J* = 6.5 Hz, 6 H), 0.88 (d, *J* = 6.5 Hz, 6 H), 1.77 (m, 2 H), 1.93 (d, *J* = 7.3 Hz, 2 H), 2.08 (d, *J* = 7.3 Hz, 2 H), 6.01 (d, *J* = 11.0 Hz, 1 H), 6.41 (d, *J* = 15.5 Hz, 1 H), 6.99 (dd, *J* = 11.0, 15.5 Hz, 1 H), 7.13 (m, 1 H), 7.27 (m, 2 H), 7.31 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.9 (q), 23.0 (q), 27.0 (d), 27.7 (d), 40.1 (t), 47.6 (t), 126.0 (d), 126.3 (d), 127.1 (d), 127.7 (d), 128.8 (d), 130.1 (d), 138.2 (s), 143.4 (s) ppm.

Julia Olefination with Sodium Amalgam (General Procedure): Compound **17d**–**f**, **j**–**l** (0.134 mmol) was dissolved in THF (1 mL) and methanol (2 mL) under a nitrogen atmosphere. Sodium amalgam (67 mg, 0.31 mmol) was added at –20 °C. After 3 h at this temperature, the reaction mixture was diluted with diethyl ether and decanted from mercury. The organic layer was washed with brine and the aqueous layer was extracted with diethyl ether (3× 25 mL). The combined organic extracts were dried with $MgSO_4$, filtered and the solvents evaporated. Purification by column chromatography (EtOAc/hexane, 1:30) afforded olefins **18d**–**f**, **j**–**l**.

(4-Ethylhex-3-en-1-yl)benzene (18d): Yield 19 mg (76%) as a colorless oil. R_f (EtOAc/hexane, 1:10) = 0.91. IR: $\tilde{\nu}$ = 2964, 2929, 2874, 2856, 1496, 1456, 1261, 1082, 1029, 802, 746, 698 cm^{-1}. MS (EI): *m*/*z* (%) = 188 (20) [M$^+$], 97 (60), 91 (40), 55 (100). HRMS (EI): *m*/*z* [M$^+$] calcd. for $C_{14}H_{20}^+$: 188.1565, found 188.1560. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.82 (t, *J* = 7.5 Hz, 3 H), 0.89 (t, *J* = 7.5 Hz, 3 H), 1.91 (2×q, *J* = 7.5 Hz, 4 H), 2.23 (m, 2 H), 2.55 (m, 2 H), 5.04 (t, *J* = 7.1 Hz, 1 H), 7.09 (m, 3 H), 7.18 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.1 (q), 13.4 (q), 23.4 (t), 29.4 (t), 29.9 (t), 36.8 (t), 122.0 (d), 125.9 (d), 128.4 (d), 128.7 (d), 142.5 (s), 144.0 (s) ppm.

3-Ethylnon-3-ene (18e): Yield 13 mg (64%) as a colorless volatile liquid. R_f (EtOAc/hexane, 1:10) = 0.91. IR: $\tilde{\nu}$ = 2964, 2929, 2874, 2856, 1456, 1261 cm^{-1}. MS (EI): *m*/*z* (%) = 154 (40) [M$^+$], 125 (20), 111 (20), 97 (30), 83 (40), 55 (100), 41 (40). $C_{11}H_{22}$ (154.29): calcd. C 85.63, H 14.37; found C 85.80, H 14.16. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.82 (t, *J* = 6.9 Hz, 3 H), 0.88 (t, *J* = 7.4 Hz, 3 H), 0.91 (t, *J* = 7.4 Hz, 3 H), 1.21 (m, 6 H), 1.83–2.02 (m, 6 H), 5.00 (t, *J* = 7.1 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.2 (q), 13.5 (q), 14.3 (q), 22.9 (t), 23.3 (t), 27.7 (t), 29.5 (t), 30.1 (t), 31.9 (t), 123.2 (d), 142.8 (s) ppm.

3-Ethylpentadec-3-ene (18f): Yield 29 mg (92%) as a colorless liquid. R_f (EtOAc/hexane, 1:10) = 0.95. IR: $\tilde{\nu}$ = 2963, 2925, 2873, 2854, 1664, 1464, 1378 cm^{-1}. MS (CI+): *m*/*z* (%) = 239 (100) [M + H$^+$], 125 (20), 111 (20), 97 (40). HRMS (CI+): *m*/*z* [M + H$^+$] calcd. for $C_{17}H_{35}^+$: 239.2739, found 239.2738. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.84 (t, *J* = 6.8 Hz, 3 H), 0.91 (t, *J* = 7.6 Hz, 3 H), 0.94 (t, *J* = 7.4 Hz, 3 H), 1.22 (m, 18 H), 1.97 (m, 6 H), 5.03 (t, *J* = 7.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.2 (q), 13.5 (q), 14.3 (q), 22.9 (t), 23.4 (t), 27.8 (t), 29.4 (t), 29.6 (t), 29.7 (t), 29.86 (t), 29.90 (t, 2 C), 29.93 (t), 30.5 (t), 32.2 (t), 123.2 (d), 142.8 (s) ppm.

(4-Isobutyl-6-methylhept-3-en-1-yl)benzene (18j): Yield 44 mg (79%) as a colorless liquid. R_f (EtOAc/hexane, 1:10) = 0.93. IR: $\tilde{\nu}$ = 2953, 2926, 2868, 1496, 1462, 1383, 1365, 909, 735, 698 cm^{-1}. MS (EI): *m*/*z* (%) = 244 (10) [M^+], 97 (100), 91 (40), 55 (90). HRMS (EI): *m*/*z* [M^+] calcd. for $C_{18}H_{28}^+$: 244.2191, found 244.2192. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.76 (d, *J* = 6.5 Hz, 6 H), 0.79 (d, *J* = 6.5 Hz, 6 H), 1.63 (m, 2 H), 1.75 (d, *J* = 7.2 Hz, 2 H), 1.79 (d, *J* = 7.3 Hz, 2 H), 2.27 (m, 2 H), 2.57 (m, 2 H), 5.13 (t, *J* = 7.1 Hz, 1 H), 7.12 (m, 3 H), 7.21 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.8 (q), 22.9 (q), 26.4 (d, 2 C), 30.2 (t), 36.8 (t), 39.1 (t), 47.1 (t), 125.9 (d), 126.6 (d), 128.4 (d), 128.8 (d), 138.2 (s), 142.8 (s) ppm.

4-Isobutyl-2-methyldec-4-ene (18k): Yield 25 mg (89%) as a colorless liquid. R_f (EtOAc/hexane, 1:10) = 0.96. IR: $\tilde{\nu}$ = 2954, 2926, 2868, 1465, 1366, 1166, 1135 cm^{-1}. MS (EI): *m*/*z* (%) = 210 (50) [M^+], 154 (30), 153 (30), 111 (40), 97 (100), 83 (95), 69 (90), 55 (60), 43 (30), 41 (30). HRMS (EI): *m*/*z* [M^+] calcd. for $C_{15}H_{30}^+$: 210.2348, found 210.2345. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.82 (m, 15 H), 1.18 (m, 6 H), 1.67 (m, 2 H), 1.77 (d, *J* = 7.1 Hz, 2 H), 1.82 (d, *J* = 7.1 Hz, 2 H), 1.95 (m, 2 H), 5.10 (t, *J* = 7.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.3 (q), 22.8 (q), 22.86 (t), 22.89 (q), 26.4 (d), 27.0 (d), 28.1 (t), 30.1 (t), 31.9 (t), 39.1 (t), 47.1 (t), 127.6 (d), 137.3 (s) ppm.

4-Isobutyl-2-methylhexadec-4-ene (18l): Yield 25 mg (64%) as a colorless liquid. R_f (EtOAc/hexane, 1:10) = 0.94. IR: $\tilde{\nu}$ = 2953, 2923, 2854, 1464, 1382, 1365 cm^{-1}. MS (EI): *m*/*z* (%) = 294 (40) [M^+], 238 (40), 125 (80), 111 (40), 97 (100), 83 (95), 69 (90), 55 (80), 43 (40), 41 (40). HRMS (EI): *m*/*z* [M^+] calcd. for $C_{21}H_{42}^+$: 294.3287, found 294.3280. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.78 (m, 15 H), 1.18 (m, 18 H), 1.63 (m, 2 H), 1.73 (d, *J* = 7.2 Hz, 2 H), 1.78 (d, *J* = 7.2 Hz, 2 H), 1.90 (m, 2 H), 5.06 (t, *J* = 7.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2 (q), 22.7 (q), 22.78 (q), 22.82 (t), 26.3 (d), 26.9 (d), 28.0 (t), 29.49 (t), 29.51 (t), 29.7 (t), 29.79 (t, 2 C), 29.80 (t), 30.3 (t), 32.1 (t), 38.9 (t), 46.9 (t), 127.5 (d), 137.1 (s) ppm.

Supporting Information (see footnote on the first page of this article): Experimental procedures, analytical data for all compounds, X-ray crystallographic data of compounds **7d**, **7g** and **7k**, and copies of ^1H and ^{13}C NMR spectra of all new compounds.

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