Stereoselective Radical Aryl Migration Reactions from Sulfur to Carbon

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Stereoselective aryl migration reactions from sulfur in sulfonates and sulfonamides to *C*-centered radicals are reported. The 1,5-aryl migration from sulfur to differently substituted *C*-centered radicals could be performed with high yields and selectivities. Functionalized aryl groups could also be transferred by this new method. A model to explain the stereochemical outcome of the reaction is presented and some mechanistic aspects of this reaction are discussed. Aryl migration reactions from sulfur in sulfinates to carbon radicals were less efficient, and the corresponding migrations in aryl sulfoxides were not observed at all.

Introduction

Many pharmaceuticals, such as Sertaline (Zoloft),[1] Paroxetine (Paxil),[2] and Diltiazem (Cardizem),[3] contain functionalized aryl groups connected to a chiral center (Figure 1). This structural motif, an aryl group connected to an sp^3-carbon atom, also often occurs in natural products. However, there are only a few methods that allow direct stereoselective $C(sp^2)-C(sp^3)$ bond formation. The stereoselective Friedel–Crafts-type alkylation is a topic of current research, but is not yet well developed.[4] Stereoselective arylations of sp^3-carbon atoms with transition metals as mediators have been successfully performed,[5] while anionic stereoselective arylations have found only scant application in organic synthesis.[6]

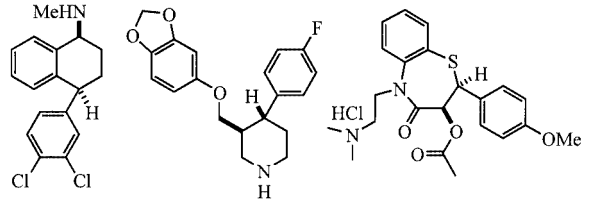
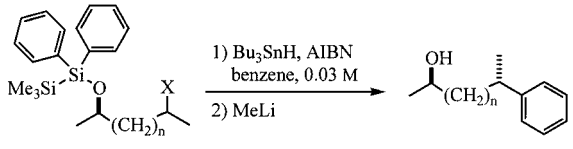


Figure 1. Some pharmaceuticals containing functionalized aryl groups connected to a chiral center

As an alternative to these methods, we recently reported stereoselective radical aryl migration reactions from silicon to carbon.[7,8] In contrast to anionic or cationic processes, these radical arylations could be performed under mild conditions. For instance, treatment of alkoxydisilane **1** under radical conditions afforded the 1,5-phenyl migration product **2** in good yield and selectivity after desilylation (Scheme 1). We further showed that functionalized aryl groups could also be transferred by this approach. The analogous 1,4-aryl migration worked even better, as was shown for the transformation of the alkoxydisilane **3** into the β-arylated alcohol **4**. Unfortunately, efficient aryl migration reactions were only observed for alkoxydisilanes. Arylated alkoxysilanes derived from commercially available silyl protecting groups, such as *tert*-butyldiphenylsilyl ethers or triphenylsilyl ethers, did not undergo the desired aryl migration reaction in acceptable yields and selectivities. This was certainly a drawback of the method, since the starting disilanes bearing functionalized aryl groups were not readily preparable. We therefore decided to look for other functional groups (tethers) that would allow highly stereoselective radical aryl migrations to carbon radicals. Furthermore, the substrates in these new systems should be readily preparable on a large scale from commercially available starting materials.



1 (X = I, n = 1)
3 (X = SePh, n = 0)

2 (70%, dr = 10:1, n = 1)
4 (74%, dr = 14:1, n = 0)

Scheme 1. Stereoselective radical phenyl migration from silicon to carbon

In the 1970s, Speckamp studied radical 1,4-aryl migrations from sulfur to carbon radicals in rigid arene sulfonamides.[9] Later, Motherwell developed a new biaryl synthesis using both 1,4- and 1,5-aryl migrations from sulfur to aryl radicals.[10] On the basis of these results and our own work

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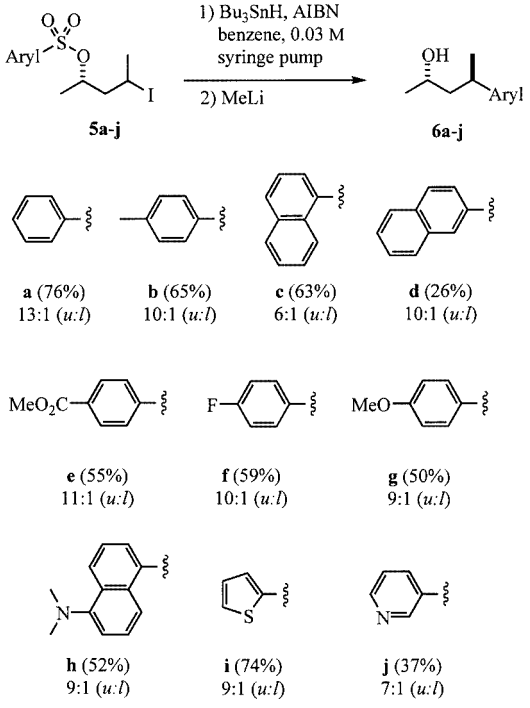
on stereoselective radical aryl migration reactions from silicon to carbon we decided to study stereoselective radical aryl migration reactions from sulfur to carbon. In this paper we report in full detail[11] the stereoselective 1,5-aryl migration reaction from sulfur in sulfonates and sulfonamides to *C*-centered radicals. Furthermore, we show that radical aryl migrations from sulfur to carbon in sulfinates were less efficient and that the corresponding aryl migrations in aryl sulfoxides did not occur.

Results and Discussion

Radical Aryl Migration Reactions in Sulfonates

The starting arenesulfonates **5a**−**j** were readily prepared from 4-iodo-2-pentanol[12] and the corresponding arenesulfonyl chloride in pyridine[13] or in CH_2Cl_2, with Et_3N and a catalytic amount of $Me_3N{\cdot}HCl$ as a combined base[14] (49−97%). The aryl transfer reactions were conducted under optimized conditions: slow addition (syringe pump, 7 h) of Bu_3SnH (1.5 equiv.) to a solution of the arenesulfonate **5a**−**j** in refluxing benzene (0.03 M) afforded the corresponding aryl transfer products **6a**−**j** in moderate to good yields and with high selectivities after treatment of the reaction mixture with methyllithium (MeLi) (Scheme 2). Addition of MeLi was used to transform the tin by-products into tributyl(methyl)stannane, which is easily removed by chromatography.[15] The relative configuration of the major isomer of **6a** was assigned by comparison of the ^1H NMR spectroscopic data with literature values.[16] All the other compounds **6b**−**j** were assigned by analogy. Diastereoisomeric ratios were determined either by GC analysis or by ^1H NMR spectroscopy.

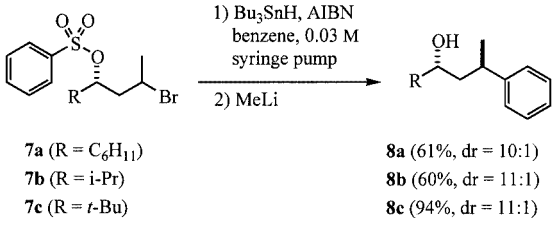


Scheme 2. Stereoselective 1,5-aryl migration

Phenyl migration (**5a** → **6a**) occurred with high yield (76%) and high selectivity (*dr* = 13:1). For the migration of the tolyl group, γ-arylated alcohol **6b** was isolated in 65% yield and with a 10:1 selectivity. A marked decrease in the selectivity was observed for the migration of the 1-naphthyl group (*dr* = 6:1, 63%), but for the transfer of the 2-naphthyl group, selectivity remained high (*dr* = 10:1). However, the yield dropped to 26% (**5d** → **6d**). Both electron-poor and electron-rich arenes could be stereoselectively transferred in similar yields, indicating that polar effects were not so important in these aryl migration reactions. Thus, the *p*-methoxycarbonyl derivative **6e** was obtained in 55% yield with good selectivity (*u*/*l* = 11:1). In addition, the *p*-fluorophenyl compound **5f** was transformed into the corresponding aryl migration product **6f** in 59% yield (*u*/*l* = 10:1). In the case of the electron-rich anisyl and dansyl derivatives, the transfer products **6g** and **6h** were isolated in 50 and 52% yields, respectively (**6g**: *dr* = 9:1; **6h**: *dr* = 9:1). Even heteroarenes could be transferred by our method, as shown for the migration of the thienyl group (**6i**: 74%, 9:1). Migration of the 3-pyridyl group (**5j** → **6j**) occurred with lower yield (37%) and lower selectivity (7:1).

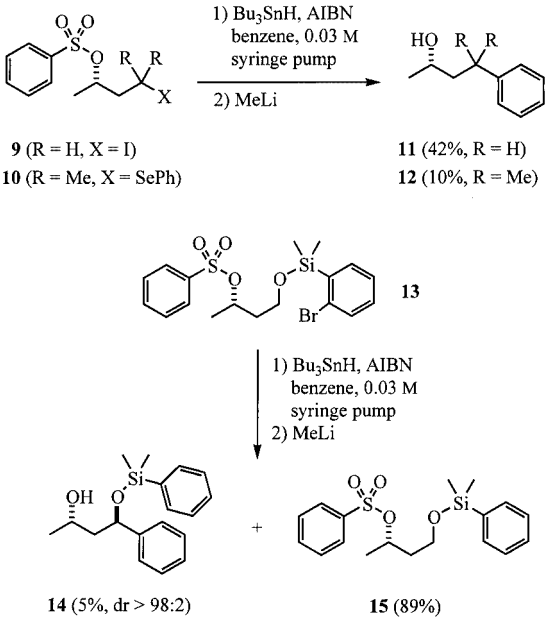
One can conclude from the variety of substrates tested that our 1,5-aryl migration reaction to secondary carbon radicals is a very general reaction. For every arenesulfonate tested to date, aryl migration could be accomplished. Yields and selectivities, however, vary significantly. At the moment, it is not possible for us to predict for which aryl group the reaction will occur with high yield and selectivity. We could not identify a clear reactivity trend.

We then studied the effect of the size of the substituent R at the α-position of the sulfonate moiety on the 1,3-stereoinduction in the phenyl migration to secondary *C*-centered radicals. The sulfonates **7a**−**c** were readily prepared from the corresponding alcohols. Phenyl migration reactions were conducted under the standard conditions described above. It turned out that the substituent R had no profound effect on the selectivity of the reaction. The cyclohexyl- (→ **8a**), isopropyl- (→ **8b**), and the *tert*-butyl-substituted derivatives (→ **8c**) all gave similar selectivities (ca. 11:1, *like*/*unlike*, Scheme 3).



Scheme 3. Effect of the substituent R on the 1,3-stereoinduction

To elucidate steric effects on the intramolecular *ipso* substitution, the nature of the attacking radical was varied. To this end, radical precursors **9** and **10** (primary and tertiary alkyl radical precursors) were prepared by standard methods. To our surprise, *ipso* substitution with the primary alkyl radical deriving from iodide **9** was not as efficient, the



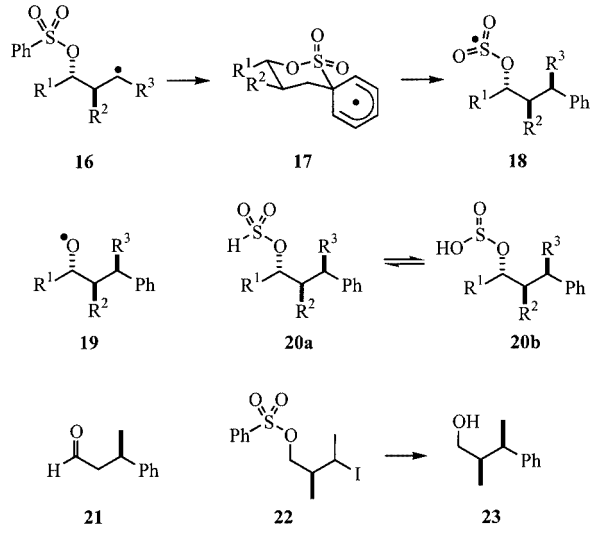
Scheme 4. Variation of the attacking radical

transfer product **11** being isolated in 42% yield (Scheme 4). As already shown in Scheme 2, the analogous phenyl transfer to the secondary alkyl radical generated from **5a** afforded the phenyl migration product in 76% yield. Aryl migration onto the tertiary alkyl radical generated from **10** was even less efficient, alcohol **12** being isolated in 10% yield. The increased steric bulk of the tertiary alkyl radical probably accounts for the decrease in the yield.

We also varied the polarity of the attacking radical. For the generation of a nucleophilic α-oxy radical we chose the sulfonate **13**, bearing Curran's radical translocating protecting group.[17] Initial Br abstraction with the tin radical generates the corresponding aryl radical, which should react further in a 1,5-H abstraction reaction to give the desired α-oxy-substituted *C*-centered radical. Phenyl migration onto this nucleophilic radical occurred with complete stereocontrol, but in only 5% yield (→ **14**). The major product was the dehalogenated sulfonate **15** (89%). At that moment it was not clear whether the low yield was the result of inefficient generation of the desired α-oxy-centered carbon radical (inefficient 1,5-H transfer) or of an inefficient 1,5-aryl migration reaction. We therefore repeated the experiment using Bu_3SnD. Again, the aryl migration product **14** was obtained in only 4% yield, while the reduction product was isolated in 70% yield. A careful NMR analysis revealed 47% incorporation of deuterium at the position α to the oxygen atom. This result established that the 1,5-aryl migration reaction to an α-oxy-substituted *C*-centered radical was an inefficient reaction (47% direct reduction versus 4% aryl migration).

Obviously, the nature of the attacking carbon radical (primary, secondary, tertiary, electron-rich secondary radical) strongly affected the outcome of the 1,5-aryl migration reaction. All attempts to prepare a radical precursor that would afford an electrophilic *C*-centered radical with an appropriately positioned phenyl sulfonate group failed.

To explain the stereochemical outcome of the aryl migration reaction, we suggest the following model (phenyl transfer discussed, Scheme 5). Radical **16** undergoes intramolecular *ipso* attack at the phenyl group of the sulfonate to form cyclohexadienyl radical **17**. We assume that the low-energy transition state for the formation of radical **17** resembles a chair with the substituents in pseudoequatorial positions (late transition state). Rearomatization then affords the alkoxysulfonyl radical **18**.[18] It was not clear whether SO_2 extrusion to form a reactive alkoxy radical **19** preceded the reduction with tin hydride to form the tautomeric compounds **20a** and **20b**. To distinguish between these two possible reaction pathways, the aryl migration was performed with the *tert*-butyl derivative **7c**. If an alkoxy radical **19** (R^1 = *t*Bu, R^2 = H, R^3 = Me) were to be generated, it should β-fragment with a rate constant of about $> 10^8\ s^{-1}$ to the corresponding aldehyde **21**.[19] In the experiment, none of the aldehyde was formed, which clearly indicated that the radical SO_2 extrusion was a slow process that could not compete with the reduction of **18** to form **20a** and **20b**.[20] The product alcohol must therefore have been formed by ionic SO_2 extrusion from **20a** and **20b**. In general, large amounts of tin hydride (> 1.5 equiv.) and AIBN (0.3−0.5 equiv.) were necessary in order to achieve quantitative conversion in these aryl migration reactions. We believe that the reduction of the alkoxysulfonyl radical **18** with tin hydride was a very inefficient reaction and therefore resulted in chain termination.[21] Furthermore, the compounds **20a** and **20b** were probably able to react with tin hydride in an ionic process, therefore consuming additional tin hydride.



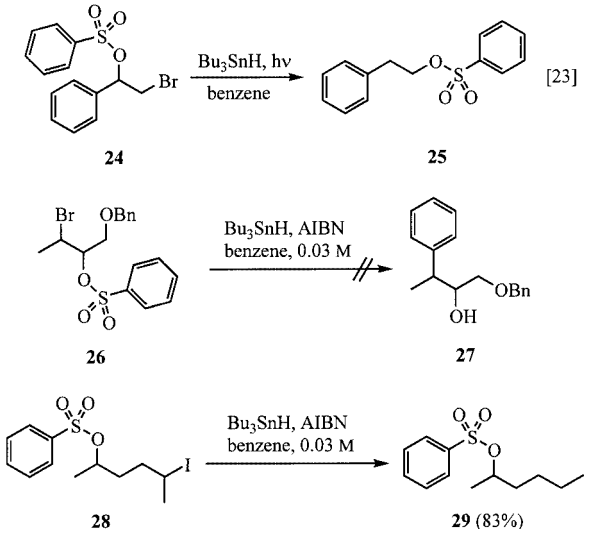
Scheme 5. A model to explain the stereochemical outcome of the reaction

To obtain further corroboration of our model to explain the stereochemical course of the reaction, we also investigated a system bearing a chiral center next to the secondary radical. Radical precursor **22** was prepared as a 1:1 mixture of diastereoisomers. Treatment of iodide **22** under the standard aryl migration conditions provided alcohol **23** in

49% yield. As predicted by the model, the *like* product was formed as the major isomer with 88% diastereoselectivity (*l*/*u* = 7:1). The relative configuration of the major isomer was assigned as previously described.[7b]

We further studied the effect of the temperature on the diastereoselectivity. Toluenesulfonate **5b** was chosen as the model substrate. As already reported (see Scheme 2), migration at 80 °C in benzene had provided the aryl transfer product **6b** in 65% yield with a 10:1 (*u*/*l*) selectivity. Reaction at 140 °C in xylene with di-*tert*-butyl peroxide as initiator afforded alcohol **6b** with lower selectivity (*dr* = 6:1) and in 31% yield. A slightly higher selectivity (*dr* = 13:1) was obtained upon running the reaction at room temperature in benzene using the Et_3B/O_2 initiation method.[22] However, the aryl migration product was isolated in only 33% yield. We also tried to run the aryl migration at −78 °C in CH_2Cl_2 with Et_3B/O_2. Under these conditions none of the aryl migration product **6b** was identified, with only the dehalogenation product being isolated. Thus, the best results in terms of selectivity and yield were provided by running the reaction at 80 °C.

As an extension of the method we also studied the 1,4- and 1,6-phenyl migration reactions. Crich previously reported the reaction of bromide **24** under tin hydride conditions to provide sulfonate **25** in high yield (Scheme 6).[23] The primary radical derived from bromide **24** underwent clean 1,2-migration of the benzenesulfonate moiety, with subsequent reduction of the corresponding secondary benzylic radical to give **25**. No 1,4-phenyl migration was observed. As an additional example, we tested the 1,4-phenyl migration with sulfonate **26**. Treatment of **26** with tin hydride under the standard aryl migration conditions provided a complex reaction mixture, the desired aryl migration product **27** not being observed.

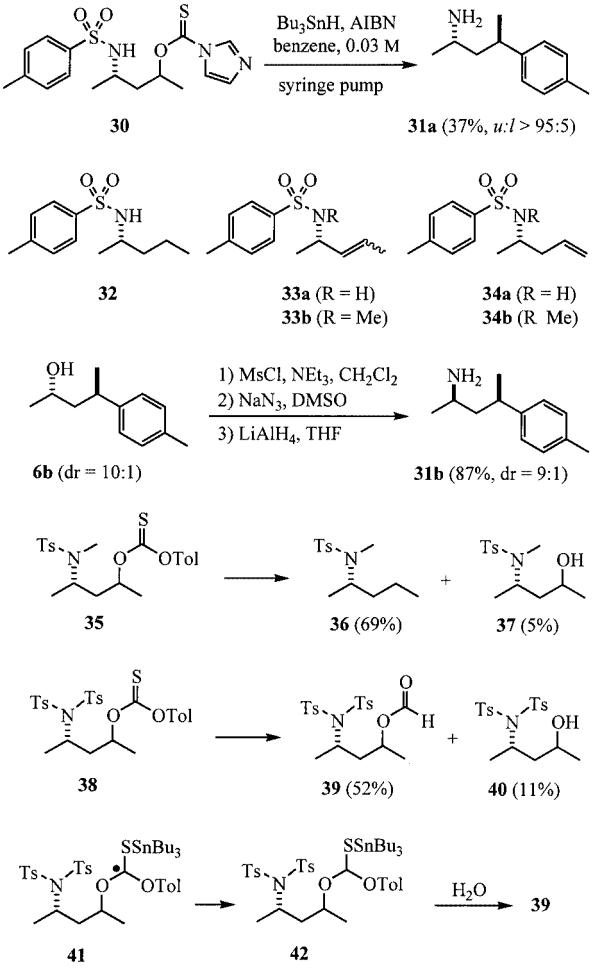


Scheme 6. 1,4- and attempted 1,6-aryl migration reactions

The 1,6-phenyl migration was studied with sulfonate **28** (1:1 diastereoisomeric mixture). Treatment of iodide **28** under the standard aryl migration conditions did not provide the desired 1,6-phenyl transfer product. The dehalogenation product **29** was isolated in 83% yield. The initial *ipso* attack to generate a seven-membered ring was too slow to compete with the direct reduction.

Radical Aryl Migration Reactions in Sulfonamides

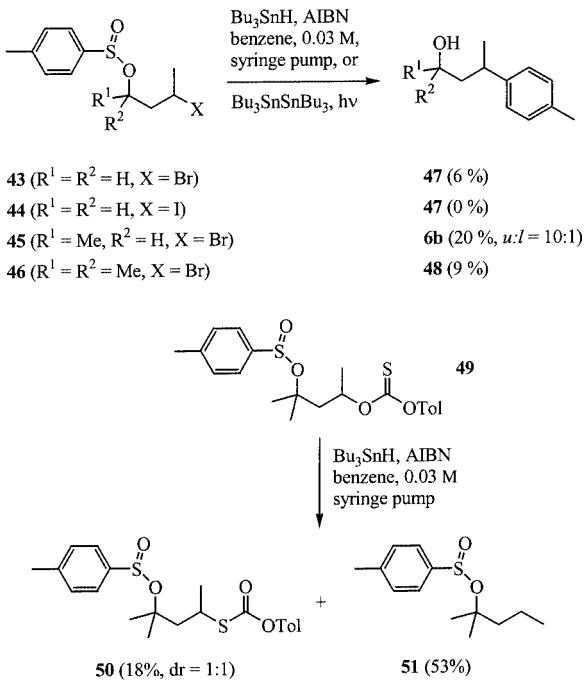
The radical precursors **30**, **35**, and **38** were prepared as described in the Exp. Sect. It turned out that the radical 1,5-aryl migration in these sulfonamides was not as efficient as in the sulfonate series described above. Treatment of sulfonamide **30** with tin hydride under the aryl migration conditions provided amine **31a** in 37% yield (Scheme 7).[24] We were pleased to see that the migration occurred with *complete stereocontrol*, none of the other diastereoisomer being detected in the GC reading. An authentic sample of amine **31** enriched in the other isomer was prepared from alcohol **6b** as described in Scheme 7. With the authentic sample to hand, we were able to unambiguously assign the relative *unlike* configuration to amine **31a** formed in the aryl migration reaction. In his 1,4-aryl migration reactions, Speckamp had reported higher yields at higher temperatures.[9] In our system, reaction conditions of 140 °C in xylene did not afford a higher yield (37%), but the selectivity dropped sharply (*dr* = 6:1). As side products, the direct reduction prod-



Scheme 7. Stereoselective radical aryl migration in sulfonamides

uct **32** and the elimination products **33a** and **34a** were formed under these conditions. Analogous eliminations have previously been reported to occur at fairly low temperatures.[25] The stereochemical outcome of the reaction can be explained by application of the model presented in Scheme 5 for the sulfonate series to the sulfonamide case.

We further studied the effect of the *N*-substituent on the tolyl migration reaction. The H atom was replaced with a methyl or an additional tosyl group. To our surprise, tolyl migration did not occur for the methylated tosylate **35** in benzene at 80 °C. The reduction product **36** was isolated as main product in 69% yield, together with 5% of alcohol **37**. Reaction at 140 °C afforded a mixture of reduction product **36** and elimination products **33b** and **34b**. The desired aryl migration product was not identified. Treatment of ditosylate **38** under standard aryl migration conditions but omitting the MeLi treatment unexpectedly yielded the formyl derivative **39** in 52% yield, along with the alcohol **40** (11%). Again, none of the tolyl migration product was observed. For the formation of the formyl compound **39** we suggest the following mechanism: stannyl radical addition onto the thiocarbonate generates the tertiary radical **41**, which does not undergo the desired β-fragmentation but is reduced to form **42**. Hydrolysis eventually gives **39**. A similar transformation of a thiocarbonate to a formate has been reported in the literature.[26]



Scheme 8. Radical aryl migration in sulfinates

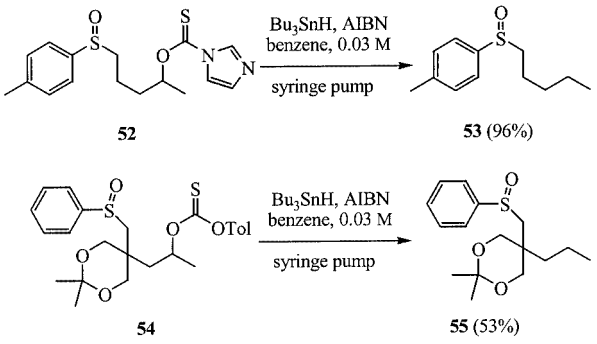
Radical Aryl Migration Reactions in Sulfinates and Sulfoxides

We next decided to investigate stereoselective aryl migration reactions in aryl sulfinates. In contrast to the examples discussed above, it should be possible for chirality to be transferred from the sulfur atom to the newly formed chirality center at the carbon atom. No additional chirality center at the carbon backbone would be necessary to induce selectivity. To study the intrinsic reactivity in these systems, racemic sulfinates **43**−**46** were prepared (see Exp. Sect.). It turned out that the tolyl migration was not as efficient as the analogous migrations in the sulfonate series. Treatment of sulfinate **43** under radical aryl migration conditions afforded the corresponding tolyl transfer product **47** in 6% yield, along with 73% of the debromination product (direct reduction, Scheme 8). We further tried to conduct the aryl migration reaction under atom-transfer conditions.[27] Iodide **44** was irradiated in the presence of $Bu_3SnSnBu_3$ in benzene. However, none of the desired product was formed, the starting sulfinate being almost quantitatively recovered.

From the sulfonate studies we had learned that migrations in systems bearing additional substituents at the α-position of the sulfonate functionality generally afforded higher yields. We therefore performed the tolyl transfer with sulfinate **45** (mixture of three diastereoisomers) deriving from a secondary alcohol. Aryl transfer worked slightly better and the product **6b** was isolated in 20% yield as a 10:1 (*unlike*/*like*) mixture of diastereoisomers. Encouraged by this result, we decided to introduce an additional methyl group at the α-position of the sulfinate moiety. The well-known Thorpe−Ingold effect[28] should accelerate the radical *ipso* substitution reaction. Tolyl migration with sulfinate **46** indeed gave the transfer product **48**, but in only 9% yield, together with 68% of direct reduction product **51**. Probably, the additional methyl group had hindered the attack of the secondary carbon radical on the tolyl group of the sulfinate. We also tested the tolyl migration with sulfinate **49**, bearing a thiocarbonate radical precursor. However, the main product in the transformation of **49** was again the reduction product **51** (53%). As a side product, rearranged[29] sulfinate **50** was formed as a 1:1 mixture of diastereoisomers (18%).[30]

Since we had never been able to achieve high yields for the aryl migration reactions with sulfinates, the reactions were not repeated with enantiomerically pure sulfinates. We could conclude that the 1,5-aryl migration from sulfur to carbon in sulfinates was not a preparative useful reaction.

Finally, we studied 1,5-tolyl migration reactions in sulfoxides. The model compounds **52** and **54** were prepared as diastereoisomeric mixtures by standard methods. The aryl migration reactions were conducted under our standard conditions, omitting the MeLi treatment. For sulfoxide **52** (*dr* = 1:1) no aryl migration occurred, and the reduction product **53** was isolated in 96% yield (Scheme 9). In order to increase the rate of the *ipso* attack, we decided to prepare a radical precursor geminally disubstituted (Thorpe−Ingold effect)[28] at the β-position of the sulfoxide moiety (→ **54**). However, the aryl migration product was also not observed in the ^1H NMR spectrum of the crude product with sulfoxide **54**.[32] The direct reduction product **55** was isolated in 53% yield. As with the sulfinates, the *ipso* attack in the sulfoxides was too slow to compete with the direct reduction.



Scheme 9. Attempted radical tolyl migration in sulfoxides

Conclusions

The 1,5-aryl migration from sulfur to secondary *C*-centered radicals in sulfonates is a very efficient new method for stereoselective $C(sp^2)-C(sp^3)$ bond formation. The starting arenesulfonates are readily preparable from alcohols bearing a radical precursor at the γ-position and the corresponding arenesulfonyl chlorides. More than 200 arenesulfonyl chlorides are commercially available! Standard radical precursors are used in these processes. The reactions are easy to conduct and no special equipment is necessary. For all the arenesulfonates tested to date in our laboratory, the 1,5-aryl migration could successfully be accomplished. The phenyl, tolyl, *p*-fluorophenyl, *p*-(methoxycarbonyl)phenyl, *p*-methoxyphenyl, 1-naphthyl, 2-naphthyl, 2-thienyl, 3-pyridyl, and the dansyl group could be transferred to secondary carbon radicals in moderate to good yields with fairly high selectivity (*dr* up to 13:1). Aryl migrations to primary and tertiary carbon radicals were less efficient.

Functionalized aryl groups connected to a chirality center can be found in many important pharmaceuticals, and we believe that our method is perfectly suited for library synthesis in medicinal chemistry. Studies along this line are underway and will be reported in due course.

The 1,5-migration from sulfur to carbon in arenesulfonamides occurs with complete stereocontrol, but in lower yields. Analogous 1,5-aryl migrations in arenesulfinates are far less efficient. For the arenesulfoxides the 1,5-migration of the aryl group to a secondary *C*-centered radical did not occur at all.

Experimental Section

General: TLC: Merck silica gel 60 F_{254} plates; detection by UV or by dipping into a solution of $KMnO_4$ (1.5 g in 333 mL of 1 M NaOH) or of $Ce(SO_4)_2 \cdot H_2O$ (10 g), phosphomolybdic acid hydrate (25 g), concd. H_2SO_4 (60 mL), and H_2O (940 mL), followed by heating. FC: Fluka or Merck silica gel 60 (40−63 μm); at ca. 0.3 bar. GC: Carlo−Erba Fractovap 4160-HR, column Supelco γ-DEX® 120 (30 m × 0.25 mm); or HP 6890 series, column HP 1 (100% dimethylpolysiloxane, 30 m). M.p.: Büchi 510 apparatus or Büchi SMP-20 apparatus; uncorrected values. IR spectra: Perkin−Elmer 782 spectrophotometer or Bruker IFS 200 interferometer or Nicolet Magna-IR 750 spectrometer (ṽ, *s* = strong, *m* = medium, *w* = weak). NMR spectra: Bruker AMX 500 (^{1}H 500 MHz, ^{13}C 125 MHz), AMX 400 (^{1}H 400 MHz, ^{13}C 100 MHz), ARX 300 (^{1}H 300 MHz, ^{13}C 75 MHz), Varian Gemini 300 (^{1}H 300 MHz, ^{13}C 75 MHz), Varian Gemini 200 (^{1}H 200 MHz, ^{13}C 50 MHz), Bruker AMX 200 (^{1}H 200 MHz, ^{13}C 50 MHz) or Bruker AC 200 (^{1}H 200 MHz, ^{13}C 50 MHz); chemical shifts [δ, relative to $SiMe_4$ (δ = 0 ppm)]. Mass spectra: VG Tribrid (EI), Varian CH7 (EI), MAT 95S (HRMS) or IonSpec-Ultima (ESI) [*m*/*z* (% of base peak)]. Elemental analyses were performed by the Microanalytical Laboratories of the Laboratorium für Organische Chemie, ETH-Zürich and the University of Marburg. Tetrahydrofuran (THF) (from potassium) and benzene (from sodium) were freshly distilled.

***l*-3-Iodo-1-methylbutyl Benzenesulfonate (5a):** *l*-4-Iodo-2-pentanol (400 mg, 1.87 mmol, see Supporting Information) was treated according to a procedure reported by Tipson[13] with pyridine (15 mL) and benzenesulfonyl chloride (0.58 mL, 4.52 mmol). After purification by FC (ether/pentane, 1:8), **5a** (347 mg, 52%) was obtained as colorless crystals. M.p. 55 °C. IR ($CHCl_3$): 3098*m*, 3010*s*, 2983*m*, 1492*m*, 1447*m*, 1405*s*, 1368*s*, 1176*s*, 1128*s*, 1094*s*, 1015*s*, 980*m*, 912*s*, 855*s*. ^{1}H NMR (400 MHz): 1.38 (*d*, *J* = 6.3 Hz, 3 H, CH_3); 1.83−2.03 (*m*, 2 H, CH_2); 1.86 (*d*, *J* = 6.9 Hz, 3 H, CH_3); 3.90−4.00 (*m*, 1 H, HCI); 4.76−4.84 (*m*, 1 H, HCO); 7.54−7.60 (*m*, 2 aromat. H); 7.64−7.69 (*m*, 1 aromat. H); 7.95−7.99 (*m*, 2 aromat. H) ppm. ^{13}C NMR (100 MHz): 21.2 (CH_3); 24.0 (CH); 26.3 (CH_3); 49.9 (CH_2); 80.7 (CH); 127.9 (CH); 129.3 (CH); 133.7 (CH); 137.1 (C) ppm. EI-MS: 354.9 (2) $[M + H]^+$, 338.9 (1) $[M - CH_3]^+$, 227.0 (29), 196.9 (27), 141.0 (83), 77.1 (78), 69.1 (100). $C_{11}H_{15}IO_3S$ (353.96): calcd. C 37.30, H 4.27; found C 37.29, H 4.29.

3-Iodo-1-methylbutyl *p*-Toluenesulfonate (5b): 4-Iodo-2-pentanol (1.36 g, 6.34 mmol, see Supporting Information) was treated according to a procedure reported by Tanabe[14] with NEt_3 (1.32 mL, 9.51 mmol), $NMe_3 \cdot HCl$ (602 mg, 6.34 mmol), and tosyl chloride (1.81 g, 9.51 mmol) in CH_2Cl_2 (20 mL). After workup, unchanged tosyl chloride was removed by stirring the crude product with imidazole (800 mg, 11.8 mmol) in CH_2Cl_2 (10 mL) for 1 h at room temp. After purification by FC (ether/pentane, 1:5), **5b** (1.77 g, 76%) was obtained as colorless crystals as a mixture of diastereomers (1.5:1). M.p. 43 °C. IR ($CHCl_3$): 2981*w*, 2922*w*, 1657*w*, 1598*w*, 1495*m*, 1362*s*, 1189*s*, 1177*s*, 1097*m*, 1018*w*, 902*s*, 816*m*, 758*m*, 664*m*. ^{1}H NMR (300 MHz): 1.22 (*d*, *J* = 6.2 Hz, 3 H, CH_3, isomer A); 1.34 (*d*, *J* = 6.2 Hz, 3 H, CH_3, isomer B); 1.80 (*d*, *J* = 6.7 Hz, 3 H, CH_3, isomer B); 1.85 (*d*, *J* = 7.0 Hz, 3 H, CH_3, isomer A); 1.89−1.96 (*m*, 1 H, CH_2); 2.21−2.36 (*m*, 1 H, CH_2); 2.44 (*s*, 3 H, CH_3); 3.88−4.13 (*m*, 1 H, HCI); 4.58−4.79 (*m*, 1 H, HCO); 7.36 (*d*, *J* = 6.9 Hz, 2 aromat. H); 7.75−7.84 (*m*, 2 aromat. H) ppm. ^{13}C NMR (50 MHz): 20.5; 21.6; 21.8; 22.1; 24.8; 28.6; 29.7; 49.5 (CH_2); 50.2 (CH_2); 79.7 (CH); 80.6 (CH); 128.1 (CH); 128.3 (CH); 130.3 (CH); 130.4 (CH); 134.3 (C); 134.4 (C); 145.1 (C); 145.3 (C) ppm. EI-MS: 241.1 (2) $[M - I]^+$, 155.1 (20), 91.0 (61), 69.0 (100). $C_{12}H_{17}IO_3S$ (368.23): calcd. C 39.14, H 4.65; found C 39.27, H 4.61.

3-Iodo-1-methylbutyl α-Naphthalenesulfonate (5c): 4-Iodo-2-pentanol (1.31 g, 6.13 mmol, see Supporting Information) was treated according to a procedure reported by Tanabe[14] with NEt_3 (1.20 mL, 8.62 mmol), $NMe_3 \cdot HCl$ (558 mg, 5.84 mmol), and α-naphthalenesulfonyl chloride (1.53 g, 6.73 mmol) in CH_2Cl_2 (20 mL). After purification by FC (MTBE/pentane, 1:5), **5c** (1.70 g, 69%) was obtained as a mixture of diastereoisomers (1.5:1). IR (nujol): 3061*w*, 2980*m*, 1508*m*, 1361*s*, 1203*m*, 1179*s*, 1141*m*, 980*m*, 898*s*, 805*m*, 772*s*, 677*m*, 595*m*, 521*m*. ^{1}H NMR (200 MHz): 1.18 (*d*, *J* = 6.2 Hz, 3 H, CH_3, isomer B); 1.34 (*d*, *J* = 6.4 Hz, 3 H, CH_3,

isomer A); 1.66 (*d*, *J* = 6.8 Hz, 3 H, CH_3, isomer B); 1.72−2.25 (*m*, 2 H, CH_2); 1.84 (*d*, *J* = 6.8 Hz, 3 H, CH_3, isomer A); 3.76−3.91 (*m*, 1 H, HCI); 4.58−4.77 (*m*, 1 H, HCO); 7.58−7.68 (*m*, 3 aromat. H); 8.00−8.21 (*m*, 3 aromat. H); 8.57−8.62 (*m*, 1 aromat. H) ppm. ^{13}C NMR (50 MHz): 20.0 (CH_3); 20.7 (CH_3); 21.3 (CH_3); 24.0 (CH); 28.0 (CH_3); 29.1 (CH_3); 49.1 (CH_2); 49.9 (CH_2); 79.9 (CH); 81.1 (CH); 124.1 (CH); 124.2 (CH); 124.9 (CH); 125.0 (CH); 127.1 (CH); 127.2 (CH); 128.4 (CH); 128.6 (CH); 128.9 (CH); 129.0 (CH); 130.2 (CH); 130.4 (CH); 132.2 (C); 134.1 (C); 134.3 (C); 135.2 (CH) ppm. EI-MS: 403.9 (8) $[M]^+$, 277.0 (17), 208.0 (52), 190.9 (34) 69.0 (100).

3-Iodo-1-methylbutyl β-Naphthalenesulfonate (5d): 4-Iodo-2-pentanol (1.00 g, 4.7 mmol, see Supporting Information) was treated according to a procedure reported by Tanabe[14] with NEt_3 (1.0 mL, 7.0 mmol), NMe_3·HCl (450 mg, 4.7 mmol), and β-naphthalenesulfonyl chloride (1.6 g, 7.0 mmol) in CH_2Cl_2 (10 mL). After purification by FC (MTBE/pentane, 1:3), **5d** (1.70 g, 90%) was obtained as a mixture of diastereoisomers (1.5:1). IR (nujol): 3058*w*, 2980*w*, 2932*w*, 1416*w*, 1352*s*, 1179*s*, 1133*m*, 1078*m*, 901*s*, 817*m*, 754*m*, 660*m*, 554*m*, 477*w*. ^{1}H NMR (200 MHz): 1.18−1.40 (*m*, 1 H, CH_2, isomer B); 1.26 (*d*, *J* = 6.1 Hz, 3 H, CH_3, isomer A); 1.39 (*d*, *J* = 6.3 Hz, 3 H, CH_3, isomer B); 1.78−1.90 (*m*, 1 H, CH_2); 1.79 (*d*, *J* = 6.8 Hz, 3 H, CH_3, isomer A); 1.83 (*d*, *J* = 6.8 Hz, 3 H, CH_3, isomer B); 2.30−2.33 (*m*, 1 H, CH_2, isomer A); 3.90−3.97 (*m*, 1 H, HCI); 4.76−4.85 (*m*, 1 H, HCO); 7.61−7.71 (*m*, 2 aromat. H); 7.86−8.03 (*m*, 4 aromat. H); 8.48−8.53 (*m*, 1 aromat. H) ppm. ^{13}C NMR (50 MHz): 20.2 (CH_3); 20.9 (CH); 21.3 (CH_3); 24.0 (CH); 28.2 (CH_3); 29.2 (CH_3); 49.1 (CH_2); 49.8 (CH_2); 79.6 (CH); 80.7 (CH); 122.4 (CH); 122.5 (CH); 127.7 (CH); 127.8 (CH); 128.0 (CH); 129.2 (CH); 129.3 (CH); 129.4 (CH); 129.5 (CH); 129.6 (CH); 129.7 (CH); 131.9 (C); 132.1 (C); 133.8 (C); 135.2 (C) ppm. EI-MS: 403.9 (5) $[M]^+$, 277.0 (21), 207.9 (61), 190.9 (54) 69.0 (100).

3-Iodo-1-methylbutyl *p*-(Methoxycarbonyl)benzenesulfonate (5e): 4-Iodo-2-pentanol (1.11 g, 5.18 mmol, see Supporting Information) was treated according to a procedure reported by Tanabe[14] with NEt_3 (1.4 mL, 10.0 mmol), NMe_3·HCl (770 mg, 5.0 mmol), and *p*-(methoxycarbonyl)benzenesulfonyl chloride (2.85 g, 11.7 mmol) in CH_2Cl_2 (30 mL). The crude product was dissolved in CH_2Cl_2 (5 mL) and the solution was cooled to 0 °C. Imidazole (340 mg, 5 mmol) and TMSCl (633 μL, 5 mmol) were added, and the solution was stirred for 1 h. The reaction mixture was diluted with CH_2Cl_2, the organic phase was washed with aq. sat. NH_4Cl and brine and dried ($MgSO_4$), and the solvent was evaporated. After purification (pentane/MTBE, 3:1), **5e** (528 mg, 26%) was obtained as a mixture of diastereoisomers. IR (neat): 2981*w*, 2953*m*, 1732*s*, 1436*m*, 1401*m*, 1366*s*, 1282*s*, 1188*s*, 1116*m*, 1094*m*, 1017*m*, 903*s*, 765*m*, 692*m*, 614*s*. ^{1}H NMR (200 MHz): 1.27 (*d*, *J* = 6.2 Hz, 3 H, CH_3, isomer A); 1.44 (*d*, *J* = 6.3 Hz, 3 H, CH_3, isomer B); 1.78−1.97 (*m*, 2 H, CH_2); 1.85 (*d*, *J* = 6.8 Hz, 3 H, CH_3, isomer A); 1.87 (*d*, *J* = 6.7 Hz, 3 H, CH_3, isomer B); 2.21−2.37 (*m*, 1 H, CH_2, isomer A); 3.85−4.05 (*m*, 1 H, HCI); 3.98 (*s*, 3 H, OCH_3); 4.68−4.89 (*m*, 1 H, HCO); 7.98−8.08 (*m*, 2 aromat. H); 8.19−8.26 (*m*, 2 aromat. H) ppm. ^{13}C NMR (50 MHz): isomer A: 20.0 (CH_3); 20.5 (CH_3); 28.2 (CH_3); 48.9 (CH_2); 52.7 (CH_3); 80.3 (CH); 127.7 (CH); 130.4 (CH); 134.8 (C); 140.9 (C); 165.3 (C); isomer B: 21.2 (CH_3); 23.7 (CH_3); 29.1 (CH_3); 49.6 (CH_2); 52.7 (CH_3); 81.4 (CH); 127.9 (CH); 130.4 (CH); 134.8 (C); 140.9 (C); 165.3 (C) ppm. EI-MS: 381 (2) $[M - OMe]^+$, 285 (24), 217 (12), 199 (66), 135 (51), 69 (100). $C_{13}H_{17}IO_5S$ (412.24): calcd. C 37.88, H 4.16; found C 38.23, H 4.21.

***l*-3-Iodo-1-methylbutyl *p*-Fluorobenzenesulfonate (5f):** *l*-4-Iodo-2-pentanol (170 mg, 0.79 mmol, see Supporting Information) was treated according to a procedure reported by Tipson[13] with pyridine (7 mL) and *p*-fluorobenzenesulfonyl chloride (618 mg, 3.18 mmol). After purification by FC (ether/pentane, 1:5), **5f** (228 mg, 78%) was obtained as an oil. IR ($CHCl_3$): 3011*m*, 2983*m*, 1906*w*, 1594*s*, 1496*s*, 1408*m*, 1368*s*, 1294*m*, 1178*s*, 1157*s*, 1095*s*, 1014*m*, 980*m*, 904*s*, 840*s*. ^{1}H NMR (400 MHz): 1.41 (*d*, *J* = 6.2 Hz, 3 H, CH_3); 1.84−2.00 (*m*, 2 H, CH_2); 1.88 (*d*, *J* = 6.9 Hz, 3 H, CH_3); 3.88−3.97 (*m*, 1 H, HCI); 4.76−4.83 (*m*, 1 H, HCO); 7.22−7.28 (*m*, 2 aromat. H); 7.96−8.01 (*m*, 2 aromat. H) ppm. ^{13}C NMR (100 MHz): 21.3 (CH_3); 24.0 (CH); 29.2 (CH_3); 49.7 (CH_2); 81.0 (CH); 116.7 (*d*, $J_{C,F}$ = 22.6 Hz, CH); 130.8 (*d*, $J_{C,F}$ = 9.5 Hz, CH); 133.1 (C); 165.8 (*d*, $J_{C,F}$ = 256.4 Hz, C) ppm. EI-MS: 372.9 (< 1) $[M + H]^+$, 245.0 (24), 203.0 (16), 197.0 (25), 159.0 (97), 95.0 (100), 75.0 (17), 69.1 (100). $C_{11}H_{14}FIO_3S$ (372.20): calcd. C 35.50, H 3.79; found C 35.61, H 3.88.

***l*-3-Iodo-1-methylbutyl p-Methoxybenzenesulfonate (5g):** *l*-4-Iodo-2-pentanol (340 mg, 1.59 mmol, see Supporting Information) was treated according to a procedure reported by Tipson[13] with pyridine (8 mL) and *p*-methoxybenzenesulfonyl chloride (1.30 g, 6.36 mmol). After purification by FC (ether/pentane, 1:5), **5g** (567 mg, 93%) was obtained as an oil. IR ($CHCl_3$): 3011*m*, 2980*m*, 1903*w*, 1598*s*, 1580*s*, 1499*s*, 1417*m*, 1363*s*, 1263*s*, 1166*s*, 1096*s*, 1028*s*, 980*m*, 904*s*, 834*s*, 628*w*. ^{1}H NMR (400 MHz): 1.37 (*d*, *J* = 6.3 Hz, 3 H, CH_3); 1.84−1.99 (*m*, 2 H, CH_2); 1.87 (*d*, *J* = 6.9 Hz, 3 H, CH_3); 3.89 (*s*, 3 H, CH_3); 3.93−4.02 (*m*, 1 H, HCI); 4.70−4.78 (*m*, 1 H, HCO); 7.00−7.04 (*m*, 2 aromat. H); 7.87−7.91 (*m*, 2 aromat. H) ppm. ^{13}C NMR (100 MHz): 21.3 (CH_3); 24.3 (CH); 29.3 (CH_3); 49.9 (CH_2); 55.7 (CH_3); 80.1 (CH); 114.6 (CH); 128.5 (C); 130.2 (CH); 163.8 (C) ppm. EI-MS: 384.0 (< 1) $[M]^+$, 257.1 (17), 189.0 (17), 171.0 (90), 123.1 (18), 107.1 (33), 92.1 (18), 77.1 (18), 69.1 (100). $C_{12}H_{17}IO_4S$ (384.23): calcd. C 37.51, H 4.46; found C 37.62, H 4.46.

***l*-3-Iodo-1-methylbutyl 5-(Dimethylamino)naphthalenesulfonate (5h):** *l*-4-Iodo-2-pentanol (466 mg, 2.18 mmol, see Supporting Information) was treated according to a procedure reported by Tipson[13] with pyridine (15 mL) and 5-(dimethylamino)naphthalenesulfonyl chloride (500 mg, 1.85 mmol). After purification by FC (ether/pentane, 1:10), **5h** (258 mg 31%) was obtained as an oil. IR ($CHCl_3$): 3008*w*, 2945*w*, 2834*w*, 2792*w*, 1573*m*, 1455*m*, 1359*s*, 1176*s*, 1128*m*, 1072*m*, 1017*w*, 980*w*, 946*m*, 901*s*, 872*m*, 628*m*. ^{1}H NMR (400 MHz): 1.36 (*d*, *J* = 6.3 Hz, 3 H, CH_3); 1.68 (*d*, *J* = 6.9 Hz, 3 H, CH_3); 1.84−1.87 (*m*, 2 H, CH_2); 2.90 [*s*, 6 H, $N(CH_3)_2$]; 3.63−3.72 (*m*, 1 H, HCI); 4.64−4.72 (*m*, 1 H, HCO); 7.19−7.21 (*m*, 1 aromat. H); 7.54−7.60 (*m*, 2 aromat. H); 8.26−8.29 (*m*, 1 aromat. H); 8.32−8.35 (*m*, 1 aromat. H); 8.60−8.62 (*m*, 1 aromat. H) ppm. ^{13}C NMR (100 MHz): 21.4 (CH_3); 24.2 (CH); 29.1 (CH_3); 45.4 (CH_3); 49.9 (CH_2); 80.9 (CH); 115.4 (CH); 119.4 (CH); 123.3 (CH); 128.5 (CH); 130.0 (C); 130.1 (C); 130.5 (CH); 131.6 (CH); 132.3 (C); 151.9 (C) ppm. EI-MS: 447.0 (9) $[M]^+$, 251.0 (100), 170.1 (22), 169.1 (11), 168.1 (22), 154.1 (11), 127.0 (10), 69.1 (10). $C_{17}H_{22}INO_3S$ (447.34): calcd. C 45.65, H 4.96, N 3.13; found C 45.80, H 4.93, N 2.91.

***l*-3-Iodo-1-methylbutyl 2-Thiophenesulfonate (5i):** *l*-4-Iodo-2-pentanol (127 mg, 0.59 mmol, see Supporting Information) was treated according to a procedure reported by Tipson[13] with pyridine (5 mL) and thiophene-2-sulfonyl chloride (452 mg, 2.37 mmol). After purification by FC (ether/pentane, 1:5), **5i** (104 mg, 49%) was obtained as yellowish crystals. Slight epimerization (7%) was observed. M.p. 67 °C. IR ($CHCl_3$): 3098*m*, 3011*s*, 2983*m*, 2936*m*, 1509*m*, 1447*m*, 1405*s*, 1368*s*, 1176*s*, 1128*s*, 1094*s*, 1071*m*, 1015*s*,

980*m*, 912*s*, 855*s*. ^{1}H NMR (400 MHz): 1.43 (*d*, *J* = 6.3 Hz, 3 H, CH_3); 1.88 (*d*, *J* = 6.9 Hz, 3 H, CH_3); 1.88−2.03 (*m*, 2 H, CH_2); 3.95−4.04 (*m*, 1 H, HCI); 4.78−4.86 (*m*, 1 H, HCO); 7.16 (*dxd*, J_1 = 5.1 Hz, J_2 = 3.8 Hz, 1 aromat. H); 7.71 (*dxd*, J_1 = 5.1 Hz, J_2 = 1.4 Hz, 1 aromat. H); 7.78 (*dxd*, J_1 = 3.8 Hz, J_2 = 1.4 Hz, 1 aromat. H) ppm. ^{13}C NMR (100 MHz): 21.2 (CH_3); 24.1 (CH); 29.3 (CH_3); 49.8 (CH_2); 81.5 (CH); 127.7 (CH); 133.8 (CH); 134.5 (CH); 136.8 (C) ppm. EI-MS: 360.0 (< 1) $[M]^+$, 233.1 (16), 197.0 (9), 191.0 (9), 149.0 (11), 147.0 (100), 84.0 (11), 69.1 (38). $C_9H_{13}IO_3S_2$ (360.24): calcd. C 30.01, H 3.64; found C 29.95, H 3.55.

3-Iodo-1-methylbutyl 3-Pyridinesulfonate (5j): 4-Iodo-2-pentanol (1.40 g, 6.52 mmol, see Supporting Information) was treated according to a procedure reported by Tanabe[14] with NEt_3 (1.25 mL, 9.00 mmol), NMe_3·HCl (574 mg, 6.00 mmol), and 3-pyridinesulfonyl chloride (1.61 g, 9.00 mmol) in CH_2Cl_2 (17 mL). After purification by FC (MTBE/pentane, 1:1), **5j** (1.53 g, 72%) was obtained as a mixture of diastereoisomers (1:1). IR (neat): 3052*w*, 2981*m*, 2933*w*, 1575*m*, 1417*m*, 1365*s*, 1186*s*, 1125*m*, 1109*m*, 904*s*, 701*m*, 622*m*, 596*m*. ^{1}H NMR (200 MHz): 1.31 (*d*, *J* = 6.2 Hz, 3 H, CH_3, isomer B); 1.46 (*d*, *J* = 6.2 Hz, 3 H, CH_3, isomer A); 1.80−2.40 (*m*, 2 H, CH_2); 1.88 (*d*, *J* = 6.8 Hz, 3 H, CH_3, isomer B); 1.93 (*d*, *J* = 6.8 Hz, 3 H, CH_3, isomer A); 3.84−4.02 (*m*, 1 H, HCI); 4.77−4.92 (*m*, 1 H, HCO); 7.53−7.57 (*m*, 1 aromat. H); 8.21−8.25 (*m*, 1 aromat. H); 8.88−8.91 (*m*, 1 aromat. H); 9.10−9.30 (*m*, 1 aromat. H) ppm. ^{13}C NMR (50 MHz): 20.2 (CH_3); 20.6 (CH_3); 21.4 (CH); 23.7 (CH); 28.3 (CH_3); 29.1 (CH_3); 48.9 (CH_2); 49.5 (CH_2); 80.8 (CH); 81.8 (CH); 123.8 (CH); 123.9 (CH); 134.0 (C); 135.3 (CH); 135.5 (CH); 148.5 (C); 148.7 (C); 154.3 (C) ppm. EI-MS: 228.2 (22) $[M - I]^+$, 142.0 (21), 69.0 (100). $C_{10}H_{14}INO_3S$ (355.19): calcd. C 33.81, H 3.97, N 3.94; found C 33.96, H 3.96, N 4.30.

General Procedure for the Aryl Migration Reactions (GP 1): The sulfonate was dissolved under argon in benzene and heated to 80 °C. A solution of tributyltin hydride and AIBN in benzene (0.5 mL) was added by syringe pump over 7 h. After complete addition, stirring was continued at that temperature for 30 min. The solution was then allowed to cool to room temp., and MeLi was added. After the mixture had been stirred overnight (14 h) at room temp., H_2O was slowly added and the reaction mixture was diluted with ether. The organic phase was washed with sat. aq. NH_4Cl and brine and dried ($MgSO_4$), and the solvents were evaporated to yield the crude product.

4-Phenyl-2-pentanol (6a): This compound was obtained by GP 1, from sulfonate **5a** (88 mg, 0.25 mmol), benzene (8 mL), Bu_3SnH (99 μL, 0.37 mmol), AIBN (12 mg, 0.07 mmol) in benzene (0.5 mL), and MeLi (0.6 mL, 1.0 mmol). Purification by FC (ether/pentane, 1:4) afforded **6a** (31 mg, 76%). The diastereoisomer ratio (*u*/*l* = 13:1) was determined by GC analysis. The physical data were in agreement with the values reported in the literature.[16]

4-(*p*-Tolyl)-2-pentanol (6b): This compound was obtained by GP 1, from sulfonate **5b** (671 mg, 1.82 mmol), benzene (36 mL), Bu_3SnH (880 μL, 3.32 mmol), AIBN (150 mg, 0.91 mmol) in benzene (3 mL), and MeLi (4.1 mL, 7.3 mmol). Purification by FC (ether/pentane, 1:4) afforded **6b** (210 mg, 65%). The diastereoisomer ratio (*u*/*l* = 10:1) was determined by GC analysis. The physical data were in agreement with the values reported in the literature.[33]

4-(1-Naphthyl)-2-pentanol (6c): This compound was obtained by GP 1, from sulfonate **5c** (180 mg, 0.45 mmol), benzene (14 mL), Bu_3SnH (203 μL, 0.77 mmol), AIBN (34 mg, 0.22 mmol) in benzene (0.5 mL), and MeLi (1.1 mL, 1.8 mmol). Purification by FC (MTBE/pentane, 1:5) afforded **6c** (60 mg, 63%). The diastereoisomer ratio (*u*/*l* = 6:1) was determined by GC analysis. IR ($CHCl_3$): 3380*br*, 3047*w*, 2965*s*, 2927*m*, 1597*w*, 1510*m*, 1456*m*, 1396*m*, 1376*m*, 1127*m*, 1063*w*, 1034*m*, 1007*m*, 798*m*, 778*s*. ^{1}H NMR (200 MHz): 1.21 (*d*, *J* = 6.2 Hz, 3 H, CH_3); 1.43 (*d*, *J* = 7.0 Hz, 3 H, CH_3); 1.64−2.18 (*m*, 2 H, CH_2); 3.77−3.95 (*m*, 1 H, HCI); 4.20−4.25 (*m*, 1 H, HCO); 7.41−7.62 (*m*, 4 aromat. H); 7.72−7.95 (*m*, 2 aromat. H); 8.19−8.23 (*m*, 1 aromat. H) ppm. ^{13}C NMR (50 MHz): 21.7 (CH_3); 24.7 (CH_3); 30.6 (CH); 47.8 (CH_2); 66.7 (CH); 123.0 (CH); 123.6 (CH); 125.8 (CH); 126.0 (CH); 126.3 (CH); 126.9 (CH); 129.4 (CH); 131.8 (C); 134.4 (C); 143.9 (C) ppm. EI-MS: 214.3 (48) $[M]^+$, 155.2 (100), 129.1 (13). HRMS: $C_{15}H_{18}O$ $[M]^+$: calcd. 214.1358; found 214.1365.

4-(2-Naphthyl)-2-pentanol (6d): This compound was obtained by GP 1, from sulfonate **5d** (180 mg, 0.45 mmol), benzene (15 mL), Bu_3SnH (213 μL, 0.80 mmol), AIBN (36 mg, 0.22 mmol) in benzene (0.5 mL), and MeLi (1.1 mL, 1.8 mmol). Purification by FC (MTBE/pentane, 1:4) afforded **6d** (25 mg, 26%). The diastereoisomer ratio (*u*/*l* = 10:1) was determined by GC analysis. IR ($CHCl_3$): 3372*br*, 3053*w*, 2963*s*, 2926*m*, 1456*m*, 1378*m*, 1127*m*, 1033*w*, 945*w*, 857*w*, 818*m*, 747*s*, 478*m*. ^{1}H NMR (200 MHz): 1.20 (*d*, *J* = 7.2 Hz, 3 H, CH_3); 1.34 (*d*, *J* = 6.8 Hz, 3 H, CH_3); 1.71−1.97 (*m*, 2 H, CH_2); 3.04 (*sx*, *J* = 7.2 Hz, 1 H, HCAr); 4.19−4.31 (*m*, 1 H, HCO); 7.39−7.45 (*m*, 3 aromat. H); 7.64 (*s*, 1 aromat. H); 7.77−7.84 (*m*, 3 aromat. H) ppm. ^{13}C NMR (50 MHz): 18.0 (CH_3); 19.4 (CH_3); 32.7 (CH); 43.3 (CH_2); 62.1 (CH); 120.7 (CH); 120.9 (CH); 121.2 (CH); 121.6 (CH); 123.2 (CH); 123.3 (CH); 123.9 (CH); 127.9 (C); 129.3 (C); 140.4 (C) ppm. EI-MS: 214.5 (18) $[M]^+$, 156.4 (100), 112.3 (18). HRMS: $C_{15}H_{18}O$ $[M]^+$: calcd. 214.1358; found 214.1359.

4-[*p*-(Methoxycarbonyl)phenyl]-2-pentanol (6e): This compound was obtained by GP 1, from sulfonate **5e** (142 mg, 0.34 mmol), benzene (12 mL), Bu_3SnH (164 μL, 0.62 mmol), and AIBN (29 mg, 0.17 mmol) in benzene (0.5 mL), without addition of MeLi. Purification by FC (ether/pentane, 1:4) afforded **6e** (42 mg, 55%). The diastereoisomer ratio (*u*/*l* = 11:1) was determined by GC analysis. IR ($CHCl_3$): 3424*br*, 2963*m*, 2929*m*, 1722*s*, 1610*m*, 1437*m*, 1418*w*, 1281*s*, 1181*m*, 1115*s*, 1018*m*, 858*w*, 775*m*, 709*m*. ^{1}H NMR (200 MHz): 1.20 (*d*, *J* = 6.0 Hz, 3 H, CH_3); 1.28 (*d*, *J* = 7.0 Hz, 3 H, CH_3); 1.58−1.90 (*m*, 2 H, CH_2); 3.69−3.81 (*m*, 1 H, HCAryl); 3.87 (*s*, 3 H, OCH_3, isomer B); 3.90 (*s*, 3 H, OCH_3, isomer A); 7.25−7.31 (*m*, 2 aromat. H); 7.92−8.00 (*m*, 2 aromat. H) ppm. ^{13}C NMR (50 MHz): 22.2 (CH_3); 24.2 (CH_3); 37.1 (CH); 47.8 (CH_2); 52.4 (CH_3); 66.4 (CH); 127.3 (CH); 128.4 (C); 130.4 (CH); 153.4 (C); 167.5 (C) ppm. EI-MS: 204 (29) $[M - H_2O]^+$, 145 (100), 105 (57), 69 (63). HRMS: $C_{13}H_{18}O_3$ $[M]^+$: calcd. 222.1256; found 222.1254.

4-(*p*-Fluorophenyl)-2-pentanol (6f): This compound was obtained by GP 1, from sulfonate **5f** (101 mg, 0.27 mmol), benzene (9 mL), Bu_3SnH (108 μL, 0.41 mmol), AIBN (13 mg, 0.08 mmol) in benzene (0.5 mL), and MeLi (0.9 mL, 1.4 mmol). Purification by FC (ether/pentane, 1:2) afforded **6f** (29 mg, 59%). The diastereoisomer ratio (*u*/*l* = 10:1) was determined by GC analysis. The physical data were in agreement with the values reported in the literature.[7b]

4-(*p*-Methoxyphenyl)-2-pentanol (6g): This compound was obtained by GP 1, from sulfonate **5g** (206 mg, 0.54 mmol), benzene (18 mL), Bu_3SnH (214 μL, 0.81 mmol), AIBN (26 mg, 0.16 mmol) in benzene (0.5 mL), and MeLi (1.5 mL, 2.4 mmol). Purification by FC (ether/pentane, 1:2) afforded **6g** (52 mg, 50%). The diastereoisomer ratio (*u*/*l* = 9:1) was determined by GC analysis. The physical data were in agreement with the values reported in the literature.[7b]

4-[5-(Dimethylamino)-1-naphthyl]-2-pentanol (6h): This compound was obtained by GP 1, from sulfonate **5h** (165 mg, 0.37 mmol), benzene (12 mL), Bu_3SnH (147 µL, 0.55 mmol), AIBN (18 mg, 0.11 mmol) in benzene (0.5 mL), and MeLi (1.7 mL, 1.1 mmol). Purification by FC (ether/pentane, 1:2) afforded **6h** (49 mg, 52%). The diastereoisomer ratio (*u*/*l* = 11:1) was determined by ^1H NMR spectroscopy. IR ($CHCl_3$): 3602*w*, 3444*w*, 2967*s*, 2830*m*, 1592*m*, 1510*m*, 1455*m*, 1404*s*, 1306*m*, 1139*m*, 1049*w*, 1003*w*, 959*m*, 840*w*. ^1H NMR (400 MHz): 1.17 (*d*, *J* = 6.2 Hz, 3 H, CH_3); 1.38 (*d*, *J* = 7.0 Hz, 3 H, CH_3); 1.87−1.95 (*m*, 2 H, CH_2); 3.22 [*s*, 6 H, $N(CH_3)_2$]; 3.60−3.70 (*m*, 1 H, CHAryl); 4.10−4.20 (*m*, 1 H, CHO); 7.21 (*d*, *J* = 6.7 Hz, 1 aromat. H); 7.57−7.64 (*m*, 2 aromat. H); 8.32−8.39 (*m*, 2 aromat. H); 8.61 (*d*, *J* = 8.4 Hz, 1 aromat. H) ppm. ^{13}C NMR (100 MHz): 23.1 (CH_3); 24.1 (CH_3); 30.7 (CH); 44.2 (CH_3); 47.5 (CH_2); 66.2 (CH); 115.2 (CH); 118.3 (CH); 122.7 (CH); 123.5 (CH); 128.8 (CH); 131.4 (C); 132.2 (C); 143.5 (C); 152.4 (C) ppm. EI-MS: 257.1 (100, $[M]^+$), 239.1 (10), 212.1 (12), 199.1 (88), 168.1 (22), 183.1 (22), 168.0 (13), 153.0 (21). HRMS: $C_{17}H_{23}NO$ $[M]^+$: calcd. 257.1774; found 257.1779.

4-(2-Thienyl)-2-pentanol (6i): This compound was obtained by GP 1, from sulfonate **5i** (103 mg, 0.29 mmol), benzene (9 mL), Bu_3SnH (114 µL, 0.43 mmol), AIBN (14 mg, 0.08 mmol) in benzene (0.5 mL), and MeLi (0.8 mL, 1.3 mmol). Purification by FC (ether/pentane, 1:3) afforded **6i** (36 mg, 74%). The diastereoisomer ratio (*u*/*l* = 9:1) was determined by GC analysis. IR ($CHCl_3$): 3607*w*, 3451*m*, 3008*s*, 2969*s*, 2928*s*, 1601*w*, 1456*m*, 1379*m*, 1261*w*, 1093*m*, 1038*w*, 944*m*, 907*w*, 848*m*, 826*m*. ^1H NMR (300 MHz): 1.22 (*d*, *J* = 6.2 Hz, 3 H, CH_3); 1.35 (*d*, *J* = 6.8 Hz, 3 H, CH_3); 1.63−1.75 (*m*, 1 H, CH_2); 1.82−1.92 (*m*, 1 H, CH_2); 3.23 (*sx*, *J* = 7.2 Hz, 1 H, HCAryl); 3.83−3.89 (*m*, 1 H, HCO); 6.82−6.84 (*m*, 1 aromat. H); 6.91−6.94 (*m*, 1 aromat. H); 7.12−7.15 (*m*, 1 aromat. H) ppm. ^{13}C NMR (75 MHz): 23.2 (CH_3); 23.9 (CH_3); 32.5 (CH); 48.9 (CH_2); 66.3 (CH); 122.7 (CH); 122.9 (CH); 126.8 (CH); 152.0 (C) ppm. EI-MS: 170.1 (11) $[M]^+$, 152.1 (29), 137.1 (53), 111.1 (100), 97.0 (16), 77.1 (8). $C_9H_{14}OS$ (170.28): calcd. C 63.48, H 8.29; found C 63.46, H 8.43.

4-(3-Pyridyl)-2-pentanol (6j): This compound was obtained by GP 1, from sulfonate **5j** (173 mg, 0.49 mmol), benzene (16 mL), Bu_3SnH (233 µL, 0.88 mmol), AIBN (40 mg, 0.25 mmol) in benzene (0.5 mL), and MeLi (1.2 mL, 1.9 mmol). Purification by FC (MTBE/acetone, 4:1) afforded **6j** (30 mg, 37%). The diastereoisomer ratio (*u*/*l* = 7:1) was determined by GC analysis. IR (nujol): 3353*br*, 3037*w*, 2964*s*, 2927*m*, 2874*w*, 1654*w*, 1459*m*, 1427*s*, 1375*m*, 1131*m*, 1029*m*, 809*m*, 716*s*. ^1H NMR (200 MHz): 1.14 (*d*, *J* = 6.2 Hz, 3 H, CH_3); 1.21 (*d*, *J* = 7.0 Hz, 3 H, CH_3); 1.61−1.74 (*m*, 2 H, CH_2); 2.86 (*sx*, *J* = 7.5 Hz, 1 H, CHAryl); 3.74−3.81 (*m*, 1 H, HCO); 7.17−7.25 (*m*, 1 aromat. H); 7.44−7.48 (*m*, 1 aromat. H); 8.35−8.40 (*m*, 2 aromat. H) ppm. ^{13}C NMR (100 MHz): 21.7 (CH_3); 24.0 (CH_3); 34.1 (CH); 47.4 (CH_2); 65.7 (CH); 123.5 (CH); 134.2 (C); 142.0 (C); 147.5 (C); 148.9 (C) ppm. EI-MS: 147.1 (100) $[M - H_2O]^+$, 106.1 (100). HRMS: $C_{10}H_{13}N$ $[M - H_2O]^+$: calcd. 147.1048; found 147.1056.

3-Bromo-1-cyclohexylbutyl Benzenesulfonate (7a): 3-Bromo-1-cyclohexyl-1-butanol (470 mg, 2.0 mmol, see Supporting Information) was treated according to a procedure reported by Tipson[13] with pyridine (5 mL) and benzenesulfonyl chloride (1.0 mL, 8.0 mmol). After workup, unchanged sulfonyl chloride was removed by stirring the crude product with imidazole (1.0 g, 14.7 mmol) in CH_2Cl_2 (5 mL) for 1 h at room temp. After purification by FC (ether/pentane, 1:4), **7a** (500 mg, 80%) was obtained. IR ($CHCl_3$): 3035*w*, 2933*s*, 2856*m*, 1588*w*, 1449*s*, 1361*s*, 1174*s*, 1096*m*, 900*s*. ^1H NMR (400 MHz): isomer A: 0.88−1.26 (*m*, 5 H, C_6H_{11}); 1.43−1.90 (*m*, 6 H, C_6H_{11}); 1.64 (*d*, *J* = 6.7 Hz, 3 H, CH_3); 1.92−2.07 (*m*, 2 H, CH_2); 3.86−3.94 (*m*, 1 H, HCBr); 4.76−4.79 (*m*, 1 H, HCO); 7.54−7.59 (*m*, 2 aromat. H); 7.64−7.68 (*m*, 1 aromat. H); 7.92−7.98 (*m*, 2 aromat. H); isomer B: 0.88−1.26 (*m*, 5 H, C_6H_{11}); 1.43−1.90 (*m*, 6 H, C_6H_{11}); 1.65 (*d*, *J* = 6.6 Hz, 3 H, CH_3); 1.92−2.07 (*m*, 1 H, CH_2); 2.21−2.28 (*m*, 1 H, CH_2); 3.97−4.05 (*m*, 1 H, HCBr); 4.56−4.60 (*m*, 1 H, HCO); 7.54−7.59 (*m*, 2 aromat. H); 7.64−7.68 (*m*, 1 aromat. H); 7.92−7.98 (*m*, 2 aromat. H) ppm. ^{13}C NMR (100 MHz): isomer A: 25.9 (CH_2); 26.1 (CH_2); 26.3 (CH_2); 26.9 (CH_3); 27.2 (CH_2); 28.3 (CH_2); 42.2 (CH); 42.5 (CH_2); 47.4 (CH); 86.9 (CH); 127.8 (CH); 129.2 (CH); 133.6 (CH); 137.4 (C); isomer B: 25.8 (CH_3); 25.9 (CH_2); 26.0 (CH_2); 26.1 (CH_2); 27.1 (CH_2); 28.3 (CH_2); 40.6 (CH); 42.2 (CH_2); 45.2 (CH); 85.7 (CH); 127.7 (CH); 129.2 (CH); 133.7 (CH); 137.3 (C) ppm. EI-MS: 293.0 (29) $[M - C_6H_{11}]^+$, 253.1 (14), 218.1 (51), 141.0 (100), 109.1 (20), 95.1 (92), 77.1 (64), 55.1 (28). $C_{16}H_{23}BrO_3S$ (375.33): calcd. C 51.20, H 6.18; found C 51.42, H 6.05.

3-Bromo-1-isopropylbutyl Benzenesulfonate (7b): 5-Bromo-2-methyl-3-hexanol (574 mg, 2.94 mmol, see Supporting Information) was treated according to a procedure reported by Tipson[13] with pyridine (15 mL) and benzenesulfonyl chloride (1.5 mL, 11.7 mmol). After workup, unchanged sulfonyl chloride was removed by stirring the crude product with imidazole (400 mg, 5.9 mmol) in CH_2Cl_2 (10 mL) for 1 h at room temp. After purification by FC (ether/pentane, 1:4), **7b** (740 mg, 75%) was obtained. IR ($CHCl_3$): 3566*w*, 3011*m*, 2970*s*, 1467*m*, 1448*s*, 1363*s*, 1175*s*, 1096*s*, 952*m*, 895*s*, 827*m*, 605*s*. ^1H NMR (400 MHz): isomer A: 0.88 (*d*, *J* = 6.9 Hz, 6 H, CH_3); 1.66 (*d*, *J* = 6.7 Hz, 3 H, CH_3); 1.85−2.09 (*m*, 3 H); 3.89−3.99 (*m*, 1 H, HCBr); 4.77−4.81 (*m*, 1 H, HCO); 7.52−7.59 (*m*, 2 aromat. H); 7.64−7.68 (*m*, 1 aromat. H); 7.90−7.97 (*m*, 2 aromat. H); isomer B: 0.88 (*d*, *J* = 7.0 Hz, 6 H, CH_3); 1.66 (*d*, *J* = 6.6 Hz, 3 H, CH_3); 1.85−2.09 (*m*, 2 H, CH_2); 2.22−2.29 (*m*, 1 H); 3.99−4.06 (*m*, 1 H, HCBr); 4.59−4.63 (*m*, 1 H, HCO); 7.52−7.59 (*m*, 2 aromat. H); 7.64−7.68 (*m*, 1 aromat. H); 7.90−7.97 (*m*, 2 aromat. H) ppm. ^{13}C NMR (100 MHz): isomer A: 16.6 (CH_3); 17.8 (CH_3); 26.9 (CH_3); 32.0 (CH); 41.6 (CH_2); 47.4 (CH); 87.0 (CH); 129.2 (CH); 133.7 (CH); 137.3 (C); isomer B: 16.5 (CH_3); 17.8 (CH_3); 25.8 (CH_3); 30.6 (CH); 42.0 (CH_2); 45.1 (CH); 85.9 (CH); 127.7 (CH); 129.2 (CH); 133.7 (CH); 137.2 (C) ppm. EI-MS: 335.1 (6) $[M + H]^+$, 317.0 (8), 293.0 (28), 291.0 (27), 220.9 (15), 213.0 (19), 178.0 (10), 141.0 (100), 97.1 (54), 78.0 (21), 77.0 (94), 71.0 (51), 56.1 (14).

3-Bromo-1-*tert*-butylbutyl Benzenesulfonate (7c): 5-Bromo-2,2-dimethyl-3-hexanol (544 mg, 2.6 mmol, see Supporting Information) was treated according to a procedure reported by Tipson[13] with pyridine (15 mL) and benzenesulfonyl chloride (1.35 mL, 10.3 mmol). After workup, unchanged sulfonyl chloride was removed by stirring the crude product with imidazole (350 mg, 5.2 mmol) in CH_2Cl_2 (10 mL) for 1 h at room temp. After purification by FC (ether/pentane, 1:4), **7c** (380 mg, 42%) was obtained. IR ($CHCl_3$): 3569*s*, 3032*m*, 2971*s*, 2874*m*, 1673*s*, 1480*s*, 1448*s*, 1400*s*, 1361*s*, 1290*m*, 1262*m*, 1174*s*, 1096*s*, 988*m*, 928*s*, 886*s*, 600*s*. ^1H NMR (400 MHz): isomer A: 0.89 [*s*, 9 H, $C(CH_3)_3$]; 1.66 (*d*, *J* = 6.6 Hz, 3 H, CH_3); 1.94−2.07 (*m*, 2 H, CH_2); 4.06−4.16 (*m*, 1 H, HCBr); 4.78 (*dxd*, J_1 = 8.9 Hz, J_2 = 1.4 Hz, 1 H, HCO); 7.52−7.58 (*m*, 3 aromat. H); 7.93−7.97 (*m*, 2 aromat. H); isomer B: 0.90 [*s*, 9 H, $C(CH_3)_3$]; 1.74 (*d*, *J* = 6.5 Hz, CH_3); 2.06−2.12 (*m*, 1 H, CH_2); 2.34−2.41 (*m*, 1 H, CH_2); 4.16−4.23 (*m*, 1 H, HCBr); 4.47 (*dxd*, J_1 = 9.7 Hz, J_2 = 2.1 Hz, 1 H, HCO); 7.62−7.68 (*m*, 3 aromat. H); 7.90−7.93 (*m*, 2 aromat. H) ppm. ^{13}C NMR (100 MHz): isomer A: 26.1 (CH_3); 27.1 (CH_3); 35.1 (C); 42.7 (CH_2); 48.1 (CH); 90.9 (CH); 127.6 (CH); 129.0 (CH); 133.5 (CH); 137.7

(C); isomer B: 25.0 (CH_3); 26.1 (CH_3); 35.2 (C); 43.0 (CH_2); 45.3 (CH); 88.7 (CH); 127.4 (CH); 129.1 (CH); 133.6 (CH); 137.6 (C) ppm. EI-MS: 351.0 (< 1) $[M + H]^+$, 292.9 (66) $[M - C(CH_3)_3]^+$, 222.9 (15), 220.9 (15), 213.0 (28), 193.0 (26), 191.0 (27), 159.0 (23), 141.0 (100), 111.1 (47), 77.0 (76), 57 (96). $C_{14}H_{21}BrO_3S$ (349.29): calcd. C 48.14, H 6.06; found C 48.29, H 5.94.

***l*-1-Cyclohexyl-3-phenyl-1-butanol (8a):** This compound was obtained by GP 1, from sulfonate **7a** (188 mg, 0.5 mmol), benzene (16 mL), Bu_3SnH (200 μL, 0.75 mmol), AIBN (25 mg, 0.15 mmol) in benzene (0.8 mL), and MeLi (1.25 mL, 2.0 mmol). Purification by FC (ether/pentane, 1:4) afforded **8a** (70.8 mg, 61%). The diastereoisomer ratio (*l*/*u* = 10:1) was determined by GC analysis. IR ($CHCl_3$): 3602*w*, 3454*w*, 3008*m*, 2927*s*, 2854*s*, 1602*w*, 1494*m*, 1451*s*, 1377*m*, 976*m*, 893*w*, 840*w*. ^1H NMR (400 MHz): 0.90−1.36 (*m*, 7 H, C_6H_{11}); 1.26 (*d*, *J* = 6.9 Hz, 3 H, CH_3); 1.54−1.76 (*m*, 6 H, CH_2, C_6H_{11}); 2.89−2.98 (*m*, 1 H, HCPh); 3.45−3.49 (*m*, 1 H, HCO); 7.16−7.32 (*m*, 5 aromat. H) ppm. ^{13}C NMR (100 MHz): 21.4 (CH_3); 26.2 (CH_2); 26.4 (CH_2); 26.6 (CH_2); 27.5 (CH_2); 29.3 (CH_2); 36.7 (CH); 43.1 (CH_2); 44.0 (CH); 74.3 (CH); 126.1 (CH); 126.9 (CH); 128.5 (CH); 148.0 (C) ppm. EI-MS: 232.2 (< 1) $[M]^+$, 214.2 (12) $[M - H_2O]^+$, 131.1 (16), 118.1 (55), 105.1 (100), 95.1 (21), 79.1 (7), 55.1 (10), 41.0 (4). $C_{16}H_{24}O$ (232.37): calcd. C 82.70, H 10.41; found C 82.74, H 10.47.

***l*-2-Methyl-5-phenyl-3-hexanol (8b):** This compound was obtained by GP 1, from sulfonate **7b** (84 mg, 0.25 mmol), benzene (8 mL), Bu_3SnH (99 μL, 0.37 mmol), AIBN (12 mg, 0.07 mmol) in benzene (0.5 mL), and MeLi (0.5 mL, 1.0 mmol). Purification by FC (ether/pentane, 1:4) afforded **8b** (29 mg, 60%). The diastereoisomer ratio (*l*/*u* = 11:1) was determined by GC analysis. The physical data were in agreement with the values reported in the literature.[7b]

***l*-2,2-Dimethyl-5-phenyl-3-hexanol (8c):** This compound was obtained by GP 1, from sulfonate **7c** (50 mg, 0.14 mmol), benzene (4.5 mL), Bu_3SnH (56 μL, 0.21 mmol), AIBN (7 mg, 0.04 mmol) in benzene (0.33 mL), and MeLi (0.4 mL, 0.56 mmol). Purification by FC (ether/pentane, 1:4) afforded **8c** (27 mg, 94%). The diastereoisomer ratio (*l*/*u* = 11:1) was determined by GC analysis. The physical data were in agreement with the values reported in the literature.[7b]

3-Iodo-1-methylpropyl Benzenesulfonate (9): 1-Benzenesulfonyl-1*H*-imidazole (4.2 g, 20 mmol) was dissolved in THF (20 mL) under argon and the solution was cooled to 0 °C. Methyl triflate (2.2 mL, 20 mmol) was added dropwise over 3 min, and the reaction mixture was stirred at 0 °C for 30 min. A solution of 4-iodo-2-butanol (1.0 g, 5 mmol)[34] and *N*-methylimidazole (0.39 g, 5.0 mmol) in THF (5 mL) was added. The reaction mixture was allowed to warm to room temp. and stirred for 13 h. It was then quenched with H_2O (30 mL) and extracted with ethyl acetate. The organic phase was washed with 0.5 M H_3PO_4, sat aq. $NaHCO_3$, and brine, and dried ($MgSO_4$), and the solvent was evaporated. After purification by FC (pentane/ether, 8:1), **9** (420 mg, 25%) was obtained. IR ($CHCl_3$): 3568*w*, 3011*m*, 2937*w*, 1586*w*, 1448*s*, 1364*s*, 1177*s*, 1126*m*, 1096*s*, 1024*w*, 1000*w*, 910*s*. ^1H NMR (400 MHz): 1.30 (*d*, *J* = 6.3 Hz, 3 H, CH_3); 1.97−2.06 (*m*, 1 H, CH_2); 2.15−2.22 (*m*, 1 H, CH_2); 2.93−2.99 (*m*, 1 H, H-CI); 3.07−3.12 (*m*, 1 H, H-CI); 4.67−4.75 (*m*, 1 H, HCO); 7.55−7.60 (*m*, 2 aromat. H); 7.64−7.69 (*m*, 1 aromat. H); 7.92−7.96 (*m*, 2 aromat. H) ppm. ^{13}C NMR (100 MHz): 0.6 (CH_2); 20.6 (CH_3); 40.4 (CH_2); 80.0 (CH); 127.8 (CH); 129.4 (CH); 133.8 (CH); 137.1 (C) ppm. EI-MS: 340.0 (1) $[M]^+$, 325.0 (< 1) $[M - CH_3]^+$, 213.1 (51), 182.0 (40), 159.0 (67), 141.0 (100), 77.0 (98), 55.1 (59).

4-Phenyl-2-butanol (10): This compound was obtained by GP 1, from sulfonate **9** (102 mg, 0.3 mmol), benzene (10 mL), Bu_3SnH (119 μL, 0.45 mmol), AIBN (14.8 mg, 0.09 mmol) in benzene (0.3 mL), and MeLi (0.75 mL, 1.2 mmol). Purification by FC (ether/pentane, 1:2) afforded **10** (19 mg, 42%). The physical data were in agreement with the values reported in the literature.[35]

1,3-Dimethyl-3-(phenylselanyl)butyl Benzenesulfonate (11): 4-Methyl-4-(phenylselanyl)-2-pentanol (576 mg, 2.24 mmol) was treated according to a procedure reported by Tanabe[14] with NEt_3 (0.78 mL, 3.6 mmol), NMe_3·HCl (214 mg, 2.24 mmol), and benzenesulfonyl chloride (0.43 mL, 3.36 mmol) in CH_2Cl_2 (8 mL). After purification by FC (ether/pentane, 1:5), **11** (0.86 g, 97%) was obtained. The product has to be protected from direct sunlight! M.p. 61 °C. IR ($CHCl_3$): 2960*s*, 1576*w*, 1475*s*, 1446*s*, 1173*s*, 1127*s*, 1035*m*, 1016*s*, 996*s*, 863*w*. ^1H NMR (400 MHz): 1.31 (*s*, 3 H, CH_3); 1.32 (*d*, *J* = 6.2 Hz, 3 H, CH_3); 1.33 (*s*, 3 H, CH_3); 1.75 (*dxd*, J_1 = 15.4 Hz, J_2 = 3.5 Hz, 1 H, CH_2); 2.01 (*dxd*, J_1 = 15.4 Hz, J_2 = 7.3 Hz, 1 H, CH_2); 5.07 (*qxdxd*, J_1 = 7.3 Hz, J_2 = 6.2 Hz, J_3 = 3.5 Hz, 1 H, HCO); 7.27−7.31 (*m*, 2 aromat. H); 7.35−7.39 (*m*, 1 aromat. H); 7.51−7.57 (*m*, 4 aromat. H); 7.61−7.65 (*m*, 1 aromat. H); 7.92−7.95 (*m*, 2 aromat. H) ppm. ^{13}C NMR (100 MHz): 22.8 (CH_3); 28.7 (CH_3); 30.9 (CH_3); 45.0 (C); 49.7 (CH_2); 79.1 (CH); 127.4 (C); 127.7 (CH); 128.8 (CH); 129.1 (CH); 133.6 (CH); 137.8 (C); 138.3 (CH) ppm. EI-MS: 398.1 (< 1) $[M + H]^+$, 314.0 (1), 267.1 (1), 240.1 (24) 157.0 (24), 83.1 (100). $C_{18}H_{22}O_3SSe$ (397.40): calcd. C 54.40, H 5.58; found C 54.50, H 5.71.

4-Methyl-4-phenyl-2-pentanol (12): This compound was obtained by GP 1, from sulfonate **11** (268 mg, 0.68 mmol), benzene (23 mL), Bu_3SnH (269 μL, 1.01 mmol), and AIBN (29 mg, 0.20 mmol) in benzene (0.5 mL), without addition of MeLi. Purification by FC (ether/pentane, 1:5) afforded **12** (12 mg, 10%) and the direct reduction product 1,3-dimethylbutyl benzenesulfonate (135 mg, 83%).

1,3-Dimethylbutyl Benzenesulfonate: IR ($CHCl_3$): 3570*m*, 2959*s*, 2871*m*, 1587*m*, 1448*s*, 1364*s*, 1172*s*, 1095*s*, 1000*m*, 912*s*. ^1H NMR (400 MHz): 0.74 (*d*, *J* = 6.6 Hz, 3 H, CH_3); 0.81 (*d*, *J* = 6.5 Hz, 3 H, CH_3); 1.26−1.30 (*m*, 1 H, CH); 1.28 (*d*, *J* = 6.2 Hz, 3 H, CH_3); 1.53−1.60 (*m*, 2 H, CH_2); 4.66−4.73 (*m*, 1 H, HCO); 7.52−7.57 (*m*, 2 aromat. H); 7.62−7.66 (*m*, 1 aromat. H); 7.91−7.94 (*m*, 2 aromat. H) ppm. ^{13}C NMR (100 MHz): 21.3 (CH_3); 21.9 (CH_3); 22.7 (CH_3); 44.3 (CH); 45.8 (CH_2); 79.5 (CH); 127.7 (CH); 129.1 (CH); 133.5 (CH); 137.6 (C) ppm. EI-MS: 243.1 (< 1) $[M + H]^+$, 227.0 (2), 185.0 (63), 140.9 (100). $C_{12}H_{18}O_3S$ (242.34): calcd. C 59.48, H 7.49; found C 59.33, H 7.38.

3-[(*o*-Bromophenyl)dimethylsiloxy]-1-methylpropyl Benzenesulfonate (13): 3-Hydroxy-1-methylpropyl benzenesulfonate (348 mg, 1.51 mmol, see Supporting Information) was dissolved in THF (5 mL) and the solution was cooled to 0 °C. After addition of NEt_3 (237 μL, 1.7 mmol), (*o*-bromophenyl)dimethylsilyl chloride (374 mg, 1.5 mmol)[36] and cat. DMAP, the reaction mixture was allowed to warm to room temp. and stirred for 18 h. The reaction mixture was diluted with pentane and the precipitate was removed by filtration. The solvent was evaporated. After purification (pentane/MTBE 5:1), **13** (525 mg, 79%) was obtained. IR (neat): 3060*w*, 2957*w*, 2878*w*, 1449*m*, 1360*m*, 1253*m*, 1187*s*, 1097*m*, 1018*m*, 902*s*, 830*m*, 754*m*, 689*w*, 592*s*. ^1H NMR (200 MHz): 1.33 (*d*, *J* = 6.3 Hz, 3 H, CH_3); 1.68−2.01 (*m*, 2 H, CH_2); 3.45−3.67 (*m*, 2 H, CH_2O); 4.80−4.96 (*m*, 1 H, HCO); 7.20−7.34 (*m*, 2 aromat. H); 7.45−7.65 (*m*, 5 aromat. H); 7.88−7.92 (*m*, 2 aromat. H) ppm. ^{13}C NMR (100 MHz): −1.3 (CH_3); −1.2 (CH_3); 21.1 (CH_3); 39.3 (CH_2); 58.7 (CH_2); 78.2 (CH); 126.5 (CH); 127.6 (CH); 129.1 (CH); 130.2 (CH); 131.3 (CH); 132.7 (CH); 133.4 (CH); 136.5 (CH); 137.4 (C); 139.1 (C) ppm. EI-MS: 429 (1) $[M - CH_3]^+$, 357 (41), 355 (45), 217 (100) 215 (38), 159 (24), 141 (22), 91 (44). $C_{18}H_{23}BrO_4SSi$ (443.43): calcd. C 48.75, H 5.23; found C 48.54, H 5.17.

4-[Dimethyl(phenyl)siloxy]-4-phenyl-2-butanol (14) and 3-[Dimethyl-(phenyl)siloxy]-1-methylpropyl Benzenesulfonate (15): These compounds were obtained by GP 1, from sulfonate **13** (118 mg, 0.27 mmol), benzene (9 mL), Bu_3SnH (106 μL, 0.35 mmol), and AIBN (12 mg, 0.08 mmol) in benzene (0.5 mL), without addition of MeLi. Purification by FC (ether/pentane, 1:6) afforded **14** (4 mg, 5%) and the direct reduction product **15** (86 mg, 89%). The second diastereoisomer of **14** could not be observed in the ^1H NMR spectrum.

4-[Dimethyl(phenyl)siloxy]-4-phenyl-2-butanol (14): IR ($CHCl_3$): 3492*s*, 3069*m*, 3007*s*, 1590*w*, 1494*m*, 1427*s*, 1376*s*, 1063*s*, 989*s*, 930*s*, 870*m*, 826*s*, 625*w*. ^1H NMR (400 MHz): 0.26 (*s*, 3 H, CH_3); 0.33 (*s*, 3 H, CH_3); 1.10 (*d*, J = 6.3 Hz, 3 H, CH_3); 1.62−1.64 (*m*, 1 H, CH_2); 1.74−1.78 (*m*, 1 H, CH_2); 2.66 (*d*, J = 3.1 Hz, 1 H, OH); 3.90−3.98 (*m*, 1 H, HCO); 4.98 (*dxd*, J_1 = 9.9 Hz, J_2 = 3.8 Hz, 1 H, HCO); 7.21−7.42 (*m*, 8 aromat. H); 7.54−7.56 (*m*, 2 aromat. H) ppm. ^{13}C NMR (100 MHz): −1.9 (CH_3); −1.2 (CH_3); 20.5 (CH_3); 47.9 (CH_2); 64.4 (CH); 73.3 (CH); 125.8 (CH); 127.1 (CH); 128.0 (CH); 128.2 (CH); 129.9 (CH); 133.5 (CH); 137.2 (C); 144.1 (C) ppm. EI-MS: 300.2 (< 1) $[M]^+$, 282.2 (7), 241.1 (98), 181.1 (16), 167.1 (51), 135.1 (100). $C_{18}H_{24}O_2Si$ (300.47): calcd. C 71.95, H 8.05; found C 71.77, H 8.09.

3-[Dimethyl(phenyl)siloxy]-1-methylpropyl Benzenesulfonate (15): ^1H NMR (400 MHz): 0.31 (*s*, 3 H, CH_3); 0.31 (*s*, 3 H, CH_3); 1.29 (*d*, J = 6.2 Hz, 3 H, CH_3); 1.63−1.73 (*m*, 1 H, CH_2); 1.79−1.90 (*m*, 1 H, CH_2); 3.43−3.56 (*m*, 2 H, H_2CO); 4.76−4.87 (*m*, 1 H, HCO); 7.34−7.52 (*m*, 7 aromat. H); 7.58−7.64 (*m*, 1 aromat. H); 7.87−7.91 (*m*, 2 aromat. H) ppm. ^{13}C NMR (100 MHz): −2.1 (CH_3); −1.9 (CH_3); 21.1 (CH_3); 39.3 (CH_2); 58.6 (CH_2); 78.2 (CH); 127.7 (CH); 127.9 (CH); 129.1 (CH); 129.7 (CH); 133.41 (CH); 133.44 (CH); 137.5 (C); 137.6 (C).

3-Iodo-2-methylbutyl Benzenesulfonate (22): 3-Iodo-2-methylbutanol (190 mg, 0.88 mmol, mixture of diastereoisomers) was treated according to a procedure reported by Tipson[13] with pyridine (8 mL) and benzenesulfonyl chloride (0.546 mL, 3.55 mmol). After purification by FC (ether/pentane, 1:8), **22** (216 mg, 69%) was obtained as a mixture of diastereoisomers (1:1). IR ($CHCl_3$): 3011*m*, 2973*m*, 1586*w*, 1449*s*, 1366*s*, 1176*s*, 1146*m*, 1097*m*, 976*s*, 837*s*. ^1H NMR (400 MHz): isomer A: 0.88 (*d*, J = 6.6 Hz, 3 H, CH_3); 1.19−1.26 (*m*, 1 H, CH); 1.87 (*d*, J = 7.1 Hz, 3 H, CH_3); 3.76−3.83 (*m*, 1 H, H_2CO); 3.91−4.01 (*m*, 1 H, H_2CO); 4.38−4.43 (*m*, 1 H, HCI); 7.56−7.60 (*m*, 2 aromat. H); 7.65−7.69 (*m*, 1 aromat. H); 7.90−7.95 (*m*, 2 aromat. H); isomer B: 1.01 (*d*, J = 6.2 Hz, 3 H, CH_3); 1.84 (*d*, J = 7.1 Hz, 3 H, CH_3); 3.91−4.01 (*m*, 1 H, H_2CO); 4.04−4.14 (*m*, 1 H, H_2CO); 4.18−4.29 (*m*, 1 H, HCI); 7.56−7.60 (*m*, 2 aromat. H); 7.65−7.69 (*m*, 1 aromat. H); 7.90−7.95 (*m*, 2 aromat. H) ppm. ^{13}C NMR (100 MHz): 13.7 (CH_3); 15.5 (CH_3); 25.3 (CH_3); 26.2 (CH_3); 30.8 (CH); 33.4 (CH); 40.1 (CH); 41.5 (CH); 74.0 (CH_2); 74.8 (CH_2); 127.9 (CH); 128.0 (CH); 129.3 (CH); 129.4 (CH); 133.8 (CH); 133.9 (CH); 135.8 (C); 136.6 (C) ppm. EI-MS: 355.1 (< 1) $[M + H]^+$, 227.1 (7), 159.1 (12), 141.0 (100), 77.1 (76), 69.1 (65).

***l*-2-Methyl-3-phenyl-1-butanol (23):** This compound was obtained by GP 1, from sulfonate **22** (109 mg, 0.31 mmol), benzene (10 mL), Bu_3SnH (122 μL, 0.46 mmol), AIBN (15 mg, 0.09 mmol) in benzene (0.5 mL), and MeLi (0.9 mL, 1.4 mmol). Purification by FC (ether/pentane, 1:5) afforded **23** (25 mg, 49%). The diastereoisomer ratio (*l*/*u* = 7:1) was determined by ^1H NMR spectroscopy. The physical data were in agreement with the values reported in the literature.[37] However, in ref.[37] the relative configuration was not correctly assigned. We oxidized alcohol **23** under Swern conditions to afford the corresponding known aldehyde[38] to assign the relative configuration.

1-(Benzyloxymethyl)-2-bromopropyl Benzenesulfonate (26): 1-(Benzyloxy)but-2-ene oxide (1.025 g, 5.76 mmol)[39] was treated according to a procedure reported by Bonini[40] with LiBr (1.69 g, 19.5 mmol) and Amberlyst 15 (3.29 g) in acetonitrile (49 mL). After purification by FC (pentane/MTBE, 1:2), 1-(benzyloxy)-3-bromo-2-butanol (732 mg, 49%) was obtained. ^1H NMR (200 MHz): 1.72 (*d*, J = 6.7 Hz, 3 H, CH_3); 2.60 (*d*, J = 5.2 Hz, 1 H, OH); 3.60−3.74 (*m*, 2 H, H_2CO); 3.82−3.93 (*m*, 1 H, HCBr); 4.20 (*qui*, 1 H, J = 6.6 Hz, HCO); 4.56 (*s*, 2 H, OCH_2); 7.29−7.42 (*m*, 5 aromat. H). 1-(Benzyloxy)-3-bromo-2-butanol (699 mg, 2.70 mmol) was treated according to a procedure reported by Tanabe[14] with NEt_3 (0.57 mL, 4.05 mmol), NMe_3·HCl (388 mg, 2.70 mmol), and benzenesulfonyl chloride (0.52 mL, 4.05 mmol) in CH_2Cl_2 (8 mL). After purification by FC (MTBE/pentane, 1:6), **26** (868 mg, 81%) was obtained. IR (neat): 3064*w*, 2978*w*, 2924*w*, 1449*m*, 1368*s*, 1188*s*, 1117*m*, 1097*m*, 999*m*, 906*s*, 805*w*, 754*m*, 584*m*. ^1H NMR (300 MHz): 1.65 (*d*, J = 6.9 Hz, 3 H, CH_3); 3.66 (*dxd*, J_1 = 10.9 Hz, J_2 = 3.8 Hz, 1 H, OCH_2); 3.80 (*dxd*, J_1 = 10.9 Hz, J_2 = 4.8 Hz, 1 H, OCH_2); 4.27−4.40 (*m*, 1 H, HCBr); 4.41 (*s*, 2 H, OCH_2); 4.70−4.78 (*m*, 1 H, CHO); 7.19−7.52 (*m*, 8 aromat. H); 7.60 (*d*, J = 6.7 Hz, 2 aromat. H) ppm. ^{13}C NMR (50 MHz): 21.5 (CH_3); 45.2 (CH); 69.0 (CH_2); 73.4 (CH_2); 83.6 (CH); 127.7 (CH); 127.8 (CH); 128.0 (CH); 128.4 (CH); 129.0 (CH); 133.8 (CH); 136.7 (C); 137.3 (C) ppm. EI-MS: 399.9 (3) $[M]^+$, 397.9 (3) $[M]^+$, 161.0 (39), 107.1 (100), 91.1 (43), 77.0 (11). $C_{17}H_{19}BrO_4S$ (399.30): calcd. C 51.13, H 4.80; found C 50.95, H 4.54.

4-Iodo-1-methylpentyl Benzenesulfonate (28): 5-Iodo-2-hexanol (0.48 g, 2.27 mmol) was treated according to a procedure reported by Tanabe[14] with NEt_3 (0.79 mL, 5.68 mmol), NMe_3·HCl (217 mg, 2.27 mmol), and benzenesulfonyl chloride (0.44 mL, 3.4 mmol) in CH_2Cl_2 (5 mL). After purification by FC (ether/pentane, 1:5), **28** (591 mg, 71%) was obtained as a mixture of diastereoisomers (2:1). IR ($CHCl_3$): 3032*m*, 2984*m*, 2916*w*, 1586*w*, 1480*m*, 1448*s*, 1355*s*, 1176*s*, 1096*m*, 1024*w*, 899*s*. ^1H NMR (400 MHz): isomer A: 1.27 (*d*, J = 6.3 Hz, 3 H, CH_3); 1.43−1.85 (*m*, 4 H, CH_2); 1.84 (*d*, J = 6.8 Hz, 3 H, CH_3); 4.00−4.09 (*m*, 1 H, HCI); 4.62−4.72 (*m*, 1 H, HCO); 7.54−7.59 (*m*, 2 aromat. H); 7.91−7.94 (*m*, 2 aromat. H); isomer B: 1.28 (*d*, J = 6.3 Hz, 3 H, CH_3); 1.43−1.85 (*m*, 4 H, CH_2); 1.85 (*d*, J = 6.8 Hz, 3 H, CH_3); 4.00−4.09 (*m*, 1 H, HCI); 4.62−4.72 (*m*, 1 H, HCO); 7.54−7.59 (*m*, 2 aromat. H); 7.64−7.68 (*m*, 1 aromat. H); 7.91−7.94 (*m*, 2 aromat. H) ppm. ^{13}C NMR (100 MHz): isomer A: 20.9 (CH_3); 28.9 (CH); 36.6 (CH_2); 37.5 (CH_2); 79.4 (CH); 127.7 (CH); 129.2 (CH); 133.7 (CH); 137.4 (C); isomer B: 21.0 (CH_3); 28.9 (CH); 36.9 (CH_2); 38.2 (CH_2); 80.1 (CH); 127.7 (CH); 129.2 (CH); 133.7 (CH); 136.6 (C) ppm. EI-MS: 369.1 (< 1) $[M + H]^+$, 241.1 (9), 211.0 (61), 141.0 (72), 83.1 (100). $C_{12}H_{17}IO_3S$ (368.24): calcd. C 39.14, H 4.65; found C 39.23, H 4.63.

1-Methylpentyl Benzenesulfonate (29): This compound was obtained by GP 1, from sulfonate **28** (148 mg, 0.40 mmol), benzene (13 mL), Bu_3SnH (159 μL, 0.60 mmol), and AIBN (17 mg, 0.12 mmol) in benzene (0.5 mL), without addition of MeLi. Purification by FC (ether/pentane, 1:5) afforded the direct reduction product **29** (80 mg, 83%). IR ($CHCl_3$): 3011*m*, 2873*m*, 1587*w*, 1448*s*, 1360*s*, 1292*w*, 1176*s*, 1095*m*, 915*s*, 834*w*. ^1H NMR (300 MHz): 0.78−0.83 (*m*, 3 H, CH_3); 1.15−1.24 (*m*, 4 H, CH_2); 1.26 (*d*, J = 6.2 Hz, 3 H, CH_3); 1.43−1.67 (*m*, 2 H, CH_2); 4.64 (*sx*, J = 6.2 Hz, 1 H, HCO); 7.51−7.57 (*m*, 2 aromat. H); 7.61−7.66 (*m*, 1 aromat. H); 7.90−7.94 (*m*, 2 aromat. H) ppm. ^{13}C NMR

(75 MHz): 13.8 (CH_3); 20.9 (CH_3); 22.2 (CH_2); 27.0 (CH_2); 36.2 (CH_2); 81.1 (CH); 127.7 (CH); 129.1 (CH); 133.4 (CH); 137.6 (C) ppm. EI-MS: 241.1 (< 1) $[M - H]^+$, 199.0 (1), 185.0 (44), 141.0 (100). $C_{12}H_{18}O_3S$ (242.34): calcd. C 59.48, H 7.49; found C 59.55, H 7.30.

***O*-{1-Methyl-3-[(*p*-tolylsulfonyl)amino]butyl} 1*H*-Imidazole-1-carbothioate (30):** A solution of *N*-(3-hydroxy-1-methylbutyl)-*p*-toluenesulfonamide (300 mg, 1.17 mmol, see Supporting Information) and 1,1′-thiocarbonylbis(imidazole) (416 mg, 2.33 mmol) in CH_2Cl_2 (15 mL) was stirred for 14 h at room temp. The yellow reaction mixture was washed with sat. aq. NH_4Cl and brine and dried ($MgSO_4$), and the solvents were evaporated to yield the crude product. After purification by FC (ether/pentane 3:1), **30** (0.41 g, 95%) was obtained as a colorless solid. M.p. 119 °C. IR (KBr): 3082*s*, 2866*s*, 1597*m*, 1470*s*, 1384*s*, 1287*s*, 1238*s*, 1163*s*, 1145*s*, 1113*s*, 999*s*, 960*s*. ^{1}H NMR (300 MHz): 1.10 (*d*, *J* = 6.6 Hz, 3 H, CH_3); 1.42 (*d*, *J* = 6.3 Hz, 3 H, CH_3); 1.79−1.87 (*m*, 1 H, CH_2); 1.93−2.06 (*m*, 1 H, CH_2); 2.38 (s, 3 H, CH_3Ph); 3.38−3.53 (*m*, 1 H, CHN); 5.34 (*d*, *J* = 8.5 Hz, 1 H, NH); 5.51-5.69 (*m*, 1 H, CHO); 7.03 (*s*, 1 aromat. H, $C_3H_3N_2$); 7.21 (*d*, *J* = 8.1 Hz, 2 aromat. H); 7.57 (*s*, 1 aromat. H, $C_3H_3N_2$); 7.69 (*d*, *J* = 8.1 Hz, 2 aromat. H); 8.27 (*s*, 1 aromat. H, $C_3H_3N_2$) ppm. ^{13}C NMR (75 MHz): 19.6 (CH_3); 21.9 (CH_3); 22.5 (CH_3); 27.4 (CH_2); 43.9 (CH_2); 47.2 (CH); 78.6 (CH); 118.2 (CH); 127.3 (CH); 130.1 (CH); 130.9 (CH); 137.1 (C); 138.1 (C); 143.9 (C); 183.4 (C) ppm. EI-MS: 234.2 (100), 198.1 (15), 155.1 (88), 133.2 (40), 124.1 (61), 91.1 (86). $C_{16}H_{21}N_3O_3S_2$ (367.49): calcd. C 52.29, H 5.76, N 11.43; found C 52.03, H 5.62, N 11.43.

2-Amino-4-(*p*-tolyl)pentane (31a)

a) Reaction at 80 °C in Benzene: The compound was obtained by GP 1, from thiocarbamate **30** (201 mg, 0.55 mmol), benzene (18 mL), Bu_3SnH (261 μL, 0.98 mmol), AIBN (45 mg, 0.27 mmol) in benzene (0.5 mL), and MeLi (1.41 mL, 2.2 mmol). The yield (37%) was determined by ^{1}H NMR spectroscopy, with acetophenone [δ = 2.59 ppm (*s*, 3 H, CH_3)] as internal standard. The diastereoisomer ratio (*u*/*l* > 95:5) was determined by GC analysis.

b) Reaction at 140 °C in Xylene: The compound was obtained by GP 1, from thiocarbamate **30** (324 mg, 0.88 mmol), xylene (29 mL), Bu_3SnH (421 μL, 1.59 mmol), *t*BuOO*t*Bu (81 μL, 0.44 mmol) in xylene (0.5 mL), and MeLi (2.26 mL, 3.52 mmol). The yield (37%) was determined by ^{1}H NMR spectroscopy, with acetophenone [δ = 2.59 ppm (*s*, 3 H, CH_3)] as internal standard. The diastereoisomer ratio (*u*/*l* = 6:1) was determined by GC analysis.

***N*-(1-Methylbutyl)-*p*-toluenesulfonamide (32):** IR (Nujol): 3280*s*, 3030*w*, 2961*s*, 2933*w*, 2873*w*, 1599*m*, 1427*s*, 1325*s*, 1305*w*, 1164*s*, 1094*s*, 815*m*, 666*s*, 580*s*, 553*s*. ^{1}H NMR (300 MHz): 0.79 (*t*, *J* = 6.8 Hz, 3 H, CH_3); 1.01 (*d*, *J* = 6.6 Hz, 3 H, CH_3); 1.09−1.91 (*m*, 4 H, CH_2); 2.43 (*s*, 3 H, CH_3Ph); 3.21−3.36 (*m*, 1 H, CHN); 4.62 (*d*, *J* = 8.1 Hz, 1 H, NH); 7.29 (*d*, *J* = 8.0 Hz, 2 aromat. H); 7.77 (*d*, *J* = 8.3 Hz, 2 aromat. H) ppm. ^{13}C NMR (75 MHz): 14.0 (CH_3); 19.0 (CH_2); 21.8 (CH_3); 22.0 (CH_3); 39.9 (CH_2); 50.1 (CH); 127.4 (CH); 129.9 (CH); 138.6 (C); 143.4 (C) ppm. EI-MS: 241.0 (< 1) $[M]^+$, 226.0 (6) $[M - CH_3]^+$, 198.0 (100), 155.0 (90), 91.0 (50). $C_{12}H_{19}NO_2S$ (241.35): calcd. C 59.72, H 7.93; found C 59.55, H 7.86.

2-Amino-4-(*p*-tolyl)pentane (31b): 4-(*p*-Tolyl)-2-pentanol (**6b**, 2.12 g, 11.89 mmol, *u*/*l* = 10:1) was dissolved in CH_2Cl_2 (30 mL) and the solution was cooled to 0 °C. After addition of NEt_3 (1.99 mL, 14.27 mmol) and MsCl (1.11 mL, 14.27 mmol), the reaction mixture was allowed to warm to room temp. and stirred for 14 h. The reaction mixture was diluted with CH_2Cl_2 and then washed with sat. aq. NH_4Cl and brine and dried ($MgSO_4$). The solvents were evaporated to yield the crude mesylate, which was purified by FC (pentane/ether, 3:1) to yield 1-methyl-3-(*p*-tolyl)butyl methanesulfonate (3.02 g, 99%). ^{1}H NMR (200 MHz): 1.27 (*d*, *J* = 7.0 Hz, 3 H, CH_3); 1.41 (*d*, *J* = 6.2 Hz, 3 H, CH_3); 1.72−2.25 (*m*, 2 H, CH_2); 2.32 (*s*, 3 H, CH_3Ph); 2.80-2.88 (*m*, 1 H, CHPh); 2.89 (*s*, 3 H, CH_3SO_3); 4.60−4.73 (*m*, 1 H, CHO); 7.05-7.14 (*m*, 4 aromat. H) ppm. The mesylate (3.02 g, 11.78 mmol) and NaN_3 (1.16 g, 17.79 mmol) were mixed in DMSO (24 mL) and stirred for 74 h at 70 °C. After cooling to room temp., the suspension was diluted with ether and the reaction mixture was washed with sat. aq. NH_4Cl and brine, dried ($MgSO_4$), and carefully evaporated (HN_3!) to yield the crude product. After purification by FC (pentane/ether, 100:1), 2-azido-4-(*p*-tolyl)pentane (2.13 g, 89%) was obtained. ^{1}H NMR (200 MHz): 1.19 (*d*, *J* = 6.5 Hz, 3 H, CH_3); 1.24 (*d*, *J* = 7.0 Hz, 3 H, CH_3); 1.62−1.72 (*m*, 2 H, CH_2); 2.33 (*s*, 3 H, CH_3Ph); 2.79-2.98 (*m*, 1 H, CH); 3.05−3.21 (*m*, 1 H, CH); 7.03−7.15 (*m*, 4 aromat. H). A solution of the azide (101 mg, 0.50 mmol) in Et_2O (2 mL) was added dropwise to a suspension of $LiAlH_4$ (38 mg, 1.0 mmol) in Et_2O (3 mL) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C and then heated to reflux for 30 min. After the mixture had been cooled to 0 °C, H_2O (50 μL) was carefully added and the reaction mixture was stirred for 5 min. After addition of 15% aq. NaOH (50 μL), the reaction mixture was stirred for an additional 5 min and H_2O (100 μL) was then added. The reaction mixture was allowed to warm to room temp. and stirred for 20 min. The white precipitate formed was removed by filtration and washed three times with ether. The organic phase was dried ($MgSO_4$) and the solvent was evaporated to yield **31b** (88 mg, 99%). The diastereoisomer ratio (*l*/*u* = 9:1) was determined by GC analysis. ^{1}H NMR (200 MHz): 1.01 (*d*, *J* = 6.2 Hz, 3 H, CH_3); 1.23 (*d*, *J* = 7.0 Hz, 3 H, CH_3); 1.43−1.71 (*m*, 2 H, CH_2); 2.32 (*s*, 3 H, CH_3Ph); 2.60−2.91 (*m*, 2 H, 2 × CH); 7.10 (*s*, 4 aromat. H). HRMS: $C_{12}H_{19}N$ $[M]^+$: calcd. 177.1517; found 177.1522.

***N*-(3-Hydroxy-1-methylbutyl)-*N*-methyl-*p*-toluenesulfonamide (37):** K_2CO_3 (4.51 g, 32.64 mmol) was suspended in a solution of *N*-(3-hydroxy-1-methylbutyl)-*p*-toluenesulfonamide (1.40 g, 5.44 mmol, see Supporting Information) in acetone (100 mL). After addition of iodomethane (1.02 mL, 16.32 mmol), the reaction mixture was heated to reflux for 4 h. Iodomethane (340 μL, 5.44 mmol) was added and the reaction mixture was further heated under reflux for 4 h. After the mixture had cooled to room temp., the solvent was evaporated at reduced pressure and the residue was dissolved in ether. The resulting solution was washed with sat. aq. NH_4Cl and brine, and dried ($MgSO_4$), and the solvent was evaporated. After purification by FC (ether/pentane, 1:1), *N*-(3-hydroxy-1-methylbutyl)-*N*-methyl-*p*-toluenesulfonamide (1.39 g, 95%) was obtained. ^{1}H NMR (200 MHz): 0.71 (*d*, *J* = 6.8 Hz, 3 H, CH_3); 1.21 (*d*, *J* = 6.3 Hz, 3 H, CH_3); 1.29−1.53 (*m*, 2 H, CH_2); 2.43 (*s*, 3 H, CH_3Ph); 2.70 (*s*, 3 H, NCH_3); 3.94−4.10 (*m*, 1 H, CH); 4.10−4.30 (*m*, 1 H, CH); 7.32 (*d*, *J* = 8.3 Hz, 2 aromat. H); 7.70 (*d*, *J* = 8.3 Hz, 2 aromat. H) ppm.

***O*-{1-Methyl-3-[methyl(*p*-toluenesulfonyl)amino]butyl} *O*-(*p*-Tolyl) Thiocarbonate (35):** *O*-(*p*-Tolyl) chlorothiocarbonate (0.74 mL, 4.82 mmol) was added at room temp. to a solution of *N*-(3-hydroxy-1-methylbutyl)-*N*-methyl-*p*-toluenesulfonamide (**37**, 1.19 g, 4.38 mmol) in CH_2Cl_2 (40 mL) and the resulting reaction mixture was heated at reflux for 3 h. After cooling to room temp., the reaction mixture was diluted with CH_2Cl_2, the organic phase was washed with sat. aq. NH_4Cl and brine and dried ($MgSO_4$), and the solvent was evaporated. After purification by FC (ether/pentane,

1:5) **35** (1.79 g, 97%) was obtained as a colorless solid. M.p. 108 °C. IR (KBr): 3016*w*, 2976*w*, 1751*m*, 1506*s*, 1339*s*, 1290*s*, 1223*s*, 1200*s*, 1158*s*, 1124*s*, 718*s*, 570*s*. ^{1}H NMR (300 MHz): 0.86 (*d*, *J* = 6.9 Hz, 3 H, CH_3); 1.45 (*d*, *J* = 6.0 Hz, 3 H, CH_3); 1.62−1.75 (*m*, 1 H, CH_2); 1.83−1.95 (*m*, 1 H, CH_2); 2.35 (*s*, 3 H, CH_3Ph); 2.41 (*s*, 3 H, CH_3Ph); 2.66 (*s*, 3 H, NCH_3); 4.21−4.34 (*m*, 1 H, CHN); 5.33−5.41 (*m*, 1 H, CHO); 7.04−7.08 (*m*, 2 aromat. H); 7.19 (*d*, *J* = 8.1 Hz, 2 aromat. H); 7.25−7.31 (*m*, 2 aromat. H); 7.73 (*d*, *J* = 8.4 Hz, 2 aromat. H) ppm. ^{13}C NMR (75 MHz): 17.2 (CH_3); 19.7 (CH_3); 21.4 (CH_3); 21.9 (CH_3); 28.1 (CH_3); 40.7 (CH_2); 49.9 (CH); 78.9 (CH); 122.2 (CH); 127.7 (CH); 130.1 (CH); 130.4 (CH); 136.5 (C); 137.1 (C); 143.6 (C); 151.8 (C); 195.0 (C) ppm. EI-MS: 254.4 (16), 238.4 (19), 212.4 (100), 155.2 (33), 91.1 (25). $C_{21}H_{27}NO_4S_2$ (421.14) calcd. C 59.83, H 6.46, N 3.32; found C 59.85, H 6.32, N 3.58.

***N*-Methyl-*N*-(1-methylbutyl)-*p*-toluenesulfonamide (36)**

a) Reaction at 80 °C in Benzene: The compound was obtained by GP 1, from thiocarbonate **35** (600 mg, 1.42 mmol), benzene (48 mL), Bu_3SnH (680 µL, 2.56 mmol), AIBN (117 mg, 0.71 mmol) in benzene (3 mL), and MeLi (3.48 mL, 2.56 mmol). Purification by FC (ether/pentane, 1:6) afforded the direct reduction product **36** (250 mg, 69%) and alcohol **37** (vide supra, 17 mg, 5%). No aryl migration product was observed.

Compound 36: IR (Nujol): 3029*w*, 2959*s*, 1599*m*, 1457*m*, 1337*s*, 1157*s*, 1090*s*, 947*m*, 713*s*, 695*s*, 567*m*, 551*s*. ^{1}H NMR (300 MHz): 0.83−0.91 (*m*, 6 H, CH_3); 1.22−1.39 (*m*, 4 H, CH_2); 2.41 (*s*, 3 H, CH_3Ph); 2.66 (*s*, 3 H, NCH_3); 3.98−4.05 (*m*, 1 H, CHN); 7.28 (*d*, *J* = 8.1 Hz, 2 aromat. H); 7.69 (*d*, *J* = 8.3 Hz, 2 aromat. H) ppm. ^{13}C NMR (75 MHz): 14.0 (CH_3); 17.4 (CH_3); 19.8 (CH_2); 21.7 (CH_3); 27.5 (CH_3); 36.7 (CH_2); 52.7 (CH); 127.3 (CH); 129.8 (CH); 137.5 (C); 143.1 (C) ppm. EI-MS: 240.3 (6) $[M - CH_3]^+$, 212.3 (100) $[M - C_3H_7]^+$, 155.1 (31), 91.1 (39). $C_{13}H_{21}NO_2S$ (255.38): calcd. C 61.14, H 8.29, N 5.48; found C 61.34, H 8.21, N 5.70.

b) Reaction at 140 °C in Xylene: The compound was obtained by GP 1, from thiocarbonate **35** (300 mg, 0.71 mmol), xylene (24 mL), Bu_3SnH (340 µL, 1.28 mmol), *t*BuOO*t*Bu (66 µL, 0.36 mmol) in xylene (2 mL), and MeLi (1.74 mL, 2.84 mmol). The reaction afforded an inseparable mixture of direct reduction product **36** and the elimination products **33b** and **34b**.

***O*-{3-[Bis(*p*-toluenesulfonyl)amino]-1-methylbutyl} *O*-(*p*-Tolyl) Thiocarbonate (38):** 2-(*tert*-Butyldimethylsiloxy)-4-[bis(*p*-toluenesulfonyl)amino]pentane (590 mg, 1.12 mmol, isomer A, see Supporting Information) was dissolved in CH_2Cl_2 (2 mL) and the solution was cooled to 0 °C. HF·pyridine (60.5 µL, 1.23 mmol, ca. 70% HF) was added by syringe and the resulting reaction mixture was stirred for 30 min at 0 °C, allowed to warm to room temp., and stirred for an additional 60 min. The reaction mixture was diluted with CH_2Cl_2, washed with sat. aq. NH_4Cl and brine, and dried ($MgSO_4$), and the solvent was evaporated. The crude product (447 mg, 1.09 mmol) was dissolved in CH_2Cl_2 (10 mL) and cooled to 0 °C. After addition of pyridine (106 µL, 1.30 mmol) and *O*-(*p*-tolyl) chlorothiocarbonate (249 µL, 1.64 mmol) the reaction mixture was allowed to warm to room temp. and stirred for 16 h. The solution was diluted with CH_2Cl_2, washed twice with 2 N aq. NaOH and brine and dried ($MgSO_4$), and the solvent was evaporated. After purification by FC (pentane/ether, 5:1), **38** (581 mg, 95%) was obtained as a colorless solid. M.p. 55−56 °C. IR (KBr): 3035*w*, 2973*w*, 1760*m*, 1596*m*, 1507*m*, 1365*s*, 1288*s*, 1224*s*, 1199*s*, 1165*s*, 850*s*, 814*s*, 661*s*, 560*s*. ^{1}H NMR (300 MHz): 1.44 (*d*, *J* = 6.3 Hz, 3 H, CH_3); 1.50 (*d*, *J* = 6.9 Hz, 3 H, CH_3); 1.91−2.14 (*m*, 1 H, CH_2); 2.20−2.55 (*m*, 1 H, CH_2); 2.35 (*s*, 3 H, $OPhCH_3$, one isomer); 2.38 (*s*, 3 H, $OPhCH_3$, one isomer); 2.45 (s, 6 H, SO_2PhCH_3); 4.28−4.49 (*m*, 1 H, CHN); 5.03−5.26 (*m*, 1 H, CHO, one isomer); 5.32−5.51 (*m*, 1 H, CHO, one isomer); 7.03−7.37 (*m*, 8 aromat. H); 7.90−7.95 (*m*, 4 aromat. H) ppm. ^{13}C NMR (75 MHz): 19.2 (CH_3); 19.3 (CH_3); 19.8 (CH_3); 20.4 (CH_3); 21.1 (CH_3); 21.8 (CH_3); 41.6 (CH_2); 42.6 (CH_2); 56.0 (CH); 56.9 (CH); 79.0 (CH); 79.2 (CH); 120.9 (C); 121.1 (C); 121.7 (CH); 121.8 (CH); 128.6 (CH); 128.6 (CH); 129.8 (*br*, CH); 130.1 (CH); 130.3 (CH); 136.3 (C); 136.5 (C); 144.97 (C); 144.99 (C); 150.2 (C); 151.4 (C); 195.2 (C); 196.8 (C) ppm. EI-MS: 394.2 (1), 352.2 (21), 326.1 (2), 238.1 (20), 155.0 (69), 108.1 (100). FD-MS: 561 (100) $[M]^+$, 394 (22). $C_{27}H_{31}NO_6S_3$ (561.74) calcd. C 57.73, H 5.56; found C 57.61, H 5.47.

3-[Bis(*p*-toluenesulfonyl)amino]-1-methylbutyl Formate (39): This compound was obtained by GP 1, from thiocarbonate **38** (201 mg, 0.36 mmol), benzene (12 mL), Bu_3SnH (190 µL, 0.72 mmol), and AIBN (59 mg, 0.36 mmol) in benzene (1 mL), without addition of MeLi. Purification by FC (ether/pentane, 1:2) afforded **39** (81 mg, 52%) and **40** (16 mg, 11%). No aryl migration product or direct reduction product was observed.

Compound 39 (Mixture of Diastereoisomers 1:2.9): ^{1}H NMR (300 MHz): 1.17 (*d*, *J* = 6.3 Hz, 3 H, CH_3, isomer B); 1.21 (*d*, *J* = 6.1 Hz, 3 H, CH_3, isomer A); 1.30 (*d*, *J* = 6.8 Hz, 3 H, CH_3, isomer B); 1.39 (*d*, *J* = 6.8 Hz, 3 H, CH_3, isomer A); 1.91−2.12 (*m*, 1 H, CH_2); 2.23−2.40 (*m*, 1 H, CH_2); 2.46 (*s*, 6 H, CH_3Ph); 4.13−4.32 (*m*, 1 H, CHN); 4.71−4.85 (*m*, 1 H, HCO, isomer B); 4.92−5.05 (*m*, 1 H, HCO, isomer A); 7.34 (*m*, *J* = 8.3 Hz, 4 aromat. H); 7.88 (*d*, *J* = 7.8 Hz, 4 aromat. H); 7.98 (*s*, 1 H, OCHO, isomer B); 8.00 (*s*, 1 H, OCHO, isomer A) ppm. ^{13}C NMR (50 MHz): 19.0 (CH_3, isomer A); 20.3 (CH_3, isomer B); 20.6 (CH_3, isomer B); 20.6 (CH_3, isomer A); 21.8 (CH_3); 41.7 (CH_2, isomer B); 42.2 (CH_2, isomer A); 56.3 (CH, isomer A); 57.0 (CH, isomer B); 68.3 (CH, isomer A); 69.0 (CH, isomer B); 128.7 (CH); 129.7 (CH, isomer B); 129.8 (CH, isomer A); 145.3 (C); 160.7 (C); 160.8 (C) ppm. EI-MS: 424.3 (2, $[M - CH_3]^+$), 352.2 (54), 284.3 (38), 155.1 (100), 91.1 (96). FD-MS: 878 (100) $[2\cdot M]^+$, 833 (9) $[2\cdot M - COHO]^+$, 440 (16) $[M + H]^+$.

3-Bromobutyl *p*-Toluenesulfinate (43): 3-Bromo-1-butanol (667 mg, 4.36 mmol) was treated according to a procedure reported by Solladié[41] with sodium *p*-toluenesulfinate (777 mg, 4.36 mmol), thionyl chloride (1.50 mL, 20.93 mmol), benzene (8 mL), pyridine (0.8 mL), and Et_2O (8 mL). After careful purification by FC (pentane/MTBE, 10:1), **43** (497 mg, 39%) was obtained. IR ($CHCl_3$): 2972*w*, 2922*w*, 1596*w*, 1445*w*, 1380*w*, 1182*w*, 1135*s*, 1081*w*, 1017*w*, 939*m*, 862*m*, 813*m*, 712*m*, 627*m*. ^{1}H NMR (300 MHz): 1.69 (*d*, *J* = 6.8 Hz, 3 H, CH_3, isomer A); 1.71 (*d*, *J* = 6.8 Hz, 3 H, CH_3, isomer B); 1.98−2.17 (*m*, 2 H, CH_2); 2.43 (*s*, 3 H, CH_3); 3.64−3.71 (*m*, 1 H, HCBr, isomer B); 3.81−3.88 (*m*, 1 H, HCBr, isomer A); 4.10−4.27 (*m*, 2 H, H_2CO); 7.32−7.36 (*m*, 2 aromat. H); 7.58−7.63 (*m*, 2 aromat. H) ppm. ^{13}C NMR (75 MHz): 21.5 (CH_3); 21.8 (CH_3); 26.3 (CH_3); 40.7 (CH_2); 40.8 (CH_2); 46.6 (CH); 46.7 (CH); 61.5 (CH_2); 63.1 (CH_2); 125.0 (CH); 125.2 (CH); 129.68 (CH); 129.70 (CH); 141.2 (C); 141.6 (C); 142.8 (C) ppm. EI-MS: 292 (< 1) $[M]^+$, 290 (< 1) $[M]^+$, 212 (15), 157 (48), 139 (84), 62 (50), 55 (100). $C_{11}H_{15}BrO_2S$ (291.21): calcd. C 45.37, H 5.19; found C 45.06, H 5.08.

3-Iodobutyl *p*-Toluenesulfinate (44): 3-Iodo-1-butanol (1.82 g, 9.12 mmol) was treated according to a procedure reported by Solladié[41] with sodium *p*-toluenesulfinate (1.62 g, 9.12 mmol), thionyl chloride (3.17 mL, 43.78 mmol), benzene (16 mL), pyridine (1.6 mL), and Et_2O (16 mL). After careful purification by FC

(pentane/MTBE, 10:1), **44** (736 mg, 24%) was obtained. IR ($CHCl_3$): 2954*w*, 2918*w*, 1446*w*, 1378*w*, 1159*m*, 1334*s*, 1081*m*, 1017*m*, 937*s*, 860*s*, 812*s*, 711*m*, 627*m*. ^{1}H NMR (300 MHz): 1.89 (*d*, J = 6.8 Hz, 3 H, CH_3, isomer A); 1.93 (*d*, J = 7.1 Hz, 3 H, CH_3, isomer B); 2.02−2.16 (*m*, 2 H, CH_2); 2.43 (*s*, 3 H, CH_3); 3.52−3.64 (*m*, 1 H, HCI, isomer B); 3.79−3.91 (*m*, 1 H, HCI, isomer A); 4.04−4.28 (*m*, 2 H, H_2CO); 7.30−7.38 (*m*, 2 aromat. H); 7.56−7.65 (*m*, 2 aromat. H) ppm. ^{13}C NMR (75 MHz): 21.5 (CH_3); 21.6 (CH_3); 24.2 (CH); 24.4 (CH); 28.7 (CH_3); 40.8 (CH_2); 42.3 (CH_2); 42.4 (CH_2); 63.1 (CH_2); 64.7 (CH_2); 125.0 (CH); 125.2 (CH); 129.69 (CH); 129.73 (CH); 141.6 (C); 142.8 (C) ppm. EI-MS: 211 (30) $[M - I]^+$, 183 (29), 157 (72), 139 (86), 91 (26), 55 (100). $C_{11}H_{15}IO_2S$ (338.21): calcd. C 39.06, H 4.47; found C 39.07, H 4.56.

3-Bromo-1-methylbutyl *p*-Toluenesulfinate (45): 4-Bromo-2-pentanol (1.00 g, 5.99 mmol) was treated according to a procedure reported by Solladié[41] with sodium *p*-toluenesulfinate (1.07 g, 6.00 mmol), thionyl chloride (2.09 mL, 28.8 mmol), benzene (10 mL), pyridine (1.0 mL), and Et_2O (10 mL). After careful purification by FC (pentane/MTBE, 10:1), **45** (1.06 g, 58%) was obtained as a mixture of three isomers. IR ($CHCl_3$): 2975*m*, 2925*w*, 1597*w*, 1450*m*, 1381*m*, 1139*s*, 1083*m*, 1018*w*, 937*w*, 896*w*, 848*s*, 813*w*, 737*m*, 628*m*. ^{1}H NMR (300 MHz): 1.21 (*d*, J = 6.3 Hz, 3 H, CH_3, isomer A); 1.37 (*d*, J = 6.2 Hz, 3 H, CH_3, isomer B); 1.42 (*d*, J = 6.2 Hz, 3 H, CH_3, isomer C); 1.65 (*d*, J = 6.5 Hz, 3 H, CH_3, isomer C); 1.71 (*d*, J = 6.8 Hz, 3 H, CH_3, isomer B); 1.76 (*d*, J = 6.5 Hz, 3 H, CH_3, isomer A); 1.82−2.38 (*m*, 2 H, CH_2); 2.43 (*s*, 3 H, CH_3); 3.99−4.25 (*m*, 1 H, HCBr); 4.49−4.85 (*m*, 1 H, HCO); 7.32−7.36 (*m*, 2 aromat. H); 7.58−7.68 (*m*, 2 aromat. H) ppm. ^{13}C NMR (50 MHz): 21.8 (CH_3); 21.9 (CH_3); 22.0 (CH_3); 22.9 (CH_3); 26.2 (CH_3); 26.6 (CH_3); 27.1 (CH_3); 46.0 (CH); 46.2 (CH); 47.9 (CH); 48.6 (CH_2); 48.8 (CH_2); 49.0 (CH_2); 74.36 (CH); 74.41 (CH); 76.7 (CH); 125.0 (CH); 125.3 (CH); 130.1 (C); 142.9 (C); 143.2 (C); 143.2 (C) ppm. EI-MS: 306 (< 1) $[M]^+$, 225 (8), 157 (54), 139 (56), 92 (63), 69 (100). $C_{12}H_{17}BrO_2S$ (305.23): calcd. C 47.22, H 5.61; found C 47.23, H 5.68.

3-Bromo-1,1-dimethylbutyl *p*-Toluenesulfinate (46): 4-Bromo-2-methyl-2-pentanol (1.50 g, 8.3 mmol) was treated according to a procedure reported by Solladié[41] with sodium *p*-toluenesulfinate (1.48 g, 8.3 mmol), thionyl chloride (3.02 mL, 41.5 mmol), benzene (15 mL), pyridine (1.5 mL), and Et_2O (15 mL). After careful purification by FC (pentane/MTBE, 10:1), **46** (472 mg, 18%) was obtained as a single diastereoisomer of unknown configuration. A side product could not be separated from the other diastereoisomer. IR ($CHCl_3$): 3007*s*, 2926*m*, 1596*w*, 1493*w*, 1373*m*, 1109*s*, 1083*m*, 1018*w*, 916*w*, 849*s*, 628*w*. ^{1}H NMR (400 MHz): 1.63 (*s*, 3 H, CH_3); 1.64 (*s*, 3 H, CH_3); 1.74 (*d*, J = 6.7 Hz, 3 H, CH_3); 2.38 (*d*, J = 5.8 Hz, 2 H, CH_2); 2.42 (*s*, 3 H, CH_3); 4.26−4.34 (*m*, 1 H, HCBr); 7.31−7.34 (*m*, 2 aromat. H); 7.56 (*txd*, J_1 = 4.1 Hz, J_2 = 1.8 Hz, 2 aromat. H) ppm. ^{13}C NMR (50 MHz): 21.5 (CH_3); 27.2 (CH_3); 28.5 (CH); 29.4 (CH_3); 44.8 (CH); 53.5 (CH_2); 83.7 (C); 124.7 (CH); 129.7 (CH); 142.3 (C); 143.3 (C) ppm. EI-MS: 318.1 (< 1) $[M]^+$, 214.2 (2), 165.1 (3), 157.1 (10), 139.1 (56), 91.1 (55), 83.1 (100). $C_{13}H_{19}BrO_2S$ (319.26): calcd. C 48.91, H 6.00; found C 48.99, H 5.86.

3-(*p*-Tolyl)-1-butanol (47)

a) From 43: This compound was obtained by GP 1, from sulfinate **43** (151 mg, 0.52 mmol), benzene (17 mL), Bu_3SnH (207 μL, 0.78 mmol), and AIBN (43 mg, 0.26 mmol) in benzene (1 mL), without addition of MeLi. Purification by FC (ether/pentane, 1:8) afforded **47** (5 mg, 6%) and the direct reduction product butyl *p*-toluenesulfinate (80 mg, 73%). The physical data were in agreement with the values reported in the literature.[42]

b) From 44: The iodide **44** (135 mg, 0.40 mmol) was dissolved in benzene (4 mL) under argon. $Bu_3SnSnBu_3$ (199 μL, 0.04 mmol) was added. The reaction mixture was exposed to an OSRAM sunlamp (300 W) for 14 h. After evaporation of the solvent, the ^{1}H NMR spectrum showed only the substrate **44** and the distannane. No aryl migration product **47** was observed.

4-(*p*-Tolyl)-2-pentanol (6b) from 45: This compound was obtained by GP 1, from sulfinate **45** (147 mg, 0.48 mmol), benzene (16 mL), Bu_3SnH (191 μL, 0.72 mmol), AIBN (39 mg, 0.24 mmol) in benzene (1 mL), and MeLi (1.66 mL, 2.39 mmol). Purification by FC (ether/pentane, 1:4) afforded **6b** (17 mg, 20%, vide supra).

2-Methyl-4-(*p*-tolyl)-2-pentanol (48) from 46: This compound was obtained by GP 1, from sulfinate **46** (142 mg, 0.44 mmol), benzene (15 mL), Bu_3SnH (176 μL, 0.66 mmol), and AIBN (22 mg, 0.13 mmol) in benzene (0.5 mL), without addition of MeLi. Purification by FC (ether/pentane, 1:8) afforded **48** (7.5 mg, 9%) and the direct reduction product 1,1-dimethylbutyl *p*-toluenesulfinate (72 mg, 68%).

1,1-Dimethyl-3-(*p*-tolyloxythiocarbonyloxy)butyl *p*-Toluenesulfinate (49): *O*-(*p*-Tolyl) chlorothiocarbonate (295 μL, 1.93 mmol) was added at room temp. to a solution of 3-hydroxy-1,1-dimethylbutyl *p*-toluenesulfinate (450 mg, 1.76 mmol, see Supporting Information) and pyridine (170 μL, 2.11 mmol) in CH_2Cl_2 (5 mL) at 0 °C. The reaction mixture was allowed to warm to room temp. and stirred for 15 h. After addition of CH_2Cl_2, the resulting solution was washed with sat. aq. NH_4Cl and brine and dried ($MgSO_4$), and the solvent was evaporated. After purification by FC (MTBE/pentane, 1:5), **49** (454 mg, 64%) was obtained. IR (neat): 3034*w*, 2979*m*, 2926*w*, 1508*m*, 1374*m*, 1279*s*, 1220*s*, 1197*s*, 1121*s*, 1045*m*, 1018*w*, 855*m*, 814*m*, 721*m*. ^{1}H NMR (200 MHz): 1.40 (*d*, J = 6.2 Hz, 3 H, CH_3, one isomer); 1.43 (*d*, J = 6.5 Hz, 3 H, CH_3, one isomer); 1.62 (*s*, 3 H, CH_3, one isomer); 1.63 (*s*, 3 H, CH_3, one isomer); 1.65 (*s*, 3 H, CH_3, one isomer); 1.66 (*s*, 3 H, CH_3, one isomer); 2.02−2.33 (*m*, 2 H, CH_2); 2.37 (*s*, 3 H, CH_3); 2.39 (*s*, 3 H, CH_3, one isomer); 2.41 (*s*, 3 H, CH_3, one isomer); 5.54−5.73 (*m*, 1 H, HCO); 6.89−6.98 (*m*, 2 aromat. H); 7.17−7.32 (*m*, 4 aromat. H); 7.57−7.62 (*m*, 2 aromat. H) ppm. ^{13}C NMR (50 MHz): 20.5 (CH_3); 20.6 (CH_3); 20.9 (CH_3); 21.4 (CH_3); 27.0 (CH_3); 27.7 (CH_3); 28.8 (CH_3); 29.5 (CH_3); 48.1 (CH_2); 48.2 (CH_2); 78.7 (CH); 78.8 (CH); 82.9 (C); 83.1 (C); 121.6 (CH); 124.9 (CH); 125.0 (CH); 129.6 (CH); 129.97 (CH); 130.01 (CH); 136.2 (C); 136.3 (C); 142.2 (C); 143.3 (C); 151.2 (C); 194.4 (C) ppm. EI-MS: 251 (21) $[M - TolSO_2]^+$, 157 (14), 139 (51), 108 (24), 83 (100). $C_{21}H_{26}O_4S_2$ (406.56): calcd. C 62.04, H 6.45; found C 62.32, H 6.65.

1,1-Dimethylbutyl *p*-Toluenesulfinate (50) and 1,1-Dimethyl-3-(*p*-tolyloxycarbonylsulfanyl)butyl *p*-Toluenesulfinate (51): These compounds were obtained by GP 1, from sulfinate **49** (113 mg, 0.28 mmol), benzene (9 mL), Bu_3SnH (110 μL, 0.42 mmol), and AIBN (14 mg, 0.08 mmol) in benzene (0.5 mL), without addition of MeLi. Purification by FC (ether/pentane, 1:6) afforded the direct reduction product **50** (35 mg, (53%), **51** (20 mg, 18%), and the unchanged starting material **49** (21 mg, 19%).

***O*-[1-Methyl-4-(*p*-toluenesulfinyl)butyl] 1*H*-Imidazole-1-carbothioate (52):** A Grignard solution was prepared from 1-bromo-3-(*tert*-butyldimethylsiloxy)pentane[43] (1.5 g, 5.34 mmol) and Mg (400 mg, 16.0 mmol) in Et_2O (10 mL). This solution was added according to a procedure reported by Solladié[41] to (−)-menthyl (*S*)-*p*-toluenesulfinate[41] (1.34 g, 4.45 mmol) in benzene (7 mL) at 0 °C.

The reaction mixture was stirred for 2 h at that temperature. After addition of sat. aq. NH_4Cl, the reaction mixture was diluted with MTBE and the resulting solution was washed with sat. aq. NH_4Cl and brine and dried ($MgSO_4$), and the solvent was evaporated. After purification by FC (MTBE/pentane, 1:10), *tert*-butyldimethyl[1-methyl-4-(*p*-toluenesulfinyl)butyl]silane (620 mg, 47%) was obtained. The silyl ether (465 mg, 1.37 mmol) was dissolved in CH_2Cl_2 (4 mL) and the solution was cooled to 0 °C. HF·pyridine (108 μL, 2.0 mmol) was added and the reaction mixture was stirred for 30 min. The reaction mixture was diluted with MTBE, the organic phase was washed with aq. sat. NH_4Cl and brine and dried ($MgSO_4$), and the solvent was evaporated. The crude product was directly dissolved in CH_2Cl_2 (10 mL) and the solution was cooled to 0 °C. 1,1′-Thiocarbonylbis(imidazole) (610 mg, 3.43 mmol) was added. The reaction mixture was allowed to warm to room temp. and stirred for 14 h. The reaction mixture was diluted with MTBE, the organic phase was washed with aq. sat. NH_4Cl and brine and dried, ($MgSO_4$), and the solvent was evaporated. After purification by FC (CH_2Cl_2/MeOH, 40:1), **52** (376 mg, 82% over two steps) was obtained as a mixture of diastereoisomers (1:1). IR (nujol): 3118*w*, 2977*w*, 2931*w*, 1465*m*, 1385*s*, 1324*s*, 1285*s*, 1235*s*, 1094*m*, 1041*m*, 967*m*, 811*w*, 745*w*, 657*w*. ^{1}H NMR (200 MHz): 1.44 (*d*, J = 6.3 Hz, 3 H, CH_3); 2.04−2.15 (*m*, 4 H, CH_2); 2.40 (*s*, 3 H, CH_3, isomer B); 2.41 (*s*, 3 H, CH_3, isomer A); 2.78−2.85 (*m*, 2 H, H_2CS); 5.58−5.67 (*m*, 1 H, HCO); 7.03 (*s*, 1 aromat. H); 7.27−7.33 (*m*, 2 aromat. H); 7.45−7.59 (*m*, 3 aromat. H); 8.29 (*d*, J = 6.0 Hz, 1 aromat. H) ppm. ^{13}C NMR (75 MHz): 17.6 (CH_3); 18.2 (CH_3); 18.9 (CH_3); 21.3 (CH_2); 21.3 (CH_2); 34.1 (CH_2); 34.2 (CH_2); 55.9 (CH_2); 56.4 (CH_2); 80.2 (CH); 80.4 (CH); 117.7 (CH); 123.8 (CH); 123.9 (CH); 129.8 (CH); 129.9 (CH); 130.68 (CH); 130.70 (CH); 136.7 (CH); 139.9 (C); 140.2 (C); 141.5 (C); 141.6 (C); 183.4 (C) ppm. EI-MS: 225 (3) $[M - TolOCS]^+$, 209 (15), 197 (58), 140 (44), 85 (64), 69 (100). $C_{16}H_{20}N_2O_2S_2$ (336.47): calcd. C 57.11, H 5.99, N 8.33; found C 57.36, H 6.23, N 8.05.

1-Methyl-4-(pentylsulfinyl)benzene (53): This compound was obtained by GP 1, from sulfoxide **52** (67 mg, 0.20 mmol), benzene (7 mL), Bu_3SnH (80 μL, 0.3 mmol), and AIBN (17 mg, 0.1 mmol) in benzene (0.5 mL), without addition of MeLi. Purification by FC (CH_2Cl_2/MeOH, 40:1) afforded **53** (40 mg, 96%). The physical data were in agreement with the values reported in the literature.[44]

***O*-{2-[5-(Phenylsulfinylmethyl)-2,2-dimethyl-1,3-dioxan-5-yl]-1-methylethyl} *O*-(*p*-Tolyl) Thiocarbonate (54):** MCPBA (447 mg, 2.26 mmol, 77%) was dissolved in CH_2Cl_2 (60 mL) under argon. After addition of Na_2CO_3 (435 mg, 4.1 mmol), the reaction mixture was cooled to 0 °C. A solution of 1-(2,2-dimethyl-5-phenylsulfanylmethyl-1,3-dioxan-5-yl)-2-propanol (607 mg, 2.05 mmol, see Supporting Information) in CH_2Cl_2 (20 mL) was then added. After the mixture had been stirred for 90 min at 0 °C, brine (5 mL) was added. The reaction mixture was dissolved in CH_2Cl_2, the organic phase was washed with brine and dried ($MgSO_4$), and the solvent was evaporated. After purification by FC (pure MTBE), 1-[5-(phenylsulfinylmethyl)-2,2-dimethyl-1,3-dioxan-5-yl]-2-propanol (571 mg, 89%) was obtained. 1-[5-(Phenylsulfinylmethyl)-2,2-dimethyl-1,3-dioxan-5-yl]-2-propanol (457 mg, 1.46 mmol) was dissolved in THF (7 mL) and the solution was cooled to −78 °C. After addition of butyllithium (1 mL, 1.61 mmol, 1.61 M in hexane), the reaction mixture was stirred for 45 min at that temperature. *O*-(*p*-Tolyl) chlorothiocarbonate (267 μL, 1.75 mmol) was then added. The solution was stirred for 2 h at −78 °C and then allowed to warm to 0 °C. The reaction mixture was quenched with sat. aq. $NaHCO_3$, diluted with MTBE, washed with sat. aq. $NaHCO_3$ and brine, and dried ($MgSO_4$), and the solvent was evaporated. After purification by FC (pentane/MTBE, 3:2), **54** (410 mg, 61%) was obtained as a mixture of diastereoisomers (3:1). IR (KBr): 2987*m*, 2926*m*, 2869*w*, 1506*m*, 1375*m*, 1276*s*, 1221*s*, 1197*s*, 1128*m*, 1085*m*, 854*s*, 828*s*. ^{1}H NMR (300 MHz): 1.10−1.50 (*m*, 2 H, CH_2); 1.43 (*s*, 3 H, CH_3); 1.47 (*s*, 3 H, CH_3); 1.49 (*d*, J = 6.3 Hz, 3 H, CH_3); 2.17 (s, 3 H, CH_3, isomer B); 2.19 (s, 3 H, CH_3, isomer A); 2.36 (*s*, 3 H, CH_3); 2.95 (*d*, J = 14.0 Hz, 1 H, CH_2S, isomer B); 3.05 (*d*, J = 14.0 Hz, 1 H, CH_2S, isomer A); 3.21 (*d*, J = 14.0 Hz, 1 H, CH_2S, isomer B); 3.26 (*d*, J = 14.0 Hz, 1 H, CH_2S, isomer A); 3.74-4.10 (*m*, 4 H, CH_2O); 5.72−5.91 (*m*, 1 H, HCO); 6.89 (*d*, J = 8.5 Hz, 2 aromat. H); 7.19 (*d*, J = 8.2 Hz, 2 aromat. H); 7.47−7.57 (*m*, 3 aromat. H); 7.67−7.76 (*m*, 2 aromat. H) ppm. ^{13}C NMR (75 MHz): 20.7 (CH_3); 20.9 (CH_3); 21.3 (CH_3); 26.1 (CH_3); 38.8 (CH_2); 49.4 (C); 62.2 (CH_2); 66.8 (CH_2); 67.6 (CH_2); 78.9 (CH); 98.5 (C); 121.5 (CH); 123.9 (CH); 129.3 (CH); 130.0 (CH); 130.9 (CH); 136.4 (C); 144.7 (C); 151.0 (C); 194.4 (C) ppm. EI-MS: 295.1 (17), 219.0 (3), 185.1 (22), 123.0 (13), 108.0 (74), 97.0 (100). $C_{24}H_{30}O_5S_2$ (462.62): calcd. C 62.31, H 6.54; found C 61.94, H 6.38.

5-(Phenylsulfinylmethyl)-2,2-dimethyl-5-propyl-1,3-dioxane (55): This compound was obtained by GP 1, from sulfoxide **54** (137 mg, 0.30 mmol), benzene (10 mL), Bu_3SnH (142 μL, 0.53 mmol), and AIBN (49 mg, 0.30 mmol) in benzene (1 mL), without addition of MeLi. Purification by FC (pentane/MTBE, 5:1 then acetone) afforded **55** (47 mg, 53%). No aryl migration product was observed.

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