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# Synthesis of substituted tetrahydrofurans via intermolecular reactions of $\gamma$ -chlorocarbanions of 3-substituted 3-chloro-propylphenyl sulfones with aldehydes

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#### A R T I C L E I N F O

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Dedicated to Professor Vladimir Minkin to celebrate his 75th birthday

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#### 1. Introduction

In our previous papers, we have shown that  $\gamma$ -halocarbanions generated from 3-chloropropyl aryl sulfones, 4-chlorobutyronitrile and *tert*-butyl 4-chlorobutyrate, in spite of fast intramolecular substitution leading to cyclopropanes, can be trapped by active electrophilic partners. Thus, generation of such  $\gamma$ -halocarbanions in the presence of aldehydes results in formation of the intermediate anionic aldol-type adducts that undergo 1,5-intramolecular substitution producing substituted tetrahydrofurans.<sup>1</sup> Similar reactions of  $\gamma$ -halocarbanions with electron-deficient imines<sup>2</sup> and Michael acceptors<sup>3</sup> give rise to substituted pyrrolidines and cyclopentanes. This simple and valuable method of synthesis of hetero- and carbocyclic five-membered rings is severely limited because of a high rate of 1,3-intramolecular substitution in the 3-chlorocarbanion. As a result, the desired reactions proceed only with highly active electrophilic partners (Scheme 1).

In order to expand the scope of the reaction we have studied the effect of substituents in the chain of the  $\gamma$ -halocarbanions on the reaction course. In our early paper, we reported that a phenyl group

# A B S T R A C T

Carbanions of 3-substituted-3-chloropropyl phenyl sulfones add to carbonyl groups of aldehydes to produce aldol type adducts that undergo 1,5-intramolecular substitution giving 2,3,5-trisubstituted tetrahydrofurans. The effect of substituents in the 3-position of these sulfones on the relative rates of 1,3-intramolecular substitution of the corresponding  $\gamma$ -chlorocarbanions and their intramolecular addition are disclosed.

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Y =  $SO_2Ar$ , CN, COO*t*Bu, COPh; Z = O, N-EWG, CH-EWG

#### Scheme 1.

in position 2- of 4-chlorobutyronitrile favours intramolecular 1,3-substitution leading to the cyclopropane at the expense of intermolecular addition.<sup>1a</sup> On the other hand, preliminary observations indicated that a methyl group in position 3- of 3-chloropropyl phenyl sulfone substantially decelerates the 1,3-intramolecular substitution, so the respective  $\gamma$ -halocarbanion can enter readily into intermolecular reactions.<sup>1c</sup> In this paper, we report that substituents in position  $\gamma$  of the  $\gamma$ -halocarbanion generated from 3-chloro-3-phenylpropyl phenyl sulfone **1**, 3-chlorobutyl phenyl sulfone **2** and 3-chloro-3-phenylthiopropyl phenyl sulfone **3**, affect the rates of 1,3-intramolecular substitution and, as a consequence, there is



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competition between this reaction and intermolecular addition to aldehydes leading to tetrahydrofurans.

A phenyl group in position 3- of 3-chloro-3-phenylpropyl phenyl sulfone **1** can affect rates of intramolecular substitution in two opposite ways. Since the halogen in **1** occupies the benzylic position, its nucleophilic substitution can be accelerated as compared to the parent 3-chloropropyl phenyl sulfone. On the other hand, substitution of the halogen in **1** proceeds at the secondary carbon atom, so it should be a slower process, decelerated as compared with that at the primary carbon. A methyl group in position 3- of 3-chlorobutyl phenyl sulfone **2** and phenylsulfide group in position 3- of (3-chloro-3-phenylthio)propylphenyl sulfone **3** should decelerate 1,3-intramolecular nucleophilic substitution of chlorine in the corresponding carbanions due to electron-donating and steric effects.

In the literature, we have found only two examples of reactions of similar carbanions. 3-Bromo-3-phenylpropyl phenyl sulfone, synthesized via bromination of 3-phenylpropyl phenyl sulfone with NBS, when treated with strong base was converted into 1-phenylsulfonyl-2-phenylcyclopropane (*cis* and *trans* isomers).<sup>4</sup> Similarly, base-induced reaction of [1-chloro-3-(*N*-methyl-S-phenylsulfonimidoyl)propyl]benzene gave the expected di-substituted cyclopropane.<sup>5</sup> No attempts of intermolecular reaction of the intermediate  $\gamma$ -halocarbanions with aldehydes or other electrophilic partners were reported in these papers.

3-Chloro-3-phenylpropyl phenyl sulfone was obtained via reaction of phenylsulfinic acid with 3-(trimethyl-ammonium)-1-phenylpropanone iodide,<sup>6</sup> borohydride reduction of the produced ketosulfone and conversion of the alcohol into chloride **1** by reaction with hydrochloric acid (Scheme 2).

#### Scheme 2.

3-Chlorobutyl phenyl sulfone **2** was obtained from the reaction of methyl-vinyl ketone with sodium phenylsulfinate followed by reduction of the ketosulfone with sodium borohydride and the Appel reaction of the alcohol with PPh<sub>3</sub> and CCl<sub>4</sub> (Scheme 3). 3-Chloro-3-phenylthiopropyl phenyl sulfone **3** was obtained as shown in Scheme 4.





All these carbanion precursors **1**, **2** and **3**, when treated with *t*-BuOK in THF are deprotonated, subsequent intramolecular 1,3-substitution gave the expected disubstituted cyclopropanes **1a**, **1b** and **1c** in good yields. Even better yields were obtained when the reaction was carried out in toluene. Substituents in the cyclopropane rings of **1a**, **1b** and **1c** are always trans and this was established on the basis of <sup>1</sup>H NMR spectra, 1D NOE experiments and comparison with literature data.

In order to estimate the effect of substituents on the rate of intramolecular substitution solutions of **1**, **2** and **3** in THF and toluene at low temperature were treated with *t*-BuOK and after a short time the mixtures were quenched with an aqueous solution of NH<sub>4</sub>Cl (Scheme 5). On the basis of such experiments, the time of half-conversion ( $\tau_{1/2}$ ) of the  $\gamma$ -chlorocarbanion into the cyclopropane was estimated. The results are presented in Table 1.



Scheme 5

Table 1	
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Reactant	Yield [%]		$(\tau_{1/2})$
	In THF	In toluene	
3-Chloro-3-phenylpropyl phenyl sulfone <b>1</b>	84	98	less than 1 s
3-Chlorobutylphenyl sulfone 2	71	71	60 s
(3-Chloro-3-phenylthio)propylphenyl sulfone <b>3</b>	74	96	120 s <sup>a</sup>

<sup>a</sup> Reaction in toluene at 0 °C.

As we expected, intramolecular substitution in carbanion of **1** proceeds with a rate similar to that of 3-chloropropyl phenyl sulfone, whereas cyclization of the carbanions of **2** and **3** is much slower.

When a solution of **1** and benzaldehyde in THF was treated at low temperature with *t*-BuOK, the expected 2,5-diphenyl-3-phenyl-sulfonyl tetrahydrofuran **1b** was produced as a mixture of two diastereoisomers. Cyclopropane **1a** was also formed but in small quantities.

On the other hands the reaction of **2** with benzaldehyde under these conditions gave the expected 5-methyl-2-phenyl-3-phenylsulfonyl tetrahydrofuran **2b** (also a mixture of two diastereoisomers) only in moderate yield, along with cyclopropane **2a**.

This is because the methyl group in position 3 of  $2^-$  decelerates not only 1,3-intramolecular substitution, but also 1,5-intramolecular substitution in the aldol-type adduct. Thus, due to reversibility of the addition, the cyclopropane was formed in substantial amounts. Formation of **2b** was the main process when the reaction was carried out in toluene. It seems that strong association of the potassium cations with the negatively charged oxygen of the aldol type adduct favours the addition and consequently formation of tetrahydrofurans.

This effect is even stronger in the reactions of **3**. Treatment of a solution of **3** and benzaldehyde in THF with *t*-BuOK gave mainly the cyclopropane **3a**, whereas in toluene the desired tetrahydro-furan **3b** was obtained, although in moderate yield.

Under these standard conditions: *t*-BuOK in THF or toluene a series of reactions between **1**, **2** and **3** and aromatic aldehydes were carried out giving the expected 2,3,5-trisubstituted tetrahydrofurans, usually in good yields (Table 3). Moderate yields of tetrahydrofurans obtained from **3** are mostly because these compounds, being in fact monothioacetals, are of moderate stability, so we encountered difficulties due to decomposition during chromatographic purification. In order to avoid these problems the crude products **3b–e** were oxidized with MCPBA to disulfones **4b–e** that were more stable and could be purified. The same conditions were also used for reaction without aldehyde and *trans*-cyclopropane **4a** was obtained in 63% yield. The results of these experiments are shown in Table 2.

Table 2

Comparison of the reactions of carbanions  $\mathbf{1}, \mathbf{2}$  and  $\mathbf{3}$  with benzaldehyde under various conditions

Reactant <sup>a</sup>	ıt <sup>a</sup> Yield [%]					
	In THF		In toluene			
	1b-3b	1a-3a	1b-3b	1a-3a		
1	68	10	90	_		
2	60	16	78	15		
3	_	80 <sup>b</sup>	42	Traces <sup>b</sup>		

<sup>a</sup> Sulfones identified by numbers **1–3** as shown in Scheme 6.

<sup>b</sup> Yield after oxidation by MCPBA.

### Table 3 Results of the reactions of carbanions 1. 2 and 3 with aldehydes as in Scheme 6

Reactant <sup>a</sup>	R in aldehyde	Tetrahydrofuran			Cyclopropane	
		Product	Yield [%]	Ratio of isomers 2,5- <i>trans-cis</i> <sup>d</sup>	Product	Yield [%]
1	Ph	1b	68	38:62	1a	10
	p-MeO-C <sub>6</sub> H <sub>4</sub>	1c	70	67:33	1a	16
	p-Me-C <sub>6</sub> H <sub>4</sub>	1d	56	57:43	1a	6
	p-Cl-C <sub>6</sub> H <sub>4</sub>	1e	53	29:71	1a	15
	Ph-CH=CH	1f	53	31:69	1a	17
	$(CH_3)_3C$	1g	60	62:38	1a	25
2	Ph	2b	60	84:16	2a	16
	Ph <sup>b</sup>	2b	78	91:9	2a	15
	p-MeO-C <sub>6</sub> H4 <sup>b</sup>	2c	82	97:3	2a	12
	p-Me-C <sub>6</sub> H <sub>4</sub> <sup>b</sup>	2d	92	97:3	2a	5
	$p-Cl-C_6H_4^b$	2e	53	93:7	2a	28
	$(CH_3)_3C^b$	2f	79	100:0	2a	<1
	$n-C_4H_9^b$	2g	11	100:0	2a	35
3	Ph <sup>b,c</sup>	4b	42 <sup>c</sup>	100:0	4a	_
	p-MeO-C <sub>6</sub> H4 <sup>b</sup>	4c	50 <sup>c</sup>	100:0	4a	_
	p-Me-C <sub>6</sub> H <sub>4</sub> <sup>b</sup>	4d	45 <sup>c</sup>	100:0	4a	_
	p-Cl-C <sub>6</sub> H <sub>4</sub> <sup>b</sup>	4e	28 <sup>c</sup>	100:0	4a	_

<sup>a</sup> Sulfones identified by numbers **1–3** as shown in Scheme 6.

<sup>b</sup> Reaction in toluene.

<sup>c</sup> Yield after oxidation of the initially formed **3c-e** by MCPBA.

<sup>d</sup> According to GC.

The reported earlier reactions of carbanion of 3-chloropropyl phenyl sulfone with aromatic aldehydes gave 2-aryl-3-phenyl-sulfonyl tetrahydrofurans as single diastereoisomers with *trans* 2,3-substituents.<sup>1</sup> Products of the reaction of **1** and **2** with aromatic aldehydes were obtained as mixtures of two diastereoisomers in which substituents in positions 2 and 3 are always in *trans* relation, whereas substituent in position 5 was *cis* or *trans* in relation to aryl or alkyl group in position 2. On the other hand, upon oxidation of the crude product of the reaction of **3** with aldehydes 2-aryl-3,5-diphenylsulfonyltetrahydrofurans **4b–e** were obtained as single

isomers with substituents in positions 2,3- and 2,5- in relation *trans* (Table 3).

In most of the cases the diastereoisomers of the obtained tetrahydrofurans were separated and the relation (*cis*- or *trans*-) of 2-aryl and 5-phenyl group was determined by analysis of <sup>1</sup>H, 2D COSY NMR spectra and 1D NOE experiments. On Figure 1 correlation between protons as a result of NOE experiment for the product **1f** was presented.

The assignments were confirmed for **1d** by X-ray determination of the crystal structure of its *trans*-isomer (Fig. 2). These type of analysis were made only for one compound because in all cases the structure of multiplets was characteristic for *cis* as well as *trans* isomer.

Some 3-phenylsulfonyl-2,5-disubstituted tetrahydrofurans, among them **2b**, were obtained earlier *via* intramolecular addition of alkoxide anion in homoallylic alcohols in which the double bond was activated by phenylsulfonyl substituents.<sup>7</sup>

Attempts of the reaction of carbanions of **1**, **2** and **3** with chalcone, an active Michael acceptor, gave a positive result only for 3-chlorobutyl phenyl sulfone **2**. In this case, it was possible to generate the carbanion before chalcone was added to the reaction mixture. The reaction carried out in a mixture THF-toluene (3:10) at -78 °C gave the expected tetrasubstituted cyclopentane as a mixture of three diastereoisomers along with a moderate amount of cyclopropane **2a**.

The stereochemistry of these three tetrasubstituted cyclopentanes **2h**, **2i** and **2k** was determined on the basis of 1D NOE experiments. In all cases, the phenylsulfonyl group in position 1 is in a *trans* relation to the phenyl group in position 2. In the diastereoisomer obtained with the highest yield, **2h**, substituents in positions 3 and 4 are in a *cis* relation to each other and in a *trans* relation to the substituent in postion 2. In the two remaining cases, substituents in positions 3 and 4 are in a *trans* relation to each other and in a *cis* or *trans* relation to the phenyl group in position 2, as shown in Scheme 7.





Figure 1.







#### 2. Conclusions

Substituents in the 3-positions of carbanions of 3-chloropropyl phenyl sulfones affect the rates of intramolecular 1,3-substitution and leads to competition between this process and intermolecular addition to aldehydes. The aldol type anions produced in such addition reactions undergo intramolecular 1,5-substitution giving trisubstituted tetrahydrofurans. It was shown that a variety of 2,3,5-trisubstituted tetrahydrofurans could be obtained according to this procedure.

#### 3. Experimental section

#### 3.1. General

Reactions of carbanions were conducted in flame-dried apparatus under atmosphere of argon. Column chromatography was performed on Fisher Scientific Matrex Silica 60 (35–70  $\mu$ ). Melting points were measured on a Griffin electrothermal apparatus. IR spectra were recorded on a Perkin–Elmer Spectrum One FTIR spectrometer <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Brücker DPX300 or DRX500 Fourier Transform spectrometers using an internal deuterium lock. Electron spray ionisation (ES) was performed on either a Micromass LCT TOF spectrometer or a Waters-Micromass ZMD spectrometer. High resolution mass spectrometry (HRMS) was obtained by peak matching using polyethylene glycols as a standard.

3.1.1. Synthesis of 3-chloro-3-phenyl-propyl phenyl sulfone (1). 1-Phenyl-3-(phenylsulfonyl)propan-1-ol<sup>8</sup> (2.0 g, 7.31 mmol) was dissolved in  $CH_2Cl_2$  (4 mL) and stirred with 35% HCl (4 mL). The progress of the reaction was monitored by TLC. After the reaction was completed the mixture was poured onto cold 10% solution of HCl (10 mL), saturated aqueous solution of NaHCO<sub>3</sub> (20 mL) was added, and mixture was extracted with  $CH_2Cl_2$  (2×10 mL). The organic phase was washed with water (20 mL), dried over MgSO<sub>4</sub>, the solvent was evaporated and the product was purified by recrystalization from ethanol, yield 1.49 g, 70%.

White crystals; mp: 73–74 °C (EtOH); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$ =2.48–2.51 (m, 2H), 3.10–3.37 (m, 2H), 4.97 (t, *J* (H, H)=7.2 Hz, 1H), 7.26–7.39 (m, 5H), 7.53–7.73 (m, 3H), 7.88–7.94 (m, 2H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$ =32.9, 53.6, 61.0, 126.7, 127.9,

128.7, 128.8, 129.4, 133.9, 138.8, 139.9; IR (KBr,  $\nu_{max}/cm^{-1}$ ): 3058, 2943, 1448, 1310, 1299, 1249, 1149, 1131, 1085, 814, 760, 717, 692, 561, 537, 526; MS (EI, 70 eV) m/z (%): 294(M<sup>+</sup>, 43), 259(17), 152(74), 143(40), 125(18), 117(100), 91(13), 77(15); HRMS (EI): calculated for C<sub>15</sub>H<sub>15</sub><sup>35</sup>ClO<sub>2</sub>S: 294.0481, found: 294.0476; anal. elem. calculated for C<sub>15</sub>H<sub>15</sub><sup>35</sup>ClO<sub>2</sub>S: C 61.11, H 5.13, Cl 12.03, S 10.88, found: C 61.02, H 5.16, Cl 12.08, S 10.72.

3.1.2. Synthesis of 3-chlorobutyl phenyl sulfone (**2**). To a solution of triphenylphosphine (9.81 g, 37.44 mmol) in CH<sub>3</sub>CN (100 mL) at 35 °C CCl<sub>4</sub> (5.9 mL, 51.4 mmol) was added, the mixture was warmed to 60 °C and 4-(phenylsulfonyl)butan-2-ol (5 g, 23.4 mmol) was added. After two days the solvent was evaporated, water (50 mL) was added and the mixture was extracted with diethyl ether (2×50 mL). The product was purified by column chromatography, yield 4.08 g, 75%.

White crystals; mp: 39–40 °C (EtOH); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =1.52 (d, *J*(H,H)=6.5 Hz, 3H), 1.98–2.08 (m, 1H), 2.20–2.28 (m, 1H), 3.23 (ddd, *J*(H,H)=5.2, 10.3, 14.0 Hz, 1H), 3.35 (ddd, *J*(H,H)=5.2, 10.3, 14.0 Hz, 1H), 4.05–4.15 (m, 1H), 7.55–7.63 (m, 2H), 7.65–7.72 (m, 1H), 7.90–7.94 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$ =25.2, 32.9, 53.7, 56.2, 128.0, 129.4, 133.9, 139.1; IR (film in CH<sub>2</sub>Cl<sub>2</sub>,  $\nu_{max}/cm^{-1}$ ): 3628, 3546, 3066, 2977, 2929, 1981, 1906, 1820, 1777, 1688, 1615, 1585, 1479, 1447, 1407, 1382, 1306, 1290, 1231, 1179, 1145, 1086, 1024, 999, 941, 910, 887, 800, 745, 689, 616, 589, 562, 537; MS (EI, 70 eV) *m*/*z* (%): 232(M<sup>+</sup>, 2), 156(34), 143(53), 132(18), 125(12), 117(11), 91(21), 77(92), 63(19), 55(100), 51(50), 39(20); HRMS (EI): calculated for C<sub>10</sub>H<sub>13</sub>O<sub>2</sub>S<sup>35</sup>Cl: 232.0325, found: 232.0320; anal. elem. calculated for: C<sub>10</sub>H<sub>13</sub>O<sub>2</sub>S<sup>35</sup>Cl: C 51.61, H 5.63, S 13.78, Cl 15.23, found: C 51.64, H 5.59, S 14.04, Cl 15.28.

3.1.3. Synthesis of 3-chloro-1-phenylsulfonyl-3-(phenylthio)propane (**3**). To a stirred solution of 1-phenylsulfonyl-3-(phenylthio)propane (18 g, 61.6 mmol) in CCl<sub>4</sub> (70 mL), *N*-chlorosuccinimide (9.02 g, 67.8 mmol) was added in small portions. The mixture was stirred for 24 h the precipitate was filtered of, washed with CCl<sub>4</sub>, and the solvent was evaporated. Crude product, yield 19.10 g, 95% was used without further purification.

Oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =2.39–2.49 (m, 1H), 2.48–2.56 (m, 1H), 3.36–3.45 (m, 2H), 5.31–5.36 (m, 1H), 7.23–7.42 (m, 5H), 7.49–753 (m, 2H), 7.66–7.71 (m, 1H), 7.89–7.95 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$ =32.3, 53.3, 67.9, 128.0, 129.2, 129.3, 129.4, 130.9, 133.7, 134.0, 138.8; IR (film in CH<sub>2</sub>Cl<sub>2</sub>,  $\nu_{max}/cm^{-1}$ ): 3060, 2989, 2927, 1718, 1584, 1477, 1447, 1440, 1402, 1318, 1308, 1150, 1086, 1024, 999, 973, 814, 746, 689, 590, 560; MS (EI, 70 eV) m/z (%): 149(100), 134(14), 116(33), 77(18); HRMS (EI): calculated for C<sub>15</sub>H<sub>15</sub>O<sub>2</sub>S<sub>2</sub><sup>35</sup>Cl: 326.0202, found: 326.0188.

3.1.4. Synthesis of trans-2-phenyl-phenylsulfonyl cyclopropane (**1a**). To a solution of 3-chloro-3-phenyl-propylphenylsulfone (**1**) (100 mg, 0.34 mmol) in THF (10 mL), at -30 °C a solution of *t*-BuOK (76 mg, 0.68 mmol) in THF (2 mL) was added dropwise. The mixture was stirred at -30 °C for 20 min, the cooling was removed and aqueous solution of NH<sub>4</sub>Cl (10 mL) was added. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2×20 mL), organic layer was washed with brine, dried over MgSO<sub>4</sub> and solvent was evaporated. The product was purified by column chromatography, yield 73 mg, 84%.

White crystals; mp: 96–98 °C (EtOH), lit. 96–97 °C;<sup>8</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ =1.49 (ddd, *J*(H,H)=8.3, 2.6, 1.6 Hz, 1H), 1.89 (dt, *J*(H,H)=9.7, 5.5 Hz, 1H), 2.66 (ddd, *J*(H,H)=8.3, 3.8, 2.9, 1H), 2.86–2.91(m, 1H), 6.99–7.02 (m, 2H), 7.17–7.26 (m, 3H), 7.54–7.59 (m, 2H), 7.63–7.67 (m, 1H), 7.93–7.95 (m, 2H).<sup>9</sup>

3.1.5. Synthesis of trans-1-phenylsulfonyl-2-methyl cyclopropane (**2a**). To a solution of 3-chlorobutyl phenyl sulfone (**2**) (232 mg, 1 mmol) in toluene (6 mL), at 0 °C solid *t*-BuOK (224 mg, 2 mmol)

was added. After 1 h aqueous solution of NH<sub>4</sub>Cl (5 mL) was added and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> ( $2 \times 50$  mL). Organic layer was dried over MgSO<sub>4</sub>, the solvent was evaporated and the product was purified by column chromatography, yield 140 mg, 71%.

Oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =0.81–0.88 (m, 1H), 1.11 (d, *J*(H,H)=6.2 Hz, 3H), 1.47 (dt, *J*(H,H)=5.0, 9.5 Hz, 1H), 1.72–1.84 (m, 1H), 2.14–2.20 (m, 1H), 7.52–7.57(m, 2H), 7.60–7.66 (m, 1H), 7.86–7.93 (m, 2H); <sup>10</sup> <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$ =14.6, 15.6, 17.4, 40.5, 127.9, 129.7, 133.8, 141.5; IR (film in CH<sub>2</sub>Cl<sub>2</sub>,  $\nu_{max}/cm^{-1}$ ): 3622, 3548, 3064, 3039, 2964, 2934, 2874, 1976, 1905, 1821, 1776, 1688, 1622, 1584, 1480, 1447, 1393, 1371, 1305, 1203, 1147, 1089, 1070, 997, 922, 889, 843, 794, 766, 734, 703, 689, 587, 547; MS (EI, 70 eV) *m/z* (%): 196(M<sup>+</sup>,2), 142(3), 126(6), 77(17), 55(100), 51(16), 39(11); HRMS (EI): calculated for C<sub>10</sub>H<sub>12</sub>O<sub>2</sub>S: P33.0558, found: 196.0561; anal. elem. calculated for: C<sub>10</sub>H<sub>12</sub>O<sub>2</sub>S: C 61.20, H 6.16, S 16.34, found: C 61.06, H 6.28, 16.47.

3.1.6. Synthesis of trans-1-phenylsulfonyl-2-(phenylthio) cyclopropane (**3a**). To a solution of 3-chloro-1-phenylsulfonyl-3-(phenyl-thio)propane (**3**) (326 mg, 1 mmol) in THF (6 mL) at -30 °C, solid *t*-BuOK (224 mg, 2 mmol) was added. After 30 min the mixture was warmed to room temperature and after 30 min aqueous solution of NH<sub>4</sub>Cl (5 mL) was added. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2×50 mL), combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, the solvent evaporated and the product was purified by column chromatography, yield 278 mg, 96%.

White crystals; mp: 125–127 °C (EtOH); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =1.38 (dt, *J*(H,H)=5.8, 8.8 Hz, 1H), 1.96 (dt, *J*(H,H)=5.6, 8.8 Hz, 1H), 2.67–2.73 (ddd, *J*(H,H)=3.7, 5.6, 9.1 Hz, 1H), 3.06–3.00 (ddd, *J*(H,H)=3.7, 5.6, 9.1 Hz, 1H), 7.12–7.25 (m, 5H), 7.56–7.50 (m, 2H), 7.62–7.67 (m, 1H), 7.83–7.87 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$ =14.4, 21.0, 42.5, 126.5, 127.7, 128.4, 129.0, 129.4, 133.7, 134.9, 139.9; IR (KBr,  $\nu_{max}/cm^{-1}$ ): 3095, 3062, 3042, 3014, 1582, 1480, 1447, 1438, 1321, 1297, 1185, 1146, 1090, 1073, 1025, 995, 903, 890, 770, 746, 736, 686, 588, 542; MS (EI, 70 eV) *m/z* (%): 290(M<sup>+</sup>, 2), 150(11), 149(100), 147(23), 134(16), 116(43), 115(25), 77(13), 51(11); HRMS (EI): calculated for: C<sub>15</sub>H<sub>14</sub>O<sub>2</sub>S<sub>2</sub>: C 62.04, H 4.86, S 22.08, found: C 61.97, H 4.74, S 21.94.

#### **3.2.** General procedure for the reaction of 3-chloro-3-phenylpropyl phenyl sulfone (1) with aldehydes

To a solution of 3-chloro-3-phenyl-propylphenylsulfone (1) (100 mg, 0.34 mmol) and aldehydes (0.51 mmol) in THF (10 mL), at -30 °C a solution of *t*-BuOK (76 mg, 0.68 mmol) in THF (2 mL) was added dropwise. The mixture was stirred at -30 °C for 20 min, the cooling was removed and aqueous solution of NH<sub>4</sub>Cl (10 mL) was added. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2×20 mL), organic layer was washed with brine, dried over MgSO<sub>4</sub> and solvent was evaporated. The products were isolated and purified by column chromatography.

3.2.1. 2,5-Diphenyl-3-phenylsulfonyl tetrahydrofuran (**1b**). Yield 68%, diastereoisomers ratio *trans-cis*: 38:62. 2,5-*cis* Isomer; white crystals; mp: 106–108 °C (Et<sub>2</sub>O); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ =2.24 (dt, *J*(H,H)=14.0, 10.3 Hz, 1H), 2.85 (ddd, *J*(H,H)=7.7, 5.3, 2.2 Hz, 1H), 3.78 (ddd, *J*(H,H)=7.8, 5.5, 2.2 Hz, 1H), 5.22 (dd, *J*(H,H)=10.6, 5.3 Hz, 1H), 5.45 (d, *J*(H,H)=5.5 Hz, 1H), 7.20–7.28 (m, 4H), 7.28–7.33 (m, 1H), 7.33–7.41 (m, 3H), 7.41–7.47 (m, 2H), 7.50–7.58 (m, 2H), 7.62–7.68 (m, 1H), 7.87–7.95 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ =36.7, 71.4, 80.0, 81.0, 126.0, 126.1, 128.08, 128.14, 128.52, 128.55, 128.7, 129.4, 134.0, 138.2, 139.6, 140.1; IR (KBr,  $\nu_{max}/cm-1$ ): 3039, 2948, 2895, 1494, 1459, 1445, 1302, 1291, 1142, 1086, 1054, 1015, 758, 750, 721, 699, 690, 598; MS (EI, 70 eV) *m/z* (%): 364(M<sup>+</sup>, <1), 223(100),

117(32), 105(56), 77(14); HRMS (ESI): calculated for C<sub>22</sub>H<sub>20</sub>O<sub>3</sub>SNa: 387.1025, found 387.1034.

2,5-*trans* Isomer; white crystals; mp: 168–169 °C (Et<sub>2</sub>O); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =2.43–2.57 (m, 2H), 4.04 (dt, *J*(H,H)=9.0, 5.3 Hz, 1H), 5.12 (dd, *J*(H,H)=10.0, 5.7 Hz, 1H), 5.78 (d, *J*(H,H)=5.7, 1H), 7.23–7.26 (m, 1H), 7.29–7.26 (m, 9H), 7.50–7.53 (m, 2H), 7.61–7.65 (m, 1H), 7.89–7.95 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$ =37.8, 71.9, 79.3, 80.8, 125.5, 126.0, 127.8, 128.2, 128.6, 128.7, 129.4, 134.0, 138.1, 139.8, 140.8; IR (KBr, *v*<sub>max</sub>/cm<sup>-1</sup>): 3058, 3032, 2898, 2846, 1497, 1448, 1307, 1147, 1085, 1055, 1026, 758, 747, 722, 697, 608, 555; MS (EI, 70 eV) *m/z* (%): 364(M<sup>+</sup>, <1), 222(100), 117(42), 105(39), 91(10), 77(15); HRMS (ESI): calculated for C<sub>22</sub>H<sub>20</sub>O<sub>3</sub>SNa: 378.1025, found: 378.1039; anal. elem. calculated for C<sub>22</sub>H<sub>20</sub>O<sub>3</sub>S: C 72.50, H 5.53, S 8.80, found: C 72.35, H 5.61, S 9.05.

3.2.2. 2-(4-Methoxyphenyl)-5-phenyl-3-phenylsulfonyl tetrahydrofuran (1c). Yield 70%, diastereoisomers ratio trans-cis: 67:33. 2,5cis Isomer; white crystals; mp: 90-91 °C (Et<sub>2</sub>O); <sup>1</sup>H NMR  $(400 \text{ MHz}, \text{CDCl}_3)$ :  $\delta = 2.24 (dt, J(H,H) = 13.9, 10.5 \text{ Hz}, 1\text{H}), 2.87 (ddd, J(H,H) = 13.9, 10.5 \text{ Hz}, 1\text{H}), 2.87 (ddd, J(H,H) = 13.9, 10.5 \text{ Hz}, 1\text{H}), 2.87 (ddd, J(H,H) = 13.9, 10.5 \text{ Hz}, 1\text{H}), 2.87 (ddd, J(H,H) = 13.9, 10.5 \text{ Hz}, 1\text{H}), 2.87 (ddd, J(H,H) = 13.9, 10.5 \text{ Hz}, 1\text{H}), 2.87 (ddd, J(H,H) = 13.9, 10.5 \text{ Hz}, 1\text{H}), 2.87 (ddd, J(H,H) = 13.9, 10.5 \text{ Hz}, 1\text{H}), 2.87 (ddd, J(H,H) = 13.9, 10.5 \text{ Hz}, 1\text{H}), 2.87 (ddd, J(H,H) = 13.9, 10.5 \text{ Hz}, 1\text{H}), 2.87 (ddd, J(H,H) = 13.9, 10.5 \text{ Hz}, 1\text{H}), 2.87 (ddd, J(H,H) = 13.9, 10.5 \text{ Hz}, 1$ J(H,H)=8.0, 5.5, 2.4 Hz, 1H), 3.73-3.78 (m, 1H), 3.77 (s, 3H), 5.18 (dd, J(H,H)=10.5, 5.7 Hz, 1H), 5.38 (d, J(H,H)=5.7 Hz, 1H), 6.73-6.84 (m, 2H), 7.07-7.17 (m, 2H), 7.26-7.33 (m, 1H), 7.33-7.39 (m, 2H), 7.39-7.47 (m, 2H), 7.47-7.58 (m, 2H), 7.58-7.69 (m, 1H), 7.84-7.92 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ =36.7, 55.2, 71.2, 79.9, 80.8, 113.9, 126.0, 127.4, 128.0, 128.5, 128.6, 129.4, 132.1, 134.0, 138.2, 139.7, 159.4; IR (KBr,  $\nu_{max}/cm^{-1}$ ): 3064, 3033, 2970, 2891, 1611, 1512, 1445, 1304, 1294, 1146, 1086, 1063, 1031, 827, 760, 752, 701, 689, 650, 600, 520; MS (EI, 70 eV) m/z (%): 394(M<sup>+</sup>, <1), 252(100), 147(15), 135(66), 117(61), 105(12), 91(14), 77(18); HRMS (ESI): calculated for C23H22O4SNa: 417.1131, found: 401.1145; anal. elem. calculated for C<sub>23</sub>H<sub>22</sub>O<sub>4</sub>S: C 70.03, H 5.62, S 8.13, found: C 69.98, H 5.59, S 8.21.

2,5-*trans* Isomer; white crystals; mp: 134–135 °C (Et<sub>2</sub>O); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ =2.43–2.59 (m, 2H), 3.78 (s, 3H), 4.02 (dt, *J*(H,H)=9.3, 5.7 Hz, 1H), 5.12 (dd, *J*(H,H)=9.9, 5.7 Hz, 1H), 5.7 (d, *J*(H,H)=5.7 Hz, 1H), 6.80–6.86 (m, 2H), 7.20–7.27 (m, 3H), 7.27–7.34 (m, 2H), 7.34–7.39 (m, 3H), 7.48–7.56 (m, 2H), 7.84–7.92 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ =37.7, 55.3, 71.7, 79.2, 80.6, 114.0, 126.0, 127.0, 128.2, 128.6, 128.7, 129.4, 132.6, 134.0, 138.1, 140.0, 159.2; IR (KBr,  $\nu_{max}/cm^{-1}$ ): 3063, 3033, 2935, 2837, 1612, 1513, 1447, 1305, 1250, 1176, 1148, 1086, 1031, 831, 758, 720, 700, 689, 607, 565; MS (EI, 70 eV) *m*/*z* (%): 394(M<sup>+</sup>, <1), 252(100), 237(4), 221(9), 135(73), 117(51), 91(11), 77(13); HRMS (EI): calculated for C<sub>23</sub>H<sub>22</sub>O<sub>4</sub>S: C 70.03, H 5.62, S 8.13, found: C 70.05, H 5.88, S 8.16.

3.2.3. 5-Phenyl-3-phenylsulfonyl-2-(4-methylphenyl) tetrahydrofuran (1d). Yield 56%, diastereoisomers ratio trans-cis: 57:43. 2,5-cis Isomer; white crystals; mp: 130–132 °C (Et<sub>2</sub>O); <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ ):  $\delta = 2.23$  (dt, J(H,H) = 13.9, 10.4, 1H), 2.31 (s, 3H), 2.86 (ddd, *I*(H,H)=7.7, 5.4, 2.2 Hz, 1H), 3.76 (ddd, *J*(H,H)=7.9, 5.5, 2.2 Hz, 1H), 5.21 (dd, J(H,H)=10.6, 5.5 Hz, 1H), 5.41 (d, J(H,H)=5.41 Hz, 1H), 7.02-7.14, (m, 4H), 7.27-7.33 (m, 1H), 7.33-7.40 (m, 2H), 7.40-7.47 (m, 2H), 7.50–7.58 (m, 2H), 7.62–7.70 (m, 1H), 7.87–7.94 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ=21.1, 36.8, 71.4, 80.0, 80.9, 126.00, 126.02, 128.1, 128.5, 128.7, 129.2, 129.4, 134.0, 137.2, 137.9, 138.2, 139.7; IR (KBr,  $\nu_{max}/cm^{-1}$ ): 3062, 3034, 2969, 2891, 1515, 1443, 1315, 1146, 1087, 1064, 1011, 820, 782, 748, 723, 698, 688, 649, 600; MS (EI, 70 eV) m/z (%): 236(100), 221(19), 131(21), 119(82), 105(60), 91(28), 77(16); HRMS (ESI): calculated for C<sub>23</sub>H<sub>22</sub>O<sub>3</sub>SNa: 401.1181, found: 401.1178; anal. elem. calculated for C<sub>23</sub>H<sub>22</sub>O<sub>3</sub>S: C 72.99, H 5.86, S 8.47, found: C 73.00, H 6.01, S 8.75.

2,5-*trans* Isomer; white crystals; mp:  $141-142 \degree C$  (Et<sub>2</sub>O); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ =2.32 (s, 3H), 2.39–2.57 (m, 2H), 4.03 (dt, *J*(H,H)=8.6, 5.3 Hz, 1H), 5.11 (dd, *J*(H,H)=10.0, 5.8 Hz, 1H), 5.76 (d, *J*(H,H)=5.3 Hz, 1H), 7.09–7.15 (m, 2H), 7.21–7.24 (m, 2H), 7.27–7.37

(m, 5H), 7.49–7.56 (m, 2H), 7.61–7.67 (m, 1H), 7.87–7.93 (m, 2H);  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ =21.0, 37.8, 71.8, 79.2, 80.7, 125.4, 126.1, 128.2, 128.6, 128.7, 129.34, 129.37, 134.0, 137.5, 137.7, 138.1, 139.9; IR (KBr,  $\nu_{max}/cm^{-1}$ ): 3060, 3025, 2924, 2899, 1514, 1445, 1294, 1144, 1086, 1063, 1048, 1020, 932, 800, 756, 718, 702, 689, 600, 564, 549, 515, 495; MS (EI, 70 eV) m/z (%): 236(76), 221(22), 131(24), 119(100), 105(15), 91(39), 77(30), 65(7), 51(9); HRMS (ESI): calculated for C<sub>23</sub>H<sub>22</sub>O<sub>3</sub>SNa: 401.1182, found: 401.1179; anal. elem. calculated for C<sub>23</sub>H<sub>22</sub>O<sub>3</sub>S: C 72.99, H 5.86, S 8.47, found: C 72.88, H 5.81, S 8.42.

3.2.4. 2-(4-Chlorophenyl)-5-phenyl-3-phenylsulfonyl tetrahydrofuran (**1e**). Yield 53%, diastereoisomers ratio *trans*-*cis*: 29:71. 2,5-*cis* Isomer; Oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ =2.22 (dt, *J*(H,H)=13.9, 10.4 Hz, 1H), 2.83 (ddd, *J*(H,H)=7.8, 5.5, 2.4 Hz, 1H), 3.72 (ddd, *J*(H,H)=8.0, 5.7, 2.3 Hz, 1H), 5.20 (dd, *J*(H,H)=10.5, 5.4 Hz, 1H), 5.45 (d, *J*(H,H)=5.7 Hz, 1H), 7.14–7.23 (m, 2H), 7.23–7.28 (m, 2H), 7.28–7.35 (m, 1H), 7.35–7.47 (m, 4H), 7.51–7.63 (m, 2H), 7.63–7.75 (m, 1H), 7.86–7.97 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ =36.7, 71.3, 79.3, 81.0, 126.0, 127.5, 128.2, 128.61, 128.65, 128.71, 129.5, 134.0, 134.2, 138.1, 138.7, 139.3; IR (KBr,  $\nu_{max}/cm^{-1}$ ): 3057, 3029, 2945, 1492, 1446, 1334, 1306, 1286, 1152, 1086, 1036, 1014, 835, 818, 767, 751, 720, 700, 688, 608, 520; MS (EI, 70 eV) *m/z* (%): 256(37), 221(11), 151(20), 139(47), 117(85), 105(100), 91(17), 77(46), 51(18); HRMS (ESI): calculated for C<sub>22</sub>H<sub>19</sub><sup>35</sup>ClO<sub>3</sub>SNa: 421.0636, found: 421.0640.

2,5-*trans* Isomer; white crystals; mp: 139–141 °C (Et<sub>2</sub>O); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ =2.49 (m, 2H), 3.97 (ddd, *J*(H,H)=9.5, 3.8, 1.2 Hz, 1H), 5.10 (dd, *J*(H,H)=9.9, 5.7 Hz, 1H), 5.76 (d, *J*(H,H)=5.7 Hz, 1H), 7.26–7.33 (m, 4H), 7.33–7.40 (m, 5H), 7.49–7.60 (m, 2H), 7.62–7.71 (m, 1H), 7.85–7.96 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ =38.1, 71.9, 78.7, 81.0, 126.0, 127.0, 128.4, 128.63, 128.65, 128.8, 129.5, 133.6, 134.2, 138.0, 139.4, 139.5; IR (KBr,  $\nu_{max}/cm^{-1}$ ): 3064, 3032, 1492, 1447, 1305, 1144, 1085, 1014, 766, 725, 700, 689, 595, 575, 545, 525; MS (EI, 70 eV) *m/z* (%): 256(100), 221(21), 151(11), 139(29), 117(35), 105(9), 77(32), 51(14); HRMS (ESI): calculated for C<sub>22</sub>H<sub>19</sub><sup>35</sup>ClO<sub>3</sub>SNa: 421.0636, found: 421.0620.

3.2.5. 5-Phenyl-3-phenylsulfonyl-2-(2-phenylvinyl) tetrahydrofuran (1f). Yield 53%, diastereoisomers ratio trans-cis: 31:69. 2,5-cis Isomer; white crystals; mp: 142–143 °C (Et<sub>2</sub>O); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): *δ*=2.22 (dt, *J*(H,H)=13.6, 10.3 Hz, 1H), 2.92 (ddd, *J*(H,H)=9.5, 6.0, 3.5 Hz, 1H), 3.68 (ddd, J(H,H)=10.3, 6.8, 3.7 Hz, 1H), 4.95 (dt, *I*(H,H)=6.6, 1.1 Hz, 1H), 5.11 (dd, *I*(H,H)=9.7, 6.0 Hz, 1H), 6.03 (dd, J(H,H)=15.9, 6.6 Hz, 1H), 6.39 (d, J(H,H)=15.7 Hz, 1H), 7.15–7.33 (m, 6H), 7.33-4.47 (m, 5H), 7.54-7.61 (m, 2H), 7.61-7.68 (m, 1H), 7.93-8.02 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ =36.2, 69.0, 79.6, 80.6, 126.0, 126.52, 126.58, 128.04, 128.09, 128.48, 128.54, 128.7, 129.5, 132.6, 134.1, 135.8, 138.2, 139.8; IR (film in  $CH_2Cl_2$ ,  $\nu_{max}/cm^{-1}$ ): 3061, 3029, 1495, 1447, 1306, 1147, 1086, 1051, 967, 752, 720, 690, 650, 601, 552; MS (EI, 70 eV) m/z (%): 248(100), 157(13), 144(21), 131(35), 117(37), 105(25), 91(30), 77(32), 65(5), 51(11); HRMS (ESI): calculated for C24H22O3SNa: 413.1182, found: 413.1198; anal. elem. calculated for C<sub>24</sub>H<sub>22</sub>O<sub>3</sub>S: C 73.82, H 5.68, S 8.21, found: C 73.61, H 5.61, S 8.41.

2,5-*trans* Isomer; white crystals; mp:  $134-135 \,^{\circ}C$  (Et<sub>2</sub>O); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ =2.46 (dt, *J*(H,H)=12.8, 10.1 Hz, 1H), 2.58 (ddd, *J*(H,H)=13.0, 7.7, 5.1 Hz, 1H), 3.82 (ddd, *J*(H,H)=9.9, 3.5, 2.0 Hz, 1H), 5.07 (dd, *J*(H,H)=10.1, 5.3 Hz, 1H), 5.26 (dt, *J*(H,H)=6.8, 1.3 Hz, 1H), 6.07 (dd *J*(H,H)=16.0, 5.9 Hz, 1H), 6.51 (dd, *J*(H,H)=16.0, 1.5 Hz, 1H), 7.18-7.41 (m, 10H), 7.50-7.59 (m, 2H), 7.59-7.68 (m, 1H), 7.89-7.97 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ =37.1, 69.8, 78.7, 80.4, 126.0, 126.5, 127.3, 128.0, 128.2, 128.50, 128.56, 128.6, 129.4, 131.3, 134.1, 135.9, 138.2, 139.8; IR (film in CH<sub>2</sub>Cl<sub>2</sub>,  $\nu_{max}$ /cm<sup>-1</sup>): 3061, 3029, 1495, 1147, 1305, 1148, 1086, 966, 755, 723, 691, 606, 561; MS (EI, 70 eV) *m*/*z* (%): 248(45), 157(14), 144(20), 131(57), 115(56), 105(49),

91(57), 77(100), 65(16), 51(54), 39(20); HRMS (ESI): calculated for  $C_{24}H_{22}O_3SNa$ : 413.1181, found: 413.1200; anal. elem. calculated for  $C_{24}H_{22}O_3S$ : C 73.82, H 5.68, S 8.21, found: C 73.89, H 5.76, S 8.23.

3.2.6. 2-tert-butyl-5-phenyl-3-phenylsulfonyl tetrahydrofuran (**1g**). Yield 60%, diastereoisomers ratio *trans-cis*: 62:38. 2,5-*cis* Isomer; Oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ =0.89 (s, 9H), 1.79–2.00 (m, 1H), 2.67 (ddd, J(H,H)=13.9, 4.9, 0.7 Hz, 1H), 3.56 (dd, J(H,H)=9.3, 3.8 Hz, 1H), 4.32 (d, J(H,H)=3.6 Hz, 1H), 5.09 (dd, J(H,H)=11.4, 4.8 Hz, 1H), 7.30–7.42 (m, 5H), 7.57–7.65 (m, 2H), 7.65–7.76 (m, 1H), 7.94–8.05 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ =25.7, 34.8, 37.6, 66.2, 80.1, 85.4, 125.8, 127.8, 128.4, 129.0, 129.4, 134.0, 138.3. 140.2; IR (film in CH<sub>2</sub>Cl<sub>2</sub>,  $\nu_{max}/cm^{-1}$ ): 3064, 2960, 2906, 1478, 1447, 1307, 1148, 1087, 1070, 1029, 759, 718, 700, 690, 601, 654; MS (EI, 70 eV) *m/z* (%): 344(M<sup>+</sup>, 1), 287(12), 202(18), 145(100), 117(95), 104(38), 91(20), 77(27), 57(42), 51(12), 41(22); HRMS (EI): calculated for C<sub>20</sub>H<sub>24</sub>O<sub>3</sub>S: 344.1446, found: 344.1435.

2,5-*trans* Isomer; Oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ =0.95 (s, 9H), 2.31–2.44 (m, 1H), 2.44–2.57 (m, 1H), 3.73–3.84 (m, 1H), 4.50 (d, *J*(H,H)=4.2 Hz, 1H), 5.02 (dd, *J*(H,H)=9.1, 6.7 Hz, 1H), 7.18–7.38 (m, 5H), 7.49–7.58 (m, 2H), 7.63–7.71 (m, 1H), 7.87–7.92 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ =26.3, 36.5, 38.3, 66.0, 81.7, 86.9, 126.2, 127.9, 128.5, 128.9, 129.3, 133.9, 138.2, 141.2; IR (film in CH<sub>2</sub>Cl<sub>2</sub>,  $\nu_{max}/$  cm<sup>-1</sup>): 3065, 2962, 2872, 1478, 1447, 1306, 1145, 1086, 1067, 1031, 986, 746, 717, 690, 649, 591, 552, 528; MS (EI, 70 eV) *m/z* (%): 344(M<sup>+</sup>, 7), 202(26), 185(9), 161(10), 145(75), 117(83), 105(100), 91(43), 77(37), 57(47), 41(26); HRMS (EI): calculated for C<sub>20</sub>H<sub>24</sub>O<sub>3</sub>S: 344.1446, found: 344.1459.

#### 3.3. General procedure for the reactions of 2 with aldehydes

To a solution of 3-chlorobutyl phenyl sulfone (**2**) (232 mg, 1 mmol) and aldehyde (1.5 mmol) in toluene (8 mL), at 0 °C solid *t*-BuOK (224 mg, 2 mmol) was added, warmed slowly to room temperature during 6 h, and kept for 18 h. Aqueous solution of NH<sub>4</sub>Cl (5 mL) was added and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>(2×25 mL). Organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, the solvent was evaporated and the products were purified by column chromatography.

3.3.1. 2-Phenyl-3-phenylsulfonyl-5-methyl tetrahydrofuran, 2,5-cis isomer (**2b**). Yield 78%; white crystals; mp: 128–129 °C (EtOH), lit. 125–126 °C (CH<sub>2</sub>Cl<sub>2</sub>);<sup>7b</sup> <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =1.38 (d, *J*(H,H)=6.0 Hz, 3H), 1.82–1.94 (m, 1H), 2.58 (ddd, *J*(H,H)=2.2, 5.0, 13.7 Hz, 1H), 3.65–3.70 (m, 1H), 4.26–4.36 (m, 1H), 5.26 (d, *J*(H,H)=5.5 Hz, 1H), 7.08–7.16 (m, 2H), 7.16–7.24 (m, 3H), 7.48–7.55 (m, 2H), 7.59–7.66 (m, 1H), 7.82–7.88 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$ =19.7, 35.8, 71.7, 75.9, 80.1, 126.0, 128.0, 128.4, 128.6, 129.3, 133.9, 138.3, 140.3; IR (KBr,  $\nu_{max}/cm^{-1}$ ): 3060, 3035, 2976, 2957, 2871, 1962, 1906, 1820, 1776, 1697, 1584, 1457, 1446, 1388, 1370, 1344, 1301, 1288, 1257, 1146, 1102, 1083, 149, 1022, 9687, 910, 856, 785, 761, 751, 719, 699, 689, 624, 610, 554, 507; HRMS (ESI): calculated for C<sub>17</sub>H<sub>18</sub>O<sub>3</sub>SNa: 325.0869, found: 325.0854; anal. elem. calculated for: C<sub>17</sub>H<sub>18</sub>O<sub>3</sub>S: C 67.52, H 6.00, S 10.60, found: C 67.29, H 5.83, S 10.69.

3.3.2. 3-Phenylsulfonyl-2-(4-methoxyphenyl)-5-methyl tetrahydro-furan, 2,5-cis isomer (**2c**). Yield 82%; white crystals; mp: 93–94 °C (EtOH); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =1.37 (d, *J*(H,H)=5.9 Hz, 3H), 1.89 (dt, *J*(H,H)=10.2, 13.7 Hz, 1H), 2.59 (ddd, *J*(H,H)=2.7, 5.3, 13.7 Hz, 1H), 3.64 (ddd, *J*(H,H)=2.7, 5.9, 10.3 Hz, 1H), 3.76 (s, 3H), 4.23–4.32 (m, 1H), 5.19 (d, *J*(H,H)=5.8 Hz, 1H), 6.72–6.78 (m, 2H), 7.06 (m, 2H), 7.48–7.54 (m, 2H), 7.59–7.63 (m, 1H), 7.82–7.86 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$ =19.8, 35.9, 55.2, 71.6, 75.7, 80.0, 113.8, 127.4, 128.6, 129.3, 132.2, 133.8, 138.4, 159.4; IR (KBr,  $\nu_{max}/$  cm<sup>-1</sup>): 3087, 3075, 3017, 2977, 2955, 2878, 2862, 2843, 2043, 1896,

1654, 1614, 1587, 1516, 1465, 1448, 1389, 1372, 1342, 1307, 1300, 1250, 1184, 1163, 1145, 1112, 1101, 1084, 1051, 1027, 970, 920, 833, 788, 751, 720, 690, 638, 611, 559, 518; HRMS (ESI): calculated for  $C_{18}H_{20}O_4SNa$ : 355.0975, found: 355.0961; anal. elem. calculated for:  $C_{18}H_{20}O_4S$ : C 65.04, H 6.06, S 9.65, found: C 65.05, H 6.09, S 9.87.

3.3.3. 3-Phenylsulfonyl-5-methyl-2-(4-methylphenyl) tetrahydrofuran, 2,5-cis isomer (**2d**). Yield 92%; white crystals; mp: 113–114 °C (EtOH); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =1.38 (d, *J*(H,H)=6.0 Hz, 3H), 1.87 (dt, *J*(H,H)=10.2, 13.7 Hz, 1H), 2.28 (s, 3H), 2.58 (ddd, *J*(H,H)=2.4, 5.2, 13.7 Hz, 1H), 3.64 (ddd, *J*(H,H)=2.4, 5.6, 10.2 Hz, 1H), 5.22 (d, *J*(H,H)=5.6 Hz, 1H), 4.25–4.37 (m, 1H), 7.55–7.48 (m, 2H), 6.94–7.10 (m, 4H), 7.82–7.88 (m, 2H), 7.59–7.66 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$ =19.7, 21.1, 35.8, 71.8, 75.8, 80.1, 125.9, 128.6, 129.1, 129.3, 133.8, 137.3, 137.7, 138.4; IR (KBr,  $\nu_{max}/cm^{-1}$ ): 3058, 3027, 2990, 2966, 2937, 2884, 1900, 1818, 1770, 1674, 1614, 1583, 1516, 1478, 1446, 1392, 1370, 1351, 1304, 1233, 1213, 1180, 1152, 1146, 1098, 1085, 1073, 1040, 1020, 998, 946, 906, 849, 825, 777, 746, 722, 687, 639, 623, 564, 536, 516; HRMS (ESI): calculated for C<sub>18</sub>H<sub>20</sub>O<sub>3</sub>SNa: 339.1025, found: 339.1014; anal. elem. calculated for: C<sub>18</sub>H<sub>20</sub>O<sub>3</sub>S: C 68.33, H 6.37, S 10.13, found: C 68.13, H 6.61, S 10.21.

3.3.4. 2-(4-Chlorophenyl)-3-phenylsulfonyl-5-methyl tetrahydrofuran, 2,5-cis isomer (**2e**). Yield 53%; white crystals; mp: 141–144 °C (EtOH); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =1.37 (d, *J*(H,H)=6.0 Hz, 3H), 1.84 (dt, *J*(H,H)=10.2, 13.5 Hz, 1H), 2.55 (ddd, *J*(H,H)=2.5, 5.2, 13.5 Hz, 1H), 3.59 (ddd, *J*(H,H)=2.5, 5.7, 10.2 Hz, 1H), 4.25–4.35 (m, 1H), 5.26 (d, *J*(H,H)=5.7 Hz, 1H), 7.18–7.25 (m, 2H), 7.08–7.12 (m, 2H), 7.50–7.58 (m, 2H), 7.62–7.68 (m,1H), 7.83–7.90 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$ =19.7, 35.9, 71.7, 76.0, 79.4, 127.4, 128.6, 129.4, 133.8, 134.0, 138.3, 138.9; IR (KBr,  $\nu_{max}/cm^{-1}$ ): 3092, 3069, 2968, 2948, 2879, 1940, 1913, 1687, 1599, 1583, 1492, 1445, 1416, 1388, 1346, 1302, 1261, 1147, 1084, 1054, 1023, 1014, 998, 967, 913, 844, 825, 754, 721, 689, 634, 611, 554, 516; HRMS (ESI): calculated for C<sub>18</sub>H<sub>20</sub>O<sub>3</sub>SNa: 339.1025, found: 339.1014; anal. elem. calculated for: C<sub>17</sub>H<sub>17</sub>O<sub>3</sub><sup>35</sup>CIS: C 60.62, H 5.09, CI 10.53, S 9.52, found: C 60.48H 5.13, CI 10.41, S 9.60.

3.3.5. 2-tert-Butyl-3-phenylsulfonyl-5-methyl tetrahydrofuran, 2,5-cis isomer (**2f**). Yield 79%; white crystals; mp: 138–139 °C (EtOH); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =0.80 (s, 9H), 1.22 (d, *J*(H,H)=6.0 Hz, 3H), 1.50–1.64 (m, 1H), 2.38 (dd, *J*(H,H)=4.6, 13.9 Hz, 1H), 3.44 (dd, *J*(H,H)=3.5, 9.5 Hz, 1H), 4.14 (d, *J*(H,H)=3.5 Hz, 1H), 4.15–4.23 (m, 1H), 7.56–7.62 (m, 2H), 7.63–7.69 (m, 1H), 7.90–7.95 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$ =19.7, 25.5, 34.3, 36.5, 66.7, 74.9, 85.4, 128.9, 129.3, 133.9, 138.4; IR (KBr, *v*<sub>max</sub>/cm<sup>-1</sup>): 3076, 2970, 2954, 2894, 2872, 1909, 1821, 1585, 1481, 1446, 1383, 1361, 1313, 1302, 1295, 1281, 1217, 1149, 1096, 1084, 1043, 1015, 964, 933, 900, 836, 782, 759, 720, 693, 641, 573, 551, 518; HRMS (ESI): calculated for C<sub>15</sub>H<sub>22</sub>O<sub>3</sub>SNa: 305.1182, found: 305.1174; anal. elem. calculated for: C<sub>15</sub>H<sub>22</sub>O<sub>3</sub>S: C 63.80, H 7.85, S 11.35, found: C 63.75, H 8.03, S 11.46.

3.3.6. 3-Phenylsulfonyl-5-methyl-2-propyl tetrahydrofuran, 2,5-cis isomer (**2g**). The reaction was performed according to general procedure but using of methodology of the separation in time: a solution of butyric aldehyde in toluene (2 mL) was added 15 s after addition of solid *t*-BuOK to a solution of 3-chlorobutyl-phenyl sulfone (**2**).

Yield 11%; oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =0.80–0.85 (m, 3H), 1.24 (d, *J*(H,H)=6.0 Hz, 3H), 1.29–1.50 (m, 4H), 1.69 (dt, *J*(H,H)=10.2, 13.6 Hz, 1H), 2.45 (ddd, *J*(H,H)=3.1, 5.5, 13.6 Hz, 1H), 3.32–3.38 (m, 1H), 3.97–4.05 (m, 1H), 4.20–4.26 (m, 1H), 7.57–7.62 (m, 2H), 7.66– 7.70 (m, 1H), 7.89–7.94 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$ =13.8, 18.9, 19.8, 35.8, 37.6, 68.7, 74.9, 78.4, 128.6, 129.4, 133.9, 138.5; IR (KBr,  $\nu_{max}/cm^{-1}$ ): 3065, 2962, 2934, 2873, 1585, 1447, 1379, 1306, 1148, 1087, 986, 913, 861, 752, 718, 690, 607; MS (EI, 70 eV) *m/z* (%): 225(35), 143(43), 141(23), 126(75), 98(100), 83(55), 77(51); HRMS (ESI): calculated for C<sub>14</sub>H<sub>20</sub>O<sub>3</sub>SNa: 291.1025, found: 291.1038.

3.3.7. 1-Benzyl-2-phenyl-3-phenylsulfonyl-5-methyl cyclopentane. To a solution of 3-chlorobutyl-phenyl sulfone (**2**) (232 mg, 1 mmol) in THF (3 mL) cooled to  $-78 \degree C t$ -BuOK (224 mg, 2 mmol) in THF (1 mL) was added dropwise and after 15 s chalkon (309 mg, 1.5 mmol) in toluene (10 mL) cooled to  $-78 \degree C$  was added dropwise. The mixture was warmed slowly to room temperature during 6 h and kept for 18 h. Aqueous solution of NH<sub>4</sub>Cl (5 mL) was added and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2×50 mL). Organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, the solvent was evaporated and the product was purified by column chromatography.

*Compound* **2h** Yield 15%; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =1.04 (d, *J*(H,H)=6.6 Hz, 3H), 2.00–2.12 (m, 1H), 2.58–2.69 (m, 1H), 2.82 (ddd, *J*(H,H)=3.4, 7.5, 14.4 Hz, 1H), 3.59 (t, *J*(H,H)=10.1 Hz, 1H), 3.91–4.01 (m, 2H), 6.87–6.92 (m, 2H), 7.00–7.07 (m,3H), 7.28–7.33 (m, 2H), 7.35–7.41 (m, 2H), 7.43–7.53 (m, 2H), 7.59–7.66 (m, 2H), 7.76–7.83 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$ =18.4, 35.4, 39.8, 52.0, 63.1, 69.3, 126.8, 127.0, 128.1, 128.4, 128.5, 128.6, 128.9, 133.0, 133.4, 137.8, 138.1, 140.5, 200.4; IR (KBr,  $\nu_{max}/cm^{-1}$ ): 3317, 2969, 2958, 2870, 1669, 1594, 1579, 1497, 1479, 1447, 1377, 1358, 1302, 1285, 1253, 1146, 1086, 1005, 973, 845, 785, 769, 757, 738, 698, 599, 599; MS (EI, 70 eV) *m*/*z* (%): 263(17), 105(100), 77(16); HRMS (ESI): calculated for C<sub>25</sub>H<sub>24</sub>O<sub>3</sub>SNa: 427.1338, found: 427.1330.

*Compound* **2i** Yield 35%; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =0.89 (d, *J*(H,H)=7.1 Hz, 3H), 2.30 (ddd, *J*(H,H)=4.4, 7.2, 14.1 Hz, 1H), 2.64–2.74 (m, 1H), 2.77–2.88 (m, 1H), 3.96 (ddd, *J*(H,H)=7.2, 10.1, 20.1 Hz, 1H), 4.01 (dd, *J*(H,H)=8.2, 10.4 Hz, 1H), 4.14 (t, *J*(H,H)=10.3 Hz, 1H), 6.93–7.02 (m, 5H), 7.25–7.30 (m, 3H), 7.35–7.44 (m, 2H), 7.46–7.52 (m, 1H), 7.65–7.69 (m, 2H), 7.78–7.83 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$ =17.1, 34.5, 35.8, 47.2, 60.4, 69.2, 126.5, 127.7, 128.0, 128.2, 128.4, 128.6, 128.7, 133.16, 133.21, 137.0, 138.4, 140.5, 197.5; IR (KBr,  $\nu_{max}$ /cm<sup>-1</sup>): 3086, 2959, 2899, 2872, 1677, 1596, 1581, 1495, 1480, 1447, 1383, 1350, 1303, 1276, 1245, 1225, 1191, 1144, 1083, 1021, 997, 959, 842, 774, 754, 709, 685, 634, 592; HRMS (ESI): calculated for C<sub>25</sub>H<sub>24</sub>O<sub>3</sub>SNa: 427.1338, found: 427.1318; anal. elem. calculated for: C<sub>25</sub>H<sub>24</sub>O<sub>3</sub>S: C 74.23, H 5.98, S 7.93, found: C 74.27, H 6.19, S 7.95.

*Compound* **2k** Yield 3%; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =1.16 (d, *J*(H,H)=6.4 Hz, 3H), 2.00–2.12 (m, 1H), 2.42 (dt, *J*(H,H)=7.5, 13.4 Hz, 1H), 2.83–2.99 (m, 1H), 3.86 (t, *J*(H,H)=10.1 Hz, 1H), 3.90–3.94 (m, 1H), 4.15 (dd, *J*(H,H)=5.9, 9.9 Hz, 1H), 6.59–6.63 (m, 2H), 6.85–6.96 (m, 3H), 7.30–7.36 (m, 2H), 7.38–7.43 (m, 2H), 7.44–7.48 (m, 1H), 7.49 (m, 1H), 7.60–7.64 (m, 2H), 7.76–7.80 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$ =18.8, 34.5, 35.7, 49.6, 59.6, 70.5, 126.8, 127.9, 128.0, 128.2, 128.3, 128.4, 129.1, 132.8, 133.5, 137.6, 138.6, 139.4, 198.7; IR (KBr,  $\nu_{max}/cm^{-1}$ ): 3055, 3032, 2977, 2962, 2908, 1681, 1592, 1582, 1495, 1447, 1376, 1322, 1301, 1290, 1249, 1208, 1148, 1087, 1016, 856, 764, 724, 691, 594; HRMS (ESI): calculated for C<sub>25</sub>H<sub>24</sub>O<sub>3</sub>SNa: 427.1338, found: 427.1322.

# 3.4. General procedure for the reaction of carbanion generated from 3 with aldehydes

To a solution of 3-chloro-1-phenylsulfonyl-3-(phenylthio)propane (**3**) (326 mg, 1 mmol) and aldehyde (2 mmol) in toluene (8 mL) at 0 °C solid *t*-BuOK (224 mg, 2 mmol) was added. After 3 h aqueous solution of NH<sub>4</sub>Cl (5 mL) was added, the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2×50 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. To the solution solid NaHCO<sub>3</sub> (0.84 g, 10 mmol) and MCPBA (0.86 g, 5 mmol) were added. After 24 h the mixture was filtered through celit<sup>®</sup>, to the filtrate the water was added and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2×50 mL), Organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> the solvent was evaporated and the crude product was purified using column chromatography. 3.4.1. 2-Phenyl-3-phenylsulfonyl-5-(phenylthio) tetrahydrofuran, 2,5cis isomer (**3b**). This compound was obtained according to general procedure without oxidation with MCPBA. Yield 162 mg, 38%.

White crystals; mp: 106–108 °C (EtOH); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =2.28–2.37 (m, 1H), 2.86–2.94 (ddd, *J*(H,H)=4.4, 6.1, 14.2 Hz, 1H), 3.75 (q, *J*(H,H)=4.7 Hz, 1H), 5.46–5.50 (d, *J*(H,H)=5.7 Hz, 1H), 5.67 (dd, *J*(H,H)=6.1, 8.2 Hz, 1H), 7.14–7.34 (m, 8H), 7.50–7.55 (m, 4H), 7.61–7.66 (m, 1H), 7.83–7.88 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$ =4.2, 70.5, 81.6, 86.4, 126.3, 127.7, 128.2, 128.5, 128.6, 129.0, 129.5, 132.0, 133.5, 134.2, 137.9, 139.7; IR (KBr,  $\nu_{max}/cm^{-1}$ ): 3082, 3057, 3045, 2970, 2920, 1583, 1482, 1453, 1445, 1359, 1317, 1255, 1188, 1145, 1084, 1060, 1029, 969, 913, 802, 757, 739, 715, 690, 630, 566; MS (EI, 70 eV) *m*/*z* (%): 145(100), 143(11), 141(13), 117(14), 115(11), 77(17); HRMS (ESI): calculated for C<sub>22</sub>H<sub>20</sub>O<sub>3</sub>S<sub>2</sub>Na: 419.0746, found: 419.0762; anal. elem. calculated for: C<sub>22</sub>H<sub>20</sub>O<sub>3</sub>S<sub>2</sub>: C 66.64, H 5.08, S 16.17, found: C 66.73, H 4.86, S 16.03.

*3.4.2. 1,2-Bis(phenylsulfonyl)cyclopropane* (**4a**). *1,2-Bis(phenylsulfonyl)cyclopropane* (**4a**) was obtained according to the general procedure without aldehyde. Yield 202 mg, 63%.

White crystals; mp: 175–180 °C (EtOH); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =1.89 (m, 2H), 3.12 (t, *J*(H,H)=7.6 Hz, 2H), 7.36–7.42 (m, 4H), 7.50–7.59 (m, 2H), 7.65–7.71 (m, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$ =10.6, 38.8, 127.6, 129.5, 134.1, 138.9; IR (KBr,  $\nu_{max}/cm^{-1}$ ): 3107, 3029, 1790, 1765, 1582, 1573, 1450, 1413, 1324, 1220, 1150, 1084, 1035, 1011, 997, 901, 812, 784, 753, 726, 699, 586; MS (EI, 70 eV) *m/z* (%): 322(M<sup>+</sup>, 22), 181(18), 156(11), 141(47), 139(12), 125(100), 117(14), 97(16), 77(82), 51(25); HRMS (EI): calculated forC<sub>15</sub>H<sub>14</sub>O<sub>4</sub>S<sub>2</sub>: 322.0334, found: 322.0327; anal. elem. calculated for: C<sub>15</sub>H<sub>14</sub>O<sub>4</sub>S<sub>2</sub>: C 55.88, H 4.38, S 19.89, found: C 55.85, H 4.41, S 20.08.

3.4.3. 2-Phenyl-3,5-bis(phenylsulfonyl) tetrahydrofuran, 2,5-cis isomer (4b). Yield 42%; white crystals; mp with decomposition: 159 °C (EtOH); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =3.00–3.14 (m, 2H), 4.17 (q, J(H,H)=8.0, 1H), 5.10 (dd, J(H,H)=4.5, 7.8 Hz, 1H), 5.39 (d, J(H,H)=8.0 Hz, 1H), 7.24-7.30 (m, 3H), 7.35-7.40 (m, 2H), 7.42-7.46 (m, 2H), 7.47-7.52 (m, 2H), 7.54-7.59 (m, 1H), 7.60-7.65 (m, 1H), 7.74-7.78 (m, 2H), 7.84-7.88 (m,2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): *δ*=28.7, 68.2, 84.2, 92.2, 127.3, 128.3, 128.6, 129.0, 129.2, 129.35, 129.39, 134.23, 134.29, 136.0, 137.1, 137.7; IR (KBr, v<sub>max</sub>/ cm<sup>-1</sup>): 3068, 3036, 2961, 2900, 1584, 1479, 1446, 1309, 1258, 1147, 1083, 998, 915, 743, 718, 700, 685, 621, 604, 579, 556, 531; MS (EI, 70 eV) m/z (%): 252(10), 250(15), 145(80), 144(21), 141(22), 125(36), 117(29), 116(12), 115(49), 109(30), 105(11), 91(14), 77(100) 65(25); HRMS (ESI): calculated 78(22), for C<sub>22</sub>H<sub>20</sub>O<sub>5</sub>S<sub>2</sub>Na: 451.0644, found: 451.0628; anal. elem. calculated for: C<sub>22</sub>H<sub>20</sub>O<sub>5</sub>S<sub>2</sub>: C 61.66, H 4.70, S 14.97, found: C 61.49, H 4.58, S 14.96.

3.4.4. 3,5-*Bis*(*phenylsulfonyl*)-2-(4-*methoxyphenyl*) tetrahydrofuran, 2,5-*cis* isomer (**4c**). Yield 50%; white crystals; mp with decomposition: 144 °C (EtOH); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =3.00–3.13 (m, 2H), 3.79 (s, 3H), 4.12–4.22 (m, 1H), 5.05 (dd, *J*(H,H)=4.1, 7.9 Hz, 1H), 5.35 (d, *J*(H,H)=8.4 Hz, 1H), 6.78–6.82 (m, 2H), 7.30–7.34 (m, 2H), 7.41–7.54 (m, 4H), 7.55–7.67 (m, 2H), 7.72–7.78 (m, 2H), 7.81–7.87 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$ =28.8, 55.3, 67.9, 84.2, 92.0, 114.0, 128.3, 128.9, 129.0, 129.2, 129.3, 129.4, 134.2, 134.3, 136.0, 137.8, 160.1; IR (KBr,  $\nu_{max}/cm^{-1}$ ): 3058, 2998, 2969,

2937, 2919, 2841, 1612, 1586, 1516, 1480, 1447, 1377, 1304, 1249, 1198, 1140, 1074, 1021, 976, 930, 920, 843, 819, 756, 735, 721, 685, 638, 606; MS (EI, 70 eV) m/z (%): 250(29), 175(25), 174(28), 159(22), 141(27), 125(80), 109(35), 94(12), 78(21), 77(100); HRMS (ESI): calculated for C<sub>23</sub>H<sub>22</sub>O<sub>6</sub>S<sub>2</sub>Na: 481.0750, found: 481.0747; anal. elem. calculated for: C<sub>23</sub>H<sub>22</sub>O<sub>6</sub>S<sub>2</sub> C 60.24, H 4.84, S 13.99, found: C 60.38, H 4.75, S 13.86.

3.4.5. 3,5-Bis(phenylsulfonyl)-2-(4-methylphenyl) tetrahydrofuran, *2,5-cis isomer* (*4d*). Yield 45%; white crystals; mp with decomposition: 159 °C (EtOH); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =2.32 (s, 3H), 3.00-3.10 (m, 2H), 4.15 (q, *I*(H,H)=8.0, 1H), 5.08 (dd, J(H,H)=4.6, 7.7 Hz, 1H), 5.37 (d, J(H,H)=8.0 Hz, 1H), 7.05-7.10 (m, 2H), 7.24-7.28 (m, 2H), 7.41-7.46 (m, 2H), 7.46-7.52 (m, 2H), 7.55–7.64 (m, 2H), 7.73–7.77 (m, 2H), 7.83–7.88 (m, 2H); <sup>13</sup>C NMR  $(125 \text{ MHz}, \text{CDCl}_3)$ ;  $\delta = 21.2, 28.8, 68.2, 84.2, 92.1, 127.3, 128.3, 129.1, 129.1, 127.3, 128.3, 129.1, 127.3, 128.3, 129.1, 127.3, 128.3, 129.1, 127.3, 128.3, 129.1, 127.3, 128.3, 129.1, 127.3, 128.3, 129.1, 127.3, 128.3, 129.1, 127.3, 128.3, 129.1, 1$ 129.26, 129.31, 129.40, 134.10, 134.11, 134.2, 136.0, 137.8, 138.9; IR (KBr, *v*<sub>max</sub>/cm<sup>-1</sup>): 3090, 3064, 2977, 2954, 2909, 2857, 1616, 1585, 1519, 1446, 1304, 1289, 1219, 1173, 1143, 1077, 1061, 998, 918, 807, 766, 739, 720, 689, 606, 579, 551; MS (EI, 70 eV) m/z (%): 160(14), 159(100), 158(28), 131(30), 129(21), 125(19), 116(10), 115(16), 91(12), 78(17), 77(41); HRMS (ESI): calculated for C<sub>23</sub>H<sub>22</sub>O<sub>5</sub>S<sub>2</sub>Na: 465.0801, found: 465.0818; anal. elem. calculated for: C23H22O5S2: C 62.42, H 5.01, S 14.49, found: C 62.32, H 5.06, S 14.42.

3.4.6. 2-(4-Chlorophenyl)-3,5-bis(phenylsulfonyl) tetrahydrofuran, 2.5-cis isomer (4e). Yield 28%: white crystals: mp: 152-153 °C (EtOH): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =2.98–3.08 (m, 2H), 4.11 (q, *I*(H,H)=8.3 Hz, 1H), 5.08 (dd, *I*(H,H)=4.6, 7.6 Hz, 1H), 5.38 (d, J(H,H)=8.0 Hz, 1H) 7.22-7.26 (m, 2H), 7.32-7.36 (m, 2H), 7.44-7.52 (m, 4H), 7.58–7.66 (m, 2H), 7.74–7.78 (m, 2H) 7.82–7.86 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ=28.9, 68.3, 83.6, 92.3, 128.4, 128.84, 128.86, 129.2, 129.35, 129.40, 129.49, 134.3, 135.0, 135.8, 136.2, 137.9; IR (KBr,  $\nu_{max}/cm^{-1}$ ): 3092, 3066, 2960, 2927, 2851, 1600, 1493, 1446, 1418, 1302, 1214, 1149, 1089, 1063, 1016, 990, 980, 931, 833, 767, 744, 728, 686, 604, 578, 564, 542; MS (EI, 70 eV) m/z (%): 286(16), 250(39), 218(22), 181(17), 180(30), 179(50), 178(79), 151(21), 149(42), 144(13), 143(15), 142(10), 141(38), 139(13), 126(11), 125(75), 116(13), 115(53), 114(10), 110(25), 109(48), 97(13), 78(43), 77(100); HRMS (ESI): calculated for C<sub>22</sub>H<sub>19</sub>O<sub>5</sub>S<sub>2</sub><sup>35</sup>ClNa: 485.0255, found: 485.0276; anal. elem. calculated for: C<sub>22</sub>H<sub>19</sub>O<sub>5</sub>S<sub>2</sub><sup>35</sup>Cl: C 57.07, H 4.14, Cl 7.66, S 13.85, found: C 56.97, H 4.11, Cl 7.78, S 13.86.

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