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Conjugate addition reaction of THF-2-yl radical with α,β-unsaturated *N*-tosyl imines using a dimethylzinc–air initiator

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ABSTRACT

The reaction of tetrahydrofuran-2-yl radical, generated directly from THF by the action of dimethylzinc–air, with α,β-unsaturated *N*-tosyl aldimines was demonstrated to proceed preferentially in a conjugate addition manner to give 2-(3-hydroxyalkyl)- or 2-(3-aminoalkyl)tetrahydrofurans in good yield. The slow addition of the enimines and the use of dimethylzinc, rather than diethylzinc or triethylborane, were found to be the keys for the efficiency of the THF conjugate addition. The observed chemoselectivity could be rationalized by the larger coefficient of LUMO at the corresponding reaction site of the enimine.

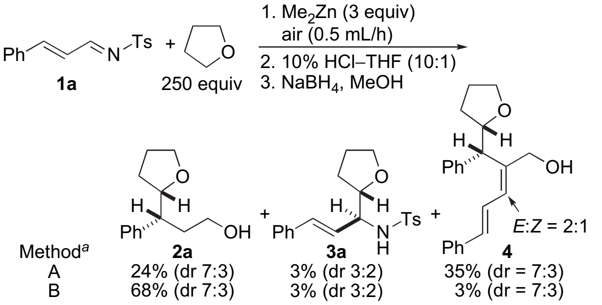
1. Introduction

Reactions involving radical species have led to synthetically useful transformations that would have been otherwise impossible or at least difficult to achieve.[1] The development of new radical initiators is one of the most important efforts for widening the applicability of radical reactions. We have studied dimethylzinc–air-initiated radical reactions[2] and have developed the direct generation of α-alkoxyalkyl radicals from ethers through hydrogen abstraction and the direct functionalization of ethers by the reaction of the resulting radicals with achiral imines,[3] chiral imines,[4] aldehydes,[5] and amines.[6] We also succeeded in the dimethylzinc–air-initiated direct generation of cycloalkyl radicals and their aminoalkylation by the reaction with *N*-tosyl imines.[7] In these reactions, dimethylzinc was assumed to react with air-oxygen[8] to initiate radical reactions by forming a methyl radical, which has a high ability in abstracting a hydrogen atom due to the strong Me–H bond (the bond dissociation energy=429 kJ/mol).[9] As part of our continuing studies, we describe a conjugate addition reaction[10,11] of directly generated THF-2-yl radical with α,β-unsaturated *N*-tosyl aldimines.

2. Results and discussions

2.1. Reaction of THF with *N*-tosyl cinnamaldimine (1a)

A solution of cinnamaldehyde *N*-tosyl imine **1a** (285 mg, 1.0 mmol) and dimethylzinc (1.0 M hexane solution, 3.0 mL, 3.0 mmol) in THF (20 mL, 0.25 mol) was stirred at room temperature for 1 h under a constant introduction of air (0.5 mL/h) into the solution (Scheme 1). Usual work-up gave a crude mixture, which was then hydrolyzed with 10% HCl/THF (10:1). Sodium borohydride reduction of the resulting mixture in methanol gave 1,4-adduct alcohol **2a** (24% yield), 1,2-adduct **3a** (3% yield), and diene **4** (35% yield). The diastereomeric ratio (dr) of **2**–**4** was 7:3, 3:2, and 7:3, respectively, and *E*/*Z* ratio of the trisubstituted alkene moiety of **4** was 2:1 as shown in Scheme 1. The relative configuration of the 1,4-adduct **2a** was undoubtedly determined by the conversion of the major isomer into the known compound with the established stereochemistry (vide infra). The relative configuration of the 1,2-adduct **3a** was tentatively assigned by analogy to the corresponding reaction of *N*-tosyl aldimines[3a] and the major isomers were depicted in the scheme. The geometry of the trisubstituted alkene was determined by NOE enhancement observed between the



Scheme 1. Addition of THF to **1a** using Me_2Zn–air initiator and formation of **2a**, **3a**, and **4**. [a]Method A: Me_2Zn was added to a THF solution of **1a** within 1 min. Method B: a THF solution of **1a** was added to a THF solution of Me_2Zn over 6 h.

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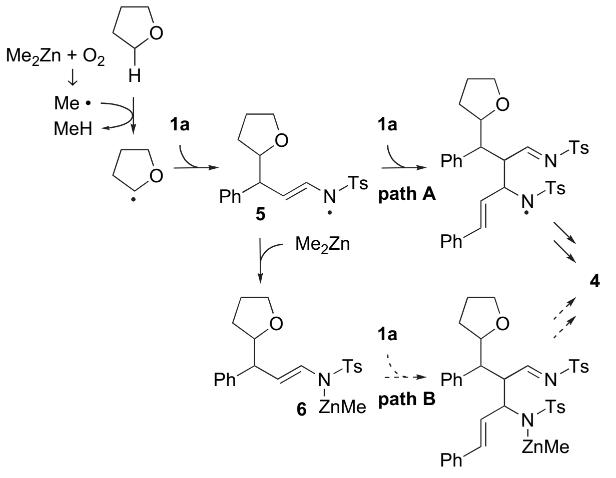
olefinic CH of the trisubstituted alkene and carbinol CH_2 or benzylic CH. The production of undesirable **4** is probably ascribable to the further reaction of 1,4-adduct intermediates **5** and/or **6** with **1a** (path A and/or path B in Scheme 2, respectively).

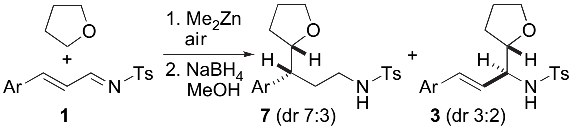


Scheme 2. Plausible mechanism for the production of **4**.

Slow addition of **1a** over 6 h to a mixture of dimethylzinc and THF, under a constant introduction of air, was effective to improve the production of **2a** in 68% yield after imine hydrolysis and aldehyde reduction, and to suppress the formation of **4** in 3% yield. The same slow addition conditions were followed by sodium borohydride reduction (acidic hydrolysis step of imines into aldehydes was omitted) to give 1,4-addition product tosylamide **7a** with dr of 7:3 in 76% yield along with 1,2-adduct **3a** (3:2 dr) in 3% yield (Table 1, entry 1).

The suppressed production of **4** by the slow addition of **1a** clearly indicates the vital role of radical intermediate **5** in the production of **4**. Low concentration of **1a** reduces the possibility of the reaction of **5** with **1a** (Scheme 2, path A), and hence **5** would be converted to a zinc enamide **6**. If path B is the main pathway to **4**, then **4** should not be suppressed in spite of the slow addition because reaction rates of both THF-2-yl radical and **6** are probably first-order with respect to the concentration of **1a** and should be affected to the same degree: the slow addition would make the whole reaction slow with no difference in the product ratio. Accordingly, the results indicate that the reaction of zinc enamide **6** with **1a**, i.e., path B, should be negligible and path A is mainly responsible to the formation of **4**.

Table 1
Radical addition of THF to unsaturated imines **1** using dimethylzinc–air initiator[a]



Entry	**1**	Ar	Yield of **7** (%)	Yield of **3** (%)
1	**1a**	Ph	76	3
2	**1b**	4-ClC_6H_4	55	5
3	**1c**	4-$MeOC_6H_4$	59	4
4	**1d**	4-MeC_6H_4	70	5
5	**1e**	2-MeC_6H_4	60	7
6	**1f**	2-Naphthyl	51	6

[a] The reaction was conducted in 250 equiv of THF with 6 equiv of Me_2Zn under continuous introduction of air (0.5 mL/h). Imines **1** (1 mmol) were added over 6 h as a THF solution.

The presence of a Lewis acid as an additive did not affect this 1,4-preference in the addition of THF-2-yl radical. Thus, in the presence of 1 equiv of boron trifluoride diethyl etherate, under the conditions corresponding to entry 1 in Table 1, the reaction still proceeded in 1,4-manner to give **7** in 32% yield along with **3** in 5% yield, although the reaction efficacy significantly decreased by competitive formation of unidentified byproducts. This is in contrast to the reported triethylborane-mediated 1,2-selective addition of an ethyl radical to an α,β-unsaturated oxime ether derived from cinnamaldehyde in the presence of boron trifluoride diethyl etherate.[12]

Other approaches to high yield production of **2a** by sterically and electronically modified imines such as *N*-(2,4,6-triisopropylbenzenesulfonyl)-, *N*-(4-methoxyphenyl)-, and *N*-(2,6-diispropylphenyl)imine failed to improve the yield of **2a**. Direct use of cinnamaldehyde as a Michael acceptor did not lead to any fruitful results.

2.2. Reactions of other *N*-tosyl α,β-unsaturated aldimines with THF

The reaction of THF with other β-aryl *N*-tosyl α,β-unsaturated aldimines having an electron-withdrawing 4-chlorophenyl group (**1b**), electron-donating 4-methoxy- and 4-methylphenyl groups (**1c**, **1d**), a sterically demanding 2-methylphenyl group (**1e**), and 2-naphthyl group (**1f**) was proven to be promising under the slow addition protocol (Table 1). Whether the β-aryl group of imines had an electron-withdrawing (entry 2) or an electron-donating substituent (entries 3 and 4), the 1,4-addition of THF-2-yl radical mainly took place to give 2-(3-aminoalkyl)-THF **7** as a major product in 55–70% yield, whilst 1,2-adducts **3** were minor products (range of **7**/**3**=ca. 11:1 to 25:1). Even with sterically demanding 2-methylphenyl (entry 5) or 2-naphthyl group (entry 6), the 1,4-addition was still preferred with a slightly increased amount of 1,2-adducts **3** (**7**/**3**=17:2).

The relative configuration of major isomers of **7b**–**7f** was assigned to be the same as **7a** based on ^1H and ^{13}C NMR chemical shifts and coupling constants of the benzylic and adjacent methines (Table 2). The coupling constants between these protons of the major isomers of **7a** and **7b** were smaller (5.8 and 5.5 Hz) than those of the minor isomers (9.2 and 8.8 Hz). This tendency of the coupling constants was in good agreement with those calculated by Karplus equation based on MMFF conformer distribution (2.6, 2.7, 9.6, and 8.2 Hz).[13] Except for **7e**, the peaks of these methine protons of the major diastereomers appear at lower δ ppm than those of the minor diastereomers, while those of the methine carbons of the major diastereomers appear at higher δ ppm than those of the minor diastereomers. Chemical shifts of methylene protons of the tetrahydrofuran ring are also characteristic: those of the minor diastereomers are better resolved and appear at higher δ ppm than those of the major diastereomers. The peaks of the amide protons of minor diastereomers also appear at higher δ ppm than those of the major diastereomers.

The reaction of 4,4,5,5-tetramethyl-1,3-dioxolane[14] with **1a** under 10 h slow addition conditions proceeded in 1,4-manner to give 1,4-adduct **8** in 15% yield and 1,2-adduct **9** in 2% yield (Scheme 3).

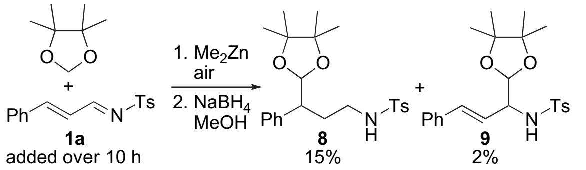
2.3. Reactions initiated by diethylzinc and triethylborane

The reaction of **1a** with THF was performed using other established radical initiators, diethylzinc,[15,16] and triethylborane,[17] to compare the reaction efficiency (Scheme 4). The reaction initiated by diethylzinc gave **7a** in slightly lower yield of 65%, while a significant amount (12%) of ethyl-adduct **10** was produced. Using triethylborane initiator, the production of **10** increased to 20% yield and 1,4-adducts **7a** and **2a** were obtained in 33% and 9% yields,

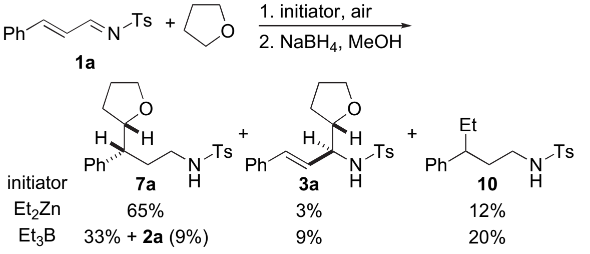
Table 2
Coupling constant (*J*, Hz) and chemical shift (*δ*, ppm) values of ^1H and ^{13}C NMR of methines, ^1H of oxygenated methylene, and amide NH of adduct **7**

		$^3J_{H-H}$[a]	*δ* ArCH		*δ* OCH		*δ* OCH_2	*δ* NH
			^1H	^{13}C	^1H	^{13}C	^1H	^1H
7a	Major	5.8	2.68	32.2	3.95	82.3	3.66, 3.71	4.44
	Minor	9.2	2.49	33.6	3.88	83.0	3.76, 3.84	4.87
7b	Major	5.5	2.67	32.5	3.91	82.0	3.64, 3.67	4.72
	Minor	8.8	2.53	33.3	3.84	82.7	3.76, 3.84	4.75
7c	Major		2.63	46.7	3.91	82.3	3.65, 3.70	4.45
	Minor		2.45	48.1	3.84	83.1	3.75, 3.84	4.76
7d	Major		2.63	47.3	3.92	82.4	3.65, 3.71	4.41
	Minor		2.45	48.8	3.85	83.0	3.76, 3.84	4.75
7e	Major			41.6	3.90	82.2	3.66, 3.70	4.67
	Minor			41.7	3.94	82.2	3.77, 3.88	4.99
7f	Major		2.76	47.7	4.04	82.3	3.66, 3.70	4.75
	Minor		2.68	49.5	4.00	82.9	3.78, 3.87	4.98

[a] The coupling constants between the benzylic and the adjacent methine protons.



Scheme 3. Attempted reaction of C1 unit ether to **1a** using Me_2Zn–air initiator.



Scheme 4. Radical reaction of THF with **1a** using Et_2Zn or Et_3B–air initiator.

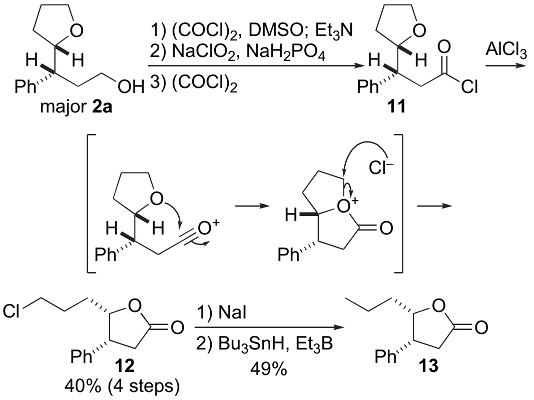
respectively.[18,19] These results suggest that the addition of ethyl radical to **1a** is competing with the hydrogen atom abstraction from THF by the ethyl radical, indicating the privilege of dimethylzinc for the efficient generation of THF-2-yl radical from THF.

2.4. Acylative tetrahydrofuran ring opening to convert 1,4-adduct 2a into lactones 12 and 13, and determination of the relative configuration of 2a

The THF moiety of the adduct is convertible into an α,ω-functionalized C4 chain unit as shown in Scheme 5. Sequential Swern and Pinnick oxidations of the major isomer of **2a** gave the corresponding carboxylic acid, which was then converted into acyl chloride **11**. Treatment of **11** with aluminum chloride at room temperature provided lactone **12** via the known acylative tetrahydrofuran ring opening.[20] Dehalogenation of **12** gave the known lactone **13**[21] to establish the relative stereochemistry of **2a**.

2.5. MO calculation rationale for selective 1,4-conjugate addition reaction[22]

Because α-alkoxyalkyl radicals are classified as nucleophilic radicals having relatively high energy SOMOs, the most important MO interaction between the radicals and the α,β-unsaturated imine (**1a**) should be the SOMO of the radicals and LUMO of the imine. The optimized geometries and the energy and MO coefficients of the LUMO were calculated by the B3LYP/6-31G* level DFT method for *s*-cis and *s*-trans conformers of *N*-(3-phenylprop-2-enylidene)-benzenesulfonamide (**14**) (Fig. 1). The LUMO energy of the *s*-cis conformer was found to be lower than that of the *s*-trans conformer (−2.45 vs −2.38 eV), although the population of the conformers at 27 °C was calculated to be trans/cis=97.5:2.5 (ΔG^0=9.14 kJ/mol). In the *s*-cis conformer, the β-carbon C3 was found to have largest coefficient (|LUMO|=0.4477) and the azomethine carbon C1 has the second largest coefficient (|LUMO|=0.3817), apparently suggesting that 1,4-conjugate addition is much more favorable than 1,2-addition.[23] Qualitatively the same results (0.4341 at C3 and 0.3622 at C1) were obtained for the *s*-trans conformer.



Scheme 5. Conversion of major isomer of **2a** into lactones **12** and **13**.

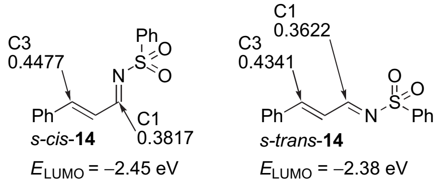


Figure 1. LUMO energy and coefficients on β-carbon (C3) and azomethine carbon (C1) of *s*-cis and *s*-trans conformers of α,β-unsaturated *N*-benzensulfonyl imine **14** by B3LYP/6–31G*.

3. Conclusions

We have shown that THF-2-yl radical, directly generated from THF by dimethylzinc–air, undergoes addition to α,β-unsaturated *N*-

tosyl aldimines preferentially in 1,4-manner to give 2-(3-hydroxyalkyl)- or 2-(3-aminoalkyl)-tetrahydrofurans in good yield. The use of dimethylzinc, rather than diethylzinc or triethylborane, was the key for the efficiency of the THF addition. The slow addition of the enimines **1** efficiently improved the production of the desired adduct **2** or **7**, by suppressing the formation of **4**, which suggests that **4** was produced through the reaction of **1a** and intermediate radical **5**, and not zinc amide **6**. The adduct **2** was converted into lactones **12** and **13**. The observed selective 1,4-conjugate addition was rationalized by the larger LUMO coefficient at the corresponding reaction site of the enimine.

4. Experimental section

4.1. General

All melting points were uncorrected. IR spectra were expressed in cm^{-1}. ^{1}H and ^{13}C NMR spectra were measured in CDCl$_3$ at 500 and 125 MHz, respectively. ^{13}C NMR peak multiplicity assignments were made based on DEPT. Chemical shift values are expressed in parts per million relative to internal TMS. *J* values were presented in hertz. Abbreviations are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Column chromatography was performed using silica gel. A hexane solution of dimethylzinc, diethylzinc, and triethylborane was purchased from Kanto chemical co., Inc. 4,4,5,5-Tetramethyl-1,3-dioxolane was prepared according to the reported procedure.[14] α,β-Unsaturated *N*-tosyl aldimines **1** were prepared by the reported procedure[24] from the corresponding aldehydes.[25] Before introduction to a reaction mixture, air was passed through a drying tube filled with NaOH.

*4.1.1. 4-Methyl-N-(3-phenylpropenylidene)benzenesulfonamide (**1a**)*

Yield: 63%, 119–121 °C. IR (KBr): 1624, 1582, 1315, 1153, 1091. ^{1}H NMR: 8.59 (d, *J*=9.5, 1H), 7.86 (d, *J*=8.3, 2H), 7.56–7.53 (m, 2H), 7.48 (d, *J*=15.9, 1H), 7.44–7.39 (m, 3H), 7.33 (d, *J*=7.9, 2H), 6.97 (dd, *J*=9.5, 15.9, 1H), 2.42 (s, 3H). ^{13}C NMR: 170.9, 153.8, 144.5, 135.3, 134.1, 131.6, 129.8, 129.2, 128.6, 127.9, 124.6, 21.5. EIMS *m*/*z*: 284 (M$^+$), 155 (Ts), 130 (M−Ts), 91. These spectroscopic data were identical to those reported.[26]

*4.1.2. N-[3-(4-Chlorophenyl)propenylidene]-4-methylbenzenesulfonamide (**1b**)*

Yield: 83%, mp 178–180 °C. IR (KBr): 1620, 1574, 1319, 1173, 1088. ^{1}H NMR: 8.76 (d, *J*=9.5, 1H), 7.85 (d, *J*=8.3, 2H), 7.48 (d, *J*=8.6, 2H), 7.42 (d, *J*=15.8, 1H), 7.40 (d, *J*=8.6, 2H), 7.34 (d, *J*=8.3, 2H), 6.95 (dd, *J*=9.5, 15.8, 1H), 2.44 (s, 3H). ^{13}C NMR: 170.5, 152.0, 144.6, 137.6, 135.2, 132.6, 129.8, 129.7, 129.5, 128.0, 125.2, 21.5. FABMS *m*/*z*: 322 (M+2+H), 320 (M+H). FABMS *m*/*z*: 320.0506 (calcd for $C_{16}H_{15}ClNO_2S$: 320.0512).

*4.1.3. N-[3-(4-Methoxyphenyl)propenylidene]-4-methylbenzenesulfonamide (**1c**)*

Yield: 82%, mp 105–106.5 °C. IR (KBr): 1624, 1601, 1574, 1512, 1315, 1245, 1157, 1091. ^{1}H NMR: 8.74 (d, *J*=9.8, 1H), 7.85 (d, *J*=8.5, 2H), 7.51 (d, *J*=8.5, 2H), 7.44 (d, *J*=15.6, 1H), 7.33 (d, *J*=8.5, 2H), 6.93 (d, *J*=8.5, 2H), 6.86 (dd, *J*=9.8, 15.6, 1H), 3.86 (s, 3H), 2.43 (s, 3H). ^{13}C NMR: 171.1, 162.6, 153.9, 144.2, 135.7, 130.6, 129.7, 127.8, 127.0, 122.2, 114.6, 55.4, 21.4. FABMS *m*/*z*: 316 (M+H). Anal. Calcd for $C_{17}H_{17}NO_3S$: C, 64.74; H, 5.43; N, 4.44. Found: C, 64.77; H, 5.45; N, 4.38.

*4.1.4. 4-Methyl-N-[3-(4-methylphenyl)propenylidene]-benzenesulfonamide (**1d**)*

Yield: 25%, mp 153–155 °C. IR (KBr): 2924, 1612, 1574, 1312, 1150, 1088. ^{1}H NMR: 8.76 (d, *J*=9.5, 1H), 7.85 (d, *J*=8.3, 2H), 7.48 (d, *J*=15.9, 1H), 7.45 (d, *J*=7.9, 2H), 7.34 (d, *J*=8.3, 2H), 7.34 (d, *J*=7.9, 2H), 6.95 (dd, *J*=9.5, 15.9, 1H), 2.44 (s, 3H), 2.40 (s, 3H). ^{13}C NMR: 171.1 (CH), 154.0 (CH), 144.4 (C), 142.6 (C), 135.6 (C), 131.6 (C), 130.0 (CH), 129.8 (CH), 128.7 (CH), 127.9 (CH), 123.8 (CH), 21.5 (CH$_3$×2). FABMS *m*/*z*: 300 (M+H). FABMS *m*/*z*: 300.1056 (calcd for $C_{17}H_{18}NO_2S$: 300.1058).

*4.1.5. 4-Methyl-N-[3-(2-methylphenyl)propenylidene]-benzenesulfonamide (**1e**)*

Yield: 49%, mp 126–128 °C. IR (KBr): 3040, 2924, 1612, 1582, 1319, 1157, 1088. ^{1}H NMR: 8.82 (d, *J*=9.5, 1H), 7.87 (d, *J*=8.3, 2H), 7.79 (d, *J*=15.6, 1H), 7.59 (d, *J*=7.7, 1H), 7.36–7.32 (m, 3H), 7.26–7.23 (m, 2H), 6.94 (dd, *J*=9.5, 15.6, 1H), 2.46 (s, 3H), 2.44 (s, 3H). ^{13}C NMR: 171.2, 151.5, 144.5, 138.3, 135.4, 133.0, 131.5, 131.2, 129.8, 128.0, 126.8, 126.7, 125.5, 21.6, 19.7. FABMS *m*/*z*: 300 (M+H). FABMS *m*/*z*: 300.1056 (calcd for $C_{17}H_{18}NO_2S$: 300.1058).

*4.1.6. 4-Methyl-N-(3-naphth-2-ylpropenylidene)-benzenesulfonamide (**1f**)*

Yield: 61%, mp 167–170 °C. IR (KBr): 3047, 3009, 2916, 1612, 1582, 1312, 1157, 1088. ^{1}H NMR: 8.83 (d, *J*=9.5, 1H), 7.97 (s, 1H), 7.89–7.84 (m, 5H), 7.66 (m, 1H), 7.65 (d, *J*=15.6, 1H), 7.58–7.53 (m, 2H), 7.35 (d, *J*=8.2, 2H), 7.10 (dd, *J*=9.5, 15.6, 1H), 2.44 (s, 3H). ^{13}C NMR: 170.9, 153.9, 144.5, 135.4, 134.8, 133.2, 131.7, 131.3, 129.8, 129.2, 128.9, 128.1, 128.0, 127.9, 127.1, 124.9, 123.3, 21.6. FABMS *m*/*z*: 336 (M+H). FABMS *m*/*z*: 336.1060 (calcd for $C_{20}H_{18}NO_2S$, 336.1058).

4.2. 3-Phenyl-3-(tetrahydrofuran-2-yl)propane-1-ol (2a), and (2*Z*,4*E*)- and (2*E*,4*E*)-5-phenyl-2-(phenyl(tetrahydrofuran-2-yl)methyl)penta-2,4-dien-1-ol (4) (Scheme 1)

THF (18.5 mL, 0.23 mol) and 1.0 M solution of Me$_2$Zn in hexane (6.0 mL, 6.0 mmol) were placed in a three-neck flask attached with NaOH tube. A solution of cinnamaldehyde imine **1a** (285 mg, 1.0 mmol) in 1.5 mL of THF was added (0.25 mL/h) over 6 h to the stirred mixture at room temperature, while air was injected to the solution (0.5 mL/h), using a syringe pump. After the addition of **1a**, the mixture was stirred for additional 0.5 h and quenched with NH$_4$Cl (15 mL). The mixture was diluted with EtOAc and the organic layer was separated. The aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, and concentrated. The resulting pale-yellow oil was dissolved in EtOAc and passed through Al$_2$O$_3$ (10 g), which was successively eluted with EtOAc. After concentration, the resulting pale-yellow solid was dissolved in methanol (3 mL) and then NaBH$_4$ (39 mg, 1.0 mmol) was added to the solution. After 15 min, the reaction was quenched with water (3 mL) and the resulting aqueous layer was extracted with EtOAc. The organic layer was washed with brine and dried over Na$_2$SO$_4$. Concentration and column chromatography (hexane/EtOAc=1:1) gave a 7:3 diastereomeric mixture of **2a** (139.7 mg, 68%) as colorless oil, and a 7:3 diastereomeric mixture of a 2:1 mixture of (*E*,*E*)- and (*E*,*Z*)-**4** (1.1 mg, 3%) as pale-yellow oil.

*A 7:3 diastereomeric mixture of **2a**.* IR (neat): 3382, 1064. ^{1}H NMR: 7.31–7.16 (m, 5H), 4.08–4.04 (m, 0.7H), 4.03–3.97 (m, 0.3H), 3.94–3.89 (m, 0.3H), 3.85–3.80 (m, 0.3H), 3.80–3.75 (m, 0.7H), 3.72–3.68 (m, 0.7H), 3.61–3.57 (m, 1H), 3.49–3.45 (m, 1H), 2.91–2.86 (m, 0.7H), 2.72–2.65 (m, 0.3H), 2.20–1.40 (m, 6H). ^{13}C NMR: major 141.8, 128.5, 128.2, 126.4, 82.7, 68.2, 60.9, 47.2, 35.4, 29.2, 25.8; minor 143.0, 128.4, 127.8, 126.4, 83.4, 68.2, 61.5, 49.6, 37.9, 30.8, 25.5. MS *m*/*z*: 206 (M$^+$). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.94; H, 8.92. The diastereomers were separated by column chromatography (hexane/EtOAc=3:2).

*The minor less polar diastereomer of **2a**.* Colorless oil. IR (neat): 3387, 2955, 2870, 1597, 1458, 1404, 1119, 1057, 918, 864, 764, 702. ^{1}H NMR: 7.29 (dd, *J*=7.3, 7.4, 2H), 7.21 (dt, *J*=7.4, 1.5, 1H), 7.17 (dd, *J*=1.5, 7.3, 2H), 4.00 (ddd, *J*=6.4, 8.3, 8.9, 1H), 3.91 (ddd, *J*=6.7, 6.7, 8.3, 1H), 3.82 (ddd, *J*=5.8, 8.0, 8.3, 1H), 3.64 (ddd, *J*=5.3, 5.3, 11.0, 1H), 3.54 (ddd, *J*=4.6, 8.6, 11.0, 1H), 2.83 (br s, 1H), 2.68 (ddd, *J*=7.0, 7.0, 8.9, 1H), 2.21 (m, 1H), 1.73–1.94 (m, 3H), 1.60 (m, 1H), 1.40 (dddd, *J*=8.5, 8.5, 8.5, 12.5, 1H). ^{13}C NMR: 143.2 (C), 128.6 (CH), 128.0 (CH), 126.6 (CH), 83.4 (CH), 68.1 (CH$_2$), 61.5 (CH$_2$), 49.6 (CH), 37.9 (CH$_2$), 30.7 (CH$_2$), 25.4 (CH$_2$). FABMS *m*/*z*: 207 (M+H). FABMS *m*/*z*: 207.1390 (calcd for $C_{13}H_{19}O_2$: 207.1385).

*The major more polar diastereomer of **2a***. Colorless oil. IR (neat): 3387, 2947, 2870, 1597, 1450, 1057, 918, 733, 702. ^{1}H NMR: 7.20–7.31 (m, 5H), 4.06 (ddd, *J*=6.1, 6.1, 8.6, 1H), 3.76 (ddd, *J*=7.1, 7.1, 7.8, 1H), 3.69 (ddd, *J*=6.1, 7.8, 7.8, 1H), 3.58 (ddd, *J*=5.8, 5.8, 10.7, 1H), 3.47 (ddd, *J*=6.1, 7.9, 10.7, 1H), 2.88 (ddd, *J*=5.5, 5.5, 9.8, 1H), 1.90–2.06 (m, 3H), 1.65–1.84 (m, 3H), 1.57 (dddd, *J*=8.4, 8.4, 8.4, 12.2, 1H). ^{13}C NMR: 141.9 (C), 128.7 (CH), 128.3 (CH), 126.6 (CH), 82.7 (CH), 68.1 (CH$_2$), 60.9 (CH$_2$), 47.1 (CH), 35.3 (CH$_2$), 29.0 (CH$_2$), 25.7 (CH$_2$). FABMS *m*/*z*: 207 (M+H). FABMS *m*/*z*: 207.1396 (calcd for $C_{13}H_{19}O_2$: 207.1385).

*A 2:1 mixture of (2Z,4E)- and (2E,2E)-**4***. IR (neat): 3406, 1061. ^{1}H NMR: 7.44–7.06 (m, 10H), 6.67–6.60 (m, 0.87H), 6.57 (d, *J*=15.9, 0.13H), 6.46 (d, *J*=11.3, 0.27H), 6.39 (d, *J*=11.3, 0.48H), 6.35 (d, *J*=11.3, 0.12H), 6.27 (d, *J*=11.6, 0.13H), 4.55 (m, 0.75H), 4.46 (m, 0.25H), 4.37 (d, *J*=11.9, 0.13H), 4.28 (d, *J*=12.2, 0.12H), 4.25–4.19 (m, 1.27H), 4.09 (d, *J*=13.5, 0.48H), 3.99–3.90 (m, 1.63H), 3.82 (m, 1H), 3.77 (m, 0.12H), 3.65 (d, *J*=6.4, 0.12H), 3.58 (d, *J*=8.9, 0.13H), 2.06–1.75 (m, 3H), 1.70–1.60 (m, 1H). ^{13}C NMR: 142.0, 141.3, 141.2, 140.3, 137.5, 137.4, 134.6, 134.5, 128.8, 128.73, 128.69, 128.68, 128.6, 128.5, 128.2, 127.84, 127.77, 126.7, 126.61, 126.55, 124.0, 123.8, 80.1, 79.7, 68.5, 68.3, 65.5, 64.9, 50.5, 50.4, 30.8, 30.1, 25.6, 25.3. MS *m*/*z*: 320 (M$^+$).

The major diastereomer of (2*Z*,4*E*)-**4** was isolated as pale-yellow oil by preparative silica gel TLC (hexane/acetone=6:1). The (2*Z*)-geometry was determined by NOE (8% between benzylic CH at 3.58 ppm and C3 olefinic CH at 6.28 ppm). IR (neat): 3359, 1045. ^{1}H NMR: 7.39 (d, *J*=7.3, 2H), 7.33–719 (m, 8H), 7.14 (dd, *J*=11.0, 15.6, 1H), 6.57 (d, *J*=15.6, 1H), 6.28 (d, *J*=11.0, 1H), 4.46 (dt, *J*=9.15, 12.9, 1H), 4.37 (d, *J*=13.9, 1H), 4.24 (d, *J*=11.4, 1H), 3.99 (dd, *J*=7.8, 14.6, 1H), 3.85 (dd, *J*=7.8, 14.6, 1H), 3.58 (d, *J*=8.9, 1H), 2.30–2.36 (m, 2H), 2.01–1.97 (m, 2H). ^{13}C NMR: 142.4, 141.4, 137.5, 133.9, 131.2, 128.74, 128.67, 128.4, 127.7, 126.9, 126.6, 124.4, 81.4, 68.4, 60.1, 57.1, 29.7, 25.5. MS *m*/*z*: 320 (M$^+$). EIMS *m*/*z*: 320.1783 (calcd for $C_{22}H_{24}O_2$: 320.1176).

4.3. General procedure of the reaction of α,β-unsaturated *N*-tosyl imines 1

*4.3.1. 4-Methyl-N-(3-phenyl-3-(tetrahydrofuran-2-yl)propyl)-benzenesulfonamide (**7a**) and (E)-4-methyl-N-(3-phenyl-1-(tetrahydrofuran-2-yl)allyl)benzenesulfonamide (**3a**) (Table 1, entry 1)*

THF (20.0 mL, 0.25 mol) and 1.0 M solution of Me_2Zn in hexane (6.0 mL, 6.0 mmol) were placed in a three-neck flask attached with NaOH in a drying tube. THF solution (4.7 mL) of **1a** (289 mg, 1.0 mmol) was added (0.78 mL/h) over 6 h to the stirred solution at room temperature, while air was injected to the solution (0.5 mL/h) using a syringe pump. After the addition of **1a**, the mixture was stirred for additional 0.5 h and quenched with methanol (20 mL), and then $NaBH_4$ (47 mg, 1.2 mmol) was added. After 15 min, the whole was quenched with water (20 mL). The resulting aqueous solution was extracted with EtOAc three times. The combined organic layers were washed with brine and dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc=2:1) gave a 7:3 diastereomeric mixture of **7a** (273.0 mg, 76%) as white solid of mp 108–110 °C and a 6:4 diastereomeric mixture of **3a** (10.7 mg, 3%) as white solid of mp 85–88 °C.

*A 7:3 diastereomeric mixture of **7a***. IR (neat): 3279, 1320, 1150, 1072. ^{1}H NMR: major 7.65 (d, *J*=7.0, 2H), 7.20–7.29 (m, 5H), 7.13 (d, *J*=7.0, 2H), 1.64 (m, 1H), 4.44 (t, 6.0, 1H), 1.76 (m, 1H), 3.95 (ddd, *J*=5.8, 6.4, 8.2, 1H), 3.71 (ddd, *J*=6.8, 6.8, 8.3, 1H), 3.66 (ddd, *J*=5.8, 7.6, 8.3, 1H), 2.87 (m, 1H), 2.79 (m, 1H), 2.68 (ddd, *J*=5.2, 5.2, 10.1, 1H), 2.42 (s, 3H), 1.82–1.96 (m, 3H), 1.44 (dddd, *J*=8.2, 8.2, 8.2, 12.2, 1H); minor 7.66 (d, *J*=7.0, 2H), 7.19–7.28 (m, 5H), 7.03 (d, *J*=7.0, 2H), 4.87 (t, *J*=5.7, 1H), 3.88 (ddd, *J*=6.4, 7.6, 9.2, 1H), 3.84 (ddd *J*=7.0, 7.0, 8.3, 1H), 3.76 (ddd, *J*=6.1, 8.0, 8.3, 1H), 2.91 (m, 1H), 2.84 (m, 1H), 2.49 (ddd, *J*=5.2, 8.8, 9.2, 1H), 2.42 (s, 3H), 2.11 (m, 1H), 1.71–1.84 (m, 3H), 1.56 (m, 1H), 1.32 (dddd, *J*=8.2, 8.2, 8.2, 12.5, 1H). ^{13}C NMR: major 143.3 (C), 140.9 (C), 137.0 (C), 129.64 (CH), 128.64 (CH), 128.4 (CH), 127.10 (CH), 126.78 (CH), 82.3 (CH), 68.1 (CH$_2$), 47.7 (CH), 41.4 (CH$_2$), 32.2 (CH$_2$), 29.0 (CH$_2$), 25.7 (CH$_2$), 21.4 (CH$_3$); minor 143.2 (C), 142.0 (C), 137.1 (C), 129.60 (CH), 128.65 (CH), 128.0 (CH), 127.11 (CH), 126.83 (CH), 83.0 (CH), 68.0 (CH$_2$), 49.3 (CH), 41.7 (CH$_2$), 33.6 (CH$_2$), 30.6 (CH$_2$), 25.4 (CH$_2$), 21.4 (CH$_3$). FABMS *m*/*z*: 360 (M+H). FABMS *m*/*z*: 360.1632 (calcd for $C_{20}H_{26}NO_3S$: 360.1633).

*A 6:4 diastereomeric mixture of **3a***. IR (neat): 3271, 2870, 1327, 1157, 1065. ^{1}H NMR: 7.71–7.68 (m, 2H), 7.27–7.07 (m, 7H), 6.24 (d, *J*=15.9, 0.4H), 6.22 (d, *J*=15.9, 0.6H), 5.77 (dd, *J*=7.9, 15.9, 0.6H), 5.75 (dd, *J*=8.4, 16, 0.4H), 5.00 (br d, *J*=6.4, 1H), 4.02–3.94 (m, 0.8H), 3.92–3.70 (m, 3.2H), 2.28 (s, 1.8H), 2.27 (s, 1.2H), 1.95–1.79 (m, 3.6H), 1.70 (m, 0.4H). ^{13}C NMR: major 143.2 (C), 136.2 (C), 133.8 (C), 132.7 (CH), 129.4 (CH), 128.36 (CH), 127.8 (CH), 127.5 (CH), 126.4 (CH), 124.4 (CH), 80.7 (CH), 68.7 (CH$_2$), 59.44 (CH), 28.0 (CH$_2$), 25.7 (CH$_2$), 21.3 (CH$_3$); minor 143.3 (C), 136.2 (C), 133.8 (C), 132.7 (CH), 129.5 (CH), 128.42 (CH), 127.9 (CH), 127.4 (CH), 126.6 (CH), 124.4 (CH), 80.8 (CH), 68.8 (CH$_2$), 59.45 (CH), 28.0 (CH$_2$), 25.7 (CH$_2$), 21.3 (CH$_3$). MS *m*/*z*: 286 (M−C_4H_8O). Anal. Calcd for $C_{20}H_{23}O_3NS$: C, 67.20; H, 6.49; N, 3.92. Found: C, 66.91; H, 6.51; N, 3.74.

*4.3.2. N-(3-(4-Chlorophenyl)-3-(tetrahydrofuran-2-yl)propyl)-4-methylbenzenesulfonamide (**7b**) and (E)-N-(3-(4-chlorophenyl)-1-(tetrahydrofuran-2-yl)allyl)-4-methylbenzenesulfonamide (**3b**) (entry 2)*

The same procedure except for the addition of **1b** (320 mg, 1.0 mmol) as a solution in THF (9.0 mL, 1.5 mL/h) gave **7b** (216.2 mg, 55%) as white solid and **3b** (19.5 mg, 5%) as white solid.

*A 7:3 diastereomeric mixture of **7b***. Mp 98–99 °C. IR (neat): 3278, 1327, 1157, 1088. ^{1}H NMR: major 7.66 (d, *J*=7.0, 2H), 7.27 (d, *J*=7.0, 1H), 7.20 (d, *J*=8.0, 2H), 7.06 (d, *J*=8.0, 2H), 4.72 (t, *J*=6.0, 1H), 3.91 (ddd, *J*=5.5, 7.3, 7.3, 1H), 3.67 (m, 1H), 3.64 (m, 1H), 2.82 (m, 1H), 2.71 (m, 1H), 2.67 (m, 1H), 2.42 (s, 3H), 1.92–1.80 (m, 3H), 1.75 (m, 1H), 1.61 (m, 1H), 1.38 (m, 1H); minor 7.67 (d, *J*=8.0, 2H), 7.28 (d, *J*=8.0, 2H), 7.22 (d, *J*=8.3, 2H), 6.98 (d, *J*=8.3, 2H), 4.75 (t, *J*=6.0, 1H), 3.87–3.81 (m, 2H), 3.76 (ddd, *J*=6.0, 8.0, 8.0, 1H), 2.89 (m, 1H), 2.81 (m, 1H), 2.53 (ddd, *J*=5.2, 8.8, 8.9, 1H), 2.43 (s, 3H), 2.09 (m, 1H), 1.82–1.72 (m, 3H), 1.58 (m, 1H), 1.30 (m, 1H). ^{13}C NMR: major 143.4 (C), 139.4 (C), 136.8 (C), 132.5 (C), 130.0 (CH), 129.7 (CH), 128.5 (CH), 127.1 (CH), 82.0 (CH), 68.1 (CH$_2$), 46.9 (CH), 41.1 (CH$_2$), 32.5 (CH$_2$), 29.2 (CH$_2$), 25.6 (CH$_2$), 21.4 (CH$_3$); minor 143.3 (C), 140.3 (C), 136.9 (C), 132.5 (C), 129.6 (CH), 129.3 (CH), 128.8 (CH), 127.7 (CH), 82.7 (CH), 68.1 (CH$_2$), 48.3 (CH), 41.3 (CH$_2$), 33.3 (CH$_2$), 30.4 (CH$_2$), 25.4 (CH$_2$), 21.4 (CH$_3$). MS *m*/*z*: 395 (M+2), 393 (M$^+$). Anal. Calcd for $C_{20}H_{24}O_3NS$: C, 60.98; H, 6.14; N, 3.56. Found: C, 60.79; H, 6.17; N, 3.57.

*A 6:4 diastereomeric mixture of **3b***. Mp 87–90. IR (neat): 3271, 2970, 2870, 1327, 1157, 1088. ^{1}H NMR: 7.70–7.67 (m, 2H), 7.23–7.20 (m, 2H), 7.17–7.14 (m, 2H), 7.04 (d, *J*=8.6, 0.8H), 7.01 (d, *J*=8.2, 1.2H), 6.21 (d, *J*=15.9, 0.4H), 6.18 (d, *J*=15.9, 0.6H), 5.76 (dd, *J*=15.9, 8.0, 0.6H), 5.74 (dd, *J*=15.9, 8.3, 0.4H), 5.04 (br d, *J*=7.7, 0.4H), 5.02 (br d, *J*=6.8, 0.6H), 3.99–3.93 (m, 0.8H), 3.91–3.76 (m, 2.2H), 3.75–3.70 (m, 1H), 2.30 (s, 1.8H), 2.29 (s, 1.2H), 1.94–1.64 (m, 4H). ^{13}C NMR: major 143.25 (C), 138.03 (C), 134.7 (C), 133.4 (C), 131.4 (CH), 129.45 (CH), 128.5 (CH), 127.6 (CH), 127.40 (CH), 125.3 (CH), 80.6 (CH), 68.77 (CH$_2$), 59.2 (CH), 28.0 (CH$_2$), 25.7 (CH$_2$), 21.3 (CH$_3$); minor 143.26 (C), 138.02 (C), 134.7 (C), 133.4 (C), 132.5 (CH), 129.48 (CH), 128.57 (CH), 127.6 (CH), 127.36 (CH), 125.3 (CH), 80.9 (CH), 68.83

(CH$_2$), 59.5 (CH), 29.2 (CH$_2$), 27.3 (CH$_2$), 21.3 (CH$_3$). FABMS *m*/*z*: 392 (M+2−H), 390 (M−H). FABMS *m*/*z*: 390.0936 (calcd for $C_{20}H_{21}O_3ClNS$: 390.0936).

*4.3.3. N-(3-(4-Methoxyphenyl)-3-(tetrahydrofuran-2-yl)propyl)-4-methylbenzenesulfonamide (**7c**) and (E)-4-methyl-N-[1-(tetrahydrofuran-2-yl)-3-(4-methoxyphenyl)allyl]-benzenesulfonamide (**3c**) (entry 3)*

The general procedure gave a 7:3 diastereomeric mixture of **7c** (229.6 mg, 59%) as white solid and 6:4 diastereomeric mixture of **3c** (16.3 mg, 4%) as pale-yellow oil.

*A 7:3 diastereomeric mixture of **7c***. Mp 94–96 °C. IR (KBr): 3279, 1612, 1512, 1327, 1250, 1157, 1065. ^{1}H NMR: 7.67–7.64 (m, 2H), 7.28–7.26 (m, 2H), 7.05–7.03 (m, 1.4H), 6.96–6.94 (m, 0.6H), 6.81–6.78 (m, 2H), 4.74–4.73 (t, 0.3H), 4.42–4.40 (t, 0.7H), 3.93–3.89 (m, 0.7H), 3.87–3.81 (m, 0.6H), 3.77–3.75 (m, 0.3H), 3.78 (s, 3H), 3.72–3.63 (m, 1.4H), 2.94–2.74 (m, 2H), 2.65–2.61 (m, 0.7H), 2.47–2.44 (m, 0.3H), 2.42 (s, 3H), 2.11–2.04 (m, 0.3H), 1.93–1.70 (m, 3.7H), 1.68–1.60 (m, 1H), 1.48–1.39 (m, 0.7H), 1.34–1.25 (m, 0.3H). ^{13}C NMR: major 158.2 (C), 143.2 (C), 136.9 (C), 132.8 (C), 129.6 (CH), 129.47 (CH), 127.0 (CH), 113.7 (CH), 82.3 (CH), 68.0 (CH$_2$), 55.0 (CH$_3$), 46.7 (CH), 41.3 (CH$_2$), 32.3 (CH$_2$), 29.0 (CH$_2$), 25.6 (CH$_2$), 21.3 (CH$_3$); minor 158.3 (C), 143.1 (C), 137.0 (C), 133.8 (C), 129.52 (CH), 128.8 (CH), 127.0 (CH), 113.9 (CH), 83.1 (CH), 68.0 (CH$_2$), 55.0 (CH$_3$), 48.1 (CH), 41.5 (CH$_2$), 33.4 (CH$_2$), 30.4 (CH$_2$), 25.3 (CH$_2$), 21.3 (CH$_3$). MS *m*/*z*: 389 (M$^+$). Anal. Calcd for $C_{21}H_{27}O_4NS$: C, 64.75; H, 6.99; N, 3.60. Found: C, 64.68; H, 6.95; N, 3.60.

*A 6:4 diastereomeric mixture of **3c***. IR (neat): 3279, 2939, 2862, 1604, 1512, 1327, 1157, 1096. ^{1}H NMR: 7.69 (d, *J*=8.6, 1.2H), 7.68 (d, *J*=8.6, 0.8H), 7.15 (d, *J*=8.6, 1.2H), 7.14 (d, *J*=8.6, 0.8H), 7.05 (d, *J*=8.6, 0.8H), 7.02 (d, *J*=8.6, 1.2H), 6.79 (d, *J*=8.6, 0.8H), 6.77 (d, *J*=8.6, 1.2H), 6.18 (d, *J*=15.9, 0.4H), 6.17 (d, *J*=15.9, 0.6H), 5.62 (dd, *J*=7.9, 15.9, 0.6H), 5.61 (dd, *J*=8.6, 15.9, 0.4H), 5.03–5.01 (m, 1H), 4.00–3.69 (m, 4H), 3.80 (s, 1.2H), 3.79 (s, 1.8H), 2.30 (s, 1.8H), 2.29 (s, 1.2H), 1.95–1.67 (m, 4H). ^{13}C NMR: major 159.38 (C), 143.13 (C), 138.2 (C), 132.3 (CH), 129.40 (CH), 129.01 (C), 127.7 (CH), 127.47 (CH), 124.3 (CH), 113.8 (CH), 80.8 (CH), 68.7 (CH$_2$), 59.6 (CH), 55.2 (CH$_3$), 28.0 (CH$_2$), 25.7 (CH$_2$), 21.3 (CH$_3$); minor 159.44 (C), 143.10 (C), 138.2 (C), 132.3 (CH), 129.42 (CH), 129.04 (C), 127.7 (CH), 127.4 (CH), 122.2 (CH), 113.8 (CH), 31.2 (CH), 68.8 (CH$_2$), 59.7 (CH), 55.26 (CH$_2$), 27.3 (CH$_2$), 25.7 (CH$_2$), 21.3 (CH$_3$). FABMS *m*/*z*: 386 (M−H). FABMS *m*/*z*: 386.1429 (calcd for $C_{21}H_{24}O_4NS$: 386.1426).

*4.3.4. 4-Methyl-N-[3-(tetrahydrofuran-2-yl)-3-(4-tolyl)propyl]-benzenesulfonamide (**7d**) and (E)-4-methyl-N-[1-(tetrahydrofuran-2-yl)-3-(4-tolyl)allyl]benzenesulfonamide (**3d**) (entry 4)*

The general procedure gave **7d** (261.4 mg, 70%) as white solid and **3d** (18.6 mg, 5%) as colorless oil.

*A 7:3 diastereomeric mixture of **7d***. Mp 80–81 °C. IR (KBr): 3279, 2970, 2862, 1319, 1150, 1072. ^{1}H NMR: 7.67–7.64 (m, 2H), 7.29–7.26 (m, 2H), 7.06 (d, *J*=8.0, 2H), 7.01 (d, *J*=8.0, 1.4H), 6.91 (d, *J*=8.0, 0.6H), 4.75 (br t, *J*=6, 0.3H), 4.41 (br t, *J*=6, 0.7H), 3.92 (m, 0.7H), 3.88–3.82 (m, 0.6H), 3.76 (m, 0.3H), 3.73–3.63 (m, 1.4H), 2.93–2.74 (m, 2.3H), 2.63 (m, 0.7H), 2.43 (s, 0.9H), 2.42 (s, 2.1H), 2.312 (s, 0.9H), 2.306 (s, 2.1H), 2.8 (m, 0.3H), 1.93–1.71 (m, 4H), 1.65 (m, 0.7H), 1.44 (m, 0.7H), 1.31 (m, 0.3H). ^{13}C NMR: major 143.2 (C), 137.8 (C), 136.9 (C), 136.2 (C), 129.59 (CH), 129.1 (CH), 128.4 (CH), 127.07 (CH), 82.4 (CH), 68.0 (CH$_2$), 47.3 (CH), 41.4 (CH$_2$), 32.2 (CH$_2$), 29.0 (CH$_2$), 25.6 (CH$_2$), 21.4 (CH$_3$), 20.9 (CH$_3$); minor 143.2 (C), 138.8 (C), 137.1 (C), 136.3 (C), 129.55 (CH), 129.3 (CH), 127.8 (CH), 127.08 (CH), 83.0 (CH), 68.0 (CH$_2$), 48.8 (CH), 41.6 (CH$_2$), 33.5 (CH$_2$), 30.5 (CH$_2$), 25.4 (CH$_2$), 21.4 (CH$_3$), 20.9 (CH$_3$). MS *m*/*z*: 373 (M$^+$). Anal. Calcd for $C_{21}H_{27}O_3NS$: C, 67.53; H, 7.29; N, 3.75. Found: C, 67.36; H, 7.36; N, 3.73.

*A 6:4 diastereomeric mixture of **3d***. IR (neat): 3279, 2924, 1327, 1157, 1065. ^{1}H NMR: 7.70–7.67 (m, 2H), 7.17–7.14 (m, 2H), 7.07–6.97 (m, 4H), 6.20 (d, *J*=15.9, 0.4H), 6.18 (d, *J*=15.9, 0.6H), 5.74–5.67 (m, 1H), 4.99 (br d, *J*=6, 1H), 4.01–3.69 (m, 4H), 2.32 (s, 1.2H), 2.31 (s, 1.8H), 2.29 (s, 1.8H), 2.28 (s, 1.2H), 1.94–1.68 (m, 4H). ^{13}C NMR: major 143.2 (C), 138.0 (C), 137.6 (C), 133.4 (C), 132.6 (CH), 129.42 (CH), 129.0 (CH), 127.43 (CH), 126.4 (CH), 125.5 (CH), 80.7 (CH), 68.7 (CH$_2$), 59.5 (CH), 28.0 (CH$_2$), 25.7 (CH$_2$), 21.1 (CH$_3$), 14.1 (CH$_3$); minor 143.1 (C), 138.0 (C), 137.6 (C), 133.7 (CH), 133.4 (C), 129.43 (CH), 129.1 (CH), 127.39 (CH), 126.4 (CH), 123.3 (CH), 81.1 (CH), 68.8 (CH$_2$), 59.7 (CH), 27.2 (CH$_2$), 25.7 (CH$_2$), 21.3 (CH$_3$), 14.1 (CH$_3$). FABMS *m*/*z*: 370 (M−H). FABMS *m*/*z*: 370.1472 (calcd for $C_{21}H_{24}O_3NS$: 370.1482).

*4.3.5. 4-Methyl-N-[3-(tetrahydrofuran-2-yl)-3-(2-tolyl)propyl]-benzenesulfonamide (**7e**) and (E)-4-methyl-N-[1-(tetrahydrofuran-2-yl)-3-(2-tolyl)allyl]benzenesulfonamide (**3e**) (entry 5)*

The general procedure gave **7e** (224.1 mg, 60%) and **3e** (26.0 mg, 7%) as colorless oil.

*A 7:3 diastereomeric mixture of **7e***. IR (neat): 3279, 2947, 1327, 1157, 1065. ^{1}H NMR: 7.67–7.64 (m, 2H), 7.28–7.25 (m, 2H), 7.17 (d, *J*=7.3, 0.7H), 7.14–7.07 (m, 3H), 6.99 (d, *J*=7.0, 0.3H), 4.99 (br s, 0.3H), 4.67 (br t, *J*=6, 0.7H), 3.95–3.86 (m, 1.3H), 3.77 (m, 0.3H), 3.72–3.64 (m, 1.4H), 3.07 (m, 0.7H), 2.90–2.85 (m, 0.6H), 2.83–2.76 (m, 1.7H), 2.42 (s, 0.9H), 2.41 (s, 2.1H), 2.25 (s, 3H), 2.07 (m, 0.3H), 1.97–1.70 (m, 4.4H), 1.62–1.58 (m, 0.3H), 1.42 (m, 0.7H), 1.24 (m, 0.3H). ^{13}C NMR: major 143.2 (C), 139.4 (C), 136.8 (C), 136.7 (C), 130.3 (CH), 129.6 (CH), 127.0 (CH), 126.31 (CH), 126.2 (CH), 82.2 (CH), 67.9 (CH$_2$), 41.6 (CH and CH$_2$ overlapping), 31.7 (CH$_2$), 28.7 (CH$_2$), 25.8 (CH$_2$), 21.4 (CH$_3$), 20.0 (CH$_3$); minor 143.1 (C), 140.7 (C), 136.93 (C), 136.91 (C), 130.6 (CH), 129.55 (CH), 126.8 (CH), 126.4 (CH), 126.27 (CH), 82.2 (CH), 68.1 (CH$_2$), 41.8 (CH$_2$), 41.7 (CH), 30.8 (CH$_2$), 30.3 (CH$_2$), 25.4 (CH$_2$), 21.4 (CH$_3$), 20.1 (CH$_3$). MS *m*/*z*: 374 (M$^+$). FABMS *m*/*z*: 373.1707 (calcd for $C_{21}H_{27}O_3NS$: 373.1712).

*A 6:4 diastereomeric mixture of **3e***. IR (neat): 3271, 2970, 1443, 1327, 1157, 1065. ^{1}H NMR: 7.73–7.70 (m, 2H), 7.19–7.01 (m, 6H), 6.50 (d, *J*=15.9, 0.6H), 6.49 (d, *J*=15.9, 0.4H), 5.70 (dd, *J*=8.0, 15.9, 0.6H), 5.65 (dd, *J*=8.3, 15.9, 0.4H), 5.10–5.07 (m, 1H), 4.03–3.96 (m, 0.8H), 3.93–3.70 (m, 3.2H), 2.305 (s, 1.8H), 2.297 (s, 1.2H), 2.22 (s, 1.2H), 2.20 (s, 1.8H), 1.96–1.80 (m, 3.6H), 1.73 (m, 0.4H). ^{13}C NMR: major 143.2 (C), 138.0 (C), 135.29 (C), 135.25 (C), 130.5 (CH), 130.09 (CH), 129.5 (CH), 128.0 (CH), 127.65 (CH), 127.35 (CH), 125.9 (CH), 125.7 (CH), 80.8 (CH), 68.7 (CH$_2$), 59.7 (CH), 28.0 (CH$_2$), 25.7 (CH$_2$), 21.3 (CH$_3$), 19.5 (CH$_3$); minor 143.20 (C), 138.0 (C), 135.30 (C), 135.29 (C), 131.6 (CH), 130.1 (CH), 129.5 (CH), 128.0 (CH), 127.7 (CH), 127.31 (CH), 125.8 (CH), 125.7 (CH), 81.2 (CH), 68.8 (CH$_2$), 59.7 (CH), 27.1 (CH$_2$), 25.7 (CH$_2$), 21.3 (CH$_3$), 19.6 (CH$_3$). MS *m*/*z*: 371 (M$^+$). Anal. Calcd for $C_{21}H_{25}O_3NS$: C, 67.89; H, 6.78; N, 3.77. Found: C, 67.62; H, 6.82; N, 3.48.

*4.3.6. 4-Methyl-N-[3-(naphthalen-2-yl)-3-(tetrahydrofuran-2-yl)propyl]benzenesulfonamide (**7f**) and (E)-4-methyl-N-[3-(naphthalen-2-yl)-1-(tetrahydrofuran-2-yl)allyl]-benzenesulfonamide (**3f**) (entry 6)*

The same procedure except for the addition of **1f** as a THF solution (9.4 mL, 1.57 mL/h) gave **7f** (225.2 mg, 51%) and **3f** (24.4 mg, 6%) as white solid.

*A 7:3 diastereomeric mixture of **7f***. IR (neat): 3279, 2947, 1327, 1157, 1072. ^{1}H NMR: 7.81–7.76 (m, 1H), 7.75–7.72 (m, 2H), 7.63–7.59 (m, 2H), 7.56 (s, 0.7H), 7.49 (s, 0.3H), 7.47–7.40 (m, 2H), 7.31–7.28 (m, 1H), 7.19 (d, *J*=8.2, 0.6H), 7.16 (d, *J*=8.3, 1.4H), 4.98 (m, 0.3H), 4.75 (m, 0.7H), 4.05–3.97 (m, 1H), 3.85 (m, 0.3H), 3.77 (m, 0.3H), 3.72–3.63 (m, 1.4H), 2.94–2.79 (m, 2H), 2.77–2.66 (m, 1H), 2.38 (s, 0.9H), 2.35 (s, 2.1H), 2.22–2.17 (m, 0.3H), 2.01–1.97 (m, 1.4H), 1.92–1.85 (m, 1H), 1.80–1.71 (m, 1.3H), 1.65–1.52 (m, 1H), 1.47 (m, 0.7H), 1.37 (m, 0.3H). ^{13}C NMR: major 143.2 (C), 138.4 (C), 136.7 (C), 133.36 (C), 132.51 (C), 129.6 (CH), 128.1 (CH), 127.69 (CH), 127.65 (CH), 127.56 (CH), 127.0 (CH), 126.5 (CH), 125.92 (CH), 125.5 (CH), 82.3 (CH), 68.1 (CH$_2$), 47.7 (CH), 41.3 (CH$_2$), 32.3 (CH$_2$), 29.2 (CH$_2$), 25.6 (CH$_2$), 21.4 (CH$_3$); minor 143.1 (C), 139.3 (C), 136.7 (C), 133.42 (C), 132.46 (C), 129.6 (CH), 128.4

(CH), 127.63 (CH), 127.1 (CH), 126.9 (CH), 126.1 (CH), 125.87 (CH), 125.6 (CH), 82.9 (CH), 68.1 (CH_2), 49.2 (CH), 41.6 (CH_2), 33.4 (CH_2), 30.6 (CH_2), 25.4 (CH_2), 21.4 (CH_3). MS *m*/*z*: 409 (M^+). FABMS *m*/*z*: 409.1718 (calcd for $C_{24}H_{27}O_3NS$: 409.1712).

*A 6:4 diastereomeric mixture of **3f**.* IR (neat): 3279, 3055, 1327, 1157, 1065. ^{1}H NMR: 7.80–7.68 (m, 3H), 7.49–7.43 (m, 3H), 7.29–7.24 (m, 2H), 7.18–7.11 (m, 3H), 6.41–6.36 (m, 1H), 5.91–5.83 (m, 1H), 5.04 (d, *J*=6.1, 1H), 4.06–4.00 (m, 1H), 3.96–3.91 (m, 1H), 3.88–3.72 (m, 2H), 2.21 (s, 1.5H), 2.19 (s, 1.5H), 1.97–1.81 (m, 3H), 1.77–1.70 (m, 1H); ^{13}C NMR: major 143.23 (C), 138.0 (C), 133.6 (C), 133.4 (C), 133.05 (C), 132.8 (CH), 129.47 (CH), 127.95 (CH), 127.7 (CH), 127.4 (CH), 127.0 (CH), 126.50 (CH), 126.3 (CH), 126.1 (CH), 124.8 (CH), 123.50 (CH), 80.8 (CH), 68.9 (CH_2), 59.5 (CH), 28.0 (CH_2), 25.7 (CH_2), 21.26 (CH_3); minor 143.26 (C), 138.1 (C), 133.9 (CH), 133.6 (C), 133.4 (C), 133.04 (C), 129.46 (CH), 128.00 (CH), 127.7 (CH), 127.5 (CH), 127.0 (CH), 126.51 (CH), 126.4 (CH), 126.0 (CH), 124.8 (CH), 123.47 (CH), 81.1 (CH), 68.8 (CH_2), 59.7 (CH), 27.3 (CH_2), 25.7 (CH_2), 21.24 (CH_3). FABMS *m*/*z*: 406 (M+H). FABMS *m*/*z*: 406.1483 (calcd for $C_{24}H_{24}O_3NS$: 406.1482).

*4.3.7. 4-Methyl-N-[3-phenyl-3-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)propyl]benzenesulfonamide (**8**) and (E)-4-methyl-N-[3-phenyl-1-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)allyl]benzenesulfonamide (**9**) (Scheme 2)*

The general procedure except for the use of 4,4,5,5-tetramethyl-1,3-dioxolane (36.5 mL, 0.25 mol) and **1a** (1.0 mmol, 0.45 mL/h) in 4.5 mL of benzene gave **8** (62.6 mg, 15%) as a white solid and **9** (8.3 mg, 2%) as a white solid by column chromatography (toluene/Et_2O=19:1).

Compound **8**: mp 107–110 °C. IR (KBr): 3279, 2978, 1435, 1327, 1157. ^{1}H NMR: 7.66 (d, *J*=8.3, 2H), 7.27–7.19 (m, 5H), 7.09 (d, *J*=7.4, 2H), 5.03 (d, *J*=5.5, 1H), 4.48 (br s, 1H), 2.94–2.81 (m, 2H), 2.68 (ddd, *J*=4.9, 5.5, 9.8, 1H), 2.42 (s, 3H), 2.02 (m, 1H), 1.81 (m, 1H), 1.15 (s, 3H), 1.11 (s, 3H), 1.08 (s, 3H), 1.06 (s, 3H); ^{13}C NMR: 143.2 (C), 139.7 (C), 137.0 (C), 129.6 (CH), 128.8 (CH), 128.4 (CH), 127.1 (CH), 126.9 (CH), 102.6 (CH), 82.1 (C), 81.8 (C), 48.8 (CH), 41.5 (CH_2), 30.6 (CH_2), 24.06 (CH_3), 24.02 (CH_3), 22.2 (CH_3), 22.0 (CH_3), 21.4 (CH_3). FABMS *m*/*z*: 416 (M−H). FABMS *m*/*z*: 416.1889 (calcd for $C_{23}H_{30}O_4NS$: 416.1901).

Compound **9**: mp 120–122 °C. IR (KBr): 3302, 2978, 1412, 1327, 1157. ^{1}H NMR: 7.73 (d, *J*=8.3, 2H), 7.27–7.16 (m, 7H), 6.36 (d, *J*=15.9, 1H), 5.86 (dd, *J*=7.4, 15.9, 1H), 4.99 (d, *J*=3.4, 1H), 4.84 (d, *J*=7.6, 1H), 4.03 (m, 1H), 2.32 (s, 3H), 1.17 (s, 3H), 1.16 (s, 3H), 1.11 (s, 6H). ^{13}C NMR: 143.2 (C), 138.1 (C), 136.3 (C), 133.6 (CH), 129.4 (CH), 128.4 (CH), 127.8 (CH), 127.5 (CH), 126.5 (CH), 124.3 (CH), 100.2 (CH), 82.9 (C), 82.6 (C), 58.7 (CH), 24.2 (CH_3), 24.1 (CH_3), 22.2 (CH_3), 22.1 (CH_3), 21.3 (CH_3). MS *m*/*z*: 415 (M^+). Anal. Calcd for $C_{23}H_{29}O_4NS$: C, 66.48; H, 7.03; N, 3.37. Found: C, 66.42; H, 7.21; N, 3.09.

*4.3.8. 4-Methyl-N-(3-phenylpentyl)benzenesulfonamide (**10**) (Scheme 4)*

The same procedure except for the use of diethylzinc instead of dimethylzinc gave **7a** (235 mg, 65%), **3a** (13.9 mg, 3%), and **10** (36.9 mg, 12%) as pale-yellow oil. Compound **10**: IR (neat): 3279, 2924, 1327, 1157. ^{1}H NMR: 7.65–7.64 (d, *J*=8.2, 2H), 7.27–7.17 (m, 5H), 7.04–7.03 (m, 2H), 4.22 (br s, 1H), 2.84–2.74 (m, 2H), 2.44–2.31 (m, 1H), 2.42 (s, 3H), 1.87–1.81 (m, 1H), 1.72–1.64 (m, 1H), 1.63 (m, 2H), 0.73–0.70 (t, *J*=7.3, 3H). ^{13}C NMR: 144.0 (C×2), 143.3 (C), 129.6 (CH), 128.6 (CH), 127.6 (CH), 127.1 (CH), 126.4 (CH), 45.0 (CH), 41.5 (CH_2), 36.1 (CH_2), 29.6 (CH_2), 21.4 (CH_3), 11.9 (CH_3). FABMS *m*/*z*: 318 (M+H). FABMS *m*/*z*: 318.1533 (calcd for $C_{18}H_{24}O_2NS$: 318.1528).

*4.3.9. (RS,SR)-5-(3-Chloropropyl)-4-phenyldihydrofuran-2(3H)-one (**12**) (Scheme 5)*

To a solution of oxalyl chloride (0.04 mL, 0.4 mmol) in CH_2Cl_2 (1 mL) in a 10 mL round-bottom flask cooled in a dry ice–ethanol bath was added DMSO (0.06 mL, 0.9 mmol) and the mixture was stirred for 2 min at the same temperature. To the mixture was added a solution of (*RS*,*SR*)-alcohol **2a** (44.5 mg, 0.216 mmol) in CH_2Cl_2 (0.2 mL+0.1 mL washing twice) at the same temperature, and the whole was stirred for 15 min at the same temperature before the addition of Et_3N (0.15 mL, 1.1 mmol) at the same temperature. After stirring for 5 min, the cooling bath was removed to allow the reaction mixture warm up to room temperature. After 4.5 h, water was added to the mixture and the whole was extracted with $CHCl_3$ three times. The combined organic layers were washed with water and brine, dried over Na_2SO_4, and concentrated to give pale-yellow oil (49.5 mg) including mainly (*RS*,*SR*)-3-phenyl-3-tetrahydrofuran-2-yl-propanal. ^{1}H NMR: 1.53 (m, 1H), 1.66 (m, 1H), 1.72–1.83 (m, 2H), 2.82 (ddd, *J*=1.7, 7.5, 16.6, 1H), 2.89 (ddd, *J*=2.3, 6.9, 16.6, 1H), 3.48 (ddd, *J*=4.6, 7.5, 7.5, 1H), 3.68–3.71 (m, 2H), 4.11 (m, 1H), 7.21–7.26 (m, 3H), 7.29–7.31 (m, 2H), 9.67 (dd, *J*=1.7, 2.3, 1H). ^{13}C NMR: 25.8 (CH_2), 28.2 (CH_2), 43.8 (CH), 45.6 (CH_2), 68.1 (CH_2), 81.9 (CH), 126.9 (CH), 128.4 (CH), 128.5 (CH), 140.3 (C), 201.2 (CH). IR (neat): 2970, 2870, 2723, 1960, 1720, 1489, 1450, 1381, 1180, 1057, 934, 764, 702, 532. EIMS *m*/*z*: 204 (M^+), 160 ($M-CH_2CHOH$), 71 (C_4H_7O). The crude aldehyde (49.5 mg) was placed in a 10 mL round-bottom flask cooled in an ice–water bath, to which was added a 2 M solution of 2-methylbut-2-ene in THF (2.2 mL, 4.4 mmol), and then a mixture of NaH_2PO_4 and $NaClO_2$ in water (2.7 M each, 0.80 mL, 2.2 mmol each). The cooling bath was removed and the mixture was stirred for 1 h before addition of 5% HCl. The whole was extracted with $CHCl_3$ five times. The combined organic layers were extracted with 10% NaOH five times and the combined aqueous layers were washed with $CHCl_3$. The basic extract was acidified by addition of concd HCl and extracted with $CHCl_3$ five times. The combined organic layers were dried over $MgSO_4$ and concentrated to give colorless oil (44.9 mg) including mainly (*RS*,*SR*)-3-phenyl-3-tetrahydrofuran-2-yl-propanoic acid. ^{1}H NMR: 1.43–1.62 (m, 2H), 1.70–1.88 (m, 2H), 2.76 (dd, *J*=8.5, 16.0, 1H), 2.89 (dd, *J*=6.4, 16.0, 1H), 3.79 (m, 1H), 3.70 (t, *J*=6.7, 2H), 4.11 (m, 1H), 7.19–7.29 (m, 5H), 10.4 (br s, 1H). ^{13}C NMR: 25.7 (CH_2), 28.6 (CH_2), 36.9 (CH_2), 45.6 (CH), 68.3 (CH_2), 81.6 (CH), 126.9 (CH), 128.3 (CH), 128.7 (CH), 140.3 (C), 178.1 (CH). IR (neat): 3032, 2978, 2878, 2684, 1713, 1450, 1412, 1265, 1165, 1072, 918, 733, 710, 617. EIMS *m*/*z*: 220 (M^+), 203 (M−OH), 160 ($M-CH_2C(OH)_2$), 71 (C_4H_7O). The crude carboxylic acid (44.9 mg) was stirred with oxalyl chloride (0.17 mL, 2.0 mmol) for 30 min and the mixture was concentrated under reduced pressure to give pale-yellow oil (46.7 mg) including mainly (*RS*,*SR*)-3-phenyl-3-tetrahydrofuran-2-yl-propanoyl chloride. ^{1}H NMR: 1.48 (m, 1H), 1.56 (m, 1H), 1.75 (m, 1H), 1.84 (m, 1H), 3.34 (dd, *J*=6.6, 13.9, 1H), 3.40 (m, 1H), 3.44 (dd, *J*=5.2, 13.9, 1H), 3.68–3.75 (m, 2H), 4.12 (ddd, *J*=4.0, 6.9, 7.4, 1H), 7.24–7.28 (m, 3H), 7.3 (m, 2H). EIMS *m*/*z*: 240 (M+2), 238 (M^+), 203 (M−Cl), 71 (C_4H_7O). The crude chloride (46.7 mg) was dissolved in benzene (2 mL) and cooled in an ice–water bath. To the solution was added $AlCl_3$ (41 mg, 0.31 mmol) and the cooling bath was removed to allow the reaction mixture warm up to room temperature. The mixture was stirred for 3 h at the same temperature and then 10% HCl was added. The whole was extracted with $CHCl_3$ five times, and the combined organic layers were dried over $MgSO_4$ and concentrated to give pale-purple oil (43.1 mg). Purification of the crude material by column chromatography (hexane/EtOAc=4:1) gave the titled chloro lactone **12** (19.3 mg, 40% over four steps) as colorless oil. ^{1}H NMR: 1.30–1.43 (m, 2H), 1.76 (m, 1H), 1.94 (m, 1H), 2.79 (dd, *J*=4.9, 17.5, 1H), 2.89 (dd, *J*=8.6, 17.5, 1H), 3.42 (ddd, *J*=5.8, 7.3, 11.0, 1H), 3.49 (ddd, *J*=5.8, 6.9, 11.0, 1H), 3.76 (ddd, *J*=4.9, 6.4, 8.6, 1H), 4.74 (ddd, *J*=3.8, 6.4, 10.0, 1H), 7.15 (d, *J*=7.1, 2H), 7.29–7.38 (m, 3H). ^{13}C NMR: 28.6 (CH_2), 29.0 (CH_2), 35.6 (CH_2), 44.2 (CH_2), 44.4 (CH), 83.2 (CH), 127.75 (CH), 127.82 (CH), 129.0 (CH), 137.7 (C), 176.5 (CH). IR (neat): 2955, 1774, 1450, 1412, 1180, 756, 702. EIMS *m*/*z*: 240

(M+2), 238 (M$^+$), 149, 104. FABMS *m*/*z*: 239.0831 (calcd for C$_{13}$H$_{16}$ClO$_2$: 239.0839).

*4.3.10. (RS,SR)-4-Phenyl-5-propyldihydrofuran-2(3H)-one (**13**) (Scheme 5)*

Chloro lactone **12** (17.8 mg, 74.6 μmol) was placed in a 10 mL round-bottom flask and dissolved in dry acetone (0.4 mL). To the solution was added NaI (56 mg, 0.37 mmol) and the mixture was stirred for 36 h at 50 °C. To the mixture cooled to room temperature was added 10% Na$_2$S$_2$O$_3$. The mixture was extracted with CHCl$_3$ three times, and the combined organic layers were dried over Na$_2$SO$_4$ and concentrated to give pale-yellow oil (17.6 mg). Purification of the crude material by column chromatography (hexane/EtOAc=4:1) gave pale-yellow oil (17.1 mg) including chloro lactone **12** and iodo lactone in a ratio of 3:7 (23% and 53%, respectively). ^{1}H NMR (iodo lactone): 1.30–1.36 (m, 2H), 1.81 (m, 1H), 1.96 (m, 1H), 2.79 (dd, *J*=5.1, 17.6, 1H), 2.99 (dd, *J*=8.7, 17.6, 1H), 3.06 (ddd, *J*=6.9, 6.9, 9.8, 1H), 3.49 (ddd, *J*=6.9, 6.9, 9.8, 1H), 3.76 (m, 1H), 4.73 (ddd, *J*=6.4, 6.4, 7.7, 1H), 7.14 (d, *J*=8.0, 2H), 7.31 (m, 1H), 7.37 (m, 2H). ^{13}C NMR (iodo lactone): 5.5 (CH$_2$), 29.7 (CH$_2$), 32.1 (CH$_2$), 35.5 (CH$_2$), 44.4 (CH), 82.8 (CH), 127.75 (CH), 127.83 (CH), 129.0 (CH), 137.7 (C), 176.5 (CH). The mixture was dissolved in benzene (0.1 mL). To the solution at room temperature were added Bu$_3$SnH (0.10 mL, 0.38 mmol) and then a 1.0 M solution of Et$_3$B in hexane (0.01 mL, 0.01 mmol). The mixture was stirred for 1 h at the same temperature and concentrated. The resulting residue was dissolved in EtOAc (2 mL), and KF (0.1 g) and satd. KF (0.2 mL) were added. The whole was vigorously stirred for 2.5 h and filtered through Celite pad. The filtrate was concentrated and purified by column chromatography (hexane/EtOAc=4:1) to give the titled lactone **13** (7.4 mg, 49% over two steps) as pale-yellow oil along with the recovered **12** (3.7 mg, 21%) as pale-yellow oil. The spectroscopic data of **13** were in good agreement with those reported.[21] ^{1}H NMR: 0.82 (t, *J*=7.2, 3H), 1.11 (m, 1H), 1.24–1.32 (m, 2H), 1.46 (m, 1H), 2.78 (dd, *J*=4.9, 11.2, 1H), 2.96 (dd, *J*=8.6, 11.2, 1H), 3.73 (ddd, *J*=4.9, 6.3, 8.6, 1H), 4.72 (ddd, *J*=4.1, 6.3, 9.5, 1H), 7.15 (d, *J*=7.0, 2H), 7.30 (t, *J*=7.0, 1H), 7.35 (dd, *J*=7.0, 7.0, 2H). ^{13}C NMR: 13.6 (CH$_3$), 19.1 (CH$_2$), 33.2 (CH$_2$), 35.7 (CH$_2$), 44.6 (CH), 84.0 (CH), 127.6 (CH), 127.8 (CH), 128.8 (CH), 138.1 (C), 176.9 (C). IR (neat): 3963, 1774, 1180, 957, 748, 702. EIMS *m*/*z*: 205 (M+1), 204 (M$^+$).

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