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Reactions of Carbanions of 1-Chloro-5-(phenylsulfonyl)pent-2-enes: Synthesis of Vinyl-Substituted Tetrahydrofurans

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Dedicated to Professor Binne Zwanenburg on the occasion of his 75th birthday

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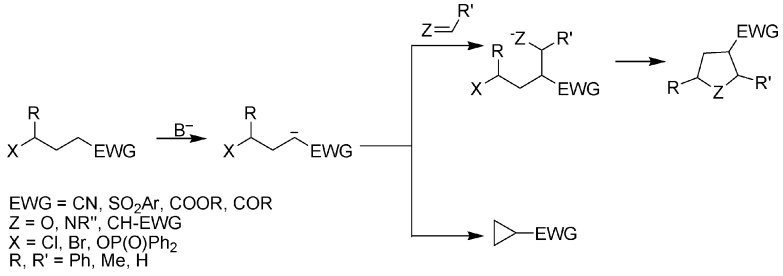
The carbanions of (*E*)- and (*Z*)-1-chloro-5-(phenylsulfonyl)-pent-2-enes can be considered as vinylogues of γ-chlorocarbanions. Because in these cases intramolecular 1,3-substitution by a S_N2' mechanism leading to vinylcyclopropanes is a relatively slow process these carbanions can be efficiently trapped by active electrophilic reagents such as aldehydes. Subsequent intramolecular S_N2' 1,5-substitution of the aldol anions produced gives vinyl-substituted tetrahydrofurans. Thus, an efficient method for the synthesis of 2,3-disubstituted-5-vinyltetrahydrofurans has been elaborated.

Introduction

γ-Halocarbanions are short-lived species that undergo rapid intramolecular substitution to produce cyclopropanes.[1] Because of the high rate of this reaction, which is often named a γ-elimination reaction, intermolecular reactions of γ-halocarbanions with electrophilic partners were not considered a valuable synthetic tool. In our previous publications we have shown that γ-halocarbanions, even though they undergo very fast intramolecular replacement of the halogen atom to form substituted cyclopropanes, can be efficiently trapped by active electrophilic partners like aldehydes, Michael acceptors, and electrophilic imines to form substituted tetrahydrofurans,[2,3] cyclopentanes,[3,4] and pyrrolidines,[3,5] respectively (Scheme 1).

The main problem in these reactions is the competition between two processes: Intramolecular 1,3-substitution in γ-halocarbanions, which gives cyclopropanes, and intermolecular addition to an electrophilic partner followed by intramolecular 1,5-substitution, which gives five-membered ring compounds. Thus, manipulation of the relative rates of these processes is of key importance. In our studies we have tried to shift this competition in favor of intermolecular addition and hence expand the scope of the synthesis of five-membered-ring compounds by reactions of γ-halocarbanions. To achieve this goal two approaches can be used: Changing the leaving group to a less active one and introducing an additional substituent into the γ position. Although it is known that trialkylammonium substituents can act as moderately active leaving groups in S_N2-type substitution reactions, treatment of phenyl 3-(trimethylammonio)-propyl sulfone, alone or in the presence of benzaldehyde, with a strong base did not result in the formation of cyclo-



Scheme 1. Intra- and intermolecular reactions of γ-halocarbanions.

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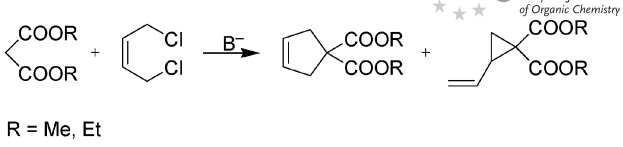
propane nor a tetrahydrofuran ring.[2] Although the carbanion generated added to aldehydes, the aldol-type anions produced did not undergo 1,5-substitution. They were sufficiently stable to be *O*-methylated and subsequent Hofmann elimination gave substituted butadienes.[6] On the other hand, an analogue of γ-halocarbanions that contains a phosphanyloxy group instead of chlorine when treated with base underwent slow cyclization; thus it was shown to be a valuable intermediate in the synthesis of tetrahydrofurans.[7] Also, the introduction of methyl, phenyl, and other similar groups into the 3-position of 3-chloropropyl phenyl sulfone substantially decelerates the intramolecular 1,3-substitution in the corresponding carbanions, which favors their intermolecular reactions with aldehydes to produce 2,3,5-trisubstituted tetrahydrofurans.[8]

It seems that another possible way of changing the relative rates of the inter- and intramolecular reactions of γ-halocarbanions is to separate the β and γ carbon atoms in the carbon chain of γ-halocarbanions by a C=C double bond. In this case the chlorine atom will then be in an allylic position and intramolecular reaction of such vinylogues of γ-halocarbanions could proceed by S_N2' 1,3-substitution to give vinyl cyclopropanes or by S_N2 1,5-substitution to give cyclopentenes. The latter reaction is possible when the double bond has a *Z* geometry.[9] It is known that in analogous systems the S_N2' reactions are slower than those proceeding by S_N2 substitution.[10] Hence, we expected that the life-time of a vinylogue of a γ-halocarbanion would be much longer and, as a consequence, the competition between intramolecular substitution and intermolecular addition should be shifted in favor of the intermolecular addition. The relative rates of the reactions proceeding by S_N2' and S_N2 mechanisms have been thoroughly studied.[9]

Bonete and Najera[11] examined the reaction of lithiated 3-tosylpropanal dimethyl ketal with (*Z*)- and (*E*)-1,4-dichlorobut-2-ene (Scheme 2). They found that the reaction with the *Z* isomer gave the corresponding cyclopentene by intramolecular S_N2 substitution, whereas with the *E* isomer intramolecular S_N2' 1,3-substitution took place to give the more stable *trans*-substituted vinylcyclopropane stereoselectively. Depres and Greene[12] found that in the cycloalkylation reaction of diethyl or dimethyl malonate with (*Z*)-1,4-dichlorobut-2-ene, the vinylcyclopropane as well as the cyclopentene were produced (Scheme 3).



Scheme 3. Reactions of (*Z*)-1,4-dichlorobut-2-ene with dialkyl malonate.

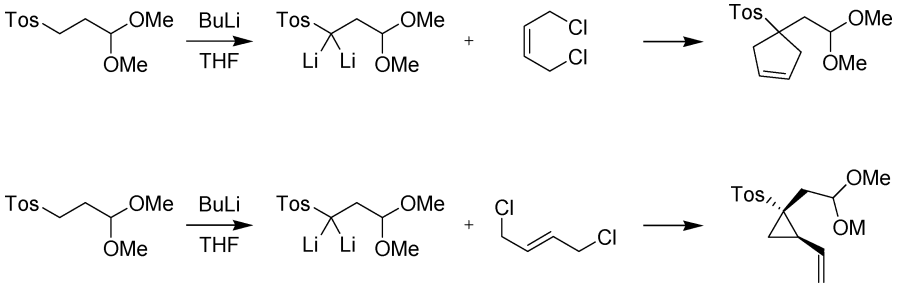
The ratio of vinylcyclopropane to cyclopentene, in general, increases with increasing hardness of the cation, on going from protic to aprotic solvents, and slightly, on changing from diethyl to dimethyl malonate.

A number of cases have been reported in the literature of the intramolecular S_N2'-type reaction of carbanions of amides,[13] esters,[14] ketones,[15] or sulfones.[16] These reactions involve the *trans* isomers of allylic chlorides and give relatively good yields of the expected products.

The stereochemistry of the S_N2' reaction has been investigated by many researchers. The earliest suggestion of a stereoelectronic preference was by Winstein and coworkers[17] who postulated that nucleophilic attack occurs on the face of the allylic system *syn* to the leaving group. The essence of the argument seems to be that this approach displaces the π electrons in such a direction as to allow them to attack the C_α–X bond from the rear. Clearly, *syn* attack would be required in those cases in which a cyclic transition state is implicated. Subsequent theoretical studies have, for the most part, supported the *syn* attack notion.[18–21]

Results and Discussion

As model compounds for the generation of vinylogues of the γ-halocarbanions we have chosen (*E*)-1-chloro-5-(phenylsulfonyl)pent-2-ene (**1**) and (*Z*)-1-chloro-5-(phenylsulfonyl)pent-2-ene (**2**). The *E* isomer was obtained in a moderate yield of 35% in the reaction of (*E*)-1,4-dichlorobut-2-ene with the carbanion of methyl phenyl sulfone in THF generated by using butyllithium as base. Because the yield of **1** was low, we tried an alternative pathway: The alkylation of ethyl 2-(phenylsulfonyl)acetate with (*E*)-1,4-dichlorobut-2-ene followed by hydrolysis and decarboxylation. In the alkylation reaction the yield was even worse (23%) despite a long reaction time. There were also some problems in the hydrolysis and decarboxylation of the product ob-



Scheme 2. Reactions of tosyl-stabilized carbanions with (*Z*)- and (*E*)-1,4-dichlorobut-2-ene.

tained. Neither heating at reflux with NaCl in a mixture of water and DMSO nor reaction with KOH in ethanol at room temperature gave the desired product. Finally, (*E*)-1-chloro-5-(phenylsulfonyl)pent-2-ene (**1**) was obtained in the reaction of (*E*)-1,4-dichlorobut-2-ene with the carbanion of methyl phenyl sulfone in a mixture of THF and DMF generated with butyllithium and CuI as the base in 90% yield (Scheme 4).

When methyl phenyl sulfone was directly alkylated with (*Z*)-1,4-dichlorobut-2-ene, the majority of the starting material was recovered and only about 1% of the desired product was obtained. On the other hand, the addition of CuI gave the *E* isomer **1** in 94% yield. However, reaction of the lithium carbanion of methyl phenyl sulfoxide, generated by reaction with LDA, with (*Z*)-1,4-dichlorobut-2-ene gave the expected substituted sulfoxide, which was subsequently oxidized to give the desired sulfone **2** in an overall yield of 38% after two steps (Scheme 4).

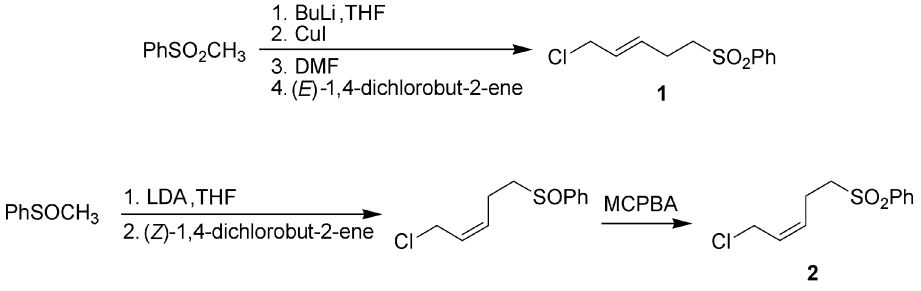
Preliminary experiments have shown that (*E*)-1-chloro-5-(phenylsulfonyl)pent-2-ene (**1**) treated with *t*BuOK in DMF at –40 °C gives vinylcyclopropane **3** in 30% yield. On the other hand, the reaction of (*Z*)-1-chloro-5-(phenylsulfonyl)-pent-2-ene (**2**) under the same conditions gave a mixture of vinylcyclopropane **3** (25%) and cyclopentene **5** (4%). In both cases the main process was the elimination of HCl, which gives the diene **4** (Scheme 5). This diene is rather unstable and polymerizes during the reaction. Nevertheless, when the reaction was arrested after a few minutes at –40 °C, we could isolate the diene **4** in moderate yield (47%).

In contrast to the rather discouraging results of the intramolecular reactions of the carbanions of **1** and **2**, they could be efficiently trapped with active external electrophiles. Thus, the treatment of concentrated THF solutions of sulfone **1** (1 equiv.) and aldehydes (1.5 equiv.) with *t*BuOK at –78 °C resulted in relatively fast reactions that gave 2,3,5-trisubstituted derivatives of tetrahydrofuran (Scheme 6). The competing formation of cyclopropane was not observed. The results are presented in Table 1.

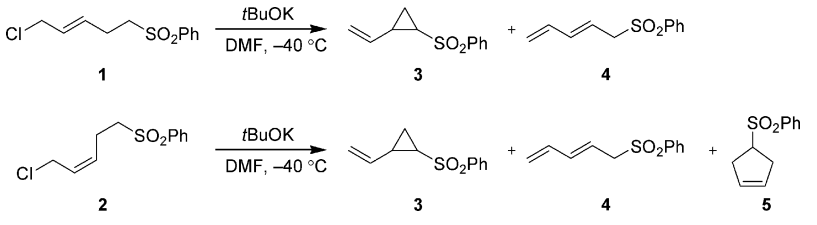
Table 1. Synthesis of vinyltetrahydrofurans by the reaction of the carbanion of **1** with aldehydes.

Entry	R	Product	% Yield	*trans*/*cis* diastereoisomeric ratio
1	Ph	**6a**	82	85:15
2	*p*-MeC_6H_4	**6b**	80	86:14
3	*p*-ClC_6H_4	**6c**	76	84:16
4	*p*-$MeOC_6H_4$	**6d**	85	82:18
5	PhCH=CH	**6e**	85	63:35
6	2-thienyl	**6f**	79	75:25
7	3-pyridyl	**6g**	90	82:18
8	2-furyl	**6h**	50	63:37
9	$(CH_3)_3C$	**6i**	49	72:28

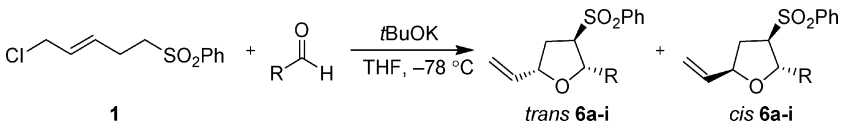
In the reactions of (*E*)-1-chloro-5-(phenylsulfonyl)pent-2-ene with aromatic aldehydes as well as with heterocyclic aldehydes and cinnamaldehyde, yields of the substituted tetrahydrofurans exceeded 75%. The reaction with pivalaldehyde gave a lower yield of the tetrahydrofuran, but is still



Scheme 4. Synthesis of sulfones **1** and **2**.



Scheme 5. Reaction of sulfones **1** and **2** with base.



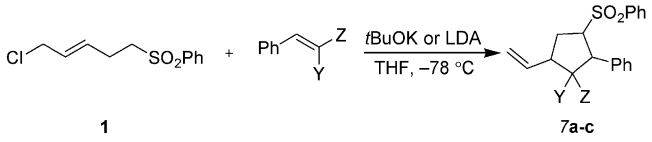
Scheme 6. Reaction of the carbanion of **1** with aldehydes.

of preparative value. Pivalaldehyde is a weaker electrophile and its addition to the carbanion is not sufficiently fast to preclude some side-reactions such as elimination and the formation of unidentified byproducts.

Note that treatment of **1** with *t*BuOK resulted in two reactions, intramolecular S_N2' substitution leading to vinylcyclopropane and, preferentially, elimination of HCl giving 5-(phenylsulfonyl)penta-1,3-diene, whereas in the presence of aldehydes vinyltetrahydrofurans were formed in high yields. We can therefore assume that the initial process common to both these former reactions is deprotonation to give the carbanion of **1**, which reacts in two ways: S_N2' substitution and a form of E1cb elimination. Both of these processes are relatively slow. When an aldehyde is present in the reaction mixture the intermolecular aldol-type addition, leading to the aldol adduct, and the subsequent intramolecular 1,5-substitution, giving vinyltetrahydrofuran, proceeds much faster than either of these intramolecular processes.

In our previous studies we found that the substituents at the 2- and 3-positions in 2-aryl-3-(phenylsulfonyl)tetrahydrofurans produced by the reaction of γ-halocarbanions with aldehydes are always *trans* relative to each other.[2,3] Also in this case, the phenylsulfonyl group and the R group coming from the aldehyde are always *trans* to each other. The vinyl group can be situated *cis* or *trans* to the phenylsulfonyl group and accordingly we observed the formation of two diastereoisomeric products. In all cases the major product was the diastereoisomer in which the vinyl group is located *trans* to the phenylsulfonyl group.

Because of the relatively long life-time of the carbanion generated from (*E*)-1-chloro-5-(phenylsulfonyl)pent-2-ene, it was possible to deprotonate the starting sulfone and then add the electrophilic partner to the reaction mixture. This procedure was useful for the reaction of **1** with Michael acceptors (Scheme 7, Table 2).



1 **7a-c**

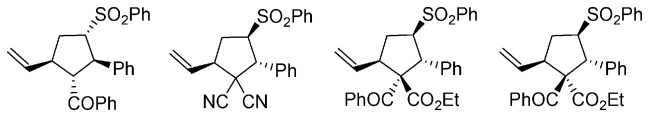
Scheme 7. Reaction of the carbanion of **1** with Michael acceptors.

Table 2. Synthesis of vinylcyclopentanes by the reaction of the carbanion of **1** with Michael acceptors.

Entry	Z, Y	Product	% Yield
1	Z = COPh, Y = H	**7a**	68
2	Z = Y = CN	**7b**	48
3	Z = COPh, Y = CO_2Et	**7c**	70

Reactions with Michael acceptors are much more stereoselective than those with aldehydes; in the cases of **7a** and **7b** only one diastereoisomer was formed and two in the case of **7c** when two different orientations of Y and Z substituents are possible. The stereochemistries of compounds **7a**–**c** are shown in Scheme 8. The yields of the cyclopentane derivatives are lower than those obtained in the analogous reactions with aldehydes. The Michael acceptors are less active electrophiles than aldehydes, which is the reason why their addition reactions are much slower. Hence, some side-reactions may occur to give undefined byproducts.

The reactions of (*Z*)-1-chloro-5-(phenylsulfonyl)pent-2-ene (**2**) with aldehydes were also studied under conditions analogous to the reactions of **1** with aldehydes (Scheme 9). The results are presented in Table 3.



7a **7b** **7c *trans*** **7c *cis***

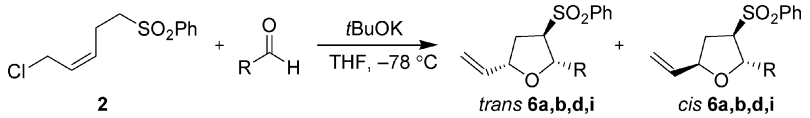
Scheme 9. Reaction of carbanion of **2** with aldehydes.

Table 3. Synthesis of vinyltetrahydrofurans by the reaction of the carbanion of **2** with aldehydes.

Entry	R	Product	% Yield	*trans*/*cis* diastereoisomeric ratio
1	Ph	**6a**	90	85:15
2	*p*-MeC_6H_4	**6b**	75	90:10
3	*p*-$MeOC_6H_4$	**6d**	86	94:6
4	$(CH_3)_3C$	**6i**	82	95:5

In the reactions of (*Z*)-1-chloro-5-(phenylsulfonyl)pent-2-ene (**2**) with aldehydes two diastereoisomeric tetrahydrofurans were also produced. Here the major product was also the diastereoisomer in which the vinyl group is located *trans* to the phenylsulfonyl group. Thus, the geometry of the C=C double bond does not affect the stereochemical outcome of the reaction. In most cases the diastereoselectivity was somewhat better that obtained with the *E* isomer **1**.

In the reaction of **2** with aromatic aldehydes, the yields of the substituted tetrahydrofurans were similar to those obtained with the *E* isomer. However, the high yield produced in the reaction with pivalaldehyde was somewhat surprising; a yield of 82% was obtained in the reaction of the *Z* isomer and only 49% in the reaction of the *E* isomer, but the intramolecular S_N2' 1,5-substitution was probably faster than side-reactions that could lead to byproducts and a lower yield.



2 *trans* **6a,b,d,i** *cis* **6a,b,d,i**

Scheme 8. Stereochemistries of compounds **7a**–**c**.

Conclusions

Carbanions of the (*E*)- (**1**) and (*Z*)-1-chloro-5-(phenylsulfonyl)pent-2-enes (**2**) react intramolecularly by two pathways: intramolecular S_N2' substitution to give vinylcyclopropane and elimination of the chloride anion in a kind of homo-E1cb process to give substituted butadienes, the latter process being somewhat faster. When these carbanions are generated in the presence of active electrophilic aldehydes, the addition of the carbanions followed by intramolecular S_N2' substitution of the resulting aldol anion is the fastest process, which produces vinyl-substituted tetrahydrofurans in good yields. The intramolecular reactions (1,3- and 1,5-substitutions, and the elimination of Cl^-) of the carbanions **1** and **2** are relatively slow processes. Thus, the carbanions can be generated in advance before addition of base-sensitive electrophiles such as Michael acceptors and hence substituted vinylcyclopentanes can be produced in these reactions.

Experimental Section

General: Reactions requiring anhydrous conditions were conducted in flame-dried apparatus under a static atmosphere of argon. Organic extracts were evaporated at 5–20 Torr by using a rotary evaporator. Samples were freed of remaining traces of solvents under high vacuum (0.1 Torr). Tetrahydrofuran was distilled from potassium/benzophenone. All reactions were magnetically stirred and monitored by thin-layer chromatography using Macherey–Nagel Alugram SiO_2 G/UV254 precoated aluminium foil sheets (layer thickness 0.25 mm). Compounds were visualized by UV irradiation (254 nm). Column chromatography was performed on Fisher Scientific Matrex silica 60 (35–70 micron). Melting points were measured with a Griffin electrothermal apparatus and are uncorrected. IR spectra were recorded with a Perkin–Elmer Spectrum One FT-IR spectrometer as thin films supported on sodium chloride plates or in a diffuse reflectance sampling cell. Absorptions are reported in cm^{-1}. ^1H and ^{13}C NMR spectra were recorded with Bruker DPX300 or DRX500 Fourier Transform spectrometers using an internal deuterium lock. All spectra were obtained in $CDCl_3$ solution in 5 mm diameter tubes and the chemical shift in ppm is quoted relative to the residual signals of chloroform (δ_H = 7.26 ppm, δ_C = 77.0 ppm) as the internal standard unless otherwise specified. Multiplicities in the ^1H NMR spectra are described as: s = singlet, d = doublet, t = triplet, q = quartet, quint. = quintet, m = multiplet. Coupling constants (*J*) are reported in Hz. Electron spray ionization (ES) mass spectrometry was performed with either a Micromass LCT TOF spectrometer or a Waters-Micromass ZMD spectrometer. High-resolution mass spectra (HRMS) were obtained by peak matching using polyethylene glycols as a standard. Ion mass/charge (*m*/*z*) ratios are reported in atomic mass units followed, in parentheses, by the peak intensity relative to the base peak (100%). Mass spectra were recorded of samples judged to be ≥95% pure by ^1H and ^{13}C NMR spectroscopy unless otherwise stated.

(*E*)-1-Chloro-5-(phenylsulfonyl)pent-2-ene (1): To a solution of methyl phenyl sulfone (156 mg, 1 mmol) in THF (5 mL), cooled to –40 °C, *n*BuLi (1.05 mmol, 0.66 mL, 1.6 M solution in hexane) was added dropwise. After 5 min, CuI (96 mg, 0.5 mmol) was added, and, after an additional 1 min, DMF (3 mL) was added. The mixture was stirred at –40 °C for additional 0.5 h and at 0 °C for further 0.5 h, followed by the addition of (*E*)-1,4-dichlorobut-2-ene (180 mg, 1.4 mmol). The mixture was stirred at 0 °C for 1 h and quenched by addition of an aqueous solution of NH_4Cl. The mixture was extracted with CH_2Cl_2 (3 × 10 mL), washed with water (2 × 10 mL), and dried with $MgSO_4$. The solvent was evaporated and the product purified by chromatography; yield 107 mg, 90%. Oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.47–2.53 (m, 2 H), 3.14–3.19 (m, 2 H), 3.95 [d, ^3J(H,H) = 5.75 Hz, 2 H], 5.61–5.73 (m, 2 H), 7.56–7.59 (m, 2 H), 7.65–7.70 (m, 1 H), 7.89–7.93 (m, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.33, 44.26, 55.17, 128.05, 128.60, 129.32, 130.35, 133.80, 138.89 ppm. IR (film): $\tilde{\nu}$ = 3065, 2955, 2930, 1585, 1479, 1447, 1306, 1148, 1086, 971, 734, 689, 598, 567, 535 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 244 (<1) $[M]^+$, 209 (76), 143 (100), 125 (14), 102 (14), 77 (18), 67 (50), 41 (18). HRMS (ESI): calcd. for $C_{11}H_{13}ClNaO_2S$ 267.0217; found 267.0205. $C_{11}H_{13}ClO_2S$ (244.74): calcd. C 53.98, H 5.35, Cl 14.49, S 13.10; found C 53.83, H 5.36, Cl 14.57, S 13.13.

(*Z*)-1-Chloro-5-(phenylsulfinyl)pent-2-ene: Phenyl methyl sulfoxide (5 g, 35.5 mmol) dissolved in THF (20 mL) was added to a solution of LDA in THF (37.4 mmol) cooled to –20 °C. The mixture was stirred for 1 h, cooled to –70 °C, and (*Z*)-1,4-dichlorobut-2-ene (5.35 g, 42 mmol) in THF (20 mL) was added. The mixture was stirred at –70 °C for 1 h, warmed to room temperature, stirred for an additional 24 h, and treated with aqueous NH_4Cl. The product was extracted with CH_2Cl_2 (3 × 100 mL), washed with water (2 × 100 mL), and dried with $MgSO_4$. The solvent was evaporated and the product purified by chromatography; yield 3.5 g, 45%. Oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.35–2.43 (m, 1 H), 2.59–2.68 (m, 1 H), 2.79–2.92 (m, 2 H), 4.04 [d, ^3J(H,H) = 7.8 Hz, 2 H], 5.58–5.64 (m, 1 H), 5.70–5.77 (m, 1 H), 7.49–7.56 (m, 3 H), 7.60–7.64 (m, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.77, 38.62, 55.73, 123.84, 127.78, 129.16, 130.72, 130.96, 143.34 ppm. IR (film): $\tilde{\nu}$ = 3466, 3056, 3028, 2963, 1652, 1477, 1443, 1251, 1086, 1042, 748, 692 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 228 (<1) $[M]^+$, 193 (89), 126 (48), 78 (53), 67 (100), 41 (61). HRMS (ESI): calcd. for $C_{11}H_{13}ClNaOS$ 251.0270; found 251.0259. $C_{11}H_{13}ClOS$ (228.74): calcd. C 57.76, H 5.73, Cl 15.50, S 14.02; found C 57.66, H 5.91, Cl 15.30, S 13.85.

(*Z*)-1-Chloro-5-(phenylsulfonyl)pent-2-ene (2): MCPBA (2.12 g, 10.44 mmol) and $NaHCO_3$ (0.74 g, 8.7 mmol) in CH_2Cl_2 (25 mL) were stirred for 1 h at room temperature. The mixture was then cooled to –40 °C and (*Z*)-1-chloro-5-(phenylsulfinyl)pent-2-ene (2 g, 8.7 mmol) in CH_2Cl_2 (5 mL) was added. The mixture was warmed to room temperature and stirred for 2 h. The organic layers were separated, the water phase was extracted with CH_2Cl_2 (3 × 100 mL), and the combined organic phases were washed with water (2 × 100 mL) and dried with $MgSO_4$. The solvent was evaporated and the product purified by chromatography; yield 1.83 g, 85%. Oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.56 [dq, ^3J(H,H) = 1.46, 7.90 Hz, 2 H], 3.14–3.18 (m, 2 H), 4.00 [d, ^3J(H,H) = 7.90 Hz, 2 H], 5.51–5.57 (m, 1 H), 5.69–5.75 (m, 1 H), 7.57–7.61 (m, 2 H), 7.66–7.70 (m, 1 H), 7.91–7.94 (m, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.68, 38.443, 55.22, 128.01, 128.03, 129.36, 129.81, 133.85, 138.84 ppm. IR (film): $\tilde{\nu}$ = 3065, 3032, 2972, 2927, 1978, 1906, 1820, 1776, 1653, 1585, 1479, 1447, 1403, 1305, 1231, 1148, 1086, 1024, 999, 986, 952, 799, 732, 689, 594, 561, 532, 439 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 244 (<1) $[M]^+$, 209 (39), 143 (55), 125 (7), 102 (14), 77 (23), 67 (100), 51 (12), 41 (31), 39 (10). HRMS (EI): calcd. for $C_{11}H_{13}ClO_2S$ 244.0325; found 244.0316. $C_{11}H_{13}ClO_2S$ (244.74): C 53.98, H 5.35, Cl 14.49, S 13.10; found C 54.06, H 5.37, Cl 14.50, S 12.82.

(*E*)-1-Chloro-5-(phenylsulfinyl)pent-2-ene: Obtained in a similar way as the (*Z*) isomer. Yield 1.62 g, 20%. Oil. ^1H NMR (500 MHz,

$CDCl_3$): δ = 2.29–2.38 (m, 1 H), 2.50–2.59 (m, 1 H), 2.78–2.90 (m, 2 H), 3.99–4.00 (m, 2 H), 5.64–5.77 (m, 2 H), 7.46–7.54 (m, 3 H), 7.58–7.62 (m, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 24.54, 44.50, 55.74, 124.00, 128.46, 129.26, 131.07, 131.55, 143.47 ppm. IR (film): $\tilde{\nu}$ = 3463, 3055, 2956, 1720, 1665, 1477, 1443, 1250, 1087, 1042, 970, 748, 692 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) =228 (1) $[M]^+$, 193 (100), 126 (49), 78 (23), 67 (49), 41 (12). HRMS (EI): calcd. for $C_{11}H_{13}ClOS$ 228.0377; found 228.0386. $C_{11}H_{13}ClOS$ (228.74): calcd. C 57.76, H 5.73, Cl 15.50, S 14.02; found C 57.63, H 5.59, Cl 15.55, S 14.26.

2-Phenylsulfonyl-1-vinylcyclopropane (3): *t*BuOK (224 mg, 2 mmol) in DMF (2 mL) was added dropwise to a solution of 1-chloro-5-(phenylsulfonyl)pent-2-ene **1** or **2** (244 mg, 1 mmol) in DMF (4 mL) at –30 °C under argon. After 30 min the mixture was warmed to room temperature and after an additional 2 h an aq. solution of NH_4Cl was added, the mixture was extracted with CH_2Cl_2 (3 × 50 mL), washed with brine, and dried with $MgSO_4$. Column chromatography with hexane/EtOAc the gave expected product; yield 30%. Oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.18 [ddd, ^3J(H,H) = 5.4, 6.8, 7.8 Hz, 1 H], 1.70 [dt, ^3J(H,H) = 5.4, 9.3 Hz, 1 H], 2.41–2.52 (m, 2 H), 5.07 [dd, ^3J(H,H) = 1.5, 10.1 Hz, 1 H], 5.22 [dd, ^3J(H,H) = 1.4, 17.1 Hz, 1 H], 5.35–5.53 (m, 1 H), 7.50–7.95 (m, 5 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.97, 22.81, 40.00, 116.69, 127.45, 129.26, 133.39, 135.14, 140.67 ppm. IR (KBr): $\tilde{\nu}$ = 2924, 2853, 1640, 1447, 1306, 1148, 1088, 738, 688, 650, 586, 544 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 208 (1) $[M]^+$, 77 (11), 67 (100), 41 (14). HRMS (EI): calcd. for $C_{11}H_{12}O_2S$ 208.0558; found 208.0566.

Reactions of Carbanions of 1 and 2 with Aromatic Aldehydes and Michael Acceptors. General Procedure: *t*BuOK (224 mg, 2 mmol) in THF (2 mL) was added dropwise to a solution of 1-chloro-5-(phenylsulfonyl)pent-2-ene **1** or **2** (244 mg, 1 mmol) and an aldehyde (1.5 mmol) in THF (4 mL) at –30 °C under argon. After 30 min the mixture was warmed to room temperature and after an additional 30 min an aq. solution of NH_4Cl was added, the mixture was extracted with CH_2Cl_2 (3 × 50 mL), and the extracts were washed with brine and dried with $MgSO_4$. The products were isolated and purified by column chromatography using hexane/ethyl acetate as eluent.

2-Phenyl-3-(phenylsulfonyl)-5-vinyltetrahydrofuran (6a): *trans*-**6a**: M.p. 114–115 °C (EtOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.06 [dt, ^3J(H,H) = 10.17, 13.80 Hz, 1 H], 2.63 [ddd, ^3J(H,H) = 2.43, 5.30, 13.80 Hz, 1 H], 2.68 [ddd, ^3J(H,H) = 2.43, 5.35, 10.17 Hz, 1 H], 4.67 [dt, ^3J(H,H) = 6.4, 10.17 Hz, 1 H], 5.24 [d, J(H,H) = 1.10, 10.4 Hz, 1 H], 5.34 [d, ^3J(H,H) = 5.35 Hz, 1 H], 5.41 [dt, ^3J(H,H) = 1.10, 17.2 Hz, 1 H], 5.94 [ddd, ^3J(H,H) = 6.4, 10.4, 17.2 Hz, 1 H], 7.12–7.16 (m, 2 H), 7.21–7.26 (m, 3 H), 7.51–7.56 (m, 2 H), 7.62–7.67 (m, 1 H), 7.86–7.90 (m, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 34.28, 71.34, 80.01, 80.49, 117.74, 125.94, 128.07, 128.46, 128.64, 129.40, 133.99, 136.21, 138.20, 140.18 ppm. IR (KBr): $\tilde{\nu}$ = 3033, 2997, 2957, 2875, 1603, 1583, 1494, 1456, 1447, 1366, 1303, 1287, 1144, 1084, 1048, 1002, 971, 938, 913, 855, 788, 761, 751, 720, 700, 690, 607, 561, 545, 515, 488 cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{18}NaO_3S$ 337.0869, found 337.0875. $C_{18}H_{18}O_3S$ (314.41): calcd. C 68.76, H 5.77, S 10.20; found C 68.62, H 5.96, S 10.41.

cis-**6a**: Oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.34–2.46 (m, 2 H), 3.95 [ddd, ^3J(H,H) = 5.81, 8.66, 14.47 Hz, 1 H], 4.62–4.68 (m, 1 H), 5.24 [dt, ^3J(H,H) = 1.10, 10.34 Hz, 1 H], 5.34 [dt, ^3J(H,H) = 1.10, 17.14 Hz, 1 H], 5.55 [d, ^3J(H,H) = 5.81 Hz, 1 H], 5.95 [ddd, ^3J(H,H) = 6.77, 10.34, 17.14 Hz, 1 H], 7.24–7.32 (m, 5 H), 7.53–7.57 (m, 2 H), 7.64–7.68 (m, 1 H), 7.90–7.92 (m, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 34.89, 71.52, 79.40, 80.22, 117.54, 125.71, 127.85, 128.60, 128.63, 129.33, 133.96, 136.67, 138.22, 140.47 ppm. IR (KBr): $\tilde{\nu}$ = 3058, 3032, 2944, 2883, 1651, 1602, 1583, 1496, 1446, 1426, 1301, 1281, 1148, 1084, 1070, 1046, 1025, 992, 943, 905, 865, 836, 757, 721, 700, 688, 630, 596, 560, 501 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 172 (85), 117 (18), 105 (100), 91 (16), 77 (28), 67 (38), 51 (8), 41 (7). HRMS (ESI): calcd. for $C_{18}H_{18}NaO_3S$ 337.0869, found 337.0860.

2-(*p*-Methylphenyl)-3-(phenylsulfonyl)-5-vinyltetrahydrofuran (6b): *trans*-**6b**: M.p. 102–103 °C (EtOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.05 [dt, ^3J(H,H) = 10.77, 13.89 Hz, 1 H], 2.29 (s, 3 H), 2.62 [ddd, ^3J(H,H) = 2.47, 5.17, 13.89 Hz, 1 H], 3.65 [ddd, ^3J(H,H) = 2.47, 5.17, 10.45 Hz, 1 H], 4.61–4.68 (m, 1 H), 5.23 [dt, ^3J(H,H) = 1.20, 10.45 Hz, 1 H], 5.30 [d, ^3J(H,H) = 5.17 Hz, 1 H], 5.40 [dt, ^3J(H,H) = 1.2, 17.18 Hz, 1 H], 5.93 [ddd, ^3J(H,H) = 6.6, 10.45, 17.18 Hz, 1 H], 6.98–7.06 (m, 4 H), 7.51–7.56 (m, 2 H), 7.62–7.67 (m, 1 H), 7.85–7.90 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.10, 34.31, 71.34, 79.93, 80.44, 117.75, 125.87, 128.66, 129.13, 129.40, 133.97, 136.27, 137.20, 137.84, 138.20 ppm. IR (KBr): $\tilde{\nu}$ = 3060, 2997, 2946, 2877, 1618, 1548, 1519, 1477, 1446, 1369, 1304, 1287, 1144, 1084, 1056, 1047, 1019, 1003, 988, 972, 940, 922, 864, 844, 820 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 186 (78), 131 (23), 119 (100), 115 (12), 105 (8), 91 (20), 77 (17), 67 (35). HRMS (ESI): calcd. for $C_{19}H_{20}NaO_3S$ 351.1025; found 351.1009. $C_{19}H_{20}O_3S$ (328.43): calcd. C 69.48, H 6.14, S 9.76; found C 69.39, H 6.22, S 9.84.

cis-**6b**: Oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.28–2.42 (m, 2 H), 2.30 (s, 3 H), 3.89 [ddd, ^3J(H,H) = 5.8, 8.6, 14.4 Hz, 1 H], 4.57–4.63 (m, 1 H), 5.19 [dt, ^3J(H,H) = 1.1, 10.3 Hz, 1 H], 5.29 [dt, ^3J(H,H) = 1.1, 17.2 Hz, 1 H], 5.49 [d, ^3J(H,H) = 5.8 Hz, 1 H], 5.91 [ddd, ^3J(H,H) = 6.8, 10.3, 17.2 Hz, 1 H], 7.06–7.13 (m, 4 H), 7.49–7.54 (m, 2 H), 7.60–7.65 (m, 1 H), 7.86–7.90 (m, 2 H) ppm. ^{13}C NMR (125 MHz, CHCl3): δ = 21.04, 34.86, 71.51, 79.35, 80.10, 117.46, 125.67, 128.66, 129.26, 129.31, 133.90, 136.77, 137.45, 137.60, 138.28 ppm. IR (film, CH_2Cl_2): $\tilde{\nu}$ = 3062, 2922, 1585, 1514, 1447, 1305, 1180, 1149, 1086, 1070, 991, 928, 813, 757, 720, 689, 607, 560, 508 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 186 (41), 131 (14), 119 (100), 105 (11), 91 (28), 77 (25), 67 (33), 51 (10), 41 (10). HRMS (ESI): calcd. for $C_{19}H_{20}NaO_3S$ 351.1025; found 351.1042.

2-(*p*-Chlorophenyl)-3-(phenylsulfonyl)-5-vinyltetrahydrofuran (6c): *trans*-**6c**: Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.02 [dt, ^3J(H,H) = 10.17, 13.88 Hz, 1 H], 2.60 [ddd, ^3J(H,H) = 2.47, 5.50, 13.88 Hz, 1 H], 3.61 [ddd, ^3J(H,H) = 2.61, 5.50, 10.17 Hz, 1 H], 4.61–4.69 (m, 1 H), 5.25 [dt, ^3J(H,H) = 1.24, 10.45 Hz, 1 H], 5.33 [d, ^3J(H,H) = 5.50 Hz, 1 H], 5.41 [dt, ^3J(H,H) = 1.24, 17.19 Hz, 1 H], 5.92 [ddd, ^3J(H,H) = 6.46, 10.45, 17.19 Hz, 1 H], 7.09–7.13 (m, 2 H), 7.20–7.24 (m, 2 H), 7.53–7.59 (m, 2 H), 7.65–7.70 (m, 1 H), 7.86–7.90 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 34.36, 71.26, 79.21, 80.54, 118.04, 127.35, 128.60, 128.64, 129.51, 133.89, 134.15, 135.91, 138.05, 138.71 ppm. IR (KBr): $\tilde{\nu}$ = 3069, 2992, 2948, 2881, 1600, 1582, 1492, 1446, 1414, 1367, 1303, 1286, 1145, 1083, 1057, 1046, 1013, 987, 972, 928, 860, 840, 826, 754, 723, 689, 632, 608, 564, 548, 531, 496, 457 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 307 (13), 279 (19), 215 (16), 201 (36), 187 (43), 171 (66), 143 (17), 106 (34), 92 (25), 77 (17), 63 (28), 43 (100). HRMS (ESI): calcd. for $C_{18}H_{17}ClNaO_3S$ 371.0479; found 371.0497.

cis-**6c**: Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.27–2.40 (m, 2 H), 3.83 [ddd, ^3J(H,H) = 6.05, 8.93, 14.71 Hz, 1 H], 4.55–4.62 (m, 1 H), 5.22 [dt, ^3J(H,H) = 1.10, 10.31 Hz, 1 H], 5.31 [dt, ^3J(H,H) = 1.10, 17.19 Hz, 1 H], 5.50 [d, ^3J(H,H) = 6.05 Hz, 1 H], 5.91 [ddd, ^3J(H,H) = 6.88, 10.31, 17.19 Hz, 1 H], 7.20–7.28 (m, 4 H), 7.51–7.57 (m, 2 H), 7.63–7.68 (m, 1 H), 7.85–7.90 (m, 2 H) ppm. ^{13}C

NMR (100 MHz, $CDCl_3$): δ = 35.12, 71.49, 78.65, 80.33, 117.79, 127.18, 128.55, 128.72, 129.41, 133.69, 134.11, 136.38, 138.06, 139.07 ppm. IR (KBr): $\tilde{\nu}$ = 3083, 3068, 2939, 2885, 1599, 1582, 1493, 1446, 1412, 1313, 1303, 1295, 1287, 1148, 1085, 1054, 1012, 986, 930, 919, 844, 815, 758, 724, 688, 619, 603, 592, 554, 512 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 206 (78), 151 (9), 139 (100), 115 (22), 77 (22), 67 (44), 51 (8), 41 (10). HRMS (ESI): calcd. for $C_{18}H_{17}ClNaO_3S$ 371.0479; found 371.0476.

2-(*p*-Methoxyphenyl)-3-(phenylsulfonyl)-5-vinyltetrahydrofuran (6d): *trans*-**6d**: M.p. 70–71 °C (EtOH). ^1H NMR (400 MHz, $CDCl_3$): δ = 2.07 [dt, ^3J(H,H) = 10.20, 13.80 Hz, 1 H], 2.64 [ddd, ^3J(H,H) = 2.71, 5.65, 13.80 Hz, 1 H], 3.65 [ddd, ^3J(H,H) = 2.71, 5.65, 10.20 Hz, 1 H], 3.76 (s, 3 H), 4.60–4.67 (m, 1 H), 5.24 [dt, ^3J(H,H) = 1.24, 10.40 Hz, 1 H], 5.26 [d, ^3J(H,H) = 5.65 Hz, 1 H], 5.40 [dt, ^3J(H,H) = 1.24, 17.18 Hz, 1 H], 5.93 [ddd, ^3J(H,H) = 6.61, 10.40, 17.18 Hz, 1 H], 6.71–6.80 (m, 2 H), 7.00–7.08 (m, 2 H), 7.48–7.59 (m, 2 H), 7.59–7.69 (m, 1 H), 7.83–7.90 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 34.32, 55.24, 71.09, 79.86, 80.27, 113.82, 117.73, 127.31, 128.59, 129.37, 132.05, 133.95, 136.24, 138.19, 159.38 ppm. IR (KBr): $\tilde{\nu}$ = 3035, 2997, 2945, 2874, 2836, 1616, 1589, 1517, 1466, 1446, 1438, 1375, 1308, 1301, 1249, 1183, 1144, 1113, 1084, 1044, 1032, 1004, 988, 926, 866, 834, 788, 750, 719, 688, 635, 606, 562, 555, 518 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 344 (<1) $[M]^+$, 202 (78), 147 (13), 135 (100), 77 (10), 67 (11). HRMS (EI): calcd. for $C_{19}H_{20}O_4S$ 344.1082; found 344.1090. $C_{19}H_{20}O_4S$ (344.43): calcd. C 66.26, H 5.85, S 9.31; found C 66.36, H 5.79, S 9.41.

cis-**6d**: Oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.28–2.47 (m, 2 H), 3.77 (s, 3 H), 3.89 [ddd, ^3J(H,H) = 6.18, 8.70, 14.95 Hz, 1 H], 4.57–4.66 (m, 1 H), 5.20 [dt, ^3J(H,H) = 1.24, 10.31 Hz, 1 H], 5.30 [dt, ^3J(H,H) = 1.24, 17.19 Hz, 1 H], 5.44 [d, ^3J(H,H) = 6.18 Hz, 1 H], 5.91 [ddd, ^3J(H,H) = 6.87, 10.31, 17.19 Hz, 1 H], 6.75–6.84 (m, 2 H), 7.10–7.19 (m, 2 H), 7.46–7.55 (m, 2 H), 7.59–7.66 (m, 1 H), 7.83–7.89 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 34.79, 55.27, 71.26, 79.21, 79.94, 113.94, 117.47, 127.15, 128.57, 129.29, 132.25, 133.92, 136.76, 138.20, 159.33 ppm. IR (film, CH_2Cl_2): $\tilde{\nu}$ = 3065, 2935, 2838, 1612, 1585, 1513, 1447, 1305, 1250, 1176, 1149, 1086, 1070, 1032, 927, 836, 756, 720, 689, 608 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 202 (33), 147 (10), 135 (100), 121 (9), 115 (8), 103 (9), 91 (11), 77 (28), 67 (15). HRMS (ESI): calcd. for $C_{19}H_{20}NaO_4S$ 367.0975; found 367.0974.

3-(Phenylsulfonyl)-2-styryl-5-vinyltetrahydrofuran (6e): *trans*-**6e**: Oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.05 [ddd, ^3J(H,H) = 10.03, 10.03, 13.61 Hz, 1 H], 2.68 [ddd, ^3J(H,H) = 3.72, 6.05, 13.61 Hz, 1 H], 3.58 [ddd, ^3J(H,H) = 3.72, 6.73, 10.03 Hz, 1 H], 4.50–4.57 (m, 1 H), 4.82 [dt, ^3J(H,H) = 1.10, 6.73 Hz, 1 H], 5.22 [dt, ^3J(H,H) = 1.24, 10.45 Hz, 1 H], 5.37 [dt, ^3J(H,H) = 1.24, 17.19 Hz, 1 H], 5.86 [ddd, ^3J(H,H) = 6.60, 10.45, 17.19 Hz, 1 H], 5.93 [dd, ^3J(H,H) = 6.73, 15.81 Hz, 1 H], 6.33 [d, ^3J(H,H) = 15.81 Hz, 1 H], 7.17–7.30 (m, 5 H), 7.53–7.59 (m, 2 H), 7.60–7.66 (m, 1 H), 7.88–7.96 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.87, 68.82, 79.42, 80.02, 117.86, 126.55, 126.60, 128.00, 128.45, 128.65, 129.43, 132.61, 134.08, 135.85, 136.33, 138.18 ppm. IR (KBr): $\tilde{\nu}$ = 3058, 2955, 2886, 1599, 1583, 1496, 1477, 1443, 1370, 1301, 1145, 1084, 1051, 973, 965, 931, 873, 846, 778, 748, 717, 689, 630, 602, 577, 549 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 198 (100), 143 (14), 131 (49), 115 (16), 91 (14), 77 (11), 67 (11). HRMS (ESI): calcd. for $C_{20}H_{20}NaO_3S$ 363.1025; found 363.1020.

cis-**6e**: Oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.31 [dt, ^3J(H,H) = 9.3, 12.9 Hz, 1 H], 2.42 [ddd, ^3J(H,H) = 5.8, 8.3, 12.9 Hz, 1 H], 3.69 [ddd, ^3J(H,H) = 6.8, 8.3, 9.3 Hz, 1 H], 4.50–4.56 (m, 1 H), 4.98–5.02 (m, 1 H), 5.20 [dt, ^3J(H,H) = 0.9, 10.3 Hz, 1 H], 5.28–5.33 (m, 1 H), 5.89 [ddd, ^3J(H,H) = 6.8, 10.3, 17.1 Hz, 1 H], 5.94 [dd, ^3J(H,H) = 6.1, 15.8 Hz, 1 H], 6.43 [dd, ^3J(H,H) = 0.9, 15.8 Hz, 1 H], 7.20–7.4 (m, 3 H), 7.26–7.29 (m, 2 H), 7.53–7.57 (m, 2 H), 7.60–7.65 (m, 1 H), 7.91–7.96 (m, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 34.29, 69.60, 78.61, 79.67, 117.56, 126.57, 127.06, 127.97, 128.49, 128.65, 129.40, 131.71, 134.07, 135.96, 136.62, 138.35 ppm. IR (film CH_2Cl_2): $\tilde{\nu}$ = 3061, 3028, 2934, 1725, 1495, 1447, 1305, 1149, 1086, 967, 929, 847, 752, 723, 690, 604, 554 cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{20}NaO_3$ 363.1025; found 363.1020.

3-Phenylsulfonyl-2-(2-thienyl)-5-vinyltetrahydrofuran (6f): *trans*-**6f**: Oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.14 [dt, ^3J(H,H) = 10.04, 13.89 Hz, 1 H], 2.70 [ddd, ^3J(H,H) = 3.02, 5.78, 13.89 Hz, 1 H], 3.75 [ddd, ^3J(H,H) = 3.02, 5.50, 10.04 Hz, 1 H], 4.60–4.67 (m, 1 H), 5.22 [dt, ^3J(H,H) = 1.24, 10.45 Hz, 1 H], 5.39 [dt, ^3J(H,H) = 1.24, 17.19 Hz, 1 H], 5.54 [d, ^3J(H,H) = 5.50 Hz, 1 H], 5.90 [ddd, ^3J(H,H) = 6.60, 10.45, 17.19 Hz, 1 H], 6.59 [dt, ^3J(H,H) = 1.24, 3.58 Hz, 1 H], 6.80 [dd, ^3J(H,H) = 3.58, 5.09 Hz, 1 H], 7.16 [dd, ^3J(H,H) = 1.24, 5.09 Hz, 1 H], 7.51–7.57 (m, 2 H), 7.63–7.68 (m, 1 H), 7.85–7.90 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.89, 71.28, 76.64, 80.54, 117.88, 124.74, 125.36, 126.70, 128.59, 129.42, 134.10, 136.06, 137.93, 143.34 ppm. IR (KBr): $\tilde{\nu}$ = 3065, 2977, 2929, 2873, 1584, 1479, 1447, 1306, 1206, 1148, 1119, 1084, 1056, 1037, 998, 939, 872, 857, 844, 782, 754, 717, 705, 691, 638, 607, 594, 557, 504 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 178 (56), 123 (18), 111 (100), 97 (11), 77 (12), 67 (29), 45 (8), 39 (8). HRMS (ESI): calcd. for $C_{16}H_{16}NaO_3S_2$ 343.0433; found 343.0424.

cis-**6f**: Oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.37 [dt, ^3J(H,H) = 9.07, 13.06 Hz, 1 H], 2.45–2.53 (m, 1 H), 3.99 [ddd, ^3J(H,H) = 5.91, 9.07, 14.44 Hz, 1 H], 4.60–4.67 (m, 1 H), 5.21 [dt, ^3J(H,H) = 1.24, 10.31 Hz, 1 H], 5.31 [dt, ^3J(H,H) = 1.24, 17.19 Hz, 1 H], 5.68 [d, ^3J(H,H) = 5.91 Hz, 1 H], 5.89 [ddd, ^3J(H,H) = 6.87, 10.31, 17.19 Hz, 1 H], 6.75 [dt, ^3J(H,H) = 1.24, 3.58 Hz, 1 H], 6.85 [dd, ^3J(H,H) = 3.58, 5.08 Hz, 1 H], 7.18 [dd, ^3J(H,H) = 1.24, 5.08 Hz, 1 H], 7.50–7.56 (m, 2 H), 7.61–7.67 (m, 1 H), 7.86–7.90 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.89, 71.53, 76.25, 79.97, 117.89, 125.10, 125.41, 126.92, 128.58, 129.37, 134.07, 136.16, 138.00, 143.97 ppm. IR (KBr): $\tilde{\nu}$ = 3070, 2934, 2872, 1447, 1305, 1150, 1086, 1038, 927, 852, 758, 722, 689, 597, 556 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{16}NaO_3S_2$ 343.0433; found 343.0416.

3-Phenylsulfonyl-2-(3-pyridyl)-5-vinyltetrahydrofuran (6g): *trans*-**6g**: M.p. 98 °C (EtOH). ^1H NMR (400 MHz, $CDCl_3$): δ = 2.06 [dt, ^3J(H,H) = 10.17, 13.89 Hz, 1 H], 2.65 [ddd, ^3J(H,H) = 2.75, 5.64, 13.89 Hz, 1 H], 3.66 [ddd, ^3J(H,H) = 2.75, 5.77, 10.17 Hz, 1 H], 4.64–4.72 (m, 1 H), 5.27 [dt, ^3J(H,H) = 1.23, 10.45 Hz, 1 H], 5.36 [d, ^3J(H,H) = 5.77 Hz, 1 H], 5.42 [dt, ^3J(H,H) = 1.23, 17.18 Hz, 1 H], 5.92 [ddd, ^3J(H,H) = 6.60, 10.45, 17.18 Hz, 1 H], 7.20 [dd, ^3J(H,H) = 0.41, 4.81 Hz, 1 H], 7.53–7.59 (m, 3 H), 7.65–7.70 (m, 1 H), 7.86–7.91 (m, 2 H), 8.35 [d, ^3J(H,H) = 1.93 Hz, 1 H], 8.49 [dd, ^3J(H,H) = 1.38, 4.81 Hz, 1 H] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 34.36, 70.96, 78.01, 80.65, 118.16, 123.30, 128.57, 129.58, 133.80, 134.32, 135.58, 135.70, 137.88, 147.78, 149.53 ppm. IR (KBr): $\tilde{\nu}$ = 3065, 3016, 2961, 2893, 1591, 1576, 1480, 1447, 1424, 1361, 1339, 1324, 1303, 1145, 1085, 1062, 1024, 1005, 938, 816, 781, 750, 722, 690, 626, 571, 536, 521 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 316 (<1) $[M]^+$, 173 (100), 158 (11), 145 (10), 118 (28), 106 (91), 91 (10), 77 (18), 67 (39), 51 (9), 41(8). HRMS (ESI): calcd. for $C_{17}H_{17}NO_3S$ 316.1002; found 316.0991. $C_{17}H_{17}NO_3S$ (315.39): calcd. C 64.74, H 5.43, N 4.44, S 10.17; found C 64.61, H 5.41, N 4.33, S 10.29.

cis-**6g**: Oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.34–2.45 (m, 2 H), 3.87 [dt, ^3J(H,H) = 6.5, 8.8 Hz, 1 H], 4.60–4.66 (m, 1 H), 5.24 [dt, ^3J(H,H) = 1.0, 10.3 Hz, 1 H], 5.33 [dt, ^3J(H,H) = 1.0, 17.1 Hz, 1

H], 5.54 [d, ^3J(H,H) = 6.5 Hz, 1 H], 5.93 [ddd, ^3J(H,H) = 6.8, 10.3, 17.1 Hz, 1 H], 7.23–7.25 (m, 1 H), 7.52–7.57 (m, 2 H), 7.63–7.69 (m, 2 H), 7.86–7.90 (m, 2 H), 8.51 (br. s, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 35.15, 71.24, 77.48, 80.56, 117.98, 123.51, 128.52, 128.60, 129.51, 134.27, 136.20, 136.28, 138.04, 147.37, 148.96 ppm.. IR (film, CH_2Cl_2): $\tilde{\nu}$ = 3062, 2935, 1580, 1479, 1447, 1429, 1305, 1150, 1086, 1071, 1024, 929, 757, 723, 689, 600, 562 cm^{-1}. HRMS (EI): calcd. for $C_{17}H_{17}NO_3S$ 316.1002; found 316.1014.

2-(2-Furyl)-3-(phenylsulfonyl)-5-vinyltetrahydrofuran (6h): *trans*-**6h**: M.p. 96–97 °C (EtOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.21 [ddd, ^3J(H,H) = 10.33, 10.33, 13.69 Hz, 1 H], 2.76 [ddd, ^3J(H,H) = 4.12, 6.34, 13.69 Hz, 1 H], 4.03 [ddd, ^3J(H,H) = 4.12, 6.45, 10.33 Hz, 1 H], 4.56–4.62 (m, 1 H), 5.19 [dt, ^3J(H,H) = 1.14, 10.39 Hz, 1 H], 5.21 [d, ^3J(H,H) = 6.45 Hz, 1 H], 5.33 [dt, ^3J(H,H) = 1.14, 17.18 Hz, 1 H], 5.87 [ddd, ^3J(H,H) = 6.46, 10.39, 17.18 Hz, 1 H], 6.06 [d, ^3J(H,H) = 3.27 Hz, 1 H], 6.16 [dd, ^3J(H,H) = 1.80, 3.27 Hz, 1 H], 7.23 [d, ^3J(H,H) = 1.80 Hz, 1 H], 7.47–7.51 (m, 2 H), 7.57–7.63 (m, 1 H), 7.81–7.85 (m, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 33.64, 66.95, 74.13, 80.35, 109.17, 110.34, 117.87, 128.40, 129.25, 133.91, 136.35, 137.98, 142.88, 150.50 ppm. IR (film, CH_2Cl_2): $\tilde{\nu}$ = 3066, 2985, 2885, 1504, 1447, 1307, 1251, 1149, 1086, 1047, 923, 884, 750, 721, 689, 600, 565 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{16}NaO_4S$ 327.0662; found 327.0675. $C_{16}H_{16}O_4S$ (304.37): calcd. C 63.14, H 5.30, S 10.53; found C 62.92, H 5.17, S 10.75.

cis-**6h**: Oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.36 [dt, ^3J(H,H) = 9.36, 12.91 Hz, 1 H], 2.54 [ddd, ^3J(H,H) = 5.69, 8.36, 12.91 Hz, 1 H], 4.19 [ddd, ^3J(H,H) = 6.38, 8.36, 9.36 Hz, 1 H], 4.59–4.65 (m, 1 H), 5.19 [dt, ^3J(H,H) = 1.15, 10.35 Hz, 1 H], 5.30 [dt, ^3J(H,H) = 1.15, 17.17 Hz, 1 H], 5.36 [d, ^3J(H,H) = 6.38 Hz, 1 H], 5.86 [ddd, ^3J(H,H) = 6.85, 10.35, 17.17 Hz, 1 H], 6.09 [d, ^3J(H,H) = 3.28 Hz, 1 H], 6.19 [dd, ^3J(H,H) = 1.84, 3.28 Hz, 1 H], 7.25 [d, ^3J(H,H) = 1.84 Hz, 1 H], 7.47–7.53 (m, 2 H), 7.58–7.63 (m, 1 H), 7.83–7.86 (m, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 33.92, 67.45, 73.49, 80.10, 108.77, 110.40, 117.81, 128.46, 129.25, 133.92, 136.29, 138.09, 142.88, 151.67 ppm. IR (film, CH_2Cl_2): $\tilde{\nu}$ = 3121, 3067, 2988, 2884, 1585, 1504, 1447, 1306, 1248, 1150, 1086, 1014, 933, 917, 884, 749, 723, 689, 603, 562 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{16}NaO_4S$ 327.0662; found 327.0661.

2-*tert*-Butyl-3-(phenylsulfonyl)-5-vinyltetrahydrofuran (6i): *trans*-**6i**: M.p. 121–122 °C (EtOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.80 (s, 9 H), 1.75 [ddd, ^3J(H,H) = 9.4, 11.2, 14.0 Hz, 1 H], 2.45 [ddd, ^3J(H,H) = 0.8, 5.0, 14.0 Hz, 1 H], 3.46 [ddd, ^3J(H,H) = 0.8, 3.6, 9.4 Hz, 1 H], 4.20 [d, ^3J(H,H) = 3.6 Hz, 1 H], 4.49–4.56 (m, 1 H), 5.15 [ddd, ^3J(H,H) = 1.1, 1.6, 10.4 Hz, 1 H], 5.33 [ddd, ^3J(H,H) = 1.1, 1.6, 17.2 Hz, 1 H], 5.78 [ddd, ^3J(H,H) = 6.7, 10.4, 17.2 Hz, 1 H], 7.57–7.63 (m, 2 H), 7.66–7.71 (m, 1 H), 7.92–7.96 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.44, 34.53, 35.10, 66.22, 79.84, 85.49, 117.08, 128.97, 129.41, 133.99, 136.63, 138.18 ppm. IR (KBr): $\tilde{\nu}$ = 2967, 2883, 1478, 1468, 1449, 1410, 1304, 1284, 1183, 1149, 1126, 1085, 1050, 1025, 1004, 932, 788, 762, 722, 697, 634, 563, 547 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{22}NaO_3S$ 317.1182; found 317.1171. $C_{16}H_{22}O_3S$ (294.42): calcd. C 65.27, H 7.53, S 10.89; found C 65.25, H 7.34, S 10.71.

cis-**6i**: Oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.85 (s, 9 H), 2.23–2.30 (m, 1 H), 2.32–2.40 (m, 1 H), 3.65 [ddd, ^3J(H,H) = 3.8, 5.8, 9.6 Hz, 1 H], 4.28 [d, ^3J(H,H) = 3.8 Hz, 1 H], 4.51 [q, ^3J(H,H) = 7.4 Hz, 1 H], 5.07–5.11 (m, 1 H), 5.16 [dt, ^3J(H,H) = 1.1, 17.2 Hz, 1 H], 5.82 [ddd, ^3J(H,H) = 7.4, 10.1, 17.2 Hz, 1 H], 7.54–7.61 (m, 2 H), 7.64–7.69 (m, 1 H), 7.91–7.95 (m, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.99, 34.88, 36.08, 66.16, 81.58, 87.01, 116.75, 129.01, 129.33, 133.88, 138.24, 138.30 ppm. IR (film, CH_2Cl_2): $\tilde{\nu}$ = 2959, 2906, 1479, 1447, 1365, 1307, 1149, 1086, 1029, 997, 930, 758, 719, 690, 597, 551 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{22}NaO_3S$ 317.1182; found 317.1187.

2-Benzoyl-3-phenyl-4-(phenylsulfonyl)-1-vinylcyclopentane (7a): M.p. 191 °C (EtOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.23–2.31 (m, 1 H), 2.79 [ddd, ^3J(H,H) = 3.5, 7.6, 14.00 Hz, 1 H], 3.16–3.24 (m, 1 H), 3.72–3.78 (m, 1 H), 3.92–3.97 (m, 2 H), 4.92 [d, ^3J(H,H) = 10.3 Hz, 1 H], 5.00 [d, ^3J(H,H) = 17.1 Hz, 1 H], 5.69 [ddd, ^3J(H,H) = 7.6, 10.3, 17.1 Hz, 1 H], 6.86–6.90 (m, 2 H), 6.99–7.03 (m, 3 H), 7.22–7.27 (m, 2 H), 7.33–7.36 (m, 2 H), 7.38–7.42 (m, 1 H), 7.44–7.48 (m, 1 H), 7.51–7.55 (m, 2 H), 7.74–7.78 (m, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 33.01, 48.30, 51.64, 61.23, 68.99, 116.51, 126.91, 127.06, 128.18, 128.26, 128.56, 128.65, 128.92, 132.95, 133.45, 137.49, 137.99, 140.13, 199.74 ppm. IR (KBr): $\tilde{\nu}$ = 3069, 1661, 1596, 1580, 1446, 1303, 1243, 1218, 1142, 1085, 1002, 922, 841, 789, 768, 758, 731, 720, 698, 687, 591, 560, 537 cm^{-1}. HRMS (ESI): calcd. for $C_{26}H_{24}NaO_3S$ 439.1338; found 439.1334. $C_{26}H_{24}O_3S$ (416.54): calcd. C 74.97, H 5.81, S 7.70; found C 74.84, H 5.93, S 7.94.

2,2-Dicyano-3-phenyl-4-(phenylsulfonyl)-1-vinylcyclopentane (7b): M.p. 117–119 °C (EtOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.65–2.72 (m, 1 H), 2.74–2.81 (m, 1 H), 3.41 [dt, ^3J(H,H) = 7.0, 7.8 Hz, 1 H], 4.07 [d, ^3J(H,H) = 10.0 Hz, 1 H], 4.16 [ddd, ^3J(H,H) = 8.0, 10.0, 17.6 Hz, 1 H], 5.50 [d, ^3J(H,H) = 7.0 Hz, 1 H], 5.53 (s, 1 H), 6.04–6.12 (m, 1 H), 7.05–7.09 (m, 2 H), 7.16–7.30 (m, 5 H), 7.42–7.46 (m, 1 H), 7.61–7.64 (m, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 30.23, 48.92, 51.44, 54.87, 65.45, 112.75, 113.41, 122.43, 128.07, 128.38, 129.02, 129.10, 129.29, 132.18, 132.55, 134.08, 137.32 ppm. IR (KBr): $\tilde{\nu}$ = 3013, 2992, 2956, 2252, 1447, 1308, 1146, 1084, 990, 941, 751, 719, 704, 683, 603, 582, 551, 498, 426 cm^{-1}. HRMS (ESI): calcd. for $C_{21}H_{18}N_2NaO_2S$ 385.0981; found 385.0989. $C_{21}H_{18}N_2O_2S$ (362.45): C 69.59, H 5.01, N 7.73, S 8.85; found C 69.61, H 5.12, N 7.72, S 8.78.

Ethyl 1-Benzoyl-2-phenyl-3-(phenylsulfonyl)-5-vinylcyclopentanecarboxylate (7c): LDA (0.55 mmol, 0.34 mL, 1.6 M solution in THF, heptane and ethylbenzene) was added dropwise to a solution of (*E*)-1-chloro-5-(phenylsulfonyl)pent-2-ene (**1**; 122 mg, 0.5 mmol) and ethyl 2-benzoyl-3-phenylacrylate (210 mg, 0.75 mmol) in THF (10 mL) at –70 °C under argon. After 30 min the mixture was warmed to room temperature and after an additional 22.5 h an aq. solution of NH_4Cl was added, the mixture was extracted with CH_2Cl_2 (3 × 50 mL), and the extracts were washed with brine and dried with $MgSO_4$. Products were isolated and purified by column chromatography using hexane/ethyl acetate as eluent; yield 70%, *trans*/*cis* = 62:38.

trans-**7c**: M.p. 104–105 °C (EtOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.58 [t, ^3J(H,H) = 7.2 Hz, 3 H], 2.66–2.82 (m, 2 H), 3.40–3.47 (m, 1 H), 3.52–3.57 (m, 1 H), 3.76–3.84 (m, 1 H), 4.34–4.41 (m, 2 H), 4.96–5.03 (m, 2 H), 6.01 [ddd, ^3J(H,H) = 7.9, 10.3, 17.9 Hz, 1 H], 6.88–6.98 (m, 5 H), 7.10–7.14 (m, 2 H), 7.20–7.24 (m, 2 H), 7.26–7.37 (m, 4 H), 7.63–7.66 (m, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.99, 30.03, 51.14, 54.68, 60.58, 66.01, 73.22, 118.11, 127.15, 127.30, 127.76, 128.54, 128.67, 129.19, 129.47, 132.15, 133.25, 135.38, 138.30, 136.53, 138.05, 169.79, 194.93 ppm. IR (KBr): $\tilde{\nu}$ = 3059, 2985, 2898, 1716, 1668, 1597, 1579, 1447, 1305, 1274, 1246, 1224, 1145, 1084, 748, 700, 688, 594, 567, 541 cm^{-1}. HRMS (ESI): calcd. for $C_{29}H_{28}NaO_5S$ 511.1550; found 511.1530. $C_{29}H_{28}O_5S$ (488.60): calcd. C 71.29, H 5.78, S 6.56; found C 71.43, H 5.63, S 6.43.

cis-**7c**: M.p. 171–172 °C (EtOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.37 [t, ^3J(H,H) = 7.2 Hz, 3 H], 2.46 [ddd, ^3J(H,H) = 4.2, 7.2,

14.3 Hz, 1 H], 3.09 [ddd, ^3J(H,H) = 8.1, 10.2, 14.3 Hz, 1 H], 3.23–3.30 (m, 1 H), 3.68–3.78 (m, 2 H), 4.19 [ddd, ^3J(H,H) = 7.2, 10.4, 10.6 Hz, 1 H], 4.76–4.82 (m, 3 H), 5.70 [dt, ^3J(H,H) = 10.2, 16.7 Hz, 1 H], 6.93–7.05 (m, 5 H), 7.19–7.24 (m, 2 H), 7.30–7.39 (m, 3 H), 7.42–7.46 (m, 1 H), 7.58–7.62 (m, 2 H), 7.67–7.71 (m, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.64, 32.55, 49.24, 51.20, 61.00, 66.44, 73.57, 117.60, 126.98, 127.61, 128.06, 128.40, 128.50, 128.61, 132.51, 133.14, 136.32, 136.37, 136.64, 138.42, 171.98, 192.60 ppm. IR (KBr): $\tilde{\nu}$ = 3078, 2985, 2952, 1721, 1678, 1583, 1449, 1290, 1255, 1238, 1215, 1143, 1084, 998, 931, 753, 735, 693, 593, 580, 546 cm^{-1}. HRMS (ESI): calcd. for $C_{29}H_{28}NaO_5S$ 511.1550; found 511.1564. $C_{29}H_{28}O_5S$ (488.60): calcd. C 71.29, H 5.78, S 6.56; found C 71.30, H 5.76, S 6.34.

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