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α-Sulfonyl Succinimides: Versatile Sulfinate Donors in Fe-Catalyzed, Salt-Free, Neutral Allylic Substitution

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Abstract: Allyl sulfones are versatile intermediates in organic chemistry. The presence of two distinct functional groups sets the stage for a plethora of subsequent transformations. However, despite these advantages the preparation of regioisomerically enriched sulfones is not easy. The use of sulfinate salts as nucleophiles in substitutions is frequently accompanied by side reactions such as π-bond migration, β-elimination, and so on. Herein we present a preparatively simple way to synthesize a variety of different aryl or alkyl allyl sulfones starting from readily accessible allylic carbonates. By employing aryl or alkyl α-sulfonyl succinimides as sulfinate synthons, mild and regioselective *ipso* substitution of diverse allylic carbonates was realized.

Keywords: allylic compounds · iron · sulfones · sulfonylation · synthetic methods

Introduction

Sulfones are an important subclass of organosulfur compounds. They can be regarded as S analogues of carbonyl compounds and hence have reactivities that are somewhat comparable.[1] A variety of functional-group transformations using sulfones as auxiliaries have been published. The fact that the sulfone group can also serve as a leaving group opens up novel strategies for direct functionalization of C–H bonds. Hence, reductive, oxidative, or methylenating desulfurization allows for transformation of the C–S bond into a C–H, C–O, or C=C bond. Furthermore, sulfones are important intermediates in olefination processes such as the Julia–Kocienski, Julia–Lythgoe, and Ramberg–Bäcklund reactions. Using the α-sulfonyl anion in Michael-type additions to α,β-unsaturated carbonyl compounds led to desulfurization with concomitant formation of a cyclopropane unit. The implementation of further proximal functional groups such as olefins expands the scope of application significantly (Scheme 1).[2–21]

Due to the versatility of sulfones as building blocks in organic synthesis, a variety of methods for their preparation has been developed. The most commonly used transformations are replacement of a leaving group (halide, sulfonate, etc.) by nucleophilic displacement[22] and Mitsunobu-type exchange of a hydroxyl group for a mercapto substituent followed by oxidation to the corresponding sulfone.[23] Both protocols are hampered by synthetic problems. Whereas nucleophilic displacement faces regioselectivity problems in the case of allylic leaving groups, the latter method is a two-step protocol that involves the use of hazardous reagents. Furthermore, allylic thioethers are prone to undergo radical isomerization.[24]

Transition metal complexes are an interesting alternative for direct nucleophilic displacement of allylic leaving groups for a sulfonyl moiety, a field that was long dominated by the use of Pd catalysts.[25] The dynamic character of the intermediate fluxional allyl metal species in combination with the use of chiral ligands allows for good to high levels of asymmetric induction,[25] but in most cases strict control of the regioselectivity is still problematic. Hartwig et al. showed that this problem can in part be overcome by using Ir complexes.[26,27] Independent of the structure of the starting material, excellent levels of regio- and stereocontrol were observed in favor of the branched sulfone having a monosubstituted olefin. Complementary to this method, catalytic protocols for the regioselective *ipso* substitution of allylic carbonates based on Rh[28] and Fe complexes[29] were reported recently. Nucleophilic Fe complex $Bu_4N[Fe(CO)_3(NO)]$ (TBAFe) allows for regio- and stereoconserving exchange of an allylic C–O for a C–C, or C–N bond. Furthermore, good levels of regio- and stereoselectivity were observed in the corresponding allylic sulfonylation using aryl sulfinates as nucleophiles.[29e] However, this method proved to be restricted to the formation of primary and tertiary aryl sulfones.

Whereas aliphatic sulfinates proved to be unreactive, secondary sulfones were shown to undergo an undesired shift of the double bond to give the corresponding vinyl sulfones. Moreover, the existing methodologies for transition metal catalyzed allylic sulfonylation are restricted to the use of simple unfunctionalized sulfinate salts. This fact is not a consequence of an incompatibility of functionalized sulfinates with the metal catalysts, but rather due to a lack of reactive

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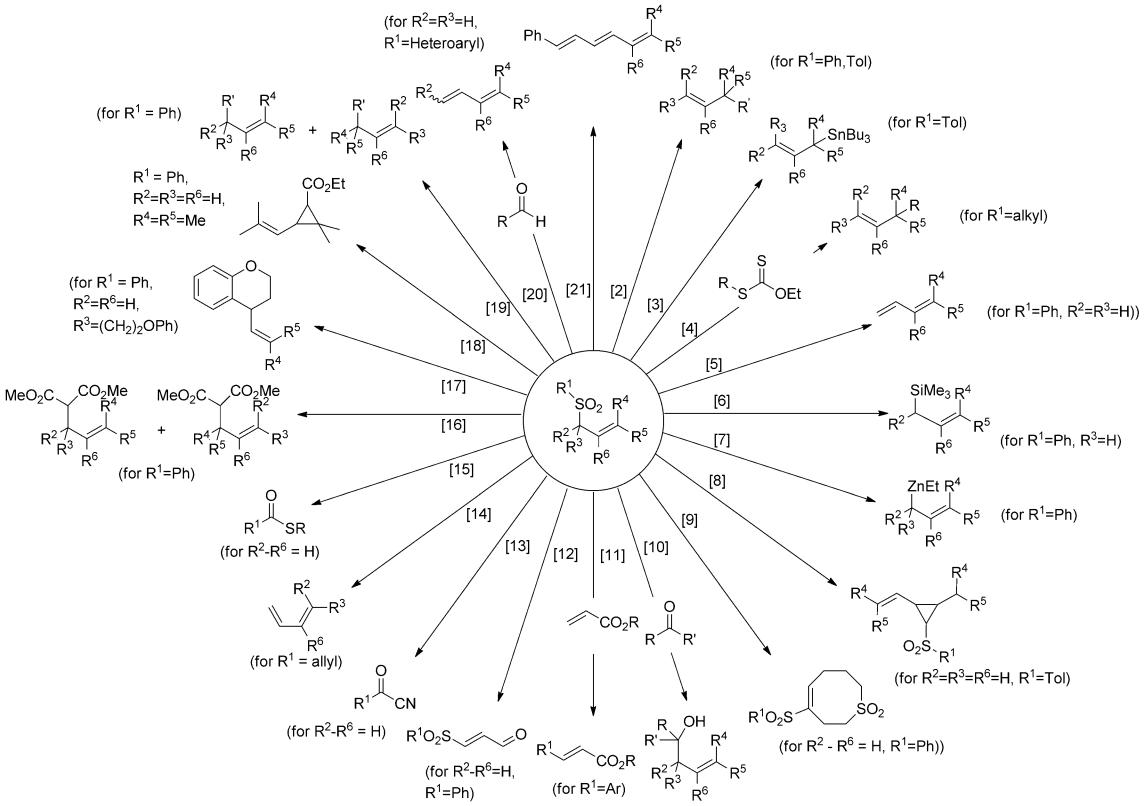


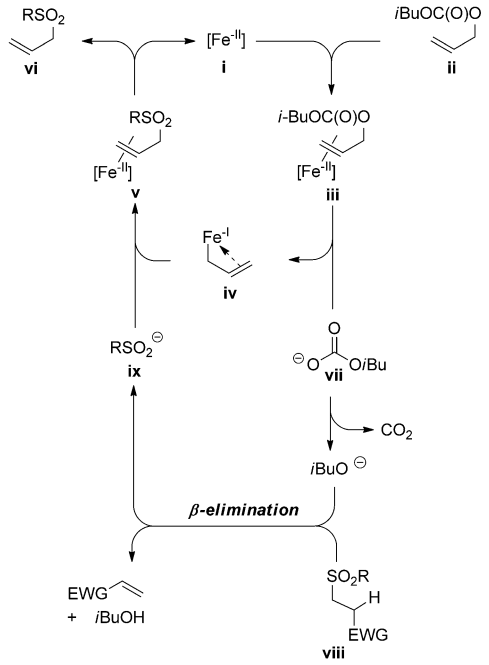
Scheme 1. Allylic sulfones: versatile building blocks in organic chemistry.

sulfinate surrogates. Here we summarize the results of an in-depth study which finally led to the development of salt-free, Fe-catalyzed regioselective allylic sulfonylation using readily available functionalized α-sulfonyl succinimides as pronucleophiles. With this species in hand, a variety of allyl, alkyl, aryl, and heteroaromatic sulfonyl groups are allylated with moderate to excellent levels of regio- and stereoconservation.

Results and Discussion

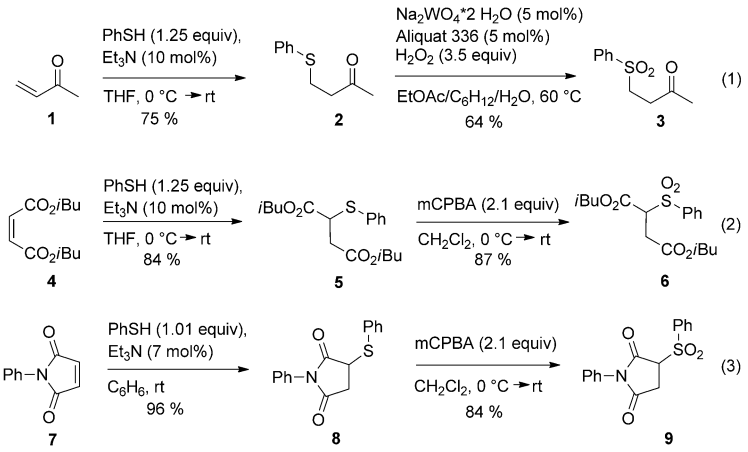
As noted above, undesired π-bond isomerization and the strict limitation to aryl sulfinates are serious synthetic drawbacks that needed to be addressed. We envisioned two factors to be a source for these problems. Firstly, the use of preformed nucleophiles (the aryl sulfinates were employed as their sodium salts) leads to formation of free base in each catalytic cycle and hence may be the reason for the base-promoted isomerization reaction. Secondly, the established procedures for preparation of sulfinates do not allow for the preparation of functionalized sulfinates. To circumvent both problems we wondered whether in situ generation of reactive sulfinate by base-promoted β-elimination would solve the problem of π-bond isomerization, since the leaving group would serve as a base generated in situ (Scheme 2).

We prepared different potential sulfinate donors by a two-step procedure of Michael addition of a mercaptan and



Scheme 2. Neutral allylic sulfonylation with sulfinates generated in situ.

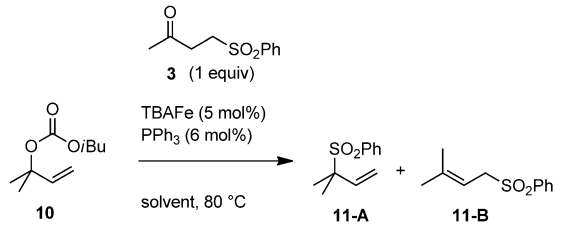
subsequent oxidation of the thioether to the corresponding sulfone (Scheme 3). β-Sulfonyl butanone **3** was recently reported to be a versatile precursor for the preparation of sulfinate and served as a prototype for a sulfinate donor.[30]



Scheme 3. Preparation of potential sulfinate donors.

Allyl carbonate **10** was transformed into corresponding allyl sulfone **11** with almost full conversion and good regioselectivity in favor of *ipso* substitution product **11-A**. Subjecting secondary carbonate **12** to the reaction conditions gave desired product **13** in good yields, albeit with moderate regioselectivities and significant amounts of vinyl sulfone **13-D** (Table 2). Although the addition of water as a cosolvent suppressed the π-bond isomerization to some extent (Table 2, entry 2), this undesired side reaction was observed over the prolonged reaction times in alcoholic solvents (Table 2, entry 3). At this point an in depth ligand screening was performed (Table 3).

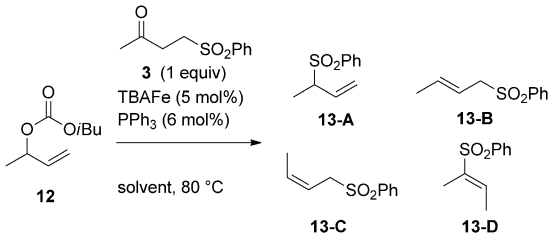
Table 1. Influence of solvent and temperature.[a]



Entry	Solvent	**11-A**:**11-B**[b]	Conv. [%][c]
1	DMF/$MeOC_2H_4OH$	91:9	29
2	THF	96:4	29
3	MTBE	97:3	96
4	DMF	94:6	50
5	acetonitrile	95:5	39
6	butanone	96:4	15
7	*n*-hexane	97:3	27

[a] Reactions were performed under an N_2 atmosphere on a 0.5 mmol scale with sulfinate donor **3** (1 equiv), TBAFe (5 mol%), and PPh_3 (6 mol%) in the given solvent (0.5 mL) at 80 °C and stopped after 24 h. [b] Determined by GC integration of the crude reaction mixture. [c] Determined by GC integration of the crude reaction mixture with dodecane as internal standard.

Table 2. Influence of solvent.[a]



Entry	Solvent	Conv. [%][b] (time)	**13-A**:**13-B**:**13-C**:**13-D**[c]
1	MTBE (500 μL)	80 (3 days)	36:12:1:50
2	MTBE (500 μL) + H_2O (10 μL)	54 (2 days)	75:7:1:18
3	*i*BuOH (250 μL)	94 (17 h)	69:18:3:10
4	*t*BuOH (250 μL)	93 (3 days)	50:18:1:31

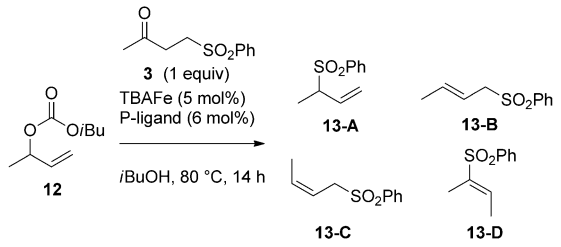
[a] Reactions were performed on a 0.5 mmol scale with sulfinate donor **3** (1 equiv), TBAFe (5 mol%), and PPh_3 (6 mol%) in the given solvent at 80 °C. [b] Determined by GC integration of the crude reaction mixture with dodecane as internal standard. [c] Determined by GC integration of the crude reaction mixture.

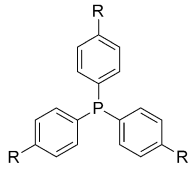
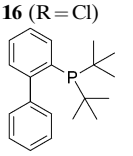
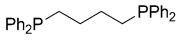
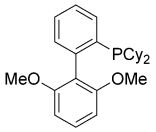
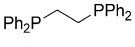
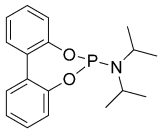
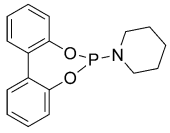
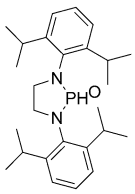
Maleic acid-derived sulfinate donors **6** and **9** were chosen as alternative pronucleophiles, since they open the chance for potential immobilization and hence for a regeneration of the sulfonylating agent. When commercially unavailable thiols are used, a procedure of Kotake et al. can be employed for synthesis of thioethers.[34] By employing thiosaccharine, the C–S bond in the desired thiols is formed on nucleophilic substitution. Cleavage of the resulting thioether in the presence of maleimide **7** gives thioethers of type **8** in a one-pot fashion.

Initial experiments focused on the use of methyl vinyl ketone derived sulfone **3** as a pronucleophilic sulfinate donor. The previously established standard allylation conditions for salt-free allylic substitutions were chosen as a starting point with allyl carbonate **10** as test substrate (Table 1).

As previously observed,[29e] *p*-methoxy triaryl phosphine **15** proved to be the best ligand, resulting in clean formation of products **13** in good yield. However, the improved yield is at the expense of π-bond isomerization. Apparently, the nucleophilicity of the catalyst combination of TBAFe/P ligand is not sufficient for a fast reaction. The use of more electron rich *N*-heterocyclic carbene ligands (NHC) might increase the nucleophilicity. To suppress undesired reactions between ligand and protic solvent we initially tested several NHC ligands, employing methyl tert-butyl ether (MTBE) as an aprotic solvent that was shown to be suitable for TBAFe-catalyzed allylic substitutions in earlier investigations (Table 4).[29c,d]

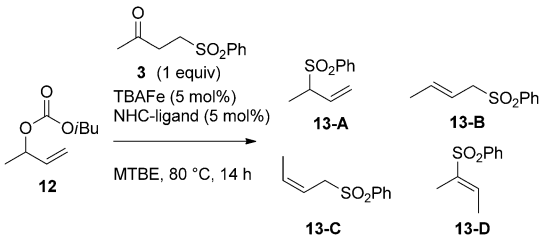
Table 3. Ligand screening: P ligands.[a]

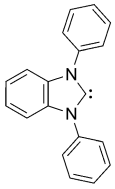
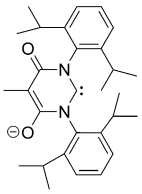
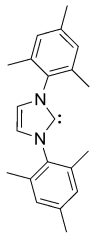
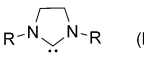
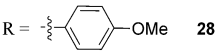
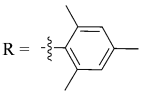
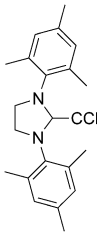


Entry	P ligand	Yield [%][b]	13-A:13-B:13-C:13-D[c]
1	 **14** (R=CH_3)	80	69:16:3:12
2	**15** (R = OCH_3)	88	54:17:4:24
3	**16** (R = Cl)	< 10	n.d.
4	 **17**	84	38:13:2:47
5	 **18**	< 10	n.d.
6	 **19**	79	52:12:2:34
7	 **20**	traces	n.d.
8	 **21**	61	52:16:2:29
9	 **22**	35	72:16:4:9
10	 **23**	40	75:13:2:10

[a] Reactions were performed on a 0.5 mmol scale in *i*BuOH (0.25 mL) with sulfinate donor **3** (1 equiv), TBAFe (5 mol%), and the given ligand (6 mol%) at 80°C and were stopped after 14 h. [b] Determined by GC integration of the crude reaction mixture with dodecane as internal standard. [c] Determined by GC integration of the crude reaction mixture.

Table 4. Ligand screening: carbene ligands.[a]



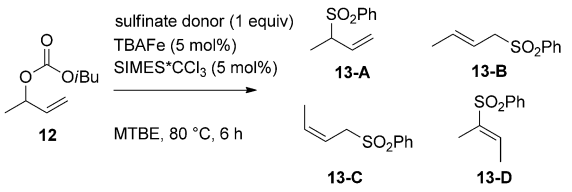
Entry	Carbene ligand	Yield [%][e]	13-A:13-B:13-C:13-D[f]
1[b]	 **24**	65	44:41:3:13
2[c]	 **25**	6	62:20:3:15
3[b]	 **26**	35	44:53:3:n.d.
4[b]	 **27** (R = *i*Pr)	26	71:22:3:5
5[b]	 **28**	16	86:11:1:2
6[b]	 **29**	99	4:53:6:37
7[d]	 **30** (SIMES*CCl_3)	98	81:14:2:3

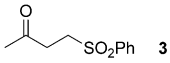
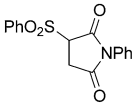
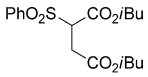
[a] Reactions were performed on a 0.5 mmol scale in MTBE (0.5 mL) with sulfinate donor **3** (1 equiv), TBAFe (5 mol%), and the given NHC ligand (5 mol%) at 80°C and were stopped after 14 h. [b] Ligands were generated from their BF_4 or PF_6 salts by using KO*t*Am in MTBE at 60°C. [c] Ligand generated from neutral precursor using KO*t*Am in MTBE at 60°C. [d] Ligand generated thermally in a microwave reactor (MTBE, 80°C, 30 min) from its $CHCl_3$ adduct. [e] Determined by GC integration of the crude reaction mixture with dodecane as internal standard. [f] Determined by GC integration of the crude reaction mixture.

Whereas most of the NHC ligands did not show any significant improvement, mesityl-substituted NHC ligand 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (SIMES, **29**) gave a first positive indication (Table 4, entry 6). However, although the yields were almost quantitative, the regioselectivity and π-bond stability were poor. To investigate the role of the counteranion and/or added base we finally employed the chloroform adduct of ligand **29**, SIMES·CCl_3 (**30**),[31] and

were surprised to find that base-free, thermal liberation of the SIMES ligand allowed for full conversion and reasonable regioselectivity (Table 4, entry 7). More importantly, almost no π-bond isomerization was detected. At this point the influence of the sulfinate donor was investigated (Table 5).

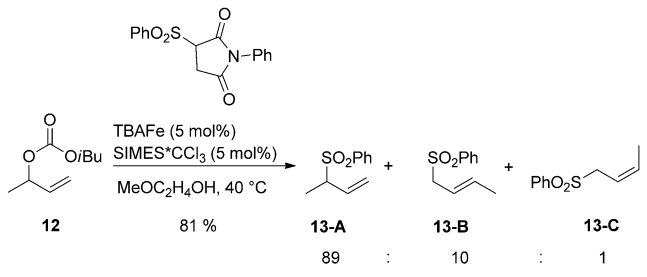
Table 5. Influence of the sulfinate donor.[a]



Entry	Sulfinate donor		Yield [%][b]	13-A:13-B:13-C:13-D[c]
1		**3**	96	81:14:2:3
2		**9**	100	89:5:2:3
3		**6**	17	91:5:1:3

[a] Reactions were performed on a 0.5 mmol scale in MTBE (0.5 mL) with the given sulfinate donor (1 equiv), TBAFe (5 mol%), and SIMES (5 mol%, generated thermally from SIMES·CCl_3 in a microwave reactor) at 80 °C and were stopped after 6 h. [b] Determined by GC integration of the crude reaction mixture with dodecane as internal standard. [c] Determined by GC integration of the crude reaction mixture.

Maleimide-derived sulfinate donor **9** proved to be superior to the other tested substrates. The corresponding sulfonylation product **13** was formed in quantitative yield and good regioselectivity in favor of *ipso* substitution product **13-A**. π-Bond isomerization was almost undetectable. Fine-tuning of solvent and temperature finally led to a protocol that allowed sulfonylation at 40 °C with only 5 mol% of iron catalyst and 5 mol% of SIMES·CCl_3. The desired product **13-A** was obtained in high yield with good *ipso* selectivity and no π-bond isomerization (Scheme 4). Furthermore, this reaction shows that NHC ligands like SIMES can be employed for reactions in alcoholic solvents. Undesired side reactions

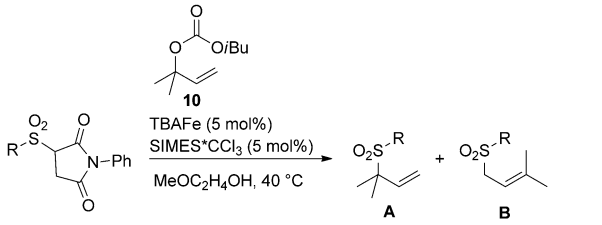


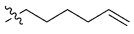
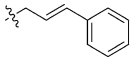
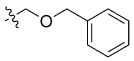
Scheme 4. Regioselective allylic sulfonylation (yields of isolated products, product composition determined by GC analysis).

that might be envisioned due to the use of a nucleophilic carbene in protic solvents were not observed.

Subsequently, different substituted sulfinate donors **31**–**39** were prepared and subjected to the reaction conditions using carbonate **10** as the allylating agent (Table 6). The

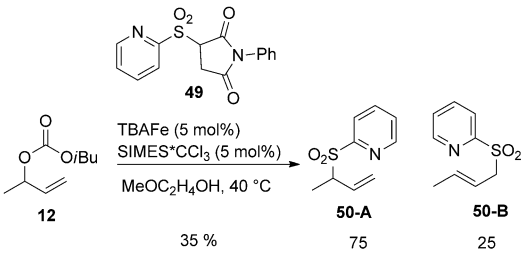
Table 6. Iron-catalyzed allylic sulfonylation: scope of sulfinate donors.[a]



Entry	R	Sulfinate donor	Product (A:B)[b]	Yield [%][c]
1		**31**	**40** (94:6)	87
2		**32**	**41** (96:4)	83
3		**33**	**42** (92:8)	71
4		**34**	**43** (97:3)	86
5		**35**	**44** (98:2)	81
6		**36**	**45** (94:6)	81
7		**37**	**46** (92:8)	84
8		**38**	**47** (94:6)	54
9		**39**	**48** (94:6)	54

[a] Reactions were performed on a 0.5 mmol scale in 2-methoxyethanol (0.5 mL) with the given sulfinate donor (1 equiv), TBAFe (5 mol%), and SIMES (5 mol%, generated thermally from SIMES·CCl_3 in a microwave reactor) at 40 °C. [b] Determined by GC or ^{1}H NMR integration of the crude product. [c] Yield of isolated product.

concept of generating the active sulfinate in situ proved to be broadly applicable. A variety of different aromatic and aliphatic allyl sulfones **40**–**48** were isolated in good to excellent yields and regioselectivities. The method displays broad tolerance of functional groups. Esters, ethers, and strained carbocycles are tolerated (Table 6, entries 7–9). Heteroaromatic sulfones are important structural motifs that allow for Julia–Kocienski-type olefination reactions. We wondered whether this new sulfonylation method would also be applicable to heteroaromatic sulfinate donors such as pyridyl derivative **49**, and found that corresponding allylic sulfone **50** was formed with 3:1 regioselectivity in favor of the *ipso* substitution product. π-Bond isomerization was not observed (Scheme 5). However, although this sulfonylation reaction is an interesting method for direct preparation of Julia–Ko-

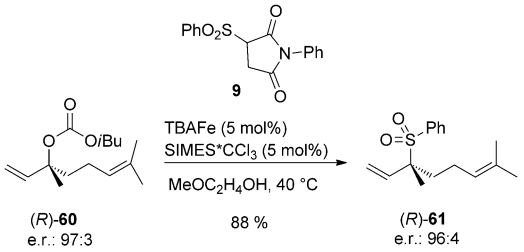


Scheme 5. Preparation of heteroaromatic sulfones.

cienski-type olefination precursors, the moderate regioselectivity must be improved in future work.

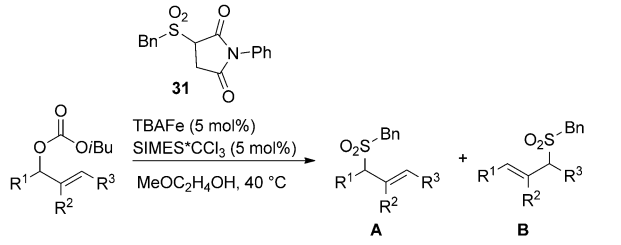
Having found a suitable sulfinate donor, we investigated the regioselective course of the allylation using different allylic carbonates. Apart from regioselectivity, π-bond isomerization was another focus of these studies (Table 7). Various allylic carbonates were sulfonylated in moderate to good yields and regioselectivities. The regioselectivities observed in this study clearly point to a π-allyl mechanism.[29c] The amount of the sterically less hindered product increased with increasing size of substituent R^1 (Table 7, entries 1, 2, 5, and 6). Another driving force for a change in the regioselectivity is the preferred formation of the regioisomer in which the C=C-bond is in conjugation with unsaturated substituents (Table 7, entries 3 and 7–10). The preference for a π-allyl mechanism when SIMES is used as ligand is in line with our previous observations in the corresponding allylic alkylation.[29c,d] However, in no case was π-bond isomerization observed. Furthermore, the electronic nature of substituent R^3 plays a crucial role in the reactivity of the starting material. In general the transformations are slower in the case of disubstituted C=C bonds. While electron-releasing substituents like alkyl groups slow down the reaction, –I substituents such as aryl groups maintain the reactivity of the starting material (Table 7, entries 7 and 8).

Apart from the regioselective course of this transformation, the stereoselectivity of C–S bond formation is of similar importance. To confirm that the stereochemical information is conserved in the catalytic process, enantiomerically enriched (*R*)-linalyl carbonate **60** was subjected to the standard sulfonylation conditions, and desired product **61** was obtained with good enantiomeric purity in high yield (Scheme 6). The new C–S bond was formed with a high preference for the *ipso*-substitution product (>92%) and almost perfect retention of configuration. Test experiments with the same system in the absence of sulfone **9** revealed configurational stability of the allylic carbonate under the reaction conditions.



Scheme 6. Stereochemical course of the allylic sulfonylation (yields of isolated products, e.r. determined by chiral HPLC analysis).

Table 7. Iron-catalyzed allylic sulfonylation: scope of allylic carbonates.[a]



Entry	R^1	R^2	R^3	Product (**A**:**B**)[b]	Yield [%][c]
1	CH_3	H	H	**51** (91:9)	86
2	$(CH_2)_3CH_3$	H	H	**52** (79:21)	81
3	Ph	H	H	**53** (59:41)	23
4	CO_2CH_3	H	H	**54** (9:91)	42
5	$CH(CH_3)_2$	H	H	**55** (50:50)	30
6	CH_2OCH_2Ph	H	H	**56** (61:39)	62
7	CH_3	H	Ph	**57** (81:19)	83
8	Ph	H	CH_3	**57** (19:81)	39
9	H	H	Ph	**53** (77:23)	44
10	Ph	$CO_2C(CH_3)_3$	H	**58** (1:99)	52
11	Me	H	Me	**59** (–)	88

[a] Reactions were performed on a 0.5 mmol scale in 2-methoxyethanol (0.5 mL) with sulfinate donor **31** (1 equiv), TBAFe (5 mol%), and SIMES (5 mol%, generated thermally from SIMES·CCl_3 in a microwave reactor) at 40 °C. [b] Determined by GC or ^{1}H NMR integration of the crude product. [c] Yield of isolated product.

Conclusion

We have reported broadly applicable, practical, iron-catalyzed allylic sulfonylation under salt-free and neutral reaction conditions at slightly elevated temperature of 40 °C in short reaction times. The use of an α-sulfonyl succinimide as a sulfinate donor that liberates the sulfinate by base-mediated β-elimination is the key feature of this protocol. A variety of functionalized aromatic, heteroaromatic, and aliphatic sulfinate donors were prepared and successfully employed in the allylation process. Although the regioselectivity of the allylation reaction needs to be improved in future studies, the good reactivity of the readily accessible α-sulfonyl succinimides and the lack of any π-bond isomerization may open a new synthetic pathway for the preparation of functionalized allylic sulfones as building blocks in organic synthesis.

Experimental Section

General remarks: All reactions and manipulations which are sensitive to air or moisture were performed under dry nitrogen by using standard Schlenk techniques. All solvents were purified prior to use. All chemicals

were purchased from Acros Organics, Sigma Aldrich, or Alfa Aesar. GC experiments were conducted on a Thermo Finnigan Focus GC with dodecane as internal standard. Microwave experiments were conducted in a CEM Discovery microwave reactor. NMR spectra were recorded on a Bruker AV300 spectrometer at 300 MHz (^{1}H NMR), 75 MHz (^{13}C NMR) or a Bruker AV500 spectrometer at 500 MHz (^{1}H NMR), 125.6 MHz (^{13}C NMR). Chemical shifts are reported in ppm downfield versus tetramethylsilane as internal standard. Signals are indicated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), or m_c (multiplet centered). IR spectra were measured on a Bruker Vector 22 FTIR spectrometer in ATR mode. Mass spectra were measured on a GC-MS HP6890 or on a Bruker Micro-TOF-Q. Thiosaccharine sodium salt,[32] *N*-phenylmaleimide,[33] $Bu_4N[Fe(CO)_3NO]$,[29d] and SIMES·CCl_3[31] were prepared according to known methods.

General procedure for preparation of thioethers by thio Michael addition (GPI): Thioethers were prepared according to a modified literature procedure from Kotake et al.[34] A solution of alkyl bromide or chloride in DMF (3 mL) was added to a solution of thiosaccharine sodium salt (1.11 g, 5 mmol) in DMF (3.5 mL) under N_2 atmosphere at room temperature. The solution was heated to 50 °C and stirred overnight. Then deionized water was added to precipitate the product, which was collected by filtration and recrystallized from ethanol. The obtained product (3.5 mmol) was then dissolved in CH_3CN (6 mL) under N_2 atmosphere, treated with a solution of piperidine (302 mg, 3.5 mmol) in CH_3CN (3 mL), and stirred for 30 min at room temperature. Then a solution of *N*-phenylmaleimide (607 mg, 3.5 mmol) in CH_3CN (9 mL) was added. After stirring for 3 h at room temperature triethylamine (7 drops) was added, and the mixture stirred for a further 1.5 h. The solvent was evaporated and the residue purified by flash column chromatography.

General procedure for the preparation of thioethers by thio Michael addition (GPII): A solution of mercaptan (20.2 mmol) was added to a solution of *N*-phenylmaleimide (20 mmol) and triethylamine (210 μL, 1.4 mmol) in benzene (35 mL) over 30 min. The solution was diluted with benzene (20 mL) and stirred at room temperature over night. The solvent was then evaporated and the resulting product washed with petroleum ether (for solid products) and dried in vacuo.

General procedure for the oxidation of thioethers to sulfones (GPIII): A solution of thioether (20 mmol) in dichloromethane (100 mL) was cooled to 0 °C and *meta*-chloroperoxybenzoic acid (mCPBA; 70 %, 10.4 g, 42 mmol) was added. After stirring for 10 min the solution was warmed to room temperature and stirred for one hour. Then the solution was filtered to remove the white precipitate, washed with a saturated Na_2CO_3 solution, dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting product was purified by recrystallization from EtOH or column chromatography.

General procedure for the oxidation of thioethers to sulfones (GPIV): A solution of oxone (2.8 g, 4.5 mmol) in demineralized water was added to a suspension of the thioether (1.5 mmol) in methanol (30 mL). The reaction mixture was stirred over night and extracted with ethyl acetate. The combined organic phases were dried over Na_2SO_4, filtered, and the solvent evaporated in vacuo. The residue was purified by chromatography on silica gel.

1-Phenyl-3-(phenylthio)pyrrolidine-2,5-dione (8): Thioether **8** was prepared according to GPII and obtained as a white solid (2.74 g, 9.6 mmol, 96 % yield). R_f = 0.29 (petroleum ether/ethyl acetate 3/1); m.p. 191–192 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62–7.56 (m, 2H; Ar-H), 7.48–7.33 (m, 6H; Ar-H), 7.09–7.03 (m, 2H; Ar-H), 4.16 (dd, J = 9.2, 3.8 Hz, 1H; SCH), 3.34 (dd, J = 18.8, 9.2 Hz, 1H; SCHCH_2), 2.92 ppm (dd, J = 18.8, 3.8 Hz, 1H; SCHCH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.5 (C=O), 173.5 (C=O), 135.2 (2C; Ar-C), 131.5 (Ar-C), 129.8 (Ar-C), 129.7 (Ar-C), 129.5 (2C; Ar-C), 129.2 (2C; Ar-C), 128.3 (Ar-C), 126.3 (2C; Ar-C), 44.2 (SCH), 36.4 ppm (SCHCH_2); IR (neat): $\tilde{\nu}$ = 3471, 3063, 2931, 1777, 1705, 1594, 1573, 1497, 1473, 1456, 1440, 1390, 1303, 1290, 1277, 1198, 1157, 1069, 1024, 1003, 942, 922, 778, 737, 694 cm^{-1}; MS (ESI): *m/z* (%): 306 (100) [*M*+Na$^+$], 284 (42) [*M*+H$^+$], 174 (9), 163 (2), 146 (14), 139 (5); HRMS (ESI): *m/z* calcd for $C_{16}H_{13}NO_2S$+Na: 306.0559, found: 306.0570.

1-Phenyl-3-(phenylsulfonyl)pyrrolidine-2,5-dione (9): Sulfone **9** was prepared according to GPIII. After recrystallization from ethanol the product was obtained as a white solid (2.54 g, 8.1 mmol, 84 % yield). R_f = 0.39 (petroleum ether/ethyl acetate 1/1); m.p. 190–192 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.00–7.94 (m, 2H; Ar-H), 7.76 (t, J = 7.5 Hz, 1H; Ar-H), 7.66–7.59 (m, 2H; Ar-H), 7.50–7.37 (m, 3H; Ar-H), 7.20–7.13 (m, 2H; Ar-H), 4.48 (dd, J = 9.7, 3.7 Hz, 1H; SO_2CH), 3.56 (dd, J = 19.3, 3.7 Hz, 1H; SO_2CHCH_2), 3.26 ppm (dd, J = 19.3, 9.7 Hz, 1H; SO_2CHCH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.9 (C=O), 167.7 (C=O), 136.4 (Ar-C), 135.1 (Ar-C), 131.0 (Ar-C), 129.6 (2C; Ar-C), 129.5 (2C; Ar-C), 129.3 (2C; Ar-C), 129.2 (Ar-C), 126.3 (2C; Ar-C), 63.6 (SO_2CH), 29.2 ppm (SO_2CHCH_2); IR (neat): $\tilde{\nu}$ = 3000, 2943, 1778, 1710, 1594, 1584, 1498, 1447, 1390, 1332, 1322, 1308, 1197, 1179, 1157, 1135, 1084, 1072, 1030, 999, 928, 797, 760, 689 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 316 (17) [*M*+H$^+$], 174 (6), 143 (2), 125 (2); HRMS (ESI): *m/z* calcd for $C_{16}H_{13}NO_4S$+Na: 338.0459, found: 338.0457.

3-(Benzylsulfonyl)-1-phenylpyrrolidine-2,5-dione (31): Thioether **31** was prepared according to GPII and obtained as a white solid (4.83 g, 16.2 mmol, 81 % yield). R_f = 0.21 (petroleum ether/ethyl acetate 3/1); m.p. 141–142 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53–7.27 (m, 10H; Ar-H), 4.29 (d, J = 13.7 Hz, 1H; SCH_2), 3.90 (d, J = 13.7 Hz, 1H; SCH_2), 3.65 (dd, J = 9.5, 3.8 Hz, 1H; SCH), 3.16 (dd, J = 18.9, 9.5 Hz, 1H; SCHCH_2), 2.58 ppm (dd, J = 18.9, 3.8 Hz, 1H; SCHCH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.7 (C=O), 173.7 (C=O), 136.7 (Ar-C), 131.6 (Ar-C), 129.3 (2C; Ar-C), 129.2 (2C; Ar-C), 128.8 (Ar-C), 128.7 (2C; Ar-C), 127.6 (Ar-C), 126.4 (2C; Ar-C), 37.2 (SC), 36.0 (SC), 35.5 ppm (SCHCH_2); IR (neat) $\tilde{\nu}$ = 3064, 3029, 2947, 1780, 1701, 1594, 1490, 1454, 1393, 1210, 1186, 1165, 1070, 1025, 928, 780, 749, 697, 630 cm^{-1}; MS (ESI): *m/z* (%): 320 (100) [*M*+Na$^+$], 242 (1); HRMS (ESI): *m/z* calcd for $C_{17}H_{15}NO_2S$+Na: 320.0716, found: 320.0695. The thioether was then oxidized to sulfone **31** according to GPIII. After recrystallization from EtOH the product was obtained as a white solid (4.48 g, 13.6 mmol, 84 % yield). R_f = 0.62 (petroleum ether/ethyl acetate 1/1); m.p. 174–175 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67–7.28 (m, 10H; Ar-H), 4.98 (d, J = 14.2 Hz, 1H; SO_2CH_2), 4.49 (d, J = 14.2 Hz, 1H; SO_2CH_2), 4.28 (dd, J = 9.9, 4.2 Hz, 1H; SO_2CH), 3.41 (dd, J = 19.2, 4.2 Hz, 1H; SO_2CHCH_2), 3.05 ppm (dd, J = 19.2, 9.9 Hz, 1H; SO_2CHCH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.9 (C=O), 169.2 (C=O), 137.4 (Ar-C), 135.2 (Ar-C), 131.3 (2C; Ar-C), 129.6 (Ar-C), 129.4 (2C; Ar-C), 129.3 (2C; Ar-C), 127.0 (Ar-C), 126.5 (2C; Ar-C), 58.5 (SO_2C), 56.9 (SO_2C), 27.9 ppm (SO_2CHCH_2); IR (neat): $\tilde{\nu}$ = 3059, 2935, 1788, 1717, 1702, 1599, 1501, 1456, 1389, 1297, 1174, 1162, 1124, 1029, 932, 829, 798, 781, 748, 697, 635, 623, 613, 567, 544 cm^{-1}; MS (ESI): *m/z* (%): 352 (100) [*M*+Na$^+$], 301 (1); HRMS (ESI): *m/z* calcd for $C_{17}H_{15}NO_4S$+Na: 352.0614, found: 352.9614.

3-(Naphthalen-1-ylmethylsulfonyl)-1-phenylpyrrolidine-2,5-dione (32): The thioether was prepared according to GPI and obtained after flash column chromatography (petroleum ether/ethyl acetate gradient 10/1→5/1) as a white solid (1.25 g, 3.6 mmol, 72 % yield). R_f = 0.19 (petroleum ether/ethyl acetate 5/1); m.p. 121–123 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.18 (d, J = 8.3 Hz, 1H; Ar-H), 7.92–7.80 (m, 2H; Ar-H), 7.63–7.28 (m, 9H; Ar-H), 4.73 (d, J = 13.6 Hz, 1H; SCH_2), 4.49 (d, J = 13.6 Hz, 1H; SCH_2), 3.73 (dd, J = 9.3, 3.8 Hz, 1H; SCH), 3.12 (dd, J = 18.9, 9.32 Hz, 1H; SCHCH_2), 2.53 ppm (dd, J = 18.9, 3.8 Hz, 1H; SCHCH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 176.0 (C=O), 173.7 (C=O), 134.2 (Ar-C), 132.0 (Ar-C), 131.6 (Ar-C), 131.3 (Ar-C), 129.3 (2C; Ar-C), 129.0 (Ar-C), 128.9 (Ar-C), 128.8 (Ar-C), 128.1 (Ar-C), 126.4 (3C; Ar-C), 126.1 (Ar-C), 125.2 (Ar-C), 123.9 (Ar-C), 37.8 (SC), 35.4 (SC), 33.8 ppm (SCHCH_2); IR (neat): $\tilde{\nu}$ = 3055, 2935, 1781, 1703, 1594, 1498, 1454, 1393, 1205, 1184, 1075, 1018, 948, 929, 793, 777, 750, 695, 629 cm^{-1}; MS (ESI): *m/z* (%): 370 (100) [*M*+Na$^+$], 303 (5), 279 (2), 242 (10), 226 (44), 201 (2), 158 (2), 141 (64); HRMS (ESI): *m/z* calcd for $C_{21}H_{17}NO_2S$+Na: 370.0872, found: 370.0864. The thioether was then oxidized to sulfone **32** according to GPIII. After column chromatography (petroleum ether/ethyl acetate 1/1) the product was obtained as a white solid (400 mg, 1.05 mmol, 70 % yield). R_f = 0.60 (petroleum ether/ethyl acetate 1/1); m.p. 198–199 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.28 (d, J = 8.3 Hz, 1H; Ar-H), 7.95 (d, J = 8.1 Hz, 1H; Ar-H), 7.92 (d, J = 8.5 Hz, 1H; Ar-H), 7.87 (d, J = 7.1 Hz, 1H; Ar-H), 7.67–7.44 (m, 6H; Ar-H), 7.38–7.32 (m, 2H; Ar-H), 5.40 (d, J = 14.7 Hz, 1H; SO_2CH_2), 5.17 (d, J = 14.7 Hz, 1H; SO_2CH_2), 4.50 (dd,

J=9.8, 4.2 Hz, 1H; SO_2CH), 4.41 (dd, J=19.3, 4.2 Hz, 1H; SO_2CHCH_2), 3.03 ppm (dd, J=19.3, 9.8 Hz, 1H; SO_2CHCH_2); ^{13}C NMR (125 MHz, $CDCl_3$): δ=172.0 (C=O), 169.4 (C=O), 134.1 (Ar-C), 132.4 (Ar-C), 131.1 (Ar-C), 131.0 (Ar-C), 130.7 (Ar-C), 129.5 (3C; Ar-C), 129.0 (Ar-C), 127.3 (Ar-C), 126.6 (Ar-C), 126.5 (2C; Ar-C), 125.4 (Ar-C), 124.0 (Ar-C), 123.2 (Ar-C), 57.6 (SO_2C), 55.9 (SO_2C), 27.7 ppm (SO_2CHCH_2); IR (neat): $\tilde{\nu}$= 2985, 1966, 1712, 1596, 1498, 1386, 1313, 1192, 1129, 928, 776, 691, 655 cm^{-1}; MS (APCI): m/z (%): 380 (2) [M+H^+], 316 (8), 240 (8), 223 (2), 176 (11), 141 (100), 115 (2); HRMS (APCI): m/z calcd for $C_{21}H_{17}NO_4S$+H: 380.0951, found: 380.0962.

3-(Hexadecylsulfonyl)-1-phenylpyrrolidine-2,5-dione (33): The thioether was prepared according to GPII and obtained as a white solid (1.81 g, 4.2 mmol, 84% yield). R_f=0.64 (petroleum ether/ethyl acetate 3/1); m.p. 65–67°C; ^1H NMR (300 MHz, $CDCl_3$): δ=7.53–7.27 (m, 5H; Ar-H), 3.87 (dd, J=9.1, 3.6 Hz, 1H; SCH), 3.31 (dd, J=18.7, 9.1 Hz, 1H; $SCHCH_2$), 3.01–2.90 (m, 1H; SCH_2), 2.86–2.75 (m, 1H; SCH_2), 2.69 (dd, J=18.7, 3.6 Hz, 1H; $SCHCH_2$), 1.66 (m_c, 2H; SCH_2CH_2), 1.49–1.17 (m, 26H; S-$(CH_2)_2(CH_2)_{13}$), 0.88 ppm (m_c, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=175.6 (C=O), 173.8 (C=O), 131.7 (Ar-C), 129.2 (2C; Ar-C), 128.8 (Ar-C), 126.4 (2C; Ar-C), 39.1 (SCH), 36.2 ($SCHCH_2$), 31.9 (2C; CH_2), 29.7 (3C; CH_2), 29.6 (3C; CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 29.0 (CH_2), 28.8 (CH_2), 22.7 (CH_2), 14.1 ppm (CH_3); IR (neat): $\tilde{\nu}$=2916, 2849, 1782, 1701, 1597, 1502, 1466, 1393, 1174, 1074, 930, 747, 722, 697, 623, 570 cm^{-1}; MS (EI, 70 eV): m/z (%): 454 (100) [M+Na^+]; HRMS (ESI): m/z calcd for $C_{26}H_{41}NO_2S$: 454.2750, found: 454.2753. The thioether was then oxidized to sulfone **33** according to GPIII. After column chromatography (petroleum ether/ethyl acetate 2/1) the product was obtained as a white solid (689 mg, 1.49 mmol, 74% yield). R_f=0.47 (petroleum ether/ethyl acetate 2/1); m.p. 136–137°C; ^1H NMR (300 MHz, $CDCl_3$): δ=7.54–7.40 (m, 3H; Ar-H), 7.32–7.27 (m, 2H; Ar-H), 4.37 (dd, J=9.8, 4.0 Hz, 1H; SO_2CH), 3.56–3.43 (m, 3H; SO_2CHCH_2 and SO_2CH_2), 3.20 (dd, J=19.2, 9.8 Hz, 1H; SO_2CHCH_2), 2.02–1.89 (m, 2H; $SO_2CH_2CH_2$), 1.55–1.45 (m, 2H; $SO_2(CH_2)_2CH_2$), 1.41–1.21 (m, 24H; $SO_2(CH_2)_3(CH_2)_{12}$), 0.88 ppm (m_c, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=172.1 (C=O), 168.9 (C=O), 131.0 (Ar-C), 129.4 (2C; Ar-C), 129.3 (Ar-C), 126.4 (2C; Ar-C), 59.9 (SO_2CH), 52.7 (SO_2CH_2), 31.9 (CH_2), 29.7 (2C; CH_2), 29.7 (2C; CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 29.0 (CH_2), 28.4 (CH_2), 27.9 (CH_2), 22.7 (CH_2), 21.7 (CH_2), 14.1 ppm (CH_3); IR (neat) $\tilde{\nu}$=2852, 2916, 2850, 1782, 1710, 1598, 1500, 1471, 1396, 2390, 1269, 1201, 1185, 1120, 928, 825, 734, 720, 695, 626, 584 cm^{-1}; MS (ESI): m/z (%): 486 (100) [M+Na^+], 398 (13), 342 (1), 311 (1); HRMS (ESI): m/z calcd for $C_{26}H_{41}NO_4S$+Na: 486.2649, found: 486.2635.

3-(Cyclohexylsulfonyl)-1-phenylpyrrolidine-2,5-dione (34): The thioether was prepared according to GPI and obtained after flash column chromatography (petroleum ether/ethyl acetate gradient 5/1→4/1) as a colorless solid (340 mg, 1.17 mmol, 23% yield). R_f=0.27 (petroleum ether/ethyl acetate 5/1); m.p. 95–96°C; ^1H NMR (300 MHz, $CDCl_3$): δ=7.52–7.44 (m, 2H; Ar-H), 7.44–7.36 (m, 1H; Ar-H), 7.33–7.27 (m, 2H; Ar-H), 3.97 (dd, J=9.0, 3.7 Hz, 1H; OCCH), 3.31 (dd, J=18.4, 9.0 Hz, 1H; $OCCH_2$), 3.33–3.21 (m, 1H; SCH), 2.69 (dd, J=18.4, 3.7 Hz, 1H; $OCCH_2$), 2.25–2.13 (m, 1H; Cyclohexyl-H), 2.02–1.90 (m, 1H; Cyclohexyl-H), 1.86–1.73 (m, 2H; Cyclohexyl-H), 1.69–1.59 (m, 1H; Cyclohexyl-H), 1.48–1.19 ppm (m, 5H; Cyclohexyl-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=175.5 (C=O), 173.9 (C=O), 131.7 (Ar-C), 129.2 (2C; Ar-C), 128.8 (Ar-C), 126.4 (2C; Ar-C), 43.9 (OCCH), 37.7 (SCH), 36.5 (CH_2), 33.5 (CH_2), 32.9 (CH_2), 26.0 (CH_2), 25.7 (CH_2), 25.6 ppm (CH_2); IR (neat): $\tilde{\nu}$=2930, 2851, 2555, 2185, 2107, 1967, 1703, 1594, 1504, 1455, 1383, 1203, 1164, 1074, 967, 752, 698 cm^{-1}; MS (ESI): m/z (%): 312 (100) [M+Na^+], 208 (19); HRMS (ESI): m/z calcd for $C_{16}H_{19}NO_2S$+Na: 312.1029, found: 312.1023. The thioether was then oxidized to sulfone **34** according to GPIV. After column chromatography (petroleum ether/ethyl acetate 2/1) the product was obtained as a white solid (265 mg, 0.82 mmol, 70% yield). R_f=0.23 (petroleum ether/ethyl acetate 2/1); m.p. 147–149°C; ^1H NMR (300 MHz, $CDCl_3$): δ=7.54–7.39 (m, 3H; Ar-H), 7.31–7.25 (m, 2H; Ar-H), 4.51 (dd, J=9.8, 3.8 Hz, 1H; OCCH), 3.68 (tt, J=12.1, 3.5 Hz, 1H; SO_2CH), 3.51 (dd, J=19.2, 3.8 Hz, 1H; $OCCH_2$), 3.19 (dd, J=19.2, 9.8 Hz, 1H; $OCCH_2$), 2.33–2.22 (m, 2H; Cyclohexyl-H), 2.04–1.91 (m, 2H; Cyclohexyl-H), 1.81–1.57 (m, 3H; Cyclohexyl-H), 1.51–1.19 ppm (m, 3H; Cyclohexyl-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=172.3 (C=O), 169.0 (C=O), 131.0 (Ar-C), 129.4 (2C; Ar-C), 129.3 (Ar-C), 126.4 (2C; Ar-C), 60.1 (OCCH), 56.8 (SO_2CH), 28.0 (CH_2), 26.8 (CH_2), 25.0 (CH_2), 24.9 (CH_2), 24.7 (CH_2), 22.6 ppm (CH_2); IR (neat): $\tilde{\nu}$=2933, 2853, 1967, 1781, 1708, 1598, 1499, 1454, 1391, 1308, 1267, 1184, 1124, 926, 851, 821, 773, 695, 604 cm^{-1}; MS (APCI): m/z (%): 322 (38) [M+H^+], 240 (99), 198 (3), 176 (100), 149 (17); HRMS (APCI): m/z calcd for $C_{16}H_{19}NO_4S$+H: 322.1108, found: 322.1102.

3-(Hex-5-enylsulfonyl)-1-phenylpyrrolidine-2,5-dione (35): The thioether was prepared according to GPI and obtained after flash column chromatography (petroleum ether/ethyl acetate gradient 10/1→5/1) as a colorless solid (876 mg, 3.03 mmol, 61% yield). R_f=0.22 (petroleum ether/ethyl acetate 5/1); m.p.: 42–43°C; ^1H NMR (300 MHz, $CDCl_3$): δ=7.53–7.45 (m, 2H; Ar-H), 7.44–7.37 (m, 1H; Ar-H), 7.33–7.27 (m, 2H; Ar-H), 5.80 (ddt, J=17.2, 10.2, 6.7 Hz, 1H; =CH), 5.06–4.94 (m, 2H; $=CH_2$), 3.87 (dd, J=9.1, 3.4 Hz, 1H; SCH), 3.31 (dd, J=18.9, 9.1 Hz, 1H; $SCHCH_2$), 2.98 (ddd, J=12.5, 8.0, 6.1 Hz, 1H; SCH_2), 2.82 (ddd, J=12.5, 7.8, 6.4 Hz, 1H; SCH_2), 2.68 (dd, J=18.9, 3.4 Hz, 1H; $SCHCH_2$), 2.09 (q, J=7.0 Hz, 2H; $=CHCH_2$), 1.80–1.60 (m, 2H; SCH_2CH_2), 1.60–1.45 ppm (m, 2H; $=CHCH_2CH_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ=175.5 (C=O), 173.8 (C=O), 138.2 (=CH), 131.6 (Ar-C), 129.2 (2C; Ar-C), 128.8 (Ar-C), 126.4 (2C; Ar-C), 114.9 ($=CH_2$), 39.0 (SCH), 36.2 ($SCHCH_2$), 33.2 (CH_2), 31.7 (CH_2), 28.4 (CH_2), 27.9 ppm (CH_2); IR (neat): $\tilde{\nu}$=3071, 2941, 2920, 2856, 1966, 1780, 1703, 1492, 1455, 1430, 1391, 1299, 1210, 1182, 1157, 992, 905, 790, 751, 697, 629 cm^{-1}; MS (ESI): m/z (%): 312 (100) [M+Na^+], 290 (79), 242 (4), 208 (44), 182 (1), 149 (4), 117 (1); HRMS (ESI): m/z calcd for $C_{16}H_{19}NO_2S$+Na: 312.1029, found: 312.1031. The thioether was then oxidized to sulfone **35** according to GPIV. After column chromatography (petroleum ether/ethyl acetate 1/1) the product was obtained as a white solid (566 mg, 1.76 mmol, 58% yield). R_f=0.52 (petroleum ether/ethyl acetate 1/1); m.p. 123–124°C; ^1H NMR (300 MHz, $CDCl_3$): δ=7.54–7.40 (m, 3H; Ar-H), 7.31–7.25 (m, 2H; Ar-H), 5.78 (ddt, J=17.1, 10.3, 6.8 Hz, 1H; =CH), 5.05 (d, J=17.1 Hz, 1H; $=CH_2$), 5.01 (d, J=10.3 Hz, 1H; $=CH_2$), 4.37 (dd, J=9.7, 4.0 Hz, 1H; SO_2CH), 3.55–3.45 (m, 3H; SO_2CH_2 and SO_2CHCH_2), 3.20 (dd, J=19.2, 9.7 Hz, 1H; SO_2CH_2), 2.14 (q, J= 7.2 Hz, 2H; $=CHCH_2$), 2.06–1.91 (m, 2H; $SO_2CH_2CH_2$), 1.67–1.57 ppm (m, 2H; $SO_2(CH_2)_2CH_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ= 172.1 (C=O), 168.9 (C=O), 137.3 (=CH), 130.8 (Ar-C), 129.4 (2C; Ar-C), 129.3 (Ar-C), 126.4 (2C; Ar-C), 115.7 ($=CH_2$), 59.9 (SO_2CH), 52.5 (SO_2CH_2), 33.0 ($=CHCH_2$), 27.8 (CH_2), 27.5 (CH_2), 21.1 ppm (CH_2); IR (neat): $\tilde{\nu}$=3075, 2971, 2951, 2875, 1966, 1784, 1707, 1639, 1598, 1498, 1456, 1393, 1307, 1270, 1187, 1119, 996, 915, 811, 783, 726, 694 cm^{-1}; MS (APCI): m/z (%): 322 (17) [M+H^+], 240 (62), 176 (100), 149 (10), 131 (3); HRMS (APCI): m/z calcd for $C_{16}H_{19}NO_4S$+H: 322.1108, found: 322.1116.

3-(Cinnamylsulfonyl)-1-phenylpyrrolidine-2,5-dione (36): The thioether was prepared according to GPI and obtained after flash column chromatography (petroleum ether/ethyl acetate gradient 10/1→5/1) as a white solid (1.17 g, 3.6 mmol, 72% yield). R_f=0.17 (petroleum ether/ethyl acetate 5/1); m.p. 119–120°C; ^1H NMR (300 MHz, $CDCl_3$): δ=7.51–7.22 (m, 10H; Ar-H), 6.64 (d, J=15.8 Hz, 1H; PhCH), 6.24 (ddd, J=15.8, 9.4, 6.2 Hz, 1H; PhCHCH), 3.95 (dd, J=14.0, 9.4 Hz, 1H; SCH_2), 3.88 (dd, J=9.4, 3.8 Hz, 1H; SCH), 3.46 (ddd, J=14.0, 6.2, 1.4 Hz, 1H; SCH_2), 3.27 (dd, J=18.4, 9.4 Hz, 1H; $SCHCH_2$), 2.69 ppm (dd, J=18.4, 3.8 Hz, 1H; $SCHCH_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ=175.9 (C=O), 173.7 (C=O), 136.2 (Ar-C), 134.2 (PhCH), 131.6 (Ar-C), 129.2 (2C; Ar-C), 128.8 (PHCHCH), 128.7 (2C; Ar-C), 128.0 (Ar-C), 126.5 (2C; Ar-C), 126.4 (2C; Ar-C), 123.7 (Ar-C), 36.7 (SCH), 35.5 ($SCHCH_2$), 34.5 ppm (SCH_2); IR (neat): $\tilde{\nu}$=3057, 3026, 2958, 1782, 1705, 1593, 1490, 1391, 1202, 1188, 1165, 965, 925, 785, 749, 699, 687, 629, 551 cm^{-1}; MS (ESI): m/z (%): 346 (100) [M+Na^+], 263 (7), 177 (2), 159 (2), 117 (52), 99 (2); HRMS (ESI): m/z calcd for $C_{19}H_{17}NO_2S$+Na: 346.0872, found: 346.0889. The thioether was then oxidized to sulfone **36** according to GPIV. After column chromatography (petroleum ether/ethyl acetate 1/1) the product was obtained as a white solid (362 mg, 1.02 mmol, 68% yield). R_f=0.73 (petroleum ether/ethyl acetate 1/1); m.p. 160–161°C; ^1H NMR (300 MHz, $CDCl_3$): δ=7.57–7.24 (m, 10H; Ar-H), 6.99 (d, J=16.2 Hz, 1H; PhCH), 6.30 (ddd, J=16.2, 9.6, 5.6 Hz, 1H; PhCHCH), 4.67–4.58 (m, 2H; SO_2CH and SO_2CH_2), 4.13 (ddd, J=14.2, 5.6, 1.5 Hz, 1H; SO_2CH_2), 3.47 (dd, J=19.3, 4.2 Hz, 1H; SO_2CHCH_2), 3.15 ppm (dd, J=19.3, 9.6 Hz, 1H;

SO_2CHCH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.0 (C=O), 169.0 (C=O), 141.0 (PhCH), 135.2 (Ar-C), 131.0 (Ar-C), 129.5 (2C; Ar-C), 129.4 (Ar-C), 129.1 (Ar-C), 128.4 (2C; Ar-C), 126.9 (2C; Ar-C), 126.4 (2C; Ar-C), 114.1 (PhCHCH), 57.2 (SO_2C), 56.6 (SO_2C), 27.5 ppm (SO_2CHCH_2); IR (neat): $\tilde{\nu}$ = 2981, 2363, 1966, 1713, 1377, 1257, 1079, 1045, 1009, 913, 862, 647, 605 cm^{-1}; MS (ESI): *m/z* (%): 378 (100) [*M*+Na^+], 314 (9), 285 (17), 117 (52); HRMS (ESI): *m/z* calcd for $C_{19}H_{17}NO_4S$+Na: 378.0770, found: 378.0778.

3-(Cyclopropylmethylsulfonyl)-1-phenylpyrrolidine-2,5-dione (37): The thioether was prepared according to GPI and obtained after column chromatography (petroleum ether/ethyl acetate 5/1) as a white solid (685 mg, 2.62 mmol, 53% yield). R_f = 0.16 (petroleum ether/ethyl acetate 5/1); m.p. 75–76 °C; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.53–7.45 (m, 2H; Ar-H), 7.44–7.36 (m, 1H; Ar-H), 7.33–7.27 (m, 2H; Ar-H), 4.04 (dd, *J* = 9.0, 3.5 Hz, 1H; SCH), 3.33 (d, *J* = 18.8, 9.0 Hz, 1H; $SCHCH_2$), 2.93 (dd, *J* = 13.1, 7.5 Hz, 1H; SCH_2), 2.74 (dd, *J* = 13.1, 6.7 Hz, 1H; SCH_2), 2.70 (dd, *J* = 18.8, 3.5 Hz, 1H; $SCHCH_2$), 1.06 (m_c, 1H; SCH_2CH), 0.70–0.53 (m, 2H; Cyclopropyl-H), 0.43–0.33 (m, 1H; Cyclopropyl-H), 0.29–0.18 ppm (m, 1H; Cyclopropyl-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.7 (C=O), 173.8 (C=O), 131.6 (Ar-C), 129.2 (2C; Ar-C), 128.8 (Ar-C), 126.4 (2C; Ar-C), 38.6 (SC), 37.3 (SC), 36.2 ($SCHCH_2$), 10.6 (SCH_2CH), 6.0 (CH_2), 4.9 ppm (CH_2); IR (neat): $\tilde{\nu}$ = 3051, 3007, 2949, 2915, 1966, 1781, 1701, 1594, 1499, 1488, 1389, 1254, 1206, 1175, 1021, 944, 927, 829, 784, 747, 698, 628, 567 cm^{-1}; MS (ESI): *m/z* (%): 284 (100) [*M*+Na^+], 266 (2); HRMS (ESI): *m/z* calcd for $C_{14}H_{15}NO_2S$+Na: 284.0716, found: 284.0714. The thioether was then oxidized to sulfone **37** according to GPIII. After column chromatography (petroleum ether/ethyl acetate 1/1) the product was obtained as a white solid (205 mg, 0.7 mmol, 70% yield). R_f = 0.46 (petroleum ether/ethyl acetate 1/1); m.p. 128–130 °C; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.55–7.40 (m, 3H; Ar-H), 7.31–7.27 (m, 2H; Ar-H), 4.63 (dd, *J* = 9.9, 4.2 Hz, 1H; SO_2CH), 3.53 (dd, *J* = 19.1, 4.2 Hz, 1H; SO_2CHCH_2), 3.44 (d, 3.7 Hz, 1H; SO_2CH_2), 3.41 (d, *J* = 5.8 Hz, 1H; SO_2CH_2), 3.22 (dd, *J* = 19.1, 9.9 Hz, 1H; SO_2CHCH_2), 1.38–1.23 (m, 1H; SO_2CH_2CH), 0.88–0.75 (m, 2H; Cyclopropyl-H), 0.74–0.64 (m, 1H; Cyclopropyl-H), 0.57–0.49 ppm (m, 1H; Cyclopropyl-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.1 (C=O), 169.1 (C=O), 131.0 (Ar-C), 129.4 (2C; Ar-C), 129.3 (Ar-C), 126.4 (2C; Ar-C), 58.9 (SO_2C), 57.4 (SO_2C), 27.7 (SO_2CHCH_2), 5.0 (SO_2CH_2CH), 4.4 (CH_2), 4.2 ppm (CH_2); IR (neat): $\tilde{\nu}$ = 2922, 2852, 1785, 1713, 1597, 1498, 1458, 1386, 1313, 1189, 1132, 1028, 928, 803, 729, 696, 624 cm^{-1}; MS (ESI): *m/z* (%): 316 (100) [*M*+Na^+]; HRMS (ESI): *m/z* calcd for $C_{14}H_{15}NO_4S$+Na: 316.0614, found: 316.0592.

***tert*-Butyl 2-(2,5-dioxo-1-phenylpyrrolidin-3-ylsulfonyl)acetate (38)**: The thioether was prepared according to GPI and obtained after flash column chromatography (petroleum ether/ethyl acetate gradient 5/1→4/1) as a colorless liquid (1.04 g, 3.23 mmol, 65% yield). R_f = 0.16 (petroleum ether/ethyl acetate 4/1); ^1H NMR (300 MHz, $CDCl_3$): δ = 7.53–7.27 (m, 5H; Ar-H), 4.21 (brd, *J* = 6.1 Hz, 1H; SCH), 3.85 (d, *J* = 15.9 Hz, 1H; SCH_2), 3.37 (d, *J* = 15.9 Hz, 1H; SCH_2), 3.33 (dd, *J* = 18.7, 8.6 Hz, 1H; $SCHCH_2$), 2.72 (d, *J* = 18.7 Hz, 1H; $SCHCH_2$), 1.49 ppm (s, 9H; $C(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.2 (C=O), 173.5 (C=O), 168.7 (CO_2), 131.5 (Ar-C), 129.2 (2C; Ar-C), 128.8 (Ar-C), 126.5 (2C; Ar-C), 82.5 (OC), 38.5 (SC), 35.7 (SC), 34.3 ($SCHCH_2$), 28.0 ppm (3C; $C(CH_3)_3$); IR (neat): $\tilde{\nu}$ = 2979, 2933, 1965, 1782, 1706, 1597, 1500, 1456, 1369, 1300, 1258, 1168, 1125, 952, 851, 744, 694, 619, 572 cm^{-1}; MS (ESI): *m/z* (%): 344 (100) [*M*+Na^+], 322 (11), 288 (9), 266 (41), 248 (5), 220 (19), 174 (4); HRMS (ESI): *m/z* calcd for $C_{16}H_{19}NO_4S$+Na: 344.0927, found: 344.0940. The thioether was then oxidized to sulfone **38** according to GPIV. After column chromatography (petroleum ether/ethyl acetate 1/1) the product was obtained as a white solid (892 mg, 2.52 mmol, 78% yield). R_f = 0.63 (petroleum ether/ethyl acetate 1/1); m.p. 153–155 °C; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.54–7.41 (m, 3H; Ar-H), 7.31–7.26 (m, 2H; Ar-H), 5.23 (dd, *J* = 9.8, 4.5 Hz, 1H; SO_2CH), 4.82 (d, *J* = 15.5 Hz, 1H; SO_2CH_2), 4.04 (d, *J* = 15.5 Hz, 1H; SO_2CH_2), 3.49 (dd, *J* = 19.2, 4.5 Hz, 1H; SO_2CHCH_2), 3.23 (dd, *J* = 19.2, 9.8 Hz, 1H; SO_2CHCH_2), 1.53 ppm (s, 9H; $C(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.9 (C=O), 169.0 (C=O), 162.1 (CO_2), 130.9 (Ar-C), 129.4 (3C; Ar-C), 126.4 (2C; Ar-C), 85.0 (OC), 59.6 (SO_2C), 56.8 (SO_2C), 27.9 (3C; $C(CH_3)_3$), 27.5 ppm (SO_2CHCH_2); IR (neat): $\tilde{\nu}$ = 2986, 1967, 1721, 1503, 1390, 1326, 1190, 1134, 1108, 1032, 926, 787, 746, 692, 586 cm^{-1}; MS (CI): *m/z* (%): 353 (18) [M^+], 338 (2), 326 (5), 312 (4), 298 (100), 280 (11), 254 (1), 202 (1), 188 (2), 174 (18), 146 (1), 119 (2), 91 (1), 65 (1), 57 (9), 43 (1); HRMS (ESI): *m/z* calcd for $C_{16}H_{19}NO_4S$+Na: 376.0825, found: 376.0814.

3-(Benzyloxymethylsulfonyl)-1-phenylpyrrolidine-2,5-dione (39): The thioether was prepared according to GPI and obtained after flash column chromatography (petroleum ether/ethyl acetate 4/1) as a light yellow solid (470 mg, 1.44 mmol, 29% yield). R_f = 0.15 (petroleum ether/ethyl acetate 4/1); m.p. 90–91 °C; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.48–7.30 (m, 8H; Ar-H), 7.26–7.21 (m, 2H; Ar-H), 5.27 (d, *J* = 12.0 Hz, 1H; $PhCH_2$), 4.75 (d, *J* = 11.7 Hz, 1H; SCH_2), 4.71 (d, *J* = 12.0 Hz, 1H; $PhCH_2$), 4.61 (d, *J* = 11.7 Hz, 1H; SCH_2), 4.08 (dd, *J* = 9.5, 4.2 Hz, 1H; SCH), 3.36 (dd, *J* = 19.0, 9.5 Hz, 1H; $SCHCH_2$), 2.90 ppm (dd, *J* = 19.0, 4.2 Hz, 1H; $SCHCH_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.5 (C=O), 173.8 (C=O), 136.6 (Ar-C), 131.7 (Ar-C), 129.2 (2C; Ar-C), 128.8 (Ar-C), 128.6 (2C; Ar-C), 128.3 (2C; Ar-C), 128.1 (Ar-C), 126.5 (2C; Ar-C), 71.5 ($PhCH_2$), 70.5 (SCH_2), 38.2 (SCH), 36.2 ppm ($SCHCH_2$); IR (neat): $\tilde{\nu}$ = 3065, 2949, 2926, 2872, 1966, 1778, 1701, 1594, 1496, 1455, 1388, 1205, 1171, 1055, 1029, 997, 927, 890, 777, 741, 696, 675, 607 cm^{-1}; MS (ESI): *m/z* (%): 350 (100) [*M*+Na^+], 328 (6), 298 (19), 251 (2), 220 (5), 91 (5); HRMS (ESI): *m/z* calcd for $C_{18}H_{17}NO_3S$+Na: 350.0821, found: 350.0835. The thioether was then oxidized to sulfone **39** according to GPIII. After column chromatography (petroleum ether/ethyl acetate 1/1) the product was obtained as a light yellow solid (282 mg, 0.78 mmol, 54% yield). R_f = 0.67 (petroleum ether/ethyl acetate 1/1); m.p. 117–118 °C; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.53–7.35 (m, 8H; Ar-H), 7.29–7.24 (m, 2H; Ar-H), 5.33 (d, *J* = 12.5 Hz, 1H; $PhCH_2$), 5.07 (d, *J* = 11.6 Hz, 1H; SO_2CH_2), 4.89 (d, *J* = 11.6 Hz, 1H; SO_2CH_2), 4.77 (dd, *J* = 10.2, 5.4 Hz, 1H; SO_2CH), 4.56 (d, *J* = 12.5 Hz, 1H; $PhCH_2$), 3.48 (dd, *J* = 19.3, 4.4 Hz, 1H; SO_2CHCH_2), 3.22 ppm (dd, *J* = 19.3, 10.2 Hz, 1H; SO_2CHCH_2); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.0 (C=O), 168.5 (C=O), 135.3 (Ar-C), 131.0 (Ar-C), 129.4 (2C; Ar-C), 129.3 (Ar-C), 128.9 (Ar-C), 128.8 (2C; Ar-C), 128.6 (2C; Ar-C), 126.4 (2C; Ar-C), 81.8 (SO_2CH_2), 75.1 ($PhCH_2$), 57.1 (SO_2CH), 27.5 ppm (SO_2CHCH_2); IR (neat): $\tilde{\nu}$ = 3064, 2946, 1965, 1783, 1703, 1955, 1499, 1455, 1387, 1304, 1245, 1184, 1173, 1147, 1105, 1077, 1026, 989, 928, 892, 746, 693, 620, 586 cm^{-1}; MS (ESI): *m/z* (%): 382 (100) [*M*+Na^+], 343 (11), 318 (14), 266 (34), 251 (14), 186 (1), 149 (2), 91 (9); HRMS (ESI): *m/z* calcd for $C_{18}H_{17}NO_5S$+Na: 382.0720, found: 382.0714.

1-Phenyl-3-(pyridin-2-ylsulfonyl)pyrrolidine-2,5-dione (49): *N*-Phenylmaleimide (868 mg, 5 mmol) was dissolved in acetonitrile (15 mL) and triethylamine (10 drops) was added. After slow addition of a solution of 2-mercaptopyridine in acetonitrile (20 mL), the reaction mixture was stirred at room temperature overnight. The solvent was evaporated in vacuo and the residue purified by flash chromatography on silica gel (petroleum ether/ethyl acetate gradient 2/1→1/2). The thioether[35] was obtained as a white solid (1.07 g, 3.8 mmol, 75% yield). R_f = 0.28 (petroleum ether/ethyl acetate 2/1); m.p. 145–146 °C; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.31 (m_c, 1H; Ar-H), 7.59–7.32 (m, 6H; Ar-H), 7.23 (d, *J* = 8.0 Hz, 1H; Ar-H), 7.03 (ddd, *J* = 7.6, 4.9, 1.3 Hz, 1H; Ar-H), 4.28 (dd, *J* = 9.8, 5.5 Hz, 1H; SCH), 3.41 (dd, *J* = 18.5, 9.8 Hz, 1H; $SCHCH_2$), 3.15 ppm (dd, *J* = 18.5, 5.5 Hz, 1H; $SCHCH_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.1 (C=O), 174.5 (C=O), 155.9 (Ar-C), 149.1 (Ar-C), 136.8 (Ar-C), 132.5 (Ar-C), 129.2 (2C; Ar-C), 128.6 (Ar-C), 126.5 (2C; Ar-C), 122.2 (Ar-C), 120.3 (Ar-C), 41.0 (SCH), 36.6 ppm ($SCHCH_2$); IR (neat): $\tilde{\nu}$ = 3469, 3049, 2981, 2914 2850, 1964, 1784, 1704 1597, 1578, 1556, 1498, 1453, 1415, 1383, 1281, 1184, 1126, 1078, 944, 753, 720, 696, 628, 547 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 284 (100) [M^+], 251 (18), 229 (1), 191 (9), 174 (9), 164 (94), 136 (48), 119 (9), 111 (84), 91 (7), 79 (14), 67 (12), 55 (16). The obtained thioether (284 mg, 1 mmol) was then dissolved in dichloromethane (5 mL) and cooled to 0 °C. After addition of mCPBA (75%, 483 mg, 2.1 mmol) the mixture was stirred for 15 min at 0 °C and for 2 h at room temperature. The reaction mixture was then diluted with dichloromethane (2.5 mL), and saturated $NaHCO_3$ solution (5 mL) was added. After stirring for 20 min the phases were separated and the aqueous phase extracted with chloroform. The combined organic phases were washed with saturated $NaHCO_3$ solution and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. After column chromatography on silica gel (petroleum ether/ethyl acetate 1/4) the product was obtained as

a white solid (186 mg, 0.59 mmol, 59% yield). R_f = 0.66 (petroleum ether/ethyl acetate 1/5); m.p. 150–152 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.79 (m_c, 1H; Ar-H), 8.12 (d, J = 8.0 Hz, 1H; Ar-H), 8.01 (td, J = 7.9, 1.7 Hz, 1H; Ar-H), 7.61 (ddd, J = 7.6, 4.6, 1.2 Hz, 1H; Ar-H), 7.49–7.36 (m, 3H; Ar-H), 7.24–7.18 (m, 2H; Ar-H), 5.17 (dd, J = 10.0, 4.3 Hz, 1H; SO_2CH), 3.64 (dd, J = 19.1, 4.3 Hz, 1H; SO_2CHCH_2), 3.34 ppm (dd, J = 19.1, 10.0 Hz, 1H; SO_2CHCH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.0 (C=O), 167.8 (C=O), 155.4 (Ar-C), 150.5 (Ar-C), 138.5 (Ar-C), 131.0 (Ar-C), 129.3 (2C; Ar-C), 129.2 (Ar-C), 128.2 (Ar-C), 126.3 (2C; Ar-C), 123.6 (Ar-C), 59.9 (SO_2CH), 29.2 ppm (SO_2CHCH_2); IR (neat): $\tilde{\nu}$ = 3085, 2951, 1787, 1713, 1597, 1581, 1500, 1434, 1390, 1317, 1193, 1167, 1111, 1085, 990, 790, 763, 749, 733, 697, 623, 606, 553 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 316 (27) [M^+], 299 (1), 252 (30), 234 (7), 207 (2), 196 (28), 174 (72), 156 (16), 132 (11), 119 (15), 91 (9), 79 (100), 64 (4), 55 (29); HRMS (ESI): *m/z* calcd for $C_{15}H_{12}N_2O_4S$+H: 317.0591, found: 317.0597.

General procedure for the preparation of allylic sulfones by Fe-catalyzed allylic substitution (GPV): A 10 mL-microwave vial was charged with SIMES·CCl_3 (10.6 mg, 0.025 mmol), evacuated and filled with nitrogen. Then dry 2-methoxyethanol (0.5 mL) was added and the mixture heated for 30 min at 80 °C in a microwave reactor. This solution was then added via syringe to a 10 mL-Schlenk tube under N_2 atmosphere charged with $Bu_4N[Fe(CO)_3(NO)]$ (10.3 mg, 0.025 mmol). After closing the tube, the reaction mixture was heated at 60 °C for 60 min in an oil bath. After cooling to room temperature sulfinate precursor (0.5 mmol) and allylic carbonate (0.5 mmol) were added to the mixture, and the Schlenk tube closed and heated at 40 °C in an oil bath. After full conversion the solvent was evaporated and the residue purified by chromatography on silica gel.

1-(But-3-en-2-ylsulfonyl)benzene (13-A):[36] Sulfone **13** was prepared according to GPV. After column chromatography (petroleum ether/ethyl acetate 5/1) the product was obtained as a colorless oil (79 mg, 0.41 mmol, 81% yield). Regioisomers were separated by semi-preparative HPLC (petroleum ether/ethyl acetate 5/1). R_f = 0.24 (petroleum ether/diethyl ether 3/1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87–7.82 (m, 2H; Ar-H), 7.69–7.61 (m, 1H; Ar-H), 7.58–7.50 (m, 2H; Ar-H), 5.83 (ddd, J = 17.2, 10.3, 7.9 Hz, 1H; =CH), 5.26 (d, J = 10.3 Hz, 1H; =CH_2), 5.09 (d, J = 17.4 Hz, 1H; =CH_2), 3.72 (m_c, 1H; SO_2CH), 1.44 ppm (d, J = 6.9 Hz, 3H; CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 136.8 (Ar-C), 133.7 (=CH), 131.2 (Ar-C), 129.3 (2C; Ar-C), 128.8 (2C; Ar-C), 121.8 (=CH_2), 64.2 (SO_2CH), 13.0 ppm (CH_3); IR (neat): $\tilde{\nu}$ = 1416, 1305, 1290, 1145, 1085, 1075, 1024, 998, 970, 798, 752, 715 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 196 (10) [M^+], 170 (19), 141 (19), 125 (10), 77 (61), 55 (100).

1-((*E*)-But-2-enylsulfonyl)benzene (13-B):[37] R_f = 0.24 (petroleum ether/diethyl ether 3/1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90–7.82 (m, 2H; Ar-H), 7.70–7.50 (m, 3H; Ar-H), 5.58 (dq, J = 15.3, 6.0 Hz, 1H; CH_3CH), 5.42 (dtq, J = 15.3, 7.1, 1.5 Hz, 1H; CH_2CH), 3.73 (d, J = 7.3 Hz, 2H; CH_2), 1.68 ppm (d, J = 6.1 Hz, 3H; CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.6 (Ar-C), 136.6 (=CH), 133.7 (Ar-C), 128.9 (2C; Ar-C), 128.5 (2C; Ar-C), 117.0 (=CH), 60.2 (CH_2), 18.3 ppm (CH_3); IR (neat): $\tilde{\nu}$ = 1667, 1447, 1319, 1298, 1142, 966, 730, 689 cm^{-1}; MS (EI, 70 eV)): *m/z* (%): 196 (1) [M^+], 142 (3), 131 (1), 126 (13), 117 (4), 97 (1), 92 (2), 77 (21), 71 (1), 65 (1), 55 (100), 51 (26).

1-[(*Z*)-But-2-enylsulfonyl)benzene (13-C):[37] R_f = 0.24 (petroleum ether/diethyl ether 3/1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92–7.86 (m, 2H; Ar-H), 7.69–7.61 (m, 1H; Ar-H), 7.59–7.50 (m, 2H; Ar-H), 5.89–5.76 (m, 1H; =CH), 5.50–5.37 (m, 1H; =CH), 3.86 (d, J = 7.9 Hz, 2H; CH_2), 1.35 ppm (d, J = 7.2 Hz, 3H; CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.5 (Ar-C), 134.0 (=CH), 133.6 (Ar-C), 129.1 (2C; Ar-C), 128.5 (2C; Ar-C), 116.2 (=CH), 54.8 (CH_2), 12.7 ppm (CH_3); IR (neat): $\tilde{\nu}$ = 1716, 1447, 1377, 1307, 1143, 1085, 925 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 196 (1) [M^+], 142 (3), 131 (1), 126 (11), 117 (2), 97 (1), 91 (2), 77 (22), 71 (2), 65 (1), 55 (100), 51 (17).

1-[(2-Methylbut-3-en-2-ylsulfonyl)methyl]benzene (40-A):[38] Sulfone **40** was prepared according to GPV. After column chromatography (petroleum ether/ethyl acetate 5/1) the product was obtained as colorless oil (97 mg, 0.44 mmol, 87% yield). Regioisomers were separated by semi-preparative HPLC (petroleum ether/ethyl acetate 5/1). R_f = 0.19 (petroleum ether/diethyl ether 3/1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.33 (m, 5H; Ar-H), 6.18 (dd, J = 17.5, 10.8 Hz, 1H; =CH), 5.44 (d, J = 10.8 Hz, 1H; =CH_2), 5.41 (d, J = 17.5 Hz, 1H; =CH_2), 4.16 (s, 2H; SO_2CH_2), 1.52 ppm (s, 6H; 2×CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.5 (=CH), 131.3 (2C; Ar-C), 128.7 (Ar-C), 128.6 (2C; Ar-C), 127.0 (Ar-C), 118.7 (=CH_2), 64.8 (SO_2C), 52.9 (SO_2CH_2), 20.5 ppm (2C; 2×CH_3); IR (neat): $\tilde{\nu}$ = 2989, 2940, 1494, 1455, 1410, 1283, 1156, 1136, 1106, 996, 951, 830, 779, 726, 704, 647 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 160 (6), 117 (1), 104 (3), 91 (68), 77 (2), 69 (100), 65 (21), 53 (9).

1-((2-Methylbut-3-en-2-ylsulfonyl)methyl)naphthalene (41-A): Sulfone **41** was prepared according to GPV. After column chromatography (petroleum ether/ethyl acetate 4/1) the product was obtained as a colorless oil (114 mg, 0.42 mmol, 83% yield). Regioisomers were separated by semi-preparative HPLC (petroleum ether/ethyl acetate 4/1). R_f = 0.22 (petroleum ether/ethyl acetate 5/1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.01 (d, J = 8.1 Hz, 1H; Ar-H), 7.88–7.82 (m, 2H; Ar-H), 7.60–7.41 (m, 4H; Ar-H), 6.30 (dd, J = 17.6, 10.8 Hz, 1H; =CH), 5.52 (d, J = 10.7 Hz, 1H; =CH_2), 5.49 (d, J = 17.6 Hz, 1H; =CH_2), 4.63 (s, 2H; CH_2), 1.61 ppm (s, 6H; 2×CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.6 (=CH), 133.9 (Ar-C), 132.8 (Ar-C), 131.1 (Ar-C), 129.7 (Ar-C), 128.7 (Ar-C), 126.7 (Ar-C), 126.0 (Ar-C), 125.2 (Ar-C), 124.1 (Ar-C), 123.2 (Ar-C), 118.9 (=CH_2), 64.9 (SO_2C), 49.2 (SO_2CH_2), 20.4 ppm (2C; 2×CH_3); IR (neat): $\tilde{\nu}$ = 2979, 1509 1412, 1394, 1288, 1214, 1155, 1104, 992, 942, 869, 807, 784, 744, 652, 617 cm^{-1}; MS (ESI): *m/z* (%): 297 (100) [M+Na$^+$], 229 (5), 207 (12), 165 (6), 141 (25), 115 (2), 102 (2); HRMS (ESI): *m/z* calcd for $C_{16}H_{18}O_2S$+Na: 297.0920, found: 297.0905.

1-(2-Methylbut-3-en-2-ylsulfonyl)hexadecane (42-A): Sulfone **42** was prepared according to GPV. After column chromatography (petroleum ether/ethyl acetate 10/1) the product was obtained as a colorless solid (112 mg, 0.36 mmol, 71% yield). Regioisomers were separated by semi-preparative HPLC (petroleum ether/ethyl acetate 10/1). R_f = 0.27 (petroleum ether/ethyl acetate 10/1); m.p. 52–53 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.12 (dd, J = 17.8, 11.2 Hz, 1H; =CH), 5.39 (d, J = 11.0 Hz, 1H; =CH_2), 5.37 (d, J = 17.8 Hz, 1H; =CH_2), 2.87 (m_c, 2H; SO_2CH_2), 1.90–1.78 (m, 2H; CH_2), 1.50 (s, 6H; $C(CH_3)_2$), 1.45–1.19 (m, 26H; 13x CH_2), 0.88 ppm (m_c, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.6 (=CH), 118.4 (=CH_2), 63.8 (SO_2C), 46.1 (SO_2CH_2), 31.9 (CH_2), 29.7 (3C; CH_2), 29.7 (2C; CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 28.8 (CH_2), 22.7 (CH_2), 20.6 (CH_2), 20.2 (2C; $C(CH_3)_2$), 14.1 ppm (CH_3); IR (neat): $\tilde{\nu}$ = 2916, 2848, 2563, 2372, 2169, 1971, 1470, 1276, 1105, 943, 781, 631, 542 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 359 (<1) [M+H$^+$], 294 (1), 273 (3), 255 (1), 224 (2), 139 (1), 125 (1), 97 (2), 83 (3), 69 (100), 57 (9), 41 (13); HRMS (EI): *m/z* calcd for $C_{21}H_{42}O_2S$+H$^+$: 359.2984, found: 359.3007.

(2-Methylbut-3-en-2-ylsulfonyl)cyclohexane (43-A): Sulfone **43** was prepared according to GPV. After column chromatography (petroleum ether/ethyl acetate 5/1) the product was obtained as a colorless solid (93 mg, 0.43 mmol, 86% yield). Regioisomers were separated by semi-preparative HPLC (petroleum ether/ethyl acetate 5/1). R_f = 0.35 (petroleum ether/ethyl acetate 5/1); m.p. 63–64 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.17 (dd, J = 17.7, 10.7 Hz, 1H; =CH), 5.34 (d, J = 17.7 Hz, 1H; =CH_2), 5.33 (d, J = 10.7 Hz, 1H; =CH_2), 3.09 (tt, J = 11.9, 3.5 Hz, 1H; SO_2CH), 2.16–2.06 (m, 2H; Cyclohexyl-H), 1.93–1.82 (m, 2H; Cyclohexyl-H), 1.70–1.54 (m, 3H; Cyclohexyl-H), 1.51 (s, 6H; 2×CH_3), 1.35–1.15 ppm (m, 3H; Cyclohexyl-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.2 (=CH), 117.3 (=CH_2), 65.2 (SO_2C), 57.8 (SO_2CH), 26.9 (2C; CH_2), 25.5 (2C; CH_2), 25.1 (CH_2), 21.0 ppm (2C; 2×CH_3); IR (neat): $\tilde{\nu}$ = 2982, 2920, 2857, 1965, 1728, 1448, 1413, 1272, 1265, 1155, 1129, 1101, 999, 939, 892, 849, 817, 789, 738, 655 cm^{-1}; MS (EI, 70 EV): *m/z* (%): 216 (2) [M^+], 149 (1), 109 (2), 96 (9), 83 (34), 69 (100), 55 (22), 41 (26); HRMS (EI): *m/z* calcd for $C_{11}H_{20}O_2S$: 216.1184, found: 216.1174.

6-(2-Methylbut-3-en-2-ylsulfonyl)hex-1-ene (44-A): Sulfone **44** was prepared according to GPV. After column chromatography (pentane/diethyl ether 5/3) the product was obtained as a colorless oil (88 mg, 0.41 mmol, 81% yield). Regioisomers were separated by semi-preparative HPLC (pentane/diethyl ether 5/3). R_f = 0.51 (pentane/diethyl ether 5/3); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.11 (dd, J = 17.5, 10.9 Hz, 1H; CCH), 5.78 (ddt, J = 17.1, 10.2, 6.8 Hz, 1H; CH_2CH), 5.39 (d, J = 10.9 Hz, 1H; CCH=CH_2), 5.37 (d, J = 17.5 Hz, 1H; CCH=CH_2), 5.02 (dq, J = 17.1,

1.6 Hz, 1H; $CH_2CH{=}CH_2$), 4.98 (dq, J=6.8, 1.4 Hz, 1H; $CH_2CH{=}CH_2$), 2.88 (m_c, 2H; SO_2CH_2), 2.09 (q, J=7.2 Hz, 2H; CH_2), 1.93–1.80 (m, 2H; CH_2), 1.58–1.49 ppm (m, 8H; CH_2 and 2×CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=137.7 (=CH), 137.5 (=CH), 118.5 (=CH_2), 115.3 (=CH_2), 63.9 (SO_2C), 45.9 (SO_2CH_2), 33.2 ($CHCH_2$), 28.0 (CH_2), 20.2 (CH_2), 20.1 ppm (2C; 2×CH_3); IR (neat): $\tilde{\nu}$=2979, 2937, 1969, 1640, 1463, 1414, 1312, 1282, 1156, 1106, 998, 913, 800, 755, 720, 634 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 216 (<1) [M^+], 149 (1), 109 (1), 83 (2), 69 (100), 55 (2), 41 (16); HRMS (EI): *m/z* calcd for $C_{11}H_{20}O_2S$: 216.1184, found: 216.1189.

1-((*E*)-3-(2-Methylbut-3-en-2-ylsulfonyl)prop-1-enyl)benzene (45-A): Sulfone **45** was prepared according to GPV. After column chromatography (petroleum ether/ethyl acetate 4/1) the product was obtained as a colorless oil (101 mg, 0.41 mmol, 81% yield). Regioisomers were separated by semi-preparative HPLC (petroleum ether/ethyl acetate 4/1). R_f=0.21 (petroleum ether/ethyl acetate 5/1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.42–7.23 (m, 5H; Ar-H), 6.66 (d, J=15.9 Hz, 1H; PhCH), 6.22 (dt, J=15.9, 7.5 Hz, 1H; CH_2CH), 6.16 (dd, J=17.5, 10.7 Hz, 1H; =CH), 5.43 (d, J=10.7 Hz, 1H; =CH_2), 5.40 (d, J=17.5 Hz, 1H; =CH_2), 3.85 (dd, J=7.5, 1.2 Hz, 2H; SO_2CH_2), 1.55 ppm (s, 6H; 2×CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=138.7 (=CH), 137.4 (=CH), 135.9 (Ar-C), 128.7 (2C; Ar-C), 128.4 (Ar-C), 126.7 (2C; Ar-C), 118.7 (CH_2CH), 114.9 (=CH_2), 64.8 (SO_2C), 51.8 (SO_2CH_2), 20.5 ppm (2C; CH_3); IR (neat): $\tilde{\nu}$=2374, 2108, 1965, 1717, 1645, 1600, 1573, 1473, 1455, 1416, 1288, 1220, 1165, 1102, 1010, 905, 798, 726, 693, 649 cm^{-1}; MS (ESI): *m/z* (%): 273 (100) [M+Na$^+$], 205 (10), 141 (2); HRMS (ESI): *m/z* calcd for $C_{14}H_{18}O_2S$+Na: 273.0920, found: 273.0919.

1-[(*E*)-3-(3-Methylbut-2-enylsulfonyl)prop-1-enyl]benzene (45-B):[39] R_f=0.21 (petroleum ether/ethyl acetate 5/1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.44–7.27 (m, 5H; Ar-H), 6.67 (d, J=15.8 Hz, 1H; PhCH), 6.25 (dt, J=15.8, 7.6 Hz, 1H; PhCHC*H*), 5.32 (m_c, 1H; C=CH), 3.82 (d, J=7.6 Hz, 2H; PhCHCHCH_2), 3.71 (d, J=7.8 Hz, 2H; SO_2CH_2), 1.84 (s, 3H; CH_3), 1.72 ppm (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=142.8 (Ar-C), 138.8 (PhCH), 135.6 (=C), 128.8 (2C; Ar-C), 128.7 (Ar-C), 126.7 (2C; Ar-C), 115.4 (=CH), 110.2 (=CH), 56.0 (PhCHCHCH_2), 51.9 (SO_2CH_2), 26.1 (CH_3), 18.7 ppm (CH_3); IR (neat): $\tilde{\nu}$=3050, 2980, 2911, 1671, 1598, 1578, 1494, 1448, 1416, 1374, 1290, 1280, 1225, 1152, 1111, 1057, 976, 914, 847, 754, 732, 720, 695, 593, 565, 539 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 250 (<1) [M^+], 186 (1), 117 (100), 102 (1), 91 (13), 77 (2), 69 (18), 63 (3), 51 (3).

[(2-Methylbut-3-en-2-ylsulfonyl)methyl]cyclopropane (46-A): Sulfone **46** was prepared according to GPV. After column chromatography (petroleum ether/ethyl acetate 5/1) the product was obtained as a colorless oil (79 mg, 0.42 mmol, 84% yield). Regioisomers were separated by semi-preparative HPLC (petroleum ether/ethyl acetate 5/1). R_f=0.26 (petroleum ether/ethyl acetate 5/1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=6.12 (dd, J=17.4, 10.6 Hz, 1H; =CH), 5.38 (d, J=10.6 Hz, 1H; =CH_2), 5.36 (d, J=17.4 Hz, 1H; =CH_2), 2.85 (d, J=7.1 Hz, 2H; SO_2CH), 1.51 (s, 6H; 2×CH_3), 1.25–1.11 (m, 1H; SO_2CH_2CH), 0.77–0.68 (m, 2H; CH_2), 0.42–0.35 ppm (m, 2H; CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ=137.6 (=CH), 118.3 (=CH_2), 63.8 (SO_2C), 51.8 (SO_2CH_2), 20.2 (2C; CH_3), 4.7 (2C; CH_2), 3.3 ppm (CH); IR (neat): $\tilde{\nu}$=3088, 2984, 2936, 1966, 1464, 1415, 1289, 1258, 1155, 1105, 1024, 1004, 917, 829, 803, 731, 632 cm^{-1}; MS (ESI): *m/z* (%): 211 (100) [M+Na$^+$], 206 (1), 143 (5), 102 (3); HRMS (ESI): *m/z* calcd for $C_9H_{16}O_2S$+Na: 211.0763, found: 211.0761.

***tert*-Butyl 2-(2-methylbut-3-en-2-ylsulfonyl)acetate (47-A)**: Sulfone **47** was prepared according to GPV. After column chromatography (petroleum ether/ethyl acetate 5/1) the product was obtained as a colorless solid (67 mg, 0.27 mmol, 54% yield). Regioisomers were separated by semi-preparative HPLC (petroleum ether/ethyl acetate 5/1). R_f=0.24 (petroleum ether/ethyl acetate 5/1); m.p. 37–38 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=6.13 (dd, J=17.4, 10.8 Hz, 1H; =CH), 5.45 (d, J=10.8 Hz, 1H; =CH_2), 5.43 (d, J=17.4 Hz, 1H; =CH_2), 3.83 (s, 2H; SO_2CH_2), 1.54 (s, 6H; 2×CH_3), 1.50 ppm (s, 9H; C(CH_3)$_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ=161.5 (C=O), 136.8 (=CH), 120.0 (=CH), 83.7 (OC), 66.1 (SO_2C), 53.7 (SO_2CH_2), 27.8 (3C; C(CH_3)$_3$), 20.1 ppm (2C; C(CH_3)$_2$); IR (neat): $\tilde{\nu}$=2981, 2938, 1967, 1730, 1463, 1395, 1369, 1314, 1288, 1260, 1156, 1108, 1002, 937, 902, 833, 799, 715, 678, 619 cm^{-1}; MS (ESI): *m/z* (%): 271 (100) [M+Na$^+$], 266 (65) [M+NH$_4^+$], 210 (6), 193 (7), 125 (2); HRMS (ESI): *m/z* calcd for $C_{11}H_{20}O_4S$+Na: 271.0975, found: 271.0962.

1-{[(2-Methylbut-3-en-2-ylsulfonyl)methoxy]methyl}benzene (48-A): Sulfone **48** was prepared according to GPV. After column chromatography (petroleum ether/ethyl acetate 5/1) the product was obtained as a colorless oil (69 mg, 0.27 mmol, 54% yield). Regioisomers were separated by semi-preparative HPLC (petroleum ether/ethyl acetate 5/1). R_f=0.31 (petroleum ether/ethyl acetate 5/1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.42–7.28 (m, 5H; Ar-H), 6.11 (dd, J=17.4, 10.7 Hz, 1H; =CH), 5.41 (d, J=17.4 Hz, 1H; =CH_2), 5.39 (d, J=10.7 Hz, 1H; =CH_2), 4.92 (s, 2H; SO_2CH_2), 4.59 (s, 2H; $PhCH_2$), 1.57 ppm (s, 6H; 2×CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=136.8 (=CH), 136.0 (Ar-C), 128.6 (2C; Ar-C), 128.4 (3C; Ar-C), 119.0 (=CH_2), 80.3 (SO_2CH_2), 74.6 ($PhCH_2$), 64.6 (SO_2C), 20.4 ppm (2C; CH_3); IR (neat): $\tilde{\nu}$=2984, 2938, 1966, 1455, 1415, 1313, 1285, 1157, 1119, 1092, 998, 933, 915, 897, 736, 698, 612, 544 cm^{-1}; MS (CI): *m/z* (%): 255 (17) [M+H$^+$], 247 (4), 225 (11), 185 (8), 157 (23), 132 (2), 121 (5), 105 (17), 91 (100), 69 (27), 65 (5), 57 (2); HRMS (ESI): *m/z* calcd for $C_{13}H_{18}O_3S$+NH$_4$: 272.1315, found: 272.1304.

2-(But-3-en-2-ylsulfonyl)pyridine (50-A): Sulfone **50** was prepared according to GPV. After column chromatography (petroleum ether/ethyl acetate 1/3) the product was obtained as a light yellow oil (35 mg, 0.18 mmol, 35% yield). Regioisomers could not be separated. R_f=0.48 (petroleum ether/ethyl acetate 1/3); ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.81–8.75 (m, 1H; Ar-H), 8.08–8.03 (m, 1H; Ar-H), 7.99–7.91 (m, 1H; Ar-H), 7.60–7.52 (m,1H; Ar-H), 5.80 (ddd, J=17.0, 10.2, 8.3 Hz, 1H; =CH), 5.24 (d, J=10.1 Hz, 1H; =CH_2), 5.14 (d, J=17.1 Hz, 1H; =CH_2), 4.39–4.27 (m, 1H; SO_2CH), 1.51 ppm (d, J=6.8 Hz, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=156.1 (Ar-C), 150.2 (Ar-C), 137.8 (Ar-C), 130.8 (=CH), 127.3 (Ar-C), 123.7 (=CH_2), 122.5 (Ar-C), 60.5 (SO_2CH), 12.3 ppm (CH_3); IR (neat) $\tilde{\nu}$=2934, 1378, 1309, 1161, 1110, 992, 934, 782, 746, 638 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 197 (5), 182 (2), 132 (75), 130 (3), 118 (100), 106 (7), 93 (8), 79 (51), 55 (58), 51 (17), 39 (8); HRMS (APCI): *m/z* calcd for $C_9H_{11}NO_2S$+H: 198.0583, found: 198.0577.

(*E*)-2-(But-2-enylsulfonyl)pyridine (50-B): R_f=0.48 (petroleum ether/ethyl acetate 1/3); ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.77 (d, J=4.4 Hz, 1H; Ar-H), 8.05 (d, J=7.9 Hz, 1H; Ar-H), 7.95 (dt, J=7.5, 1.8 Hz, 1H; Ar-H), 7.55 (ddd, J=7.6, 5.0, 1.2 Hz, 1H; Ar-H), 5.75–5.60 (m, 1H; =CH), 5.49–5.35 (m, 1H; =CH), 4.06 (d, J=7.2 Hz, 2H; SO_2CH_2), 1.65 ppm (d, J=6.5 Hz, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=150.2 (Ar-C), 137.9 (Ar-C), 137.0 (CH_3CH), 127.3 (Ar-C), 122.8 (Ar-C), 116.3 (CH_2CH), 55.8 (SO_2CH_2), 18.2 ppm (CH_3); IR (neat): ν=3035, 2919, 1452, 1314, 1152, 968 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 197 (5), 182 (2), 132 (75), 130 (3), 118 (100), 106 (7), 93 (8), 79 (51), 55 (58), 51 (17), 39 (8); HRMS (APCI): *m/z* calcd for $C_9H_{11}NO_2S$+H: 198.0583, found: 198.0577.

1-((But-3-en-2-ylsulfonyl)methyl)benzene (51-A):[38] Sulfone **51** was prepared according to GPV. After column chromatography (petroleum ether/ethyl acetate 5/1) the product was obtained as colorless oil (90 mg, 0.43 mmol, 86% yield). Regioisomers were separated by semi-preparative HPLC (petroleum ether/ethyl acetate 5/1). R_f=0.33 (petroleum ether/ethyl acetate 3/1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.44–7.36 (m, 5H; Ar-H), 5.98 (ddd, J=17.2, 10.4, 8.6 Hz, 1H; =CH), 5.48 (d, J=10.4 Hz, 1H; =CH_2), 5.39 (d, J=17.2 Hz, 1H; =CH_2), 4.26 (d, J=13.9 Hz, 1H; SO_2CH_2), 4.19 (d, J=13.9 Hz, 1H; SO_2CH_2), 3.65–3.52 (m, 1H; SO_2CH), 1.47 ppm (d, J=7.0 Hz, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=132.3 (=CH), 130.9 (2C; Ar-C), 129.0 (Ar-C), 128.9 (2C; Ar-C), 127.6 (Ar-C), 122.0 (=CH_2), 60.3 (SO_2CH), 56.0 (SO_2CH_2), 12.3 ppm (CH_3); IR (neat): $\tilde{\nu}$=2987, 2939, 1495, 1455, 1415, 1307, 1116, 1030, 995, 935, 873, 773, 697, 650 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 210 (<1) [M^+], 146 (3), 131 (3), 117 (1), 104 (2), 91 (100), 65 (12), 55 (11).

1-{[(*E*)-But-2-enylsulfonyl)methyl]benzene (51-B):[40] R_f=0.20 (petroleum ether/ethyl acetate 5/1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.40 (s, 5H; Ar-H), 5.84 (dqt, J=15.2, 6.7, 1.1 Hz, 1H; CH_3CH), 5.55 (dtq, J=15.2, 7.5, 1.5 Hz, 1H; CH_2CH), 4.20 (s, 2H; $PhCH_2$), 3.52 (d, J=7.5 Hz, 2H; SO_2CH_2), 1.81 ppm (d, J=6.7 Hz, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=136.6 (CH_3CH), 130.7 (2C; Ar-C)), 129.0 (3C; Ar-C), 127.9 (Ar-C), 117.2 (CH_2CH), 57.8 (SO_2CH_2), 55.3 (SO_2CH_2), 18.3 ppm (CH_3); IR (neat): $\tilde{\nu}$=3034, 2971, 2818, 1856, 1967, 1496, 1455, 1405, 1296, 1259,

1237, 1115, 1091, 966, 930, 870, 786, 769, 697, 593 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 210 (<1) [M^+], 146 (4), 131 (3), 117 (1), 104 (2), 91 (100), 65 (19), 55 (15).

1-[(Hept-1-en-3-ylsulfonyl)methyl]benzene (52-A): Sulfone **52** was prepared according to GPV. After column chromatography (petroleum ether/ethyl acetate 5/1) the product was obtained as a colorless oil (102 mg, 0.41 mmol, 81% yield). Regioisomers were separated by semi-preparative HPLC (petroleum ether/ethyl acetate 5/1). R_f=0.37 (petroleum ether/ethyl acetate 5/1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.44–7.33 (m, 5H; Ar-H), 5.84 (dt, *J*=17.1, 10.1 Hz, 1H; =CH), 5.54 (d, *J*=10.1 Hz, 1H; =CH_2), 5.36 (d, *J*=17.1 Hz, 1H; =CH_2), 4.27 (d, *J*=13.9 Hz, 1H; SO_2CH_2), 4.17 (d, *J*=13.9 Hz, 1H; SO_2CH_2), 3.37 (ddd, *J*=11.0, 10.0, 3.3 Hz, 1H; SO_2CH), 2.11–1.98 (m, 1H; SO_2CHCH_2), 1.76–1.60 (m, 1H; SO_2CHCH_2), 1.44–1.07 (m, 4H; 2×CH_2), 0.87 ppm (t, *J*=7.1 Hz, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=131.6 (=CH), 131.0 (2C; Ar-C), 128.9 (2C; Ar-C), 128.8 (Ar-C), 127.6 (Ar-C), 123.6 (=CH_2), 65.7 (SO_2CH), 56.4 (SO_2CH_2), 28.5 ($CHCH_2$), 25.1 (CH_2), 22.2 (CH_2), 13.8 ppm (CH_3); IR (neat): $\tilde{\nu}$=2957, 2931, 2871, 1965, 1495, 1456, 1303, 1117, 995, 935, 919, 768, 730, 696, 648, 548 cm^{-1}; MS (ESI): *m/z* (%): 275 (100) [*M*+Na^+], 157 (22), 91 (2); HRMS (ESI): *m/z* calcd for $C_{14}H_{20}O_2S$+Na: 275.1076, found: 275.1085.

1-{[(*E*)-Hept-2-enylsulfonyl]methyl}benzene (52-B): R_f=0.29 (petroleum ether/ethyl acetate 5/1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.40 (s, 5H; Ar-H), 5.81 (dt, *J*=15.4, 6.8 Hz, 1H; CH_2CH), 5.53 (dtt, *J*=15.4, 7.2, 1.5 Hz, 1H; SO_2CH_2CH), 4.20 (s, 2H; $PhCH_2$), 3.53 (d, *J*=7.2 Hz, 2H; SO_2CH_2), 2.14 (dt, *J*=6.8, 6.6 Hz, 2H; $CHCH_2$), 1.48–1.26 (m, 4H; 2×CH_2), 0.91 ppm (t, *J*=7.0 Hz, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=141.9 (CH_2CH), 130.8 (2C; Ar-C), 129.0 (2C; Ar-C), 128.9 (Ar-C), 127.9 (Ar-C), 116.0 (SO_2CH_2CH), 57.7 (SO_2CH_2), 55.3 (SO_2CH_2), 32.4 ($CHCH_2$), 30.9 (CH_2), 22.2 (CH_2), 13.9 ppm (CH_3); IR (neat): $\tilde{\nu}$=2957, 2927, 2858, 1966, 1496, 1456, 1302, 1259, 1117, 1073, 971, 923, 873, 786, 768, 697, 594 cm^{-1}; MS (ESI): *m/z* (%): 275 (100) [*M*+Na^+], 157 (14), 91 (1); HRMS (ESI): *m/z* calcd for $C_{14}H_{20}O_2S$+Na: 275.1076, found: 275.1085.

1-[1-(Benzylsulfonyl)allyl]benzene (53-A):[38] Sulfone **53** was prepared according to GPV. After column chromatography (petroleum ether/ethyl acetate 4/1) the product was obtained as a white solid (31 mg, 0.12 mmol, 23% yield). Regioisomers were separated by semi-preparative HPLC (petroleum ether/ethyl acetate 4/1). R_f=0.27 (petroleum ether/ethyl acetate 4/1); m.p. 77–79 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.45–7.30 (m, 10H; Ar-H), 6.35 (ddd, *J*=17.0, 10.1, 9.1 Hz, 1H; =CH), 5.56 (d, *J*=10.1 Hz, 1H; =CH_2), 5.42 (d, *J*=17.0 Hz, 1H; =CH_2), 4.61 (d, *J*=9.1 Hz, 1H; SO_2CH), 4.19 (d, *J*=14.2 Hz, 1H; SO_2CH_2), 4.11 ppm (d, *J*=14.2 Hz, 1H; SO_2CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ=131.6 (Ar-C), 131.0 (2C; Ar-C), 129.9 (=CH), 129.7 (2C; Ar-C), 129.2 (Ar-C), 129.0 (2C; Ar-C), 128.9 (Ar-C), 128.9 (2C; Ar-C), 127.5 (Ar-C), 123.6 (Ar-C), 71.0 (SO_2CH), 56.8 ppm (SO_2CH_2); IR (neat): $\tilde{\nu}$=3060, 3033, 2982, 2943, 1959, 1492, 1455, 1416, 1310, 1282, 1218, 1120, 1071, 985, 959, 936, 769, 712, 695, 650, 638, 559 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 208 (9), 117 (100), 91 (53), 77 (6), 65 (18), 51 (10).

1-[(*E*)-3-(Benzylsulfonyl)prop-1-enyl]benzene (53-B):[41] R_f=0.21 (petroleum ether/ethyl acetate 4/1); m.p. 122–123 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.46–7.27 (m, 10H; Ar-H), 6.63 (d, *J*=15.9 Hz, 1H; PhCH), 6.22 (dt, *J*=15.9, 7.6 Hz, 1H; CH_2CH), 4.25 (s, 2H; $PhCH_2$), 3.74 ppm (d, *J*=7.6 Hz, 1H; SO_2CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ=139.2 (PhCH), 135.5 (Ar-C), 130.8 (2C; Ar-C), 129.1 (Ar-C), 129.0 (2C; Ar-C), 128.8 (2C; Ar-C), 128.7 (Ar-C), 127.8 (Ar-C), 126.7 (2C; Ar-C), 115.2 (CH_2CH), 58.2 (SO_2CH_2), 55.8 ppm (SO_2CH_2); IR (neat): $\tilde{\nu}$=3059, 3030, 2981, 2936, 1965, 1716, 1491, 1449, 1410, 1279, 1162, 1115, 1074, 1055, 1026, 974, 912, 824, 776, 749, 726, 696, 603, 546 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 272 (<1) [M^+], 208 (4), 117 (100), 102 (1), 91 (38), 77 (2), 65 (13), 51 (4).

(*E*)-Methyl-4-(benzylsulfonyl)but-2-enoate (54-B): Sulfone **54** was prepared according to GPV. After column chromatography (petroleum ether/ethyl acetate 2/1) the product was obtained as a white solid (53 mg, 0.21 mmol, 42% yield). Regioisomers were separated by semipreparative HPLC (petroleum ether/ethyl acetate 2/1). R_f=0.21 (petroleum ether/ethyl acetate 2/1); m.p. 102–104 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.45–7.37 (m, 5H; Ar-H), 6.87 (dt, *J*=15.7, 7.7 Hz, 1H; CH_2CH), 6.07 (d, *J*=15.7 Hz, 1H; CH_2CHCH), 4.25 (s, 2H; $PhCH_2$), 3.78 (s, 3H; CH_3), 3.70 ppm (d, *J*=7.7 Hz, 2H; SO_2CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ=165.2 (C=O), 133.1 (CH_2CH), 130.7 (2C; Ar-C), 129.4 (Ar-C), 129.2 (2C; Ar-C), 129.1 (CH_2CHCH), 127.3 (Ar-C), 59.2 (SO_2CH_2), 54.1 (SO_2CH_2), 52.0 ppm (CH_3); IR (neat): $\tilde{\nu}$=3035, 2988, 2955, 2941, 1962, 1718, 1653, 1493, 1441, 1323, 1304, 1283, 1206, 1189, 1144, 1118, 1052, 1027, 1003, 979, 926, 829, 780, 726, 699 cm^{-1}; MS (ESI): *m/z* (%): 277 (100) [*M*+Na^+], 223 (3), 122 (1), 91 (7); HRMS (ESI): *m/z* calcd for $C_{12}H_{14}O_4S$+Na: 277.0505, found: 277.0497.

1-[(4-Methylpent-1-en-3-ylsulfonyl)methyl]benzene (55-A): Sulfone **55** was prepared according to GPV. After column chromatography (petroleum ether/ethyl acetate 4/1) the product was obtained as a colorless oil (36 mg, 0.15 mmol, 30% yield). Regioisomers were separated by semi-preparative HPLC (petroleum ether/ethyl acetate 4/1). R_f=0.40 (petroleum ether/ethyl acetate 4/1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.38 (s, 5H; Ar-H), 6.02 (dt, *J*=17.2, 10.2 Hz, 1H; =CH), 5.60 (dd, *J*=10.2, 1.5 Hz, 1H; =CH_2), 5.33 (dd, *J*=17.2, 1.3 Hz, 1H; =CH_2), 4.26 (d, *J*=14.0 Hz, 1H; SO_2CH_2), 4.13 (d, *J*=14.0 Hz, 1H; SO_2CH_2), 3.25 (dd, *J*=10.2, 3.4 Hz, 1H; SO_2CH), 2.68–2.51 (m, 1H; CH), 1.08 (d, *J*=7.0 Hz, 3H; CH_3), 0.93 ppm (d, *J*=7.0 Hz, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=130.9 (2C; Ar-C), 129.0 (=CH), 128.9 (2C; Ar-C), 128.8 (Ar-C), 127.9 (Ar-C), 124.4 (=CH_2), 69.9 (SO_2CH), 57.5 (SO_2CH_2), 26.1 (CH), 21.6 (CH_3), 18.0 ppm (CH_3); IR (neat): $\tilde{\nu}$=2965, 2367, 2001, 1968, 1457, 1312, 1127, 782, 696, 642 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 238 (<1) [M^+], 174 (5), 133 (5), 118 (3), 104 (9), 91 (100), 83 (36), 65 (8), 55 (32), 41 (8); HRMS (ESI): *m/z* calcd for $C_{13}H_{18}O_2S$+Na: 261.0920, found: 261.0902.

1-{[(*E*)-4-Methylpent-2-enylsulfonyl]methyl}benzene (55-B): R_f=0.40 (petroleum ether/ethyl acetate 4/1); m.p. 75–76 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.40 (s, 5H; Ar-H), 5.77 (dd, *J*=15.5, 6.7 Hz, 1H; CH_2CHCH), 5.49 (ddt, *J*=15.5, 7.3, 1.4 Hz, 1H; CH_2CH), 4.19 (s, 2H; $PhCH_2$), 3.52 (d, *J*=7.3 Hz, 2H; SO_2CH_2), 2.40 (m_c, 1H; CH), 1.05 ppm (d, *J*=6.8 Hz, 6H; 2×CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=148.5 (CH_2CHCH), 130.8 (2C; Ar-C), 129.0 (3C; Ar-C), 127.9 (Ar-C), 113.5 (CH_2CH), 57.6 (SO_2CH_2), 55.4 (SO_2CH_2), 31.4 (CH), 21.9 ppm (2C; CH_3); IR (neat): $\tilde{\nu}$=2967, 2956, 2926, 2895, 2868, 1966, 1497, 1456, 1407, 1306, 1261, 1250, 1148, 1116, 967, 878, 786, 728, 698, 595, 562 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 238 (<1) [M^+], 174 (5), 133 (5), 118 (4), 104 (9), 91 (100), 83 (45), 65 (7), 55 (34), 41 (8); HRMS (ESI): *m/z* calcd for $C_{13}H_{18}O_2S$+Na: 261.0920, found: 261.0903.

1-{[2-(Benzylsulfonyl)but-3-enyloxy]methyl}benzene (56-A): Sulfone **56** was prepared according to GPV. After column chromatography (petroleum ether/ethyl acetate gradient 3/1→1/1) the product was obtained as a colorless oil (78 mg, 0.31 mmol, 62% yield). R_f=0.42 (petroleum ether/ethyl acetate 3/1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.43–7.26 (m, 10H; Ar-H), 5.91 (ddd, *J*=17.2, 10.4, 8.5 Hz. 1H; =CH), 5.52 (d, *J*=10.4 Hz, 1H; =CH_2), 5.44 (d, *J*=17.2 Hz, 1H; =CH_2), 4.59 (s, 2H; $PhCH_2$), 4.40 (d, *J*=13.6 Hz, 1H; SO_2CH_2), 4.29 (d, *J*=13.6 Hz, 1H; SO_2CH_2), 4.01 (dd, *J*=9.8, 6.3 Hz, 1H; $CHCH_2$), 3.91 (dd, *J*=9.8, 4.9 Hz, 1H; $CHCH_2$), 3.81–3.72 ppm (m, 1H; SO_2CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=137.1 (=CH), 131.2 (2C; Ar-C), 128.8 (Ar-C), 128.8 (2C; Ar-C), 128.6 (2C; Ar-C), 128.1 (Ar-C), 128.0 (Ar-C), 127.5 (2C; Ar-C), 127.2 (Ar-C), 124.4 (=CH_2), 73.9 ($PhCH_2$), 67.8 (OCH_2), 65.1 (SO_2CH), 59.2 ppm (SO_2CH_2); IR (neat): $\tilde{\nu}$=3032, 2921, 2886, 1966, 1715, 1495, 1455, 1363, 1309, 1257, 1023, 1116, 1028, 991, 937, 739, 696, 648 cm^{-1}; MS (ESI): *m/z* (%): 339 (100) [*M*+Na^+], 317 (7), 181 (8), 91 (2); HRMS (ESI): *m/z* calcd for $C_{18}H_{20}O_3S$+Na: 339.1025, found: 339.1013.

1-{[(*E*)-4-(Benzylsulfonyl)but-2-enyloxy]methyl}benzene (56-B): R_f=0.16 (petroleum ether/ethyl acetate 3/1); m.p. 68–69 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.40 (s, 5H; Ar-H), 7.40–7.27 (m, 5H; Ar-H), 5.95 (dt, *J*=15.7, 5.1 Hz, 1H; OCH_2CH), 5.83 (dt, *J*=15.7, 7.0 Hz, 1H; SO_2CH_2CH), 4.54 (s, 2H; $PhCH_2$), 4.21 (s, 2H; SO_2CH_2), 4.08 (d, *J*=5.1 Hz, 2H; OCH_2), 3.59 ppm (d, *J*=7.0 Hz, 2H; $CHCH_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ=137.8 (Ar-C), 137.2 (OCH_2CH), 130.8 (2C; Ar-C), 129.1 (Ar-C), 129.0 (2C; Ar-C), 128.5 (2C; Ar-C), 127.9 (Ar-C), 127.8 (2C; Ar-C), 127.7 (Ar-C), 118.6 (SO_2CH_2CH), 72.6 ($PhCH_2$), 69.6 (OCH_2), 58.3 (SO_2CH_2), 54.8 ppm (SO_2CH_2); IR (neat): $\tilde{\nu}$=3033, 2938, 2861, 2843, 1957, 1726, 1494, 1453, 1410, 1360, 1301, 1280, 1220, 1166, 1119, 1111, 1067, 1026, 1008, 963, 773, 749, 726, 695, 605, 550 cm^{-1}; MS (ESI): *m/z*

(%): 339 (100) [M+Na^+], 233 (1), 181 (2), 143 (1), 91 (3); HRMS (ESI): m/z calcd for $C_{18}H_{20}O_3S$+Na: 339.1025, found: 339.1029.

1-[(*E*)-3-(Benzylsulfonyl)but-1-enyl]benzene (57-A): Sulfone **57** was prepared according to GPV. After column chromatography (petroleum ether/ethyl acetate 4/1) the product was obtained as a white solid (119 mg, 0.42 mmol, 83% yield). Regioisomers were separated by semi-preparative HPLC (petroleum ether/ethyl acetate 4/1). R_f=0.25 (petroleum ether/ethyl acetate 4/1); m.p. 126–128°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.45–7.28 (m, 10H; Ar-H), 6.60 (d, J=15.9 Hz, 1H; PhCH), 6.24 (dd, J=15.9, 9.1 Hz, 1H; PhCHC*H*), 4.29 (d, J=14.0 Hz, 1H; SO_2CH_2), 4.21 (d, J=14.0 Hz, 1H; SO_2CH_2), 3.73 (dq, J=9.1, 6.8 Hz, 1H; OCH), 1.55 ppm (d, J=6.8 Hz, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=136.6 (PhCH), 135.5 (Ar-C), 130.9 (2C; Ar-C), 128.9 (3C; Ar-C), 128.8 (2C; Ar-C), 128.7 (Ar-C), 127.6 (Ar-C), 126.7 (2C; Ar-C), 122.8 (PhCH*C*H), 60.4 (SO_2CH), 56.4 (SO_2CH_2), 12.8 ppm (CH_3); IR (neat): $\tilde{\nu}$=3029, 2981, 2937, 1493, 1453, 1312, 1282, 1261, 1211, 1121, 1071, 1020, 969, 774, 758, 725, 700, 623, 588 cm^{-1}; MS (ESI): m/z (%): 309 (70) [M+Na^+], 279 (6), 179 (25), 131 (100), 98 (4); HRMS (ESI): m/z calcd for $C_{17}H_{18}O_2S$+Na: 309.0920, found: 309.0915.

{[(*E*)-1-Phenylbut-2-enylsulfonyl]methyl}benzene (57-B): R_f=0.43 (petroleum ether/ethyl acetate 4/1); m.p. 106–107°C (decomp.); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.44–7.29 (m, 10H; Ar-H), 6.05–5.90 (m, 1H; PhCHC*H*), 5.84 (dq, J=15.2, 6.0 Hz, 1H; CH_3C*H*), 4.56 (d, J=8.8 Hz, 1H; SO_2CH), 4.17 (d, J=14.1 Hz, 1H; SO_2CH_2), 4.10 (d, J=14.1 Hz, 1H; SO_2CH_2), 1.81 ppm (dd, J=6.0, 1.0 Hz, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=135.3 (CH_3*C*H), 132.4 (Ar-C), 130.9 (2C; Ar-C), 129.6 (2C; Ar-C), 129.0 (3C; Ar-C), 128.9 (Ar-C), 128.8 (2C; Ar-C), 127.7 (Ar-C), 122.5 (Ar-C), 70.5 (PhCH), 56.8 ($PhCH_2$), 18.4 ppm (CH_3); IR (neat): $\tilde{\nu}$=3063, 3033, 2980, 2936, 2916, 1494, 1455, 1316, 1287, 1123, 1074, 966, 802, 764, 711, 697, 637, 593, 525 cm^{-1}; MS (ESI): m/z (%): 309 (67) [M+Na^+], 304 (98) [M+NH_4^+], 279 (4), 179 (15), 131 (100), 91 (2); HRMS (ESI): m/z calcd for $C_{17}H_{18}O_2S$+Na: 309.0920, found: 309.0915.

(*Z*)-*tert*-Butyl-2-[(benzylsulfonyl)methyl]-3-phenylacrylate 58B: Sulfone **58** was prepared according to GPV. After column chromatography (petroleum ether/ethyl acetate 5/1) the product was obtained as a white solid (97 mg, 0.26 mmol, 52% yield). Regioisomers were separated by semi-preparative HPLC (petroleum ether/ethyl acetate 5/1). R_f=0.23 (petroleum ether/ethyl acetate 5/1); m.p. 114–115°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.00 (s, 1H; CH), 7.53–7.31 (m, 10H; Ar-H), 4.33 (s, 2H; SO_2CH_2), 4.19 (s, 2H; SO_2CH_2), 1.58 ppm (s, 9H; 3x CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=166.0 (C=O), 145.6 (PhCH), 134.1 (Ar-C), 131.1 (2C; Ar-C), 129.5 (Ar-C), 129.3 (2C; Ar-C), 129.0 (Ar-C), 128.9 (2C; Ar-C), 128.8 (2C; Ar-C), 127.9 (Ar-C), 122.7 (=C), 82.3 (OC), 60.8 ($PhCH_2$), 51.3 (SO_2CH_2), 28.1 ppm (3C; CH_3); IR (neat): $\tilde{\nu}$=3052, 3977, 2929, 1964, 1702, 1622, 1496, 1447, 1367, 1320, 1279, 1245, 1204, 1163, 1148, 1975, 889, 853, 779, 765, 754, 697, 681, 591, 569, 526 cm^{-1}; MS (ESI): m/z (%): 390 (100) [M+NH_4^+], 373 (13) [M+H^+], 339 (11), 317 (76), 299 (23), 167 (3), 91 (3); HRMS (ESI): m/z calcd for $C_{21}H_{24}O_4S$+NH_4: 390.1734, found: 390.1749.

1-{[(*E*)-Pent-3-en-2-ylsulfonyl]methyl}benzene (59): Sulfone **59** was prepared according to GPV. After column chromatography (petroleum ether/ethyl acetate 5/1) the product was obtained as colorless oil (98 mg, 0.44 mmol, 88% yield). R_f=0.19 (petroleum ether/ethyl acetate 5/1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.44–7.34 (m, 5H; Ar-H), 5.80 (dqd, J=15.4, 6.5, 0.7 Hz, 1H; CH_3C*H*), 5.56 (ddq, J=15.4, 8.7, 1.7 Hz, 1H; SO_2CHC*H*), 4.21 (q, J=14.1 Hz, 2H; SO_2CH_2), 3.53 (dq, J=8.5, 7.1 Hz, 1H; SO_2CH), 1.81 (dd, J=6.4, 1.5 Hz, 3H; CH_3), 1.43 ppm (d, J=7.1 Hz, 3H; SO_2CHC*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ=133.5 (CH_3*C*H), 130.9 (2C; Ar-C), 128.9 (2C; Ar-C), 128.8 (Ar-C), 127.8 (Ar-C), 125.0 (SO_2CH*C*H), 59.8 (SO_2CH), 56.0 (SO_2CH_2), 18.2 (CH_3), 12.8 ppm (SO_2CH*C*H$_3$); IR (neat): $\tilde{\nu}$=2033, 1980, 2938, 1965, 1495, 1455, 1298, 1256, 1116, 1020, 969, 872, 772, 722, 698, 609, 546 cm^{-1}; MS (EI, 70 eV): m/z (%): 225 (3) [M+H^+], 197 (1), 160 (5), 131 (1), 118 (1), 91 (26), 69 (100), 53 (1), 41 (22); HRMS (ESI): m/z calcd for $C_{12}H_{16}O_2S$+Na: 247.0763, found: 247.0758.

1-[(*R*)-3,7-Dimethylocta-1,6-dien-3-ylsulfonyl]benzene (61):[29e] Sulfone **61** was prepared according to GPV. After column chromatography (petroleum ether/ethyl acetate 5/1) the product was obtained as a colorless oil (123 mg, 0.44 mmol, 88% yield). Regioisomers were separated by semi-preparative HPLC (petroleum ether/ethyl acetate 5/1). R_f=0.47 (petroleum ether/ethyl acetate 5/1); $[\alpha]_D^{20}$=−10 (c=1.0 in diethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.84–7.78 (m, 2H; Ar-H), 7.66–7.59 (m, 1H; Ar-H), 7.55–7.47 (m, 2H; Ar-H), 5.92 (dd, J=17.4, 10.7 Hz, 1H; =CH), 5.37 (d, J=10.8 Hz, 1H; =CH_2), 5.06 (d, J=17.4 Hz, 1H; =CH_2), 5.09–5.01 (m, 1H; =CH), 1.96–1.84 (m, 4H; 2×CH_2), 1.67 (s, 3H; CH_3), 1.56 (d, J=0.8 Hz, 3H; CH_3), 1.37 ppm (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=135.3 (Ar-C), 135.2 (CH_2=CH), 133.5 (Ar-C), 132.6 (=C), 130.8 (2C; Ar-C), 128.3 (2C; Ar-C), 123.0 (C=*C*H), 120.6 (=CH_2), 68.3 (SO_2C), 32.7 (CCH_2), 25.6 (CH_3), 22.5 (CH_2), 17.7 (CH_3), 16.2 ppm (CH_3); IR (neat): $\tilde{\nu}$=2970, 2917, 1446, 1413, 1376, 1293, 1143, 1068, 999, 929, 758, 724, 689, 622 cm^{-1}; MS (EI, 70 EV): m/z (%): 137 (17), 121 (9), 107 (3), 93 (34), 81 (42), 69 (100), 53 (12); HPLC analysis: DAICEL CHIRALCEL OJ, heptane/isopropyl alcohol 95/5, flow rate: 1.0 mL min^{-1}, detector: 220 nm, t_R(R)=12.8 min, t_R(S)=16.1 min.

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