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Trisubstituted highly activated benzo[*d*]thiazol-2-yl-sulfone-containing olefins as building blocks in organic synthesis

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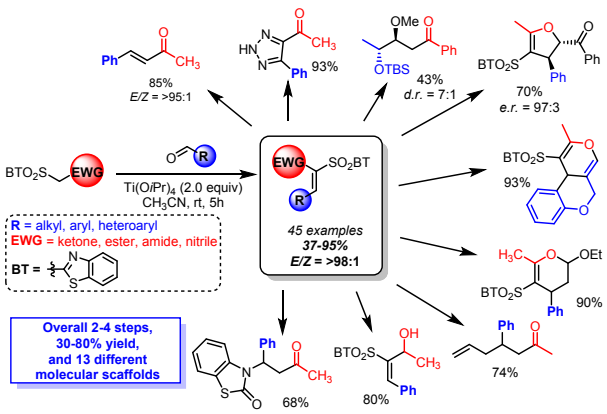


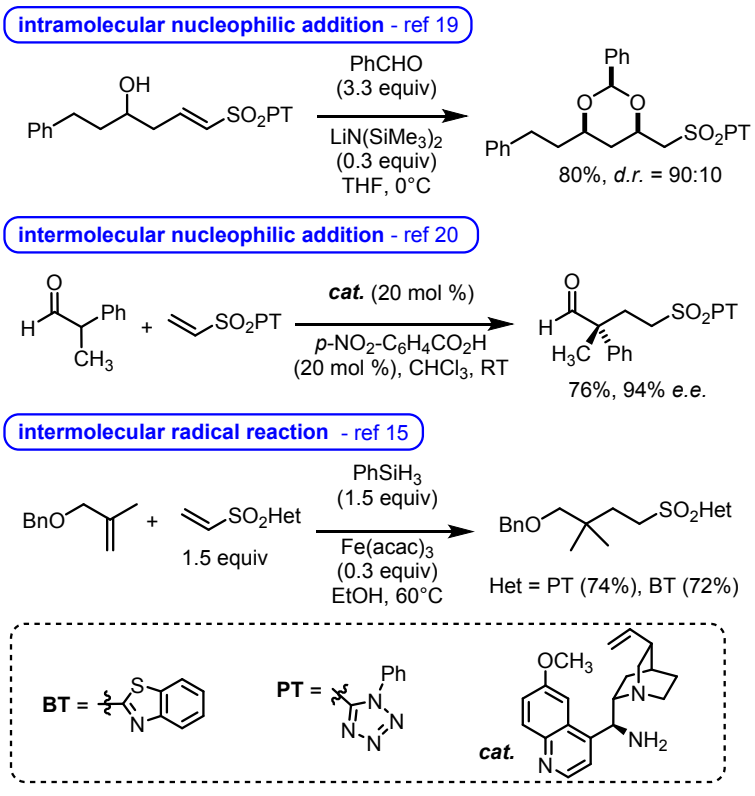
ABSTRACT: In this paper we report formation of highly electrophilic 1,1-diactivated olefins, their use as novel synthetic building block, and their transformation to structurally diverse molecular scaffolds. Synthesis of 1,1-diactivated olefins substituted with a BT-sulfonyl group and a carbonyl or nitrile, respectively, consists of unusual Ti(OPr^i)$_4$-mediated Knoveneagel-type condensation and proceed in good to excellent yields. Generated olefins can be further transformed in highly stereoselective manner and in good yield to various polyfunctionalized heterocycles and acyclic molecular scaffolds. Overall, obtained structures are accessed in two to four steps starting from the (mostly) commercially available aldehydes. In addition, the presence of the BT-sulfonyl group in prepared structures allows for further chemoselective functionalization/post-synthetic transformations to provide structurally diverse final compounds.

Introduction

Diversity-oriented synthesis (DOS) is a synthetic strategy of choice when a chemical library of small organic molecules with a high degree of structural and functional variety have to be prepared.[1–4] In this strategy, rapid (3-5 steps) and efficient (high scaffold diversity) synthesis of structurally distinct molecules is achieved using specially designed readily available building blocks. Such building blocks are further transformed to structurally diverse frameworks.

For some time, our group has been interested in the development of such building blocks.[5,6] More recently Michael-type acceptors, namely aryl vinyl sulfones, have attracted our attention. Indeed, Michael-type additions to vinylic group of aryl vinyl sulfones have attracted, over the past two decades, much attention of both the synthetic[7–11] and medicinal[12–14] community. At the same time, the use of heteroaryl vinyl sulfones as powerful electrophilic substrates was somewhat limited. Only roughly a dozen of seminal works (for selected examples see Scheme 1) focusing on the use of vinyl and/or 1,2-disubstituted olefin-bearing heteroaryl sulfones were reported.[15–22] Such olefins proved to be highly superior in their reactivity in comparison to aryl vinyl sulfones and even to 1,1-diphenylvinylsulfones.[16] We speculated that additional substitution with electron-withdrawing group on heteroaryl vinyl sulfone should broader the synthetic utility of the vinyl sulfones (Figure 1). Newly generated Michael-type adducts should not only be more reactive towards external nucleophiles and radicals but should also react as substrates in cycloaddition reactions. In addition, the presence of heteroaryl sulfonyl group in final adducts should allow further chemo selective transformations of obtained products.

In our group we have a long-standing experience with benzo[d]thiazol-2-yl-sulfone chemistry thus we have designed the synthesis of sulfone **1** as a two-step protocol based on the Knoveneagel condensation[23] of aldehydes with readily available electron-withdrawing α-substituted BT-sulfones **2**[24,25,26] (Figure 2). Herewith we would like to present scope and limitations of such approach and selected synthetic applications of prepared olefins **1**.



Scheme 1. Selected examples of previous use of heteroaryl vinyl sulfones as substrates in intramolecular, intermolecular and radical reactions.

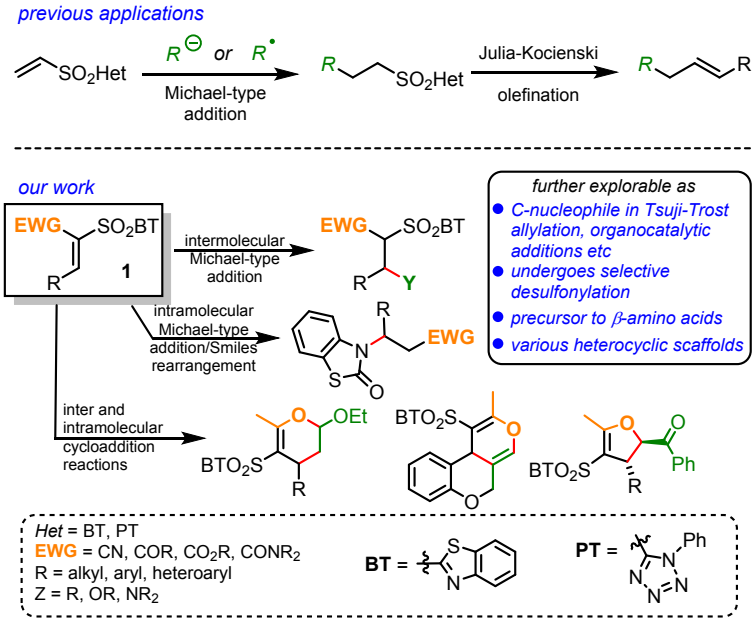


Figure 1. Comparison of previously exploited vinyl sulfones and our newly developed trisubstituted vinyl sulfones **1**.

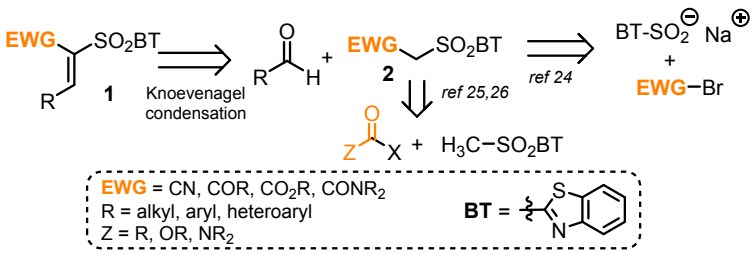


Figure 2. Retrosynthesis of trisubstituted vinyl sulfone **1**.

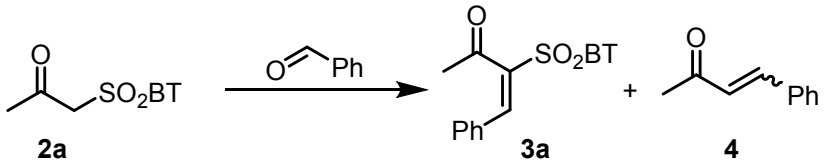
Results and discussions

Reaction conditions optimization

Our approach to BT-sulfone **1** synthesis started with the condensation of BT-sulfone **2a** and benzaldehyde (for selected examples see Table 1). Surprisingly, the reaction proved to be more challenging than expected and all our efforts to obtain the desired product **3a** under the "classical" Knoveneagel reaction conditions failed (Table 1, entry 1).[27] In all cases, only the formation of olefin **4**, the product of Julia-Kocienski olefination,[28] was observed.[27] Interestingly when EDDA was used to promote the condensation, product **3a** was isolated in 26% yield (Table 1, entry 2). However further optimization and studies demonstrated that olefin **3a** is not stable under the reaction conditions and undergoes under prolonged reaction times to retro Knoveneagel reaction.[27] Observed olefin **3a** instability under basic conditions prompted us to attempt the Knoveneagel condensation under Lewis acid catalysis (Table 1, entries 3-7). Gratifyingly it was observed that the use of Ti(O*i*Pr)$_4$ promotes the

reaction yielding the desired BT-sulfone **3a** not only as the only product of the reaction, but also as the single *E*-izomer (Table 1, entry 3). Further reaction optimization revealed that the condensation proceeds best when carried out in CH_3CN at rt in the presence of 2.0 equiv. of Ti(O*i*Pr)$_4$ (Table 1, entry 6). The presence of two Ti(O*i*Pr)$_4$ equivalents proved to be crucial for the reaction to drive it to completion. To shed some light on this intriguing observation we carried out some additional experiments[27] that led us to propose the dual role of Ti(O*i*Pr)$_4$ during the reaction; (a) it promotes enolate formation, and (b) it works as a water molecule scavenger. The exclusive E-olefin formation can be also attributed to the presence of bulky Lewis acid during the condensation step.[27]

Table 1. Knoveneagel condensation of **1** with benzaldehyde: Reaction optimization.



2a **3a** **4**

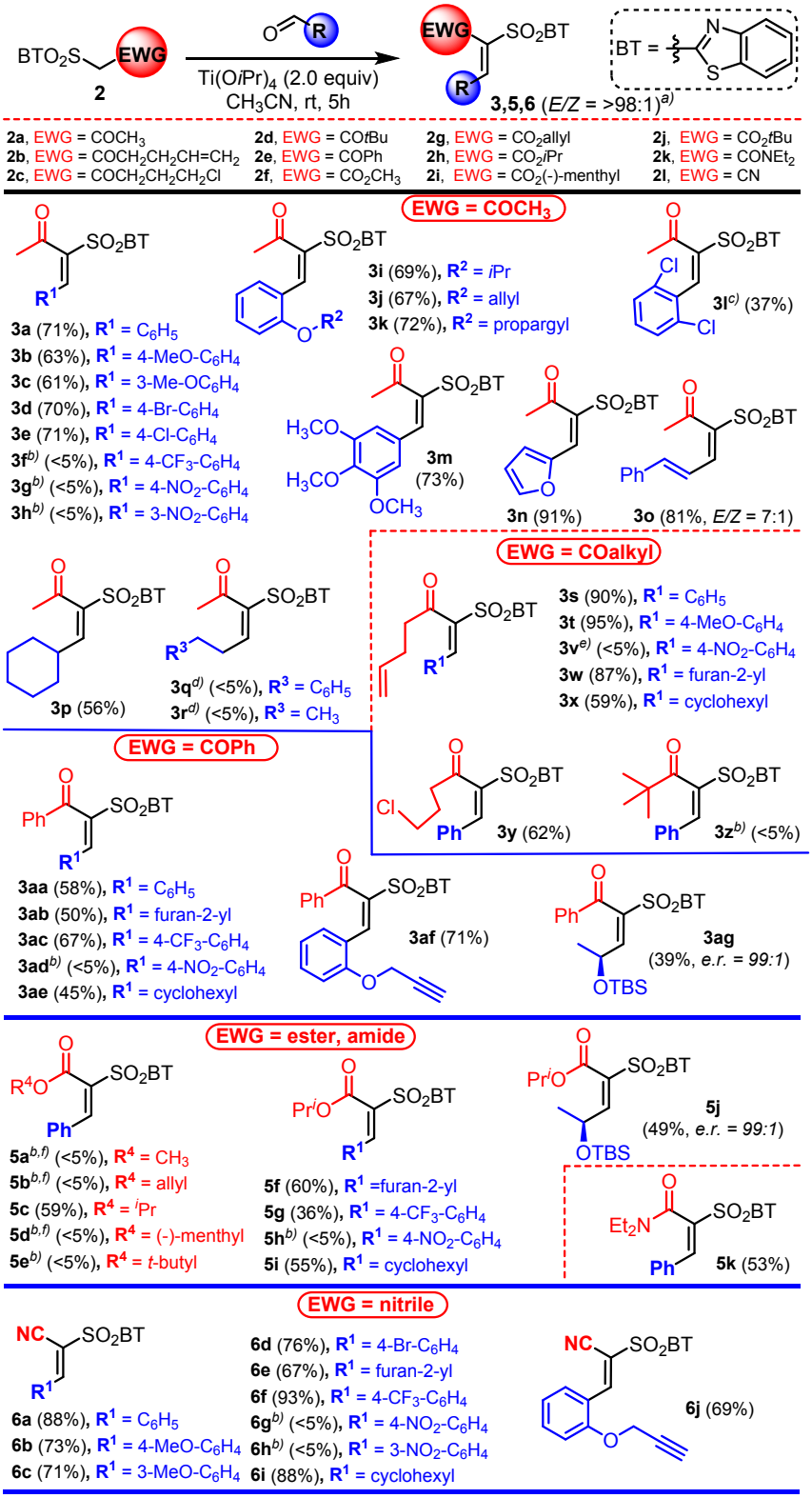
Entry	Conditions	**3a**/**4** ratio[a]	Yield[b] of **3a** (%)
1	Various "standard" Knoevenagel reaction conditions[c]	<5:>95	n.d.
2	EDDA (10 mol%), DCE, reflux, 3h	>95:<5	26%
3	Ti(O-*i*Pr)$_4$ (2.0 equiv), toluene, r.t., 5h	>95:<5	70%
4	Ti(O-*i*Pr)$_4$ (1.0 equiv), CH_3CN, r.t., 5h	>95:<5	35%
5	Ti(O-*i*Pr)$_4$ (3.0 equiv), CH_3CN, r.t., 5h	>95:<5	52%
6	Ti(O-*i*Pr)$_4$ (2.0 equiv), CH_3CN, r.t., 5h	>95:<5	71%
7	Ti(O-*i*Pr)$_4$ (2.0 equiv), CH_3CN, reflux, 5h	>95:<5	52%

[a] Based on the ^{1}H NMR spectra of the crude reaction mixture. [b] Isolated yields. [c] For further details see Supplementary Informations.

Scope and limitations of Knoveneagel condensation

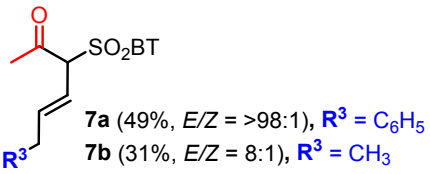
Having determined the optimal reaction conditions, the reaction partners' scope and limitations were evaluated (Table 2). From the *E/Z* olefin stereochemistry viewpoint, the condensations proceed with virtually exclusive *E* selectivity. The only exception was observed in case of the olefin **3s** (prepared from sulfone **2a** and cinnamaldehyde) that was formed as a 7:1 *E/Z* mixture. From the substrate viewpoint the influence of aldehyde coupling partner to reaction yield was first evaluated. It was observed that aryl and heteroaryl aldehydes substituted with alkoxy and halogen substituents including sterically crowded *ortho*-monosubstituted- or *o,o'*-disubstituted-ones are well tolerated. In contrary, strong electron-withdrawing substituents on the aryl ring (NO_2 and CF_3) led to the (partial in case of CF_3) product degradation under the reaction conditions or during the reaction work up. Indeed, it seems that the product of olefination **3f-h**, **3v**, **3ad**, **5h**, **6f-h** are formed under the reaction conditions but immediately undergo reaction with *i*PrOH (or another nucleophile) present in the media.[29] Only in the case of nitrile bearing condensation product **6f** no degradation occurred and the product was isolated in 93% yield.

Table 2. Scope and limitations of the condensation reaction.

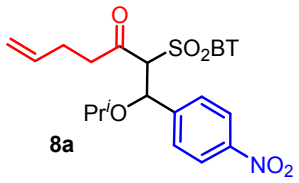


a) Based on the ^{1}H NMR spectra of the crude reaction mixture. b) No traces of product observed. c) Reaction carried out at 80 °C for 6h. d) Only olefin migration products **7a** and **7b** were isolated as the products of the reaction. e) only the product of 1,4-addition of *i*-PrOH to **3v** (compound **8a**) were detected suggesting that trace amount of the desired product was formed. Similar observations were made when 4-cyanobenzaldehyde and 3-

cyanobenzaldehyde were used as reaction substrates (not shown). [f] Only product **5c** was isolated in 58-61% yields.



7a (49%, *E/Z* = >98:1), $R^3 = C_6H_5$
7b (31%, *E/Z* = 8:1), $R^3 = CH_3$



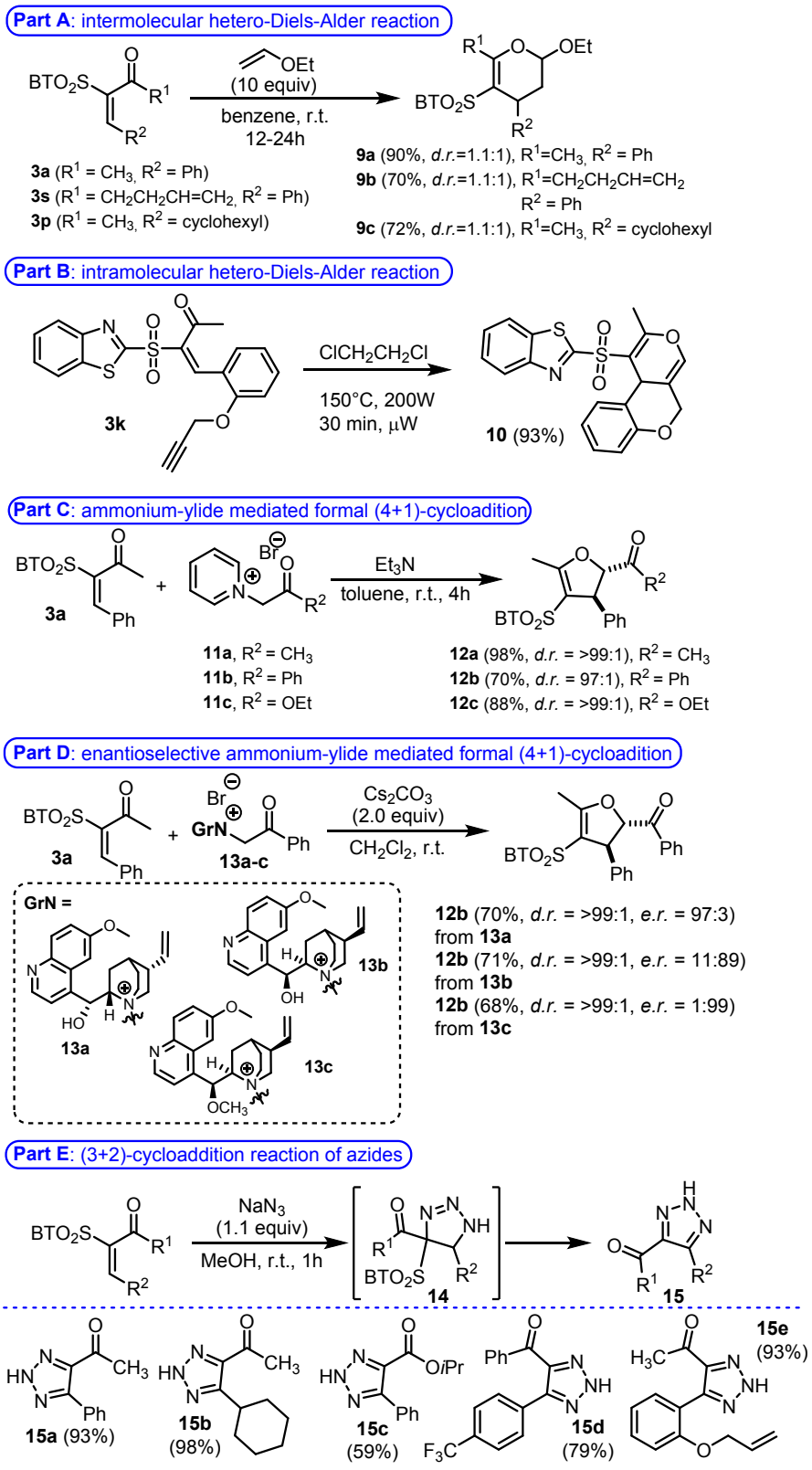
8a

α-Unbranched aldehydes represent the second limitation of the condensation reaction. In those cases the products **7a** and **7b**, the products of the olefin migration, were isolated instead of expected condensation products **3q** and **3r**.[27] Gratifyingly, when α-branched aldehydes were used, the desired products **3p**, **3x**, **3ae**, **3ag**, **5i**, **5j**, and **6i** were obtained in good to excellent yields. More importantly, when α-chiral aldehydes were used as the starting material, no stereo erosion was observed. When ketones were used as the condensation partners (not showed), no product of condensation was observed.

Next, the influence of the electron-withdrawing (EWG) group in **2** on the condensation was evaluated. It was observed that the condensation of alkyl ketone bearing sulfone **2d** is sensitive to the steric hindrance in carbonyl proximity (sulfone **2d** failed to yield adduct **3z**); methyl and α-unbranched functionalized BT-sulfoketones **2a-c** yielded the corresponding adducts **3a-y** in good to excellent yields; and arylketosulfone **2e** yielded the products **3aa-ag** in yields slightly lower to the corresponding alkyl sulfones **2a-c**. Ester, amide and nitrile bearing sulfones **2h**,**k**, and **2l** reacted under the condensation conditions smoothly and yielded the corresponding adducts **5** and **6** in good to excellent yields and exclusive *E*-selectivity. In case of esters, however, only *i*-propyl bearing ester adducts might be isolated after the reaction, since rapid *in situ* transesterification process of ester sulfones **2f**, **2g** and **2i** to the sulfone **2h** occurs during the condensation.[27] In the case of *t*-butyl-bearing ester sulfone **2j**, no traces of transesterification was observed, however, no product of condensation either.

Applications of activated olefins in organic synthesis

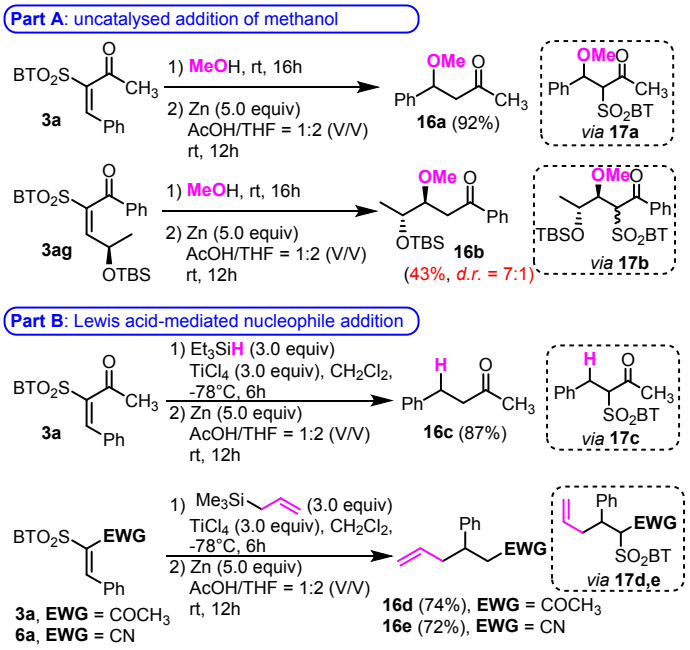
Having desired activated olefins **3**, **5** and **6** in hands, their reactivity in cycloadditions (Scheme 2), Michael-type (Lewis acid-mediated) nucleophilic additions (Scheme 3 and 4), hydride reductions, and radical reactions (Scheme 5) were evaluated. First, hetero-Diels-Alder cycloaddition reaction of ketosulfones **3** with ethyl vinyl ether was investigated (Scheme 2, part A). It was observed that the reaction proceeds well and yields the desired dihydropyran **9** in excellent yields. Similarly, intramolecular hetero-Diels-Alder reaction of ketosulfone function to alkynes can be performed albeit under harsher reaction conditions (μW, 150°C, 200W) (Scheme 2, part B). Ketosulfones **3** can also react with ammonium ylides to generate products of formal [4+1]-cycloaddition reaction in both racemic (Scheme 2, part C) and enantioselective manner (Scheme 2, part D). In both cases the desired dihydrofurans **12** are formed in very good to excellent yields and, in the case of nonracemic ammonium ylides,[30] enantioselectivity. Lastly, activated olefins **3a**, **3p**, **3ac** and **5c** were used as dipolarophiles in 1,3-cycloaddition reaction of sodium azide (Scheme 2, part E). In this case, products of [3+2]-cycloaddition **14** undergoes to spontaneous *in situ* $BTSO_2$-group elimination to provide solely corresponding triazoles **15** in good to excellent yields. In the case of compound **15e** the reaction was chemoselective towards the activated olefin.



Scheme 2. Cycloaddition reactions – attempted examples.

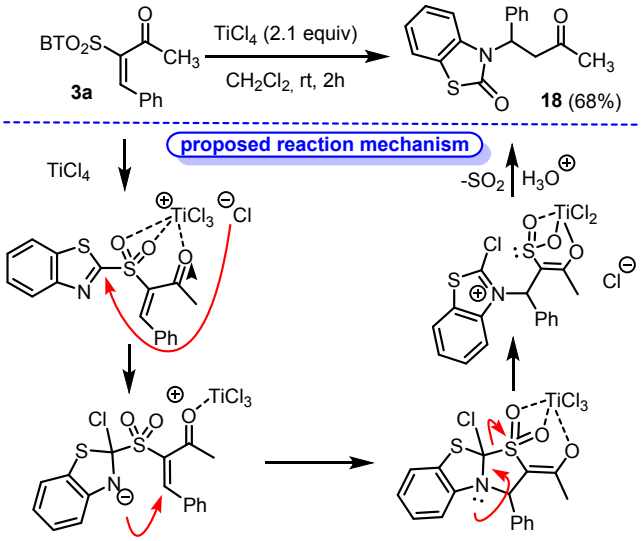
The reactivity of activated olefins towards nucleophiles under uncatalyzed (Scheme 3, part A) and Lewis acid mediated (Scheme 3, part B, and Scheme 4) reaction conditions was also evaluated. It was observed that simple treatment of olefins **3a** and **3ag** with methanol at rt under prolonged reaction times results in the formation of 1,4-adducts **17**, that can be further selectively desulfonylated[31] to

yield β-methoxy ketones **16a** and **16b** (Scheme 3, part A). Interestingly, even under unoptimized reaction conditions, the addition of methanol to homochiral olefin **3ag** proceeds with high diastereoselectivity.[27] Similarly, olefins **3a** and **6a** were reacted with the Et_3SiH and allylsilane in the presence of $TiCl_4$ (Scheme 3, part B). Rapid 1,4-addition followed by *in situ* desulfonylation[31] then yielded β-adducts **19a-c** in very good yield.



Scheme 3. Uncatalyzed and Lewis acid-mediated reactions of activated olefins **3a**, **3ag** and **6a**.

Another interesting reaction was observed when olefin **3a** was treated with $TiCl_4$ at rt without any additional additive (Scheme 4). In this case, an intramolecular Smiles-like rearrangement followed with desulfonylation yielded β-functionalized ketone **18**.[32]

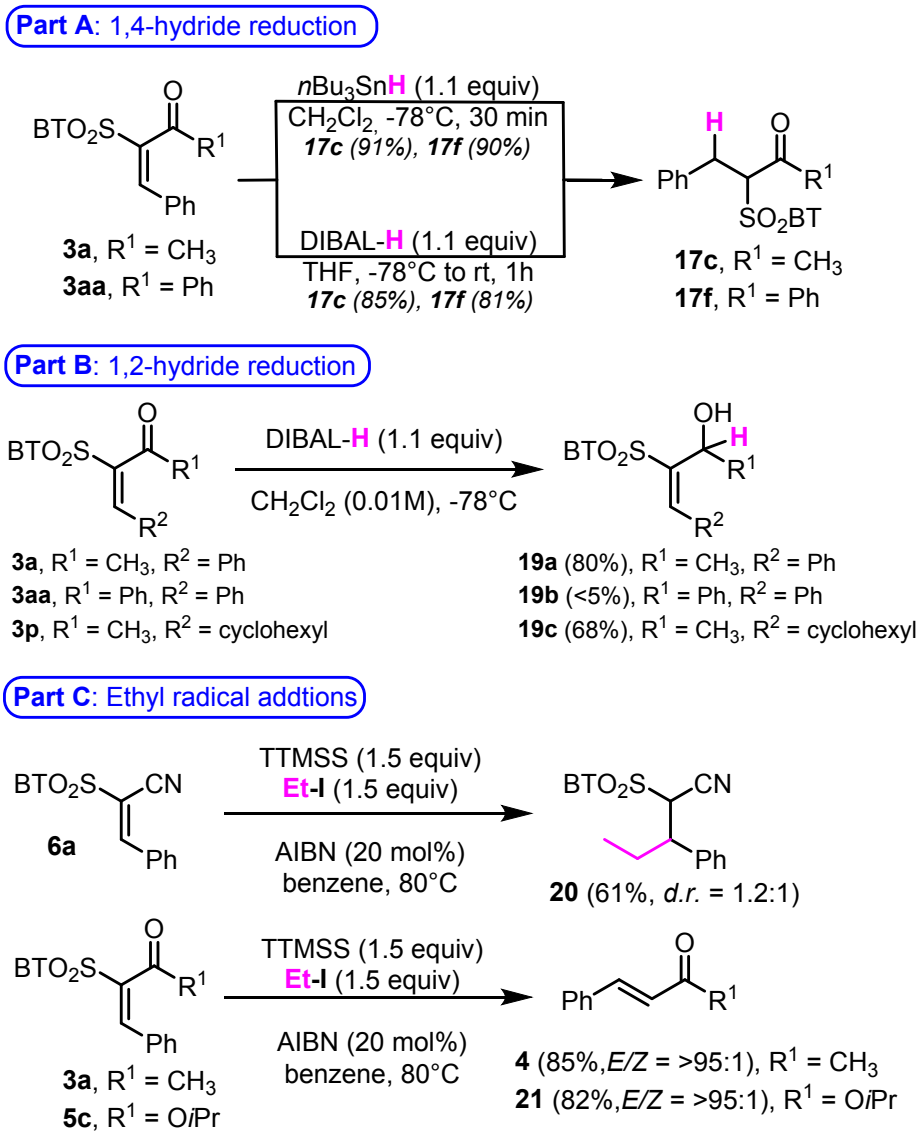


Scheme 4. $TiCl_4$-mediated rearrangement of **3a** to ketone **18**.

Since the Lewis acid-mediated Et_3SiH addition proceeded with exclusive 1,4-addition, selectivity of 1,2- vs. 1,4-hydride reduction was investigated (Scheme 5).[27] It was observed that vast majority of standard

reducing agents, to mention just a few (nBu$_3$SnH[33] or DIBAL-H in THF), favors 1,4-reduction products **17c,f** (Scheme 5, part A). In contrary, the selective 1,2-hydride reduction could be performed if DIBAL-H reduction was carried out in CH_2Cl_2 at -78°C under high (0.01M) dilution (Scheme 5, part B). Using such conditions, the desired allylic alcohols **19a,c** could be obtained in very good yields.[27] Interestingly, phenyl-substituted ketone **3aa** do not undergo to 1,2-reduction under such conditions, and only 1,4-adduct **17f** is isolated.

Finally, we have decided to evaluate the radicophilic behavior of activated olefins **3**, **5** and **6**. The original hypothesis was that these newly generated olefins will behave similarly as vinyl BT sulfone explored in the pioneering work of Baran *et al* (Fe(acac)$_3$ promoted radical addition).[15] However, quick 1,4-addition of EtOH to **3** excluded such possibility.[34] Thus we have focused on classical Giese addition, in which an electron-deficient alkene (our olefins) is attacked by a nucleophilic alkyl radical.[35–38] Unfortunately, such conditions in general require a tin reagent. Since in our case nBu$_3$SnH spontaneously adds in a 1,4-manner to olefin **3a** even at low temperature, tris(trimethylsilyl)silane (TTMS) was used instead (Scheme 5, part C). Thus, olefins **3a**, **5c**, and **6a** were reacted with the ethyl radical generated in a TTMS/EtI/AIBN system. Surprisingly, only nitrile bearing olefin **6a** yielded the desired adduct **20**, while carbonyl bearing olefins **3a** and **5c** gave unsaturated carbonyl compounds **4** and **21**, respectively. Such observation suggests that in the case of carbonyl-substituted olefins, the generated radical preferentially attacks the BT-sulfonyl group and, as suggested by the (*E*)-olefin **4** and **21** formation,[39] generates a vinylic radical as a reaction intermediate.



Scheme 5. Selective hydride reductions and radical addition.

Conclusions

In conclusion, synthesis of highly electrophilic olefins that can be in one or two steps transformed into valuable (enantio-enriched) heterocyclic and acyclic scaffolds has been developed. Prepared olefins can be used as hetero-dienes, dienophiles and Michael-acceptors, respectively, and can be reacted in various hetero-Diels-Alder, 1,3-dipolar, or formal [4+1]-cycloaddition reactions. Selective 1,2 and 1,4-hydride addition, respectively, are possible in the case of carbonyl bearing olefins **3**. Such olefins also undergo Lewis acid-mediated 1,4-addition of allylsilanes or to unprecedented Smiles-like rearrangement products. Finally, classical Giese 1,4-radical addition of nucleophilic ethyl radical was observed in case of nitrile-bearing olefin **6a**, but not in case of the two carbonyl-group bearing analogs **3a** and **5c**. The last two transformations (Smiles-like rearrangement and nucleophilic radical additions) are currently being further investigated in our group.

Experimental section

General information. All starting materials were purchased from commercial suppliers and used without further purification, unless otherwise stated. Chiral aldehydes,[40] pyridium salts **11a-c**,[41] chiral ammonium salts **13a-c**,[30,42] BT-sulfones **2d**,[43] **2g**,[25,26] (–)-2-menthyl 2-bromoacetate,[44] and 2-

(methylsulfonyl)benzo[d]thiazole[25,26] were prepared using reported procedures. Progress of reactions was monitored by thin-layer chromatography (TLC) - aluminum plates pre-coated with silica gel (silica gel 60 F254). Column chromatography was performed on silica gel 60 (40-63 µm) or neutralized silica gel (40-63 µm) using 5% solution of Et_3N in petroleum ether. Reactions run at elevated temperatures were carried out using the oil bath and indicated temperatures refers to the oil bath temperature. Determination of melting points were done on a Büchi melting point apparatus and were uncorrected. ^1H NMR and $^{13}C\{^1H\}$ NMR spectra were measured on Jeol ECA400II (400 and 101 MHz) or Jeol 500 ECA (500 and 126 MHz) in $CDCl_3$ or DMSO. Chemical shifts are reported in ppm and their calibration was performed (a) in case of ^1H NMR experiments on residual peak of non-deuterated solvent δ ($CHCl_3$) = 7.26 ppm; δ (DMSO) = 2.50 ppm, (b) in case of ^{13}C NMR experiments on the middle peak of the ^{13}C signal in deuterated solvent δ ($CDCl_3$) = 77.2 ppm; δ (DMSO-d_6) = 39.5 ppm, and (c) in case of $^{19}F\{^1H\}$ NMR experiments on the external calibrant $CFCl_3$ (δ ($CFCl_3$) = 0 ppm). Proton coupling patterns are represented as singlet (s), doublet (d), doublet of doublet (dd), triplet (t), triplet of triplet (tt) and multiplet (m). HRMS data were obtained using quadrupole/ion trap mass analyzer. HPLC was performed using a Dionex Summit HPLC system with a CHIRAL ART Cellulose-SB (250 x 4.6 mm, 5 µm) or CHIRALPAK IE-3 chiral stationary phase with mobile phase 2-propanol/hexane, 2-propanol/CO_2, MeOH/CO_2. HRMS analysis was performed using LC chromatograph (Dionex UltiMate 3000, Thermo Fischer Scientific, MA, USA) + mass spectrometer Exactive Plus Orbitrap high-resolution (Thermo Fischer Scientific, MA, USA) with electrospray ionization; Chromatographic separation: column Phenomenex Gemini (C18, 50 x 2 mm, 3 µm particle), isocratic elution, MP: 80 % ACN and 20 % buffer (0,01M ammonium acetate) or 95% MeOH + 5% water + 0.1% HCOOH. Microwave irradiation experiments were carried out in a dedicated CEM-Discover mono-mode microwave apparatus. The reactor was used in the standard configuration as delivered, including proprietary software. The reactions were carried out in 30 mL glass vials sealed with an Silicone/PTFE Vial caps top, which can be exposed to a maximum of 250 °C and 20 bar internal pressure. The temperature was measured with an IR sensor on the outer surface of the process vial. After the irradiation period, the reaction vessel was cooled to ambient temperature by gas jet cooling.

Synthesis of α-electron withdrawing BT-sulfones (2). Method A.[45] *Synthesis of sulfide intermediate.* A mercaptobenzthiazole (10.0 g, 1.0 equiv) and α-halo compound (1.0 equiv) were dissolved in CH_2Cl_2 (0.2 M) and the mixture was cooled to 0°C. Triethylamine (8.6 mL, 2.0 equiv) was added dropwise and resulting mixture was allowed warm to r.t. and stirred for 4 hours. 2 M aq. HCl (20 mL) was added and the resulting layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3x20mL) and the resulting organic extracts were combined, washed with water (30 mL), brine (20 mL), dried over $MgSO_4$ and solvents were evaporated under reduced pressure. Crude product was used in the next step without further purification. *Synthesis of targeted sulfone.* Sulfide (1.1 g, 1.0 equiv) and periodic acid (2.8 g, 3.0 equiv) were dissolved in acetonitrile (0.2 M) and mixture was cooled to 0°C. CrO_3 (0.123 g, 0.3 equiv) was added portion wise and the resulting mixture stirred for 30 minutes, before it was warmed to r.t. The reaction was stirred for another 4 hours before it was cooled to 0°C and quenched by adding sat. aq. Na_2SO_3. Filtration over the Celite®, washed (5x25 mL EtOAc). Layers were separated, and organic phase was washed with sat. Na_2SO_3 (2x20 mL), water (2x20mL), brine (2x20mL) and dried over $MgSO_4$. Solvents were removed under the reduced pressure. **Method B.**[25] A solution of -(methylsulfonyl)benzo[d]thiazole[25,26] (0.300 g, 1.41 mmol, 1.0 equiv) in dry THF (7.0 mL, 0.2 M) was cooled to -78°C and LiHMDS (1.0 M sol. in THF) (3.7 mL, 2.2 equiv) was added dropwise. A color of the reaction mixture turned from colorless or slightly yellow to orange/red. Immediately after, a solution of acyl halide (1.69 mmol, 1.2 equiv) in THF (3 mL) was added. The color of the reaction mixture faded within few minutes. The resulting mixture was stirred at -78°C for 60 min, allowed to warm to r.t. within 1h, and stirred at r.t. for additional 60 min before sat. aq. NH_4Cl (15 mL) was added. The whole

mixture was extracted with EtOAc (3x75 mL) and the combined organic layers were washed with brine (50 mL), dried over $MgSO_4$, filtered and the solvents were removed under reduced pressure. Resulting crude product was used further without any purification, if not stated otherwise.

*1-(benzo[d]thiazol-2-ylsulfonyl)propan-2-one (**2a**)*. Crude product was prepared using the method A and obtained with enough purity as yellow solid (4.2 g, 89%). M.p. = 125-127°C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (dd, *J* = 7.6, 2.0 Hz, 1H), 8.03 – 7.99 (m, 1H), 7.67 – 7.57 (m, 2H), 4.57 (s, 2H), 2.45 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 194.7, 164.9, 152.5, 137.0, 128.4, 127.9, 125.7, 122.5, 65.5, 31.6; MS (ESI), m/z (%) 256 $[M+H]^+$ (100); HRMS (ESI) *m/z*: $[M - H]^-$ Calcd for $C_{10}H_8NO_3S_2$ 253.9951; Found 253.9950.

*1-(benzo[d]thiazol-2-ylsulfonyl)hex-5-en-2-one (**2b**)*. Crude product was prepared using the method B and purified using flash column chromatography (SiO_2; EtOAc: P.E. = 1: 6), isolated as a yellow oil (1.4 g, 71%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 – 8.19 (m, 1H), 8.05 – 8.00 (m, 1H), 7.67 – 7.58 (m, 2H), 5.81 – 5.70 (m, 1H), 5.08 – 4.95 (m, 2H), 4.59 (s, 2H), 2.85 (t, *J* = 7.2 Hz, 2H), 2.41 – 2.29 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 196.4, 165.0, 152.5, 137.0, 136.0, 128.4, 127.9, 125.7, 122.5, 116.1, 64.7, 43.6, 27.1; MS (ESI), m/z (%) 294 $[M-H]^-$ (100); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{14}NO_3S_2$ 296.0410; Found 296.0407.

*1-(benzo[d]thiazol-2-ylsulfonyl)-5-chloropentan-2-one (**2c**)*. Crude product was prepared using method B and purified using flash column chromatography (SiO_2; Diethylether: P.E. = 3: 1), isolated as an orange oil (0.485 g, 82%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.23 – 8.20 (m, 1H), 8.04 – 8.01 (m, 1H), 7.68 – 7.59 (m, 2H), 4.61 (s, 2H), 3.55 (t, *J* = 6.8 Hz, 2H), 2.96 (t, *J* = 6.8 Hz, 2H), 2.12 – 2.02 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 196.2, 164.9, 152.5, 137.0, 128.5, 128.0, 125.7, 122.6, 64.9, 43.8, 41.3, 26.0; MS (ESI), m/z (%) 282 $[M-Cl]^+$ (100); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{13}ClNO_3S_2$ 318.0020; Found 318.0021.

*2-(benzo[d]thiazol-2-ylsulfonyl)-1-phenylethan-1-one (**2e**)*. Crude product was prepared using the method A and obtained with enough purity as a light brown solid (3.9 g, 92%). M.p. = 118-120°C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 – 8.18 (m, 1H), 8.02 – 7.99 (m, 1H), 7.95 – 7.90 (m, 2H), 7.66 – 7.57 (m, 3H), 7.50 – 7.44 (m, 2H), 5.20 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 187.3, 165.4, 152.6, 137.2, 135.6, 134.8, 129.1, 129.1, 128.3, 127.8, 125.7, 122.5, 61.3; MS (ESI), m/z (%) 318 $[M+H]^+$ (100); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{12}NO_3S_2$ 318.0253; Found 318.0251.

*methyl 2-(benzo[d]thiazol-2-ylsulfonyl)acetate (**2f**)*. Crude product was prepared using the method A and obtained as a yellow solid (2.8 g, 88%). M.p. = 68-70°C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 – 8.21 (m, 1H), 8.04 – 8.01 (m, 1H), 7.68 – 7.59 (m, 2H), 4.58 (s, 2H), 3.74 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 165.0, 162.3, 152.6, 137.1, 128.4, 127.9, 125.7, 122.5, 58.7, 53.5; MS (ESI), m/z (%) 272 $[M+H]^+$ (27); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{10}NO_4S_2$ 272.0046; Found 272.0043.

*isopropyl 2-(benzo[d]thiazol-2-ylsulfonyl)acetate (**2h**)*. Crude product was prepared using the method B and obtained as a light yellow solid (0.199 g, 90%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 – 8.21 (m, 1H), 8.08 – 7.99 (m, 1H), 7.68 – 7.58 (m, 2H), 5.00 (hept, *J* = 6.4 Hz, 1H), 4.54 (s, 2H), 1.15 (d, *J* = 6.4 Hz, 6H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 165.2, 161.2, 152.6, 137.1, 128.4, 127.9, 125.7, 122.5, 71.1, 59.1, 21.6; MS (ESI), m/z (%) 298 $[M-H]^-$ (100); HR-MS (ESI) *m/z*: $[M]^+$ Calcd for $C_{12}H_{13}NO_4S_2$ 299.0286; Found 299.0284.

*(2S,5R)-2-isopropyl-5-methylcyclohexyl 2-(benzo[d]thiazol-2-ylsulfonyl)acetate (**2i**)*. Crude product was prepared using the method A from (–)-2-menthyl 2-bromoacetate[44] and obtained with enough purity as a green viscose syrup (2.24 g, 95%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 – 8.17 (m, 1H), 8.07 – 7.97 (m, 1H), 7.69 – 7.54 (m, 2H), 4.65 (td, *J* = 10.8, 4.4 Hz, 1H), 4.62 (d, *J* = 15.2 Hz, 1H), 4.52 (d, *J* =

15.2 Hz, 1H) 1.97 – 1.85 (m, 1H), 1.69 – 1.52 (m, 3H), 1.47 – 1.31 (m, 1H), 1.24 – 1.10 (m, 1H), 1.03 – 0.84 (m, 2H), 0.83 (d, *J* = 6.4 Hz, 3H), 0.84 – 0.67 (m, 1H), 0.68 (d, *J* = 7.2 Hz, 3H), 0.61 (d, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, Chloroform-*d*) δ 165.3, 161.3, 152.6, 137.0, 128.3, 127.9, 125.6, 122.5, 58.9, 46.7, 40.4, 34.1, 31.4, 26.0, 23.1, 22.0, 20.6, 16.0; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd. for $C_{19}H_{26}NO_4S_2$ 396.1298; Found 396.1300; α_D^{22}= - 32.5 (c 0.2, $CHCl_3$).

*2-(benzo[d]thiazol-2-ylsulfonyl)-N,N-diethylacetamide (**2k**)*. Crude product was prepared using the method B and purified using flash column chromatography (SiO_2; EtOAc: P.E. = 3:1), isolated as a yellow solid (0.366 g, 84%). M.p. = 125-126°C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.23 – 8.20 (m, 1H), 8.01 – 7.98 (m, 1H), 7.64 – 7.55 (m, 2H), 4.63 (s, 2H), 3.46 (q, *J* = 7.2 Hz, 2H), 3.35 (q, *J* = 7.2 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.08 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, Chloroform-*d*) δ 165.5, 160.0, 152.6, 137.4, 128.1, 127.7, 125.7, 122.6, 58.0, 43.3, 41.1, 14.6, 12.9; MS (ESI), m/z (%) 313 $[M+H]^+$ (100); HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{13}H_{16}N_2NaO_3S_2$ 335.0495; Found 335.0494.

*2-(benzo[d]thiazol-2-ylsulfonyl)acetonitrile (**2l**)*. Crude product was prepared using the method A and obtained with enough purity as a brown solid (3.4 g, 95%). M.p. = 172-174°C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.29 – 8.25 (m, 1H), 8.09 – 8.05 (m, 1H), 7.74 – 7.65 (m, 2H), 4.56 (s, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, Chloroform-*d*) δ 162.5, 152.4, 137.3, 129.1, 128.4, 126.0, 122.7, 109.2, 44.1; MS (ESI), *m/z* (%) 237 $[M-H]^-$ (25); HRMS (ESI) *m/z*: $[M - H]^-$ calcd for $C_9H_5N_2O_2S_2$: 236.9798, found 236.9798.

Ti(O-*i*Pr)$_4$-mediated transesterification of 2f to 2h. To solution of sulfone **2f** (0.200 g, 0.73 mmol, 1.0 equiv) in CH_3CN (4.0 mL, 0.2 M), Ti(O-*i*Pr)$_4$ (0.435 mL, 1.46 mmol, 2.0 equiv) was added dropwise at r.t. and the resulting mixture was stirred for 2h. CH_2Cl_2 (15 mL) and sat. aq. NH_4Cl (5 mL) were added and the resulting mixture was filtered through Celite®. Filtrate cake was washed with CH_2Cl_2 (5x20mL) and combined filtrates were washed with sat. aq. NH_4Cl (2x15 mL), brine (2x15 mL), and dried over $MgSO_4$. Solvents were removed under reduced pressure and the crude product was isolated as a light yellow solid (0.219 g, 95%)

General procedure for Knoveneagel condensation reaction. To a sulfone (1.0 mmol, 1.0 equiv) in CH_3CN (5.0 mL, 0.2 M) at r.t. was added Ti(O-*i*Pr)$_4$ (0.925 mL, 3.0 equiv) and the resulting mixture was stirred for 30 minutes. An aldehyde (2.0 mmol, 2.0 equiv) was added dropwise and the mixture was stirred for the indicated time. The reaction was quenched upon addition of CH_2Cl_2 (15 mL) and sat. NH_4Cl (5 mL) and the resulting suspension was filtered through Celite®. The filtrate cake was rinsed with CH_2Cl_2 (5x20mL), and the combined filtrates were washed with sat. NH_4Cl (2x15 mL), brine (2x15 mL), dried over $MgSO_4$, filtered, and the solvents removed under reduced pressure to provide the crude product.

*(E)-3-(benzo[d]thiazol-2-ylsulfonyl)-4-phenylbut-3-en-2-one (**3a**)*. Reaction was carried out using the described procedure with 1.5g (4.37 mmol) of sulfone **2a**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:4) and concentration of the relevant fractions provided the **3a** as a light yellow solid (1.43 g, 71%). M.p. = 104-107°C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.20 – 8.18 (m, 1H), 8.14 (s, 1H), 8.01 – 7.98 (m, 1H), 7.59 (ddd, *J* = 7.2, 6.4, 1.6 Hz, 2H), 7.41 (s, 5H), 2.38 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, Chloroform-*d*) δ 198.3, 166.0, 152.9, 145.1, 139.3, 137.6, 132.2, 131.3, 130.3, 129.4, 128.1, 127.6, 125.7, 122.40, 31.92; MS (ESI), *m/z* (%) 344 $[M+H]^+$ (100); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{14}NO_3S_2$ 344.0410; Found 344.0413.

*(E)-3-(benzo[d]thiazol-2-ylsulfonyl)-4-(4-methoxyphenyl)but-3-en-2-one (**3b**).* Reaction was carried out using the described procedure with 0.200 g (0.79 mmol) of sulfone **2a**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:3) and concentration of the relevant fractions provided the **3b** as a yellow solid (0.143 g, 63%). M.p. = 119-121°C; ^1H NMR (500 MHz, Chloroform-*d*) δ 8.20 – 8.18 (m, 1H), 8.07 (s, 1H), 8.00 – 7.98 (m, 1H), 7.62 – 7.55 (m, 2H), 7.39 – 7.36 (m, 2H), 6.94 –

6.91 (m, 2H), 3.85 (s, 3H), 2.43 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, Chloroform-*d*) δ 198.7, 166.5, 163.0, 152.8, 145.1, 137.5, 136.2, 132.8, 128.0, 127.6, 125.7, 123.7, 122.4, 114.9, 55.7, 31.9; MS (ESI), *m/z* (%) 374 $[M+H]^+$ (50); HRMS (ESI) *m/z*: $[M]^+$ calcd. for $C_{18}H_{16}NO_4S_2$ 374.0515; Found 374.0519.

*(E)-3-(benzo[d]thiazol-2-ylsulfonyl)-4-(3-methoxyphenyl)but-3-en-2-one (**3c**).* Reaction was carried out using the described procedure with 0.200 g (0.79 mmol) of sulfone **2a**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:3) and concentration of the relevant fractions provided the **3c** as a yellow oil (0.138 g, 61%). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.20 – 8.17 (m, 1H), 8.10 (s, 1H), 8.00 – 7.97 (m, 1H), 7.62 – 7.54 (m, 2H), 7.37 – 7.28 (m, 1H), 7.06 – 6.94 (m, 3H), 3.78 (s, 3H), 2.37 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, Chloroform-*d*) δ 198.3, 165.9, 160.1, 152.8, 145.0, 139.5, 137.6, 132.5, 130.4, 128.1, 127.6, 125.7, 122.6, 122.4, 118.1, 115.0, 55.5, 32.0; MS (ESI), *m/z* (%) 374 $[M+H]^+$; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{16}NO_4S_2$: 374.0515; Found 374.0518.

*(E)-3-(benzo[d]thiazol-2-ylsulfonyl)-4-(4-bromophenyl)but-3-en-2-one (**3d**)*. Reaction was carried out using the described procedure with 0.200 g (0.79 mmol) of sulfone **2a**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:4) and concentration of the relevant fractions provided the **3d** as a yellow oil (0.231 g, 70%). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.22 – 8.19 (m, 1H), 8.05 (s, 1H), 8.03 – 8.00 (m, 1H), 7.65 – 7.59 (m, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 2.41 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, Chloroform-*d*) δ 198.0, 165.7, 152.9, 143.5, 140.1, 137.6, 132.8, 131.6, 130.2, 128.3, 127.8, 127.1, 125.8, 122.5, 32.0; MS (ESI), *m/z* (%) 422 $[M]^+$ (100); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{13}BrNO_3S_2$ 421.9515; Found 421.9514.

*(E)-3-(benzo[d]thiazol-2-ylsulfonyl)-4-(4-chlorophenyl)but-3-en-2-one (**3e**)*. Reaction was carried out using the described procedure with 0.200 g (0.79 mmol) of sulfone **2a**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:3) and concentration of the relevant fractions provided the **3e** as a colorless oil (0.212 g, 71%). ^1H NMR (500 MHz, Chloroform-*d*) δ 8.24 – 8.17 (m, 1H), 8.06 (s, 1H), 8.03 – 7.99 (m, 1H), 7.64 – 7.56 (m, 2H), 7.44 – 7.39 (m, 2H), 7.37 – 7.33 (m, 2H), 2.41 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, Chloroform-*d*) δ 198.0, 165.8, 152.9, 143.5, 140.0, 138.6, 137.6, 131.5, 129.8, 128.3, 127.8, 125.8, 122.4, 32.0; MS (ESI), *m/z* (%) 378 $[M+H]^+$ (100); HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{12}ClNaNO_3S_2$ 399.0939; Found 399.0940.

*(E)-3-(benzo[d]thiazol-2-ylsulfonyl)-4-(2-isopropoxyphenyl)but-3-en-2-one (**3i**)*. Reaction was carried out using the described procedure with 0.233 g (0.92 mmol) of sulfone **2a**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:3) and concentration of the relevant fractions provided the **3i** as a yellow oil (0.274 g, 69%). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.51 (s, 1H), 8.18 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.01 (dd, *J* = 6.8, 2.4 Hz, 1H), 7.58 (tt, *J* = 7.2, 5.6 Hz, 2H), 7.43 (ddd, *J* = 8.8, 7.2, 1.6 Hz, 1H), 7.20 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.02 – 6.85 (m, 2H), 4.63 (hept, *J* = 6.0 Hz, 1H), 2.30 (s, 3H), 1.35 (d, *J* = 6.0 Hz, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, Chloroform-*d*) δ 197.8, 167.0, 157.0, 142.9, 138.2, 137.5, 133.8, 131.1, 127.9, 127.4, 125.5, 122.3, 121.5, 120.7, 114.0, 71.9, 53.6, 31.3, 21.9; MS (ESI), *m/z* (%) 402 $[M]^+$ (100); HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{19}NNaO_4S_2$ 424.0653; Found 424.0648.

*(E)-4-(2-(allyloxy)phenyl)-3-(benzo[d]thiazol-2-ylsulfonyl)but-3-en-2-one (**3j**)*. Reaction was carried out using the described procedure with 0.255 g (1.0 mmol) of sulfone **2a**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:3) and concentration of the relevant fractions provided the **3j** as a yellow oil (0.267 g, 67%). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.53 (s, 1H), 8.23 – 8.16 (m, 1H), 8.05 – 7.95 (m, 1H), 7.66 – 7.52 (m, 2H), 7.49 – 7.40 (m, 1H), 7.21 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.01 – 6.90 (m, 2H), 6.02 (ddt, *J* = 17.2, 10.4, 5.2 Hz, 1H), 5.42 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.30 (dd, *J* = 10.8, 1.2 Hz, 1H), 4.70 – 4.59 (m, 2H), 2.33 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, Chloroform-*d*) δ 197.8, 166.8, 157.4, 152.8, 142.2, 138.5, 137.5, 133.9, 132.2, 131.1, 128.0, 127.5, 125.6, 122.4, 121.1, 120.8, 118.3,

112.8, 69.4, 31.5; MS (ESI), *m/z* (%) 400 $[M+H]^+$ (100); HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{17}NNaO_4S_2$ 422.0497; Found 422.0490.

*(E)-3-(benzo[d]thiazol-2-ylsulfonyl)-4-(2-(prop-2-yn-1-yloxy)phenyl)but-3-en-2-one (**3k**)*. Reaction was carried out using the described procedure with 0.200 g (0.79 mmol) of sulfone **2a**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:2) and concentration of the relevant fractions provided the **3k** as a brown solid (0.224 g, 72%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.45 (s, 1H), 8.19 (dd, *J* = 7.2, 2.0 Hz, 1H), 8.00 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.63 – 7.53 (m, 2H), 7.51 – 7.45 (m, 1H), 7.24 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 7.01 (t, *J* = 7.4 Hz, 1H), 4.78 (d, *J* = 2.4 Hz, 2H), 2.54 (t, *J* = 2.4 Hz, 1H), 2.33 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 197.8, 166.7, 156.2, 152.9, 141.7, 139.0, 137.6, 133.8, 131.4, 128.0, 127.6, 125.7, 122.4, 121.9, 121.3, 113.1, 56.2, 31.6; MS (ESI), *m/z* (%) 397 $[M]^+$ (100); HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{15}NNaO_4S_2$ 420.0340, Found 420.0335.

*(E)-3-(benzo[d]thiazol-2-ylsulfonyl)-4-(2,6-dichlorophenyl)but-3-en-2-one (**3l**)*. Reaction was carried out using the described procedure with 0.100 g (0.4 mmol) of sulfone **2a**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:3) and concentration of the relevant fractions provided the **3l** as a yellow oil (0.06 g, 37%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.31 (s, 1H), 8.21 – 8.18 (m, 1H), 8.04 – 8.01 (m, 1H), 7.65 – 7.58 (m, 2H), 7.41 – 7.38 (m, 2H), 7.35 – 7.30 (m, 1H), 2.26 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, Chloroform-*d*) δ 193.6, 166.2, 152.7, 143.8, 137.5, 133.9, 131.6, 130.7, 128.6, 128.3, 127.7, 126.6, 125.8, 122.5, 30.2; MS (ESI), *m/z* (%) 412 $[M]^+$ (100); HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{11}Cl_2NNaO_3S_2$ 433.9455; Found 433.9449.

*(E)-3-(benzo[d]thiazol-2-ylsulfonyl)-4-(3,4,5-trimethoxyphenyl)but-3-en-2-one (**3m**)*. Reaction was carried out using the described procedure with 0.100 g (0.4 mmol) of sulfone **2a**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:4) and concentration of the relevant fractions provided the **3m** as a yellow oil (0.131 g, 73%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.23 – 8.19 (m, 1H), 8.04 (s, 1H), 8.03 – 7.99 (m, 1H), 7.66 – 7.55 (m, 2H), 6.64 (s, 2H), 3.90 (s, 3H), 3.82 (s, 6H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, Chloroform-*d*) δ 198.7, 166.0, 153.6, 152.9, 145.1, 141.6, 138.1, 137.6, 128.2, 127.7, 126.4, 125.8, 122.4, 107.7, 61.2, 56.3, 32.2; MS (ESI), *m/z* (%) 434 $[M+H]^+$ (100); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{20}NO_6S_2$: 423.0727, found 423.0728.

*(E)-3-(benzo[d]thiazol-2-ylsulfonyl)-4-(furan-2-yl)but-3-en-2-one (**3n**)*. Reaction was carried out using the described procedure with 0.200 g (0.79 mmol) of sulfone **2a**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:4) and concentration of the relevant fractions provided the **3n** as a yellow oil (0.237 g, 91%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20 – 8.17 (m, 1H), 7.99 – 7.96 (m, 1H), 7.74 (s, 1H), 7.62 – 7.58 (m, 3H), 7.04 (d, *J* = 3.6 Hz, 1H), 6.57 (dd, *J* = 3.6, 1.6 Hz, 1H), 2.61 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 196.8, 166.1, 152.9, 148.1, 147.6, 137.5, 134.3, 129.7, 128.1, 127.6, 125.7, 122.3, 122.0, 113.6, 32.3; MS (ESI), *m/z* (%) 334 $[M+H]^+$ (49); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{12}NO_4S_2$ 334.0202; Found 334.0203.

*(3E,5E)-3-(benzo[d]thiazol-2-ylsulfonyl)-6-phenylhexa-3,5-dien-2-one (**3o**)*. Reaction was carried out using the described procedure with 0.740 g (2.9 mmol) of sulfone **2a**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:5) and concentration of the relevant fractions provided the **3o** as a yellow solid (0.866 g, 81%, *E*/*Z*=7:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20 – 8.14 (m, 1H), 8.02 – 7.97 (m, 2H), 7.69 (dd, *J* = 15.2, 11.6 Hz, 1H), 7.62 – 7.56 (m, 4H), 7.41 (m, 3H), 7.37 (d, *J* = 15.2 Hz, 1H), 2.65 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 194.1, 167.5, 152.7, 152.4, 152.3, 137.0, 135.7, 135.1, 131.4, 129.3, 128.9, 128.2, 127.7, 125.7, 123.0, 122.4, 31.9; MS (ESI), *m/z* (%) 370 $[M+1]^+$ (60); HRMS (ESI) *m/z*: Calcd for $C_{19}H_{16}NO_3S_2$ $[M + H]^+$ 370.0566; Found 370.0568.

*(E)-3-(benzo[d]thiazol-2-ylsulfonyl)-4-cyclohexylbut-3-en-2-one (**3p**)*. Reaction was carried out using the described procedure with 1.0 g (3.9 mmol) of sulfone **2a**. Purification using flash chromatography

(SiO_2; EtOAc/petroleum ether = 1:3) and concentration of the relevant fractions provided the **3p** as a colorless oil (0.764 g, 56%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20 – 8.16 (m, 1H), 8.00 – 7.97 (m, 1H), 7.64 – 7.54 (m, 2H), 7.25 (d, *J* = 10.8 Hz, 1H), 2.57 (s, 3H), 1.76 (bs, 5H), 1.28 (bs, 6H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 195.1, 166.5, 159.0, 152.6, 139.8, 137.1, 128.1, 127.7, 125.7, 122.4, 39.5, 32.2, 31.6, 25.5, 25.0; MS (ESI), *m/z* (%) 350 $[M+1]^+$ (100); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{20}NO_3S_2$ 350.0879; Found 350.0877.

*(E)-2-(benzo[d]thiazol-2-ylsulfonyl)-1-phenylhepta-1,6-dien-3-one (**3s**)*. Reaction was carried out using the described procedure with 0.200 g (0.68 mmol) of sulfone **2b**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:5) and concentration of the relevant fractions provided the **3s** as a yellow oil (0.234 g, 90%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 – 8.19 (m, 1H), 8.16 (s, 1H), 8.02 – 7.99 (m, 1H), 7.64 – 7.56 (m, 2H), 7.52 – 7.46 (m, 1H), 7.45 – 7.40 (m, 2H), 7.39 – 7.35 (m, 2H), 5.69 (ddt, *J* = 16.8, 10.0, 6.8 Hz, 1H), 5.01 – 4.92 (m, 2H), 2.74 (t, *J* = 7.2 Hz, 2H), 2.39 – 2.32 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 200.1, 166.0, 153.0, 145.2, 139.2, 137.7, 136.1, 132.2, 131.4, 130.4, 129.4, 128.2, 127.7, 125.8, 122.4, 116.2, 43.5, 27.4; MS (ESI), *m/z* (%) 384 $[M+1]^+$ (100); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{18}NO_3S_2$ 384.0723; Found 384.0720.

*(E)-2-(benzo[d]thiazol-2-ylsulfonyl)-1-(4-methoxyphenyl)hepta-1,6-dien-3-one (**3t**)*. Reaction was carried out using the described procedure with 0.200 g (0.68 mmol) of sulfone **2b**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:5) and concentration of the relevant fractions provided the **3t** as a yellow oil (0.266 g, 95%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 – 8.17 (m, 1H), 8.07 (s, 1H), 8.01 – 7.97 (m, 1H), 7.62 – 7.54 (m, 2H), 7.35 – 7.31 (m, 2H), 6.93 – 6.89 (m, 2H), 5.73 (ddt, *J* = 16.8, 10.0, 6.8 Hz, 1H), 5.04 – 4.94 (m, 2H), 3.85 (s, 3H), 2.81 (t, *J* = 7.2 Hz, 2H), 2.42 – 2.35 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 200.5, 166.5, 163.0, 152.9, 145.2, 137.6, 136.3, 136.0, 132.9, 128.0, 127.6, 125.8, 123.8, 122.4, 116.1, 114.9, 55.7, 43.5, 27.5; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{20}NO_4S_2$ 414.0828; Found 414.0827.

*(E)-2-(benzo[d]thiazol-2-ylsulfonyl)-1-(furan-2-yl)hepta-1,6-dien-3-one (**3w**)*. Reaction was carried out using the described procedure with 0.200 g (0.68 mmol) of sulfone **2b**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:6) and concentration of the relevant fractions provided the **3w** as a yellow oil (0.220 g, 87%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 – 8.18 (m, 1H), 8.00 – 7.97 (m, 1H), 7.74 (s, 1H), 7.63 – 7.53 (m, 3H), 7.00 – 6.98 (m, 1H), 6.57 (dd, *J* = 3.6, 1.6 Hz, 1H), 5.85 (ddt, *J* = 16.8, 10.0, 6.4 Hz, 1H), 5.06 (dq, *J* = 17.2, 1.6 Hz, 1H), 4.99 (ddt, *J* = 10.0, 1.6, 1.2 Hz, 1H), 3.02 (t, *J* = 7.2 Hz, 2H), 2.50 – 2.43 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 198.6, 166.1, 152.9, 148.0, 147.7, 137.6, 136.8, 134.5, 129.7, 128.1, 127.7, 125.8, 122.4, 121.7, 115.7, 113.6, 43.9, 27.5; MS (ESI), *m/z* (%) 374 $[M+1]^+$ (100); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{16}NO_4S_2$ 374.0515; Found 374.0513.

*(E)-2-(benzo[d]thiazol-2-ylsulfonyl)-1-cyclohexylhepta-1,6-dien-3-one (**3x**)*. Reaction was carried out using the described procedure with 0.200 g (0.68 mmol) of sulfone **2b**. Product **3x** was obtained with enough purity as a yellow oil (0.155 g, 59%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20 – 8.16 (m, 1H), 8.01 – 7.97 (m, 1H), 7.64 – 7.55 (m, 2H), 7.21 (d, *J* = 10.8 Hz, 1H), 5.79 (ddt, *J* = 16.8, 10.4, 6.4 Hz, 1H), 5.07 – 4.94 (m, 2H), 2.99 (t, *J* = 7.2 Hz, 2H), 2.54 – 2.43 (m, 1H), 2.39 (dtd, *J* = 7.2, 6.0, 1.6 Hz, 2H), 1.82 – 1.68 (m, 5H), 1.33 – 1.22 (m, 5H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 197.4, 166.5, 158.1, 152.8, 139.9, 137.3, 136.5, 128.2, 127.7, 125.8, 122.4, 115.8, 43.7, 39.5, 31.7, 27.5, 25.6, 25.0; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{23}NNaO_3S_2$ 412.1012; Found 412.1013.

*(E)-2-(benzo[d]thiazol-2-ylsulfonyl)-6-chloro-1-phenylhex-1-en-3-one (**3y**)*. Reaction was carried out using the described procedure with 0.100 g (0.68 mmol) of sulfone **2c**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:3) and concentration of the relevant fractions

provided the **3y** as a yellow oil (0.079 g, 62%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.23 – 8.18 (m, 1H), 8.17 (s, 1H), 8.03 – 7.98 (m, 1H), 7.64 – 7.55 (m, 2H), 7.52 – 7.47 (m, 1H), 7.46 – 7.41 (m, 2H), 7.39 – 7.35 (m, 2H), 3.50 (t, *J* = 6.4 Hz, 2H), 2.84 (t, *J* = 6.8 Hz, 2H), 2.13 – 2.03 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 199.9, 165.9, 152.9, 145.5, 139.0, 137.6, 132.3, 131.3, 130.2, 129.5, 128.2, 127.7, 125.8, 122.4, 43.7, 41.2, 26.4; MS (ESI), *m/z* (%) 406 $[M]^+$ (100), 407 $[M+1]^+$ (23); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{17}ClNO_3S_2$ 406.0333; Found 406.0333.

*(E)-2-(benzo[d]thiazol-2-ylsulfonyl)-1,3-diphenylprop-2-en-1-one (**3aa**)*. Reaction was carried out using the described procedure with 0.200 g (0.68 mmol) of sulfone **2e**. Purification using flash chromatography (passive SiO_2; EtOAc/petroleum ether = 1:3) and concentration of the relevant fractions provided the **3aa** as a yellow solid (0.367 g, 58%). M.p. = 150-153°C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.33 (s, 1H), 8.24 – 8.16 (m, 1H), 8.00 – 7.93 (m, 1H), 7.91 – 7.82 (m, 2H), 7.65 – 7.51 (m, 2H), 7.47 (tt, *J* = 7.2, 1.2 Hz, 1H), 7.38 – 7.27 (m, 5H), 7.24 – 7.13 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 191.2, 166.0, 152.9, 145.9, 137.7, 136.7, 135.3, 134.7, 131.9, 131.2, 130.9, 129.9, 129.1, 128.9, 128.1, 127.6, 125.8, 122.4; MS (ESI), *m/z* (%) 406 $[M+1]^+$ (100); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{16}NO_3S_2$ 406.0566; Found 406.0563.

*(E)-2-(benzo[d]thiazol-2-ylsulfonyl)-3-(furan-2-yl)-1-phenylprop-2-en-1-one (**3ab**)*. Reaction was carried out using the described procedure with 0.200 g (0.68 mmol) of sulfone **2e**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:1) and concentration of the relevant fractions provided the **3ab** as a yellow solid (0.120 g, 50%). M.p. = 168-170°C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 (m, 1H), 8.00 (s, 1H), 7.96 – 7.93 (m, 1H), 7.92 – 7.89 (m, 2H), 7.61 – 7.54 (m, 2H), 7.53 – 7.49 (m, 1H), 7.39 – 7.33 (m, 2H), 7.24 (dq, *J* = 1.6, 0.8 Hz, 2H), 6.85 (d, *J* = 3.2 Hz, 1H), 6.41 (dd, *J* = 3.6, 1.6 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 190.1, 166.2, 152.9, 147.9, 147.5, 137.7, 136.4, 134.3, 132.3, 130.9, 129.7, 128.8, 128.0, 127.5, 125.7, 122.3, 121.4, 113.2; MS (ESI), *m/z* (%) 396 $[M+1]^+$ (100); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{14}NO_4S_2$ 396.0359; Found 396.0359.

*(E)-2-(benzo[d]thiazol-2-ylsulfonyl)-1-phenyl-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (**3ac**)*. Reaction was carried out using the described procedure with 0.200 g (0.68 mmol) of sulfone **2e**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:1) and concentration of the relevant fractions provided the **3ac** as a white solid (0.200 g, 67%). M.p. = 57-59°C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.34 (s, 1H), 8.23 – 8.20 (m, 1H), 8.00 – 7.97 (m, 1H), 7.88 – 7.85 (m, 1H), 7.65 – 7.56 (m, 2H), 7.54 – 7.44 (m, 5H), 7.36 – 7.31 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 190.6, 165.3, 153.0, 143.5, 139.5, 137.8, 135.1, 135.0, 134.5, 133.1 (q, *J* = 32.9 Hz), 130.8, 129.9, 129.1, 128.3, 128.2, 126.7 (d, *J* = 272.1 Hz), 126.0 (q, *J* = 3.7 Hz), 125.8, 122.4; ^{19}F{^{1}H} NMR (376 MHz, Chloroform-*d*) δ -63.17(s, 3F); MS (ESI), *m/z* (%) 474 $[M]+1^+$ (100); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{15}F_3NO_3S_2$ 474.0440; Found 474.0438.

*(E)-2-(benzo[d]thiazol-2-ylsulfonyl)-3-cyclohexyl-1-phenylprop-2-en-1-one (**3ae**)*. Reaction was carried out using the described procedure with 0.050 g (0.16 mmol) of sulfone **2e**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:4) and concentration of the relevant fractions provided the **3ae** as a colorless oil (0.029 g, 45%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 – 8.15 (m, 1H), 7.97 – 7.93 (m, 1H), 7.91 – 7.87 (m, 2H), 7.63 – 7.58 (m, 2H), 7.57 – 7.53 (m, 1H), 7.43 (td, *J* = 8.4, 7.6, 0.8 Hz, 2H), 7.37 (d, *J* = 10.8 Hz, 1H), 2.12 – 1.99 (m, 1H), 1.75 – 1.57 (m, 4H), 1.39 – 1.14 (m, 5H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 190.0, 166.2, 155.5, 152.8, 137.7, 137.6, 136.5, 134.7, 129.9, 128.9, 128.0, 127.5, 125.7, 122.3, 39.8, 31.3, 25.3, 24.8; MS (ESI), *m/z* (%) 413 $[M+1]^+$ (100); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{22}NO_3S_2$ 412.1036; Found 412.1038.

*(E)-2-(benzo[d]thiazol-2-ylsulfonyl)-1-phenyl-3-(2-(prop-2-yn-1-yloxy)phenyl)prop-2-en-1-one (**3af**)*. Reaction was carried out using the described procedure with 0.100 g (0.31 mmol) of sulfone **2e**.

Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:2) and concentration of the relevant fractions provided the **3af** as a light brown solid (0.103 g, 71%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.72 (s, 1H), 8.22 – 8.17 (m, 1H), 7.97 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.87 – 7.82 (m, 2H), 7.57 (pd, *J* = 7.2, 1.2 Hz, 2H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.27 (td, *J* = 8.4, 3.2 Hz, 3H), 7.12 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.72 (t, *J* = 7.6 Hz, 1H), 4.72 (d, *J* = 2.4 Hz, 2H), 2.51 (t, *J* = 2.4 Hz, 1H).; ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 191.1, 166.6, 156.3, 152.9, 142.0, 137.7, 136.2, 135.6, 134.3, 133.4, 131.4, 129.7, 128.7, 127.9, 127.5, 125.7, 122.3, 121.5, 121.1, 112.7, 77.7, 76.5, 56.0; MS (ESI) *m/z* (%) 460 $[M+H]^+$ (100); HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{25}H_{17}NNaO_4S_2$ 482.0497; Found 482.0490.

*(S,E)-2-(benzo[d]thiazol-2-ylsulfonyl)-4-((tert-butyldimethylsilyl)oxy)-1-phenylpent-2-en-1-one (**3ag**)*. Reaction was carried out using the described procedure with 0.100 g (0.31 mmol) of sulfone **2e**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:5) and concentration of the relevant fractions provided the **3ag** as a colorless oil (0.059 g, 39%, e.r.= >99:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 – 8.19 (m, 1H), 7.97 – 7.94 (m, 1H), 7.90 – 7.85 (m, 2H), 7.64 – 7.57 (m, 2H), 7.57 – 7.54 (m, 1H), 7.45 (d, *J* = 6.4 Hz, 1H), 7.44 – 7.39 (m, 2H), 4.49 (p, *J* = 6.4 Hz, 1H), 1.28 (d, *J* = 6.4 Hz, 3H), 0.70 (s, 9H), -0.15 (s, 3H), -0.19 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 189.3, 165.6, 153.0, 137.8, 137.6, 136.6, 134.5, 130.2, 128.8, 128.1, 127.6, 125.8, 122.4, 67.0, 25.8, 23.3, 18.2, -4.8, -5.1; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{30}NO_4S_2Si$ 488.1380; Found 488.1383; α_D^{27}= + 31.4 (c 0.7,$CHCl_3$); HPLC (CHIRALPAK IE-3, eluent: CO_2: MeOH = 95:5, 2.2 mL/min, 38°C, retention time: t = 13.22 min).

*isopropyl (E)-2-(benzo[d]thiazol-2-ylsulfonyl)-3-phenylacrylate (**5c**)*. Reaction was carried out using the described procedure with 2.4 g (8.86 mmol) of sulfone **2f**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:1) and concentration of the relevant fractions provided the **5c** as a yellow solid (2.0 g, 59%). M.p. = 76-78°C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 (s, 1H), 8.21 – 8.18 (m, 1H), 8.03 – 7.99 (m, 1H), 7.64 – 7.55 (m, 4H), 7.51 – 7.39 (m, 3H), 5.15 (hept, *J* = 6.0 Hz, 1H), 1.16 (d, *J* = 6.4 Hz, 6H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 166.6, 161.8, 152.8, 148.2, 137.4, 132.3, 132.2, 131.4, 130.8, 129.0, 128.1, 127.6, 125.7, 122.3, 71.2, 21.4; MS (ESI), *m/z* (%) 328 $[M-OiPr]^+$ (100); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{18}NO_4S_2$ 388.0672; Found 388.0672.

*isopropyl (E)-2-(benzo[d]thiazol-2-ylsulfonyl)-3-(furan-2-yl)acrylate (**5f**)*. Reaction was carried out using the described procedure with 0.200 g (0.74 mmol) of sulfone **2f**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:3) and concentration of the relevant fractions provided the **5f** as a yellow oil (0.164 g, 60%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 – 8.14 (m, 1H), 8.06 (s, 1H), 8.01 – 7.97 (m, 1H), 7.65 (d, *J* = 1.6 Hz, 1H), 7.61 – 7.52 (m, 2H), 7.43 (d, *J* = 3.6 Hz, 1H), 6.61 (dd, *J* = 3.6, 1.6 Hz, 1H), 5.15 (hept, *J* = 6.4 Hz, 1H), 1.16 (d, *J* = 6.4 Hz, 6H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 167.3, 161.1, 152.7, 148.4, 148.0, 137.3, 134.6, 127.9, 127.6, 126.3, 125.6, 123.6, 122.3, 114.0, 70.8, 21.6; MS (ESI): *m/z* (%) 318 $[M]^+$ (100), 378 $[M+1]^+$(21); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{16}NO_5S_2$ 378.0464; Found 378.0461.

*isopropyl (E)-2-(benzo[d]thiazol-2-ylsulfonyl)-3-(4-(trifluoromethyl)phenyl)acrylate (**5g**)*. Reaction was carried out using the described procedure with 0.200 g (0.74 mmol) of sulfone **2f**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:5) and concentration of the relevant fractions provided the **5g** as a white solid (0.120 g, 36%). M.p. = 135-137°C; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.27 (s, 1H), 8.22 – 8.19 (m, 1H), 8.05 – 8.01 (m, 1H), 7.68 (s, 4H), 7.65 – 7.57 (m, 2H), 5.12 (hept, *J* = 6.4 Hz, 1H), 1.13 (d, *J* = 6.4 Hz, 6H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 166.0, 161.1, 152.7, 146.4, 137.4, 135.0, 134.8, 133.2 (q, *J* = 33.0 Hz), 130.6, 128.2, 127.7, 125.8 (q, *J* = 3.7 Hz), 125.7, 123.6 (q, *J* = 273.2 Hz), 122.3, 71.5, 21.3; ^{19}F{^{1}H} NMR (376 MHz, Chloroform-*d*) δ -63.04 (s, 3F); MS (ESI), *m/z* (%)

414 $[M]^+$ (100), 456 $[M+1]^+$(32); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{17}F_3NO_4S_2$ 456.0546; found 456.0548.

*isopropyl (E)-2-(benzo[d]thiazol-2-ylsulfonyl)-3-cyclohexylacrylate (**5i**)*. Reaction was carried out using the described procedure with 0.200 g (0.74 mmol) of sulfone **2f**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:3) and concentration of the relevant fractions provided the **5i** as a yellow oil (0.160 g, 55%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20 – 8.12 (m, 1H), 8.03 – 7.94 (m, 1H), 7.63 (d, *J* = 10.4 Hz, 1H), 7.60 – 7.53 (m, 2H), 5.05 (hept, *J* = 6.0, 1H), 3.17 – 3.04 (m, 1H), 1.90 – 1.68 (m, 5H), 1.37 – 1.24 (m, 5H), 1.13 (d, *J* = 6.0 Hz, 6H; ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 167.7, 164.5, 160.8, 152.9, 137.4, 132.3, 128.2, 127.8, 125.8, 122.6, 70.8, 39.9, 31.9, 26.0, 25.5, 21.9; MS (ESI), *m/z* (%) 352 $[M]^+$ (100), 394 $[M+1]^+$ (53); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{24}NO_4S_2$ 394.1141; Found 394.1141.

*isopropyl (S,E)-2-(benzo[d]thiazol-2-ylsulfonyl)-4-((tert-butyldimethylsilyl)oxy)pent-2-enoate (**5j**)*. Reaction was carried out using the described procedure with 0.100 g (0.37 mmol) of sulfone **2f**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:3) and concentration of the relevant fractions provided the **5j** as a yellow oil (0.084 g, 49%, e.r.= >99:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 – 8.12 (m, 1H), 8.02 – 7.99 (m, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.63 – 7.54 (m, 2H), 5.22 (dq, *J* = 7.6, 6.4 Hz, 1H), 5.04 (hept, *J* = 6.4 Hz, 1H), 1.40 (d, *J* = 6.4 Hz, 3H), 1.15 (d, *J* = 6.4 Hz, 3H), 1.07 (d, *J* = 6.4 Hz, 3H), 0.90 (s, 9H), 0.08 (d, *J* = 6.4 Hz, 6H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 166.9, 162.9, 160.0, 152.6, 137.1, 131.2, 128.0, 127.6, 125.5, 122.3, 70.8, 66.6, 25.9, 23.0, 21.6, 21.5, 18.3, -4.5, -4.7; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{32}NO_5S_2Si$ 470.1486; Found 470.1489; α_D^{27}= + 41.2 (c 1.0,$CHCl_3$) ; HPLC (CHIRALPAK IE-3, eluent: CO_2: *i*-PrOH = 95:5, 2.2 mL/min, 38°C, retention time: t = 5.14 min).

*(E)-2-(benzo[d]thiazol-2-ylsulfonyl)-N,N-diethyl-3-phenylacrylamide (**5k**)*. Reaction was carried out using the described procedure with 0.070 g (0.22 mmol) of sulfone **2k**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:1) and concentration of the relevant fractions provided the **5k** as a white solid (0.048 g, 53%). M.p.= 158-161°C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 – 8.19 (m, 1H), 8.01 (s, 1H), 7.98 – 7.95 (m, 1H), 7.60 – 7.51 (m, 4H), 7.48 – 7.41 (m, 1H), 7.41 – 7.33 (m, 2H), 3.62 (dq, *J* = 14.4, 7.2 Hz, 1H), 3.38 (dq, *J* = 14.4, 7.2 Hz, 1H), 3.27 (q, *J* = 7.2 Hz, 2H), 1.19 (t, *J* = 7.2 Hz, 3H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 166.3, 162.1, 152.9, 143.0, 138.0, 134.5, 132.0, 131.7, 130.3, 129.2, 128.0, 127.5, 125.9, 122.4, 43.5, 39.7, 13.7, 12.0; MS (ESI), *m/z* (%) 401 $[M+1]^+$ (100); HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{20}N_2NaO_3S_2$ 423.0808; Found 423.0809.

*(E)-2-(benzo[d]thiazol-2-ylsulfonyl)-3-phenylacrylonitrile (**6a**)*. Reaction was carried out using the described procedure with 2.0 g (8.4 mmol) of sulfone **2l**. Crude product **6a** was isolated with enough purity as a light yellow solid (2.4 g, 88%). M.p. = 158-160°C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.45 (s, 1H), 8.26 – 8.23 (m, 1H), 8.06 – 8.03 (m,1H), 8.03 – 7.99 (m, 2H), 7.69 – 7.60 (m, 3H), 7.58 – 7.52 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 164.0, 156.0, 153.3, 138.0, 135.5, 132.2, 130.5, 130.1, 129.0, 128.5, 126.4, 122.8, 112.8, 112.2; MS (ESI), *m/z* (%) 327 $[M+1]^+$ (100); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{11}N_2O_2S_2$ 327.0256; Found 327.0254.

*(E)-2-(benzo[d]thiazol-2-ylsulfonyl)-3-(4-methoxyphenyl)acrylonitrile (**6b**)*. Reaction was carried out using the described procedure with 0.100 g (0.42 mmol) of sulfone **2l**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:3) and concentration of the relevant fractions provided the **6b** as a yellow oil (0.109 g, 73%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.34 (s, 1H), 8.24 – 8.21 (m, 1H), 8.04 – 7.99 (m, 3H), 7.66 – 7.58 (m, 2H), 7.03 – 7.00 (m, 2H), 3.91 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 165.5, 164.4, 155.0, 152.9, 137.6, 134.7, 128.5, 128.0, 125.9, 123.0, 122.5,

115.3, 113.2, 107.7, 56.0; MS (ESI), *m/z* (%) 374 $[M+H_2O]^+$ (100); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{13}N_2O_3S_2$ 357.0362; Found 357.0359.

*(E)-2-(benzo[d]thiazol-2-ylsulfonyl)-3-(3-methoxyphenyl)acrylonitrile (**6c**)*. Reaction was carried out using the described procedure with 0.100 g (0.42 mmol) of sulfone **2l**. Purification using flash chromatography (SiO_2; acetone/petroleum ether = 1:3) and concentration of the relevant fractions provided the **6c** as a yellow solid (0.106 g, 71%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.40 (s, 1H), 8.28 – 8.19 (m, 1H), 8.08 – 7.99 (m, 1H), 7.70 – 7.57 (m, 2H), 7.61 – 7.50 (m, 2H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.18 (ddd, *J* = 8.4, 2.4, 1.2 Hz, 1H), 3.85 (s, 3H).; ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 55.7, 112.0, 112.5, 114.9, 122.1, 122.5, 125.1, 126.0, 128.1, 128.7, 130.7, 131.2, 137.7, 152.9, 155.8, 160.3, 163.7; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{13}N_2O_3S_2$ 357.0362; Found 357.0360.

*(E)-2-(benzo[d]thiazol-2-ylsulfonyl)-3-(4-bromophenyl)acrylonitrile (**6d**)*. Reaction was carried out using the described procedure with 0.100 g (0.42 mmol) of sulfone **2l**. Purification using flash chromatography (SiO_2; acetone/petroleum ether = 1:3) and concentration of the relevant fractions provided the **6d** as a light-yellow syrup (0.129 g, 76%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.38 (s, 1H), 8.27 – 8.22 (m, 1H), 8.06 – 8.03 (m, 1H), 7.89 – 7.85 (m, 2H), 7.71 – 7.67 (m, 2H), 7.67 – 7.61 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ(ppm): 163.5, 154.1, 153.0, 137.7, 133.3, 132.8, 130.5, 128.9, 128.8, 128.2, 126.1, 122.5, 112.6, 112.3; MS (ESI), *m/z* (%) 406 $[M+H]^+$ (100); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{10}BrN_2O_2S_2$ 404.9362; Found 404.9360.

*(E)-2-(benzo[d]thiazol-2-ylsulfonyl)-3-(furan-2-yl)acrylonitrile (**6e**)*. Reaction was carried out using the described procedure with 0.100 g (0.42 mmol) of sulfone **2l**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:3) and concentration of the relevant fractions provided the **6e** as a yellow oil (0.089 g, 67%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 – 8.22 (m, 1H), 8.18 (s, 1H), 8.05 – 8.02 (m, 1H), 7.83 (dt, *J* = 1.6, 0.4 Hz, 1H), 7.67 – 7.59 (m,2H), 7.43 (d, *J* = 3.6 Hz, 1H), 6.72 (dd, *J* = 3.6, 1.6 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 164.0, 152.9, 150.3, 147.3, 139.5, 137.6, 128.6, 128.0, 125.9, 125.3, 122.5, 114.7, 112.2, 107.2; MS (ESI), *m/z* (%) 334 $[M+H_2O]^+$ (100), 317 $[M+1]^+$ (34); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_9N_2O_3S_2$ 317.0049; Found 317.0047.

*(E)-2-(benzo[d]thiazol-2-ylsulfonyl)-3-(4-(trifluoromethyl)phenyl)acrylonitrile (**6f**)*. Reaction was carried out using the described procedure with 0.100 g (0.42 mmol) of sulfone **2l**. Crude product **6f** was isolated with enough purity as a colorless oil (0.157 g, 93%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.48 (s, 1H), 8.26 – 8.22 (m, 1H), 8.11 (d, *J* = 8.4 Hz, 2H), 8.07 – 8.04 (m, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.70 – 7.62 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 163.0, 153.5, 152.9, 137.7, 135.7 (q, *J* = 33.4 Hz), 133.0, 131.7, 128.9, 128.2, 126.7 (q, *J* = 3.7 Hz), 126.5, 126.0, 123.4 (d, *J* = 272.7 Hz), 114.9, 111.9; ^{19}F{^{1}H} NMR (376 MHz, Chloroform-d) δ -63.34 (s, 3F); MS (ESI), *m/z* (%) 177 $[M]^+$ (100); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{10}F_3N_2O_2S_2$ 395.0130; Found 395.0128.

*(E)-2-(benzo[d]thiazol-2-ylsulfonyl)-3-cyclohexylacrylonitrile (**6i**)*. Reaction was carried out using the described procedure with 0.050 g (0.21 mmol) of sulfone **2l**. Crude product **6i** was isolated with enough purity as a yellow solid (0.060 g, 88%). M.p.= 112-114°C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26 – 8.23 (m, 1H), 8.05 – 8.02 (m, 1H), 7.76 (d, *J* = 10.4 Hz, 1H), 7.69 – 7.60 (m, 2H), 2.77 – 2.67 (m, 1H), 1.89 – 1.70 (m, 5H), 1.41 – 1.22 (m, 5H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 169.0, 163.5, 152.9, 137.6, 128.7, 128.1, 126.1, 122.5, 116.5, 110.6, 42.0, 31.1, 25.3, 24.8; MS (ESI), *m/z* (%) 333 $[M+1]^+$ (100); HR-MS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{17}N_2O_2S_2$ 333.0726; Found 333.0725.

*(E)-2-(benzo[d]thiazol-2-ylsulfonyl)-3-(2-(prop-2-yn-1-yloxy)phenyl)acrylonitrile (**6j**)*. Reaction was carried out using the described procedure with 0.100 g (0.42 mmol) of sulfone **2l**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:3) and concentration of the relevant fractions provided the **6j** as a brown solid (0.110 g, 69%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.96 (s, 1H), 8.35

– 8.20 (m, 2H), 8.05 – 8.00 (m, 1H), 7.63 (ddd, *J* = 9.2, 5.6, 2.0 Hz, 3H), 7.19 – 7.07 (m, 2H), 4.88 (d, *J* = 2.4 Hz, 2H), 2.58 (s, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, Chloroform-*d*) δ 164.0, 157.9, 152.9, 149.9, 137.6, 136.9, 129.7, 128.6, 128.0, 126.0, 122.5, 122.2, 119.8, 113.3, 112.9, 111.1, 77.3, 56.6; MS (ESI), *m/z* (%) 381 $[M]^+$ (100); HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{19}H_{12}N_2NaO_3S_2$ 403.0187; Found 403.0181.

*(E)-3-(benzo[d]thiazol-2-ylsulfonyl)-6-phenylhex-4-en-2-one (**7a**)*. Reaction was carried out using the described procedure with 0.050 g (0.2 mmol) of sulfone **2a**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:3) and concentration of the relevant fractions provided the **7a** as a white solid (0.036 g, 49%). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.24 – 8.16 (m, 1H), 8.01 – 7.95 (m, 1H), 7.69 – 7.56 (m, 2H), 7.13 – 7.06 (m, 3H), 6.94 – 6.86 (m, 2H), 5.92 – 5.77 (m, 2H), 5.22 (d, *J* = 9.2 Hz, 1H), 3.35 (d, *J* = 6.0 Hz, 2H), 2.51 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, Chloroform-*d*) δ 196.6, 164.2, 152.6, 142.5, 138.1, 137.1, 128.6, 128.4, 128.3, 127.8, 126.5, 125.7, 122.5, 117.5, 78.0, 39.1, 31.2; MS (ESI), *m/z* (%) 372 $[M+1]^+$ (37); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{18}NO_3S_2$ 372.0723; Found 372.0725.

*(E)-3-(benzo[d]thiazol-2-ylsulfonyl)hept-4-en-2-one (**7b**)*. Reaction was carried out using the described procedure with 0.050 g (0.2 mmol) of sulfone **2a**. Crude product proved to be unstable on SiO_2. The yield of the crude material was 0.019 g, 31%, (keto/enol = 1.7:1). *Peaks attributed to enol form marked with **; ^1H NMR (400 MHz, Chloroform-*d*) δ(ppm): 0.84 (t, *J* = 7.6 Hz, 3H*), 1.00 (t, *J* = 7.6 Hz, 3H), 2.04 (qd, *J* = 7.6, 6.8, 5.2 Hz, 2H), 2.48 (dd, *J* = 7.6, 3.6 Hz, 1H*), 2.50 (s, 3H*), 2.52 (dd, *J* = 7.6, 0.4 Hz, 1H*), 2.57 (s, 3H), 5.16 (d, *J* = 9.2 Hz, 1H), 5.65 – 5.85 (m, 2H), 7.50 (t, *J* = 7.6 Hz, 1H*), 7.55 – 7.69 (m, 2H & 2H*), 7.98 – 8.04 (m, 1H & 1H*), 8.17 – 8.20 (m, 1H), 8.24 (ddd, *J* = 8.4, 1.6, 0.8 Hz, 1H*); HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{15}NNaO_3S_2$ 332.0391, found 332.0393.

General procedure for dihydropyran 9 synthesis. A vinyl-sulfone **3** (0.100 g, 0.29 mmol) was dissolved in benzene (1.5 mL, 0.2 M) and vinyl-ether (0.278 mL, 2.9 mmol) was added in one portion. Mixture was stirred for 24 hours. Volatilities were evaporated under reduced pressure to yield the crude product.

*2-(((4S)-2-ethoxy-6-methyl-4-phenyl-3,4-dihydro-2H-pyran-5-yl)sulfonyl)benzo[d]thiazole (**9a**)*. Reaction was carried out using the described procedure with 0.100 g (0.29 mmol) of vinyl-sulfone **3a**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:3) and concentration of the relevant fractions provided the **9a** as a yellow oil (0.129 g, 90%, *d.r.* = 1 : 1.1). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.15 – 8.08 (m, 2H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.60 – 7.54 (m, 2H), 7.53 – 7.44 (m, 2H), 7.08 (bs, 5H), 7.02 (d, *J* = 7.2 Hz, 2H), 6.91 (t, *J* = 7.2 Hz, 1H), 6.84 (t, *J* = 7.6 Hz, 2H), 5.11 (dd, *J* = 6.8, 2.4 Hz, 1H), 4.95 (t, *J* = 6.0 Hz, 1H), 4.31 (t, *J* = 4.4 Hz, 1H), 4.19 (t, *J* = 7.6 Hz, 1H), 3.99 – 3.88 (m, 2H), 3.62 – 3.52 (m, 2H), 2.68 (bs, 3H), 2.64 (bs, 3H), 2.35 (ddd, *J* = 14.0, 7.6, 2.4 Hz, 1H), 2.12 – 2.04 (m, 3H), 1.19 (t, *J* = 6.0 Hz, 3H), 1.16 (t, *J* = 6.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, Chloroform-*d*) δ 170.2, 169.6, 168.1, 167.8, 152.7, 152.5, 142.7, 141.6, 137.2, 136.9, 128.9, 128.6, 128.1, 127.8, 127.4, 127.2, 127.2, 127.0, 126.8, 126.4, 125.3, 125.2, 122.1, 121.9, 113.9, 110.6, 100.2, 98.7, 65.6, 65.2, 39.1, 38.5, 37.7, 35.9, 21.2, 20.7, 15.2, 15.1; MS (ESI), *m/z* (%) 416 $[M+H]^+$ (62); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{22}NO_4S_2$ 416.0985; Found 416.0987.

*2-(((4S)-6-(but-3-en-1-yl)-2-ethoxy-4-phenyl-3,4-dihydro-2H-pyran-5-yl)sulfonyl)benzo[d]thiazole (**9b**)*. Reaction was carried out using the described procedure with 0.100 g (0.26 mmol) of vinyl-sulfone **3s**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:3) and concentration of the relevant fractions provided the **9b** as a yellow oil (0.109 g, 70%, *d.r.* = 1 : 1.1). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.11 (t, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.53 – 7.45 (m, 2H), 7.09 (bs, 5H), 7.01 (d, *J* = 7.2 Hz, 2H), 6.91 (t, *J* = 7.2 Hz, 1H), 6.84 (t, *J* = 7.2 Hz, 2H), 5.97 (dddt, *J* = 20.8, 16.8, 10.4, 6.8 Hz, 2H), 5.19 – 5.07 (m, 3H), 5.06 – 4.98 (m, 2H), 4.96 – 4.89 (m, 1H), 4.33 (t, *J* = 4.8 Hz, 1H), 4.22 (t, *J* = 8.0 Hz, 1H), 3.94 (dqd, *J* = 9.6, 7.2, 2.4 Hz, 2H), 3.56 (ddq, *J* =

18.8, 9.6, 7.2 Hz, 2H), 3.33 – 3.15 (m, 3H), 3.09 – 3.01 (m, 1H), 2.60 – 2.48 (m, 4H), 2.35 (ddd, *J* = 14.0, 7.6, 2.4 Hz, 1H), 2.11 – 2.02 (m, 3H), 1.18 (dt, *J* = 14.0, 7.2 Hz, 6H); $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*) δ 170.4, 170.1, 170.0, 169.7, 152.6, 152.5, 142.7, 141.6, 137.6, 137.4, 137.3, 137.0, 128.9, 128.5, 128.1, 127.8, 127.5, 127.3, 127.0, 126.8, 126.4, 125.2, 125.1, 122.1, 121.9, 115.6, 115.5, 114.4, 111.1, 100.1, 98.6, 65.5, 65.2, 39.3, 38.6, 37.8, 35.8, 33.3, 32.7, 32.1, 32.1, 29.8, 15.2, 15.1; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{26}NO_4S_2$ 456.1298; Found 456.1300.

*2-((4-cyclohexyl-2-ethoxy-6-methyl-3,4-dihydro-2H-pyran-5-yl)sulfonyl)benzo[d]thiazole (**9c**)*. Reaction was carried out using the described procedure with 0.070 g (0.2 mmol) of vinyl-sulfone **3p**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:6) and concentration of the relevant fractions provided the **9c** as a colorless oil (0.069 g, 72%, *d.r.* = 1.1:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 (dddd, *J* = 8.0, 2.4, 1.6, 0.8 Hz, 2H), 7.96 (dddd, *J* = 8.0, 6.0, 1.6, 0.8 Hz, 2H), 7.61 – 7.49 (m, 4H), 5.16 (dd, *J* = 9.6, 3.6 Hz, 1H), 4.91 (dd, *J* = 7.6, 3.2 Hz, 1H), 3.95 (ddq, *J* = 14.0, 9.6, 7.2 Hz, 2H), 3.61 (dq, *J* = 9.6, 7.2 Hz, 2H), 2.05-2.97 (m,1H), 2.95-2.88 (m,1H), 2.45 (d, *J* = 1.2 Hz, 3H), 2.39 (d, *J* = 0.8 Hz, 3H), 2.18 (dt, *J* = 14.0, 3.6 Hz, 1H), 2.10 – 1.88 (m, 2H), 1.88 – 1.75 (m, 3H), 1.73 – 1.57 (m, 9H), 1.55 – 1.46 (m, 1H), 1.41 – 1.31 (m, 1H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.22 (t, *J* = 7.2 Hz, 3H), 1.20 – 0.81 (m, 8H), 0.77 – 0.59 (m, 1H); $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*) δ 170.0, 169.8, 168.5, 166.8, 152.7, 152.6, 136.5, 136.5, 127.6, 127.6, 127.4, 125.3, 122.2, 114.9, 112.5, 101.5, 99.7, 65.5, 65.3, 41.1, 39.6, 38.5, 37.5, 31.8, 31.6, 30.2, 30.1, 29.4, 27.1, 27.0, 26.9, 26.8, 26.6, 26.5, 26.0, 21.3, 20.9, 15.2.; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{28}NO_4S_2$ 422.1454; Found 422.1456.

General procedure for intramolecular Het. Diels-Alder reaction. A vinyl-sulfone (0.017 g, 0.04 mmol, 1.0 equiv) was dissolved in DCE (4.0 mL, 0.01 M) and the reaction mixture was stirred under microwave conditions (200W, 150°C, 5 min ramp, 30 min hold). The solvent was evaporated under reduced pressure to yield the crude product.

*2-((2-methyl-5H,10bH-pyrano[3,4-c]chromen-1-yl)sulfonyl)benzo[d]thiazole (**10**)*. Reaction was carried out using the described procedure with 0.017 g (0.04 mmol) of vinyl-sulfone **3k**. Desired product **10** was isolated as a yellow oil (0.016 g, 93%) in sufficient purity. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 – 8.18 (m, 1H), 8.06 – 7.97 (m, 1H), 7.61 (dtd, *J* = 20.0, 7.6, 1.2 Hz, 2H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.20 – 7.10 (m, 1H), 6.98 (td, *J* = 7.6, 1.2 Hz, 1H), 6.83 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.44 – 6.32 (m, 1H), 4.88 – 4.81 (m, 1H), 4.69 (s, 1H), 4.59 (d, *J* = 12.0 Hz, 1H), 2.45 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*) δ(ppm): 19.5, 33.7, 67.8, 110.9, 113.7, 117.3, 121.3, 122.4, 125.7, 126.3, 127.7, 128.0, 128.2, 129.6, 134.4, 136.8, 152.8, 153.8, 165.2, 168.4; MS (ESI), *m/z* (%) 398 $[M+H]^+$ (30); HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{15}NNaO_4S_2$ 420.0340; Found 420.0336.

General procedure for dihydrofurane 12 synthesis. Racemic protocol: A vinyl-sulfone **3a** (0.050 g, 0.15 mmol, 1.0 equiv) and pyridinium salt **11a-c** (0.217 mmol, 1.5 equiv) were dissolved in toluene (1.5 mL, 0.1 M). After 5 minutes, Et_3N (0.030 mL, 1.5 equiv) was added and mixture was stirred for an additional 4 hours at r.t.. H_2O (10 mL) followed by EtOAc (10 mL) were added and the resulting layers were separated. The aqueous phase was extracted with EtOAc (4x10 mL) and the combined organic layers were washed brine (2x10 mL), dried over $MgSO_4$, filtered, and the solvents were removed under reduced pressure to provide the crude product. Asymmetric protocol: A vinyl-sulfone **3a** (0.030 g, 0.086 mmol, 2.0 equiv) and chiral ammonium salt **13a-c** (0.043 mmol, 1.0 equiv.) were dissolved in dry CH_2Cl_2 (1.0 mL, 0.043 M). After 5 minutes, Cs_2CO_3 (0.028 mg, 2.0 equiv.) was added in one portion and the mixture was stirred for an additional 20 hours. H_2O (10 mL) and EtOAc (10 mL) were added and the aqueous phase was extracted with EtOAc (4x10 mL). The combined organic layers were washed with

brine (2x10 mL), dried over $MgSO_4$, filtered, and the solvents were removed under reduced pressure to provide the crude product.

*1-((2S,3R)-4-(benzo[d]thiazol-2-ylsulfonyl)-5-methyl-3-phenyl-2,3-dihydrofuran-2-yl)ethan-1-one (**12a**)*. Reaction was carried out using the described racemic procedure with 0.050 g (0.15 mmol) of vinyl-sulfone **3a**. Product **12a** was isolated in good crude purity as a yellow oil (0.062 g, 98%, d.r.= 99:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 8.05 (m, 1H), 7.80 – 7.77 (m, 1H), 7.58 – 7.54 (m, 1H), 7.51 – 7.47 (m, 1H), 7.04 – 7.01 (m, 2H), 6.97 – 6.91 (m, 3H), 4.83 (d, *J* = 5.2 Hz, 1H), 4.58 (dd, *J* = 5.2, 1.2 Hz, 1H), 2.63 (d, *J* = 1.2 Hz, 3H), 2.26 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 203.7, 171.2, 168.9, 152.6, 139.5, 137.3, 128.7, 127.9, 127.7, 127.5, 127.2, 125.4, 122.0, 112.1, 93.2, 52.0, 26.1, 14.5; MS (ESI), *m/z* (%) 400 $[M+1]^+$ (62); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{18}NO_4S_2$ 400.0672; Found 400.0669.

*((2S,3R)-4-(benzo[d]thiazol-2-ylsulfonyl)-5-methyl-3-phenyl-2,3-dihydrofuran-2-yl)(phenyl)methanone (**12b**)*. Reaction was carried out using the described asymmetric or racemic procedure with 0.050 g (0.2 mmol) of vinyl-sulfone **3a**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:2) and concentration of the relevant fractions provided the **12b** as a colorless oil (0.068 g, 98%, *d.r.* = 97:1). Product **12b** was also prepared in enantioenriched form purified using flash column chromatography (SiO_2; CH_2Cl_2:heptane=6:1) and isolated as a light red oil in following manner: starting from salt **13a**: 0.013 g, 70%, *e.r.* = 97:3, *d.r.*=99:1; starting from salt **13c**: 0.012 g, 68%, e.r. = 1:99, *d.r.*=99:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 8.03 (m, 1H), 7.79 – 7.74 (m, 3H), 7.63 – 7.53 (m, 2H), 7.50 – 7.41 (m, 3H), 7.07 – 7.04 (m, 2H), 7.01 – 6.95 (m, 3H), 5.77 (d, *J* = 4.8 Hz, 1H), 4.64 (dd, *J* = 4.8, 1.2 Hz, 1H), 2.66 (d, *J* = 1.2 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 191.9, 172.0, 169.0, 152.6, 139.2, 137.3, 134.4, 133.0, 129.1, 129.0, 128.8, 128.2, 127.9, 127.4, 127.1, 125.4, 122.0, 111.9, 90.3, 52.2, 14.4; MS (ESI), *m/z* (%) 462 $[M+1]^+$ (54); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{20}NO_4S_2$ 462.0828; Found 462.0827; α_D^{25}=+161.4 (c 0.5,$CHCl_3$) – first enantiomer (ret. Time – 29.35 min); α_D^{25}=-148.2 (c 0.5,$CHCl_3$) – second enantiomer (ret. Time – 32.7 min); HPLC (CHIRAL ART Cellulose-SB, eluent: *n*-hexane: *i*-PrOH = 4:1, 0.5 mL/min, 10°C, retention times: t = 29.3 and t = 32.7 min).

*ethyl (2S,3R)-4-(benzo[d]thiazol-2-ylsulfonyl)-5-methyl-3-phenyl-2,3-dihydrofuran-2-carboxylate (**12c**)*. Reaction was carried out using the described racemic procedure with 0.050 g (0.2 mmol) of vinyl-sulfone **3a**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:2) and concentration of the relevant fractions provided the **12c** as a colorless oil (0.054 g, 88%, *d.r.* = 99:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 8.05 (m, 1H), 7.80 – 7.77 (m, 1H), 7.58 – 7.53 (m, 1H), 7.51 – 7.46 (m, 1H), 7.04 – 7.01 (m, 2H), 6.97 – 6.91 (m, 3H), 4.90 (d, *J* = 4.8 Hz, 1H), 4.62 (dd, *J* = 4.8, 1.2 Hz, 1H), 4.30 – 4.20 (m, 2H), 2.62 (d, *J* = 1.2 Hz, 3H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 171.8, 168.9, 168.7, 152.6, 139.4, 137.3, 128.6, 127.8, 127.8, 127.5, 127.2, 125.4, 122.0, 111.9, 86.7, 62.3, 53.3, 14.4, 14.2; MS (ESI), *m/z* (%) 430 $[M+1]^+$ (48); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{20}NO_5S_2$ 430.0777; Found 430.0777.

General procedure for triazole 15 synthesis. To a vinyl-sulfone (0.291 mmol, 1.0 equiv) in MeOH (1.5 mL, 0.2 M) at r.t. was added sodium azide (0.021 g, 0.32 mmol, 1.1 equiv) in one portion and the mixture was stirred for 20 hours. H_2O (10 mL) and EtOAc (10 mL) were added and aqueous phase was extracted with EtOAc (4x10 mL). The combined organic layers were washed with brine (2x10 mL), dried over $MgSO_4$, filtered, and the solvents were removed under reduced pressure to provide the crude product.

*1-(5-phenyl-2H-1,2,3-triazol-4-yl)ethan-1-one (**15a**)*. Reaction was carried out using the described procedure with 0.100 g (0.4 mmol) of vinyl-sulfone **3a**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:1) and concentration of the relevant fractions provided the **15a** as a pale

yellow solid (0.032 g, 93%). M.p. = 108-110°C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.77 (m, 2H), 7.51 – 7.34 (m, 3H), 2.73 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 193.6, 141.9, 130.2, 129.2, 128.7, 127.5, 28.8; MS (ESI), *m/z* (%) 186 [M-H]$^{-}$ (100); HRMS (ESI) *m/z*: [M + H]$^{+}$ Calcd for $C_{10}H_{10}O$ 188.0818; Found 188.0819.

*1-(5-cyclohexyl-2H-1,2,3-triazol-4-yl)ethan-1-one (**15b**)*. Reaction was carried out using the described procedure with 0.050 g (0.14 mmol) of vinyl-sulfone **3p**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:4) and concentration of the relevant fractions provided the **15b** as a white solid (0.027 g, 98%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.42 (tt, *J* = 11.5, 3.5 Hz, 1H), 2.71 (s, 3H), 2.04 – 1.95 (m, 2H), 1.84 (dq, *J* = 13.5, 3.5 Hz, 2H), 1.78 (dqd, *J* = 12.5, 3.0, 1.5 Hz, 1H), 1.57 – 1.39 (m, 4H), 1.29 (qt, *J* = 13.0, 4.0 Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, Chloroform-*d*) δ 25.9, 26.3, 28.3, 31.9, 34.2, 141.9, 149.7, 194.4; MS (ESI), *m/z* (%) 192 [M-H]$^{-}$ (100); HRMS (ESI) *m/z*: [M + H]$^{+}$ Calcd for $C_{10}H_{16}N_3O$ 194.1288; Found 194.1289.

*isopropyl 5-phenyl-2H-1,2,3-triazole-4-carboxylate (**15c**)*. Reaction was carried out using the described procedure with 0.100 g (0.26 mmol) of vinyl-sulfone **5c**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:1) and concentration of the relevant fractions provided the **15c** as a yellow oil (0.034 g, 59%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.75 (m, 2H), 7.42 – 7.38 (m, 3H), 5.23 (h, *J* = 6.4 Hz, 1H), 1.27 (d, *J* = 6.4 Hz, 6H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 160.8, 134.4, 129.7, 129.4, 128.3, 114.0, 69.8, 21.8; MS (ESI), *m/z* (%) 230 [M-H]$^{-}$ (100); HRMS (ESI) *m/z*: [M + H]$^{+}$ Calcd for $C_{12}H_{14}N_3O_2$ 232.1081; Found 232.1082.

*phenyl(5-(4-(trifluoromethyl)phenyl)-2H-1,2,3-triazol-4-yl)methanone (**15d**)*. Reaction was carried out using the described procedure with 0.100 g (0.21 mmol) of vinyl-sulfone **3ac**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:1) and concentration of the relevant fractions provided the **15d** as a yellow oil (0.051 g, 79%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.04 (d, *J* = 6.4 Hz, 2H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 187.7, 156.0, 141.6, 136.9, 133.5, 130.1, 129.3, 128.4, 128.1, 125.4, 125.3 (q, *J* = 3.6 Hz), 122.7; ^{19}F{^{1}H} NMR (376 MHz, DMSO-d_6) δ -61.15 (s, 3F); MS (ESI): *m/z* (%) 316 [M-H]$^{-}$ (100); HRMS (ESI) *m/z*: [M + H]$^{+}$ Calcd for $C_{16}H_{11}F_3N_3O$ 318.0849; Found 318.0850.

*1-(5-(2-(allyloxy)phenyl)-2H-1,2,3-triazol-4-yl)ethan-1-one (**15e**)*. Reaction was carried out using the described procedure with 0.050 g (0.125 mmol) of vinyl-sulfone **3j**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:3) and concentration of the relevant fractions provided the **15e** as a colorless oil (0.028 g, 93%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 13.00 (bs, 1H), 8.10 (d, *J* = 7.6 Hz, 1H), 7.42 (ddd, *J* = 8.4, 7.6, 1.6 Hz, 1H), 7.09 (td, *J* = 7.6, 1.2 Hz, 1H), 7.04 – 6.95 (m, 1H), 6.01 (ddt, *J* = 17.2, 10.8, 5.6 Hz, 1H), 5.42 – 5.27 (m, 2H), 4.62 (dt, *J* = 5.4, 1.4 Hz, 2H), 2.76 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 29.0, 29.8, 69.9, 112.6, 115.0, 119.1, 121.5, 132.0, 132.1, 132.3, 142.5, 155.6, 193.6; MS (ESI): *m/z* (%) 200 [M-allyl]$^{-}$ (100), 242 [M-H]$^{-}$ (45); HRMS (ESI) *m/z*: [M + H]$^{+}$ Calcd for $C_{13}H_{14}N_3O_2$ 244.1081; Found 244.1079.

General procedure for Michael type addition and desulfonation. A vinyl-sulfone (0.69 mmol, 1.0 equiv) was dissolved in MeOH (4.0 mL, 0.2 M) and solution was stirred for 16 hours. After consumption of the starting material the solvent was evaporated under reduced pressure to yield the crude product, that was used in the next step without further purification. The resulting methoxy sulfone adduct was dissolved in THF (7.0 mL, 0.1 M) and AcOH (4.0 mL, 0.2 M). Zn (0.226 g, 5.0 equiv) was added in one portion and the resulting mixture was stirred overnight. The reaction was quenched upon addition of EtOAc (20 mL) and the resulting suspension filtered through Celite®, and filtrate cake was washed with EtOAc (5x20mL). The combined filtrates were washed with sat. $NaHCO_3$ (2x20 mL), brine (2x20 mL),

dried over $MgSO_4$, filtered, and the solvents were removed under reduced pressure to provide the crude product.

*4-methoxy-4-phenylbutan-2-one (**16a**)*. Reaction was carried out using the described procedure with 0.238 g (0.69 mmol) of vinyl-sulfone **3a**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:9) and concentration of the relevant fractions provided the **16a** as a colorless liquid (0.051 g, 92% over 2 steps). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36–7.26 (m, 5H), 4.62 (dd, *J* = 8.8, 4.4 Hz, 1H), 3.18 (s, 3H), 2.95 (dd, *J* = 15.6, 8.8 Hz, 1H), 2.57 (dd, *J* = 15.6, 4.4 Hz, 1H), 2.14 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 206.4, 140.9, 128.5, 127.9, 126.4, 79.5, 56.6, 51.9, 31.0; HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{11}H_{14}NaO_2$ 201.0886; Found 201.0887.

*(3S,4S)-4-((tert-butyldimethylsilyl)oxy)-3-methoxy-1-phenylpentan-1-one (**16b**)*. Reaction was carried out using the described procedure with 0.336 g (0.69 mmol) of vinyl-sulfone **3ag**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:20) and concentration of the relevant fractions provided the **16b** as a colorless liquid (0.102 g, 43% over 2 steps, *d.r.*=7:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.95 (m, 2H), 7.60 – 7.53 (m, 1H), 7.49 – 7.43 (m, 2H), 4.08 (qd, *J* = 6.4, 4.4 Hz, 1H), 3.88 (ddd, *J* = 8.0, 4.4, 3.6 Hz, 1H), 3.37 (s, 3H), 3.19 – 3.06 (m, 2H), 1.17 (d, *J* = 6.4 Hz, 3H), 0.88 (s, 9H), 0.07 (d, *J* = 7.2 Hz, 6H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 199.4, 137.6, 133.1, 128.7, 128.4, 80.8, 68.1, 58.6, 38.5, 26.0, 18.2, 17.9, -4.5, -4.7; HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{18}H_{30}NaO_3Si$ 345.1862; Found 345.1855; α_D^{22} =-7.1 (c 0.65,$CHCl_3$).

General procedure for Michael type allylation or reduction and desulfonation. A vinyl-sulfone (0.290 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (3.0 mL, 0.1 M) and the solution was cooled down to -78°C (acetone/dry ice). After 30 minutes, **Nu** (0.290 mmol, 3.0 equiv) was added and the mixture stirred for another 30 minutes, followed by addition of $TiCl_4$ (0.870 mL, 3.0 equiv, 1.0M solution in CH_2Cl_2). The mixture was stirred for 6 hours. $NaHCO_3$ (10 mL) was added and the suspension warmed to r.t.. The aqueous phase was extracted with CH_2Cl_2 (4x10 mL) and the combined organic layers were washed with brine (2x10 mL), dried over $MgSO_4$, filtered, and the solvents were removed under reduced pressure. The crude product was used in the next step without further purification. Crude sulfone was dissolved in THF (3.0 mL, 0.1 M) and AcOH (1.5 mL, 0.2 M) and Zn (0.019 g, 5.0 equiv) was added in one portion. The resulting heterogenic mixture was stirred overnight before it was quenched with the addition of EtOAc (20 mL). The resulting slurry was filtered through Celite® and the filtrate cake was washed with EtOAc (5x15mL). The filtrates were washed with sat. $NaHCO_3$ (2x15 mL), brine (2x15 mL), dried over $MgSO_4$, filtered, and the solvents removed under reduced pressure to yield the crude product.

*4-phenylbutan-2-one (**16c**)*. Reaction was carried out using the described procedure with 0.100 g (0.29 mmol) of vinyl-sulfone **3a**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:10) and concentration of the relevant fractions provided the **16c** as a colorless liquid (0.037 g, 87% over 2 steps). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28-7.26 (m, 2H), 7.22–7.16 (m, 3H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.76-2.72 (m, 2H), (t, *J* = 7.6 Hz, 2H), 2.14 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 207.8, 140.9, 128.4, 128.2, 126.0, 45.1, 30.1, 29.6; HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{10}H_{13}O$ 149.0961; Found 149.0961.

*4-phenylhept-6-en-2-one (**16d**)*. Reaction was carried out using the described procedure with 0.100 g (0.29 mmol) of vinyl-sulfone **3a**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:8) and concentration of the relevant fractions provided the **16d** as a colorless oil (0.040 g, 74% over 2 steps). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.26 (m, 2H), 7.22 – 7.16 (m, 3H), 5.72 – 5.58 (m, 1H), 5.03 – 4.94 (m, 2H), 3.26 (p, *J* = 7.2 Hz, 1H), 2.82 – 2.68 (m, 2H), 2.39 – 2.33 (m, 2H), 2.02 (s, 3H);

$^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*) δ 207.8, 144.2, 136.3, 128.6, 127.6, 126.6, 116.9, 49.7, 41.0, 40.9, 30.8; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{17}O$: 189.1274, found 189.1274.

*3-phenylhex-5-enenitrile (**16e**)*. Reaction was carried out using the described procedure with 0.050 g (0.153 mmol) of vinyl-sulfone **6a**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:6) and concentration of the relevant fractions provided the **16e** as a colorless oil (0.019 g, 72% over 2 steps). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.32 (m, 2H), 7.30 – 7.27 (m, 1H), 7.25 – 7.21 (m, 2H), 5.66 (ddt, *J* = 17.2, 10.0, 7.2 Hz, 1H), 5.12 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.07 (ddt, *J* = 10.0, 2.0, 1.2 Hz, 1H), 3.04 (p, *J* = 7.2 Hz, 1H), 2.70 – 2.57 (m, 2H), 2.55 (tt, *J* = 7.2, 1.2 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*) δ 141.4, 134.7, 128.9, 127.6, 127.3, 118.5, 118.2, 41.8, 39.2, 24.0; HRMS (ESI) *m/z*: $[M]^+$ Calcd for $C_{12}H_{13}N$ 171.1048; Found 171.1049.

General procedure for Lewis acid-mediated rearrangement. A vinyl-sulfone (0.050 g, 0.145 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (1.5 mL, 0.1 M) at r.t., and $TiCl_4$ (0.580 mL, 4.0 equiv, 1.0M solution in CH_2Cl_2) was added. The mixture was stirred for 1 hour at r.t. prior to addition of CH_2Cl_2 (10 mL) and sat. NH_4Cl (5 mL). The resulting suspension was filtered through Celite® and the filter cake was washed with CH_2Cl_2 (5x10mL). The combined organic layers were washed with brine (2x10 mL), dried over $MgSO_4$, filtered, and the solvent removed under reduced pressure to yield the crude product.

*3-(3-oxo-1-phenylbutyl)benzo[d]thiazol-2(3H)-one (**18**)*. Reaction was carried out using the described procedure with 0.050 g (0.145 mmol) of vinyl-sulfone **3a**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:6) and concentration of the relevant fractions provided the **18** as a pale-yellow oil (0.043 g, 68%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.35 (m, 3H), 7.35 – 7.27 (m, 1H), 7.16 – 7.10 (m, 2H), 6.01 (dd, *J* = 8.0, 6.0 Hz, 1H), 3.96 (dd, *J* = 18.0, 8.0 Hz, 1H), 3.44 (dd, *J* = 18.0, 6.0 Hz, 1H), 2.22 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*) δ 205.4, 138.2, 137.2, 129.1, 128.3, 127.0, 126.4, 122.9, 122.7, 111.9, 54.5, 45.8, 30.3.; MS (ESI), *m/z* (%) 297 $[M+1]^+$ (100); HRMS (ESI) *m/z*: $[M]^+$ Calcd for $C_{17}H_{15}NO_2S$ 297.0823; Found 297.0825.

General procedure for 1,4 reduction of vinyl-sulfones. Procedure A: A vinyl-sulfone (0.582 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (6.0mL, 0.1 M) and solution was cooled down to -78°C (acetone/dry ice). After 15 minutes, *n*Bu_3SnH (0.138 mL, 1.1 equiv) was added and the mixture was stirred for additional 30 minutes. After consumption of the starting material, CH_2Cl_2 (10 mL) was added and the reaction mixture was washed with brine (2x10 mL), dried over $MgSO_4$, filtered, and the volatiles were removed under reduced pressure. The crude material was dissolved in CH_3CN (25mL) and washed with hexane (2x20mL) to remove any remaining organotin compounds. The resulting acetonitrile solution was concentrated under reduced pressure to provide the crude product. Procedure B: A vinyl-sulfone (0.582 mmol, 1.0 equiv) was dissolved in THF (0.1 M) and solution was cooled down to -78°C (acetone/dry ice). After 15 minutes, DIBAL (0.640 mL, 1.1 equiv, 1M solution in hexane) was added dropwise and the mixture was stirred at -78°C for 10 min and at r.t. for another 1 h (consumption of the SM monitored by TLC). After consumption of starting material, the reaction mixture was cooled down to -78°C, and saturated aq. solution of Rochelle salt (5 mL) was added. The resulting mixture was allowed to warm to r.t. and stirred until the solution became clear (cca 6 hours). The whole mixture was extracted with CH_2Cl_2 (3x5 mL). The combined organic layers were washed with brine (2x10 mL), dried over $MgSO_4$, filtered, and solvents were removed under reduced pressure to provide the crude product.

*3-(benzo[d]thiazol-2-ylsulfonyl)-4-phenylbutan-2-one (**17c**)*. Reaction was carried out using the described procedure with 0.200 g (0.583 mmol) of vinyl-sulfone **3a**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:4) and concentration of the relevant fractions provided the **17c** as a yellow solid **Procedure A** (0.181 g, 91%); **Procedure B** (0.170 g, 85%). ^{1}H NMR

(400 MHz, Chloroform-*d*) δ 8.32 – 8.23 (m, 1H), 8.09 – 7.95 (m, 1H), 7.76 – 7.55 (m, 2H), 7.25 – 7.16 (m, 3H), 7.14 – 7.08 (m, 2H), 4.91 (dd, *J* = 9.2, 5.6 Hz, 1H), 3.55 – 3.36 (m, 2H), 2.27 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, Chloroform-*d*) δ 32.8, 32.9, 75.6, 122.5, 125.9, 127.5, 128.0, 128.5, 129.0, 129.1, 135.4, 137.3, 152.7, 164.1, 198.2; MS (ESI), *m/z* (%) 346 $[M+1]^+$ (100); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{16}NO_3S_2$ 346.0566; Found 346.0563.

*2-(benzo[d]thiazol-2-ylsulfonyl)-1,3-diphenylpropan-1-one (**17f**)*. Reaction was carried out using the described procedure with 0.100 g (0.246 mmol) of vinyl-sulfone **3aa**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:3) and concentration of the relevant fractions provided the **17f** as a colorless oil: **Procedure A:** (0.090 g, 90%); **Procedure B:** (0.081 g, 81%). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.23 – 8.18 (m, 1H), 8.01 – 7.92 (m, 1H), 7.79 – 7.69 (m, 2H), 7.68 – 7.53 (m, 2H), 7.49 – 7.38 (m, 1H), 7.35 – 7.24 (m, 2H), 7.20 – 7.04 (m, 5H), 5.82 (dd, *J* = 10.8, 3.6 Hz, 1H), 3.82 – 3.62 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, Chloroform-*d*) δ 33.7, 70.6, 122.4, 125.8, 127.3, 127.8, 128.4, 128.7, 128.9, 129.2, 134.1, 135.6, 137.0, 137.4, 152.6, 164.3, 191.0; MS (ESI), *m/z* (%) 408 $[M+1]^+$ (100); HRMS (ESI) *m/z*: $[M+ H]^+$ Calcd for $C_{22}H_{18}NO_3S_2$ 408.0723; found 408.0725.

General procedure for 1,2 reduction of vinyl sulfones. A vinyl-sulfone (0.290 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (30 mL, 0.01 M) and resulting solution was cooled to -78°C (acetone/dry ice). After 15 minutes, DIBAL-H (0.320 mL, 1.1 equiv, 1M solution in hexane) was added dropwise and the mixture was stirred at -78°C for an additional 4 hours. After consumption of the starting material (checked via TLC), a saturated aqueous solution of Rochelle salt (5 mL) was added and the reaction mixture was allowed to warm to r.t.. The resulting mixture was stirred until the solution became clear (cca 6 hours). The whole mixture was extracted with CH_2Cl_2 (3x10 mL). The combined organic layers were washed with brine (2x10 mL), dried over $MgSO_4$, filtered, and the solvents were removed under reduced pressure to provide the crude product.

*(E)-3-(benzo[d]thiazol-2-ylsulfonyl)-4-phenylbut-3-en-2-ol (**19a**)*. Reaction was carried out using the described procedure with 0.100 g (0.291 mmol) of vinyl-sulfone **3a**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:4) and concentration of the relevant fractions provided the **19a** as a pale-yellow oil (0.080 g, 80%). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.20 – 8.14 (m, 1H), 8.07 (s, 1H), 8.02 – 7.97 (m, 1H), 7.67 – 7.52 (m, 4H), 7.45 (dd, *J* = 5.2, 2.0 Hz, 3H), 5.23 (q, *J* = 6.8 Hz, 1H), 1.63 (d, *J* = 6.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, Chloroform-*d*) δ 22.2, 64.8, 122.5, 125.4, 127.7, 128.1, 129.0, 130.6, 130.6, 132.7, 136.7, 142.1, 145.3, 152.3, 169.2; MS (ESI), *m/z* (%) 346 $[M+1]^+$ (100); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{16}NO_3S_2$ 346.0566; Found 346.0565.

*(E)-3-(benzo[d]thiazol-2-ylsulfonyl)-4-cyclohexylbut-3-en-2-ol (**19c**)*. Reaction was carried out using the described procedure with 0.050 g (0.143 mmol) of vinyl-sulfone **3p**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:5) and concentration of the relevant fractions provided the **19c** as a colorless oil (0.034 g, 68%). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.18 – 8.12 (m, 1H), 8.02 – 7.93 (m, 1H), 7.65 – 7.51 (m, 2H), 6.98 (d, *J* = 10.8 Hz, 1H), 5.04 (dt, *J* = 13.2, 6.8 Hz, 1H), 2.94 (d, *J* = 6.0 Hz, 1H), 2.76 (tdt, *J* = 10.8, 6.8, 3.6 Hz, 1H), 1.84 – 1.64 (m, 5H), 1.54 (d, *J* = 6.8 Hz, 3H), 1.34 – 1.17 (m, 5H); $^{13}C\{^1H\}$ NMR (101 MHz, Chloroform-*d*) δ 23.6, 25.2, 25.2, 25.7, 31.8, 31.9, 38.3, 65.1, 122.4, 125.4, 127.6, 128.0, 136.7, 140.7, 152.3, 154.2, 169.0; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{22}NO_3S_2$ 352.1036; Found 352.1034.

General procedure for radical addition. To a vinyl-sulfone (0.050 g, 0.153 mmol, 1.0 equiv) in benzene (1.5 mL, 0.1 M) was added ethyl iodide (0.019 mL, 1.5 equiv), $(Me_3Si)_3SiH$ (0.071 µL, 1.5 equiv) and AIBN (0.005 g, 0.2 equiv) and reaction mixture was heated (oil bath) to reflux. After consumption of starting vinyl-sulfone (8 hours), the volatilities were evaporated under reduced pressure to yield the crude product.

*2-(benzo[d]thiazol-2-ylsulfonyl)-3-phenylpentanenitrile (**20**)*. Reaction was carried out using the described procedure with 0.050 g (0.153 mmol) of vinyl-sulfone **6a**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:5) and concentration of the relevant fractions provided the **20** as a colorless oil (0.033 g, 61%, *d.r.*=1.2 : 1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 – 8.18 (m,2H), 8.01 (ddd, *J* = 9.6, 7.6, 2.0 Hz, 2H), 7.72 – 7.57 (m, 4H), 7.45 – 7.35 (m, 2H), 7.39 – 7.23 (m, 8H), 4.96 (d, *J* = 5.6 Hz, 1H), 4.88 (d, *J* = 3.6 Hz, 1H), 3.75 – 3.62 (m, 2H), 2.36 (dqd, *J* = 13.6, 7.2, 3.6 Hz, 1H), 2.21 – 1.95 (m, 3H), 0.91 (t, *J* = 7.2 Hz, 3H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 163.4, 163.2, 152.4, 138.2, 137.5, 136.7, 129.3, 129.3, 128.9, 128.8, 128.7, 128.7, 128.5, 128.4, 128.2, 128.1, 128.0, 128.0, 125.9, 125.8, 122.5, 122.5, 112.3, 112.1, 62.1, 61.2, 44.6, 44.1, 27.8, 25.1, 11.8, 11.7; MS (ESI), *m/z* (%) 357 $[M+H]^+$ (100); HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{16}N_2NaO_2S_2$ 379.0551; Found 379.0546.

*(E)-4-phenylbut-3-en-2-one (**4**)*. Reaction was carried out using the described procedure with 0.100 g (0.291 mmol) of vinyl-sulfone **3a**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:4) and concentration of the relevant fractions provided the **4** as a yellowish solid (0.036 g, 85%, >*E*/*Z*= 95 : 1). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.56 – 7.54 (m, 2H), 7.52 (d, *J* = 16.5 Hz, 1H), 7.42 – 7.38 (m, 3H), 6.72 (d, *J* = 16.5 Hz, 1H), 2.39 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, Chloroform-*d*) 198.5, 143.5, 134.6, 130.7, 129.1, 128.4, 127.3, 27.7. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{11}O$ 147.0804; Found 147.0806.

*(E)-isopropyl cinnamate (**21**)*. Reaction was carried out using the described procedure with 0.100 g (0.258 mmol) of vinyl-sulfone **5c**. Purification using flash chromatography (SiO_2; EtOAc/petroleum ether = 1:5) and concentration of the relevant fractions provided the **21** as a viscose oil (0.046 g, 82%, >*E*/*Z*= 95 : 1). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 16.0 Hz, 1H), 7.52 (dd, *J* = 7.0, 3.0 Hz, 2H), 7.41 – 7.35 (m, 3H), 6.42 (d, *J* = 16.0 Hz, 1H), 5.14 (hept, *J* = 6.0 Hz, 1H), 1.32 (d, *J* = 6.5 Hz, 6H). ^{13}C{^{1}H} NMR (126 MHz, Chloroform-*d*) δ 166.7, 144.4, 134.6, 130.3, 129.0, 128.1, 118.9, 67.9, 22.1; MS (ESI), *m/z* (%) 191 $[M+1]^+$ (10), 149 (100); HRMS (ESI) *m/z*: $[M+ H]^+$ Calcd for $C_{12}H_{15}O_2$ 191.1067; found 191.1068.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Relevant optimization tables, discussion relevant stereochemical outcomes of reactions, discussion of the stereochemistry of obtained compounds, and a copy of ^{1}H and ^{13}C{^{1}H} NMR spectra. (PDF)

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O.K., F.Z. and D.J.-Y.D.B. performed most of the experiments and analyzed experimental data. L.V.B. and O.K. carried out the Smiles-like rearrangement. L.R., O.K. and M.W. performed and optimized [4+1]-cycloaddition reaction. O.K. and D.J.-Y.D.B. partially designed the experimental plans. J.P. initiated the project, led the project team, designed experiments, analyzed results, and wrote the

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Notes

The authors declare no competing financial interest.

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