DOI: 10.1002/adsc.201800466
Advanced Synthesis & Catalysis

Sulfinate-Organocatalyzed (3+2) Annulation of Allenyl Sulfones with 1,1-Dicyano Olefins in the Presence of a Quaternary Ammonium Phase Transfer Agent

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Received: April 11, 2018; Revised: May 7, 2018; Published online: ■■, ■■■■

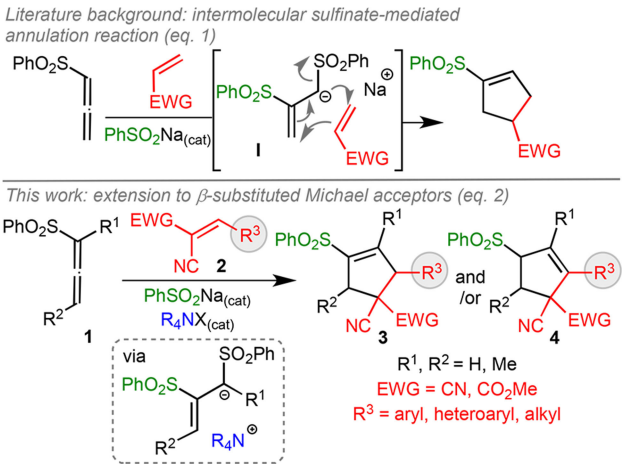
Abstract: The benzenesulfinate-catalyzed (3+2) annulation between allenyl sulfones and aryl(alkyl)-idenemalononitriles has been developed under mild phase transfer conditions, affording a breadth of functionalized sulfonyl cyclopentenes in good to excellent yields (22 examples, 49–99%) and high diastereoselectivities. These adducts were likely generated, *via* an allylsulfone anion featuring a quaternary ammonium cation.

Keywords: phase-transfer catalysis; sulfinate; annulation; allene; carbocycle

1 Introduction

The (3+2) annulation reaction between electron-poor allenes and Michael acceptors has emerged as a powerful strategy for the construction of cyclopentene derivatives.[1] This synthetic sequence has been promoted by a catalytic amount of a tertiary phosphine as Lewis base, and paved the way for efficient syntheses of medicinally important architectures.[2] At the end of the 1980s, the group of Padwa described a unique and complementary process with parent allenyl sulfone in the presence of a benzenesulfinate organocatalyst[3] ($PhSO_2^-$ Na^+), which resulted in the formation of versatile sulfonyl cyclopentene platforms (Scheme 1, equation 1).[4,5] This sequence was initiated by the catalytic addition of the sulfur catalyst on the central carbon atom of the cumulene to generate the highly reactive allyl sulfone anion **I**. Notwithstanding the synthetic values offered by this strategy, very few developments have been described so far.[6–8] To date and to the best of our knowledge, intermolecular examples are confined to non-substituted Michael acceptors (if the few cyclic ones[6,7] are excluded) and the reactivity of the α- or γ-substituted allenyl sulfones[6] has being seldom examined.

Following our current interest in exploring nucleophilic sulfinate catalysis,[9] herein we report an efficient (3+2) annulation reaction of allenyl sulfones **1** (R^1, R^2) with substituted cyano-based olefins[10] **2** (EWG, R^3), which proceeds under mild conditions and with operational simplicity (Scheme 1, equation 2). The protocol takes profit of phase transfer conditions, which probably allows the formation of a lipophilic sulfinate ammonium ($PhSO_2^-$ R_4N^+) species and enhances the reactivity of the anionic intermediates successively formed.[11,12] This investigation also revealed an original reactivity pattern, which involves a subtle prototropic shift and leads, in most cases, to the formation of products of structural type **4**. Very recently, while the manuscript was in progress, Kuwano's research group briefly reported the related annulation reaction of parent allenyl sulfone (R^1=



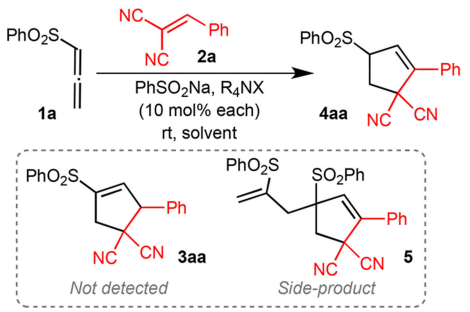
Scheme 1. Background and objectives.

R^2 = H) with arylidenemalononitriles (EWG = CN, R^3 = Ar), initiated by an *N*-heterocyclic carbene catalyst.[13]

2 Results and Discussion

We commenced our study (Table 1) by investigating parent allenyl sulfone **1a** (1.5 equiv.) and 2-benzylidenemalononitrile **2a** in the presence of catalytic amounts of sodium benzenesulfinate and *n*-tetrabutylammonium bromide (10 mol% each). The reaction was initially conducted at room temperature for 24 h in THF as solvent and delivered cleanly two products, which were readily separated by column chromatography on silica gel (entry 1). Standard spectral identification techniques rapidly showed that none of them corresponds to the anticipated cycloadduct **3aa**. The structures were unambiguously assigned by single crystal X-ray analyses (see Supporting Information). The major compound **4aa**, isolated in a 67% yield, is position isomer of **3aa**, in which the carbon-carbon double bond is conjugated with the phenyl group. The minor compound, produced in a 20% yield, was identified as the disulfonyl cyclopentene **5**.[14]

Table 1. Proof and reaction optimization.[a]

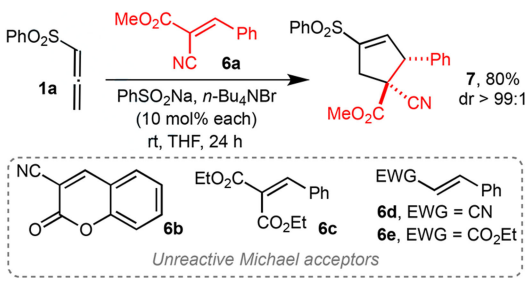


Entry	R_4NX	Solvent, time (h)	**4aa**/**5**[b]	Isolated yield (%)
1	*n*-Bu_4NBr	THF, 24	76/24	67 (20)[c]
2	*n*-Bu_4NBr	CH_2Cl_2, 24	89/11	75
3	*n*-Bu_4NBr	PhMe, 4	84/16	78
4	*n*-Bu_4NBr	MeCN, 4	>99/1	84
5[d]	***n*-Bu_4NBr**	**MeCN, 16**	**>99/1**	**82**
6	–	MeCN, 16	65/35	57
7	Me_3BnNCl	MeCN, 0.33	67/33	63

[a] Reaction performed with **2a** (0.1 mmol) and **1a** (1.5 equiv.) in solvent (1 mL) in the presence of $PhSO_2Na/R_4NX$ catalytic system (10 mol%).
[b] Ratio determined by ^1H NMR on the crude product.
[c] Isolated yield of **5** under brackets.
[d] With 1.2 equiv. of **1a**.

Optimization of the reaction conditions was then investigated. Although significant improvements for the conversion into **4aa**, up to a 78% yield, were noticed in dichloromethane or toluene solutions, the formation of the side-product **5** was not totally suppressed (entries 2 and 3). Gratifyingly, a complete selectivity was achieved in acetonitrile, which resulted in the isolation of **4aa** in an 84% yield (entry 4). Furthermore, the reaction is particularly faster in this medium (4 h versus 24 h in THF for example). A similar efficiency of the process was still observed by decreasing the amount of allene **1a** to 1.2 equivalent (entry 5). The beneficial effect of the PT-catalyst was then clearly pointed. The yield for **4aa** dropped to 57% without the addition of *n*-Bu_4NBr, along with the appearance of unwanted side-product **5** (entry 6). Finally, the use of Me_3BnNCl led to a faster process, in which the reagents were consumed within 20 min (entry 7). However, the desired product **4aa** was isolated only in a 63% yield, with concomitant formation of **5**. Interestingly, the procedure does not require a large excess nor dropwise addition of allenyl sulfone **1a** as already mentioned,[8a] thus exhibiting the specific and high reactivity of benzylidenemalononitrile **2a** under the PT conditions.

The reaction outcome of the process is highly dependent on the nature of the activating groups of the electron deficient alkene employed, as outlined in Scheme 2. An experiment carried out with the related cyanoester **6a** showcased the formation of the adduct **7**, with a diastereoselective ratio >99:1 in an 80% yield. The carbon-carbon double bond in **7** is conjugated with the sulfur substituent, and not with the phenyl group as previously observed with *bis*-nitrile **2a**. The observed stereochemical outcome for **7** reflects perfectly the *trans* relationship of the phenyl substituent and the ester group in the starting olefin **6a**.[15] It can be interpreted by a (3+2) cycloaddition type mechanism taking place in a concerted fashion or a non-concerted manner (1,4-addition followed by a formal SN_2' reaction), incorporating a rapid cyclization step.[16] In contrast, coumarine **6b** and malonate derivative **6c** were unreactive under identical conditions. A similar failure was also observed with cinnamonitrile **6d** and ethyl cinnamate **6e**. This result clearly highlights the specific reactivity of the 1,1-



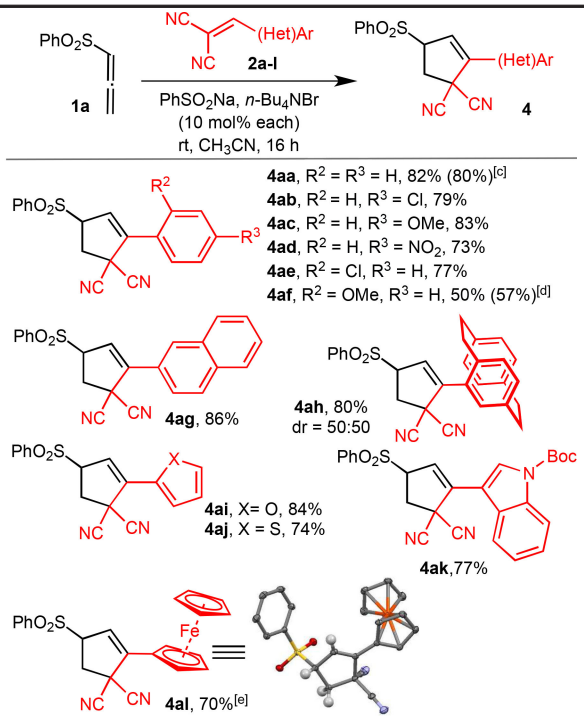
Scheme 2. Comparison with other Michael acceptors **6**.

diactivated olefins and also the crucial requirement of at least one cyano group.

We then explored the generality of the sulfinate-mediated annulation reaction in the presence of allene **1a**. As shown in Table 2, arylidene derivatives **2b–e** with various substitution on the benzene ring (4-Cl, 4-OMe, 4-NO_2, 2-Cl) were tolerated, leading to the corresponding cyclopentene targets **4ab–4ae** with yields higher than 72%. A lower yield of 50% (**4af**) was obtained with a methoxy substituent in the *ortho* position, but a slight improvement to a 57% yield was obtained when switching to THF as solvent. 2-Naphthyl and [2.2]paracyclophan-4-yl derived acceptors can also participate in the process (**4ag** and **4ah**, 86 and 80% respectively). Introduction of heterocyclic motifs was also successful, as exemplified by products flanked with furan (**4ai**, 84%), thiophene (**4aj**, 74%) or indole (**4ak**, 77%) rings. Moreover, ferrocene **4al** was synthesized in a 70% yield and its structure was confirmed by a single-crystal X-ray diffraction analysis. In order to highlight the practicality of the protocol, a 1.1 mmol scale reaction was carried out with **2a** and provided **4aa** without any loss of efficiency (80% yield versus 82% previously).

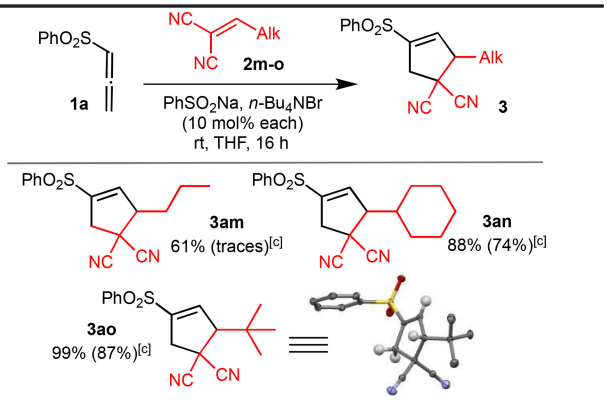
Pleasingly, alkylidenemalononitriles turned out to be compatible substrates, but a markedly different reaction outcome, leading exclusively to products **3**, was observed (Table 3). The conjugation of the carbon-carbon double bond with the sulfonyl group was determined by ^{1}H NMR analyses. This was also confirmed in the case of the *t*-Bu derivative **3ao** by an X-ray experiment (see Supporting Information). THF turned out to be the suitable reaction solvent in this series, providing better yields. As the most prominent example, compound **3am** displaying an *n*-propyl group was produced in a 61% yield in THF, whereas only trace amounts were detected in a CH_3CN medium.

Table 2. Substrate scope with allenyl sulfone **1a**.[a,b]



[a] Reaction performed with **2** (0.1 mmol) and **1a** (1.2 equiv.) in CH_3CN (1 mL) in the presence of $PhSO_2Na$/*n*-Bu_4NBr catalytic system (10 mol%).
[b] Isolated yields.
[c] Reaction on a 1.1 mmol scale under brackets.
[d] Under brackets reaction carried out in THF.
[e] With Me_3BnNCl as the PT-catalyst.

Table 3. Extension to alkylidenemalononitriles.[a,b]

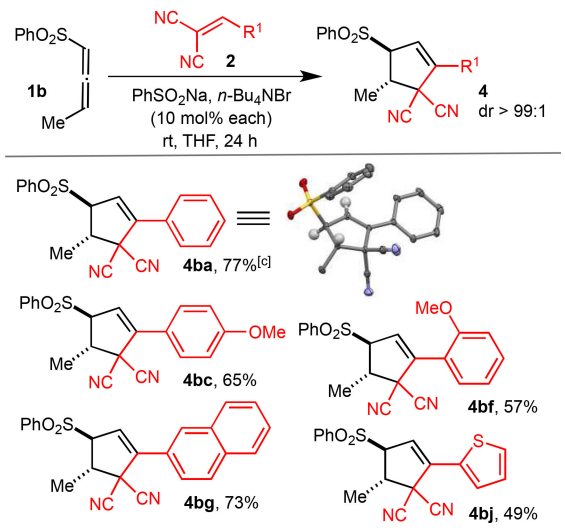


[a] Reaction performed with **2** (0.1 mmol) and **1a** (1.2 equiv.) in THF (1 mL) in the presence of $PhSO_2Na$/*n*-Bu_4NBr catalytic system (10 mol%).
[b] Isolated yields.
[c] Reaction carried out in CH_3CN under brackets.

Next, we wondered whether γ-methyl allenyl sulfone **1b** could also be exploited in the process (Table 4). Reaction of the five (het)arylidenemalononitriles **2** in the presence of $PhSO_2Na$/*n*-Bu_4NBr as the catalytic system in THF led to the isomerized adducts **4**, with chemical yields in the range of 49 to 77%. A control experiment carried out with **2a** showed that no reaction took place without the ammonium catalyst. A single diastereoisomer of **4**, displaying a *trans* geometry, was invariably formed, as confirmed by an X-ray structural analysis of **4ba** (R^1 = Ph). In contrast, the three alkylidene derivatives **2m–o** we tested (R^1 = *n*-Pr, Cy, *t*-Bu) were not accommodated in this series. A similar failure was observed with the Michael acceptors **6a–c** displaying an ester function as activating group (see Scheme 2 for the structures).

We finally turned our attention to α-methyl allenyl sulfone **1c**, for which the transformation was successful. However, more contrasted and unpredictable

Table 4. Extension to γ-methyl allenyl sulfone **1b**.[a,b]

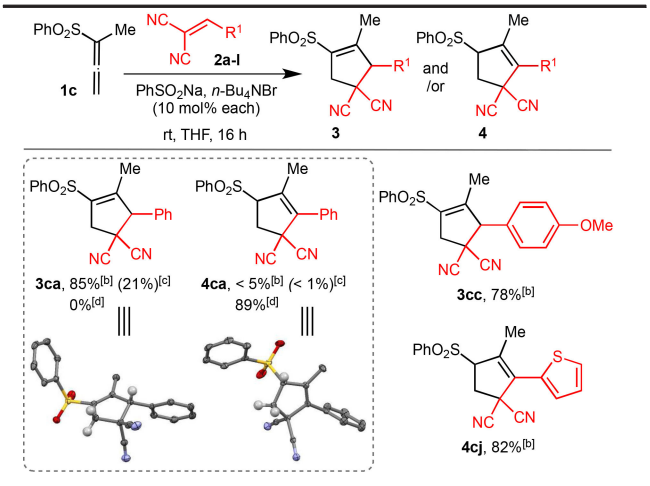


[a] Reaction performed with **1b** (0.1 mmol) and **2** (1.5 equiv.) in THF (1 mL) in the presence of $PhSO_2Na$/n-Bu_4NBr catalytic system (10 mol%).
[b] Isolated yields.
[c] No reaction without n-Bu_4NBr.

results were observed for the structure of the isolated product (Table 5). The reaction with benzylidenemalononitrile **2a** led to the adduct **3ca** in an excellent 85% yield, along with trace amounts of the readily separable isomer **4ca** (**3ca**:**4ca**, 96/4 ratio). The structures of both isomers **3ca** and **4ca** were unequivocally proven by single-crystal X-ray analyses. The effect of the PT-catalyst was again ascertained, as only a 21% yield of **3ca** was obtained after 24 h without n-Bu_4NBr (**3ca**:**4ca**, >99:1 ratio). A rapid screening of ammonium salts (see Supporting Information) showed that n-Bu_4NBr was the optimal catalyst, while the anion had a dramatic impact on **3ca** and **4ca** distribution. Interestingly, n-Bu_4NOAc furnished exclusively the isomerized compound **4ca** in an 89% yield. Conditions using n-Bu_4NBr also led to **3cc** displaying a 4-methoxyphenyl substituent (78% yield). In contrast, the isomerized adduct **4cj** was produced directly in the presence of n-Bu_4NBr in an 82% yield from the 2-thienyl malononitrile **2j**.

Based on these results and literature background,[4,6] we propose the catalytic cycle outlined in Figure 1. The process probably begins with the extraction of the sulfinate catalyst into the organic phase through sodium/ammonium counterion exchange. The equilibrated addition of the lipophilic ammonium sulfinate on the electrophilic β carbon atom of **1** would generate a small amount of allyl sulfone anion **II**. Regioselective conjugate addition of **2**, through the carbon centre in α-position to the sulfone moiety (**II**) would provide the conjugate addition intermediate **III**, which would then undergo cyclization to generate the sulfonyl anion **IV**. Elimination of the sulfinate can take place at this stage to furnish adduct **3** (route A, R^3 = alkyl and $R^1 = R^2 = H$). When R^3 = (het)aryl, a spontaneous intramolecular proton transfer is speculated, leading to the benzylic carbanion **V** (route B, $R^1 = R^2 = H$), from which $PhSO_2^-$ would be released to afford the isomerized product **4**.[17] In the γ-methyl series (R^2 = Me), the proton shift proceeds with complete diastereoselectivity in favor of a *trans* configuration, probably to minimize steric hindrance.

Table 5. Extension to α-methyl allenyl sulfone **1c**.[a,b]



[a] Isolated yields.
[b] Reaction performed with **1c** (0.1 mmol) and **2** (1.5 equiv.) in THF (1 mL) in the presence of $PhSO_2Na$/n-Bu_4NBr catalytic system (10 mol%).
[c] Under brackets, reaction performed without n-Bu_4NBr.
[d] Reaction carried out with n-Bu_4NOAc (10 mol%) as PT-catalyst, instead of n-Bu_4NBr (10 mol%).

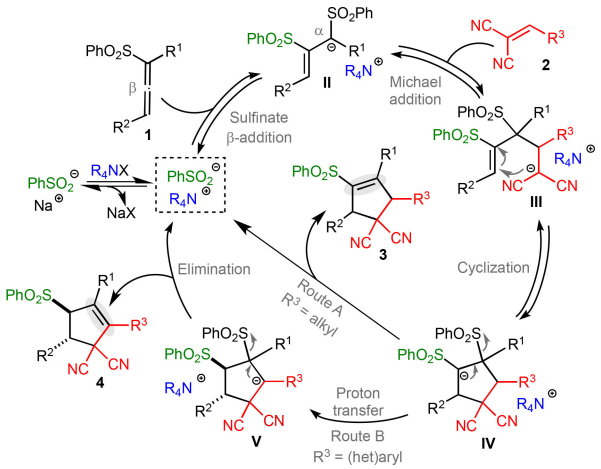
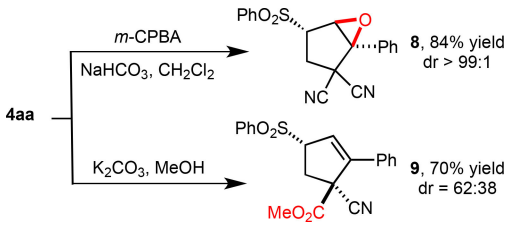


Figure 1. Proposed sulfinate-mediated catalytic cycle under PT conditions.

Competition between routes A and B is observed from the α-methyl precursor **1c**, the selectivity being highly dependent on the nature of **2**. In some case, we cannot also rule out isomerization of the kinetic product **3** into the thermodynamic isomer **4** displaying an aryl-conjugated C=C bond. This option could account of the role of AcO^- as a basic proton-shift promoter (Table 5).

To illustrate the potential of our substrates, some representative transformations were performed (Scheme 3).



Scheme 3. Synthetic applications of **4aa**.

Treatment of sulfonyl cyclopentene **4aa** with *m*-CBPA (3 equiv.) led to the epoxide **8** as a single diastereoisomer in an 84% yield (See Supporting Information for the stereochemical assignment based on the recorded ^{1}H NMR data). Conversion into the methyl ester **9** could also be achieved in a 70% yield by solvolysis[18] of one of the cyano groups in methanol in the presence of K_2CO_3, thus broadening the use of dicyano compounds to cyano-ester derivatives. Worthy of note is that product **9** is an isomer of cyclopentene **7**, previously obtained in Scheme 2 from cyanoester **6a**.

3 Conclusion

In summary, we have successfully developed a straightforward (3+2) annulation, under phase transfer conditions, between allenyl sulfones and 2-substituted-1,1-dicyano olefins in the presence of catalytic $PhSO_2Na$. The reaction provides a facile access to original sulfonyl cyclopentenes and extends thereby the initial Padwa process with a unique proton shift. The salient features of the methodology include mild reaction conditions, operational simplicity (no need of a syringe pump for a slow addition of the allene), atom-economy, wide substrate scope with regard to both reaction partners, high chemo- and diastereoselectivity and good yields of isolated product. The reaction is a valuable complement to currently existing methods for accessing synthetically useful multifunctional cyclopentenes[1,10,19] and has also potential to be further applied through manipulation of the functional groups. First attempts to render the process enantioselective, in the presence of chiral quaternary ammonium salts, unfortunately failed and led to low asymmetric inductions.[20] Further studies to expand synthetic approaches mediated by sulfinate catalysts are ongoing in our laboratory.

Experimental Section

General

Dry THF, CH_2Cl_2 and acetonitrile were obtained by a passage down an activated alumina column. All other reagents and solvents were used as purchased from commercial sources. All reactions were performed in oven-dried glassware, under an atmosphere of dry nitrogen. Low reaction temperatures stated were those of the reaction mixtures. Reactions were purified by column chromatography with silica gel Si 60 (0.040–0.063 nm). Thin layer chromatography was carried out on silica gel 60 F_{254} (1.1 mm) with spot detection under UV light and/or through $KMnO_4$ oxidation. Melting points were obtained on a capillary apparatus and are uncorrected. All chemical shifts (δ) and coupling constants (J) in the NMR spectra are quoted in parts per million (ppm) and Hertz (Hz) respectively. The following abbreviations are used to designate the multiplicity of the signals: s=singlet; d=doublet; t=triplet; m=multiplet; br=broad; app=apparent and combinations thereof. The chemical shifts are calibrated to TMS (δ H 0.00) or residual proton and carbon resonances of the solvent $CDCl_3$ (δ H 7.26 and δ C 77.16). IR spectra were recorded on an ATR-FT-IR instrument equipped with a diamond ATR probe. Wavenumbers are quoted in cm^{-1}. Low resolution mass spectra were recorded on a GC/MS/MS instrument and only peaks of an intensity >10% (except decisive ones) are listed. High resolution mass spectra (HRMS) were recorded on a QTOF LC/MC instrument. X-ray diffraction experiments were performed with a graphite–monochromatized Mo Kα radiation on a CCD area detector diffractometer.

Typical Procedures for (3+2) Annulations with Allenes 1a and 1b

Procedure A in MeCN: Allenyl sulfone **1a** or **1b** (1.2 equiv.), Michael acceptor **2** (1 equiv.), *n*-Bu_4NBr (10 mol%) were diluted in MeCN (0.1 M) and $PhSO_2Na$ (10 mol%) was added. After stirring at room temperature for 16 hours, the reaction mixture was concentrated under reduced pressure and directly purified by column chromatography on silica gel to afford the pure cyclopentene **3** or **4**.

Procedure B in THF: Allenyl sulfone **1a** or **1b** (1.5 equiv.), Michael acceptor **2** or **6a** (1 equiv.), *n*-Bu_4NBr (10 mol%) were diluted in THF (0.1 M) and $PhSO_2Na$ (10 mol%) was added. After stirring at room temperature for 24 hours, the reaction mixture was concentrated under reduced pressure and directly purified by column chromatography on silica gel to afford the pure cyclopentene **3** or **4**.

2-Phenyl-4-(phenylsulfonyl)cyclopent-2-ene-1,1-dicarbonitrile (4aa): According to procedure A, cyclopentene **4aa** was

obtained from allene **1a** (21.6 mg, 0.12 mmol), malononitrile derivative **2a** (15.4 mg, 0.1 mmol), *n*-Bu_4NBr (3.3 mg, 0.01 mmol) and $PhSO_2Na$ (1.8 mg, 0.01 mmol) in MeCN (1 mL). Column chromatography with petroleum ether/AcOEt/CH_2Cl_2 = 7/1.5/1.5. Yield 82% (27 mg, 0.082 mmol). The reaction was repeated on a larger scale, starting with **1a** (200 mg, 1.11 mmol), **2a** (258 mg, 1.67 mmol), *n*-Bu_4NBr (36 mg, 0.11 mmol) and $PhSO_2Na$ (20 mg, 0.11 mmol) in MeCN (10 mL). Yield 80% (267 mg, 0.799 mmol). Beige solid, mp: 158–159 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.20 and 3.25 (AB part of ABX, $^2J_{AB}$ = 15.0, $^3J_{AX}$ = 5.5 and $^3J_{BX}$ = 8.4, 1H each), 4.67 (ddd, ^3J = 2.6, 5.5 and 8.4, 1H), 6.44 (d, ^3J = 2.6, 1H), 7.46–7.49 (m, 3H), 7.58–7.70 (m, 4H), 7.73–7.77 (m, 1H), 7.92–7.95 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 38.4, 40.1, 69.8, 113.5, 114.5, 126.0, 126.8 (2C), 129.0 (2C), 129.2, 129.4 (2C), 129.9 (2C), 130.8, 135.0, 136.0, 143.0. IR (neat, ATR probe, cm^{-1}): 2913, 2438, 2160, 2030, 1977, 1447, 1307, 1222, 1139, 1087. HRMS (ESI): Calculated for $C_{19}H_{14}N_2O_2SNa$ [$(M+Na)^+$]: 357.0674, found: 357.0670.

2-(4-Chlorophenyl)-4-(phenylsulfonyl)cyclopent-2-ene-1,1-dicarbonitrile (4ab): According to procedure A, cyclopentene **4ab** was obtained from allene **1a** (21.6 mg, 0.12 mmol), malononitrile derivative **2b** (18.8 mg, 0.1 mmol), *n*-Bu_4NBr (3.3 mg, 0.01 mmol) and $PhSO_2Na$ (1.8 mg, 0.01 mmol) in MeCN (1 mL). Column chromatography with petroleum ether/AcOEt/CH_2Cl_2 = 6.5/1.75/1.75. Yield 79% (29.2 mg, 0.079 mmol). White solid, mp: 72–73 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.18 and 3.26 (AB part of ABX system, $^2J_{AB}$ = 15.0, $^3J_{AX}$ = 5.2 and $^3J_{BX}$ = 8.4, 1H each), 4.64–4.69 (m, 1H), 6.43 (d, ^3J = 2.4, 1H), 7.43–7.45 (m, 2H), 7.53–7.55 (m, 2H), 7.62–7.66 (m, 2H), 7.73–7.77 (m, 1H), 7.92–7.94 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 38.4, 40.1, 69.8, 113.3, 114.3, 126.7, 127.7, 128.1 (2C), 129.0 (2C), 129.7 (2C), 130.0 (2C), 135.1, 136.0, 137.1, 141.9. IR (neat, ATR probe, cm^{-1}): 2924, 2159, 1977, 1594, 1493, 1447, 1404, 1307, 1148, 1084. HRMS (ESI): Calculated for $C_{19}H_{13}ClN_2O_2SNa$ [$(M+Na)^+$] with ^{35}Cl isotope: 391.0284, found: 391.0283.

2-(4-Methoxyphenyl)-4-(phenylsulfonyl)cyclopent-2-ene-1,1-dicarbonitrile (4ac): According to procedure A, cyclopentene **4ac** was obtained from allene **1a** (21.6 mg, 0.12 mmol), malononitrile derivative **2c** (18.4 mg, 0.1 mmol), *n*-Bu_4NBr (3.3 mg, 0.01 mmol) and $PhSO_2Na$ (1.8 mg, 0.01 mmol) in MeCN (1 mL). Column chromatography with petroleum ether/AcOEt/CH_2Cl_2 = 6.5/1.75/1.75. Yield 83% (30.2 mg, 0.083 mmol). Orange solid, mp: 144–145 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.17 and 3.23 (AB part of ABX system, $^2J_{AB}$ = 15.0, $^3J_{AX}$ = 5.4 and $^3J_{BX}$ = 8.2, 1H each), 3.85 (s, 3H), 4.67 (ddd, ^3J = 2.6, 5.4 and 8.2, 1H), 6.30 (d, ^3J = 2.6, 1H), 6.95–6.97 (m, 2H), 7.53–7.56 (m, 2H), 7.61–7.65 (m, 2H), 7.72–7.76 (m, 1H), 7.91–7.94 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 38.4, 40.0, 55.5, 69.9, 113.6, 114.7 (3C, signals overlapping), 121.7, 123.3, 128.3 (2C), 129.1 (2C), 129.9 (2C), 135.0, 136.0, 142.5, 161.5. IR (neat, ATR probe, cm^{-1}): 2452, 2159, 1976, 1644, 1480, 1446, 1308, 1146, 1083, 1022. HRMS (ESI): Calculated for $C_{20}H_{16}N_2O_3SNa$ [$(M+Na)^+$]: 387.0779, found: 387.0775.

2-(4-Nitrophenyl)-4-(phenylsulfonyl)cyclopent-2-ene-1,1-dicarbonitrile (4ad): According to procedure A, cyclopentene **4ad** was obtained from allene **1a** (21.6 mg, 0.12 mmol), malononitrile derivative **2d** (19.9 mg, 0.1 mmol), *n*-Bu_4NBr (3.3 mg, 0.01 mmol) and $PhSO_2Na$ (1.8 mg, 0.01 mmol) in MeCN (1 mL). Column chromatography with petroleum ether/AcOEt/CH_2Cl_2 = 6/2/2. Yield 73% (27.7 mg, 0.073 mmol). Pale yellow solid, mp: 65–66 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.21 and 3.31 (AB part of ABX system, $^2J_{AB}$ = 15.0, $^3J_{AX}$ = 5.4 and $^3J_{BX}$ = 8.3, 1H each), 4.71 (ddd, ^3J = 2.6, 5.4 and 8.3, 1H), 6.63 (d, ^3J = 2.6, 1H), 7.65–7.69 (m, 2H), 7.77–7.80 (m, 3H), 7.94–7.96 (m, 2H), 8.33–8.35 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 38.4, 40.2, 69.8, 112.9, 113.9, 124.6 (2C), 127.9 (2C), 128.9 (2C), 130.1 (2C), 130.3, 135.2, 135.3, 136.0, 141.1, 148.8. IR (neat, ATR probe, cm^{-1}): 2160, 1977, 1599, 1518, 1447, 1347, 1308, 1149, 1083, 847. HRMS (ESI): Calculated for $C_{19}H_{13}N_3O_4SNa$ [$(M+Na)^+$]: 402.0524, found: 402.0520.

2-(2-Chlorophenyl)-4-(phenylsulfonyl)cyclopent-2-ene-1,1-dicarbonitrile (4ae): According to procedure A, cyclopentene **4ae** was obtained from allene **1a** (21.6 mg, 0.12 mmol), malononitrile derivative **2e** (18.8 mg, 0.1 mmol), *n*-Bu_4NBr (3.3 mg, 0.01 mmol) and $PhSO_2Na$ (1.8 mg, 0.01 mmol) in MeCN (1 mL). Column chromatography with petroleum ether/AcOEt = 7.5/2.5. Yield 77% (28.4 mg, 0.077 mmol). White solid, mp: 143–144 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.19–3.29 (m, 2H), 4.70–4.75 (m, 1H), 6.33 (d, ^3J = 2.2, 1H), 7.34–7.42 (m, 2H), 7.47–7.51 (m, 2H), 7.64–7.67 (m, 2H), 7.75–7.79 (m, 1H), 7.95–7.97 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 37.9, 43.0, 70.0, 113.0, 113.9, 127.3, 128.9, 129.2 (2C), 129.7, 129.9 (2C), 130.7, 131.4, 133.0, 133.8, 135.1, 136.0, 139.5. IR (neat, ATR probe, cm^{-1}): 2927, 1470, 1448, 1318, 1147, 1083, 1042, 757, 727, 714. HRMS (ESI): Calculated for $C_{19}H_{13}ClN_2O_2SNa$ [$(M+Na)^+$] with ^{35}Cl isotope: 391.0284, found: 391.0278.

2-(2-Methoxyphenyl)-4-(phenylsulfonyl)cyclopent-2-ene-1,1-dicarbonitrile (4af): According to procedure A, cyclopentene **4af** was obtained from allene **1a** (27 mg, 0.15 mmol), malononitrile derivative **2f** (18.4 mg, 0.1 mmol), *n*-Bu_4NBr (3.3 mg, 0.01 mmol) and $PhSO_2Na$ (1.8 mg, 0.01 mmol) in THF (1 mL). Column chromatography with pentane/AcOEt/CH_2Cl_2 = 6.5/1.75/1.75. Yield 57% (20.7 mg, 0.057 mmol). White solid, mp: 139–140 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.09 and 3,13 (AB part of ABX system, $^2J_{AB}$ = 14, $^3J_{AX}$ = $^3J_{AX}$ = 7.4, 1H each), 3.92 (s, 3H), 4.67 (dt, ^3J = 2.3 and 7.4, 1H), 6.51 (d, ^3J = 2.3, 1H), 6.98–7.04 (m, 2H), 7.41–7.45 (m, 2H), 7.63–7.67 (m, 2H), 7.73–7.77 (m, 1H), 7.94–7.96 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 39.4, 42.0, 55.0, 69.2, 111.7, 113.9, 115.0, 118.8, 121.2, 128.1, 129.0 (2C), 129.8 (2C), 129.9, 132.1, 134.9, 136.4, 157.0. IR (neat, ATR probe, cm^{-1}): 2160, 2030, 1599, 1489, 1448, 1310, 1265, 1151, 1087, 1017. HRMS (ESI): Calculated for $C_{20}H_{16}N_2O_3SNa$ [$(M+Na)^+$]: 387.0779, found: 387.0774.

2-(2-Naphthyl)-4-(phenylsulfonyl)cyclopent-2-ene-1,1-dicarbonitrile (4ag): According to procedure A, cyclopentene **4ag** was obtained from allene **1a** (21.6 mg, 0.12 mmol), malononitrile derivative **2g** (20.4 mg, 0.1 mmol), *n*-Bu_4NBr (3.3 mg, 0.01 mmol) and $PhSO_2Na$ (1.8 mg, 0.01 mmol) in MeCN (1 mL). Column chromatography with pentane/AcOEt/CH_2Cl_2 = 6.5/1.75/1.75. Yield 86% (33.2 mg, 0.086 mmol). Yellow solid, mp: 186–187 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.24 and 3.31 (AB part of ABX system, $^2J_{AB}$ = 15.0, $^3J_{AX}$ = 5.4

and $^3J_{AX}$=8.4, 1H each), 4.72 (ddd, ^3J=2.6, 5.4 and 8.4, 1H), 6.57 (d, ^3J=2.6, 1H), 7.55–7.60 (m, 2H), 7.62–7.66 (m, 3H), 7.73–7.77 (m, 1H), 7.85–7.87 (m, 1H), 7.90–7.97 (m, 4H), 8.08–8.10 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 38.6, 40.0, 70.0, 113.6, 114.7, 123.4, 126.1, 126.4, 126.9, 127.3, 127.8, 128.0, 128.9, 129.1 (2C), 129.4, 129.9 (2C), 132.9, 133.9, 135.1, 136.0, 142.9. IR (neat, ATR probe, cm^{-1}): 2925, 2159, 1446, 1308, 1147, 1083, 854, 814, 751, 722. HRMS (ESI): Calculated for $C_{23}H_{16}N_2O_2SNa$ [(M+Na)$^+$]: 407.0830, found: 407.0825.

2-([2.2]Paracyclophan-4-yl)-4-(phenylsulfonyl)cyclopent-2-ene-1,1-dicarbonitrile (4ah): According to procedure A, cyclopentene **4ah** was obtained from allene **1a** (21.6 mg, 0.12 mmol), malononitrile derivative **2h** (28.4 mg, 0.1 mmol), *n*-Bu_4NBr (3.3 mg, 0.01 mmol) and $PhSO_2Na$ (1.8 mg, 0.01 mmol) in MeCN (1 mL). Column chromatography pentane/AcOEt/CH_2Cl_2=7/1.5/1.5. Yield 80% (37 mg, 0.080 mmol). The product was obtained as a mixture of two non separable diastereoisomers (dr=50:50). Yellow solid, mp: 112–113 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.97–3.25 (m, 9.5H), 3.39 (ddd, J=3.9 9.2 and 13.4, 0.5H), 4.68–4.75 (m, 1H), 6.28 (d, ^3J=2.3, 0.5H), 6.33 (d, ^3J=2.3, 0.5H), 6.35–6.37 (m, 0.5H), 6.43–6.47 (m, 1H), 6.50–6.55 (m, 3H), 6.62–6.69 (m, 2.5H), 7.67–7.73 (m, 2H), 7.77–7.83 (m, 1H), 8.00–8.04 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 34.6, 34.7, 35.0, 35.18, 35.22, 35.4, 35.6, 37.8, 38.2, 41.4, 43.5, 69.8, 70.1, 113.1, 113.7, 114.2, 114.5, 128.1, 128.4, 128.90, 128.95, 129.01, 129.11, 130.0, 130.2, 130.6, 131.75, 131.80, 132.3, 132.52, 132.56, 132.59, 132.9, 133.2, 135.1, 135.4, 135.6, 136.2, 136.4, 136.6, 136.8, 138.6, 138.76, 138.84, 139.1, 139.4, 139.7, 140.2, 142.4, 144.3. IR (neat, ATR probe, cm^{-1}): 2927, 1585, 1446, 1308, 1147, 1083, 903, 815, 721, 688. HRMS (ESI): Calculated for $C_{29}H_{24}N_2O_2SNa$ [(M+Na)$^+$]: 487.1456, found: 487.1458.

2-(2-Furyl)-4-(phenylsulfonyl)cyclopent-2-ene-1,1-dicarbonitrile (4ai): According to procedure A, cyclopentene **4ai** was obtained from allene **1a** (21.6 mg, 0.12 mmol), malononitrile derivative **2i** (14.4 mg, 0.1 mmol), *n*-Bu_4NBr (3.3 mg, 0.01 mmol) and $PhSO_2Na$ (1.8 mg, 0.01 mmol) in MeCN (1 mL). Column chromatography with pentane/AcOEt/CH_2Cl_2=6.5/1.75/1.75. Yield 84% (27.3 mg, 0.084 mmol). Orange solid, mp: 66–67 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.16 and 3.26 (AB part of ABX system, $^2J_{AB}$=15.3, $^3J_{AX}$=4.6 and $^3J_{BX}$=8.6, 1H each), 4.65 (ddd, ^3J=2.8, 4.6 and 8.6, 1H), 6.30 (d, ^3J=2.8, 1H), 6.54 (dd, ^3J=1.7 and 3.5, 1H), 6.84 (d, ^3J=3.5, 1H), 7.54 (d, ^3J=1.7, 1H), 7.61–7.65 (m, 2H), 7.72–7.76 (m, 1H), 7.91–7.93 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 37.8, 39.0, 70.3, 112.3, 112.4, 113.1, 114.2, 122.6, 129.1 (2C), 129.9 (2C), 132.7, 135.0, 135.9, 144.7, 145.3. IR (neat, ATR probe, cm^{-1}): 2452, 2160, 1977, 1644, 1480, 1447, 1308, 1146, 1083, 1022. HRMS (ESI): Calculated for $C_{17}H_{12}N_2O_3SNa$ [(M+Na)$^+$]: 347.066, found: 347.0461.

4-(Phenylsulfonyl)-2-(2-thienyl)cyclopent-2-ene-1,1-dicarbonitrile (4aj): According to procedure A, cyclopentene **4aj** was obtained from allene **1a** (21.6 mg, 0.12 mmol), malononitrile derivative **2j** (16 mg, 0.1 mmol), *n*-Bu_4NBr (3.3 mg, 0.01 mmol) and $PhSO_2Na$ (1.8 mg, 0.01 mmol) in MeCN (1 mL). Column chromatography with pentane/AcOEt/CH_2Cl_2=6.5/1.75/1.75. Yield 74% (25.3 mg, 0.074 mmol). Pale yellow solid, mp: 164–165 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.19 and 3.26 (AB part of ABX system, $^2J_{AB}$=15.3, $^3J_{AX}$=4.7 and $^3J_{BX}$=8.6, 1H each), 4.64 (ddd, ^3J=2.8, 4.7 and 8.6, 1H), 6.25 (d, ^3J=2.8, 1H), 7.11 (dd, ^3J=3.8 and 5.1, 1H), 7.43–7.46 (m, 2H), 7.61–7.65 (m, 2H), 7.73–7.76 (m, 1H), 7.90–7.93 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 38.1, 40.4, 70.2, 113.2, 114.3, 123.9, 128.2, 128.5, 128.9, 129.1 (2C), 129.9 (2C), 132.1, 135.1, 135.7, 136.8. IR (neat, ATR probe, cm^{-1}): 3106, 2904, 2160, 1448, 1307, 1225, 1138, 1085, 864, 731. HRMS (ESI): Calculated for $C_{17}H_{12}N_2O_2S_2Na$ [(M+Na)$^+$]: 363.0238, found: 363.0237.

2-(3-(*N*-Boc)indolyl)-4-(phenylsulfonyl)cyclopent-2-ene-1,1-dicarbonitrile (4ak): According to procedure A, cyclopentene **4ak** was obtained from allene **1a** (21.6 mg, 0.12 mmol), malononitrile derivative **2k** (29.3 mg, 0.1 mmol), *n*-Bu_4NBr (3.3 mg, 0.01 mmol) and $PhSO_2Na$ (1.8 mg, 0.01 mmol) in MeCN (1 mL). Column chromatography with petroleum ether/AcOEt/CH_2Cl_2=7/1.5/1.5. Yield 77% (36.4 mg, 0.077 mmol). Yellow solid, mp: 151–152 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.69 (s, 9H), 3.18 and 3.24 (AB part of ABX system, $^2J_{AB}$=15.2, $^3J_{AX}$=5.0 and $^3J_{BX}$=8.4, 1H each), 4.74–4.78 (m, 1H), 6.56 (d, ^3J=2.5, 1H), 6.54 (dd, ^3J=1.7 and 3.5, 1H), 6.84 (d, ^3J=3.5, 1H), 7.35–7.46 (m, 2H), 7.60–7.76 (m, 4H), 7.94–7.96 (m, 2H), 8.10 (s, 1H), 8.24–8.26 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.1 (3C), 37.4, 41.2, 70.9, 85.3, 110.7, 113.6, 114.8, 115.9, 119.7, 123.9, 124.6, 125.8, 126.0, 127.5, 129.2 (2C), 129.9 (2C), 135.0, 135.7, 136.1, 148.8 (1 signal missing, probably overlapping with another one). IR (neat, ATR probe, cm^{-1}): 2159, 1737 (C=O), 1493, 1447, 1370, 1308, 1147, 1083, 826, 722. HRMS (ESI): Calculated for $C_{26}H_{23}N_3O_4SNa$ [(M+Na)$^+$]: 496.1307, found: 496.1304.

2-(2-Ferrocenyl)-4-(phenylsulfonyl)cyclopent-2-ene-1,-dicarbonitrile (4al): According to procedure A, cyclopentene **4al** was obtained from allene **1a** (21.6 mg, 0.12 mmol), malononitrile derivative **2l** (26.2 mg, 0.1 mmol), Me_3BnNCl (1.9 mg, 0.01 mmol) and $PhSO_2Na$ (1.8 mg, 0.01 mmol) in MeCN (1 mL). Column chromatography with pentane/AcOEt/CH_2Cl_2=7.5/1.25/1.25. Yield 70% (31 mg, 0.07 mmol). Brown solid, mp: 162–163 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.10 and 3.21 (AB part of ABX system, $^2J_{AB}$=15.2, $^3J_{AX}$=4.2 and $^3J_{BX}$=8.5, 1H each), 4.25 (s, 4H), 4.41–4.49 (m, 3H), 4.61–4.65 (m, 2H), 6.05 (d, ^3J=2.1, 1H), 7.64–7.68 (m, 2H), 7.74–7.78 (m, 1H), 7.94–7.96 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 38.4, 40.0, 67.1, 67.7, 70.2, 70.8 (4C), 70.9, 71.7, 72.7, 114.1, 115.1, 119.9, 129.1 (2C), 129.8 (2C), 134.8, 136.5, 144.2. IR (neat, ATR probe, cm^{-1}): 2925, 1625, 1450, 1306, 1292, 1155, 1075, 1034, 1000, 727. HRMS (ESI): Calculated for $C_{23}H_{18}N_2O_2SFe$ [(M+H)$^+$]: 442.0438, found: 442.0442.

2-(*n*-Butyl)-4-(phenylsulfonyl)cyclopent-3-ene-1,1-dicarbonitrile (3am): According to procedure B, cyclopentene **3am** was obtained from allene **1a** (27 mg, 0.15 mmol), malononitrile derivative **2m** (12 mg, 0.1 mmol), *n*-Bu_4NBr (3.3 mg, 0.01 mmol) and $PhSO_2Na$ (1.8 mg, 0.01 mmol) in THF (1 mL). Column chromatography with pentane/AcOEt/CH_2Cl_2=8/1/1. Yield 61% (18.3 mg, 0.061 mmol). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.02 (t, ^3J=7.2, 3H), 1.49–1.58 (m, 2H), 1.70–1.89 (m, 2H), 3.28 (s, 2H), 3.45–3.48 (m, 1H), 6.70–6.71 (m, 1H), 7.59–7.63 (m, 2H), 7.70–7.73 (m, 1H), 7.89–7.91 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7, 20.5, 32.6, 38.6, 42.4, 54.8, 113.0, 114.8, 128.0 (2C), 129.8 (2C), 134.6, 137.7, 141.1, 141.7. IR (neat, ATR probe, cm^{-1}):

2963, 1599, 1519, 1447, 1320, 1308, 1154, 1082, 846, 754. HRMS (ESI): Calculated for $C_{16}H_{16}N_2O_2SNa$ [$(M+Na)^+$]: 323.0830, found: 323.0829.

2-Cyclohexyl-4-(phenylsulfonyl)cyclopent-3-ene-1,1-dicarbonitrile (3an): According to procedure B, cyclopentene **3an** was obtained from allene **1a** (27 mg, 0.15 mmol), malononitrile derivative **2n** (16 mg, 0.1 mmol), *n*-Bu_4NBr (3.3 mg, 0.01 mmol) and $PhSO_2Na$ (1.8 mg, 0.01 mmol) in THF (1 mL). Column chromatography with petroleum ether/AcOEt = 8/2. Yield 88% (29.8 mg, 0.088 mmol). White solid, mp: 144–145 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 1.06–1.39 (m, 5H), 1.71–1.90 (m, 5H), 1.98–2.03 (m, 1H), 3.21–3.32 (m, 3H), 6.81 (br s, 1H), 7.59–7.63 (m, 2H), 7.70–7.73 (m, 1H), 7.89–7.91 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.47, 25.50, 25.6, 30.8, 31.4, 37.5, 39.5, 43.0, 61.0, 113.4, 115.1, 128.0 (2C), 129.8 (2C), 134.6, 137.8, 139.8, 141.9. IR (neat, ATR probe, cm^{-1}): 3093, 2933, 2854, 1623, 1446, 1309, 1158, 1086, 759, 718. HRMS (ESI): Calculated for $C_{19}H_{20}N_2O_2SNa$ [$(M+Na)^+$]: 363.1143, found: 363.1140.

2-(*tert*-Butyl)-4-(phenylsulfonyl)cyclopent-3-ene-1,1-dicarbonitrile (3ao): According to procedure B, cyclopentene **3ao** was obtained from allene **1a** (27 mg, 0.15 mmol), malononitrile derivative **2o** (13.4 mg, 0.1 mmol), *n*-Bu_4NBr (3.3 mg, 0.01 mmol) and $PhSO_2Na$ (1.8 mg, 0.01 mmol) in THF (1 mL). Column chromatography with pentane/AcOEt/CH_2Cl_2 = 8/1/1. Yield 99% (31.3 mg, 0.099 mmol). White solid, mp: 146–147 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 1.22 (s, 9H), 3.29–3.34 (m, 3H), 6.80–6.82 (m, 1H), 7.60–7.64 (m, 2H), 7.70–7.74 (m, 1H), 7.89–7.91 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.8 (3C), 34.3, 35.8, 43.9, 65.5, 114.6, 115.6, 128.0 (2C), 129.8 (2C), 134.6, 137.8, 140.4, 142.1. IR (neat, ATR probe, cm^{-1}): 2968, 2464, 2160, 1976, 1625, 1317, 1294, 1154, 1106, 887. HRMS (ESI): Calculated for $C_{17}H_{18}N_2O_2SNa$ [$(M+Na)^+$]: 337.0987, found: 337.0987.

(1*S,2*R**)-1-Cyano-2-phenyl-4-(phenylsulfonyl)cyclopent-3-enecarboxylic Acid Methyl Ester (7):** According to procedure B, cyclopentene **7** was obtained from allene **1a** (27 mg, 0.15 mmol), (*E*)-configured cyanoester derivative **6a** (18.7 mg, 0.1 mmol), *n*-Bu_4NBr (3.3 mg, 0.01 mmol) and $PhSO_2Na$ (1.8 mg, 0.01 mmol) in THF (1 mL). Yield 80% (29.5 mg, 0.080 mmol). Column chromatography with pentane/AcOEt/CH_2Cl_2 = 6.5/1.75/1.75. The product was obtained as a single diastereoisomer (dr > 99:1). Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 3.24 (dt, ^2J = 16.3 and ^4J = 1.7, 1H), 3.39 (dt, ^2J = 16.3 and ^4J = 2.0, 1H), 3.83 (s, 3H), 4.75–4.78 (m, 1H), 6.77–6.79 (m, 1H), 7.15–7.20 (m, 2H), 7.31–7.40 (m, 3H), 7.61–7.65 (m, 2H), 7.70–7.74 (m, 1H), 7.96–7.98 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 41.3, 54.4, 55.1, 58.5, 116.5, 128.1 (2C), 128.4 (2C), 129.17 (2C), 129.24, 129.7 (2C), 134.3, 134.8, 138.3, 141.0, 143.2, 167.7. IR (neat, ATR probe, cm^{-1}): 3105, 2160, 1744(C=O), 1447, 1307, 1241, 1151, 1083, 755, 722. HRMS (ESI): Calculated for $C_{20}H_{17}NO_4SNa$ [$(M+Na)^+$]: 390.0776, found: 390.0770.

***Trans*-(±)-5-methyl-2-phenyl-4-(phenylsulfonyl)cyclopent-2-ene-1,1-dicarbonitrile (4ba):** According to procedure B, cyclopentene **4ba** was obtained from allene **1b** (19.4 mg, 0.1 mmol), malononitrile derivative **2a** (23.1 mg, 0.15 mmol), *n*-Bu_4NBr (3.3 mg, 0.01 mmol) and $PhSO_2Na$ (1.8 mg, 0.01 mmol) in THF (1 mL). Yield 77% (26.8 mg, 0.077 mmol). Column chromatography with pentane/AcOEt/CH_2Cl_2 = 8/1/1. The product was obtained as a single diastereoisomer (dr > 99:1). White solid, mp: 190–191 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 1.56 (d, ^3J = 7.1, 3H), 3.39 (quint, ^3J = 7.1, 1H), 4.24 (dd, ^3J = 2.2 and 7.7, 1H), 6.30 (d, ^3J = 2.2, 1H), 7.44–7.47 (m, 3H), 7.53–7.58 (m, 2H), 7.63–7.68 (m, 2H), 7.73–7.78 (m, 1H), 7.94–7.98 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.2, 45.9, 47.0, 75.1, 112.1, 113.7, 126.2, 126.6 (2C), 129.0 (2C), 129.3 (2C), 129.6, 129.9 (2C), 130.7, 135.0, 136.3, 142.2. IR (neat, ATR probe, cm^{-1}): 2451, 2159, 2022, 1977, 1446, 1309, 1218, 1142, 1086, 806. HRMS (ESI): Calculated for $C_{20}H_{16}N_2O_2SNa$ [$(M+Na)^+$]: 371.0830, found: 371.0837.

***Trans*-(±)-2-(4-methoxyphenyl)-5-methyl-4-(phenylsulfonyl)-cyclopent-2-ene-1,1-dicarbonitrile (4bc):** According to procedure B, cyclopentene **4bc** was obtained from allene **1b** (19.4 mg, 0.1 mmol), malononitrile derivative **2c** (27.6 mg, 0.15 mmol), *n*-Bu_4NBr (3.3 mg, 0.01mmol) and $PhSO_2Na$ (1.8 mg, 0.01 mmol) in THF (1 mL). Yield 65% (24.5 mg, 0.065 mmol). Column chromatography with pentane/AcOEt/CH_2Cl_2 = 7/1.5/1.5. The product was obtained as a single diastereoisomer (dr > 99:1). Yellow solid, mp: 173–174 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 1.56 (d, ^3J = 7.1, 3H), 3.36 (quint, ^3J = 7.1, 1H), 3.84 (s, 3H), 4.22 (dd, ^3J = 2.1 and 7.5, 1H), 6.16 (d, ^3J = 2.1, 1H), 6.93–6.97 (m, 2H), 7.50–7.53 (m, 2H), 7.63–7.67 (m, 2H), 7.73–7.77 (m, 1H), 7.94–7.96 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.3, 45.8, 47.0, 55.5, 75.3, 112.2, 113.9, 114.7 (2C), 122.0, 123.5, 128.1 (2C), 129.0 (2C), 129.8 (2C), 134.9, 136.3, 141.7, 161.4. IR (neat, ATR probe, cm^{-1}): 2927, 2160, 1600, 1517, 1447, 1347, 1308, 1150, 1084, 846. HRMS (ESI): Calculated for $C_{21}H_{18}N_2O_3SNa$ [$(M+Na)^+$]: 401.0936, found: 401.0928.

***Trans*-(±)-2-(2-methoxyphenyl)-5-methyl-4-(phenylsulfonyl)-cyclopent-2-ene-1,1-dicarbonitrile (4bf):** According to procedure B, cyclopentene **4bf** was obtained from allene **1b** (19.4 mg, 0.1 mmol), malononitrile derivative **2f** (27.6 mg, 0.15 mmol), *n*-Bu_4NBr (3.3 mg, 0.01 mmol) and $PhSO_2Na$ (1.8 mg, 0.01 mmol) in THF (1 mL). Column chromatography with pentane/AcOEt/CH_2Cl_2 = 8/1/1. Yield 57% (21.7 mg, 0.057 mmol). The product was obtained as a single diastereoisomer (dr > 99:1). White solid, mp: 148–149 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 1.60 (d, ^3J = 6.9, 3H), 3.21–3.29 (m, 1H), 3.91 (s, 3H), 4.26 (dd, ^3J = 1.9 and 8.7, 1H), 6.31 (d, ^3J = 1.9, 1H), 6.95–7.02 (m, 2H), 7.32 (dd, ^3J = 1.5 and 7.7, 1H), 7.38–7.43 (m, 1H), 7.64–7.68 (m, 2H), 7.73–7.77 (m, 1H), 7.95–7.98 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.1, 47.0, 48.9, 54.9, 73.9, 111.6, 112.6, 114.0, 119.2, 121.2, 128.5, 129.0 (2C), 129.7 (2C), 129.8 (1C), 132.0, 134.9, 136.6, 141.1, 156.9. IR (neat, ATR probe, cm^{-1}): 2527, 2160, 1976, 1597, 1489, 1468, 1307, 1268, 1144, 1023. HRMS (ESI): Calculated for $C_{21}H_{18}N_2O_3SNa$ [$(M+Na)^+$]: 401.0936, found: 401.0929.

***Trans*-(±)-2-(2-naphthyl)-5-methyl-4-(phenylsulfonyl)cyclopent-2-ene-1,1-dicarbonitrile (4bg):** According to procedure B, cyclopentene **4bg** was obtained from allene **1b** (19.4 mg, 0.1 mmol), malononitrile derivative **2g** (30.6 mg, 0.15 mmol), *n*-Bu_4NBr (3.3 mg, 0.01 mmol) and $PhSO_2Na$ (1.8 mg, 0.01 mmol) in THF (1 mL). Column chromatography with pentane/AcOEt/CH_2Cl_2 = 8/1/1. Yield 73% (29.1 mg, 0.073 mmol). The product was obtained as a single diaster-

eoisomer (dr > 99:1). White solid, mp: 171–172 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.60 (d, ^3J = 7.0, 3H), 3.45 (quint$_{app}$, J = 7.2, 1H), 4.29 (dd, ^3J = 2.2 and 7.6, 1H), 6.43 (d, ^3J = 2.2, 1H), 7.54–7.60 (m, 3H), 7.65–7.69 (m, 2H), 7.74–7.78 (m, 1H), 7.84–7.93 (m, 3H), 7.97–8.00 (m, 2H), 8.05–8.07 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.3, 46.0, 47.0, 75.3, 112.2, 113.9, 123.3, 126.3, 126.6, 126.8, 127.2, 127.8, 127.9, 128.9, 129.0 (2C), 129.3, 129.9 (2C), 132.9, 133.9, 135.0, 136.4, 142.1. IR (neat, ATR probe, cm^{-1}): 2442, 2159, 1976, 1446, 1308, 1211, 1140, 1084, 860, 801. HRMS (ESI): Calculated for $C_{24}H_{18}N_2O_2SNa$ [(M + Na)$^+$]: 421.0987, found: 421.0983.

***Trans*-(±)-5-methyl-4-(phenylsulfonyl)-2-(2-thienyl)-cyclopent-2-ene-1,1-dicarbonitrile (4bj):** According to procedure B, cyclopentene **4bj** was obtained from allene **1b** (19.4 mg, 0.1 mmol), malononitrile derivative **2j** (24 mg, 0.15 mmol), *n*-Bu_4NBr (3.3 mg, 0.01 mmol) and $PhSO_2Na$ (1.8 mg, 0.01 mmol) in THF (1 mL). Column chromatography with pentane/AcOEt/CH_2Cl_2 = 7.5/1.25/1.25. Yield 49% (17.5 mg, 0.049 mmol). The product was obtained as a single diastereoisomer (dr > 99:1). Pink solid, mp: 197–198 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.55 (d, ^3J = 7.1, 3H), 3.38 (quint, J = 7.1, 1H), 4.21 (dd, ^3J = 2.4 and 6.9, 1H), 6.15 (d, ^3J = 2.4, 1H), 7.10 (dd, ^3J = 3.8 and 5.0, 1H), 7.42 (d, ^3J = 5.0, 1H), 7.45 (d, ^3J = 3.8, 1H), 7.63–7.67 (m, 2H), 7.73–7.77 (m, 1H), 7.92–7.94 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.8, 45.4, 47.2, 75.8, 111.7, 113.6, 123.9, 127.8, 128.4, 128.6, 129.0 (2C), 129.9 (2C), 132.5, 135.0, 135.8, 136.0. IR (neat, ATR probe, cm^{-1}): 2447, 2160, 2030, 1977, 1582, 1446, 1309, 1221, 1142, 1084. HRMS (ESI): Calculated for $C_{18}H_{14}N_2O_2S_2Na$ [(M + Na)$^+$]: 377.0394, found: 377.0393.

Typical Procedure for (3 + 2) Annulations with Allenyl Sulfone 1c: Allenyl sulfone **1c** (1 equiv.), Michael acceptor **2** (1.5 equiv.), *n*-Bu_4NBr (10 mol%) were diluted in THF (0.1 M) and $PhSO_2Na$ (10 mol%) was added. After stirring at room temperature for 16 hours, the reaction mixture was concentrated under reduced pressure and directly purified by column chromatography on silica gel to afford the pure cyclopentenes **3** or **4**.

3-Methyl-2-phenyl-4-(phenylsulfonyl)cyclopent-3-ene-1,1-dicarbonitrile (3ca): Cyclopentene **3ca** was obtained from allene **1c** (19.4 mg, 0.1 mmol), malononitrile derivative **2a** (23.1 mg, 0.15 mmol), *n*-Bu_4NBr (3.3 mg, 0.01mmol) and $PhSO_2Na$ (1.8 mg, 0.01 mmol) in THF (1 mL). Column chromatography with pentane/AcOEt/CH_2Cl_2 = 8/1/1. Yield 85% (29.6 mg, 0.085 mmol). White solid, mp: 128–129 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.16 (s, 3H), 3.36–3.48 (m, 2H), 4.43 (s, 1H), 7.07–7.10 (m, 2H), 7.39–7.46 (m, 3H), 7.63–7.68 (m, 2H), 7.72–7.77 (m, 1H), 7.95–7.98 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.5, 38.3, 43.5, 66.3, 112.8, 115.6, 127.4 (2C), 128.6 (2C), 129.75 (2C), 129.83 (2C), 130.2, 131.7, 133.9, 134.5, 139.5, 151.4. IR (neat, ATR probe, cm^{-1}): 2925, 1640, 1446, 1321, 1306, 1149, 1093, 752, 725, 687. HRMS (ESI): Calculated for $C_{20}H_{16}N_2O_2SNa$ [(M + Na)$^+$]: 371.0830, found: 371.0822.

3-Methyl-2-phenyl-4-(phenylsulfonyl)cyclopent-2-ene-1,1-dicarbonitrile (4ca): Cyclopentene **4ca** was obtained from allene **1c** (19.4 mg, 0.1 mmol), malononitrile derivative **2a** (23.1 mg, 0.15 mmol), *n*-Bu_4NOAc (3 mg, 0.01 mmol) and $PhSO_2Na$ (1.8 mg, 0.01 mmol) in THF (1 mL). Column chromatography with pentane/AcOEt/CH_2Cl_2 = 7/1.5/1.5. Yield 89% (31 mg, 0.089 mmol). White solid, mp: 171–172 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.05 (s, 3H), 2.98 and 3.04 (AB part of ABX system, $^2J_{AB}$ = 15.2, $^3J_{AX}$ = 5.2 and $^3J_{BX}$ = 8.5, 1H each), 4.49–4.54 (m, 1H), 7.29–7.32 (m, 2H), 7.44–7.48 (m, 3H), 7.66–7.70 (m, 2H), 7.76–7.81 (m, 1H), 7.94–7.97 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.7, 37.6, 42.6, 72.8, 113.3, 114.8, 128.7 (2C), 129.0 (2C), 129.2 (2C), 129.89, 129.94 (2C), 130.5, 135.1, 136.2, 137.1, 139.0. IR (neat, ATR probe, cm^{-1}): 2925, 1445, 1316, 1306, 1148, 1085, 1070, 768, 753, 726. HRMS (ESI): Calculated for $C_{20}H_{16}N_2O_2SNa$ [(M + Na)$^+$]: 371.0830, found: 371.0844.

2-(4-Methoxyphenyl)-3-methyl-4-(phenylsulfonyl)cyclopent-3-ene-1,1-dicarbonitrile (3cc): Cyclopentene **3cc** was obtained from allene **1c** (19.4 mg, 0.1 mmol), malononitrile derivative **2c** (27.6 mg, 0.15 mmol), *n*-Bu_4NBr (3.3 mg, 0.01 mmol) and $PhSO_2Na$ (1.8 mg, 0.01 mmol) in THF (1 mL). Column chromatography with pentane/AcOEt/CH_2Cl_2 = 8/1/1. Yield 78% (29.3 mg, 0.078 mmol). Yellow solid, mp: 58–59 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.15 (s, 3H), 3.34–3.45 (m, 2H), 3.81 (s, 3H), 4.39 (s, 1H), 6.90–6.92 (m, 2H), 6.99–7.02 (m, 2H), 7.63–7.67 (m, 2H), 7.72–7.76 (m, 1H), 7.95–7.97 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.4, 38.4, 43.3, 55.4, 65.8, 113.0, 115.1 (2C), 115.7, 123.4, 127.4 (2C), 129.8 (2C), 129.9 (2C), 133.4, 134.4, 139.5, 151.8, 160.8. IR (neat, ATR probe, cm^{-1}): 2925, 1640, 1446, 1321, 1306, 1149, 1093, 752, 725, 687. HRMS (ESI): Calculated for $C_{21}H_{18}N_2O_3SNa$ [(M + Na)$^+$]: 401.0936, found: 401.0937.

3-Methyl-4-(phenylsulfonyl)-2-(2-thienyl)-cyclopent-2-ene-1,1-dicarbonitrile (4cj): Cyclopentene **4cj** was obtained from allene **1c** (19.4 mg, 0.1 mmol), malononitrile derivative **2j** (24 mg, 0.15 mmol), *n*-Bu_4NBr (3.3 mg, 0.01 mmol) and $PhSO_2Na$ (1.8 mg, 0.01 mmol) in THF (1 mL). Column chromatography with pentane/AcOEt/CH_2Cl_2 = 7/1.5/1.5. Yield 82% (29.2 mg, 0.082 mmol). White solid, mp: 166–167 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.31 (br s, 3H), 3.03 and 3.08 (AB part of ABX system, $^2J_{AB}$ = 15.4, $^3J_{AX}$ = 4.7 and $^3J_{BX}$ = 8.6, 1H each), 4.05–4.53 (m, 1H), 7.16 (dd, ^3J = 3.8 and 5.1, 1H), 7.40–7.42 (m, 1H), 7.52 (dd, ^3J = 5.1 and ^4J = 0.9, 1H), 7.62–7.66 (m, 2H), 7.73–7.76 (m, 1H), 7.90–7.92 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.7, 37.3, 41.9, 73.9, 113.4, 115.1, 127.7, 128.8, 128.9, 129.0 (2C), 130.0 (2C), 130.4, 131.6, 135.1, 135.9, 137.2. IR (neat, ATR probe, cm^{-1}): 2502, 2160, 2029, 1977, 1443, 1313, 1306, 1146, 1085, 813. HRMS (ESI): Calculated for $C_{18}H_{14}N_2O_2S_2Na$ [(M + Na)$^+$]: 377.0394, found: 377.0392.

Chemical Transformations of Cyclopentene 4aa

1-Phenyl-4-(phenylsulfonyl)-6-oxabicyclo[3.1.0]hexane-2,2-dicarbonitrile (8): To a solution of cyclopentene **4aa** (80 mg, 0.24 mmol, 1 equiv.) in dry CH_2Cl_2, $NaHCO_3$ (60 mg, 0.72 mmol, 3 equiv.) and 3-chloroperbenzoic acid (*m*-CPBA 70%, 177 mg, 0.72 mmol, 3 equiv.) were added. After stirring the reaction mixture at room temperature for 48 hours, the volatiles were removed under reduced pressure. The crude product was then purified by column chromatography (pentane/AcOEt = 4/1) on silica gel to afford the pure epoxide **8** as a single diastereoisomer (dr > 99:1). Yield 84% (71 mg, 0.20 mmol). White solid, mp: 193–194 °C. ^{1}H NMR

(600 MHz, $CDCl_3$): δ 2.67 (dd, ^2J=15.6 and ^3J=8.8, 1H), 3.14 (d_{app}, ^2J=15.6, 1H), 4.08 (s_{app}, 1H), 4.08 (d_{app}, ^3J=8.8, 1H), 7.49–7.53 (m, 3H), 7.67–7.70 (m, 2H), 7.73–7.75 (m, 2H), 7.77–7-80 (m, 1H), 8.02–8.04 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 35.8, 40.4, 63.7 (2C), 71.0, 112.3, 113.1, 128.2, 128.6, 128.9, 129.1, 130.3, 131.0, 135.4, 136.8. IR (neat, ATR probe, cm^{-1}): 2924, 1310, 1151, 747, 727, 696, 591, 564, 547, 513. HRMS (ESI): Calculated for $C_{19}H_{14}N_2O_3SNa$ [$(M+Na)^+$]: 373.0623, found: 373.0622.

1-Cyano-2-phenyl-4-(phenylsulfonyl)cyclopent-2-enecarboxylic Acid Methyl Ester (9): To a solution of cyclopentene **4aa** (54 mg, 0.16 mmol, 1 equiv.) in methanol, K_2CO_3 (110 mg, 0.80 mmol, 5 equiv.) was added. After stirring the reaction mixture at room temperature for 16 hours, the solvent was removed under reduced pressure. ^{1}H NMR analysis of the crude product indicated the formation of the two diastereoisomers of **9** in a 68:32 ratio. Separation of both products was readily achieved through purification by column chromatography (toluene/AcOEt=15/1) on silica gel.

Major diastereoisomer (1*S,4*S**)-9:** Yield 48% (27.9 mg, 0,075 mmol). White solid, mp: 125–126 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.99 (d, ^3J=7.2, 2H), 3.77 (s, 3H), 4.68 (dt, ^3J=2.4 and 7.2, 1H), 6.39 (d, ^3J=2.4, 1H), 7.36–7.38 (m, 3H), 7.44–7.46 (m, 2H), 7.61 (t, ^3J=7.8, 2H), 7.71 (t, ^3J=7.5, 1H), 7.93 (d, ^3J=7.5, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 37.5, 54.3, 54.5, 70.7, 117.2, 125.9, 126.7, 129.1, 129.2, 129.8, 130.0, 131.0, 134.8, 136.3, 145.6, 168.4. IR (neat, ATR probe, cm^{-1}): 2887, 1739, 1285, 1198, 1133, 1081, 752, 719, 690, 650, 578, 511. HRMS (ESI): Calculated for $C_{20}H_{17}NO_4SNa$ [$(M+Na)^+$]: 390.0776, found: 390.0777.

Minor diastereoisomer (1*S,4*R**)-9:** Yield 22% (13.12 mg, 0,035 mmol). White solid, mp: 129–130 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.02 (AB part of ABX system ^2J=14.2, ^3J=7.5 and 8.0, 1H each), 3.66 (s, 3H), 4.70 (dt_{app}, ^3J=2.2 and 7.7, 1H), 6.33 (d, ^3J=2.2, 1H), 7.35–7.37 (m, 3H), 7.43–7.45 (m, 2H), 7.63 (t, ^3J=7.8, 2H), 7.72 (t, ^3J=7.5, 1H), 7.94 (d, ^3J=7.5, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 37.6, 54.3, 54.6, 70.0, 117.9, 125.7, 126.6, 129.0, 129.1, 129.7, 129.9, 131.3, 134.6, 136.9, 145.7, 167.3. IR (neat, ATR probe, cm^{-1}): 3078, 1759, 1290, 1207, 1137, 1081, 687, 644, 581, 539. HRMS (ESI): Calculated for $C_{20}H_{17}NO_4SNa$ [$(M+Na)^+$]: 390.0776, found: 390.0777.

Acknowledgements

We acknowledge financial support from Region Normandie (CRUNCh network), CNRS, EFRD and Labex SynOrg (ANR-11-LABX-0029). This work has been also partially supported by INSA Rouen, ENSICAEN, University of Rouen and Caen Normandy.

References

[1] a) Y. Wei, M. Shi, *Org. Chem. Front.* **2017**, *4*, 1876; b) T. Wang, X. Han, F. Zhong, W. Yao, Y. Lu, *Acc. Chem. Res.* **2016**, *49*, 1369; c) Z. Wang, X. Xu, O. Kwon, *Chem. Soc. Rev.* **2014**, *43*, 2927.

[2] C. Gomez, J.-F. Betzer, A. Voituriez, A. Marinetti, *ChemCatChem* **2013**, *5*, 1055.

[3] An original feature of the catalytic cycle is that the expelled sulfinate originates from the starting allenyl sulfone. This characteristic implies the use of identical sulfur motifs within the allene and the sulfinate salt.

[4] For intermolecular versions: a) A. Padwa, P. E. Yeske, *J. Am. Chem. Soc.* **1988**, *110*, 1617; b) A. Padwa, P. E. Yeske, *J. Org. Chem.* **1991**, *56*, 6386.

[5] For intramolecular versions: a) A. Padwa, S. H. Watterson, Z. Ni, *J. Org. Chem.* **1994**, *59*, 3256; b) A. Padwa, S. S. Murphree, Z. Ni, S. H. Watterson, *J. Org. Chem.* **1996**, *61*, 3829; c) A. Padwa, H. Lipka, S. H. Watterson, S. S. Murphree, *J. Org. Chem.* **2003**, *68*, 6238.

[6] A. Núñez, M. Rosario Martín, A. Fraile, J. L. García Ruano, *Chem. Eur. J.* **2010**, *16*, 5443.

[7] a) J. T. Flasz, K. J. Hale, *Org. Lett.* **2012**, *14*, 3024; b) Z. Xiong, K. J. Hale, *Org. Lett.* **2016**, *18*, 4254.

[8] For related intermolecular extensions leading to 3-pyrrolines and chromans, see: a) E. Moreno-Clavijo, A. T. Carmona, H.-U. Reissig, A. J. Moreno-Vargas, E. Alvarez, I. Robina, *Org. Lett.* **2009**, *11*, 4778; b) F. Hu, X. Guan, M. Shi, *Tetrahedron* **2012**, *68*, 4782.

[9] T. Martzel, J.-F. Lohier, A.-C. Gaumont, J.-F. Brière, S. Perrio, *Adv. Synth. Catal.* **2017**, *359*, 96.

[10] For a review dedicated to α,α-dicyano olefins: J. Kaur, P. Chauhan, S. S. Chimni, *Org. Biomol. Chem.* **2016**, *14*, 7832.

[11] For reviews, see: a) S. Shirakawa, K. Maruoka, *Angew. Chem. Int. Ed.* **2013**, *52*, 4312. *Angew. Chem.* **2013**, *125*, 4408; b) J. Tan, N. Yasuda, *Org. Proc. Res. Dev.* **2015**, *19*, 1731; c) J. Schörgenhumer, M. Tiffner, M. Waser, *Beilstein J. Org. Chem.* **2017**, *13*, 1753; d) S. Oudeyer, V. Levacher, J.-F. Brière, *Chiral Quaternary Ammonium Salts in Organocatalysis*, *in Radical and Ion-pairing Strategies in Asymmetric Organocatalysis*, Chapter 2, ISTE Press and Elsevier, **2017**, pp. 87.

[12] See ref. 6 for the beneficial use of PT conditions through the introduction of ammonium salts or crown ethers.

[13] In a Special Issue of *Heterocycles* journal: S. Kuwano, T. Masuda, K. Yamaguchi, T. Arai, *Heterocycles* **2017**, *95*, 232.

[14] A retrosynthetic disconnection indicated that **5** might be produced from two molecules of **1a** and a single molecule of **2a** (see Supporting Information).

[15] D. Blanco-Ania, C. Valderas-Cortina, P. H. H. Hermkens, L. A. J. M. Sliedregt, H. W. Scheeren, F. P. J. T. Rutjes, *Molecules* **2010**, *15*, 2269.

[16] a) P. Beak, D. A. Burg, *J. Org. Chem.* **1989**, *54*, 1647; b) V. Gembus, S. Postikova, V. Levacher, J.-F. Brière, *J. Org. Chem.* **2011**, *76*, 4194.

[17] For a recent phosphine-catalyzed (4+1) annulation with allenoates, in which a rapid proton transfer/double-bond migration reaction was observed: K. Zielke, M. Waser, *Org. Lett.* **2018**, *20*, 768.

[18] O. Lahtigui, F. Emmetiere, W. Zhang, L. Jirmo, S. Toledo-Roy, J. C. Hershberger, J. M. Macho, A. J. Grenning, *Angew. Chem. Int. Ed.* **2016**, *55*, 15792; *Angew. Chem.* **2016**, *128*, 16024.

[19] A. Vlasceanu, B. N. Frandsen, A. B. Skov, A. S. Hansen, M. G. Rasmussen, H. G. Kjaergaard, K. V. Mikkelsen, M. B. Nielsen, *J. Org. Chem.* **2017**, *82*, 10398.

[20] See Supporting Information for some results with commercially available chiral catalysts in THF solution with allenyl sulfones **1a** and **1b**.

COMMUNICATIONS

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Adv. Synth. Catal. **2018**, *360*, 1–12

T. Martzel, J.-F. Lohier, A.-C. Gaumont, J.-F. Brière, S. Perrio*