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Diastereoselective Aza-Baylis–Hillman Reactions: Synthesis of Chiral α-Allenylamines and 2-Azetines from Allenic Esters

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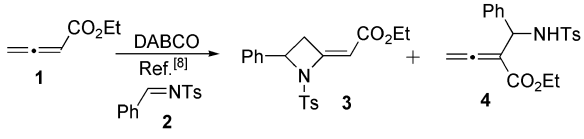
The reactivity of allenic esters towards activated *N*-sulfonylimines in the presence of DABCO was explored. A formal [2+2] cycloaddition of benzyl buta-2,3-dienoate and *N*-arylidenebenzenesulfonamides yielded mainly 2-methyleneazetidines. Interestingly, a DABCO-catalysed reaction of 2,3-allenoates, bearing a chiral auxiliary on the ester moiety, with *N*-arylidenebenzenesulfonamides led to optically active aza-Baylis–Hillman products and 2-azetine derivatives.

Introduction

2-Azetines[1,2] can be considered as enamines with a highly strained double bond. They are difficult to prepare and have received increasing interest in the last years because they are very versatile synthons for the preparation of acyclic and cyclic derivatives.[3] These heterocyclic compounds are mainly prepared from the corresponding four-membered azetidines[2,3a–3c] and 1-amino-2-azetines or 3-pyrrolines. They can also be obtained when electron-rich α-allenyl hydrazines are treated with *n*-butyllithium or from reaction of lithiomethoxyallenes with hydrazones.[4] However, preparative methods for 2- and 4-substituted 2-azetines are scarce, and 2-azetinyl carboxylates specifically have not been described.

Since the first report of Baylis and Hillman in 1972,[5] the aza-Baylis–Hillman reaction has become an important carbon–carbon bond-forming reaction,[6] and it is one of the most fundamental reactions for the construction of molecular frameworks.[7] Furthermore, this synthetic methodology can be considered an efficient process, as it meets the requirements of atom economy and generation of functional groups. Typically, the process involves the reaction of a Michael acceptor such as electron-deficient alkenes with imines in the presence of Lewis bases to form highly functionalized allylic amines. For example, Shi et al. proved that allenoates can act as Michael acceptors in the aza-Baylis–Hillman reaction to yield functionalized allenes as well as azetidines (Scheme 1).[8] The enantioselective aza-Baylis–Hillman reaction of α,β-unsaturated ketones has been reported,[9] whereas only one example of the asymmetric version of the aza-Baylis–Hillman reaction of allenes with imines is known.[10]



Conditions	Yield [%]	
	3	**4**
r.t., 5 h	57	43
4 Å MS, r.t., 1 h	82	–

Scheme 1. DABCO-catalysed reaction of ethyl 2,3-butadienoate with *N*-tosylimine.

We have been interested in the preparation of three,[11] four, five[12] and six-membered[13] nitrogen-containing heterocycles, as well as in the use of allenes as starting materials for the preparation of acyclic and cyclic derivatives.[14] In this context, we decided to further explore the reactivity of allenes towards activated imines in the presence of DABCO (1,4-diazabicyclo[2.2.2]octane). In particular, we are interested in the development of asymmetric versions of these reactions to synthesize optically active four-membered nitrogen heterocycles.

Results and Discussion

The reaction of benzyl buta-2,3-dienoate (**5**[15]) with *N*-benzylidenebenzenesulfonamide (**6**[16]) and DABCO at room temperature was explored (Scheme 2 and Table 1). By carrying out the reaction for 1 h, 2-methyleneazetidine **7** was obtained in moderate yield (40%); aza-Baylis–Hillman

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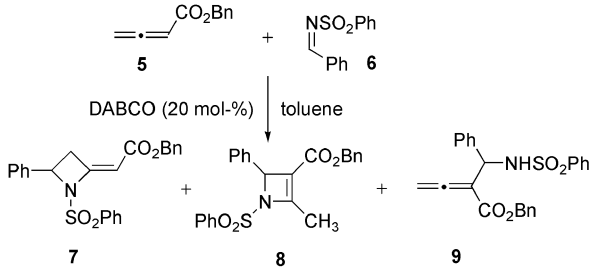
adduct **9** was also isolated (25% yield). Interestingly, a new kind of four-membered heterocycle, 2-methyl-4-phenyl-1-phenylsulfonamido-2-azetine-3-carboxylate (**8**), could also be detected and isolated from the same reaction (Table 1, Entry 1). As far as we know, the occurrence of azetine-3-carboxylates has never been reported for the reaction of allenoates with imines. The ^{1}H NMR spectrum of **8** shows a signal at δ = 2.03 ppm, corresponding to the methyl group, and a signal at δ = 4.97 ppm, corresponding to the benzylic proton, which are in agreement with the assigned structure. When the reaction was performed under the same reaction conditions but with a longer reaction time (6 h), 2-methyleneazetidine **7** and 2-azetine **8** were isolated in 35 and 5% yield, respectively (Table 1, Entry 2). However, no evidence for the aza-Baylis–Hillman adduct was observed. The DABCO-catalysed reaction of imine **6** and **5** was also carried at room temperature for 1 h in the presence of 4 Å molecular sieves and, as observed for allene **1** (Scheme 1, vide supra),[8] azetidine **7** was obtained as the main product together with a small proportion of aza-Baylis–Hillman adduct **9** (9%); 2-azetine **8** could also be detected (Table 1, Entry 3). Increasing the reaction time to 6 h led to the isolation of **7** and **8** in 39 and 7% yield, respectively (Table 1, Entry 4). Likewise, the microwave-mediated [2+2] annulation reaction produced **7** and **8** in 42 and 8.5% yield, respectively (Table 1, Entry 5).

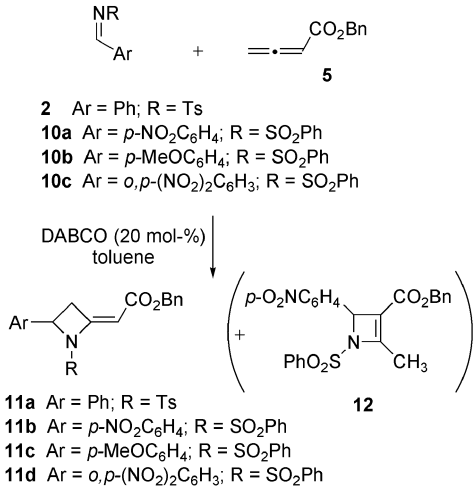


Scheme 2. DABCO-catalysed reaction of benzyl buta-2,3-dienoate (**5**) with imine **6**.

Table 1. DABCO-catalysed reaction of benzyl buta-2,3-dienoate (**5**) with imine **6**.

Entry	Reaction conditions	Yield [%]		
		7	**8**	**9**
1	r.t.., 1 h	40	1	25
2	r.t.., 6 h	35	5	–
3	4 Å MS, r.t., 1 h	39	0.2	9
4	4 Å MS, r.t., 6 h	39	7	–
5	MW, 100 °C, 5 min	42	8.5	–

We then investigated the reactivity of **5** towards *N*-arylidenebenzenesulfonamides **2** and **10** in the presence of DABCO (Scheme 3 and Table 2). The reaction of allene **5** with *N*-tosylimine **2** and DABCO at room temperature for 1 h gave 2-methyleneazetidine **11a** in 49% yield (Table 2, Entry 1). A more efficient reaction was observed when allene **5** was treated with *N*-(4-nitrobenzylidene)benzenesulfonamide (**10a**[17]). The DABCO-catalysed reaction carried out at room temperature for 1 h gave only azetidine **11b** in 67% yield (Table 2, Entry 2), whereas a longer reaction time (6 h) resulted in the formation of azetidine **11b** (50% yield) as the major product and 2-azetine **12** (5% yield; Table 2, Entry 3). The microwave-assisted reaction at 100 °C produced azetidine **11b** regioselectively in 66% yield after only 5 min (Table 2, Entry 4).



Scheme 3. DABCO-catalysed reaction of benzyl buta-2,3-dienoate (**5**) with *N*-arylidenebenzenesulfonamides **2** and **10**.

Table 2. DABCO-catalysed reaction of benzyl buta-2,3-dienoate (**5**) with *N*-arylidenebenzenesulfonamides **2** and **10**.

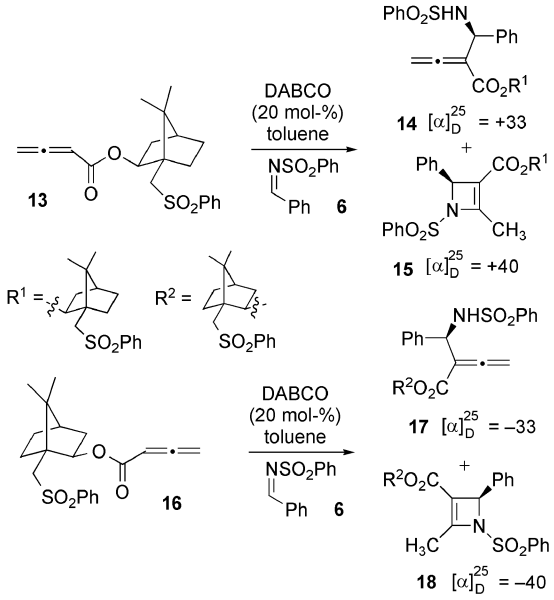
Entry	Imine	Reaction conditions	Product, Yield [%]
1	**2**	4 Å MS, r.t., 1 h	**11a**, 49
2	**10a**	4 Å MS, r.t., 1 h	**11b**, 67
3	**10a**	4 Å MS, r.t., 6 h	**11b**, 50; **12**, 5
4	**10a**	MW, 100 °C, 5 min	**11b**, 66
5	**10b**	4 Å MS, r.t., 1 h	**11c**, 59
6	**10c**	4 Å MS, r.t., 1 h	**11d**, 22

Treatment of allene **5** with other imines such as **10b** and **10c** at room temperature for 1 h in the presence of DABCO gave 2-methyleneazetidines **11c** and **11d**, respectively, as the only products (Table 2, Entries 5 and 6).

The results described in Schemes 2 and 3 demonstrate that the main pathway for the condensation of **5** with *N*-arylidenebenzenesulfonamides in the presence of DABCO is a formal [2+2] cycloaddition leading to 2-methyleneazetidines **7** and **11**. This reaction was, however, accompanied by the simultaneous formation of four-membered heterocycles **8** and **12**, which were also isolated.

Next, the behaviour of optically active allenes was explored. The DABCO-catalysed reaction of chiral allenes **13**[18] and **16**[18] with imine **6** at room temperature in the presence of 4 Å molecular sieves gave different results (Scheme 4 and Table 3). The reaction of (1*R*)-(–)-10-phenylsulfonylisobornyl buta-2,3-dienoate (**13**) with **6** at room temperature for 24 h afforded optically active 2-azetine **15** as the major product, and chiral α-allenylamine **14** in 31 and 18% yield, respectively (Table 3, Entry 1). Under the same conditions but with shorter reaction times an increase in the conversion and the formation of optically active 2-

azetine **15** was observed (Table 3, Entries 2 and 3). The effect of the temperature was also investigated. At 0 °C identical products were formed in significantly higher overall yield (81%), although 2-azetine **15** and allene **14** were isolated in 44 and 37% yield, respectively (Table 3, Entry 4). Interestingly, by lowering the temperature even further to –20 °C, chiral α-allenylamine **14** was isolated as the major product in 52% yield (Table 3, Entry 5).



Scheme 4. DABCO-catalysed reaction of chiral allenes **13** and **16** with *N*-benzylidenebenzenesulfonamide (**6**).

Table 3. DABCO-catalysed reaction of chiral allenes **13** and **16** with *N*-benzylidenebenzenesulfonamide (**6**).

Entry	Allene	Reaction conditions	Product, Yield [%]
1	**13**	4 Å MS, r.t., 24 h	**14**, 18; **15**, 31
2	**13**	4 Å MS, r.t., 3 h	**14**, 12.5; **15**, 48
3	**13**	4 Å MS, r.t., 1 h	**14**, 8; **15**, 45
4	**13**	4 Å MS, 0 °C, 24 h	**14**, 37; **15**, 44
5	**13**	4 Å MS, –20 °C, 24 h	**14**, 52; **15**, 9
6	**13**	MW, 100 °C, 15 min	**15**, 24
7	**16**	4 Å MS, r.t., 24 h	**17**, 9; **18**, 44
8	**16**	4 Å MS, r.t., 1 h	**17**, 4; **18**, 55
9	**16**	4 Å MS, –20 °C, 24 h	**17**, 46; **18**, 12
10	**16**	4 Å MS, –20 °C, 6 h	**17**, 38
11	**16**	MW, 100 °C, 15 min	**18**, 16

Concerning the enantiomeric allene, the aza-Baylis–Hillman reaction of (1*S*)-(+)-10-phenylsulfonylisobornyl buta-2,3-dienoate (**16**) with imine **6** at room temperature for 24 h gave 2-azetine **18** as the major product (44% yield) and optically active α-allenylamine **17**, the enantiomer of **14**, in 9% yield (Table 3, Entry 7). By performing the reaction with a significantly shorter reaction time (1 h), 2-azetine **18** could be obtained in higher yield (55%; Table 3, Entry 8). Carrying out the reaction at lower temperature (–20 °C for 24 h) led to the formation of α-allenylamine **17** (46%; Table 3, Entry 9) as the major product. Efforts to reduce the reaction time gave α-allenylamine **17** as the only product in moderate yield (38%; Table 3, Entry 10). Notice that 2-azetines **15** and **18** show identical NMR spectra but that the values for the optical rotation have opposite signs, indicating that they are enantiomers. As far as we know, this strategy represents the first example of preparation of optically active 2-azetines **15** and **18**.

The structure of allene **14** was determined by X-ray crystallography (Figure 1). The absolute structure was determined by taking advantage of the significant anomalous dispersion of sulfur at the Mo-K_α wavelength. Both Flack analysis of the diffraction data and the results of separate refinements of the possible enantiomers unambiguously assigned the *S*,*S*,*S*,*R* absolute configurations to the C5, C18, C20 and C26 stereogenic centres, respectively. The phenyl ring attached to S1 is disordered over two positions with approximately 50% occupancy each.

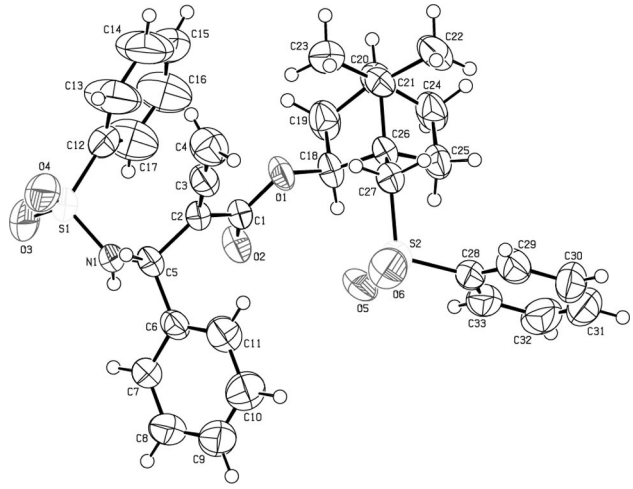


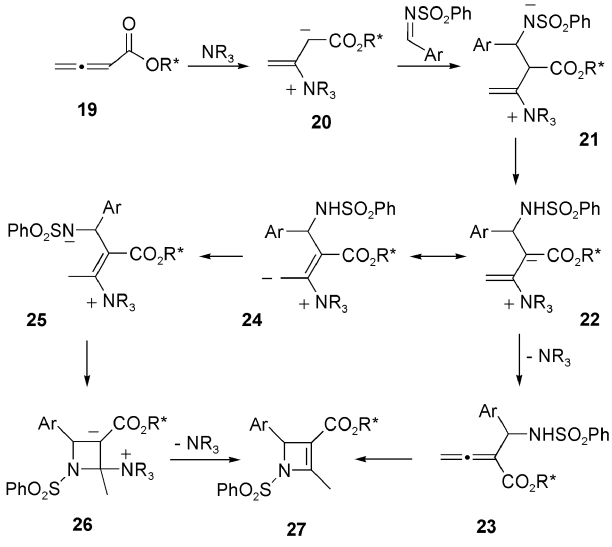
Figure 1. X-ray structure of **14**. Some disordered atoms were omitted for clarity.

The preceding results show that the selectivity of the condensation of chiral allenoates **13** and **16** with **6** depends on the choice of reaction conditions. When the reaction is done at room temperature 2-azetines are formed as the major product, whereas at –20 °C the α-allenylamines are formed preferentially (Scheme 4). It is noteworthy that the presence of a (1*R*)- or (1*S*)-10-phenylsulfonylisobornyl substituent seems to hinder the formation of 2-methyleneazetidines (i.e., **3**, **7**, **11**; Schemes 1–3) as has been observed for allenoates **1** and **5**.

The microwave-assisted reaction of imine **6** with allenes **13** and **16** at 100 °C for 15 min afforded heterocycle **15** (Table 3, Entry 6) and 2-azetine **18** (Table 3, Entry 11), respectively. Allenes **14** and **17** were formed in less than 1% yield and could only be detected by NMR spectroscopy. On the other hand, a significant amount of benzenesulfonamide was isolated, suggesting a lack of stability of the products upon microwave irradiation.

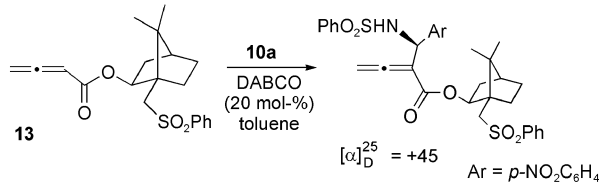
The formation of aza-Baylis–Hillman adducts **14** and **17** and 2-azetines **15** and **18** can be explained as outlined in Scheme 5. Nucleophilic addition of DABCO to 2,3-alleno-

ate **19** produces zwitterionic intermediate **20**, which in turn reacts with the imine to give **21**. Proton transfer gives intermediate **22**, which then undergoes elimination of DABCO to give α-allenylaminealkylallene **23**. A similar mechanism was previously reported for the formation of α-allenylamines.[8] The synthesis of these allenes as single stereoisomers is explained by selective addition of the imine to **20**, leading to intermediate **21**. Resonance-stabilized zwitterionic intermediate **24** can also undergo proton transfer to give intermediate **25**. Cyclization of **25** leads to another zwitterionic intermediate **26**, which can then expel DABCO to produce 2-azetine **27**. Because intermediate **21** is common to both pathways, the chirality of both α-allenylamine and 2-azetine is expected to originate from the same chiral allene. Alternatively, the 2-azetines could result from a 4-*exo*-*dig* cyclization of α-allenylamines **23**. This mechanistic pathway was ruled out, as attempts to convert α-allenylamines into the corresponding 2-azetines were unsuccessful. In fact, treatment of allene **14** with DABCO at room temperature for 24 h led only to the recovery of the starting material.

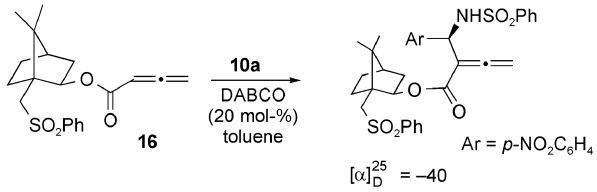


Scheme 5. Proposed mechanism for the formation of aza-Baylis–Hillman adducts and 2-azetines.

The reaction of chiral allenes **13** and **16** with **10a** in the presence of DABCO at room temperature led, in both cases, to the corresponding chiral α-allenylamines **28** and **29** in moderate yield and in a selective fashion. By carrying out this reaction at –20 °C the chiral allenes could be obtained in higher yield (Scheme 6). Lower temperatures and the presence of an electron-withdrawing group on the imine may favour the formation of optically active acyclic α-allenylamines over the cyclic 2-azetine derivatives. These results could be explained by invoking the proposed mechanism (Scheme 5). At lower temperatures or by the use of more reactive electron-poor imines, the elimination of DABCO to produce α-allenylamines **23** could be more favourable than the [1,3]-prototropic rearrangement between intermediates **24** and **25**, which leads to 2-azetines **27**.



Conditions	% Yield of **28**
4 Å MS, r.t., 24 h	38
4 Å MS, –20 °C, 48 h	52

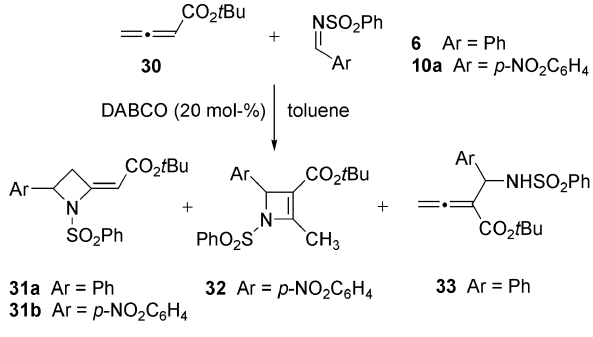


Conditions	% Yield of **29**
4 Å MS, r.t., 24 h	25
4 Å MS, –20 °C, 48 h	57

Scheme 6. DABCO-catalysed reaction of chiral allenes **13** and **16** with *N*-(4-nitrobenzylidene)benzenesulfonamide (**10a**).

We can conclude that the DABCO-catalysed reaction of (1*R*)-(–)-10-phenylsulfonylisobornyl buta-2,3-dienoate with *N*-arylidenebenzenesulfonamide leads to chiral products with *S* configuration at the new stereogenic centre. Conversely, the use of (1*S*)-(+)-10-phenylsulfonylisobornyl buta-2,3-dienoate gives products with *R* configuration. It is noteworthy that the careful choice of reaction conditions can be used to favour the formation of optically active acyclic α-allenylamines or cyclic 2-azetines.

In order to determine if the presence of the (1*R*)- or (1*S*)-10-phenylsulfonylisobornyl substituent on the allene is required to prevent the formal [2+2] cycloaddition, the DABCO-catalysed reaction of allene **30** bearing a sterically demanding ester group with *N*-arylidenebenzenesulfonamides was studied (Scheme 7). The reaction of allene **30** with **6** and DABCO was carried out either at room temperature or under microwave irradiation to give 2-methyleneazetidine **31a** and α-allenylamine **33** (Table 4, Entries 1–4). The best results were obtained by performing the reac-



Scheme 7. DABCO-catalysed reaction of *tert*-butyl buta-2,3-dienoate (**30**) with *N*-arylidenebenzenesulfonamides **6** and **10a**.

tion at room temperature for 24 h to afford heterocycle **31a** and allene **33** in 37 and 40% yield, respectively (Table 4, Entry 3). The reaction of **30** with **10a** did not produce the corresponding aza-Baylis–Hillman adduct; instead, 2-methyleneazetidine **31b** was formed exclusively as the major product (Table 4, Entries 5–8). In fact, the reaction done at room temperature for 1 h afforded azetidines **31b** and **32** in 24 and 5% yield, respectively (Table 4, Entry 5). Longer reaction times led to 2-azetidine **31b** as the sole product (47–54%; Table 4, Entries 6 and 7). The microwave-induced, DABCO-catalysed reaction gave only azetidine **31b** in 48% (Table 4, Entry 8).

Table 4. DABCO-catalysed reaction of *tert*-butyl buta-2,3-dienoate (**30**) with *N*-arylidenebenzenesulfonamides **6** and **10a**.

Entry	Imine	Reaction conditions	Product, Yield [%]
1	**6**	4 Å MS, r.t., 1 h	**31a**, 24; **33**, 30
2	**6**	4 Å MS, r.t., 6 h	**31a**, 21; **33**, 24
3	**6**	4 Å MS, r.t., 24 h	**31a**, 37; **33**, 40
4	**6**	MW, 100 °C, 5 min	**31a**, 35; **33**, 22
5	**10a**	4 Å MS, r.t., 1 h	**31b**, 24; **32**, 9
6	**10a**	4 Å MS, r.t., 6 h	**31b**, 47
7	**10a**	4 Å MS, r.t., 24 h	**31b**, 54
8	**10a**	MW, 100 °C, 5 min	**31b**, 48

These results have shown that 2-methyleneazetidines can be obtained from the reaction of **30** with *N*-arylidenebenzenesulfonamides. The reactivities of allene **30** and **5** are similar. However, the use of allene **30** instead of **5** favours the formation of α-allenylamines in the condensation reaction with imine **6**. On the other hand, the DABCO-catalysed reaction of **30** with imine **10a** gave mainly the corresponding 2-methyleneazetidine, as previously observed for the reaction of allene **5** with the same imine. The reactivities of chiral allenes **13** and **16** are different from those shown by allenes **5** and **30**. In fact, 2-methyleneazetidines are not formed from the reaction of the chiral allenes and *N*-arylidenebenzenesulfonamides, which leads to optically active aza-Baylis–Hillman products and 2-azetine derivatives. The outcome of the reaction can be controlled by the selection of the reaction conditions or by the nature of the imine counterpart.

Conclusions

Optically active α-allenylamines and 2-azetines were prepared by using a DABCO-catalysed reaction of 2,3-allenoates, bearing a chiral auxiliary on the ester moiety, with *N*-arylidenebenzenesulfonamides. The use of (1*R*)-(–)-10-phenylsulfonylisobornyl buta-2,3-dienoate as a starting material affords products with *S* configuration, whereas (1*S*)-(+)-10-phenylsulfonylisobornyl buta-2,3-dienoate leads to products with *R* configuration. The outcome of the reaction can be controlled by carefully selecting the reaction conditions or by tuning the electronic properties of the imine. Functionalized chiral α-allenylamines have great potential as building blocks for the synthesis of chiral pyrrolines and pyrroles.[19] On the other hand, strained cyclic enamines, such as 2-azetines, show particularly interesting reactivity.[1–3]

Experimental Section

Unless otherwise noted ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 400 and 100 MHz, respectively. Mass spectra were recorded on an instrument operating in ESI mode.

General Procedure for the Synthesis of Abnormal and Normal Aza-Baylis–Hillman Adducts

Method A: To a mixture of *N*-arylidenebenzenesulfonamide (1.0 mmol), DABCO (22 mg, 0.2 mmol) and 4 Å MS (400 mg) in toluene (2 mL) was added a solution of the corresponding allene (1.1 mmol) in toluene (1 mL). The reaction mixture was stirred under an atmosphere of nitrogen for the duration indicated in the individual procedures. The reaction mixture was then washed with water (3 × 20 mL) and extracted with dichloromethane (2 × 20 mL). The organic layer was dried with anhydrous $MgSO_4$, and solvents were removed under reduced pressure. The crude product was purified by flash column chromatography (ethyl acetate/hexane).

Method B: A suspension of *N*-arylidenebenzenesulfonamide (0.5 mmol), DABCO (11 mg, 0.10 mmol) and the corresponding allene (0.55 mmol) in toluene (3 mL) was irradiated in a microwave reactor (CEM Focused Synthesis System, Discover S-Class) at 100 °C for 15 min. The reaction mixture was then washed with water (3 × 20 mL) and extracted with dichloromethane (2 × 20 mL). The organic layer was dried with anhydrous $MgSO_4$, and solvents were removed under reduced pressure. The crude product was purified by flash column chromatography (ethyl acetate/hexane).

(*E*)-Benzyl 2-[4-Phenyl-1-(phenylsulfonyl)azetindin-2-ylidene]ethanoate (7), Benzyl 4-methyl-2-phenyl-1-(phenylsulfonamido)-2-azetine-3-carboxylate (8) and Benzyl 2-[phenyl(phenylsulfonamido)methyl]buta-2,3-dienoate (9): Yield (method A; r.t., 1 h): 0.2 (for **8**), 39 (for **7**) and 9% (for **9**); Yield (method B): 8.5 (for **8**) and 42% (for **7**). Purification by flash chromatography (hexane/ethyl acetate, 1:4) gave (in order of elution) **8**, **7** and **9**. Data for **8**: Oil. IR (film): $\tilde{\nu}$ = 3134, 1715, 1623, 1401, 1166 cm^{-1}. ^{1}H NMR: δ = 2.04 (s, 3 H, CH_3), 4.98 (s, 1 H, C*H*Ph), 5.15 (s, 2 H, CH_2Ph), 7.30–7.42 (m, 10 H, Ar-H), 7.51–7.55 (m, 2 H, Ar-H), 7.59–7.63 (m, 1 H, Ar-H), 7.90 (d, ^3J = 7.6 Hz, 2 H, Ar-H) ppm. ^{13}C NMR: δ = 19.8, 48.0, 65.9, 96.3, 127.1, 128.2, 128.3, 128.6, 129.3, 133.3, 135.8, 140.5, 153.1, 168.8 ppm. MS (ESI): *m*/*z* (%) = 420 (1) [M + 1]$^+$, 407 (3), 386 (2), 354 (21), 332 (8), 247 (1), 215 (100). HRMS (ESI): calcd. for $C_{24}H_{22}NO_4S$ 420.12641; found 420.12776. Data for **7**: Oil. IR (film): $\tilde{\nu}$ = 1706, 1655, 1168, 1119 cm^{-1}. ^{1}H NMR: δ = 3.11 (ddd, ^2J = 16.8 Hz, ^3J = 4.2 Hz, ^4J = 2.1 Hz, 1 H, CHCH_2), 3.51 (ddd, ^2J = 16.8 Hz, ^3J = 7.0 Hz, ^4J = 2.1 Hz, 1 H, CHCH_2), 5.10 (d, ^2J = 12.4 Hz, 1 H, CH_2Ph), 5.16 (d, ^2J = 12.4 Hz, 1 H, CH_2Ph), 5.22 (dd, ^3J = 7.0, 4.2 Hz, 1 H, C*H*CH$_2$), 5.92–5.93 (m, 1 H, =C*H*), 7.30–7.36 (m, 10 H, Ar-H), 7.41–7.46 (m, 2 H, Ar-H), 7.56–7.65 (m, 3 H, Ar-H) ppm. ^{13}C NMR: δ = 37.5, 65.7, 66.4, 94.3, 126.8, 127.3, 128.1, 128.5, 128.7, 129.0, 129.2, 133.8, 136.2, 136.8, 137.4, 158.7, 167.0 ppm. MS (ESI): *m*/*z* (%) = 420 (100) [M + 1]$^+$, 312 (3), 197 (5). HRMS (ESI): calcd. for $C_{24}H_{22}NO_4S$ 420.12641; found 420.12491. Data for **9**: Oil. IR (film): $\tilde{\nu}$ = 3280, 1965, 1706, 1330, 1165 cm^{-1}. ^{1}H NMR: δ = 5.01 (d, ^2J = 12.8 Hz, 1 H, CH_2Ph), 5.05 (d, ^2J = 12.8 Hz, 1 H, CH_2Ph), 5.09 (d, ^2J = 14.8 Hz, 1 H, C=CH_2), 5.16 (d, ^2J = 14.8 Hz, 1 H, C=CH_2), 5.36 (d, ^3J = 10.0 Hz, 1 H,

C*H*NH), 5.84 (d, ^3J = 10.0 Hz, 1 H, CHN*H*), 7.17–7.19 (m, 2 H, Ar-H), 7.22–7.24 (m, 5 H, Ar-H), 7.31–7.37 (m, 5 H, Ar-H), 7.47 (m, 1 H, Ar-H), 7.76 (d, ^3J = 7.6 Hz, 2 H, Ar-H) ppm. ^{13}C NMR: δ = 55.6, 65.8, 80.4, 99.5, 125.5, 126.1, 126.8, 126.9, 127.2, 127.5, 127.5, 127.8, 131.5, 134.4, 137.9, 139.8, 164.1, 212.2 ppm. MS (ESI): *m*/*z* (%) = 420 (41) [M + 1]$^+$, 263 (100), 245 (14), 215 (16). HRMS (ESI): calcd. for $C_{24}H_{22}NO_4S$ 420.12641; found 420.12603.

(*E*)-Benzyl 2-(4-Phenyl-1-tosylazetindin-2-ylidene)ethanoate (11a): Yield (method A; r.t., 1 h): 49%. Purification by flash chromatography (hexane/ethyl acetate, 1:6 to 1:5) gave **11a** as a white solid. M.p. 116.1–117.0 °C. IR (film): $\tilde{\nu}$ = 1709, 1661, 1165, 1119 cm^{-1}. ^{1}H NMR: δ = 2.42 (s, 3 H, CH_3), 3.10 (ddd, ^2J = 16.8 Hz, ^3J = 4.4 Hz, ^4J = 1.6 Hz, 1 H, CHCH_2), 3.49 (ddd, ^2J = 16.8 Hz, ^3J = 6.8 Hz, ^4J = 1.6 Hz, 1 H, CHCH_2), 5.12–5.18 (m, 2 H, CH_2Ph), 5.19 (dd, ^3J = 6.8, 4.4 Hz, 1 H, C*H*CH$_2$), 5.90 (s, 1 H, =C*H*), 7.24 (d, ^3J = 8.4 Hz, 2 H, Ar-H), 7.32–7.36 (m, 10 H, Ar-H), 7.55 (d, ^3J = 8.4 Hz, 2 H, Ar-H) ppm. ^{13}C NMR: δ = 21.6, 37.5, 65.7, 66.3, 94.3, 126.8, 127.4, 128.1, 128.1, 128.5, 128.7, 128.9, 129.8, 134.4, 136.3, 137.2, 144.9, 158.8, 167.1 ppm. MS (ESI): *m*/*z* (%) = 434 (100) [M + 1]$^+$, 359 (4), 315 (5), 230 (3), 201 (25). HRMS (ESI): calcd. for $C_{25}H_{24}NO_4S$ 434.14206; found 434.14067.

(*E*)-Benzyl 2-[4-(4-Nitrophenyl)-1-(phenylsulfonyl)azetindin-2-ylidene]ethanoate (11b) and Benzyl 4-Methyl-2-(4-nitrophenyl)-1-(phenylsulfonamido)-2-azetine-3-carboxylate (12): Yield (method A; r.t., 6 h): 5 (for **12**) and 50% (for **11b**); yield (method B): 66% (for **11b**). Purification by flash chromatography (hexane/ethyl acetate, 1:2) gave (in order of elution) **12** and **11b**. Data for **12**: Oil. IR (film): $\tilde{\nu}$ = 3132, 1716, 1400, 1162 cm^{-1}. ^{1}H NMR: δ = 2.26 (s, 3 H, CH_3), 4.76 (d, ^2J = 12.0 Hz, 1 H, CH_2Ph), 4.97 (d, ^2J = 12.0 Hz, 1 H, CH_2Ph), 5.70 (s, 1 H, C*H*Ph), 7.45–7.47 (m, 2 H, Ar-H), 7.51–7.56 (m, 8 H, Ar-H), 7.69–7.73 (m, 2 H, Ar-H), 8.22 (d, ^3J = 8.8 Hz, 2 H, Ar-H) ppm. ^{13}C NMR: δ = 20.6, 67.0, 71.8, 120.3, 124.4, 126.9, 127.4, 127.5, 128.6, 128.7, 130.1, 131.3, 139.9, 144.3, 148.1, 163.3 ppm. MS (ESI): *m*/*z* (%) = 465 (7) [M + 1]$^+$, 420 (66), 391 (100), 301 (49), 210 (39). HRMS (ESI): calcd. for $C_{24}H_{21}N_2O_6S$ 465.10756; found 465.11148. Data for **11b**: Yellow solid, m.p. 138.0–140.0 °C. IR (film): $\tilde{\nu}$ = 1701, 1661, 1522, 1345, 1168, 1120 cm^{-1}. ^{1}H NMR: δ = 2.98 (ddd, ^2J = 16.8 Hz, ^3J = 4.0 Hz,^4J = 1.6 Hz, 1 H, CHCH_2), 3.48 (ddd, ^2J = 16.8 Hz, ^3J = 7.2 Hz, ^4J = 1.6 Hz, 1 H, CHCH_2), 5.03 (d, ^2J = 12.4 Hz, 1 H, CH_2Ph), 5.08 (d, ^2J = 12.4 Hz, 1 H, CH_2Ph), 5.17 (dd, ^3J = 7.2, 4.0 Hz, 1 H, C*H*CH$_2$), 5.90 (s, 1 H, =C*H*), 7.27 (br. s, 5 H, Ar-H), 7.44–7.47 (m, 4 H, Ar-H), 7.58–7.62 (m, 1 H, Ar-H), 7.68 (d, ^3J = 8.4 Hz, 2 H, Ar-H), 8.11 (d, ^3J = 8.4 Hz, 2 H, Ar-H) ppm. ^{13}C NMR: δ = 36.5, 63.7, 64.9, 94.7, 123.1, 126.4, 127.2, 127.6, 128.5, 133.3, 135.0, 135.7, 143.4, 147.1, 156.5, 165.6 ppm. MS (ESI): *m*/*z* (%) = 465 (100) [M + 1]$^+$, 447 (21), 391 (12), 210 (18). HRMS (ESI): calcd. for $C_{24}H_{21}N_2O_6S$ 465.11148; found 465.11119.

(*E*)-Benzyl 2-[4-(4-Methoxyphenyl)-1-(phenylsulfonyl)azetindin-2-ylidene]ethanoate (11c): Yield (method A; r.t., 1 h): 59%. Purification by flash chromatography (hexane/ethyl acetate, 1:3 to 1:2) gave **11c** as a yellow solid, m.p. 87.2–88.9 °C. IR (film): $\tilde{\nu}$ = = 1714, 1666, 1248, 1090 cm^{-1}. ^{1}H NMR: δ = 3.11 (ddd, ^2J = 16.8 Hz, ^3J = 4.0 Hz, ^4J = 1.6 Hz, 1 H, CHCH_2), 3.49 (ddd, ^2J = 16.8 Hz, ^3J = 6.8 Hz, ^4J = 1.6 Hz, 1 H, CHCH_2), 3.80 (s, 3 H, OCH_3), 5.11 (d, ^2J = 12.4 Hz, 1 H, CH_2Ph), 5.15 (d, ^2J = 12.4 Hz, 1 H, CH_2Ph), 5.20 (dd, ^3J = 6.8, 4.0 Hz, 1 H, C*H*CH$_2$), 5.90 (s, 1 H, =C*H*), 6.81 (d, ^3J = 8.8 Hz, 2 H, Ar-H), 7.21 (d, ^3J = 8.8 Hz, 2 H, Ar-H), 7.30–7.36 (m, 6 H, Ar-H), 7.43 (m, 2 H, Ar-H), 7.62–7.63 (m, 2 H, Ar-H) ppm. ^{13}C NMR: δ = 37.5, 55.4, 65.7, 66.3, 94.0, 114.1, 127.2, 128.2, 128.4, 128.6, 128.8, 129.2, 133.7, 136.3, 137.7, 158.8, 160.1, 167.1 ppm. MS (ESI): *m*/*z* (%) = 450 (100) [M + 1]$^+$, 382 (12), 359 (22), 291 (20). HRMS (ESI): calcd. for $C_{25}H_{24}NO_5S$ 450.13697; found 450.13744.

(*E*)-Benzyl 2-[4-(2,4-Dinitrophenyl)-1-(phenylsulfonyl)azetindin-2-ylidene]ethanoate (11d): Yield (method A; r.t., 1 h): 22%. Purification by flash chromatography (hexane/ethyl acetate, 1:3 to 1:2) gave **11d** as a yellow oil. IR (film): $\tilde{\nu}$ = 1709, 1665, 1536, 1345, 1118 cm^{-1}. ^{1}H NMR: δ = 2.96 (ddd, ^2J = 17.2 Hz, ^3J = 4.4 Hz, ^4J = 1.6 Hz, 1 H, CHCH_2), 3.74 (ddd, ^2J = 17.2 Hz, ^3J = 7.6 Hz, ^4J = 1.6 Hz, 1 H, CHCH_2), 5.09 (d, ^2J = 12.4 Hz, 1 H, CH_2Ph), 5.13 (d, ^2J = 12.4 Hz, 1 H, CH_2Ph), 5.63 (dd, ^3J = 7.6, 4.4 Hz, 1 H, C*H*CH$_2$), 6.06 (s, 1 H, =C*H*), 7.33–7.37 (m, 6 H, Ar-H), 7.62–7.66 (m, 2 H, Ar-H), 7.75–7.79 (m, 1 H, Ar-H), 7.87 (d, ^3J = 7.6 Hz, 2 H, Ar-H), 8.39 (d, ^3J = 8.8 Hz, 1 H, Ar-H), 8.58–8.63 (m, 1 H, Ar-H), 8.98–9.00 (m, 1 H, Ar-H) ppm. ^{13}C NMR: δ = 38.0, 62.7, 66.1, 98.0, 120.7, 127.8, 128.2, 128.3, 128.5, 128.6, 129.9, 130.4, 131.5, 134.9, 135.9, 140.5, 146.6, 147.8, 156.7, 166.2, 186.3 ppm. MS (ESI): *m*/*z* (%) = 510 (48) [M + 1]$^+$, 476 (39), 450 (46), 354 (75), 332 (100), 291 (52), 251 (73). HRMS (ESI): calcd. for $C_{24}H_{20}N_3O_8S$ 510.09656; found 510.09753.

(1*R*)-(–)-10-Phenylsulfonylisobornyl (*S*)-2-[Phenyl(phenylsulfonamido)methyl]buta-2,3-dienoate (14) and (1*R*)-(–)-10-Phenylsulfonylisobornyl (*S*)-3-Methyl-4-phenyl-1-phenylsulfonamido-2-azetine-3-carboxylate (15): Yield (method A; r.t., 1 h): 45 (for **15**) and 8% (for **14**); yield (method A; –20 °C, 24 h): 9 (for **15**) and 52% (for **14**); yield (method B): 24% (for **15**). Purification by flash chromatography (hexane/ethyl acetate, 1:2) gave (in order of elution) **15** and **14**. Data for **15**: Oil. IR (film): $\tilde{\nu}$ = 2959, 1711, 1318, 1168 cm^{-1}. ^{1}H NMR: δ = 0.86 (s, 3 H), 0.92 (s, 3 H), 1.17–1.22 (m, 1 H), 1.64 (br. s, 2 H), 1.75–1.78 (m, 2 H), 1.86–1.96 (m, 2 H), 2.05 (s, 3 H, =CCH_3), 3.00 (d, ^2J = 14.4 Hz, 1 H), 3.54 (d, ^2J = 14.4 Hz, 1 H), 4.76–4.78 (m, 1 H), 4.80 (s, 1 H, C*H*Ph), 7.31–7.33 (m, 1 H, Ar-H), 7.38–7.71 (m, 9 H, Ar-H), 7.83 (d, ^3J = 7.6 Hz, 2 H, Ar-H), 7.93 (d, ^3J = 7.6 Hz, 2 H, Ar-H) ppm. ^{13}C NMR: δ = 19.7, 19.9, 20.3, 27.1, 29.7, 39.6, 44.1, 49.3, 49.9, 53.4, 55.2, 78.9, 96.6, 126.4, 127.1, 127.7, 129.2, 129.4, 133.3, 133.5, 140.5, 141.2, 152.7, 167.6 ppm. MS (ESI): *m*/*z* (%) = 606 (56) [M + 1]$^+$, 518 (100), 401 (10), 277 (28), 197 (6). HRMS (ESI): calcd. for $C_{33}H_{36}NO_6S_2$ 606.19786; found 606.19708. $[\alpha]_D^{20}$ = +33 (*c* = 0.75, CH_2Cl_2). Data for **14**: White solid, m.p. 135.0–137.0 °C. IR (film): $\tilde{\nu}$ = 3256, 1970, 1709, 1309, 1162 cm^{-1}. ^{1}H NMR: δ = 0.67 (s, 3 H), 0.80 (s, 3 H), 1.10–1.16 (m, 1 H), 1.47–1.60 (m, 2 H), 1.70 (br. s, 2 H), 1.81–1.86 (m, 2 H), 2.88 (d, ^2J = 14.0 Hz, 1 H), 3.34 (d, ^2J = 14.0 Hz, 1 H), 4.73 (dd, ^3J = 7.6, 2.8 Hz, 1 H), 4.98 (d, ^2J = 14.4 Hz, 1 H, C=CH_2), 5.03 (d, ^2J = 14.4 Hz, 1 H, C=CH_2), 5.32 (d, ^3J = 9.6 Hz, 1 H, C*H*NH), 6.15 (d, ^3J = 9.6 Hz, 1 H, CHN*H*), 7.31–7.33 (m, 2 H, Ar-H), 7.39–7.59 (m, 8 H, Ar-H), 7.78–7.84 (m, 4 H, Ar-H), 7.92 (d, ^3J = 7.6 Hz, 1 H, Ar-H) ppm. ^{13}C NMR: δ = 19.6, 20.2, 27.0, 29.5, 39.3, 44.0, 49.5, 49.8, 54.9, 57.0, 78.6, 80.2, 100.3, 126.4, 126.6, 127.2, 127.6, 127.9, 128.6, 128.9, 129.1, 129.2, 132.5, 133.6, 138.9, 163.8, 213.8 ppm. MS (ESI): *m*/*z* (%) = 606 (31) [M + 1]$^+$, 449 (18), 401 (13), 277 (100), 197 (18). HRMS (ESI): calcd. for $C_{33}H_{36}NO_6S_2$ 606.19786; found 606.19761. $[\alpha]_D^{20}$ = +40 (*c* = 0.1, CH_2Cl_2).

(1*S*)-(+)-10-Phenylsulfonylisobornyl (*R*)-2-[Phenyl(phenylsulfonamido)methyl]buta-2,3-dienoate (17) and (1*S*)-(+)-10-Phenylsulfonylisobornyl (*R*)-3-Methyl-4-phenyl-1-phenylsulfonamido-2-azetine-3-carboxylate (18): Yield (method A; r.t., 1 h): 55 (for **18**) and 4% (for **17**); yield (method A; –20 °C, 24 h): 12 (for **18**) and 46% (for **17**); yield (method B): 16% (for **18**). Purification by flash chromatography (hexane/ethyl acetate, 1:2) gave (in order of elution) **18** and **17**: Data for **18**: Oil. IR (film): $\tilde{\nu}$ = 2958, 1714, 1317, 1166 cm^{-1}. ^{1}H NMR: δ = 0.86 (s, 3 H), 0.92 (s, 3 H), 1.17–1.24 (m,

1 H), 1.59–1.63 (m, 2 H), 1.75–1.76 (m, 2 H), 1.88–1.96 (m, 2 H), 2.05 (s, 3 H, =CCH_3), 3.00 (d, ^2J = 14.4 Hz, 1 H), 3.54 (d, ^2J = 14.4 Hz, 1 H), 4.75–4.78 (m, 1 H), 4.79 (s, 1 H, C*H*Ph), 7.30–7.33 (m, 1 H, Ar-H), 7.35–7.71 (m, 10 H, Ar-H), 7.83 (d, ^3J = 7.6 Hz, 2 H, Ar-H), 7.93 (d, ^3J = 7.6 Hz, 2 H, Ar-H) ppm. ^{13}C NMR: δ = 19.7, 19.9, 20.3, 27.1, 29.7, 39.6, 44.1, 49.3, 49.9, 53.4, 55.2, 96.5, 127.2, 127.7, 129.2, 129.4, 133.3, 133.5, 140.5, 141.2, 152.7, 167.6 ppm. MS (ESI): *m*/*z* (%) = 606 (47) [M + 1]$^+$, 518 (100), 277 (30). HRMS (ESI): calcd. for $C_{33}H_{36}NO_6S_2$ 606.19786; found 606.19986. $[\alpha]_D^{20}$ = –33 (*c* = 0.75, CH_2Cl_2). Data for **17**: White solid, m.p. 135.0–137.0 °C. IR (film): $\tilde{\nu}$ = 3256, 1964, 1710, 1309, 1161 cm^{-1}. ^{1}H NMR: δ = 0.68 (s, 3 H), 0.80 (s, 3 H), 1.11–1.17 (m, 1 H), 1.48–1.60 (m, 2 H), 1.70 (br. s, 2 H), 1.81–1.86 (m, 2 H), 2.88 (d, ^2J = 14.0 Hz, 1 H), 3.35 (d, ^2J = 14.0 Hz, 1 H), 4.72 (dd, ^3J = 7.6, 2.8 Hz, 1 H), 4.98 (d, ^2J = 14.4 Hz, 1 H, C=CH_2), 5.03 (d, ^2J = 14.4 Hz, 1 H, C=CH_2), 5.31 (d, ^3J = 9.2 Hz, 1 H, C*H*NH), 6.10 (d, ^3J = 9.2 Hz, 1 H, CHN*H*), 7.21–7.59 (m, 10 H, Ar-H), 7.78–7.84 (m, 4 H, Ar-H), 7.92–7.93 (m, 1 H, Ar-H) ppm. ^{13}C NMR: δ = 19.6, 20.2, 27.1, 29.5, 39.3, 44.0, 49.6, 49.8, 55.0, 57.0, 78.7, 80.2, 100.5, 126.7, 127.3, 127.6, 128.6, 128.9, 129.2, 132.5, 133.6, 139.0, 163.8, 213.8 ppm. MS (ESI): *m*/*z* (%) = 606 (62) [M + 1]$^+$, 518 (10), 449 (16), 277 (100), 197 (63). HRMS (ESI): calcd. for $C_{33}H_{36}NO_6S_2$ 606.19786; found 606.19898. $[\alpha]_D^{20}$ = –40 (*c* = 0.1, CH_2Cl_2).

(1*R*)-(+)-10-Phenylsulfonylisobornyl (*S*)-2-[Nitrophenyl(phenylsulfonamido)methyl]buta-2,3-dienoate (28): Yield (method A; –20 °C, 48 h): 52%. Purification by flash chromatography (hexane/ethyl acetate, 1:2) gave **28** as a yellow solid, m.p. 115.0–117.0 °C. IR (KBr): $\tilde{\nu}$ = 3265, 1966, 1707, 1522, 1347, 1165 cm^{-1}. ^{1}H NMR: δ = 0.61 (s, 3 H), 0.70 (s, 3 H), 1.09–1.12 (m, 1 H), 1.55–1.58 (m, 2 H), 1.65 (br. s, 2 H), 1.70–1.83 (m, 2 H), 2.85 (d, ^2J = 14.0 Hz, 1 H), 3.25 (d, ^2J = 14.0 Hz, 1 H), 4.85 (dd, ^3J = 7.6, 3.2 Hz, 1 H), 4.92 (d, ^2J = 14.4 Hz, 1 H, C=CH_2), 5.06 (d, ^2J = 14.4 Hz, 1 H, C=CH_2), 5.31 (d, ^3J = 9.2 Hz, 1 H, C*H*NH), 6.18 (d, ^3J = 9.2 Hz, 1 H, CHN*H*), 7.39–7.59 (m, 12 H, Ar-H), 7.77–7.79 (m, 4 H, Ar-H), 7.87 (d, ^3J = 7.2 Hz, 1 H, ArH), 8.06 (d, ^3J = 8.4 Hz, 1 H, ArH) ppm. ^{13}C NMR: δ = 18.4, 19.1, 26.0, 28.8, 38.2, 43.0, 48.8, 54.3, 55.7, 59.4, 78.1, 79.6, 98.3, 122.7, 125.4, 126.3, 126.6, 126.8, 128.0, 128.3, 131.8, 132.7, 139.5, 140.1, 146.4, 162.8, 212.8 ppm. MS (ESI): *m*/*z* (%) = 651 (47) [M + 1]$^+$, 442 (46), 401 (26), 321 (96), 271 (100). HRMS (ESI): calcd. for $C_{33}H_{35}N_2O_8S_2$ 651.18293; found 651.18424. $[\alpha]_D^{20}$ = +45 (*c* = 0.1, CH_2Cl_2).

(1*S*)-(–)-10-Phenylsulfonylisobornyl (*R*)-2-[Nitrophenyl(phenylsulfonamido)methyl]buta-2,3-dienoate (29): Yield (method A; –20 °C, 48 h): 57%. Purification by flash chromatography (hexane/ethyl acetate, 1:2) gave **29** as a yellow solid, m.p. 85.0–86.4 °C. IR (KBr): $\tilde{\nu}$ = 3270, 1964, 1708, 1522, 1346, 1166 cm^{-1}. ^{1}H NMR: δ = 0.69 (s, 3 H), 0.77 (s, 3 H), 1.11–1.16 (m, 1 H), 1.49–1.56 (m, 2 H), 1.72 (br. s, 2 H), 1.77–1.89 (m, 2 H), 2.92 (d, ^2J = 14.0 Hz, 1 H), 3.33 (d, ^2J = 14.0 Hz, 1 H), 4.92 (dd, ^3J = 8.0, 3.2 Hz, 1 H), 4.99 (d, ^2J = 14.4 Hz, 1 H, C=CH_2), 5.13 (d, ^2J = 14.4 Hz, 1 H, C=CH_2), 5.38 (d, ^3J = 9.2 Hz, 1 H, C*H*NH), 6.26 (d, ^3J = 9.2 Hz, 1 H, CHN*H*), 7.46–7.65 (m, 12 H, Ar-H), 7.81–7.86 (m, 4 H, Ar-H), 7.93–7.95 (m, 1 H, Ar-H), 8.13 (d, ^3J = 8.8 Hz, 2 H, Ar-H) ppm. ^{13}C NMR: δ = 19.5, 20.1, 27.0, 29.8, 37.4, 39.2, 44.1, 49.8, 55.3, 56.7, 79.1, 80.6, 99.3, 123.7, 127.3, 127.6, 127.8, 129.3, 132.8, 133.7, 140.5, 141.2, 146.2, 147.5, 163.8, 213.8 ppm. MS (ESI): *m*/*z* (%) = 651 (38) [M + 1]$^+$, 494 (6), 401 (9), 277 (100). HRMS (ESI): calcd. for $C_{33}H_{35}N_2O_8S_2$ 651.18293; found 651.18148. $[\alpha]_D^{20}$ = –40 (*c* = 0.1, CH_2Cl_2).

(*E*)-*tert*-Butyl 2-[4-Phenyl-1-(phenylsulfonyl)azetindin-2-ylidene]-ethanoate (31a) and *tert*-Butyl 2-[Phenyl(phenylsulfonamido)methyl]buta-2,3-dienoate (33): Yield (method A; r.t., 24 h): 37 (for **31a**) and 40% (for **33**); yield (method B): 24 (for **31a**) and 22% (for **33**). Purification by flash chromatography (hexane/ethyl acetate, 1:4) gave (in order of elution) **31a** and **33**. Data for **31a**: Oil. IR (film): $\tilde{\nu}$ = 1701, 1665, 1324, 1150 cm^{-1}. ^{1}H NMR: δ = 1.46 [s, 9 H, C(CH_3)$_3$], 3.09 (ddd, ^2J = 16.7 Hz, ^3J = 4.2 Hz, ^4J = 2.1 Hz, 1 H, CHCH_2), 3.50 (ddd, ^2J = 16.7 Hz, ^3J = 7.1, 2.1 Hz, 1 H, CHCH_2), 5.21 (dd, ^3J = 7.0, 4.2 Hz, 1 H, C*H*CH$_2$), 5.77–5.79 (m, 1 H, =C*H*), 7.31–7.39 (m, 5 H, Ar-H), 7.44–7.49 (m, 2 H, Ar-H), 7.58–7.68 (m, 3 H, Ar-H) ppm. ^{13}C NMR: δ = 28.3, 37.4, 66.2, 80.0, 96.7, 126.8, 127.3, 128.7, 128.9, 129.1, 133.6, 137.1, 137.5, 157.0, 166.6 ppm. MS (ESI): *m*/*z* (%) = 408 (19) [M + Na]$^+$, 330 (100), 312 (42), 191 (8). HRMS (ESI): calcd. for $C_{21}H_{23}NNaO_4S$ 408.12400; found 408.12401. Data for **33**: Oil. IR (film): $\tilde{\nu}$ = 3279, 1967, 1703, 1329, 1167 cm^{-1}. ^{1}H NMR: δ = 1.31 [s, 9 H, C(CH_3)$_3$], 5.01 (dd, ^2J = 14.2 Hz, ^4J = 1.2 Hz, 1 H, C=CH_2), 5.09 (dd, ^2J = 14.2 Hz, ^4J = 1.3 Hz, 1 H, C=CH_2), 5.30 (d, ^3J = 9.9 Hz, 1 H, C*H*NH), 5.86 (d, ^3J = 9.9 Hz, 1 H, CHN*H*), 7.21–7.26 (m, 5 H, Ar-H), 7.42–7.54 (m, 3 H, Ar-H), 7.79–7.82 (m, 2 H, Ar-H) ppm. ^{13}C NMR: δ = 27.8, 56.6, 80.7, 82.1, 101.5, 126.4, 127.1, 127.6, 128.3, 128.8, 132.4, 139.2, 140.8, 164.3, 212.8 ppm. MS (ESI): *m*/*z* (%) = 408 (100) [M + Na]$^+$, 352 (14), 143 (18). HRMS (ESI): calcd. for $C_{21}H_{23}NNaO_4S$ 408.12400; found 408.12342.

(*E*)-*tert*-Butyl 2-[4-(4-Nitrophenyl)-1-(phenylsulfonyl)azetindin-2-ylidene]ethanoate (31b) and *tert*-Butyl 4-Methyl-2-phenyl-1-(phenylsulfonamido)-2-azetine-3-carboxylate (32): Yield (method A; r.t., 1 h): 24 (for **31a**) and 9% (for **32**); yield (method B): 48% (for **31b**). Purification by flash chromatography (hexane/ethyl acetate, 1:4) gave (in order of elution) **32** and **31b**. Data for **32**: Yellow oil. IR (film): $\tilde{\nu}$ = 3122, 1713, 1619, 1168 cm^{-1}. ^{1}H NMR: δ = 1.36 [s, 9 H, C(CH_3)$_3$], 2.17 (br. s, 3 H, CH_3), 5.68 (br. s, 1 H, C*H*Ph), 7.39–7.59 (m, 5 H, Ar-H), 7.75–7.80 (m, 2 H, Ar-H), 8.22–8.25 (m, 2 H, Ar-H) ppm. ^{13}C NMR: δ = 20.4, 28.0, 71.7, 82.9, 122.3, 124.1, 127.4, 130.1, 131.5, 132.7, 134.5, 144.4, 147.5, 148.1, 162.8 ppm. MS (ESI): *m*/*z* (%) = 453 (27) [M + Na]$^+$, 375 (67), 357 (100), 331 (12). HRMS (ESI): calcd. for $C_{21}H_{22}N_2NaO_6S$ 453.10908; found 453.10964. Data for **31b**: Yellow oil. IR (film): $\tilde{\nu}$ = 1700, 1661, 1523, 1347, 1168, 1120 cm^{-1}. ^{1}H NMR: δ = 1.46 [s, 9 H, C(CH_3)$_3$], 3.04 (ddd, ^2J = 16.8 Hz, ^3J = 4.2 Hz, ^4J = 2.1 Hz, 1 H, C=CH_2), 3.55 (ddd, ^2J = 16.8 Hz, ^3J = 7.3 Hz, ^4J = 2.1 Hz, 1 H, C=CH_2), 5.22 (dd, ^3J = 7.3, 4.3 Hz, 1 H, C*H*CH$_2$), 5.83–5.85 (m, 1 H, =C*H*), 7.37–7.66 (m, 5 H, Ar-H), 7.75–7.79 (m, 2 H, Ar-H), 8.20–8.23 (m, 2 H, Ar-H) ppm. ^{13}C NMR: δ = 28.3, 37.5, 64.5, 80.4, 98.1, 124.1, 127.4, 129.5, 134.2, 136.7, 144.7, 148.0, 155.9, 166.2 ppm. (ESI): *m*/*z* (%) = 431 (26) [M + H]$^+$, 375 (100), 357 (97), 331 (6). HRMS (ESI): calcd. for $C_{21}H_{23}N_2O_6S$ 431.12713; found 431.12723.

X-ray Crystallography: The structure of compound **14** was determined by taking advantage of the significant anomalous dispersion of sulfur at the Mo-K_α wavelength. Both a Flack analysis of the diffraction data and the results of separate refinements of the possible enantiomers unambiguously assigned the *S*,*S*,*S*,*R* absolute configurations to the C5, C18, C20 and C26 stereogenic centres, respectively. The phenyl ring attached to S1 is disordered over two positions with approximately 50% occupancy each. The X-ray data were collected with an APEX2 single-crystal diffractometer, at 298(3) K, by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Intensities were recorded as full profiles of ω–θ scans. The structures were solved by direct methods as implemented in SHELXS97 and refined by full-matrix least-squares using SHELXL97. Examination of the structure with PLATON confirmed the absence of voids that might be occupied by solvent molecules in the crystal structures. CCDC-774953 contains the supplementary crystallographic data for this paper. These data can be

obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystallographic Data for (1*R*)-(–)-10-Phenylsulfonylisobornyl (*S*)-2-[Phenyl(phenylsulfonamido)methyl]buta-2,3-dienoate (14): $C_{33}H_{35}NO_6S_2$, M = 605.74, monoclinic, $P2_1$ with unit cell, a = 11.1501(6) Å, b = 11.3696(6) Å, c = 12.1303(6) Å, α = 90°, β = 90°, γ = 88.851(3)°, V = 1537.48(14) Å^3. It contains two molecules/unit cell. $\rho_{calcd.}$ = 1.308 g cm^{-3}, Z = 2, μ = 0.219 mm^{-1}. R [$I > 2\sigma(I)$] = 0.0637 and R_w = 0.1504 for 5989 independent reflections. H atoms were placed at calculated positions and refined as riding on their parent atoms. The phenyl ring attached to S1 is disordered over two positions, occupancies refined to 0.546(16)/0.454(16). The disordered atoms were refined isotropically.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra.

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