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# Gold(I)-catalysed synthesis of cyclic sulfamidates: current scope, stereochemistry and competing ene-allene cycloisomerisation

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ABSTRACT

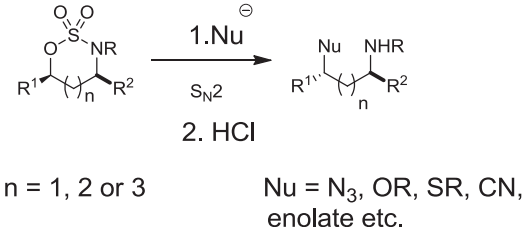
Six-membered cyclic sulfamidates are prepared in high yields by treatment of allenic sulfamates with readily available $Ph_3PAuNTf_2$. The reaction enables formation of *N*-substituted quaternary centres in high yields. The relative stereochemistry has been unambiguously determined. A π-rearrangement is faster than hydroamination in the case of an allyl-substituted sulfamate and a mechanism is proposed for this process.



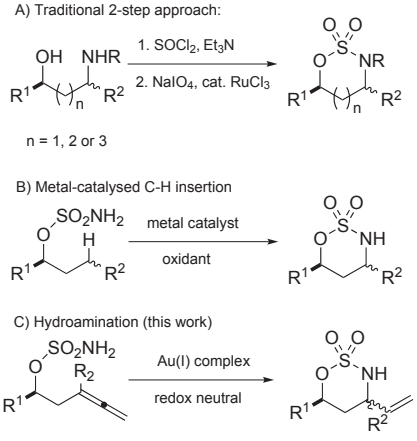
## 1. Introduction

Cyclic sulfamidates are versatile intermediates for the synthesis of substituted amines, and the development of their chemistry is of ongoing and increasing interest.[1]

They readily undergo $S_N2$ reaction at the oxygen-bearing carbon with a variety of heteroatoms and carbon nucleophiles including stabilised enolates (Scheme 1). The traditional two-step route to sulfamidates involves treatment of amino alcohols with thionyl chloride to give an intermediate sulfamidite that is then subjected to Ru-catalysed oxidation to the corresponding sulfamidate (Scheme 2, A).[1]




**Scheme 1.** Reactivity of cyclic sulfamidates.




**Scheme 2.** Synthetic approaches to sulfamidates.

The requirement for the strongly oxidising step limits the functional group tolerance of this method—alkenes and alkynes are normally incompatible with these conditions. Notably, perhaps the most self-evident approach—direct reaction of amino alcohols with sulfuryl chloride ($SO_2Cl_2$) does not usually lead to sulfamidate products, but instead to aziridines, or more commonly, to substrate decomposition.[1]

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0040-4020/

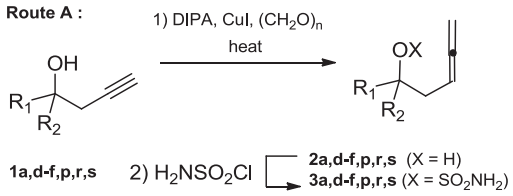
In recent years, a number of procedures have emerged for the preparation of this useful class of compounds via catalytic C–N bond formation.[2] This area has to-date been dominated by metal-catalysed generation of a reactive nitrenoid from a linear sulfamate precursor under oxidising conditions (Scheme 2, B). This species can undergo insertion into an appropriately positioned C–H bond, usually to form six-membered rings. Alternatively, addition to a pendant alkene gives fused aziridines. These approaches have been successfully employed in a number of complex target syntheses.[3]

Transition metal-catalysed hydroamination is an increasingly useful method for the preparation of amines.[4–8] Given the high reactivity of allenes and the use of gold complexes to promote hydroamination with unsaturated tosyl sulfonamides, we decided to investigate the viability of gold-catalysed sulfamidate synthesis using allenic sulfamates and recently reported the first results of these studies (Scheme 2, C).[9,10] We now wish to give a full account of our work so far on this new route to cyclic sulfamidates, including elucidation of and a tentative explanation for the unusual diastereoselectivity found in the reaction of one of the substrates, some substrates, which illustrate the current limitations of this reaction and an unusual amidine synthesis that fully demonstrates the sterically encumbered environment around the nitrogen atom in the products.

## 2. Results and discussion

The allenic sulfamates used in this study were prepared by either of two routes: (A) Johnson–Claisen rearrangement[11] of substituted propargyl alcohols to give allenic esters, followed by reduction and sulfamoylation[12] (Table 1A, or B) Crabbe homologation[13] of substituted homopropargyl alcohols then sulfamoylation (Table 1B).

**Table 1A**
Sulfamate preparation via Crabbé homologation[a]



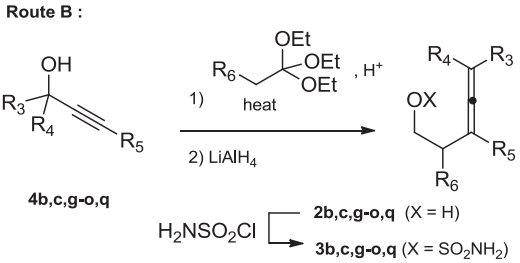

| Starting alcohol | $R_1$ | $R_2$ |
|---|---|---|
| **1a** | H | *c*-$C_6H_{11}$ |
| **1d** | H | *i*-$C_4H_9$ |
| **1e** | H | *t*-$C_4H_9$ |
| **1f** | H | $CH_2CH_2Ph$ |
| **1p** | –$(CH_2)_5$– | |
| **1r** | H | *E*-CH=CH–Ph |
| **1s** | H | *E*-CH=CH–$C_3H_7$ |

[a] For experimental details see Supplementary data.

Our initial test substrate **3a** (Table 2) was prepared by route A in three steps from cyclohexane carbaldehyde. We were pleased to find that treatment of **3a** with commercially available $PPh_3AuNTf_2$ (Gagosz's complex)[14] or $PPh_3AuCl/AgOTf$[15] at room temperature in dichloromethane led to the clean formation of the expected sulfamidate **5a** (entries 4 and 5). Use of other ligands and counterions on gold (entries 6–8) gave better diastereoselectivity in some cases, but with diminished yield. Control experiments without any catalyst, with AgOTf only and with TfOH confirmed that the gold complex was necessary for reaction to occur (entries 1–3).

We then prepared a range of substituted substrates designed to demonstrate the scope of the reaction using Gagosz's complex,

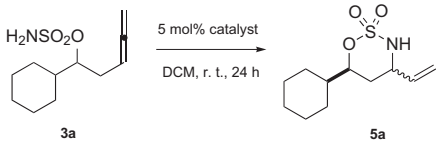
**Table 1B**
Sulfamate preparation via Johnson–Claisen rearrangement[a]




| Starting alcohol | $R_3$ | $R_4$ | $R_5$ | $R_6$ |
|---|---|---|---|---|
| **4b** | *n*-$C_5H_{11}$ | H | H | H |
| **4c** | –$(CH_2)_5$– | | H | H |
| **4g** | H | H | H | Me |
| **4h** | H | H | *n*-$C_3H_7$ | H |
| **4i** | H | H | *n*-$C_6H_{13}$ | H |
| **4j** | H | H | $CH_2$-*c*-$C_6C_{11}$ | H |
| **4k** | H | H | $(CH_2)_2OBn$ | H |
| **4l** | H | H | $CH_2OBn$ | H |
| **4m** | H | H | $CH_2OMe$ | H |
| **4n** | H | H | *i*-$C_3H_7$ | H |
| **4o** | H | H | *n*-$C_4H_9$ | Me |
| **4q** | H | H | Ph | Me |

[a] For experimental details see Supplementary data.

**Table 2**
Initial catalyst screen and controls[a]




| Entry | Catalyst | Yield **5a**/% | dr cis:trans |
|---|---|---|---|
| 1 | None | 0 | NA |
| 2 | AgOTf | 0 | NA |
| 3 | TfOH | 0 | NA |
| 4 | $(Ph_3P)AuCl/AgOTf$ | 74 | 1.7:1 |
| 5 | $(Ph_3P)AuNTf_2$ | 99 | 1.2:1 |
| 6 | IPrAuCl/AgOTf | 48 | 1:1 |
| 7 | (2,4-Di-*t*BuPhO)$_3$PAuCl/AgOTf | 43 | 2:1 |
| 8 | (2,4-Di-*t*BuPhO)$_3$PAuCl/$AgNTf_2$ | 82 | 1:1 |

[a] Reactions conducted on a 50 mg scale.

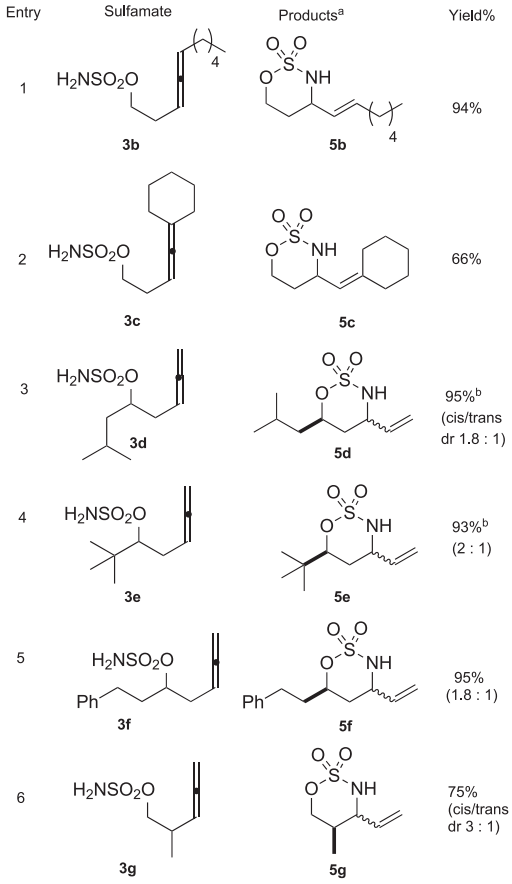
which had given us the highest yield of **5a**, as catalyst (Table 3). Sulfamidate **5b** was formed as exclusively the *E*-alkene (entry 1) in excellent yield. Sulfamate **3c**, leading to the formation of sulfamidate **5c** containing a trisubstituted olefin, was also a viable substrate under these conditions. Sulfamates **3d**–**f**, derived from secondary alcohols, gave mixtures of 1,3-cis and trans isomers.

It would not be possible to prepare these sulfamidates regioselectively from the Rh-nitrene chemistry of sulfamates, where insertion into tertiary C–H bonds is faster than that into allylic and benzylic C–H bonds, and aziridination often predominates over allylic C–H insertion.[16–19] The hydroamination route thus described provides access to sulfamidate substitution patterns complementary to those available by other means.

In the case of sulfamidate **5a** the diastereomers were separable and the major product was shown to be the 1,3-cis isomer (*cis*-**5a**) by a single crystal X-ray diffraction study (see Supplementary data); the other 1,3-disubstituted products were assigned by analogy.[20]

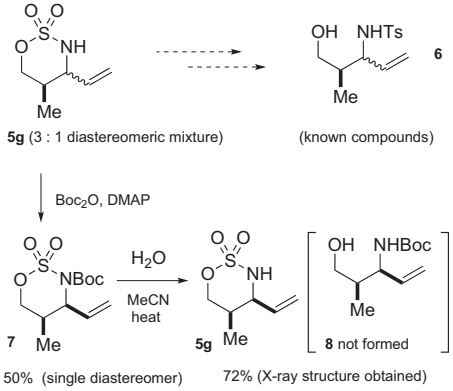
The 2-substituted product **5g** was formed as a 3:1 mixture of diastereomers. Initially, we were unable to separate these diastereomers by chromatography or determine the relative

**Table 3**
Mono- and disubstituted sulfamidates




[a] 5 mol% $Ph_3PAuNTf_2$, DCM, r.t. 24-120 h, see ESI.[b] Solvent DCE, temperature 40 °C.

stereochemistry of the major isomer by NMR experiments. We therefore planned to convert the diastereomeric mixture into the corresponding known[21] *syn*- and *anti*-tosyl-protected amino alcohols **6** (Scheme 3) to elucidate the nature of the major product.

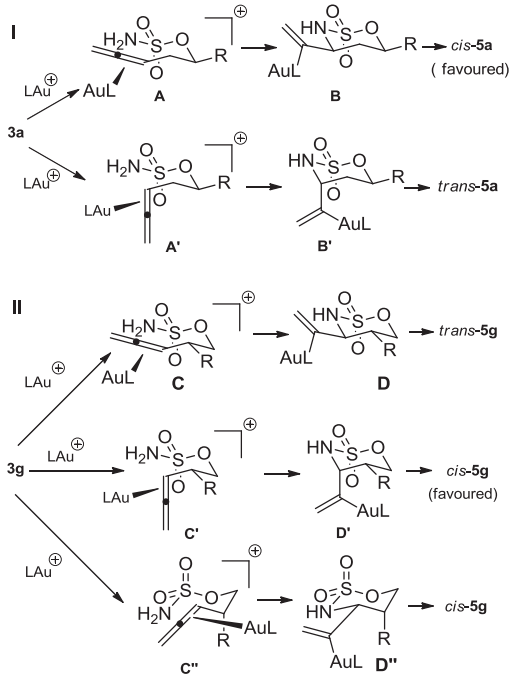



**Scheme 3.** Determination of diastereoselectivity for **5g**.

However, we did not ultimately need to carry out this lengthy sequence in full. Boc-protection of the mixture **5g** led unexpectedly to the isolation of a single diastereomeric product **7** in moderate yield. We were once again unable to crystallise this compound, but attempted ring-opening using water in boiling acetonitrile led only to slow loss of the Boc group (presumably by a thermal mechanism[22]) to give a single diastereomer of **5g**. Crystals suitable for an X-ray diffraction study were then obtained, revealing this product to be 2,3-*cis*-**5g**. Comparison of the $^1H$ and $^{13}C$ NMR data with those obtained from the mixture arising from the gold-catalysed cyclisation confirmed that the cis diastereomer was indeed the original major product.

A control experiment, performed by subjecting the separable diastereomer *cis*-**5a** to the original reaction conditions, showed that no equilibrium existed between the diastereomers. This is consistent with a kinetically controlled cyclisation, which is common in other gold-catalysed hydroaminations.[4–6]

Mechanistically, we anticipate that the reaction occurs via an outer sphere mechanism[23–28] (Scheme 4) leading to *anti* amino-auration of the allene. The cis and trans diastereomeric products may arise from the conformations **A** and **A′** indicated.




**Scheme 4.** Working stereochemical hypothesis.

Protonation of the vinyl gold intermediates **B** and **B′** would then give the observed products and regenerate the catalyst. Addition of protic additives ($H_2O$, AcOH, TfOH) to the reaction mixture did not accelerate the reaction to a measurable extent, suggesting that the final protonation is not the rate-determining step of this process.

The diastereoselectivity observed in the formation of **5a**, **5d**, **5e** and **5f** is lower than that normally found in related cyclisations.[23] The explanation for this is currently unclear. At present, we postulate that **A** and **A′** (Scheme 4, part I) are in equilibrium[29] and that the observed diastereoselectivity for the cis-products is due to faster and irreversible cyclisation of **A**, which has both the substituent R and the allene in equatorial positions. This would compare favourably with cyclisation of **A′**, where the allene is in the axial position.

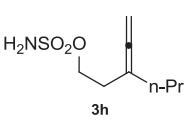
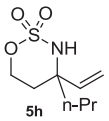
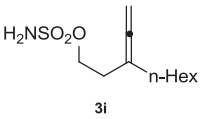
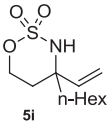
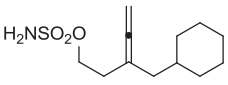
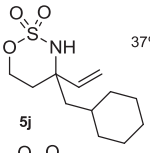
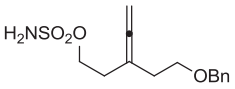
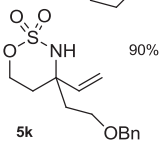
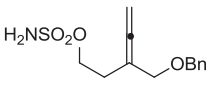
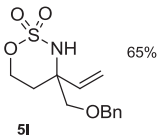
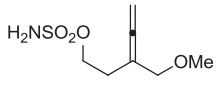
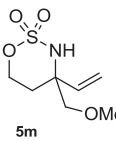
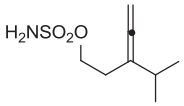
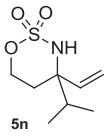
The observed diastereoselectivity in the formation of the 2-substituted system **5g** was initially somewhat surprising and does not seem to have such a straightforward explanation. If the major product arose simply from a reactive conformation with the maximum possible number of equatorial substituents, then the major diastereomer would be expected to arise from conformation **C** (Scheme 4, part II), with both the gold-bound allene and the methyl group in equatorial positions. This would lead to the preferential formation of the trans product, but we have demonstrated unequivocally that the major product is *cis*-**5g**. Assuming a chair-like

transition state, two reactive conformations leading to the cis-products are **C′** and **C″** leading to **D′** and **D″**, respectively. There is no obvious reason why **C′**, with the allene in the axial position, would be favoured over **C**, and indeed the steric bulk of the nearby substituent R is likely to clash with the metal–ligand assembly. Conformation **C″** is thus probably more likely to be responsible for the formation of the major product—the gold-bound allene is equatorial, and although the group R is now axial, it is now less likely to interfere with the metal–allene binding. This would also be consistent with our analysis of the 1,3-disubstituted systems—the allene is equatorial in the suggested favoured conformation **A**, but substituent R is perhaps in this case sufficiently distant not to affect the metal–allene interaction when in the equatorial position. A fourth possible conformation of **3g** that would give rise to *trans*-**5g**, with *both* substituents in axial positions, was considered energetically unlikely.

We continued our studies by preparing substrates that could lead to the formation of *N*-substituted quaternary centres[30] (Table 4), since this is very rare for catalytic hydroaminations.[31–33] Gratifyingly, cyclisation of sulfamates **3h**–**j** occurred cleanly to give the respective products **5h**–**j** (entries 1–3). Substrates **3k**–**m**, bearing protected hydroxyl groups, were also compatible with these conditions, leading to densely functionalised products **5k**–**m** (entries 4–6). The current limit of the method was reached in the case of substrate **3n**, which gave only a trace (~3%) of product **5n** after 5 days at 40 °C (entry 7), presumably for steric reasons. These polyfunctional unsaturated amine derivatives are difficult to access by other methods[34,35] and can potentially participate in a number of chemoselective transformations. General catalytic asymmetric approaches to *C*-tertiary amines have so far proved very difficult to realise. We feel that this new hydroamination reaction can potentially contribute to solving this important problem.[34–40]

We also prepared a number of substrates **3o**–**r**, **9** and **10**, which served to demonstrate the current limitations of this process (Fig. 1). Sulfamate **3o** (bearing adjacent substituents) and **9** (requiring formation of a seven-membered ring) were found to be unreactive under all conditions attempted, with various Au complexes. Tertiary alcohol-derived sulfamate **3p** and compound **3q**, bearing a phenyl-substituted allene, underwent decomposition to unidentifiable products upon treatment with any of the potential catalysts, with no evidence of product formation, as judged by $^1$H NMR spectra of the crude reaction mixtures. Compounds **3r** and **3s** could not be purified chromatographically and did not appear to be stable under ambient conditions (although evidence for their formation was seen in the crude $^1$H NMR spectra of the sulfamoylation reactions).

**Table 4**
Formation of *N*-substituted quaternary centres

| Entry | Sulfamate | Product[a] | Yield% |
|---|---|---|---|
| 1 |  **3h** |  **5h** | 92% |
| 2 |  **3i** |  **5i** | 68% |
| 3 |  **3j** |  **5j** | 37% |
| 4 |  **3k** |  **5k** | 90% |
| 5 |  **3l** |  **5l** | 65% |
| 6 |  **3m** |  **5m** | 44% |
| 7 |  **3n** |  **5n** | trace[b] |

[a] $Ph_3PAuNTf_2$, DCM, r.t. 24-120 h, see ESI. [b] ~3% of 90% pure product isolated.

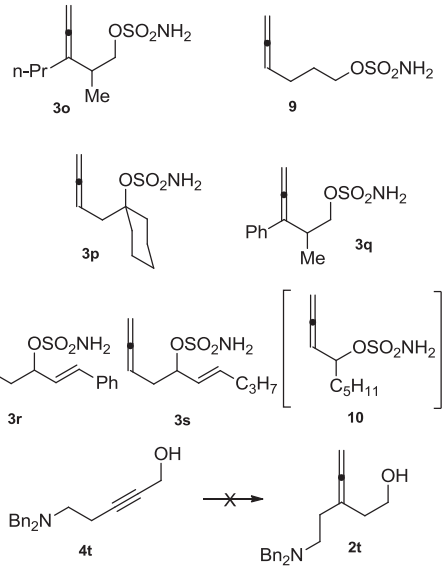
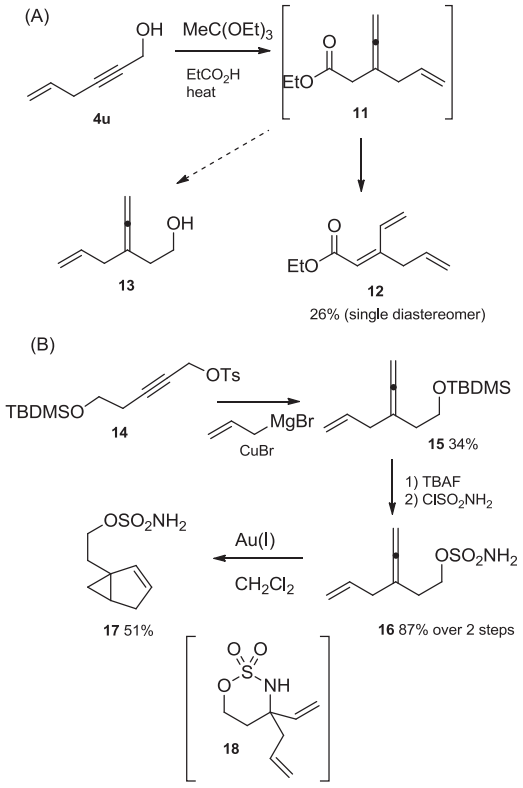



**Fig. 1.** Unsuccessful substrates.

Compound **10**, which would in theory lead to a five-membered sulfamidate, could not be prepared and all attempts at sulfamoylation of the corresponding alcohol led only to complete decomposition. Robertson and co-workers made similar observations regarding related compounds[9] and it seems likely that these particular allenic sulfamates are not viable reagents. Our attempts to prepare alcohol **2t**, intended for subsequent sulfamate formation, were stalled by a lack of reactivity in the desired Johnson–Claisen rearrangement step. To the best of our knowledge, there appear to be no examples in the literature of such rearrangements involving substrates containing basic amines.

Intriguingly, our attempts to conduct the Johnson–Claisen rearrangement of 3-allyl propargyl alcohol **4u** resulted in very small and variable amounts of the expected ester **11** (Scheme 5A). The major product from this reaction was found to be conjugated diene **12**, isolated as a single diastereomer,[41] but which obviously could not easily be converted to the desired alcohol **13**. This product presumably results from acid-catalysed isomerisation[42] of the first-

formed allene under the reaction conditions. Further investigations are continuing into optimising the yield, scope and selectivity of this process. As an alternative route to our desired ene-allene substrate **16** (Scheme 5B), we prepared the known tosylate[43] **14** and conducted an $S_N2'$ reaction using an allyl cuprate[44] to give protected ene-allene **15** in modest yield. Removal of the silyl group and sulfamoylation then gave the desired hydroamination substrate **16**.

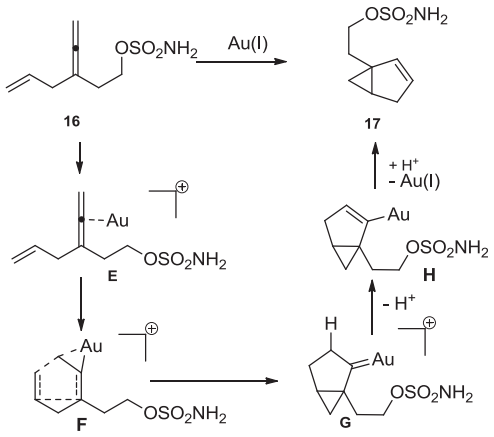



**Scheme 5.** (A) Unexpected isomerisation to give diene **12** and (B) successful synthesis and ene-allene cycloisomerisation of **16** to give cyclopropane **17**.

Treatment of **16** with the gold(I) complex under our standard conditions did not lead to formation of the hydroamination product **18**. Instead, the sole product isolated after only 30 min was found to possess some alkyl protons with $^1$H NMR signals at very low chemical shift ($\delta$=0.68 and 0.0 ppm relative to $CDCl_3$ at 7.27 ppm). It was identified by 1D and 2D NMR studies as fused cyclopropane **17**.

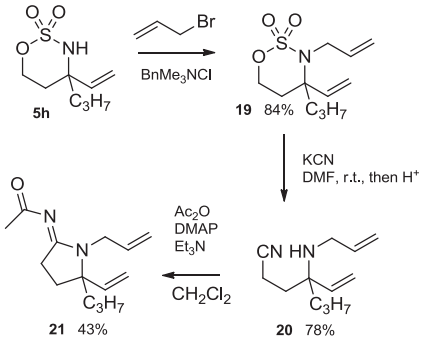
Mechanistically, product **17** may result from ene-allene cycloisomerisation as depicted in Scheme 6. Thus, co-ordination of Au(I) to the allene initiates an intramolecular cyclopropanation to give carbene **G** via transition state **F**. Loss of a proton then gives vinyl gold intermediate **H**, after which protodemetallation leads to **17**. This mechanism is related to one, which was elucidated by Fensterbank, Malacria and Nolan from computational and experimental studies on Au(I)- and Pt(II)-catalysed reactions on more elaborate allenenyl esters.[45] The fact that none of the expected product **18** was detected at all suggests that the rearrangement is more than one order of magnitude faster than the hydroamination, with the sulfamate nucleophile acting as merely a spectator.

Finally, during our investigations into the reactivity of these sulfamidates, we discovered unusual behaviour leading to a novel acyl amidine synthesis (Scheme 7). Allylation[46] of **5h** to give **19** and ring-opening with cyanide ion occurred as expected to give the cyanoamine **20** after acid hydrolysis of the *N*-sulfate intermediate.[1] Exposure of **20** to standard acylation conditions gave not the expected acetamide, but a product ultimately identified as the




**Scheme 6.** Possible cycloisomerisation mechanism.

amidine **21**. It is currently unclear whether acylation of the nitrile occurs before or after the 5-*exo*-*dig* cyclisation of the amine onto the nitrile, leading to **21**. Related reactions are normally carried out in strong acid or base in two separate steps, rather than the relatively mild one-pot conditions found here.[47]




**Scheme 7.** An unusual acyl amidine synthesis.

## 3. Conclusion

In summary, we have presented our full results on the first gold-catalysed preparation of cyclic sulfamidates, leading to a range of unusually substituted and sterically hindered products under mild conditions. We have proposed a model for the diastereoselectivity of these reactions for different substitution patterns and demonstrated the current scope and limitations of this new reaction. We are currently exploring further improvements to the catalyst system, development of an asymmetric version of this process and broadening our studies to other metal-catalysed reactions of sulfamates and related compounds. We are also examining the scope of the unexpected cycloisomerisation and amidine cyclisations.

## 4. Experimental

### 4.1. General

$^1$H NMR spectra were recorded on Bruker AV 300, DPX 400 and AV 400 spectrometers at 300 and 400 MHz, respectively, and referenced to residual solvent. $^{13}$C NMR spectrum was recorded using the same spectrometers at 75 and 100 MHz, respectively. Chemical shifts ($\delta$ in parts per million (ppm)) were referenced to tetramethylsilane (TMS) or to residual solvent peaks ($CDCl_3$ at $\delta_H$ 7.26). *J* values are given in hertz (Hz) and s, d, dd, t, q and m abbreviations correspond to singlet, doublet, doublet of doublet, triplet, quartet

and multiplet. Mass spectra were obtained at the EPSRC National Mass Spectrometry Service Centre in Swansea. Infrared spectra were obtained on Perkin–Elmer Spectrum 100 FT-IR Universal ATR Sampling Accessory, deposited neat or as a chloroform solution to a diamond/ZnSe plate.

Flash column chromatography was carried out using Matrix silica gel 60 from Fisher Chemicals and TLC was performed using Merck silica gel 60 $F_{254}$ precoated sheets and visualised by UV (254 nm) or stained by the use of aqueous acidic $KMnO_4$. Anhydrous dichloromethane (DCM) and anhydrous dichloroethane (DCE) were distilled from $CaH_2$.

## 4.2. Experimental section

Homopropargyl alcohols (**1a**,[48] **1d**,[49] **1e**,[50] **1f**,[48] **1p**,[51] **1r**,[48] **1s**[52]) were prepared by Barbier-type reactions.[48,53] Propargyl alcohols **4c**, **4g**, **4h**, **4o** and **4q** are commercially available. Propargyl alcohols (**4b**,[11] **4i**,[54] **4j**,[55] **4k**,[56] **4l**,[57] **4m**,[58] **4n**,[59] **4t**,[60] **4u**[61]) were prepared by known methods.

Allenic alcohols (**2a**,[62] **2d**,[63] **2e**,[64] **2f**,[63] **2p**,[65] **2r**[63] and **2s**[63]) were prepared by the Crabbé homologation of homopropargyl alcohols.[66] Allenic alcohols (**2b**,[67] **2c**,[11] **2g**,[10] **2h**,[68] **2i**,[69] **2j**, **2k**, **2l**, **2m**, **2n**, **2o**[11] and **2q**[11]) were prepared by the Johnson–Claisen rearrangement of the corresponding propargyl alcohol.[11]

*4.2.1. 3-(Cyclohexylmethyl)penta-3,4-dien-1-ol (**2j**).* Wt 2.0 g; 66%; colourless oil; $\nu_{max}/cm^{-1}$ 3326, 2920, 2850, 1957, 1448, 1045, 1015, 842; $\delta_H$ (300 MHz, $CDCl_3$) 4.74–4.68 (2H, m, $CH_2$=), 3.74 (2H, dd, *J* 11.1, 5.6 Hz, C$H_2$OH), 2.25–2.12 (2H, m, C$H_2$CH$_2$OH), 1.90–1.71 (2H, m, C$H_2$C), 1.70–1.58 (4H, m, $C_6H_{11}$), 1.53–1.32 (1H, m, CH$_2$C*H*), 1.31–1.09 (4H, m, $C_6H_{11}$), 1.07–0.75 (2H, m, $C_6H_{11}$). Further characterised by preparation of the 4-nitrobenzoate ester due to instability.

*4.2.2. 3-(Cyclohexylmethyl)penta-3,4-dien-1-yl 4-nitrobenzoate ester.* To a solution of 3-(cyclohexylmethyl)penta-3,4-dien-1-ol (108 mg, 0.6 mmol) in dichloromethane (1 mL) were added triethylamine (85 mg, 0.8 mmol) and dimethylaminopyridine (6.8 mg, 56 μmol). To the stirring solution at 0 °C was added *p*-nitro benzoylchloride (128 mg, 0.7 mmol) in dichloromethane (1 mL) dropwise and stirred for 30 min. The reaction mixture was stirred at room temperature for 18 h. Water (10 mL) was added. The separated organic layer was washed with hydrochloric acid (10%; 2×1 mL), water (5 mL) then brine (5 mL) and dried ($Na_2SO_4$) and concentrated in vacuo. Purification by column chromatography (20:1 petroleum ether/ethyl acetate) afforded the title compound. Wt 140 mg; 76%; colourless oil; $\nu_{max}/cm^{-1}$ 2922, 2850, 1957, 1724, 1527, 1347, 1268, 842; $\delta_H$ (300 MHz, $CDCl_3$) 8.33–8.22 (2H, m, 2×*C*HCNO$_2$), 8.22–8.14 (2H, m, 2×*C*HCCO), 4.67–4.62 (2H, m, C$H_2$=), 4.45 (2H, t, *J* 6.7 Hz, C$H_2$O), 2.39 (2H, tt, *J* 6.7, 3.2 Hz, C$H_2$CH$_2$O), 1.89 (2H, dt, *J* 6.7, 2.7 Hz, C$H_2$CH), 1.80–1.54 (5H, m, $C_6H_{11}$), 1.53–1.32 (1H, m, $C_6H_{11}$), 1.32–1.06 (2H, m, $C_6H_{11}$), 1.00–0.76 (3H, m, $C_6H_{11}$); $\delta_C$ (75 MHz, $CDCl_3$) 206.3, 164.6, 150.5, 135.8, 130.7, 123.5, 97.4, 75.7, 64.1, 40.5, 35.9, 33.3, 31.0, 26.5, 26.2; *m*/*z* (ESI$^+$) 347 ($M+NH_4^+$, 100%); HRMS (ESI$^+$) found 347.1963, $C_{19}H_{27}O_4N_2$ $(M+NH_4)^+$ requires 347.1965.

*4.2.3. 3-(2-(Benzyloxy)ethyl)penta-3,4-dien-1-ol (**2k**).* Wt 2.4 g; 42%; colourless oil; $\nu_{max}/cm^{-1}$ 3406, 2927, 2881, 1715, 1453,1273, 713; $\delta_H$ (300 MHz, $CDCl_3$) 7.39–7.25 (5H, m, Ph), 4.77–4.73 (2H, m, C$H_2$=), 4.52 (2H, s, C$H_2$OPh), 3.75 (2H, dd, *J* 6.0 Hz, C$H_2$OH), 3.60 (2H, t, *J* 6.6 Hz, C$H_2$OCH$_2$Ph), 2.30 (2H, td, *J* 6.6, 3.2 Hz, C$H_2$CH$_2$OCH$_2$Ph), 2.24 (2H, td, *J* 6.0, 3.2 Hz, C$H_2$CH$_2$OH); $\delta_C$ (75 MHz, $CDCl_3$) 206.0, 134.6, 129.1, 128.5, 127.9, 97.5, 77.4, 73.2, 68.7, 60.8, 35.7, 32.3; *m*/*z* (ESI$^+$) 219 ($M+H^+$, 30%), 213 (100%), 197 (50%), 195 (95%); HRMS (ESI$^+$) found 437.2683, $C_{28}H_{37}O_4$ $(2M+H)^+$ requires 437.2686.

*4.2.4. 3-((Benzyloxy)methyl)penta-3,4-dien-1-ol (**2l**).* Wt 2.4 g; 88%; colourless oil; $\nu_{max}/cm^{-1}$ 3371, 3030, 2859, 1956, 1496, 1453, 1355, 1205, 1027, 849, 687, 737; $\delta_H$ (300 MHz, $CDCl_3$) 7.43–7.26 (5H, m, Ph), 4.86–4.82 (2H, m, $CH_2$=), 4.56 (2H, s, C$H_2$Ph), 4.08 (2H, t, *J* 1.9 Hz, C$H_2$OCH$_2$Ph), 3.78 (2H, t, *J* 6.0 Hz, C$H_2$OH), 2.59–2.50 (1H, s, OH), 2.37 (2H, tt, *J* 6.0, 1.9 Hz, C$H_2$CH$_2$OH); $\delta_C$ (75 MHz, $CDCl_3$) 207.5, 137.7, 128.5, 128.0, 127.8, 97.7, 75.8, 72.0, 71.4, 61.3, 33.5; *m*/*z* (ESI$^+$) 205 ($M+H^+$, 100%), 113 (39%), 107 (67%); HRMS (ESI$^+$) found 205.1223, $C_{13}H_{17}O_2$ $(M+H)^+$ requires 205.1223.

*4.2.5. 3-(Methoxymethyl)penta-3,4-dien-1-ol (**2m**).* Wt 3.30 g; 52%; colourless oil; $\nu_{max}/cm^{-1}$ 3385, 2927, 2822, 1957, 1728, 1450, 1375, 1179, 1084, 848; $\delta_H$ (300 MHz, $CDCl_3$) 4.84–4.75 (2H, m, $CH_2$=), 3.94 (2H, t, *J* 2.0 Hz, C$H_2$OCH$_3$), 3.74 (2H, t, J 5.9 Hz, C$H_2$OH), 3.34 (3H, s, $CH_3$), 2.55 (1H, br s, OH), 2.30 (2H, tt, *J* 5.9, 2.0 Hz, C$H_2$CH$_2$OH); $\delta_C$ (100 MHz, $CDCl_3$) 207.3, 97.5, 75.5, 73.6, 61.1, 57.6, 33.3; *m*/*z* (ESI$^+$) 129 ($M+H^+$, 68%), 97 (100%); HRMS (ESI$^+$) found 129.0909, $C_7H_{13}O_2$ $(M+H)^+$ requires 129.0910.

*4.2.6. 3-Isopropylpenta-3,4-dien-1-ol (**2n**).* Wt 1.1 g; 72%; colourless oil; $\nu_{max}/cm^{-1}$ 3316, 2962, 2931, 2871, 1953, 1465, 1041, 844; $\delta_H$ (300 MHz, $CDCl_3$) 4.81–4.77 (2H, m, $CH_2$=), 3.75 (2H, dd, *J* 6.0 Hz, C$H_2$OH), 2.30–2.16 (2H, m, C$H_2$CH$_2$OH), 2.16–2.03 (1H, m, C*H*(CH$_3$)$_2$), 1.78–1.56 (1H, m, OH), 1.04 (6H, d, *J* 6.8 Hz, CH(C$H_3$)); $\delta_C$ (75 MHz, $CDCl_3$) 204.3, 106.7, 77.6, 61.1, 33.3, 30.7, 21.5; *m*/*z* (ESI$^+$) 127 ($M+H^+$, 100%), 110 (30%), 109 (35%); HRMS (ESI$^+$) found 126.1038, $C_8H_{14}O$ ($M^+$) requires 126.1039.

## 4.3. General procedure for the preparation of allenic sulfamates[18,70]

Allenic sulfamates **3a**,[70] **3b**,[67] **3c**, **3d**, **3e**, **3f**, **3g**, **3h**,[54] **3i**, **3j**, **3k**, **3l**, **3m**, **3n**,[55] **3o**, **3p**, **3q** and **3s** were prepared as outlined below.

Under an inert atmosphere (nitrogen), formic acid (2.5 equiv) was added dropwise to neat chlorosulfonylisocyanate (2.5 equiv), at 0 °C with vigorous stirring. Acetonitrile (0.8 mL/mmol alcohol) was added and the reaction mixture stirred overnight. The allenic alcohol was dissolved in dimethylacetamide (1.7 mL/mmol alcohol) and added dropwise to the sulfamoyl chloride solution at 0 °C. Transfer of the alcohol was made quantitative with an additional 0.5 mL of dimethylacetamide. The resulting white suspension was stirred for 2 h at 0 °C. Once TLC indicated consumption of starting material, the reaction mixture was diluted with ethyl acetate and brine and poured into a separating funnel containing ethyl acetate and water. The separated aqueous phase was further extracted with ethyl acetate and the combined organic layer washed with brine, dried ($Na_2SO_4$) and concentrated in vacuo. Purification by column chromatography provided the desired sulfamate ester.

*4.3.1. 4-Cyclohexylidene-3-en-1-yl sulfamate (**3c**).* Wt 429 mg; 58%; colourless oil; $\nu_{max}/cm^{-1}$ 3385, 3282, 2925, 2853, 1966, 1554, 1446, 1359, 1266, 1239, 1175, 978, 924, 851, 825, 797, 739; $\delta_H$ (300 MHz, $CDCl_3$) 5.10–4.85 (1H, m, C*H*=), 4.68 (2H, s, $NH_2$), 4.25 (2H, t, *J* 6.9 Hz, C$H_2$O), 2.41 (2H, dt, *J* 13.3, 6.9 Hz, C$H_2$CH$_2$O), 2.17–2.05 (4H, m, $C_6H_{10}$), 1.69–1.35 (6H, m, $C_6H_{10}$); $\delta_C$ (75 MHz, $CDCl_3$) 199.3, 104.0, 83.2, 70.8, 31.5, 28.9, 27.3, 26.0; *m*/*z* (ESI$^+$) 249 ($M+NH_4^+$, 100%), 232 ($M+H^+$, 40%); HRMS (ESI$^+$) found 232.1004, $C_{10}H_{18}O_3NS$ $(M+H)^+$ requires 232.1002.

*4.3.2. 2-Methylocta-6,7-dien-4-yl sulfamate (**3d**).* Wt 421 mg; 71%; yellow oil; $\nu_{max}/cm^{-1}$ 3362, 3283, 2951, 2935, 1957, 1539, 1351, 1329, 1178; $\delta_H$ (300 MHz, $CDCl_3$) 5.15–5.10 (1H, m, CH=), 4.86–4.39 (3H,

m, $CH_2$= and C*H*O), 2.58–2.42 (3H, m, 1×C$H_2$CH= and CHC$H_2$CHO), 1.88–1.66 (3H, m, 1×C$H_2$CH and $NH_2$), 1.61–1.38 (1H, m, C*H*($CH_3$)$_2$), 0.96 (3H, d, *J* 6.2 Hz, CH(C$H_3$)($CH_3$)), 0.94 (3H, d, *J* 6.2 Hz, CH($CH_3$)(C$H_3$)); $\delta_C$ (75 MHz, $CDCl_3$) 209.7, 84.6, 82.7, 75.3, 42.8, 33.8, 24.3, 22.9, 22.2; *m*/*z* (ESI$^+$) 218 (M−H$^+$, 100%); HRMS (ESI$^+$) found 218.0852, $C_9H_{16}O_3NS$ (M−H)$^+$ requires 218.0856.

*4.3.3. 2,2-Dimethylhepta-5,6-dien-3-yl sulfamate (**3e**).* Wt 257 mg; 41%; yellow oil; $\nu_{max}$/cm$^{-1}$ 3381, 2964, 2881, 1957, 1365, 1176, 907; $\delta_H$ (300 MHz, $CDCl_3$) 5.28 (1H, ddt, *J* 8.2, 6.6 Hz), 4.86–4.62 (4H, m, $CH_2$= and $NH_2$), 4.47–4.43 (1H, m, CHO), 2.62–2.31 (2H, m, C$H_2$CHO), 1.03 (9H, s, C($CH_3$)$_3$); $\delta_C$ (75 MHz, $CDCl_3$) 209.2, 92.6, 87.4, 75.6, 35.4, 30.4, 26.1; *m*/*z* (ESI$^+$) 220 (M+H$^+$, 100%), HRMS (ESI$^+$) found 220.0853, $C_9H_{17}O_3NS$ (M+H)$^+$ requires 220.0856.

*4.3.4. 1-Phenylhepta-5,6-dien-3-yl sulfamate (**3f**).* Wt 614 mg; 86%; colourless oil; $\nu_{max}$/cm$^{-1}$ 3379, 3281, 2928, 1956, 1355, 1177, 912; $\delta_H$ (300 MHz, $CDCl_3$) 7.36–7.14 (5H, m, Ph), 5.19–5.03 (1H, m, CH=), 4.70 (5H, m, $CH_2$=, $NH_2$ and CHO), 2.88–2.66 (2H, m, C$H_2$Ph), 2.55–2.49 (2H, m, C$H_2$CH=), 2.15–2.02 (2H, m, $CH_2$C$H_2$CHO); $\delta_C$ (75 MHz, $CDCl_3$) 209.7, 141.0, 128.6, 128.4, 126.2, 84.4, 83.3, 75.4, 35.2, 33.4, 31.2; *m*/*z* (ESI$^+$) 268 (M+H$^+$, 100%), 204 (45%), 163 (30%); HRMS (ESI$^+$) found 268.1272, $C_{13}H_{18}O_3NS$ (M+H)$^+$ requires 268.1267.

*4.3.5. 2-Methylpenta-3,4-dien-1-yl sulfamate (**3g**).* Wt 60 mg; 67%; colourless oil; $\nu_{max}$/cm$^{-1}$ 3376, 3283, 2974, 1956, 1357, 1175, 972, 919; $\delta_H$ (300 MHz, $CDCl_3$) 5.14 (1H, dd, *J* 13.1, 6.4 Hz, CHC*H*=), 4.85–4.77 (2H, m, $CH_2$=), 4.76 (2H, s, $NH_2$), 4.14 (1H, dd, *J* 9.4, 6.4 Hz, 1×C$H_2$OSO$_2$NH$_2$), 4.04 (1H, dd, *J* 9.4, 7.0 Hz, 1×C$H_2$OSO$_2$NH$_2$), 2.72–2.52 (1H, m, C*H*CH$_3$), 1.12 (3H, d, *J* 6.9 Hz, $CH_3$); $\delta_C$ (75 MHz, $CDCl_3$) 208.0, 91.2, 77.2, 75.0, 32.2, 16.5; *m*/*z* (ESI$^+$) 250 (M+OAc$^+$, 100%), 236 (15%); HRMS (ESI$^+$) found 178.0529, $C_6H_{11}O_3NS$ (M+H)$^+$ requires 178.0532.

*4.3.6. 3-Vinylidenenonyl sulfamate (**3i**).* Wt 1.3 g; 43%; colourless oil; $\nu_{max}$/cm$^{-1}$ 3283, 2957, 2927, 2858, 1958, 1724, 1361, 1125; $\delta_H$ (300 MHz, $CDCl_3$) 4.86–4.64 (4H, m, $CH_2$= and $NH_2$), 4.30 (2H, t, *J* 7.1 Hz, C$H_2$O), 2.38 (2H, tt, *J* 6.9, 3.3 Hz, $CH_2CH_2CH_2C$=), 2.03–1.89 (2H, m, C$H_2$CH$_2$O), 1.70–1.19 (8H, m, (C$H_2$)$_4$CH$_3$), 0.89 (3H, dd, *J* 9.4, 4.2 Hz, $CH_3$); $\delta_C$ (75 MHz, $CDCl_3$) 205.5, 98.7, 77.2, 69.5, 32.3, 31.7, 31.0, 28.9, 27.3, 22.6, 14.1; *m*/*z* (ESI$^+$) 265 (M + $NH_4^+$, 100%), 255 (15%); HRMS (ESI$^+$) found 265.1584, $C_{11}H_{25}O_3N_2S$ (M+$NH_4$)$^+$ requires 265.1580.

*4.3.7. 3-(Cyclohexylmethyl)penta-3,4-dien-1-yl sulfamate (**3j**).* Wt 1.1 g; 76%; colourless oil; $\nu_{max}$/cm$^{-1}$ 3274, 2921, 2851, 1959, 1709, 1561, 1448, 1363, 1176; $\delta_H$ (300 MHz, $CDCl_3$) 4.79–4.50 (4H, m, $CH_2$= and $NH_2$), 4.29 (2H, t, *J* 7.0 Hz, C$H_2$O), 2.36 (2H, tt, *J* 7.0, 3.4 Hz, C$H_2$CH$_2$O), 1.91–1.82 (2H, m, C$H_2$C$_6$H$_{11}$), 1.82–1.57 (4H, m, 4×C$_6$H$_{11}$), 1.51–1.32 (1H, m, CH$_2$C*H*), 1.31–0.99 (4H, m, 4×C$_6$H$_{11}$), 0.99–0.73 (2H, m, 2×C$_6$H$_{11}$); $\delta_C$ (75 MHz, $CDCl_3$) 206.0, 96.9, 76.4, 69.5, 40.5, 35.8, 33.3, 31.0, 26.5, 26.2. This compound decomposed rapidly; good MS/HRMS data could not be obtained. It had to be subjected to the hydroamination conditions immediately for reproducible yields of **5j**.

*4.3.8. 3-(2-(Benzyloxy)ethyl)penta-3,4-dien-1-yl sulfamate (**3k**).* Wt 609 mg; 76%; colourless oil; $\nu_{max}$/cm$^{-1}$ 3280, 2866, 1958, 1716, 1363, 1176; $\delta_H$ (300 MHz, $CDCl_3$) 7.44–7.20 (5H, m, Ph), 4.93–4.63 (4H, m, $CH_2$= and $NH_2$), 4.53 (2H, s, C$H_2$Ph), 4.33 (2H, t, *J* 6.7 Hz, C$H_2$OSO$_2$NH$_2$), 3.63 (2H, t, *J* 6.4 Hz, CH$_2$C$H_2$OCH$_2$Ph), 2.44 (2H, tt, *J* 6.7, 3.2 Hz, C$H_2$CH$_2$OSO$_2$NH$_2$), 2.33 (2H, tt, *J* 6.4, 3.2 Hz, C$H_2$CH$_2$OCH$_2$Ph); $\delta_C$ (100 MHz, $CDCl_3$) 205.6, 161.0, 129.6, 128.4, 127.7, 127.6, 77.2, 73.0, 68.5, 62.1, 32.4, 31.1; *m*/*z* (ESI$^+$) 315 (M + $NH_4^+$, 100%), 298 (M+H$^+$, 35%); HRMS (ESI$^+$) found 298.1115, $C_{14}H_{20}O_4NS$ (M+H)$^+$ requires 298.1108.

*4.3.9. 3-((Benzyloxy)methyl)penta-3,4-dien-1-yl sulfamate (**3l**).* Wt 1.1 g; 88%; colourless solid; mp 45–46 °C; $\nu_{max}$/cm$^{-1}$ 3277, 1959, 1559, 1454, 1363, 1185, 1065, 978, 924, 857, 747, 699; $\delta_H$ (300 MHz, $CDCl_3$) 7.36–7.18 (5H, m, Ph), 4.82–4.77 (2H, m, $CH_2$=), 4.75 (2H, s, $NH_2$), 4.52 (2H, s, C$H_2$Ph), 4.37 (2H, t, *J* 6.8 Hz, C$H_2$OSO$_2$NH$_2$), 4.10 (2H, t, *J* 2.6 Hz, PhCH$_2$OC$H_2$), 2.53 (2H, tt, *J* 6.8 2.6 Hz, C$H_2$CH$_2$O-SO$_2$NH$_2$); $\delta_C$ (75 MHz, $CDCl_3$) 207.0, 137.8, 128.5, 128.0, 127.9, 95.9, 77.0, 71.9, 71.1, 69.4, 28.8; *m*/*z* (ESI$^+$) 306 (M+Na$^+$, 100%), 328 (30%), 301 (97%); HRMS (ESI$^+$) found 306.0775, $C_{13}H_{17}NaNO_4S$ (M+Na)$^+$ requires 306.0770.

*4.3.10. 3-(Methoxymethyl)penta-3,4-dien-1-yl sulfamate (**3m**).* Wt 0.5 g; 48%; colourless oil; $\nu_{max}$/cm$^{-1}$ 3273, 2929, 1958, 1563, 1452, 1361, 1180, 1079, 975, 924, 856, 774; $\delta_H$ (300 MHz, $CDCl_3$) 4.94 (2H, br s, $NH_2$), 4.89–4.81 (2H, m, $CH_2$=), 4.33 (2H, t, *J* 6.8 Hz, =CCH$_2$O), 3.95 (2H, t, *J* 2.1 Hz, C$H_2$OSO$_2$NH$_2$), 3.32 (3H, s, $OCH_3$), 2.54–2.40 (2H, m, C$H_2$CH$_2$OSO$_2$NH$_2$); $\delta_C$ (75 MHz, $CDCl_3$) 206.8, 95.7, 76.9, 73.4, 69.3, 57.7, 28.6; *m*/*z* (ESI$^+$) 230 (M+Na$^+$, 100%), 208 (40%), 176 (32%), 149 (9%); HRMS (ESI$^+$) found 230.0459, $C_7H_{13}O_4NSNa$ (M+Na)$^+$ requires 230.0457.

*4.3.11. 2-Methyl-3-vinylideneheptyl sulfamate (**3o**).* Wt 925 mg; 78%; colourless oil; $\nu_{max}$/cm$^{-1}$ 3286, 2958, 2931, 2874, 1954, 1363, 1181, 908; $\delta_H$ (300 MHz, $CDCl_3$) 4.84–4.60 (2H, m, $CH_2$=), 4.23 (1H, dd, *J* 9.4, 5.7 Hz, 1×C$H_2$OSO$_2$NH$_2$), 3.98 (1H, dd, *J* 9.4, 8.0 Hz, 1×C$H_2$OSO$_2$NH$_2$), 2.50–2.27 (1H, m, C*H*CH$_3$), 2.11–1.90 (2H, m, $NH_2$), 1.50–1.15 (6H, m, C$H_2$C$H_2$C$H_2$CH$_3$), 1.13 (3H, d, *J* 6.8 Hz, CHC$H_3$), 0.90 (3H, t, *J* 7.1 Hz, CH$_2$C$H_3$); $\delta_C$ (75 MHz, $CDCl_3$) 205.1, 104.3, 78.0, 74.5, 35.3, 30.5, 29.7, 22.4, 16.5, 13.9; *m*/*z* (ESI$^+$) 273 (M + $NH_4^+$, 100%), 241 (15%), 154 (15%), 137 (70%); HRMS (ESI$^+$) found 251.1423, $C_{10}H_{23}O_3N_2S$ (M+$NH_4$)$^+$ requires 251.1424.

*4.3.12. 1-(Buta-2,3-dien-1-yl)cyclohexyl sulfamate (**3p**).* Wt 191 mg; 74%; white solid; mp 71 °C; $\nu_{max}$/cm$^{-1}$ 3277, 2927, 2854, 1645, 1408, 1361, 1175, 870; $\delta_H$ (300 MHz, $CDCl_3$) 5.48 (1H, ddd, *J* 8.6, 3.5, 1.4 Hz, =CH), 5.16–4.99 (2H, m, =CH$_2$), 2.64 (2H, d, *J* 8.6 Hz, CH$_2$CH=), 1.98–1.47 (12H, m, C$_6$H$_{10}$ and $NH_2$); $\delta_C$ (75 MHz, $CDCl_3$) 208.9, 136.3, 121.9, 88.4, 74.3, 37.4, 28.2, 25.2, 22.9, 22.5; *m*/*z* (ESI$^+$) 249 (M + $NH_4^+$, 100%), 244 (70%); HRMS (ESI$^+$) found 249.0774, $C_{10}H_{21}O_3N_2S$ (M$^+$) requires 249.0779.

*4.3.13. 2-Methyl-3-phenylpenta-3,4-dien-1-yl sulfamate (**3q**).* Wt 655 mg; 65%; white solid; mp 79–81 °C; $\nu_{max}$/cm$^{-1}$ 3416, 3310, 2982, 2970, 1933, 1542, 1464, 1330, 1170; $\delta_H$ (300 MHz, $CDCl_3$) 7.44–7.16 (5H, m, Ph), 5.27–5.11 (2H, m, $CH_2$=), 4.62 (2H, s, $NH_2$), 4.34 (1H, dd, *J* 9.6, 5.3 Hz, 1×C$H_2$OSO$_2$NH$_2$), 4.06 (1H, dd, *J* 9.6, 8.1 Hz, 1×C$H_2$OSO$_2$NH$_2$), 3.23–3.01 (1H, m, C*H*CH$_3$), 1.27 (3H, d, *J* 6.8 Hz, $CH_3$); $\delta_C$ (75 MHz, $CDCl_3$) 207.9, 135.1, 128.7, 127.2, 126.3, 106.7, 80.4, 74.5, 32.6, 17.0; *m*/*z* (ESI$^+$) 271 (M + $NH_4^+$, 100%), 157 (60%); HRMS (ESI$^+$) found 271.1115, $C_{12}H_{19}O_3N_2S$ (M+$NH_4$)$^+$ requires 271.1111.

### 4.4. Cyclic sulfamidates (5a–5n)[10]

*General procedure for gold-catalysed hydroamination*

Under an inert atmosphere (nitrogen), the sulfamate was dissolved in dry dichloromethane (0.3 M). $PPh_3AuNTf_2$ (5 mol %) was added and the reaction mixture stirred at room temperature. When starting material was consumed, as determined by TLC, the reaction mixture was filtered through a plug of silica with diethyl ether, and concentrated in vacuo. Purification by column chromatography afforded the title compounds **5a**–**n**.

*4.4.1. 6-Cyclohexyl-4-vinyl-1,2,3-oxathiazinane 2,2-dioxide (**5a**).* Wt 60 mg; 99%; cis/trans 1.2:1. *cis*-**5a**: white solid; $R_f$ 0.31 (2:1 dichloromethane/hexane); mp 90–91 °C; $\nu_{max}/cm^{-1}$ 3276, 2927, 2852, 1650, 1436, 1347, 1175; $\delta_H$ (400 MHz, $CDCl_3$) 5.81 (1H, ddd, *J* 17.3, 10.6, 5.1 Hz, C*H*=$CH_2$), 5.38–5.18 (2H, m, CH=C$H_2$), 4.56 (1H, ddd, *J* 11.9, 6.4, 2.0 Hz, C*H*$C_6H_{11}$), 4.31–4.17 (1H, m, C*H*CH=$CH_2$), 3.98 (1H, d, *J* 10.3 Hz, NH), 1.98–1.43 (8H, m, 6×$C_6H_{11}$ and C$H_2$CHO), 1.36–0.96 (5H, m, 5×$C_6H_{11}$); $\delta_C$ (101 MHz, $CDCl_3$) 135.3, 117.3, 88.3, 56.4, 42.2, 32.5, 28.3, 28.0, 26.3, 25.9, 25.7; *m*/*z* ($ESI^+$) 263 ($M+NH_4^+$, 100%), 246 (15%); HRMS ($ESI^+$) found 263.1428, $C_{11}H_{23}O_3N_2S$ $(M+NH_4)^+$ requires 263.1424. The X-ray diffraction data have been submitted to the Cambridge Structural Database (Ref. number CCDC 871548) and the structure was included in our previous communication.[10]

*trans*-**5a**: colourless oil; $R_f$ 0.15 (2:1 dichloromethane/hexane); $\nu_{max}/cm^{-1}$ 3277, 2927, 2854, 1645, 1408, 1361, 1175, 870; $\delta_H$ (400 MHz, $CDCl_3$) 6.18 (1H, ddd, *J* 17.4, 10.7, 5.5 Hz, C*H*=$CH_2$), 5.28 (1H, ddd, *J* 10.7, 1.8, 0.7 Hz, 1×CH=C$H_2$), 5.25 (1H, ddd, *J* 17.4, 1.8, 0.7 Hz, 1×CH=C$H_2$), 4.67–4.56 (1H, m, C*H*$C_6H_{11}$), 4.48 (1H, d, *J* 6.6 Hz, NH), 4.29–4.13 (1H, m, C*H*CH=$CH_2$), 2.08–1.91 (1H, m, 1×C$H_2$CHO), 1.99–1.92 (1H, m, 1×C$H_2$CHO), 1.88 (1H, ddd, *J* 14.5, 3.9, 2.9 Hz, C*H*CHO), 1.83–1.61 (5H, m, 5×$C_6H_{11}$), 1.34–0.96 (5H, m, 5×$C_6H_{11}$); $\delta_C$ (101 MHz, $CDCl_3$) 136.0, 117.2, 86.3, 55.3, 41.7, 30.4, 28.4, 28.2, 26.3, 25.8, 25.6; *m*/*z* ($ESI^+$) 263 ($M+NH_4^+$, 100%), 246 (15%), 149 (15%); HRMS ($ESI^+$) found 263.1428, $C_{11}H_{23}O_3N_2S$ $(M+NH_4)^+$ requires 263.1424.

*4.4.2. (E)-4-(Hept-1-en-1-yl)-1,2,3-oxathiazinane 2,2-dioxide (**5b**).* Wt 42 mg; 94%; colourless oil; $\nu_{max}/cm^{-1}$ 3245, 2926, 1433, 1346, 1190, 1170; $\delta_H$ (300 MHz, $CDCl_3$) 5.81–5.68 (1H, m, =CH), 5.44–5.33 (1H, m, =CH), 4.73 (1H, td, *J* 11.9, 3.1 Hz, C*H*NH), 4.58–4.48 (1H, m, 1×$CH_2O$), 4.32–4.16 (2H, m, 1×$CH_2O$ and NH), 2.09–1.96 (2H, m, C$H_2(CH_2)_3CH_3$), 1.95–1.72 (2H, m, C$H_2$CHNH), 1.42–1.16 (6H, m, $(CH_2)_3CH_3$), 0.87 (3H, t, *J* 6.8 Hz, $CH_3$); $\delta_C$ (75.5 MHz, $CDCl_3$) 134.9, 126.8, 71.8, 56.9, 32.3, 31.4, 29.9, 28.7, 22.6, 14.1; *m*/*z* ($ESI^+$) 251 ($M+NH_4^+$, 100%), 216 (6%), 156 (6%); HRMS ($ESI^+$) found 251.1428, $C_{10}H_{23}O_3N_2S$ $(M+NH_4)^+$ requires 251.1424.

*4.4.3. 4-(Cyclohexylidenemethyl)-1,2,3-oxathiazinane 2,2-dioxide (**5c**).* Wt 33 mg; 66%; colourless oil; $\nu_{max}/cm^{-1}$ 3246, 2922, 1421, 1347, 1187; $\delta_H$ (400 MHz, $CDCl_3$) 5.56–5.42 (1H, m, C*H*=$CH_2$), 4.78–4.66 (1H, m, 1×$CH_2O$), 4.59–4.49 (1H, m, 1×$CH_2O$), 4.05–3.71 (2H, m, CHNH), 2.19–2.15 (2H, m, C$H_2CH_2O$), 2.06–1.50 (10H, m, $C_6H_{10}$); $\delta_C$ (101 MHz, $CDCl_3$) 132.1, 126.5, 72.2, 53.8, 44.2, 30.2, 28.5, 25.4, 22.8, 22.2; *m*/*z* ($ESI^+$) 440 ($M+NH_4^+$, 100%), 232 (43%), 199 (20%), 149 (27%); HRMS ($ESI^+$) found 249.1271, $C_{10}H_{21}O_3N_2S$ $(M+NH_4)^+$ requires 249.1267.

*4.4.4. 6-Isobutyl-4-vinyl-1,2,3-oxathiazinane 2,2-dioxide (**5d**).* Wt 49 mg; 94%; colourless oil; cis/trans 1.8:1: $\nu_{max}/cm^{-1}$ 3245, 2960, 2874, 1650, 1413, 1356, 1185; $\delta_H$ (300 MHz, $CDCl_3$) cis-isomer: 5.81 (1H, ddd, *J* 17.3, 10.6, 5.0 Hz, C*H*=$CH_2$), 5.37–5.22 (2H, m, CH=C$H_2$), 4.90–4.79 (2H, m, CHO and C*H*NH), 3.90 (1H, d, *J* 10.2 Hz, NH), 1.96–1.80 (2H, m, C$H_2$CHNH), 1.80–1.66 (1H, m, $CH(CH_3)_2$), 1.60–1.45 (2H, m, C$H_2CH(CH_3)_2$), 1.00–0.87 (6H, m, $CH(CH_3)_2$) *trans*-isomer: 6.18 (1H, ddd, *J* 17.3, 10.7, 5.5 Hz, C*H*=$CH_2$), 5.37–5.22 (2H, m, CH=C$H_2$), 5.00–4.91 (2H, m, CHO and C*H*NH), 4.44 (1H, d, *J* 7.1 Hz, NH), 1.96–1.80 (2H, m, C$H_2$CHNH), 1.80–1.66 (1H, m, C$H(CH_3)_2$), 1.44–1.32 (2H, m, C$H_2CH(CH_3)_2$), 1.00–0.87 (6H, m, $CH(CH_3)_2$); $\delta_C$ (75 MHz, $CDCl_3$) cis-isomer: 135.1, 117.4, 82.7, 56.3, 44.3, 35.6, 23.8, 23.0, 22.0; trans-isomer: 135.9, 117.4, 81.1, 55.2, 43.6, 33.5, 24.1, 23.0, 21.9; *m*/*z* ($ESI^+$) 237 ($M+NH_4^+$, 100%), HRMS ($ESI^+$) found 237.1270, $C_9H_{21}O_3N_2S$ $(M+NH_4)^+$ requires 237.1267.

*4.4.5. 6-(tert-Butyl)-4-vinyl-1,2,3-oxathiazinane 2,2-dioxide (**5e**).* Wt 53 mg; 93%; colourless oil; cis/trans 2:1: $\nu_{max}/cm^{-1}$ 3252, 2962, 2877, 1650, 1413, 1346, 1183; $\delta_H$ (300 MHz, $CDCl_3$) cis-isomer: 5.82 (1H, ddd, *J* 17.3, 10.6, 5.0 Hz, C*H*=$CH_2$), 5.42–5.15 (2H, m, CH=C$H_2$), 4.58–4.39 (1H, m, CHO), 4.28–4.15 (2H, m, CHNH), 1.95–1.82 (1H, m, 1×C$H_2$CHNH), 1.65–1.46 (1H, m, 1×C$H_2$CHNH), 0.98 (9H, s, $(CH_3)_3C$); trans-isomer: 6.20 (1H, ddd, *J* 17.4, 10.7, 5.4 Hz, C*H*=$CH_2$), 5.42–5.15 (2H, m, CH=C$H_2$), 4.58–4.39 (1H, m, CHO), 4.30–4.01 (2H, m, CHNH), 2.10–1.97 (1H, m, 1×C$H_2$CHNH), 1.95–1.82 (1H, m, 1×C$H_2$CHNH), 0.98 (9H, s, $(CH_3)_3C$); $\delta_C$ (75 MHz, $CDCl_3$) cis-isomer 135.2, 117.3, 91.3, 56.3, 34.5, 29.9, 25.4; trans-isomer 135.9, 117.1, 88.5, 55.2, 34.4, 27.8, 25.2; *m*/*z* ($ESI^+$) 237 ($M+NH_4^+$, 100%) HRMS ($ESI^+$) found 237.1269, $C_9H_{21}O_3N_2S$ $(M+NH_4)^+$ requires 237.1267.

*4.4.6. 6-Phenethyl-4-vinyl-1,2,3-oxathiazinane 2,2-dioxide (**5f**).* Wt 48 mg; 95%; colourless oil; cis/trans 1.8:1: $\nu_{max}/cm^{-1}$ 3263, 3028, 2931, 1603, 1497, 1416, 1360, 1183; $\delta_H$ (400 MHz, $CDCl_3$) cis-isomer: 7.42–7.19 (5H, m, Ph), 5.85 (1H, ddd, *J* 17.3, 10.6, 5.0 Hz, C*H*=$CH_2$), 5.41–5.25 (2H, m, CH=C$H_2$), 4.86–4.76 (1H, m, CHO), 4.37–4.24 (1H, m, C*H*NH), 4.04 (1H, d, *J* 10.4 Hz, NH), 3.00–2.71 (2H, m, C$H_2$Ph), 2.22–2.04 (1H, m, 1×C$H_2$CHNH), 2.03–1.86 (2H, m, C$H_2CH_2$Ph), 1.63 (1H, dt, *J* 14.3, 11.9 Hz, 1×C$H_2$CHNH); trans-isomer: 7.42–7.19 (5H, m, Ph), 6.16 (1H, ddd, *J* 17.2, 10.7, 5.5 Hz, C*H*=$CH_2$), 5.41–5.25 (2H, m, CH=C$H_2$), 4.91 (1H, m, CHO), 4.54 (1H, d, *J* 6.8 Hz, NH), 4.37–4.24 (1H, m, C*H*NH), 3.00–2.71 (2H, m, C$H_2$Ph), 2.36 (1H, dtd, *J* 14.4, 9.2, 5.3 Hz, 1×C$H_2$CHNH), 2.03–1.86 (3H, m, C$H_2CH_2$Ph and 1×C$H_2$CHNH); $\delta_C$ (75 MHz, $CDCl_3$) cis-isomer: 140.4, 135.0, 128.8, 128.6, 126.5, 117.5, 83.1, 56.3, 37.1, 35.2, 30.7; trans-isomer: 140.5, 135.6, 128.7, 128.6, 126.4, 117.5, 81.9, 55.0, 36.5, 33.1, 31.1; *m*/*z* ($ESI^+$) 285 ($M+NH_4^+$, 100%), 214 (60%); HRMS ($ESI^+$) found 285.1272, $C_{13}H_{21}O_3N_2S$ $(M+NH_4)^+$ requires 285.1267.

*4.4.7. 5-Methyl-4-vinyl-1,2,3-oxathiazinane 2,2-dioxide (**5g**).* Wt 36 mg; 75%; colourless oil; major/minor 3:1: mp 113 °C; $\nu_{max}/cm^{-1}$ 3266, 2977, 1647, 1423, 1358, 1185, 919; $\delta_H$ (400 MHz, $CDCl_3$) major-isomer: 5.81–5.66 (1H, m, C*H*=$CH_2$), 5.42–5.23 (2H, m, CH=C$H_2$), 4.84 (1H, dd, *J* 11.1, 2.5 Hz, 1×$CH_2O$), 4.58–4.42 (2H, m, NH and C*H*NH), 4.33 (1H, dd, *J* 11.5, 1.9 Hz, 1×$CH_2O$), 2.00–1.79 (1H, m, C*H*$CH_3$), 1.08 (3H, d, *J* 7.2 Hz, $CH_3$); minor-isomer: 5.81–5.66 (1H, m, C*H*=$CH_2$), 5.42–5.23 (2H, m, CH=C$H_2$), 4.42–4.35 (2H, m, $CH_2O$), 3.87 (1H, dd, *J* 17.6, 9.8 Hz, C*H*NH), 2.00–1.79 (1H, m, C*H*$CH_3$), 0.89 (3H, d, *J* 6.8 Hz, $CH_3$); $\delta_C$ (101 MHz, $CDCl_3$) major-isomer: 133.9, 117.0, 77.7, 59.8, 30.8, 9.7; minor-isomer: 133.7, 120.1, 76.4, 63.4, 33.3, 12.0; *m*/*z* ($ESI^+$) 195 ($M+NH_4^+$, 100%), 187 (10%); HRMS ($ESI^+$) found 195.0794, $C_6H_{15}O_3N_2S$ $(M+NH_4)^+$ requires 195.0798.

*4.4.8. 4-Propyl-4-vinyl-1,2,3-oxathiazinane 2,2-dioxide (**5h**).* Wt 50 mg; 92%; colourless oil; $\nu_{max}/cm^{-1}$ 3263, 2963, 2876, 1641, 1407, 1354; $\delta_H$ (400 MHz, $CDCl_3$) 5.97–5.85 (1H, m, C*H*=$CH_2$), 5.30 (1H, d, *J* 11.1 Hz, 1×CH=C$H_2$), 5.12 (1H, d, *J* 17.7 Hz, 1×CH=C$H_2$), 4.73–4.64 (1H, m, 1×C$H_2$O), 4.60 (1H, ddd, *J* 11.8, 5.6, 4.0 Hz, 1×$CH_2O$), 4.28 (1H, s, NH), 2.04–1.96 (1H, m, 1×C$H_2CH_2O$), 1.91–1.81 (1H, m, 1×C$H_2CH_2O$), 1.81–1.20 (4H, m, $(CH_2)_2CH_3$), 0.91 (3H, t, *J* 7.2 Hz, $CH_3$); $\delta_C$ (101 MHz, $CDCl_3$) 139.9, 115.1, 69.2, 63.0, 43.2, 32.2, 16.2, 14.2; *m*/*z* ($ESI^+$) 223 ($M+NH_4^+$, 100%), 185 (5%); HRMS ($ESI^+$) found 223.1113, $C_8H_{19}O_3N_2S$ $(M+NH_4)^+$ requires 223.1111.

*4.4.9. 4-Hexyl-4-vinyl-1,2,3-oxathiazinane 2,2-dioxide (**5i**).* Wt 35 mg; 70%; yellow oil; $\nu_{max}/cm^{-1}$ 3264, 2956, 2931, 2859, 1642, 1407, 1356, 1186, 777; $\delta_H$ (300 MHz, $CDCl_3$) 5.91 (1H, dd, *J* 17.5, 10.8 Hz, C*H*=$CH_2$), 5.30 (1H, d, *J* 11.1 Hz, 1×CH=C$H_2$), 5.12 (1H, d, *J* 17.7 Hz, 1×CH=C$H_2$), 4.77–4.48 (2H, m, $CH_2O$), 4.16 (1H, s, NH), 2.01 (1H, m, 1×C$H_2CH_2O$), 1.92–1.70 (2H, m, C$H_2$C), 1.60–1.51 (1H, m, C$H_2CH_2O$), 1.44–1.14 (8H, m, $(CH_2)_4CH_3$), 0.88 (3H, dd, *J* 9.3, 4.2 Hz, $CH_3$); $\delta_C$ (75 MHz, $CDCl_3$) 140.0, 115.2, 69.2, 63.0, 41.1, 32.3,

31.7, 29.4, 22.8, 22.7, 14.2; *m*/*z* ($ESI^+$) 270 ($M+Na^+$, 100%); HRMS ($ESI^+$) found 270.1138, $C_{11}H_{21}O_3NNaS$ $(M+Na)^+$ requires 270.1134.

*4.4.10. 4-(Cyclohexylmethyl)-4-vinyl-1,2,3-oxathiazinane 2,2-dioxide (**5j**).* Wt 37 mg; 37%; colourless oil; $\nu_{max}/cm^{-1}$ 3381, 2921, 2850, 1557, 1449, 1348, 1176, 926; $\delta_H$ (300 MHz, $CDCl_3$) 6.00 (1H, dd, *J* 17.8, 11.1 Hz, C*H*=$CH_2$), 5.31 (1H, d, *J* 11.1 Hz, 1×CH=C$H_2$), 5.15 (1H, d, *J* 17.8 Hz, 1×CH=C$H_2$), 4.77–4.64 (1H, ddd, *J* 11.8, 9.4, 3.2 Hz, 1×$CH_2O$), 4.56 (1H, ddd, *J* 11.8, 5.0, 4.1 Hz, 1×$CH_2O$), 4.12 (1H, s, NH), 2.06–1.83 (2H, m, C$H_2CH_2O$), 1.72–1.37 (6H, m, 6×$CH_2C_6H_{11}$), 1.31–1.04 (4H, m, 4×$CH_2C_6H_{11}$), 1.04–0.82 (3H, m, 3×$CH_2C_6H_{11}$); $\delta_C$ (101 MHz, $CDCl_3$) 140.2, 115.0, 69.1, 63.4, 49.4, 35.3, 35.0, 33.3, 33.0, 26.4, 26.4, 26.1; *m*/*z* ($ESI^+$) 282 ($M+Na^+$, 100%), 278 (40%), 163 (30%); HRMS ($ESI^+$) found 260.1319, $C_{12}H_{22}O_3NS$ $(M+H)^+$ requires 260.1315.

*4.4.11. (4-(2-Benzyloxy)ethyl)-4-vinyl-1,2,3-oxathiazinane 2,2-dioxide (**5k**).* Wt 45 mg; 90%; colourless oil; $\nu_{max}/cm^{-1}$ 3247, 2874, 1703, 1496, 1455, 1407, 1358, 1187, 778; $\delta_H$ (300 MHz, $CDCl_3$) 7.47–7.26 (5H, m, Ph), 6.00 (1H, ddd, *J* 17.7, 11.0, 0.6 Hz, C*H*=$CH_2$), 5.78 (1H, s, NH), 5.34–5.12 (2H, m, CH=C$H_2$), 4.72 (1H, td, *J* 11.4, 2.4 Hz, 1×$CH_2O$), 4.60–4.41 (3H, m, 1×$CH_2O$ and PhC$H_2O$), 3.73–3.53 (2H, m, C$H_2OCH_2Ph$), 2.15–1.94 (2H, m, $CH_2CN$), 1.89–1.74 (2H, m, C$H_2$C); $\delta_C$ (75 MHz, $CDCl_3$) 140.3, 137.1, 128.7, 128.1, 128.0, 115.4, 73.5, 68.8, 65.6, 62.4, 40.1, 30.6; *m*/*z* ($ESI^+$) 315 ($M+NH_4^+$, 90%), 298 ($(M+H)^+$, 100%), 149 (25%); HRMS ($ESI^+$) found 298.1115, $C_{14}H_{20}O_4NS$ $(M+H)^+$ requires 298.1108.

*4.4.12. 4-((Benzyloxy)methyl)-4-vinyl-1,2,3-oxathiazinane 2,2-dioxide (**5l**).* Wt 33 mg; 65%; colourless oil; $\nu_{max}/cm^{-1}$ 3298, 2864, 1454, 1402, 1350, 1195, 1076, 779; $\delta_H$ (300 MHz, $CDCl_3$) 7.35–7.18 (5H, m), 5.95 (1H, ddd, *J* 17.9, 11.1, 0.9 Hz, C*H*=$CH_2$), 5.26 (1H, d, *J* 11.1 Hz, H of $CH_2$=), 5.12 (1H, d, *J* 17.9 Hz, H of $CH_2$=), 4.91 (1H, s, NH), 4.73–4.63 (1H, m, H of $CH_2OSO_2^-$), 4.55–4.37 (3H, m, H of $CH_2OSO_2^-$, 2×H of PhC$H_2O$), 3.33 (1H, roofed d, *J* 9.5 Hz, H of C$H_2$OBn), 3.19 (1H, roofed d, *J* 9.5 Hz, H of C$H_2$OBn), 2.43 (1H, ddd, *J* 13.2, 4.7, 3.8 Hz, H of C$H_2CH_2O$), 1.66 (1H, dt, *J* 13.2, 2.1 Hz, H of C$H_2CH_2O$); $\delta_C$ (75 MHz, $CDCl_3$) 137.1, 136.7, 128.7, 128.3, 128.0, 117.1, 74.3, 73.5, 68.9, 63.0, 27.1; *m*/*z* ($ESI^+$) 284 ($M+H^+$, 100%); HRMS ($ESI^+$) found 284.0955, $C_{13}H_{18}NO_4S$ $(M+H)^+$ requires 284.0951.

*4.4.13. 4-(Methoxymethyl)-4-vinyl-1,2,3-oxathiazinane 2,2-dioxide (**5m**).* Wt 22 mg; 44%; colourless oil; $\nu_{max}/cm^{-1}$ 3263, 2899, 1402, 1352, 1255, 1187, 1114, 1013, 972; $\delta_H$ (300 MHz, $CDCl_3$) 6.06 (1H, dd, *J* 17.0 11.0 Hz, C*H*=$CH_2$), 5.41–5.20 (2H, m, CH=$CH_2$), 4.95 (1H, s, NH), 4.83–4.67 (1H, m, 1×$CH_2CH_2O$), 4.55–4.42 (1H, m, 1××$CH_2CH_2O$), 3.38 (3H, s, $OCH_3$), 3.18 (2H, apparent q, *J* 9.4 Hz, C$H_2OCH_3$), 2.55–2.31 (1H, m, 1×C$H_2CH_2O$), 1.74 (1H, dt, *J* 14.7, 2.2 Hz, C$H_2CH_2O$); $\delta_C$ (75 MHz, $CDCl_3$) 137.1, 117.0, 76.8, 68.8, 63.0, 59.1, 27.1; *m*/*z* ($ESI^+$) 284 ($M+H^+$, 100%); HRMS ($ESI^+$) found 284.0955, $C_{13}H_{18}NO_4S$ $(M+H)^+$ requires 284.0951.

*4.4.14. tert-Butyl 5-methyl-4-vinyl-1,2,3-oxathiazinane-3-carboxylate 2,2-dioxide (**7**).* 5-Methyl-4-vinyl-1,2,3-oxathiazinane 2,2-dioxide (188 mg, 1.0 mmol) was dissolved in dry dichloromethane (10 mL) and di-*tert*-butyl dicarbonate (255 mg, 1.2 mmol) was added followed by pyridine (94 μL, 1.2 mmol) and dimethylaminopyridine (13 mg, 0.1 mmol). The reaction mixture was stirred for 18 h. The reaction mixture was poured into brine (10 mL) and extracted with dichloromethane (3×10 mL), dried ($Na_2SO_4$) and concentrated in vacuo. Purification by column chromatography (1:1 dichloromethane/hexane to dichloromethane) afforded the title compound. Wt 146 mg; 50%; colourless oil; $\nu_{max}/cm^{-1}$ 3266, 2976, 1647, 1424, 1360, 1187, 920; $\delta_H$ (300 MHz, $CDCl_3$) 6.02 (1H, ddd, *J* 17.2, 10.0, 8.4 Hz, C*H*=$CH_2$), 5.46–5.27 (2H, m, CH=C$H_2$), 4.75 (1H, ddd, *J* 10.9, 4.5, 0.6 Hz, 1×C$H_2O$), 4.55 (1H, ddd, *J* 10.9, 6.5, 0.9 Hz, 1×$CH_2O$), 4.30–4.16 (1H, m, CHN), 2.95–2.73 (1H, m, C*H*$CH_3$), 1.53 (9H, s, $C(CH_3)_3$), 0.98 (3H, d, *J* 7.0 Hz, CHC$H_3$); $\delta_C$ (75 MHz, $CDCl_3$); 150.4, 130.0, 121.5, 85.2, 74.5, 64.7, 31.5, 28.0, 13.4; *m*/*z* ($ESI^+$) 295 ($M+NH_4^+$, 100%), 222 (30%); HRMS ($ESI^+$) found 295.1326, $C_{11}H_{23}O_5N_2S$ $(M+NH_4)^+$ requires 295.1322.

*4.4.15. (4S,5R)-5-Methyl-4-vinyl-1,2,3-oxathiazinane 2,2-dioxide (**5g**, single diastereomer). tert*-Butyl 5-methyl-4-vinyl-1,2,3-oxathiazinane-3-carboxylate 2,2-dioxide (100 mg, 0.4 mmol) was dissolved in acetonitrile (4 mL) and water (3 mL) and was stirred at 75 °C for 24 h. After cooling to room temperature aqueous hydrochloric acid (1 M; 2 mL) and ethyl acetate (2 mL) were added and the reaction mixture stirred for 1 h, then basified with aqueous sodium hydroxide (1 M). The biphasic mixture was extracted with ethyl acetate (three times). The combined organic layer washed with brine, dried ($MgSO_4$) and concentrated in vacuo affording the title compound as a yellow oil. Crystallisation from diethyl ether afforded the title compound as a colourless solid (46 mg, 0.26 mmol, 72%): mp 112–113 °C; $\delta_H$ (300 MHz, $CDCl_3$) 5.76 (1H, ddd, *J* 17.2, 10.8, 4.3 Hz, C*H*=$CH_2$), 5.30 (1H, dd, *J* 17.2, 1.9 Hz, 1×CH=C$H_2$), 4.86 (1H, dd, *J* 10.8, 2.5 Hz, 1×CH=C$H_2$), 4.64–4.45 (1H, m, 1×$CH_2O$), 4.33 (1H, dd, *J* 11.5, 1.8 Hz, 1×$CH_2O$), 4.28–4.19 (1H, m, C*H*NH), 2.03–1.79 (1H, m, C*H*$CH_3$), 1.09 (3H, d, *J* 7.2 Hz, $CH_3$); $\delta_C$ (75 MHz, $CDCl_3$) 133.8, 116.9, 77.6, 59.7, 30.7, 9.5. Other data as above. The X-ray diffraction data have been submitted to the Cambridge Structural Database (Ref. number CCDC 898464).

*4.4.16. Hexa-4,5-dien-1-yl sulfamate (**9**).* Wt 445 mg; 48%; colourless oil; $\nu_{max}/cm^{-1}$ 3391, 3291, 2939, 1958, 1539, 1455, 1344, 1169, 895; $\delta_H$ (300 MHz, $CDCl_3$) 5.16–5.11 (1H, m, CH=), 4.92–4.66 (4H, m, $CH_2$= and $NH_2$), 4.26 (2H, t, *J* 6.4 Hz, $CH_2O$), 2.22–2.06 (2H, m, C$H_2$CH=), 1.97–1.81 (2H, m, C$H_2CH_2CH$=); $\delta_C$ (75 MHz, $CDCl_3$) 208.6, 88.5, 75.7, 70.7, 27.9, 23.9; *m*/*z* ($ESI^+$) 178 ($M+H^+$, 100%), 154 (10%), 115 (10%); HRMS ($ESI^+$) found 178.0533, $C_6H_{12}O_3NS$ $(M+H)^+$ requires 178.0533.

### 4.5. (*Z*)-Ethyl 3-vinylhexa-2,5-dienoate (12)

5-Hexen-2-yn-1-ol **4u**[61] (2.28 g, 25.5 mmol) was dissolved in triethyl orthoacetate (14.8 mL). Propionic acid (0.4 mL) was added and heated to reflux under nitrogen, with a Dean–Stark apparatus, for 5 h. Reaction mixture was allowed to cool, extracted with diethyl ether and washed with deionised water. Purification by column chromatography (20:1 petroleum ether/ethyl acetate) afforded the title compound. Wt 1.07 g; 26%; yellow tinted oil; $\nu_{max}/cm^{-1}$ 2980, 1710, 1632, 1369, 1149, 1038, 998, 914, 859; $\delta_H$ (400 MHz, $CDCl_3$) 7.69 (1H, ddd, *J* 17.7, 11.1, 0.9 Hz, $CH_2$=C*H*–C), 5.87–5.67 (1H, m, $CH_2CH$=$CH_2$), 5.62 (1H, s, =C*H*C(O)), 5.55–5.51 (1H, m, C$H_{trans}$ of alkene) 5.36 (1H, ddd, *J* 11.1, 1.6, 1.2 Hz, C$H_{cis}$ of alkene), 5.09–4.97 (2H, m, 2×C*H* of terminal alkenes superposed), 4.09 (2H, q, *J* 7.1 Hz, C$H_2O$), 3.02 (2H, apparent dq, *J* 6.6, 1.2 Hz, C–C$H_2$–CH=), 1.20 (3H, t, *J* 7.1 Hz, C$H_3$); $\delta_C$ (101 MHz, $CDCl_3$) 166.0, 152.3, 134.9, 133.1, 120.2, 118.2, 117.4, 59.8, 37.4, 14.2; *m*/*z* ($ESI^+$) 167 ($M+H^+$, 100%), HRMS ($ESI^+$) found 167.1064, $C_{10}H_{15}O_2$ $(M+H^+)$ requires 167.1067.

### 4.6. *tert*-Butyldimethyl((3-vinylidenehex-5-en-1-yl)oxy)silane (15)

5-((*tert*-Butyldimethylsilyl) oxy)pent-2-yn-1-yl 4-methylbenzenesulfonate **14**[71] (11.09 g, 30.1 mmol) was dissolved in dry THF (60 mL) under nitrogen. Copper(I) bromide (404 mg, 3 mmol) was added. 1 M Allylmagnesium bromide (11.43 mL, 11.43 mmol) was added dropwise and stirred for 2 h at room temperature. The reaction was quenched with ammonium chloride and extracted with diethyl ether. Organic layer was dried with $Na_2SO_4$ and the

solvent was evaporated. Purification by column chromatography (100% petroleum ether) afforded the title compound. Wt 6.21 g; 85%; yellow tinted oil; $\nu_{max}/cm^{-1}$ 2954, 2926, 2895, 2856, 1958, 1638, 1471, 1255, 1253, 1095, 833, 773; $\delta_H$ (300 MHz, $CDCl_3$) 5.86–5.55 (1H, m, C*H*=$CH_2$), 5.13–4.83 (2H, m, C$H_2$=CH), 4.70–4.52 (2H, m, C$H_2$=C), 3.65 (2H, t, *J* 7.2 Hz, $CH_2O$), 2.74–2.66 (2H, m, =CHC$H_2$), 2.12 (2H, tt, *J* 7.2, 3.0 Hz, C$H_2CH_2O$), 0.84 (9H, s, SiC($CH_3$)$_3$), 0.00 (6H, s, Si($CH_3$)$_2$); $\delta_C$ (75 MHz, $CDCl_3$); 206.3, 135.7, 115.9, 98.6, 75.5, 61.8, 37.4, 34.9, 25.9, 18.3, −5.3; *m*/*z* ($ESI^+$) 255 ($(M+O+H)^+$, 100%), HRMS ($ESI^+$) found 255.1775, $C_{14}H_{27}O_2Si$ $(M+O+H)^+$ requires 255.1780.

### 4.7. 3-Vinylidenehex-5-en-1-yl sulfamate (16)[70]

*tert*-Butyldimethyl((3-vinylidenehex-5-en-1-yl)oxy)silane (**15**) (1.76 g, 7.4 mmol) was in dissolved THF and 1 M TBAF (14.8 mL, 14.8 mmol) was added and stirred at room temperature for 4 h. Water was added and extracted with diethyl ether. Organic layer was dried with $Na_2SO_4$ and the solvent was evaporated giving 3-vinylidenehex-5-en-1-ol. Wt 800.9 mg; 87%, yellow tinted oil, was reacted on without purification. Formic acid (0.2 mL, 5.3 mmol) was added chlorosulfonylisocyanate (0.46 mL, 5.3 mmol) at 0 °C under $N_2$. Acetonitrile (0.4 mL) was added and allowed to come to room temperature overnight. 3-Vinylidenehex-5-en-1-ol (262.6 mg, 2.1 mmol) was added at 0 °C and stirred for 24 h allowing to come to room temperature gradually. Water was added and extracted with diethyl ether. Organic layer was dried with $Na_2SO_4$ and the solvent was evaporated. Purification by column chromatography (1:1 petroleum ether/dichloromethane) afforded the title compound. Wt 138.9 mg; 33%; caramel coloured oil; $\nu_{max}/cm^{-1}$ 3380, 3285, 3076, 2979, 2902, 1958, 1638, 1556, 1359, 1176, 973, 911; $\delta_H$ (400 MHz, $CDCl_3$) 5.82 (1H, ddt, *J* 16.9, 10.1, 6.8 Hz, C*H*=$CH_2$), 5.18–5.05 (2H, m, CH=C$H_2$), 4.99 (2H, s, N$H_2$), 4.83–4.79 (2H, m, C$H_2$=C), 4.32 (2H, t, *J* 7.0 Hz, C$H_2$O), 2.85–2.67 (2H, m, C$H_2$CH=), 2.46–2.37 (2H, m, C$H_2CH_2$O); $\delta_C$ (101 MHz, $CDCl_3$) 205.9, 135.0, 116.7, 97.1, 77.1, 69.3, 37.3, 30.5.

### 4.8. 2-(Bicyclo[3.1.0]hex-2-en-1-yl)ethyl sulfamate (17)

3-Vinylidenehex-5-en-1-yl sulfamate (**16**) (42.7 mg, 0.24 mmol) was dissolved in $CDCl_3$. [Bis(trifluoromethanesulfonyl)imidate](triphenylphosphine)gold(I) (2:1) toluene adduct (18.9 mg, 0.012 mmol) was added under $N_2$. Purification by column chromatography (1:1 petroleum ether/dichloromethane) afforded the title compound. Wt 21.5 mg; 51%; clear oil; $\nu_{max}/cm^{-1}$ 3366, 3281, 3057, 2983, 2903, 2837, 2360, 1577, 1360, 1179, 907; $\delta_H$ (400 MHz, $CDCl_3$) 5.73–5.66 (1H, m, =C*H*–$CH_2$), 5.35–5.25 (1H, m, =C*H*–C), 4.72 (2H, s, $NH_2$), 4.17 (2H, dd, *J* 7.3 6.6 Hz, C$H_2$–O), 2.51 (1H, dd, *J* 17.9, 7.0 Hz, H of allylic $CH_2$), 2.18 (1H, apparent dt, *J* 17.9, 2.4 Hz, H of allylic $CH_2$), 2.00 (1H, dt, *J* 14.5, 6.6 Hz, H of C$H_2$–$CH_2$O), 1.75 (1H, dt, *J* 14.5, 7.3 Hz, H of C$H_2CH_2$O), 1.37–1.28 (1H, m, $CH_2$C*H*$CH_2$), 0.72–0.66 (1H, m, H of cyclopropyl $CH_2$), 0.04-(-0.02) (1H, m, H of cyclopropyl $CH_2$); $\delta_C$ (101 MHz, $CDCl_3$); 135.8, 128.1, 70.8, 36.2, 32.7, 32.6, 21.9, 21.1; *m*/*z* ($ESI^+$) 221 ($(M+NH_4)^+$, 100%), HRMS ($ESI^+$) found 221.0954, $C_8H_{17}N_2O_3S$ $(M+NH_4)^+$ requires 221.0960.

### 4.9. 3-Allyl-4-propyl-4-vinyl-1,2,3-oxathiazinane 2,2-dioxide (19)

To a stirring solution of 4-propyl-4-vinyl-1,2,3-oxathiazinane 2,2-dioxide (735 mg, 3.6 mmol) in dichloromethane (26 mL) were added benzyltributylammonium bromide (64 mg, 179 μmol), allyl bromide (1.2 mL, 14.3 mmol) and sodium hydroxide solution (5 M). The reaction mixture was stirred for 24 h. Purification by column chromatography (4:1 petroleum ether/ethyl acetate) afforded the title compound. Wt 728 mg; 84%; colourless oil; $\nu_{max}/cm^{-1}$ 3087, 2964, 2876, 1642, 1379, 1352, 1175; $\delta_H$ (300 MHz, $CDCl_3$) 6.09 (1H, dd, *J* 17.7, 11.1 Hz, $CH_2$C*H*=), 5.94 (1H, dddd, *J* 17.1, 10.2, 6.2, 5.5 Hz, CC*H*=$CH_2$), 5.34–5.08 (4H, m, $CH_2$= and $CH_2$=), 4.72–4.52 (2H, m, C$H_2$O), 3.93 (1H, ddt, *J* 17.0, 5.4, 1.6 Hz, 1×$CH_2$CH=), 3.74 (1H, ddt, *J* 17.0, 6.2, 1.4 Hz, 1×$CH_2$CH=), 2.24–2.08 (1H, m, 1×C$H_2CH_2$O), 2.05–1.68 (3H, m, 1×C$H_2CH_2$O and C$H_2CH_2CH_3$), 1.51–1.19 (2H, m, C$H_2CH_3$), 0.92 (3H, t, *J* 7.3 Hz, $CH_3$); $\delta_C$ (75 MHz, $CDCl_3$) 139.3, 135.5, 117.1, 115.5, 68.5, 67.4, 48.3, 39.4, 31.3, 17.2, 14.3; *m*/*z* ($ESI^+$) 263 ($M+NH_4^+$, 70%), 246 ($M+H^+$, 100%); HRMS ($ESI^+$) found 246.1162, $C_{11}H_{20}O_3NS$ $(M+H)^+$ requires 246.1158.

### 4.10. 4-(Allylamino)-4-vinylheptanenitrile (20)

3-Allyl-4-propyl-4-vinyl-1,2,3-oxathiazinane 2,2-dioxide (100 mg, 0.41 mmol) was dissolved in dry dimethylformamide (1.4 mL) and potassium cyanide (133 mg, 2.04 mmol) was added and stirred at 40 °C for 2 days. The reaction mixture was diluted with ether (2 mL) and $H_2SO_4$ (20% aqueous; 2 mL) was added and stirred for 5 h. The mixture was neutralised with solid sodium carbonate and extracted with diethyl ether (3×5 mL). The combined organic phase was washed with water (×2), brine and concentrated in vacuo to give the title compound. Wt 61 mg; 78%; colourless oil; $\nu_{max}/cm^{-1}$ 3083, 2959, 2933, 2873, 2246, 1643, 1458, 1416, 918; $\delta_H$ (300 MHz, $CDCl_3$) 5.90 (1H, ddt, *J* 17.1, 10.2, 5.8 Hz, C*H*=$CH_2$), 5.58 (1H, dd, *J* 17.5, 10.9 Hz, C*H*=$CH_2$), 5.27–5.01 (4H, m, =$CH_2$ and =$CH_2$), 3.02 (2H, dt, *J* 5.8, 1.5 Hz, $CH_2$N), 2.32 (2H, ddd, *J* 8.3, 6.9, 1.0 Hz, $CH_2$CN), 1.95–1.63 (2H, m, C$H_2CH_2$CN), 1.54–1.08 (4H, m, C$H_2CH_2CH_3$), 0.92 (3H, t, *J* 7.2 Hz, $CH_3$); $\delta_C$ (75 MHz, $CDCl_3$) 143.0, 137.0, 120.8, 115.5, 114.9, 58.5, 44.3, 39.0, 31.5, 16.4, 14.4, 11.3; *m*/*z* ($ESI^+$) 193 ($M+H^+$, 100%); HRMS ($ESI^+$) found 193.1695, $C_{12}H_{21}N_2$ $(M+H)^+$ requires 193.1699.

### 4.11. (*E*)-*N*-(1-Allyl-5-propyl-5-vinylpyrrolidin-2-ylidene) acetamide (21)

Under an inert atmosphere (nitrogen), diisopropylethylamine (134 mg, 180 μl, 1.04 mmol) was added dropwise to 4-(allylamino)-4-vinylheptanitrile in dry dichloromethane (2.2 mL). The reaction mixture was cooled to 0 °C and acetic anhydride (32 mg, 29 μL, 0.31 mmol) was added dropwise followed by dimethylaminopyridine (32 mg, 0.26 mmol). The reaction mixture was heated to reflux for 48 h. The room temperature reaction mixture was quenched with water (2 mL) followed by $H_3PO_4$ (5% wt/v; 1 mL) and the organic layer was separated. The aqueous layer was further extracted with dichloromethane (2×5 mL) and the combined organic phase was washed with saturated sodium bicarbonate solution and dried ($Na_2SO_4$) and concentrated in vacuo. Purification by column chromatography (1:1 petroleum ether/ethyl acetate) afforded the title compound. Wt 24 mg; 43%; yellow oil; $\nu_{max}/cm^{-1}$ 2961, 2875, 1642, 1540, 1263, 1249, 990, 925; $\delta_H$ (400 MHz, $CDCl_3$) 5.90 (1H, dddd, *J* 17.1, 10.2, 6.9, 4.7 Hz, =C*H*$CH_2$N), 5.78 (1H, dd, *J* 17.4, 10.8 Hz, =C*H*C), 5.20–5.00 (4H, m, =$CH_2$ and =$CH_2$), 4.09 (1H, dd, *J* 15.3, 4.7 Hz, 1×C$H_2$N), 3.69 (1H, dd, *J* 15.3, 6.9 Hz, 1×$CH_2$N), 3.13–2.94 (1H, m, 1×$CH_2$C=N), 2.94–2.76 (1H, m, 1×$CH_2$C=N), 2.14 (3H, s, $CH_3$C=O), 1.95 (2H, t, *J* 7.9 Hz, C$H_2CH_2CH_3$), 1.72 (1H, ddd, *J* 13.7, 12.1, 5.0 Hz, 1×C$H_2$C), 1.58 (1H, ddd, *J* 13.7, 12.1, 4.4 Hz, 1×$CH_2$C), 1.43–1.05 (2H, m, C$H_2CH_3$), 0.92 (3H, t, *J* 7.3 Hz, $CH_3$); $\delta_C$ (100 MHz, $CDCl_3$) 184.3, 170.1, 140.1, 133.7, 117.1, 114.7, 69.3, 44.8, 38.9, 31.6, 29.1, 28.0, 17.0, 14.3; *m*/*z* ($ESI^+$) 235 ($M+H^+$, 100%), 194 (70%); HRMS ($ESI^+$) found 235.1806, $C_{14}H_{23}ON_2$ $(M+H)^+$ requires 235.1805.

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## Supplementary data

$^{1}$H and $^{13}$C NMR spectra for all new compounds. Crystallographic data (excluding structure factors) for *cis*-**5a** and *cis*-**5g** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 871548 and CCDC 898464, respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax:+44 (0)1223 336033 or email:deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2014.11.058.

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