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Graphical Abstract

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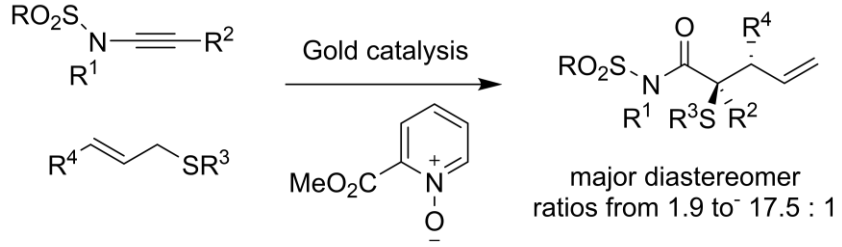

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ABSTRACT

The [2,3]-sigmatropic rearrangement of sulfonium ylides bearing substituted allyl groups creates two contiguous stereocentres. Low diastereoselectivity is typically observed from commonly used α-diazocarboxylic ester precursors. High diastereoselectivity was previously revealed in a gold-catalysed multicomponent route into allyl sulfonium ylides by reaction of ynamide, oxidant and allyl sulfides. The effect of substrate modifications on the diastereoselectivity have been studied with *N*-phenyl methanesulfonamide derived ynamides proving the most effective. This report includes an enhanced experimental procedure, and a demonstration that the gold-catalysed process remains highly effective at -78 °C.

1. Introduction

The formation and rearrangement of allyl sulfonium ylides provides a powerful, convenient and mild method for simultaneous C-C and C-*S* bond formation and the production of complex tertiary and quaternary carbon centres.[1,2] Compared with preformation of the sulfonium salt, *in-situ* ylide formation using metal carbenes and sulfides provides greatly improved practicality and applicability, and is the basis of the Doyle-Kirmse reaction which has been demonstrated across many different metal sources (Scheme 1a).[3] Several groups including ours have introduced alternative processes that ultimately see alkynes act as diazo-surrogates for the formation of allyl sulfonium ylides (Scheme 1b-g).[4] These approaches provide new opportunities for synthesis as they can access carbenoid environments that complement those available from diazo chemistry and they bypass the handling risks and synthetic inefficiencies associated with the introduction of ultimately sacrificial diazo groups.

Using substituted allyl groups in these rearrangements can produce a sulfur substituted quaternary carbon with an adjacent tertiary carbon, both potentially stereogenic (Scheme 2a).[2] The value of quaternary centres featuring sulfur atoms in biologically active molecules and natural products makes such protocols attractive.[5] Variants using sulfides featuring substituted allyl groups have focused upon enantio- and diastereocontrol.[6] The methods used for stereo induction have typically employed chiral catalysts[6a, 6c, 6e, 6h] and substrate control[4a, 6b, 6d, 6f, 6g, 6i-k] to direct the initial sulfur attack and following [2,3]-sigmatropic rearrangement through a 5-membered envelope transition states (Scheme 2b).[3c, 3e, 3f, 3h, 6a, 6b, 6e, 6f] While high enantioenrichment has been achieved, strategies that aim to provide diastereo control over the rearrangement step have been only moderately successful and are typically indifferent to the catalyst used.

Our group reported a three component process that combines an ynamide, a nucleophilic oxidant, and a sulfide under gold catalysis to access the rearrangement products from allyl sulfonium ylides (Scheme 2c).[7] High diastereocontrol was revealed when (*E*)-cinnamyl phenyl sulfide was employed in this efficient three component coupling. The observed ratio of diastereomers approaches the levels achieved with custom designed esters under asymmetric catalysis and is far in excess of those typical in similar rearrangements featuring diazocompounds.

Substrates that provide good diastereocontrol over the [2,3]-sigmatropic rearrangement would provide a route to highly complex stereoenriched products from achiral starting materials when combined with existing strategies to control the chirality of the intermediate sulfonium ylide. Diazoesters are most commonly used in these stereoselective Doyle-Kirmse reactions and increasing steric bulk on the ester group appears to be a key feature in achieving good diastereoselectivity (Scheme 2).[6j] The inherently more substituted diazoamide analogues might therefore be of value in such transformations and with ynamides functioning as readily accessible[8] diazoamide surrogates[9] we considered that they may be of wider use for stereoselective processes. However only one example of a diastereoselective reaction was produced in

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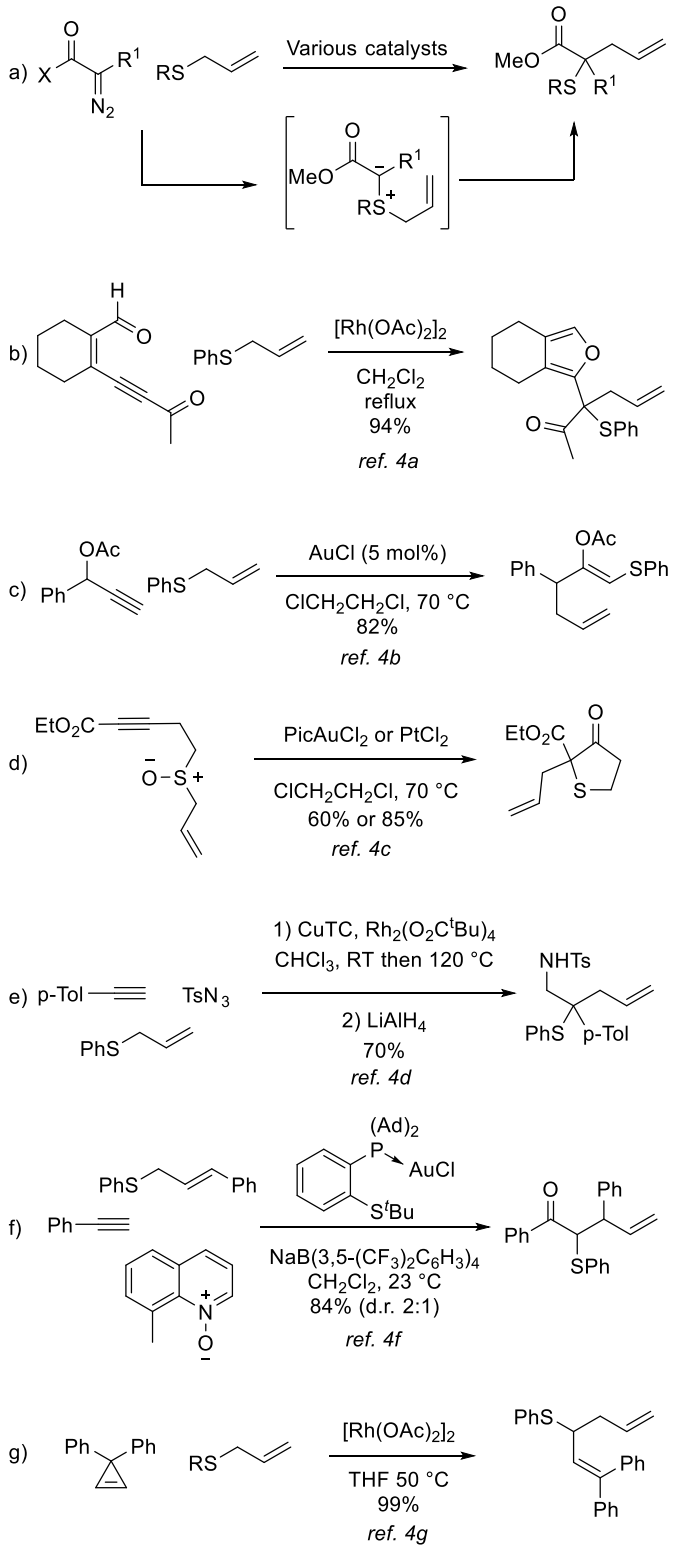
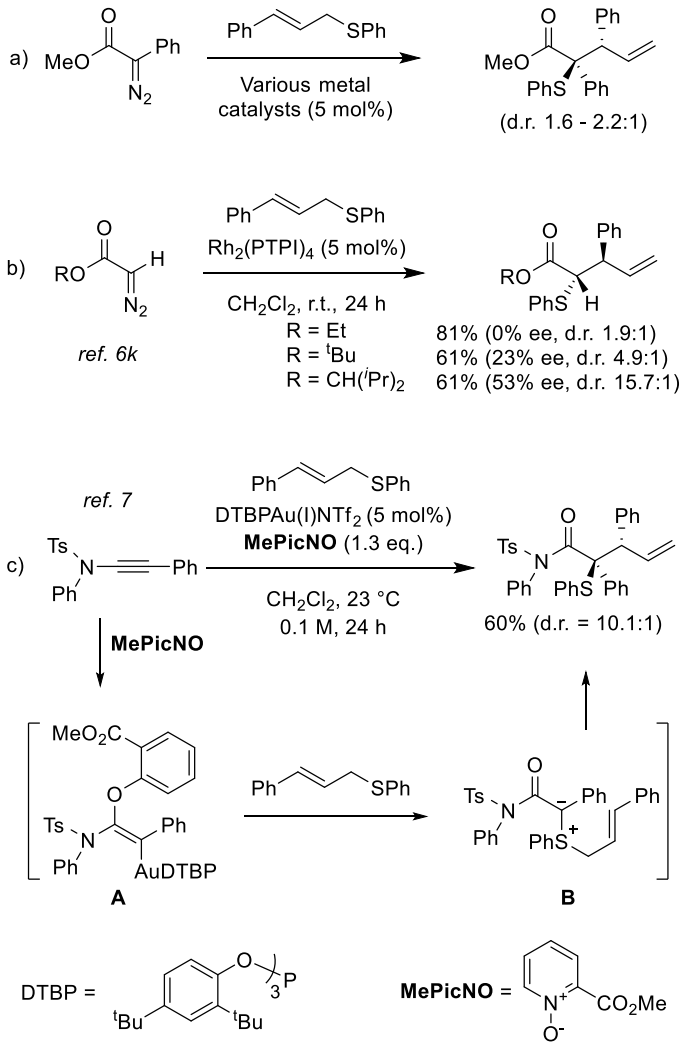
the initial study.[7] Here we report a wider investigation of the effect of structural modifications of the ynamide and sulfides on the diastereoselective gold-catalyzed three-component coupling sequence.



Scheme 1 Cascade reactions featuring the formation and rearrangement reactions of allyl sulfonium ylides.

2. Results and discussion

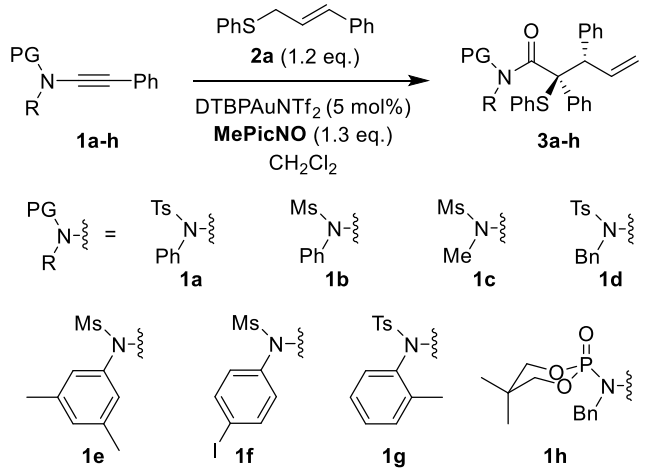
We began by varying the ynamide *N*-substituents to investigate the effect of substrate modifications on diastereoselectivity with a cinnamyl derived sulfide (Table 1). It soon became clear that while the reactions proceeded well, separating these products from residual ynamide and an oxidation byproduct was difficult and led to reduced yields of isolated products. Under the developed conditions, the three coupling reactants (ynamide, oxidant and sulfide) are employed in close-stoichiometry and added in single batches at the start of the reaction. The byproduct, an α-ketoamide,[9a, 11] arises from the nucleophilic oxidant reacting in preference to the sulfide from the electrophilic gold carbenoid **A** (Scheme 2c).



Scheme 2 Diastereoselectivity in [2,3]-sigmatropic rearrangements of sulfonium ylides.[6e, 6f, 10]

A modified protocol was developed that incorporated a slow addition of the oxidant **MePicNO** was assessed in order to maintain a relatively low concentration of oxidant in solution. Addition of the oxidant in solution over 2 h using a syringe pump was found to be generally superior in these cases, providing good yields while minimising byproducts and facilitating isolation of the desired product. For instance, using the batch addition saw reasonable yields of **3b**/**c** as determined by analysis of the ^{1}H NMR spectra against an internal standard (49% and 61% respectively, Table 1, Entries 2 and 6), but the low isolation efficiency afforded 35% and 40% yields of **3b** and **3c** respectively. However, using the slow addition afforded significantly higher isolated yields for both products (Table 1, Entries 3 and 7).

Table 1. Exploring how different ynamide substituents affect the diastereoselective Doyle-Kirmse type reaction



Entry	Ynamide	Temp (°C)	**3**	Yield (%) (Time)	d.r.[a]
1[b,c]	**1a**	23	**3a**	60	10.1:1
2[c]	**1b**	23	**3b**	61[d] (24 h)	13.0:1
3	**1b**	23	**3b**	79[e] (5 h)	13.0:1
4	**1b**	1	**3b**	77 (8 h)	15.9:1
5	**1b**	-78	**3b**	77 (9 h)	17.5:1
6[c]	**1c**	23	**3c**	49[d] (4 h)	5.6:1
7	**1c**	23	**3c**	86 (7 h)	5.6:1
8	**1d**	23	**3d**	54 (7 h)	5.5:1
9	**1e**	23	**3e**	82 (12 h)	13.1:1
10	**1f**	23	**3f**	73 (9 h)	14.2:1
11	**1g**	23	**3g**	38 (5 h)	2.1:1
12	**1h**	23	**3h**	- (6 h)[f]	n/a

Reaction conditions: ynamide (0.2 mmol), sulfide **2a** (0.24 mmol) and catalyst (5 mol%) were dissolved in dry CH_2Cl_2 (1.0 mL) held at the specified temperature before the addition of oxidant **Ox** (0.26 mmol) as a solution in CH_2Cl_2 (1.0 mL) via syringe pump over 2 h, the reaction was then stirred for the remainder of the reaction time indicated. Major isomer shown, see Fig. 1.

[a] Diastereomeric ratio determined from ^{1}H NMR of crude reaction mixture.

[b] Comparative result from ref. 7.

[c] All reagents combined in CH_2Cl_2 (0.1 M) without slow addition of **MePicNO**.

[d] NMR yield calculated using 1,2,4,5-tetramethylbenzene as the internal standard.

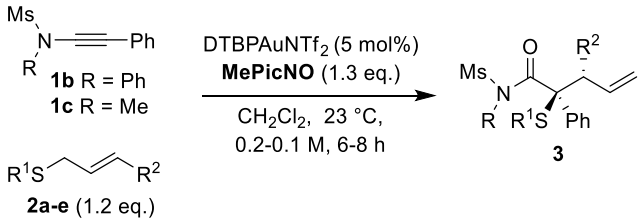
[e] At 0.4 mmol of **1b** 86% of **3b** was isolated after 14 h reaction time.

[f] No product observed although all of **1h** was consumed.

Changing from a tosyl to a mesyl substituent increases diastereoselectivity (Table 1, Entries 1 and 2). Methyl and benzyl substituents gave worse outcomes than a phenyl group (Entries 3, 7, and 8). Increasing the size of the aromatic group with meta- and para-substitution was productive, but an ortho-substituted *N*-aryl group led to substantially reduced selectivity and reaction efficiency (Table 1, Entries 9-11). The phosphoramide derivative **1h** proved unreactive.

Lower reaction temperatures led to higher diastereomeric ratios and without any significant effect on the efficacy of the catalysis reaction even at -78 °C (Table 1, Entries 3-5).

Table 2. Exploring the interplay between sulfides and ynamides in the diastereoselective Doyle-Kirmse type reaction



Entry	**2**	R	R^1	R^2	**3**	Yield (%) (Time)	d.r.[a]
1	**2a**	Ph	Ph	Ph	**3b**	79 (6 h)	13.0:1
2	**2b**	Ph	Cy	Ph	**3i**	56 (8 h)	12.3:1
3	**2c**	Ph	Bn	Ph	**3j**	61 (8 h)	5.6:1
4	**2d**	Ph	Et	Ph	**3k**	59 (8 h)	7.2:1
5	**2d**	Me	Et	Ph	**3l**	78 (8 h)	1.9: 1
6	**2e**	Ph	Ph	^{n}Pr	**3m**	81 (5 h)	5.7:1[b]
7	**2e**	Me	Ph	^{n}Pr	**3n**	81 (6 h)	3.6:1

Reaction conditions: ynamide (0.2 mmol), sulfide (0.24 mmol) and catalyst (5 mol%) were dissolved in dry CH_2Cl_2 (1.0 mL) held at 23 °C before the addition of oxidant **MePicNO** (0.26 mmol) as a solution in CH_2Cl_2 (1.0 mL) via syringe pump over 2 h, the reaction was then stirred for the remainder of the reaction time indicated.

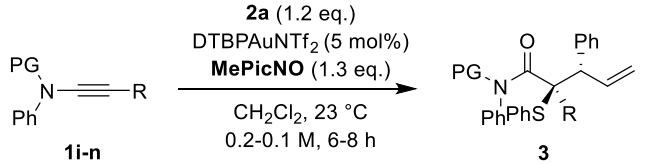
[a] Diastereomeric ratio determined from NMR of crude reaction mixture.

[b] Lowering the temperature to 0°C provided no increase in d.r..

Changing the non-migrating substituent on the sulfide reactant saw a mild loss in selectivity going from phenyl to cyclohexyl, and a significant reduction with benzyl and ethyl substituents (Table 2, Entries 1-4). Replacing the phenyl substituent on the migrating group with an isopropyl group saw an erosion of the d.r. which was insensitive to improvement by lowering the reaction temperature (Table 2, Entry 6). The influence of the ynamide *N*-substituent remained pronounced across these modified allyl sulfides, with methyl substituents leading to substantially lower diastereoselectivity than seen with phenyl groups (Table 2, Entries 5 and 7 vs. 4 and 6).

A range of ynamides with different groups covering steric and electronic variety at the C-terminus were then employed in the reaction. Interestingly the addition of a *para*- or *meta*-bromo substituent leads to a significant increase in the observed diastereoselectivity (Table 3, Entries 2-3). However no coupling product was seen with the ortho-bromo isomer **1k**, suggesting the limit of steric encumbrance has been surpassed. No desired product was seen with the ester-substituted ynamide **1m** with only the product matching double oxidation identified.[9a, 11] Terminal ynamide **1n** reacted was tolerated and gave good diastereoselectivity, for instance when compared to that obtained with the same sulfide using a three component coupling from phenyl acetylene (cf. Scheme 1f).[4f]

Table 3. The effect of different alkyne C-substituents on the reaction with (*E*)-cinnamyl phenyl sulfide.



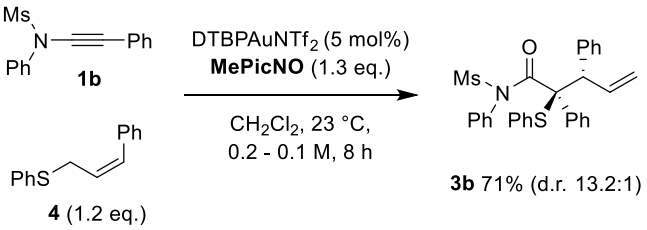
Entry	1	PG	R	3	Yield (%) (Time)	d.r.[a]
1	**1i**	Ms	*p*-ClC_6H_4	**3o**	82 (5 h)	13.2:1
2	**1j**	Ms	*p*-BrC_6H_4	**3p**	87 (6 h)	15.2:1
3	**1k**	Ms	*m*-BrC_6H_4	**3q**	63 (6 h)	16.8:1
4	**1l**	Ms	*o*-BrC_6H_4	**3r**	-[b]	-
5	**1m**	Ts	CO_2Et	**3s**	-[b]	-
6	**1n**	Ts	H	**3t**	38 (6 h)	5.9:1

Reaction conditions: ynamide (0.2 mmol), sulfide (0.24 mmol) and catalyst (5 mol%) were dissolved in dry CH_2Cl_2 (1.0 mL) held at 23 °C before the addition of oxidant **MePicNO** (0.26 mmol) as a solution in CH_2Cl_2 (1.0 mL) via syringe pump over 2 h, the reaction was then stirred for the remainder of the reaction time indicated.

[a] Diastereomeric ratio determined from NMR of crude reaction mixture.

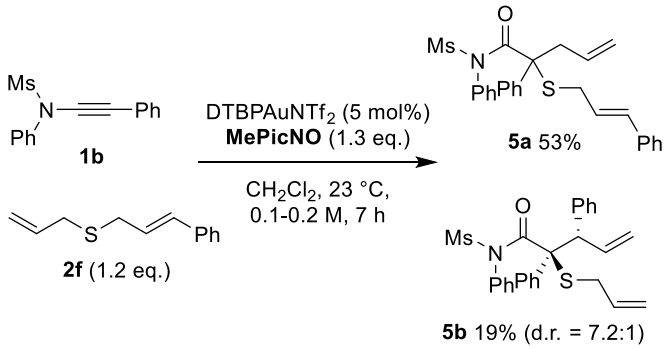
[b] Only starting material and double oxidation product observed.

The reaction with (*Z*)-cinnamyl phenyl sulfide **4** produced the same major diastereomer of **3b** as with (*E*)-cinnamyl phenyl sulfide **2a** with very similar selectivity (Scheme 3).[6b]



Scheme 3. Reaction with (*Z*)-cinnamyl sulfide

Allyl (*E*)-cinnamyl sulfide **5** was then subjected to our standard reaction conditions (Scheme 4). The unsubstituted allyl group underwent preferential rearrangement over the cinnamyl group, affording **5a** in a 2.8:1 ratio to **5b**. The diastereomeric ratio of the minor product is similar to that observed from methyl or benzyl sulfides **2c**/**d** (Table 2, Entries 3 and 4).



Scheme 4. Use of an unsymmetrical bis-allyl sulfide in the three component coupling reaction

Analysis of the X-ray crystal structure of **3p**, reveals an *anti* (R/S, S/R) stereochemical relationship which was inferred for all other products (Figure 1).

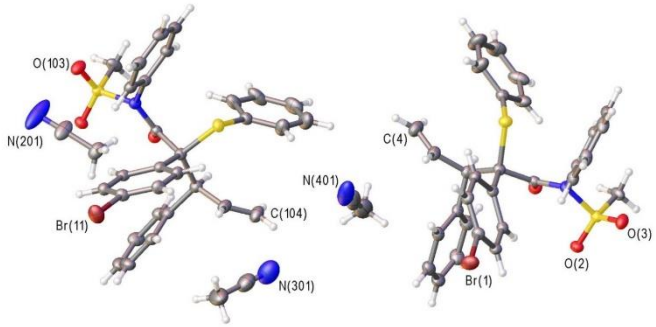


Figure 1. X-ray crystal structure of **3p** with ellipsoids drawn at the 50% probability level. The structure contains two crystallographically independent molecules with three molecules of acetonitrile per two molecules.

The preferential formation of **5a** over **5b** confirms the increased steric resistance resulting arising from the cinnamyl substituent. Analysis of the four diastereomeric envelope transition states **C** to **F** (Figure 2) identifies that the favoured *anti* configuration could derive from states **C** and **E** which differ only through the configuration of the sulfur atom and in which interactions between amide and alkene substituent are minimized relative to their gauche relationship in states **B** and **D**. For the reaction of *tert*-butyldiazoacetate and (*E*)-cinnamyl substituted sulfide **2a** Fukada et al. calculated that state **C** was the lowest energy transition state when R is a *tert*-butoxy group and R^1 is a proton.[6b] With a more heavily substituted system, the preference between **A** and **C** is less clear. That both *E* and *Z* cinnamyl sulfides afford essentially the same outcome supports that the dominant role is avoidance of the steric clash between the cinnamyl group's phenyl ring and the *N*-sulfonyl amide formed through oxidation of the ynamide. However, the observed diastereoselectivity across the structural changes outlined above, shows that all positions can influence the outcome and that ordering across all the positions is important. Ortho-substituted aryl groups that enforce a twist around critical aryl-substituent axes play a critical role, affecting both stereoselectivity as well as the viability of the desired transformation, potentially by raising the energy of the pathway to C-C bond formation sufficiently to see competing oxidation of the gold carbene to take precedent.

The highly congested nature of these compounds is apparent in their ^1H and ^{13}C NMR spectra. Significant broadening is observed in resonances related to aryl substituents appending *N* or the quaternary C α to the sulfonyl imide.[7] A similar effect is not present in the products previously obtained from unsubstituted allyl sulfides. The impact of this congestion on the reactivity of the potentially useful *N*-sulfonyl amide[ref] was tested by comparison to the simple allylated analogue **6**, which was prepared on 3.0 mmol scale using the established protocol.

Both **6** and **2b** underwent smooth reduction with $LiAlH_4$ to give the primary alcohols **7** and **8**, with THF required with **2b** to aid solubility. In contrast different outcomes were observed on reaction with allyl magnesium bromide. The addition product, tertiary alcohol **9**, was obtained from the less substituted **6**. In contrast the demesylated amide **10** was observed on reaction with **2c**, presumably as a consequence of the amide being inaccessible (Scheme 6). Loss of the methanesulfonyl substituent alleviates the steric congestion, with the severe broadening observed in the NMR spectra of **2c** not being observed in the NMR spectra of **10**.

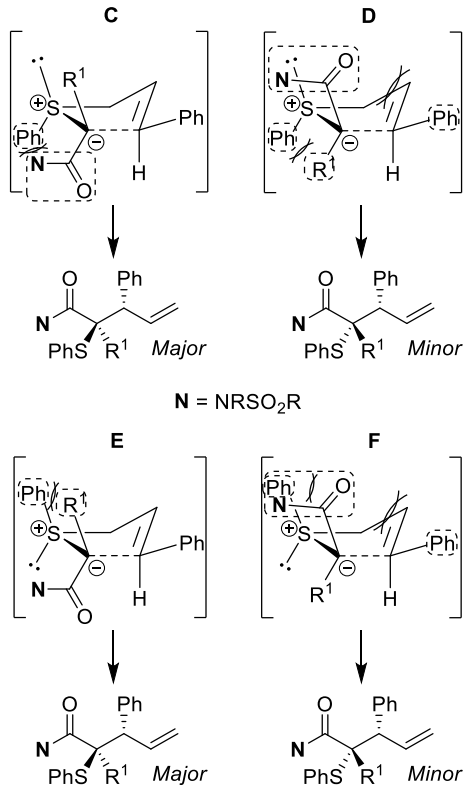
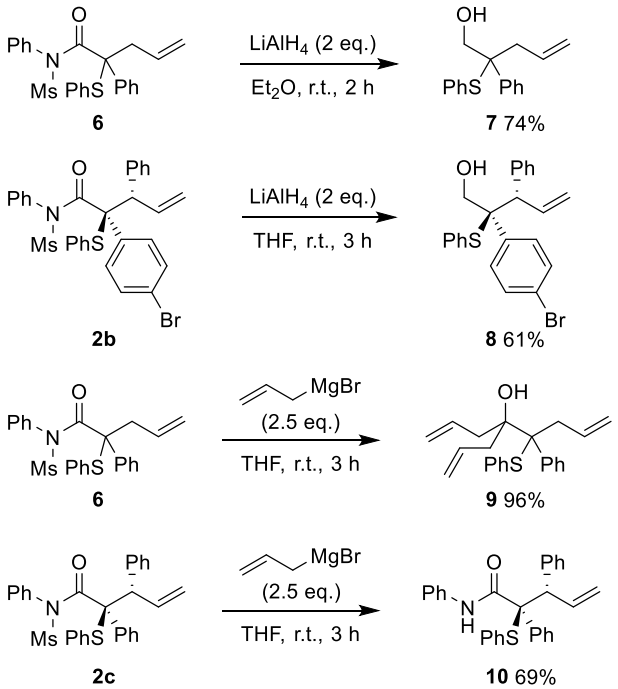


Figure 2. Model for diastereocontrol with clashing groups highlighted and the configurations of the major pair of isomers indicated.



Scheme 6 Reactions of the homoallylic sulfide products.

3. Conclusion

The fully intermolecular coupling between an ynamide, an oxidant and an allyl sulfide which leads to a C-O, C-S and C-C bond forming sequence has been studied in reactions that lead to the formation of two new stereogenic centres in the α-sulfido amide products. The experimental method has been refined to allow for higher yield and simpler recovery of the desired products. The effect of changing substitutes across the sulfide and the ynamide have been explored. These gold catalyzed oxidation reactions of ynamides were found to be highly productive even at cryogenic temperatures. The resulting products are demonstrated to have considerable steric congestion, speaking to the assembly potential of the three component approach. Notably a simple *N*-methanesulfonyl-phenyl substitution pattern on the ynamide delivers very high diastereoselectivity relative to that achieved from α-diazoesters under substrate control. This study highlights the potential of using *N*-sulfonyl amide motifs more widely, and in place of the ubiquitous esters, when bulky substituents can be beneficial for diazo based transformations.

Acknowledgements

We acknowledge the University of Birmingham and the EPSRC for financial support (DTP studentship to JDP). The authors gratefully acknowledge support from the Centre for Chemical and Materials analysis in the School of Chemistry and Dr Louise Male (XRD).

Dedicated to the memory of Professor Jonathan Williams whose scientific contributions in the field of transition metal catalysis. and character, were an inspiration.

4. Experimental Section

4.1. General details

Commercially available solvents and reagents were used without further purification unless otherwise stated. CH_2Cl_2, CH_3CN, PhMe, MeOH, Et_2O and tetrahydrofuran (THF) were purified *via* an Innovative Technology PureSolv-EN™ solvent purification system. Commercially supplied 1,4-dioxane, and *N*,*N*-dimethylformamide (DMF) were freshly dried over Linde type 3 or 4 Å molecular sieves and degassed before use. Argon was used as the inert atmosphere and all reactions were stirred using PTFE coated magnetic stir bars unless stated otherwise. Cooling bath mixture, ice/water (0–1 °C), dry ice/CH_3CN (-40 °C) or dry ice/acetone (-78 °C), a temperature probe controlled stirrer hotplate and paraffin oil bath were employed for all other temperatures. Thin layer chromatography (TLC) was carried out on Merck-Kiesegel $60F_{254}$ aluminium backed SiO_2 plates with visualisation by UV_{254} and heat developed $KMnO_4$, *p*-anisaldehyde or vanillin stain. Merck Gelduran 60 (40-63 μm particle size) SiO_2 was utilised for flash column chromatography with the eluent specified. Melting points were measured on a Stuart Scientific melting point machine and are quoted without correction. NMR spectra were recorded on a Brüker AVIII300 or AVIII400 machine, in the indicated TMS free solvent at 298 K. Chemical shifts presented in ppm, coupling constants (*J*) in Hz, and multiplicities are expressed in the standard format (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, dd = doublet of doublets, m = multiplet, br. = broad, obs. = obscured, app. = apparent). $CDCl_3$ (Sigma-Aldrich) and d_6 DMSO (Goss Scientific) used as solvent with spectra calibrated from residual solvent peaks relative to TMS, for $CHCl_3$ ^1H (7.26 ppm resonance) and ^{13}C (77.00 ppm resonance). ^{13}C spectra were recorded using the UDEFT pulse sequence from the Brüker pulse program library. ^{13}C DEPT and 2D COSY, HSQC and HMBC spectra were recorded as necessary for assignment. IR spectra were completed on a Perkin-Elmer 100 FT-IR spectrometer with ATR attachment, all significant peaks are reported in cm^{-1}. HR-MS spectra were obtained using Waters LCT (ES), Water Synapt (ES)) or Waters Xevo G2-XS (ES) spectrometers, using a lock-mass to adjust the calibrated mass scale. Ynamides **1a**,[7] **1b**,[12] **1c**,[13] **1d**,[8a] **1h**,[14] **1m**,[15] **1n**,[8f] prepared as reported, sulfides were prepared from the corresponding thiol (**2a-e**)[4b, 16] or thioate (**2f**)[17] and alkyl bromide or from the activated alcohol (**4**).[6b] Alkynes for the novel ynamides were prepared from the precursor aldehyde using the Bestmann-

Ohira reagent.[18] **1e-g**, **1i-l** and **2f** were prepared as reported below. **MePicNO** and **3a** were prepared as previously reported.[7]

*4.2. General procedure for the $CuCl_2$ based coupling of alkynes and sulfonamides to form ynamides **1e**, **1f**, **1i-l***

Following a literature method.[19] In a flame dried 500 mL 3-necked flask originally filled with argon, was added the sulfonamide (5.0 eq.), $CuCl_2$ (0.2 eq.) and Na_2CO_3 (2.0 eq.) before purging the flask with O_2 for 15 mins. Pyridine (2.0 eq.) was then added as a solution in dry PhMe (0.2 M) and the mixture was heated to 70 °C for 15 mins while maintaining an O_2 atmosphere with a balloon. The alkyne (1.0 eq.) was then added as a solution in dry PhMe (0.2 M) by syringe pump over 4 h and following complete addition the reaction mixture was held at 70 °C and typically stirred overnight (total reaction time indicated in each case). The reaction mixture was then cooled to r.t. and vacuum filtered through a pad of celite, eluted with CH_2Cl_2, and the filtrate obtained concentrated by rotary evaporation under reduced pressure. The crude residue produced was then purified as described in each case.

*4.2.1. N-(3,5-Dimethylphenyl)-N-(phenylethynyl)methanesulfonamide (**1e**).* Following general procedure **4.2** (16 h) using *N*-(3,5-dimethylphenyl)methanesulfonamide (1.3 g, 6.5 mmol)[20] and phenylacetylene (0.15 mL, 1.4 mmol), purified by SiO_2 flash column chromatography (^{n}hexane:EtOAc [9:1–4:1]) to give **1e** as a white solid; mp: 84–85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.42 (m, 2H), 7.34–7.29 (m, 3H), 7.18 (s, 2H), 7.01 (s, 1H), 3.17 (s, 3H), 2.36 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.4, 138.4, 131.5, 130.2, 128.3, 128.1, 123.4, 122.4, 82.3, 70.6, 36.9, 21.3; IR (neat): ν_{max} 3018, 2934, 2243, 1610, 1592, 1470, 1445, 1363, 1336, 1316, 1283, 1166, 1154, 1086, 1070, 1018, 959, 944, 856, 801, 755, 687 cm^{-1}; HR-MS (ESI-TOF): *m/z* calcd for $C_{17}H_{17}NO_2SNa$: 322.0878 found 322.0881 $[M+Na]^+$.

*4.2.2. N-(4-Iodophenyl)-N-(phenylethynyl)methanesulfonamide (**1f**).* Following general procedure **4.2** (16 h) using *N*-(4-iodophenyl)methanesulfonamide (1.5 g, 5.0 mmol)[9d] and phenylacetylene (0.11 mL, 1.0 mmol), purified by SiO_2 flash column chromatography (^{n}hexane:EtOAc [9:1–4:1]) to give **1f** as a white solid; mp: 75-76 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.74 (m, 2H), 7.47–7.42 (m, 2H), 7.36–7.30 (m, 5H), 3.16 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 138.5, 131.6, 128.4, 128.4, 127.1, 121.9, 93.4, 81.3, 71.6, 37.0; IR (neat): ν_{max} 3031, 2930, 2240, 1598, 1477, 1398, 1358, 1329, 1200, 1163, 1115, 1099, 1071, 1056, 1024, 1007, 966, 898, 823, 778, 755, 747, 688 cm^{-1}; HR-MS (EI-TOF): *m/z* calcd for $C_{15}H_{12}O_2SINa$: 419.9531 found 419.9533 $[M+Na]^+$.

*4.2.3. N-((4-Chlorophenyl)ethynyl)-N-phenylmethanesulfonamide (**1i**).* Following general procedure **4.2** (8 h) using *N*-phenylmethanesulfonamide (1.27 g, 7.42 mmol)[20-21] and 1-chloro-4-ethynylbenzene (197 mg, 1.44 mmol),[18a] further purified by flash SiO_2 column chromatography (^{n}hexane:EtOAc [9:1–4:1]). **1i** was obtained as a white solid (385 mg, 87%); mp: 111–112 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.5 Hz, 2H), 7.48–7.43 (m, 2H), 7.41–7.35 (m, 3H), 7.31–7.27 (m, 2H), 3.16 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 134.2, 132.7, 129.6, 128.7, 128.5, 125.6, 120.8, 82.9, 69.9, 37.0; IR (neat): ν_{max} 2241, 1592, 1488, 1354, 1329, 1160, 1090, 1076, 1029, 1013, 967, 934, 905, 844, 824, 796, 763, 749, 696, 680 cm^{-1}; HR-MS (ESI-TOF): *m/z* calcd for $C_{15}H_{12}NO_2SClNa$: 328.0175 found 328.0170 $[M+Na]^+$.

*4.2.4. N-((4-Bromophenyl)ethynyl)-N-phenylmethanesulfonamide (**1j**).* Following general procedure **4.2** (15 h) using *N*-phenylmethanesulfonamide (1.89 g, 11.0 mmol)[20-21] and 1-bromo-4-ethynylbenzene (372 mg, 2.05 mmol),[18a] further purified by flash SiO_2 column chromatography (^{n}hexane:EtOAc [9:1–4:1]). **1j** was obtained as a white solid (481 mg, 65%); mp: 113–114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.55 (m, 2H), 7.49–7.42 (m, 4H), 7.41–7.36 (m, 1H), 7.32–7.28 (m, 2H), 3.16 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 132.9, 131.6, 129.6, 128.5, 125.6, 122.4, 121.3, 83.0, 70.0, 37.0; IR (neat): ν_{max} 3007, 2926, 2235, 1590, 1486, 1458, 1395, 1349, 1332, 1206, 1158, 1081, 1027, 1011, 971, 937, 908, 835, 818, 795, 766, 746, 695, 677 cm^{-1}; HR-MS (ESI-TOF): *m/z* calcd for $C_{15}H_{13}NO_2S^{79}Br$: 349.9850 found 349.9847 $[M+H]^+$.

*4.2.5. N-((3-Bromophenyl)ethynyl)-N-phenylmethanesulfonamide (**1k**).* Following general procedure **4.2** (15 h) using *N*-phenylmethanesulfonamide (1.93 g, 11.3 mmol)[20-21] and 1-bromo-3-ethynylbenzene (401 mg, 2.22 mmol),[18a, 22] further purified by flash SiO_2 column chromatography (^{n}hexane:EtOAc [9:1–4:1]). **1k** was obtained as a pale yellow oil (686 mg, 88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (app. t, *J* = 1.7 Hz, 1H), 7.59–7.54 (m, 2H), 7.49–7.42 (m, 3H), 7.42–7.35 (m, 2H), 7.18 (t, *J* = 7.9 Hz, 1H), 3.16 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 134.0, 131.2, 129.9, 129.8, 129.6, 128.5, 125.6, 124.3, 122.1, 83.3, 69.7, 37.1; IR (neat): ν_{max} 3020, 2240, 1733, 1591, 1555, 1490, 1476, 1412, 1365, 1323, 1203, 1165, 1080, 1064, 959, 924, 895, 814, 782, 748, 692, 680, 667, 659 cm^{-1}; HR-MS (ESI-TOF): *m/z* calcd for $C_{15}H_{12}NO_2S^{79}BrNa$: 371.9670 found 371.9673 $[M+Na]^+$.

*4.2.6. N-((2-Bromophenyl)ethynyl)-N-phenylmethanesulfonamide (**1l**).* Following general procedure **4.2** (14 h) using *N*-phenylmethanesulfonamide (1.67 g, 9.75 mmol)[20-21] and 1-bromo-2-ethynylbenzene (345 mg, 1.91 mmol),[18a, 22] further purified by flash SiO_2 column chromatography (^{n}hexane:EtOAc [9:1–4:1]). **1l** was obtained as a pale yellow oil (387 mg, 58%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.9 Hz, 2H), 7.59 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.46 (app. t, *J*= 7.9 Hz, 3H), 7.41–7.36 (m, 1H), 7.26 (td, *J* = 7.9, 0.9 Hz, 1H), 7.16 (td, *J* = 7.9, 1.7 Hz, 1H), 3.22 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 133.1, 132.3, 129.5, 129.3, 128.4, 127.1, 125.6, 125.6, 124.6, 86.2, 70.3, 36.9; IR (neat): ν_{max} 3012, 2930, 2240, 1592, 1490, 1474, 1433, 1364, 1321, 1203, 1166, 1087, 1034, 1025, 958, 923, 893, 790, 746, 691, 674, 652 cm^{-1}; HR-MS (ESI-TOF): *m/z* calcd for $C_{15}H_{13}NO_2S^{79}Br$: 349.9850 found 349.9849 $[M+H]^+$.

4.2.7. *4-Methyl-N-(phenylethynyl)-N-(o-tolyl)benzenesulfonamide (**1g**).* In a flame dried Schlenk tube under argon *N*-(1,2-dichlorovinyl)-4-methyl-*N*-(o-tolyl)benzenesulfonamide (714 mg, 2.00 mmol)[23] was dissolved in dry THF (5.0 mL) and cooled to -78 °C before the addition of ^{n}BuLi (1.6 M in hexanes, 1.50 mL, 2.4 mmol) dropwise, the reaction mixture was then warmed to -40 °C and stirred for 30 mins before cooling again to -78 °C. ^{n}BuLi (1.6 M in hexanes, 1.25 mL, 2.0 mmol) was then added dropwise, following complete addition the reaction mixture was warmed to -40 °C and stirred for a further 30 mins. The reaction mixture was held at -40 °C and diluted with dry THF (5.0 mL) before the addition of anhydrous $ZnBr_2$ (543 mg, 2.41 mmol), the reaction mixture was then allowed to warm to r.t. and stirred for 30 mins. The solution obtained was then transferred by syringe and added dropwise to a stirred solution of $Pd_2(dba)_3$ (88.8 mg, 97.0 μmol.), PPh_3 (105 mg, 0.400 mmol) and PhI (0.27 mL, 2.4 mmol) in dry THF (15 mL) in a pre-prepared flame dried 3-necked round bottomed flask under argon, following complete addition the reaction mixture was stirred at r.t. for 20 h. The reaction mixture was then concentrated by rotary evaporation and the residue obtained purified by SiO_2 column chromatography (^{n}hexane:EtOAc [19:1–9:1]) and recrystallisation (^{n}hexane). **1g** was obtained as an off-white solid (294 mg, 41%); mp: 96–98 °C °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.38–7.33 (m, 4H), 7.30–7.26 (m, 5H), 7.18–7.12 (m, 1H), 6.96 (d, *J* = 7.8 Hz, 1H), 2.48 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (101 MHz,

$CDCl_3$) δ 144.9, 137.8, 137.5, 134.3, 131.6, 131.4, 129.6, 129.3, 128.4, 128.2, 128.1, 127.8, 126.7, 122.9, 83.3, 69.4, 21.7, 18.0; IR (neat): ν_{max} 3025, 2237, 1651, 1597, 1488, 1444, 1365, 1304, 1172, 1158, 1118, 1089, 1070, 1044, 1027, 918, 812, 760, 713, 693, 675, 652 cm^{-1}. Spectroscopic data in accordance with the literature.[9d]

4.3. General procedure for gold catalyzed reaction of ynamides.

In a flame dried 2-necked round bottomed flask held under an argon atmosphere the ynamide (0.200 mmol, 1.0 eq.) was dissolved in anhydrous CH_2Cl_2 (1.0 mL). The relevant allyl sulfide (0.240 mmol, 1.2 eq.) and $DTBPAuNTf_2$ (11.2 mg, 9.97 μmol., 5 mol%) were added and the reaction mixture stirred, held in a temperature controlled 23 °C oil bath, or alternatively the appropriate cooling bath. 2-(Methoxycarbonyl)pyridine 1-oxide (**MePicNO**) (39.8 mg, 0.260 mmol, 1.3 eq.) was then added as a solution in anhydrous CH_2Cl_2 (1.0 mL) by syringe pump over 2 h, unless stated otherwise. Following the complete addition of **MePicNO** the reaction mixture was stirred at the stated temperature until TLC revealed complete consumption of the starting material or until the reaction appeared to progress no further. The reaction mixture was then filtered through a cotton wool plugged pipette containing a short column of SiO_2 eluting with CH_2Cl_2 to remove any catalyst residues; the filtrate was concentrated under reduced pressure and the crude residue was further purified by SiO_2 flash column chromatography as described in each case.

*4.3.1. N-(Methylsulfonyl)-N,2,3-triphenyl-2-(phenylthio)pent-4-enamide (**3b**).* Following general procedure **4.3** using **1b** (54.9 mg, 0.202 mmol) with sulfide **2a** at either 23 °C (5 h), 1 °C (8 h) or -78 °C (9 h); further purified by flash SiO_2 column chromatography (^{n}hexane:EtOAc [9:1–4:1]). **3b** was isolated as a mixture of diastereomers (d.r. from crude reaction mixture using **2a** at 23 °C was 13.0:1; at 1 °C was 15.9:1 and at -78 °C was 17.5:1), NMR data is provided for the major diastereomer only. **3b** was obtained as a colourless solid; isolated yield when performed with **2a** at 23 °C (59.6 mg, 79%); mp: 71–72 °C; ^{1}H signals featured very significant broadening in the aromatic region, a very broad 1H signal appeared from 6.2 -5.8 ppm, a feature of many of these compounds. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.71 (m, 2H), 7.48–7.30 (m, 3H), 7.26 (t, *J* = 7.4 Hz, 2H), 7.06–6.91 (m, 7H), 6.89–6.79 (m, 2H), 6.79–6.74 (m, 2H), 5.98 (ddd, *J* = 17.1, 10.2, 9.3 Hz, 1H), 5.03 (dd, *J* = 10.2, 1.0 Hz, 1H), 4.67 (d, *J* = 17.1 Hz, 1H), 4.29 (d, *J* = 9.3 Hz, 1H), 3.47 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 141.0, 137.1, 135.7, 133.9, 133.3, 132.8, 132.0, 130.2, 129.9, 129.5, 128.9, 128.8 (2C), 128.3, 127.2, 126.7, 126.5, 117.3, 66.3, 53.9, 42.3; IR (neat): ν_{max} 3060, 3031, 1681, 1594, 1582, 1491, 1475, 1452, 1351, 1318, 1245, 1187, 1151, 1075, 1027, 1004, 962, 934, 911, 749, 692 cm^{-1}; HR-MS (ESI-TOF): *m/z* calcd for $C_{30}H_{27}NO_3S_2Na$: 536.1330 found 536.1320 $[M+Na]^+$. Alternatively as a modification to procedure **4.3**, **1b** (41.1 mg, 0.150 mmol), sulfide **4** (40.3 mg, 0.178 mmol), and $DTBPAuNTf_2$ (8.5 mg, 7.6 μmol.) were dissolved in CH_2Cl_2 (0.75 mL). **MePicNO** (30.1 mg, 0.197 mmol) added over 2h as a solution in CH_2Cl_2 (0.75 mL), reaction time 8h at 23 °C, purified by flash SiO_2 column chromatography (^{n}hexane:EtOAc [9:1–17:3]). **3b** was isolated as a mixture of diastereomers (d.r. from crude reaction mixture 13.2:1), colourless solid (54.8 mg, 71%), data as above.

*4.3.2. N-Methyl-N-(methylsulfonyl)-2,3-diphenyl-2-(phenylthio)pent-4-enamide (**3c**).* Following general procedure **4.3** using **1c** (41.8 mg, 0.200 mmol) with sulfide **2a** for 4 h; further purified by flash SiO_2 column chromatography (^{n}hexane:EtOAc [9:1–4:1]). **3c** was isolated as a mixture of diastereomers (d.r. from crude reaction mixture 5.6:1), NMR data is provided for the major diastereomer only. **3c** was obtained as a colourless solid (31.3 mg, 35%); mp: 246–247 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68–7.60 (m, 2H), 7.51–7.08 (m, 7H), 7.07–7.00 (m, 1H), 6.97 (t, *J* = 7.4 Hz, 2H), 6.63 (d, *J* = 7.3 Hz, 2H), 6.47–6.35 (m, 1H), 6.57–5.99 (m, 1H), 5.27 (dd, *J* = 10.4, 1.0 Hz, 1H), 5.05 (d, *J* = 17.1 Hz, 1H), 4.50 (d, *J* = 9.4 Hz, 1H), 3.09 (s, 3H), 2.91 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 140.7, 137.8, 136.5, 135.9, 134.4, 131.3, 130.3, 129.6, 129.1, 128.4, 128.0, 126.8, 126.4, 117.8, 67.3, 54.4, 41.9, 34.9; IR (neat): ν_{max} 3060, 2934, 1676, 1581, 1491, 1439, 1340, 1318, 1266, 1156, 1100, 965, 931, 899, 883, 751, 721, 701, 692 cm^{-1}; HR-MS (ESI-TOF): *m/z* calcd for $C_{25}H_{25}NO_3S_2Na$: 474.1174 found 474.1157 $[M+Na]^+$.

*4.3.3. N-Benzyl-2,3-diphenyl-2-(phenylthio)-N-tosylpent-4-enamide (**3d**).* Following general procedure **4.3** using **1d** (72.3 mg, 0.200 mmol.) with sulfide **2a** for 7 h; further purified by flash SiO_2 column chromatography (^{n}hexane:EtOAc [95:5 - 9:1]). **3d** was isolated as a mixture of diastereomers (d.r. from crude reaction mixture 5.5:1), NMR data is provided for the major diastereomer only. **3d** was obtained as a colourless solid (65.2 mg, 54%); mp: 91–93 °C; 1H missing by integration, a very broad approximately 1H signal appears 6.3 -5.7 ppm, in similarity to other molecules in the series, one of the ^{13}C signals at 128.0 is very broad and is included tentatively; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.41 – 7.27 (m, 8H), 7.25 – 7.14 (m, 8H), 6.97 (t, *J* = 7.3 Hz, 1H), 6.86 (t, *J* = 7.6 Hz, 2H), 6.49 (d, *J* = 7.3 Hz, 2H), 6.32 – 5.69 (br. s, 1H), 6.21 (d app. t, *J* = 17.0, 10.0 Hz, 1H), 5.06 (dd, *J* = 10.3, 1.4 Hz, 1H), 4.85 (d, *J* = 16.1 Hz, 1H), 4.60 (d, *J* = 17.0 Hz, 1H), 4.17 (d, *J* = 9.5 Hz, 1H), 4.15 (d, *J* = 16.1 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 144.2, 140.6, 136.7, 136.4, 136.2, 136.1, 133.9, 131.4, 129.6, 129.5, 129.3, 128.6, 128.6, 128.4, 128.0, 128.0, 127.9, 127.1, 126.6, 126.0, 117.6, 65.2, 53.0, 52.8, 21.6; IR (neat): ν_{max} 3066, 2922, 2847, 1680, 1596, 1494, 1438, 1353, 1210, 1165, 1084, 1026, 913, 863, 813, 701 cm^{-1}; HR-MS (ESI-TOF): *m/z* calcd for $C_{37}H_{34}NO_3S_2$: 604.1980 found 604.1989 $[M+H]^+$.

*4.3.4. N-(3,5-Dimethylphenyl)-N-(methylsulfonyl)-2,3-diphenyl-2-(phenylthio)pent-4-enamide (**3e**).* Following general procedure **4.3** using **1e** (60.5 mg, 0.202 mmol) with sulfide **2a** for 12 h, further purified by flash SiO_2 column chromatography (^{n}hexane:EtOAc [9:1–17:3]). **3e** was isolated as a mixture of diastereomers (d.r. from crude reaction mixture 13.1:1), NMR data is provided for the major diastereomer only. **3e** was obtained as a pale yellow solid (88.3 mg, 82%); mp: 147–148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.68 (m, 2H), 7.49–7.40 (m, 3H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.14–6.99 (m, 6H), 6.93–6.75 (m, 4H), 6.71 (s, 1H), 6.00 (ddd, *J* = 17.1, 10.3, 9.3 Hz, 1H), 5.50 (br. s, 1H), 5.03 (dd, *J* = 10.3, 0.9 Hz, 1H), 4.71 (d, *J* = 17.1 Hz, 1H), 4.30 (d, *J* = 9.3 Hz, 1H), 3.46 (s, 3H), 2.18 (br. s, 3H), 1.82 (br. s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 141.1, 137.3, 135.3, 133.6, 133.4, 132.0, 130.7, 130.7, 130.4, 129.8, 129.3, 128.9, 128.0, 127.0, 126.7, 126.5, 117.3, 66.3, 54.1, 42.3, 20.9; IR (neat): ν_{max} 3057, 2928, 1679, 1611, 1596, 1492, 1474, 1446, 1358, 1344, 1316, 1218, 1172, 1148, 1064, 958, 917, 797, 789, 745, 703, 690 cm^{-1}; HR-MS (ESI-TOF): *m/z* calcd for $C_{32}H_{31}NO_3S_2Na$: 564.1643 found 564.1645 $[M+H]^+$.

*4.3.5. N-(4-Iodophenyl)-N-(methylsulfonyl)-2,3-diphenyl-2-(phenylthio)pent-4-enamide (**3f**).* Following general procedure **4.3** using **1f** (80.1 mg, 0.202 mmol) with sulfide **2a** for 9 h, further purified by flash SiO_2 column chromatography (^{n}hexane:EtOAc [9:1–17:3]). **3f** was isolated as a mixture of diastereomers (d.r. from crude reaction mixture 14.2:1), NMR data is provided for the major diastereomer only. **3f** was obtained as a pale yellow solid (93.5 mg, 73%); mp: 158–159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.58–6.90 (br. m, 4H), 7.51–7.41 (m, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.17–7.06 (m, 3H), 7.03 (t, *J* =

7.3 Hz, 2H), 6.88–6.71 (m, 2H), 6.77 (d, *J* = 7.3 Hz, 2H), 6.03–5.93 (m, 1H), 5.90–5.37 (br. s, 1H), 5.04 (d, *J* = 10.8 Hz, 1H), 4.68 (d, *J* = 17.1 Hz, 1H), 4.27 (d, *J* = 9.3 Hz, 1H), 3.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.7, 140.8, 137.0, 136.4, 135.7, 134.4, 133.6, 133.2, 132.0, 129.9, 129.7, 129.0, 128.5, 127.4, 126.8, 126.6, 117.5, 95.2, 66.4, 53.8, 42.5; IR (neat): ν_{max} 2929, 1698, 1479, 1455, 1438, 1350, 1322, 1233, 1186, 1151, 1074, 1058, 1007, 969, 926, 915, 883, 813, 769, 759, 748, 702, 666 cm^{-1}; HR-MS (ESI-TOF): *m/z* calcd for $C_{30}H_{26}NO_3S_2INa$: 662.0296 found 662.0290 $[M+Na]^+$.

*4.3.6. 2,3-Diphenyl-2-(phenylthio)-N-(o-tolyl)-N-tosylpent-4-enamide (**3g**).* Following general procedure **4.3** using **1g** (46.5 mg, 0.129 mmol) with sulfide **2a** for 5 h, further purified by flash SiO_2 column chromatography (^{n}hexane:EtOAc [9:1]) and was then recrystalised (^{n}hexane). **3g** was isolated as a mixture of diastereomers (d.r. from crude reaction mixture 2.1:1), NMR data is provided for the major diastereomer only. **3g** was obtained as a white powder (29.7 mg, 38%); mp: 152–153 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.57 (m, 2H), 7.38–7.31 (m, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 7.09–6.99 (m, 4H), 6.99–6.94 (m, 1H), 6.93–6.84 (m, 3H), 6.74–6.54 (m, 3H), 6.52–6.25 (m, 3H), 5.73 (d app. t, *J* = 16.9, 10.2 Hz, 1H), 5.51 (d, *J* = 7.9 Hz, 1H), 4.65 (dd, *J* = 10.2, 1.3 Hz, 1H), 4.27 (d, *J* = 10.2 Hz, 1H), 4.06 (d, *J* = 16.9 Hz, 1H), 2.45 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 144.6, 142.2, 140.7, 136.7, 135.7, 135.3, 134.3, 134.0, 133.3, 132.6, 131.9, 130.0, 129.9, 129.1, 128.7, 128.7, 128.6, 128.3, 128.2, 127.9, 127.0, 126.2, 125.8, 124.7, 116.5, 64.0, 53.4, 21.6, 20.0; IR (neat): ν_{max} 3062, 1681, 1597, 1488, 1476, 1439, 1362, 1349, 1243, 1197, 1190, 1177, 1162, 1154, 1114, 1086, 1027, 988, 921, 905, 882, 817, 804, 790, 771, 747, 706, 688, 681, 653 cm^{-1}; HR-MS (ESI-TOF): *m/z* calcd for $C_{37}H_{33}NO_3S_2Na$: 626.1801 found 626.1800 $[M+Na]^+$.

*4.3.7. 2-(Cyclohexylthio)-N-(methylsulfonyl)-N,2,3-triphenylpent-4-enamide (**3i**).* Following general procedure **4.3** using **1b** (54.9 mg, 0.202 mmol) with sulfide **2b** for 8 h, further purified by flash SiO_2 column chromatography (^{n}hexane:EtOAc [9:1–17:3]). **3i** was isolated as the major diastereomer only (d.r. from crude reaction mixture 12.3:1); in this case major and minor diastereomers were separable, however the low abundance of the minor diastereomer and co-elution with the starting material prevented its accurate characterisation. NMR data is therefore provided for the major diastereomer only. Thus **3i** was obtained as colourless crystals (58.1 mg, 56%); mp: 128–129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19–7.01 (m, 6H), 6.97 (dd, *J* = 8.3, 7.6 Hz, 2H), 6.97–6.74 (br. m, 2H) 6.82 (d, *J*= 7.1 Hz, 2H), 6.67 (br. s, 2H), 5.95 (app. dt, *J* = 17.4, 9.9 Hz, 1H), 5.07–5.04 (m, 1H), 5.02 (s, 1H), 4.92 (d, *J* = 9.9 Hz, 1H), 3.44 (s, 3H), 3.20–3.09 (m, 1H), 2.38–2.28 (m, 1H), 2.03–1.93 (m, 1H), 1.91–1.82 (m, 1H), 1.82–1.72 (m, 1H), 1.71–1.60 (m, 2H), 1.60–1.47 (m, 1H), 1.47–1.39 (m, 2H), 1.36–1.24 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 141.5, 137.9, 134.2, 133.6, 133.0, 131.6, 130.1 (v. br. s), 128.7, 128.1, 127.2, 127.1, 127.0, 126.8, 116.2, 63.8, 53.5, 42.9, 42.0, 35.2, 34.5, 27.0, 26.5, 25.7; IR (neat): ν_{max} 2932, 2852, 1670, 1489, 1446, 1351, 1248, 1188, 1152, 1078, 1000, 957, 904, 879, 776, 763, 697, 677, 663 cm^{-1}; HR-MS (ESI-TOF): *m/z* calcd for $C_{30}H_{33}NO_3S_2Na$: 542.1800 found 542.1804 $[M+Na]^+$.

*4.3.8. 2-(Benzylthio)-N-(methylsulfonyl)-N,2,3-triphenylpent-4-enamide (**3j**).* Following general procedure 4.2 using **1b** (54.9 mg, 0.202 mmol) with sulfide **2c** for 8 h, further purified by flash SiO_2 column chromatography (^{n}hexane:EtOAc [9:1–17:3]) followed by recrystallisation from CH_2Cl_2/^{n}hexane to remove trace co-eluting impurities. **3j** was isolated as a mixture of diastereomers (d.r. from crude reaction mixture 5.6:1), NMR data is provided for the major diastereomer only. **3j** was obtained as pale orange crystals (64.0 mg, 61%); mp: 146–147 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.35 (m, 4H), 7.36–7.28 (m, 1H), 7.18–7.06 (m, 4H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.96 (t, *J* = 7.9 Hz, 2H), 6.92–6.78 (br. s, 2H), 6.86 (d, *J* = 6.9 Hz, 2H), 6.68 (d, *J* = 7.3 Hz, 2H), 6.11 (d app. t, *J* = 16.8, 10.1 Hz, 1H), 5.23 (d, *J* = 16.8 Hz, 1H), 5.14 (dd, *J* = 10.1, 1.3 Hz, 1H), 4.82 (d, *J* = 10.1 Hz, 1H), 3.99 (d, *J* = 10.7 Hz, 1H), 3.92 (d, *J* = 10.7 Hz, 1H), 3.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 140.9, 137.1, 135.8, 134.6, 133.5, 132.3, 131.3, 129.9, 129.7, 129.0, 129.0, 128.1, 127.8, 127.5, 127.4, 127.1, 126.9, 115.9, 65.0, 53.4, 42.2, 34.6; IR (neat): ν_{max} 3027, 1667, 1492, 1454, 1347, 1252, 1190, 1153, 1068, 1031, 991, 956, 935, 919, 899, 885, 767, 696, 675 cm^{-1}; HR-MS (ESI-TOF): *m/z* calcd for $C_{31}H_{29}NO_3S_2Na$: 550.1487 found 550.1484 $[M+Na]^+$.

*4.3.9. 2-(Ethylthio)-N-(methylsulfonyl)-N,2,3-triphenylpent-4-enamide (**3k**).* Following general procedure **4.3** using **1b** (54.9 mg, 0.202 mmol) with sulfide **2d** for 8 h, further purified by flash SiO_2 column chromatography (^{n}hexane:EtOAc [9:1–17:3]). **3k** was successfully separated into its pure major diastereomer (54.6 mg) and a mixture of minor diastereomer and the double oxidised ynamide (d.r. from crude reaction mixture 7.2:1), NMR data is provided for the major diastereomer only. **3k** major diastereomer was obtained as pale yellow crystals (54.6 mg, 59%); mp: 132–133 °C; 2H missing by integration, although a very broad 2H singlet appears δ 7.23–6.21 and is tentatively included; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–6.21 (br. s, 2H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.11–7.03 (m, 4H), 6.99 (t, *J* = 7.5 Hz, 2H), 6.99–6.82 (br. s, 2H), 6.85–6.80 (m, 2H), 6.71 (d, *J* = 7.5 Hz, 2H), 6.04 (d app. t, *J* = 17.0, 10.0 Hz, 1H), 5.10 (d, *J* = 17.0 Hz, 1H), 5.03 (dd, *J* = 10.0, 1.5 Hz, 1H), 4.64 (d, *J* = 10.0 Hz, 1H), 3.46 (s, 3H), 2.83–2.68 (m, 2H), 1.31 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 140.9, 137.2, 134.8, 134.0, 132.2, 131.2, 129.8, 129.0, 128.0, 127.5, 127.3, 127.1, 126.8, 115.8, 64.5, 53.9, 42.0, 23.7, 13.0; IR (neat): ν_{max} 2972, 2928, 1683, 1590, 1489, 1452, 1367, 1344, 1316, 1245, 1190, 1164, 1150, 1079, 964, 915, 883, 780, 762, 706, 692, 667 cm^{-1}; HR-MS (ESI-TOF): *m/z* calcd for $C_{26}H_{27}NO_3S_2Na$: 488.1330 found 488.1332 $[M+Na]^+$.

*4.3.10. 2-(Ethylthio)-N-methyl-N-(methylsulfonyl)-2,3-diphenylpent-4-enamide (**3l**).* Following general procedure **4.3** using **1c** (41.8 mg, 0.200 mmol) with sulfide **2d** for 8 h, further purified by flash SiO_2 column chromatography (^{n}hexane:EtOAc [9:1–17:3]). **3l** was partially separated into the major and minor diastereomers during chromatography (d.r. from crude reaction mixture 1.9:1); and thus both major and minor diastereomer receive characterisation. The major isomer of **3l** was obtained as colourless crystals (34.7 mg, 43%), following this a small amount of mixed major and minor isomer was collected as a colourless solid (7.4 mg, 9%) and finally a mixture of mostly the minor isomer (9:1) of **3l** was obtained as a colourless solid (21.0 mg, 26%), overall major plus minor (63.1 mg, 78%); *major isomer*: mp: 97–98 °C; 2H missing by integration from Ar region resonances, integration of the entire broad overlapping signals from δ 7.41–6.90 gives matching integration overall; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.10 (m, 3H), 7.10–6.97 (m, 3H), 6.72 (d, *J* = 7.2 Hz, 2H), 6.26 (d app. t, *J* = 16.9, 10.1 Hz, 1H), 5.17–5.08 (m, 2H), 4.63 (d, *J* = 10.1 Hz, 1H), 3.35 (s, 3H), 2.80–2.70 (m, 4H), 2.61 (dq, *J* = 10.8, 7.5 Hz, 1H), 1.28 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 140.4, 136.7, 134.8, 130.8, 128.2, 128.0, 127.1 (2C), 126.5, 116.2, 63.8, 53.8, 41.9, 35.2, 23.5, 13.2; IR (neat): ν_{max} 2968, 2930, 1673, 1496, 1453, 1355, 1343, 1258, 1171, 1101, 1038, 1003, 962, 935, 928, 900, 876, 769, 727, 709, 697, 681, 652 cm^{-1}; HR-MS (ESI-TOF): *m/z* calcd for $C_{21}H_{25}NO_3S_2Na$: 426.1174 found 426.1170 $[M+Na]^+$; *minor isomer*: mp: 104–105 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41–7.27 (m, 3H), 7.24–7.08 (m, 5H), 6.70–6.63 (m, 2H), 5.95 (ddd, *J* =

17.1, 10.1, 8.3 Hz, 1H), 5.21–5.07 (m, 2H), 4.48 (d, *J* = 8.3 Hz, 1H), 3.40 (s, 3H), 2.80 (s, 3H), 2.84–2.71 (m, 1H), 2.66–2.53 (m, 1H), 1.24 (t, *J* = 7.5 Hz, 3H); HR-MS (ESI-TOF): *m/z* calcd for $C_{21}H_{25}NO_3S_2Na$: 426.1174 found 426.1176 $[M+Na]^+$.

*4.3.11. N-(Methylsulfonyl)-N,2-diphenyl-2-(phenylthio)-3-vinylhexanamide (**3m**).* Following general procedure **4.3** using **1b** (54.9 mg, 0.202 mmol) with sulfide **2e** for 5 h; further purified by flash SiO_2 column chromatography (^{n}hexane:EtOAc [9:1–17:3]). **3m** was isolated as a mixture of diastereomers (d.r. from crude reaction mixture 5.5:1), NMR data is provided for the major diastereomer only. **3m** was obtained as a colourless solid (77.4 mg, 81%); mp: 127–128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.51 (m, 2H), 7.40–7.32 (m, 5H), 7.30–7.22 (m, 5H), 7.14 (t, *J* = 7.3 Hz, 1H), 7.03–6.64 (br. s, 1H), 6.51–5.94 (br. s, 1H), 5.12–5.01 (m, 1H), 4.99 (dd, *J* = 10.4, 2.4 Hz, 1H), 4.58 (dd, *J* = 16.8, 2.4 Hz, 1H), 3.52 (s, 3H), 2.63 (app. t, *J* = 9.4 Hz, 1H), 1.79–1.70 (m, 1H), 1.24–1.11 (m, 1H), 1.11–0.98 (m, 1H), 0.78 (t, *J* = 7.3 Hz, 3H), 0.78–0.73 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 135.5, 135.5 134.6, 134.4, 132.5, 129.2, 129.2, 129.0, 128.9, 128.7, 128.0, 127.7, 127.5, 117.7, 65.8, 49.3, 42.2, 33.9, 20.8, 13.9; IR (neat): ν_{max} 3054, 2958, 2863, 1686, 1491, 1446, 1347, 1320, 1234, 1185, 1150, 1004, 963, 940, 915, 898, 775, 762, 748, 703, 692 cm^{-1}; HR-MS (ESI-TOF): *m/z* calcd for $C_{27}H_{29}NO_3S_2Na$: 502.1487 found 502.1484 $[M+Na]^+$.

*4.3.12. N-Methyl-N-(methylsulfonyl)-2-phenyl-2-(phenylthio)-3-vinylhexanamide (**3n**).* Following general procedure **4.3** using **1c** (41.8 mg, 0.200 mmol) with sulfide **2e** for 6 h, further purified by flash SiO_2 column chromatography (^{n}hexane:EtOAc [9:1–17:3]). **3n** was isolated as a mixture of diastereomers (d.r. from crude reaction mixture 3.6:1), NMR data is provided for the major diastereomer only. **3m** was obtained as a colourless solid (67.7 mg, 81%); mp: 124–125 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.51 (m, 2H), 7.48–7.31 (m, 8H), 5.44 (d app. t, *J* = 17.1, 10.2 Hz, 1H), 5.27 (dd, *J* = 10.2, 2.0 Hz, 1H), 5.02 (dd, *J* = 17.1, 2.0 Hz, 1H), 3.13 (s, 3H), 2.97 (s, 3H), 2.93 (app. t, *J* = 10.2 Hz, 1H), 1.61–1.51 (m, 1H), 1.32–1.10 (m, 2H), 0.76 (t, *J* = 7.3 Hz, 3H), 0.47 (d app. td, *J* = 12.5, 10.2, 4.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 136.5, 136.4, 134.6, 130.1, 130.0, 129.0, 128.3, 128.1, 128.1 (br.), 118.4, 66.6, 50.0, 42.1, 35.1, 34.1, 20.9, 13.9; IR (neat): ν_{max} 2958, 2872, 1680, 1497, 1464, 1440, 1417, 1346, 1321, 1258, 1168, 1155, 1104, 1081, 1001, 965, 941, 913, 894, 846, 777, 754, 745, 704, 694, 682 cm^{-1}; HR-MS (ESI-TOF): *m/z* calcd for $C_{22}H_{27}NO_3S_2Na$: 440.1330 found 440.1331 $[M+Na]^+$.

*4.3.13. 2-(4-Chlorophenyl)-N-(methylsulfonyl)-N,3-diphenyl-2-(phenylthio)pent-4-enamide (**3o**).* Following general procedure **4.3** using **1i** (61.2 mg, 0.200 mmol) with sulfide **2a** for 5 h, purified by SiO_2 flash column chromatography (^{n}hexane:EtOAc [9:1–17:3]) to give **3o** as a mix of isomers (d.r. from crude reaction mixture 13.2:1), NMR data is provided for the major diastereomer only; colourless solid (89.9 mg, 82%); mp: 83–84 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.70 (m, 2H), 7.54–7.32 (m, 4H), 7.19–6.86 (m, 8H), 6.81 (d, *J* = 7.1 Hz, 2H), 6.74 (d, *J* = 6.8 Hz, 2H), 6.41–5.72 (br. s, 1H), 5.92 (ddd, *J* = 17.1, 10.6, 9.2 Hz, 1H), 5.06 (d, *J* = 10.6 Hz, 1H), 4.69 (d, *J* = 17.1 Hz, 1H), 4.30 (d, *J* = 9.2 Hz, 1H), 3.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 140.7, 136.7, 135.9, 134.4, 133.7, 132.8, 132.0, 131.8, 131.2, 129.8, 129.8, 129.0, 129.0, 127.3, 127.3, 127.0, 126.8, 117.8, 65.8, 53.4, 42.3; IR (neat): ν_{max} = 3062, 1682, 1592, 1491, 1352, 1244, 1187, 1151, 1094, 963, 917, 828, 750, 730, 692 cm^{-1}; HR-MS (ESI-TOF): *m/z* calcd for $C_{30}H_{26}NO_3S_2ClNa$: 570.0940 found 570.0941 $[M+Na]^+$.

*4.3.14. 2-(4-Bromophenyl)-N-(methylsulfonyl)-N,3-diphenyl-2-(phenylthio)pent-4-enamide (**3p**).* Following general procedure **4.3** using **1j** (70.0 mg, 0.200 mmol) with sulfide **2a** for 6 h, further purified by flash SiO_2 column chromatography (^{n}hexane:EtOAc [9:1–17:3]). **3p** was isolated as a mixture of diastereomers (d.r. from crude reaction mixture 15.2:1), NMR data is provided for the major diastereomer only. **3p** was obtained as a white solid (103 mg, 87%); mp: 125–126 °C; ^{1}H signal apparently missing a proton by integration (although broadening of both the *N*-Ph and 4-Br Ph protons was evident). This structure was fully confirmed by SC-XRD and the NMR issues experienced here are shared by many of the other molecules in the series, ^{1}H NMR reported below as observed, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76–7.69 (m, 2H), 7.53–7.41 (m, 3H), 7.21 (d, *J* = 8.8 Hz, 2H), 7.17–7.04 (m, 4H), 7.17–6.76 (br. s, 2H), 6.82 (d, *J* = 7.0 Hz, 2H), 6.68 (d, *J* = 6.8 Hz, 2H), 6.41–5.74 (br. s, 1H), 5.92 (ddd, *J* = 17.1, 10.6, 9.2 Hz, 1H), 5.06 (d, *J* = 10.6 Hz, 1H), 4.70 (d, *J* = 17.1 Hz, 1H), 4.30 (d, *J* = 9.2 Hz, 1H), 3.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 140.7, 136.7, 136.0, 133.7, 132.8, 132.3, 132.0, 131.5, 130.2, 129.9, 129.7, 129.0, 129.0, 127.3, 127.0, 126.8, 122.6, 117.8, 65.9, 53.3, 42.3; IR (neat): ν_{max} 2954, 2931, 1691, 1488, 1473, 1454, 1352, 1239, 1187, 1153, 1077, 1008, 958, 934, 921, 901, 877, 832, 754, 727, 693, 661 cm^{-1}; HR-MS (ESI-TOF): *m/z* calcd for $C_{30}H_{26}NO_3S_2{}^{79}BrNa$: 614.0435 found 614.0433 $[M+Na]^+$.

*4.3.15. 2-(3-Bromophenyl)-N-(methylsulfonyl)-N,3-diphenyl-2-(phenylthio)pent-4-enamide (**3q**).* Following general procedure **4.3** using **1k** (70.0 mg, 0.200 mmol) with sulfide **2a** for 6 h, further purified by flash SiO_2 column chromatography (^{n}hexane:EtOAc [9:1–17:3]). **3q** was isolated as a mixture of diastereomers (d.r. from crude reaction mixture 16.8:1), NMR data is provided for the major diastereomer only. **3q** was obtained as a white solid (74.7 mg, 63%); mp: 86–87 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 6.8 Hz, 2H), 7.55–7.44 (m, 3H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.33–6.65 (br. s, 2H), 7.19–7.07 (m, 4H), 6.97 (t, *J* = 7.9 Hz, 1H), 6.86–6.69 (br. s, 2H), 6.82 (d, *J* = 7.2 Hz, 2H), 6.46–5.80 (br. s, 1H), 5.95 (ddd, *J* = 17.1, 10.5 Hz, 9.1 Hz, 1H), 5.11 (d, *J* = 10.5 Hz, 1H), 4.74 (d, *J* = 17.1 Hz, 1H), 4.35 (d, *J* = 9.1 Hz, 1H), 3.49 (s, 3H), ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 140.6, 136.7, 136.2, 135.5, 133.5, 133.2, 132.9, 131.9, 131.2, 130.0, 129.4, 129.0, 128.6, 128.2, 127.3, 126.9, 126.8, 121.2, 117.9, 66.0, 53.4, 42.4; IR (neat): ν_{max} 2987, 2902, 1683, 1591, 1562, 1490, 1474, 1409, 1354, 1242, 1185, 1153, 1076, 962, 937, 918, 879, 786, 751, 692 cm^{-1}; HR-MS (ESI-TOF): *m/z* calcd for $C_{30}H_{26}NO_3S_2{}^{79}BrNa$: 614.0435 found 614.0427 $[M+Na]^+$.

*4.3.16. N,3-Diphenyl-2-(phenylthio)-N-tosylpent-4-enamide (**3t**).* Following general procedure **4.3** using **1n** (54.3 mg, 0.200 mmol) with sulfide **2a** for 6 h, further purified by flash SiO_2 column chromatography (^{n}hexane:EtOAc [9:1–17:3]). **3t** was isolated as a mixture of diastereomers (d.r. from crude reaction mixture 5.9:1), NMR data is provided for the major diastereomer only. **3t** was obtained as a pale yellow oil (33.0 mg, 38%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.40–7.34 (m, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.28–7.24 (m, 4H), 7.23–7.16 (m, 3H), 7.11 (t, *J* = 7.4 Hz, 2H), 6.89–6.85 (m, 2H), 6.52–6.07 (br. s, 2H), 6.01 (ddd, *J* = 17.0, 10.2, 9.0 Hz, 1H), 5.15 (d, *J* = 10.2 Hz, 1H), 5.05 (d, *J* = 17.0 Hz, 1H), 3.71 (dd, *J* = 11.2, 9.0 Hz, 1H), 3.50 (d, *J* = 11.2 Hz, 1H), 2.51 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 144.5, 140.9, 136.9, 136.0, 135.5, 134.9, 130.9, 130.5, 129.8, 129.4, 129.3, 129.1, 129.0, 128.9, 128.5, 128.4, 127.0, 118.3, 54.5, 50.6, 21.7; IR (neat): ν_{max} 3065, 2924, 1697, 1596, 1489, 1361, 1330, 1274, 1240, 1188, 1172, 1144, 1118, 1087, 915, 883, 813, 748, 694, 652 cm^{-1}; HR-MS (ESI-TOF): *m/z* calcd for $C_{30}H_{27}NO_3S_2Na$: 536.1330 found 536.1329 $[M+H]^+$.

*4.3.17. 2-(Cinnamylthio)-N-(methylsulfonyl)-N,2-diphenylpent-4-enamide (**5a**) and 2-(allylthio)-N-(methylsulfonyl)-N,2,3-triphenylpent-4-enamide (**5b**).* Following general procedure **4.3** using **1b** (54.9 mg, 0.202 mmol) with sulfide **2f** for 7 h, further

purified by flash SiO_2 column chromatography (^{n}hexane:EtOAc [9:1–17:3]). The 2 products **5a** and **5b** were isolated individually and are characterised below. The major product **5a** was obtained as a pale yellow oil (50.2 mg, 53%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.29 (m, 4H), 7.25–7.21 (m, 1H), 7.18–7.10 (m, 4H), 7.00–6.93 (m, 4H), 6.83–6.82 (br. s, 2H), 6.54 (d, *J* = 15.7 Hz, 1H), 6.23–6.14 (m, 1H), 5.63–5.51 (m, 1H), 5.07–4.99 (m, 2H), 3.44 (s, 3H), 3.36 (ddd, *J* = 12.4, 7.6, 1.0 Hz, 1H), 3.30 (ddd, *J* = 12.4, 7.3, 1.1 Hz, 1H), 3.07 (dd, *J* = 15.4, 7.6 Hz, 1H), 2.91 (dd, *J* = 15.4, 5.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 138.0, 136.5, 133.6, 133.6, 132.3, 131.8, 129.0, 128.6, 128.4, 127.8, 127.5, 126.7, 126.3, 123.9, 118.5, 77.2, 62.6, 42.0, 41.6, 31.8; IR (neat): ν_{max} 3028, 2928, 1676, 1594, 1491, 1448, 1417, 1351, 1319, 1260, 1191, 1153, 1121, 1076, 1029, 1004, 960, 917, 891, 843, 756, 692 cm^{-1}; HR-MS (ESI-TOF): m/z calcd for $C_{27}H_{27}NO_3S_2Na$: 500.1330 found 500.1331 $[M+Na]^+$. The minor product **5b** was obtained as a mixture of diastereomers (d.r. from crude reaction mixture 7.2:1), NMR data is provided for the major diastereomer only, and appeared as a colourless oil (18.0 mg, 19%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (t, *J* = 7.4 Hz, 1H), 7.11–7.03 (m, 4H), 6.99 (t, *J* = 7.9 Hz, 2H), 6.98–6.80 (br. m, 3H), 6.83 (d, *J* = 7.9 Hz, 2H), 6.70 (d, *J* = 7.6 Hz, 2H), 6.12–5.98 (m, 1H), 5.98–5.84 (m, 1H), 5.35 (dd, *J* = 16.9, 1.3 Hz, 1H), 5.24 (d, *J* = 10.0 Hz, 1H), 5.14 (d, *J* = 17.0 Hz, 1H), 5.07 (dd, *J* = 10.1, 1.5 Hz, 1H), 4.66 (d, *J* = 10.0 Hz, 1H), 3.46 (s, 3H), 3.43 (d, *J* = 7.2 Hz, 2H); HR-MS (ESI-TOF): m/z calcd for $C_{27}H_{27}NO_3S_2Na$: 500.1330 found 500.1329 $[M+Na]^+$.

4.1. Transformation of catalysis products using $LiAlH_4$

*4.4.1. 2-Phenyl-2-(phenylthio)pent-4-en-1-ol (**7**).* In a flame dried Schlenk tube under argon $LiAlH_4$ (12.4 mg, 0.327 mmol) was suspended in anhydrous Et_2O (2.0 mL), **6** (71.1 mg, 0.162 mmol) was then added as a single portion and the reaction stirred at r.t. and monitored by TLC until all starting material had been consumed (2 h). The reaction was then carefully quenched with saturated aqueous Na/K tartrate solution, diluted with EtOAc and transferred to a separating funnel. The organic fraction was separated and the aqueous further extracted with EtOAc, the combined organic extracts were then dried over Na_2SO_4, filtered and evaporated to dryness under reduced pressure. The crude residue was then purified by SiO_2 flash column chromatography (^{n}hexane:EtOAc [17:3]) providing **7** as a colourless oil (32.3 mg, 74%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.33 (m, 2H), 7.32–7.13 (m, 8H), 5.60–5.48 (m, 1H), 5.05 (d, *J* = 17.1, 1H), 5.00 (d, *J* = 10.1 Hz, 1H), 3.85 (dd, *J* = 11.6, 5.5 Hz, 1H), 3.81 (dd, *J* = 11.6, 7.7 Hz, 1H), 2.82 (dd, *J* = 14.0, 6.2 Hz, 1H), 2.69 (dd, *J* = 14.0, 8.0 Hz, 1H), 2.42 (dd, *J* = 8.0, 6.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.6, 136.5, 132.8, 130.0, 129.1, 128.6, 128.2, 127.6, 127.1, 118.7, 63.1, 60.7, 41.0; IR (neat): ν_{max} 3440, 3058, 1496, 1473, 1445, 1438, 1389, 1208, 1062, 1024, 995, 918, 747, 691 cm^{-1}; HR-MS (EI-TOF): *m/z* calcd for $C_{17}H_{18}OS$: 270.1078 found 270.1088 $[M+H]^+$.

*4.4.2. 2-(4-Bromophenyl)-3-phenyl-2-(phenylthio)pent-4-en-1-ol (**8**).* In a flame dried Schlenk tube under argon $LiAlH_4$ (21.3 mg, 0.561 mmol) was suspended in anhydrous THF (2.5 mL), **3p** (149 mg, 0.251 mmol) was then added as a single portion and the reaction stirred at r.t. and monitored by TLC until all starting material had been consumed (3 h). The reaction was then carefully quenched with saturated aqueous Na/K tartrate solution, diluted with Et_2O and transferred to a separating funnel. The organic fraction was separated and the aqueous further extracted with Et_2O, the combined organic extracts were then dried over Na_2SO_4, filtered and evaporated to dryness under reduced pressure. The crude residue was then purified by SiO_2 flash column chromatography (^{n}hexane:EtOAc [95:5–9:1]) providing **8** as a colourless oil (65.3 mg, 61%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.8 Hz, 2H), 7.31–7.08 (m, 10H), 6.67 (dd, *J* = 7.6, 1.8 Hz, 2H), 6.31 (ddd, *J* = 16.9, 10.1, 9.3 Hz, 1H), 5.27 (dd, *J* = 10.1, 1.1 Hz, 1H), 5.21 (d, *J* = 16.9 Hz, 1H), 3.98 (d, *J* = 9.3 Hz, 1H), 3.68 (dd, *J* = 11.4, 8.7 Hz, 1H), 3.43 (d, *J* = 11.4 Hz, 1H), 2.84–2.64 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 137.3, 136.3, 135.4, 131.3, 130.7, 130.3, 129.5, 129.0, 128.9, 127.9, 127.1, 121.7, 118.4, 65.6, 61.8, 54.9; IR (neat): ν_{max} 3449, 3062, 2921, 1583, 1489, 1453, 1438, 1391, 1209, 1075, 1008, 919, 830, 746, 729, 701, 691 cm^{-1}; HR-MS (ESI-TOF): *m/z* calcd for $C_{23}H_{21}OS^{79}BrNa$: 447.0394 found 447.0389 $[M+Na]^+$.

4.2. Transformation of catalysis products using allyl magnesium bromide

*4.5.1. 4-Allyl-5-phenyl-5-(phenylthio)octa-1,7-dien-4-ol (**9**).* In a flame dried Schlenk tube under argon **6** (52.2 mg, 0.118 mmol) was dissolved in anhydrous THF (1.0 mL), a solution of allyl magnesium bromide (1 M in Et_2O, 0.30 mL, 0.30 mmol) was then added and the reaction stirred at r.t. and monitored by TLC until all starting material had been consumed (3 h). The reaction was then carefully quenched with a saturated aqueous NH_4Cl solution, diluted with EtOAc and H_2O and transferred to a separating funnel. The organic fraction was separated and the aqueous further extracted with EtOAc, the combined organic extracts were then dried over Na_2SO_4, filtered and evaporated to dryness under reduced pressure. The crude residue was then purified by SiO_2 flash column chromatography (^{n}hexane:EtOAc [95:5]) providing **9** as a colourless oil (39.7 mg, 96%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 – 7.72 (m, 2H), 7.37 – 7.13 (m, 8H), 6.05 (ddt, *J* = 16.5, 10.3, 6.1 Hz, 1H), 5.84 – 5.69 (m, 2H), 5.11 – 4.92 (m, 6H), 3.23 (ddt, *J* = 16.6, 6.2, 1.6 Hz, 1H), 3.09 (ddt, *J* = 16.6, 6.0, 1.7 Hz, 1H), 2.76 (dd, *J* = 14.4, 6.5 Hz, 1H), 2.57 (dd, *J* = 14.4, 7.1 Hz, 1H), 2.43 (s, 1H), 2.39 (dd, *J* = 14.4, 7.2 Hz, 1H), 2.26 (dd, *J* = 14.4, 8.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 136.7, 135.6, 134.8, 134.8, 132.9, 130.4, 128.5, 128.3, 127.5, 127.1, 118.1, 118.0, 116.3, 78.5, 69.7, 41.9, 41.5, 38.0; IR (neat): ν_{max} 3548, 3074, 2977, 2926, 1635, 1496, 1474, 1438, 1414, 1347, 1308, 1237, 1154, 1126, 1026, 999, 910, 747, 703, 691 cm^{-1}; HR-MS (ESI-TOF): *m/z* calcd for $C_{23}H_{26}OSNa$: 373.1602 found 373.1603 $[M+Na]^+$.

*4.5.2. N,2,3-Triphenyl-2-(phenylthio)pent-4-enamide (**10**).* In a flame dried Schlenk tube under argon **3b** (106 mg, 0.207 mmol) was dissolved in anhydrous THF (1.0 mL), a solution of allyl magnesium bromide (1 M in Et_2O, 0.52 mL, 0.52 mmol) was then added and the reaction stirred at r.t. and monitored by TLC until all starting material had been consumed (3 h). The reaction was then carefully quenched with a saturated aqueous NH_4Cl solution, diluted with Et_2O and H_2O and transferred to a separating funnel. The organic fraction was separated and the aqueous further extracted with Et_2O, the combined organic extracts were then dried over Na_2SO_4, filtered and evaporated to dryness under reduced pressure. The crude residue was then purified by SiO_2 flash column chromatography (^{n}hexane:EtOAc [95:5–9:1]) providing **10** as a white solid (61.8 mg, 69%); mp: 111–112 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.38 – 7.27 (m, 6H), 7.24 – 7.10 (m, 12H), 7.09 – 7.02 (m, 2H), 6.41 (ddd, *J* = 17.1, 10.3, 8.6 Hz, 1H), 5.12 (d, *J* = 10.3 Hz, 1H), 5.05 (d, *J* = 17.1 Hz, 1H), 4.72 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 139.5, 137.5, 137.3, 137.2, 135.4, 131.2, 130.5, 130.2, 128.9, 128.9, 128.6, 127.7, 127.5, 127.4, 127.2, 124.5, 119.9, 117.7, 71.0, 57.1; IR (neat): ν_{max} 3322, 3059, 3025, 1670, 1599, 1519, 1497, 1473, 1439, 1314, 1232, 1179, 1159, 1080, 1027, 991, 915, 883, 832, 746, 726, 704, 687, 665 cm^{-1}; HR-MS (ESI-TOF): *m/z* calcd for $C_{29}H_{25}NOSNa$: 458.1559 found 458.1555 $[M+Na]^+$.

Supplementary Material

CCDC 2034141 contain 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.

ESI shows ^{1}H and ^{13}C NMR spectra for new compounds and HSQC for **3e** and experimental details for cyrtallography.

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