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Heterocycles via intramolecular platinum-catalyzed propargylic substitution

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ABSTRACT

We report a Pt(II)-catalyzed cyclization of nucleophile-tethered propargylic acetates yielding substituted heterocycles containing multiple heteroatoms including morpholines, dioxanes, and sulfamates with high cis-selectivity.

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1. Introduction

Heterocyclic compounds continue to dominate the curiosity of biologists and chemist alike.[1] With a seemingly limitless range of structures and substitution patterns, all of which possess inherent value in medicinal chemistry and as synthetic building blocks, the need for improved and increasingly creative methods for their preparation persists. Tetrahydropyrans in particular are important substructures found in many polyketide-derived natural products, which bear the 1,3-dioxygenation pattern. Recently, we reported a novel platinum-catalyzed propargylic substitution of ω-hydroxy propargylic esters.[2] This cyclization yielded 2,6-*cis*-disubstituted tetrahydropyrans and tetrahydrofurans by way of a Pt(II)-templated activation of the ester and subsequent intramolecular S_N2' substitution (Fig. 1). Given the importance of heterocyclic compounds in chemistry and biology, we wondered if it would be feasible to access heterocycles with multiple heteroatoms using this methodology. In the context of biologically important tetrahydropyran-containing natural products, this strategy would allow access to heterocyclic analogs with potential improved potency.[3] Herein, we describe that this can be achieved by incorporation of heteroatoms within the tether linking the propargylic acetate and the cyclizing nucleophile (see box in Fig. 1). We also demonstrate that in addition to alcohols, sulfonamides, and sulfamates are equally competent nucleophiles in this chemistry.

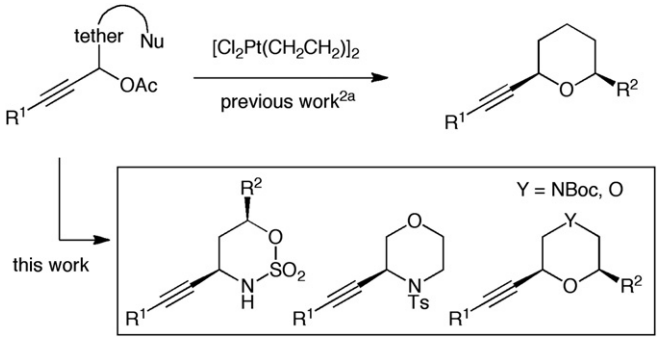

Fig. 1 Pt(II)-catalyzed propargylic substitution.

2. Results and discussion

First, we explored the possibility of implementing the intramolecular propargylic substitution for the construction of non-symmetrical 2,6-disubstituted morpholines. The 1,4-morpholine unit is prevalent in nature and is featured in compounds with a range of functions including antidepressant,[4] antiparasitic,[5] antitumor,[6] antioxidant,[7] and anti-inflammatory[8] activities.[9] Over 100 compounds listed in the world drug index contain a morpholine subunit. Additionally, morpholines have enjoyed use as tools in chemical synthesis.[10] Given the ubiquity of morpholines it is unsurprising that many preparatory methods have been developed.[11,12] Despite these notable advances, to the best of our

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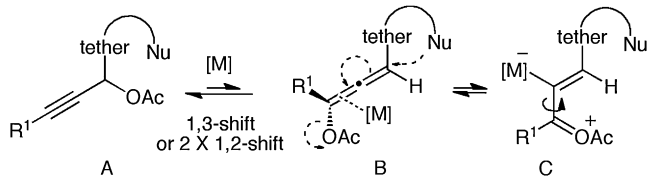
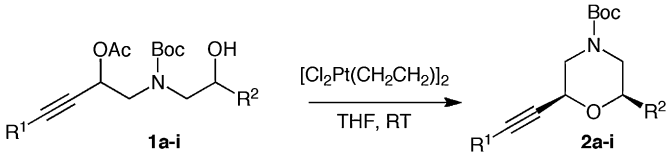
knowledge there are few examples of selective formation of non-C_2-symmetrical *cis*-2,6-disubstituted morpholines.[11e,f,l,o]

As alluded to earlier, our approach toward 2,6-disubstituted morpholines hinges on the cyclization of ω-hydroxy propargylic acetates containing a Boc-protected nitrogen atom in the tether, materials that were readily prepared on scale and in high yield.[13] As shown in Table 1, treatment of propargylic acetates **1a**–**i** with a catalytic amount of Zeise's dimer ($[(CH_2CH_2)Cl_2Pt]_2$, 2.5 mol %) in tetrahydrofuran at rt provided morpholines **2a**–**i** in excellent yields. When diastereomeric mixtures of secondary alcohols **1b**–**d**, **1f**, or **1h** were used as starting materials, only *cis*-products were obtained in high diastereomeric excess (>10:1 ratio). This dynamic kinetic resolution, via epimerization at the propargylic position,[14] was also observed in our previous study for the synthesis of alkyne-substituted tetrahydropyrans.[2a,15] As shown in Eq. 1, we had previously postulated that the propargylic substitution occurs from a metal-templated allenyl acetate (**B**) via S_N2' substitution.



(**1**)

Table 1
Formation of 2,6-disubstituted morpholines **2**[a]



Entry	Substrate	R^1	R^2	Yield[b]	*cis*/*trans*[c]
1	**1a**	$PhCH_2CH_2$	H	85	—
2	**1b**	$PhCH_2CH_2$	Et	82	13:1
3	**1c**	$PhCH_2CH_2$	*i*-Pr	86	10:1
4	**1d**	$PhCH_2CH_2$	Ph	88	14:1
5	**1e**	Ph	H	88	—
6	**1f**	Ph	Ph	85	20:1
7	**1g**	$CH_3(CH_2)_5$	H	84	—
8	**1h**	$CH_3(CH_2)_5$	Et	98	10:1
9	**1i**	$CH_3(CH_2)_3$	H	87	—

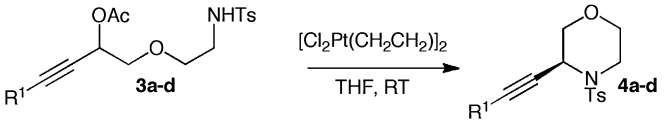
[a] Reaction conditions: propargylic acetate (0.1 M in THF), 2.5 mol % $[Cl_2Pt(CH_2H_2)]_2$, rt.
[b] Isolated yield (%).
[c] Determined by ^{1}H NMR spectroscopy.

The allenylester arises from a 1,3-acetate or double 1,2-acetate shift of propargylic acetate **A**.[16] Both the stepwise rearrangement and a hapto-2 to hapto-1 isomerization (**B** to **C**) would permit epimerization at the propargylic carbon.

With these results in hand, it was of interest to assess whether the nucleophilic residue could be switched to nitrogen and the tether residue to oxygen as an entry to alternatively substituted morpholines. As shown in Table 2, cyclization of oxygen-tethered sulfonamides **3a**–**d**, readily prepared from simple starting materials,[13] under the standard conditions provided 3-substituted morpholines **4a**–**d** in good yield (65–76%).[17]

We next pursued 2,6-disubstituted-1,4-dioxanes, which have previously been prepared by a number of methods including epoxide opening,[18] cyclodimerization of epoxides,[19] selenylation[20] and by use of iron-promoted intramolecular cyclizations of allylic ethers.[21] As their utility in a number of applications continues to be

Table 2
Formation of 3-substituted morpholines **4**[a]

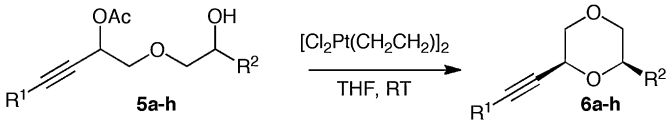


Entry	Substrate	R^1	Yield[b]
1	**3a**	Ph	65
2	**3b**	$PhCH_2CH_2$	76
3	**3c**	$CH_3(CH_2)_5$	74
4	**3d**	$CH_3(CH_2)_3$	71

[a] Reaction conditions: propargylic acetate (0.1 M in THF), 2.5 mol % $[Cl_2Pt(CH_2H_2)]_2$, rt.
[b] Isolated yield (%).

investigated, for example, in use as photoreceptors,[22] in perfumes,[23] and as anti-tumoral[24] and anti-viral agents,[25] there remains a pressing need for additional methods for their preparation. A simple derivation of the original substrates by inclusion of an oxygen atom in the tether was envisaged to allow access to 1,4-dioxanes of varying substitution patterns. Satisfyingly, stirring oxygen-tethered ω-hydroxy propargylic acetates **5a**–**h**, materials which were readily prepared on gram scale,[13] with a catalytic amount of Zeise's dimer in THF at rt, afforded the *cis*-2,6-disubstituted-1,4-dioxanes **6a**–**h** in excellent yields (85–90%) and diastereoselectivity (**6e**–**h**, 14:1 to 19:1) as illustrated in Table 3. There are few preparations in the literature for *cis*-2,6-disubstited-1,4-dioxanes where the substituents are non-identical.[26] Therefore, this methodology represents a valuable route to these synthetically useful synthons without the need for desymmetrization before further elaboration.

Table 3
Formation of 2,6-disubstituted-1,4-dioxanes **6**[a]



Entry	Substrate	R^1	R^2	Yield[b]	*cis*/*trans*[c]
1	**5a**	$PhCH_2CH_2$	H	86	—
2	**5b**	Ph	H	88	—
3	**5c**	$CH_3(CH_2)_5$	H	85	—
4	**5d**	$CH_3(CH_2)_3$	H	87	—
5	**5e**	Ph	Ph	89	14:1
6	**5f**	$CH_3(CH_2)_5$	Ph	90	19:1
7	**5g**	$CH_3(CH_2)_5$	Et	85	14:1
8	**5h**	$CH_3(CH_2)_3$	Et	85	14:1

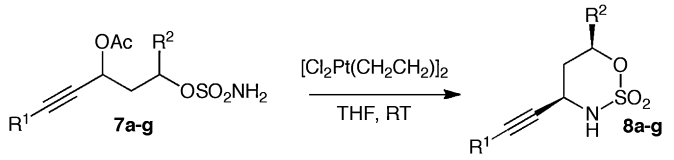
[a] Reaction conditions: propargylic acetate (0.1 M in THF), 2.5 mol % $[Cl_2Pt(CH_2H_2)]_2$, rt.
[b] Isolated yield (%).
[c] Determined by ^{1}H NMR spectroscopy.

Cyclic sulfamates, while only rarely occurring in nature,[27] have enjoyed use as building blocks in synthetic chemistry. Du Bois and Wehn elegantly demonstrated their use in cross-coupling reactions[28] and subsequently as intermediates in the synthesis of the bis-guanidinium toxin (+)-saxitoxin.[29] Despite a promising future for their continued use as intermediates toward amino alcohols and polyamines, preparations of cyclic sulfamates have been relatively limited; including, for example, rhodium-catalyzed C–H insertions[28] and reduction of the corresponding sulfamidates.[30]

We envisaged a route toward these increasingly important heterocycles by incorporation of a terminal, unsubstituted sulfamate as the nucleophilic residue for propargylic substitution. The

substrates **7a**–**g** were prepared from commercially available materials in good yield.[13] Armed with the knowledge from the morpholine preparation that sulfonamides were effective nucleophiles in these propargylic substitutions (Table 2), we were pleased to confirm that unsubstituted sulfamates were equally competent in this chemistry, as illustrated in Table 4. Gratifyingly, the transformations to cyclic sulfamates proceeded in high yields (81–88%), and *syn*/*anti* mixtures of starting materials **7c**–**g** (1:1) converged to single *cis*-disubstituted products **8** with excellent diastereoselectivity (20:1 to 25:1).[15]

Table 4
Formation of cyclic sulfamates **8**[a]



Entry		R^1	R^2	Yield[b]	*cis*/*trans*[c]
1	**7a**	$PhCH_2CH_2$	H	88	—
2	**7b**	Ph	H	85	—
3	**7c**	$PhCH_2CH_2$	CH_3	81	22:1
4	**7d**	Ph	CH_3	82	25:1
5	**7e**	$CH_3(CH_2)_5$	CH_3	82	20:1
6	**7f**	$CH_3(CH_2)_5$	$CH_2OTBDPS$	84	25:1
7	**7g**	Ph	$CH_2OTBDPS$	84	20:1

[a] Reaction conditions: propargylic acetate (0.1 M in THF), 2.5 mol % $[Cl_2Pt(CH_2H_2)]_2$, rt.
[b] Isolated yield (%).
[c] Determined by ^1H NMR spectroscopy.

3. Conclusion

In conclusion, we have demonstrated the usefulness of the intramolecular propargylic substitution of nucleophile-tethered propargylic acetates. Particularly noteworthy is the incorporation of a range of functionality to produce a range of mono- and disubstituted heterocycles containing multiple heteroatoms, such as morpholines, dioxanes, and cyclic sulfamates. The methodology described herein provides these heterocycles from readily available starting materials under operationally mild conditions and with high diastereoselectivity. Further extension of this work to gain entry to other classes of heterocycles is currently underway.

4. Experimental section

4.1. General experimental

Unless otherwise stated, commercially available materials were used without further purification. All solvents were of HPLC or ACS grade. Solvents used for moisture-sensitive operations were dried over molecular sieves (4 Å, Aldrich). Pyridine was dried over solid KOH; anhydrous *N*,*N*-dimethylformamide and CH_3CN were purchased from commercial sources. Reactions were performed under an atmosphere of nitrogen with magnetic stirring unless noted otherwise. Flash chromatography was performed using *E. Merck* silica gel 60 (240–400 mesh) according to the protocol of Still et al.[31] TLC was performed using pre-coated plates purchased from *E. Merck* (silica gel 60 PF254, 0.25 mm) and were visualized using a $KMnO_4$ or Ce (IV) stain. NMR spectra were recorded with an internal deuterium lock and referenced to the residual solvent peak[32] on the following instruments: 500 MHz: Varian Inova-500; 400 MHz: Varian Inova-400; 300 MHz Mercury-300 spectrometers. ^1H NMR data are presented as follows: chemical shift (in ppm), integration, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, br=broad, app.=apparent), and coupling constants (H/Hz). ^1H–^1H coupling constants were taken from the spectra. Infrared spectra were recorded on a *Perkin–ElmerI* 1000 series FTIR, with wavenumbers expressed in cm^{-1}, using samples prepared as thin films between NaCl plates. Electrospray ionization mass spectra (ESI-MS) were recorded on a Shimadzu 2010-LCMS. Procedures for the preparation of all substrate materials **1a**–**i**, **3a**–**d**, **5a**–**h**, and **7a**–**g** can be found in the Supplementary data.

4.2. Propargylic acetates 1a–i

*4.2.1. 1-((tert-Butoxycarbonyl)(2-hydroxyethyl)-amino)-6-phenylhex-3-yn-2-yl acetate (**1a**).* δ_H (400 MHz, $CDCl_3$) 7.28–7.24 (2H, m), 7.20–7.15 (3H, m), 5.53 (1H, m), 3.67 (2H, m), 3.58–3.14 (4H, m), 2.78 (2H, t, *J*=7.6 Hz), 2.46 (2H, t, *J*=7.6 Hz), 2.04 (3H, s), 1.44 (9H, s); δ_C (75 MHz, $CDCl_3$) 169.6, 156.6, 140.1, 128.3, 128.2, 126.3, 86.6, 80.8, 76.2, 62.7, 62.0, 52.4, 51.5, 34.5, 28.2, 20.9, 20.8; ν_{max} (liquid film) 3436, 2959, 1728, 1638, 1463, 1274, 1123, 1072, 742 cm^{-1}; MS (ESI): MNa^+, found 398.1. $C_{21}H_{29}NO_5$ requires 398.1.

*4.2.2. 1-((tert-Butoxycarbonyl)(2-hydroxybutyl)amino)-6-phenylhex-3-yn-2-yl acetate (**1b**).* δ_H (300 MHz, $CDCl_3$) 7.31–7.26 (2H, m), 7.23–7.17 (3H, m), 5.57 (1H, m), 3.68 (1H, m), 3.55–3.18 (4H, m), 2.81 (2H, app. t, *J*=7.5 Hz), 2.48 (2H, app. t, *J*=6.6 Hz), 2.05 (3H, s), 1.46 (11H, s), 0.96 (3H, t, *J*=7.8 Hz); δ_C (75 MHz, $CDCl_3$) 169.8, 157.2, 140.5, 128.6, 128.5, 126.6, 86.9, 81.2, 76.5, 73.1, 62.9, 55.3, 53.2, 52.7, 34.8, 28.3, 21.2, 21.1, 10.0; ν_{max} (liquid film) 3474, 2974, 1746, 1694, 1455, 1411, 1368, 1230, 1157, 1025, 749, 700 cm^{-1}; MS (ESI): MNa^+, found 426.2. $C_{23}H_{33}NO_5$ requires 426.2.

*4.2.3. 1-((tert-Butoxycarbonyl)(2-hydroxy-3-methyl-butyl)amino)-6-phenylhex-3-yn-2-yl acetate (**1c**).* δ_H (500 MHz, $CDCl_3$) 7.31–7.27 (2H, m), 7.23–7.19 (3H, m), 5.64 (1H, m), 3.55 (2H, m), 3.50 (1H, m), 3.32 (2H, m), 2.83 (2H, t, *J*=7.0 Hz), 2.51 (2H, app. td, *J*=8.0, 2.0 Hz), 2.07 (3H, s), 1.61–1.69 (1H, m), 1.48 (9H, s), 0.96 (3H, m), 0.95 (3H, m); δ_C (75 MHz, $CDCl_3$) 169.9, 157.3, 140.5, 128.6, 128.5, 126.6, 86.9, 81.2, 76.6, 76.1, 62.7, 53.6, 52.9, 34.9, 32.5, 28.5, 21.2, 21.1, 18.9, 17.4; ν_{max} (liquid film) 3477, 2962, 1745, 1692, 1454, 1411, 1367, 1229, 1166, 1022, 889, 748, 699 cm^{-1}; MS (ESI): MNa^+, found 440.2. $C_{24}H_{35}NO_5$ requires 440.2.

*4.2.4. 1-((tert-Butoxycarbonyl)(2-hydroxy-2-phenyl-ethyl)amino)-6-phenylhex-3-yn-2-yl acetate (**1d**).* δ_H (500 MHz, $CDCl_3$) 7.40–7.25 (10H, m), 5.61 (1H, m), 4.94 (1H, m), 3.54 (2H, m), 3.48 (1H, d, *J*=3.0 Hz), 3.45 (1H, d, *J*=3.0 Hz), 2.81 (2H, t, *J*=7.5 Hz), 2.48 (2H, td, *J*=7.5, 2.0 Hz), 2.04 (3H, s), 1.51 (9H, s); δ_C (75 MHz, $CDCl_3$) 169.8, 157.6, 142.4, 140.5, 128.7, 128.6, 127.8, 126.6, 126.0, 87.1, 81.6, 76.5, 74.2, 62.8, 57.6, 52.8, 34.8, 28.5, 21.2, 21.1; ν_{max} (liquid film) 3452, 2929, 1744, 1693, 1454, 1409, 1367, 1229, 1164, 1024, 750, 700 cm^{-1}; MS (ESI): MNa^+, found 464.4. $C_{27}H_{33}NO_5$ requires 474.2.

*4.2.5. 1-((tert-Butoxycarbonyl)(2-hydroxyethyl)-amino)-4-phenylbut-3-yn-2-yl acetate (**1e**).* δ_H (400 MHz, $CDCl_3$) 7.43–7.41 (2H, m), 7.32–7.25 (3H, m), 5.85 (1H, m), 3.77 (2H, m), 3.65 (2H, m), 3.53 (2H, m), 2.64 (1H, br s), 2.10 (3H, s), 1.46 (9H, s); δ_C (75 MHz, $CDCl_3$) 169.9, 157.0, 132.1, 129.1, 128.5, 121.9, 86.7, 84.4, 81.4, 63.1, 62.6, 52.6, 52.1, 28.5, 21.2; ν_{max} (liquid film) 3446, 2976, 1747, 1695, 1478, 1410, 1368, 1225, 1166, 1032, 758, 691 cm^{-1}; MS (ESI): MNa^+, found 370.1. $C_{19}H_{25}NO_5$ requires 370.1.

*4.2.6. 1-((tert-Butoxycarbonyl)(2-hydroxy-2-phenyl-ethyl)amino)-4-phenylbut-3-yn-2-yl acetate (**1f**).* δ_H (400 MHz, $CDCl_3$) 7.41–7.25 (10H, m), 5.86 (1H, m), 4.97 (1H, m), 3.46 (4H, m), 2.68 (1H, br s), 2.09 (3H, s), 1.49 (9H, s); δ_C (75 MHz, $CDCl_3$) 169.9, 157.4, 142.3, 132.1, 129.1, 128.7, 128.5, 128.4, 127.8, 125.5, 84.4, 81.6, 74.1, 63.0, 57.8, 53.2, 28.5, 28.4, 21.3; ν_{max} (liquid film) 2360, 1747, 1692, 1408,

1367, 1223, 1164, 1026, 757 cm^{-1}; MS (ESI): MNa^+, found 446.3. $C_{25}H_{29}NO_5$ requires 446.2.

*4.2.7. 1-((tert-Butoxycarbonyl)(2-hydroxyethyl)-amino)dec-3-yn-2-yl acetate (**1g**).* δ_H (400 MHz, $CDCl_3$) 5.60 (1H, m), 3.74 (2H, m), 3.51 (2H, m), 3.48 (2H, m), 2.18 (2H, td, *J*=7.2, 2.0 Hz), 2.06 (3H, s), 1.52–1.46 (2H, m), 1.46 (9H, s), 1.38–1.24 (6H, m), 0.88 (3H, t, *J*=7.2 Hz); δ_C (75 MHz, $CDCl_3$) 169.9, 157.1, 88.0, 81.3, 75.5, 63.1, 62.4, 52.8, 51.9, 31.4, 28.6, 28.4, 22.7, 21.2, 18.8, 14.2; ν_{max} (liquid film) 3463, 2933, 1748, 1697, 1466, 1409, 1367, 1226, 1158, 1023, 775 cm^{-1}; MS (ESI): MNa^+, found 378.1. $C_{19}H_{33}NO_5$ requires 378.2.

*4.2.8. 1-((tert-Butoxycarbonyl)(2-hydroxy-3-methyl-butyl)amino) dec-3-yn-2-yl acetate (**1h**).* δ_H (400 MHz, $CDCl_3$) 5.61 (1H, m), 3.71 (1H, m), 3.54 (2H, m), 3.29 (2H, m), 2.18 (2H, app. t, *J*=7.2 Hz), 2.05 (3H, s), 1.52–1.41 (4H, m), 1.46 (9H, s), 1.38–1.26 (6H, m), 0.96 (3H, t, *J*=7.6 Hz), 0.88 (3H, t, *J*=7.2 Hz); δ_C (75 MHz, $CDCl_3$) 169.8, 157.2, 88.0, 81.1, 75.6, 73.1, 63.1, 55.3, 54.8, 52.8, 31.4, 28.7, 28.5, 28.3, 22.7, 21.2, 18.8, 14.2, 10.0; ν_{max} (liquid film) 2932, 2360, 1747, 1693, 1467, 1410, 1367, 1228, 1156, 1023, 766 cm^{-1}; MS (ESI): MNa^+, found 405.9. $C_{21}H_{37}NO_5$ requires 406.2.

*4.2.9. 1-((tert-Butoxycarbonyl)(2-hydroxyethyl)-amino)oct-3-yn-2-yl acetate (**1i**).* δ_H (400 MHz, $CDCl_3$) 5.59 (1H, m), 3.73 (2H, app. t, *J*=2.8 Hz), 3.49–3.43 (4H, m), 2.18 (2H, td, *J*=6.8, 2.0 Hz), 2.05 (3H, s), 1.50–1.43 (2H, m), 1.47 (9H, s), 1.41–1.29 (2H, m), 0.88 (3H, t, *J*=7.2 Hz); δ_C (75 MHz, $CDCl_3$) 169.9, 157.1, 87.9, 81.3, 75.5, 63.1, 62.4, 52.8, 51.9, 30.5, 28.5, 22.1, 21.2, 18.5, 13.7; ν_{max} (liquid film) 3455, 2935, 1747, 1697, 1466, 1409, 1367, 1227, 1160, 1023, 878, 775 cm^{-1}; MS (ESI): MNa^+, found 350.0. $C_{17}H_{29}NO_5$ requires 350.1.

4.3. General procedure for the preparation of 2,6-substituted morpholines 2a–i

To a 0.1 M solution of propargylic ester **1a**–**i**[13] in THF at rt was added $[Cl_2Pt(CH_2CH_2)]_2$ (2.5 mol %). The resulting yellow solution was stirred for 0.5–2.0 h[13] before being quenched by the addition of NEt_3 (0.5 mL/mmol substrate). The solution was concentrated in vacuo and the crude material was filtered through a plug of silica gel to give the title compound **2a**–**i** as a colorless oil.

*4.3.1. tert-Butyl 2-(4-phenylbut-1-yn-1-yl)-morpholine-4-carboxylate (**2a**).* δ_H (500 MHz, $CDCl_3$) 7.31–7.27 (2H, m), 7.22–7.19 (3H, m), 4.18 (1H, m), 3.88 (1H, dt, *J*=12.5, 4.0 Hz), 3.78 (1H, br d, *J*=12.5 Hz), 3.60 (1H, app. dt, *J*=13.5, 3.0 Hz), 3.49 (1H, ddd, *J*=13.5, 9.0, 3.0 Hz), 3.22–3.14 (2H, m), 2.84 (2H, t, *J*=7.5 Hz), 2.52 (2H, td, *J*=8.0, 2.0 Hz), 1.49 (9H, s); δ_C (125 MHz, $CDCl_3$) 154.6, 140.7, 128.6, 128.4, 126.5, 86.5, 80.2, 77.4, 66.2, 65.1, 49.1, 43.6, 35.1, 28.6, 20.9; ν_{max} (liquid film) 2975, 1698, 1454, 1417, 1250, 1171, 1099, 1016, 868, 748, 699 cm^{-1}; MS (ESI): MNa^+, found 338.1. $C_{19}H_{25}NO_3$ requires 338.1.

*4.3.2. tert-Butyl 2-ethyl-6-(4-phenylbut-1-yn-1-yl)-morpholine-4-carboxylate (**2b**).* δ_H (500 MHz, $CDCl_3$) 7.31–7.27 (2H, m), 7.22–7.20 (3H, m), 4.12 (1H, m), 4.02 (1H, br d, *J*=12.5 Hz), 3.93 (1H, br d, *J*=12.5 Hz), 3.31–3.25 (1H, m), 2.85 (2H, t, *J*=7.5 Hz), 2.79 (1H, app. t, *J*=12.5 Hz), 2.53 (2H, app. td, *J*=7.5, 1.5 Hz), 2.49 (1H, m), 1.64–1.57 (1H, m), 1.53–1.47 (1H, m), 1.49 (9H, s), 0.98 (3H, t, *J*=7.5 Hz); δ_C (125 MHz, $CDCl_3$) 154.5, 140.7, 128.6, 128.5, 126.5, 86.1, 80.3, 77.7, 77.5, 67.0, 49.0, 47.8, 35.1, 28.6, 26.3, 21.1, 9.6; ν_{max} (liquid film) 3449, 2923, 2107, 1703, 1654, 1453, 1419, 1365, 1232, 1171, 1084, 880, 699 cm^{-1}; MS (ESI): MNa^+, found 366.0. $C_{21}H_{29}NO_3$ requires 366.1.

*4.3.3. tert-Butyl 2-isopropyl-6-(4-phenylbut-1-yn-1-yl)morpholine-4-carboxylate (**2c**).* δ_H (500 MHz, $CDCl_3$) 7.31–7.27 (2H, m), 7.23–7.20 (3H, m), 4.10 (1H, br d, *J*=10.5 Hz), 3.98 (2H, m), 3.06 (1H, t, *J*=7.5 Hz), 2.85 (2H, t, *J*=7.5 Hz), 2.77 (1H, t, *J*=12.5 Hz), 2.55 (3H, m), 1.76 (1H, m), 1.49 (9H, s), 1.01 (3H, d, *J*=7.0 Hz), 0.94 (3H, d, *J*=7.0 Hz); δ_C (125 MHz, $CDCl_3$) 154.7, 140.7, 128.6, 128.5, 126.5, 85.9, 81.1, 80.3, 77.8, 77.4, 67.1, 35.1, 31.3, 28.6, 21.1, 18.8, 18.3; ν_{max} (liquid film) 3432, 2964, 2929, 1699, 1454, 1366, 1250, 1150, 1082, 886, 699 cm^{-1}; MS (ESI): MNa^+, found 380.1. $C_{22}H_{31}NO_3$ requires 380.2.

*4.3.4. tert-Butyl 2-phenyl-6-(4-phenylbut-1-yn-1-yl)morpholine-4-carboxylate (**2d**).* δ_H (400 MHz, $CDCl_3$) 7.39–7.18 (10H, m), 4.42 (1H, dd, *J*=10.8, 2.4 Hz), 4.30 (1H, m), 4.10 (2H, m), 2.90 (1H, dd, *J*=12.8, 11.2 Hz), 2.84 (2H, t, *J*=7.6 Hz), 2.78 (1H, m), 2.52 (2H, td, *J*=7.6, 1.2 Hz), 1.49 (9H, s); δ_C (125 MHz, $CDCl_3$) 154.4, 140.6, 138.7, 128.6, 128.5, 128.4, 126.6, 126.5, 86.5, 80.6, 78.2, 67.3, 60.6, 49.0, 34.9, 28.6, 21.2, 14.4; ν_{max} (liquid film) 3419, 2976, 2929, 2859, 2243, 1694, 1454, 1416, 1366, 1305, 1251, 1168, 1120, 1074, 1029, 886, 750, 699 cm^{-1}; MS (ESI): MNa^+, found 414.2. $C_{25}H_{29}NO_3$ requires 414.2.

*4.3.5. tert-Butyl 2-(phenylethynyl)morpholine-4-carboxylate (**2e**).* δ_H (400 MHz, $CDCl_3$) 7.44–7.42 (2H, m), 7.33–7.25 (3H, m), 4.43 (1H, dd, *J*=8.0, 2.8 Hz), 3.98 (1H, app. d, *J*=11.2 Hz), 3.89 (1H, br d, *J*=8.0 Hz), 3.65–3.55 (2H, m), 3.36–3.24 (2H, m), 1.46 (9H, s); δ_C (125 MHz, $CDCl_3$) 154.6, 132.1, 128.8, 128.4, 122.5, 86.5, 85.4, 80.4, 66.4, 65.2, 48.8, 43.7, 28.6; ν_{max} (liquid film) 2975, 1698, 1490, 1454, 1417, 1366, 1250, 1168, 1127, 1085, 757, 691 cm^{-1}; MS (ESI): MNa^+, found 310.1. $C_{17}H_{21}NO_3$ requires 310.1.

*4.3.6. tert-Butyl 2-phenyl-6-(phenylethynyl)-morpholine-4-carboxylate (**2f**).* δ_H (500 MHz, $CDCl_3$) 7.49–7.27 (10H, m), 4.59 (1H, dd, *J*=3.0, 11.0 Hz), 4.53 (1H, dd, *J*=11.0, 2.5 Hz), 4.29 (1H, br d, *J*=11.5 Hz), 4.18 (1H, br d, *J*=9.0 Hz), 3.11 (1H, app. t, *J*=12.0 Hz), 2.88 (1H, app. t, *J*=12.0 Hz), 1.49 (9H, s); δ_C (125 MHz, $CDCl_3$) 154.5, 138.8, 132.1, 128.8, 128.6, 128.4, 128.3, 126.6, 122.5, 86.2, 85.4, 80.7, 78.3, 67.7, 49.7, 48.6, 28.6; ν_{max} (liquid film) 2360, 1694, 1413, 1249, 1165, 1125, 1071, 756 cm^{-1}; MS (ESI): MNa^+, found 386.1. $C_{23}H_{25}NO_3$ requires 386.1.

*4.3.7. tert-Butyl 2-(oct-1-yn-1-yl)morpholine-4-carboxylate (**2g**).* δ_H (500 MHz, $CDCl_3$) 4.17 (1H, m), 3.89 (1H, app. dt, *J*=12.0, 4.0 Hz), 3.80 (1H, br d, *J*=12.0 Hz), 3.61 (1H, dt, *J*=12.0, 3.5 Hz), 3.49 (1H, ddd, *J*=14.5, 11.5, 3.5 Hz), 3.19–3.10 (2H, m), 2.20 (2H, td, *J*=7.0, 2.0 Hz), 1.53–1.48 (2H, m), 1.46 (9H, s), 1.44–1.24 (6H, m), 0.88 (3H, t, *J*=7.0 Hz); δ_C (125 MHz, $CDCl_3$) 154.6, 87.4, 80.2, 76.5, 66.3, 65.2, 49.1, 43.1, 31.4, 28.6, 28.5, 22.6, 18.8, 14.0; ν_{max} (liquid film) 3445, 2931, 2859, 2360, 1702, 1455, 1417, 1250, 1172, 1100, 1015, 869, 767 cm^{-1}; MS (ESI): MNa^+, found 318.2. $C_{17}H_{29}NO_3$ requires 318.2.

*4.3.8. tert-Butyl 2-ethyl-6-(oct-1-yn-1-yl)-morpholine-4-carboxylate (**2h**).* δ_H (500 MHz, $CDCl_3$) 4.12 (1H, m), 4.03 (1H, br d, *J*=11.0 Hz), 3.91 (1H, br d, *J*=11.0 Hz), 3.27 (1H, m), 2.80 (1H, t, *J*=12.0 Hz), 2.50 (1H, t, *J*=12.0 Hz), 2.21 (2H, td, *J*=7.0, 2.0 Hz), 1.64–1.55 (1H, m), 1.54–1.43 (3H, m), 1.47 (9H, s), 1.24–1.41 (6H, m), 0.97 (3H, t, *J*=7.5 Hz), 0.89 (3H, t, *J*=7.0 Hz); δ_C (125 MHz, $CDCl_3$) 154.5, 86.9, 80.3, 77.5, 76.8, 67.1, 49.1, 47.7, 31.4, 28.7, 28.6, 28.5, 26.3, 22.6, 18.9, 14.1, 9.7; ν_{max} (liquid film) 2931, 2858, 1703, 1415, 1318, 1235, 1173, 1147, 1083, 882 cm^{-1}; MS (ESI): M^+, found 323.1. $C_{19}H_{33}NO_3$ requires 323.2.

4.4. Propargylic acetates 3a–d

*4.4.1. 1-(2-(4-Methylphenylsulfonamido)ethoxy)-4-phenylbut-3-yn-2-yl acetate (**3a**).* δ_H (400 MHz, $CDCl_3$) 7.74 (2H, d, *J*=8.4 Hz), 7.45–7.42 (2H, m), 7.36–7.27 (5H, m), 5.73 (1H, dd, *J*=7.2, 4.0 Hz), 5.05 (1H, m), 3.73–3.63 (2H, m), 3.61–3.53 (2H, m), 3.12 (2H, br dd, *J*=10.0, 5.6 Hz), 2.41 (3H, s), 2.13 (3H, s); δ_C (75 MHz, $CDCl_3$) 170.2, 143.6, 137.0, 132.1, 129.9, 129.8, 129.1, 128.5, 127.2, 126.5, 121.8, 86.6, 83.3, 72.5, 69.8, 63.3, 42.9, 21.6, 21.2; ν_{max} (liquid film) 3278, 1744,

1492, 1371, 1329, 1228, 1161, 1093, 815 cm^{-1}; MS (ESI): MNa^+, found 424.5. $C_{21}H_{23}NSO_5$ found 424.2.

*4.4.2. 1-(2-(4-Methylphenylsulfonamido)ethoxy)-6-phenylhex-3-yn-2-yl acetate (**3b**).* δ_H (400 MHz, $CDCl_3$) 7.73 (2H, d, J=8.4 Hz), 7.27 (4H, app. t, J=8.0 Hz), 7.21–7.17 (3H, m), 5.45 (1H, m), 4.90 (1H, br t, J=5.6 Hz), 3.56–3.44 (4H, m), 3.08 (2H, dd, J=10.8, 6.0 Hz), 2.80 (2H, t, J=7.2 Hz), 2.49 (2H, td, J=7.6, 2.0 Hz), 2.40 (3H, s), 2.07 (3H, s); δ_C (75 MHz, $CDCl_3$) 170.2, 143.6, 140.4, 137.0, 129.9, 128.6, 128.5, 127.2, 126.5, 87.0, 75.5, 72.6, 69.7, 63.2, 42.9, 34.8, 21.7, 21.2, 21.0; ν_{max} (liquid film) 2360, 1741, 1371, 1329, 1231, 1161, 1092, 1037, 815, 667 cm^{-1}; MS (ESI): MNa^+, found 452.1. $C_{23}H_{27}NSO_5$ requires 452.1.

*4.4.3. 1-(2-(4-Methylphenylsulfonamido)ethoxy)dec-3-yn-2-yl acetate (**3c**).* δ_H (400 MHz, $CDCl_3$) 7.71 (2H, d, J=8.4 Hz), 7.27 (2H, app. t, J=8.4 Hz), 5.46 (1H, m), 4.96 (1H, br t, J=6.0 Hz), 3.57–3.45 (4H, m), 3.07 (2H, m), 2.39 (3H, s), 2.17 (2H, td, J=7.2, 1.6 Hz), 2.06 (3H, s), 1.49–1.42 (2H, m), 1.36–1.21 (6H, m), 0.86 (3H, t, J=7.2 Hz); δ_C (75 MHz, $CDCl_3$) 170.3, 143.6, 137.1, 129.9, 127.2, 88.0, 74.5, 72.8, 69.7, 63.3, 43.0, 31.4, 28.6, 28.4, 22.7, 21.7, 21.2, 18.8, 14.2; ν_{max} (thin film) 3288, 2930, 1738, 1599, 1428, 1372, 1329, 130, 1160, 1092, 945, 814, 661 cm^{-1}; MS (ESI): MNa^+, found 432.2. $C_{21}H_{31}NSO_5$ requires 432.1.

*4.4.4. 1-(2-(4-Methylphenylsulfonamido)ethoxy)oct-3-yn-2-yl acetate (**3d**).* δ_H (400 MHz, $CDCl_3$) 7.75–7.71 (2H, m), 7.31–7.25 (2H, m), 5.47 (1H, m), 4.93 (1H, br t, J=6.0 Hz), 3.59–3.46 (4H, m), 3.13–3.05 (2H, m), 2.40 (3H, s), 2.18 (2H, td, J=7.2, 2.0 Hz), 2.07 (3H, s), 1.49–1.42 (2H, m), 1.40–1.31 (2H, m), 0.88 (3H, t, J=7.2 Hz); δ_C (75 MHz, $CDCl_3$) 170.3, 143.6, 137.1, 129.9, 127.3, 88.0, 74.5, 72.8, 69.7, 63.3, 43.0, 30.5, 22.1, 21.7, 21.2, 18.5, 13.7; ν_{max} (liquid film) 3284, 2933, 2873, 1743, 1431, 1372, 1330, 1231, 1161, 1093, 1037, 944, 815 cm^{-1}; MS (ESI): MNa^+, found 404.2. $C_{19}H_{27}NSO_5$ requires 404.1.

4.5. General procedure for the preparation of 3-substituted morpholines 4a–d

To a 0.1 M solution of propargylic ester **3a**–**d** in THF at rt was added $[Cl_2Pt(CH_2CH_2)]_2$ (2.5 mol %). The resulting yellow solution was stirred for 3–4 h[13] before being quenched by the addition of NEt_3 (0.5 mL/mmol substrate). The solution was concentrated in vacuo and the crude material was filtered through a plug of silica gel.

*4.5.1. 3-(Phenylethynyl)-4-tosylmorpholine (**4a**).* δ_H (500 MHz, $CDCl_3$) 7.73 (2H, d, J=8.5 Hz), 7.29–7.20 (5H, m), 6.99 (2H, dd, J=8.5, 1.0 Hz), 4.79 (1H, m), 3.99 (2H, m), 3.83 (1H, dd, J=11.0, 3.0 Hz), 3.70 (1H, td, J=11.0, 3.0 Hz), 3.58 (1H, m), 3.18 (1H, td, J=12.0, 3.0 Hz), 2.27 (3H, s); δ_C (75 MHz, $CDCl_3$) 144.0, 134.4, 131.8, 129.6, 128.6, 128.4, 128.2, 122.2, 86.9, 82.8, 71.4, 66.9, 47.2, 42.3, 21.6; ν_{max} (liquid film) 2933, 1597, 1491, 1443, 1346, 1260, 1165, 1111, 936 cm^{-1}; MS (ESI): MNa^+, found 364.3. $C_{19}H_{19}NSO_3$ requires 364.1.

*4.5.2. 3-(4-Phenylbut-1-yn-1-yl)-4-tosylmorpholine (**4b**).* δ_H (400 MHz, $CDCl_3$) 7.65 (2H, d, J=8.0 Hz), 7.27–7.17 (5H, m), 7.08 (2H, m), 4.55 (1H, m), 3.88–3.80 (2H, m), 3.68 (1H, dd, J=11.2, 2.8 Hz), 3.60 (1H, td, J=11.2, 2.8 Hz), 3.41 (1H, m), 2.98 (1H, td, J=12.0, 3.2 Hz), 2.51 (2H, m), 2.38 (3H, s), 2.11 (2H, m); δ_C (75 MHz, $CDCl_3$) 143.7, 140.5, 134.7, 129.3, 128.6, 128.5, 126.5, 86.6, 82.6, 74.3, 71.5, 66.8, 46.7, 41.9, 34.7, 21.8, 20.8; ν_{max} (liquid film) 2921, 2858, 1598, 1494, 1453, 1346, 1261, 1166, 1110, 936 cm^{-1}; MS (ESI): MNa^+, found 392.2. $C_{21}H_{23}NSO_3$ requires 392.1.

*4.5.3. 3-(Oct-1-yn-1-yl)-4-tosylmorpholine (**4c**).* δ_H (400 MHz, $CDCl_3$) 7.71–7.68 (2H, m), 7.30–7.25 (2H, m), 4.55 (1H, m), 3.88 (1H, dd, J=11.2, 3.2 Hz), 3.83 (1H, m), 3.69 (1H, dd, J=11.2, 3.2 Hz), 3.65–3.62 (1H, td, J=11.6, 2.8 Hz), 3.47–3.41 (1H, m), 3.05 (1H, td, J=11.2, 3.2 Hz), 2.41 (3H, s), 1.79 (2H, d, J=1.6 Hz), 1.26–1.21 (2H, m), 1.17–1.16 (6H, m), 0.87 (3H, t, J=7.2 Hz); δ_C (75 MHz, $CDCl_3$) 143.6, 134.7, 129.4, 128.5, 73.5, 71.6, 68.4, 66.8, 46.7, 41.9, 31.5, 28.7, 28.4, 22.7, 21.7, 18.7, 14.2; ν_{max} (liquid film) 2929, 2858, 1348, 1261, 1167, 1113, 937 cm^{-1}; MS (ESI): MNa^+, found 372.0. $C_{19}H_{27}NSO_3$ requires 372.1.

*4.5.4. 3-(Hex-1-yn-1-yl)-4-tosylmorpholine (**4d**).* δ_H (400 MHz, $CDCl_3$) 7.69 (2H, d, J=8.4 Hz), 7.27 (2H, d, J=8.4 Hz), 4.55 (1H, m), 3.88 (1H, dd, J=11.6, 2.8 Hz), 3.82 (1H, app. d, J=10.8 Hz), 3.70 (1H, dd, J=11.2, 2.8 Hz), 3.61 (1H, td, J=11.6, 2.8 Hz), 3.46 (1H, m), 3.05 (1H, td, J=11.6, 3.2 Hz), 2.41 (3H, s), 1.80 (2H, t, J=6.8 Hz), 1.24–1.14 (4H, m), 0.81 (3H, t, J=7.2 Hz); δ_C (75 MHz, $CDCl_3$) 143.6, 134.7, 129.4, 128.5, 87.5, 73.4, 71.6, 66.9, 46.7, 41.9, 30.5, 22.1, 21.7, 18.4, 13.7; ν_{max} (liquid film) 2929, 2859, 2360, 1598, 1444, 1346, 1261, 1167, 1111, 936 cm^{-1}; MS (ESI): MNa^+, found 344.3. $C_{17}H_{23}NSO_3$ requires 344.2.

4.6. Propargylic acetates 5a–h

*4.6.1. 1-(2-Hydroxyethoxy)-6-phenylhex-3-yn-2-yl acetate (**5a**).* δ_H (400 MHz, $CDCl_3$) 7.30–7.25 (2H, m), 7.22–7.17 (3H, m), 5.54 (1H, m), 3.71–3.55 (6H, m), 2.80 (2H, td, J=7.6, 2.4 Hz), 2.51–2.46 (2H, m), 2.09 (3H, s); δ_C (75 MHz, $CDCl_3$) 170.3, 140.5, 128.6, 128.5, 126.5, 86.8, 75.6, 72.8, 72.7, 63.4, 61.8, 34.8, 21.2, 21.1; ν_{max} (liquid film) 3455, 2931, 2239, 1741, 1495, 1454, 1371, 1231, 1131, 1037, 946, 748 cm^{-1}; MS (ESI): MNa^+, found 299.1. $C_{16}H_{20}O_4$ requires 299.1.

*4.6.2. 1-(2-Hydroxyethoxy)-4-phenylbut-3-yn-2-yl acetate (**5b**).* δ_H (400 MHz, $CDCl_3$) 7.46–7.43 (2H, m), 7.36–7.26 (3H, m), 5.84 (1H, dd, J=4.0, 6.8 Hz), 3.88–3.73 (2H, m), 3.73–3.64 (4H, m), 2.10 (3H, s); δ_C (75 MHz, $CDCl_3$) 170.3, 132.1, 129.1, 128.5, 121.9, 86.6, 83.6, 72.9, 72.7, 63.5, 61.9, 21.2; ν_{max} (liquid film) 3432, 2935, 2229, 1742, 1644, 1491, 1443, 1372, 1226, 1131, 1039, 844, 758, 692 cm^{-1}; MS (ESI): MNa^+, found 271.1. $C_{14}H_{16}O_4$ requires 271.1.

*4.6.3. 1-(2-Hydroxyethoxy)dec-3-yn-2-yl acetate (**5c**).* δ_H (400 MHz, $CDCl_3$) 5.55–5.53 (1H, m), 3.69–3.54 (6H, m), 2.31 (1H, br s), 2.15 (2H, td, J=7.2, 2.0 Hz), 2.06 (3H, s), 1.48–1.41 (2H, m), 1.34–1.20 (6H, m), 0.84 (3H, t, J=6.0 Hz); δ_C (75 MHz, $CDCl_3$) 170.2, 87.6, 74.6, 72.8, 72.7, 63.3, 61.6, 31.3, 28.5, 28.3, 22.5, 21.0, 18.7, 14.0; ν_{max} (liquid film) 3440, 2931, 2240, 1745, 1454, 1371, 1230, 1132, 1036 cm^{-1}; MS (ESI): MNa^+, found 279.1. $C_{14}H_{24}O_4$ requires 279.1.

*4.6.4. 1-(2-Hydroxyethoxy)oct-3-yn-2-yl acetate (**5d**).* δ_H (400 MHz, $CDCl_3$) 5.55–5.52 (1H, m), 3.69–3.54 (6H, m), 2.34 (1H, br s), 2.18–2.13 (2H, m), 2.06 (3H, s), 1.47–1.39 (2H, m), 1.38–1.29 (2H, m), 0.88–0.83 (3H, m); δ_C (75 MHz, $CDCl_3$) 170.3, 87.7, 74.7, 72.9, 72.8, 63.4, 61.7, 30.5, 22.0, 21.2, 18.5, 13.7; ν_{max} (liquid film) 3448, 2934, 2360, 1743, 1371, 1228, 1131, 1035 cm^{-1}; MS (ESI): MNa^+, found 251.1. $C_{12}H_{20}O_4$ requires 251.1.

*4.6.5. 1-(2-Hydroxy-2-phenylethoxy)-4-phenylbut-3-yn-2-yl acetate (**5e**).* δ_H (400 MHz, $CDCl_3$) 7.45–7.25 (10H, m), 5.84 (1H, m), 4.91 (1H, m), 3.86–3.83 (2H, m), 3.75 (1H, m), 3.62–3.51 (1H, m), 2.93 (1H, m), 2.14 (3H, s); δ_C (75 MHz, $CDCl_3$) 170.2, 139.9, 132.1, 129.1, 128.6, 128.5, 128.1, 126.3, 121.9, 86.7, 83.6, 77.6, 72.8, 72.7, 63.5, 21.2; ν_{max} (liquid film) 2913, 1745, 1491, 1443, 1371, 1226, 1129, 1028, 757, 700 cm^{-1}; MS (ESI): MNa^+, found 347.1. $C_{20}H_{20}O_4$ requires 347.1.

*4.6.6. 1-(2-Hydroxy-2-phenylethoxy)dec-3-yn-2-yl acetate (**5f**).* δ_H (400 MHz, $CDCl_3$) 7.37–7.25 (5H, m), 5.58 (1H, m), 4.86 (1H, m), 3.73–3.69 (2H, m), 3.66 (1H, dd, J=10.0, 3.2 Hz), 3.49 (1H, m), 2.95 (1H, dd, J=6.4, 2.0 Hz), 2.18 (2H, m), 2.08 (3H, s), 1.48 (2H, m), 1.37–1.22 (6H, m), 0.87 (3H, t, J=6.8 Hz); δ_C (75 MHz, $CDCl_3$) 170.3, 140.0, 128.6, 128.1, 126.3, 88.0, 74.7, 73.0, 72.8, 72.7, 63.4, 31.4, 28.7,

28.5, 22.7, 21.2, 18.9, 14.2; ν_{max} (liquid film) 2930, 2858, 1743, 1453, 1371, 1230, 1128, 1028, 757, 700 cm^{-1}; MS (ESI): MH^+, found 333.2. $C_{20}H_{28}O_4$ requires 333.2.

*4.6.7. 1-(2-Hydroxybutoxy)dec-3-yn-2-yl acetate (**5g**).* δ_H (400 MHz, $CDCl_3$) 5.54 (1H, m), 3.72–3.60 (3H, m), 3.54 (1H, m), 3.32 (1H, m), 2.42 (1H, d, *J*=2.8 Hz), 2.17 (2H, m), 2.08 (3H, s), 1.48–1.40 (4H, m), 1.36–1.23 (6H, m), 0.93 (3H, t, *J*=6.4 Hz), 0.86 (3H, t, *J*=6.4 Hz); δ_C (75 MHz, $CDCl_3$) 170.3, 87.9, 75.7, 74.8, 73.0, 71.7, 63.4, 31.4, 28.6, 28.4, 26.1, 22.6, 21.2, 18.8, 14.2, 10.0; ν_{max} (liquid film) 2931, 2858, 1744, 1635, 1457, 1371, 1231, 1118, 1039 cm^{-1}; MS (ESI): M^+, found 284.2. $C_{16}H_{28}O_4$ requires 284.2.

*4.6.8. 1-(2-Hydroxybutoxy)oct-3-yn-2-yl acetate (**5h**).* δ_H (400 MHz, $CDCl_3$) 5.56–5.53 (1H, m), 3.72–3.59 (3H, m), 3.54 (1H, m), 3.2 (1H, m), 2.42 (1H, br s), 2.18 (2H, m), 2.08 (3H, s), 1.51–1.28 (6H, m), 0.93 (3H, t, *J*=7.2 Hz), 0.87 (3H, t, *J*=7.2 Hz); δ_C (75 MHz, $CDCl_3$) 170.3, 87.9, 75.7, 73.0, 72.9, 71.7, 63.5, 30.5, 26.1, 22.0, 21.2, 18.5, 13.7, 10.0; ν_{max} (liquid film) 2933, 1747, 1464, 1372, 1231, 1119, 1039 cm^{-1}; MS (ESI): MNa^+, found 279.1. $C_{14}H_{24}O_4$ requires 279.1.

4.7. General procedure for the preparation of 3,5-substituted-1,4-dioxanes 6a–h

To a 0.1 M solution of propargylic ester **5a**–**h** in THF at rt was added $[Cl_2Pt(CH_2CH_2)]_2$ (2.5 mol %). The resulting yellow solution was stirred for 0.5–1.0 h[13] before being quenched by the addition of NEt_3 (0.5 mL/mmol substrate). The solution was concentrated in vacuo and the crude material was filtered through a plug of silica gel.

*4.7.1. 2-(4-Phenylbut-1-yn-1-yl)-1,4-dioxane (**6a**).* δ_H (400 MHz, $CDCl_3$) 7.30–7.27 (2H, m), 7.26–7.18 (3H, m), 4.31–4.28 (1H, m), 3.87–3.76 (2H, m), 3.70–3.55 (3H, m), 3.54–3.49 (1H, m), 2.86–2.81 (2H, m), 2.54–2.48 (2H, m); δ_C (75 MHz, $CDCl_3$) 140.6, 128.6, 128.5, 126.6, 87.0, 76.5, 70.8, 66.6, 66.4, 65.9, 35.1, 21.1; ν_{max} (liquid film) 2962, 2854, 1603, 1453, 1338, 1260, 1119, 1091, 876, 699 cm^{-1}; MS (ESI): MNa^+, found 239.0. $C_{14}H_{16}O_2$ requires 239.1.

*4.7.2. 2-(Phenylethynyl)-1,4-dioxane (**6b**).* δ_H (400 MHz, $CDCl_3$) 7.45–7.44 (2H, m), 7.32–7.25 (3H, m), 4.56 (1H, dd, *J*=8.8, 3.2 Hz), 3.95–3.89 (2H, m), 3.77–3.65 (4H, m); δ_C (75 MHz, $CDCl_3$) 132.0, 128.9, 128.5, 122.2, 86.7, 84.5, 70.6, 66.6, 66.5, 66.0; ν_{max} (liquid film) 2853, 1491, 1443, 1337, 1263, 1119, 1092, 903, 874, 756, 691 cm^{-1}; MS (ESI): M^+, found 187.9. $C_{12}H_{12}O_2$ requires 188.0.

*4.7.3. 2-(Oct-1-yn-1-yl)-1,4-dioxane (**6c**).* δ_H (400 MHz, $CDCl_3$) 4.28 (1H, ddd, *J*=8.8, 4.8, 2.4 Hz), 3.80 (2H, m), 3.68–3.61 (3H, m), 3.50 (1H, dd, *J*=11.2, 8.8 Hz), 2.18 (2H, td, *J*=7.2, 2.0 Hz), 1.47 (2H, td, *J*=15.2, 7.2 Hz), 1.37–1.20 (6H, m), 0.85 (3H, t, *J*=7.2 Hz); δ_C (75 MHz, $CDCl_3$) 87.8, 75.5, 70.9, 66.5, 66.0, 31.4, 28.7, 28.6, 22.7, 18.8, 14.2; ν_{max} (liquid film) 2958, 2885, 2245, 1452, 1337, 1259, 1120, 912, 877 cm^{-1}; MS (ESI): MH^+, found 197.1. $C_{12}H_{21}O_2$ requires 197.1.

*4.7.4. 2-(Hex-1-yn-1-yl)-1,4-dioxane (**6d**).* δ_H (400 MHz, $CDCl_3$) 4.28 (1H, ddd, *J*=8.8, 4.8, 2.4 Hz), 3.86–3.76 (2H, m), 3.69–3.58 (3H, m), 3.50 (1H, dd, *J*=11.2, 8.8 Hz), 2.19 (2H, td, *J*=7.2, 2.0 Hz), 1.50–1.45 (2H, m), 1.44–1.34 (2H, m), 0.87 (3H, t, *J*=7.2 Hz); δ_C (75 MHz, $CDCl_3$) 87.8, 75.5, 70.9, 66.5, 66.0, 30.6, 22.1, 18.5, 13.7; ν_{max} (liquid film) 2959, 2856, 2359, 1451, 1336, 1259, 1119, 1092, 915, 874 cm^{-1}; MS (ESI): MH^+, found 169.0. $C_{10}H_{16}O_2$ requires 169.1.

*4.7.5. 2-Phenyl-6-(phenylethynyl)-1,4-dioxane (**6e**).* δ_H (400 MHz, $CDCl_3$) 7.49–7.26 (10H, m), 4.80 (1H, dd, *J*=10.4, 2.8 Hz), 4.72 (1H, dd, *J*=10.4, 2.6 Hz), 4.03 (1H, dd, *J*=11.5, 2.8 Hz), 3.87 (1H, dd, *J*=11.7, 2.7 Hz), 3.70 (1H, app. t, *J*=10.8 Hz), 3.50 (1H, dd, *J*=11.6, 10.8 Hz); δ_C (75 MHz, $CDCl_3$) 137.4, 132.1, 128.9, 128.6, 128.5, 128.4, 126.7, 122.2, 86.8, 84.1, 78.3, 71.8, 70.0, 67.5; ν_{max} (liquid film) 2962, 2852, 1490, 1450, 1311, 1116, 1075, 909, 756, 698 cm^{-1}; MS (ESI): MH^+, found 265.0. $C_{18}H_{16}O_2$ requires 265.1.

*4.7.6. 2-(Oct-1-yn-1-yl)-6-phenyl-1,4-dioxane (**6f**).* δ_H (400 MHz, $CDCl_3$) 7.42–7.20 (5H, m), 4.64 (1H, dd, *J*=10.4, 2.8 Hz), 4.54 (1H, ddd, *J*=10.4, 4.4, 2.0 Hz), 3.89 (1H, dd, *J*=11.6, 2.8 Hz), 3.82 (1H, dd, *J*=11.6, 2.8 Hz), 3.55 (1H, app. t, *J*=10.8 Hz), 3.43 (1H, dd, *J*=10.8, 10.4 Hz), 2.21 (2H, td, *J*=7.2, 2.0 Hz), 1.58–1.45 (2H, m), 1.44–1.21 (6H, m), 0.88 (3H, t, *J*=6.8 Hz); δ_C (75 MHz, $CDCl_3$) 137.6, 128.6, 128.4, 126.7, 88.0, 78.2, 75.3, 71.7, 70.4, 67.4, 31.4, 28.7, 28.5, 22.7, 18.9, 14.2; ν_{max} (liquid film) 2957, 2929, 1452, 1305, 1227, 1116, 1075, 911, 754, 698 cm^{-1}; MS (ESI): MH^+, found 296.1. $C_{18}H_{24}O_2$ requires 295.1.

*4.7.7. 2-Ethyl-6-(oct-1-yn-1-yl)-1,4-dioxane (**6g**).* δ_H (400 MHz, $CDCl_3$) 4.32 (1H, ddd, *J*=10.4, 4.4, 2.0 Hz), 3.78 (1H, dd, *J*=11.4, 2.8 Hz), 3.72–3.64 (1H, m), 3.51–3.43 (1H, m), 3.39 (1H, app. t, *J*=10.8 Hz), 3.20 (1H, app. t, *J*=10.8 Hz), 2.19 (2H, td, *J*=7.2, 2.0 Hz), 1.56–1.18 (10H, m), 0.93 (3H, t, *J*=7.6 Hz), 0.87 (3H, t, *J*=6.8 Hz); δ_C (75 MHz, $CDCl_3$) 87.7, 77.1, 75.4, 70.6, 70.5, 67.0, 31.4, 28.7, 28.5, 24.8, 22.7, 18.9, 14.2, 9.8; ν_{max} (liquid film) 2960, 2931, 2853, 1456, 1320, 1101, 1077, 904 cm^{-1}; MS (ESI): MH^+, found 247.1. $C_{14}H_{24}O_2$ requires 247.1.

*4.7.8. 2-Ethyl-6-(hex-1-yn-1-yl)-1,4-dioxane (**6h**).* δ_H (400 MHz, $CDCl_3$) 4.32 (1H, d, *J*=10.4 Hz), 3.78 (1H, dd, *J*=11.2, 2.8 Hz), 3.69 (1H, m), 3.50–3.40 (1H, m), 3.39 (1H, app. t, *J*=10.8 Hz), 3.20 (1H, t, *J*=10.8 Hz), 2.20 (2H, t, *J*=7.2 Hz), 1.55–1.23 (6H, m), 0.93 (3H, t, *J*=7.5 Hz), 0.88 (3H, t, *J*=7.3 Hz); δ_C (75 MHz, $CDCl_3$) 87.7, 77.1, 75.5, 70.6, 70.5, 67.0, 30.7, 24.8, 22.2, 18.7, 13.8, 9.9; ν_{max} (liquid film) 2961, 2933, 2853, 1464, 1320, 1101, 1077, 909 cm^{-1}; MS (ESI): MH^+, found 197.0. $C_{12}H_{20}O_2$ requires 197.1.

4.8. Propargylic acetates 7a–g

*4.8.1. 7-Phenyl-1-(sulfamoyloxy)hept-4-yn-3-yl acetate (**7a**).* δ_H (500 MHz, $CDCl_3$) 7.33–7.27 (2H, m), 7.25–7.21 (3H, m), 5.49 (1H, t, *J*=7.0 Hz), 5.04 (2H, s), 4.25 (2H, m), 2.83 (2H, t, *J*=7.0 Hz), 2.52 (2H, td, *J*=7.5, 1.5 Hz), 2.22–2.07 (2H, m), 2.09 (3H, s); δ_C (125 MHz, $CDCl_3$) 170.6, 140.6, 128.8, 128.7, 126.7, 105.0, 86.9, 67.1, 61.3, 34.8, 34.4, 21.3, 21.0; ν_{max} (liquid film) 3335, 3281, 2933, 2246, 1728, 1559, 1372, 1241, 1183, 1020, 931, 751, 700 cm^{-1}; MS (ESI): MNa^+, found 348.0. $C_{15}H_{19}NSO_5$ requires 348.0.

*4.8.2. 1-Phenyl-5-(sulfamoyloxy)pent-1-yn-3-yl acetate (**7b**).* δ_H (400 MHz, $CDCl_3$) 7.44–7.41 (2H, m), 7.33–7.25 (3H, m), 5.74 (1H, t, *J*=6.4 Hz), 5.34 (2H, s), 4.36 (2H, m), 2.34–2.23 (2H, m), 2.10 (3H, s); δ_C (125 MHz, $CDCl_3$) 170.6, 132.0, 129.1, 128.5, 121.8, 86.4, 85.1, 66.9, 61.3, 34.2, 21.1; ν_{max} (liquid film) 3281, 2234, 1731, 1557, 1491, 1372, 1237, 1183, 1022, 932, 759 cm^{-1}; MS (ESI): MNa^+, found 319.9. $C_{13}H_{15}NSO_5$ requires 320.0.

*4.8.3. 8-Phenyl-2-(sulfamoyloxy)oct-5-yn-4-yl acetate (**7c**).* δ_H (400 MHz, $CDCl_3$) 7.30–7.25 (2H, m), 7.21–7.18 (3H, m), 5.34–5.29 (1H, m), 5.06–4.98 (1H, m), 4.82 (2H, s), 2.82 (2H, t, *J*=7.6 Hz), 2.49 (2H, td, *J*=8.0, 2.0 Hz), 2.10 (1H, ddd, *J*=10.6, 8.8, 6.4 Hz), 2.02 (3H, s), 1.81 (1H, ddd, *J*=10.6, 8.8, 6.4 Hz), 1.25 (3H, d, *J*=6.0 Hz); δ_C (75 MHz, $CDCl_3$) 170.7, 140.6, 128.6, 128.5, 126.5, 86.5, 77.7, 68.1, 62.8, 41.2, 34.9, 21.5, 21.1, 20.3; ν_{max} (liquid film) 2360, 1722, 1371, 1243, 1043, 668 cm^{-1}; MS (ESI): MNa^+, found 361.9. $C_{16}H_{21}NSO_5$ requires 362.1.

*4.8.4. 1-Phenyl-5-(sulfamoyloxy)hex-1-yn-3-yl acetate (**7d**).* δ_H (400 MHz, $CDCl_3$) 7.45–7.40 (2H, m), 7.35–7.15 (3H, m), 5.73 (1H, dd, *J*=8.0, 6.0 Hz), 5.12 (2H, s), 4.98–4.90 (1H, m), 2.38–2.27 (1H, m), 2.15–2.03 (1H, m), 2.08 (3H, s), 1.53 (3H, d, *J*=6.8 Hz); δ_C

(75 MHz, $CDCl_3$) 170.3, 132.1, 129.2, 128.6, 121.7, 86.7, 85.4, 77.6, 61.8, 41.5, 21.3, 21.2; ν_{max} (liquid film) 3277, 2360, 1729, 1491, 1370, 1239, 1183, 1023, 918, 759, 692 cm^{-1}; MS (ESI): MNa^+, found 333.9. $C_{14}H_{17}NSO_5$ requires 334.1.

*4.8.5. 2-(Sulfamoyloxy)dodec-5-yn-4-yl acetate (**7e**).* δ_H (400 MHz, $CDCl_3$) 5.50–5.45 (1H, m), 4.95 (2H, s), 4.90–4.82 (1H, m), 2.26–2.18 (3H, m), 2.07 (3H, s), 1.95 (1H, ddd, *J*=12.4, 8.8, 4.4 Hz), 1.53–1.45 (2H, m), 1.48 (3H, d, *J*=6.4 Hz), 1.38–1.24 (6H, m), 0.87 (3H, t, *J*=6.4 Hz); δ_C (75 MHz, $CDCl_3$) 170.3, 88.2, 77.9, 76.8, 61.8, 41.8, 31.4, 28.7, 28.5, 22.7, 21.4, 21.3, 18.8, 14.2; ν_{max} (liquid film) 3374, 2927, 2360, 1729, 1457, 1370, 1239, 1182, 1023, 923, 668 cm^{-1}; MS (ESI): MNa^+, found 342.1. $C_{14}H_{25}NSO_5$ requires 342.1.

*4.8.6. 1-((tert-Butyldiphenylsilyl)oxy)-2-(sulfamoyloxy)dodec-5-yn-4-yl acetate (**7f**).* δ_H (400 MHz, $CDCl_3$) 7.78–7.55 (m, 4H), 7.42 (6H, m), 5.48 (1H, m), 4.81 (3H, m), 3.87 (2H, d, *J*=4.4 Hz), 2.32–2.08 (4H, m), 2.02 (3H, s), 1.56–1.40 (2H, m), 1.43–1.17 (6H, m), 1.06 (9H, s), 0.87 (3H, t, *J*=7.2 Hz); δ_C (75 MHz, $CDCl_3$) δ170.0, 135.8, 135.7, 133.0, 132.7, 130.25, 130.22, 128.1, 88.1, 80.9, 76.6, 65.4, 61.8, 36.8, 31.4, 28.7, 28.5, 27.0, 22.7, 21.2, 19.4, 18.8, 14.2; ν_{max} (liquid film) 3279, 2930, 2857, 1730, 1427, 1370, 1236, 1185, 1112, 933, 702 cm^{-1}; MS (ESI): M^+, found 573.2. $C_{30}H_{43}NO_6SSi$ requires 573.2.

*4.8.7. 6-((tert-Butyldiphenylsilyl)oxy)-1-phenyl-5-(sulfamoyloxy) hex-1-yn-3-yl acetate (**7g**).* δ_H (400 MHz, $CDCl_3$) 7.78–7.57 (4H, m), 7.52–7.20 (11H, m), 5.89–5.62 (1H, dd, *J*=6.8, 6.0 Hz), 4.91 (2H, s), 4.88 (1H, dd, *J*=7.6 Hz, 4.8 Hz), 3.91 (2H, d, *J*=4.8 Hz), 2.45–2.21 (2H, m), 2.05 (3H, s), 1.08 (9H, s); δ_C (75 MHz, $CDCl_3$) 170.0, 135.9, 135.7, 133.0, 132.7, 132.1, 130.26, 130.24, 129.1, 128.5, 128.1, 121.9, 86.7, 85.4, 80.6, 65.4, 61.8, 36.6, 27.0, 21.2, 19.4; ν_{max} (liquid film) 3389, 2931, 1731, 1428, 1371, 1233, 1186, 1113, 1022, 922, 758 cm^{-1}; MS (ESI): MNa^+, found 588.5. $C_{30}H_{35}NSiSO_6$ requires 588.2.

4.9. General procedure for the preparation of cyclic sulfamates 8a–g

To a 0.1 M solution of sulfamate **7a–g** in THF at rt was added $[Cl_2Pt(CH_2CH_2)]_2$ (2.5 mol %). The resulting yellow solution was stirred for 0.5–5.0 h[13] before being quenched by the addition of NEt_3 (0.5 mL/mmol substrate). The solution was concentrated in vacuo and the crude material was filtered through a plug of silica gel.

*4.9.1. 4-(4-Phenylbut-1-yn-1-yl)-1,2,3-oxathiazinane 2,2-dioxide (**8a**).* δ_H (400 MHz, $CDCl_3$) 7.32–7.24 (2H, m), 7.23–7.18 (3H, m), 4.67 (1H, td, *J*=12.0, 2.8 Hz), 4.51–4.47 (2H, m), 4.10 (1H, d, *J*=10.4 Hz), 2.80 (2H, t, *J*=7.2 Hz), 2.49 (2H, app. td, *J*=7.2, 1.6 Hz), 2.04–1.88 (2H, m); δ_C (75 MHz, $CDCl_3$) 140.3, 128.6, 128.5, 126.6, 86.4, 76.0, 71.4, 47.8, 34.6, 31.2, 20.8; ν_{max} (liquid film) 3268, 2360, 2089, 1651, 1417, 1368, 1188, 1061, 1012, 781 cm^{-1}; MS (ESI): $M-H^-$, found 264.0. $C_{13}H_{15}NSO_3$ requires 264.0.

*4.9.2. 4-(Phenylethynyl)-1,2,3-oxathiazinane 2,2-dioxide (**8b**).* δ_H (400 MHz, $CDCl_3$) 7.43–7.41 (2H, m), 7.38–7.30 (3H, m), 4.80–4.71 (2H, m), 4.56 (1H, ddd, *J*=12.0, 4.8, 2.0 Hz), 4.49 (1H, d, *J*=9.2 Hz), 2.25–2.14 (1H, m), 2.09–2.03 (1H, m); δ_C (75 MHz, $CDCl_3$) 132.0, 129.4, 128.6, 121.5, 86.1, 84.1, 71.5, 48.2, 30.9; ν_{max} (liquid film) 3263, 2360, 1491, 1420, 1373, 1189, 1064, 1002, 934, 874, 783, 758, 691 cm^{-1}; MS (ESI): $M-H^-$, found 235.9. $C_{11}H_{11}NSO_3$ requires 236.0.

*4.9.3. 6-Methyl-4-(4-phenylbut-1-yn-1-yl)-1,2,3-oxathiazinane 2,2-dioxide (**8c**).* δ_H (400 MHz, $CDCl_3$) 7.32–7.28 (2H, m), 7.25–7.18 (3H, m), 4.84–4.76 (1H, m), 4.43 (1H, app. td, *J*=10.0, 2.0 Hz), 4.02 (1H, d, *J*=10.4 Hz), 2.80 (2H, t, *J*=7.2 Hz), 2.48 (2H, td, *J*=7.2, 2.0 Hz), 1.96 (1H, dt, *J*=17.5, 2.0 Hz), 1.70–1.58 (1H, m), 1.40 (3H, d, *J*=6.4 Hz); δ_C (75 MHz, $CDCl_3$) 140.3, 128.6, 126.7, 86.2, 80.2, 76.6, 47.2, 38.5, 34.7, 21.1, 20.8; ν_{max} (liquid film) 2388, 1414, 1360, 1189, 1069, 867, 700 cm^{-1}; MS (ESI): MNa^+, found 301.8. $C_{14}H_{17}NSO_3$ requires 302.0.

*4.9.4. 6-Methyl-4-(phenylethynyl)-1,2,3-oxathiazinane 2,2-dioxide (**8d**).* δ_H (400 MHz, $CDCl_3$) 7.42–7.37 (2H, m), 7.36–7.25 (3H, m), 4.93–4.85 (1H, m), 4.73 (1H, app. t, *J*=10.0 Hz), 4.22 (1H, d, *J*=10.0 Hz), 2.14 (1H, m), 1.86 (1H, dt, *J*=14.4, 12.0 Hz), 1.45 (3H, d, *J*=6.4 Hz); δ_C (75 MHz, $CDCl_3$) 132.0, 129.4, 128.6, 121.5, 86.0, 84.1, 80.3, 47.6, 38.2, 21.2; ν_{max} (thin film) 3254, 2360, 1422, 1365, 1189, 1076, 929, 865, 758 cm^{-1}; MS (ESI): M^+, found 250.9. $C_{12}H_{13}NSO_3$ requires 251.0.

*4.9.5. 6-Methyl-4-(oct-1-yn-1-yl)-1,2,3-oxathiazinane 2,2-dioxide (**8e**).* δ_H (400 MHz, $CDCl_3$) 4.81 (1H, m), 4.45 (1H, m), 4.06 (1H, d, *J*=10.0 Hz), 2.16 (2H, td, *J*=7.2, 2.0 Hz), 2.01 (1H, dt, *J*=14.4, 2.4 Hz), 1.69 (1H, dt, *J*=14.8, 12.0 Hz), 1.50–1.45 (2H, m), 1.44 (3H, d, *J*=6.8 Hz), 1.37–1.20 (6H, m), 0.88 (3H, t, *J*=6.8 Hz); δ_C (75 MHz, $CDCl_3$) 87.1, 80.2, 75.6, 47.3, 38.6, 31.4, 28.6, 28.4, 22.7, 21.1, 18.7, 14.2; ν_{max} (liquid film) 2931, 2359, 1415, 1363, 1190, 1070, 869 cm^{-1}; MS (ESI): M^+, found 259.0. $C_{12}H_{21}NSO_3$ requires 259.1.

*4.9.6. 6-(((tert-Butyldiphenylsilyl)oxy)methyl)-4-(oct-1-yn-1-yl)-1,2,3-oxathiazinane 2,2-dioxide (**8f**).* δ_H (500 MHz, $CDCl_3$) 7.82–7.59 (4H, m), 7.58–7.35 (6H, m), 4.77 (1H, m), 4.51 (1H, app. t, *J*=10.0 Hz), 4.09 (1H, d, *J*=10.0 Hz), 3.79 (2H, d, *J*=4.5 Hz), 2.20 (2H, td, *J*=17.0, 8.5 Hz), 2.04 (1H, dt, *J*=14.5, 2.5 Hz), 1.92 (1H, dt, *J*=14.5, 12.0 Hz), 1.56–1.47 (2H, m), 1.45–1.22 (6H, m), 1.08 (9H, s), 0.91 (3H, t, *J*=7.0 Hz); δ_C (125 MHz, $CDCl_3$) 135.8, 135.7, 132.8, 132.7, 130.2, 128.1, 128.0, 87.3, 82.9, 75.8, 65.1, 47.2, 33.5, 31.4, 28.6, 28.4, 26.9, 22.7, 19.4, 18.7, 14.2; ν_{max} (liquid film) 2927, 2855, 1718, 1427, 1374, 1191, 1113, 1067, 823, 702 cm^{-1}; MS (ESI): M^+, found 513.1. $C_{28}H_{39}NSSiO_4$ requires 513.2.

*4.9.7. 6-(((tert-Butyldiphenylsilyl)oxy)methyl)-4-(phenylethynyl)-1,2,3-oxathiazinane 2,2-dioxide (**8g**).* δ_H (500 MHz, $CDCl_3$) 7.88–7.60 (4H, m), 7.55–7.32 (11H, m), 4.96–4.64 (2H, m), 4.24 (1H, d, *J*=10.5 Hz), 3.81 (2H, br d, *J*=4.5 Hz), 2.24–2.12 (1H, m), 2.06 (1H, m), 1.10 (9H, s); δ_C (125 MHz, $CDCl_3$) 135.85, 135.81, 132.8, 132.7, 132.09, 132.07, 130.2, 129.4, 128.7, 128.14, 128.13 121.5, 86.1, 84.2, 83.0, 65.2, 47.5, 33.2, 27.0, 19.5; ν_{max} (liquid film) 3272, 2931, 1427, 1377, 1192, 1113, 1072, 873, 824, 702 cm^{-1}; MS (ESI): M^+, found 505.0. $C_{28}H_{31}NSSiO_4$ requires 505.2.

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Supplementary data

Additional experimental details, spectroscopic data, and copies of ^1H and ^{13}C NMR spectra for new compounds are available. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2011.03.115.

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