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Synthesis of unsaturated 1,4-heteroatom-containing benzo-fused heterocycles using a sequential isomerization–ring-closing metathesis strategy

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ABSTRACT

A small library of 1,4-benzodioxins and 4*H*-1,4-benzoxazines was synthesized from the corresponding bis-allyloxy precursors by way of an initial isomerization to the bis-vinyloxy compounds, followed by a ring-closing metathesis using the second generation Grubbs' catalyst (G2). A related strategy, starting from benzene-1,2-dithiol and 2-mercaptophenol, afforded benzodithiin and 1,4-benzoxathiin, respectively.

1. Introduction

Substituted 1,4-benzodioxin **1a**, 4*H*-1,4-benzoxazine **2a**, 1,4-dihydroquinoxaline **3a**, 1,4-benzodithiin **4a**, 1,4-benzoxathiin **5a**, 4*H*-1,4-benzothiazine **6a** derivatives and their corresponding hydrogenated analogues **1b**–**6b** are all six-membered heterocycles containing two heteroatoms in a 1,4-relationship, fused to an aromatic ring (Fig. 1). Owing to an interest in their structural features and chemical properties, the synthesis of these compounds has elicited much research activity and the literature pertaining to some of these compounds has been reviewed.[1]

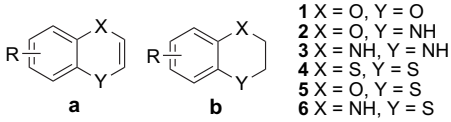

Figure 1.

Natural products with a six-membered ring containing two heteroatoms and unsaturation as in **1a**–**6a** are quite rare. An example is cappamensin A **7**, which possesses a benzoxazinol/benzoxazinone backbone and has promising anti-cancer activity (Fig. 2). It was isolated from the roots of the Taiwanese shrub *Capparis sikkimensis* (subsp. *formosana*).[2] However, natural products containing the hydrogenated heterocycles, as in **1b**–**6b**, are more plentiful. Examples include purpurenol **8**, a substituted 2,3-dihydro-1,4-benzodioxin derivative, which also contains a coumarin skeleton (Fig. 2). This compound was obtained from the aerial component of the Argentinean plant, *Pterocaulon purpurascens*.[3]

Compounds **1a**–**6a**, containing the heterocyclic ring unsaturation, have also been investigated as potential medicinal scaffolds. For instance, 1,4-benzodioxin **9**, synthesized by Guillaumet and coworkers, was tested as a potential lipid peroxidation inhibitor (Fig. 3).[4] Guillaumet's interests have also involved the testing of substituted benzo[1,4]dioxin scaffolds as melatonin ligands.[5] Benzoxazines have also been screened for their pharmaceutical

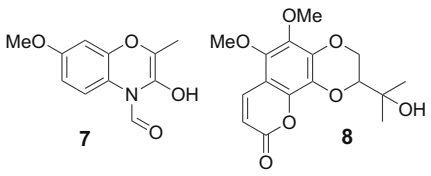

Figure 2.

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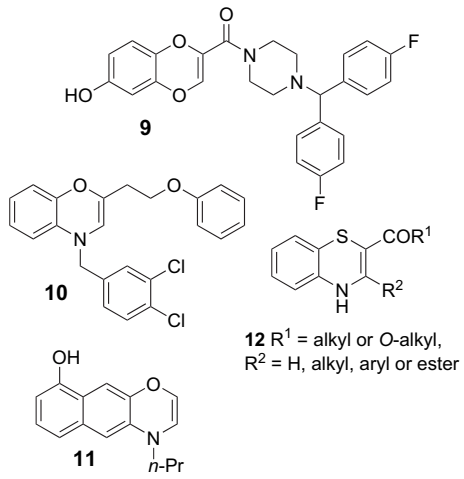


Figure 3.

properties. Examples include compound **10**, tested as a PPARγ agonist,[6] and compound **11** (also named PHNO), a known dopamine D_2 agonist.[7] Finally, some 4*H*-1,4-benzothiazines, as represented by the generalized structure **12**, proved to be moderately active against a range of microbes.[8]

It can be seen from the examples shown in Figures 2 and 3 that compounds **1a**–**6a** and their dihydro derivatives are important scaffolds as potential medicinal leads. Perusal of the chemical literature shows that the direct derivatization of the core structures **1a**–**6a** is an important way of obtaining substituted versions of these scaffolds.[9] It would thus be of synthetic benefit to explore new methods of synthesizing these unsaturated benzo-fused compounds and a possible solution to this challenge is presented in this paper.

Over the last few years one of our main research thrusts has involved the synthesis of ring systems by way of the ubiquitous ring-closing metathesis (RCM) reaction and related transformations.[10,11] The catalyst that has been the stalwart for the metathesis transformations in our work has usually been the ruthenium-based Grubbs' second generation catalyst (G2) **13** (Fig. 4).[11] Another important theme in our work has been the preparation of the metathesis precursors using an isomerization reaction, frequently mediated by the ruthenium hydride **14**, to place the alkene functionalities into the desired position.[12] This has developed into a sequential isomerization–metathesis strategy that has been applied successfully to the synthesis of various classes of benzo-fused heterocycles.[13]

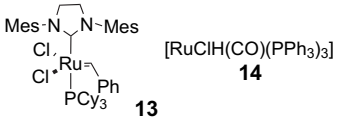
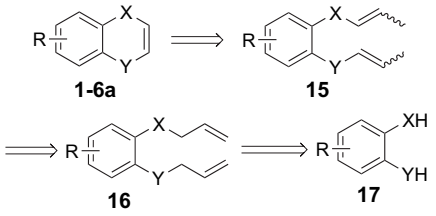


Figure 4.

When looking at the structure of compounds **1a**–**6a** it should be quite clear that use of a RCM strategy would involve the intramolecular metatheses of two vinyl fragments.[14] If benzo[1,4]dioxin compound **1a** (X=Y=O) is used as an example, it can be seen that it can be disconnected to the bis-vinyloxy species **15**. Compound **15** could furthermore be disconnected to the bis-allyloxy compound **16**, which in turn could be obtained from the readily available catechol **17** (Scheme 1). In this paper novel approaches towards the synthesis of 1,4-, *O*,*O*-, *O*,*N*-, *N*,*S*-, *O*,*S*- and *S*,*S*-containing six-membered benzo-fused compounds, using the isomerization–RCM strategy, will be described.[15]

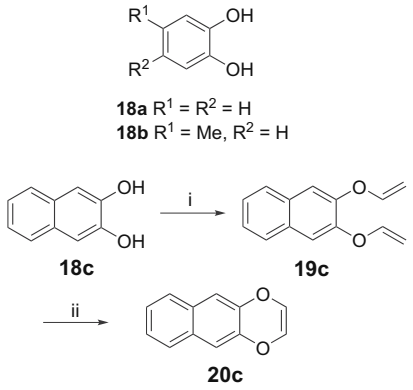


Scheme 1.

2. Results and discussion

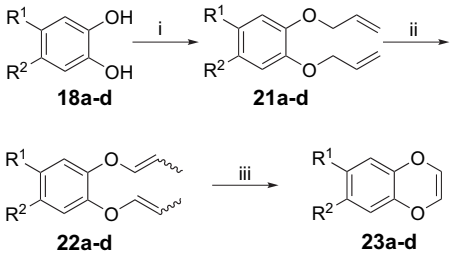
2.1. Synthesis of 1,4-benzodioxins

Earlier work from our group[16] focused on the synthesis of substituted 1,4-benzodioxins **1a** using novel methodology involving the metathesis reactions on substituted catechols containing two *O*-vinyl groups. Unfortunately, when three differently substituted catechols **18a**–**c** were subjected to vinylation with tetravinylstannane and copper(II) acetate,[17] the results were very disappointing (Scheme 2). Only compound **19c** was obtained in a poor yield, the other substrates giving rise to mixtures of products, which were difficult to purify. It was postulated that competing formation of copper–catechol complexes probably contributed to the limited success of this divinylation reaction. 2,3-Bis(vinyloxy)naphthalene **19c** was subsequently treated with catalyst **13** and the corresponding known compound, naphtho[2,3-*b*][1,4]dioxin **20c**,[18] was produced by this novel direct ring-closure method. However, our success with the synthesis of this compound was somewhat marred by the problematic assembly of the desired 1,2-bis(vinyloxy)benzenes. Apart from the irreproducible low yields, other disadvantages encountered included the need for stoichiometric amounts of copper acetate and tetravinylstannane. Bearing these factors in mind we decided to find an alternative approach to the benzo[1,4]dioxin skeletons.[19]



Scheme 2. Reagents and conditions: (i) $Cu(OAc)_2$, $Sn(CH{=}CH_2)_4$, acetonitrile, O_2, rt, 22 h, 47%; (ii) **13** (5+5 mol %), toluene, 60 °C, Ar, 5+6 h, 64%.

Our research group has frequently made use of the allylation of phenolic compounds to form the corresponding aryl allyloxy compounds.[20] We also became aware of the ease of the isomerization of these compounds using metal catalysts. In particular, the use of the compound $[RuClH(CO)(PPh_3)_3]$ **14**, extensively investigated by Krompiec, Kuźnik and co-workers, looked particularly interesting.[21] A small number of substituted catechols **18** were therefore converted into their corresponding 1,2-



Scheme 3. Reagents and conditions: (i) allyl bromide, K_2CO_3, acetone, reflux; (ii) **14** (1 mol %), toluene-d_8 or toluene, 65–100 °C; (iii) **13** (5 mol %), toluene-d_8 or toluene, 65–80 °C. See Table 1 for yields.

bis(allyloxy)benzene compounds **21** in good yields (Scheme 3). These compounds were then subjected to an in situ isomerization, which was monitored by ^{1}H NMR spectroscopy. Formation of the more thermodynamically favoured aryl bis(vinyl) ether compounds was evident by the disappearance of the usual signals in the ^{1}H NMR spectra for the allyloxy functional group and the appearance of new signals for the newly formed methyl groups in the alkyl region. It was initially decided not to isolate the enol ether intermediates **22** and Grubbs' catalyst (G2) **13** was then added directly to the reaction mixture in the NMR spectroscopy tubes. Based on NMR spectroscopy evidence, the desired 1,4-benzodioxins **23a–d** were obtained in good conversions and their spectroscopic data compared well to published literature data.[22,23] To prove the synthetic feasibility of this approach, compound **23a** was successfully synthesized on a multigram scale (~25 mmol), utilizing low catalyst loadings (0.5 mol % of **13** and **14**) (entry 4 in Table 1), in acceptable yields.

Table 1
Reaction yields for synthesis of the substituted 1,4-benzodioxins

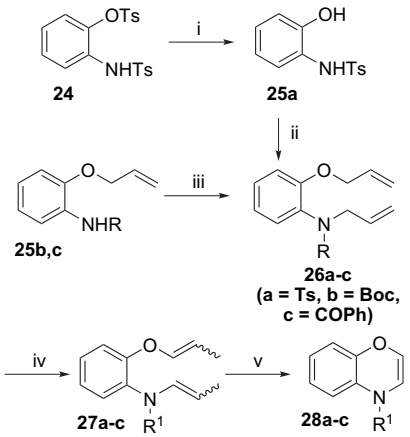
Entry	R^1,R^2=	21	22	23
1	(a) H, H	96%	[a]	>70%[b,c]
2	(b) Me, H	93%	[a]	>70%[b,c,d]
3	(c) Fused benzene ring	76%	[a]	>90%[b,c]
4	(a) H, H	90%[e]	95%[f,g]	73%[h,g]

[a] Not isolated, deemed complete by ^{1}H NMR spectroscopy.
[b] Estimated by ^{1}H NMR spectroscopy.
[c] Yield over two steps.
[d] After chromatography compound was obtained in a yield of 58% over two steps.
[e] Performed on 199 mmol scale.
[f] Performed on 26.3 mmol scale.
[g] Catalyst loading: 0.5 mol %.
[h] Performed on 23.5 mmol scale.

The synthesis of compounds with the 1,4-benzodioxin structure was thus successful. This approach used a simple three-step process suitable for the synthesis of substituted 1,4-benzodioxins on a reasonable scale, with the added benefit of being able to use low catalyst loadings.[24]

2.2. Synthesis of 4*H*-1,4-benzoxazines

Next, it was decided to synthesize the analogous 1,4-benzoxazine compounds, where the unsaturated benzannulated heterocycle now contained an oxygen and nitrogen atom.[25] *N*,*O*-Diallyl compounds **26a–c** were thus synthesized from the *N*-protected substrates **25a–c**, which in turn had been obtained from derivatives of 2-aminophenol such as compound **24** (readily obtained from the ditosylation of 2-aminophenol). Again the isomerization catalyst **14** proved highly successful in mediating the bis-isomerizations to afford compounds **27a–c** in high yields (Scheme 4). Satisfyingly, addition of Grubbs' second generation catalyst (G2) **13** to compounds **27a–c** cleanly afforded the substituted 4*H*-[1,4]-



Scheme 4. Reagents and conditions: (i) Mg, MeOH, 94%; (ii) K_2CO_3, allyl bromide, acetone, 60 °C, N_2, 18–23 h; (iii) NaH, allyl bromide, DMF, rt, 18 h; (iv) **14** (1–6 mol %), toluene-d_8 or toluene, 60–105 °C, N_2, 2–98 h; (v) **13** (5–8 mol %), toluene, 80 °C to reflux, N_2, 2.5–24 h. See Table 2 for yields and experimental section for specific details.

Table 2
Reaction yields for synthesis of the substituted 4*H*-1,4-benzoxazines

Entry	R=	26	27	28
1	(a) Ts	91%	95%	70%
2	(b) Boc	61%	81%	75%
3	(c) COPh	90%	98%	96%

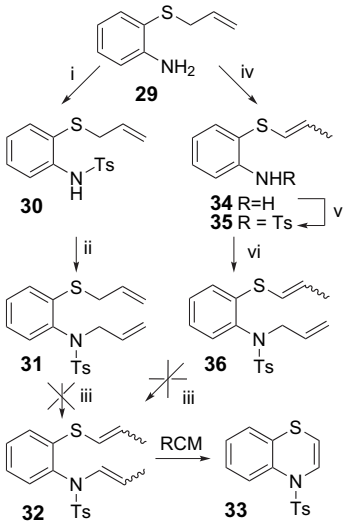
benzoxazines **28a–c** in good yields.[26] RCM using Grubbs' catalysts on substrates containing electron-rich vinylic olefins is known to be synthetically challenging and to our knowledge these results are the first examples of high-yielding metathesis reactions between phenolic vinyl enol ethers and protected enamines.[14]

2.3. Attempted synthesis of 4*H*-1,4-benzothiazine and synthesis of benzodithiin and 1,4-benzoxathiin

The RCM of sulfur-containing ring systems has seen much less research activity when compared to the application of ruthenium-mediated RCM to systems containing nitrogen and oxygen atoms.[27] In fact, few applications of metathesis to vinyl sulfides have been reported.[28] It was thus of interest to investigate whether the isomerization–RCM approach could be applied to the synthesis of benzo-fused compounds containing sulfur atoms in the heterocyclic ring.

The first substrate targeted to be investigated was the *S*,*N*-bis-isomerized compound **32**. Compound **31**, the proposed precursor to this material, was readily synthesized from 2-aminobenzenethiol in good yield (Scheme 5). This was performed by way of an *S-allylation*[29] to afford compound **29**, an *N-tosylation* to give **30**, followed by an *N-allylation* reaction to afford compound **31**. However, we were never able to accomplish bis-isomerization of compound **31**. In addition, decomposition of the starting material started to occur under harsher reaction conditions. Of interest is that the problems associated with the isomerization of *S*-allyl groups has been reported before by Krompiec and co-workers.[21a,d,e]

It was next decided to try two sequential allylation–isomerizations to afford compound **32**. 2-(Allylthio)aniline **29** was thus subjected to isomerization with potassium *tert*-butoxide to afford compound **34** with an *E*/*Z* ratio of ~1:1.[30] Tosylation of **34**, followed by a further allylation then afforded compound **36**, by way of **35**, in near quantitative yields (Scheme 5). However, all the attempts to isomerize the *N*-allyl functional group of **36**, to afford the desired **32**, also met with failure and resulted in the loss of the tosyl and/or

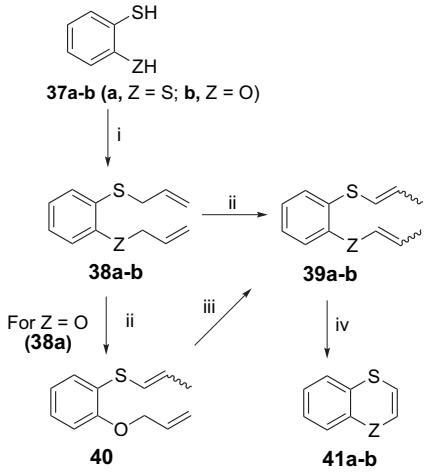


Scheme 5. Reagents and conditions: (i) TsCl, pyridine, CH_2Cl_2, 0 °C to reflux, N_2, 24 h, 97%; (ii) K_2CO_3, allyl bromide, acetone, rt, 24 h, 99%; (iii) **14** (5 mol %), toluene, reflux, 24 h no reaction, or 48 h decomposition; (iv) ^{t}BuOK, DMSO, rt, 18 h, 85%; (v) TsCl, pyridine, CH_2Cl_2, 0 °C to rt, N_2, 18 h, 99%; (vi) K_2CO_3, allyl bromide, acetone, rt, 24 h, 98%.

N-allyl group. It was thus realized that this synthetic route was not a realistic strategy to obtain the desired 4*H*-1,4-benzothiazine **33**.

Despite the failure of the methodology to afford the 1,4-*S*,*N*-system, the isomerization–RCM strategy was attempted on two other sulfur-containing substrates. To this end, benzene-1,2-dithiol **37a** and 2-mercaptophenol **37b** were converted into their bis(allyl) derivatives **38a** and **38b**, respectively, in good yields (Scheme 6). Initial attempts at using catalyst **14** to facilitate the isomerization of the allyl groups proved problematic as predicted by work from Krompiec and co-workers.[21e] Fortunately, it was found that other classical isomerization methodologies readily afforded the desired 2-propenyl compounds.[31] With substrate **38a** (Z=S), treatment with excess sodium ethoxide provided **39a** in a good yield of 92%. Of interest was that when **38b**, bearing the *O*- and *S*-allyl groups, was treated with sodium ethoxide only compound **40**, with an isomerized *S*-allyl group, was isolated in quantitative yield. Potassium *tert*-butoxide was therefore required to isomerize the other allyl group to afford compound **39b**.

To our satisfaction, application of the Grubbs' second generation catalyst (G2) **13** to ring-close substrates **39a** and **39b** afforded the desired six-membered heterocyclic compounds benzodithiin **41a**[32] and 1,4-benzoxathiin **41b**[33] in acceptable yields. To the best of our knowledge these results represent the first application of RCM to make these types of compounds.



Scheme 6. Reagents and conditions: (i) K_2CO_3, allyl bromide, acetone, 60 °C, N_2, 48 h; (ii) Na, EtOH, microwave, 50 W, 90 °C, 3 h; (iii) ^{t}BuOK, DMSO, 60 °C, 18 h, 72%; (iv) **13** (5–10 mol %), CH_2Cl_2, reflux, N_2, 18–38 h. See Table 3 for yields.

Table 3
Reaction yields for synthesis of benzodithiin and 1,4-benzoxathiin

Entry	Z=	**38**	**39**	**41**
a	S	92%	92%	77%
b	O	70%	72%[a]	77%

[a] Over two isomerization steps [**38b**→**40** (quantitative) and **40**→**39b** (72%)]—see experimental section for details.

3. Conclusion

In this paper we have shown that the isomerization–RCM approach can be successfully applied to the synthesis of a selection of benzo-fused, six-membered heterocycles containing two heteroatoms in a 1,4-relationship, namely 1,4-benzodioxins, 4*H*-1,4-benzoxazines, benzodithiins and 1,4-benzoxathiins. In addition, it demonstrates the power of the isomerization–RCM approach to generate these versatile aromatic benzo-fused ring systems. We hope that this general approach to these compounds will stimulate further research into their use as scaffolds for potentially bioactive molecules.

4. Experimental

4.1. General

^{1}H NMR and ^{13}C NMR spectra were recorded either on a Bruker AC-200, Bruker AVANCE 300 spectrometer or on a Bruker DRX-400 spectrometer at the frequency indicated. DEPT, C–H correlated and COSY spectra were run on some samples to enable a more complete assignment of signals. *J* Values are given in hertz. Assignments with the same superscript may be interchanged. Infrared spectra were recorded on a Bruker Vector 22 Fourier Transform spectrometer. Mass spectra were recorded on a Kratos MS 9/50, VG 70E MS or a VG 70 SEQ mass spectrometer. All microwave reactions were performed in a CEM Corporation Discover Focused Microwave Synthesis system. Macherey–Nagel Kieselgel 60 (particle size 0.063–0.200 mm) was used for conventional silica gel chromatography. All solvents used for reactions and chromatography were distilled prior to use to remove residual non-volatiles. Anhydrous/oxygen-free solvents (THF and Et_2O) were obtained according to standard procedures. Removal or concentration of solvent in vacuo implies the evaporation of solvent at 20–25 Torr utilizing a rotary evaporator.

*4.1.1. 2,3-Bis(vinyloxy)naphthalene **19c**.* $Cu(OAc)_2$ (0.22 g, 1.2 mmol) was added to a solution of naphthalene-2,3-diol **18c** (0.16 g, 1.0 mmol) in CH_3CN (3.0 mL) under O_2 (1 atm, balloon) and tetravinyl tin (0.54 g, 2.4 mmol, 0.44 mL) was added by syringe. The mixture was left to react for 22 h at rt and quenched with aqueous NH_4OAc (25 mL). The mixture was extracted with EtOAc (3×20 mL), which was dried ($MgSO_4$) and reduced under vacuum. Silica gel column chromatography (10% EtOAc/hexane) afforded the desired product **19c** as a light yellow oil (0.10 g, 47%). R_f (10% EtOAc/hexane) 0.36; IR ν_{max} ($CHCl_3$)/cm^{-1}: 1643, 1263; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)=4.55 (2H, d, *J* 6.1 Hz, 2×OCHCH_aH_b), 4.86 (2H, dd, *J* 13.7, 0.8 Hz, 2×OCHCH_aH_b), 6.72 (2H, dd, *J* 13.7, 6.0 Hz, 2×OC*H*CH_2), 7.38–7.42 (4H, m, 4×ArH), 7.70–7.73 (2H, m, 2×ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)=96.0, 114.2, 125.3, 126.8, 130.3, 146.5, 148.3; HRMS: found: M^+, 212.0838, $C_{14}H_{12}O_2$ requires 212.0837; *m*/*z*=212 (M^+, 68%), 184 (62), 171 (100), 141 (38), 128 (43), 115 (47), 114 (30), 102 (29), 77 (18).

*4.1.2. Naphtho[2,3-b][1,4]dioxin **20c**[18].* Grubbs' catalyst (G2) **13** (0.014 g, 0.02 mmol, 5 mol %) was added to a solution of 2,3-bis

(vinyloxy)naphthalene **19c** (0.090 g, 0.42 mmol) in toluene (25 mL, 0.02 M) under Ar. The reaction mixture was then heated at 60 °C for 5 h and then another portion of the catalyst **13** (0.014 g, 0.02 mmol) was added. The reaction was left to continue for a further 6 h after which the reaction was judged complete by TLC analysis. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (5% EtOAc/hexane) to afford compound **20**[18] (0.050 g, 64%) as a light-coloured semi-solid. R_f (10% EtOAc/hexane) 0.34; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)=5.95 (2H, s, 2×OCH), 6.99–7.05 (2H, m, 2×ArH), 7.25–7.31 (2H, m, 2×ArH), 7.50–7.58 (2H, m, 2×ArH); ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm)=111.8, 125.2, 126.4, 126.7, 131.2, 142.4.

*4.1.3. General procedure for the allylation of substituted catechols **18** to produce 1,2-bis(allyloxy)benzenes **21**.* Allyl bromide (2.5–4 mol equiv) and K_2CO_3 (2.5–4 mol equiv) were added to the catechol **18** (8.1–10 mmol) dissolved in acetone (20 mL), and the reaction slurry was then stirred at 60 °C for 2 h. After cooling, the base was removed by filtration and the solvent was removed under reduced pressure. The brown residue was then purified using silica gel column chromatography (EtOAc/hexane) to afford compounds **21**. The following compounds were prepared using this procedure:

*4.1.4. 1,2-Bis(allyloxy)benzene **21a**[34].* The product **21a** (1.82 g, 96%) was obtained as a clear oil from **18a** (1.10 g, 10 mmol) according to the general procedure. In addition, the reaction was performed on a much large scale: Allyl bromide (98.7 g, 799 mmol), K_2CO_3 (110 g, 799 mmol) and catechol (22.0 g, 199 mmol) dissolved in acetone (500 mL), at reflux for 36 h. Chromatography (5% EtOAc/hexane) afforded the desired compound **21a** as a pale yellow oil (34.2 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)=4.58–4.61 (4H, m, 2×CH_2CHCH$_2$), 5.24–5.28 (2H, m, 2×CH$_2$CHCH_aH$_b$), 5.38–5.44 (2H, m, 2×CH$_2$CHCH$_a$$H_b$), 6.01–6.14 (2H, m, 2×CH$_2$CHCH$_2$), 6.86 (4H, br s, 4×ArH). The rest of compound's spectra compared well to that described in the literature.[34]

*4.1.5. 1,2-Bis(allyloxy)-4-methylbenzene **21b**.* The product **21b** (1.54 g, 93%) was obtained as a clear oil from **18b** (1.00 g, 8.1 mmol) according to the general procedure. R_f (10% EtOAc/hexane) 0.56; IR ν_{max} (film)/cm^{-1} 1608, 1589, 1508, 1455, 1421, 1381, 1362; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)=2.26 (3H, s, ArCH$_3$), 4.53–4.57 (4H, m, 2×CH_2CHCH$_2$), 5.20–5.26 (2H, m, 2×CH$_2$CHCH_aH$_b$), 5.35–5.43 (2H, m, 2×CH$_2$CHCH$_a$$H_b$), 6.02–6.12 (2H, m, 2×CH$_2$CHCH$_2$), 6.65–6.76 (2H, m, 2×ArH), 6.77 (1H, d, J 8.0 Hz, 4×ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)=20.8, 69.8, 70.1, 114.6, 115.3, 117.1, 117.1, 121.3, 130.9, 133.5, 133.7, 146.3, 148.4; HRMS: calculated for $C_{13}H_{16}O_2$ 204.1150, found 204.1148; m/z (EI): 204 (M$^+$, 100%), 181 (37), 163 (88), 153 (33), 148 (37), 135 (44), 133 (69), 123 (69).

*4.1.6. 2,3-Bis(allyloxy)naphthalene **21c**[35].* The product **21c** (1.83 g, 76%) was obtained as a clear oil from **18c** (1.6 g, 10 mmol) according to the general procedure. ^{1}H NMR (300 MHz, toluene-d): δ (ppm)=4.22–4.29 (4H, m, 2×CH_2CHCH$_2$), 5.11 (2H, d, J 6.0 Hz, 2×CH$_2$CHCH_aH$_b$), 5.39 (2H, d, J 13.4 Hz, 2×CH$_2$CHCH$_a$$H_b$), 5.87–6.00 (2H, m, 2×CH$_2$CHCH$_2$), 6.95 (2H, br s, 2×ArH), 7.28–7.31 (2H, m, 2×ArH), 7.59–7.62 (2H, m, 2×ArH). The other spectra of this compound compared well with that published in the literature.[35]

*4.1.7. General procedure for the isomerization of substituted 1,2-bis(allyloxy)benzenes **21** to produce 1,2-bis(1-propenyloxy)benzenes **22** performed on an NMR spectroscopy scale.* Typically, 1,2-bis(allyloxy) benzene **21** (0.050 g) and [RuClH(CO)(PPh$_3$)$_3$] 14 (0.1–0.5 mol %) were dissolved in degassed toluene-d_8 or benzene-d_6 (2.5 mL) in an NMR spectroscopy tube. The tube was heated at 65–100 °C in an oil bath and the completion of the reaction was confirmed by NMR spectroscopy. The reaction solution was purified by filtration through a short silica gel pad (5% EtOAc/hexane) and evaporated under reduce pressure to afford the product, **22**, as a mixture of *E,Z*-isomers. The following compounds, some of which were used in the next reaction without further characterization, were prepared using this procedure, unless otherwise mentioned:

*4.1.8. 1,2-Bis(1-propenyloxy)benzene **22a**.* The product **22a** was obtained by the isomerization of **21a** (0.050 g, 0.26 mmol) with catalyst **14** (1 mg, 1 μmol, 0.4 mol %) in toluene-d_8 for 18 h at 90–100 °C. As the isomerization was still incomplete another portion of **14** (1 mg, 1 μmol, 0.4 mol %) was added and the reaction mixture was heated at 90–100 °C for a further 18 h. Compound **22a** was not isolated and was used directly for the next reaction. This compound was also generated on a larger scale in the following way: 1,2-bis(allyloxy)benzene **22a** (5.01 g, 26.3 mmol) and **14** (0.125 g, 0.13 mmol, 0.49 mol %) were heated according to the described procedure for 80 °C at 23 h under Ar. The cooled solution was taken up into 5% EtOAc/hexane (20 mL) and filtered through a pad of SiO_2. The pad was rinsed with additional 5% EtOAc/hexane (100 mL), and the pooled organic fractions were evaporated to give a complex mixture of *E,Z*-isomers of 1,2-bis(1-propenyloxy)benzene **22a** as a yellow oil (4.73 g, 95%). IR ν_{max} (film)/cm^{-1} 1668, 1593, 1495, 1395, 1360, 1265; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)=1.63–1.75 (6H, m, 2×OCHCHCH_3), 4.79–5.35 (2H, m, 2×OCHCHCH$_3$), 6.29–6.35 (2H, m, 2×OCHCHCH$_3$), 6.96–7.03 (4H, m, 4×ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)=9.3, 9.4 and 12.2 (CH$_3$), 107.1, 107.4 and 107.6, 117.1, 117.3 and 118.0, 122.9, 123.0 and 123.3, 141.5, 141.8 and 143.0, 147.6 (C); HRMS: calculated for $C_{12}H_{14}O_2$ 190.0994, found 190.0987; m/z (EI): 190 (M$^+$, 20%), 134 (72), 121 (100), 81 (14).

*4.1.9. 4-Methyl-1,2-bis(1-propenyloxy)benzene **22b**.* The product **22b** was obtained by the isomerization of **21b** (0.048 g, 0.23 mmol) with catalyst **14** (1 mg, 1 μmol, 0.4 mol %) in benzene-d_6 for 18 h at 60 °C. As the isomerization was still incomplete another portion of **14** (1 mg, 1 μmol, 0.4 mol %) was added and the reaction mixture was heated at 60 °C for a further 18 h. Compound **22b** was not isolated and was used directly in the next reaction.

*4.1.10. 2,3-Bis(1-propenyloxy)naphthalene **22c**.* The product **23c** was obtained by the isomerization of **21c** (0.050 g, 0.21 mmol) with catalyst **14** (1 mg, 1 μmol, 0.5 mol %) in toluene-d_8 for 18 h at 80 °C. Compound **22c** was not isolated and used directly in the next reaction.

*4.1.11. General procedure for the RCM of substituted bis(1-propenyloxy) compounds **22** to produce substituted dioxenes **23**, performed on an NMR spectroscopy scale.* Typically, 1,2-bis(1-propenyloxy) benzenes **22** (0.050 g, 0.25 mmol) and catalyst **13** (5 mol %) were dissolved in degassed toluene-d_8 or benzene-d_6 (2.5 mL) in an NMR spectroscopy tube. The tube was heated at 65–70 °C in an oil bath and the completion of the reaction was checked by NMR spectroscopy of the crude sample. After the reaction was deemed complete by ^{1}H NMR spectroscopy, unsaturated gases were allowed to diffuse from the solvent before final ^{1}H and ^{13}C NMR spectroscopy were performed to confirm the product structure. Where necessary, the solvent was replaced with $CDCl_3$ to facilitate comparison with literature data. The following compounds were synthesized in this manner.

*4.1.12. 1,4-Benzodioxin **23a**[36].* The product **23a** (>70% by ^{1}H NMR spectroscopy, over two steps) was obtained as a clear oil from **21a** (0.050 g, 0.26 mmol) according to the general procedure. ^{1}H NMR (300 MHz, toluene-d): δ (ppm)=5.35 (2H, s, 2×OCH), 6.42–6.50 (4H, m, 4×ArH). The other spectra of this compound compared well with that published in the literature.[36] This reaction was also performed on a larger scale in a more conventional manner.

Compound **22a** (4.48 g, 23.5 mmol) and catalyst **13** (0.102 g, 0.12 mmol, 0.51 mol %) were dissolved in degassed toluene (50 mL) and heated for 18 h at 80 °C under a blanket of Ar. The reaction mixture was carefully concentrated to a third of its volume on a rotary evaporator, after which 5% EtOAc/hexane (20 mL) was added. The mixture was then filtered through a pad of SiO_2, and the filter pad was washed with an additional 5% EtOAc/hexane (100 mL). The solvent was concentrated to about 10 mL on a rotary evaporator. The mixture was then subjected to fractional vacuum distillation and the fraction boiling at 120 °C (13 mmHg) afforded **23a** (2.30 g, 73%) as a colourless oil.

*4.1.13. 6-Methyl-1,4-benzodioxin **23b**.* The product **23b** (>70% by ^{1}H NMR spectroscopy, over two steps) was isolated after chromatography (10% EtOAc/hexane) as a clear oil (0.020 g, 58% over two steps) from **21b** (0.048 g, 0.24 mmol) according to the general procedure. R_f (10% EtOAc/hexane) 0.64; IR ν_{max} (film)/cm^{-1} 2923, 1672, 1628, 1596, 1504, 1295; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm)=2.18 (3H, s, $ArCH_3$), 5.84 (2H, s, 2×OCH), 6.44 (1H, br s, 5-H), 6.49 (1H, d, *J* 8.1 Hz, 8-H), 6.60 (1H, dd, *J* 8.1, 1.2 Hz, 7-H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm)=20.3, 115.8, 116.8, 124.3, 126.6, 126.8, 134.0, 140.3, 142.2; HRMS: calculated for $C_9H_8O_2$ 148.0524, found 148.0519; *m*/*z* (EI): 148 (M^+, 100%), 119 (14), 92 (18), 91 (57), 65 (10).

*4.1.14. Naphtho[2,3-b][1,4]dioxin **23c**[18].* The product **23c** (>90% by ^{1}H NMR spectroscopy, over two steps) was obtained as a clear oil from **21c** (0.050 g) according to the general procedure. ^{1}H NMR (300 MHz, toluene-*d*): δ (ppm)=5.37 (2H, s, 2×OCH), 6.61 (2H, s, 5-H and 10-H), 6.82–6.87 (2H, m, 2×ArH), 7.02–7.11 (2H, m, 2×ArH). The other spectra of this compound compared well with that published in the literature.[18]

*4.1.15. N-(2-Hydroxyphenyl)-4-methylbenzenesulfonamide **25a**.* 2-{[(4-Methylphenyl)sulfonyl]amino}phenyl 4-methylbenzenesulfonate (2.01 g, 4.81 mmol) was reacted with magnesium (1.16 g, 47.7 mmol) in MeOH (50 mL) in a round-bottomed flask fitted with condenser and a calcium chloride guard tube.[37,38] The reaction mixture was stirred at rt in a H_2O bath for 8 h. The reaction mixture was then neutralized with chilled aqueous 5% HCl solution and the reaction mixture was subsequently extracted with Et_2O (3×50 mL), which was dried ($MgSO_4$). The solvent was then evaporated under reduced pressure to give red-coloured crystals of **25a** (1.18 g, 94%), which was used without further purification. See Ref. 40 for full characterization of **25a**.

*4.1.16. N-Allyl-N-[2-(allyloxy)phenyl]-4-methylbenzenesulfonamide **26a**.* Compound **25a** (0.91 g, 3.5 mmol) was reacted with allyl bromide (1.20 mL, 14.2 mmol) and K_2CO_3 (1.82 g, 13.2 mmol) in acetone (30 mL) at 60 °C with stirring under N_2 for 23 h. The K_2CO_3 was then removed by filtration and the solvent was removed under reduced pressure. The residue was then purified by silica gel column chromatography (10–20% EtOAc/hexane) to give **26a** as a clear oil (1.18 g, 91%). IR: ν_{max} (film)/cm^{-1} 1596, 1494, 1451, 1424, 1343; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)=2.41 (3H, s, $ArCH_3$), 4.17–4.23 (4H, br m, 2×CH_2CHCH$_2$), 4.97–5.17 (4H, m, 2×CH_2CHCH_2), 5.60–5.80 (2H, m, 2×CH_2CHCH$_2$), 6.75–6.78 (1H, m, ArH), 6.92–6.94 (1H, m, ArH), 7.19–7.31 (4H, m, 4×ArH), 7.58 (2H, d, *J* 8.1 Hz, 2×ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)=21.4, 52.5, 68.5, 112.4, 117.1, 117.9, 120.6, 126.6, 127.5, 129.1, 129.5, 132.5, 133.5, 133.7, 137.5, 142.7, 155.4; HRMS: calculated for $C_{19}H_{21}NO_3S$ 343.1242, found 343.1272; *m*/*z* (EI): 343 (M^+, 26%), 187 (44), 188 (100), 160 (12), 147 (57), 146 (47), 120 (43), 91 (32), 65 (15).

*4.1.17. 4-Methyl-N-(prop-1-en-1-yl)-N-{2-(prop-1-en-1-yloxy)phenyl} benzenesulfonamide **27a**.* Compound **26a** (0.19 g, 0.55 mmol) was added to an NMR tube containing ca. 1 mL deuterated toluene. To this solution was added catalyst **14** (0.0054 g, 1 mol %). The tube was capped and placed into an oil bath pre-heated to 105 °C. After 2 h the reaction was deemed completed as evidenced by ^{1}H NMR spectroscopy. Column chromatography (10% EtOAc/hexane) then afforded **27a** as a yellow oil (0.178 g, 95%). R_f (10% EtOAc/hexane) 0.31; ν_{max} (film)/cm^{-1} 1672, 1597, 1494, 1464, 1406, 1338, 1307; ^{1}H NMR (300 MHz, $CDCl_3$): 1.36–1.61 (6H, m, 2×CHCHCH_3), 2.35, 2.39 and 2.41 (3H, 3×s, $ArCH_3$), 4.36–4.43, 4.70–4.77 and 5.20–5.25 (2H, 3×m, 2× HCHCH$_3$), 5.92–5.98 and 6.19–6.24 (1H, 2×m, CHCHCH$_3$), 6.83–7.49 (7H, m, 6×ArH and CHCHCH$_3$), 7.54–7.61 (2H, m, 2×ArH); ^{13}C NMR (75 MHz; $CDCl_3$): δ 9.1 and 11.7, 14.8, 21.5, 106.6, 107.8 and 108.4, 115.7 and 119.8, 122.5 and 122.6, 127.4 and 127.5, 127.6 and 127.9, 129.2 and 129.3, 130.4, 132.1 and 132.6, 136.6 and 136.9, 139.8 and 140.1, 143.3 and 143.4, 153.7 and 154.3; HRMS: calculated for $C_{21}H_{19}NO_3S$ 343.1242, found 343.1244; *m*/*z* (EI): 343 (M^+, 17%), 287 (38), 274 (100), 188 (74), 173 (29), 160 (29), 132 (77), 120 (39), 91 (38), 69 (24).

*4.1.18. 4-[(4-Methylphenyl)sulfonyl]-4H-1,4-benzoxazine **28a**[25].* Compound **27a** (0.144 g, 0.42 mmol) was diluted with toluene (8 mL) and degassed with N_2. Grubbs' catalyst (G2) **13** (0.018 g, 0.021 mmol, 5 mol %) was then added. The solution was degassed again and allowed to stir under N_2 at 90 °C for 6 h. Column chromatography (10 EtOAc/hexane) afforded **28a** as a colourless solid (0.084 g, 70%). ^{1}H NMR (300 MHz, $CDCl_3$): 2.39 (3H, s, CH_3), 5.97 (1H, d, *J* 4.1 Hz, *H*C=CH), 6.18 (1H, d, *J* 4.1 Hz, HC=C*H*), 6.61–6.57 (1H, m, ArH), 7.07–7.03 (2H, m, 2×ArH), 7.19 (2H, d, *J* 8.2 Hz, 2×ArH), 7.43 (d, 2H, *J* 8.2 Hz, 2×ArH), 7.63–7.60 (1H, m, ArH). See Ref. 25 for the full characterization of this compound.

*4.1.19. tert-Butyl allyl(2-allyloxy)phenylcarbamate **26b**.* *tert*-Butyl [2-(allyloxy)phenyl]carbamate **25b**[9d] (0.36 g, 1.4 mmol) was dissolved in DMF (20 mL) followed by the sequential addition of NaH (60% in oil, 0.07 g, 1.7 mmol) and allyl bromide (0.15 mL, 1.8 mmol). The reaction mixture was then stirred at rt for 18 h. H_2O (20 mL) was added to the reaction mixture after which it was extracted with EtOAc (3×100 mL). The combined fractions were dried ($MgSO_4$) and then the solvent was removed under vacuum. Silica gel column chromatography (10% EtOAc/hexane) was performed to afford the product **26b** as a brown oil (0.25 g, 61%). The NMR spectra of this compound indicated the presence of rotamers due to the *N*-Boc group. R_f (10% EtOAc/hexane) 0.63; IR: ν_{max} (film)/cm^{-1} 1699, 1598, 1502, 1454, 1385, 1280; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)=1.32 and 1.50 (9H, 2×br s, 3×CH_3), 4.07–4.35 (2H, br m, NCH_2CHCH$_2$), 4.52–4.54 (2H, m, OCH_2CHCH$_2$), 5.00–5.09 (2H, m, CH_2CHCH_2), 5.25 (1H, dd, *J* 10.6, 1.0 Hz, CH_2CHCH_aH$_b$), 5.41 (1H, dd, *J* 17.3, 1.5 Hz, CH_2CHCH$_a$H$_b$), 5.81–5.92 (1H, m, CH_2CHCH$_2$), 5.95–6.08 (1H, m, CH_2CHCH$_2$), 6.86–6.91 (2H, m, 2×ArH), 7.07–7.20 (2H, m, 2×ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)=28.2, 52.0, 68.0, 79.4, 112.5, 116.5, 116.9, 120.3, 127.8, 129.6, 131.1, 132.9, 134.4, 154.1, 155.0; HRMS: calculated for $C_{17}H_{23}NO_3$ 289.1678, found 289.1680; *m*/*z* (EI): 289 (M^+, 19%), 233 (22), 148 (100), 57 (78), 41 (32).

*4.1.20. tert-Butyl prop-1-en-1-yl[2-(prop-1-en-1-yloxy)phenyl]carbamate **27b**.* Carbamate **26b** (0.106 g, 0.37 mmol) was dissolved in toluene (2 mL) and catalyst **14** (0.004 g, 0.004 mmol, 1 mol %) was added. The reaction mixture was then stirred at 90–100 °C for 98 h after which the solvent was removed by rotary evaporation. Silica gel column chromatography (20% EtOAc/hexane) then afforded the isomerized product **27b** as a brown oil (0.086 g, 81%). The NMR spectra of this compound indicated a complex mixture of *E*,*Z*-isomers and rotamers. R_f (20% EtOAc/hexane) 0.84; IR: ν_{max} (film)/cm^{-1} 1710, 1669, 1589, 1499, 1454, 1388, 1366, 1322; ^{1}H NMR

(300 MHz, toluene-d_8): δ (ppm)=1.36–1.72 [15H, br m, 2×CHCHCH_3 and C(CH_3)$_3$], 4.30–4.41 (1H, m, CHCHCH$_3$), 4.58–4.68 (1H, m, CHCHCH$_3$), 6.14–6.17 (1H, m, CHCHCH$_3$), 6.74–7.12 (5H, m, 4×ArH and CHCHCH$_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 2 CH signals missing in spectrum): δ (ppm)=9.4, 12.0, 28.3, 80.5, 108.8, 114.2, 118.6, 122.3, 122.9, 128.6, 140.7, 145.5, 152.6; HRMS: calculated for $C_{17}H_{23}NO_3$ 289.1678, found 289.1676; m/z (EI): 289 (M$^+$, 8%), 233 (15), 160 (56), 133 (25), 120 (93), 57 (100).

4.1.21. tert-Butyl 4H-1,4-benzoxazine-4-carboxylate ***28b***[9d]. Carbamate **27b** (0.070 g, 0.24 mmol) was dissolved in toluene (15 mL) and Grubbs' second generation catalyst (G2) **13** (0.010 g, 0.01 mmol, 5 mol %) was added. The reaction mixture was then heated at reflux for 18 h after which the solvent was removed in vacuo. The crude product was purified by silica gel column chromatography (10% EtOAc/hexane) to afford the desired compound **28b**[9d] as a brown oil (0.041 g, 75%). R_f (20% EtOAc/hexane) 0.86; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)=1.55 (9H, s, 3×CH$_3$), 5.98 (1H, d, J 4.6 Hz, NCH), 6.19 (1H, d, J 4.6 Hz, OCH), 6.71–6.74 (1H, m, ArH), 6.92–6.96 (2H, m, 2×ArH), 7.79 (1H, br s, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)=28.2, 82.1, 110.4, 116.2, 121.4, 123.5, 125.5, 127.7, 130.9, 147.3, 150.1.

4.1.22. N-[2-(Allyloxy)phenyl]benzamide ***25c***[39]. *N*-(2-Hydroxyphenyl) benzamide (1.34 g, 6.29 mmol) was dissolved in acetone (25 mL), followed by the addition of K_2CO_3 (1.81 g, 13.1 mmol) and allyl bromide (0.67 mL, 7.7 mmol). The reaction mixture was stirred at rt for 24 h under N_2, after which it was filtered through Celite and the solvent removed under vacuum. Silica gel column chromatography (20% EtOAc/hexane) was performed to afford product **25c** as a yellow solid. (1.26 g, 79%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)=4.64 (2H, dt, J 5.3, 1.3 Hz, OCH_2CHCH$_2$), 5.33 (1H, dd, J 10.5, 1.3 Hz, OCH$_2$CHCH_aH$_b$), 5.43 (1H, dd, J 17.3, 1.5 Hz, OCH$_2$CHCH$_a$H$_b$), 6.08 (1H, tdd, J 17.3, 10.5, 5.3 Hz, OCH$_2$CHCH$_2$), 6.89–6.95 (1H, m, ArH), 6.89–7.10 (2H, m, 2×ArH), 7.44–7.58 (3H, m, 3×ArH), 7.89 (2H, dd, J 8.0, 1.5 Hz, 2×ArH), 8.53–8.58 (1H, m, 2×ArH), 8.63 (1H, br s, NH). The rest of the spectra of this compound compared well with that in the literature.[39]

4.1.23. N-Allyl-N-[2-(allyloxy)phenyl]benzamide ***26c***. Benzamide **25c** (1.05 g, 4.13 mmol) was dissolved in DMF (30 mL) and the temperature of the mixture lowered to 0 °C, followed by the sequential addition of NaH (60% in oil, 0.255 g, 4.96 mmol) and allyl bromide (0.70 mL, 8.1 mmol). The reaction mixture was then stirred at rt for 24 h under N_2. H_2O was added to the reaction mixture after which it was extracted with EtOAc (3×50 mL) and the combined fractions dried ($MgSO_4$) and the solvent removed under vacuum. Silica gel column chromatography (15% EtOAc-hexane) was performed to afford the product **26c** as a yellow oil (1.1 g, 90%). R_f (20% EtOAc/hexane) 0.30; IR: ν_{max} (ATR)/cm^{-1} 1647, 1601, 1518, 1496, 1481, 1452, 1324, 1294, 1265; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)=4.18–4.37 (2H, m, CH_2CHCH$_2$), 4.44–4.50 and 4.55–4.60 (2H, 2×m, CH_2CHCH$_2$), 5.04–5.17 (2H, m, CH$_2$CHCH_2), 5.26 (1H, dd, J 10.6, 1.1 Hz, OCH$_2$CHCH_2), 5.36 (1H, dd, J 17.2, 1.2 Hz, OCH$_2$CHCH_2), 5.85–6.09 (2H, m, 2×CH$_2$CHCH$_2$), 6.71 (1H, d, J 8.0 Hz, ArH), 6.75–6.85 (1H, m, ArH), 7.00–7.23 (5H, m, 5×ArH), 7.32 (2H, d, J 7.0 Hz, 2×ArH); ^{13}C NMR (75 MHz, $CDCl_3$, 2CH peaks not observed in spectrum): δ (ppm)=52.5, 69.0, 113.1, 117.7, 118.0, 121.1, 127.7, 128.5, 129.0, 129.8, 130.4, 132.5, 133.1, 133.9, 136.9, 154.0, 171.6; HRMS: $C_{19}H_{19}NO_2$ 293.1424, found: 293.1416; m/z (EI): 293 (M$^+$, 28%), 236 (11), 188 (10), 120 (5), 105 (100), 77 (32), 41 (7).

4.1.24. N-(Prop-1-enyl)-N-[2-(prop-1-enyloxy)phenyl]benzamide ***27c***. Benzamide **26c** (0.329 g, 1.12 mmol) was reacted directly with ruthenium isomerization catalyst **14** (0.064 g, 0.067 mmol, 6 mol %) under solventless conditions. The reaction mixture was stirred at 60 °C for 24 h under Ar after which it was diluted with a 10% EtOAc/hexane mixture and filtered slowly though a compacted Celite plug (3×) to remove the catalyst. The solvent was then removed under vacuum and silica gel column chromatography (10% EtOAc/hexane) was performed to afford the product **27c** as a yellow oil (0.321 g, 98%). The NMR spectra of this compound indicated the presence of *E*/*Z* isomers. R_f (10% EtOAc/hexane) 0.17; IR: ν_{max} (ATR)/cm^{-1} 1650, 1588, 1495, 1447, 1386, 1355, 1319; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)=1.61 (3H, dd, J 7.1, 1.2 Hz, CHCHCH_3), 1.66 (3H, dd, J 6.7, 1.4 Hz, CHCHCH_3), 4.60–4.73 (1H, m, CHCHCH$_3$), 4.84–4.94 and 5.34 (1H, m and dq, J 14.0, 7.0 Hz, CHCHCH$_3$), 6.09 (1H, br, CHCHCH$_3$), 6.80–7.53 (10H, m, 9×ArH and CHCHCH$_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 1CH signal not observed in spectrum): δ (ppm)=9.9 and 12.5, 15.5, 109.2 and 109.8, 109.8 and 110.4, 116.2 and 116.6, 123.0, 127.9, 128.5, 129.8 and 129.7, 130.1, 131.3 and 131.2, 136.3, 140.5 and 141.5, 153.3 and 153.4, 169.5 and 169.4; HRMS: calculated for $C_{19}H_{19}NO_2$ 293.1416, found: 293.1416; m/z (EI): 293 (M$^+$, 34%), 264 (68), 236 (100), 220 (15), 188 (10), 176 (4).

4.1.25. (4H-Benzo[b][1,4]oxazin-4-yl)(phenyl)methanone ***28c***[40]. Benzamide **27c** (0.362 g, 1.24 mmol) was dissolved in degassed toluene (20 mL) and Grubbs' second generation catalyst (G2) **13** (0.084 g, 0.099 mmol, 8 mol %) added. The reaction mixture was then stirred at 80 °C for 18 h under Ar. The reaction mixture was then diluted with a 10% EtOAc/hexane mixture and filtered slowly though a compacted Celite plug (3×) to remove the catalyst. The solvent was then removed under vacuum and silica gel column chromatography (10% EtOAc/hexane) was performed to afford the product **28c** as a yellow oil (0.281 g, 96%). R_f (10% EtOAc/hexane) 0.30; IR: ν_{max} (ATR)/cm^{-1} 1640, 1585, 1492, 1462, 1444, 1352, 1304; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)=6.05 (1H, d, J 4.5 Hz, OCH), 6.27 (1H, br s, NCH), 6.84 (1H, dd, J 8.0, 1.1 Hz, ArH), 6.87–6.93 (1H, m, ArH), 7.04–7.07 (1H, m, ArH), 7.37–7.48 (3H, m, 3×ArH), 7.53–7.60 (2H, m, 2×ArH), 7.65 (1H, br s, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, 1CH not observed in spectrum): δ (ppm)=112.0, 117.1, 122.9, 124.0, 126.9, 128.4, 129.0, 131.2, 132.2, 135.4, 147.9, 167.1; HRMS: calculated for $C_{15}H_{11}NO_2$ 237.0798, found: 237.0789; m/z (EI): 237 (M$^+$, 33%), 238 (6), 219 (23), 132 (18), 105 (100), 77 (62), 51 (16).

4.1.26. 2-(Allylthio)aniline ***29***[29]. 2-Aminobenzenethiol (0.706 g, 5.64 mmol) was stirred in MeOH (20 mL) at 0 °C under an Ar blanket. Aqueous $NaHCO_3$ [prepared from $NaHCO_3$, 0.569 g, 6.77 mmol, and H_2O (20 mL)] was added and stirring continued until effervescence had ceased. Allyl bromide (0.82 g, 0.59 mL, 6.8 mmol) in MeOH (20 mL) was then added dropwise over 10 min. The solution was allowed to gradually warm to rt over 18 h after which most of the MeOH was evaporated. The aqueous oily residue was extracted with EtOAc (50 mL) and washed with H_2O (2×20 mL) and brine (20 mL). Drying (Na_2SO_4) and evaporation of the solvent afforded an orange oil, which was purified by silica gel flash chromatography (5% EtOAc/hexane) to afford **29** as a yellow oil (0.709 g, 76%). R_f (10% EtOAc/hexane) 0.33; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)=3.33–3.36 (2H, m, CH_2CHCH$_2$), 4.27 (2H, br s, NH$_2$), 4.91–4.99 (2H, 2m, CH$_2$CHCH_2), 5.73–5.90 (1H, m, CH$_2$CHCH$_2$), 6.66–6.71 (2H, m, 2×ArH), 7.07–7.10 (1H, m, ArH), 7.33–7.35 (1H, m, ArH). The rest of compound's spectra corresponded well with that reported in the literature.[29]

4.1.27. N-[2-(Allylthio)phenyl]-4-methylbenzenesulfonamide ***30***. 2-(Allylthio)aniline **29** (1.02 g, 6.20 mmol) was added to a solution of CH_2Cl_2 (20 mL) containing pyridine (1 mL). The reaction mixture was cooled to 0 °C and toluenesulfonyl chloride (1.30 g, 6.82 mmol) was added. Stirring was continued for 30 min at 0 °C and the mixture finally allowed to warm-up to rt over 90 min. The reaction mixture was then heated at reflux for 24 h. The solvent was evaporated and the

residue taken up into a mixture of H_2O (50 mL) and CH_2Cl_2 (20 mL). The aqueous fraction was furthermore extracted with CH_2Cl_2 (3×20 mL), which was separated and dried (Na_2SO_4). Evaporation gave a yellow oil that was purified by column chromatography (10% EtOAc/hexane) to afford **30** as a yellow oil (1.92 g, 97%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)=2.35 (3H, s, $ArCH_3$), 3.11 (2H, d, *J* 7.3 Hz, SCH_2CHCH_2), 4.72 (1H, dd, *J* 17.0, 1.2 Hz, $CH_2CHCH_aH_b$), 4.88 (1H, d, *J* 9.9 Hz, $CH_2CHCH_aH_b$), 5.65 (1H, ddt, *J* 7.3, 9.9, 17.0 Hz, CH_2CHCH_2), 6.98–7.02 (1H, m, ArH), 7.19–7.30 (3H, m, 3×ArH), 7.36 (1H, dd, *J* 7.7, 1.5 Hz, ArH), 7.64 (1H, dd, *J* 8.2, 1.2 Hz, ArH), 7.69 (2H, d, *J* 8.3 Hz, 2×ArH), 7.85 (1H, br s, NH); ^{13}C NMR (75 MHz, $CDCl_3$, one quaternary signal not observed in spectrum): δ (ppm)=21.4, 39.5, 118.3, 119.3, 123.5, 124.4, 127.2, 129.5, 129.8, 132.5, 136.1, 138.8, 143.9; HRMS: calculated for $C_{16}H_{17}NO_2S_2$ 319.0701, found 319.0687; *m*/*z* (EI): 319.06 (M^+, 100%), 289 (7), 213 (34).

*4.1.28. N-Allyl-N-[2-(allylthio)phenyl]-4-methylbenzenesulfonamide **31**.* Allyl bromide (0.48 g, 4.0 mmol) and K_2CO_3 (0.55 g, 4.0 mmol) were added to 4-methylbenzenesulfonamide **30** (0.64 g, 2.0 mmol) dissolved in acetone (50 mL), and the reaction slurry was then stirred at rt for 24 h. The base was removed by filtration and the solvent was removed under reduced pressure to afford **31** as a yellow oil, which required no further purification (0.72 g, 99%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)=2.43 (3H, s, $ArCH_3$), 3.50–3.56 (2H, m, SCH_2CHCH_2), 4.10–4.20 (2H, m, NCH_2CHCH_2), 4.89–5.05 (2H, m, CH_2CHCH_2), 5.11 (1H, dd, *J* 10.1, 1.0 Hz, $CH_2CHCH_aH_b$), 5.22 (1H, dd, *J* 17.0, 1.3 Hz, $CH_2CHCH_aH_b$), 5.72–5.94 (2H, m, 2×CH_2CHCH_2), 6.88 (1H, d, *J* 7.7 Hz, ArH), 6.98–7.10 (1H, m, ArH), 7.22–7.27 (4H, m, 4×ArH), 7.68 (2H, d, *J* 8.3 Hz, 2×ArH); ^{13}C NMR (75 MHz, $CDCl_3$, one quaternary signal not observed in spectrum): δ (ppm)=21.5, 35.2, 53.9, 118.1, 119.0, 125.1, 127.5, 128.1, 128.7, 129.3, 130.2, 132.7, 132.9, 136.5, 136.6, 139.8, 143.4; *m*/*z* (EI): 360 (M^++H, 18%), 205 (100), 164 (8), 91 (6).

*4.1.29. 2-(Prop-1-en-1-ylthio)aniline **34**.* ^{t}BuOK (0.400 g, 3.56 mmol) was added to solution of 2-(allylthio)aniline **29** (0.533 g, 3.22 mmol) in DMSO (10 mL). Stirring was continued for 18 h after which H_2O (100 mL) and hexane (100 mL) were added. The phases were separated and the aqueous phase was extracted with additional hexane (100 mL). The pooled hexane fractions were washed with additional H_2O (50 mL) and brine (50 mL). The extract was dried (Na_2SO_4) and evaporated to give a red oil. Flash silica gel column chromatography (5% EtOAc/hexane) afforded **34**, in a ~1:1 *E*/*Z* ratio, as an orange oil (0.449 g, 85%). IR ν_{max} (film)/cm^{-1} 3461, 3368, 1606, 1478, 1446, 1307; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm)=1.72 (1.5H, dd, *J* 1.5, 6.7 Hz, CH_3), 1.83 (1.5H, dd, *J* 1.4, 6.7 Hz, CH_3), 4.20 (2H, br s, NH_2), 5.60 (0.5H, dq, *J* 14.8, 6.7 Hz, $CHCHCH_3$), 5.72 (0.5H, dq, *J* 9.2, 6.7 Hz, $CHCHCH_3$), 5.80–5.90 (1H, m, CHCH), 6.67–6.69 (2H, m, 2×ArH), 7.08–7.13 (1H, m, ArH), 7.34 (1H, d, *J* 7.6 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)=14.4 and 18.1, 115.1, 116.2 and 117.5, 118.5 and 118.6, 122.4 and 127.0, 125.3 and 125.5, 129.6 and 129.9, 134.5 and 135.1, 147.4 and 147.6; HRMS: calculated for $C_9H_{11}N_1S$ 165.0612, found 165.0609; *m*/*z* (EI): 165 (M^+, 56%), 135 (100), 123 (35), 117 (13), 93 (13), 80 (23).

*4.1.30. 4-Methyl-N-[2-(prop-1-en-1-ylthio)phenyl]benzenesulfonamide **35**.* 2-(Prop-1-en-1-ylthio)aniline **34** (0.361 g, 2.19 mmol) was added to a solution of CH_2Cl_2 (10 mL) containing pyridine (1 mL). The reaction mixture was cooled to 0 °C and toluenesulfonyl chloride (0.460 g, 2.41 mmol) was added. Stirring was continued for 30 min at 0 °C and the mixture finally allowed to warm-up to rt over 18 h. The solvent was evaporated and the residue taken up into EtOAc (50 mL). The organic solution was washed with H_2O (2×25 mL) and brine (25 mL). Drying (Na_2SO_4) followed by evaporation gave an orange gum that was purified by flash chromatography (10% EtOAc/hexane) to afford compound **35** as an orange-coloured oil, an *E*/*Z* mixture with ratio ~1:1 (0.692 g, 99%). R_f (10% EtOAc/hexane) 0.25; IR ν_{max} (film)/cm^{-1} 3253, 1495, 1400, 1337, 1165; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)=1.67 (1.5H, br d, *J* 5.3 Hz, CH_3), 1.79 (1.5H, dd, *J* 6.7, 1.5 Hz, CH_3), 2.36 (3H, s, $ArCH_3$), 5.46–5.80 (2H, m, $SCHCHCH_3$), 6.98–7.07 (1H, m, ArH), 7.18–7.39 (4H, m, 4×ArH), 7.45 (1H, br s, NH), 7.61–7.69 (3H, m, 3×ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)=14.4 and 18.2, 21.5, 120.3 and 120.7, 121.6 and 123.9, 123.5 and 125.0, 124.9 and 125.1, 127.3, 127.7, 129.3 and 129.9, 129.5, 134.2 and 135.0, 136.0, 137.6 and 137.0, 143.9 and 144.0; HRMS: calculated for $C_{16}H_{17}NO_2S_2$ 319.0701, found 319.0697; *m*/*z* (EI): 319 (M^+, 6%), 165 (22), 164 (51), 149 (51), 131 (45), 130 (35).

*4.1.31. N-Allyl-4-methyl-N-[2-(prop-1-en-1-ylthio)phenyl]benzenesulfonamide **36**.* Allyl bromide (0.468 g, 0.33 mL, 3.87 mmol) was added to a solution of acetone (20 mL) containing K_2CO_3 (0.535 g, 3.87 mmol) and sulfonamide **35** (0.619 g, 1.76 mmol). The reaction mixture was stirred at rt for 18 h and filtered to remove most of the inorganic solids. The solvent was evaporated to afford an orange gum, and the gum was filtered through a small pad of silica with 10% EtOAc/hexane as the eluent (100 mL). Evaporation of the solvent then afforded **36** as an orange gum, which was used without further purification (0.685 g, 98%). NMR spectroscopy showed that the product was a ~1:1 mixture of *E*/*Z* isomers. R_f (10% EtOAc/hexane) 0.26; IR ν_{max} (film)/cm^{-1} 1468, 1439, 1347, 1216, 1160; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)=1.76–1.88 (3H, m, CH_3), 2.43 (3H, s, $ArCH_3$), 3.98–4.30 (2H, br m, NCH_2CHCH_2), 4.85–5.14 (2H, m, NCH_2CHCH_2), 5.75–6.16 (3H, m, NCH_2CHCH_2 and $SCHCHCH_3$), 6.81–6.97 (1H, m, ArH), 7.01–7.12 (1H, m, ArH), 7.20–7.32 (4H, m, 4×ArH), 7.67 (2H, d, *J* 8.2 Hz, 2×ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)=14.6 and 18.6, 21.5, 53.9, 119.0, 120.5 and 122.1, 125.5 and 125.7, 128.0 and 128.1, 128.2 and 128.6, 128.8 and 128.9, 129.4, 130.2, 130.4 and 130.5, 132.7 and 132.8, 134.9, 135.9 and 136.4, 136.5 and 136.6, 139.8 and 140.4, 143.4; HRMS: calculated for $C_{19}H_{21}N_1O_2S_2$ 359.1014, found 359.1017; *m*/*z* (EI): 359 (M^+, 4%), 205 (20), 204 (100), 176 (21), 163 (34), 162 (57), 136 (74).

*4.1.32. Attempted synthesis of 4-methyl-N-(prop-1-en-1-yl)-N-[2-(prop-1-en-1-ylthio)phenyl]benzenesulfonamide **32**.* The isomerization catalyst **14** (0.012 g, 0.013 mmol, 5 mol%) was added to benzenesulfonamide **36** (0.103 g, 0.26 mmol) in toluene (5 mL) and the mixture was stirred at reflux for 24 h under Ar. Examination of the crude proton NMR showed no appreciable reaction had occurred. In a further reaction, the reaction mixture was heated at reflux for 48 h under Ar; this time significant decomposition was evident in the NMR spectrum. Similar reactions were attempted on substrate **31**, unfortunately without success.

*4.1.33. 1,2-Bis(allylthio)benzene **38a**.* Benzene-1,2-dithiol **37a** (0.858 g, 6.03 mmol) was reacted with allyl bromide (2.04 mL, 24.1 mmol) and K_2CO_3 (3.33 g, 24.1 mmol) in acetone (20 mL) at 60 °C with stirring under Ar for 48 h. The K_2CO_3 was then removed by filtration and the solvent was removed under reduced pressure. The residue was then purified by silica gel column chromatography (2% EtOAc/hexane) to give product **38a** as a colourless oil (1.23 g, 92%). The oil was stored in the dark as it tended to turn pink in colour on exposure to sunlight. R_f (5% EtOAc/hexane) 0.50; IR: ν_{max} (film)/cm^{-1} 3081, 2978, 1636, 1571, 1446, 1427, 1406, 1225; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)=3.56 (4H, d, *J* 6.8 Hz, 2×SCH_2CHCH_2), 5.08 (2H, br d, *J* 9.9 Hz, 2×$SCH_2CHCH_aH_b$), 5.16 (2H, br d, *J* 16.9 Hz, 2×$SCH_2CHCH_aH_b$), 5.89 (2H, tdd, *J* 6.8, 9.9, 16.9 Hz, 2×SCH_2CHCH_2), 7.08–7.18 (2H, m, 2×ArH), 7.23–7.34 (2H, m, 2×ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)=36.5, 117.9, 126.4, 129.8, 133.1, 136.73; HRMS: calculated for $C_{12}H_{14}S_2$ 222.0537, found 222.0533; *m*/*z* (EI): 222 (M^+, 67%), 181 (100), 153 (85), 148 (93), 147 (67), 139 (32), 135 (25), 96 (24).

*4.1.34. 1,2-Bis(prop-1-en-1-ylthio)benzene **39a**.* A solution of **38a** (0.17 g, 0.77 mmol) in EtOH (1.0 mL) was added to a solution of

NaOEt in EtOH [prepared by dissolving Na (0.151 g, 6.55 mmol) in EtOH (3.0 mL)] in a microwave reactor vial. The vial was sealed and reacted in a microwave for 3 h at 90 °C (max. power=50 W). The reaction was poured into H_2O (10 mL) and extracted with EtOAc (2×25 mL). The organic fraction was washed with additional H_2O (20 mL) and brine (10 mL). Drying (Na_2SO_4), followed by evaporation afforded a yellow oil. Flashed silica gel chromatography (100% hexane) then afforded product **39a** as a colourless oil and as an inseparable mixture of *E*,*E*-, *Z*,*Z*- and *E*,*Z*-isomers (0.157 g, 92%). R_f (5% EtOAc/hexane) 0.50; IR: ν_{max} (film)/cm^{-1} 1613, 1571, 1445, 1430, 1377, 1333; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)=1.82–1.87 (6H, m, 2×CH_3), 5.89–6.15 (4H, m, 2×SC*H*CHCH$_3$ and 2×SCHC*H*CH$_3$), 7.12–7.15 (2H, m, 2×ArH), 7.26–7.30 (2H, m, 2×ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)=14.6 and 14.7 (SCHCH*C*H$_3$), 18.5 and 18.6 (SCH*C*HCH$_3$), 120.9 and 121.0, 122.8, and 123.0, 126.5 and 126.6, 126.7 and 126.8, 128.6 and 129.1, 129.0 and 129.3, 129.5 and 129.6, 133.3 and 133.8, 135.5 and 136.1, 136.3 and 137.0; HRMS: calculated for $C_{12}H_{14}S_2$ 222.0537, found 222.0532; *m*/*z* (EI): 222 (M$^+$, 30%), 181 (20), 167 (24), 166 (41), 153 (100), 147 (100), 147 (27), 134 (25).

4.1.35. 1,4-Benzodithiin ***41a***[32]. To a solution of **39a** (0.067 g, 0.30 mmol) in CH_2Cl_2 (8 mL), was added Grubbs' second generation catalyst (G2) **13** (0.013 g, 0.015 mmol, 5 mol %). The reaction mixture was then heated at reflux for 18 h after which the solvent was removed in vacuo. The crude product was purified by silica gel column chromatography (100% hexane) to afford the known compound **41a** as a yellow oil (0.039 g, 77%). The colour of the oil changed to pink on standing in air. The spectra of this compound compared well with that published in the literature.[32] R_f (Hexane) 0.48; IR: ν_{max} (film)/cm^{-1} 3055, 3031, 1617, 1552, 1449, 1427, 1251; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)=6.51 (2H, s, 2×SC*H*) 7.19–7.23 (2H, m, 2×ArH), 7.25–7.30 (2H, m, 2×ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)=123.7, 127.7, 128.2, 133.1 (C).

4.1.36. 1-(Allyloxy)-2-(allylthio)benzene ***38b***. 2-Mercaptophenol **37b** (1.00 g, 7.53 mmol) was added to a solution of dry acetone (25 mL) containing K_2CO_3 (5.48 g, 39.7 mmol) and allyl bromide (4.80 g, 3.35 mL, 39.7 mmol). The mixture was stirred under Ar for 48 h after which the reaction mixture was filtered through a pad of Celite. The Celite pad was washed with additional acetone (2×25 mL). The filtrate was evaporated and subjected to column chromatography (4% EtOAc/hexane) to afford **38b** as a colourless oil (1.087 g, 70%). R_f (5% EtOAc/hexane) 0.51; IR: ν_{max} (film)/cm^{-1} 3081, 2919, 1637, 1579, 1475, 1276, 1240; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)=3.55 (2H, d, *J* 6.9 Hz, SCH_2CHCH$_2$), 4.61 (2H, m, OCH_2CHCH$_2$), 5.05 (1H, d, *J* 10.0 Hz, SCH$_2$CHCH_aH$_b$), 5.14 (1H, dd, *J* 1.3, 17.0 Hz, SCH$_2$CHCH$_a$H$_b$), 5.29 (1H, dd, *J* 10.4, 1.4 Hz, OCH$_2$CHCH_aH$_b$), 5.47 (1H, dd, *J* 17.2, 1.5 Hz, OCH$_2$CHCH$_a$H$_b$), 5.88 (1H, ddt, *J* 6.9, 10.0, 17.0 Hz, SCH$_2$C*H*CH$_2$), 6.08 (1H, ddt, *J* 5.0, 10.4, 17.2 Hz, OCH$_2$C*H*CH$_2$), 6.84 (1H, d, *J* 8.0 Hz, ArH), 6.90 (1H, td, *J* 7.6, 1.0 Hz, ArH), 7.15 (1H, td, *J* 8.0, 1.6 Hz, ArH), 7.28 (1H, dd, *J* 7.6, 1.5 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)=35.3 (SCH_2), 69.3 (OCH_2), 112.0, 117.5 (2×CH), 121.1, 124.5, 127.2, 130.3, 133.0, 133.7, 156.6 (C); HRMS: calculated for $C_{12}H_{14}OS$ 206.0765, found 206.0761; *m*/*z* (EI): 206 (M$^+$, 48%), 165 (100), 150 (28), 137 (77), 132 (98), 131 (59), 103 (21).

4.1.37. 1-(Allyloxy)-2-(prop-1-en-1-ylthio)benzene ***40***. Compound **38b** (0.12 g, 0.59 mmol) in EtOH (abs, 1 mL) was added to a solution of Na (0.151 g, 6.57 mmol) in EtOH (abs, 3 mL) in a microwave pressure vessel. The vessel was sealed and reacted for 3 h (50 W, 90 °C). The reaction mixture was poured into H_2O (30 mL) and extracted with EtOAc (50 mL). Drying (Na_2SO_4) and evaporation of the solvent afforded **40** as an orange oil (0.12 g, quantitative, *E*:*Z* ratio ~1:1). IR: ν_{max} (film)/cm^{-1} 1649, 1614, 1578, 1475, 1443, 1423, 1335, 1299, 1276, 1240; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)=1.84–1.87 (3H, m, CH_3), 4.59–4.62 (2H, m, OCH_2), 5.26–5.30 (1H, m, OCH$_2$CHCH_aH$_b$), 5.43–5.50 (1H, m, OCH$_2$CHCH$_a$H$_b$), 5.91–6.21 (3H, m, OCH$_2$C*H*CH$_2$ and SC*H*C*H*CH$_3$), 6.82–6.86 (1H, m, ArH), 6.90–6.95 (1H, m, ArH), 7.10–7.16 (1H, m, ArH), 7.20–7.27 (1H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)=14.6, and 18.6, 69.3, 112.0 and 112.1, 117.3 and 117.4, 120.4 and 121.3, 121.4 and 122.3, 125.3 and 126.0, 126.6 and 126.8, 128.0 and 128.5, 129.0, 132.9 and 133.5, 155.0 and 155.5; HRMS: calculated for $C_{12}H_{14}OS$ 206.0765, found 206.0760; *m*/*z* (EI): 206 (M$^+$, 67%), 165 (100), 150 (56), 137 (60), 132 (36), 131 (25).

4.1.38. 1-(Prop-1-en-1-yloxy)-2-(prop-1-en-1-ylthio)benzene ***39b***. Compound **40** (0.095 g, 0.46 mmol) was dissolved in dry DMSO (5 mL). ^{t}BuOK (0.103 g, 0.92 mmol) was added and the solution was stirred under Ar at 60 °C for 18 h. The solution was then poured into H_2O (10 mL) and extracted with hexane (5×20 mL). The hexane fraction was washed with H_2O (2×10 mL) and dried (Na_2SO_4). Evaporation of the solvent afforded the desired product **39b** as a yellow oil (0.068 g, 72%, *E*:*Z* ratio ~1:1 for SCHCHCH$_3$). IR: ν_{max} (film)/cm^{-1} 1668, 1575, 1471, 1443, 1394, 1252, 1228; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)=1.74–1.77 (3H, m, OCHCHC*H*$_3$), 1.84–1.88 (3H, m, SCHCHC*H*$_3$), 4.88–4.98 (1H, m, OCHC*H*CH$_3$), 5.92–6.22 (2H, m, SC*H*C*H*CH$_3$), 6.34–6.37 (1H, m, OC*H*CHCH$_3$), 6.90–6.94 (1H, m, ArH), 6.97–7.02 (1H, m, ArH), 7.11–7.18 (1H, m, ArH), 7.25–7.30 (1H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)=9.4 and 14.6, 18.6, 108.2 and 108.3, 114.7 and 114.8, 120.4 and 122.2, 122.9 and 122.9, 126.0 and 126.5, 126.8 and 126.9, 128.5 and 128.9, 129.3 and 133.5, 140.7, 154.2 and 154.7; HRMS: calculated for $C_{12}H_{14}OS$ 206.0765, found 206.0760; *m*/*z* (EI): 206 (M$^+$, 47%), 165 (18), 150 (45), 137 (100).

4.1.39. 1,4-Benzoxathiin ***41b***[33]. Grubbs' second generation catalyst (G2) **13** (0.013 g, 0.015 mmol, 5 mol %) was added to a solution of sulfane **39b** (0.062 g, 0.30 mmol) in CH_2Cl_2 (5 mL). The solution was degassed and heated at reflux under Ar for 20 h. An additional quantity of Grubbs' II **13** (0.013 g, 0.015 mmol, 5 mol %) was added and heating at reflux was continued for an additional 18 h. The reaction mixture was evaporated and the residue purified by silica gel column chromatography (hexane) to afford **41b** as a yellow oil (0.035 g, 77%). The spectra of this compound compared well with that available in the literature.[33] IR: ν_{max} (film)/cm^{-1} 1634, 1573, 1471, 1443, 1341, 1268, 1227; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)=5.20 (1H, d, *J* 5.8 Hz, SCH), 6.41 (1H, d, *J* 5.8 Hz, OCH), 6.69 (1H, d, *J* 8.0 Hz, ArH), 6.84–6.94 (2H, m, 2×ArH), 6.99–7.05 (1H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)=97.4, 117.3, 118.2, 124.9, 126.9, 127.9, 140.0, 150.8.

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