Activation by allylic alcohols of sulfur-containing dienes to ruthenium-catalysed ring-closing metathesis

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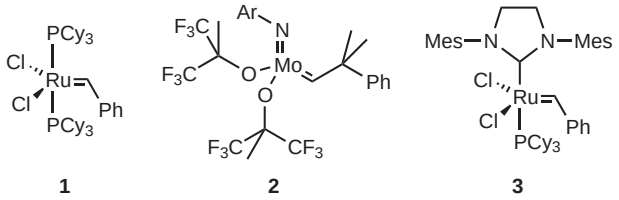
The presence of an allylic alcohol facilitates ring-closing metathesis of sulfur-containing substrates with Grubbs' dihydroimidazole ruthenium complex.

Keywords: ring-closing metathesis, organosulfur, allylic alcohol, alkene activation, NHC ligands

Ring-closing metathesis (RCM) has rapidly become a fundamental tool in organic synthesis for the preparation of medium to large ring systems.[1] This is largely the consequence of the development of well-defined metal alkylidene catalysts such as the ruthenium catalysts of Grubbs[2] **1** and the molybdenum catalysts of Schrock[3] **2** (Fig. 1). Whilst the molybdenum catalyst exhibits superior reactivity over a range of substrates, from a practical perspective, the ruthenium catalysts are undeniably more attractive due to wider functional group compatibility, air and moisture insensitivity and thermal stability. With the advent of the dihydroimidazole carbene ligands,[4] so called "second-generation" Grubbs' ruthenium catalysts **3** have overcome many of their initial limitations, showing increased reactivity and even greater stability.

Despite the tremendous advances in metathesis utilising ruthenium catalysts there remains a dearth of examples involving substrates containing sulfides.[5] Such a deficiency has partly been attributed to the match of the "soft" ruthenium centre with the "soft" sulfur functionality allowing favourable coordination and catalyst deactivation. Recently a number of reports have appeared that surmount this obstacle, either by steric shielding, preventing coordination[5b] or by attenuating the electronic environment of the sulfur sufficiently to permit catalysis.[5c] However, limitations in the scope of ruthenium-catalysed RCM on sulfur-containing substrates remain, as recently highlighted by both Mioskowski[5d] and Singh.[5e] This, in conjunction with value of any information that adds definition to the gamut of substrates that can be tolerated in ruthenium catalysed RCM has prompted us to disclose our results which demonstrate a potential solution to this problem *via* alkene activation with an allylic alcohol.[6]

During the course of our studies into the sila-Pummerer[7] reaction we required a variety of medium ring α-thiosilacycles **13–16** (Scheme 2). The most expedient route to this class of substrate appeared to be RCM of the dienes **7–10**. The cyclisation precursors could be synthesised from thioanisole in two steps (Scheme 1). Silylation with the appropriate chlorosilane[8,9] proceeded without incident to furnish **4–6** in moderate to excellent yields. Subsequent deprotonation of **4** or **6** with *n*-butyl lithium followed by alkylation with alkyl halides 3-(chloromethoxy)prop-1-ene or 5-bromopentene gave the desired cyclisation precursors **7** and **8** respectively.

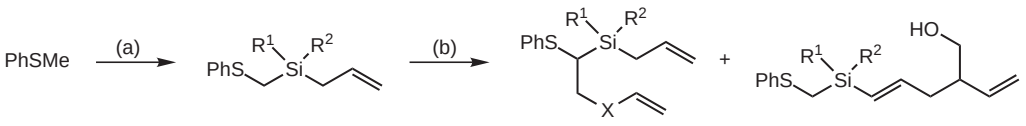


1 **2** **3**

Fig. 1.

Addition of butadiene monoxide proved more problematic. Deprotonation of **4** followed by the addition of butadiene monoxide resulted in formation of 5-phenylsulfanyl-1-penten-3-ol only. Presumably the desired alkylation was followed by 1,4-Brook rearrangement and subsequent hydrolysis. Use of the more hindered silanes **5** and **6** prevented desilylation but led to the formation of complex reaction mixtures. In both cases only two isomeric alcohols **9** and **11** or **10** and **12** could be isolated. Characterisation and isolation was hampered by the formation of mixtures of diastereoisomers. Whilst **9** was isolated as a single diastereoisomer, analysis of the crude nmr spectrum suggested the presence of at least three other diastereoisomers of the desired product. These arose from chiral centres at the silicon atom, alcohol functionality and the sulfide position. In addition to these diastereoisomers, compounds resulting from the non-selective deprotonation and non-selective addition to butadiene monoxide prevented isolation of any other compounds in meaningful amounts or purity. To half the number of possible diastereoisomers, diisopropylsilane **6** was utilised. Unfortunately, the lack of chemoselectivity in the reaction meant we saw no improvement in yield.

Initial investigations of the metathesis utilised Grubbs' catalyst **1** (Scheme 2; Table 1). It was hoped that the silane moiety would offer a sufficient steric buttress to prevent sulfur



4 R^1=R^2=Me (53 %)
5 R^1=Me R^2=*t*-Bu (93 %)
6 R^1=R^2=*i*-Pr (65 %)

7 R^1=R^2=Me X=OCH_2 (47 %)
8 R^1=R^2=*i*-Pr X=$(CH_2)_2$ (49 %)
9 R^1=Me R^2=*t*-Bu X=CH(OH) (15 %)
10 R^1=R^2=*i*-Pr X=CH(OH) (14 %)

11 R^1=Me R^2=*t*-Bu (30 %)
12 R^1=R^2=*i*-Pr (1.5 %)

Scheme 1 (a) i. *n*-BuLi, THF, -78°C; ii. $ClSiR^1R^2CH_2CH=CH_2$. (b) i. *n*-BuLi, TMEDA, hexanes, -78°C; ii. 3-(chloromethoxy)prop-1-ene or 5-bromopentene or butadiene monoxide.

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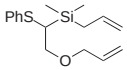
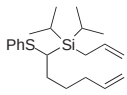
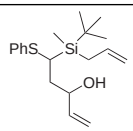
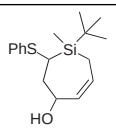
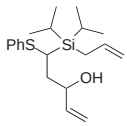
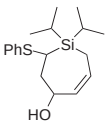
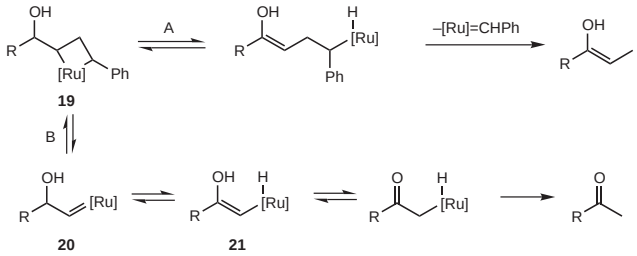
Table 1 Ring-closing metathesis of sulfur-containing compounds

Entry	Substrate	Catalyst	Mol. %	Temp./°C	Product	Yield/%
1		**1**	5	20		0
2		**1**	15	40		0
3		**3**	5	20		0
4	**7**	**3**	10	40		0
5		**1**	5	20		0
6		**3**	5	20		0
7		**3**	5	40		0
	8					
8		**1**	5	20		0
9		**1**	10	40		<20[a]
10		**3**	5	20		76
	9				**15**	
11		**3**	5	20		77
	10				**16**	

[a]The major products were the two ketones **17** (64 %) and **18** (10 %) *c.f.* Scheme 2

coordination and catalyst deactivation. Unfortunately none of the substrates reacted under standard conditions of 5 mol % **1** at room temperature (Table 1. Entries 1, 5, 8). Increasing the catalyst loading (15 mol %) and elevating the temperature (reaction heated to reflux in dichloromethane) had no effect on the allyl ether (Entry 2). Interestingly, allyl alcohol **9** did react under these new conditions but not in the anticipated manner (Entry 9). Only traces of the desired silacycle **15** (<20 %) could be isolated. The predominant compound was the ethyl ketone **17** (64 %) and a trace of the methyl ketone **18** (10 %) (Scheme 2).

A number of recent reports have observed similar isomerisation and fragmentation reactions of allylic alcohols during RCM.[10] It is postulated that they occur *via* two competing pathways. Initially both pathways undergo cycloaddition to furnish the ruthenocycle **19** (Scheme 3). Formation of the ethyl ketone *via* isomerisation (A) is thought to occur *via* hydrogen transfer with concomitant ring opening of the ruthenocycle **19** and subsequent loss of the propagating carbenoid. Alternatively, fragmentation (B) to give the methyl ketone occurs *via* cyclo-reversion of the ruthenocycle followed by tautomerisation of the resultant carbene **20** to give a ruthenium hydride species **21** that undergoes reductive elimination. Isolation of the ketone-containing substrates alludes to the formation of the metallocycle, the first step of RCM. Evidently the free hydroxyl group has a significant activating effect on the adjacent vinyl group[6] which is



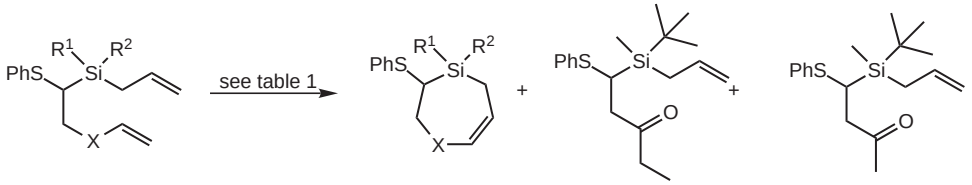
Scheme 3

sufficient to overcome the normal deactivating interaction between sulfur and the ruthenium catalyst. If isomerisation could be suppressed then RCM should proceed even in the presence of the sulfur moiety.

Ruthenium alkylidene complexes containing a bulky dihydroimidazole carbene ligand have been shown to be far more efficient catalysts for RCM.[4] It was hoped that the increased reactivity would allow RCM to occur more rapidly than isomerisation / fragmentation.[10a,b] Indeed, treatment of allyl alcohols **9** and **10** with 5 mol % **3** at room temperature resulted in formation of the desired silacycles **15** and **16** in high yields (Entries 10 and 11). Neither the allyl ether **7** or the simple diene **8** underwent RCM with complex **3** even at elevated temperatures (Entries 3, 4, 6 and 7). It could be argued that differences in ring size might account for the propensity of each of compounds to undergo RCM; all dienes forming 7-membered rings successfully cyclised under optimised conditions whilst all dienes forming 8-membered rings failed. Grubbs' has shown that silyl ethers readily undergo RCM to give 7-rings (88–91% yield), 8-rings (90–96%) and even 9-rings (73%), thus suggesting that the formation of cyclic silyl ethers by RCM is tolerant of a variety of ring sizes and that this is not a factor in the chemistry described.[11] A test compound incorporating an extra methylene unit could have been synthesised but as it would have provided a compound unsuitable for our proposed work it was deemed unnecessary.

It is clear that allylic hydroxyl groups greatly accelerate the formation of the metallocyclobutane,[6a] possibly *via* rapid and reversible ligand exchange or hydrogen bonding resulting in the carbene and alkene residing in close proximity, thus predisposing the complex to cycloaddition rather than unproductive interaction with the sulfur atom. It is further evident that for this activation to be profitable the subsequent metathesis must be rapid in order to prevent isomerisation of the secondary allylic alcohol. Thus the more reactive dihydroimidazole carbene derived catalysts must be employed.

In conclusion, we have shown that allylic alcohol activation in conjunction with the "second generation" Grubbs' catalyst provides sufficient enhancement of RCM to overcome the deactivating effect of the sulfur moiety.



7 R^1=R^2=Me X=OCH_2
8 R^1=R^2=*i*-Pr X=$(CH_2)_2$
9 R^1=Me R^2=*t*-Bu X=CH(OH)
10 R^1=R^2=*i*-Pr X=CH(OH)

13 R^1=R^2=Me X=OCH_2
14 R^1=R^2=*i*-Pr X=$(CH_2)_2$
15 R^1=Me R^2=*t*-Bu X=CH(OH)
16 R^1=R^2=*i*-Pr X=CH(OH)

Scheme 2

Experimental

^{1}H NMR spectra were recorded on Bruker DPX300, Varian unityINOVA-300 or Varian unityINOVA-400 Fourier transform spectrometers at 300, 300 or 400 MHz respectively using $CDCl_3$ as solvent. Chemical shifts (δ) are quoted in ppm using tetramethylsilane as internal reference (δ = 0.00 ppm), and coupling constants (*J*) are quoted in Hz. ^{13}C NMR spectra were recorded using the same instruments at 75, 75 or 100 MHz respectively, and chemical shifts (δ) are quoted in ppm using $CDCl_3$ as internal reference (δ = 77.0 ppm). IR spectra were recorded on Perkin-Elmer Spectrum One Fourier transform instruments, by the method of Attenuated Total Reflectance (ATR). Low- and high-resolution electron impact (EI) mass spectra were recorded using a Fisons Autospect instrument. Low-resolution GC-EI analysis was performed on a Hewlett Packard HP 6890 GC-system with a Hewlett Packard 5973 mass selective detector. All starting materials were obtained from the normal suppliers unless otherwise stated. The anhydrous solvents, THF and diethyl ether (ether), were obtained from Aldrich Chemicals in Sure/Seal™ bottles and were used without further purification. Petrol refers to petroleum ether with a boiling range of 40 – 60 °C. Flash column chromatography was performed using Fisher Matrix 60 (35 – 70 μm) silica. Analytical thin layer chromatography (TLC) was performed using Whatman K6F silica gel plates (60Å porosity) and visualised with UV light or an alkaline solution of potassium permanganate.

Allyl(tert-butyl)chloro(methyl)silane: Copper (I) cyanide (0.45 g, 5 mmol) was added to a solution of allyldichloromethylsilane (13 ml, 90.1 mmol) in THF (90 ml) and the mixture cooled to 0 °C under a nitrogen atmosphere. A solution of *tert*-butylmagnesium chloride (1.0 M in THF; 100 ml, 100 mmol) was added to the reaction mixture *via* a syringe pump over 2 hours, keeping the temperature of the reaction at 0 °C. The reaction was stirred for 2 hours at 0 °C before being allowed to warm to room temperature and stirred overnight. The mixture was concentrated, before being diluted with *iso*-hexane (90 ml) and filtered. The filtrated was evaporated and the residue distilled under vacuum to give allyl(*tert*-butyl)chloro(methyl)silane (7.5 g, 47 %) as a colourless oil; b.p. 55–57°C at 25mmHg; υ_{max} (thin film) 2933, 1472, 1256, 1163, 932, 900, 825, 810, 774, 724, 694, 609, 574 and 553 cm^{-1}; δ_H (400MHz; $CDCl_3$; Me_4Si) 5.85 (1H, m, CH), 4.95 (2H, m, CH_2), 1.85 (2H, m, CH_2Si), 1.00 (9H, s, *t*-Bu), 0.35 (3H, s, CH_3); GC / MS (96.5%) *m/z* 176 (M+, 9%), 135 (M-allyl, 19%), 119 (M-*t*-Bu, 20%), 93 (100%), 79 (15%).

Allylchlorodiisopropylsilane: A stirred mixture of dimethyl imidazolidinone (DMI) (20 ml), zinc powder (3.5 g, 54 mmol) and dichlorodiisopropylsilane (10 g, 54 mmol) was heated under a nitrogen atmosphere, and stirred at 70 °C for 1 hour. Allyl chloride (4.4 ml, 54 mmol) was then added dropwise over 15 minutes [CAUTION: the addition is very exothermic even at 70 °C]. Once the addition was complete the mixture was held at 70 °C for 2 hours before being allowed to cool to room temperature and stirred overnight. The mixture was diluted with diethyl ether (30 ml) and the precipitated salts removed by filtration. The filtrate was concentrated to yield a crude mixture of the intended product and the bulk of the DMI. The crude mixture was purified by distillation under water pump vacuum (b.p. 94–97°C at 20mmHg) to give allylchlorodiisopropylsilane (7.32 g) of a colourless oil. The product contains approximately 1 mol of DMI, which can be tolerated in the subsequent reaction. The effective yield of allylchlorodiisopropylsilane, accounting for DMI, is 4.6g (45%); δ_H (300MHz; $CDCl_3$; Me_4Si) 5.80 (1H, ddd, *J* 16.9 10.0 9.0, CH=CH_2), 4.95 (1H, d, *J* 16.9, $CH_{2(trans)}$), 4.90 (1H, d, *J* 10.0, $CH_{2(cis)}$), 1.85 (2H, d, *J* 9.0, $SiCH_2$), 1.20 (2H, m, CH), 1.10 (12H, s, CH_3); δ_C (75MHz; $CDCl_3$; Me_4Si) 133.0 (CH), 115.5 (CH_2), 21.3 (CH_2), 17.0 (CH_3), 13.9 (CH); HRMS (EI+) calcd. (M) 190.094457 found 190.094863.

Allyldimethyl(phenylthiomethyl)silane **(4)**: To a solution of thioanisole (5.0 g, 0.04 mol) in THF (50 ml) was added TMEDA (6 ml, 0.04 mol) and the mixture cooled to –40 °C under a nitrogen atmosphere. A solution of *n*-BuLi (2.5 M in hexanes; 11.1 ml, 0.04 mol) was added dropwise keeping the reaction temperature at –40 °C. The mixture was cooled and stirred for 1 hour at –60 °C before a solution of allylchlorodimethylsilane (7.0 ml, 0.05 mol) in THF (15 ml) was added dropwise keeping the reaction temperature at –60 °C. Once the addition was complete the mixture was held at –60 °C for 1 hour before warming to room temperature and stirring overnight. The reaction was quenched by the addition of water (100 ml) and the product extracted into petrol (2 × 100 ml). The organic layers were combined and washed with 3M $HCl_{(aq)}$ (2 × 200 ml), and sat. $NaHCO_{3(aq)}$ (200 ml), dried ($MgSO_4$), filtered and evaporated. The residue was purified by vacuum distillation to give **4** as a colourless oil (4.7 g, 53 %); b.p. 130–132°C at 15mmHg; υ_{max} (thin film) 3076, 2890, 1630, 1583, 1479, 1438, 1391, 1250, 1192, 1157, 1025, 895, 834, 735 and 688 cm^{-1}; δ_H (300MHz; $CDCl_3$; Me_4Si) 7.35 (4H, m, Ar–H), 7.15 (1H, m, Ar–H), 5.80 (1H, ddd, *J* 15.0, 12.0, 10.0, CH), 4.95 (1H, d, J 15.0, $CH_{2(trans)}$), 4.90 (1H, d, *J* 10.0, $CH_{2(cis)}$), 2.20 (2H, s, CH_2SPh), 1.75 (2H, d, *J* 12.0, CH_2Si), 0.2 (6H, s, CH_3); δ_C (75MHz; $CDCl_3$; Me_4Si) 140.5 (C), 134.4 (CH), 129.1 (2 × CH), 126.5 (2 × CH), 125.1 (CH), 114.2 (CH_2), 23.1 (CH_2), 16.8 (CH_2), 11.8 (2 × CH_3); *m/z* (EI) 222 (M+H, 31%), 181 (M-allyl, 100%), 165 (93%), 151 (26%), 135 (70%), 91 (50%), 59 (46%); HRMS (EI+) calcd. (M+H) 223.0977 found 223.0979.

Allyl(tert-butyl)(methyl)(phenylthiomethyl)silane **(5)**: Thioanisole (3.5 g, 28.3 mmol) was dissolved in THF (40 ml) and cooled to 0°C under nitrogen. A solution of *n*-BuLi (2.5M in hexane; 11.9 ml, 29.7 mmol) was added dropwise keeping the temperature below 0 °C. The reaction mixture was stirred at 0 °C for 1 hour resulting in a bright yellow suspension. A solution of allyl(*tert*-butyl)chloro(methyl)silane (5 g, 28.3 mmol) in THF (10 ml) was added dropwise to the reaction mixture, keeping the temperature below 0 °C. After a further 1 hour at 0 °C the mixture was allowed to warm to room temperature and diluted with diethyl ether (100 ml). The resulting mixture was washed with sat. $NH_4Cl_{(aq)}$ (2 × 100 ml), dried ($MgSO_4$), filtered and evaporated. The resulting crude product was purified by distillation to give **5** as a clear oil (7.0 g, 93 %); b.p. 220–225°C at 6mBar; υ_{max} (thin film) 2928, 2856, 1479, 1470, 1463, 1389, 1254, 934, 894, 825, 816, 800, 736, 697, 688, 653, 599, 563 and 554 cm^{-1}; δ_H (400MHz; $CDCl_3$; Me_4Si) 7.30 (4H, m, Ar–H), 7.10 (1H, m, Ar–H), 5.85 (1H, m, CH), 4.95 (1H, dd, *J* 17.2, 4.4, $CH_{2(trans)}$), 4.85 (1H, dd, *J* 10.0, 4.4, $CH_{2(cis)}$), 2.25 (2H, d, *J* 4.0, CH_2SPh), 1.85 (2H, m, CH_2Si), 1.00 (9H, s, *t*-Bu), 0.35 (3H, s, CH_3); δ_C (75MHz; $CDCl_3$; Me_4Si) 141.5 (C), 134.6 (CH), 128.7 (2 × CH), 126.0 (2 × CH), 124.7 (CH), 113.8 (CH_2), 26.9 (3 × CH_3), 19.2 (CH_2), 17.3 (C), 13.5 (CH_2), -7.1 (CH_3); HRMS (EI+) calcd. (M+H) 265.1446 found 265.1449.

Allyldiisopropyl(phenylthiomethyl)silane **(6)**: Thioanisole (2.96 ml, 25.3 mmol) was dissolved in THF (20 ml) and the mixture cooled to 0 °C under a nitrogen atmosphere. *n*-BuLi (2.5M in hexanes; 11.1 ml, 27.8 mmol) was added dropwise keeping the reaction temperature at 0 °C. The mixture was then stirred for 1 hour at 0 °C before a solution of allylchlorodiisopropylsilane (25.3 mmol) (containing 1 mol DMI) in THF (5 ml) was added dropwise keeping the reaction temperature at 0 °C. Once the addition was complete the mixture was allowed to warm to room temperature and stirred for 2 hours. The reaction mixture was quenched by the addition of saturated $NH_4Cl_{(aq)}$ (200 ml) and the product extracted into dichloromethane (2 × 40 ml). The organic layers were combined and washed with water (2 × 100 ml), dried ($MgSO_4$), filtered and evaporated. The residue was purified by Kugelrohr distillation, to give **6** as a colourless oil (6.3 g, 65 %); b.p. 205–210 °C at 5 mmHg; υ_{max} (thin film) 2941, 2865, 1629, 1586, 1479, 1462, 1386, 1158, 1025, 993, 919, 882, 777, 710 and 688 cm^{-1}; δ_H (300MHz; $CDCl_3$; Me_4Si) 7.25 (4H, m, Ar–H), 7.10 (1H, m, Ar–H); 5.80 (1H, ddd, *J* 16.9, 10.0, 9.0, CH=CH_2), 4.95 (1H, d, J 16.9, $CH_{2(trans)}$), 4.90 (1H, d, *J* 10.0, $CH_{2(cis)}$), 2.20 (2H, s, CH_2SPh), 1.85 (2H, d, *J* 9.0, CH_2Si), 1.05 (2H, m, CH), 1.05 (12H, s, CH_3); δ_C (75MHz; $CDCl_3$; Me_4Si) 140.1 (C), 135.0 (CH), 129.0 (2 × CH), 126.3 (2 × CH), 125.0 (CH), 114.2 (CH_2), 18.5 (4 × CH_3), 18.0 (CH_2), 12.5 (CH_2), 11.8 (CH); *m/z* (EI) 278 (M+, 15%), 237 (M-allyl, 100%), 193 (60%), 165 (64%), 151 (67%), 91 (62%); HRMS (EI+) calcd. (M+H) 279.1597245 found 279.1585850.

Allyl(2-(allyloxy)-1-(phenylthio)ethyl)dimethylsilane **(7)**: Allyldimethyl(phenylthiomethyl)silane **4** (2.6 g, 11.7 mmol) was dissolved in THF (10 ml) and the mixture cooled to 0 °C under a nitrogen atmosphere. A solution of *n*-BuLi (2.5M in hexanes; 5.6 ml, 14.0 mmol) was added dropwise keeping the reaction temperature at 0 °C. The mixture was stirred for 1 hour at 0 °C before a solution of allylchloromethyl ether (1.87 g, 17.6 mmol) in THF (5 ml) was added dropwise keeping the reaction temperature at 0 °C. The reaction was allowed to warm to room temperature and stirred for 2 hours resulting in a white suspension. The mixture was partitioned between diethyl ether (50 ml) and sat. $NH_4Cl_{(aq)}$ (50 ml), and the organic layer, separated, dried ($MgSO_4$), filtered and evaporated. The residue was purified by flash chromatography (0.5% v/v diethyl ether / *iso*-hexane) and the product **7** obtained as a colourless oil (1.6 g, 47 %); R_f = 0.40 (1 : 200 diethyl ether : *iso*-hexane); υ_{max} (thin film) 2957, 1629, 1583, 1479, 1439, 1248, 1155, 1138, 1091, 1069, 1025, 965, 927, 895, 836, 821, 737, 690, 658, 627, 604 and 580 cm^{-1}; δ_H (400MHz; $CDCl_3$; Me_4Si) 7.4 (2H, d, *J* 8.4, Ar-$H_{(ortho)}$), 7.25 (2H, dd, *J* 8.4, 6.4, Ar-$H_{(meta)}$), 7.15 (1H, t, *J* 6.4, Ar-$H_{(para)}$), 5.90 (2H, m, 2 × CH=CH_2), 5.20 (1H, dd, *J* 17.2, 1.8, $OCH_2CH=CH_{2(trans)}$), 5.15 (1H, dd, *J* 10.4, 1.8, $OCH_2CH=CH_{2(cis)}$), 4.90 (1H, dd, *J* 14.2, 1.8, $SiCH_2CH=CH_{2(trans)}$), 4.85 (1H, dd, *J* 9.0, 1.8, $SiCH_2CH=CH_{2(cis)}$), 3.95 (2H, m, CH_2O), 3.65 (2H, d, *J* 10.0, H-2), 2.80 (1H, t, *J* 10.0, H-1), 1.75 (2H, m, CH_2Si),

0.1 (6H, s, CH_3); δ_C (75MHz; $CDCl_3$; Me_4Si) 137.8 (C), 134.7 (CH), 134.6 (CH), 129.4 (2 × CH) 128.9 (2 × CH), 125.9 (CH), 116.7 (CH_2), 113.6 (CH_2), 72.0 (CH_2), 71.6 (CH_2), 33.3 (CH), 22.5 (CH_2), –4.1 (2 × CH_3); HRMS (EI+) calcd. (M+H) 293.1395 found 293.1405.

Allyldiisopropyl(1-(phenylthio)hex-5-enyl)silane **(8)**: Allyldiisopropyl(phenylthiomethyl)silane **6** (0.5 g, 1.8 mmol) was dissolved in hexanes (5 ml) and TMEDA (0.4 ml, 2.7 mmol) added. The mixture was then cooled to 0 °C under a nitrogen atmosphere and a solution of *n*-BuLi (2.5M in hexanes, 1.4 ml, 3.4 mmol) was added dropwise keeping the reaction temperature at 0 °C. The mixture was stirred for 5 hours at 0 °C, before 5-bromopentene (0.3 ml, 2.7 mmol) was added dropwise to maintain the reaction temperature at 0 °C. Once the addition was complete the mixture was allowed to warm to room temperature and stirred for 2 hours. The reaction mixture was then partitioned between dichloromethane (50 ml) and sat. $NH_4Cl_{(aq)}$ (50 ml). The layers were separated and the aqueous layer was extracted with fresh dichloromethane (50 ml), before the organic layers were combined, dried ($MgSO_4$), filtered and evaporated. The residue was purified by gravity chromatography (petrol), and the product **8** was obtained as a colourless oil (0.305 g, 49 %); R_f = 0.95 (40–60 °C petrol); υ_{max} (thin film) 2926, 2892, 2865, 1629, 1584, 1479, 1462, 1438, 1386, 1159, 1086, 1025, 992, 909, 882, 779, 735 and 689 cm^{-1}; δ_H (400MHz; $CDCl_3$; Me_4Si) 7.35 (2H, d, *J* 7.5, Ar–$H_{(ortho)}$), 7.25 (2H, m, *J* 7.5, 6.9, Ar–$H_{(meta)}$), 7.15 (1H, t, *J* 6.9, Ar–$H_{(para)}$), 5.90 (1H, m, $SiCH_2CH=CH_2$), 5.70 (1H, m, H-5), 4.90–4.80 (4H, m, 2 × $CH=CH_2$), 2.75 (1H, dd, *J* 9.4, 3.7, H-1), 1.95 (2H, m, H-2), 1.80 (2H, d, *J* 8.1, $SiCH_2$), 1.60 (2H, m, H-4), 1.20 (2H, m, H-3), 1.10 (2H, m, $CHMe_2$), 1.0 (12H, m, CH_3); δ_C (75MHz; $CDCl_3$; Me_4Si) 139.4 (C), 138.6 (CH), 135.2 (CH), 128.7 (4 × CH), 125.5 (CH), 114.4 (CH_2), 113.8 (CH_2), 33.7 (CH_2), 33.3 (CH_2), 31.0 (CH), 28.3 (CH) 18.7 (4 × CH_3), 18.0 (CH_2), 11.6 (2 × CH); *m/z* (EI) 346 (M+, 8%), 305 (M-allyl, 23%), 237 (M-PhS,17%), 223 (75%), 151 (35%), 109 (30%), 85 (53%), 59 (62%), 41 (100%), 27 (40%); HRMS (EI+) calcd. (M) 346.215052 found 346.216070.

5-(Allyl(tert-butyl)(methyl)silyl)-5-(phenylthio)pent-1-en-3-ol **(9)** *and (E)-5-(tert-butyl(methyl)(phenylthiomethyl)silyl)-2-vinylpent-4-en-1-ol* **(11)**: To a solution of TMEDA (7.1 ml, 47.1 mmol) in hexane (60 ml) at 0 °C, under a nitrogen atmosphere, was added n-BuLi (2.5M in hexanes; 23.7 ml, 59.7 mmol) dropwise maintaining a reaction temperature of 0 °C. A solution of allyl(tert-butyl)(methyl)(phenylthiomethyl)silane **5** (8.25 g, 31.4 mmol) in iso-hexane (20 ml) was added, maintaining a reaction temperature of 0 °C. The yellow solution was stirred at 0 °C for 5 hours, whereupon a solution of butadiene monoxide (3.5 ml, 44.0 mmol) in hexane (10 ml) was added dropwise, maintaining a reaction temperature of 0 °C. The mixture was allowed to warm to room temperature and stirred for 3 hours. The reaction mixture was diluted with diethyl ether (200 ml) and washed with sat. $NH_4Cl_{(aq)}$ (2 × 200ml), dried ($MgSO_4$), filtered and evaporated. The resulting crude product was purified by flash chromatography (2 : 1 iso-hexane : DCM), to give a mixture of diastereoisomers of **9** as a colourless oil (1.5 g, 15 %) and (E)-5-(tert-butyl(methyl)(phenylthiomethyl)silyl)-2-vinylpent-4-en-1-ol **11** as a colourless oil (30 %); 5-(allyl(tert-butyl)(methyl)silyl)-5-(phenylthio)pent-1-en-3-ol **9** R_f = 0.35 (2 : 1 iso-hexane : DCM); υ_{max} (thin film) 2928, 2857, 1471, 1438, 1253, 1158, 991, 921, 895, 823, 797, 738, 689, 642, 622, 601, 583 and 556 cm^{-1}; δ_H (400MHz; $CDCl_3$; Me_4Si) 7.45 (2H, d, J 8.4, Ar–$H_{(ortho)}$), 7.25 (2H dd, J 8.4, 7.2, Ar–$H_{(meta)}$), 7.15 (1H, t, J 7.2, Ar–$H_{(para)}$), 5.80 (2H, m, 2 × CH), 5.15 (1H, dd, J 17.2, 2.8, ($SiCH_2CH$)$CH_{2(trans)}$), 5.05 (1H, dd, J 10.4, 2.8, ($SiCH_2CH$)$CH_{2(cis)}$), 4.95 (1H, dd, J 16.8, 3.2, $CH_{2(trans)}$), 4.90 (1H, dd, J 6.8, 3.2, $CH_{2(cis)}$), 4.30 (1H, bs, H-3), 3.05 (1H, m, H-5), 1.80 (4H, m, 2 × CH_2), 1.45 (1H, m, OH), 1.00 (9H, s, t-Bu), 0.10 (3H, s, CH_3); δ_C (75MHz; $CDCl_3$; Me_4Si) 141.3 (CH), 139.1 (C), 135.0 (CH), 128.9 (2 × CH), 128.5 (2 × CH), 125.7 (CH), 113.9 (2 × CH_2), 70.1 (CH), 41.2 (CH_2), 28.2 (CH), 28.0 (3 × CH_3), 19.0 (CH_2), 18.5 (C), -7.6 (CH_3); GC/MS (96.2%) m/z 334 (M+, 0.5%), 293 (M-allyl, 10%), 277 (M-^{t}Bu, 5%), 239 (19%), 169 (100%), 151 (46%), 101 (48%), 75 (71%), 59 (22%); HRMS (EI+) calcd. (M+H) 335.1865 found 335.1849. (E)-5-(tert-butyl(methyl)(phenylthiomethyl)silyl)-2-vinylpent-4-en-1-ol **11**; R_f = 0.15 (2 : 1 isohexane : DCM); υ_{max} (thin film) 2926, 2855, 1616, 1585, 1479, 1470, 1463, 1438, 1253, 1085, 1067, 1025, 1007, 990, 914, 823, 793, 736, 716, 689, 669, 618, 606 and 598 cm^{-1}; δ_H (400MHz; $CDCl_3$; Me_4Si) 7.30 (4H, m, Ar–H), 7.10 (1H, m, Ar–H), 6.10 (1H, m, H-4), 6.15 (2H, m, H-5 & $CH=CH_2$), 5.10 (2H, m, $CH=CH_2$), 3.55 (2H, m, H-1), 2.40 (1H, m, H-2), 2.25 (4H, m, H-3 & CH_2SPh), 1.45 (1H, m, OH), 0.95 (9H, s, t-Bu), 0.20 (3H, s, CH_3); δ_C (75MHz; $CDCl_3$; Me_4Si) 147.9 (CH), 140.6 (C), 139.1 (CH) 128.6 (2 × CH), 126.1 (CH), 126.0 (2 × CH), 124.6 (CH), 117.2 (CH_2), 65.0 (CH_2), 46.0 (CH), 38.6 (CH_2), 26.6 (3 × CH_3), 17.1 (C), 13.9 (CH_2), -8.1 (CH_3); GC/MS (96.7%) m/z 334 (M+, 0.5%), 277 (M-^{t}Bu, 2%), 183 (41%), 165 (100%), 151 (21%), 137 (20%), 75 (31%); HRMS (EI+) calcd. (M+H) 335.1865 found 335.1862.

5-(Allyldiisopropylsilyl)-5-(phenylthio)pent-1-en-3-ol **(10)** *and (E)-5-(diisopropyl(phenylthiomethyl)silyl)-2-vinylpent-4-en-1-ol* **(12)**: To a solution of allyldiisopropyl(phenylthiomethyl)silane **6** (3.0 g, 10.8 mmol) and TMEDA (2.4 ml, 16.2 mmol) in hexane (30 ml) at 0 °C under a nitrogen atmosphere was added *n*-BuLi (2.5M in hexanes; 8.2 ml, 20.5 mmol) dropwise maintaining the temperature of 0 °C. The yellow solution was stirred at 0 °C for 5 hours, before a solution of butadiene monoxide (1.2 ml, 15.1 mmol) in hexanes (5 ml) was added dropwise, maintaining a reaction temperature of 0 °C. The reaction was stirred at 0 °C for 1 hour before warming to room temperature and stirred for 3 hours. The reaction mixture was diluted with dichloromethane (100 ml) and washed with saturated $NH_4Cl_{(aq)}$ (100 ml). The aqueous layer was re-extracted with a further portion of dichloromethane (100 ml) and the organic layers were combined, dried ($MgSO_4$), filtered and evaporated to yield an orange oil. The resulting crude product was purified by flash chromatography (2 : 1 petrol : DCM) to give 5-(allyldiisopropylsilyl)-5-(phenylthio)pent-1-en-3-ol **10** as a colourless oil (0.51g, 14%) and (*E*)-5-(diisopropyl(phenylthiomethyl)silyl)-2-vinylpent-4-en-1-ol **12** (1.5 %); 5-(Allyldiisopropylsilyl)-5-(phenylthio)pent-1-en-3-ol **10** R_f = 0.35 (1 : 1 petrol : DCM); υ_{max} (thin film) 2941, 2892, 2865, 1629, 1582, 1480, 1463, 1438, 1420, 1367, 1246, 1159, 1085, 1024, 991, 882, 841, 777, 710, 690 and 656 cm^{-1}; δ_H (400MHz; $CDCl_3$; Me_4Si) 7.50 (2H, d, *J* 7.6, Ar–$H_{(ortho)}$), 7.25 (2H, dd, *J* 8.0, 7.5, Ar–$H_{(meta)}$), 7.15 (1H, t, *J* 8.0, Ar–$H_{(para)}$), 5.90 (2H, m, H-2 & $CH=CH_2$), 5.15 (1H, dd, *J* 15.2, 1.8, $CH=CH_{2(trans)}$), 5.05 (1H, dd, *J* 10.4, 1.8, $CH=CH_{2(cis)}$), 4.95 (1H, dd, *J* 15.2, 1.8, H-$1_{(trans)}$), 4.90 (1H, dd, *J* 10.0, 1.8, H-$1_{(cis)}$), 4.25 (1H, bs, H-3), 3.15 (1H, dd, *J* 12.8 3.2, H-5), 1.85 (2H, m, H-4), 1.80 (2H, d, $SiCH_2$), 1.45 (1H, m, OH), 1.25 (2H, m, $CHMe_2$), 1.15–1.05 (12H, m, CH_3); δ_C (75MHz; $CDCl_3$; Me_4Si) 141.8 (CH), 139.8 (C), 135.5 (CH), 129.3 (2 × CH), 128.5 (2 × CH) 126.0 (CH), 114.2 (2 × CH_2), 70.5 (CH), 41.9 (CH_2), 27.0 (CH), 19.0 (4 × CH_3), 18.1 (CH_2), 11.8 (2 × CH); HRMS (EI+) calcd. (M+H) 349.2015893 found 349.2012710. (*E*)-5-(diisopropyl(phenylthiomethyl)silyl)-2-vinylpent-4-en-1-ol **12** R_f = 0.15 (1 : 1 40–60 °C Petrol ether : DCM); υ_{max} (thin film) 2940 (m), 2864, 1616, 1586, 1479, 1462, 1438, 1384, 1084, 1067, 1025, 917, 881, 776 and 688 cm^{-1}; δ_H (400MHz; $CDCl_3$; Me_4Si) 7.20 (4H, m, Ar–H), 7.00 (1H, t, *J* 8.0, Ar–$H_{(para)}$), 6.05 (1H, dt, *J* 18.8, 6.4, H–4), 5.60 (1H, m, $CH=CH_2$), 5.50 (1H, d, *J* 18.8, H-5), 5.10 (1H, d, *J* 8.4, $CH=CH_{2(trans)}$), 5.05 (1H, d, *J* 6.8, $CH=CH_{2(cis)}$), 3.65 (1H, bs, OH), 3.45 (2H, m, H-1), 2.25 (1H, m, H-2), 2.25 (1H, m, H-3), 2.20 (2H, s, CH_2SPh), 2.15 (1H, m, H-3), 1.15 (2H, m, $CHMe_2$), 1.10–1.05 (12H, m, CH_3); δ_C (75MHz; $CDCl_3$; Me_4Si) 148.6 (CH), 141.0 (C), 139.5 (CH), 128.9 (2 × CH), 126.2 (2 × CH), 124.9 (CH), 124.6 (CH), 116.9 (CH_2), 65.3 (CH_2), 46.4 (CH), 39.1 (CH_2), 18.2 (4 × CH_3), 12.3 (CH_2), 11.5 (2 × CH); HRMS (EI+) calcd. (M+H) 349.2015893 found 349.2013617.

(Z)-1-tert-Butyl-1-methyl-2-(phenylthio)-2,3,4,7-tetrahydro-1H-silepin-4-ol **(15)**: To a solution of **9** (1.5 g) in dichloromethane (150 ml), under nitrogen was added tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimazol-2-ylidene][benzylidine]ruthenium (IV) dichloride **3** (0.19 g, 5 mol%) and the mixture stirred for 18 hours at room temperature. The crude product was isolated by evaporation. Purification by flash chromatography (2 : 1 dichloromethane : *iso*-hexane) gave a mixture of two diastereoisomers of **15** as a colourless oil (1.05 g, 76 %); R_f = 0.25 (1 : 1 *iso*-hexane : DCM); υ_{max} (thin film) 2925, 2899, 2850, 1648, 1470, 1449, 1438, 1281, 1253, 1162, 1049, 1024, 1005, 824, 807, 786, 771, 731, 691, 661, 628, 612, 601, 594 and 556 cm^{-1}; δ_H (400MHz; $CDCl_3$; Me_4Si) (Diastereoisomer 1) 7.40 (2H, d, *J* 8.0, Ar–$H_{(ortho)}$), 7.30 (2H, dd, *J* 8.0, 7.0, Ar–$H_{(meta)}$), 7.10 (1H, t, *J* 7.0, Ar–$H_{(para)}$), 5.75 (1H, m, H-5), 5.55 (1H, ddd, *J* 10.8, 5.1, 2.6, H-6), 5.00 (1H, m, H-4), 2.85 (1H, dd, *J* 6.7, 4.4, H-2), 2.05 (2H, m, H-3), 1.90 (1H, m, H-7), 1.40 (1H, m, H-7), 1.35 (1H, d, *J* 4.0, OH), 1.05 (9H, s, *t*-Bu), 0.10 (3H, m, CH_3); (Diastereoisomer 2) 7.40 (2H, d, *J* 8.0, Ar–$H_{(ortho)}$), 7.30 (2H, dd, *J* 8.0, 7.0, Ar–$H_{(meta)}$), 7.10 (1H, t, *J* 7.0, Ar–$H_{(para)}$), 5.75 (1H, m, H-5), 5.55 (1H, ddd, *J* 11.5, 3.6, 1.0, H-6), 4.65 (1H, m, H-4), 3.35 (1H, dd, *J* 8.0, 2.8, H-2), 2.20 (2H, m, H-3), 1.70 (1H, m, H-7), 1.60 (1H, m, H-7), 1.35 (1H, d, *J* 4.0, OH), 1.00 (9H, s, *t*-Bu), 0.15 (3H, m, CH_3); δ_C (75MHz; $CDCl_3$; Me_4Si) (diastereoisomer 1) 135.9 (C) 131.2 (CH), 129.8 (2 × CH), 128.7 (2 × CH), 126.0 (CH), 125.1 (CH), 66.9 (CH), 38.0 (CH_2), 30.7 (CH), 27.0 (3 × CH_3), 17.5 (C), 12.0 (CH_2), –7.2 (CH_3); (diastereoisomer 2) 136.4 (C), 133.9 (CH), 129.2 (2 × CH), 128.8 (2 × CH), 125.8 (CH), 125.5 (CH), 68.1 (CH), 37.7 (CH_2), 27.0 (3 × CH_3), 24.2 (CH), 17.1 (C), 12.3 (CH_2), –8.5 (CH_3); GC/MS (96.1%) *m/z* 306 (M+, 3%), 288 (M-H_2O, 4%), 249 (M-^{t}Bu, 12%), 239 (15%),

169 (100%), 151 (70%), 75 (39%); HRMS (EI+) calcd. (M+H) 307.1552 (M-H_2O) 289.1446 found 289.1438.

1-(Allyl(tert-butyl)(methyl)silyl)-1-(phenylthio)pentan-3-one **(17)** *and 4-(allyl(tert-butyl)(methyl)silyl)-4-(phenylthio)butan-2-one* **(18)**: To solution of 5-(allyl(tert-butyl)(methyl)silyl)-5-(phenylthio)pent-1-en-3-ol **9** (0.5 g, 1.5 mmol) in dichloromethane (50 ml) under nitrogen was added Grubbs' catalyst [bis(tricyclohexylphosphine)benzylidine ruthenium (IV) dichloride] **1** (65 mg, 5 mol%) and the mixture heated to reflux. After 5 hours at reflux a further portion of Grubbs' catalyst (65 mg, 5 mol%) was added and heating continued overnight. Concentration and column chromatography (5 : 1 iso-hexane : DCM) gave a mixture of diastereoisomers of ethyl ketone **17** (320 mg, 64 %) as a colourless oil and the methyl ketone **18** (47 mg, 10 %); 1-(allyl(tert-butyl)(methyl)silyl)-1-(phenylthio)pentan-3-one **17**; R_f = 0.45 (5 : 1 isohexane : DCM); υ_{max} (thin film) 2929, 2857, 1713, 1470, 1463, 1438, 1363, 1254, 1160, 1110, 1025, 991, 971, 584 cm^{-1}; δ_H (400MHz; $CDCl_3$; Me_4Si) 7.35 (2H, m, Ar–$H_{(ortho)}$), 7.30 (2H, m, Ar–$H_{(meta)}$), 7.15 (1H, m, Ar–$H_{(para)}$), 5.90 (1H, m, CH=CH_2), 4.90 (2H, m, CH=CH_2), 3.40 (1H, m, H-1), 2.90–2.70 (2H, m, H-2), 2.25 (2H, t, J 9.6, H-4), 1.90–1.75 (2H, m, $SiCH_2$), 1.00 (9H, s, t-Bu), 0.90 (3H, q, J 9.6, H-5), 0.00 (3H, s, CH_3); δ_C (75MHz; $CDCl_3$; Me_4Si) 208.1 (C), 136.7 (CH), 134.7 (CH), 129.5 (2 × CH), 128.9 (2 × CH), 126.0 (CH) 114.0 (CH_2), 45.8 (CH_2), 36.2 (CH_2), 27.6 (3 × CH_3), 24.6 (CH), 19.0 (CH_2), 18.5 (C), 7.6 (CH_2), –8.1 (CH_3); GC/MS (87.5%) m/z 305 (M-Et, 1%), 293 (M-allyl, 32%), 277 (M-^{t}Bu, 20%), 183 (100%), 167 (55%), 151 (32%), 139 (70%), 125 (60%), 110 (61%), 99 (49%), 75 (81%), 57 (78%), 29 (45%); HRMS (EI+) calcd. (M+H) 335.1865 found 335.1860. 4-(Allyl(tert-butyl)(methyl)silyl)-4-(phenylthio)butan-2-one **18**; R_f = 0.35 (5 : 1 iso-hexane : DCM); υ_{max} (thin film) 3075, 2929, 1714, 1629, 1583, 1480, 1470, 1438, 1254, 1155, 1024, 824, 805, 786, 768, 738, 690 and 601 cm^{-1}; δ_H (400MHz; $CDCl_3$; Me_4Si) 7.35 (2H, m, Ar–$H_{(ortho)}$), 7.30 (2H, m, Ar–$H_{(meta)}$), 7.15 (1H, m, Ar–$H_{(para)}$), 5.90 (1H, m, CH=CH_2), 4.90 (2H, m, CH=CH_2), 3.40 (1H, m, H-4), 2.90–2.70 (2H, m, H-3), 2.00 (3H, s, $COCH_3$), 1.90–1.75 (2H, m, $SiCH_2$), 1.05 (9H, s, t-Bu), 0.10 (3H, m, CH_3); δ_C (75MHz; $CDCl_3$; Me_4Si) 207.1 (C), 136.7 (CH), 134.8 (CH), 129.5 (2 × CH), 128.7 (2 × CH), 126.0 (CH), 114.0 (CH_2), 47.2 (CH_2), 30.1 (CH_3), 27.6 (3 × CH_3), 24.4 (CH), 19.0 (CH_2), 18.5 (C), -8.1 (CH_3); GC/MS (81.6%) m/z 279 (M-allyl, 26%), 263 (M-CH_3C=O, 7%), 169 (100%), 153 (52%), 125 (62%), 110 (50%), 75 (63%), 43 (81%); HRMS (EI+) calcd. (M+H) 321.1708 found 321.1701.

(Z)-1,1-Diisopropyl-2-(phenylthio)-2,3,4,7-tetrahydro-1H-silepin-4-ol **(16)**: To a solution of **10** (0.55 g, 1.6 mmol) in dichloromethane (50 ml), under nitrogen was added tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimazol-2-ylidene] [benzylidene] ruthenium (IV) dichloride **3** (67 mg, 5 mol%) and the mixture stirred for 18 hours at room temperature. The crude product was isolated by evaporation. Purification by flash chromatography (1 : 1 dichloromethane : *iso*-hexane) gave **16** as a colourless oil as mixture of two diastereoisomers (0.38 g, 77%); R_f = 0.25 (1 : 1 isohexane : DCM); υ_{max} (thin film) 2938, 2889, 2863, 1583, 1479, 1463, 1438, 1383, 1254, 1162, 1045, 1023, 736 and 691 cm^{-1}; δ_H (300MHz; $CDCl_3$; Me_4Si) 7.40 (2H, d, *J* 8.7, Ar–$H_{(ortho)}$), 7.30 (2H, dd, *J* 8.7, 7.2, Ar–$H_{(meta)}$), 7.10 (1H, t, *J* 7.2, Ar–$H_{(para)}$), 5.75 (1H, m, H-6), 5.40 (1H, dd, *J* 5.2, 2.3, H-5), 4.80 (1H, m, H-4), 3.00 (1H, dd, *J* 8.4, 4.5, H-2), 2.10 (2H, m, H-3), 1.80 (1H, dd, *J* 14.4, 1.8, H-7), 1.50 (1H, dd, *J* 14.4, 9.0, H-7), 1.30–1.00 (14H, m, 2 × $CHMe_2$ & 4 × CH_3); δ_C (75MHz; $CDCl_3$; Me_4Si) 136.8 (C), 132.5 (CH), 130.0 (2 × CH), 129.3 (2 × CH), 126.5 (CH), 126.1 (CH), 68.6 (CH), 38.8 (CH_2), 26.7 (CH), 19.1 (CH_3), 18.9 (CH_3), 18.8 (CH_3), 18.7 (CH_3), 11.9 (CH), 11.6 (CH), 11.0 (CH_2); HRMS (EI+) calcd. (M-OH) 303.1603 found 303.1599.

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