Pergamon

Tetrahedron 57 (2001) 4411–4422

TETRAHEDRON

Polylithiation of thioethers: a versatile route for polyanionic synthons

Miguel Yus,* Ana Gutiérrez and Francisco Foubelo*

Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Alicante, Apdo. 99, E-03080 Alicante, Spain

Received 5 January 2001; revised 5 March 2001; accepted 29 March 2001

Abstract—The successive reaction of phenyl vinyl thioether (**1**) with *n*-butyllithium and an electophile [E_1=PhCHO, $(CH_2)_4CO$, $(CH_2)_5CO$] in THF at −78°C gives, after hydrolysis, the expected methylenic hydroxy thioethers (**2**). Deprotonation of **2** with *n*-butyllithium followed by a DTBB-catalysed lithiation and reaction with a second electrophile [E_2=^{t}BuCHO, PhCHO, Me_2CO, $(CH_2)_5CO$], at −78°C, gives after hydrolysis the corresponding methylenic diols **3**. The same diols can be prepared starting from **1** in a one-pot process without isolation of the hydroxy thioether **2**. The same methodology was applied to the cyclopropyl phenyl thioether (**4**), cyclopropyl 1,3-diols 5 {E_1=^{t}BuCHO, PhCHO, $[Me(CH_2)_4]_2CO$, $(CH_2)_5CO$, $(CH_2)_7CO$; E_2=^{t}BuCHO, Me_2CO, $(CH_2)_5CO$} being isolated in moderate yields. The successive treatment of bis(phenylthio)methane (**7**) with: (a) *n*-butyllithium at 0°C, (b) a carbonyl compound [E_1=^{t}BuCHO, Me_2CO, Et_2CO, $(CH_2)_5CO$] at −40°C, (c) lithium and catalytic amount of DTBB (5%) and (d) a second carbonyl compound [E_2=^{i}PrCHO, ^{t}BuCHO, Me_2CO, Et_2CO, $(CH_2)_5CO$] both at −78°C leads, after hydrolysis, to the expected dihydroxy thioethers **8**. When after step (d), a second DTBB-catalysed lithiation is performed at temperatures ranging between −78 and 20°C, the corresponding allylic alcohols **9** were isolated. Finally, treatment of alcohols **9** with a few drops of 6 M hydrochloric acid gives dienes **10** in almost quantitative yields.

---

1. Introduction

Polylithium organic compounds[1] exhibit fascinating structures[2] and their stability depends strongly and mainly on the relative position of the lithium atoms and also on the hybridisation of the carbon atom bonded to the lithium atoms. These systems are accessible by applying the same methodology as for single organolithium compounds[3] and they are important intermediates in synthetic organic chemistry because polyfunctionalised molecules[4] can be prepared in a single step by reaction with electrophiles. More interesting would be to introduce different electrophilic fragments in the polyanionic unit, the reiterative sequential lithiation-reaction with the electrophile being the only way to achieve this goal.[5] It is known that direct deprotonation with apropriate bases of dithioacetals[6] or phenyl thioethers[7] yields sulfur-stabilised carbanions, which act as typical acyl anion equivalents in the first case. On the other hand, in the last few years, a new methodology for the preparation of organolithium compounds starting from phenyl thioethers has being developed, using either a stoichiometric[8] or a catalytic amount[9] of an arene as electron carrier.[10] Taking into account these both methodologies, α-deprotonation of thioethers and sulfur–lithium exchange, we thought that it would be of interest to combine them in order to generate different geminal polylithium synthons starting from phenyl vinyl thioether (**1**), cyclopropyl phenyl thioether (**4**) and bis(phenylthio)methane (**7**).[11]

2. Results and discussion

2.1. Lithiation of phenyl vinyl thioether: an ethylene 1,1-dianion synthon[12]

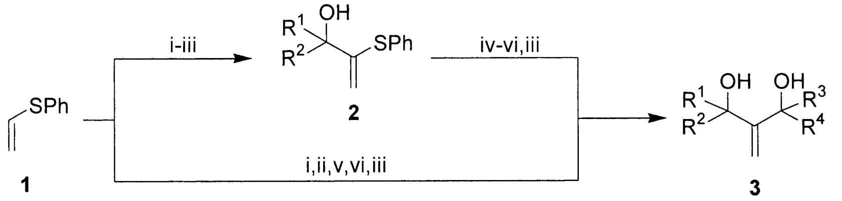
The reaction of commercially available phenyl vinyl thioether (**1**) with *n*-butyllithium in the presence of tetramethylethylenediamine (TMEDA)[13] in THF at −78°C followed by treatment with a carbonyl compound [E_1=PhCHO, $(CH_2)_4CO$, $(CH_2)_5CO$] led, after hydrolysis, to the expected unsaturated hydroxy thioethers **2**. These compounds, after deprotonation with *n*-butyllithium in THF at 0°C, were reductively lithiated using an excess of lithium and a catalytic amount of 4,4′-di-*tert*-butylbiphenyl (DTBB; 5 mol%). The reaction with a second carbonyl compound [E_2=^{t}BuCHO, PhCHO, Me_2CO, $(CH_2)_5CO$] gave, after hydrolysis with water, the expected methylenic 1,3-diols **3** (Scheme 1 and Table 1).

As intermediates in the reaction, compounds **I** and **II** (Scheme 2) should be involved in the first (**1**→**2**) and second step (**2**→**3**), respectively. On the other hand, when two prochiral carbonyl compounds are used as electrophiles, a mixture of diastereomers was obtained (Table 1, entry 1).

Keywords: lithiation; deprotonation; 1,3-diols; thioacetals; 1,3-dienes.

* Corresponding authors. Tel.: +34-965903548; fax: +34-965903549; e-mail: yus@ua.es

PII: S0040-4020(01)00374-X

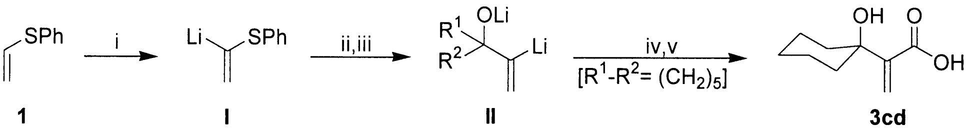


Scheme 1. *Reagents and conditions*: (i) ^{n}BuLi, TMEDA, THF, −78°C; (ii) E_1=PhCHO, $(CH_2)_4CO$, $(CH_2)_5CO$, −78°C; (iii) H_2O, −78–20°C; (iv) ^{n}BuLi, THF, 0°C; (v) Li, DTBB cat. (5 mol%), −78°C; (vi) E_2=^{t}BuCHO, PhCHO, Me_2CO, $(CH_2)_5CO$, −78°C.

Table 1. Preparation of compounds **2** and **3** (step by step process)

Entry	Compound **2**[a]				Compound **3**[a]			
	No.	R^1	R^2	Yield (%)[b,c]	No.	R^3	R^4	Yield (%)[b,d]
1	**2a**	H	Ph	66	**3aa**	H	Ph	41[e]
2	**2b**	$(CH_2)_4$		56	**3ba**	H	^{t}Bu	43
3	**2b**	$(CH_2)_4$		56	**3bb**	H	Ph	46
4	**2b**	$(CH_2)_4$		56	**3bc**	$(CH_2)_5$		35
5	**2c**	$(CH_2)_5$		74	**3ca**	Me	Me	33

[a] All compounds **2** and **3** were >95% pure (GLC and/or 300 MHz ^{1}H NMR).
[b] Isolated yield after column chromatography (silica gel, hexane/ethyl acetate).
[c] Based on the starting thioether **1**.
[d] Based on the hydroxythioether **2**.
[e] Isolated as a ca. 2:1 diastereomeric mixture (75 MHz ^{13}C NMR) and separated by column chromatography.



Scheme 2. *Reagents and conditions*: (i) ^{n}BuLi, TMEDA, THF, −78°C; (ii) R^1R^2CO, −78°C; (iii) Li, DTBB cat. (5 mol%), −78°C; (iv) CO_2, −78°C; (v) H_3O^+, −78–20°C.

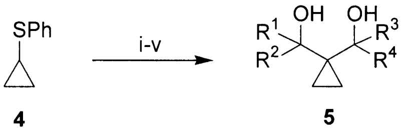
As a demonstration that other electrophiles different from carbonyl compounds can be used in the reaction, we used carbon dioxide in the second step after having introduced cyclohexanone as the first electrophile, and in this way the methylenic hydroxy acid **3cd** (Scheme 2) was obtained in 35% isolated yield.

Alternatively, the preparation of compounds **3** can more easily be achieved in a one-pot process, without isolation of alcohols **2**. Thus, once the lithium alcoholate derived from **2** was obtained, it was directly lithiated under the above mentioned reaction conditions and reacted with a second electrophile giving compound **3**, after hydrolysis (Scheme 1 and Table 2). For the same type of structures **3**, yields are better in the case of the one-pot procedure.

Table 2. Direct preparation of compounds **3** (one-pot process)

Entry	No.[a]	R^1	R^2	R^3	R^4	Yield (%)[b]
1	**3ab**	H	Ph	Me	Me	42
2	**3ac**	H	Ph	$(CH_2)_5$		31
3	**3cb**	$(CH_2)_5$		$(CH_2)_5$		62
4	**3da**	H	^{t}Bu	Me	Me	20
5	**3db**	H	^{t}Bu	$(CH_2)_5$		50

[a] All compounds **3** were >94% pure (GLC and/or 300 MHz ^{1}H NMR).
[b] Isolated yield after column chromatography (silica gel, hexane/ethyl acetate), based on the starting thioether **1**.



Scheme 3. *Reagents and conditions*: (i) ^{n}BuLi, TMEDA, THF, 0°C; (ii) E_1=^{t}BuCHO, PhCHO, $[Me(CH_2)_4]_2CO$, $(CH_2)_5CO$, $(CH_2)_7CO$, −78°C; (iii) Li, DTBB cat. (5 mol%), −78°C; (iv) E_2=^{t}BuCHO, Me_2CO, $(CH_2)_5CO$, −78°C; (v), H_2O, −78–20°C.

2.2. Lithiation of cyclopropyl phenyl thioether: a cyclopropane 1,1-dianion synthon

The reaction of commercially available cyclopropyl phenyl thioether (**4**) with *n*-butyllithium[14] in the presence of

Table 3. Preparation of compounds **5**

Entry	No.[a]	R^1	R^2	R^3	R^4	Yield (%)[b,c]
1	**5a**	H	^{t}Bu	H	^{t}Bu	41+15 (31)[d]
2	**5b**	H	Ph	Me	Me	35 (48)
3	**5c**	$Me(CH_2)_4$	$Me(CH_2)_4$	Me	Me	21 (51)
4	**5d**	$(CH_2)_5$		H	^{t}Bu	30 (45)
5	**5e**	$(CH_2)_5$		$(CH_2)_5$		22 (53)
6	**5f**	$(CH_2)_7$		Me	Me	27 (44)

[a] All compounds **5** were >94% pure (GLC and/or 300 MHz ^{1}H NMR).
[b] Isolated yield after column chromatography (silica gel, hexane/ethyl acetate), based on the starting thioether **4**.
[c] In parenthesis, yield of the corresponding alcohol **6** based on GLC is given.
[d] Isolated as a *anti–syn* diastereomeric mixture and separated by column chromatography.

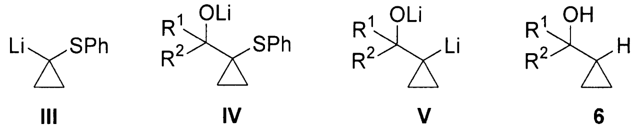
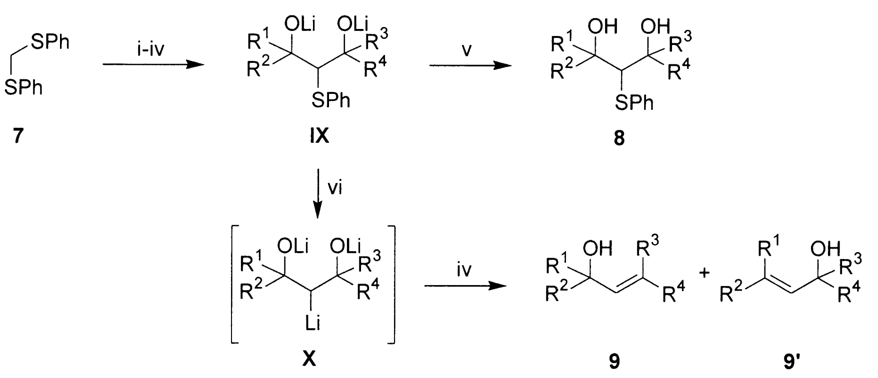


Chart 1.



Scheme 4. *Reagents and conditions*: (i) ^{n}BuLi, THF, 0°C; (ii) E_1=^{t}BuCHO, Me_2CO, Et_2CO, $(CH_2)_5CO$, −40°C; (iii) Li, DTBB cat. (5 mol%), −78°C; (iv) E_2=^{i}PrCHO, ^{t}BuCHO, Me_2CO, Et_2CO, $(CH_2)_5CO$, −78°C; (v) H_2O, −78–20°C; (vi) Li, DTBB (5 mol%), −78–20°C.

Table 4. Preparation of compounds **8**

Entry	No.[a]	R^1	R^2	R^3	R^4	Yield (%)[b]
1	**8a**	H	^{t}Bu	H	^{t}Bu	45[c]
2	**8b**	Me	Me	Me	Me	50
3	**8c**	Et	Et	Me	Me	65
4	**8d**	Et	Et	Et	Et	48
5	**8e**	$(CH_2)_5$		H	^{i}Pr	55[d]
6	**8f**	$(CH_2)_5$		H	^{t}Bu	75[d]
7	**8g**	$(CH_2)_5$		H	Ph	75[d]
8	**8h**	$(CH_2)_5$		Me	Me	46
9	**8i**	$(CH_2)_5$		Et	Et	38
10	**8j**	$(CH_2)_5$		$(CH_2)_5$		52

[a] All compounds **5** were >94% pure (GLC and/or 300 MHz ^{1}H NMR).

[b] Isolated yield after column chromatography (silica gel, hexane/ethyl acetate), based on the starting dithioacetal **7**.

[c] A ca. 1:1:1 diastereomeric mixture (75 MHz ^{13}C NMR) was obtained.

[d] Isolated as a ca. 1:1 diastereomeric mixture and separated by column chromatography.

TMEDA in THF at −78°C, and a carbonyl compound {E_1= ^{t}BuCHO, PhCHO, $[Me(CH_2)_4]_2CO$, $(CH_2)_5CO$, $(CH_2)_7CO$}, was followed by treatment with an excess of lithium powder and a catalytic amount of 4,4′-di-*tert*-butylbiphenyl (DTBB; 5 mol%) at the same temperature, and finally reaction with a second carbonyl compound [E_2=^{t}BuCHO, Me_2CO, $(CH_2)_5CO$] giving, after hydrolysis with water, the expected cyclopropane 1,3-diols derivatives **5** (Scheme 3 and Table 3).

Organolithium compounds **III**, **IV** and **V** (Chart 1) act probably as intermediates in the whole process (**4**→**5**). Yields are in general modest and cyclopropyl alcohols **6** (Chart 1) being found in a significant amount in all these cases (Table 3). A possible explanation for these results could be that β-functionalised tertiary organolithium compounds **V** is an extremely reactive species and takes a proton from the reaction medium before reacting with the corresponding second electrophile (E_2). Finally, in the case of using prostereogenic carbonyl compounds as electrophiles such as ^{t}BuCHO, an almost mixture around 3/1 of *anti*/*syn* diastereomeric diols was obtained (Table 3, entry 1).

2.3. Lithiation of bis(phenylthio)methane (7): a methane polyanion synthon[15]

Deprotonation of the dithioacetal **7** with *n*-butyllithium[6] in THF at 0°C followed by reaction with a carbonyl compound [E_1=^{t}BuCHO, Me_2CO, Et_2CO, $(CH_2)_5CO$] at −40°C gave an alcoholate of type **VII**, which was further lithiated with an excess of lithium and a catalytic amount of 4,4′-di-*tert*-butylbiphenyl (DTBB; 5 mol%) at −78°C to give β-oxido-functionalised organolithium compound **VIII**. The reaction of this intermediate with a second carbonyl compound [E_2=^{i}PrCHO, ^{t}BuCHO, Me_2CO, Et_2CO, $(CH_2)_5CO$] at −78°C gave the corresponding dialcoholate **IX** which, after hydrolysis, yielded the expected dihydroxy thioethers **8** (Scheme 4, Table 4). Intermediates **IX** were lithiated in the same way as for alcoholates **VII**, giving in this case trilithio derivatives of type **X**, which were unstable under these reaction conditions (−78 to 20°C) yielding a mixture of allylic alcohols **9**+**9**′ (Scheme 4, Charts 2 and 3 and Table 5). All attempts to react intermediates **X** with a third electrophile (D_2O or a carbonyl compound) at −78°C failed: in all cases, only lithium–hydrogen exchange was observed giving the corresponding 1,3-diols as the only reaction products. This behaviour indicated that the non-stabilised double β-oxidofunctionalised secondary organolithium intermediates **X** are unstable at −78°C taking a proton

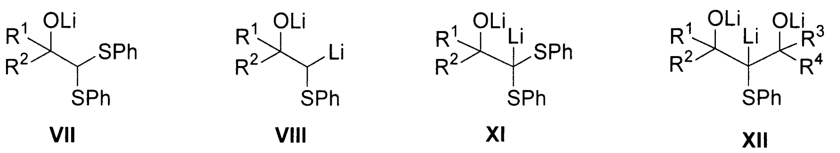


Chart 2.

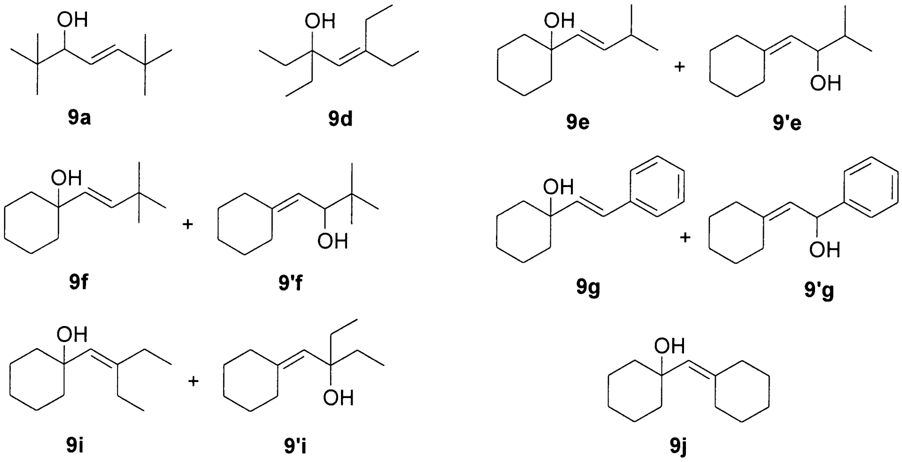


Chart 3.

from the reaction mixture. Due to the mentioned instability of intermediates **X**, we took advantage of the β-elimination process[16] at temperatures ranging from −78 to 20°C in order to achieve the corresponding allylic alcohols **9**.

All attempts of preparing intermediates **XI** and **XII** by deprotonation of **VII** and **IX** with *n*-butyllithium (Chart 2), respectively, failed, so it was not possible to prepare a tetralithiomethane synthon using this methodology.

We found of interest the preparation of 1,3-dienes **10** from either pure allylic alcohols **9j** (Table 5, entry 7) or mixtures **9**+**9′** (Table 5, entries 3–6) in almost quantitative yields when they were treated with a few drops of 6 M hydrochloric acid in chloroform at 20°C (Chart 4 and Table 5). A mixture of regioisomers was only obtained in the case of dienes **10**+**10′**. In the other cases, only one 1,3-diene **10** was obtained, probably the most thermodinamically stable one, even when more than one was possible to be formed.

Table 5. Preparation of allylic alcohols **9** and dienes **10**

	Allyl alcohol[a]		Diene[a]	
Entry	No.	Yield (%)[b,c]	No.	Yield (%)[c,d]
1	**9a**	42	–	–
2	**9d**	32	–	–
3	**9e**+**9′e**	62 (0.4:1)	**10e**	>95
4	**9f**+**9′f**	56 (1:1)	**10f**	>95
5	**9g**+**9′g**	29 (0.4:1)	**10g**	>95
6	**9i**+**9′I**	40 (1:1)	**10i**+**10′I**	>95 (1:0.3)
7	**9j**	73	**10j**	>95

[a] All compounds **9** and **10** were >95% pure (GLC and/or 300 MHz ^{1}H NMR).
[b] Isolated yield after column chromatography (silica gel, hexane/ethyl acetate), based on the starting dithioacetal **7**.
[c] In parenthesis the corresponding regioisomers ratio from 75 MHz ^{13}C NMR.
[d] Crude.

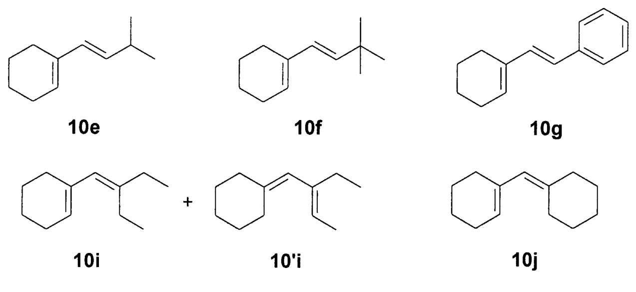


Chart 4.

3. Conclusions

We have described here a simple way to generate a 1,1-dilithioethylene synthon and a 1,1-dilithiocyclopropane synthon starting from phenyl vinyl thioether (**1**) and cyclopropyl phenyl thioether (**4**), respectively, taking advantage of two well established reactions: (a) α-deprotonation of a thioether and (b) sulfur–lithium exchange. Following this procedure it is possible to introduce two different electrophilic fragments at the same position of ethylene in the first case and cyclopropane in the second case. When carbonyl compounds were used as electrophiles, 1,3-diols (**3** and **5**, respectively) were obtained. Finally, it is possible to prepare 1,3-dihydroxythioethers **8**, allylic alcohols **9**+**9′** and 1,3-dienes **10**, starting from bis(phenylthio)methane (**7**) and using the same combination of α-deprotonation and sulfur–lithium exchange. In general, yields corresponding to the double lithiation and S_E reactions are modest: β-functionalised intermediates **II**, **V** and **X** bearing a substituted carbanionic centre are very unstable and have a tendency to decompose, even at low temperatures, by abstracting a proton from the reaction medium.[16]

4. Experimental

4.1. General

For general information see Ref. 5(b).

4.2. Lithiation of phenyl vinyl thioether (1) and reaction with electrophiles

Isolation of compounds **2**. *General procedure*. To a 1.6 M solution of *n*-butyllithium in hexane (0.75 ml, 1.2 mmol) and TMEDA (0.15 ml, 1.0 mmol) in THF (3 ml) at −78°C was added phenyl vinyl thioether (**1**; 0.12 ml, 1.0 mmol) allowing the temperature to rise to 20°C during ca. 30 min. After that a carbonyl compound (1.2 mmol) was added to the resulting mixture at −78°C and after 5 min it was hydrolysed with water (10 ml) and extracted with ethyl acetate (3×25 ml). The organic layer was dried with anhydrous Na_2SO_4 and evaporated (15 Torr) to yield a residue which was purified by column chromatography (silica gel, hexane/ethyl acetate) to give the title pure compounds **2**. Yields are included in Table 1. Physical, spectroscopic and analytical data follow.

4.2.1. 1-Phenyl-2-phenylsulfanyl-2-propen-1-ol (2a). Colourless oil; R_f 0.33 (hexane/ethyl acetate: 5/1); ν (film) 3737–3069 cm^{-1} (OH); δ_H 2.46 (1H, d, *J*=4.0 Hz, OH), 5.14 (1H, s, C*H*H=C), 5.24 (1H, d, *J*=4.0 Hz, C*H*OH), 5.60 (1H, s, CH*H*=C), 7.28–7.39 (10H, m, ArH); δ_C 76.1 (CHOH), 115.1 (*C*H$_2$=C), 125.9, 126.7, 127.9, 128.4, 129.2, 132.7, 132.9, 141.0 (ArC), 148.05 (CH$_2$=*C*); *m/z* 242 (M^+, 37%), 137 (10), 136 (47), 135 (100), 134 (10), 115 (19), 110 (12), 107 (31), 105 (24), 91 (71), 79 (63), 78 (15), 77 (76), 65 (19), 59 (10), 58 (11), 55 (17), 51 (49), 50 (15); HRMS: M^+, found 242.0761. $C_{15}H_{14}OS$ requires 242.0765.

4.2.2. 1-(1-Phenylsulfanylvinyl)cyclopentanol (2b). Colourless oil; R_f 0.31 (hexane/ethyl acetate: 5/1); ν (film) 3737–3131 cm^{-1} (OH); δ_H 1.72–2.07 (9H, m, 4CH$_2$, OH), 4.80 (1H, s, C*H*H=C), 5.54 (1H, s, CH*H*=C), 7.25–7.36 (3H, m, ArH), 7.46–7.49 (2H, m, ArH); δ_C 23.6 [CH$_2$(*C*H$_2$)$_2$CH$_2$], 36.6 [*C*H$_2$(CH$_2$)$_2$*C*H$_2$], 84.6 (COH), 111.55 (*C*H$_2$=C), 127.9, 129.2, 133.3, 133.7 (ArC), 152.25 (CH$_2$=*C*); *m/z* 220 (M^+, 40%), 137 (12), 136 (57), 135 (100), 111 (54), 110 (79), 109 (18), 93 (12), 92 (10), 91 (88), 85 (28), 83 (12), 81 (15), 78 (10), 77 (40), 69 (13), 67 (45), 66 (18), 65 (34), 59 (20), 58 (15), 57 (17), 55 (51), 53 (16), 51 (32), 45 (20), 43 (45), 42 (10), 41 (75); HRMS: M^+, found 220.0918. $C_{13}H_{16}OS$ requires 220.0922.

4.2.3. 1-(1-Phenylsulfanylvinyl)cyclohexanol (2c). Colourless oil; R_f 0.45 (hexane/ethyl acetate: 3/1); ν (film) 3697–3086 cm^{-1} (OH); δ_H 1.18–1.85 (11H, m, 5CH$_2$, OH), 4.79 (1H, s, C*H*H=C), 5.50 (1H, s, CH*H*=C), 7.25–7.36 (3H, m, ArH), 7.44–7.48 (2H, m, ArH); δ_C 21.9, 22.25, 25.4, 36.8, 37.4 (5CH$_2$), 74.6 (COH), 111.55 (*C*H$_2$=C), 127.8, 129.2, 133.35, 134.0 (ArC), 155.0 (CH$_2$=*C*); *m/z* 234 (M^+, 37%), 137 (15), 136 (71), 135 (100), 110 (17), 109 (12), 99 (21), 91 (44), 81 (469, 79 (14), 77 (17), 65 (15), 59 (11), 55 (36), 53 (12), 51 (17), 45 (100), 43 (31), 41 (41); HRMS: M^+, found 234.1074. $C_{14}H_{18}OS$ requires 234.1078.

Isolation of compounds **3** *from hydroxy thioethers* **2**. *General procedure*. To a solution of hydroxy thioether **2** (1.0 mmol) in THF (5 ml) was added dropwise a 1.6 M solution of *n*-butyllithium in hexane (0.75 ml, 1.2 mmol) at 0°C, after 15 min at this temperature, the mixture was added to a dark green suspension of lithium powder (100 mg, 14.0 mmol) and a catalytic amount of DTBB (30 mg, 0.11 mmol) in THF (5 ml) at −78°C. The resulting mixture was stirred for 1 h and a carbonyl compound (1.2 mmol) was added. The mixture was stirred for 10 min, was hydrolysed with water (10 ml) and extracted with ethyl acetate (3×25 ml). The organic layer was dried with anhydrous Na_2SO_4 and evaporated (15 Torr) to yield a residue which was purified by column chromatography (silica gel, hexane/ethyl acetate) to give the title pure compounds **3**. Yields are included in Table 1. Physical, spectroscopic and analytical data follow.

4.2.4. 2-Methylene-1,3-diphenyl-1,3-propanediol (3aa). Major isomer: Colourless oil; R_f 0.11 (hexane/ethyl acetate: 3/1); ν (film) 3677–3112 cm^{-1} (OH); δ_H 2.65 (2H, br s, 2OH), 5.14, 5.19 (4H, 2s, 2CH, C*H*$_2$=C), 7.20–7.36 (10H, m, ArH); δ_C 75.4 (2CHOH), 114.5 (*C*H$_2$=C), 126.6, 128.1, 128.4, 141.7 (ArC), 151.6 (CH$_2$=*C*); *m/z* 222 (M^+-H_2O, 2%), 179 (14), 79 (11), 77 (12), 71 (100), 44 (15), 43 (46), 41 (15); HRMS: M^+-H_2O, found 222.1044. $C_{16}H_{14}O$ requires 222.1045. Minor isomer: White solid, mp 66–67°C (pentane/dichloromethane); (Found: C, 79.82; H, 6.81. $C_{16}H_{16}O_2$ requires C, 79.97; H, 6.71); R_f 0.18 (hexane/ethyl acetate: 3/1); ν (KBr) 3597–3110 cm^{-1} (OH); δ_H 2.84 (2H, br s, 2OH), 5.09, 5.25 (4H, 2s, 2C*H*, C*H*$_2$=C), 7.18–7.34 (10H, m, ArH); δ_C 75.0 (2CHOH), 114.2 (*C*H$_2$=C), 126.6, 127.7, 128.35, 141.65 (ArC), 152.7 (CH$_2$=*C*); *m/z* 222 (M^+-H_2O, 41%), 221 (41), 161 (10), 131 (21), 117 (14), 116 (51), 115 (61), 107 (33), 105 (79), 91 (17), 79 (71), 78 (20), 77 (100), 55 (36), 53 (10), 51 (40), 50 (12), 44 (23), 43 (14).

4.2.5. 2-(1-Hydroxycyclopentyl)-4,4-dimethyl-1-penten-3-ol (3ba). White solid, mp 78–79°C (pentane/dichloromethane) (found: C, 72.60; H, 11.23. $C_{12}H_{22}O_2$ requires C, 72.68; H, 11.18); R_f 0.23 (hexane/ethyl acetate: 3/1); ν (KBr) 3598–3097 cm^{-1} (OH); δ_H 1.00 (9H, s, (CH$_3$)$_3$C), 1.69–1.89 [8H, m, (CH$_2$)$_4$], 2.25 (2H, br s, 2OH), 4.04 (1H, s, C*H*OH), 5.19 (1H, s, C*H*H=C), 5.27 (1H, s, CH*H*=C); δ_C 23.25 (CH$_2$), 23.3 (CH$_2$), 26.95 [(*C*H$_3$)$_3$C], 35.8 [(CH$_3$)$_3$*C*], 40.0 (CH$_2$), 41.0 (CH$_2$), 79.3 (CHOH), 85.0 (COH), 111.85 (*C*H$_2$=C), 155.0 (CH$_2$=*C*); *m/z* 180 (M^+-H_2O, 2%), 141 (20), 124 (38), 123 (22), 109 (17), 105 (12), 95 (44), 93 (12), 91 (14), 85 (11), 81 (16), 79 (18), 77 (12), 67 (39), 66 (24), 57 (90), 55 (32), 53 (12), 44 (15), 43 (57), 41 (100).

4.2.6. 2-(1-Hydroxycyclopentyl)-1-phenyl-2-propen-1-ol (3bb). White solid, mp 80–81°C (pentane/dichloromethane) (found: C, 76.99; H, 8.33. $C_{14}H_{18}O_2$ requires C, 77.03; H, 8.31); R_f 0.21 (hexane/ethyl acetate: 3/1); ν (KBr) 3611–3112 cm^{-1} (OH); δ_H 1.64–1.84 (8H, m, 4 CH$_2$), 2.48 (1H, br s, OH), 3.43 (1H, br s, OH), 4.88, 5.21, 5.47 (3H, 3s, C*H*OH, C*H*$_2$=C), 7.06–7.39 (5H, m, ArH); δ_C 22.9 (CH$_2$), 23.1 (CH$_2$), 40.0 (2CH$_2$), 75.7 (COH), 84.75 (CHOH), 112.5 (*C*H$_2$=C), 126.7, 127.35, 128.0, 128.2, 142.7 (ArC), 154.4 (CH$_2$=*C*); *m/z* 218 (M^+, 84%), 200 (19), 199 (35), 185 (15), 171 (10), 154 (19), 141 (10), 129 (21), 128 (11), 117 (11), 116 (14), 115 (29), 110 (10), 109 (100), 107 (16), 105 (25), 104 (13), 91 (19), 82 (11), 81 (14), 80 (10), 79 (61), 78 (12), 77 (66), 69 (19), 67 (15), 66 (11), 65 (61), 57 (13), 55 (37), 53 (11), 52 (12), 51 (32), 50 (14), 45 (11), 44 (37), 43 (29), 42 (14), 41 (45).

4.2.7. 1-[1-(1-Hydroxycyclopentyl)vinyl]cyclohexanol (3bc). White solid, mp 75–76°C (pentane/dichloromethane); (found: C, 74.18; H, 10.61. $C_{13}H_{22}O_2$ requires C, 74.24; H, 10.54); R_f 0.50 (hexane/ethyl acetate: 3/1); ν (KBr) 3619–3025 cm^{-1} (OH); δ_H 1.54–1.69, 1.83–1.92 (12 and 6H, respectively, 2m, 9CH$_2$), 3.14 (2H, br s, 2OH), 4.89 (1H, s, C*H*H=C), 5.04 (1H, s; CH*H*=C); δ_C 21.9, 23.3, 25.4, 39.9, 40.8 (9CH$_2$), 76.3 (COH), 107.9 (*C*H$_2$=C), 159.5 (CH$_2$=*C*); *m/z* 192 (M$^+$−H$_2$O, 26%), 163 (31), 150 (14), 149 (60), 145 (14), 136 (13), 135 (31), 131 (26), 121 (15), 117 (11), 108 (14), 107 (21), 105 (12), 99 (11), 95 (19), 94 (16), 93 (32), 91 (33), 83 (14), 81 (33), 80 (12), 79 (62), 77 (25), 69 (13), 67 (43), 65 (14), 57 (13), 55 (78), 53 (20), 43 (61), 42 (23), 41 (100).

4.2.8. 1-[1-(1-Hydroxy-1-methylethyl)vinyl]cyclohexanol (3ca). Colourless oil; R_f 0.31 (hexane/ethyl acetate: 3/1); ν (film) 3730–3036 cm^{-1} (OH); δ_H 1.47 [6H, s, (CH$_3$)$_2$], 1.53–1.68 (8H, m, 3CH$_2$, 2C*H*H), 1.92–1.96 (2H, m, 2CH*H*), 3.33, 3.38 (2H, br s, 2OH), 4.90 (1H, s, C=C*H*H), 4.96 (1H, s, C=CH*H*); δ_C 21.8 (CH$_2$), 25.5 (CH$_2$), 32.4 (CH$_3$), 39.15 (CH$_2$), 75.6 (COH), 76.4 (COH), 108.4 (*C*=CH$_2$), 160.85 (C=*C*H$_2$); *m/z* 184 (M$^+$, 0.5%), 166 (18), 151 (24), 123 (28), 110 (44), 109 (46), 99 (10), 95 (24), 93 (13), 91 (11), 82 (16), 81 (29), 79 (16), 69 (17), 68 (18), 67 (40), 59 (15), 54 (50), 53 (13), 43 (100), 42 (22), 41 (60); HRMS: M$^+$, found 184.1466. $C_{11}H_{20}O_2$ requires 184.1463.

4.2.9. 2-(1-Hydroxycyclohexyl)propenoic acid (3cd). White solid, mp 81–82°C (pentane/dichloromethane); (found: C, 63.39; H, 8.40. $C_9H_{14}O_3$ requires C, 63.51; H, 8.29); R_f 0.19 (hexane/ethyl acetate: 1/1); ν (KBr) 3700–2205 cm^{-1} (OH, COOH); δ_H 1.25–1.91 [11H, m, (CH$_2$)$_5$, COH], 5.85 (1H, s, C*H*H=C), 6.35 (1H, s, CH*H*=C), 9.50 (1H, br s, COOH); δ_C 21.55, 25.5, 35.95 [(CH$_2$)$_5$], 72.25 (COH), 125.9 (*C*H$_2$=C), 145.35 (CH$_2$=*C*), 171.8 (COOH); *m/z* 152 (M$^+$−H$_2$O, 26%), 127 (21), 124 (20), 110 (21), 109 (73), 107 (16), 99 (11), 97 (15), 96 (44), 95 (11), 91 (16), 83 (12), 82 (13), 81 (36), 79 (28), 77 (22), 70 (10), 69 (18), 68 (30), 67 (24), 57 (12), 55 (100), 54 (40), 53 (32), 51 (15), 45 (13), 44 (31), 43 (45), 42 (29), 41 (76).

Isolation of compounds ***3*** *in a one-pot process. General procedure*. To a 1.6 M solution of *n*-butyllithium in hexane (0.75 ml, 1.2 mmol) and TMEDA (0.15 ml, 1.0 mmol) in THF (3 ml) at −78°C was added phenyl vinyl thioether (**1**; 0.12 ml, 1.0 mmol) allowing the temperature to rise to 20°C during ca. 30 min. After that a carbonyl compound (1.2 mmol) was added to the resulting mixture at −78°C and after 5 min stirring at the same temperature, the mixture was added to a dark green suspension of lithium powder (100 mg, 14.0 mmol) and a catalytic amount of DTBB (30 mg, 0.11 mmol) in THF (5 ml) at −78°C. The resulting mixture was stirred for 1 h and then the second electrophile (1.2 mmol, CO$_2$ was bubbled for 30 min) was added. The mixture was stirred for 10 min, was hydrolysed with water (10 ml) and extracted with ethyl acetate (3×25 ml). The organic layer was dried with anhydrous Na$_2$SO$_4$ and evaporated (15 Torr) to yield a residue which was purified by column chromatography (silica gel, hexane/ethyl acetate) to give the title pure compounds **3**. Yields are included in Table 2. Physical, spectroscopic and analytical data follow:

4.2.10. 3-(Hydroxyphenylmethyl)-2-methyl-3-buten-1-ol (3ab). Colourless oil; R_f 0.27 (hexane/ethyl acetate: 2/1); ν (film) 3400–3050 cm^{-1} (OH); δ_H 1.37, 1.43 (6H, 2s, (C*H*$_3$)$_2$COH), 2.92 (2H, br s, 2OH), 4.84, 5.16, 5.51 (3H, 3s, C*H*OH, C*H*$_2$=C), 7.25–7.40 (5H, m, ArH); δ_C 30.8, 30.85 [(CH$_3$)$_2$COH], 74.1 (COH), 74.8 (CHOH), 112.5 (*C*H$_2$=C), 125.6, 126.7, 127.35, 128.2, 142.7 (ArC), 156.4 (*C*=CH$_2$); *m/z* 174 (M$^+$−H$_2$O, 3.5%), 107 (11), 105 (15), 85 (20), 79 (11), 77 (18), 71 (33), 69 (14), 57 (68), 56 (13), 55 (27), 51 (12), 44 (44), 43 (100), 42 (12); HRMS: M$^+$−H$_2$O, found 174.1044. $C_{12}H_{14}O$ requires 174.1045.

4.2.11. 2-(1-Hydroxycyclohexyl)-1-phenyl-2-propen-1-ol (3ac). Colourless oil; R_f 0.45 (hexane/ethyl acetate: 2/1); ν (film) 3365–3060 cm^{-1} (OH); δ_H 1.17–2.14 [10H, m, COH(C*H*$_2$)$_5$], 2.33, 3.57 (2H, 2 br s, 2OH), 4.89, 5.18, 5.49 (3H, 3s, C*H*OH, C*H*$_2$=CH), 7.22–7.39 (5H, m, ArH); δ_C 21.8 (COHCH$_2$CH$_2$*C*H$_2$CH$_2$CH$_2$), 25.4 [COH(CH$_2$)$_2$*C*H$_2$], 37.95 [COH*C*H$_2$(CH$_2$)$_3$*C*H$_2$], 74.75, 74.85 (COH, CHOH), 113.05 (*C*H$_2$=C), 126.6, 127.2, 128.1, 128.3, 128.4, 142.9 (ArC), 156.7 (*C*=CH$_2$); *m/z* 214 (M$^+$−H$_2$O, 61%), 213 (42), 196 (38), 185 (16), 183 (13), 181 (18), 171 (20), 168 (13), 167 (23), 165 (13), 158 (35), 157 (10), 155 (12), 153 (14), 145 (12), 143 (24), 141 (25), 131 (11), 130 (21), 129 (37), 128 (19), 118 (13), 117 (30), 116 (64), 115 (64), 108 (19), 107 (33), 105 (64), 104 (18), 95 (15), 93 (30), 91 (44), 89 (11), 83 (12), 81 (49), 80 (17), 79 (100), 78 (21), 77 (92), 69 (16), 67 (21), 65 (18), 63 (11), 57 (10), 55 (75), 53 (24), 52 (13), 51 (35), 44 (47), 43 (51), 42 (25); HRMS: M$^+$−H$_2$O, found 214.1359. $C_{15}H_{18}O$ requires 214.1358.

4.2.12. 1-[1-(1-Hydroxycyclohexyl)vinyl]cyclohexanol (3cb). White solid, mp 109–110°C (pentane/dichloromethane) (found: C, 74.86; H, 10.88. $C_{14}H_{24}O_2$ requires C, 74.94; H, 10.79); R_f 0.38 (hexane/ethyl acetate: 5/1); ν (KBr) 3664–3026 cm^{-1} (OH); δ_H 1.11–1.31, 1.51–1.69, 1.91–1.95 (6, 8 and 6H, respectively, 3m, 10CH$_2$), 3.44 (2H, br s, 2OH), 4.95 (2H, s, C*H*$_2$=C); δ_C 21.8, 25.5, 39.2 (10CH$_2$), 76.4 (COH), 108.6 (*C*H$_2$=C), 161.4 (CH$_2$=*C*); *m/z* 206 (M$^+$−H$_2$O, 33%), 163 (51), 150 (26), 149 (100), 145 (18), 135 (10), 131 (13), 122 (11), 121 (15), 108 (13), 107 (20), 95 (100), 93 (27), 91 (22), 83 (12), 81 (36), 80 (11), 79 (44), 77 (16), 69 (16), 67 (27), 55 (67), 53 (19), 43 (51), 42 (21), 41 (86), 40 (10).

4.2.13. 2,2,6-Trimethyl-4-methylene-3,5-heptanediol (3da). Colourless oil; R_f 0.27 (hexane/ethyl acetate: 2/1); ν (film) 3711–3046 cm^{-1} (OH); δ_H 1.00 [9H, s, (C*H*$_3$)$_3$C], 1.42 (3H, s, C*H*$_3$COH), 1.43 (1H, s, C*H*$_3$COH), 2.40, 2.53 (2H, 2 br s, 2OH), 4.11 (1H, s, C*H*OH), 5.13, 5.19 (2H, 2s, CH$_2$=C); δ_C 27.0 [(*C*H$_3$)$_3$C], 30.7, 31.6 [(*C*H$_3$)$_2$COH], 35.85 [(CH$_3$)$_3$*C*], 74.0 (COH), 79.3 (CHOH), 111.6 (*C*H$_2$=C), 156.6 (CH$_2$=*C*); *m/z* 172 (M$^+$, 19%), 171 (100), 157 (15), 155 (14), 127 (11), 115 (10), 113 (55), 98 (17), 83 (18), 77 (18), 75 (65), 59 (31), 57 (40), 55 (14), 47 (12), 45 (19), 43 (44), 41 (53), 40 (22); HRMS: M$^+$, found 172.1462. $C_{10}H_{20}O_2$ requires 172.1463.

4.2.14. 2-(1-Hydroxycyclohexyl)-4,4-dimethyl-2-penten-3-ol (3db). Colourless oil; R_f 0.45 (hexane/ethyl acetate: 3/1); ν (film) 3696–3049 cm^{-1} (OH); δ_H 0.99 [9H, s, C(CH$_3$)$_3$], 1.55–1.77 [10H, m, COH(C*H*$_2$)$_5$], 2.17 (2H, br s, 2OH), 4.10 (1H, s, C*H*OH), 5.17, 5.19 (2H, 2s, CH$_2$=C); δ_C 21.75, 21.8 (COHCH$_2$CH$_2$CH$_2$CH$_2$*C*H$_2$), 25.4 [COH(CH$_2$)$_2$-*C*H$_2$], 27.05 [(*C*H$_3$)$_3$C], 35.8, 37.55 [COH*C*H$_2$(CH$_2$)$_3$*C*H$_2$], 38.3 [(CH$_3$)$_3$*C*], 74.6 (COH), 79.05 (CHOH), 111.85 (*C*H$_2$=C), 157.4 (CH$_2$=*C*); *m/z* 212 (M$^+$, 0.51%), 155 (17), 138 (38), 137 (24), 123 (12), 119 (13), 113 (15), 110 (11), 109 (28), 99 (24), 98 (34), 97 (14), 96 (13), 95 (34), 91

(20), 85 (17), 83 (17), 81 (38), 80 (15), 79 (29), 71 (27), 70 (20), 69 (24), 67 (32), 58 (11), 57 (100), 56 (15), 55 (70), 53 (15), 43 (90), 42 (28); HRMS: M^+, found 212.1775. $C_{13}H_{24}O_2$ requires 212.1776.

4.3. Lithiation of cyclopropyl phenyl thioether (4) and reaction with carbonyl compounds

Isolation of compounds **5**. *General procedure.* To a 1.6 M solution of *n*-butyllithium in hexane (0.75 ml, 1.2 mmol) and TMEDA (0.15 ml, 1.0 mmol) in THF (3 ml) at −78°C was added cyclopropyl vinyl thioether (**4**; 0.13 ml, 1.0 mmol) allowing the temperature to rise to 20°C during ca. 30 min. After that a carbonyl compound (1.2 mmol) was added to the resulting mixture at −78°C and after 5 min stirring at the same temperature, the mixture was added to a dark green suspension of lithium powder (100 mg, 14.0 mmol) and a catalytic amount of DTBB (30 mg, 0.11 mmol) in THF (5 ml) at −78°C. The resulting mixture was stirred for 1 h at the same temperature and then the second carbonyl compound (1.2 mmol) was added. The mixture was stirred for 10 min, was hydrolysed with water (10 ml) and extracted with ethyl acetate (3×25 ml). The organic layer was dried with anhydrous Na_2SO_4 and evaporated (15 Torr) to yield a residue which was purified by column chromatography (silica gel, hexane/ethyl acetate) to give the title pure compounds **5**. Yields are included in Table 3. Physical, spectroscopic and analytical data follow.

4.3.1. (*R,*R**)-1-[1-(1-Hydroxy-2,2-dimethylpropyl)cyclopropyl]-2,2-dimethyl-1-propanol (*anti*-5a).** Colourless oil; R_f 0.39 (hexane/ethyl acetate: 5/1); ν (film) 3778–3040 cm^{-1} (OH); δ_H 0.61–0.66, 0.77–0.93 [2 and 2H, respectively, 2m, $C(CH_2)_2$], 0.98 [18H, s, $2C(CH_3)_3$], 1.39 (2H, br s, 2OH), 3.07 (2H, s, $2C\mathit{H}OH$); δ_c 8.4 [$(\mathit{C}H_2)_2C$], 26.8 [$2(\mathit{C}H_3)_3C$], 30.0 [$2(CH_3)_3\mathit{C}$], 36.2 [$(CH_2)_2\mathit{C}$], 81.5 (2CHOH); *m*/*z* 196 (M^+-H_2O, 0.1%), 181 (10), 139 (38), 121 (19), 97 (89), 95 (16), 93 (16), 83 (11), 71 (11), 69 (47), 67 (10), 57 (63), 55 (56), 53 (10), 43 (100), 41 (89); HRMS: M^+-H_2O, found 196.1833. $C_{13}H_{24}O$ requires 196.1827.

4.3.2. (*R,*S**)-1-[1-(1-Hydroxy-2,2-dimethylpropyl)cyclopropyl]-2,2-dimethyl-1-propanol (*syn*-5a).** Colourless oil; R_f 0.24 (hexane/ethyl acetate: 5/1); ν (film) 3708–3099 cm^{-1} (OH); δ_H 0.76–0.80, 0.91–0.96 [2 and 2H, respectively, 2m, $C(CH_2)_2$], 0.98 [18H, s, $2C(CH_3)_3$], 2.73 (2H, br s, $2CHO\mathit{H}$), 3.24 (2H, s, $2C\mathit{H}OH$); δ_c 11.9 [$(\mathit{C}H_2)_2C$], 26.0 [$(CH_2)_2\mathit{C}$], 27.4 [$2(\mathit{C}H_3)_3C$], 36.5 [$(CH_3)_3\mathit{C}$], 86.3 (2COH); *m*/*z* 196 (M^+-H_2O, 0.2%), 181 (10), 139 (40), 121 (18), 97 (81), 95 (21), 93 (15), 83 (10), 81 (10), 69 (56), 67 (11), 57 (64), 55 (64), 53 (11), 43 (100), 41 (94); HRMS: M^+-H_2O, found 196.1835. $C_{13}H_{24}O$ requires 196.1827.

4.3.3. 2-[1-(Hydroxyphenylmethyl)cyclopropyl]-2-propanol (5b). Colourless oil; R_f 0.43 (hexane/ethyl acetate: 5/1); ν (film) 3708–3090 cm^{-1} (OH); δ_H (−0.19)–(− 0.12), 0.24–0.32, 0.42–0.49, 0.61–0.69 [4H, 4m, $C(\mathit{CH}_2)_2$], 1.02, 1.49 [6H, 2s, $COH(CH_2)_3$], 3.51 (2H, br s, COH, $CHO\mathit{H}$), 5.40 (1H, s, $C\mathit{H}OH$), 7.19–7.35 (5H, m, ArH); δ_c 3.4, 8.6 [$(\mathit{C}H_2)_2C$], 26.7, 28.3 [$(\mathit{C}H_3)_2COH$], 31.55 [$(CH_2)_2\mathit{C}$], 74.2 (COH), 74.9 (CHOH), 127.2, 127.4, 127.6, 140.9 (ArC); *m*/*z* 188 (M^+-H_2O, 6%), 173 (18), 159 (18), 145 (11), 129 (20), 115 (14), 107 (43), 105 (24), 104 (14), 91 (13), 82 (51), 79 (35), 77 (41), 67 (54), 59 (27), 51 (19), 43 (100), 41 (29), 40 (10); HRMS: M^+-H_2O, found 188.1202. $C_{13}H_{16}O$ requires 188.1201.

4.3.4. 6-[1-(1-Hydroxy-1-methylethyl)cyclopropyl]-6-undecanol (5c). Colourless oil; R_f 0.32 (hexane/ethyl acetate: 5/1); ν (film) 3708–3088 cm^{-1} (OH); δ_H 0.52 [4H, s, $[(\mathit{CH}_2)_2C]$, 0.89 [6H, t, J=7.0 Hz, $2(CH_2)_4C\mathit{H}_3$], 1.23 [6H, s, $COH(C\mathit{H}_3)_2$], 1.25–1.59 [16H, m, 2 $COH(C\mathit{H}_2)_4$], 3.00 (2H, br s, 2COH); δ_c 7.95 [$(\mathit{C}H_2)_2C$], 14.1 ($2CH_2\mathit{C}H_3$), 22.65, 23.5, 32.4 [$2COHCH_2(\mathit{C}H_2)_3$], 29.9 [$(\mathit{C}H_3)_2COH$], 31.7 [$(CH_2)_2\mathit{C}$], 38.9 ($2COH\mathit{C}H_2$), 74.7 (2COH); *m*/*z* 234 (M^+-2H_2O, 0.4%), 181 (33), 99 (15), 82 (12), 81 (11), 71 (17), 69 (17), 67 (19), 59 (15), 57 (12), 55 (34), 43 (100), 41 (55); HRMS: M^+-2H_2O, found 234.2343. $C_{17}H_{30}$ requires 234.2347.

4.3.5. 1-[1-(1-Hydroxy-2,2-dimethylpropyl)cyclopropyl]-cyclohexanol (5d). Colourless oil; R_f 0.23 (hexane/ethyl acetate: 5/1); ν (film) 3740–3110 cm^{-1} (OH); δ_H 0.45–0.53, 0.65–0.75 (2 and 2H, respectively, 2m, CH_2CH_2C), 0.91 [9H, s, $(CH_3)_3C$], 1.04–1.27, 1.36–1.77 [6 and 4H, respectively, 2m, $COH(C\mathit{H}_2)_5$], 2.03 (2H, br s, COH, $CHO\mathit{H}$), 3.78 (1H, s, $C\mathit{H}OH$); δ_c 4.9 [$(\mathit{C}H_2)_2C$], 21.7, 21.8, 25.5, 34.6 [$COH(\mathit{C}H_2)_5$], 26.5 [$(\mathit{C}H_3)_3C$], 32.8 [$(CH_2)_2\mathit{C}$], 35.4 [$(CH_3)_3\mathit{C}$], 73.2 (COH), 76.3 (CHOH); *m*/*z* 190 (M^+-2H_2O,7%), 175 (11), 165 (14), 151 (53), 133 (30), 123 (11), 95 (20), 93 (18), 91 (47), 83 (17), 81 (46), 79 (37), 77 (19), 71 (10), 69 (21), 67 (57), 65 (10), 57 (55), 55 (55), 53 (19), 44 (34), 43 (56), 42 (15), 41 (100); HRMS: M^+-2H_2O, found 190.1716. $C_{14}H_{22}$ requires 190.1721.

4.3.6. 1-[1-(1-Hydroxycyclohexyl)cyclopropyl]cyclohexanol (5e). Colourless oil; R_f 0.31 (hexane/ethyl acetate: 5/1); ν (film) 3759–2998 cm^{-1} (OH); δ_H 0.94–1.11, 1.19–1.55, 1.77–1.82 [2, 2 and 20H, respectively, 3m, $2COH(C\mathit{H}_2)_5$, $(CH_2)_2C$], 3.61 (2H, br s, 2COH); δ_c 6.8 [$(\mathit{C}H_2)_2C$], 21.8, 25.6, 36.1 [$2COH(\mathit{C}H_2)_5$], 36.2 [$(CH_2)_2\mathit{C}$], 75.2 (2COH); *m*/*z* 220 (M^+-H_2O, 6%), 177 (21), 173 (17), 164 (57), 163 (12), 149 (27), 145 (12), 136 (12), 135 (17), 131 (15), 125 (13), 122 (24), 121 (11), 117 (10), 107 (31), 105 (11), 99 (29), 95 (12), 94 (12), 93 (34), 91 (31), 83 (10), 81 (66), 80 (23), 79 (54), 78 (11), 77 (23), 69 (16), 67 (41), 65 (13), 57 (11), 55 (71), 53 (21), 44 (10), 43 (51), 42 (16), 41 (100), 40 (19); HRMS: M^+-H_2O, found 220.1810. $C_{15}H_{24}O$ requires 220.1827.

4.3.7. 1-[1-(1-Hydroxy-1-methylethyl)cyclopropyl]cyclooctanol (5f). Colourless oil; R_f 0.08 (hexane/ethyl acetate: 5/1); ν (film) 3772–3072 cm^{-1} (OH); δ_H 0.47–0.51, 0.60–0.64 [2 and 2H, respectively, 2m, $2C(C\mathit{H}_2)_2$], 1.24 [6H, s, $COH(C\mathit{H}_3)_2$], 1.11–1.80 [14H, m, $(C\mathit{H}_2)_7$], 3.05 (2H, br s, 2COH); δ_c 7.5 [$(\mathit{C}H_2)_2C$], 22.15, 25.0, 28.3, 35.25 [$COH(\mathit{C}H_2)_7$], 30.6 [$(\mathit{C}H_3)_2COH$], 33.8 [$(CH_2)_2\mathit{C}$], 75.0 [$(CH_3)_2\mathit{C}OH$], 78.2 [$\mathit{C}OH(CH_2)_7$]; *m*/*z* 208 (M^+-H_2O, 0.3%), 135 (13), 122 (21), 121 (10), 119 (11), 109 (17), 107 (21), 105 (18), 95 (26), 94 (11), 93 (33), 91 (30), 82 (19), 81 (32), 80 (13), 79 (37), 77 (20), 69 (13), 68 (11), 67 (54), 65 (12), 59 (82), 55 (41), 53 (19), 44 (27), 43 (100), 41 (86), 40 (57); HRMS: M^+-H_2O, found 208.1831. $C_{14}H_{24}O$ requires 208.1827.

4.4. Lithiation of bis(phenylthio)methane (7) and reaction with carbonyl compounds

Isolation of compounds **8***. General procedure*. To a solution of bis(phenylthio)methane (**7**; 0.23 g, 1.0 mmol) in THF (2 ml) was added a 1.6 M solution of *n*-butyllithium in hexane (0.63 ml, 1.0 mmol) at 0°C. The reaction mixture was stirred for 15 min at 20°C. After that a carbonyl compound (1.0 mmol) was added to the resulting mixture at −40°C and after 5 min stirring at the same temperature, the mixture was added to a dark green suspension of lithium powder (100 mg, 14.0 mmol) and a catalytic amount of DTBB (30 mg, 0.11 mmol) in THF (5 ml) at −78°C. The resulting mixture was stirred for 1 h at the same temperature and then the second carbonyl compound (1.0 mmol) was added. The mixture was stirred for 10 min, was hydrolysed with water (10 ml) and extracted with ethyl acetate (3×25 ml). The organic layer was dried with anhydrous Na_2SO_4 and evaporated (15 Torr) to yield a residue which was purified by column chromatography (silica gel, hexane/ethyl acetate) to give the title pure compounds **8**. Yields are included in Table 4. Physical, spectroscopic and analytical data follow.

4.4.1. 2,2,6,6-Tetramethyl-4-phenylsulfanyl-3,5-heptanediol (8a). Diastereomeric mixture: Pale yellow solid, mp 120–125°C (pentane/dichloromethane) (found: C, 68.75; H, 9.60; S, 9.98. $C_{17}H_{28}O_2S$ requires C, 68.87; H, 9.52; S, 10.81); R_f 0.55 (hexane/ethyl acetate: 5/1); ν (KBr) 3689–3036 cm^{-1} (OH); δ_H 0.84, 0.97, 1.12 [18H, 3s, $(CH_3)_3C$], 2.93 (1H, d, *J*=4.3 Hz, CH), 3.23 (1H, d, *J*=3.7 Hz, CH), 3.35 (1H, d, *J*=4.9 Hz, CH), 3.36 (1H, d, *J*=4.3 Hz, CH), 3.60–3.72 (3H, m, SCH, 2OH), 4.05 (1H, d, *J*=3.7 Hz, SCH), 7.23–7.33 (3H, m, ArH), 7.41–7.45 (2H, m, ArH); δ_C 26.7, 27.2, 27.6 [$(\mathit{C}H_3)_3C$], 35.8, 36.0 [$(CH_3)_3\mathit{C}$], 49.8, 52.9 (CHS), 76.8, 83.2, 84.4 (CHOH), 127.1, 127.5, 129.0, 129.0, 132.4, 132.6 (ArC); *m*/*z* 278 (M^+-H_2O, 0.62%), 193 (14), 192 (92), 177 (74), 153 (20), 135 (10), 123 (22), 111 (19), 110 (22), 109 (13), 83 (58), 73 (13), 69 (21), 65 (11), 57 (84), 55 (24), 45 (36), 43 (47), 41 (100), 40 (11).

4.4.2. 2,4-Dimethyl-3-phenylsulfanyl-2,4-pentanediol (8b). White solid, mp 92–93°C (pentane/dichloromethane) (found: C, 64.81; H, 8.36; S, 12.84. $C_{13}H_{20}O_2S$ requires C, 64.96; H, 8.39; S, 13.34); R_f 0.31 (hexane/ethyl acetate: 2/1); ν (KBr) 3550–3040 cm^{-1} (OH); δ_H 1.43 (6H, s, $2CH_3$), 1.50 (6H, s, $2CH_3$), 3.27 (1H, s, CHS), 3.97 (2H, br s, 2OH), 7.16–7.29 (3H, m, ArH), 7.43–7.46 (2H, m, ArH); δ_C 27.2 (CH_3), 32.2 (CH_3), 68.45 (CHS), 76.75 (COH), 126.5, 129.1, 129.8, 138.0 (ArC); *m*/*z* 222 (M^+-H_2O, 0.5%), 164 (52), 149 (18), 110 (12), 91 (15), 65 (11), 59 (28), 58 (10), 56 (10), 55 (50), 53 (13), 51 (15), 45 (35), 44 (16), 43 (100), 41 (26).

4.4.3. 4-Ethyl-2-methyl-3-phenylsulfanyl-2,4-hexanediol (8c). White solid, mp 71–73°C (pentane/dichloromethane) (found: C, 67.01; H, 9.16; S, 11.26. $C_{15}H_{24}O_2S$ requires C, 67.12; H, 9.01; S, 11.94]; R_f 0.33 (hexane/ethyl acetate: 5/1); ν (KBr) 3567–3032 cm^{-1} (OH); δ_H 0.87, 0.92 [6H, 2t, *J*=7.4 Hz, $(C\mathit{H}_3CH_2)_2C$], 1.40, 1.50 (6H, 2s, $(CH_3)_2C$), 1.77, 1.92 [4H, 2q, *J*=7.4 Hz, $(CH_3C\mathit{H}_2)_2C$], 3.08, 3.68 (2H, 2 br s, 2OH), 3.46 (1H, s, CHS), 7.18–7.30 (3H, m, ArH), 7.43–7.47 (2H, m, ArH); δ_C 7.6, 8.1 [$(\mathit{C}H_3CH_2)_2C$], 28.05, 31.65 [$(CH_3)_2C$], 29.8, 30.65 [$(CH_3\mathit{C}H_2)CH$], 65.95 (CHS), 76.6, 79.1 (2COH), 126.4, 129.0, 129.9, 137.9 (ArC); *m*/*z* 232 (M^+-2H_2O, 3%), 192 (45), 164 (24), 163 (11), 149 (11), 135 (13), 123 (14), 110 (42), 109 (13), 91 (14), 83 (16), 81 (20), 79 (13), 69 (10), 67 (12), 65 (15), 59 (31), 57 (29), 55 (60), 53 ((15), 51 (12), 45 824), 44 (11), 43 (100), 41 (46).

4.4.4. 3,5-Diethyl-4-phenylsulfanyl-3,5-heptanediol (8d). White solid, mp 92–93°C (pentane/dichloromethane) (found: C, 68.91; H, 9.73; S, 9.70. $C_{17}H_{28}O_2S$ requires C, 68.88; H, 9.53; S, 10.79); R_f 0.35 (hexane/ethyl acetate: 5/1); ν (KBr) 3531–3023 cm^{-1} (OH); δ_H 0.87, 0.89 (12H, 2t, *J*=7.3 Hz, $4CH_3$), 1.68–2.02 (8H, m, $4CH_2$), 2.97 (2H, br s, 2OH), 3.66 (1H, s, CHS), 7.17–7.30 (3H, m, ArH), 7.46–7.51 (2H, m, ArH); δ_C 7.6, 8.35 ($4CH_3$), 30.3, 30.4 ($4CH_2$), 64.85 (CHS), 78.45 (COH), 126.6, 129.0, 130.35, 137.8 (ArC); *m*/*z* 278 (M^+-H_2O, 0.15%), 193 (16), 192 (100), 177 (10), 163 (19), 135 (18), 110 (27), 109 (10), 91 (12), 83 (20), 65 (11), 57 (44), 55 (59), 53 (11), 45 (20), 43 (18), 41 (44).

4.4.5. 1-[(2-Hydroxy-3-methyl-1-phenylsulfanyl)butyl]cyclohexanol (8e). First isomer: Pale yellow solid, mp 153–154°C (pentane/dichloromethane) (found: C, 69.28; H, 9.01; S, 10.29. $C_{17}H_{26}O_2S$ requires C, 69.34; H, 8.90; S, 10.89); R_f 0.30 (hexane/ethyl acetate: 5/1); ν (KBr) 3588–3074 cm^{-1} (OH); δ_H 0.69, 0.97 [6H, 2d, *J*=7.3 Hz, $(C\mathit{H}_3)_2CH$], 1.55–1.68 (8H, m, $4CH_2$), 1.85–1.89 (1H, m, C*H*HOH), 2.13–2.24 (1H, m, CH*H*OH), 2.45 [1H, hept. d, *J*=2.4, 6.7 Hz, $(CH_3)_2C\mathit{H}$], 3.13 (1H, d, *J*=9.8 Hz, CHSPh), 3.21 (1H, br s, OH), 3.62 (1H, br s, OH), 3.85 (1H, d, *J*=9.8 Hz, C*H*OH), 7.15–7.30 (3H, m, ArH), 7.40–7.48 (2H, m, ArH); δ_C 20.6, 21.45 ($2CH_2$), 21.5 [$(\mathit{C}H_3)_2CH$], 25.6, 32.1, 36.95 ($2CH_2$), 29.95 [$\mathit{C}H(CH_3)_2$], 61.1 (CHS), 76.35 (COH), 78.1 (CHOH), 126.45, 129.0, 130.2, 130.97, 137.05 (ArC); *m*/*z* 294 (M^+, 0.20%), 204 (11), 179 (13), 178 (100), 163 (27), 110 (42), 99 (14), 95 (10), 91 (12), 81 (24), 79 (12), 77 (11), 71 (12), 69 (77), 67 (11), 55 (40), 45 (20), 43 (55), 41 (54). Second isomer: White solid, mp 93–94°C (pentane/dichloromethane) (found: C, 69.30; H, 9.01; S, 10.41. $C_{17}H_{26}O_2S$ requires C, 69.34; H, 8.90; S, 10.89); R_f 0.29 (hexane/ethyl acetate: 5/1); ν (KBr) 3588–3074 cm^{-1} (OH); δ_H 0.67, 1.03 [6H, 2d, *J*=6.7 Hz, $(C\mathit{H}_3)_2CH$], 1.42–1.70 (8H, m, $4CH_2$), 1.85–1.87 (1H, m, C*H*HOH), 1.97–2.12 [2H, m, CH*H*COH, $C\mathit{H}(CH_3)_2$], 2.95 (2H, br s, 2OH), 3.34 (1H, s, C*H*SPh), 7.14–7.29 (3H, m, ArH), 7.39–7.48 (2H, m, ArH); δ_C 19.2, 19.25 [$(\mathit{C}H_3)_2CH$], 21.9, 22.05, 25.6, 35.5, 37.1 [$(CH_2)_5$], 32.0 [$\mathit{C}H(CH_3)_2$], 63.55 (CHS), 75.4 (COH), 77.1 (CHOH), 126.55, 129.0, 130.90, 130.95, 137.1 (ArC); *m*/*z* 276 (M^+-H_2O, 0.18%), 204 (12), 179 (13), 178 (100), 163 (27), 123 (14), 110 (43), 99 (11), 95 (13), 91 (12), 81 (21), 79 (12), 77 (12), 71 (14), 69 (76), 67 (13), 55 (40), 45 (20), 43 (53), 41 (55).

4.4.6. 1-[(2-Hydroxy-3,3-dimethyl-1-phenylsulfanyl)butyl]cyclohexanol (8f). First isomer: White solid, mp 117–118°C (pentane/dichloromethane) (found: C, 69.99; H, 9.24; S, 9.88. $C_{18}H_{28}O_2S$ requires C, 70.09; H, 9.15; S, 10.39); R_f 0.44 (hexane/ethyl acetate: 5/1); ν (KBr) 3530–3073 cm^{-1} (OH); δ_H 0.98 [9H, s, $(CH_3)_3C$], 1.49–1.80 [10H, m, $(CH_2)_5$], 3.25 (1H, d, *J*=7.3 Hz, CHS), 3.30 (1H, br s, OH), 3.43 (1H, d, *J*=4.5 Hz, CHO*H*), 3.88 (1H, dd, *J*=4.5 Hz, 7.3, C*H*OH), 7.11–7.48 (5H, m, ArH); δ_C 21.45, 21.65, 25.55, 33.3, 37.2 $[(CH_2)_5]$, 26.45 $[(CH_3)_3C]$, 36.75 $[(CH_3)_3C]$, 55.8 (CHS), 77.5 (COH), 84.0 (CHOH), 125.6, 128.0, 129.0, 137.6 (ArC); *m*/*z* 308 (M^+, 0.21%), 204 (10), 193 (14), 192 (100), 177 (73), 124 (18), 123 (20), 110 (16), 99 (19), 95 (11), 91 (12), 83 (52), 81 (28), 77 (10), 69 (11), 67 (11), 57 (49), 55 (40), 45 (22), 43 (37), 41 (67), 40 (12). Second isomer: White solid, mp 103–104°C (pentane/dichloromethane) (found: C, 69.92; H, 9.31; S, 9.59. $C_{18}H_{28}O_2S$ requires C, 70.09; H, 9.15; S, 10.39); R_f 0.39 (hexane/ethyl acetate: 5/1); ν (KBr) 3530–3073 cm^{-1} (OH); δ_H 0.87 [9H, s, $(CH_3)_3C$], 1.54–1.70 [10H, m, $(CH_2)_5$], 2.55 (1H, br s, OH), 2.68 (1H, d, *J*=9.8 Hz, CHS), 3.39 (1H, br s, OH), 3.68 (1H, d, *J*=9.8 Hz, C*H*OH), 7.09–7.34 (3H, m, ArH), 7.42–7.48 (2H, m, ArH); δ_C 21.45, 22.1, 25.55, 33.8, 34.9 $[(CH_2)_5]$, 26.5 $[(CH_3)_3C]$, 36.65 $[(CH_3)_3C]$, 64.6 (CHS), 74.3 (COH), 75.95 (CHOH), 126.2, 129.0, 129.5, 137.0 (ArC); *m*/*z* 308 (M^+, 0.16%), 204 (13), 193 (14), 192 (100), 177 (71), 123 (20), 110 (17), 109 (10), 99 (12), 95 (15), 91 (11), 83 (51), 81 (21), 79 (12), 77 (10), 71 (10), 69 (11), 67 (13), 57 (49), 55 (40), 45 (20), 43 (34), 41 (68), 40 (11).

4.4.7. 1-[(2-Hydroxy-2-phenyl-1-phenylsulfanyl)ethyl]-cyclohexanol (8g). First isomer: White solid, mp 180–182°C (pentane/dichloromethane) (found: C, 73.10; H, 7.46; S, 9.29. $C_{20}H_{24}O_2S$ requires C, 73.13; H, 7.36; S, 9.76); R_f 0.23 (hexane/ethyl acetate: 5/1); ν (KBr) 3668–3007 cm^{-1} (OH); δ_H 1.25–1.34, 1.56–2.04 [10H, 2m, $(CH_2)_5$], 3.25 (1H, d, *J*=9.5 Hz, CHS), 3.63, 3.72 (2H, 2 br s, 2OH), 5.02 (1H, d, *J*=9.5 Hz, CHOH), 6.75–6.79 (3H, m, ArH), 6.87–6.90 (3H, m, ArH), 6.98–7.07 (2H, m, ArH), 7.21–7.43 (2H, m, ArH); δ_C 21.5, 22.3, 25.6, 35.55, 37.0 $[(CH_2)_5]$, 66.1 (CHS), 72.15 (CHOH), 77.2 (COH), 126.3, 127.2, 128.0, 128.6, 128.6, 131.6, 131.7, 142.45 (ArC); *m*/*z* 292 (M^+-2H_2O, 14%), 212 (25), 211 (13), 207 (16), 183 (20), 179 (13), 178 (19), 167 (17), 165 (16), 152 (10), 142 (10), 141 (46), 129 (11), 128 (14), 121 (14), 117 (11), 115 (24), 110 (66), 109 (39), 105 (53), 104 (32), 103 (13), 91 (46), 89 (11), 84 (14), 82 (15), 81 (30), 80 (12), 79 (31), 78 (20), 77 (73), 71 (13), 69 (21), 67 (15), 66 (33), 65 (33), 63 (14), 57 (31), 56 (11), 55 (34), 53 (15), 52 (10), 51 (64), 50 (25), 45 (37), 44 (100), 43 (53), 42 (24), 41 (58). Second isomer: White solid, mp 122–123°C (pentane/dichloromethane) (found: C, 73.07; H, 7.41; S, 9.41. $C_{20}H_{24}O_2S$ requires C, 73.13; H, 7.36; S, 9.76); R_f 0.26 (hexane/ethyl acetate: 5/1); ν (KBr) 3668–3007 cm^{-1} (OH); δ_H 1.23–1.33, 1.55–1.85, 1.99–2.06 [2, 4 and 4H, respectively, 3m, $(CH_2)_5$], 2.56 (1H, br s, OH), 3.19 (1H, s, CHS), 3.72 (1H, br s, OH), 5.59 (1H, s, C*H*OH), 6.75–6.78, 6.97–7.04, 7.21–7.43 (2, 1 and 7H, respectively, 3m, ArH); δ_C 21.9, 22.3, 25.5, 35.5, 37.2 $[(CH_2)_5]$, 69.8 (CHS), 72.1 (CHOH), 76.2 (COH), 126.3, 126.6, 127.2, 127.95, 128.55, 128.6, 131.7, 136.7, 142.4 (ArC); *m*/*z* 328 (M^+, 1%), 327(16), 115 (12), 114 (100), 59 (16), 42 (60), 41 (12).

4.4.8. 1-[(2-Hydroxy-2-methyl-1-phenylsulfanyl)propyl]-cyclohexanol (8h). White solid, mp 113–114°C (pentane/dichloromethane) (found: C, 68.50; H, 8.76; S, 10.94. $C_{16}H_{24}O_2S$ requires C, 68.53; H, 8.63; S, 11.43); R_f 0.45 (hexane/ethyl acetate: 2/1); ν (KBr) 3557–3019 cm^{-1} (OH); δ_H 1.40, 1.51 [6H, 2s, $(CH_3)_2C$], 1.15–1.80 (8H, m, $4CH_2$), 2.01–2.15 (2H, m, CH_2), 3.20 (1H, s, CHS), 3.42 (1H, br s, OH), 3.98 (1H, br s, OH), 7.14–7.29 (3H, m, ArH), 7.42–7.45 (2H, m, ArH); δ_C 21.7, 25.2, 33.7, 37.7 (CH_2), 27.8, 32.2 $[(CH_3)_2C]$, 69.25 (CHS), 76.8, 77.8 (2COH), 126.25, 129.0, 129.5, 138.3 (ArC); *m*/*z* 262 (M^+-H_2O, 0.92%), 244 (10), 204 (62), 165 (11), 164 (100), 149 (16), 110 (42), 95 (50), 94 (22), 93 (18), 91 (37), 79 (31), 77 (25), 69 (13), 67 (25), 66 (15), 65 (21), 55 (59), 53 (19), 51 (20), 45 (28), 44 (17), 43 (43), 42 (17), 41 (55).

4.4.9. 1-[(2-Ethyl-2-hydroxy-1-phenylsulfanyl)butyl]-cyclohexanol (8i). Pale yellow oil; R_f 0.26 (hexane/ethyl acetate: 5/1); ν (film) 3744–3072 cm^{-1} (OH); δ_H 0.86, 0.94 (6H, 2t, *J*=7.3 Hz, $2CH_3$), 1.50–2.05 (14H, m, $7CH_2$), 3.30 (2H, br s, 2OH), 3.39 (1H, s, CHS), 7.14–7.29 (3H, m, ArH), 7.41–7.46 (2H, m, ArH); δ_C 7.35, 7.95 ($2CH_3$), 21.55, 25.1, 30.1, 30.9, 34.5, 37.2 ($7CH_2$), 66.6 (CH), 76.4, 78.8 (2COH), 126.0, 128.8, 129.35, 138.1 (ArC); *m*/*z* 290 (M^+-H_2O, 0.24%), 272 (10), 205 (15), 204 (100), 192 (53), 163 (14), 135 (14), 110 (62), 109 (21), 95 (47), 94 (19), 93 (15), 91 (30), 34 (10), 83 (13), 81 (12), 79 (27), 77 (25), 69 (16), 67 (26), 66 (21), 65 (24), 57 (33), 55 (73), 53 (18), 51 (19), 45 (32), 44 (31), 43 (36), 42 (25), 41 (88); HRMS: M^+-H_2O, found 290.1703. $C_{18}H_{26}OS$ requires 290.1704.

4.4.10. 1-[(1-Hydroxycyclohexylphenylsulfanyl)methyl]-cyclohexanol (8j). White solid, mp 155–156°C (pentane/dichloromethane) (found: C, 71.18; H, 8.86; S, 9.37. $C_{19}H_{28}O_2S$ requires C, 71.21; H, 8.81; S, 9.99); R_f 0.24 (hexane/ethyl acetate: 5/1); ν (KBr) 3718–3026 cm^{-1} (OH); δ_H 0.88–1.64, 1.77–1.88, 1.98–2.17 (14, 2, and 4H, respectively, 3m, $10CH_2$), 3.12 (1H, s, CH), 3.52 (2H, 2 br s, 2OH), 7.13–7.19 (1H, m, ArH), 7.23–7.29 (2H, m, ArH), 7.41–7.45 (2H, m, ArH); δ_C 21.7, 21.75, 25.3, 34.15, 38.0 $[(CH_2)_5]$, 69.6 (CHS), 78.1 (COH), 126.0, 129.0, 129.1, 138.7 (ArC); *m*/*z* 284 (M^+-2H_2O, 36%), 251 (17), 209 (11), 207 (55), 175 (30), 147 (11), 133 (15), 131 (20), 119 (11), 115 (12), 111 (10), 110 (100), 109 (32), 105 (20), 96 (14), 95 (24), 93 (34), 92 (12), 91 (56), 84 (21), 82 (12), 81 (36), 80 (13), 79 (80), 78 (19), 77 (47), 73 (15), 69 (24), 67 (43), 66 850), 65 (34), 58 (17), 57 (15), 55 (44), 54 (10), 53 (20), 52 (55), 51 (50), 50 (37), 45 (34), 44 (72), 43 (37), 42 (17), 41 (78).

Isolation of compounds ***9****. General procedure*. To a solution of bis(phenylthio)methane (**7**; 0.23 g, 1.0 mmol) in THF (2 ml) was added a 1.6 M solution of *n*-butyllithium in hexane (0.63 ml, 1.0 mmol) at 0°C. The reaction mixture was stirred for 15 min at 20°C. After that a carbonyl compound (1.0 mmol) was added to the resulting mixture at −40°C and after 5 min stirring at the same temperature, the mixture was added to a dark green suspension of lithium powder (100 mg, 14.0 mmol) and a catalytic amount of DTBB (30 mg, 0.11 mmol) in THF (5 ml) at −78°C. The resulting mixture was stirred for 1 h at the same temperature and then the second carbonyl compound (1.0 mmol) was added. The mixture was allowed to reach room temperature for about 2 h, was hydrolysed with water (10 ml) and extracted with ethyl acetate (3×25 ml). The organic layer was dried with anhydrous Na_2SO_4 and evaporated (15 Torr) to yield a residue which was purified by column chromatography (silica gel, hexane/ethyl acetate) to give the title pure compounds **9**. Yields are included in Table 5. Physical, spectroscopic and analytical data follow.

4.4.11. 2,2,6,6-Tetramethyl-4-hepten-3-ol (9a). Colourless oil; R_f 0.51 (hexane/ethyl acetate: 6/1); ν (film) 3695–3118 cm^{-1} (OH); δ_H 0.82 [9H, s, $(CH_3)_3CCHOH$], 0.95 [9H, s, $(CH_3)_3CCH{=}CH$], 3.61 (1H, d, J=6.7 Hz, CHOH), 5.34 (1H, dd, J=6.7, 16.5 Hz, CHOH–C*H*=CH), 5.56 (1H, d, J=16.5 Hz, CHOHCH=C*H*); δ_C 25.7, 29.6 [$(CH_3)_3CCHOH$, $(CH_3)_3CCH$], 32.9, 34.85 [$(CH_3)_3CCHOH$, $(CH_3)_3CCH$], 81.2 (CHOH), 124.4 (*C*H=CHCHOH), 144.5 (CH=*C*HCHOH); *m/z* 155 (M^+-CH_3, 0.11%), 113 (20), 95 (26), 57 (42), 43 (100), 41 (41); HRMS: M^+-CH_3, found 155.1433. $C_{10}H_{19}O$ requires 155.1436.

4.4.12. 3,5-Diethyl-4-hepten-3-ol (9d). Colourless liquid; R_f 0.60 (hexane); ν (film) 3696–3146 cm^{-1} (OH); δ_H 0.88 [6H, t, J=7.3 Hz, $(CH_3CH_2)_2C$], 1.00 [6H, t, J=7.3 Hz, $(CH_3CH_2)_2C$], 1.28 (1H, br s, OH), 1.58 [4H, q, J=7.3 Hz, $(CH_3CH_2)_2C$], 2.02 (2H, qd, J=1.2, 7.3 Hz, $CH_3CH_2C{=}CH$), 2.35 (2H, q, J=7.3 Hz, $CH_3CH_2C{=}CH$), 5.03 (1H, s, CH=C); δ_C 8.15 (CH_3), 13.35 (CH_3), 13.4 ($2CH_3$), 23.2, 29.75, 34.2 ($4CH_2$),76.2 (COH), 127.7 (*C*H=C), 145.75 (CH=*C*); *m/z* 152 (M^+-H_2O, 8%), 141 (89), 123 (16), 99 (35), 95 (13), 85 (91), 81 (54), 79 (13), 69 (18), 67 (23), 57 (100), 55 (47), 53 (17), 45 (13), 43 (77), 41 (81); HRMS: M^+-H_2O, found 152.1562. $C_{11}H_{20}$ requires 152.1565.

4.4.13. (*E*)-1-(3-Methyl-1-butenyl)cyclohexanol (9e) and 1-cyclohexylene-3-methyl-2-butanol (9′e). Colourless oil; R_f 0.41 (hexane/ethyl acetate: 5/1); ν (film) 3715–3098 cm^{-1} (OH); δ_H 0.86 [3H, d, J=6.7 Hz, CH_3 (**9e**)], 0.95 [3H, d, J=6.7 Hz, CH_3 (**9′e**)], 0.98 [6H, d, J=6.7 Hz, $(CH_3)_2CH$ (**9e**)], 1.26–1.67 [19H, m, $3CH_2$ (**9′e**), $5CH_2$ (**9e**), 2OH, C*H*CHOH (**9′e**)], 2.09–2.33 [5H, m, C*H*CH=CH (**9e**), $CH_2(CH_2)_3CH_2C{=}CH$ (**9′e**)], 4.09 [1H, dd, J=6.7, 9.2 Hz, C*H*OH (**9′e**)], 5.12 [1H, d, J=9.2 Hz, CHOHC*H*=C (**9′e**)], 5.50 [1H, d, J=15.9 Hz, C*H*COH (**9e**)], 5.63 [1H, dd, J=6.1, 15.9 Hz, CHC*H*=CH (**9e**)]; δ_C 18.15, 18.4 ($2CH_3$ (**9′e**)), 22.2, 22.5 [$2CH_3$ (**9e**)], 22.2, 25.6, 27.8, 28.55, 29.4, 37.4, 38.1 ($10CH_2$), 30.75, 34.3 (2CH), 71.1 (COH), 72.3 (CHOH), 123.1 (*C*H=C), 134.7 (*C*H=CHCOH), 135.05 (CH=*C*HCOH), 143.4 (CH=*C*); (**9e**): *m/z* 168 (M^+, 6%), 125 (90), 112 (18), 107 (21), 97 (33), 91 (12), 83 (31), 81 (27), 79 (34), 77 (12), 69 (30), 67 (16), 57 (11), 55 (97), 53 (16), 43 (100), 41 (90); HRMS: M^+, found 168.1514. $C_{11}H_{20}O$ requires 168.1514. (**9′e**): *m/z* 168 (M^+, 2%), 125 (82), 107 (14), 81 (25), 79 (38), 69 (11), 67 (15), 57 (100), 55 (32), 53 (11), 43 (39), 41 (45), 40 (10); HRMS: M^+, found 168.1512. $C_{11}H_{20}O$ requires 168.1514.

4.4.14. (*E*)-1-(3,3-Dimethyl-1-butenyl)cyclohexanol (9f) and 1-cyclohexylene-3,3-dimethyl-2-butanol (9′f). Colourless oil; R_f 0.46 (hexane/ethyl acetate: 5/1); ν (film) 3772–3077 cm^{-1} (OH); δ_H 0.90, 1.01 [18H, 2s, $(CH_3)_3CH$, $(CH_3)_3CCHOH$], 1.07–1.62 (18H, m, $9CH_2$), 2.05–2.47 (4H, m, CH_2, 2OH), 4.05 [1H, d, J=9.5 Hz, C*H*OH (**9′f**)], 5.17 [1H, d, J=9.5 Hz, CH=C (**9′f**)], 5.46 [1H, d, J=16.2 Hz, C*H*=CH (**9f**)], 5.68 [1H, d, J=16.2 Hz, CH=C*H* (**9f**)]; δ_C 25.5 ($6CH_3$), 22.25, 25.6, 26.7, 29.4, 29.6, 37.45, 38.2 ($10CH_2$), 32.5, 35.1 (2C), 121.51 (*C*H=C), 132.27 (*C*H=CHCOH), 138.87 (CH=*C*HCOH), 143.59 (CH=*C*); first isomer: *m/z* 182 (M^+, 15%), 139 (34), 126 (15), 125 (54), 112 (13), 111 (82), 107 (13), 97 (32), 95 (14), 93 (18), 91 (12), 83 (52), 81 (26), 79 (18), 77 (14), 69 (33), 67 (19), 57 (59), 55 (85), 53 (16), 43 (90), 42 (10), 41 (100); HRMS: M^+, found 182.1668. $C_{12}H_{22}O$ requires 182.1670. Second isomer: *m/z*182 (M^+, 0.30%), 125 (94), 107 (12), 81 (22), 79 (31), 67 (12), 57 (100), 54 (24), 43 (24), 40 (48); HRMS: M^+, found 182.1671. $C_{12}H_{22}O$ requires 182.1670.

4.4.15. (*E*)-1-(2-Phenyl-1-ethenyl)cyclohexanol (9g) and 2-cyclohexylene-1-phenyl-1-ethanol (9′g). Colourless oil; R_f 0.31 (hexane/ethyl acetate: 5/1); ν (film) 3737–3125 cm^{-1} (OH); δ_H 1.20–1.76 (18H, m, $6CH_2$, 4C*H*H, 2OH), 2.28–2.32, 2.86–2.92 (2 and 2H, respectively, 2m, $2CH_2$), 5.34 [1H, d, J=8.9 Hz, C*H*OH (**9′g**)], 5.52 [1H, d, J=8.9 Hz, CH=C (**9′g**)], 6.33 [1H, d, J=16.2 Hz, CHPh (**9g**)], 6.62 [1H, d, J=16.2 Hz, C*H*COH (**9g**)], 7.17–7.40 (10H, m, ArH); δ_C 22.1, 25.5, 26.55, 27.8, 28.3, 29.35, 37.1 ($10CH_2$), 71.7 (COH), 78.3 (CHOH), 120.7 (*C*H=C), 124.5 (CH=*C*HPh), 126.4, 127.1, 127.15, 127.35, 127.85, 128.3, 128.4, 128.5, 137.45, 142.3, 143.1, 144.4 (*C*H=CHPh, CH=*C*, ArC); (**9g**) *m/z* 202 (M^+, 31%), 184 (28), 159 (100), 155 (13), 146 (10), 145 (40), 142 (16), 141 (81), 131 (27), 129 (15), 115 (18), 111 (31), 103 (21), 91 (63), 55 (28), 43 (43), 41 (37); HRMS: M^+, found 202.1351. $C_{14}H_{18}O$ requires 202.1357. (**9′g**) *m/z* 202 (M^+, 57%), 184 (45), 169 (14), 160 (13), 159 (100), 156 (14), 155 (23), 146 (22), 145 (73), 144 (11), 143 (11), 142 (37), 141 (90), 131 (57), 130 (10), 129 (38), 128 (37), 127 (24), 120 (19), 117 (28), 116 (16), 115 (46), 111 (21), 105 (21), 104 (18), 103 (31), 102 (13), 92 (15), 91 (92), 83 (12), 81 (25), 79 (19), 78 (21), 77 (62), 76 (13), 67 (10), 65 (17), 63 (14), 55 (40), 53 (16), 52 (10), 51 (36), 50 (11), 43 (53), 41 (47); HRMS: M^+, found 202.1354. $C_{14}H_{18}O$ requires 202.1357.

4.4.16. 1-(2-Ethyl-1-butenyl)cyclohexanol (9i) and 3-(cyclohexylenemethyl)-3-pentanol (9′i). Colourless oil; R_f 0.53 (hexane/ethyl acetate: 5/1); ν (film) 3695–3049 cm^{-1} (OH); δ_H 0.89 [6H, t, J=7.3 Hz, $(CH_3CH_2)_2C$], 1.00 (6H, td, J=2.4, 7.3 Hz, $(CH_3CH_2)_2C$), 1.25–1.63 (20H, m, $10CH_2$), 1.98–2.06 [5H, m, $CH_2(CH_2)_3CH_2$, COH], 2.38 [4H, q, J=7.3 Hz, $(CH_3CH_2)_2C$], 2.44 (1H, br s, OH), 5.06 (1H, s, CH=C), 5.24 (1H, s, CH=C); δ_C 8.2 ($2CH_3$), 13.3 ($2CH_3$), 22.7, 22.7, 23.6, 25.5, 26.7, 28.0, 29.0, 29.1, 29.7, 30.1, 34.15, 38.5, 39.85 (CH_2), 71.8 (COH), 75.95 (COH), 126.6 (CH), 129.6 (CH), 143.1 (*C*=CH), 146.4 (*C*=CH); first isomer *m/z* 182 (M^+, 3%), 153 (48), 111 (61), 85 (33), 79 (28), 57 (52), 55 (55), 43 (38), 41 (100); HRMS: M^+, found 182.1665. $C_{12}H_{22}O$ requires 182.1670. Second isomer: *m/z* 182 (M^+, 6%), 164 (21), 153 (70), 139 (14), 135 (35), 126 (10), 112 (11), 111 (79), 107 (21), 97 (10), 95 (14), 93 (38), 91 (22), 85 (59), 83 (14), 81 (35), 79 (45), 77 (22), 69 (22), 67 (33), 65 (12), 57 (77), 55 (76), 53 (21), 43 (64), 41 (100); HRMS: M^+, found 182.1669. $C_{12}H_{22}O$ requires 182.1670.

4.4.17. 1-(Cyclohexylenemethyl)cyclohexanol (9j). Colourless oil; R_f 0.56 (hexane/ethyl acetate: 5/1); ν (film) 3669–3097 cm^{-1} (OH); δ_H 1.40–1.66 (17H, m, $8CH_2$, OH), 2.04 (2H, m, CH_2CCH_2), 2.48 (2H, m, CH_2CCH_2), 5.25 (1H, s, CH=C); δ_C 22.6, 25.4, 26.6, 27.9, 28.9, 30.0, 38.1, 39.8 ($10CH_2$), 71.5 (COH), 128.4 (CH), 143.6 (*C*=CH); *m/z* 176 (M^+-H_2O, 45%), 147 (18), 134 (13), 133 (22), 119 (15), 105 (27), 95 (29), 94 (83), 93 (28), 91 (63), 81 (36), 80 (29), 79 (100), 78 (13), 77 (30), 67 (38), 65 (19), 55 (24), 53 (21), 51 (12), 44 (10), 43 (38), 41 (70); HRMS: $M^+ - H_2O$, found 176.1559. $C_{13}H_{20}$ requires 176.1565.

4.5. Dehydration of allylic alcohols 9

Isolation of compounds ***10****. General procedure*. To a solution of allylic alcohol **9** (0.25 mmol) in chloroform (3 ml) was added six drops of a 6N solution of hydrochloric acid at 20°C. The reaction mixture was stirred for 12 h at the same temperature. After that ethyl acetate (20 ml) was added, and the reaction solution was dried with anhydrous Na_2SO_4 and evaporated (15 Torr) to yield a residue which was the title pure compounds **10**. Yields are included in Table 5. Physical, spectroscopic and analytical data follow.

4.5.1. (*E*)-1-(3-Methyl-1-butenyl)cyclohexene (10e). Colourless oil; R_f 0.81 (hexane); ν (film) 3022 cm^{-1} (C=C–H); δ_H 1.01 [6H, d, J=6.7 Hz, $(CH_3)_2CH$], 1.03–1.78 [4H, m, $CH_2(CH_2)_2CH_2$], 2.10–2.14 [4H, m, $CH_2(CH_2)_2CH_2$], 2.29–2.34 (1H, m, $(CH_3)_2CH$), 5.51 (1H, dd, J=6.7, 15.9 Hz, CH=CHCH), 5.65 (1H, m, C=CH), 5.99 (1H, d, J=15.9 Hz, CH=CHCH); δ_C 22.6, 22.7 [$(CH_3)_2CH$], 24.6, 25.8, 31.2 ($4CH_2$), 127.25 (CH=C), 130.4 (CHCH=CH), 133.8 (CHCH=CH), 135.6 (CH=C); m/z 150 (M^+, 41%), 135 (63), 121 (10), 108 (10), 107 (57), 105 (11), 95 (10), 94 (30), 93 (51), 91 (40), 82 (21), 81 (31), 80 (14), 79 (100), 77 (32), 69 (20), 67 (36), 65 (17), 55 (27), 53 (17), 51 (13), 43 (12), 41 (73); HRMS: M^+, found 150.1410. $C_{11}H_{18}$ requires 150.1408.

4.5.2. (*E*)-1-(3,3-Dimethyl-1-butenyl)cyclohexene (10f). Colourless oil; R_f 0.75 (hexane); ν (film) 3023 cm^{-1} (C=C–H); δ_H 1.03 [9H, s, $(CH_3)_3C$], 1.09–1.70 (4H, m, $CH_2CH_2CH_2CH_2$), 2.10–2.12 (4H, m, $CH_2CH{=}CH_2$), 5.58 [1H, d, J=17.1 Hz, $(CH_3)_3CCH$], 5.66–5.68 (1H, m, CH_2CH), 5.97 (1H, d, J=15.9 Hz, CH=CCH=CH); δ_C 22.3, 22.6, 22.7, 25.8 ($4CH_2$), 29.8 [$(CH_3)_3C$], 37.4 [$(CH_3)_3C$], 127.4, 128.1, 137.6 (3CH), 135.6 (CHC); m/z 164 (M^+, 23%), 149 (58), 121 (32), 107 (30), 99 (46), 95 (14), 94 (11), 93 (44), 91 (24), 81 (51), 79 (43), 77 (21), 69 (21), 67 (33), 65 (13), 58 (18), 57 (29), 55 (47), 53 (17), 45 (10), 44 (12), 43 (100), 42 (13), 41 (94); HRMS: M^+, found 164.1562. $C_{12}H_{20}$ requires 164.1565.

4.5.3. (*E*)-1-(2-Phenylethenyl)cyclohexene (10g). Colourless oil; R_f 0.46 (hexane); ν (film) 3059, 3026 (C=C–H), 1632 cm^{-1} (C=C); δ_H 0.79–1.76, 2.15–2.27 (4 and 4H, respectively, 2m, $4CH_2$), 5.89 (1H, s, $CH_2CH{=}C$), 6.43 (1H, d, J=15.9 Hz, CH=CH), 6.76 (1H, d, J=16.5 Hz, CH=CH), 7.15–7.41 (5H, m, ArH); δ_C 22.5, 24.5, 26.1, 37.4 ($4CH_2$), 124.6, 126.1, 127.1, 128.3, 128.5, 130.8, 132.6, 135.8, 138.0 (ArC, C=C); m/z 184 (M^+, 63%), 169 (18), 156 (19), 155 (30), 143 (11), 142 (49), 141 (100), 129 (20), 128 (32), 115 (29), 91 (42), 79 (12), 78 (12), 77 (24), 65 (11), 51 (16), 41 (16); HRMS: M^+, found 184.1246. $C_{14}H_{16}$ requires 184.1252.

4.5.4. 1-(2-Ethyl-1-butenyl)cyclohexene (10i) and (*E*)-3-(cyclohexylenemethyl)-2-pentene (10′i). Colourless oil; R_f 0.53 (hexane); ν (film) 1650, 1645 cm^{-1} (C=C); δ_H 0.86–1.03 (12H, m, $4CH_3$), 1.26–1.36, 1.48–1.66, 1.99–2.32 (6, 8 and 8H, respectively, 3m, $12CH_2$), 5.15–5.31 [1H, m, $CH_3CH{=}C$ (**10′i**)], 5.49 [1H, s, CH=C (**10i**)], 5.52 [2H, s, 2CH (**10i–10′i**)]; δ_C 12.9, 13.8, 14.8 (CH_3), 22.3, 23.1, 24.1, 25.5, 26.8, 26.85, 27.5, 28.2, 28.8, 29.98, 36.77, 37.9 ($12CH_2$), 124.6, 124.8, 125.2, 126.0 (4CH=C), 132.8, 135.2, 135.5, 140.3 (4CH=C); (**10i**): m/z 164 (M^+, 57%), 136 (11), 135 (95), 121 (20), 107 (51), 105 (12), 95 (11), 94 (16), 93 (74), 91 (41), 82 (11), 81 (53), 80 (14), 79 (85), 77 (35), 69 (14), 67 (58), 65 (19), 55 (44), 53 (25), 51 (13), 43 (23), 41 (100), 40 (21); HRMS: M^+, found 164.1563. $C_{12}H_{20}$ requires 164.1565. (**10′i**): m/z 164 (M^+, 55%), 136 (11), 135 (100), 121 (20), 107 (56), 105 (14), 95 (10), 94 (16), 93 (80), 91 (46), 82 (10), 81 (47), 80 (14), 79 (92), 78 (10), 77 (38), 69 (14), 67 (51), 65 (19), 55 (46), 53 (22), 51 (13), 43 (21), 41 (89); HRMS: M^+, found 164.1559. $C_{12}H_{20}$ requires 164.1565.

4.5.5. 1-(Cyclohexylenemethyl)cyclohexene (10j). Colourless oil; R_f 0.73 (hexane); ν (film) 1691, 1650 cm^{-1} (C=C); δ_H 1.25–1.72, 2.02–2.10, 2.29–2.33 (10, 6 and 2H, respectively, 3m, $9CH_2$), 5.47–5.50 (2H, m, 2CH); δ_C 22.3, 23.0, 25.5, 26.8, 28.2, 28.8, 29.5, 30.0, 37.9 ($9CH_2$), 124.8, 125.2 (2CH), 104.25 (C=CH); m/z 176 (M^+, 48%), 147 (20), 134 (14), 133 822), 119 (16), 107 (10), 105 (29), 95 (28), 94 (83), 93 (27), 92 (15), 91 (62), 81 (34), 80 (29), 79 (100), 78 (13), 77 (30), 767 836), 66 (10), 65 (20), 55 (22), 53 (19), 51 (12), 43 (17), 41 (70); HRMS: M^+, found 176.1564. $C_{13}H_{20}$ requires 176.1565.

Acknowledgements

This work was financially supported by the DGES from the Spanish ministerio de Educación y Cultura (MEC) (project no. PB-97-0133).

References

1. (a) Maercker, A. In *Lithium Chemistry, A Theoretical and Experimental Overview*, Sapse, A. M., Schleyer, P. v. R., Eds.; Wiley: New York, 1995. (b) Foubelo, F.; Yus, M. *Trends Org. Chem.* **1998**, *7*, 1–26.
2. (a) Bolton, E. E.; Laidig, W. D.; Schleyer, P. v. R.; Schaefer III, H. F. *J. Am. Chem. Soc.* **1994**, *116*, 9602–9612. (b) Collins, J. B.; Dill, J. D.; Jemmis, E. D.; Apeloig, Y.; Schleyer, P. v. R.; Seeger, R.; Pople, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5419–5427. (c) Kos, A. J.; Jemmis, E. D.; Schleyer, P. v. R.; Gleiter, R.; Fischbach, U.; Pople, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 4996–5002.
3. (a) Bates, R. B.; Ogle, C. A. *Carbanion Chemistry*, Springer: Berlin, 1983. (b) Wakefield, B. *Organolithium Methods*, Academic Press: London, 1988. (c) Jones, R. G.; Gilman, H. *Chem. Rev.* **1954**, *54*, 835–890.
4. For reviews, see: (a) Nájera, C.; Yus, M. *Trends Org. Chem.* **1991**, *2*, 155–181. (b) Nájera, C.; Yus, M. *Recent Res. Devel. Org. Chem.* **1997**, *1*, 67–96.
5. Recent papers on this topic from our laboratory: (a) Foubelo, F.; Yus, M. *Tetrahedron Lett.* **1999**, *40*, 743–746. (b) Foubelo, F.; Saleh, S. A.; Yus, M. *J. Org. Chem.* **2000**, *65*, 3478–3483. (c) Foubelo, F.; Yus, M. *Tetrahedron Lett.* **2000**, *41*, 5047–5051.

6. (a) Corey, E. J.; Seebach, D. *Angew. Chem. Int. Ed. Engl.* **1965**, *4*, 1075–1076. (b) Corey, E. J.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 1077.
7. Seebach, D.; Corey, E. J. *J. Org. Chem.* **1966**, *31*, 4097–4099.
8. (a) Screttas, C. G.; Micha-Screttas, M. *J. Org. Chem.* **1978**, *43*, 1064–1071. (b) Screttas, C. G.; Micha-Screttas, M. *J. Org. Chem.* **1979**, *44*, 713–719. (c) Cohen, T.; Bhupathy, M. *Acc. Chem. Res.* **1989**, *22*, 152–161.
9. (a) Foubelo, F.; Gutiérrez, A.; Yus, M. *Tetrahedron Lett.* **1997**, *38*, 4837–4840. (b) Foubelo, F.; Gutiérrez, A.; Yus, M. *Synthesis* **1999**, 503–514 (Feature article).
10. For reviews, see: (a) Yus, M. *Chem. Soc. Rev.* **1996**, 155–161. (b) Ramón, D. J.; Yus, M.; Eur *J. Org. Chem.* **2000**, 225–237.
11. For step by step related procedures, see: (a) Ager, D. J. *Tetrahedron Lett.* **1981**, *22*, 2923–2926. (b) Guo, B.-S.; Doubleday, W.; Cohen, T. *J. Am. Chem. Soc.* **1987**, *109*, 4710–4711. (c) Tanaka, K.; Minami, K.; Funaki, I.; Suzuki, H. *Tetrahedron Lett.* **1990**, *31*, 2727–2730.
12. Preliminary communication: Foubelo, F.; Gutiérrez, A.; Yus, M. *Tetrahedron Lett.* **1999**, *40*, 8173–8176.
13. Cookson, R. C.; Parsons, P. J. *J. Chem. Soc., Chem. Commun.* **1978**, 821–822.
14. (a) Trost, B. M.; Keeley, D. E.; Arndt, H. C.; Rigby, J. H.; Bogdanowicz, M. J. *J. Am. Chem. Soc.* **1977**, *99*, 3080–3087. (b) Trost, B. M.; Keeley, D. E.; Arndt, H. C.; Bogdanowicz, M. J. *J. Am. Chem. Soc.* **1977**, *99*, 3088–3100. (c) Witulski, B.; Bergsträsser, U.; Gössmann, M. *Tetrahedron* **2000**, *56*, 4747–4752.
15. Preliminary communication: Foubelo, F.; Gutiérrez, A.; Yus, M. *Tetrahedron Lett.* **1999**, *40*, 8177–8180.
16. For reviews on functionalised organolithium compounds and their elimination reactions, see reference 4.