SUPPORTING INFORMATION

NaOH-Catalyzed Thiolysis of α,β-Epoxyketones in Water. A Key Step in the Synthesis of target Molecules Starting from α,β-Unsaturated Ketones.

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CONTENTS

page S2 Experimental Section

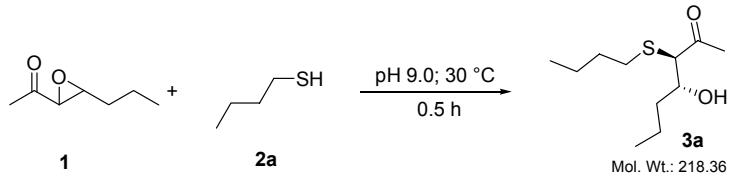
page S3-S25 Full characterization charts (^{1}H NMR, ^{13}C NMR, IR, GC-MS, R_f) for compounds ***anti*-3a-d**, **(*Z*)-4a-d**, **7c**, **7d**, **8b**, **8c**, **9c**, **9d**, **10c**, **10d**, **13**, **14** and significant spectral ^{1}H and ^{13}C NMR data for compounds ***syn*-3a-b, 5a, 5d**, **(*E*)-4a**, **(*E*)-4d** and for **Rel(2R,3S)-3-hydroxy-3,5,5-trimethyl-2-(phenylthio)-cyclohexanone** (coming from the thiolysis of **8**).

Experimental Section

All chemicals were purchased and used without any further purification. In this work we have used de-ionized water. GC analyses were performed with an SPB-5 fused silica capillary column (30 m, 0.25 mm diameter), an "on column" injector system, a FID detector and hydrogen as the carrier gas. GC-MS analyses were carried out with 70 eV electron energy. All ^{1}H NMR and ^{13}C NMR spectra were recorded at 200 MHz or 400 MHz, and at 50.3 or 100.6 MHz respectively, using a convenient deuterated solvent (reported in the characterization charts) and the residual peak as internal standard, or TMS in the case of $CDCl_3$. The pH values of the reactions were controlled using a pH-meter apparatus equipped with a combined refillable pH electrode and with an Autocompensating Temperature Control (ATC) probe. All melting points are uncorrected. Thin Layer Cromatography analyses were performed on silica gel on aluminum plates and UV and/or $KMnO_4$ or phosphomolybdic acid were used as revealing agents. Column chromatography were performed by using silica gel 230-400 mesh and eluting as reported in the following characterization charts.

Chem. Name	Rel(3R,4R)-3-buthylthio-4-hydroxyheptan-2-one (*anti*-3a)
Lit. Ref.	

Scheme



Method: 189 mg (2.1 mmol) of buthylthiol (**2a**) were added to 3.75 mL of water and 0.25 mL of NaOH 0.1 M aq sol to obtain a resulting pH = 9.0. Then after 5 minutes 256 mg (2.0 mmol) of 3,4-epoxy-heptan-2-one (**1a**) were added and after additional 0.5 h under vigorous magnetic stirring at 30 °C, the reaction mixture was extracted with Et_2O (3 x 5 mL). The combined organic layers were dried over Na_2SO_4 and evaporated under vacuum to give the crude hydroxysulfide. ***anti*-3a** was isolated as an oil in ≥ 98% purity after silica-gel column chromatography (Etp/AcOEt: 8:2 (gradient), silica/sample: 30:1) in 94% yield.

Exp. Ref.	Table 1, entry 2	Spectra Refs	
Mol Formula	$C_{11}H_{22}O_2S$	m.p./b.p.	Oil
Tlc - R_f (eluent)	0.54 (Etp/AcOEt 8:2)		-

comments:

ν_{max}/cm^{-1}

FT-IR ($CHCl_3$, cm^{-1}): 1225 (m), 1275 (m), 1358 (s), 1462 (m), 1698 (s), 2251 (m), 2872 (s), 2961 (s), 3997 (s)

Elemental Analysis : C. 60.51; H. 10.16. Found: C 60.38; H. 10.11.

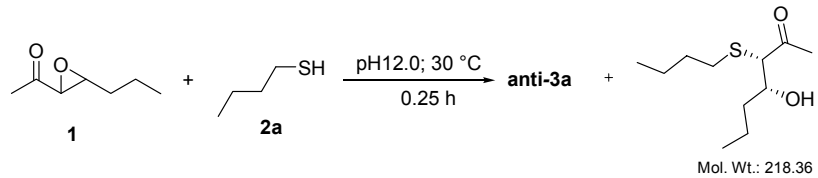
^{1}H NMR 400 MHz $CDCl_3$	δ value	No. H	Mult.	j value/Hz
	0.90	3	*t*	*J* = 7.2 Hz
	0.95	3	*t*	*J* = 7.2 Hz
	1.30-1.60	7	*m*	
	1.85-1.92	1	*m*	
	2.32	3	*s*	
	2.35-2.51	2	*m*	
	3.17	1	*d*	*J* = 9.2 Hz
	3.31	1	*bs*	
	3.90	1	*m*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 13.4, 13.8, 18.4, 21.7, 27.2, 30.2, 31.3, 36.1, 58.8, 70.2, 205.7

GC/EIMS (*m/z*) : decomposed

Chem. Name	Rel(3S,4R)-3-butylthio-4-hydroxyheptan-2-one (*syn*-3a)

Scheme



Method: 189 mg (2.1 mmol) of buthylthiol (**2a**) were added to 3.9 mL of water and 0.1 mL of NaOH 1.0 M aq sol to obtain a resulting pH = 12.0. Then after 5 minutes 256 mg (2.0 mmol) of 3,4-epoxy-heptan-2-one (**1**) were added and after additional 0.25 h under vigorous magnetic stirring at 30 °C, the reaction mixture was extracted with Et_2O (3 x 5 mL). The combined organic layers were over Na_2SO_4 and evaporated under vacuum to give the crude reaction mixture of ***syn*-3a** (20%) and ***anti*-3a** (80%) in 98% yield.

comments: Analyses performed on the crude reaction mixture (Table 1 entry 3). Characteristic signals are reported.

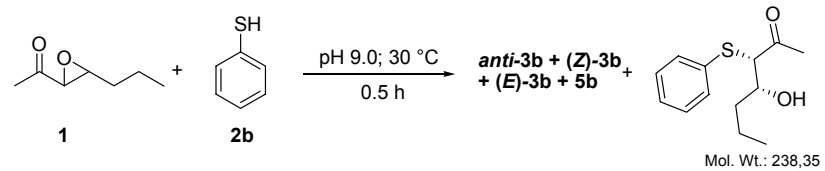
^{1}H NMR 400 MHz $CDCl_3$	δ value	No. H	Mult.	j value/Hz
	2.29	3	*s*	
	3.19	1	*d*	*J* = 9.2 Hz
	3.88	1	*m*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 13.9, 13.5, 19.0, 21.9, 28.3, 30.4, 31.5, 36.6, 60.2, 68.5, 204.8

GC/EIMS (*m/z*) : decomposed

Chem. Name	Rel(3S,4R)-4-hydroxy-2-(phenylthio)-heptan-2-one (*syn*-3b)

Scheme



Method: 0.220 mL (2.1 mmol) of thiophenol (**2b**) and 256 mg (2.0 mmol) of 3,4-epoxy-heptan-2-one (**1a**) were added to 3.4 mL of water, and 0.6 mL of NaOH 1M aq sol to obtain a pH around 12.0. After 0.5 h under vigorous magnetic stirring at 30 °C, the reaction mixture was extracted with Et_2O (3 x 10 mL). The combined organic layers were dried over Na_2SO_4 and evaporated under vacuum to give the mixture of products ***anti*-3b** (13%), ***syn*-3b** (8%), **(*Z*)-4b** (55%), **(*E*)-4b** (< 1%), and **5b** (24%). 97% yield.

comments: Analyses performed on the crude reaction mixture (Table 1 entry 6). Characteristic signals are reported.

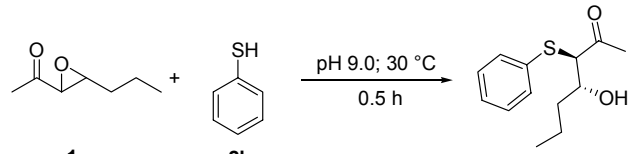
^{1}H NMR 200 MHz $CDCl_3$	δ value	No. H	Mult.	j value/Hz
	2.31	3	*s*	
	3.58	1	*d*	*J* = 6.0 Hz
	4.02-4.07	1	*m*	

^{13}C NMR (50.3 MHz, $CDCl_3$) δ : 13.6, 18.9, 20.4, 29.4, 36.4, 64.2, 69.4, (4 C not identified), 205.8

GC/EIMS (*m/z*) : decomposed

Chem. Name	Rel(3S,4R)-4-hydroxy-2-(phenylthio)-heptan-2-one (*anti*-3b)
Lit. Ref.	

Scheme



1 **2b** Mol. Wt.: 238,35

Method: 0.220 mL (2.1 mmol) of thiophenol (**2b**) and 256 mg (2.0 mmol) 3,4-epoxy-heptan-2-one (**1**) were added to in 3.4 mL of water, then 0.6 mL of NaOH 1M aq sol were slowly added to maintain the pH around 9.0. After 0.5 h under vigorous magnetic stirring at 30 °C, the reaction mixture was extracted with Et_2O (3 x 10 mL). The combined organic layers were dried over Na_2SO_4 and evaporated under vacuum to give ***anti*-3b** in 97% yield.

Exp Ref	Table 1, entry 5	Spectra Refs	
Mol Formula	$C_{13}H_{18}O_2S$	m.p./b.p.	Oil
Tlc - R_f (solv)	0.27 (Etp/AcOEt 8:2)		

comments:

ν_{max}/cm^{-1}

FT-IR (neat, cm^{-1}): 720 (m), 790 (m), 1213 (m), 1358 (m), 1439 (m), 1476 (m), 1582 (m), 1703 (s), 2874 (s), 2965 (s), 3019 (s), 3068 (w)

Elemental Analysis : C, 65.51; H, 7.61. Found: C 65.57; H. 7.68.

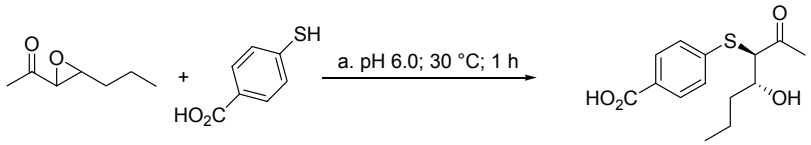
^{1}H NMR 200 MHz $CDCl_3$	δ value	No. H	Molt.	j value/Hz
	0.95	3	*t*	*J* = 7.2 Hz
	1.40-1.60	4	*m*	
	2.31	3	*s*	
	3.58	1	*d*	*J* = 8.3 Hz
	3.94	1	*m*	
	7.20-7.50	5	*m*	

^{13}C NMR (50.3 MHz, $CDCl_3$) δ : 13.9, 18.6, 20.9, 28.8, 36.0, 62.0, 70.7, 128.3, 129.3, 132.3, 205.8, 132.8,

GC/EIMS (*m/z*) : decomposed

Chem. Name	Rel(3R,4R)-3-(4'-carboxy-phenylthio)-4-hydroxy-heptan-2-one (*anti*-3c)
Lit. Ref.	

Scheme



1 **2c** Mol. Wt.: 282.36

Method: 323 mg (2.1 mmol) of 4-mercaptobenzoic acid (**2c**) were added to 3.4 mL of water and 0.6 mL of NaOH 1.0 M aq sol. Then after 5 minutes 224 mg (2.0 mmol) of 3,4-epoxy-hepten-2-one (**1**) were added. After 1 h under vigorous stirring at 30 °C, the reaction mixture was acidified to pH 2.0 and extracted with AcOEt (3 x 5 mL). dried over Na_2SO_4 and evaporated under vacuum to give ***anti*-3d** in 98% yield. ***anti*-3d** was re-crystallized from AcOEt

Exp Ref	Table 1, entry 7	Spectra Refs	
Mol Formula	$C_{14}H_{18}O_4S$	m.p./b.p.	115-117 °C
Tlc - R_f (solv)	0.24 (Etp/AcOEt/AcOH 6:3.5:0.5)		

comments:

ν_{max}/cm^{-1}

FT-IR ($CHCl_3$, cm^{-1}): 1015 (m), 1088 (m), 1119 (m), 1182 (m), 1278 (s), 1359 (m), 1414 (s), 1594 (s), 1700 (s), 2549 (m), 2661 (m), 2874 (s), 2964 (s), 3020 (s)

Elemental Analysis : C, 59.55; H, 6.43. Found: C 59.61; H. 6.48.

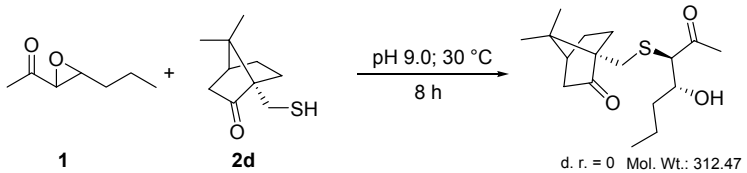
^{1}H NMR 400 MHz Aceton$_{d-6}$	δ value	No. H	Mult.	j value/Hz
	0.91	3	*t*	*J* = 7.2 Hz
	1.39-1.60	3	*m*	
	1.79-1.88	1	*m*	
	3.89	1	*d*	*J* = 8.3 Hz
	4.01	1	*m*	
	7.50	2	*d*	*J* = 8.4 Hz
	7.95	2	*d*	*J* = 8.4 Hz

^{13}C NMR (100.6 MHz,$CDCl_3$) δ : 14.0, 19.0, 27.1, 37.7, 62.3, 71.5, 129.3, 129.6, 131.2, 141.8, 166.9, 204.5

GC/EIMS (*m/z*) : decomposed

Chem. Name	**Rel(3R,4R)3-((1′*S*)-camphoryl-10′-thio)-4-hydroxy-heptan-2-one (*anti*-3d)**

Scheme



Method: 390 mg (2.0 mmol) of (1S)-camphor-10-thiol (**2d**) were added to 3.8 mL of water and 0.2 mL of NaOH 0.1 M aq sol to obtain a resulting pH = 9.0. Then after 5 minutes 256 mg (2.0 mmol) 3,4-epoxy-heptan-2-one (**1**) were added and the pH maintained around 9.0. After 8 h under vigorous magnetic stirring at 30 °C, the reaction mixture has been extracted with Et_2O (3 x 5 mL). The combined organic layers were dried over Na_2SO_4 and evaporated under vacuum to give the crude hydroxysulfides. The mixture of the diastereoisomers ***anti*-3d** was then obtained in ≥ 98% purity by a silica-gel column chromatography (Etp/AcOEt: 7:3, silica/sample: 30:1) in 93% yield. Analyses refer to the mixture of two diastereoisomers (d.r. = 0)

Exp Ref	Table 1, entry 10	**Spectra Refs**	
Mol Formula	$C_{17}H_{28}O_3S$	**m.p./b.p.**	oil
Tlc - R_f (solv)	0.5 (Etp/AcOEt 6:4)		

comments:

ν_{max}/cm^{-1}

FT-IR (neat, cm^{-1}): 733(m) , 1048 (m), 1355 (s), 1416 (s), 1700 (s), 1742 (s), 2873 (s), 2960 (s) , 3465 (s broad)

Elemental Analysis : C. 65.34; H. 9.03; Found: C 65.28; H. 9.11.

^{1}H NMR 200 MHz $CDCl_3$

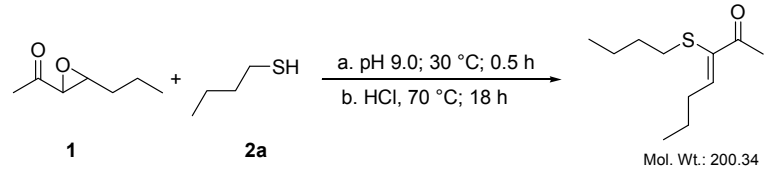
δ value	No. H	Mult.	j value/Hz
0.79	6	*s*	
0.80-0.90	6	*m*	
0.92	6	*s*	
1.05-1.55	10	*m*	
1.67-2.01	10	*m*	
2.15-2.34	4	*m*	
2.26	3	s	
2.27	3	s	
3.17	1	d	*J* = 1.9 Hz
3.12	1	d	*J* = 2.2
3.75-3.95	2	m	

^{13}C NMR (50.3 MHz, $CDCl_3$) δ : 13.9, 18.5, 19.8, 20.1, 26.7, 27.2, 27.7, 27.9, 35.9, 36.0, 42.9, 44.0, 47.7, 59.2, 59.6, 60.5, 60.6, 70.0, 70.3, 205.4, 205.7, 216.9

GC/EIMS (*m/z*) : 312 (M^+ not detected), 294 (21), 251 (100), 109 (41), 81 (22)

Chem. Name	**(*Z*)-3-(buthylthio)-hepten-2-one ((*Z*)-4a)**
Lit. Ref.	

Scheme



Method: 189 mg (2.1 mmol) of buthylthiol (**2a**) were added to 3.75 mL of water and 0.25 mL of NaOH 0.1 M aq sol to obtain a resulting pH = 9.0. Then after 5 minutes 256 mg (2.0 mmol) of 3,4-epoxy-heptan-2-one (**1**) were added and after additional 0.5 h under vigorous magnetic stirring at 30 °C, 0.4 mL of HCl_{conc} were added and the reaction mixture was warmed to 70 °C. After 18 h the reaction mixture was extracted with Et_2O (3 x 5 mL). The combined organic layers were washed with brine (1 x 5 mL), dried over Na_2SO_4 and evaporated under vacuum to give the crude vinyl sulfide. **(*Z*)-4a** was then isolated as an oil in ≥ 98% purity after silica-gel column chromatography (Etp/AcOEt: 9:1 (gradient), silica/sample: 20:1) in 90% yield.

Exp Ref	Scheme 1	**Spectra Refs**	
Mol Formula	$C_{11}H_{20}OS$	**m.p./b.p.**	oil
Tlc - R_f (solv)	0.33 (Etp/AcOEt 9:1)		

comments:

ν_{max}/cm^{-1}

FT-IR ($CHCl_3$, cm^{-1}): 1213 (s), 1358 (w), 1461 (w), 1593 (w), 1675 (s), 2873 (w), 2933 (m), 2965 (s), 3019 (w)

Elemental Analysis : C. 65.95; H. 10.06. Found: C 65.98; H. 10.15.

^{1}H NMR 400 MHz $CDCl_3$

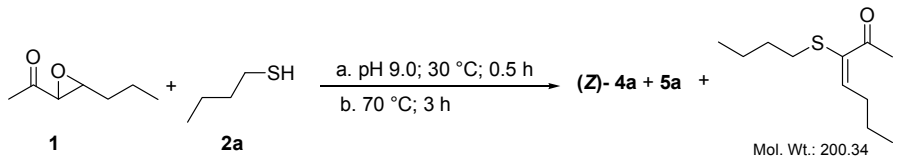
δ value	No. H	Mult.	j value/Hz
0.86	3	*t*	*J* = 7.2 Hz
0.95	3	*t*	*J* = 7.4 Hz
1.30-1.55	6	*m*	
2.39	3	*s*	
2.47	2	*q*	*J* = 7.4 Hz
2.61	2	*t*	*J* = 7.2 Hz
6.98	1	*t*	*J* = 7.4 Hz

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 13.5, 13.9, 21.7, 21.8, 27.0, 31.9, 32.8, 33.2, 137.2, 150.0,197.3

GC/EIMS (*m/z*) : 200 (M^+ 100), 157 (25), 143 (28), 115 (33), 95 (29), 67 (30), 43 (69)

Chem. Name	(*E*)-3-(buthylthio)-hepten-2-one ((*E*)-4a)
Lit. Ref.	

Scheme



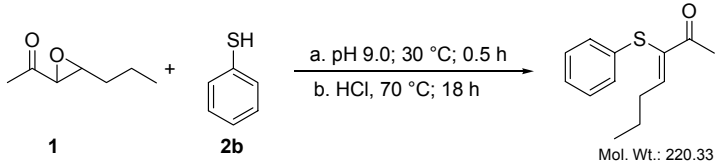
Method: 189 mg (2.1 mmol) of buthylthiol (**2a**) were added to 3.75 mL of water and 0.25 mL of NaOH 0.1 M aq sol to obtain a resulting pH = 9.0. Then after 5 minutes 256 mg (2.0 mmol) of 3,4-epoxy-heptan-2-one (**1**) were added and after additional 0.5 h under vigorous magnetic stirring at 30 °C, the reaction mixture was warmed to 70 °C. After 3 h the reaction mixture was extracted with Et_2O (3 x 5 mL). The combined organic layers were dried over Na_2SO_4 and evaporated under vacuum to give the mixture of products **(*Z*)-4a** (26%), **(*E*)-4a** (14%), and **5a** (60%) in 98% yield.

comments: Analyses performed on the crude reaction mixture (Table 3 entry 1). Characteristic signal of vinylic proton is reported.

^{1}H NMR 400 MHz $CDCl_3$	δ value	No. H	Mult.	j value/Hz
	6.41	1	*t*	*J* = 7.5 Hz

Chem. Name	(*Z*)-3-(phenylthio)-hept-3-en-2-one ((*Z*)-4b)
Lit. Ref.	

Scheme



Method: 0.220 mL (2.1 mmol) of thiophenol (**2b**) and 256 mg (2.0 mmol) 3,4-epoxy-heptan-2-one were added to 3.4 mL of water. Then 0.6 mL of NaOH 1 M aq sol were slowly added maintaining the pH around 9.0. After 0.5 h, under vigorous magnetic stirring at 30 °C, 1 mL of HCl was added and the reaction mixture was warmed to 70 °C. After 18 h the reaction mixture was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine (1 x 10 mL), dried over Na_2SO_4 and evaporated under vacuum to give the crude vinyl sulfide. **(*Z*)-4b** was then obtained in ≥ 99% purity by a silica-gel column chromatography (Etp/AcOEt: 9:1, silica/sample: 30:1) in 89% yield.

Exp Ref	Scheme 1	Spectra Refs	
Mol Formula	$C_{13}H_{16}OS$	m.p./b.p.	oil
Tlc - R_f (solv)	0.41 (Etp/AcOEt 9:1)		

comments:

ν_{max}/cm^{-1}

FT-IR (neat, cm^{-1}): 691 (m), 741 (m), 1208 (s), 1356 (m), 1439 (m), 1479 (m), 1585 (m), 1592 (m), 1688 (s), 2872 (s), 2932 (s), 2961 (s), 3060 (w)

Elemental Analysis : C. 70.87; H. 7.32. Found: C 70.88; H. 7.38.

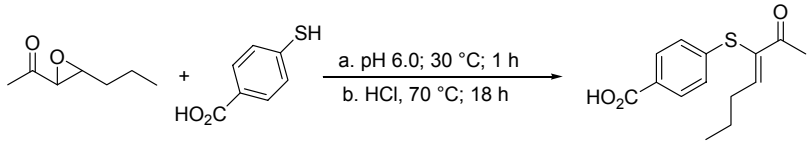
^{1}H NMR 200 MHz $CDCl_3$	δ value	No. H	Mult.	j value/Hz
	0.96	3	*t*	*J* = 7.3 Hz
	1.53	2	*app. sextet*	*J* = 7.5 Hz
	2.28	3	*s*	
	2.49	2	*app. quartet*	*J* = 7.4 Hz
	7.10-7.40	6	*m*	

^{13}C NMR (50.3 MHz, $CDCl_3$) δ : 14.0, 21.8, 27.5, 32.7, 126.0, 127.5, 129.2, 134.5, 135.9, 151.9, 197.8.

GC/EIMS (*m/z*) : 220 (M^+, 100), 177 (18), 135 (44), 110 (26), 95 (29)

Chem. Name	**(*Z*)-3-(4'-carboxy-phenylthio)-hepten-2-one ((*Z*)-4c)**
Lit. Ref.	

Scheme



1 **2c** Mol. Wt.: 264.34

Method: 323 mg (2.1 mmol) of 4-mercaptobenzoic acid (**2c**) were added to 3.4 mL of water and 0.6 mL of NaOH 1.0 M aq sol. Then after 5 minutes 224 mg (2.0 mmol) of 3,4-epoxy-hepten-2-one (**1**) were added. After 1 h under vigorous stirring at 30 °C, 0.4 mL of $HCl_{conc.}$ were added and the reaction mixture was warmed to 70 °C. After 18 h the reaction mixture was cooled to r.t., acidified to pH 2.0 and extracted with AcOEt (3 x 5 mL). The combined organic layers were washed with brine (1 x 5 mL), dried over Na_2SO_4 and evaporated under vacuum to give the crude vinyl sulfide. **(*Z*)-4c** was isolated in ≥ 99% purity and 94% yield after re-crystallization from AcOEt.

Exp Ref	Scheme 1	**Spectra Refs**	
Mol Formula	$C_{14}H_{16}O_3S$	**m.p./b.p.**	93-94 °C
Tlc - R_f (solv)	0.34 (Etp/AcOEt/AcOH 1:1:0.05)		

comments:

ν_{max}/cm^{-1}

FT-IR ($CHCl_3$, cm^{-1}): 1015 (m), 1086 (m), 1182 (m), 1219 (s), 1291 (s), 1418 (s), 1594 (s), 1697 (s), 2553 (m), 2670 (m), 2877 (s), 2966 (s), 3020 (s)

Elemental Analysis : C. 63.61; H. 6.10. Found: C 63.64; H. 6.18.

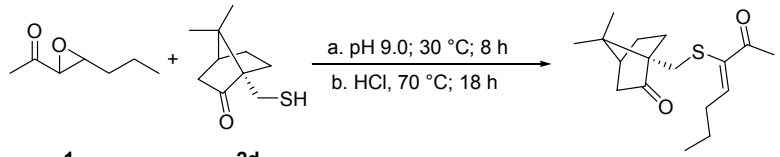
^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	0.96	3	*t*	*J* = 7.4 Hz
	1.54	2	*sextet*	*J* = 7.4 Hz
	2.34	3	*s*	
	2.50	2	*q*	*J* = 7.4 Hz
	7.18	2	*d*	*J* = 8.2 Hz
	7.44	1	*t*	*J* = 7.4 Hz
	7.99	2	*d*	*J* = 8.2 Hz

^{13}C NMR (100.6 MHz,$CDCl_3$) δ : 13.9, 21.7, 27.3, 33.0, 126.0, 126.5, 130.9, 133.0, 144.0, 154.6, 171.6, 196.8

GC/EIMS (*m/z*) : 264 (M^+ 100), 135 (24), 110 (25), 95 (29), 67 (22)

Chem. Name	**(*Z*)-3-((1'*S*)-camphoryl-10'-thio)-hept-3-en-2-one ((*Z*)-4d)**
Lit. Ref.	

Scheme



1 **2d** Mol. Wt.: 294.45

Method: 390 mg (2.0 mmol) of (1S)-camphor-10-thiol (**2d**) were added to 3.8 mL of water and 0.2 mL of NaOH 0.1 M aq sol to obtain a resulting pH of 9.0. Then after 5 minutes 256 mg (2.0 mmol) of 3,4-epoxy-heptan-2-one (**1**) were added. After 8 h under vigorous magnetic stirring at 30 °C, 1 mL of HCl_{conc} was added and the reaction mixture was warmed to 70 °C. After 18 h the reaction mixture was cooled to r.t. and extracted with AcOEt (3 x 10 mL). The combined organic layers were washed with brine (1 x 10 mL), dried over Na_2SO_4 and evaporated under vacuum to give the vinyl sulfide. **(*Z*)-4d** was then obtained in ≥ 98% purity by a silica-gel column chromatography (Etp/Et_2O: 8/2, gradient, silica/sample: 200:1) in 89% yield.

Exp Ref	Scheme 1	**Spectra Refs**	
Mol Formula	$C_{17}H_{26}O_2S$	**m.p./b.p.**	oil
Tlc - R_f (solv)	0.33 (Etp/AcOEt 8:2)	**$[\alpha]_D^{25}$ (c. solv)**	4.31 (c = 1.132, $CHCl_3$)

comments: NOESY experiments confirmed the *E*-stereochemistry of the double bond

ν_{max}/cm^{-1}

FT-IR ($CHCl_3$, cm^{-1}): 1051 (w), 1214 (m), 1415 (m), 1675 (s), 1738 (s), 2876 (m), 2964 (s), 3009 (m)

Elemental Analysis : C. 69.34; H. 8.90; Found: C 69.28; H. 8.91.

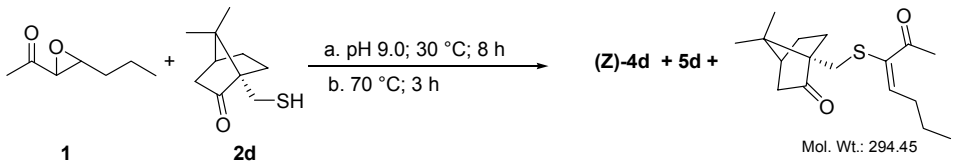
^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	0.89	3	*s*	
	0.95	3	*t*	*J* = 7.4 Hz
	1.04	3	*s*	
	1.35-1.60	4	*m*	
	1.80-1.90	2	*m*	
	1.90-2.10	2	*m*	
	2.26-2.38	1	m	
	2.41	3	s	
	2.48	2	apparent q	*J* = 7.3 Hz
	2.58	1	*d*	*J* = 13.1
	2.93	1	*d*	*J* = 13.1
	6.90	1	t	*J* = 7.3 Hz

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 13.9, 19.9, 20.0, 21.7, 26.7, 27.0, 30.6, 32.7, 38.5, 42.9, 43.4, 47.7, 60.9, 138.8, 148.9, 197.0, 216.9

GC/EIMS (*m/z*) : 294 (M^+ 23), 251 (100), 183 (23), 123 (20), 109 (48), 81 (41)

Chem. Name	(*E*)-3-((1'*S*)-camphoryl-10'-thio)-hept-3-en-2-one ((*E*)-4d)
Lit. Ref.	

Scheme



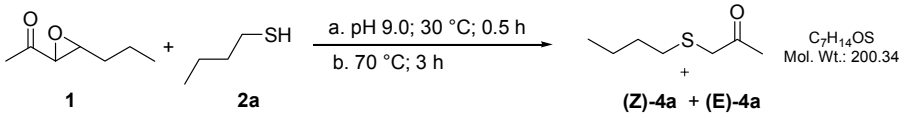
Method: 390 mg (2.0 mmol) of (1*S*)-camphor-10-thiol (**2d**) were added to 3.8 mL of water and 0.2 mL of NaOH 0.1 M aq sol to obtain a resulting pH of 9.0. Then after 5 minutes 256 mg (2.0 mmol) 3,4-epoxy-heptan-2-one (**1**) were added and after additional 8 h under vigorous magnetic stirring at 30 °C, the reaction mixture was warmed to 70 °C. After 3 h the reaction mixture was extracted with Et_2O (3 x 5 mL). The combined organic layers were dried over Na_2SO_4 and evaporated under vacuum to give the mixture of products **(*Z*)-4d** (33%), **(*E*)-4d** (13%), and **5d** (54%). in 97% yield.

comments: Analyses performed on the crude reaction mixture (Table 3 entry 7). Characteristic signal of vinylic proton is reported.

^{1}H NMR 400 MHz $CDCl_3$	δ value	No. H	Mult.	j value/Hz
	6.90	1	*t*	*J* = 7.3 Hz

Chem. Name	1-(butylthio)propan-2-one (5a)

Scheme



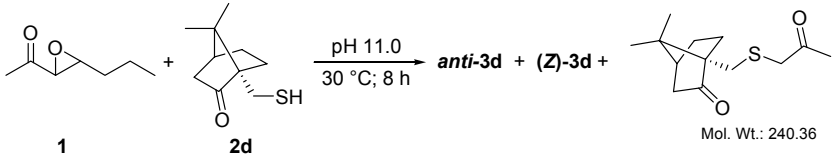
Method: 189 mg (2.1 mmol) of buthylthiol (**2a**) were added to 3.75 mL of water and 0.25 mL of NaOH 0.1 M aq sol to obtain a resulting pH = 9.0. Then after 5 minutes 256 mg (2.0 mmol) of 3,4-epoxy-heptan-2-one (**1**) were added and after additional 0.5 h under vigorous magnetic stirring at 30 °C, the reaction mixture was warmed to 70 °C. After 3 h the reaction mixture was extracted with Et_2O (3 x 5 mL). The combined organic layers were dried over Na_2SO_4 and evaporated under vacuum to give the mixture of products **(*Z*)-4a** (26%), **(*E*)-4a** (14%), and **5a** (60%) in 98% yield.

comments: Analyses performed on the crude reaction mixture (Table 3 entry 1). Characteristic signal of CH_3-C1 and CH_2-C3 are reported.

^{1}H NMR 400 MHz $CDCl_3$	δ value	No. H	Mult.	j value/Hz
	2.27	3	*s*	
	3.19	2	s	

Chem. Name	3-((1'*S*)-camphoryl-10'-thio)-propan-2-one (5d)
Lit. Ref.	

Scheme



Method: 390 mg (2.0 mmol) of (1S)-camphor-10-thiol (**2d**) were added to 3.9 mL of water and 0.1 mL of NaOH 1.0 M aq sol to obtain a resulting pH = 11.0. Then after 5 minutes 256 mg (2.0 mmol) of 3,4-epoxy-heptan-2-one (**1**) were added and the pH maintained around 11.0. After 8 h under vigorous magnetic stirring at 30 °C, the reaction mixture was extracted with AcOEt (3 x 5 mL). The combined organic layers were dried over Na_2SO_4 and evaporated under vacuum to give a mixture of products ***anti*-3d** (18%), **(*Z*)-3d** (9%) **5d** 73%. **5d** was then obtained in ≥ 99% purity by a silica-gel column chromatography (Etp/AcOEt: 7:3, silica/sample: 50:1) in 67% yield.

Exp Ref	Table 1, entry 11	Spectra Refs	
Mol Formula	$C_{13}H_{20}O_2S$	m.p./b.p.	oil
Tlc - R_f (solv)	0.4 (Etp/AcOEt 6:4)	$[\alpha]_D^{25}$ (c. solv)	+ 8.51 (c = 1.41, $CHCl_3$)

comments:

ν_{max}/cm^{-1}

FT-IR (CsI, cm^{-1}): 1051 (w), 1238 (w), 1357 (w), 1417 (w), 1706 (m), 1743 (s), 2965 (m broad)

Elemental Analysis : C. 64.96; H. 8.39. Found: C 64.91; H. 8.28.

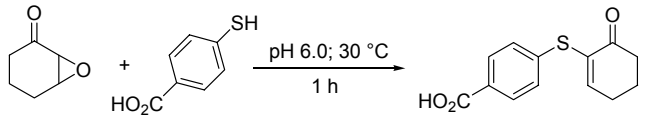
^{1}H NMR 400 MHz $CDCl_3$	δ value	No. H	Mult.	j value/Hz
	0.83	3	*s*	
	0.96	3	*s*	
	1.28-1.36	1	*m*	
	1.45-1.55	1	*m*	
	1.75-2.10	4	*m*	
	2.24	3	*s*	
	2.25-2.35	1	*m*	
	2.40	1	*d*	*J* = 13.0 Hz
	2.71	1	*d*	*J* = 13.0 Hz
	3.24	2	*dd*	*J* = 14.1, 22.3 Hz

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 19.8, 20.1, 26.7, 26.8, 27.7, 29.1, 42.9, 43.4, 44.0, 47.7, 60.8, 203.8, 217.0

GC/EIMS (*m/z*) : 240 (M^+ 100), 197 (17), 182 (59), 167 (9), 139 (53), 123 (32), 109 (67), 93 (32), 81 (73), 67 (48)

Chem. Name	2-(4′-carboxy-phenylthio)-cyclohexene-2-one (7c)
Lit. Ref.	

Scheme



7 **2c** Mol. Wt.: 248.30

Method:
320 mg (2.0 mmol) of 4-mercaptobenzoic (**2c**) acid were dissolved in 3.4 mL of water and 0.6 mL of NaOH 1.0 M aq sol. Then after 5 minutes 224 mg (2.0 mmol) of -2,3-epoxy-cycloxexan-2-one (**7**) were added. After 1 h under vigorous magnetic stirring at 30 °C, the reaction mixture was acidified to pH 2.0 and extracted with AcOEt (3 x 5 mL). The combined organic layers were dried over Na_2SO_4 and evaporated under vacuum to give the crude vinyl sulfide in 98% yield. **7c** was then obtained as solid in ≥ 99% purity by a silca-gel column chromatography (Etp/AcOEt, gradient, silica/sample: 20:1) in 95% yield. The solid was re-crystallizated from acetone.

Exp Ref	Table 3, entry 3	Spectra Refs	
Mol Formula	$C_{13}H_{12}O_3S$	m.p./b.p.	178-179 °C
Tlc - R_f (solv)	0.28 (Etp/AcOEt/AcOH 1:1:0.05)		

comments:

ν_{max}/cm^{-1}

FT-IR ($CHCl_3$, cm^{-1}): 1015 (m), 1088 (m), 1128 (m), 1277 (s), 1290 (s), 1418 (s), 1595 (s), 1693 (s), 2548 (w), 2665 (w), 3011 (w)

Elemental Analysis : C. 62.88; H. 4.87. Found: C 62.64; H. 4.78.

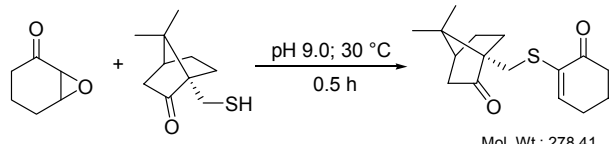
^{1}H NMR 400 MHz acetone$_{d-6}$	δ value	No. H	Mult.	j value/Hz (coupled proton)	Proton
	2.06-215	2	*m*		H-5
	2.50-2.65	4	*m*		H-4,6
	7.27	1	*t*	*J* = 4.2 Hz (H-4)	H-3
	7.37	2	*d*	*J* = 8.2 Hz (H-3′,5′)	H-2′,6′
	7.94	2	*d*	*J* = 8.2 Hz (H-2′,6′)	H-3′,5′

^{13}C NMR (100.6 MHz, acetone$_{d-6}$) δ : 23.2, 28.1, 39.1, 129.0, 129.6, 130.8, 133.8, 142.4, 155.1, 167.0, 194.0

GC/EIMS (*m/z*) : 248 (M^+ 100), 204 (23), 191 (23), 115 (16), 71 (29)

Chem. Name	2-((1′*S*)-camphoryl-10′-thio)-cyclohex-2-en-1-one (7d)
Lit. Ref.	

Scheme



7 **2d** Mol. Wt.: 278.41

Method: 390 mg (2.0 mmol) of (1S)-camphor-10-thiol (**2d**) were added to 3.8 mL of water and 0.2 mL of NaOH 0.1 M aq sol to obtain a resulting pH = 9.0. Then after 5 minutes 224 mg 2,3-epoxy-cyclohexan-1-one (**7**) were added and the pH remained around 9.0. After 0.5 h under vigorous magnetic stirring at 30 °C, the reaction mixture was extracted with Et_2O (3 x 10 mL). The combined organic layers were dried over Na_2SO_4 and evaporated under vacuum to give the crude vinyl sulfide. **7d** was then obtained as an oil in ≥ 98% purity by a silica-gel column chromatography (Etp/Et_2O: gradient, silica/sample: 25:1) in 93% yield.

Exp Ref	Table 3, entry 4	Spectra Refs	
Mol Formula	$C_{16}H_{22}O_2S$	m.p./b.p.	oil
Tlc - R_f (solv)	0.38 (Etp/AcOEt 8:2)	$[\alpha]_D^{25}$ (c. solv)	+ 22.2 (c = 1.28, $CHCl_3$)

comments:

ν_{max}/cm^{-1}

FT-IR (CsI, cm^{-1}): 1051 (m), 1063 (m), 1679 (s), 1741 (s), 2890 (s), 2934 (s), 2958 (s)

Elemental Analysis : C. 69.02; H. 7.96. Found: C 69.11; H. 7.98.

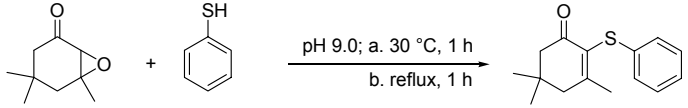
^{1}H NMR 200 MHz $CDCl_3$	δ value	No. H	Mult.	j value/Hz
	0.89	3	*s*	
	1.07	3	*s*	
	1.22-1.57	2	*m*	
	1.80-2.60	11	*m*	
	2.58	1	*d*	*J* = 14.4 Hz
	2.99	1	*d*	*J* = 14.4 Hz
	6.73	1	*t*	*J* = 4.5 Hz

^{13}C NMR (50.3 MHz, $CDCl_3$) δ : 19.6, 19.9, 22.2, 26.0, 26.4, 26.6, 27.0, 38.1, 42.5, 42.8, 47.7, 50.7, 131.6, 141.6, 195.3, 216.4

GC/EIMS (*m/z*) : 278 (M^+ 100), 235 (21), 222 (24), 191 (41), 128 (61), 107 (49), 81 (82), 67 (58), 55 (49)

Chem. Name	3,5,5-methyl-2-(phenylthio)-cyclohexen-2-one (8b)
Lit. Ref.	

Scheme



8 **2b** Mol. Wt.: 246.37

Method: 0.215 mL (2.1 mmol) of thiophenol (**2b**) were added to 3.4 mL of water and 0.6 mL of NaOH 1 M aq sol. Then after 5 minutes 308 mg (2.0 mmol) of isophorone oxide (**8**) were added and the reaction mixture left under vigorous magnetic stirring at 30 °C for 1 h and then warmed to reflux. After 1 h the reaction mixture was extracted with AcOEt (3 x 5 mL). The combined organic layers were dried over Na_2SO_4 and evaporated under vacuum. **8b** was then obtained in ≥ 99% purity by a silica-gel column chromatography (Etp/AcOEt: 9:1 (gradient), silica/sample: 20:1) in 90% yield. 8b was re-crystallized from Et_2O/Hexane: 1/9

Exp Ref	Table 3, entry 5	Spectra Refs	
Mol Formula	$C_{15}H_{18}OS$	m.p./b.p.	white crystals 55-56 °C
Tlc - R_f (solv)	0.6 (Etp/AcOEt 6:4)		

comments:

ν_{max}/cm^{-1}

FT-IR ($CHCl_3$, cm^{-1}): 1371(m) , 1478(m), 1586 (m), 1675(s), 2247 (w) 2871 (w), 2963 (m)

Elemental Analysis : C. 73.13; H. 7.36. Found: C 73.21; H. 7.28.

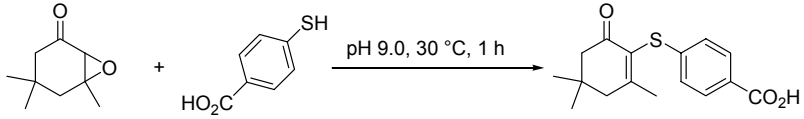
^{1}H NMR 400 MHz $CDCl_3$	δ value	No. H	Mult.	j value/Hz
	1.07	6	*s*	
	2.24	3	*s*	
	2.40	2	*s*	
	2.48	2	*s*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 24.5, 28.2, 32.6, 48.1, 51.6, 125.4, 127.4, 128.6, 136.7, 166.8, 194.6

GC/EIMS (*m/z*) : 246 (M^+ 100), 189 (26), 129 (53), 105 (25) 81 (26), 77 (50)

Chem. Name	3,5,5-methyl-2-(4'carboxy-phenylthio)-cyclohexen-2-one (8c)
Lit. Ref.	

Scheme



8 **2c** Mol. Wt.: 290.38

Method: 323 mg (2.1 mmol) of 4-mercaptobenzoic acid (**2c**) were added to 3.4 mL of water and 0.6 mL of NaOH 1 M aq sol. Then after 5 minutes 308 mg (2.0 mmol) of isophorone oxide (**8**) were added and the reaction mixture left under vigorous stirring at 30 °C. After 1 h the reaction mixture was acidified to pH 2.0 and extracted with AcOEt (3 x 5 mL). The combined organic layers were dried over Na_2SO_4 and evaporated under vacuum to give the crude product in 95% yield. **8c** was then obtained in ≥ 99% purity by re-crystallization from AcOEt

Exp Ref	Table 3, entry 6	Spectra Refs	
Mol Formula	$C_{16}H_{18}O_3S$	m.p./b.p.	white crystals 155-156 °C
Tlc - R_f (solv)	0.41 (Etp/AcOEt/AcOH 1:1:0.2)		

comments:

ν_{max}/cm^{-1}

FT-IR ($CHCl_3$, cm^{-1}): 1083 (w), 1223 (w), 1285 (m), 1586 (s), 1675 (s) 2536 (w), 3082 (w)

Elemental Analysis : C. 66.18; H. 6.25. Found: C 66.21; H. 6.18.

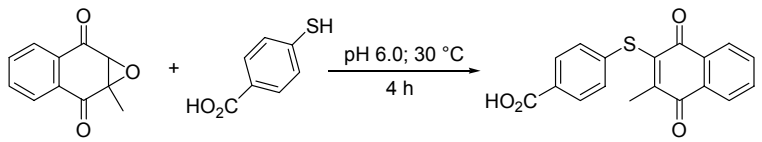
^{1}H NMR 400 MHz Acetone$_{d-6}$	δ value	No. H	Mult.	j value/Hz
	1.09	6	*s*	
	2.28	3	*s*	
	2.44	2	*s*	
	2.65	2	*s*	
	7.20	2	*d*	*J* = 8.3 Hz (H-3' and H-5')
	7.87	2	*d*	*J* = 8.3 Hz (H-2' and H-6')

^{13}C NMR (100.6 MHz, Acetone$_{d-6}$) δ : 24.3, 28.1, 33.0, 48.2, 51.9, 126.5, 127.0, 127.6, 130.6, 144.9, 167.1, 169.1, 193.7

GC/EIMS (*m/z*) : 290 (M^+ 100), 189 (34), 161 (24) 85 (40), 77 (50)

Chem. Name	2-(4'-carboxy-phenylthio)-3-methylnaphtoquinone (9c)
Lit. Ref.	

Scheme



Mol. Wt.: 324.35

Method: 323 mg (2.1 mmol) of 4-mercaptobenzoic acid (**2c**) were added to 3.8 mL of water and 0.2 mL of NaOH 1.0 M aq sol. Then after 5 minutes 376 mg (2.0 mmol) of 2-methyl-naphtoquinone-2,3-oxide (**9**) were added and the reaction mixture left at 30 °C under vigorous magnetic stirring for 4 h. Then the reaction mixture was acidified to pH 2.0 and was extracted with AcOEt (3 x 5 mL). The combined organic layers were dried over Na_2SO_4 and evaporated under vacuum to give the vinyl sulfide in 98% yield. **9c** was then obtained as solid in ≥ 99% purity by a silica-gel column chromatography (Etp/AcOEt, gradient, silica/sample: 20:1) in 96% yield. **9c** was re-crystallized from AcOEt.

Exp Ref	Table 3, entry 7	Spectra Refs	
Mol Formula	$C_{18}H_{12}O_4S$	m.p./b.p.	orange crystals: >250°C (dec.)
Tlc - R_f (solv)	0.49 (Etp/AcOEt/AcOH 1:1:0.05)		

comments:

ν_{max}/cm^{-1}

FT-IR ($CHCl_3$, cm^{-1}): 1110 (m), 1119 (m), 1281 (s), 1595 (s), 1667 (s), 1719 (s), 3014 (w), 3021 (w)

Elemental Analysis : C. 66.65; H. 3.73; Found: C 66.48; H. 3.58.

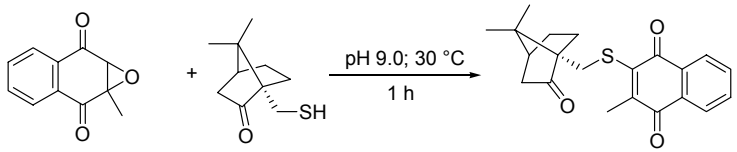
^{1}H NMR 400 MHz THF_{d-8}	δ value	No. H	Mult.	j value/Hz
	2.34	3	*s*	
	7.39	2	*d*	*J* = 8.2 Hz
	7.70-7.80	2	*m*	
	7.88	2	*d*	*J* = 8.2 Hz
	8.00-8.03	1	*m*	
	8.05-8.11	1	*m*	

^{13}C NMR (100.6 MHz, THF_{d-8}) δ : 17.0, 127.9, 128.2, 130.4, 130.8, 131.8, 134.0, 134.4, 135.2, 135.2, 142.4, 144.8, 152.4, 167.9, 181.0, 184.0

GC/EIMS (*m/z*) : (on the methyl ester derivative) **:** 338 (M^+ 100), 323 (32), 307 (20), 279 (82), 115 (24)

Chem. Name	2-((1'*S*)-camphoryl-10'-thio)-3-methylnaphtoquinone (9d)
Lit. Ref.	

Scheme



Mol. Wt.: 354.46

Method: 390 mg (2.0 mmol) of (*1S*)-camphor-10-thiol (**2d**) were added to 3.75 mL of water and 0.25 mL of NaOH 0.1 M aq sol. to obtain a resulting pH = 9.0. Then after 5 minutes 376 mg (2.0 mmol) of 2-methyl-naphtoquinone-2,3-oxide (**9**) were added. After 1 h under vigorous magnetic stirring at 30 °C, the reaction mixture was extracted with AcOEt (3 x 5 mL). The combined organic layers were dried over Na_2SO_4 and evaporated under vacuum to give the title vinyl sulfide. **9d** was then obtained as solid in ≥ 99% purity by a silica-gel column chromatography (Etp/Et_2O: 8/2 gradient, silica/sample: 20:1) in 91% yield. **9d** was obtained re-crystallizated from Et_2O/Hexane: 2/8.

Exp Ref	Table 3, entry 8	Spectra Refs	
Mol Formula	$C_{21}H_{22}O_3S$	m.p./b.p.	orange crystals: 103-104 °C
Tlc - R_f (solv)	0.57 (Etp/AcOEt 6:4)	$[\alpha]_D$ (c. solv)	- 40.6 ($CHCl_3$ c = 1.28)

comments:

ν_{max}/cm^{-1}

FT-IR ($CHCl_3$, cm^{-1}): 1212 (s), 1221 (s), 1656 (m), 1663 (m), 1736 (m), 2978 (m), 3015 (s), 3021 (m), 3027 (s)

Elemental Analysis : C. 71.16; H. 6.26. Found: C 71.11; H. 6.38.

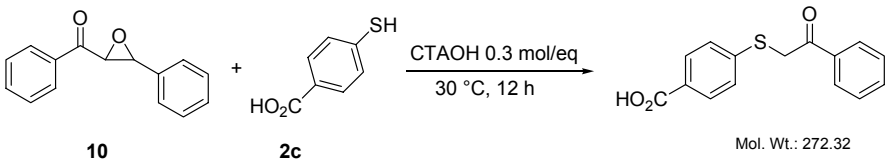
^{1}H NMR 400 MHz $CDCl_3$	δ value	No. H	Mult.	j value/Hz
	0.89	3	*s*	
	1.12	3	*s*	
	1.30-1.45	1	*m*	
	1.55-1.72	1	*m*	
	1.80-2.15	4	*m*	
	2.36	3	*s*	
	2.32-2.40	1	*m*	
	3.15	1	*d*	*J* = 13.6 Hz
	2.54	1	*d*	*J* = 13.6 Hz
	7.60-8.11	4		

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 15.6, 19.8, 20.2, 26.7, 26.9, 31.1, 43.0, 43.5, 48.0, 61.1, 126.4, 126.7, 132.0, 133.1, 133.2, 133.4, 146.0, 148.0, 181.0, 182.3, 216.8

GC/EIMS (*m/z*) : 354 (M^+ 100), 204 (21), 109 (20), 67 (23)

Chem. Name	2-(4'-carboxy-phenylthio)-1-phenylethanone (10c)
Lit. Ref.	

Scheme



Method: 323 mg (2.1 mmol) of 4-mercaptobenzoic acid (**2c**) were added to 2.2 mL of water and 1.8 mL of CTAOH 0.33 M aq sol. Then after 5 minutes 448 mg (2.0 mmol) of calchone oxide (**10**) were added. After 12 h under vigorous magnetic stirring at 30 °C, the reaction mixture was extracted with AcOEt (3 x 5 mL). The combined organic layers were dried over Na_2SO_4 and evaporated under vacuum to give the title retroaldol product in 95% yield. **10c** was re-crystallizated from ethyl AcOEt.

Exp Ref	Table 3, entry 13	Spectra Refs	
Mol Formula	$C_{15}H_{12}O_3S$	m.p./b.p.	177-178 °C
Tlc - R_f (solv)	0.36 (Etp/AcOEt/AcOH 1:1:0.05)		

comments:

ν_{max}/cm^{-1}

FT-IR (nujol, cm^{-1}): 1179 (w), 1291 (w), 1376 (m), 1458 (s), 1592 (s), 1682 (s), 2886 (s), 2909 (s), 2959 (s)

Elemental Analysis : C. 66.16; H. 4.44. Found: C 66.24; H. 4.48.

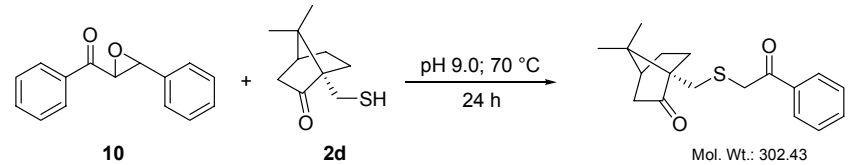
^{1}H NMR 400 MHz acetone$_{d-6}$	δ value	No. H	Mult.	j value/Hz
	4.71	2	*s*	
	7.45-8.0	9	*m*	

^{13}C NMR (100.6 MHz, acetone$_{d-6}$) δ : 39.9, 127.6, 128.6, 129.3, 129.4, 130.7, 134.2, 136.4, 143.6, 167.0, 194.0

GC/EIMS (*m/z*) : (on the methyl ester derivative)**:** 286 (M$^+$ 25), 105 (100), 77 (38)

Chem. Name	3-((1'*S*)-camphoryl-10'-thio)-acetophenone (10d)
Lit. Ref.	

Scheme



Method: 390 mg (2.0 mmol) of (1*S*)-camphor-10-thiol (**2d**) were added to3.6 mL of water and 0.4 mL of NaOH 0.1 M aq sol. to obtain a resulting pH = 9.0. Then after 5 minutes 448 mg (2.0 mmol) of calchone oxide (**10**) were added and the reaction mixture warmed to 70 °C. After 24 h under vigorous magnetic stirring, the reaction was extracted with AcOEt (3 x 5 mL). The combined organic layers were dried over Na_2SO_4 and evaporated under vacuum. **10d** was then obtained in ≥ 99% purity by a silica-gel column chromatography (Etp/AcOEt: 9:1 (gradient), silica/sample: 50:1) in 82% yield.

Exp Ref	Table 3, entry 15	Spectra Refs	
Mol Formula	$C_{18}H_{22}O_2S$	m.p./b.p.	oil
Tlc - R_f (solv)	0.4 (Etp/AcOEt 6:4)	$[\alpha]_D$ (c. solv)	+ 13.3 (c = 1.70, $CHCl_3$)

comments:

ν_{max}/cm^{-1}

FT-IR ($CHCl_3$, cm^{-1}): 1216 (m), 1279 (m), 1415 (w), 1449 (w), 1673 (s), 1737 (s), 2963 (m), 3546 (m)

Elemental Analysis : C. 71.48; H. 7.33. Found: C 71.41; H. 7.28.

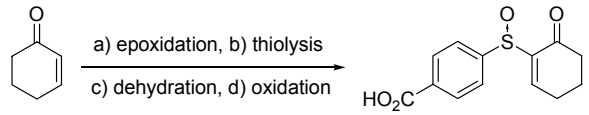
^{1}H NMR 400 MHz $CDCl_3$	δ value	No. H	Mult.	j value/Hz
	0.84	3	*s*	
	0.97	3	*s*	
	1.27-1.35	1	*m*	
	1.45-1.55	1	*m*	
	1.75-2.10	4	*m*	
	2.31	1	*ddd*	*J* = 2.3, 4.8, 18.3 Hz
	2.55	1	*d*	*J* = 13.1 Hz
	2.85	1	*d*	*J* = 13.1 Hz
	3.86	2	*s*	
	7.38-7.58	3	*m*	
	7.90-7.98	2	*m*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 19.8, 20.1, 26.7, 26.8, 29.3, 39.5, 43.0, 43.5, 47.8, 61.0, 128.5 128.6, 133.2, 135.3, 194.5, 217.1

GC/EIMS (*m/z*) : 302 (M$^+$ 100), 183 (30), 182 (36), 139 (41), 120 (23), 109 (25), 105 (97) 81 (26), 77 (50)

Chem. Name	2-(4′-carboxy-phenylsulfinyl)-cyclohexene-1-one (13)
Lit. Ref.	

Scheme



11 Mol. Wt.: 264.30

Method: 0.196 g. (2.0 mmol) of cyclohex-2-en-1-one (**11**) and 0.25 mL (0.5 molar equiv) of 2 M NaOH aqueous solution were added to 1.62 mL of water at 0-2° C. After magnetic stirring at this temperature for 10 minutes, 0.13 mL (1.1 molar equiv) of 35 wt.% aqueous hydrogen peroxide was added (pH ~ 11). After 0.5 h, 340 mg (2.2 mmol) of 4-mercaptobenzoic acid (**2c**) were added and the pH maintained around 6.0 by adding NaOH 1 M aq sol. After 1 h, 416 mg (2.0 molar equiv) of powdered $NaIO_4$ were added and the reaction left under stirring at r.t. for 12 under vigorous magnetic stirring, then the final reaction mixture was acidified to pH 2.0 and extracted with AcOEt (3 x 5 mL). The combined organic layers were dried over Na_2SO_4 and evaporated under vacuum to give the crude title vinyl sulfoxide. **13** was then obtained as solid in ≥ 99% purity by a silica-gel column chromatography (Etp/AcOEt, gradient, silica/sample: 20:1) in 61% yield. **13** was re-crystallizated from acetone.

Exp Ref	Scheme 3	Spectra Refs	
Mol Formula	$C_{13}H_{12}O_3S$	m.p./b.p.	205-206 °C
Tlc - R_f (solv)	0.25 (AcOEt/AcOH 98:2)		

comments:

ν_{max}/cm^{-1}

FT-IR (nujol, cm^{-1}): 1054 (m), 1290 (m), 1314 (m), 1461 (m), 1674 (m), 1687 (m), 2854 (s), 2922 (s),

Elemental Analysis : C. 59.08; H. 4.58. Found: C 59.04; H. 4.47.

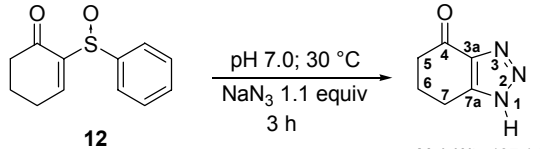
^{1}H NMR 400 MHz DMSO$_{d-6}$	δ value	No. H	Mult.	j value/Hz
	1.80-1.90	1	*m*	
	1.90-200	1	*m*	
	2.26-2.70	4	*m*	
	7.78	2	*d*	*J* = 8.2 Hz
	8.04	2	*d*	*J* = 8.2 Hz

^{13}C NMR (100.6 MHz, DMSO$_{d-6}$) δ : 21.4, 25.6, 37.5, 125.1, 129.7, 133.0, 142.1, 148.2, 151.5, 166.1, 194.6

GC/EIMS (*m/z*) : decomposed

Chem. Name	1,5,6,7-Tetrahydro-4*H*-1,2,3-benzotriazol-4-one (14)
Lit. Ref.	

Scheme



12 Mol. Wt.: 137.14

Method: 450 mg (2.05 mmol) of 2-(phenylsulfinyl)-2-cyclohexenone were added to 4 mL of water and 147 mg (1.1 molar equiv) of powdered NaN_3 were added. The resulting pH was 7.0. After 3 h under magnetic stirring at 30 °C, the pH was adjusted at ca.11 and extracted with AcOEt (3 x 10 mL). The aqueous layer was then acidified to pH 2 and extracted with AcOEt (3 x 10 mL) the latter combined organic layers were dried over Na_2SO_4 and evaporated under vacuum to give **14** in 95% purity. Yield 91%. The product was obtained pure after re-crystallization from acetone

Exp Ref	Scheme 4	Spectra Refs	
Mol Formula	$C_6H_7N_3O$	m.p./b.p.	white crystals 226-227 °C
Tlc - R_f (solv)	0.25 (absolute AcOEt)		

comments:

ν_{max}/cm^{-1}

FT-IR (nujol, cm^{-1}): 846 (w), 992 (w), 1077(w), 1477 (m), 1666 (s), 2889 (m), 2944 (m), 3205 (m broad),

Elemental Analysis : C. 52.55; H. 5.14; N. 30.64; Found: C. 52.59; H. 5.32; N. 30.80.

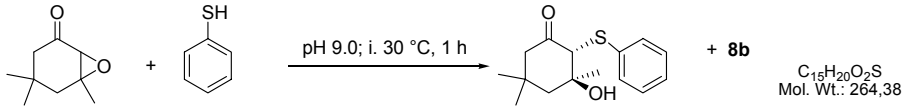
^{1}H NMR 400 MHz DMSO$_{d-6}$	δ value	No. H	Mult.	j value/Hz
	2.04	2	*quintet*	*J* = 6.2 Hz
	2.48	2	*triplet*	*J* = 6.2 Hz
	2.89	2	*triplet*	*J* = 6.2 Hz

^{13}C NMR (100.6 MHz, 330 K, DMSO$_{d-6}$) δ : 19.8, 22.7, 38.4, 139.4, 148.1, 190.2

GC/EIMS (*m/z*) : 137 (76), 109 (100), 108 (43), 80 (33), 53 (62), 52 (55)

Chem. Name	Rel(2R,3S)-3-hydroxy-3,5,5-trimethyl-2-(phenylthio)-cyclohexanone

Scheme



Method: 0.215 mL (2.1 mmol) of thiophenol (**2b**) were added to 3.4 mL of water and 0.6 mL of NaOH 1 M aq sol. Then after 5 minutes 308 mg (2.0 mmol) of isophorone oxide (**8**) were added and the reaction mixture left under stirring at 30 °C for 1h. The reaction mixture was extracted with AcOEt (3 x 5 mL). The combined organic layers were dried over Na_2SO_4 and evaporated under vacuum. The mixture of compound **8b** (20%) and the title hydroxyl sulfide (80%) was isolated in 94% yield.

Rel(2R,3S)-3-hydroxy-3,5,5-trimethyl-2-(phenylthio)-cyclohexanone was characterizated by ^{1}H and ^{13}C NMR analyses of the crude reaction mixture.

^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	1.08	3	*s*	
	1.14	3	*s*	
	1.47	3	*s*	
	1.68	1	*d*	*J* = 14.6 Hz
	1.91	1	*d*	*J* = 14.6 Hz
	2.01	1	*d*	*J* = 13.4 Hz
	3.01	1	*d*	*J* = 13.4 Hz
	3.53	1	*bs*	
	7.25-7.40	5	*m*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 29.1, 29.2, 33.1, 34.9, 46.6, 49.0, 64.9, 77.2, 127.5, 129.0, 131.3,

136.6, 208.7