Pergamon

Tetrahedron: *Asymmetry* 10 (1999) 1369–1380

TETRAHEDRON: *ASYMMETRY*

Enantioselective hydrogenation of β-keto sulfones with chiral Ru(II)-catalysts: synthesis of enantiomerically pure butenolides and γ-butyrolactones

P. Bertus,[a] P. Phansavath,[a] V. Ratovelomanana-Vidal,[a] J.-P. Genêt,[a,*] A. R. Touati,[b] T. Homri [b] and B. Ben Hassine [b]

[a]*Laboratoire de Synthèse Sélective Organique et Produits Naturels, Associé au C.N.R.S., Ecole Nationale Supérieure de Chimie de Paris, 11 rue P. et M. Curie, 75231 Paris Cedex 05, France*

[b]*Faculté des Sciences, Laboratoire de Synthèse Organique et Photochimie, Avenue de l'Environnement, 5000 Monastir, Tunisia*

Received 5 March 1999; accepted 25 March 1999

Abstract

A series of β-hydroxy sulfones were synthesized with high enantioselectivities via a new enantioselective ruthenium-catalyzed hydrogenation using MeO-BIPHEP as a ligand. Some β-hydroxy sulfones were used in the synthesis of optically active butenolides and γ-butyrolactones with high yields and enantioselectivities over 95%.

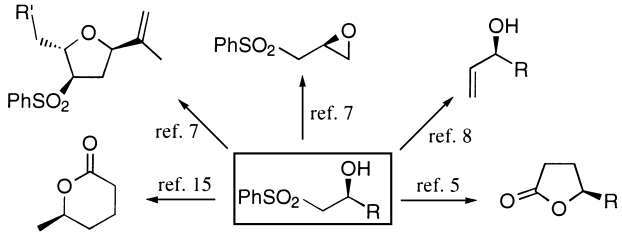
1. Introduction

Recent investigations in this laboratory have focused on the development of asymmetric catalysts for the enantioselective hydrogenation of prochiral olefins and keto groups.[1] Initial work in this area resulted in the first general method[1] for the preparation of chiral Ru(II)-catalysts and their uses in the asymmetric hydrogenation of a wide range of prochiral keto groups.[2] The chiral Ru(II)-catalysts, readily prepared in situ from commercially available CODRu(methylallyl)$_2$ and the chiral diphosphine by addition of methanolic HBr, are highly effective catalysts for the enantioselective hydrogenation of functionalized ketones containing sulfur groups.[1] Because of the potential usefulness of optically active hydroxy sulfones as chiral synthons in organic synthesis, their preparation in enantiomerically pure form has stimulated a great deal of interest.[3,4] These compounds have been used in the synthesis of optically active γ-butyrolactones[5] and δ-valerolactones.[15] They are also key intermediates in obtaining

* Corresponding author. E-mail: genet@ext.jussieu.fr

0957-4166/99/$ - see front matter
PII: S0957-4166(99)00113-5

enantiomerically pure 2,5-disubstituted tetrahydrofuran units or chiral epoxides containing an electron-withdrawing sulfonyl group at the β-position.[7] The alkylation of β-hydroxy sulfones with electrophilic reagents has also been reported, leading to enantiomerically enriched allylic alcohols[8] (Scheme 1).



Scheme 1.

One of the most practical routes to enantiomerically enriched sulfones is the baker's yeast-mediated reduction of β-keto sulfones.[9] However, the corresponding β-hydroxy sulfones were prepared in enantiomeric excesses depending on the substrate: 1-(phenylsulfonyl)propan-2-one was reduced to the (*S*)-alcohol in 98% yield and 95% e.e. If the pentyl or phenyl analogues were submitted to microbial transformation instead, the corresponding hydroxy sulfones were obtained in 10 and 15% e.e., respectively (Scheme 1, R=*n*-C_5H_{11} or Ph), and this is one critical limitation of this reduction.[6,9,10] The kinetic resolution of β-hydroxy sulfones has been described with porcine pancreatic lipase (PPL) with moderate selectivities.[11] A tartaric acid-modified Raney nickel reagent has been employed to perform the chemical reductions of β-keto sulfones in moderate (70%) e.e.[12] This report describes the ruthenium-catalyzed asymmetric hydrogenation of β-keto sulfones as a new application of our simple in situ preparation of chiral Ru(II)-catalysts[1] and a practical route to optically active lactones.

2. Results and discussion

All β-hydroxy sulfones were conveniently prepared through (*S*)-BINAP or (*S*)-MeO-BIPHEP/ruthenium catalyzed hydrogenation of the corresponding β-keto sulfones **1**–**11** easily prepared by condensation of the dianion of methyl phenyl sulfone with various acid chlorides or esters.[13] As a preliminary evaluation of the best experimental reaction conditions, we have examined the ruthenium-promoted hydrogenations of 1-phenylsulfonyl-butan-2-one **1**. The screening tests were carried out on a mmol scale (Table 1). At high pressure (100 bar) and 30°C, a moderate conversion was obtained (entry 1). In decreasing hydrogen pressure to 75 bar at 50°C, very good conversion and enantioselectivity were obtained (entry 2). In lowering the hydrogen pressure to 10 bar at a higher temperature (80°C), the (*R*)-alcohols were synthesized with excellent enantiofacial discrimination with (*R*)-BINAP (entry 3, 92% e.e.) and (*R*)-MeO-BIPHEP (entry 4, e.e. >95%). Finally, the hydrogenation reaction was readily carried out using very mild conditions at atmospheric pressure in refluxing methanol using the (*S*)-configuration of the ligand to afford alcohol (*S*)-**12** in an enantiomerically pure form (entry 5).

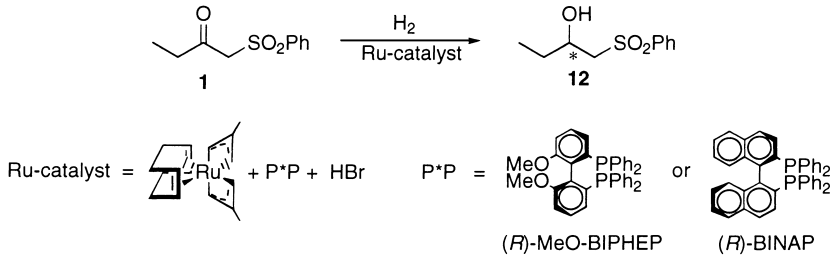


Table 1
Ruthenium-catalyzed hydrogenation of 1-(phenylsulfonyl) butan-2-one **1**

Entry	Ligand	Conditions			alcohol	Conv.	e.e.
		P(bar)	T(°C)	Time	(conf.)		
1	(*R*)-BINAP	100	30	35	(*R*)-**12**	41	-
2	(*R*)-BINAP	75	50	35	(*R*)-**12**	92	90
3	(*R*)-BINAP	10	80	17	(*R*)-**12**	100	92
4	(*R*)-MeO-BIPHEP	10	80	17	(*R*)-**12**	100	>95[a]
5	(*S*)-MeO-BIPHEP	1	65	17	(*S*)-**12**	100	>95[a]

(a) Only one enantiomer was detectable by ^{1}H NMR (250MHz) with Eu(tfc)$_3$.

Hydrogenation reactions of functionalized β-keto sulfones **2**–**5** were therefore conducted at atmospheric pressure in refluxing methanol using 1 mol% of the chiral ruthenium(II) catalyst. Our results are summarized in Table 2. 1-(Phenylsulfonyl)propan-2-one **2** was reduced to (*R*)-1-(phenylsulfonyl)propan-2-ol **13** with a slightly better enantioselectivity using (*R*)-MeO-BIPHEP compared to (*R*)-BINAP (entries 1 and 2). Both enantiomers (*R*)-**13** and (*S*)-**13** were synthesized in enantiomerically pure forms with (*R*)- and (*S*)-MeO-BIPHEP, respectively (entries 2 and 3). However, in the hydrogenation reaction of 1-(phenylsulfonyl) heptan-2-one **3** promoted by ruthenium–BINAP complexes, both the activity and enantiomeric excess were moderate (entry 4, 82% e.e.) in contrast to the high enantiofacial discrimination and complete conversion observed with (*R*)-MeO-BIPHEP (entry 5, e.e. >95%).

When the β-keto sulfone **4** was substituted with a cyclohexyl ring, both (*R*)-BINAP and (*S*)-MeO-BIPHEP led to comparable yields and enantioselectivities (entries 6 and 7, 91% and >95% e.e.). The ruthenium-mediated hydrogenation of 3-chloro-1-(phenylsulfonyl) propan-2-one **5** proceeded smoothly to afford (*R*)-**16** with high enantioselectivity (entry 8, 90% e.e.). The ruthenium-mediated hydrogenation of β-keto sulfones **6**, **7** and **8**, bearing a long alkyl chain, required 10 bar and 80°C to afford the corresponding enantiomerically pure β-hydroxy sulfones **17**, **18** and **19** with complete conversions (entries 9 to 13). Finally, the hydrogenation reaction of β-keto sulfones bearing an aromatic substituent **9**, **10** and **11** required more drastic conditions: 1-phenyl-2-(phenylsulfonyl)ethan-1-one **9** was not completely hydrogenated at atmospheric pressure (entry 14). When conducted at 75 bar and 80°C, the hydrogenation reaction quantitatively yielded the corresponding β-hydroxy sulfone **20** with 88% e.e. (entry 15). When the temperature was decreased to 40°C (entry 16), a significant increase in the enantiofacial discrimination was observed, leading to the corresponding β-hydroxy sulfone (*S*)-**20** with excellent enantioselectivity (over 95%). The influence of the temperature was also observed when the phenyl ring was substituted with a chlorine or fluorine group in the *para*-position, and the corresponding β-hydroxysulfones (*R*)-**21** and (*R*)-**22** were synthesized with high selectivities (entries 17 and 18).

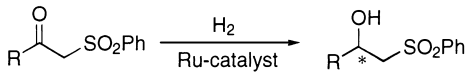


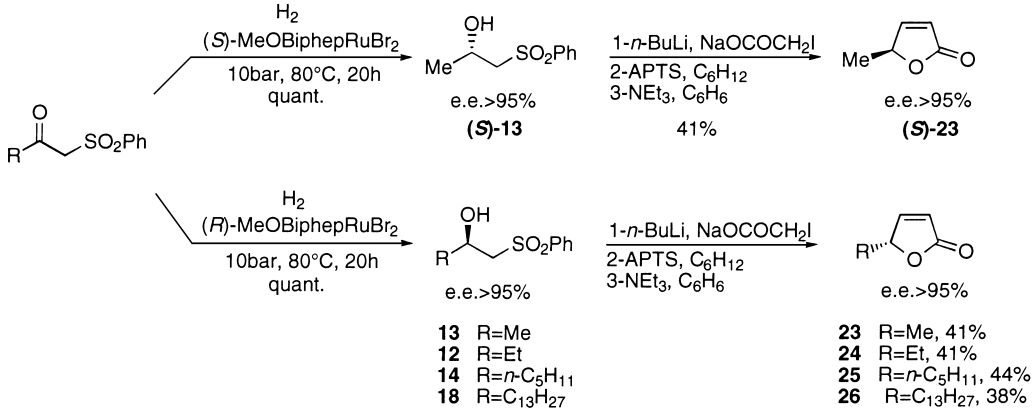
Table 2
Ruthenium-catalyzed hydrogenation of functionalized sulfones

Entry	Substrate	Ligand P*P	Conditions[a,b] P(bar)	T(°C)	Time(h)	Conv	Conf. / e.e.[c]
1	$MeCOCH_2SO_2Ph$ **2**	(*R*)-BINAP	1bar	65°C	24h	90	(*R*)-**13** (91%)
2	**2**	(*R*)-MeO-BIPHEP	1bar	65°C	24h	100	(*R*)-**13** (>95%)
3	**2**	(*S*)-MeO-BIPHEP	1bar	65°C	24h	100	(*S*)-**13** (>95%)
4	$nC_5H_{11}COCH_2SO_2Ph$ **3**	(*S*)-BINAP	1bar	65°C	24h	67	(*S*)-**14** (82%)
5	**3**	(*R*)-MeO-BIPHEP	1bar	65°C	24h	100	(*R*)-**14** (>95%)
6	$C_6H_{11}COCH_2SO_2Ph$ **4**	(*R*)-BINAP	1bar	65°C	24h	100	(*R*)-**15** (91%)
7	**4**	(*S*)-MeO-BIPHEP	1bar	65°C	24h	100	(*S*)-**15** (>95%)
8	$ClCH_2COCH_2SO_2Ph$ **5**	(*S*)-MeO-BIPHEP	1bar	65°C	24h	100	(*R*)-**16** (90%)
9	$C_{11}H_{23}COCH_2SO_2Ph$ **6**	(*R*)-MeO-BIPHEP	10bar	80°C	18h	100	(*R*)-**17** (>95%)
10	**6**	(*S*)-MeO-BIPHEP	10bar	80°C	18h	100	(*S*)-**17** (>95%)
11	$C_{13}H_{27}COCH_2SO_2Ph$ **7**	(*R*)-MeO-BIPHEP	10bar	80°C	18h	100	(*R*)-**18** (>95%)
12	$C_{15}H_{31}COCH_2SO_2Ph$ **8**	(*R*)-MeO-BIPHEP	10bar	80°C	18h	100	(*R*)-**19** (>95%)
13	**8**	(*S*)-MeO-BIPHEP	10bar	80°C	18h	100	(*S*)-**19** (>95%)
14	$PhCOCH_2SO_2Ph$ **9**	(*S*)-MeO-BIPHEP	1bar	65°C	24h	54	(*S*)-**20** (92%)
15	**9**	(*S*)-MeO-BIPHEP	75bar	80°C	24h	100	(*S*)-**20** (88%)
16	**9**	(*S*)-MeO-BIPHEP	75bar	40°C	24h	100	(*S*)-**20** (>95%)
17	*p*-Cl-$PhCOCH_2SO_2Ph$ **10**	(*R*)-MeO-BIPHEP	75bar	40°C	24h	100	(*R*)-**21** (>95%)
18	*p*-F-$PhCOCH_2SO_2Ph$ **11**	(*R*)-MeO-BIPHEP	75bar	40°C	24h	100	(*R*)-**22** (94%)

(a) Chiral Ru(II)-catalyst (1 or 2 mol %). (b) Reaction times are not optimized. (c) Enantiomeric excesses were determined by ^1H NMR (250 or 400 MHz) with $Eu(tfc)_3$ (e.e.>95% means that only one enantiomer was detectable). The absolute configurations of the β-hydroxy sulfones **13**, **14**, **16**, **18**, **20** were assigned by comparison of their specific rotations with those described in the literature.[9,14,15] We assumed that for compounds **15**, **17**, **19**, **21** and **22**, the hydrogenation reaction follows the same stereochemical course as above.[2]

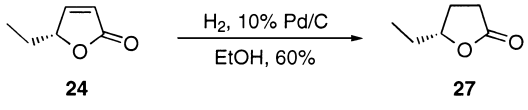
Butenolides and saturated γ-lactones are incorporated in the structures of a variety of natural compounds such as flavor components and insect pheromones.[16,17] Having in hand a highly practical and enantioselective route to both enantiomers of various β-hydroxy sulfones, we applied this methodology to the stereoselective synthesis of some butenolides and γ-butyrolactones. All butenolides were con-

veniently prepared from the corresponding β-hydroxysulfones via a three-step sequence:[18] reaction of the dianion of the β-hydroxy sulfones **12**–**14** and **18** with sodium acetate followed by acid catalyzed lactonization and elimination of phenyl sulfonyl group with triethylamine. The syntheses of (*R*)- and (*S*)-angelica lactone **23**, which are interesting synthons for the preparation of natural products bearing a γ-lactone moiety, were reported for the first time by Font in 11 steps from tartaric acid.[19] Since then a considerable number of syntheses have been described, including a one-step procedure from methyl *trans*-3-pentenoate affording (*S*)-angelica lactone in 78% e.e.[20] Thus, we prepared both enantiomers (*R*)- and (*S*)-β-angelica lactone **23**, from the corresponding enantiomerically pure β-hydroxysulfones **13**, in equal overall yields (41%) and in almost enantiomerically pure forms (Scheme 2). A butenolide bearing a long alkyl chain (i.e. γ-tridecylbutenolide **26**) was synthesized in 38% overall yield and enantiomerically pure form. This compound is a key intermediate in the synthesis of the natural lactone fatty acid (−)-protolichesterinic.[18,21]



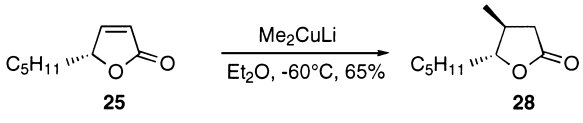
Scheme 2.

Following the same general sequence (Scheme 2) with an additional hydrogenation step (Scheme 3), we achieved the synthesis of optically pure (*R*)-hexanolide, a component of the pheromone secreted by the female dermestid beetle *Trogoderma glabrum* L.[5,22]



Scheme 3.

The *trans* tetrahydro-4-methyl-5-pentylfuran-2-one **28**, identified as an aroma component of cognac, was obtained from the pure butenolide **25** (Scheme 2) by conjugate addition of lithium dimethyl cuprate in 65% yield (Scheme 4).[23]



Scheme 4.

3. Conclusion

When comparing the present results of reductions of the β-keto sulfones to those using baker's yeast, the following comments can be made: in the case of baker's yeast mediated reductions, an increase in the number of carbon atoms adjacent to the carbonyl group decreases the e.e. values. Enzymatic reduction and ruthenium-catalyzed hydrogenation give similar yields and enantioselectivities for compound **2**.[9] However, the ruthenium-promoted hydrogenation reaction of β-keto sulfones can be conducted at atmospheric pressure and gives, in most cases, more satisfactory e.e. values compared to those using baker's yeast[9] and this was the most efficient method. Our technique is advantageous for several reasons, i.e. its wide scope and predictable absolute configurations of the chiral β-hydroxy sulfones because of the ready availability of the chiral Ru(II)-catalyst in either enantiomeric forms. Furthermore, this simple process gives high yields and a practical route to enantiomerically pure butenolides and γ-lactones.

4. Experimental

4.1. General

All NMR spectra were measured in $CDCl_3$ using a Bruker AC 200 or 400 instrument, and chemical shifts are expressed in ppm relative to internal $CHCl_3$ (7.26 ppm). Infrared spectra were recorded on a Perkin–Elmer 783 spectrometer. Optical rotations were measured on a Perkin–Elmer 241 polarimeter. Enantiomeric excesses were determined by ^{1}H NMR with $Eu(tfc)_3$.

4.2. General procedure for the preparation of 2-ketosulfones[13b]

Butyllithium (11.2 mL of a 2.5 M solution, 28 mmol) was added slowly under argon to a solution of methyl phenyl sulfone (2.0 g, 13 mmol) in 40 mL of anhydrous THF at −30°C. After 30 min, the acid chloride (15 mmol) was slowly added by syringe. Subsequently, the reaction mixture was poured into 150 mL of a saturated NH_4Cl solution and stirred. The β-keto sulfone was extracted with dichloromethane and the organic phase was washed with a saturated NaCl solution, dried with magnesium sulfate, filtered and concentrated. Recrystallization from CCl_4 or column chromatography of the crude product afforded the β-keto sulfones **1**, **3**, **4** and **6**–**9**.

1-(Phenylsulfonyl)propan-2-one **2** is commercially available from Aldrich. Compound **5** was prepared by condensation of methylphenylsulfone with ethyl chloroacetate[13a] while syntheses of **10** and **11** were performed in two steps according to a literature procedure.[13c]

4.2.1. (Phenylsulfonyl)butan-2-one *1*

A white solid (2.0 g, 73%): mp 48°C. IR ($CHCl_3$): 1720, 1330, 1150 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.08 (3H, t, J=7.2 Hz), 2.75 (2H, q, J=7.2 Hz), 4.17 (2H, s), 7.54 (3H, m), 7.85–7.95 (2H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ 7.3, 37.8, 66.7, 128.2, 129.3, 134.2, 138.7, 198.6. MS (EI): m/e=212 (14, M^+), 183 (18), 141 (27).

4.2.2. (Phenylsulfonyl)heptan-2-one *3*

A pale yellow solid (1.75 g, 73%): mp 38°C. IR ($CHCl_3$): 1710, 1310, 1150 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (3H, t, J=6.6 Hz), 1.15–1.35 (4H, m), 1.55 (2H, quint, J=7.2 Hz), 2.69 (2H, t, J=7.2

Hz), 4.15 (2H, s), 7.53–7.73 (3H, m), 7.86–7.90 (2H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.8, 22.3, 22.7, 30.9, 44.3, 66.7, 128.2, 129.3, 134.2, 138.7, 198.2. MS (EI): m/e=255 (10, M+H), 198 (19), 141 (42).

4.2.3. Cyclohexyl-2-phenylsulfonyl-ethan-1-one ***4***

A white solid (2.4 g, 69%): mp 89°C. IR ($CHCl_3$): 1710, 1310, 1150 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.10–1.40 (5H, m), 1.60–1.90 (5H, m), 2.50–2.70 (1H, m), 4.20 (2H, s), 7.5–7.7 (3H, m), 7.88 (2H, d, J=7.0 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 25.2, 25.5, 27.8, 51.4, 64.7, 128.3, 129.2, 134.1, 138.9, 201.2. MS (EI) m/e=267 (4, $M-H^+$), 141 (18), 124 (66).

4.2.4. Chloro-1-phenylsulfonyl-propan-2-one ***5***

A white solid (1.4 g, 60%): mp 48°C. IR ($CHCl_3$): 1720, 1310, 1160 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.39 (4H, s), 7.58–7.78 (3H, m), 7.89–7.94 (2H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ 48.7, 64.1, 128.3, 129.5, 134.6, 138.1, 190.2. MS (EI): m/e=232 (9, M^+), 183 (35), 141 (85).

4.2.5. (Phenylsulfonyl)tridecan-2-one ***6***

A white solid (2.2 g, 50%): mp 74°C. IR ($CHCl_3$): 1725, 1320, 1160 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.87 (3H, t, J=6.3 Hz), 1.23 (18H, s), 1.57 (2H, m), 2.69 (2H, t, J=7.2 Hz), 4.14 (2H, s), 7.53–7.72 (3H, m), 7.85–7.90 (2H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0, 22.6, 23.0, 28.7, 29.2, 29.5, 31.8, 44.4, 66.7, 128.2, 129.2, 134.2, 138.5, 198.0.

4.2.6. (Phenylsulfonyl)pentadecan-2-one ***7***

A white solid (2.5 g, 52%): mp 75°C. IR ($CHCl_3$): 1710, 1320, 1160 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.87 (3H, t, J=6.4 Hz), 1.24 (2H, s), 1.54 (22H, m), 2.69 (2H, t, J=7.2 Hz), 4.14 (2H, s), 7.53–7.72 (3H, m), 7.85–7.90 (2H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.1, 22.6, 23.1, 28.8, 29.3, 29.6, 32.0, 44.4, 66.7, 128.2, 129.3, 134.2, 138.7, 198.2.

4.2.7. (Phenylsulfonyl)heptadecan-2-one ***8***

A white solid (4.2 g, 41%): mp 77°C. IR ($CHCl_3$): 1710, 1320, 1160 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.87 (3H, t, J=6.5 Hz), 1.25 (25H, s), 1.57 (2H, m), 2.69 (2H, t, J=7.2 Hz), 4.14 (2H, s), 7.53–7.72 (3H, m), 7.85–7.90 (2H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0, 22.6, 23.0, 28.7, 29.2, 29.6, 31.8, 44.4, 66.7, 128.2, 129.2, 134.2, 138.6, 198.2.

4.2.8. Phenyl-2-phenylsulfonyl-ethan-1-one ***9***

A white solid (2.6 g, 76%): mp 100°C. IR ($CHCl_3$): 1700, 1320, 1160 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.77 (2H, s), 7.47–7.74 (6H, m), 7.90–8.00 (4H, m). ^{13}C NMR (50 MHz, $CDCl_3$): δ 63.2, 128.4, 128.7, 129.1, 134.1, 134.2, 135.5, 138.6, 187.9. MS (EI): m/e=260 (0.5, M^+), 196 (45), 105 (100).

4.2.9. p-*Chlorophenyl-2-phenylsulfonyl-ethan-2-one* ***10***

A white solid: mp 118°C. IR ($CHCl_3$): 1690, 1330, 1170 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.73 (2H, s), 7.28–7.70 (5H, m), 7.87–7.94 (4H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ 63.5, 128.4, 129.2, 130.6, 133.9, 134.3, 138.5, 141.0, 186.7. MS (EI): m/e=294 (0.9, M^+), 139 (100), 77 (54).

4.2.10. p-*Fluorophenyl-2-phenylsulfonyl-ethan-2-one* ***11***

A white solid: mp 115°C. IR ($CHCl_3$): 1670, 1310, 1160 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.73 (2H, s), 7.14–7.75 (5H, m), 7.89–8.06 (4H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ 63.5, 128.4, 129.2, 132.0, 132.2, 134.2, 138.5, 186.3. MS (EI): m/e=278 (0.5, M^+), 123 (100), 77 (50).

*4.3. Typical procedure for the asymmetric hydrogenation of β-keto sulfones **1–11** to β-hydroxysulfones **12–22***

(*R*)-MeO-BIPHEP (7.0 mg, 0.012 mmol) and CODRu(2-methylallyl)$_2$ (3.2 mg, 0.01 mmol, commercially available from Acros), were placed in a Schlenk tube and dissolved in 1 mL of acetone (degassed by three cycles of vacuum/argon at room temperature). To this suspension was added 147 μL of a 0.15 N methanolic HBr solution (0.022 mmol) and the mixture was stirred at room temperature for 30 min. A yellow solid precipitated. The solvent was evaporated under vacuum and keto sulfone (1 mmol) in MeOH (1 mL) was added to the Ru(II)-catalyst. The resulting mixture was placed under the desired hydrogen pressure and temperature for 18–35 h. After removal of the solvent, the residue was purified by silica gel chromatography to afford the hydroxysulfone.

All reactions were run on a 1 mmol scale and led to the corresponding β-hydroxysulfones in quantitative yields except where specified.

*4.3.1. (*S*)-1-(Phenylsulfonyl)propan-2-ol (*S*)-**13***

Starting from 1.4 g (7 mmol) of **2**, the reaction yielded 1.4 g (7 mmol, 100%) of **13** as a pale yellow oil. $[\alpha]_D^{20}$=+15 (*c* 1.6, $CHCl_3$), lit.[11] $[\alpha]_D^{25}$=+15.1 (*c* 1.3, $CHCl_3$). IR ($CHCl_3$): 3500, 1310, 1150 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.25 (3H, d, J=6.4 Hz), 3.13–3.43 (3H, m), 4.27–4.42 (1H, m), 7.47–7.71 (3H, m), 7.93–7.98 (2H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.6, 62.3, 63.3, 127.9, 129.5, 134.1, 139.13. MS (EI): m/e=201 (8, M−H$^+$), 141 (39).

*4.3.2. (*R*)-1-(Phenylsulfonyl)butan-2-ol (*R*)-**12***

Starting from 414 mg (1.95 mmol) of **1**, the reaction yielded 380 mg (1.77 mmol, 91%) of **12** as a white solid: mp 50°C. $[\alpha]_D^{20}$=−22 (*c* 1.0, $CHCl_3$). IR ($CHCl_3$): 3500, 1300, 1150 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.94 (3H, t, J=7.4 Hz), 1.44–1.67 (2H, m), 3.16–3.32 (2H, m), 3.40 (1H, s, OH), 4.02–4.20 (1H, m), 7.59–7.75 (3H, m), 7.92–7.97 (2H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ 9.3, 29.4, 61.9, 67.1, 127.8, 129.4, 134.0, 139.2. MS (EI): m/e=214 (15, M−H$^+$), 185 (65), 141 (48).

*4.3.3. (*R*)-1-(Phenylsulfonyl)heptan-2-ol (*R*)-**14***

Starting from 1.38 g (5.4 mmol) of **3**, the reaction yielded 1.26 g (4.9 mmol, 91%) of **14** as a colorless oil. $[\alpha]_D^{20}$=−15 (*c* 1.04, $CHCl_3$), lit.[12] $[\alpha]_D^{20}$=−19.9 (*c* 5, EtOH). IR ($CHCl_3$): 3450, 1310, 1150 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.81–0.95 (3H, m), 1.20–1.80 (8H, m), 3.20–3.40 (3H, m), 4.10–4.25 (1H, m), 7.51–7.80 (3H, m), 7.90–8.00 (2H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.9, 22.4, 24.6, 31.4, 36.4, 62.2, 65.9, 127.9, 129.4, 134.0, 139.3. MS (EI): m/e=255 (M−H$^+$), 198 (13), 141 (21).

*4.3.4. (*R*)-1-Cyclohexyl-2-phenylsulfonyl-ethan-1-ol (*R*)-**15***

A colorless oil. $[\alpha]_D^{20}$=−20 (*c* 1.0, $CHCl_3$). IR ($CHCl_3$): 3550, 1310, 1150 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.95–1.90 (11H, m), 3.20–3.30 (2H, m), 3.47 (1H, s, OH), 3.91–3.98 (1H, m), 7.55–7.73 (3H, m), 7.91–7.96 (2H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ 25.8, 25.9, 26.1, 27.4, 28.4, 43.1, 60.2, 69.7, 127.8, 129.4, 133.9, 139.2. MS (EI): m/e=269 (5, M−H$^+$), 185 (100), 141 (55).

*4.3.5. (*S*)-1-Phenyl-2-phenylsulfonyl-ethan-1-ol (*S*)-**20***

A white solid: mp 112°C. $[\alpha]_D^{20}$=+29 (*c* 1.0, $CHCl_3$). IR ($CHCl_3$): 3450, 1310, 1150 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.35 (1H, dd, J=14.3 and 2.0 Hz), 3.50 (1H, dd, J=14.3 and 9.8 Hz), 3.67 (1H, s, OH), 5.28 (1H, dd, J=9.8 and 2.0 Hz), 7.25–7.31 (5H, m), 7.50–7.78 (3H, m), 7.94–7.98 (2H, m). ^{13}C

NMR (50 MHz, $CDCl_3$) δ 63.9, 68.4, 125.6, 128.0, 128.3, 128.8, 129.5, 134.1, 139.2, 140.6. MS (EI): m/e=262 (8, M^+), 244 (12), 120 (100).

*4.3.6. (2*R*)-1-(Phenylsulfonyl)tridecan-2-ol (*R*)-**17** and (2*S*)-1-(phenylsulfonyl)tridecan-2-ol (*S*)-**17***

A white solid: mp 69°C. $[\alpha]_D^{20}$=−11 for (*R*)-**17** or +11 for (*S*)-**17** (*c* 1.0, $CHCl_3$). IR ($CHCl_3$): 3450, 1310, 1150 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ 0.90 (3H, t, J=7.0 Hz), 1.26–1.59 (20H, m), 3.21–3.32 (3H, m), 4.18 (1H, m), 7.59–7.72 (3H, m), 7.96 (2H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0, 22.6, 24.9, 29.2, 29.4, 29.5, 30.4, 31.8, 36.4, 62.2, 65.9, 127.8, 129.4, 133.9, 139.2.

*4.3.7. (2*R*)-1-Phenylsulfonylpentadecan-2-ol (*R*)-**18***

Starting from 2 g (5.4 mmol) of **7**, the reaction yielded 1.8 g (4.8 mmol, 90%) of **18** as a white solid: mp 78°C. $[\alpha]_D^{20}$=−19 (*c* 1.0, $CHCl_3$), lit.[24] $[\alpha]_{365}^{22}$=−2.0 (*c* 1.10, MeOH). IR ($CHCl_3$): 3500, 1310, 1160 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ 0.89 (3H, t, J=6.8 Hz), 1.20–1.75 (24H, m), 3.21–3.40 (3H, m), 4.18 (1H, m), 7.58–7.71 (3H, m), 7.97 (2H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0, 22.6, 24.8, 29.2, 29.4, 29.5, 31.8, 36.3, 62.1, 65.8, 127.8, 129.3, 133.9, 139.2.

*4.3.8. (2*R*)-1-Phenylsulfonylheptadecan-2-ol (*R*)-**19** and (2*S*)-1-phenylsulfonylheptadecan-2-ol (*S*)-**19***

A white solid: mp 84°C. $[\alpha]_D^{20}$=−10 for (*R*)-**19** or +10 for (*S*)-**19** (*c* 1.0, $CHCl_3$). IR ($CHCl_3$): 3500, 1310, 1160 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ 0.91 (3H, t, J=7.0 Hz), 1.25–1.58 (28H, m), 3.21–3.35 (3H, m), 4.20 (1H, m), 7.62–7.72 (3H, m), 7.96 (2H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.1, 22.7, 25.0, 29.3, 29.6, 31.9, 36.4, 62.3, 65.9, 127.9, 129.5, 134.0, 139.3.

*4.3.9. (2*R*)-3-Chloro-1-phenylsulfonyl-propan-2-ol (*R*)-**16***

A white solid: mp 93°C. $[\alpha]_D^{20}$=+7 (*c* 1.0, MeOH), lit.[18] $[\alpha]_D^{24}$=+10.15 (*c* 1.0, MeOH). IR ($CHCl_3$): 3450, 1310, 1160 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ 3.39 (3H, m), 3.63 (2H, d, J=5.0 Hz), 4.40 (1H, s), 7.57–7.72 (3H, m), 7.94–7.98 (2H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ 47.5, 59.5, 66.1, 127.9, 129.4, 134.2, 138.9.

*4.3.10. (1*R*)-1-*p*-Chlorophenyl-2-phenylsulfonyl-ethan-1-ol (*R*)-**21***

A white solid: mp 92°C. $[\alpha]_D^{20}$=−20 (*c* 5.0, $CHCl_3$). IR ($CHCl_3$): 3500, 1300, 1143 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ 3.34 (1H, dd, J=14.3 and 2.4 Hz), 3.51 (1H, dd, J=14.3 and 9.6 Hz), 3.94 (1H, s), 5.28 (1H, dd, J=9.6 and 2.1 Hz), 7.08–7.28 (4H, m), 7.52–7.72 (3H, m), 7.90–8.32 (2H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ 63.7, 67.7, 127.0, 127.8, 128.4, 128.8, 129.4, 134.0, 134.1, 139.0. MS (EI): m/e=296 (11, M^+), 154 (100), 77 (53).

*4.3.11. (1*R*)-1-*p*-Fluorophenyl-2-phenylsulfonyl-ethan-1-ol (*R*)-**22***

A white solid: mp 68°C. $[\alpha]_D^{20}$=−23 (*c* 3.0, $CHCl_3$). IR ($CHCl_3$): 3510, 1300, 1143 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ 3.34 (1H, dd, J=14.3 and 2.3 Hz), 3.52 (1H, dd, J=14.3 and 9.7 Hz), 3.80 (1H, s), 5.29 (1H, dd, J=9.7 and 2.3 Hz), 6.93–7.02 (2H, m), 7.23–7.30 (2H, m), 7.54–7.69 (3H, m), 7.91–7.96 (2H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ 63.7, 67.7, 127.3, 127.5, 127.9, 129.4, 134.1, 136.5, 139.0. MS (EI): m/e=262 (8, M^+), 244 (12), 120 (100).

*4.4. General procedure for the preparation of butenolides **23–26**[18]*

A solution of *n*-butyllithium (15.5 mmol) in hexane was added dropwise to a solution of β-hydroxy sulfone (7 mmol) in tetrahydrofuran (50 mL) at −78°C under an argon atmosphere. After being stirred

at −78°C for 30 min and at −10°C for 2 h, sodium iodoacetate (1.77 g, 8.5 mmol) was added at −78°C. The resulting mixture was allowed to warm to 0°C with stirring for 15 h, then quenched with aqueous saturated ammonium chloride (10 mL), and acidified with 10% hydrochloric acid (10 mL). The organic layer was separated, the aqueous layer extracted with ether (150 mL), and the combined organic phase dried with magnesium sulfate and concentrated. The residue was dissolved in benzene (80 mL) and a catalytic amount of *p*-toluenesulfonic acid was added. The solution was refluxed for 2 h, the water being removed with a Dean–Stark apparatus. The cooled benzene layer was washed with aqueous 5% sodium hydrogen carbonate (50 mL), and dried with magnesium sulfate. After filtering off the magnesium sulfate, triethylamine (2.53 g, 25 mmol) was added to the benzene solution and the resulting mixture was stirred at room temperature for 15 h, washed with 10% hydrochloric acid (50 mL), and dried with magnesium sulfate. The solvent was evaporated and the residue purified by column chromatography on silica gel affording enantiomerically pure butenolides **23**–**26**.

*4.4.1. (*S*)-(+)-Methyl-2(5*H*)-furanone [(S)-(+)-β-angelica lactone)]* ***23***

A colorless oil (280 mg, 41%). $[\alpha]_D^{20}$=+95 (*c* 0.5, $CHCl_3$), lit.[24] $[\alpha]_D^{20}$=+93.8 (*c* 0.5, $CHCl_3$). IR ($CHCl_3$): 1810, 1570, 1470, 1220 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ 1.44 (3H, d, J=6.9 Hz), 5.14 (1H, m), 6.08 (1H, dd, J=1.9 and 5.6 Hz), 7.45 (1H, dd, J=1.1 and 5.6 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 18.7, 79.5, 121.1, 157.3, 173.0.

*4.4.2. (*R*)-5-Ethyl-2(5*H*)-furanone* ***24***

A colorless oil (82 mg, 41%). $[\alpha]_D^{20}$=−94 (*c* 1.05, CH_2Cl_2), lit.[21a] $[\alpha]_D^{23}$=−95 (liq. l=1 dm). ^1H NMR (200 MHz, $CDCl_3$) δ 0.97 (3H, t, J=7.4 Hz), 1.65–1.91 (2H, m), 5.00 (1H, m), 6.11 (1H, dd, J=1.9 and 5.8 Hz), 7.44 (1H, dd, J=1.4 and 5.6 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 8.9, 26.1, 84.2, 121.6, 155.9, 173.0.

*4.4.3. (*R*)-5-Pentyl-2(5*H*)-furanone* ***25***

A colorless oil (320 mg, 44%). $[\alpha]_D^{20}$=−84 (*c* 1.30, $CHCl_3$), lit.[23a] $[\alpha]_D^{20}$=−85 (*c* 1.36, $CHCl_3$). IR ($CHCl_3$): 1760, 1620, 1310, 1160 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ 0.89 (3H, t, J=6.6 Hz), 1.22–1.79 (8H, m), 5.04 (1H, m), 6.10 (1H, dd, J=1.9 and 5.8 Hz), 7.45 (1H, dd, J=1.4 and 5.6 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.8, 22.3, 24.5, 31.3, 33.0, 83.3, 121.4, 156.2, 173.1.

*4.4.4. (*R*)-5-Tridecyl-2(5*H*)-furanone* ***26***

A white solid (370 mg, 38%): mp 50°C. $[\alpha]_D^{20}$=−49 (*c* 2.0, dioxane), lit.[21b] $[\alpha]_D^{25}$=−51.7 (*c* 2.0, dioxane). IR ($CHCl_3$): 1750, 1610, 1580, 1170 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ 0.88 (3H, t, J=6.4 Hz), 1.10–1.76 (24H, m), 5.04 (1H, m), 6.11 (1H, dd, J=1.9 and 5.6 Hz), 7.44 (1H, dd, J=1.4 and 5.6 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0, 22.5, 24.8, 29.2, 29.4, 29.5, 31.8, 33.0, 83.3, 121.3, 156.3, 173.0.

4.5. Preparation of γ-lactones ***27***–***28***

*4.5.1. (*R*)-(+)-4-Hexanolide* ***27***

To a degassed solution of **24** (63 mg, 0.56 mmol) in MeOH (5 mL) was added 10% Pd/C (100 mg). The resulting mixture was placed under a hydrogen atmosphere and stirred overnight. After filtration through Celite and removal of the solvent, the residue was purified by silica gel chromatography to afford **27** as a colorless oil (38 mg, 60%). $[\alpha]_D^{20}$=+50 (*c* 1.7, MeOH), lit.[22b] $[\alpha]_D^{24.2}$=+48.8 (*c* 1.72, MeOH). ^1H NMR (200 MHz, $CDCl_3$) δ 1.01 (3H, t, J=7.5 Hz), 1.65–1.96 (3H, m), 2.24–2.40 (1H, m), 2.50–2.58 (2H, m), 4.44 (1H, quint, J=6.4 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 9.3, 27.4, 28.4, 28.7, 82.1, 177.2.

*4.5.2. (4*S*,5*R*)-Methyl-5-pentyl-4,5-dihydro-2(3*H*)-furanone [(+)-*trans*-cognac lactone]* ***28***

A solution of **25** (100 mg, 0.65 mmol) in Et_2O (6 mL) was added dropwise to a stirred solution of lithium dimethyl cuprate [3.25 mmol, prepared from addition of a solution of methyllithium (1.4 M) in ether (4.1 mL, 6.5 mmol) to a suspension of CuI (619 mg, 3.25 mmol) in Et_2O (8.3 mL) at −20°C] at −60°C. The reaction mixture was then stirred for 2 h at the same temperature. After the addition of 10% HCl (6 mL), the mixture was stirred for 30 min then filtered through Celite, and the organic layer was separated. The aqueous solution was extracted with Et_2O, the combined organic layers were dried with magnesium sulfate, filtered and concentrated. The residue was purified by column chromatography (cyclohexane:AcOEt, 3:1) affording **28** (72 mg, 65%) as a colorless oil. $[\alpha]_D^{20}$=+72, lit.[23] $[\alpha]_D^{25}$=+75 (*c* 1.0, CH_2Cl_2). IR ($CHCl_3$): 2930, 2870, 1780, 1200, 1170 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ 0.89 (3H, t, J=7.0 Hz), 1.13 (3H, d, J=6.5 Hz), 1.26–1.70 (8H, m), 2.15–2.24 (2H, m), 2.63–2.70 (1H, m), 4.01 (1H, dt, J=7.9 and 4.1 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.9, 17.4, 22.4, 25.3, 31.5, 33.9, 36.0, 37.0, 87.4, 176.5.

Acknowledgements

We are grateful to the CMCU (Comité Mixte Franco-Tunisien pour la Coopération Universitaire) for grants to A.R.T. and T.H. and we wish to thank Dr. R. Schmid (Hoffmann La Roche) for samples of (*R*)- and (*S*)-MeO-BIPHEP=(*R*)-(+)-6,6′-dimethoxy-2,2′-bis(diphenylphosphino)-1,1′-biphenyl.

References

1. (a) Genêt, J.-P.; Pinel, C.; Ratovelomanana-Vidal, V.; Mallart, S.; Pfister, X.; Caño de Andrade, M. C.; Laffitte, J. A. *Tetrahedron: Asymmetry* **1994**, *5*, 665–674. (b) Genêt, J.-P.; Pinel, C.; Ratovelomanana-Vidal, V.; Mallart, S.; Pfister, X.; Bischoff, L.; Caño de Andrade, M. C.; Darses, S.; Galopin, C.; Laffitte, J. A. *Tetrahedron: Asymmetry* **1994**, *5*, 675–690. (c) Genêt, J.-P.; Ratovelomanana-Vidal, V.; Caño de Andrade, M. C.; Pfister, X.; Guerreiro, P.; Lenoir, J. Y. *Tetrahedron Lett*. **1995**, *36*, 4801–4804. (d) Ratovelomanana-Vidal, V.; Genêt, J. P. *J. Organomet. Chem*. **1998**, *567*, 163–171. (e) Tranchier, J.-P.; Ratovelomanana-Vidal, V.; Genêt, J.-P.; Tong, S.; Cohen, T. *Tetrahedron Lett*. **1997**, *38*, 2951–2954.
2. For reviews on this technology, see: (a) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; John Wiley: New York, 1994; pp. 1–93. (b) Noyori, R. *Acc. Chem. Res*. **1997**, *30*, 97–102. (c) Genêt, J.-P. *Reductions in Organic Synthesis, A.C.S. Symposium Series*; Abdel Magid, A. F., Ed., 1996; Vol. 641, pp. 31–51. (d) Genêt, J.-P. *Acros Organics Acta* **1995**, *1*, 4–9.
3. (a) *The Chemistry of Sulfur-Containing Functional Groups*; Patai, S.; Rappoport, Z., Eds.; Wiley Interscience: New York, 1993. (b) Oae, S. *Organic Sulfur Chemistry*; CRC Press: Boca Raton, 1991. (c) *Chemistry of Organosulfur Compounds*; Belen'Kii, L. I., Ed.; Ellis Horwood: New York, 1990.
4. Simpkins, N. S. *Sulphones in Organic Synthesis*; Pergamon Press: New York, 1993.
5. Sato, T.; Okumura, Y.; Itai, J.; Fujisawa, T. *Chem. Lett*. **1988**, 1537–1540.
6. Crumbie, R. L.; Deol, B. S.; Nemorin, J. E.; Ridley, D. D. *Aust. J. Chem*. **1978**, *31*, 1965–1980.
7. Tanikaga, R.; Hosoya, K.; Kaji, A. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1799–1802.
8. Tanikaga, R.; Hosoya, K.; Kaji, A. *Chem. Lett*. **1987**, 829–832.
9. Reviews on baker's yeast reductions including examples of ketones bearing sulfur groups: (a) Servi, S. *Synthesis* **1990**, 1–25. (b) Csuk, R.; Glänzer, B. I. *Chem. Rev*. **1991**, *91*, 49–97. See also references cited therein.
10. Nakamura, K.; Ushio, K.; Oka, S.; Ohno, A.; Yasui Y. *Tetrahedron Lett*. **1984**, 3979–3982.
11. Chinchilla, R.; Najera, C.; Pardo, J.; Yus, M. *Tetrahedron: Asymmetry* **1990**, *1*, 575–578.
12. Hiraki, Y.; Ito, K.; Harada, T.; Tai, A. *Chem. Lett*. **1981**, 131–132.
13. (a) Berdardi, R.; Bravo, P.; Cardillo, R.; Ghiringhelli, D.; Resnati, G. *J. Chem. Soc., Perkin Trans. 1* **1988**, 2831–2834. (b) Thomsen, M. W.; Handwerker, B. M.; Katz, S. A.; Belser, R. B. *J. Org. Chem*. **1988**, *53*, 906–907. (c) Long Fan, A.; Cao, S.; Zhang, Z. *J. Heterocycl. Chem*. **1997**, *34*, 1657.
14. Iriuchjima, S.; Kojima, N. A. *Agric. Biol. Chem*. **1978**, *42*, 451–455.
15. Kozikowski, A. P.; Mugrage, B. B.; Li, C. S.; Felder, L. *Tetrahedron Lett*. **1986**, *27*, 4817–4820.

16. Rao, Y. S. *Chem. Rev*. **1976**, *76*, 625–694. For recent synthesis of non-racemic γ-chiral-lactones, see: Koch, S. S. C.; Chamberlin, A. R. *J. Org. Chem*. **1993**, *58*, 2725–2737 and references cited therein.
17. For recent synthesis of non-racemic γ-chiral butenolides, see: Knight, D. W. *Contemp. Org. Synth*. **1994**, *1*, 287–315.
18. Tanikaga, R.; Hosoya, K.; Kaji, A. *Synthesis* **1987**, 389–390.
19. Camps, P.; Cardellach, J.; Corbera, J.; Font, J.; Ortuno, R. M.; Ponsati, O. *Tetrahedron* **1983**, *39*, 395–400.
20. (a) Harcken, C.; Bruckner, R.; Rank, E.; *Chem. Eur. J*. **1998**, *4*, 2342–2352. (b) Robin, S.; Huet, F.; Fauve, A.; Veschambre, H. *Tetrahedron: Asymmetry* **1993**, *4*, 239–246.
21. (a) Murta, M. M.; De Azevedo, M. B. M.; Greene, A. E. *J. Org. Chem*. **1993**, *58*, 7537–7541. (b) Vigneron, J.-P.; Blanchard, J.-M. *Tetrahedron Lett*. **1980**, *21*, 1739–1742.
22. For some syntheses of (*R*)-hexanolide, see: (a) Utaka, M.; Watabu, H.; Takeda, A. *J. Org. Chem*. **1987**, *52*, 4363–4368. (b) Ravid, U.; Silverstein, M.; Smith, L. R. *Tetrahedron* **1978**, *34*, 1449–1452. (c) Vigneron, J.-P.; Bloy, V. *Tetrahedron Lett*. **1980**, *21*, 1735–1738. (d) Mori, K.; Mori, H.; Sugai, T. *Tetrahedron* **1985**, *41*, 919–925.
23. For some syntheses of (+)-*trans* cognac lactone, see: (a) Takahata, H.; Uchida, Y.; Momose, T. *J. Org. Chem*. **1995**, *60*, 5628–5633. (b) Pai, Y.-C.; Fang, J.-M.; Wu, S.-H. *J. Org. Chem*. **1994**, *59*, 6018–6025. (c) Takahata, H.; Uchida, Y.; Momose, T. *Tetrahedron Lett*. **1994**, *35*, 4123–4124. (d) Jefford, C. W.; Sledeski, A. W.; Boukouvalas, J. *Helv. Chim. Acta* **1989**, *72*, 1362–1370. (e) Ortuno, R. M.; Merce, R.; Font, J. *Tetrahedron* **1987**, *43*, 4497–4506.
24. Ortuno, R. M.; Alonso, D.; Font, J. *Tetrahedron Lett*. **1986**, *27*, 1079–1080.