Aryl(chloro)methyl 4-Tolyl Sulfoxides: Synthesis and Application to the Synthesis of α-Aryl Ketones

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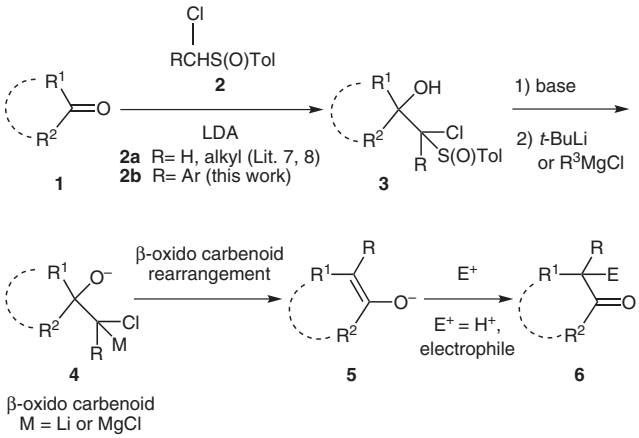
Received 21 July 2011; revised 25 August 2011

Abstract: Aryl(chloro)methyl 4-tolyl sulfoxides were synthesized from arylmethyl 4-tolyl sulfoxides in moderate-to-good yields by sequential treatment with lithium diisopropylamide and tosyl chloride at low temperatures. Treatment of the lithium α-sulfinyl carbanion of the aryl(chloro)methyl 4-tolyl sulfoxides with aldehydes or ketones resulted in the formation of adducts in good-to-high yields. Treatment of these adducts with *tert*-butylmagnesium chloride gave the corresponding magnesium alkoxides. On treatment with isopropylmagnesium chloride, the alkoxides gave the corresponding magnesium β-oxido carbenoids, which rearranged to give α-aryl ketones in good-to-high yields. The magnesium enolate intermediates generated by rearrangement of the β-oxido carbenoids could also be trapped with electrophiles to give α-aryl α-substituted ketones. These procedures offer a good method for the synthesis of a variety of α-aryl ketones from aldehydes and ketones.

Key words: sulfoxides, α-aryl ketones, homologations, aldehydes

The β-oxido carbenoid rearrangement is one of the most useful reactions for the homologation or elongation of carbonyl compounds.[1] Several methods for the homologation of carbonyl compounds by using the β-oxido carbenoid rearrangement as the key reaction have been reported.[2–6] We have been interested for long time in the homologation and elongation of carbonyl compounds by the β-oxido carbenoid rearrangement as the key reaction. Our previous method[7] was based on the rearrangement of lithium β-oxido carbenoids **4a** (M = Li) derived from adducts of carbonyl compounds **1** with the lithium α-sulfinyl carbanion of 1-chloroalkyl 4-tolyl sulfoxides **2a** (Scheme 1). The rearrangement gives enolates **5a** as the intermediates, and one-carbon homologated carbonyl compounds **6a** are obtained on treating enolates **5a** with a range of electrophiles.[7] Later, we found that magnesium β-oxido carbenoids (**4a**, M = MgCl) are better for our homologation reaction, and we established a versatile procedure for homologation of ketones and aldehydes.[8] In all our investigations mentioned above, we used 1-chloroalkyl 4-tolyl sulfoxides **2a** as the one-carbon homologating agents.

If the procedures could be carried out with aryl(chloro)methyl 4-tolyl sulfoxides **2b** (R = Ar), α-aryl carbonyl compounds **6b** (R = Ar) should be obtained. However, no general method for the synthesis of sulfoxides **2b** has been reported so far.[9] In a continuation of our interest in the homologation and elongation of carbonyl compounds through the magnesium β-oxido carbenoid rearrangement, we recently began to study the synthesis of aryl(chloro)methyl 4-tolyl sulfoxides **2b** and their use in the synthesis of α-aryl carbonyl compounds **6b** from carbonyl compounds by a one-carbon homologation or elongation process (Scheme 1). Here, we wish to report a general method for the synthesis of aryl(chloro)methyl 4-tolyl sulfoxides **2b** and for the elongation and homologation of aldehydes and ketones, respectively, to give α-aryl ketones **6b** (R = Ar) by using sulfoxides **2b** as the one-carbon homologating agents.

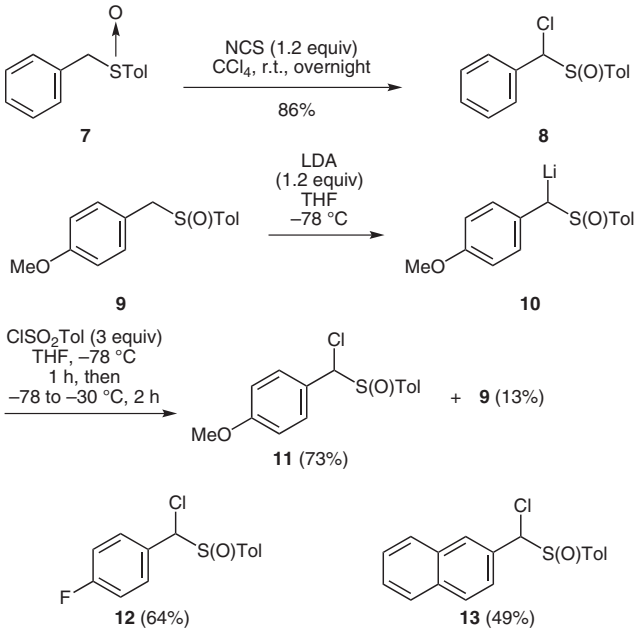


Scheme 1

In our previous studies, we synthesized 1-chloroalkyl 4-tolyl sulfoxides **2a** by treating the corresponding alkyl 4-tolyl sulfoxides with *N*-chlorosuccinimide (NCS) in carbon tetrachloride.[10] On the basis of this experience and a report on the chlorination of benzyl phenyl sulfoxide,[9d] we treated benzyl 4-tolyl sulfoxide (**7**) with NCS in carbon tetrachloride at room temperature overnight. This reaction worked well and gave the desired chloro(phenyl)methyl 4-tolyl sulfoxide (**8**) cleanly as a mixture of two diastereomers in 86% yield (Scheme 2).

Next, to synthesize aryl(chloro)methyl 4-tolyl sulfoxides other than **8**, we treated 4-methoxybenzyl 4-tolyl sulfoxide (**9**) with NCS under the same conditions as described above. Somewhat surprisingly, the chlorination did not proceed at all, and prolonging the reaction time resulted only in decomposition of **9** to give a complex mixture. We

SYNTHESIS 2011, No. 22, pp 3615–3626
Advanced online publication: 05.10.2011
DOI: 10.1055/s-0031-1260251; Art ID: F71511SS



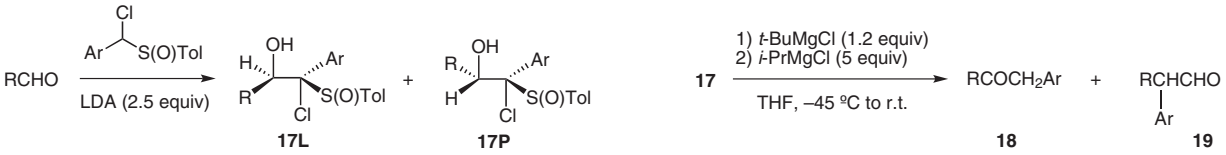
Scheme 2 Synthesis of aryl(chloro)methyl 4-tolyl sulfoxides by the chlorination of lithium α-sulfinyl carbanions with tosyl chloride

tried other chlorinating reagents, such as (dichloroiodo)benzene,[11] but none gave any promising results.

Next, we attempted to chlorinate of lithium α-sulfinyl carbanion **10** with an electrophilic chlorinating agent. After searching for a suitable chlorinating agent, we found that sequential treatment of sulfoxide **9** with lithium diisopropylamide (LDA) and tosyl chloride at –78 °C gave the desired chlorinated sulfoxide **11** in moderate yield. Investigations to find the best conditions for the reaction resulted in an improvement of the yield of **11** to 73% (Scheme 2). Thus, treatment of 4-methoxybenzyl 4-tolyl sulfoxide (**9**) with 1.2 equivalents of LDA in tetrahydrofuran at –78 °C gave the lithium α-sulfinyl carbanion **10**. A solution of tosyl chloride (3 equivalents) in tetrahydrofuran was then added to the reaction mixture, which was stirred at –78 °C for one hour and then slowly warmed to –30 °C for two hours. These optimal conditions gave **11** in 73% yield, together with recovered starting material **9** (13%). Chloro(4-fluorophenyl)methyl 4-tolyl sulfoxide (**12**) and chloro(2-naphthyl)methyl 4-tolyl sulfoxide (**13**) were similarly obtained in moderate yields from the corresponding arylmethyl 4-tolyl sulfoxides under the conditions described above.

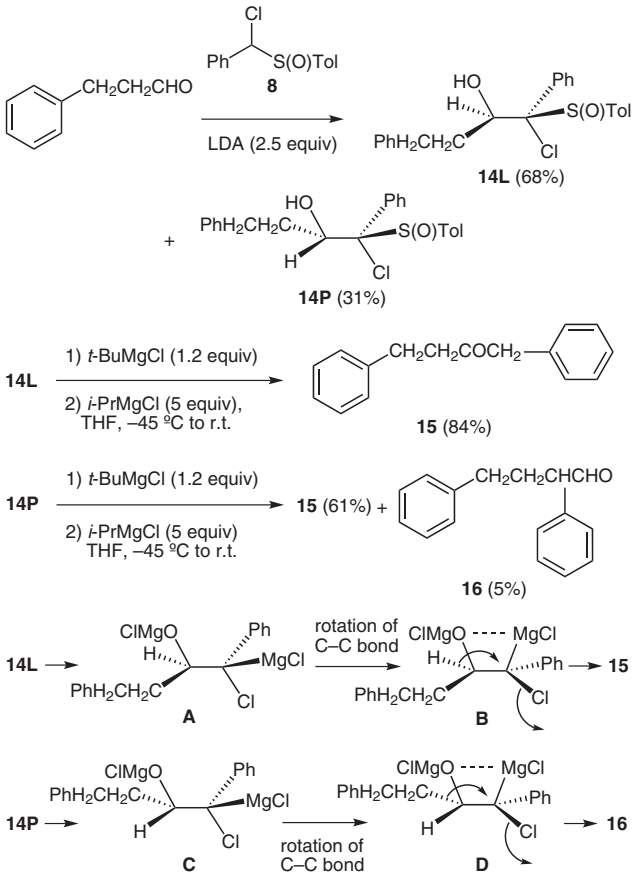
Having obtained the desired aryl(chloro)methyl 4-tolyl sulfoxides, we next investigated the properties of these compounds and their synthetic uses (Scheme 3). First, chloro(phenyl)methyl 4-tolyl sulfoxide (**8**) was treated with 2.5 equivalents of LDA in tetrahydrofuran at –78 °C for 20 minutes. The colorless reaction mixture became yellow and the lithium α-sulfinyl carbanion of **8** was generated instantaneously. To this reaction mixture we added a solution of 3-phenylpropanal (3 equivalents) in tetrahydrofuran to give adduct **14L** [the less polar adduct on silica gel thin-layer chromatography (TLC)] and **14P** (the more polar adduct on silica gel TLC) in 68% and 31% yields, respectively. On the basis of our previous study[8d] and a report by García-Martínez and co-workers,[9d] we assumed that the configuration of these two products are those shown in Scheme 3.

Table 1 Synthesis of α-Aryl Ketones from Aldehydes with Aryl(chloro)methyl 4-Tolyl Sulfoxides as One-Carbon Elongating Agents



Entry	Aldehyde	Ar(Cl)CHS(O)Tol	α-Aryl carbonyl compounds		
	R	Ar	Product **17** [yield (%)]	Product **18** [yield (%)]	Product **19** [yield (%)]
1	$(CH_2)_2Ph$	2-naphthyl (**13**)	**17aL** (78)	**18a** (70)	**19a** (0)
2			**17aP** (22)	**18a** (63)	**19a** (9)
3	$(CH_2)_2Ph$	4-$MeOC_6H_4$ (**11**)	**17bL** (63)	**18b** (82)	**19b** (0)
4			**17bP** (35)	**18b** (82)	**19b** (0)
5	$(CH_2)_2Ph$	4-FC_6H_4 (**12**)	**17c** (99)[a]	**18c** (75)	**19c** (5)
6	Ph	Ph (**8**)	**17dL** (72)	**18d** (95)	**19d** (0)
7			**17dP** (27)	**18d** (30)	**19d** (9)
8	Ph	4-$MeOC_6H_4$ (**11**)	**17eL** (71)	**18e** (85)	**19e** (0)
9			**17eP** (28)	**18e** (75)	**19e** (14)
10	Ph	4-FC_6H_4 (**12**)	**17fL** (73)	**18f** (86)	**19f** (0)
11			**17fP** (27)	**18f** (31)	**19f** (16)

[a] ~3:1 mixture of two inseparable diastereomers.



Scheme 3 Synthesis of α-phenyl ketone **15** from 3-phenylpropanal and sulfoxide **8** with the β-oxido carbenoid rearrangement as the key reaction

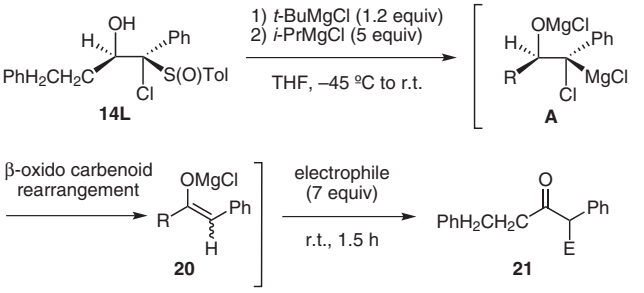
The major adduct **14L** was treated sequentially with 1.2 equivalents of *tert*-butylmagnesium chloride, to form the magnesium alkoxide, and then with 5 equivalents of isopropylmagnesium chloride at –45 °C, to generate the magnesium β-oxido carbenoid **A** by means of a sulfoxide–magnesium exchange reaction.[12] The mixture was then allowed to warm slowly to room temperature to give 1,4-diphenylbutan-2-one (**15**) in 84% yield. Interestingly, the same treatment of **14P** gave the α-phenyl ketone **15** in a somewhat lower yield (61%), together with the α-phenyl aldehyde **16** in 5% yield.

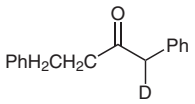
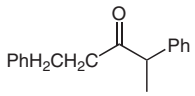
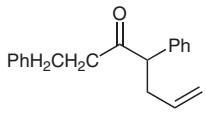
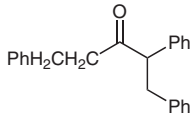
The difference in the reactivity of **14L** and **14P** with isopropylmagnesium chloride can be explained as follows (see Scheme 3). As the sulfoxide–magnesium exchange reaction[12] is known to occur with retention of the configuration at the carbon bearing a sulfinyl group,[13] the sulfoxide–magnesium exchange reaction of the magnesium alkoxide of **14L** gives magnesium β-oxido carbenoid **A**. The conformation of **A** must be fixed to give **B** by formation of a chelate ring. The hydrogen at the rear of the chlorine in the β-oxido carbenoid **B** rearranges smoothly to give ketone **15** via a magnesium enolate. On the other hand, the sulfoxide–magnesium exchange reaction of the magnesium alkoxide of **14P** gives β-oxido carbenoid **D** via the initially generated intermediate **C**. From **D**, the 2-phenylethyl group rearranges to give aldehyde **16** via an enolate intermediate. However, the alkyl group is known to have a poor migratory ability so that rearrangement of the hydrogen is the main reaction, giving **15** as a major product.

The scope of the elongation of aldehydes to α-aryl ketones, as described above, was investigated by using various aryl(chloro)methyl 4-tolyl sulfoxides **8** and **11**–**13** with 3-phenylpropanal and benzaldehyde as representative examples of an alkyl aldehyde and an aryl aldehyde, respectively. The results are summarized in Table 1.

As shown in Table 1, the addition of the lithium α-sulfinyl carbanion of aryl(chloro)methyl 4-tolyl sulfoxides with either the alkylaldehyde or the arylaldehyde gave an almost quantitative yield of the corresponding adducts **17**. In all cases, the less-polar adduct **17L** was the major product. Treatment of **17L** with Grignard reagents as described above gave the expected α-aryl ketones **18** in good-to-high yields, without any α-aryl aldehydes **19**. The same reaction of the minor adducts **17P** with Grignard reagents gave the α-aryl ketones **18** in somewhat variable yields and, in some cases, the corresponding α-aryl aldehydes **19** were also obtained in less than 16% yield. These

Table 2 Synthesis of α-Phenyl α-Substituted Ketones **21** from **14L** by Trapping the Enolate Intermediate **20** with Electrophiles



Entry	Electrophile	Additive	Product **21** [Yield (%)]
1	MeOD	none	 **21a** (84)[b]
2	MeI	HMPA[a]	 **21b** (66)
3	CH_2=$CHCH_2$I	HMPA[a]	 **21c** (69)
4	BnBr	HMPA[a]	 **21d** (43)

[a] HMPA (5 equiv) was added.
[b] Deuterium content 94%.

results confirmed that the procedure for the elongation of aldehydes to α-aryl ketones has general applicability.

As reported previously, the product of the β-oxido carbenoid rearrangement has been shown to be a magnesium enolate.[8] We hoped that if such enolate intermediates could be trapped with electrophiles, we might realize a synthesis of an α-aryl α-substituted ketones. We prepared the enolate intermediate **20** from adduct **14L** by treatment with Grignard reagents, via the β-oxido carbenoid intermediate **A**, and we attempted to trap the enolate **20** with some haloalkanes. This procedure did indeed work well and gave α-phenyl α-substituted ketones **21** in moderate-to-good yields (Table 2).

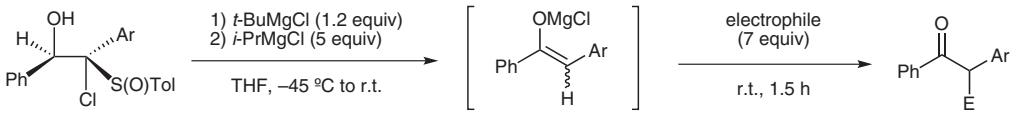
When adduct **14L** was treated sequentially with *tert*-butylmagnesium chloride and isopropylmagnesium chloride, and the reaction was quenched with an excess of methanol-d_1, we obtained the α-deuterio α-phenyl ketone **21a** with a 94% deuterium content in 84% yield (Table 2, entry 1). When alkyl halides were used as the electrophiles, hexamethylphosphoramide (HMPA) was found to be useful additive in the alkylation reaction, giving α-alkyl α-phenyl ketones **21b–d** in moderate yields (entries 2 to 4, respectively). Disappointingly, attempt to trap the enolate intermediate **20** with benzaldehyde, benzoyl chloride, or ethyl chloroformate resulted in the formation of complex mixtures.

Next, we applied the procedure to the adducts **17L**, derived from an aryl aldehyde (benzaldehyde) and an aryl(chloro)methyl 4-tolyl sulfoxide; the results are summarized in Table 3. Thus, treatment of **17dL** with *tert*-butylmagnesium chloride and isopropylmagnesium chloride gave the magnesium enolate intermediate, which was trapped with iodomethane or allyl iodide to give the expected α-alkyl α-aryl ketones **22a** and **22b**, respectively, in moderate yields (Table 3, entries 1 and 2). The reaction with benzoyl chloride gave the expected β-diketone **22c** in 45% yield (entry 3). Interestingly, the reaction with ethyl chloroformate gave the enol carbonate **22d** in a low yield (entry 4). The reaction starting from **17eL** and **17fL** with allyl iodide gave relatively good yields of the desired products **22e** and **22f**, respectively (entries 5 and 6).

Next, we investigated the reaction of the lithium α-sulfinyl carbanion of aryl(chloro)methyl 4-tolyl sulfoxides with ketones, and our results are summarized in Table 4. The addition reaction of the lithium α-sulfinyl carbanion of chloro(phenyl)methyl 4-tolyl sulfoxide (**8**) with cyclobutanone, cyclopentanone, or cyclohexanone gave the desired adducts **23a–c**, respectively, in almost quantitative yields (Table 4, entries 1 to 3). The same reaction of the lithium α-sulfinyl carbanions of **8**, **13**, **11**, and **12** with cyclohexane-1,4-dione monoethylene ketal (1,4-dioxaspiro[4.5]decan-8-one) gave adducts **23d–g**, respectively, in high-to-quantitative yields (entries 4 to 7).

Interestingly, the lithium α-sulfinyl carbanion of chloro(phenyl)methyl 4-tolyl sulfoxide (**8**) did not react at all with cycloalkanones larger than cyclohexanone (entries 8 and 9) or with acyclic ketones other than acetone (entries 10 to 12). The results are in sharp contrast to those for the lithium α-sulfinyl carbanions of 1-chloroalkyl 4-tolyl sulfoxides, the carbanions of which reacted with large cyclic ketones and acyclic ketones larger than acetone to give adducts in good yields.[7b] This can be rationalized in terms

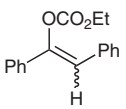
Table 3 Synthesis of α-Aryl α-Substituted Ketones from Adduct **17L** by Trapping the Enolate Intermediates



17L **22**

Entry	Adduct **17**	Ar	Electrophile	E	Product **22** [Yield (%)]
1	**17dL**	Ph	MeI[a]	Me	**22a** (41)
2	**17dL**	Ph	CH_2=$CHCH_2I$[a]	CH_2CH=CH_2	**22b** (71)
3	**17dL**	Ph	BzCl	Bz	**22c** (45)
4	**17dL**	Ph	$ClCO_2Et$	CO_2Et	**22d** (30)[b]
5	**17eL**	4-$MeOC_6H_4$	CH_2=$CHCH_2I$[a]	CH_2CH=CH_2	**22e** (67)
6	**17fL**	4-FC_6H_4	CH_2=$CHCH_2I$[a]	CH_2CH=CH_2	**22f** (52)

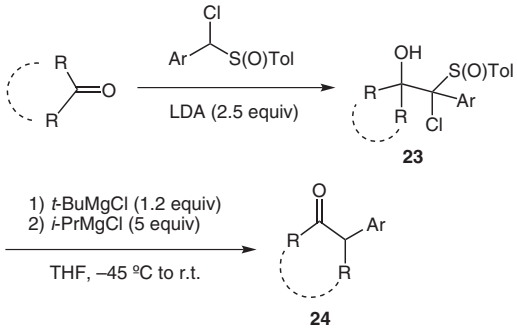
[a] HMPA (5 equiv) was present as an additive.
[b] The product **22d** was found to be an enol carbonate (single isomer, *E*/*Z* not determined).

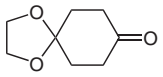


22d

of the bulk of the lithium α-sulfinyl carbanion of aryl(chloro)methyl 4-tolyl sulfoxides and the highly acidic nature of the hydrogen atoms on the carbon atoms bearing the sulfinyl group in comparison with those of the corresponding 1-chloroalkyl 4-tolyl sulfoxides. The formation of the magnesium β-oxido carbenoids from the adducts **23** and their rearrangement reaction proceeded without any problem to give the desired one-carbon ring-expanded α-aryl ketones **24** in up to 94% yield.

Table 4 Synthesis of α-Aryl Ketones from Ketones with Aryl(chloro)methyl 4-Tolyl Sulfoxides as One-Carbon Homologating Agents

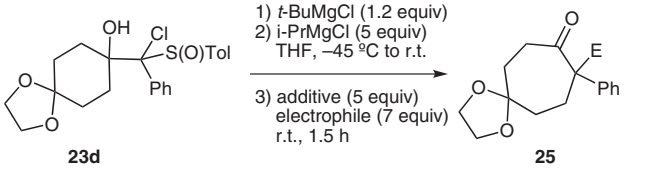


Entry	Ketone[a]	Ar(Cl)CHS(O)Tol Ar	**23** [Yield (%)]	**24** [Yield (%)]
1	cyclobutanone	Ph (**8**)	**23a** (99)	**24a** (94)
2	cyclopentanone	Ph (**8**)	**23b** (95)	**24b** (92)
3	cyclohexanone	Ph (**8**)	**23c** (98)	**24c** (85)
4		Ph (**8**)	**23d** (99)	**24d** (91)
5		2-naphthyl (**13**)	**23e** (98)	**24e** (80)
6		4-$MeOC_6H_4$ (**11**)	**23f** (99)	**24f** (44)
7		4-FC_6H_4 (**12**)	**23g** (88)	**24g** (86)
8	cycloheptanone	Ph (**8**)	nr[b]	
9	cyclooctanone	Ph (**8**)	nr	
10	acetone	Ph (**8**)	**23h** (90)	**24h** (73)
11	pentan-3-one	Ph (**8**)	nr	
12	heptan-4-one	Ph (**8**)	nr	

[a] The ketone (3 equiv) was treated with the lithium α-sulfinyl carbanion of the aryl(chloro)methyl 4-tolyl sulfoxide.
[b] nr = no reaction.

Next, we examined the synthesis of α-aryl α-substituted ketones from ketones with one-carbon homologation by using **23d** as a representative example, and the results are summarized in Table 5. Adduct **23d** (see Table 4, entry 4) was treated sequentially with *tert*-butylmagnesium chloride and isopropylmagnesium chloride in tetrahydrofuran at –45 °C and the mixture was slowly allowed to warm to room temperature. Seven equivalents of electrophile were added and the mixture was stirred at room temperature for 1.5 hours. α-Alkyl α-phenyl cycloheptanone derivatives **25b–d** were obtained in up to 85% yield (entries 2 to 4). Benzoyl chloride also reacted with the magnesium enolate intermediate to give the β-diketone **25e** in 51% yield (entry 5).

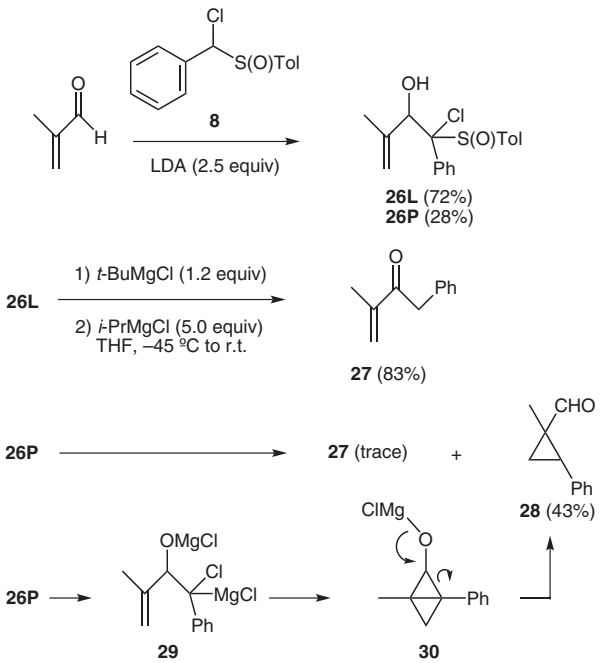
Table 5 Synthesis of 9-Substituted 9-Phenyl-1,4-dioxaspiro[4.6]undecan-8-ones **25**



entry	Electrophile	Additive	**25** [Yield (%)]
1	MeOD	none	**25a** (91)[a]
2	MeI	HMPA	**25b** (72)
3	CH_2=$CHCH_2$I	HMPA	**25c** (85)
4	BnBr	HMPA	**25d** (58)
5	BzCl	none	**25e** (51)

[a] Degree of deuteration = 99%.

Finally, we examined the reactions with the α,β-unsaturated aldehyde methacrolein, and the results are shown in Scheme 4. Thus, the addition reaction of the lithium α-sulfinyl carbanion of **8** with methacrolein gave adducts **26L** and **26P** in 72% and 28% yields, respectively. The reaction of the major adduct **26L** with Grignard reagents under the conditions discussed above gave the expected α-phenyl ketone **27** in 83% yield. In contrast, the reaction of **26P** with the Grignard reagents gave a trace of ketone **27** together with the cyclopropanecarbaldehyde **28** as a single diastereomer in 43% yield.



Scheme 4

The mechanism responsible for this interesting result is as follows. Initially, the reaction of **26P** with the Grignard reagents gives the β-oxido carbenoid intermediate **29**. As mentioned above, the rearrangement of the alkenyl group in this intermediate must be slow and, instead, addition of the magnesium carbenoid to the double bond must occur to give highly strained intermediate **30**. Carbon–carbon bond cleavage between the carbon bearing the alkoxide and the carbon bearing the phenyl group occurs next to give a cyclopropyl anion with a negative charge on the carbon bearing the phenyl group. This anion is protonated by water during the workup to afford aldehyde **28**. Actually, when this reaction was quenched with methanol-d_1, the hydrogen on the carbon bearing the phenyl group was almost completely replaced by deuterium.

In conclusion, we have developed a method for the synthesis of aryl(chloro)methyl 4-tolyl sulfoxides from arylmethyl 4-tolyl sulfoxides by sequential treatment with LDA and 4-tosyl chloride. The lithium α-sulfinyl carbanions generated from the aryl(chloro)methyl 4-tolyl sulfoxides and LDA reacted with either alkyl or aryl aldehydes to afford the corresponding adducts in high-to-quantitative yields, whereas the scope of the corresponding addition reaction with ketones was quite limited. Sequential treatment of the adducts with *tert*-butylmagnesium chloride and isopropylmagnesium chloride gave the corresponding one-carbon homologated or elongated α-aryl ketones in good-to-high yields via magnesium enolate intermediates. α-Substituted α-aryl ketones were obtained by trapping the magnesium enolate intermediates with electrophiles. As the synthesis of α-aryl carbonyl compounds is still recognized as being relatively difficult,[14] our results contribute to the synthesis of α-aryl ketones from aldehydes and ketones by one-carbon homologation and/or elongation.

All melting points were measured on a Yanaco MP-S3 apparatus and are uncorrected. ^{1}H NMR spectra were recorded in $CDCl_3$ soln by using a JEOL JNM-LA 500, a Bruker DPX 300 or a Bruker UltraShield 400 spectrometer. IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR instrument. Electron-impact mass spectra were recorded at 70 eV by direct insertion into a JEOL JMS-SX102A spectrometer. Silica gel 60N containing 0.5% fluorescence reagent 254 (Kanto Chemical) and a quartz column were used for column chromatography, and products showing a UV absorption were detected by UV irradiation. In experiments requiring dry solvents and reagents, THF was distilled from sodium diphenylketyl, and *i*-Pr_2NH was distilled from CaH_2. Acetone and HMPA were dried over $CaSO_4$ and distilled before use. Allyl iodide, MeI, BnBr, PhCHO, BzCl, and EtO_2CCl were distilled before use. Compounds **7**,[15] **18d**,[16] **18e**,[16] **18f**,[17] **22a**,[18] **24a**,[16] **24b**,[16] **24c**,[16] **24h**,[19] and **27**[20] are known in the literature.

Chloro(phenyl)methyl 4-Tolyl Sulfoxide (8)

NCS (1.39 g; 10.4 mmol) was added to a soln of 4-TolS(O)Bn (**7**; 2.00 g; 8.7 mmol) in CCl_4 (21 mL) and the suspension was stirred at r.t. for 15 h. The precipitate was filtered off and the solvent was evaporated. The residue was purified by column chromatography (silica gel, hexane–EtOAc) to give a white solid; yield: 1.97 g (86%, ~3:2 mixture of two diastereomers). The major isomer was isolated by crystallization; mp 153.0–153.5 °C (hexane–EtOAc).

IR (KBr): 2945, 1593, 1493, 1453, 1087 (SO), 1056, 807, 697, 514 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.37 (s, 3 H), 5.46 (s, 1 H), 7.06 (d, *J* = 8.3 Hz, 2 H), 7.10–7.15 (m, 4 H), 7.26 (t, *J* = 7.7 Hz, 2 H), 7.35 (t, *J* = 7.4 Hz, 1 H).

Anal. Calcd for $C_{14}H_{13}ClOS$: C, 63.51; H, 4.95; Cl, 13.39; S, 12.11. Found: C, 63.50; H, 4.81; Cl, 13.11; S, 11.99.

4-Methoxybenzyl 4-Tolyl Sulfoxide (9)

A soln of 4-TolSH (1.98 g; 16.0 mmol) in EtOH (5 mL) was added dropwise to a soln of NaOEt (1.20 g; 17.6 mmol) in EtOH (5 mL) at 0 °C with stirring, and the soln was stirred for 15 min. 4-Methoxybenzyl chloride (1.1 mL, 8.0 mmol) was then added dropwise with stirring and the mixture was stirred for 15 min. The reaction was quenched with 5% aq NaOH (20 mL) and the mixture was extracted with benzene (2 × 20 mL). The organic layer was dried ($MgSO_4$) and concentrated to give the crude sulfide.

A stirred soln of the crude sulfide in $CHCl_3$ (16 mL) was treated with MCPBA (2.39 g; 10.4 mmol) at 0 °C, and the mixture was stirred for 30 min. The reaction was quenched with sat. aq Na_2SO_3 (10 mL) and $NaHCO_3$ (10 mL), and the mixture was extracted with $CHCl_3$ (2 × 20 mL). The product was purified by column chromatography (silica gel, hexane–EtOAc) to give the sulfoxide **9** as colorless crystals; yield: 1.75 g (84%, two steps); mp 128.0–129.0 °C (hexane–EtOAc).

IR (KBr): 2960, 1610, 1514, 1253, 1037 (SO), 811, 519 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.40 (s, 3 H), 3.79 (s, 3 H), 3.92 (d, *J* = 12.6 Hz, 1 H), 4.03 (d, *J* = 12.6 Hz, 1 H), 6.78 (d, *J* = 8.7 Hz, 2 H), 6.91 (d, *J* = 8.7 Hz, 2 H), 7.23 (d, *J* = 8.3 Hz, 2 H), 7.28 (d, *J* = 8.3 Hz, 2 H).

Chloro(4-methoxyphenyl)methyl 4-Tolyl Sulfoxide (11); Typical Procedure

A soln of sulfoxide **9** (1.04 g; 4.0 mmol) in anhyd THF (50 mL) was added dropwise with stirring to a soln of LDA (4.8 mmol) in anhyd THF (6.6 mL) in a flame-dried flask at –78 °C under argon, and the soln was stirred at –78 °C for 20 min. A soln of TsCl (2.29 g; 12.0 mmol) in anhyd THF (10 mL) was then added dropwise with stirring. The mixture was stirred at –78 °C for 1 h and then slowly allowed to warm to –30 °C for 1.5 h. The reaction was quenched with sat. aq NH_4Cl (60 mL), and the mixture was extracted with $CHCl_3$ (2 × 60 mL). The organic layer was dried ($MgSO_4$) and the product was purified by column chromatography (silica gel, hexane–EtOAc) to give a white solid; yield 859 mg (73%; ~2:1 mixture of two diastereomers).

IR (KBr): 2948, 1609, 1512, 1256, 1176, 1087, 1056 (SO), 811, 515 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.38 (s, 2 H), 2.42 (s, 1 H), 3.81 (s, 2 H), 3.83 (s, 1 H), 5.38 (s, 0.33 H), 5.42 (s, 0.67 H), 6.77 (d, *J* = 8.8 Hz, 1.33 H), 6.87 (d, *J* = 8.8 Hz, 0.67 H), 6.98 (d, *J* = 8.8 Hz, 1.33 H), 7.10–7.28 (m, 4 H), 7.36 (d, *J* = 8.2 Hz, 0.67 H).

MS (FAB): *m/z* (%) = 295 (4) $[M + 1]^+$, 155 (100).

HRMS (FAB): *m/z* $[M + H]^+$ calcd for $C_{15}H_{16}ClO_2S$: 295.0560; found: 295.0556.

Chloro(4-fluorophenyl)methyl 4-Tolyl Sulfoxide (12)

White solid (~ 3:2 mixture of two diastereomers).

IR (KBr): 2958, 1596, 1508, 1229, 1058 (SO), 814, 746, 522, 462 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.39 (s, 1.2 H), 2.42 (s, 1.8 H), 5.39 (s, 0.6 H), 5.48 (s, 0.4 H), 6.92–7.35 (m, 8 H).

Anal. Calcd for $C_{14}H_{12}ClFOS$: C, 59.47; H, 4.28; Cl, 12.54; F, 6.72; S, 11.34. Found: C, 59.50; H, 4.08; Cl, 12.20; F, 6.48, S, 11.26.

Chloro(2-naphthyl)methyl 4-Tolyl Sulfoxide (13)
White solid (~ 2:1 mixture of two diastereomers).

IR (KBr): 2947, 1508, 1087 (SO), 1059, 809, 755, 626, 478 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ 2.34 (s, 1 H), 2.41 (s, 2 H), 5.60 (s, 0.67 H), 5.62 (s, 0.33 H), 7.05–7.59 (m, 7 H), 7.69–7.89 (m, 4 H).

Anal. Calcd for $C_{18}H_{15}ClOS$: C, 68.67; H, 4.80; Cl, 11.26; S, 10.18. Found: C, 68.67; H, 4.69; Cl, 11.07; S, 10.18.

1-Chloro-1,4-diphenyl-1-[(4-tolyl)sulfinyl]butan-2-ol (14L and 14P)
A soln of sulfoxide **8** (212 mg, 0.80 mmol) in anhyd THF (6 mL) was added dropwise to a stirred soln of LDA (2.00 mmol) in anhyd THF (2 mL) at –78 °C under argon. The resulting mixture was stirred at –78 °C for 20 min and then 3-phenylpropanal (0.32 mL, 2.40 mmol) was added dropwise with stirring. The mixture was stirred at –78 °C for 10 min before the reaction was quenched by sequential addition of MeOH (5 mL) and sat. aq NH_4Cl (10 mL). The mixture was extracted with $CHCl_3$ (2 × 10 mL) and the organic layer was dried ($MgSO_4$). The product was purified by column chromatography (silica gel, hexane–EtOAc) to give the less-polar isomer **14L** as a colorless oil [yield: 217 mg (68%] and the more-polar isomer **14P** as colorless crystals [yield: 99 mg (31%)].

14L
IR (neat): 3402 (OH), 1597, 1494, 1454, 1081 (SO), 1042, 811, 750, 700 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.40 (td, *J* = 8.6, 13.9 Hz, 1 H), 1.76–1.88 (m, 1 H), 2.33 (s, 3 H), 2.66 (td, *J* = 8.3, 13.7 Hz, 1 H), 2.87 (ddd, *J* = 4.5, 8.6, 13.7 Hz, 1 H), 4.68 (br s, 1 H), 4.88 (d, *J* = 10.1 Hz, 1 H), 6.76 (d, *J* = 8.1 Hz, 2 H), 7.03 (d, *J* = 8.1 Hz, 2 H), 7.08 (d, *J* = 7.3 Hz, 2 H), 7.11 (d, *J* = 7.7 Hz, 2 H), 7.17 (t, *J* = 7.3 Hz, 1 H), 7.20–7.32 (m, 4 H), 7.36 (t, *J* = 7.3 Hz, 1 H).

MS (FAB): *m/z* (%) = 399 (74) $[M + 1]^+$, 241 (100), 223 (97), 205 (38), 154 (18), 140 (16), 91 (42).

HRMS (FAB): *m/z* $[M + H]^+$ calcd for $C_{23}H_{24}ClO_2S$: 399.1186; found: 399.1185.

14P
Mp 153.5–154.0 °C (hexane–EtOAc).

IR (KBr): 3305 (OH), 1597, 1492, 1446, 1082 (SO), 1044, 750, 698, 507 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.40–1.52 (m, 1 H), 1.96 (td, *J* = 8.4, 13.9 Hz, 1 H), 2.32 (s, 3 H), 2.69 (ddd, *J* = 7.3, 9.3, 14.1 Hz, 1 H), 2.89 (ddd, *J* = 4.8, 10.1, 14.1 Hz, 1 H), 3.90 (d, *J* = 6.3 Hz, 1 H), 4.56 (dd, *J* = 6.2, 9.0 Hz, 1 H), 6.81 (d, *J* = 8.0 Hz, 2 H), 7.03 (d, *J* = 8.0 Hz, 2 H), 7.14 (d, *J* = 7.7 Hz, 2 H), 7.15 (d, *J* = 5.0 Hz, 1 H), 7.23 (t, *J* = 7.6 Hz, 2 H), 7.34 (t, *J* = 7.4 Hz, 2 H), 7.38 (t, *J* = 7.2 Hz, 1 H), 7.66 (d, *J* = 7.6 Hz, 2 H).

Anal. Calcd for $C_{23}H_{23}ClO_2S$: C, 69.24; H, 5.81; Cl, 8.89; S, 8.04. Found: C, 69.14; H, 5.81; Cl, 8.85; S, 8.09.

1,4-Diphenylbutan-2-one (15); Typical Procedure
A soln of adduct **14L** (40.0 mg, 0.1 mmol) in anhyd THF (1.8 mL) was added dropwise with stirring to a soln of *t*-BuMgCl (0.12 mmol) in anhyd THF (0.2 mL) in a flame-dried flask at –45 °C under argon, and the mixture was stirred at –45 °C for 10 min. The resulting soln of magnesium alkoxide was stirred and treated by dropwise addition of *i*-PrMgCl (0.5 mmol). The mixture was then slowly warmed to r.t. for 1.7 h before the reaction was quenched with sat. aq NH_4Cl (10 mL). The mixture was extracted with $CHCl_3$ (2 × 10 mL), and the organic layer was washed with sat. aq NH_4Cl then dried ($MgSO_4$). The product was purified by column chromatography (silica gel) to give a colorless oil; yield: 18.8 mg (84%).

IR (neat): 3028, 1710 (CO), 1603, 1498, 1455, 1412, 702 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.72–2.81 (m, 2 H), 2.81–2.92 (m, 2 H), 3.66 (s, 2 H), 7.09–7.21 (m, 5 H), 7.21–7.36 (m, 5 H).

MS: *m/z* (%) = 224 (24) $[M]^+$, 133 (48), 105 (87), 91 (100), 65 (14).

HRMS: *m/z* $[M]^+$ calcd for $C_{16}H_{16}O$: 224.1201; found: 224.1200.

2,4-Diphenylbutanal (16)
Colorless oil.

IR (neat): 1722 (CHO), 1603, 1454, 699 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.02–2.11 (m, 1 H), 2.37–2.47 (m, 1 H), 2.51–2.67 (m, 2 H), 3.51 (ddd, *J* = 1.8, 6.3, 8.2 Hz, 1 H), 7.13–7.16 (m, 2 H), 7.19–7.35 (m, 6 H), 7.40 (t, *J* = 7.4 Hz, 2 H), 9.67 (d, *J* = 1.7 Hz, 1 H).

MS: *m/z* (%) = 224 (6) $[M]^+$, 133 (23), 120 (46), 105 (45), 91 (100), 77 (12), 65 (13).

HRMS: *m/z* $[M]^+$ calcd for $C_{16}H_{16}O$: 224.1201; found: 224.1200.

1-Chloro-1-(2-naphthyl)-4-phenyl-1-[(4-tolyl)sulfinyl]butan-2-ol (17aL and 17aP)
17aL
Colorless amorphous.

IR (KBr): 3379 (OH), 1596, 1494, 1455, 1081 (SO), 1040, 812, 756 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.41 (td, *J* = 8.5, 15.5 Hz, 1 H), 1.78–1.95 (m, 1 H), 2.28 (s, 3 H), 2.69 (td, *J* = 8.4, 13.5 Hz, 1 H), 2.85 (ddd, *J* = 4.5, 8.1, 13.5 Hz, 1 H), 4.72 (br s, 1 H), 4.98 (d, *J* = 10.3 Hz, 1 H), 6.72 (d, *J* = 8.2 Hz, 2 H), 6.94 (d, *J* = 8.2 Hz, 2 H), 7.01–7.08 (m, 2 H), 7.12–7.26 (m, 4 H), 7.47–7.61 (m, 3 H), 7.63–7.71 (m, 1 H), 7.75 (d, *J* = 8.7 Hz, 1 H), 7.85 (d, *J* = 8.2 Hz, 1 H).

MS (FAB) *m/z* (%) = 449 (13) $[M + 1]^+$, 391 (23), 291 (58), 273 (50), 167 (21), 149 (100), 91 (20).

HRMS (FAB): *m/z* $[M + H]^+$ Calcd for $C_{27}H_{26}ClO_2S$: 449.1342; found: 449.1341.

17aP
Colorless crystals; mp 140.0–141.0 °C (hexane–EtOAc).

IR (KBr): 3279 (OH), 1597, 1493, 1083, 1048 (SO), 807, 758, 699, 511 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.37–1.54 (m, 1 H), 1.92–2.06 (m, 1 H), 2.28 (s, 3 H), 2.63–2.76 (m, 1 H), 2.89 (ddd, *J* = 4.9, 10.0, 14.3 Hz, 1 H), 3.85 (br s, 1 H), 4.64 (ddd, *J* = 1.7, 6.3, 10.6 Hz, 1 H), 6.79 (d, *J* = 8.3 Hz, 2 H), 6.96 (d, *J* = 8.3 Hz, 2 H), 7.08–7.16 (m, 3 H), 7.16–7.24 (m, 2 H), 7.47–7.60 (m, 2 H), 7.78–7.91 (m, 4 H), 8.05 (d, *J* = 1.7 Hz, 1 H).

MS (FAB) *m/z* (%) = 449 (27) $[M + 1]^+$, 291 (100), 273 (85), 246 (24), 185 (53), 154 (80), 137 (64), 93 (82).

HRMS (FAB): *m/z* $[M + H]^+$ Calcd for $C_{27}H_{26}ClO_2S$: 449.1342; found: 449.1347.

1-Chloro-1-(4-methoxyphenyl)-4-phenyl-1-[(4-tolyl)sulfinyl]butan-2-ol (17bL and 17bP)
17bL
Colorless crystals; mp 105.0–106.0 °C (hexane–EtOAc).

IR (KBr): 3284 (OH), 1610, 1511, 1259, 1081, 1033 (SO), 815, 753, 540 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.42 (m, 1 H), 1.81 (m, 1 H), 2.34 (s, 3 H), 2.65 (td, *J* = 8.4, 13.6 Hz, 1 H), 2.87 (ddd, *J* = 4.7, 8.6, 13.6 Hz, 1 H), 3.83 (s, 3 H), 4.63 (t, *J* = 2.2 Hz, 1 H), 4.80 (td, *J* = 2.2, 10.1 Hz, 1 H), 6.79 (d, *J* = 9.0 Hz, 2 H), 6.80 (d, *J* = 8.2 Hz, 2 H),

7.00 (d, *J* = 9.0 Hz, 2 H), 7.06 (d, *J* = 8.2 Hz, 2 H), 7.09 (d, *J* = 7.7 Hz, 2 H), 7.13–7.27 (m, 3 H).

MS (FAB): *m/z* (%) = 429 (10) $[M + 1]^+$, 393 (27), 289 (59), 271 (49), 253 (100), 121 (87), 91 (34).

HRMS (FAB): *m/z* $[M + H]^+$ calcd for $C_{24}H_{26}ClO_3S$: 429.1291; found: 429.1292.

17bP

Colorless crystals; mp 119.0–120.0 °C (hexane–EtOAc).

IR (KBr): 3326 (OH), 1610, 1510, 1260, 1045 (SO), 1032, 810, 704, 512 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.46 (m, 1 H), 1.94 (td, *J* = 8.5, 15.6 Hz, 1 H), 2.33 (s, 3 H), 2.68 (ddd, *J* = 7.0, 9.4, 14.1 Hz, 1 H), 2.89 (ddd, *J* = 4.8, 10.1, 14.1 Hz, 1 H), 3.83 (s, 3 H), 4.04 (d, *J* = 5.6 Hz, 1 H), 4.54 (dd, *J* = 6.8, 9.9 Hz, 1 H), 6.85 (d, *J* = 8.3 Hz, 4 H), 7.06 (d, *J* = 8.2 Hz, 2 H), 7.10–7.18 (m, 3 H), 7.22 (t, *J* = 7.5 Hz, 2 H), 7.57 (d, *J* = 8.9 Hz, 2 H).

Anal. Calcd for $C_{24}H_{25}ClO_3S$: C, 67.20; H, 5.87; Cl, 8.26; S, 7.47. Found: C, 67.05; H, 5.77; Cl, 8.31; S, 7.50.

1-Chloro-1-(4-fluorophenyl)-4-phenyl-1-[(4-tolyl)sulfinyl]butan-2-ol (17c)

Colorless amorphous (~3:1 mixture of two diastereomers).

IR (KBr): 3295 (OH), 1596, 1509, 1239, 1081, 1039 (SO), 1017, 806, 703, 536 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.32–1.50 (m, 1 H), 1.77–1.95 (m, 1 H), 2.33 (s, 0.75 H), 2.34 (s, 2.25 H), 2.62–2.74 (m, 1 H), 2.82–2.94 (m, 1 H), 4.13 (br s, 0.25 H), 4.46 (dd, *J* = 1.7, 3.3 Hz, 0.75 H), 4.55 (ddd, *J* = 1.7, 6.1, 10.5 Hz, 0.25 H), 4.75 (ddd, *J* = 1.9, 3.3, 10.5 Hz, 0.75 H), 6.79–6.87 (m, 2 H), 6.78–6.88 (m, 2 H), 6.92–7.32 (m, 8.5 H), 7.62–7.69 (m, 0.5 H).

MS (FAB) *m/z* (%) = 417 (42) $[M + 1]^+$, 259 (100), 242 (69), 223 (20), 140 (14), 91 (45).

HRMS (FAB): *m/z* $[M + H]^+$ calcd for $C_{23}H_{23}ClFO_2S$: 417.1091; found: 417.1092.

2-Chloro-1,2-diphenyl-2-[(4-tolyl)sulfinyl]ethanol (17dL and 17dP)

17dL

Colorless crystals; mp 137.5–138.5 °C (hexane–$CHCl_3$).

IR (KBr): 3349 (OH), 1595, 1492, 1447, 1078, 1064, 1048 (SO), 815, 699, 519 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.31 (s, 3 H), 5.50 (d, *J* = 1.0 Hz, 1 H), 6.14 (s, 1 H), 6.85 (d, *J* = 8.2 Hz, 2 H), 7.04 (d, *J* = 8.2 Hz, 2 H), 7.06–7.17 (m, 5 H), 7.23–7.41 (m, 5 H).

MS (FAB) *m/z* (%) = 371 (65) $[M + 1]^+$, 246 (19), 231 (33), 195 (100), 154 (48), 137 (45), 93 (68), 75 (11).

HRMS (FAB): *m/z* $[M + H]^+$ calcd for $C_{21}H_{20}ClO_2S$: 371.0873; found: 371.0874.

17dP

Colorless crystals; mp 165.0–165.5 °C (hexane–$CHCl_3$).

IR (KBr): 3267 (OH), 1596, 1492, 1445, 1084, 1050 (SO), 699, 509 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.30 (s, 3 H), 3.75 (br s, 1 H), 5.64 (d, *J* = 5.0Hz, 1 H), 6.90 (d, *J* = 8.0 Hz, 2 H), 7.02 (d, *J* = 8.0 Hz, 4 H), 7.11 (t, *J* = 7.6 Hz, 2 H), 7.18 (t, *J* = 7.2 Hz, 1 H), 7.31 (t, *J* = 7.7 Hz, 2 H), 7.39 (t, *J* = 7.3 Hz, 1 H), 7.63 (d, *J* = 7.8 Hz, 2 H).

MS (FAB) *m/z* (%) = 371 (42) $[M + 1]^+$, 246 (23), 231 (24), 195 (83), 154 (66), 137 (64), 93 (100), 75 (16).

HRMS (FAB): *m/z* $[M + H]^+$ calcd for $C_{21}H_{20}ClO_2S$: 371.0873; found: 371.0874.

2-Chloro-2-(4-methoxyphenyl)-1-phenyl-2-[(4-tolyl)sulfinyl]ethanol (17eL and 17eP)

17eL

Colorless amorphous.

IR (KBr): 3343 (OH), 1607, 1510, 1261, 1180, 1063 (SO), 1024, 829, 705 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.32 (s, 3 H), 3.81 (s, 3 H), 5.50 (s, 1 H), 6.09 (s, 1 H), 6.80 (d, *J* = 9.0 Hz, 2 H), 6.88 (d, *J* = 8.3 Hz, 2 H), 7.03–7.25 (m, 9 H).

MS (FAB): *m/z* (%) = 401 (10) $[M + 1]^+$, 365 (8), 261 (100), 225 (90), 197 (32), 154 (23), 137 (22), 93 (37).

HRMS (FAB): *m/z* $[M + H]^+$ calcd for $C_{22}H_{22}ClO_3S$: 401.0978; found: 401.0975.

17eP

Colorless crystals; mp 127.0–128.0 °C (hexane–EtOAc).

IR (KBr): 3244 (OH), 1609, 1509, 1256, 1181, 1083 (SO), 1043, 702, 509 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.31 (s, 3 H), 3.49 (d, *J* = 4.8 Hz, 1 H), 3.85 (s, 3 H), 5.60 (d, *J* = 4.8 Hz, 1 H), 6.84 (d, *J* = 9.0 Hz, 2 H), 6.93 (d, *J* = 8.3 Hz, 2 H), 6.98–7.23 (m, 7 H), 7.54 (d, *J* = 9.0 Hz, 2 H).

MS (FAB): *m/z* (%) = 401 (12) $[M + 1]^+$, 261 (100), 246 (23), 225 (80), 197 (28), 185 (72), 154 (52), 137 (56), 107 (15), 93 (93).

HRMS (FAB): *m/z* $[M + H]^+$ calcd for $C_{22}H_{22}ClO_3S$: 401.0978; found: 401.0977.

2-Chloro-2-(4-fluorophenyl)-1-phenyl-2-[(4-tolyl)sulfinyl]ethanol (17fL and 17fP)

17fL

Colorless amorphous.

IR (KBr): 3392 (OH), 1596, 1507, 1232, 1095, 1082 (SO), 805, 696, 514 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.33 (s, 3 H), 5.39 (d, *J* = 1.1 Hz, 1 H), 6.07 (br s, 1 H), 6.90 (d, *J* = 8.3 Hz, 2 H), 6.95–7.03 (m, 2 H), 7.06–7.18 (m, 7 H), 7.25–7.34 (m, 1 H), 7.38 (d, *J* = 4.3 Hz, 1 H).

MS (FAB): *m/z* (%) = 389 (43) $[M + 1]^+$, 249 (46), 213 (100), 185 (36), 154 (9).

HRMS (FAB): *m/z* $[M + H]^+$ calcd for $C_{21}H_{19}ClFO_2S$: 389.0778; found: 389.0783.

17fP

Colorless crystals; mp 168.0–169.0 °C (hexane–EtOAc).

IR (KBr): 3254 (OH), 1595, 1507, 1237, 1083 (SO), 1057, 700 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.32 (s, 3 H), 3.45 (d, *J* = 4.8 Hz, 1 H), 5.61 (d, *J* = 4.8 Hz, 1 H), 6.94 (d, *J* = 8.3 Hz, 2 H), 6.98–8.28 (m, 4 H), 7.07 (d, *J* = 8.3 Hz, 2 H), 7.13 (t, *J* = 7.5 Hz, 2 H), 7.17–7.23 (m, 1 H), 7.59–7.65 (m, 2 H).

MS (FAB): *m/z* (%) = 389 (34) $[M + 1]^+$, 249 (35), 213 (80), 185 (74), 154 (79), 137 (71), 107 (22), 93 (100), 75 (16).

HRMS (FAB): *m/z* $[M + H]^+$ calcd for $C_{21}H_{19}ClFO_2S$: 389.0778; found: 389.0782.

1-(2-Naphthyl)-4-phenylbutan-2-one (18a)

White solid; mp 83.5–84.5 °C.

IR (KBr): 1712 (CO), 745, 699 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.75–2.93 (m, 4 H), 3.82 (s, 2 H), 7.06–7.31 (m, 6 H), 7.41–7.52 (m, 2 H), 7.61 (s, 1 H), 7.71–7.85 (m, 3 H).

MS: *m/z* (%) = 274 (90) $[M]^+$, 141 (82), 133 (40), 115 (37), 105 (100), 91 (72).

HRMS: *m/z* $[M]^+$ calcd for $C_{20}H_{18}O$: 274.1358; found: 274.1355.

1-(4-Methoxyphenyl)-4-phenylbutan-2-one (18b)
Colorless crystals; mp 64.0–65.0 °C (hexane–EtOAc).

IR (KBr): 1710 (CO), 1518, 1251, 1035, 747, 700 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.75 (dt, *J* = 1.7, 7.7 Hz, 2 H), 2.80–2.91 (m, 2 H), 3.60 (s, 2 H), 3.79 (s, 3 H), 6.85 (d, *J* = 8.7 Hz, 2 H), 7.04–7.21 (m, 5 H), 7.21–7.31 (m, 2 H).

MS: *m/z* (%) = 254 (40) $[M]^+$, 121 (100), 105 (19), 91 (22).

HRMS: *m/z* $[M]^+$ calcd for $C_{17}H_{18}O_2$: 254.1307; found: 254.1307.

1-(4-Fluorophenyl)-4-phenylbutan-2-one (18c)
Colorless crystals; mp 38.0–38.5 °C (hexane).

IR (KBr): 1714 (CO), 1509, 1218, 747, 699 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.77 (dt, *J* = 1.7, 7.7 Hz, 2 H), 2.82–2.93 (m, 2 H), 3.63 (s, 2 H), 6.99 (t, *J* = 8.7 Hz, 2 H), 7.06–7.31 (m, 7 H).

MS: *m/z* (%) = 242 (26) $[M]^+$, 133 (60), 105 (100), 91 (85), 77 (13).

HRMS: *m/z* $[M]^+$ calcd for $C_{16}H_{15}FO$: 242.1107; found: 242.1106.

Aldehydes 19a, 19c, 19d, 19e, and 19f
These aldehydes were not completely isolated; only the NMR data for the protons on the aldehyde carbon are reported.

19a: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.74 (d, *J* = 1.7 Hz, 1 H).

19c: ^{1}H NMR (300 MHz, $CDCl_3$): d = 9.64 (d, *J* = 1.7 Hz, 1 H).

19d: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.96 (d, *J* = 2.4 Hz, 1 H).

19e: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.92 (d, *J* = 2.3 Hz, 1 H).

19f: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.93 (d, *J* = 2.3 Hz, 1 H).

1,4-Diphenylbutan-2-one-d_1 (21a)
Colorless oil.

IR (neat): 3029, 1709 (CO), 1604, 1498, 1454, 702 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.72–2.81 (m, 2 H), 2.81–2.92 (m, 2 H), 3.64 (t, *J* = 1.9 Hz, 1 H), 7.08–7.21 (m, 5 H), 7.21–7.35 (m, 5 H).

MS: *m/z* (%) = 225 (27) $[M]^+$, 133 (57), 105 (100), 91 (88), 77 (12).

HRMS: *m/z* $[M]^+$ calcd for $C_{16}H_{15}DO$: 225.1264; found: 225.1263.

1,4-Diphenylpentan-3-one (21b); Typical Procedure
A soln of **14L** (40.0 mg, 0.1 mmol) in anhyd THF (1.8 mL) was added dropwise with stirring to a soln of *t*-BuMgCl (0.12 mmol) in anhyd THF (0.2 mL) in a flame-dried flask at –45 °C under argon. The mixture was stirred at –45 °C for 10 min to give the magnesium alkoxide. *i*-PrMgCl (0.5 mmol) was then added to the mixture, which was slowly allowed to warm to r.t. for 1.7 h. HMPA (0.5 mmol) and MeI (0.7 mmol) were added sequentially and the mixture was stirred at r.t. for 1.5 h. The reaction was quenched with sat. aq NH_4Cl (10 mL). The mixture was extracted with $CHCl_3$ (2 × 10 mL) and the product was purified by column chromatography (silica gel) to give a colorless oil; yield: 15.8 mg (66%).

IR (neat): 3028, 1713 (CO), 1495, 1453, 752, 700 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.37 (d, *J* = 7.0 Hz, 3 H), 2.60–2.70 (m, 2 H), 2.70–2.92 (m, 2 H), 3.70 (q, *J* = 7.0 Hz, 1 H), 7.02–7.10 (m, 2 H), 7.11–7.18 (m, 3 H), 7.18–7.34 (m, 5 H).

MS: *m/z* (%) = 238 (19) $[M]^+$, 133 (44), 105 (100), 91 (45), 77 (13).

HRMS: *m/z* $[M]^+$ calcd for $C_{17}H_{18}O$: 238.1358; found: 238.1357.

1,4-Diphenylhept-6-en-3-one (21c)
Colorless oil.

IR (neat): 1714 (CO), 1495, 1454, 752, 700 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.43 (td, *J* = 7.2, 14.3 Hz, 1 H), 2.60–2.89 (m, 5 H), 3.66 (t, *J* = 7.5 Hz, 1 H), 4.94 (dd, *J* = 1.3, 10.2 Hz, 1 H), 4.98 (dd, *J* = 1.3, 17.1 Hz, 1 H), 5.63 (tdd, *J* = 6.9, 10.2, 17.1 Hz, 1 H), 7.05 (d, *J* = 7.2 Hz, 2 H), 7.12–7.18 (m, 3 H), 7.18–7.27 (m, 3 H), 7.29 (t, *J* = 7.2 Hz, 2 H).

MS: *m/z* (%) = 264 (12) $[M]^+$, 133 (64), 105 (100), 91 (94).

HRMS: *m/z* $[M]^+$ calcd for $C_{19}H_{20}O$: 264.1514; found: 264.1512.

1,2,5-Triphenylpentan-3-one (21d)
White solid; mp 49.0–50.0 °C.

IR (KBr): 3026, 1709 (CO), 1699 (CO), 1495, 1453, 1069, 726, 698 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.47–2.61 (m, 1 H), 2.61–2.85 (m, 3 H), 2.89 (dd, *J* = 7.1, 13.7 Hz, 1 H), 3.41 (dd, *J* = 7.7, 13.7 Hz, 1 H), 3.87 (t, *J* = 7.4 Hz, 1 H), 6.95–7.05 (m, 4 H), 7.08–7.35 (m, 11 H).

MS: *m/z* (%) = 314 (49) $[M]^+$, 209 (22), 181 (77), 165 (21), 133 (74), 105 (100), 91 (88), 77 (18).

HRMS: *m/z* $[M]^+$ calcd for $C_{23}H_{22}O$: 314.1671; found: 314.1671.

1,2-Diphenylpent-4-en-1-one (22b)
Colorless oil.

IR (neat): 3064, 1682 (CO), 1448, 918, 759, 699 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.57 (td, *J* = 7.1, 14.2 Hz, 1 H), 2.95 (td, *J* = 7.1, 14.2 Hz, 1 H), 4.63 (t, *J* = 7.1 Hz, 1 H), 4.97 (d, *J* = 10.2 Hz, 1 H), 5.04 (dd, *J* = 1.5, 17.1 Hz, 1 H), 5.75 (tdd, *J* = 7.1, 10.2, 17.1 Hz, 1 H), 7.15–7.24 (m, 1 H), 7.26–7.34 (m, 4 H), 7.38 (t, *J* = 7.5 Hz, 2 H), 7.48 (t, *J* = 7.3 Hz, 1 H), 7.96 (d, *J* = 7.4 Hz, 2 H).

MS: *m/z* (%) = 236 (8) $[M]^+$, 105 (100), 77 (25).

HRMS: *m/z* $[M]^+$ calcd for $C_{17}H_{16}O$: 236.1201; found: 236.1200.

1,2,3-Triphenylpropane-1,3-dione (22c); Typical Procedure
A soln of sulfoxide **17dL** (37.0 mg, 0.1 mmol) in anhyd THF (1.8 mL) was added dropwise with stirring to a soln of *t*-BuMgCl (0.12 mmol) in dry THF (0.2 mL) in a flame-dried flask at –45 °C under argon, and the mixture was stirred at –45 °C for 10 min. *i*-PrMgCl (0.5 mmol) was added dropwise with stirring, and the mixture was slowly allowed to warm to r.t. for 1.7 h. BzCl (0.7 mmol) was added dropwise with stirring, and the mixture was stirred at r.t. for 1.5 h. The reaction was quenched by adding sat. aq NH_4Cl (10 mL) and the mixture was extracted with $CHCl_3$ (2 × 10 mL). The product was purified by column chromatography (silica gel) to give colorless crystals; 13.5 mg (45%); mp 152.5–153.5 °C (hexane–EtOAc).

IR (KBr): 1697 (CO), 1670 (CO), 1594, 1448, 693 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.57 (s, 1 H), 7.27–7.35 (m, 1 H), 7.35–7.40 (m, 4 H), 7.43 (t, *J* = 7.7 Hz, 4 H), 7.55 (t, *J* = 7.4 Hz, 2 H), 7.97 (d, *J* = 7.5 Hz, 4 H).

MS: *m/z* (%) = 300 (36) $[M]^+$, 105 (100), 77 (31).

HRMS: *m/z* $[M]^+$ calcd for $C_{21}H_{16}O_2$: 300.1150; found: 300.1150.

Enol Carbonate (22d)
This compound was not isolated in a pure form, and only the carbonyl absorption in the IR is reported.

IR (neat): 1759 cm^{-1}.

2-(4-Methoxyphenyl)-1-phenylpent-4-en-1-one (22e)
Colorless oil.

IR (KBr): 1682 (CO), 1511, 1251, 1035 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.54 (td, *J* = 7.1, 14.2 Hz, 1 H), 2.91 (td, *J* = 7.1, 14.2 Hz, 1 H), 3.75 (s, 3 H), 4.57 (t, *J* = 7.1 Hz, 1 H), 4.92–5.10 (m, 2 H), 5.75 (tdd, *J* = 7.1, 10.2, 17.1 Hz, 1 H), 6.82 (d, *J* = 9.0 Hz, 2 H), 7.21 (d, *J* = 9.0 Hz, 2 H), 7.38 (t, *J* = 7.4 Hz, 2 H), 7.48 (t, *J* = 7.3 Hz, 1 H), 7.91–7.98 (m, 2 H).

MS: *m/z* (%) = 266 (10) $[M]^+$, 161 (100), 105 (17), 77 (15).

HRMS: *m/z* $[M]^+$ calcd for $C_{18}H_{18}O_2$: 266.1307; found: 266.1307.

2-(4-Fluorophenyl)-1-phenylpent-4-en-1-one (22f)
Colorless oil.

IR (KBr): 1685 (CO), 1508, 1225, 691 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.55 (ttd, *J* = 1.2, 7.1, 14.2 Hz, 1 H), 2.92 (m, 1 H), 4.61 (t, *J* = 7.1 Hz, 1 H), 4.92–5.09 (m, 2 H), 5.73 (tdd, *J* = 7.1, 10.2, 17.1 Hz, 1 H), 6.98 (t, *J* = 8.7 Hz, 2 H), 7.21–7.32 (m, 2 H), 7.40 (t, *J* = 7.4 Hz, 2 H), 7.50 (t, *J* = 7.3 Hz, 1 H), 7.90–7.98 (m, 2 H).

MS: *m/z* (%) = 254 (8) $[M]^+$, 105 (100), 77 (22).

HRMS: *m/z* $[M]^+$ calcd for $C_{17}H_{15}FO$: 254.1107; found: 254.1108.

1-{Chloro(phenyl)[(4-tolyl)sulfinyl]methyl}cyclobutanol (23a)
Colorless crystals; mp 140.0–141.0 °C (hexane–EtOAc).

IR (KBr): 3269 (OH), 1594, 1489, 1444, 1154, 1080 (SO), 1034, 809, 698 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.56–1.72 (m, 1 H), 1.96–2.13 (m, 2 H), 2.14–2.28 (m, 1 H), 2.32 (s, 3 H), 2.70–2.85 (m, 1 H), 2.92–3.05 (m, 1 H), 3.57 (br s, 1 H), 6.93 (d, *J* = 8.3 Hz, 2 H), 7.04 (d, *J* = 8.3 Hz, 2 H), 7.30–7.43 (m, 3 H), 7.61–7.70 (m, 2 H).

MS (FAB): *m/z* (%) = 335 (63) $[M + 1]^+$, 281 (22), 246 (24), 185 (65), 159 (100), 137 (66), 123 (17), 117 (75), 107 (20), 93 (99).

HRMS (FAB): *m/z* $[M + H]^+$ calcd for $C_{18}H_{20}ClO_2S$: 335.0873; found: 335.0874.

1-{Chloro(phenyl)[(4-tolyl)sulfinyl]methyl}cyclopentanol (23b)
Colorless crystals; mp 146.5–147.0 °C (hexane–EtOAc).

IR (KBr): 3312 (OH), 2956, 1595, 1492, 1446, 1080, 1043 (SO), 809, 698, 512 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.48–2.12 (m, 7 H), 2.24–2.41 (m, 4 H), 3.55 (br s, 1 H), 6.90 (d, *J* = 8.2 Hz, 2 H), 7.02 (d, *J* = 8.2 Hz, 2 H), 7.30–7.43 (m, 3 H), 7.73–7.84 (m, 2 H).

Anal. Calcd for $C_{19}H_{21}ClO_2S$: C, 65.41; H, 6.07; Cl, 10.16; S, 9.19. Found: C, 65.39; H, 6.1; Cl, 10.15; S, 9.17.

1-{Chloro(phenyl)[(4-tolyl)sulfinyl]methyl}cyclohexanol (23c)
Colorless crystals; mp 138.5–139.0 °C (hexane–EtOAc).

IR (KBr): 3288 (OH), 2937, 1596, 1491, 1444, 1080, 1047 (SO), 805, 697, 512 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.88–1.15 (m, 2 H), 1.45 (d, *J* = 13.2 Hz, 1 H), 1.51–1.74 (m, 3 H), 1.76–1.89 (m, 1 H), 1.93 (dt, *J* = 3.7, 12.7 Hz, 1 H), 2.09–2.26 (m, 2 H), 2.29 (s, 3 H), 4.31 (s, 1 H), 6.95 (d, *J* = 8.1 Hz, 2 H), 7.02 (d, *J* = 8.1 Hz, 2 H), 7.38 (br s, 3 H), 7.72 (br s, 2 H).

Anal. Calcd for $C_{20}H_{23}ClO_2S$: C, 66.19; H, 6.39; Cl, 9.77; S, 8.83. Found: C, 66.13; H, 6.44; Cl, 9.71; S, 8.88.

8-{Chloro(phenyl)[(4-tolyl)sulfinyl]methyl}-1,4-dioxaspiro[4.5]decan-8-ol (23d)
Colorless crystals; mp 143.5–144.0 °C (hexane–EtOAc).

IR (KBr): 3337 (OH), 2965, 1597, 1377, 1103, 1079 (SO), 1033, 996, 718, 512 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.36–1.55 (m, 2 H), 1.63–1.74 (m, 1 H), 1.99 (dt, *J* = 4.2, 13.9 Hz, 1 H), 2.11–2.26 (m, 4 H), 2.30 (s, 3 H), 3.75–3.95 (m, 4 H), 4.47 (d, *J* = 1.6 Hz, 1 H), 6.93 (d, *J* = 8.3 Hz, 2 H), 7.03 (d, *J* = 8.3 Hz, 2 H), 7.32–7.45 (m, 3 H), 7.72 (br s, 2 H).

MS (FAB): *m/z* (%) = 421 (44) $[M + 1]^+$, 281 (50), 245 (100), 185 (38), 154 (31), 137 (29), 93 (46).

HRMS (FAB): *m/z* $[M + H]^+$ calcd for $C_{22}H_{25}ClO_4S$: 421.1240; found: 421.1240.

8-{Chloro(2-naphthyl)[(4-tolyl)sulfinyl]methyl}-1,4-dioxaspiro[4.5]decan-8-ol (23e)
Colorless crystals; mp 145.0–146.0 °C (hexane–EtOAc).

IR (KBr): 3381 (OH), 1596, 1416, 1160, 1106, 1078, 1045 (SO), 760 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.35–1.51 (m, 2 H), 1.65–1.72 (m, 1 H), 2.00 (dt, *J* = 4.4, 14.3 Hz, 1 H), 2.16–2.24 (m, 5 H), 2.34–2.39 (m, 2 H), 3.70–3.83 (m, 2 H), 3.86–3.90 (m, 2 H), 4.59 (d, *J* = 1.6 Hz, 1 H), 6.91–6.98 (m, 4 H), 7.52–7.63 (m, 2 H), 7.76–7.97 (m, 4 H), 8.18 (br s, 1 H).

MS (FAB): *m/z* (%) = 471 (10) $[M + 1]^+$, 331 (27), 295 (44), 246 (25), 185 (68), 154 (77), 137 (70), 93 (100), 75 (17).

HRMS (FAB): *m/z* $[M + H]^+$ calcd for $C_{26}H_{28}ClO_4S$: 471.1397; found: 471.1399.

8-{Chloro(4-methoxyphenyl)[(4-tolyl)sulfinyl]methyl}-1,4-dioxaspiro[4.5]decan-8-ol (23f)
Colorless crystals; mp 120.0–121.0 °C (hexane–EtOAc).

IR (KBr): 3382 (OH), 1605, 1509, 1256, 1106, 1034 (SO), 815 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.34–1.44 (m, 1 H), 1.44–1.54 (m, 1 H), 1.66–1.72 (m, 1 H), 1.99 (dt, *J* = 4.4, 13.5 Hz, 1 H), 2.07–2.22 (m, 2 H), 2.23–2.33 (m, 5 H), 3.77–3.94 (m, 7 H), 4.49 (s, 1 H), 6.90 (d, *J* = 8.5 Hz, 2 H), 6.96 (d, *J* = 8.3 Hz, 2 H), 7.06 (d, *J* = 8.3 Hz, 2 H), 7.62 (br s, 2 H).

MS (FAB): *m/z* (%) = 451 (10) $[M + 1]^+$, 311 (88), 275 (100), 246 (22), 185 (58), 154 (65), 137 (60), 93 (86).

HRMS (FAB): *m/z* $[M + H]^+$ calcd for $C_{23}H_{28}ClO_5S$: 451.1346; found: 451.1347.

8-{Chloro(4-fluorophenyl)[(4-tolyl)sulfinyl]methyl}-1,4-dioxaspiro[4.5]decan-8-ol (23g)
Colorless crystals; mp 150.0–151.0 °C (hexane–EtOAc).

IR (KBr): 3302 (OH), 1601, 1504, 1374, 1227, 1108, 1040 (SO), 1001, 844, 792, 510 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.40–1.56 (m, 2 H), 1.61–1.75 (m, 1 H), 1.98 (dt, *J* = 4.4, 13.5 Hz, 1 H), 2.07–2.26 (m, 4 H), 2.31 (s, 3 H), 3.77–3.97 (m, 4 H), 4.35 (s, 1 H), 6.95 (d, *J* = 8.3 Hz, 2 H), 7.02–7.14 (m, 4 H), 7.71 (br s, 2 H).

MS (FAB): *m/z* (%) = 439 (26) $[M + 1]^+$, 299 (40), 263 (100), 219 (13), 185 (45), 154 (47), 137 (44), 93 (68), 75 (12).

HRMS (FAB): *m/z* $[M + H]^+$ calcd for $C_{22}H_{25}ClFO_4S$: 439.1146; found: 439.1146.

1-Chloro-2-methyl-1-phenyl-1-[(4-tolyl)sulfinyl]propan-2-ol (23h)
Colorless crystals; mp 143.0–144.0 °C (hexane–EtOAc).

IR (KBr): 3280 (OH), 1595, 1141, 1080 (SO), 1040, 728, 698, 513 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.31 (s, 3 H), 1.76 (s, 3 H), 2.30 (s, 3 H), 4.55 (s, 1 H), 6.94 (d, *J* = 8.3 Hz, 2 H), 7.04 (d, *J* = 8.3 Hz, 2 H), 7.34–7.42 (m, 3 H), 7.69–7.78 (m, 2 H).

MS (FAB): *m/z* (%) = 323 (100) $[M + 1]^+$, 246 (25), 219 (12), 183 (74), 147 (91), 137 (58), 93 (62), 77 (12).

HRMS (FAB): *m/z* $[M + H]^+$ calcd for $C_{17}H_{20}ClO_2S$: 323.0873; found: 323.0877.

9-Phenyl-1,4-dioxaspiro[4.6]undecan-8-one (24d)
Colorless oil.

IR (neat): 2948, 2884, 1704 (CO), 1450, 1111, 699, 454 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.79 (t, *J* = 12.2 Hz, 1 H), 1.90–2.11 (m, 4 H), 2.30–2.46 (m, 2 H), 2.94 (ddd, *J* = 4.7, 10.9, 13.6 Hz, 1 H), 3.70 (dd, *J* = 3.8, 11.6 Hz, 1 H), 3.97–4.04 (m, 4 H), 7.19–7.28 (m, 3 H), 7.28–7.36 (m, 2 H).

MS: *m/z* (%) = 246 (35) $[M]^+$, 218 (14), 142 (12), 113 (12), 104 (100), 99 (49), 86 (36), 28 (26).

HRMS: *m/z* $[M]^+$ calcd for $C_{15}H_{18}O_3$: 246.1256; found: 246.1253.

9-(2-Naphthyl)-1,4-dioxaspiro[4.6]undecan-8-one (24e)
Colorless crystals; mp 109.0–110.0 °C (hexane–EtOAc).

IR (KBr): 2944, 1697 (CO), 1105, 826, 753, 477 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.77–1.95 (m, 1 H), 1.96–2.06 (m, 2 H), 2.06–2.19 (m, 2 H), 2.37–2.59 (m, 2 H), 3.00 (ddd, *J* = 5.5, 10.0, 13.8 Hz, 1 H), 3.86 (dd, *J* = 3.7, 11.4 Hz, 1 H), 3.97–4.06 (m, 4 H), 7.36 (dd, *J* = 8.6, 1.7 Hz, 1 H), 7.40–7.53 (m, 2 H), 7.67 (s, 1 H), 7.74–7.87 (m, 3 H).

MS: *m/z* (%) = 296 (10) $[M]^+$, 154 (100).

HRMS: *m/z* $[M]^+$ calcd for $C_{19}H_{20}O_3$: 296.1412; found: 296.1414.

9-(4-Methoxyphenyl)-1,4-dioxaspiro[4.6]undecan-8-one (24f)
Colorless oil.

IR (neat): 2951, 1704 (CO), 1610, 1512, 1250, 833 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.70–1.85 (m, 1 H), 1.87–2.09 (m, 4 H), 2.25–2.43 (m, 2 H), 2.92 (ddd, *J* = 4.5, 11.0, 13.5 Hz, 1 H), 3.65 (dd, *J* = 3.7, 11.6 Hz, 1 H), 3.79 (s, 3 H), 3.95–4.04 (m, 4 H), 6.86 (d, *J* = 8.8 Hz, 2 H), 7.15 (d, *J* = 8.8 Hz, 2 H).

MS: *m/z* (%) = 276 (13) $[M]^+$, 134 (100), 99 (23).

HRMS: *m/z* $[M]^+$ calcd for $C_{16}H_{20}O_4$: 276.1362; found: 276.1358.

9-(4-Fluorophenyl)-1,4-dioxaspiro[4.6]undecan-8-one (24g)
Colorless crystals; mp 109.0–110.0 °C (hexane–EtOAc).

IR (KBr): 2884, 1701 (CO), 1602, 1512, 1223, 844 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.72–1.88 (m, 1 H), 1.92–2.09 (m, 4 H), 2.24–2.36 (m, 1 H), 2.36–2.47 (m, 1 H), 2.82–2.98 (m, 1 H), 3.69 (dd, *J* = 3.5, 11.4 Hz, 1 H), 3.99 (s, 4 H), 7.00 (t, *J* = 8.7 Hz, 2 H), 7.18 (dd, *J* = 5.4, 8.7 Hz, 2 H).

Anal. Calcd for $C_{15}H_{17}FO_3$: C, 68.17; H, 6.48; F, 7.19. Found: C, 68.22; H, 6.5; F, 7.17.

9-Deuterio-9-Phenyl-1,4-dioxaspiro[4.6]undecan-8-one (25a)
Colorless oil.

IR (neat): 2948, 2884, 1702 (CO), 1447, 1116, 699 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.71–1.86 (m, 1 H), 1.93–2.10 (m, 4 H), 2.30–2.46 (m, 2 H), 2.94 (ddd, *J* = 4.7, 10.9, 13.6 Hz, 1 H), 3.97–4.04 (m, 4 H), 7.19–7.28 (m, 3 H), 7.28–7.36 (m, 2 H).

MS: *m/z* (%) = 247 (28) $[M]^+$, 219 (15), 142 (12), 113 (12), 105 (100), 99 (50), 86 (36), 28 (32).

HRMS: *m/z* $[M]^+$ calcd for $C_{15}H_{17}DO_3$: 247.1319; found: 247.1317.

9-Methyl-9-phenyl-1,4-dioxaspiro[4.6]undecan-8-one (25b)
Colorless oil.

IR (neat): 2965, 1705 (CO), 1443, 1110, 701 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.38 (s, 3 H), 1.67 (dd, *J* = 10.9, 14.4 Hz, 1 H), 1.77–1.86 (m, 1 H), 1.86–1.96 (m, 2 H), 2.04 (dd, *J* = 9.5, 14.8 Hz, 1 H), 2.26 (ddd, *J* = 2.8, 7.1, 11.9 Hz, 1 H), 2.67 (dd, *J* = 10.8, 14.7 Hz, 1 H), 2.71 (dt, *J* = 2.6, 12.2 Hz, 1 H), 3.86–4.03 (m, 4 H), 7.17–7.26 (m, 3 H), 7.32 (t, *J* = 7.7 Hz, 2 H).

MS: *m/z* (%) = 260 (5) $[M]^+$, 232 (7), 118 (100), 99 (29), 86 (24).

HRMS: *m/z* $[M]^+$ calcd for $C_{16}H_{20}O_3$: 260.1412; found: 260.1411.

9-Allyl-9-phenyl-1,4-dioxaspiro[4.6]undecan-8-one (25c)
Colorless oil.

IR (neat): 2952, 1704 (CO), 1444, 1112 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.56–1.69 (m, 1 H), 1.75–1.94 (m, 3 H), 2.10–2.26 (m, 2 H), 2.39 (dd, *J* = 8.8, 14.2 Hz, 1 H), 2.52 (dd, *J* = 10.8, 14.9 Hz, 1 H), 2.63 (dt, *J* = 2.8, 12.3 Hz, 1 H), 2.77 (dd, *J* = 5.4, 14.2 Hz, 1 H), 3.85–4.02 (m, 4 H), 4.92 (d, *J* = 17.2 Hz, 1 H), 4.94 (d, *J* = 9.5 Hz, 1 H), 5.35 (m, 1 H), 7.19 (d, *J* = 7.6 Hz, 2 H), 7.24 (t, *J* = 7.4 Hz, 1 H), 7.32 (t, *J* = 7.6 Hz, 2 H).

MS: *m/z* (%) = 286 (22) $[M]^+$, 245 (18), 144 (100), 129 (73), 115 (32), 99 (48), 86 (36).

HRMS: *m/z* $[M]^+$ calcd for $C_{18}H_{22}O_3$: 286.1569; found: 286.1571.

9-Benzyl-9-phenyl-1,4-dioxaspiro[4.6]undecan-8-one (25d)
Colorless crystals; mp 120.0–120.5 °C (hexane–EtOAc).

IR (KBr): 2953, 1709 (CO), 1450, 1139, 1094, 704 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.69 (dd, *J* = 10.5, 14.7 Hz, 1 H), 1.81–1.95 (m, 3 H), 2.05 (dd, *J* = 9.5, 15.2 Hz, 1 H), 2.19 (ddd, *J* = 2.9, 6.3, 11.8 Hz, 1 H), 2.41 (dd, *J* = 10.7, 15.1 Hz, 1 H), 2.65 (dt, *J* = 3.4, 12.1 Hz, 1 H), 2.99 (d, *J* = 13.9 Hz, 1 H), 3.27 (d, *J* = 13.9 Hz, 1 H), 3.85–4.01 (m, 4 H), 6.53 (d, *J* = 7.2 Hz, 2 H), 6.99–7.13 (m, 5 H), 7.21–7.30 (m, 3 H).

Anal. Calcd for $C_{22}H_{24}O_3$: C, 78.54; H, 7.19. Found: C, 78.54; H, 7.16.

9-Benzoyl-9-phenyl-1,4-dioxaspiro[4.6]undecan-8-one (25e)
Colorless oil.

IR (neat): 2956, 1722 (CO), 1664 (CO), 1447, 1239, 1113, 700 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.78–2.04 (m, 4 H), 2.55–2.73 (m, 2 H), 2.77–2.90 (m, 2 H), 3.87–4.00 (m, 4 H), 7.19–7.28 (m, 4 H), 7.28–7.43 (m, 4 H), 7.47–7.55 (m, 2 H).

MS: *m/z* (%) = 350 (23) $[M]^+$, 149 (22), 105 (100), 77 (18).

HRMS: *m/z* $[M]^+$ calcd for $C_{22}H_{22}O_4$: 350.1518; found: 350.1519.

1-Chloro-3-methyl-1-phenyl-1-[(4-tolyl)sulfinyl]but-3-en-2-ol (26L and 26P)
26L
Colorless oil.

IR (neat): 3394 (OH), 1647, 1596, 1446, 1085 (SO), 911, 809 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.48 (s, 3 H), 2.32 (s, 3 H), 4.84 (s, 1 H), 4.97 (s, 2 H), 5.54 (s, 1 H), 6.80 (d, *J* = 8.0 Hz, 2 H), 7.04 (d, *J* = 8.0 Hz, 2 H), 7.30–7.45 (m, 5 H).

MS: *m/z* (%) = 334 (4) $[M]^+$, 298 (3), 246 (10), 193 (12), 158 (14), 123 (27), 105 (100), 91 (18), 77 (36).

HRMS: *m/z* $[M]^+$ calcd for $C_{18}H_{19}ClO_2S$: 334.0794; found: 334.0793.

26P

Colorless crystals; mp 140.0–141.0 °C (hexane–EtOAc).

IR (KBr): 3269 (OH), 1645, 1596, 1492, 1445, 1081 (SO), 1036, 913, 807, 697, 510 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.37 (s, 3 H), 2.31 (s, 3 H), 3.44 (br s, 1 H), 4.93 (t, *J* = 1.5 Hz, 1 H), 4.99 (br s, 1 H), 5.08 (d, *J* = 5.3 Hz, 1 H), 6.82 (d, *J* = 8.2 Hz, 2 H), 7.02 (d, *J* = 8.2 Hz, 2 H), 7.30–7.44 (m, 3 H), 7.69–7.77 (m, 2 H).

MS (FAB): *m/z* (%) = 335 (54) $[M + 1]^+$, 177 (20), 159 (100), 131 (18), 93 (12).

HRMS (FAB): *m/z* $[M + H]^+$ calcd for $C_{18}H_{20}ClO_2S$: 335.0873; found: 335.0873.

1-Methyl-2-phenylcyclopropanecarbaldehyde (28)

Colorless oil.

IR (neat): 1708 (CHO), 1603, 903, 699 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.98 (s, 3 H), 1.44 (dd, *J* = 5.3, 7.1 Hz, 1 H), 1.68 (dd, *J* = 5.3, 9.3 Hz, 1 H), 2.73 (dd, *J* = 7.1, 9.3 Hz, 1 H), 7.12–7.41 (m, 5 H), 8.95 (s, 1 H).

MS: *m/z* (%) = 160 (100) $[M]^+$, 145 (73), 131 (72), 115 (39), 103 (15), 91 (85), 77 (19), 69 (22), 51 (13).

HRMS: *m/z* $[M]^+$ calcd for $C_{11}H_{12}O$: 160.0888; found: 160.0889.

Acknowledgment

This work was supported by a Grant-in-Aid for Scientific Research No. 19590018 and 22590021 from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and a TUS Grant for Research Promotion from Tokyo University of Science, which is gratefully acknowledged.

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