1-Haloalkyl Aryl Sulfoxides as Useful Agents in Synthesis of α-Halo Ketones: A New Synthesis of α-Halo Ketones, α-Halo α,β-Unsaturated Ketones, and α-Halo Cross Dienones from Aldehydes

Tsuyoshi SATOH, Norifumi ITOH, Ken-ichi ONDA, Yasushi KITOH, and Koji YAMAKAWA*
Faculty of Pharmaceutical Sciences, Science University of Tokyo, Ichigaya-funagawaramachi, Shinjuku-ku, Tokyo 162
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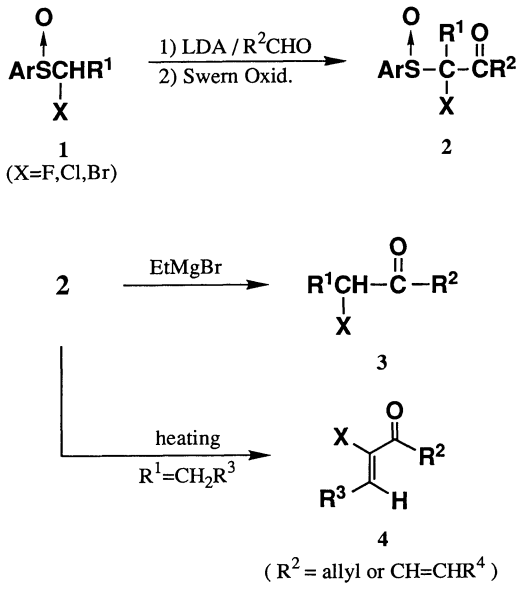
α-Halo α-sulfinyl ketones were synthesized in two steps from 1-haloalkyl aryl sulfoxides and aldehydes in high yields. Desulfinylation of the α-halo α-sulfinyl ketones was performed with ethylmagnesium bromide in ether at low temperature to afford α-halo ketones via magnesium enolates in high yields. The magnesium enolate intermediates were trapped with various electrophiles such as deuterium oxide, ethyl chloroformate, and chlorotrimethylsilane. Trapping of the magnesium enolate intermediate with carbonyl compounds afforded a new type of the directed aldol reaction. Desulfinylation of the sulfinyl group of the α-halo α-sulfinyl ketones under thermal conditions gave α-halo α,β-unsaturated ketones or α-halo cross dienones.

α-Halo ketones are quite useful compounds in synthetic organic chemistry. Especially, α-fluoro ketones have received much attention as key substances for preparation of fluorine-containing medicines and agricultural chemicals.[1] Extensive studies have been made on the chemistry and the synthesis of α-halo ketones;[2] however, new and efficient methods for preparing these compounds are eagerly sought.

In our recent studies, 1-chloroalkyl aryl sulfoxides (**1**: X=Cl) were proved to be useful agents for homologation of carbonyl compounds.[3] We envisioned that 1-haloalkyl aryl sulfoxides **1** could be used as good starting materials for the synthesis of α-halo ketones. In this paper we report a versatile method for the synthesis of α-fluoro, α-chloro, and α-bromo ketones **3** and several α-halo α,β-unsaturated ketones **4** from 1-haloalkyl aryl sulfoxides **1** and aldehydes (Scheme 1).[4]



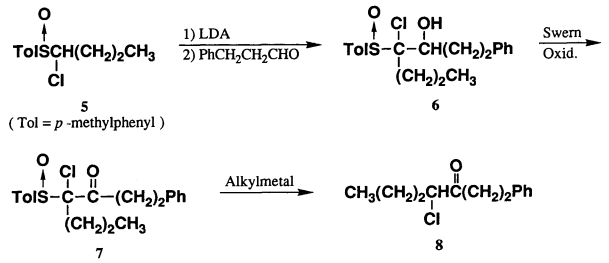
Scheme 1.

Results and Discussion

A Synthesis of α-Halo Ketones from α-Halo α-Sulfinyl Ketones 2 by Ethylmagnesium Bromide Promoted Desulfinylation and Trapping of the Magnesium Enolate. 1-Fluoroalkyl aryl sulfoxides (**1**: X=F),[5] 1-chloroalkyl aryl sulfoxides (**1**: X=Cl),[6] and 1-bromoalkyl aryl sulfoxides (**1**: X=Br)[7] are now quite easily prepared from alkyl aryl sulfides or alkyl aryl sulfoxides in practical quantities. Generation of the α-sulfinyl carbanion of **1** is easily carried out with lithium diisopropylamide (LDA) in THF at low temperature. The carbanion reacts with aldehydes to afford the adducts usually in quantitative yields; then the Swern oxidation of the hydroxyl group of the adducts gives α-halo α-sulfinyl ketones **2** in high yields.[4] It was anticipated that if the sulfinyl group of **2** was desulfurized, α-halo ketone **3** could be obtained. To this end, we studied the removal of the sulfinyl group of **2** and found a novel way completely different from the conventional method.

An example illustrating the preparation of 4-chloro-1-phenyl-3-heptanone **8** from 1-chlorobutyl *p*-tolyl sulfoxide **5** and 3-phenylpropanal will be described (Scheme 2).

Treatment of **5** with 1.2 equivalents of LDA in THF at −78 °C and with 3-phenylpropanal gave the chloro alcohol **6** (a mixture of two diastereomers) in 99% yield.



Scheme 2.

Swern oxidation[8] of **6** afforded the desired ketone **7** in 96% yield. This ketone **7** was found to be slightly unstable under heating; even at room temperature thermal elimination of the sulfinyl group of **7** took place slowly to afford an enone.

Next, the reaction for removal of the sulfinyl group in **7** was investigated. In our previous work we reported the stereospecific desulfinylation of sulfinyloxiranes[9] and sulfinylaziridines[10] with butyllithium (*n*-BuLi) or ethylmagnesium bromide (EtMgBr). We thought that the reaction could be applied to the desulfinylation of the α-chloro α-sulfinyl ketone **7**. Actually, treatment of **7** with 1.1 equivalents of *n*-BuLi in ether at −78 °C gave the desulfinylated product **8** in 86% yield. Interestingly, no product from the reaction of *n*-BuLi with the carbonyl group of **7** was detected.

Table 1 shows the results of the desulfinylation of **7** with several alkylmetals at −78 °C. Both alkyllithium and Grignard reagents are almost equally effective for the desulfinylation. The best result was obtained when **7** was treated with EtMgBr in ether as a solvent; these conditions were used throughout this study.

The results for the synthesis of α-fluoro, α-chloro, and α-bromo ketones from 1-halobutyl aryl sulfoxides and aldehydes through the desulfinylation of **2** with 1.1 equivalents of EtMgBr in ether are summarized in Table 2. Both the α-fluoro ketones and α-chloro ketones were synthesized through the corresponding α-halo α-sulfinyl ketones without any problem (Entries a—h). Because of the unstable nature of the bromides, the yields of the α-bromo α-sulfinyl ketones and α-bromo ketones were somewhat lower than those of the fluorides and chlorides (Entries i—l).

Table 1. Reaction Conditions and Yield of the Desulfinylation of **7**

Entry	Alkylmetal[a]	Solvent	**8** Yield[b]/%
1	MeLi	Ether	84
2	*n*-BuLi	Ether	86
3	*n*-BuLi	THF	82
4	MeMgBr	Ether	90
5	EtMgBr	THF	88
6	EtMgBr	Ether	91

a) All reactions were carried out at −78 °C with 1.1 equivalents of alkylmetal. b) Isolated yield.

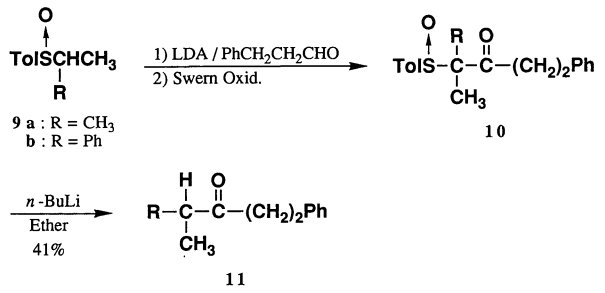
Table 2. Synthesis of α-Halo Ketones **3** from 1-Halobutyl Aryl Sulfoxide **1** ($R^1=(CH_2)_2CH_3$) and Aldehydes

Entry	**1** X	**1** Ar	Aldehyde	**2** Yield (%)[a]	**3** Yield (%)[b]
a	F[c]	Ph	$PhCH_2CH_2CHO$	**2a** (90)	**3a** (79)
b			$CH_3(CH_2)_8CHO$	**2b** (81)	**3b** (90)
c			PhCHO	**2c** (96)	**3c** (82)
d			Cyc-HexCHO	**2d** (78)	**3d** (85)
e	Cl	Tol	$PhCH_2CH_2CHO$	**7** (98)	**8** (91)
f			$CH_3(CH_2)_8CHO$	**2f** (75)	**3f** (93)
g			PhCHO	**2g** (76)	**3g** (78)
h			Cyc-HexCHO	**2h** (86)	**3h** (95)
i	Br[d]	Tol	$PhCH_2CH_2CHO$	**2i** (70)	**3i** (68)
j			$CH_3(CH_2)_8CHO$	**2j** (89)	**3j** (70)
k			PhCHO	**2k** (67)	**3k** (56)
l			Cyc-HexCHO	**2l** (65)	**3l** (59)

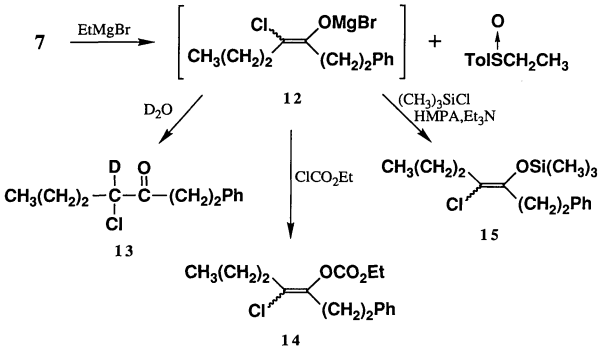
a) Two-step overall yield from **1** and aldehyde. b) Isolated yield. c) Prepared according to the method by Wnuk.[5] d) Prepared according to the method by Iriuchijima.[7]

This desulfinylation was thought to be a ligand-exchange reaction of sulfoxide,[9b,11] and the product would be a magnesium enolate (this is discussed later). First, we examined the role of the halogen in this desulfinylation of the α-halo α-sulfinyl ketones **2**. Instead of the halogens, the corresponding α-sulfinyl ketones having a methyl (**10a**: R=CH_3) and phenyl (**10b**: R=Ph) group were synthesized from sulfoxide **9** and 3-phenylpropanal. The desulfinylation of **10** was carried out with EtMgBr under the same conditions described above; however, this reaction gave a complex mixture. With *n*-BuLi the reaction afforded the desired desulfinylated ketone **11** as a major product with several by-products, but the yields were in both cases only 41%. From these results, it was proved that the halogen of the α-halo α-sulfinyl ketones **2** plays an important role in this desulfinylation.

As described above, this desulfinylation was thought to result in the production of a magnesium enolate (for example **12**). To confirm this expectation and develop this reaction to new synthetic method, the reaction was



Scheme 3.

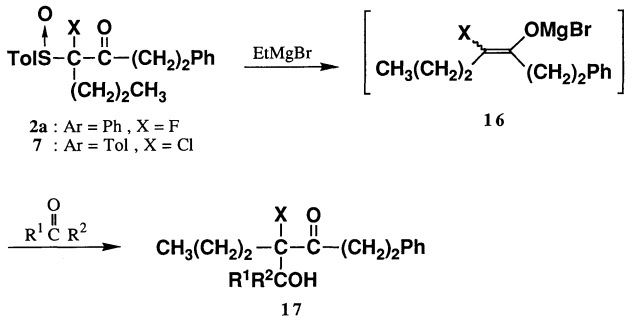


Scheme 4.

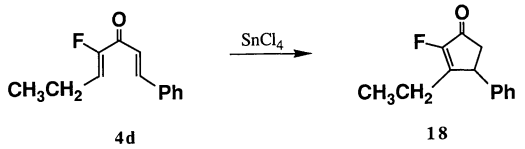
quenched with several electrophiles (Scheme 4). α-Chloro α-sulfinyl ketone **7** was treated with 1.1 equivalents of EtMgBr in ether at −78 °C for 10 min followed by deuterium oxide to give α-deuterated α-chloro ketone **13** in 87% yield with ethyl *p*-tolyl sulfoxide (84%). The reaction was quenched with ethyl chloroformate to give enol carbonate **14** in 86% yield. Treatment with chlorotrimethylsilane in the presence of hexamethylphosphoric triamide (HMPA) and triethylamine gave enol silyl ether **15** (detected by ^{1}H NMR), which was converted to the α-chloro ketone **8** by silica gel in 82% yield.

It is interesting to note that this desulfinylation gave a regioselective enolate between the carbonyl carbon and the carbon bearing the sulfinyl group. Magnesium enolates have been reported to be useful intermediates in aldol reactions,[12] and we utilized the magnesium enolate for carrying out the directed aldol reaction[12] (Scheme 5 and Table 3). For example, **2a** was treated with 1.1 equivalents of EtMgBr in ether and then with cyclohexanone to give the aldol **17a** (Table 3) in 66% yield. This reaction gave the directed aldol products in moderate to good yields, which are summarized in Table 3.

A Synthesis of α-Halo α,β-Unsaturated Ketones and α-Halo Cross Dienones from Aldehydes. Thermal elimination is one of the most remarkable chemical properties of sulfoxides in organic synthesis.[13] As mentioned above, thermal elimination of the sulfinyl group in the α-halo α-sulfinyl ketones **2** tends to take place under relatively low temperature. For example, **2a** was heated at reflux in benzene for 25 min to give (*Z*)-4-fluoro-1-phenyl-4-hepten-3-one (**4a**) in 81% yield (Entry 1 in Table 4). When **2** was synthesized from α,β-unsaturated aldehydes, the useful α-halo cross dienones were obtained in good yields without any problem



Scheme 5.



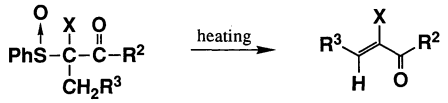
Scheme 6.

Table 3. Synthesis of the Aldol **17** from **2** or **7** and Carbonyl Compounds via the Ethylmagnesium Bromide Promoted Desulfinylation

Entry	2 or 7		R^1COR^2		17
	Ar	X	R^1	R^2	Yield (%)[a]
a	Ph	F	$-(CH_2)_5-$		**17a** (66)
b			CH_3	CH_3	**17b** (52)
c			Ph	H	**17c** (64)
d	Tol	Cl	Ph	H	**17d** (86)

a) Isolated yield.

Table 4. Synthesis of α-Halo α,β-Unsaturated Ketones and α-Halo Cross Dienones **4** from **2**



2 **4**

Entry	2				4
		X	R^3	R^2	Yield (%)[a]
1	**2a**	F	CH_3CH_2	$Ph(CH_2)_2$	**4a** (81)
2	**2b**	F	CH_3CH_2	$CH_3(CH_2)_8$	**4b** (90)
3	**2c**	F	CH_3CH_2	Ph	**4c** (75)
4	**2m**	F	CH_3CH_2	(*E*)-CH=CHPh	**4d** (91)
5	**2n**	F	H	(*E*)-CH=CHPh	**4e** (79)
6	**2o**	F	$CH_3(CH_2)_7$	(*E*)-CH=CHCH$_3$	**4f** (77)
7	**2p**	Cl	CH_3CH_2	$Ph(CH_2)_2$	**4g** (85)
8	**2q**	Cl	CH_3CH_2	(*E*)-CH=CHPh	**4h** (79)
9	**2r**	Cl	$CH_3(CH_2)_7$	(*E*)-CH=CHCH$_3$	**4i** (79)

a) Isolated yield.

(Entryies 4—6, 8, 9). Nazarov cyclization[14] of dienone **4d** gave 2-fluoro-2-cyclopenten-1-one **18** in 46% yield.

In conclusion, we developed a versatile method for the synthesis of α-halo ketones and α-halo α,β-unsaturated ketones from aldehydes and 1-haloalkyl aryl sulfoxides. Because the procedure is simple and the yields are pretty good, the presented method will prove to be valuable in the synthesis of α-halo ketones.

Experimental

^{1}H NMR spectra were measured in a $CDCl_3$ solution with a JEOL FX-100 spectrometer. Electron-impact mass spectra (MS) were obtained at 70 eV by direct insertion. Silica gel BW-127 ZH (Fuji-Devison) containing 2% fluorescence reagent 254 and a quartz column were used for column chromatography, and the products having UV absorption were detected by UV irradiation. In experiments requiring a dry solvent, THF and ether were distilled from diphenylketyl; diisopropylamine, triethylamine, HMPA, and benzene were dried over CaH_2 and distilled. Special precautions were taken in the purification of CH_2Cl_2. To remove methanol, 3 L of commercial CH_2Cl_2 was washed successively with concentrated sulfuric acid (100 ml×2), water (100 ml×2), saturated aqueous $NaHCO_3$ (100 ml×2), and finally saturated brine (100 ml×3). The CH_2Cl_2 was dried over $CaCl_2$ overnight and then distilled in the presence of CaH_2. Oily compounds did not give

acceptable data for combustion analysis; however, the purity of all title compounds was judged to be over 95% by ^{1}H NMR spectral determination and chromatographic analyses.

4-Chloro-1-phenyl-4-(*p*-tolylsulfinyl)-3-heptanol (6). A solution of 1-chlorobutyl *p*-tolyl sulfoxide (595 mg; 2.6 mmol) in 1 ml of THF was added dropwise to a solution of LDA (3 mmol) in 10 ml of THF at −78 °C under N_2 atmosphere. The mixture was stirred for 10 min, then 3-phenylpropanal (0.47 ml; 3.6 mmol) was added. The reaction mixture was stirred for 5 min, then the reaction was quenched with sat. aq NH_4Cl. The reaction mixture was extracted with benzene–ether. The extract was washed with sat. aq NH_4Cl, dried, and the solvent was evaporated. The residue was purified by silica-gel column chromatography to give a mixture of two diastereomers of **6** (928 mg; 99% yield). A part of this mixture was separated to give the less polar adduct and the more polar adduct (ratio about 4:5).

The less polar adduct: Colorless oil; IR (neat) 3370 (OH), 1090, 1040, 1020 (SO) cm^{-1}; ^{1}H NMR δ=1.04 (3H, t, *J*=7 Hz), 1.5—3.0 (8H, m), 2.44 (3H, s), 3.83 (1H, dd, *J*=7, 6 Hz), 7.0—7.9 (9H, m).

The more polar adduct: Colorless oil; IR (neat) 3350 (OH), 1080, 1040 (SO) cm^{-1}; ^{1}H NMR δ=0.91 (3H, t, *J*=7 Hz), 1.4—3.0 (8H, m), 2.41 (3H, s), 3.82 (1H, dd, *J*=10, 2 Hz), 7.0—7.7 (9H, m).

4-Chloro-1-phenyl-4-(*p*-tolylsulfinyl)-3-heptanone (7). To a solution of oxalyl dichloride (2 mmol) in 10 ml of dry CH_2Cl_2 at −60 °C was added dropwise with stirring a solution of dimethyl sulfoxide (4 mmol) in 2 ml of dry CH_2Cl_2. After 5 min, a solution of **6** (diastereomeric mixture; 364 mg; 1 mmol) in 2 ml of CH_2Cl_2 was added to the mixture. The reaction mixture was stirred at −60 °C for 15 min, then triethylamine (1.4 ml; 10 mmol) was added. The reaction mixture was allowed to warm to 0 °C for 2 h, then 10 ml of water was added to the reaction mixture. The whole was extracted with CH_2Cl_2. After the usual workup, the product was purified by silica-gel column chromatography to give 347 mg (96%) of **7** as a colorless oil. IR (neat) 1705 (CO), 1090, 1070 (SO) cm^{-1}; ^{1}H NMR δ=0.94 (3H, t, *J*=7 Hz), 1.0—3.0 (8H, m), 2.40 (3H, s), 6.9—7.6 (9H, m); MS *m/z* (%) 362 (M^+, trace), 262 (7), 246 (9), 214 (22), 193 (19), 139 (100).

4-Chloro-1-phenyl-3-heptanone (8). A solution of **7** (76 mg; 0.21 mmol) in 2 ml of dry ether was added dropwise to a stirring solution of EtMgBr (0.23 mmol) in 5 ml of dry ether at −78 °C. The reaction mixture was stirred for 5 min, then the reaction was quenched with sat. aq NH_4Cl. The whole was extracted with AcOEt, then the usual workup followed by silica-gel column chromatography gave **8** (43 mg; 91%) and ethyl *p*-tolyl sulfoxide (29.5 mg; 84%).

8: Colorless oil; IR (neat) 1730 (CO) cm^{-1}; ^{1}H NMR δ=0.89 (3H, t, *J*=7 Hz), 1.1—2.0 (4H, m), 2.95 (4H, m), 4.16 (1H, dd, *J*=8, 7 Hz), 7.2 (5H, m); MS *m/z* (%) 224 (M^+, 8), 133 (44), 105 (100). Found: *m/z* 224.0975. Calcd for $C_{13}H_{17}ClO$: M, 224.0967.

α-Halo α-Sulfinyl Ketones (2a—2d, 2f—2l: Table 1). These ketones were synthesized from 1-haloalkyl aryl sulfoxides and aldehydes in a similar way as described for **7**.

4-Fluoro-1-phenyl-4-(phenylsulfinyl)-3-heptanone (2a). Colorless oil; IR (neat) 1710 (CO), 1080, 1055 (SO) cm^{-1}; ^{1}H NMR δ=0.92 (3H, t, *J*=7 Hz), 1.1—2.8 (8H, m), 6.8—7.7 (10H, m); MS *m/z* (%) 332 (M^+, 1), 205 (0.5), 177 (50), 91 (100). Found: *m/z* 332.1247. Calcd for $C_{19}H_{21}FO_2S$: M, 332.1245.

4-Fluoro-4-(phenylsulfinyl)-5-tetradecanone (2b). Light yellow oil; IR (neat) 1725 (CO), 1095, 1065 (SO) cm^{-1}; ^{1}H NMR δ=0.87, 0.93 (each 3H, t, *J*=7 Hz), 0.8—2.7 (methylene, m), 7.3—7.7 (5H, m); MS *m/z* (%) 354 (M^+, 0.7), 229 (20), 199 (5), 155 (15), 116 (100). Found: *m/z* 354.2020. Calcd for $C_{20}H_{31}FO_2S$: M, 354.2026.

2-Fluoro-1-phenyl-2-(phenylsulfinyl)-1-pentanone (2c). Light yellow oil; IR (neat) 1665 (CO), 1085, 1055 (SO) cm^{-1}; ^{1}H NMR δ=0.97 (3H, t, *J*=7 Hz), 1.2—1.7 (2H, m), 2.2—2.8 (2H, m), 7.1—7.8 (10H, m); MS *m/z* (%) 304 (M^+, 1), 179 (31), 126 (20), 105 (100). Found: *m/z* 304.0938. Calcd for $C_{17}H_{17}FO_2S$: M, 304.0932.

1-Cyclohexyl-2-fluoro-2-(phenylsulfinyl)-1-pentanone (2d). Light yellow oil; IR (neat) 1705 (CO), 1085, 1050 (SO) cm^{-1}; ^{1}H NMR δ=0.91 (3H, t, *J*=7 Hz), 1.0—2.6 (15H, m), 7.3—7.7 (5H, m); MS *m/z* (%) 310 (M^+, 1.5), 218 (2), 185 (33), 83 (100). Found: *m/z* 310.1403. Calcd for $C_{17}H_{23}FO_2S$: M, 310.1402.

4-Chloro-4-(*p*-tolylsulfinyl)-5-tetradecanone (2f). Colorless oil; IR (neat) 1710 (CO), 1095, 1075 (SO) cm^{-1}; ^{1}H NMR δ=0.84 (3H, t, *J*=7 Hz), 0.95 (3H, t, *J*=7 Hz), 1.0—2.8 (methylene, m), 2.41 (3H, s), 7.1—7.6 (4H, m); MS *m/z* (%) 384 (M^+ trace), 262 (1), 215 (16), 155 (19), 132 (100). Found: *m/z* 384.1870. Calcd for $C_{21}H_{33}ClO_2S$: M, 384.1887.

2-Chloro-1-phenyl-2-(*p*-tolylsulflnyl)-1-pentanone (2g). Colorless oil; IR (neat) 1680 (CO), 1095, 1070 (SO) cm^{-1}; ^{1}H NMR δ=0.90 (3H, t, *J*=7 Hz), 1.0—2.6 (4H, m), 2.35 (3H, s), 7.1—8.0 (9H, m); MS *m/z* (%) 334 (M^+ trace), 278 (1), 214 (2), 194 (10), 105 (100). Found: *m/z* 334.0793. Calcd for $C_{18}H_{19}ClO_2S$: M, 334.0793.

2-Chloro-1-cyclohexyl-2-(*p*-tolylsulfinyl)-1-pentanone (2h). Colorless oil; IR (neat) 1705 (CO), 1095, 1075 (SO) cm^{-1}; ^{1}H NMR δ=0.91 (3H, t, *J*=7 Hz), 0.9—2.0 (14H, m), 2.2—2.7 (1H, m), 2.41 (3H, s), 7.2—7.7 (4H, m); MS *m/z* (%) 340 (M^+, 0.7), 262 (1), 246 (1.7), 171 (36), 83 (100). Found: *m/z* 340.1285. Calcd for $C_{18}H_{25}ClO_2S$: M, 340.1262.

4-Bromo-1-phenyl-4-(*p*-tolylsulfinyl)-3-heptanone (2i). Colorless oil; IR (neat) 1705 (CO), 1090, 1070 (SO) cm^{-1}; ^{1}H NMR δ=0.95 (3H, t, *J*=7 Hz), 1.1—3.1 (8H, m), 2.40 (3H, s), 6.9—7.7 (9H, m); MS *m/z* (%) 408, 406 (M^+ trace), 239, 237 (44), 91 (100). Found: *m/z* (%) 406.0625. Calcd for $C_{20}H_{23}BrO_2S$: M, 406.0602.

4-Bromo-4-(*p*-tolylsulfinyl)-5-tetradecanone (2j). Colorless oil; IR (neat) 1705 (CO), 1090, 1070 (SO) cm^{-1}; ^{1}H NMR δ=0.88, 0.97 (each 3H, t, *J*=7 Hz), 1.0—2.8 (methylene, m), 2.41 (3H, s), 7.2—7.7 (4H, m); MS *m/z* (%) 430, 428 (M^+ trace), 291, 289 (5), 261, 259 (31), 176 (100). Found: *m/z* 428.1386. Calcd for $C_{21}H_{33}BrO_2S$: M, 428.1384.

2-Bromo-1-phenyl-2-(*p*-tolylsulfinyl)-1-pentanone (2k). Colorless oil; IR (neat) 1710 (CO), 1095, 1075 (SO) cm^{-1}; ^{1}H NMR δ=0.89 (3H, t, *J*=7 Hz), 1.0—2.5 (4H, m), 2.35 (3H, s), 7.1—8.1 (9H, m); MS *m/z* (%) 380, 378 (M^+ trace), 240 (6), 211 (4), 105 (100). Found: *m/z* 378.0289. Calcd for $C_{18}H_{19}BrO_2S$: M, 378.0289.

2-Bromo-1-cyclohexyl-2-(*p*-tolylsulfinyl)-1-pentanone (2l). Colorless oil; IR (neat) 1700 (CO), 1095, 1075 (SO) cm^{-1}; ^{1}H NMR δ=0.92 (3H, t, *J*=7 Hz), 0.8—2.7 (methylene, m), 2.41 (3H, s), 7.2—7.7 (4H, m); MS *m/z* (%) 386, 384 (M^+, 0.3), 290 (18), 246 (10), 179 (60), 83 (100). Found: *m/z* 384.0746. Calcd for $C_{18}H_{25}BrO_2S$: M, 384.0757.

α-Halo Ketones (3a—3d, 3f—3l). These α-halo ketones were synthesized from α-halo α-sulfinyl ketones **2** in a similar way as described for **8**.

4-Fluoro-1-phenyl-3-heptanone (3a). Light yellow oil; IR

(neat) 1715 (CO) cm^{-1}; ^1H NMR δ=0.92 (3H, t, J=7 Hz), 1.2—2.0 (4H, m), 2.90 (4H, m), 4.68 (1H, ddd, J=50, 7, 5 Hz), 7.0—7.4 (5H, m); MS m/z (%) 208 (M^+, 20), 133 (41), 105 (100). Found: m/z 208.1270. Calcd for $C_{13}H_{17}FO$: M, 208.1263.

4-Fluoro-5-tetradecanone (3b). Light yellow oil; IR (neat) 1715 (CO) cm^{-1}; ^1H NMR δ=0.88, 0.95 (each 3H, t, J=7 Hz), 1.0—2.0 (18H, m), 2.4—2.8 (2H, m), 4.67 (1H, ddd, J=50, 7, 6 Hz); MS m/z 230 (M^+, 0.6), 205 (0.6), 183 (1), 155 (100). Found: m/z 230.2049. Calcd for $C_{14}H_{27}FO$: M, 230.2045.

2-Fluoro-1-phenyl-1-pentanone (3c). Light yellow oil; IR (neat) 1695 (CO) cm^{-1}; ^1H NMR δ=0.99 (3H, t, J=7 Hz), 1.1—2.2 (4H, m), 5.56 (1H, dt, J=49, 5 Hz), 7.3—8.1 (5H, m); MS m/z (%) 180 (M^+, 5), 138 (3), 105 (100). Found: m/z 180.0944. Calcd for $C_{11}H_{13}FO$: M, 180.0949.

1-Cyclohexyl-2-fluoro-1-pentanone (3d). Light yellow oil; IR (neat) 1710 (CO) cm^{-1}; ^1H NMR δ=0.95 (3H, t, J=7 Hz), 1.0—2.0 (14H, m), 2.6—3.0 (1H, m), 4.80 (1H, dt, J=50, 6 Hz); MS m/z (%) 186 (M^+, 4), 111 (25), 83 (100). Found: m/z 186.1425. Calcd for $C_{11}H_{19}FO$: 186.1219.

4-Chloro-5-tetradecanone (3f). Colorless oil; IR (neat) 1725 cm^{-1}; ^1H NMR δ=0.87, 0.94 (each 3H, t, J=7 Hz), 1.1—2.0 (18H, m), 2.64 (2H, t, J=7 Hz), 4.19 (1H, dd, J=8, 6 Hz); MS m/z (%) 246 (M^+, 0.8), 204 (0.9), 155 (100). Found: m/z 246.1752. Calcd for $C_{14}H_{27}ClO$: M, 246.1749.

2-Chloro-1-phenyl-1-pentanone (3g). Colorless oil; IR (neat) 1695 (CO) cm^{-1}; ^1H NMR δ=0.98 (3H, t, J=7 Hz), 1.1—2.2 (4H, m), 5.11 (1H, dd, J=7, 6 Hz), 7.3—8.1 (5H, m); MS m/z (%) 196 (M^+, 0.2), 154 (0.7), 105 (100). Found: m/z 196.0654. Calcd for $C_{11}H_{13}ClO$: M, 196.0654.

2-Chloro-1-cyclohexyl-1-pentanone (3h). Colorless oil; IR (neat) 1730 cm^{-1}; ^1H NMR δ=0.93 (3H, t, J=7 Hz), 1.0—2.0 (14H, m), 2.76 (1H, m), 4.29 (1H, dd, J=8, 6 Hz); MS m/z (%) 202 (M^+, 0.2), 160 (0.1), 111 (32), 83 (100). Found: m/z 202.1124. Calcd for $C_{11}H_{19}ClO$: M, 202.1123.

4-Bromo-1-phenyl-3-heptanone (3i). Colorless oil; IR (neat) 1725 (CO) cm^{-1}; ^1H NMR δ=0.89 (3H, t, J=7 Hz), 1.1—1.6 (2H, m), 1.85 (2H, t, J=7 Hz), 2.96 (4H, m), 4.19 (1H, t, J=7 Hz), 7.0—7.4 (5H, m); MS m/z (%) 270, 268 (M^+, 6), 189 (14), 160 (7), 133 (40), 105 (100). Found: m/z 268.0448. Calcd for $C_{13}H_{17}BrO$: M, 268.0461.

4-Bromo-5-tetradecanone (3j). Colorless oil; IR (neat) 1725 (CO) cm^{-1}; ^1H NMR δ=0.87, 0.94 (each 3H, t, J=7 Hz), 1.1—2.1 (18H, m), 2.66 (2H, t, J=6 Hz), 4.24 (1H, t, J=7 Hz); MS m/z (%) 292, 290 (M^+, 1), 250, 248 (1), 211 (2), 155 (100). Found: m/z 290.1240. Calcd for $C_{14}H_{27}BrO$: M, 290.1243.

2-Bromo-1-phenyl-1-pentanone (3k). Colorless oil; IR (neat) 1695 (CO) cm^{-1}; ^1H NMR δ=0.98 (3H, t, J=7 Hz), 1.1—1.8 (2H, m), 2.14 (2H, q, J=7 Hz), 5.14 (1H, t, J=7 Hz), 7.3—8.1 (5H, m); MS m/z (%) 242, 240 (M^+, 1), 213, 211 (2), 161 (6), 105 (100). Found: m/z 240.0146. Calcd for $C_{11}H_{13}BrO$: M, 240.0149.

2-Bromo-1-cyclohexyl-1-pentanone (3l). Colorless oil; IR (neat) 1720 (CO) cm^{-1}; ^1H NMR δ=0.94 (3H, t, J=7 Hz), 1.0—2.1 (14H, m), 2.76 (1H, m), 4.37 (1H, t, J=7 Hz); MS m/z (%) 248, 246 (M^+, 0.4), 206, 204 (0.6), 167 (1), 111 (37), 83 (100). Found: m/z 246.0603. Calcd for $C_{11}H_{19}BrO$: M, 246.0618.

4-Methyl-1-phenyl-3-pentanone (11a). To a solution of **10a** (40.2 mg; 0.13 mmol) in dry ether (3 ml) at −78 °C was added with stirring a solution of *n*-BuLi (0.14 mmol) and the reaction mixture was stirred for 15 min. The reaction was quenched with sat. aq NH_4Cl. The usual workup followed by silica-gel column chromatography afforded **11a** (13.6 mg; 41%) as a colorless oil. IR (neat) 1720 (CO) cm^{-1}; ^1H NMR δ=1.06 (6H, d, J=7 Hz), 2.3—3.0 (5H, m), 7.0—7.4 (5H, m); MS m/z (%) 176 (M^+, 32), 133 (32), 105 (100). Found: m/z 176.1198. Calcd for $C_{12}H_{16}O$: M, 176.1200.

2,5-Diphenyl-3-pentanone (11b). The sulfoxide **10b** was treated with 1.1 equivalents of *n*-BuLi as above to afford **11b** (41% yield) as a colorless oil. IR (neat) 1720 (CO) cm^{-1}; ^1H NMR δ=1.36 (3H, d, J=7), 1.5—2.0 (4H, m), 3.68 (1H, q, J=7 Hz), 6.9—7.4 (10H, m); MS m/z (%) 238 (M^+, 8), 133 (45), 105 (100). Found: m/z 238.1353. Calcd for $C_{17}H_{18}O$: M, 138.1355.

4-Chloro-4-deuterio-1-phenyl-3-heptanone (13). A solution of EtMgBr (0.19 mmol) in THF was added to a solution of **7** (63 mg; 0.17 mmol) in 3 ml of ether at −78 °C. The reaction mixture was stirred at −78 °C for 10 min, then D_2O (0.5 ml) was added to the reaction mixture. The whole was extracted with AcOEt. After the usual workup **13** (33.8 mg; 87%) was obtained as a colorless oil. IR (neat) 1730 (CO) cm^{-1}; ^1H NMR δ=0.89 (3H, t, J=7 Hz), 1.1—2.0 (4H, m), 2.94 (4H, m), 7.0—7.4 (5H, m); MS m/z (%) 225 (M^+, 9), 133 (51), 105 (100). Found: m/z 225.1032. Calcd for $C_{13}H_{16}ClDO$: M, 225.1030.

4-Chloro-3-ethoxycarbonyloxy-1-phenyl-3-heptanone (14). A solution of EtMgBr (0.11 mmol) was added to a solution of **7** (37.5 mg; 0.1 mmol) in 3 ml of ether at −78 °C. The reaction mixture was stirred at −78 °C for 10 min, then ethyl chloroformate (0.23 mmol) was added. The reaction mixture was stirred at 0 °C for 5 h, and at room temperature for 1 h. The reaction was quenched with sat. aq NH_4Cl and after the usual workup, the crude product was purified by silica-gel column chromatography to afford 26.3 mg (86%) of **14** as a colorless oil. IR (neat) 1775 (CO) cm^{-1}; ^1H NMR δ=0.86 (3H, t, J=7 Hz), 1.2—1.7 (2H, m), 1.34 (3H, t, J=7 Hz), 2.29 (2H, t, J=7 Hz), 2.79 (1.6H, s), 2.96 (0.4H, s), 4.24 (2H, q, J=7 Hz), 7.20 (5H, m); MS m/z (%) 296 (M^+, 0.8), 252 (3), 224 (10), 91 (100). Found: m/z 296.1176. Calcd for $C_{16}H_{21}ClO_3$: M, 296.1177.

4-Chloro-1-phenyl-3-trimethylsilyloxy-3-heptene (15). A solution of EtMgBr (0.27 mmol) was added to a solution of **7** (89 mg; 0.24 mmol) in 3 ml of ether at −78 °C. The mixture was stirred for 10 min, then chlorotrimethylsilane (0.61 mmol), triethylamine (0.61 mmol), and HMPA (0.73 mmol) were successively added. The reaction mixture was stirred at 0 °C for 1 h, then at room temperature for 2 h. The reaction was quenched with sat. aq NH_4Cl. The whole was extracted with ether, which was successively washed with sat. aq $NaHCO_3$ and sat. brine. The solution was dried over $MgSO_4$ and the solvent was evaporated to give crude silyl enol ether **15**. ^1H NMR δ=0.00, 0.15 (each s, $SiCH_3$), 0.6—3.0 (methylene), 7.0—7.5 (aromatic-H). In this spectrum, no ^1H-signal on the carbon bearing the chlorine atom was detected. A solution of this silyl enol ether **15** in AcOEt–hexane was treated with silica-gel to afford **8** (60 mg; 82%).

4-Fluoro-4-(1-hydroxycyclohexyl)-1-phenyl-3-heptanone (17a). A solution of EtMgBr (0.24 mmol) was added dropwise with stirring to a solution of **2a** (70 mg; 0.21 mmol) in 5 ml of ether at −78 °C under argon atmosphere. The reaction mixture was stirred at −78 °C for 15 min, then cyclohexanone (0.63 mmol) was added. The reaction mixture was stirred for 20 min, then sat. aq NH_4Cl was added. The whole was extracted with ether–benzene and the organic layer was washed once with sat. aq NH_4Cl. After the usual workup, the

crude product was purified by silica-gel column chromatography to give **17a** (43 mg; 66%) as a colorless oil. IR (neat) 3540 (OH), 1720 (CO) cm^{-1}; ^1H NMR δ=0.85 (3H, t, J=7 Hz), 0.9—2.4 (methylene, m), 2.90 (4H, m), 7.0—7.4 (5H, m); MS m/z (%) 306 (M^+, 0.5), 288 (1.5), 268 (0.7), 208 (100). Found: m/z 306.1993. Calcd for $C_{19}H_{27}FO_2$: M, 306.1993.

4-Fluoro-4-(1-hydroxy-1-methylethyl)-1-phenyl-3-heptanone (17b). Colorless oil; IR (neat) 3480 (OH), 1715 (CO) cm^{-1}; ^1H NMR δ=0.7—1.0 (3H, m), 1.19 (6H, s), 2.90 (4H, m), 7.1—7.3 (5H, m); MS m/z (%) 266 (M^+, 2), 248 (4), 208 (48), 91 (100). Found: m/z 266.1686. Calcd for $C_{16}H_{23}FO_2$: M, 266.1681.

4-Fluoro-4-(α-hydroxybenzyl)-1-phenyl-3-heptanone (17c). Colorless oil; IR (neat) 3480 (OH), 1710 (CO) cm^{-1}; ^1H NMR δ=0.7—1.0 (3H, m), 1.0—2.9 (8H, m), 4.78 (1H, dd, J=21, 4 Hz), 6.9—7.4 (10H, m); MS m/z (%) 314 (M^+, trace), 296 (0.7), 208 (100). Found: m/z 314.1679. Calcd for $C_{20}H_{23}FO_2$: M, 314.1680.

4-Chloro-4-(α-hydroxybenzyl)-1-phenyl-3-heptanone (17d). Diastereomeric mixture; colorless oil; IR (neat) 3500 (OH), 1720 (CO) cm^{-1}; ^1H NMR δ=0.6—1.0 (3H, m), 1.0—3.2 (methylene, m), 4.93, 5.03 (each 0.5H, s), 6.9—7.4 (10H, m); MS m/z (%) 312 ($[M-H_2O]^+$, 0.4), 255 (1), 224 (45), 91 (100).

Synthesis of α-Halo α,β-Unsaturated Ketones (4a—4i). α-Halo α-sulfinyl ketones **2m—2r** (Table 4) were synthesized in a similar way as described above; the selected data are reported.

(*E*)-4-Fluoro-1-phenyl-4-(phenylsulfinyl)-1-hepten-3-one (**2m**); light yellow oil; 75% yield; IR (neat) 1675 (CO), 1610 (C=C) cm^{-1}; ^1H NMR δ=0.97 (3H, t, J=7 Hz), 1.1—1.8 (2H, m), 2.0—2.8 (2H, m), 6.5—6.9 (1H, m), 7.2—7.7 (11H, m).

(*E*)-4-Fluoro-1-phenyl-4-(phenylsulfinyl)-1-penten-3-one (**2n**); light yellow oil; 78% yield; IR (neat) 1680 (CO), 1605 (C=C) cm^{-1}; ^1H NMR δ=1.84, 1.93 (each 3H, d, J=22 Hz), 6.5—7.0 (1H, m), 7.2—7.7 (11H, m).

(*E*)-5-Fluoro-5-(phenylsulfinyl)-2-tetradecen-4-one (**2o**); light yellow oil; 96% yield; IR (neat) 1680 (CO), 1620 (C=C) cm^{-1}; ^1H NMR δ=0.87 (3H, t, J=7 Hz), 1.1—1.3 (14H, m), 1.74 (3H, dd, J=7, 1 Hz), 1.9—2.6 (2H, m), 5.9—6.2 (1H, m), 6.6—7.0 (1H, m), 7.3—7.7 (5H, m).

4-Chloro-1-phenyl-4-(phenylsulfinyl)-3-heptanone (**2p**); colorless oil; 98% yield; IR (neat) 1700 (CO) cm^{-1}; ^1H NMR δ=0.95 (3H, t, J=7 Hz), 1.1—3.0 (8H, m), 6.8—7.8 (10H, m).

(*E*)-4-Chloro-1-phenyl-4-(phenylsulfinyl)-1-hepte-3-one (**2q**); light yellow oil; 97% yield; IR (neat) 1685, 1665 (CO), 1600 (C=C) cm^{-1}; ^1H NMR δ=1.00 (3H, t, J=7 Hz), 1.1—2.8 (4H, m), 6.93 (1H, d, J=16 Hz), 7.2—7.8 (6H, m).

(*E*)-5-Chloro-5-(phenylsulfinyl)-2-tetradecen-4-one (**2r**); colorless oil; 94% yield; IR (neat) 1690, 1675 (CO), 1620 (C=C), cm^{-1}; ^1H NMR δ=0.88 (3H, t, J=7 Hz), 1.1—1.5 (14H, m), 1.81 (3H, dd, J=7, 1 Hz), 1.9—2.7 (2H, m), 6.40 (1H, dq, J=15, 1 Hz), 6.82 (1H, dq, J=15, 7 Hz), 7.3—7.8 (5H, m).

(*Z*)-4-Fluoro-1-phenyl-4-hepten-3-one (4a). A solution of **2a** (100 mg) in 5 ml of benzene was heated at reflux temperature for 25 min. The solvent was evaporated under vacuum to leave a residue, which was purified by silica-gel column chromatography to give **4a** (50 mg; 81%) as a light yellow oil. IR (neat) 1705, 1685 (CO), 1650 (C=C) cm^{-1}; ^1H NMR δ=1.05 (3H, t, J=7 Hz), 2.25 (2H, double quintet, J=7, 3 Hz), 2.93 (4H, s), 6.00 (1H, dt, J=34, 7 Hz), 7.0—7.4 (5H, m); MS m/z (%) 206 (M^+, 32), 177 (100). Found: m/z 206.1098. Calcd for $C_{13}H_{15}FO$: M, 206.1105.

(*Z*)-4-Fluoro-3-tetradecen-5-one (4b). Light yellow oil; IR (neat) 1700, 1680 (CO), 1645 (C=C) cm^{-1}; ^1H NMR δ=0.87 (3H, t, J=7 Hz), 1.07 (3H, t, J=7 Hz), 1.0—1.8 (14H, m), 2.25 (2H, double quintet, J=7, 2 Hz), 2.59 (2H, dt, J=7, 2 Hz), 5.99 (1H, dt, J=34, 7 Hz); MS m/z (%) 228 (M^+, 0.7), 199 (5), 155 (13), 116 (100). Found: m/z 228.1886. Calcd for $C_{14}H_{25}FO$: M, 228.1888.

(*Z*)-2-Fluoro-1-phenyl-2-penten-1-one (4c). Light yellow oil; IR (neat) 1665 (CO), 1645 (C=C) cm^{-1}; ^1H NMR δ=1.11 (3H, t, J=7 Hz), 2.35 (double quintet, J=7, 2 Hz), 6.01 (1H, dt, J=34, 7 Hz), 7.3—7.9 (5H, m).

(1*E*,4*Z*)-4-Fluoro-1-phenyl-1,4-heptadien-3-one (4d). Light yellow oil; IR (neat) 1665, 1645 (CO), 1605 (C=C) cm^{-1}; ^1H NMR δ=1.11 (3H, t, J=7 Hz), 2.32 (2H, double quintet, J=7, 2 Hz), 6.16 (1H, dt, J=35, 8 Hz), 7.0—7.9 (7H, m); MS m/z (%) 204 (M^+, 100), 203 (96), 189 (12). Found: m/z 204.0962. Calcd for $C_{13}H_{13}FO$: M, 204.0949.

(*E*)-4-Fluoro-1-phenyl-1,4-petadien-3-one (4e). Light yellow oil; IR (neat) 1665, 1640 (CO), 1610, 1590 (C=C) cm^{-1}; ^1H NMR δ=5.28 (1H, dd, J=14, 3 Hz), 5.68 (1H, dd, J=46, 3 Hz), 7.19 (1H, dd, J=16, 2 Hz), 7.3—7.7 (5H, m), 7.82 (1H, d, J=16 Hz); MS m/z (%) 176 (M^+, 86), 175 (100), 147 (7), 131 (50), 103 (62). Found: m/z 176.0637. Calcd for $C_{11}H_{19}FO$: M, 176.0637.

(2*E*,5*Z*)-5-Fluoro-2,5-tetradecadien-4-one (4f). Light yellow oil; IR (neat) 1675, 1650 (CO), 1620 (C=C) cm^{-1}; ^1H NMR δ=0.88 (3H, t, J=7 Hz), 1.2—1.4 (10H, m), 1.46 (2H, quintet, J=7 Hz), 1.95 (3H, dd, J=7, 1 Hz), 2.26 (2H, m), 6.08 (1H, dt, J=35, 7.5 Hz), 6.61 (1H, d, J=15 Hz), 7.09 (1H, m); MS m/z (%) 226 (M^+, 4), 211 (3), 191 (3), 115 (53), 69 (100). Found: m/z 226.1731. Calcd for $C_{14}H_{23}FO$: M, 226.1731.

(*Z*)-4-Chloro-1-phenyl-4-hepten-3-one (4g). Light yellow oil; IR (neat) 1710 (CO), 1650 (C=C) cm^{-1}; ^1H NMR δ=1.07 (3H, t, J=7 Hz), 2.38 (2H, quintet, J=7 Hz), 2.7—3.2 (4H, m), 6.89 (1H, t, J=7 Hz), 7.1—7.4 (5H, m); MS m/z (%) 222 (M^+, 10), 193 (72), 175 (10), 157 (10), 133 (24), 91 (100). Found: m/z 222.0811. Calcd for $C_{13}H_{15}ClO$: M, 222.0811.

(1*E*,4*Z*)-4-Chloro-1-phenyl-1,4-heptadien-3-one (4h). Light yellow oil; IR (neat) 1665 (CO), 1615 (C=C) cm^{-1}; ^1H NMR δ=1.14 (3H, t, J=7 Hz), 2.44 (2H, quintet, J=7 Hz), 7.02 (1H, t, J=7 Hz), 7.2—7.7 (6H, m), 7.73 (1H, d, J=7 Hz); MS m/z (%) 220 (M^+, 35), 185 (3), 131 (100). Found: m/z 220.0668. Calcd for $C_{13}H_{13}ClO$: M, 220.0654.

(2*E*,5*Z*)-5-Chloro-2,5-tetradecadien-4-one (4i). Light yellow oil; IR (neat) 1675 (CO), 1625 (C=C) cm^{-1}; ^1H NMR δ=0.88 (3H, t, J=7 Hz), 1.1—1.9 (12H, m), 1.95 (3H, dd, J=7, 1 Hz), 2.40 (2H, q, J=7 Hz), 6.6—7.3 (3H, m); MS m/z (%) 242 (M^+, 1), 207 (7), 69 (100). Found: m/z 242.1432. Calcd for $C_{14}H_{23}ClO$: M, 242.1436.

3-Ethyl-2-fluoro-4-phenyl-2-cyclopenten-1-one (18). $SnCl_4$ (0.59 mmol) was added dropwise to a solution of **4d** (40 mg; 0.2 mmol) in 4 ml of dry CH_2Cl_2. The reaction mixture was stirred and refluxed for 4 h. The reaction was quenched with sat. aq $NaHCO_3$, and then the whole was extracted with ether–benzene. The organic layer was washed once with sat. aq $NaHCO_3$. The usual workup gave a crude product, which was purified by silica-gel column chromatography to give **18** (18 mg; 46%) as a light yellow oil. IR (neat) 1720 (CO) cm^{-1}; ^1H NMR δ=1.01 (3H, t, J=7 Hz), 1.9—3.2 (4H, m), 4.06 (1H, dd, J=7, 2 Hz), 7.0—7.5 (5H, m).

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