A New Synthesis of 2-Sulfanyl Allylic Alcohols and α-Sulfanyl Ketones from Carbonyl Compounds and 1-Chloroalkyl *p*-Tolyl Sulfoxides with Carbon–Carbon Bond-Formation

Tsuyoshi SATOH,* Yoshinori TAKAHASHI, Yuuichi SHIRAI, and Yukie YAMADA

Department of Chemistry, Faculty of Science, Tokyo University of Science; Ichigaya-Funagawara-machi, Shinjuku-ku, Tokyo 162–0826, Japan. Received July 21, 2006; accepted September 6, 2006

Reaction of lithium α-sulfinyl carbanions of 1-chloroalkyl *p*-tolyl sulfoxides with ketones or aldehydes at low temperature gave adducts in almost quantitative yields. Treatment of the adducts derived from ketones with trifluoroacetic anhydride (TFAA) in the presence of NaI in acetone gave α-sulfanyl allylic alcohols in good to quantitative yields. On the other hand, treatment of the adducts derived from aldehydes with TFAA and NaI resulted in the formation of α-sulfanyl ketones and/or α-sulfanyl allylic alcohols. These reactions offer a good method for the synthesis of the above-mentioned compounds from ketones and aldehydes with carbon–carbon bond-formation in two steps and in good yields.

Key words sulfoxide; Pummerer reaction; 2-sulfanyl allylic alcohol; α-sulfanyl ketone

Organosulfur compounds are very valuable in organic synthesis and innumerable studies for their chemistry and applications in organic synthesis have been reported.[1—6] Especially, sulfoxides have a variety of reactivity and are most extensively used in organic synthesis.[7—9] We also have long been interested in the organosulfur compounds in organic synthesis. We recently focused our attention on 1-chloroalkyl aryl sulfoxides as useful compounds in organic synthesis, many novel synthetic methods of which have appeared.[10—20] In continuation of our interest in the use of 1-chloroalkyl aryl sulfoxides in organic synthesis, we recently treated the α-chloro-β-hydroxy sulfoxides, which were synthesized from carbonyl compounds and 1-chloroalkyl *p*-tolyl sulfoxide, with trifluoroacetic anhydride (TFAA) in the presence of NaI, and quite interesting results were obtained (Chart 1).

Thus, addition reaction of lithium α-sulfinyl carbanion of 1-chloroalkyl *p*-tolyl sulfoxides **2** to carbonyl compounds **1** gave adducts, β-hydroxy sulfoxides **3**, in high to quantitative yields. The adducts **3** were treated with TFAA and NaI in acetone at 0 °C to give 2-sulfanylated allylic alcohols **4** in high to quantitative yields. On the other hand, the adducts derived from aldehydes (**3**, R^2=H) were treated with TFAA-NaI to give α-sulfanylated ketones **5** and/or the allylic alcohols **4**, depending on the substituents on the adducts **3**, in good to high yields. These products, **4** and **5**, are quite important compounds in organic synthesis. Details of this procedure and the reaction mechanisms are discussed.

A representative example of the reaction is described as follows (Chart 2). Thus, treatment of 1-chloroalkyl *p*-tolyl sulfoxide **2a**[13] with slight excess of LDA in THF at −78 °C resulted in the formation of lithium α-sulfinyl carbanion. To this reaction mixture was added cyclohexanone to afford the adduct **3a** in 91% yield as a single product. The adduct **3a** was next treated with excess TFAA in the presence of NaI in acetone at 0 °C for 10 min.[21,22] A quite clean reaction took place and the product was found to have a hydroxyl group and one vinylic hydrogen and the structure was found to be the allylic alcohol having a sulfanyl group **4a**.

Obviously, this reaction was recognized to be a very interesting method for synthesis of allylic alcohols having a sul-

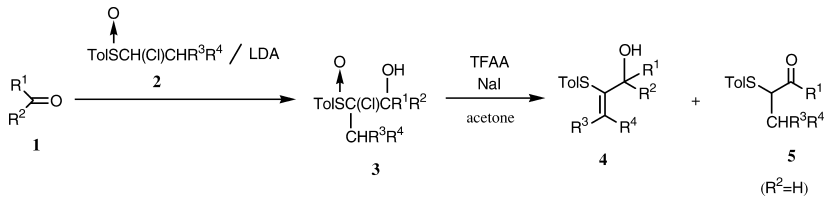


Chart 1

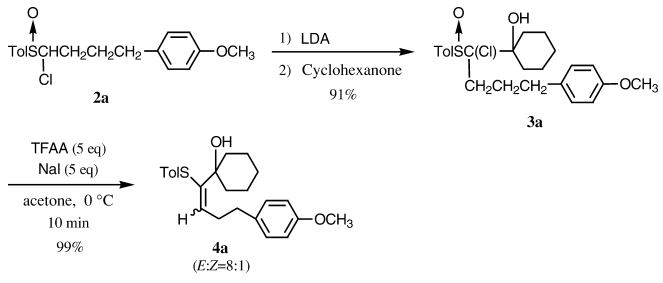
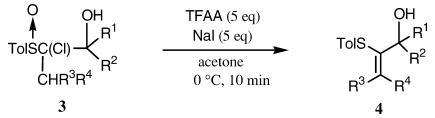


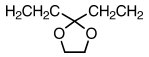
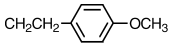
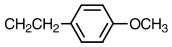
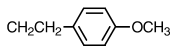
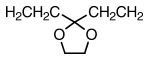
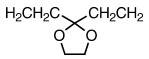
Chart 2

* To whom correspondence should be addressed. e-mail: tsatoh@rs.kagu.tus.ac.jp

Table 1. Treatment of the α-Chloro β-Hydroxy Sulfoxides **3** Derived from Ketones with TFAA in the Presence of NaI in Acetone at 0 °C



3 **4**

Entry	**3**					**4**	
		R^1	R^2	R^3	R^4		Yield/%
1	**3b**			H		**4b**	97[a]
2	**3c**	Ph	Ph	H		**4c**	97[b]
3	**3d**	CH_3	CH_3	H		**4d**	97[c]
4	**3e**	$-(CH_2)_5-$		H	H	**4e**	92[d]
5	**3f**			H	H	**4f**	96
6	**3g**	$CH_3CH_2CH_2$	$CH_3CH_2CH_2$	H	H	**4g**	96
7	**3h**	Ph	Ph	H	H	**4h**	99
8	**3i**	CH_3	CH_3	H	H	**4i**	97
9	**3j**	$-(CH_2)_{14}-$		H	H	**4j**	97
10	**3k**	CH_3	CH_3	CH_3	CH_3	**4k**	85
11	**3l**			CH_3	CH_3	**4l**	85
12	**3m**	$-(CH_2)_5-$		CH_3	CH_3	**4m**	95

a) $E:Z=8:2$. *b*) $E:Z=5:4$. *c*) $E:Z=7:1$. *d*) The reaction was conducted at −50 °C.

fanyl group at the β-position from two components, 1-chloroalkyl *p*-tolyl sulfoxides and ketones, with carbon–carbon bond-formation in only two steps. We first examined the generality of these reactions and the results are summarized in Table 1.

Cyclohexane-1,4-dione mono ethylene ketal, benzophenone, acetone, cyclohexanone, 4-heptanone, and cyclopentadecanone were used as the representative examples of the ketones. 1-Chloro-4-(4-methoxyphenyl)butyl *p*-tolyl sulfoxide, 1-chloroethyl *p*-tolyl sulfoxide, and 1-chloro-2-methylpropyl *p*-tolyl sulfoxide were used as the sulfoxides. The addition reaction of the 1-chloroalkyl *p*-tolyl sulfoxides to ketones took place without any problem to give the adducts **3** in almost quantitative yields.

All the reactions of **3** were carried out with 5 eq of TFAA in the presence of NaI (5 eq) in acetone at 0 °C for 10 min. The reaction of the adducts **3b**—**d** gave the allylic alcohols **4b**—**d** as a mixture of two geometrical isomers (entries 1—3). *E*-Isomers were obtained as main products and the ratio of the configurational isomers was found to be variable with the substrates.[23] All the other adducts (**3e**—**m**) gave the allylic alcohols (**4e**—**m**) in high to quantitative yields (entries 5—12). From these results, we are sure this reaction is of value for the synthesis of allylic alcohol having a sulfanyl group at the β-position **4** from ketones in short steps and in high yield.

At this stage of the investigation, we thought that it should be better to clarify the necessity of the chlorine atom in the sulfoxide and NaI as the reagent. We synthesized β-hydroxy sulfoxide **6** and treated it with TFAA in the presence of NaI;

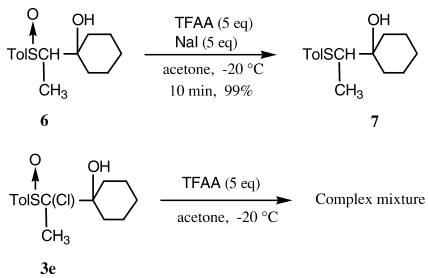


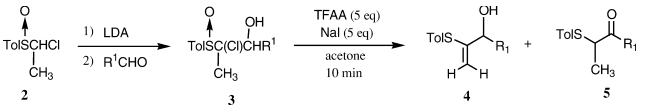
Chart 3

however, only a reduced product,[24] β-hydroxy sulfide **7**, was obtained in quantitative yield (Chart 3). On the other hand, treatment of the β-hydroxy sulfoxide having a chlorine atom **3e** with TFAA without NaI resulted in the formation of a complex mixture. From these results, the chlorine atom and NaI are proved to be essential for this reaction.

We next investigated the above-mentioned reaction with the α-chloro β-hydroxysulfoxides derived from aldehydes and the results are summarized in Table 2.

First, 2-chloro-2-(*p*-tolylsulfinyl)-1-phenyl-1-propanol **3n** was synthesized from 1-chloroethyl *p*-tolyl sulfoxide and benzaldehyde in quantitative yield as a mixture of two diastereomers. The sulfoxide **3n** was treated with TFAA-NaI in acetone at 0 °C for 10 min. Somewhat surprisingly, the main product was α-sulfanyl ketone **5n** (49%) with a trace amount of the expected allylic alcohol **4n** (entry 1). The reaction was conducted at 25 and 40 °C (entries 2, 3), and total yield of **4n** and **5n** was found to be variable with the reaction tempera-

Table 2. Synthesis of 2-Sulfanyl Allylic Alcohols **4** and α-Sulfanyl Ketones **5** from 1-Chloroethyl *p*-Tolyl Sulfoxide **2** and Aldehydes through the α-Chloro β-Hydroxy Sulfoxides **3**



Entry	3		Temperature	4		5	
		R^1	°C		Yield/%		Yield/%
1	**3n**	Ph	0	**4n**	Trace	**5n**	49
2			25		23		40
3			40		26		71
4	**3o**	$PhCH_2$	0	**4o**	0	**5o**	50
5			40		0		54
6	**3p**	$PhCH_2CH_2$	0	**4p**	0	**5p**	58
7			40		0		75

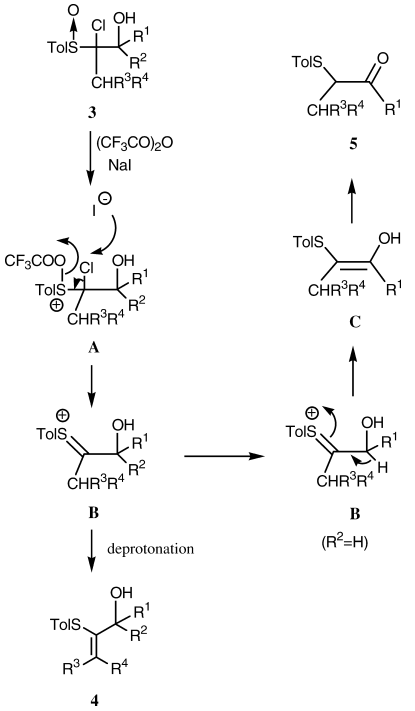


Chart 4

ture. As shown in entry 3, α-sulfanyl ketone **5n** was obtained in 71% yield as a main product. α-Sulfanyl ketones also are quite interesting and important compounds in organic synthesis.[25]

We finally investigated the generality of this reaction and the results are summarized in Table 2. The adducts derived from 1-chloroethyl *p*-tolyl sulfoxide and phenylacetaldehyde and 3-phenylpropanal (**3o**, **3p**) gave α-sulfanyl ketones **5o** and **5p** in up to 75% yield without the allylic alcohol **4** (entries 4—7).

The mechanism of this reaction is presumed to be the Pummerer-type reaction[26—28] as shown in Chart 4. At first, the reaction of the sulfoxide **3** with TFAA gives an acyloxysulfonium ion **A**. The iodide anion then attacks the chlorine atom in **A** to afford thionium ion **B**. Deprotonation from the thionium ion takes place to give the allylic alcohol having a sulfanyl group **4**. When this reaction was carried out with **3** derived from aldehydes, competitive deprotonation of the hydrogen on the carbon bearing R^3 and R^4, and the hydrogen on the carbon bearing the hydroxyl group takes place. In the latter case, the product is an enolate **C** and tautomerism gives the α-sulfanyl ketone **5**.

Experimental

All melting points are uncorrected. ^{1}H-NMR spectra were measured in a $CDCl_3$ solution with JEOL JNM-LA 400 and 500 spectrometer. Electron-impact mass spectra (MS) were obtained at 70 eV by direct insertion. Silica gel 60 (MERCK) containing 0.5% 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 reagent and solvent, diisopropylamine was distilled from CaH_2 and THF was distilled from diphenylketyl and acetone was dried over $CaSO_4$ and distilled before use.

1-[1-Chloro-4-(4-methoxyphenyl)-1-(*p*-tolylsulfinyl)butyl]cyclohexanol (3a) To a solution of LDA (11.8 mmol) in THF (50 ml) at −78 °C was added dropwise with stirring a solution of **2a** (3.32 g, 9.86 mmol) in 5 ml of THF and the solution was stirred for 15 min. Cyclohexanone (1.27 ml, 12.3 mmol) was added to the reaction mixture and the stirring was continued for 15 min. The reaction was quenched with sat. aq. NH_4Cl, and the whole was extracted with CH_2Cl_2. The organic layer was washed with water and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography to give **3a** (3.90 g, 91%) as colorless crystals; mp 105—106 °C (AcOEt–hexane); IR (KBr) 3307 (OH), 2931, 1511, 1241, 1030 (SO), 829, 814, 512 cm^{-1}; ^{1}H-NMR δ 1.07—1.19 (1H, m), 1.20—1.32 (1H, m), 1.43—1.50 (1H, m), 1.54—1.88 (10H, m), 1.86—2.00 (2H, m), 2.18—2.23 (1H, m), 2.35—2.42 (1H, m), 2.43 (3H, s), 3.80 (3H, s), 6.80 (2H, d, J=8.3 Hz), 6.93 (2H, d, J=8.3 Hz), 7.26 (2H, d, J=7.0 Hz), 7.52 (2H, d, J=7.0 Hz); *Anal.* Calcd for $C_{24}H_{32}ClO_3S$: C, 66.26; H, 7.18; Cl, 8.15; S, 7.37. Found: C, 66.29; H, 7.12; Cl, 8.04; S, 7.70.

Other adducts **3b**—**q** were synthesized in the same manner described above.

1-[4-(4-Methoxyphenyl)-1-(*p*-tolylsulfanyl)-1-butenyl]cyclohexanol (4a) To a solution of **3a** (48 mg, 0.11 mmol) in acetone (5 ml) in a flame-dried flask was added NaI (84 mg, 0.56 mmol) and $(CF_3CO)_2O$ (0.56 mmol) at 0 °C under argon atmosphere. After 5 min, the reaction was quenched with sat. aq. Na_2SO_3 and sat. aq. $NaHCO_3$, and the whole was extracted with CH_2Cl_2. The organic solution was washed with water and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography to give **4a** (42.4 mg, 99%) (*E*/*Z*=8 : 1). *E*-**4a**; colorless oil. IR (neat) 3564 (OH), 2927, 1513, 1245, 1033, 807 cm^{-1}; ^{1}H-NMR δ 1.08—1.15 (1H, m), 1.46—1.64 (8H, m), 1.80 (2H, dt, J=14.1, 4.0 Hz), 2.32 (3H, s), 2.61 (2H, t, J=7.4 Hz), 2.75 (2H, q, J=7.6 Hz), 3.78 (3H, s), 5.72 (1H, t, J=7.6 Hz), 6.81 (2H, d, J=8.5 Hz), 7.04 (2H, d, J=8.5 Hz), 7.06 (2H, d, J=7.3 Hz), 7.16 (2H, d, J=7.3 Hz); MS *m*/*z* (%) 382 (M^+, 57), 261 (31), 243 (27), 149 (29), 137 (67), 121 (100), 119 (17), 91 (19). Calcd for $C_{24}H_{30}O_2S$: M, 382.1966. Found: *m*/*z* 382.1959. *Z*-**4a**; colorless oil. IR (neat) 3480 (OH), 2929, 1513, 1247, 1037, 805 cm^{-1}; ^{1}H-NMR δ 1.15—1.21 (1H, m), 1.48—1.73 (9H, m), 2.00 (1H, s, OH), 2.27 (3H, s),

2.48—2.61 (4H, m), 3.77 (3H, s), 6.39 (1H, t, J=6.7 Hz), 6.77 (2H, d, J=8.9 Hz), 6.99 (2H, d, J=8.9 Hz), 7.01 (2H, d, J=8.0 Hz), 7.07 (2H, d, J=8.0 Hz); MS m/z (%) 382 (M^+, 53), 261 (27), 243 (29), 149 (27), 137 (56), 121 (100), 119 (19), 91 (19). Calcd for $C_{24}H_{30}O_2S$: M, 382.1966. Found: m/z 382.1971.

The Allylic Alcohols 4b—m in Table 1 **4b**: *E*-**4b**; colorless oil. IR (neat) 3481 (OH), 2929, 1615, 1515, 1246, 1104, 1036, 965, 808 cm^{-1}; ^{1}H-NMR δ 1.52—1.63 (4H, m), 1.91 (2H, dt, J=13.5, 4.0 Hz), 2.16 (2H, dt, J=13.5, 4.0 Hz), 2.32 (3H, s), 2.62 (2H, t, J=7.3 Hz), 2.73 (2H, q, J=7.6 Hz), 3.79 (3H, s), 3.93 (4H, t, J=2.8 Hz), 5.77 (1H, t, J=8.0 Hz), 6.18 (2H, d, J=8.3 Hz), 7.07 (4H, d, J=8.9 Hz), 7.16 (2H, d, J=8.0 Hz); MS m/z (%) 440 (M^+, 46), 319 (28), 301 (11), 195 (69), 151 (16), 121 (100), 99 (23). Calcd for $C_{26}H_{32}O_4S$: M, 440.2022. Found: m/z 440.2026. *Z*-**4b**; colorless oil. IR (neat) 3480 (OH), 2928, 1514, 1247, 1096, 1036, 980, 806 cm^{-1}; ^{1}H-NMR δ 1.57—1.78 (4H, m), 1.89—2.01 (4H, m), 2.10 (1H, s), 2.27 (3H, s), 2.50—2.60 (4H, m), 3.77 (3H, s), 3.91—3.97 (4H, m), 6.40 (1H, t, J=7.0 Hz), 6.78 (2H, d, J=8.3 Hz), 7.00 (4H, t, J=8.3 Hz), 7.06 (4H, d, J=8.3 Hz); MS m/z (%) 440 (M^+, 26), 319 (22), 301 (11), 257 (7), 239 (4), 195 (42), 151 (14), 121 (100), 99 (24), 91 (13). Calcd for $C_{26}H_{32}O_4S$: M, 440.2021. Found: m/z 440.2021.

4c: *E*-**4c**; colorless oil. IR (neat) 3504 (OH), 2925, 1511, 1247, 805, 701 cm^{-1}; ^{1}H-NMR δ 2.29 (3H, s), 2.24—2.51 (4H, m), 3.67 (1H, s, OH), 3.80 (3H, s), 5.63 (1H, t, J=7.1 Hz), 6.79 (2H, d, J=8.5 Hz), 6.91 (2H, d, J=8.5 Hz), 7.04 (2H, d, J=8.0 Hz), 7.16 (2H, d, J=8.0 Hz), 7.20—7.22 (4H, m), 7.24—7.31 (8H, m); MS m/z (%) 466 (M^+, 38), 284 (41), 221 (24), 191 (32), 163 (37), 121 (100), 105 (63), 77 (21). Calcd for $C_{31}H_{30}O_2S$: M, 466.1964. Found: m/z 466.1968. *Z*-**4c**; colorless oil. IR (neat) 3472 (OH), 3023, 2922, 1612, 1514, 1447, 1246, 1178, 1035, 809, 762, 701 cm^{-1}; ^{1}H-NMR δ 1.72 (2H, q, J=7.4 Hz), 2.26 (2H, t, J=7.7 Hz), 2.33 (3H, s), 3.54 (1H, s, OH), 3.77 (3H, s), 5.95 (1H, t, J=7.6 Hz), 6.72 (4H, s), 7.07 (2H, d, J=8.3 Hz), 7.22 (2H, d, J=8.3 Hz), 7.26—7.30 (10H, m); MS m/z (%) 466 (M^+, 24), 448 (6), 284 (24), 221 (43), 187 (27), 163 (30), 121 (100), 105 (64). Calcd for $C_{31}H_{30}O_2S$: M, 466.1964. Found: m/z 466.1962.

4d: *E*-**4d**; colorless oil. IR (neat) 3401 (OH), 2982, 2940, 1513, 1247, 1036, 732 cm^{-1}; ^{1}H-NMR δ 1.38 (6H, s), 1.95 (1H, s, OH), 2.32 (3H, s), 2.60—2.73 (4H, m), 3.79 (3H, s), 5.72 (1H, t, J=7.5 Hz), 6.82 (2H, d, J=8.5 Hz), 7.05 (2H, d, J=8.5 Hz), 7.08 (2H, d, J=8.0 Hz), 7.18 (2H, d, J=8.0 Hz); MS m/z (%) 342 (M^+, 51), 221 (48), 203 (22), 149 (37), 121 (100), 97 (79), 91 (16). Calcd for $C_{21}H_{26}O_2S$: M, 342.1652. Found: m/z 342.1656. *Z*-**4d**; colorless oil. IR (neat) 3448 (OH), 2923, 1511, 1246, 1037, 805 cm^{-1}; ^{1}H-NMR δ 1.39 (6H, s), 2.28 (3H, s), 2.52 (2H, t, J=7.1 Hz), 2.59 (2H, t, J=7.1 Hz), 3.77 (3H, s), 6.40 (1H, t, J=6.7 Hz), 6.79 (2H, d, J=8.6 Hz), 7.00 (2H, d, J=8.6 Hz), 7.02 (2H, d, J=8.2 Hz), 7.07 (2H, d, J=8.2 Hz); MS m/z (%): 342 (M^+, 54), 221 (50), 203 (23), 149 (37), 121 (100), 97 (68), 91 (14). Calcd for $C_{21}H_{26}O_2S$: M, 342.1652. Found: m/z 342.1652.

4e: Colorless crystals; mp 94—95 °C (AcOEt–hexane); IR (KBr) 3335 (OH), 2925, 2854, 1599, 1447, 1121, 979, 873, 813 cm^{-1}; ^{1}H-NMR δ 1.20—1.29 (1H, m), 1.56—1.84 (9H, m), 2.35 (3H, s), 4.67 (1H, s), 5.41 (1H, s), 7.15 (2H, d, J=8.0 Hz), 7.36 (2H, d, J=8.0 Hz); MS m/z (%) 248 (M^+, 100), 150 (72), 149 (27), 135 (65), 99 (35), 81 (41). Calcd for $C_{15}H_{20}OS$: M, 248.1235. Found: m/z 248.1235. *Anal.* Calcd: C, 72.53; H, 8.12; S, 12.91. Found: C, 72.67; H, 8.26; S, 12.99.

4f: Colorless crystals; mp 81—83 °C (AcOEt–hexane). IR (KBr) 3445 (OH), 2961, 1489, 1096, 950, 811 cm^{-1}; ^{1}H-NMR δ 1.64—1.67 (2H, m), 1.83 (1H, s, OH), 1.84—1.87 (2H, m), 1.98—2.05 (2H, m), 2.07—2.13 (2H, m), 2.34 (3H, s), 3.93—3.99 (4H, m), 4.72 (1H, s), 5.44 (1H, s) 7.16 (2H, d, J=7.9 Hz), 7.35 (2H, d, J=7.9 Hz); MS m/z (%) 306 (M^+, 97), 278 (23), 150 (30), 135 (26), 105 (26), 99 (100), 91 (19). Calcd for $C_{17}H_{22}O_3S$: M, 306.1289. Found: m/z 306.1289.

4g: Colorless oil. IR (neat) 3483 (OH), 2959, 1492, 1105, 810 cm^{-1}; ^{1}H-NMR δ 0.94 (6H, t, J=7.4 Hz), 1.33—1.42 (4H, m), 1.60—1.66 (2H, m), 1.73—1.79 (2H, m), 2.36 (3H, s), 4.54 (1H, s), 5.23 (1H, s), 7.17 (2H, d, J=8.0 Hz), 7.37 (2H, d, J=8.0 Hz); MS m/z (%): 264 (M^+, 25), 222 (100), 193 (15), 151 (51), 150 (43), 135 (51), 71 (46). Calcd for $C_{16}H_{24}OS$: M, 264.1546. Found: m/z 264.1547.

4h: Colorless oil. IR (neat) 3505 (OH), 3025, 1491, 1447, 1019, 759, 701 cm^{-1}; ^{1}H-NMR δ 2.31 (3H, s), 3.49 (1H, s, OH), 4.98 (1H, s), 5.12 (1H, s), 7.12 (2H, d, J=7.9 Hz), 7.19—7.37 (8H, m), 7.43—7.45 (4H, m); MS m/z (%) 332 (M^+, 35), 191 (15), 183 (77), 150 (100), 135 (18), 105 (77), 77 (39). Calcd for $C_{22}H_{20}OS$: M, 332.1235. Found: m/z 332.1236.

4i[29]: Colorless oil. IR (neat) 3401 (OH), 2978, 1492, 1364, 1104, 810 cm^{-1}; ^{1}H-NMR δ 1.51 (6H, s), 2.35 (3H, s), 4.61 (1H, s), 5.37 (1H, s), 7.16 (2H, d, J=8.0 Hz), 7.36 (2H, d, J=8.0 Hz); MS m/z (%) 208 (M^+, 87), 150 (49), 149 (47), 135 (100), 105 (28), 91 (24), 77 (8), 59 (49). Calcd for $C_{12}H_{16}OS$: M, 208.0921. Found: m/z 208.0921.

4j: Colorless oil. IR (neat) 3296 (OH), 2927, 2854, 1491, 1458, 808 cm^{-1}; ^{1}H-NMR δ 1.32—1.38 (26H, m), 1.63—1.69 (2H, m), 1.80—1.86 (2H, m), 1.93 (1H, s, OH), 2.35 (3H, s), 4.67 (1H, d, J=0.9 Hz), 5.26 (1H, d, J=0.9 Hz), 7.16 (2H, d, J=7.9 Hz), 7.36 (2H, d, J=7.9 Hz); MS m/z (%) 374 (M^+, 100), 251 (7), 225 (4), 150 (35), 124 (12), 105 (10), 91 (7). Calcd for $C_{24}H_{38}OS$: M, 374.2643. Found: m/z 374.2659.

4k: Colorless oil. IR (neat) 3400 (OH), 2928, 1599, 1490, 1366, 1119, 804 cm^{-1}; ^{1}H-NMR δ 1.49 (6H, s), 2.04 (3H, s), 2.15 (3H, s), 2.28 (3H, s), 2.53 (1H, s, OH), 7.05 (4H, s). MS m/z (%) 236 (M^+, 96), 218 (21), 203 (14), 178 (100), 163 (58), 143 (32), 133 (33), 105 (21), 91 (30). Calcd for $C_{14}H_{20}OS$: M, 236.1234. Found: m/z 236.1234.

4l: Colorless oil. IR (neat) 3468 (OH), 2928, 1596, 1491, 1375, 1099, 1035, 805, 768 cm^{-1}; ^{1}H-NMR δ 1.54—1.60 (2H, m), 1.67—1.71 (2H, m), 1.97 (2H, dt, J=13.2, 4.3 Hz), 2.05 (3H, s), 2.19 (3H, s), 2.28 (3H, s), 2.32 (2H, dt, J=13.2, 4.3 Hz), 2.33 (1H, s, OH), 3.93 (4H, t, J=2.1 Hz), 7.04 (4H, s). MS m/z (%) 334 (M^+, 52), 316 (29), 178 (100), 163 (28), 149 (27), 124 (20), 101 (73), 91 (32). Calcd for $C_{19}H_{26}O_3S$: M, 334.1601. Found: m/z 334.1611.

4m: Colorless oil. IR (neat) 3468 (OH), 2927, 2856, 1491, 1447, 1258, 1084, 803 cm^{-1}; ^{1}H-NMR δ 1.50—1.53 (2H, m), 1.56—1.66 (4H, m), 1.71 (2H, d, J=12.5 Hz), 1.90—1.97 (3H, m), 2.03 (3H, s), 2.21 (3H, s), 2.28 (3H, s), 7.03 (4H, s). MS m/z (%) 276 (M^+, 51), 258 (33), 178 (100), 163 (27), 143 (12), 133 (16), 107 (20), 91 (31). Calcd for $C_{17}H_{24}OS$: M, 276.1546. Found: m/z 276.1544.

Allylic Alcohol 4n and α-Sulfanyl Ketones 5n, 5o, and 5p in Table 2 **4n**: Colorless oil. IR (neat) 3419 (OH), 1679, 1448, 1233, 1019, 950, 799 cm^{-1}; ^{1}H-NMR δ 2.34 (3H, s), 5.04 (1H, s), 5.27 (1H, s), 5.51 (1H, s), 7.13 (2H, d, J=7.9 Hz), 7.30—7.32 (3H, m), 7.34—7.37 (2H, m), 7.41 (2H, d, J=7.9 Hz). MS m/z (%) 256 (M^+, 100), 246 (7), 150 (37), 149 (53), 135 (61), 115 (15), 105 (63), 91 (30). Calcd for $C_{16}H_{16}OS$: M, 256.0920. Found: m/z 256.0918.

5n[30]: Colorless oil. IR (neat) 2926, 1681 (CO), 1448, 1233, 1178, 950, 812, 718 cm^{-1}; ^{1}H-NMR δ 1.50 (3H, d, J=6.8 Hz), 2.31 (3H, s), 4.55 (1H, q, J=6.8 Hz), 7.07 (2H, d, J=8.0 Hz), 7.21—7.24 (2H, m), 7.43 (2H, t, J=7.6 Hz), 7.54 (1H, m), 7.95 (2H, m) . MS m/z (%) 256 (M^+, 33), 151 (100), 123 (25), 105 (29), 91 (8), 77 (27). Calcd for $C_{16}H_{16}OS$: M, 256.0920. Found: m/z 256.0912.

5o: Colorless oil. IR (neat) 2924, 1713 (CO), 1493, 1454, 1375, 1032, 809 cm^{-1}; ^{1}H-NMR δ 1.33 (3H, d, J=7.0 Hz), 2.32 (3H, s), 3.76 (1H, q, J=7.0 Hz), 3.88 (1H, d, J=15.3 Hz), 3.95 (1H, d, J=15.3 Hz), 7.09 (2H, d, J=7.9 Hz), 7.17 (2H, d, J=7.0 Hz), 7.23—7.25 (3H, m), 7.30 (2H, t, J=7.9 Hz). MS m/z (%) 270 (M^+, 22), 151 (100), 147 (12), 123 (17), 91 (36). Calcd for $C_{17}H_{18}OS$: M, 270.1078. Found: m/z 270.1083.

5p: Colorless oil. IR (neat) 3027, 2926, 1709 (CO), 1493, 1454, 811, 699 cm^{-1}; ^{1}H-NMR δ 1.32 (3H, d, J=7.2 Hz), 2.32 (3H, s), 2.83—2.89 (3H, m), 3.01—3.06 (1H, m), 3.63 (1H, q, J=7.2 Hz), 7.07 (2H, d, J=8.4 Hz), 7.16—7.21 (5H, m), 7.27 (2H, t, J=7.2 Hz). MS m/z (%) 284 (M^+, 34), 151 (100), 123 (13), 105 (10), 91 (19). Calcd for $C_{18}H_{20}OS$: M, 284.1235. Found: m/z 284.1230.

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