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Rongalite® promoted highly regioselective synthesis of β-hydroxy sulfides by ring opening of epoxides with disulfides

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ABSTRACT

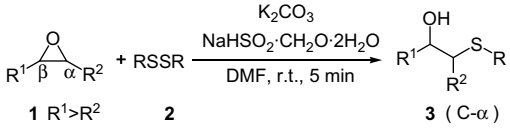
Rongalite® promotes cleavage of disulfides generating thiolate anions that then undergo facile ring opening of epoxides in the presence of K_2CO_3 to afford α-addition products **3** with good to excellent yields. The important features of this methodology are broad substrates scope, high yielding, reasonably rapid reaction rate, high regioselectivity and no requirement of metal catalysts. It should be noted that the thiolate anion attacks the epoxides derived from styrene to produce the corresponding α-addition products **3** with high regioselectivity, instead of the β-addition regioisomer **4** that could be formed from the attack of the nucleophile at the benzylic position.

1. Introduction

Epoxides are important precursors in organic synthesis[1] and their reactions with different nucleophiles (e.g., amines, thiols, alcohols, etc.) have been the subject of extensive studies.[2] Among them, thiolysis of epoxides has attracted comparatively more attention since it produces β-hydroxy sulfides as important intermediates in organic chemistry,[3] especially in the fields of pharmaceuticals[4] and natural products chemistry.[5] Classical synthesis of β-hydroxy sulfides involves the ring opening of an epoxide by an excess of thiol, which inevitably incurs unpleasant odor, either catalyzed by Lewis acid,[6] PBu_3[7] or under microwave irradiation conditions.[8] Recently, we have studied the thiolysis reaction of epoxides in ionic liquids without any catalyst[9] or with gallium(III) triflate as a catalyst.[10]

In addition, disulfide bond cleavage could lead to interesting products by the reaction of the resulting nucleophilic sulfur[11] species to a variety of organic substrates. Thus, the method has been developed in recent years for the synthesis of β-hydroxy sulfides by the reaction of epoxides with disulfides using different promoting agents. These promoting agents include tetrathiomolybdate,[12] $NaBH_4$/Amberlite IRA 400,[13] ytterbium(III) chalcogenolate complexes,[14] InI–$InCl_3$,[15] Zn–$Bi(OTf)_3$ or Zn–$Bi(TFA)_3$.[16] However, these methods usually suffer from one or more limitations such as the use of unpleasant odor substrates[6–10] and expensive, toxic or metallic catalysts,[12,14–16] long reaction times,[12–15] unsatisfactory yields[14,15] as well as elevated temperature.[13,15,16] Therefore, developing versatile approaches to synthesize β-hydroxy sulfides selectively still remains a highly desired goal in organic synthesis.

In continuation of our researches in developing novel synthetic routes for the formations of carbon–carbon and carbon-heteroatom bonds,[9,10,17] we herein report a highly efficient and regioselective synthesis of β-hydroxy sulfides by Rongalite® (sodium formaldehyde sulfoxylate, $NaHSO_2 \cdot CH_2O \cdot 2H_2O$ as an inexpensive reagent) promoted thiolysis of epoxides with disulfides (Scheme 1).



Scheme 1. Ring opening of epoxides with disulfides.

2. Results and discussion

The model ring opening reaction of 2-phenyloxirane **1a** with 1,2-diphenyldisulfide **2a** was conducted to screen the optimal reaction conditions and the results were listed in Table 1. Initially, the effect of solvents was tested. Among all the solvents screened, (acetonitrile, water, HMPA, and DMF), DMF afforded an interesting

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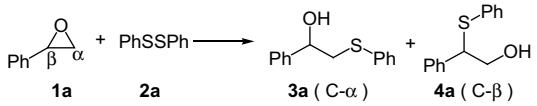
Table 1
Screening conditions for the thiolysis of 2-phenyloxirane with 1,2-diphenyldisulfide[a]



1a **2a** **3a** (C-α) **4a** (C-β)

Entry	Rongalite® (equiv)	Base	Solvent	Yield[b] (%)
1	2	Cs_2CO_3	CH_3CN	11
2	2	Cs_2CO_3	Toluene	NR
3	2	Cs_2CO_3	HMPA	Trace
4	2	Cs_2CO_3	H_2O	NR
5	2	Cs_2CO_3	DMF	79
6	3	—	DMF	6
7	3	K_3PO_4	DMF	NR
8	3	Et_3N	DMF	6
9	3	$KF·2H_2O$	DMF	10
10	3	K_2CO_3	DMF	5
11	3	K_2CO_3	DMF	98
12	—	K_2CO_3	DMF	NR[c]
13	1	K_2CO_3	DMF	64
14	2	K_2CO_3	DMF	83
15	3	K_2CO_3	DMF	35[d]
16	3	K_2CO_3	DMF	87[e]
17	3	K_2CO_3	DMF	98[f]
18	3	K_2CO_3	DMF	89[g]

NR=No reaction.
[a] All reactions were run with **1a** (0.4 mmol), **2a** (0.2 mmol), and solvent (2 mL) at room temperature for 5 min.
[b] Isolated total yield of **3a**, the regioisomer **4a** was not detected.
[c] Without Rongalite®.
[d] 0.2 equiv of K_2CO_3.
[e] 1 equiv of K_2CO_3.
[f] 3 equiv of K_2CO_3.
[g] At 50 °C.

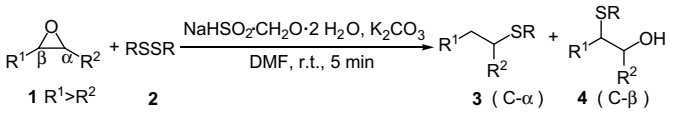
result, where **1a** undergoes the cleavage with **2a** to produce only α-addition products **3a** in 79% yield with Cs_2CO_3 as a base (Table 1, entry 5). Encouraged by this promising result, we further optimized the reaction conditions including the effect of bases, reaction temperature, and the amount of Rongalite®.

It was found that **3a** was not obtained in the absence of a base (Table 1, entry 7). Among the screened bases, $KF·2H_2O$, Et_3N, and K_3PO_4 provided only 5%, 10%, and 6% yield of **3a**, respectively (Table 1, entries 8–10). However, it was satisfying to find that the reaction could reach to completion in as short as 5 min and afforded **3a** in 98% yield regiospecifically when the combination of K_2CO_3 and DMF was employed at room temperature in the presence of 3 equiv of Rongalite® (Table 1, entry 11). Moreover, the yield was significantly affected by the amount of Rongalite® (Table 1, entries 11–14) and K_2CO_3 (Table 1, entries 11, 15–17). The results indicated that the yield was decreased to some extent when 2 equiv of Rongalite® was added, and no reaction was observed even for longer time in the absence of Rongalite® (Table 1, entry 12). Decreasing the amount of K_2CO_3 (Table 1, entries 15–16) in the system reduced the yield slightly. The yield was decreased to some extent when the reaction was carried out at the elevated temperature (Table 1, entry 18). As a result, the model reaction was carried out under optimized conditions with 3 equiv of Rongalite® and 1.5 equiv of K_2CO_3 at room temperature in DMF, which led to the desired product **3** with 98% yield and high regioselectivity.

With the optimal conditions in hand, the scope of both disulfides and epoxides was explored and the results are summarized in Table 2. In all cases, Rongalite®-catalyzed reactions proceeded smoothly and gave the corresponding products in good to excellent yields. The highly regioselective nucleophilic attack of thiophenols occurred almost exclusively on the less hindered α-carbon of the oxirane ring.

A series of aromatic disulfides bearing either electron-donating or electron-withdrawing groups on the aromatic ring were investigated. The substitution groups on the aromatic ring had no

Table 2
Ring opening of epoxides with disulfides in the presence of Rongalite® and K_2CO_3[a]



1 R^1>R^2 **2** **3** (C-α) **4** (C-β)

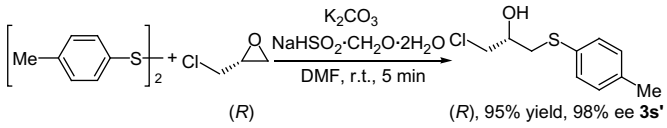
Entry	Epoxide		*R*	Product	Yield[b] (%)
	R^1	R^2			
1	C_6H_5	H	C_6H_5	**3a**	98
2	C_6H_5	H	*p*-$(CH_3)C_6H_4$	**3b**	99
3	C_6H_5	H	*p*-$(Cl)C_6H_4$	**3c**	97
4	C_6H_5	H	*p*-$(F)C_6H_4$	**3d**	83
5	C_6H_5	H	*o*-$(NH_2)C_6H_4$	**3e**	97
6	*p*-$(Cl)C_6H_4$	H	C_6H_5	**3f**	95
7	*p*-$(Cl)C_6H_4$	H	*p*-$(CH_3)C_6H_4$	**3g**	94
8	*p*-$(Cl)C_6H_4$	H	*p*-$(Cl)C_6H_4$	**3h**	91
9	*p*-$(Cl)C_6H_4$	H	*p*-$(F)C_6H_4$	**3i**	84
10	*p*-$(Cl)C_6H_4$	H	*o*-$(NH_2)C_6H_4$	**3j**	95
11	$C_6H_5OCH_2$	H	C_6H_5	**3k**	95
12	$C_6H_5OCH_2$	H	*p*-$(CH_3)C_6H_4$	**3l**	98
13	$C_6H_5OCH_2$	H	*p*-$(Cl)C_6H_4$	**3m**	95
14	$C_6H_5OCH_2$	H	*p*-$(F)C_6H_4$	**3n**	80
15	$C_6H_5OCH_2$	H	*o*-$(NH_2)C_6H_4$	**3o**	95
16	$-(CH_2)_4-$		C_6H_5	**3p**	84
17	$-(CH_2)_4-$		*p*-$(CH_3)C_6H_4$	**3q**	83
18	$ClCH_2$	H	C_6H_5	**3r**	93
19	$ClCH_2$	H	*p*-$(CH_3)C_6H_4$	**3s**	97
20	$ClCH_2$	H	*p*-$(Cl)C_6H_4$	**3t**	94
21	$ClCH_2$	H	*p*-$(F)C_6H_4$	**3u**	81
22	$ClCH_2$	H	*o*-$(NH_2)C_6H_4$	**3v**	99
23	*n*-C_6H_{13}	H	C_6H_5	**3w**	85
24	*n*-C_6H_{13}	H	*p*-$(CH_3)C_6H_4$	**3x**	87
25	*n*-C_6H_{13}	H	*p*-$(Cl)C_6H_4$	**3y**	83
26	*n*-C_6H_{13}	H	*p*-$(F)C_6H_4$	**3z**	91

[a] All reactions were run with epoxide **1** (0.5 mmol), disulfide **2** (0.2 mmol), $NaHSO_2·CH_2O·2H_2O$ (0.6 mmol), K_2CO_3 (0.3 mmol) and DMF (2 mL) at room temperature for 5 min.
[b] Isolated yield of **3**, the regioisomer **4** was not detected.

obvious effect on the yield. When less nucleophilic thiophenol (*R*=*p*-FC_6H_4) (Table 2, entries 4, 9, 14, 21, and 26) was used, the reactions could also work efficiently compared to electron-rich thiophenol (*R*=*p*-MeC_6H_4) (Table 2, entries 2, 7, 12, 17, 19, and 24) under the same conditions. On the other hand, the chemoselective thiolysis in the presence of unprotected reactive functional groups such as -NH_2 also proved to be successful. The corresponding products of **3e**, **3j**, **3o**, and **3z** were obtained in high yields (Table 2, entries 5, 10, 15, and 26).

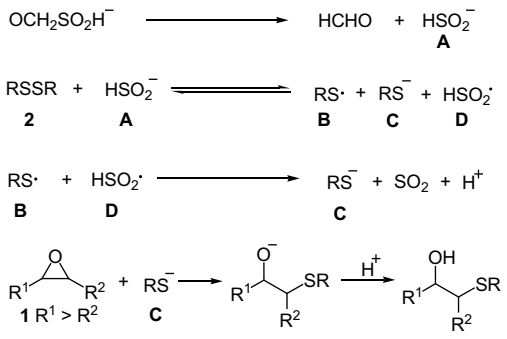
It should be especially noted that the epoxides derived from styrene, such as 2-phenyloxirane underwent cleavage with disulfide to afford only one corresponding α-addition products **3a**–**3e** in our procedure (Table 2, entries 1–5). Their structures were confirmed by ^1H NMR and ^{13}C NMR spectral data in comparison with those reported in literature.[9,18] This regioselectivity is not similar to that obtained from thiolysis of epoxides in the presence of ytterbium(III) chalcogenolate complexes,[14] InI–$InCl_3$,[15] Zn–$Bi(OTf)_3$ or Zn–$Bi(TFA)_3$[16] in which the regioisomer **4** as the major product was formed from attack of the nucleophile at the benzylic position. Similarly, the thiolysis of 2-(4-chlorophenyl)oxirane with disulfide was also examined and the corresponding α-addition products **3f**–**3j** were obtained with high regioselectivity in excellent yields (Table 2, entries 6–10). On the other hand, the ring opening of symmetrical epoxide, such as cyclohexene oxide with disulfides to produce the corresponding β-hydroxy sulfides with high stereoselectivity in good yields (Table 2, entries 16 and 17). Only the products of *trans*-isomer were formed based on ^1H NMR spectrum. If the epoxide is unsymmetrical, attack by the thiolate anion occurs primarily at the less substituted carbon atom. For example, 2-(chloromethyl)oxirane or 2-hexyloxirane reacts with the thiolate anion selectively at its primary carbon atom (Table 2, entries 18–26).

Finally, to extend the scope of this reaction, the thiolysis of chiral epoxide, such as (*R*)-2-(chloromethyl)oxirane (99% ee) was also examined using the present protocol. It was found that optically pure epoxide was converted into the corresponding β-hydroxy sulfide **3s′** without any racemization or inversion (Scheme 2).



Scheme 2. The thiolysis of chiral epoxides.

According to the previous proposed mechanism,[19] Rongalite® promotes mainly the cleavage of disulfides and produces the thiolate anion, which undergoes ring opening of epoxides in the presence of K_2CO_3. A tentative mechanism for the formation of β-hydroxy sulfides was proposed in Scheme 3. Rongalite® can be readily decomposed into HCHO and HSO_2^- anion (**A**). Intermediate (**A**) then reacts with RSSR (**2**) to generate two radical intermediates (**B** and **D**) and the thiolate anion (**C**). The radical (**B**) can also be converted into the anion (**C**) by reacting with intermediate (**D**). Finally, the nucleophilic attack of the thiolate anion (**C**) to the less hindered position of the epoxide (**1**) affords the target product.



Scheme 3. A possible mechanism.

3. Conclusion

In summary, a highly regioselective synthesis of β-hydroxy sulfides has been developed by ring opening of epoxides by disulfides promoted by inexpensive Rongalite®. Especially, the epoxides resulting from styrenes undergo the ring opening and the corresponding α-addition products **3** were obtained in good to excellent yields. Besides, the present method allows the reaction to be carried out under mild conditions and completed in short time (5 min), which is an additional advantage of this protocol. Efforts to explore the detailed mechanism and further applications of the present system in other transformations using disulfide as a reaction partner are ongoing in our group.

4. Experimental section

4.1. General

Chemicals and solvents were either purchased or purified by standard techniques. Melting points were uncorrected and recorded on Digital Melting Point Apparatus WRS-1B. IR spectra were recorded on an AVATAR 370 FI-Infrared Spectrophotometer. NMR spectroscopy was performed on both a Bruck-300 spectrometer operating at 300 MHz (^{1}H NMR) and 75 MHz (^{13}C NMR). TMS (tetramethylsilane) was used as an internal standard and $CDCl_3$ was used as the solvent. Mass spectrometric analysis was performed on GC–MS analysis (SHIMADZU GCMS-QP2010). Optical rotations were measured with Autopol IV RUDOLPH RESEARCH ANALYTICAL (U.S.A.) automatic polarimeter in chloroform solution. Enantiomeric excesses (ee) were determined with a HPLC apparatus fitted with a Chiralcel OJ-H (Daicel, Germany) chiral column. Elemental analysis was determined on a Carlo–Erba 1108 instrument.

4.2. General procedure for synthesis of β-hydroxy sulfides

A mixture of epoxides **1** (0.4 mmol), disulfide **2** (0.2 mmol), Rongalite® (3 equiv), and K_2CO_3 (1.5 equiv) in DMF (2 mL) was stirred at room temperature for 5 min under air. The reaction mixture washed with water, extracted with ethyl acetate, the organic phase was separated and dried over anhydrous sodium sulfate, filtered and the solvent was evaporated under vacuum. The residue was purified by flash column chromatography (ethyl acetate or hexane/ethyl acetate) to afford the desired product **3**.

*4.2.1. 2-(4-Fluorophenylthio)-1-phenylethanol (**3d**) (Table 2, entry 4)*

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.44–7.31 (m, 7H), 7.05–6.99 (m, 2H), 4.69 (dd, J=9.2, 3.7 Hz, 1H), 3.25 (dd, J=13.7, 3.7 Hz, 1H), 3.11–3.03 (m, 1H), 2.89 (br s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.1 (d, $^1J_{C-F}$=245.8 Hz), 142.0, 133.1 (d, $^3J_{C-F}$=8.0 Hz), 129.9, (d, $^4J_{C-F}$=3.2 Hz) 128.5, 128.0, 125.8, 116.2 (d, $^2J_{C-F}$=21.8 Hz), 71.7, 45.1; IR (KBr, cm^{-1}): 3433, 3032, 2922, 1594, 1532, 1490, 1441; MS (EI, 70 eV) m/z (%): 248 (M^+, 12), 142 (100). Anal. Calcd for $C_{14}H_{13}FOS$: C, 67.72; H, 5.28. Found: C, 67.66; H, 5.33.

*4.2.2. 1-(4-Chlorophenyl)-2-(4-chlorophenylthio)ethanol (**3h**) (Table 2, entry 8)*

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.32–7.22 (m, 8H), 4.66 (dd, J=9.0, J=3.9, 1H), 3.21 (dd, J=13.8, 3.9 Hz, 1H), 3.07–3.00 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.3, 133.5, 133.1, 132.8, 131.4, 129.6, 129.1, 128.5, 127.0, 126.8, 125.1, 70.9, 43.8; IR (KBr, cm^{-1}): 3218, 3069, 2923, 1577, 1545, 1455, 1417; MS (EI, 70 eV) m/z (%): 298 (M^+, 12), 158 (100). Anal. Calcd for $C_{14}H_{12}Cl_2OS$: C, 56.20; H, 4.04. Found: C, 56.15; H, 3.98.

*4.2.3. 1-(4-Chlorophenyl)-2-(4-fluorophenylthio)ethanol (**3i**) (Table 2, entry 9)*

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.42–7.37 (m, 2H), 7.31–7.22 (m, 4H), 7.01 (t, J=6.7 Hz, 2H), 4.64 (dd, J=9.0, 3.9 Hz, 1H), 3.19 (dd, J=3.8, 13.8 Hz, 1H), 3.04–2.97 (m, 2H, including br s, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.2 (d, $^1J_{C-F}$=246.2 Hz), 140.4, 133.6, 133.3 (d, $^3J_{C-F}$=8.0 Hz), 129.5 (d, $^4J_{C-F}$=3.3 Hz), 128.6, 127.2, 116.3 (d, $^2J_{C-F}$= 21.8 Hz), 71.0, 45.0; IR (KBr, cm^{-1}): 3223, 3064, 2922, 1588, 1545, 1460, 1407; MS (EI, 70 eV) m/z (%): 282 (M^+, 10), 142 (100). Anal. Calcd for $C_{14}H_{12}ClFOS$: C, 59.47; H, 4.28. Found: C, 59.51; H, 4.23.

*4.2.4. 2-(2-Aminophenylthio)-1-(4-chlorophenyl)ethanol (**3j**) (Table 2, entry 10)*

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.48–7.44 (m, 1H), 7.33–7.19 (m, 6H), 6.79 (t, J=7.6 Hz, 2H), 4.53 (dd, J=9.4, 3.2 Hz, 1H), 4.42 (br s, 2H, NH_2), 3.60 (br s, 1H, OH), 3.13 (dd, J=13.4, 3.3 Hz, 1H), 2.91–2.84 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.5, 141.0, 136.6, 133.5, 130.6, 128.7, 119.5, 117.0, 115.7, 71.5, 44.7. IR (KBr, cm^{-1}): 3406, 3283, 3063, 2920, 1659, 1612, 1507, 1476; MS (EI, 70 eV) m/z (%): 279 (M^+, 14), 139 (100). Anal. Calcd for $C_{14}H_{14}ClNOS$: C, 60.10; H, 5.04. Found: C, 60.14; H, 4.99.

*4.2.5. 1-(2-Aminophenylthio)-3-phenoxypropan-2-ol (**3o**) (Table 2, entry 15)*

White solid, mp 65–68 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.50–7.47 (m, 1H), 7.35 (t, J=7.5 Hz, 2H), 7.19 (t, J=1.1 Hz, 1H), 7.04–6.92 (m, 3H), 6.77 (t, J=7.7 Hz, 2H), 4.4 7 (br s, 2H, NH_2), 4.07–4.01 (m, 3H), 3.39 (br s, 1H, OH), 3.15–2.95 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$)

δ 158.6, 148.5, 136.5, 130.5, 129.7, 121.3, 119.3, 117.4, 115.6, 114.8, 70.5, 69.0, 39.0; IR (KBr, cm^{-1}): 3405, 3333, 3055, 2928, 1660, 1593, 1514, 1454; MS (EI, 70 eV) *m*/*z* (%): 275 (M^+, 40), 125 (100). Anal. Calcd for $C_{15}H_{17}NO_2S$: C, 65.43; H, 6.22. Found: C, 65.49; H, 6.29.

*4.2.6. 1-(p-Tolylthio)octan-2-ol (**3x**) (Table 2, entry 24)*

^1H NMR ($CDCl_3$, 300 MHz) δ 7.27 (d, *J*=8.1 Hz, 2H), 7.07 (d, *J*=7.9 Hz, 2H), 3.58 (s, 1H), 3.06 (dd, *J*=13.5, 3.3 Hz, 1H), 2.79–2.72 (m, 1H), 2.47 (s, 1H), 2.28 (s, 3H), 1.49–1.23 (m, 10H), 0.84 (t, *J*=6.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.8, 131.4, 130.8, 129.8, 69.2, 42.9, 36.0, 31.7, 29.2, 25.6, 22.5, 21.0, 14.0; IR (KBr, cm^{-1}): 3287, 3023, 2983, 2884, 2835, 1725, 1560, 1472, 1431; MS (EI, 70 eV) *m*/*z* (%): 252 (M^+, 34), 138 (100). Anal. Calcd for $C_{15}H_{24}OS$: C, 71.37; H, 9.58. Found: C, 71.45; H, 9.62.

*4.2.7. 1-(4-Fluorophenylthio)octan-2-ol (**3z**) (Table 2, entry 26)*

^1H NMR ($CDCl_3$, 300 MHz) δ 7.41–7.37 (m, 2H), 7.02–6.96 (m, 2H), 3.66–3.58 (m, 1H), 3.07 (dd, *J*=13.5, 3.5 Hz, 1H), 2.84–2.77 (m, 1H), 2.49 (s, 1H), 1.52–1.26 (m, 10H), 0.87 (t, *J*=6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.0 (d, $^1J_{C-F}$=245.5 Hz), 132.9(d, $^3J_{C-F}$=8.0 Hz), 130.3, 116.1 (d, $^2J_{C-F}$=21.8 Hz), 69.3, 43.4, 36.0, 31.7, 29.2, 25.5, 22.5, 14.0; IR (KBr, cm^{-1}): 3279, 2926, 1678, 1654, 1624, 1575; MS (EI, 70 eV) *m*/*z* (%): 256 (M^+, 30), 142 (100). Anal. Calcd for $C_{14}H_{21}FOS$: C, 65.59; H, 8.26. Found: C, 65.63; H, 8.20.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.04.085.

References and notes

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