

Zinc-Catalyzed Regioselective Addition of Alkyl Thiols to Alkenes via Anion or Radical Reactions

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Dedicated to Prof. Dr. Lanny L. Liebeskind on the occasion of his 70th birthday

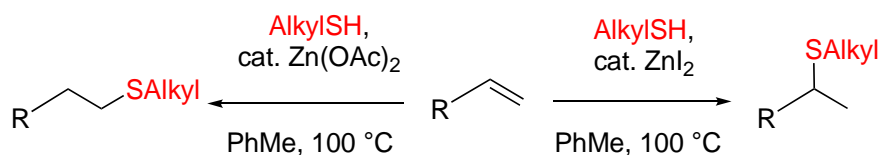
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Abstract

Zn-catalyzed reactions of alkenes with alkyl thiols could afford alkyl sulfides regioselectively. When the ZnI₂-catalyzed hydrothiolation of alkenes was achieved using alkyl thiols at 100 °C, Markovnikov-type alkyl sulfides were obtained in excellent yields without the formation of linear products. To the contrary, Zn(OAc)₂-catalyzed reaction gave rise only to *anti*-Markovnikov-type products regioselectively. The reaction proceeded via a radical process.

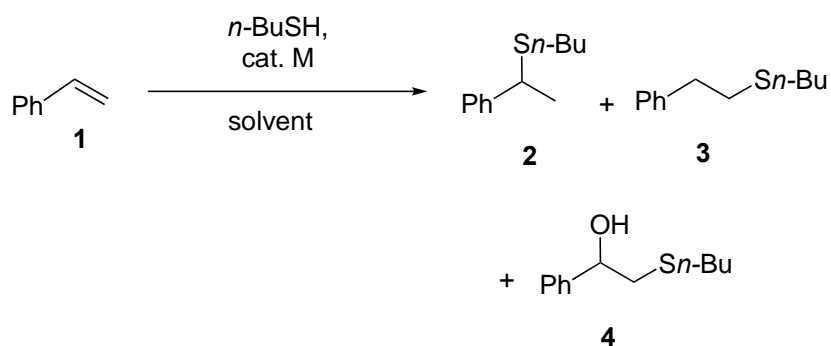


Keywords: Zinc catalyst, Anion, Radical, Alkene, Alkyl thiol

Results and Discussion

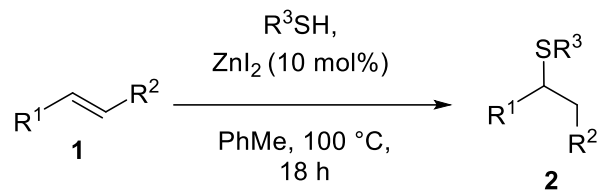
To establish the hydrothiolation of alkenes using alkyl thiols, various conditions were investigated. As shown in Table 1, when the ZnI_2 -catalyzed reaction of styrene with 1-butanethiol was performed in dichloromethane or toluene at room temperature, the expected sulfide **2** was not obtained (Entries 1-2). Also the reaction did not proceed in acetic acid at 100 °C did not proceed (Entry 3). However, when the solvent was changed to toluene, the corresponding branched sulfide **3** was obtained in a 79% yield without the formation of other products (Entry 4). Similarly, the reaction using ZnBr_2 produced the same result (Entry 5). Notably, the reactions using ZnF_2 or Zn(OAc)_2 catalysts afforded linear sulfide **3** in 38% or 49% yields, regioselectively (Entry 7). Furthermore, when the Zn(OAc)_2 -catalyzed reaction was performed for 36 h, the production of **3** increased to 87% yield (Entry 9). The reactivity of other metal catalysts were examined similarly, but these led to unsatisfactory results (Entries 10-14).

Table 1. Investigation of suitable conditions^a



Entry	solv.	M	°C	2/3/4 ^b	2 (%) ^c	3 (%) ^c
1	CH_2Cl_2	ZnI_2	rt	0/100/0	0	trace
2	PhMe	ZnI_2	rt	0/100/0	0	trace
3	AcOH	ZnI_2	100	-	0	0
4	PhMe	ZnI_2	100	100/0/0	79	0
5	PhMe	ZnBr_2	100	100/0/0	77	0
6	PhMe	ZnCl_2	100	91/9/0	27	trace
7	PhMe	ZnF_2	100	0/100/0	0	38
8	PhMe	Zn(OAc)_2	100	0/100/0	0	49
9 ^d	PhMe	Zn(OAc)_2	100	0/100/0	0	87
10	PhMe	NiCl_2	100	0/75/25	0	17
11	PhMe	NiBr_2	100	9/91/0	trace	41
12	PhMe	FeBr_3	100	100/0/0	51	0
13	PhMe	CuBr_2	100	95/5/0	16	trace
14	PhMe	CuI	100	0/75/25	0	17

^aReaction conditions: A mixture of **1** (0.3 mmol), *n*-BuSH (0.33 mmol) and cat. M (10 mol%) in solvent (0.3 mL). ^bDetermined by ^1H NMR. ^cIsolated yield after silica gel chromatography. ^dThe reaction was performed for 36 h.

Table 2. Zn-catalyzed hydrothiolation of alkenes^a

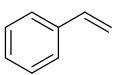
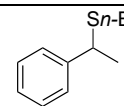
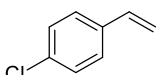
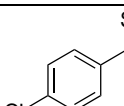
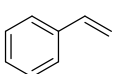
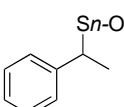
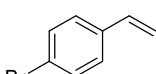
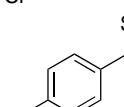
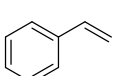
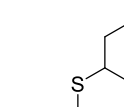
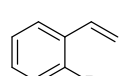
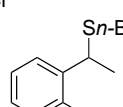
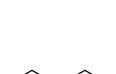
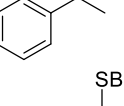
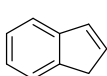
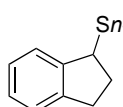
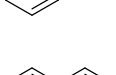
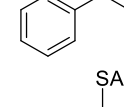
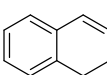
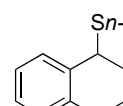
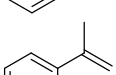
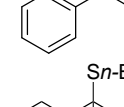

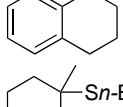
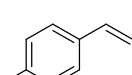
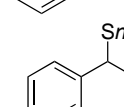
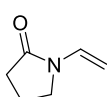
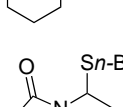
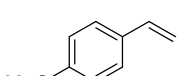
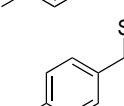
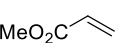
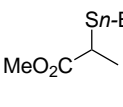
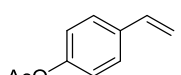
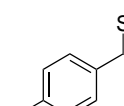
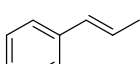
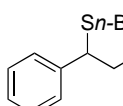
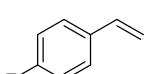
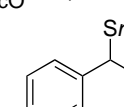
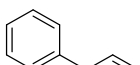
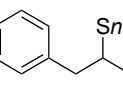
Entry	1	2	2 (%) ^b	Entry	1	2	2 (%) ^b
1			2a 79	11			2k 74
2			2b 66	12			2l 81
3			2c 83	13			2m 69
4			2d 78	14			2n 74
5			2e 7	15			2o 80
6			2f 90	16			2p 86
7			2g 88	17			2q 81
8			2h 75	18			2r 0 ^d
9 ^c			2i 62	19			2s trace
10			2j 79	20			2t 0

Table 2. Continued

^aReaction conditions: A mixture of **1** (0.3 mmol), R³SH (0.33 mmol) and ZnI₂ (10 mol%) in PhMe (0.15 mL) was heated at 100 °C. ^bIsolated yield after silica gel chromatography. ^cThe reaction was performed for 42 h. ^dMethyl 3-(1-butylthio)propionate was obtained in 90% yield.

Sequentially, the Zn(OAc)₂-catalyzed reactions were also surveyed for the preparation of *anti*-Markovnikov-type sulfides (Table 3). When a mixture of alkene with alkyl thiol was heated at 100 °C for 36 h, the expected products **3** were regioselectively obtained in excellent yields (Entries 1-5). Similarly, the procedure worked with various styrene derivatives (Entries 6-9). Regrettably, using internal or terminal alkyl alkenes produced lower yields (Entries 10-12).

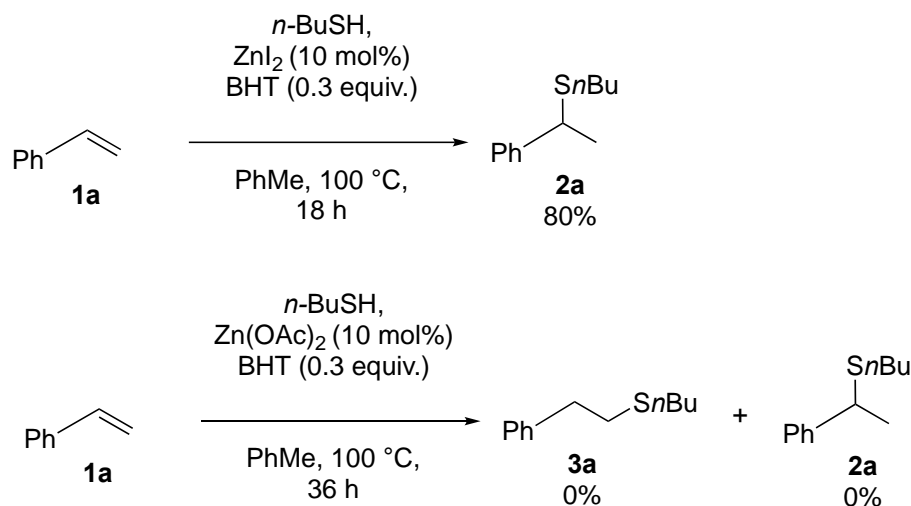
On the basis of developed procedure, numerous substrates were next investigated (Table 2). When styrene was reacted with different alkyl thiols, the expected products were obtained in excellent yields without the formation of linear sulfides (Entries 1-6). Numerous styrene derivatives were suitable substrates for the procedure (Entries 7-13). Furthermore, cyclic alkenes afforded **2** in excellent yields, regioselectively (Entries 14-16). A using vinyl pyrrolidine gave only the expected sulfide **2** with an 81% yield (Entry 17). On the other hand, the reaction of methyl acrylate produced linear products in a 90% yield (Entry 18). Regrettably, other internal alkenes or terminal alkyl alkenes did not undergo the reaction satisfactorily (Entries 19-20).

Table 3. Zn-catalyzed hydrothiolation of alkenes^a

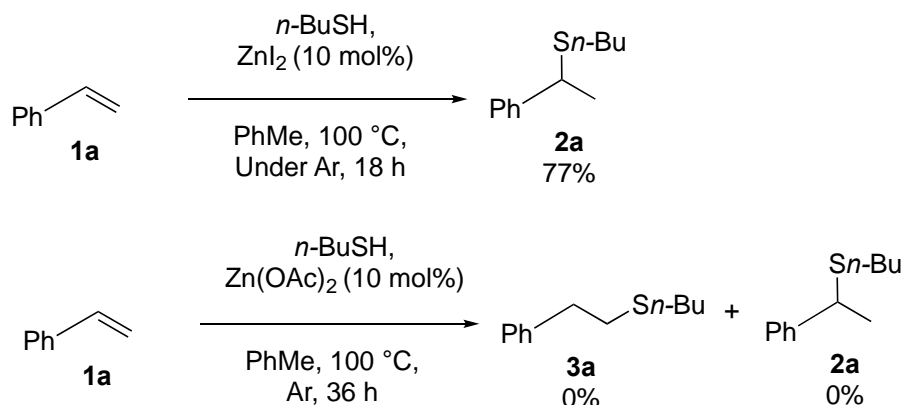
Entry	1	3	3 (%) ^b	Entry	1	3	3 (%) ^b
1			3a 87	7			3g 64
2			3b 81	8			3h 64
3			3c 79	9			3i 72
4			3d 78	10			3j 15
5			3e 67	11			3k 31
6			3f 81	12			3l trace

^aReaction conditions: A mixture of **1** (0.3 mmol), R³SH (0.33 mmol) and Zn(OAc)₂ (10 mol%) in PhMe (0.15 mL) was heated at 100 °C. ^bIsolated yield after silica gel chromatography. ^cDetermined by ¹H NMR.

To clarify these reaction mechanisms, several experiments were then carried out. Initially, the reactions were performed in the presence of 2,6-di-*tert*-butyl-4-methylphenol (BHT) as a radical scavenger (Scheme 2). Although the ZnI₂-catalyzed reactions gave the corresponding product in an 80% yield, Zn(OAc)₂ did not promote the reaction. These results indicate that the reaction using Zn(OAc)₂ as catalyst might involve a radical process. Furthermore, reactions in the absence of oxygen were also examined. When a mixture of styrene with 1-butanethiol was treated by ZnI₂ under an argon atmosphere, the corresponding sulfide **2a** was obtained in a 77% yield. However, again, Zn(OAc)₂ catalysis did not occur (Scheme 3). It is conceivable that the thiyl radicals are generated in the presence of oxygen.



Scheme 2. A reaction in the presence of BHT.



Scheme 3. A reaction in the absence of oxygen.

From these results, a plausible reaction mechanism is considered to be as follows (Figure 2).¹¹ In the ZnI₂-catalyzed reaction, after the reaction of ZnI₂ with the alkyl thiol produces an alkylS-ZnI complex,⁹ Markovnikov-type products are produced by the addition of the complex to the alkene. Alternatively, in reactions using a Zn(OAc)₂ catalyst in oxygen, thiyl radicals are efficiently produced. Ultimately, anti-Markovnikov-type products are obtained.

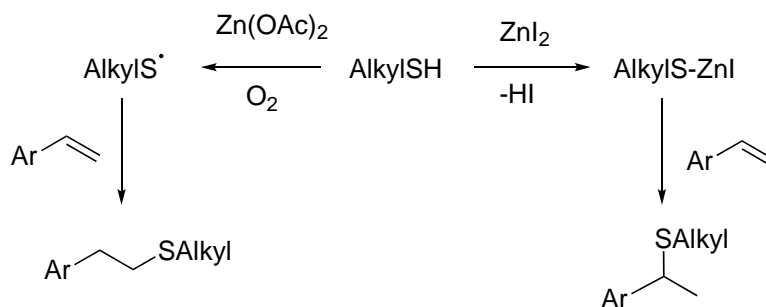


Figure 2. A plausible reaction mechanism.

Conclusions

In conclusion, the ZnI₂-catalyzed hydrothiolation of alkenes using alkyl thiols was achieved at 100 °C. The procedure regioselectively affords excellent yields of Markovnikov-type products. However, Zn(OAc)₂-catalyzed hydrothiolation regioselectively produces *anti*-Markovnikov-type products via a radical process. Thus, regioselective additions of alkyl thiols to alkenes were achieved using different zinc catalysts.

Experimental Section

General Procedure and Chemicals. All reactions were carried out in air. ¹H and ¹³C NMR spectra were recorded on a JEOL EX-270 spectrometer (270 MHz for ¹H, 67.8 MHz for ¹³C). Chemical shifts are reported in δ ppm referenced to an internal tetramethylsilane standard for ¹H NMR and chloroform-d (δ 77.0) for ¹³C NMR. IR spectra were recorded on a PerkinElmer Frontier FT-IR spectrometer.

Typical procedure for zinc-catalyzed hydrothiolation of alkenes: Synthesis of 1-(1-Butylthio)-1-phenylethane (2a) (Table 2, entry 1)

To a mixture of styrene (31.2 mg, 0.3 mmol), 1-butanethiol (56.8 mg, 0.33 mmol), in PhCH₃ (0.3 mL), ZnI₂ (9.6 mg, 0.03 mmol) was added, and the mixture was stirred at 100 °C for 18 h in the presence of air in 15 mL glass test tube with plastic screw cap. After, the residue was dissolved in Et₂O, the solution was washed with H₂O and saturated aq NaCl and dried over anhydrous MgSO₄. Chromatography on silica gel (hexane) gave 1-(1-butylthio)-1-phenylethane **2a** (45.9 mg, 79%): Colorless oil; ¹H NMR (270 MHz, CDCl₃) δ 7.36–7.20 (m, 5H, Ar-H), 3.94 (q, *J* = 7.0 Hz, 1H, CH), 2.34–2.24 (m, 2H, CH₂), 1.56 (d, *J* = 7.0 Hz, 3H, CH₃), 1.53–1.38 (m, 2H, CH₂), 1.38–1.27 (m, 2H, CH₂), 0.84 (t, *J* = 7.2 Hz, 3H, CH₃); ¹³C{¹H} NMR (67.8 MHz, CDCl₃) δ 144.2, 128.4, 127.2, 126.9, 44.0, 31.4, 30.9, 22.6, 22.0, 13.6; IR (neat, NaCl cell, *v*_{max}, cm⁻¹) 2959 (C-H), 2927 (C-H), 1602 (C=C), 1491 (C=C), 1451 (C-H), 1373 (C-H), 1217 (SC-H); Anal. Calcd for C₁₂H₁₈S (194.34): C, 74.17; H, 9.34. Found: C, 73.88; H, 9.28.

1-(1-Octylthio)-1-phenylethane (2b). The title compound was obtained as a colorless oil (49.2 mg, 66%). ¹H NMR (270 MHz, CDCl₃) δ 7.36–7.19 (m, 5H, Ar-H), 3.94 (q, *J* = 7.0 Hz, 1H, CH), 2.38–2.21 (m, 2H, CH₂), 1.57 (d, *J* = 7.0 Hz, 3H, CH₃), 1.48–1.43 (m, 2H, CH₂), 1.31–1.22 (m, 10H, CH₂), 0.87 (t, *J* = 6.8 Hz, 3H, CH₃); ¹³C{¹H} NMR (67.8 MHz, CDCl₃) δ 144.2, 128.4, 127.2, 126.9, 44.0, 31.8, 31.3, 29.3, 29.1, 28.9, 22.6, 22.5, 14.1; IR (neat, NaCl

cell, ν_{\max} , cm^{-1}) 2925 (C-H), 2854 (C-H), 1602 (C=C), 1491 (C=C), 1452 (C-H), 1372 (C-H), 1220 (S C-H), 1026 (C-H); Anal. Calcd for $\text{C}_{16}\text{H}_{26}\text{S}$ (264.47): C, 76.73; H, 10.46. Found: C, 76.77; H, 10.48.

1-Cyclohexylthio-1-phenylethane (2c). The title compound was obtained as a colorless oil (54.8 mg, 83%). ^1H NMR (270 MHz, CDCl_3) δ 7.37–7.18 (m, 5H, Ar-H), 4.04 (q, $J = 7.0$ Hz, 1H, CH), 2.42–2.34 (m, 1H, CH_2), 1.99–1.94 (m, 1H, CH_2), 1.75–1.65 (m, 3H, CH_2), 1.56–1.53 (m, 1H, CH_2), 1.55 (d, $J = 6.9$ Hz, 3H, CH_3), 1.40–1.18 (m, 5H, CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.8 MHz, CDCl_3) δ 144.7, 128.4, 127.1, 126.8, 42.7, 42.4, 33.8, 33.2, 26.0, 25.8, 23.1 IR (neat, NaCl cell, ν_{\max} , cm^{-1}) 2927 (C-H), 2852 (C-H), 1601 (C=C), 1491 (C=C), 1448 (C-H); Anal. Calcd for $\text{C}_{14}\text{H}_{20}\text{S}$ (220.37): C, 76.30; H, 9.15. Found: C, 76.50; H, 9.17.

1-Benzylthio-1-phenylethane (2d). The title compound was obtained as a colorless oil (53.4 mg, 78%). ^1H NMR (270 MHz, CDCl_3) δ 7.33–7.18 (m, 10H, Ar-H), 3.80 (q, $J = 7.0$ Hz, 1H, CH), 3.48 (dd, $J = 29.0$ and 13.5 Hz, 2H, CH_2), 1.53 (d, $J = 7.0$ Hz, 3H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.8 MHz, CDCl_3) δ 143.8, 138.4, 128.9, 128.5, 128.4, 127.4, 127.0, 126.8, 43.5, 35.7, 25.5; IR (neat, NaCl cell, ν_{\max} , cm^{-1}) 3027 (C-H), 2966 (C-H), 1601 (C=C), 1492 (C=C), 1452 (C-H), 1222 (S C-H); Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{S}$ (228.35): C, 79.95; H 6.71. Found: C, 79.99; H, 6.82.

2-(1-Butylthio)-2-phenylpropane (2f). The title compound was obtained as a colorless oil (56.5 mg, 90%). ^1H NMR (270 MHz, CDCl_3) δ 7.55–7.52 (m, 2H, Ar-H), 7.34–7.17 (m, 3H, Ar-H), 2.21 (t, $J = 7.1$ Hz, 2H, CH_2), 1.70 (s, 6H, CH_3), 1.39–1.22 (m, 4H, CH_2), 0.79 (t, $J = 7.1$ Hz, 3H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.8 MHz, CDCl_3) δ 146.8, 128.0, 126.4, 126.3, 47.3, 31.2, 30.3, 29.1, 22.1, 13.6; IR (neat, NaCl cell, ν_{\max} , cm^{-1}) 2959 (C-H), 2871 (C-H), 1600 (C=C), 1493 (C=C), 1446 (C-H), 1381 (C-H), 1364 (C-H); Anal. Calcd for $\text{C}_{13}\text{H}_{20}\text{S}$ (208.36): C, 74.94; H, 9.68. Found: C, 74.66; H 9.74.

1-(1-Butylthio)-1-(4-tolyl)ethane (2g). The title compound was obtained as a colorless oil (54.8 mg, 88%). ^1H NMR (270 MHz, CDCl_3) δ 7.22 (d, $J = 8.2$ Hz, 2H, Ar-H), 7.11 (d, $J = 8.2$ Hz, 2H, Ar-H), 3.91 (q, $J = 7.0$ Hz, 1H, CH), 2.34–2.24 (m, 5H, CH_2), 1.54 (d, $J = 6.9$ Hz, 3H, CH_3), 1.55–1.31 (m, 4H, CH_2), 0.85 (t, $J = 7.2$ Hz, 3H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.8 MHz, CDCl_3) δ 141.2, 136.5, 129.1, 127.1, 43.7, 31.5, 30.9, 22.7, 22.0, 21.0, 13.6; IR (neat, NaCl cell, ν_{\max} , cm^{-1}) 2925 (C-H), 2870 (C-H), 1512 (C=C), 1448 (C-H), 1372 (C-H), 1219 (SC-H); Anal. Calcd for $\text{C}_{13}\text{H}_{20}\text{S}$ (208.36): C, 79.94; H, 9.68. Found: C, 74.84; H, 9.62.

1-(1-Butylthio)-1-(4-methoxyphenyl)ethane (2h). The title compound was obtained as a colorless oil (50.5 mg, 75%). ^1H NMR (270 MHz, CDCl_3) δ 7.25 (d, $J = 8.5$ Hz, 2H, Ar-H), 6.85 (d, $J = 8.5$ Hz, 2H, Ar-H), 3.92 (q, $J = 6.9$ Hz, 1H, CH), 3.79 (s, 3H, OCH_3), 2.35–2.26 (m, 2H, CH_2), 1.53 (d, $J = 6.9$ Hz, 3H, CH_3), 1.59–1.29 (m, 4H, CH_2), 0.85 (t, $J = 7.2$ Hz, 3H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.8 MHz, CDCl_3) δ 158.4, 136.2, 128.2, 113.7, 55.2, 43.3, 31.5, 30.9, 22.7, 22.0, 13.6; IR (neat, NaCl cell, ν_{\max} , cm^{-1}) 2958 (C-H), 2871 (C-H), 1611 (C=C), 1511 (C=C), 1464 (C-H), 1247 (SC-H); Anal. Calcd for $\text{C}_{13}\text{H}_{20}\text{OS}$ (224.36): C, 69.59; H, 8.99. Found: C, 69.77; H, 8.96.

1-(4-Acetoxyphenyl)-1-(1-Butylthio)ethane (2i). The title compound was obtained as a colorless oil (46.7 mg, 62%). ^1H NMR (270 MHz, CDCl_3) δ 7.35 (d, $J = 8.2$ Hz, 2H, Ar-H), 7.03 (d, $J = 8.2$ Hz, 2H, Ar-H), 3.94 (q, $J = 7.0$ Hz, 1H, CH), 2.34–2.29 (m, 2H, CH_2), 2.29 (s, 3H, COCH_3), 1.54 (d, $J = 7.0$ Hz, 3H, CH_3), 1.58–1.26 (m, 4H, CH_2), 0.85 (t, $J = 7.2$ Hz, 3H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.8 MHz, CDCl_3) δ 169.4, 149.4, 141.8, 128.2, 121.4, 43.4, 31.4, 30.9, 22.7, 22.0, 21.1, 13.6; IR (neat, NaCl cell, ν_{\max} , cm^{-1}) 2960 (C-H), 2928 (C-H), 1767 (C=O), 1505 (C=C), 1369 (C-H); Anal. Calcd for $\text{C}_{14}\text{H}_{20}\text{OS}$ (252.37): C, 66.63; H, 7.99. Found: C, 66.61; H, 7.97.

1-(1-Butylthio)-1-(4-fluorobenzene)ethane (2j). The title compound was obtained as a colorless oil (50.5 mg, 79%). ^1H NMR (270 MHz, CDCl_3) δ 7.33–7.26 (m, 2H, Ar-H), 7.03–6.96 (m, 2H, Ar-H), 3.93 (q, $J = 7.1$ Hz, 1H, CH), 2.35–2.34 (m, 2H, CH_2), 1.55–1.26 (m, 4H, CH_2), 1.54 (d, $J = 6.9$ Hz, 3H, CH_3), 0.85 (t, $J = 7.1$ Hz, 3H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.8 MHz, CDCl_3) δ = 161.7 (d, $^1J_{\text{C-F}} = 244.8$ Hz), 139.7 (d, $^4J_{\text{C-F}} = 3.4$ Hz), 128.7 (d, $^3J_{\text{C-F}} = 8.8$ Hz), 115.2 (d, $^2J_{\text{C-F}} = 21.7$ Hz), 43.3, 31.4, 30.9, 22.7 (d, $J = 0.7$ Hz), 22.0, 13.6; IR (neat, NaCl cell, ν_{\max} , cm^{-1}) 2960 (C-H), 2872 (C-H), 1603 (C=C), 1508 (C=C), 1452 (C-H), 1223 (SC-H); Anal. Calcd for $\text{C}_{12}\text{H}_{17}\text{FS}$ (212.33): C, 67.88; H, 8.07. Found: C, 68.15; H, 8.25

1-(1-Butylthio)-1-(4-chlorophenyl)ethane (2k). The title compound was obtained as a colorless oil (50.6 mg, 74%). ^1H NMR (270 MHz, CDCl_3) δ 7.27 (s, 4H, Ar-H), 3.91 (q, $J = 7.1$ Hz, 1H, CH), 2.35–2.21 (m, 2H, CH_2), 1.56–1.25 (m, 4H, CH_2), 1.55 (d, $J = 6.9$ Hz, 3H, CH_3), 0.85 (t, $J = 7.2$ Hz, 3H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.8 MHz, CDCl_3) δ 142.8, 132.5, 128.6, 128.5, 43.4, 31.4, 30.9, 22.6, 22.0, 13.6; IR (neat, NaCl cell, ν_{max} , cm^{-1}) 2959 (C-H), 2871 (C-H), 1491 (C-H), 1465 (C-H), 1215 (SC-H), 1092 (C-H); Anal. Calcd for $\text{C}_{12}\text{H}_{17}\text{ClS}$ (228.78): C, 63.00; H, 7.49. Found: C, 63.11; H 7.62.

1-(1-Butylthio)-1-(4-bromophenyl)ethane (2l). The title compound was obtained as a colorless oil (66.3 mg, 81%). ^1H NMR (270 MHz, CDCl_3) δ 7.45–7.41 (m, 2H, Ar-H), 7.24–7.20 (m, 2H), 3.90 (q, $J = 7.0$ Hz, 1H, CH), 2.33–2.25 (m, 2H, CH_2), 1.56–1.28 (m, 4H, CH_2), 1.52 (dd, $J = 6.9$ and 0.7 Hz, 3H, CH_3), 0.88 (t, $J = 7.4$ Hz, 3H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.8 MHz, CDCl_3) δ 143.4, 131.5, 128.9, 120.5, 43.4, 31.3, 30.9, 22.5, 22.0, 13.6; IR (neat, NaCl cell, ν_{max} , cm^{-1}) 2959 (C-H), 2870 (C-H), 1487 (C-H), 1450 (C-H), 1213 (SC-H); Anal. Calcd for $\text{C}_{12}\text{H}_{17}\text{BrS}$ (273.23): C, 52.75; H, 6.27. Found: C, 52.68; H, 6.21.

1-(1-Butylthio)-1-(2-bromophenyl)ethane (2m). The title compound was obtained as a colorless oil (56.2 mg, 69%). ^1H NMR (270 MHz, CDCl_3) δ 7.62 (d, $J = 7.9$ Hz, 1H, Ar-H), 7.50 (d, $J = 8.2$ Hz, 1H, Ar-H), 7.31 (dd, $J = 7.9$ and 8.2 Hz, 1H, Ar-H), 7.05 (d, $J = 7.9$ and 8.2 Hz, 1H, Ar-H), 4.53 (q, $J = 7.0$ Hz, 1H, CH), 2.42–2.30 (m, 2H, CH_2), 1.51 (d, $J = 6.9$ Hz, 3H, CH_3), 1.56–1.30 (m, 4H, CH_2), 0.85 (t, $J = 7.2$ Hz, 3H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.8 MHz, CDCl_3) δ 143.3, 132.5, 128.6, 128.2, 127.9, 123.8, 42.4, 31.5, 31.0, 22.2, 21.9, 13.5; IR (neat, NaCl cell, ν_{max} , cm^{-1}) 2958 (C-H), 2870 (C-H), 1565 (C=C), 1466 (C-H), 1438 (C-H), 1373 (C-H), 1221 (SC-H); Anal. Calcd for $\text{C}_{12}\text{H}_{17}\text{BrS}$ (273.23): C, 52.75; H 6.27. Found: C, 52.93; H, 6.32.

1-(1-Butylthio)indane (2n). The title compound was obtained as a colorless oil (45.8 mg, 74%). ^1H NMR (270 MHz, CDCl_3) δ 7.36–7.33 (m, 1H, Ar-H), 7.24–7.16 (m, 3H, Ar-H), 4.34–4.29 (m, 1H, CH), 3.10–2.93 (m, 1H, CH_2), 2.91–2.80 (m, 1H, CH_2), 2.59–2.45 (m, 3H, CH_2), 2.17–2.09 (m, 1H, CH_2), 1.65–1.54 (m, 2H, CH_2), 1.48–1.34 (m, 2H, CH_2), 0.91 (t, $J = 7.2$ Hz, 3H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.8 MHz, CDCl_3) δ 143.6, 143.5, 127.3, 126.4, 124.6, 48.8, 34.1, 31.8, 31.0, 30.6, 22.1, 13.7; IR (neat, NaCl cell, ν_{max} , cm^{-1}) 2959 (C-H), 2929 (C-H), 1459 (C-H), 1378 (C-H); Anal. Calcd for $\text{C}_{13}\text{H}_{18}\text{S}$ (206.35): C, 75.67; H, 8.79. Found: C, 75.92; H 8.86.

1,2,3,4-Tetrahydro-1-(1-Butylthio)naphthaene (2o). The title compound was obtained as a colorless oil (52.8 mg, 80%). ^1H NMR (270 MHz, CDCl_3) δ 7.40–7.36 (m, 1H, Ar-H), 7.13–7.03 (m, 3H, Ar-H), 4.09 (t, $J = 4.1$ Hz, 1H, CH), 2.82–2.73 (m, 2H, CH_2), 2.67–2.49 (m, 2H, CH_2), 2.16–2.05 (m, 3H, CH_2), 1.80–1.74 (m, 1H, CH_2), 1.64–1.54 (m, 2H, CH_2), 1.47–1.39 (m, 2H, CH_2), 0.92 (t, $J = 7.1$ Hz, 3H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.8 MHz, CDCl_3) δ 137.3, 136.8, 130.2, 129.1, 126.6, 125.6, 43.8, 31.7, 31.3, 29.2, 29.1, 22.2, 19.1, 13.7; IR (neat, NaCl cell, ν_{max} , cm^{-1}) 2931 (C-H), 2870 (C-H), 1693 (C=C), 1487 (C-H), 1452 (C-H), 1269 (SC-H); Anal. Calcd for $\text{C}_{14}\text{H}_{20}\text{S}$ (220.37): C, 76.30; H, 9.15. Found: C, 76.27; H, 9.11.

1-(1-Butylthio)-1-methylcyclohexane (2p). The title compound was obtained as a colorless oil (48.1 mg, 86%). ^1H NMR (270 MHz, CDCl_3) δ 2.44 (t, $J = 7.2$ Hz, 2H, Ar-H), 1.69–1.65 (m, 2H, CH_2), 1.59–1.37 (m, 12H, CH_2), 1.31 (s, 3H, CH_3), 0.91 (t, $J = 7.2$ Hz, 3H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.8 MHz, CDCl_3) δ 45.9, 38.3, 31.9, 28.8, 28.7, 26.5, 25.9, 22.4, 13.7; IR (neat, NaCl cell, ν_{max} , cm^{-1}) 2929 (C-H), 2858 (C-H), 1446 (C-H), 1375 (C-H), 1272 (SC-H); Anal. Calcd for $\text{C}_{11}\text{H}_{22}\text{S}$ (186.36): C, 70.90; H, 11.90. Found: C, 71.11; H, 11.64.

1-[(1-Butylthio)ethyl]-2-pyrrolidinone (2q). The title compound was obtained as a colorless oil (48.7 mg, 81%). ^1H NMR (270 MHz, CDCl_3) δ 5.54 (q, $J = 7.0$ Hz, 1H, CH), 3.66–3.57 (m, 1H, CH), 3.35–3.26 (m, 1H, CH), 2.54–2.29 (m, 4H, CH_2), 2.09–1.98 (m, 2H, CH_2), 1.63–1.32 (m, 4H, CH_2), 1.39 (d, $J = 6.9$ Hz, CH_3), 0.89 (t, $J = 7.2$ Hz, 3H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.8 MHz, CDCl_3) δ 174.6, 51.6, 40.9, 31.6, 31.5, 30.5, 21.9, 19.2, 17.8, 13.5; IR (neat, NaCl cell, ν_{max} , cm^{-1}) 2957 (C-H), 2873 (C-H), 1687 (C=O), 1459 (C-H), 1419 (C-H), 1267 (SC-H); Anal. Calcd for $\text{C}_{10}\text{H}_{19}\text{NOS}$ (201.33): C, 59.66; H 9.51. Found: C, 59.31; H, 9.59.

Typical procedure for zinc-catalyzed hydrothiolation of alkenes: Synthesis of 1-(1-Butylthio)-2-phenylethane (3a) (Table 3, entry 1)

To a mixture of styrene (31.2 mg, 0.3 mmol), 1-butanethiol (29.8 mg, 0.33 mmol), in PhCH₃ (0.3 mL), Zn(OAc)₂ (5.5 mg, 0.03 mmol) was added, and the mixture was stirred at 100 °C for 36 h in the presence of air in 15 mL glass test tube with plastic screw cap. After the residue was dissolved in Et₂O, the solution was washed with H₂O and saturated aq NaCl and dried over anhydrous MgSO₄. Chromatography on silica gel (hexane) gave 1-(1-butylthio)-2-phenylethane **3a** (50.9 mg, 87%): Colorless oil; ¹H NMR (270 MHz, CDCl₃) δ 7.32–7.19 (m, 5H, Ar-H), 2.92–2.85 (m, 2H, CH₂), 2.80–2.73 (m, 2H, CH₂), 2.53 (t, *J* = 7.4 Hz, 2H, CH₂), 1.63–1.52 (m, 2H, CH₂), 1.47–1.33 (m, 2H, CH₂), 0.91 (t, *J* = 7.4 Hz, 3H, CH₃); ¹³C{¹H} NMR (67.8 MHz, CDCl₃) δ 140.7, 128.4, 128.4, 126.3, 36.4, 33.6, 32.0, 31.7, 22.0, 13.7; IR (neat, NaCl cell, *v*_{max}, cm⁻¹) 2955 (C-H), 2871 (C-H), 1604 (C=C), 1496 (C-H), 1453 (C-H), 1273 (SC-H); Anal. Calcd for C₁₂H₁₈S (208.36): C, 74.17; H, 9.34. Found: C, 74.30; H, 9.42.

1-(1-Octylthio)-2-phenylethane (3b). The title compound was obtained as a colorless oil (60.8 mg, 81%). ¹H NMR (270 MHz, CDCl₃) δ 7.32–7.19 (m, 5H, Ar-H), 2.91–2.85 (m, 2H, CH₂), 2.80–2.73 (m, 2H, CH₂), 2.53 (t, *J* = 7.4 Hz, 2H, CH₂), 1.63–1.52 (m, 2H, CH₂), 1.40–1.27 (m, 10H, CH₂), 0.88 (t, *J* = 6.6 Hz, 3H, CH₃); ¹³C{¹H} NMR (67.8 MHz, CDCl₃) δ 140.7, 128.4, 128.4, 126.3, 36.4, 33.6, 32.3, 31.8, 29.6, 29.2, 29.1, 28.9, 22.6, 14.1; IR (neat, NaCl cell, *v*_{max}, cm⁻¹) 2925 (C-H), 2854 (C-H), 1604 (C=C), 1496 (C-H), 1454 (C-H); Anal. Calcd for C₁₆H₂₆S (250.44): C, 76.73; H, 10.46. Found: C, 76.80; H, 10.20.

1-(1-Cyclohexylthio)-2-phenylethane (3c). The title compound was obtained as a colorless oil (52.4 mg, 79%). ¹H NMR (270 MHz, CDCl₃) δ 7.32–7.18 (m, 5H, Ar-H), 2.91–2.75 (m, 4H, CH₂), 2.65–2.61 (m, 1H, CH), 1.99–1.95 (m, 2H, CH₂), 1.77–1.75 (m, 2H, CH₂), 1.65–1.56 (m, 1H), 1.31–1.23 (m, 5H, CH₂); ¹³C{¹H} NMR (67.8 MHz, CDCl₃) δ 140.8, 128.4, 126.3, 43.7, 36.7, 33.7, 31.7, 26.1, 25.8; IR (CHCl₃, NaCl cell, *v*_{max}, cm⁻¹) 2932 (C-H), 2854 (C-H), 1464 (C-H), 1449 (C-H), 1264 (SC-H); Anal. Calcd for C₁₄H₂₀S (220.37): C, 76.30 ; H, 9.15. Found: C, 76.37; H, 9.15.

1-(1-Benzylthio)-2-phenylethane (3d). The title compound was obtained as a colorless oil (53.4 mg, 78%). ¹H NMR (270 MHz, CDCl₃) δ 7.32–7.13 (m, 10H, Ar-H), 3.71 (s, 2H, CH₂), 2.86–2.80 (m, 2H, CH₂), 2.68–2.62 (m, 2H, CH₂); ¹³C{¹H} NMR (67.8 MHz, CDCl₃) δ 140.5, 138.4, 128.9, 128.5, 128.4, 127.0, 126.3, 36.4, 36.0, 32.7; IR (neat, NaCl cell, *v*_{max}, cm⁻¹) 3061 (C-H), 3026 (C-H), 2915 (C-H), 1602 (C=C), 1494 (C-H), 1453 (C-H); Anal. Calcd for C₁₅H₁₆S (228.35): C, 78.90; H, 7.06. Found: C, 78.91; H, 6.95.

1-(1-Buthylthio)-2-phenylpropane (3e). The title compound was obtained as a colorless oil (41.9 mg, 67%). ¹H NMR (270 MHz, CDCl₃) δ 7.34–7.28 (m, 2H, Ar-H), 7.25–7.18 (m, 3H, Ar-H), 2.98–2.90 (m, 1H, CH), 2.83–2.71 (m, 1H, CH₂), 2.67–2.64 (m, 1H, CH₂), 2.44 (t, *J* = 7.2 Hz, 2H, CH₂), 1.58–1.47 (m, 2H, CH₂), 1.43–1.30 (m, 5H, CH₂), 0.89 (d, *J* = 7.2 Hz, 3H, CH₃); ¹³C{¹H} NMR (67.8 MHz, CDCl₃) δ 146.0, 128.4, 126.9, 126.4, 40.8, 40.2, 32.4, 31.7, 22.0, 21.0, 13.7; IR (neat, NaCl cell, *v*_{max}, cm⁻¹) 2859 (C-H), 1602 (C=C), 1493 (C-H), 1452 (C-H), 1375 (C-H); Anal. Calcd for C₁₃H₂₀S (208.36): C, 74.94; H, 9.68. Found: C, 74.62; H, 9.61.

1-(1-Buthylthio)-2-(4-tolyl)ethane (3f). The title compound was obtained as a colorless oil (44.3 mg, 81%). ¹H NMR (270 MHz, CDCl₃) δ 7.13–7.07 (m, 4H, Ar-H), 2.88–2.81 (m, 2H, CH₂), 2.77–2.71 (m, 2H, CH₂), 2.53 (t, *J* = 7.4 Hz, 2H, CH₂), 2.32 (s, 3H, CH₃), 1.63–1.54 (m, 2H, CH₂), 1.52–1.33 (m, 2H, CH₂), 0.91 (d, *J* = 7.3 Hz, 3H, CH₃); ¹³C{¹H} NMR (67.8 MHz, CDCl₃) δ 137.6, 135.8, 129.1, 128.3, 35.9, 33.8, 31.9, 31.7, 22.0, 21.0, 13.7; IR (CHCl₃, NaCl cell, *v*_{max}, cm⁻¹) 2961 (C-H), 2930 (C-H), 1422 (C-H); Anal. Calcd for C₁₃H₂₀S (208.36): C, 74.94; H, 9.68. Found: C, 74.86; H, 9.81.

1-(1-Buthylthio)-2-(4-methoxyphenyl)ethane (3g). The title compound was obtained as a colorless oil (43.1 mg, 64%). ¹H NMR (270 MHz, CDCl₃) δ 7.13 (d, *J* = 8.9 Hz, 2H, Ar-H), 6.84 (d, *J* = 8.9 Hz, 2H, Ar-H), 3.78 (s, 3H, CH₃), 2.86–2.80 (m, 2H, CH₂), 2.76–2.69 (m, 2H, CH₂), 2.53 (t, *J* = 7.2 Hz, 2H, CH₂), 1.63–1.52 (m, 2H, CH₂), 1.47–1.33 (m, 2H, CH₂), 0.91 (d, *J* = 7.2 Hz, 3H, CH₃); ¹³C{¹H} NMR (67.8 MHz, CDCl₃) δ 158.1, 132.8, 129.4,

113.8, 55.2, 35.4, 33.9, 31.9, 31.7, 22.0, 13.7; IR (neat, NaCl cell, ν_{\max} , cm^{-1}) 2955 (C-H), 2871 (C-H), 1611 (C=C), 1512 (C=C), 1464 (C-H); Anal. Calcd for $\text{C}_{13}\text{H}_{20}\text{OS}$ (224.36): C, 69.59; H, 8.99. Found: C, 69.33; H, 8.89.

1-(1-Buthylthio)-2-(4-fluorophenyl)ethane (3h). The title compound was obtained as a colorless oil (40.9 mg, 64%). ^1H NMR (270 MHz, CDCl_3) δ 7.19–7.14 (m, 2H, Ar-H), 7.01–6.95 (m, 2H, Ar-H), 2.88–2.83 (m, 2H, CH_2), 2.77–2.71 (m, 2H, CH_2), 2.523 (t, $J = 7.4$ Hz, 2H, CH_2), 1.62–1.54 (m, 2H, CH_2), 1.51–1.33 (m, 2H, CH_2), 0.91 (d, $J = 7.2$ Hz, 3H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.8 MHz, CDCl_3) δ 161.5 (d, $^1J_{\text{C-F}} = 243.4$ Hz), 136.3 (d, $^4J_{\text{C-F}} = 3.4$ Hz), 129.8 (d, $^3J_{\text{C-F}} = 7.5$ Hz), 115.2 (d, $^2J_{\text{C-F}} = 21.0$ Hz), 35.5, 22.7 (d, $J_{\text{C-F}} = 1.4$ Hz), 32.0, 31.7, 21.9, 13.7; IR (neat, NaCl cell, ν_{\max} , cm^{-1}) 2957 (C-H), 2930 (C-H), 1601 (C=C), 1510 (C=C), 1465 (C-H); Anal. Calcd for $\text{C}_{12}\text{H}_{17}\text{FS}$ (212.33): C, 67.88; H, 8.07. Found: C, 67.99; H, 8.15.

1-(1-Buthylthio)-2-(4-bromophenyl)ethane (3i). The title compound was obtained as a colorless oil (58.9 mg, 72%). ^1H NMR (270 MHz, CDCl_3) δ 7.26 (d, $J = 8.2$ Hz, 2H, Ar-H), 7.13 (d, $J = 8.2$ Hz, 2H, Ar-H), 2.88–2.82 (m, 2H, CH_2), 2.77–2.71 (m, 2H, CH_2), 2.52 (t, $J = 7.4$ Hz, 2H, CH_2), 1.62–1.51 (m, 2H, CH_2), 1.44–1.36 (m, 2H, CH_2), 0.91 (d, $J = 7.2$ Hz, 3H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.8 MHz, CDCl_3) δ 139.1, 129.8, 128.5, 35.6, 33.5, 32.0, 31.7, 22.0, 13.7; IR (CHCl_3 , NaCl cell, ν_{\max} , cm^{-1}) 3019 (C-H), 2961 (C-H), 1600 (C=C), 1492 (C-H); Anal. Calcd for $\text{C}_{12}\text{H}_{17}\text{S}$ (273.23): C, 52.75; H, 6.27. Found: C, 52.94; H, 6.22.

1-(1-Buthylthio)-3-phenylpropane (3j). The title compound was obtained as a colorless oil (15.7 mg, 25%). ^1H NMR (270 MHz, CDCl_3) δ 7.31–7.26 (m, 2H, Ar-H), 7.20–7.17 (m, 3H, Ar-H), 2.72 (t, $J = 7.6$ Hz, 2H, CH), 2.55–2.48 (m, 4H, CH_2), 1.96–1.85 (m, 2H, CH_2), 1.60–1.49 (m, 2H, CH_2), 1.46–1.33 (m, 2H, CH_2), 0.91 (d, $J = 7.2$ Hz, 3H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.8 MHz, CDCl_3) δ 141.6, 128.5, 128.3, 125.9, 34.8, 31.8, 31.5, 31.2, 22.0, 13.7; IR (CHCl_3 , NaCl cell, ν_{\max} , cm^{-1}) 3019 (C-H), 2960 (C-H), 1603 (C=C), 1512 (C=C), 1454 (C-H); Anal. Calcd for $\text{C}_{13}\text{H}_{20}\text{S}$ (208.13): C, 74.94; H, 9.68. Found: C, 74.74; H, 9.65.

1-(1-Buthylthio)indane (3k). The title compound was obtained as a colorless oil (19.0 mg, 31%). ^1H NMR (270 MHz, CDCl_3) δ 7.21–7.13 (m, 4H, Ar-H), 3.69–3.58 (m, 1H, CH), 3.36–3.27 (m, 2H, CH_2), 2.98–2.89 (m, 2H, CH_2), 2.61 (t, $J = 7.4$ Hz, 2H, CH), 1.67–1.55 (m, 2H, CH_2), 1.50–1.36 (m, 2H, CH_2), 0.93 (d, $J = 7.2$ Hz, 3H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.8 MHz, CDCl_3) δ 141.9, 126.5, 124.3, 43.3, 40.7, 31.9, 31.3, 22.1, 13.7; IR (CHCl_3 , NaCl cell, ν_{\max} , cm^{-1}) 2930 (C-H), 2873 (C-H), 1460 (C-H), 1273 (SC-H); Anal. Calcd for $\text{C}_{13}\text{H}_{18}\text{S}$ (206.35): C, 75.67; H, 8.79. Found: C, 75.63; H, 8.82.

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Supplementary Material

Copies of the ^1H NMR and ^{13}C NMR Spectra are provided. This material is available free of charge via the Internet at <http://xxxxxx>

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