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

Nobukazu Taniguchi

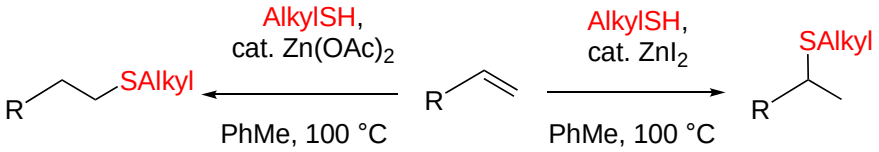
Department of Chemistry, Fukushima Medical University, Fukushima 960-1295, Japan
Email: taniguti@fmu.ac.jp

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

Received 12-09-2020 **Accepted** 02-02-2021 **Published on line** 02-06-2021

Abstract

Zn-catalyzed reactions of alkenes with alkyl thiols could afford alkyl sulfides regioselectively. When the ZnI_2-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

Introduction

Transition metal-catalyzed carbon–sulfur bond formations have been exploited by numerous researchers to date; such procedures are widely utilized in organic chemistry.[1-5] Among them, hydrothiolation of alkenes has been well investigated.[6-12] The reaction usually produces two regioisomers. Development of regioselective reactions is greatly to be desired.

As a general rule, arenethiols readily generate thiyl radicals in the presence of oxygen or light; however their formation from alkyl thiols is very slow (Figure 1).[13] To generate alkyl thiyl radicals, irradiation using UV or blue light in the presence of metal catalysts is required. Various procedures have been successful to date.[14-16] For example, the Ru-catalyzed reaction performed under irradiation with blue light affords *anti*-Markovnikov-type products in excellent yields.[14,15] Contrarily, alkyl thiols work as anion sources without light irradiation.[17-22] For instance, In- or Mont K10-catalyzed reactions of alkenes with alkyl thiols afford Markovnikov-type products regioselectively (Scheme 1).[17,22]

Recently, it was reported that the ZnI_2-catalyzed reactions of aryl alkenes with thiols produces Markovnikov-type sulfides regioselectively in the presence of 4-toluenesulfonic acid.[23] This method cannot afford radical reaction products, whereas zinc salts have the ability to promote radical reactions[24,25] thus, various zinc salts were screened. Fortunately, on one hand, it was found that ZnI_2-catalyzed reactions using alkyl thiols afforded Markovnikov-type products in the absence of 4-toluenesulfonic acid. On the other hand, $Zn(OAc)_2$-catalyzed reactions produced *anti*-Markovnikov-type sulfides. In this paper, these methods are described.

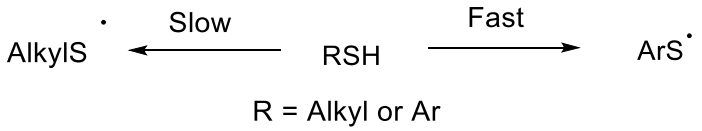
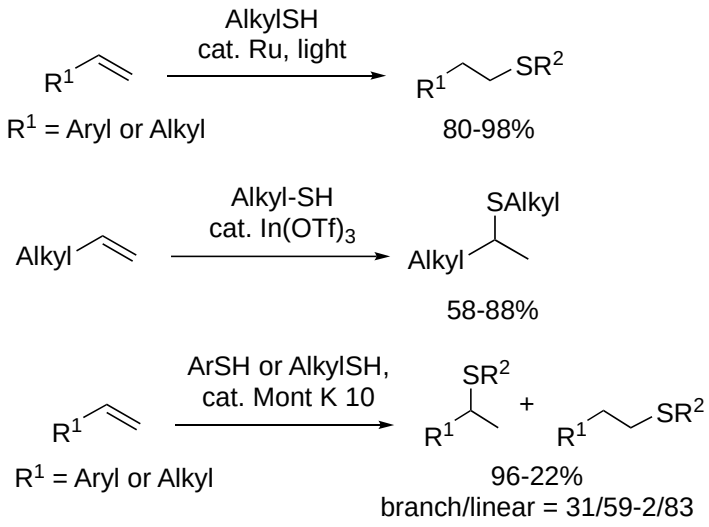


Figure 1. The formation of thiyl radicals.

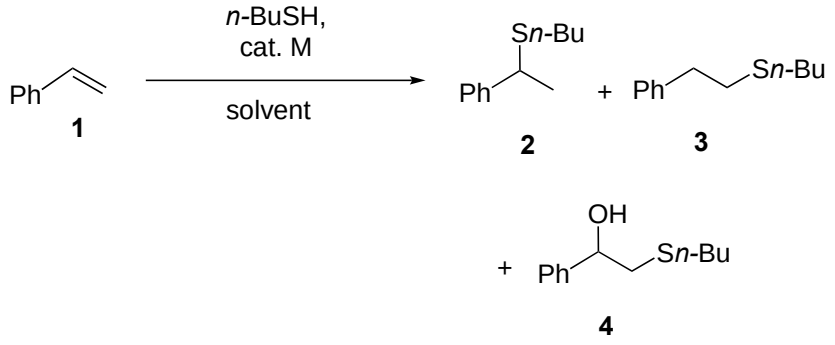


Scheme 1. Reported reactions of alkenes with alkyl thiols.

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).

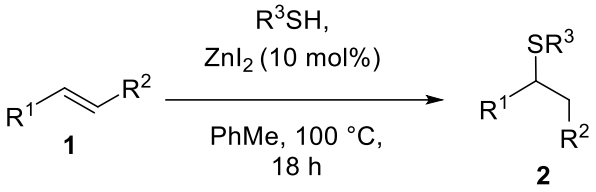
Table 1. Investigation of suitable conditions[a]



Entry	solv.	M	ºC	**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

[a]Reaction conditions: A mixture of **1** (0.3 mmol), *n*-BuSH (0.33 mmol) and cat. M (10 mol%) in solvent (0.3 mL). [b]Determined by ^{1}H NMR. [c]Isolated yield after silica gel chromatography. [d]The reaction was performed for 36 h.

Table 2. Zn-catalyzed hydrothiolation of alkenes[a]



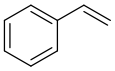
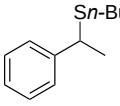
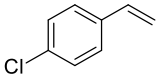
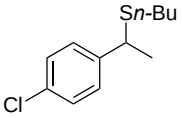
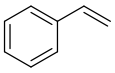
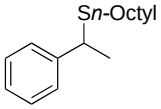
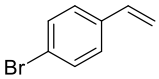
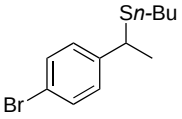
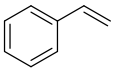
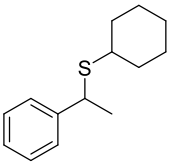
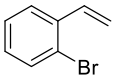
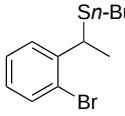
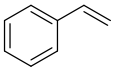
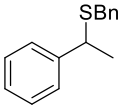
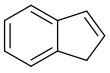
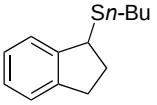
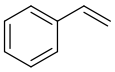
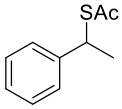
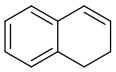
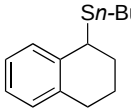
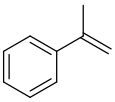
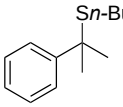
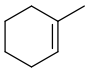
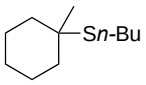
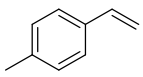
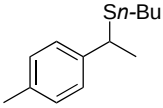
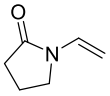
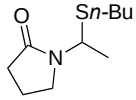
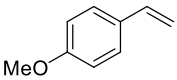
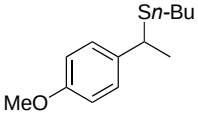
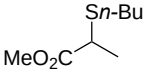
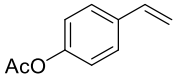
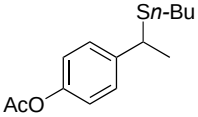
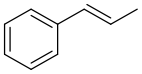
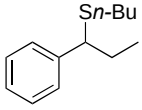
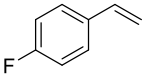
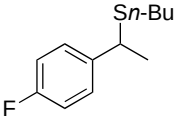
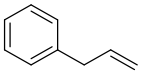
Entry	1	2		2 (%)[b]	Entry	1	2		2 (%)[b]
1			**2a**	79	11			**2k**	74
2			**2b**	66	12			**2l**	81
3			**2c**	83	13			**2m**	69
4			**2d**	78	14			**2n**	74
5			**2e**	7	15			**2o**	80
6			**2f**	90	16			**2p**	86
7			**2g**	88	17			**2q**	81
8			**2h**	75	18			**2r**	0[d]
9[c]			**2i**	62	19			**2s**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

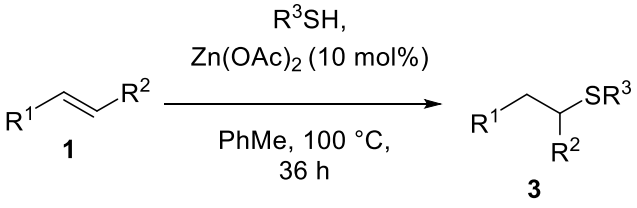
Table 2. Continued

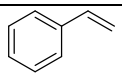
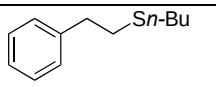
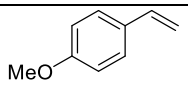
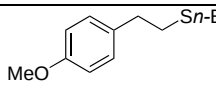
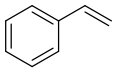
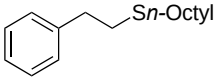
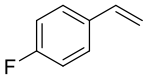
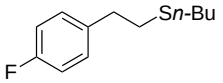
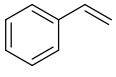
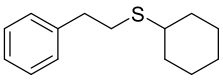
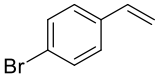
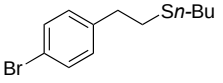
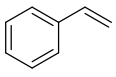
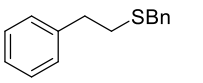
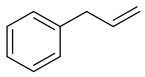
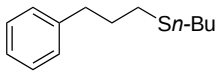
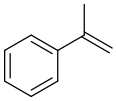
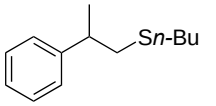
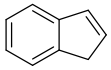
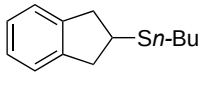
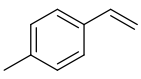
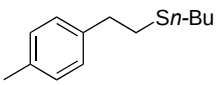
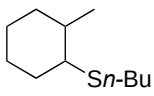
[a]Reaction conditions: A mixture of **1** (0.3 mmol), R^3SH (0.33 mmol) and ZnI_2 (10 mol%) in PhMe (0.15 mL) was heated at 100 ºC. [b]Isolated yield after silica gel chromatography. [c]The reaction was performed for 42 h. [d]Methyl 3-(1-butylthio)propionate was obtained in 90% yield.

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).

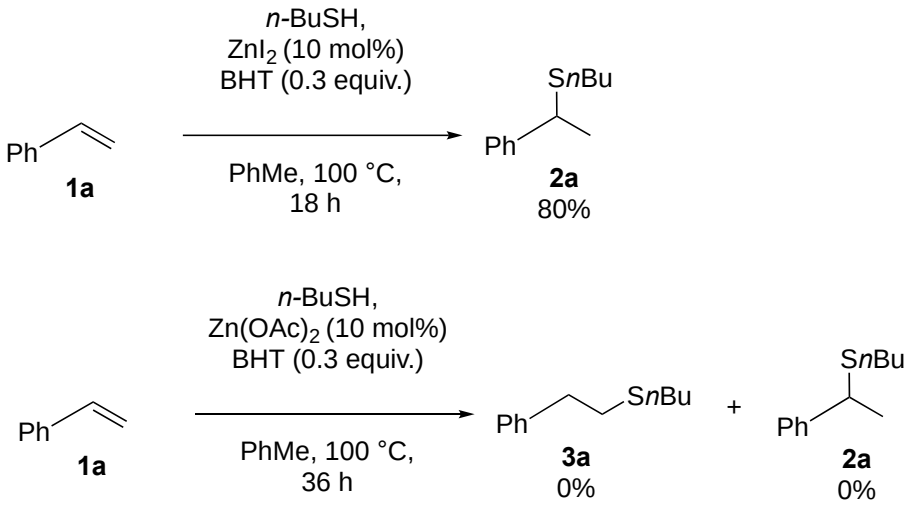
Table 3. Zn-catalyzed hydrothiolation of alkenes[a]



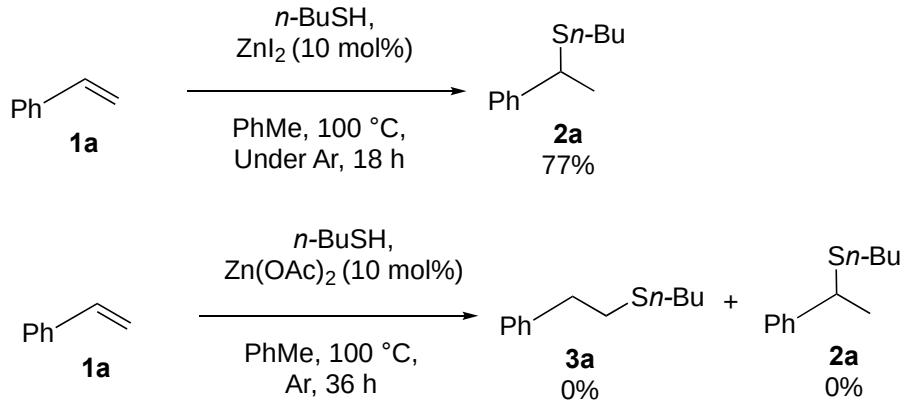
Entry	1	3		3 (%)[b]	Entry	1	3		3 (%)[b]
1			**3a**	87	7			**3g**	64
2			**3b**	81	8			**3h**	64
3			**3c**	79	9			**3i**	72
4			**3d**	78	10			**3j**	15
5			**3e**	67	11			**3k**	31
6			**3f**	81	12			**3l**	trace

[a]Reaction conditions: A mixture of **1** (0.3 mmol), R^3SH (0.33 mmol) and $Zn(OAc)_2$ (10 mol%) in PhMe (0.15 mL) was heated at 100 ºC. [b]Isolated yield after silica gel chromatography. [c]Determined 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 ZnI_2-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 ZnI_2 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 ZnI_2-catalyzed reaction, after the reaction of ZnI_2 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.

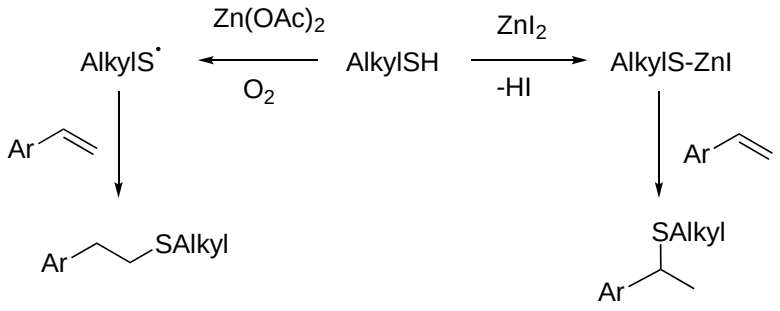


Figure 2. A plausible reaction mechanism.

Conclusions

In conclusion, the ZnI_2-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. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL EX-270 spectrometer (270 MHz for ^{1}H, 67.8 MHz for ^{13}C). Chemical shifts are reported in δ ppm referenced to an internal tetramethylsilane standard for ^{1}H NMR and chloroform-d (δ 77.0) for ^{13}C 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 $PhCH_3$ (0.3 mL), ZnI_2 (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 Et_2O, the solution was washed with H_2O and saturated aq NaCl and dried over anhydrous $MgSO_4$. Chromatography on silica gel (hexane) gave 1-(1-butylthio)-1-phenylethane **2a** (45.9 mg, 79%)**:** Colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.36–7.20 (m, 5H, Ar-H), 3.94 (q, *J* = 7.0 Hz, 1H, CH), 2.34–2.24 (m, 2H, CH_2), 1.56 (d, *J* = 7.0 Hz, 3H, CH_3), 1.53–1.38 (m, 2H, CH_2), 1.38–1.27 (m, 2H, CH_2), 0.84 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C{^{1}H} NMR (67.8 MHz, $CDCl_3$) 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, ν_{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 $C_{12}H_{18}S$ (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%).^{1}H NMR (270 MHz, $CDCl_3$) δ 7.36–7.19 (m, 5H, Ar-H), 3.94 (q, *J* = 7.0 Hz, 1H, CH), 2.38–2.21 (m, 2H, CH_2), 1.57 (d, *J* = 7.0 Hz, 3H, CH_3), 1.48–1.43 (m, 2H, CH_2), 1.31–1.22 (m, 10H, CH_2), 0.87 (t, *J* = 6.8 Hz, 3H, CH_3); ^{13}C{^{1}H} NMR (67.8 MHz, $CDCl_3$) 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 $C_{16}H_{26}S$ (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%).^{1}H 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); $^{13}C\{^1H\}$ 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 $C_{14}H_{20}S$ (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%).^{1}H 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); $^{13}C\{^1H\}$ 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 $C_{16}H_{16}S$ (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%). ^{1}H 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); $^{13}C\{^1H\}$ 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 $C_{13}H_{20}S$ (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%). ^{1}H 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); $^{13}C\{^1H\}$ 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 $C_{13}H_{20}S$ (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%). ^{1}H 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); $^{13}C\{^1H\}$ 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 $C_{13}H_{20}OS$ (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%). ^{1}H 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); $^{13}C\{^1H\}$ 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 $C_{14}H_{20}OS$ (252.37): C, 66.63; H, 7.99. Found: C, 66.61; H, 7.97.

1-(1-Butylthio)-1-(4-fuluorobenzene)ethane (**2j**). The title compound was obtained as a colorless oil (50.5 mg, 79%). ^{1}H 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); $^{13}C\{^1H\}$ NMR (67.8 MHz, $CDCl_3$) δ = 161.7 (d, $^1J_{C-F}$ = 244.8 Hz), 139.7 (d, $^4J_{C-F}$ = 3.4 Hz), 128.7 (d, $^3J_{C-F}$ = 8.8 Hz), 115.2 (d, $^2J_{C-F}$ = 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 $C_{12}H_{17}FS$ (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%). ^{1}H 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}C{^{1}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 $C_{12}H_{17}ClS$ (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%). ^{1}H 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}C{^{1}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 $C_{12}H_{17}BrS$ (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%). ^{1}H 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}C{^{1}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 $C_{12}H_{17}BrS$ (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%). ^{1}H 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}C{^{1}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 $C_{13}H_{18}S$ (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%). ^{1}H 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}C{^{1}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 $C_{14}H_{20}S$ (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%). ^{1}H 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– 137 (m, 12H, CH_2), 1.31 (s, 3H, CH_3), 0.91 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C{^{1}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 $C_{11}H_{22}S$ (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%). ^{1}H 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}C{^{1}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 $C_{10}H_{19}NOS$ (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 $PhCH_3$ (0.3 mL), $Zn(OAc)_2$ (5.5 mg, 0.03 mmol) was added, and the mixture was stirred at 100 ºC for 36 h in the presence of air in 15 mL glass test tube with plastic screw cap. After the residue was dissolved in Et_2O, the solution was washed with H_2O and saturated aq NaCl and dried over anhydrous $MgSO_4$. Chromatography on silica gel (hexane) gave 1-(1-butylthio)-2-phenylethane **3a** (50.9 mg, 87%)**:** Colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.32–7.19 (m, 5H, Ar-H), 2.92–2.85 (m, 2H, CH_2), 2.80–2.73 (m, 2H, CH_2), 2.53 (t, *J* = 7.4 Hz, 2H, CH_2), 1.63–1.52 (m, 2H, CH_2), 1.47–1.33 (m, 2H, CH_2), 0.91 (t, *J* = 7.4 Hz, 3H, CH_3); ^{13}C{^{1}H} NMR (67.8 MHz, $CDCl_3$) 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, ν_{max}, cm^{-1}) 2955 (C-H), 2871 (C-H), 1604 (C=C), 1496 (C-H), 1453 (C-H), 1273 (SC-H); Anal. Calcd for $C_{12}H_{18}S$ (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%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.32–7.19 (m, 5H, Ar-H), 2.91–2.85 (m, 2H, CH_2), 2.80–2.73 (m, 2H, CH_2), 2.53 (t, *J* = 7.4 Hz, 2H, CH_2), 1.63–1.52 (m, 2H, CH_2), 1.40–1.27 (m, 10H, CH_2), 0.88 (t, *J* = 6.6 Hz, 3H, CH_3); ^{13}C{^{1}H} NMR (67.8 MHz, $CDCl_3$) 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, ν_{max}, cm^{-1}) 2925 (C-H), 2854 (C-H), 1604 (C=C), 1496 (C-H), 1454 (C-H); Anal. Calcd for $C_{16}H_{26}S$ (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%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.32–7.18 (m, 5H, Ar-H), 2.91–2.75 (m, 4H, CH_2), 2.65–2.61 (m, 1H, CH), 1.99–1.95 (m, 2H, CH_2), 1.77–1.75 (m, 2H, CH_2), 1.65–1.56 (m, 1H), 1.31–1.23 (m, 5H, CH_2); ^{13}C{^{1}H} NMR (67.8 MHz, $CDCl_3$) δ 140.8, 128.4, 126.3, 43.7, 36.7, 33.7, 31.7, 26.1, 25.8; IR ($CHCl_3$, NaCl cell, ν_{max}, cm^{-1}) 2932 (C-H), 2854 (C-H), 1464 (C-H), 1449 (C-H), 1264 (SC-H); Anal. Calcd for $C_{14}H_{20}S$ (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%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.32–7.13 (m, 10H, Ar-H), 3.71 (s, 2H, CH_2), 2.86–2.80 (m, 2H, CH_2), 2.68–2.62 (m, 2H, CH_2); ^{13}C{^{1}H} NMR (67.8 MHz, $CDCl_3$) 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, ν_{max}, cm^{-1}) 3061 (C-H), 3026 (C-H), 2915 (C-H), 1602 (C=C), 1494 (C-H), 1453 (C-H); Anal. Calcd for $C_{15}H_{16}S$ (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%). ^{1}H NMR (270 MHz, $CDCl_3$) 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, CH_2), 2.67–2.64 (m, 1H, CH_2), 2.44 (t, *J* = 7.2 Hz, 2H, CH_2), 1.58–1.47 (m, 2H, CH_2), 1.43–1.30 (m, 5H, CH_2), 0.89 (d, *J* = 7.2 Hz, 3H, CH_3); ^{13}C{^{1}H} NMR (67.8 MHz, $CDCl_3$) 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, ν_{max}, cm^{-1}) 2859 (C-H), 1602 (C=C), 1493 (C-H), 1452 (C-H), 1375 (C-H); Anal. Calcd for $C_{13}H_{20}S$ (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%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.13–7.07 (m, 4H, Ar-H), 2.88–2.81 (m, 2H, CH_2), 2.77–2.71 (m, 2H, CH_2), 2.53 (t, *J* = 7.4 Hz, 2H, CH_2), 2.32 (s, 3H, CH_3), 1.63–1.54 (m, 2H, CH_2), 1.52–1.33 (m, 2H, CH_2), 0.91 (d, *J* = 7.3 Hz, 3H, CH_3); ^{13}C{^{1}H} NMR (67.8 MHz, $CDCl_3$) δ 137.6, 135.8, 129.1, 128.3, 35.9, 33.8, 31.9, 31.7, 22.0, 21.0, 13.7; IR ($CHCl_3$, NaCl cell, ν_{max}, cm^{-1}) 2961 (C-H), 2930 (C-H), 1422 (C-H); Anal. Calcd for $C_{13}H_{20}S$ (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%). ^{1}H NMR (270 MHz, $CDCl_3$) 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, CH_3), 2.86–2.80 (m, 2H, CH_2), 2.76–2.69 (m, 2H, CH_2), 2.53 (t, *J* = 7.2 Hz, 2H, CH_2), 1.63–1.52 (m, 2H, CH_2), 1.47–1.33 (m, 2H, CH_2), 0.91 (d, *J* = 7.2 Hz, 3H, CH_3); ^{13}C{^{1}H} NMR (67.8 MHz, $CDCl_3$) 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 $C_{13}H_{20}OS$ (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%). ^{1}H 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); $^{13}C\{^1H\}$ NMR (67.8 MHz, $CDCl_3$) δ 161.5 (d, $^1J_{C-F}$ = 243.4 Hz), 136.3 (d, $^4J_{C-F}$ = 3.4 Hz), 129.8 (d, $^3J_{C-F}$ = 7.5 Hz), 115.2 (d, $^2J_{C-F}$ = 21.0 Hz), 35.5, 22.7 (d, J_{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 $C_{12}H_{17}FS$ (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%). ^{1}H 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); $^{13}C\{^1H\}$ 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 $C_{12}H_{17}S$ (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%). ^{1}H 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); $^{13}C\{^1H\}$ 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 $C_{13}H_{20}S$ (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%). ^{1}H 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); $^{13}C\{^1H\}$ 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 $C_{13}H_{18}S$ (206.35): C, 75.67; H, 8.79. Found: C, 75.63; H, 8.82.

Acknowledgements

This work was supported by The Foundation for Japanese Chemical Research and Daicel Corporation

Supplementary Material

Copies of the ^{1}H 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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