Tetrahedron 67 (2011) 10212–10215

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Ruthenium-catalyzed reaction of alkenyl triflates with zinc thiolates

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ARTICLE INFO

Article history:
Received 6 September 2011
Received in revised form 30 September 2011
Accepted 30 September 2011
Available online 6 October 2011

Keywords:
Ruthenium catalyst
Alkenyl triflates
Thiolation
Alkenyl sulfides
Zinc thiolates

ABSTRACT

A ruthenium complex coordinated with 3,4,7,8-tetramethyl-1,10-phenanthroline catalyzed the reaction of alkenyl triflates with zinc dithiolates to give alkenyl sulfides.

1. Introduction

During the past few decades, a wide variety of ruthenium-catalyzed reactions, such as hydrogenation, oxidation, olefin metathesis, and C–H bond functionalization have been developed.[1] Most of these reactions involve transformation of C–C unsaturated bonds and/or C–H bonds. In contrast, activation of C(sp^2)–X bonds in aryl and alkenyl halides under ruthenium catalysis is much less common than that under palladium or nickel catalysis.[2] The pioneering work on catalytic activation of C(sp^2)–X bonds by a ruthenium complex is the coupling reaction of β-bromostyrene with Grignard reagents or organolithium compounds reported by Murahashi and co-workers in 1979.[3] After a long while, the coupling reaction of aryl or alkenyl (pseudo)halides with arenes bearing a directing group was extensively studied.[4] Only a few reports are available for other types of substitution reactions, such as the Mizoroki–Heck reaction, Suzuki–Miyaura coupling, and Sonogashira coupling reactions.[5] On the other hand, we have recently reported the ruthenium-catalyzed transformation of alkenyl triflates to alkenyl halides using lithium halides as the first example on the ruthenium-catalyzed reaction of aryl or alkenyl (pseudo)halides with heteroatom nucleophiles.[6,7] Here we report the ruthenium-catalyzed reaction of alkenyl triflates or halides with zinc thiolates to give alkenyl sulfides,[8] which are important moieties of synthetic precursors[9] and biologically active compounds.[10]

2. Results and discussion

A ruthenium complex coordinated with 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4-phen) was found to catalyze the thiolation of alkenyl triflates. Thus, in the presence of a ruthenium complex prepared from $Ru(acac)_3$ (3 mol %) and Me_4-phen (3 mol %), 1-cyclohexenyl triflate (**1a**: 1 equiv) was treated with NaSPh (**2m**: 1.2 equiv) in 1,3-dimethyl-2-imidazolidinone (DMI) at 120 °C for 24 h[11] to give 46% yield of 1-cyclohexenyl phenyl sulfide (**3am**) (entry 1 of Table 1). Use of PhSSPh (**4m**: 1.2 equiv) as a phenylthio source in combination with zinc powder (1.35 equiv) improved the yield to 78% (entry 2). A 1:1 mixture of Zn and **4m** is known to be transformed to $Zn(SPh)_2$,[12] which is likely to react with the ruthenium complex. Only a trace amount of **3am** was obtained by use of $Zn(SPh)_2$ prepared beforehand in a manner that zinc metal does not remain (entry 3), showing that the active species is a low valent ruthenium complex generated by reduction of $Ru(acac)_3$ by zinc.[13] Use of $[RuCl_2(p\text{-cymene})]_2$ instead of $Ru(acac)_3$ gave **3am** in a higher yield (entry 4). Use of a reduced amount (1.0 equiv) of **4m** gave a comparable yield of **3am** (entry 5). Thioether **3am** was obtained in an amount larger than that of **4m** used (entry 6), showing that both of the two thiolate moieties of $Zn(SPh)_2$ have potential ability to participate in the thiolation. In order to restore the nucleophilicity of the PhS moiety diminished upon transformation to PhSZnOTf through the first transfer of PhS, NaOAc was added to form more nucleophilic PhSZnOAc and the yield was increased to 81% even in use of 0.6 equiv of **4m** (entry 7). Phenylthiol also was used as a phenylthio source in combination with Et_2Zn (entry 8). Non-substituted 1,10-phenanthroline (phen) and 2,2′-bipyridyl (bpy)

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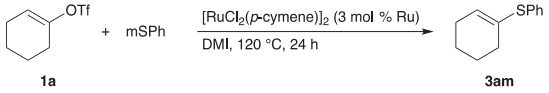
doi:10.1016/j.tet.2011.09.145

Table 1
Ruthenium-catalyzed phenylthiolation of 1-cyclohexenyl triflate[a]



1a 3am

Entry	Ligand (mol %)	Phenylthio source and other reagents (equiv)	Yield[b] (%)
1[c]	Me_4-phen (3)	NaSPh (**2m**: 1.2)	46
2[c]	Me_4-phen (3)	PhSSPh (**4m**: 1.2), Zn (1.35)	78
3[c,d]	Me_4-phen (3)	PhSSPh (**4m**: 1.2), Zn (1.0)	4
4	Me_4-phen (3)	PhSSPh (**4m**: 1.2), Zn (1.35)	94
5	Me_4-phen (3)	PhSSPh (**4m**: 1.0), Zn (1.15)	93
6	Me_4-phen (3)	PhSSPh (**4m**: 0.6), Zn (0.75)	68
7	Me_4-phen (3)	PhSSPh (**4m**: 0.6), Zn (0.75), NaOAc (1.2)	81
8	Me_4-phen (3)	PhSH (2.0), Et_2Zn (1.1)	87
9	phen (3)	PhSSPh (**4m**: 1.0), Zn (1.15)	58
10	bpy (3)	PhSSPh (**4m**: 1.0), Zn (1.15)	58
11	PPh_3 (6)	PhSSPh (**4m**: 1.0), Zn (1.15)	7
12	dppp (3)	PhSSPh (**4m**: 1.0), Zn (1.15)	5
13[e]	Me_4-phen (3)	PhSSPh (**4m**: 1.0), Zn (1.15)	86
14[f]	Me_4-phen (3)	PhSSPh (**4m**: 1.0), Zn (1.15)	53
15[g]	Me_4-phen (3)	PhSSPh (**4m**: 1.0), Zn (1.15)	1
16[h]	Me_4-phen (3)	PhSSPh (**4m**: 1.0), Zn (1.15)	23

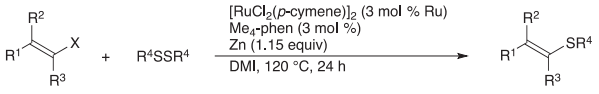
[a] The reaction was carried out in DMI (1.0 mL) at 120 °C for 24 h under a nitrogen atmosphere using 1-cyclohexenyl triflate (**1a**: 0.25 mmol), a phenylthio source and other reagents in the presence of $[RuCl_2(p\text{-cymene})]_2$ (3.8 μmol) and a ligand.
[b] Determined by GC.
[c] $Ru(acac)_3$ (7.5 μmol) was used instead of $[RuCl_2(p\text{-cymene})]_2$.
[d] PhSSPh and Zn was stirred at 120 °C for 24 h in DMI before addition of $Ru(acac)_3$ and **1a**.
[e] NMP was used as a solvent.
[f] DMF was used as a solvent.
[g] DMSO was used as a solvent.
[h] 1,4-Dioxane was used as a solvent.

were less effective as ligands than Me_4-phen, and only a trace amount of **3am** was obtained by use of a phosphine ligand (entries 9–12). *N*-Methylpyrrolidone (NMP) also was effective as a solvent, whereas the reaction was sluggish in DMF, DMSO, or 1,4-dioxane (entries 13–16).

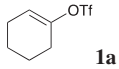
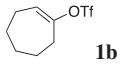
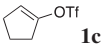
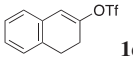
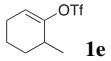
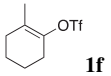
Various alkenyl triflates and iodides were thiolated under the reaction conditions of entry 5 of Table 1. In addition to diphenyl disulfide (**4m**), methoxy- or bromo-substituted ones reacted with 1-cyclohexenyl triflate (**1a**) in high yields (entries 1–3 of Table 2). The reaction of primary and secondary alkyl disulfides gave the corresponding alkyl sulfides, whereas no thiolation took place with ^{t}BuSS^{t}Bu (**4r**) (entries 4–6). The thiolation reaction is applicable to various cyclic alkenyl triflates (entries 7–11), which have advantages over cyclic alkenyl halides in facility of preparation, in particular in regioselective synthesis from unsymmetrical ketones.[14] For example, methylcyclohexenyl trifltates **1e** and **1f** were prepared regioselectively from the same ketone, and were converted to the corresponding alkenyl sulfides without migration of the double bond (entries 10 and 11).[8b] For trisubstituted alkenyl triflate **1f**, 4,7-dimethoxy-1,10-phenanthroline [$(MeO)_2$-phen] as a ligand was effective. The reaction of acyclic alkenyl triflates and iodides took place in high yields (entries 12–15). Although 1-octen-2-yl triflate was unstable under the reaction conditions,[15] the corresponding iodide (**1g**) underwent the coupling without decomposition (entry 12). Both *E*- and *Z*-isomers of 1-octen-1-yl iodide (**1i**) reacted with **4m** to give a mixture of stereoisomers of the same *E*/*Z* ratio (entries 14 and 15).

To clarify when the *E*/*Z* isomerization takes place, stereochemical stabilities of an alkenyl triflate and the corresponding alkenyl sulfide were examined (Scheme 1). Analysis of a reaction mixture at the middle stage showed that the *E*/*Z* ratio of the starting alkenyl iodide (**1i**) was conserved during the thiolation. Under the conditions where thiolation of **1h** proceeds, alkenyl sulfide **3im** was

Table 2
Ruthenium-catalyzed thiolation of alkenyl electrophiles with zinc thiolates[a]

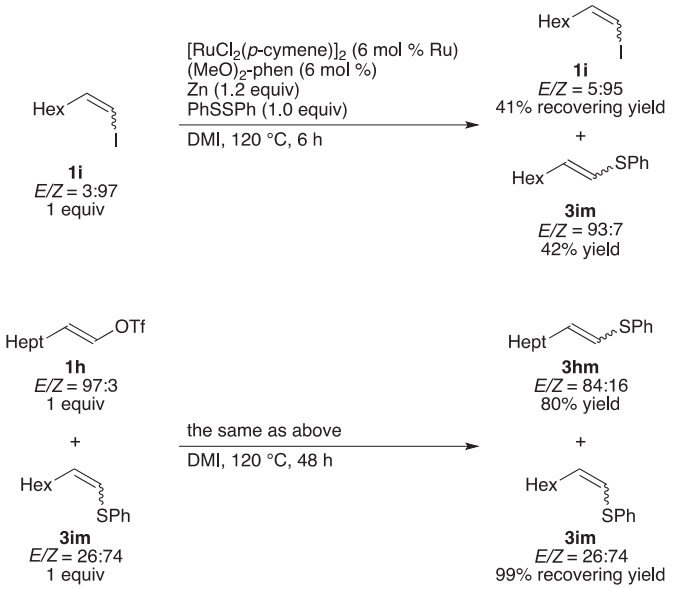


1 (1 equiv, X = OTf, I) 4 (1 equiv) 3

Entry	1	R^4	Yield[b] (%)	Product
1	 **1a**	Ph (**4m**)	93	**3am**
2	**1a**	4-$MeOC_6H_4$ (**4n**)	95	**3an**
3[c,d]	**1a**	4-BrC_6H_4 (**4o**)	77	**3ao**
4	**1a**	Bu (**4p**)	68	**3ap**
5	**1a**	Cyclohexyl (**4q**)	85	**3aq**
6	**1a**	^{t}Bu (**4r**)	0	**3ar**
7	 **1b**	Ph (**4m**)	83	**3bm**
8[c]	 **1c**	Ph (**4m**)	78	**3cm**
9[d]	 **1d**	Ph (**4m**)	89	**3dm**
10[c,d]	 **1e** (**1e**/**1f** = 95:5)	Ph (**4m**)	80 (**3em**/**3fm**=98:2)	**3em**
11[c,e]	 **1f** (**1f**/**1e** = 94:6)	Ph (**4m**)	69 (**3fm**/**3em**=93:7)	**3fm**
12[d]	 [f] Hex **1g**	Ph (**4m**)	71[g]	**3gm**
13	Hept OTf **1h** (*E*/*Z* = 97:3)	Ph (**4m**)	82 (*E*/*Z*=86:14)	**3hm**
14[c,h]	Hex I **1i** (*E*/*Z* = 100:0)	Ph (**4m**)	84 (*E*/*Z*=92:8)	**3im**
15[c,h]	Hex I **1i** (*E*/*Z* = 3:97)	Ph (**4m**)	77 (*E*/*Z*=92:8)	**3im**

[a] The reaction was carried out in DMI (1.0 mL) at 120 °C for 24 h under a nitrogen atmosphere using an alkenyl triflate (**1**: 0.25 mmol), a disulfide (**4**: 0.25 mmol), and zinc powder (0.29 mg atom) in the presence of $[RuCl_2(p\text{-cymene})]_2$ (3.8 μmol) and Me_4-phen (7.5 μmol).
[b] Isolated yield.
[c] The reaction was carried out for 48 h.
[d] $[RuCl_2(p\text{-cymene})]_2$ (7.5 μmol), Me_4-phen (15 μmol), and Zn (0.30 mg atom) were used.
[e] The reaction was carried out at 140 °C using $[RuCl_2(p\text{-cymene})]_2$ (12.5 μmol), $(MeO)_2$-phen (25 μmol), and Zn (0.31 mg atom).
[f] Containing 13% of 2-iodo-2-octene.
[g] Containing 7% of 2-octen-2-yl phenyl sulfide.
[h] $[RuCl_2(p\text{-cymene})]_2$ (7.5 mmol), $(MeO)_2$-phen (15 μmol), and Zn (0.30 mg atom) were used.

configurationally stable. These results show that the isomerization takes place during transformation from alkenyl (pseudo)halides to sulfides, suggesting that the ruthenium-catalyzed thiolation proceeds through a different mechanism from that of palladium-catalyzed one, which consists of oxidative addition, transmetalation, and reductive elimination and thus proceeds with retention of stereochemistry.[8e]



Scheme 1.

In a competition reaction, alkenyl triflate **1h** was much more reactive than alkenyl iodide **1i** under the ruthenium catalysis (Scheme 2). Thus, 43% of **1h** and 14% of **1i** were consumed in the presence of $[RuCl_2(p\text{-cymene})]_2$ (6 mol % Ru) and Me_4-phen (6 mol %) in DMI at 120 °C for 30 min to give 33% of **3hm** and 5% of **3im**. In contrast, iodide **1i** showed fourfold reactivity compared with triflate **1h** in the presence of $Pd(PPh_3)_4$ (3 mol %). The opposite reactivity order also may be ascribed to the different mechanism. Although the reaction mechanism is unclear at present, the ruthenium-catalyzed reaction possibly proceeds via alkenyl radical or cation intermediates in a similar manner to the ruthenium-catalyzed transformation of alkenyl triflates to alkenyl halides.[6]

catalyst	conv.[a] 1h	conv.[a] 1i	yield (E/Z)[a] 3hm	yield (E/Z)[a] 3im
$[RuCl_2(p\text{-cymene})]_2$ (6 mol % Ru) Me_4-phen (6 mol %)	43%	14%	33% (93:7)	5% (92:8)
$Pd(PPh_3)_4$ (3 mol %)	14%	68%	13% (96:4)	57% (97:3)

[a]Determined by GC.

Scheme 2.

In conclusion, we have described the reaction of alkenyl triflates with zinc thiolates as a new entry of ruthenium-catalyzed reaction of sp^2-carbon electrophiles.

3. Experimental section

3.1. General

All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a nitrogen atmosphere. Nuclear magnetic resonance spectra were taken on a JEOL JNM LA500 (^1H, 500 MHz; ^{13}C, 125 MHz) spectrometer. High-resolution mass spectra (APCI) were obtained with a Bruker Daltonics microTOF-Q spectrometer. Unless otherwise noted, reagents were commercially available and used without further purification. 1,3-Dimethyl-2-imidazolidinone (DMI) was distilled from CaH_2. Alkenyl triflates and iodides were prepared according to the literature procedures.[14,16]

3.2. General procedure for ruthenium-catalyzed reaction of alkenyl electrophiles with zinc thiolates (Table 2)

To a mixture of $[RuCl_2(p\text{-cymene})]_2$ (2.3 mg, 3.8 μmol), 3,4,7,8-tetramethyl-1,10-phenanthroline (1.8 mg, 7.5 μmol), zinc powder (18.8 mg, 0.288 mg atom), a disulfide (0.25 mmol), and DMI (1.0 mL) placed in a flame-dried 20 mL Schlenk tube was added an alkenyl electrophile (0.25 mmol). After stirring at 120 °C for 24 h, the reaction mixture was extracted with diethyl ether (3×10 mL). The combined organic layer was washed with water (2×15 mL) and brine (15 mL), and dried over $MgSO_4$. After filtration and evaporation, the crude product was subjected to column chromatography on silica gel (hexane/NEt_3 97:3) or alumina (hexane) to give the corresponding product.

*3.2.1. 1-Cyclohexenyl phenyl sulfide (**3am**)*[8b]. A colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 1.58–1.72 (m, 4H), 2.12–2.20 (m, 4H), 6.06–6.10 (m, 1H), 7.19 (t, *J*=7.1 Hz, 1H), 7.26–7.34 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.8, 23.8, 26.9, 30.2, 126.4, 129.0, 130.3, 131.6, 132.9, 135.4.

*3.2.2. 1-Cyclohexenyl 4-methoxyphenyl sulfide (**3an**).* A colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 1.55–1.68 (m, 4H), 2.06–2.13 (m, 4H), 3.80 (s, 3H), 5.77–5.82 (m, 1H), 6.85 (d, *J*=8.9 Hz, 2H), 7.32 (d, *J*=8.9 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.0, 23.7, 26.7, 29.7, 55.4, 114.7, 124.7, 128.0, 133.5, 134.2, 159.3. HRMS (APCI) calcd for $C_{13}H_{17}OS$: $[M+H]^+$ 221.0995. Found *m*/*z* 221.1001.

*3.2.3. 4-Bromophenyl 1-cyclohexenyl sulfide (**3ao**).* A colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 1.58–1.72 (m, 4H), 2.08–2.20 (m, 4H), 6.09–6.13 (m, 1H), 7.16 (d, *J*=8.6 Hz, 2H), 7.39 (d, *J*=8.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.7, 23.8, 27.0, 30.1, 120.3, 131.0, 131.6, 132.1, 134.1, 134.9. HRMS (APCI) calcd for $C_{12}H_{13}BrS$: $[M]^+$, 267.9916. Found *m*/*z* 267.9913.

*3.2.4. Butyl 1-cyclohexenyl sulfide (**3ap**).* A colorless oil. H NMR (500 MHz, $CDCl_3$) δ 0.92 (t, *J*=7.4 Hz, 3H), 1.42 (sext, *J*=7.3 Hz, 2H), 1.52–1.63 (m, 4H), 1.65–1.72 (m, 2H), 2.05–2.17 (m, 4H), 2.65 (t, *J*=7.4 Hz, 2H), 5.59–5.64 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.8, 22.2, 22.3, 23.5, 26.5, 30.1, 30.6, 31.4, 123.1, 132.3. HRMS (APCI) calcd for $C_{10}H_{19}S$: $[M+H]^+$, 171.1202. Found *m*/*z* 171.1208.

*3.2.5. 1-Cyclohexenyl cyclohexyl sulfide (**3aq**)*[8b]. A colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ1.18–1.36 (m, 5H), 1.55–1.63 (m, 3H), 1.65–1.71 (m, 2H), 1.72–1.81 (m, 2H), 1.89–1.98 (m, 2H), 2.07–2.12 (m, 2H), 2.13–2.18 (m, 2H), 2.89–2.98 (m, 1H), 5.78–5.82 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.1, 23.7, 26.0, 26.2, 26.7, 30.9, 33.6, 42.8, 127.8, 131.3.

*3.2.6. 1-Cycloheptenyl phenyl sulfide (**3bm**).* A colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 1.50–1.58 (m, 4H), 1.72–1.77 (m, 2H), 2.17–2.23 (m, 2H), 2.32–2.38 (m, 2H), 6.16 (t, *J*=6.6 Hz, 1H), 7.20 (t, *J*=7.0 Hz, 1H), 7.26–7.35 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.9, 27.2, 29.5, 32.1, 35.5, 126.5, 129.0, 130.6, 135.8, 135.9, 137.4. HRMS (APCI) calcd for $C_{13}H_{17}S$: $[M+H]^+$, 205.1045. Found *m*/*z* 205.1047.

*3.2.7. 1-Cyclopentenyl phenyl sulfide (**3cm**).* A colorless oil. Contains 2% of PhSSPh. ^1H NMR (500 MHz, $CDCl_3$) δ 1.97 (quint, *J*=7.5 Hz, 2H), 2.37–2.45 (m, 4H), 5.71–5.75 (m, 1H), 7.24 (t, *J*=7.5 Hz, 1H), 7.31 (t, *J*=7.7 Hz, 2H), 7.39 (d, *J*=7.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$)

δ 23.9, 33.1, 35.9, 127.1, 129.0, 131.4, 131.5, 134.4, 135.9. HRMS (APCI) calcd for $C_{11}H_{13}S$: $[M+H]^+$, 177.0732. Found *m*/*z* 177.0729.

*3.2.8. 1,2-Dihydro-3-(phenylthio)naphthalene (**3dm**)*[17]. A colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.45 (t, *J*=8.0 Hz, 2H), 2.87 (t, *J*=8.0 Hz, 2H), 6.49 (s, 1H), 6.95 (d, *J*=7.0 Hz, 1H), 7.08–7.16 (m, 3H), 7.28–7.33 (t, *J*=7.3 Hz, 1H), 7.36 (t, *J*=7.5 Hz, 2H), 7.49 (d, *J*=8.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.0, 29.1, 125.8, 126.8, 127.10, 127.13, 127.5, 127.7, 129.3, 132.3, 133.6, 134.2, 134.4, 136.2.

*3.2.9. 6-Methyl-1-cyclohexenyl phenyl sulfide (**3em**)*[8b]. A colorless oil. Contains 2% of regioisomer (**3fm**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.14 (d, *J*=7.1 Hz, 3H), 1.50–1.83 (m, 4H), 2.09–2.23 (m, 2H), 2.26–2.30 (m, 1H), 6.06 (t, *J*=3.8 Hz, 1H), 7.19 (t, *J*=7.2 Hz, 1H), 7.29 (t, *J*=7.4 Hz, 2H), 7.33 (d, *J*=7.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.5, 20.2, 27.3, 31.4, 32.9, 126.2, 129.0, 130.1, 134.0, 136.2, 137.1.

*3.2.10. 2-Methyl-1-cyclohexenyl phenyl sulfide (**3fm**)*[8b]. A colorless oil. Contains 7% of regioisomer (**3em**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.60–1.71 (m, 4H), 1.96 (s, 3H), 2.12–2.24 (m, 4H), 7.13 (t, *J*=7.2 Hz, 1H), 7.20 (d, *J*=8.3 Hz, 2H), 7.25 (t, *J*=7.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.9, 23.0, 24.4, 32.1, 33.1, 123.3, 125.3, 128.2, 128.9, 137.0, 141.9.

*3.2.11. 1-Octen-2-yl phenyl sulfide (**3gm**).* A colorless oil. Contains 9% of 2-octen-2-yl phenyl sulfides. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89 (t, *J*=7.0 Hz, 3H), 1.20–1.34 (m, 6H), 1.50–1.59 (m, 2H), 2.22 (t, *J*=7.6 Hz, 2H), 4.87 (s, 1H), 5.14 (s, 1H), 7.28 (t, *J*=7.3 Hz, 1H), 7.33 (t, *J*=7.2 Hz, 2H), 7.44 (d, *J*=8.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.2, 22.7, 28.5, 28.7, 31.7, 36.7, 112.6, 127.8, 129.2, 133.4, 133.5, 146.3. HRMS (APCI) calcd for $C_{14}H_{21}S$: $[M+H]^+$, 221.1358. Found *m*/*z* 221.1352.

*3.2.12. 1-Nonen-1-yl phenyl sulfide (**3hm**).* A colorless oil. *E*/*Z*=87/13. The italicized peaks could not be assigned to each isomer. The peaks in ^{13}C NMR were characterized by a comparison of ^{13}C NMR spectra between a mixture of stereoisomers in 87/13 (*E*/*Z*) ratio and that in 52/48 ratio, which was obtained through isomerization on silica gel. ^{1}H NMR (500 MHz, $CDCl_3$) δ *0.90* (*t*, *J*=*6.9* Hz, *3H*), *1.24–1.37* (*m*, *8H*), *1.38–1.48* (*m*, *2H*), 2.17/2.26 (q, *J*=7.0/7.4 Hz, 2H), 6.00/5.83 (dt, *J*=15.0, 7.0/9.3, 7.4 Hz, 1H), 6.14/6.19 (d, *J*=15.0/9.3 Hz, 1H), *7.18* (*t*, *J*=*6.9* Hz, *1H*), *7.26–7.36* (*m*, *4H*). ^{13}C NMR (125 MHz, $CDCl_3$) ***E*-3hm**: δ 14.2, 22.8, 29.16, 29.21, 29.24, 31.97, 33.2, 120.8, 126.1, 128.5, 129.0, 136.9, 138.0. ***Z*-3hm**: δ 14.2, 22.8, 29.19, 29.28, 29.34, 31.99, 33.2, 122.8, 126.2, 128.9, 129.1, 133.9, 136.7. HRMS (APCI) calcd for $C_{15}H_{23}S$: $[M+H]^+$, 235.1515. Found *m*/*z* 235.1519.

*3.2.13. 1-Octen-1-yl phenyl sulfide (**3im**)*[16b]. A colorless oil. *E*/*Z*=92/8. The italicized peaks could not be assigned to each isomer. ^{1}H NMR (500 MHz, $CDCl_3$) δ *0.90* (*t*, *J*=*6.8* Hz, *3H*), *1.24–1.33* (*m*, *6H*), *1.34–1.47* (*m*, *2H*), 2.17/2.25 (q, *J*=7.2/6.6 Hz, 2H), 6.00/5.83 (dt, *J*=15.0, 7.0/9.2, 7.3 Hz, 1H), 6.14/6.19 (d, *J*=15.0/9.2 Hz, 1H), *7.18* (*t*, *J*=*6.9* Hz, *1H*), *7.26–7.36* (*m*, *4H*).

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