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Radical Additions of Arenethiols to Ynamides for the Selective Synthesis of *N*-[(*Z*)-2-(Arylsulfanyl)-1-alkenyl]amides†

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A variety of ynamides undergo highly regio- and stereoselective radical addition of arenethiols with the aid of triethylborane as a radical initiator. The products, *N*-[(*Z*)-2-arylsulfanyl-1-alkenyl]amides, can be reduced with triethylsilane in trifluoroacetic acid to yield *N*-[2-(arylsulfanyl)alkyl]amides.

Key Words: Radical addition, Hydrothiolation, Ynamide, Hydrogenation

Introduction

Sulfides are a versatile class of compounds that are extensively used in organic synthesis. Development of carbon-sulfur bond forming reactions is thus important.[1] Radical addition of thiols to alkenes or alkynes is a representative method to introduce a sulfanyl moiety.[2,3] Whereas radical addition of thiols to terminal alkynes is facile, addition to internal alkynes is rather difficult and rarely reported.[4]

Addition of thiols to heteroatom-substituted internal alkynes can provide a rapid access to 1-heteroatom-substituted 2-sulfanyl 1-alkenes and can be useful in organic synthesis. However, such addition reactions have scarcely been reported.[5,6] We focused on *N*-alkynylamides (ynamides)[7] as nitrogen-substituted internal alkynes, and radical hydrothiolation of ynamides is reported in detail.[8,9]

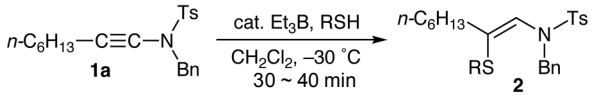
Results and Discussion

A mixture of *N*-benzyl-*N*-(1-octynyl)-*p*-toluenesulfonamide (**1a**) and benzenethiol was treated with a catalytic amount of triethylborane[10] in dichloromethane at −30 ºC for 30 min under air. The reaction proceeded with exclusive regio- and stereoselectivities to yield *N*-benzyl-*N*-[(*Z*)-2-(phenylsulfanyl)-1-octenyl]-*p*-toluenesulfonamide (**2a**) in 89% isolated yield (Table 1, entry 1).

A plausible mechanism is outlined in Scheme 1. As the initiation step, an ethyl radical generated from triethylborane abstracts hydrogen atom from benzenethiol to form a phenylsulfanyl radical. Arylsulfanyl radicals are known to behave as electron-deficient radicals.[11] Addition of the phenylsulfanyl radical thus naturally takes place at the more electron rich *sp*-hybridized carbon of ynamide **1a**. The newly formed nitrogen-substituted vinyl radical **3** should have *Z* geometry,[12] and the isomerization of **(*Z*)-3** into the *E* isomer **(*E*)-3** would be so slow because of the electronegative nitrogen[13] that **(*Z*)-3** abstracts hydrogen atom from benzenethiol. Product **2a** is thus selectively formed.

†This paper is dedicated to Professor Sunggak Kim on the occasion of his honorable retirement.

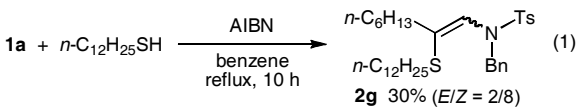
Table 1. Radical addition of various arenethiols to ynamide **1a**



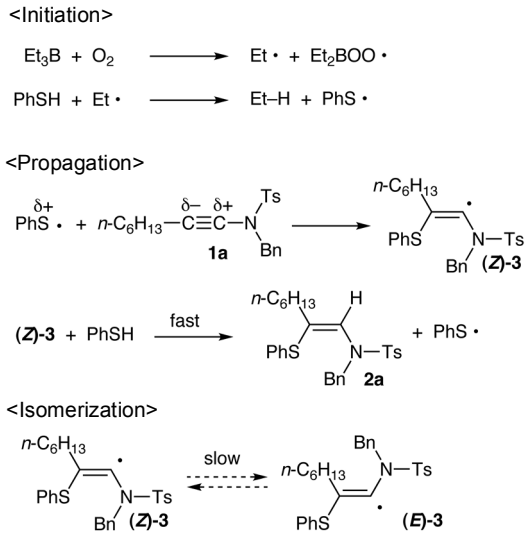
entry	RSH	product	yield / %[a]
1	PhSH	**2a**	89
2	*p*-BrC_6H_4SH	**2b**	88
3	C_6F_5SH	**2c**	93
4	*o*-MeC_6H_4SH	**2d**	31[e,f]
5	*p*-MeC_6H_4SH	**2e**	23[e,f]
6[b]	*p*-$MeOC_6H_4SH$	**2f**	35
7[c]	PhSH	**2a**	6[e,g]
8[d]	PhSH	**2a**	< 2[e,f]

[a]Isolated yield. [b]Performed at room temperature. [c]Performed with TEMPO (0.10 mmol). [d]Performed without triethylborane. [e]NMR yield. [f]*E*/*Z* ratio could not be determined. [g]*E*/*Z* ratio was 4/6.

The radical addition of electron-deficient arenethiols proceeded smoothly (Table 1, entries 2 and 3). On the other hand, electron-rich arenethiols added less efficiently (entries 4-6). The inefficiency would result from the low reactivity of the electrophilic sulfanyl radicals that are stabilized by electron-donating aryl groups. The presence of TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl) or the absence of triethylborane significantly suppressed the reaction, which support a radical mechanism (entries 7 and 8). The addition of dodecanethiol to **1a** did not proceed at −30 ºC. The reaction proceeded in refluxing benzene with the aid of AIBN [2,2'-azobis(isobutyronitrile)], albeit with low yield and stereoselectivity (eq 1).

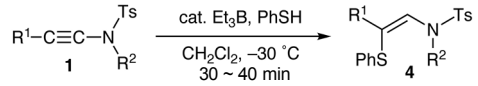


The scope of ynamides in the radical addition of benzenethiol is summarized in Table 2. Functional groups such as an acid-sen-



Scheme 1. Plausible mechanism

Table 2. Radical hydrothiolation of *p*-toluenesulfonyl-substituted ynamides with benzenethiol

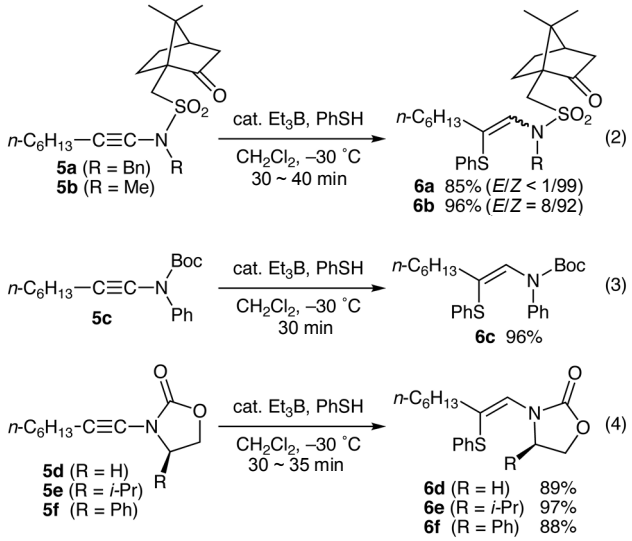


entry	R^1	R^2	**1**	product	yield / %[a]
1	*n*-C_6H_{13}	Bn	**1a**	**4a**[b]	89
2	$THPOCH_2$	Bn	**1b**	**4b**	90
3	$EtO_2C(CH_2)_4$	Bn	**1c**	**4c**	97
4	*n*-$C_5H_{11}CH(OH)$	Bn	**1d**	**4d**	(74)[c]
5	*c*-C_6H_{11}	Bn	**1e**	**4e**	73[d]
6	*t*-Bu	Bn	**1f**	**4f**	15[e,f]
7	Ph	Bn	**1g**	**4g**	–[g]
8	*n*-C_6H_{13}	Me	**1h**	**4h**	97[h]
9	*n*-C_6H_{13}	allyl	**1i**	**4i**	84
10	*n*-C_6H_{13}	Ph	**1j**	**4j**	60

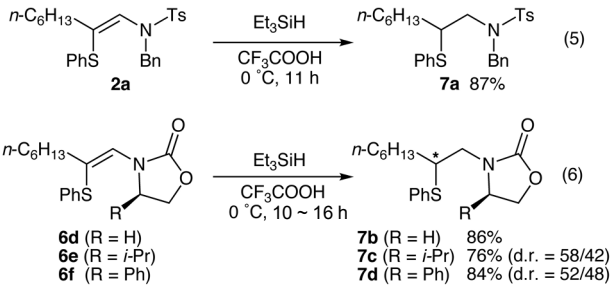
[a]Isolated yield. [b]**4a** = **2a**. [c]Determined by NMR analysis. [d]*E*/*Z* ratio was 3/97. [e]NMR yield. [f]*E*/*Z* ratio was not determined. [g]A complex mixture of regio- and stereoisomers. [h]*E*/*Z* ratio was 4/96.

sitive THP ether moiety and a base-sensitive ester moiety were compatible under the conditions (entries 2 and 3). The radical conditions allowed us to use hydroxy-containing substrate **1d** although the product decomposes during chromatographic purification (entry 4). The cyclohexyl group of ynamide **1e** retarded the addition reaction as well as diminished stereoselectivity slightly (entry 5). Ynamide **1f** having a *t*-butyl group resisted the addition reaction (entry 6). The addition reaction to phenyl-substituted ynamide **1g** afforded a complex mixture of stereo- and regioisomers (entry 7). Replacement of the benzyl group of **1a** by a methyl group slightly decreased the stereoselectivity of the reaction (entry 1 *vs*. entry 8). The allyl group of **1i** remained untouched under the reaction conditions (entry 9). *N*-Phenyl ynamide **1j** was less reactive than the *N*-benzyl analogue **1a** (entry 10).

Camphorsulfonamides **5a** and **5b** and Boc-protected ynamide **5c** as well as tosylamides **1** also underwent the radical addition smoothly (eqs 2 and 3). *N*-(1-Alkynyl)oxazolidinones **5d-5f** were good substrates to yield the corresponding *Z* adducts exclusively (eq 4).



Hydrogenation of the olefinic moiety of adducts **2**, **4**, and **6** can create a sulfur-substituted chiral center. Many attempts to reduce **2a** with 1 atm of molecular hydrogen under transition metal catalysis resulted in failure, suffering from no conversions. On the other hand, **2a** was efficiently reduced with triethylsilane in trifluoroacetic acid[14] (eq 5). Unfortunately, no diastereoselectivity was observed in the reduction of chiral *N*-(1-alkenyl)oxazolidinones **6e** and **6f** (eq 6). As each diastereomer was separable by flash column chromatography on silica gel, we could readily obtain enantiomerically pure **7c** and **7d**.



Conclusion

We have found that arenethiols can add to ynamides, a class of electron-rich internal alkynes, by a radical process. The addition takes place with high regio- and stereoselectivities to yield *N*-[(*Z*)-2-(arylsulfanyl)-1-alkenyl]amides. The products will be useful precursors that undergo a number of transformations. As an example, we have disclosed triethylsilane-mediated reduction of the double bonds. The reduced products have asymmetric carbons, and they can be useful as chiral building blocks[15] and chiral bidentate *N*,*S*-ligands of transition metal catalysts.[16]

Experimental Section

Instrumentation. ^{1}H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer and were obtained in $CDCl_3$ with tetramethylsilane as an internal standard. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra were determined on a JEOL Mstation 700 spectrometer. Specific rotations were determined on a HORIBA SEPA-200 polarimeter. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel 60F_{254}. Silica gel (Wakogel 200 mesh) was used for column chromatography. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Materials. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Neat triethylborane was obtained from Aldrich and was diluted with dry hexane to prepare a 1.0 M solution, which was stored under argon. Triethylsilane was available from TCI. Trifluoroacetic acid was purchased from Wako Pure Chemicals. Dichloromethane was dried with molecular sieves 4A. Thiols were commercially available or readily prepared by the conventional methods. Ynamides were synthesized from the corresponding bromoalkynes and amides.[17]

Preparation of ynamide. Synthesis of *N*-benzyl-*N*-(1-octynyl)-*p*-toluenesulfonamide (**1a**) is representative. Under argon atmosphere, copper sulfate pentahydrate (0.12 g, 0.50 mmol), 1,10-phenanthroline (0.18 g, 1.0 mmol), and potassium carbonate (1.4 g, 10 mmol) were added to a solution of 1-bromo-1-octyne (1.1 g, 5.9 mmol) and *N*-benzyl-*p*-toluenesulfonamide (1.3 g, 5.0 mmol) in toluene (6.0 mL). The resulting mixture was heated at 80 °C for 11 h. The mixture was then cooled down to room temperature, filtered through a pad of Florisil® with ethyl acetate, and concentrated in vacuo. Silica gel column chromatography (hexane/ethyl acetate = 10/1) afforded *N*-benzyl-*N*-(1-octynyl)-*p*-toluenesulfonamide (**1a**) as a pale yellow oil in 78% yield (1.4 g, 3.9 mmol). Since ynamides are more or less unstable under air at room temperature, ynamides must be stored in a refrigerator under inert atmosphere.

Procedure for additions of thiols to ynamides. Addition of benzenethiol to ynamide **1a** is representative (Table 1, entry 1). Under air, triethylborane (1.0 M hexane solution, 0.050 mL, 0.050 mmol) was added to a solution of ynamide **1a** (0.18 g, 0.50 mmol) and benzenethiol (0.062 mL, 0.60 mmol) in dichloromethane (2.0 mL) at −30 °C. The solution was stirred for 30 min at the same temperature and concentrated in vacuo. Silica gel column chromatography (hexane/ethyl acetate = 10/1 to 5/1) afforded *N*-benzyl-*N*-[(*Z*)-2-(phenylsulfanyl)-1-octenyl]-*p*-toluenesulfonamide (**2a**) as a white solid in 89% yield (0.21 g, 0.45 mmol). The Z configuration was assigned by NOE analysis that showed correlation between the vinylic proton and C_5H_{11}-$C\underline{H}_2$).

In the addition of dodecanethiol (eq 1), AIBN (0.10 mmol), dodecanethiol (0.75 mmol), and benzene (2.0 mL) were used. In the addition to *N*-(1-alkynyl)oxazolidinone **5d-5f** (eq 4), benzenethiol (1.2 mmol) and triethylborane (0.10 mmol) were used.

Hydrogenations of the double bonds of enamides. Hydrogenation of the double bond of **2a** is representative (eq 5). Under argon atmosphere, triethylsilane (0.048 mL, 0.30 mmol) was added to a solution of **2a** (0.096 g, 0.20 mmol) in trifluoroacetic acid (1.0 mL, 13.5 mmol) at 0 °C. The solution was stirred for 11 h at the same temperature. Then the reaction was quenched with a saturated $NaHCO_3$ solution and extracted with ethyl acetate (10 mL × 2). The organic extracts were dried over Na_2SO_4 and concentrated in vacuo. Silica gel column chromatography (hexane/ethyl acetate = 20/1) afforded *N*-benzyl-*N*-(2-phenylsulfanyl)octyl-*p*-toluenesulfonamide (**7a**) as a colorless oil in 87% yield (0.084 g, 0.17 mmol).

***N*-Benzyl-*N*-(1-octynyl)-*p*-toluenesulfonamide (1a):** IR (Nujol) 2925, 2855, 2255, 1597, 1454, 1169, 1093, 1056, 812, 655 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.86 (t, J = 7.5 Hz, 3H), 1.14-1.29 (m, 6H), 1.32-1.39 (m, 2H), 2.16 (t, J = 7.0 Hz, 2H), 2.44 (s, 3H), 4.44 (s, 2H), 7.26-7.31 (m, 7H), 7.72-7.76 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.03, 18.35, 21.58, 22.52, 28.26, 28.70, 31.29, 55.54, 70.89, 73.32, 127.68, 128.05, 128.35, 128.68, 129.51, 134.78, 134.83, 144.20. Found: C, 71.64; H, 7.37%. Calcd for $C_{22}H_{27}NO_2S$: C, 71.51; H, 7.37%.

***N*-Benzyl-*N*-[3-(2-oxacyclohexyloxy)-1-propynyl]-*p*-toluenesulfonamide (1b):** IR (Nujol) 2923, 2243, 1596, 1365, 1172, 1015 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.45-1.67 (m, 5H), 1.72-1.83 (m, 1H), 2.44 (s, 3H), 3.41-3.47 (m, 1H), 3.77 (ddd, J = 11.5, 8.5, 3.0 Hz, 1H), 4.30 (s, 2H), 4.48 (d, J = 14.0 Hz, 1H), 4.53 (d, J = 14.0 Hz, 1H), 4.58 (dd, J = 4.0, 4.0 Hz, 1H), 7.26-7.33 (m, 7H), 7.72-7.76 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 19.20, 21.61, 25.33, 30.24, 54.17, 55.41, 62.10, 67.91, 79.34, 96.15, 127.68, 128.20, 128.45, 128.64, 129.64, 134.50, 134.72, 144.54. Found: C, 65.92; H, 6.25%. Calcd for $C_{22}H_{25}NO_4S$: C, 66.14; H, 6.31%.

***N*-Benzyl-*N*-(6-ethoxycarbonyl-1-hexynyl)-*p*-toluenesulfonamide (1c):** IR (neat) 2935, 2255, 1733, 1597, 1456, 1366, 1170, 1092, 1027, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25 (t, J = 7.0 Hz, 3H), 1.36-1.44 (m, 2H), 1.50-1.58 (m, 2H), 2.19 (t, J = 7.0 Hz, 2H), 2.21 (t, J = 7.5 Hz, 2H), 2.45 (s, 3H), 4.12 (q, J = 7.0 Hz, 2H), 4.44 (s, 2H), 7.25-7.34 (m, 7H), 7.73-7.77 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.25, 18.09, 21.63, 23.83, 28.10, 33.71, 55.47, 60.24, 70.20, 73.61, 127.66, 128.10, 128.39, 128.73, 129.60, 134.65, 134.73, 144.33, 173.40. Found: C, 66.76; H, 6.57%. Calcd for $C_{23}H_{27}NO_4S$: C, 66.80; H, 6.58%.

***N*-Benzyl-*N*-(2-cyclohexylethynyl)-*p*-toluenesulfonamide (1e):** IR (neat) 2929, 2854, 2249, 2043, 1598, 1497, 1449, 1367, 1170, 1091 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.17-1.34 (m, 5H), 1.37-1.47 (m, 1H), 1.49-1.58 (m, 2H), 1.60-1.67 (m, 2H), 2.34-2.42 (m, 1H), 2.45 (s, 3H), 4.44 (s, 2H), 7.27-7.32 (m, 7H), 7.73-7.77 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.63, 24.46, 25.82, 28.60, 32.57, 55.57, 73.63, 74.79, 127.74, 128.06, 128.32, 128.84, 129.47, 134.60, 134.76, 144.21. Found: C, 71.73; H, 6.87%. Calcd for $C_{22}H_{25}NO_2S$: C, 71.90; H, 6.86%.

***N*-Methyl-*N*-(1-octynyl)-*p*-toluenesulfonamide (1h):** IR (neat) 2931, 2858, 2255, 1597, 1456, 1366, 1173, 676 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J = 7.0 Hz, 3H), 1.22-1.37 (m, 6H), 1.43-1.50 (m, 2H), 2.23 (t, J = 7.0 Hz, 2H), 2.46 (s, 3H), 3.01 (s, 3H), 7.33-7.37 (m, 2H), 7.76-7.80 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.02, 18.31, 21.59, 22.53, 28.41, 28.81, 31.30, 39.35, 68.62, 74.78, 127.79, 129.57, 133.13, 144.39. Found: C, 65.67; H, 7.72%. Calcd for $C_{16}H_{23}NO_2S$: C, 65.49; H, 7.90%.

***N*-Allyl-*N*-(1-octynyl)-*p*-toluenesulfonamide (1i):** IR (neat) 2930, 2858, 2253, 1597, 1367, 1171, 1091, 814, 665 cm^{-1}; ^{1}H

NMR ($CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 1.20-1.36 (m, 6H), 1.41-1.49 (m, 2H), 2.24 (t, J = 7.0 Hz, 2H), 2.45 (s, 3H), 3.92 (ddd, J = 6.5, 1.5, 1.0 Hz, 2H), 5.18 (ddt, J = 10.0, 1.0, 1.0 Hz, 1H), 5.22 (ddt, J = 17.0, 1.5, 1.0 Hz, 1H), 5.73 (ddt, J = 17.0, 10.0, 6.5 Hz, 1H), 7.31-7.35 (m, 2H), 7.77-7.81 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.05, 18.40, 21.63, 22.57, 28.38, 28.85, 31.31, 54.27, 70.48, 72.95, 119.59, 127.74, 129.56, 131.20, 134.73, 144.30. Found: C, 67.96; H, 8.04%. Calcd for $C_{18}H_{25}NO_2S$: C, 67.67; H, 7.89%.

***N*-(1-Octynyl)-*N*-phenyl-*p*-toluenesulfonamide (1j):** IR (neat) 2930, 2255, 1596, 1489, 1373, 1177, 1091, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J = 7.0 Hz, 3H), 1.22-1.39 (m, 6H), 1.46-1.53 (m, 2H), 2.29 (t, J = 7.0 Hz, 2H), 2.44 (s, 3H), 7.23-7.34 (m, 7H), 7.53-7.57 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.05, 18.45, 21.66, 22.57, 28.47, 28.77, 31.31, 70.38, 73.79, 126.08, 127.84, 128.23, 128.87, 129.28, 132.92, 139.36, 144.57. Found: C, 70.81; H, 7.08%. Calcd for $C_{21}H_{25}NO_2S$: C, 70.95; H, 7.09%.

***N*-Benzyl-*N*-[(*Z*)-2-(phenylsulfanyl)-1-octenyl]-*p*-toluene sulfonamide (2a):** IR (Nujol) 2925, 1456, 1351, 1339, 1161, 1089, 1024, 741, 661 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.83 (t, J = 7.5 Hz, 3H), 1.02-1.15 (m, 4H), 1.16-1.35 (m, 4H), 1.89 (t, J = 7.0 Hz, 2H), 2.45 (s, 3H), 4.46 (s, 2H), 5.64 (s, 1H), 6.90-6.94 (m, 2H), 7.13-7.21 (m, 3H), 7.26-7.35 (m, 5H), 7.36-7.41 (m, 2H), 7.76-7.80 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.04, 21.57, 22.50, 28.09, 28.25, 31.40, 33.36, 54.15, 124.26, 127.14, 127.62, 127.67, 128.32, 128.58, 128.77, 129.60, 132.31, 133.10, 135.63, 135.83, 142.86, 143.59. Found: C, 70.00; H, 6.94%. Calcd for $C_{28}H_{33}NO_2S_2$: C, 70.11; H, 6.93%.

***N*-Benzyl-*N*-[(*Z*)-2-(4-bromophenylsulfanyl)-1-octenyl]-*p*-toluenesulfonamide (2b):** IR (Nujol) 2924, 1471, 1352, 1340, 1162, 1087, 1008, 813, 740, 659 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.85 (t, J = 7.5 Hz, 3H), 1.05-1.17 (m, 4H), 1.18-1.27 (m, 2H), 1.27-1.34 (m, 2H), 1.89 (t, J = 7.0 Hz, 2H), 2.46 (s, 3H), 4.41 (s, 2H), 5.63 (s, 1H), 6.69-6.73 (m, 2H), 7.23-7.30 (m, 5H), 7.31-7.38 (m, 4H), 7.73-7.77 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.04, 21.58, 22.51, 28.09, 28.24, 31.42, 33.40, 54.22, 121.22, 125.27, 127.64, 127.72, 128.37, 128.85, 129.68, 131.68, 132.66, 133.49, 135.48, 135.65, 142.26, 143.73. Found: C, 60.14; H, 5.71%. Calcd for $C_{28}H_{32}BrNO_2S_2$: C, 60.21; H, 5.77%.

***N*-Benzyl-*N*-[(*Z*)-2-(pentafluorophenylsulfanyl)-1-octenyl]-*p*-toluenesulfonamide (2c):** IR (Nujol) 2923, 1514, 1484, 1340, 1162, 1094, 979, 856, 739, 659 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.86 (t, J = 7.5 Hz, 3H), 1.07-1.18 (m, 4H), 1.19-1.34 (m, 4H), 1.85 (td, J = 7.0, 1.0 Hz, 2H), 2.46 (s, 3H), 4.47 (s, 2H), 5.64 (t, J = 1.0 Hz, 1H), 7.24-7.31 (m, 3H), 7.31-7.36 (m, 4H), 7.72-7.76 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.95, 21.53, 22.41, 27.96, 28.11, 31.32, 33.72, 54.12, 106.73 (td, J = 20.5, 3.8 Hz), 124.45, 127.63, 127.75, 128.33, 128.62, 129.69, 135.35, 135.38, 137.52 (ddddd, J = 253.5, 16.0, 13.5, 5.0, 2.0 Hz), 139.84, 141.63 (dtt, J = 255.3, 27.1, 9.5 Hz), 143.92, 147.33 (ddddd, J = 247.3, 10.5, 4.0, 4.0, 4.0 Hz). Found: C, 59.16; H, 4.89%. Calcd for $C_{28}H_{28}F_5NO_2S_2$: C, 59.04; H, 4.95%.

***N*-Benzyl-*N*-[(*Z*)-2-(4-methoxyphenylsulfanyl)-1-octenyl]-*p*-toluenesulfonamide (2f):** IR (Nujol) 2924, 1593, 1492, 1455, 1351, 1339, 1246, 1161, 1039, 739 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.84 (t, J = 7.5 Hz, 3H), 1.02-1.14 (m, 4H), 1.17-1.32 (m, 4H), 1.81 (t, J = 7.0 Hz, 2H), 2.45 (s, 3H), 3.77 (s, 3H), 4.44 (s, 2H), 5.49 (s, 1H), 6.69-6.73 (m, 2H), 6.88-6.92 (m, 2H), 7.28-7.35 (m, 5H), 7.39-7.42 (m, 2H), 7.76-7.80 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.06, 21.56, 22.50, 28.12, 28.16, 31.42, 33.03, 54.21, 55.25, 114.18, 122.13, 123.13, 127.59, 127.69, 128.26, 128.85, 129.56, 134.96, 135.60, 135.89, 143.51, 144.69, 159.41. Found: C, 68.47; H, 6.94%. Calcd for $C_{29}H_{35}NO_3S_2$: C, 68.33; H, 6.92%.

***N*-Benzyl-*N*-[(*Z*)-3-(2-oxacyclohexyloxy)-2-(phenylsulfanyl)-1-propenyl]-*p*-toluenesulfonamide (4b):** IR (Nujol) 2923, 1348, 1163, 1033, 743, 699, 665 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.39-1.61 (m, 5H), 1.67-1.78 (m, 1H), 2.45 (s, 3H), 3.29-3.35 (m, 1H), 3.62 (ddd, J = 11.0, 9.0, 3.0 Hz, 1H), 3.83 (dd, J = 14.0, 1.0 Hz, 1H), 3.97 (dd, J = 14.0, 1.5 Hz, 1H), 4.30 (dd, J = 6.5, 6.0 Hz, 1H), 4.58 (d, J = 14.5 Hz, 1H), 4.68 (d, J = 14.5 Hz, 1H), 6.29 (dd, J = 1.5, 1.0 Hz, 1H), 6.92-6.96 (m, 2H), 7.10-7.18 (m, 3H), 7.24-7.30 (m, 3H), 7.30-7.36 (m, 4H), 7.74-7.78 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 19.17, 21.57, 25.31, 30.29, 53.11, 61.94, 66.80, 96.89, 127.11, 127.57 (Two signals merge.), 127.66, 128.34, 128.45, 128.68, 129.69, 131.49, 132.20, 132.90, 135.73, 135.86, 143.79. Found: C, 65.78; H, 5.95%. Calcd for $C_{28}H_{31}NO_4S_2$: C, 65.98; H, 6.13%.

***N*-Benzyl-*N*-[(*Z*)-6-(ethoxycarbonyl)-2-(phenylsulfanyl)-1-hexenyl]-*p*-toluenesulfonamide (4c):** IR (Nujol) 2924, 1726, 1341, 1160, 737, 659 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.24 (t, J = 7.0 Hz, 3H), 1.31-1.45 (m, 4H), 1.91 (t, J = 7.0 Hz, 2H), 2.15 (t, J = 7.5 Hz, 2H), 2.46 (s, 3H), 4.10 (q, J = 7.0 Hz, 2H), 4.44 (s, 2H), 5.62 (s, 1H), 6.89-6.93 (m, 2H), 7.13-7.21 (m, 3H), 7.26-7.31 (m, 3H), 7.33-7.41 (m, 4H), 7.76-7.80 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.23, 21.58, 23.70, 27.67, 30.93, 32.99, 33.92, 54.18, 60.19, 124.62, 127.25, 127.66, 128.34, 128.64, 128.79, 129.69, 132.29, 132.91, 135.41, 135.70, 142.49, 143.67, 173.45. HRMS Found: 523.1851 (Δ = +0.0 ppm); Calcd for $C_{29}H_{33}NO_4S_2$: 523.1851 [M]$^+$.

***N*-Benzyl-*N*-[(*Z*)-2-cyclohexyl-2-(phenylsulfanyl)ethenyl]-*p*-toluenesulfonamide (4e):** IR (Nujol) 2923, 1456, 1352, 1162, 738 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88-1.12 (m, 5H), 1.50-1.57 (m, 1H), 1.58-1.65 (m, 2H), 1.68-1.75 (m, 3H), 2.45 (s, 3H), 4.49 (s, 2H), 5.73 (d, J = 0.5 Hz, 1H), 6.81-6.86 (m, 2H), 7.10-7.18 (m, 3H), 7.25-7.29 (m, 3H), 7.30-7.35 (m, 4H), 7.72-7.76 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.58, 26.04, 26.41, 33.30, 42.54, 53.94, 124.67, 126.65, 127.59, 127.68, 128.27, 128.58, 128.93, 129.58, 131.22, 134.29, 135.58, 135.77, 143.57, 146.10. Found: C, 70.46; H, 6.51%. Calcd for $C_{28}H_{31}NO_2S_2$: C, 70.40; H, 6.54%.

***N*-Methyl-*N*-[(*Z*)-2-(phenylsulfanyl)-1-octenyl]-*p*-toluenesulfonamide (4h):** IR (neat) 2929, 1598, 1476, 1440, 1353, 1166, 1090, 745, 666 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.85 (t, J = 7.5 Hz, 3H), 1.13-1.30 (m, 6H), 1.36-1.44 (m, 2H), 2.05 (td, J = 7.5, 1.0 Hz, 2H), 2.44 (s, 3H), 3.06 (s, 3H), 6.16 (t, J = 1.0 Hz, 1H), 7.20-7.28 (m, 5H), 7.30-7.34 (m, 2H), 7.70-7.74 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.02, 21.55, 22.52, 28.27, 28.35, 31.45, 34.24, 37.02, 127.02, 127.54, 127.55, 128.85, 129.61, 131.43, 133.35, 134.21, 134.81, 143.63. Found: C, 65.48; H, 7.25%. Calcd for $C_{22}H_{29}NO_2S_2$: C, 65.47; H, 7.24%.

***N*-Allyl-*N*-[(*Z*)-2-(phenylsulfanyl)-1-octenyl]-*p*-toluenesulfonamide (4i):** IR (neat) 2928, 2856, 1598, 1440, 1354, 1164, 1091, 665 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.85 (t, J = 7.5 Hz, 3H), 1.11-1.19 (m, 4H), 1.20-1.28 (m, 2H), 1.33-1.42 (m, 2H), 2.03 (td, J = 7.5, 1.0 Hz, 2H), 2.43 (s, 3H), 4.00 (ddd, J = 6.5, 1.5, 1.5 Hz, 2H), 5.16 (ddt, J = 10.0, 1.5, 1.5 Hz, 1H), 5.23 (ddt, J = 17.5,

1.5, 1.5 Hz, 1H), 5.80 (t, J = 1.0 Hz, 1H), 5.83 (ddt, J = 17.5, 10.5, 6.5 Hz, 1H), 7.21-7.28 (m, 5H), 7.28-7.32 (m, 2H), 7.72-7.76 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.05, 21.55, 22.53, 28.19, 28.29, 31.43, 33.52, 52.99, 118.50, 124.30, 127.29, 127.64, 128.79, 129.53, 132.26, 132.97, 132.99, 135.83, 141.28, 143.52. Found: C, 67.22; H, 7.29%. Calcd for $C_{24}H_{31}NO_2S_2$: C, 67.09; H, 7.27%.

***N*-Phenyl-*N*-[(*Z*)-2-(phenylsulfanyl)-1-octenyl]-*p*-toluenesulfonamide (4j):** IR (neat) 2928, 2028, 1595, 1490, 1360, 1168, 1092, 693, 665 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.83 (t, J = 7.5 Hz, 3H), 1.07-1.25 (m, 6H), 1.31-1.39 (m, 2H), 2.04 (td, J = 7.5, 1.0 Hz, 2H), 2.42 (s, 3H), 6.53 (t, J = 1.0 Hz, 1H), 7.12-7.17 (m, 4H), 7.18-7.30 (m, 8H), 7.53-7.57 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.00, 21.58, 22.49, 28.22, 28.24, 31.37, 33.76, 126.06, 127.06, 127.22, 127.80, 127.82, 128.69, 128.73, 129.42, 132.25, 132.75, 135.02, 135.70, 140.97, 143.80. Found: C, 69.49; H, 6.55%. Calcd for $C_{27}H_{31}NO_2S_2$: C, 69.64; H, 6.71%.

***N*-Benzyl-*N*-(1-octynyl)-10-camphorsulfonamide (5a):** IR (neat) 2956, 2931, 2858, 2254, 2044, 1747, 1456, 1363, 1165, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.82 (s, 3H), 0.87 (t, J = 7.0 Hz, 3H), 1.11 (s, 3H), 1.19-1.35 (m, 6H), 1.38-1.49 (m, 3H), 1.68 (ddd, J = 14.0, 9.5, 5.0 Hz, 1H), 1.93 (d, J = 18.5 Hz, 1H), 2.00-2.12 (m, 2H), 2.25 (t, J = 7.0 Hz, 2H), 2.37 (ddd, J = 18.5, 4.0, 4.0 Hz, 1H), 2.48 (ddd, J = 14.5, 11.5, 4.0 Hz, 1H), 2.87 (d, J = 15.0 Hz, 1H), 3.55 (d, J = 15.0 Hz, 1H), 4.56 (d, J = 14.0 Hz, 1H), 4.63 (d, J = 14.0 Hz, 1H), 7.31-7.40 (m, 3H), 7.42-7.46 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.05, 18.48, 19.64, 20.00, 22.54, 25.24, 26.92, 28.42, 28.81, 31.32, 42.52, 42.80, 47.85, 47.97, 55.68, 58.37, 71.36, 73.15, 128.37, 128.60, 128.96, 135.14, 214.39. Found: C, 70.03; H, 8.38%. Calcd for $C_{25}H_{35}NO_3S$: C, 69.89; H, 8.21%.

***N*-Methyl-*N*-(1-octynyl)-10-camphorsulfonamide (5b):** IR (neat) 2932, 2256, 1748, 1456, 1363, 1153, 1053 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J = 7.0 Hz, 3H), 0.91 (s, 3H), 1.15 (s, 3H), 1.23-1.54 (m, 9H), 1.70 (ddd, J = 14.0, 9.5, 4.5 Hz, 1H), 1.95 (d, J = 18.5 Hz, 1H), 2.02-2.14 (m, 2H), 2.28 (t, J = 7.0 Hz, 2H), 2.37-2.44 (m, 1H), 2.45-2.53 (m, 1H), 3.10 (d, J = 14.5 Hz, 1H), 3.20 (s, 3H), 3.63 (d, J = 14.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.04, 18.40, 19.72, 20.00, 22.53, 25.10, 26.89, 28.49, 28.88, 31.31, 39.26, 42.52, 42.80, 45.91, 47.92, 58.20, 69.15, 74.40, 214.68. Found: C, 64.49; H, 8.84%. Calcd for $C_{19}H_{31}NO_3S$: C, 64.55; H, 8.84%.

***t*-Butyl *N*-(1-octynyl)-*N*-phenylcarbamate (5c):** IR (neat) 2932, 2270, 1733, 1597, 1494, 1369, 1302, 1291, 1254, 1155 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J = 7.5 Hz, 3H), 1.24-1.35 (m, 4H), 1.37-1.45 (m, 2H), 1.52 (s, 9H), 1.48-1.57 (m, 2H), 2.32 (t, J = 7.0 Hz, 2H), 7.19-7.23 (m, 1H), 7.32-7.38 (m, 2H), 7.44-7.48 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.06, 18.50, 22.57, 28.00, 28.56, 28.90, 31.36, 69.33, 74.31, 82.87, 124.51, 126.16, 128.58, 140.24, 153.59. Found: C, 75.94; H, 9.26%. Calcd for $C_{19}H_{27}NO_2$: C, 75.71; H, 9.03%.

3-(1-Octynyl)oxazolidin-2-one (5d): IR (neat) 2929, 2858, 2272, 1767, 1416, 1206, 1116, 1036, 751 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J = 7.5 Hz, 3H), 1.23-1.34 (m, 4H), 1.34-1.42 (m, 2H), 1.49-1.56 (m, 2H), 2.30 (t, J = 7.0 Hz, 2H), 3.85-3.90 (m, 2H), 4.39-4.44 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.04, 18.39, 22.52, 28.52, 28.73, 31.30, 47.01, 62.73, 69.93, 71.27, 156.63. Found: C, 67.82; H, 8.92%. Calcd for $C_{11}H_{17}NO_2$: C, 67.66; H, 8.78%.

(*R*)-4-Isopropyl-3-(1-octynyl)oxazolidin-2-one (5e): IR (neat) 2932, 2859, 2266, 1778, 1771, 1414, 1201, 1117, 1050 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J = 7.0 Hz, 3H), 0.97 (d, J = 6.5 Hz, 3H), 0.98 (d, J = 7.0 Hz, 3H), 1.23-1.43 (m, 6H), 1.49-1.57 (m, 2H), 2.21 (qqd, J = 7.0, 6.5, 4.0 Hz, 1H), 2.31 (t, J = 7.5 Hz, 2H), 3.91 (ddd, J = 9.0, 6.0, 4.0 Hz, 1H), 4.12 (dd, J = 9.0, 6.0 Hz, 1H), 4.34 (dd, J = 9.0, 9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.01, 14.98, 17.21, 18.45, 22.52, 28.48, 28.73, 28.92, 31.26, 61.75, 64.44, 69.26, 72.30, 156.73; $[\alpha]^{25}_D$ −26 (*c* 0.82, cyclohexane). Found: C, 70.97; H, 9.82%. Calcd for $C_{14}H_{23}NO_2$: C, 70.85; H, 9.77%.

(*R*)-4-Phenyl-3-(1-octynyl)oxazolidin-2-one (5f): IR (neat) 2931, 2858, 2268, 1771, 1407, 1187, 1106, 1039, 751, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.84 (t, J = 7.0 Hz, 3H), 1.10-1.30 (m, 6H), 1.30-1.38 (m, 2H), 2.16 (t, J = 7.0 Hz, 2H), 4.22 (dd, J = 9.0, 7.0 Hz, 1H), 4.71 (dd, J = 9.0, 8.5 Hz, 1H), 5.00 (dd, J = 8.5, 7.0 Hz, 1H), 7.32-7.36 (m, 2H), 7.38-7.47 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 14.02, 18.26, 22.46, 28.14, 28.48, 31.20, 62.11, 68.97, 70.55, 72.90, 126.85, 129.17, 129.30, 136.37, 156.31; $[\alpha]^{25}_D$ −159 (*c* 0.82, cyclohexane). Found: C, 74.95; H, 7.95%. Calcd for $C_{17}H_{21}NO_2$: C, 75.25; H, 7.80%.

***N*-Benzyl-*N*-[(*Z*)-2-(phenylsulfanyl)-1-octenyl]-10-camphorsulfonamide (6a):** IR (Nujol) 2923, 1751, 1441, 1338, 1147, 1049, 698, 665 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.81 (t, J = 7.5 Hz, 3H), 0.85 (s, 3H), 1.01-1.22 (m, 6H), 1.15 (s, 3H), 1.28-1.36 (m, 2H), 1.43 (ddd, J = 12.5, 9.5, 4.0 Hz, 1H), 1.68 (ddd, J = 14.0, 9.5, 4.5 Hz, 1H), 1.94 (d, J = 18.0 Hz, 1H), 1.99 (t, J = 7.5 Hz, 2H), 2.01-2.12 (m, 2H), 2.39 (ddd, J = 18.0, 4.0, 3.5 Hz, 1H), 2.54-2.62 (m, 1H), 2.97 (d, J = 14.5 Hz, 1H), 3.57 (d, J = 14.5 Hz, 1H), 4.75 (s, 2H), 6.04 (s, 1H), 7.12-7.17 (m, 2H), 7.20-7.25 (m, 3H), 7.26-7.35 (m, 3H), 7.41-7.45 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.04, 19.72, 20.08, 22.43, 25.18, 26.93, 28.05, 28.27, 31.37, 33.54, 42.59, 42.82, 47.86, 48.54, 53.61, 58.52, 124.67, 127.37, 127.68, 128.41, 128.73, 128.84, 132.25, 132.71, 136.27, 140.32, 215.15. Found: C, 68.92; H, 7.50%. Calcd for $C_{31}H_{41}NO_3S_2$: C, 68.98; H, 7.66%.

***N*-Methyl-*N*-[(*Z*)-2-(phenylsulfanyl)-1-octenyl]-10-camphorsulfonamide (6b):** IR (neat) 2956, 2930, 1747, 1349, 1147, 745 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.84 (t, J = 7.0 Hz, 3H), 0.86 (s, 3H), 1.13 (s, 3H), 1.16-1.28 (m, 6H), 1.39-1.48 (m, 3H), 1.67 (ddd, J = 14.0, 9.0, 4.5 Hz, 1H), 1.93 (d, J = 18.0 Hz, 1H), 2.01-2.12 (m, 2H), 2.12 (td, J = 7.5, 1.0 Hz, 2H), 2.38 (ddd, J = 18.0, 4.0, 4.0 Hz, 1H), 2.53 (ddd, J = 15.0, 12.0, 4.0 Hz, 1H), 2.89 (d, J = 14.5 Hz, 1H), 3.23 (s, 3H), 3.50 (d, J = 14.5 Hz, 1H), 6.44 (t, J = 1.0 Hz, 1H), 7.22-7.26 (m, 1H), 7.28-7.32 (m, 2H), 7.34-7.37 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.02, 19.75, 20.05, 22.48, 25.07, 26.92, 28.29, 28.41, 31.43, 34.39, 36.83, 42.57, 42.80, 47.25, 47.86, 58.32, 127.09, 128.07, 129.02, 131.21, 132.67, 133.33, 214.92. Found: C, 64.44; H, 8.01%. Calcd for $C_{25}H_{37}NO_3S_2$: C, 64.76; H, 8.04%.

***t*-Butyl *N*-phenyl-*N*-[(*Z*)-2-(phenylsulfanyl)-1-octenyl]carbamate (6c):** IR (neat) 2930, 2856, 1714, 1596, 1496, 1367, 1300, 1160, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.85 (t, J = 7.0 Hz, 3H), 1.16-1.30 (m, 6H), 1.43-1.52 (m, 2H), 1.49 (s, 9H), 2.12 (t, J = 7.5 Hz, 2H), 6.60 (br s, 1H), 7.12-7.25 (m, 8H), 7.26-7.31 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.05, 22.52, 28.21, 28.38, 28.43, 31.50, 34.20, 81.38, 125.45, 126.13, 126.63, 128.31, 128.64 (Two signals merge.), 129.02, 131.15, 133.93, 141.55, 153.32. Found: C, 72.98; H, 8.09%. Calcd for $C_{25}H_{33}NO_2S$: C, 72.95; H, 8.08%.

3-[(*Z*)-2-(Phenylsulfanyl)-1-octenyl]oxazolidin-2-one (6d):

IR (neat) 2929, 1761, 1641, 1478, 1398, 1225, 1061, 742 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (t, J = 7.0 Hz, 3H), 1.17-1.31 (m, 6H), 1.46-1.55 (m, 2H), 2.20 (td, J = 7.5, 1.0 Hz, 2H), 4.23-4.28 (m, 2H), 4.30-4.35 (m, 2H), 7.02 (t, J = 1.0 Hz, 1H), 7.15-7.20 (m, 1H), 7.21-7.25 (m, 2H), 7.26-7.31 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.04, 22.53, 28.50, 28.66, 31.57, 36.87, 44.82, 62.90, 114.49, 125.83, 127.61, 129.02, 129.12, 135.78, 156.91. Found: C, 66.83; H, 7.64%. Calcd for $C_{17}H_{23}NO_2S$: C, 66.85; H, 7.59%.

(*R*)-4-Isopropyl-3-[(*Z*)-2-(phenylsulfanyl)-1-octenyl]oxazolidin-2-one (6e): IR (neat) 2929, 1761, 1637, 1477, 1392, 1303, 1211, 1054, 742, 691 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.83 (d, J = 7.0 Hz, 3H), 0.85 (t, J = 7.0 Hz, 3H), 0.87 (d, J = 7.0 Hz, 3H), 1.17- 1.31 (m, 6H), 1.46-1.55 (m, 2H), 2.12-2.27 (m, 3H), 4.07 (dd, J = 9.0, 9.0 Hz, 1H), 4.14 (dd, J = 9.0, 3.0 Hz, 1H), 4.67 (ddd, J = 9.0, 3.0, 3.0 Hz, 1H), 6.72 (s, 1H), 7.18-7.22 (m, 1H), 7.24-7.31 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.01, 14.08, 17.52, 22.53, 27.69, 28.41, 28.65, 31.48, 36.26, 59.26, 63.20, 120.93, 125.09, 126.38, 128.89, 129.07, 134.05, 156.77; $[\alpha]^{25}_D$ −113 (*c* 0.82, cyclohexane). Found: C, 69.29; H, 8.48%. Calcd for $C_{20}H_{29}NO_2S$: C, 69.12; H, 8.41%.

(*R*)-4-Phenyl-3-[(*Z*)-2-(phenylsulfanyl)-1-octenyl]oxazolidin-2-one (6f): IR (neat) 2929, 1761, 1639, 1394, 1207, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.81 (t, J = 7.5 Hz, 3H), 0.96-1.22 (m, 6H), 1.31-1.38 (m, 2H), 1.95-2.10 (m, 2H), 4.16 (dd, J = 8.5, 4.0 Hz, 1H), 4.56 (dd, J = 8.5, 8.5 Hz, 1H), 5.83 (dd, J = 8.5, 4.0 Hz, 1H), 6.66 (s, 1H), 6.91-6.95 (m, 2H), 7.12-7.19 (m, 3H), 7.20-7.24 (m, 2H), 7.29-7.35 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 14.02, 22.45, 28.04, 28.31, 31.44, 35.34, 59.22, 70.48, 122.48, 124.83, 126.35, 126.42, 128.55, 128.79, 129.05, 129.45, 133.76, 138.89, 156.94; $[\alpha]^{25}_D$ −33 (*c* 0.80, cyclohexane). HRMS Found: 381.1766 (Δ = +0.9 ppm); Calcd for $C_{23}H_{27}NO_2S$: 381.1762 $[M]^+$.

***N*-Benzyl-*N*-[2-(phenylsulfanyl)octyl]-*p*-toluenesulfonamide (7a):** IR (neat) 2926, 2855, 1599, 1456, 1439, 1342, 1162, 1092, 737, 654 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 7.5 Hz, 3H), 1.02-1.31 (m, 8H), 1.34-1.46 (m, 1H), 1.65-1.75 (m, 1H), 2.42 (s, 3H), 2.95-3.05 (m, 2H), 3.26-3.34 (m, 1H), 4.05 (d, J = 14.5 Hz, 1H), 4.31 (d, J = 14.5 Hz, 1H), 7.17-7.32 (m, 12H), 7.57-7.61 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.07, 21.49, 22.58, 26.62, 28.94, 30.82, 31.64, 47.40, 53.96, 54.26, 126.75, 127.30, 127.96, 128.58, 128.62, 128.83, 129.69, 131.62, 134.66, 135.82, 136.21, 143.37. Found: C, 70.03; H, 7.38%. Calcd for $C_{28}H_{35}NO_2S_2$: C, 69.81; H, 7.32%.

3-[2-(Phenylsulfanyl)octyl]oxazolidin-2-one (7b): IR (neat) 2928, 2856, 1750, 1482, 1438, 1425, 1264, 1043, 748, 693 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 1.22-1.37 (m, 6H), 1.44-1.69 (m, 4H), 3.32-3.48 (m, 3H), 3.51-3.63 (m, 2H), 4.09-4.19 (m, 2H), 7.22-7.26 (m, 1H), 7.28-7.34 (m, 2H), 7.41-7.46 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.04, 22.55, 26.78, 29.08, 31.61, 32.25, 45.94, 47.61, 49.42, 61.76, 127.05, 129.02, 131.67, 134.59, 158.63. Found: C, 66.29; H, 8.24%. Calcd for $C_{17}H_{25}NO_2S$: C, 66.41; H, 8.20%.

(*R*)-4-Isopropyl-3-[2-(phenylsulfanyl)octyl]oxazolidin-2-one (7c): < the faster moving band: R_f = 0.47, hexane/ethyl acetate = 3/1> IR (neat) 2929, 1750, 1439, 1423, 1240, 1051, 745, 693 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.76 (d, J = 7.0 Hz, 3H), 0.83 (d, J = 7.0 Hz, 3H), 0.88 (t, J = 7.0 Hz, 3H), 1.22-1.34 (m, 6H), 1.42-1.68 (m, 4H), 1.89 (qqd, J = 7.0, 7.0, 4.0 Hz, 1H), 2.98 (dd, J = 14.5, 8.0 Hz, 1H), 3.44-3.51 (m, 1H), 3.74 (dd, J = 14.5, 7.5 Hz, 1H), 3.78 (ddd, J = 8.5, 4.5, 4.0 Hz, 1H), 3.86 (dd, J = 9.0, 8.5 Hz, 1H), 3.96 (dd, J = 9.0, 4.5 Hz, 1H), 7.21-7.25 (m, 1H), 7.27-7.32 (m, 2H), 7.38-7.42 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.04, 14.22, 17.54, 22.53, 26.60, 27.43, 29.07, 31.60, 32.60, 46.87, 47.16, 59.97, 62.78, 126.89, 129.01, 131.11, 134.94, 158.20; $[\alpha]^{25}_D$ −7.5 (*c* 1.5, cyclohexane). Found: C, 68.71; H, 8.73%. Calcd for $C_{20}H_{31}NO_2S$: C, 68.73; H, 8.94%. < The slower moving band: R_f = 0.43, hexane/ethyl acetate = 3/1> IR (neat) 2929, 1750, 1438, 1421, 1240, 1052, 747, 693 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.79 (d, J = 7.0 Hz, 3H), 0.83 (d, J = 7.0 Hz, 3H), 0.88 (t, J = 7.0 Hz, 3H), 1.23-1.38 (m, 6H), 1.45-1.72 (m, 4H), 1.93 (qqd, J = 7.0, 7.0, 3.5 Hz, 1H), 3.11 (dd, J = 14.5, 5.5 Hz, 1H), 3.31-3.38 (m, 1H), 3.65 (ddd, J = 8.5, 5.5, 3.5 Hz, 1H), 3.74 (dd, J = 14.5, 7.5 Hz, 1H), 3.97 (dd, J = 9.0, 8.5 Hz, 1H), 4.00 (dd, J = 9.0, 5.5 Hz, 1H), 7.22-7.26 (m, 1H), 7.27-7.33 (m, 2H), 7.44-7.48 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.04, 14.15, 17.61, 22.55, 26.99, 27.33, 29.12, 31.63, 32.16, 46.04, 47.31, 59.74, 62.55, 127.05, 129.01, 131.81, 134.57, 158.52; $[\alpha]^{25}_D$ −16 (*c* 1.0, cyclohexane). Found: C, 68.54; H, 8.74%. Calcd for $C_{20}H_{31}NO_2S$: C, 68.73; H, 8.94%.

(*R*)-4-Phenyl-3-[2-(phenylsulfanyl)octyl]oxazolidin-2-one (7d): < The faster moving band: R_f = 0.46, hexane/ethyl acetate = 3/1> IR (neat) 2928, 1756, 1458, 1439, 1411, 1232, 1168, 1088, 1039, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (t, J = 7.0 Hz, 3H), 1.19-1.32 (m, 6H), 1.36-1.48 (m, 2H), 1.50-1.62 (m, 2H), 2.81 (dd, J = 14.5, 8.0 Hz, 1H), 3.40-3.47 (m, 1H), 3.64 (dd, J = 14.5, 7.0 Hz, 1H), 4.06 (dd, J = 8.5, 6.0 Hz, 1H), 4.35 (dd, J = 9.0, 8.5 Hz, 1H), 4.89 (dd, J = 9.0, 6.0 Hz, 1H), 7.15-7.26 (m, 7H), 7.35-7.41 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 14.02, 22.53, 26.54, 29.04, 31.58, 32.40, 46.59, 47.08, 60.71, 69.89, 126.56, 127.06, 128.95, 129.09, 129.33, 130.44, 134.98, 137.85, 158.26; $[\alpha]^{25}_D$ -28 (*c* 0.63, $CDCl_3$). HRMS Found: 383.1919 (Δ = +0.0 ppm); Calcd for $C_{23}H_{29}NO_2S$: 383.1919 $[M]^+$. < The slower moving band: Rf = 0.42, hexane/ethyl acetate = 3/1> IR (neat) 2928, 1756, 1459, 1438, 1414, 1214, 1168, 1089, 1039, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (t, J = 7.0 Hz, 3H), 1.15-1.37 (m, 7H), 1.41-1.53 (m, 2H), 1.56-1.65 (m, 1H), 3.01-3.08 (m, 2H), 3.51-3.59 (m, 1H), 4.09 (dd, J = 9.0, 6.5 Hz, 1H), 4.41 (dd, J = 9.0, 9.0 Hz, 1H), 4.62 (dd, J = 9.0, 6.5 Hz, 1H), 7.18-7.32 (m, 7H), 7.36-7.41 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 14.02, 22.53, 26.73, 28.94, 31.59, 31.92, 46.96, 47.10, 60.66, 69.83, 126.95, 127.05, 128.97, 129.21, 129.31, 131.69, 134.58, 137.79, 158.80; $[\alpha]^{25}_D$ −47 (*c* 0.81, $CDCl_3$). HRMS Found: 383.1918 (Δ = −0.3 ppm); Calcd for $C_{23}H_{29}NO_2S$: 383.1919 $[M]^+$.

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