Synthesis of vinyl sulfides using glycerol as a recyclable solvent

Eder J. Lenardão, Márcio S. Silva, Renata G. Lara, Júnior M. Marczewski, Maraisa Sachini, Raquel G. Jacob, Diego Alves, and Gelson Perin*

Instituto de Química e Geociências, LASOL, Universidade Federal de Pelotas, UFPel, P.O. Box 354, 96010-900 Pelotas, RS, Brazil
E-mail: gelson_perin@ufpel.edu.br

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Abstract
A new, clean, and efficient protocol is described for the hydrothiolation of terminal alkynes promoted by KF/Al_2O_3, using glycerol as recyclable solvent. This improved method furnishes selectively the corresponding *anti*-Markovnikov vinyl sulfides in good to excellent yields starting from terminal alkynes and aliphatic or aromatic thiols. The irradiation with microwaves facilitated the procedure and accelerates the reaction. The catalytic system and the glycerol can be re-used up to four times without previous treatment, and with comparable activity.

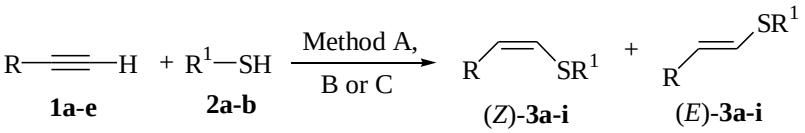
Keywords: Microwave-assisted, hydrothiolation, glycerol, KF/alumina

Introduction

Vinyl sulfides are present in natural occurring compounds such as griseoviridin and benzylthiocredillidone, with important biological activities.[1,2] The first compound is a type A streptogramin antibiotic, firstly isolated from *Streptomyces graminofaciens*,[1] while benzylthiocredillidone is a yellow pigment isolated from the brightly red colored sponge *Crella spinulata*.[2] Besides, vinyl sulfides are a very useful tool in organic reactions, acting as key intermediate in organic synthesis.[3] Various methods are described for the preparation of vinyl sulfides and the most common protocols involve the addition of thiol, or the respective anions, to terminal or internal alkynes.[4-10] Most of the described methods make use of toxic organic solvents and are catalyzed by transition-metals[4] or promoted by base.[5] More recently, some improvements on selective preparation of vinyl sulfides have been described.[6-11] These comprise the use of catalytic phenylselenenyl bromide,[6] nickel,[7] gold[8] or native silica nanoparticle[9] under solvent-free conditions, β-cyclodextrin in the presence of water and acetone[10] or under catalyst-free conditions.[11] In recent years, the use of potassium fluoride supported on alumina (KF/Al_2O_3) as a green catalytic system for a number of transformations has been increased.[12] By using

KF/Al_2O_3, the products can be easily isolated by filtration and the generation of large amounts of salts at the end of the synthesis, as well as the use of stoichiometric strong bases, can be avoided. On the other hand, the development of green solvents from renewable resources has gained much interest recently, because of the extensive use of solvents in almost all of the chemical industry, and of the predicted disappearance of fossil oil.[13] The wanted characteristics for a green solvent include no flammability, high availability, obtaining from renewable sources and biodegradability.[14] Thus, the use of glycerol as a promising medium for organic reactions was recently demonstrated by us[15,16] and others.[17-21] These include Pd-catalyzed Heck[17-19] and Suzuki[17] cross-couplings, base[18] and acid[15] promoted condensations, catalytic hydrogenation[19,20] and asymmetrical reduction.[19]

More recently, we have described several efficient approaches using KF/Al_2O_3.[22,23] As a continuation of our studies we report herein the full results of the hydrothiolation of alkynes **1** using KF/Al_2O_3 without any solvent (Method A),[22] as well as the use of glycerol as recyclable solvent for this reaction (Scheme 1).



Scheme 1

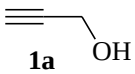
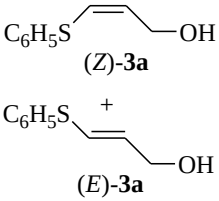
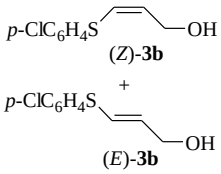
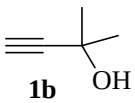
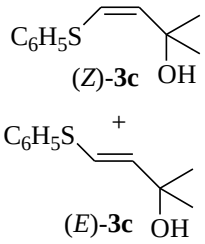
Results and Discussion

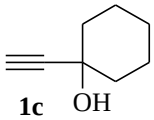
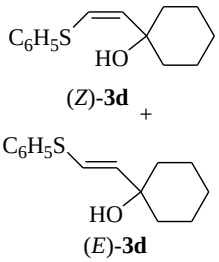
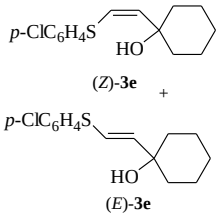
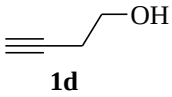
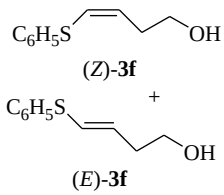
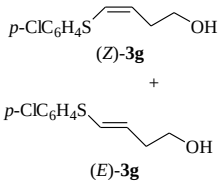
In a recent communication, we described the optimum conditions to perform the solvent-free hydrothiolation of several alkynes using KF/Al_2O_3 as solid catalyst.[22] It was found that the best conditions for the hydrothiolation consists in stirring a mixture of **1a** (2 mmol) and **2a** (1 mmol) in presence of 0.08g (51 mol%) of KF/Al_2O_3 (40%) at gently heating (60 ˚C) and under N_2 atmosphere, (Table 1, entry 1).

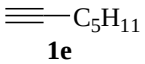
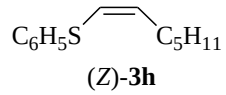
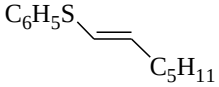
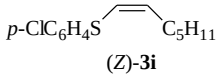
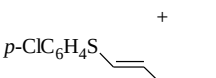
Despite the good yields and generality of the solvent-free protocol described above, the method is restricted to thiols and/or alkynes that are liquid at room temperature or with low melting points. To circumvent this limitation, but maintaining our focal point, i.e., a cleaner procedure for the hydrothiolation, we decide to expand the studies using of a recyclable solvent. Thus, glycerol, a renewable feed-stock which is easily available as a co-product in biodiesel production, was studied as a solvent in this reaction (Method B, Table 1). The best yields were obtained when a mixture of the alkyne **1** (1.0 mmol) and the thiol **2** (1.0 mmol) and KF/Al_2O_3 (40%, 0.08 g) in glycerol (3 mL), was vigorously stirred at 90 °C for 2-6 hours (Method B, Table 1). Thus, by using glycerol as solvent, benzenethiol **2a** reacted with propargyl alcohol **1a** to afford the respective adduct **3b** in 80% yield after stirring at 90 °C for 2 hours, a 25% increasing in yield, compared with the solvent-free protocol (Table 1, entries 1 and 2). This augmentation in

yield was observed for all the tested examples, indicating that glycerol is a very good solvent for this reaction. Aiming to reduce the reaction time, the mixture in glycerol was irradiated with focused microwaves at the same temperature (90 °C, Method C). It was observed complete consume of thiol **1a** after irradiation for 10 min and **3a** was obtained in 95% yield (Table 1, entry 3).

Table 1. Hydrothiolation of alkynes using KF/Al_2O_3 and glycerol

Entry	Alkyne **1**	Product **3**	Method[a]	Time	Ratio[b] *Z*:*E*	Yield,[c] %
1	 **1a**	 (*Z*)-**3a** + (*E*)-**3a**	A[22]	3.5 h	86 : 14	63 (64:36)[d]
2	**1a**	**3a**	B	2 h	62 : 38	80 (87:13)[d]
3	**1a**	**3a**	C	10 min	65 : 35	95 (91:9)[d]
4	**1a**	 (*Z*)-**3b** + (*E*)-**3b**	A[22]	1 h	75 : 25	57 (51:49)[d]
5	**1a**	**3b**	B	2.5 h	66 : 34	94 (95:5)[d]
6	**1a**	**3b**	C	10 min	67: 33	97 (96 :4)[d]
7	 **1b**	 (*Z*)-**3c** + (*E*)-**3c**	A[22]	4 h	31 : 69	90 (93 :7)[d]
8	**1b**	**3c**	B	3 h	33 : 67	87 (98 :2)[d]
9	**1b**	**3c**	C	15 min	45 : 55	91 (95 :5)[d]

10	 **1c**	 (*Z*)-**3d** + (*E*)-**3d**	A[22]	3 h	13 : 87	56 (94 :6)[d]
11	**1c**	**3d**	B	3 h	37 : 63	75 (84:16)[d]
12	**1c**	**3d**	C	30 min	44 : 56	81 (82:18)[d]
13	**1c**	 (*Z*)-**3e** + (*E*)-**3e**	A[22]	5 h	20 : 80	63 (93 :7)[d]
14	**1c**	**3e**	B	4 h	30 : 70	78 (98 :2)[d]
15	**1c**	**3e**	C	30 min	30 : 70	82 (99 : 1)[d]
16	 **1d**	 (*Z*)-**3f** + (*E*)-**3f**	A[22]	2 h	53 : 47	62 (92 : 8)[d]
17	**1d**	**3f**	B	3 h	52 : 48	84 (85:15)[d]
18	**1d**	**3f**	C	25 min	54 : 46	72 (91 : 9)[d]
19	**1d**	 (*Z*)-**3g** + (*E*)-**3g**	A[22]	2 h	50 : 50	55 (54 : 46)[d]
20	**1d**	**3g**	B	2 h	52 : 48	80 (92 : 8)[d]
21	**1d**	**3g**	C	25 min	54 : 46	79 (87:13)[d]

22	 **1e**	 (*Z*)-**3h** +  (*E*)-**3h**	A[22]	5.5 h	48 : 52	52 (100:0)[d]
23	**1e**	**3h**	B	4.5 h	44 : 56	87 (100:0)[d]
24	**1e**	**3h**	C	30 min	46 : 54	88 (100:0)[d]
25	**1e**	 (*Z*)-**3i** +  (*E*)-**3i**	A[22]	7 h	45 : 55	53 (100:0)[d]
26	**1e**	**3i**	B	6 h	64 : 36	89 (100: 0)[d]
27	**1e**	**3i**	C	30 min	56 : 44	82 (100: 0)[d]

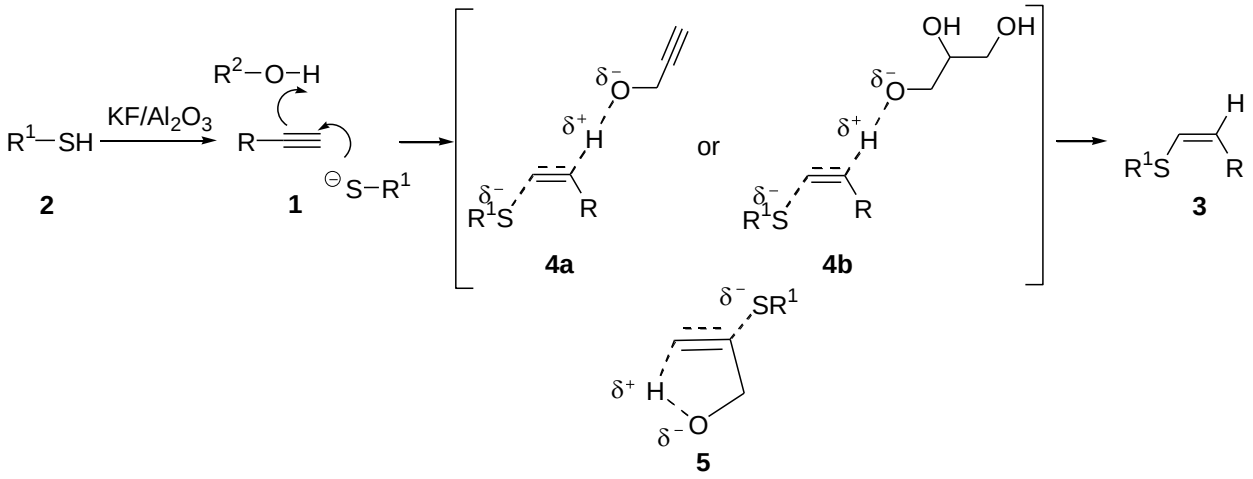
[a]**Method A.**[22] The experiments were performed at 60 °C. **Method B**: The experiments were performed at 90 °C using glycerol (3 mL/mmol) as solvent. **Method C**: The experiments were performed using glycerol and MW at 90 °C. [b]Determined by ^{1}H NMR of the crude reaction mixture and confirmed after isolation of the mixture of formed isomers. [c]Yields of the mixture of isomers obtained by column chromatography eluting with hexanes **3h**-**3i** or with hexane/ethyl acetate **3a**-**3g** (98:2). [d]The regioselectivity of the hydrothiolation (the ratio of anti-Markovnikov to Markovnikov adducts).

Concerning the stereochemistry of products, for all the studied examples, the anti-Markovnikov adduct **3** were obtained in higher amount than the Markovnikov one. The results depicted in Table shown that glycerol was an excellent solvent, affording the vinyl sulfides in better yields and with a very good selectivity for the anti-Markovnikov adducts, compared to the solvent-free protocol. This higher selectivity is evident for the alkynes **1a** and **1d** (Table 1, entries 1, 3, 4, 6, 19 and 21).

To check the efficacy of this method, a reuse study of the glycerol/KF/Al_2O_3 medium was carried out for the model reaction involving propargyl alcohol **1a** and benzenethiol **2a**. After completion of the hydrothiolation of **1a**, the product was extracted simply by washing the reaction mixture with three portions of hexanes. The remained lower phase containing glycerol/KF/Al_2O_3 was then recovered, dried under vacuum and reused for further reactions. Fortunately, the catalytic system maintained a good level of efficiency after being reused by five times (95%, 94%, 90%, 89% and 80% yield of **3a**). However, after the fifth reuse, the catalytic

system loose drastically its activity, affording **3a** in only 53% and 42% yields after successive cycles.

A tentative mechanism for explaining the regiochemistry of the hydrothiolation is depicted in Scheme 2. The formation of the Markovnikov adduct starting from propargyl alcohols suggests that the transition state **5** can be involved, while the formation of the *anti*-Markovnikov adduct involves the intermediate **4**. This proposition is corroborated by the increasing in the ratio *anti*-Markovnikov: Markovnikov adduct when glycerol is used as solvent, via a transition state like **4b**.



Scheme 2

Conclusions

In summary, an efficient and clean protocol was developed for the selective synthesis of vinyl sulfides using KF/Al_2O_3 and glycerol as recyclable solvent. The reaction proceeds easily and the products were obtained in good to excellent yields. Glycerol was successfully used as a renewable, non-toxic, and recyclable solvent, opening new possibilities for future applications of glycerol in green and sustainable chemistry. The procedure is very simple and the solvent/catalyst system can be directly re-used. The use of microwaves accelerates the reaction with comparable yields in most of examples. Applications of glycerol in other organic reactions are ongoing in our laboratory.

Experimental Section

General. The ^{1}H- and ^{13}C- NMR spectra of $CDCl_3$ solutions were recorded with a 200 MHz or a 400 MHz spectrometer (Bruker DPX), as noted. Spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$ (for ^{13}C spectra) or tetramethylsilane (TMS, for ^{1}H) as the internal reference. Data are reported as follows: chemical shift (δ), multiplicity, coupling constant *(J)* in Hertz and peak intensity. Low Resolution Mass Spectra (LRMS, EI) were obtained at 70 eV with a Hewlett Packard EM/CG HP-5988A spectrometer. High-Resolution Mass Spectra: HR-ESI-MS were performed in the positive mode (UltrOTOF-Q system, version 1.10, Bruker Daltonics, MA, USA). Merck's silica gel (230-400 mesh) was used for flash chromatography. All microwave tests were conducted using a CEM Discover, mode operating systems working at 2.45 GHz, with a power programmable from 1 to 300 W.

General preparation of alumina- supported potassium fluoride.[22-24] To a 100 mL beaker was added alumina (6.0 g of Al_2O_3 90, 0.063-0.200 mm, Merck), $KF.2H_2O$ (5.2 g) and water (10 mL). The suspension was stirred for 1 h at 65 °C, dried at 80 °C for 1 h and for an additional 4 h at 300 °C in an oven and then cooled in a desiccator. The content of KF is about 40% (m/m).

General procedure for the synthesis of vinyl sulfides 3

Method A.[22] To a mixture of appropriate alkyne **1** (2 mmol) and thiol **2** (1 mmol) under N_2 atmosphere, KF/Al_2O_3 (0.08g, obtained as described above) was added at room temperature. Then, the temperature was slowly raised to 60 °C. The reaction progress was followed by TLC. After consuming the starting materials (see Table 1), the crude product was filtered off the solid supported catalyst by washing with ethyl acetate (10 mL). The solvent was evaporated under reduced pressure and the residue was purified by column chromatography over silica gel eluting with hexanes **3h-3i** or with hexane/ethyl acetate **3a-3g** (98:2), yielding the products, according Table 1.

Method B. To a mixture of appropriate alkyne **1** (1 mmol) and thiol **2** (1 mmol) in glycerol (3 mL) under stirring and N_2 atmosphere, was added KF/Al_2O_3 (0.08 g) at room temperature. Then, the temperature was slowly raised to 90 °C. The reaction progress was followed by TLC. After consuming the starting materials (see Table 1), the product was extracted from the glycerol by washing the mixture with hexanes (3 × 5 mL). The hexanes were evaporated under reduced pressure and the residue was purified according to that described in Method A.

Method C. To a mixture of appropriate alkyne **1** (1 mmol) and thiol **2** (1 mmol) in glycerol (3 mL) under stirring and N_2 atmosphere, was added KF/Al_2O_3 (0.08 g) at room temperature in a 10 mL glass tube. The vessel was then sealed with a septum, placed into the microwave cavity and irradiated with stirring at 90 °C for the time given in Table 1. After allowing the mixture to cool to room temperature, the reaction vessel was opened and the product was purified according to described in Method A. The remaining mixture of glycerol and KF/Al_2O_3 was re-used up to 7

times by the simple addition of more thiol and alkyne to the remaining mixture in the reaction vessel. Spectral data of vinyl sulfides prepared are listed below.

3-(Phenylthio)prop-2-en-1-ol (3a).[25] ^{1}H NMR (400 MHz, $CDCl_3$) δ *Z* isomer: 7.21-7.42 (m, 5H); 6.35 (dt, *J* 9.2 and 1.2, 1H); 5.96 (dt, *J* 9.2 and 6.6, 1H); 4.37 (dd, *J* 6.6 and 1.2, 2H); 1.92 (broad s, 1H); *E* isomer: 7.21-7.42 (m, 5H); 6.46 (dt, *J* 15.6 and 1.2, 1H); 5.95 (dt, *J* 15.6 and 6.8, 1H); 4.20 (dd, *J* 6.8 and 1.2, 2H); 1.92 (broad s, 1H); Markovnikov adduct: 7.21-7.42 (m, 5H); 5.57 (s, 1H); 5.24 (s, 1H); 4.16 (s, 2H); 1.92 (broad s, 1H).

3-(4-Chlorophenylthio)prop-2-en-1-ol (3b). ^{1}H NMR (400 MHz, $CDCl_3$) δ *Z* isomer: 7.26-7.37 (m, 4H); 6.29 (dt, *J* 9.2 and 1.2, 1H); 5.99 (dt, *J* 9.2 and 6.4, 1H); 4.36 (dd, *J* 6.4 and 1.2, 2H); 1.63 (broad s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 63.9, 125.5, 127.8, 129.1, 132.8, 133.5, 170.3; *E* isomer: 7.26-7.37 (m, 4H); 6.41 (dt, *J* 15.2 and 1.2, 1H); 5.97 (dt, *J* 15.2 and 5.6, 1H); 4.21 (dd, *J* 5.6 and 1.2, 2H); 1.88 (broad s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 65.1, 118.0, 128.4, 129.2, 132.4, 134.0, 169.9; Markovnikov adduct: 7.26-7.37 (m, 4H); 5.60 (s, 1H); 5.25 (s, 1H); 4.15 (s, 2H); 1.64 (broad s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 60.8, 125.9, 129.0, 130.5, 131.4, 133.3, 170.4; MS *m*/*z* (rel. int., %) *Z* isomer: MS *m*/*z* (rel. int., %) 200 (M^+, 13.8), 182 (28.0), 144 (72.8); 99 (82.4), 43 (100.0); *E* isomer: 201 (M^+ +1, 7.6), 181 (30.3), 144 (96.1); 99 (42.6), 43 (100.0); Markovnikov adduct: 201 (M^+ + 1, 6.7), 183 (23.9), 144 (88.7), 43 (100.0). HRMS (ESI): *m/z* Calcd for C_9H_9ClOS $[M + H]^+$: 222.9960. Found: 223.0980.

2-Methyl-4-(phenylthio)but-3-en-2-ol (3c). ^{1}H NMR (400 MHz, $CDCl_3$) δ *Z* isomer: 7.22-7.45 (m, 5H); 6.19 (d, *J* 10.6 1H); 5.80 (d, *J* 10.6, 1H); 1.85 (broad s, 1H); 1.45 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.4, 29.6, 54.3, 123.0, 126.7, 128.9, 129.5, 133.2, 135.1; *E* isomer: 7.22-7.45 (m, 5H); 6.41 (d, *J* 15.0 1H); 5.99 (d, *J* 15.0, 1H); 1.78 (broad s, 1H); 1.35 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.4, 29.8, 72.0, 116.0, 123.2, 126.8, 129.0, 129.7, 134.5; Markovnikov adduct:[7,26] 7.26-7.37 (m, 4H); 5.45 (s, 1H); 4.72 (s, 1H); 2.21 (broad s, 1H); 1.51 (s, 6H); MS *m*/*z* (rel. int., %) *Z* isomer: 194 (M^+, 11.9), 135 (100.0), 77 (16.4); *E* isomer: 193 (M^+ - 1, 2.3), 110 (24.3), 82 (100.0); Markovnikov adduct: 194 (5.8), 110 (100.0), 77 (4.3). HRMS (ESI): *m/z* Calcd for $C_{11}H_{14}OS$ $[M + Na]^+$, 217.0663. Found: 217.0661.

1-(1-Phenylsulfanylvinyl)cyclohexanol (3d). ^{1}H NMR (400 MHz, $CDCl_3$) δ *Z* isomer: 7.16-7.37 (m, 5H); 6.22 (d, *J* 10.0, 1H); 5.77 (d, *J* 10.0, 1H); 2.09 (broad s, 1H), 1.20-1.80 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 23.0, 25.0, 39.7, 72.2, 123.6, 126.7, 128.9, 129.2, 135.4, 136.2; *E* isomer: 7.16-7.37 (m, 5H); 6.44 (d, *J* 15.2, 1H); 6.00 (d, *J* 15.2, 1H); 2.47 (broad s, 1H); 1.20-1.80 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.9, 25.3, 37.8, 72.0, 121.2, 126.5, 128.9, 129.2, 129.5, 140.6. Markovnikov adduct:[26,27] 7.16-7.37 (m, 5H); 5.48 (s, 1H); 4.76 (s, 1H); 2.47 (broad s, 1H); 1.20-1.80 (m, 10H); MS *m*/*z* (rel. int., %) *Z* isomer: 234 (M^+, 34.1), 216 (50.4), 139 (79.6), 79 (100.0); *E* isomer: 234 (M^+, 43.3), 216 (71.9), 139 (93.2), 79 (100.0); Markovnikov adduct: 234 (M^+ 34.6), 135 (100.0), 91 (55.5). HRMS (ESI): *m/z* Calcd for $C_{14}H_{18}OS$ $[M + Na]^+$: 257.0976; Found: 257.0973.

1-[1-(4-Chlorophenyl)sulfanylvinyl]cyclohexanol (3e). ^{1}H NMR (400 MHz, $CDCl_3$) δ *Z* isomer: 7.25-7.26 (m, 4H); 6.15 (d, *J* 10.2, 1H); 5.79 (d, *J* 10.2, 1H); 2.16 (broad s, 1H); 1.25-2.16 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.2, 24.3, 25.2, 73.0, 116.6, 128.9, 129.3, 130.2,

135.2, 136.5; *E* isomer: 7.25-7.26 (m, 4H); 6.40 (d, *J* 15.2, 1H); 6.02 (d, *J* 15.2, 1H); 2.13 (broad s, 1H); 1.25-2.16 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.9, 23.0, 25.0, 72.0, 123.1, 129.0, 129.8, 130.7, 134.4, 138.4; Markovnikov adduct: 7.25-7.26 (m, 4H); 5.52 (s, 1H); 4.78 (s, 1H); 1.90 (broad s, 1H); 1.25-2.16 (m, 10H). MS *m*/*z* (rel. int., %) *Z* isomer: 270 (M^+ + 2, 9.3), 268 (M^+, 23.0), 139 (64.0), 79 (100.0); *E* isomer: 270 (M^+ + 2, 8.2), 268 (M^+, 21.6), 139 (3.7), 79 (100.0); Markovnikov adduct: 270 (M^+ + 2, 10.5), 268 (M^+, 27.8), 170 (42.7), 135 (100.0), 81 (91.2). HRMS (ESI): *m/z* Calcd for $C_{14}H_{17}ClOS$ $[M + Na]^+$: 291.0586; Found: 291.0572.

4-(Phenylthio)but-3-en-1-ol (3f).[28] ^{1}H NMR (400 MHz, $CDCl_3$) δ *Z* isomer: 7.15-7.43 (m, 5H); 6.31 (dt, *J* 9.6 and 1.6, 1H); 5.83 (dt, *J* 9.6 and 6.4, 1H); 3.65 (t, *J* 6.4, 2H); 2.56 (broad s, 1H); 2.47-2.53 (m, 2H); *E* isomer: 7.15-7.43 (m, 5H); 6.24 (dt, *J* 15.2 and 1.6, 1H); 5.90 (dt, *J* 15.2 and 6.8, 1H); 3.69 (t, *J* 6.8, 2H); 2.56 (broad s, 1H); 2.35-2.41 (m, 2H); Markovnikov adduct:[7] 7.15-7.43 (m, 5H); 5.23 (s, 1H); 4.99 (s, 1H); 3.76 (t, *J* 6.4, 2H); 2.56 (broad s, 1H); 2.47-2.53 (m, 2H). MS *m*/*z* (rel. int., %) *Z* isomer: 180 (M^+, 49.1), 149 (100.0), 116 (83.0); *E* isomer: 180 (M^+, 49.1), 149 (100.0), 116 (83.0); Markovnikov adduct: 180 (M^+, 12.9), 135 (84.7), 110 (100.0).

4-(4-Chlorophenylthio)but-3-en-1-ol (3g). ^{1}H NMR (200 MHz, $CDCl_3$) δ *Z* isomer: 7.24-7.26 (m, 4H); 6.28 (dt, *J* 9.6 and 1.0, 1H); 5.88 (dt, *J* 9.6 and 6.6, 1H); 3.71 (t, *J* 6.6, 2H); 2.36-2.57 (m, 2H); 1.96 (broad s, 1H); *E* isomer: 7.24-7.26 (m, 4H); 6.22 (dt, *J* 15.2 and 1.2, 1H); 5.93 (dt, *J* 15.2 and 6.6, 1H); 3.71 (t, *J* 6.6, 2H); 2.36-2.57 (m, 2H); 1.96 (broad s, 1H); Markovnikov adduct: 7.32-7.34 (m, 4H); 5.27 (s, 1H); 5.02 (s, 1H); 3.76 (t, *J* 6.6, 2H); 2.36-2.57 (m, 2H); 2.03 (broad s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ *Z* + *E* + Markovnikov adduct: 28.6, 32.3, 39.1, 59.1, 62.9, 63.1, 124.0, 125.3, 125.4, 128.7, 129.1, 129.2, 129.3, 129.4, 130.1, 130.2, 131.1, 131.6, 132.4, 134.2, 134.3, 134.4. MS *m*/*z* (rel. int., %) *Z* isomer: 216 (M^+ + 2, 26.1), 214 (M^+, 69.4), 183 (100.0), 148 (99.1); *E* isomer: 216 (M^+ + 2, 26.1), 214 (M^+, 69.4), 183 (100.0), 148 (99.1); Markovnikov adduct: 214 (M^+, 33.5), 144 (100.0), 109 (60.2). HRMS (ESI): *m/z* Calcd for $C_{10}H_{11}ClOS$ $[M + Na]^+$: 237.0117; Found: 237.0117.

Hept-1-enyl(phenyl)sulfide (3h). ^{1}H NMR (200 MHz, $CDCl_3$) δ *Z* isomer: 7.13-7.50 (m, 5H); 6.18 (d, *J* 9.2, 1H); 5.82 (dt, *J* 9.2 and 6.4, 1H); 2.10-2.30 (m, 2H); 1.30-1.47 (m, 6H); 0.90 (t, *J* 6.4, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0, 22.5, 29.1, 31.4, 33.0, 126.0, 127.1, 128.7, 128.9, 129.1, 137.8; *E* isomer: 7.13-7.50 (m, 5H); 6.13 (d, *J* 15.0, 1H); 5.99 (dt, *J* 15.0 and 6.2, 1H); 2.10-2.30 (m, 2H); 1.30-1.47 (m, 6H); 0.90 (t, *J* 6.2, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0, 22.4, 28.7, 31.3, 33.0, 126.0, 127.5, 128.4, 128.9, 129.0, 132.7. MS *m*/*z* (rel. int., %) *Z* isomer: 206 (M^+, 63.0), 149 (96.6), 110 (100.0), 55 (81.3); *E* isomer: 206 (M^+, 66.2), 149 (100.0), 110 (93.7), 55 (77.6). HRMS (ESI): *m/z* Calcd for $C_{13}H_{19}S$ $[M + H]^+$: 207.1207; Found: 207.1202.

(4-Chlorophenyl)(hept-1-enyl)sulfide (3i). ^{1}H NMR (400 MHz, $CDCl_3$) δ *Z* isomer: 7.20-7.26 (m, 4H); 6.10 (dt, *J* 10.4 and 1.2, 1H); 5.84 (dt, *J* 10.4 and 7.2, 1H); 2.25 (q, *J* 7.2, 2H); 1.31-1.43 (m, 6H); 0.92 (t, *J* 7.2, 3H); *E* isomer: 7.20-7.26 (m, 4H); 6.07 (d, *J* 15.2, 1H); 6.0 (dt, *J* 15.2 and 7.2, 1H); 2.17 (q, *J* 7.2, 2H); 1.31-1.43 (m, 6H); 0.91 (t, *J* 7.2, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ *Z* + *E*: 14.0, 22.4, 22.43, 28.5, 28.6, 29.0, 31.2, 31.3, 33.0, 120.0, 121.8, 128.9, 129.0, 129.1, 129.2, 129.4, 129.7, 133.5, 134.0, 134.6, 135.0, 138.8. MS *m*/*z* (rel. int., %) *Z*

isomer: 240 (M^+, 43.5), 183 (49.7), 55 (100.0); *E* isomer: 242 (M^+ + 2, 16.0), 240 (M^+, 42.3), 183 (46.5), 148 (75.9), 55 (100.0). HRMS (ESI): *m/z* Calcd for $C_{13}H_{17}ClS$ $[M + H]^+$: 263.0637; Found: 262.9876.

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References

1. (a) Marcantoni, E.; Massaccesi, M.; Petrini, M. *J. Org. Chem.* **2000**, *65*, 4553; (b) Kuligowski, C.; Bezzenine-Lafollée, S.; Chaume, G.; Mahuteau, J.; Barrière, J.-C.; Bacqué, E.; Pancrazi, A.; Ardisson, J. *J. Org. Chem.* **2002**, *67*, 4565.
2. Lan, H. W; Cooke, P. A.; Pattenden, G.; Bandaranayake, W. M.; Wickramasinghe, W. A. *J. Chem. Soc., Perkin Trans. 1* **1999**, 847.
3. For the synthetic utility of vinyl sulfides, see, for example: (a) Aucagne, V.; Lorin, C.; Tatibouët, A.; Rollin, P. *Tetrahedron Lett*. **2005**, *46*, 4349. (b) Muraoka, N.; Mineno, M.; Itami, K.; Yoshida, J.-I. *J. Org. Chem.* **2005**, *70*, 6933. (c) Woodland, C. A.; Crawley, G. C.; Hartley, R. C. *Tetrahedron Lett*. **2004**, *45*, 1227. (d) McReynolds, M. D.; Dougherty, J. M.; Hanson, P. R. *Chem. Rev*. **2004**, *104*, 2239. (e) Oae, S. *Organic Sulfur Chemistry: Structure and Mechanism*; CRC Press: Boca Raton, FL, 1991; Cremlyn, R. J. *An Introduction to Organosulfur Chemistry*; Wiley & Sons: New York, 1996.
4. (a) Kondo, T.; Mitsudo, T. *Chem. Rev*. **2000**, *100*, 3205. (b) Cao, C.; Fraser, L. R.; Love, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 17614. (c) Weiss, C. J.; Wobser, S. D.; Marks, T. J. *J. Am. Chem. Soc.* **2009**, *131*, 2062. (d) Ogawa, A.; Ikeda, T.; Kimura, K.; Hirao, T. *J. Am. Chem. Soc.* **1999**, *121*, 5108. (e) Malyshev, D. A.; Scott, N. M.; Marion, N.; Stevens, E. D.; Ananikov, V. P.; Beletskaya, I. P.; Nolan, S. P. *Organometallics* **2006**, *25*, 4462.
5. (a) Waters, M. S.; Cowen, J. A.; McWilliams, J. C.; Maligres, P. E.; Askin, D. *Tetrahedron Lett*. **2000**, *41*, 141. (b) Dabdoub, M. J.; Dabdoub, V. B.; Lenardão, E. J.; Hurtado, G. R.; Barbosa, S. L.; Guerrero Jr., P. G.; Nazário, C. E. D.; Viana, L. H.; Santana, A. S.; Baroni, A. C. M. *Synlett* **2009**, 986. (c) Wadsworth, D. H.; Detty, M. R. *J. Org. Chem.* **1980**, *45*, 4611.
6. Manarin, F.; Roehrs, J. A.; Prigol, M.; Alves, D.; Nogueira, C. W.; Zeni, G. *Tetrahedron Lett*. **2007**, *48*, 4805.
7. Ananikov, V. P.; Orlov, N. V.; Beletskaya, I. P. *Organometallics* **2006**, *25*, 1970.
8. Corma, A.; González-Arellano, C.; Iglesias, M.; Sánchez, F. *Appl. Catal. A: Gen.* **2010**, *375*, 49.

9. Banerjee, S.; Das, J.; Santra, S. *Tetrahedron Lett*. **2009**, *50*, 124.
10. Sridhar, R.; Surendra, K.; Krishnaveni, N. S.; Srinivas, B.; Rao, K. R. *Synlett* **2006**, 3495.
11. Schneider, C. C.; Godoi, B.; Prigol, M.; Nogueira, C. W.; Zeni, G. *Organometallics* **2007**, *26*, 4252.
12. Basu, B.; Das, P.; Das, S. *Curr. Org. Chem.* **2008**, *12*, 141; Blass, B. E. *Tetrahedron* **2002**, *58*, 9301.
13. (a) Handy, S. T. *Chem. Eur. J.* **2003**, *9*, 2938. (b) Leitner, W. *Green Chem.* **2007**, *9*, 923; (c) Horváth, I. T. *Green Chem.* **2008**, *10*, 1024. (d) Giovanni, I.; Silke, H.; Dieter, L.; Burkhard, K. *Green Chem.* **2006**, *8*, 1051. (e) Clark, J. H. *Green Chem.* **1999**, *1*, 1 and references cited therein.
14. Nelson, W. M. *Green Solvents for Chemistry: Perspectives and Practice*, Oxford University Press: Oxford, 2003.
15. Silveira, C. C.; Mendes, S. R.; Líbero, F. M.; Lenardão, E. J.; Perin, G. *Tetrahedron Lett.* **2009**, *50*, 6060.
16. (a) Lenardão, E. J.; Trecha, D. O.; Ferreira, P. C.; Jacob, R. G.; Perin, G. *J. Braz. Chem. Soc.* **2009**, *20*, 93. (b) Lenardão, E. J.; Silva, M. S.; Sachini, M.; Lara, R. G.; Jacob, R. G.; Perin, G. *Arkivoc* **2009**, (*xi)*, 221-227. (c) Perin, G.; Mello, L. G.; Radatz, C. S.; Savegnago, L.; Alves, D.; Jacob, R. G.; Lenardão, E. J. *Tetrahedron Lett.* **2010**, *51*, 4354.
17. Wolfson, A.; Dlugy, C. *Chem. Pap.* **2007**, *61*, 228.
18. Wolfson, A.; Litvak, G.; Dlugy, C. Shotland, Y; Tavor, D. *Ind. Crops Prod.* **2009**, *30*, 78.
19. Wolfson, A.; Dlugy, C.; Shotland, Y. Environ. *Chem. Lett*. **2007**, *5*, 67.
20. Wolfson, A.; Dlugy, C.; Shotland, Y; Tavor, D. *Tetrahedron Lett*. **2009**, *50*, 5951.
21. (a) He, F.; Li, P.; Gu, Y.; Li, G. *Green Chem.* **2009**, *11*, 1767. (b) Karam, A.; Villandier, N.; Delample, M.; Koerkamp, C. K.; Douliez, J.-P.; Granet, R.; Krausz, P.; Barrault, J.; Jérôme, F. *Chem. Eur. J*. **2008**, *14*, 10196. (c) Gu, Y.; Barrault, J.; Jérôme, F. *Adv. Synth. Catal*. **2008**, *350*, 2007.
22. Silva, M. S.; Lara, R. G.; Marczewski, J. M.; Jacob, R. G.; Lenardão, E. J.; Perin, G. *Tetrahedron Lett.* **2008**, *49*, 1927.
23. (a) Lenardão, E. J.; Ferreira, P. C.; Jacob, R. G.; Perin, G.; Leite, F. P. L. *Tetrahedron Lett.* **2007**, *48*, 6763. (b) Lenardão, E. J.; Lara, R. G.; Silva, M. S.; Jacob, R. G.; Perin, G. *Tetrahedron Lett.* **2007**, *48*, 7668. (c) Victoria, F. N.; Radatz, C. S.; Sachini, M.; Jacob, R. G.; Perin, G.; da Silva, W. P.; Lenardão, E. J. *Tetrahedron Lett.* **2009**, *50*, 6761.
24. Wang, S.-X.; Li, J.-T.; Yang, W.-Z.; Li, T.-S. *Ultrason. Sonochem.* **2002**, *9*, 159.
25. Ritter, R. H.; Cohen, T. *J. Am. Chem. Soc.* **1986**, *108*, 3718.
26. Kuniyasu, H.; Ogawa, A.; Sato, K.-I.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1992**, *114*, 5902.
27. Yus, M.; Gutiérrez, A.; Foubelo, F. *Tetrahedron* **2001**, *57*, 4411.
28. Ihara, M.; Katsumata, A.; Setsu, F.; Tokunaga, Y.; Fukumoto, K. *J. Org. Chem.* **1996**, *61*, 677.

