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A One-Pot Synthesis of Alkynyl Sulfides from Terminal Alkynes

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ABSTRACT: *A one-pot synthesis of alkynyl sulfide from terminal alkyne has been reported via lithiation of the alkyne, oxidative addition of sulfur, consecutively followed by the nucleophilic substitution of lithium alkynyl thiolate to various halides.* © 2011 Wiley Periodicals, Inc. Heteroatom Chem 23:105–110, 2012; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.20744

INTRODUCTION

Sulfur-containing compounds exist widely in nature and the sulfur moiety serves as important auxiliary functional group in synthetic sequences, owing to which the selective formation of C—S bonds have attached much attention in the organic synthesis [1].

Among the compounds containing sulfur groups, the alkynyl sulfides have been found to be essential building blocks in organic synthesis [2]. Because of the activity of the alkylthio group to the carbon–carbon triple bonds, alkynyl sulfides have been involved in hydrostannation [3], [2 + 2] [4] or [4 + 2] -type [5] cycloaddition, silacyclo-propenation [6], and cross-coupling reactions [7] as well as in the preparation of self-assembled monolayers in the production of composite materials [8].

In this way, some methodologies have been mentioned for the syntheses of alkynyl sulfides. The nucleophilic substitution reactions of the lithium acetylide to the RSX compounds involving an electron-withdrawing X as the leaving groups (X= tosyl [8], chloro [9], bromo [10], cyano [11],) could give the alkynyl sulfides, in which the sulfur moiety should be generated from odorous thiol. The alkynyl sulfides are also obtained *via* the reaction of terminal alkynes with phenylsulfuryl halides [9b] or dialkyl disulfides [12] as well as alkynyl bromides with disulfides [13] in the presence of copper iodide (I) in polar solvent. These conversions should be carried out in toxic solvent and with the cupric salts that are necessary. The appointed materials containing sulfur should be supplied and some of them, for instance, sulfuryl halides and the precursor thiophenol, are stenchy and highly toxic. An alternative preparation has been reported via the cleavage of an S—S bond of the disulfides by alkynyl metallic species formed in situ from terminal alkynes. However, the losing moiety of thiolate should be trapped by the extra halides to avoid further addition of the thiolate anion to the formed alkynyl sulfide to give bisphenylthio alkenes [4b,14]. The generation of the monosulfide as the byproduct is inevitable. Other protocols, such as the cleavage of 5-chloro-1, 2, 3-thiadiazoles, the dehydrobromination of vinyl sulfides, and the substitution of the silyl group in the silyl alkyne, have suffered from astricting the broad spectrum of the methodologies [15]. Owing to the

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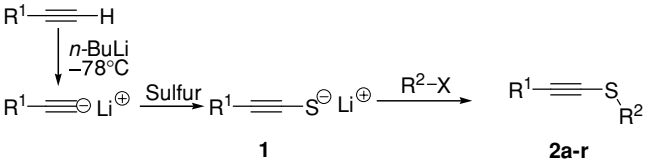

R^1 = C_6H_5 *n*-C_4H_9, *n*-C_6H_{13}
R^2 = CH_3, C_2H_5, *n*-C_3H_7, *i*-C_3H_7, *n*-C_4H_9, $CH_2C_6H_5$, $CH_2COC_6H_5$, $CH_2COOC_2H_5$
X = Cl, Br, I

SCHEME 1

above, we conceived that the elementary sulfur could be addressed as the precursor of the thio group to avoid the use of the toxic and stenchy materials and to accord with the atomic economics.

Herein, we have developed a one-pot synthesis of alkyl alkynyl sulfides from various alkyl halides and terminal alkynes. Although the preparation of lithium alkynyl thiolate is a classical way [16], there has been no report on the synthesis of the alkynyl sulfides via lithium alkynyl thiolate generated in situ from terminal alkyne and *n*-BuLi in the presence of sulfur, to the best of our knowledge. In this study, we report the ready coupling of lithium alkynyl thiolate with different alkyl halides to afford various alkynyl sulfides in good yields (Scheme 1).

RESULTS AND DISCUSSION

Our procedure is as follows. To a THF solution of lithium acetylide prepared in situ and generated from terminal acetylene and *n*-BuLi at –78°C, one equivalent of sulfur powder was added. The reaction was gradually warmed from –78°C to 0°C untill the sulfur was consumed completely to afford the red lithium alkynyl thiolate **1.** Alkyl bromide at the same temperature. The solution gradually changed to pale orange. Hydrolysis of the completed reaction mixture with saturated aqueous ammonium chloride afforded **2** (Scheme 1) in good yields based on the terminal alkynes.

Ethyl magnesium bromide was used instead of *n*-BuLi, and the disappearance of sulfur powder was also observed. However, the yield of the target product was poor, owing to the formation of some byproducts. When the reaction temperature was higher than 0°C in the step of the coupling of lithium alkynyl thiolate **1** and alkyl bromide, we could not get a good yield of the desired sulfide as a result of the polymerization of the alkyne. Both alkynl and aromatic alkyne are receivable in this protocol. Alkyl halides, which are readily available commercially are generally more varied and cheaper than alkyl thiols or disulfides [12–14]. The results are summarized in Table 1.

TABLE 1 Preparation of Alkynyl Sulfides **2**

Entry	R^1	R^2	*X*	*Product* **2**	*Time (h)*	*Yield*[a]
1	C_6H_5	CH_3	I	**2a**	3	86
2	C_6H_5	C_2H_5	Br	**2b**	4	84
3	C_6H_5	*n*-C_3H_7	Br	**2c**	4	79
4	C_6H_5	*i*-C_3H_7	Br	**2d**	4	15 (39[b])
5	C_6H_5	$CH_2C_6H_5$	Br	**2e**	3	85
6	C_6H_5	CH_2COPh	Br	**2f**	1	80
7	C_6H_5	CH_2COOEt	Br	**2g**	1	82
8	*n*-C_4H_9	CH_3	I	**2h**	3	88
9	*n*-C_4H_9	C_2H_5	Br	**2i**	4	80
10	*n*-C_4H_9	*n*-C_3H_7	Br	**2j**	5	79
11	*n*-C_4H_9	*n*-C_3H_7	Cl	—	24	—
12	*n*-C_4H_9	*i*-C_3H_7	Br	**2k**	5	14 (40[b])
13	*n*-C_4H_9	*i*-C_3H_7	I	**2k**	4	26 (47[b])
14	*n*-C_4H_9	*n*-C_4H_9	Br	**2l**	5	77
15	*n*-C_4H_9	*n*-C_4H_9	Cl	—	24	—
16	*n*-C_4H_9	*s*-C_4H_9	I	**2m**	4	33 (40[b])
17	*n*-C_4H_9	$CH_2C_6H_5$	Br	**2n**	4	79
18	*n*-C_4H_9	$CH_2C_6H_5$	Cl	**2n**	5	56
19	*n*-C_6H_{13}	CH_3	I	**2o**	4	81
20	*n*-C_6H_{13}	C_2H_5	Br	**2p**	4	72
21	*n*-C_6H_{13}	*n*-C_3H_7	Br	**2q**	5	78
22	*n*-C_6H_{13}	*n*-C_4H_9	Br	**2r**	5	75
23	*n*-C_6H_{13}	$CH_2C_6H_5$	Br	**2s**	4	74

[a]Isolated yields based on the alkynes.
[b]5 mol% of CuCl was added to the reaction.

When 2-bromophenylacetone and the 2-bromoethyl acetate (entries 6 and 7) were used as reactants, good yields were achieved and the reactions progressed faster than others. It was realized that the reaction rate of the bromide with the electron-withdrawing group was more reactive than that with the electron-donating group. The yield of **2f** and **2g** indicated the favorable chemoselectivity of nucleophilic substitution of the alkynyl thiolate to the halides rather than the nucleophilic addition to the carbonyl group and the abstraction of the active hydrogen atom in the α-position of the carbonyl group as well. The reaction of the benzyl chloride resulted in the moderate yield of benzyl alkynyl sulfide **2n** (entry 18). Yet no reaction could be detected in the case of entries 11 and 15, chain alkyl chloride, even in the presence of CuCl. As the carbon chain in R^2 became longer, the yield of the alkynyl sulfides was slightly lower (entries 1–3, entries 8–10, entry 14, and entries 19–22). However, when the Br was attached to a secondary carbon in the halide, the decline of the yield of the alkynyl sulfide was observed (entries 4 and 12), which was caused mainly by the elimination reaction of the secondary bromide. To decrease the alkalinity of the organometallic reagent, 5 mol% of CuCl was added and the yields improved markedly. When the secondary iodide was involved instead of the bromide, a better yield was obtained and the copper catalyst also led to a moderate yield (entries 13 and 16).

CONCLUSION

In summary, we have developed a one-pot synthesis of the alkynyl sulfide from sulfur simple substance, terminal alkyne, and diverse alkyl halides. All of the substances are readily and commercially available. The alkylthio moiety in the product derived from the sulfur powder and halide, avoiding the preparation of other sulfur-containing compounds. Considering both the reactivity and cost, the bromide is suitable for the primary substance and the iodide for the secondary. Therefore, this procedure has the advantages of convenience, safety, and atomic economy, owing to the avoidance of the loss of alkylthio moiety.

EXPERIMENTAL

General Information

The thermometer was uncorrected. All reactions were conducted under a slightly positive pressure of dry, prepurified nitrogen using standard Schlenk line techniques when appropriate. Standard column chromatography was performed on 300–400 meshes of silica gel using flash column chromatography techniques. All glassware, syringes, and needles were flame dried above 100°C. ^{1}H and ^{13}C NMR spectra were recorded over Bruker AdvanceDMX 400 in $CDCl_3$, using Me_4Si as the internal standard. Chemical shifts (δ) were reported in parts per million (ppm). IR spectra were recorded on BrukerTENSOR 27. Low resolution MS were carried out on Bruker Daltonics Esquire 3000 plus. HRMS were recorded on GCT Premier. Unless stated otherwise, commercial reagents were used without further purification. Solvents were purified by distillation under dry nitrogen from sodium/benzophenone (THF).

A Typical Procedure for the Preparation of Lithium Alkynyl Thiolate 1. To a THF (5 mL) solution of terminal alkyne (1.0 mmol) at –78°C was added *n*-BuLi (1.1 mmol, 1.6 M in hexane). The above reaction solution was then stirred for 1 h, to which was added 1.0 mmol of sulfur powder followed by further stirring at −78°C for 1 h. The mixture was gradually warmed to 0°C untill the sulfur was completely consumed to give red lithium alkynyl thiolate **1.**

A Typical Procedure for the Synthesis of Alkynyl Sulfide 2. To the in situ prepared lithium alkynyl thiolate **1** in THF at 0°C was added 1.0 mmol of halide via a syringe and 5 mol% of CuCl if necessary, which was monitored by TLC. Then the saturated aqueous NH_4Cl was added into the pale orange solution to quench the reaction. The inorganic layer was extracted with diethyl ether three times. The combined extract was washed with brine and dried over $MgSO_4$. After rotary evaporation, the residue was purified by column chromatograph (silica gel, petroleum ether) to afford alkynyl sulfide **2**. The reaction time and the yields are listed in Table 1. The analytical data for the products are shown as follows.

Methyl(2-phenylethynyl)sulfide (2a) [15a]

Yellow oil, isolated yield 86%; IR cm^{-1} (neat) υ 3060, 2926, 2826, 2167 (C≡C), 1595, 1500, 1440 (CH_3), 1069(C—S), 754, 689; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 2.46 (s, 3H), 7.26-7.29(m, 3H), 7.38–7.41(m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si)19.3, 80.9, 91.8, 123.3, 128.0, 128.2, 131.4; MS (EI 70 ev): m/e 57 (100), 148 (M^+, 2).

Ethyl (2-phenylethynyl) sulfide (2b) [4b]

Yellow oil, isolated yield 84%; IR cm^{-1} (neat) υ 3031, 2964, 2926, 2166 (C≡C), 1595, 1486, 1442, 1375 (CH_3), 1069 (C—S), 690, 754; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.46 (t, J = 7.2 Hz, 3H), 2.82 (q, J = 7.2 Hz, 2H), 7.26–7.31 (m, 3H), 7.40–7.43 (m, 2H); MS (EI 70 ev): m/e 91 (100), 162(M^+, 3).

(2-Phenylethynyl)propyl sulfide (2c)

Yellow oil, isolated yield 79%; IR cm^{-1} (neat) υ 3061, 2964, 2873, 2167 (C≡C), 1596, 1487, 1292, 1237, 1069 (C—S), 754, 690; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.06 (t, J = 7.2 Hz, 3H), 1.81–1.86 (m, 2H), 2.78 (t, J = 7.2 Hz, 2H), 7.25-7.42 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si)13.0, 22.7, 37.8, 79.6, 92.8, 123.6, 128.0, 128.3, 131.4; MS (EI 70 ev): m/e 57 (100), 176 (M^+, 8). HRMS: m/z for $C_{11}H_{12}S$, calcd: 176.0660. Found: 176.0669.

Isopropyl(2-phenylethynyl)sulfide (2d) [17]

Yellow oil, isolated yield 39%; IR cm^{-1} (neat) υ 3061, 2962, 2926, 2856, 2166 (C≡C), 1596, 1572, 1486, 1367, 1238, 1155, 1069 (C—S), 754, 689; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.42 (s, 3H), 1.44 (s, 3H), 3.25 (m, 1H), 7.24–7.42 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) 23.0, 39.9, 77.4, 78.6, 94.8, 123.7, 128.0, 128.3, 131.4; MS (EI 70 ev): m/e 57 (100), 176 (M^+, 1).

Benzyl (2-phenylethynyl) sulfide (2e) [4b]

Yellow oil, isolated yield 85%; IR cm^{-1} (neat) υ 3030, 2927, 2164(C≡C), 1596, 1489, 1447, 1069(C—S), 757, 696; ^1H NMR ($CDCl_3$, Me_4Si) δ 4.01 (s, 2H), 7.25–7.39 (m, 10H); MS (EI 70 ev): m/e 224 (M^+, 100); HRMS: m/z for $C_{15}H_{12}S$, calcd: 224.0660. Found: 224.0659.

Phenyl-2-(2-phenylethynylthio) ethanone (2f) [18]

Yellow oil, isolated yield 80%; IR cm^{-1} (neat) υ 2982, 2170 (C≡C), 1736 (C=O), 1595, 1571, 1487, 1089 (C—S), 756, 690; ^1H NMR ($CDCl_3$, Me_4Si) δ 4.29 (s, 2H), 7.25–7.61 (m, 8H), 7.69–7.99 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si)42.3, 77.7, 94.4, 122.9, 128.3, 128.4, 128.7, 128.8, 131.5, 133.8, 135.1, 193.0; MS (EI 70 ev): m/e 105 (100), 262 (M^+, 1).

Ethyl 2-(2-phenylenylethynylthio) acetate (2g) [19]

Yellow oil, isolated yield 82%; IR cm^{-1} (neat) υ 3060, 2915, 2190 (C≡C), 1680 (C=O), 1596, 1579, 1486, 1196 (C—O—C), 1070 (C—S), 753, 688; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.30 (t, J= 7.2 Hz, 3H), 3.56 (s, 2H), 4.25(q, J= 7.2 Hz, 2H), 7.29–7.31 (m, 3H), 7.40–7.42 (m, 2H);^{13}C NMR ($CDCl_3$, Me_4Si)14.1, 37.6, 61.8, 77.3, 94.4, 122.9, 128.2, 128.4, 131.5, 168.2; MS (EI 70 ev): m/e 105 (100), 220 (M^+, 5).

Hexa-1-ynyl (methyl) sulfide (2h) [14c]

Yellow oil, isolated yield 88%; IR cm^{-1} (neat) υ 3060, 2926, 2167 (C≡C), 1595, 1340 (CH_3), 1169 (C—S), 754; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.91 (t, J = 7.4 Hz, 3H), 1.38–1.55 (m, 4H), 2.29 (t, J= 7.0 Hz, 2H), 2.35(s, 3H); ^{13}C NMR ($CDCl_3$, Me_4Si)13.6, 19.3, 19.7, 21.9, 30.8, 69.7, 93.3; MS (EI 70 ev): m/e 59 (100), 128(M^+, 10).

Ethyl (hexa-1-ynyl) sulfide (2i) [20]

Yellow oil, isolated yield 80%; IR cm^{-1} (neat) υ 2958, 2929, 2871, 1456, 1376(CH_3), 1055 (C—S), 745; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.91 (t, J = 7.6 Hz, 3H), 1.37 (t, J = 7.2 Hz, 3H), 1.38–1.57 (m, 4H), 2.31 (t, J = 7.2 Hz, 2H), 2.68 (q, J = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si)13.5, 14.6, 19.8, 21.9, 29.5, 30.9, 31.3, 35.1, 67.8, 94.8; MS (EI 70 ev): m/e 57 (100), 142(M^+, 1).

Hexa-1-ynyl (propyl) sulfide (2j)

Yellow oil, isolated yield 79%; IR cm^{-1} (neat) υ 2961, 2933, 2873, 1462(CH_3), 1378, 1294, 1237, 1094 (C—S), 896, 837, 782, 743; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.91 (t, J = 7.2 Hz,3H), 1.01 (t, J = 7.2 Hz, 3H), 1.36–1.45 (m, 2H), 1.46-1.53 (m, 2H), 1.71–1.80 (m, 2H), 2.30 (t, J = 7.2 Hz, 2H), 2.64 (t, J = 7.2Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si)12.9, 13.6, 19.8, 21.9, 22.6, 30.9, 37.4, 68.2, 77.0, 94.1; MS (EI 70 ev): m/e 57 (100), 156 (M^+, 27); HRMS: m/z for $C_9H_{16}S$, calcd: 156.0973. Found: 156.0982.

*Hexa-1-ynyl (*iso*-propyl) sulfide (2k)*

Yellow oil, isolated yield 40%; IR cm^{-1} (neat) υ 2961, 2930, 2864, 1463, 1381 (CH_3), 1237, 1052 (C—S), 929, 881, 745, 627; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.91 (t, J= 7.2 Hz, 3H), 1.34 (s, 3H), 1.36 (s, 3H), 1.39–1.47 (m, 2H), 1.48–1.53 (m, 2H), 2.33 (t, J = 7.2 Hz, 3H), 3.10 (m, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si)13.6, 19.9, 21.9, 22.8, 30.9, 39.0, 67.1, 77.0, 96.1; MS (EI 70 ev): m/e 57 (100), 156(M^+, 9); HRMS: m/z for $C_9H_{16}S$, calcd: 156.0973. Found: 156.0977.

Butyl (hexa-1-ynyl) sulfide (2l) [21]

Yellow oil, isolated yield 77%; IR cm^{-1} (neat) υ 2958, 2858, 1464, 1378 (CH_3), 1325, 1224, 1100 (C—S), 916, 726; ^1H NMR ($CDCl_3$, Me_4Si), δ 0.89–0.95 (m, 6H), 1.36–1.54 (m, 6H), 1.67–1.74 (m, 2H), 2.30 (t, J= 7.2 Hz, 2H), 2.67 (t, J= 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si)13.6, 13.7, 19.8, 21.4, 21.9, 30.9, 31.3, 35.1, 68.3, 94.2; MS (EI 70 ev): m/e 57 (100), 198(M^+, 5).

Hexa-1-ynyl (sec-butyl) sulfide (2m)

Yellow oil, isolated yield 40%; IR cm^{-1} (neat) υ 2962, 2931, 2874, 2361, 1687, 1458, 1378 (CH_3), 1293, 1220, 1058 (C—S), 999, 956, 793, 745; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.91 (t, J= 7.2 Hz, 3H), 0.99 (t, J= 7.6 Hz, 3H), 1.35 (d, J= 6.8 Hz, 3H), 1.39–1.74 (m, 6H), 2.32 (t, J = 6.8 Hz, 2H), 2.82 (q, J = 6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si)11.6, 13.6, 19.9, 20.6, 21.9, 29.2, 31.0, 45.7, 66.9, 95.6; MS (EI 70 ev): m/e 57 (100), 170 (M^+, 2). HRMS: m/z for $C_{10}H_{18}S$, calcd: 170.1127. Found: 170.1130.

Benzyl (hexa-1-ynyl) sulfide (2n)

Yellow oil, isolated yield 79%; IR cm^{-1} (neat) υ 3063, 3030, 2957, 2929, 2987, 1602, 1494, 1454, 1378(CH_3), 1070 (C—S), 763, 697; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.88 (t, J = 7.2 Hz, 3H, $CH_3(CH_2)_3$), 1.29–1.48 (m, 4H), 2.26 (t, J = 6.8 Hz, 2H), 3.87 (s, 2H), 7.24–7.32 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) 13.6, 19.7, 21.8, 30.7, 40.2, 67.9, 96.0, 127.6, 128.4, 129.0, 137.0; MS (EI 70 ev): m/z 91 (100), 113 (4), 204(M^+, 2); HRMS: m/z for $C_{13}H_{16}S$, calcd: 204.0973. Found: 204.0963.

Methyl (octa-1-ynyl) sulfide (2o)[6]

Yellow oil, isolated yield 81%; IR cm^{-1} (neat) υ 2954, 2922, 2852, 1376(CH_3), 1090(C—S); ^1H NMR ($CDCl_3$, Me_4Si) δ 0.89 (t, J = 7.2 Hz, 3H), 1.26–1.41 (m, 6H), 1.47–1.54 (m, 2H), 2.28 (t, J= 7.2 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, Me_4Si) 14.0, 15.5, 16.7, 23.1, 28.3, 28.8, 31.6, 66.7, 92.5; MS (EI 70 ev): m/z 71 (100), 156(M^+, 16).

Ethyl (octa-1-ynyl) sulfide (2p)

Yellow oil, isolated yield 72%; IR cm^{-1} (neat) υ 2957, 2929, 2858, 1456, 1376 (CH_3), 1056(C—S),770; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.86 (t, J= 7.0 Hz, 3H), 1.18–1.40 (m, 9H), 1.45–1.55 (m, 2H), 2.27 (t, J = 7.2 Hz, 2H), 2.65 (q, J = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si)14.0, 14.6,20.1, 22.5, 28.5, 28.7, 29.5, 31.3, 67.9, 94.8; MS (EI 70 ev): m/z 71 (100), 170(M^+, 2); HRMS: m/z for $C_{10}H_{18}S$, calcd: 170.1129. Found: 170.1131.

Octa-1-ynyl (propyl) sulfide (2q)

Yellow oil, isolated yield 68%; IR cm^{-1} (neat) υ 2961, 2931, 2858, 1460, 1378, 1294, 1237, 1061 (C—S), 896, 838, 783, 726; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.89 (t, J = 6.8 Hz, 3H), 1.02 (t, J = 7.2 Hz, 3H), 1.26–1.41 (m, 6H), 1.51 (m, 2H), 1.71–1.80 (m, 2H), 2.29 (t, J = 7.2 Hz, 2H), 2.64 (t, J = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) 12.9, 14.1, 16.7, 20.1, 22.6, 28.5, 28.8, 31.3, 37.4, 68.2, 94.2; MS (EI 70 ev): m/e 71 (100), 184 (M^+, 13). HRMS: m/z for $C_{11}H_{20}S$, calcd: 184.1286. Found: 184.1299.

Butyl (octa-1-ynyl) sulfide (2r) [22]

Yellow oil, isolated yield 75%; IR cm^{-1} (neat) υ 2959, 2937, 2872, 1486, 1363(CH_3), 1074 (C—S), 874, 744; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.87–0.95 (m, 6H), 1.26–1.54 (m, 10H), 1.67–1.74 (m, 2H), 2.29 (t, J = 7.2 Hz, 2H), 2.67 (t, J = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si)13.6, 14.1, 16.7, 20.1, 21.4, 22.6, 28.5, 28.8, 31.3, 35.1, 68.2, 94.2; MS (EI 70 ev): m/e 57 (100), 198(M^+, 1).

Benzyl (octa-1-ynyl) sulfide (2s)

Yellow oil, isolated yield 70%; IR cm^{-1} (neat) υ 3063, 2929, 2857, 1602, 1494, 1454, 1446, 1378 (CH_3) 1070 (C—S), 763, 696; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.89 (t, J = 7.2 Hz, 3H), 1.23–1.36 (m, 6H), 1.42–1.47 (m, 2H), 2.26 (t, J = 7.2 Hz, 2H), 3.88 (s, 2H), 7.25–7.33 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) 14.0, 20.1, 22.5, 28.5, 28.6, 31.3, 40.2, 67.9, 96.1, 127.5, 128.4, 129.0, 137.0; MS (EI 70 ev): m/z 91 (100), 232(M^+, 1); HRMS: m/z for $C_{15}H_{20}S$, calcd: 232.1686. Found: 232.1687.

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