A convenient synthesis of new functionalized thioether compounds

Amira Hafedh, Abderrahmen Abdelli*, Mohamed Lotfi Efrit and Hédi Mrabet*

Laboratory of Selective Organic and Heterocyclic Synthesis & Biological Activity Evaluation, Faculty of Sciences of Tunis, Tunis El Manar University, 2092 Tunis, Tunisia.

(Received: 06 February 2017, accepted: 18 July 2017)

Abstract: An efficient synthesis of new thioether compounds through the thia-Michael protocol under mild condition is described. The reaction of thiols and dithiols with β-carbonylethoxyallylic sulfones and sulfides, leads to the formation of di- and tetra-thioethers respectively. The methodology could be extended to the synthesis of new cyclic thioethers in high yields.

Keywords: Michael acceptor, thiols, allylicsulfure, thioethers.

INTRODUCTION

The conjugated addition of thiols [1-9] onto Michael's acceptors is a key reaction leading to organo-sulfur compounds and derivatives.[10] We have recently reported the addition of a series of thiols into β-ethoxycarbonylallyl phosphonate. [11] As part of our continued interest in the acrylic derivative [12-17], and in order to access, among others, to 1,3-dithioethers widely used as ligands in organometallic coordination chemistry [18-23], we herein describe the reaction of thiols with different type of Michael's acceptors such as β-carbonylallylic sulfides **1** and sulfones **2.**

RESULTS AND DISCUSSIONS

1. Reaction of thiols with ethyl 2-((arylthio) methyl)acrylate 1

In our initial approach we investigated the thia-Michael reaction by reacting simple thiols and 2-(thioarylmethyl)ethylacrylates **1a** and **1b** in a polar and protic solvent in the presence of thriethylamine. Multiple reactions were carried out and optimum yields were achieved when the triethylamine was used in a slight excess with respect to the substrates (Scheme 1). Monitoring the reaction by TLC showed that a full conversion of substrates **1** requires 18 hours of stirring at room temperature.

In absence of base, the conversion proved to be much slower even after extending the reaction time to 48 hours. The slow conversion could possibly be attributed to the retro-thia-Michael reaction [24]. An attempt to accelerate the reaction was to operate at higher temperatures, turned out to be unsuccessful as degradation of the substrate was observed.

In order to extend the reaction scope and access to new varieties of functionalized sulfur adducts, we envisioned to study the addition of dithiols on allylic sulfide **1**. The reaction was undertaken in

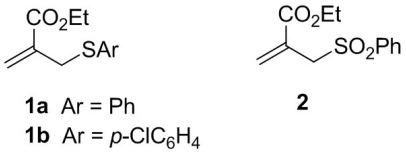
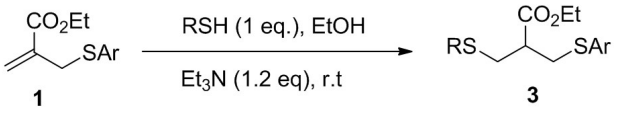


Figure 1



Scheme 1

* Corresponding authors, e-mail addresses : abdelli.abderrahmen@gmail.com (A. Abdelli) Tel.: +21621205389, mrabet.fst@gmail.com (H. Mrabet) Tel.: +21698616488

Table I. Result of the above study

Substrate	Ar	R	Product	Yield%
1a	Ph	Et	**3a1**	78
		$PhCH_2$	**3a2**	90
1b	*p*-ClC_6H_4-	Et	**3b1**	64
		$PhCH_2$	**3b2**	96

Table II. Preparation of thioethers **4**.

Substrate	Ar	n	Product	Yield %
1a	Ph	2	**4a1**	93
		3	**4a2**	45
1b	*p*-ClC_6H_4-	2	**4b1**	67
		3	**4b2**	43

the same conditions as used for simple thiol reported earlier. These conditions allowed us to synthesize a new family of functionalized tetrathioethers **4**, to the best of our knowledge, unreported in the literature (scheme 2).

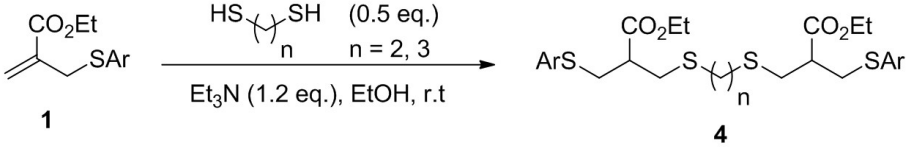
The initial results showed that the yields were substantially lower in the case of propane dithiols (n=3), compared to the ethanedithiol. This is probably due to the added flexibility induced by an additional methylene group into the dithiol system. It is worth noting that in contrast to previous reports[11], among multiple byproducts formed along with compounds **4a2** and **4b2**, none of them corresponds to either a mono addition or cyclic products (figure 2).

2. Reaction of thiols with ethyl 2-((phenylsulfonyl)methyl)acrylate

Our initial target behind studying this reaction was the access to compounds bearing both functionalities sulfide and sulfones. These compounds proved to be challenging to obtain by selective oxidation of disulfide precursors [25-26]. We have used the same strategy adopted in the synthesis of di- and tetrasulfides. Unexpectedly, the reaction did not proceed as predicted. A substitution product was isolated instead of an addition product as evidenced by NMR analysis. The latter shows that the aromatic group has been totally removed whereas the ethylenic protons are still present (scheme 3).

A similar result was obtained when the reaction was extended to dithiol system. Indeed, when sulfone **2** was reacted with ethane-dithiol or propane-1,3-dithiol, diacrylate **6a** and **6b** were isolated respectively (Scheme 4).

This result, eventhough unexpected, does not seem to be totally new to the literature. As a matter of fact, a few recent reports have confirmed the possibility for allylic sulfone to undergo nucleophilic substitution reactions [27-34].



Scheme 2

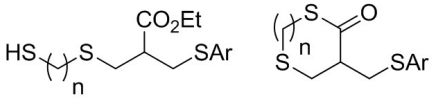
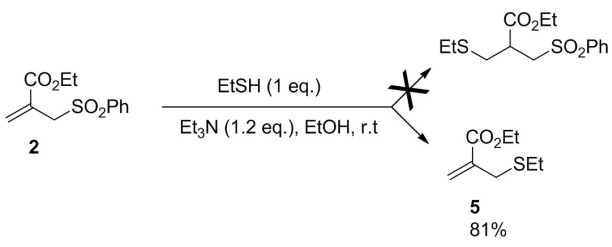
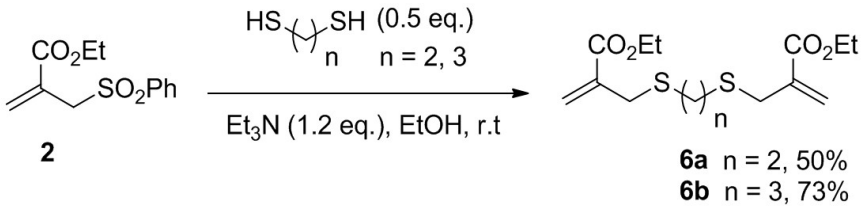


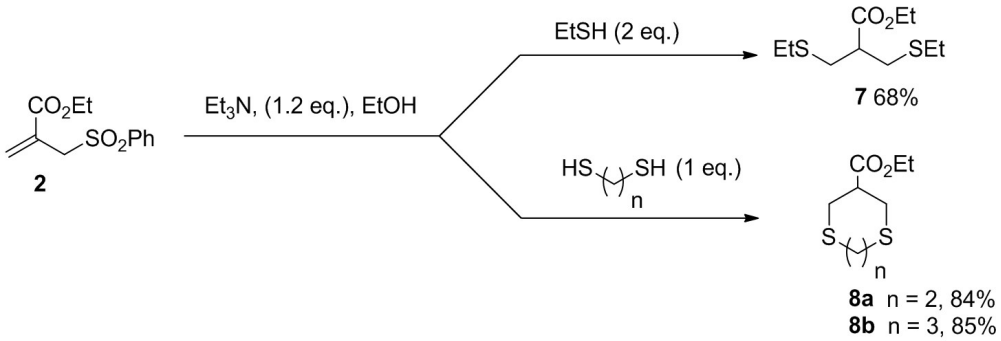
Figure 2



Scheme 3



Scheme 4



Scheme 5

Furthermore, the acrylic derivatives **5** and **6** can themselves undergo a subsequent conjugate addition of monothiols to generate other type of thioethers. In this perspective, we envisioned the direct access to dithioethers **7** simply by reacting sulfone **2** with two equivalents of ethanethiol. However one equivalent of dithiol leads in the same condition, to cyclic thioethers **8a** and **8b** in high yields (Scheme 5).

It is important to outline that operating in high dilution is crucial to the formation of cyclic thioethers **8a** and **8b**. Indeed, when the reaction was conducted at higher concentration, a pasty residue was obtained and could not be identified.

CONCLUSION

In summary, we have described an efficient and straightforward synthesis of a variety of di and tetra-functionalized thioethers starting form allylic sulfides and sulfones. We have by the same token proved that the arylsulfones constitute a good leaving group as they are easily displaced by alkyl sulfides. The isolated products are being investigated as ligands in metal complex studies.

Acknowledgments: The authors wish to thank Dr. Salim BARKALLAH, Group Leader at Cambridge Isotope Laboratories, for helpful discussion.

EXPERIMENTAL SECTION

1. General

^{1}H and ^{13}C-NMR spectra were recorded with $CDCl_3$ as solvent, on a Bruker-300 spectrometer. The chemical shifts are reported in ppm relative to TMS (internal reference) for ^{1}H spectra and (77.00 ppm for $CDCl_3$) for ^{13}C spectra. Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiple.

Purification of products was performed by column chromatography using silica gel 60 silice 60 (70-230 mesh).

2. Synthesis of ethyl 2-((arylthio)methyl) acrylates 1a-b :

To a solution of ethyl 2-bromomethylacrylate (0.05 mol) in 50 mL of acetone was added 0.05 mol of arylthiol and 0.055 mol of potassium carbonate. The reaction was heated under acetone reflux for 6 hours.

After cooling, the solution must be filtered to remove the potassium bromide formed. The solvent was then evaporated under vacuum and the residue was treated with 50 mL of diethyl ether and washed twice with 25 mL of water. The organic phase was dried with sodium sulfate. The solvent was evaporated and the reaction residue was purified by column chromatography using a

mixture of diethyl ether/petroleum ether (1/9) as eluent or by distillation under reduced pressure.
The crude product **1b** was purified by silica gel column chromatography using the same condition of the product **1a**.

2.1. Ethyl 2-((phenylthio)methyl)acrylate 1a

Yield = 80% ; Viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ = 1.31 (t, ^{3}J = 6.0, 3H), 3.77 (d, 2H), 4.24 (q, ^{3}J = 6.0, 2H), 5.54 (s, 1H), 6.16 (s, 1H), 7.20-7.37 (m, 5H). ^{13}C NMR (75.43 MHz, $CDCl_3$, δ ppm): δ = 14.25, 35.75, 61.11, 126.65, 126.82, 128.95, 130.85, 135.56, 136.51, 166.15.

2.2. Ethyl 2-(((4-Chlorophenyl)thio)methyl) acrylate 1b

Yield = 92 % ; Viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm, *J* Hz): δ = 1.31 (t, ^{3}J = 6.0, 3H), 3.77 (d, 2H), 4.25 (q, ^{3}J = 6.0 Hz, 2H), 5.52 (s, 1H), 6,16 (s, 1H), 7.23-7.30 (m, 4H). ^{13}C NMR (75.43 MHz, $CDCl_3$, δ ppm): δ = 14.31, 61.25, 36.17, 126.82, 129.17, 132.47, 133.09, 134.10, 136.41, 166.09.

3. Synthesis of Ethyl 2-((phenylsulfone)methyl) acrylate 2 :

To a solution of ethyl 2-bromomethylacrylate 0,02 mol (3.85 g) in 25 mL EtOH, was added 0.02 mol of sodium benzenesulfonate. The mixture was refluxed for 5 hours.
After cooling, the solution was filtered to remove the sodium bromide formed. The solvent was then removed under vacuum and the residue was treated with 25 mL of diethyl ether and then washed twice with 25 mL of water. The organic phase was dried with sodium sulfate and the solvent was removed under vacuum. The residue was purified by column chromatography using a mixture of diethyl ether/ petroleum ether (1/9) as eluent.

3.1. Ethyl 2-((phenylsulfone)methyl)acrylate 2

Yield = 59 % ; Viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ = 1.22 (t, ^{3}J = 6.0, 3H), 4.06 (q, ^{3}J = 6.0, 2H), 4.21 (s, 2H), 5.96 (s, 1H), 6.55 (s, 1H), 7.56-7.92 (m, 5H). ^{13}C NMR (75.43 MHz, $CDCl_3$, δ ppm): δ = 14.07, 57.60, 61.55, 128.85, 129.12, 129.20, 133.42, 133.95, 138.47, 164.83.

4. General procedure for the synthesis of dithioethers 3 and thioether 5

To a solution of ethyl 2-((arylthio)methyl)acrylates **2** (5 mmol) in 15 mL of ethanol and triethylamine (6 mmol) was added dropwise 1 eq. of thiol. The reaction mixture was stirred for 18 hours at room temperature. The solvent was removed, the residue diluted in 20 mL of chloroform and washed twice with 15 mL of distilled water. The solvent was next removed and the reaction residue purified by silica gel column chromatography using diethyl ether / petroleum ether mixture (2/8) as eluent.

4.1. Ethyl 3-(ethylthio)-2-((phenylthio)methyl) propanoate 3a1

Yield = 78 % ; Viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ = 1.29 (m, 6H), 2.48 (m, 2H), 2.92 (m, 2H), 2,87 (m, 1H), 3.25 (m, 2H), 4.21 (m, 2H), 7.21-7.39 (m, 5H). ^{13}C NMR (75.43 MHz, $CDCl_3$, δ ppm): δ = 14.41, 14.7, 25.8, 30.4, 34.8, 46.1, 61.6, 125.1, 128.9, 129.3, 155.6, 173.0.

4.2. Ethyl 3-(benzylthio)-2-((phenylthio)methyl) propanoate 3a2

Yield = 90 % ; Viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ = 1.29 (t, ^{3}J = 6.0, 3H), 2.92 (m, 2H), 2.87 (m, 1H), 3.25 (m, 2H), 3.70 (s, 2H), 4.21 (q, ^{3}J = 6.0, 2H), 7.21-7.40 (m, 10H). ^{13}C NMR (75.43 MHz, $CDCl_3$, δ ppm): δ = 14.1, 30.3, 34.8, 36.8, 46.1, 128.8, 129.3, 138.8, 155.6, 173.0.

4.3. Ethyl 3-((4-chlorophenyl)thio)-2-((ethylthio) methyl)propanoate 3b1

Yield = 64 % ; Viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ = 1.29 (m, 6H), 2.48 (q, ^{3}J = 6.0, 2H), 2.92 (m, 2H), 2.87 (m, 1H), 3.25 (m, 2H), 4.21 (q, ^{3}J = 6.0, 2H), 7.33-7.39 (m, 4H). ^{13}C NMR (75.43 MHz, $CDCl_3$, δ ppm): δ = 14.1, 14.8, 25.8, 30.4, 34.8, 46.1, 61.4, 129.0, 130.7, 134.5, 131.12, 173.0.

4.4. Ethyl 3-(benzylthio)-2-(((4-chlorophenyl) thio)methyl)propanoate 3b2

Yield = 96 % ; Viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ = 1.29 (m, 3H), 2.92 (m, 2H), 2.87 (m, 1H), 3.25 (m, 2H), 3.70 (s, 2H), 4.21 (q, ^{3}J = 6.0, 2H), 7.26-7.40 (m, 9H). ^{13}C NMR (75.43 MHz, $CDCl_3$, δ ppm): δ = 14.1, 30.3, 34.8, 36.6, 61.4, 128.7, 129.0, 138.8, 134.5, 173.0.

4.5. Ethyl 2-((ethylthio)methyl)acrylate 5

Yield = 81 % ; Viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ = 1.29 (m, 6H), 2.48 (q, ^{3}J = 6.0, 2H), 4.20 (q, ^{3}J = 6.0, 2H). 3.27 (s, 2H), 5.54 (s, 1H), 6.37 (s, 1H).^{13}C NMR (75.43 MHz, $CDCl_3$, δ ppm): δ = 14.2, 26.2, 32.8, 61.7, 167.2, 125.2, 138.0.

5. Typical procedure for the synthesis of tetrathioethers 4 and dithioethers 6

To a solution of ethyl 2-((arylthio)methyl)acrylates **2** (5 mmol) in 15 mL of ethanol and triethylamine

(6 mmol) were added, 2.5 mmol of dithiol. The reaction mixture was stirred for 18 hours at room temperature. The solvent was removed; the residue diluted in 20 mL of chloroform and washed twice with 15 mL of distilled water. The solvent was next removed and the reaction residue purified by silica gel column chromatography using diethyl ether / petroleum ether mixture (1/1) as eluent for product **4** and (7/3) as eluent for compounds **6a** and **6b**.

5.1. Diethyl 3,3'-(ethane-1,2-diylbis (sulfanediyl))bis(2-((phenylthio)methyl) propanoate) 4a1

Yield = 93 % ; Viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ = 1.29 (m, 6H), 2.92 (m, 4H), 2.81 (s, 4H), 2.87 (m, 2H), 3.25 (m, 4H), 4,21 (q, ^{3}J = 6.0, 4H), 7.21-7.39 (m, 10H).^{13}C NMR (75.43 MHz, $CDCl_3$, δ ppm): δ = 14.1, 30.0, 34.4, 34.8, 46.1, 61.1, 125.1, 128.9, 129.3, 155.6, 173.0.

5.2. Diethyl 3,3'-(propane-1,3-diylbis (sulfanediyl))bis(2-((phenylthio)methyl) propanoate) 4a2

Yield = 45 % ; Viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ = 1.23 (m, 6H), 2.18 (m, 2H), 2.74-2.83 (m, 5H), 3.15-3.28 (m, 7H), 4.02-4.16 (m, 4H), 7.15-7.33 (m, 10 H). ^{13}C NMR (75.43 MHz, $CDCl_3$, δ ppm): δ = 16.1, 32.0, 34.4, 34.8, 36.3, 46.1, 61.1, 125.1, 128.9, 129.3, 155.6, 173.0.

5.3. Diethyl 3,3'-(ethane-1,2-diylbis (sulfanediyl))bis(2-(((4-chlorophenyl)thio) methyl)-propanoate) 4b1

Yield = 67 % ; Viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ = 1.29 (m, 6H), 2.92 (m, 4H), 2.81 (s, 4H), 2.87 (m, 2H), 3.25 (m, 2H), 4.21 (q, ^{3}J = 6.0, 4H), 7.33-7.39 (m, 8H).^{13}C NMR (75.43 MHz, $CDCl_3$, δ ppm): δ = 14.1, 30.0, 34.4, 34.8, 46.1, 61.6, 129.0, 130.7, 131.2, 134.6, 173.0.

5.4. Diethyl 3,3'-(propane-1,3-diylbis (sulfanediyl))bis(2-(((4-chlorophenyl)thio) methyl)-propanoate) 4b2

Yield = 43 % ; Viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ = 1.24 (m, 6H), 2.12 (m, 2H), 4.11 (m, 4H), 2.75 (m, 4H), 3.08 (m, 2H), 3.15 (m, 4H), 3.18 (m, 4H), 7.23 (m, 10H).^{13}C NMR (75.43 MHz, $CDCl_3$, δ ppm): δ = 14.15, 30.85, 31.22, 35.27, 46.01, 61.19, 129.15, 131.80, 132.95, 133.41, 172.95.

5.5. Ethyl 2,2'-((ethane-1,2-diylbis(sulfanediyl) bis(methylene))diacrylate 6a

Yield = 50 % ; Viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ = 1.29 (t, ^{3}J = 6.0, 6H), 2.81 (s, 4H), 4.20 (q, ^{3}J = 6.0, 4H), 3.27 (s, 4H), 5.54 (s, 2H), 6.37 (s, 2H).^{13}C NMR (75.43 MHz, $CDCl_3$, δ ppm): δ = 14.2, 32.4, 34.6, 61.7, 125.2, 138.0, 167.2.

5.6. Diethyl 2,2'-((propane-1,3-diylbis (sulfanediyl))bis(methylene))diacrylate 6b

Yield = 73 % ; Viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ = 1.31 (m, 6H), 1.84 (m, 2H), 2.55 (m, 4H), 4.23 (m, 4H), 3.37 (s, 4H), 5.65 (s, 2H), 6.20 (s, 2H).^{13}C NMR (75.43 MHz, $CDCl_3$, δ ppm): δ = 13.78, 28.22, 29.99, 32.33, 60.59, 125.30, 138.0, 165.73.

6. Synthesis of dithioether 7

To a solution of ethyl 2-((phenylsulfone)methyl) acrylate 2 (5 mmol) in 15 mL of ethanol and triethylamine (6 mmol) were added, dropwise 10 mmol of ethanthiol. The reaction mixture was stirred for 18 hours at room temperature. The solvent was removed, the residue diluted in 20 mL of chloroform and washed twice with 15 mL of distilled water. The solvent was next removed and the reaction residue purified by silica gel column chromatography using diethyl ether / petroleum ether mixture (2/3) as eluent.

6.1. Ethyl 3-(ethylthio)-2-((ethylthio)methyl) propanoate 7

Yield = 73 % ; Viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ = 1.10 (m, 9H), 2.39 (m, 4H), 2,62 (m, 5H), 4.02 (q, ^{3}J = 6.0, 2H).^{13}C NMR (75.43 MHz, $CDCl_3$, δ ppm): δ = 13.97, 14.44 (2C), 26.06 (2C), 32.36 (2C), 45.96, 60.52, 172.90.

7. Synthesis of thioether 8

To a solution of ethyl 2-((phenylsulfone)methyl) acrylate 2 (5 mmol) in 4 mL of ethanol and triethylamine (6 mmol) were added, dropwise of dithiol (5 mmol). The reaction mixture was stirred for 18 hours at room temperature. The solvent was removed; the residue diluted in 20 mL of chloroform and washed twice with 15 mL of distilled water. The solvent was next removed and the reaction residue was purified by silica gel column chromatography using diethyl ether / petroleum ether mixture (1/1) as eluent.

7.1. Ethyl 1,4-dithiepane-6-carboxylate 8a

Yield = 84 % ; Viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): δ = 1.29 (t, ^{3}J = 6.0, 3H), 2.74 (m, 4H), 2.87 (m, 5H), 4.20 (q, ^{3}J = 6.0, 2H).^{13}C NMR (75.43 MHz, $CDCl_3$, δ ppm): δ = 14.31, 33.08, 33.47, 46.80, 61.12, 172.70.

7.2. Ethyl 1,5-dithiocane-3-carboxylate 8b

Yield = 85 % ; Viscous oil; ^{1}H NMR (300 MHz,

$CDCl_3$, δ ppm, J Hz): δ = 1.28 (t, ^3J = 6.0, 3H), 1.87 (m, 2H), 2.62 (m, 4H), 2.81 (m, 4H), 3.14 (m, 1H), 4.19 (q, ^3J = 6.0, 2H). ^{13}C NMR (75.43 MHz, $CDCl_3$, δ ppm): δ = 14.31, 31.64, 33.43, 46.66, 46.93, 60.93, 172.87.

BIBLIOGRAPHICAL REFERENCES

[1] R. Chintakunta, L. Po-Min, K. Veerababurao, K. Chun-Wei, Y. Ching-Fa, *Molecules,* **2012**, *17*, 5081.

[2] E. Emori, T. Arai, H. Sasai, M. Shibasaki, *J. Am. Chem. Soc*. **1998**, *120*, 4043.

[3] S. Kanemasa, Y. Oderaotoshi, E. Wada, *J. Am. Chem. Soc*. **1999**, *121*, 8675.

[4] C. C. Silveira, S. R. Mendes, F. M. Líbero, *Synlett*, **2010**, *5*, 790.

[5] T. Mukaiyama, T. Izawa, K. Saigo, H. Takei, *Chem. Lett*. **1973**, 355.

[6] M. Belley, R. Zamboni, *J. Org. Chem*. **1989**, *54*, 1230.

[7] H.Firouzabadi, N. Iranpoor, A. A. Jafari, *SYNLETT*. **2005**, *2*, 0299.

[8] H.Firouzabadi, N. Iranpoor, A. A. Jafari, *Adv. Synth. Catal.***2005**, *347*, 655.

[9] I. Erraya, J. Obleb, G. Polib, F. Rezgui, *Journal of Sulfur Chemistry*, **2014**, *35*, 128.

[10] R. A. Sheldon, *Chirotechnologies. In Industrial Synthesis of Optically Active Compounds*; Dekker: New York, **1993**.

[11] A. Abdelli, H. M'rabet, M. L. Efrit, A. Gaucher, D. Primb, *Journal of Sulfur Chemistry*, **2014**, *35*, 674.

[12] H. M'Rabet, M. Ould M'Hamed, A. Ayari, M. L. Efrit. *J. Soc. Chim. Tunisie*, **2009**,*11*, 1.

[13] N. Azizi, A. K. Amiri, H. Ghafuri, M. Bolourtchian*, Green Chem. Lett. Rev.*, **2009**, *2*, 43.

[14] S. Kundu, B. Roy and B. Basu *Beilstein J. Org. Chem.,* **2014,** *10,* 26.

[15] A. Peng, R. Rosenblatt, K. Nolin, *Tetrahedron Lett.,* **2012**, *53*, 2712.

[16] C. Ramesh, P. Lei, V. Kavala, C. Kuo, C. Yao, *Molecules,* **2012**, *17*, 5081.

[17] B. Movassagh, A. Rakhshani, *Chinese Chem. Lett.*, **2011**, *22*, 1179.

[18] I. Yoon, K.M. Park, J.H. Jung, J. Kim, S.B. Park, S.S. Lee, *J. Inclusion Phenom. Mol. Recognit Chem.***2002**, *42*, 45.

[19] F. Arnesano, S. Scintilla, G. Natile, *Angew Chem Int Ed*, **2007**, *46*, 9062.

[20] R. Kannan, N. Pillarsetty, H. Gali, J. T. Hoffman, L. C. Barnes, S. S Jurisson, J. C. Smith, W. A. Volkert, *Inorg. Chem.* **2011,** *50,* 6210.

[21] J.-R. Li, X.-H. Bu, J. Jiao, W.-P. Du, X.-H. Xu, R.-H. Zhang, *Dalton Trans.* **2005,** 464.

[22] W. Levason, G. Reid, W. Zhang, *Dalton Trans.* **2011,** *40,* 8491.

[23] M. O. Awaleh, A. Badia, F. Brisse, X.-H. Bu, *Inorg. Chem.* **2006,** *45,*1560.

[24] D. A. Baldwin, K. L. Kiick, *Bioconjug. Chem.***2011**, *22*, 1946.

[25] H. Suzuki, S. Kawato, A. Nasu,*Bull. Chem. Soc. Jpn.* **1992**, 65.

[26] Z. Lasemi, R. Hosseinzadeh, M. Tajbakhsh, M. Mohadjerani, *Bulg. Chem. Commun*, **2013**, *45*, 379.

[27] Darmency, E. M. Scanlan, A. P. Schaffner, P. Renaud, *Organic Syntheses*, **2006**, *83*, 24-30 ; Coll. **2009**, *11*, 308.

[28] T. Llamas, R. G. Arrayas, J. C. Carretero, *Adv. Synth. Catal*. **2004**, *346*, 1651.

[29] M. Nambo, C. M. Crudden, *ACS Catal*. **2015**, *5*, 4734.

[30] J. Marc, A. Righini-Tapie, J. Noel, *Tetrahedron*, **1983**, *39*, 3283.

[31] L. Deqiang, H. Wenzhong, Y. Lin, M. Yinhai, O. Liping, R. Yuqin Rao, Y. Yuxian, *Synth. Comm.* **2014**, *44*, 1930.

[32] C. Jonathan, J. Jonathan, A. Cooney, J. Marc, *J. Chem. Soc., Perkin Trans. 1*, **1995**, 7.

[33] F. Le Guyader, B. Quiclet-Sire, S. Seguin, S. Z. Zard, *J. Am. Chem. Soc.* **1997**, *119*, 7410.

[34] J. Xiang, J. Evarts, A. Rivkin, D. P. Curran, P. L. Fuchs, *Tetrahedron Lett.* **1998**, *39*, 4163.