Tetrahedron Letters 54 (2013) 5492–5495

Contents lists available at ScienceDirect

Tetrahedron Letters

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

Regio- and stereoselective synthesis of (Z)-2-Arylsulfanyl allylic alcohols using anhydrous $CeCl_3$ as catalyst under solvent free conditions

Claudio C. Silveira [a,*], Guilherme M. Martins [a], Samuel R. Mendes [b]

[a] Departamento de Química, Universidade Federal de Santa Maria, 97105-900 Santa Maria, RS, Brazil
[b] GAPAM–Departamento de Química, Universidade do Estado de Santa Catarina, 89219-710 Joinville, SC, Brazil

ARTICLE INFO

Article history:
Received 14 May 2013
Revised 25 July 2013
Accepted 27 July 2013
Available online 2 August 2013

Keywords:
Click chemistry
Solvent free
Propargylic alcohols
Thiols
Cerium(III) chloride

ABSTRACT

Anhydrous $CeCl_3$ was successfully employed as catalyst for the synthesis of (Z)-2-Arylsulfanyl allylic alcohols from propargylic alcohols and thiols under solvent free conditions. The products were obtained in good to excellent yields.

Click chemistry is a concept introduced in 2001 by Sharpless[1] to describe reactions capable of connecting two molecules with high yields, under simple reaction conditions. To be characterized as click chemistry the reaction must be rapid, stereospecific, and generate inoffensive by-products. Furthermore, it must be performed without solvents or in nontoxic solvents, using stable starting materials and of simple production.

In recent years, the number of publications involving the use of click reaction for the preparation of new molecules has grown exponentially. Many researchers reported this application for the synthesis of polymers,[2] *N,N'*-disubstituted thioureas,[3] copper-catalyzed azide-alkyne cycloaddition (CuAAC),[4] and many others.[5] The thiol-clock chemistry has been the subject of a recently published detailed review article.[6] The thiol addition is also a very useful reaction in material chemistry.[6,7]

Allylic alcohols are important intermediates in organic synthesis such as for cyclopropanation reactions[8] and allylic substitution;[9] they can be isomerized into carbonyl compounds in the presence of a transition metal catalyst.[10] They are also very important in the synthesis of natural products and pharmaceuticals.[11] The synthesis of allylic alcohols containing metals or heteroatoms is also of considerable interest for organic synthesis,[12] as they provide a useful intermediate for change through the introduction and removal of the metal or heteroatom.[13] Substituted allylic alcohols are generally prepared by a Reformatsky reaction[14] of the corresponding ketones or by the Horner–Wadsworth–Emmons reaction,[15] but a mixture of isomers has been usually obtained.

Organochalcogen compounds play an important role in modern organic synthesis in view of their chemo, regio, and stereoselective reactions[16] and their useful biological activities.[17] Among the different classes of organochalcogen compounds, vinylic chalcogenides constitute a very useful group and have attracted considerable attention in recent years as synthetic precursors.[18] Vinyl sulfides are particularly interesting, serving as intermediaries for various organic transformations.[19] The most common method to prepare vinyl sulfides involves the addition of thiols or its anions, to terminal or internal alkynes, usually by metal-catalyzed reactions.[20] From the various classes of alkynes, propargylic alcohols are particularly interesting since the sulfanyl allylic alcohols, resulting from the corresponding thiol addition, can be functionalized in many ways.[21] Another very important alternative for the preparation of vinyl sulfides is the metal-catalyzed reaction of thiols with vinyl halides.[22]

On the other hand, lanthanide salts have been shown to be excellent catalysts, widely used as Lewis acids. Many of these salts have attracted great interest in organic syntheses due to their ease of handling, low toxicity, high resistance to water, and stability.[23] In this context, there has been a series of articles reporting the use of $CeCl_3$ as catalyst.[24] $CeCl_3$ has been used in different ways, as heptahydrate, anhydrous, and in combination with NaI.[25] Due

* Corresponding author. Fax: +55 55 32208754.
E-mail addresses: silveira@quimica.ufsm.br (C.C. Silveira), samuel.mendes@udesc.br (S.R. Mendes).

0040-4039/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tetlet.2013.07.142

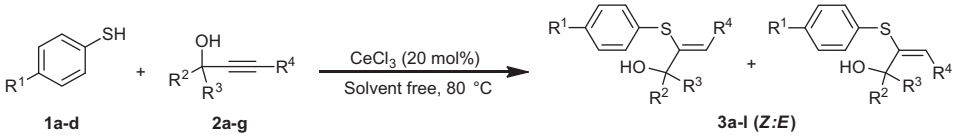
Table 1
Optimization of conversion **1a**–**3a**[a]

Entry	Solvent	Catalyst (equiv)	Time (h)	Yield[b] (%)
1	—	$CeCl_3$ (0.3)	0.5	86
2	$MeNO_2$	$CeCl_3$ (0.3)	6	—[c]
3	MeCN	$CeCl_3$ (0.3)	6	—[c]
4	*i*-propanol	$CeCl_3$ (0.3)	6	—[c]
5	—	$CeCl_3{\cdot}7H_2O$ (0.3)	6	30
6	—	$Ce(OTf)_3$ (0.3)	0.5	45
7	—	$Ce(NO_3)_3{\cdot}6H_2O$ (0.3)	0.5	50
8	—	$CeCl_3$ (0.2)	0.5	86

[a] Reaction conditions: benzenethiol (**1a**, 1.1 mmol), 2,4-diphenylbut-3-yn-2-ol (**2a**, 1.0 mmol), at 80 °C.
[b] Isolated yields.
[c] No reaction.

to our interest in developing new methods and new applications of salts of cerium(III) in organic synthesis, we decided to study the reaction of propargylic alcohols with thiols using a cerium(III) salt as catalyst. We observed previously that cerium salts are efficient acid catalysts, capable of promoting several reactions with high regio and stereoselectivity.[26,24c] Therefore, the main goal was in obtaining a regio- and stereoselective addition, since most of the described methods of thiol addition to alkynes give rise to mixtures of regio- and/or stereoisomers.

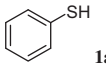
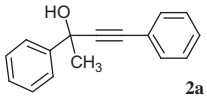
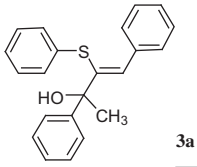
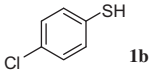
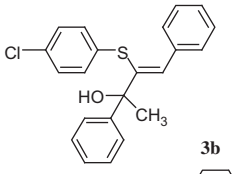
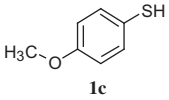
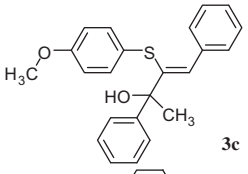
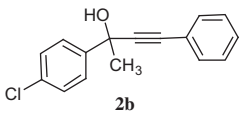
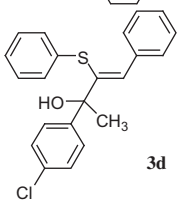
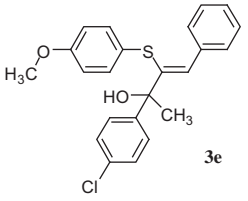
In preliminary experiments, the best reaction conditions were pursued by the use of benzenethiol (**1a**, 1.1 mmol) and 2,4-diphenylbut-3-yn-2-ol (**2a**, 1.0 mmol) as starting materials (Table 1). First, the solvent effect was tested using $MeNO_2$, MeCN, and *i*-propanol under solvent-free conditions (entries 1–4). The results revealed that the best yields were obtained under solvent-free



R^1 = H, Cl, MeO; R^2 = Ph, *p*-ClPh, Me; R^3 = H, Ph, Me; R^4 = Ph, C_4H_9; $R^2 = R^3 = C_5H_{10}$

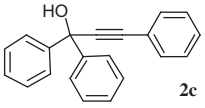
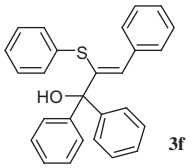
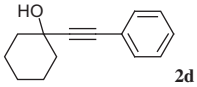
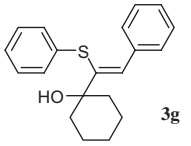
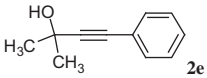
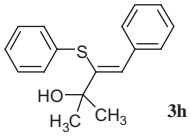
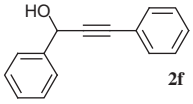
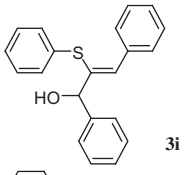
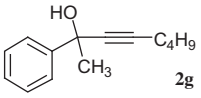
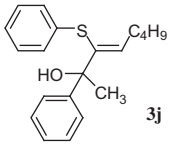
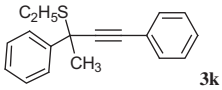
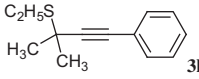
Scheme 1.

Table 2
Synthesis of (*Z*)-2-Arylsulfanyl allylic alcohols using anhydrous $CeCl_3$ as catalyst[a]

Entry	Thiol	Propargylic alcohol	Product[c]	Time (h)	Ratio *Z*:*E*	Yield[d] (%)
1	 **1a**	 **2a**	 **3a**	0.5	98:2	86
2	 **1b**	**2a**	 **3b**	0.5	96:4	53
3	 **1c**	**2a**	 **3c**	0.25	98:2	91
4	**1a**	 **2b**	 **3d**	0.5	100:0	95
5	**1c**	**2b**	 **3e**	0.25	100:0	80

(*continued on next page*)

Table 2 (*continued*)

Entry	Thiol	Propargylic alcohol	Product[c]	Time (h)	Ratio *Z*:*E*	Yield[d] (%)
6	**1a**	 **2c**	 **3f**	1.25	55:45	86
7	**1a**	 **2d**	 **3g**	0.5	100:0	84
8	**1a**	 **2e**	 **3h**	0.5	100:0	81
9	**1a**	 **2f**	 **3i**	0.5	100:0	75
10	**1a**	 **2g**	 **3j**	3.5	94:6	65
11	C_2H_5SH 1d	**2a**	 **3k**	1.5	–	50[b]
12	**1d**	**2e**	 **3l**	3.0	–	42[b]

[a] Reaction performed at 80 °C, using anhydrous $CeCl_3$ (20 mol %) under solvent free.
[b] $MeNO_2$ (2 mL) was used as solvent.
[c] Product was detected by ^1H NMR, ^{13}C NMR, and GC–MS.
[d] Isolated yields.

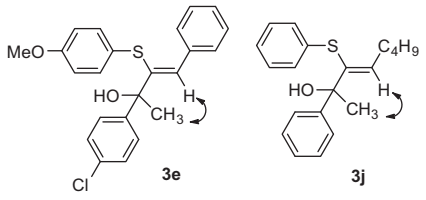


Figure 1. Results of the NOESY studies.

conditions. The type of catalyst and its amountwere also evaluated using anhydrous $CeCl_3$, $Ce(OTf)_3$, $CeCl_3{\cdot}7H_2O$, and $Ce(NO_3)_3{\cdot}6H_2O$ (entries 5–8). The best yield was obtained by the use of anhydrous $CeCl_3$ (0.2 equiv, entry 8). Next, the amount of $CeCl_3$ was checked; it was observed a decrease in the yields when 0.1 equiv was used, while the use of 0.3 equiv did not increase significantly the performance. The temperature was also evaluated. The best results were obtained at 80 °C (entry 8), yields were lower at 50 °C, while at room temperature only traces of the product were observed. On the other hand, at 100 °C there was a complete lack of selectivity, with a formation of *Z*/*E* mixtures.

In order to explore the scope and limitations of the method, the transformation of Scheme 1 was extended to other examples, under the optimized conditions (Table 2).[27]

Reactions of propargyl alcohols with various thiols were performed. The corresponding products resulting from addition to the triple bond were obtained from aromatic compounds such as benzenethiol, 4-chlorobenzenethiol, and 4-methoxy benzenethiol. Surprisingly, however, when the reaction was carried out using ethanethiol, under the standard conditions, no reaction was observed. When $MeNO_2$ was employed as solvent and under these conditions, the nucleophilic substitution reaction wasobserved, furnishing the corresponding propargylic thiol, albeit in low yields (entries 11 and 12). Catalysts for the OH/SR substitution on propargylic alcohols include PTSA,[28] Ru,[29] Au,[30] and $FeCl_3$.[31] When employing arylthiols carrying electron withdrawing groups, such as 4-chlorobenzenethiol, the yield decrease considerably to 53% (entry 2). Using an electron releasing group, as 4-methoxybenzenethiol, the yield increased from 86% to 91%, and the reaction time was reduced by half (Table 2, entry 3). The reaction with aromatic thiols proved to be regio- and stereoselective, as determined by ^1H NMR, ^{13}C NMR, and GC/MS, with a very high preference for the formation of the *Z* isomers, with the exception of alcohol **2c** (entry 6). A NOESY experiment on the major isomer of **3e** (Fig. 1) exhibited a clear coupling between the vinyl hydrogen δ 7.29 (s, 1H) with the methyl hydrogens δ 1.81 (s, 3H); revealing its geometry as *Z*. A similar pattern was observed for compound **3j**. The

stereochemistry of the other examples was assigned from these examples.

In summary, we have developed a simple and efficient method for the stereoselective synthesis of (Z)-2-Arylsulfanyl allylic alcohols using anhydrous $CeCl_3$ as catalyst, by addition of thiols into propargyl alcohols under solvent-free conditions. Thereaction showed excellent stereoselectivity leading to isomers of *Z* configuration for most of the compounds. The products were obtained in good yields and in short reaction times.

Acknowledgments

The authors thank FAPERGS (1014315/2010), CAPES and MCTI/CNPq for financial support.

References and notes

1. Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004.
2. (a) Brady, S. E.; Tyler, D. R. *J. Inorg. Organomet. Polym.* **2013**, *23*, 158; (b) Gunay, U. S.; Durmaz, H.; Gungor, E.; Dag, A.; Hizal, G.; Tunca, U. J. Polym. Sci., Part A:Polym. Chem. **2012**, *50*, 729; (c) Brändle, A.; Khan, A. *Polym. Chem.* **2012**, *3*, 3224.
3. Štrukil, V.; Margetić, D.; Igrc, M. D.; Eckert-Maksić, M.; Friščič, T. *Chem. Commun.* **2012**, 9705.
4. (a) Zarei, A.; Khazdooz, L.; Hajipour, A. R.; Aghaei, H.; Azizi, G. *Synthesis* **2012**, *44*, 3353; (b) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2596.
5. (a) Meldal, M. *Macromol. Rapid Commun.* **2008**, *29*, 1016; (b) Fahrenbach, A. C.; Stoddart, J. F. *Chem. AsianJ.* **2011**, *6*, 2660.
6. Hoyle, C. E.; Lowe, A. B.; Bowman, C. N. *Chem. Soc. Rev.* **2010**, *39*, 1355.
7. (a) Yang, M.; Mao, J.; Nie, W.; Dong, Z.; Wang, D.; Zhao, Z.; Ji, X. J. Polym. Sci., Part A: Polym.Chem. **2012**, *50*, 2075; (b) Shen, Y.; Ma, Y.; Li, Z. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 708.
8. Hoveyda, A. H.; Evans, D. A.; Fu, G. C. *Chem. Rev.* **1993**, *93*, 1307.
9. Alexakis, A.; Bäckvall, J. E.; Krause, N.; Pàmies, O.; Diéguez, M. *Chem. Rev.* **2008**, *108*, 2796.
10. Uma, R.; Crévisy, C.; Grée, R. *Chem. Rev.* **2003**, *103*, 27.
11. (a) Barchi, J. J., Jr.; Moore, R. E.; Patterson, G. M. L. *J. Am. Chem. Soc.* **1984**, *106*, 8193; (b) Bollag, D. M.; McQueney, P. A.; Zhu, J.; Hensens, O.; Koupal, L.; Liesch, J.; Goetz, M.; Lazarides, E.; Woods, C. M. *CancerRes.* **1995**, *55*, 2325; (c) Oka, M.; Iimura, S.; Tenmyo, O.; Sawada, Y.; Sugawara, M.; Ohkusa, N.; Yamamoto, H.; Kawano, K.; Hu, S.-L.; Fukagawa, Y.; Oki, T. *J.Antibiot.* **1993**, *46*, 367; (d) Burke, S. D.; Hong, J.; Lennox, J. R.; Mongin, A. P. *J. Org. Chem.* **1998**, *63*, 6952; (e) Jamison, F.; Chan, J. *J. Am. Chem. Soc.* **2003**, *125*, 11514.
12. (a) Takai, K.; Kataoka, Y.; Utimoto, K. *J. Org. Chem.* **1990**, *55*, 1707; (b) Magriotis, P. A.; Brown, J. T.; Scott, M. E. *Tetrahedron Lett.* **1991**, *32*, 5050; (c) Ogawa, A.; Tsuboi, Y.; Obayashi, R.; Yokoyama, K.; Ryu, I.; Sonoda, N. *J. Org. Chem.* **1994**, *59*, 1600; (d) Dabdoub, M. J.; Begnini, M. L.; Guerrero, P. G., Jr.; Baroni, A. C. M. *J. Org. Chem.* **2000**, *65*, 61; (e) Langille, N. F.; Jamison, T. F. *Org. Lett.* **2006**, *8*, 3761; (f) Kerrigan, M. H.; Jeon, S.; Chen, Y. K.; Salvi, L.; Carroll, P. J.; Walsh, P. J. *J. Am. Chem. Soc.* **2009**, *131*, 8434.
13. (a) Doi, T.; Yanagisawa, A.; Miyazawa, M.; Yamamoto, K. *Tetrahedron: Asymmetry* **1995**, *6*, 389; (b) Lee, T.; Kim, S. *Tetrahedron: Asymmetry* **2003**, *14*, 1951.
14. Murphy, J. A.; Patterson, C. W. *J. Chem Soc., Perkin Trans 1* **1993**, 405.
15. (a) Stille, J. K. *Angew. Chem.* **1986**, *25*, 508; (b) Farina, V.; Krishnamurthy, V.; Scott, W. *Org.React.* **1997**, *50*, 1.
16. (a) Whitham, G. H. In *Organosulfur Chemistry*; Davies, S. G., Ed.; Oxford Chemistry Primers, Oxford University University Press: Oxford, 1995; (b) Irgolic, K. I. In *Houben-Weyl Methods of Organic Chemistry*; Klaman, D., Ed.; Georg Thieme: Stuttgart, 1990; 4th ed.; Vol. E12b, (c) Paulmier, C. *Selenium Reagents and Intermediates in OrganicSynthesis*; Pergamon Press: Oxford, 1986; (d) Petragnani, N.; Stefani, H. A. *Tellurium in Organic Synthesis – Best Synthetic Methods*, 2nd ed.; Academic Press: London, 2007; (e) Cremlyn, R. J. *An Introduction to Organo-Sulfur Chemistry*; Wiley & Sons: New York, 1996.
17. (a) Nogueira, C. W.; Zeni, G.; Rocha, J. B. T. *Chem. Rev.* **2004**, *104*, 6255; (b) Zheng, Y. F.; Dodd, S. S.; Oehlschlager, A. C.; Hartman, P. G. *Tetrahedron* **1995**, *51*, 5255; (c) Ceruti, M.; Balliano, G.; Rocco, F.; Milla, P.; Arpico, S.; Cattel, L.; Viola, F. *Lipids* **2001**, *36*, 629; (d) Zhao, G.; Zhou, Z. S. *Bioorg. Med. Chem. Lett.* **2001**, *11*, 2331; (e) Marcantoni, E.; Massaccesi, M.; Petrini, M. *J. Org.Chem.* **2000**, *65*, 4553; (f) Kabir, M. S.; Lorenz, M.; Van Linn, M. L.; Namjoshi, O. A.; Ara, S.; Cook, J. M. *J. Org.Chem.* **2010**, *75*, 3626. and references therein..
18. (a) Zeni, G.; Ludtke, D. S.; Panatieri, R. B.; Braga, A. L. *Chem. Rev.* **2006**, *106*, 1032; (b) Silveira, C. C.; Perin, G.; Jacob, R. G.; Braga, A. L. Phosphorus, Sulfur, Silicon Relat. Elem. **2001**, *172*, 309; (c) Perin, G.; Lenardão, E. J.; Jacob, R. G.; Panatieri, R. B. *Chem. Rev.* **2009**, *109*, 1277.
19. (a) Beletskaya, I. P.; Ananikov, V. P. *Chem. Rev.* **2011**, *111*, 1596; (b) Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2004**, *104*, 3079; (c) Gerard, J.; Hevesi, L. *Tetrahedron* **2001**, *57*, 9109; (d) Kondo, T.; Mitsudo, T. *Chem.Rev.* **2000**, *100*, 3205.
20. (a) Riduan, S. N.; Ying, J. Y.; Zhang, Y. *Org. Lett.* **2012**, *14*, 1780; (b) Malyshev, D. A.; Scott, N. M.; Marion, N.; Steven, E. D.; Ananikov, V. P.; Beletskaya, I. P.; Nola, S. P. *Organometallics* **2006**, *25*, 4462; (c) Yamashita, F.; Kuniyasu, H.; Terao, J.; Kambe, N. *Org. Lett.* **2008**, *10*, 101; (d) Cao, C.; Fraser, L. R.; Love, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 17614; (e) Ananikov, V. A.; Orlov, N. V.; Beletskaya, I. P. *Organometallics* **2007**, *26*, 740; (f) Kondo, A. K.; Takami, K.; Yorimitsu, H.; Oshima, K. *J. Org. Chem.* **2005**, *70*, 6468; (g) Trofimov, B. A. *Curr. Org.Chem.* **2002**, *6*, 1121; (h) Ogawa, A.; Ikeda, T.; Kimura, K.; Hirao, T. *J. Am. Chem. Soc.* **1999**, *121*, 5108; (i) Manarin, F.; Roehrs, J. A.; Progol, M.; Alves, D.; Nogueira, C. W.; Zeni, G. *Tetrahedron Lett.* **2007**, *48*, 4805; (j) Corma, A.; González-Arellano, C.; Iglesias, M.; Sánchez, F. *Appl. Catal., A* **2010**, *375*, 49.
21. (a) Waters, M. S.; Cowen, J. A.; McWilliams, J. C.; Maligres, P. E.; Askin, D. *Tetrahedron Lett.* **2000**, *41*, 141; (b) Ananikov, V. P.; Orlov, N. V.; Beletskaya, I. P. *Organometallics* **2006**, *25*, 1970; (c) Xu, Y.; Hao, W.; Wang, D.; Cai, M. *Heteroat. Chem.* **2008**, *19*, 639; (d) Arcadi, A.; Alfonsi, M.; Marinelli, F. *Tetrahedron Lett.* **2009**, *50*, 2060; (e) Jin, Z.; Xu, B.; Hammond, G. B. *Eur. J. Org. Chem.* **2010**, 168; (f) Biswas, S.; Samec, S. M. *Chem.Commun.* **2012**, *48*, 6586.
22. (a) Kao, H. L.; Lee, C. F. *Org. Lett.* **2011**, *13*, 5204; (b) Lin, Y. Y.; Wang, Y. J.; Lin, C. H.; Cheng, J. H.; Lee, C. F. *J. Org. Chem.* **2012**, *77*, 6100. and references therein..
23. Bartoli, G.; De Nino, A.; Dalpozzo, R.; Maiuolo, L.; Nardi, M.; Procopio, A.; Tagarelli, A. *Lett. Org.Chem.* **2005**, *2*, 51.
24. (a) Tsuruta, H.; Yamaguchi, K.; Imamoto, T. *Tetrahedron Lett.* **2003**, *59*, 10419; (b) Bartoli, G.; Dalpozzo, R.; DeNino, A.; Maiuo-lo, L.; Nardi, M.; Procopio, A.; Tagarelli, A. *Eur. J. Org. Chem.* **2004**, 2176; (c) Silveira, C. C.; Mendes, S. R.; Wolf, L.; Martins, G. M. *Tetrahedron Lett.* **2010**, *51*, 2014; (d) Bartoli, G.; Marcantoni, E.; Marcolini, M.; Sambri, L. *Chem. Rev.* **2010**, *110*, 6104.
25. (a) Sabitha, G.; Yadav, J. S. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; Wiley-VCH: Weinheim, 2006; (b) Bartoli, G.; DiAntonio, G.; Giovannini, R.; Giuli, S.; Lanari, S.; Paoletti, M.; Marcantoni, E. *J. Org. Chem.* **2008**, *73*, 1919; (c) Yadav, J. S.; SubbaReddy, B. V.; Suresh Reddy, Ch.; Krishna, A. D. *Tetrahedron Lett.* **2007**, *48*, 2029; (d) Meng, Q.; Sun, Y.; Ratovelomanana-Vidal, V.; Genêt, J. P.; Zhang, Z. *J. Org. Chem.* **2008**, *73*, 3842; Cerium chloride was dried accordingto: (e) Dimitrov, V.; Kostova, K.; Genov, M. *Tetrahedron Lett.* **1996**, *37*, 6787.
26. (a) Silveira, C. C.; Mendes, S. R. *Tetrahedron Lett.* **2007**, *48*, 7469; (b) Silveira, C. C.; Mendes, S. R.; Líbero, F. *Synlett* **2010**, *5*, 790; (c) Silveira, C. C.; Mendes, S. R.; Wolf, L.; Martins, G. M. *Tetrahedron Lett.* **2010**, *51*, 4560; (d) Silveira, C. C.; Mendes, S. R.; Martins, G. M. *Tetrahedron Lett.* **2012**, *53*, 1567; (e) Silveira, C. C.; Mendes, S. R.; Villetti, M. A.; Back, D. F.; Kaufman, T. S. *Green Chem.* **2012**, *14*, 2912. and references therein..
27. *Typical procedure*: To a mixture of propargylic alcohol (1.0 mmol) and anhydrous $CeCl_3$ (0.049 g, 20 mol %), was added the thiol (1.1 mmol). The reaction progress was followed by GC–MS, the reaction mixture was stirred at 80 °C in an oil bath for the time indicated in Table 2. The resulting reaction mixture was extracted with EtOAc (3 × 10 mL). The organic phase was washed with water and brine. Then, it was dried over anhydrous $MgSO_4$, the solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel (EtOAc:hexanes 10/90). Spectral data of selected products. Compound (**3d**): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.60–7.55 (m, 2H), 7.45–7.38 (m, 3H), 7.28–7.15 (m, 5H), 7.09–6.99 (m, 5H), 2.89 (s, 1H), 1.84 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 144.5, 139.1, 135.5, 135.2, 135.1, 133.0, 129.3, 128.6, 128.2, 128.1, 127.9, 127.6, 127.2, 125.6, 78.3, 28.8. MS (EI): *m*/*z* 366 (M^+, 27), 257 (13), 239 (10), 212 (100), 211 (55), 178 (45), 167 (35), 155 (36), 121 (25), 77 (15). Anal. Calcd for $C_{22}H_{19}ClOS$: C, 72.02; H, 5.22. Found: C, 71.63; H, 5.45. Compound (**3e**): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (d, 2H, *J* = 8.7), 7.40 (d, 2H, *J* = 8.8), 7.28 (s, 1H), 7.24–7.14 (m, 5H), 6.92 (d, 2H, *J* = 8.9), 6.55 (d, 2H, *J* = 8.9), 3.66 (s, 3H), 3.03 (s, 1H), 1.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.4, 144.8, 141.5, 135.6, 134.4, 132.9, 130.7, 129.4, 128.1, 127.9, 127.8, 127.2, 125.5, 114.4, 78.2, 55.2, 29.0. MS (EI): *m*/*z* 396 (M^+, 16), 395 (63), 241 (100), 225 (55), 210 (36), 197 (53), 165 (32), 139 (58), 77 (25). Anal. Calcd for $C_{23}H_{21}ClO_2S$: C, 69.60; H, 5.33. Found: C, 69.32; H, 5.33. Compound (**3g**): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.58–7.54 (m, 2H), 7.43 (s, 1H), 7.19–6.97 (m, 8H), 2.16 (s, 1H), 1.88–1.63 (m, 9H), 1.29–1.11 (m, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 140.5, 136.5, 135.9, 135.3, 129.2, 128.6, 127.8, 127.7, 126.9, 125.1, 76.0, 36.3, 25.3, 21.9. MS (EI): *m*/*z* 310 (M^+, 7), 292 (38), 183 (55), 167 (20), 141 (100), 125 (17), 115 (28), 91 (34), 77 (17), 55 (11). Anal. Calcd for $C_{20}H_{22}OS$: C, 77.38; H, 7.14. Found: C, 77.19; H, 7.01. Compound (**3h**): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.60–7.56 (m, 2H), 7.43 (s, 1H), 7.24–6.98 (m, 8H), 2.49 (s, 1H), 1.52 (s, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 139.8, 136.2, 135.7, 134.9, 129.2, 128.6, 127.8, 127.8, 127.0, 125.2, 75.3, 29.4. MS (EI): *m*/*z* 270 (M^+, 9), 252 (17), 211 (8), 143 (100), 128 (69), 115 (21), 77 (16). Anal. Calcd for $C_{17}H_{18}OS$: C, 75.51; H, 6.71 Found: C, 75.28; H, 6.71. Compound (**3j**):[21c] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, 2H, *J* = 8.4), 7.35–7.17(m, 8H), 6.43 (t, 1H, *J* = 6.8), 2.82 (s, 1H), 2.35–2.22 (m, 1H), 2.21–2.04 (m, 1H), 1.75 (s, 3H), 1.43–1.21 (m, 4H),0.84 (t, 3H, *J* = 7.2). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.4, 139.4, 139.1, 136.8, 128.7, 128.0, 127.1, 126.9, 125.5, 125.2, 78.0, 30.7, 30.1, 28.8, 22.3, 13.7. MS (EI): *m*/*z* 312 (M^+, 33), 192 (86), 149 (83), 121 (57), 110 (100), 77 (34).
28. Sanz, R.; Martínez, A.; Lvarez-Gutiérrez, J. M.; Rodríguez, F. *Eur. J. Org. Chem.* **2006**, 1383.
29. Inada, Y.; Nishibayashi, Y.; Hisai, M.; Uemura, S. *J. Am. Chem. Soc.* **2002**, *124*, 15172.
30. Georgy, M.; Boucard, V.; Campagne, J. M. *J. Am. Chem. Soc.* **2005**, *127*, 14180.
31. Zhan, Z. P.; Yu, J. L.; Liu, H. J.; Cui, Y. Y.; Yang, R. F.; Yang, W. Z.; Li, J. P. *J. Org.Chem.* **2006**, *71*, 8298.