Green Chemistry

Cite this: *Green Chem.*, 2012, **14**, 456

www.rsc.org/greenchem

PAPER

Synthesis of selenol esters from diorganyl diselenides and acyl chlorides under solvent-free conditions and microwave irradiation†

Marcelo Godoi,[a] Eduardo W. Ricardo,[a] Giancarlo V. Botteselle,[a] Fabio Z. Galetto,[a,b] Juliano B. Azeredo[a] and Antonio L. Braga*[a]

Received 6th October 2011, Accepted 18th November 2011
DOI: 10.1039/c1gc16243h

Herein, we report an efficient, quick and eco-friendly new method for the synthesis of a variety of selenol esters. This novel solvent-free methodology gave good to excellent isolated yields of desired products after just 2 min under microwave irradiation. Furthermore, by using the same green approach, we were also able to synthesize selenocarbonates bearing interesting functionalities.

Introduction

Organoselenium compounds have been gaining increasing attention in recent years, mainly due to their properties as antioxidant and antitumor agents, apoptosis inducers and in the effective chemoprevention of cancer in a variety of organs.[1,2]

Moreover, this class of compounds has become an attractive synthetic target in chemo-, regio- and stereoselective reactions.[3,4] Notably in this context, organoselenium compounds have been used as chiral catalysts in asymmetric catalysis,[5,6] as well as electrophilic, nucleophilic and radical species in cross-coupling reactions.[7]

The most convenient methodologies for the incorporation of selenium into organic compounds generally involve the preparation of selenolate anions, which can be generated *via* reductive cleavage of Se–Se bonds. The most commonly used protocols for generating selenolates *in situ* have employed several reducing agents, such as $NaBH_4$, $LiAlH_4$ and other expensive metal sources such as La, In, Yb, Sm, *etc.*[8,9] Thus, research aimed at improving these transformations is currently of great interest. In particular, studies on the use of Zn dust for the cleavage of diselenides have received special attention due to the unique properties of this material, including easy manipulation and better stability in air compared to other metals.[10,11]

Selenol esters have been shown to be of great importance as intermediates in several organic transformations.[12] For instance, these kinds of compounds have been successfully employed as precursors of acyl radicals[13] and anions[14] and also have attracted special attention for the synthesis of new molecular materials, including superconducting materials and liquid crystals.[15] Furthermore, applications of selenol esters have been expanded to the synthesis of proteins by chemical ligation of chalcogenol esters,[16] to the synthesis of substrates which undergo facile and efficient radical decarbonylation, as well as to the synthesis of the natural alkaloid.[17]

Although several methods were reported in the past,[18] new methods for the synthesis of selenol esters have still been described. In this context, these compounds have been prepared under different reaction conditions, for instance, from aldehydes using both i-Bu_2AlSeR[19] and SeCO,[20] from anhydride using rongalite/base system.[21] Moreover, employing selenoacetylenes[22] as selenium source and by coupling of aryl iodides with CO and $PhSeSnBu_3$ catalyzed by Pd.[23] However, the vast majority of methodologies reported have used acyl chlorides with nucleophilic species of selenium involving reagents such as $Hg(SePh)_2$,[24] $PhSeSiMe_3$[25] and $PhSeSnBu_3/Pd$,[26] or reductive cleavage of diselenides with indium,[27] indium(I) iodide[28] and magnesium.[29] Furthermore, the reductive coupling of diselenide and acyl chloride in an Rh/H_2 system has also been reported.[30] All of the methods cited above are detailed in Fig. 1.

Despite the variety of methodologies described to date, it is well recognized that most of the protocols shown in Fig. 1 have their respective drawbacks, such as air reactivity of some selenium compounds, use of toxic and carcinogenic solvents, and long reaction time. In addition, some procedures which do not require the use of an inert atmosphere, such as the synthesis of selenol esters from selenoacetylenes, also have their own limitations since these compounds are not readily available.

Alternatively, in order to minimize these limitations concerning the synthesis of selenol esters, we have recently reported new methods employing the use of ionic liquids as eco-friendly solvents in different reaction systems.[31] However, the development of new methodologies to carry out the preparation of selenol esters under mild reaction conditions, open to the

---

[a] *Departamento de Química, Universidade Federal de Santa Catarina, Florianópolis, SC, Brazil. E-mail: albraga@qmc.ufsc.br; Fax: +55-48 3721 6427; Tel: +55-48 3721 6844*
[b] *Departamento de Química, Universidade Federal de Santa Maria, Santa Maria, RS, Brazil; Fax: +55-55 3220 8998; Tel: +55-55 3220 8761*

† Electronic supplementary information (ESI) available: Detailed experimental procedures, NMR spectra of all isolated compounds. See DOI: 10.1039/c1gc16243h

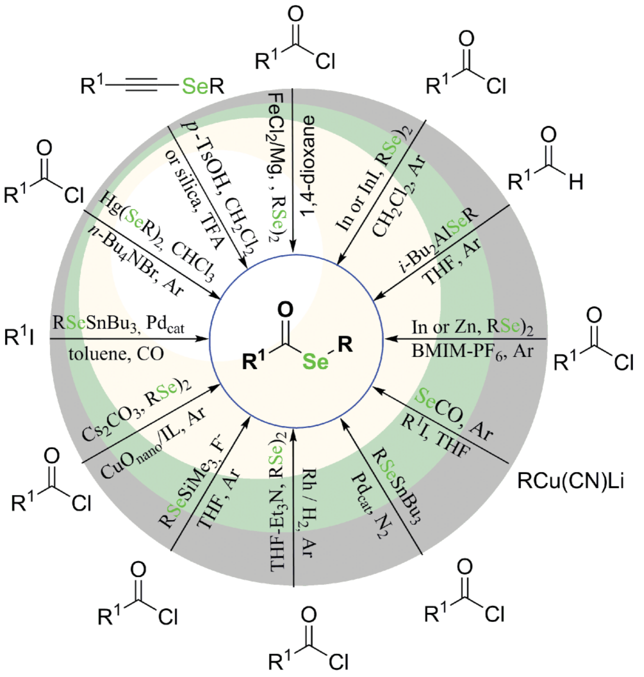
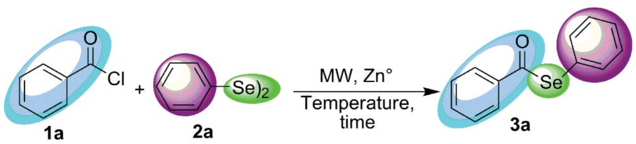


Fig. 1 General methodologies for the synthesis of selenol esters.

Table 1 Optimization of the reaction conditions[a]



Entry	MW power (W)	T (°C)	Time (min)	Yield (%)[b]
1	100	80	0.5	61
2	100	80	1.0	72
3	100	80	2.0	88
4	100	80	5.0	90
5	100	80	2.0	88[c]
6	100	50	2.0	63
7	100	130	2.0	91
8	150	80	2.0	88
9	50	80	2.0	40
10	—	80	90.0	67[d]

[a] *Reaction conditions*: benzoyl chloride (0.5 mmol), diphenyl diselenide (0.25 mmol), Zn dust (0.25 mmol), MW. [b] Isolated yields. [c] Reaction was carried out under argon atmosphere. [d] Conventional heating.

air, employing stable and non-hazardous starting materials and short reaction time coupled with neat conditions, is still highly desirable.

On the other hand, microwave (MW) irradiation has provided higher yields, avoiding the synthesis of side products and allowing milder conditions and shorter reaction times in several transformations.[32] From an environmental point of view, the use of microwave irradiation associated with neat conditions has been described and is emerging as an environmentally benign alternative.[33] Nonetheless, this irradiation source has not been widely employed in organoselenium chemistry and studies exploring a combination of microwaves and solvent-free conditions are rare in this area.[34]

Thus, in connection with our continuing interest in organoselenium chemistry using eco-friendly conditions,[31,35] herein we describe a novel method for the synthesis of selenol esters in the absence of solvent, under microwave irradiation in a very short reaction time (Scheme 1).

Scheme 1 Synthesis of selenol esters.

Results and discussion

In order to optimize our protocol, we performed the reaction using benzoyl chloride, diphenyl diselenide and zinc dust in the absence of solvent with an irradiation power of 100 W (Table 1). Firstly, the reaction was carried out for only 0.5 min, affording the desired product in 61% yield (entry 1). However, on increasing the reaction time to 1 min, the selenol ester **3a** was obtained with 72% yield (entry 2). Similarly, when the reaction was carried out for 2 min the corresponding product was enhanced, in this case to 88% yield (entry 3). On further extension of the irradiation time, no significant change in the yield was observed (Table 1, entry 4).

Furthermore, it was observed in this study that the inert atmosphere did not influence the reaction, since we obtained the desired product in the same yield compared with open atmosphere (entry 3 *vs.* 5).

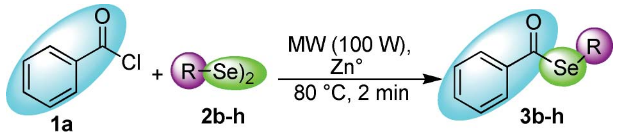
On the other hand, the reaction temperature proved to have a great influence on the yield values (entries 3, 6 and 7). Screening this reaction parameter revealed that a value of 80 °C was most appropriate, since on decreasing the temperature to 50 °C the desired selenol ester was obtained in lower yield, whilst on increasing the temperature from 80 to 130 °C no significant change in the yield was observed (entry 3 *vs.* 7).

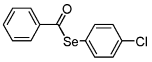
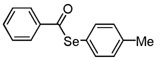
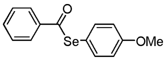
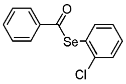
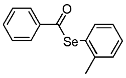
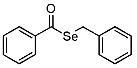
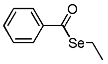
Focusing on the influence of the microwave irradiation on the system we carried out the reaction with different levels of microwave power (50–150 W). An increase in the power from 100 to 150 W did not affect the reaction since the desired product **3a** was obtained in the same yield (entry 8). However, on decreasing the power to 50 W the yield decreased considerably (entry 9). Therefore, this optimization of the irradiation power showed that 100 W was the best choice for the synthesis of selenol esters (entry 3). Moreover, we also carried out the reaction under conventional heating and even after a long reaction time only 67% yield of the desired product was achieved (entry 10). Thus, these results indicated that the reaction performed under microwave irradiation has significant advantages compared to conventional heating, since the reaction time was reduced and the desired product was obtained in better yield.

Once we had established the best conditions, we then examined the scope of the reaction (Table 2). At first, a variety of diorganyl diselenides were reacted with benzoyl chloride in order to synthesize different selenol esters (entries 1–6).

The electronic effects of substituents in the aryl diselenides were evaluated and showed a remarkable effect on the reaction. For instance, when diselenides containing withdrawing groups

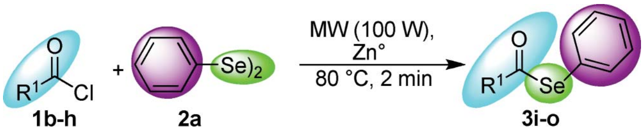
Table 2 Synthesis of selenol esters with a variety of diselenides[a]

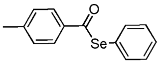
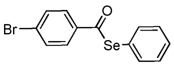
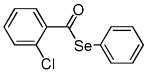
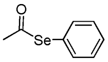
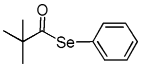
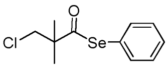


Entry	R	Product	Yield (%)[b]
1	*p*-ClPh, **2b**	 **3b**	90
2	*p*-MePh, **2c**	 **3c**	66
3	*p*-MeOPh, **2d**	 **3d**	61
4	*o*-ClPh, **2e**	 **3e**	92
5	*o*-MePh, **2f**	 **3f**	70
6	Bn, **2g**	 **3g**	71
7	Et, **2h**	 **3h**	70

[a] *Reaction conditions*: acyl chloride (0.5 mmol), diorganyl diselenide (0.25 mmol), Zn dust (0.25 mmol), MW (100 W), 80 °C, 2 min. [b] Isolated yields.

Table 3 Synthesis of several selenol esters[a]



Entry	R¹	Product	Yield (%)[b]
1	*p*-MePh, **1b**	 **3i**	80
2	*p*-BrPh, **1c**	 **3j**	95
3	*o*-ClPh, **1d**	 **3l**	64
4	Me, **1e**	 **3m**	86
5	*t*-Bu, **1f**	 **3n**	40
6	ClC_4H_8, **1g**	 **3o**	41

[a] *Reaction conditions*: acyl chloride (0.5 mmol), diorganyl diselenide (0.25 mmol), Zn dust (0.25 mmol), MW (100 W), 80 °C, 2 min. [b] Isolated yields.

attached to the aromatic ring were used, a significant improvement in the yield values was observed and the desired products were achieved in 90% and 92% yields, respectively (entries 1 and 4). Meanwhile, by using either a weak or a strong electron donating group, the corresponding products were obtained in lower yields (entries 2, 3 and 5). These considerable decreases in the yield values may be explained by the stronger Se–Se bond of electron-rich aryl diselenides.

It is well recognized that diaryl diselenides are more reactive than aliphatic ones and are also much more easily cleaved.[36] Applying the same methodology, we prepared the selenol ester starting from aliphatic diselenides. Using both dibenzyl diselenide and diethyl diselenide as a source of selenolate anions, the corresponding compounds **3f** and **3g** were obtained in good yields (entries 6 and 7).

In our reaction system we also investigated the combination of a range of structurally diverse acid chlorides with diphenyl diselenide (Table 3). When compound **1b**, with a soft electron-donor group in the *para* position of the aromatic ring, was used the corresponding product was obtained with 80% yield (entry 1).

Notably, when *p*-bromo benzoyl chloride was employed as the acyl source the yield increased to 95% (entry 2). However, benzoic acid chloride with a halide in the *ortho* position did not provide an active substrate under the same reaction conditions, affording the desired product in only 64% yield (entry 3).

Some aliphatic acyl chlorides were also used in order to synthesize alkylic selenol esters (entries 4–6). It was noted that when the acyl chloride **1e** was used the corresponding product was achieved with 86% yield (entry 4).

However, the aliphatic acyl chlorides which were sterically hindered proved to be less reactive substrates in the present methodology. Thus, using either 2,2-dimethylpropionyl chloride or 3-chloro-2,2-dimethylpropanoyl chloride afforded the corresponding products **3n** and **3o** in lower yields (entries 5 and 6).

It is well known that selenium-containing protecting groups make these reagents particularly valuable for efficient application in palladium-catalyzed decarboxylation.[37] Thus, we also attempted to synthesize different selenocarbonates bearing interesting functionalities by using the same methodology. Gratifyingly, the corresponding products were obtained with satisfactory yields, as depicted in Fig. 2.

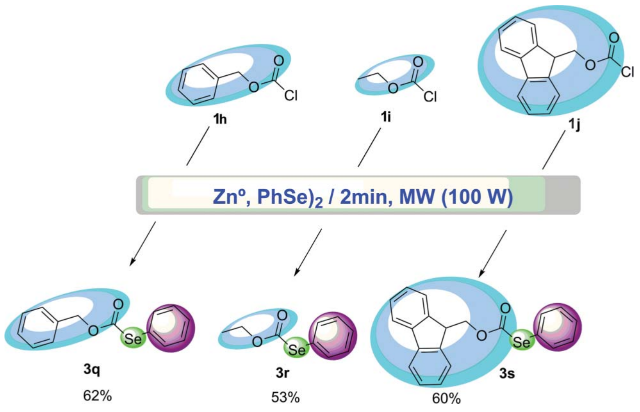
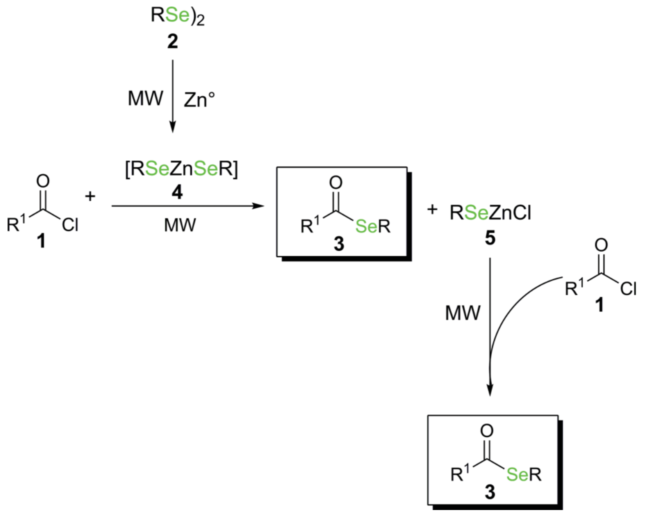


Fig. 2 Synthesis of selenocarbonates.

Interestingly, as described previously by our group,[27] the FMOC-modified substrate **1j** is an efficient protecting group for organic selenium compounds and can also be extended to the synthesis of seleno amino acids.

It is well established that metallic zinc can be inserted into a diselenide bond, and an RSeZnSeR complex is formed in the reaction medium.[9] A plausible pathway for the synthesis of selenol esters is illustrated in Scheme 2. We assumed that initially the diselenide bridge is rapidly cleaved by Zn dust, affording the complex di(organylselenyl)zinc **4**, which reacts with acyl chloride furnishing the product **3** and RSeZnCl. Subsequently, compound **5**, which is a versatile reagent according to Santi *et al.*,[38] undergoes a nucleophilic attack on another equivalent of acyl chloride **1**, giving another equivalent of the desired selenol ester.



Scheme 2 Plausible reaction pathway.

Conclusions

In summary, we have described an efficient, rapid and eco-friendly approach to the synthesis of selenol esters. Applying this new methodology, we obtained the desired compounds in good to excellent yields. Moreover, this procedure is highly efficient and environmentally benign, allowing the synthesis of selenol esters by carrying out all reactions in the absence of solvent, open to the air, with a short reaction time and under microwave irradiation.

We believe that the chemistry described fulfils most of the aims of "green chemistry" and may represent an environmentally-benign alternative for the synthesis of different types of selenol esters, including selenocarbonates ,which can be used either as protecting groups for organoselenium compounds or in the synthesis of selenoamino acids. Intensive research in this area remains in progress in our laboratory.

Experimental section

Detailed experimental procedures, ^{1}H and ^{13}C NMR spectra for all compounds are available in the supporting information, ESI†.

Acknowledgements

We are grateful to CAPES, CNPq (INCT-Catálise) and FAPESC for financial support. CAPES is also acknowledged for the doctorate fellowship received by M. G.

Notes and references

1 (*a*) D. L. Klayman and H. H. Günter, *Organoselenium Compounds: Their Chemistry and Biology*, Wiley-Interscience, New York, 1973; (*b*) J. T. Rotruck, A. L. Pope, H. E. Ganther, A. B. Swanson, D. G. Hafeman and W. G. Hoekstra, *Science*, 1973, **179**, 588; (*c*) L. Flohé, E. A. Günzler and H. H. Schock, *FEBS Lett.*, 1973, **32**, 132; (*d*) R. J. Shamberger, *Biochemistry of Selenium*, Plenum Press, New York, 1983; (*e*) L. Flohé, J. R. Andreesen, R. Brigelius-Flohé, M. Maiorino and F. Ursini, *IUBMB Life*, 2000, **49**, 411; (*f*) C. Jacob, G. I. Giles, N. M. Giles and H. Sies, *Angew. Chem. Int. Ed.*, 2003, **42**, 4742; (*g*) E. E. Alberto and A. L. Braga, in *Selenium and Tellurium Chemistry – From Small Molecules to Biomolecules and Materials*, ed. W. J. Derek and L. Risto, Springer-Verlag, Berlin, Heidelberg, 2011, p. 251.

2 (*a*) G. Mugesh and H. Singh, *Chem. Soc. Rev.*, 2000, **29**, 347; (*b*) G. Mugesh, W. W. Du Mont and H. Sies, *Chem. Rev.*, 2001, **101**, 2125; (*c*) C. W. Nogueira, G. Zeni and J. B. T. Rocha, *Chem. Rev.*, 2004, **104**, 6255; (*d*) B. K. Sarma and G. Mugesh, *Org. Biomol. Chem.*, 2008, **6**, 965; (*e*) E. E. Alberto, V. Nascimento and A. L. Braga, *J. Braz. Chem. Soc.*, 2010, **21**, 2032.

3 (*a*) T. Wirth, Topics in Current Chemistry in *Organoselenium Chemistry*, ed., Springer, Heidelberg, 2000, p. 208; (*b*) A. Krief, In *Comprehensive Organometallic Chemistry II*, ed. E. V. Abel, F. G. A. Stone and G. Wilkinson, Pergamon Press, New York, 1995; Vol. 11, Chapter 13, p. 515; (*c*) C. Paulmier, in *Selenium Reagents and Intermediates in Organic Synthesis; Organic Chemistry Series 4*, ed. J. E. Baldwin, Pergamon Press, Oxford, 1986.

4 (*a*) D. M. Freudendahl, M. Iwaoka and T. Wirth, *Eur. J. Org. Chem.*, 2010, 3934; (*b*) L. Zhao, Z. Li and T. Wirth, *Eur. J. Org. Chem.*, 2011, 176; (*c*) S. A. Shahzad, C. Vivant and T. Wirth, *Org. Lett.*, 2010, **12**, 1364; (*d*) A. L. Braga, G. Zeni, L. H. Andrade and C. C. Silveira, *Synlett*, 1997, 595; (*e*) D. M. Browne, O. Niyomura and T. Wirth, *Org. Lett.*, 2007, **9**, 3169; (*f*) M. Tiecco, L. Testaferri, M. Tingoli, L. Bagnoli and C. Santi, *Synlett*, 1993, 798.

5 (*a*) S. Fukuzawa and K. Tsudsuki, *Tetrahedron: Asymmetry*, 1995, **6**, 1039; (*b*) T. Wirth, *Tetrahedron Lett.*, 1995, **36**, 7849; (*c*) A. L. Braga, F. Vargas, J. A. Sehnem and R. C. Braga, *J. Org. Chem.*, 2005, **70**, 9021; (*d*) M. Zielińska-Blajet, R. Siedlecka and J. Skażewski, *Tetrahedron: Asymmetry*, 2007, **18**, 131; (*e*) R. S. Schwab, L. C. Soares, L. Dornelles, O. E. D. Rodrigues, M. W. Paixão, M. Godoi and A. L. Braga, *Eur. J. Org. Chem.*, 2010, 3574; (*f*) F. Vargas, J. A. Sehnem, F. Z. Galetto and A. L. Braga, *Tetrahedron*, 2008, **64**, 392; (*g*) T. Wirth, K. J. Kulicke and G. Fragale, *Helv. Chim. Acta*, 1996, **79**, 1957; (*h*) E. Wojaczyńska and J. Skażewski, *Tetrahedron: Asymmetry*, 2008, **19**, 593.

6 For reviews, see: (*a*) T. Wirth, *Tetrahedron*, 1999, **55**, 1; (*b*) T. Wirth, *Angew. Chem., Int. Ed.*, 2000, **39**, 3741; (*c*) A. L. Braga, D. S. Lüdtke, F. Vargas and R. C. Braga, *Synlett*, 2006, 1453; (*d*) A. L. Braga, D. S. Lüdtke, F. Vargas and R. C. Braga, *Curr. Org. Chem.*, 2006, **10**, 1921; (*e*) M. Godoi, M. W. Paixão and A. L. Braga, *Dalton Trans.*, 2011, **40**, 11347.

7 (*a*) A. L. Braga, T. Barcellos, M. W. Paixao, A. M. Deobald, M. Godoi, H. A. Stefani, R. Cella and A. Sharma, *Organometallics*, 2008, **27**, 4009; (*b*) G. Perin, E. J. Lenardao, R. G. Jacob and R. B. Panatieri, *Chemical Reviews*, 2009, **109**, 1277.

8 (*a*) T. R. Hoye and A. J. Caruso, *Tetrahedron Lett.*, 1978, **19**, 4611; (*b*) D. Liotta, U. Sunay, H. Santiesteban and W. Markiewicz, *J. Org. Chem.*, 1981, **46**, 2605; (*c*) M. Yoshimatsu, T. Sato, H. Shimizu, M. Hori and T. Kataoka, *J. Org. Chem.*, 1994, **59**, 1011; (*d*) I. Andreadou, W. M. P. B. Menge, J. N. M. Commandeur, E. A. Worthington and N. P. E. Vermeulen, *J. Med. Chem.*, 1996, **39**, 2040; (*e*) T. Nishino, M. Okada, T. Kuroki, T. Watanabe, Y. Nishiyama and N. Sonoda, *J. Org. Chem.*, 2002, **67**, 8696; (*f*) B. C. Ranu, T. Mandal and S. Samanta, *Org. Lett.*, 2003, **5**, 1439; (*g*) B. C. Ranu and T. Mandal, *J. Org. Chem.*, 2004, **69**, 579; (*h*) R. J. Cohen, D. L. Fox and R. N. Salvatore, *J. Org. Chem.*, 2004, **69**, 4265; (*i*) M. Bonaterra, S. E. Martín and R. A. Rossi, *Tetrahedron Lett.*, 2006, **47**, 3511; (*j*) A. Ouchi, S. Liu, Z. Li, S. A. Kumar, T. Suzuki, T. Hyugano and H. Kitahara, *J. Org. Chem.*, 2007, **72**, 8700.

9 (*a*) J. Dowsland, F. McKerlie and D. J. Procter, *Tetrahedron Lett.*, 2000, **41**, 4923; (*b*) W. Su, N. Gao and Y. Zhang, *J. Chem. Res. Syn.*, 2002, **4**, 168; (*c*) N. Taniguchi and T. Onami, *J. Org. Chem.*, 2004, **69**, 915; (*d*) L. Wang, M. Wang and F. Huang, *Synlett*, 2005, 2007; (*e*) K. Ajiki, M. Hirano and K. Tanaka, *Org. Lett.*, 2005, **7**, 4193.

10 (*a*) B. Movassagh and M. Shamsipoor, *Synlett*, 2005, 121; (*b*) A. Krief, M. Derock and D. Lacroixa, *Synlett*, 2005, 2832; (*c*) B. Movassagh and A. Tatar, *Synlett*, 2007, 1954; (*d*) M. Nazari and B. Movassagh, *Tetrahedron Lett.*, 2009, **50**, 438; (*e*) A. L. Braga, P. H. Schneider, M. W. Paixão and A. M. Deobald, *Tetrahedron Lett.*, 2006, **47**, 7195; (*f*) X. Zhao, Z. Yu, S. Yan, S. Wu, R. Liu, W. He and L. Wang, *J. Org. Chem.*, 2005, **70**, 7338.

11 (*a*) L. W. Bieber, F. A. C. P. de Sá, P. H. Menezes and S. M. C. Goncalves, *Tetrahedron Lett.*, 2001, **42**, 4597; (*b*) B. Movassagh and M. Shamsipoor, *Synlett*, 2005, 1316; (*c*) C. Santi, S. Santoro, L. Testaferri and M. Tiecco, *Synlett*, 2008, 1471; (*d*) A. L. Braga, R. S. Schwab, E. E. Alberto, S. M. Salman, J. Vargas and J. B. Azeredo, *Tetrahedron Lett.*, 2009, **50**, 2309; (*e*) C. Santi, S. Santoro, L. Testaferri and M. Tiecco, *Eur. J. Org. Chem.*, 2008, 5387.

12 (*a*) T. Mukaiyama, M. Araki and H. Takei, *J. Am. Chem. Soc.*, 1973, **95**, 4763; (*b*) R. J. Anderson, C. A. Henrick and L. D. Rosenblum, *J. Am. Chem. Soc.*, 1974, **96**, 3654; (*c*) A. F. Sviridov, M. S. Ermolenko, D. V. Yashunsky and N. K. Kochetkov, *Tetrahedron Lett.*, 1983, **24**, 4355; (*d*) T. Mukaiyama, H. Uchiro, I. Shiina and S. Kobayashi, *Chem. Lett.*, 1990, 1019; (*e*) S. Kobayashi, H. Uchiro, Y. Fujishita, I. Shiina and T. Mukaiyama, *J. Am. Chem. Soc.*, 1991, **113**, 4247; (*f*) K.-H. Suh and D.-J. Choo, *Tetrahedron Lett.*, 1995, **36**, 6109.

13 (*a*) G. Keck and M. C. Grier, *Synlett*, 1999, 1657; (*b*) D. L. Boger and R. J. Mathvink, *J. Org. Chem.*, 1992, **57**, 1429; (*c*) C. Chen, D. Crich and A. Papadatos, *J. Am. Chem. Soc.*, 1992, **114**, 8313.

14 T. Hiiro, Y. Morita, T. Inoue, N. Kambe, A. Ogawa, I. Ryuand and N. Sonoda, *J. Am. Chem. Soc.*, 1990, **112**, 455.

15 (*a*) G. Heppke, J. Martens, K. Praefcke and H. Simon, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 318; (*b*) R. Cristiano, F. Ely and H. Gallardo, *Liq. Cryst.*, 2005, **32**, 15; (*c*) R. Cristiano, E. Westphal, I. H. Bechtold, A. J. Bortoluzzi and H. Gallardo, *Tetrahedron*, 2007, **63**, 2851; (*d*) D. R. Gamota, P. Brazis, K. Kalyanasundaram and J. Zhang, *Printed Organic and Molecular Electronics*, Kluwer Academic, New York, NY, 2004; (*e*) V. Balzani, A. Credi, F. M. Raymo and J. F. Stoddart, *Angew. Chem. Int. Ed.*, 2000, **39**, 3348; (*f*) K. L. Woon, M. P. Aldred, P. Vlachos, G. H. Mehl, T. Stirner, S. M. Kelly and M. O'Neill, *Chem. Mater.*, 2006, **18**, 2311; (*g*) H. Gallardo, C. Zucco and L. Da Silva, *Mol. Cryst. Liq. Cryst.*, 2002, **373**, 181; (*h*) J. Yamada, H. Akutsu, H. Nishikawa and K. Kikuchi, *Chem. Rev.*, 2004, **104**, 5057; (*i*) R. Cristiano, A. Vieira, F. Ely and H. Gallardo, *Liq. Cryst.*, 2006, **33**, 381; (*j*) D. S. Rampon, F. S. Rodembusch, J. M. F. M. Schneider, I. H. Bechtold, P. F. B. Goncalves, A. A. Merlo and P. H. Schneider, *J. Mater. Chem.*, 2010, **20**, 715.

16 (*a*) M. Baca, T. Muir, M. Schonolzer and S. Kent, *J. Am. Chem. Soc.*, 1995, **117**, 1881; (*b*) M. Inoue, S. Yamahita, Y. Ishihara and M. Hirama, *Org. Lett.*, 2006, **8**, 5805.

17 S. F. Martin, K. X. Chen and C. T. Eary, *Org. Lett.*, 1999, **1**, 79.

18 (*a*) P. A. Grieco, Y. Yokoyama and E. Williams, *J. Org. Chem.*, 1978, **43**, 1283; (*b*) M. R. Detty and G. P. Wood, *J. Org. Chem.*, 1980, **45**, 80; (*c*) P. A. Grieco and J. Y. Jaw, *J. Org. Chem.*, 1981, **46**, 1215; (*d*) G. P. Mullen, N. P. Luthra, R. B. Dunlap and J. D. Odom, *J. Org. Chem.*, 1985, **50**, 811; (*e*) H. Ishihara, N. Matsunami and Y. Yamada, *Synthesis*, 1987, 371.

19 T. Inoue, T. Takeda, N. Kambe, A. Ogawa, I. Ryu and N. Sonoda, *J. Org. Chem.*, 1994, **59**, 5824.

20 S.-I. Fujiwara, A. Asai, T. Shin-ike, N. Kambe and Noboru Sonoda, *J. Org. Chem.*, 1998, **63**, 5.

21 W. Dan, H. Deng, J. Chen, M. Liu, J. Ding and H. Wu, *Tetrahedron*, 2010, **66**, 7384.

22 (*a*) A. L. Braga, T. L. C. Martins, C. C. Silveira and O. E. D. Rodrigues, *Tetrahedron Lett.*, 2001, **57**, 3297; (*b*) M. Tiecco, L. Testaferri, A. Temperini, L. Bagnoli, F. Marini, C. Santi and R. Terlizzi, *Eur. J. Org. Chem.*, 2004, 3447.

23 Y. Nishiyama, K. Tokunaga, H. Kawamatsu and N. Sonoda, *Tetrahedron Lett.*, 2002, **43**, 1507.

24 C. C. Silveira, A. L. Braga and E. L. Larghi, *Organometallics*, 1999, **18**, 5183.

25 A. Capperucci, A. Degl'Innocenti and C. Tiberi, *Synlett*, 2011, 2248.

26 (*a*) I. P. Beletskaya, A. S. Sigeev, A. S. Peregudov and P. V. Petrovskii, *Russ. J. Org. Chem.*, 2001, **37**, 1703; (*b*) Y. Nishiyama, H. Kawamatsu, S. Funato, K. Tokunaga and N. Sonoda, *J. Org. Chem.*, 2003, **68**, 3599.

27 G. Marin, A. L. Braga, A. S. Rosa, F. Z. Galetto, R. A. Burrow, H. Gallardo and M. W. Paixao, *Tetrahedron*, 2009, **65**, 4614.

28 B. C. Ranu and T. Mandal, *J. Org. Chem.*, 2004, **69**, 5793.

29 K. Ren, M. Wang, P. Liu and L. Wang, *Synthesis*, 2010, 1078.

30 K. Ajiki, M. Hirano and K. Tanaka, *Org. Lett.*, 2005, **7**, 4193.

31 (*a*) D. Singh, S. Narayanaperumal, K. Gul, M. Godoi, O. E. D. Rodrigues and A. L. Braga, *Green Chem.*, 2010, **12**, 957; (*b*) G. Tabarelli, A. M. Deobald, G. Marin, O. E. D. Rodrigues, L. Dornelles and A. L. Braga, *Tetrahedron Lett.*, 2010, **51**, 5728; (*c*) S. Narayanaperumal, E. E. Alberto, K. Gul, C. Y. Kawasoko, L. Dornelles, O. E. D. Rodrigues and A. L. Braga, *Tetrahedron*, 2011, **67**, 4723.

32 (*a*) Y. Ju, D. Kumar and R. S. Varma,, *J. Org. Chem.*, 2006, **71**, 6697; (*b*) D. Kumar and R. S. Varma, *J. Org. Chem.*, 2007, **72**, 7420; (*c*) M. A. Herrero, J. M. Kremsner and C. O. Kappe, *J. Org. Chem.*, 2008, **73**, 36; (*d*) K. Görmer, H. Waldmann and G. Triola, *J. Org. Chem.*, 2010, **75**, 1811; (*e*) C. R. Strauss and D. W. Rooney, *Green Chem.*, 2010, **12**, 1340; (*f*) S. Herrero, R. Jiménez-Aparicio, J. Perles, J. L. Priego and F. A. Urbanos, *Green Chem.*, 2010, **12**, 965; (*g*) M. Najeebullah, D. W. Knight, M. A. Munawar, M. Yaseenx and F. Vincenzo, *Tetrahedron*, 2010, **66**, 6761; (*h*) M. T. Barros, K. T. Petrova, P. Correia-da-Silva and T. M. Potewar, *Green Chem.*, 2011, **13**, 1897; (*i*) M. N. Nadagouda, T. F. Speth and R. S. Varma, *Acc. Chem. Res.*, 2011, **44**, 469.

33 (*a*) M. Jida, R. Deprez-Poulain, S. Malaquin, P. Roussel, F. Agbossou-Niedercorn, B. Deprezand and G. Laconde, *Green Chem.*, 2010, **12**, 961; (*b*) G. Epane, J. C. Laguerre, A. Wadouachi and D. Marek, *Green Chem.*, 2010, **12**, 502; (*c*) F. Zhang and G. Zhang, *Green Chem.*, 2011, **13**, 178; (*d*) R. Sarma and D. Prajapati, *Green Chem.*, 2011, **13**, 718; (*e*) Z.-J. Liu, J.-P. Vors, E. R. F. Gesing and C. Bolm, *Green Chem.*, 2011, **13**, 42.

34 (*a*) G. Perin, R. G. Jacob, L. G. Dutra, F. Azambuja, G. F. F. Santos and E. J. Lenardão, *Tetrahedron Lett.*, 2006, **47**, 935; (*b*) G. Perin, S. R. Mendes, M. S. Silva, E. J. Lenardão, R. G. Jacob and P. C. Santos, *Synth. Commun.*, 2006, **36**, 2587.

35 D. Singh, E. E. Alberto, O. E. D. Rodrigues and A. L. Braga, *Green Chem.*, 2009, **11**, 1521.

36 V. P Ananikov, K. A. Gayduk, I. P. Beletskaya, V. N. Khrustalev and M. Y. Antipin, *Chem. Eur. J.*, 2008, **14**, 2420.

37 S. R. Waetzig and J. A. Tunge, *Chem. Comm.*, 2008, 3311.

38 (*a*) C. Santi, S. Santoro, B. Battistelli, L. Testaferri and M. Tiecco, *Eur. J. Org. Chem.*, 2008, 5287; (*b*) B. Battistelli, T. Lorenzo, M. Tiecco and C. Santi, *Eur. J. Org. Chem.*, 2011, 1848; (*c*) S. Santoro, B. Battistelli, L. Testaferri, M. Tiecco and C. Santi, *Eur. J. Org. Chem.*, 2009, 4921; (*d*) C. Santi, *Phenylselenenylzinc halides*, Encyclopedia of Reagents for Organic Synthesis, John Wiley & Sons Ltd. 2011, in press, 10.1002/047084289X.rn01352.