PAPER www.rsc.org/obc | Organic & Biomolecular Chemistry

Lewis acid $InBr_3$-catalyzed arylation of diorgano diselenides and ditellurides with arylboronic acids†

Kai Ren,[a] Min Wang[a] and Lei Wang*[a,b]

Received 20th July 2009, Accepted 18th August 2009
First published as an Advance Article on the web 23rd September 2009
DOI: 10.1039/b914533h

A novel Lewis acid $InBr_3$-catalyzed direct cross-coupling reaction of arylboronic acids with diorgano diselenides and ditellurides without any additive has been developed. The reactions generated the corresponding unsymmetrical diorgano monoselenides and monotellurides in good to excellent yields. The method has advantages of broad substrate scope, simple operation, mild reaction conditions and high effectiveness. A possible reaction mechanism was proposed.

Introduction

Organic chalcogens, especially with selenium and tellurium as structural motifs, are generally found in a variety of biological and pharmaceutical molecules[1] and in materials science.[2] Additionally, organoselenium compounds have emerged as an exceptional class of structures that exemplify a role in biochemical processes, serving as important therapeutic compounds ranging from antiviral and anticancer agents to naturally occurring food supplements.[3] To synthesize these compounds, a number of synthetic methods have been explored.[4] The generally used method to introduce a selenium or tellurium moiety into organic molecules is the reaction of a metal selenolate or tellurolate with appropriate electrophiles, such as organic halides and acyl chlorides, but aryl halides failed because of the less reactivity of $C(sp^2)$–X bonds.[5]

On the other hand, transition metal-catalyzed aryl carbon–chalcogen bond formation reactions for the preparation of unsymmetrical organochalcogenides have received more attention.[6] For the preparation of aryl chalcogenides, C–S and C–Se coupling reactions of aryl halides with thiols and selenols have been successfully carried out in the presence of palladium[7] and nickel,[8] as well as copper,[9] as catalyst under basic reaction conditions. Recently, dichalcogenides are used as substrates in the synthesis of monoselenides and tellurides since they are stable in air and are easy to treat. However, this is limited to alkyl halides.[10] In the metal-catalyzed chalcogenylation of aryl halides with dichalcogenide, an efficient reductant is often necessary for the generation of the corresponding anion[11] or metal–monochalcogenide complex.[12] As drawbacks, most of these synthetic protocols suffer from lengthy synthetic steps, harsh reaction conditions, and usually require the handling of air- and moisture-sensitive reagents.

Over the past few years, indium(III) salts have received increasing attention as a novel type of water-tolerant green Lewis acid catalyst for organic synthesis with highly chemo-, regio- and stereoselectivity. Compared to conventional Lewis acids, they have advantages of water stability, recyclability, operational simplicity, strong tolerance to oxygen and nitrogen-containing reaction substrates and functional groups.[13] As green Lewis acid catalysts, In(III) salts used in the Diels–Alder,[14] Friedel–Crafts,[15] Mukaiyama aldol,[16] and Sakurai–Hosomi allylation reactions[17] have been extensively investigated.[18] However, In(III)-catalyzed preparation of unsymmetrical organochalcogenides has not so far been described, despite the fact that a reaction of dichalcogenides with alkyl and acyl halides using a stoichiometric indium(I) iodide has been reported.[19]

Organoboronic acids are widely used as reagents in organic synthesis because they are commercially available, stable, generally nontoxic, and compatible with a variety of functional groups. Recently, a copper-catalyzed C–Se and C–Te coupling reaction of arylboronic acids with diselenides and ditellurides has been demonstrated by our group.[20] After that, synthesis of unsymmetrical monochalcogenides, including sulfides, selenides and tellurides from dichalcogenides with organoboronic acids in presence of CuI and a ligand 2,2′-dipyridyl was investigated.[21] As part of our ongoing efforts devoted to the synthesis of unsymmetrical organochalcogenides using a new and practical procedure, herein we wish to report a novel and highly efficient $InBr_3$-catalyzed direct cross-coupling reaction of diorgano diselenides and ditellurides with arylboronic acids in air in the absence of any additive. The reactions generated the corresponding unsymmetrical diorgano monoselenides and monotellurides in good to excellent yields (Scheme 1).

$$(R^1Y)_2 \;+\; R^2B(OH)_2 \xrightarrow[\text{DMSO, 130 °C}]{\text{InBr}_3\text{ (5 mol\%)}} R^1\text{–}Y\text{–}R^2$$

Y = Se, Te

Scheme 1

Results and discussion

In our preliminary investigations aimed at the preparation of 4-methoxyphenyl phenyl selenide, we undertook a detailed study using diphenyl diselenide and 4-methoxyphenyboronic acid as model coupling partners in order to probe the optimized reaction conditions with respect to a variety of indium salts and indium

---

[a] *Department of Chemistry, Huaibei Coal Teachers College, Huaibei Anhui 235000, P R China. E-mail: leiwang@hbcnc.edu.cn; Fax: + 86 (0)561 3090 518; Tel: + 86 (0)561 3802 069*
[b] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai, 200032, P R China*

† Electronic supplementary information (ESI) available: Full experimental details and further results. See DOI: 10.1039/b914533h

Table 1 Screening of catalysts and solvents for the reaction of arylboronic acid with diphenyl diselenide[a]

$$4\text{-MeOC}_6\text{H}_4\text{B(OH)}_2 + \text{C}_6\text{H}_5\text{SeSeC}_6\text{H}_5 \xrightarrow{\text{[In] Catal.}} 4\text{-MeOC}_6\text{H}_4\text{SeC}_6\text{H}_5$$

Entry	Indium source (amount)	Solvent/temp.	Yield (%)[b]
1	$InCl_3$ (5 mol%)	DMSO/130 °C	82
2	$InBr_3$ (5 mol%)	DMSO/130 °C	98 76[c]
3	InI_3 (5 mol%)	DMSO/130 °C	97
4	$In(CF_3SO_3)_3$ (5 mol%)	DMSO/130 °C	40
5	$In(CH_3COO)_3$ (5 mol%)	DMSO/130 °C	35
6	InCl (5 mol%)	DMSO/130 °C	0
7	InBr (5 mol%)	DMSO/130 °C	0
8	In metal (5 mol%)	DMSO/130 °C	0
9	In metal (5 mol%)	H_2O/100 °C	0
10	$InBr_3$ (2.5 mol%)	DMSO/130 °C	81
11	$InBr_3$ (10 mol%)	DMSO/130 °C	98
12	$InBr_3$ (5 mol%)	DMF/130 °C	0
13	$InBr_3$ (5 mol%)	DMA/130 °C	0
14	$InBr_3$ (5 mol%)	toluene/130 °C	0
15	$InBr_3$ (5 mol%)	benzene/80 °C	0
16	$InBr_3$ (5 mol%)	THF/67 °C	0
17	$InBr_3$ (5 mol%)	DCE/84 °C	0
18	$InBr_3$ (5 mol%)	DMSO/100 °C	30

[a] Reaction conditions: 4-methoxyphenylboronic acid (1.00 mmol), diphenyl diselenide (0.50 mmol), In catalyst (its amount indicated in this Table) in solvent (1.0 mL) at the indicated temperature for 20 h. [b] Isolated yields. [c] A commercially available Sale WP 650 microwave oven was utilized at 2450 MHz at 100% power for 0.25 h.

Table 2 $InBr_3$-catalyzed C–Se (Te) direct cross-coupling reactions[a]

$$(\text{R}^1\text{Y})_2 + \text{R}^2\text{B(OH)}_2 \xrightarrow[\text{DMSO, 130° C}]{\text{In Br}_3\text{ (5 mol\%)}} \text{R}^1-\text{Y}-\text{R}^2$$

Entry	$(R^1Y)_2$	$R^2B(OH)_2$	Yield (%)[b]
1	$(C_6H_5Se)_2$	$4\text{-MeOC}_6H_4B(OH)_2$	98
2	$(C_6H_5Se)_2$	$3\text{-MeOC}_6H_4B(OH)_2$	90
3	$(C_6H_5Se)_2$	$2\text{-MeOC}_6H_4B(OH)_2$	95
4	$(C_6H_5Se)_2$	$2,4\text{-MeOC}_6H_4B(OH)_2$	98
5	$(C_6H_5Se)_2$	$2,6\text{-MeOC}_6H_4B(OH)_2$	88[c]
6	$(C_6H_5Se)_2$	$4\text{-MeSC}_6H_4B(OH)_2$	96
7	$(C_6H_5Se)_2$	$4\text{-MeO}_2CC_6H_4B(OH)_2$	85
8	$(C_6H_5Se)_2$	$2\text{-OHCC}_6H_4B(OH)_2$	73
9	$(4\text{-MeOC}_6H_4Se)_2$	$C_6H_5B(OH)_2$	91
10	$(4\text{-MeOC}_6H_4Se)_2$	$4\text{-ClC}_6H_4B(OH)_2$	72
11	$(4\text{-MeOC}_6H_4Se)_2$	$4\text{-BrC}_6H_4B(OH)_2$	70
12	$(4\text{-MeOC}_6H_4Se)_2$	$4\text{-FC}_6H_4B(OH)_2$	85
13	$(4\text{-MeOC}_6H_4Se)_2$	$4\text{-MeC}_6H_4B(OH)_2$	93
14	$(4\text{-MeOC}_6H_4Se)_2$	$3\text{-MeC}_6H_4B(OH)_2$	77
15	$(4\text{-MeOC}_6H_4Se)_2$	$2\text{-MeC}_6H_4B(OH)_2$	89
16	$(4\text{-MeOC}_6H_4Se)_2$	$4\text{-}t\text{-}C_4H_9C_6H_4B(OH)_2$	83
17	$(4\text{-MeOC}_6H_4Se)_2$	$n\text{-}C_4H_9B(OH)_2$	trace
18	$(n\text{-}C_4H_9Se)_2$	$4\text{-MeOC}_6H_4B(OH)_2$	71
19	$(C_6H_5CH_2Se)_2$	$4\text{-MeOC}_6H_4B(OH)_2$	90
20	$(C_6H_5Te)_2$	$4\text{-MeOC}_6H_4B(OH)_2$	98
21	$(C_6H_5Te)_2$	$3\text{-MeOC}_6H_4B(OH)_2$	95
22	$(C_6H_5Te)_2$	$2\text{-MeOC}_6H_4B(OH)_2$	94
23	$(C_6H_5Te)_2$	$4\text{-MeO}_2CC_6H_4B(OH)_2$	95
24	$(4\text{-MeOC}_6H_4Te)_2$	$C_6H_5B(OH)_2$	99

[a] Reaction conditions: organoboronic acid (1.0 mmol), dichalcogenide (0.5 mmol), $InBr_3$ (0.05 mmol) in DMSO (1.0 mL), 130 °C, 20 h. [b] Isolated yields. [c] At 130 °C for 36 h.

metal, and the results are summarized in Table 1. Notably, when the reaction was ongoing on DMSO at 130 °C, $InBr_3$ or InI_3 was the judicious catalyst of choice, delivering 4-methoxyphenyl phenyl selenide exclusively, in very high yield and purity (Table 1, entries 2 and 3). On the other hand, other indium(III) salts, such as $InCl_3$, $In(CF_3SO_3)_3$, and $In(CH_3COO)_3$ under the same reaction conditions, were inferior and generated the desired products in 82, 40 and 35% yields, respectively (Table 1, entries 1, 4 and 5). However, when InCl, InBr or In metal was used as catalyst, no desired product was isolated and starting materials were recovered (Table 1, entries 6–9). Considering that $InBr_3$ is relatively cheap compared to InI_3, it was therefore chosen as catalyst for the following experiments. With respect to the catalyst loading, when 2.5 mol% of $InBr_3$ was used, the reaction did not go to completion (Table 1, entry 10), but that a higher loading (5 mol%) of the catalyst gave a very good result (Table 1, entry 2). However, with an increased loading of the catalyst up to 10 mol% there was no increase in the isolated yield of the product (Table 1, entry 11). Thus, 5 mol% of $InBr_3$ is enough to accomplish this reaction.

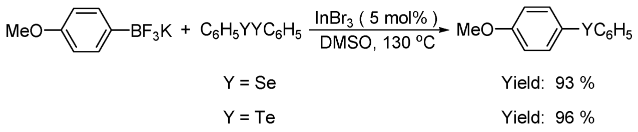
We next screened the effect of solvent on the model reaction by using 5 mol% of $InBr_3$ as catalyst at 130 °C, and the nature of the reaction media significantly affects the reaction. What is noteworthy is that the choice of DMSO as the solvent was crucial, and 98% yield of the desired product was isolated (Table 1, entry 2). Unfortunately, none of the desired product was isolated when the reactions were carried out in *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMA), toluene, benzene, tetrahydrofuran (THF) and 1,2-dichloroethane (DCE) (Table 1, entries 12–17).

Microwave irradiation conditions could significantly shorten the reaction time from 20 h to 0.25 h, but the yield of the product was reduced from 98% to 76% (Table 1, entry 2). Meanwhile, the effect of reaction temperature was also investigated. High yield was obtained when the reaction was carried out in DMSO at 130 °C for 20 h. The reaction at 100 °C for 20 h only gave product in 30% yield (Table 1, entry 18). Thus, the optimized reaction conditions for the cross-coupling of arylboronic acids with diselenides and ditellurides are $InBr_3$ (5 mol%) in DMSO at 130 °C for 20 h without any additive.

After obtaining the optimized reaction conditions, the scope of this transformation on the direct cross-coupling reaction of a variety of dichalcogenides with different substituted arylboronic acids was evaluated. The results are delineated in Table 2. At first, we set out to explore $InBr_3$-catalyzed arylation of diselenides by the use of various arylboronic acids. In general, the reaction is unaffected by electronic factors and steric hindrance of substituted groups on benzene rings in arylboronic acids. When diphenyl diselenide or di(4-methoxyphenyl) diselenide was served as dichalcogenide partner, a variety of electron-rich, electron-neutral, and electron-deficient arylboronic acids underwent C–Se cross-coupling reactions smoothly to generate the corresponding diaryl monoselenides in good to excellent yields (Table 2, entries 1–16). More distal steric bulk has, as expected, little effect upon reactivity as demonstrated by the 4-*tert*-butylphenylboronic acid case which reacted with di(4-methoxyphenyl) diselenide under the present reaction conditions to generate the desired product in 83% yield (Table 2, entry 16). Furthermore, sterically demanding *ortho* substituents did not hamper the cross-coupling reaction and the corresponding unsymmetrical diaryl monoselenides were obtained in good yields (Table 2, entries 3–5, 8, and 15). Remarkable observation was that more strongly sterically hindered substitution does not significantly affect the reaction rate or over yield, with 2,6-dimethoxyphenylboronic acid producing good yield of the expected product within a reasonable time (Table 2, entry 5). What's more, the tolerance of potentially reactive functional group, such as carbonyl and ester group to the described protocol was remarkable (Table 2, entries 7 and 8). However, only a trace amount of the product was isolated when an alkylboronic acid, such as n-$C_4H_9B(OH)_2$ was used as the substrate (Table 2, entry 17). Fortunately, dialkyl diselenide, such as n-$C_4H_9SeSeC_4H_9$-n, and dibenzyl diselenide ($C_6H_5CH_2SeSeCH_2C_6H_5$) also reacted with 4-methoxyphenylboronic acid to generate the corresponding products in 71, 90% yields, respectively (Table 2, entries 18 and 19).

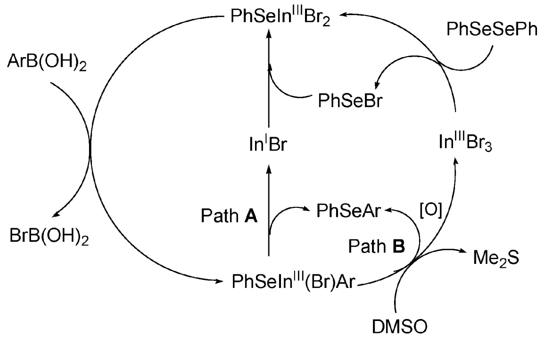
Then, we explored the cross-coupling reaction using other dichalcogenides, such as ditellurides and disulfides. According to the previously developed procedure, $InBr_3$-catalyzed coupling of ditellurides with a number of arylboronic acids also underwent C–Te bond formation smoothly to afford the desired diaryl monotellurides in good yields, which also were not affected by electronic effects or steric hindrance of the reaction center (Table 2, entries 20–24). However, all attempts to use diaryl disulfides as chalcogen source for directly C–S coupling with arylboronic acids were met with failure, probably due to the stronger S–S bond, and starting materials were recovered unconsumed.

As an alternative to organoboronic acids and esters, organotrifluoroborate salts have emerged as a new class of air-stable boron derivatives, facile to prepare in high yields and purities, easy to handle, and feasible to utilize in a number of useful synthetic processes.[22] When the reaction of potassium 4-methoxyphenyltrifluoroborates with diphenyl diselenide or ditelluride was performed under the present reaction conditions, as expected, excellent yields of the desired products were obtained (Scheme 2).



Scheme 2

A possible mechanism of $InBr_3$-catalyzed reaction was shown in Scheme 3. Initially, $InBr_3$ reacted with PhSeSePh to form $PhSeIn^{III}Br_2$ and PhSeBr through a heterolytic cleavage of Se–Se bond.[23] The obtained $PhSeIn^{III}Br_2$ then reacted with $ArB(OH)_2$ *via* transmetallation to generate $PhSeIn^{III}(Br)Ar$, which produced the desired cross-coupling product PhSeAr and InBr according to path **A** route *via* reductive elimination. On the other hand, $PhSeIn^{III}(Br)Ar$ also could generate the cross-coupling product PhSeAr and re-generate $InBr_3$ in path **B** way in the presence of an oxidant. DMSO, not only as the solvent, but also as the oxidant in path **B** might be reduced into dimethyl sulfide under the present reaction conditions.[24] The formed dimethyl sulfide could, in small amounts, be observed in gas chromatography analysis. Also we assumed that the generated dimethyl sulfide can stabilize the formed boronic acid in the transmetallation step.



Scheme 3 Possible mechanism of the reaction

The generated InBr in path **A** next reacted with PhSeBr, which is from initially step to provide $PhSeIn^{III}Br_2$ *via* oxidative addition. The proposed mechanism here also indicated that the cross-coupling of diorgano diselenide with arylboronic acid is able to use both selenide groups on diselenide.

Conclusions

In conclusion, we have successfully developed a novel and highly efficient procedure for the synthesizing unsymmetrical diorgano monoselenides and diorgano monotellurides in good to excellent yields through the directly C–Se and C–Te cross-coupling reaction of arylboronic acids and potassium aryltrifluoroborates with diorgano diselenides and diphenyl ditelluride in the presence of a catalytic amount of $InBr_3$ in DMSO without any additive in air. The present method displays a broad substrate scope, and is mild, simple, effective and convenient. Furthermore, this method can tolerate arylation of both organochalcogenide groups in a dichalcogenide. Althought the similar results including the reaction conditions, substrate scopes and yields, *etc.* were achieved by our previous work using copper catalysts,[20] it may open a new way for using $InBr_3$ as Lewis acid-catalyzed cleavage of Se–Se and Te–Te bond in diorgano diselenides and ditellurides without any activating agent and ligand in organic synthesis. Further work on In-catalyzed organic transformation is being in progress in our laboratory.

Experimental

For full details, see the ESI.† General remarks: All reactions were carried out under an air atmosphere. All reagents were purchased from commercial suppliers and used after further purification. Products were purified by flash chromatography on 230–400 mesh silica gel, SiO_2. All ^1H NMR, ^{13}C NMR spectra were measured on a Bruker Avance NMR spectrometer (400 MHz or 100 MHz, respectively) with $CDCl_3$ as solvent and recorded in ppm relative to internal tetramethylsilane standard. High resolution mass spectroscopy data of the product were collected on a Waters Micromass GCT instrument.

General procedure for $InBr_3$-catalyzed preparation of monochalcogenides from dichalcogenides with arylboronic acids without any additive: A 10 mL of reaction tube was charged with dichalcogenide (0.5 mmol), arylboronic acid (1.0 mmol), $InBr_3$ (0.05 mmol), and DMSO (1.0 mL). The reaction vessel was placed in an oil bath at 130 °C. After the reaction was carried out at this temperature for 20 h, it was cooled to room temperature, diluted with H_2O and extracted twice with Et_2O. The organic layers were combined, dried over Na_2SO_4, and concentrated to yield the crude product, which was further purified by flash chromatography on silica gel (eluant: petroleum ether) to give the desired cross-coupling product.

Acknowledgements

We gratefully acknowledge financial support by the National Natural Science Foundation of China (No. 20772043).

Notes and references

1 (*a*) K. C. Nicolaou, N. A. Petasis, in *Selenium in Natural Products Synthesis*, CIS, Pennsylvania, 1984; (*b*) S. Patai, Z. Rappoport and C. Wiley, in *The Chemistry of Organic Selenium and Tellurium Compounds*, 1987, vol. 2; (*c*) T. G. Back, in *Organoselenium Chemistry: A Practical Approach*, Oxford University Press, New York, 1999; (*d*) G. Liu, J. R. Huth, E. T. Olejniczak, R. Mendoza, P. DeVries, S. Leitza, E. B. Reilly, G. F. Okasinski, S. W. Fesik and T. W. Geldern, *J. Med. Chem.*, 2001, **44**, 1202–1210; (*e*) G. Mugesh, W. W. Mont and H. Sies, *Chem. Rev.*, 2001, **101**, 2125–2179; (*f*) M. G. Szczepina, B. D. Johnston, Y. Yuan, B. Svensson and B. M. Pinto, *J. Am. Chem. Soc.*, 2004, **126**, 12458–12469.

2 (*a*) Y. Okamoto, in *The Chemistry of Organic Selenium and Tellurium Compounds*, ed. S. Patai and Z. Rappoport, Wiley, Chichester, U.K., 1986, vol. 1, ch. 10; (*b*) J. Hellberg, T. Remonen, M. Johansson, O. Inganäs, M. Theander, L. Engman and P. Eriksson, *Synth. Met.*, 1997, **84**, 251–252; (*c*) T. Ando, T. S. Kwon, A. Kitagawa, T. Tanemura, S. Kondo, H. Kunisada and Y. Yuki, *Macromol. Chem. Phys.*, 1996, **197**, 2803–2810.

3 (*a*) A. Krief and M. Derock, *Tetrahedron Lett.*, 2002, **43**, 3083–3086; (*b*) D. L. Klayman and W. H. H. Günther, in *Organoselenium Compounds: Their Chemistry and Biology*, Wiley-Interscience, New York, 1973.

4 For selected reviews: (*a*) B. M. Trost and I. Fleming, in *Comprehensive Organic Synthesis*, Pergamon Press, New York, 1991, vol. 4; (*b*) A. Krief, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon Press, New York, 1995, vol. 11, ch. 13; (*c*) N. Miyaura, in *Metal-Catalyzed Cross-Coupling Reactions, vol. 1*, ed. A. Meijere, F. Diederich), Wiley-VCH, Weinheim, 2004, pp 41–123; (*d*) H. R. Ahn, Y. A. Cho, D.-S. Kim, J Chin, Y.-S. Gyoung, S Lee, H Kang and J Ham, *Org. Lett.*, 2009, **11**, 361–364; (*e*) V. P. Reddy, A. V. Kumar, K Swapna and K. R. Rao, *Org. Lett.*, 2009, **11**, 951–953.

5 (*a*) W. Bao, Y. Zheng, Y. Zhang and J. Zhou, *Tetrahedron Lett.*, 1996, **37**, 9333–9334; (*b*) S. Fukuzawa, Y. Niimoto, T. Fujinami and S. Sakai, *Heteroat. Chem.*, 1990, **1**, 491–495; (*c*) M. Sakakibara, K. Katsumata, Y. Watanabe, T. Toru and Y. Ueno, *Synthesis*, 1992, 377–379; (*d*) M. R. Detty, *J. Org. Chem.*, 1980, **45**, 274–279; (*e*) L. Wang and Y. Zhang, *Heteroat. Chem.*, 1999, **10**, 203–208.

6 For selected reviews, see: (*a*) S. V. Ley and A. W. Thomas, *Angew. Chem., Int. Ed.*, 2003, **42**, 5400–5449; (*b*) T. Kondo and T. Mitsudo, *Chem. Rev.*, 2000, **100**, 3205–3220.

7 For selected papers using Pd catalyst: (*a*) T. Migita, T. Shimizu, Y. Asami, J. Shiobara and M. Kosugi, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 1385–1389; (*b*) M. Kosugi, T. Ogata, M. Terada, H. Sano and T. Migita, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 3657–3658; (*c*) D. Barrañano and J. F. Hartwig, *J. Am. Chem. Soc.*, 1995, **117**, 2937–2938; (*d*) P. G. Ciattini, E. Morera and G. Ortar, *Tetrahedron Lett.*, 1995, **36**, 4133–4136; (*e*) N. Zheng, J. C. McWilliams, F. J. Fleitz, J. D. Armstrong, III and R. P. Volante, *J. Org. Chem.*, 1998, **63**, 9606–9607; (*f*) Y. Nishiyama, K. Tokunaga and N. Sonoda, *Org. Lett.*, 1999, **1**, 1725–1727; (*g*) T. Itoh and T. Mase, *Org. Lett.*, 2004, **6**, 4587–4590.

8 The synthetic method using Ni catalyst: (*a*) H. J. Cristau, B. Chabaud, A. Chêne and H. Christol, *Synthesis*, 1981, 892–894; (*b*) K. Takagi, *Chem. Lett.*, 1987, 2221–2224.

9 Selected methods using Cu catalyst: (*a*) H. Suzuki, H. Abe and A. Osuka, *Chem. Lett.*, 1981, 151–152; (*b*) W. R. Bowman, H. Heaney and P. H. G. Smith, *Tetrahedron Lett.*, 1984, **25**, 5821–5824; (*c*) F. Y. Kwong and S. L. Buchwald, *Org. Lett.*, 2002, **4**, 3517–3520; (*d*) R. K. Gujadhur and D. Venkataruman, *Tetrahedron Lett.*, 2003, **44**, 81–84.

10 Chalcogenations of alkyl halides or alkenyl borane with dichalcogenide: (*a*) A. Kundu and S. Roy, *Organometallics*, 2000, **19**, 105–108; (*b*) T. Nishino, M. Okada, T. Kuroki, T. Watanabe, Y. Nishiyama and N. Sonoda, *J. Org. Chem.*, 2002, **67**, 8696–8698; (*c*) K. Ajiki and K. Tanaka, *Org. Lett.*, 2005, **7**, 4193–4195.

11 C. Millois and P. Diaz, *Org. Lett.*, 2000, **2**, 1705–1708.

12 (*a*) N. Taniguchi and T. Onami, *Synlett*, 2003, 829–832; (*b*) N. Taniguchi and T. Onami, *J. Org. Chem.*, 2004, **69**, 915–920; (*c*) N. Taniguchi, *J. Org. Chem.*, 2004, **69**, 6904–6906; (*d*) N. Taniguchi, *Synlett*, 2005, 1687–1690; (*e*) V. Gómez-Betez, O. Baldovino-Pantaleón, C. Herrera-Álvarez, R. A. Toscano and D. Morales-Morales, *Tetrahedron Lett.*, 2006, **47**, 5059–5062; (*f*) S. Kumar and L. Engman, *J. Org. Chem.*, 2006, **71**, 5400–5403; (*g*) D. Cheng and W. Bao, *Synlett*, 2006, 1786–1788; (*h*) S. I. Fukuzawa, D. Tanihara and S. Kikuchi, *Synlett*, 2006, 2145–2147.

13 Reviews for indium Lewis acids: (*a*) C. G. Frost and K. K. Chauhan, *J. Chem. Soc., Perkin Trans., 1*, 2000, 3015–3019; (*b*) F. Fringuelli, O. Piermatti, F. Pizzo and L. Vaccaro, *Curr. Org. Chem.*, 2003, **7**, 1661–1689; (*c*) C. G. Frost and J. P. Hartley, *Mini-Rev. Org. Chem.*, 2004, **1**, 1–7; (*d*) Z.-H. Zhang, *Synlett*, 2005, 711–712.

14 (*a*) Y.-C. Teo and T.-P. Loh, *Org. Lett.*, 2005, **7**, 2539–2541; (*b*) G. Babu and P. T. Perumal, *Tetrahedron Lett.*, 1998, **39**, 3225–3228.

15 T. Miyai, Y. Onishi and A. Baba, *Tetrahedron Lett.*, 1998, **39**, 6291–6294.

16 T.-P. Loh and L.-L. Wei, *Tetrahedron Lett.*, 1998, **39**, 323–326.

17 (*a*) G. K. Friestad, C. S. Korapala and H. Ding, *J. Org. Chem.*, 2006, **71**, 281–289; (*b*) Y. Onishi, T. Ito, M. Yasuda and A. Baba, *Eur. J. Org. Chem.*, 2002, 1578–1581.

18 Allylation of carbonyl compounds with allyltributylstannanes: (*a*) Y.-U. Teo, J.-D. Goh and T.-P. Loh, *Org. Lett.*, 2005, **7**, 2743–2745; (*b*) J. Lu, S.-J. Ji, Y.-C. Teo and T.-P. Loh, *Org. Lett.*, 2005, **7**, 159–161; (*c*) J. A. Marshall and K. W. Hinkle, *J. Org. Chem.*, 1995, **60**, 1920–1921; (*d*) Other reactions, see: S. Harada, S. Handa, S. Matsunaga and M. Shibasaki, *Angew. Chem., Int. Ed.*, 2005, **44**, 4365–4368; (*e*) R. Yanada, S. Obika, Y. Kobayashi, T. Inokuma, M. Oyama, K. Yanada and Y. Takemoto, *Adv. Synth. Catal.*, 2005, **347**, 1632–1642; (*f*) R. Yanada, S. Obika, M. Oyama and Y. Takemoto, *Org. Lett.*, 2004, **6**, 2825–2828; (*g*) A. P. Dobbs, S. J. J. Guesné, S. Martinović, S. J. Coles and M. B. Hursthouse, *J. Org. Chem.*, 2003, **68**, 7880–7883; (*h*) Y. Onishi, D. Ogawa, M. Yasuda and A. Baba, *J. Am. Chem. Soc.*, 2002, **124**, 13690–13691; (*i*) Y. S. Cho, H. Y. Kim, J. H. Cha, A. N. Pae, H. Y. Koh, J. H. Choi and M. H. Chang, *Org. Lett.*, 2002, **4**, 2025–2028; (*j*) M. Yasuda, Y. Onishi, M. Ueba, T. Miyai and A. Baba, *J. Org. Chem.*, 2001, **66**, 7741–7744.

19 (*a*) B. C. Ranu, T. Mandal and S. Samanta, *Org. Lett.*, 2003, **5**, 1439–1441; (*b*) B. C. Ranu and T. Mandal, *J. Org. Chem.*, 2004, **69**, 5793–5795.

20 L. Wang, M. Wang and F. Huang, *Synlett*, 2005, 2007–2010.

21 N. Taniguchi, *J. Org. Chem.*, 2007, **72**, 1241–1245.

22 (*a*) G. A. Molander and M. Ribagorda, *J. Am. Chem. Soc.*, 2003, **125**, 11148–11149; (*b*) G. A. Molander and M. R. Rivero, *Org. Lett.*, 2002, **4**, 107–109; (*c*) G. A. Molander and B. J. Biolatto, *J. Org. Chem.*, 2003, **68**, 4302–4314; (*d*) R. A. Batey and A. N. Thadani, *Org. Lett.*, 1999, **1**, 1683–1686; (*e*) A. N. Thadani and R. A. Batey, *Org. Lett.*, 2002, **4**, 3827–3830; (*f*) G. W. Kabalka, B. Venkataiah and G. Dong, *Org. Lett.*, 2003, **5**, 3803–3805; (*g*) T. E. Barder and S. L. Buchwald, *Org. Lett.*, 2004, **6**, 2649–2652.

23 S. Usugi, H. Yorimitsu, H. Shinokubo and K. Oshima, *Org. Lett.*, 2004, **6**, 601–603.

24 (*a*) A. J. Mancuso and D. Swern, *Synthesis*, 1981, 165–185; (*b*) B. Karimi, H. Hazarkhani and D. Zareyee, *Synthesis*, 2002, 2513–2516; (*c*) L. W. Bieber, M. F. Silva and P. H. Menezes, *Tetrahedron Lett.*, 2004, **45**, 2735–2737.