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Copper-free Sandmeyer Cyanation of Arenediazonium *o*-Benzenedisulfonimides

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Keywords: Diazonium salts, Sandmeyer reaction, *o*-Benzenedisulfonimide, Electron transfer agent, Aryl nitriles.

Abstract

Arene and heteroarenediazonium *o*-benzenedisulfonimides can be used as efficient reagents in Sandmeyer cyanation. This work reports such reactions being carried out in very mild conditions using tetrabutyl ammonium cyanide as a safe cyanide source and, interestingly, without the need for a Cu catalyst. The reaction has given rise to aryl nitriles in good yields (25 examples, average yield 75%). A good amount of *o*-benzenedisulfonimide was recovered from each reaction and then reused to prepare other salts. Mechanistic insights have allowed us to highlight the fundamental role of the *o*-benzenedisulfonimide anion as an electron transfer agent.

Introduction

Aryl nitriles are an important class of organic compounds that is widely used in organic synthesis and a common structural motif in natural products.¹ They are in fact versatile building blocks in the synthesis of not only more complex natural products, but also pharmaceuticals, agricultural chemicals, dyes and other commercially important materials.^{2a,b} Moreover, aryl nitriles are easily transformed into a variety of functional groups, such as amines, aldehydes, amides, ketones, carboxylic acids and many others.^{2c}

Although several protocols for aryl nitriles preparation have been proposed,³ they have been conventionally synthesized via either Sandmeyer⁴ or Rosenmund-von Braun^{5a,b} reactions using stoichiometric amounts of CuCN and diazonium salts⁴ or aryl halides.^{5a,b}

Over the years, the cyanation of aryl halides has also been carried out using various reagents, such as KCN, Zn(CN)₂, NaCN and cyanohydrins, always in the presence of Cu catalysts.^{1a} Although these protocols have found a number of applications, they sometimes suffer from various drawbacks including limited substrate

scope, harsh reaction conditions and the release of dangerous gasses. A number of research groups have thus reported the formation of aryl nitriles by means of other metal catalysts^{5c} such as nickel,^{5d} rhodium,^{5e} palladium^{5f-j} and even using non-metallic CN sources.^{1b-c,5k} Finally, an interesting variant of the Rosenmund protocol involves the use of boronic acids instead of aryl halides.^{5l}

On the other hand, few studies⁶ have been carried out (many by the Beletskaya group^{6b,d}) on the Sandmeyer cyanation than the Rosenmund protocol. However, it must be stressed that there has been a renewed interest in the Sandmeyer reaction very recently. In fact, Li and coworkers have investigated other cyanide sources, namely trimethylsilyl cyanide^{7a} and acetonitrile^{7b} (in the presence of PdCl₂ as a metal catalyst) as an alternative to CuCN in order to find milder and safer reaction conditions.

Since 1998, our own researches has resulted in a new and large family of dry diazonium salts: arenediazonium *o*-benzenedisulfonimides **1** (Figure 1).^{8a}

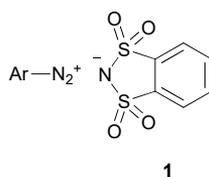
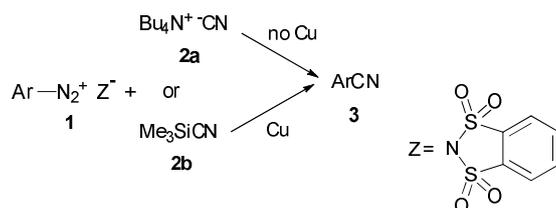


Figure 1 Arenediazonium *o*-benzenedisulfonimides **1**.

Their properties lend them great potential in numerous synthetic applications. These salts are, in fact, easy to prepare and isolate, extremely stable, and can also be stored indefinitely.

We have therefore advantageously employed them in several classical diazonium salts reactions.^{8b-h} The paper reports the results of a detailed study on the Sandmeyer reaction of arenediazonium *o*-benzenedisulfonimides **1**, using tetrabutylammonium cyanide (**2a**) or, alternatively, trimethylsilyl cyanide (**2b**; Scheme 1) as cyanide sources.



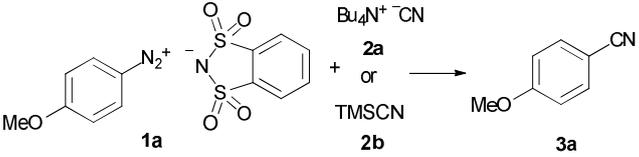
Scheme 1 Sandmeyer reaction between arenediazonium *o*-benzenedisulfonimides **1** and cyanides **2a** or **2b**.

Results and discussion

A model reaction between 4-methoxybenzenediazonium *o*-benzenedisulfonimide (**1a**) and tetrabutylammonium cyanide (**2a**) was studied under various conditions (Table 1), in order to optimize the reaction conditions.

Differing solvents (polar or slightly polar) and various Cu catalysts were tested (Table 1). The optimal combination was MeCN as solvent and Cu₂O as catalyst (10 mol%, Table 1; entry 10); 4-methoxybenzonitrile (**3a**) was obtained in an excellent yield (95%) at room temperature and was easily purified from the only by-product (anisole) using a short chromatographic column.

Table 1 Trial reactions: optimization of reaction conditions.

					
Entry	Solvent	Source of CN	Catalyst	Time (min)	Yield of 3a (%) ^{a,b}
1	THF	2a	Cu ₂ O	60	18
2	THF	2a	Cu	60	12
3	DMF	2a	Cu ₂ O	90	-
4	EtOH	2a	Cu ₂ O	30	22

5	DMSO	2a	Cu ₂ O	30	36
6	MeCN	2a	Cu	30	54
7	MeCN	2a	CuI	30	- ^c
8	MeCN	2a	CuCl	30	- ^d
9	MeCN	2a	Cu(OAc) ₂	30	-
10	MeCN	2a	Cu ₂ O	20	95
11	MeCN	2a	-	40	92
12	MeCN	2a	-	240	44 ^e
13	MeCN	2a	-	90	^f
14	THF	2b	Cu ₂ O	60	-
15	DMF	2b	Cu ₂ O	60	-
16	EtOH	2b	Cu ₂ O	10	75
17	DMSO	2b	Cu ₂ O	10	74
18	DMSO	2b	Cu	10	47
19	MeCN	2b	Cu ₂ O	30	45
20	DMSO	2b	-	90	-
21	EtOH	2b	-	90	-
22	DMSO	CuCN	-	60	62

^a All the reactions were performed at r.t. with 10 mol% of appropriate Cu catalyst. **1: 2a** or **2b** ratio was 1:1.2 (2.5 and 3 mmol respectively). ^b Yields refer to pure and isolated **3a**, purified from anisole, MS (EI) $m/z = 108 [M]^+$ (only by-product) on a silica gel chromatography column. The eluent was petroleum ether/diethyl ether (9:1). ^c The only detected products were iodobenzene, MS (EI) $m/z = 204 [M]^+$ and anisole. ^d The only detected products were chlorobenzene, MS (EI) $m/z = 112 [M]^+$ and anisole. ^e The reaction was carried out in

the presence of 1,3-dinitrobenzene (2.5 mmol, 0.41g).^f The reaction was performed using 4-methoxybenzenediazonium tetrafluoroborate (2.5 mmol, 0.55 g)

The reaction (Table 1, entry 11) was subsequently performed without Cu catalyst under optimized conditions. Interestingly and gratifyingly, very good **3a** yield was obtained (92%).

In order to further exploit this reaction, we decided to change the cyanide source to trimethylsilyl cyanide (TMSCN; **2b**), which was used in different solvents. Good results were also obtained here, especially in DMSO and EtOH (Table 1, entries 16, 17): yields of **3a** were good (74% and 75% respectively). However, the Cu catalyst was strictly required. In fact, no **3a** was obtained without the Cu catalyst (Table 1, entries 20,21)

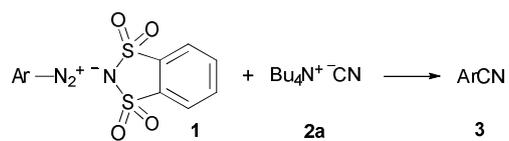
Encouraged by this excellent result and with optimized conditions in hand, a number of other diazonium salts **1**, bearing either electron withdrawing or electron donating groups, were reacted. In light of previous results, we decided to use **2a** as cyanide source. In fact, solid **2a** was easier to handle and safer than **2b** while, most importantly, allowed us to carry out the reaction without the Cu catalyst. Moreover, it is important to note that **2a** has never been used as a cyanating agent in Sandmeyer protocol, to the best of our knowledge.

Good yields of target nitriles **3** were obtained (Table 2), although even higher yields were obtained in the presence of electron donating groups (Table 2, entries 1, 4, 5, 13). The influence of steric hindrance was evident: when there were one (Table 2, entries 3, 9, 12) or two groups (Table 2, entries 18,19, 20) on the *ortho* positions to the diazonium group, reaction times were significantly longer and smaller yields of **3** were obtained. The reaction was chemoselective and no traces of terephthalonitrile (**3p**) were detected in the reactions of diazonium salts containing a bromine or iodine atom, which could potentially react in the same way as a diazonium group (Table 2, entries 6, 8).

We have not so far synthesized heteroarene diazonium *o*-benzenedisulfonimides, with few exceptions.^{8g,h} In order to address this shortcoming, we decided to prepare stable salts **1u–y** which provided target heteroaryl nitriles **3u–y** with satisfactory yields upon reaction with **2a** (Table 2, entries 21–25).

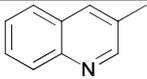
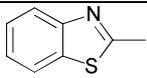
It is worth nothing that is possible to recover *o*-benzenedisulfonimide (**6**) in excess of 70% yield from all the reactions described above. **6** was recycled for the preparation of other salts **1**.

Table 2 Synthesis of aryl cyanides **3**.



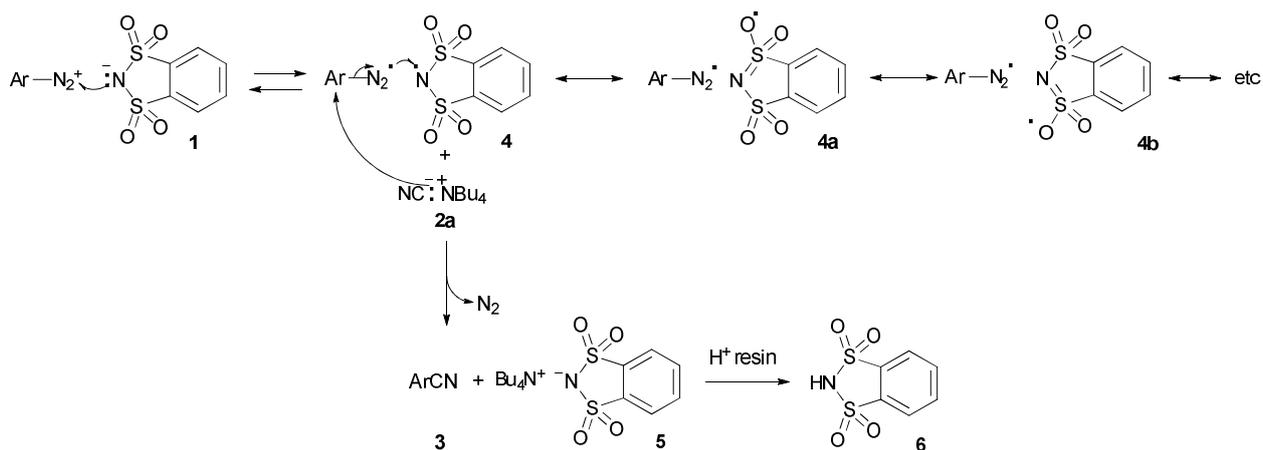
Entry	Ar in 1 and 3	Time (min)	Product	Yield (%) ^{a,b}
1	4-MeOC ₆ H ₄	40	3a	92
2	Ph	45	3b	88
3	2-MeC ₆ H ₄	90	3c	65
4	3-MeC ₆ H ₄	30	3d	92
5	4-MeC ₆ H ₄	15	3e	96
6	4-BrC ₆ H ₄	45	3f	88
7	4-ClC ₆ H ₄	30	3g	82
8	4-IC ₆ H ₄	30	3h	79
9	2-NO ₂ C ₆ H ₄	100	3i	62

10	3-NO ₂ C ₆ H ₄	45	3j	87
11	4-NO ₂ C ₆ H ₄	30	3k	84
12	2-OHC ₆ H ₄	90	3l	54
13	4-OHC ₆ H ₄	30	3m	90
14	4-MeCOC ₆ H ₄	60	3n	82
15	4-MeOCOC ₆ H ₄	60	3o	74
16	4-CN	30	3p	78
17	2-naphthyl	20	3q	82
18	2,6-Me ₂ C ₆ H ₃	120	3r	45
19	2,6-Cl ₂ C ₆ H ₃	150	3s	37
20	2,6-Br ₂ C ₆ H ₃	150	3t	34
21	3-thienyl	60	3u	81

22	3-pyridyl	45	3v	73
23	2-pyrimidyl	60	3w	69
24		60	3x	78
25		45	3y	80

^a All the reactions were performed in MeCN at r.t.. **1**: **2a** ratio was 1: 1.2. ^b Yields refer to pure and isolated **3**, purified from corresponding arenes or heteroarenes, (only by-products) on a silica gel chromatography column. The eluent was always petroleum ether/diethyl ether (9:1).

The results obtained here have provided us with useful insights into the mechanism of cyanodediazotiation without Cu catalyst. We firstly carried out a reaction between **1a** and **2a** in the presence of 1,3-dinitrobenzene, an excellent electron acceptor.⁹ This reaction was very much slower (4 h) than the reaction without 1,3-dinitrobenzene and yielded much less **3a** (Table 1, entry 12). We therefore confirmed its homolytic course by means of this known diagnostic test. We assumed that the anion in salts **1** would act as an electron donor toward the arenediazonium cations, most likely giving rise to the electron transfer complex **4**, where the partner of the aryldiazenyl radical is highly resonance stabilized (**4a**, **4b**, etc). Complex **4** would subsequently react with the CN⁻ of **2a** to create aryl nitrile **3**, as shown in Scheme 2. The role of the anion of **6** as an electron donor can be confirmed by the fact that 4-methoxybenzenediazonium tetrafluoroborate did not react with **2a** in the absence of a Cu catalyst (Table 1, entry 13).

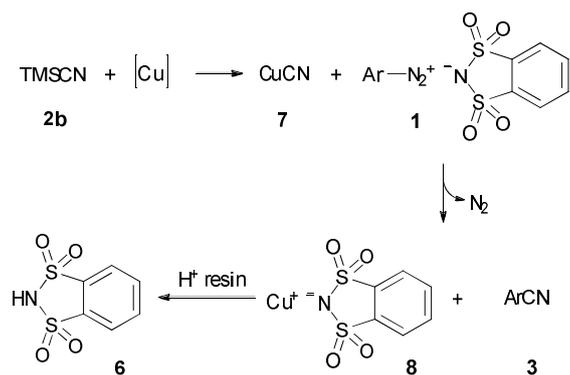


Scheme 2 Reaction mechanism.

It is interesting to note that we have already described the fascinating role as an electron transfer agent in bromodiazonation of salts **1**, played by the *o*-benzenedisulfonamide anion (**5**).¹⁰

Further theoretical investigations into the role of **6** as an electron donor are currently underway.

As mentioned above, **2b** did not react without Cu (Table 1; entries 20, 21). The fact that **2b** is a good source of CN in the presence of a Cu catalyst has clearly demonstrated by Li and coworkers.^{7a} However, no mechanistic insights were reported. Moreover, the literature shows that the Sandmeyer trifluoromethylation of arenediazonium tetrafluoroborates has been performed using TMSCF₃ in the presence of Cu catalyst.¹¹ The authors assumed that a trifluoromethyl copper (I) species, generated from Cu and TMSCF₃ in the presence of a cesium base, was the real trifluoromethylating agent. In light of this, we hypothesized that the cyanating agent is most probably CuCN (**7**), which is derived from the interaction between **2b** and the Cu catalyst (Scheme 3).



Scheme 3 Cu catalyzed reaction between **1** and **2b**.

In order to confirm this hypothesis, we carried out the same reaction using CuCN (normally used as a cyanating agent in the classical Sandmeyer protocol)^{4c} instead of **2b** (Table 1; entry 22). **3a** was obtained under reaction conditions and yield similar to those reported using **2b** (Table1; entry 17)

Conclusion

We have proposed a mild, easy, safe and efficient method for the synthesis of aryl and heteroaryl nitriles according to Sandmeyer protocol. Target products are generally obtained in satisfactory yields (25 examples, average yield 75%).

Arenediazonium *o*-benzenedisulfonimides **1** have several advantages over other diazonium salts. These include high stability, ease of preparation and *o*-benzenedisulfonimide recovery at the end of the reaction. Unlike other acids (e.g. tetrafluoroboric acid), *o*-benzenedisulfonimide is a non-risk acid that can be reused to prepare other salts, with ecological and economic advantages.

It is noteworthy that no copper or other metal catalysts are needed, confirming the interesting role that the anion of *o*-benzenedisulfonimide plays as an electron transfer agent. To the best of our knowledge, this is the first example of Sandmeyer cyanation being carried out without Cu catalyst.

Moreover, tetrabutylammonium cyanide (**2a**) has been used as a safe cyanating agent for the first time.

Experimental

General

All the reactions were carried out in open air glassware. Analytical grade reagents and solvents (purchased from Sigma Aldrich or Alfa-Aesar) were used and reactions were monitored by GC, GC-MS and TLC. Column chromatography and TLC were performed on Merck silica gel 60 (70-230 mesh ASTM) and GF 254, respectively. Petroleum ether refers to the fraction boiling in the range 40–70 °C. Room temperature is 22 °C. Mass spectra were recorded on an HP 5989B mass selective detector connected to an HP 5890 GC with a methyl silicone capillary column. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance 200

spectrometer at 200 and 50 MHz respectively. IR spectra were recorded on IR Perkin-Elmer UATR-two spectrometer.

Dry arene and heteroarenediazonium *o*-benzenedisulfonimides **1** were prepared as described previously by us.⁸ Crude salts **1** were virtually pure (by ¹H NMR spectroscopy) and were used in subsequent reactions with **2** without further crystallization. Physical data, spectroscopic data and NMR spectra of heteroarenediazonium *o*-benzenedisulfonimides **1u**, **1v**, **1w**, **1x** and **1y** are reported in Electronic Supplementary Information (ESI). Satisfactory microanalyses were obtained for all new compounds.

4-Methoxybenzenediazonium tetrafluoroborate was prepared as reported in the literature.¹² Structures and purity of aryl nitriles **3** were confirmed by their spectral (NMR, MS, IR) and physical data, substantially identical to those of commercial (Sigma-Aldrich) samples. Yields of pure (GC, GC-MS, TLC and NMR) isolated aryl cyanides **3** are collected in Table 2; their physical data, spectroscopic data and NMR spectra are reported in ESI.

4-Methoxybenzonitrile (3a); typical procedure

Tetrabutylammonium cyanide (**2a**, 0.81 g, 3 mmol) was added to a stirred solution of 4-methoxybenzenediazonium *o*-benzenedisulfonimide (**1a**, 0.88 g, 2.5 mmol) in anhydrous MeCN (10 ml). Immediately, the colour of the solution turned black and evolution of nitrogen was observed. The mixture was stirred at room temperature for 40 min; the completion of the reaction was confirmed by the absence of azo coupling with 2-naphthol. Then, the reaction mixture was poured into diethyl ether/water (100 mL, 1:1). The aqueous layer was separated and extracted with diethyl ether (50 mL). The combined organic extracts were washed with water (50 mL), dried with Na₂SO₄ and evaporated under reduced pressure. GC-MS analyses of the crude residue showed 4-methoxybenzonitrile (**3a**, MS (EI): *m/z* = 133 [M]⁺) as the major product, besides traces of anisole, MS (EI) *m/z* = 108 [M]⁺. The crude residue was purified on a short column, eluting with petroleum ether/diethyl ether (9:1). The only isolated product was title compound (**3a**, 0.31 g, 93% yield). The aqueous layer and aqueous washings were collected and evaporated under reduced pressure. The tarry residue was passed through a column of Dowex HCR-W2 ion exchange resin (1.6 g/1 g of product), eluting with water (about 50 mL). After removal of water under reduced pressure, virtually pure (¹H NMR) *o*-benzenedisulfonimide was recovered (0.42 g, 76% yield; mp 191–193 °C. Lit.^{8a} 191–193 °C).

All other aryl nitriles **3** were prepared according to this procedure.

Trial reactions

The reactions between **1a** and **2a** or **2b** in the presence of Cu catalyst (Table 1) were performed as described above.

1a (0.88 g, 2.5 mmol) was dissolved in the appropriate solvent (10 ml) and appropriate Cu catalyst was added (10 mol%). Then cyanating agent **2a** (0.81 g, 3 mmol) or **2b** (0.30 g, 3 mmol) was added.

The completion of the reactions was confirmed by the absence of azo coupling with 2-naphthol and the crude residues were purified on short columns (eluent: petroleum ether/diethyl ether 9:1).

Acknowledgments

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Electronic Supplementary Information (ESI) available:

1. Synthesis of heteroarenediazonium o-benzenedisulfonimides **1u–y**; pag. 2.
2. Physical and spectroscopic data of heteroarenediazonium o-benzenedisulfonimides **1u–y** ; pag. 3.
3. Physical and spectroscopic data of aryl cyanides **3** pag. 4–7.
4. NMR spectra of heteroarenediazonium o-benzenedisulfonimides **1u–y**; pag. 8–12.
5. NMR spectra of aryl nitriles **3**, pag. 13–37.

References

1. For recent reviews see: (a) Q. Wen, J. Jin, L. Zhang, Y. Luo, P. Lu and Y. Wang, *Tetrahedron Lett.*, 2014, **55**, 1271 and references reported therein; (b) T. Wang and N. Jiao, *Acc. Chem. Res.*, 2014, **47**, 1137; (c) J. Kim, H. J. Kim and S. Chang, *Angew. Chem. Int. Ed.*, 2012, **51**, 11948 and references cited therein;
2. (a) J. S. Miller and J. L. Manson, *Acc. Chem. Res.*, 2001, **34**, 563; (b) for books see: A. Kleemann, J. Engel, B. Kutschner and D. Reichert, *Pharmaceutical substances: Syntheses, Patents, Applications*, Thieme, Stuttgart, New York, 4th edn, 2001; (c) Z. Rappoport, *The Chemistry of the Cyano Group*, Interscience Publishers, New York, 1970.
3. For recent examples see: (a) S. Guo, G. Wan, S. Sun, Y. Jiang, J.-T. Yu and J. Cheng, *Chem. Commun.*, 2015, **51**, 5085; (b) X. Jiang, J.-M. Wang, Y. Zhang, Z. Chen, Y.-M. Zhu and

- S.-J. Ji, *Tetrahedron*, 2015, **71**, 4883 and references cited therein; (c) L. Gu and C. Jin, *Chem. Commun.*, 2015, **51**, 6572; (d) G. Lu, M. Bu and C. Cai, *Synlett*, 2014, **25**, 547; (e) W. Yin, R. Liu, G. He, W. Lv and H. Zhu, *RSC Adv.*, 2014, **4**, 37773; (f) A. B. Khemnar and B. M. Bhanage, *RSC Adv.*, 2014, **4**, 13405; (g) K. Zheng, B. Liu, S. Chen and F. Chen, *Tetrahedron Lett.*, 2013, **54**, 5250; (h) Y. Luo, Q. Wen, Z. Wu, J. Jin, P. Lu and Y. Wang, *Tetrahedron*, 2013, **69**, 8400; (i) C. Tao, F. Liu, Y. Zhu, W. Liu and Z. Cao, *Org. Biomol. Chem.*, 2013, **11**, 3349.
4. (a) T. Sandmeyer, *Ber. Dtsch. Chem. Ges.*, 1884, **17**, 1633; (b) for a review see H. H. Hodgson, *Chem. Rev.*, 1947, **40**, 251; (c) H. T. Clarke and R. R. Read, *Org. Synth.*, 1941, **1**, 514; (d) J. K. Kochi, *J. Am. Chem. Soc.*, 1957, **79**, 2942.
5. (a) K. W. Rosenmund and E. Struck, *Chem. Ber.*, 1919, **52**, 1749; (b) J. Lindley, *Tetrahedron*, 1984, **40**, 1433; (c) Y. Nakao, *Top. Curr. Chem.* 2014, **346**, 33; (d) L. Cassar, M. Foà, F. Montanari and G. P. Marinelli, *J. Organomet. Chem.*, 1979, **173**, 335; (e) A. B. Khenmar, D. N. Sawant and B. M. Bhanage, *Tetrahedron Lett.* 2013, **54**, 2682; (f) T. Chatterjee, R. Dey and B. C. Ranu, *J. Org. Chem.*, 2014, **79**, 5875 and references cited therein; (g) T. D. Senecal, W. Shu and S. L. Buchwald, *Angew. Chem. Int. Ed.*, 2013, **52**, 10035 and references cited therein; (h) S. Ding and N. Jiao, *J. Am. Chem. Soc.*, 2011, **133**, 12374; (i) G. Zhang, J. Yu, M. Hu and J. Cheng, *J. Org. Chem.*, 2013, **78**, 2710; (j) T. Schareina, A. Zapf and M. Beller, *J. Organomet. Chem.*, 2004, **689**, 4576; (k) G. Zhang, X. Ren, J. Chen, M. Hu and J. Cheng, *Org. Lett.*, 2011, **13**, 5005; (l) G. Zhang, L. Zhang, J. Chen, M. Hu and J. Cheng, *Adv. Synth. Catal.*, 2011, **353**, 291.
6. (a) P. Hanson, S. C. Rowell, A. B. Taylor, P. H. Walton, A. W. Timms, *J. Chem. Soc., Perkin Trans. 2*, 2002, **6**, 1126; (b) I. P. Beletskaya, A. S. Sigeev, A. S. Peregudov and P. V. Petrovskii, *J. Organomet. Chem.*, 2004, **689**, 3810; (c) M. A. K. Zarchi and N. Ebrahimi, *J. Appl. Polym. Sci.* 2012, **125**, 2163; (d) A. S. Sigeev, I. P. Beletskaya, P. V. Petrovskii and A. S. Peregudov, *Russ. J. Org. Chem.*, 2012, **48**, 1055; (e) D. Habibi, S. Heydari and M. Nasrollahzadeh, *J. Chem. Res.*, 2012, **10**, 573.
7. (a) W.-B. Xu, Q.-H. Xu, Z.-F. Zhang and J.-Z. Li, *Asian J. Org. Chem.*, 2014, **3**, 1062; (b) W.-B. Xu, Q.-H. Xu and J.-Z. Li, *Org. Chem. Front.*, 2015, **2**, 231.
8. (a) M. Barbero, M. Crisma, I. Degani, R. Fochi and P. Perracino, *Synthesis*, 1998, 1171; for recent publications see: (b) E. Artuso, M. Barbero, I. Degani, S. Dughera and R. Fochi, *Tetrahedron*, 2006, **62**, 3146. (c) S. Dughera, *Synthesis*, 2006, 1117; (d) M. Barbero, S. Cadamuro and S. Dughera, *Synthesis*, 2008, 474; (e) M. Barbero, S. Cadamuro, S. Dughera and C. Giaveno, *Eur. J. Org. Chem.*, 2006, 4884; (f) M. Barbero, S. Cadamuro, S. Dughera,

- and G. Ghigo, *Eur. J. Org. Chem.*, 2008, 862; (g) M. Barbero; S. Cadamuro and S. Dughera, *Eur. J. Org. Chem.* 2014, 598; (h) M. Barbero, S. Cadamuro and S. Dughera, *Tetrahedron*, 2014, **70**, 8010.
9. G. Briegleb, *Angew. Chem. Int. Ed.*, 1964, **3**, 617.
 10. M. Barbero, I. Degani, S. Dughera and R. Fochi, *J. Org. Chem.*, 1999, **64**, 3448.
 11. G. Danoun, B. Bayarmagnai, M. F. Grünberg, and L. J. Gooßen, *Angew. Chem. Int. Ed.*, 2013, **52**, 7972.
 12. A. Roe, *Organic Reactions*, 1949, **5**, 193.