

A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

Accepted Article

Title: Metal-Free Direct C-H Cyanation of Alkenes

Authors: Xi Wang and Armido Studer

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201807303 Angew. Chem. 10.1002/ange.201807303

Link to VoR: http://dx.doi.org/10.1002/anie.201807303 http://dx.doi.org/10.1002/ange.201807303



COMMUNICATION

Metal-Free Direct C-H Cyanation of Alkenes

Xi Wang^[a] and Armido Studer*^[a]

Abstract: A metal-free direct alkene C-H cyanation is described. Directing groups are not required and the mechanism involves electrophilic activation of the alkene by a cyano iodine(III) species generated in situ from a [bis(trifluoroacetoxy)iodo]arene and trimethylsilyl cyanide as the cyanide source. This C-H functionalization can be conducted at gram-scale and for non-cyclic 1,1- and 1,2-disubstuted alkenes high stereoselectivity is achieved, rendering the method highly valuable.

The nitrile functionality is an important structural moiety that can be found in various natural products, drugs, agrochemicals, and in polymers.^[1] Moreover, the cyano group can be used as a synthetic equivalent for primary amines, tetrazoles, aldehydes/ketones and their related functionalities.^[2]

Aryl nitriles are generally prepared by cyanation of halides, pseudohalides, diazonium salts, and organometallic reagents.^[3] Step- and atom-economy in the synthesis of cyanated arenes and alkenes can be improved following a direct C-H cyanation strategy. Significant advances in directing group (DG) assisted arene C-H cyanation have been achieved using transition metal catalysis (e.g., Pd, Cu, and Rh).^[4] Along these lines, direct C-H cyanation of indoles has also been reported.^[5] Recently, Wang and coworkers disclosed a Fe-catalyzed electrophilic cyanation of arenes and heteroarenes using aryl(cyano)iodonium triflates,^[6a] and the Nicewicz group reported aromatic C-H cyanation with trimethylsilyl cyanide using photoredox catalysis.^[6b]



Scheme 1. Direct C-H cyanation of alkenes.

Established approaches for the synthesis of acrylonitriles comprise carbocyanation,^[7] heterocyanation,^[8] and hydrocyanation^[9] of alkynes with X-CN-type reagents (X = C, Si, B, Sn, Ge, S, O, Br, H). However, as compared to arene C-H cyanation, direct alkene C-H cyanation has not been well investigated. Anbarasan^[10a] and Fu^[10b] reported Rh-catalyzed direct C(sp²)-H cyanation of alkenes bearing directing groups with

 [a] Dr. X. Wang, Prof. Dr. A. Studer Westfälische Wilhelms-Universität Organisch-Chemisches Institut Corrensstraβe 40, 48149 Münster, Germany E-mail: studer@uni-muenster.de

Supporting information for this article is given via a link at the end of the document.

NCTS (*N*-cyano-*N*-phenyl-*p*-methylbenzenesulfonamide) as the cyanation reagent. However, non-directed alkene C-H cyanation has not yet been described. We report herein transition-metal-free alkene cyanation using an aryl(biscyano)iodine(III)reagent as alkene activator and cyanide source.



Figure 1. Various "CN" sources and oxidants tested (Ts = *p*-tolylsulfonyl, Tf = trifluoromethylsulfonyl, TMS = trimethylsilyl).

α-Phenylstyrene 1a was chosen as a model substrate and various electrophilic cyanation reagents were screened in combination with or without an additive in dichloroethane (DCE) at 70 °C for 15 h (Table 1, Figure 1).^[3g,4b,4c,4i,5d,11] C-H cyanation of 1a with reagents 2a-d, 2i and 2j failed (Table 1, entries 1-6). Traces of nitrile 4a were detected when benziodoxole 2e was employed in combination with catalytic CuCl or Fe(OAc)₂ (Table 1, entries 7 and 8). No improvement was noted by using reagent 2f (Table 1, entries 9 and 10). TMSCN paired with oxone, (NH₄)₂S₂O₈, or t-BuOOH did not provide 1a (Table 1, entries 11-13). Product 4a was obtained in 7% yield using reagent 2e in combination with TMSCN (Table 1, entry 14). Replacing 2e by 2f led to a significant improvement of the yield (Table 1, entry 15, 32%). The electronic nature of the substituents at the aryl moiety in the I(III)-reagent is important: the activity of 2h was superior to that of 2f and 2g (Table 1, entries 15-17). Pleasingly, direct C-H cyanation using the more stable and easily accessible [bis(trifluoroacetoxy)iodo]arene 3d, that reacts in situ via sequential ligand exchange with TMSOTf and TMSCN to aryl(cyano)iodonium triflate 2h,[12] gave a comparable result (Table 1, entry 18, 88%). The best yield (90%) was achieved upon lowering the temperature to 40 °C (Table 1, entries 19 and 20). With 2 equivalents of TMSCN, a lower yield resulted but using 3 and 4 equivalents provided good results (Table 1, entries 22-24). Benziodoxole 3e as an oxidant provided a worse result (Table 1, entry 21, 34%). Other cyanide sources such as NaCN, KCN and Bu₄NCN did not lead 4a (Table 1, entries 25-27).

COMMUNICATION

Table 1. Optimization studies.ª

	Ph Is u				oxidant promoter		Ph Is on	
Ph	\sim	+ "	CN" source	-	DCE, temp	Ph		
	⊣ 1a		2			4	⊣ 4a	
_								
Entry [a]	"CN" 2 (equiv)		Oxidant (equiv)		Additive (eq	uiv)	Yield (%) ^[b]	
1	2a (2.0)		none		none		NP	
2	2b (2.0)		none		AuCl₃ (0.05)		NP	
3	2c (2.0)		none		CuCl (0.1)		NP	
4	2d (2.0)		none		BF3 ⁻ Et ₂ O (2.	0)	NP	
5	2i (2.0)		none		none		NP	
6	2j (2.0)		none		none		NP	
7	2e (2.0)		none		CuCl (0.1)		traces	6
8	2e (2.0)		none		Fe(OAc) ₂ (0.	1)	traces	6
9	2f (2.0)		none		none		traces	6
10	2f (2.0)		none		Fe(OAc) ₂ (0.	1)	traces	6
11	2k (2.0)		3a (2.0)		none		NP	
12	2k (2.0)		3b (2.0)		none		NP	
13	2k (2.0)		3c (2.0)		none		NP	
14	2k (4.0)		2e (1.5)		none		7	
15	2k (4.0)		2f (1.5)		none		32	
16	2k (4.0)		2g (1.5)		none		44	
17	2k (4.0)		2h (1.5)		none		87	
18	2k (5.5)		3d (1.5)		TMSOTf (1.	5)	88	
19 ^[c]	2k (5.5)		3d (1.5)		TMSOTf (1.	5)	90 ^[d]	
20 ^[e]	2k (5.5)		3d (1.5)		TMSOTf (1.	5)	14	1
21	2k (5.5)		3e (1.5)		TMSOTf (1.	5)	34	
22 ^[c]	2k (2.0)		3d (1.5)		TMSOTf (1.	5)	27	
23 ^[c]	2k (3.0)		3d (1.5)		TMSOTf (1.	5)	81	
24 ^[c]	2k (4.0)		3d (1.5)		TMSOTf (1.	5)	85	
25 ^[c]	NaCN (5.	5)	3d (1.5)		TMSOTf (1.	5)	NP	
26 ^[c]	KCN (5.5))	3d (1.5)		TMSOTf (1.	5)	NP	
27 ^[c]	Bu₄NCN (5.5)	3d (1.5)		TMSOTf (1.	5)	NP	

[a] Reaction condition: **1a** (0.20 mmol, 1.0 equiv), **2**, oxidant, additive, DCE (2 mL), 70 °C, 15 h. [b] Yield determined by ¹H NMR analysis using MeNO₂ as an internal standard. [c] Conducted at 40 °C. [d] Isolated in 87% yield. [e] Conducted at room temperature.

Under optimized conditions, various alkenes were tested (Table 2). α -Methylstyrenes possessing electron withdrawing or electron donating groups at the *para* position of the arene ring afforded acrylonitriles **4b-I** in moderate to high yields with good to excellent *E*-selectivity. Generally, systems bearing electron-withdrawing groups provided lower *E*-selectivities in this series. An α -methylstyrene bearing a *meta*-substituent (**4m**) worked well and the β -naphthyl congener reacted with similar efficiency (**4n**). Increasing the size of the α -alkyl substituent in the styrene substrate leads to diminished selectivity, as shown by switching from α -methylstyrene to the n-propyl derivative (**4o**) and reversed selectivity was obtained for the α -cyclohexyl styrene (**4p**).



[a] Reaction condition: **1** (0.20 mmol, 1.0 equiv), **2k** (1.1 mmol, 5.5 equiv), **3d** (0.30 mmol, 1.5 equiv), TMSOTf (0.30 mmol, 1.5 equiv), DCE (2 mL), 40 °C, 15 h. [b] Yields refer to the isolated yield of the major isomer if not otherwise noted. [c] Conducted at 70 °C. [d] These yields are based on ¹H NMR analysis with MeNO₂ as internal standard. [e] Combined yield of both isomers. [f] **2k** (1.1 mmol, 7.0 equiv), **3d** (0.30 mmol, 1.5 equiv), TMSOTf (0.30 mmol, 1.5 equiv). [g] **2k** (0.30 mmol, 1.5 equiv), **2h** (0.30 mmol, 1.5 equiv). [h] The ratio of the major isomer to other isomers is given in parentheses.

A bicyclic styrene with exocyclic double bond reacted in excellent selectivity (4q) and 1,3-enynes engage in this transformation providing the Z-product as major isomer (see 4r). Reaction works on β -substituted styrenes and indene was converted to 4s in a good yield. A *trans*- β -methylstyrene and *trans*-stilbene reacted with complete regio and good stereoselectivity (4t, 4u). Both acyclic and cyclic trisubstituted

COMMUNICATION

styrenes could be converted (**4v-x**) and conjugated dienes were also competent reaction partners, affording the monocyanated products with high regioselectivity (**4y-4aa**). To document the practicability, reaction of **1a** in gram scale gave **4a** in 91% yield. Unfortunately, styrene did not react to cinnamonitrile.

Notably, *Z*-selectivity of **4p** could be improved from 1.2:1 to 17:1 upon $E \rightarrow Z$ isomerization under UV-irradiation (402 nm) following a Gilmour protocol in presence of (–)-riboflavin (Scheme 2).^[13] This method was also applied to isomerize (*E*)-**4q** to its *Z*-derivative, showing that both isomers are accessible using our approach.



Scheme 2. $E \rightarrow Z$ isomerization.

To elucidate the mechanism, control experiments were conducted. A radical pathway^[14] could be excluded based on the result obtained with the radical probe 1y that reacted to 4y without formation of any ring-opening product 5 (Scheme 3a). In the absence of Lewis acid, the cyanation did not occur, indicating that TMSOTf is essential for generating the active I(III) species (Scheme 3b, left). Arl(CN)OTf 2h (1.5 equiv) in combination with TMSCN (4 equiv) provided 4a in comparable yield showing that Arl(CN)OTf 2h is a potential active reagent that can be formed by reaction of 3d with TMSCN and TMSOTf (Scheme 3b, right). However, we found that 2h is not an active I(III) species, since cyanation of 1a with 2h did not provide 4a, and 1a decomposed (Scheme 3c, left). Other nucleophilic CN-reagents such as NaCN, KCN, (n-Bu)₄NCN did not work in combination with 2h showing the importance of the TMS-moiety (Scheme 3c, right). Replacing TMSCN by TMSCI provided the chlorination product 6 in 34% yield and nitrile 4a was not formed (Scheme 3d). The analogue Ph₂IOTf was not a competent oxidant for cyanation of 1a with TMSCN and the phenylated product 7 was also not identified (Scheme 3e). These results revealed that the active I(III) reagent is likely the highly electrophilic [bis(cyano)iodo]arene[15] formed in situ from 2h and TMSCN.

We also determined intermolecular and intramolecular kinetic isotope effects (KIE). α -Phenylstyrene (**1a**) and [D2]-**1a** (1:1) were subjected to the reaction conditions and a $k_{\rm H}/k_{\rm D}$ value of 1.1 was measured for the intermolecular KIE (Scheme 3f). A significant intramolecular KIE of 3.3 was determined for cyanation of [D1]-**1a** (Scheme 3g). These KIE experiments indicate that activation of the alkene by the I(III) reagent is likely reversible and C–H bond cleavage is a slow step.^[16]



Scheme 3. Mechanistic studies.

Based on these investigations, the following mechanism is suggested (Scheme 4). The aryl(cyano)iodonium triflate **2h** generated from **3d** through ligand exchange undergoes renewed ligand exchange with TMSCN to give the active species [bis(cyano)iodo]arene **A** and TMSOTf. The electrophilic activation of alkene **1** with **A**, which is additionally supported by interaction with TMSOTf, then reversibly leads to the cyclic iodonium intermediate **B**.^[17] Regioselective ring-opening of **B** by the cyanide anion provides the intermediate **C** and diastereoselective deprotonation of **C** in a conformation where the cyano group is positioned anti to the bulkier R_L-substituent eventually provides **4**.



Scheme 4. Suggested mechanism.

COMMUNICATION

In summary, we have described a metal-free $C(sp^2)$ –H cyanation of various alkenes using TMSCN in combination with [bis(trifluoroacetoxy)iodo]arene **3d**. Reactions proceed under mild conditions and show broad substrate scope: 1,1-disubstituted, 1,2-disubstituted, and trisubstituted alkenes are smoothly converted into the corresponding cyanated products in high yield and good to excellent diastereoselectivity.

Acknowledgements

We thank the European Research Council (ERC Advanced Grant agreement No. 692640) for financial support.

Keywords: Cyanation • Hypervalent Iodine(III) Reagents • C-H functionalization • Acrylonitriles

- (a) R. C. Larock, Comprehensive Organic Transformations: A Guide to Functional Group Preparations, VCH, New York, **1989**; (b) F. F. Fleming, L. Yao, P. C. Ravikumar, L. Funk, B. C. Shook, *J. Med. Chem.* **2010**, *53*, 7902; (c) A. Kleemann, J. Engel, B. Kutscher, D. Reichert, Pharmaceutical Substances: Syntheses, Patents, Applications, *4th edn*, Thieme: Stuttgart, **2001**.
- [2] (a) Z. Rappoport, Chemistry of the Cyano Group, John Wiley & Sons, London, **1970**; (b) R. C. Larock, Comprehensive Organic Transformations: A Guide to Functional Group Preparations, John Wiley & Sons, New York, **1999**.
- (a) T. Sandmeyer, Ber. Dtsch. Chem. Ges. 1884, 17, 1633-1635; (b) J. [3] Lindley, Tetrahedron, 1984, 40, 1433-1456; (c) C. Galli, Chem. Rev. 1988, 88, 765-792; For reviews: (d) P. Anbarasan, T. Schareina, M. Beller, Chem. Soc. Rev. 2011, 40, 5049-5067; (e) S. Ding, N. Jiao, Angew. Chem. 2012, 124, 9360-9371; Angew. Chem. Int. Ed. 2012, 51, 9226-9237; (f) J. Kim, H. J. Kim, S. Chang, Angew. Chem. 2012, 124, 12114-12125; Angew. Chem. Int. Ed. 2012, 51, 11948-11959; (g) G. Yan, Y. Zhang, J. Wang, Adv. Synth. Catal. 2017, 359, 4068-4105; Selected examples: (h) G. Kaupp, J. Schmeyers, J. Boy, Chem. Eur. J. 1998, 4, 2467–2474; (i) F.-H. Luo, C. Chu, C.-H. Cheng, Organometallics, 1998, 17, 1025-1030; (j) M. Sundermeier, S. Mutyala, A. Zapf, A. Spannenberg, M. Beller, J. Organomet, Chem. 2003, 684, 50-55; (k) N. Sato, Q. Yue, Tetrahedron, 2003, 59, 5831-5836; (I) P. Anbarasan, H. Neumann, M. Beller, Angew. Chem. 2011, 123, 539-542; Angew. Chem. Int. Ed. 2011, 50, 519–522; (m) Z. Jiang, Q. Huang, S. Chen, L. Long, X. Zhou, Adv. Synth. Catal. 2012, 354, 589-592; (n) K. Okamoto, N. Sakata, K. Ohe. Org. Lett. 2015. 17. 4670-4673.
- [4] DG-assisted arene C-H cyanation: (a) X. Chen, X.-S. Hao, C. E. Goodhue, J.-Q. Yu, J. Am. Chem. Soc. 2006, 128, 6790-6791; (b) X. Jia, D. Yang, S. Zhang, J. Cheng, Org. Lett. 2009, 11, 4716-4719; (c) J. Kim, S. Chang, J. Am. Chem. Soc. 2010, 132, 10272-10274; (d) M. Chaitanya, D. Yadagiri, P. Anbarasan, Org. Lett. 2013, 15, 4960-4963; (e) T.-J. Gong, B. Xiao, W.-M. Cheng, W. Su, J. Xu, Z.-J. Liu, L. Liu, Y. Fu, J. Am. Chem. Soc. 2013, 135, 10630-10633; (f) W. Liu, L. Ackermann, Chem. Commun. 2014, 50, 1878-1881; (g) D. G. Yu, T. Gensch, F. Azambuja, S. V. Céspedes, F. Glorius, J. Am. Chem. Soc. 2014, 136, 17722-17725; (h) J. Dong, Z. Wu, Z. Liu, P. Liu, P. Sun, A. B. Pawar, S. Chang, Org. Lett. 2015, 17, 660-663. (i) J. Li, L. Ackermann, Angew. Chem. 2015, 127, 3706-3709; Angew. Chem. Int. Ed. 2015, 54, 3635-3638.
- Indole C-H cyanation: (a) G. Yan, C. Kuang, Y. Zhang, J. Wang, Org. Lett. 2010, 12, 1052–1055; (b) Y. Yang, Y. Zhang, J. Wang, Org. Lett.
 2011, 13, 5608–5611; (c) S.-T. Ding, N. Jiao, J. Am. Chem. Soc. 2011, 133, 12374–12377; (d) J. Kim, H. Kim, S. Chang, Org. Lett. 2012, 14, 3924–3927; (e) K. Okamoto, M. Watanabe, M. Murai, R. Hatano, K. Ohe, Chem. Commun. 2012, 48, 3127–3129.

- [6] Direct C-H cyanation of arenes: (a) Z. Shu, W. Ji, X. Wang, Y. Zhou, Y. Zhang, J. Wang, *Angew. Chem.* 2014, *126*, 2218–2221; *Angew. Chem. Int. Ed.* 2014, *53*, 2186–2189; (b) J. B. McManus, D. A. Nicewicz, *J. Am. Chem. Soc.* 2017, *139*, 2880–2883.
- [7] TM-catalyzed carbocyanations: (a) Y. Nakao, S. Oda, T. Hiyama, J. Am. Chem. Soc. 2004, 126, 13904–13905; (b) Y. Nakao, T. Yukawa, Y. Hirata, S. Oda, J. Satoh, T. Hiyama, J. Am. Chem. Soc. 2006, 128, 7116–7117; (c) S. Arai, T. Sato, Y. Koike, M. Hayashi, A. Nishida, Angew. Chem. Int. Ed. 2009, 48, 4528–4531; (d) Y. Hirata, A. Yada, E. Morita, Y. Nakao, T. Hiyama, M. Ohashi, S. Ogoshi, J. Am. Chem. Soc. 2010, 132, 10070–10077; (e) Y. Nakao, A. Yada, S. Ebata, T. Hiyama, J. Am. Chem. Soc. 2007, 129, 2428–2429; (f) N. R. Rondla, S. M. Levi, J. M. Ryss, R. A. V. Berg, C. J. Douglas, Org. Lett. 2011, 13, 1940–1943; (g) S. Arai, Y. Amako, X. Yang, A. Nishida, Angew. Chem. 2013, 125, 8305–8308; Angew. Chem. Int. Ed. 2013, 52, 8147–8150. (h) F. Wang, D. Wang, X. Wan, L. Wu, P. Chen, G. Liu, J. Am. Chem. Soc. 2016, 138, 15547–15550.
- [8] TM-catalyzed heterocyanations: (a) N. Chatani, T. Hanafusa, J. Chem. Soc. Chem. Commun. 1985, 838–839; (b) N. Chatani, N. Horiuchi, T. Hanafusa, J. Org. Chem. 1990, 55, 3393–3395; (c) M. Suginome, H. Kinugasa, Y. Ito, Tetrahedron Lett. 1994, 35, 8635–8638; (d) Y. Obora, A. S. Baleta, M. Tokunaga, Y. Tsuji, J. Organomet. Chem. 2002, 660, 173–177; (e) M. Suginome, A. Yamamoto, M. Murakami, J. Am. Chem. Soc. 2003, 125, 6358–6359; (f) M. Suginome, A. Yamamoto, M. Murakami, Angew. Chem. 2005, 117, 2432–2434; Angew. Chem. Int. Ed. 2005, 44, 2380–2382; (g) M. Murai, R. Hatano, S. Kitabata, K. Ohe, Chem. Commun. 2011, 47, 2375–2377; (h) D. C. Koester, M. Kobayashi, D. B. Werz, Y. Nakao, J. Am. Chem. Soc. 2012, 134, 6544–6547; (i) X. Wang, A. Studer, J. Am. Chem. Soc. 2016, 138, 2977–2980.
- [9] TM-catalyzed hydrocyanation: (a) T. Funabiki, Y. Yamazaki, K. Tarama, J. Chem. Soc. Chem. Commun. **1978**, 63–65; (b) W. R. Jackson, C. G.
 Lovel, J. Chem. Soc. Chem. Commun. **1982**, 1231–1232; (c) P. Alonso, P. Pardo, A. Galván, F. J. Fañanás, F. Rodríguez, Angew. Chem. **2015**, 127,15726–15730; Angew. Chem. Int. Ed. **2015**, *54*, 15506–15510; (d) F. Ye, J. Chen, T. Ritter, J. Am. Chem. Soc. **2017**, *139*, 7184–7187.

[10] DG-assisted alkene C–H cyanation: (a) M. Chaitanya, P. Anbarasan, Org.
 Lett. 2015, 17, 3766–3769; (b) W. Su, T.-J. Gong, B. Xiao, Y. Fu, Chem.
 Commun. 2015, 51, 11848–11851.

- [11] Electrophilic cyanation: (a) T. Dohi, K. Morimoto, N. Takenaga, A. Goto, A. Maruyama, Y. Kiyono, H. Tohma, Y. Kita, J. Org. Chem. 2007, 72, 109–116; (b) P. Anbarasan, H. Neumann, M. Beller, Chem. Eur. J. 2010, 16, 4725–4728; (c) J. P. Brand, D. F. González, S. Nicolai, J. Waser, Chem. Commun. 2011, 47, 102–115; (d) S. Kamijo, T. Hoshikawa, M. Inoue, Org. Lett. 2011, 13, 5928-5931; (e) Y. Yang, S. L. Buchwald, Angew. Chem. 2014, 126, 8821–8825; Angew. Chem. Int. Ed. 2014, 53, 8677–8681; (f) R. Frei, T. Courant, M. D. Wodrich, J. Waser, Chem. Eur. J. 2015, 21, 2662–2668; (g) M. V. Vita, P. Caramenti, J. Waser, Org. Lett. 2015, 17, 5832–5835; (h) G. Talavera, J. Peña, M. Alcarazo, J. Am. Chem. Soc. 2015, 137, 8704–8707; (i) J. T. Reeves, C. A. Malapit, F. G. Buono, K. P. Sidhu, M. A. Marsini, C. A. Sader, K. R. Fandrick, C. A. Busacca, C. H. Senanayake, J. Am. Chem. Soc. 2015, 137, 9481–9488; (j) W. Zhao, J. Montgomery, J. Am. Chem. Soc. 2016, 138, 9763–9766.
- [12] V. V. Zhdankin, M. C. Scheuller, P. J. Stang, *Tetrahedron Lett.* **1993**, *34*, 6853–6856.
- [13] J. B. Metternich, D. G. Artiukhin, M. C. Holland, M. von Bremen-Kühne, J. Neugebauer, R. Gilmour, J. Org. Chem. 2017, 82, 9955–9977.
- [14] X. Wang, A. Studer, Acc. Chem. Res. 2017, 50, 1712–1724.
- [15] H.-J. Frohna, M. E. Hirschberga, R. Boesea, D. Bläsera, U. Z. Flörke, Anorg. Allg. Chem. 2008, 634, 2539–2550.
- [16] E. M. Simmons, J. F. Hartwig, Angew. Chem. 2012, 124, 3120–3126; Angew. Chem. Int. Ed. 2012, 51, 3066–3072.
- [17] (a) T. Dohi, M. Ito, N. Yamaoka, K. Morimoto, H. Fujioka, Y. Kita, Angew. Chem. 2010, 122, 3406–3409; Angew. Chem. Int. Ed. 2010, 49, 3334–3337. (b) F. Wang, D. Wang, X. Mu, P. Chen, G. Liu, J. Am. Chem. Soc. 2014, 136, 10202–10205.

COMMUNICATION

COMMUNICATION

Xi Wang, Armido Studer*

Page No. – Page No.

Metal-Free Direct C-H Cyanation of Alkenes

Dual role. An in situ generated aryl(biscyano)iodine(III)reagent activates various styrene derivatives and additionally also acts as a cyanide source in the direct C–H cyanation of various alkenes. Reactions occur under mild conditions in the absence of any transition metal in good chemical yield and high stereoselectivity.

