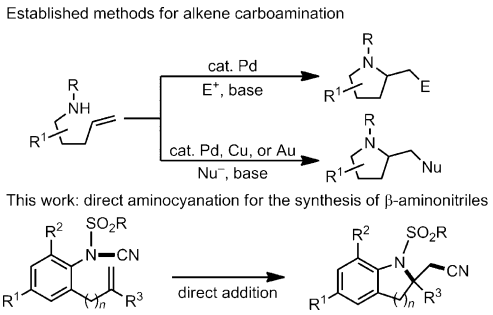
Synthetic Methods

DOI: 10.1002/anie.201310983

Intramolecular Aminocyanation of Alkenes by N–CN Bond Cleavage**

*Zhongda Pan, Sarah M. Pound, Naveen R. Rondla, and Christopher J. Douglas**

Abstract: *A metal-free, Lewis acid promoted intramolecular aminocyanation of alkenes was developed. $B(C_6F_5)_3$ activates N-sulfonyl cyanamides, thus leading to a formal cleavage of the N–CN bonds in conjunction with vicinal addition of sulfonamide and nitrile groups across an alkene. This method enables atom-economical access to indolines and tetrahydroquinolines in excellent yields, and provides a complementary strategy for regioselective alkene difunctionalizations with sulfonamide and nitrile groups. Labeling experiments with ^{13}C suggest a fully intramolecular cyclization pattern due to the lack of label scrambling in double crossover experiments. Catalysis with Lewis acid is realized and the reaction can be conducted under air.*



Scheme 1. Carboamination of alkenes.

Alkene addition reactions are a hallmark of organic chemistry, yet significant problems remain unsolved.[1] Recent successes include forming new C–N bonds in conjunction with vicinal C–C,[2,3] C–O,[4] C–N,[5] C–H,[6] or C–X[7] bonds. These alkene aminofunctionalization reactions represent a unique strategy for the synthesis of valuable nitrogen-containing heterocycles. Despite significant developments, the established aminofunctionalization methods typically rely upon an exogenous electrophile (e.g., aryl halides) or nucleophile (e.g., halides, amines, carboxylates) to furnish the subsequent C–C or C–heteroatom bonds vicinal to the nitrogen atom (Scheme 1).[8] To our knowledge, a direct intramolecular addition approach to aminocyanation is unexplored.

Recently, our group[9] and Nakao's group[10] independently reported two metal-catalyzed oxyfunctionalization reactions of alkenes through the activation of O–CO and O–CN bonds of esters and cyanates, respectively. Though this early work was pioneering, the corresponding chemistry to install a nitrogen atom is potentially more powerful. Due to the versatile synthetic utility of the cyano group[11] and the persistent demand for methods to prepare functionalized nitriles,[12] we envisioned that the aminocyanation of alkenes (Scheme 1) would allow straightforward access to β-aminonitriles. These compounds are versatile precursors to the biologically and pharmacologically important β-amino acids.[13] To our surprise, the well-developed strategies for alkene aminofunctionalization[2–7] have only recently been applied to the introduction of cyano groups onto the alkene double bond. In 2013, Xiong, Li, Zhang, and co-workers reported the first example of alkene aminocyanation. Their work focused on aminocyanation of styrenes in an intermolecular context and was thought to proceed by a copper-promoted radical addition pathway using TMSCN as the cyanide source and *N*-fluorobenzenesulfonimide as the nitrogen source.[14]

Cyanamides (R^1R^2N–CN) are versatile one-carbon, two-nitrogen building blocks for heterocycle synthesis.[15] These bench-stable compounds are easily prepared by reaction of the corresponding secondary or tertiary amine with BrCN (von Braun reaction).[16] While most transformations of cyanamides occur at the cyano group, methods for cleaving the N–CN bond of cyanamides are rare, presumably due to the double-bond character of N–CN bonds.[17] Owing to this challenge, catalytic cleavage of N–CN bonds has only recently been reported.[18,19] Notably, Falck and Wang reported a rhodium-catalyzed cyano-group transfer from an *ortho* cyanamide to the alkene of an α-methyl styrene. They proposed metal-mediated N–CN bond cleavage as a key step and the reaction required a relatively high catalyst loading (20 mol% of Rh).[19] This N–CN bond activation was conceptually in accord with our early mechanistic thinking regarding alkene aminocyanation. Nevertheless, to the best of our knowledge, intramolecular aminocyanation of alkenes—by any mechanism—has never been described. Herein we report a Lewis acid promoted intramolecular aminocyanation of alkenes. We report the construction of 2,2-disubstituted indolines[20] and 2,2-disubstituted tetrahydroquinolines in an atom-economical fashion. The highlight of our approach is

[*] Z. Pan, S. M. Pound, N. R. Rondla, Prof. Dr. C. J. Douglas
Department of Chemistry, University of Minnesota—Twin Cities
207 Pleasant St. SE, Minneapolis, MN 55455 (USA)
E-mail: cdouglas@umn.edu

[**] We thank the National Institutes of Health for primary support of this work (R01 GM095559). C.J.D. thanks Research Corporation for Science Advancement for additional support through a Cottrell Scholar Award. We thank Dr. Joe Dalluge and Sean Murray for assistance with HRMS measurements. NMR spectra were recorded on an instrument purchased with support from the National Institutes of Health (S10OD011952).

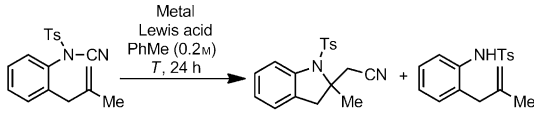
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201310983.

a novel mechanism for aminocyanation of alkenes by a non-degradative rupture at the N–CN bond.

Recently, *N*-cyano-*N*-phenyl-*p*-toluene sulfonamide (NCTS) has been employed as a bench-stable and less-toxic cyanation reagent in metal-catalyzed cross-coupling[21] and arene C–H cyanations,[22] thus implying a metal-mediated N–CN cleavage process. Meanwhile, Lewis acid cocatalysts, particularly BPh_3, have proven effective at accelerating metal-catalyzed carbocyanation[23] and oxycyanation[10] of alkenes.

We attempted to take advantage of the electron-withdrawing tosyl group to weaken the N–CN bond of NCTS-type cyanamides while incorporating the activating effect of a Lewis acid on the cyano group. Therefore, we initiated our investigation of aminocyanation conditions by treating the *N*-tosyl cyanamide **1a** with a variety of transition-metal and Lewis acid additives (see the Supporting Information for details on discovery and optimization). We quickly identified that the combination of rhodium(I) complexes and boron Lewis acids were effective (Table 1, entries 1–4). As Lewis acid strength increased from BPh_3 to $B(C_6F_5)_3$, the yield of **2a** improved from 49 to 72% with minimal amounts of the reductive de-cyanation byproduct **3a** observed (entry 2).[24] Also, the temperature required for acceptable conversion of **1a** could be decreased, with 90°C proving optimal (entries 2–4). Dramatically, a reaction employing $B(C_6F_5)_3$ in the absence of added rhodium still gave **2a** in a 90% yield (entry 5). This observation prompted us to examine other Lewis acids to promote aminocyanation. The isoelectronic Lewis acids $BF_3{\cdot}OEt_2$, $AlCl_3$, and Me_2AlCl each provided **2a**, albeit in lower yields than $B(C_6F_5)_3$ (entries 6–8). The reaction of AgOTf or $Cu(OTf)_2$ with **1a** failed to produce detectable amounts of **2a**, and instead gave complex mixtures (entries 9 and 10). $Zn(OTf)_2$ or $Sc(OTf)_3$ were also ineffective, returning **1a** without a detectable amount of **2a** (entries 11 and 12). Reaction of **1a** with $SnCl_4$ provided **2a** in 49% (entry 13), but also provided an insoluble black precipitate as a byproduct. Interestingly, BPh_3 was an ineffective promoter, even at 150°C (entry 14).

Table 1: Development of aminocyanation conditions.



1a 2a 3a

Entry	Metal[a]	Lewis acid[b]	T [°C]	Yield [%]
1	$[\{Rh(C_2H_4)_2Cl\}_2]$	BPh_3 (1.2 equiv)	110	49[c]
2	$[\{Rh(C_2H_4)_2Cl\}_2]$	$B(C_6F_5)_3$	110	72[d]
3	$[\{Rh(C_2H_4)_2Cl\}_2]$	$B(C_6F_5)_3$	90	89[d]
4	$[\{Rh(C_2H_4)_2Cl\}_2]$	$B(C_6F_5)_3$	80	71[d]
5	–	$B(C_6F_5)_3$	90	90[d]
6	–	$BF_3{\cdot}OEt_2$	90	31[d]
7	–	$AlCl_3$	90	52[d]
8	–	Me_2AlCl	90	11[c]
9	–	$Ag(OSO_2CF_3)$	90	–[e]
10	–	$Cu(OSO_2CF_3)_2$	90	–[e]
11	–	$Zn(OSO_2CF_3)_2$	90	–[f]
12	–	$Sc(OSO_2CF_3)_3$	90	–[f]
13	–	$SnCl_4$	90	49[c]
14	–	BPh_3	150	–[f]

[a] 5 mol% Rh complex used. [b] 1.0 equiv of Lewis acid was used unless otherwise specified. [c] Determined by ^1H NMR analysis using *p*-methoxyacetophenone as the internal standard. [d] Yield after column chromatography. [e] No **2a** detected by NMR spectroscopy. Complex mixture formed. [f] No **2a** detected by NMR spectroscopy. Only **1a** was detected. Ts = *p*-toluenesulfonyl.

With the identification of suitable reaction conditions, the scope of the Lewis acid promoted intramolecular aminocyanation was investigated. Substrates bearing alkyl (Table 2, entries 1 and 2) or halo groups on the aromatic ring (entries 3–5) provided the corresponding indolines in excellent yields. It is worth noting that the presence of bromide *para* to the cyanamide moiety (entry 5) was well-tolerated, as this offers a convenient handle for further functionalization. The electronic effects of *para* substituents on the aryl ring appeared to be inconsequential as substrates containing either electron-donating (R = Me, OMe; entries 1 and 7) or electron-withdrawing (R = F, CF_3; entries 3 and 6) groups *para* to the cyanamide underwent the reaction in excellent yields ($\geq$92%). Substitution at the alkene, either alkyl or phenyl, was tolerated and, in fact, necessary for the reaction. The ethyl- and phenyl-substituted alkenes **1i** and **1j**, respectively, (entries 8 and 9) afforded the corresponding indolines in high yields. However, the allyl substrate **1n** returned only unconsumed starting material (entry 13). Substrates with internal alkenes (including trisubstituted) provided complex mixtures of products, and alkene substitution remains a limitation at this time. The benzyloxymethyl-substituted alkene **1m** also failed to provide product (entry 12), which was tentatively attributed to the inductive effect of the benzyloxy group.[25] An extended alkene tether found in the substrate **1k** afforded the tetrahydroquinoline **2k** in 93% yield (entry 10). Changing the protecting group at the nitrogen atom from tosyl to nosyl (**1l**) provided the *para*-nosyl indoline **2l** in almost quantitative yield (99%, entry 11). The relatively mild reaction conditions for cleaving nosyl groups should allow convenient post-functionalization on the nitrogen atom.[26] Additionally, methyl substitution *ortho* to the cyanamide moiety (entry 14) was tolerated, giving **2o** in 90% yield.

Based on the ability of $B(C_6F_5)_3$ to promote intramolecular aminocyanation, we needed to revise our mechanistic thinking. Wang and co-workers recently reported that electrophilic cyanations of indoles[27] is accomplished using NCTS and a Lewis acid. This provides precedence for the nucleophilic cleavage of N–CN bonds and cyano-group transfer under Lewis acid conditions. In aminocyanation, however, both groups are transferred to the alkene. We hypothesized that the N_{CN} lone pair of electrons of **1a** initially coordinated to $B(C_6F_5)_3$, affording the adduct **I1** (Scheme 2).[28] This coordination set the stage for an intramolecular nucleophilic attack of the alkene, but the mode of attack was unclear.

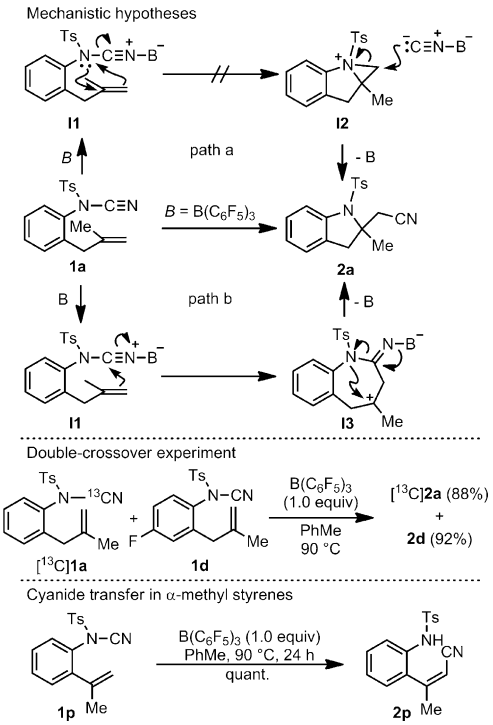
We considered a mechanism involving N–CN cleavage by aziridinium ion formation (path a, Scheme 2) and a nonfragmenting pathway involving nucleophilic attack of the alkene at the central cyanamide carbon atom (path b, Scheme 2). Aziridinium ion formation by $B(C_6F_5)_3$-promoted loss of

Table 2: Scope of alkene aminocyanation.[a]

Entry	Substrate	Product	Yield [%][b]
1	**1b**, R = Me	**2b**	92
2	**1c**, R = *t*Bu	**2c**	92[c]
3	**1d**, R = F	**2d**	> 99
4	**1e**, R = Cl	**2e**	95
5	**1f**, R = Br	**2f**	96
6	**1g**, R = CF_3	**2g**	94
7	**1h**, R = OMe	**2h**	99
8	**1i**	**2i**	> 99
9	**1j**	**2j**	> 99
10[d]	**1k**	**2k**	93
11	**1l**	**2l**	99
12	**1m**	–[e]	0
13	**1n**	–[e]	0
14	**1o**	**2o**	90

[a] Reaction conditions: substrate (0.1 mmol), $B(C_6F_5)_3$ (0.1 mmol), PhMe (0.5 mL), 90 °C, 24 h. [b] Yields after column chromatography. [c] Average of two runs. [d] Reaction time: 28 h. [e] Unconsumed starting material. Ns = *p*-nitrobenzenesulfonyl.

cyanide was attractive due to the remarkable "anion abstracting properties of this special boron compound".[29,30] The hypothesis involving nucleophilic attack of the alkene at the central cyanamide carbon atom was attractive since this is the typical site of nucleophile attack on cyanamides.[31] These hypotheses were tested by a double-crossover experiment (Scheme 2). A mixture of **1d** and the ^{13}C-labeled cyanamide **1a** ([^{13}C]**1a**) afforded only the non-crossover products **2d** and

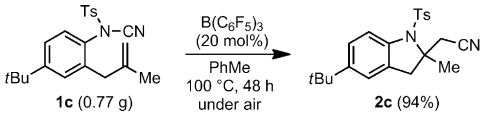


Scheme 2. Mechanistic experiments and considerations.

[^{13}C]**2a**. The lack of crossover in the experiment indicated that alkene aminocyanation proceeds in a fashion which is inconsistent with the aziridinium ion hypothesis (Path A).[32]

The crossover experiments ruled out path a (Scheme 2). We note that the success of cyanamides bearing more nucleophilic alkenes (such as **1i** and **1j**) and the failure of cyanamides bearing less nucleophilic alkenes (**1m** and **1n**) is consistent with rate-limiting alkene attack. The mechanism by which the intermediate **I3** is converted into product is not yet clear. In principle, formation of the new C–N_{Ts} bond could occur either before or after rupture of the N_{Ts}–CN bond. Intriguingly, instead of giving the corresponding four-membered benzazetidine,[33] the reaction of the *o*-isopropenyl-substituted cyanamide **1p** led to the alkenyl nitrile **2p**in quantitative yield (Scheme 2, bottom).[34] These results show that the type of cyano group transfer developed by Wang and Falck does not require added rhodium. Future work will explore the mechanistic consequence of this observation for aminocyanation.

Our mechanistic hypothesis suggested that $B(C_6F_5)_3$ might act as a catalyst. To test this hypothesis, **1a** was treated with 20 mol% $B(C_6F_5)_3$ in toluene and heated at 90 °C for an extended period (48 h). We were pleased to find that **2a** was formed in 91% yield. These results indicate that the coordination of $B(C_6F_5)_3$ to the product is not so strong as to preclude turnover. Due to the relatively high cost of commercial $B(C_6F_5)_3$, cost-saving by catalysis may be achieved at the expense of reaction time. After a successful small-scale reaction of **1c** with 20 mol% $B(C_6F_5)_3$ under nitrogen, we repeated the reaction on larger scale, heating at 100 °C for 48 hours under an atmosphere of air. We obtained **2c** in 94% yield (Scheme 3).



Scheme 3. Catalysis with $B(C_6F_5)_3$ and reaction under air.

In summary, we have developed a Lewis acid promoted intramolecular aminocyanation of alkenes. The addition of transition-metal catalysts or initiators is not required. We believe we have identified a new mechanistic pathway for aminative alkene difunctionalization by the addition of bench-stable, readily available cyanamides. We demonstrated the aminocyanation reaction in the preparation of two important classes of nitrogen heterocycles, indolines and tetrahydroquinolines, in excellent yields. Current efforts are directed towards further elucidating the mechanism and expanding the scope, as well as developing intermolecular variants of aminocyanation. Further work will be directed towards development of a catalytic asymmetric variant of the reaction and further studies on the mechanism by probing the stereochemistry of the addition process.

Received: December 18, 2013
Revised: February 6, 2014
Published online: April 9, 2014

Keywords: alkenes · boron · heterocycles · Lewis acids · reaction mechanisms

[1] Reviews: a) K. H. Jensen, M. S. Sigman, *Org. Biomol. Chem.* **2008**, *6*, 4083; b) R. I. McDonald, G. Liu, S. S. Stahl, *Chem. Rev.* **2011**, *111*, 2981.

[2] Review: J. P. Wolfe, *Top. Heterocycl. Chem.* **2013**, *32*, 1. Selected Examples a) L. S. Hegedus, G. F. Allen, D. J. Olsen, *J. Am. Chem. Soc.* **1980**, *102*, 3583; b) Y. Tamaru, M. Hojo, H. Higashimura, Z. Yoshida, *J. Am. Chem. Soc.* **1988**, *110*, 3994; c) J. E. Ney, J. P. Wolfe, *Angew. Chem.* **2004**, *116*, 3689; *Angew. Chem. Int. Ed.* **2004**, *43*, 3605; d) C. C. Scarborough, S. S. Stahl, *Org. Lett.* **2006**, *8*, 3251; e) E. S. Sherman, P. H. Fuller, D. Kasi, S. R. Chemler, *J. Org. Chem.* **2007**, *72*, 3896; f) S. Hayashi, H. Yorimitsu, K. Oshima, *Angew. Chem.* **2009**, *121*, 7360; *Angew. Chem. Int. Ed.* **2009**, *48*, 7224; g) C. F. Rosewall, P. A. Sibbald, D. V. Liskin, F. E. Michael, *J. Am. Chem. Soc.* **2009**, *131*, 9488; h) L. M. Rossiter, M. L. Slater, R. E. Giessert, S. A. Sakwa, R. J. Herr, *J. Org. Chem.* **2009**, *74*, 9554; i) L. Bagnoli, S. Cacchi, G. Fabrizi, A. Goggiamani, C. Scarponi, M. Tiecco, *J. Org. Chem.* **2010**, *75*, 2134; j) W. E. Brenzovich, D. Benitez, A. D. Lackner, H. P. Shunatona, E. Tkatchouk, W. A. Goddard, F. D. Toste, *Angew. Chem.* **2010**, *122*, 5651; *Angew. Chem. Int. Ed.* **2010**, *49*, 5519; k) S. Jaegli, W. Erb, P. Retailleau, J.-P. Vors, L. Neuville, J. Zhu, *Chem. Eur. J.* **2010**, *16*, 5863; l) T. H. Jepsen, M. Larsen, M. B. Nielsen, *Tetrahedron* **2010**, *66*, 6133; m) E. Borsini, G. Broggini, A. Fasana, S. Galli, M. Khansaa, U. Piarulli, M. Rigamonti, *Adv. Synth. Catal.* **2011**, *353*, 985; n) S. Nicolai, C. Piemontesi, J. Waser, *Angew. Chem.* **2011**, *123*, 4776; *Angew. Chem. Int. Ed.* **2011**, *50*, 4680; o) R. Jana, T. P. Pathak, K. H. Jensen, M. S. Sigman, *Org. Lett.* **2012**, *14*, 4074.

[3] Diazoalkane cycloadditions accomplish simultaneous C–C and C–N bond forming across alkenes: "Diazoalkanes": G. Maas in *Synthetic Applications of 1,3-Dipolar Cycloaddition Chemistry Toward Heterocycles and Natural Products* (Eds.: A. Padwa, W. H. Pearson), Wiley-Interscience, New York, **2002**, pp. 539–623.

[4] Review: T. J. Donohoe, C. K. A. Callens, A. Flores, A. R. Lacy, A. H. Rathi, *Chem. Eur. J.* **2011**, *17*, 58.

[5] Review: a) F. Cardona, A. Goti, *Nat. Chem.* **2009**, *1*, 269; b) K. Muñiz, C. Martínez, *J. Org. Chem.* **2013**, *78*, 2168.

[6] Review: a) T. E. Mueller, K. C. Hultzsch, M. Yus, F. Foubelo, M. Tada, *Chem. Rev.* **2008**, *108*, 3795; b) G. Zi, *Dalton Trans.* **2009**, 9101.

[7] Review: a) G. Li, K. S. R. S. Saibau, C. Timmons, *Eur. J. Org. Chem.* **2007**, 2745; b) S. R. Chemler, M. T. Bovino, *ACS Catal.* **2013**, *3*, 1076.

[8] Intramolecular diamination of alkenes is an exception (Ref. [5]).

[9] G. T. Hoang, V. J. Reddy, H. H. K. Nguyen, C. J. Douglas, *Angew. Chem.* **2011**, *123*, 1922; *Angew. Chem. Int. Ed.* **2011**, *50*, 1882.

[10] D. C. Koester, M. Kobayashi, D. B. Werz, Y. Nakao, *J. Am. Chem. Soc.* **2012**, *134*, 6544.

[11] *Three Carbon-Heteroatom Bonds: Nitriles, Isocyanides, and Derivatives*, *Vol. 19* (Ed.: S. Murahashi), Georg Thieme, Stuttgart, **2004**.

[12] A. Fatiadi in *Preparation and Synthetic Application of Cyano Compounds* (Eds.: S. Patai, Z. Rappaport), Wiley, New York, **1983**.

[13] a) G. Cardillo, C. Tomasini, *Chem. Soc. Rev.* **1996**, *25*, 117; b) "Biosynthesis of β-Amino Acids": P. Spiteller, F. von Nussbaum in *Highlights in Bioorganic Chemistry*: *Methods and Application* (Eds.: C. Schumck, H. Wennemers), Wiley-VCH, Weinheim, **2004**, pp. 63–89; c) E. Juaristi, V. A. Soloshonok, *Enantioselective Synthesis of β-Amino Acids*, Wiley-VCH, New York, **2005**; d) B. Weiner, W. Szymanski, D. B. Janssen, A. J. Minnaard, B. L. Feringa, *Chem. Soc. Rev.* **2010**, *39*, 1656.

[14] H. Zhang, W. Pu, T. Xiong, Y. Li, X. Zhou, K. Sun, Q. Liu, Q. Zhang, *Angew. Chem.* **2013**, *125*, 2589; *Angew. Chem. Int. Ed.* **2013**, *52*, 2529.

[15] a) D. D. Nekrasov, *Chem. Heterocycl. Compd.* **2004**, *40*, 1107; b) M.-H. Larraufie, G. Maestri, M. Malacria, C. Ollivier, L. Fensterbank, E. Lacote, *Synthesis* **2012**, 1279.

[16] a) J. von Braun, *Ber. Dtsch. Chem. Ges. Chem.* **1907**, *40*, 3914; Reviews: b) H. A. Hageman, *Org. React.* **1953**, *7*, 198; c) S. Thavaneswaran, K. McCamley, P. J. Scammells, *Nat. Prod. Commun.* **2006**, *1*, 885. **CAUTION!** Cyanogen bromide (BrCN) is highly toxic and hydrolyzes readily to release hydrogen cyanide. Reactions using BrCN must be carried out in a well-ventilated fume hood.

[17] a) I. D. Cunningham, M. E. Light, M. B. Hursthouse, *Acta Crystallogr. Sect. C* **1999**, *55*, 1833; b) For an early example of cleaving cyanamide N–CN bonds under harsh reaction conditions, see: E. B. Vliet, *Org. Synth.* **1925**, *5*, 43; c) cleaving cyanamide N–CN bond via aminocyanation of benzyne: B. Rao, X. Zeng, *Org. Lett.* **2014**, *16*, 314.

[18] K. Fukumoto, T. Oya, M. Itazaki, H. Nakazawa, *J. Am. Chem. Soc.* **2009**, *131*, 38.

[19] R. Wang, J. R. Falck, *Chem. Commun.* **2013**, *49*, 6516.

[20] For syntheses of 2,2-disubstituted indolines, see: a) R. C. Larock, P. Pace, H. Yang, C. E. Russell, S. Cacchi, G. Fabrizi, *Tetrahedron* **1998**, *54*, 9961; b) F. Zhou, J. Guo, J. Liu, K. Ding, S. Yu, Q. Cai, *J. Am. Chem. Soc.* **2012**, *134*, 14326; c) Q. Cai, F. Zhou, *Synlett* **2013**, 408; d) F. Nowrouzi, R. A. Batey, *Angew. Chem.* **2013**, *125*, 926; *Angew. Chem. Int. Ed.* **2013**, *52*, 892.

[21] P. Anbarasan, H. Neumann, M. Beller, *Angew. Chem.* **2011**, *123*, 539; *Angew. Chem. Int. Ed.* **2011**, *50*, 519.

[22] a) M. Chaitanya, D. Yadagiri, P. Anbarasan, *Org. Lett.* **2013**, *15*, 4960; b) 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.

[23] Recent review: Y. Nakao, *Bull. Chem. Soc. Jpn.* **2012**, *85*, 731.

[24] Nakao and co-workers observed reductive decyanation of the cyanate substrates from the oxycyanation reactions (see Ref. [19]).
[25] Subjecting **1m** to the aminocyanation conditions with [{Rh(C_2H_4)$_2$Cl}$_2$] (5 mol%) and BPh_3 (1.0 equiv) in toluene at 110°C gave the product of decyanation (**3m**) and unconsumed starting material.
[26] T. Kan, T. Fukuyama, *Chem. Commun.* **2004**, 353.
[27] Y. Yang, Y. Zhang, J.-B. Wang, *Org. Lett.* **2011**, *13*, 5608.
[28] Lewis acid/base pairs between isonitriles or nitriles and B(C_6F_5)$_3$: a) H. Jacobsen, H. Berke, S. Döring, G. Kehr, G. Erker, R. Froehlich, O. Meyer, *Organometallics* **1999**, *18*, 1724; b) Lewis acid/base pair adducts between B(C_6F_5)$_3$ and cyanamides (and other nitrogen-containing compounds) F. Focante, P. Mercandelli, A. Sironi, L. Resconi, *Coord. Chem. Rev.* **2006**, *250*, 170, and references therein.
[29] G. Erker, *Dalton Trans.* **2005**, 1883.
[30] B(C_6F_5)$_3$ is estimated to be in between BCl_3 and BF_3 in Lewis acidity: S. Döring, G. Erker, R. Froehlich, O. Meyer, K. Bergander, *Organometallics* **1998**, *17*, 2183.
[31] For a recent example, see: R. L. Giles, J. D. Sullivan, A. M. Steiner, R. E. Looper, *Angew. Chem.* **2009**, *121*, 3162; *Angew. Chem. Int. Ed.* **2009**, *48*, 3116.
[32] Similarly, an equimolar mixture of **1d** and **1l** was subjected to the aminocyanation conditions, and only the corresponding indoline products **2d** and **2l** were observed. This indicates the N–S bond also remains intact during aminocyanation.
[33] Synthesis of *N*-acyl benzazetidines: K. Kobayashi, K. Miyamoto, O. Morikawa, H. Konishi, *Bull. Chem. Soc. Jpn.* **2005**, *78*, 886.
[34] **2o** was identified by comparing its ^{1}H and ^{13}C NMR spectra and HRMS data with the prior report (see Ref. [19]).

