ChemComm

Ruthenium-catalyzed *ortho* alkenylation of aromatic nitriles with activated alkenes *via* C–H bond activation†

Mallu Chenna Reddy and Masilamani Jeganmohan*

The ruthenium-catalyzed *ortho* alkenylation of substituted aromatic and heteroaromatic nitriles with activated alkenes providing *ortho* alkenylated aromatic and heteroaromatic nitriles in a highly regio- and stereoselective manner is described.

Selective transformation of the C–H bond of organic moieties into C–C and C–heteroatom bond catalyzed by transition metal complexes *via* C–H bond activation is one of the most versatile and well-acknowledged methods in organic synthesis.[1] This transformation has gained tremendous attention in chemical and pharmaceutical industries, because it provides step- and atom-economical routes to synthesize useful organic molecules from the readily available starting materials.[2] Particularly, a transition metal-catalyzed oxidative cross-coupling of hetero-atom substituted aromatics with alkenes has proven to be a highly efficient route to synthesize disubstituted alkenes without having any prefunctionalized starting materials in a highly regio- and stereoselective manner.[3] The selectivity of the C–H bond of organic moieties can be controlled by using suitable directing groups. In most cases, the lone pair of electrons of nitrogen or oxygen atom of the directing groups coordinate with the metal complex through σ-coordination and activate the C–H bond of organic moieties selectively (Fig. 1, eqn (1)).[4,5] The search for new variants to activate the C–H bond of aromatics is very important to expand the synthetic scope of the alkenylation reaction. Very recently, Cheng's group disclosed an alkene assisted alkenylation of aromatics with activated alkenes in the presence of a palladium catalyst *via* an unusual carbon–carbon π-bond coordination (Fig. 1, eqn (2)).[6]

Nitrile is a versatile functional group which can be efficiently used for various organic transformations.[7] In addition, nitrile group containing organic molecules are used as pharmaceuticals, pesticides and dyes.[8] The strong electron withdrawing nature and
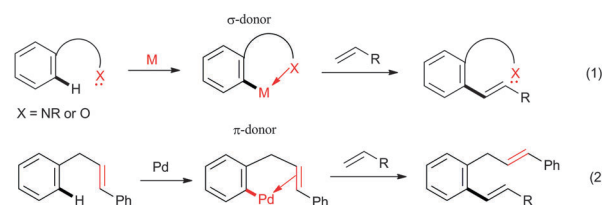

Fig. 1 Chelation-assisted C–H bond alkenylation.

better hydrogen bond accepting properties of the nitrile group allow it to be used widely in designing drug molecules. Meanwhile, the cyano group can also be used as a directing group for the C–H bond activation reactions.[9–11] It is known that the lone pair of electrons of the nitrogen atom of the nitrile group of benzonitrile coordinate with the metal complex through σ-coordination, and this process leads to the formation of a linear metal complex.[9] Also, a less likely, C≡N π-bond of benzonitrile coordinates with the metal, yielding the π-coordinated metal complexes.[10] Recently, by employing the σ-coordination of the nitrile moiety, the *meta* C–H bond of aromatics could be activated efficiently for the alkenylation reaction (Fig. 2, eqn (1)).[11] To date, there is no report on the C≡N π-bond assisted alkenylation at the *ortho* position of aromatic nitriles with alkenes due to the difficulty in coordination of the π-bond of C≡N with metals.

Our ongoing interest in the finding of a new C–H bond transformation reaction prompted us to explore the possibility of C≡N π-bond assisted *ortho* alkenylation of substituted aromatic

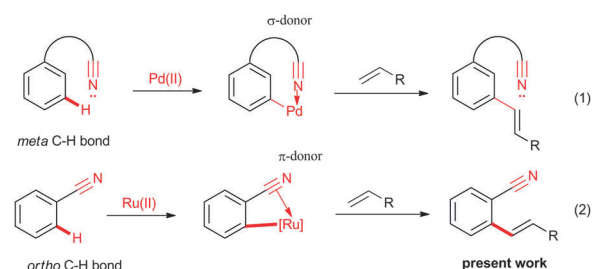Department of Chemistry, Indian Institute of Science Education and Research, Pune 411021, India. E-mail: mjeganmohan@iiserpune.ac.in

† Electronic supplementary information (ESI) available: Detailed experimental procedures and spectroscopic data. See DOI: 10.1039/c5cc03112e

Fig. 2 C–H bond alkenylation of aromatic nitriles.

nitriles with alkenes. Herein, we wish to report for the first time nitrile as a π-bond coordinating group for the *ortho* alkenylation of aromatic and heteroaromatic nitriles with activated alkenes in the presence of a ruthenium catalyst (Fig. 2, eqn (2)). The alkenylation reaction was compatible with functional group substituted aromatic nitriles. Later, the *ortho* alkenylated aromatic nitrile was converted into a chiral phthalide in the presence of AD-mix-β. By employing nitrile as a directing group, arylation was performed at the alkene C–H bond of the *ortho* alkenylated aromatic nitriles with aromatic iodides in the presence of a Pd catalyst.

Initially, the ruthenium-catalyzed alkenylation reaction was examined using benzonitrile (1a) and *n*-butyl acrylate (2a) (Scheme 1). It is expected that the nitrogen atom of 1a prefers to coordinate with the metal *via* the lone pair electrons rather than π-coordination. However, for successful *ortho* C–H bond activation, π-coordination of nitrile is crucial. Meanwhile, a metal acetate base is needed for the deprotonation of the C–H bond of weak coordinating group substituted aromatics. Thus, a combination of the ruthenium catalyst and metal acetate having a Lewis acidic nature was selected. The main idea behind the selection of the Lewis acidic metal acetate is that the lone pair of nitrogen of the nitrile moiety would coordinate with the Lewis acid prior to the ruthenium catalyst reaction and block the corresponding site. Therefore, a possibility is created for the π-bond coordination of the nitrile moiety with the ruthenium catalyst and initiates the C–H bond activation. With this idea, a combination of [{RuCl$_2$(*p*-cymene)}$_2$] (5 mol%), AgSbF$_6$ (20 mol%) and Cu(OAc)$_2$·H$_2$O (2.0 equiv.) was used for the reaction. As a nitrile is a weak coordinating group, AgSbF$_6$ was used to generate a cationic ruthenium species for the C–H bond reaction. However, in the reaction, hydration takes place at the nitrile group and only benzamide (3a) was observed. If the same reaction is run for a long time, a cyclic isoindolin-1-one derivative was observed.[12] Later, the reaction was examined using various Lewis acids such as Co(OAc)$_2$, Mn(OAc)$_2$, Ag$_2$O, AgOAc, Ag$_2$CO$_3$, Ag(CF$_3$CO$_2$) and Fe(OAc)$_2$ (2.0 equiv.). Very interestingly, in AgOAc, the *ortho* C–H bond activation takes place selectively and further reaction with *n*-butyl acrylate (2a) provides the *ortho* alkenylated benzonitrile 4aa in 75% isolated yield. In the reaction, benzamide 3a was observed only in a very minor 3% yield. In other silver salts such as Ag$_2$O, Ag$_2$CO$_3$ and Ag(CF$_3$CO$_2$), the product 4aa was observed in 45%, 49% and 61% yields. Benzamide 3a was observed in 25%, 19% and 14% yields, respectively. But, in Co(OAc)$_2$ and Mn(OAc)$_2$, benzamide 3a was observed in more than 45% and 51% yields and product 4aa was observed in 15% and 19% yields, respectively. Meanwhile, the acidic solvent AcOH is crucial for the reaction. Other solvents such as 1,2-dichloroethane, THF,

1,4-dioxane, DMF, toluene and CF$_3$COOH were not suitable for the reaction. However, in iso-PrOH, the product 4aa was observed only in 10% yield without benzamide 3a formation.
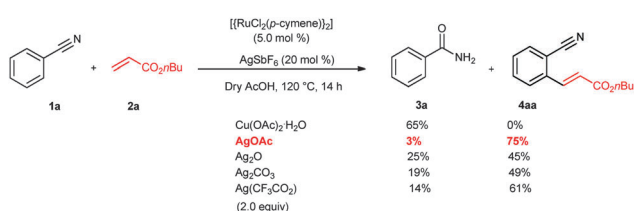
The scope of the alkenylation reaction was examined with various activated alkenes 2 under the optimized reaction conditions (Table 1). Ethyl acrylate (2b), cyclohexyl acrylate (2c), phenyl acrylate (2d), benzyl acrylate (2e) and 2-phenoxyethyl acrylate (2f) reacted efficiently with 1a, providing the expected *ortho* alkenylated benzonitriles 4ab–af in 64%, 79%, 69%, 67% and 59% yields, respectively (entries 1–5). Further, *n*-butyl acrylate (2a), ethyl acrylate (2b), methyl acrylate (2g) and 2,2,2-trifluoroethyl acrylate (2h) also efficiently reacted with 2-naphthonitrile (1b), yielding *ortho* alkenylated 2-naphthonitriles 4ba–bh in 75%, 65%, 62% and 57% yields, respectively (entries 6–9). In the reaction, C–H bond activation takes place selectively at the C3 position of 2-naphthonitrile (1b). Interestingly, phenyl vinyl sulphone (2i) was also efficiently involved in the reaction, providing product 4bi in 52% yield (entry 10).

The alkenylation reaction was compatible for a variety of sensitive functional groups such as Br, Cl, I, OMe, SMe and CO$_2$Me substituted aromatic nitriles (Table 2). *ortho* Bromo (1c), chloro (1d) and methoxy (1e) substituted benzonitriles reacted efficiently with *n*-butyl acrylate (2a), providing the corresponding *ortho* alkenylated aromatic nitriles 4ca–ea in 51%, 50% and 47% yields, respectively (entries 1–3). Subsequently, *meta* methylester (1f), iodo (1g), bromo (1h), chloro (1i) and methoxy (1j) benzonitriles also efficiently participated in the reaction, providing the corresponding *ortho* alkenylated benzonitriles 4fa–ja in 53%, 48%, 45%, 44% and 42% yields, respectively, in a highly regioselective manner (entries 4–8). In all these reactions, C–H bond activation takes place at a less hindered *ortho* C6–H bond of the

Table 1 Reaction of benzonitrile (1a) or 2-naphthonitrile (1b) with activated alkenes 2b–i[a]

Entry	Alkenes 2	Product 4	Yield[b] (%)
	CO$_2$R^1 2b-f	4ab-af	
1	2b: R^1 = Et	4ab: R^1 = Et	64
2	2c: R^1 = cyclohexyl	4ac: R^1 = cyclohexyl	79
3	2d: R^1 = Ph	4ad: R^1 = Ph	69
4	2e: R^1 = CH$_2$Ph	4ae: R^1 = CH$_2$Ph	67
5	2f: R^1 = (CH$_2$)$_2$OPh	4af: R^1 = (CH$_2$)$_2$OPh	59
	CO$_2$R^1 2a-h	4ba-bh	
6	2a: R^1 = *n*-Bu	4ba: R^1 = *n*-Bu	75
7	2b: R^1 = Et	4bb: R^1 = Et	65
8	2g: R^1 = Me	4bg: R^1 = Me	62
9	2h: R^1 = CH$_2$CF$_3$	4bh: R^1 = CH$_2$CF$_3$	57
10	SO$_2$Ph 2i	4bi	52[c]

[a] All the reactions were carried out using 1a or 1b (75 mg), alkenes 2a–h (4.0 equiv.) and 2i (2.0 equiv.), [{RuCl$_2$(*p*-cymene)}$_2$] (5 mol%), AgSbF$_6$ (20 mol%) and AgOAc (2.0 equiv.) in dry acetic acid (3.0 mL) at 120 °C for 14 h. [b] Isolated yield. [c] In this reaction, DCE (3.0 mL) + pivalic acid (0.5 mL) was used instead of AcOH.

|		3a	4aa
Cu(OAc)$_2$·H$_2$O		65%	0%
AgOAc		**3%**	**75%**
Ag$_2$O		25%	45%
Ag$_2$CO$_3$		19%	49%
Ag(CF$_3$CO$_2$)		14%	61%
(2.0 equiv)			

Scheme 1 *ortho* Alkenylation of benzonitrile.

Table 2 Reaction of benzonitrile (**1a**) or 2-naphthonitrile (**1b**) with activated alkenes **2b–i**[a]

Entry	Alkenes 2	Product 4	Yield[b] (%)
	1c-e	**4ca-ea**	
1	**1c**: R^2 = Br	**4ca**: R^2 = Br	51
2	**1d**: R^2 = Cl	**4da**: R^2 = Cl	50
3	**1e**: R^2 = OMe	**4ea**: R^2 = OMe	47
	1f-j	**4fa-ja**	
4	**1f**: R^2 = CO$_2$Me	**4fa**: R^2 = CO$_2$Me	53
5	**1g**: R^2 = I	**4ga**: R^2 = I	48
6	**1h**: R^2 = Br	**4ha**: R^2 = Br	45
7	**1i**: R^2 = Cl	**4ia**: R^2 = Cl	44
8	**1j**: R^2 = OMe	**4ja**: R^2 = OMe	42
	1k-l	**4ka-la**	
9	**1k**: R^2 = OMe	**4ka**: R^2 = OMe	42[c]
10	**1l**: R^2 = SMe	**4la**: R^2 = SMe	57
11	**1m**	**4ma**	38[c]
12	**1n**	**4nb**	29[c]
	1o		
13		**4oa**: R^2 = n-Bu	52[c]
14		**4og**: R^2 = Me	48[c]

[a] All the reactions were carried out using **1c–o** (75 mg), alkenes **2** (4.0 equiv.), [{RuCl$_2$(p-cymene)}$_2$] (5 mol%), AgSbF$_6$ (20 mol%) and AgOAc (2.0 equiv.) in dry acetic acid (3.0 mL) at 120 °C for 14 h. [b] Isolated yield. [c] The reaction time was 16 h.

benzonitriles (**1f–j**). 4-Methoxy (**1k**) and 4-SMe (**1l**) substituted benzonitriles provided the corresponding alkenylation products **4ka** and **4la** in 42% and 57% yields, respectively (entries 9 and 10). The alkenylation reaction was also examined with disubstituted benzonitriles (**1m–o**). 2,3-Dimethoxy (**1m**) and 3,4-dimethoxy (**1n**) benzonitriles reacted with **2a** or **2b**, affording *ortho* alkenylated benzonitriles **4ma** and **4nb** in moderate 38% and 29% yields, respectively (entries 11 and 12). In the substrate **1n**, the C–H bond activation takes place at the less hindered *ortho* C6–H bond. In contrast, a sterically hindered *ortho* C–H bond of piperonylonitrile (**1o**) reacted with **2a** or **2g** providing products **4oa** and **4og** in 52% and 48% yields, respectively (entries 13 and 14). The present result clearly reveals that a strong electron donating OMe group as the substituent on the benzonitrile decreases the yield of the product, and SMe, halogens and electron withdrawing substituents on the benzonitrile moderately increases the yield. In unsubstituted benzonitrile and 2-naphthonitrile substrates, good yields were observed.

The alkenylation reaction was also successfully extended with heteroaromatic nitriles (Scheme 2). Treatment of 2-nitrile
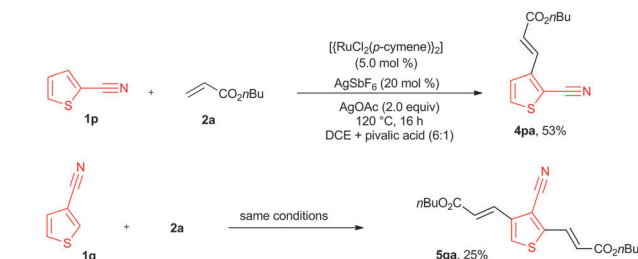
Scheme 2 Alkenylation of 2-cyano and 3-cyanothiophenes.

thiophene (**1p**) with *n*-butyl acrylate (**2a**) in the presence of [{RuCl$_2$(p-cymene)}$_2$] (5 mol%), AgSbF$_6$ (20 mol%) and AgOAc (2.0 equiv.) at 120 °C for 16 h provided 2-alkenyl-3-nitrile thiophene (**4pa**) in 53% yield. 3-Nitrile thiophene (**1q**) reacted with *n*-butyl acrylate (**2a**) affording bis alkenylated 3-nitrile thiophene **5qa** in 25% yield. Next, the same reaction was examined using Cu(OAc)$_2$·H$_2$O without AgOAc. Interestingly, in this reaction, bis alkenylated 3-nitrile thiophene **5qa** was observed in 57% yield (Scheme 3). Similarly, *n*-ethyl acrylate (**2b**), cyclohexyl acrylate (**2c**), phenyl acrylate (**2d**), benzyl acrylate (**2e**), 2-phenoxyethyl acrylate (**2f**) and methyl acrylate (**2g**) also reacted with **1q**, affording bis alkenylated 3-nitrile thiophenes **5qb–qg** in 65%, 48%, 49%, 47%, 45% and 69% yields, respectively (Scheme 3).

A substituted *ortho* alkenyl aromatic nitrile is a versatile synthetic intermediate which can be used for synthesizing various useful organic molecules.[7,8] *ortho* Alkenyl benzonitrile **4ab** underwent an intramolecular cyclization in the presence of AD-mix-β, yielding a chiral phthalide **6** in 93% yield in 99 ee% (Scheme 4).[13] By using AD-mix-α, the reverse chiral phthalide derivative can be prepared in a highly enantioselective manner.[13] Further,
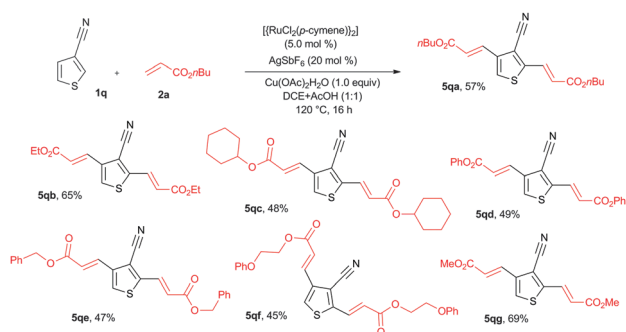
Scheme 3 bis Alkenylation of 3-cyanothiophene.
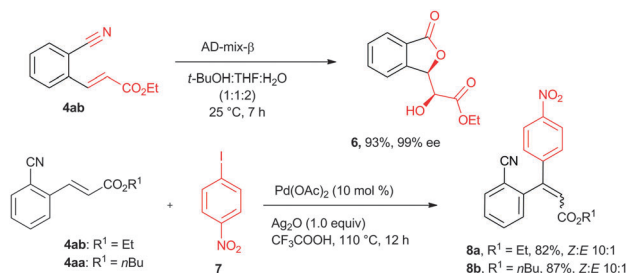
Scheme 4 Transformation of *ortho* alkenyl benzonitriles **4**.
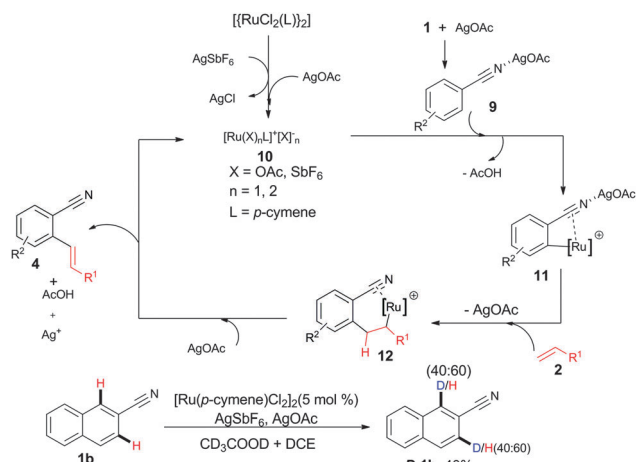
Scheme 5 Proposed mechanism.

by employing nitrile as a directing group, arylation was performed at the alkene C–H bond of **4ab** and **4aa** with 4-iodo nitrobenzene (**7**) in the presence of Pd(OAc)$_2$ and Ag$_2$O in CF$_3$COOH at 110 °C for 12 h, giving trisubstituted alkenes **8a** and **8b** in 82% and 87% yields in a 10 : 1 $Z:E$ ratio.

A possible reaction mechanism is proposed to account for the present alkenylation reaction in Scheme 5. It is strongly believed that first the lone electron pair of the nitrogen atom of benzonitrile **1** coordinates with the Lewis acid AgOAc, providing a linear benzonitrile silver complex **9**. A similar observation is strongly supported by DFT calculations.[14] Subsequently, AgSbF$_6$ likely removes the Cl$^-$ ligand from the [{RuCl$_2$(p-cymene)}$_2$] complex, providing a cationic ruthenium species **10**. Coordination of the C≡N π-bond of **9** into the ruthenium species **10** followed by *ortho*-metalation provides intermediate **11**. Coordinative insertion of activated alkene **2** into the Ru–carbon bond of intermediate **11** affords intermediate **12**. Subsequent β-hydride elimination of intermediate **12** in the presence of AgOAc gives product **4** and regenerates the active ruthenium species **10**. To support the hypothesis that *ortho* C–H bond cleavage of **9** is a reversible and rate determining process, the reaction of **1b** was carried out in the presence of CD$_3$COOD under similar reaction conditions. In this reaction, the product **D-1b** was observed in 40% yield, in which 40% of deuterium incorporation was observed at both C-1 as well as C-3 carbons of **1b**.

In conclusion, we have demonstrated a ruthenium-catalyzed C≡N π-bond assisted *ortho* alkenylation of substituted aromatic and heteroaromatic nitriles with activated alkenes providing *ortho* alkenylated aromatic and heteroaromatic nitriles in good to moderate yields in a highly regio- and stereoselective manner.

Notes and references

1 Selected references: (*a*) S. R. Neufeldt and M. S. Sanford, *Acc. Chem. Res.*, 2012, **45**, 936; (*b*) P. B. Arockiam, C. Bruneau and P. H. Dixneuf, *Chem. Rev.*, 2012, **112**, 5879; (*c*) K. M. Engle, T.-S. Mei, M. Wasa and J.-Q. Yu, *Acc. Chem. Res.*, 2012, **45**, 788; (*d*) L. Ackermann, *Chem. Rev.*,

2011, **111**, 1315; (*e*) T. Satoh and M. Miura, *Chem. – Eur. J.*, 2010, **16**, 11212; (*f*) G. Song, F. Wang and X. Li, *Chem. Soc. Rev.*, 2012, **41**, 3651.
2 Selected papers: (*a*) A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz and A. B. Holmes, *Chem. Rev.*, 2009, **109**, 897; (*b*) A. Kraft, A. C. Grimsdale and A. B. Holmes, *Angew. Chem., Int. Ed.*, 1998, **37**, 402; (*c*) D. A. Colby, R. G. Bergman and J. A. Ellman, *Chem. Rev.*, 2010, **110**, 624.
3 (*a*) J. L. Bras and J. Muzart, *Chem. Rev.*, 2011, **111**, 1170; (*b*) C. S. Yeung and V. M. Dong, *Chem. Rev.*, 2011, **111**, 1215; (*c*) L. Ackermann, *Acc. Chem. Res.*, 2014, **47**, 281.
4 (*a*) X. Huang, J. Huang, C. Du, X. Zhang, F. Song and J. You, *Angew. Chem., Int. Ed.*, 2013, **52**, 12970; (*b*) T. Ueyama, S. Mochida, T. Fukutani, K. Hirano, T. Satoh and M. Miura, *Org. Lett.*, 2011, **13**, 706; (*c*) K. Padala, S. Pimparkar, P. Madasamy and M. Jeganmohan, *Chem. Commun.*, 2012, **48**, 7140; (*d*) K. Padala and M. Jeganmohan, *Org. Lett.*, 2011, **13**, 6144; (*e*) K. Nobushige, K. Hirano, T. Satoh and M. Miura, *Org. Lett.*, 2014, **16**, 1188; (*f*) D. Zhao, C. Nimphius, M. Lindale and F. Glorius, *Org. Lett.*, 2013, **15**, 4504; (*g*) K. Padala and M. Jeganmohan, *Org. Lett.*, 2012, **14**, 1134; (*h*) W. Ma, R. Mei, G. Tenti and L. Ackermann, *Chem. – Eur. J.*, 2014, **20**, 15248; (*i*) W. Ma and L. Ackermann, *Chem. – Eur. J.*, 2013, **19**, 13925; (*j*) M. C. Reddy and M. Jeganmohan, *Eur. J. Org. Chem.*, 2013, 1150; (*k*) L. Ackermann, L. Wang, R. Wolfram and A. V. Lygin, *Org. Lett.*, 2012, **14**, 728; (*l*) G. Li, D. Leow, L. Wan and J.-Q. Yu, *Angew. Chem., Int. Ed.*, 2013, **52**, 1245.
5 (*a*) H.-L. Wang, R.-B. Hu, H. Zhang, A.-X. Zhou and S.-D. Yang, *Org. Lett.*, 2013, **15**, 5302; (*b*) K. Parthasarathy and C. Bolm, *Chem. – Eur. J.*, 2014, **20**, 4896; (*c*) Y. Yokoyama, Y. Unoh, K. Hirano, T. Satoh and M. Miura, *J. Org. Chem.*, 2014, **79**, 7649; (*d*) F. W. Patureau, T. Besset and F. Glorius, *Angew. Chem., Int. Ed.*, 2011, **50**, 1064; (*e*) K. M. Engle, D.-H. Wang and J.-Q. Yu, *Angew. Chem., Int. Ed.*, 2010, **49**, 6169; (*f*) C. Wang, H. Chen, Z. Wang, J. Chen and Y. Huang, *Angew. Chem., Int. Ed.*, 2012, **51**, 7242; (*g*) P. B. Arockiam, C. Fischmeister, C. Bruneau and P. H. Dixneuf, *Green Chem.*, 2011, **13**, 3075; (*h*) C. Wang and H. B. Ge, *Chem. – Eur. J.*, 2011, **17**, 14371; (*i*) B. Li, K. Devaraj, C. Darcel and P. H. Dixneuf, *Green Chem.*, 2012, **14**, 2706; (*j*) K. S. Singh and P. H. Dixneuf, *Organometallics*, 2012, **31**, 7320; (*k*) K. J. Stowers, K. C. Fortner and M. S. Sanford, *J. Am. Chem. Soc.*, 2011, **133**, 6541; (*l*) W. Dong, K. Parthasarathy, Y. Cheng, F. Pan and C. Bolm, *Chem. – Eur. J.*, 2014, **20**, 15732.
6 (*a*) P. Gandeepan and C.-H. Cheng, *Chem. – Asian J.*, 2015, **10**, 824; (*b*) P. Gandeepan and C.-H. Cheng, *J. Am. Chem. Soc.*, 2012, **134**, 5738.
7 (*a*) Z. Rappoport, *The Chemistry of the Cyano Group*, Interscience Publishers, London, 1970; (*b*) R. C. Larock, *Comprehensive Organic Transformations: A Guide to Functional Group Preparations*, VCH, NewYork, 1989; (*c*) P. Anbarasan, T. Schareina and M. Beller, *Chem. Soc. Rev.*, 2011, **40**, 5049.
8 (*a*) K. Friedrich and K. Wallenfels, in *The Chemistry of the Cyano Group*, ed. Z. Rappaport, Wiley, New York, 1970; (*b*) F. F. Fleming, L. Yao, P. C. Ravikumar, L. Funk and B. C. Shook, *J. Med. Chem.*, 2010, **53**, 7902.
9 (*a*) J. A. Davies and F. R. Hartley, *Chem. Rev.*, 1981, **81**, 79; (*b*) R. A. Michelin, M. Mozzon and R. Bertani, *Coord. Chem. Rev.*, 1996, **147**, 299; (*c*) M. F. Farona and N. J. Bremer, *J. Am. Chem. Soc.*, 1966, **88**, 3735.
10 (*a*) F. Kakiuchi, M. Sonoda, T. Tsujimoto, N. Chatani and S. Murai, *Chem. Lett.*, 1999, 1083; (*b*) W. Li, Z. Xu, P. Sun, X. Jiang and M. Fang, *Org. Lett.*, 2011, **13**, 1286; (*c*) J.-C. Wan, J.-M. Huang, Y.-H. Jhan and J.-C. Hsieh, *Org. Lett.*, 2013, **15**, 2742; (*d*) W. Li and P. Sun, *J. Org. Chem.*, 2012, **77**, 8362; (*e*) B. Du, X. Jiang and P. Sun, *J. Org. Chem.*, 2013, **78**, 2786.
11 (*a*) H.-X. Dai, G. Li, X.-G. Zhang, A. F. Stepan and J.-Q. Yu, *J. Am. Chem. Soc.*, 2013, **135**, 7567; (*b*) R.-Y. Tang, G. Li and J.-Q. Yu, *Nature*, 2014, **507**, 215; (*c*) M. Bera, A. Modak, T. Patra, A. Maji and D. Maiti, *Org. Lett.*, 2014, **16**, 5760.
12 M. C. Reddy and M. Jeganmohan, *Org. Lett.*, 2014, **16**, 4866.
13 R. S. Reddy, I. N. C. Kiran and A. Sudalai, *Org. Biomol. Chem.*, 2012, **10**, 3655.
14 T. Shoeib, H. E. Aribi, K. W. M. Siu and A. C. Hopkinson, *J. Phys. Chem. A*, 2001, **105**, 710.