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An N-heterocyclic carbene-catalyzed switchable reaction of 9-(trimethylsilyl)fluorene and aldehydes: chemoselective synthesis of dibenzofulvenes and fluorenyl alcohols†

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An N-heterocyclic carbene-catalyzed synthesis of dibenzofulvenes and fluorenyl alcohols was developed. In the presence of 10 mol% NHC (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) and 4 Å molecular sieves, 9-(trimethylsilyl)fluorene undergoes an olefination reaction with aldehydes to produce dibenzofulvenes in 43–99% yields. However, on reducing the NHC loading to 1 mol% and with the addition of water, 9-(trimethylsilyl)fluorene selectively undergoes nucleophilic addition with aldehydes to afford fluorenyl alcohols in 40–95% yields.

Introduction

Dibenzofulvenes and fluorenyl alcohols are important structural motifs existing widely in many natural products, pharmaceuticals, biologically active compounds[1] and optoelectronic materials.[2] Due to the remarkable importance of these fluorene frameworks, considerable effort has been exerted to develop efficient methods for the synthesis of these versatile scaffolds. Typically, Wittig olefination,[3] Peterson olefination,[4] and transition-metal catalyzed reactions[5] provide efficient approaches for the synthesis of dibenzofulvenes, while strong base promoted nucleophilic addition of fluorene anions and carbonyl compounds allows facile access to fluorenyl alcohols.[6] However, stoichiometric amounts of strong bases, such as *n*-BuLi, LDA and Grignard reagent, harsh reaction conditions and expensive transition-metal catalysts are usually required for these reactions. Therefore, the development of a more mild and convenient method for the synthesis of dibenzofulvenes and fluorenyl alcohols is highly significant. As an important type of organocatalyst, NHCs have been used in a wide range of reactions,[7] such as umpolung reactions,[8] cycloadditions,[9] redox reactions[10] and other transformations.[11] In particular, NHCs exhibit high reactivity toward activation of silylated nucleophiles.[12] As a result, the NHC-catalyzed cyanation reaction,[13] trifluoromethylation reaction,[14a] Mukaiyama aldol reaction[14b] and ring-opening reaction[15] have been developed by different groups. Our group has also independently developed NHC-catalyzed vinylogous Mukaiyama type additions, silyl-Reformatsky reaction, Peterson olefination and other reactions.[16] In line with our continuous interest in NHC catalysis, we envisaged that NHCs can be used as a nucleophilic catalyst to catalyze the reaction between 9-TMSF and carbonyl compounds to produce dibenzofulvenes and fluorenyl alcohols.

Results and discussion

With this idea in mind, we commenced our study using the commercially available 9-(trimethylsilyl)fluorene (9-TMSF) and *p*-chlorobenzaldehyde as the model substrates. In the presence of 10 mol% stable NHC **A** (1,3-bis(diisopropylphenyl)imidazole-2-ylidene, IPr),[17] the reaction proceeded in THF at room temperature to afford 18% yield of dibenzofulvene **3a** and 37% yield of fluorenyl alcohol **4a** (Table 1, entry 1). The following evaluation of the reaction media showed that the polar aprotic solvents acetonitrile, DMSO, and chlorinated solvents gave dibenzofulvene **3a** as the major product, whereas DMF, toluene and ethers afforded fluorenyl alcohol **4a** as the major product (Table 1, entries 2–8). Protic solvents, such as methanol and ethanol, were inefficient (Table 1, entries 9 and 10). Surprisingly, using DMSO as the solvent, NHCs derived from both imidazolium precursors and the saturated imidazolinium

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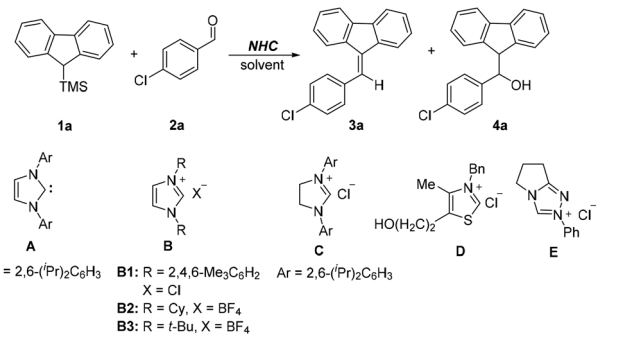
Table 1 Optimization of the reaction conditions[a]



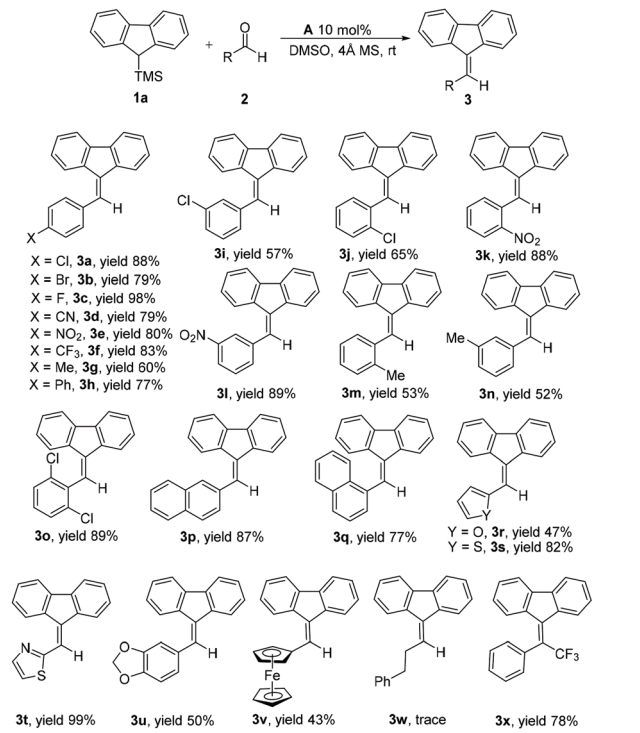
Entry	Conditions	*T* (°C)	Yield **3a** [b] (%)	Yield **4a** [b] (%)
1	THF, **A** (10 mol%), 12 h	rt	18	37
2	CH_3CN, **A** (10 mol%), 12 h	rt	57	16
3	DMSO, **A** (10 mol%), 12 h	rt	79	5
4	DCM, **A** (10 mol%), 12 h	rt	36	15
5	DCE, **A** (10 mol%), 12 h	rt	32	3
6	DMF, **A** (10 mol%), 12 h	rt	12	33
7	Toluene, **A** (10 mol%), 12 h	rt	8	35
8	1,4-Dioxane, **A** (10 mol%), 12 h	rt	6	37
9	MeOH, **A** (10 mol%), 24 h	rt	0	0
10	EtOH, **A** (10 mol%), 24 h	rt	0	0
11	DMSO, **B1** (12 mol%) *t*-BuOK (10 mol%), 12 h	rt	7	41
12	DMSO, **B2** (12 mol%) *t*-BuOK (10 mol%), 12 h	rt	5	40
13	DMSO, **B3** (12 mol%) *t*-BuOK (10 mol%), 12 h	rt	8	60
14	DMSO, **C** (12 mol%) *t*-BuOK (10 mol%), 12 h	rt	4	55
15	DMSO, **D** (12 mol%) *t*-BuOK (10 mol%), 24 h	rt	0	0
16	DMSO, **E** (12 mol%) *t*-BuOK (10 mol%), 24 h	rt	0	0
17	DMSO, **A** (10 mol%), 4 Å MS, 12 h	rt	88	3
18	DMSO, **A** (10 mol%), 4 Å MS, 5 h	60	89	0
19	DMSO, **A** (1 mol%), 12 h	rt	6	62
20	DMSO, **A** (0.1 mol%), 12 h	rt	0	43
21	DMSO, **A** (1 mol%), H_2O (100 μL), 12 h	10	3	74
22	DMSO, **A** (1 mol%), H_2O (500 μL), 12 h	10	0	0
23	DMSO, **A** (1 mol%), H_2O (100 μL), 4 h	60	16	67
24	DMSO, 48 h	rt	0	0

[a] **1a** (1.0 equiv.), **2a** (1.0 equiv.), NHC **A** (10 mol%) or NHC precursor (12 mol%), *t*-BuOK (10 mol%). [b] Isolated yield.

salt catalyzed the reaction to produce fluorenyl alcohol **4a** as the major product (Table 1, entries 11–14). NHCs derived from thiazolium and triazolium could not catalyze the reaction (Table 1, entries 15 and 16). The addition of 4 Å molecular sieves could improve the reaction yield of **3a** to 88% (Table 1, entry 17). Raising the reaction temperature led to a shorter reaction time (Table 1, entry 18). Interestingly, reducing the NHC loading to 1 mol% resulted in a switch of the chemoselectivity and fluorenyl alcohol **4a** was formed as the major product (Table 1, entry 19). On further reduction of the catalyst loading to 0.1 mol%, fluorenyl alcohol **4a** could still be obtained in 43% yield (Table 1, entry 20). Intriguingly, the addition of H_2O and lowering of the reaction temperature to 10 °C could improve the reaction yield of **4a** to 74% (Table 1, entry 21). However, further increasing the amount of H_2O led to a dramatic decrease of the yield (Table 1, entry 22). On conducting the reaction at an elevated temperature, the addition could be completed in a shorter time but the chemoselectivity was decreased obviously (Table 1, entry 23). Finally, the control experiment showed that in the absence of NHC, no desired products were formed (Table 1, entry 24).

Having evaluated the optimal reaction conditions, we then examined the substrate scope of the olefination reaction and the results are presented in Table 2. Aromatic aldehydes with electron-withdrawing, electron-neutral and electron-donating groups participated in the reaction well, producing the corresponding dibenzofulvenes in moderate to high yields (Table 2, **3a–3h**). It's noteworthy that aromatic aldehydes with electron-withdrawing substituents gave a higher yield than those bearing electron-neutral or electron-donating substituents (Table 2, **3a–3h**). In addition, substitutions at the *ortho*-, *meta*- and *para*-positions of the aromatic ring could be well tolerated for the reaction (Table 2, **3i–3o**). Both α- and β-naphthaldehydes were proved to be competent substrates for the olefination, affording **3p** and **3q** in 87% and 77% yields, respectively (Table 2, **3p** and **3q**). Heteroaromatic aldehydes, such as furfural, 2-thienal and 2-thiazol aldehyde, underwent the reaction to produce the corresponding products in moderate to excellent yields (Table 2, **3r–3t**). Heliotropine reacted with 9-TMSF to afford dibenzofulvene **3u** in 50% yield (Table 2, **3u**). Ferrocenealdehyde was proved to be a successful candidate for

Table 2 NHC-catalyzed synthesis of dibenzofulvenes[a]



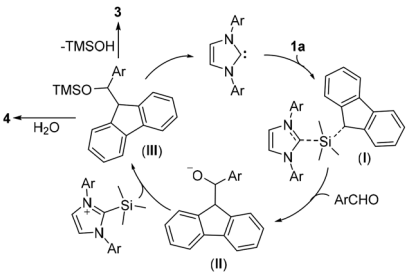
[a] Reaction conditions: **1a** (0.10 mmol), **2** (0.10 mmol), NHC **A** (1 mol%), DMSO (1.0 mL), 2–24 h, room temperature; isolated yield.

the reaction, providing **3v** in 43% yield (Table 2, **3v**). However, when aliphatic aldehyde was used for this olefination, only a trace amount of the desired product was detected and the starting materials were recovered in high yields (Table 2, **3w**). The active 2,2,2-trifluoroacetophenone could also undergo the olefination efficiently to give **3x** in 78% yield (Table 2, **3x**). It's noteworthy that fluorenyl alcohols were obtained as side products in 3–10% yields for these reactions.

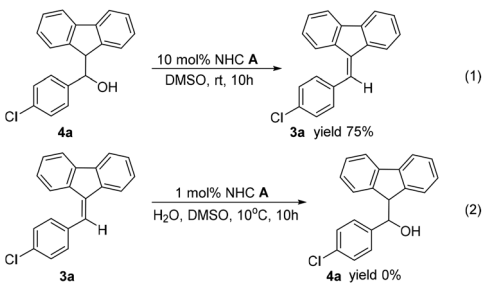
The generality of the synthesis of fluorenyl alcohols was next investigated. As shown in Table 3, aromatic aldehydes bearing electron-withdrawing substituents have higher yields than that bearing an electron-donating group (Table 3, **4a–4h**). Different positions of the substituents could be tolerated for the addition reaction (Table 3, **4i–4k**). Both naphthaldehyde and biphenyl aldehyde performed very well, producing the corresponding products in good yields (Table 3, **4l–4n**). Heliotropine underwent the addition to give **4o** in 40% yield (Table 3, **4o**). 2-Benzofurancarboxaldehyde coupled efficiently with 9-TMSF to furnish **4p** in an excellent yield (Table 3, **4p**). Electron-rich heteroaromatic aldehydes, such as furfural and 2-thienal, reacted with 9-TMSF to produce the desired products in moderate yields, while electron-deficient 2-thiazo aldehyde underwent the addition to give **4s** in a high yield (Table 3, **4q–4s**).

On conducting the reaction in undried DMSO, the product was delivered in a comparable yield (Table 3, **4a**). Similarly, the corresponding dibenzofulvenes were formed as side products for these additions in 4–21% yields.

Based on the pioneering studies on NHC-catalyzed additions of silylated nucleophiles,[13–16] a plausible mechanism was proposed for the reaction (Scheme 1). NHC acts as a Lewis base to attack the silicon atom of 9-TMSF to generate the reactive hypervalent silicon species **I**, which might trigger the subsequent nucleophilic addition with aldehyde to produce intermediate **II**. The following migration of TMS from NHC to **II** results in the formation of intermediate **III**. At this time, NHC can act as a carbon-centered Brønsted base[16g,18] to catalyze the elimination of **III** to produce dibenzofulvene, while the direct hydrolysis of **III** will give fluorenyl alcohol.



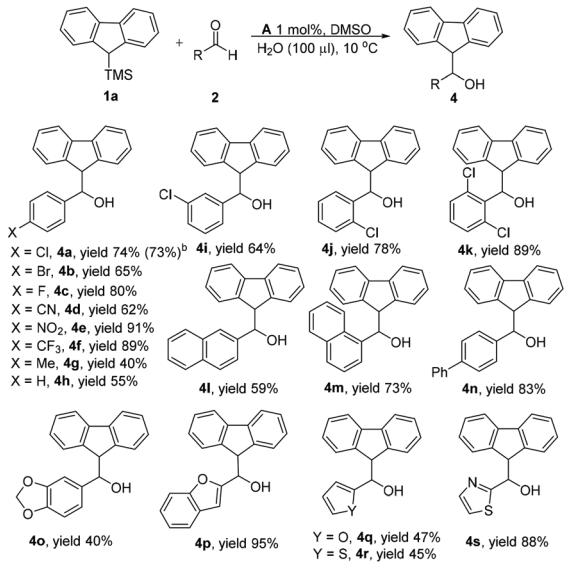
Scheme 1 Proposed mechanism.



Scheme 2 Control experiment.

The control experiment showed that 10 mol% NHC **A** can act as a Brønsted base to catalyze dehydration[19] of **4a** to afford **3a** in 75% yield. However, under the catalysis of 1 mol% NHC **A**, **3a** cannot react with H_2O to produce **4a**. We concluded that **3a** is thermodynamically more stable than **4a**, which should be responsible for this result (Scheme 2).

Table 3 NHC-catalyzed synthesis of fluorenyl alcohols[a]



[a] Reaction conditions: **1** (0.10 mmol), **2a** (0.10 mmol), NHC **A** (1 mol%), DMSO (1.0 mL), H_2O (100 μl), 2–24 h, 10 °C; isolated yield. [b] Using undried DMSO as the reaction solvent.

Conclusions

In summary, using the unique nucleophilicity and Brønsted characteristics of NHCs, we have developed an efficient method for the synthesis of dibenzofulvenes. We have also described an organocatalytic method for the preparation of fluorenyl alcohols *via* the activation of 9-TMSF by NHCs. The mild conditions, simple procedure and switchable chemoselectivity provide an efficient protocol for the synthesis of these important fluorene-derived compounds.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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References

1 (*a*) D. Dunn, G. Hostetler, M. Iqbal, V. R. Marcy, Y. G. Lin, B. Jones, L. D. Aimone, J. Gruner, M. A. Ator, E. R. Bacon and S. Chatterjee, *Bioorg. Med. Chem. Lett.*, 2012, **22**, 3751–3753; (*b*) H.-S. Hong, I. Maezawa, M. Budamagunta, S. Rana, A. Shi, R. Vassar, R. Liu, K. S. Lam, R. H. Cheng, D. H. Hua, J. C. Voss and L.-W. Jin, *Neurobiol. Aging*, 2010, **31**, 1690–1699; (*c*) G. Kumar, R. Agarwal and S. Swaminathan, *Chem. Commun.*, 2012, **48**, 2412–2414; (*d*) S. J. Gould and C. R. Melville, *Bioorg. Med. Chem. Lett.*, 1995, **5**, 51–54.

2 (*a*) S. Beaupré, P.-L. T. Boudreault and M. Leclerc, *Adv. Mater.*, 2010, **22**, E6–E27; (*b*) Y. Duan, H. Ma, H. Tian, J. Liu, X. Deng, Q. Peng and Y. Q. Dong, *Chem. – Asian J.*, 2019, **14**, 864–870; (*c*) X. Gu, J. Yao, G. Zhang, Y. Yan, C. Zhang, Q. Peng, Q. Liao, Y. Wu, Z. Xu, Y. Zhao, H. Fu and D. Zhang, *Adv. Funct. Mater.*, 2012, **22**, 4862–4872; (*d*) Z. Kahveci, M. J. Martínez-Tomé, R. Mallavia and C. R. Mateo, *Biomacromolecules*, 2013, **14**, 1990–1998; (*e*) A. Shimizu and Y. Tobe, *Angew. Chem., Int. Ed.*, 2011, **50**, 6906–6910; (*f*) Z. Zeng, Y. M. Sung, N. Bao, D. Tan, R. Lee, J. L. Zafra, B. S. Lee, M. Ishida, J. Ding, J. T. López Navarrete, Y. Li, W. Zeng, D. Kim, K.-W. Huang, R. D. Webster, J. Casado and J. Wu, *J. Am. Chem. Soc.*, 2012, **134**, 14513–14525.

3 (*a*) M. Banerjee, S. J. Emond, S. V. Lindeman and R. Rathore, *J. Org. Chem.*, 2007, **72**, 8054–8061; (*b*) S. Schraff, Y. Sun and F. Pammer, *Macromolecules*, 2018, **51**, 5323–5335; (*c*) H. Shao, X. Chen, Z. Wang and P. Lu, *J. Lumin.*, 2007, **127**, 349–354; (*d*) R. Yi, J. Chen, X. Wang, Z. Liang and X. Xu, *Eur. J. Org. Chem.*, 2018, 1347–1351.

4 (*a*) N. S. Mills, C. Tirla, M. A. Benish, A. J. Rakowitz, L. M. Bebell, C. M. M. Hurd and A. L. M. Bria, *J. Org., Chem.*, 2005, **70**, 10709–10716; (*b*) Y. Ooyama, R. Sagisaka, T. Enoki, N. Tsunoji and J. Ohshita, *New J. Chem.*, 2018, **42**, 13339–13350.

5 (*a*) N. Chernyak and V. Gevorgyan, *J. Am. Chem. Soc.*, 2008, **130**, 5636–5637; (*b*) N. Chernyak and V. Gevorgyan, *Adv. Synth. Catal.*, 2009, **351**, 1101–1114; (*c*) R. C. Larock and Q. Tian, *J. Org. Chem.*, 2001, **66**, 7372–7379; (*d*) M. A. Shaikh, S. G. Agalave, A. S. Ubale and B. Gnanaprakasam, *J. Org., Chem.*, 2020, **85**, 2277–2290; (*e*) Q. Tian and R. C. Larock, *Org. Lett.*, 2000, **2**, 3329–3332; (*f*) J. Zhao, N. Asao, Y. Yamamoto and T. Jin, *J. Am. Chem. Soc.*, 2014, **136**, 9540–9543; (*g*) D. Zhu, Y. Wu, B. Wu, B. Luo, A. Ganesan, F.-H. Wu, R. Pi, P. Huang and S. Wen, *Org. Lett.*, 2014, **16**, 2350–2353.

6 (*a*) R. D. Crocker, B. Zhang, D. P. Pace, W. W. H. Wong and T. V. Nguyen, *Chem. Commun.*, 2019, **55**, 11591–11594; (*b*) A. G. Giuglio-Tonolo, T. Terme and P. Vanelle, *Molecules*, 2016, **21**, 1408.

7 (*a*) A. T. Biju, N. Kuhl and F. Glorius, *Acc. Chem. Res.*, 2011, **44**, 1182–1195; (*b*) X.-Y. Chen, Z.-H. Gao and S. Ye, *Acc. Chem. Res.*, 2020, **53**, 690–702; (*c*) D. Enders, O. Niemeier and A. Henseler, *Chem. Rev.*, 2007, **107**, 5606–5655; (*d*) D. M. Flanigan, F. Romanov-Michailidis, N. A. White and T. Rovis, *Chem. Rev.*, 2015, **115**, 9307–9387; (*e*) M. N. Hopkinson, C. Richter, M. Schedler and F. Glorius, *Nature*, 2014, **510**, 485–496; (*f*) Q. Liu and X.-Y. Chen, *Org. Chem. Front.*, 2020, **7**, 2082–2087; (*g*) M. Melaimi, R. Jazzar, M. Soleilhavoup and G. Bertrand, *Angew. Chem., Int. Ed.*, 2017, **56**, 10046–10068.

8 (*a*) L. Dai and S. Ye, *ACS Catal.*, 2020, **10**, 994–998; (*b*) D. A. DiRocco and T. Rovis, *Angew. Chem., Int. Ed.*, 2012, **51**, 5904–5906; (*c*) K. Hirano, A. T. Biju, I. Piel and F. Glorius, *J. Am. Chem. Soc.*, 2009, **131**, 14190–14191; (*d*) M.-Q. Jia and S.-L. You, *ACS Catal.*, 2013, **3**, 622–624; (*e*) S. M. Langdon, M. M. D. Wilde, K. Thai and M. Gravel, *J. Am. Chem. Soc.*, 2014, **136**, 7539–7542; (*f*) Q. Liu, S. Perreault and T. Rovis, *J. Am. Chem. Soc.*, 2008, **130**, 14066–14067; (*g*) A. Patra, S. Mukherjee, T. K. Das, S. Jain, R. G. Gonnade and A. T. Biju, *Angew. Chem., Int. Ed.*, 2017, **56**, 2730–2734; (*h*) L.-H. Sun, Z.-Q. Liang, W.-Q. Jia and S. Ye, *Angew. Chem., Int. Ed.*, 2013, **52**, 5803–5806; (*i*) J. Zhang, C. Xing, B. Tiwari and Y. R. Chi, *J. Am. Chem. Soc.*, 2013, **135**, 8113–8116.

9 (*a*) X.-L. Huang, L. He, P.-L. Shao and S. Ye, *Angew. Chem., Int. Ed.*, 2009, **48**, 192–195; (*b*) T.-Y. Jian, X.-Y. Chen, L.-H. Sun and S. Ye, *Org. Biomol. Chem.*, 2013, **11**, 158–163; (*c*) T.-Y. Jian, L. He, C. Tang and S. Ye, *Angew. Chem., Int. Ed.*, 2011, **50**, 9104–9107; (*d*) P.-L. Shao, X.-Y. Chen and S. Ye, *Angew. Chem., Int. Ed.*, 2010, **49**, 8412–8416; (*e*) L. Shen, W. Jia and S. Ye, *Chin. J. Chem.*, 2014, **32**, 814–818; (*f*) Y.-R. Zhang, L. He, X. Wu, P.-L. Shao and S. Ye, *Org. Lett.*, 2008, **10**, 277–280.

10 (*a*) C. Burstein and F. Glorius, *Angew. Chem., Int. Ed.*, 2004, **43**, 6205–6208; (*b*) L. Candish, A. Levens and D. W. Lupton, *Chem. Sci.*, 2015, **6**, 2366–2370; (*c*) K.-Q. Chen, Z.-H. Gao and S. Ye, *Org. Chem. Front.*, 2019, **6**, 405–409; (*d*) L. Dai and S. Ye, *Org. Lett.*, 2020, **22**, 986–990; (*e*) J. Izquierdo, A. Orue and K. A. Scheidt, *J. Am. Chem. Soc.*, 2013, **135**, 10634–10637; (*f*) H. Lv, W.-Q. Jia, L.-H. Sun and S. Ye, *Angew. Chem., Int. Ed.*, 2013, **52**, 8607–8610; (*g*) J. Mo, X. Chen and Y. R. Chi, *J. Am. Chem. Soc.*, 2012, **134**, 8810–8813; (*h*) S. S. Sohn, E. L. Rosen and J. W. Bode, *J. Am. Chem. Soc.*, 2004, **126**, 14370–14371; (*i*) T. Zhu, C. Mou, B. Li, M. Smetankova, B.-A. Song and Y. R. Chi, *J. Am. Chem. Soc.*, 2015, **137**, 5658–5661.

11 (*a*) S. Bae, C. Zhang, R. M. Gillard and D. W. Lupton, *Angew. Chem., Int. Ed.*, 2019, **58**, 13370–13374; (*b*) J. Chen, P. Yuan, L. Wang and Y. Huang, *J. Am. Chem. Soc.*, 2017,

139, 7045–7051; (*c*) K.-Q. Chen, Z.-H. Gao and S. Ye, *Angew. Chem., Int. Ed.*, 2019, **58**, 1183–1187; (*d*) Y. Zhang, F. Xin, Z.-N. Feng, G.-F. Du, C.-Z. Gu and L. He, *Chin. J. Org. Chem.*, 2020, **40**, 1608–1617; (*e*) L. Dai, Z.-H. Xia, Y.-Y. Gao, Z.-H. Gao and S. Ye, *Angew. Chem., Int. Ed.*, 2019, **58**, 18124–18130; (*f*) E. S. Devi, T. Pavithra, A. Tamilselvi, S. Nagarajan, V. Sridharan and C. U. Maheswari, *Org. Lett.*, 2020, **22**, 3576–3580; (*g*) Z. Huang, X. Huang, B. Li, C. Mou, S. Yang, B.-A. Song and Y. R. Chi, *J. Am. Chem. Soc.*, 2016, **138**, 7524–7527; (*h*) K. Satyam, B. Harish, J. B. Nanubolu and S. Suresh, *Chem. Commun.*, 2020, **56**, 2803–2806; (*i*) X. Wu, L. Hao, Y. Zhang, M. Rakesh, R. N. Reddi, S. Yang, B.-A. Song and Y. R. Chi, *Angew. Chem., Int. Ed.*, 2017, **56**, 4201–4205.

12 (*a*) M. J. Fuchter, *Chem. – Eur. J.*, 2010, **16**, 12286–12294; (*b*) L. He, H. Guo, Y. Wang, G.-F. Du and B. Dai, *Tetrahedron Lett.*, 2015, **56**, 972–980.

13 For NHC-catalysed cyanation reactions, see: (*a*) Y. Fukuda, Y. Maeda, S. Ishii, K. Kondo and T. Aoyama, *Synthesis*, 2006, 589–590; (*b*) J. J. Song, F. Gallou, J. T. Reeves, Z. Tan, N. K. Yee and C. H. Senanayake, *J. Org. Chem.*, 2006, **71**, 1273–1276; (*c*) Y. Suzuki, M. D. A. Bakar, K. Muramatsu and M. Sato, *Tetrahedron*, 2006, **62**, 4227–4231; (*d*) J. Wu, X. Sun, S. Ye and W. Sun, *Tetrahedron Lett.*, 2006, **47**, 4813–4816; (*e*) Y. Suzuki, K. Muramatsu, K. Yamauchi, Y. Morie and M. Sato, *Tetrahedron*, 2006, **62**, 302–310; (*f*) Y. Fukuda, K. Kondo and T. Aoyama, *Synthesis*, 2006, 2649–2652; (*g*) Y. Fukuda, Y. Maeda, K. Kondo and T. Aoyama, *Synthesis*, 2006, 1937–1939.

14 (*a*) J. J. Song, Z. Tan, J. T. Reeves, F. Gallou, N. K. Yee and C. H. Senanayake, *Org. Lett.*, 2005, **7**, 2193–2196; (*b*) J. J. Song, Z. Tan, J. T. Reeves, N. K. Yee and C. H. Senanayake, *Org. Lett.*, 2007, **9**, 1013–1016.

15 (*a*) J. Wu, X. Sun and H.-G. Xia, *Eur. J. Org. Chem.*, 2005, 4769–4772; (*b*) J. Wu, X. Sun, S. Ye and W. Sun, *Tetrahedron Lett.*, 2006, **47**, 4813–4816; (*c*) X. Sun, S. Ye and J. Wu, *Eur. J. Org. Chem.*, 2006, 4787–4790; (*d*) Y.-K. Liu, R. Li, L. Yue, B.-J. Li, Y.-C. Chen, Y. Wu and L.-S. Ding, *Org. Lett.*, 2006, **8**, 1521–1524.

16 (*a*) Y. Wang, F. Xing, M. Xue, G.-F. Du, X.-H. Guo, K.-W. Huang and B. Dai, *Synthesis*, 2016, **48**, 79–84; (*b*) Y. Wang, G.-F. Du, F. Xing, K.-W. Huang, B. Dai and L. He, *Asian J. Org. Chem.*, 2015, **4**, 1362–1365; (*c*) Y. Wang, F. Xing, C.-Z. Gu, W.-J. Li, L. He, B. Dai and G.-F. Du, *Tetrahedron*, 2017, **73**, 4501–4507; (*d*) Y. Wang, G.-F. Du, C.-Z. Gu, F. Xing, B. Dai and L. He, *Tetrahedron*, 2016, **72**, 472–478; (*e*) Z.-S. Cong, Y.-G. Li, G.-F. Du, C.-Z. Gu, B. Dai and L. He, *Chem. Commun.*, 2017, **53**, 13129–13132; (*f*) L. He, H. Guo, Y.-Z. Li, G.-F. Du and B. Dai, *Chem. Commun.*, 2014, **50**, 3719–3721; (*g*) F. Xing, Z.-N. Feng, Y. Wang, G.-F. Du, C.-Z. Gu, B. Dai and L. He, *Adv. Synth. Catal.*, 2018, **360**, 1704–1710; (*h*) Y. Zhang, F. Xing, Z.-N. Feng, G.-F. Du, C.-Z. Gu and L. He, *Chin. J. Org. Chem.*, 2020, **40**, 1608–1617.

17 (*a*) A. J. Arduengo, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshall and M. Unverzagt, *Tetrahedron*, 1999, **55**, 14523–14534.

18 J. Chen and Y. Huang, *Nat. Commun.*, 2014, **5**, 3437.

19 (*a*) P. K. Hota, S. Maji, J. Ahmed, N. M. Rajendran and S. K. Mandal, *Chem. Commun.*, 2020, **56**, 575–578; (*b*) S. Marrot, F. Bonnette, T. Kato, L. Saint-Jalmes, E. Fleury and A. Baceiredo, *J. Organomet. Chem.*, 2008, **693**, 1729–1732.