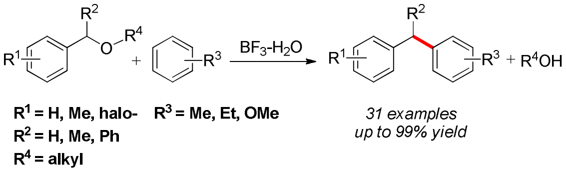
Green Chemistry

This article can be cited before page numbers have been issued, to do this please use: Y. Li, Y. Xiong, X. li, X. Ling, R. Huang, X. Zhang and J. Yang, *Green Chem.*, 2014, DOI: 10.1039/C4GC00005F.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/greenchem

View Article Online
DOI: 10.1039/C4GC00005F



An efficient *in situ* generated BF_3-H_2O-promoted benzylation of arenes gives a series of structurally diverse diarylmethanes (yields up to 99%).

View Article Online
DOI: 10.1039/C4GC00005F

Green Chemistry RSCPublishing

COMMUNICATION

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Benzylation of arenes with benzyl ethers promoted by *in situ* prepared superacid BF_3-H_2O

Yu Li,[a] Yan Xiong,[a,*] Xueming Li,[a,*] Xuege Ling,[a] Ruofeng Huang,[a] Xiaohui Zhang[a] and Jianchun Yang [b]

An efficient and environmentally friendly benzylation of arenes with benzyl ethers as benzyl donors using BF_3-Et_2O to generate *in situ* the superacid BF_3-H_2O as an efficient promotor has been described. A wide variety of functional groups have been investigated and found to be compatible to give the desired diarylmethanes in yields of up to 99%. The crucial role of moisture content in this transformation has been demonstrated by detailed investigations.

Diarylmethanes are key architectures in molecules of biological interest[1] as well as building blocks in supramolecular structures such as calixarene, cryptophane and pillar[n]arene (Figure 1).[2] Thus, considerable research attention has been drawn to the preparation of diarylmethanes, which mainly includes reductions of diarylketones or diarylcarbinols,[3] transition-metal-catalyzed coupling reactions,[4-10] and Friedel-Crafts reactions.[11-18] Transition-metal-catalyzed cross-coupling reactions have been intensively developed for the preparation of a variety of diarylmethanes over the past decades, in which palladium,[5] zinc,[6] copper,[7] nickel,[8] scandium[9] and iron[10] are involved. The Friedel-Crafts reaction of benzyl halides has also been considered to be one of the most powerful methods to afford diarylmethanes. In addition to benzyl halides, various reagents such as alcohols, [12] ethers, [13] styrenes[14] and benzylic acetates[15] have been recently introduced in Friedel-Crafts benzylation to meet the requirement of green chemistry. Compared to benzyl alcohols and esters, benzyl ethers are relatively stable organic compounds. Due to their commercial availability, recent research efforts have focused on the activation of benzyl ether C-O bonds to construct C-C bonds.[16-19] Several examples of synthesis of diarylmethanes starting from benzyl ethers catalyzed by metal catalyst such as Ir/Sn,[13a] $Hf(OTf)_4$,[13b] $FeCl_3$,[17] $Sc(OTf)_3$[18] and $HfCl_4/HfO_2$[19] have been reported. The development of metal-free benzylation of arenes using benzyl alkyl ethers as benzylating agents is still a synthetic challenge to prepare functionalized diarylmethanes *via* an environmentally sound technology.

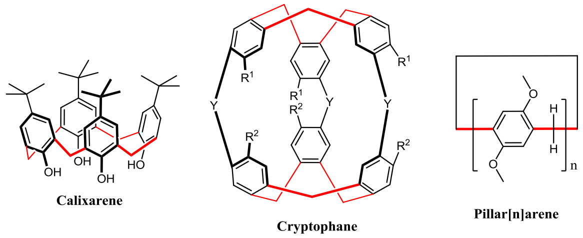


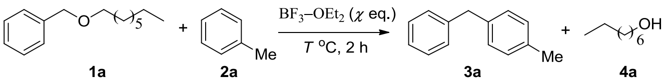
Figure 1. Examples of diarylmethanes in supramolecules.

BF_3 is a commonly used Lewis acid and has shown strong interaction with numerous ligands due to the boron atom acting as an acceptor to form a large number of coordination compounds containing carbon, nitrogen, oxygen, fluorine, phosphorus and sulfur.[20] For instance, BF_3-OEt_2 is an adduct of BF_3 and Et_2O through a donor-acceptor bonding.[21] Various synthetic procedures such as alkylation,[22a-b] cyclization,[22c] rearrangement[22d] and coupling reactions[22e] employing BF_3-OEt_2 have been reported. The superacid boron trifluoride monohydrate (BF_3-H_2O) formed by mixing BF_3 and water with equal amount has been used as a highly effective acid catalyst for several reactions.[23] Compared to Et_2O, the interaction of H_2O with BF_3 is relatively stonger, and the ligand exchange and rearrangement between BF_3-OEt_2 and water has been observed.[24] We describe herein an efficient benzylation of arenes with benzyl ethers promoted by the superacid BF_3-H_2O, which is generated *in situ* from BF_3-OEt_2.[24]

Our initial investigation concentrated on the study of the effect of the loading of BF_3-OEt_2 and temperature in the benzylation of benzyl *n*-octyl ether **1a** with undistilled toluene under open-flask conditions. In the presence of a catalytic amount (20 mol%) of BF_3-OEt_2, the desired monobenzylated product **3a** was obtained in

25% yield with regioselectivity of 51:39:10 (*o*- :*p*- :*m*-) under reflux (Table 1, entry 1). Then, different amounts of BF_3-OEt_2 were screened (entries 2-6), and the results showed that increasing the amount of BF_3-OEt_2 was beneficial for the reaction. A slight increase of the loading of BF_3-OEt_2 from 0.2 equiv. to 0.5 equiv. allowed the synthesis of **3a** in 81% yield with the remaining starting material recovered in 15% yield (entry 2). Further increase of the amount of BF_3-OEt_2 gave better results and therefore, 1.2 equiv. was chosen as the best conditions in the following investigations. The influence of different temperatures on the reaction outcome was then studied and similar levels of yield were observed for temperatures ranging from 60 ℃ to 100 ℃ (entries 7-9). Nevertheless, only traces of product **3a** were detected when the reaction was conducted at 25 ^{o}C (entry 10). The optimal open-flask conditions were established as follows: benzylating agent (1.0 mmol) in refluxing undistilled toluene (2.0 mL) using 1.2 equivalents of BF_3-OEt_2. The reaction under N_2 atmosphere using anhydrous toluene was performed, and the desired product **3a** was obtained in a low yield of 24% with regioselectivity of 56:36:8 (entry 11). As a result, exclusion of moisture is detrimental to the reaction by preventing the formation of the superacid BF_3-H_2O.

Table 1. Optimization of reaction conditions[a]

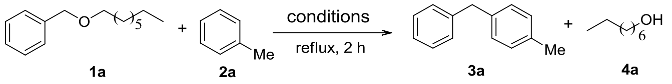


Entry	BF_3-OEt_2 (χ mmol)	Temperature (^{o}C)	Yield (%)[b], Ratio (*o*- : *p*- : *m*-)[c]
1	0.2	reflux [d]	25 (51:39:10)
2	0.5	reflux [d]	81 (50:42:8), 15[e]
3	0.8	reflux [d]	95 (51:41:8)
4	1.0	reflux [d]	97 (50:42:8)
5	1.2	reflux [d]	99 (50:41:9)
6	2.0	reflux [d]	99 (49:42:9)
7	1.2	60	77 (58:36:6)
8	1.2	80	97 (53:41:6)
9	1.2	100	98 (52:41:7)
10	1.2	25	trace
11[f]	1.2	reflux [d]	24 (56:36:8)

[a] Conditions: benzyl ether (**1a**, 1.0 mmol), undistilled toluene (**2a**, 2.0 mL), BF_3-OEt_2 (specified), temperature (specified), in air for 2 h. [b] Yields of isolated products after silica gel column chromatography. [c] Isomer ratios determined by ^{13}C NMR. [d] Oil bath at 120 ℃. [e] Recoverable yield of starting materials. [f] Conducted under N_2 atmosphere using anhydrous toluene.

A set of different boron species was then tested in the benzylation of toluene with **1a** under optimized reaction conditions (Table 2). HBF_4 promoted the reaction efficiently to give rise to the desired product **3a** in 94% yield with regioselectivity of 52:40:8 (entry 1), while no desired product was observed by using H_3BO_3 (entry 2). Unlike BF_3-OEt_2, conducting the reaction under N_2 atmosphere and using dry toluene as a reagent did not lower the reactivity of HBF_4 (Table 2, entry 3 vs Table 1, entry 11). The reaction of **1a** in the presence of BF_3-OEt_2 proceeded in excellent yields under open-flask conditions with anhydrous toluene or by using undistilled toluene under protective atmosphere (entries 4 and 5). In light of the results obtained in Table 1 (entry 11), traces of residual water from air or toluene are required to promote the reaction and therefore, this encouraged us to further study the influence of water on the reaction outcome. The use of 1.2 equivalent of water and 0.2 equivalent of BF_3-Et_2O under N_2 atmosphere using anhydrous toluene resulted in a significantly higher yield compared to dry conditions (Table 2, entry 6 vs Table 1, entry 11). The desired product **3a** was obtained in 93% yield with regioselectivity of 50:43:7 by the addition of 1.2 equivalents of the system BF_3-Et_2O/H_2O (1/1) (entry 7). Increasing the ratio of water led to lower yields (entries 8 and 9), which shows that excessive water is detrimental to the reaction's efficiency.

Table 2. Reaction of benzyl ether with toluene under different conditions[a]



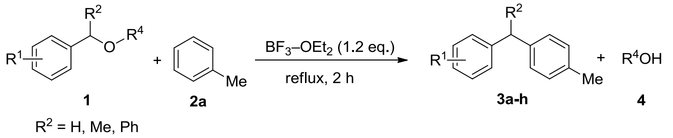
Entry	Boron Sources	H_2O	Atmosphere	Yield (%)[b], Ratio (*o*- : *p*- : *m*-)[c]
1	HBF_4 (1.2 eq.)	-	air	94 (52:40:8)
2[d]	H_3BO_3 (1.2 eq.)	-	air	0
3	HBF_4 (1.2 eq.)	-	N_2	95 (53:38:9)
4[d]	BF_3-OEt_2 (1.2 eq.)	-	air	89 (52:42:6)
5	BF_3-OEt_2 (1.2 eq.)	-	N_2	84 (51:41:8)
6[d]	BF_3-OEt_2 (1.2 eq.),	0.2 eq.	N_2	84 (51:41:8)
7[d]	BF_3-OEt_2 (1.2 eq.)	1.2 eq.	N_2	93 (50:43:7)
8[d]	BF_3-OEt_2 (1.2 eq.),	2.4 eq.	N_2	24 (49:41:10)
9[d]	BF_3-$2H_2O$ (1.2 eq.)	-	N_2	25 (50:41:9)

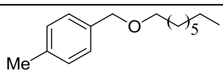
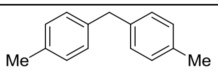
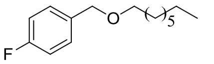
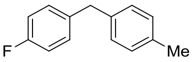
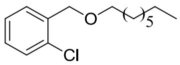
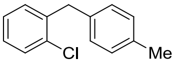
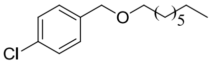
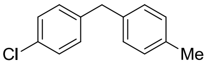
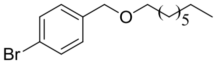
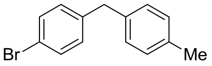
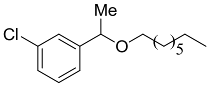
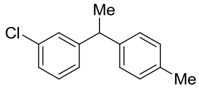
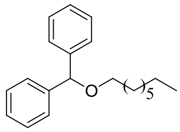
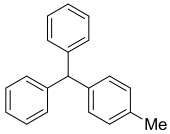
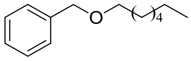
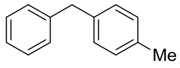
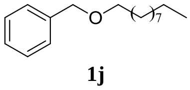
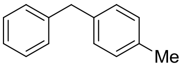
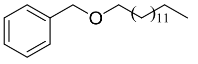
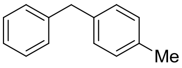
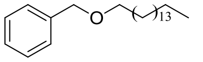
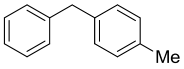
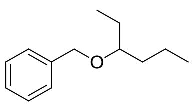
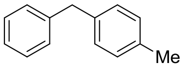
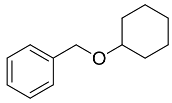
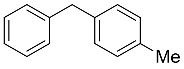
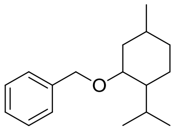
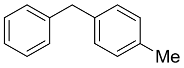
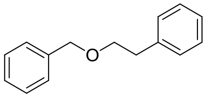
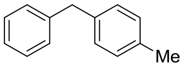
[a] Conditions: benzyl ether (**1a**, 1.0 mmol), undistilled toluene (**2a**, 2.0 mL), reflux in air for 2 h. [b] Yields of isolated products after silica gel column chromatography. [c] Isomer ratios determined by ^{13}C NMR. [d] The reaction was performed in anhydrous toluene.

Having explored the reaction conditions, our interest then focused on the influence of the benzyl ether substitution in the Friedel-Crafts reaction with undistilled toluene (Table 3). Using the optimal reaction conditions described above (Table 1, entry 5), the desired products **3a-h** were obtained in good-to-excellent yields. Friedel-Crafts reaction of diversely functionalized benzyl ethers proceeded smoothly to give rise to products **3b-f** in good to excellent yields regardless of the nature and the position of the substituents on the aromatic ring (entries 1-5). Secondary ethers gave also excellent yields and high *para* regioselectivities of 79% and 92%, respectively (entrie 6 and 7), while no reaction occurred when nitro, cyano or ester group were present on the benzene ring. The use of benzyl ethers derived from various alkyl or cycloalkyl alcohols as starting materials has also been studied. Ethers bearing linear and/or branched alkyl chains **1i-m** gave rise to the corresponding targets in good-to-excellent yields (entries 8-12). Cycloalkyl ether compounds **1o** and **1p** were amenable to Friedel-Crafts reactions by providing the desired products in 94% and 90%

yield respectively (entries 13 and 14). Benzyl phenethyl ether was a suitable substrate for this reaction and the desired product was obtained in 92% yield (entry 15). Interestingly, the release of alcohols from the reaction provides an efficient debenzylation strategy of benzyl ethers (entries 9-11). Like the model substrate (Table 1, entry 11), diminished yields for **1h**, **1j** and **1m** were obtained under dry conditions. With the addition of 1.2 equivalents of water the yields were increased to levels similar to that of open-flask conditions (entries 7 and 9). However, the yields dropped again when the amount of water increased to 2.4 eq. (entry 12), which further demonstrates that the amount of water is a strict requirement in this transformation. The corresponding remaining starting materials for **1h**, **1j** and **1m** after reactions have been recovered as well, and from the calculation of recoverable ratio, it has been deduced that very small amounts of by-products were produced in these reactions.

Table 3. Benzyl ether scope[a]

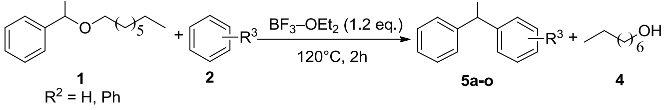


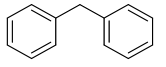
Entry	Benzyl ethers	Products	Yield (%)[b], Ratio (p- : o- : m-)[c]
1	 **1b**	 **3b**	78 (64 : 32 : 4)
2	 **1c**	 **3c**	96 (53 : 40 : 7)
3	 **1d**	 **3d**	88 (49 : 37 : 14)
4	 **1e**	 **3e**	94 (49 : 41 : 10)
5	 **1f**	 **3f**	97 (49 : 41 : 10)
6	 **1g**	 **3g**	98 (79 : 15 : 6)
7	 **1h**	 **3h**	96 (92 : 8 : 0) 75[d], 15[e] (90 : 10: 0) 91[f], 4[e] (91 : 9 : 0)
8	 **1i**	 **3a**	87 (52 : 41 : 7)
9	 **1j**	 **3a**	92, 50 : 42 : 8 (**4j**, 76)[g] 34[d], 59[e] (53 : 43 : 4) 87[f], 7[e] (51 :40 : 9)
10	 **1k**	 **3a**	83 (51 : 40 : 9) (**4k**, 96)[g]
11	 **1l**	 **3a**	89 (50 : 41 : 9) (**4l**, 96)[g]
12	 **1m**	 **3a**	91 (51 : 41 : 8) 20[d], 72[e] (52 : 41 : 7) 91[f], 4[e] (51 : 40 : 9) 25[h], 69[e] (53 : 38 : 9)
13	 **1o**	 **3a**	94 (53 : 39 : 8)
14	 **1p**	 **3a**	90 (54 : 37 : 9)
15	 **1q**	 **3a**	92 (55 : 38 : 7)

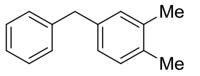
[a] Conditions: **1** (1.0 mmol), BF_3-OEt_2 (1.2 mmol), undistilled toluene (2.0 mL), reflux in air for 2 h. [b] Yields of isolated products after silica gel column chromatography are given. [c] Isomer ratios of p- : o- : m- determined by ^{13}C NMR. [d] Corresponding isolated yields under N_2 atmosphere using anhydrous arenes. [e] Yields of isolated remaining starting materials. [f] Corresponding isolated yields under N_2 atmosphere using anhydrous arenes with extra 1.2 equivalents of H_2O. [g] Isolated yields of the corresponding alcohol products. [h] Corresponding isolated yields under N_2 atmosphere using anhydrous arenes with extra 2.4 equivalents of H_2O.

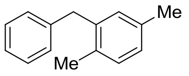
Primary and secondary benzyl ether were taken to further explore the scope of arenes. Various arenes were investigated and the results were summarized in Table 4. The reaction of **1a** with benzene produced **5a** in 62% yield. Mesitylene as well as xylenes were converted into the corresponding benzylation products in good to excellent yields (**5b-e** and **5j-m)**, while *p*-xylene (**5c** and **5l**) showed relatively lower reactivity than *o*-xylene and *m*-xylene due to its stronger steric hindrance. Ethylbenzene was also well tolerated as a substrate by providing **5f** and **5n** in good yields. The reaction of anisole with benzyl *n*-octyl ether gave rise to desired product in 35% yield with *ortho* regioselectivity of 99% (**5g**). An excellent *para*-selectivity was obtained by reacting anisole with secondary benzyl ether and the compound **5o** was produced in 97% yield. Polycyclic and hetero arenes such as naphthalene and thiophene were also suitable substrates for this reaction to afford the corresponding products with moderate yields (**5h** and **5i**). It is worth pointing out that all the reactions of arenes with secondary dibenzyl ether gave corresponding products with excellent regioselectivities (>99%) (**5j-5o**).

Table 4. Benzylation of different arenes[a]







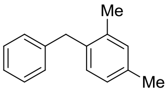


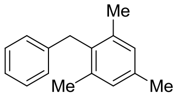
View Article Online
DOI: 10.1039/C4GC00005F

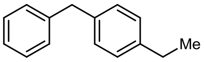
5a, 62%[b]

5b, 95%, *4-* : *3-* = 66 : 34

5c, 88%



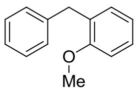


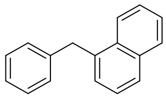


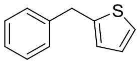
5d, 92%, *4-* : *5-* = 80 : 20

5e, 96%

5f, 81%, *p-* : *o-* : *m-* = 55 : 35 : 10



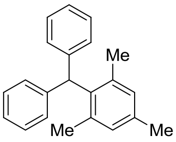


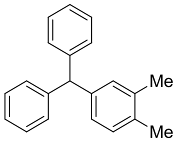


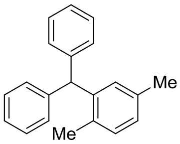
5h, 75%[c], *1-* : *2-* = 74 : 26
45%[d] (*1-* : *2-* = 76 : 24), 49%[e]
65%[f] (*1-* : *2-* = 75 : 25), 26%[e]
22%[g], 70%[e]
1- : *2-* = 75 : 25

5g, 35%, *o-* > 99%

5i, 50%,[b] *2-* : *3-* = 52 : 48



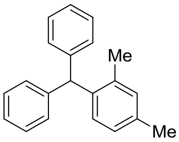


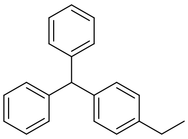


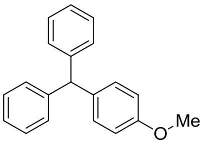
5j, 96%

5k, 92%, *4-* > 99%

5l, 62%,







5m, 86%, *4-* > 99%

5n, 69%, *p-* > 99%

5o, 97%, *p-* > 99%

---

[a] Conditions: **1** (1.0 mmol), BF_3-OEt_2 (1.2 mmol), arene (2.0 mL), 120 °C, in air for 2 h; yields of isolated products after silica gel column chromatography are given; isomer ratios of *p-* : *o-* : *m-* determined by ^{13}C NMR. [b] The reaction was carried out under reflux of the arene. [c] BF_3-OEt_2 (1.2 mmol), arene (4.0 mmol), $CHCl_3$ (2.0 mL). [d] Isolated yields under N_2 atmosphere using anhydrous arenes. [e] Yields of isolated remaining starting materials. [f] Isolated yields under N_2 atmosphere using anhydrous arenes with extra 1.2 equivalents of H_2O. [g] Isolated yields under N_2 atmosphere using anhydrous arenes with extra 2.4 equivalents of H_2O.

Conclusions

In summary, BF_3-H_2O produced *in-situ* from BF_3-OEt_2 and residual water was found to be an efficient acid to promote the reaction of arenes with different benzyl ethers in good-to-excellent yields. This environmentally friendly and highly efficient procedure shows wide functional group compatibilities to provide a practical synthetic method for the preparation of diarylmethanes with good regioselectivities especially for secondary benzyl ethers.

Acknowledgements

We are grateful for the financial support of the National Science Foundation of China (No. 21372265 and No. 61271059), the Scientific Research Fundings of the Scientific Research Foundation for the Returned Overseas Chinese Scholars, the State Education Ministry, the Natural Science Foundation Project of CQ CSTC (No. cstc2013jcyjA0217), and the Fundamental Research Funds for the Central Universities (No. CDJRC10220004, No. CDJZR11220005 and No. CQDXWL-2013-Z012).).

Notes and references

[a] College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400030, China. Email: xiong@cqu.edu.cn (Y. X.); xuemingli@cqu.edu.cn (X. L.)
[b] Key Laboratory for Optoelectronic Technology and Systems of Education Ministry of China, College of Optoelectronic Engineering, Chongqing University, Chongqing 400044, China.

† Electronic supplementary information (ESI) available: Experimental procedures, characterisation data. See DOI: 10.1039/c000000x/

1 (*a*) H. H. Sun, V. J. Paul and W. Fenical, *Phytochemistry*, 1983, **22**, 743; (*b*) M. G. Nordberg, K. Kolmodin, J. Aquist, S. F. Queener and A. Hallberg, *J. Med. Chem*., 2001, **44**, 2391.

2 (*a*) M. M. Conn and J. Rebek, Jr., *Chem. Rev*., 1997, **97**, 1647; (*b*) A. Jasat and J. C. Sherman, *Chem. Rev*., 1999, **99**, 931; (*c*) J. S. Kim and D. T. Quang, *Chem. Rev*., 2007, **107**, 3780; (*d*) T. Brotin and J.-P. Dutasta, *Chem. Rev*., 2009, **109**, 88; for our former work, see: (*e*) C. Y. Tao, X. M. Li, J. C. Yang and Y. Q. Shi, *Sensors and Actuators B*, 2011, **156**, 553; (*f*) Y. Q. Shi, X. M. Li, J. C. Yang, F Gao and C. Y. Tao, *J. Fluoresc*., 2011, **21**, 531.

3 (*a*) M. Mirza-Aghayan, R. Boukherroub, and M. Rahimifard, *Tetrahedron Lett*., 2009, **50**, 5930; (*b*) F. Zaccheria, N. Ravasio, M. Ercoli and P. Allegrini, *Tetrahedron Lett*., 2005, **46**, 7743.

4 For recent reviews on transition-metal catalyzed direct benzylation, see: (*a*) B. Liégault, J. L. Renaud and C. Bruneau, *Chem. Soc. Rev*., 2008, **37**, 290; (*b*) L. Ackermann, *Chem. Commun*., 2010, **46**, 4866.

5 (*a*) J.-Y. Yu and R. Kuwano, *Org. Lett*., 2008, **10**, 973; (*b*) G. A. Molander and M. D. Elia, *J. Org. Chem*., 2006, **71**, 9198; (*c*) M. McLaughlin, *Org. Lett*., 2005, **7**, 4875; (*d*) A, Bej, D. Srimani, and A. Sarkar, *Green Chem*., 2012, **14**, 661.

6 (*a*) A. Metzger, M. A. Schade and P. Knochel, *Org. Lett*., 2008, **10**, 1107; (*b*) C. Duplais, A. Krasovskiy, A. Wattenberg and B. H. Lipshutz, *Chem. Commun*., 2010, **46**, 562.

7 (*a*) W.Dohle, D. M. Lindsay and P. Knochel, *Org. Lett*., 2001, **3**, 2871; (*b*) C. C. Kofink and P. Knochel, *Org. Lett*., 2006, **8**, 4121.

8 M. A. Schade, A. Metzger, S. Hug and P. Knochel, *Chem. Commun*., 2008, 3046.

9 V. D. Sarcaab and K. K. Laali, *Green Chem*., 2006, **8**, 615.

10 R. B. Bedford, M. Huwea and M. C. Wilkinson, *Chem. Commun*., 2009, 600.

11 (*a*) R. M. Roberts and A. A. Khalaf, *Friedel-Crafts Alkylation Chemistry: a Century of Discovery*, ed. Marcel Dekker, New York, 1984; (*b*) G. A. Olah, *Friedel-Crafts and Related Reactions*, Interscience Publishers, New York, 1963; (*c*) G. A. Olah, *Friedel-Crafts Chemistry*, Wiley, New York, 1973.

12 (*a*) T. Tsuchimoto, K. Tobita, T. Hiyama and S. Fukuzawa, *J. Org. Chem*., 1997, **62**, 6997; (*b*) S. Podder, J. Choudhury and S. Roy, *J. Org. Chem*., 2007, **72**, 3129.

13 (*a*) S. Podder and S. Roy, *Tetrahedron*, 2007, **63**, 9146; (*b*) I. Shiina and M. Suzuki, *Tetrahedron Lett*., 2002, **43**, 6391; (*c*) A. Prades, R. Corberán, M. Poyatos, and E. Peris. *Chem.-Eur. J*. 2009, **15**, 4610.

14 (*a*) M.Rueping, B. J. Nachtsheim and T. Scheidt, *Org. Lett*., 2006, **8**, 3717; (*b*) J. Kischel, I. Jovel, K. Mertins, A. Zapf and M. Beller, *Org. Lett*., 2006, **8**, 19.

15 (*a*) K. Mertins, I. Lovel, J. Kischel, A. Zapf and M. Beller, *Adv. Synth. Catal*., 2006, **348**, 691; (*b*) K. Mertins, I. Iovel, J. Kischel, A. Zapf and M. Beller, *Angew. Chem. Int. Ed*., 2005, **44**, 238.

View Article Online
DOI: 10.1039/C4GC00005F

16 S. Murai, *Activation of Unreactive Bonds and Organic Synthesis*, Springer, Berlin, 1999.

17 B. Q. Wang, S. K. Xiang, Z. P. Sun, B. T. Guan, P. Hu, K. Q. Zhao and Z. J. Shi, *Tetrahedron Lett*., 2008, **49**, 4310.

18 T. Tsuchimoto, K. Tobita, T. Hiyama and S. Fukuzawa, *J. Org. Chem*., 1997, **62**, 6997.

19 C. Y. Zhang, X. Q. Gao, J. H. Zhang and X. J. Peng, *Chin. Chem. Lett*., 2009, **20**, 913.

20 H. S. Booth and D. R. Martin, *J. Am. Chem. Soc*., 1942, **64**, 2198.

21 A. W. Laubengayer and G. R. Finlay, *J. Am. Chem. Soc*., 1943, **65**, 884.

22 (*a*) G. Schäfer and J. W. Bode, *Angew. Chem. Int. Ed*., 2011, **123**, 10913; (*b*) X. F. Xu, Y. Xiong, X. G. Ling, X. M. Xie, J. Yuan, S. T. Zhang and Z. R. Song, *Chin. Chem. Lett*., 2014, **25**, 406; (*c*) E. O. Onyango, L. F. Fu and G. W. Gribble, *Org. Lett*., 2013, dx.doi.org/10.1021/ol403289y; (*d*) L. X. Shao, Y. P. Zhang, M. H. Qi and M. Shi, *Org. Lett*., 2007, **9**, 117; (*e*) L. Shi, Y. Q. Tu, M. Wang, F. M. Zhang, C. A. Fan, Y. M. Zhao and W. J. Xia, *J. Am. Chem. Soc*., 2005, **127**, 10836.

23 (*a*) G. K. S. Prakash, F. Paknia, T. Mathew, G. Mloston, J. P. Joschek and G. A. Olah, *Org. Lett*., 2011, **13**, 4128; (*b*) G. K. S. Prakash, T. Mathew, D. Hoole, P. M. Esteves, Q. Wang, G. Rasul and G. A. Olah, *J. Am. Chem. Soc*., 2004, **126**, 15770; (*c*) G. K. S. Prakash, C. Panja, A. Shakhmin, E. Shah, T. Mathew and G. A. Olah, *J. Org. Chem*., 2009, **74**, 8659; (*d*) H. Yu and C. Z. Li, *J. Org. Chem*., 2004, **69**, 142; (*e*) L. Liu, X. Wang and C. Z. Li, *Org. Lett*., 2003, **5**, 361.

24 (*a*) V .S. Tkach, D. S. Suslov, G. Myagmarsuren, O. V. Gubaydulina, M. V. Bykov and V. A. Umanets, *Catal. Commun*., 2009, **10**, 1813; (*b*) J. W. Huang and M. Shi, *Tetrahedron Lett*., 2003, **44**, 9343; (*c*) H. Yu, T. Wu and C. Z. Li, *J. Am. Chem. Soc*., 2002, **124**, 10302; (*d*) X. Q. Fang, K. Liu and C. Z. Li, *J. Am. Chem. Soc*., 2010, **132**, 2274.