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Deaminative coupling of benzylamines and arylboronic acids†

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A metal-free deaminative coupling of non-prefunctionalised benzylamines and arylboronic acids is reported. In this operationally simple reaction, a primary amine in benzylamine is converted into a good leaving group *in situ* using inexpensive and commercially available isoamyl nitrite as a nitrosating reagent. Lewis-acidic arylboronic acids are shown to replace mineral acids such as HCl or HBF_4 that are conventionally used in the preparation of aryl diazonium salts. This unlocked the formation of the corresponding diarylmethanes by forging a new C–C bond in good yields.

Introduction

Although primary amines are highly attractive handles for late-stage modification and downstream functionalisation due to their prevalence in biologically active molecules and industrially relevant chemicals,[1–5] their poor leaving group ability renders the cleavage of the C–N bond particularly challenging.[6–8] A direct use of ubiquitous primary amines as coupling partners has been underexploited in deaminative cross-coupling reactions despite the potential to streamline organic synthesis. Among the limited examples addressing this challenge, the cleavage of unactivated C–N single bonds in primary amines has been largely achieved by acid-assisted transition metal-catalysed oxidative addition.[7,8] Notably, the Tian group has developed Pd-catalysed deaminative couplings of non-prefunctionalised allylic amines with various nucleophiles such as boronic acids, boronates, sulfonate salts and phosphonium ylides (Fig. 1a).[9–15] The proposed mechanism is suggested to proceed through a palladium allyl intermediate in analogy to the Tsuji–Trost reaction.[9,16,17] An alternative, mechanistically distinct approach for the deaminative functionalization of primary amines relies on diazotisations. While such reactions using *aromatic* amines are commonly encountered in both academic and industrial settings, as highlighted by the plethora of reports employing aryldiazonium species for cross-coupling and other functionalisation reactions,[18–21] successful utilisation of *alkyl* amines in deaminative reactions usually relies on the presence of a neighbouring electron-withdrawing group to form the alkyl diazo compound instead of the notoriously unstable, high-energy alkyl diazonium species.[22–29] A notable exception is the deaminative functionalisation of electronically non-biased primary amines reported by the Lebel group (Fig. 1b).[30–33] The reaction was suggested to proceed *via* a transient diazonium intermediate, however the transformation was limited to the use of carboxylic acids or electron-poor phenols as highly acidic coupling partners to form and trap the high-energy diazonium species. Thus, the reaction was restricted to the formation of C–O bonds, while the formation of C–C bonds has so far remained elusive. The scarce literature precedent for the direct deaminative cross-coupling of primary amines, as well as their limitations, calls for the development of new, efficient approaches to harness the underexplored potential of amines as carbon-centered coupling partners.

To overcome the difficulty of breaking a strong C(sp^3)–N bond under mild conditions, existing indirect deaminative cross-coupling reactions of benzylamines with arylboronic acids require an additional prefunctionalisation step to transform the primary amine into a good leaving group and a transition metal to perform the desired reaction (Fig. 1c).[34–36] The Watson group has developed a nickel-catalysed deaminative cross-coupling of arylboronic acids with Katritzky's salts along with an analogous reaction using methylated quaternary amines. Rhee and coworkers have disclosed a conceptually related approach using *N*,*N*-ditosylbenzylamines under palladium catalysis. In all these reports, an additional step for the conversion of an amine into a better leaving group was necessary, thus limiting the step and atom economy of the reactions.

In this work, we present an interrupted diazotisation strategy for the direct coupling of benzylamines with arylboronic acids to forge a new carbon–carbon bond (Fig. 1d). The reaction is operationally simple, proceeds under mild reaction conditions in the absence of any catalyst and tolerates a wide range of functional groups.

Results and discussion

Although, in analogy to aromatic amines, there are numerous reports attempting to functionalise electronically non-biased

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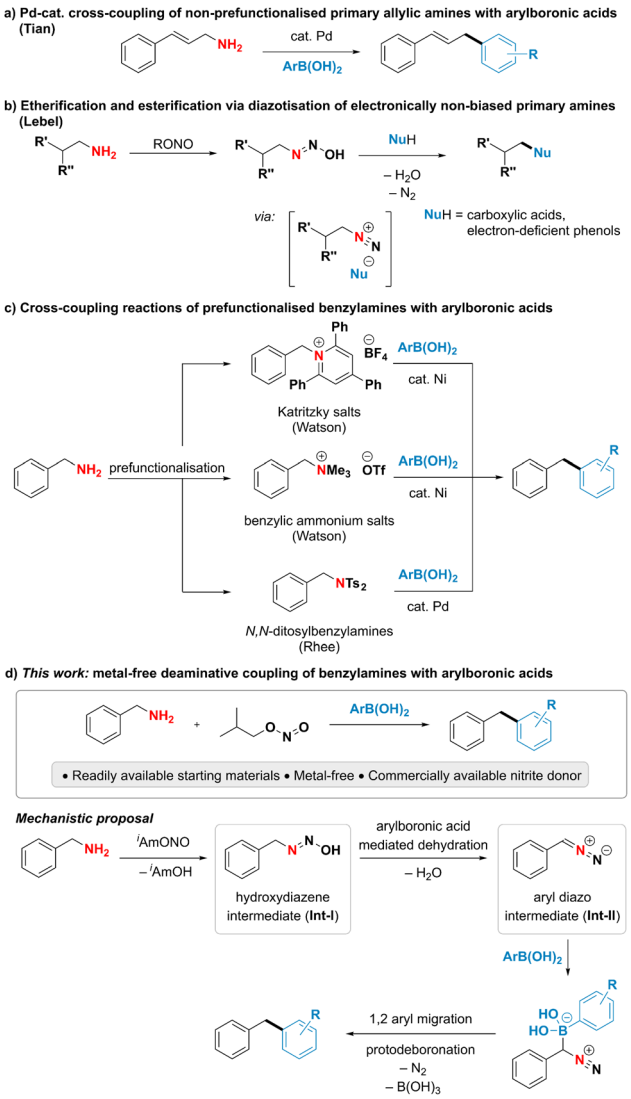


Fig. 1 Context of this work.

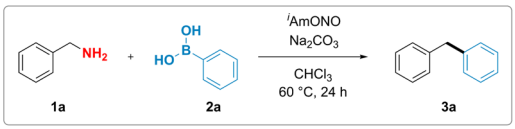
primary aliphatic amines by diazotisation, formation of highly reactive alkyldiazonium intermediates rendered those reactions inefficient and made them suffer from poor functional group tolerance and low yields.[37–42] We hypothesized that substitution of conventional mineral acids, such as HCl and HBF_4, used for the synthesis of aromatic diazonium salts, by a mild organic Lewis acid might suppress the unproductive formation of the high-energy alkyl diazonium species and thus unlock a divergent reaction outcome (Fig. 1d). More specifically, we proposed that benzylamine could react with the nitrite donor, producing a hydroxy diazene intermediate (**Int-I**). Arylboronic acid-facilitated dehydration of this intermediate would form the corresponding semi-stabilised diazo compound (**Int-II**).[43] This intermediate could then subsequently react with arylboronic acid as described by Barluenga and coworkers[44] and furnish the desired diarylmethane along with dinitrogen and boric acid as benign stoichiometric byproducts.

To test this hypothesis, benzylamine (**1a**) was reacted with commercially available isoamyl nitrite and phenylboronic acid (**2a**). We observed that the formation of the desired diphenylmethane product **3a** occurred upon mixing stoichiometric amounts of the three reagents, thereby validating our hypothesis experimentally.

With these initial reaction conditions in hand, the deaminative coupling reaction between benzylamine and phenylboronic acid was further optimized by evaluating various reaction parameters. The highest yield for the formation of the desired diphenylmethane product was observed upon incorporation of one equivalent of sodium carbonate as a base relative to phenylboronic acid. Control experiments revealed that deaminative coupling is contingent upon addition of the organic nitrite (Table 1, entry 2). Using phenylboronic pinacol ester instead of phenylboronic acid completely shut down the desired reactivity (Table 1, entry 4). Lower loadings of either the isoamyl nitrite or benzylamine led to diminished yields (see ESI†). Substitution of isoamyl nitrite with either *tert*-butyl nitrite or nitrosonium tetrafluoroborate also resulted in lower yield or no formation of the product, respectively (see Table 1, entry 5 and ESI†). Interestingly, addition of 1.0 equivalent of boric acid (Table 1, entry 6), which is believed to be formed as a stoichiometric byproduct in the reaction, gave lower yields of the desired product, suggesting that byproduct formation might suppress the desired reaction pathway.

With the optimized conditions in hand, the benzylamine substrate scope of this synthetic transformation was explored (Fig. 2). Electron-rich *p*-tolyl- and 4-*tert*-butylbenzylamines gave the corresponding products **3b** and **3c** in moderate yields. 4-Phenylbenzylamine gave the product **3d** in 60% yield. 4-Fluoro, 4-chloro, 4-bromo and 4-iodobenzylamines could be transformed to target diarylmethanes **3e–h** in 51%, 76%, 85% and 89% yields, respectively. Furthermore, diarylmethanes bearing electron-withdrawing functional groups, such as nitrile (**3i**), nitro (**3j**), ester (**3k**) and methylsulfonyl (**3l**), were synthesised

Table 1 Optimisation of the reaction conditions. Reaction conditions: benzylamine (**1a**, 2.0 mmol), phenylboronic acid (**2a**, 0.5 mmol), isoamyl nitrite (2.5 mmol), sodium carbonate (0.5 mmol), chloroform (1.25 mL), 60 °C, 24 h



Entry	Deviation from standard conditions	Yield[a] [%]
1	No deviation	80 (70)[b]
2	No ^{i}AmONO	0
3	No base	72
4	Pinacol ester instead of phenylboronic acid	0
5	^{t}BuONO instead of ^{i}AmONO	23
6	1 equiv. of boric acid ($B(OH)_3$)	70

[a] GC yield of the crude reaction mixture using *n*-dodecane as an internal standard. [b] Isolated yield.

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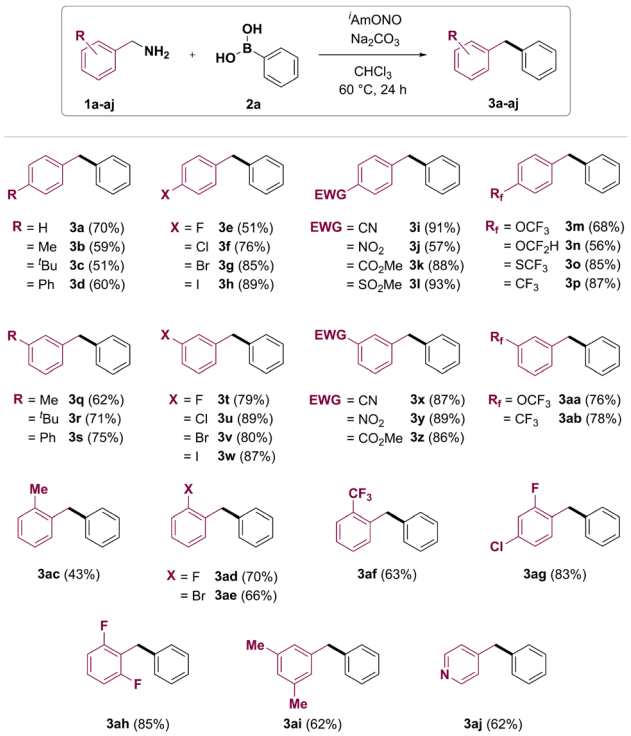

Fig. 2 Benzylamine scope of the deaminative coupling between benzylamines and arylboronic acids. Reaction conditions: benzylamine (**1a–aj**, 2.0 mmol), phenylboronic acid (**2a**, 0.5 mmol), isoamyl nitrite (2.5 mmol), sodium carbonate (0.5 mmol), chloroform (1.25 mL), 60 °C, 24 h. Isolated yields after flash column chromatography.

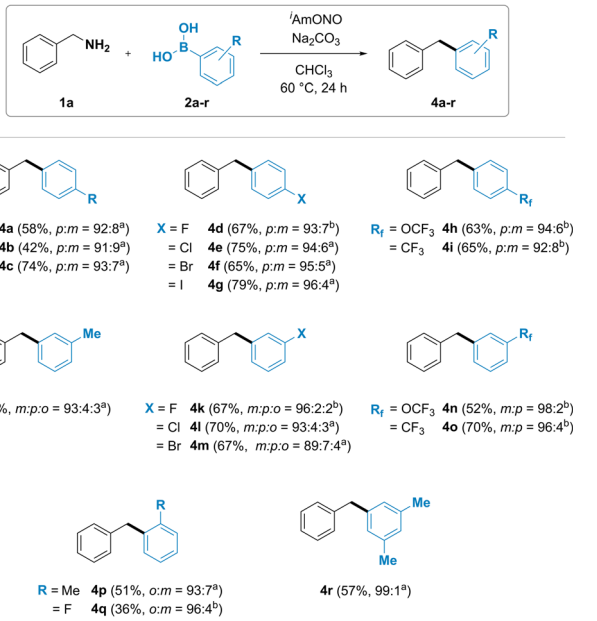

Fig. 3 Arylboronic acid scope of the deaminative coupling between benzylamines and arylboronic acids. Reaction conditions: benzylamine (**1a**, 2.0 mmol), arylboronic acid (**2a–r**, 0.5 mmol), isoamyl nitrite (2.5 mmol), sodium carbonate (0.5 mmol), chloroform (1.25 mL), 60 °C, 24 h. Isolated yields after flash column chromatography. [a] Isomer ratio determined by ^{13}C NMR. [b] Isomer ratio determined by ^{19}F NMR.

from the corresponding benzylamines in good to excellent yields. Fluorine-containing functional groups such as trifluoromethoxy (**3m**), difluoromethoxy (**3n**), trifluoromethylsulfane (**3o**) and trifluoromethyl (**3p**) were also found to be tolerated under reaction conditions. *Meta*-substituted benzylamines have also been found to be good coupling partners in the transformation, affording products **3q–ab**. Deaminative coupling between benzylamines and arylboronic acids was also shown to tolerate *ortho* substitution on the benzylamine partner, with yields of the corresponding diarylmethanes depending on both electronic and steric properties of the benzylamine substrate. 2-Methylbenzylamine (**1ac**) gave the desired product **3ac** in 43% yield. Diarylmethanes **3ad**, **3ag** and **3ah** bearing *ortho*-fluoro group were obtained in 70%, 83% and 85% yield, respectively. Introduction of 2-bromo or 2-trifluoromethyl group was also shown to furnish the corresponding products in good yields (**3ae** and **3af**, respectively). Importantly, a pyridine heterocycle was also tolerated under reaction conditions, and 4-benzylpyridine (**3aj**) was obtained from 4-picolylamine (**1aj**) in 62% yield.

The substrate scope of arylboronic acids was then investigated (Fig. 3). A wide range of products were obtained in good yields and high selectivity. Unexpectedly, substituted arylboronic acids gave trace amounts of a minor regioisomeric product. *Para*-substituted arylboronic acids (**2a–i**) have been found to give a mixture of *para*- and *meta*-substituted diarylmethanes **4a–i** in 96 : 4 to 91 : 9 *p* : *m* isomer ratio. Similar trend was also observed with *meta*-substituted arylboronic acids. Formation of a mixture of all three possible isomers was observed for diarylmethanes **4j**, **4k**, **4l** and **4m**, synthesized using 3-methyl, 3-fluoro, 3-chloro and 3-bromophenylboronic acids, respectively, with the desired *meta* isomeric product obtained in 89 to 96% selectivity. Introduction of an electron withdrawing group such as trifluoromethoxy (**4n**) or trifluoromethyl (**4o**) in the *meta* position led to the formation of *meta* and *para* isomers. *Ortho*-substituted phenylboronic acids **4p** and **4q** were also observed to furnish both the *ortho* and the *meta* isomer of diarylmethane product.

To better understand the unusual reactivity of substituted phenylboronic acids not only through the *ipso* but also through the *ortho* position, the mechanistic aspects of the deaminative coupling were investigated (Fig. 4). To probe whether the isomer formation is feasible under the originally proposed diazo pathway, 1-benzyl-4-methylbenzene (**3b**) was synthesised using conditions described by Barluenga and coworkers[44] from benzaldehyde tosylhydrazone (**6**) and *p*-tolylboronic acid (**2b**) (Fig. 4a). The desired product **3b** was obtained in 60% yield, however no formation of the minor *meta* isomer was observed. To gain further insight into the mechanism of the deaminative coupling, a *p*-tolylbenzylamine deuterated on the benzylic position (**1b-d_2**) was subjected to the reaction conditions using phenylboronic acid (**2a**) as a coupling partner (Fig. 4b). A high extent of scrambling was observed in the benzylic position of the diarylmethane product **7**. This suggests that the reaction

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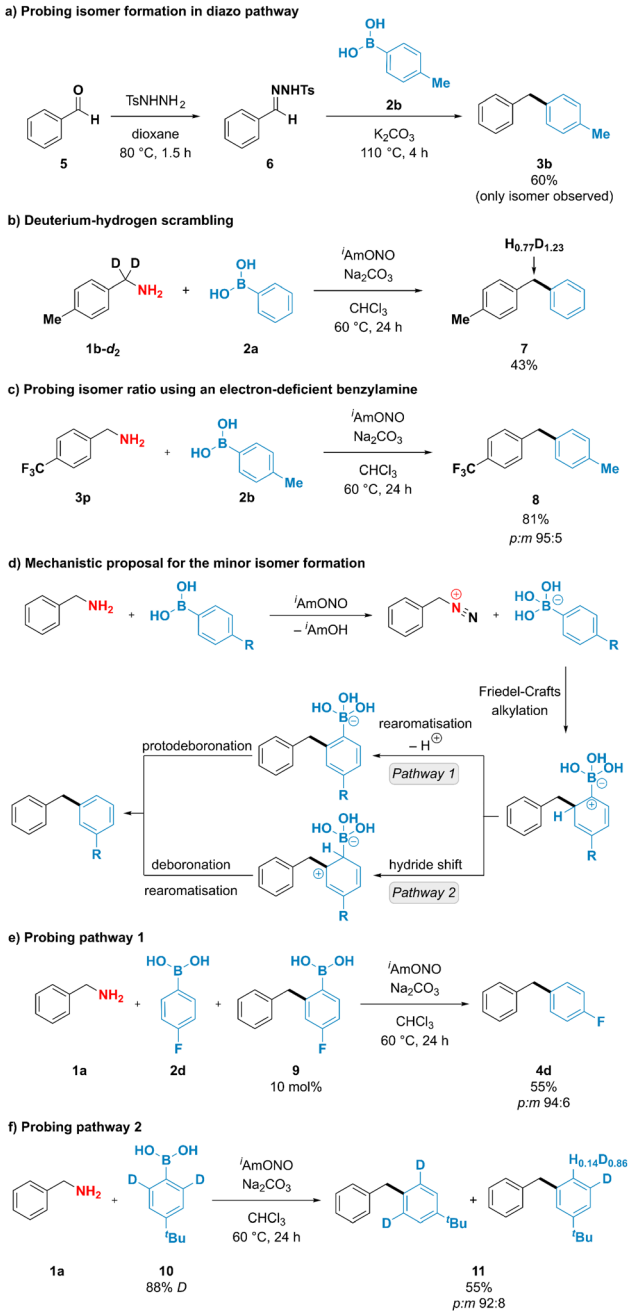

Fig. 4 Mechanistic experiments and proposed mechanism for the formation of minor isomer.

likely proceeds through diazo species **Int-II** (Fig. 1d), however the deprotonation of the intermediate species might not be strictly necessary for the formation of the desired product. Formation of one isomer in the diazo pathway and incomplete hydrogen–deuterium scrambling in the benzylic position of benzylamine indicate that more than one mechanistically distinct pathway is accessible for the formation of diarylmethane products. This observation was indirectly supported by reacting 4-(trifluoromethyl)benzylamine (**3p**) with *p*-tolylboronic acid (**2b**) using optimized reaction conditions (Fig. 4c). In contrast to the unsubstituted benzylamine, formation of the diazo compound from 4-(trifluoro-methyl) benzylamine is expected to be favoured due to the ability of the neighbouring electron-withdrawing groups to stabilise diazo compounds.[26–28] It was therefore anticipated that subjecting the benzylamine bearing electron-withdrawing group to the deaminative coupling with *p*-tolylboronic acid would almost exclusively furnish the desired *para* isomer. However, a mixture of both *para* and *meta* isomers was still obtained in 95 : 5 ratio, which is similar to that of unsubstituted benzylamine (93 : 7).

Exclusive formation of the major isomer in the diazo pathway, incomplete deuterium–hydrogen scrambling, and formation of both isomeric products when using electron-deficient benzylamines suggest that at least two mechanistically distinct pathways are operating under reaction conditions, with one being responsible for the formation of the minor product. Interestingly, boronate salts have been reported to engage in electrophilic aromatic substitution reactions if exposed to highly reactive species, such as NO_2^+, Cl^+ or F^+, among others.[45–52] To explain the formation of the minor product, it could be envisioned that arylboronic acids participate in electrophilic substitution reaction through their *ortho* position with a subsequent loss of boron (Fig. 4d). After arylboronic acid-assisted elimination of the hydroxy group from the hydroxydiazene intermediate **Int-I**, a benzyldiazonium–arylboronate ion pair might be formed, and the aryl ring of the arylboronic acid could engage in an intramolecular Friedel–Crafts alkylation reaction, furnishing the minor isomer either after (1) rearomatisation and subsequent protodeboronation or after (2) hydride shift and subsequent deboronation. Mechanistic pathway (1) has been probed by adding 10 mol% of the putative intermediate arylboronic acid **9** to the deaminative coupling reaction between 4-fluorophenylboronic acid (**2d**) and benzylamine (**1a**), which under optimized conditions was reported to furnish the isomeric products in 67% yield and 94 : 6 *p* : *m* isomer ratio (Fig. 3, entry **4d**). Upon spiking the reaction mixture with 10% of the putative intermediate **9**, diarylmethane products were obtained in 55% yield and 94 : 6 *p* : *m* isomer ratio, suggesting that addition of the arylboronic acid **9** to the reaction mixture did not increase the amount of the minor isomer formed and that compound **9** is likely not an intermediate in the formation of the minor product. To check whether mechanistic pathway (2) is operative under the reaction conditions, deuterium-enriched arylboronic acid **10** was subjected to the deaminative coupling with benzylamine **1a**. Deuterium enrichment was observed in the position *para* to the *tert*-butyl group in the minor isomer, suggesting that hydride/deuteride shift is likely to operate under the reaction conditions. Therefore, we propose that mechanistic pathway (2) is likely to be responsible for the formation of the minor isomer, thus providing the rationale for the formation of isomeric products when using substituted arylboronic acids as coupling partners.

Conclusions

In this report, a deaminative coupling between benzylamines and arylboronic acids under basic conditions is disclosed. Utilisation of inexpensive isoamyl nitrite for diazotisation of

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benzylamines along with arylboronic acids as Lewis-acidic coupling partners enabled the forging of a C–C bond to give diarylmethane products in good to excellent yields with a broad functional group tolerance. Mechanistic experiments supported the operation of at least two mechanistically distinct reaction pathways under optimised conditions to furnish desired deamination products. Intramolecular Friedel–Crafts reaction followed by hydride shift and deboronation was proposed to be the pathway responsible for the formation of isomeric diarylmethane products when using substituted arylboronic acids as deaminative coupling partners.

Author contributions

B. M. and G. S. designed the project. G. S. and J. C. R. carried out the experiments. B. M., G. S. and J. C. R. analysed the data and wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 N. A. McGrath, M. Brichacek and J. T. Njardarson, *J. Chem. Educ.*, 2010, **87**, 1348–1349.
2 R. Vardanyan and V. Hruby, *Synthesis of best-seller drugs*, Academic press, 2016.
3 S. A. Lawrence, *Amines: synthesis, properties and applications*, Cambridge University Press, 2004.
4 K. Weissermel and H.-J. Arpe, *Industrial organic chemistry*, John Wiley & Sons, 2008.
5 A. Ricci, *Amino group chemistry: from synthesis to the life sciences*, John Wiley & Sons, 2008.
6 K. J. Berger and M. D. Levin, *Org. Biomol. Chem.*, 2021, **19**, 11–36.
7 Q. Wang, Y. Su, L. Li and H. Huang, *Chem. Soc. Rev.*, 2016, **45**, 1257–1272.
8 K. Ouyang, W. Hao, W.-X. Zhang and Z. Xi, *Chem. Rev.*, 2015, **115**, 12045–12090.
9 M.-B. Li, Y. Wang and S.-K. Tian, *Angew. Chem., Int. Ed.*, 2012, **51**, 2968–2971.
10 X.-S. Wu, Y. Chen, M.-B. Li, M.-G. Zhou and S.-K. Tian, *J. Am. Chem. Soc.*, 2012, **134**, 14694–14697.
11 X.-T. Ma, Y. Wang, R.-H. Dai, C.-R. Liu and S.-K. Tian, *J. Org. Chem.*, 2013, **78**, 11071–11075.
12 Y. Wang, J.-K. Xu, Y. Gu and S.-K. Tian, *Org. Chem. Front.*, 2014, **1**, 812–816.
13 M.-B. Li, H. Li, J. Wang, C.-R. Liu and S.-K. Tian, *Chem. Commun.*, 2013, **49**, 8190–8192.
14 T.-T. Wang, F.-X. Wang, F.-L. Yang and S.-K. Tian, *Chem. Commun.*, 2014, **50**, 3802–3805.
15 X.-S. Wu, M.-G. Zhou, Y. Chen and S.-K. Tian, *Asian J. Org. Chem.*, 2014, **3**, 711–714.
16 J. Tsuji, H. Takahashi and M. Morikawa, *Tetrahedron Lett.*, 1965, **6**, 4387–4388.
17 B. M. Trost and T. J. Fullerton, *J. Am. Chem. Soc.*, 1973, **95**, 292–294.
18 F. Mo, G. Dong, Y. Zhang and J. Wang, *Org. Biomol. Chem.*, 2013, **11**, 1582–1593.
19 F. Mo, D. Qiu, L. Zhang and J. Wang, *Chem. Rev.*, 2021, **121**, 5741–5829.
20 S. S. Babu, P. Muthuraja, P. Yadav and P. Gopinath, *Adv. Synth. Catal.*, 2021, **363**, 1782–1809.
21 J. Chen, X. Xie, J. Liu, Z. Yu and W. Su, *React. Chem. Eng.*, 2022, **7**, 1247–1275.
22 G. Maas, *Angew. Chem., Int. Ed.*, 2009, **48**, 8186–8195.
23 M. Rosenberger, P. Yates, J. B. Hendrickson and W. Wolf, *Tetrahedron Lett.*, 1964, **5**, 2285–2289.
24 M. Regitz and J. Rüter, *Chem. Ber.*, 1968, **101**, 1263–1270.
25 R. L. Danheiser, R. F. Miller, R. G. Brisbois and S. Z. Park, *J. Org. Chem.*, 1990, **55**, 1959–1964.
26 M. Regitz, *Diazo compounds: properties and synthesis*, Elsevier, 2012.
27 M. P. Doyle, M. A. McKervey and T. Ye, *Modern catalytic methods for organic synthesis with diazo compounds*, Wiley, 1998.
28 H. Zollinger, *Diazo Chemistry, Diazo Chemistry II: Aliphatic, Inorganic and Organometallic Compounds*, Wiley, 1995.
29 G. Wu, Y. Deng, C. Wu, Y. Zhang and J. Wang, *Angew. Chem., Int. Ed.*, 2014, **53**, 10510–10514.
30 G. Reynard, E.-M. Joseph-Valcin and H. Lebel, *Chem. Commun.*, 2020, **56**, 10938–10941.
31 G. Reynard, H. Mayrand and H. Lebel, *Can. J. Chem.*, 2020, **98**, 480–484.
32 C. Audubert and H. Lebel, *Org. Lett.*, 2017, **19**, 4407–4410.
33 R. M. Jacobson, *Synth. Commun.*, 1978, **8**, 33–37.
34 J. Liao, W. Guan, B. P. Boscoe, J. W. Tucker, J. W. Tomlin, M. R. Garnsey and M. P. Watson, *Org. Lett.*, 2018, **20**, 3030–3033.
35 P. Maity, D. M. Shacklady-McAtee, G. P. A. Yap, E. R. Sirianni and M. P. Watson, *J. Am. Chem. Soc.*, 2013, **135**, 280–285.
36 S. Yoon, M. C. Hong and H. Rhee, *J. Org. Chem.*, 2014, **79**, 4206–4211.
37 R. J. Baumgarten, *J. Chem. Educ.*, 1966, **43**, 398.
38 L. G. Cannell and R. W. Taft, *J. Am. Chem. Soc.*, 1956, **78**, 5812–5817.
39 A. T. Jurewicz, J. H. Bayless and L. Friedman, *J. Am. Chem. Soc.*, 1965, **87**, 5788–5790.
40 J. H. Bayless, F. D. Mendicino and L. Friedman, *J. Am. Chem. Soc.*, 1965, **87**, 5790–5791.

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41 L. Friedman, A. T. Jurewicz and J. H. Bayless, *J. Am. Chem. Soc.*, 1969, **91**, 1795–1799.
42 J. H. Bayless and L. Friedman, *J. Am. Chem. Soc.*, 1967, **89**, 147–148.
43 A. Greb, J.-S. Poh, S. Greed, C. Battilocchio, P. Pasau, D. C. Blakemore and S. V. Ley, *Angew. Chem., Int. Ed.*, 2017, **56**, 16602–16605.
44 J. Barluenga, M. Tomás-Gamasa, F. Aznar and C. Valdés, *Nat. Chem.*, 2009, **1**, 494–499.
45 T. Kamei, A. Ishibashi and T. Shimada, *Tetrahedron Lett.*, 2014, **55**, 4245–4247.
46 I. Vints, J. Gatenyo and S. Rozen, *J. Org. Chem.*, 2013, **78**, 11794–11797.
47 P. Appukkuttan, W. Dehaen and E. Van der Eycken, *Chem.–Eur. J.*, 2007, **13**, 6452–6460.
48 G. Wu, S. Xu, Y. Deng, C. Wu, X. Zhao, W. Ji, Y. Zhang and J. Wang, *Tetrahedron*, 2016, **72**, 8022–8030.
49 G. Berionni, V. Morozova, M. Heininger, P. Mayer, P. Knochel and H. Mayr, *J. Am. Chem. Soc.*, 2013, **135**, 6317–6324.
50 G. A. Molander and L. N. Cavalcanti, *J. Org. Chem.*, 2011, **76**, 7195–7203.
51 J. Kim and M. Movassaghi, *J. Am. Chem. Soc.*, 2011, **133**, 14940–14943.
52 G. A. Olah, M. Piteau, K. Laali, C. B. Rao and O. Farooq, *J. Org. Chem.*, 1990, **55**, 46–48.

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