Chemical Science

EDGE ARTICLE



Cite this: Chem. Sci., 2024, 15, 3249

have been paid for by the Royal Society of Chemistry

Received 8th December 2023 Accepted 17th January 2024

DOI: 10.1039/d3sc06600b

rsc.li/chemical-science

Introduction

Small aliphatic rings attract considerable attention in contemporary research.¹ For example, the cyclobutane ring is common within modern bioactive compounds² and can be found in the structures of at least ten market-approved drugs.³ This motivated substantial development of cyclobutyl boronate chemistry during the past decade owing to the fact that the carbon-boron bond provides an excellent site for functionalization.⁴ The known approaches to the preparation of cyclobutyl boronates include the C–H activation of cyclobutanes,⁵ electrocyclization,⁶ functionalization of bicyclo [1.1.0]butanes,⁷ borylation⁸ and hydrogenation of cyclobutenes,⁹ along with other methods.^{10,11}

The most frequently used approach is a [2 + 2]-cycloaddition. Strikingly, while the photochemical version of this transformation has been elaborated in numerous studies by Hollis, Bach, Hiemstra, Grygorenko, Yoon, Swierk with Brown, Romanov-Michailidis with Knowles, and Fürstner,¹² the thermal approach remained underdeveloped for unclear reasons (Scheme 1). We found only a single example in the literature on non-catalyzed thermal [2 + 2]-cycloaddition between alkene 1 and ketene 2 (Scheme 1). In 1969, Fish demonstrated that heating this mixture in a sealed vial for 15 days afforded the target cyclobutane 3 in 23% yield.¹³ Also, recently Brown showed an example of a thermal [2 + 2]-cycloaddition between a borylated alkene and an allene that required, however, Lewis acid catalysis.¹⁴

In this work, we developed a one-step approach to borylated cyclobutanes by thermal [2 + 2]-cycloaddition between vinyl boronates and *in situ*-generated keteniminium salts.

Borylated cyclobutanes *via* thermal [2 + 2]cycloaddition[†]

Kateryna Prysiazhniuk, Oleksandr Polishchuk, Stanislav Shulha, Kyrylo Gudzikevych, Oleksandr P. Datsenko, Vladimir Kubyshkin b and Pavel K. Mykhailiuk *

A one-step approach to borylated cyclobutanes from amides of carboxylic acids and vinyl boronates is elaborated. The reaction proceeds *via* the thermal [2 + 2]-cycloaddition of *in situ*-generated keteniminium salts.

Results and discussion

From the pioneering study of Fish (Scheme 1),¹³ it seemed reasonable to assume that vinyl boronates are amenable to noncatalytic thermal [2 + 2] cycloadditions; however, a more active partner than a ketene was needed. We turned our attention to keteniminium salts that are known to be more active than ketenes.¹⁵ Moreover, the [2 + 2]-cycloaddition of keteniminium salts with alkenes has been reported.^{16,17} Despite the substantial recent progress in keteniminium chemistry,¹⁵ we found no literature mentioning the reaction of borylated alkenes with keteniminium salts. Initially, we suspected that the conditions for their generation, which typically involved treatment with triflic anhydride,¹⁷ do not tolerate the Bpin group and the latter might decompose. Nonetheless, we decided to examine the feasibility of this transformation.



Scheme 1 Retrosynthetic disconnection of borylated cyclobutanes *via* a [2 + 2]-reaction: photochemical *vs.* thermal strategies.



View Article Online

View Journal | View Issue

Enamine Ltd, Winston Churchill St. 78, 02094 Kyiv, Ukraine. E-mail: Pavel. Mykhailiuk@gmail.com; Web: https://www.mykhailiukchem.org

[†] Electronic supplementary information (ESI) available. CCDC 2312008, 2312007, 2312010, 2312009, 2312011, 2321052 and 2321392. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d3sc06600b



Scheme 2 Reaction conditions: (i) vinyl Bpin/allyl Bpin (1.0 equiv.), amide (1.2 equiv.), triflic anhydride (1.4 equiv.), collidine or lutidine (1.4 equiv.), 1,2-dichloroethane, reflux, and 16 h; (ii) aqueous NaHCO₃; (iii) purification (vacuum distillation or column chromatography). The scale of the synthesis: ^a 100–500 mg; ^b 1–7 g; ^c 10–50 g of the isolated product. ^d Product **25** (d.r. = 7 : 1) was obtained with *ca.* 70% purity. ^e Additional purification by column chromatography provided the pure product **25** as a single diastereomer in 3% yield. ^f Product **26** (d.r. = 2 : 1) was obtained with *ca.* 50% purity. ^g Additional purification by column chromatography provided the pure product **25** as a single diastereomer in 1% yield. X-ray crystal structures of compounds **14–16**, **20**, and **22** are shown as thermal ellipsoids at a 50% probability level; carbon – white, oxygen – red, boron – brown, and fluorine – green; hydrogen atoms are omitted for clarity.

The model reaction between *N*,*N*-dimethylacetamide and vinyl Bpin did not produce the desired product **4** even at trace amounts when performed in refluxed dichloroethane. Lowering the

temperature to 60 $^{\circ}$ C or increasing the number of keteniminium equivalents from 1.2 to 3, 4, and 5 were as unsuccessful (Scheme 2, part limitations). Only the starting vinyl Bpin along with



Scheme 3 Unexpected synthesis of ketone 33

Modifications



Scheme 4 Modifications of borylated cyclobutanes. (a) Synthesis of borylated cyclobutane 23. (b) Synthesis of *N*-Boc amino boronates 38 and 40. (c) An attempted synthesis of bicyclo[1.1.1]pentanes 41 and 42.

unidentified side products was detected in the reaction mixture. We were quite discouraged by the futility of our initial efforts, yet we attempted another reaction involving the homologous *N*,*N*- dimethylpropanamide. Serendipitously, the reaction worked out. Activation of the amide with $(CF_3SO_2)_2O$ /collidine (*in situ* formation of the keteniminium salt) followed by its reaction with vinyl Bpin produced the desired product 5 (Scheme 2).

After short optimization of the reaction conditions, we found that performing the reaction in refluxing dichloroethane for 12 hours produced excellent conversion of the starting vinyl boronate (see Table S1 in the ESI†). Thus, we examined the reaction scope by taking various amide counterparts and obtained borylated cyclobutanes **5–16** in decent yields (Scheme 2). The reaction was found compatible with the presence of the cyclopropyl ring (7), the active chlorine atom (8), and the *gem*difluoro motif (**10** and **15**) in the product substances. Substituted alkenes, $CH_2=C(Me)$ -Bpin and $CH_2=C(Ph)$ -Bpin, gave the desired borylated cyclobutanes **17–22** as well. Products **5**, **7**, **8**, **12**, and **18** were obtained as inseparable mixtures of two diastereomers. The structure of products **14–16**, **20** and **22** was confirmed by X-ray crystallographic analysis.¹⁸

The developed reaction showed few limitations, however. The keteniminium salt obtained from *N*,*N*-dimethylacetamide reacted with substituted vinyl boronates (products **17** and **21**) but failed to react with vinyl Bpin (**4**). Attempts towards the synthesis of compounds **23**, **24** and **27** failed as well. Analysis of the reaction mixture revealed either the presence of unreacted vinyl Bpin (**23**, **27**) or the formation of a complex mixture (**24**). Some products, such as **25** and **26**, were obtained in low isolated yields because they required rather tedious purification. The purification led to isolation of a single diastereomer in each case, and the *trans*-configuration of compounds **25** and **26** was revealed by X-ray crystallography.¹⁸

The analogous reaction between amides of carboxylic acids and the homologous CH_2 =CH-CH₂-Bpin also produced the desired products **28–31** (Scheme 2).

It is important to note that the reaction demonstrated good performance on milligram, gram, and even multigram scales (10, 12, and 20). When carrying out the reaction on a small scale, we purified products by silica gel column chromatography. On a gram-to-multigram scale, we isolated the products by distillation under reduced pressure, which is more practical. Despite the seeming simplicity of the current approach to borylated cyclobutanes, to the best of our knowledge, none of the obtained products depicted in Scheme 2 has been reported in the literature.

Somewhat unexpectedly, the reaction between β , β -disubstituted vinyl boronate **32** and *N*,*N*-dimethylacetamide produced ketone **33** rather than the borylated cyclobutane **34** (Scheme 3). While we did not examine the exact mechanism of this transformation,¹⁹ we found a fairly reasonable explanation for the observed outcome. We reasoned that the bulky C==NMe₂ moiety approached the tertiary rather than quaternary carbon of the amide in the course of the cycloaddition probably due to steric reasons (Scheme 3, proposed explanation). Effectively, this steered the reaction towards the formation of the intermediate compound **35**, which is related to the class of unstable α -borylated ketones²⁰ prone to hydrolytic protodeborylation, thus producing ketone **33**.

Next, we performed transformations of the obtained products. For example, despite the failed attempt to direct synthesis of cyclobutane 23 from amide 36 (Scheme 2, limitations), we



Scheme 5 Synthesis of potassium trifluoroborate salts 6a, 9a, and 13; and diol 44.

were able to obtain compound **23** by an intramolecular cyclization of the previously synthesized chloride **8** in 84% yield (Scheme 4a). From ketone **6**, the corresponding amino boronate **37** was synthesized in two steps (Scheme 4b). The subsequent *N*protection provided *N*-Boc amino boronate **38**, which represents a useful medicinal chemistry precursor. Analogously, the *N*-Boc amino boronate **40** was obtained from ketone **9** *via* amine **39**.

In 2021, Qin and colleagues developed an elegant intramolecular coupling towards multi-substituted bicycloalkyl boronates.^{11*a*} The corresponding starting materials were synthesized in multiple steps. In this work, we obtained ketones **29** and **30** in one step, and we also attempted their cyclization into the desired bicyclo[1.1.1]pentanes **41** and **42** (Scheme 4c). Unfortunately, under the original conditions reported by the Qin group, the formation of the desired products was not observed. Our unsuccessful efforts corroborate the seminal conclusion that the presence of an additional substituent at the cyclobutane ring is crucial for the formation of bicyclo[1.1.1]pentane in this reaction.^{11*a*}

Finally, we performed a few other representative modifications. The reaction of pinacol boronates 6, 9, and 13 with KHF_2 produced potassium trifluoroborates 6a, 9a, and 13a (Scheme 5). The reduction of the ketone group in 13 with $NaBH_4$ gave alcohol 43. The oxidative cleavage of the Bpin group in the latter substance gave diol 44. We assume that similar modifications could be performed with the other obtained Bpin ketones following our protocols.

Conclusions

Here, we elaborated a thermal [2 + 2]-cycloaddition between vinyl boronates and *in situ* generated keteniminium salts. This practical approach allows the preparation of borylated cyclobutanes in one step. The obtained compounds can be used in the syntheses of various functionalized cyclobutanes.

Data availability

The ESI† contains method description, product characterization data, and NMR spectra.

Author contributions

O. P. D. and P. K. M. designed the project. K. P., O. P., S. S., K. G., and O. P. D. carried out experiments. V. K. analysed the data. V. K. and P. K. M. wrote the manuscript and all authors provided comments.

Conflicts of interest

The authors are employees of a chemical supplier Enamine.

Acknowledgements

The authors are grateful to Prof. A. A. Tolmachov for the support and to Dr S. Shishkina for the X-Ray analysis. This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (grant agreement No. 101000893 – BENOVELTY).

Notes and references

- 1 M. R. Bauer, P. Di Fruscia, S. C. C. Lucas, I. N. Michaelides, J. E. Nelson, R. I. Storer and B. C. Whitehurst, Put a ring on it: application of small aliphatic rings in medicinal chemistry, *RSC Med. Chem.*, 2021, **12**, 448–471.
- 2 M. R. van der Kolk, M. A. C. H. Janssen, F. P. J. T. Rutjes and D. Blanco-Ania, Cyclobutanes in Small-Molecule Drug Candidates, *ChemMedChem*, 2022, **17**, e202200020.
- 3 Chemical structure search drugbank online, https:// go.drugbank.com/structures/search/small_molecule_drugs/ structure, accessed December 2023, filters used: "substucture"+"approved"+"vet approved".
- 4 (a) R. J. Armstrong and V. Aggarwal, 50 Years of Zweifel Olefination: a Transition-Metal-Free Coupling, *Synthesis*, 2017, **49**, 3323–3336; (b) C. Sandford and V. K. Aggarwal, Stereospecific Functionalizations and Transformations of Secondary and Tertiary Boronic Esters, *Chem. Commun.*, 2017, **53**, 5481–5494; (c) J. W. B. Fyfe and A. J. B. Watson, Recent Developments in Organoboron Chemistry: Old Dogs, New Tricks, *Chem*, 2017, **3**, 31–55.
- 5 (a) J. He, Q. Shao, Q. Wu and J.-Q. Yu, Pd(II)-Catalyzed Enantioselective C(sp³)-H Borylation, J. Am. Chem. Soc., 2017, 139, 3344–3347; (b) R. Murakami, K. Tsunoda, T. Iwai and M. Sawamura, Stereoselective C-H Borylations of Cyclopropanes and Cyclobutanes with Silica-Supported Monophosphane-Ir Catalysts, Chem.-Eur. J., 2014, 20, 13127–13131; (c) X. Chen, L. Chen, H. Zhao, Q. Gao, Z. Shen and S. Xu, Iridium-Catalyzed Enantioselective C(sp³)-H Borylation of Cyclobutanes, Chin. J. Chem., 2020, 38, 1533–1537; (d) Q. Gao and S. Xu, Site- and Stereoselective C(sp³)-H Borylation of Strained (Hetero) Cycloalkanols Enabled by Iridium Catalysis, Angew. Chem., Int. Ed., 2023, 62, e202218025.
- 6 Z. X. Giustra, X. Yang, M. Chen, H. F. Bettinger and S.-Y. Liu, Accessing 1,2-Substituted Cyclobutanes Through 1,2-

This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

Open Access Article. Published on 25 January 2024. Downloaded on 8/22/2025 6:17:59 PM.

Azaborine Photoisomerization, Angew. Chem., Int. Ed., 2019, 58, 18918-18922.

- 7 (a) M. Silvi and V. K. Aggarwal, Radical Addition to Strained σ-Bonds Enables the Stereocontrolled Synthesis of Cyclobutyl Boronic Esters, J. Am. Chem. Soc., 2019, 141, 9511-9515; (b) A. Fawcett, T. Biberger and V. K. Aggarwal, Carbopalladation of C-C σ -Bonds Enabled by Strained Boronate Complexes, Nat. Chem., 2019, 11, 117-122; (c) J. Michalland, N. Casaretto and S. Z. Zard, A Modular Access to 1,2- and 1,3-Disubstituted Cyclobutylboronic Esters by Consecutive Radical Additions, Angew. Chem., Int. Ed., 2022, 61, e202113333.
- 8 (a) L. Brener and H. C. Brown, Hydroboration. 47. Unique Stereospecificity of the Hydroboration of 1, 3-Dimethylcycloalkenes with 9-Borabicyclo [3.3.1] Nonane, J. Org. Chem., 1977, 42, 2702-2704; (b) M. Guisan-Ceinos, A. Parra, V. Martin-Heras and M. Tortosa, Enantioselective Synthesis of Cyclobutylboronates via a Copper-Catalyzed Desymmetrization Approach, Angew. Chem., Int. Ed., 2016, (c) H. A. Clement, 55, 6969-6972; M. Boghi, R. M. McDonald, L. Bernier, J. W. Coe, W. Farrell, C. J. Helal, M. R. Reese, N. W. Sach, J. C. Lee and D. G. Hall, High-Throughput Ligand Screening Enables the Enantioselective Conjugate Borylation of Cyclobutenones to Access Synthetically Versatile Tertiary Cyclobutylboronates, Angew. Chem., Int. Ed., 2019, 58, 18405-18409; (d) A. K. Simlandy, M.-Y. Lyu and M. K. Brown, Catalytic Arylboration of Spirocyclic Cyclobutenes: Rapid Access to Highly Substituted Spiro [3.n]alkanes, ACS Catal., 2021, 11, 12815-12820; (e) L. Nóvoa, L. Trulli, A. Parra and M. Tortosa, Stereoselective Diboration of Spirocyclobutenes: A Platform for the Synthesis of Spirocycles with Orthogonal Exit Vectors, Angew. Chem., Int. Ed., 2021, 60, 11763-11768; (f) L. Novoa, L. Trulli, I. Fernandez, A. Parra and M. Tortosa, Regioselective Monoborylation of Spirocyclobutenes, Org. Lett., 2021, 23, 7434-7438; (g) J. Proessdorf, C. Jandl, T. Pickl and T. Bach, Synthesis of Boronates with a Protoilludane Skeleton, Synthesis, 2023, 55, 2311-2318; (h) M. Cui, Z.-Y. Zhao and M. Oestreich, Boosting the Enantioselectivity of Conjugate Borylation of α , β -Disubstituted Cyclobutenones with Monooxides of Chiral C2-Symmetric Bis(phosphine) Ligands, Chem.-Eur. J., 2022, 62, e202202163.
- 9 M. M. Parsutkar, V. V. Pagar and T. V. RajanBabu, Catalytic Enantioselective Synthesis of Cyclobutenes From Alkynes and Alkenyl Derivatives, J. Am. Chem. Soc., 2019, 141, 15367-15377.
- 10 (a) D. P. Hari, J. C. Abell, V. Fasano and V. K. Aggarwal, Ring-Expansion Induced 1,2-Metalate Rearrangements: Highly Diastereoselective Synthesis of Cyclobutyl Boronic Esters, J. Am. Chem. Soc., 2020, 142, 5515-5520; (b) T. R. McDonald and S. A. L. Rousseaux, Synthesis of 3-borylated epihalohydrins or epoxy alcohol cyclobutanols from derivatives, Chem. Sci., 2023, 14, 963-969; (c)P. Dominguez-Molano, R. Weeks, R. J. Maza, J. J. Carbo and E. Fernández, Boron-Copper 1,3-Rearrangement: the

New Concept Behind the Boryl Migration from C(sp²) in Alkenvl Boranes to C(sp³), Angew. Chem., Int. Ed., 2023, 62, e202304791.

- 11 Borylated bicyclo[1.1.1]pentanes: (a) Y. Yang, J. Tsien, J. M. E. Hughes, B. K. Peters, R. R. Merchant and T. Qin, An intramolecular coupling approach to alkyl bioisosteres for the synthesis of multisubstituted bicycloalkyl boronates, Nat. Chem., 2021, 13, 950-955; (b) Y. Yang, J. Tsien, R. Dykstra, S.-J. Chen, J. B. Wang, R. R. Merchant, J. M. E. Hughes, B. K. Peters, O. Gutierrez and T. Qin, Programmable late-stage functionalization of bridgesubstituted bicyclo[1.1.1]pentane bis-boronates, Nat. Chem., 2023, DOI: 10.1038/s41557-023-01342-7; (c) S. Kim, H. Oh, W. Dong, J. Majhi, M. Sharique, B. Matsuo, S. Keess and G. A. Molander, Metal-Free Photoinduced Acylboration of [1.1.1]Propellane via Energy Transfer Catalysis, ACS Catal., 2023, 13, 9542-9549; (d) W. Dong, E. Yen-Pon, L. Li, A. Bhattacharjee, A. Jolit and G. A. Molander, Exploiting the sp² character of bicyclo[1.1.1]pentyl radicals in the transition-metal-free multi-component difunctionalization of [1.1.1]propellane, Nat. Chem., 2022, 14, 1068-1077; (e) I. F. Yu, J. L. Manske, A. Diéguez-Vázquez, A. Misale, A. E. Pashenko, P. K. Mykhailiuk, S. V. Ryabukhin, D. M. Volochnyuk and J. F. Hartwig, Catalytic undirected borylation of tertiary C-H bonds in bicyclo[1.1.1]pentanes and bicyclo[2.1.1]hexanes, Nat. Chem., 2023, 15, 685-693.
- 12 (a) W. G. Hollis Jr., W. C. Lappenbusch, K. A. Everberg and C. M. Woleben, The Use of Alkenylboronate Esters in [2 +2] Enone-Olefin Photocycloadditions, Tetrahedron Lett., 1993, 34, 7517-7520; (b) S. C. Coote and T. Bach, Enantioselective Intermolecular [2 + 2] Photocycloadditions of Isoquinolone Mediated by a Chiral Hydrogen-Bonding Template, J. Am. Chem. Soc., 2013, 135, 14948-14951; (c) R. A. Kleinnijenhuis, B. J. J. Timmer, G. Lutteke, J. M. M. Smits, R. de Gelder, J. H. van Maarseveen and Hiemstra, Formal Synthesis of Solanoeclepin a: H. Enantioselective Allene Diboration and Intramolecular [2 + 2] Photocycloaddition for the Construction of the Tricyclic Chem.-Eur. J., 2016, 22, 1266-1269; (d)Core, O. P. Demchuk, O. V. Hryshchuk, B. V. Vashchenko, A. V. Kozytskiy, A. V. Tymtsunik, I. V. Komarov and O. O. Grygorenko, Photochemical [2 + 2] Cycloaddition of Alkenyl Boronic Derivatives: an Entry Into 3-Azabicyclo [3.2.0]Heptane Scaffold, J. Org. Chem., 2020, 85, 5927-5940; (e) S. O. Scholz, J. B. Kidd, L. Capaldo, N. E. Flikweert, R. M. Littlefield and T. P. Yoon, Construction of Complex Cyclobutane Building Blocks by Photosensitized [2 + 2] Cycloaddition of Vinyl Boronate Esters, Org. Lett., 2021, 23, 3496-3501; (f) Y. Liu, D. Ni, B. G. Stevenson, V. Tripathy, S. E. Braley, K. Raghavachari, J. R. Swierk and M. K. Brown, Photosensitized [2 + 2]-Cycloadditions of Alkenylboronates and Alkenes, Angew. Chem., Int. Ed., 2022, 61, e202200725; (g)P. R. D. Murray. W. M. M. Bussink, G. H. M. Davies, F. W. van der Mei, A. H. Antropow, J. T. Edwards, L. A. D'Agostino, J. M. Ellis, L. G. Hamann, F. Romanov-Michailidis and R. R. Knowles, Intermolecular Crossed [2+2] Cycloaddition Promoted by

Visible-Light Triplet Photosensitization: Expedient Access to Polysubstituted 2-Oxaspiro[3.3]Heptanes, *J. Am. Chem. Soc.*, 2021, **143**, 4055–4063; (*h*) Y. Liu, D. Ni and M. K. Brown, Boronic Ester Enabled [2 + 2]-Cycloadditions by Temporary Coordination: Synthesis of Artochamin J and Piperarborenine B, *J. Am. Chem. Soc.*, 2022, **144**, 18790– 18796; (*i*) S. M. Spohr and A. Fürstner, Studies toward Providencin: The Furanyl-Cyclobutanol Segment, *Org. Lett.*, 2023, **25**, 1536–1540.

- 13 R. H. Fish, The Cycloaddition of Diphenylketene to 2-Vinyl-4,6,6-trimethyl-1,3,2-dioxaborinane, *J. Org. Chem.*, 1969, **34**, 1127–1128.
- 14 M. L. Conner and M. K. Brown, Synthesis of 1,3-Substituted Cyclobutanes by Allenoate-Alkene [2 + 2] Cycloaddition, *J. Org. Chem.*, 2016, 81, 8050–8060.
- 15 (a) C. Madelaine, V. Valerio and N. Maulide, Revisiting Keteniminium Salts: More than the Nitrogen Analogs of Ketenes, *Chem.-Asian J.*, 2011, 6, 2224–2239; (b) G. Evano, M. Lecomte, P. Thilmany and C. Theunissen, Keteniminium Ions: Unique and Versatile Reactive Intermediates for Chemical Synthesis, *Synthesis*, 2017, 49, 3183–3214.

- 16 (a) J. Marchand-Brynaert and L. Ghosez, Cycloadditions of Keteneimmonium Cations to Olefins and Dienes. A new Synthesis of Four-Membered Rings, J. Am. Chem. Soc., 1972, 94, 2870–2872; (b) A. Sidani, J. Marchand-Brynaert and L. Ghosez, A Convenient Procedure for the Synthesis of Cyclobutanones, Angew. Chem., Int. Ed., 1974, 13, 267.
- 17 J.-B. Falmagne, J. Escudero, S. Taleb-Sahraoui and L. Ghosez, Cyclobutanone and Cyclobutenone Derivatives by Reaction of Tertiary Amides with Alkenes or Alkynes, *Angew. Chem.*, *Int. Ed.*, 1981, **20**, 879–880.
- 18 Cambridge Crystallographic Data Centre (CCDC) deposition numbers: 2312008 (14), 2312007 (15), 2312010 (16), 2312009 (20), 2312011 (22), 2321052 (25), and 2321392 (26).
- 19 H. Saimoto, C. Houge, A.-M. Hesbain-Frisque, A. Mockel and L. Ghosez, Nonstereospecificity in the cycloadditions of keteneiminium salts to olefins. Evidence for a stepwise mechanism, *Tetrahedron Lett.*, 1983, 24, 2251–2254.
- 20 Z. He, A. Zajdlik and A. K. Yudin, α-Borylcarbonyl compounds: from transient intermediates to robust building blocks, *Dalton Trans.*, 2014, **43**, 11434–11451.