Chemical Science

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Cite this: *Chem. Sci.*, 2020, **11**, 3301

All publication charges for this article have been paid for by the Royal Society of Chemistry

Received 13th January 2020
Accepted 27th February 2020

DOI: 10.1039/d0sc00230e

rsc.li/chemical-science

meta-Selective C–H functionalisation of aryl boronic acids directed by a MIDA-derived boronate ester†

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N-Methyliminodiacetic acid (MIDA) boronates are boronic acid derivatives which are stable to reduction, oxidation and transmetalation. This has led to their widespread use as boronic acid protecting groups (PGs) and in iterative cross-couplings. We describe herein the development of a novel MIDA derivative that acts in a dual manner, as a protecting group and a directing group (DG) for *meta* C(sp^2)–H functionalisation of arylboronic acids. Palladium catalysed C–H alkenylations, acetoxylations and arylations are possible, at room temperature and under aerobic conditions. Deprotection to reveal the functionalised boronic acids is rapid and allows for full recovery of the DG. The technique allows the facile diversification of aryl boronic acids and their subsequent use in a range of reactions or in iterative processes.

Introduction

In recent years, directed C–H functionalisation has rapidly progressed from a new concept to an indispensable synthetic technique.[1] Directing groups (DGs) have emerged as powerful tools to achieve these transformations, often over-riding the inherent steric or electronic bias of the substrate.[2] While numerous methods for the directed *ortho* C(sp^2)–H functionalisation of aryl systems have been developed, directed, *meta*-selective processes remain relatively underexplored.[3] The distal nature of the *meta* C–H bond, its proximity to the *ortho* and *para* positions and often unfavourable electronic properties pose unique challenges. In 2012, Yu was able to address these challenges with the seminal design of U-shaped DGs for the *meta* alkenylation of hydrocinnamic acid and toluene derivatives.[4]

Numerous DG designs have since been developed, expanding on Yu's work.[3d,5] However, the DGs are often bespoke for a particular substitution process, require stepwise syntheses and attachment *via* functional groups (FGs) which are themselves non-ideal for subsequent derivatisation (*e.g.* amides).[6] Consequently, the synthetic versatility of the DGs is limited. A single, more general, *meta*-selective DG, tethered *via* a synthetically versatile FG would reduce the current need for many individually bespoke systems (Scheme 1).

We identified the boronic acid FG as an attractive foundation for such a *meta*-selective DG. Boronic acids are ubiquitous in organic synthesis, with a wealth of transformations available for their derivatisation.[7,8] Their propensity to undergo transmetalation precludes their direct use in metal catalysed C–H functionalisations however.[9,10] Selective transition metal insertion into the desired, comparatively inert, C–H bond over the C–B bond must therefore be engineered to allow boronic acids to be exploited as the foundation of the envisioned DG.

Such selectivity has been demonstrated by Suginome *et al.*, who developed anthranilamide (aam) and 2-(1*H*-pyrazole-3-yl)aniline (pza) boronate DGs which enable *ortho*-directed C–H functionalisations.[11] Using these DGs, selective C–H silylations, alkynylations and borylations are possible using iridium, ruthenium or rhodium catalysts, with retention of the protected boronic acid FGs.

N-Methyliminodiacetic acid (MIDA) boronate esters, popularised by Burke *et al.*, similarly suppress B → M transmetalation, allowing the selective Suzuki–Miyaura coupling of boronic acids in the presence of masked MIDA boronates, under anhydrous conditions.[12] This reactivity profile, combined with their ease of introduction and deprotection, and the fact that *N*-tethered moieties are held in enforced proximity to the parent boronic acid by the rigid bicyclic system, make the MIDA boronate an attractive scaffold upon which to base a DG.[13]

We describe herein the development of a novel MIDA derivative for the *meta* selective C(sp^2)–H functionalisation of aryl boronic acids. The MIDA-DG is simple to attach and remove, with quantitative recovery possible. The DG enables Pd-catalysed C–H functionalisation of aryl boronic acids, at room temperature and under aerobic conditions, with retention of

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† Electronic supplementary information (ESI) available. CCDC 1961105. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0sc00230e

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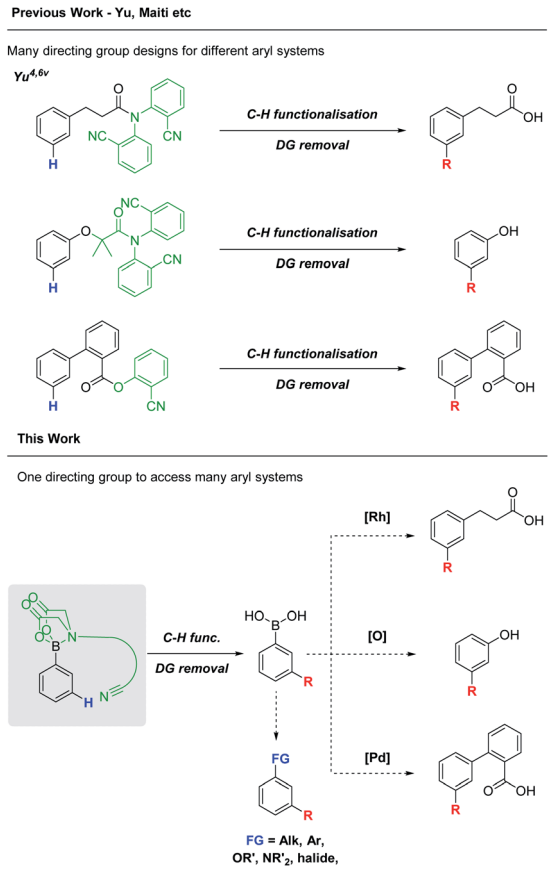


Scheme 1 A comparison between previously developed, bespoke *meta*-DGs and a general boron-tethered *meta*-DG.

the boronic acid FG. On deprotection, the functionalised boronic acids can be derivatised into numerous other FGs using established boronic acid chemistry. Lastly, we demonstrate the utility of MIDA-DG boronates by using iterative C–H functionalisation/cross-coupling procedures to access diverse polysubstituted aromatic systems.

When considering the design of a MIDA-tethered DG, two general principles were identified: that MIDA boronates are unstable towards strongly basic reagents and nucleophilic solvents,[12b] and that electron-withdrawing groups adjacent to the B–N bond were anticipated to weaken the strength of this interaction, causing the MIDA ligand to become more labile.

Consequently, DG design focused on a cyanophenol moiety, attached *via* an *O*-alkyl linker to the nitrogen of the iminodiacetic acid.

The aryl ether linkage was anticipated to impart a minimal detrimental effect on the MIDA B–N bond, while allowing for a cyclophane-like macrocyclic transition state to be accessed.[3d,4]

A number of DGs were synthesised and screened using conditions based on those reported for *meta* C–H alkenylation (Fig. 1).[3d,4,5] Product formation was initially observed with the simple 2-cyanophenol based system **2**, as well as ethyl cinnamate **1**, formed after deprotection and oxidative Heck coupling. Changes to the 2-cyanophenol motif, investigating sterically biasing the direction of the nitrile DG (**3** and **4**), increasing its Lewis basicity (**5**), or varying the nitrile position (**6**) did not lead

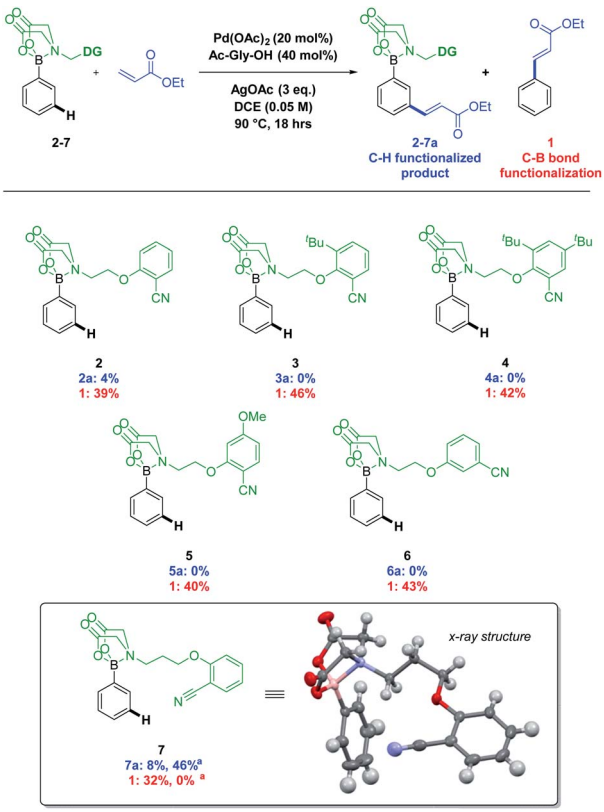
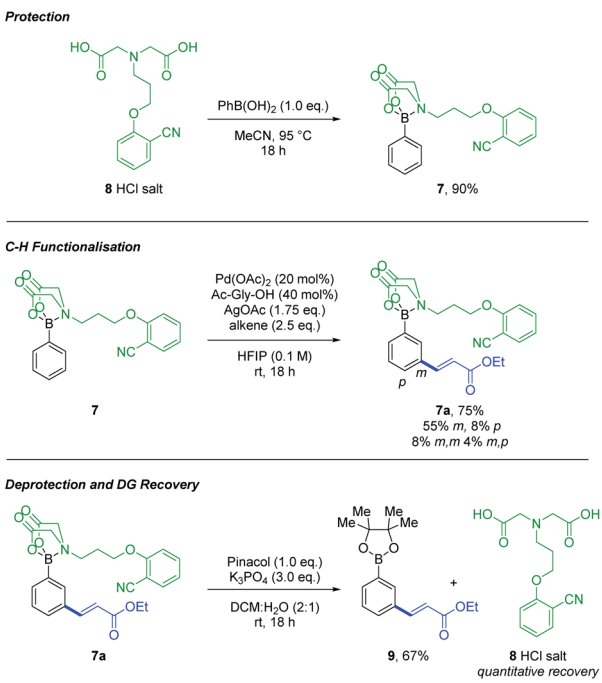


Fig. 1 Screening of DG designs against C–H alkenylation conditions. Reactions performed on 0.05 mmol scale, yields calculated using ^{1}H NMR against a CH_2Br_2 internal standard. [a] HFIP (0.1 M), AgOAc (1.0 eq.), 50 °C used with **7**, resulting in 46% yield as a mixture of 32% *meta* (**7a**), 6% *para*, 5% di *meta*–*meta* and 3% di *meta*–*para* isomers.



Scheme 2 MIDA-DG **8** allows protection of boronic acids, functionalisation *via* C–H insertion and is simple to deprotect with quantitative recovery.

to improved performance. However, increasing the length of the linker from ethyl to propyl (**7**) resulted in a doubling of the yield and a concomitant drop in formation of by-product **1**.

Switching solvent to HFIP, a privileged solvent in C–H functionalisation protocols,[14,15] and lowering temperature to 50 °C, led to a further increase in yield (Fig. 1, **7**[a]), along with the formation of *para* and di-functionalised products. A design of experiment (DOE) approach was taken to optimise the conditions (see ESI†). The optimisation process led to the surprising discovery that functionalisation occurred at room temperature, which is unusual for a transition metal catalysed C–H functionalisation process (Scheme 2, middle).[6u]

The MIDA-DG boronate **7** can easily be accessed from the MIDA-DG **8** simply by heating with phenylboronic acid (Scheme 2). All MIDA-DG boronates synthesised thus far have been bench-stable, free-flowing solids, stable for extended periods (>6 months) and to column chromatography using silica gel. Lastly, the MIDA-DG salt **8** is fully recoverable and reusable after deprotection. An unmodified phenylboronic acid MIDA ester was submitted to the optimised conditions, yielding no alkenylated product and indicating the necessity of the directing motif for achieving reactivity (see ESI†).

A 3 × 3 array was devised to investigate the reaction scope, incorporating electron-donating to electron-withdrawing substituents in the *ortho*, *meta* and *para* positions (Fig. 2, left). Yields varied from 33% to 79%, with electron-withdrawing ester groups (**16a–18a**) requiring longer reaction times. *Ortho* substituents gave a more complex mixture of regioisomers, as the *meta* positions are no longer equivalent or blocked. It appears that electron-withdrawing groups strengthen the PG ability of the MIDA-DG, while the opposite was true for electron-donating substituents, especially the *para*-methoxy analogue (**12a**), where significant degradation occurred. This may reflect donation of electron density weakening the B–N dative bond. The regioselectivity could be increased by employing a more sterically encumbered Ac-Val-OH ligand in place of Ac-Gly-OH (**14a**[b]).

Other functionalised aryl boronic acids were also investigated. Bromo (**19a** and **20a**) and fluoro (**21a**) substituents are tolerated under the conditions, with selective C–H functionalisation occurring in preference to oxidative insertion. The alkenylated products provide interesting handles for further S_NAr or cross-coupling chemistry. 2-Naphthylboronic acid (**22a**) gave two regioisomers at the 4- and 8-positions, with the former being the major product. 3,5-Dimethyl analogue **23a** gave a good yield of the *para* product selectively. The reaction is amenable to scale-up to gram scale (**7a**[c]), with quantitative recovery of the DG after further functionalisations (see Scheme 4).

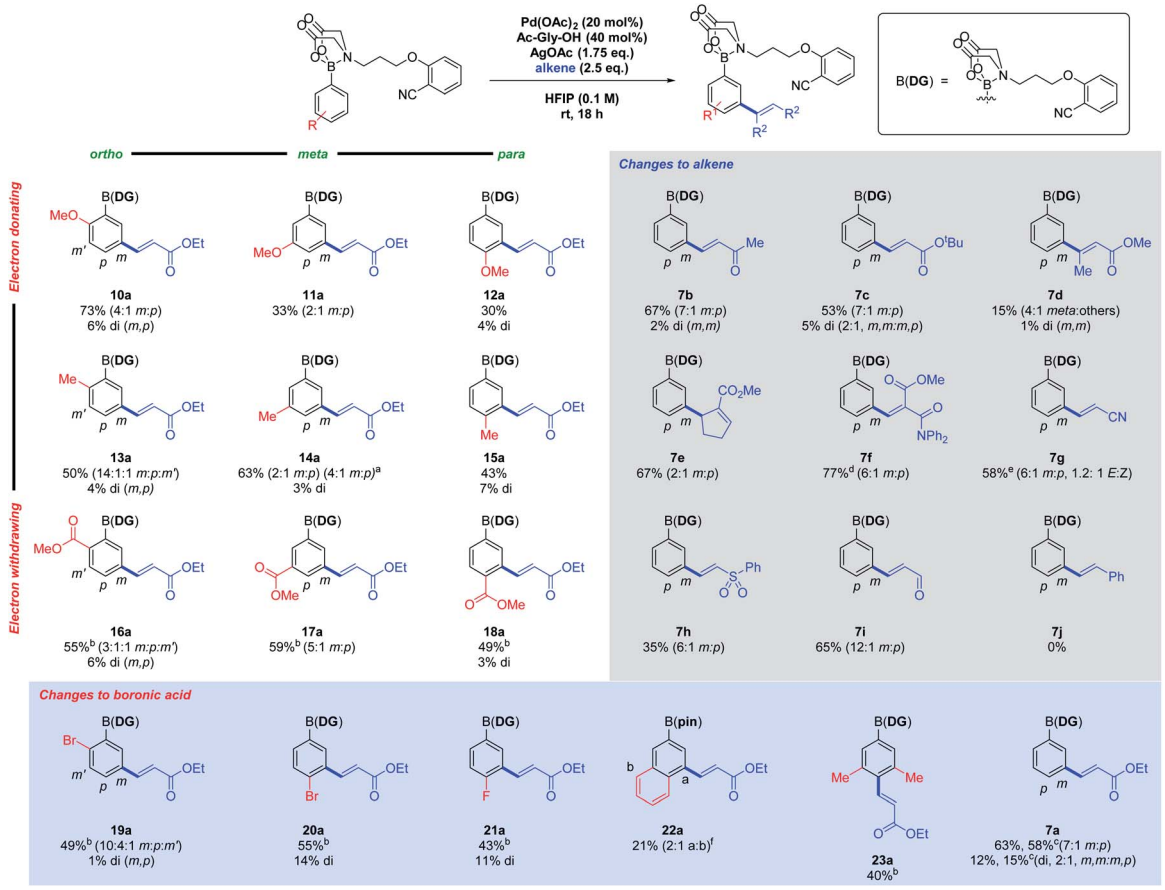


Fig. 2 The scope of the C–H alkenylation reaction. Reactions performed on 0.3 mmol scale, isolated yields. [a] Ac-Val-OH (40 mol%), 40 °C used. [b] Reaction time 48 h. [c] Average yield of 4 and 3 mmol scale reactions. [d] 1.2 eq. of alkene used. [e] 2.0 eq. alkene used, reaction time 48 h. [f] Reported yield is over 2 steps following synthesis of the pinacol boronate ester.

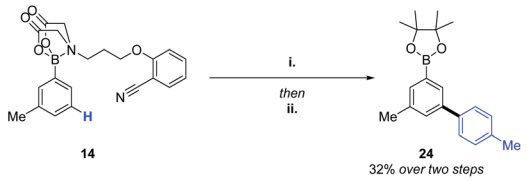
The scope of the alkene coupling partner was next investigated (Fig. 2, right). Ketone (**7b**), nitrile (**7g**), sulfone (**7h**) and aldehyde (**7i**), FGs were all suitable alkene activating groups. Competition between the acrylonitrile and the MIDA-DG **7** for catalyst co-ordination led to extended reaction times. A cyclic alkene was tolerated, yielding only one alkene regioisomer (**7e**). A 1,1-heterodisubstituted alkene featuring a diphenylamide was successful (**7f**), demonstrating the tolerance of secondary amide FGs and that fewer equivalents of alkene can be utilised. *N*,*N*-Dimethylacrylamide, styrene (**7j**) and diethyl vinylphosphonate were unreactive under the standard conditions.

In all cases, the alkenylated products were converted to the pinacol esters using a one-pot procedure (see ESI†), allowing unambiguous characterisation of products.

Nitrile DGs have shown activity in C(sp^2)–H acetoxylations, using a suitable oxidant to access a putative Pd^{IV} intermediate.[5] Building upon this, *meta* selective C–H acetoxylations were successfully achieved using $PhI(OAc)_2$ as oxidant. Using a 3-methylboronic acid MIDA-DG ester **14** model system, a DOE approach was again applied to optimise the reaction conditions (see ESI†). The scope of the reaction was then investigated using the same 3 × 3 grid to assess the effects of sterics and electronics on yield and regioselectivity (Fig. 3).

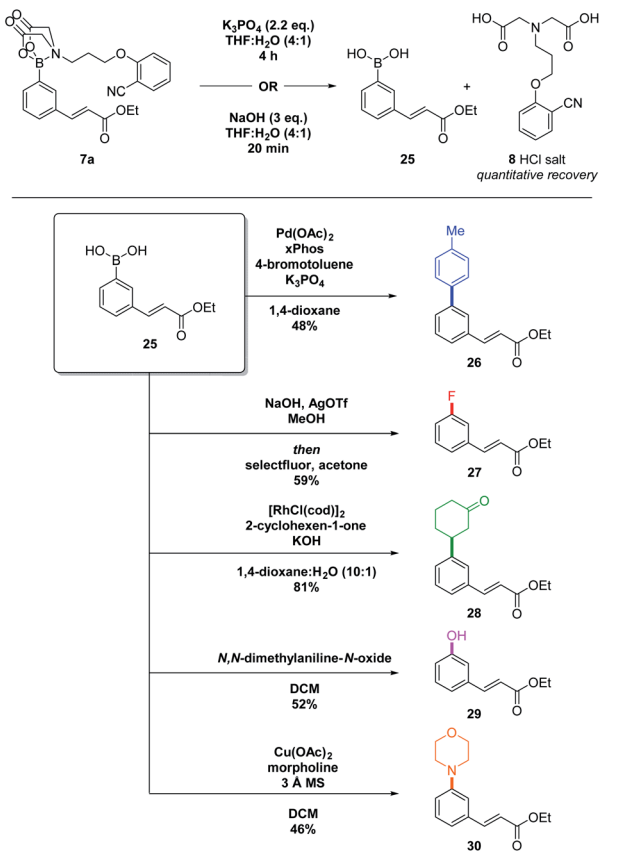
Electron-donating groups (**10b–12b**) again resulted in increased degradation – lowering the reaction temperature from 40 °C to room temperature reduced this and led to an increase in yield. Increased sensitivity to steric bulk was observed relative to the alkenylation reactions particularly with methyl substituents (**13b–15b**), potentially due to the involvement of a sterically encumbered hexacoordinate Pd^{IV} intermediate. The rate was also reduced when using electron-withdrawing groups (**16b–18b**) and full conversions were not achieved. With the phenylboronic acid MIDA-DG ester **7**, 70% yield (6 : 1 *meta* : *para*) was obtained (see ESI†).

The success of the MIDA-DG in achieving C–H alkenylations and acetoxylations, led us to perform a brief screen of C–H arylation conditions.[16] Gratifyingly, the transformation was successful, allowing access to biphenyl product **24** *via* the selective C–H coupling of one organoboron species in the presence of another (Scheme 3).



Scheme 3 (i) $Pd(OAc)_2$ (40 mol%), Ac-Gly-OH (40 mol%), 4-methylphenylboronic acid pinacol ester (2.0 eq.), Ag_2CO_3 (2.0 eq.), Cs_2CO_3 (2.0 eq.), HFIP (0.1 M), rt, 18 h, 52%. (ii) Pinacol (1.0 eq.), K_3PO_4 (3.0 eq.), H_2O, THF, DCM, rt, 18 h, 62%.

Removal of the DG is facile and can be performed using NaOH, or K_3PO_4, with quantitative recovery of the MIDA-DG **8** (Scheme 4, top).[17]



Scheme 4 Deprotection and derivatisation of C–H functionalised aryl MIDA-DG boronate. The boronic acid was used directly after deprotection without purification. All yields given are over two steps.

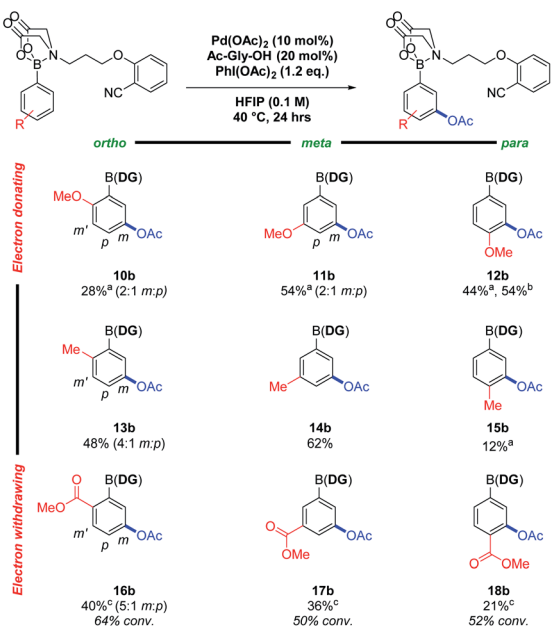
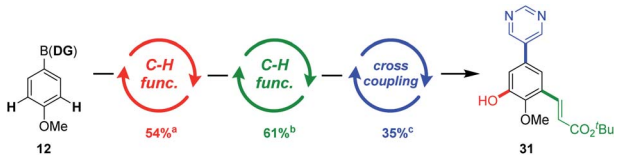


Fig. 3 Scope of the C–H acetoxylation reaction. Reactions were performed on a 0.2 mmol scale, isolated yields. [a] Reactions performed at room temperature. [b] Reaction performed at room temperature, for 18 h, on 0.9 mmol scale. [c] Reaction time 48 h.

The deprotected boronic acid can subsequently be used in numerous transformations (Scheme 4). Suzuki–Miyaura (→**26**), Chan–Lam (→**30**) and Rh-catalysed conjugate addition reactions (→**28**) all proceeded well. A chemoselective oxidation using *N*,*N*-dimethylaniline-*N*-oxide (→**29**) and a fluorination reaction (→**27**) also achieved good yields over the two-steps. The telescoped deprotection–functionalisation procedure allows access to a broad range of motifs, including those that would be difficult to access *via* alternative methods.

Burke *et al.* were able to develop an automated iterative synthesis platform using the unusual properties of MIDA boronates on silica.[12e] Pleasingly, MIDA-DG boronates display similar properties, allowing for their facile purification using the 'catch and release' method. Reaction mixtures can be loaded directly onto silica and washed with Et_2O to remove organic by-products, while the MIDA-DG-containing components remain 'caught'. After washing, MIDA-DG boronates can be selectively 'released' using a more polar solvent.

In this manner, an iterative C–H functionalisation/cross-coupling procedure was envisaged, enabling access to polysubstituted aromatic systems, in just three catalytic steps using the 'catch and release' purifications (Scheme 5). To demonstrate the feasibility of this approach, the heterotetrasubstituted arene **31** was expediently accessed using this method. Importantly, the procedures appear to be amenable to automation using the platform developed by Burke.



Scheme 5 An iterative C–H functionalisation/cross-coupling procedure allows access to 1,3,5-trisubstituted aromatic systems. [a] $Pd(OAc)_2$ (10 mol%), Ac-Gly-OH (20 mol%), $PhI(OAc)_2$ (1.2 eq.), HFIP (0.1 M), rt, 18 h. [b] $Pd(OAc)_2$ (20 mol%), Ac-Gly-OH (40 mol%), *tert*-butyl acrylate (2.5 eq.), AgOAc (1.75 eq.), HFIP (0.1 M), rt, 18 h. [c] $Pd(OAc)_2$ (10 mol%), xPhos (20 mol%), 5-bromopyrimidine (1.0 eq.), K_3PO_4 (3.0 eq.), 1,4-dioxane : H_2O (4 : 1), 75 °C, 18 h.

Conclusions

In conclusion, a new MIDA derivative **8** has been developed which condenses to aryl boronic acids, enabling their *meta*-selective C–H functionalisation at room temperature. Installation of the DG and subsequent C–H functionalisation are operationally simple and use commercially available reagents. Removal of the DG is fast, occurs under mild conditions and provides access to synthetically useful aryl boronic acids with quantitative recovery of the MIDA-DG **8**. Finally, the technique enables iterative C–H functionalisation/cross-coupling pathways and holds the potential for future automation. Studies to expand the breadth of transformations possible with the MIDA-DG **8** are underway.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We acknowledge financial support from Imperial College London, the EPSRC (PhD Studentship, A. F. W.), and the Royal Society for a University Research Fellowship (C. J. C.). We thank Dr Li-Jie Cheng for early prototype work, Alexander Dudnik for helpful discussions during the concept stage, Ben Deadman for assistance performing DOE optimisation and Peter Haycock for NMR assistance.

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