

Direct Light-Enabled Access to α -Boryl Radicals: Application in the Stereodivergent Synthesis of Allyl Boronic Esters

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Abstract: Operationally simple strategies to assemble boron containing organic frameworks are highly enabling in organic synthesis. While conventional retrosynthetic logic has engendered many platforms focusing on the direct formation of C–B bonds, α -boryl radicals have recently reemerged as versatile open-shell alternatives to access organoborons via adjacent C–C bond formation. Direct light-enabled α -activation is currently contingent on photo- or transition metal-catalysis activation to efficiently generate radical species. Here, we disclose a facile activation of α -halo boronic esters using only visible light and a simple Lewis base to enable homolytic scission. Intermolecular addition to styrenes facilitates the rapid construction of highly versatile *E*-allylic boronic esters. The simplicity of activation permits the strategic merger of this construct with selective energy transfer catalysis to enable the complimentary stereodivergent synthesis of *Z*-allylic boronic esters.

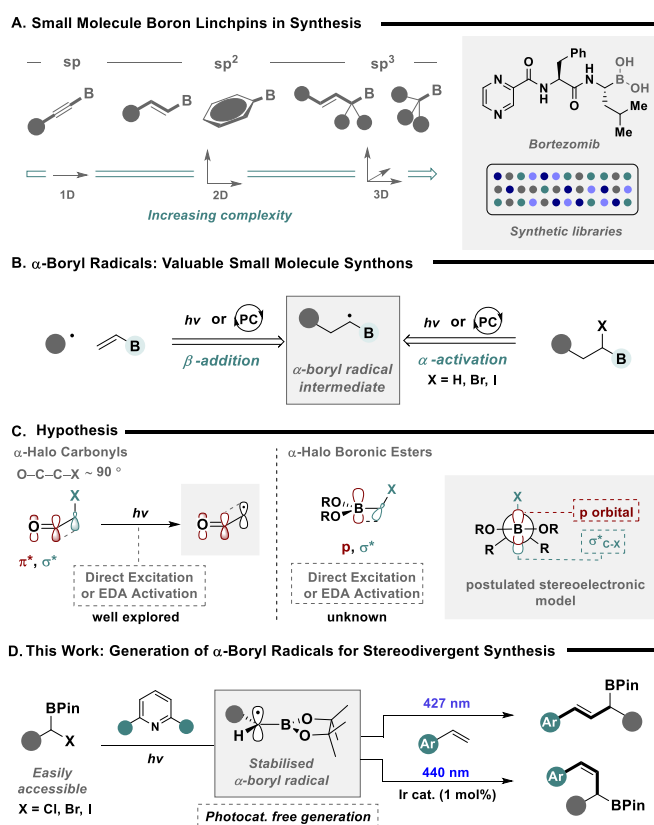
The prominence of organoboron motifs in contemporary synthesis reflects the operational advantages and dexterity conferred by this unique exit vector.¹ The ability to modulate the hybridisation state of the adjacent carbon atom enables practitioners of organic synthesis to manipulate 1D, 2D, or 3D chemical space at will, and to replace the C(sp²/sp³)–B bond using a suite of well-established methods (Figure 1A).² Importantly, the structural and electronic nuances of organoboron species are not restricted to synthesis and are finding application in chemical sensing³ and medicinal chemistry:⁴ boronic acids or esters are frequently leveraged as molecular antennae for (bio)molecular recognition.⁵ The versatility of organoboron motifs across the small molecule spectrum, and particularly in medicinal chemistry where 3D topologies are being intensively investigated,⁶ has created demand for the development of efficient methods to generate C(sp³)–B centres containing a boron linchpin.

Whilst conventional retrosynthetic logic has culminated in a plenum of C–B bond forming processes,⁷ disconnecting the adjacent σ -bond has been less-intensively investigated.⁸ Motivated by the emergent popularity of α -boryl radicals as promising open-shell alternatives,⁹ opportunities exist to complement existing borylation methods by radical-based paradigms to enable the rapid construction of saturated organoboron motifs (Figure 1B). Whereas early reports on the generation of α -boryl radicals leveraged radical initiators,¹⁰ this has been superseded by photochemical platforms to enable in situ generation via two distinct pathways; β -addition or α -activation.⁹ The former has gained much attention in recent years and relies on independent radical generation via direct excitation or photoredox activation, followed by addition to a vinyl or strained organoboron species.^{9b} Intriguingly, subsequent reactivity of the α -boryl radical is often governed by boron hybridisation.¹¹ Addition to organometallic-derived boronates has been leveraged to generate elegant pairing with 1,2-metalate rearrangements,¹² while addition to vinyl boronic esters,¹³ has also resulted in fruitful mergers with transition metal cascades.¹⁴ Light-enabled α -activation strategies, are however, comparatively under-explored but are attractive based on considerations of operational simplicity and atom economy.¹⁵ Studer and coworkers have demonstrated that H-atom abstraction of organometallic-derived organoborates enable the intramolecular transfer of carbon and boron units to the α -position.¹⁶ In addition, the activation of easily accessible α -iodides is currently achieved via photoredox,¹⁷ halogen atom transfer¹⁸ or unique examples via photoactivation in the presence of transition metal complexes.¹⁹ Since photoredox or transition-metal

catalysts are prerequisites for photo-activation in these examples, strategies that would facilitate the reactivity to be emulated by direct irradiation using only visible light would be highly enabling.

The unique stereoelectronic properties of the α -halocarbonyl system serves as a guiding tool,²⁰ with methods to generate stabilised α -radicals readily achieved using visible light.^{12a,21} Access via direct excitation or activation of Lewis base derived electron donor-acceptor (EDA) complexes (Figure 1C) enables the practitioner to combine this mild activation mode with other reactivity platforms for the controlled construction of sp^3 carbon centres.²² Given the structural similarities of α -halo boron systems (p -orbital vs. π^*),²³ we were intrigued to find that similar activation had thus far been unexplored, presumably due to formidable complications that arise by undesired boron p -orbital activation in the presence of Lewis basic additives.²⁴ Should this obstacle be overcome, we envisaged that the conformation and stereoelectronic properties could give rise to a weakened C–X bond creating a prominent precursor for mild, catalyst-free generation of α -boryl radicals.

Herein we describe the direct, visible light-enabled activation of α -halo boronic esters to readily generate α -boryl radicals in the presence of 2,6-disubstituted pyridines (Figure 1D). Intermolecular quench by styrenes enables expedient access to synthetically versatile *E*-allylic boronic esters after *in situ* elimination. Studies to determine the origin of activation revealed a substrate dependent mechanistic dichotomy, suggesting both EDA, and direct excitation enabled homolytic cleavage is operational. Capitalising on the mild reaction conditions, the introduction of a sensitizer enabled efficient stereodivergent access to the analogous *Z*-isomer, via selective energy transfer, further expanding accessibility of chemical space.



Scheme 1. A) Synthetic utility of organoboron compounds. B) Light-enabled *in situ* formation α -boryl radicals. C) Inspiration and hypothetical origin of catalyst-free activation mode. D) Catalyst-free generation of α -boryl radicals: A platform for stereodivergent access to allylic boronic esters.

Cognizant of the electron-deficient nature of the α -boryl radical,²⁵ reaction optimization was explored using α -iodo BPIn (**2a**) in the presence of styrene (**3**) as an electron-rich SOMOphile (Table 1). In the absence of additives using UV-light no conversion to product was observed (Entry 1), however detection of iodine was

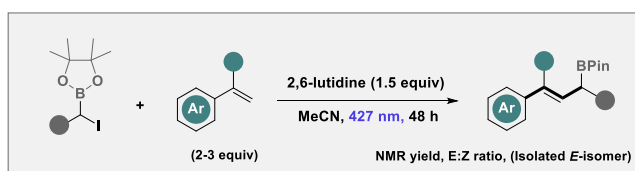
noted indicating homolytic cleavage (see SI for full details). Judicious choice of 2,6-lutidine as an additive enabled the formation of product (*E-1*) with appreciable yield and selectivity at both 370 nm and 390 nm (Entry 2 and 3). Intriguingly, longer wavelengths enhanced stereoselectivity but led to unsatisfactory conversion to product (Entry 4). This subtle nuance could be easily rectified by an increase in photon flux to afford the product in good yield and excellent selectivity (Entry 5). While translation to longer wavelengths improved selectivity, conversion to product in the given timeframe was insufficient (Entry 6). We were interested to find that the reaction was highly specific to the use of 2,6-disubstituted pyridine additives with little to no reactivity observed with a range of other additives (Entry 7, see SI for full additive screen). Translation of model reaction conditions to α -iodo BPin (**2b**) was inefficient, presumably due to a loss in steric hinderence at the α -halo precursor leading to undesired reactivity (Entry 8). Modulating steric properties of the additive restored reactivity and selectivity (Entry 9), while control reactions demonstrated that both additive and light were required for the target transformation (Entries 10 and 11).

Table 1. Optimisation of reaction conditions.^[a]

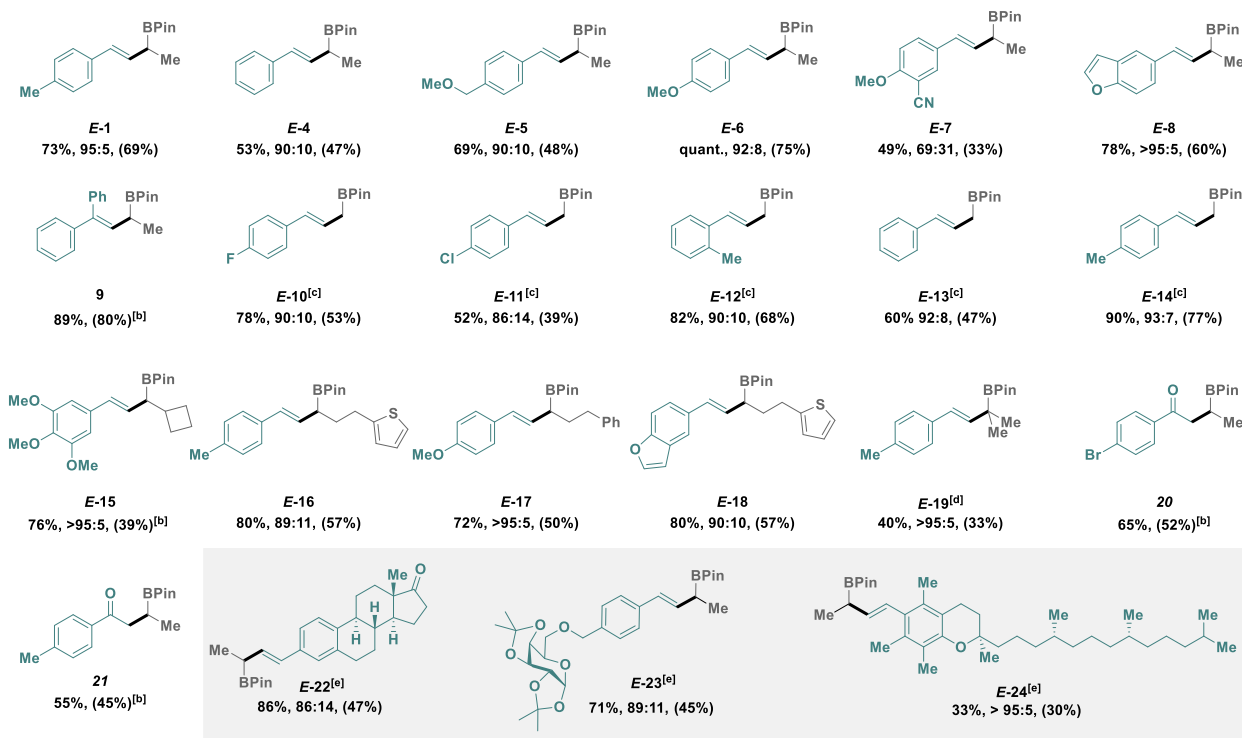
Entry	●	Irradiation wavelength	Additive	Yield ^[b] [%]	<i>E/Z</i> ^[b]
1	Me	370 nm	–	0	n.d.
2	Me	370 nm	2,6-lutidine	53	85:15
3	Me	390 nm	2,6-lutidine	57	79:21
4	Me	427 nm	2,6-lutidine	18	94:6
5^[c]	Me	427 nm	2,6-lutidine	73	95:5
6 ^[c]	Me	440 nm	2,6-lutidine	37	99:1
7 ^[c]	Me	427 nm	Et ₃ N	0	n.d.
8 ^[c]	H	427 nm	2,6-lutidine	26	69:31
9^[c]	H	427 nm	2,6-dtbpy	90	93:7
10	Me	–	2,6-lutidine	0	n.d.
11 ^[c]	Me	427 nm	–	0	n.d.

[a] Standard conditions: 2a or 2b (0.2 mmol, 1 equiv.), 3 (3 equiv.), additive (1.5 equiv.), Kessil lamp, MeCN (0.05 M), rt, 48 h. [b] Determined by ¹H NMR spectroscopy against a known internal standard (1,3,5-trimethoxybenzene). [c] Reaction carried out using two Kessil lamps. Dtbpy = di-tert-butylpyridine.

Having established a set of general reaction conditions, the scope and limitations were established (Scheme 2). Pleasingly, the protocol was amenable to a range of styrenes including electron-rich (*E-1*, *E-5*, and *E-6*) and electron-neutral systems (*E-4* and *E-12*) which favoured the *E*-isomer in good yield and selectivity. Intriguingly, electron-rich heterocycles, typically prone to reactivity with electron-deficient radicals, were also permitted (*E-8*, *E-16*, and *E-18*). Furthermore, while electron-deficient halides (*E-10* and *E-11*) were tolerated as styrene coupling partners, mesomerically electron-withdrawing groups led to depreciated yields (< 40% NMR yield, see SI for full details), presumably due to a mismatch in radical philicity with the electron deficient α -boryl radical.²⁵ The α -phenyl derivative (**9**), was isolated in 80% yield, while ortho-substituted examples (*E-12*) also proved to be effective. The reaction was very much tolerant of modifications to the α -iodo boronic ester, enabling efficient reactivity with secondary (*E-10* to *E-14*), tertiary (*E-15* to *E-18*) and quaternary (*E-19*) precursors. It is pertinent to note, increased substitution (*E-19*) required an increase in reaction temperature for appreciable coupling. Intermolecular radical traps could be efficiently extended to silyl enol ethers enabling the rapid generation of β -boryl ketones (**20** and **21**). Finally, expansion of the scope to common, biologically relevant frameworks included a modified estrone derivative (*E-22*), D-galactose derivative (*E-23*) and the sterically encumbered natural product-derived tocopherol example (*E-24*). Despite concerted efforts, non-styrenyl systems were found to be unreactive under model reaction conditions (see SI for full details).



Substrate Scope ^[a]



Scheme 2. Exploring the substrate scope. [a] Reactions were performed in MeCN on a 0.2 mmol scale using α -iodo BPin (1 equiv.), styrene (3 equiv.), 2,6-lutidine (1.5 equiv.) under 427 nm irradiation. NMR yield and *E:Z* ratio was determined by ¹H NMR spectroscopy against a known internal standard (1,3,5-trimethoxybenzene). To aid characterisation of isolated material, the *E*-isomer was isolated after *in situ* oxidation to the corresponding allylic alcohol; [b] Isolated as the boronic acid, pinacol ester; [c] 2,6-dtbpy (1.5 equiv.) was used; [d] The reaction was heated to 60 °C; [e] Styrene (2.0 equiv.) was used.

Given our initial stereoelectronic rationale as a means of postulated activation, we aimed to discern this on a structural basis investigating single point modifications of the core scaffold (Figure 1A). Introducing a stronger C–X bond suppressed reactivity, suggesting bond dissociation energy as a pivotal factor.²⁶ However, formal activation of these substrates could be readily enabled by the simple inclusion of NaI via an *in situ* Finkelstein exchange.²⁷ Occupation of the boron p-orbital inhibited activation, further supporting stereoelectronic effects as the origin for bond activation. X-ray crystallography unveiled a dihedral angle of ca. 86°,²⁸ increasing the stereoelectronic similarities in the ground state to the venerable Ahn-Eisenstein model (Figure 1B).²⁰ Having suitably established the requirement of the boron p-orbital, additive and C–I bond as a prerequisite for activation, we investigated the origin of photoactivation via UV/vis spectroscopy (Figure 1C). The presence of α -iodo precursor **2a** at model reaction concentration showed no absorption in the emission region of the Kessil light source suggesting direct irradiation and homolytic cleavage was inefficient (Figure 1C (i), grey). However, after stirring with 2,6-lutidine, a band with a substantial bathochromic shift appeared ($\lambda_{\text{max}} \sim 400$ nm) most likely due to the formation of an EDA complex (Figure 1C (i), red).^[22d] Consciously aware of the stark differences in steric parameters of the 2,6-dtbpy system we also investigated precursor **2b** in the presence of 2,6-dtbpy (Figure 1C (i), green). To our surprise, no EDA was detected despite this system showing comparable reactivity under model reaction conditions. Irradiating a reaction mixture at 427 nm containing precursor **2b** and 2,6-dtbpy revealed a new band with $\lambda_{\text{max}} \sim 364$ nm (Figure 1C (ii), grey). While this band and coloration may suggest formation of an EDA complex, this was instead attributed to triiodide formation based on commercial reagents and control experiments [$\lambda_{\text{max}} \sim 364$ nm] (Figure 1C (ii), red and green respectively).²⁹ The formation of the

triiodide species, does however, indicate efficient homolytic cleavage of the C–X bond to generate the respective α -boryl and iodine radical.³⁰ It is pertinent to note, the inclusion of styrene reagent had no effect on UV/Vis properties of the EDA or triiodide (see SI for full details). With these data describing the origin of photoactivation, we investigated the presence of radicals and possible chain processes. Radical clock experiments provided strong evidence for the generation of both an α -boryl and benzylic radical while quantum yield excluded the possibility of an efficient chain process (see SI for full details). With the absence of a chain process we looked to push the boundaries of this reactivity further in a competition experiment (Figure 1D). Despite an excess of α -iodo silane **30**, reactivity was completely selective for α -halo boron activation underpinning the opportunity for chemoselective activation.

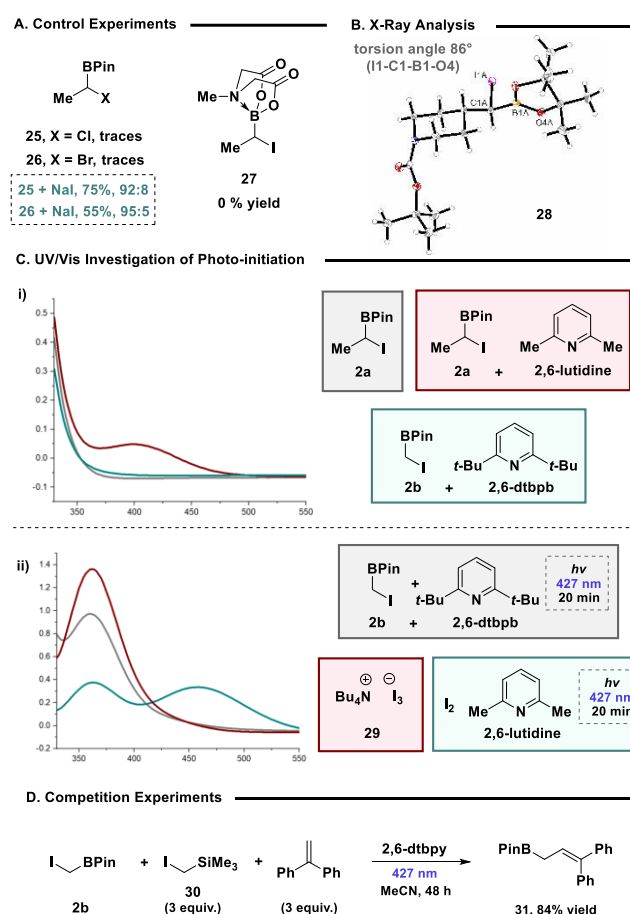


Figure 1. Mechanistic studies. A) Structural analysis of core scaffold. B) Crystal structure of compound **28** CCDC number - 2249285. Thermal ellipsoids are shown at 50% probability. C) UV/Vis analysis of reaction components. D) Competition experiments highlighting selective activation of **2b**.

Taking all results in to consideration, we tentatively propose the following mechanism as operational (Figure 2). While the formation of an EDA complex using **2a** and 2,6-lutidine is clear by UV/Vis, the large oxidation potentials of pyridine derivatives renders single electron-transfer (SET) unlikely.³¹ We propose in this case, EDA or aggregation³² aids in homolytic cleavage of the weak C–I bond to form the desired α -boryl radical **32** (supported by radical clock) and an iodine radical stabilised by 2,6-lutidine (**34**).³³ The electron-deficient α -boryl radical can then engage styrene to form a benzylic radical **33** (supported by radical clock). Translation of the benzylic radical to the *E*-isomer product can proceed via two possible mechanisms. Recombination or radical polar cross-over to the benzylic iodide, can allow closed shell elimination via the pyridine derived base. The absence of a chain mechanism suggests SET occurs from an iodine radical and not another molecule of **2**. The presence of iodine radicals can also enable H-atom abstraction via an open shell mechanism as observed in literature.³⁴ Further evidence of homolytic cleavage comes from the detection of iodine and the triiodide salt (**35**). This occurs via iodine radical recombination and subsequent salt quenching of iodine by the base.

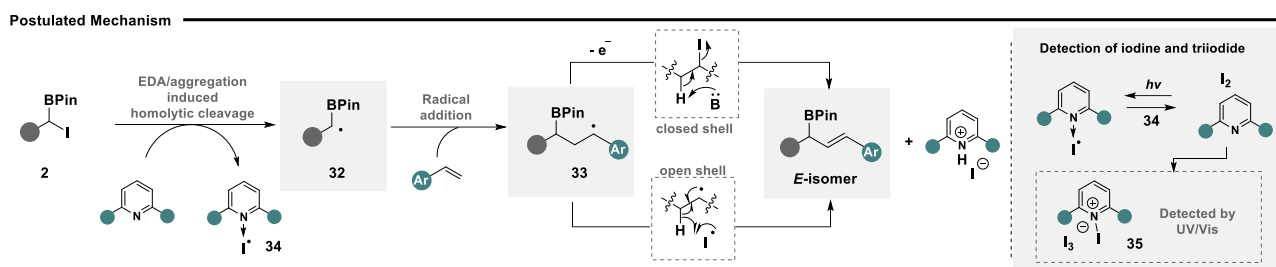
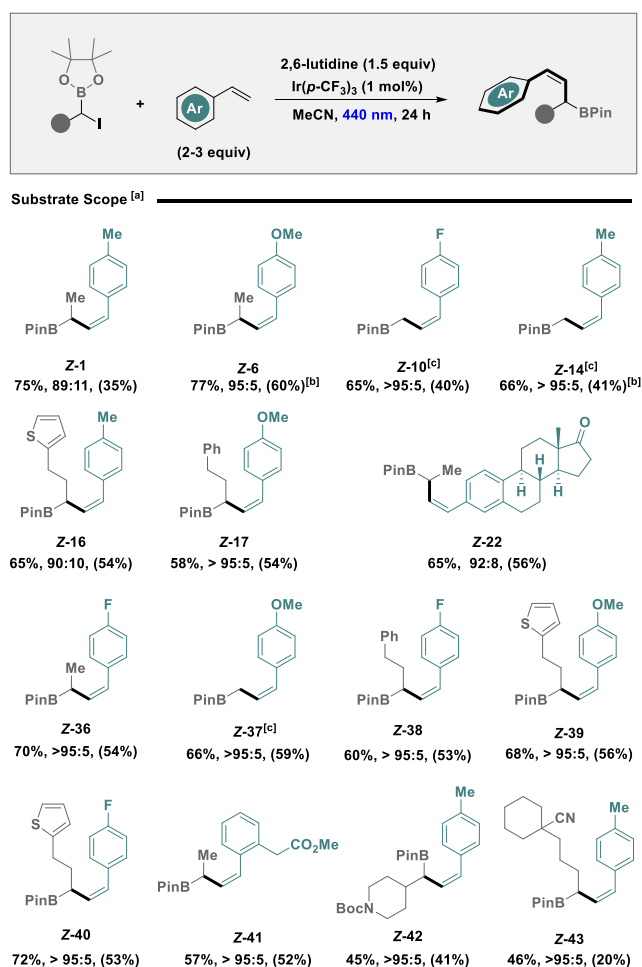


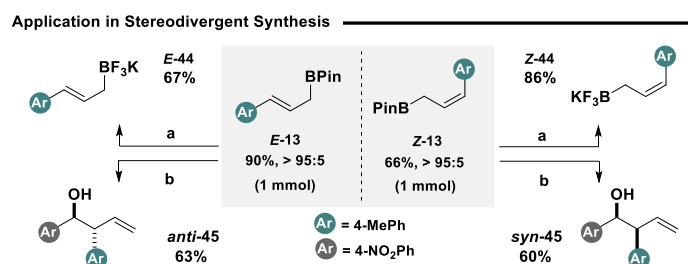
Figure 2. Postulated mechanism.

The overarching goal of this study was to develop a mild photocatalyst free method for the generation of α -boryl radicals, with the vision to easily pair this activation mode with other catalysis paradigms. Given the synthetic utility of the generated *E*-allylic boronic esters, we anticipated that merging our protocol with photocatalytic energy transfer would enable the efficient translation to the corresponding *Z*-isomer via geometric isomerisation (Scheme 3).³⁵ The realisation of which would provide the user with stereodivergent access to both isomers, significantly expanding the accessible chemical space. Optimisation identified Ir(*p*-CF₃)₃ as a suitable sensitizer enabling the reaction to be run at longer wavelength (440 nm) and shorter reaction times (See SI for full details). Intriguingly, reaction efficiency was contingent on catalyst triplet energies and not photoredox properties, as determined by catalyst screening and cyclic voltammetry analysis. The developed conditions enabled reactivity with both electron-rich (**Z-1**, **Z-6**, **Z-14**, **Z-16**, and **Z-17**) and electron-deficient styrenes (**Z-10**, **Z-36**, **Z-38**, and **Z-40**) furnishing the *Z*-isomer with excellent levels of stereoselectivity. The reaction could also proceed in the presence of electron-rich heterocycles (**Z-16**, **Z-39**, **Z-40**, and **Z-42**) and biologically relevant frameworks (**Z-22**) with high efficiency. Finally, the use of various α -iodo boronic esters was also tolerated including secondary (**Z-10**, **Z-14**, **Z-37**) and tertiary (**Z-38** to **Z-43**) examples.



Scheme 3. Exploring the substrate scope of Z-isomer. [a] Reactions were performed in MeCN on a 0.2 mmol scale using α -iodo BPin (1 equiv.), styrene (3 equiv.), 2,6-lutidine (1.5 equiv.), Ir(*p*-CF₃)₃ (1 mol%) under 440 nm irradiation. NMR yield and *E*:*Z* ratio was determined by ¹H NMR spectroscopy against a known internal standard (1,3,5-trimethoxybenzene). To aid characterisation of isolated material, the *Z*-isomer was isolated after *in situ* oxidation to the corresponding allylic alcohol; [b] The *Z*-isomer was isolated as the boronic acid, pinacol ester; [c] 2,6-dtbpv (1.5 equiv.) was used.

To demonstrate the power of our complimentary divergent process, we looked to probe our reaction at larger scale, and explore subsequent reactivity of the corresponding isomers (Scheme 4). Despite an apparent dependence on photon flux, the reaction was unperturbed on 1 mmol scale enabling efficient formation of **E-13** and **Z-13** in 90% and 66% respectively.³⁶ Both isomers could be easily transformed to the trifluoroborate (**E-44** and **Z-44**) with retention of stereochemistry. Similarly, stereospecific allylation with an electron-deficient aldehyde was successful with both isomers to access **anti-45** and **syn-45** in good yields.



Scheme 4. Stereodivergent applications in synthesis: a) **13** (1 equiv.), KF (4 equiv.), L-tartaric acid (2.05 equiv.), MeCN/MeOH, rt; b) **13** (1 equiv.), 4-nitro benzaldehyde (1 equiv.), MeCN, 50 °C.

In summary, we have developed an efficient, operationally simple method for the *in situ* generation of α -boryl radicals using only light, α -halo boronic esters, and an inexpensive additive. When exposed to styrenes, this photocatalyst-free platform enables the rapid construction of synthetically useful *E*-allylic boronic esters. Capitalising on the benign activation mode, the inclusion of a sensitizer facilitated a stereodivergent approach to the corresponding *Z*-isomer. The translation of this protocol for the mild generation of α -boryl radicals to other catalysis platforms may prove expansive for the future construction of highly desirable 3D organoboron scaffolds.

Acknowledgements

We gratefully acknowledge financial support from the Max-Planck Society. A.M. and J.J.M thank the Fonds der Chemischen Industrie, FCI for funding. J.J.M thanks the Daimler and Benz Foundation for financial support. H. F. thanks the Chinese Scholarship Council for funding. C.E.A thanks the Royal Society of Edinburgh for a Saltire Early Career Fellowship. We thank Prof. Peter H. Seeberger, Dr. Oliver Dumele, Dr Craig Johnston, and Dr. Bart Pieber for scientific discussions. We thank Anna Stepanova and Mayar Elbendary for preliminary results. We thank the Mass Spec department of Freie Universität.

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