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# Chan–Lam Amination of Secondary and Tertiary Benzylic Boronic Esters

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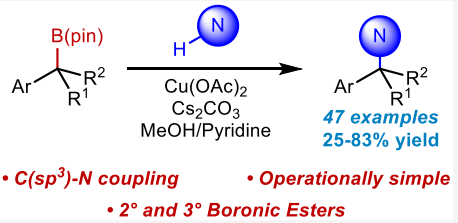
**ABSTRACT:** We report a Chan–Lam coupling reaction of benzylic and allylic boronic esters with primary and secondary anilines to form valuable alkyl amine products. Both secondary and tertiary boronic esters can be used as coupling partners, with mono-alkylation of the aniline occurring selectively. This is a rare example of a transition-metal-mediated transformation of a tertiary alkylboron reagent. Initial investigation into the reaction mechanism suggests that transmetalation from B to Cu occurs through a single-electron, rather than a two-electron process.






Advances in catalysis have enabled chemists to prepare aryl amines in a reliable and predictable manner, using methods such as the Buchwald–Hartwig,[1] Chan–Lam,[2] and Ullmann reactions.[1c,2b,3] These reactions allow amine formation from common chemical building blocks (e.g., aryl halides or arylboronic acids) and are typically operationally simple to carry out. As a result, they have found application in a range of disciplines from drug discovery and manufacture to materials science.[1b]

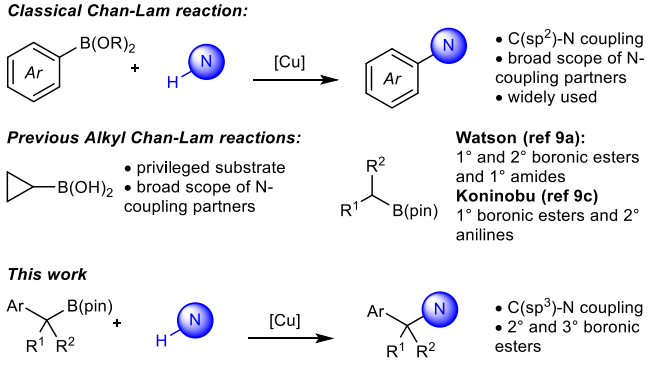
While highly desirable, the corresponding coupling methods that form alkyl C–N bonds are underdeveloped.[4] For Pd catalysis, the reductive elimination step to form alkyl–N bonds is challenging.[5] More progress has been made using Cu catalysis, through the coupling of amines with alkyl radicals, generated under photoredox catalysis from alkyl halides[6] and carboxylic acids.[7]

Because of the versatility of organoboron reagents, we are interested in developing an alkyl variant of the Chan–Lam reaction (Scheme 1). This reaction has been studied in detail for the coupling of cyclopropyl boronic acid,[8] but the reaction of alkylboronic esters has only been rarely reported.[9] Advances in this area would complement traditional methods to form alkyl amines, such as nucleophilic substitution and reductive amination.[10] These often suffer from the necessity of protecting group strategies, over-alkylation, and, in the case of nucleophilic substitution, the need for toxic alkylating agents.

Herein, we report a Chan–Lam coupling of secondary and tertiary benzylic boronic esters with anilines. This complements a recent report of Cu-catalyzed decarboxylative amination of benzylic carboxylic acids which was proposed to occur through a Chan–Lam type mechanism.[11,12]

As part of the ongoing investigation into Cu-catalyzed oxidative transformations of boronic esters,[13] we explored the reaction of boronic ester **1** with aniline **2a** in the presence of $Cu(OAc)_2$ and $Cs_2CO_3$ (see Table 1).[14] Heating these reagents in a mixture of MeOH and pyridine at 50 °C under air gave amine **3a**, alongside oxidation products **4** and **5** which are consistent with our previous observations.[13] The remainder of the mass is likely to be accounted for by protodeboronation of boronic ester **1** to give ethylbenzene, whose volatility means it was unable to be detected after workup. Reducing the loading of base led to an increase in amine **3a** and a decrease in the amount of alcohol **5** formed. However, in the absence of $Cs_2CO_3$, formation of ketone **4** dominated. Pleasingly, oxidation side products could be minimized by conducting the reaction under an inert atmosphere. However, this requires the use of stoichiometric loadings of $Cu(OAc)_2$, to act as both catalyst

**Scheme 1. Context of This Research**[a]




[a]pin = pinacol boronic ester.

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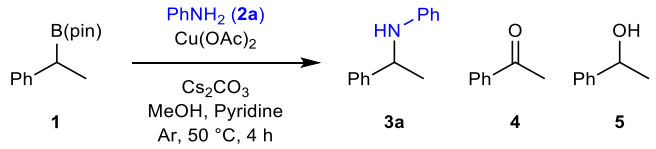
**Table 1. Evaluation of Reaction Conditions on the Yield of 3a**[a]




| | | | | | yield (%)[b] | | | |
|---|---|---|---|---|---|---|---|---|
| entry | equiv [Cu] | equiv **2a** | MeOH:Pyr | equiv $Cs_2CO_3$ | **1** | **3a** | **4** | **5** |
| 1[c] | 2 | 2 | 3:2 | 2 | 0 | 16 | 34 | 48 |
| 2[c] | 2 | 2 | 3:2 | 0.5 | 0 | 30 | 32 | 5 |
| 3[c] | 2 | 2 | 3:2 | | 0 | 6 | 60 | <5 |
| 4 | 2 | 2 | 3:2 | 0.5 | 0 | 39 | 6 | 6 |
| 5 | 2 | 4 | 3:2 | 0.5 | 23 | 48 | <5 | 6 |
| 6 | 2 | 4 | 3:1 | 0.5 | 51 | 38 | <5 | <5 |
| 7[d,e] | 2 | 4 | 3:1 | 0.5 | | 73[f] | | |
| 8[d,e] | 1 | 2 | 3:1 | 0.5 | | 36[f] | | |
| 9[d,e] | 1.5 | 3 | 3:1 | 0.5 | | 67[f] | | |
| 10[d,e] | 2 | 1 | 3:1 | 0.5 | | 46[f] | | |
| 11[d] | 0 | 4 | 3:1 | 0.5 | n.d. | 0 | <5 | 33 |
| 12[d] | 2 | 4 | 1:0 | 0.5 | 45 | 37 | <5 | 0 |

[a]Reactions performed using 0.05 mmol of **1a**. [b]Determined using $^1$H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. [c]Reaction conducted under air. [d]16 h reaction time. [e]Reactions performed using 0.50 mmol of **1a**. [f]Yield is of isolated material. n.d. = not determined.

and oxidant in the reaction. Because of the relatively low cost and benign safety profile of $Cu(OAc)_2$, we chose this compromise rather than using other chemical oxidants that have been used previously in Chan–Lam reactions.[9a,c,15] Increasing the amount of aniline **2a** led to an improved yield of **3a**, with a ratio of **2a**:$Cu(OAc)_2$ of 2:1 found to be best. Lowering the amount of pyridine in the solvent mixture gave a better mass balance, presumably due to lower levels of protodeboronation. Finally, extending the reaction time led to complete conversion of boronic ester **1**, giving amine **3a** in excellent yield. A series of control experiments showed the necessity of $Cu(OAc)_2$ for amination to occur (entry 11). In the absence of pyridine, the efficiency of amination is reduced (entry 12). This suggests that pyridine acts to break up aggregates of $Cu(OAc)_2$, providing a higher concentration of active catalyst in solution.[16] Switching the stoichiometry to make the amine the limiting reagent did lead to coupling, albeit in moderate yield (entry 10). However, these conditions would allow an isolable amount of coupling product to be obtained if the aniline substrate is prohibitively expensive.

Scheme 2 details the scope of the reaction of boronic ester **1** with a variety of anilines. In all cases, only mono-substitution of the aniline was observed. There is a clear trend that electron rich anilines react in higher yield over a 16 h time frame. Anilines substituted with electron withdrawing groups did react successfully but often required higher temperatures and prolonged reaction times for acceptable yields. Functional groups tolerated include alkenes (**3j**), amides (**3g**), aryl halides (**3e**, **3k**, **3n**), esters (**3h**), sulfides (**3d**), and trifluoromethyl groups (**3f**, **3i**). Importantly, no Ullmann coupling was observed when using substrates containing an aryl bromide or chloride.[3] C–N coupling also occurred exclusively at the aniline in the presence of a primary amide, which complements reports of amide coupling from Watson and co-workers.[9a,17] Heteroaromatic anilines were successfully coupled in modest to good yield (**3p**, **3q**). Secondary anilines can also be coupled successfully, with examples including methyl- and isopropyl-substituted anilines (**3r**, **3s**), and tetrahydroquinoline (**3t**). However, amine **3b**, when resubjected to the coupling conditions, reacted in low conversion after 48 h (**3u**). This suggests why only the product of monoalkylation is typically observed as the rate of the second alkylation is much slower by comparison. We have briefly explored the generality of our conditions with alkylamines. Morpholine did undergo coupling to form amine **3v**, though with low efficiency. However, primary alkyl amines **6** and **7** were found to be unreactive.

We next explored the scope of the boronic ester using *p*-anisidine as the coupling partner (Scheme 3). Benzylic boronic esters containing both electron donating and electron withdrawing groups on the arene are tolerated. Trifluoromethyl-substituted boronic ester **8f**, however, reacted slowly. Aryl halides and ortho substituents on the arene are also tolerated. Extension of the alkyl chain was possible, with groups containing ethers, azides, and alcohols tolerated (**9l**–**9o**). Primary benzylic boronic ester **8p** reacted smoothly and only gave the product of monoalkylation. The reaction conditions were successfully applied to allylic boronic esters **8q** and **8r** to form allylic amines in good yield. The reaction of 2-methylallylboronic ester **8r** with *p*-anisidine did give a mixture of mono- and dialkylated products, but this is the only boronic ester for which we have observed dialkylation. In comparison, aliphatic boronic ester **8s** showed low reactivity under these conditions.

Methods using tertiary boronic esters to form C–N bonds are currently limited to the preparation of primary amines.[18] Using our conditions, we were pleased to observe the successful coupling of boronic ester **10a** with a range of primary anilines (Scheme 4). This is a rare example of a tertiary boronic ester reacting under transition metal catalysis.[19] Unlike secondary boronic esters, no reaction occurred between *N*-methylaniline and boronic ester **10a**, presumably due to the increased steric congestion from these substrates. Interestingly, amination of dibenzylboronic esters proceeded at room temperature, except $CF_3$-containing boronic ester (**11f**). Monobenzylic tertiary boronic ester, however, required a reaction temperature of 50 °C to give **11g** in reasonable yield within 16 h. In contrast, *tert*-butyl pinacol boronic ester was unreactive under the reaction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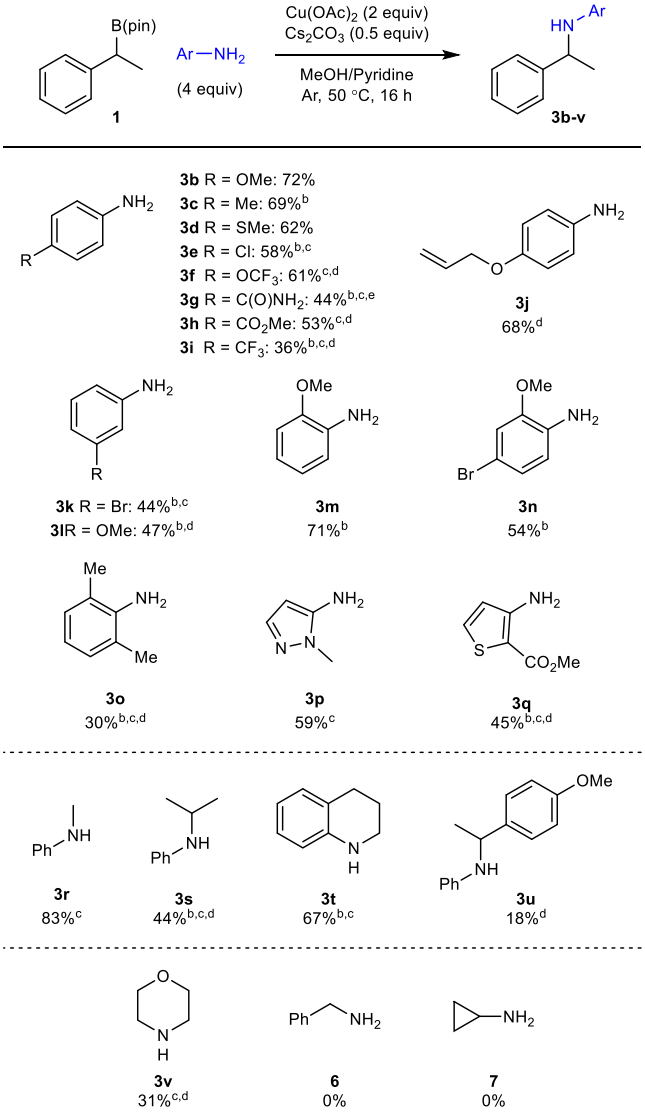
**Scheme 2. Scope of Anilines in the Amination of Boronic Ester 1**[a]

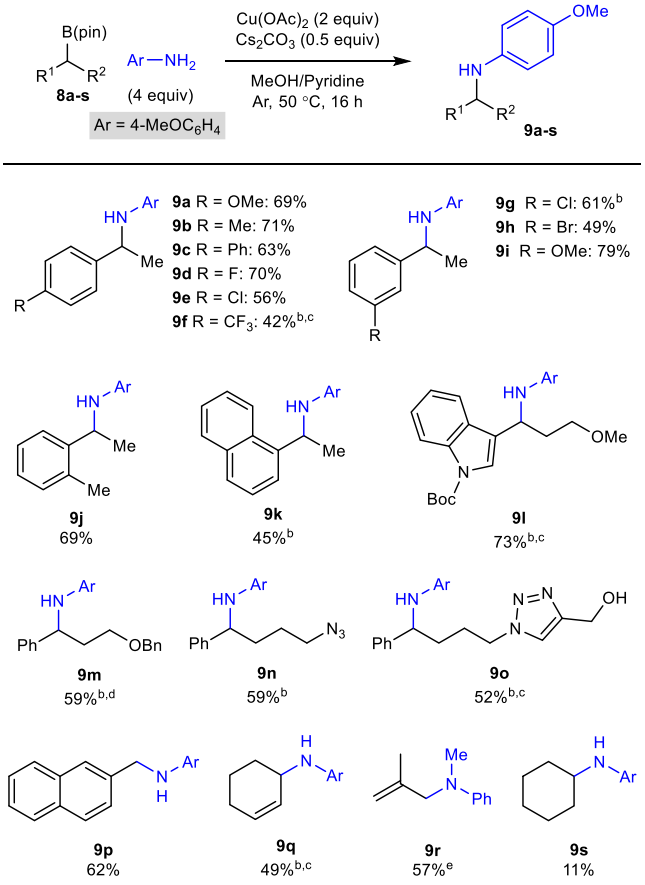



[a]Reactions were conducted on a 0.5 mmol scale. Yields reported are of isolated material of the corresponding product. [b]Oxidation of remaining boronic ester using $H_2O_2$/NaOH was performed prior to isolation of the amine product. [c]Reaction conducted at 65 °C. [d]Reaction time of 48 h. [e]Reaction time of 36 h.

conditions. While the yields of coupling are generally lower than with secondary boronic esters, the method can produce useful amounts of these otherwise hard to make C-tertiary amines.

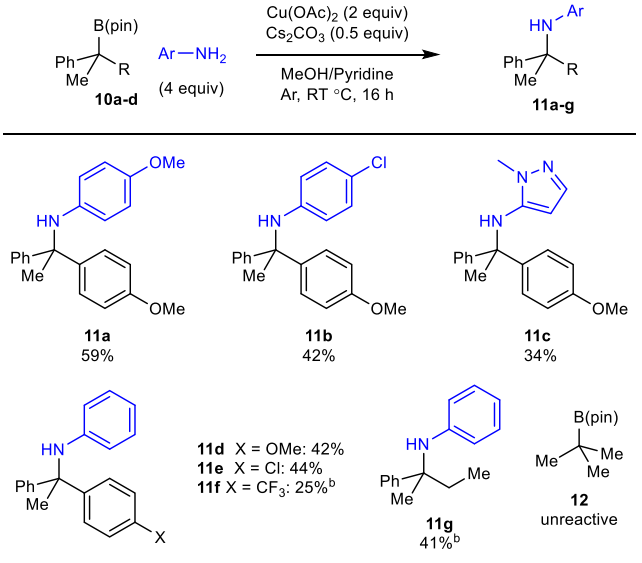
Interestingly, when *p*-anisidine was reacted with tertiary boronic ester **13**, alongside C-N coupling product **14**, we also observed a product of C-C coupling (**15**, isolated as thiourea **16**, Scheme 5). While this reactivity was not seen between *p*-anisidine and secondary boronic esters, a reaction of 4-aminophenol with **1** did give a mixture of products from C-N (**17**), C-O (**18**), and C-C (**19**) coupling. Single isomers of both **15** and **19** were observed, with X-ray crystallography of the corresponding thiourea of **19** confirming arylation occurs ortho to nitrogen.[20] We have assigned **16** through analogy. The selectivity is consistent with electrophilic aromatic substitution reactions, suggesting the formation of **15** and **19** may involve a carbocation intermediate.

**Scheme 3. Scope of Boronic Esters in the Amination with *p*-Anisidine**[a]




[a]Yields reported are of isolated material. [b]Reaction conducted at 65 °C. [c]Reaction time of 48 h. [d]Reaction time of 32 h. [e]Reaction conducted with *N*-methylaniline instead of *p*-anisidine.

**Scheme 4. Amination of Tertiary Boronic Esters**[a]




[a]Reactions were conducted on a 0.5 mmol scale. Yields reported are of isolated material. [b]Reaction conducted at 50 °C.

We wanted to learn more about the reaction mechanism, as little information is available about the reaction of alkylboronic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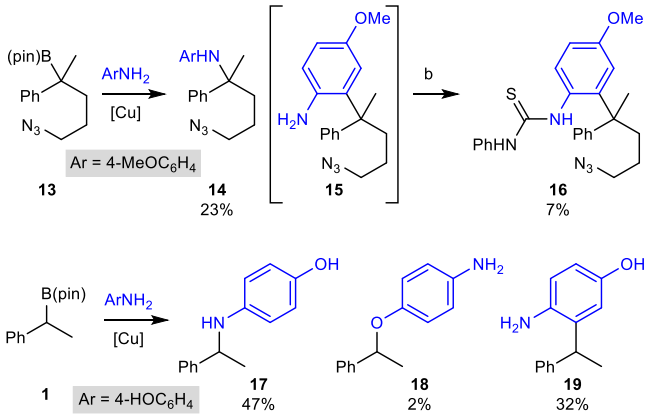
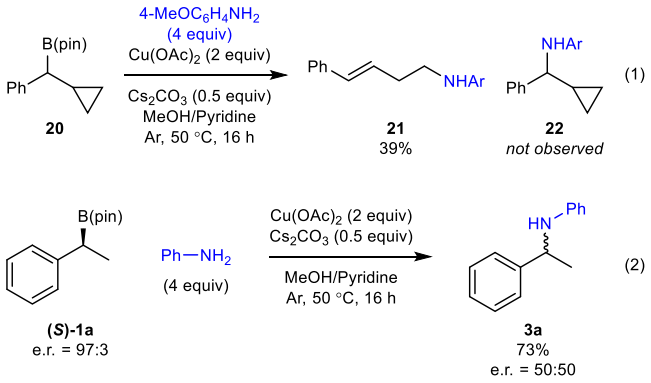
**Scheme 5. Observation of C−C Bond Formation**[a]




[a]Reaction conditions for amination reactions: $Cu(OAc)_2$ (2 equiv), $Cs_2CO_3$ (0.5 equiv), MeOH/Pyr (3:1), 25 °C (reaction with **13**) or 50 °C (reaction with **1**). Yields reported are of isolated material. [b]Phenyl isothiocyanate (1.1 equiv), hexane:MeCN:$Et_3N$ (1:0.1:0.1).

esters with Cu salts. We started by performing a radical clock experiment, using cyclopropane containing boronic ester **20** (eq 1). This reacted to give amine **21**, with ring opening of the cyclopropane, without observation of the corresponding benzyl amine **22**. This suggests that the boronic ester serves as a radical precursor,[21] with a two-electron transmetalation to Cu unlikely. This is in contrast to our previous investigation into the Cu-catalyzed oxidation of benzylic boronic esters, where oxidation of **20** occurred without ring opening of the cyclopropane.[13] While we cannot rule out further oxidation of the radical to a carbocation, the observed product distribution indicates this is likely to be a minor pathway, due to stability of cyclopropylcarbinyl cations which would presumably promote formation of **22**.




Consistent with the formation of a benzyl radical is the reaction of enantiomerically enriched boronic ester (*S*)-**1a** (eq 2). This reacted smoothly to form amine **3a**, but with complete loss of stereochemical information. However, we cannot rule out whether configurational instability of an alkyl-Cu intermediate is the cause of stereoablation.[22]

In conclusion, we have developed an operationally simple Chan−Lam coupling of secondary and tertiary boronic esters with anilines. The amination reaction is a rare example of a transition-metal-mediated reaction using a tertiary alkylboron coupling partner. Monoalkylation of the amine occurs selectively, and the conditions tolerate a diverse range of functional groups. Initial investigation into the reaction mechanism suggests that transmetalation from boron to copper is likely to occur through a single-electron process. Further C−heteroatom bond forming processes from alkylboronic esters are under development and will be reported in due course.

## EXPERIMENTAL SECTION

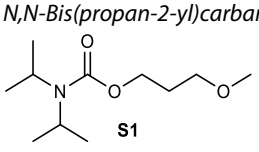
**General.** All reagents and solvents used were supplied by commercial sources without further purification unless specified. Aniline (distillation) and *p*-anisidine (recrystallization from ethanol) were purified before use. All air-sensitive reactions were carried out under a nitrogen or argon atmosphere using oven-dried apparatus. Anhydrous $Et_2O$, THF, and toluene were dried and purified by passage through activated alumina columns using a solvent purification system. All petroleum ether used was 40−60 °C petroleum ether. All reactions which required elevated temperatures were heated using a stirrer hot plate and oil bath with an external probe to control the temperature. Thin layer chromatography (TLC) was performed on aluminum-backed plates precoated with silica. Compounds were visualized by exposure to UV light or by dipping the plates into solutions of vanillin or $KMnO_4$, followed by heating. All flash chromatography was carried out using silica gel mesh 40−63. It should be noted that the time taken for chromatography of boronic esters should be kept to a minimum to avoid extensive decomposition and reduced yields.

Infrared spectra were recorded on a PerkinElmer 100 FT instrument on the neat compound. NMR spectra were recorded on Bruker Advance 400 and 500 instruments at the indicated 101, 128, 126, 377, 400, and 500 MHz as dilute solutions in the indicated deuterated solvent. NMR spectra were recorded at ambient temperature unless otherwise stated. All chemical shifts ($\delta$) are reported in parts per million (ppm) relative to the residual protio solvent ($\delta$H: $CHCl_3$ = 7.27 ppm, DMSO = 2.50 ppm, or $CH_3CN$ = 1.94 ppm) or the solvent itself ($\delta$C: $CDCl_3$ = 77.0 ppm, DMSO = 39.5 ppm, or $CH_3CN$ = 1.32, 118.3 ppm). All multiplets are designated by the following abbreviations: s = singlet, br s = broad singlet, d = doublet, dt = doublet triplet, td = triplet doublet, ddd = doublet of doublets of doublets, q = quartet, br q = broad quartet, m = multiplet. All coupling constants ($J$) are reported in Hertz (Hz). Assignments of $^1$H NMR signals were made using 2D NMR spectra, typically HSQC and HMBC experiments. $^{13}$C NMR data were acquired as DEPT-Q experiments as standard. For samples where quaternary carbons were not observed by DEPT-Q, $^{13}$C NMR spectra were acquired as decoupled spectra. $^{19}$F NMR spectra were acquired as decoupled spectra. High-resolution mass spectra were recorded using either electrospray ionization (ESI) or electron ionization (EI) by the Chemistry Mass Spectrometry Facility in the Faculty of Science, University of Sheffield. HPLC analysis was carried out using the Chromatography Facility at the Department of Chemistry, University of Sheffield. Melting points were measured using a Linkam HFs91 heating stage, used in conjunction with a TC92 controller, and are uncorrected.

Single crystal X-ray intensity data were collected at 100 K on a Bruker D8 Venture diffractometer equipped with a Photon 100 CMOS detector using a Cu K$\alpha$ microfocus X-ray source from crystals mounted in fomblin oil on a MiTiGen microloop and cooled in a stream of cold $N_2$. Data were corrected for absorption using empirical methods (SADABS)[23] based upon symmetry equivalent reflections combined with measurements at different azimuthal angles.[24] The crystal structures were solved and refined against $F^2$ values using ShelXT[25] for solution and ShelXL[26] for refinement accessed via the Olex2 program.[27] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions with idealized geometries and then refined by employing a riding model and isotropic displacement parameters.

**Synthesis of Substrates.** Boronic esters (**1**, **8a**−**p**, **20**)[13] and boronic esters (**8q**, **8r**)[28] were prepared by literature methods.

*3-Methoxypropyl N,N-Bis(propan-2-yl)carbamate (**S1**).*





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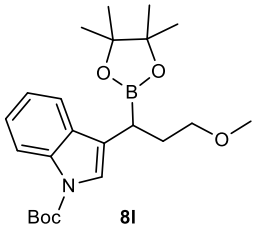
*N*,*N*-Diisopropylcarbamoyl chloride (3.96 g, 24.2 mmol) was added to a solution of 3-methoxy propanol (2.2 mL, 23 mmol) and triethylamine (3.4 mL, 24 mmol) in $CH_2Cl_2$ (77 mL). The mixture was heated at reflux for 18 h, cooled to room temperature, and diluted with $H_2O$ (30 mL). The mixture was extracted with DCM (3 × 20 mL). The combined organic layers were washed with brine (20 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude material was purified by flash chromatography (10% EtOAc/petroleum ether) to give *carbamate* **S1** (3.88 g, 77%) as a yellow oil. **IR** 2969, 2932, 1687, 1435, 1289 $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 4.16 (2H, t, $J$ = 6.4 Hz, C(O)OC**$H_2$**), 4.13−3.55 (2H, m, 2 × $CH_3$C**H**), 3.47 (2H, t, $J$ = 6.4 Hz, C**$H_2$**O$CH_3$), 3.34 (3H, s, OC**$H_3$**), 1.92 (2H, p, $J$ = 6.4 Hz, O$CH_2$C**$H_2$**), 1.25−1.15 (12H, m, 4 × CHC**$H_3$**). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 155.7 (C), 69.6 ($CH_2$), 61.7 ($CH_2$), 58.6 ($CH_3$), 46.3 (br, 2 × CH), 29.4 ($CH_2$), 20.9 (4 × $CH_3$). **HRMS** (Q-TOF) $m/z$: [M + H]$^+$ Calcd for $C_{11}H_{24}NO_3^+$ 218.1756; found 218.1751.

*(±)-tert-Butyl 3-[3-Methoxy-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl]-1H-indole-1-carboxylate (**8l**).*



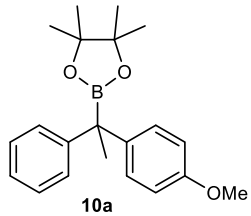
**8l**

Using a modification of the procedure by Aggarwal and co-workers,[29] a Schlenck flask containing carbamate **S1** (0.576 g, 2.65 mmol) was backfilled with nitrogen three times. TMEDA (0.55 mL, 3.7 mmol) and anhydrous $Et_2O$ (10.2 mL) were added, and the mixture was cooled to −78 °C. *s*-BuLi (1.3 M in cyclohexane, 2.8 mL, 3.7 mmol) was added dropwise, and the mixture was stirred at −78 °C for 4 h. *t*-Butyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole-1-carboxylate (0.700 g, 2.04 mmol) was added dropwise. A solution of $MgBr_2$ in $Et_2O$ (0.378 g, 2.04 mmol, 1 M) was added dropwise, and the mixture was stirred at 34 °C for 18 h. Toluene (10 mL) was added, and the mixture was heated to 90 °C for 18 h. $H_2O$ (20 mL) and $Et_2O$ (15 mL) were added, and the mixture was extracted with $Et_2O$ (3 × 15 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude material was purified by column chromatography (5% EtOAc/petroleum ether) to give *boronic ester* **8l** (0.422 g, 50%) as a colorless oil. **IR** 2977, 2930, 1729, 1452, 1368, 1142 $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 8.11 (s, 1H), 7.66−7.61 (1H, m, Ar**H**), 7.41 (1H, s, Ar**H**), 7.31−7.27 (1H, m, Ar**H**), 7.24−7.17 (1H, m, Ar**H**), 3.48−3.36 (2H, m, C**$H_2$**O$CH_3$), 3.33 (3H, s, OC**$H_3$**), 2.66−2.57 (1H, m, BC**H**), 2.25−2.14 (1H, m, BCHC**$H_A$**C**$H_B$**), 2.05−1.93 (1H, m, BCHC$H_A$C**$H_B$**), 1.66 (9H, s, 3 × C(O)OCC**$H_3$**), 1.22 (6H, s, 2 × BOCC**$H_3$**), 1.21 (6H, s, 2 × BOCC**$H_3$**). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 149.8 (C), 135.6 (C), 130.7 (C), 124.0 (CH), 122.3 (C), 122.0 (CH), 121.5 (CH), 119.6 (CH), 115.0 (CH), 83.5 (2 × C), 83.0 (C), 72.0 ($CH_2$), 58.5 ($CH_3$), 31.0 ($CH_2$), 28.2 (3 × $CH_3$), 24.7 (4 × $CH_3$), 18.4 (BCH). **$^{11}$B NMR** (128 MHz, $CDCl_3$) $\delta$ 33.7. **HRMS** (Q-TOF) $m/z$: [M + Na]$^+$ Calcd for $C_{23}H_{34}BNNaO_5^+$ 438.2428; found 438.2422.

*(S)-4,4,5,5-Tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane (**(S)-1**).* Following the procedure by Yun and co-workers,[30] a mixture of CuCl (20.8 mg, 0.211 mmol), KOtBu (56.7 mg, 0.506 mmol), and (*R*)-DTBM-Segphos (250.0 mg, 0.211 mmol) in anhydrous toluene (5.0 mL) was stirred for 30 min under an atmosphere of nitrogen. Pinacolborane (10.1 mmol, 1.46 mL) was added to the reaction mixture and stirred for 10 min. Styrene (8.44 mmol, 0.97 mL) was added, and the mixture was stirred at 60 °C for 18 h. The reaction mixture was cooled, filtered through a pad of Celite eluting with EtOAc, and concentrated *in vacuo*. The product was purified by column chromatography (5% $Et_2O$/petroleum ether) to give boronic ester (***S***)-**1** (1.10 g, 54%) as a colorless oil. The data were consistent with the literature.[31] $[\alpha]_D^{21}$ +12.0 (*c* 1.00, $CHCl_3$); lit. $[\alpha]_D^{23}$ +11.9 (*c* 1.08, $CHCl_3$) 97:3 e.r. (*S*).[32] **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.33−7.19 (4H, m, Ar**H**), 7.19−7.08 (1H, m, Ar**H**), 2.45 (1H, q, $J$ = 7.5 Hz, C**H**), 1.34 (3H, d, $J$ = 7.5 Hz, CHC**$H_3$**), 1.22 (6H, s, 2 × CC**$H_3$**), 1.21 (6H, s, 2 × CC**$H_3$**). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 144.9 (C), 128.3 (2 × CH), 127.8 (2 × CH), 125.1 (CH), 83.3 (2 × C), 24.6 (2 × $CH_3$), 24.6 (2 × $CH_3$), 17.0 ($CH_3$). **$^{11}$B NMR** (128 MHz, $CDCl_3$) $\delta$ 33.5. e.r. = 97:3, measured through chiral HPLC analysis of the corresponding alcohol obtained after oxidation. HPLC (Phenomenex Cellulose-1 column (250 × 4.6 mm), IPA/hexane 10/90, flow rate = 1.0 mL/min, *l* = 254 nm), $t_R$ = 6.2 min (minor), 7.1 min (major).

*General Procedure 1: Lithiation-Borylation.* Using a modification of the procedure by Aggarwal and co-workers,[29] a Schlenk flask containing the corresponding carbamate (1.2 equiv) was backfilled with nitrogen three times. Anhydrous $Et_2O$ (0.2 M) was added, and the mixture was cooled to −78 °C. *s*-BuLi (1.3 equiv) was added dropwise, and the mixture was stirred at −78 °C for 1 h. The boronic ester (1 equiv) was added dropwise, and the mixture was stirred at −78 °C for 1 h and then at room temperature for 2 h. $H_2O$ (20 mL) and $Et_2O$ (15 mL) were added, and the mixture was extracted with $Et_2O$ (3 × 15 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*.

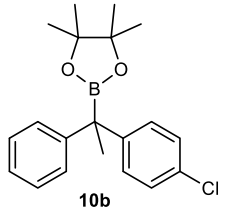
*(±)-2-[1-(4-Methoxyphenyl)-1-phenylethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**10a**).*



**10a**

The title compound was prepared according to *General Procedure 1* using 1-phenylethyl diisopropylcarbamate[33] (1.60 g, 6.42 mmol), *s*-BuLi (1.3 M in cyclohexane, 5.6 mL, 7.3 mmol), and 4-methoxyphenylboronic acid pinacol ester (1.00 g, 4.27 mmol) added in $Et_2O$ (2 mL). Flash chromatography (2% EtOAc/petroleum ether) of the crude material gave boronic ester **10a** (1.25 g, 87%) as a white solid. The data were consistent with the literature.[29] **m.p.** 64−66 °C (petroleum ether); no literature value available. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.31−7.24 (2H, m, Ar**H**), 7.25−7.20 (2H, m, Ar**H**), 7.20−7.15 (3H, m, Ar**H**), 6.86−6.80 (2H, m, Ar**H**), 3.81 (3H, s, OC**$H_3$**), 1.68 (3H, s, CC**$H_3$**), 1.22 (12H, s, 4 × OCC**$H_3$**). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 157.3 (C), 148.1 (C), 139.4 (C), 129.4 (2 × CH), 128.4 (2 × CH), 127.9 (2 × CH), 125.3 (CH), 113.3 (2 × CH), 83.7 (2 × C), 55.1 ($CH_3$), 25.9 ($CH_3$), 24.4 (4 × $CH_3$). **$^{11}$B NMR** (128 MHz, $CDCl_3$) $\delta$ 33.6.

*(±)-2-[1-(4-Chlorophenyl)-1-phenylethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**10b**).*



**10b**

The title compound was prepared according to *General Procedure 1* using 1-phenylethyl diisopropylcarbamate[33] (1.25 g, 5.03 mmol), *s*-BuLi (1.3 M in cyclohexane, 4.2 mL, 5.5 mmol), and 4-chlorophenylboronic acid pinacol ester (1.00 g, 4.19 mmol) added in $Et_2O$ (2 mL). Flash chromatography (4% EtOAc/petroleum ether) of the crude material gave boronic ester **10b** (1.38 g, 96%) as an off-white solid. The data were consistent with the literature.[29] **m.p.** 74−75 °C (petroleum ether); no literature value available. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.30−7.27 (1H, m, Ar**H**), 7.26−7.15 (8H, m, Ar**H**), 1.67 (3H, s, CC**$H_3$**), 1.21 (6H, s, 2 × OCC**$H_3$**), 1.21 (6H, s, 2 × OCC**$H_3$**). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 147.2 (C), 146.2 (C), 131.1 (C), 129.9 (2 × CH), 128.4 (2 × CH), 128.1 (2 × CH), 128.0 (2 × CH), 125.6 (CH), 83.9 (2 × C), 25.7 ($CH_3$), 24.4 (4 × $CH_3$). **$^{11}$B NMR** (128 MHz, $CDCl_3$) $\delta$ 33.1.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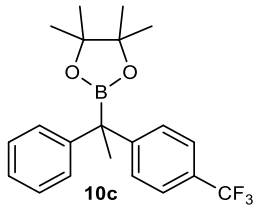
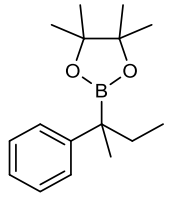
*(±)-2-[1-(4-Trifluoromethylphenyl)-1-phenylethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**10c**).*




**10c**

The title compound was prepared according to *General Procedure 1* using 1-phenylethyl diisopropylcarbamate[33] (0.551 g, 2.21 mmol), *s*-BuLi (1.3 M in cyclohexane, 1.8 mL, 2.4 mmol), and 4-trifluoromethlphenylboronic acid pinacol ester (0.50 g, 1.84 mmol) added in $Et_2O$ (2 mL). Flash chromatography (4% EtOAc/petroleum ether) of the crude material gave *boronic ester* **10c** (0.575 g, 83%) as an off white solid. **m.p.** 65−66 °C (petroleum ether). **IR** 2977, 2932, 1616, 1317, 1113 $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.53−7.49 (2H, m, Ar**H**), 7.36−7.28 (4H, m, Ar**H**), 7.22−7.18 (3H, m, Ar**H**), 1.71 (3H, s, CC**H$_3$**), 1.22 (6H, s, 2 × OCC**H$_3$**), 1.21 (6H, s, 2 × OCC**H$_3$**). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 152.2 (C), 146.6 (C), 128.8 (2 × CH), 128.4 (2 × CH), 128.2 (2 × CH), 127.6 (q, $J_F$ = 32.2 Hz, C), 125.8 (CH), 124.8 (q, $J_F$ = 3.8 Hz, 2 × CH), 124.4 (q, $J_F$ = 271.6 Hz, $CF_3$), 84.0 (2 × C), 25.6 ($CH_3$), 24.5 (2 × $CH_3$), 24.4 (2 × $CH_3$). **$^{11}$B NMR** (128 MHz, $CDCl_3$) $\delta$ 33.3. **$^{19}$F NMR** (377 MHz, $CDCl_3$) $\delta$ −62.2. **HRMS** (Q-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{21}H_{25}BF_3O_2^+$ 377.1900; found 377.1894.

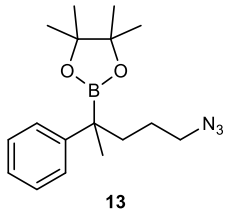
*(±)-2-(2-Phenylbut-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**10d**).*




**10d**

The title compound was prepared according to *General Procedure 1* using 1-phenylethyl diisopropylcarbamate[33] (1.92 g, 7.69 mmol), *s*-BuLi (1.3 M in cyclohexane, 6.4 mL, 8.3 mmol), and ethylboronic acid pinacol ester (1.00 g, 6.41 mmol). Flash chromatography (4% EtOAc/petroleum ether) of the crude material gave boronic ester **10d** (1.51 g, 90%) as a yellow oil. The data were consistent with the literature.[29] **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.34−7.26 (4H, m, Ar**H**), 7.17−7.11 (1H, m, Ar**H**)), 1.89 (1H, dq, *J* = 14.7, 7.4 Hz, CC**H$_A$**H$_B$), 1.72 (1H, dq, *J* = 14.7, 7.4 Hz, CCH$_A$**H$_B$**), 1.34 (3H, s, BCC**H$_3$**), 1.22 (6H, s, 2 × OCC**H$_3$**), 1.22 (6H, s, 2 × OCC**H$_3$**), 0.84 (3H, t, *J* = 7.4 Hz, $CH_2$C**H$_3$**). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 147.3 (C), 128.0 (2 × CH), 126.9 (2 × CH), 125.0 (CH), 83.2 (2 × C), 31.9 ($CH_2$), 24.6 (4 × $CH_3$), 21.0 ($CH_3$), 10.0 ($CH_3$). **$^{11}$B NMR** (128 MHz, $CDCl_3$) $\delta$ 33.7.

*(±)-2-(5-Azido-2-phenylpentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**13**).*




**13**

The title compound was prepared according to *General Procedure 1* using 1-phenylethyl diisopropylcarbamate[33] (1.19 g, 4.77 mmol), *s*-BuLi (1.3 M in cyclohexane, 4.2 mL, 5.4 mmol), and 2-(3-bromopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[34] (0.700 g, 3.32 mmol). Flash chromatography (1% EtOAc/petroleum ether) of the crude material gave *boronic ester* **13** (0.540 g, 52%) as a colorless oil. **IR** 2977, 2932, 2092, 1350, 1312, 1145 $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.33−7.28 (4H, m, Ar**H**), 7.18−7.12 (1H, m, Ar**H**), 3.25−3.17 (2H, m, C**H$_2$**N), 1.88−1.72 (2H, m, C**H$_2$**CH$_2$N), 1.55−1.42 (2H, m, CC**H$_2$**), 1.36 (3H, s, BCC**H$_3$**), 1.22 (6H, s, 2 × OCC**H$_3$**), 1.21 (6H, s, 2 × OCC**H$_3$**). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 146.4 (C), 128.2 (2 × CH), 126.8 (2 × CH), 125.3 (CH), 83.5 (2 × C), 52.1 ($CH_2$), 36.5 ($CH_2$), 24.9 ($CH_2$), 24.6 (2 × $CH_3$), 24.5 (2 × $CH_3$), 21.3 ($CH_3$). **$^{11}$B NMR** (128 MHz, $CDCl_3$) $\delta$ 33.7. **HRMS** (Q-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{17}H_{26}BN_3O_2Na^+$ 338.2016; found 338.2017.

**Experimental Procedure for the Cu-Promoted Amination of Alkylboronic Esters.** *General Procedure 2: Preparative Scale Cu-Catalyzed Amination of Alkylboronic Esters.* A flask containing the corresponding boronic ester (0.50 mmol, 1 equiv), aniline (2.00 mmol, 4 equiv), $Cu(OAc)_2$ (0.182 g, 1.00 mmol), and $Cs_2CO_3$ (0.0820 g, 0.252 mmol) was purged with argon. Methanol (1.0 mL) and pyridine (0.33 mL) were added, and the mixture was stirred at 50 or 65 °C until the reaction was complete (as determined by TLC). The mixture was cooled to room temperature, $NH_4OH$ (10 mL) was added, and the mixture was extracted with $Et_2O$ (3 × 10 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude material was purified by column chromatography.

*General Procedure 3: Preparative Scale Cu-Catalyzed Amination of Alkylboronic Esters with Oxidative Workup.* A flask containing the corresponding boronic ester (0.50 mmol, 1 equiv), aniline (2.00 mmol, 4 equiv), $Cu(OAc)_2$ (0.182 g, 1.00 mmol), and $Cs_2CO_3$ (0.082 g, 0.25 mmol) was purged with argon. Methanol (1.0 mL) and pyridine (0.33 mL) were added, and the mixture was stirred at 50 or 65 °C until the reaction was complete (as determined by TLC). The mixture was cooled to room temperature, $NH_4OH$ (10 mL) was added, and the mixture was extracted with $Et_2O$ (3 × 10 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. THF (1 mL), $H_2O$ (1 mL), and sodium perborate (0.382 g, 2.50 mmol) were added, and the mixture was stirred at RT for 1 h. The mixture was diluted with $H_2O$ (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic phases were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude material was purified by column chromatography.

*General Procedure 4: Preparative Scale Tertiary Alkyl Chan−Lam Coupling.* A flask containing the corresponding boronic ester (0.50 mmol, 1 equiv), aniline (2.00 mmol, 4 equiv), $Cu(OAc)_2$ (0.182 g, 1.00 mmol), and $Cs_2CO_3$ (0.0820 g, 0.252 mmol) was purged with argon. Methanol (1.0 mL) and pyridine (0.33 mL) were added, and the mixture was stirred at RT for 16 h. $NH_4OH$ (10 mL) was added, and the mixture was extracted with $Et_2O$ (3 × 10 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude material was purified by column chromatography.

*(±)-N-(1-Phenylethyl)aniline (**3a**).* The title compound was prepared according to *General Procedure 3* using boronic ester **1** (0.116 g, 0.501 mmol) and aniline (0.18 mL, 2.0 mmol), heating at 50 °C for 16 h. Flash chromatography (2% EtOAc/petroleum ether) of the crude material gave amine **3a** (0.0719 g, 73%) as a brown oil. The data were consistent with the literature.[35] **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.41−7.36 (2H, m, Ar**H**), 7.36−7.30 (2H, m, Ar**H**), 7.26−7.21 (1H, m, Ar**H**), 7.14−7.06 (2H, m, Ar**H**), 6.69−6.61 (1H, m, Ar**H**), 6.56−6.48 (2H, m, Ar**H**), 4.50 (1H, q, *J* = 6.7 Hz, C**H**), 4.05 (1H, s, N**H**), 1.53 (3H, d, *J* = 6.7 Hz, CHC**H$_3$**). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 147.2 (C), 145.2 (C), 129.1 (2 × CH), 128.6 (2 × CH), 126.8 (CH), 125.8 (2 × CH), 117.2 (CH), 113.2 (2 × CH), 53.4 (CH), 25.0 ($CH_3$).

*(±)-4-Methoxy-N-(1-phenylethyl)aniline (**3b**).* The title compound was prepared according to *General Procedure 2* using boronic ester **1** (0.116 g, 0.501 mmol) and *p*-anisidine (0.246 g, 2.00 mmol), heating at 50 °C for 16 h. Flash chromatography (4% EtOAc/petroleum ether) of the crude material gave amine **3b** (0.0823 g, 72%) as a yellow oil. The data were consistent with the literature.[35] **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.45−7.39 (2H, m, Ar**H**), 7.39−7.33 (2H, m, Ar**H**), 7.39−7.33 (1H, m, Ar**H**), 6.75 (2H, d, *J* = 8.9 Hz, Ar**H**), 6.52 (2H, d, *J* = 8.9 Hz, Ar**H**), 4.46 (1H, q, *J* = 6.7 Hz, C**H**), 3.82 (1H, s, N**H**), 3.74 (3H, s, OC**H$_3$**), 1.54 (3H, d, *J* = 6.7 Hz, CHC**H$_3$**). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 151.8 (C), 145.4 (C), 141.5 (C), 128.5 (2 × CH), 126.8 (CH), 125.8 (2 × CH), 114.7 (2 × CH), 114.5 (2 × CH), 55.7 ($CH_3$), 54.2 (CH), 25.1 ($CH_3$).

*(±)-4-Methyl-N-(1-phenylethyl)aniline (**3c**).* The title compound was prepared according to *General Procedure 3* using boronic ester **1** (0.116 g, 0.499 mmol) and *p*-toluidine (0.216 g, 2.00 mmol), heating at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50 °C for 16 h. Flash chromatography (2% EtOAc/petroleum ether) of the crude material gave amine **3c** (0.0729 g, 69%) as a brown oil. The data were consistent with the literature.[35] **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.41−7.34 (2H, m, Ar**H**), 7.35−7.29 (2H, m, Ar**H**), 7.25−7.18 (1H, m, Ar**H**), 6.91 (2H, d, $J$ = 8.3 Hz, Ar**H**), 6.45 (2H, d, $J$ = 8.3 Hz, Ar**H**), 4.47 (1H, q, $J$ = 6.7 Hz, NC**H**), 3.92 (1H, s, N**H**), 2.20 (3H, s, CC**H$_3$**), 1.51 (3H, d, $J$ = 6.7 Hz, CHC**H$_3$**). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 145.4 (C), 145.0 (C), 129.6 (2 × CH), 128.6 (2 × CH), 126.8 (CH), 126.3 (C), 125.8 (2 × CH), 113.3 (2 × CH), 53.6 (CH), 25.1 ($CH_3$), 20.3 ($CH_3$).

*(±)-4-(Methylthio)-N-(1-phenylethyl)aniline (**3d**).* The title compound was prepared according to *General Procedure 2* using boronic ester **1** (0.115 g, 0.495 mmol) and 4-(methylthio)aniline (0.25 mL, 2.0 mmol), heating at 50 °C for 16 h. Flash chromatography (5% EtOAc/petroleum ether) of the crude material gave amine **3d** (0.0743 g, 62%) as a brown oil. The data were consistent with the literature.[36] **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.28−7.20 (4H, m, Ar**H**), 7.17−7.12 (1H, m, Ar**H**), 7.04 (2H, d, $J$ = 8.7 Hz, Ar**H**), 6.37 (2H, d, $J$ = 8.7 Hz, Ar**H**), 4.37 (1H, q, $J$ = 6.7 Hz, NC**H**), 3.96 (1H, s, N**H**), 2.27 (3H, s, SC**H$_3$**), 1.42 (3H, d, $J$ = 6.7 Hz, CHC**H$_3$**). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 146.1 (C), 144.9 (C), 131.3 (2 × CH), 128.7 (2 × CH), 126.9 (CH), 125.8 (2 × CH), 124.0 (C), 113.8 (2 × CH), 53.5 (CH), 25.0 ($CH_3$), 19.1 ($CH_3$).

*(±)-4-Chloro-N-(1-phenylethyl)aniline (**3e**).* The title compound was prepared according to *General Procedure 3* using boronic ester **1** (0.116 g, 0.501 mmol) and 4-chloroaniline (0.256 g, 2.01 mmol), heating at 65 °C for 16 h. Flash chromatography (2% EtOAc/petroleum ether) of the crude material gave amine **3e** (0.0672g, 58%) as a brown oil. The data were consistent with the literature.[35] **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.40−7.30 (4H, m, Ar**H**), 7.27−7.21 (1H, m, Ar**H**), 7.10−7.01 (2H, m, Ar**H**), 6.52−6.32 (2H, m, Ar**H**), 4.45 (1H, q, $J$ = 6.7 Hz, NC**H**), 4.06 (1H, s, N**H**), 1.52 (2H, d, $J$ = 6.7 Hz, CHC**H$_3$**). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 145.8 (C), 144.7 (C), 128.9 (2 × CH), 128.7 (2 × CH), 127.0 (CH), 125.8 (2 × CH), 121.8 (C), 114.4 (2 × CH), 53.6 (CH), 25.0 ($CH_3$).

*(±)-α-Methyl-N-[4-(trifluoromethoxy)phenyl]-benzenemethanamine (**3f**).* The title compound was prepared according to *General Procedure 2* using boronic ester **1** (0.116 g, 0.499 mmol) and 4-(trifluoromethoxy)aniline (0.27 mL, 2.01 mmol), heating at 65 °C for 48 h. Flash chromatography (2% EtOAc/petroleum ether) of the crude material gave *amine* **3f** (0.0853g, 61%) as a yellow oil. **IR** 3420, 2968, 1613, 1512, 1248, 1153 cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.38−7.31 (4H, m, Ar**H**), 7.27−7.24 (1H, m, Ar**H**), 6.95 (2H, d, $J$ = 8.9 Hz, Ar**H**), 6.46 (2H, d, $J$ = 8.9 Hz, Ar**H**), 4.45 (1H, q, $J$ = 6.9 Hz, NC**H**), 4.10 (1H, s, N**H**), 1.53 (3H, d, $J$ = 6.9 Hz, C**H$_3$**). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 146.0 (C), 144.7 (C), 140.3 (C, q, $J_F$ = 1.9 Hz), 128.7 (2 × CH), 127.1 (CH), 125.7 (2 × CH), 122.2 (2 × CH), 120.64 ($OCF_3$, q, $J_F$ = 255.2 Hz), 113.4 (2 × CH), 53.7 (CH), 25.0 ($CH_3$). **$^{19}$F NMR** (377 MHz, $CDCl_3$) $\delta$ −58.5. **HRMS** (Q-TOF) $m/z$: $[M + H]^+$ Calcd for $C_{15}H_{15}F_3NO^+$ 282.1106; found 282.1095.

*(±)-4-(1-Phenylethylamino)benzamide (**3g**).* The title compound was prepared according to a modification of *General Procedure 3* using boronic ester **1** (0.117 g, 0.502 mmol) and 4-aminobenzamide (0.272 g, 2.01 mmol), heating at 65 °C for 36 h. The mixture was cooled to room temperature, $Et_2O$ (5 mL) was added, and the mixture was passed through a plug of Celite. Flash chromatography (3% MeOH/DCM) of the crude material gave a mixture of amine **3g** and pinacol (1:0.3, 0.0623 g). THF (1 mL), $H_2O$ (1 mL), and sodium periodate (0.060 g, 0.281 mmol) were added, and the mixture was stirred at RT for 16 h. The mixture was diluted with $H_2O$ (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic phases were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Flash chromatography (3% MeOH/DCM) of the crude material gave amine **3g** (0.0526 g, 44%) as an off-white solid. The data were consistent with the literature.[37] **m.p** 153−155 °C ($CH_2Cl_2$). No literature value. **$^1$H NMR** (400 MHz, DMSO) $\delta$ 7.53 (2H, d, $J$ = 8.6 Hz, Ar**H**), 7.46 (1H, s, N**H**), 7.39−7.33 (2H, m, Ar**H**), 7.33−7.25 (2H, m, Ar**H**), 7.22−7.14 (1H, m, Ar**H**), 6.81 (1H, s, N**H**), 6.72−6.66 (1H, m, N**H**), 6.47 (2H, d, $J$ = 8.6 Hz, Ar**H**), 4.54 (1H, q, $J$ = 6.8 Hz, NC**H**), 1.42 (3H, d, $J$ = 6.8 Hz, C**H$_3$**). **$^{13}$C{$^1$H} NMR** (101 MHz, DMSO) $\delta$ 168.4 (C), 150.8 (C), 146.1 (C), 129.3 (2 × CH), 128.8 (2 × CH), 127.0 (CH), 126.3 (2 × CH), 121.4 (C), 111.9 (2 × CH), 52.2 (CH), 24.9 ($CH_3$).

*(±)-Methyl 4-(1-Phenylethylamino)benzoate (**3h**).* The title compound was prepared according to *General Procedure 2* using boronic ester **1** (0.117 g, 0.503 mmol) and 4-methoxycarbonylaniline (0.302 g, 2.01 mmol), heating at 65 °C for 48 h. Flash chromatography (10% EtOAc/petroleum ether) of the crude material gave amine **3h** (0.0648 g, 53%) as a white solid. The data were consistent with the literature.[38] **m.p.** 101−103 °C (petroleum ether); no literature value available. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.79 (2H, d, $J$ = 8.8 Hz, Ar**H**), 7.35−7.33 (4H, m, Ar**H**), 7.27−7.22 (1H, m, Ar**H**), 6.48 (2H, d, $J$ = 8.8 Hz, Ar**H**), 4.57 (1H, q, $J$ = 6.6, NC**H**), 4.48 (1H, s, N**H**), 4.48 (1H, s, OC**H$_3$**), 1.56 (3H, d, $J$ = 6.6 Hz, CHC**H$_3$**). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 167.2 (C), 150.9 (C), 144.1 (C), 131.4 (2 × CH), 128.8 (2 × CH), 127.1 (CH), 125.7 (2 × CH), 118.3 (C), 112.1 (2 × CH), 53.0 (CH), 51.5 ($CH_3$), 24.7 ($CH_3$).

*(±)-N-(1-Phenylethyl)-4-(trifluoromethyl)aniline (**3i**).* The title compound was prepared according to *General Procedure 3* using boronic ester **1** (0.116 g, 0.501 mmol) and 4-trifluoromethylaniline (0.25 mL, 2.0 mmol), heating at 65 °C for 48 h. Flash chromatography (2% EtOAc/petroleum ether) of the crude material gave amine **3i** (0.0479 g, 36%) as a colorless oil. The data were consistent with the literature.[39] **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.39−7.34 (6H, m, Ar**H**), 7.32−7.27 (1H, m, Ar**H**), 6.57−6.53 (2H, m, Ar**H**), 4.55 (1H, q, $J$ = 6.7 Hz, NC**H**), 4.42 (1H, s, N**H**), 1.58 (3H, d, $J$ = 6.7 Hz, CHC**H$_3$**). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 149.6 (C), 144.2 (C), 128.8 (2 × CH), 127.2 (CH), 126.4 (2 × CH, q, $J_F$ = 3.8 Hz), 125.7 (2 × CH), 125.0 (C, q, $J_F$ = 270.4 Hz), 118.6 (C, q, $J_F$ = 32.5 Hz), 112.4 (2 × CH), 53.2 (CH), 24.8 ($CH_3$). **$^{19}$F NMR** (377 MHz, $CDCl_3$) $\delta$ −61.1.

*(±)-N-(1-Phenylethyl)-4-(prop-2-en-1-yloxy)aniline (**3j**).* The title compound was prepared according to *General Procedure 2* using boronic ester **1** (0.116 g, 0.500 mmol) and 4-[(prop-2-en-1-yl)oxy]aniline (0.299 g, 2.00 mmol), heating at 50 °C for 48 h. Flash chromatography (6% EtOAc/petroleum ether) of the crude material gave *amine* **3j** (0.0863 g, 68%) as a yellow oil. **IR** 3404, 3025, 2866, 1508, 1229 cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.40−7.36 (2H, m, Ar**H**), 7.36−7.30 (2H, m, Ar**H**), 7.26−7.21 (1H, m, Ar**H**), 6.72 (2H, d, $J$ = 8.9 Hz, Ar**H**), 6.47 (2H, d, $J$ = 8.9 Hz, Ar**H**), 6.03 (1H, ddt, $J$ = 17.2, 10.6, 5.4 Hz, C**H**═$CH_2$), 5.37 (1H, dd, $J$ = 17.2, 1.5 Hz, CH═C**H$_A$**H$_B$), 5.24 (1H, dd, $J$ = 10.6, 1.5 Hz, CH═CH$_A$**H$_B$**), 4.46−4.39 (3H, m, NC**H**, OC**H$_2$**), 3.80 (1H, s, N**H**), 1.51 (3H, d, $J$ = 6.7 Hz, C**H$_3$**). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 150.8 (C), 145.4 (C), 141.7 (C), 133.9 (CH), 128.6 (2 × CH), 126.8 (CH), 125.9 (2 × CH), 117.3 ($CH_2$), 115.8 (2 × CH), 114.4 (2 × CH), 69.6 ($CH_2$), 54.2 (CH), 25.1 ($CH_3$). **HRMS** (Q-TOF) $m/z$: $[M + H]^+$ Calcd for $C_{17}H_{20}NO^+$ 254.1545; found 254.1539.

*(±)-3-Bromo-N-(1-phenylethyl)aniline (**3k**).* The title compound was prepared according to *General Procedure 3* using boronic ester **1** (0.116 g, 0.501 mmol) and 3-bromoaniline (0.344 g, 2.00 mmol), heating at 65 °C for 16 h. Flash chromatography (2% EtOAc/petroleum ether) of the crude material gave amine **3k** (0.0613 g, 44%) as a brown oil. The data were consistent with the literature.[40] **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.38−7.31 (4H, m, Ar**H**), 7.29−7.23 (1H, m, Ar**H**), 6.96−6.90 (1H, m, Ar**H**), 6.78−6.74 (1H, m, Ar**H**), 6.70−6.67 (1H, m, Ar**H**), 6.44−6.37 (1H, m, Ar**H**), 4.47 (1H, q, $J$ = 6.6 Hz, C**H**), 4.10 (1H, s, N**H**), 1.53 (3H, d, $J$ = 6.6 Hz, CHC**H$_3$**). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 148.4 (C), 144.4 (C), 130.4 (CH), 128.7 (2 × CH), 127.1 (CH), 125.7 (2 × CH), 123.0 (C), 120.0 (CH), 116.0 (CH), 111.8 (CH), 53.3 (CH), 24.8 ($CH_3$).

*(±)-3-Methoxy-N-(1-phenylethyl)aniline (**3l**).* The title compound was prepared according to *General Procedure 3* using boronic ester **1** (0.120 g, 0.519 mmol) and *m*-methoxyaniline (0.251 g, 2.04 mmol), heating at 50 °C for 48 h. Flash chromatography (5% EtOAc/petroleum ether) of the crude material gave amine **3l** (0.0552 g, 47%) as a yellow oil. The data were consistent with the literature.[41] **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.39−7.31 (4H, m, Ar**H**), 7.24 (1H, t, $J$ = 7.1 Hz, Ar**H**), 7.01 (1H, t, $J$ = 8.1 Hz, Ar**H**), 6.23 (1H, dd, $J$ = 8.1, 2.1 Hz, Ar**H**), 6.16 (1H, dd, $J$ = 8.1, 1.8 Hz, Ar**H**), 6.08 (1H, dd, $J$ = 2.1, 1.8 Hz, Ar**H**), 4.49 (1H, q, $J$ = 6.7 Hz, C**H**), 4.11 (1H, s, N**H**), 3.70 (3H, s, OC**H$_3$**), 1.53 (3H, d, $J$ = 6.7 Hz, C**H$_3$**). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$


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160.6 (C), 148.6 (C), 145.1 (C), 129.8 (CH), 128.6 (2 × CH), 126.9 (CH), 125.8 (2 × CH), 106.4 (CH), 102.4 (CH), 99.3 (CH), 54.9 ($CH_3$), 53.5 (CH), 24.9 ($CH_3$).

*(±)-2-Methoxy-N-(1-phenylethyl)aniline (**3m**).* The title compound was prepared according to *General Procedure 3* using boronic ester **1** (0.116 g, 0.499 mmol) and *o*-methoxyaniline (0.23 mL, 2.0 mmol), heating at 50 °C for 16 h. Flash chromatography (4% EtOAc/petroleum ether) of the crude material gave amine **3m** (0.0801 g, 71%) as a colorless oil. The data were consistent with the literature.[42] **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.41−7.37 (2H, m, ArH), 7.36−7.30 (2H, m, ArH), 7.26−7.21 (1H, m, ArH), 6.81−6.76 (1H, m, ArH), 6.75−6.69 (1H, m, ArH), 6.66−6.59 (1H, m, ArH), 6.39−6.33 (1H, m, ArH), 4.65 (1H, s, NH), 4.50 (1H, q, $J$ = 6.6 Hz, CH), 3.91 (3H, s, $OCH_3$), 1.57 (3H, d, $J$ = 6.6 Hz, $CHCH_3$). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 146.5 (C), 145.4 (C), 137.2 (C), 128.6 (2 × CH), 126.7 (CH), 125.8 (2 × CH), 121.1 (CH), 116.3 (CH), 111.0 (CH), 109.2 (CH), 55.4 ($CH_3$), 53.3 (CH), 25.2 ($CH_3$).

*(±)-4-Bromo-2-methoxy-N-(1-phenylethyl)aniline (**3n**).* The title compound was prepared according to *General Procedure 3* using boronic ester **1** (0.119 g, 0.514 mmol) and 4-bromo-2-methoxyaniline (0.409 g, 2.02 mmol), heating at 50 °C for 16 h. Flash chromatography (2% EtOAc/petroleum ether) of the crude material gave *amine* **3n** (0.0843 g, 54%) as a light brown solid. **m.p.** 95−97 °C (petroleum ether). **IR** 3425, 2963, 2933, 1590, 1506, 1223 cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.36−7.29 (4H, m, ArH), 7.26−7.20 (1H, m, ArH), 6.85 (1H, d, $J$ = 2.1 Hz, ArH), 6.79 (1H, dd, $J$ = 8.4, 2.1 Hz, ArH), 6.17 (1H, d, $J$ = 8.4 Hz, ArH), 4.60 (1H, s, NH), 4.49−4.39 (1H, m, CH), 3.88 (3H, s, $OCH_3$), 1.55 (3H, d, $J$ = 6.7 Hz, $CHCH_3$). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 147.1 (C), 144.8 (C), 136.2 (C), 128.6 (2 × CH), 126.9 (CH), 125.7 (2 × CH), 123.6 (CH), 112.6 (CH), 111.8 (CH), 107.7 (C), 55.7 ($CH_3$), 53.2 (CH), 25.1 ($CH_3$). **HRMS** (Q-TOF) $m/z$: $[M + H]^+$ Calcd for $C_{15}H_{18}{}^{79}BrNO^+$ 306.0494; found 306.0488.

*(±)-N-(1-Phenylethyl)-2,6-dimethylbenzenamine (**3o**).* The title compound was prepared according to *General Procedure 3* using boronic ester **1** (0.116 g, 0.501 mmol) and 2,6-dimethylaniline (0.25 mL, 2.0 mmol), heating at 65 °C for 48 h. Flash chromatography (2% EtOAc/petroleum ether) of the crude material gave amine **3o** (0.0339 g, 30%) as a red oil. The data were consistent with the literature.[43] **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.33−7.28 (4H, m, ArH), 7.26−7.21 (1H, m, ArH), 6.96 (2H, d, $J$ = 7.4 Hz, ArH), 6.79 (1H, t, $J$ = 7.4 Hz, ArH), 4.33 (1H, q, $J$ = 6.7 Hz, NCH), 3.21 (1H, s, NH), 2.28 (6H, s, 2 × $CCH_3$), 1.52 (3H, d, $J$ = 6.7 Hz, $CHCH_3$). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 145.3 (C), 144.9 (C), 129.4 (C), 128.8 (2 × CH), 128.4 (2 × CH), 126.9 (CH), 126.1 (2 × CH), 121.5 (CH), 56.7 ($CH_3$), 22.6 (CH), 18.9 (2 × $CH_3$).

*(±)-1-Methyl-N-(1-phenylethyl)-1H-pyrazol-5-amine (**3p**).* The title compound was prepared according to *General Procedure 2* using boronic ester **1** (0.116 g, 0.499 mmol) and 1*H*-pyrazol-5-amine (0.194 g, 2.01 mmol), heating at 65 °C for 16 h. Flash chromatography (1:1 → 2:1 EtOAc/petroleum ether) of the crude material gave *amine* **3p** (0.0589 g, 59%) as a colorless oil. **IR** 3293, 2967, 2926, 1550, 1501 cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.42−7.37 (2H, m, ArH), 7.35−7.30 (2H, m, ArH), 7.26−7.20 (1H, m, ArH), 7.00 (1H, d, $J$ = 2.3 Hz, ArH), 5.29 (1H, d, $J$ = 2.3 Hz, ArH), 4.46 (1H, q, $J$ = 6.7 Hz, NCH), 4.07 (1H, s, NH), 3.68 (3H, s, $NCH_3$), 1.50 (3H, d, $J$ = 6.7 Hz, $CHCH_3$). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 156.6 (C), 145.6 (C), 130.8 (CH), 128.4 (2 × CH), 126.8 (CH), 126.0 (2 × CH), 91.3 (CH), 54.7 (CH), 38.4 ($CH_3$), 24.5 ($CH_3$). **HRMS** (Q-TOF) $m/z$: $[M + H]^+$ Calcd for $C_{12}H_{16}N_3{}^+$ 202.1344; found 202.1339.

*(±)-Methyl 3-[(1-Phenylethyl)amino]thiophene-2-carboxylate (**3q**).* The title compound was prepared according to *General Procedure 3* using boronic ester **1** (0.117 g, 0.504 mmol) and methyl 3-amino-2-thiophenecarboxylate (0.316 g, 2.01 mmol), heating at 65 °C for 48 h. Flash chromatography (6% EtOAc/petroleum ether) of the crude material gave *amine* **3q** (0.0595 g, 45%) as a yellow oil. **IR** 3364, 2950, 1663, 1566, 1246 cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.34−7.32 (4H, m, ArH), 7.25−7.23 (1H, m, ArH), 7.19−7.18 (1H, d, $J$ = 5.4 Hz, ArH), 6.36 (1H, d, $J$ = 5.4 Hz, ArH), 4.60 (1H, p, $J$ = 6.8 Hz, NHCH), 3.86 (3H, s, $OCH_3$), 1.58 (3H, d, $J$ = 6.8 Hz, $CHCH_3$). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 165.5 (C), 155.4 (C), 144.9 (C), 132.0 (CH), 128.7 (2 × CH), 127.1 (CH), 125.7 (2 × CH), 117.2 (CH), 98.9 (C), 54.8 ($CH_3$), 51.1 (CH), 24.9 ($CH_3$). **HRMS** (Q-TOF) $m/z$: $[M + H]^+$ Calcd for $C_{14}H_{16}NO_2S^+$ 262.0896; found 262.0905.

*(±)-N-Methyl-N-(1-phenylethyl)aniline (**3r**).* The title compound was prepared according to *General Procedure 2* using boronic ester **1** (0.116 g, 0.501 mmol) and *N*-methylaniline (0.22 mL, 2.0 mmol), heating at 65 °C for 16 h. Flash chromatography (2% EtOAc/petroleum ether) of the crude material gave amine **3r** (0.0877 g, 83%) as a yellow oil. The data were consistent with the literature.[44] **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.40−7.35 (4H, m, ArH), 7.33−7.27 (3H, m, ArH), 6.92−6.87 (2H, m, ArH), 6.81−6.75 (1H, m, ArH), 5.18 (1H, q, $J$ = 6.9 Hz, CH), 2.73 (3H, s, $NCH_3$), 1.60 (3H, d, $J$ = 6.9 Hz, $CHCH_3$). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 150.2 (C), 142.8 (C), 129.2 (2 × CH), 128.4 (2 × CH), 126.9 (2 × CH), 126.8 (CH), 116.6 (CH), 113.0 (2 × CH), 56.5 (CH), 31.8 ($CH_3$), 16.3 ($CH_3$).

*(±)-N-(1-Phenylethyl)-N-(propan-2-yl)aniline (**3s**).* The title compound was prepared according to *General Procedure 3* using boronic ester **1** (0.116 g, 0.498 mmol) and *N*-isopropylaniline (0.29 mL, 2.0 mmol), heating at 65 °C for 48 h. Flash chromatography (100% pentane) of the crude material gave *amine* **3s** (0.0525 g, 44%) as a colorless oil. **IR** 2670, 2931, 1595, 1500, 1263 cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.47−7.40 (2H, m, ArH), 7.38−7.30 (2H, m, ArH), 7.26−7.21 (1H, m, ArH), 7.20−7.11 (2H, m, ArH), 6.85−6.74 (3H, m, ArH), 4.79 (1H, q, $J$ = 6.9 Hz, NCHAr), 3.89 (1H, sept, $J$ = 6.7 Hz, CH($CH_3$)$_2$), 1.53 (3H, d, $J$ = 6.9 Hz, $NCHCH_3$), 1.20 (3H, d, $J$ = 6.7 Hz, $CH(CH_3CH_3)$), 1.16 (3H, d, $J$ = 6.7 Hz, $CH(CH_3CH_3)$). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 147.0 (C), 144.9 (C), 128.3 (2 × CH), 128.3 (2 × CH), 126.8 (CH), 126.3 (2 × CH), 119.5 (2 × CH), 118.4 (CH), 54.1 (CH), 48.7 (CH), 20.4 ($CH_3$), 20.3 ($CH_3$), 19.4 ($CH_3$). **HRMS** (Q-TOF) $m/z$: $[M + H]^+$ Calcd for $C_{17}H_{22}N^+$ 240.1752; found 240.1747.

*(±)-1-(1-Phenylethyl)-1,2,3,4-tetrahydroquinoline (**3t**).* The title compound was prepared according to *General Procedure 3* using boronic ester **1** (0.116 g, 0.499 mmol) and 1,2,3,4-tetrahydroquinoline (0.266 mg, 2.00 mmol), heating at 65 °C for 16 h. Flash chromatography (2% EtOAc/petroleum ether) of the crude material gave amine **3t** (0.0789 g, 67%) as a clear oil. The data were consistent with the literature.[45] **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.40−7.33 (4H, m, ArH), 7.29−7.24 (1H, m, ArH), 7.08−7.03 (1H, m, ArH), 7.03−6.98 (1H, m, ArH), 6.75−6.69 (1H, m, ArH), 6.63−6.57 (1H, m, ArH), 5.16 (1H, q, $J$ = 6.9 Hz, NCH), 3.21−3.14 (1H, m, $NCH_ACH_B$), 3.10−3.02 (1H, m, $NCH_ACH_B$), 2.86−2.74 (2H, m, $ArCH_2$), 1.94−1.85 (2H, m, $NCH_2CH_2$), 1.61 (3H, d, $J$ = 6.9 Hz, $CH_3$). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 145.6 (C), 142.7 (C), 129.2 (CH), 128.4 (2 × CH), 127.1 (CH), 126.9 (2 × CH), 126.7 (CH), 122.8 (C), 115.4 (CH), 110.6 (CH), 54.6 (CH), 42.5 ($CH_2$), 28.5 ($CH_2$), 22.2 ($CH_2$), 16.0 ($CH_3$).

*(±)-4-Methoxy-N,N-bis(1-phenylethyl)aniline (**3u**).* The title compound was prepared according to *General Procedure 2* using boronic ester **1** (0.0603 g, 0.260 mmol) and (±)-4-methoxy-*N*-(1-phenylethyl)-aniline (**3b**) (0.226 g, 1.00 mmol), heating at 50 °C for 48 h. Flash chromatography (5% EtOAc/petroleum ether) of the crude material (d.r. 1:1) gave *amine* **3u** (0.0016 g, 18%, isolated d.r = 1.8:1 A:B) as a yellow oil, and amine **3b** was recovered (182.8 mg, 80%). Upon further purification, diastereomer B was isolated as a single diastereomer. **IR** 3028, 2971, 1507, 1243, 1036, 699 cm$^{-1}$. **$^1$H NMR (diastereomer A)** (400 MHz, $CDCl_3$) 7.33−7.29 (4H, m, ArH), 7.25−7.19 (6H, m, ArH), 6.73−6.71 (4H, m, ArH), 4.26 (2H, q, $J$ = 6.8 Hz, 2 × CH), 3.80 (3H, s, $OCH_3$), 1.18 (6H, d, $J$ = 6.8 Hz, 2 × $CH_3$). **$^1$H NMR (diastereomer B)** (400 MHz, $CDCl_3$) $\delta$ 7.30−7.29 (8H, m, ArH), 7.24−7.20 (2H, m, ArH), 6.71 (2H, d, $J$ = 9.0 Hz, ArH), 6.65 (2H, d, $J$ = 9.0 Hz, ArH), 4.45 (2H, q, $J$ = 6.7 Hz, 2 × CH), 3.74 (3H, s, $CH_3$), 1.27 (6H, d, $J$ = 6.7 Hz, 2 × $CH_3$). **$^{13}$C{$^1$H} NMR (mixed diastereomer A +B) (101 MHz, $CDCl_3$)** $\delta$ 156.4 (C), 155.5 (C), 145.0 (2 × C), 143.7 (2 × C), 138.9 (C), 138.0 (C), 130.8 (CH), 128.7 (2 × CH), 128.0 (4 × CH), 128.0 (2 × CH), 127.9 (4 × CH), 127.8 (2 × CH), 126.7 (CH), 126.6 (CH), 112.8 (2 × CH), 112.5 (2 × CH), 58.3 (CH), 57.9 (CH), 55.2 ($CH_3$), 22.0 ($CH_3$), 18.2 ($CH_3$). **HRMS** (Q-TOF) $m/z$: $[M + H]^+$ Calcd for $C_{23}H_{25}NO^+$ 332.2009; found 332.2007.


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*(±)-4-(1-Phenylethyl)-morpholine (**3v**).* The title compound was prepared according to *General Procedure 2* using boronic ester **1** (0.116 g, 0.502 mmol) and morpholine (0.18 mL, 2.0 mmol), heating at 65 °C for 48 h. Flash chromatography (5−10% EtOAc/petroleum ether) of the crude material gave amine **3v** (0.0301 g, 31%) as a yellow oil. The data were consistent with the literature.[46] **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.34−7.29 (4H, m, Ar**H**), 7.26−7.21 (1H, m, Ar**H**), 3.73−3.66 (4H, m, 2 × OC**H**$_2$), 3.31 (1H, q, $J$ = 6.6 Hz, NC**H**), 2.56−2.44 (2H, m, 2 × NC**H**$_A$H$_B$), 2.41−2.34 (2H, m, 2 × NCH$_A$**H**$_B$), 1.36 (3H, d, $J$ = 6.6 Hz, C**H**$_3$). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 143.9 (C), 128.3 (2 × CH), 127.6 (2 × CH), 127.0 (CH), 67.2 (2 × $CH_2$), 65.4 (H), 51.3 (2 × $CH_2$), 19.8 ($CH_3$).

*(±)-4-Methoxy-N-(1-(4-methoxyphenyl)ethyl)aniline (**9a**).* The title compound was prepared according to *General Procedure 2* using boronic ester **8a** (0.143 g, 0.507 mmol) and *p*-anisidine (0.249 g, 2.02 mmol), heating at 50 °C for 16 h. Flash chromatography (6% EtOAc/petroleum ether) of the crude material gave amine **9a** (0.0899 g, 69%) as a yellow oil. The data were consistent with the literature.[35] **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.29 (2H, d, $J$ = 8.7 Hz, Ar**H**), 6.87 (2H, d, $J$ = 8.7 Hz, Ar**H**), 6.71 (2H, d, $J$ = 8.9 Hz, Ar**H**), 6.49 (2H, d, $J$ = 8.9 Hz, Ar**H**), 4.39 (1H, q, $J$ = 6.7 Hz, C**H**), 3.80 (3H, s, OC**H**$_3$), 3.71 (3H, s, OC**H**$_3$), 1.48 (3H, d, $J$ = 6.7 Hz, C**H**$_3$). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 158.4 (C), 151.8 (C), 141.6 (C), 137.5 (C), 126.9 (2 × CH), 114.7 (2 × CH), 114.6 (2 × CH), 113.9 (2 × CH), 55.7 ($CH_3$), 55.2 ($CH_3$), 53.6 (CH), 25.1 ($CH_3$).

*(±)-4-Methoxy-N-(1-p-tolylethyl)aniline (**9b**).* The title compound was prepared according to *General Procedure 2* using boronic ester **8b** (0.123 g, 0.500 mmol) and *p*-anisidine (0.246 g, 2.00 mmol), heating at 50 °C for 16 h. Flash chromatography (6% EtOAc/petroleum ether) of the crude material gave amine **9b** (0.0853 g, 71%) as an orange oil. The data were consistent with the literature.[35] **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.26 (2H, d, $J$ = 7.9 Hz, Ar**H**), 7.14 (2H, d, $J$ = 7.9 Hz, Ar**H**), 6.70 (2H, d, $J$ = 8.9 Hz, Ar**H**), 6.49 (2H, d, $J$ = 8.9 Hz, Ar**H**), 4.40 (1H, q, $J$ = 6.7 Hz, NC**H**), 3.75 (1H, br. s, N**H**), 3.71 (3H, s, OC**H**$_3$), 2.33 (3H, s, CC**H**$_3$), 1.49 (3H, d, $J$ = 6.7 Hz, CHC**H**$_3$). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 151.8 (C), 142.4 (C), 141.6 (C), 136.3 (C), 129.3 (2 × CH), 125.8 (2 × CH), 114.7 (2 × CH), 114.5 (2 × CH), 55.7 ($CH_3$), 53.9 (CH), 25.2 ($CH_3$), 21.1 ($CH_3$).

*(±)-N-(1-(Biphenyl-4-yl)ethyl)-4-methoxyaniline (**9c**).* The title compound was prepared according to *General Procedure 2* using boronic ester **8c** (0.156 g, 0.507 mmol) and *p*-anisidine (0.247 g, 2.01 mmol), heating at 50 °C for 16 h. Flash chromatography (6% EtOAc/petroleum ether) of the crude material gave amine **9c** (0.0975 g, 63%) as an orange solid. The data were consistent with the literature.[47] **m.p.** 85−86 °C (petroleum ether); no literature value available. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.64−7.50 (4H, m, Ar**H**), 7.48−7.38 (4H, m, Ar**H**), 7.37−7.31 (1H, m, Ar**H**), 6.72 (2H, d, $J$ = 8.9 Hz, Ar**H**), 6.51 (2H, d, $J$ = 8.9 Hz, Ar**H**), 4.47 (1H, q, $J$ = 6.7 Hz, NC**H**), 3.79 (1H, s, N**H**), 3.71 (3H, s, OC**H**$_3$), 1.55 (3H, d, $J$ = 6.7 Hz, CHC**H**$_3$). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 152.0 (C), 144.6 (C), 141.6 (C), 141.0 (C), 139.7 (C), 128.7 (2 × CH), 127.4 (2 × CH), 127.1 (CH), 127.0 (2 × CH), 126.3 (2 × CH), 114.8 (2 × CH), 114.6 (2 × CH), 55.7 ($CH_3$), 54.0 (CH), 25.1 ($CH_3$).

*(±)-N-(1-(4-Fluorophenyl)ethyl)-4-methoxyaniline (**9d**).* The title compound was prepared according to *General Procedure 2* using boronic ester **8d** (0.122 g, 0.488 mmol) and *p*-anisidine (0.246 g, 2.00 mmol), heating at 50 °C for 16 h. Flash chromatography (6% EtOAc/petroleum ether) of the crude material gave amine **9d** (0.0839 g, 70%) as an orange oil. The data were consistent with the literature.[35] **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.36−7.30 (2H, m, Ar**H**), 7.04−6.97 (2H, m, Ar**H**), 6.70 (2H, d, $J$ = 8.7 Hz, Ar**H**), 6.45 (2H, d, $J$ = 8.7 Hz, Ar**H**), 4.40 (1H, q, $J$ = 6.7 Hz, C**H**), 3.77 (1H, s, N**H**), 3.71 (3H, s, OC**H**$_3$), 1.48 (3H, d, $J$ = 6.7 Hz, CHC**H**$_3$). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 161.7 (C, d, $J_F$ = 244.1 Hz), 151.9 (C), 141.1 (C, d, $J_F$ = 3.0 Hz), 127.3 (2 × CH, d, $J_F$ = 8.0 Hz), 115.4 (2 × CH, $J_F$ = 21.3 Hz), 114.7 (2 × CH), 114.5 (2 × CH), 55.7 ($CH_3$), 53.6 (CH), 25.3 ($CH_3$). **$^{19}$F NMR** (377 MHz, $CDCl_3$) $\delta$ −116.3.

*(±)-4-Methoxy-N-(1-4-chlorophenylethyl)aniline (**9e**).* The title compound was prepared according to *General Procedure 2* using boronic ester **8e** (0.133 g, 0.499 mmol) and *p*-anisidine (0.246 g, 2.00 mmol), heating at 50 °C for 16 h. Flash chromatography (6% EtOAc/petroleum ether) of the crude material gave amine **9e** (0.0729 g, 56%) as an orange oil. The data were consistent with the literature.[48] **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.33−7.27 (4H, m, Ar**H**), 6.70 (2H, d, $J$ = 8.9 Hz, Ar**H**), 6.44 (2H, d, $J$ = 8.9 Hz, Ar**H**), 4.39 (1H, q, $J$ = 6.7 Hz, NC**H**), 3.70 (3H, s, OC**H**$_3$), 1.48 (3H, d, $J$ = 6.7 Hz, CHC**H**$_3$). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 152.1 (C), 144.1 (C), 141.3 (C), 132.4 (C), 128.8 (2 × CH), 127.3 (2 × CH), 114.8 (2 × CH), 114.6 (2 × CH), 55.7 ($CH_3$), 53.8 (CH), 25.1 ($CH_3$).

*(±)-4-Methoxy-N-(1-(4-(trifluoromethyl)phenyl)ethyl)aniline (**9f**).* The title compound was prepared according to *General Procedure 2* using boronic ester **8f** (0.148 g, 0.493 mmol) and *p*-anisidine (0.249 g, 2.02 mmol), heating at 65 °C for 48 h. Flash chromatography (6% EtOAc/petroleum ether) of the crude material gave amine **9f** (0.0609 g, 42%) as a yellow oil. The data were consistent with the literature.[35] **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.58 (2H, d, $J$ = 8.2 Hz, Ar**H**), 7.49 (d, $J$ = 8.2 Hz, 2H), 6.70 (d, $J$ = 8.9 Hz, 2H), 6.43 (d, $J$ = 8.9 Hz, 2H), 4.46 (q, $J$ = 6.8 Hz, 1H), 3.70 (s, 3H), 1.51 (d, $J$ = 6.8 Hz, 3H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 152.2 (C), 149.8 (C), 141.0 9 (C), 129.1 (C, q, $J_F$ = 32.3 Hz), 126.2 (2 × CH), 125.6 (2 × CH q, $J_F$ = 3.7 Hz), 124.2 (C, q, $J_F$ = 270.4 Hz), 114.8 (2 × CH), 114.5 (2 × CH), 55.7 ($CH_3$), 54.0 (CH), 25.1 ($CH_3$). **$^{19}$F NMR** (377 MHz, $CDCl_3$) $\delta$ −62.4.

*(±)-N-[1-(3-Chlorophenyl)ethyl]-4-methoxyaniline (**9g**).* The title compound was prepared according to *General Procedure 2* using boronic ester **8g** (0.133 g, 0.497 mmol) and *p*-anisidine (0.247 g, 2.00 mmol), heating at 65 °C for 16 h. Flash chromatography (6% EtOAc/petroleum ether) of the crude material gave amine **9g** (0.0792 g, 61%) as an orange oil. The data were consistent with the literature.[48] **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.38 (1H, s, Ar**H**), 7.27−7.24 (2H, m, Ar**H**), 7.24−7.19 (1H, m, Ar**H**), 6.71 (2H, d, $J$ = 8.8 Hz, Ar**H**), 6.46 (2H, d, $J$ = 8.8 Hz, Ar**H**), 4.38 (1H, q, $J$ = 6.7 Hz, C**H**), 3.77 (1H, s, N**H**), 3.71 (3H, s, OC**H**$_3$), 1.49 (3H, d, $J$ = 6.7 Hz, CHC**H**$_3$). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 152.1 (C), 147.9 (C), 141.2 (C), 134.5 (C), 129.9 (CH), 127.0 (CH), 126.1 (CH), 124.1 (CH), 114.8 (2 × CH), 114.5 (2 × CH), 55.7 ($CH_3$), 54.0 (CH), 25.1 ($CH_3$).

*(±)-N-[1-(3-Bromophenyl)ethyl]-4-methoxyaniline (**9h**).* The title compound was prepared according to *General Procedure 2* using boronic ester **8h** (0.153 g, 0.490 mmol) and *p*-anisidine (0.252 g, 2.04 mmol), heating at 50 °C for 16 h. Flash chromatography (6% EtOAc/petroleum ether) of the crude material gave amine **9h** (0.0738 g, 49%) as a brown oil. The data were consistent with the literature.[49] **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.53 (1H, s, Ar**H**), 7.36 (1H, d, $J$ = 7.7 Hz, Ar**H**), 7.30 (1H, d, $J$ = 7.7 Hz, Ar**H**), 7.19 (t, $J$ = 7.7 Hz, Ar**H**), 6.71 (2H, d, $J$ = 8.9 Hz, Ar**H**), 6.45 (2H, d, $J$ = 8.9 Hz, Ar**H**), 4.37 (1H, q, $J$ = 6.7 Hz, C**H**), 3.79 (1H, s, N**H**), 3.71 (3H, s, OC**H**$_3$), 1.49 (3H, d, $J$ = 6.7 Hz, CHC**H**$_3$). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 152.1 (C), 148.2 (C), 141.1 (C), 130.2 (CH), 130.0 (CH), 129.0 (CH), 124.5 (CH), 122.8 (C), 114.8 (2 × CH), 114.5 (2 × CH), 55.7 ($CH_3$), 54.0 (CH), 25.2 ($CH_3$).

*(±)-4-Methoxy-N-(1-(3-methoxyphenyl)ethyl)aniline (**9i**).* The title compound was prepared according to *General Procedure 2* using boronic ester **8i** (0.129 g, 0.493 mmol) and *p*-anisidine (0.246 g, 2.03 mmol), heating at 50 °C for 16 h. Flash chromatography (6% EtOAc/petroleum ether) of the crude material gave amine **9i** (0.0998 g, 79%) as a yellow oil. The data were consistent with the literature.[42] **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.27−7.22 (1H, m, Ar**H**), 7.00−6.96 (1H, m, Ar**H**), 6.94 (1H, s, Ar**H**), 6.80−6.75 (1H, m, Ar**H**), 6.71 (2H, d, $J$ = 8.8 Hz, Ar**H**), 6.49 (2H, d, $J$ = 8.8 Hz, Ar**H**), 4.39 (1H, q, $J$ = 6.7 Hz, NC**H**), 3.80 (3H, s, CCHCOC**H**$_3$), 3.71 (3H, s, CHCHCOC**H**$_3$), 1.50 (3H, d, $J$ = 6.7 Hz, CHC**H**$_3$). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 159.9 (C), 151.8 (C), 147.4 (C), 141.5 (C), 129.6 (CH), 118.2 (CH), 114.7 (2 × CH), 114.5 (2 × CH), 111.9 (CH), 111.6 (CH), 55.7 ($CH_3$), 55.1 ($CH_3$), 54.3 (CH), 25.1 ($CH_3$).

*(±)-4-Methoxy-N-(1-o-tolylethyl)aniline (**9j**).* The title compound was prepared according to *General Procedure 2* using boronic ester **8j** (0.120 g, 0.487 mmol) and *p*-anisidine (0.251 g, 2.04 mmol), heating at 50 °C for 16 h. Flash chromatography (6% EtOAc/petroleum ether) of the crude material gave amine **9j** (0.0809 g, 69%) as a brown oil. The data were consistent with the literature.[50] **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.46−7.40 (1H, m, Ar**H**), 7.20−7.10 (3H, m, Ar**H**), 6.70 (2H, d, $J$ =


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8.9 Hz, ArH), 6.42 (2H, d, $J$ = 8.9 Hz, ArH), 4.62 (1H, q, $J$ = 6.6 Hz, NCH), 3.77 (1H, s, NH), 3.70 (3H, s, $OCH_3$), 2.44 (3H, s, $CCH_3$), 1.47 (3H, d, $J$ = 6.6 Hz, $CHCH_3$). **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$) $\delta$ 151.8 (C), 143.0 (C), 141.6 (C), 134.6 (C), 130.6 (CH), 126.6 (CH), 126.5 (CH), 124.6 (CH), 114.8 (2 × CH), 114.1 (2 × CH), 55.7 ($CH_3$), 50.4 (CH), 23.1 ($CH_3$), 19.0 ($CH_3$).

*(±)-N-(4-Methoxyphenyl)-α-methyl-1-naphthalenemethanamine (**9k**).* The title compound was prepared according to *General Procedure 2* using boronic ester **8k** (0.141 g, 0.499 mmol) and *p*-anisidine (0.249 g, 2.02 mmol), heating at 65 °C for 16 h. Flash chromatography (6% EtOAc/petroleum ether) of the crude material gave amine **9k** (0.0623 g, 45%) as a yellow solid. The data were consistent with the literature.[51] **$^1H$ NMR** (400 MHz, $CDCl_3$) $\delta$ 8.20–8.18 (1H, m, ArH), 7.93–7.91 (1H, m, ArH), 7.77–7.75 (1H, m, ArH), 7.68–7.66 (1H, m, ArH), 7.60–7.51 (2H, m, ArH), 7.44–7.41 (1H, m, ArH), 6.67 (2H, d, $J$ = 8.8 Hz, ArH), 6.45 (2H, d, $J$ = 8.8 Hz ArH), 5.23 (1H, q, $J$ = 6.6 Hz, NCH), 3.96 (1H, br s, NH), 3.69 (3H, s, $OCH_3$), 1.66 (3H, d, $J$ = 6.6 Hz, $CHCH_3$). **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$) $\delta$ 151.8 (C), 141.3 (C), 140.1 (C), 134.1 (C), 130.7 (C), 129.1 (CH), 127.3 (CH), 126.0 (CH), 125.9 (CH), 125.4 (CH), 122.6 (CH), 122.3 (CH), 114.7 (2 × CH), 114.2 (2 × CH), 55.7 ($CH_3$), 50.1 (CH), 23.8 ($CH_3$).

*(±)-tert-Butyl 3-(3-Methoxy-1-[(4-methoxyphenyl)amino]-propyl)-1H-indole-1-carboxylate (**9l**).* The title compound was prepared according to *General Procedure 2* using boronic ester **8l** (0.208 g, 0.500 mmol) and *p*-anisidine (0.249 g, 2.02 mmol), heating at 65 °C for 48 h. Flash chromatography (10% EtOAc/petroleum ether) of the crude material gave *amine* **9l** (0.151 g, 73%) as a dark yellow oil. **IR** 2932, 2832, 2248, 1726, 1510, 906 $cm^{-1}$. **$^1H$ NMR** (400 MHz, $CDCl_3$) $\delta$ 8.15 (1H, s, ArH), 7.65 (1H, d, $J$ = 7.7 Hz, ArH), 7.53 (1H, s, ArH), 7.36–7.32 (1H, m, ArH), 7.26–7.24 (1H, m, ArH), 6.73 (2H, d, $J$ = 8.9 Hz, ArH), 6.60 (2H, d, $J$ = 8.9 Hz, ArH), 4.77 (1H, t, $J$ = 6.3 Hz, NCH), 3.72 (3H, s, $ArOCH_3$), 3.60–3.55 (1H, m, $CH_AH_BO$), 3.51–3.46 (1H, m, $CH_AH_BO$), 3.37 (3H, s, $CH_2OCH_3$), 2.26–2.18 (2H, m, $CHCH_2$), 1.67 (9H, s, 3 × $CCH_3$). **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$) $\delta$ 152.0 (C), 149.7 (C), 141.7 (C), 135.8 (C), 129.0 (C), 124.4 (2 × CH), 123.0 (CH), 122.4 (2 × CH), 119.3 (CH), 115.4 (CH), 114.7 (2 × CH), 83.6 (C), 70.3 ($CH_2$), 58.8 ($CH_3$), 55.7 ($CH_3$), 50.4 (CH), 36.3 ($CH_2$), 28.2 (3 × $CH_3$). **HRMS** (Q-TOF) $m/z$: $[M + Na]^+$ Calcd for $C_{24}H_{30}N_2O_4^+$ 433.2106; found 433.2098.

*(±)-N-[3-(Benzyloxy)-1-phenylpropyl]-4-methoxyaniline (**9m**).* The title compound was prepared according to *General Procedure 2* using boronic ester **8m** (0.177 g, 0.501 mmol) and *p*-anisidine (0.247 g, 2.02 mmol), heating at 65 °C for 32 h. Flash chromatography (8% EtOAc/petroleum ether) of the crude material gave *amine* **9m** (0.103 g, 59%) as an orange oil. **IR** 3385, 3028, 2857, 1510, 1235 $cm^{-1}$. **$^1H$ NMR** (400 MHz, $CDCl_3$) $\delta$ 7.38–7.28 (9H, m, ArH), 7.25–7.19 (1H m, ArH), 6.67 (2H, d, $J$ = 8.9 Hz, ArH), 6.42 (2H, d, $J$ = 8.9 Hz, ArH), 4.61 (1H, s, NH), 4.51 (2H, s, $ArCH_2$), 4.49–4.45 (1H, m, NCH), 3.69 (3H, s, $OCH_3$), 3.63–3.52 (2H, m, $CH_2CH_2O$), 2.12–2.05 (2H, m, $CHCH_2$). **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$) $\delta$ 151.6 (C), 144.0 (C), 141.9 (C), 138.1 (C), 128.5 (2 × CH), 128.4 (2 × CH), 127.7 (2 × CH), 127.7 (CH), 126.8 (CH), 126.4 (2 × CH), 114.6 (2 × CH), 114.3 (2 × CH), 73.2 ($CH_2$), 68.1 ($CH_2$), 57.8 ($CH_3$), 55.7 (CH), 38.3 ($CH_2$). **HRMS** (Q-TOF) $m/z$: $[M + H]^+$ Calcd for $C_{23}H_{26}NO_2^+$ 348.1964; found 348.1958.

*(±)-N-(4-Azido-1-phenylbutyl)-4-methoxyaniline (**9n**).* The title compound was prepared according to *General Procedure 2* using boronic ester **8n** (0.151 g, 0.500 mmol)and *p*-anisidine (0.247 g, 2.01 mmol), heating at 65 °C for 16 h. Flash chromatography (5% EtOAc/petroleum ether) of the crude material gave *amine* **9n** (0.0869 g, 59%) as a brown oil. **IR** 3396, 2930, 2093, 1509, 1451, 1233 $cm^{-1}$. **$^1H$ NMR** (400 MHz, $CDCl_3$) $\delta$ 7.36–7.29 (4H, m, ArH), 7.26–7.21 (1H, m, ArH), 6.70 (2H, d, $J$ = 8.9 Hz, ArH), 6.49 (2H, d, $J$ = 8.9 Hz, ArH), 4.32–4.23 (1H, m, NCH), 3.70 (3H, s, $OCH_3$), 3.34–3.25 (2H, m, $CH_2$), 1.96–1.81 (2H, m, $CH_2$), 1.77–1.69 (1H, m, $CH_2$), 1.66–1.59 (1H, m, $CH_2$). **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$) $\delta$ 152.0 (C), 143.6 (C), 141.3 (C), 128.7 (2 × CH), 127.1 (CH), 126.4 (2 × CH), 114.8 (2 × CH), 114.6 (2 × CH), 58.6 ($CH_3$), 55.7 (CH), 51.2 ($CH_2$), 35.7 ($CH_2$), 25.8 ($CH_2$). **HRMS** (Q-TOF) $m/z$: $[M + H]^+$ Calcd for $C_{17}H_{21}N_4O^+$ 297.1715; found 297.1717.

*(±)-(1-{4-[(4-Methoxyphenyl)amino]-4-phenylbutyl}-1H-1,2,3-triazol-4-yl)methanol (**9o**).* The title compound was prepared according to a modification of *General Procedure 2* using boronic ester **8o** (0.0899 g, 0.252 mmol), *p*-anisidine (0.124 g, 1.00 mmol), $Cu(OAc)_2$ (0.0910 g, 0.501 mmol), $Cs_2CO_3$ (0.0410 g, 0.126 mmol), methanol (0.5 mL), and pyridine (0.17 mL). The mixture was stirred at 65 °C for 48 h. Flash chromatography (2%–5% EtOAc/petroleum ether) of the crude material gave *amine* **9o** (0.0457 g, 52%) as an off white solid. **m.p.** 135–136 °C ($CHCl_3$). **IR** 3333, 3207, 2928, 2858, 1737, 1513, 1234 $cm^{-1}$. **$^1H$ NMR** (400 MHz, $CDCl_3$) $\delta$ 7.45 (1H, s, ArH), 7.35–7.28 (4H, m, ArH), 7.26–7.20 (1H, m, ArH), 6.68 (2H, d, $J$ = 8.8 Hz, ArH), 6.48 (2H, d, $J$ = 8.8 Hz, ArH), 4.78 (2H, s, $CH_2OH$), 4.38–4.32 (2H, m, $CH_2N$), 4.29–4.24 (1H, m, CHN), 3.69 (3H, s, $OCH_3$), 2.10–2.02 (1H, m, $CHCH_ACH_B$), 1.96–1.89 (1H, m, $CHCH_ACH_B$), 1.85–1.75 (2H, m, $CH_2CH_2N$). **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$) $\delta$ 152.4 (C), 147.7 (C), 142.9 (C), 140.6 (C), 128.7 (2 × CH), 127.3 (CH), 126.4 (2 × CH), 121.5 (CH), 115.1 (2 × CH), 114.8 (2 × CH), 58.8 (CH), 56.6 ($CH_2$), 55.7 ($CH_3$), 50.0 ($CH_2$), 35.0 ($CH_2$), 27.1 ($CH_2$). **HRMS** (Q-TOF) $m/z$: $[M + H]^+$ Calcd for $C_{20}H_{25}N_4O_2^+$ 353.1978; found 353.1972.

*4-Methoxy-N-(naphthalen-2-ylmethyl)aniline (**9p**).* The title compound was prepared according to *General Procedure 2* using boronic ester **8p** (0.135 g, 0.505 mmol) and *p*-anisidine (0.249 g, 2.02 mmol), heating at 50 °C for 16 h. Flash chromatography (6% EtOAc/petroleum ether) of the crude material gave amine **9p** (0.0825 g, 62%) as a yellow solid. The data were consistent with the literature.[52] **m.p.** 106–108 °C (petroleum ether); no literature value available. **$^1H$ NMR** (400 MHz, $CDCl_3$) $\delta$ 7.88–7.78 (4H, m, ArH), 7.54–7.42 (3H, m, ArH), 6.79 (2H, d, $J$ = 8.9 Hz, ArH), 6.66 (2H, d, $J$ = 8.9 Hz, ArH), 4.46 (2H, s, $CH_2$), 3.75 (3H, s, $OCH_3$). **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$) $\delta$ 152.2 (C), 142.4 (C), 137.2 (C), 133.5 (C), 132.7 (C), 128.3 (CH), 127.7 (CH), 127.7 (CH), 126.1 (CH), 125.9 (CH), 125.8 (CH), 125.7 (CH), 114.9 (2 × CH), 114.2 (2 × CH), 55.8 ($CH_3$), 49.4 ($CH_2$).

*(±)-N-(4-Methoxybenzyl)cyclohex-2-enamine (**9q**).* The title compound was prepared according to *General Procedure 2* using boronic ester **8q** (0.104 g, 0.501 mmol) and *p*-anisidine (0.247 g, 2.00 mmol), heating at 65 °C for 48 h. Flash chromatography (3% EtOAc/petroleum ether) of the crude material gave amine **9q** (0.0498 g, 49%) as a yellow oil. The data were consistent with the literature.[53] **$^1H$ NMR** (400 MHz, $CDCl_3$) $\delta$ 6.79 (2H, d, $J$ = 9.0 Hz, ArH), 6.61 (2H, d, $J$ = 9.0 Hz, ArH), 5.88–5.79 (1H, m, CHCH=CH), 5.80–5.72 (1H, m, CHCH=CH), 3.92 (1H, s, NCH), 3.76 (3H, s, $OCH_3$), 3.34 (1H, s, NH), 2.13–1.99 (2H, m, $CH=CHCH_2$), 1.95–1.85 (1H, m, $NCHCH_AH_B$), 1.81–1.69 (1H, m, $NCHCH_2CH_AH_B$), 1.67–1.52 (2H, m, $NCHCH_2CH_AH_B$ + $NCHCH_AH_B$). **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$) $\delta$ 152.0 (C), 141.3 (C), 129.9 (CH), 128.9 (CH), 115.0 (2 × CH), 114.9 (2 × CH), 55.8 ($CH_3$), 49.0 (CH), 29.0 ($CH_2$), 25.2 ($CH_2$), 19.8 ($CH_2$).

*N-Methyl-N-(3-methylbut-2-en-1-yl)aniline (**9r**).* The title compound was prepared according to *General Procedure 2* using boronic ester **8r** (0.093 g, 0.509 mmol) and *N*-methyl aniline (0.216 g, 2.01 mmol), heating at 50 °C for 16 h. Flash chromatography (6% EtOAc/petroleum ether) of the crude material gave amine **9r** (0.0464 g, 57%) as a yellow oil. The data were consistent with the literature.[54] **$^1H$ NMR** (400 MHz, $CDCl_3$) $\delta$ 7.25–7.21 (2H, m, ArH), 6.71–6.68 (3H, m, ArH), 4.86 (1H, s, $C=CH_AH_B$), 4.81 (1H, s, $C=CH_AH_B$) 3.81 (2H, s, $NCH_2$), 2.97 (3H, s, $NCH_3$), 1.74 (3H, s, $CCH_3$). **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$) $\delta$ 149.6 (C), 141.5 (C), 129.0 (2 × CH), 116.1 (CH), 111.9 (2 × CH), 110.7 ($CH_2$), 58.8 ($CH_2$), 38.2 ($CH_3$), 20.0 ($CH_3$).

*N-Cyclohexyl-4-methoxyaniline (**9s**).* Methanol (1.0 mL) and pyridine (0.33 mL) were added to a flask containing cyclohexylboronic acid pinacol ester (0.106 g, 0.503 mmol), *p*-anisidine (0.248 g, 2.03 mmol), $Cu(OAc)_2$ (0.182 g, 1.00 mmol), and $Cs_2CO_3$ (0.0820 g, 0.252 mmol), and the mixture was stirred at 80 °C for 16 h. The mixture was cooled to room temperature, $NH_4OH$ (10 mL) was added, and the mixture was extracted with $Et_2O$ (3 × 10 mL). The combined organic phases were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Flash chromatography (5% EtOAc/petroleum ether) of the crude material


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gave amine **9s** (0.0114 g, 11%) as an orange oil. The data were consistent with the literature.[55] **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 6.77 (2H, d, $J$ = 8.2 Hz, Ar**H**), 6.58 (2H, d, $J$ = 8.2 Hz, Ar**H**), 3.75 (3H, s, $OCH_3$), 3.21−3.13 (1H, m, NC**H**), 2.08−2.02 (2H, m, $CHCH_AH_B$), 1.80−1.69 (2H, m, $CHCH_2CH_AH_B$), 1.69−1.63 (1H, m, $CHCH_2CH_2CH_AH_B$), 1.40−1.31 (2H, m, $CHCH_2CH_AH_B$), 1.27 (1H, s, N**H**), 1.25−1.18 (1H, m, $CHCH_2CH_2CH_AH_B$), 1.18−1.08 (2H, m, $CHCH_AH_B$). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 151.9 (C), 141.6 (C), 114.9 (2 × CH), 114.8 (2 × CH), 55.8 ($CH_3$), 52.8 (CH), 33.6 (2 × $CH_2$), 26.0 ($CH_2$), 25.1 (2 × $CH_2$).

*(±)-4-Methoxy-N-[1-(4-methoxyphenyl)-1-phenylethyl]aniline (**11a**).* The title compound was prepared according to *General Procedure 4* using boronic ester **10a** (0.168 g, 0.498 mmol) and *p*-anisidine (0.246 g, 2.00 mmol). Flash chromatography (2% EtOAc/petroleum ether) of the crude material gave *amine* **11a** (0.0977 g, 59%) as a yellow oil. **IR** 3396, 2991, 2932, 2833, 1608, 1507, 1237 cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.49−7.43 (2H, m, Ar**H**), 7.37 (2H, d, $J$ = 8.8 Hz, Ar**H**), 7.35−7.29 (2H, m, Ar**H**), 7.26−7.20 (1H, m, Ar**H**), 6.85 (2H, d, $J$ = 8.8 Hz, Ar**H**), 6.64 (2H, d, $J$ = 8.9 Hz, Ar**H**), 6.41 (2H, d, $J$ = 8.9 Hz, Ar**HH**), 4.03 (1H, s, N**H**), 3.80 (3H, s, $OCH_3$), 3.70 (3H, s, $OCH_3$), 2.03 (3H, s, $CCH_3$). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 158.2 (C), 152.4 (C), 147.7 (C), 139.8 (C), 139.7 (C), 128.3 (2 × CH), 128.0 (2 × CH), 126.8 (2 × CH), 126.6 (CH), 118.2 (2 × CH), 114.2 (2 × CH), 113.6 (2 × CH), 62.2 (C), 55.6 ($CH_3$), 55.2 ($CH_3$), 26.7 ($CH_3$). **HRMS** (Q-TOF) $m/z$: $[M]^+$ Calcd for $C_{22}H_{23}NO_2^+$ 333.1723; found 333.1719.

*(±)-4-Chloro-N-[1-(4-methoxyphenyl)-1-phenylethyl]aniline (**11b**).* The title compound was prepared according to *General Procedure 4* using boronic ester **10a** (0.170 g, 0.501 mmol) and 4-chloroaniline (0.257 g, 2.01 mmol). Flash chromatography (2% EtOAc/petroleum ether) of the crude material gave *amine* **11b** (0.0710 g, 42%) as a yellow oil. **IR** 3473, 3383, 3006, 1601, 1493, 1247 cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.46−7.40 (2H, m, $J$ = 8.9 Hz, Ar**H**), 7.37−7.31 (4H, m, Ar**H**), 7.27−7.23 (1H, m, Ar**H**), 6.97 (2H, d, $J$ = 8.9 Hz, Ar**H**), 6.86 (2H, d, $J$ = 8.9 Hz, Ar**H**), 6.35 (2H, d, $J$ = 8.9 Hz, Ar**H**), 4.39 (1H, s, N**H**), 3.81 (3H, s, $OCH_3$), 2.07 (3H, s, $CCH_3$). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 158.4 (C), 146.8 (C), 144.5(C), 138.7 (C), 128.5 (2 × CH), 128.5 (2 × CH), 128.0 (2 × CH), 126.9 (CH), 126.7 (2 × CH), 122.2 (C), 117.0 (2 × CH), 113.7 (2 × CH), 62.0 (C), 55.2 ($CH_3$), 26.9 ($CH_3$). **HRMS** (Q-TOF) $m/z$: $[M + Na]^+$ Calcd for $C_{21}H_{20}{}^{35}ClNNaO^+$ 360.1131; found 360.1135.

*(±)-N-[1-(4-Methoxyphenyl)-1-phenylethyl]-1-methyl-1H-pyrazol-5-amine (**11c**).* The title compound was prepared according to *General Procedure 4* using boronic ester **10a** (0.169 g, 0.501 mmol) and 1-methyl-1*H*-pyrazol-3-amine (0.194 g, 2.00 mmol). Flash chromatography (1:5 EtOAc/petroleum ether) of the crude material gave *amine* **11c** (0.0522 g, 34%) as a yellow oil. **IR** 3267, 2933, 2835, 1547, 1509, 1249 cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.50−7.45 (2H, m, Ar**H**), 7.39 (2H, d, $J$ = 8.9 Hz, Ar**H**), 7.33−7.28 (2H, m, Ar**H**), 7.25−7.19 (1H, m, Ar**H**), 6.92 (1H, d, $J$ = 2.3 Hz, Ar**H**), 6.84 (2H, d, $J$ = 8.9 Hz, Ar**H**), 4.84 (1H, d, $J$ = 2.3 Hz, Ar**H**), 4.58 (1H, s, N**H**), 3.79 (3H, s, $OCH_3$), 3.68 (3H, s, $NCH_3$), 2.00 (3H, s, $CCH_3$). **$^{13}$C{$^1$H} NMR** (126 MHz, $CDCl_3$) $\delta$ 158.1 (C), 155.0 (C), 147.7 (C), 139.6 (C), 130.3 (CH), 128.2 (2 × CH), 128.0 (2 × CH), 126.7 (2 × CH), 126.5 (CH), 113.4 (2 × CH), 94.0 (CH), 61.8 (C), 55.2 ($CH_3$), 38.3 ($CH_3$), 27.7 ($CH_3$). **HRMS** (Q-TOF) $m/z$: $[M + H]^+$ Calcd for $C_{19}H_{22}N_3O^+$ 308.1763; found 308.1757.

*(±)-N-[1-(4-Methoxyphenyl)-1-phenylethyl]aniline (**11d**).* The title compound was prepared according to *General Procedure 4* using boronic ester **10a** (0.169 g, 0.499 mmol) and aniline (0.18 mL, 2.0 mmol). Flash chromatography (2% EtOAc/petroleum ether) of the crude material gave *amine* **11d** (0.0642 g, 42%) as a yellow oil. **IR** 3409, 2989,2834, 1599, 1497, 1249 cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.46 (2H, d, $J$ = 8.8 Hz, Ar**H**), 7.38−7.30 (4H, m, Ar**H**), 7.26−7.21 (1H, m, Ar**H**), 7.07−7.00 (2H, m, Ar**H**), 6.86 (2H, d, $J$ = 8.8 Hz, Ar**H**), 6.68−6.63 (1H, m, Ar**H**), 6.47−6.41 (2H, m, Ar**H**), 4.36 (1H, s, N**H**), 3.80 (3H, s, $OCH_3$), 2.10 (3H, s, $CCH_3$). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 158.3 (C), 147.3 (C), 146.0 (C), 139.3 (C), 128.6 (2 × CH), 128.4 (2 × CH), 128.0 (2 × CH), 126.8 (2 × CH), 126.7 (CH), 117.4 (CH), 116.0 (2 × CH), 113.6 (2 × CH), 61.9 (C), 55.2 ($CH_3$), 26.6 ($CH_3$). **HRMS** (Q-TOF) $m/z$: $[M + Na]^+$ Calcd for $C_{21}H_{21}NNaO^+$ 326.1521; found 326.1536.

*(±)-N-[1-(4-Chlorophenyl)-1-phenylethyl]aniline (**11e**).* The title compound was prepared according to *General Procedure 4* using boronic ester **10b** (0.171 g, 0.499 mmol) and aniline (0.18 mL, 2.0 mmol), heating at 25 °C. Flash chromatography (2% EtOAc/petroleum ether) of the crude material gave *amine* **11e** (0.0681 g, 44%) as a yellow oil. **IR** 3150, 1492, 1097, 1012, 750 cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.46−7.41 (4H, m, Ar**H**), 7.37−7.28 (5H, m, Ar**H**), 7.08−7.03 (2H, m, Ar**H**), 6.73−6.66 (1H, m, Ar**H**), 6.47−6.42 (2H, m, Ar**H**), 4.34 (1H, s, N**H**), 2.11 (3H, s, $CH_3$). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 146.8 (C), 145.6 (C), 145.4 (C), 132.6 (C), 128.7 (2 × CH), 128.5 (6 × CH), 127.1 (CH), 126.6 (2 × CH), 117.8 (CH), 116.1 (2 × CH), 62.1 (C), 26.7 ($CH_3$). **HRMS** (ESI) $m/z$: $[M + H]^+$ Calcd for $C_{20}H_{18}{}^{35}ClN^+$ 308.1201; found 308.1194.

*(±)-N-{1-Phenyl-1-[4-(trifluoromethyl)phenyl]ethyl}aniline (**11f**).* The title compound was prepared according to *General Procedure 4* using boronic ester **10c** (0.189 g, 0.502 mmol) and aniline (0.18 mL, 2.0 mmol), heating at 50 °C. Flash chromatography (2% EtOAc/petroleum ether) of the crude material gave *amine* **11f** (0.0432 g, 25%) as a yellow oil. **IR** 3450, 2928, 1600, 1497, 1325 cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.56−7.48 (4H, m, Ar**H**), 7.34 (2H, d, $J$ = 7.7 Hz, Ar**H**), 7.28−7.23 (2H, m, Ar**H**), 7.20−7.16 (1H, m, Ar**H**), 7.00−6.93 (2H, m, Ar**H**), 6.64−6.57 (1H, m, Ar**H**), 6.34 (2H, d, $J$ = 7.7 Hz, Ar**H**), 4.27 (1H, s, N**H**), 2.05 (3H, s, $CH_3$). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 150.7 (C), 146.5 (C), 145.5 (C), 129.0 (C, q, $J_F$ = 32.6 Hz), 128.7 (2 × CH), 128.6 (2 × CH), 127.4 (2 × CH), 127.2 (CH), 126.6 (2 × CH), 125.4 (2 × CH, q, $J_F$ = 3.7 Hz), 124.2 ($CF_3$, q, $J_F$ = 271.8 Hz,), 118.0 (CH), 116.2 (2 × CH), 62.4 (C), 26.6 ($CH_3$). **$^{19}$F NMR** (377 MHz, $CDCl_3$) $\delta$ −62.3. **HRMS** (EI) $m/z$: $[M]^+$ Calcd for $C_{21}H_{18}F_3N^+$ 341.1386; found 341.1399.

*(±)-N-(2-Phenylbutan-2-yl)aniline (**11g**).* The title compound was prepared according to *General Procedure 4* using boronic ester **10d** (0.130 g, 0.500 mmol) and aniline (0.18 mL, 2.0 mmol), heating at 50 °C. Flash chromatography (1% EtOAc/petroleum ether) of the crude material gave amine **11g** (0.0466 g, 41%) as a yellow oil. The data were consistent with the literature.[56] **IR** 3359, 2918, 2850, 1600, 1468, 1263. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.52−7.45 (2H, m, Ar**H**), 7.36−7.30 (2H, m, Ar**H**), 7.26−7.21 (1H, m, Ar**H**), 7.04−6.95 (2H, m, Ar**H**), 6.65−6.56 (1H, m, Ar**H**), 6.38−6.30 (2H, m, Ar**H**), 4.01 (1H, s, N**H**), 1.92 (2H, q, $J$ = 7.4, $CH_2$), 1.63 (3H, s, $CCH_3$), 0.83 (3H, t, $J$ = 7.4 Hz, $CH_2CH_3$). **$^{13}$C{$^1$H} NMR** (400 MHz, CDCl3) $\delta$ 146.3 (C), 146.0 (C), 128.7 (2 × CH), 128.3 (2 × CH), 126.2 (3 × CH), 116.9 (CH), 115.1 (2 × CH), 58.4 (C), 36.4 ($CH_2$), 25.3 ($CH_3$), 8.2 ($CH_3$). **HRMS** (ESI) $m/z$: $[M + H]^+$ Calcd for $C_{16}H_{19}N^+$ 226.1590; found 226.1597.

**Reaction of Boronic Ester 13 with *p*-Anisidine.** (See Scheme S1 in the Supporting Information.)

According to *General Procedure 4*, boronic ester **13** (0.159 g, 0.503 mmol) and *p*-anisidine (0.246 g, 2.00 mmol) were heated at 25 °C. Flash chromatography (5% EtOAc/petroleum ether) of the crude material gave *amine* **14** (0.0365 g, 23%) as a yellow oil, and an inseparable mixture of *alcohol* **S2** and *amine* **15** (40.9 mg).

Phenyl isothiocyanate (1.1 equiv) was added to a solution of a mixture of **S2** and **15** in hexane:$Et_3N$:MeCN (1:0.1:0.1, 0.1 M), and the mixture was stirred for 16 h at room temperature. The precipitate was collected and washed with hexane (2 × 5 mL) to give *thiourea* **16** (16.0 mg, 7%). Flash chromatography (petroleum ether → 20% EtOAc/petroleum ether) of the mother liquor gave *alcohol* **S2** (18.1 mg, 18%).

*(±)-N-(5-Azido-2-phenylpentan-2-yl)-4-methoxyaniline (**14**).* **IR** 3390, 2932, 2831, 2093, 1508, 1235, cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.53−7.45 (2H, m, Ar**H**), 7.39−7.32 (2H, m, Ar**H**), 7.27−7.23 (1H, m, Ar**H**), 6.62 (2H, d, $J$ = 8.8 Hz, Ar**H**), 6.31 (2H, d, $J$ = 8.8 Hz, Ar**H**), 3.69 (4H, s, N**H**, $OCH_3$), 3.26−3.12 (2H, m, $CH_2N$), 2.01−1.88 (2H, m, $CH_2CH_2N$), 1.61 (3H, s, $CCH_3$), 1.55−1.47 (2H, m, $CCH_2$). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 152.0 (C), 146.2 (C), 139.7 (C), 128.5 (2 × CH), 126.5 (CH), 126.2 (2 × CH), 117.0 (2 × CH), 114.3 (2 × CH), 58.3 (C), 55.6 ($CH_3$), 51.6 ($CH_2$), 40.6 ($CH_2$), 26.3 ($CH_3$), 23.5 ($CH_2$). **HRMS** (Q-TOF) $m/z$: $[M + H]^+$ Calcd for $C_{18}H_{23}N_4O^+$ 311.1872; found 311.1866.


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*(±)-1-[2-(5-Azido-2-phenylpentan-2-yl)-4-methoxyphenyl]-3-phenylthiourea (**16**).* **m.p.** 150−151 °C (hexane). **IR** 3334, 3170, 2959, 2096, 1508, 1214 $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.57 (1H, s, N**H**), 7.35−7.29 (1H, m, Ar**H**), 7.26−7.21 (2H, m, Ar**H**), 7.18−7.13 (2H, m, Ar**H**), 7.04 (6H, m, Ar**H**), 6.90−6.87 (1H, m, Ar**H**), 6.38 (1H, s, Ar**H**), 3.90 (3H, s, OC**H$_3$**), 3.38−3.28 (1H, m, C**H$_A$**H$_B$N), 3.28−3.18 (1H, m, CH$_A$**H$_B$**N), 2.23−2.03 (2H, m, C**H$_2$**CH$_2$N$_3$), 1.57 (3H, s, CC**H$_3$**), 1.44−1.31 (2H, m, CC**H$_2$**). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 179.7 (C), 158.5 (C), 148.2 (C), 145.1 (C), 136.8 (C), 131.9 (CH), 129.6 (CH), 128.8 (4 × CH), 126.6 (2 × CH), 126.3 (2 × CH), 125.4 (CH), 123.8 (C), 115.4 (CH), 110.8 (CH), 55.5 ($CH_3$), 51.9 ($CH_2$), 45.5 (C), 36.1 ($CH_2$), 27.8 ($CH_3$), 24.8 ($CH_2$). **HRMS** (Q-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{25}H_{28}N_5OS^+$ 446.2015; found 446.2009.

*(±)-5-Azido-2-phenylpentan-2-ol (**S2**).* **IR** 3420, 2930, 2092, 1602, 1146, 1260 $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.48−7.39 (2H, m, Ar**H**), 7.40−7.33 (2H, m, Ar**H**), 7.29−7.24 (1H, m, Ar**H**), 3.26−3.19 (2H, m, C**H$_2$**N$_3$), 1.95−1.83 (2H, m, C**H$_2$**CH$_2$N$_3$), 1.80 (1H, s, O**H**), 1.64−1.57 (4H, m, CH$_3$, CC**H$_A$**H$_B$), 1.53−1.38 (1H, m, CCH$_A$**H$_B$**). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 147.2 (C), 128.3 (2 × CH), 126.7 (CH), 124.6 (2 × CH), 74.3 (C), 51.6 ($CH_2$), 41.1 ($CH_2$), 30.5 ($CH_3$), 23.7 ($CH_2$). **HRMS** (Q-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{11}H_{15}N_3ONa^+$ 228.1113; found 228.1107.

**Reaction of Boronic Ester 1 with *p*-Aminophenol.** The title compounds were prepared according to *General Procedure 2* using boronic ester **1** (0.116 g, 0.500 mmol) and 4-aminophenol (0.218 g, 2.00 mmol), heating at 65 °C for 48 h. Flash chromatography (20% EtOAc/petroleum ether) of the crude material gave amine **17** (0.0499 g, 47%), *amine* **18** (0.0023 g, 2%), and *amine* **19** (0.0338 g, 32%) as red oils.

*(±)-4-[(1-Phenylethyl)amino]phenol (**17**).* The data were consistent with the literature.[57] **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.38−7.30 (4H, m, Ar**H**), 7.25−7.21 (1H, m, Ar**H**), 6.62 (2H, d, *J* = 8.8 Hz, Ar**H**), 6.43 (2H, d, *J* = 8.8 Hz, Ar**H**), 4.41 (1H, q, *J* = 6.7 Hz, C**H**), 2.19 (1H, s, N**H**), 1.50 (3H, d, *J* = 6.7 Hz, C**H$_3$**). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 147.4 (C), 145.4 (C), 141.6 (C), 128.6 (2 × CH), 126.8 (CH), 125.9 (2 × CH), 116.0 (2 × CH), 114.7 (2 × CH), 54.3 (CH), 25.1 ($CH_3$).

*(±)-4-(1-Phenylethoxy)aniline (**18**).* **IR** 3446, 3360, 2920, 2850, 1624, 1508, 1230 $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.39−7.30 (4H, m, Ar**H**), 7.27−7.21 (1H, m, Ar**H**), 6.70 (2H, d, *J* = 8.7 Hz, Ar**H**), 6.56 (2H, d, *J* = 8.7 Hz, Ar**H**), 5.17 (1H, q, *J* = 6.5 Hz, C**H**), 3.44 (2H, s, N**H$_2$**), 1.60 (3H, d, *J* = 6.5 Hz, C**H$_3$**). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 151.1 (C), 143.6 (C), 139.9 (C), 128.5 (2 × CH), 127.3 (CH), 125.7 (2 × CH), 117.4 (2 × CH), 116.3 (2 × CH), 76.9 (CH), 24.3 ($CH_3$). **HRMS** (Q-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{14}H_{16}NO^+$ 214.1232; found 214.1226.

*(±)-4-Amino-3-(1-phenylethyl)phenol (**19**).* **IR** 3363, 2966, 2929, 1600, 1498, 1450, 1214 $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.32−7.27 (2H, m, Ar**H**), 7.23−7.18 (3H, m, Ar**H**), 6.82 (1H, d, *J* = 2.7 Hz, Ar**H**), 6.60 (1H, dd, *J* = 8.4, 2.7 Hz, Ar**H**), 6.55 (1H, d, *J* = 8.4 Hz, Ar**H**), 4.09 (1H, q, *J* = 7.2 Hz, C**H**), 1.59 (3H, d, *J* = 7.2 Hz, C**H$_3$**). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 148.8 (C), 145.3 (C), 137.5 (C), 132.1 (C), 128.7 (2 × CH), 127.5 (2 × CH), 126.4 (CH), 117.6 (CH), 114.6 (CH), 113.8 (CH), 40.1 (CH), 21.7 ($CH_3$). **HRMS** (Q-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{14}H_{16}NO^+$ 214.1232; found 214.1226.

*(±)-3-[4-Hydroxy-2-(1-phenylethyl)phenyl]-1-phenylthiourea (**S3**).* (See Scheme S2 in the Supporting Information.)

Phenyl isothiocyanate (23.8 mg, 0.176 mmol) was added to a solution of amine **19** (33.8 mg, 0.158 mmol) in hexane (1.6 mL), $Et_3N$ (0.16 mL), and MeCN (0.16 mL), and the mixture was stirred for 16 h at room temperature. The precipitate was collected and washed with hexane (2 × 5 mL) to give *thiourea* **S3** (37.2 mg, 68%). **m.p.** 155−157 °C (hexane). **IR** 3339, 3152, 2967, 1747, 1533, 1275 $cm^{-1}$. **$^1$H NMR** (400 MHz, $CD_3CN$) $\delta$ 7.73 (1H, s, N**H**), 7.33−7.23 (8H, m, Ar**H**), 7.21−7.15 (2H, m, Ar**H**), 7.09−7.06 (1H, m, Ar**H**), 6.79 (1H, s, Ar**H**), 6.73−6.68 (1H m, Ar**H**), 4.33 (1H, q, *J* = 7.2 Hz, C**H**), 1.55 (3H, d, *J* = 7.2 Hz, CHC**H$_3$**). **$^{13}$C{$^1$H} NMR** (101 MHz, $CD_3CN$) $\delta$ 182.8 (C), 157.9 (C), 147.0 (C), 146.4 (C), 131.6 (CH), 129.6 (C), 129.4 (4 × CH), 128.5 (4 × CH), 127.1 (CH), 126.9 (C), 126.8 (CH), 115.5 (CH), 114.8 (CH), 40.4 (CH), 21.6 ($CH_3$). **HRMS** (Q-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{21}H_{21}N_2OS^+$ 349.1375; found 349.1369. Crystals suitable for X-ray diffraction were obtained through recrystallization of **S3** from hexane and slow evaporation.

**Reaction of Cyclopropane-Containing Boronic Ester 12.** A flask containing boronic ester **20** (0.131 g, 0.507 mmol), *p*-anisidine (0.251 g, 2.04 mmol), $Cu(OAc)_2$ (0.184 g, 1.01 mmol), and $Cs_2CO_3$ (0.0858 g, 0.263 mmol) was purged with argon. Methanol (1.0 mL) and pyridine (0.33 mL) were added, and the mixture was stirred at 65 °C for 48 h. The mixture was cooled to room temperature, $NH_4OH$ (10 mL) was added, and the mixture was extracted with $Et_2O$ (3 × 10 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Flash chromatography (6% EtOAc/petroleum ether) of the crude material gave *amine* **21** (0.0501g, 39%) as an orange oil. **IR** 3390, 2929, 2831, 1510, 1233 $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.41−7.35 (2H, m, Ar**H**), 7.36−7.29 (2H, m, Ar**H**), 7.27−7.20 (1H, m, Ar**H**), 6.81 (2H, d, *J* = 8.9 Hz, Ar**H**), 6.62 (2H, d, *J* = 8.9 Hz, Ar**H**), 6.51 (1H, d, *J* = 15.9 Hz, PhC**H**), 6.24 (1H, dt, *J* = 15.9 7.1 Hz, PhCH=C**H**), 3.77 (3H, s, OC**H$_3$**), 3.47 (1H, s, N**H**), 3.25 (2H, t, *J* = 6.7 Hz, C**H$_2$**N), 2.55 (2H, dtd, *J* = 7.1, 6.7, 1.1 Hz, C**H$_2$**CH$_2$N). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 152.2 (C), 142.5 (C), 137.3 (C), 132.2 (CH), 128.5 (2 × CH), 127.5 (CH), 127.2 (CH), 126.1 (2 × CH), 115.0 (2 × CH), 114.3 (2 × CH), 55.8 ($CH_3$), 44.3 ($CH_2$), 33.0 ($CH_2$). **HRMS** (Q-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{17}H_{20}NO^+$ 254.1545; found 254.1539.

**Reaction of Enantiomerically Enriched Boronic Ester (*S*)-1.** According to *General Procedure 2*, boronic ester (*S*)-**1** (0.0502 g, 0.216 mmol) and aniline (0.0803 g, 0.862 mmol) were reacted, heating at 50 °C for 16 h. Flash chromatography (4% EtOAc/petroleum ether) of the crude material gave amine **3a** (0.0311 g, 73%) as a yellow oil. The data were consistent with the literature.[35] See above for data. e.r. = 50:50. HPLC (Phenomenex Cellulose-1 column (250 × 4.6 mm), IPA/hexane 6/94, flow rate = 1.0 mL/min, *l* = 254 nm), $t_R$ = 6.5 min (minor), 8.0 min (major).

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00976.

Experimental details and characterization data (PDF)

### Accession Codes

CCDC 2073100 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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### Author Contributions

The manuscript was written through contributions of all authors.

### Notes

The authors declare no competing financial interest.

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