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(54) Title: METHODS FOR PREPARING A BORONIC ACID OR A BORONIC ESTER

(57) Abstract: Methods are disclosed for converting a carboxylic acid by using a diboron reagent to convert the carboxylic acid or imide ester derivative of a carboxylic acid to a boronic ester. The method may involve providing an imide ester, such as a phthalimide ester, of a carboxylic acid, and treating the imide ester with a diboron reagent, thereby forming a boronic ester. The diboron reagent may be selected from bis(catecholato)diboron, B2(OH)4 or a mixture thereof, optionally in the presence of catechol.



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METHODS FOR PREPARING A BORONIC ACID OR A BORONIC ESTER

The present invention relates to methods for converting carboxylic acids into boronic acids or esters, more particular to methods for borylation of carboxylic acids
5 and even more particularly to methods for decarboxylative borylation of carboxylic acids.

Carboxylic acids are among the most prevalent class of organic molecules found in Nature and thus methods for the conversion of the carboxyl functional group into other functional groups are highly sought after. In contrast, the isoelectronic
10 boronic acids are hardly found in Nature at all, yet arguably bear the most versatile functional group available to the synthetic organic chemist.

Boronic acids and their ester derivatives can be converted into almost any functional group in one step, through either transition-metal-mediated coupling reactions, 1,2-metallate rearrangements, or deborylative nucleophilic addition.
15 Therefore, the conversion of carboxylic acid groups into the highly versatile boronic acid moiety would facilitate more rapid diversification of this important class of feedstock molecules. Also, boronic acids are important target molecules in their own right. Specifically, they share a number of features with carboxylic acids that make them potent bioisosteres in medicinal chemistry. For example, boronic acids form
20 hydrogen bonds of similar geometries to carboxylic acids, despite their lower acidity, and they can switch reversibly between stable tricoordinate and tetracoordinate forms, thus allowing them to mimic the tetrahedral intermediates involved in, for example, the enzymatic hydrolysis of amide group. A straightforward method for converting libraries of bioactive carboxylic acids into the corresponding boronic acids would lead
25 to enhanced screening libraries and would facilitate bioisosteric lead optimisation.

Although the decarboxylative borylation of carboxylic acid derivatives has not previously been described, reaction conditions for decarboxylative borylation of carboxylic derivatives have recently been disclosed. However, these transformations, which involve the oxidative addition of a catalytically active Ni(0) or Rh(I) species
30 into the C–O, C–S, or C–N bond of an ester, thioester, or amide derivative,

respectively, only give high yields for carboxylic acid derivatives bearing sp^2 carbon centers. When these conditions have been applied to simple carboxylic acid derivatives bearing sp^3 carbon centers, the yields have been low.

It is an aim of the present invention to provide improved synthetic methods and more particularly methods for borylation of carboxylic acids.

In first and second aspects, the present invention accordingly provides a method as set out in claim 1 and a method as set out in claim 2, respectively.

Preferred, advantageous and optional aspects of the invention are set out in claims 3 to 16.

In a third aspect, the present invention additionally provides a method as set out in claim 17, with the optional aspect as set out in claim 18.

In a fourth aspect, the present invention provides a method as set out in claim 19.

The invention is illustrated, but not limited, by the following examples.

Preliminary Studies

Using *N*-hydroxyphthalimide ester **1** as our test substrate as a solution in *N,N*-dimethylformamide (DMF; 0.1 M) with Cs_2CO_3 (1.5 equivalent) and the diboron reagent, bis(catecholato)diboron (B_2cat_2 , 1.00 equivalent), under the illumination of blue LED light for 14 hours, followed by a workup that involved adding pinacol and NEt_3 , so as to effect ligand exchange to form the more stable pinacol boronic ester, we obtained the desired boronic ester **2** in a noteworthy 8% yield. Carrying out the reaction with B_2cat_2 in the absence of Cs_2CO_3 delivered boronic ester **2** in 69% yield.

A solvent screen revealed that the amide-based solvents were effective for this transformation, with the use of *N,N*-dimethylacetamide (DMAc) being marginally better than DMF. Increasing the amount of B_2cat_2 in increments from 1.00 equivalent to 2.00 equivalents revealed that a slight excess of the reagent (1.25 equivalents; 91% yield) was optimal; there was a slight drop in yield with larger amounts. The transformation conducted in the dark delivered the desired product in 5% yield. Light

from a regular white bulb placed in the vicinity of the reaction vessel was effective at increasing yield (91% yield), ambient light also led to efficient reaction (43% yield). The transformation was moderately sensitive to concentration (0.1 M being optimal) the reaction was complete within 4 hours. Investigation of reaction setup showed that although the reaction was tolerant of small amounts of water, the presence of O₂ was detrimental and therefore conducting the reaction under an inert atmosphere (N₂ or Ar) was advantageous for higher yields.

Reaction Scope

The substrate scope of the transformation was broad.

Primary carboxylic acids, including a benzylic substrate and substrates bearing heteroatoms, heterocycles (thiophene, indole), β -positioned alkenes, alkynes, esters, carbon–bromine bonds, and perfluoroalkyl chains, were converted into the corresponding primary pinacol boronic esters in good to high yields. The isolation of these products was facile, for example, a quick filtration through a plug of silica gel, or washing with mild aqueous base being sufficient for providing material of high purity.

Secondary carboxylic acids, either as part of an acyclic chain or as part of a carbo- or heterocycle of a variety of ring sizes (cyclohexyl, cyclopentyl, cyclopropyl, 2,2,2-bridged bicyclic, pyranyl), and containing functional groups, such as difluoromethylene, a carbamate, and an ester, were converted into the corresponding boronic esters in good to high yield.

We also investigated a number of carbocyclic substrates containing two stereogenic centers, at least one of which bears the carboxylic acid moiety. Here, the boronic ester products were obtained with varying levels of diastereoselectivity, depending on the relative position of substituents and ring size. For example, although the 1,3-substituted cyclopentane, **17**, was obtained with low levels of diastereoselectivity, the 1,2-substituted cyclohexane **21** (derived from the corresponding dicarboxylic acid) and 1,2-disubstituted cyclopropane **15** were obtained in 90:10 and 98:2 d.r., respectively.

Tertiary carboxylic acids, in which the three carbon atoms are tied back into a ring structure, for example adamantyl, cubyl, and bicyclo[1.1.1]pentyl carboxylic acids, were transformed into the corresponding boronic esters in good yield. Notably, over one gram of adamantyl pinacol boronic ester **25** was prepared in a single reaction, thus showing that the conditions are suitable for preparing significant quantities of material for further applications.

Boronic acids derived from stearic, oleic, lithocholic, pinonic, gibberellic, and arachidonic acids were obtained in moderate to good yields (Figure 2d).

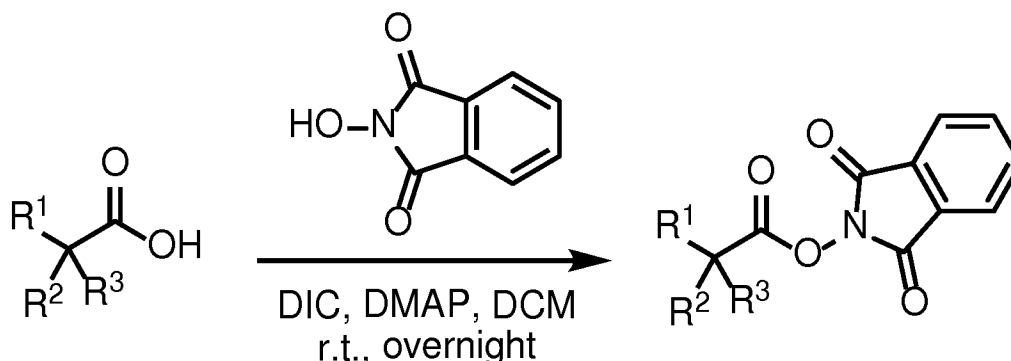
Transformation of the bis(*N*-hydroxyphthalimide ester) of succinic acid gave the corresponding 1,2-bis(boronic ester) **39** in 41% yield.

Fenbufen, a protected form of glutamic acid, and indometacin were converted into the corresponding boronic esters in moderate to good yields. These examples highlight that the transformation is also tolerant of free hydroxy groups, silyl ethers, and ketones.

Examples of the invention will be further described below.

1. General Procedures

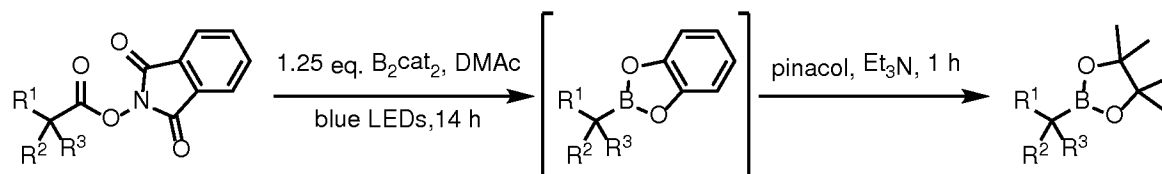
1.1 Synthesis of *N*-Hydroxyphthalimide (NHPI) Esters



- General Procedure A:** *N*-Hydroxyphthalimide (1.0 eq), DMAP (0.1 eq.) and, if solid, carboxylic acid (1.0 eq.) was added to a round-bottomed flask. Dichloromethane (0.1 M) and, if liquid, carboxylic acid (1.0 eq) were then added, followed by DIC (1.0 eq.). The reaction mixture was allowed to stir at room temperature overnight, before concentrating under reduced pressure. The crude residue was directly purified by flash-

column chromatography (SiO₂; typically DCM with either pentane or Et₂O) to yield pure NHPI ester. If solid and not pure, the NHPI ester can be recrystallized from DCM/MeOH or EtOAc to give pure material.

5 1.2 Conditions 1: Decarboxylative Borylation of Alkyl Carboxylic Acids

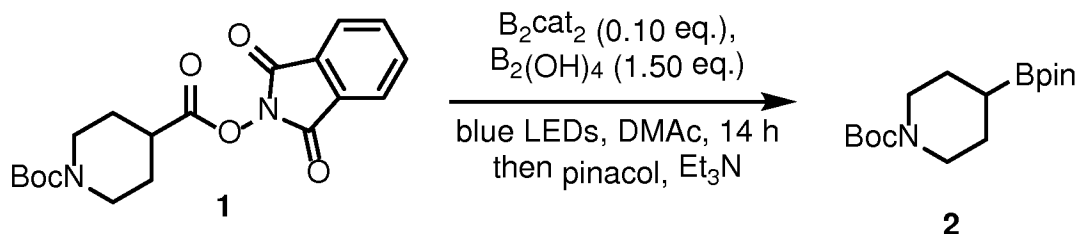


General Procedure B: NHPI ester (1.0 eq., 0.13 mmol) and B₂cat₂ (40 mg, 1.25 eq., 0.16 mmol) were carefully weighed into a flame-dried 7 mL vial containing a small magnetic stirrer bar. DMAc (1.3 mL, 0.1 M) was added and then the headspace of the vial was purged with a gentle stream of argon for approximately 10 seconds. The vial was tightly sealed and stirred under blue LED irradiation for 14 h. Pinacol (63 mg, 0.53 mmol, 4 eq.) was dissolved in Et₃N (0.45 mL), added to the reaction mixture and stirred for 1 h. **For workup,** the reaction mixture was transferred into a vial containing EtOAc (15 mL), H₂O (3 mL), NH₄Cl (saturated aqueous solution, 3 mL). After vigorously shaking and allowing the two layers to separate, the top organic layer was carefully removed with a pipette. This was repeated twice more with EtOAc (5 mL). The organic layers were combined and concentrated under reduced pressure. The crude residue was directly purified using a short silica gel column to yield the desired boronic ester.

Alternative workup: The crude reaction mixture was diluted with Et₂O (10 mL) and washed with NaOH (aqueous, 0.10 M, 6 mL), and then the aqueous layer was extracted with Et₂O (10 mL). The combined organic layers were washed with NaOH (aqueous, 0.10 M, 6 mL) and water (6 mL), then dried over MgSO₄, filtered and concentrated under reduced pressure to yield the desired boronic ester.

Notes: Solvent: Also works in DMF, DMPU, DMI, NMP and tetramethylurea.
Starting material: Also works with the tetrachlorophthalimide.

1.3 Conditions 2: Decarboxylative Borylation of Alkyl Carboxylic Acids with Catalytic Catechol or B₂cat₂



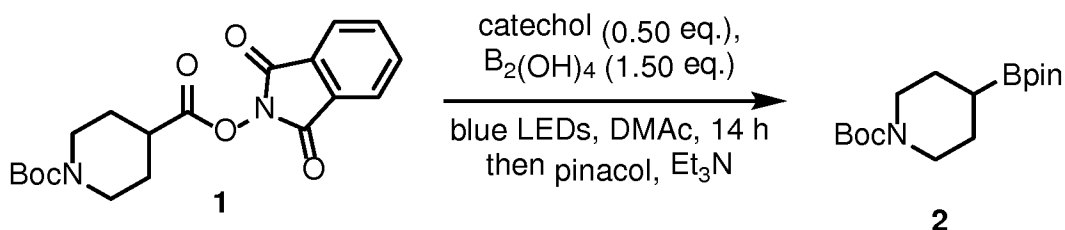
General procedure C (catalytic B₂cat₂):

- 5 NHPI ester (50 mg, 1.0 eq., 0.13 mmol), B₂cat₂ (3 mg, 0.10 eq., 0.013 mmol) and B₂(OH)₄ (18 mg, 1.50 eq., 0.195 mmol) were carefully weighed into a flame-dried 7 mL vial containing a small magnetic stirrer bar. DMAc (1.3 mL, 0.1 M) was added and then the headspace of the vial was purged with a gentle stream of argon for approximately 10 seconds. The vial was tightly sealed and stirred under blue LED
- 10 irradiation for 14 h. Pinacol (63 mg, 0.53 mmol, 4 eq.) was dissolved in Et₃N (0.45 mL), added to the reaction mixture and stirred for 1 h. The reaction mixture was transferred into a vial containing EtOAc (15 mL), H₂O (3 mL), NH₄Cl (saturated aqueous solution, 3 mL). After vigorously shaking and allowing the two layers to separate, the top organic layer was carefully removed with a pipette. This was repeated
- 15 twice more with EtOAc (5 mL). The organic layers were combined and concentrated under reduced pressure. The crude residue was directly purified using a short silica gel column to yield the desired boronic ester.

Notes: Solvents: Also works in DMF, DMPU, DMI, NMP and tetramethylurea.

Diboron source: Also works with 0 – 100% B₂cat₂ and 95 – 150% B₂(OH)₄. **Starting**

- 20 **material:** Also works with the tetrachlorophthalimide.

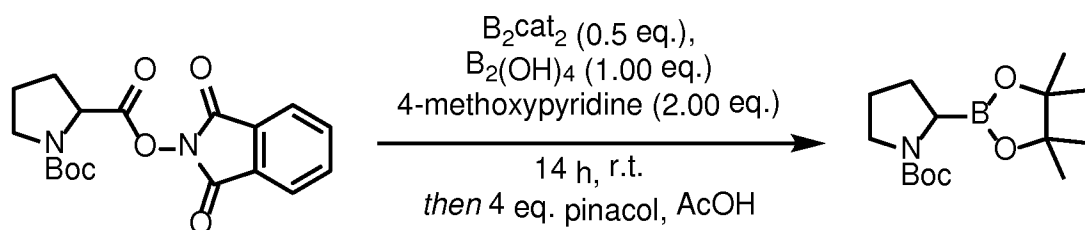


General procedure D (catalytic catechol):

NHPI ester (50 mg, 1.0 eq., 0.13 mmol), catechol (4.5 mg, 0.50 eq., 0.065 mmol) and $B_2(OH)_4$ (18 mg, 1.50 eq., 0.195 mmol) were carefully weighed into a flame-dried 7 mL vial containing a small magnetic stirrer bar. DMAc (1.3 mL, 0.1 M) was added and then the headspace of the vial was purged with a gentle stream of argon for approximately 10 seconds. The vial was tightly sealed and stirred under blue LED irradiation for 14 h. Pinacol (63 mg, 0.53 mmol, 4 eq.) was dissolved in Et_3N (0.45 mL), added to the reaction mixture and stirred for 1 h. The reaction mixture was transferred into a vial containing EtOAc (15 mL), H_2O (3 mL), NH_4Cl (saturated aqueous solution, 3 mL). After vigorously shaking and allowing the two layers to separate, the top organic layer was carefully removed with a pipette. This was repeated twice more with EtOAc (5 mL). The organic layers were combined and concentrated under reduced pressure. The crude residue was directly purified using a short silica gel column to yield the desired boronic ester.

Notes: Solvents: Also works in DMF, DMPU, DMI, NMP and tetramethylurea. **Diboron source:** Also works with 5 – 100% catechol and 95 – 150% $B_2(OH)_4$. **Starting material:** Also works with the tetrachlorophthalimide.

1.4 Conditions 3: Decarboxylative Borylation of α -Amino Carboxylic Acids with Pyridine Derivatives and No Light

**General procedure E:**

NHPI ester (48 mg, 1.0 eq., 0.13 mmol), B_2cat_2 (16 mg, 0.10 eq., 0.065 mmol) and $B_2(OH)_4$ (12 mg, 1.0 eq., 0.13 mmol) were carefully weighed into a flame-dried 7 mL vial containing a small magnetic stirrer bar. DMAc (1.3 mL, 0.1 M) and 4-methoxypyridine (29 μ L, 2.0 eq., 0.26 mmol) were added and then the headspace of the

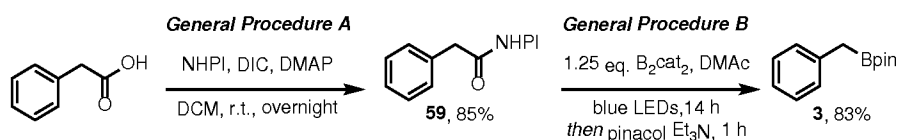
vial was purged with a gentle stream of argon for approximately 10 seconds. The vial was tightly sealed and stirred at room temperature for 14 h. Pinacol (63 mg, 0.53 mmol, 4 eq.) and glacial acetic acid (0.03 mL) was added to the reaction mixture and stirred for 4 h. The reaction mixture was transferred into a vial containing EtOAc (15 mL),
 5 H₂O (3 mL), NH₄Cl (saturated aqueous solution, 3 mL). After vigorously shaking and allowing the two layers to separate, the top organic layer was carefully removed with a pipette. This was repeated twice more with EtOAc (5 mL). The organic layers were combined and concentrated under reduced pressure. The crude residue was directly purified using a short silica gel column to yield the desired boronic ester.

- 10 **Notes: Solvents:** Also works in DMF, DMPU, DMI, NMP, tetramethylurea, MeCN, DCM, DME, Et₂O, 1,4-dioxane, acetone, EtOAc, hexane, toluene, THF, chloroform. **Diboron source:** Also works with 5 – 100% B₂cat₂ and 95 – 150% B₂(OH)₄. **Additive:** Also works with DMAP, pyridine, DABCO, DBU, quinuclidine, TMG, TBD, MTBD, 2-picoline, 4-picoline, 3-picoline, imidazole, K₂CO₃, AcOH, triethylamine, 4-
 15 cyanopyridine, 4-phenylpyridine. **Starting material:** Also works with the tetrachlorophthalimide.

2. Substrate Scope

2.1.1 Substrate Scope: Primary

20 2-Benzyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3)



- Activation:** The carboxylic acid (1.30 g, 10.0 mmol) was coupled with *N*-hydroxyphthalimide according to **General Procedure A**. The crude residue was purified by flash column chromatography (SiO₂; 90:10 hexane:EtOAc) to afford the
 25 corresponding NHPI ester **59** (2.28 g, 85%) as a white solid.

m.p.: 54 – 58 °C (DCM/MeOH)

TLC: *R*_f = 0.24 (90:10 hexane:EtOAc)

¹H NMR (400 MHz, CDCl₃) δ 7.89 – 7.84 (m, 2H, phthalimide ArH), 7.79 – 7.74 (m, 2H, phthalimide ArH), 7.40 – 7.30 (m, 5H, ArH), 4.00 (s, 2H, CH₂) ppm

¹³C NMR (101 MHz, CDCl₃) δ 167.8 (C=O), 161.9 (C=O), 134.9 (phthalimide ArCH), 131.6 (ArC), 129.4 (ArCH), 129.0 (phthalimide ArC), 127.9 (ArCH), 124.1 (phthalimide ArCH), 37.8 (ArCH₂) ppm (*ArC of phenyl ring not observed*)

HRMS (*m/z*): (ESI) calc'd for C₁₆H₁₁NO₄Na [M+Na]⁺: 304.0580, found: 304.0591

IR (solid state) ν_{max} : 1736, 1363, 1184, 1133, 1060, 969 and 876 cm⁻¹

Borylation: NHPI ester **59** (37 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO₂; 80:20 pentane:Et₂O) to afford boronic ester **3** (24 mg, 83%) as a colorless oil.

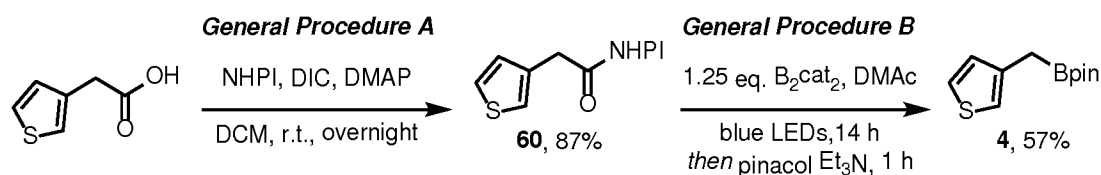
TLC: *R*_f = 0.77 (95:5 pentane:Et₂O)

¹H NMR (400 MHz, CDCl₃) δ 7.26 – 7.10 (m, 5H, ArH), 2.29 (s, 2H, CH₂Bpin), 1.23 (s, 12H, Bpin) ppm

¹³C NMR (101 MHz, CDCl₃) δ 138.8 (ArC), 129.1 (ArCH), 128.4 (ArCH), 125.0 (ArCH), 83.6 (C(CH₃)₂), 24.9 (C(CH₃)₂) ppm

All data matched that reported in the literature.

4,4,5,5-Tetramethyl-2-(thiophen-3-ylmethyl)-1,3,2-dioxaborolane (**4**)



Activation: The carboxylic acid (500 mg, 3.52 mmol) was coupled with *N*-hydroxyphthalimide according to **General Procedure A**. The crude residue was purified by flash column chromatography (SiO₂; 20:80 pentane:DCM) to afford the corresponding NHPI ester **60** (878 mg, 87%) as a colorless oil.

TLC: *R*_f = 0.36 (20:80 pentane:DCM)

¹H NMR (400 MHz, CDCl₃) δ 7.90 – 7.86 (m, 2H, phthalimide ArH), 7.81 – 7.77 (m, 2H, phthalimide ArH), 7.36 – 7.32 (m, 2H, ArH), 7.14 – 7.12 (m, 1H, ArH), 4.03 (s, 2H, CH₂) ppm

¹³C NMR (101 MHz, CDCl₃) δ 167.3 (C=O), 161.9 (C=O), 135.0 (phthalimide ArCH), 130.9 (ArC), 129.0 (phthalimide ArC), 128.3 (ArH), 126.4 (ArH), 124.1 (phthalimide ArCH), 123.9 (ArH), 32.6 (CH₂) ppm

HRMS (*m/z*): (ESI) calc'd for C₁₄H₉NO₄SNa [M+Na]⁺: 310.0144, found: 310.0145

IR (neat) ν_{max} : 3103, 1786, 1735, 1357, 1185, 1063, 974, 876 and 783 cm⁻¹

Borylation: NHPI ester **60** (38 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO₂; 90:10 pentane:Et₂O) to afford boronic ester **4** (17 mg, 57%) as a colorless oil. **Note:** Product volatile! Product unstable on silica gel.

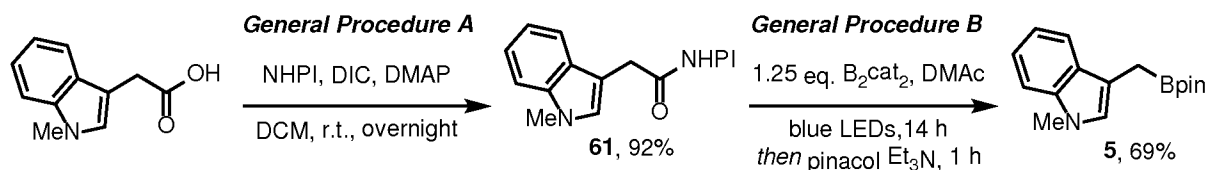
TLC: *R*_f = 0.34 (90:10 pentane:Et₂O)

¹H NMR (400 MHz, CDCl₃) δ 7.20 (dd, *J* = 4.7, 3.0 Hz, 1H, ArH), 6.95 – 6.93 (m, 2H, ArH), 2.28 (s, 2H, CH₂), 1.25 (s, 12H, C(CH₃)₂) ppm

¹³C NMR (101 MHz, CDCl₃) δ 137.7 (ArC), 129.6 (ArCH), 124.9 (ArCH), 120.2 (ArCH), 83.6 (C(CH₃)₂), 24.9 (C(CH₃)₂) ppm

All data matched that reported in the literature.

20 1-Methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1H-indole (**5**)



Activation: The carboxylic acid (500 mg, 2.64 mmol) was coupled with *N*-hydroxyphthalimide according to **General Procedure A**. The crude residue was purified by flash column chromatography (SiO₂; 20:80 pentane:DCM) to afford the corresponding NHPI ester **61** (809 mg, 92%) as a white solid.

m.p.: 120 – 122 °C (DCM/MeOH)

TLC: R_f = 0.26 (20:80 pentane:DCM)

^1H NMR (400 MHz, CDCl_3) δ 7.89 – 7.84 (m, 2H, phthalimide ArH), 7.78 – 7.74 (m, 2H, phthalimide ArH), 7.64 (d, J = 7.9 Hz, 1H, NCH), 7.31 (d, J = 8.1 Hz, 1H, ArH),
5 7.25 (t, J = 7.5 Hz, 1H, ArH), 7.18 – 7.15 (m, 2H, ArH), 4.14 (s, 2H, CH_2), 3.77 (s, 3H, NCH₃) ppm

^{13}C NMR (101 MHz, CDCl_3) δ 168.2 (C=O), 162.1 (C=O), 137.0 (ArC), 134.9 (phthalimide ArCH), 129.1 (phthalimide ArC), 128.2 (ArCH), 127.5 (ArC), 124.1 (phthalimide ArCH), 122.2 (ArCH), 119.6 (ArCH), 118.9 (NCH), 109.5 (ArCH), 104.4
10 (ArC), 32.9 (NCH₃), 28.1 (CH_2) ppm

HRMS (m/z): (ESI) calc'd for $\text{C}_{19}\text{H}_{14}\text{NO}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 357.0846, found: 357.0853

IR (solid state) ν_{max} : 3074, 2917, 1729, 1187, 1061, 970, 876, 736, 693 and 518 cm^{-1}

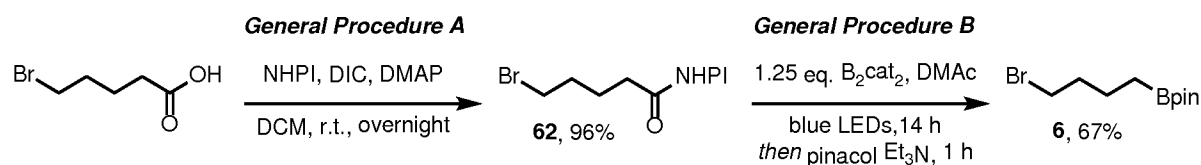
Borylation: NHPI ester **61** (45 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO_2 ;
15 70:30 pentane: Et_2O) to afford boronic ester **5** (25 mg, 69%) as a colorless oil.

TLC: R_f = 0.40 (70:30 pentane: Et_2O)

^1H NMR (400 MHz, CDCl_3) δ 7.61 (d, J = 7.9 Hz, 1H, ArH), 7.27 (d, J = 8.2 Hz, 1H, ArH), 7.21 (t, J = 7.5 Hz, 1H, ArH), 7.09 (t, J = 7.4 Hz, 1H, ArH), 6.94 (s, 1H, NCH),
3.74 (s, 3H, NCH₃), 2.34 (s, 2H, CH_2), 1.29 (s, 12H, $\text{C}(\text{CH}_3)_2$) ppm

^{13}C NMR (101 MHz, CDCl_3) δ 137.1 (ArC), 128.9 (ArC), 126.7 (NCH), 121.3 (ArCH),
20 119.3 (ArCH), 118.3 (ArCH), 110.2 (ArC), 109.0 (ArCH), 83.5 ($\text{C}(\text{CH}_3)_3$), 32.7 (CH_3), 25.0 ($\text{C}(\text{CH}_3)_2$) ppm

All data matched that reported in the literature.

2-(4-Bromobutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6)

Activation: The carboxylic acid (2.37 g, 13.1 mmol) was coupled with *N*-hydroxyphthalimide according to **General Procedure A**. The crude residue was purified by flash column chromatography (SiO₂; 90:10 hexane:EtOAc) to afford the corresponding NHPI ester **62** (4.10 g, 96%) as a white solid.

m.p.: 53 – 56 °C (DCM/MeOH)

TLC: *R*_f = 0.24 (90:10 hexane:EtOAc)

¹H NMR: (400 MHz, CDCl₃) δ 7.91 – 7.86 (m, 2H, phthalimide ArCH), 7.81 – 7.77 (m, 2H, phthalimide ArCH), 3.46 (t, *J* = 5.9 Hz, 2H, CH₂C=O), 2.72 (t, *J* = 7 Hz, 2H, CH₂Br), 2.07 – 1.92 (m, 4H, 2×CH₂) ppm

¹³C NMR: (101 MHz, CDCl₃) δ 169.2 (C=O), 162.0 (C=O), 134.9 (phthalimide ArCH), 129.0 (phthalimide ArC), 124.1 (phthalimide ArCH), 32.7 (CH₂C=O), 31.5 (CH₂), 30.2 (CH₂Br), 23.3 (CH₂) ppm

HRMS (*m/z*): (ESI) calc'd for C₁₃H₁₂BrNO₄Na [M+Na]⁺: 347.9842, found: 347.9840

IR (solid state) ν_{max}: 1738, 1374, 1186, 1138, 1065, 968 and 858 cm⁻¹

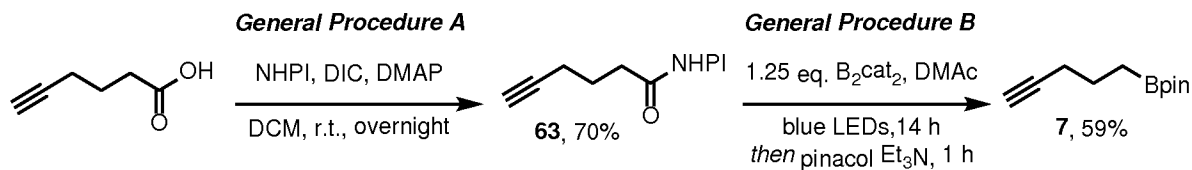
Borylation: NHPI ester **62** (44 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO₂; 80:20 pentane:Et₂O) to afford boronic ester **6** (23 mg, 67%) as a colorless oil. **Note:** Product volatile!

¹H NMR: (400 MHz, CDCl₃) δ 3.40 (t, *J* = 7.4 Hz, 2H, CH₂Br), 1.87 (p, *J* = 7.4 Hz, 2H, CH₂CH₂Br), 1.54 (p, *J* = 7.4 Hz, 2H, CH₂CH₂Bpin), 1.24 (s, 12H, C(CH₃)₂), 0.79 (t, *J* = 7.4 Hz, 2H, CH₂Bpin) ppm

¹³C NMR: (101 MHz, CDCl₃) δ 83.2 (C(CH₃)₂), 35.5 (CH₂Br), 33.8 (CH₂), 25.0 (C(CH₃)₂), 22.9 (CH₂) ppm

All data matched that reported in the literature.

4,4,5,5-Tetramethyl-2-(pent-4-yn-1-yl)-1,3,2-dioxaborolane (7)



- 5 **Activation:** The carboxylic acid (0.23 mL, 2.0 mmol) was coupled with *N*-hydroxyphthalimide according to **General Procedure A**. The crude residue was purified by flash column chromatography (SiO₂; 90:10 hexane:EtOAc) to afford the corresponding NHPI ester **63** (360 mg, 70%) as a white solid.

m.p.: 48 – 52 °C (DCM/MeOH)

- 10 **TLC:** *R*_f = 0.28 (90:10 hexane:EtOAc)

¹H NMR: (400 MHz, CDCl₃) δ 7.90 – 7.85 (m, 2H, phthalimide ArH), 7.81 – 7.76 (m, 2H, phthalimide ArH), 2.83 (t, *J* = 7.1 Hz, 2H, CH₂C=O), 2.37 (td, *J* = 7.1, 2.6 Hz, 2H, ≡CCH₂), 2.03 (t, *J* = 2.6 Hz, ≡CH), 2.00 (p, *J* = 7.1 Hz, 2H, ≡CCH₂CH₂) ppm

- 15 **¹³C NMR:** (101 MHz, CDCl₃) δ 169.2 (C=O), 162.0 (C=O), 134.9 (phthalimide ArCH), 129.0 (phthalimide ArC), 124.1 (phthalimide ArCH), 82.6 (≡CH), 70.0 (≡C), 29.8 (CH₂C=O), 23.5 (≡CCH₂CH₂), 17.8 (≡CCH₂) ppm

HRMS (*m/z*): (ESI) calc'd for C₁₄H₁₁NO₄Na [M+Na]⁺: 280.0580, found: 280.0573

IR (solid state) ν_{max}: 3273, 1741, 1182, 1062, 969 and 876 cm⁻¹

- 20 **Borylation:** NHPI ester **63** (33 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO₂; 95:5 pentane:Et₂O) to afford boronic ester **7** (15 mg, 59%) as a colorless oil. **Note:** Product volatile!

TLC: *R*_f = 0.80 (95:5 pentane:Et₂O)

¹H NMR: (400 MHz, CDCl₃) δ 2.19 (td, J = 7.5, 2.6 Hz, 2H, $\equiv$ CH₂), 1.93 (t, J = 2.6 Hz, 1H, $\equiv$ CH), 1.65 (p, J = 7.5, 2H, $\equiv$ CH₂CH₂), 1.24 (s, 12H, C(CH₃)₂), 0.89 (t, J = 7.5 Hz, 2H, CH₂Bpin) ppm

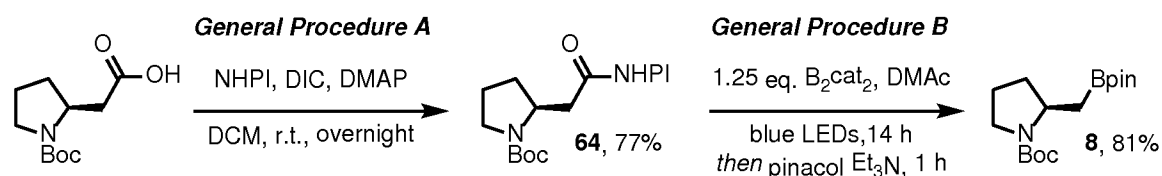
¹³C NMR: (101 MHz, CDCl₃) δ 84.7 ($\equiv$ CH), 83.1 (C(CH₃)₂), 68.3 ($\equiv$ C), 24.9

5 (C(CH₃)₂, 23.3 ($\equiv$ CCH₂CH₂), 20.8 ($\equiv$ CCH₂) ppm

LRMS (m/z): (EI) 179 ([M-Me]⁺, 36%), 194 ([M+H]⁺, 3%). *Despite repeated attempts, a HRMS could not be obtained.*

IR (CHCl₃) $\nu_{\max}$: 3297, 2979, 2936, 1374, 1318, 1233, and 1145 cm⁻¹

10 ***tert*-Butyl-(*R*)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pyrrolidine-1-carboxylate (**8**)**



Activation: The carboxylic acid (500 mg, 2.18 mmol) was coupled with *N*-hydroxyphthalimide according to **General Procedure A**. The crude residue was
 15 purified by flash column chromatography (SiO₂; 98:2 DCM:Et₂O) to afford the corresponding NHPI ester **64** (628 mg, 77%) as a colorless oil that crystallized over several days to give a white amorphous solid.

TLC: R_f = 0.21 (98:2 DCM:Et₂O)

¹H NMR (400 MHz, CDCl₃) δ 7.93 – 7.71 (br m, 4H, phthalimide ArCH), 4.31 – 4.08
 20 (br m, NCH), 3.48 – 3.09 (br m, 3H, NCH₂ and CH^aH^bC=O), 2.83 – 2.60 (br m, CH^aH^bC=O), 2.24 – 2.09 (br m, CH^aH^b), 2.01 – 1.78 (br m, CH₂ and CH^aH^b) ppm

¹³C NMR (126 MHz, CDCl₃) δ 167.6 and 167.5 (C=O), 162.0 (C=O), 154.5 and 154.2 (C=O), 134.9 and 134.8 (phthalimide ArCH), 129.0 (phthalimide ArC), 124.1 (phthalimide ArCH), 80.2 and 79.7 (OC(CH₃)₃), 54.2 and 54.1 (NCH), 46.9 and 46.5

(CH₂C=O), 36.3 and 35.2 (CH₂), 31.2 and 30.3 (CH₂), 28.6 (C(CH₃)₃), 23.8 and 23.0 (CH₂) ppm (*Doubling up of signals due to presence of rotamers*)

HRMS (*m/z*): (ESI) calc'd for C₁₉H₂₂N₂NaO₆ [M+Na]⁺: 397.1370, found: 397.1372

IR (solid state) $\nu_{\max}$: 2973, 2893, 1739 (C=O), 1698 (C=O), 1678 (C=O), 1365,

1165, 1108, 1081, 956, 877, 697 and 519 cm⁻¹

Borylation: NHPI ester **64** (50 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO₂; 95:5 pentane:acetone) to afford boronic ester **8** (34 mg, 81%) as a colorless oil.

TLC: *R_f* = 0.34 (60:40 pentane:Et₂O)

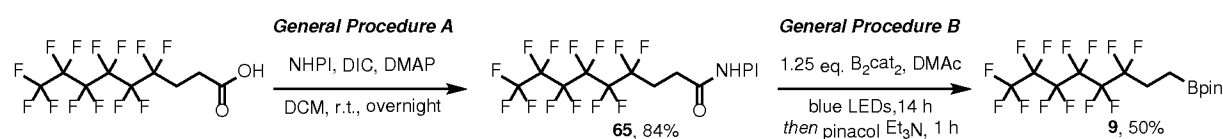
¹H NMR (400 MHz, CDCl₃) δ 4.01 – 3.82 (br m, 1H, NCH), 3.45 – 3.21 (br m, 2H, NCH₂), 2.06 – 1.94 (m, 1H, CH^aH^b), 1.87 – 1.77 (m, 1H, CH^aH^b), 1.75 – 1.66 (m, CH^aH^b), 1.63 – 1.36 (br m, 2H, CH^aH^b and CH^aH^bBpin), 1.43 (s, 9H, OC(CH₃)₃), 1.21 (s, 6H, C(CH₃)₂), 1.20 (s, 6H, C(CH₃)₂), 1.04 – 0.81 (br m, 1H, CH^aH^bBpin) ppm

¹³C NMR (101 MHz, CDCl₃) δ 154.6 and 154.4 (C=O), 83.0 (C(CH₃)₂), 78.9 (OC(CH₃)₃), 54.3 (NCH), 46.5 and 46.3 (NCH₂), 33.4 and 33.1 (CH₂), 28.7 (OC(CH₃)₃), 25.0 and 24.8 (C(CH₃)₂), 23.8 and 23.3 (CH₂) ppm (*Doubling up of signals due to presence of rotamers*)

HRMS (*m/z*): (ESI) calc'd for C₁₆H₃₁NBO₄ [M+H]⁺: 312.2344, found: 312.2341

IR (neat) $\nu_{\max}$: 2975, 1691 (C=O), 1365, 1166, 1141, 1108 and 848 cm⁻¹

4,4,5,5-Tetramethyl-2-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-1,3,2-dioxaborolane (**9**)



Activation: The carboxylic acid (500 mg, 2.23 mmol) was coupled with *N*-hydroxyphthalimide according to **General Procedure A**. The crude residue was

purified by flash column chromatography (SiO₂; 5:1 petroleum ether 40-60:EtOAc) to afford the corresponding NHPI ester **65** (690 mg, 84%) as a white solid.

m.p.: 104 – 106 °C (DCM/MeOH)

TLC: *R*_f = 0.50 (3:1 petroleum ether 40-60:EtOAc)

5 **¹H NMR** (400 MHz, CDCl₃) δ 7.90 – 7.85 (m, 2H, Ar-H), 7.80 – 7.76 (m, 2H, Ar-H), 3.02 (t, *J* = 7.7 Hz, 2H, CH₂), 2.68 – 2.52 (m, 2H, CH₂) ppm

¹³C NMR (101 MHz, CDCl₃) δ 167.7 (C=O), 161.6 (C=O), 134.9 (HC_{Ar}), 128.8 (C_{Ar}), 124.1 (HC_{Ar}), 26.3 (t, *J* = 23.3 Hz, CH₂), 22.9 (t, *J* = 4.8 Hz, CH₂) ppm. *The carbon atoms bearing fluorine atoms were observed (see NMR spectrum) but were not*
10 *assigned.*

¹⁹F NMR (377 MHz, CDCl₃) δ –80.8, –114.6, –121.8, –122.8, –123.3, –126.1 ppm

HRMS (*m/z*): (ESI) calc'd for C₁₇H₈F₁₃NNaO₄ [M+Na]⁺: 560.0138, found: 560.0139

IR (solid state) *v*_{max}: 1744, 1225, 1136, 1073, 965 and 877 cm^{–1}

Borylation: NHPI ester **65** (70 mg, 0.13 mmol) was borylated according to **General**
15 **Procedure B**. The crude residue was purified by flash column chromatography (SiO₂; 10:1 petroleum ether 40-60:Et₂O) to afford boronic ester **9** (31 mg, 50%) as a colorless oil. **Note:** product unstable on silica gel.

TLC: *R*_f = 0.75 (3:1 petroleum ether 40-60:EtOAc)

20 **¹H NMR** (400 MHz, CDCl₃) δ 2.25 – 2.01 (m, 2H, CH₂), 1.18 (s, 12H, 2×OC(CH₃)₂), 1.02 – 0.88 (m, 2H, CH₂) ppm

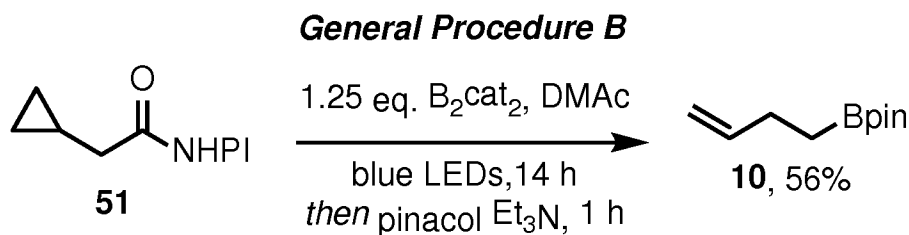
¹³C NMR (101 MHz, CDCl₃) δ 83.6 (OC(CH₃)₂), 25.7 (t, *J* = 23.4 Hz, CF₂CH₂), 24.7 (OC(CH₃)₂) ppm. *The carbon atoms bearing fluorine atoms were observed (see NMR spectrum) but were not assigned.*

25 **¹⁹F NMR** (377 MHz, CDCl₃) δ –80.91, –116.12, –122.00, –122.91, –123.57, –126.20 ppm

HRMS (*m/z*): (ESI) calc'd for C₁₄H₁₆BF₁₃NaO₂ [M+Na]⁺: 497.0931, found: 497.0947

IR (neat) ν_{max} : 2984, 1385, 1235, 1195, 1141, 1072 and 847 cm^{-1}

2-(But-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10)



Activation: NHPI ester **51** was prepared according to a known procedure (36).

- 5 **Borylation:** NHPI ester **51** (33 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO_2 ; 95:5 pentane: Et_2O) to afford boronic ester **10** (14 mg, 56%) as a colorless oil. **Note:** the intermediate alkyl radical undergoes radical ring opening, and the product is volatile!

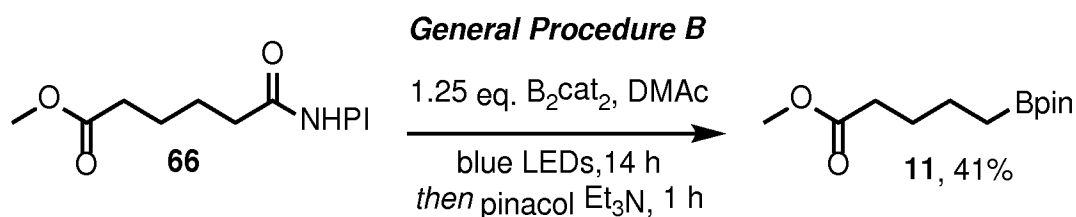
TLC: R_f = 0.29 (95:5 pentane: Et_2O)

- 10 **^1H NMR:** (400 MHz, CDCl_3) δ 5.88 (ddt, J = 17.0, 10.2, 7.3 Hz, 1H, CH=), 5.03 – 4.95 (m, 1H, $=\text{CH}^a\text{H}^b$), 4.92 – 4.87 (m, 1H, $=\text{CH}^a\text{H}^b$), 2.17 (app q, J = 7.3 Hz, 2H, $\text{CH}_2\text{CH=}$), 1.24 (s, 12H, $\text{C}(\text{CH}_3)_2$), 0.88 (t, J = 7.3 Hz, 2H, CH_2Bpin) ppm

^{13}C NMR: (101 MHz, CDCl_3) δ 140.8 ($=\text{CH}$), 113.3 ($=\text{CH}_2$), 83.1 ($\text{C}(\text{CH}_3)_2$), 28.1 (CH_2), 25.0 ($\text{C}(\text{CH}_3)_2$) ppm

- 15 All data matched that reported in the literature.

Methyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (11)



Activation: NHPI ester **66** was prepared according to a known procedure.

Borylation: NHPI ester **66** (40 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO₂; 4:1 petroleum ether 40-60:Et₂O) to afford boronic ester **11** (13 mg, 41%) as a colorless oil.

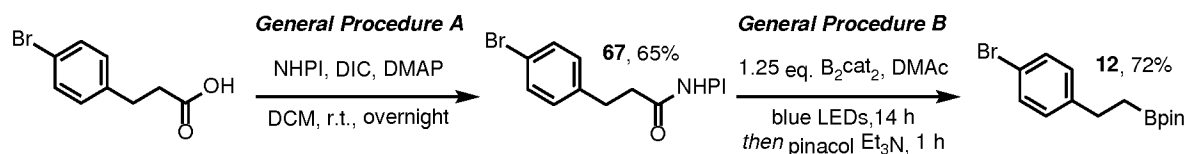
5 **TLC:** R_f = 0.65 (1:1 petroleum ether 40-60:EtOAc)

¹H NMR (400 MHz, CDCl₃) δ 3.67 (s, 3H, CO₂CH₃), 2.32 (t, J = 7.2 Hz, 2H, CH₂), 1.70 – 1.60 (m, 2H, CH₂), 1.50 – 1.40 (m, 2H, CH₂), 1.27 (s, 12H, 2×OC(CH₃)₂), 0.80 (t, J = 8.0 Hz, 2H, CH₂Bpin) ppm

¹³C NMR (101 MHz, CDCl₃) δ 174.2 (CO₂CH₃), 82.9 (OC(CH₃)₂), 51.4 (CO₂CH₃),
10 33.9 (CH₂), 27.5 (CH₂), 24.8 (OC(CH₃)₂), 23.6 (CH₂) ppm

All data matched that reported in the literature.

2-(4-Bromophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**12**)



15 **Activation:** The carboxylic acid (500 mg, 2.18 mmol) was coupled with *N*-hydroxyphthalimide according to **General Procedure A**. The crude product was filtered quickly through a short column (~5 cm silica gel). After concentrated to a ~10 mL solution, 30 mL of MeOH was added. The precipitate was collected by filtration and washed with 10 mL of MeOH to afford the corresponding NHPI ester **67** (530 mg,
20 65%) as a white solid.

m.p.: 154 – 156 °C (DCM/MeOH)

TLC: R_f = 0.38 (3 : 1 petroleum ether 40-60:EtOAc)

¹H NMR (400 MHz, CDCl₃) δ 7.84 – 7.79 (m, 2H, Ar-H), 7.74 – 7.68 (m, 2H, Ar-H), 7.36 (d, J = 8.1 Hz, 2H, Ar-H), 7.06 (d, J = 8.1 Hz, 2H, Ar-H), 2.98 (t, J = 7.3 Hz, 2H, CH₂), 2.88 (t, J = 7.2 Hz, 2H, CH₂) ppm
25

¹³C NMR (101 MHz, CDCl₃) δ 168.6 (C=O), 161.8 (C=O), 138.1 (C_{Ar}), 134.8 (HC_{Ar}), 131.8 (HC_{Ar}), 130.1 (HC_{Ar}), 128.8 (C_{Ar}), 124.0 (HC_{Ar}), 120.6 (C_{Ar}), 32.4 (CH₂), 29.9 (CH₂) ppm

HRMS (*m/z*): (ESI) calc'd for C₁₇H₁₂BrNNaO₄ [M+Na]⁺: 395.9842, found: 395.9854

5 **IR (solid state) $\nu_{\max}$:** 1789, 1741, 1487, 1371, 1070, 964, 877 and 821 cm⁻¹

Borylation: NHPI ester **67** (49 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO₂; 10:1 petroleum ether 40-60:Et₂O) to afford boronic ester **12** (29 mg, 72%) as a colorless oil.

10 **TLC:** *R_f* = 0.68 (3:1 petroleum ether 40-60:EtOAc)

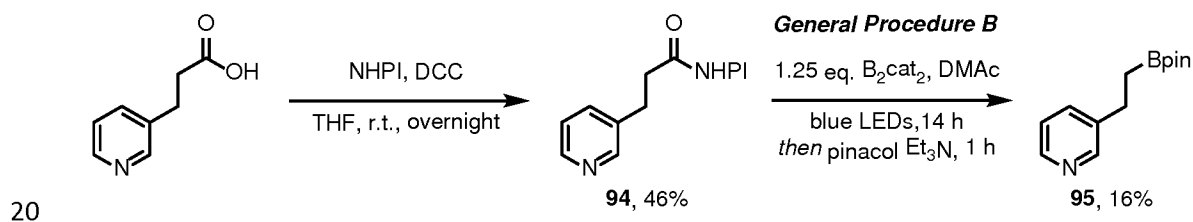
¹H NMR (400 MHz, CDCl₃) δ 7.29 (d, *J* = 8.3 Hz, 2H, Ar-H), 7.01 (d, *J* = 8.3 Hz, 2H, Ar-H), 2.67 – 2.55 (t, *J* = 8.1 Hz, 2H, CH₂), 1.14 (s, 12H, 2×OC(CH₃)₂), 1.03 (t, *J* = 8.1 Hz, 2H, CH₂) ppm

¹³C NMR (101 MHz, CDCl₃) δ 143.3 (C_{Ar}), 131.1 (HC_{Ar}), 129.8 (HC_{Ar}), 119.1 (C_{Ar}),
15 83.1 (OC(CH₃)₂), 29.4 (CH₂), 24.8 (OC(CH₃)₂) ppm

HRMS (*m/z*): (ESI) calc'd for C₁₄H₂₀BBrNaO₂ [M+Na]⁺: 333.0635, found: 333.0647

IR (neat) $\nu_{\max}$: 2976, 1679, 1369, 1315, 1140, 967 and 827 cm⁻¹

3-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)pyridine (**95**):



Activation: The carboxylic acid (500 mg, 3.31 mmol) was coupled with *N*-hydroxyphthalimide according to **General Procedure A**. The crude residue was purified by flash column chromatography (SiO₂; 70:30 pentane:acetone) to afford the

corresponding NHPI ester **94** (447 mg, 46%) as a pale yellow solid. **Note:** product unstable on silica gel.

m.p.: 111 – 115 °C (cryst. EtOAc)

TLC: R_f = 0.21 (pentane:acetone 70:30)

5 **¹H NMR:** (400 MHz, CDCl₃) δ 8.54 (d, J = 2.3 Hz, 1H, Ar-H), 8.50 (dd, J = 4.9, 1.6 Hz, 1H, Ar-H), 7.87 (dd, J = 5.5, 3.1 Hz, 2H, 2×Ar-H), 7.78 (dd, J = 5.5, 3.1 Hz, 2H, 2×Ar-H), 7.60 (ddd, J = 7.8, 2.3, 1.6 Hz, 1H, Ar-H), 7.26 (dd, J = 7.8, 4.9 Hz, 1H, Ar-H), 3.11 (t, J = 7.4 Hz, 2H, pyridyl-CH₂), 2.99 (t, J = 7.4 Hz, 2H, CH₂CO₂R) ppm

10 **¹³C NMR:** (101 MHz, CDCl₃) δ 168.6 (CO₂R), 161.9 (2×CO), 149.9 (HC_{Ar}), 148.4 (HC_{Ar}), 136.0 (HC_{Ar}), 134.9 (2×HC_{Ar}), 134.6 (C_{Ar}), 129.0 (2×C_{Ar}), 124.1 (2×HC_{Ar}), 123.7 (HC_{Ar}), 32.4 (CH₂CO₂R), 27.9 (pyridyl-CH₂) ppm

HRMS (m/z): (ESI) calc'd for C₁₆H₁₂N₂NaO₄ [M+Na]⁺: 319.0689, found: 319.0692

IR (neat) $\nu_{\max}$: 3100, 3055, 2943, 2324 (br.), 1812, 1783, 1742, 1714, 1188 and 1079 cm⁻¹

15 **Borylation:** NHPI ester **94** (77 mg, 0.26 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO₂; 90:10 hexane:acetone) to afford boronic ester **95** (10 mg, 16%) as a colorless oil. **Note:** product unstable on silica gel.

TLC: R_f = 0.54 (pentane:acetone 80:20)

20 **¹H NMR:** (500 MHz, CDCl₃) δ 8.48 (d, J = 1.7 Hz, 1H, Ar-H), 8.41 (dd, J = 4.8, 1.2 Hz, 1H, Ar-H), 7.52 (ddd, J = 7.7, 1.7, 1.2 Hz, 1H, Ar-H), 7.18 (dd, J = 7.7, 4.8 Hz, 1H, Ar-H), 2.74 (t, J = 8.0 Hz, 2H, CH₂), 1.21 (s, 12H, 4×CH₃), 1.14 (t, J = 8.0 Hz, 2H, CH₂) ppm

25 **¹³C NMR:** (126 MHz, CDCl₃) δ 149.9 (HC_{Ar}), 147.2 (HC_{Ar}), 139.6 (HC_{Ar}), 135.6 (HC_{Ar}), 123.3 (HC_{Ar}), 83.4 (2×OC(CH₃)₂), 27.3 (pyridyl-CH₂), 24.9 (4×CH₃) ppm

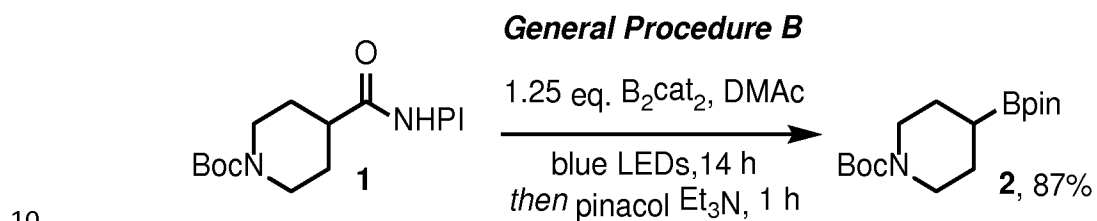
HRMS (m/z): (ESI) calc'd for C₁₃H₂₀BNNaO₂ [M+Na]⁺: 256.1482, found: 256.1480

IR (neat) ν_{max} : 2978, 2929, 1575, 1479, 1422, 1372, 1311, 1144, 968, 849 and 714 cm^{-1}

5

2.1.2 Substrate Scope: Secondary

***tert*-Butyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine-1-carboxylate (**2**)**



Activation: NHPI ester **1** was prepared according to a known procedure.

Borylation: NHPI ester **1** (50 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO_2 ; 75:25 pentane: Et_2O) to afford boronic ester **2** (35 mg, 87%) as a colorless oil.

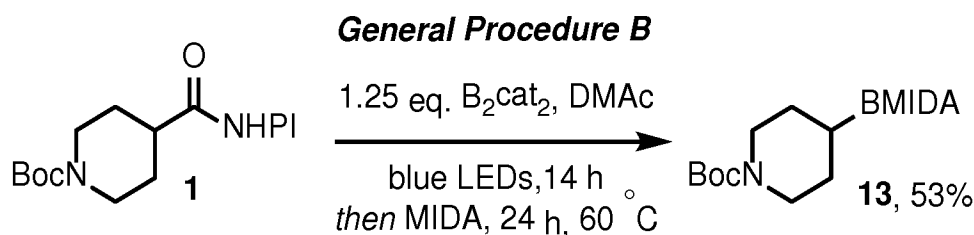
15 **TLC:** R_f = 0.28 (75:25 pentane: Et_2O)

^1H NMR (400 MHz, CDCl_3) δ 3.85 – 3.70 (m, 2H, NCH^aH^b), 2.95 – 2.88 (m, 2H, NCH^aH^b), 1.65 – 1.60 (m, 2H, CH^aH^b), 1.51 – 1.38 (m, 2H, CH^aH^b), 1.43 (s, 9H, $\text{OC}(\text{CH}_3)_3$), 1.22 (s, 12H, $\text{C}(\text{CH}_3)_2$), 1.06 (m, 1H, CHBpin) ppm

20 **^{13}C NMR** (126 MHz, CDCl_3) δ 155.0 ($\text{C}=\text{O}$), 83.3 ($\text{C}(\text{CH}_3)_2$), 79.1 ($\text{OC}(\text{CH}_3)_3$), 45.0 (NCH_2), 28.6 ($\text{OC}(\text{CH}_3)_3$), 27.1 (CH_2), 24.9 ($\text{C}(\text{CH}_3)_2$) ppm

All data matched that reported in the literature.

***tert*-Butyl 4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)piperidine-1-carboxylate (**13**)**



5

Activation: NHPI ester **1** was prepared according to a known procedure.

Borylation: NHPI ester **1** (50 mg, 0.13 mmol) was borylated according to **General Procedure B** but with a modified workup. After the 14 h stir under irradiation with blue LEDs methyliminodiacetic acid (MIDA, 79 mg, 0.53 mmol, 4.0 eq.) was added and the reaction mixture was stirred for 24 h at 60 °C (oil bath). The reaction mixture was transferred into a vial containing EtOAc (15 mL) and H₂O (6 mL). After vigorously shaking and allowing to two layers to separate, the top organic layer was carefully removed with a pipette. This was repeated twice more with EtOAc (5 mL). The organic layers were combined and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (SiO₂; THF) to afford boronic ester **13** (24 mg, 53%) as a white amorphous solid. **Note:** The THF must be BHT free.

15

TLC: $R_f = 0.21$ (THF)

¹H NMR (500 MHz, CDCl₃) δ 4.07 – 4.04 (br m, 2H, NCH^aH^b), 3.95 (d, $J = 16.9$ Hz, 2H, C=OCH^aH^b), 3.78 (d, $J = 16.9$ Hz, 2H, C=OCH^aH^b), 2.93 (s, 3H, NCH₃), 2.73 – 2.60 (br m, 2H, NCH^aH^b), 1.61 – 1.58 (br m, 2H, CH^aH^b), 1.44 (s, 9H, C(CH₃)₃), 1.31 – 1.19 (m, 2H, CH^aH^b), 0.93 (tt, $J = 12.3, 3.2$ Hz, CHBpin) ppm

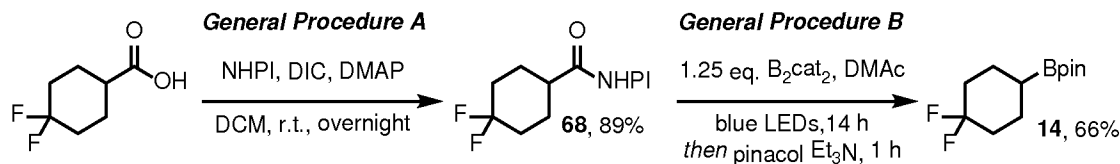
20

¹³C NMR (126 MHz, CDCl₃) δ 169.0 (C=O), 155.4 (C=O), 79.4 (OC(CH₃)₃), 63.2 (C=OCH₂), 46.4 (NCH₃), 28.6 (C(CH₃)₃), 27.9 (CH₂) ppm. NCH₂ not observed.

HRMS (m/z): (ESI) calc'd for C₁₅H₂₅BN₂NaO₆ [M+Na]⁺: 363.1701, found: 363.1697

IR (solid state) ν_{max} : 2924, 2853, 1752, 1676, 1288, 1163, 1111 and 1030 cm^{-1}

2-(4,4-Difluorocyclohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14)



- 5 **Activation:** The carboxylic acid (250 mg, 1.52 mmol) was coupled with *N*-hydroxyphthalimide according to **General Procedure A**. The crude residue was purified by flash column chromatography (SiO_2 ; 75:25 pentane: Et_2O) to afford the corresponding NHPI ester **68** (417 mg, 89%) as a white solid.

m.p.: 109 – 112 $^{\circ}\text{C}$ (DCM/MeOH)

- 10 **TLC:** R_f = 0.19 (90:10 pentane: EtOAc)

^1H NMR (400 MHz, CDCl_3) δ 7.91 – 7.87 (m, 2H, phthalimide ArCH), 7.82 – 7.77 (phthalimide ArCH), 2.92 – 2.85 (m, 1H, $\text{CHC}=\text{O}$), 2.26 – 2.04 (m, 6H, $\text{CH}^a\text{H}^b \times 2$ and $\text{CH}_2 \times 2$), 1.97 – 1.84 (m, 2H, $\text{CH}^a\text{H}^b \times 2$) ppm

- 15 **^{13}C NMR** (126 MHz, CDCl_3) δ 170.6 ($\text{C}=\text{O}$), 162.0 ($\text{C}=\text{O}$), 135.0 (phthalimide ArCH), 129.0 (phthalimide ArC), 124.1 (phthalimide ArCH), 122.3 (t, J = 241.3 Hz, CF_2), 37.9 ($\text{CHC}=\text{O}$), 32.2 (t, J = 24.8 Hz, CF_2CH_2), 25.1 (t, J = 5.1 Hz, CH_2) ppm

^{19}F NMR: (377 MHz, CDCl_3) δ –95.6 (d, J = 239.8 Hz), –98.4 (d, J = 239.8 Hz)

HRMS (m/z): (ESI) calc'd for $\text{C}_{15}\text{H}_{13}\text{F}_2\text{NNaO}_4$ $[\text{M}+\text{Na}]^+$: 332.0705, found: 332.0708

- 20 **IR (solid state) ν_{max} :** 2973, 2948, 1809, 1782, 1740 ($\text{C}=\text{O}$), 1374, 1360, 1147, 1114, 1115, 1079, 981, 947, 875 and 697 cm^{-1}

Borylation: NHPI ester **68** (40 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO_2 ; 95:5 pentane: Et_2O) to afford boronic ester **14** (21 mg, 66%) as a colorless oil.

TLC: R_f = 0.51 (pentane: Et_2O 85:15)

¹H NMR (400 MHz, CDCl₃) δ 1.99 (m, 2H), 1.85 – 1.52 (m, 6H), 1.23 (s, 12H, 4×CH₃), 0.97 (m, 1H, CHBpin) ppm

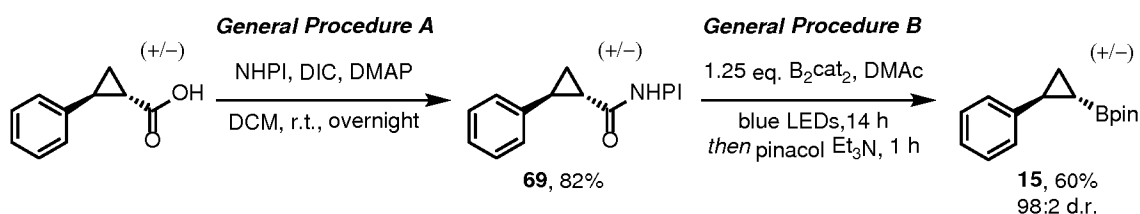
¹³C NMR (101 MHz, CDCl₃) δ 123.9 (t, J = 240.5 Hz, CF₂), 83.4 (2×OC(CH₃)₂), 34.5 (t, J = 23.2 Hz, 2×CH₂CF₂), 24.9 (4×CH₃), 24.4 (m, 2×CH₂CH₂CF₂) ppm

5 **¹⁹F NMR:** (377 MHz, CDCl₃) δ –91.6 (d, J = 234 Hz), –98.7 (d, J = 234 Hz)

MS (m/z): Despite repeated attempts, a HRMS or LRMS could not be obtained by any means.

IR (neat) $\nu_{\max}$: 2925, 2854, 1454, 1330, 1144 and 847 cm^{–1}

10 **4,4,5,5-Tetramethyl-2-(*trans*-2-phenylcyclopropyl)-1,3,2-dioxaborolane (15)**



Activation: The carboxylic acid (1.00 g, 6.17 mmol) was coupled with *N*-hydroxyphthalimide according to **General Procedure A**. The crude residue was purified by flash column chromatography (SiO₂; 80:20 → 60:40 pentane:Et₂O) to afford the corresponding NHPI ester **69** (1.55 g, 82%) as a white solid.

15

m.p.: 116 – 119 °C (Et₂O)

TLC: R_f = 0.34 (pentane:Et₂O 70:30)

¹H NMR: (400 MHz, CDCl₃) δ 7.90 (m, 2H, 2×Ar-H), 7.79 (m, 2H, 2×Ar-H), 7.34 (m, 2H, 2×Ar-H), 7.27 (m, 1H, Ar-H), 7.28 (m, 2H, 2×Ar-H), 2.79 (ddd, J = 9.1, 6.9, 4.0 Hz, 1H, PhCH), 2.23 (ddd, J = 8.4, 5.2, 4.0 Hz, 1H, CHCO₂R), 1.83 (ddd, J = 9.1, 5.2, 4.9 Hz, 1H, CH^aH^b), 1.64 (ddd, J = 8.4, 6.9, 4.9 Hz, 1H, CH^aH^b) ppm

20

^{13}C NMR: (101 MHz, CDCl_3) δ 169.8 (CO_2R), 162.1 ($2\times\text{CO}$), 138.6 (C_{Ar}), 134.8 ($2\times\text{HC}_{\text{Ar}}$), 129.1 ($2\times\text{C}_{\text{Ar}}$), 128.8 ($2\times\text{HC}_{\text{Ar}}$), 127.3 (HC_{Ar}), 126.5 ($2\times\text{HC}_{\text{Ar}}$), 124.1 ($2\times\text{HC}_{\text{Ar}}$), 28.4 (PhCH), 21.1 (CHCO_2R), 18.6 (CH_2) ppm

HRMS (m/z): (ESI) calc'd for $\text{C}_{18}\text{H}_{13}\text{NNaO}_4$ $[\text{M}+\text{Na}]^+$: 330.0737, found: 330.0748

5 **IR (neat) ν_{max} :** 3065, 3031, 1806, 1778, 1738, 1467, 1401, 1360, 1186, 1100 and 877 cm^{-1}

Borylation: NHPI ester **69** (40 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO_2 ; 95:5 pentane: Et_2O) to afford boronic ester **15** (19 mg, 60%) as a colorless oil.

10 **TLC:** R_f = 0.35 (pentane: Et_2O 95:5)

^1H NMR: (400 MHz, CDCl_3) δ 7.24 (m, 2H, $2\times\text{Ar-H}$), 7.14 (m, 1H, Ar-H), 7.08 (m, 2H, $2\times\text{Ar-H}$), 2.11 (ddd, J = 8.1, 5.5, 5.2 Hz, 1H, PhCH), 1.26 (s, 6H, $2\times\text{CH}_3$), 1.24 (s, 6H, $2\times\text{CH}_3$), 1.16 (ddd, J = 8.1, 6.8, 3.7 Hz, 1H, $\text{CH}^{\text{a}}\text{H}^{\text{b}}$), 1.01 (ddd, J = 9.5, 5.2, 3.7 Hz, 1H, $\text{CH}^{\text{a}}\text{H}^{\text{b}}$), 0.31 (ddd, J = 9.5, 6.8, 5.5 Hz, 1H, CHBpin) ppm

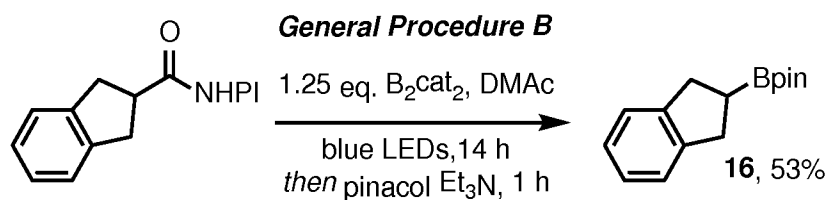
15 **^{13}C NMR:** (101 MHz, CDCl_3) δ 143.5 (C_{Ar}), 128.4 ($2\times\text{HC}_{\text{Ar}}$), 125.8 ($2\times\text{HC}_{\text{Ar}}$), 125.7 (HC_{Ar}), 83.3 ($2\times\text{OC}(\text{CH}_3)_2$), 24.9 ($2\times\text{CH}_3$), 24.8 ($2\times\text{CH}_3$), 22.0 (PhCH), 15.2 (CH_2) ppm

HRMS (m/z): (EI) calc'd for $\text{C}_{15}\text{H}_{21}\text{BO}_2$: 244.1635, found: 244.1634

IR (neat) ν_{max} : 3027, 2978, 2931, 1419, 1357, 1321, 1217, 1144 and 860 cm^{-1}

20 All data matched that reported in the literature.

2-(2,3-Dihydro-1H-inden-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**16**)



Activation: NHPI ester **70** was prepared according to a known procedure.

Borylation: NHPI ester **70** (40 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO₂; 5:1 petroleum ether 40-60:Et₂O) to afford boronic ester **16** (17 mg, 53%) as a colorless oil.

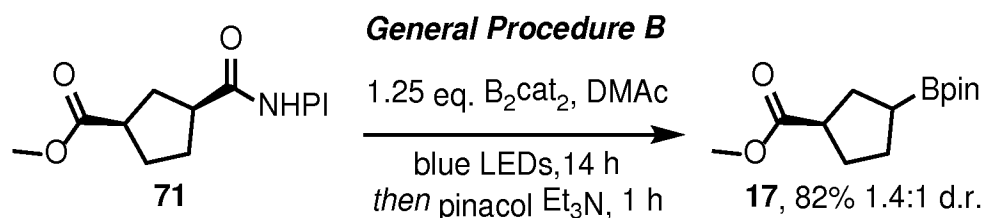
TLC: R_f = 0.68 (3:1 petroleum ether 40-60:EtOAc)

¹H NMR (400 MHz, CDCl₃) δ 7.16 – 7.11 (m, 2H, Ar-H), 7.08 – 7.00 (m, 2H, Ar-H), 3.05 – 2.83 (m, 4H, 2×CH₂), 1.80 (p, J = 9.9 Hz, 1H, CHBpin), 1.19 (s, 12H, 2×OC(CH₃)₂) ppm

¹³C NMR (101 MHz, CDCl₃) δ 144.4 (C_{Ar}), 125.8 (HC_{Ar}), 124.1 (HC_{Ar}), 83.2 (OC(CH₃)₂), 35.1 (CH₂), 24.7 (OC(CH₃)₂) ppm

All data matched that reported in the literature.

Methyl (1R)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane-1-carboxylate (17)



Activation: NHPI ester **71** was prepared according to a known procedure.

Borylation: NHPI ester **71** (42 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO₂; 70:30 pentane:Et₂O) to afford boronic ester **17** (28 mg, 82%, 1.4:1 d.r.) as a colorless oil.

TLC: R_f = 0.36 (70:30 pentane:Et₂O)

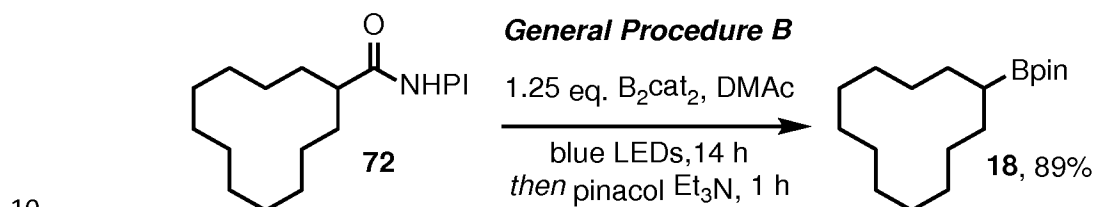
¹H NMR (400 MHz, CDCl₃) δ 3.64 and 3.64 (s, 3H C=OOCH₃), 2.82 – 2.67 (m, 1H, CHC=O), 2.12 – 1.35 (m, 7H, CHBpin and CH₂ ×3), 1.22 and 1.21 (s, 12H, C(CH₃)₂) ppm

¹³C NMR (101 MHz, CDCl₃) δ 177.3 and 177.0 (C=O), 83.2 and 83.1 (C(CH₃)₂), 51.7 and 51.6 (C=OOCH₃), 45.2 and 44.3 (CHC=O), 33.3 and 32.3 (CH₂), 31.3 and 30.5 (CH₂), 28.9 and 27.9 (CH₂), 24.9 and 24.8 (C(CH₃)₂) ppm

HRMS (*m/z*): (ESI) calc'd for C₁₃H₂₃BNaO₄ [M+Na]⁺: 277.1584, found: 277.1580

IR (neat) *v*_{max}: 2977, 2952, 2872, 1733, 1381, 1315, 1197, 1143, 973 and 858 cm⁻¹

2-Cyclododecyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18)



Activation: NHPI ester **72** was prepared according to a known procedure.

Borylation: NHPI ester **72** (46 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO₂; 10:1 petroleum ether 40-60:Et₂O) to afford boronic ester **18** (34 mg, 89%) as a colorless oil.

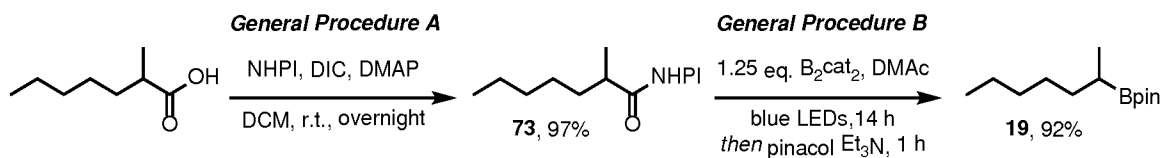
TLC: *R*_f = 0.54 (10:1 petroleum ether 40-60:EtOAc)

¹H NMR (400 MHz, CDCl₃) δ 1.45 – 1.20 (m, 22H, 11×CH₂), 1.16 (s, 12H, 2×OC(CH₃)₂), 1.04 – 0.94 (m, 1H, CHBpin) ppm

¹³C NMR (101 MHz, CDCl₃) δ 82.7 (OC(CH₃)₂), 24.9 (CH₂), 24.7 (OC(CH₃)₂), 24.2 (CH₂), 24.1 (CH₂), 23.4 (CH₂), 23.4 (CH₂), 23.3 (CH₂) ppm

HRMS (*m/z*): (ESI) calc'd for C₁₈H₃₅BNaO₂ [M+Na]⁺: 317.2626, found: 317.2628

IR (neat) *v*_{max}: 2928, 2848, 1469, 1305, 1144, 967, 858 and 708 cm⁻¹

2-(Heptan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (19)

Activation: The carboxylic acid (1.44 g, 10.0 mmol) was coupled with *N*-hydroxyphthalimide according to **General Procedure A**. The crude residue was purified by flash column chromatography (SiO₂; 5:1 petroleum ether 40-60:EtOAc) to afford the corresponding NHPI ester **73** (2.81 g, 97%) as a colorless oil.

TLC: R_f = 0.51 (3:1 petroleum ether 40-60:EtOAc)

¹H NMR (400 MHz, CDCl₃) δ 7.78 – 7.73 (m, 2H, Ar-H), 7.70 – 7.65 (m, 2H, Ar-H), 2.80 – 2.67 (m, 1H, CH), 1.79 – 1.66 (m, 1H, CH₂), 1.58 – 1.47 (m, 1H, CH₂), 1.41 – 1.33 (m, 2H, CH₂), 1.29 – 1.19 (m, 7H, 2×CH₂ + CH₃), 0.90 – 0.76 (m, 3H, CH₃) ppm

¹³C NMR (101 MHz, CDCl₃) δ 172.7 (C=O), 161.9 (C=O), 134.6 (HC_{Ar}), 128.9 (C_{Ar}), 123.8 (HC_{Ar}), 37.1 (CH), 33.6 (CH₂), 31.5 (CH₂), 26.4 (CH₂), 22.4 (CH₂), 16.9 (CH₃), 13.9 (CH₃) ppm

HRMS (m/z): (ESI) calc'd for C₁₆H₁₉NNaO₄ [M+Na]⁺: 312.1206, found: 312.1201

IR (neat) ν_{max} : 2931, 1739, 1466, 1363, 1185, 1047, 876 and 710 cm⁻¹

Borylation: NHPI ester **73** (38 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO₂; 10:1 petroleum ether 40-60:Et₂O) to afford boronic ester **19** (27 mg, 92%) as a colorless oil.

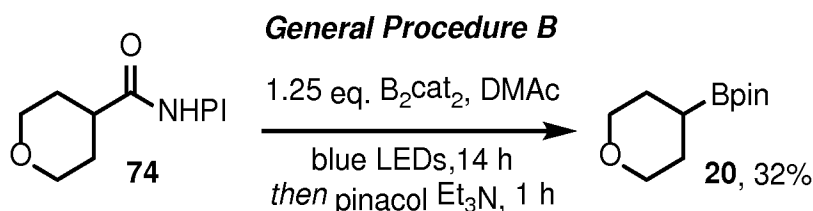
TLC: R_f = 0.54 (10:1 petroleum ether 40-60:EtOAc)

¹H NMR (400 MHz, CDCl₃) δ 1.38 – 1.15 (m, 20H, 8×CH₂ + 2×OC(CH₃)₂), 0.95 – 0.86 (m, 4H, CHBpin + CH₃), 0.80 (t, J = 6.9 Hz, 3H, CH₃) ppm

¹³C NMR (101 MHz, CDCl₃) δ 82.7 (OC(CH₃)₂), 33.2 (CH₂), 32.0 (CH₂), 28.6 (CH₂), 24.7 (OC(CH₃)₂), 24.7 (OC(CH₃)₂), 22.6 (CH₂), 15.5 (CH₃), 14.0 (CH₃) ppm

All data matched that reported in the literature.

4,4,5,5-Tetramethyl-2-(tetrahydro-2H-pyran-4-yl)-1,3,2-dioxaborolane (20)



Activation: NHPI ester **74** was prepared according to a known procedure.

- 5 **Borylation:** NHPI ester **74** (36 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO₂; 3:1 petroleum ether 40-60:Et₂O) to afford boronic ester **20** (9 mg, 32%) as a colorless oil. **Note:** the product is unstable on silica gel.

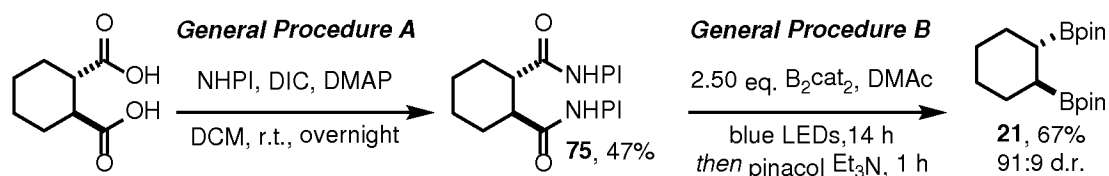
TLC: $R_f = 0.48$ (3:1 petroleum ether 40-60:EtOAc)

- 10 **¹H NMR** (400 MHz, CDCl₃) δ 3.76 (dt, $J = 11.2, 3.9$ Hz, 2H, OCH₂), 3.48 – 3.34 (m, 2H, OCH₂), 1.59 – 1.51 (m, 4H, 2×CH₂), 1.23 – 1.15 (m, 13H, CHBpin + 2×OC(CH₃)₂) ppm

¹³C NMR (101 MHz, CDCl₃) δ 83.1 (OC(CH₃)₂), 68.8 (OCH₂), 27.6 (CH₂), 24.7 (OC(CH₃)₂) ppm

- 15 All data matched that reported in the literature.

1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexane (21)



- 20 **Activation:** The carboxylic acid (500 mg, 3.24 mmol) was coupled with *N*-hydroxyphthalimide according to **General Procedure A** with all reagents doubled in quantity. The crude residue was purified by flash column chromatography (SiO₂; DCM) to afford the corresponding NHPI ester **75** (709 mg, 47%) as a white solid.

m.p.: 188 – 192 °C (DCM/MeOH)

TLC: R_f = 0.21 (DCM)

^1H NMR (400 MHz, CDCl_3) δ 7.89 – 7.85 (m, 2H, phthalimide ArH), 7.79 – 7.75 (m, 2H, phthalimide ArH), 3.28 – 3.21 (m, 2H, $\text{CHC}=\text{O}$), 2.44 – 2.37 (br m, 2H, CHCH^aH^b ×2), 1.94 – 1.87 (br m, 2H, CH^aH^b ×2), 1.84 – 1.75 (br m, 2H, CHCH^aH^b ×2), 1.53 – 1.46 (br m, 2H, CH^aH^b ×2) ppm

^{13}C NMR (101 MHz, CDCl_3) δ 170.3 ($\text{C}=\text{O}$), 161.8 ($\text{C}=\text{O}$), 134.8 (phthalimide ArCH), 129.2 (phthalimide ArC), 124.1 (phthalimide ArC), 41.7 ($\text{CHC}=\text{O}$), 28.4 ($\text{CH}_2\text{CHC}=\text{O}$), 24.4 ($\text{CH}_2\text{CH}_2\text{CHC}=\text{O}$) ppm

HRMS (m/z): (ESI) calc'd for $\text{C}_{24}\text{H}_{18}\text{N}_2\text{NaO}_8$ $[\text{M}+\text{Na}]^+$: 485.0955, found: 485.0955

IR (solid state) ν_{max} : 2937, 2862, 1783, 1734, 1468, 1358, 1186, 1123, 1082, 997, 970, 876, 693 and 518 cm^{-1}

Borylation: NHPI ester **75** (62 mg, 0.13 mmol) was borylated according to **General Procedure B** with double the amount of B_2cat_2 . The crude residue was purified by flash column chromatography (SiO_2 ; 90:10 pentane: Et_2O) to afford boronic ester **21** (30 mg, 67%, 91:9 d.r.) as an amorphous white solid.

TLC: R_f = 0.31 (90:10 pentane: Et_2O)

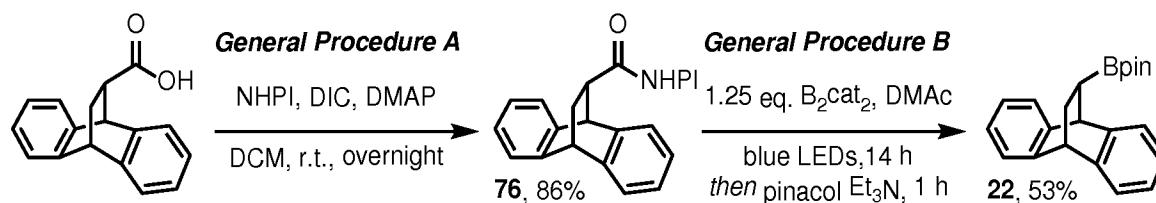
^1H NMR (400 MHz, CDCl_3) δ 1.72 – 1.62 (br m, 4H, CH_2 ×2), 1.25 – 1.17 (m, 4H, CH_2 ×2), 1.21 (s, 24H, $\text{C}(\text{CH}_3)_2$), 1.01 – 0.94 (br m, 2H, CHBpin) ppm

^{13}C NMR (101 MHz, CDCl_3) δ 82.8 ($\text{C}(\text{CH}_3)_2$), 28.5 (CH_2), 27.3 (CH_2), 25.0 ($\text{C}(\text{CH}_3)_2$), 24.8 ($\text{C}(\text{CH}_3)_2$) ppm

HRMS (m/z): (ESI) calc'd for $\text{C}_{18}\text{H}_{34}\text{B}_2\text{NaO}_4$ $[\text{M}+\text{Na}]^+$: 359.2542, found: 359.2543

IR (solid state) ν_{max} : 2977, 2918, 2848, 1370, 1312, 1138, 972 and 861 cm^{-1}

2-((9s,10s)-9,10-Dihydro-9,10-ethanoanthracen-11-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (22)



Activation: The carboxylic acid (52) (500 mg, 2.00 mmol) was coupled with *N*-hydroxyphthalimide according to **General Procedure A**. The crude residue was purified by flash column chromatography (SiO₂; 40:60 pentane:DCM) to afford the corresponding NHPI ester **76** (677 mg, 86%) as a white solid.

m.p.: 180 – 184 °C (DCM/MeOH)

TLC: *R*_f = 0.29 (30:70 pentane:DCM)

¹H NMR (400 MHz, CDCl₃) δ 7.89 – 7.82 (m, 2H, phthalimide ArH), 7.78 – 7.74 (m, 2H, phthalimide ArH), 7.52 – 7.48 (m, 1H, ArH), 7.41 – 7.37 (m, 1H, ArH), 7.35 – 7.25 (m, 2H, ArH), 7.18 – 7.11 (m, 4H, ArH), 4.90 (d, *J* = 2.3 Hz, 1H, CHCHC=O), 4.42 (t, *J* = 2.6 Hz, 1H, CHCH₂), 3.30 – 3.26 (m, 1H, CHC=O), 2.22 – 2.12 (m, 2H, CH₂) ppm

¹³C NMR (101 MHz, CDCl₃) δ 170.2 (C=O), 162.0 (C=O), 143.5 (ArC), 143.4 (ArC), 141.9 (ArC), 138.6 (ArC), 134.8 (phthalimide ArCH), 129.1 (phthalimide ArC), 126.8 (ArCH), 126.7 (ArCH), 126.2 (ArCH), 126.1 (ArCH), 125.9 (ArCH), 124.1 (phthalimide ArCH), 123.9 (ArCH), 123.8 (ArCH), 123.2 (ArCH), 47.2 (CHCHC=O), 43.7 (CHCH₂), 41.8 (CHC=O), 31.4 (CH₂) ppm

HRMS (*m/z*): (ESI) calc'd for C₂₅H₁₇NNaO₄ [*M*+Na]⁺: 418.1050, found: 418.1048

IR (solid state) ν_{max}: 3024, 2954, 1743 (C=O), 1466, 1087, 996, 964, 762 and 695 cm⁻¹

Borylation: NHPI ester **76** (53 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO₂; 98:2 pentane:Et₂O) to afford boronic ester **22** (23 mg, 53%) as an amorphous white solid.

TLC: *R*_f = 0.21 (95:5 pentane:Et₂O)

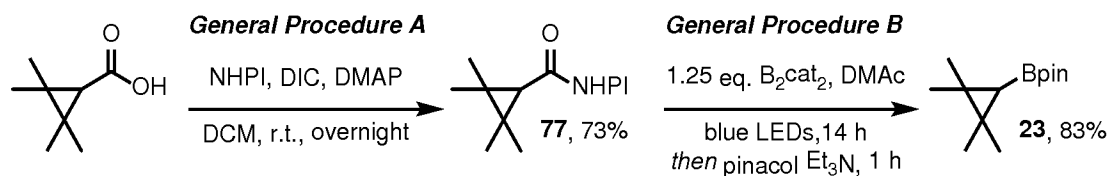
¹H NMR (400 MHz, CDCl₃) δ 7.28 – 7.24 (m, 4H, ArH), 7.10 – 7.01 (m, 4H, ArH), 4.47 (d, J = 2.3 Hz, 1H, CHCHBpin), 4.33 (t, J = 2.6 Hz, 1H, CHCH₂), 1.90 (ddd, J = 11.8, 5.4, 2.5 Hz, 1H, CH^aH^b), 1.82 (app td, J = 11.8, 2.5 Hz, 1H, CH^aH^b), 1.43 (ddd, J = 10.7, 5.4, 2.5 Hz, 1H, CHBpin), 1.12 (s, 6H, C(CH₃)₂), 1.02 (s, 6H, C(CH₃)₂) ppm

5 **¹³C NMR** (101 MHz, CDCl₃) δ 145.2 (ArC), 144.3 (ArC), 143.9 (ArC), 142.8 (ArC), 125.7 (ArCH), 125.5 (ArCH), 125.4 (ArCH), 125.1 (ArCH), 124.3 (ArCH), 123.4 (ArCH), 123.3 (ArCH), 122.8 (ArCH), 83.4 (C(CH₃)₂), 45.7 (CHCHBpin), 44.6 (CHCH₂), 29.6 (CH₂), 24.9 (C(CH₃)₂) ppm

HRMS (m/z): (ESI) calc'd for C₂₂H₂₅BNaO₂ [M+Na]⁺: 355.1844, found: 355.1837

10 **IR (solid state)** ν_{max} : 2982, 2940, 2870, 1458, 1366, 1315, 1249, 1138, 981, 854, 753, 743 and 701 cm⁻¹

4,4,5,5-tetramethyl-2-(2,2,3,3-tetramethylcyclopropyl)-1,3,2-dioxaborolane (23)



15 **Activation:** The carboxylic acid (500 mg, 3.52 mmol) was coupled with *N*-hydroxyphthalimide according to **General Procedure A**. The crude residue was purified by flash column chromatography (SiO₂; 40:60 pentane:DCM) to afford the corresponding NHPI ester **77** (740 mg, 73%) as a white solid.

m.p.: 78 – 80 °C (DCM/MeOH)

TLC: R_f = 0.21 (40:60 pentane:DCM)

20 **¹H NMR** (400 MHz, CDCl₃) δ 7.89 – 7.84 (m, 2H, phthalimide ArCH), 7.78 – 7.74 (m, 2H, phthalimide ArCH), 1.52 (s, 1H, CHC=O), 1.30 (s, 6H, CH₃ ×2), 1.27 (6H, CH₃ ×2) ppm

25 **¹³C NMR** (101 MHz, CDCl₃) δ 167.8 (C=O), 162.6 (C=O), 134.7 (phthalimide ArCH), 129.2 (phthalimide ArC), 124.0 (phthalimide ArCH), 33.4 (C(CH₃)₂), 32.4 (CHC=O), 23.4 (CH₃), 16.5 (CH₃) ppm

HRMS (m/z): (ESI) calc'd for $C_{16}H_{17}NNaO_4$ $[M+Na]^+$: 310.1050, found: 310.1052

IR (solid state) ν_{max} : 2950, 2924, 1773, 1731, 1467, 1357, 1094, 1021, 997, 977, 877, 847, 783 and 691 cm^{-1}

Borylation: NHPI ester **77** (38 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO_2 ; 95:5 pentane:Et₂O) to afford boronic ester **23** (25 mg, 83%) as an amorphous white solid.

TLC: R_f = 0.60 (80:20 pentane:Et₂O)

1H NMR (400 MHz, CDCl₃) δ 1.21 (s, 12H, Bpin $C(CH_3)_2$), 1.15 (s, 6H, $C(CH_3)_2 \times 2$), 1.14 (s, 6H, $C(CH_3)_2 \times 2$), -0.46 (s, 1H, CHBpin) ppm

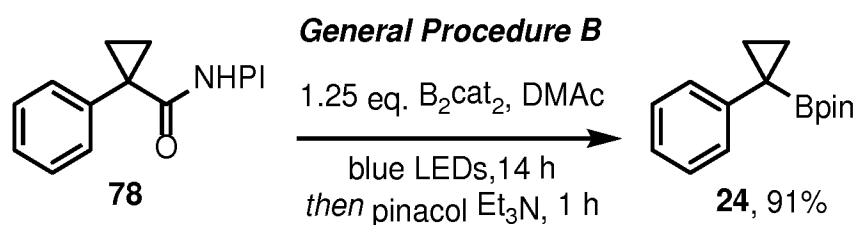
^{13}C NMR (101 MHz, CDCl₃) δ 82.5 (Bpin $C(CH_3)_2$), 27.2 ($C(CH_3)_2$), 25.0 (Bpin $C(CH_3)_2$), 24.7 (CH_3), 19.9 (CH_3) ppm

HRMS (m/z): (ESI) calc'd for $C_{13}H_{25}BNaO_2$ $[M+Na]^+$: 247.1842, found: 247.1840

IR (solid state) ν_{max} : 2979, 2925, 2867, 1418, 1396, 1343, 1311, 1235, 1142, 1106, 857 and 706 cm^{-1}

2.1.3 Substrate Scope: Tertiary

4,4,5,5-Tetramethyl-2-(1-phenylcyclopropyl)-1,3,2-dioxaborolane (**24**)



Activation: NHPI ester **78** was prepared according to a known procedure.

Borylation: NHPI ester **78** (40 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO_2 ; 80:20 pentane:Et₂O) to afford boronic ester **24** (29 mg, 91%) a colorless oil.

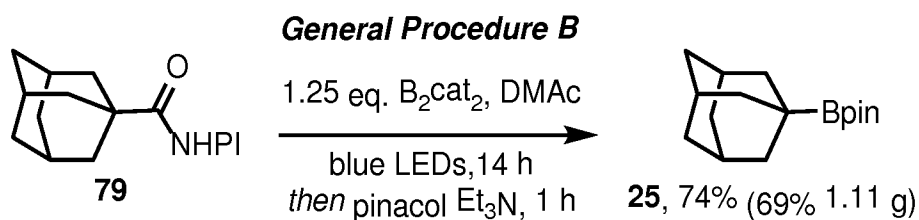
TLC: $R_f = 0.59$ (70:30 pentane:Et₂O)

¹H NMR (400 MHz, CDCl₃) δ 7.28 – 7.21 (m, 4H, ArH), 7.14 – 7.10 (m, 1H, ArH), 1.21 (s, 12H, C(CH₃)₂), 1.11 (q, $J = 3.5$ Hz, 2H, CH₂), 0.91 (q, $J = 3.5$ Hz, 2H, CH₂) ppm

5 **¹³C NMR** (101 MHz, CDCl₃) δ 145.0 (ArC), 129.1 (ArCH), 128.1 (ArCH), 125.4 (ArCH), 83.5 (C(CH₃)₂), 24.7 (C(CH₃)₂), 13.5 (CH₂) ppm

All data matched that reported in the literature.

2-((3r,5r,7r)-Adamantan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (25)



10 **Activation:** NHPI ester **79** was prepared according to a known procedure.

Borylation: NHPI ester **79** (43 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO₂; 80:20 pentane:Et₂O) to afford boronic ester **25** (26 mg, 74%) an amorphous white solid.

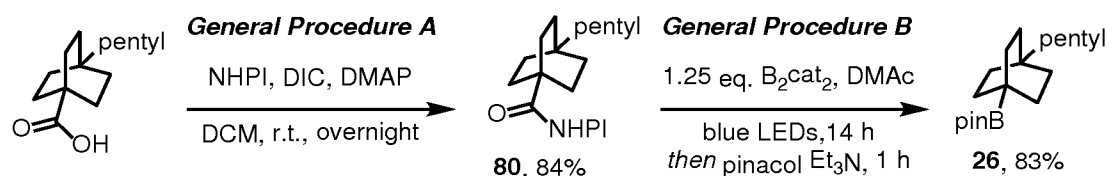
Gram Scale Borylation: NHPI ester **79** (2.0 g, 6.15 mmol) and B₂cat₂ (1.83 g, 7.68 mmol) were carefully weighed into a flame-dried Schlenk tube containing a small magnetic stirrer bar. DMAc (12.3 mL, 0.5 M) was added and then the headspace of the vial was purged with a gentle stream of argon for approximately 30 seconds. The tube was sealed and stirred under blue LED irradiation for 14 h. Pinacol (2.91 g, 24.59 mmol) was dissolved in Et₃N (4.14 mL) and added to the reaction mixture and stirred for 1 h. The reaction mixture was transferred into a separating funnel containing EtOAc (40 mL), H₂O (20 mL), NH₄Cl (saturated aqueous solution, 20 mL). After vigorously shaking and allowing to two layers to separate, the organic layer was collected. This was repeated twice more with EtOAc (40 mL). The organic layers were combined, dried over MgSO₄, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (SiO₂; 80:20 pentane:Et₂O) to afford boronic ester **25** (1.11 g, 69%) as an amorphous white solid.

¹H NMR (400 MHz, CDCl₃) δ 1.91 – 1.71 (br m, 15H, CH ×3 and CH₂ ×6), 1.21 (s, 12H, C(CH₃)₂) ppm

¹³C NMR (101 MHz, CDCl₃) δ 82.7 (C(CH₃)₂), 38.1 (CH₂), 37.7 (CH₂), 27.7 (CH), 24.8 (C(CH₃)₃) ppm

5 All data matched that reported in the literature.

4,4,5,5-Tetramethyl-2-(4-pentylbicyclo[2.2.2]octan-1-yl)-1,3,2-dioxaborolane (26)



10 **Activation:** The carboxylic acid (500 mg, 2.23 mmol) was coupled with *N*-hydroxyphthalimide according to **General Procedure A**. The crude residue was purified by flash column chromatography (SiO₂; 20:1 petroleum ether 40-60:EtOAc) to afford the corresponding NHPI ester **80** (690 mg, 84%) as a white solid.

m.p.: 121 – 123 °C (DCM/MeOH)

TLC: *R*_f = 0.24 (10:1 petroleum ether 40-60:EtOAc)

15 **¹H NMR** (400 MHz, CDCl₃) δ 7.86 – 7.82 (m, 2H, Ar-H), 7.77 – 7.72 (m, 2H, Ar-H), 2.07 – 1.92 (m, 6H, 3×CH₂), 1.53 – 1.39 (m, 6H, 3×CH₂), 1.35 – 1.07 (m, 8H, 4×CH₂), 0.87 (t, *J* = 7.1 Hz, 3H, CH₃) ppm

20 **¹³C NMR** (101 MHz, CDCl₃) δ 174.0 (C=O), 162.1 (C=O), 134.6 (HC_{Ar}), 129.1 (C_{Ar}), 123.9 (HC_{Ar}), 41.2 (CH₂), 38.7 (C), 32.8 (CH₂), 30.4 (C), 30.1 (CH₂), 28.5 (CH₂), 23.4 (CH₂), 22.7 (CH₂), 14.1 (CH₃) ppm

HRMS (*m/z*): (ESI) calc'd for C₂₂H₂₇NNaO₄ [M+Na]⁺: 392.1832, found: 392.1832

IR (neat) ν_{max}: 2917, 2855, 1774, 1738, 1369, 1183, 1139, 980, 876 and 734 cm⁻¹

Borylation: NHPI ester **80** (48 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO₂;

10:1 petroleum ether 40-60:Et₂O) to afford boronic ester **26** (33 mg, 83%) as an amorphous white solid.

TLC: *R_f* = 0.51 (10:1 petroleum ether 40-60:EtOAc)

¹H NMR (400 MHz, CDCl₃) δ 1.52 – 1.41 (m, 6H, 3×CH₂), 1.26 – 1.08 (m, 24H, 6×CH₂ + 2×OC(CH₃)₂), 0.98 – 0.89 (m, 2H, CH₂), 0.79 (t, *J* = 7.2 Hz, 3H, CH₃) ppm

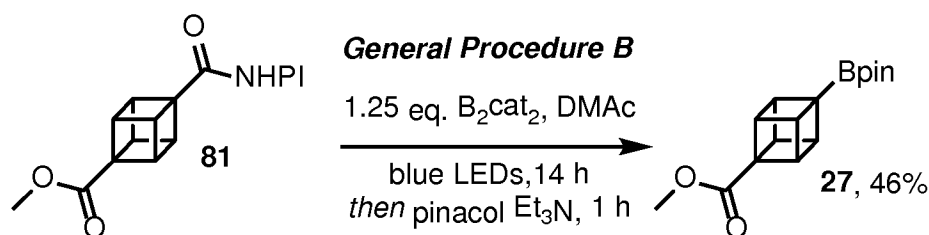
¹³C NMR (101 MHz, CDCl₃) δ 82.6 (OC(CH₃)₂), 42.2 (CH₂), 32.9 (CH₂), 30.7 (CH₂), 29.8 (C), 27.4 (CH₂), 24.6 (OC(CH₃)₂), 23.1 (CH₂), 22.7 (CH₂), 14.1 (CH₃) ppm

HRMS (*m/z*): (ESI) calc'd for C₁₉H₃₅BNaO₂ [M+Na]⁺: 329.2626, found: 329.2641

IR (neat) *ν*_{max}: 2925, 2855, 1750, 1383, 1306, 1145, 1125 and 849 cm⁻¹

10

Methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cubane-1-carboxylate (**27**)



Activation: NHPI ester **81** was prepared according to a known procedure.

Borylation: NHPI ester **81** (47 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO₂; 60:40 pentane:Et₂O) to afford boronic ester **27** (18 mg, 46%) an amorphous solid.

15

TLC: *R_f* = 0.42 (50:50 pentane:Et₂O)

¹H NMR (400 MHz, CDCl₃) δ 4.31 – 4.27 (m, 3H, CH), 4.04 – 3.99 (m, 3H, CH), 3.69 (s, 3H, C=OOCH₃), 1.25 (s, 12H, C(CH₃)₂) ppm

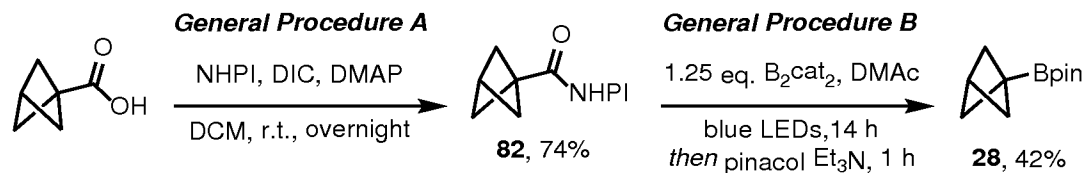
¹³C NMR (126 MHz, CDCl₃) δ 172.6 (C=O), 83.2 (C(CH₃)₂), 55.3 (CC=O), 51.5 (C=OOCH₃), 49.8 (CH), 45.1 (CH), 24.8 (C(CH₃)₂) ppm

20

HRMS (*m/z*): (ESI) calc'd for C₁₆H₂₁BNaO₄ [M+Na]⁺: 311.1428, found: 311.1420

IR (solid state) ν_{max} : 2976, 1715, 1429, 1395, 1307, 1224, 1142, 1085 and 845 cm^{-1}

2-(Bicyclo[1.1.1]pentan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (28)



- 5 **Activation:** The carboxylic acid (110 mg, 0.98 mmol) was coupled with *N*-hydroxyphthalimide according to **General Procedure A**. The crude residue was purified by flash column chromatography (SiO_2 ; 60:40 pentane: Et_2O) to afford the corresponding NHPI ester **82** (187 mg, 74%) as an amorphous white solid.

TLC: R_f = 0.23 (50:50 pentane:DCM)

- 10 **^1H NMR** (500 MHz, CDCl_3) δ 7.89 – 7.86 (m, 2H, phthalimide ArH), 7.80 – 7.76 (m, 2H, phthalimide ArH), 2.55 (s, 1H, CH), 2.33 (s, 6H, CH_2) ppm

^{13}C NMR (126 MHz, CDCl_3) δ 164.7 (C=O), 162.0 (C=O), 134.8 (phthalimide ArCH), 129.1 (phthalimide ArC), 124.1 (phthalimide ArCH), 52.5 (CH_2), 40.0 ($\text{CC}=\text{O}$), 29.3 (CH) ppm

- 15 **HRMS (m/z):** (ESI) calc'd for $\text{C}_{14}\text{H}_{11}\text{NNaO}_4$ $[\text{M}+\text{Na}]^+$: 280.0580, found: 280.0594

IR (solid state) ν_{max} : 3001, 2887, 1776, 1736, 1372, 1185, 1039, 875, 789, 692, 606 and 518 cm^{-1}

- Borylation:** NHPI ester **82** (34 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO_2 ; 90:10 pentane: Et_2O) to afford boronic ester **82** (11 mg, 42%) a colorless oil (due to the product's volatility, a small amount of pentane remained). **Note:** product is volatile and unstable on silica.

TLC: R_f = 0.24 (90:10 pentane: Et_2O)

- 25 **^1H NMR** (500 MHz, CDCl_3) δ 2.48 (s, 1H, CH), 1.95 (s, 6H, CH_2), 1.22 (s, 12H, $\text{C}(\text{CH}_3)_2$) ppm

^{13}C NMR (126 MHz, CDCl_3) δ 83.3 ($\text{C}(\text{CH}_3)_2$), 52.0 (CH_2), 34.7 (CH), 24.9 ($\text{C}(\text{CH}_3)_2$) ppm

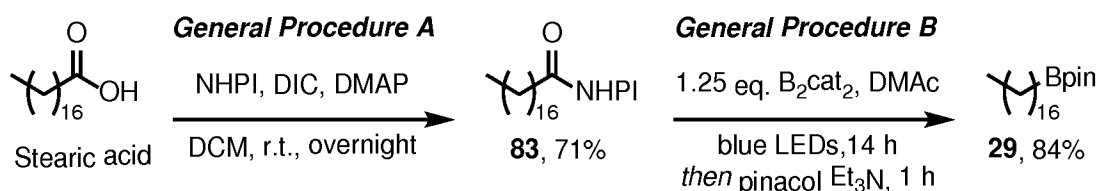
HRMS (m/z): (EI) calc'd for $\text{C}_{11}\text{H}_{19}\text{BNaO}_2$ [$\text{M}+\text{Na}$] $^+$: 217.1372, found: 217.1369

IR (neat) ν_{max} : 2923, 1399, 1317, 1216, 1135, 852 and 662 cm^{-1}

5

2.1.4 Substrate Scope: Natural Products and Drugs

10 2-Heptadecyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (29)



Activation: Stearic acid (1.0 g, 3.52 mmol) was coupled with *N*-hydroxyphthalimide according to **General Procedure A**. The crude residue was purified by flash column chromatography (SiO_2 ; 60:40 pentane:DCM) to afford the corresponding NHPI ester

15 **83** (1.07 mg, 71%) as a white solid.

TLC: R_f = 0.32 (50:50 pentane:DCM)

^1H NMR (400 MHz, CDCl_3) δ 7.91 – 7.86 (m, 2H, phthalimide ArH), 7.81 – 7.76 (m, 2H, phthalimide ArH), 2.66 (t, J = 7.5 Hz, 2H, $\text{CH}_2\text{C}=\text{O}$), 1.78 (p, J = 7.5 Hz, $\text{CH}_2\text{CH}_2\text{C}=\text{O}$), 1.44 (p, J = 7.5 Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{C}=\text{O}$), 1.37 – 1.21 (m, 26H, $\text{CH}_2 \times 13$), 0.88 (t, J = 7.0 Hz, 3H, CH_3) ppm

20

^{13}C NMR (101 MHz, CDCl_3) δ 169.8 ($\text{C}=\text{O}$), 162.1 ($\text{C}=\text{O}$), 134.8 (phthalimide ArCH), 129.1 (phthalimide ArC), 124.1 (phthalimide ArCH), 32.1 ($\text{CH}_2\text{C}=\text{O}$), 31.1 (CH_2), 29.8 – 29.7 ($\text{CH}_2 \times 9$), 29.5 (CH_2), 29.3 (CH_2), 29.0 (CH_2), 24.8 (CH_2), 22.8 (CH_2), 14.3 (CH_3) ppm

All data matched that reported in the literature.

Borylation: NHPI ester **83** (57 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO₂; 90:10 pentane:Et₂O) to afford boronic ester **29** (41 mg, 84%) as colorless oil.

5 **TLC:** R_f = 0.56 (90:10 pentane:Et₂O)

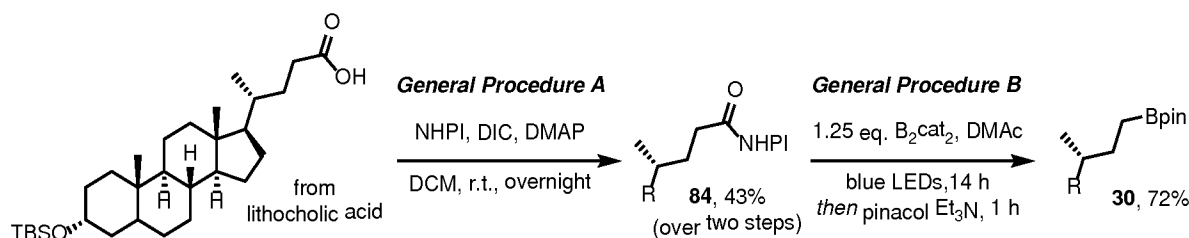
¹H NMR (400 MHz, CDCl₃) δ 1.43 – 1.17 (m, 30H, CH₂ $\times$ 15), 1.24 (s, 12H, C(CH₃)₂), 0.88 (t, J = 6.8 Hz, 3H, CH₃), 0.76 (t, J = 7.7 Hz, 2H, CH₂Bpin) ppm

¹³C NMR (101 MHz, CDCl₃) δ 83.0 (C(CH₃)₂), 32.6 (CH₂), 32.1 (CH₂), 29.9 – 29.5 (CH₂ $\times$ 9), 25.0 (C(CH₃)₂), 24.2 (CH₂), 22.9 (CH₂), 14.3 (CH₃) ppm

10 **HRMS (m/z):** (ESI) calc'd for C₂₃H₄₈BO₂ [M+H]⁺: 367.3746, found: 367.3745

IR (neat) $\nu_{\max}$: 2922, 2853, 1377, 1316, 1145, 968, 847 and 735 cm⁻¹

tert-Butyl(((3*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)dimethylsilane (**30**)



Activation: Crude TBS protected lithocholic acid (**55**) (2.45 g, 5.0 mmol) was coupled with *N*-hydroxyphthalimide according to **General Procedure A**. The crude residue was purified by flash column chromatography (SiO₂; 95:5 hexane:EtOAc) to afford the corresponding NHPI ester **84** (1.37 g, 43% over two steps) as a white solid.

m.p.: 194 – 198 (DCM/MeOH)

TLC: R_f = 0.55 (90:10 hexane:EtOAc)

¹H NMR (400 MHz, CDCl₃) δ 7.91 – 7.86 (m, 2H, phthalimide ArH), 7.80 – 7.76 (m, 2H, phthalimide ArH), 3.58 (app tt, J = 11.0, 4.7 Hz, 1H, CHOTBS), 2.76 – 2.65 (m, 1H, CH^aH^bC=O), 2.64 – 2.53 (m, 1H, CH^aH^bC=O), 1.98 – 1.72 (m, 6H), 1.58 – 0.86 (m, 20H), 0.98 (d, J = 6.3 Hz, CHCH₃), 0.90 (s, 3H, CH₃), 0.89 (s, 9H, SiC(CH₃)₃),
5 0.67 (s, 3H, CH₃), 0.06 (s, 6H, Si(CH₃)₂) ppm

¹³C NMR (101 MHz, CDCl₃) δ 170.2 (C=O), 162.1 (C=O), 134.8 (ArCH), 129.1 (ArC), 124.1 (ArCH), 73.0 (CHOTBS), 56.5, 56.1, 42.9 (C), 42.4, 40.3, 40.3 (C), 37.1 (C), 36.0, 35.7 (C), 35.4, 34.7 (C), 31.2 (CH₂), 30.9 (CH₂), 28.3 (CH₂), 28.2 (CH₂), 27.5 (CH₂), 26.5 (CH₂), 26.1 (SiC(CH₃)₃), 24.4 (CH₂), 23.5, 21.0 (CH₂), 18.5 (SiC(CH₃)₃),
10 18.4, 12.2 (CH₃), –4.4 (Si(CH₃)₂) ppm

HRMS (m/z): (ESI) calc'd for C₃₈H₅₇BNO₅SiNa [M+Na]⁺: 658.3898, found: 658.3888

IR (neat) ν_{max} : 2930, 2860, 1744, 1065, 835 and 781 cm⁻¹

$[\alpha]_{\text{D}}^{24}$: +20 (c = 1.0, CHCl₃)

15 **Borylation:** NHPI ester **84** (83 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO₂; 95:5 pentane:Et₂O) to afford boronic ester **30** (54 mg, 72%) as an amorphous white solid.

TLC: R_f = 0.38 (pentane:Et₂O 95:5)

20 **¹H NMR** (400 MHz, CDCl₃) δ 3.57 (dddd, J = 10.9, 10.7, 4.7, 4.5 Hz, 1H, CHOTBS), 1.95 (m, 1H), 1.90 – 1.70 (m, 4H), 1.59 – 1.50 (m, 3H), 1.48 – 1.28 (m, 8H), 1.28 – 1.17 (m, 15H), 1.16 – 0.98 (m, 6H), 0.98 – 0.75 (m, 17H), 0.69 – 0.54 (m, 4H), 0.05 (s, 6H, Si(CH₃)₂) ppm

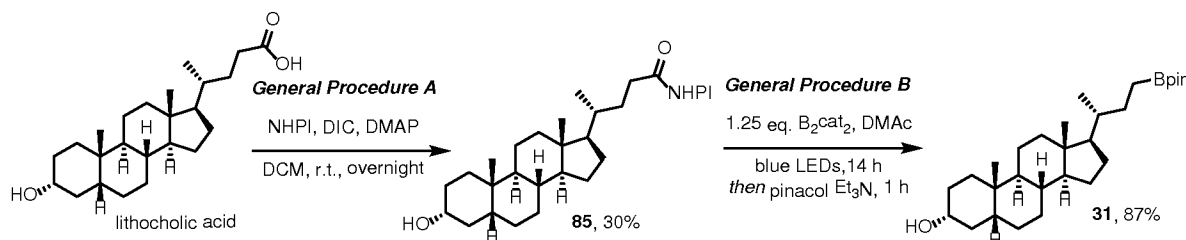
25 **¹³C NMR** (101 MHz, CDCl₃) δ 82.9 (2×OC(CH₃)₂), 73.0 (CHOTBS), 56.6 (CH), 56.2 (CH), 42.9 (C^{IV}), 42.5 (CH), 40.4 (CH), 40.3 (CH₂), 37.8 (CH), 37.1 (CH₂), 36.1 (CH), 35.8 (CH₂), 34.8 (C^{IV}), 31.2 (CH₂), 29.9 (CH₂), 28.4 (CH₂), 27.5 (CH₂), 26.6 (CH₂), 26.2 (SiC(CH₃)₃), 25.0 (OC(CH₃)₂), 24.9 (OC(CH₃)₂), 24.4 (CH₂), 23.6 (CH₃), 21.0 (CH₂), 18.5 (CH), 18.2 (CH₃), 12.2 (CH₃), –4.4 (Si(CH₃)₂) ppm

HRMS (*m/z*): (ESI) calc'd for C₃₅H₆₅BNaO₃Si [M+Na]⁺: 595.4695, found: 595.4690

IR (neat) ν_{max} : 2927, 2856, 1470, 1370, 1312, 1251, 1146, 1095, 835 and 774 cm⁻¹

$[\alpha]_{\text{D}}^{24}$: +17 (*c* = 1.0, CHCl₃)

- 5 **(3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-ol (31)**



- Activation:** The carboxylic acid (1.00 g, 2.66 mmol) was coupled with *N*-hydroxyphthalimide according to **General Procedure A**. The crude residue was purified by flash column chromatography (SiO₂; 80:20 → 60:40 pentane:EtOAc) to afford the corresponding NHPI ester **85** (418 mg, 30%) as a white solid.

m.p.: 161 – 163 °C (EtOAc)

TLC: *R*_f = 0.42 (pentane:EtOAc 50:50)

- 15 **¹H NMR:** (400 MHz, CDCl₃) δ 7.88 (m, 2H, 2×Ar-H), 7.78 (m, 2H, 2×Ar-H), 3.62 (dddd, *J* = 11.1, 11.0, 4.7, 4.6 Hz, 1H, CH₂OH), 2.71 (ddd, *J* = 15.9, 9.6, 4.8 Hz, 1H, CH^aH^bCO₂R), 2.58 (ddd, *J* = 15.9, 9.0, 6.9 Hz, 1H, CH^aH^bCO₂R), 2.05 – 1.93 (m, 2H), 1.91 – 1.83 (m, 2H), 1.81 – 1.70 (m, 2H), 1.66 (m, 1H), 1.61 – 1.46 (m, 4H), 1.44 – 1.36 (m, 5H), 1.35 – 1.21 (m, 4H), 1.19 – 1.02 (m, 5H), 1.01 – 0.95 (m, 4H), 0.92 (s, 3H, CH₃), 0.67 (s, 3H, CH₃) ppm

¹³C NMR: (101 MHz, CDCl₃) δ 170.2 (CO₂R), 162.1 (2×CO), 134.8 (2×HC_{Ar}), 129.1 (2×C_{Ar}), 124.1 (2×HC_{Ar}), 72.0 (CHOH), 56.6 (CH), 56.0 (CH), 43.0 (C^{IV}), 42.2 (CH), 40.6 (CH), 40.3 (CH₂), 36.6 (CH₂), 36.0 (CH), 35.5 (CH₂), 35.4 (CH), 34.7 (C^{IV}), 30.9

(CH₂), 30.7 (CH₂), 28.3 (CH₂), 28.2 (CH₂), 27.3 (CH₂), 26.6 (CH₂), 24.3 (CH₂), 23.5 (CH₃), 21.0 (CH₂), 18.4 (CHCH₃), 12.2 (CH₃) ppm

HRMS (*m/z*): (ESI) calc'd for C₃₂H₄₃NNaO₅ [M+Na]⁺: 544.3033, found: 544.3032

IR (neat) ν_{max} : 3366 (br.), 2928, 2863, 1816, 1788, 1741, 1467, 1365, 1067 and 732
5 cm⁻¹

$[\alpha]_{\text{D}}^{24}$: +18 (*c* 1.0, CHCl₃)

All data matched that reported in the literature.

Borylation: NHPI ester **85** (68 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO₂;
10 60:40 pentane:Et₂O) to afford boronic ester **31** (52 mg, 87%) as a white solid.

m.p.: 159 – 161 °C (Et₂O)

TLC: *R*_f = 0.24 (pentane:Et₂O 50:50)

¹H NMR: (400 MHz, CDCl₃) δ 3.61 (dddd, *J* = 11.1, 11.0, 4.7, 4.6 Hz, 1H, CHOH),
1.96 (m, 1H), 1.91 – 1.70 (m, 4H), 1.65 (m, 1H), 1.60 – 1.46 (m, 3H), 1.45 – 1.28 (m,
15 7H), 1.28 – 1.17 (m, 15H), 1.17 – 0.94 (m, 7H), 0.91 (s, 3H, CH₃), 0.88 (d, *J* = 6.5 Hz,
3H, CHCH₃), 0.79 (ddd, *J* = 15.8, 10.7, 5.1 Hz, 1H, CH^aH^bBpin), 0.68 – 0.56 (m, 4H,
CH₃ & CH^aH^bBpin) ppm

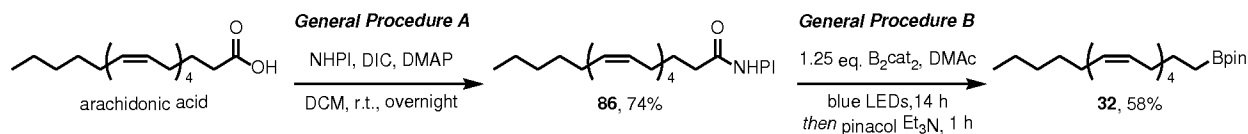
¹³C NMR: (101 MHz, CDCl₃) δ 82.9 (2×OC(CH₃)₂), 72.0 (CHOH), 56.7 (CH), 56.1
(CH), 42.8 (C^{IV}), 42.3 (CH), 40.6 (CH), 40.4 (CH₂), 37.8 (CH), 36.7 (CH₂), 36.0 (CH),
20 35.5 (CH₂), 34.7 (C^{IV}), 30.7 (CH₂), 29.9 (CH₂), 28.4 (CH₂), 27.4 (CH₂), 26.6 (CH₂),
25.0 (OC(CH₃)₂), 24.9 (OC(CH₃)₂), 24.4 (CH₂), 23.5 (CH₃), 21.0 (CH₂), 18.2 (CHCH₃),
12.2 (CH₃) ppm

HRMS (*m/z*): (ESI) calc'd for C₂₉H₅₁BNaO₃ [M+Na]⁺: 481.3829, found: 481.3827

IR (neat) ν_{max} : 3346 (br.), 2974, 2929, 2864, 1448, 1369, 1311, 1144 and 732 cm⁻¹

25 **$[\alpha]_{\text{D}}^{26}$:** +21 (*c* 1.0, CHCl₃)

4,4,5,5-Tetramethyl-2-((4Z,7Z,10Z,13Z)-nonadeca-4,7,10,13-tetraen-1-yl)-1,3,2-dioxaborolane (32)



Activation: The carboxylic acid (100 mg, 0.33 mmol) was coupled with *N*-hydroxyphthalimide according to **General Procedure A**. The crude residue was purified by flash column chromatography (SiO₂; 90:10 pentane:Et₂O) to afford the corresponding NHPI ester **86** (110 mg, 74%) as a colorless oil.

TLC: *R*_f = 0.15 (pentane:Et₂O 90:10)

¹H NMR: (400 MHz, CDCl₃) δ 7.88 (m, 2H, 2×Ar-H), 7.78 (m, 2H, 2×Ar-H), 5.50 – 5.29 (m, 8H, 8×CH), 2.87 – 2.80 (m, 6H, 3×CHCH₂CH), 2.68 (t, *J* = 7.4 Hz, 2H, CH₂CO₂R), 2.24 (td, *J* = 7.3, 7.1 Hz, 2H, CH₂(CH₂)₂CO₂R), 2.05 (td, *J* = 7.0, 6.9 Hz, 2H, C₄H₉CH₂CH), 1.87 (tt, *J* = 7.4, 7.3 Hz, 2H, CH₂CH₂CO₂R), 1.40 – 1.22 (m, 6H, 3×CH₂), 0.88 (t, *J* = 6.8 Hz, 3H, CH₃) ppm

¹³C NMR: (101 MHz, CDCl₃) δ 169.6 (CO₂R), 162.0 (2×CO), 134.8 (2×HC_{Ar}), 130.6 (CH), 129.8 (CH), 129.1 (2×C_{Ar}), 128.7 (CH), 128.5 (CH), 128.3 (CH), 128.2 (CH), 128.0 (CH), 127.7 (CH), 124.1 (2×HC_{Ar}), 31.6 (CH₂), 30.5 (CH₂CO₂R), 29.5 (CH₂), 27.3 (C₄H₉CH₂CH), 26.3 (CH₂(CH₂)₂CO₂R), 25.8 (3×CHCH₂CH), 24.7 (CH₂CH₂CO₂R), 22.7 (CH₂), 14.2 (CH₃) ppm

HRMS (*m/z*): (ESI) calc'd for C₂₈H₃₅NNaO₄ [M+Na]⁺: 472.2458, found: 472.2460

IR (neat) ν_{max}: 3012, 2927, 2856, 1816, 1789, 1743, 1467, 1367, 1185, 1081 and 877 cm⁻¹

Borylation: NHPI ester **86** (58 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO₂; 95:5 pentane:Et₂O) to afford boronic ester **32** (29 mg, 58%) as a colorless oil.

TLC: *R*_f = 0.50 (pentane:Et₂O 95:5)

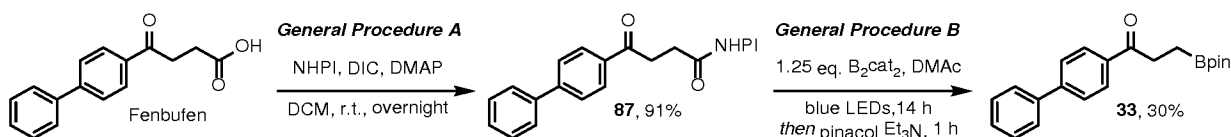
¹H NMR: (400 MHz, CDCl₃) δ 5.48 – 5.24 (m, 8H, 8×CH), 2.92 – 2.73 (m, 6H, 3×CHCH₂CH), 2.06 (app. p, $J^{app.}$ = 7.0 Hz, 4H, 2×CHCH₂CH₂), 1.48 (tt, J = 7.8, 7.7 Hz, 2H, CH₂CH₂Bpin), 1.41 – 1.27 (m, 6H, 3×CH₂), 1.24 (s, 12H, 4×CH₃), 0.89 (t, J = 6.8 Hz, 3H, CH₃), 0.80 (t, J = 7.9 Hz, 2H, CH₂B(OR)₂) ppm

5 **¹³C NMR:** (101 MHz, CDCl₃) δ 130.5 (CH), 130.2 (CH), 128.6 (CH), 128.5 (CH), 128.0 (CH), 128.0 (CH), 127.9 (CH), 127.6 (CH), 82.9 (2×OC(CH₃)₂), 31.5 (CH₂), 29.8 (CHCH₂CH₂), 29.3 (CH₂), 27.2 (CHCH₂CH₂), 25.6 (3×CHCH₂CH), 24.8 (4×CH₃), 24.1 (CH₂CH₂Bpin), 22.6 (CH₂), 14.1 (CH₃) ppm

HRMS (m/z): (EI) calc'd for C₂₅H₄₃BO₂: 386.3356, found: 386.3338

10 **IR (neat) ν_{max} :** 3012, 2927, 2858, 1371, 1316, 1140, 968 and 846 cm⁻¹

15 **1-([1,1'-Biphenyl]-4-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (33)**



Activation: Fenbufen (1.0 g, 3.93 mmol) was coupled with *N*-hydroxyphthalimide according to **General Procedure A**. The crude product was filtered quickly through a short column (~5 cm silica gel). After concentrated to a ~15 mL solution, 30 mL of MeOH was added. The precipitate was collected by filtration and washed with 10 mL of MeOH to afford the corresponding NHPI ester **87** (1.42 g, 91%) as a light pink solid.

Note: The product is not stable on silica gel.

m.p.: 165 – 168 °C (DCM/MeOH)

TLC: R_f = 0.50 (1:1 petroleum ether 40-60:EtOAc)

¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, J = 8.1 Hz, 2H, Ar-H), 7.85 – 7.79 (m, 2H, Ar-H), 7.75 – 7.67 (m, 2H, Ar-H), 7.62 (d, J = 8.1 Hz, 2H, Ar-H), 7.55 (d, J = 7.4 Hz, 2H, Ar-H), 7.39 (t, J = 7.5 Hz, 2H, Ar-H), 7.33 (t, J = 7.4 Hz, 1H, Ar-H), 3.43 (t, J = 6.9 Hz, 2H, CH₂), 3.10 (t, J = 6.9 Hz, 2H, CH₂) ppm

5 **¹³C NMR** (101 MHz, CDCl₃) δ 196.0 (C=O), 169.3 (C=O), 161.8 (C=O), 146.1 (C_{Ar}), 139.7 (C_{Ar}), 134.8 (C_{Ar}), 134.7 (HC_{Ar}), 128.9 (HC_{Ar}), 128.9 (C_{Ar}), 128.7 (HC_{Ar}), 128.3 (HC_{Ar}), 127.3 (HC_{Ar}), 127.2 (HC_{Ar}), 124.0 (HC_{Ar}), 33.2 (CH₂), 25.5 (CH₂) ppm

HRMS (m/z): (ESI) calc'd for C₂₄H₁₇NNaO₅ [M+Na]⁺: 422.0999, found: 422.1004

IR (neat) ν_{max} : 2920, 1741, 1682, 1360, 1186, 1083, 877 and 765 cm⁻¹

10 **Borylation:** NHPI ester **87** (52 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO₂; 4:1 petroleum ether 40-60:Et₂O) to afford boronic ester **33** (13 mg, 30%) as a colorless oil.

TLC: R_f = 0.63 (1:1 petroleum ether 40-60:EtOAc)

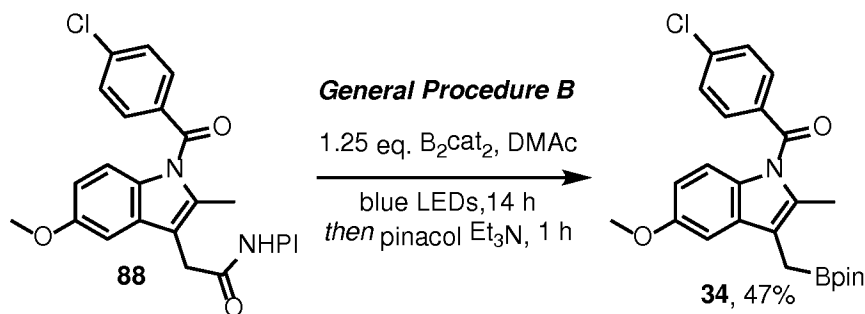
15 **¹H NMR** (400 MHz, CDCl₃) δ 8.08 (d, J = 8.3 Hz, 2H, Ar-H), 7.70 (d, J = 8.3 Hz, 2H, Ar-H), 7.65 (d, J = 7.6 Hz, 2H, Ar-H), 7.50 (t, J = 7.4 Hz, 2H, Ar-H), 7.42 (t, J = 7.3 Hz, 1H, Ar-H), 3.21 (t, J = 7.0 Hz, 2H, CH₂), 1.29 (s, 12H, 2×OC(CH₃)₂), 1.13 (t, J = 7.0 Hz, 2H, CH₂Bpin) ppm

20 **¹³C NMR** (101 MHz, CDCl₃) δ 200.1 (C=O), 145.4 (C_{Ar}), 140.0 (C_{Ar}), 135.7 (C_{Ar}), 128.9 (HC_{Ar}), 128.5 (HC_{Ar}), 128.1 (HC_{Ar}), 127.2 (HC_{Ar}), 127.1 (HC_{Ar}), 83.1 (OC(CH₃)₂), 33.7 (CH₂), 24.8 (OC(CH₃)₂) ppm

HRMS (m/z): (ESI) calc'd for C₂₁H₂₅BNaO₃ [M+Na]⁺: 359.1792, found: 359.1788

IR (neat) ν_{max} : 2972, 1745, 1679, 1369, 1313, 1221, 1137, 1074, 966 and 763 cm⁻¹

(4-Chlorophenyl)(5-methoxy-2-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1H-indol-1-yl)methanone (**34**)



Activation: NHPI ester **88** was prepared according to a known procedure.

- 5 **Borylation:** NHPI ester **88** (67 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO₂; 95:5 pentane:acetone) to afford boronic ester **34** (28 mg, 47%) a colorless oil.

TLC: R_f = 0.31 (70:30 pentane:Et₂O)

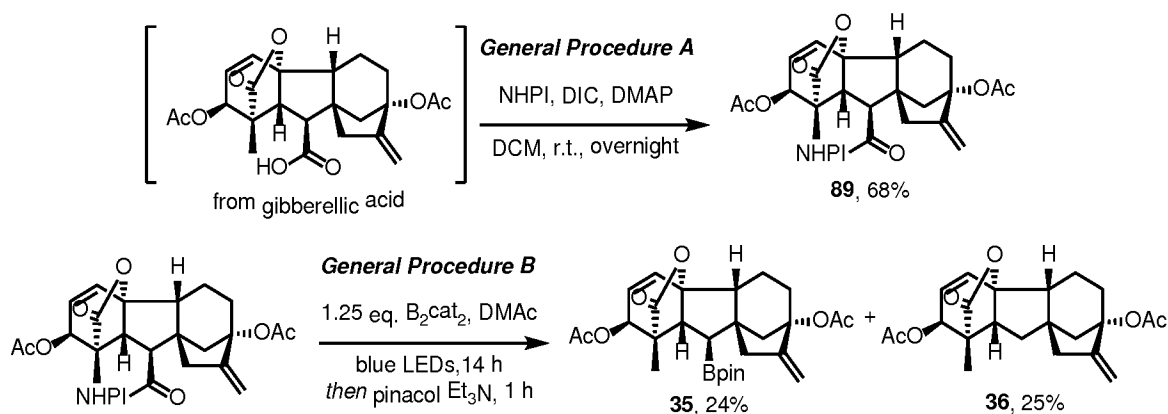
- 10 **¹H NMR** (400 MHz, CDCl₃) δ 7.64 (d, J = 8.6 Hz, 2H, ArH), 7.45 (d, J = 7.6 Hz, 2H, ArH), 6.93 (d, J = 9.0 Hz, 2H, ArH), 6.65 (dd, J = 9.0, 2.5 Hz, 1H, ArH), 3.84 (s, 3H, OCH₃), 2.29 (s, 3H, CH₃), 2.18 (s, 2H, CH₂Bpin), 1.23 (s, 12H, C(CH₃)₂) ppm

- 15 **¹³C NMR** (126 MHz, CDCl₃) δ 168.3 (C=O), 156.0 (ArC), 138.8 (ArC), 134.7 (ArC), 133.2 (ArC), 132.0 (ArC), 131.2 (ArCH), 131.1 (ArC), 129.1 (ArCH), 116.7 (ArC), 115.0 (ArCH), 111.3 (ArCH), 101.7 (ArCH), 83.7 (C(CH₃)₂), 55.8 (OCH₃), 24.9 (C(CH₃)₂), 13.8 (CH₃) ppm

HRMS (m/z): (ESI) calc'd for C₂₄H₂₇BClNNaO₄ [M+Na]⁺: 462.1618, found: 462.1618

IR (neat) $\nu_{\max}$: 2977, 1676, 1476, 1454, 1321, 1222, 1140, 1088, 1061, 846, 732 cm⁻¹

(1*S*,2*S*,4*aR*,4*bR*,7*S*,9*aR*,10*S*,10*aR*)-1-Methyl-8-methylene-13-oxo-10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,5,6,8,9,10,10a-octahydro-4a,1-(epoxymethano)-7,9a-methanobenzo[*a*]azulene-2,7(4*bH*)-diyl diacetate (**35**)



- 5 **Activation:** To a solution of Gibberellic acid (346 mg, 1 mmol, 1.0 eq.), acetic anhydride (1.2 g, 12 mmol, 12.0 eq.) and DMAP (12 mg, 0.1 mmol, 0.1 eq.) in anhydrous DCM (10 mL) at room temperature was added pyridine (1.6 g, 20 mmol, 20.0 eq.). After the addition, the mixture was allowed to stir for 48 h at room temperature before addition of 10 mL of water. After extraction with DCM (10 mL×2),
10 the organic phase was dried over MgSO₄, filtered and concentrated under reduced pressure to give a colourless oil (450 mg). The crude was used without further purification and was coupled with *N*-hydroxyphthalimide according to **General Procedure A**. The crude residue was purified by flash column chromatography (SiO₂; 2:1 petroleum ether 40-60:EtOAc) to afford the corresponding NHPI ester **89** (390 mg,
15 68%) as a colorless oil.

m.p.: 172 – 175 °C

TLC: *R*_f = 0.60 (1:1 petroleum ether 40-60:EtOAc)

¹H NMR (400 MHz, CDCl₃) δ 7.85 – 7.80 (m, 2H, Ar-H), 7.76 – 7.72 (m, 2H, Ar-H), 6.32 (d, *J* = 9.3 Hz, 1H, =CH–), 5.83 (dd, *J* = 9.3, 3.8 Hz, 1H, =CH–), 5.30 (d, *J* = 3.8 Hz, 1H, CH–OAc), 5.18 (s, 1H, =CH₂), 5.02 (s, 1H, =CH₂), 3.32 (d, *J* = 11.1 Hz, 1H), 3.07 (d, *J* = 11.1 Hz, 1H), 2.83 (dt, *J* = 15.0, 3.1 Hz, 1H), 2.46 – 2.35 (m, 3H), 2.17 (d, *J* = 15.0 Hz, 1H), 2.06 – 1.94 (m, 8H), 1.80 – 1.63 (m, 2H), 1.24 (s, 3H, CH₃) ppm

¹³C NMR (101 MHz, CDCl₃) δ 176.4 (C=O), 169.9 (C=O), 168.5 (C=O), 161.5 (C=O), 153.0 (C=O), 134.9 (CH), 133.9 (CH), 129.3 (CH), 128.8 (C), 124.1 (CH), 108.6 (=CH₂), 89.6 (C), 83.8 (C), 70.0, 54.0, 52.1 (C), 51.4 (C), 51.3, 48.0, 42.2 (CH₂), 39.7 (CH₂), 36.1 (CH₂), 21.9, 20.7, 16.9 (CH₂), 14.3 ppm

5 **HRMS (*m/z*):** (ESI) calc'd for C₃₁H₂₉NNaO₁₀ [M+Na]⁺: 598.1684, found: 598.1686

IR (solid state) $\nu_{\max}$: 2948, 1780, 1740, 1369, 1227, 1019, 972, 911 and 730 cm⁻¹

$[\alpha]_{\text{D}}^{24}$: +132 (*c* = 0.5, CHCl₃)

Borylation: NHPI ester **89** (75 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO₂; 10 90:10 pentane:acetone) to afford boronic ester **35** (16 mg, 24%), which co-eluted with the corresponding H-atom abstraction product **36** (12 mg, 25%), as a colorless oil.

TLC: *R_f* = 0.31 (80:20 pentane:acetone)

¹H NMR (400 MHz, CDCl₃) δ 6.25 (d, *J* = 9.3 Hz, 1H, C=CH), 5.69 (dd, *J* = 9.3, 3.8 Hz, 1H, C=CH), 5.19 (dd, *J* = 3.7 Hz, 1H, CHOAc), 5.01 (d, *J* = 2.1 Hz, 1H, =CH₂), 15 4.85 (d, *J* = 2.0 Hz, 1H, =CH₂), 2.89 (d, *J* = 12.2 Hz, 1H), 2.35 (dt, *J* = 14.8, 3.1 Hz, 1H), 2.31 – 2.19 (m, 1H), 2.11 – 2.03 (m, 3H), 1.98 (s, 3H, OAc), 1.90 – 1.82 (m, 4H), 1.70 – 1.60 (m, 2H), 1.55 – 1.46 (m, 1H), 1.29 (d, *J* = 12.2 Hz, 1H), 1.14 (s, 12H, 2×OC(CH₃)₂), 1.02 (s, 3H, CH₃) ppm

¹³C NMR (101 MHz, CDCl₃) δ 177.6 (C=O), 169.9 (C=O), 169.8 (C=O), 155.2 20 (C=CH₂), 135.1 (CH), 128.6 (CH), 107.4 (C=CH₂), 91.4 (C), 84.4 (C), 83.8 (OC(CH₃)₂), 70.5 (CHOAc), 53.4 (CH), 52.5 (C), 51.6 (CH), 51.0 (C), 44.7 (CH₂), 40.6 (CH₂), 36.7 (CH₂), 25.2 (OC(CH₃)₂), 24.7 (OC(CH₃)₂), 22.0 (O₂CCH₃), 20.7 (O₂CCH₃), 16.8 (CH₂), 15.0 (CH₃) ppm

HRMS (*m/z*): (ESI) calc'd for C₂₈H₃₇BNaO₈ [M+Na]⁺: 535.2479, found: 535.2476

25 **IR (neat) $\nu_{\max}$:** 2978, 1769, 1736, 1370, 1228, 1141, 1015, 970, 892 and 730 cm⁻¹

$[\alpha]_{\text{D}}^{24}$: -204 (*c* = 0.2, CHCl₃)

(1*S*,2*S*,4*aR*,4*bR*,7*S*,9*aR*,10*aR*)-1-Methyl-8-methylene-13-oxo-1,2,5,6,8,9,10,10a-octahydro-4*a*,1-(epoxymethano)-7,9a-methanobenzo[*a*]azulene-2,7(4*bH*)-diyl diacetate (36)

m.p.: 193 – 195 °C

5 **¹H NMR** (400 MHz, CDCl₃) δ 6.40 (d, *J* = 9.2 Hz, 1H, C=CH), 5.86 (dd, *J* = 9.3, 3.8 Hz, 1H, C=CH), 5.34 (d, *J* = 3.7 Hz, 1H, CHOAc), 5.13 (s, 1H, =CH₂), 4.97 (s, 1H, =CH₂), 2.85 (dd, *J* = 11.2, 7.9 Hz, 1H), 2.55 (dt, *J* = 15.2, 3.0 Hz, 1H), 2.43 – 2.34 (m, 1H), 2.34 – 2.27 (m, 1H), 2.21 (dd, *J* = 10.8, 2.7 Hz, 1H), 2.12 (m, 4H), 2.05 – 1.94 (m, 5H), 1.86 – 1.78 (m, 2H), 1.75 – 1.66 (m, 2H), 1.22 (s, 3H, CH₃) ppm

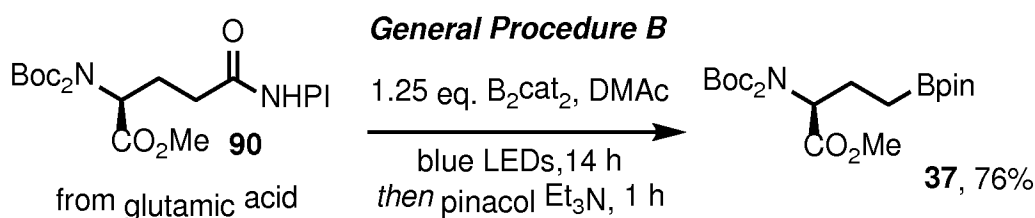
10 **¹³C NMR** (101 MHz, CDCl₃) δ 177.5 (C=O), 169.8 (C=O), 154.9 (C=CH₂), 134.7 (CH), 128.9 (CH), 106.9 (C=CH₂), 91.6 (C), 84.9 (C), 70.4 (CHOAc), 52.3 (C), 51.0 (CH), 50.4 (CH), 48.2 (C), 46.7 (CH₂), 39.8 (CH₂), 36.8 (CH₂), 34.9 (CH₂), 22.1 (O₂CCH₃), 20.8 (O₂CCH₃), 16.5 (CH₂), 14.5 (CH₃) ppm

HRMS (*m/z*): (ESI) calc'd for C₂₂H₂₆NaO₆ [M+Na]⁺: 409.1622, found: 409.1630

15 **IR (neat) ν_{max} :** 2939, 1774, 1735, 1369, 1227, 1157, 1019, 964, 896 and 731 cm⁻¹

$[\alpha]_{\text{D}}^{24}$: +138 (*c* = 0.5, CHCl₃)

Glutamic acid derived pinacol boronic ester (37)



20 **Activation:** Glutamic acid derived NHPI ester **90** was prepared according to a known procedure.

Borylation: NHPI ester **90** (66 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO₂;

5:1 petroleum ether 40-60:Et₂O) to afford boronic ester **37** (44 mg, 76%) as a colorless oil.

TLC: *R*_f = 0.48 (3:1 petroleum ether 40-60:EtOAc)

¹H NMR (400 MHz, CDCl₃) δ 4.85 (dd, *J* = 9.9, 5.1 Hz, 1H, CHCO₂CH₃), 3.70 (s, 3H, CO₂CH₃), 2.22 (dddd, *J* = 14.1, 8.9, 7.7, 5.1 Hz, 1H, CH₂), 1.99 (dtd, *J* = 14.3, 9.5, 6.6 Hz, 1H, CH₂), 1.49 (s, 18H, NBoc₂), 1.24 (s, 12H, 2×OC(CH₃)₂), 0.80 (ddd, *J* = 9.3, 7.0, 2.3 Hz, 2H, CH₂Bpin) ppm

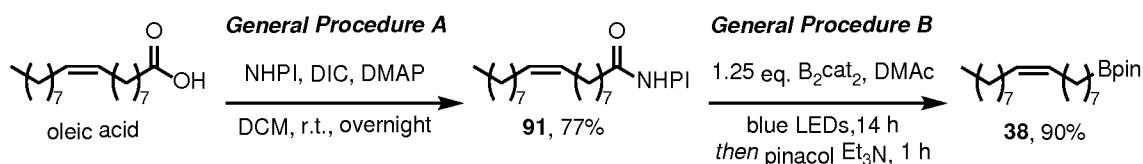
¹³C NMR (101 MHz, CDCl₃) δ 171.4 (C=O), 152.2 (C=O), 83.0 (OC(CH₃)₂), 82.7 (OC(CH₃)₃), 59.7 (CHCO₂CH₃), 51.9 (CO₂CH₃), 27.9 (OC(CH₃)₃), 24.8 (OC(CH₃)₂), 24.1 (CH₂) ppm

HRMS (*m/z*): (ESI) calc'd for C₂₁H₃₈BNaO₈ [M+Na]⁺: 466.2587, found: 466.2587

IR (neat) ν_{max}: 2978, 1743, 1700, 1367, 1235, 1131, 849 and 781 cm⁻¹

[α]_D²⁴: -24 (*c* = 1, CHCl₃)

15 **(*Z*)-2-(Heptadec-8-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**38**)**



Activation: Oleic acid (1.0 mL, 3.15 mmol) was coupled with *N*-hydroxyphthalimide according to **General Procedure A**. The crude residue was purified by flash column chromatography (SiO₂; 60:40 pentane:DCM) to afford the corresponding NHPI ester **91** (1.04 g, 77%) as a colorless oil.

TLC: *R*_f = 0.28 (50:50 pentane:DCM)

¹H NMR (400 MHz, CDCl₃) δ 7.90 – 7.86 (m, 2H, phthalimide ArH), 7.80 – 7.76 (m, 2H, phthalimide ArH), 5.39 – 5.31 (m, 2H, =CH × 2), 2.66 (t, *J* = 7.5 Hz, 2H, CH₂C=O), 2.06 – 1.97 (m, 4H, =CHCH₂ × 2), 1.78 (p, *J* = 7.5 Hz, 2H, CH₂CHC=O), 1.47 – 1.23 (m, 20H, CH₂ × 10), 0.87 (t, *J* = 7.0 Hz, 3H, CH₃) ppm

¹³C NMR (101 MHz, CDCl₃) δ 169.7 (C=O), 162.1 (C=O), 134.8 (phthalimide ArCH), 130.2 (=CH), 129.8 (=CH), 129.1 (phthalimide ArC), 124.1 (phthalimide ArCH), 32.0 (CH₂), 31.1 (CH₂C=O), 29.9 (CH₂), 29.8 (CH₂), 29.7 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 29.2 (CH₂ × 2), 28.9 (CH₂), 27.4 (=CHCH₂), 27.3 (=CHCH₂), 24.8 (CH₂CH₂C=O), 22.8 (CH₂), 14.2 (CH₃) ppm

All data matched that reported in the literature.

Borylation: NHPI ester **91** (57 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO₂; 95:5 pentane:Et₂O) to afford boronic ester **38** (44 mg, 90%) as colorless oil.

TLC: *R*_f = 0.55 (95:5 pentane:Et₂O)

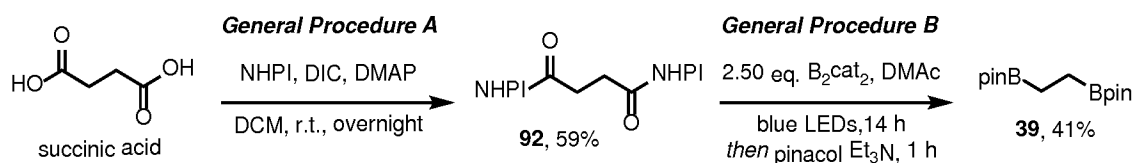
¹H NMR (400 MHz, CDCl₃) δ 5.39 – 5.30 (m, 2H, =CH × 2), 2.05 – 1.98 (m, 4H, =CHCH₂ × 2), 1.43 – 1.21 (m, 22H, CH₂ × 11), 1.24 (s, 12H, C(CH₃)₂), 0.88 (t, *J* = 7.0 Hz, 3H, CH₃), 0.76 (t, *J* = 7.7 Hz, 2H, CH₂Bpin) ppm

¹³C NMR (101 MHz, CDCl₃) δ 130.1 (=CH), 130.0 (=CH), 83.0 (C(CH₃)₂), 32.6 (CH₂), 32.1 (CH₂), 29.9 (CH₂ × 2), 29.9 (CH₂), 29.7 (CH₂), 29.5 (CH₂ × 2), 29.4 (CH₂), 27.4 (=CHCH₂), 27.4 (=CHCH₂), 25.0 (C(CH₃)₂), 24.2 (CH₂), 22.8 (CH₂), 14.3 (CH₃) ppm

HRMS (*m/z*): (ESI) calc'd for C₂₃H₄₆BO₂ [M+H]⁺: 365.3590, found: 365.3589

IR (neat) ν_{max}: 2978, 2923, 2854, 1377, 1371, 1316, 1146, 958 and 847 cm⁻¹

20 1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethane (**39**)



Activation: Succinic acid (500 mg, 4.23 mmol) was coupled with *N*-hydroxyphthalimide according to **General Procedure A** with all reagents doubled in quantity. The crude residue was purified by flash column chromatography (SiO₂; 98:2

DCM:Et₂O) to afford the corresponding NHPI ester **92** (1.02 g, 59%) as an amorphous white solid.

TLC: R_f = 0.21 (98:2 DCM:Et₂O)

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.00 – 7.93 (m, 8H, phthalimide ArH), 3.21 (s, 4H, CH₂C=O) ppm

¹³C NMR (101 MHz, DMSO-*d*₆) δ 168.8 (C=O), 161.6 (C=O), 135.5 (phthalimide ArCH), 128.1 (phthalimide ArC), 124.0 (phthalimide ArCH), 25.3 (CH₂) ppm

HRMS (m/z): (ESI) calc'd for C₂₀H₁₂N₂NaO₈ [M+Na]⁺: 431.0486, found: 431.0484

IR (solid state) $\nu_{\max}$: 3058, 2939, 1788, 1732, 1467, 1375, 1301, 1186, 1140, 1076, 972, 882, 789, 728, 694, 601 and 519 cm⁻¹

Borylation: NHPI ester **92** (53 mg, 0.13 mmol) was borylated according to **General Procedure B** with double the amount of B₂cat₂. The crude residue was purified by flash column chromatography (SiO₂; 100:0 → 90:10 pentane:Et₂O) to afford boronic ester **39** (15 mg, 41%) as a colorless oil.

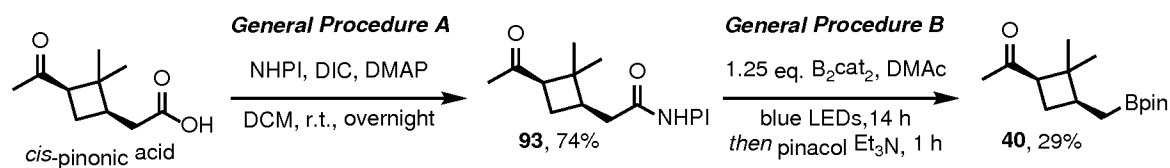
TLC: R_f = 0.30 (80:20 pentane:Et₂O)

¹H NMR (400 MHz, CDCl₃) δ 1.23 (s, 24H, 8×CH₃), 0.84 (s, 4H, 2×CH₂) ppm

¹³C NMR (101 MHz, CDCl₃) δ 83.0 (4×OC(CH₃)₂), 25.0 (8×CH₃), 4.6 (2×CH₂) ppm

All data matched that reported in the literature.

20 1-((1*R*,3*S*)-2,2-Dimethyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)cyclobutyl)ethan-1-one (40**)**



Activation: *cis*-Pinonic acid (1.0 g, 5.42 mmol) was coupled with *N*-hydroxyphthalimide according to **General Procedure A**. The crude residue was

purified by flash column chromatography (SiO₂; 3:1 petroleum ether 40-60:EtOAc) to afford the corresponding NHPI ester **93** (1.32 g, 74%) as a white solid.

m.p.: 88 – 90 °C

TLC: *R*_f = 0.23 (3:1 petroleum ether:EtOAc)

5 **¹H NMR** (400 MHz, CDCl₃) δ 7.82 – 7.77 (m, 2H, Ar-H), 7.74 – 7.69 (m, 2H, Ar-H), 2.85 (dd, *J* = 10.1, 7.6 Hz, 1H, CH), 2.67 – 2.50 (m, 2H, CH₂), 2.43 (dtd, *J* = 10.4, 8.4, 6.8 Hz, 1H, CH), 2.13 – 1.89 (m, 5H, CH₂ + CH₃), 1.30 (s, 3H, CH₃), 0.88 (s, 3H, CH₃) ppm

10 **¹³C NMR** (101 MHz, CDCl₃) δ 207.0 (C=O), 168.6 (C=O), 161.8 (C=O), 134.7 (HC_{Ar}), 128.8 (C_{Ar}), 123.9 (HC_{Ar}), 53.9 (CH), 43.3 (C), 37.8 (CH), 31.8 (CH₂), 30.1 (CH₃), 30.0 (CH₃), 22.9 (CH₂), 17.2 (CH₃) ppm

HRMS (*m/z*): (ESI) calc'd for C₁₈H₁₉NNaO₅ [M+Na]⁺: 352.1155, found: 352.1145

IR (solid state) ν_{max} : 2949, 1785, 1739, 1701, 1356, 1184, 1060, 968 and 876 cm⁻¹

15 **Borylation:** NHPI ester **93** (43 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO₂; 10:1 petroleum ether 40-60:Et₂O) to afford boronic ester **40** (10 mg, 29%) as a colorless oil.

TLC: *R*_f = 0.53 (3:1 petroleum ether 40-60:EtOAc)

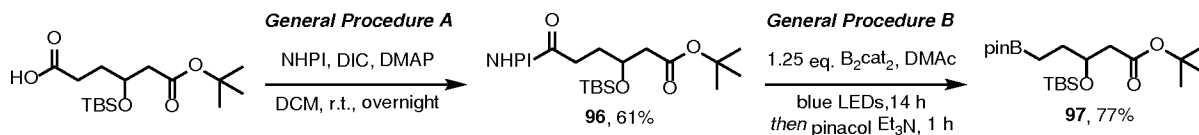
20 **¹H NMR** (400 MHz, CDCl₃) δ 2.73 (dd, *J* = 10.0, 7.7 Hz, 1H, CH), 2.12 – 1.99 (m, 1H, CH), 1.95 (s, 3H, O=CCH₃), 1.87 – 1.74 (m, 2H, CH₂), 1.20 (s, 3H, CH₃), 1.16 (s, 12H, 2×OC(CH₃)₂), 0.74 (s, 3H, CH₃), 0.71 – 0.60 (m, 2H, CH₂Bpin).

¹³C NMR (76 MHz, CDCl₃) δ 208.3 (C=O), 83.0 (OC(CH₃)₂), 54.7 (CH), 44.1 (C), 38.1 (CH), 30.1 (CH₃), 30.0 (CH₃), 25.2 (CH₂), 24.9 (OC(CH₃)₂), 24.8 (OC(CH₃)₂), 17.3 (CH₃).

25 **HRMS (*m/z*):** (ESI) calc'd for C₂₅H₂₇BNaO₃ [M+Na]⁺: 289.1948, found: 289.1945

IR (neat) ν_{max} : 2975, 1705, 1369, 1317, 1145, 968 and 846 cm⁻¹

***tert*-Butyl 3-((*tert*-butyldimethylsilyl)oxy)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate**



Activation: The carboxylic acid (577 mg, 1.74 mmol) was coupled with *N*-hydroxyphthalimide according to **General Procedure A**. The crude residue was purified by flash column chromatography (SiO_2 ; 70:30 pentane: Et_2O) to afford the corresponding NHPI ester **96** (508 g, 61%) as a white solid.

TLC: $R_f = 0.20$ (DCM)

^1H NMR (400 MHz, CDCl_3) δ 7.91 – 7.87 (phthalimide ArH), 7.81 – 7.76 (phthalimide ArH), 4.22 (p, $J = 6.7$ Hz, CHO), 2.76 (t, $J = 7.9$ Hz, 2H, $\text{CH}_2\text{C}=\text{O}$), 2.48 (dd, $J = 14.9$, 5.6 Hz, 1H, $\text{CH}^a\text{H}^b\text{C}=\text{O}$), 2.35 (dd, $J = 14.9$, 6.9 Hz, 1H, $\text{CH}^a\text{H}^b\text{C}=\text{O}$), 2.10 – 2.01 (m, 1H, CH^aH^b), 1.98 – 1.88 (m, 1H, CH^aH^b), 1.45 (s, 9H, $\text{C}(\text{CH}_3)_3$), 0.90 (s, 9H, $\text{SiC}(\text{CH}_3)_3$), 0.12 (s, 3H, SiCH_3), 0.10 (s, 3H, SiCH_3) ppm

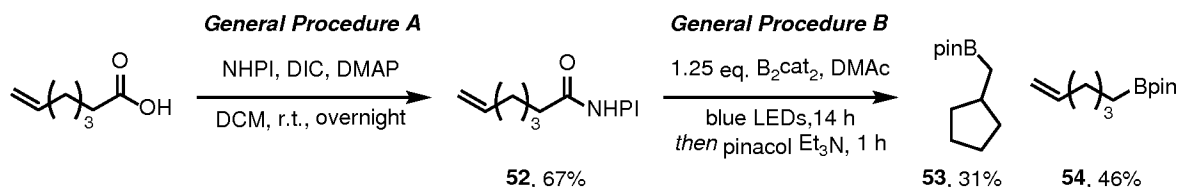
Borylation: NHPI ester **96** (64 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO_2 ; 95:5 pentane: Et_2O) to afford boronic ester **40** (43 mg, 77%) as a colorless oil.

TLC: $R_f = 0.26$ (90:10 pentane: Et_2O)

^1H NMR (400 MHz, CDCl_3) δ 4.03 (p, $J = 5.9$ Hz, 1H, CHO), 2.33 (d, $J = 6.3$ Hz, 2H, $\text{CH}_2\text{C}=\text{O}$), 1.64 – 1.51 (m, 2H, CH_2), 1.43 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.23 (s, 12H, $\text{C}(\text{CH}_3)_2$), 0.86 (s, 9H, $\text{SiC}(\text{CH}_3)_3$), 0.82 – 0.72 (2H, CH_2Bpin), 0.06 (s, 3H, SiCH_3), 0.04 (s, 3H, SiCH_3) ppm

2.1.5 Radical Cyclization

2-(Cyclopentylmethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**53**) and 2-(Hex-5-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**54**)



- 5 **Activation:** The carboxylic acid (150 mg, 1.17 mmol) was coupled with *N*-hydroxyphthalimide according to **General Procedure A**. The crude residue was purified by flash column chromatography (SiO₂; 90:10 hexane:acetone) to afford the corresponding NHPI ester **52** (215 mg, 67%) as a colorless oil.

TLC: R_f = 0.27 (hexane:acetone 80:20)

- 10 **¹H NMR:** (400 MHz, CDCl₃) δ 7.88 (m, 2H, 2×Ar-H), 7.78 (m, 2H, 2×Ar-H), 5.81 (ddt, J = 17.0, 10.2, 6.7 Hz, 1H), 5.04 (ddt, J = 17.0, 2.2, 1.7 Hz, 1H), 4.98 (ddt, J = 10.2, 2.2, 1.2 Hz, 1H), 2.67 (t, J = 7.4 Hz, 2H, CH₂CO₂R), 2.12 (dddt, J = 7.4, 6.7, 1.7, 1.2 Hz, 2H, CH₂(CH₂)₃CO₂R), 1.81 (app. p, J^{app} = 7.4 Hz, 2H, CH₂CH₂CO₂R), 1.55 (app. p, J^{app} = 7.4 Hz, 2H, CH₂(CH₂)₂CO₂R) ppm

- 15 **¹³C NMR:** (101 MHz, CDCl₃) δ 169.6 (CO₂R), 162.1 (2×CO), 138.2 (H₂C=CHR), 134.9 (2×HC_{Ar}), 129.1 (2×C_{Ar}), 124.1 (2×HC_{Ar}), 115.2 (H₂C=CHR), 33.3 (CH₂(CH₂)₃CO₂R), 31.0 (CH₂CO₂R), 28.1 (CH₂(CH₂)₂CO₂R), 24.2 (CH₂CH₂CO₂R) ppm

HRMS (m/z): (ESI) calc'd for C₁₅H₁₅NNaO₄ [M+Na]⁺: 296.0893, found: 296.0883

- 20 **IR (neat) ν_{max} :** 3076, 2934, 2865, 1815, 1787, 1738, 1467, 1362, 1185, 1081, and 877 cm⁻¹

Borylation: NHPI ester **52** (36 mg, 0.13 mmol) was borylated according to **General Procedure B**. The crude residue was purified by flash column chromatography (SiO₂; 100:0 → 90:10 pentane:Et₂O) to afford a 57:43 mixture of linear:cyclized boronic esters **54** and **53** (21 mg, 77%) as a colorless oil. **Note:** Product volatile!

- 25 **TLC:** R_f = 0.55 (pentane:Et₂O 95:5)

Linear product (54):

¹H NMR: (400 MHz, CDCl₃) δ 5.81 (ddt, J = 17.1, 10.1, 6.6 Hz, 1H, H₂CCHR), 4.98 (d, J = 17.1 Hz, 1H), 4.91 (d, J = 10.1 Hz, 1H), 2.04 (td, J = 7.0, 6.6 Hz, 2H, H₂CCHCH2), 1.45 – 1.34 (m, 4H, 2×CH₂), 1.24 (s, 12H, 4×CH₃), 0.77 (t, J = 7.3 Hz, 2H, CH₂Bpin) ppm

¹³C NMR: (101 MHz, CDCl₃) δ 139.3 (H₂CCHR), 114.2 (H₂CCHR), 83.0 (2×OC(CH₃)₂), 33.7 (CH₂(CH₂)₃Bpin), 31.8 (CH₂), 25.0 (4×CH₃), 23.7 (CH₂) ppm

All data matched that reported in the literature.

Cyclized product (53)

¹H NMR: (400 MHz, CDCl₃) δ 1.95 (m, 1H, CHCHCH₂Bpin), 1.76 (m, 2H), 1.60 (m, 2H), 1.50 (m, 2H), 1.05 (m, 2H), 0.83 (d, J = 7.4 Hz, 2H, CH₂Bpin)

¹³C NMR: (101 MHz, CDCl₃) δ 82.9 (2×OC(CH₃)₂), 36.3 (CHCH₂Bpin), 35.2 ((CH₂)₂CHCH₂Bpin), 25.3 ((CH₂CH₂)₂CHCH₂Bpin), 25.0 (4×CH₃) ppm

All data matched that reported in the literature.

Claims

1. A method for converting a carboxylic acid, the method comprising using a
diboron reagent to convert a carboxylic acid or imide ester derivative of a carboxylic
5 acid to a boronic ester.
2. A method for converting a carboxylic acid, the method comprising,
providing an imide ester of a carboxylic acid, and
treating the imide ester with a diboron reagent, thereby forming a boronic
10 ester.
3. A method as claimed in either claim 1 or claim 2, wherein the diboron reagent
is selected from bis(catecholato)diboron, $B_2(OH)_4$ or a mixture thereof.
- 15 4. A method as claimed in claim 3, wherein the diboron reagent further
comprises catechol.
5. A method as claimed in any one of the preceding claims, wherein the diboron
reagent comprises bis(catecholato)diboron and/or $B_2(OH)_4$ in the presence of catechol.
20
6. A method as claimed in either claim 4 or claim 5, wherein catechol is present
in 0.1 to 0.9 equivalents.
7. A method as claimed in any one of the preceding claims wherein the diboron
25 reagent is present in 1.0 to 2.0 equivalents, preferably 1.1 to 2.0 equivalents.

8. A method as claimed in any one of the preceding claims, wherein the imide ester is a phthalimide ester, preferably a phthalimide ester derived from N-hydroxyphthalimide or halogen-substituted N-hydroxyphthalimide, more preferably N-hydroxytetrachlorophthalimide.
9. A method as claimed in any one of the preceding claims, wherein providing an imide ester comprises a step of reacting an N-hydroxyimide with the carboxylic acid, preferably esterifying a N-hydroxyphthalimide or halogen-substituted N-hydroxyphthalimide, more preferably N-hydroxytetrachlorophthalimide with the carboxylic acid.
10. A method as claimed in any one of the preceding claims, further comprising a subsequent step of converting the boronic ester produced by the method into another boronic ester.
11. A method as claimed in claim 10, wherein converting the boronic ester comprises ligand exchange of the boronic ester, preferably with a ligand composition comprising pinacol and/or N-methyliminodiacetic acid (MIDA).
12. A method as claimed in any one of the preceding claims, wherein treating the imide ester with the diboron reagent is conducted under illumination.
13. A method as claimed in claim 12, wherein illumination is with light having a component with a wavelength in the range 410 nm to 480 nm.

14. A method as claimed in any one of the preceding claims, wherein the method is conducted in a solvent, preferably an amide solvent, more preferably an amide solvent selected from DMAc, DMF, DMPU, DMI, NMP and tetramethylurea.

5 15. A method as claimed in any one of the preceding claims, wherein the method is conducted in the presence of an additive, preferably selected from one or more of 4-methoxypyridine, DMAP, pyridine, DABCO, DBU, quinuclidine, TMG, TBD, MTBD, 2-picoline, 4-picoline, 3-picoline, imidazole, K₂CO₃, AcOH, triethylamine, 4-cyanopyridine, and 4-phenylpyridine.

10

16. A method as claimed in claim 15, wherein there is no illumination other than, optionally, ambient light.

17. A method for converting a carboxylic acid, the method comprising,

15 providing a phthalimide ester of a carboxylic acid, the phthalimide ester being a derivative of N-hydroxyphthalimide or N-hydroxytetrachlorophthalimide, and

treating the phthalimide ester with a diboron reagent selected from bis(catecholato)diboron and/or B₂(OH)₄ and catechol, thereby forming a boronic ester of the carboxylic acid.

20

18. A method as claimed in claim 17, further comprising converting the boronic ester by ligand exchange of the boronic ester, preferably by treatment with a ligand composition comprising pinacol and/or N-methyliminodiacetic acid (MIDA).

25 19. A method of preparing a boronic acid or a boronic ester, the method comprising the capture of an alkyl radical with a diboron reagent.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/059121

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07B47/00 C07D207/46 C07F5/02
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07B C07D C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JIEFENG HU ET AL: "Nickel-Catalyzed Decarbonylative Borylation of Amides: Evidence for Acyl C-N Bond Activation", ANGEWANDTE CHEMIE INTERNATIONAL EDITION, vol. 55, no. 30, 18 July 2016 (2016-07-18), pages 8718-8722, XP055478348, ISSN: 1433-7851, DOI: 10.1002/anie.201603068	1,14,16
A	tables 1,2 ----- -/--	2,8-13, 17,18



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

28 May 2018

Date of mailing of the international search report

01/08/2018

Name and mailing address of the ISA/

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Eberhard, Michael

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2018/059121

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	LIN GUO ET AL: "Functional Group Interconversion: Decarbonylative Borylation of Esters for the Synthesis of Organoboronates", CHEMISTRY - A EUROPEAN JOURNAL, vol. 22, no. 47, 14 November 2016 (2016-11-14), pages 16787-16790, XP055478347, DE ISSN: 0947-6539, DOI: 10.1002/chem.201604504 tables 1,2 -----	1,14,16
X	MING GAO ET AL: "Structure and Reactivity of a Preactivated sp²-sp³ Diboron Reagent: Catalytic Regioselective Boration of [alpha],[beta]-Unsaturated Conjugated Compounds", JOURNAL OF ORGANIC CHEMISTRY, vol. 76, no. 10, 20 May 2011 (2011-05-20), pages 3997-4007, XP055476606, ISSN: 0022-3263, DOI: 10.1021/jo2003488 figures 1,4 -----	1,3-7, 14,16
X	O. K. RASHEED ET AL: "The assembly of "S₃N"-ligands decorated with an azo-dye as potential sensors for heavy metal ions", DALTON TRANSACTIONS, vol. 46, no. 16, 15 March 2017 (2017-03-15), pages 5229-5239, XP055476610, GB ISSN: 1477-9226, DOI: 10.1039/C7DT00569E * scheme 2 equation 1 * -----	1,14,16
X	MING GAO ET AL: "sp²-sp³ Hybridized Mixed Diboron: Synthesis, Characterization, and Copper-Catalyzed [beta]-Boration of [alpha],[beta]-Unsaturated Conjugated Compounds", ORGANIC LETTERS, 14(23), 6012-6015 CODEN: ORLEF7; ISSN: 1523-7052, vol. 11, no. 15, 6 August 2009 (2009-08-06), pages 3478-3481, XP055476637, ISSN: 1523-7060, DOI: 10.1021/o1901359n abstract table 1 ----- -/--	1,14,16

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	QIANG FENG ET AL: "Highly selective copper-catalyzed trifunctionalization of alkynyl carboxylic acids: an efficient route to bis-deuterated [beta]-borylated [alpha],[beta]-styrene", CHEMICAL COMMUNICATIONS, vol. 51, no. 84, 1 January 2015 (2015-01-01), pages 15394-15397, XP055476641, GB ISSN: 1359-7345, DOI: 10.1039/C5CC05084G * schemes 1, 2 * * equations (4), (8), (9) * table 1 -----	1,14,16
X	CAYETANA ZARATE ET AL: "Ipso- Borylation of Aryl Ethers via Ni-Catalyzed C-OMe Cleavage", JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 137, no. 21, 22 May 2015 (2015-05-22), pages 6754-6757, XP055476644, US ISSN: 0002-7863, DOI: 10.1021/jacs.5b03955 tables 2,3 compounds (3f), (3g), (3k), (5a), (5b), (5c), (5e) -----	1,14,16
X	FRANCIS MARIARAJ IRUDAYANATHAN ET AL: "Copper-catalyzed Decarboxylative Hydroboration: Synthesis of Vinyl Boronic Esters : Copper-catalyzed Decarboxylative Hydroboration", BULL. KOREAN CHEM. SOC., vol. 37, no. 4, 1 April 2016 (2016-04-01), pages 463-468, XP055476649, ISSN: 1229-5949, DOI: 10.1002/bkcs.10706 * scheme 1 (a), (d) * table 1 -----	1,14-16
X	ROBIN B. BEDFORD ET AL: "Iron-Catalyzed Borylation of Alkyl, Allyl, and Aryl Halides: Isolation of an Iron(I) Boryl Complex", ORGANOMETALLICS, vol. 33, no. 21, 10 November 2014 (2014-11-10), pages 5940-5943, XP055478363, US ISSN: 0276-7333, DOI: 10.1021/om500847j tables 2 entries 1,4,12,25 ----- -/--	1,14,16

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2018/059121

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	YING-WEI ZHAO ET AL: "Copper-catalyzed decarboxylative hydroboration of phenylpropionic acids under ligand-free or both ligand- and base-free conditions", CHINESE CHEMICAL LETTERS, vol. 27, no. 4, 1 April 2016 (2016-04-01), pages 571-574, XP055476650, AMSTERDAM, NL ISSN: 1001-8417, DOI: 10.1016/j.cclet.2016.02.012 table 1 * schemes 1-3 * -----	1,14-16
X	EMILY C. NEEVE ET AL: "Diboron(4) Compounds: From Structural Curiosity to Synthetic Workhorse", CHEMICAL REVIEWS, vol. 116, no. 16, 19 July 2016 (2016-07-19), pages 9091-9161, XP055477033, US ISSN: 0009-2665, DOI: 10.1021/acs.chemrev.6b00193 * schemes 90., 91.(b), 111.(a) * -----	1,14,16
X,P	Alexander Fawcett ET AL: "Photoinduced decarboxylative borylation of carboxylic acids", Science, 21 July 2017 (2017-07-21), pages 283-286, XP055477023, Retrieved from the Internet: URL:http://science.sciencemag.org/content/357/6348/283.full.pdf [retrieved on 2018-05-22] the whole document -----	1-18
X,P	WAN-MIN CHENG ET AL: "Isonicotinate Ester Catalyzed Decarboxylative Borylation of (Hetero)Aryl and Alkenyl Carboxylic Acids through N -Hydroxyphthalimide Esters", ORGANIC LETTERS, 14(23), 6012-6015 CODEN: ORLEF7; ISSN: 1523-7052, vol. 19, no. 16, 28 July 2017 (2017-07-28), pages 4291-4294, XP055476654, ISSN: 1523-7060, DOI: 10.1021/acs.orglett.7b01950 the whole document ----- -/--	1-18

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2018/059121

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	SHICHENG SHI ET AL: "Decarbonylative Cyanation of Amides by Palladium Catalysis", ORGANIC LETTERS , 14(23), 6012-6015 CODEN: ORLEF7; ISSN: 1523-7052, vol. 19, no. 12, 1 June 2017 (2017-06-01), pages 3095-3098, XP055476633, ISSN: 1523-7060, DOI: 10.1021/acs.orglett.7b01199 the whole document	1-18
X,P	CHAO LI ET AL: "Decarboxylative borylation", SCIENCE, vol. 356, no. 6342, 9 June 2017 (2017-06-09), page eaam7355, XP055476621, US ISSN: 0036-8075, DOI: 10.1126/science.aam7355 the whole document	1-18
X,P	LISA CANDISH ET AL: "Transition-Metal-Free, Visible-Light-Enabled Decarboxylative Borylation of Aryl N -Hydroxyphthalimide Esters", JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 139, no. 22, 17 May 2017 (2017-05-17) , pages 7440-7443, XP055476619, US ISSN: 0002-7863, DOI: 10.1021/jacs.7b03127 the whole document	1-18
X,P	DAWEI HU ET AL: "Decarboxylative Borylation of Aliphatic Esters under Visible-Light Photoredox Conditions", ORGANIC LETTERS , 14(23), 6012-6015 CODEN: ORLEF7; ISSN: 1523-7052, vol. 19, no. 10, 5 May 2017 (2017-05-05), pages 2770-2773, XP055476617, ISSN: 1523-7060, DOI: 10.1021/acs.orglett.7b01181 the whole document	1-18
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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2018/059121

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	SHAO-CHI LEE ET AL: "Nickel-Catalyzed Decarbonylative Silylation, Borylation, and Amination of Arylamides via a Deamidative Reaction Pathway", SYNLETT, vol. 28, no. 19, 23 October 2017 (2017-10-23), pages 2594-2598, XP055476635, DE ISSN: 0936-5214, DOI: 10.1055/s-0036-1591495 the whole document -----	1-18

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2018/059121

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-18

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-18

Methods for converting a carboxylic acid.

2. claim: 19

A method for preparing a boronic acid or a boronic ester.
