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Nickel-Catalyzed Borylation of Aryl- and Benzyltrimethylammonium Salts *via* C-N Bond Cleavage

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ABSTRACT: By developing a mild Ni-catalyzed system, a method for direct borylation of sp^2 and sp^3 C-N bonds has been established. The key to this highly efficient C-N bond borylative cleavage depends on the appropriate choice of the nickel catalyst $Ni(COD)_2$, $ICy\cdot HCl$ as a ligand and the use of 2-ethoxyethanol as the co-solvent. This transformation shows good functional group compatibility and can serve as a powerful synthetic tool for gram-scale synthesis and late-stage C-N borylation of complex compounds.

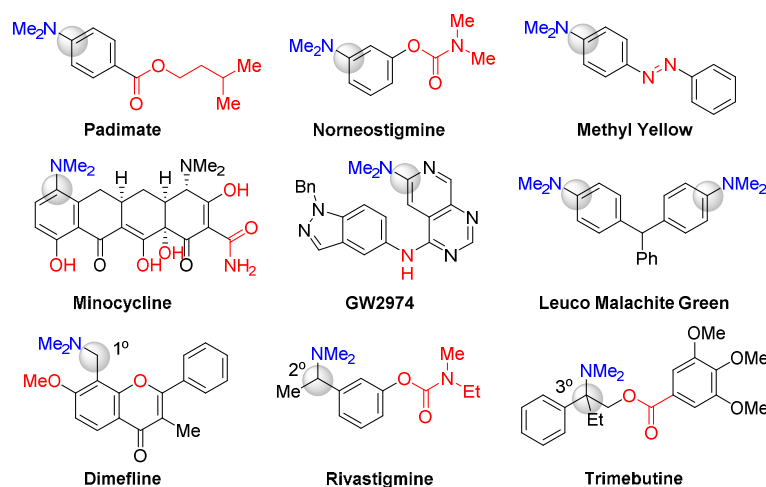
■ INTRODUCTION

The transition-metal-catalyzed functionalization of unreactive bonds has become one of the most powerful protocols available to practitioners of chemical synthesis.¹ C-N bonds are one of the most abundant and unreactive bonds in organic molecules, and the selective cleavage of them represents a challenge in the field of organometallic chemistry.² Since Wenkert et al. uncovered the first Ni-catalyzed Kumada coupling of aryltrimethylammonium iodide salts in 1988,³ other types of C-C bond cross-coupling reactions via C-N bond cleavage including Suzuki coupling⁴ and Negishi coupling⁵ have been developed in succession. Although the ruthenium-catalyzed direct arylation of C-N bond in aniline derivatives has also been developed in this context, the requirement of the substrates bearing an *ortho* directing group has restricted their general use.⁶ In addition to the C-C bond formation reactions, most recently, Garg and Houk et al. reported an important breakthrough for the conversion of amides to esters *via* nickel-catalyzed activation of amide C-N bonds.⁷

Aryl and alkyl substituted boronic acid and their derivatives are versatile synthetic intermediates.⁸ Among the routes to these compounds, the borylation of C-H,⁹ C-O,¹⁰ C-F,¹¹ and C-C¹² bonds have shown promise because it bestows these inert functional groups with the synthetic versatility. In 2014, Tobisu and Chatani developed the first Ni-catalyzed borylative cleavage of C-N bonds in *N*-aryl amides and carbamates with fused aromatic system such as naphthalenes, anthracenes and phenanthrenes at high temperature.¹³ Although polycyclic aromatic amine derivatives are not necessarily ideal substrates for certain transformations, with some not readily available, the transformation is highly important for the construction of C-B bonds from this nonconventional synthetic strategy. *N,N*-dimethylamino functional groups are widely represented in biologically active natural products, medicines and dyes (a small selection of which are shown in Scheme 1), and many of them are commercially available at low prices. Therefore, mild methods for borylative cleavage of these sp^2 and sp^3 C-N bonds will not only expand the utility of the NMe_2 substituent

as a functional group, but also provide a route to make these readily available compounds to useful synthetic intermediates and commercial chemicals. In order to achieve this goal, several difficulties need to be overcome, in particular the issues of selective cleavage of a C-N bond in a complex molecule, since, (1) generally, the C-N bond scission requires a relatively high activation energy because of the strength and stability of its linkage; (2) the discrimination of different types of C-N bonds is challenging; (3) the selective cleavage of C-N bonds instead of C-H,⁹ C-O¹⁰ and C-halogen¹⁴ bonds is hard to control; and (4) elimination process in sp³ C-N bond cleavage is a significant impediment for cross-coupling.¹⁵ Here, we report our results on nickel-catalyzed highly chemo- and regioselective C-N bond borylation by activating ammonium salts under mild and scalable conditions. This system is effective not only for high functional-group tolerance of arylamines but also for the primary, secondary and even tertiary benzylamines. Moreover, application of this method in the preparation of some important organoboronate intermediates showcases the strategic opportunity to utilize this transformation in the synthesis of biologically active compounds.

Scheme 1. Nature Products, Drugs and Dyes Involving NMe₂ Groups

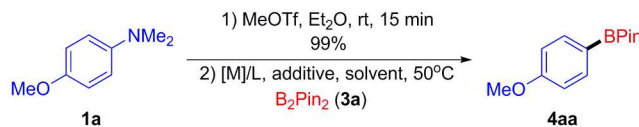


RESULTS AND DISCUSSION

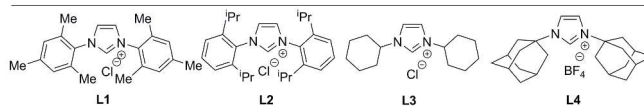
Initial studies involved the evaluation of the selective C-N borylation of 4-methoxy-*N,N*-dimethylaniline (**1a**) (Table 1). The experiments were performed with the corresponding aryltrimethylammonium triflate **2a** which was easily prepared in quantitative yield *via* methylation of **1a**, and bis(pinacolato)diboron (B₂Pin₂, **3a**) in the presence of 5 mol% Ni(COD)₂, 10 mol% IMes•HCl (**L1**) and 2.0 equiv ^tBuONa, at 50 °C under an Ar atmosphere in toluene. We indeed observed the desired product **4aa** in 5% yield after 12 h in GC-MS without any C-O bond cleavage byproducts (Table 1, entry 1). A variety of alcohols were investigated as potential promoters, and 2-ethoxyethanol (EE) showed the best result increasing the yield to 16% (Table 1, entry 2). Among various NHC ligands, a dramatic effect of ICy•HCl (**L3**) is notable, affording 78% yield of **4aa** (Table 1, entries 3-5). Under these conditions, both toluene and EE (v/v=1:1) were indispensable for this coupling. Changing the co-solvent ratio or replacing EE with MeOH or ^tBuOH resulted in much lower yields (Table 1, entries 6-10). ^tBuOLi was not as effective as ^tBuONa (Table 1, entry 11), and nearly quantitative yield was observed by employing ^tBuOK as the base (Table 1, entry 12). To our delight, other nickel sources as catalyst

such as Ni(OTf)₂ was also proven successful in this coupling reaction with a high reactivity (Table 1, entries 13-14). Notably, decreasing the Ni(COD)₂ loading to 1 mol% still resulted in a good yield (Table 1, entry 15) and no product is observed in the absence of Ni catalyst (Table 1, entry 16).

Table 1. Reaction Development^a



entry	[M]	L	Base	solvent	yield (%) ^b
1	Ni(COD) ₂	L1	^t BuONa	Toluene	5
2	Ni(COD) ₂	L1	^t BuONa	Toluene/EE (1:1)	16
3	Ni(COD) ₂	L2	^t BuONa	Toluene/EE (1:1)	18
4	Ni(COD) ₂	L3	^t BuONa	Toluene/EE (1:1)	78
5	Ni(COD) ₂	L4	^t BuONa	Toluene/EE (1:1)	25
6	Ni(COD) ₂	L3	^t BuONa	Toluene	33
7	Ni(COD) ₂	L3	^t BuONa	EE	54
8	Ni(COD) ₂	L3	^t BuONa	Toluene/EE (3:1)	68
9	Ni(COD) ₂	L3	^t BuONa	Toluene/MeOH (1:1)	42
10	Ni(COD) ₂	L3	^t BuONa	Toluene/ ⁿ BuOH (1:1)	71
11	Ni(COD) ₂	L3	^t BuOLi	Toluene/EE (1:1)	65
12	Ni(COD)₂	L3	^tBuOK	Toluene/EE (1:1)	99(94)^c
13	Ni(OTf) ₂	L3	^t BuOK	Toluene/EE (1:1)	91
14	NiCl ₂	L3	^t BuOK	Toluene/EE (1:1)	18
15 ^d	Ni(COD) ₂	L3	^t BuOK	Toluene/EE (1:1)	82
16	-	L3	^t BuOK	Toluene/EE (1:1)	0

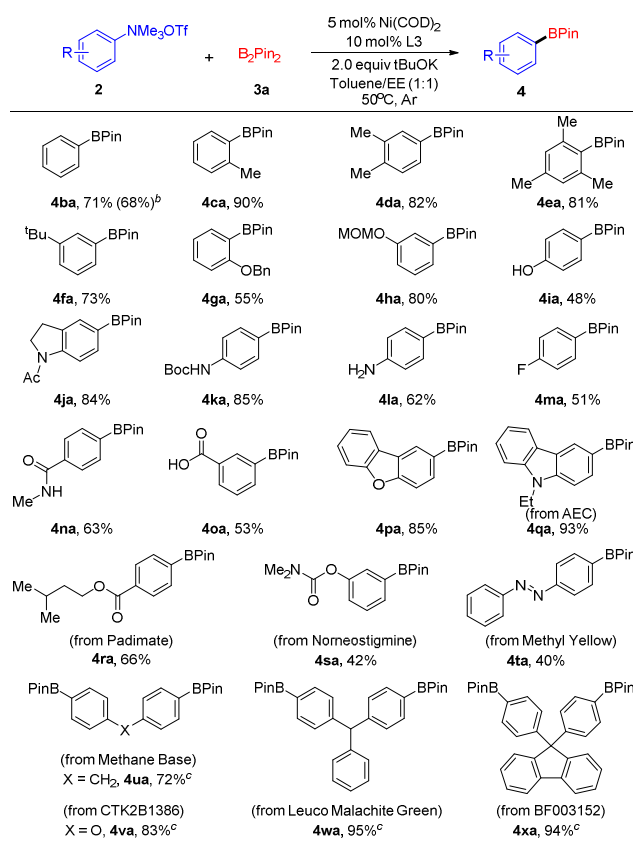


^aReaction conditions: **2a** (0.20 mmol), **3a** (0.50 mmol), 5 mol% of catalyst, 10 mol% of ligand, 2.0 equiv of base in solvent (2.0 mL), 16 h, under Ar. ^bDetermined by GC analysis. ^cYield. ^dUsing 1 mol% Ni(COD)₂ and 2 mol% **L3**. EE = 2-ethoxyethanol.

To evaluate the utility of the Ni-catalyzed borylation of C-N bonds, a series of *N,N*-dimethylanilines were tested in Table 2. Gratifyingly, a wide range of arylammonium triflates that incorporate electron- neutral, electron-donating and electron-withdrawing substituents at the *ortho*, *meta*, and *para* positions were readily tolerated (**4ba-4oa**). Among them, sterically hindered substrate **2e** resulted in good yield. Notably, this method can selectively activate the C-N bond in the presence of ether groups (**4ga** and **4ha**) and hydroxyl group (**4ia**). Moreover, the unique selectivity toward ammonium triflate was further corroborated by the presence of other types of C-N bonds such as amide, BocNH and NH₂ groups (**4ja-4la**). Transition-metal-catalyzed *ortho*-C-H borylation is a general process in the presence of directing-groups such as benzamide and benzoic acid.¹⁶ In our conditions, the directing-group-containing substrates **4na-4oa** can also selectively cleave C-N bonds, avoiding the catalyst to bind the directing groups. It's noted that only fluoro-substituted phenylammonium triflate **4ma** can be selectively borylated at the C-N bond, other halide-substituents such as aryl chlorides under-

went borylation at both the C-Cl and C-N bonds. In addition, polycyclic and hetero cyclic substrates were also compatible (**4pa-4qa**). To our delight, the -NMe₂ groups in drugs and dyes such as Padimate (**2r**), Norneostigmine (**2s**) and Methyl Yellow (**2t**) bearing ester, carbamate and diazenyl groups can be converted to the corresponding products successfully. Diborylated units are versatile synthetic intermediates, and practical and economical synthesis of them from the readily available chemicals is undoubtedly an ideal route. We observed that the desired borylation also took place when using the industrial materials such as Methane Base (**2u**), CTK2B1386 (**2v**), Leuco Malachite Green (**2w**) and BF003152 (**2x**), affording the corresponding products **4ua-4xa** in good to excellent yields.

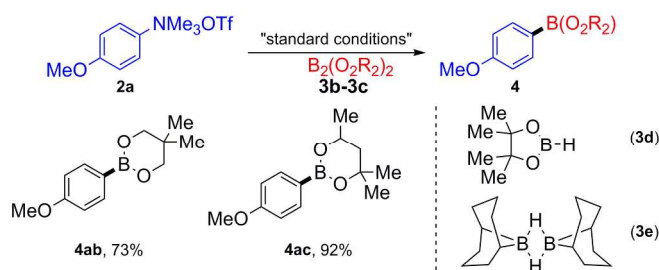
Table 2. Ni-Catalyzed Borylation of Aryl C-N Bonds^a



^aReaction conditions: **2** (0.20 mmol), **3a** (0.50 mmol), 5 mol% of Ni(COD)₂, 10 mol% of **L3**, ^tBuOK (0.4 mmol) in 2.0 mL toluene/EE (1:1) at 40 °C, 12 h, under Ar. ^bUsing phenyltrimethylammonium iodide as the substrate. ^c1.00 mmol **3a**.

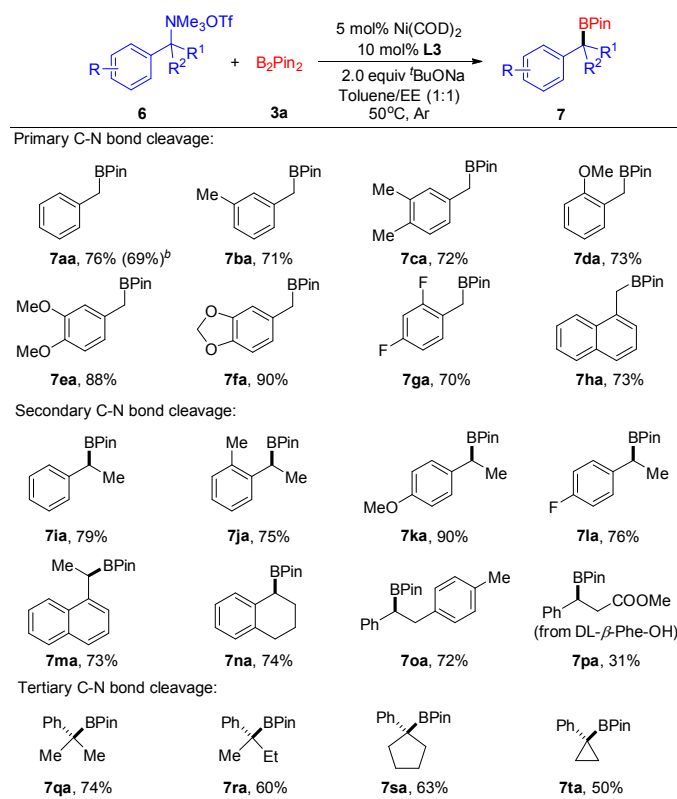
Our nickel-catalyzed system is not limited to the use of B₂Pin₂ as the sole borylating agent. Under the optimal conditions, reactions with bis(hexylene glycolato)diboron (**3b**) and bis(neopentyl glycolato)diboron (**3c**) also provided the aryl boronic esters **4ab** and **4ac** in 73% and 92% yields, respectively (Scheme 2). However, when pinacolborane (**3d**) and 9-borabicyclo[3.3.1]nonane (9-BBN dimer, **3e**) were employed, no desired products were detected, which might be attributed to the lack of the required B-B bonds in borylating agents for the transformation.

Scheme 2. Investigation of Different Borylating Agents



Further investigation revealed that benzylamines could also serve as suitable coupling partners with B_2Pin_2 (**3a**) (Table 3). Similar as the high functional-group tolerance in arylamine substituents, this substrate scope was also found to be very wide. Products containing methyl, ether, fluoro and ester substituents were formed in high yields. In the case of secondary benzylamines, β -hydrogens posed no problems. Moreover, the β -amino acid derivative **6p** is compatible with this method, giving **7pa** in an accepted yield of 31%. A particularly noteworthy point of our catalytic system is the first time report of tertiary C-N bond activation, as observed by the borylation of substrates **6q-6s** to produce desired product in moderate to good yields.

Table 3. Ni-Catalyzed Borylation of Benzylic C-N Bonds^a

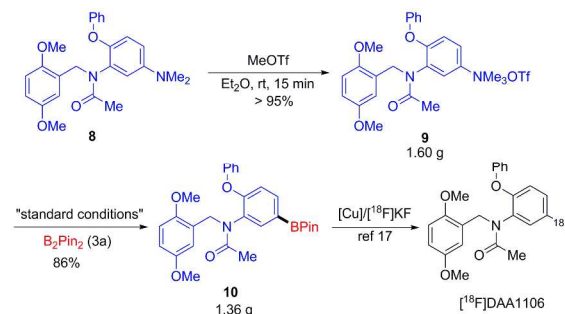


^aReaction conditions: **6** (0.20 mmol), **3a** (0.50 mmol), 5 mol% of $Ni(COD)_2$, 10 mol% of **L3**, $tBuONa$ (0.4 mmol) in 2.0 mL toluene/EE (1:1) at 50 °C, 12 h, under Ar. ^bUsing $tBuOK$.

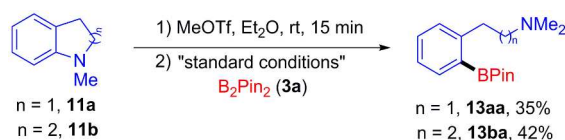
A major benefit of this mild, highly selective C-N bond borylation procedure is its amenability to gram-scale and late-stage synthetic applications (Scheme 3). To demonstrate this potential, complex molecule **8** containing a number of different types of C-O and C-N bonds was subjected to our borylation protocol and the corresponding arylammonium triflate **9** can be selectively

borylated at C-NMe₃ bond position to yield aryl boronic ester **10** in 86% yield. Subsequent copper-mediated nucleophilic ¹⁸F fluorination of **10** can provide the translocator protein (TSPO) PET ligand [¹⁸F]DAA1106.¹⁷ Nickel-catalyzed ring-opening and cross-coupling of aziridines has been developed recently.¹⁸ Remarkably, our optimized method provide an effective tool to cleave the larger rings in azaheterocyclic compounds. By employing the indoline and 1,2,3,4-tetrahydroquinoline derivatives **11a** and **11b** as substrates and B₂Pin₂ (**3a**) as the borylation reagent, the ring-opened products **13aa-13ba** can be generated in 35-42% yields at the current stage (Scheme 4).

Scheme 3. Gram-Scale Synthesis and Late-Stage Borylative C-N Bond Cleavage of Complex Molecule

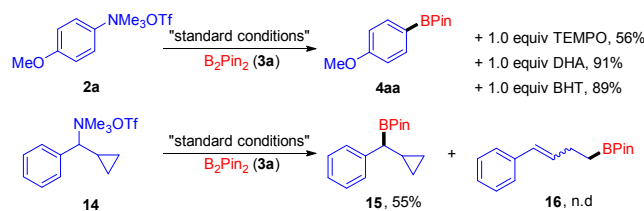


Scheme 4. Ring-Opening *via* Borylative Cleavage of C-N Bonds

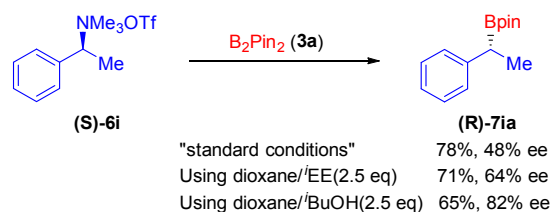


Fu and others proved that nickel-catalyzed Miyaura-type borylation of aryl and alkyl halides was proposed to be a radical involved mechanism.¹⁹ However, our reaction proceeds with comparable efficiency in the presence of 1.0 equiv of TEMPO, DHA or BHT as the radical inhibitors. Moreover, a radical-clock experiment using ammonium triflate **14** can further rule out the radical pathway (Scheme 5).

Scheme 5. Mechanistic Experiments

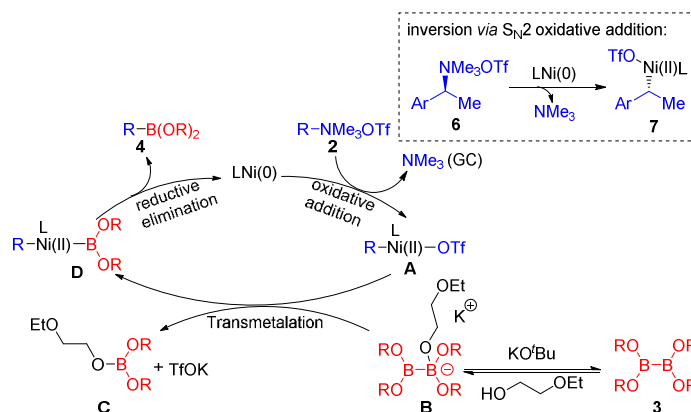


Scheme 6. Borylation of Chiral Substrate



Watson and co-workers previously uncovered that Ni-catalyzed process for the stereospecific cross-coupling of benzylic ammonium salts and boronic acids proceed *via* an S_N2 mechanism.^{4b} When (S)-**6i** (99% ee) was allowed to react with B₂Pin₂ (**3a**) in our standard conditions, only (R)-**7ia** of 48% ee was observed in 78% yield (Scheme 6).²⁰ A further improved screening revealed that solvent affects the chirality transfer with dioxane as solvent and 2.5 equiv ^tBuOH as additive providing (R)-**7ia** in good enantioselectivity (65% yield, 82% ee). This result is consistent with the inversion of configuration observed in stereospecific C-C bond formation cross couplings.^{15c, 21} On the basis of these investigations, we have hypothesized that the mechanism outlined in Scheme 7 is operative when ammonium triflates **2** or **6** are employed as electrophiles. The oxidative addition of the nickel catalyst into the benzylic C–N bond likely takes place *via* an S_N2 mechanism, leading to inversion of configuration of the benzylic stereocenter. The specific role of the co-solvent 2-ethoxyethanol (EE) is to generate the anionic adduct of borylating agent **B** from **3** in the presence of KO^tBu, which is the key to success for the transmetalation process in this catalytic cycle.²²

Scheme 7. Proposed Catalytic Cycle



In summary, we have developed a mild Ni-catalyzed system, which is capable to activate aryl and benzyl ammonium bonds for C-N bond borylation to produce various organoboronates.²³ In view of the widespread -NMe₂ group and its precursors in chemicals, this method offers a meaningful tool to enable them as valuable building blocks. This transformation showed exceptional functional group tolerance, high efficiency and excellent chemoselectivity. Due to these advantages, this reaction should be of high synthetic value.

EXPERIMENTAL SECTION

All new compounds were fully characterized. NMR-spectra were recorded either a 300 or 400 MHz spectrometer. HRMS spectra were recorded on a spectrometer with an ESI source. GC-MS spectra were recorded on a spectrometer with an EI source. All reactions were carried out in flame-dried reaction vessels with Teflon screw caps under argon. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Ni(COD)₂, 2-ethoxyethanol, toluene and ICy•HCl were purchased from Acros. KO^tBu and (Bpin)₂ was purchased from Sigma-Aldrich.

General Procedure for Preparation of Ammonium Triflates. The preparation of the dimethyl amines were described according to Eschweiler-Clarke conditions²⁴⁻²⁵. The ammonium triflates were prepared according to the literatures²⁶. To a solution of 4-methoxyaniline (1.2 g, 10.0 mmol, 1.0 eq.) in MeOH (15 mL) under Ar were added formic acid to adjust pH to 3-4. NaBH₃CN (0.9 g, 15.0 mmol, 1.5 eq.) was added to the reaction mixture and stirred for 10 min at room temperature. The mixture was cooled in a 0 °C ice-water bath, and formaldehyde (18 mL, 500 mmol, 50 eq.) was added slowly via a syringe and the mixture was allowed to warm to rt and stirred at 35 °C under Ar for 16 h. The resulting mixture was concentrated and the solution of K₂CO₃(5 M) was added to pH≈12. The aqueous layer was extracted with DCM (3 x 50 mL). The combined organic layer was dried over Na₂SO₄. The filtrate was concentrated and the crude product was purified by column chromatography on silica gel (DCM: MeOH = 20 : 1).

Dimethylamine (5 mmol, 1.0 equiv) was dissolved in Et₂O (10 mL). MeOTf (6.5 mmol, 1.3 equiv) was added dropwise at 0 °C. After complete addition the reaction mixture was stirred for an additional 15-60 minutes at 0 °C. The solution was concentrated and washed with Et₂O (2 x 20 mL). The resulting compounds were dried under vacuum to give salt.

N,N,N,3,4-Pentamethylbenzenaminium trifluoromethanesulfonate (2d). A white solid (1.4 g, 92%). ¹H NMR (400 MHz, DMSO) δ 7.73 (d, J = 2.7 Hz, 1H), 7.61 (dd, J = 8.5, 2.9 Hz, 1H), 7.34 (d, J = 8.6 Hz, 1H), 3.53 (s, 9H), 2.29 (s, 3H), 2.24 (s, 3H). ¹³C{¹H} NMR (101 MHz, DMSO) δ 145.0, 138.6, 138.4, 130.5, 120.9, 117.3, 56.3, 19.6, 18.7. HRMS m/z (ESI) calcd for C₁₁H₁₈N (M - OTf)⁺ 164.1434, found 164.1434.

3-(tert-Butyl)-N,N,N-trimethylbenzenaminium trifluoromethanesulfonate (2f). A white solid (1.5 g, 88%). ¹H NMR (400 MHz, DMSO) δ 7.87 (s, 1H), 7.75 (dd, J = 8.1, 2.6 Hz, 1H), 7.65 – 7.49 (m, 2H), 3.61 (s, 9H), 1.34 (s, 9H); ¹³C{¹H} NMR (101 MHz, DMSO) δ 153.3, 147.2, 129.6, 126.8, 117.3, 56.4, 35.1, 30.9. HRMS m/z (ESI) calcd for C₁₃H₂₂N (M - OTf)⁺ 192.1747, found 192.1748.

2-(Benzyloxy)-N,N,N-trimethylbenzenaminium trifluoromethanesulfonate (2g). A white solid (1.8 g, 92%). ¹H NMR (400 MHz, DMSO) δ 7.80 (dd, J = 8.5, 1.2 Hz, 1H), 7.59 (ddd, J = 8.3, 7.6, 2.9 Hz, 3H), 7.53 – 7.37 (m, 4H), 7.18 (ddd, J = 8.6, 7.5, 1.4 Hz, 1H), 5.38 (s, 2H), 3.64 (s, 9H); ¹³C{¹H} NMR (101 MHz, DMSO) δ 150.6, 135.5, 133.5, 131.9, 128.8, 128.5, 121.9, 121.4, 115.8, 71.0, 55.1. HRMS m/z (ESI) calcd for C₁₆H₂₀NO (M - OTf)⁺ 242.1539, found 242.1541.

3-(tert-Butyl)-N,N,N-trimethylbenzenaminium trifluoromethanesulfonate (2h). A black solid (1.3 g, 75%). ¹H NMR (400 MHz, DMSO) δ 7.67 – 7.50 (m, 3H), 7.35 – 7.19 (m, 1H), 5.31 (s, 2H), 3.59 (s, 9H), 3.41 (s, 3H); ¹³C{¹H} NMR (101 MHz, DMSO) δ 157.4, 148.2, 130.9, 117.0, 113.3, 109.4, 94.1, 56.3, 55.9. HRMS m/z (ESI) calcd for C₁₁H₁₈NO₂ (M - OTf)⁺ 196.1332, found 196.1332.

4-Hydroxy-N,N,N-trimethylbenzenaminium trifluoromethanesulfonate (2i). A colorless oil (0.9 g, 60%). ¹H NMR (400 MHz, DMSO) δ 10.17 (s, 1H), 7.81 – 7.70 (m, 2H), 6.99 – 6.87 (m, 2H), 3.55 (s, 9H); ¹³C{¹H} NMR (101 MHz, DMSO) δ 158.1, 138.7, 121.6, 115.81, 56.5. HRMS m/z (ESI) calcd for C₉H₁₄NO (M - OTf)⁺ 152.1070, found 152.1069.

1
2 **1-Acetyl-*N,N,N*-trimethylindolin-5-aminium trifluoromethanesulfonate (2j)**. A white solid (1.7 g, 92%). ^1H NMR (400 MHz,
3 DMSO) δ 8.10 (d, $J = 9.0$ Hz, 1H), 7.87 (s, 1H), 7.72 (dd, $J = 9.0, 2.6$ Hz, 1H), 4.17 (t, $J = 8.6$ Hz, 2H), 3.57 (s, 9H), 3.22 (t, $J = 8.5$
4 Hz, 2H), 2.18 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO) δ 169.3, 143.7, 142.0, 133.9, 119.3, 117.3, 115.4, 56.6, 48.6, 27.4, 23.8.
5
6 HRMS m/z (ESI) calcd for $\text{C}_{13}\text{H}_{19}\text{N}_2\text{O}(\text{M} - \text{OTf})^+$ 219.1492, found 219.1493.
7

8
9 **1-Acetyl-*N,N,N*-trimethylindolin-5-aminium trifluoromethanesulfonate (2k)**. A white solid (1.2 g, 65%). ^1H NMR (400 MHz,
10 DMSO) δ 9.72 (s, 1H), 7.91 – 7.78 (m, 2H), 7.62 (d, $J = 9.4$ Hz, 2H), 3.55 (s, 9H), 1.48 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO)
11 δ 152.6, 140.9, 140.7, 120.9, 118.3, 79.8, 56.4, 28.0. HRMS m/z (ESI) calcd for $\text{C}_{14}\text{H}_{23}\text{N}_2\text{O}_2(\text{M} - \text{OTf})^+$ 251.1754, found 251.1751.
12
13

14 **4-amino-*N,N,N*-trimethylbenzenaminium trifluoromethanesulfonate (2l)**. A white solid (0.5 g, 30%). ^1H NMR (400 MHz,
15 DMSO) δ 7.71 (d, $J = 9.3$ Hz, 2H), 6.84 (d, $J = 9.3$ Hz, 2H), 3.53 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO) δ 122.7, 122.2,
16 120.8, 119.0, 56.59.
17
18

19 **4-Fluoro-*N,N,N*-trimethylbenzenaminium trifluoromethanesulfonate (2m)**. A white solid (1.4 g, 94%). ^1H NMR (400 MHz,
20 DMSO) δ 8.17 – 7.92 (m, 2H), 7.50 (t, $J = 8.7$ Hz, 2H), 3.72 – 3.55 (m, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO) δ 163.1 (d, $J = 11.1$
21 Hz), 160.7, 143.3, 123.2 (d, $J = 9.0$ Hz), 116.8, 116.6, 56.6. HRMS m/z (ESI) calcd for $\text{C}_9\text{H}_{13}\text{FN}(\text{M} - \text{OTf})^+$ 154.1027, found
22 154.1031.
23
24

25 ***N,N,N*-Trimethyl-4-(methylcarbamoyl)benzenaminium trifluoromethanesulfonate (2n)** A white solid (1.1 g, 64%). ^1H NMR
26 (400 MHz, DMSO) δ 8.66 (d, $J = 4.0$ Hz, 1H), 8.17 – 7.97 (m, 4H), 3.63 (d, $J = 7.2$ Hz, 9H), 2.81 (d, $J = 4.5$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$
27 NMR (101 MHz, DMSO) δ 170.0, 154.1, 140.9, 133.9, 125.9, 61.6, 31.5. HRMS m/z (ESI) calcd for $\text{C}_{11}\text{H}_{17}\text{N}_2\text{O}(\text{M} - \text{OTf})^+$
28 193.1335, found 193.1336.
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30 **3-Carboxy-*N,N,N*-trimethylbenzenaminium trifluoromethanesulfonate (2o)**. A white solid (1.5 g, 91%). ^1H NMR (400 MHz,
31 DMSO) δ 13.64 (s, 1H), 8.41 (d, $J = 1.4$ Hz, 1H), 8.26 (dd, $J = 8.3, 2.6$ Hz, 1H), 8.12 (d, $J = 7.8$ Hz, 1H), 7.79 (t, $J = 8.1$ Hz, 1H),
32 3.65 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO) δ 166.0, 147.4, 132.6, 130.6, 125.0, 121.1, 56.3.
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35 ***N,N,N*-Trimethyldibenzo[*b,d*]furan-2-aminium trifluoromethanesulfonate (2p)**. A white solid (1.7 g, 90%). ^1H NMR (400
36 MHz, DMSO) δ 8.44 (dd, $J = 14.3, 5.5$ Hz, 2H), 8.28 (d, $J = 7.7$ Hz, 1H), 8.05 (dd, $J = 8.8, 2.4$ Hz, 1H), 7.82 (d, $J = 8.3$ Hz, 1H),
37 7.64 (dd, $J = 8.3, 7.4$ Hz, 1H), 7.50 (t, $J = 7.5$ Hz, 1H), 3.72 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO) δ 156.8, 154.9, 146.2, 128.9,
38 124.8, 123.8, 122.4, 115.6 (s), 112.0, 105.3, 56.9. HRMS m/z (ESI) calcd for $\text{C}_{15}\text{H}_{16}\text{NO}_2(\text{M} - \text{OTf})^+$ 226.1226, found 226.1229.
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41 **9-Ethyl-*N,N,N*-trimethyl-9*H*-carbazol-3-aminium trifluoromethanesulfonate (2q)**. A white solid (1.6 g, 80%). ^1H NMR (400
42 MHz, DMSO) δ 8.82 (d, $J = 2.5$ Hz, 1H), 8.32 (d, $J = 7.8$ Hz, 1H), 8.08 (dd, $J = 9.2, 2.7$ Hz, 1H), 7.86 (d, $J = 9.2$ Hz, 1H), 7.71 (d,
43 $J = 8.2$ Hz, 1H), 7.56 (t, $J = 7.7$ Hz, 1H), 7.33 (t, $J = 7.5$ Hz, 1H), 4.53 (q, $J = 6.9$ Hz, 2H), 3.75 (s, 9H), 1.33 (t, $J = 7.1$ Hz, 3H);
44 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO) δ 140.5, 139.3, 138.9, 126.9, 121.9, 120.9, 119.5, 117.6, 112.5, 110.0, 109.8, 57.0, 37.2, 13.7.
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47 HRMS m/z (ESI) calcd for $\text{C}_{17}\text{H}_{21}\text{N}_2(\text{M} - \text{OTf})^+$ 253.1699, found 253.1701.
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2 **4-((Isopentyloxy)carbonyl)-N,N,N-trimethylbenzenaminium trifluoromethanesulfonate (2r)**. A white solid (1.5 g, 75%). ¹H
3 NMR (400 MHz, DMSO) δ 8.20 – 8.09 (m, 4H), 4.36 (t, *J* = 6.6 Hz, 2H), 3.35 (s, 9H), 1.81 – 1.68 (m, 1H), 1.63 (q, *J* = 6.7 Hz, 2H),
4 0.94 (d, *J* = 6.6 Hz, 6H); ¹³C{¹H} NMR (101 MHz, DMSO) δ 164.3, 150.4 131.3, 130.7, 121.3, 63.8, 56.3, 36.7, 24.7, 22.3. HRMS
5 m/z (ESI) calcd for C₁₅H₂₄NO₂ (M - OTf)⁺ 250.1802, found 250.1805.
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9 **N-(3-((Dimethylcarbamoyl)oxy)phenyl)-N,N-dimethylmethanideaminium trifluoromethanesulfonate salt (2s)**. A white solid
10 (1.2 g, 65%). ¹H NMR (400 MHz, DMSO) δ 7.90 – 7.77 (m, 2H), 7.65 (t, *J* = 8.3 Hz, 1H), 7.38 (dd, *J* = 8.1, 1.5 Hz, 1H), 3.60 (s,
11 9H), 3.09 (d, *J* = 10.2 Hz, 3H), 2.94 (s, 3H); ¹³C{¹H} NMR (101 MHz, DMSO) δ 153.4, 151.9, 147.7, 130.5, 124.0, 117.1, 115.0,
12 56.4, 36.3, 36.1. HRMS m/z (ESI) calcd for C₁₂H₁₉N₂O₂ (M - OTf)⁺ 223.1441, found 223.1443.
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16 **(E)-N,N-Dimethyl-N-(4-(phenyldiazenyl)phenyl)methanideaminium, trifluoromethanesulfonate salt (2t)**. A yellow solid (0.9 g,
17 46%). ¹H NMR (400 MHz, DMSO) δ 8.22 (d, *J* = 9.1 Hz, 2H), 8.10 (d, *J* = 8.7 Hz, 2H), 7.96 (dd, *J* = 6.3, 2.8 Hz, 2H), 7.65 (d, *J* =
18 4.6 Hz, 3H), 3.69 (s, 9H); ¹³C{¹H} NMR (101 MHz, DMSO) δ 151.9, 151.7, 148.6, 132.4, 129.6, 123.6, 122.9, 122.1, 56.5. HRMS
19 m/z (ESI) calcd for C₁₅H₁₈N₃ (M - OTf)⁺ 240.1495, found 240.1497.
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23 **4,4'-Methylenebis(N,N,N-trimethylbenzenaminium) trifluoromethanesulfonate (2u)**. A white solid (2.7 g, 93%). ¹H NMR (400
24 MHz, DMSO) δ 7.88 (d, *J* = 8.3 Hz, 4H), 7.55 (d, *J* = 8.4 Hz, 4H), 4.10 (s, 2H), 3.56 (s, 18H); ¹³C{¹H} NMR (101 MHz, DMSO) δ
25 150.7, 148.0, 135.3, 125.8, 61.6.
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29 **4,4'-Oxybis(N,N,N-trimethylbenzenaminium) trifluoromethanesulfonate (2v)**. A white solid (2.6 g, 89%). ¹H NMR (400 MHz,
30 DMSO) δ 8.03 (d, *J* = 9.3 Hz, 4H), 7.30 (d, *J* = 9.3 Hz, 4H), 3.63 (s, 18H); ¹³C{¹H} NMR (101 MHz, DMSO) δ 156.5, 142.9, 122.8,
31 119.7, 56.6.
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35 **4,4'-(Phenylmethylene)bis(N,N,N-trimethylbenzenaminium) trifluoromethanesulfonate (2w)**. A white solid (1.7 g, 52%). ¹H
36 NMR (400 MHz, DMSO) δ 7.92 (dd, *J* = 9.0, 2.0 Hz, 4H), 7.46 – 7.32 (m, 6H), 7.28 (t, *J* = 7.3 Hz, 1H), 7.15 (d, *J* = 7.2 Hz, 2H),
37 5.90 (s, 1H), 3.59 (d, *J* = 2.3 Hz, 18H); ¹³C{¹H} NMR (101 MHz, DMSO) δ 150.8, 150.2, 147.3, 135.6, 134.0, 132.1, 125.9, 61.6,
38 59.2.
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42 **4,4'-(9H-Fluorene-9,9-diyl)bis(N,N,N-trimethylbenzenaminium) trifluoromethanesulfonate (2x)**. A white solid (1.8 g, 49%).
43 ¹H NMR (400 MHz, DMSO) δ 8.01 (d, *J* = 7.5 Hz, 2H), 7.87 (d, *J* = 9.2 Hz, 4H), 7.54 – 7.44 (m, 4H), 7.37 (td, *J* = 7.5, 1.0 Hz, 2H),
44 7.31 (d, *J* = 9.1 Hz, 4H), 3.56 (s, 18H); ¹³C{¹H} NMR (101 MHz, DMSO) δ 148.9, 146.7, 145.9, 128.9, 128.6, 128.5, 125.9, 121.0,
45 120.8, 63.9, 56.3.
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49 **1-(Benzo[d][1,3]dioxol-5-yl)-N,N,N-trimethylmethanaminium trifluoromethanesulfonate (6f)**. A white solid (0.9 g, 52%): ¹H
50 NMR (400 MHz, DMSO) δ 7.10 (d, *J* = 1.3 Hz, 1H), 7.08 – 6.98 (m, 2H), 6.10 (s, 2H), 4.41 (s, 2H), 3.00 (s, 9H); ¹³C{¹H} NMR
51 (101 MHz, DMSO) δ 148.83, 147.5, 127.2, 121.6, 112.4, 108.5, 101.6, 67.8, 51.6. HRMS m/z (ESI) calcd for C₁₁H₁₆NO₂ (M -
52 OTf)⁺ 194.1176, found 194.1177.
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2 **1-(2,4-Difluorophenyl)-N,N,N-trimethylmethanaminium trifluoromethanesulfonate (6g).** A white solid (1.1 g, 65%). ^1H NMR
3 (400 MHz, DMSO) δ 7.68 (td, $J = 8.6, 6.6$ Hz, 1H), 7.47 (td, $J = 10.6, 2.5$ Hz, 1H), 7.29 (td, $J = 8.4, 2.2$ Hz, 1H), 4.57 (s, 2H), 3.07
4 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO) δ 165.1 (d, $J = 12.7$ Hz), 162.6 (d, $J = 12.7$ Hz), 136.6 (dd, $J = 10.5, 4.4$ Hz), 119.0,
5 112.72 – 112.0 (m), 105.1, 104.8, 104.6, 60.9, 51.8. HRMS m/z (ESI) calcd for $\text{C}_{10}\text{H}_{14}\text{F}_2\text{N}$ (M - OTf) $^+$ 186.1089, found 186.1089.
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9 **N,N,N-Trimethyl-1,2,3,4-tetrahydronaphthalen-1-aminium trifluoromethanesulfonate (6n).** A white solid (1.0 g, 59%). ^1H
10 NMR (400 MHz, DMSO) δ 7.49 (d, $J = 7.6$ Hz, 1H), 7.43 (t, $J = 7.5$ Hz, 1H), 7.32 (t, $J = 7.5$ Hz, 2H), 4.90 (dd, $J = 7.1, 3.2$ Hz, 1H),
11 2.99 (s, 9H), 2.76 (dd, $J = 8.5, 5.5$ Hz, 2H), 2.41 (s, 1H), 2.23 – 2.11 (m, 1H), 2.11 – 1.96 (m, 1H), 1.47 (dd, $J = 13.3, 6.9$ Hz, 1H);
12 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO) δ 142.7, 133.5, 130.0, 129.5, 126.9, 125.9, 71.7, 50.6, 27.9, 22.8, 21.0.
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15 **N,N,N-Trimethyl-1-phenyl-2-(p-tolyl)ethan-1-aminium trifluoromethanesulfonate (6o).** A white solid (1.2 g, 60%). ^1H NMR
16 (400 MHz, DMSO) δ 7.90 (s, 1H), 7.60 – 7.17 (m, 4H), 7.06 – 6.89 (m, 4H), 4.90 (dd, $J = 12.3, 3.1$ Hz, 1H), 3.70 – 3.57 (m, 1H),
17 3.49 (t, $J = 12.8$ Hz, 1H), 3.10 (s, 9H), 2.15 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO) δ 135.5, 132.8, 131.0, 130.1, 129.1, 128.8,
18 77.9, 51.0, 32.2, 20.4.
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21 **3-Methoxy-N,N,N-trimethyl-3-oxo-1-phenylpropan-1-aminium trifluoromethanesulfonate (6p).** A white solid (1.2 g, 65%). ^1H NMR
22 (400 MHz, DMSO) δ 7.65 (s, 2H), 7.56 – 7.46 (m, 3H), 5.04 (dd, $J = 11.1, 4.0$ Hz, 1H), 3.64 – 3.49 (m, 2H), 3.47 (s, 3H),
23 3.02 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO) δ 169.2, 131.4, 130.4, 128.9, 72.8, 51.9, 51.0, 33.2. HRMS m/z (ESI) calcd for
24 $\text{C}_{13}\text{H}_{20}\text{NO}_2$ (M - OTf) $^+$ 222.1489, found 222.1493.
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27 **N,N,N-Trimethyl-2-phenylpropan-2-aminium trifluoromethanesulfonate (6q).** A white solid (0.9 g, 55%). ^1H NMR (400 MHz,
28 DMSO) δ 7.85 – 7.72 (m, 2H), 7.57 – 7.46 (m, 3H), 2.94 (s, 9H), 1.90 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO) δ 135.4, 129.6,
29 128.4, 74.4, 49.2, 22.5. HRMS m/z (ESI) calcd for $\text{C}_{12}\text{H}_{20}\text{N}$ (M - OTf) $^+$ 178.1590, found 178.1589.
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32 **N,N,N-Trimethyl-2-phenylbutan-2-aminium trifluoromethanesulfonate (6r).** A white solid (0.7 g, 43%). ^1H NMR (400 MHz,
33 DMSO) δ 7.60 (d, $J = 6.5$ Hz, 2H), 7.49 (d, $J = 7.2$ Hz, 3H), 3.03 (s, 9H), 2.76 (dd, $J = 12.9, 6.8$ Hz, 1H), 2.26 – 2.06 (m, 1H), 1.95
34 (s, 3H), 0.84 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO) δ 131.4, 130.1, 129.9, 128.8, 79.6, 49.3, 25.5, 19.3, 9.7. HRMS
35 m/z (ESI) calcd for $\text{C}_{12}\text{H}_{18}\text{N}$ (M - OTf) $^+$ 176.1434, found 176.1435.
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38 **N,N,N-Trimethyl-1-phenylcyclopropan-1-aminium trifluoromethanesulfonate (6t).** A white solid (0.7 g, 40%). ^1H NMR (400
39 MHz, DMSO) δ 7.73 – 7.63 (m, 2H), 7.49 (d, $J = 5.8$ Hz, 3H), 3.02 (s, 9H), 2.04 – 1.88 (m, 2H), 1.18 – 1.05 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$
40 NMR (101 MHz, DMSO) δ 133.9, 133.4, 130.1, 128.6, 58.9, 51.5, 10.1. HRMS m/z (ESI) calcd for $\text{C}_{14}\text{H}_{22}\text{N}$ (M - OTf) $^+$ 204.1747,
41 found 204.1748.
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44 **3-(N-(2,5-dimethoxybenzyl)acetamido)-N,N,N-trimethyl-4-phenoxybenzenaminium (9).** To a solution of N^i,N^i -dimethyl-4-
45 phenoxybenzene-1,3-diamine (16.6 mmol, 1.0 eq.) and Et_3N (2.8 mL, 19.9 mmol, 1.2 eq.) in DCM (20mL) was added acetyl chlo-
46 ride (3.0 mL, 19.9 mmol, 1.2 eq.) in a dropwise manner under 0 °C, and the mixture was stirred at room temperature for 3 h. After
47 the reaction mixture was concentrated under reduced pressure, the residue was quenched with AcOEt and washed with saturated
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NaCl solution. After the organic layer was dried over Na_2SO_4 , the solvent was removed to give a residue. To a solution of the residue (16.6 mmol, 1.0 eq.) in DMF (20 mL) was added NaH (60% dispersion in mineral oil, 0.80 g, 20 mmol), and the mixture was stirred for 1h at room temperature. To the mixture was added 2-(chloromethyl)-1,4-dimethoxybenzene and stirred for 5h at room temperature. The mixture was poured into ice water and extracted with AcOEt three times. The combined organic layer was washed with saturated NaCl solution. After the organic layer was dried over Na_2SO_4 , the solvent was removed to give a residue. This residue (16.6 mmol, 1.0 eq.) was dissolved in $\text{Et}_2\text{O}/\text{DCM}$ (30/5 mL). MeOTf (2.4 mL, 21.6 mmol, 1.3 equiv) was added dropwise at 0 °C. After complete addition the reaction mixture was stirred for an additional 30 minutes at 0 °C. The solution was concentrated and washed with Et_2O (2 x 20 mL). The resulting compounds purified by column chromatography on silica gel (DCM: MeOH = 20 : 1). to give **9** (6.9 g, 71%) as white solid: ^1H NMR (400 MHz, DMSO) δ 7.99 (d, J = 3.2 Hz, 1H), 7.79 (dd, J = 9.3, 2.4 Hz, 1H), 7.45 (t, J = 8.0 Hz, 2H), 7.26 (t, J = 7.4 Hz, 1H), 6.98 – 6.88 (m, 4H), 6.79 (dd, J = 10.9, 5.8 Hz, 2H), 4.84 (s, 2H), 3.59 (s, 3H), 3.53 (s, 9H), 3.50 (s, 3H), 1.91 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO) δ 169.4, 155.4, 154.2, 152.9, 151.2, 141.4, 132.8, 130.4, 125.6, 125.1, 123.7, 121.2, 119.5, 119.5, 117.0, 116.6, 112.1, 56.5, 55.7, 55.3, 45.6, 22.1.

1,1-Dimethylindolin-1-ium trifluoromethanesulfonate (12a). A white solid (0.8 g, 54%). ^1H NMR (400 MHz, DMSO) δ 7.84 (dd, J = 7.7, 4.2 Hz, 1H), 7.60 – 7.49 (m, 3H), 4.16 (t, J = 7.2 Hz, 2H), 3.49 (s, 9H), 3.38 (t, J = 7.2 Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO) δ 133.7, 130.7, 128.8, 126.5, 117.3, 67.4, 54.0, 26.6. HRMS m/z (ESI) calcd for $\text{C}_{10}\text{H}_{14}\text{N}$ (M - OTf) $^+$ 148.1121, found 148.1120.

1,1-Dimethyl-1,2,3,4-tetrahydroquinolin-1-ium trifluoromethanesulfonate (12b). A white solid (0.9 g, 58%). ^1H NMR (400 MHz, DMSO) δ 8.03 – 7.93 (m, 1H), 7.50 – 7.41 (m, 2H), 7.38 (dd, J = 5.9, 3.4 Hz, 1H), 4.01 – 3.80 (m, 2H), 3.58 (s, 6H), 2.94 (t, J = 5.9 Hz, 2H), 2.29 – 2.16 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO) δ 142.8, 131.0, 130.7, 129.6, 128.0, 121.3, 63.7, 56.7, 25.4, 16.8. HRMS m/z (ESI) calcd for $\text{C}_{11}\text{H}_{16}\text{N}$ (M - OTf) $^+$ 162.1277, found 162.1277.

1-Cyclopropyl-*N,N,N*-trimethyl-1-phenylmethanaminium trifluoromethanesulfonate (14). A white solid (0.6 g, 35%). ^1H NMR (400 MHz, DMSO) δ 7.55 (s, 2H), 7.52 – 7.48 (m, 3H), 3.94 (d, J = 10.8 Hz, 1H), 3.04 (s, 9H), 1.97 – 1.78 (m, 1H), 1.08 – 0.94 (m, 1H), 0.83 (td, J = 10.6, 5.0 Hz, 1H), 0.66 – 0.51 (m, 1H), -0.08 (qd, J = 9.6, 4.8 Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO) δ 133.1, 129.8, 128.7, 80.8, 51.0, 10.0, 3.3. HRMS m/z (ESI) calcd for $\text{C}_{13}\text{H}_{20}\text{N}$ (M - OTf) $^+$ 190.1590, found 190.1591.

General Procedure for Cleavage of the C-N Bonds.

The 25 mL Schlenk tube was added 4-methoxy-*N,N,N*-trimethyl -benzenaminium trifluoromethanesulfonate **1a** (63.6 mg, 0.2 mmol), bis(pinacolato)diboron (127.0 mg, 0.5 mmol), $\text{Ni}(\text{COD})_2$ (3.3 mg, 6 mol %), $\text{ICy}\cdot\text{HCl}$ (6.5 mg, 12 mol %), KOtBu (44.9 mg, 200 mol%), toluene (0.5 mL) and 2-ethoxyethano (0.5 mL) under argon. The formed mixture was stirred at 50 °C under Ar for 24 h as monitored by TLC. The solution was then cooled to room temperature, and the solvent was removed under vacuum directly. The crude product was purified by column chromatography on silica gel (Ethyl acetate: Petroleum ether = 1 : 100).

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2 **2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4aa)**²⁷. A colorless oil (44.0 mg, 94%). ¹H NMR (400 MHz,
3 CDCl₃) δ 7.75 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 3.83 (s, 3H), 1.33 (s, 12H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 136.5,
4 113.3, 83.54, 55.1, 24.9; ATR-FTIR (cm⁻¹): 2965, 2931, 1513, 1466, 1367, 1122, 1051, 884, 807, 746; GC-MS (EI) Calcd. for
5 C₁₃H₁₉BO₃ [M] 234.14, found 234.21.
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9 **4,4,5,5-Tetramethyl-2-phenyl-1,3,2-dioxaborolane (4ba)**²⁷. A colorless oil (28.9 mg, 71%). ¹H NMR (400 MHz, CDCl₃) δ 7.81
10 (dd, *J* = 7.9, 1.2 Hz, 2H), 7.48 – 7.44 (m, 1H), 7.39 – 7.35 (m, 2H), 1.35 (s, 12H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 134.7, 131.2,
11 127.7, 83.8, 24.9; ATR-FTIR (cm⁻¹): 2979, 2926, 2855, 2363, 1605, 1359, 1145, 1092, 1026, 963, 858, 700, 656; GC-MS (EI)
12 Calcd. for C₁₂H₁₇BO₂ [M] 204.13, found 204.20.
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15 **4,4,5,5-Tetramethyl-2-(*o*-tolyl)-1,3,2-dioxaborolane (4ca)**²⁸. A colorless oil (39.2 mg, 90 %). ¹H NMR (400 MHz, CDCl₃) δ 7.80
16 – 7.77 (m, 1H), 7.36 – 7.31 (m, 1H), 7.20 – 7.16 (m, 2H), 2.56 (s, 3H), 1.36 (s, 12H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 144.8,
17 135.8, 130.8, 129.7, 124.7, 83.4, 24.9, 22.2; ATR-FTIR (cm⁻¹): 2979, 2927, 1601, 1442, 1379, 1348, 1312, 1269, 1146, 1042, 861,
18 761, 730, 662; GC-MS (EI) Calcd. for C₁₃H₁₉BO₂ [M] 218.15, found 218.16.
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23 **2-(3,4-Dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4da)**²⁹. A colorless oil (30.1 mg, 82%). ¹H NMR (400 MHz,
24 CDCl₃) δ 7.60 (s, 1H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 1H), 2.29 (s, 3H), 2.28 (s, 3H), 1.35 (s, 12H); ¹³C{¹H} NMR
25 (101 MHz, CDCl₃) δ 140.1, 135.9, 132.4, 129.1, 83.6, 24.8, 20.0, 19.4; ATR-FTIR (cm⁻¹): 2965, 2933, 2872, 1513, 1466, 1384,
26 1364, 1262, 1125, 1052, 886, 812, 739; GC-MS (EI) Calcd. for C₁₄H₂₁BO₂ [M] 232.16, found 232.22.
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29 **2-Mesityl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ea)**²⁸. A colorless oil (40.1 mg (81%)). ¹H NMR (400 MHz, CDCl₃) δ 6.79
30 (s, 2H), 2.39 (s, 6H), 2.26 (s, 3H), 1.39 (s, 13H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 142.2, 138.9, 127.5, 83.5, 25.0, 22.2, 21.3;
31 ATR-FTIR (cm⁻¹): 2978, 2924, 1610, 1439, 1371, 1333, 1300, 1145, 1067, 855, 672; HRMS *m/z* (ESI) calcd for C₁₅H₂₄BO₂ (M +
32 H)⁺ 247.1864, found 247.1867.
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39 **2-(3-(*Tert*-butyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4fa)**³⁰. A white solid (37.7 mg, 73%): ¹H NMR (400 MHz,
40 CDCl₃) δ 7.86 (s, 1H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.52 (ddd, *J* = 7.9, 2.0, 1.3 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 1.36 (s, 21H); ¹³C{¹H}
41 NMR (101 MHz, CDCl₃) δ 150.2, 132.0, 131.4, 128.4, 127.5, 83.6, 34.6, 31.4, 24.9; ATR-FTIR (cm⁻¹): 3065, 2975, 2930, 1607,
42 1398, 1364, 1323, 1266, 1144, 1090, 859, 744, 660; GC-MS (EI) calcd for C₁₆H₂₅BO₂ [M] 260.19, found 260.30.
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47 **2-(2-(*Benzyloxy*)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ga)**. A white solid (34.3 mg, 55%). ¹H NMR (400 MHz,
48 CDCl₃) δ 7.72 (dd, *J* = 7.3, 1.7 Hz, 1H), 7.63 (d, *J* = 7.3 Hz, 2H), 7.44 – 7.35 (m, 3H), 7.31 (d, *J* = 7.2 Hz, 1H), 7.04 – 6.91 (m, 2H),
49 5.14 (s, 2H), 1.38 (s, 13H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 163.2, 137.6, 136.7, 132.5, 128.1, 127.3, 126.7, 120.6, 112.0, 83.4,
50 69.9, 24.9; ATR-FTIR (cm⁻¹): 2977, 2925, 2888, 2853, 1598, 1443, 1355, 1320, 1141, 1072, 861, 761, 744, 656; HRMS *m/z* (ESI)
51 calcd for C₁₉H₂₄BO₃ (M + H)⁺ 311.1813, found 311.1821.
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56 **2-(3-(*Methoxymethoxy*)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ha)**. A white solid (42.3 mg, 80%): ¹H NMR (300
57 MHz, CDCl₃) δ 7.50 – 7.42 (m, 2H), 7.34 – 7.27 (m, 1H), 7.13 (ddd, *J* = 8.2, 2.6, 1.2 Hz, 1H), 5.20 (s, 2H), 3.48 (s, 3H), 1.34 (s,
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12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 156.6, 128.9, 128.3, 121.8, 119.5, 94.3, 83.8, 55.9, 24.9; ATR-FTIR (cm^{-1}): 2979, 1577, 1431, 1354, 1317, 1148, 1077, 1016, 707; HRMS m/z (ESI) calcd for $\text{C}_{14}\text{H}_{22}\text{BO}_4$ ($\text{M} + \text{H}$) $^+$ 265.1606, found 265.1607.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (4ia)³¹. A white solid (21.4 mg, 48 %): ^1H NMR (400 MHz, CDCl_3) δ 7.70 (d, $J = 8.5$ Hz, 2H), 6.86 – 6.78 (m, 2H), 5.43 (s, 1H), 1.33 (s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 158.4, 136.8, 114.8, 83.7, 24.8; ATR-FTIR (cm^{-1}): 3175, 2978, 2925, 2854, 1657, 1607, 1358, 1268, 1142, 1087, 838, 655; GC-MS (EI) calcd for $\text{C}_{12}\text{H}_{17}\text{BO}_3$ [M] 220.13, found 220.22.

1-(5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)indolin-1-yl)ethan-1-one (4ja)³². A white solid (48.0 mg, 84 %): ^1H NMR (400 MHz, CDCl_3) δ 8.18 (d, $J = 8.1$ Hz, 1H), 7.66 (d, $J = 8.1$ Hz, 1H), 7.62 (s, 1H), 4.04 (t, $J = 8.5$ Hz, 2H), 3.17 (t, $J = 8.5$ Hz, 2H), 2.22 (s, 3H), 1.33 (s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 168.9, 145.4, 134.9, 130.6, 130.3, 116.2, 83.6, 48.9, 27.6, 24.9, 24.6; ATR-FTIR (cm^{-1}): 2973, 2926, 1657, 1605, 1438, 1355, 1151, 907, 735, 668; HRMS m/z (ESI) calcd for $\text{C}_{16}\text{H}_{23}\text{BNO}_3$ ($\text{M} + \text{H}$) $^+$ 288.1766, found 288.1768.

***t*-Butyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)carbamate (4ka)**²⁷. A white solid (54.2 mg, 85 %): ^1H NMR (400 MHz, CDCl_3) δ 7.77 – 7.68 (m, 2H), 7.36 (d, $J = 8.4$ Hz, 2H), 6.67 (s, 1H), 1.50 (s, 9H), 1.32 (s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 152.5, 141.1, 135.8, 117.2, 83.7, 28.3, 24.9; ATR-FTIR (cm^{-1}): 3333, 2978, 2931, 1732, 1609, 1587, 1529, 1506, 1398, 1362, 1317, 1231, 1145, 1091, 837, 656. HRMS m/z (ESI) calcd for $\text{C}_{17}\text{H}_{26}\text{BNO}_4\text{Na}$ ($\text{M} + \text{Na}$) $^+$ 342.1847, found 342.1853.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (4la)³¹. A white solid (26.8 mg, 62 %). ^1H NMR (400 MHz, CDCl_3) δ 7.62 (d, $J = 8.4$ Hz, 2H), 6.66 (d, $J = 8.4$ Hz, 2H), 1.32 (s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 149.3, 136.4, 114.1, 83.3, 24.8; ATR-FTIR (cm^{-1}): 2973, 2922, 1604, 1357, 1317, 1270, 1141, 1092, 858, 815, 738, 656. HRMS m/z (ESI) calcd for $\text{C}_{12}\text{H}_{18}\text{BNO}_2\text{Na}$ ($\text{M} + \text{Na}$) $^+$ 242.1323, found 242.1329.

2-(4-Fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ma)²⁷. A colorless oil (22.6 mg, 51 %). ^1H NMR (400 MHz, CDCl_3) δ 7.79 (dd, $J = 8.5, 6.3$ Hz, 2H), 7.10 – 6.99 (m, 2H), 1.34 (s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 166.3, 163.8, 137.0, 114.9, 114.7, 83.9, 24.8; ATR-FTIR (cm^{-1}): 2976, 2923, 2853, 2364, 1633, 1365, 1145, 802, 523; GC-MS (EI) calcd for $\text{C}_{12}\text{H}_{16}\text{BFO}_2$ [M] 222.12, found 222.16.

***N*-Methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (4na)**. A white solid (33.2 mg, 63 %). ^1H NMR (400 MHz, CDCl_3) δ 7.85 (d, $J = 8.2$ Hz, 2H), 7.74 (d, $J = 8.2$ Hz, 2H), 6.22 (s, 1H), 3.01 (d, $J = 4.9$ Hz, 3H), 1.35 (s, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 168.1, 136.8, 134.9, 125.9, 84.1, 26.8, 24.9; ATR-FTIR (cm^{-1}): 2978, 2929, 2363, 1644, 1550, 1397, 1361, 1326, 1144, 1098, 857, 658; HRMS m/z (ESI) calcd for $\text{C}_{14}\text{H}_{21}\text{BNO}_3$ ($\text{M} + \text{H}$) $^+$ 262.1609, found 262.1617.

3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic acid (4oa). A white solid (26.3 mg, 53 %). ^1H NMR (400 MHz, CDCl_3) δ 8.57 (s, 1H), 8.20 (dd, $J = 6.4, 1.4$ Hz, 1H), 8.04 (d, $J = 7.4$ Hz, 1H), 7.49 (t, $J = 7.6$ Hz, 1H), 1.37 (s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101

MHz, CDCl₃) δ 171.8, 140.0, 136.6, 132.8, 128.7, 127.9, 84.2, 24.9; ATR-FTIR (cm⁻¹): 2978, 2638, 2361, 1682, 1605, 1406, 1387, 1357, 1326, 1292, 1077, 961, 848, 761; HRMS m/z (ESI) calcd for C₁₃H₁₇BO₄Na (M + Na)⁺ 271.1112, found 271.1120.

2-(Dibenzo[b,d]furan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4pa). A white solid (50.3 mg, 85%). ¹H NMR (400 MHz, CDCl₃) δ 8.03 (s, 1H), 7.97 (dd, *J* = 7.6, 3.4 Hz, 2H), 7.81 (d, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.52 – 7.44 (m, 1H), 7.39 – 7.31 (m, 1H), 1.40 (s, 12H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 156.6, 155.9, 128.9, 127.7, 126.8, 124.1, 122.6, 121.0, 120.0, 117.6, 111.8, 84.0, 25.0; ATR-FTIR (cm⁻¹): 2978, 2926, 1633, 1501, 1355, 1326, 1189, 1067, 964, 910, 827, 795, 727, 686; HRMS m/z (ESI) calcd for C₁₈H₂₀BO₃ (M + H)⁺ 295.1500, found 295.1506.

9-Ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (4qa). A white solid (60.4 mg, 93%). ¹H NMR (400 MHz, CDCl₃) δ 8.62 (s, 1H), 8.14 (d, *J* = 7.7 Hz, 1H), 7.94 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.49 – 7.42 (m, 1H), 7.38 (dd, *J* = 8.2, 4.8 Hz, 2H), 7.27 – 7.20 (m, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 1.42 – 1.36 (m, 15H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 142.0, 140.0, 132.1, 127.8, 125.58, 123.1, 122.6, 120.6, 119.2, 108.4, 107.8, 83.5, 37.5, 24.9, 13.7; ATR-FTIR (cm⁻¹): 2977, 2931, 1595, 1476, 1429, 1351, 1326, 1301, 1264, 1231, 1143, 1231, 1077, 962, 810, 748, 627; HRMS m/z (ESI) calcd for C₂₀H₂₅BNO₂ (M + H)⁺ 322.1973, found 322.1979.

Isopentyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (4ra). A colorless oil (41.7 mg, 66%). ¹H NMR (400 MHz, CDCl₃) δ 8.04 – 7.97 (m, 2H), 7.86 (d, *J* = 8.3 Hz, 2H), 4.35 (t, *J* = 6.8 Hz, 2H), 1.85 – 1.73 (m, 1H), 1.68 (t, *J* = 6.8 Hz, 2H), 1.35 (s, 12H), 0.98 (s, 3H), 0.96 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 166.7, 134.6, 132.7, 128.5, 84.1, 63.7, 37.4, 25.2, 24.8, 22.5; ATR-FTIR (cm⁻¹): 2960, 1722, 1399, 1362, 1269, 1145, 1113, 858, 710, 651; HRMS m/z (ESI) calcd for C₁₈H₂₈BO₄(M + H)⁺ 319.2075, found 319.2080.

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl dimethylcarbamate (4sa)³³. A white solid (23.4 mg, 42%). ¹H NMR (400 MHz, CDCl₃) δ 7.65 – 7.59 (m, 1H), 7.53 (d, *J* = 1.9 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.21 (ddd, *J* = 8.1, 2.5, 1.1 Hz, 1H), 3.08 (s, 3H), 3.00 (s, 3H), 1.33 (s, 12H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 155.0, 151.1, 131.5, 128.7, 127.7, 124.8, 83.9, 36.7, 36.4, 24.8; ATR-FTIR (cm⁻¹): 2927, 1724, 1611, 1499, 1442, 1385, 1353, 1206, 1168, 849; HRMS m/z (ESI) calcd for C₁₅H₂₃BNO₄ (M + H)⁺ 292.1715, found 292.1718.

1-Phenyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)diazene (4ta)³¹. A yellow solid (24.6 mg, 40%). ¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, *J* = 8.5 Hz, 2H), 7.24 – 7.17 (m, 2H), 6.88 – 6.78 (m, 5H), 1.32 (s, 12H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 151.5, 148.5, 136.4, 129.4, 120.1, 112.4, 111.3, 83.4, 24.9; ATR-FTIR (cm⁻¹): 2977, 2925, 2261, 1604, 1395, 1358, 1271, 1143, 1087, 856, 766, 689, 654; HRMS m/z (ESI) calcd for C₁₈H₂₂BN₂O₂ (M + H)⁺ 309.1769, found 309.1777.

Bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methane (4ua)³⁴. A white solid (60.1 mg, 72%). ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 4.02 (s, 1H), 1.34 (s, 12H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 144.1,

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2 135.0, 128.4, 83.6, 42.3, 24.8; ATR-FTIR (cm⁻¹): 2979, 2927, 1608, 1515, 1464, 1399, 1360, 1322, 1269, 1143, 1089, 1019, 963,
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4 858, 736, 660; GC-MS (EI) calcd for C₂₅H₃₄B₂O₄ [M] 420.26, found 420.40.

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6 **2,2'-(Oxybis(4,1-phenylene))bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4va)**. A white solid (70.3 mg, 83%). ¹H NMR (400
7 MHz, CDCl₃) δ 7.84 – 7.75 (m, 4H), 7.05 – 6.96 (m, 4H), 1.34 (s, 24H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 159.5, 136.6, 118.2,
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9 83.8, 24.8; ATR-FTIR (cm⁻¹): 2898, 2922, 1638, 1478, 1367, 1343, 1138, 1278, 1015, 947; HRMS m/z (ESI) calcd for C₂₄H₃₃B₂O₅
10 (M + H)⁺ C₂₅H₃₄B₂O₄ [M] 423.2509, found 423.2513.

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13 **2,2'-((Phenylmethylene)bis(4,1-phenylene))bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4wa)**. A white solid (94.2 mg, 95%).
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15 ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 8.0 Hz, 4H), 7.93 (dd, *J* = 5.9, 1.5 Hz, 1H), 7.27-7.07 (m, 9H), 5.56 (s, 1H), 1.32 (s, 1H);
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17 ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 146.9, 143.4, 134.8, 129.4, 128.9, 128.3, 126.3, 83.6, 57.1, 24.8; ATR-FTIR (cm⁻¹): 2978, 2362,
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19 1608, 1399, 1361, 1323, 1271, 1144, 1089, 1021, 962, 858, 701. HRMS m/z (ESI) calcd for C₃₁H₃₀B₂O₄ (M + H)⁺ 497.3029, found
20 497.3035.

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23 **2,2'-((9H-Fluorene-9,9-diyl)bis(4,1-phenylene))bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4xa)**. A white solid (107.2 mg,
24 94%). ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, *J* = 7.5 Hz, 1H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.34 (dd, *J* = 13.1, 7.5 Hz, 2H), 7.22 (ddd, *J*
25 = 16.8, 9.2, 4.5 Hz, 3H), 1.29 (s, 12H); ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 150.7, 149.0, 140.2, 134.7, 127.8, 127.5, 126.1, 120.1,
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27 83.66, 65.9, 24.8; ATR-FTIR (cm⁻¹): 2977, 2930, 1607, 1515, 1447, 1361, 1269, 1214, 1144, 1090, 1018, 982, 962, 919, 856, 819,
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29 746, 660, 520, 443. HRMS m/z (ESI) calcd for C₃₇H₄₂B₂O₄ (M + H)⁺ 571.3185, found 571.3188.

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32 **2-(4-Methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (4ab)**³⁵. A white solid (32.3 mg, 73%). ¹H NMR (400 MHz, CDCl₃) δ
33 7.81 – 7.70 (m, 2H), 6.94 – 6.86 (m, 2H), 3.83 (s, 3H), 3.76 (s, 4H), 1.02 (s, 6H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 161.7, 135.5,
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35 113.1, 72.2, 55.0, 31.9, 21.9; ATR-FTIR (cm⁻¹): 2961, 2838, 1603, 1478, 1420, 1318, 1247, 1176, 1134, 1105, 1031, 834, 647;
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37 HRMS m/z (ESI) calcd for C₁₂H₁₈BO₃ (M + H)⁺ 221.1344, found 221.1338.

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40 **2-(4-Methoxyphenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane (4ac)**³⁶. A colorless oil (43.1 mg, 92%). ¹H NMR (400 MHz, CDCl₃)
41 δ 7.77 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 4.33 (dq, *J* = 12.3, 6.2, 3.0 Hz, 1H), 3.82 (s, 3H), 1.85 (dd, *J* = 13.9, 2.9 Hz,
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43 1H), 1.60 (dd, *J* = 15.0, 3.2 Hz, 1H), 1.36 (dd, *J* = 9.7, 5.6 Hz, 9H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 161.5, 135.4, 113.0, 70.8,
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45 64.8, 55.0, 46.0, 31.3, 28.1, 23.2; ATR-FTIR (cm⁻¹): 2974, 2935, 1603, 1511, 1411, 1384, 1359, 1330, 1305, 1245, 1208, 1168,
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47 1107, 1032, 834, 805, 768, 649; HRMS m/z (ESI) calcd for C₁₃H₂₀BO₃ (M + H)⁺ 235.1500, found 235.1500.

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49 **2-Benzyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7aa)**³⁷. The reaction of **6a** (59.8 mg, 0.20 mmol), (Bpin)₂ (127.0 mg, 0.50
50 mmol), Ni(COD)₂ (3.3 mg, 6 mol %), ICy HCl (6.5 mg, 12 mol %) and NaO^tBu (38.4 mg, 200 mol%) in toluene/2-ethoxyethano
51 (0.5/0.5 mL) at 50 °C under Ar after column chromatography on silica (Ethyl acetate: Petroleum ether = 1 : 100) to afford 33.1 mg
52 (76%) of **7aa** as colorless oil: ¹H NMR (400 MHz, CDCl₃) δ 7.23 (dd, *J* = 9.9, 4.7 Hz, 2H), 7.18 (d, *J* = 6.7 Hz, 2H), 7.11 (t, *J* = 7.1
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54 Hz, 1H), 2.29 (s, 2H), 1.23 (s, 12H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 138.7, 129.0, 128.3, 124.8, 83.4, 24.7; ATR-FTIR (cm⁻¹):
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56 2966, 2934, 1494, 1466, 1452, 1385, 1367, 1120, 1051, 882, 727, 700; GC-MS (EI) calcd for C₁₃H₁₉BO₂ [M] 218.15, found 218.15.
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2 *4,4,5,5-Tetramethyl-2-(3-methylbenzyl)-1,3,2-dioxaborolane (7ba)*³⁸. A colorless oil (33.6 mg, 71%). ¹H NMR (400 MHz,
3 CDCl₃) δ 7.14 (t, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 7.7 Hz, 2H), 6.94 (d, *J* = 7.5 Hz, 1H), 2.31 (s, 3H), 2.26 (s, 2H), 1.24 (s, 12H);
4 ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 138.4, 137.7, 129.8, 128.1, 125.9, 125.6, 83.4, 24.7, 21.4; ATR-FTIR (cm⁻¹): 2979, 2926, 1607,
5 1451, 1333, 1272, 1145, 968, 877, 848, 781, 740, 701, 674; HRMS *m/z* (ESI) calcd for C₁₄H₂₂BO₂ (M + H)⁺ 233.1707, found
6 233.1708.

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11 *2-(2,3-Dimethylbenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7ca)*. A colorless oil (35.6 mg, 72%). ¹H NMR (400 MHz,
12 CDCl₃) δ 7.04 – 6.93 (m, 3H), 2.29 (d, *J* = 2.2 Hz, 2H), 2.29 (s, 3H), 2.18 (s, 3H), 1.24 (s, 12H); ¹³C{¹H} NMR (101 MHz, CDCl₃)
13 δ 137.4, 136.3, 134.4, 127.5, 127.0, 125.2, 83.3, 24.7, 20.7, 15.8; ATR-FTIR (cm⁻¹): 2978, 2927, 1488, 1330, 1144, 968, 847;
14 HRMS *m/z* (ESI) calcd for C₁₅H₂₄BO₂ (M + H)⁺ 247.1864, found 247.1867.

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19 *2-(2-Methoxybenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7da)*³⁸. A colorless oil (36.1 mg, 73%). ¹H NMR (400 MHz,
20 CDCl₃) δ 7.13 (dd, *J* = 11.6, 4.5 Hz, 2H), 6.84 (ddd, *J* = 16.7, 11.6, 4.7 Hz, 2H), 3.80 (s, 3H), 2.19 (s, 2H), 1.24 (s, 12H); ¹³C{¹H}
21 NMR (101 MHz, CDCl₃) δ 157.1, 130.4, 127.9, 126.2, 120.4, 109.7, 83.1, 55.0, 24.7; ATR-FTIR (cm⁻¹): 2978, 2932, 1601, 1492,
22 1464, 1353, 1328, 1244, 1144, 1030, 969, 849, 754, 674; HRMS *m/z* (ESI) calcd for C₁₄H₂₂BO₃ (M + H)⁺ 249.1657, found
23 249.1661.

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29 *2-(2-Methoxybenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7ea)*. A colorless oil (48.8 mg, 88%). ¹H NMR (400 MHz,
30 CDCl₃) δ 6.80 – 6.65 (m, 3H), 3.84 (s, 3H), 3.83 (s, 3H), 2.22 (s, 2H), 1.23 (s, 12H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 148.6,
31 146.4, 130.9, 120.7, 112.4, 111.3, 83.3, 55.7, 24.7; ATR-FTIR (cm⁻¹): 2977, 2936, 2839, 1681, 1591, 1514, 1458, 1375, 1337, 1268,
32 1141, 1026, 860, 809, 763, 640; HRMS *m/z* (ESI) calcd for C₁₅H₂₄BO₄ (M + H)⁺ 279.1762, found 279.1766.

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36 *2-(Benzo[d][1,3]dioxol-5-ylmethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7fa)*. A colorless oil (47.3 mg, 90%). ¹H NMR
37 (400 MHz, CDCl₃) δ 6.72 – 6.66 (m, 2H), 6.61 (dd, *J* = 7.9, 1.6 Hz, 1H), 5.89 (s, 2H), 2.21 (s, 2H), 1.23 (s, 12H); ¹³C{¹H} NMR
38 (101 MHz, CDCl₃) δ 147.4, 144.9, 132.1, 121.4, 109.6, 108.1, 100.5, 83.4, 24.7; ATR-FTIR (cm⁻¹): 2979, 2930, 1722, 1689, 1606,
39 1447, 1376, 1252, 1148, 1099, 1039, 930, 851, 810, 674; HRMS *m/z* (ESI) calcd for C₁₄H₂₀BO₄ (M + H)⁺ 263.1449, found
40 263.1450.

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45 *2-(2,4-Difluorobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7ga)*. A colorless oil (35.7 mg, 70%). ¹H NMR (400 MHz,
46 CDCl₃) δ 7.14 (dt, *J* = 14.9, 7.4 Hz, 1H), 6.80 – 6.70 (m, 2H), 2.20 (s, 2H), 1.24 (s, 12H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ
47 164.1, 159.7, 131.4 (dd, *J* = 9.2, 6.5 Hz), 121.6 (dd, *J* = 17.1, 3.7 Hz), 110.7 (dd, *J* = 20.8, 3.8 Hz), 103.6, 103.3, 103.1, 83.6, 24.6;
48 ATR-FTIR (cm⁻¹): 2980, 2929, 2234, 1601, 1504, 1353, 1273, 1212, 1143, 966, 848; HRMS *m/z* (ESI) calcd for C₁₃H₁₈BF₂O₂(M +
49 H)⁺ 255.1362, found 255.1368.

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54 *4,4,5,5-Tetramethyl-2-(naphthalen-1-ylmethyl)-1,3,2-dioxaborolane (7ha)*³⁷. A colorless oil (39.0 mg, 73%). ¹H NMR (300
55 MHz, CDCl₃) δ 8.03 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.84 (dd, *J* = 7.3, 2.1 Hz, 1H), 7.71 – 7.65 (m, 1H), 7.53 – 7.44 (m, 2H), 7.42 – 7.34
56 (m, 2H), 2.71 (s, 2H), 1.21 (s, 12H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 135.6, 133.7, 132.4, 128.5, 126.4, 125.7, 125.3, 124.5,
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83.5, 24.6; ATR-FTIR (cm⁻¹): 3052, 2978, 2928, 1691, 1511, 1449, 1375, 1346, 1217, 1146, 1075, 1008, 885, 852, 799, 776, 673; HRMS m/z (ESI) calcd for C₁₇H₂₂BO₂ (M + H)⁺ 269.1707, found 269.1709.

4,4,5,5-Tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane (7ia)³⁹. A colorless oil (36.7 mg, 79%). ¹H NMR (400 MHz, CDCl₃) δ 7.24 – 7.11 (m, 5H), 7.10 – 7.01 (m, 1H), 2.36 (q, J = 7.5 Hz, 1H), 1.26 (d, J = 7.5 Hz, 3H), 1.13 (d, J = 5.3 Hz, 12H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 144.9, 128.3, 127.8, 125.1, 83.3, 24.6, 17.0; ATR-FTIR (cm⁻¹): 2976, 2921, 2850, 2361, 2337, 1633, 1605, 1395, 1361, 1319, 1248, 1143, 1092, 1031, 801, 654; GC-MS (EI) calcd for C₁₄H₂₁BO₃ [M] 232.16, found 232.19.

4,4,5,5-Tetramethyl-2-(1-(o-tolyl)ethyl)-1,3,2-dioxaborolane (7ja). A colorless oil (37.2 mg, 75%). ¹H NMR (400 MHz, CDCl₃) δ 7.24 – 7.20 (m, 1H), 7.14 (dd, J = 13.3, 6.7 Hz, 2H), 7.06 (td, J = 7.4, 1.4 Hz, 1H), 2.60 (q, J = 7.5 Hz, 1H), 2.33 (s, 3H), 1.35 (dd, J = 10.0, 4.4 Hz, 3H), 1.23 (d, J = 4.8 Hz, 12H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 143.3, 135.6, 130.0, 127.1, 126.0, 125.0, 83.2, 24.6, 19.9, 16.3; ATR-FTIR (cm⁻¹): 2978, 2929, 1442, 1375, 1329, 1218, 1148, 1077, 982, 850, 760, 674; GC-MS (EI) calcd for C₁₅H₂₃BO₂ [M] 246.18, found 247.21.

2-(1-(4-Methoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7ka)³⁹. A colorless oil (47.1 mg, 90%). ¹H NMR (400 MHz, CDCl₃) δ 7.18 – 7.11 (m, 2H), 6.86 – 6.79 (m, 2H), 3.78 (s, 3H), 2.38 (q, J = 7.5 Hz, 1H), 1.30 (d, J = 7.5 Hz, 3H), 1.21 (d, J = 5.1 Hz, 12H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 157.2, 137.0, 128.6, 113.7, 83.2, 55.1, 24.6, 17.3; ATR-FTIR (cm⁻¹): 2927, 2930, 1675, 1605, 1512, 1455, 1372, 1248, 1174, 1146, 1087, 1033, 832, 674; HRMS m/z (ESI) calcd for C₁₅H₂₄BO₃ (M + H)⁺ 263.1813, found 263.1817.

2-(1-(4-Fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7la)³⁹. A colorless oil (38.3 mg, 76%). ¹H NMR (400 MHz, CDCl₃) δ 7.20 – 7.12 (m, 2H), 6.98 – 6.90 (m, 2H), 2.41 (q, J = 7.5 Hz, 1H), 1.31 (d, J = 7.5 Hz, 3H), 1.20 (d, J = 4.6 Hz, 12H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 162.0, 159.6, 140.5 (d, J = 3.1 Hz), 129.0 (d, J = 7.6 Hz), 115.0, 114.8, 83.3, 24.6, 17.2; ATR-FTIR (cm⁻¹): 2978, 2929, 1604, 1510, 1445, 1376, 1267, 1224, 1147, 1084, 1011, 982, 837, 674; GC-MS (EI) calcd for C₁₄H₂₀BFO₂ [M] 250.15, found 251.2.

4,4,5,5-Tetramethyl-2-(1-(naphthalen-1-yl)ethyl)-1,3,2-dioxaborolane (7ma)⁴⁰. A colorless oil (41.3 mg, 73%). ¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, J = 8.1 Hz, 1H), 7.84 (dd, J = 7.4, 2.0 Hz, 1H), 7.71 – 7.64 (m, 1H), 7.54 – 7.37 (m, 4H), 3.13 (q, J = 7.4 Hz, 1H), 1.51 (d, J = 7.5 Hz, 3H), 1.21 (d, J = 4.1 Hz, 12H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 141.4, 133.9, 132.0, 128.7, 125.8, 125.3, 124.1, 83.4, 24.6, 16.4; ATR-FTIR (cm⁻¹): 3049, 2977, 2930, 2362, 1510, 1453, 1375, 1324, 1143, 851, 798, 777, 673; HRMS m/z (ESI) calcd for C₁₈H₂₄BO₂ (M + H)⁺ 283.1864, found 283.1867.

4,4,5,5-Tetramethyl-2-(1,2,3,4-tetrahydronaphthalen-1-yl)-1,3,2-dioxaborolane (7na)³⁹. A colorless oil (37.9 mg, 74%). ¹H NMR (400 MHz, CDCl₃) δ 7.25-7.05 (m, 4H), 2.77 (s, 2H), 2.60 (s, 1H), 1.90 (s, 3H), 1.81 – 1.68 (m, 1H), 1.25 (s, 12H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 136.6, 135.6, 128.3, 124.3, 123.7, 82.2, 28.7, 24.1, 24.0, 21.6; ATR-FTIR (cm⁻¹): 2927, 2928, 1684, 1452, 1382, 1324, 1145, 852, 740, 672; HRMS m/z (ESI) calcd for C₁₆H₂₄BO₂ (M + H)⁺ 259.1864, found 259.1869.

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2 **4,4,5,5-Tetramethyl-2-(1-phenyl-2-(p-tolyl)ethyl)-1,3,2-dioxaborolane (7oa)**. A colorless oil (46.7 mg, 72%). ^1H NMR (400
3 MHz, CDCl_3) δ 7.26 – 7.21 (m, 4H), 7.16 – 7.09 (m, 1H), 7.04 (dd, $J = 19.6, 8.0$ Hz, 4H), 3.12 (dd, $J = 13.5, 9.6$ Hz, 1H), 2.91 (dd,
4 $J = 13.5, 7.0$ Hz, 1H), 2.65 (dd, $J = 9.6, 7.0$ Hz, 1H), 2.28 (s, 3H), 1.11 (d, $J = 2.5$ Hz, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ
5 142.6, 138.6, 135.0, 128.7, 128.3, 125.3, 83.3, 38.3, 24.5, 21.0; ATR-FTIR (cm^{-1}): 2978, 2925, 1595, 1451, 1360, 1326, 1240, 1142,
6 1088, 967, 855, 700; HRMS m/z (ESI) calcd for $\text{C}_{21}\text{H}_{28}\text{BO}_2$ ($\text{M} + \text{H}$) $^+$ 322.2177, found 322.2179.

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11 **Methyl 3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (7pa)**⁴¹. A colorless oil (18.2 mg, 31%). ^1H NMR
12 (400 MHz, CDCl_3) δ 7.30 – 7.19 (m, 5H), 7.19 – 7.12 (m, 1H), 3.65 (s, 3H), 2.90 (dd, $J = 15.9, 9.8$ Hz, 1H), 2.70 – 2.63 (m, 2H),
13 1.22 (s, 6H), 1.17 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 173.8, 141.3, 128.5, 128.2, 125.7, 83.6, 51.6, 37.1, 24.5; ATR-FTIR
14 (cm^{-1}): 3061, 2977, 1736, 1637, 1371, 1324, 1261, 1171, 1140, 1050, 973, 846, 766, 701; HRMS m/z (ESI) calcd for $\text{C}_{16}\text{H}_{23}\text{BO}_4\text{Na}$
15 ($\text{M} + \text{Na}$) $^+$ 313.1582, found 313.1589.

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21 **4,4,5,5-Tetramethyl-2-(2-phenylpropan-2-yl)-1,3,2-dioxaborolane (7qa)**³⁷. A colorless oil (36.6 mg, 74%). ^1H NMR (400 MHz,
22 CDCl_3) δ 7.37 – 7.26 (m, 4H), 7.13 (ddd, $J = 6.6, 3.2, 1.6$ Hz, 1H), 1.35 (s, 6H), 1.20 (s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ
23 148.6, 128.1, 126.3, 125.0, 83.3, 25.6, 24.5; ATR-FTIR (cm^{-1}): 2872, 2802, 1432, 1344, 1208, 1192, 1054, 972, 838; HRMS m/z
24 (ESI) calcd for $\text{C}_{15}\text{H}_{24}\text{BO}_2$ ($\text{M} + \text{H}$) $^+$ 247.1864, found 247.1864.

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29 **4,4,5,5-Tetramethyl-2-(1-phenylcyclopentyl)-1,3,2-dioxaborolane (7ra)**. A white solid (33.9 mg, 63%). ^1H NMR (400 MHz,
30 CDCl_3): δ 7.31 – 7.22 (m, 5H), 7.14 – 7.07 (m, 1H), 2.32 (d, $J = 8.2$ Hz, 2H), 1.78 – 1.59 (m, 6H), 1.13 (s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR
31 (101 MHz, CDCl_3): δ 147.1, 127.9, 127.0, 124.7, 83.3, 35.2, 24.4; ATR-FTIR (cm^{-1}): 2973, 2864, 1446, 1374, 1354, 1312, 1111,
32 748, 700; HRMS m/z (ESI) calcd for $\text{C}_{17}\text{H}_{26}\text{BO}_2$ ($\text{M} + \text{H}$) $^+$ 273.2020, found 273.2026.

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36 **4,4,5,5-tetramethyl-2-(1-phenylcyclopentyl)-1,3,2-dioxaborolane (7sa)**⁴². A colorless oil (31.4 mg, 60%). ^1H NMR (400 MHz,
37 CDCl_3) δ 7.34 – 7.27 (m, 3H), 7.21 – 7.10 (m, 2H), 1.87 (dq, $J = 14.7, 7.4$ Hz, 1H), 1.70 (dq, $J = 14.6, 7.4$ Hz, 1H), 1.20 (d, $J = 3.3$
38 Hz, 12H), 1.09 (s, 3H), 0.82 (t, $J = 7.4$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 147.2, 127.7, 126.9, 126.8, 125.0, 83.3, 31.9,
39 24.6, 21.0, 1.0; ATR-FTIR (cm^{-1}): 2965, 2925, 1637, 1461, 1372, 1349, 1313, 1261, 1142, 1097, 1026, 801, 700; HRMS m/z (ESI)
40 calcd for $\text{C}_{12}\text{H}_{26}\text{BO}_2$ ($\text{M} + \text{H}$) $^+$ 261.2020, found 261.2022.

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45 **4,4,5,5-Tetramethyl-2-(1-phenylcyclopropyl)-1,3,2-dioxaborolane (7ta)**⁴³. A colorless oil (24.2 mg, 50%). ^1H NMR (400 MHz,
46 CDCl_3) δ 7.30 – 7.19 (m, 5H), 7.16 – 7.09 (m, 1H), 1.21 (s, 12H), 1.10 (q, $J = 3.5$ Hz, 2H), 0.90 (q, $J = 3.5$ Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR
47 (101 MHz, CDCl_3) δ 144.8, 128.9, 128.0, 125.2, 83.3, 24.6, 13.3; ATR-FTIR (cm^{-1}): 2946, 2932, 1643, 1421, 1353, 1312, 1127,
48 838, 737, 655; HRMS m/z (ESI) calcd for $\text{C}_{15}\text{H}_{22}\text{BO}_2$ ($\text{M} + \text{H}$) $^+$ 244.1635, found 244.1640.

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53 ***N*-(2,5-Dimethoxybenzyl)-*N*-(2-phenoxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetamide (10)**⁴⁴. A white solid
54 (90.2 mg, 84%). ^1H NMR (400 MHz, CDCl_3) δ 7.57 (dd, $J = 7.0, 1.5$ Hz, 2H), 7.31 (dd, $J = 11.2, 4.7$ Hz, 2H), 7.14 (t, $J = 7.4$ Hz,
55 1H), 6.99 (d, $J = 3.0$ Hz, 1H), 6.86 – 6.80 (m, 2H), 6.74 (d, $J = 8.7$ Hz, 1H), 6.68 (dt, $J = 5.1, 2.5$ Hz, 1H), 6.62 (d, $J = 8.9$ Hz, 1H),
56 4.98 (d, $J = 12.0$ Hz, 1H), 4.90 (d, $J = 12.0$ Hz, 1H), 3.63 (s, 3H), 3.50 (s, 3H), 1.97 (s, 3H), 1.32 (d, $J = 4.7$ Hz, 12H); $^{13}\text{C}\{^1\text{H}\}$
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NMR (101 MHz, CDCl₃) δ 171.1, 156.3, 155.3, 153.4, 151.8, 136.9, 135.5, 132.4, 129.8, 126.4, 124.3, 119.7, 116.7, 116.3, 113.6, 111.2, 83.9, 55.6, 46.4, 25.0, 24.6, 22.3; ATR-FTIR (cm⁻¹): 2979, 2834, 1663, 1588, 1498, 1422, 1384, 1357, 1245, 1222, 1142, 1048, 860, 753, 692.

N,N-Dimethyl-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-amine (**13aa**)⁴⁵. A colorless oil (19.4 mg, 35%). ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 6.9 Hz, 1H), 7.41 (t, *J* = 7.1 Hz, 1H), 7.28 (t, *J* = 6.9 Hz, 2H), 3.31 (dt, *J* = 8.9, 5.5 Hz, 2H), 3.23 (dt, *J* = 8.3, 5.4 Hz, 2H), 2.96 (s, 6H), 1.36 (s, 12H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 141.8, 137.1, 132.0, 130.2, 126.8, 84.0, 60.3, 43.6, 30.9, 24.9; ATR-FTIR (cm⁻¹): 3057, 2980, 2938, 2862, 1447, 1380, 1349, 1278, 1163, 1031, 857, 749, 640, 519; GC-MS (EI) calcd for C₁₆H₂₆BNO₂ [M] 275.21, found 275.30.

N,N-Dimethyl-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propan-1-amine (**13ba**). A colorless oil (24.5 mg, 42%). ¹H NMR (400 MHz, CDCl₃) δ 7.81 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.36 (td, *J* = 7.5, 1.5 Hz, 1H), 7.23 – 7.15 (m, 2H), 2.97 – 2.84 (m, 4H), 2.71 (s, 6H), 2.05 – 1.88 (m, 2H), 1.33 (s, 12H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 147.1, 136.6, 131.3, 129.2, 125.7, 83.6, 58.5, 43.8, 32.5, 28.0, 24.8; ATR-FTIR (cm⁻¹): 2978, 2931, 2363, 1600, 1443, 1381, 1348, 1276, 1147, 1030, 860, 639; GC-MS (EI) calcd for C₁₇H₂₈BNO₂ [M] 289.22, found 289.32.

2-(Cyclopropyl(phenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**15**). A colorless oil (28.8 mg, 55%). ¹H NMR (400 MHz, CDCl₃) δ 7.28 – 7.23 (m, 3H), 7.23 – 7.11 (m, 2H), 1.72 (d, *J* = 9.7 Hz, 1H), 1.22 (d, *J* = 1.4 Hz, 12H), 1.17 – 1.14 (m, 1H), 0.61 – 0.52 (m, 1H), 0.52 – 0.43 (m, 1H), 0.25 (td, *J* = 9.3, 5.1 Hz, 1H), 0.09 (td, *J* = 9.4, 5.1 Hz, 1H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 143.1, 128.2, 125.2, 83.3, 24.6, 13.0, 5.0, 4.7; ATR-FTIR (cm⁻¹): 2979, 2929, 2362, 1455, 1374, 1324, 1144, 971, 850, 700, 673; HRMS *m/z* (ESI) calcd for C₁₆H₂₄BO₂ (M + H)⁺ 258.1791, found 258.1794.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.xxxxxxx

NMR spectra of all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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