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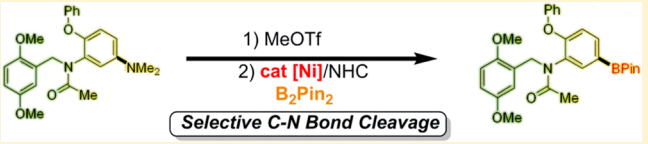
Nickel-Catalyzed Borylation of Aryl- and Benzyltrimethylammonium Salts via C−N Bond Cleavage

Jiefeng Hu, Heqing Sun, Wangshui Cai, Xinghui Pu, Yemin Zhang, and Zhuangzhi Shi*

State Key Laboratory of Coordination Chemistry, Collaborative Innovation Center of Chemistry for Life Sciences, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

Supporting Information

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 hightly efficient C−N bond borylative cleavage depends on the appropriate choice of the nickel catalyst $Ni(COD)_2$, ICy·HCl as a ligand, and the use of 2-ethoxyethanol as the cosolvent. 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.

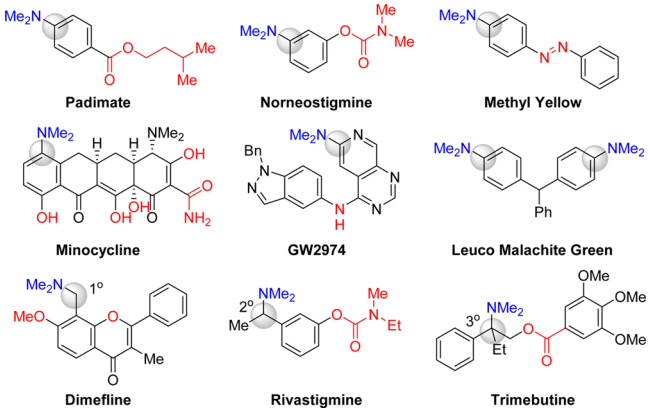


INTRODUCTION

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 coupling[4] and Negishi coupling[5] 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−C[12] bonds has 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

Scheme 1. Nature Products, Drugs and Dyes Involving NMe_2 Groups



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−O,[10] and C−halogen[14] bonds is hard to control; and (4) elimination process in sp^3 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

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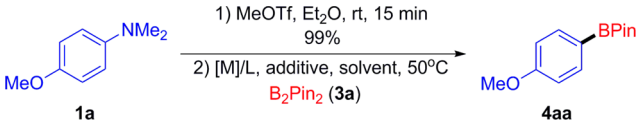
mild and scalable conditions. This system is effective not only for high functional-group tolerance of arylamines but also for the primary, secondary, and even tertiary benzylamines. Moreover, application of this method in the preparation of some important organoboronate intermediates showcases the strategic opportunity to utilize this transformation in the synthesis of biologically active compounds.

RESULTS AND DISCUSSION

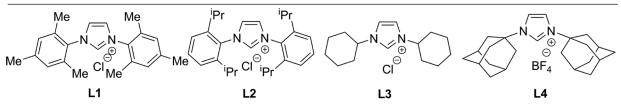
Initial studies involved the evaluation of the selective C−N borylation of 4-methoxy-*N*,*N*-dimethylaniline (**1a**) (Table 1).

Table 1. Reaction Development[a]



1a 4aa

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**	**^{t}BuOK**	**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

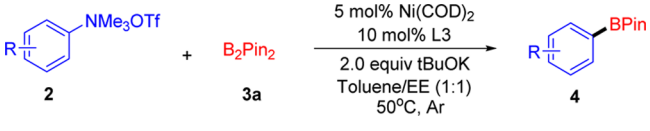


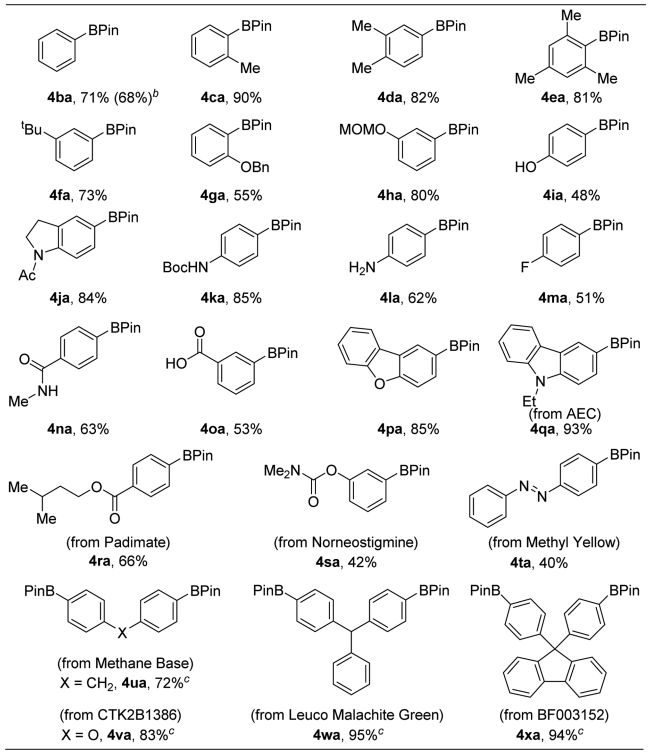
[a]Reaction conditions: **2a** (0.20 mmol), **3a** (0.50 mmol), 5 mol % of catalyst, 10 mol % of ligand, 2.0 equiv of base in solvent (2.0 mL), 16 h, under Ar. [b]Determined by GC analysis. [c]Yield. [d]Using 1 mol % $Ni(COD)_2$ and 2 mol % **L3**. EE = 2-ethoxyethanol.

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 (B_2Pin_2, **3a**) in the presence of 5 mol % of $Ni(COD)_2$, 10 mol % of IMes·HCl (**L1**), and 2.0 equiv of ^{t}BuONa, 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 cosolvent ratio or replacing EE with MeOH or ^{n}BuOH resulted in much lower yields (Table 1, entries 6−10). ^{t}BuOLi was not as effective as ^{t}BuONa (Table 1, entry 11), and nearly quantitative yield was observed by employing ^{t}BuOK as the base (Table 1, entry 12). To our delight, other nickel sources as catalyst such as $Ni(OTf)_2$ were also proven successful in this coupling reaction with a high reactivity (Table 1, entries 13 and 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).

To evaluate the utility of the Ni-catalyzed borylation of C−N bonds, a series of *N*,*N*-dimethylanilines were tested in Table 2.

Table 2. Ni-Catalyzed Borylation of Aryl C−N Bonds[a]





[a]Reaction conditions: **2** (0.20 mmol), **3a** (0.50 mmol), 5 mol % of $Ni(COD)_2$, 10 mol % of **L3**, ^{t}BuOK (0.4 mmol) in 2.0 mL of toluene/EE (1:1) at 40 °C, 12 h, under Ar. [b]Using phenyltrimethylammonium iodide as the substrate. [c]1.00 mmol of **3a**.

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**−**oa**). Among them, sterically hindered substrate **2e** resulted in a 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 NH_2 groups (**4ja**−**la**). Transition-metal-catalyzed *ortho*-C−H borylation is a general process in the presence of directing groups such as benzamide

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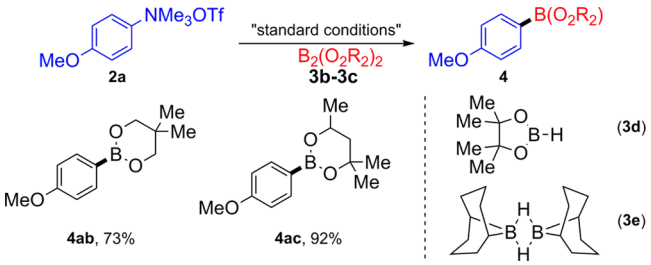
and benzoic acid.[16] Under our conditions, the directing-group-containing substrates **4na–oa** can also selectively cleave C–N bonds, avoiding the catalyst to bind the directing groups. It is noted that only fluoro-substituted phenylammonium triflate **4ma** can be selectively borylated at the C–N bond, other halide substituents such as aryl chlorides underwent borylation at both the C–Cl and C–N bonds. In addition, polycyclic and heterocyclic substrates were also compatible (**4pa–qa**). To our delight, the $-NMe_2$ 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 industrial materials such as methane base (**2u**), CTK2B1386 (**2v**), leuco malachite green (**2w**), and BF003152 (**2x**) were used, affording the corresponding products **4ua–xa** in good to excellent yields.

Our nickel-catalyzed system is not limited to the use of B_2Pin_2 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**)

Scheme 2. Investigation of Different Borylating Agents

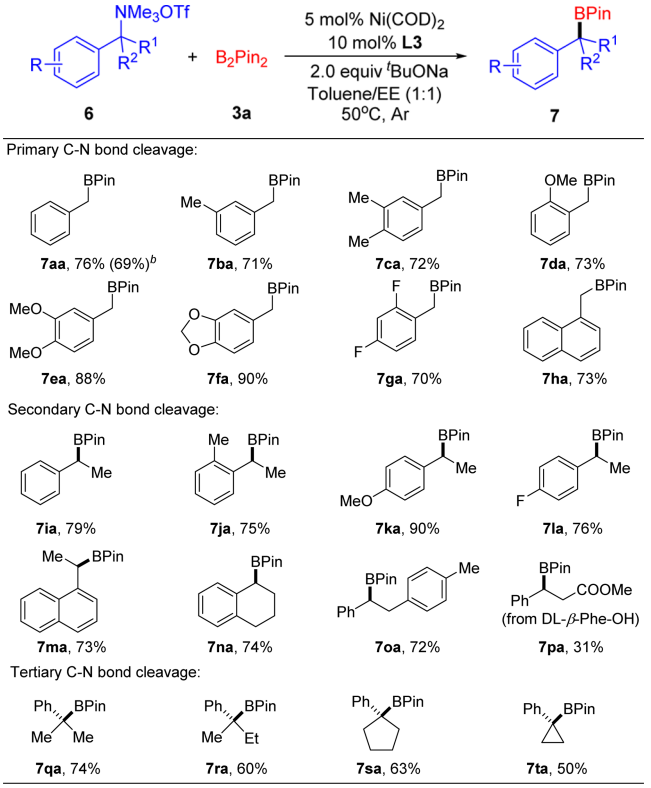


and 9-borabicyclo[3.3.1]nonane (9-BBN dimer, **3e**) were employed, no desired products were detected, which might be attributed to the lack of the required B–B bonds in borylating agents for the transformation.

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 acceptable yield of 31%. A particularly noteworthy point of our catalytic system is the first report of tertiary C–N bond activation, as observed by the borylation of substrates **6q–s**, to produce desired product in moderate to good yields.

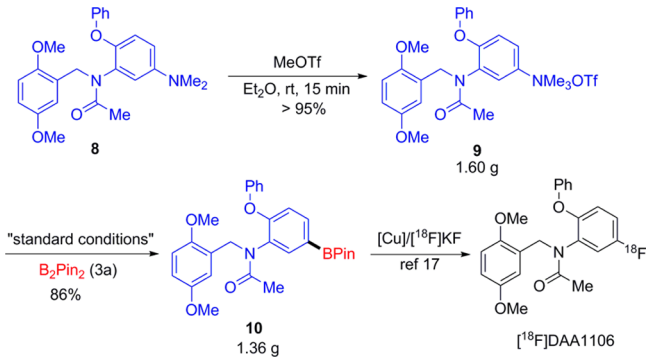
A major benefit of this mild, highly selective C–N bond borylation procedure is its amenability to gram-scale and late-stage synthetic applications (Scheme 3). To demonstrate this potential, complex molecule **8** containing a number of different types of C–O and C–N bonds was subjected to our borylation protocol, and the corresponding arylammonium triflate **9** can be selectively borylated at the C–NMe_3 bond position to yield aryl boronic ester **10** in 86% yield. Subsequent copper-

Table 3. Ni-Catalyzed Borylation of Benzylic C–N Bonds[a]



[a]Reaction conditions: **6** (0.20 mmol), **3a** (0.50 mmol), 5 mol % of $Ni(COD)_2$, 10 mol % of **L3**, ^{t}BuONa (0.4 mmol) in 2.0 mL toluene/EE (1:1) at 50 °C, 12 h, under Ar. [b]Using ^{t}BuOK.

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



mediated nucleophilic ^{18}F fluorination of **10** can provide the translocator protein (TSPO) PET ligand [^{18}F]DAA1106.[17] Nickel-catalyzed ring-opening and cross-coupling of aziridines has been developed recently.[18] Remarkably, our optimaized 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 B_2Pin_2 (**3a**) as the borylation reagent, the ring-opened products **13aa–ba** can be generated in 35–42% yields at the current stage (Scheme 4).

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-

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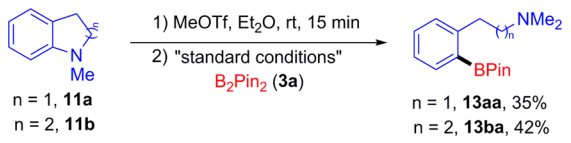
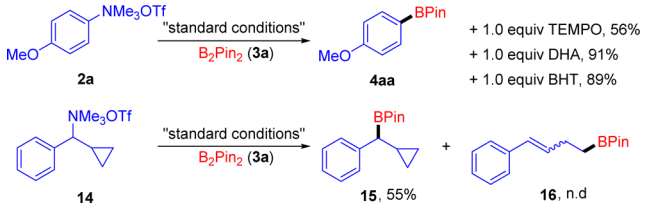
Scheme 4. Ring-Opening via Borylative Cleavage of C−N Bonds



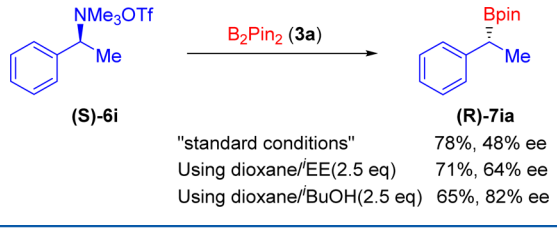
clock experiment using ammonium triflate **14** can further rule out the radical pathway (Scheme 5).

Scheme 5. Mechanistic Experiments



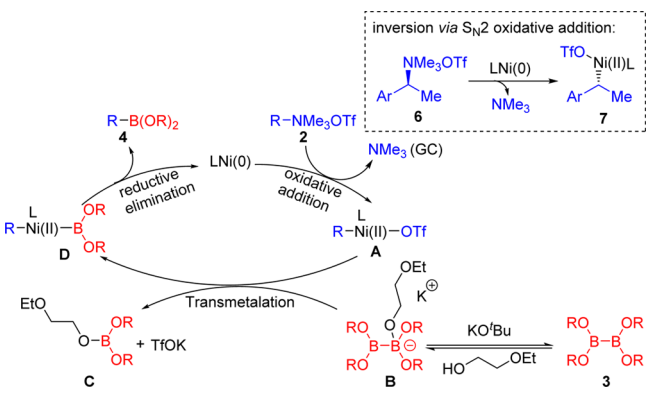
Watson and co-workers previously uncovered that Ni-catalyzed process for the stereospecific cross-coupling of benzylic ammonium salts and boronic acids proceed via an S_N2 mechanism.[4b] When (*S*)-**6i** (99% ee) was allowed to react with B_2Pin_2 (**3a**) under our standard conditions, only (*R*)-**7ia** of 48% ee was observed in 78% yield (Scheme 6).[20] A further

Scheme 6. Borylation of Chiral Substrate



improved screening revealed that solvent affects the chirality transfer with dioxane as solvent and 2.5 equiv of ^{i}BuOH as additive providing (*R*)-**7ia** in good enantiospecificity (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

Scheme 7. Proposed Catalytic Cycle



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 cosolvent 2-ethoxyethanol (EE) is to generate the anionic adduct of borylating agent **B** from **3** in the presence of KO^{t}Bu, which is the key to success for the transmetalation process in this catalytic cycle.[22]

In summary, we have developed a mild Ni-catalyzed system that is capable of activating aryl and benzyl ammonium bonds for C−N bond borylation to produce various organoboronates.[23] In view of the widespread $-NMe_2$ 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 on 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 a commercial source. KO^{t}Bu and (Bpin)$_2$ was purchased from another commercial supplier.

General Procedure for Preparation of Ammonium Triflates. The preparation of the dimethylamines was described according to Escheweiler−Clarke conditions.[24,25] The ammonium triflates were prepared according to the literature.[26] To a solution of 4-methoxyaniline (1.2 g, 10.0 mmol, 1.0 equiv) in MeOH (15 mL) under Ar was added formic acid to adjust the pH to 3−4. $NaBH_3CN$ (0.9 g, 15.0 mmol, 1.5 equiv) 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, formaldehyde (18 mL, 500 mmol, 50 equiv) 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 K_2CO_3(5 M) was added to pH ≈ 12. The aqueous layer was extracted with DCM (3 × 50 mL). The combined organic layer was dried over Na_2SO_4.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 Et_2O (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 min at 0 °C. The solution was concentrated and washed with Et_2O (2 × 20 mL). The resulting compounds were dried under vacuum to give a salt.

*N,N,N,3,4-Pentamethylbenzenaminium trifluoromethanesulfonate (**2d**):* white solid (1.4 g, 92%); ^{1}H NMR (400 MHz, D6-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); ^{13}C{^{1}H} NMR (101 MHz, D6-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 $C_{11}H_{18}N$ (M − OTf)$^+$ 164.1434, found 164.1434.

*3-tert-Butyl-N,N,N-trimethylbenzenaminium trifluoromethanesulfonate (**2f**):* white solid (1.5 g, 88%); ^{1}H NMR (400 MHz, D6-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); ^{13}C{^{1}H} NMR (101 MHz, D6-DMSO) δ 153.3, 147.2, 129.6, 126.8, 117.3, 117.2, 56.4, 35.1, 30.9; HRMS m/z (ESI) calcd for $C_{13}H_{22}N$ (M − OTf)$^+$ 192.1747, found 192.1748.

*2-(Benzyloxy)-N,N,N-trimethylbenzenaminium trifluoromethanesulfonate (**2g**):* white solid (1.8 g, 92%); ^{1}H NMR (400 MHz, D6-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

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(s, 2H), 3.64 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, D6-DMSO) δ 150.6, 135.5, 133.5, 131.9, 128.8, 128.6, 128.4, 121.9, 121.4, 115.8, 71.0, 55.1; HRMS m/z (ESI) calcd for $C_{16}H_{20}NO$ $(M - OTf)^+$ 242.1539, found 242.1541.

*3-tert-Butyl-N,N,N-trimethylbenzenaminium trifluoromethanesulfonate (**2h**):* black solid (1.3 g, 75%); ^{1}H NMR (400 MHz, D6-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); $^{13}C\{^{1}H\}$ NMR (101 MHz, D6-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 $C_{11}H_{18}NO_2$ $(M - OTf)^+$ 196.1332, found 196.1332.

*4-Hydroxy-N,N,N-trimethylbenzenaminium trifluoromethanesulfonate (**2i**):* colorless oil (0.9 g, 60%); ^{1}H NMR (400 MHz, D6-DMSO) δ 10.17 (s, 1H), 7.81−7.70 (m, 2H), 6.99−6.87 (m, 2H), 3.55 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, D6-DMSO) δ 158.1, 138.7, 121.6, 115.81, 56.5; HRMS m/z (ESI) calcd for $C_9H_{14}NO$ $(M - OTf)^+$ 152.1070, found 152.1069.

*1-Acetyl-N,N,N-trimethylindolin-5-aminium trifluoromethanesulfonate (**2j**):* white solid (1.7 g, 92%); ^{1}H NMR (400 MHz, D6-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 Hz, 2H), 2.18 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, D6-DMSO) δ 169.3, 143.7, 142.0, 133.9, 119.3, 117.3, 115.4, 56.6, 48.6, 27.4, 23.8; HRMS m/z (ESI) calcd for $C_{13}H_{19}N_2O(M - OTf)^+$ 219.1492, found 219.1493.

*1-Acetyl-N,N,N-trimethylindolin-5-aminium trifluoromethanesulfonate (**2k**):* white solid (1.2 g, 65%); ^{1}H NMR (400 MHz, D6-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); $^{13}C\{^{1}H\}$ NMR (101 MHz, D6-DMSO) δ 152.6, 140.9, 140.7, 120.9, 118.3, 79.8, 56.4, 28.0; HRMS m/z (ESI) calcd for $C_{14}H_{23}N_2O_2$ $(M - OTf)^+$ 251.1754, found 251.1751.

*4-Amino-N,N,N-trimethylbenzenaminium trifluoromethanesulfonate (**2l**):* white solid (0.5 g, 30%); ^{1}H NMR (400 MHz, D6-DMSO) δ 7.71 (d, J = 9.3 Hz, 2H), 6.84 (d, J = 9.3 Hz, 2H), 3.53 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, D6-DMSO) δ 122.7, 122.2, 120.8, 119.0, 56.59.

*4-Fluoro-N,N,N-trimethylbenzenaminium trifluoromethanesulfonate (**2m**):* white solid (1.4 g, 94%); ^{1}H NMR (400 MHz, D6-DMSO) δ 8.17−7.92 (m, 2H), 7.50 (t, J = 8.7 Hz, 2H), 3.72−3.55 (m, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, D6-DMSO) δ 163.1 (d, J = 11.1 Hz), 160.7, 143.3, 123.2 (d, J = 9.0 Hz), 116.8, 116.6, 56.6; HRMS m/z (ESI) calcd for $C_9H_{13}FN$ $(M - OTf)^+$ 154.1027, found 154.1031.

*N,N,N-Trimethyl-4-(methylcarbamoyl)benzenaminium trifluoromethanesulfonate (**2n**):* white solid (1.1 g, 64%); ^{1}H NMR (400 MHz, D6-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); $^{13}C\{^{1}H\}$ NMR (101 MHz, D6-DMSO) δ 170.0, 154.1, 140.9, 133.9, 125.9, 61.6, 31.5; HRMS m/z (ESI) calcd for $C_{11}H_{17}N_2O$ $(M - OTf)^+$ 193.1335, found 193.1336.

*3-Carboxy-N,N,N-trimethylbenzenaminium trifluoromethanesulfonate (**2o**):* white solid (1.5 g, 91%); ^{1}H NMR (400 MHz, D6-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), 3.65 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, D6-DMSO) δ 166.0, 147.4, 132.6, 130.6, 125.0, 121.1, 56.3.

*N,N,N-Trimethyldibenzo[b,d]furan-2-aminium trifluoromethanesulfonate (**2p**):* white solid (1.7 g, 90%); ^{1}H NMR (400 MHz, D6-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), 7.64 (dd, J = 8.3, 7.4 Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 3.72 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, D6-DMSO) δ 156.8, 154.9, 146.2, 128.9, 124.8, 123.8, 122.2, 122.1, 122.0, 115.6, 112.0, 105.3, 56.9; HRMS m/z (ESI) calcd for $C_{15}H_{16}NO_2$ $(M - OTf)^+$ 226.1226, found 226.1229.

*9-Ethyl-N,N,N-trimethyl-9H-carbazol-3-aminium trifluoromethanesulfonate (**2q**):* white solid (1.6 g, 80%); ^{1}H NMR (400 MHz, D6-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, 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); $^{13}C\{^{1}H\}$ NMR (101 MHz, D6-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; HRMS m/z (ESI) calcd for $C_{17}H_{21}N_2$ $(M - OTf)^+$ 253.1699, found 253.1701.

*4-((Isopentyloxy)carbonyl)-N,N,N-trimethylbenzenaminium trifluoromethanesulfonate (**2r**):* white solid (1.5 g, 75%); ^{1}H NMR (400 MHz, D6-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), 0.94 (d, J = 6.6 Hz, 6H); $^{13}C\{^{1}H\}$ NMR (101 MHz, D6-DMSO) δ 164.3, 150.4 131.3, 130.7, 121.3, 63.8, 56.3, 36.7, 24.7, 22.3; HRMS m/z (ESI) calcd for $C_{15}H_{24}NO_2$ $(M - OTf)^+$ 250.1802, found 250.1805.

*N-(3-((Dimethylcarbamoyl)oxy)phenyl)-N,N-dimethylmethanideaminium trifluoromethanesulfonate salt (**2s**):* white solid (1.2 g, 65%); ^{1}H NMR (400 MHz, D6-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, 9H), 3.09 (d, J = 10.2 Hz, 3H), 2.94 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, D6-DMSO) δ 153.4, 151.9, 147.7, 130.5, 124.0, 117.1, 115.0, 56.4, 36.3, 36.1; HRMS m/z (ESI) calcd for $C_{12}H_{19}N_2O_2$ $(M - OTf)^+$ 223.1441, found 223.1443.

*(E)-N,N-Dimethyl-N-(4-(phenyldiazenyl)phenyl)-methanideaminium, trifluoromethanesulfonate salt (**2t**):* yellow solid (0.9 g, 46%); ^{1}H NMR (400 MHz, D6-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 = 4.6 Hz, 3H), 3.69 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, D6-DMSO) δ 151.9, 151.7, 148.6, 132.4, 129.6, 123.6, 122.9, 122.1, 56.5; HRMS m/z (ESI) calcd for $C_{15}H_{18}N_3$ $(M - OTf)^+$ 240.1495, found 240.1497.

*4,4′-Methylenebis(N,N,N-trimethylbenzenaminium) trifluoromethanesulfonate (**2u**):* white solid (2.7 g, 93%). ^{1}H NMR (400 MHz, D6-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); $^{13}C\{^{1}H\}$ NMR (101 MHz, D6-DMSO) δ 150.7, 148.0, 135.3, 125.8, 61.6.

*4,4′-Oxybis(N,N,N-trimethylbenzenaminium) trifluoromethanesulfonate (**2v**):* white solid (2.6 g, 89%); ^{1}H NMR (400 MHz, D6-DMSO) δ 8.03 (d, J = 9.3 Hz, 4H), 7.30 (d, J = 9.3 Hz, 4H), 3.63 (s, 18H); $^{13}C\{^{1}H\}$ NMR (101 MHz, D6-DMSO) δ 156.5, 142.9, 122.8, 119.7, 56.6.

*4,4′-(Phenylmethylene)bis(N,N,N-trimethylbenzenaminium) trifluoromethanesulfonate (**2w**):* white solid (1.7 g, 52%); ^{1}H NMR (400 MHz, D6-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), 5.90 (s, 1H), 3.59 (d, J = 2.3 Hz, 18H); $^{13}C\{^{1}H\}$ NMR (101 MHz, D6-DMSO) δ 150.8, 150.2, 147.3, 135.6, 134.0, 133.9, 132.1, 127.5, 125.9, 124.3, 61.6, 59.2.

*4,4′-(9H-Fluorene-9,9-diyl)bis(N,N,N-trimethylbenzenaminium) trifluoromethanesulfonate (**2x**):* white solid (1.8 g, 49%); ^{1}H NMR (400 MHz, D6-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), 7.31 (d, J = 9.1 Hz, 4H), 3.56 (s, 18H); $^{13}C\{^{1}H\}$ NMR (101 MHz, D6-DMSO) δ 148.9, 146.7, 145.9, 139.6, 128.9, 128.6, 128.5, 125.9, 121.0, 120.8, 63.9, 56.3.

*1-(Benzo[d][1,3]dioxol-5-yl)-N,N,N-trimethylmethanaminium trifluoromethanesulfonate (**6f**):* white solid (0.9 g, 52%); ^{1}H NMR (400 MHz, D6-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); $^{13}C\{^{1}H\}$ NMR (101 MHz, D6-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 $C_{11}H_{16}NO_2$ $(M - OTf)^+$ 194.1176, found 194.1177.

*1-(2,4-Difluorophenyl)-N,N,N-trimethylmethanaminium trifluoromethanesulfonate (**6g**):* white solid (1.1 g, 65%). ^{1}H NMR (400 MHz, D6-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 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, D6-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, 112.72−112.0 (m), 105.1, 104.8, 104.6, 60.9, 51.8; HRMS m/z (ESI) calcd for $C_{10}H_{14}F_2N$ $(M - OTf)^+$ 186.1089, found 186.1089.

*N,N,N-Trimethyl-1,2,3,4-tetrahydronaphthalen-1-aminium trifluoromethanesulfonate (**6n**):* white solid (1.0 g, 59%); ^{1}H NMR (400 MHz, D6-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), 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); $^{13}C\{^{1}H\}$ NMR (101 MHz, D6-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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*N,N,N-Trimethyl-1-phenyl-2-p-tolylethan-1-aminium trifluoromethanesulfonate (**6o**):* white solid (1.2 g, 60%); ^{1}H NMR (400 MHz, D6-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), 3.49 (t, J = 12.8 Hz, 1H), 3.10 (s, 9H), 2.15 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, D6-DMSO) δ 135.5, 132.8, 131.0, 130.1, 129.1, 128.8, 128.7, 77.9, 51.0, 32.2, 20.4.

*3-Methoxy-N,N,N-trimethyl-3-oxo-1-phenylpropan-1-aminium trifluoromethanesulfonate (**6p**):* white solid (1.2 g, 65%); ^{1}H NMR (400 MHz, D6-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), 3.02 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, D6-DMSO) δ 169.2, 131.4, 130.4, 128.9, 72.8, 51.9, 51.0, 33.2; HRMS m/z (ESI) calcd for $C_{13}H_{20}NO_2$ (M − OTf)$^+$ 222.1489, found 222.1493.

*N,N,N-Trimethyl-2-phenylpropan-2-aminium trifluoromethanesulfonate (**6q**):* white solid (0.9 g, 55%); ^{1}H NMR (400 MHz, D6-DMSO) δ 7.85−7.72 (m, 2H), 7.57−7.46 (m, 3H), 2.94 (s, 9H), 1.90 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, D6-DMSO) δ 135.4, 129.7, 129.5, 128.4, 74.4, 49.2, 22.5; HRMS m/z (ESI) calcd for $C_{12}H_{20}N$ (M − OTf)$^+$ 178.1590, found 178.1589.

*N,N,N-Trimethyl-2-phenylbutan-2-aminium trifluoromethanesulfonate (**6r**):* white solid (0.7 g, 43%); ^{1}H NMR (400 MHz, $CDCl_3$) 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 (s, 3H), 0.84 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 131.4, 130.1, 129.9, 128.8, 79.6, 49.3, 25.5, 19.3, 9.7; HRMS m/z (ESI) calcd for $C_{12}H_{18}N$ (M − OTf)$^+$ 176.1434, found 176.1435.

*N,N,N-Trimethyl-1-phenylcyclopropan-1-aminium trifluoromethanesulfonate (**6t**):* white solid (0.7 g, 40%); ^{1}H NMR (400 MHz, D6-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}C{^{1}H} NMR (101 MHz, D6-DMSO) δ 133.9, 133.4, 130.1, 128.6, 58.9, 51.5, 10.1; HRMS m/z (ESI) calcd for $C_{14}H_{22}N$ (M − OTf)$^+$ 204.1747, found 204.1748.

*3-(N-(2,5-dimethoxybenzyl)acetamido)-N,N,N-trimethyl-4-phenoxybenzenaminium (**9**).* To a solution of N^1,N^1-dimethyl-4-phenoxybenzene-1,3-diamine (16.6 mmol, 1.0 equiv) and Et_3N (2.8 mL, 19.9 mmol, 1.2 equiv) in DCM (20 mL) was added acetyl chloride (3.0 mL, 19.9 mmol, 1.2 equiv) in a dropwise manner at 0 °C, and the mixture was stirred at room temperature for 3 h. After the reaction mixture was concentrated under reduced pressure, the residue was quenched with AcOEt and washed with saturated 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 equiv) in DMF (20 mL) was added NaH (60% dispersion in mineral oil, 0.80 g, 20 mmol), and the mixture was stirred for 1 h at room temperature. To the mixture was added 2-(chloromethyl)-1,4-dimethoxybenzene, and the resulting mixture was stirred for 5 h 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 equiv) was dissolved in Et_2O/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 min at 0 °C. The solution was concentrated and washed with Et_2O (2 × 20 mL). The resulting compound was purified by column chromatography on silica gel (DCM/MeOH = 20:1) to give **9** (6.9 g, 71%) as a white solid: ^{1}H NMR (400 MHz, D6-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}C{^{1}H} NMR (101 MHz, D6-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**):* white solid (0.8 g, 54%); ^{1}H NMR (400 MHz, D6-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}C{^{1}H} NMR (101 MHz, D6-DMSO) δ 146.9, 133.7, 130.7, 128.8, 126.5, 117.3, 67.4, 54.0, 26.6; HRMS m/z (ESI) calcd for $C_{10}H_{14}N$ (M − OTf)$^+$ 148.1121, found 148.1120.

*1,1-Dimethyl-1,2,3,4-tetrahydroquinolin-1-ium trifluoromethanesulfonate (**12b**):* white solid (0.9 g, 58%); ^{1}H NMR (400 MHz, D6-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}C{^{1}H} NMR (101 MHz, D6-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 $C_{11}H_{16}N$ (M − OTf)$^+$ 162.1277, found 162.1277.

*1-Cyclopropyl-N,N,N-trimethyl-1-phenylmethanaminium trifluoromethanesulfonate (**14**):* white solid (0.6 g, 35%); ^{1}H NMR (400 MHz, D6-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}C{^{1}H} NMR (101 MHz, D6-DMSO) δ 133.1, 129.8, 128.7, 80.8, 51.0, 9.98, 9.96, 3.3; HRMS m/z (ESI) calcd for $C_{13}H_{20}N$ (M − OTf)$^+$ 190.1590, found 190.1591.

General Procedure for Cleavage of the C−N Bonds. To a 25 mL Schlenk tube were added 4-methoxy-*N,N,N*-trimethylbenzenaminium trifluoromethanesulfonate **1a** (63.6 mg, 0.2 mmol), bis(pinacolato)diboron (127.0 mg, 0.5 mmol), Ni(COD)$_2$ (3.3 mg, 6 mol %), ICy·HCl (6.5 mg, 12 mol %), KO^{t}Bu (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).

*2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4aa**):*[27] colorless oil (44.0 mg, 94%); ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.1, 136.5, 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 $C_{13}H_{19}BO_3$ [M] 234.14, found 234.21.

*4,4,5,5-Tetramethyl-2-phenyl-1,3,2-dioxaborolane (**4ba**):*[27] colorless oil (28.9 mg, 71%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, J = 7.9, 1.2 Hz, 2H), 7.48−7.44 (m, 1H), 7.39−7.35 (m, 2H), 1.35 (s, 12H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 134.7, 131.2, 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) calcd for $C_{12}H_{17}BO_2$ [M] 204.13, found 204.20.

*4,4,5,5-Tetramethyl-2-o-tolyl-1,3,2-dioxaborolane (**4ca**):*[28] colorless oil (39.2 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80−7.77 (m, 1H), 7.36−7.31 (m, 1H), 7.20−7.16 (m, 2H), 2.56 (s, 3H), 1.36 (s, 12H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.8, 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, 761, 730, 662; GC−MS (EI) calcd for $C_{13}H_{19}BO_2$ [M] 218.15, found 218.16.

*2-(3,4-Dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4da**):*[29] colorless oil (30.1 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.1, 135.91, 135.85, 132.4, 129.1, 83.6, 24.8, 20.0, 19.4; ATR-FTIR (cm^{-1}) 2965, 2933, 2872, 1513, 1466, 1384, 1364, 1262, 1125, 1052, 886, 812, 739; GC−MS (EI) calcd for $C_{14}H_{21}BO_2$ [M] 232.16, found 232.22.

*2-Mesityl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4ea**):*[28] colorless oil (40.1 mg (81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 (s, 2H), 2.39 (s, 6H), 2.26 (s, 3H), 1.39 (s, 12H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.2, 138.9, 127.5, 83.5, 25.0, 22.2, 21.3; ATR-FTIR (cm^{-1}) 2978, 2924, 1610, 1439, 1371, 1333, 1300, 1145, 1067, 855, 672; HRMS m/z (ESI) calcd for $C_{15}H_{24}BO_2$ (M + H)$^+$ 247.1864, found 247.1867.

*2-(3-tert-Butylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4fa**):*[30] white solid (37.7 mg, 73%); ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) 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, 1398, 1364, 1323,

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1266, 1144, 1090, 859, 744, 660; GC−MS (EI) calcd for $C_{16}H_{25}BO_2$ [M] 260.19, found 260.30.

2-(2-(Benzyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4ga**): white solid (34.3 mg, 55%); ^{1}H NMR (400 MHz, $CDCl_3$) 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), 5.14 (s, 2H), 1.38 (s, 12H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 163.2, 137.6, 136.7, 132.5, 128.1, 127.3, 126.7, 120.6, 112.0, 83.4, 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) calcd for $C_{19}H_{24}BO_3$ $(M + H)^+$ 311.1813, found 311.1821.

2-(3-(Methoxymethoxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4ha**): white solid (42.3 mg, 80%); ^{1}H NMR (300 MHz, $CDCl_3$) 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, 12H); ^{13}C{^{1}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 $C_{14}H_{22}BO_4$ $(M + H)^+$ 265.1606, found 265.1607.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (**4ia**):[31] white solid (21.4 mg, 48%); ^{1}H 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}C{^{1}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 $C_{12}H_{17}BO_3$ [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] white solid (48.0 mg, 84%); ^{1}H 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}C{^{1}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 $C_{16}H_{23}BNO_3$ $(M + H)^+$ 288.1766, found 288.1768.

tert-Butyl (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenyl)carbamate (**4ka**):[27] white solid (54.2 mg, 85%); ^{1}H 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}C{^{1}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 $C_{17}H_{26}BNO_4Na$ $(M + Na)^+$ 342.1847, found 342.1853.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (**4la**):[31] white solid (26.8 mg, 62%); ^{1}H NMR (400 MHz, CDCl3) δ 7.62 (d, J = 8.4 Hz, 2H), 6.66 (d, J = 8.4 Hz, 2H), 1.32 (s, 12H); ^{13}C{^{1}H} NMR (101 MHz, CDCl3) 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 $C_{12}H_{18}BNO_2Na$ $(M + Na)^+$ 242.1323, found 242.1329.

2-(4-Fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4ma**):[27] colorless oil (22.6 mg, 51%); ^{1}H 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}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.08 (d, J = 251.5 Hz), 136.96 (d, J = 9.1 Hz), 114.82 (d, J = 20.2 Hz), 83.89, 24.84; ATR-FTIR (cm^{-1}) 2976, 2923, 2853, 2364, 1633, 1365, 1145, 802, 523; GC−MS (EI) calcd for $C_{12}H_{16}BFO_2$ [M] 222.12, found 222.16.

N-Methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-benzamide (**4na**): white solid (33.2 mg, 63%); ^{1}H 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}C{^{1}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 $C_{14}H_{21}BNO_3$ $(M + H)^+$ 262.1609, found 262.1617.

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic acid (**4oa**): white solid (26.3 mg, 53%); ^{1}H 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}C{^{1}H} NMR (101 MHz, $CDCl_3$) 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 $C_{13}H_{17}BO_4Na$ $(M + Na)^+$ 271.1112, found 271.1120.

2-(Dibenzo[b,d]furan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4pa**): white solid (50.3 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) 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 $C_{18}H_{20}BO_3$ $(M + H)^+$ 295.1500, found 295.1506.

9-Ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (**4qa**): white solid (60.4 mg, 93%); ^{1}H 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); ^{13}C{^{1}H} 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 $C_{20}H_{25}BNO_2$ $(M + H)^+$ 322.1973, found 322.1979.

Isopentyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-benzoate (**4ra**): colorless oil (41.7 mg, 66%); ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): 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 $C_{18}H_{28}BO_4(M + H)^+$ 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%). ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) 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 $C_{15}H_{23}BNO_4$ $(M + H)^+$ 292.1715, found 292.1718.

1-Phenyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenyl)diazene (**4ta**):[31] yellow solid (24.6 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) 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 $C_{18}H_{22}BN_2O_2$ $(M + H)^+$ 309.1769, found 309.1777.

Bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-methane (**4ua**):[34] white solid (60.1 mg, 72%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.0 Hz, 4H), 7.20 (d, J = 8.0 Hz, 4H), 4.02 (s, 2H), 1.34 (s, 24H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.1, 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, 858, 736, 660; GC−MS (EI) calcd for $C_{25}H_{34}B_2O_4$ [M] 420.26, found 420.40.

2,2′-(Oxybis(4,1-phenylene))bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**4va**): white solid (70.3 mg, 83%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84−7.75 (m, 4H), 7.05−6.96 (m, 4H), 1.34 (s, 24H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.5, 136.6, 118.2, 83.8, 24.8; ATR-FTIR (cm^{-1}) 2898, 2922, 1638, 1478, 1367, 1343, 1138, 1278, 1015, 947; HRMS m/z (ESI) calcd for $C_{24}H_{33}B_2O_5$ $(M + H)^+$ $C_{25}H_{34}B_2O_4$ [M] 423.2509, found 423.2513.

2,2′-((Phenylmethylene)bis(4,1-phenylene))bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**4wa**): white solid (94.2 mg, 95%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.0 Hz, 4H), 7.29−7.17 (m, 3H), 7.10 (dd, J = 17.5, 7.6 Hz, 6H), 5.56 (s, 1H), 1.32 (s, 24H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) 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, 1608, 1399, 1361, 1323, 1271, 1144, 1089, 1021, 962, 858, 701; HRMS m/z (ESI) calcd for $C_{31}H_{39}B_2O_4$ $(M + H)^+$ 497.3029, found 497.3035.

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*2,2′-((9H-Fluorene-9,9-diyl)bis(4,1-phenylene))bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4xa**):* white solid (107.2 mg, 94%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 7.5 Hz, 2H), 7.67 (d, J = 8.2 Hz, 4H), 7.34 (dd, J = 13.1, 7.5 Hz, 4H), 7.22 (ddd, J = 16.8, 9.2, 4.5 Hz, 6H), 1.29 (s, 24H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 150.7, 149.0, 140.2, 134.7, 127.8, 127.51, 127.48, 126.1, 120.1, 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, 746, 660, 520, 443; HRMS m/z (ESI) calcd for $C_{37}H_{42}B_2O_4$ $(M + H)^+$ 571.3185, found 571.3188.

*2-(4-Methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (**4ab**):*[35] white solid (32.3 mg, 73%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81−7.70 (m, 2H), 6.94−6.86 (m, 2H), 3.83 (s, 3H), 3.76 (s, 4H), 1.02 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.7, 135.5, 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; HRMS m/z (ESI) calcd for $C_{12}H_{18}BO_3$ $(M + H)^+$ 221.1344, found 221.1338.

*2-(4-Methoxyphenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane (**4ac**):*[36] colorless oil (43.1 mg, 92%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.6 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 4.33 (dqd, J = 12.3, 6.2, 3.0 Hz, 1H), 3.82 (s, 3H), 1.85 (dd, J = 13.9, 2.9 Hz, 1H), 1.60 (dd, J = 15.0, 3.2 Hz, 1H), 1.36 (dd, J = 9.7, 5.6 Hz, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.5, 135.4, 113.0, 70.8, 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, 1107, 1032, 834, 805, 768, 649; HRMS m/z (ESI) calcd for $C_{13}H_{20}BO_3$ $(M + H)^+$ 235.1500, found 235.1500.

*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 mmol), $Ni(COD)_2$ (3.3 mg, 6 mol %), ICy HCl (6.5 mg, 12 mol %), and NaO^{t}Bu (38.4 mg, 200 mol %) in toluene/2-ethoxyethanol (0.5/0.5 mL) at 50 °C under Ar after column chromatography on silica (ethyl acetate/petroleum ether = 1:100) afforded 33.1 mg (76%) of **7aa** as colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) 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 Hz, 1H), 2.29 (s, 2H), 1.23 (s, 12H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 138.7, 129.0, 128.3, 124.8, 83.4, 24.7; ATR-FTIR (cm^{-1}) 2966, 2934, 1494, 1466, 1452, 1385, 1367, 1120, 1051, 882, 727, 700; GC−MS (EI) calcd for $C_{13}H_{19}BO_2$ [M] 218.15, found 218.15.

*4,4,5,5-Tetramethyl-2-(3-methylbenzyl)-1,3,2-dioxaborolane (**7ba**):*[38] colorless oil (33.6 mg, 71%); 1H NMR (400 MHz, $CDCl_3$) 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); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) 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, 1451, 1333, 1272, 1145, 968, 877, 848, 781, 740, 701, 674; HRMS m/z (ESI) calcd for $C_{14}H_{22}BO_2$ $(M + H)^+$ 233.1707, found 233.1708.

*2-(2,3-Dimethylbenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**7ca**):* colorless oil (35.6 mg, 72%); ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) 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; HRMS m/z (ESI) calcd for $C_{15}H_{24}BO_2$ $(M + H)^+$ 247.1864, found 247.1867.

*2-(2-Methoxybenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**7da**):*[38] colorless oil (36.1 mg, 73%); ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) 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, 1464, 1353, 1328, 1244, 1144, 1030, 969, 849, 754, 674; HRMS m/z (ESI) calcd for $C_{14}H_{22}BO_3$ $(M + H)^+$ 249.1657, found 249.1661.

*2-(2-Methoxybenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**7ea**):* colorless oil (48.8 mg, 88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80−6.65 (m, 3H), 3.84 (s, 3H), 3.83 (s, 3H), 2.22 (s, 2H), 1.23 (s, 12H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.6, 146.4, 130.9 120.7, 112.4, 111.3, 83.3, 55.9, 55.7, 24.7; ATR-FTIR (cm^{-1}) 2977, 2936, 2839, 1681, 1591, 1514, 1458, 1375, 1337, 1268, 1141, 1026, 860, 809, 763, 640; HRMS m/z (ESI) calcd for $C_{15}H_{24}BO_4$ $(M + H)^+$ 279.1762, found 279.1766.

*2-(Benzo[d][1,3]dioxol-5-ylmethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**7fa**):* colorless oil (47.3 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) 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, 1447, 1376, 1252, 1148, 1099, 1039, 930, 851, 810, 674; HRMS m/z (ESI) calcd for $C_{14}H_{20}BO_4$ $(M + H)^+$ 263.1449, found 263.1450.

*2-(2,4-Difluorobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**7ga**):* colorless oil (35.7 mg, 70%); ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.8 (dd, J = 245.4, 12.1 Hz), 160.6 (dd, J = 246.4, 11.6 Hz), 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), 103.3 (t, J = 25.3 Hz), 83.6, 24.6; ATR-FTIR (cm^{-1}) 2980, 2929, 2234, 1601, 1504, 1353, 1273, 1212, 1143, 966, 848; HRMS m/z (ESI) calcd for $C_{13}H_{18}BF_2O_2(M + H)^+$ 255.1362, found 255.1368.

*4,4,5,5-Tetramethyl-2-(naphthalen-1-ylmethyl)-1,3,2-dioxaborolane (**7ha**):*[37] colorless oil (39.0 mg, 73%). ^{1}H NMR (300 MHz, $CDCl_3$) 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 (m, 2H), 2.71 (s, 2H), 1.21 (s, 12H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 135.6, 133.7, 132.4, 128.5, 126.4, 125.7, 125.33, 125.29, 124.5, 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 $C_{17}H_{22}BO_2$ $(M + H)^+$ 269.1707, found 269.1709.

*4,4,5,5-Tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane (**7ia**):*[39] colorless oil (36.7 mg, 79%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24−7.11 (m, 4H), 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); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.9, 128.3, 127.8, 125.1, 83.3, 24.60, 24.55, 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 $C_{14}H_{21}BO_3$ [M] 232.16, found 232.19.

*4,4,5,5-Tetramethyl-2-(1-o-tolylethyl)-1,3,2-dioxaborolane (**7ja**):* colorless oil (37.2 mg, 75%); ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.3, 135.6, 130.0, 127.1, 126.0, 125.0, 83.2, 24.63, 24.59, 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 $C_{15}H_{23}BO_2$ [M] 246.18, found 247.21.

*2-(1-(4-Methoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**7ka**):*[39] colorless oil (47.1 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 157.2, 137.0, 128.6, 113.7, 83.2, 55.1, 24.59, 24.55, 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 $C_{15}H_{24}BO_3$ $(M + H)^+$ 263.1813, found 263.1817.

*2-(1-(4-Fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**7la**):*[39] colorless oil (38.3 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.8 (d, J = 243.4 Hz), 140.5 (d, J = 3.1 Hz), 129.0 (d, J = 7.6 Hz), 115.0 (d, J = 21.2 Hz), 83.3, 24.6, 24.5, 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 $C_{14}H_{20}BFO_2$ [M] 250.15, found 251.2.

*4,4,5,5-Tetramethyl-2-(1-(naphthalen-1-yl)ethyl)-1,3,2-dioxaborolane (**7ma**):*[40] colorless oil (41.3 mg, 73%); ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.4, 133.9, 132.0, 128.7, 125.8, 125.3, 125.2, 124.2, 124.0, 83.4, 24.7, 24.5, 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 $C_{18}H_{24}BO_2$ $(M + H)^+$ 283.1864, found 283.1867.

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*4,4,5,5-Tetramethyl-2-(1,2,3,4-tetrahydronaphthalen-1-yl)-1,3,2-dioxaborolane (**7na**):*[39] colorless oil (37.9 mg, 74%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20−7.00 (m, 4H), 2.80−2.75 (m, 2H), 2.75−2.55 (m, 1H), 1.95−1.85 (m, 3H), 1.74−1.72 (m, 1H), 1.25 (s, 12H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 137.6, 136.6, 129.3, 129.3, 125.2, 124.7, 83.2, 29.7, 24.7, 24.6, 22.6; ATR-FTIR (cm^{-1}) 2927, 2928, 1684, 1452, 1382, 1324, 1145, 852, 740, 672; HRMS *m*/*z* (ESI) calcd for $C_{16}H_{24}BO_2$ $(M + H)^+$ 259.1864, found 259.1869.

*4,4,5,5-Tetramethyl-2-(1-phenyl-2-p-tolylethyl)-1,3,2-dioxaborolane (**7oa**):* colorless oil (46.7 mg, 72%); ^{1}H NMR (400 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, *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); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 142.6, 138.6, 135.0, 128.7, 128.4, 128.3, 125.3, 83.3, 38.3, 24.6, 24.5, 21.0; ATR-FTIR (cm^{-1}) 2978, 2925, 1595, 1451, 1360, 1326, 1240, 1142, 1088, 967, 855, 700; HRMS *m*/*z* (ESI) calcd for $C_{21}H_{28}BO_2$ $(M + H)^+$ 322.2177, found 322.2179.

*Methyl 3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-propanoate (**7pa**):*[41] colorless oil (18.2 mg, 31%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.19 (m, 4H), 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), 1.22 (s, 6H), 1.17 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 173.8, 141.3, 128.5, 128.2, 125.7, 83.6, 51.6, 37.1, 24.54, 24.45; ATR-FTIR (cm^{-1}) 3061, 2977, 1736, 1637, 1371, 1324, 1261, 1171, 1140, 1050, 973, 846,766,701; HRMS *m*/*z* (ESI) calcd for $C_{16}H_{23}BO_4Na$ $(M + Na)^+$ 313.1582, found 313.1589.

*4,4,5,5-Tetramethyl-2-(2-phenylpropan-2-yl)-1,3,2-dioxaborolane (**7qa**):*[37] colorless oil (36.6 mg, 74%); ^{1}H NMR (400 MHz, $CDCl_3$) 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); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 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* (ESI) calcd for $C_{15}H_{24}BO_2$ $(M + H)^+$ 247.1864, found 247.1864.

*4,4,5,5-Tetramethyl-2-(2-phenylbutan-2-yl)-1,3,2-dioxaborolane (**7ra**):*[42] colorless oil (31.4 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.27 (m, 3H), 7.21−7.08 (m, 2H), 1.87 (dq, *J* = 14.7, 7.4 Hz, 1H), 1.70 (dq, *J* = 14.6, 7.4 Hz, 1H), 1.32 (s, 3H), 1.21 (s, 6H), 1.20 (s, 6H), 0.82 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 147.3, 128.0, 127.5, 126.9, 125.0, 83.3, 31.9, 24.6, 24.6, 21.0, 10.0; ATR-FTIR (cm^{-1}): 2965, 2925, 1637, 1461, 1372, 1349, 1313, 1261, 1142, 1097, 1026, 801, 700; HRMS *m*/*z* (ESI) calcd for $C_{12}H_{26}BO_2$ $(M + H)^+$ 261.2020, found 261.2022.

*4,4,5,5-Tetramethyl-2-(1-phenylcyclopentyl)-1,3,2-dioxaborolane (**7sa**):* white solid (33.9 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31−7.22 (m, 4H), 7.14−7.07 (m, 1H), 2.32 (d, *J* = 8.2 Hz, 2H), 1.78−1.59 (m, 6H), 1.13 (s, 12H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 147.1, 127.9, 127.0, 124.7, 83.3, 35.2, 24.6, 24.4; ATR-FTIR (cm^{-1}): 2973, 2864, 1446, 1374, 1354, 1312, 1111, 748, 700; HRMS *m*/*z* (ESI) calcd for $C_{17}H_{26}BO_2$ $(M + H)^+$ 273.2020, found 273.2026.

*4,4,5,5-Tetramethyl-2-(1-phenylcyclopropyl)-1,3,2-dioxaborolane (**7ta**):*[43] colorless oil (24.2 mg, 50%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.19 (m, 4H), 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); $^{13}C\{^1H\}$ NMR (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, 838, 737, 655; HRMS *m*/*z* (ESI) calcd for $C_{15}H_{22}BO_2$ $(M + H)^+$ 244.1635, found 244.1640.

*N-(2,5-Dimethoxybenzyl)-N-(2-phenoxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetamide (**10**):*[44] white solid (90.2 mg, 84%); ^{1}H 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, 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), 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); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) 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, 55.7, 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] colorless oil (19.4 mg, 35%); ^{1}H NMR (400 MHz, $CDCl_3$) 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); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) 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 $C_{16}H_{26}BNO_2$ [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**):* colorless oil (24.5 mg, 42%); ^{1}H NMR (400 MHz, $CDCl_3$) 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); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) 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 $C_{17}H_{28}BNO_2$ [M] 289.22, found 289.32.

*2-(Cyclopropyl(phenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**15**):* colorless oil (28.8 mg, 55%); ^{1}H NMR (400 MHz, $CDCl_3$) 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); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 143.1, 128.4, 128.2, 125.2, 83.3, 24.60, 24.57, 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 $C_{16}H_{24}BO_2$ $(M + H)^+$ 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.5b02557.

NMR spectra of all compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: shiz@nju.edu.cn.

Notes

The authors declare no competing financial interest.

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