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2-[(Neopentyl glycolato)boryl]phenyl Triflates and Halides for Fluoride Ion-Mediated Generation of Functionalized Benzynes

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Dedicated to Prof. Stephen L. Buchwald on the occasion of his 60th birthday.

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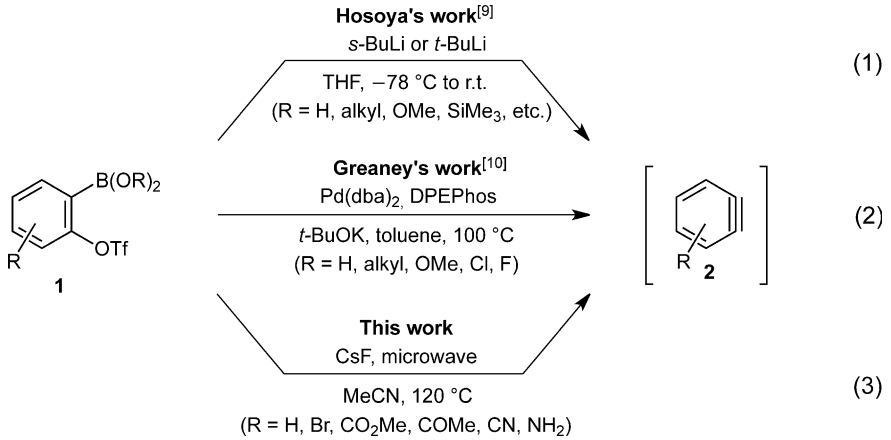
Abstract: 2-[(Neopentyl glycolato)boryl]phenyl trifluoromethanesulfonates (triflates) and halides have been developed as new benzyne precursors, which generate benzynes at 120 °C in the presence of a fluoride ion. There are two major features of these types of precursors. First, they generate benzynes bearing various reactive functional groups, such as carbonyl, cyano, bromo, and primary amino groups. Second, these precursors were directly synthesized through either the palladium-catalyzed Miyaura borylation of 2-iodophenol derivatives or *ortho*-selective iodination of the corresponding boronic acids as key steps without using any protecting groups. The *in-situ*-generated benzynes underwent [4+2], (3+2), and [2+2] cycloadditions to give the benzo-fused multicyclic compounds while maintaining such functional groups. In particular, 4-aminobenzyne was generated for the first time and underwent the Diels–Alder reaction with the free primary amino group remaining intact.

Keywords: benzynes; boronic acid esters; borylation; Diels–Alder reaction; microwave heating

Introduction

Reactions of benzynes are among the oldest and most potent multi-bond-forming processes for the synthesis of polysubstituted benzenes.[1,2] A wide variety of benzyne precursors has been developed and expanded the usefulness of benzyne reactions by providing diverse arynophiles.[3] However, the generation of "functionalized benzynes" still remains a challenge.[4] This is because most of the well-known precursors, such as 2-halophenyl trifluoromethanesulfonates (triflates)[3c,4i] and 2-(trimethylsilyl)phenyl triflates,[3b,4g] originally required highly reactive *n*-BuLi for the generation of benzynes from these precursors and/or the preparation of the precursors themselves, which resulted in poor compatibility with reactive functional groups, such as carbonyl and halo groups. Other synthetic methods for the benzyne precursors have involved [4+2] cycloadditions to construct the benzene rings; however, these required many steps, and the substituents of the benzenes were limited and relied strongly on the availability of the cycloaddition substrates.[4b,e,f]

Among the reported benzyne precursors, 2-(trimethylsilyl)phenyl triflates[5] have gained a high reputation among the most widely used precursors because benzynes can be generated from them under fluoride ion-mediated mild conditions that have led to the development of a huge variety of new benzyne reactions in the past few decades.[1,3b] However, the regioselective introduction of functional groups to 2-(trimethylsilyl)phenyl triflate was not possible,[4f] and the syntheses of these compounds from commercially available materials required lengthy processes.[4f,g] Therefore, for further extension of the synthetic utility of benzynes, the development of new benzyne precursors that meet the following three requirements has been highly desired: (i) generation of benzynes *via* the treatment of a fluoride ion, (ii) preparation of precursors under milder reaction conditions under which many reactive functional groups can be tolerated, and (iii) ready availability of the precursors in fewer steps.



Scheme 1. Previously reported generation of benzynes **2** from 2-borylphenyl triflates **1**, and this work.

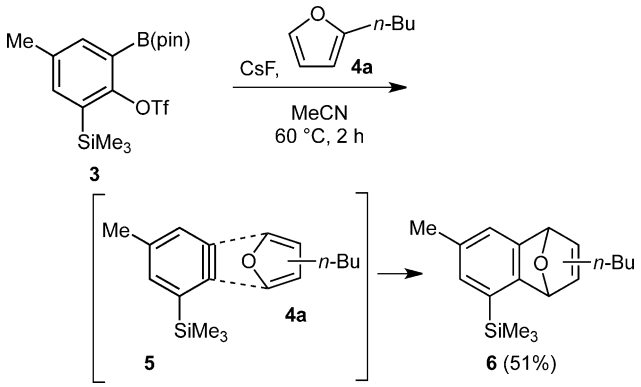
In this context, 2-borylphenyl triflates **1** can be good candidates for such new precursors because **1** would be easily synthesized through either stoichiometric[6] or catalytic[7] aromatic C–B bond-forming reactions in which many functional groups would be tolerated. More importantly, our group discovered that 3-(trimethylsilyl)benzyne was generated from 2-[(pinacolato)boryl]-6-(trimethylsilyl)phenyl triflate using a fluoride ion (*vide infra*),[8a] which was the first example of benzyne generation from 2-borylphenyl triflates **1**. Hosoya et al. then reported the generation of benzynes **2** from **1** *via* treatment with alkyllithium at −78 °C followed by warming to room temperature [Scheme 1, Eq. (1)].[9] The thus-generated **2** reacted with various arynophiles; however, the generation of benzynes with reactive functional groups was not reported, probably due to the need for *t*-BuLi or *s*-BuLi. Greaney et al. reported the palladium-catalyzed [2+2+2] cycloaddition of **2**, which was generated from **1** using $Pd(dba)_2$, *t*-BuOK, and DPEPhos in toluene at 100 °C [Scheme 1, Eq. (2)].[10] The examples were limited to this particular trimerization of benzynes possessing relatively stable substituents such as methoxy, chloro, and fluoro groups.

In this paper, we report the generation of benzynes **2**, bearing reactive functional groups, such as bromo, ester, carbonyl, cyano, and amino groups, from 2-[(neopentyl glycolato)boryl]phenyl triflates **1** using a fluoride ion under microwave heating conditions [Scheme 1, Eq. (3)]. One of the most important points in this work is the finding that the (neopentyl glycolato)boryl [B(neop)] group was the best substituent among the various boryl groups we have examined for both the generation of benzynes from **1** and the preparation of **1**.

Results and Discussion

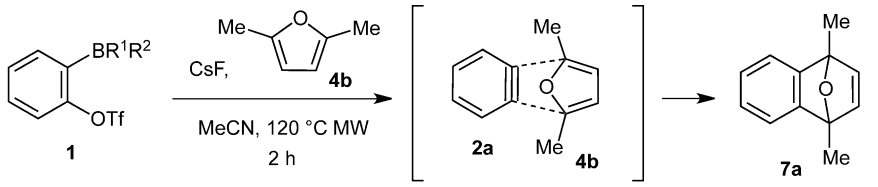
As mentioned above, we incidentally discovered the generation of 3-(trimethylsilyl)benzyne **5** from 2-[(pinacolato)boryl]-6-(trimethylsilyl)phenyl triflate **3** using CsF in MeCN at 60 °C in the presence of furan **4a** (Scheme 2)[8a] or amine.[8b] Although we originally intended to generate 3-[(pinacolato)boryl]benzyne, the fluoride ion preferentially attacked the boron of **3**, rather than the silicon, to generate **5**. These results encouraged us to develop a new method for benzyne generation using the combination of 2-borylphenyl triflates **1** and fluoride ions.

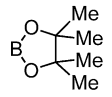
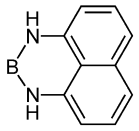
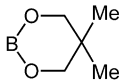
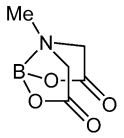
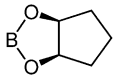
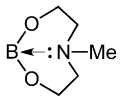
We preliminarily examined the feasibility of the generation of benzyne **2a** from a simplified precursor, 2-[(pinacolato)boryl]phenyl triflate (**1a**), by trapping with furan **4b** to afford Diels–Alder adduct **7a**. Under reaction conditions (2.0 equiv. of CsF, MeCN, 60 °C) similar to those of Scheme 2, the benzyne generation was extremely slow, and gave only a trace amount of **7a** even after 24 h (Table 1, entry 1). After investigation of the reaction temperature, we found that the benzyne generation was significantly accelerated by microwave heating at 120 °C, giving **7a** in 56% yield after 2 h (entry 2). Then, we examined other boron substituents (**1b**–**1i**) for more efficient generation of **2a** under the same reaction conditions (entries 3–11) and found that 2-[(neopentyl glycolato)boryl]phenyl triflate (**1b**) provided the best yield of **7a** (85%,



Scheme 2. Our initial findings on benzyne generation from 2-boryl-6-silylphenyl triflate **3**.[8a]

Table 1. Optimization of boryl groups for benzyne generation from 2-borylphenyl triflates **1a–1i**.[a]



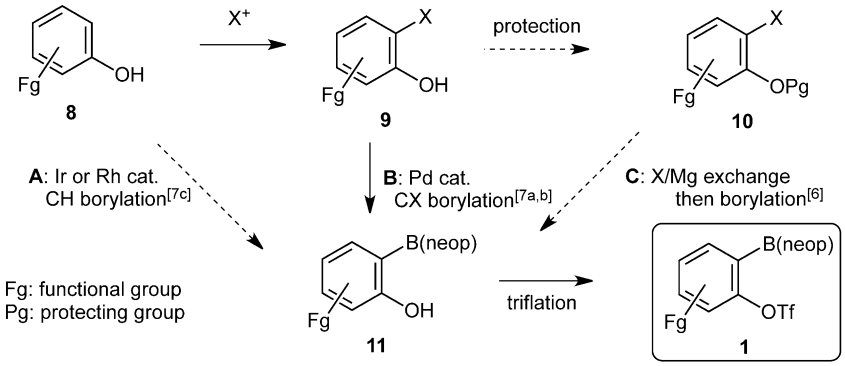
Entry	BR^1R^2	1	7a [%][b]	Entry	BR^1R^2	1	7a [%][b]
1		**1a**	3[c]	7		**1e**	15
2			56				
3		**1b**	61[c]	8		**1f**	32
4	: B(neop)		85 (84)[d]				
5		**1c**	10	9		**1g**	14
6		**1d**	22	10	BF_3K	**1h**	0
				11	$B(OH)_2$	**1i**	2

[a] *Reaction conditions:* **1** (1.0 equiv.), **4b** (10 equiv.), CsF (2.0 equiv.) in MeCN (0.10 M) at 120 °C using microwaves for 2 h unless otherwise noted.
[b] The yield was determined *via* analysis of the ^{1}H NMR spectra of crude products using 1,4-dimethoxybenzene as an internal standard.
[c] The reaction was performed at 60 °C for 24 h using an oil bath.
[d] Isolated yield of **7a** is shown in parentheses.

entry 4). Other 2-borylphenyl triflates **1c–1i** gave poor yields of **7a** (0–32%, entries 5–11). The better reactivity of **1b** than **1a** was also proven by heating in an oil bath at 60 °C for 24 h (comparison of entries 1 and 3). These results indicated that the (neopentyl glycolato)boryl [B(neop)] group should be one of the best substituents for the fluoride ion-mediated generation of benzynes from **1**.

Next, we planned three synthetic routes to functionalized benzyne precursors **1**, as shown in Scheme 3. The first route included the regioselective C–H borylation of phenol derivatives **8** reported by Hartwig et al.[7c] (route A). Although this route was the shortest, the compatibility with various functional groups was unknown, and the installation of B(neop) instead of a (pinacolato)boryl [B(pin)] group might not have been possible under the reported reaction conditions.[11] The second route was through Miyaura borylation of 2-halophenols **9** (route B).[7a] This route was thought to be promising because Wang et al. had already achieved similar borylations of hindered and functionalized 2-halophenols.[7b,12] The third route employed halogen-metal exchange using *i*-PrMgCl followed by borylation under non-cryogenic conditions (route C).[6b,c] This approach was also a good candidate owing to its functional group compatibility and the high reactivity of the intermediate Grignard reagents toward $B(OR)_3$.[13] However, this route required protection of the hydroxy group of **9** and therefore required more steps for the synthesis of **1** than did the others. Accordingly, we decided to synthesize **1** from **9** through route B.

The syntheses of several precursors **1** through route B are shown in Table 2. Notably, the key Pd-catalyzed Miyaura borylation using $B_2(neop)_2$ of all 2-iodophenol derivatives **9b–9e** bearing methoxycarbonyl, acetyl, cyano, and bromo groups provided the corresponding 2-[(neop)boryl]phenols **11b–11e** in moderate to good yields under the standard reaction conditions without loss of the functional groups (entries 2–5).[7b,12] The major by-products of this transformation were proto-deiodinated phenols. To our delight, the



Scheme 3. Synthetic strategies for functionalized benzyne precursors **1**.

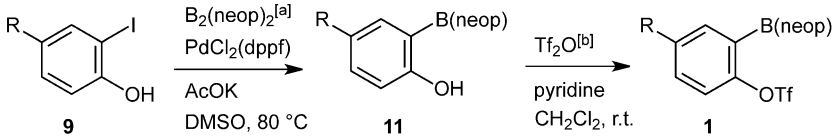
final triflation reactions of **11b–11e** using Tf_2O with pyridine also worked very well, affording functionalized benzyne precursors **1b** and **1j–1m**.

The reaction conditions for the generation of benzyne **2b** bearing a methoxycarbonyl group were optimized as a typical case for the functionalized benzynes, which was monitored by the Diels–Alder reaction with furan **4b** (Table 3). Under the microwave heating conditions, several fluoride sources and solvents were tested; it was found that CsF in MeCN gave the best yield of **7b** (79%, entries 1–7). The best reaction temperature was 120 °C among our several studies (entries 6, 10, 11, and 13). A similar 72% yield of **7b** was obtained under the same reaction conditions in a sealed Schlenk flask heated at 120 °C in an oil bath without microwave irradiation (entry 12).

It is worth noting that the yield of **7b** gradually increased from 45% (0.25 h) to 79% (1 h) over time, although **1j** was completely consumed within 0.25 h (Table 3, entries 6–9). These results suggested that a relatively stable boronate **12** was plausibly generated (Figure 1) and gradually produced **2b** while being heated at 120 °C.

The most common side reaction of this benzyne generation was the protodeborylation of **1j** to produce triflate **14** in 8–25% yield. The yield of **14** clearly increased and that of **7b** decreased when hygroscopic CsF was used without drying prior to use. The protodeborylation probably took place through the formation of boronate intermediate **13**, generated by the addition of H_2O to the boron atom ahead of a fluoride ion, followed by the intramolecular dissociation of **13** to produce **14** (Scheme 4).

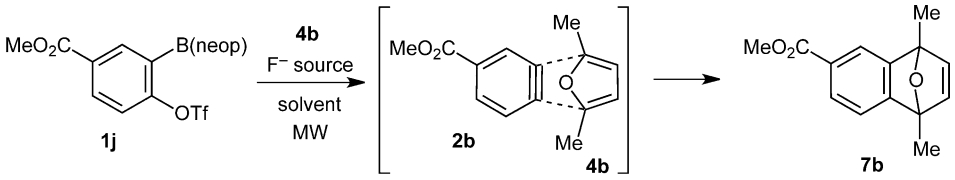
Table 2. Syntheses of various 2-[(neop)boryl]phenyl triflates **1**.



Entry	9	R	11	Yield of 11 [%][c]	1	Yield of 1 [%][c]
1	**9a**	H	**11a**	-	**1b**	95
2	**9b**	CO_2Me	**11b**	68	**1j**	93
3	**9c**	COMe	**11c**	41	**1k**	quant.
4	**9d**	CN	**11d**	30	**1l**	90
5	**9e**	Br	**11e**	62	**1m**	30[d]

[a] *Reaction conditions:* **9** (1.0 equiv.), $B_2(neop)_2$ (1.2 equiv.), $PdCl_2(dppf)$ (3.0 mol%), AcOK (3.0 equiv.) in DMSO (0.13 M) at 80 °C.
[b] *Reaction conditions:* **11** (1.0 equiv.), Tf_2O (1.5 equiv.), pyridine (3.0 equiv.) in CH_2Cl_2 (0.20 M) at room temperature.
[c] Isolated yield.
[d] Overall isolated yield from **9e**.

Table 3. Optimization of reaction conditions for benzyne generation from 2-[(neop)boryl]phenyl triflate **1j**.[a]



Entry	Solvent	F⁻ source	Temperature [°C]	Time [h]	Yield [%][b]
1	THF	KF, 18-c-6[c]	120	2	32
2	THF	$Bu_4NPh_3SiF_2$	120	2	71
3	THF	Bu_4NF	120	2	32
4	THF	CsF	120	2	19
5	MeCN	CsF	120	2	30[d]
6	MeCN	CsF	120	2	76 (67)[e]
7	MeCN	CsF	120	1	79 (67)[e]
8	MeCN	CsF	120	0.5	68
9	MeCN	CsF	120	0.25	45
10	MeCN	CsF	150	1	65
11	MeCN	CsF	100	1	57
12	MeCN	CsF	120[f]	2	72 (60)[e]
13	MeCN	CsF	60[f]	24	50

[a] *Reaction conditions:* **1j** (1.0 equiv.), **4b** (10 equiv.), F^- source (2.0 equiv.) in solvent (0.10 M) using microwaves.
[b] The yield of **7b** was determined *via* analysis of the ^1H NMR spectra of crude products using 1,1,2,2-tetrachloroethane as an internal standard.
[c] 18-c-6 = 18-crown-6.
[d] 3.0 equiv. of **4b** were used.
[e] Isolated yield of **7b** is shown in parenthesis.
[f] Oil bath heating.

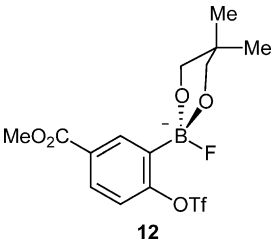
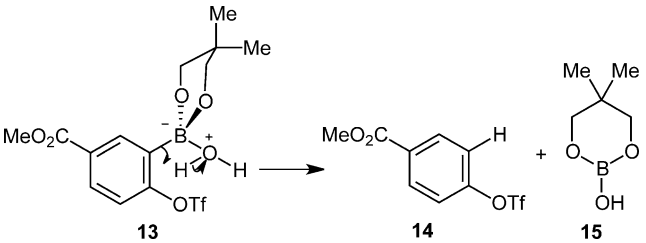


Figure 1. Proposed structure of boronate intermediate **12**.

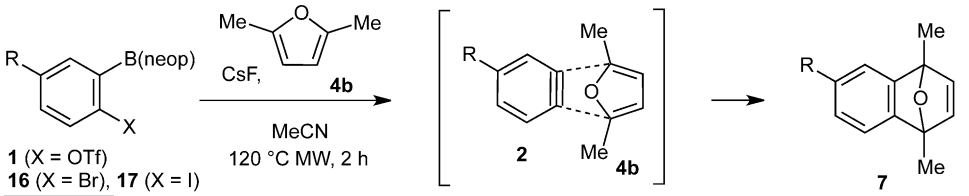


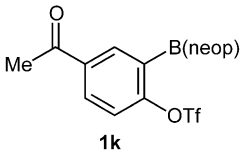
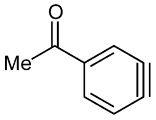
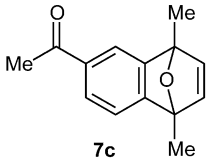
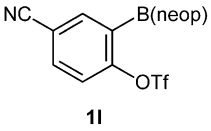
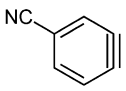
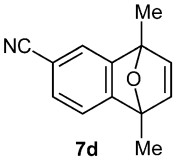
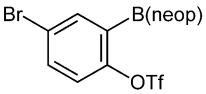
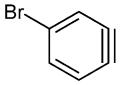
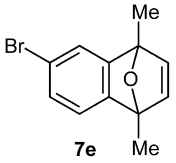
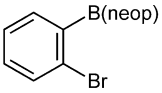
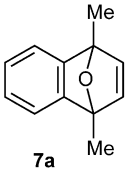
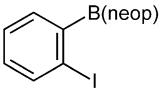
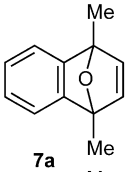
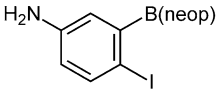
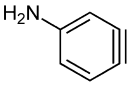
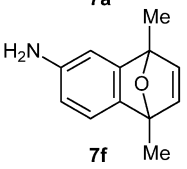
Scheme 4. A plausible mechanism for the formation of by-product **14**.

The developed new method for benzyne generation was found to be similarly effective for other functionalized precursors **1k**–**1m**, and Diels–Alder adducts **7c**–**7e** bearing acetyl, cyano, and bromo groups were obtained in 50–69% isolated yields (Table 4, entries 1–3). These results clearly indicated that 4-acetylbenzyne **2c**, 4-cyanobenzyne **2d**, and 4-bromobenzyne **2e** were generated with these reactive functional groups intact.

Benzyne **2a** could also be generated from 2-halophenylboronic acid neopentyl glycol esters **16** and **17a** under the same reaction conditions (entries 4 and

Table 4. Diels–Alder reactions of benzynes **2a** and **2c**–**2f**, generated from **1k**–**1m**, **16**, **17a**, and **17b** with 2,5-dimethylfuran (**4b**).[a]



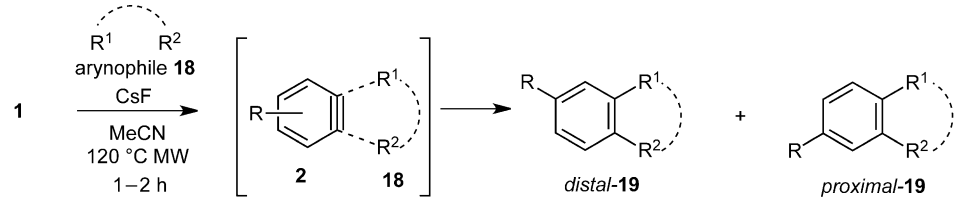
Entry	1, 16, 17	2	7	Yield [%][b]
1	 **1k**	 **2c**	 **7c**	77 (50)[c]
2	 **1l**	 **2d**	 **7d**	70 (64)[c]
3[d]	 **1m**	 **2e**	 **7e**	82 (69)[c]
4[d]	 **16**	 **2a**	 **7a**	86
5[d]	 **17a**	 **2a**	 **7a**	67 (49)[c]
6	 **17b**	 **2f**	 **7f**	65 (38)[c]

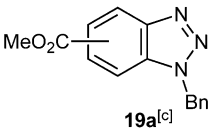
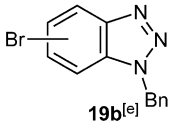
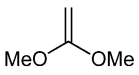
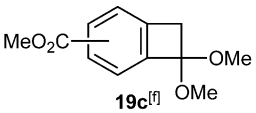
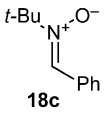
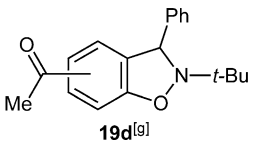
[a] *Reaction conditions:* **1** (1.0 equiv.), **4b** (10 equiv.), CsF (2.0 equiv.) in MeCN (0.10 M) at 120 °C using microwaves for 2 h.
[b] The yield of **7** was determined *via* analysis of the ^{1}H NMR spectra of crude products using 1,1,2,2-tetrachloroethane as an internal standard.
[c] Isolated yield of **7** in parentheses.
[d] Reaction was performed for 1 h.

5).[14] This discovery enabled the generation of 4-aminobenzyne **2f** from **17b**, which was effectively prepared *via* the *ortho*-selective iodination of boronic acid[15] followed by esterification. The *in-situ*-generated **2f** underwent the Diels–Alder reaction with **4b** to afford adduct **7f** (entry 6), and this is the first example of an experimentally generated benzyne bearing a free amino group.[16]

The reaction scope was explored with several arynophiles **18** in Table 5. Functionalized benzynes **2b**, **2c** and **2e**, generated from **1j**, **1k** and **1m** underwent (3+2) and [2+2] cycloaddition reactions with benzyl azide

Table 5. Reaction scope of benzynes **2b**, **2c**, and **2e**, generated from **1j**, **1k** and **1m**, with arynophiles **18a**–**18c**.



Entry	1	2	18	19	Yield (%)[b]
1	**1j** R = CO_2Me	**2b**	BnN_3 **18a**	 **19a**[c]	80 (68)[d]
2	**1m** R = Br	**2e**	**18a**	 **19b**[e]	84 (68)[d]
3	**1j** R = CO_2Me	**2b**	 **18b**	 **19c**[f]	74 (51)[d]
4	**1k** R = COMe	**2c**	 **18c**	 **19d**[g]	71 (54)[d]

[a] *Reaction conditions:* **1** (1.0 equiv.), **18** (10 equiv.), CsF (2.0 equiv.) in MeCN (0.10 M) at 120 °C using microwave for 2 h.
[b] The yield of **19** was determined *via* analysis of the ^{1}H NMR spectra of crude products using 1,1,2,2-tetrachloroethane as an internal standard. Isolated yields are given in parentheses.
[c] Ratio of *distal*-**19a** and *proximal*-**19a** = 1.0:1.
[d] Total isolated yield of *distal*-**19** and *proximal*-**19**.
[e] Ratio of *distal*-**19b** and *proximal*-**19b** = 1.4:1.
[f] Ratio of *distal*-**19c** and *proximal*-**19c** = 1.0:1.
[g] Ratio of *distal*-**19d** and *proximal*-**19d** = 1.2:1.

18a (entries 1 and 2), ketene acetal **18b** (entry 3) and nitrone **18c** (entry 4) under the same conditions to produce **19a**–**d** in 52–68% isolated yields, although the regioselectivities of these reactions were very low.

Conclusions

In conclusion, we have developed a new method for benzyne generation using 2-[(neopentyl glycolato)boryl]phenyl triflates and halides as potent precursors. These precursors, possessing reactive functional groups such as 4-methoxycarbonyl, 4-acetyl, 4-bromo, and 4-amino groups, can be directly prepared through either Miyaura borylation of the corresponding 2-iodophenols or *ortho*-selective iodination of the corresponding boronic acids as the key steps. Such functionalized precursors generated the benzynes at 120 °C (either by microwave irradiation or in an oil bath) with the aid of CsF, which immediately underwent [4+2], (3+2), and [2+2] cycloaddition reactions with a furan or an azide or a ketene acetal or a nitrone to give the corresponding benzo-fused multicyclic compounds while maintaining the functional groups.

This benzyne chemistry should be synthetically valuable because the functionalized benzyne precursors are readily synthesized from commercially available materials in a few steps and also because the benzyne generation reactions are easy to perform. Efforts to apply new functionalized benzynes to the syntheses of biologically active compounds are currently underway.

Experimental Section

General Experimental Details

All reactions were carried out under an argon or nitrogen atmosphere. Microwave reactions were conducted using a Biotage® Initiator Classic in a single purpose reaction flask for the benzyne generation from **1**, **16** and **17**. Schlenk flasks were used for benzyne generation from **1** and Miyaura borylation of **9**. A round-bottom flask with a 3-way stopcock was used for other reactions. Anhydrous THF, CH_2Cl_2 and MeCN were purchased from Wako Pure Chemical Industries and used without purification or purified with a Glass Contour solvent dispensing system (Nikko Hansen, Osaka, Japan) using two packed columns of activated molecular sieves. Anhydrous DMSO, anhydrous pyridine, and 2,5-dimethylfuran (**4b**) were distilled over CaH_2. 2-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)phenol (**11a**),[17] 1-(4-hydroxy-3-iodophenyl)ethan-1-one (**9c**),[18] 4-hydroxy-3-iodobenzonitrile (**9d**),[19] and 4-bromo-2-iodophenol (**9e**)[20] were prepared according to the literature. All other reagents were purchased from Wako Pure Chemical Industries, Tokyo Chemical Industry, Sigma–Aldrich, Combi-Blocks, Kanto Chemicals and Kishida Chemical and used without further purification. Flash chromatography was performed with Silica gel 60, spherical (40–50 μm) for aryl boronates, and Silica gel 60N, spherical neutral (40–50 μm) for other chemicals, purchased from Kanto Chemicals. Melting points were recorded on a Yanagimoto melting point apparatus and are uncorrected. IR spectra were obtained on a Shimadzu FT-IR-8400S. ^{1}H NMR, ^{13}C NMR and NOESY spectra were recorded on a JEOL JMN-ECA-500 (^{1}H: 500 MHz, ^{13}C: 125 MHz) or a JEOL JMN-ECS-400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) or a JEOL JMN-AL-300 (^{1}H: 300 MHz, ^{13}C: 75 MHz) instrument with chemical shifts reported in ppm relative to the residual deuterated solvent. The mass spectra were recorded on a JEOL JMS-S3000 (MALDI) spectrometer. Yield refers to isolated yields of compounds greater than 95% purity as determined by ^{1}H NMR analysis. ^{1}H NMR and melting points (where applicable) of all known compounds were taken. All new products were further characterized by high resolution mass spectroscopy (HR-MS). All carbons bearing boron substituents could not be observed in ^{13}C NMR due to quadrupolar relaxation.

General Procedure for Benzyne Generations (General Procedure A, Table 1, Table 3, Table 4 and Table 5)

CsF (2.0 equiv.) was added to a microwave vial and flame-dried under reduced pressure (or dried at 200 °C using an oil bath under reduced pressure overnight) and back-filled with argon. Another flask was charged with 2-borylphenyl triflate **1** or halide **16** or **17** (1.0 equiv.) and dried via azeotropic distillation with toluene and back-filled with argon. To the flask with **1** (or **16**, **17**) was added 2,5-dimethylfuran (**4b**) (10 equiv.) or benzyl azide (**10a**) (10 equiv.) or ketene acetal **18b** (10 equiv.) *via* a syringe, [or nitrone **18c** (10 equiv.) under argon flow] and the mixture was added to another flask containing CsF *via* cannula with anhydrous MeCN (0.10 M). This mixture was heated to 120 °C in a microwave reactor and stirred for 2 h. After cooling the mixture to room temperature, the reaction was quenched with H_2O. The mixture was extracted with EtOAc (this process was repeated thrice), and the combined organic phase was washed with brine and dried over $MgSO_4$. The organic phase was filtered and concentrated under reduced pressure (for calculating NMR yield, 1,4-dimethoxybenzene or 1,1,2,2-tetrachloroethane was added as an internal standard). The residue was purified by flash column chromatography on silica gel to provide **7** or **19**.

1,4-Dimethyl-1,4-dihydro-1,4-epoxynaphthalene (7a) (Table 1, entry 4):[21] Following General Procedure A, a mixture of CsF (61 mg, 0.40 mmol, dried using oil bath), **1b** (68 mg, 0.20 mmol), 2,5-dimethylfuran **4b** (0.21 mL, 2.0 mmol) in MeCN (2.0 mL, 0.10 M) was stirred at 120 °C using microwaves for 1 h. The reaction mixture (total NMR yield: 85%, 1,4-dimethoxybenzene was used as an internal standard) was purified by flash column chromatography on silica gel (hexane/EtOAc = 10:1) to provide **7a** as a pale yellow oil; yield: 29 mg (84%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.90 (6H, s), 6.78 (2H, s), 6.96–6.99 (2H, m), 7.12–7.15 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.2, 88.5, 118.3, 124.7, 146.8, 152.6.

Methyl 1,4-dimethyl-1,4-dihydro-1,4-epoxynaphthalene-6-carboxylate (7b) (Table 3, entry 6):[22] Following General Procedure A, a mixture of CsF (39 mg, 0.25 mmol, dried over a flame), **1j** (51 mg, 0.13 mmol), 2,5-dimethylfuran **4b** (0.14 mL, 1.3 mmol) in MeCN (1.3 mL, 0.10 M) was stirred at 120 °C using microwaves for 2 h. The reaction mixture (total NMR yield: 76%, 1,1,2,2-tetrachloroethane was used as an internal standard) was purified by flash column chromatography on silica gel (hexane/EtOAc = 5:1) to provide **7b** as a colorless oil; yield: 20 mg (67%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.90 (3H, s), 1.92 (3H, s), 3.89 (3H, s), 6.75 (1H, d, J = 5.0 Hz), 6.78 (1H, d, J = 5.0 Hz), 7.17 (1H, d, J = 7.5 Hz), 7.74 (1H, s), 7.76 (1H, d, J = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.1, 52.0, 88.5, 118.0, 118.8, 127.0, 127.9, 146.2, 147.0, 153.3, 158.1, 167.0.

1-(1,4-Dimethyl-1,4-dihydro-1,4-epoxynaphthalen-6-yl)-ethan-1-one (7c) (Table 4, entry 1): Following General Procedure A, a mixture of CsF (44 mg, 0.29 mmol, dried using oil bath), **1k** (51 mg, 0.13 mmol), 2,5-dimethylfuran **4b** (0.15 mL, 1.4 mmol) in MeCN (1.4 mL, 0.10 M) was stirred at 120 °C using microwaves for 2 h. The reaction mixture (total NMR yield: 77%, 1,1,2,2-tetrachloroethane was used as an internal standard) was purified by flash column chromatography on silica gel (hexane/EtOAc = 5:1) to provide **7c** as a pale yellow oil; yield: 15 mg (50%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.91 (3H, s), 1.92 (3H, s), 2.57 (3H, s), 6.75 (1H, d, J = 5.5 Hz), 6.79 (1H, d, J = 5.5 Hz), 7.18 (1H, d, J = 7.5 Hz), 7.65 (1H, brd, J = 7.5 Hz), 7.70 (1H, brs); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.1, 26.8, 88.5, 88.6, 117.1, 118.0, 127.3, 134.4, 146.0, 147.1, 153.6, 158.2, 197.7; IR (neat): ν = 1678 cm^{-1}; HR-MS (MALDI): m/z = 215.1069, calcd. for $C_{14}H_{15}O_2$ [M + H$^+$]: 215.1067.

1,4-Dimethyl-1,4-dihydro-1,4-epoxynaphthalene-6-carbonitrile (7d) (Table 4, entry 2): Following General Procedure A, a mixture of CsF (49 mg, 0.32 mmol, dried using oil bath), **1l** (59 mg, 0.16 mmol), 2,5-dimethylfuran **4b** (0.17 mL, 1.6 mmol) in MeCN (1.6 mL, 0.10 M) was stirred at 120 °C using microwaves for 2 h. The reaction mixture (total NMR yield: 70%, 1,1,2,2-tetrachloroethane was used as an internal standard) was purified by flash column chromatography on

silica gel (hexane/EtOAc = 10:1) to provide **7d** as a brown oil; yield: 21 mg (64%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.895 (3H, s), 1.900 (3H, s), 6.76 (1H, d, J = 5.5 Hz), 6.79 (1H, d, J = 5.5 Hz), 7.20 (1H, d, J = 7.0 Hz), 7.33 (1H, brs), 7.36 (1H, brd, J = 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.96, 14.99, 88.5, 88.6, 108.5, 118.7, 119.2, 120.9, 130.7, 146.3, 146.8, 154.2, 158.2; IR (neat): ν = 2226 cm^{-1}; HR-MS (MALDI): m/z = 198.0905, calcd. for $C_{13}H_{12}NO$ [M + H$^+$]: 198.0913.

6-Bromo-1,4-dimethyl-1,4-dihydro-1,4-epoxynaphthalene (7e) (Table 4, entry 3):[22] Following General Procedure A, a mixture of CsF (42 mg, 0.28 mmol, dried using oil bath), **1m** (58 mg, 0.14 mmol), 2,5-dimethylfuran **3a** (0.15 mL, 1.4 mmol) in MeCN (1.4 mL, 0.10 M) was stirred at 120 °C using microwaves for 1 h. The reaction mixture (total NMR yield: 82%, 1,1,2,2-tetrachloroethane was used as an internal standard) was purified by flash column chromatography on silica gel (hexane/EtOAc = 10:1) to provide **7e** as a colorless oil; yield: 24 mg (69%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.87 (6H, s), 6.74 (1H, d, J = 5.5 Hz), 6.78 (1H, d, J = 5.5 Hz), 6.98 (1H, d, J = 7.5 Hz), 7.11 (1H, dd, J = 1.5, 7.5 Hz), 7.25 (1H, d, J = 1.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.1, 88.45, 88.53, 118.6, 119.7, 122.2, 127.2, 146.3, 146.9, 151.9, 155.4.

6-Amino-1,4-dimethyl-1,4-dihydro-1,4-epoxynaphthalene (7f) (Table 4, entry 6): Following General Procedure A, a mixture of CsF (37 mg, 0.24 mmol, dried using oil bath), **17b** (41 mg, 0.12 mmol), 2,5-dimethylfuran **4b** (0.13 mL, 1.2 mmol) in MeCN (1.2 mL, 0.10 M) was stirred at 120 °C using microwaves for 2 h. The reaction mixture (total NMR yield: 65%, 1,1,2,2-tetrachloroethane was used as an internal standard) was purified by flash column chromatography on silica gel (hexane/EtOAc = 3:1–2:1) to provide **7f** as a brown oil; yield: 8.5 mg (38%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.84 (3H, s), 1.85 (3H, s), 6.25 (1H, dd, J = 2.0, 7.5 Hz), 6.59 (1H, d, J = 2.0 Hz), 6.70 (1H, d, J = 5.0 Hz), 6.76 (1H, d, J = 5.0 Hz), 6.89 (1H, d, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.3, 15.4, 88.38, 88.45, 108.3, 109.2, 118.8, 142.6, 143.3, 145.7, 147.3, 154.6; IR (neat): ν = 3352, 3456 cm^{-1}; HR-MS (MALDI): m/z = 188.1066, calcd. for $C_{12}H_{14}NO$ [M + H$^+$]: 188.1070.

Methyl 1-benzyl-1*H*-benzo[*d*][1,2,3]triazole-5-carboxylate[4f] **and methyl 1-benzyl-1*H*-benzo[*d*][1,2,3]triazole-6-carboxylate**[4f] **(*distal*- and *proximal*-19a) (Table 5, entry 1):** Following General Procedure A, a mixture of CsF (55 mg, 0.36 mmol, dried over a flame), **1j** (71 mg, 0.18 mmol), benzyl azide **18a** (0.23 mL, 1.8 mmol) in MeCN (1.8 mL, 0.10 M) was stirred at 120 °C using microwaves for 1 h. The reaction mixture (total NMR yield: 80%, 1,1,2,2-tetrachloroethane was used as an internal standard) was purified by flash column chromatography on silica gel (hexane/EtOAc = 3:1) to provide a mixture of *distal*-**19a** and *proximal*-**19a** as a colorless solid; yield: 33 mg (68%, *distal*/*proximal* = 1:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.95 (3/2H, s), 3.96 (3/2H, s), 5.87 (2/2H, s), 5.89 (2/2H, s), 7.27–7.38 (11/2H, m), 8.02 (1/2H, dd, J = 1.5, 9.0 Hz), 8.09 (1/2H, dd, J = 1.0, 8.5 Hz), 8.10 (1/2H, d, J = 9.0 Hz), 8.16 (1/2H, brs), 8.80 (1/2H, brs); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 52.5, 52.6, 109.6, 112.3, 120.0, 123.0, 124.7, 126.4, 127.56, 127,59, 128.3, 128.7, 129.1, 129.3, 132.5, 134.26, 134.33, 135.0, 146.1, 148.3, 166.4, 166.5.

1-Benzyl-5-bromo-1*H*-benzo[*d*][1,2,3]triazole[4f] **and 1-benzyl-6-bromo-1*H*-benzo[*d*][1,2,3]triazole**[4f] **(*distal*- and *proximal*-19b) (Table 5, entry 2):** Following General Procedure A, a mixture of CsF (49 mg, 0.32 mmol, dried using oil bath), **1m** (67 mg, 0.16 mmol), benzyl azide **18a** (0.20 mL, 1.6 mmol) in MeCN (1.6 mL, 0.10 M) was stirred at 120 °C using microwaves for 1 h. The reaction mixture (total NMR yield: 84%, 1,1,2,2-tetrachloroethane was used as an internal standard) was purified by flash column chromatography on silica gel (hexane/EtOAc = 5:1) to provide *distal*-**19b** and *proximal*-**19b** as a colorless solid; yield: 32 mg (68%, *distal*/*proximal* = 1.4:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.80 (2/2.4H, s), 5.82 (2.8/2.4H, s), 7.21–7.36 (13.4/2.4H, m), 7.43 (1/2.4H, dd, J = 1.5, 9.0 Hz), 7.47 (1.4/2.4H, dd, J = 1.5, 9.0 Hz), 7.53 (1/2.4H, brs), 7.92 (1/2.4H, d, J = 9.0 Hz), 8.21 (1.4/2.4H, d, J = 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 52.3, 52.5, 111.0, 112.6, 117.2, 121.2, 121.7, 122.6, 127.50, 127.52, 127.7, 128.6, 129.06, 129.10, 130.7, 131.7, 133.8, 134.19, 134.21, 145.1, 147.5.

Methyl 7,7-dimethoxybicyclo[4.2.0]octa-1(6),2,4-triene-3-carboxylate and methyl 8,8-dimethoxybicyclo[4.2.0]octa-1(6),2,4-triene-3-carboxylate (*distal*- and *proximal*-19c) (Table 5, entry 3): Following General Procedure A, a mixture of CsF (36 mg, 0.24 mmol, dried over a flame), **1j** (47 mg, 0.12 mmol), 1,1-dimethoxyethene **18b** (0.11 mL, 1.2 mmol) in MeCN (1.2 mL, 0.10 M) was stirred at 120 °C using microwaves for 2 h. The reaction mixture (total NMR yield: 74%, 1,1,2,2-tetrachloroethane was used as an internal standard) was purified by flash column chromatography on silica gel (hexane/EtOAc = 10:1) to provide a mixture of *distal*-**19c** and *proximal*-**19c** as a colorless oil; yield: 13 mg (51%, *distal*/*proximal* = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.38 (2/2H, s), 3.39 (2/2H, s), 3.449 (6/2H, s), 3.454 (6/2H, s), 3.906 (3/2H, s), 3.909 (3/2H, s), 7.30 (1/2H, d, J = 8.0 Hz), 7.34 (1/2H, d, J = 8.0 Hz), 7.90 (1/2H, brs), 7.95 (1/2H, brs), 8.00 (1/2H, dd, J = 8.0, 1.5 Hz), 8.08 (1/2H, dd, J = 8.0, 1.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 42.7, 43.2, 51.4, 51.5, 52.1, 52.2, 105.0, 120.9, 122.2, 123.9, 125.2, 129.07, 129.10, 131.7, 131.8, 141.4, 145.2, 147.0, 149.8, 167.0, 167.1; IR (neat): ν = 1717, 1722, 2937, 2994 cm^{-1}; HR-MS (MALDI): m/z = 223.0963, calcd. for $C_{12}H_{15}O_4$ [M + H$^+$]: 223.0965.

1-(2-(*tert*-Butyl)-3-phenyl-2,3-dihydrobenzo[*d*]isoxazol-6-yl)ethan-1-one and 1-(2-(*tert*-butyl)-3-phenyl-2,3-dihydrobenzo[*d*]isoxazol-5-yl)ethan-1-one (*distal*- and *proximal*-19d) (Table 5, entry 4): Following General Procedure A, a mixture of CsF (31 mg, 0.20 mmol, dried over a flame), **1k** (39 mg, 0.10 mmol), *N*-*tert*-butyl-α-phenylnitrone **18c** (0.12 g, 1.0 mmol) in MeCN (1.0 mL, 0.10 M) was stirred at 120 °C using microwaves for 2 h. The reaction mixture (total NMR yield: 71%, 1,1,2,2-tetrachloroethane was used as an internal standard) was purified by flash column chromatography on silica gel (hexane/EtOAc = 5:1) to provide a mixture of *distal*-**19d** and *proximal*-**19d** as a colorless oil: yield: 17 mg (54%, *distal*/*proximal* = 1.2:1).

For *distal*-**19d:** pale yellow solid; mp 84–87 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.18 (9H, s), 2.56 (3H, s), 5.62 (1H, s), 6.96 (1H, d, J = 7.5 Hz), 7.25–7.44 (7H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.4, 26.8, 61.2, 66.8, 106.4, 121.7, 123.6, 127.3, 127.7, 128.7, 135.3, 138.2, 143.0, 156.6, 197.4; IR (neat): ν = 1682, 2973 cm^{-1}; HR-MS (MALDI): m/z = 296.1644, calcd. for $C_{19}H_{22}NO_2$ [M + H$^+$]: 296.1645. The re-

giochemistry of *distal*-**19d** was confirmed by NOESY experiments.

For *proximal*-**19d:** pale yellow solid; mp 85–88 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.18 (9H, s), 2.47 (3H, s), 5.60 (1H, s), 6.83 (1H, d, *J* = 8.5 Hz), 7.25–7.41 (5H, m), 7.55 (1H, brs), 7.83 (1H, dd, *J* = 1.5, 8.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.4, 26.4, 61.4, 66.5, 106.5, 124.5, 127.3, 127.7, 128.8, 130.9, 131.06, 131.11, 143.1, 160.0, 196.2; IR (neat): ν = 1672, 2975 cm^{-1}; HR-MS (MALDI): *m/z* = 296.1647, calcd. for $C_{19}H_{22}NO_2$ [M + H$^+$]: 296.1645. The regiochemistry of *proximal*-**19d** was confirmed by NOESY experiments.

Synthesis of Benzyne Precursor Candidates 1

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl trifluoromethanesulfonate (1a) (Table 1, entries 1 and 2):[9a] A mixture of 2-hydroxyphenylboronic acid (2.1 g, 15 mmol) and pinacol (2.7 g, 23 mmol) was stirred in CH_2Cl_2 (75 mL, 0.20 M) at room temperature for 3 h. The reaction was quenched with H_2O and the mixture was extracted with CH_2Cl_2 (this process was repeated thrice). The combined organic phase was washed with brine and dried over Na_2SO_4. The organic solvent was removed under reduced pressure to provide 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (**20**)[23] as a colorless oil.

To a solution of **20** in anhydrous CH_2Cl_2 (75 mL) were added anhydrous pyridine (3.6 mL, 45 mmol) and trifluoromethanesulfonic anhydride (3.8 mL, 23 mmol) at 0 °C. The reaction mixture was stirred for 3 h at 0 °C. The reaction was quenched with H_2O and the mixture was extracted with CH_2Cl_2 (this process was repeated thrice). The combined organic phase was washed with brine and dried over $MgSO_4$. The organic solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 5:1) to provide the title compound **1a** as a colorless oil; yield: 5.4 g (quant.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.42 (12H, s), 7.22 (1H, brd, *J* = 7.5 Hz), 7.37 (1H, brt, *J* = 7.5 Hz), 7.51 (1H, dt, *J* = 2.0, 7.5 Hz), 7.88 (1H, dd, *J* = 2.0, 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.7, 84.6, 118.8 (q, *J* = 318 Hz), 121.0, 127.7, 132.9, 137.2, 154.2.

(2-{[(Trifluoromethyl)sulfonyl]oxy}phenyl)boronic acid (1i) (Table 1, entry 11):[9a] To a solution of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl trifluoromethanesulfonate **1a** (5.4 g, 15 mmol) and $NaIO_4$ (9.6 g, 45 mmol) in THF (24 mL) and H_2O (6.0 mL) was added 1.0 N HCl (45 mL, 45 mmol) at room temperature and stirred for 2 h. The reaction was quenched with saturated $Na_2S_2O_3$ solution and the mixture was extracted with EtOAc (this process was repeated thrice). The combined organic phase was washed with brine and dried over Na_2SO_4. The organic solvent was removed under reduced pressure. The residue was purified by recrystallization using cyclohexane to provide the title compound **1i** as a colorless solid; yield: 3.0 g (75%); mp 100–104 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.96 (2 OH, s), 7.30 (1H, brd, *J* = 7.5 Hz), 7.44 (1H, brt, *J* = 7.5 Hz), 7.56 (1H, brt, *J* = 7.5 Hz), 7.88 (1H, brd, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 118.6 (q, *J* = 318 Hz), 121.1, 128.3, 132.9, 136.7, 153.3.

2-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)phenyl trifluoromethanesulfonate (1b) (Table 1, entries 3 and 4, Table 2, entry 1):[9a] An oven-dried round-bottom flask (50 mL) was charged with **11a**[17] (0.66 g, 3.2 mmol) and capped with an inlet adapter with a 3-way stopcock and then evacuated and back-filled with argon. Anhydrous CH_2Cl_2 (16 mL, 0.20 M) was added *via* a syringe and the mixture was cooled to 0 °C. Anhydrous pyridine (0.77 mL, 9.6 mmol) and trifluoromethanesulfonic anhydride (0.79 mL, 4.8 mmol) were added dropwise and the reaction was allowed to warm up to room temperature and stirred for 30 min. The reaction was quenched with H_2O and the mixture was extracted with CH_2Cl_2 (this process was repeated thrice). The combined organic phase was washed with brine and dried over $MgSO_4$. The organic phase was filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 1:1) to provide the title compound **1b** as a pale yellow oil; yield: 1.0 g (95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05 (6H, s), 3.80 (4H, s), 7.17 (1H, brd, *J* = 7.5 Hz), 7.36 (1H, brt, *J* = 7.5 Hz), 7.48 (1H, dt, *J* = 1.5, 7.5 Hz), 7.86 (1H, dd, *J* = 1.5, 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.8, 31.8, 72.3, 118.9 (q, *J* = 320 Hz), 121.0, 127.6, 132.3, 136.5, 154.2.

2-{(3a*R*,6a*S*)-Tetrahydro-4*H*-cyclopenta[*d*][1,3,2]dioxaborol-2-yl}phenyl trifluoromethanesulfonate (1c) (Table 1, entry 5): A round-bottom flask (10 mL) was charged with (1*R*,2*S*)-cyclopentane-1,2-diol (18 mg, 0.18 mmol) and **1i** (35 mg, 0.13 mmol) and CH_2Cl_2 (0.65 mL, 0.20 M) was added. The mixture and stirred overnight at room temperature. The reaction was quenched with H_2O and the mixture was extracted with CH_2Cl_2 (this process was repeated thrice). The combined organic phase was washed with brine and dried over $MgSO_4$. The organic phase was filtered and concentrated under reduced pressure to provide the title compound **1c** as a pale yellow oil; yield: 49 mg (quant.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.60–1.81 (4H, m), 2.08 (2H, dd, *J* = 5.5, 13.0 Hz), 5.05 (2H, brd, *J* = 4.0 Hz), 7.22 (1H, brd, *J* = 7.5 Hz), 7.39 (1H, brt, *J* = 7.5 Hz), 7.53 (1H, brt, *J* = 7.5 Hz), 7.86 (1H, brd, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.4, 34.4, 83.3, 118.8 (q, *J* = 318 Hz), 121.0, 127.8, 133.0, 137.3, 154.2; IR (neat): ν = 1424, 2967 cm^{-1}; HR-MS (MALDI): *m/z* = 359.0348, calcd. for $C_{12}H_{12}BO_5F_3NaS$ [M + Na$^+$]: 359.0343.

2-(1,3,2-Dioxaborolan-2-yl)phenyl trifluoromethanesulfonate (1d) (Table 1, entry 6): A flame-dried round-bottom flask (10 mL) was charged with **1i** (35 mg, 0.13 mmol) and capped with inlet adapter with a 3-way stopcock and then evacuated and back-filled with argon. Anhydrous CH_2Cl_2 (0.65 mL, 0.20 M) and anhydrous ethylene glycol (7.3 μL, 0.13 mmol) were added *via* syringes. After the reaction mixture was stirred overnight at room temperature, toluene (1.0 mL) was added and the mixture was concentrated under reduced pressure to provide the title compound **1d** as a colorless oil; yield: 36 mg (93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.43 (4H, s), 7.25 (1H, d, *J* = 7.5 Hz), 7.41 (1H, t, *J* = 7.5 Hz), 7.55 (1H, dt, *J* = 1.5, 7.5 Hz), 7.88 (1H, dd, *J* = 1.5, 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 66.2, 118.8 (q, *J* = 320 Hz), 121.1, 127.9, 133.2, 137.3, 154.2; IR (neat): ν = 2915, 2996 cm^{-1}; HR-MS (MALDI): *m/z* = 319.0028, calcd. for $C_9H_8BO_5F_3NaS$ [M + Na$^+$]: 319.0030.

2-{1*H*-Naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl}phenyl trifluoromethanesulfonate (1e) (Table 1, entry 7): A mixture of **1i** (50 mg, 0.19 mmol) and 1,8-diaminonaphthalene (29 mg, 0.19 mmol) was stirred in CH_2Cl_2 (0.93 mL, 0.20 M)

at room temperature for 2 h. The reaction was quenched with H_2O and the mixture was extracted with CH_2Cl_2 (this process was repeated thrice). The combined organic phase was washed with brine and dried over $MgSO_4$. The organic phase was filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/Et_2O = 5:1) to provide the title compound **1e** as a pale yellow solid; yield: 72 mg (99%) mp 71–75 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.08 (2 NH, brs), 6.41 (2 H, d, J = 8.0 Hz), 7.08 (2 H, d, J = 8.0 Hz), 7.14 (2 H, t, J = 8.0 Hz), 7.35 (1 H, d, J = 8.0 Hz), 7.46 (1 H, t, J = 8.0 Hz), 7.54 (1 H, dt, J = 2.0, 8.0 Hz), 7.67 (1 H, dd, J = 2.0, 8.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 106.3, 118.3, 118.6 (q, J = 318 Hz), 119.9, 121.6, 127.6, 128.4, 131.8, 134.3, 136.2, 140.4, 152.4; IR (neat): ν = 3053, 3424 cm^{-1}; HR-MS (MALDI): m/z = 392.0611, calcd. for $C_{17}H_{12}BN_2O_3F_3S$ [M$^+$]: 392.0608.

2-(6-Methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)phenyl trifluoromethanesulfonate (1f) (Table 1, entry 8): A round-bottom flask with a stir bar was charged with **1i** (0.30 g, 1.1 mmol), *N*-methyliminodiacetic acid (0.16 g, 1.1 mmol) and evacuated and back-filled with argon. Anhydrous toluene (10 mL) and anhydrous DMSO (0.61 mL) were added to the mixture. The flask was equipped with a Dean–Stark trap, a Dimroth condenser with a 3-way stopcock and the reaction was stirred at 130 °C under argon. Anhydrous toluene was added to the reaction mixture at the indicated times (5 mL at 2 h 40 min, 10 mL at 13 h, 10 mL at 21 h). After stirring for 22 h, MeCN (6.0 mL) was added at room temperature and the mixture was concentrated under reduced pressure. The crude product was filtered through a pad of silica gel (MeCN/Et_2O = 1:1) and the filtrate was concentrated under reduced pressure. The residue was filtered again through a pad of silica gel (Et_2O, and MeCN/Et_2O = 1:1) and the filtrate was concentrated under reduced pressure to provide the title compound **1f** as a colorless solid; yield: 0.39 g (93%); mp 157–163 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.62 (3 H, s), 4.21 (2 H, d, J = 17.0 Hz), 4.44 (2 H, d, J = 17.0 Hz), 7.41 (1 H, brd, J = 7.5 Hz), 7.54 (1 H, dt, J = 1.5, 7.5 Hz), 7.60 (1 H, dd, J = 1.5, 7.5 Hz), 7.66 (1 H, dt, J = 1.5, 7.5 Hz); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 47.5, 62.4, 118.4 (q, J = 319 Hz), 120.7, 128.5, 132.3, 136.4, 153.6, 168.8; IR (neat): ν = 1424, 1767 cm^{-1}; HR-MS (MALDI): m/z = 404.0198, calcd. for $C_{12}H_{11}BNO_7F_3NaS$ [M + Na$^+$]: 404.0194.

2-(6-Methyl-1,3,6,2-dioxazaborocan-2-yl)phenyl trifluoromethanesulfonate (1g) (Table 1, entry 9): A flame-dried round-bottom flask (10 mL) was charged with **1i** (35 mg, 0.13 mmol) and CH_2Cl_2 (0.65 mL, 0.20 M). *N*-Methyldiethanolamine (15 μL, 0.13 mmol) was added *via* a syringe and stirred overnight at room temperature. Toluene (1.0 mL) was added to the crude mixture and the solvent was removed under reduced pressure to provide the title compound **1g** as a colorless solid; yield: 53 mg (quant.); mp 70–73 °C. ^{1}H NMR (500 MHz, $CDCl_3$); δ = 2.47 (3 H, s), 3.09–3.21 (4 H, m), 4.09–4.20 (4 H, m), 7.14 (1 H, brd, J = 8.0 Hz), 7.30–7.36 (2 H, m), 7.79 (1 H, brd, J = 6.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 46.6, 61.5, 62.2, 118.7 (q, J = 318 Hz), 120.4, 127.6, 130.0, 136.5, 155.0; IR (neat): ν = 2866 cm^{-1}; HR-MS (MALDI): m/z = 354.0792, calcd. for $C_{12}H_{16}BNO_5F_3S$ [M + H$^+$]: 354.0789.

Potassium trifluoro(2-{[(trifluoromethyl)sulfonyl]oxy}phenyl)borate (1h) (Table 1, entry 10): A mixture of **1i** (0.20 g, 0.74 mmol), KHF_2 (0.14 g, 1.8 mmol), MeOH (1.7 mL, 0.44 M), and H_2O (0.42 mL, 1.8 M) was stirred for 59 h at room temperature. The precipitate in the mixture was filtered and washed with MeCN to provide the title compound **1h** as a colorless solid; yield: 0.27 g (quant.); mp 240–244 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.07 (1 H, d, J = 7.5 Hz), 7.24 (1 H, t, J = 7.5 Hz), 7.28 (1 H, dt, J = 2.0, 7.5 Hz), 7.53 (1 H, dd, J = 2.0, 7.5 Hz); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 118.6 (q, J = 318 Hz), 119.4, 127.2, 128.0, 135.0, 153.9; IR (KBr): ν = 3038 cm^{-1}; HR-MS (MALDI): m/z = 354.9404, calcd. for $C_7H_4BO_3F_6NaSK$ [M + Na$^+$]: 354.9408.

General Procedure of Miyaura Borylation for the Synthesis of Boronate 11 (General Procedure B, Table 2)

An oven-dried Schlenk flask was charged with **9**, bis(neopentyl glycolato)diboron (1.2 equiv.), [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (0.03 equiv.), and AcOK (3.0 equiv.). After the Schlenk flask was evacuated and back-filled with argon, anhydrous DMSO (0.13 M) was added *via* a syringe, and the reaction was allowed to warm up to 80 °C and stirred for several hours. The reaction was quenched with H_2O and the mixture was extracted with Et_2O (this process was repeated thrice). The combined organic phase was washed with brine and dried over $MgSO_4$. The organic phase was filtered and concentrated under reduced pressure. Then, the residue was purified by flash column chromatography on silica gel to provide **11**.

General Procedure for Triflation in the Synthesis of Triflate 1 (General Procedure C, Table 2)

A flame-dried round-bottom flask was charged with **11**, capped with an inlet adapter with a 3-way stopcock, and then evacuated and back-filled with argon. Anhydrous CH_2Cl_2 (0.20 M) was added *via* a syringe and the mixture was cooled to 0 °C. Anhydrous pyridine (3.0 equiv.) and trifluoromethanesulfonic anhydride (1.5 equiv.) were added *via* syringes. The reaction was allowed to warm to room temperature and stirred for several hours. The reaction was quenched with H_2O and the mixture was extracted with CH_2Cl_2 (this process was repeated thrice). The combined organic phase was washed with brine and dried over $MgSO_4$. The organic phase was filtered and concentrated under reduced pressure. Then, the residue was purified by flash column chromatography on silica gel to provide **1**.

Methyl 3-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-4-hydroxybenzoate (11b) (Table 2, Entry 2): Following General Procedure B, a mixture of **9b**[23] (1.0 g, 3.6 mmol), bis(neopentyl glycolato)diboron (0.98 g, 4.3 mmol), 1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (80 mg, 0.11 mmol) and AcOK (1.1 g, 11 mmol) in anhydrous DMSO (29 mL, 0.13 M) was stirred at 80 °C for 10 h. The reaction mixture was purified by flash column chromatography (hexane/EtOAc/AcOH = 2:1:0.1) to provide **11b** as a colorless solid; yield: 0.65 g (68%); mp 66–73 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05 (6 H, s), 3.83 (4 H, s), 3.87 (3 H, s), 6.86 (1 H, d, J = 8.5 Hz), 8.01 (1 H, dd, J = 2.5, 8.5 Hz), 8.34 (1 H, d, J = 2.5 Hz), 8.72 (OH, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 21.8, 32.0, 51.7, 72.4, 115.7, 121.3, 134.8, 137.7, 167.0, 167.6;

IR (neat): $\nu = 1717$, 2961, 3376 cm^{-1}; HR-MS (MALDI): *m/z* = 265.1248, calcd. for $C_{13}H_{18}BO_5$ [M + H^+]: 265.1242.

Methyl 3-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-4-{[(trifluoromethyl)sulfonyl]oxy}benzoate (1j) (Table 2, entry 2): Following General Procedure C, a mixture of **11b** (0.38 g, 1.4 mmol), anhydrous pyridine (0.35 mL, 4.3 mmol) and trifluoromethanesulfonic anhydride (0.35 mL, 2.1 mmol) in CH_2Cl_2 (7.1 mL, 0.20 M) was stirred for 19 h at room temperature. The reaction mixture was purified by flash column chromatography on silica gel (hexane/EtOAc = 5:1) to provide **1j** as a pale yellow solid; yield: 0.52 g (93%); mp 70–74 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05 (6H, s), 3.82 (4H, s), 3.94 (3H, s), 7.25 (1H, d, *J* = 9.0 Hz), 8.14 (1H, dd, *J* = 2.5, 9.0 Hz), 8.53 (1H, d, *J* = 2.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.8, 31.8, 52.4, 72.3, 118.8 (q, *J* = 318 Hz), 121.3, 129.5, 133.7, 138.1, 156.9, 165.8; IR (neat): ν = 1732 cm^{-1}; HR-MS (MALDI): *m/z* = 419.0545, calcd. for $C_{14}H_{16}BO_7F_3NaS$ [M + Na^+]: 419.0554.

1-[3-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)-4-hydroxyphenyl]ethan-1-one (11c) (Table 2, entry 3): Following General Procedure B, a mixture of **9c** (1.0 g, 3.8 mmol), bis(neopentyl glycolato)diboron (1.0 g, 4.6 mmol), [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (94 mg, 0.11 mmol) and AcOK (1.1 g, 11 mmol) in anhydrous DMSO (31 mL, 0.13 M) was stirred at 80 °C for 18.5 h. The reaction mixture was purified by flash column chromatography on silica gel (hexane/EtOAc = 1:1) and the residue was recrystallized by cyclohexane to provide **11c** as a pale yellow solid; yield: 0.40 g (41%, contaminated with 2% of 4′-hydroxyacetophenone); mp 105–111 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.06 (6H, s), 2.56 (3H, s), 3.84 (4H, s), 6.88 (1H, d, *J* = 8.5 Hz), 7.99 (1H, dd, *J* = 2.5, 8.5 Hz), 8.26 (1H, d, *J* = 2.5 Hz), 8.77 (OH, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.7, 26.3, 32.0, 72.3, 115.9, 129.1, 133.5, 137.0, 167.8, 197.0; IR (neat): ν = 1674, 3374 cm^{-1}; HR-MS (MALDI): *m/z* = 271.1129, calcd. for $C_{13}H_{17}BO_4Na$ [M + Na^+]: 271.1112.

4-Acetyl-2-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenyl trifluoromethanesulfonate (1k) (Table 2, entry 3): Following General Procedure C, a mixture of **11c** (0.35 g, 1.4 mmol), trifluoromethanesulfonic anhydride (0.35 mL, 2.1 mmol), anhydrous pyridine (0.34 mL, 4.2 mmol) in anhydrous CH_2Cl_2 (7.0 mL, 0.20 M) was stirred for 1.5 h at room temperature. The reaction mixture was purified by flash column chromatography on silica gel (hexane/EtOAc = 1:1) to provide **1k** as a colorless solid; yield: 0.54 g (quant.); mp 42–48 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.05 (6H, s), 2.64 (3H, s), 3.82 (4H, s), 7.26 (1H, d, *J* = 9.0 Hz), 8.07 (1H, dd, *J* = 2.5, 9.0 Hz), 8.43 (1H, d, *J* = 2.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.8, 26.7, 31.8, 72.3, 118.8 (q, *J* = 318 Hz), 121.6, 132.2, 136.0, 137.0, 156.9, 196.7; IR (neat): ν = 1427, 1694, 2965 cm^{-1}; HR-MS (MALDI): *m/z* = 403.0595, calcd. for $C_{14}H_{16}BO_6F_3NaS$ [M + Na^+]: 403.0605.

3-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)-4-hydroxybenzonitrile (11d) (Table 2, entry 4): Following General Procedure B, a mixture of **9d** (1.0 g, 4.1 mmol), bis(neopentyl glycolato)diboron (1.1 g, 4.9 mmol), [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (0.10 g, 0.12 mmol) and AcOK (1.2 g, 12 mmol) in anhydrous DMSO (33 mL, 0.13 M) was stirred at 80 °C for 13.5 h. The reaction mixture was purified by flash column chromatography on silica gel (hexane/EtOAc = 1:1) to provide **11d** as a colorless solid; yield: 0.28 g (30%); mp 99–102 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.06 (6H, s), 3.84 (4H, s), 6.88 (1H, d, *J* = 8.5 Hz), 7.57 (1H, dd, *J* = 2.0, 8.5 Hz), 7.94 (1H, d, *J* = 2.0 Hz), 8.78 (OH, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.7, 32.1, 72.5, 102.8, 116.7, 119.5, 136.5, 140.3, 166.9; IR (neat): ν = 2222, 3370 cm^{-1}; HR-MS: (MALDI): *m/z* = 254.0969, calcd. for $C_{12}H_{14}BNO_3Na$ [M + Na^+]: 254.0959.

4-Cyano-2-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenyl trifluoromethanesulfonate (1l) (Table 2, entry 4): Following General Procedure C, a mixture of **11d** (0.22 mg, 1.0 mmol), trifluoromethanesulfonic anhydride (0.24 mL, 1.5 mmol) and anhydrous pyridine (0.23 mL, 2.9 mmol) in anhydrous CH_2Cl_2 (4.8 mL, 0.20 M) was stirred for 2 h at room temperature. The reaction mixture was purified by flash column chromatography on silica gel (hexane/EtOAc = 20:1 to 10:1) to provide **1l** as a pale yellow oil; yield: 0.31 g (90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.23 (6H, s), 3.81 (4H, s), 7.29 (1H, d, *J* = 8.5 Hz), 7.77 (1H, dd, *J* = 2.0, 8.5 Hz), 8.19 (1H, d, *J* = 2.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.7, 31.8, 72.4, 112.2, 117.4, 118.7 (q, *J* = 319 Hz), 122.3, 135.8, 140.8, 156.2; IR (neat): ν = 1427, 2236 cm^{-1}; HR-MS (MALDI): *m/z* = 386.0448, calcd. for $C_{13}H_{13}BNO_5F_3NaS$ [M + Na^+]: 386.0452.

4-Bromo-2-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenol (11e) (Table 2, entry 5): Following General Procedure B, a mixture of **9e** (1.0 g, 3.4 mmol), bis(neopentyl glycolato)diboron (0.76 g, 3.4 mmol), [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (82 mg, 0.10 mmol) and AcOK (0.99 g, 10 mmol) in anhydrous DMSO (23 mL, 0.13 M) was stirred at 80 °C for 15 h. The reaction mixture was purified by flash column chromatography on silica gel (hexane/EtOAc = 1:1) to provide **11e**; yield: 0.52 g (54%).

The mixture of **11e** contaminated with by-product was purified by flash column chromatography on silica gel (hexane/EtOAc = 5:1) to provide **11e** as a colorless solid; yield: 76 mg (8%); mp 85–88 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.04 (6H, s), 3.81 (4H, s), 6.73 (1H, d, *J* = 9.0 Hz), 7.39 (1H, dd, *J* = 2.5, 9.0 Hz), 7.70 (1H, d, *J* = 2.5 Hz), 8.27 (OH, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.7, 32.0, 72.4, 111.6, 117.6, 135.7, 137.3, 162.6; IR (neat): ν = 2963, 3408 cm^{-1}; HR-MS (MALDI): *m/z* = 284.0210, calcd. for $C_{11}H_{14}BO_3Br$ [M^+]: 284.0214.

4-Bromo-2-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenyl trifluoromethanesulfonate (1m) (Table 2, entry 5): Following General Procedure B, a mixture of **9e** (1.0 g, 3.4 mmol), bis(neopentyl glycolato)diboron (0.76 g, 3.4 mmol), [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (82 mg, 0.10 mmol) and AcOK (0.99 g, 10 mmol) in anhydrous DMSO (23 mL, 0.13 M) was stirred at 80 °C and stirred for 15 h. The crude product was used for next reaction without further purification.

Following General Procedure C, a mixture of the above obtained crude **11e**, trifluoromethanesulfonic anhydride (3.4 mL, 21 mmol) and anhydrous pyridine (2.5 mL, 31 mmol) in anhydrous CH_2Cl_2 (52 mL, 0.065 M) was stirred for 4 h at room temperature. The reaction mixture was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 = 5:1) to provide **1m** as a colorless solid; yield: 1.3 g (30% from **9e**); mp 30–31 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.04 (6H, s), 3.80 (4H, s), 7.05 (1H, d, *J* = 8.5 Hz), 7.58 (1H, dd, *J* = 2.5, 8.5 Hz), 7.97 (1H, d, *J* = 2.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.8, 31.8, 72.4, 118.8 (q, *J* = 318 Hz),

121.7, 122.9, 135.1, 139.3, 153.0; IR (neat): $\nu = 2965\ cm^{-1}$; HR-MS (MALDI): $m/z = 438.9590$, calcd. for $C_{12}H_{13}BO_5F_3NaSBr$ [M+Na$^+$]: 438.9604.

Synthesis of Other Benzyne Precursors, 2-Haloaryl Boronates 16, 17a and 17b

2-(2-Bromophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (16) (Table 4, entry 4): 2,2-Dimethyl-1,3-propanediol (0.62 g, 6.0 mmol) was added to a solution of 2-bromophenylboronic acid (1.0 g, 5.0 mmol) in CH_2Cl_2 (10 mL, 0.50 M) and the mixture was stirred for 3.5 h at room temperature. The reaction was quenched with H_2O and the mixture was extracted with CH_2Cl_2 (this process was repeated thrice). The combined organic phase was washed with brine and dried over $MgSO_4$. The organic phase was filtered and concentrated under reduced pressure to provide **16** as a colorless solid; yield: 1.3 g (quant.); mp 28–30 °C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.07$ (6H, s), 3.81 (4H, s), 7.20 (1H, dt, $J = 2.0$, 7.5 Hz), 7.27 (1H, dt, $J = 1.0$, 7.5 Hz), 7.52 (1H, dd, $J = 1.0$, 7.5 Hz), 7.56 (1H, dd, $J = 2.0$, 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 21.8$, 31.6, 72.4, 126.2, 126.9, 131.0, 132.5, 135.3; IR (neat): $\nu = 2961$, 3063 cm^{-1}; HR-MS (MALDI): $m/z =$ 291.0163, calcd. for $C_{11}H_{14}BO_2NaBr$ [M+Na$^+$]: 291.0162.

2-(2-Iodophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (17a) (Table 4, entry 5): 2,2-Dimethyl-1,3-propanediol (0.47 g, 4.5 mmol) was added to a solution of 2-iodophenylboronic acid (0.74 g, 3.0 mmol) in CH_2Cl_2 (20 mL, 0.15 M) and the mixture was stirred for 18 h at room temperature. The reaction was quenched with H_2O and the mixture was extracted with CH_2Cl_2 (this process was repeated thrice). The combined organic phase was washed with brine and dried over $MgSO_4$. The organic phase was filtered and concentrated under reduced pressure to provide **17a** as a pale yellow oil; yield: 0.95 g (quant.). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.08$ (6H, s), 3.80 (4H, s), 7.03 (1H, dt, $J = 2.0$, 7.5 Hz), 7.31 (1H, dt, $J = 1.0$, 7.5 Hz), 7.50 (1H, dd, $J = 2.0$, 7.5 Hz), 7.83 (1H, dd, $J = 1.0$, 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 21.9$, 31.7, 72.3, 99.7, 126.8, 131.1, 135.1, 139.3; IR (neat): $\nu =$ 2962 cm^{-1}; HR-MS (MALDI): $m/z = 339.0050$, calcd. for $C_{11}H_{14}BO_2NaI$ [M+Na$^+$]: 339.0024.

3-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)-4-iodoaniline (17b) (Table 4, entry 6): To a solution of 3-aminophenylboronic acid (0.50 g, 3.7 mmol) and silver sulfate (0.63 g, 2.0 mmol)[15] in EtOH (12 mL) was added dropwise a solution of iodine (0.93 g, 3.7 mmol) in EtOH (12 mL). The reaction mixture was stirred for 6 h at room temperature. The mixture was filtered through a short pad of Celite using CH_2Cl_2. The filtrate was washed with brine and dried over Na_2SO_4. The organic solvent was removed under reduced pressure. The crude product (0.81 g) was dissolved in CH_2Cl_2 (10 mL, 0.37 M) then 2,2-dimethylpropanediol (0.38 g, 3.7 mmol) was added to the mixture. The reaction mixture was stirred at room temperature for 9 h. The reaction was quenched with H_2O and the mixture was extracted with CH_2Cl_2 (this process was repeated twice). The combined organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (hexane/EtOAc = 2:1) to provide the titled compound **17b** as a dark blown solid; yield: 0.73 g (60%); mp 84–87 °C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.06$ (6H, s), 3.78 (4H, s), 6.43 (1H, dd, $J = 2.5$, 8.5 Hz), 6.88 (1H, d, $J = 2.5$ Hz), 7.54 (1H, d, $J = 8.5$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 21.9$, 31.7, 72.3, 85.1, 118.4, 122.1, 139.8, 145.3; IR (neat): $\nu = 2960$, 3372, 3458 cm^{-1}; HR-MS (MALDI): $m/z = 332.0317$, calcd. for $C_{11}H_{16}BNO_2I$ [M+H$^+$]: 332.0313.

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