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2-(Trimethylsilyl)phenyl Trimethylsilyl Ethers as Stable and Readily Accessible Benzyne Precursors

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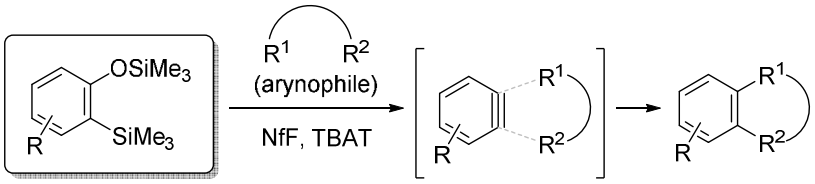


ABSTRACT: Stable 2-(trimethylsilyl)phenyl trimethylsilyl ethers, readily obtained from the corresponding halogenated phenols in two steps, were identified as novel benzyne precursors. These species were converted to benzynes by a domino reaction of *O*-desilylation, *O*-nonaflylation, and β-elimination under mild conditions using nonafluorobutanesulfonyl fluoride (NfF) and tetrabutylammonium triphenyldifluorosilicate (TBAT). The generated benzynes were trapped by various arynophiles to afford a wide variety of benzo-fused heterocycles.

■ INTRODUCTION

Benzynes have been long known as attractive reactive intermediates for the synthesis of complex polysubstituted and/or fused aromatic compounds.[1] In the last two decades, a wide variety of new

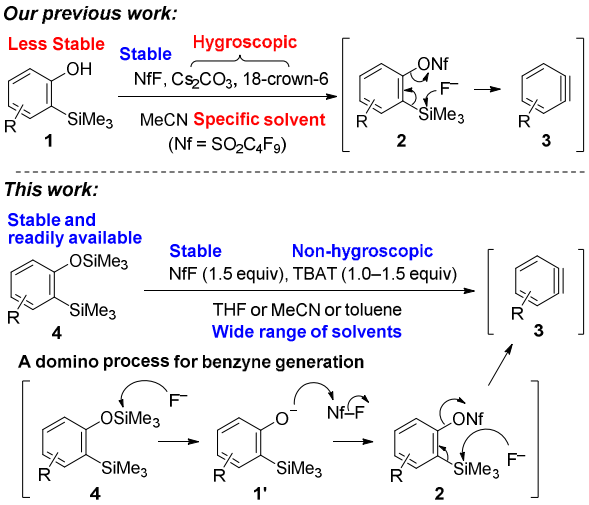
benzyne reactions including transition-metal-catalyzed multi-component coupling reactions have been developed, probably due to the conditions of benzyne generation becoming milder than before. In particular, 2-(trimethylsilyl)phenyl triflates[2] have greatly contributed to the prosperous benzyne chemistry field, currently remaining the most widely used benzyne precursors, although a number of other precursors has also been reported.[3]

Several 2-silylaryl triflates are now commercially available, and numerous other ones can be synthesized in a few steps from readily accessible starting materials. However, the diversity of substituted benzynes available from 2-silylaryl triflates has been limited by the use of relatively harsh reagents such as *n*-BuLi and trifluoromethanesulfonic anhydride (Tf_2O) for the synthesis of these species. Recently, we have developed 2-borylphenyl triflates as novel benzyne precursors that can be prepared without using *n*-BuLi and generate benzynes under fluoride-mediated mild conditions.[3g] Additionally, we have developed a novel method of benzyne generation from 2-(trimethylsilyl)phenols **1** using benchtop-stable nonafluorobutanesulfonyl fluoride (NfF), featuring a domino reaction relying on in situ formation of nonaflates **2** and benzyne generation by the attack of the produced fluoride ion on the silicon atom (Scheme 1).[3a] This method provides some advantages over the use of 2-silylaryl triflates, because it does not require the use of moisture-sensitive Tf_2O that often causes decomposition of acid-labile compounds, and also because **1** is the precursor of 2-silylaryl triflates. However, this method has some limitations. (1) Some 2-silylphenols **1** are too unstable to be isolated (*vide infra*). (2) Scrupulous attention is required when handling hygroscopic Cs_2CO_3 and 18-crown-6. (3) The specific solvent usability restricts synthetic applications. (4) A strong base (NaH) is required for the generation of 3-silylbenzyne.[4] Therefore, the development of an alternative efficient method for benzyne generation is required to overcome these limitations and open new possibilities for benzyne chemistry.

Herein, we report the use of 2-(trimethylsilyl)phenyl trimethylsilyl ethers **4** as new precursors for generating various benzynes **3**, including 3-silylbenzynes.[4] The advantages of this method include two-step preparations of **4** from halogenated phenols, high stability of **4**, direct generation of **3** via a domino

of *O*-desilylation, *O*-nonaflylation, and β-elimination, and the use of easy-to-handle NfF and non-hygroscopic tetrabutylammonium triphenyldifluorosilicate (TBAT) as a fluoride source in various solvents (Scheme 1). The generated benzynes are trapped by various arynophiles to afford a wide variety of benzo-fused heterocycles.

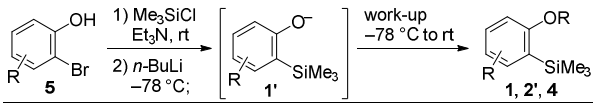
Scheme 1. Previously Reported Benzyne Generation and the Novel Method Used in This Work

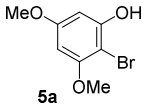
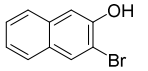
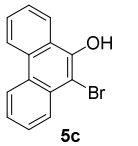


■ RESULTS AND DISCUSSION

Initially, we synthesized 2-(trimethylsilyl)phenyl trimethylsilyl ethers **4a**–**4c** from 2-bromophenols **5a**–**5c** in 72–84% overall yields via *O*-silylation, retro-Brook rearrangement in the reaction with *n*-BuLi, and work-up with Me_3SiCl (Table 1, entries 3, 6, and 9). The obtained **4a**–**4c** were stable for purification by silica gel column chromatography and could be stored for several months without decomposition. On the other hand, the corresponding phenols **1a**–**1c** and triflates **2a'**–**2c'** could hardly be isolated after work-up of 2-trimethylsilylphenolates **1'** with Tf_2O (entries 2, 5, and 8) or aqueous NH_4Cl (entries 1, 4, and 7) at –78 °C. The previously reported synthesis of **2a'**–**2c'** by trapping phenolates **1'** by Tf_2O at lower temperature (e.g. –100 °C) resulted in only moderate yields.[5–7]

Table 1. Preparation of 2-(Trimethylsilyl)phenyl Trimethylsilyl Ethers 4 from 2-Bromophenols 5[a]

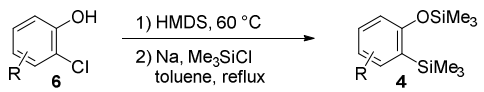


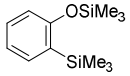
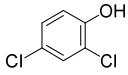
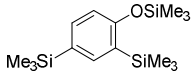
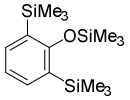
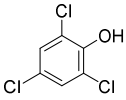
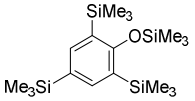
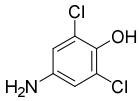
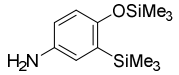
entry	substrate **5**	work-up	**1**, **2'**, **4**	OR	Yield(%)[b]
1	 **5a**	sat. aq NH_4Cl	**1a**	OH	0
2		Tf_2O	**2a'**	OTf	0
3		Me_3SiCl	**4a**	$OSiMe_3$	84
4	 **5b**	sat. aq NH_4Cl	**1b**	OH	25
5		Tf_2O	**2b'**	OTf	12
6		Me_3SiCl	**4b**	$OSiMe_3$	80
7	 **5c**	sat. aq NH_4Cl	**1c**	OH	0
8		Tf_2O	**2c'**	OTf	0
9		Me_3SiCl	**4c**	$OSiMe_3$	72

[a]Conditions: 1) **5** (1.0 mmol), Me_3SiCl (1.5 mmol), and Et_3N (1.5 mmol) in THF (0.2 M) at rt for 1 h. 2) *n*-BuLi (1.3 mmol) in THF (0.2 M) at –78 °C for 1 h except for entries 2, 5, and 8. Et_2O was used instead of THF in these three entries. Work-up) Me_3SiCl (1.5 mmol) or Tf_2O (1.5 mmol) or sat. aq NH_4Cl (excess) at –78 °C and warming up to rt. [b]Isolated yield.

We also synthesized other 2-(trimethylsilyl)phenyl trimethylsilyl ethers **4** from 2-chlorophenols **6** (Table 2).[2,8] After trimethylsilylation of the phenolic hydroxyl groups of **6** using hexamethyldisilazane (HMDS), further *C*-silylation was achieved by using an excess of sodium metal and Me_3SiCl to produce **4** (entries 1–4). In particular, two or three chlorine atoms attached to the benzene rings of **6b**–**6d** could be simultaneously replaced with the trimethylsilyl group, furnishing bis- and tris(trimethylsilyl)phenyl trimethylsilyl ethers **4e**–**4g** (entries 2–4). Interestingly, one of the chlorine atoms of 4-amino-2,6-dichlorophenol **6e** was selectively removed during silylation using sodium metal/Me_3SiCl to give 4-amino-2-(trimethylsilyl)phenyl trimethylsilyl ether **4h** in 88% yield (entry 5). Compounds **4d**–**4h** were stable for purification by silica gel chromatography and could be stored under ambient conditions. It should be noted that 2-chlorophenol derivatives such as **6a**–**6e** are commercially available at much lower prices compared to the corresponding bromo- or iodophenols.

Table 2. Preparation of 2-(Trimethylsilyl)phenyl Trimethylsilyl Ethers 4 from 2-Chlorophenols 6[a]

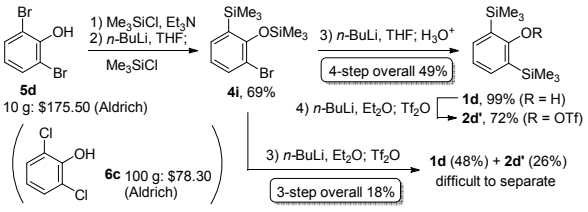


entry	substrate **6**		precursor **4**		yield (%)[b]
1		**6a**		**4d**	86
2		**6b**		**4e**	78
3		**6c**		**4f**	76
4		**6d**		**4g**	68
5[c]		**6e**		**4h**	88

[a]Conditions: 1) **6** (1.0 equiv) and HMDS (1.0 equiv) in THF (1.0 M) at 60 °C for 1 h. 2) Na metal (7.5 equiv for each chlorine atom) and Me_3SiCl (8.0 equiv for each chlorine atom) in toluene (0.5 M) at reflux for 18 h. [b]Isolated yield. [c]Conditions: 1) Me_3SiCl (3.0 equiv) and Et_3N (3.0 equiv) in THF (0.2 M). 2) The same conditions shown above.

In contrast, 2,4-bis(trimethylsilyl)phenyl triflate **2d'**,[4d,4e,4g] which corresponds to **4f** (Table 2, entry 3) and generated 3-(trimethylsilyl)benzyne **3f** under mild fluoride ion conditions, was prepared in 4-step in lower yield (49%) from a far more expensive raw material, 2,6-dibromophenol **5d** (Scheme 2).

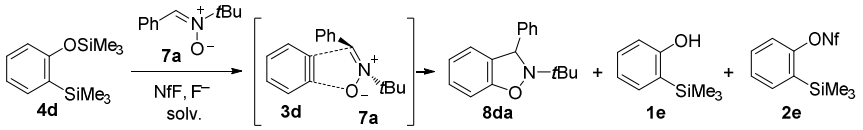
Scheme 2. Reported Route for the Synthesis of 2,6-Bis(trimethylsilyl)phenyl Triflate 2d'



Next, the conditions for generating benzyne **3d** from **4d** using fluoride ions and NfF (1.5 equiv) were optimized in the presence of 3.0 equiv of nitrone **7a** to trap **3d** (Table 3). By using 3.0 equiv of either KF/18-crown-6 or TBAT in THF at room temperature, the product of a (3+2) cycloaddition reaction between **3d** and **7a**, **8da** was obtained in 95 and 99% yield, respectively (entries 2 and 3), while

the use of 3.0 equiv of Bu_4NF (TBAF) resulted in a lower yield (53%) due to the significant hydrolysis of **4d** (entry 1). The use of CsF (3.0 equiv) gave an excellent yield in MeCN (99%, entry 5) but not in THF (18%, entry 4). When less CsF was used (2.0 equiv), a hydrolyzed product [2-(trimethylsilyl)phenol **1e**] was observed, accounting for the lower yield of **8da** (77%, entry 6). The reactions utilizing CsF (3.0 equiv) seem to be sensitive to temperature (entries 7 and 8), with the best yield observed at room temperature (entry 5). On the other hand, reactions utilizing TBAT (1.0–3.0 equiv) at 60 °C gave almost equal yields (92–98%) in THF, MeCN, and toluene (entries 3, 10–14). To sum up these results, the best conditions for benzyne generation correspond to using 1.0–1.5 equiv of anhydrous and non-hygroscopic fluoride sources such as TBAT. In addition, hygroscopic CsF and KF can also be used when present in excess in appropriate solvents.

Table 3. Optimization of Benzyne Generation from 2-(Trimethylsilyl)phenyl Trimethylsilyl Ether 4d[a]



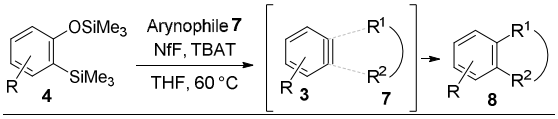
entry	F^- (equiv)		solv.	temp. (°C)	yield (%)[b] 8da	1e	2e
1	Bu_4NF	3.0	THF	rt	53	15	0
2	KF, 18-c-6	3.0	THF	rt	95 (91)[c]	0	0
3	TBAT[d]	3.0	THF	rt	99 (96)[c]	0	0
4	CsF	3.0	THF	rt	18	0	82
5	CsF	3.0	MeCN	rt	99 (93)[c]	0	0
6	CsF	2.0	MeCN	rt	77	17	0
7	CsF	3.0	MeCN	60	87	7	0
8	CsF	3.0	MeCN	0	20	0	78
9	TBAT[d]	2.0	THF	rt	89	0	11
10	TBAT[d]	2.0	THF	60	97 (93)[c]	0	0
11	TBAT[d]	1.5	THF	60	98 (91)[c]	0	0
12	TBAT[d]	1.5	toluene	60	92 (94)[c]	0	0
13	TBAT[d]	1.5	MeCN	60	98 (93)[c]	0	0
14	TBAT[d]	1.0	MeCN	60	96	0	0
15	TBAT[d]	5 mol%	MeCN	60	5	0	93 (90)

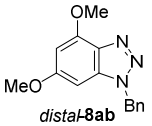
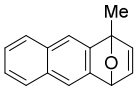
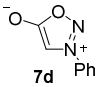
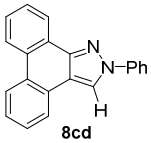
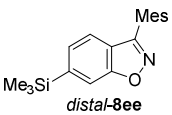
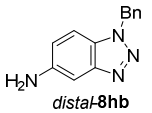
[a]Conditions: **4d** (0.10 mmol), **7a** (0.30 mmol), NfF (0.15 mmol), and F^- (given in the Table) in solvent (0.1 M) for 24 h. [b]GC yield (%) of **8da**. [c]Isolated yield (%) of **8da** is shown in parenthesis. [d]TBAT: $Bu_4NPh_3SiF_2$.

It is also worth noting that 5% of **8da** and 93% of 2-(trimethylsilyl)phenyl nonaflate **2e**[3a,9] were produced using 5 mol% TBAT (entry 15), indicating that fluoride ions generated from NfF by nonaflylation of phenolate **1'** were effectively used for the *O*-desilylation of another **4d** to complete its conversion into **2e**, followed by benzyne generation.

Subsequently, we applied our new benzyne generation method to other silyl ethers (**4a**–**4c**, **4e**, and **4h**) for performing various cycloaddition reactions with arynophiles **7**, e.g., benzyl azide **7b** (Table 4, entries 1 and 5), 2-methylfuran **7c** (entry 2), sydnone **7d** (entry 3), and nitrile oxide **7e** (entry 4), with the corresponding (3+2) and [4+2] cycloaddition products **8ab**, **8bc**, **8cd**, **8ee**, and **8hb** produced in 52–86% yields. These results clearly indicate that 3,5-dimethoxybenzyne **3a** (entry 1), 2,3-naphthalyne **3b** (entry 2), 9,10-phenanthryne **3c** (entry 3), 4-silylbenzyne **3e** (entry 4), and 4-aminobenzyne **3h** (entry 5) were successfully generated from the corresponding nonaflates **2** and were efficiently trapped by **7**.

Table 4. Scope of Substituted Benzyne Generations from Precursors 4 and Their Reactions with Arynophiles 7[a]

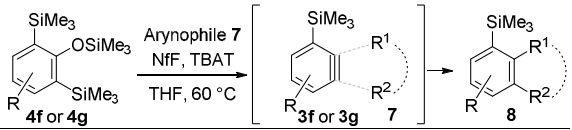


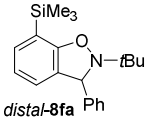
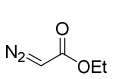
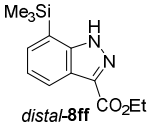
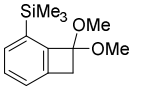
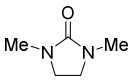
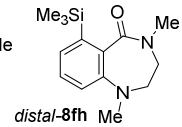
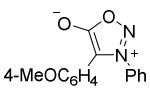
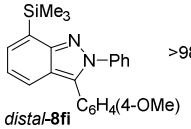
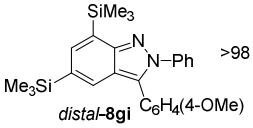
entry	precursor **4**	arynophile **7**	major product **8**	ratio[b]	yield[c]
1	**4a**	BnN_3 **7b**	 *distal*-**8ab**	>98 : 2	86
2	**4b**	 **7c**	 **8bc**	–	85
3	**4c**	 **7d**	 **8cd**	–	83
4	**4e**	Mes-NCO **7e**	 *distal*-**8ee**	76 : 24	81
5	**4h**	**7b**	 *distal*-**8hb**	50 : 50	52

[a]Conditions: **4** (0.20 mmol), **7** (0.60 mmol), NfF (0.30 mmol), and TBAT (0.30 mmol) in THF (0.1 M) at 60 °C for 5–12 h. [b]Ratio of regioisomers was determined by ^{1}H NMR spectra. [c]Isolated yield (%).

Additionally, combinations of 2,6-bis- and 2,4,6-tris(trimethylsilyl)phenyl trimethylsilyl ethers (**4f** and **4g**, respectively) as precursors of 3-silylbenzynes with various arynophiles **7** were tested under the same reaction conditions (Table 5). To our delight, 3-(trimethylsilyl)benzynes **3f** and **3g** were successfully generated from **4f** and **4g**, respectively, and their cycloadditions with nitrone **7a**, diazoacetate **7f**, 1,1-dimethoxyethylene **7g**, 1,3-dimethyl-2-imidazolidinone **7h**, and 4-arylsydnone **7i** proceeded with perfect regioselectivity in most cases (entries 1, 2, and 4–7).[4] These excellent results indicated the pronounced effect of the C3 silyl group of benzyne on controlling the orientation of

Table 5. Scope of 3-Silylbenzyne Generations from Precursors 4 and Their Regioselective Reactions with Arynophiles 7[a]



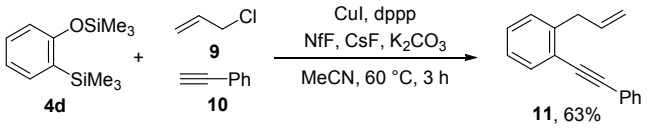
entry	precursor **4**	arynophile **7**	major product **8**	ratio[b]	yield[c]
1	**4f**	**7a**	 *distal*-**8fa**	95 : 5	84
2	**4f**	 **7f**	 *distal*-**8ff**	>98 : 2	79
3	**4f**	**7b**	 *distal*-**8fb**	75 : 25	76
4	**4f**	 **7g**	 *proximal*-**8fg**	>98 : 2	65
5	**4f**	 **7h**	 *distal*-**8fh**	>98 : 2	77
6	**4f**	 **7i**	 *distal*-**8fi**	>98 : 2	82
7	**4g**	**7i**	 *distal*-**8gi**	>98 : 2	82

[a]Conditions: **4** (0.50 mmol), **7** (1.5 mmol), NfF (0.75 mmol), and TBAT (0.75 mmol) in THF (0.1 M) at 60 °C for 3–24 h. [b]Ratio of regioisomers was determined by ^{1}H NMR spectra. [c]Isolated yield (%).

cycloaddition reactions. The better yield of a cycloaddition product **8fb** from silyl ether **4f** (76%, entry 3) was observed than that from 2-(trimethylsilyl)phenyl triflate **2d'** (52%).[4g]

Our new method is also applicable to transition-metal-catalyzed three-component coupling reactions[10] (Scheme 3). For example, a mixture of **4d**, allyl chloride **9**, and phenylacetylene **10** was heated at 60 °C for 2 h in the presence of CuI, dppp, CsF, K_2CO_3, and NfF to give **11** in 63% yield. In this case, CsF was found to be a suitable fluoride source, whereas TBAT produced a complex mixture.

Scheme 3. Application of Benzyne Precursor 4d to a Transition-Metal-Catalyzed Coupling Reaction



■ CONCLUSION

In summary, we have developed a new method for the direct generation of benzynes from 2-(trimethylsilyl)phenyl trimethylsilyl ethers, which are stable during both preparation and storage. This method avoids problematic triflylation by using easy-to-handle non-hygroscopic nonafluorobutanesulfonyl fluoride (NfF) and tetrabutylammonium triphenyldifluorosilicate (TBAT). The simple and convenient access to 3-silylbenzynes from readily available 2-chloro- or 2-bromophenol precursors is another advantage of this method. Our new benzyne precursors **4** would contribute to benzyne chemistry and take over 2-(trimethylsilyl)phenyl triflates **2'** in the near future.

■ EXPERIMENTAL SECTION

General. All reactions were carried out under a nitrogen atmosphere. A round-bottomed, two necked, three necked, or side-arm flasks containing a magnetic stir-bar with a three-way stopcock were used as reactors. 2.6 M solution of *n*-BuLi in hexane was purchased from Kanto Chemical. CsF was heated under reduced pressure with a flame torch for each reaction. 18-Crown-6 was recrystallized from anhydrous MeCN in a Schlenk flask. Anhydrous THF, Et_2O and MeCN were purchased from Kanto

Chemical, and purified with a Glass Contour solvent dispensing system (Nikko Hansen) using two packed columns of activated molecular sieves. Anhydrous toluene was purchased from Wako Pure Chemical Industries. 2-Bromo-3,5-dimethoxyphenol (**5a**),[5a] 3-bromonaphthol (**5b**),[7a] 10-bromophenanthrol (**5c**),[11] 2-(trimethylsilyl)phenol (**1e**),[3a,9] 3-phenylsydnone (**7d**),[12] 2,4,6-trimethylbenzonitrile oxide (**7e**),[13] 1,1-dimethoxyethylene (**7g**)[14] and 4-(4-methoxyphenyl)-3-phenylsydnone (**7i**)[11] were prepared according to the literature. All other reagents were purchased from Wako Pure Chemical Industries, Tokyo Chemical Industry, Sigma-Aldrich, Kishida Chemical, Nacalai Tesque, and Combi-Blocks and used without further purification. Flash chromatography[15] was performed with silica gel 60N, spherical neutral (40–50 μm), purchased from Kanto Chemical. All reactions were monitored by thin-layer chromatography (TLC) on glass-backed silica gel 60 F254, 0.2 mm plates (Merck), and compounds were visualized under UV light (254 nm). These TLC plates were also used for preparative thin-layer chromatography (PTLC).

Melting points were recorded on a Yanagimoto melting point apparatus and are uncorrected. IR spectra were obtained on a SHIMADZU IRAffinity-1S. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JMN-ECA-500 (^{1}H: 500 MHz, ^{13}C: 125 MHz), 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 undeuterated solvent. NOESY, HMBC, HMQC spectra were taken by a JEOL JMN-ECA-500, a JEOL JMN-ECS-400, a JEOL JMN-AL-300. GC chromatograms were recorded on a SHIMADZU GC-2010 and *n*-decane was used as an internal standard. The mass spectra were recorded on a JEOL JMS-S3000 (MALDI, TOF), or a JEOL JMS-700 (FAB, quadrupole). 'Yield' refers to the isolated yields of compounds showing at most only trace peaks in the ^{1}H NMR spectra that are not attributable to the assigned structure. ^{1}H NMR and melting points (where applicable) of all known compounds were taken. All new products were further characterized by ^{13}C NMR, infrared (IR) and high resolution mass (HRMS) spectra. The regiochemistry of *distal*-**8ff** was confirmed by NOESY, HMBC and HMQC spectra and all other regiochemistries of cycloaddition products *distal*-**8ab**, *distal*-

and *proximal*-**8ee**, *distal*- and *proximal*-**8hb**, *distal*- and *proximal*-**8fa**, *proximal*-**8fg**, *distal*-**8fh**, *distal*-**8fi**, *distal*-**8gi**, were confirmed by NOESY spectra.

Preparation of 2-(trimethylsilyl)phenols 1, 2-(trimethylsilyl)phenyl triflates 2, and 2-(trimethylsilyl)phenyl trimethylsilyl ethers 4 from 2-bromophenols 5 (Table 1):

General Procedure A: An oven-dried round bottom flask was charged with **5** (1.0 equiv) and a stir-bar. The flask was equipped with a three-way stopcock, and evacuated and back-filled with N_2 (This process was repeated three times). Anhydrous THF (0.20 M), Me_3SiCl (1.5 equiv), and Et_3N (1.5 equiv) were sequentially added into the flask via a syringe. The mixture was stirred at room temperature for 1 h. The reaction mixture was evaporated under reduced pressure and the residue was filtrated through a celite cake and washed with hexane to provide the 2-bromophenyl trimethylsilyl ether which can be used without further purification. The obtained silyl ether was dissolved in anhydrous THF (0.20 M, for Work-up Methods I and III) or Et_2O (0.10 M, for Work-up Method II) under N_2. After the mixture was cooled to –78 °C, 2.6 M solution of *n*-BuLi in hexane (1.2 equiv) was added dropwise into the mixture and it was stirred for 1 h. The reaction was quenched by following Work-up Method I–III.

Work-up Method I: sat. aq NH_4Cl (ca. 3–5 mL) was added to the reaction mixture at –78 °C. After the mixture was warmed to room temperature, it was extracted with hexane three times. The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/AcOEt) to afford 2-(trimethylsilyl)phenol **1**.

Work-up Method II: Tf_2O (1.5 equiv) was added to the reaction mixture at –78 °C and the mixture was stirred for 1 h at –78 °C. The reaction was quenched with sat. aq $NaHCO_3$ (ca. 3–5 mL) at –78 °C. After the mixture was warmed to room temperature, it was extracted with hexane three times. The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/AcOEt) to afford 2-(trimethylsilyl)aryl triflate **2'**.

Work-up Method III: Me_3SiCl (1.5 equiv) was added to the reaction mixture at –78 °C and the mixture was stirred for 1 h at –78 °C. The reaction was quenched with sat. aq $NaHCO_3$ (ca. 3–5 mL) at –78 °C. After the mixture was warmed to room temperature, it was extracted with hexane three times. The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/AcOEt) to afford 2-(trimethylsilyl)aryl trimethylsilyl ether **4**.

2-(Trimethylsilyl)-3,5-dimethoxyphenol (1a) (Table 1, entry 1): Following General Procedure A, a mixture of Me_3SiCl (0.15 mL, 1.2 mmol), Et_3N (0.17 mL, 1.2 mmol) and 2-bromo-3,5-dimethoxyphenol (**5a**)[5a] (0.19 g, 0.80 mmol) was stirred in THF (4.0 mL, 0.20 M) for 1 h at room temperature. To the obtained silyl ether in THF (4.0 mL, 0.20 M) was added *n*-BuLi (1.6 M in hexane, 0.60 mL, 0.96 mmol) at –78 °C and the mixture was stirred for 1 h. Following Work-up Method I, sat. aq NH_4Cl (3 mL) was added and stirred for 1 h at room temperature. However, the titled compound **1a** could not be detected by ^1H NMR analysis of the crude mixture.

2-(Trimethylsilyl)-3,5-dimethoxyphenyl trifluoromethanesulfonate (2a') (Table 1, entry 2):[5a] Following General Procedure A, a mixture of Me_3SiCl (0.15 mL, 1.2 mmol), Et_3N (0.17 mL, 0.80 mmol) and 2-bromo-3,5-dimethoxyphenol (**5a**)[5a] (0.19 g, 0.80 mmol) was stirred in THF (4.0 mL, 0.20 M) for 1 h at room temperature. To the obtained silyl ether in Et_2O (4.0 mL, 0.20 M) was added *n*-BuLi (1.6 M in hexane, 0.60 mL, 0.96 mmol) at –78 °C and stirred for 1 h. Following Work-up Method II, Tf_2O (0.20 mL, 1.2 mmol) was added and stirred for 1 h at –78 °C. However, the titled compound **2a'** could not be detected by ^1H NMR analysis of the crude mixture.

2-(Trimethylsilyl)-3,5-dimethoxyphenyl trimethylsilyl ether (4a) (Table 1, entry 3): Following General Procedure A, a mixture of Me_3SiCl (0.82 mL, 6.4 mmol), Et_3N (0.90 mL, 6.4 mmol) and 2-bromo-4,6-dimethoxyphenol (**5a**)[5a] (1.0 g, 4.3 mmol) was stirred in THF (22 mL, 0.20 M) for 1 h at room temperature. To the obtained silyl ether in THF (22 mL, 0.20 M) was added *n*-BuLi (2.6 M in hexane, 2.0 mL, 5.2 mmol) at –78 °C and stirred for 1.5 h. Following Work-up Method III, Me_3SiCl

(0.82 mL, 6.5 mmol) was added and stirred for 1 h. The crude material was purified by flash column chromatography on silica gel (hexane/EtOAc = 10:1) to provide the titled compound **4a** as a colorless oil (1.1 g, 84%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.26 (9 H, s), 0.32 (9 H, s), 3.73 (3 H, s), 3.78 (3 H, s), 6.00 (1 H, d, J = 2.0 Hz), 6.08 (1 H, d, J = 2.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 0.7, 1.5, 54.99, 55.03, 90.9, 96.7, 108.3, 162.0, 162.3, 166.6. IR (neat): 1595, 1402 cm^{-1}. HRMS (MALDI) Calcd for $C_{14}H_{26}O_3Si_2$ $[M]^+$: 298.1415, found 298.1393.

3-(Trimethylsilyl)-2-naphthol (1b) (Table 1, entry 4):[16] Following General Procedure A, a mixture of Me_3SiCl (85 μL, 0.68 mmol), Et_3N (94 μL, 0.68 mmol) and 3-bromo-2-naphthol (**5b**)[7a] (0.10 g, 0.45 mmol) was stirred in THF (2.3 mL, 0.20 M) for 1 h at room temperature. To the obtained silyl ether in THF (4.5 mL, 0.10 M) was added *n*-BuLi (2.6 M in hexane, 0.25 mL, 0.52 mmol) at –78 °C and stirred for 1 h. Following Work-up Method I, sat. aq NH_4Cl (3 mL) was added and stirred for 1 h at room temperature. The crude material was purified by flash column chromatography on silica gel (hexane/EtOAc = 10:1) to provide the titled compound **1b** as a colorless oil (23 mg, 25%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.40 (9 H, s), 6.98 (1 H, s), 7.27–7.36 (1 H, m), 7.38–7.47 (1 H, m), 7.62 (1 H, d, J = 8.0 Hz), 7.78 (1 H, d, J = 8.0 Hz), 7.88 (1 H, s).

3-(Trimethylsilyl)naphthalene-2-yl trifluoromethanesulfonate (2b') (Table 1, entry 5):[7a] Following General Procedure A, a mixture of Me_3SiCl (85 μL, 0.68 mmol), Et_3N (94 μL, 0.68 mmol) and 3-bromo-2-naphthol (**5b**)[7a] (0.10 g, 0.45 mmol) was stirred in THF (2.3 mL, 0.20 M) for 1 h at room temperature. To the obtained silyl ether in Et_2O (4.5 mL, 0.10 M) was added *n*-BuLi (2.6 M in hexane, 0.25 mL, 5.2 mmol) at –78 °C and stirred for 1.5 h. Following Work-up Method II, Tf_2O (0.16 mL, 0.66 mmol) was added and stirred for 1 h. The crude material was purified by flash column chromatography on silica gel (hexane/EtOAc = 10:1) to provide the titled compound **2b'** as a colorless oil (18 mg, 12%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.44 (9 H, s), 7.51–7.60 (2 H, m), 7.80 (1 H, s), 7.82–7.90 (2 H, m), 8.01 (1 H, s).

3-(Trimethylsilyl)naphthalene-2-yl trimethylsilyl ether (4b) (Table 1, entry 6): Following General Procedure A, a mixture of Me_3SiCl (0.19 mL, 1.5 mmol), Et_3N (0.21 mL, 1.5 mmol) and 3-bromo-2-naphthol (**5b**)[7a] (0.22 g, 1.0 mmol) was stirred in THF (5.0 mL, 0.20 M) for 1 h at room temperature. To the obtained silyl ether in THF (10 mL, 0.10 M) was added *n*-BuLi (2.6 M in hexane, 0.50 mL, 1.3 mmol) at –78 °C and stirred for 1.5 h. Following Work-up Method III, Me_3SiCl (0.19 mL, 1.5 mmol) was added and stirred for 1 h. The crude material was purified by flash column chromatography on silica gel (hexane) to provide the titled compound **4b** as a brown solid (0.23 g, 80%). Mp: 51–52 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.34 (9 H, s), 0.40 (9 H, s), 7.06 (s, 1 H), 7.31 (1 H, dd, *J* = 8.0, 8.0 Hz), 7.41 (1 H, dd, *J* = 8.0, 8.0 Hz), 7.66 (1 H, d, *J* = 8.0 Hz), 7.76 (1 H, d, *J* = 8.0 Hz), 7.86 (1 H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: –0.8, 0.6, 110.7, 123.5, 126.2, 126.4, 127.8, 128.8, 132.9, 135.4, 136.2, 157.7. IR (neat): 1587, 1445 cm^{-1}. HRMS (MALDI) Calcd for $C_{16}H_{24}OSi_2$ $[M]^+$: 288.1360, found 288.1367.

10-(Trimethylsilyl)-9-phenanthrol (1c) (Table 1, entry 7): Following General Procedure A, a mixture of Me_3SiCl (95 μL, 0.75 mmol), Et_3N (105 μL, 0.75 mmol) and 10-bromo-9-phenanthrol (**5c**)[11] (0.14 g, 0.50 mmol) was stirred in THF (2.5 mL, 0.20 M) for 1 h at room temperature. To the obtained silyl ether in THF (2.5 mL, 0.20 M) was added *n*-BuLi (2.1 M in hexane, 0.29 mL, 0.60 mmol) at –78 °C and the mixture was stirred for 1 h. Following Work-up Method I, sat. aq NH_4Cl (3 mL) was added and stirred for 1 h at room temperature. 9-Phenanthryl trimethylsilyl ether (**12**) (8% determined by ^{1}H NMR which was identical with alternatively synthesized compound **12** shown below) was observed in the crude mixture. The crude material was purified by flash column chromatography on silica gel (hexane) to provide 9-phenanthrol[17] (65 mg, 46 %) and **5c** (17 mg, 6%). However, the titled compound **1c** could not be detected by ^{1}H NMR analysis.

Alternative synthesis of 9-phenanthryl trimethylsilyl ether (12) (Table 1, entry 7): A test tube (1.0 mL) was charged with 9-phenanthrol[17] (5.0 mg, 26 μmol) and a stir-bar. THF (ca. 0.50 mL, 0.050 M) and Me_3SiCl (1 drop), Et_3N (1 drop) were sequentially added to the test tube using a Pasteur pipet. The test tube was blown with N_2 and equipped with a rubber septum. The mixture was stirred at room

temperature for 1 h. The reaction mixture was evaporated under reduced pressure and the residue was filtrated through a celite cake and washed with hexane. The resultant residue was concentrated under reduced pressure to provide the titled compound **12** as a colorless oil (6.4 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.40 (9 H, s), 7.08 (s, 1 H), 7.49–7.47 (2 H, m), 7.63 (1 H, ddd, *J* = 8.0, 8.0, 1.5 Hz), 7.68 (1 H, ddd, *J* = 8.0, 8.0, 1.5 Hz), 7.75 (1 H, dd, *J* = 8.0, 1.5 Hz), 8.25 (1 H, dd, *J* = 8.0, 1.5 Hz), 8.61 (1 H, d, *J* = 8.0 Hz), 8.67 (1 H, d, *J* = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 0.4, 110.9, 122.5, 122.6, 123.1, 124.5, 126.3, 126.7, 126.9, 127.2, 128.6, 131.6, 132.9, 149.5. IR (neat): 1450, 1317, 1229 cm^{-1}. HRMS (MALDI) Calcd for $C_{17}H_{18}OSi$ $[M]^+$: 266.1121, found 266.1128.

10-(Trimethylsilyl)-9-phenanthryl trifluoromethanesulfonate (2c') (Table 1, entry 8):[11] Following General Procedure A, a mixture of Me_3SiCl (95 μL, 0.75 mmol), Et_3N (105 μL, 0.75 mmol) and 10-bromo-9-phenanthrol (**5c**)[11] (0.14 g, 0.50 mmol) was stirred in THF (2.5 mL, 0.20 M) for 1 h at room temperature. To the obtained silyl ether in Et_2O (2.5 mL, 0.20 M) was added *n*-BuLi (2.1 M in hexane, 0.29 mL, 0.60 mmol) at –78 °C and stirred for 1 h. Following Work-up Method II, Tf_2O (96 μL, 0.57 mmol) was added and stirred for 1 h at –78 °C. However, the titled compound **2c'** could not be detected by ^{1}H NMR analysis of the crude mixture.

10-(Trimethylsilyl)phenanthren-9-yl trimethylsilyl ether (4c) (Table 1, entry 9): Following General Procedure A, a mixture of Me_3SiCl (0.19 mL, 1.5 mmol), Et_3N (0.21 mL, 1.5 mmol) and 10-bromo-9-phenanthrol (**5c**)[11] (0.22 g, 1.0 mmol) was stirred in THF (5.0 mL, 0.20 M) for 1 h at room temperature. To the obtained silyl ether in THF (10 mL, 0.10 M) was added *n*-BuLi (2.6 M in hexane, 0.50 mL, 1.3 mmol) at –78 °C and stirred for 1.5 h. Following Work-up Method III, Me_3SiCl (0.19 mL, 1.5 mmol) was added and stirred for 1 h. The crude material was purified by flash column chromatography on silica gel (hexane) to provide the titled compound **4c** as a white solid (0.24 g, 72%). Mp: 103–105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.24 (9 H, s), 0.52 (9 H, s), 7.47–7.67 (4 H, m), 8.02–8.08 (1 H, m), 8.14 (1 H, dd, *J* = 8.0, 1.5 Hz), 8.58–8.65 (2 H, m). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 1.2, 2.8, 120.3, 122.5, 122.9,

124.0, 124.2, 125.8, 125.9, 128.4, 128.5, 132.6, 136.6, 155.8. IR (neat): 1560, 1445, 1310 cm^{-1}. HRMS (MALDI) Calcd for $C_{20}H_{26}OSi_2$ $[M]^+$: 338.1517, found 338.1519.

Preparation of 2-(trimethylsilyl)phenyl trimethylsilyl ethers 4 from 2-chlorophenols 6 (Table 2):

General Procedure B: An oven-dried round bottom flask was charged with 2-chlorophenol **6** (1.0 equiv) and a stir-bar. The flask was equipped with a three-way stopcock, and evacuated and back-filled with N_2 (This process was repeated three times). Anhydrous THF (1.0 M) and hexamethyldisilazane (HMDS) (1.0 equiv) were added into the flask via a syringe. The mixture was stirred at 60 °C for 1 h and evaporated under reduced pressure to provide 2-chlorophenyl trimethylsilyl ether which can be used in the next step without further purification. Another oven-dried three necked flask was charged with a glass coated stir-bar and equipped with two septum caps and a reflux condenser which has a three-way stopcock on the top. The flask was evacuated and back-filled with N_2 (This process was repeated three times). Anhydrous toluene (0.50 M) was added to the flask via a syringe and sodium metal (Na metal) (7.5 equiv for each chlorine atom) was quickly added under N_2 flow. The mixture was refluxed for 15 min. A mixture of the above obtained 2-chlorophenyl trimethylsilyl ether and Me_3SiCl (8.0 equiv for each chlorine atom) was added dropwise to the flask via a cannula at reflux temperature and continued to be refluxed for 18 h. After the reaction mixture was cooled to room temperature, the mixture was filtrated through a celite cake and washed with hexane. The filtrate was evaporated and the resultant residue was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 or hexane/EtOAc) to afford 2-(trimethylsilyl)phenyl trimethylsilyl ether **4**.

2-(Trimethylsilyl)phenyl trimethylsilyl ether (4d) (Table 2, entry 1):[18] Following General Procedure B, a mixture of HMDS (10 mL, 50 mmol) and 2-chlorophenol (**6a**) (6.4 g, 50 mmol) was stirred in THF (50 mL, 1.0 M) for 1 h at 60 °C, and the mixture was evaporated to provide the 2-chlorophenyl trimethylsilyl ether. A mixture of the obtained silyl ether and Me_3SiCl (50 mL, 0.40 mol) was added into Na metal (9.2 g, 0.40 mol) in toluene (0.10 L, 0.50 M) and refluxed for 18 h. The crude material was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 = 100:1) to provide the titled

compound **4d** as a colorless oil (10 g, 86%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.26 (9 H, s), 0.33 (9 H, s), 6.76 (1 H, dd, *J* = 8.0, 1.0 Hz), 6.93 (1 H, ddd, *J* = 7.5, 7.5, 1.0 Hz), 7.24 (1 H, ddd, *J* = 8.0, 7.5, 2.0 Hz), 7.37 (1 H, dd, *J* = 7.5, 2.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: –1.0, 0.6, 116.4, 120.5, 129.9, 130.5, 135.3, 160.3. IR (neat): 1470, 1435, 1238 cm^{-1}. HRMS (MALDI) Calcd for $C_{12}H_{22}OSi_2$ $[M]^+$: 238.1204, found 238.1206.

2,4-Bis(trimethylsilyl)phenyl trimethylsilyl ether (4e) (Table 2, entry 2):[19] Following General Procedure B, a mixture of HMDS (2.1 mL, 10 mmol) and 2,4-dichlorophenol (**6b**) (1.6 g, 10 mmol) was stirred in THF (10 mL, 1.0 M) for 1 h at 60 °C, and the mixture was evaporated to provide the 2,4-dichlorophenyl trimethylsilyl ether. A mixture of the obtained silyl ether and Me_3SiCl (20 mL, 0.16 mol) was added into Na metal (3.4 g, 0.15 mol) in toluene (20 mL, 0.50 M) and refluxed for 18 h. The crude material was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 = 100:1) to provide the titled compound **4e** as a colorless oil (2.5 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.18 (9 H, s), 0.31 (9 H, s), 0.37 (9 H, s), 6.79 (1 H, d, *J* = 8.0 Hz), 7.44 (1 H, d, *J* = 8.0 Hz), 7.56 (1 H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: –0.95, –0.86, 0.6, 115.8, 129.1, 130.7, 135.9, 140.5, 161.2. IR (neat): 1574, 1474, 1246 cm^{-1}. HRMS (MALDI) Calcd for $C_{15}H_{30}OSi_3$ $[M]^+$: 310.1599, found 310.1590.

2,6-Bis(trimethylsilyl)phenyl trimethylsilyl ether (4f) (Table 2, entry 3): Following General Procedure B, a mixture of HMDS (2.1 mL, 10 mmol) and 2,6-dichlorophenol (**6c**) (1.6 g, 10 mmol) was stirred in THF (10 mL, 1.0 M) for 1 h at 60 °C, and the mixture was evaporated to provide the 2,6-dichlorophenyl trimethylsilyl ether. A mixture of the obtained silyl ether and Me_3SiCl (20 mL, 0.16 mol) was added into Na metal (3.4 g, 0.15 mol) in toluene (20 mL, 0.50 M) and refluxed for 18 h. The crude material was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 = 100:1) to provide the titled compound **4f** as a white solid (2.4 g, 76%). Mp: 54–56 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.24 (9 H, s), 0.32 (18 H, s), 6.99 (1 H, t, *J* = 7.0 Hz), 7.41 (2 H, d, *J* = 7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 1.0, 1.9, 121.0, 130.0, 137.3, 164.7. IR (neat): 1558, 1377 cm^{-1}. HRMS (MALDI) Calcd for $C_{15}H_{30}OSi_3$ $[M]^+$: 310.1599, found 310.1574.

2,4,6-Tris(trimethylsilyl)phenyl trimethylsilyl ether (4g) (Table 2, entry 4): Following General Procedure B, a mixture of HMDS (2.1 mL, 10 mmol) and 2,4,6-trichlorophenol (**6d**) (2.0 g, 10 mmol) was stirred in THF (10 mL, 1.0 M) for 1 h at 60 °C, and the mixture was evaporated to provide the 2,4,6-trichlorophenyl trimethylsilyl ether. A mixture of the obtained silyl ether and Me_3SiCl (30 mL, 0.24 mol) was added into Na metal (5.2 g, 0.23 mol) in toluene (20 mL, 0.50 M) and refluxed for 18 h. The crude material was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 = 100:1) to provide the titled compound **4g** as a white solid (2.4 g, 68%). Mp: 47–50 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.250 (9 H, s), 0.252 (9 H, s), 0.33 (18 H, s), 7.55 (2 H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: –0.9, 1.0, 2.0, 128.9, 130.9, 142.8, 165.8. IR (neat): 1557, 1385, 1248 cm^{-1}. HRMS (FAB, NBA) Calcd for $C_{18}H_{38}OSi_4$ $[M]^+$: 382.2000, found 382.2000.

4-Amino-2-(trimethylsilyl)phenyl trimethylsilyl ether (4h) (Table 2, entry 5): An oven dried round bottom flask was charged with 4-amino-2,6-dichlorophenol (**6e**) (1.8 g, 10 mmol) and a stir-bar. The flask was equipped with a three-way stopcock, and evacuated and back-filled with N_2 (This process was repeated three times). Then, anhydrous THF (50 mL, 0.20 M), Me_3SiCl (3.8 mL, 30 mmol), and Et_3N (4.2 mL, 30 mmol) were sequentially added into the flask via a syringe at room temperature. The mixture was stirred at room temperature for 1 h. The reaction mixture was evaporated under reduced pressure and the residue was filtered through a celite pad and washed with hexane to provide the 4-[(trimethylsilyl)amino]-2,6-dichlorophenyl trimethylsilyl ether which can be used in the next step without further purification. Another oven-dried three necked flask was charged with a glass coated stir-bar and equipped with two septums and a reflux condenser having a three-way stopcock on the top. The flask was evacuated and back-filled with N_2 (This process was repeated three times). Anhydrous toluene (20 mL, 0.50 M) was added to the flask via a syringe and Na metal (3.4 g, 0.15 mol) was quickly added under N_2 flow. The mixture was refluxed for 15 min. A mixture of the above obtained trimethylsilyl ether and Me_3SiCl (20 mL, 0.16 mol) was added dropwise to the flask via a cannula at reflux temperature and continued to be refluxed for 18 h. After the reaction mixture was cooled to room

temperature, the mixture was filtrated through a celite cake and washed with hexane. The filtrate was evaporated and the resultant residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 4:1) to provide the titled compound **4h** as a brown solid (2.1 g, 88%). Mp: 83–85 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.23 (9 H, s), 0.28 (9 H, s), 3.36 (2 H, brs), 6.58–6.60 (2 H, m), 6.71–6.73 (1 H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: –0.9, 0.6, 117.0, 117.3, 122.3, 130.6, 139.4, 153.2. IR (neat): 3308, 3215, 1473 cm^{-1}. HRMS (MALDI) Calcd for $C_{12}H_{23}NOSi_2$ $[M]^+$: 253.1313, found 253.1309.

Synthesis of 2,6-bis(trimethylsilyl)phenyl triflate 2d' from 2,6-dibromophenol 5d (Scheme 2):

2-(Trimethylsilyl)-6-bromophenyl trimethylsilyl ether (4i) (Scheme 2): Following General Procedure A, a mixture of Me_3SiCl (1.9 mL, 15 mmol) and Et_3N (2.1 mL, 15 mmol) and 2,6-dibromophenol (**5d**) (2.6 g, 10 mmol) was stirred in THF (50 mL, 0.20 M) for 1 h at room temperature. To the obtained silyl ether in THF (50 mL, 0.20 M) was added *n*-BuLi (2.6 M in hexane, 4.6 mL, 12 mmol) at –78 °C and stirred for 1 h. Following Work-up Method III, Me_3SiCl (1.9 mL, 15 mmol) was added and stirred for 1 h. The crude material was purified by flash column chromatography on silica gel (hexane) to provide the titled compound **4i** as a colorless oil (2.2 g, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.31 (9 H, s), 0.41 (9 H, s), 6.83 (1 H, dd, J = 8.0, 7.5 Hz), 7.31 (1 H, dd, J = 7.5, 1.5 Hz), 7.53 (1 H, dd, J = 8.0, 1.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: –0.2, 2.5, 114.0, 122.5, 133.0, 134.5, 135.0, 157.0. IR (neat): 1570, 1416, 1246 cm^{-1}. HRMS (FAB, NBA) Calcd for $C_{12}H_{21}BrOSi_2$ $[M]^+$: 316.0309, found 316.0315.

2,6-Bis(trimethylsilyl)phenol (1d) (Scheme 2): Anhydrous THF (34 mL, 0.20 M) was added to 2-(trimethylsilyl)-6-bromophenyl trimethylsilyl ether (**4i**) (2.2 g, 6.8 mmol) in a round bottom flask equipped with a stir-bar and a three-way stopcock. After the mixture was cooled to –78 °C, *n*-BuLi (2.6 M in hexane, 3.1 mL, 8.2 mmol) was added dropwise into the mixture and it was stirred for 1 h. sat. aq NH_4Cl (5 mL) was added to the reaction mixture at –78 °C. After the mixture was warmed to room temperature, it was extracted with hexane three times. The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column

chromatography on silica gel (hexane) to provide the titled compound **1d** as a colorless oil (1.6 g, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.34 (18 H, s), 5.00 (1 H, brs), 6.94 (1 H, t, J = 7.5 Hz), 7.38 (2 H, d, J = 7.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: –0.6, 120.4, 124.0, 136.7, 165.2. IR (neat): 3614, 1580, 1389 cm^{-1}. HRMS (FAB, NBA) Calcd for $C_{12}H_{22}OSi_2$ $[M]^+$: 238.1204, found 238.1203.

2,6-Bis(trimethylsilyl)phenyl trifluoromethanesulfonate (2d') (Scheme 2):[4g]

[Stepwise method] Anhydrous Et_2O (65 mL, 0.10 M) was added to 2,6-bis(trimethylsilyl)phenol (**1d**) (1.6 g, 6.5 mmol) in a round bottom flask equipped with a stir-bar and a three-way stopcock. After the mixture was cooled to –78 °C, *n*-BuLi (2.6 M in hexane, 3.0 mL, 7.8 mmol) was added dropwise into the mixture and it was stirred for 10 min. Tf_2O (1.6 mL, 9.8 mmol) was added to the reaction mixture at –78 °C and the mixture was stirred for 5 h at room temperature. The reaction was quenched with sat. aq $NaHCO_3$ (10 mL). And it was extracted with hexane three times. The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane) to provide the titled compound **2d'** as a colorless oil (1.7 g, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.37 (18 H, s), 7.37 (1 H, t, J = 8.0 Hz), 7.58 (1 H, d, J = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 0.33, 118.4 (CF_3, q, J = 318 Hz), 127.3, 134.9, 138.2, 154.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ: –72.3. IR (neat): 1578, 1397, 1213 cm^{-1}. HRMS (FAB, NBA) Calcd for $C_{13}H_{21}O_3SF_3Si_2Na$ $[M+Na]^+$: 393.0594, found 393.0608.

[Direct method] Anhydrous Et_2O (10 mL, 0.10 M) was added to 2-(trimethylsilyl)-6-bromophenyl trimethylsilyl ether (**4i**) (0.32 g, 1.0 mmol) in a round bottom flask equipped with a stir-bar and a three-way stopcock. After the mixture was cooled to –78 °C, *n*-BuLi (2.5 M in hexane, 0.48 mL, 1.2 mmol) was added dropwise into the mixture and it was stirred for 1 h. Tf_2O (0.25 mL, 1.5 mmol) was added to the reaction mixture at –78 °C and the mixture was stirred for 5 h at room temperature. The reaction was quenched with sat. aq $NaHCO_3$ (5 mL). And it was extracted with hexane three times. The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane) to provide the titled compound **1d**

with **2d'** as a mixture (colorless oil, 0.21 g, 48% of **1d** and 26% of **2d'**). These two compounds (**1d** and **2d'**) were hard to separate completely by silica gel column chromatography.

Optimization of benzyne generation in detail (Table 3):

Procedures for Table 3, entries 1–3, and 9–15: An oven-dried side-arm flask was charged with **4d** (24 mg, 0.10 mmol), *N*-*tert*-butyl-α-phenylnitrone (**7a**) (53 mg, 0.30 mmol) and a stir-bar. The flask was equipped with a septum, and evacuated and back-filled with N_2 (This process was repeated three times). Anhydrous THF (1.0 mL, 0.10 M) and NfF (26 μL, 0.15 mmol) were added into the flask via a syringe through the septum. Then, a fluoride source (0.050–3.0 equiv) was quickly added to the flask at room temperature with N_2 flow [A solution of Bu_4NF (3.0 equiv) was added via a syringe through the septum]. The mixture was [warmed to 60 °C and (for entries 10–15)] stirred for 5 h. The reaction mixture was filtered through a short pad of silica gel and washed with EtOAc. *n*-Decane (19 μL, 0.10 mmol) was added to the filtrate and the crude mixture (1.0 μL) was injected to a gas chromatograph (GC) to determine yields of **8da**,[20] **1e**,[3a,9] and **2e**.[3a,9] The mixture was evaporated under reduced pressure and the resultant residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 8:1) to provide **8da**.

Procedures for Table 3, entries 4–8: A side-arm flask was charged with CsF [46 mg, 0.30 mmol (for entries 4, 5, 7 and 8) or 30 mg, 0.20 mmol (for entry 6)] and a stir-bar. The flask was equipped with a septum and heated under reduced pressure with a flame torch. After cooling to room temperature under reduced pressure, the flask was back-filled with N_2. The solution of **4d** (23 mg, 0.10 mmol) and *N*-*tert*-Butyl-α-phenylnitrone (**7a**) (53 mg, 0.30 mmol) in solvent (1.0 mL) was added to the flask via a cannula at room temperature [or at 0 °C (for entry 8)] and the mixture was [warmed to 60 °C and (for entry 7)] stirred at the indicated temperature for 5 h. Then, the reaction mixture was filtered through a short pad of silica gel and washed with EtOAc. *n*-Decane (19 μL, 0.10 mmol) was added to the filtrate and the crude mixture (1.0 μL) was injected to a gas chromatograph (GC) to determine yields of **8da**,[20] **1e**,[3a,9]

and **2e**.[3a,9] The mixture was evaporated under reduced pressure and the resultant residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 8:1) to provide **8da**.

2-(*tert*-Butyl)-3-phenyl-2,3-dihydrobenzo[*d*]isoxazole (8da) (Table 3, entry 11):[20] An oven-dried side-arm flask was charged with 2-(trimethylsilyl)phenyl trimethylsilyl ether **4d** (24 mg, 0.10 mmol) and *N*-*tert*-butyl-α-phenylnitrone (**7a**) (53 mg, 0.30 mmol) and a stir-bar. The flask was equipped with a septum, and evacuated and back-filled with N_2 (This process was repeated three times). Anhydrous THF (1.0 mL, 0.10 M) and NfF (27 μL, 0.15 mmol) were added into the flask via a syringe through the septum. Then, $Bu_4NPh_3SiF_2$ (TBAT) (81 mg, 0.15 mmol) was quickly added to the flask at room temperature with N_2 flow. The mixture was warmed to 60 °C and stirred at for 5 h. After cooling to room temperature, the reaction mixture was filtered through a short pad of silica gel using EtOAc and solvents were removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc = 8:1) to afford the titled compound **8da** as a white solid (21 mg, 91%). Mp: 92–94 °C (lit. 93–95 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.18 (9 H, s), 5.59 (1 H, s), 6.77–6.82 (2 H, m), 6.88 (1 H, d, *J* = 7.5 Hz), 7.14 (1 H, dd, *J* = 8.0, 8.0 Hz), 7.22–7.26 (1 H, m), 7.32 (2 H, dd, *J* = 7.5, 7.5 Hz), 7.39 (2 H, d, *J* = 7.5 Hz).

2-(Trimethylsilyl)phenyl perfluorobutaneslufonate (2d) (Table 3, entry 15):[3a,9] An oven-dried side-arm flask was charged with 2-(trimethylsilyl)phenyl trimethylsilyl ether (**4d**) (23 mg, 0.10 mmol) and a stir-bar. The flask was equipped with a septum, and evacuated and back-filled with N_2 (This process was repeated three times). Anhydrous THF (1.0 mL, 0.10 M) and NfF (26 mL, 0.15 mmol) were added into the flask via a syringe. Then, TBAT (2.7 mg, 5.0 μmol) was quickly added to the flask with N_2 flow. The mixture was stirred at 60 °C for 24 h. After cooling to room temperature, the reaction mixture was filtered through a short pad of silica gel and washed with EtOAc and solvents were removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane) to provide the titled compound **2d** as a colorless oil (13 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.40 (9 H, s), 7.34–7.37 (2 H, m), 7.46 (1 H, ddd, *J* = 2.5, 7.5, 7.5 Hz), 7.56 (1 H, dd, *J* = 2.5, 7.5 Hz).

Reactions of 2-(trimethylsilyl)phenyl trimethylsilyl ethers 4 with arynophiles 7 (Tables 4 and 5):

General Procedure C: An oven-dried side-arm flask was charged with **4** (1.0 equiv) [and arynophile **7** (3.0 equiv) in cases where the **7** was solid] and a stir-bar. The flask was equipped with a septum, and evacuated and back-filled with N_2 (This process was repeated three times). Anhydrous THF and NfF (1.5 equiv) [and arynophile **7** (3.0 equiv) in cases where the **7** was liquid] was added into the flask via a syringe through the septum. Then, TBAT ($Bu_4NPh_3SiF_2$) (1.5 equiv) was quickly added to the flask at room temperature with N_2 flow. The mixture was warmed to 60 °C and stirred at for 5 h. After cooling to room temperature, the reaction mixture was filtered through a short pad of silica gel using EtOAc, and solvents were removed under reduced pressure. The resultant residue was filtered through a short pad of silica gel using hexane/EtOAc (10:1) to remove Ph_3SiF and then other products were washed out using hexane/EtOAc (1:1). The crude mixture was subjected to ^{1}H NMR analysis for calculating the ratio of the two regioisomers (*distal*- and *proximal*-**8**). The crude product was purified by flash column chromatography on silica gel or PTLC (hexane or CH_2Cl_2 or a mixture of hexane and EtOAc, hexane and toluene) to afford *distal*- and *proximal*-**8**.

1-Benzyl-4,6-dimethoxy-1*H*-benzo[*d*][1,2,3]triazole (*distal*-8ab) (Table 4, entry 1): Following General Procedure C, a mixture of TBAT (161 mg, 0.30 mmol), NfF (53 μL, 0.30 mmol), benzylazide (**7b**) (75 μL, 0.45 mmol) and 3,5-dimethoxy-2-(trimethylsilyl)phenyl trimethylsilyl ether (**4a**) (60 mg, 0.20 mmol) was stirred in THF (2.0 mL, 0.10 M) for 20 h at 60 °C. The crude product (*distal*-**8ab**/*proximal*-**8ab** = >98:2, determined by 400 MHz ^{1}H NMR analysis) was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to provide the titled compound *distal*-**8ab** as a pale yellow solid (47 mg, 86%) and its regiochemistry was determined by NOESY spectra. Mp: 167–169 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.76 (3 H, s), 4.04 (3 H, s), 5.74 (2 H, s), 6.16 (1 H, d, J = 1.5 Hz), 6.30 (1 H, d, J = 1.5 Hz), 7.23 (2 H, d, J = 7.0 Hz), 7.27–7.35 (3 H, m). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 51.8, 55.7, 56.1, 82.2, 96.1, 127.3, 128.2, 128.8, 134.3, 134.8, 135.3, 151.9, 161.3. IR (neat): 1620, 1516 cm^{-1}. HRMS (MALDI) Calcd for $C_{15}H_{16}N_3O_2$ $[M+H]^+$: 270.1237, found 270.1240.

1-Methyl-1,4-dihydro-1,4-epoxyanthracene (8bc) (Table 4, entry 2): Following General Procedure C, a mixture of TBAT (161 mg, 0.30 mmol), NfF (53 μL, 0.30 mmol), 2-methylfuran (**7c**) (53 μL, 0.45 mmol) and 3-(trimethylsilyl)-2-naphthyl trimethylsilyl ether (**4b**) (58 mg, 0.20 mmol) was stirred in THF (2.0 mL, 0.10 M) for 16 h at 60 °C. The crude product was purified by column chromatography on silica gel (hexane/EtOAc = 8:1) to provide the titled compound **8bc** as a colorless oil (35 mg, 85%). Mp: 71–73 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.00 (3 H, s), 5.72 (1 H, d, *J* = 1.5 Hz), 6.71 (1 H, d, *J* = 5.0 Hz), 6.96 (1 H, dd, *J* = 5.0 , 1.5 Hz), 7.41–7.45 (2 H, m), 7.48 (1 H, s), 7.54 (1 H, s), 7.69–7.75 (2 H, m). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 15.3, 81.3, 88.7, 117.1, 118.2, 126.0, 128.0, 128.1, 131.7, 131.9, 142.8, 144.3, 145.8, 147.0. IR (neat): 1662, 1307 cm^{-1}. HRMS (MALDI) Calcd for $C_{15}H_{12}O$ $[M]^+$: 208.0883, found 208.0881.

2-Phenyl-2*H*-dibenzo[*e*,*g*]indazole (8cd) (Table 4, entry 3): Following General Procedure C, a mixture of TBAT (161 mg, 0.30 mmol), NfF (53 μL, 0.30 mmol), 3-phenylsydnone (**7d**)[13] (97 mg, 0.45 mmol) and 10-(trimethylsilyl)-9-phenanthoryl trimethylsilyl ether (**4c**) (68 mg, 0.20 mmol) was stirred in THF (2.0 mL, 0.10 M) for 5 h at 60 °C. The crude product was purified by column chromatography on silica gel (hexane/EtOAc = 8:1) to provide the titled compound **8cd** as a white solid (37 mg, 63%). Mp: 104–106 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.39 (1 H, dd, *J* = 7.5, 7.5 Hz), 7.53–7.59 (4 H, m), 7.61–7.67 (2 H, m), 7.98 (2 H, m), 8.10 (1 H, m), 8.56 (2 H, m), 8.68–8.72 (2 H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 118.7, 120.1, 120.7, 123.3, 123.5, 123.9, 124.1, 125.8, 126.0, 126.8, 127.1, 127.3, 127.4, 127.6, 129.0, 129.6, 130.8, 140.5, 147.0. IR (neat): 1599, 1504 cm^{-1}. HRMS (MALDI) Calcd for $C_{21}H_{14}N_2$ $[M]^+$: 294.1151, found 294.1146.

3-(2,4,6-Trimethylphenyl)-6-(trimethylsilyl)benzo[*d*]isoxazole and 3-(2,4,6-trimethylphenyl)-5-(trimethylsilyl)benzo[*d*]isoxazole (*distal*- and *proximal*-8ee) (Table 4, entry 4): Following General Procedure C, a mixture of TBAT (162 mg, 0.30 mmol), NfF (53 μL, 0.30 mmol), 2,4,6-trimethylphenylnitriloxide (**7e**)[12] (48 mg, 0.45 mmol) and 2,4-bis(trimethylsilyl)phenyl trimethylsilyl ether (**4e**) (63 mg, 0.10 mmol) was stirred in THF (2.0 mL, 0.10 M) for 24 h at 60 °C. The crude product

(*distal*-**8ee**/*proximal*-**8ee** = 76:24, determined by 400 MHz ^{1}H NMR analysis) was purified by column chromatography on silica gel (hexane/EtOAc = 15:1) and PTLC (hexane/toluene = 1:1) to provide the titled compound *distal*- and *proximal*-**8ee** (65:35) as a colorless oil (50 mg, 88%) and its regiochemistry was determined by NOESY spectra. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.29 (9/3 H, s), 0.37 (18/3 H, s), 2.10 (12/3 H, s), 2.11 (6/3 H, s), 2.36 (6/3 H, s), 2.40 (3/3 H, s), 7.02 (4/3 H, s), 7.04 (2/3 H, s), 7.39 (2/3 H, d, J = 8.0 Hz), 7.43 (2/3 H, d, J = 8.0 Hz), 7.52 (1/3 H, s), 7.66 (1/3 H, d, J = 8.5 Hz), 7.73 (1/3 H, d, J = 8.5 Hz), 7.83 (2/3 H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ: –1.1, –0.9, 20.06, 20.13, 21.2, 109.5, 114.5, 121.2, 122.0, 122.5, 124.3, 124.4, 127.1, 128.0, 128.46, 128.53, 134.5, 135.6, 137.65, 137.73, 139.20, 139.24, 143.6, 157.6, 157.7, 163.0, 163.7. IR (neat): 1612, 1449, 1250 cm^{-1}. HRMS (MALDI) Calcd for $C_{19}H_{24}NOSi$ $[M+H]^+$: 310.1622, found 310.1617.

5-Amino-1-benzyl-1*H*-benzo[*d*][1,2,3]triazol (*distal*-8hb) (Table 4, entry 5): Following General Procedure C, a mixture of TBAT (0.40 g, 0.50 mmol), benzylazide (**7b**) (0.19 mL, 1.5 mmol), and 4-amino-2,6-bis(trimethylsilyl)phenyl trimethylsilyl ether (**4h**) (0.12 g, 67 μmol) was stirred in THF (5.0 mL) for 6 h at 60 °C. The crude product (*distal*-**8hb**/*proximal*-**8hb** = 50:50, determined by 400 MHz ^{1}H NMR analysis) was purified by column chromatography on silica gel (hexane/EtOAc = 1:2) to provide the titled compound *distal*-**8hb** as a brown solid (12 mg, 26%) and its regiochemistry was determined by NOESY spectra. Mp: 169–171 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.78 (2 H, brs), 5.75 (2 H, s), 6.82 (1 H, d, J = 8.5, 2.5 Hz), 7.10 (1 H, d, J = 8.5 Hz), 7.18 (1 H, d, J = 2.5 Hz), 7.21–7.27 (2 H, m), 7.28–7.34 (3 H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 52.3, 101.4, 110.4, 119.3, 127.5, 127.7, 128.3, 128.9, 134.9, 143.4, 147.8. IR (neat): 3433, 3341, 1506 cm^{-1}. HRMS (MALDI) Calcd for $C_{13}H_{13}N_4$ $[M+H]^+$: 225.1135, found 225.1127.

5-Amino-1-benzyl-1*H*-benzo[*d*][1,2,3]triazol (*proximal*-8hb) (Table 4, entry 5) was obtained from the above-mentioned reaction mixture as a brown solid (12 mg, 26%) and its regiochemistry was determined by NOESY spectra. Mp: 158–160 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.91 (2 H, brs), 5.70 (2 H, s), 6.40 (1 H, d, J = 2.5 Hz), 6.71 (1 H, dd, J = 8.5, 2.5 Hz), 7.22–7.26 (2 H, m), 7.28–7.35 (3 H,

m), 7.81 (1 H, d, J = 8.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ:51.7, 91.1, 115.6, 120.8, 127.4, 128.2, 128.9, 134.5, 135.1, 141.1, 146.5. IR (neat): 3325, 3217, 1624 cm^{-1}. HRMS (MALDI) Calcd for $C_{13}H_{13}N_4$ $[M+H]^+$: 225.1135, found 225.1134.

2-(*tert*-Butyl)-3-phenyl-7-(trimethylsilyl)-2,3-dihydrobenzo[*d*]isoxazole (*distal*-8fa) (Table 5, entry 1): Following General Procedure C, a mixture of TBAT (57 mg, 0.30 mmol), NfF (26 μL, 0.15 mmol), *N*-*tert*-butyl-α-phenylnitrone (**7a**) (57 mg, 0.30 mmol), and 2,6-bis(trimethylsilyl)phenyl trimethylsilyl ether (**4f**)[13] (31 mg, 0.10 mol) was stirred in THF (1.0 mL) for 24 h at 60 °C. The crude product (*distal*-**8fa**/*proximal*-**8fa** = 95:5, determined by 400 MHz ^{1}H NMR analysis) was purified by column chromatography on silica gel (hexane/EtOAc = 1:20) and PTLC (hexane/EtOAc = 1:15) to provide the titled compound *distal*-**8fa** as a yellow solid (27 mg, 80%) and its regiochemistry was determined by NOESY spectra. Mp: 60–62 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.34 (9 H, s), 1.18 (9 H, s), 5.56 (1 H, s), 6.81 (1 H, dd, J = 7.5, 7.0 Hz), 6.90 (1 H, dd, J = 7.5, 1.0 Hz), 7.21–7.26 (2 H, m), 7.32 (2 H, dd, J = 8.5, 8.5 Hz) 7.37 (2 H, d, J = 8.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ:–1.2, 25.4, 61.0, 66.7, 117.2, 120.4, 124.7, 127.3, 127.4, 128.0, 128.6, 133.7, 144.0, 161.1. IR (neat): 1416, 1364 cm^{-1}. HRMS (MALDI) Calcd for $C_{20}H_{27}NOSi$ $[M]^+$: 325.1856, found 325.1857.

2-(*tert*-Butyl)-3-phenyl-4-(trimethylsilyl)-2,3-dihydrobenzo[*d*]isoxazole (*proximal*-8fa) (Table 5, entry 1) was obtained from the above-mentioned reaction mixture as a white solid (1.3 mg, 4%) and its regiochemistry was determined by NOESY spectra. Mp: 67–70 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: –0.03 (9 H, s), 1.18 (9 H, s), 5.63 (1 H, s), 6.91 (1 H, d, J = 8.0 Hz), 7.00–7.07 (2 H, m), 7.20–7.30 (5 H, m). ^{13}C NMR (125 MHz, $CDCl_3$) δ: –1.0, 25.6, 61.3, 66.6, 107.5, 127.0, 127.6, 128.2, 128.4, 128.7, 133.3, 135.6, 143.3, 157.3. IR (neat): 1730, 1562, 1250 cm^{-1}HRMS (MALDI) Calcd for $C_{20}H_{27}NOSi$ $[M]^+$: 325.1856, found 325.1854.

Ethyl 7-(trimethylsilyl)-1*H*-indazole-3-carboxylate (*distal*-8ff) (Table 5, entry 2): Following General Procedure C, a mixture of TBAT (0.40 g, 1.5 mmol), NfF (0.13 mL, 0.75 mmol), ethyl diazoacetate (**7f**) (contain 13% of CH_2Cl_2 181 μL, 1.5 mmol), and 2,6-bis(trimethylsilyl)phenyl trimethylsilyl ether (**4f**)

(0.16 g, 0.50 mmol) was stirred in THF (5.0 mL) for 5 h at 60 °C. The crude product (*distal*-**8ff**/*proximal*-**8ff** = >98:2, determined by 400 MHz ^{1}H NMR analysis) was purified by column chromatography on silica gel (hexane/EtOAc = 1:8 to 1:2) to provide the titled compound *distal*-**8ff** as a white solid (0.10 g, 79%) and its regiochemistry was determined by NOESY, HMQC and HMBC spectra. Mp: 128–130 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.46 (9 H, s), 1.49 (3 H, t, *J* = 7.0 Hz), 4.53 (2 H, q, *J* = 7.0 Hz), 7.33 (1 H, dd, *J* = 8.0, 8.0 Hz), 7.55 (1 H, d, *J* = 8.0 Hz), 8.26 (1 H, d, *J* = 8.0 Hz), 10.48 (1 H, brs). ^{13}C NMR (100 MHz, $CDCl_3$) δ: –0.7, 14.4, 61.0, 121.4, 121.7, 122.9, 123.1, 133.4, 136.8, 145.0, 162.6. IR (neat): 3294, 1737, 1454 cm^{-1}. HRMS (MALDI) Calcd for $C_{13}H_{19}N_2O_2Si$ $[M+H]^+$: 263.1210, found 263.1219.

1-Benzyl-4-(trimethylsilyl)-1*H*-benzo[*d*][1,2,3]triazole (*distal*-8fb) (Table 5, entry 3):[4g] Following General Procedure C, a mixture of TBAT (81 mg, 0.15 mmol), NfF (26 μL, 0.15 mmol), benzylazide (**7b**) (37 μL, 0.30 mmol) and 2,6-bis(trimethylsilyl)phenyl trimethylsilyl ether (**4f**) (31 mg, 0.10 mmol) was stirred in THF (1.0 mL, 0.10 M) for 7 h at 60 °C. The crude product (*distal*-**8fb**/*proximal*-**8fb** = 75:25, determined by 400 MHz ^{1}H NMR analysis) was purified by column chromatography on silica gel (hexane/EtOAc = 8:1) to provide the titled compound *distal*-**8fb** as a colorless oil (16 mg, 57%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.49 (9 H, s), 5.83 (2 H, s), 7.27–7.44 (8 H, m).

1-Benzyl-7-(trimethylsilyl)-1*H*-benzo[*d*][1,2,3]triazole (*proximal*-8fb) (Table 5, entry 3)[4g] was obtained from the above-mentioned reaction mixture as a yellow oil (5.4 mg, 19%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.36 (9 H, s), 6.05 (2 H, s), 6.89 (2 H, d, *J* = 8.0 Hz), 7.27–7.42 (4 H, m), 7.64 (1 H, dd, *J* = 8.0, 1.5 Hz), 8.15 (1 H, d, *J* = 8.0 Hz).

3-(Trimethylsilyl)-benzocyclobutene-1-one (*proximal*-8fg) (Table 5, entry 4): Following General Procedure C, a mixture of TBAT (0.40 g, 1.5 mmol), NfF (0.13 mL, 0.75 mmol), 1,1-dimethoxyethylene (**7g**) (0.14 μL, 1.5 mmol) and 2,6-bis(trimethylsilyl)phenyl trimethylsilyl ether (**4f**) (0.16 mg, 0.50 mmol) was stirred in THF (5.0 mL, 0.10 M) for 5 h at 60 °C. The crude product (*distal*-**8fg**/*proximal*-**8fg** = 2:>98, determined by 400 MHz ^{1}H NMR analysis) was purified by column chromatography on

silica gel (hexane/EtOAc = 8:1) to provide the titled compound *proximal*-**8fg** as a colorless oil (62 mg, 65%). and its regiochemistry was determined by NOESY spectra. ^{1}H NMR (500 MHz, acetone-d_6) δ: 0.27 (9 H, s), 3.30 (6 H, s), 3.32 (2 H, s), 7.18 (1 H, d, J = 7.5 Hz), 7.27 (1 H, dd, J = 7.5, 7.5 Hz), 7.38 (1 H, d, J = 7.5 Hz). ^{13}C NMR (125 MHz, acetone-d_6) δ: –0.5, 39.9, 52.1, 108.3, 124.4, 130.2, 133.6, 136.5, 141.6, 151.7. IR (neat): 1765, 1562, 1250 cm^{-1}. HRMS (MALDI) Calcd for $C_{13}H_{21}O_2Si$ $[M+H]^+$: 237.1305, found 237.1305.

1,4-Dimethyl-6-(trimethylsilyl)-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (*distal*-8fh) (Table 5, entry 5): Following General Procedure C, TBAT (0.40 g, 1.5 mmol), 2,5-dimethylinidazolidinone (**7h**) (0.16 mL, 1.5 mmol), and 2,6-bis(trimethylsilyl)phenyl trimethylsilyl ether (**4f**) (0.16 g, 0.50 mmol) was stirred in THF (5.0 mL) for 3 h at 60 °C. The crude product (*distal*-**8fh**/*proximal*-**8fh** = >98:2, determined by 300 MHz ^{1}H NMR analysis) was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to provide the titled compound *distal*-**8fh** as a white solid (20 mg, 77%) and its regiochemistry was determined by NOESY spectra. Mp: 122–125 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.28 (9 H, s), 2.79 (3 H, s), 3.17 (2 H, d, J = 6.5 Hz), 3.20 (3 H, s), 3.40 (2 H, d, J = 6.5 Hz), 6.91 (1 H, dd, J = 8.0, 1.0 Hz), 7.23–7.26 (1 H, m), 7.32 (1 H, dd, J = 8.0, 8.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: –0.03, 33.9, 40.1, 48.2, 57.6, 118.4, 128.8, 130.0, 136.3, 141.2, 146.0, 171.5. IR (neat): 1645, 1394 cm^{-1}. HRMS (MALDI) Calcd for $C_{14}H_{23}N_2OSi$ $[M+H]^+$: 263.1574, found 263.1573.

3-(4-Methoxyphenyl)-2-phenyl-7-(trimethylsilyl)-2*H*-indazole (*distal*-8fi) (Table 5, entry 6): Following General Procedure C, a mixture of TBAT (0.16 g, 0.30 mmol), NfF (53 μL, 0.30 mmol), 4-(4-methoxyphenyl)-3-phenylsydnone (**7i**)[13] (80 mg, 0.30 mmol) and 2,6-bis(trimethylsilyl)phenyl trimethylsilyl ether (**4f**) (62 mg, 0.20 mmol) was stirred in THF (2.0 mL, 0.10 M) for 10 h at 60 °C. The crude product (*distal*-**8fi**/*proximal*-**8fi** = >98:2, determined by 400 MHz ^{1}H NMR analysis) was purified by column chromatography on silica gel (hexane/EtOAc = 8:1) to provide the titled compound *distal*-**8fi** as a white solid (50 mg, 82%) and its regiochemistry was determined by NOESY spectra. Mp: 145–

146 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.47 (9 H, s), 3.81 (3 H, s), 6.92 (2 H, d, *J* = 8.5 Hz), 7.09 (1 H, dd, *J* = 8.5, 6.5 Hz), 7.25–7.28 (2 H, m), 7.31–7.40 (3 H, m), 7.44–7.48 (3 H, m), 7.66 (1 H, d, *J* = 8.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: –0.9, 55.3, 114.2, 120.7, 121.4, 121.9, 122.7, 125.8, 127.6, 128.7, 129.8, 131.0, 132.7, 134.5, 140.6, 152.3, 159.4. IR (neat): 1504, 1250 cm^{-1}. HRMS (MALDI) Calcd for $C_{23}H_{24}N_2OSi$ $[M]^+$: 372.1652, found 372.1657.

3-(4-Methoxyphenyl)-2-phenyl-5,7-bis(trimethylsilyl)-2*H*-indazole (*distal*-8gi) (Table 5, entry 7): Following General Procedure C, a mixture of TBAT (0.16 g, 0.30 mmol), NfF (53 μL, 0.30 mmol), 4-(4-methoxyphenyl)-3-phenylsydnone (**7i**)[13] (0.16 g , 0.21 mmol) and 2,4,6-tris(trimethylsilyl)phenyl trimethylsilyl ether (**4g**) (76 mg, 0.20 mmol) was stirred in THF (2.0 mL) for 13 h at 60 °C. The crude product (*distal*-**8gi**/*proximal*-**8gi** = >98:2, determined by 300 MHz ^{1}H NMR analysis) was purified by column chromatography on silica gel (hexane/EtOAc = 16:1) to provide the titled compound *distal*-**8gi** as a white solid (74 mg, 58%) and its regiochemistry was determined by NOESY spectra. Mp: 208–209 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.31 (9 H, s), 0.49 (9 H, s), 3.86 (3 H, s), 6.96 (2 H, d, *J* = 8.5 Hz), 7.28 (2 H, d, *J* = 8.5 Hz), 7.32–7.40 (3 H, m), 7.45 (2 H, d, *J* = 7.5 Hz), 7.58 (1 H, s), 7.84 (1 H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ: –0.9, –0.8, 55.3, 144.3, 120.5, 122.7, 125.9, 127.5, 127.6, 128.6, 128.7, 131.0, 132.7, 134.5, 136.4, 140.6, 152.6, 159.4. IR (neat): 1593, 1248 cm^{-1}. HRMS (MALDI) Calcd for $C_{26}H_{32}N_2OSi_2$ $[M]^+$: 444.2048, found 444.2057.

Application to transition-metal catalyzed reaction (Scheme 3):

1-(2-Allylphenyl)-2-phenylacetylene (11) (Scheme 3):[10] An oven-dried side-arm flask was charged with CuI (5.7 mg, 30 μmol), 1,2-bis(diphenylphosphino)propane (12 mg, 30 μmol), CsF (68 mg, 0.45 mmol), K_2CO_3 (83 mg, 0.60 mmol) and a stir-bar. The flask was equipped with a septum, and evacuated and back-filled with N_2 (This process was repeated three times). Anhydrous MeCN (1.0 mL) was added to the flask. Then, the mixture of 2-(trimethylsilyl)phenyl trimethylsilyl ether (**4d**) (72 mg, 0.30 mmol), phenylacetylene (**10**) (33 μL, 0.30 mmol), allylchloride (**9**) (98 μL, 1.2 mmol) and NfF (80 μL, 0.45 mmol) in anhydrous MeCN (2.0 mL) were added into the flask via a cannula through the septum and it

was warmed to 60 °C. The mixture was stirred at for 3 h at 60 °C. After cooling to room temperature, the reaction mixture was filtered through a short pad of silica gel using EtOAc, and solvents were removed under reduced pressure. The resultant residue was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 = 100:1) to provide the titled compound **11** (42 mg, 63%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.66 (2 H, d, J = 6.5 Hz), 5.08–5.19 (2 H, m), 5.98–6.12 (1 H, m), 7.18–7.25 (2 H, m), 7.26–7.31 (1 H, m), 7.33–7.38 (3 H, m), 7.51–7.57 (3 H, m).

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Notes

The authors declare no competing financial interest.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: xxxxxxxxxxxxxxxxxxxxxxxx.

^{1}H and ^{13}C NMR chart with some two dimension spectra data (PDF)

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