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Aryne cycloaddition reactions of benzodioxasilines as aryne precursors generated by catalytic reductive *ortho*-C–H silylation of phenols with traceless acetal directing groups

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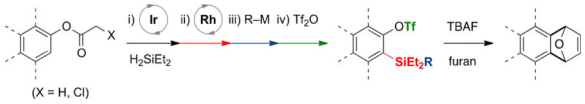
Abstract

Diversely substituted arylsilyl triflates, as aryne precursors for aryne cycloaddition reactions, were accessed from benzodioxasilines. Catalytic reductive C–H *ortho*-silylation of phenols with traceless acetal directing groups was exploited to prepare benzodioxasilines. Sequential addition of MeLi and then trifluoromethanesulfonic anhydride to benzodioxasilines provided arylsilyl triflates in a single pot. Notably, this approach was successfully utilized to prepare sterically hindered 1,2,3-trisubstituted arylsilyl triflates, which ultimately underwent fluoride-mediated aryne cycloaddition.

Graphical Abstract



Keywords

AryneArrylsilyl triflatesBenzodioxasilinesC-H; activationCycloaddition; Silyl acetals

1. Introduction

Ever since the discovery of benzynes in the mid 1950s,[1] these highly reactive intermediates have been employed in a wide variety of important applications, such as the synthesis of bioactive molecules,[2] organic materials,[3] and catalysts.[4] Additionally, benzynes enable the formation of diverse heterocyclic frameworks, which are difficult to obtain by conventional methods, via reactions with various arynophiles.[5] Among the several methods that have been developed for the efficient generation of arynes,[6] the reaction of silylaryl triflates with

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Supplementary Material

Supplementary data related to this article can be found at

fluoride is one of the most widely used approaches.[7] These stable benzyne precursors, which can undergo aryne cycloadditions under mild conditions, have led to a resurgence in aryne chemistry. Generally, these highly useful 1,2-silylaryl triflates have been prepared by one of the following three methods: 1) a sequence of directed *ortho* metalation (D*o*M),[8] silylation and triflation, 2) catalytic cross-coupling of *ortho*-haloarenes[9] and triflation, and 3) *ortho*-halo-phenols via retro-Brook rearrangement[10] followed by triflation (Scheme1). However, each of these methods suffer from challenges and/or limitations: the commercial availability of starting materials, challenging post-directing group manipulation due to potential protodesilylation, the need for either pre-functionalization of arene substrates or stoichiometric basic reagents, and limited functional group compatibility.[11] Furthermore, preparation of site-selectively installed silyl and triflate moieties within multi-substituted arenes for regioselective aryne cycloaddition is often difficult to access by these methods.

We recently developed a method to access versatile benzodioxasilines **3** from readily accessible phenyl acetates, derived from simple phenol, via catalytic reductive C–H *ortho*-silylation with traceless acetal directing groups (Scheme 2a).[12] Specifically, a relay of iridium and rhodium catalysts involving hydrosilylation of esters with dihydrosilanes and arene *ortho*-C–H silylation, respectively, which were followed by a subsequent nucleophile addition to the electrophilic silicon to remove the acetal directing group, directly provides unmasked *ortho*-silyl phenol products in a single vessel. This strategy was successfully applied to the preparation of multi-substituted arenes by exploiting a new, formal α-chloroacetyl directing group. In particular, this new directing group tactic permits access to sterically hindered *ortho*-silyl phenols. Importantly the synthesis of 1,2,3-trisubstituted phenolic arenes, which are difficult to obtain by other catalytic means, was established. Following this study, we speculated that diversely substituted benzodioxasilines **3** could be excellent precursors for preparation of silylaryl triflates. For example, addition of organometallic agents to silicon and then subsequent trapping of the resulting *ortho*-silyl oxyanion intermediates **4** by trifluoromethanesulfonic anhydride can directly afford diversely substituted silylaryl triflates (Scheme 2b).

2. Results and Discussion

Benzodioxasilines were efficiently prepared through Ircatalyzed hydrosilylation of phenyl acetates followed by Rhcatalyzed C–H silylation in a single pot. We then examined the efficiency of the nucleophilic ring-opening reaction of benzodioxasilines **3** with simple, readily available organometallic reagents (e.g., organolithium reagents), followed by direct triflation with trifluoromethanesulfonic anhydride. The single-pot, sequential reactions with benzodioxasiline **3a**, generated from phenyl acetate **1a** via catalytic reductive *ortho*-C–H silylation and used without purification, produced the desired silylaryl triflate **5a** by MeLi ring-opening and trifilation reactions in excellent yield (91% from **1a**) (Table 1). Electronically differentiated, diverse substituted benzodioxasilines provided silylaryl triflates **5** in moderate to excellent yields (four steps from **1**) under this reaction conditions. Specifically, halogens, trifluoromethyl, TBS-protected primary alcohol group, *ortho*-methyl, methoxy within benzodioxasilines **3** were tolerated by the four-step reaction conditions to furnish silylaryl triflates (**5b**–**5i**). 1- and 2-naphthyl silyl triflates (**5j** and **5k**) were produced

from **1j** and **1k** in modest yields via the reaction sequence. Moreover, disubstituted benzodioxasilines **3l** and **3m** afforded **5l** and **5m** in 53% and 72% yields, respectively. Finally, dual functionalization produced bis-silylaryl triflate **5n** in 74% yield.

During these processes, we found that noticeable, yet minor desilylation phenol byproducts **7** were also produced with most substrates (Scheme 3). Especially, substrates such as **5d, 5j**, and **5k** produced a significant amount of **7**. For the desilylation event, we reasoned that a nucleophilic attack of MeLi to dioxasilines first generates putative penta-coordinate silicate species **8**, which undergoes a fragmentation process to afford lithium *ortho*-silyl phenoxide **10** (via lithio acetal **9**) and acetaldehyde. A nucleophilic addition of MeLi to acetaldehyde can then furnish $XCH_2CH(Me)OLi$. At this moment two possible scenarios explaining the observed desilylation are feasible: 1) Intramolecular silyl transfer–a [1,3]-silatropic rearrangement can be attributed to this issue. For example, a [1,3]-Brook rearrangement[13] of *ortho*-silyl phenols to afford silyl ethers has been reported, however, this process was explored mainly under acidic conditions,[14] elevated temperatures[15] or catalytic aerobic conditions.[16] Additionally, under strong basic conditions a retro-[1,3]-silatropic process within *ortho*-silyl phenols has been well reported.[10] 2) Intermolecular silyl transfer–nucleophiles (e.g., MeLi, LiOPh, LiOR), present in the reaction, can engage with **10** to produce dianions of type **12**, which eventually afford phenols **7** upon work-up. To minimize the potential rearrangement (**10** to **11**, path 1) or reversible association of nucleophiles (**10** to **12**, path 2) to silyl moiety after the first fragmentation (**3** to **10**), we quickly quenched the reaction within <1 min with Tf_2O at −78 °C (achieving a full consumption of **3**). This procedure substantially reduced the formation of **7**, thereby enhancing yields of desirable products **6**.

Next we investigated the single-pot, sequential strategy concerning nucleophilic attack of MeLi and triflation of the sterically demanding benzodioxasilines **3** bearing substituents at *ortho* position relative to the hydroxyl group (Table 2). These substrates consistently produced substantial desilylation adducts **7** even in a short period of reaction time. We found that the purity of the dioxasilines **3** was crucial to affect the MeLi addition reaction. Specifically, when purified benzodioxasilines **3o–r**, obtained by a column chromatography after the reductive C–H silylation, were employed under the reaction conditions, we were able to isolate **5o–r** in good yields. Of note, these 1,2,3-trisubstituted arylsilyl triflates are difficult to access by other catalytic means.

We next explored fluoride-mediated [4+2] aryne cycloaddition reactions of diethylmethylsilylaryl triflates **5** with furan (Table 3). Cycloaddition reactions with electron-rich and -deficient arylsilyl triflates with furan (solvent) provided a variety of 1,4-dihydro-1,4-epoxynaphthalenes **13**, demonstrating good functional group tolerance. Under these reaction conditions, *meta* and *para*-substituted arylsilyl triflates (**5b–g**) produced the corresponding 6-substituted 1,4-dihydro-1,4-epoxynaphthalenes (**13b–g**) in good yields. In particular, a TBS-protected primary alcohol group within **5f** survived under the reaction conditions at 0 °C. The *ortho*-substituted arylsilyl triflates (**5h** and **5i**) underwent aryne cycloadditions to provide **13h** and **13i** in 86% and 67% yields, respectively. This approach is also successful with 1- and 2-silylnaphthyl triflates (**5j** and **5k**, respectively) to afford **13j**

and **13k** in modest yields. Furthermore, cycloadditions with di-substituted arylsilyl triflates (i.e., **5l** and **5m**) and tetra-substituted arylsilyl triflate (**5n**) produced **13l, 13m**, and **13n** (1:1 *dr*) in good yields. Next, we studied the cycloaddition of sterically hindered, 1,2,3-trisubstituted arylsilyl triflates **5o–r**. The corresponding cycloadducts **13o–r** were successfully produced in moderate yields.

An important component of this project was broadening the scope of the approach towards the synthesis of bioactive molecules. For this purpose, we examined the [4+2] aryne cycloaddition of arylsilyl triflates derived from estrone **14**. The C17 ketone in estrone, which was not compatible in Ircatalyzed ester hydrosilylation, was first protected with a ketal group. Next, the α-Chloroacetyl group was installed to the phenol for an effective arene C–H silylation reaction in a hindered environment. Catalytic reductive *ortho*-C–H bond silylation of the resulting phenyl acetate with the α-chloroacetyl formal directing group provided dioxasiline **16** (only C2). A MeLi addition to **16** afforded C2-silyl phenol **17** in 82% yield over 3 steps. The reaction of **17** and Tf_2O in the presence of pyridine gave arylsilyl triflate **18**, which in turn was utilized for the aryne cycloaddition with furan to afford cycloadduct **19**. During the course of the cycloaddition reaction partial deprotection of the ketal group was observed (**19:20** = 4:1). ketal deprotection of **19** afforded **20** (72% yield, 1.2:1 *dr*). (scheme 4)

3. Conclusion

To summarize, we have developed an efficient strategy to prepare diversely substituted arylsilyl triflates. The catalytic reductive *ortho*-C–H silylation of phenols via a traceless acetal directing group to afford benzodioxasilines **3**, followed by a sequential addition of MeLi and trifluoromethanesulfonic anhydride, furnished arylsilyl triflates **5** in a single pot. In particular, α-chloroacetyl formal directing group was required for the effective reductive *ortho*-C–H silylation to afford 1,2,3-trisubstitued arylsilyl triflates **5**. Furthermore, this class of arylsilyl triflates demanded purification of benzodioxasilines **3o–r** for subsequent nucleophilic ring-opening and triflation processes, in order to minimize unwanted desilylation byproduct **7**. We demonstrated that fluoride-mediated [4+2] aryne cycloaddition reaction of the resulting diethylmethylsilylaryl triflates **5** with furan to afford distinctly substituted cycloadducts **13**, some of which were not accessed previously.

4. Experimental section

4.1. General

Reactions requiring anhydrous conditions were performed under an atmosphere of nitrogen or argon in flame or oven-dried glassware. Anhydrous toluene and dichloromethane (DCM) were distilled from CaH_2. Anhydrous tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium and benzophenone. Triethylamine and pyridine were distilled from KOH. DMF and DMSO were stored over 4 Å molecular sieves. All other solvents and reagents from commercial sources were used as received. NMR spectra were recorded on a 500 or 300 MHz NMR spectrometer. ^1H NMR chemical shifts are referenced to chloroform (7.26 ppm) and DMSO-d_6 (2.50 ppm). ^{13}C NMR chemical shifts are referenced to $^{13}CDC1_3$ (77.23 ppm) and DMSO-d_6 (39.52 ppm). The following abbreviations are used to describe

multiplets: s (singlet), d (doublet), t (triplet), q (quartet), pent (pentet), m (multiplet), nfom (nonfirst-order multiplet), and br (broad). The following format was used to report peaks: chemical shift in ppm [multiplicity, coupling constant(s) in Hz, integral, and assignment]. ^{1}H NMR assignments are indicated by structure environment (e.g., CH_aH_b). ^{1}H NMR and ^{13}C NMR were processed with the iNMR software program. Infrared (IR) spectra were recorded using neat (for liquid compound) or a thin film from a concentrated DCM solution. Absorptions are reported in cm^{-1}. Only the most intense and/or diagnostic peaks are reported. MPLC refers to medium pressure liquid chromatography (25–200 psi) using hand-packed columns of silica gel (20–45 μm, spherical, 70 Å pore size), an HPLC pump, and a differential refractive index detector. High-resolution mass spectra (HRMS) were recorded in atmospheric-pressure chemical ionization and time-of-flight (APCI/TOF) mode. Samples were introduced as solutions in a mixed solution of methanol and DCM. Analytical TLC experiments were performed on an F254 plate with 250 μm thickness. Detection was performed by UV light or potassium phosphomolybdic acid, potassium permanganate, and *p*-anisaldehyde staining.

4.2. General Procedure for Preparation of Arylsilyl triflates from Phenyl Acetates (5)

(i) $[Ir(coe)_2Cl]_2$ (0.9 mg, 0.1 mol %) and aryl acetates **1** (1 mmol) were added to a flame-dried, nitrogen-purged septum-capped vial. The mixture was dissolved with THF (0.3 mL, 3.3 M), and diethylsilane (0.26 mL, 2 mmol) was added to the mixture. The septum on the vial was replaced by a screw cap with a Teflon liner under a N_2 atmosphere [note: diethylsilane (bp 56 °C and density 0.686 g/mL) is volatile]. The reaction mixture was stirred for 3–12 h at 60 °C. Volatiles were removed *in vacuo* to afford silyl acetals, which were directly used for subsequent reactions without further purification. (ii) $[Rh(nbd)Cl]_2$ (1.8 mg, 0.4 mol %), *tris*(4-methoxyphenyl)phosphine (8.4 mg, 2.4 mol %), norbornene (188 mg, 2 mmol), and THF (1 mL, 1 M) were added to the crude silyl acetals (1 mmol). The septum on the vial was replaced by a screw cap with a Teflon liner, and the mixture was stirred at 120 °C for 15 min. The reaction progress was monitored by GC/MS spectrometry. The resulting benzodioxasilines **3** were directly used for a subsequent reaction without further purification. For hindered substrates **3o–r**, the resulting benzodioxasilines **3** were purified for the subsequent reactions; volatiles were removed *in vacuo*, and the resulting mixture was dissolved with pentane, filtered through a pad of Celite®, and concentrated *in vacuo*. The crude product was purified by MPLC (hexanes/EtOAc = 80:1, 5 mL/min, retention time 5–15 min). (iii) The crude benzodioxasilines **3** (1 mmol, THF, 1 M) were diluted with diethyl ether (3 mL, 0.33 M) and cooled to −78 °C. MeLi (3 mmol, 1.6 M in Et_2O) were added into the reaction mixture at −78 °C and stirred for 1 min. (iv) Trifluoromethanesulfonyl anhydride (1.2 mmol, 0.2 mL) was added into the reaction mixture. The reaction mixture was warmed to rt and stirred for 30 min. The reaction mixture was cooled to 0 °C and saturated aqueous ammonium chloride solution was added. The mixture was extracted with diethyl ether three times. The combined organic layer was washed with water and brine, and dried over anhydrous sodium sulfate. Volatiles were removed *in vacuo*, and the crude mixture was purified by MPLC to afford arylsilyl triflates **5** (hexanes/EtOAc = 40:1, 5 mL/min, retention time 6–20 min).

4.2.1. 2-[Diethyl(methyl)silyl]-4-(trifluoromethyl)phenyl trifluoromethanesulfonate (5d)—Yield (70%, 276 mg); colorless oil; ^{1}H NMR ($CDC1_3$, 500 MHz) δ 7.76 (d, *J* = 2.4 Hz, 1H, Ar-*H*), 7.71 (dd, *J* = 8.7, 2.4 Hz, 1H, Ar-*H*), 7.49 (d, *J* = 8.7 Hz, 1H, Ar-*H*), 0.98–0.90 [m, 10H, Si($CH_2CH_3)_2$], and 0.38 (s, 3H, SiCH_3); ^{13}C NMR ($CDC1_3$, 125 MHz) δ 157.3, 134.0 (q, $^3J_{F\text{-}C}$ = 3.6 Hz), 132.6, 129.9 (q, $^2J_{F\text{-}C}$ = 32.5 Hz), 128.7 (q, $^3J_{F\text{-}C}$ = 3.6 Hz), 123.8 (q, $^1J_{F\text{-}C}$ = 273.2 Hz), 119.9, 118.8 (q, $^1J_{F\text{-}C}$ = 320.3 Hz), 7.3, 5.3, and −5.6; IR (neat) 2962 (m), 2857 (w), 1566 (w), 1421 (s), 1201 (s), 1131 (s), 1045 (m), 889 (s), and 773 (s) cm^{-1}; TLC R_f = 0.5 in 40:1 hexanes:EtOAc; HRMS (APCI/TOF) calcd for $(M+H)^+$ $(C_{13}H_{16}F_6O_3SSi)^+$: 394.0494. Found: 394.0463.

4.2.2. 4-{[(tert-Butyldimethylsilyl)oxy]methyl}-2-(diethyl[methyl] silyl)phenyl trifluoromethanesulfonate (5e)—Yield (74%, 348 mg); colorless oil; ^{1}H NMR ($CDC1_3$, 500 MHz) δ 7.48 (d, *J* = 2.2 Hz, 1H, Ar-*H*), 7.37 (dd, *J* = 8.6, 2.2 Hz, 1H, Ar-*H*), 7.30 (d, *J* = 8.6 Hz, 1H, Ar-*H*), 4.76 (s, 2H, Ar-CH_2OTBS), 0.95 [s, 9H, OSiC($CH_3)_3$], 0.97–0.85 [m, 10H, Si($CH_2CH_3)_2$], 0.34 (s, 3H, SiCH_3), and 0.11 [s, 6H, OSi($CH_3)_2$]; ^{13}C NMR ($CDC1_3$, 125 MHz) δ 154.3, 140.7, 134.3, 130.4, 128.8, 119.4, 118.7 (q, $^1J_{F\text{-}C}$ = 320.3 Hz), 64.3, 26.1, 18.5, 7.5, 5.6, −5.1, and −5.3; IR (neat) 2954 (m), 2873 (w), 1571 (w), 1454 (s), 1244 (s), 1133 (s), 1061 (m), 888 (s), and 621 (s) cm^{-1}; TLC R_f = 0.5 in 40:1 hexanes:EtOAc; HRMS (APCI/TOF) calcd for $(M+H)^+$ $(C_{19}H_{34}F_3O_4SSi_2)^+$: 471.1663. Found: 471.1689.

4.2.3. 2-[Diethyl(methyl) silyl]-4-methoxyphenyl trifluoromethanesulfonate (5f)—Yield (83%, 295 mg); colorless oil; ^{1}H-NMR ($CDC1_3$, 500 MHz) δ 7.26 (d, *J* = 9.0 Hz, 1H, Ar-*H*), 7.00 (d, *J* = 3.2 Hz, 1H, Ar-*H*), 6.90 (dd, *J* = 9.0, 3.2 Hz, 1H, Ar-*H*), 3.82 (s, 3H, Ar-OCH_3), 0.98–0.84 [m, 10H, Si($CH_2CH_3)_2$], and 0.34 (s, 3H, SiCH_3); ^{13}C NMR ($CDC1_3$, 125 MHz) δ 158.1, 148.6, 132.4, 122.2, 120.8, 118.7 (q, $^1J_{F\text{-}C}$ = 320.3 Hz), 115.0, 55.6, 7.3, 5.4, and −5.5; IR (neat) 2957 (m), 2878 (w), 1576 (w), 1467 (s), 1211 (s), 1121 (s), 1034 (m), 889 (s), and 618 (s) cm^{-1}; TLC R_f = 0.5 in 40:1 hexanes: EtOAc; HRMS (APCI/TOF) calcd for $(M+H)^+$ $(C_{13}H_{20}F_3O_4SSi)^+$: 357.0798. Found: 357.0815.

4.2.4. 2-[Diethyl(methyl)silyl]-5-methylphenyl trifluoromethanesulfonate (5g)—Yield (72%, 245 mg); colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.39 (d, *J* = 7.9 Hz, 1H, Ar-*H*), 7.17–7.14 (m, 2H, Ar-*H*), 2.39 (s, 3H, Ar-CH_3), 0.95–0.83 [m, 10H, Si($CH_2CH_3)_2$], and 0.32 (s, 3H, SiCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.6, 142.2, 136.9, 128.5, 127.0, 120.3, 118.7 (q, $^1J_{F\text{-}C}$ = 320.3 Hz), 21.5, 7.5, 5.6, and −5.3; IR (neat) 2957 (m), 2877 (w), 1610 (w), 1417 (s), 1204 (s), 1139 (s), 1046 (m), 839 (s), and 597 (s) cm^{-1}; TLC R_f = 0.5 in 40:1 hexanes:EtOAc; HRMS (APCI/TOF) calcd for $(M+H)^+$ $(C_{13}H_{20}F_3O_3SSi)^+$: 341.0849. Found: 341.0873.

4.2.5. 2-[Diethyl(methyl)silyl]-6-methylphenyl trifluoromethanesulfonate (5h)—Yield (66%, 224 mg); colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.39 (dd, *J* = 6.9, 2.2 Hz, 1H, Ar-*H*), 7.31 (dd, *J* = 7.5, 2.2 Hz, 1H, Ar-*H*), 7.28 (dd, *J* = 7.5, 6.9 Hz, 1H, Ar-*H*), 2.40 (s, 3H, Ar-CH_3), 0.99–0.87 [m, 10H, Si($CH_2CH_3)_2$], and 0.37 (s, 3H, SiCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 151.6, 135.3, 134.0, 132.8, 131.7, 128.1, 118.9 (q, $^1J_{F\text{-}C}$ = 319.8 Hz),

17.6, 7.5, 6.1, and −4.5; IR (neat) 2957 (m), 2875 (w), 1587 (w), 1455 (s), 1232 (s), 1115 (s), 1026 (m), 881 (s), and 610 (s) cm^{-1}; TLC R_f = 0.5 in 40:1 hexanes:EtOAc; HRMS (APCI/TOF) calcd for $(M+H)^+$ $(_{13}H_{20}F_3O_3SSi)^+$: 341.0849. Found: 341.0818.

4.2.6. 2-[Diethyl(methyl)silyl]-6-methoxyphenyl trifluoromethanesulfonate (5i)—Yield (65%, 231 mg); colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.30 (dd, J = 7.8, 7.8 Hz, 1H, Ar-*H*), 7.04 (dd, J = 7.8, 1.5 Hz, 1H, Ar-*H*), 7.03 (dd, J = 7.8, 1.5 Hz, 1H, Ar-*H*), 3.86 (s, 3H, Ar-OCH_3), 0.96–0.86 [m, 10H, Si(CH_2CH_3)$_2$], and 0.35 (s, 3H, SiCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 150.3, 143.6, 133.4, 128.7, 127.6, 119.2 (q, $^1J_{F\text{-}C}$ = 321.6 Hz), 114.1, 55.7, 7.5, 5.6, and −5.1; IR (neat) 2957 (m), 2879 (w), 1575 (w), 1461 (s), 1203 (s), 1137 (s), 1030 (m), 870 (s), and 631 (s) cm^{-1}; TLC R_f = 0.5 in 40:1 hexanes:EtOAc; HRMS (APCI/TOF) calcd for $(M+H)^+$ $(C_{13}H_{20}F_3O_4SSi)^+$: 357.0798. Found: 357.0776.

4.2.7. 2-[Diethyl(methyl)silyl]naphthalen-1-yl trifluoromethanesulfonate (5j)—Yield (60%, 226 mg) colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.90 (dd, J = 7.0, 1.3 Hz, 1H, Ar-*H*), 7.87 (ddd, J = 8.1, 1.1, 0.4 Hz, 1H, Ar-*H*), 7.82 (dd, J = 8.2, 1.4 Hz, 1H, Ar-*H*), 7.77 (dd, J = 8.1, 1.1 Hz, 1H, Ar-*H*), 7.53 (dd, J = 8.1, 7.0 Hz, 1H, Ar-*H*), 7.45 (dd, J = 8.1, 8.1 Hz, 1H, Ar-*H*), 0.99–0.90 [m, 10H, Si(CH_2CH_3)$_2$], and 0.40 (s, 3H, SiCH_3); ^{13}C NMR ($CDCl_3$, 76 MHz) δ 148.6, 137.9, 136.0, 132.2, 129.9, 129.3, 129.0, 126.2, 124.6, 118.9 (q, $^1J_{F\text{-}C}$ = 320.2 Hz), 114.9, 7.9, 7.3, –2.7; IR (neat) 2956 (m), 2877 (w), 1485 (s), 1192 (s), 1111 (s), 1051 (w), 890 (s), and 650 (s) cm^{-1}; TLC R_f = 0.5 in 80:1 hexanes: EtOAc; HRMS (APCI/TOF) calcd for $(M+H)^+$ $(C_{16}H_{20}F_3O_3SSi)^+$: 376.0776. Found: 376.0759.

4.2.8. 3-[Diethyl(methyl)silyl]naphthalen-2-yl trifluoromethanesulfonate (5k)—Yield (66%, 248 mg); colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.00 (s, 1H, Ar-*H*), 7.88 (dd, J = 6.8, 2.2 Hz, 1H, Ar-*H*), 7.85 (dd, J = 6.8, 2.2 Hz, 1H, Ar-*H*), 7.82 (s, 1H, Ar-*H*), 7.59–7.53 (m, 2H, Ar-*H*), 1.01–0.92 [m, 10H Si(CH_2CH_3)$_2$], and 0.42 (s, 3H, SiCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 152.9, 138.5, 134.3, 131.9, 129.2, 128.15, 127.99, 127.95, 127.1, 118.8 (q, $^1J_{F\text{-}C}$ = 320.3 Hz), 116.6, 7.5, 5.6, and −5.2; IR (neat) 2957 (m), 2874 (w), 1532 (w), 1474 (s), 1202 (s), 1109 (s), 1046 (m), 874 (s), and 637 (s) cm^{-1}; TLC R_f = 0.5 in 40:1 hexanes:EtOAc. HRMS (APCI/TOF) calcd for $(M+H)^+$ $(C_{16}H_{20}F_3O_3SSi)^+$: 377.0849. Found: 377.0817.

4.2.9. 4-[Diethyl(methyl)silyl]benzo[d][1,3]dioxol-5-yl trifluoromethanesulfonate (5l)—Yield (53%, 196 mg); colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.79 (app s, 2H, Ar-*H*), 5.98 (s, 2H, OCH_2O), 0.98–0.84 (m, 10H, Si(CH_2CH_3)$_2$], and 0.38 (s, 3H, SiCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.8, 148.7, 145.8, 118.7 (q, $^1J_{F\text{-}C}$ = 320.3 Hz), 113.5, 112.7, 109.1, 101.6, 7.4, 6.0, and −4.6; IR (neat) 2955 (m), 2865 (w), 1581 (w), 1465 (s), 1208 (s), 1124 (s), 1030 (m), 869 (s), and 661 (s) cm^{-1}; TLC R_f = 0.5 in 40:1 hexanes:EtOAc; HRMS (APCI/TOF) calcd for $(M+H)^+$ $(_{13}H_{18}F_3O_5SSi)^+$: 371.0591. Found: 371.0585.

4.2.10. 2-[Diethyl(methyl)silyl]-4,6-dimethylphenyl trifluoromethanesulfonate (5m)—Yield (72%, 255 mg); colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.18 (d, J = 2.3 Hz, 1H, Ar-*H*), 7.13 (d, J = 2.3 Hz, 1H, Ar-*H*), 2.38 (s, 3H, Ar-CH_3), 2.36 (s, 3H, Ar-CH_3), 1.01–0.92 [m, 10H Si(CH_2CH_3)$_2$], and 0.39 (s, 3H, SiCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ

149.6, 137.7, 135.7, 134.6, 132.4, 131.2, 119.0 (q, $^{1}J_{F\text{-}C}$ = 320.1 Hz), 20.9, 17.5, 7.6, 6.1, and −4.5; IR (neat) 2956 (m), 2877 (w), 1460 (s), 1221 (s), 900 (s), 1039 (m), 865 (s), and 633 (s) cm^{-1}; TLC R_f = 0.5 in 40:1 hexanes:EtOAc; HRMS (APCI/TOF) calcd for $(M+H)^+$ $(C_{14}H_{22}F_3O_3SSi)^+$: 355.1006. Found: 355.1013.

4.2.11. 2,5-bis[Diethyl(methyl)silyl]-1,4-phenylene bis(trifluoromethanesulfonate) (5n)—Yield (74%, 425 mg); colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.47 (s, 2H, Ar-*H*), 0.99–0.88 [m, 20H, Si(C*H*$_2$C*H*$_3$)$_2$], and 0.37 (s, 6H, SiC*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.5, 135.8, 127.7, 118.8 (q, $^{1}J_{F\text{-}C}$ = 320.6 Hz), 7.2, 5.2, and −5.7; IR (neat) 2958 (m), 2879 (w), 1461 (w), 1422 (s), 1223 (s), 1137 (s), 1078 (m), 884 (s), and 615 (s) cm^{-1}; TLC R_f = 0.5 in 20:1 hexanes:EtOAc; HRMS (APCI/TOF) calcd for $(M+H)^+$ $(_8H_{29}F_6O_6S_2Si_2)^+$: 575.0843. Found: 575.0817.

4.2.12. 2-[Diethyl(methyl)silyl]-6-ethylphenyl trifluoromethanesulfonate (5o)—Yield (81%, 287 mg); colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.40 (dd, *J* = 7.3, 2.1 Hz, 1H, Ar-*H*), 7.37 (dd, *J* = 7.3, 2.1 Hz, 1H, Ar-*H*), 7.33 (dd, *J* = 7.3, 7.3 Hz, 1H, Ar-*H*), 2.79 (q, *J* = 7.6 Hz, 2H, Ar-C*H*$_2$CH$_3$), 1.25 (t, *J* = 7.6 Hz, 3H, Ar-CH$_2$C*H*$_3$), 0.99–0.87 [m, 10H, Si(C*H*$_2$C*H*$_3$)$_2$], and 0.37 (s, 3H, SiC*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 150.7, 137.5, 135.3, 132.9, 131.9, 128.3, 118.9 (q, $^{1}J_{F\text{-}C}$ = 319.35 Hz), 23.5, 14.2, 7.5, 6.2, and −4.4; IR (neat) 2957 (m), 2878 (w), 1576 (w), 1467 (s), 1211 (s), 1121 (s), 1034 (m), 889 (s), and 618 (s) cm^{-1}; TLC R_f = 0.5 in 80:1 hexanes:EtOAc; HRMS (APCI/TOF) calcd for $(M+H)^+$ $(C_{14}H_{22}F_3O_3SSi)^+$: 355.1006. Found: 355.1018.

4.2.13. 2-[Diethyl(methyl)silyl]-6-isopropylphenyl trifluoromethanesulfonate (5p)—Yield (269 mg, 73%); colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.42 (dd, *J* = 7.0, 2.5 Hz, 1H, Ar-*H*), 7.38–7.33 (m, 2H, Ar-*H*), 3.31 [hept, *J* = 6.8 Hz, 1H, Ar-C*H*(CH$_3$)$_2$], 1.24 [d, *J* = 6.8 Hz, 6H, Ar-CH(C*H*$_3$)$_2$], 0.96–0.87 [m, 10H, Si(C*H*$_2$C*H*$_3$)$_2$], and 0.35 (s, 3H, SiC*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 149.5, 142.2, 135.2, 133.0, 129.3, 128.4, 118.8 (q, $^{1}J_{F\text{-}C}$ = 317.3 Hz), 27.3, 23.7, 7.6, 6.2, and − 4.3; IR (neat) 2958 (m), 2877 (w), 1571 (w), 1447 (s), 1201 (s), 1154 (s), 1027 (m), 892 (s), and 636 (s) cm^{-1}; TLC R_f = 0.5 in 80:1 hexanes:EtOAc; HRMS (APCI/TOF) calcd for $(M+H)^+$ $(C_{15}H_{24}F_3O_3SSi)^+$: 369.1162. Found: 369.1145.

4.2.14. 2-(tert-Butyl)-6-[diethyl(methyl)silyl]phenyl trifluoromethanesulfonate (5q)—Yield (70%, 267 mg); colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.55 (dd, *J* = 7.8, 1.9 Hz, 1H, Ar-*H*), 7.37 (dd, *J* = 7.2, 1.9 Hz, 1H, Ar-*H*), 7.30 (dd, *J* = 7.8, 7.2 Hz, 1H, Ar-*H*), 1.43 [s, 9H, C(C*H*$_3$)$_3$], 0.95–0.84 [m, 10H Si(C*H*$_2$C*H*$_3$)$_2$], and 0.32 (s, 3H, SiC*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 148.2, 143.8, 135.6, 134.6, 131.8, 127.6, 118.6 (q, $^{1}J_{F\text{-}C}$ = 320.3 Hz), 36.5, 32.1, 7.6, 6.9, and −3.6; IR (neat) 2957 (m), 2878 (w), 1564 (w), 1443 (s), 1236 (s), 1163 (s), 1041 (m), 874 (s), and 608 (s) cm^{-1}; TLC R_f = 0.5 in hexanes. HRMS (APCI/TOF) calcd for $(M+H)^+$ $(C_{16}H_{26}F_3O_3SSi)^+$: 383.1319. Found: 383.1304.

4.2.15. 3-[Diethyl(methyl)silyl]-(1,1'-biphenyl)-2-yl trifluoromethanesulfonate (5r)—Yield (75%, 301 mg); colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.54–7.52 (m, 1H, Ar-*H*), 7.45–7.37 (m, 7H, Ar-*H*), 1.02–0.93 [m, 10H, Si(C*H*$_2$C*H*$_3$)$_2$], and 0.42 (s, 3H, SiC*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 150.1, 137.1, 136.5, 133.96, 133.85, 129.8, 128.6,

128.2, 118.2 (q, $^{1}J_{F\text{-}C}$ = 320.7 Hz), 7.6, 6.2, and −4.3; IR (neat) 2957 (m), 2878 (w), 1556 (w), 1435 (s), 1221 (s), 1133 (s), 1024 (m), 869 (s), and 798 (s) cm^{-1}; TLC R_f = 0.5 in 80:1 hexanes:EtOAc; HRMS (APCI/TOF) calcd for $(M+H)^+$ $(C_{18}H_{22}F_3O_3SSi)^+$: 403.1006. Found: 403.9985.

4.3. General Procedure for Fluoride-Mediated Benzyne Cycloaddition Reactions (13)

Arylsilyl triflate (0.5 mmol) **5** was dissolved in furan (0.2 mL) and placed in a 4 mL vial. TBAF (1.2 equiv, 1 M in THF) was added into the reaction mixture at rt. The septum on the vial was replaced by a screw cap with a Teflon liner, and the mixture was stirred at rt for 2 h. The reaction was quenched by adding saturated aqueous ammonium chloride. The reaction mixture was extracted with diethyl ether and concentrated *in vacuo* to afford the crude mixture, which was purified by MPLC (hexanes/EtOAc = 10:1, 5 mL/min, retention time 7–15 min) to afford 1,4-dihydro-1,4-epoxynaphthalenes **13**.

4.3.1. 6-(Trifluoromethyl)-1,4-dihydro-1,4-epoxynaphthalene (13d)—Yield (83%, 88 mg) colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.46 (s, 1H, Ar-*H*), 7.33 (d, *J* = 7.4 Hz, 1H, Ar-*H*), 7.29 (d, *J* = 7.4 Hz, 1H, Ar-*H*), 7.06 (dd, *J* = 5.5, 1.7 Hz, 1H, CH(O)C*H*=CH), 7.04 (dd, *J* = 5.5, 1.8 Hz, 1H CH(O)CH=C*H*), and 5.77 (app s, 2H, C*H*OC*H*); ^{13}C NMR ($CDCl_3$, 76 MHz) δ 153.4, 150.5, 143.3, 142.9, 127.7 (q, $^{2}J_{F\text{-}C}$ = 32.3 Hz), 124.3 (q, $^{1}J_{F\text{-}C}$ = 271.6 Hz), 123.2 (q, $^{3}J_{F\text{-}C}$ = 4.3 Hz), 120.2, 117.2 (q, $^{3}J_{F\text{-}C}$ = 3.6 Hz), and 82.3 (2). IR (neat): 3035 (w), 2956 (m), 2924 (m), 2853 (m), 1703 (w), 1631 (m), 1527 (m), 1222 (s), 1087 (s), 1031 (s), and 826 (m) cm^{-1}; TLC R_f = 0.5 in 5:1 hexanes:EtOAc; HRMS (APCI/TOF) calcd for $(M+H)^+$ $(C_{11}H_8F_3O)^+$: 213.0522. Found: 213.0514.

4.3.2. tert-Butyl[(1,4-dihydro-1,4-epoxynaphthalen-6-yl)methoxy]dimethylsilane (13e)—Yield (80%, 47 mg); colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.24 (s, 1H, Ar-*H*), 7.18 (d, *J* = 7.2 Hz, 1H, Ar-*H*), 7.01 [nfom, 2H, CH(O)C*H*=C*H*], 6.91 (d, *J* = 7.2 Hz, 1H, Ar-*H*), 5.70 (s, 2H, C*H*OC*H*), 4.67 (s, 2H, Ar-CH_2OTBS), 0.93 [s, 9H, OSiC(CH_3)$_3$], and 0.09 [s, 6H, OSi(CH_3)$_2$]; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 149.5, 147.9, 143.27, 143.12, 138.8, 122.7, 120.0, 118.8, 82.58, 82.41, 65.2, 26.2, 18.6, and −5.0; IR (neat) 3053 (m), 2874 (w), 1600 (w), 1460 (m), 1415 (s), 1278 (m), 1209 (s), 1139 (s), 1045 (s), 845 (w), 695 (s), and 571 (m) cm^{-1}. TLC R_f = 0.5 in 5:1 hexanes:EtOAc; HRMS (APCI/TOF) calcd for $(M+H)^+$ $(C_{17}H_{25}O_2Si)^+$: 289.1618. Found: 289.1602.

4.3.3. 6-Methoxy-1,4-dihydro-1,4-epoxynaphthalene (13f)—Yield (65%, 94 mg); colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.13 (d, *J* = 7.8 Hz, 1H, Ar-*H*), 7.03 [dd, *J* = 5.6, 1.8 Hz, 1H CH(O)C*H*=CH], 6.99 [dd, *J* = 5.6, 1.8 Hz, 1H CH(O)CH=C*H*], 6.91 (d, *J* = 2.2 Hz, 1H, Ar-*H*), 6.42 (dd, *J* = 7.8, 2.2 Hz, 1H, Ar-*H*), 5.68 (app s, 1H, C*H*OCH), 5.66 (app s, 1H, C*H*OCH), and 3.77 (s, 3H, Ar-OCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 157.6, 151.2, 143.7, 142.4, 140.6, 120.6, 109.9, 107.4, 82.6, 82.2, and 55.8; IR (neat) 3036 (w), 2961 (w), 2909 (w), 1632 (m), 1516 (m), 1481 (m), 1264 (s), 1217 (s), 1030 (m), 812 (s), and 560 (m) cm^{-1}; TLC R_f = 0.5 in 5:1 hexanes:EtOAc; HRMS (APCI/TOF) calcd for $(M+H)^+$ $(C_{11}H_{11}O_2)^+$: 175.0754. Found: 175.0737.

4.3.4. 6-Methyl-1,4-dihydro-1,4-epoxynaphthalene (13g)—Yield (75%, 35 mg); colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.13 (d, *J* = 7.2 Hz, 1H, Ar-*H*), 7.10 (s, 1H, Ar-*H*), 7.02 [dd, *J* = 5.5, 1.7 Hz, 1H CH(O)CH=C*H*], 7.01 [dd, *J* = 5.5, 1.7 Hz, 1H CH(O)CH=C*H*], 6.77 (d, *J* = 7.2 Hz, 1H, Ar-*H*), 5.69 (app s, 1H, C*H*OCH), 5.67 (app s, 1H, CHOC*H*), and 2.30 (s, 3H, Ar-CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 149.5, 146.2, 143.4, 143.0, 135.0, 125.2, 121.8, 120.1, 82.50, 82.38, and 21.5; IR (neat) 3038 (m), 2954(w), 1620 (w), 1599 (w), 1459 (m), 1279 (s), 1165 (m), 1020 (s), 845 (s), 641 (s), and 573 (s) cm^{-1}; TLC R_f = 0.5 in 5:1 hexanes:EtOAc; HRMS (APCI/TOF) calcd for $(M+H)^+$ $(C_{11}H_{11}O)^+$: 159.0804. Found: 159.0821.

4.3.5. 5-Methyl-1,4-dihydro-1,4-epoxynaphthalene (13h)—Yield (86%, 68 mg); colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.09 (d, *J* = 6.9 Hz, 1H, Ar-*H*), 7.07–6.99 [m, 2H, CH(O)C*H*=C*H*], 6.88 (dd, *J* = 7.6, 6.9 Hz, 1H, Ar-*H*), 6.78 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 5.81 (app s, 1H, C*H*OCH), 5.71 (app s, 1H, C*H*OCH), and 2.32 (s, 3H, ArCH_3); ^{13}C NMR ($CDCl_3$, 76 MHz) δ 148.7, 147.4, 143.2, 142.7, 130.1, 126.8, 125.1, 117.9, 82.6, 80.9, and 18.2; IR (neat) 3036 (m), 2841 (w), 1632 (w), 1465 (m), 1522 (s), 1216 (s), 1347 (s), 1014 (s), 835 (m), 662 (s), and 573 (m) cm^{-1}; TLC R_f = 0.5 in 5:1 hexanes:EtOAc; HRMS (APCI/TOF) calcd for $(M+H)^+$ $(C_{11}H_{11}O)^+$: 159.0804. Found: 159.0791.

4.3.6. 5-Methoxy-1,4-dihydro-1,4-epoxynaphthalene (13i)—Yield (60%, 56 mg); colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.07 [dd, *J* = 5.5, 1.8 Hz, 1H, CH(O)C*H*=CH], 7.03 [dd, *J* = 5.5, 1.8 Hz, 1H CH(O)CH=C*H*], 6.97 (dd, *J* = 8.0, 7.0 Hz, 1H, Ar-*H*), 6.93 (dd, *J* = 7.0, 0.8 Hz, 1H, Ar-*H*), 6.59 (dd, *J* = 8.0, 0.8 Hz, 1H, Ar-*H*), 5.95 (app s, 1H, C*H*OCH), 5.70 (app s, 1H, C*H*OCH), and 3.83 (s, 3H, Ar-CH_3); ^{13}C NMR ($CDCl_3$, 76 MHz) δ 153.1, 151.7, 143.23, 143.08, 135.2, 127.2, 113.9, 110.5, 82.7, 80.3, and 55.9; IR (neat) 3042 (m), 2874 (w), 1642 (w), 1453 (m), 1538 (s), 1312 (m), 1167 (s), 1041 (m), 844 (m), and 521 (m) cm^{-1}; TLC R_f = 0.5 in 5:1 hexanes:EtOAc; HRMS (APCI/TOF) calcd for $(M+H)^+$ $(C_{11}H_{11}O_2)^+$: 175.0754. Found: 175.0731.

4.3.7. 1,4-Dihydro-1,4-epoxyphenanthrene (13j)—Yield (71%, 69 mg); pale yellow solid, mp 85–87 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.83 (dd, *J* = 8.3, 8.3 Hz, 2H, Ar-*H*), 7.56 (ddd, *J* = 7.9, 7.9, 7.9 Hz, 2H, Ar-*H*), 7.47 (dd, *J* = 8.1, 7.4 Hz, 1H, Ar-*H*), 7.39 (dd, *J* = 8.1, 7.6 Hz, 1H, Ar-*H*), 7.31–7.12 [m, 2H, CH(O)C*H*=C*H*], 6.28 (app s, 1H, C*H*OCH), and 5.94 (app s, 1H, CHOC*H*).; ^{13}C NMR ($CDCl_3$, 76 MHz) δ 148.5, 148.0, 145.1, 143.6, 132.0, 129.0, 127.8, 126.4, 125.6, 125.3, 122.9, 119.5, 83.6, and 81.4; IR (neat) 3050 (m), 2855 (w), 1655 (w), 1517 (m), 1451 (m), 1345 (s), 1147 (s), 1039 (s), 683 (s), and 482 (s); TLC R_f = 0.5 in 5:1 hexanes:EtOAc; HRMS (APCI/TOF) calcd for $(M+H)^+$ $(C_{14}H_{11}O)^+$: 194.0732. Found: 194.0741.

4.3.8. 1,4-Dihydro-1,4-epoxyanthracene (13k)—Yield (67%, 65 mg) pale yellow solid, mp 160–162 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.76–7.67 (m, 2H, Ar-*H*), 7.59 (s, 2H, Ar-*H*), 7.45–7.42 (m, 2H, Ar-*H*), 7.01–6.94 [m, 2H, CH(O)C*H*=C*H*], and 5.81 (app s, 2H, C*H*OC*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 144.3, 141.9, 132.1, 128.3, 126.3, 118.8, and 82.0; IR (neat) 3024 (m), 2929 (w), 1666 (w), 1538 (m), 1454 (s), 1193 (s), 1025 (s), 843

(s), 744 (s), and 496 (m) cm^{-1}; TLC R_f = 0.5 in 5:1 hexanes:EtOAc; HRMS (APCI/TOF) calcd for $(M+H)^+$ $(C_{14}H_{11}O)^+$: 195.0804. Found: 195.0788.

4.3.9. 6,9-Dihydro-6,9-epoxynaphtho[1,2-d][1,3]dioxole (13l)—Yield (60%, 56 mg); colorless oil; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.00 [dd, *J* = 5.6, 1.7 Hz, 1H, CH(O)CH=C*H*], 6.97 [dd, *J* = 5.6, 1.7 Hz, 1H, CH(O)C*H*=CH], 6.72 (d, *J* = 7.2 Hz, 1H, Ar-*H*), 6.38 (d, *J* = 7.2 Hz, 1H, Ar-*H*), 5.90 (d, *J* = 10.7 Hz, 1H, OCH_aH_bO), 5.90 (d, *J* = 10.7 Hz, 1H, OCH_aH_bO), 5.85 (app s, 1H, C*H*OCH), and 5.65 (app s, 1H, CHOC*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 146.5, 143.2 (2), 141.5, 140.6, 127.3, 113.3, 103.5, 101.1, 82.5, and 79.7; IR (neat) 3053 (m), 2960 (w), 2777 (w), 1650 (w), 1572 (m), 1458 (s), 1232 (s), 1042 (s), 954 (s), 829 (m), 638 (s), and 522 (m) cm^{-1}; TLC R_f = 0.5 in 5:1 hexanes:EtOAc; HRMS (APCI/TOF) calcd for $(M+H)^+$ $(C_{11}H_9O_3)^+$: 189.0546. Found: 189.0565.

4.3.10. 5,7-Dimethyl-1,4-dihydro-1,4-epoxynaphthalene (13m)—Yield (71%, 61 mg); colorless oil; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.03 [dd, *J* = 5.5, 1.7 Hz, 1H, CH(O)CH=C*H*], 7.02 [dd, *J* = 5.5, 1.7 Hz, 1H, CH(O)C*H*=CH], 6.94 (s, 1H, Ar-*H*), 6.60 (s, 1H, Ar-*H*), 5.78 (app s, 1H, CHOC*H*), 5.66 (app s, 1H, C*H*OCH), 2.28 (s, 3H, Ar-C*H*$_3$), and 2.27 (s, 3H, Ar-C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 149.2, 144.5, 143.08, 143.03, 134.9, 129.8, 127.0, 119.4, 82.7, 80.9, 21.3, and 18.2; IR (neat) 3047 (m), 2964 (m), 2872 (w), 1612 (w), 1481 (m), 1532 (s), 1214 (s), 1121 (s), 644 (s), and 521 (m) cm^{-1}; TLC R_f = 0.5 in 5:1 hexanes:EtOAc; HRMS (APCI/TOF) calcd for $(M+H)^+$ $(C_{12}H_{13}O)^+$: 173.0961. Found: 173.0942.

4.3.11. 1,4,5,8-Tetrahydro-1,4:5,8-diepoxyanthracene (13n)—Yield (69%, 72 mg) (1:1 *dr*); white sold, mp 189–191 °C ; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.20 (s, 2H, Ar-*H*), 7.06–6.99 (m, 4H, CH(O)C*H*=C*H*], and 5.63 (app s, 4H, C*H*OC*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 148.0, 143.6, 114.3, and 82.6; IR (neat) 3047 (w), 2963 (m), 2877 (w), 1640 (w), 1603 (w), 1485 (m), 1528 (s), 1222 (s), 1147 (s), 1029 (s), 845 (m), 635 (s), and 516 (m) cm^{-1}; TLC R_f = 0.5 in 3:1 hexanes:EtOAc; HRMS (APCI/TOF) calcd for $(M+H)^+$ $(C_{14}H_{11}O_2)^+$: 211.0754. Found: 211.0767.

4.3.12. 5-Ethyl-1,4-dihydro-1,4-epoxynaphthalene (13o)—Yield (70%, 60 mg); colorless oil; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.12 (d, *J* = 7.0 Hz, 1H, Ar-*H*), 7.05–7.02 [nfom, 2H, CH(O)C*H*=C*H*], 6.92 (dd, *J* = 7.9, 7.0 Hz, 1H, Ar-*H*), 6.81 (d, *J* = 7.9 Hz, 1H, Ar-*H*), 5.84 (app s, 1H, CHOC*H*), 5.72 (app s, 1H, C*H*OCH), 2.70 (dq, *J* = 14.1, 7.6 Hz, 1H, Ar-C$H_aH_bCH_3$), 2.63 (dq, *J* = 14.1, 7.6 Hz, 2H, Ar-C$H_aH_bCH_3$), and 1.21 (dd, *J* = 7.7, 7.7 Hz, 3H, Ar-$CH_aH_bCH_3$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 148.7, 146.9, 143.4, 142.9, 136.7, 125.40, 125.34, 118.2, 82.6, 81.0, 26.2, and 16.0; IR (neat) 3050 (m), 2963 (m), 2871 (w), 1643 (w), 1609 (w), 1470 (m), 1278 (m), 1141 (m), 1087 (m), 1003 (s), 870 (s), 675 (s), and 603 (m) cm^{-1}; TLC R_f = 0.5 in 10:1 hexanes:EtOAc; HRMS (APCI/TOF) calcd for $(M+H)^+$ $(C_{12}H_{13}O)^+$: 173.0961. Found: 173.0942.

4.3.13. 5-Isopropyl-1,4-dihydro-1,4-epoxynaphthalene (13p)—Yield (64%, 60 mg); colorless oil; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.11 (d, *J* = 6.9 Hz, 1H, Ar-*H*), 7.05–7.01 [nfom, 2H, CH(O)C*H*=C*H*], 6.94 (dd, *J* = 7.9, 6.9 Hz, 1H, Ar-*H*), 6.86 (d, *J* = 7.9, 0.5 Hz, 1H, Ar-*H*), 5.91 (app s, 1H, CHOC*H*), 5.70 (app s, 1H, C*H*OCH), 3.05 (hept, *J* = 6.9 Hz,

1H), 1.29 (d, J = 6.9 Hz, 3H), and 1.21 (d, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 148.7, 146.4, 143.5, 142.9, 141.2, 125.5, 122.8, 118.3, 82.6, 81.2, 31.8, 24.3, and 23.2; IR (neat) 3052 (m), 2956 (m), 2872 (w), 1641 (w), 1611 (w), 1475 (m), 1274 (m), 1121 (m), 1065 (m), 671 (s), and 653 (m) cm^{-1}; TLC R_f = 0.5 in 10:1 hexanes:EtOAc; HRMS (APCI/TOF) calcd for $(M+H)^+$ $(C_{13}H_{15}O)^+$: 187.1117. Found: 187.1103.

4.3.14. 5-(Tert-butyl)-1,4-dihydro-1,4-epoxynaphthalene (13q)—Yield (50%, 50 mg); white solid, mp 53–54 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.12 (d, J = 6.8, 1.1 Hz, 1H, Ar-*H*), 7.06–7.02 [nfom, 2H, CH(O)C*H*=C*H*], 6.97 (dd, J = 8.1, 1.1 Hz, 1H, Ar-*H*), 6.93 (dd, J = 8.1, 6.8 Hz, 1H, Ar-*H*), 6.15 (app s, 1H, CHOC*H*), 5.68 (app s, 1H, C*H*OCH), and 1.36 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 149.2, 146.7, 144.1, 143.8, 142.8, 125.2, 122.6, 118.4, 83.2, 82.1, 35.5, and 31.5; IR (neat) 3066 (m), 2963 (m), 2869 (w), 1686 (w), 1588 (w), 1470 (m), 1279 (m), 1187 (m), 1120 (m), 1008 (m), 878 (s), 710 (s), and 658 (m) cm^{-1}; TLC R_f = 0.5 in 10:1 hexanes:EtOAc; HRMS (APCI/TOF) calcd for $(M+H)^+$ $(C_{14}H_{17}O)^+$: 201.1274. Found: 201.1294.

4.3.15. 5-Phenyl-1,4-dihydro-1,4-epoxynaphthalene (13r)—Yield (67%, 74 mg); pale yellow solid, mp 63–65 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.51–7.45 (m, 2H, Ar-*H*), 7.42–7.35 (m, 3H, Ar-*H*), 7.29–7.25 (m, 1H, Ar-*H*), 7.20–7.10 [m, 2H, CH(O)C*H*=C*H*], 7.09–7.04 (m, 2H, Ar-*H*), 5.84 (app s, 1H, CHOC*H*), and 5.78 (app s, 1H, C*H*OCH). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 149.3, 147.1, 143.5, 143.0, 139.8, 135.1, 128.9, 128.3, 127.6, 125.6, 125.4, 119.5, 82.7, and 82.0; IR (neat) 3063 (m), 2962 (m), 2872 (w), 1662 (w), 1581 (w), 1473 (m), 1282 (m), 1193 (m), 1117 (m), 1003 (m), 871 (s), and 710 (s), cm^{-1}; TLC R_f = 0.5 in 10:1 hexanes:EtOAc; HRMS (APCI/TOF) calcd for $(M+H)^+$ $(C_{16}H_{13}O)^+$: 221.0961. Found: 221.0945.

4.4. Procedure for Preparation of (8*R*,9*S*,13*S*,14*S*)-13-Methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[a]phenanthrene-17,2'-[1,3]dioxolan]-3-yl 2-chloroacetate (15)

A round-bottom flask (100 mL) with a magnetic stir bar and a Dean-Stark apparatus was charged with estrone **14** (3.0 g, 11.0 mmol) and *p*-TsOH (105 mg, 5 mol %). Toluene (60 mL) and ethylene glycol (3.1 ml, 55 mmol) were added and the reaction mixture was heated at reflux for 14 h. The reaction was cooled to rt, and the solvent was removed *in vacuo*, ethyl acetate (30 mL) and brine (50 mL) were added. The mixture was extracted with ethyl acetate three times, and the combined organic extract was washed with water and brine, and dried over anhydrous sodium sulfate. The volatiles were removed *in vacuo* to afford the crude product, which was directly used for a subsequent reaction without further purification. The crude product (11 mmol) and chloroacetic acid (1.9 g, 20 mmol) and DMAP (67 mg, 5 mol %) were dissolved with CH_2Cl_2 (20 mL), the reaction mixture was cooled to 0 °C with an ice bath. DCC (2.7 g, 13 mmol) was added into the reaction mixture slowly. The reaction mixture was warmed to rt and stirred for 10 h. Diethyl ether (30 mL) was added to precipitate the urea byproduct. The mixture was filtered and the filtrate was treated with saturated aqueous sodium bicarbonate. Aqueous phase was extracted with ethyl acetate three times. The combined organic extracts were washed with water and brine, and dried over anhydrous sodium sulfate. The volatiles were removed *in vacuo*, and the crude mixture was purified by flash column (hexanes: EtOAc 3:1) to afford the ester **15** (3.27 g, 76% over two

steps). White solid, mp 113–115 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.30 [d, *J* = 8.1 Hz, 1H, *H(1)*], 6.88 [dd, *J* = 8.1, 2.6 Hz, 1H, *H(2)*], 6.83 [d, *J* = 2.6 Hz, 1H, *H(4)*], 4.28 (s, 2H, C*H*$_2$Cl), 3.98–3.88 (m, 4H, OC*H*$_2$C*H*$_2$O), 2.88–2.84 (m, 2H, alkyl-*H*), 2.32 (dddd, *J* = 13.2, 4.2, 4.2, 2.7 Hz, 1H, alkyl-*H*), 2.26 (ddd, *J* = 10.6, 10.6, 4.1 Hz, 1H, alkyl-*H*), 2.03 (ddd, *J* = 14.0, 11.2, 3.1 Hz, 1H, alkyl-*H*), 1.93–1.74 (m, 4H, alkyl-*H*), 1.63 (ddd, *J* = 12.1, 10.8, 7.0 Hz, 1H, alkyl-*H*), 1.55–1.31 (m, 5H, alkyl-*H*), and 0.88 [s, 3H, *CH(18)*$_3$]; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.4, 148.2, 138.9, 138.8, 126.8, 121.2, 119.6, 118.2, 65.5, 64.8, 49.6, 46.3, 44.0, 41.1, 38.8, 34.4, 30.9, 29.7, 26.9, 26.2, 22.6, and 14.5; IR (neat) 2935 (m), 2864 (m), 1775 (s), 1724 (m), 1493 (m), 1304 (m), 1190 (s), 1042 (m), and 804 (m) cm^{-1}. m.p. 76–78 °C; TLC R_f = 0.5 in 3:1 hexanes:EtOAc; HRMS (APCI/TOF) calcd for $(M+H)^+$ $(C_{22}H_{28}ClO_4)^+$: 391.1671. Found: 391.1659.

4.5. Procedure for Preparation of (8*R*,9*S*,13*S*,14*S*)-3-[Diethyl(methyl)silyl)]-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro(cyclopenta[a]phenanthrene-17,2'-[1,3]dioxolan)-2-yl trifluoromethanesulfonate (18)

C2-silyl phenol **17** (414 mg, 1 mmol) and pyridine (0.12 mL, 1.5 mmol) in CH_2Cl_2 (2 mL, 1 M) were cooled to 0 °C with an ice bath. Trifluoromethanesulfonyl anhydride (0.25 mL, 1.5 mmol) was added into the reaction mixture dropwise. The reaction mixture was stirred at 0 °C for 1 h and an additional 30 min at rt. The reaction was quenched by saturated aqueous sodium bicarbonate and was extracted with diethyl ether three times. The combined organic extracts were washed with water two times and brine, and dried over anhydrous sodium sulfate. The volatiles were removed *in vacuo*, and the crude mixture was purified by MPLC (hexanes/EtOAc = 5:1, 5 mL/min) to afford arylsilyl triflate **18**. White solid; Yield (90%, 491 mg) ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.39 (s, 1H, Ar-*H*), 7.01 (s, 1H, Ar-*H*), 3.99–3.88 (m, 4H, OC*H*$_2$C*H*$_2$O), 2.87 (dd, *J* = 8.4, 4.0 Hz, 2H, alkyl-*H*), 2.37–2.31 (m, 1H, alkyl-*H*), 2.30–2.25 (m, 1H, alkyl-*H*), 2.04 (ddd, *J* = 14.1, 11.6, 2.7 Hz, 1H, alkyl-*H*), 1.94–1.76 (m, 4H alkyl-*H*), 1.64 (ddd, *J* = 11.9, 10.9, 7.0 Hz, 1H alkyl-*H*), 1.56 (ddd, *J* = 12.6, 3.3, 2.6 Hz, 1H alkyl-*H*), 1.55–1.33 (m, 4H), 0.89 [s, 3H C*H(18)*$_3$], 0.97–0.80 [m, 10H, Si(C*H*$_2$C*H*$_3$)$_2$], and 0.30 (s, 3H, SiC*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.5, 141.0, 139.8, 134.1, 126.8, 119.58, 119.51, 118.7 (q, $^{1}J_{F\text{-}C}$ = 319.6 Hz), 65.5, 64.8, 49.5, 46.3, 44.0, 38.8, 34.4, 30.8, 29.9, 26.8, 26.1, 22.6, 14.5, 7.6, 5.68, 5.59, and −5.2; IR (neat) 2957 (m), 2874 (w), 1493 (m), 1304 (m), 1190 (s), 1042 (m), and 804 (m) (s) cm^{-1}; TLC R_f = 0.5 in 5:1 hexanes:EtOAc; HRMS (APCI/TOF) calcd for $(M+H)^+$ $(C_{26}H_{38}F_3O_5SSi)^+$: 547.2156. Found: 547.2139.

4.6. (3aS,3bR,11bS,13aS)-13a-Methyl-2,3,3a,3b,4,5,7,10,11b,12,13,13a-dodecahydrospiro[7,10-epoxycyclopenta[c]tetraphene-1,2'-[1,3]dioxolane] (19)

C2-Silyl triflate **18** (109 mg, 0.2 mmol) was dissolved in furan (0.2 mL). TBAF (0.6 mL, 0.24 mmol, 1 M in THF) was added to the reaction mixture at rt. The septum on the vial was replaced by a screw cap with a Teflon liner, and the mixture was stirred at rt for 2 h. Reaction progress was monitored by TLC until full conversion of **18**. TLC showed two spots, indicating formation of compound **19** and **20**. The reaction was quenched by adding saturated aqueous ammonium chloride. The reaction mixture was extracted with diethyl ether and concentrated *in vacuo* to afford a mixture of **19** and **20** (4:1), which was used for next step without further purification. White solid; Yield (60%, 44 mg) (1.2:1 *dr*). ^{1}H NMR

($CDCl_3$, 500 MHz) δ 7.25 (s, 0.45H, Ar-*H*), 7.24 (s, 0.55H, Ar-*H*), 7.02–6.98 [m, 3H, Ar-*H* and CH(O)C*H*=C*H*], 5.66–5.65 (m, 2H, C*H*OC*H*), 3.98–3.87 (m, 4H, OCH_2CH_2O), 2.85–2.72 (m, *J* = 2.9 Hz, 2H, Alkyl-*H*), 2.32–2.28 (m, 1H, Alkyl-*H*), 2.27–2.19 (m, 1H, Alkyl-*H*), 2.05–1.99 (m, 1H, Alkyl-*H*), 1.89–1.73 (m, 4H, Alkyl-*H*), 1.65–1.59 (m, 1H, Alkyl-*H*), 1.56–1.51 (m, 1H, Alkyl-*H*), 1.49–1.31 (m, 4H, Alkyl-*H*), 0.88 [s, 1.35H, C*H(18)*$_3$], and 0.86 [s, 1.65H C*H(18)*$_3$]; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 146.34, 146.32, 146.21, 146.09, 143.24, 143.20, 143.01 (2), 136.84, 136.73, 133.31, 133.27, 121.57, 121.52, 119.62, 119.60, 118.0 (2), 82.58, 82.55, 82.36, 82.28, 65.5 (2), 64.8 (2), 49.61, 49.57, 46.34, 46.32, 44.47, 44.39, 39.18, 39.13, 34.4 (2), 31.0 (2), 30.1 (2), 27.11, 27.09, 26.44, 26.30, 22.6 (2), and 14.5 (2); IR (neat) 3061 (m), 2957 (m), 2873 (w), 1491 (m), 1205 (m), 1192 (s), 1041 (m), and 814 (m) (s) cm^{-1}; TLC R_f = 0.4 in 5:1 hexanes:EtOAc; HRMS (APCI/TOF) calcd for $(M+H)^+$ $(C_{24}H_{29}O_3)^+$: 365.2111. Found: 365.2085.

4.7. Procedure for Preparation of (3a*S*,3b*R*,11b*S*,13a*S*)-13a-Methyl-2,3,3a,3b,4,5,7,10,11b,12,13,13a-dodecahydro-1H-7,10-epoxycyclopenta[c]tetraphen-1-one (20)

The crude mixture of **19** was dissolved in a mixture of THF/H_2O (0.5 mL, 1:1, 0.1 M). Hydrochloric acid (0.5 ml, 1 M) was added and the mixture was stirred at rt for 5 h. The reaction was quenched by adding saturated aqueous sodium bicarbonate. The reaction mixture was extracted with diethyl ether three times and concentrated *in vacuo* to afford the crude mixture, which was purified by MPLC (hexanes/EtOAc = 5:1, 5 mL/min, retention time 15 min) to provide **20**. Yield (72%, 46 mg) (1.2:1 *dr*); White solid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.24 (s, 0.45H, Ar-*H*), 7.24 (s, 0.55H, Ar-*H*), 7.02–6.98 [m, 3H, Ar-*H* and CH(O)C*H*=C*H*], 5.66 (app s, 2H, C*H*OC*H*), 2.86–2.82 (m, 2H, Alkyl-*H*), 2.50 (ddd, *J* = 19.0, 8.7, 2.3 Hz, 1H, Alkyl-*H*), 2.41–2.35 (m, 1H, Alkyl-*H*), 2.27–2.24 (m, 1H, Alkyl-*H*), 2.18–2.10 (m, 1H, Alkyl-*H*), 2.07–1.94 (m, 3H, Alkyl-*H*), 1.63–1.42 (m, 6H, Alkyl-*H*), 0.91 [s, 1.35H, C*H(18)*$_3$], and 0.89 [s, 1.65H, C*H(18)*$_3$]; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 221.1 (2), 146.60, 146.58, 146.44 (2), 143.25, 143.23, 142.99, 142.96, 136.17, 136.07, 133.08, 133.05, 121.58, 121.54, 117.9 (2), 82.57, 82.54, 82.35, 82.27, 50.6 (2), 48.21, 48.19, 44.81, 44.73, 38.51, 38.47, 36.1 (2), 31.8 (2), 30.0 (2), 26.7 (2), 26.23, 26.10, 21.8 (2), and 14.1 (2); IR (neat) 3053 (m), 2961 (m), 2874 (w), 1631 (w), 1442 (m), 1222 (m), 1191 (m), 1115 (m), 1001 (m), 851 (s), 706 (s), cm^{-1}; TLC R_f = 0.5 in 3:1 hexanes:EtOAc; HRMS (APCI/TOF) calcd for $(M+H)^+$ $(_{22}H_{25}O_2)^+$: 321.1849. Found: 321.1855.

Supplementary Material

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Acknowledgments

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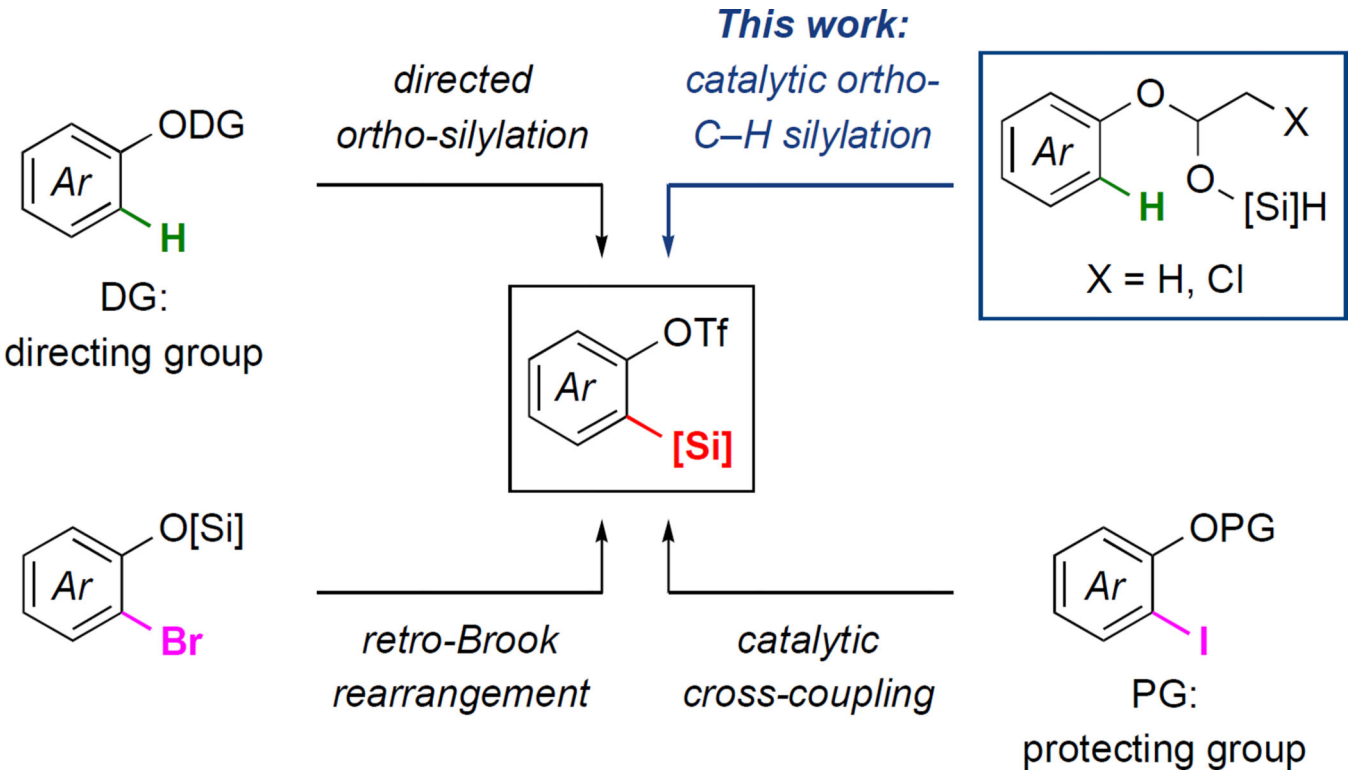
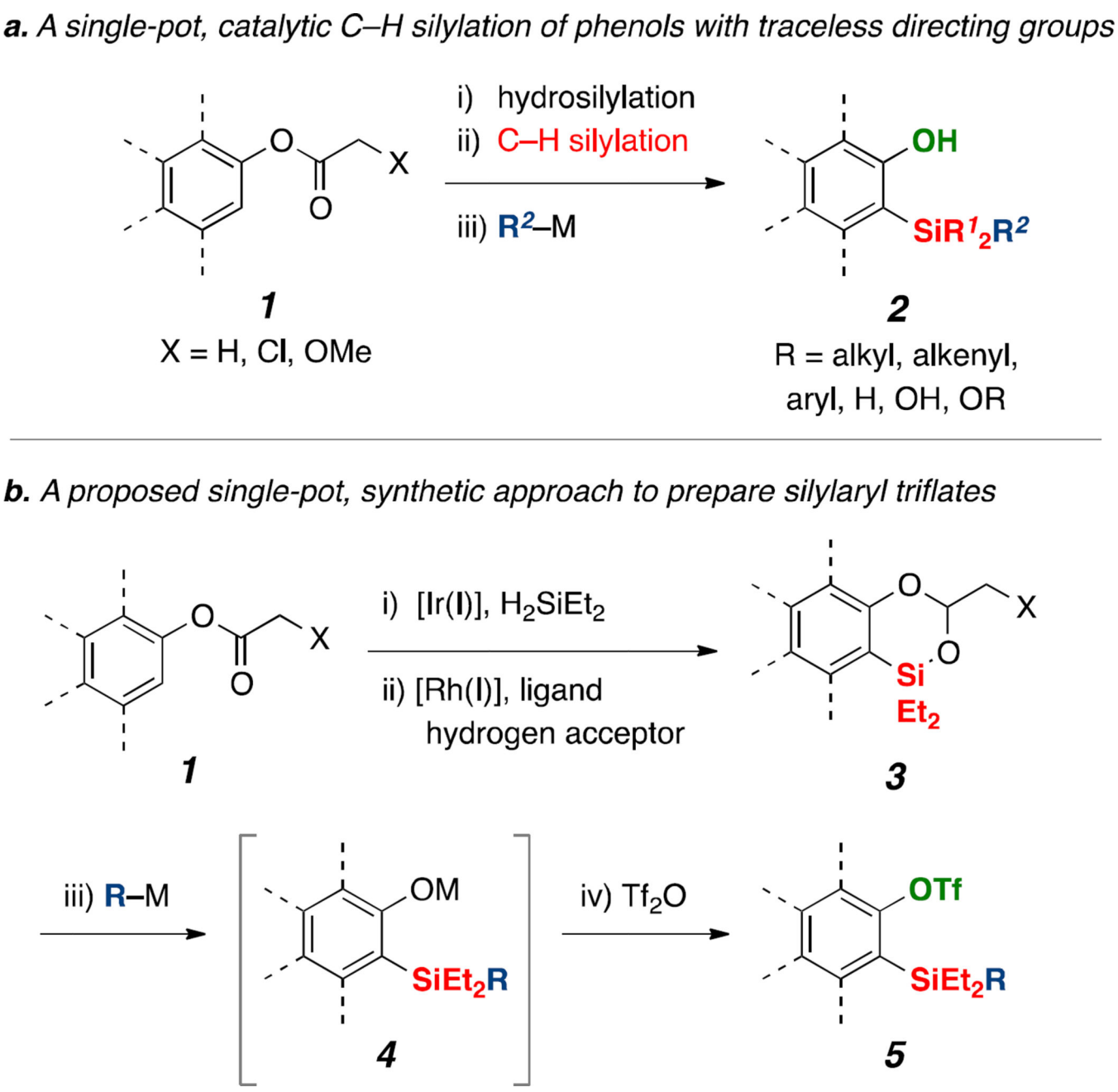
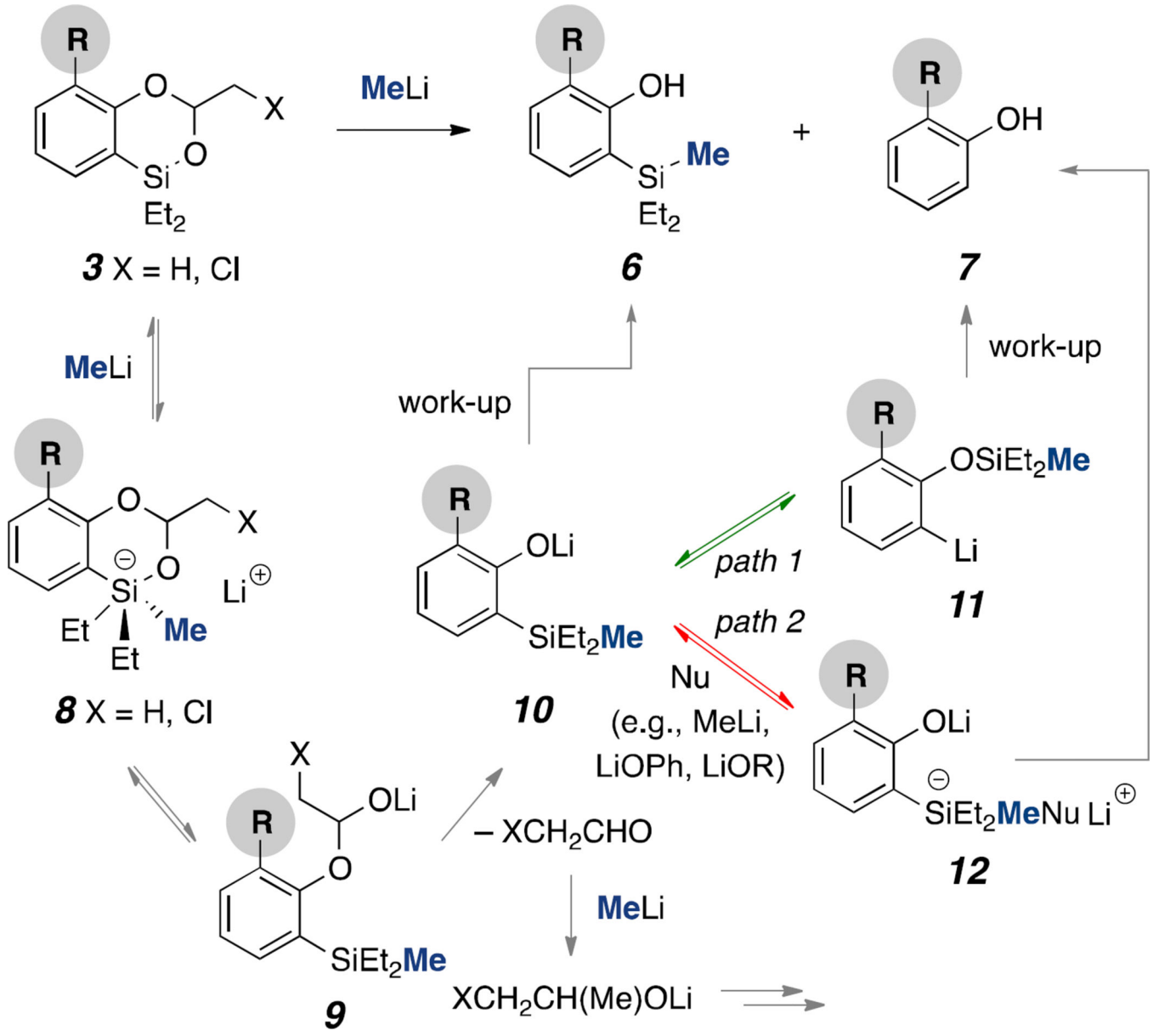


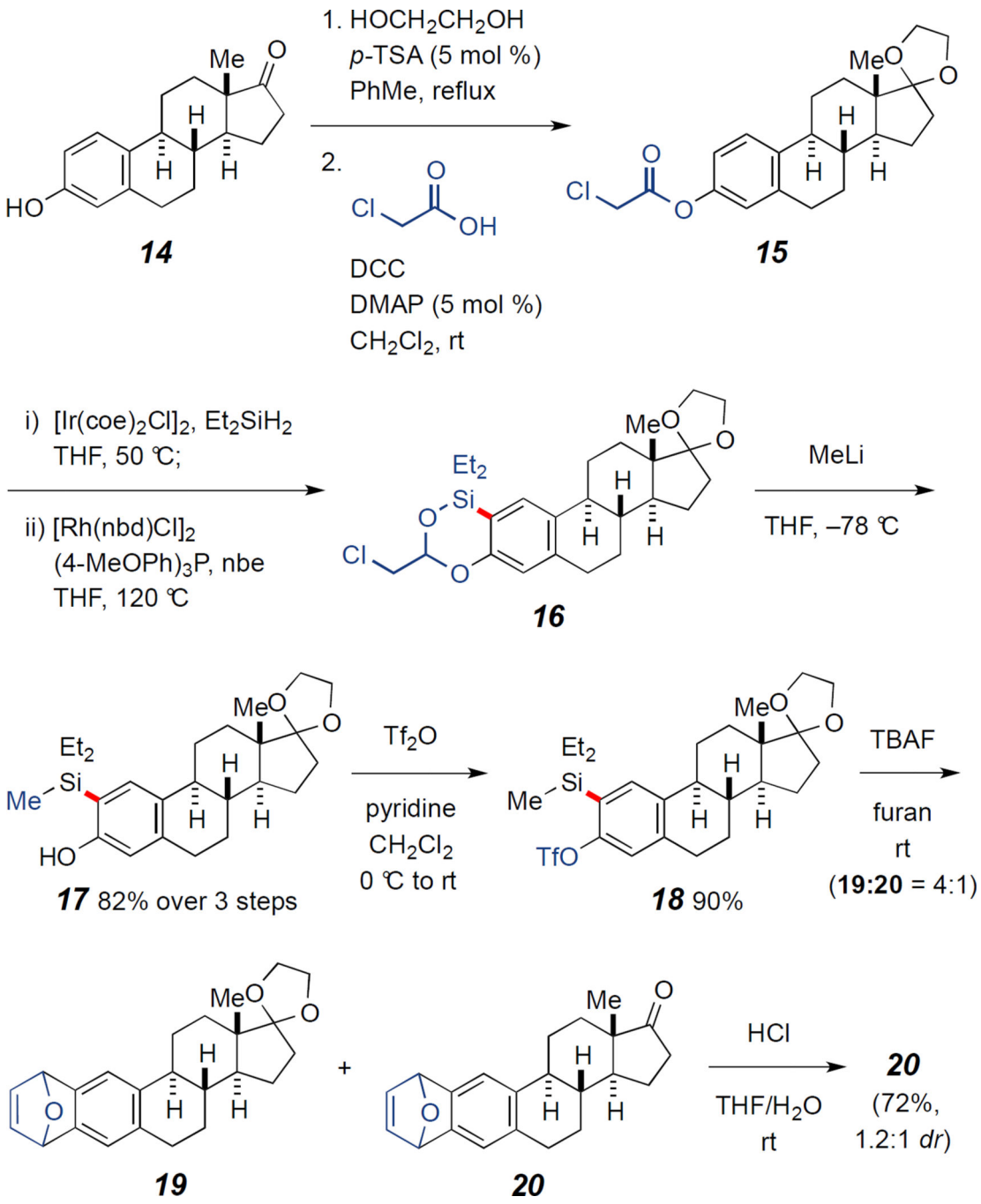
Scheme 1.
Methods to prepare silylaryl triflates



Scheme 2.
Synthetic approach to silylaryl triflates via *ortho*-C–H silylation



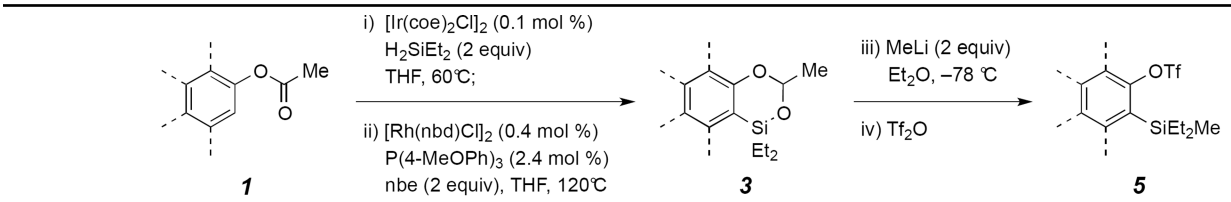
Scheme 3.
Proposed mechanism of desilylation

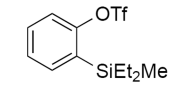


Scheme 4.
Synthetic approach to estrone derivative **20**

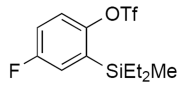
Table 1

Preparation of silylaryl triflates **5** from benzodioxasilines **3**

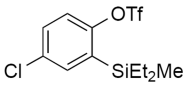




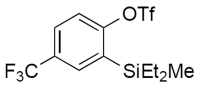
5a 91%



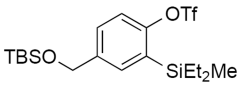
5b 88%



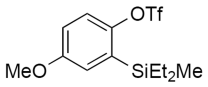
5c 82%



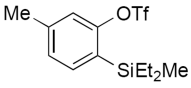
5d 70%



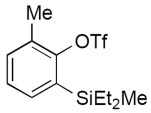
5e 74%



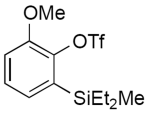
5f 83%



5g 72%



5h 66%



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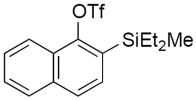
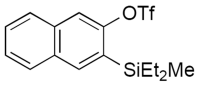
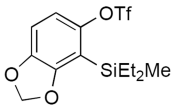


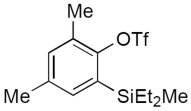
5j 60%



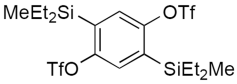
5k 66%



5l 53%



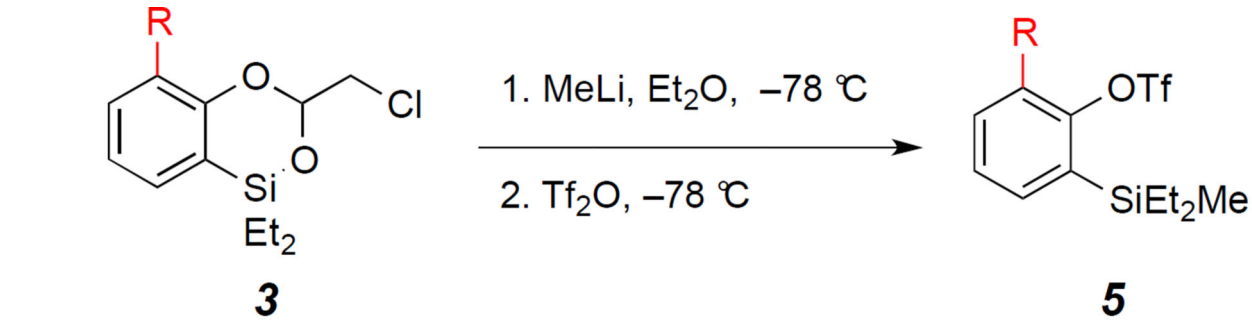
5m 72%



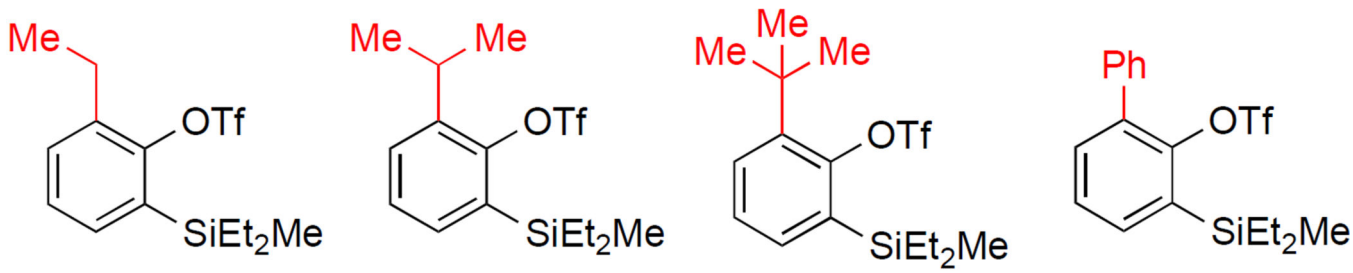
5n 74%

Table 2

Preparation of sterically hindered silylaryl triflates **5** from benzodioxasilines **3**



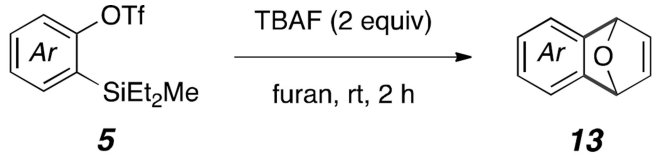
3 ***5***



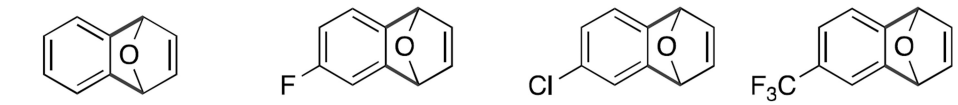
5o 81% ***5p*** 73% ***5q*** 70% ***5r*** 75%

Table 3

Fluoride-mediated [4+2] aryne cycloaddition reaction of diethylmethylsilylaryl triflates **5**



5 ***13***

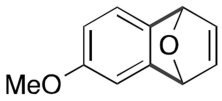


13a 81%

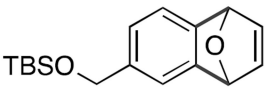
13b 71%

13c 82%

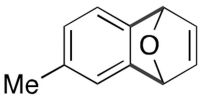
13d 83%



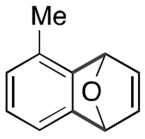
13e 80%



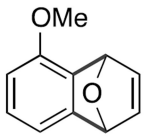
13f 65%



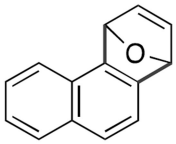
13g 75%



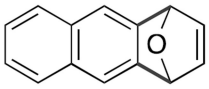
13h 86%



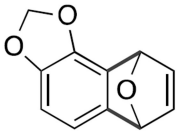
13i 67%



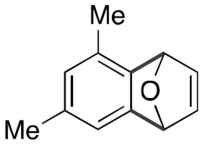
13j 71%



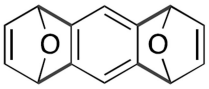
13k 67%



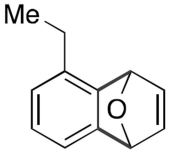
13l 60%



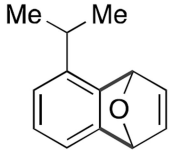
13m 71%



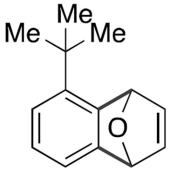
13n 69% (1:1 *dr*)



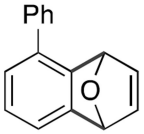
13o 70%



13p 64%



13q 50%



13r 67%