Improved and Practical Synthesis of [2,4,5-Tris(trimethylsilyl)phenyl](phenyl)iodonium Triflate and Utilization as a 1,4-Benzdiyne Synthon

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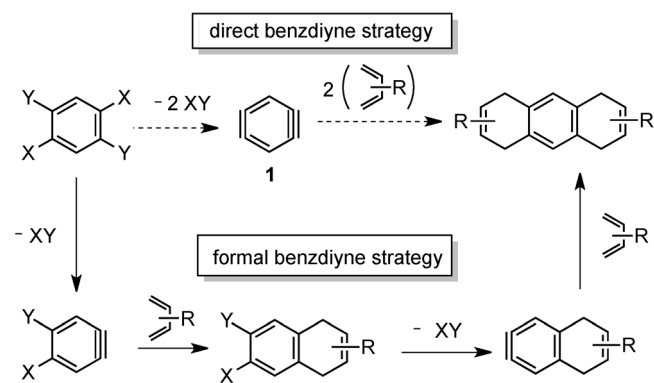
Abstract: An efficient and improved method for preparing [2,4,5-tris(trimethylsilyl)phenyl](phenyl)-iodonium triflate as a 1,4-benzdiyne synthon was developed by using phenyiodonium diacetate/boron triflouride·diethyl etherate [PhI(OAc)$_2$/BF$_3$·OEt$_2$] reagent. The iodonium triflate generated 3,4-bis(trimethylsilyl)benzyne quantitatively to give cycloadducts with tetraphenylcyclopentadienone, furan and anthracene in high yields. These cycloadducts bearing two trimethylsilyl groups were transformed into the corresponding aryne precursors, which underwent subsequent cycloaddition reactions to afford polycyclic aromatic compounds such as 1,4-dihydro-1,4-epoxyanthracene, naphthotriazole, triptycene, and anthratriazole derivatives in good to high yields. The total reactions are formally considered as double cycloaddition reactions of 1,4-benzdiyne. This practical and useful formal benzdiyne strategy is described.

Keywords: arynes; 1,4-benzdiyne; cycloaddition; hypervalent iodine; iodonium salts

1,4-Benzdiyne or 1,2,4,5-tetradehydrobenzene (**1**) is considerably higher in energy than benzyne and has been a target compound for theoretical studies[1] and for matrix isolation and characterization so far.[2] Although benzdiyne **1** is regarded as a useful intermediate to construct polycyclic aromatic molecules, there are few reports on the utilization of benzdiyne **1** for organic synthesis because of its inherent instability. Furthermore, the cycloaddition reaction of benzdiyne precursors such as tetrahaloarenes,[3] benzeneditriflates,[4] and diaminobenzobistriazoles[5] gives double cycloadducts, but it is not clear whether the generation of benzdiyne 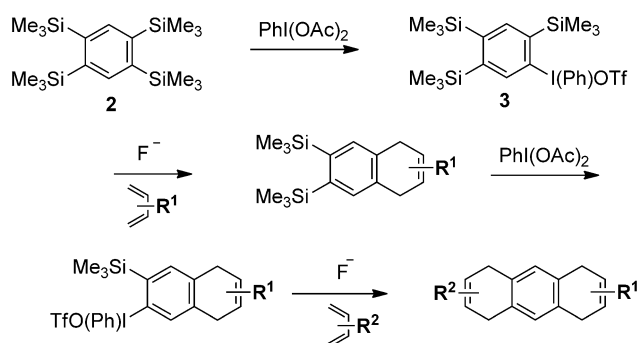**1** is involved in these reactions. Al-though the direct generation of **1** for double cycloaddition is fascinating in organic synthesis due to its simple and straightforward nature, trapping highly reactive benzdiyne **1** seems to be difficult because **1** easily isomerizes to ring-opening products such as hexatriyne.[2] Therefore, a sequential, stepwise process for double cycloaddition is superior to the direct method from the standpoint of organic synthesis. In addition, the sequential method enables the synthesis of unsymmetrical cycloadducts which are difficult to prepare by the direct method. Apart from a direct benzdiyne strategy involving generation and cycloaddition of benzdiyne **1**, a formal benzdiyne strategy *via* a sequential process as shown in Scheme 1 is more useful and practical in organic synthesis.

However, only few methods giving unsymmetrical cycloadducts with different dienes under mild and neutral conditions have been reported. Winling and Russel reported that (phenyl)[2,4,5-tris(trimethylsilyl)phenyl]iodonium triflate prepared from 1,2,4,5-tetrakis(trimethylsilyl)benzene was the good reagent for the synthesis of unsymmetrical adducts of benzdiyne **1**.[6] Furthermore, Wong and co-workers demonstrated

Scheme 1. Benzdiyne strategies for constructing aromatic compounds.

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Scheme 2. A benzdiyne strategy using [tris(trimethylsilyl)-phenyl]iodonium triflate **3**.

the synthesis of linear polycyclic aromatic hydrocarbons using 5,6-bis(trimethylsilyl)benzo[c]furan, which was prepared in two steps from [2,4,5-tris(trimethylsilyl)phenyl]iodonium triflate.[7] Lee and co-workers developed a synthesis of fused triptycenes and extended triptycene derivatives from benzobisoxadisilole as a 1,4-benzdiyne equivalent.[8] However, regrettably, [tris(trimethylsilyl)phenyl]iodonium triflate and the related iodonium triflates were not isolated but used for further reactions without isolation.

Very recently, we discovered a safe and efficient procedure for the synthesis of 1,2-bis(trimethylsilyl)-benzene from 1,2-dichlorobenzene; this procedure provides 1,2,4,5-tetrakis(trimethylsilyl)benzene (**2**) in a high yield.[9] Encouraged by this discovery, we studied a facile approach to benzdiyne adducts using hypervalent iodine compounds because a hypervalent benzyne precursor, (phenyl)[2-(trimethylsilyl)phenyl]-iodonium triflate,[10] has the highest efficiency for benzyne generation and is easy to handle. We could improve the synthesis of (phenyl)[2,4,5-tris(trimethylsilyl)phenyl]iodonium triflate (**3**) using a milder hypervalent iodine reagent system and develop a benzdiyne strategy. We want to report here a stepwise approach to benzydiyne adducts using [2,4,5-tris(trimethylsilyl)-phenyl]iodonium triflate **3**, as shown in Scheme 2.

Fist we examined the synthesis of [2,4,5-tris(trimethylsilyl)phenyl]iodonium triflate **3** from 1,2,4,5-tetrakis(trimethylsilyl)benzene (**2**). The results are given in Table 1. According to this procedure for the synthesis of [2-(trimethylsilyl)phenyl]iodonium triflate,[10] tetrakis(trimethylsilyl)benzene **2** was treated with PhI(OAc)$_2$ activated with 2 equiv. of TfOH However, The reaction with PhI(OAc)$_2$/2TfOH at $-20\,°C$ or at $-20\,°C$ to room temperature afforded a complex mixture of products (Table 1, entries 1 and 2). It was considered that the use of TfOH as an activating agent caused desilylation. Then, we examined a reagent system of PhIO and BF$_3$·Et$_2$O for phenyliodination.[11] Tetrakis(trimethylsilyl)benzene **2** was reacted with PhIO activated with BF$_3$·Et$_2$O at $0\,°C$ and the reaction mixture was then treated with aqueous NaOTf. In this procedure, the desired iodonium triflate **3** was isolated as a solid in 23% yield (entry 3). Increasing the amount of PhIO/BF$_3$·Et$_2$O improved the yield of **3** slightly (entries 4 and 5). After increasing the amount of activating agent BF$_3$·Et$_2$O, the desired iodonium triflate **3** was obtained in 58% yield (entry 6). Finally, we examined on use of PhI(OAc)$_2$ together with BF$_3$·Et$_2$O. The reaction of tetrakis(trimethylsilyl)benzene **2** with PhI(OAc)$_2$ activated by 2 equiv. of BF$_3$·Et$_2$O followed by treatment with aqueous NaOTf gave the desired iodonium triflate **3** in 84% yield (entry 7). Considering the availability and stability of PhI(OAc)$_2$, it was found that the PhI(OAc)$_2$/BF$_3$·Et$_2$O reagent was the best.

Table 1. Preparation of [tris(trimethylsilyl)phenyl]iodonium triflate **3**.
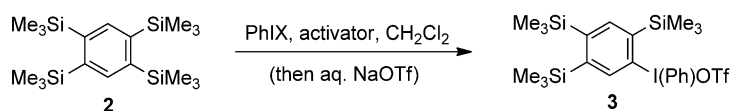
| Entry	PhIX (mmol)	Activator (mmol)	Temp. [°C]	Time [h]	Yield [%][a]
1	PhI(OAc)$_2$ (1)	TfOH (2)	-20	0.5	–[b]
2	PhI(OAc)$_2$ (2)	TfOH (3.8)	-20 to r.t.	17	–[b]
3[c]	PhIO (1.2)	BF$_3$·OEt$_2$ (1.2)	0	3	23
4[c,d]	PhIO (2)	BF$_3$·OEt$_2$ (2)	0	3	27
5[c,e]	PhIO (3)	BF$_3$·OEt$_2$ (3)	0	3	31
6[c]	PhIO (1.2)	BF$_3$·OEt$_2$ (6)	0	1	58
7[c,f]	PhI(OAc)$_2$ (1.2)	BF$_3$·OEt$_2$ (2.4)	r.t.	0.5	86

[a] Isolated yield.
[b] A complex mixture of products.
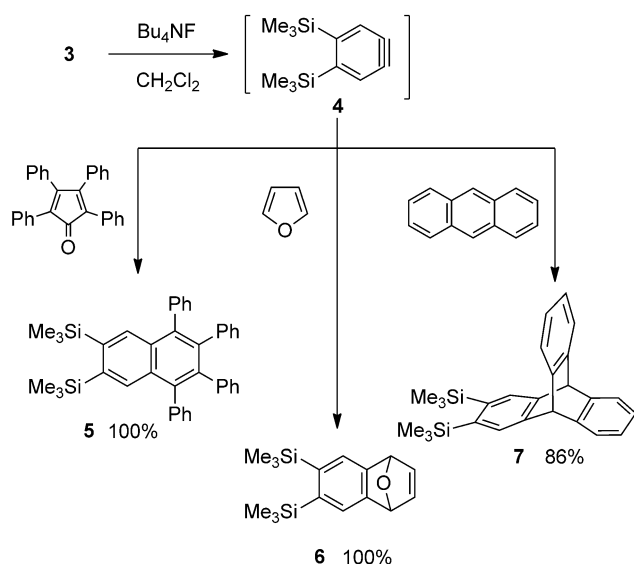[c] Product was isolated after treating the reaction mixture with aqueous NaOTf.
[d] CH$_2$Cl$_2$ (6 mL).
[e] CH$_2$Cl$_2$ (8 mL).
[f] CH$_2$Cl$_2$ (10 mL).

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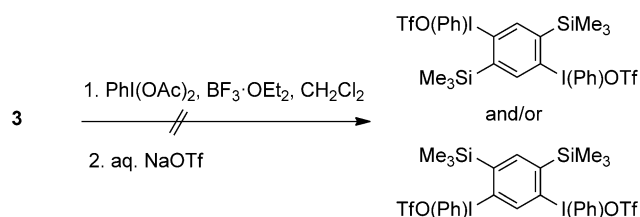
Scheme 3. Attempted synthesis of a benzdiyne precursor (see Scheme 4).
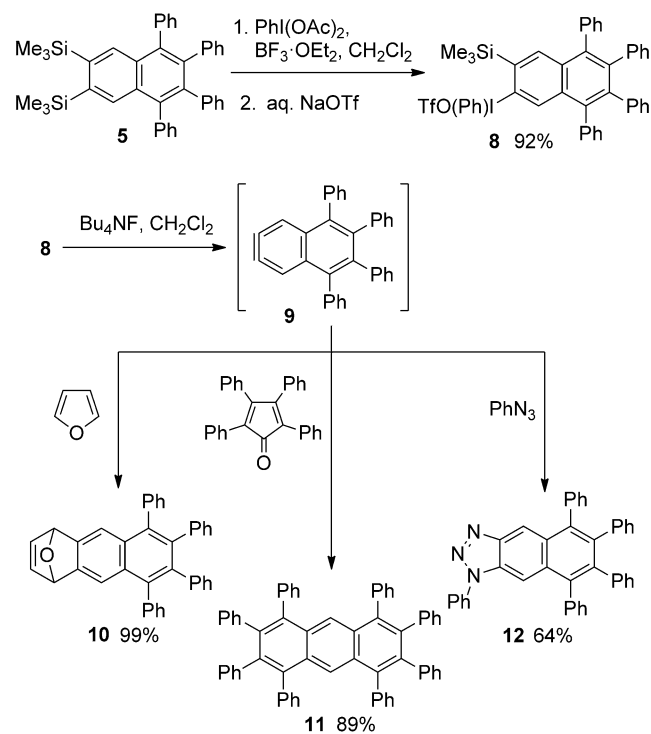

Scheme 4. Generation and reaction of bis(trimethylsilyl)benzyne **4**.

In order to explore the synthesis of a benzdiyne precursor, we attempted an additional phenyliodination of tris(trimethylsilyl)phenyliodonium triflate **3** using PhI(OAc)$_2$/BF$_3$·Et$_2$O reagent. However, no bis-iodonium ditriflates were obtained (Scheme 3). Several attempted reactions using other reagents such as PhIO/BF$_3$·Et$_2$O and PhI(OAc)$_2$/TfOH also failed. Thus, we turned our approach into a stepwise, consecutive method for the benzdiyne strategy.

To achieve the consecutive benzdiyne strategy, the trimethylsilyl group must be tolerant against fluoride ion under the reaction conditions. Then, we examined the trapping reaction of 4,5-bis(trimethylsilyl)benzyne (**4**) using furan, tetraphenylcyclopentadienone, and anthracene (Scheme 4). When iodonium triflate **3** was treated with Bu$_4$NF in CH$_2$Cl$_2$, the cycloadducts **5** and **6** of bis(trimethylsilyl)benzyne **4** with furan and tetraphenylcyclopentadienone were obtained quantitatively in both cases. In the trapping reaction with anthracene, bis(trimethysilyl)triptycene **7** was isolated in 86% yield. Two trimethylsilyl groups were tolerated under the reaction conditions and existed on the cycloadducts **5**–**7** without any damage.

Since we confirmed that the first step of the consecutive benzdiyne strategy proceeded successfully, we then conducted further transformations of cycloadducts **5**–**7**. Treatment of bis(trimethylsilyl)naphthalene **5** with PhI(OAc)$_2$/BF$_3$·Et$_2$O reagent followed by aqueous NaOTf gave (trimethylsilyl)naphthyliodonium triflate **8** in 92% yield. Reaction of the iodonium triflate **8** with Bu$_4$NF in the presence of furan afforded cycloadduct **10** in 99% yield (Scheme 5), suggesting that tetraphenyldidehydronaphthalene **9** was generated quantitatively. Next, we conducted the trapping reaction with tetraphenylpentadienone under the same conditions and obtained octaphenylanthracene **11** in 89% yield. Although the synthesis of octaphenylanthracene **11** was reported by different methods,[12] the yields were low or moderate. In addition, 1,3-dipolar cycloaddition of **9** with phenyl azide proceeded efficiently to give naphthotriazole **12** in 64% yield. These results indicate that this consecutive benzdiyne approach is excellent. Encouraged by these results, we continued examining the consecutive benzdiyne strategy.

Since the furan adduct **6** derived from bis(trimethylsilyl)benzyne **4** has a reactive double bond toward an electrophilic hypervalent iodine reagent, it must be transformed into its naphthalene derivative by deoxygenative aromatization. The deoxygenation reaction of furan adduct **6** was conducted according to the literature method using TiCl$_4$/LiAlH$_4$/Et$_3$N in THF,[13]
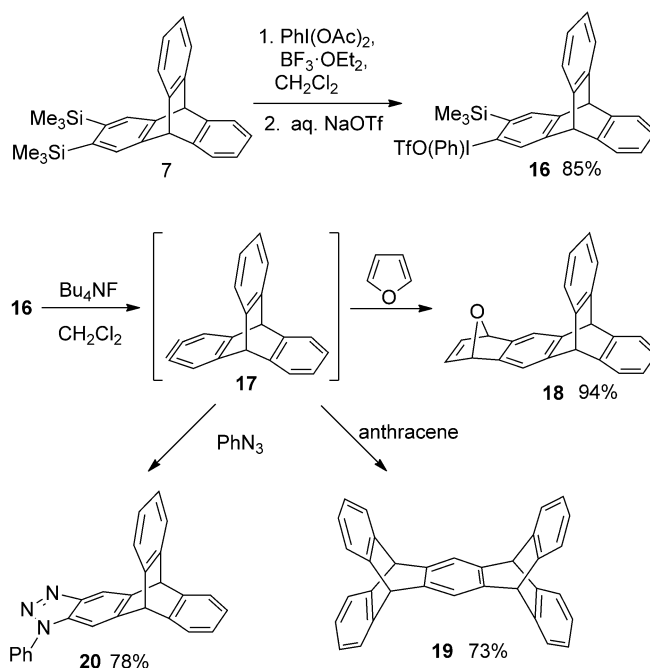

Scheme 5. Preparation and reaction of (trimethylsilyl)naphthyliodonium triflate **9**.

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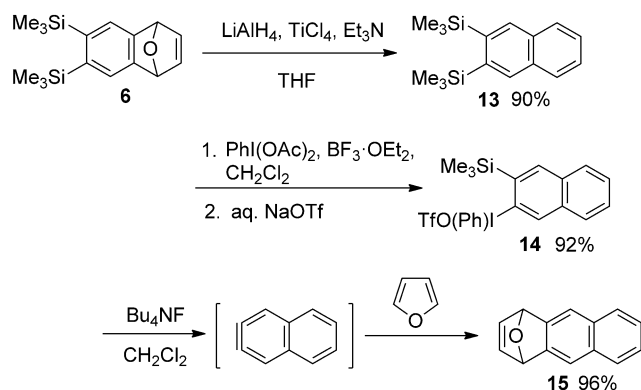
Scheme 6. Preparation and reaction of naphthyliodonium triflate **14**.

Scheme 7. Preparation and reaction of triptycenyliodonium triflate **16**.

affording 2,3-bis(trimethylsilyl)naphthalene (**13**) in 90% yield (Scheme 6). Treatment of bis(trimethylsilyl)naphthalene **13** with PhI(OAc)$_2$/BF$_3$·Et$_2$O reagent followed by aqueous NaOTf gave (phenyl)[3-(trimethylsilyl)naphthyl]iodonium triflate (**14**) in 92% yield. In the previous synthesis of the same iodonium salt **14** using PhI(OAc)$_2$/TfOH reagent, the yield was 54%.[14] Therefore, the synthesis of the benzyne precursor was much improved by use of PhI(OAc)$_2$/BF$_3$·Et$_2$O reagent. Reaction of the iodonium triflate **14** with Bu$_4$NF in the presence of furan afforded cycloadduct **15** in 96% yield.

Recently triptycene and the related compounds have attracted much attention due to their unique structures and have been applied to molecular machines, supramolecular chemistry, and material science.[15] However, there are only a few reports on the synthesis of triptycyne precursors.[8c,16] Thus, we conducted the synthesis of a 2,3-triptycyne equivalent from bis(trimethylsilyl)triptycene **7**. Treatment of bis-(trimethylsilyl)triptycene **7** with PhI(OAc)$_2$/BF$_3$·Et$_2$O reagent followed by aqueous NaOTf afforded triptycenyliodonium triflate **16** in 85% yield (Scheme 7). The triptycenyliodonium triflate **16** readily reacted with Bu$_4$NF to generate 2,3-triptycyne (**17**), which underwent cycloaddition with furan and anthracene to give the cycloadducts **18** and **19** in 94 and 73% yields, respectively. From the result of the cycloaddition with furan, 2,3-triptycyne is considered to be formed almost quantitatively. Pentiptycene (**19**) was first prepared through the addition of 2,3-triptycyne to anthracene but the yield was low.[17] A one-pot synthesis of pentiptycene was conducted by the reaction of 1,2,4,5-tetrabromobenzene with BuLi in the presence of anthracene.[16] However, there were some technical difficulties so that the yield based on 1,2,4,5-tetrabromobenzne was only 26% and the remaining anthracene must be separated from the product. Therefore, the present procedure is considered to be valuable in the synthesis of tri-/pentiptycene derivatives. Furthermore, the cycloaddition of 2,3-pentycyne **17** with

phenyl azide was conducted by reaction of iodonium triflate **16** with Bu$_4$NF in the presence of phenyl azide, affording cycloadduct **20** in 78% yield.

In conclusion, we have demonstrated that tris(trimethylsilyl)phenyliodonium triflate **3** can be isolated and applied as a synthon of 1,4-benzdiyne (**1**). In the present paper, we improved the synthesis of iodonium trifalte **3** using a PhI(OAc)$_2$/BF$_3$·OEt$_2$ reagent. Reaction of **3** with Bu$_4$NF efficiently generated 4,5-bis(trimethylsilyl)benzyne (**4**) to afford bis(trimethylsilyl)-naphthalenes **5** and **6** and bis(trimethylsilyl)triptycene **7** in high yields. These products were converted into the corresponding silyl-substituted iodonium triflates **9**, **15**, and **17**, and applied to subsequent cycloaddition reactions. The consecutive cycloaddition reactions constructed several polycyclic aromatic compounds which are formally considered as double cycloaddition products of 1,4-benzdiyne. The present results indicate that the consecutive benzdiyne strategy using tris(trimethylsilyl)phenyliodonium triflate **3** is practical and useful for the synthesis of such polycyclic aromatic compounds.

Experimental Section

Preparation of (Phenyl)[2,4,5-tris(trimethylsilyl)-phenyl]iodonium Triflate (3)

To a mixture of 1,2,4,5-tetrakis(trimethylsilyl)benzene (**2**) (5 mmol) and PhI(OAc)$_2$ (6 mmol) in CH$_2$Cl$_2$ (30 mL) was

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added $BF_3 \cdot OEt_2$ (12 mmol). The mixture was stirred at room temperature for 30 min. The reaction mixture was poured into an aqueous solution of NaOTf (25 mmol) and stirred vigorously. The product was extracted with CH_2Cl_2 (20 mL×3). The combined organic extract was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting solid was filtered and washed with hexane to give a white solid; yield: 2.28 g (86%); mp 115–117°C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.31$ (s, 9H), 0.39 (s, 9H), 0.43 (s, 9H), 7.48 (t, $J = 7.6$ Hz, 2H), 7.60 (t, $J = 7.6$ Hz, 1H), 7.82 (d, $J = 7.6$ Hz, 2H), 7.92 (s, 1H), 7.98 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -0.4$, 1.0, 1.2, 113.0, 125.1, 132.1, 132.2, 133.4, 142.6, 144.4, 151.1, 154.3 (one carbon overlapped); HR-MS (FAB): $m/z = 497.1020$, calcd. for $C_{21}H_{34}ISi$ ([M−OTf]$^+$): 497.1013.

Trapping Reaction of 4,5-Bis(trimethylsilyl)benzyne (4) with Dienophiles

To a solution of iodonium triflate **3** (2 mmol) and a dienophile (10 mmol) in CH_2Cl_2 (10 mL) was slowly added a THF solution of TBAF (2 mmol). The mixture was stirred at room temperature for 20 min. The reaction mixture was poured into water and extracted with CH_2Cl_2 (10 mL×3). The combined organic extract was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The product was separated by column chromatography on silica gel (hexane/AcOEt).

1,2,3,4-Tetraphenyl-6,7-bis(trimethylsilyl)naphthalene (5): The product was obtained as a white solid; yield: 1.118 g (97%); mp 310–312°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.22$ (s, 18H), 6.84–6.85 (m, 10H), 7.21–7.25 (m, 10H), 7.97 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 1.6$, 125.3, 126.4, 126.6, 127.4, 130.6, 131.2, 131.3, 134.6, 138.3, 139.1, 139.4, 140.5, 142.0. HR-MS (FAB): $m/z = 576.2666$, calcd. for $C_{40}H_{40}Si_2$: 576.2669.

6,7-Bis(trimethylsilyl)-1,4-dihydro-1,4-epoxynaphthalene (6): The reaction of **3** (1 mmol) with furan (5 mmol) in CH_2Cl_2 (5 mL) in the presence of a THF solution of TBAF (1 mmol) gave the product **6** as a white solid; yield: 0.288 g (100%); mp 97–99°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.35$ (s, 18H), 5.71 (s, 2H), 7.02 (s, 2H), 7.59 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 2.1$, 82.3, 126.5, 142.8, 143.4, 148.3; HR-MS (EI): $m/z = 288.1363$, calcd. for $C_{16}H_{24}OSi_2$: 288.1366.

9,10-Dihydro-2,3-bis(trimethylsilyl)-9,10[1′,2′]-benzenoanthracene (7): The reaction of **3** (1 mmol) with anthracene (5 mmol) in CH_2Cl_2 (30 mL) in the presence of a THF solution of TBAF (1 mmol) gave the product **7** as a white solid; yield; 0.342 g (86%); mp 187–189°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.31$ (s, 18H), 5.40 (s, 2H), 6.97–6.99 (m, 4H), 7.37 (m, 4H), 7.67 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 2.1$, 54.0, 123.6, 125.1, 130.2, 143.0, 144.4, 145.2; HR-MS (FAB): $m/z = 398.1884$, calcd. for $C_{26}H_{30}Si_2$: 398.1886.

General Procedure for Preparation of Functionalized Aryne Precursors 8, 14, 16

To a mixture of a bis(trimethylsilyl)arene (0.2 mmol) and $PhI(OAc)_2$ (0.24 mmol) in CH_2Cl_2 (2 mL) was added $BF_3 \cdot OEt_2$ (0.24 mmol). The mixture was stirred at room temperature for 30 min. The reaction mixture was poured

into an aqueous solution of NaOTf (2 mmol) and stirred vigorously. The product was extracted with CH_2Cl_2 (2 mL × 3). The combined organic extract was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting solid was filtered and washed with hexane to give a crystalline product.

(Phenyl)(3-trimethylsilyl-5,6,7,8-tetraphenyl-2-naphthalenyl)iodonium triflate (8): The product was obtained as a white solid; yield: 0.158 g (92%); mp 239–254°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.28$ (s, 9H), 6.78–7.28 (m, 20H), 7.41 (t, $J = 8.0$ Hz, 2H), 7.58 (t, $J = 8.0$ Hz, 1H), 7.70 (d, $J = 8.0$ Hz, 2H), 7.95 (s, 1H), 8.22 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -0.1$, 114.4, 118.2, 126.0, 126.8, 127.2, 127.5, 127.8, 128.1, 130.7, 130.8, 130.9, 132.2, 132.37, 132.44, 133.4, 134.0, 137.1, 137.6, 138.0, 138.6, 138.9, 139.1, 139.2, 140.0, 142.0, 142.7 (four carbons overlapped); HR-MS (FAB): $m/z = 707.1633$, calcd. for $C_{43}H_{36}ISi$ ([M−OTf]$^+$): 707.1631.

(Phenyl)(3-trimethylsilyl-2-naphthalenyl)iodonium triflate (14):[14] The reaction of **13** (1 mmol) and $PhI(OAc)_2$ (1.2 mmol) in CH_2Cl_2 (6 mL) in the presence of $BF_3 \cdot OEt_2$ (2.4 mmol) gave **14** as a white solid; yield: 0.530 g (96%); mp 187–188°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.45$ (s, 9H), 7.40 (t, $J = 8.0$ Hz, 2H), 7.51 (t, $J = 8.0$ Hz, 1H), 7.66–7.70 (m, 2H), 7.84 (d, $J = 8.0$ Hz, 2H), 7.91 (d, $J = 8.8$ Hz, 1H), 7.97 (d, $J = 9.2$ Hz, 1H), 8.12 (s, 1H), 8.84 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 0.2$, 114.3, 117.1, 128.21, 128.23, 128.7, 129.8, 131.9, 132.3, 133.0, 133.8, 135.1, 139.5, 140.6, 140.8.

(9,10-Dihydro-3-trimethylsilyl-9,10[1′,2′]-benzenoanthracen-2-yl)(phenyl)iodonium triflate (16): The product was obtained as a white solid; yield: 0.788 g (85%); mp 241–244°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.37$ (s, 9H), 5.49 (s, 1H), 5.58 (s, 1H), 7.02–7.05 (m, 4H), 7.36–7.50 (m, 7H), 7.65 (s, 1H), 7.83 (d, $J = 7.6$ Hz, 2H), 8.12 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 0.2$, 52.9, 53.8, 114.0, 116.3, 124.0, 124.4, 125.8, 125.9, 132.2, 132.4, 132.8, 133.6, 143.5, 143.6, 144.4, 150.3, 151.7 (one carbon overlapped); HR-MS (FAB): $m/z = 529.0850$, calcd. for $C_{29}H_{26}ISi$ ([M−OTf]$^+$): 529.0849.

Trapping Reaction of an Aryne with a Dienophile

To a solution of an aryne precursor **8**, **14**, or **16** (0.2 mmol) and a dienophile (1 mmol) in CH_2Cl_2 (2 mL) was slow added a THF solution of TBAF (0.2 mmol) and the mixture was stirred at room temperature for 20 min. The reaction mixture was poured into water and the product was extracted with CH_2Cl_2 (2 mL×3). The combined organic extract was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under a reduced pressure. The crude product was purified by column chromatography on silica gel with hexane/EtOAc as eluent.

1,4-Dihydro-5,6,7,8-tetraphenyl-1,4-epoxyanthracene (10): The product was obtained as a white solid; yield: 0.099 g (99%); mp 274–276°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.66$ (s, 2H), 6.80–6.82 (m, 8H), 6.87 (s, 2H), 7.16–7.23 (m, 12H), 7.39 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 81.8$, 117.6, 125.3, 126.4, 126.5, 126.6, 127.5, 127.6, 130.2, 131.13, 131.18, 131.21, 131.24, 138.8, 139.2, 139.7, 140.4, 141.6, 144.2 (nineteen peaks were observed by inhibiting free rotation of phenyl groups due to steric repulsion); HR-MS (FAB): $m/z = 499.2060$, calcd. for $C_{38}H_{27}O$ ([M+H]$^+$): 499.2062.

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1,2,3,4,5,6,7,8-Octaphenylanthracene (11):[5] The product was obtained as a yellow solid; yield: 0.140 g (89%). This compound did not dissolve in any organic solvents; mp >400°C. HR-MS (FAB): $m/z = 786.3290$, calcd. for $C_{62}H_{42}$: 786.3287.

5,6,7,8-Tetraphenyl-1H-naphtho[2,3-d]triazole (12): The product was obtained as a yellow solid; yield: 0.070 g (64%); mp 232–233°C; ^1H NMR (400 MHz, CDCl$_3$): $\delta =$ 6.85–7.24 (m, 10H), 7.25–7.31 (m, 10H), 7.41 (t, $J = 8.0$ Hz, 1H), 7.52 (t, $J = 8.0$ Hz, 2H), 7.74 (d, $J = 8.0$ Hz, 2H), 8.01 (s, 1H), 8.53 (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta =$ 106.0, 118.4, 121.7, 125.5, 125.6, 126.6, 126.8, 126.9, 127.77, 127.81, 127.9, 129.7, 130.2, 130.4, 131.0, 131.14, 131.16, 131.2, 133.0, 137.4, 138.0, 138.3, 139.1, 139.3, 139.4, 140.11, 140.12, 140.2, 145.7 (one carbon overlapped); HR-MS (FAB): $m/z =$ 550.2282, calcd. for $C_{40}H_{28}N_3$ ([M+H]$^+$): 550.2283.

1,4-Dhydro-1,4-epoxyanthracene (15):[14] The product was obtained as a white solid; yield: 0.037 g (96%); mp 163–165°C; ^1H NMR (400 MHz, CDCl$_3$): $\delta = 5.80$ (s, 2H), 6.97 (s, 2H), 7.41–7.45 (m, 2H), 7.59 (s, 2H), 7.69–7.73 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 81.8$, 118.6, 126.1, 128.1, 131.9, 141.6, 144.1.

1,4,6,11-Tetrahydro-6,11[1′,2′]-benzeno-1,4-epoxynaphtha-cene (18):[16] The product was obtained as a white solid; yield: 0.060 g (94%); mp 211–213°C; ^1H NMR (400 MHz, CDCl$_3$): $\delta = 5.36$ (s, 2H), 5.61 (s, 2H), 6.94 (s, 2H), 6.95–7.01 (m, 4H), 7.34 (s, 2H), 7.36–7.39 (m, 4H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 54.3$, 82.3, 116.9, 123.40, 123.44, 125.01, 125.04, 143.1, 143.2, 145.4, 145.5, 146.7.

5,7,12,14-Tetrahydro-5,14[1′,2′]:7,12[1″,2″]-dibenzenopen-tacene (19):[3c] The product was obtained as a white solid; yield: 0.063 g (73%); mp 408–410°C; ^1H NMR (400 MHz, CDCl$_3$): $\delta = 5.30$ (s, 4H), 6.89–6.92 (m, 8H), 7.26–7.30 (m, 8H), 7.43 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 53.9$, 119.7, 123.4, 125.0, 142.4, 145.4.

5,10[1′,2′]-Benzeno-1-phenyl-1H-anthra[2,3-d]triazole (20): The product was obtained as a yellow solid; yield: 0.058 g (78%); mp 197–199°C; ^1H NMR (400 MHz, CDCl$_3$): $\delta = 5.50$ (s, 1H), 5.59 (s, 1H), 7.03–7.06 (m, 4H), 7.39–7.7 (m, 10H) 8.03 (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta =$ 53.7, 54.2, 105.4, 114.2, 123.0, 123.7, 123.8, 125.6, 125.8, 128.6, 129.7, 130.9, 136.9, 142.1, 143.9, 144.5, 144.6, 146.0; HR-MS (FAB): $m/z = 372.1051$, calcd. for $C_{26}H_{18}N_3$ ([M+H]$^+$): 372.1051.

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Improved and Practical Synthesis of [2,4,5-Tris(trimethylsilyl)-phenyl](phenyl)iodonium Triflate and Utilization as a 1,4-Benzdiyne Synthon

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