A One-pot, Three-Aryne Cascade Strategy for Naphthalene Formation from 1,3-Diynes and 1,2-Benzdiyne Equivalents

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Supporting Information Placeholder

ABSTRACT: Here we disclose a cascade strategy for naphthyne formation that capitalizes on the traditional benzyne generation (i.e., from an *ortho*-silyl aryl triflate) and the thermal hexadehydro-Diels–Alder (HDDA) reaction. In this transformation, three distinct aryne species work in tandem, two of which can be formally considered as a 1,2-benzidyne, and each undergoes a different type of trapping event. Many examples were explored by varying the naphthyne capture chemistry as well as the 1,2-benzdiyne equivalent. This strategy enables rapid construction of various naphthalene products and has potential for the synthesis of extended polycyclic arenes.

The development of mild and versatile methods for generation of arynes has enabled myriad synthetic applications of these long-standing reactive intermediates.[1] The fluoride ion induced aryne formation from *ortho*-silyl aryl triflates (the Kobayashi protocol; cf. **1** to **2**, Figure 1a) is perhaps the most enabling of the classical methods that has fueled the advances in modern aryne chemistry.[2] The thermal generation of benzynes from, minimally, a triyne substrate like **3** represents a complementary strategy (Figure 1a).[3] This so-called hexadehydro-Diels–Alder (HDDA) reaction also has considerable generality.[4] In the work reported here, we have developed a strategy that capitalizes on both the Kobayashi protocol and the HDDA reaction to conveniently generate naphthynes, arynes of greater structural complexity, from relatively simple building blocks.

Two key design principles drove our study. First, Li and coworkers have pioneered the use of 1,2-benzdiyne equivalent **4** (Figure 1b).[5] Upon treatment with a silaphilic nucleophile/base (e.g., fluoride or carbonate ion), benzyne **5** can be generated in which substituent X can both direct nucleophilic addition to the *meta*-position and serve as a leaving group to regenerate a second benzyne. This net S_N2' reaction to form **6** (an example in which a thioamide has served as the initial benzyne trapping nucleophile) is followed by intramolecular capture by the amide nitrogen atom to produce the benzothiazole **7**. Second, arynes have been shown to function as diynophiles in HDDA reactions. For example, benzyne **8** can engage with a 1,3-diyne unit to form naphthyne **9** (Figure 1c).[6] This process can be extended to form higher homologs, including a tetracyne, **10**.[7] Therefore, we hypothesized that nucleophile **11**, bearing a pendant 1,3-diyne moiety, attacks the 1,2-benzdiyne equivalent **5** to give the benzyne **12** (Figure 1d). Subsequent HDDA reaction produces naphthyne **13**, which is then trapped to form product **14**. Notably, this cascade involves three distinct reactive benzyne species, each of which needs to undergo a different type of transformation [cf. maroon (1,2-benzdiyne #1) vs. blue (1,2-benzdiyne #2) vs. magenta (HDDA naphthyne), throughout].

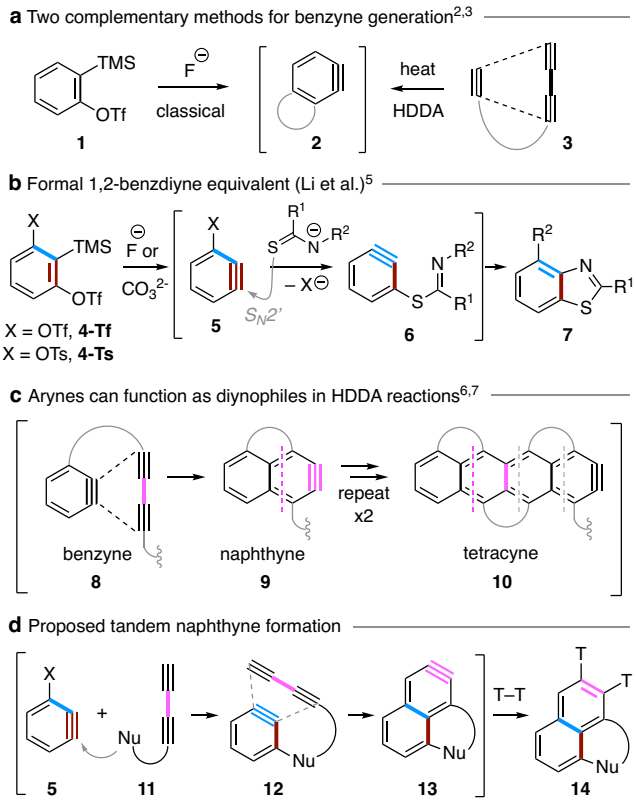
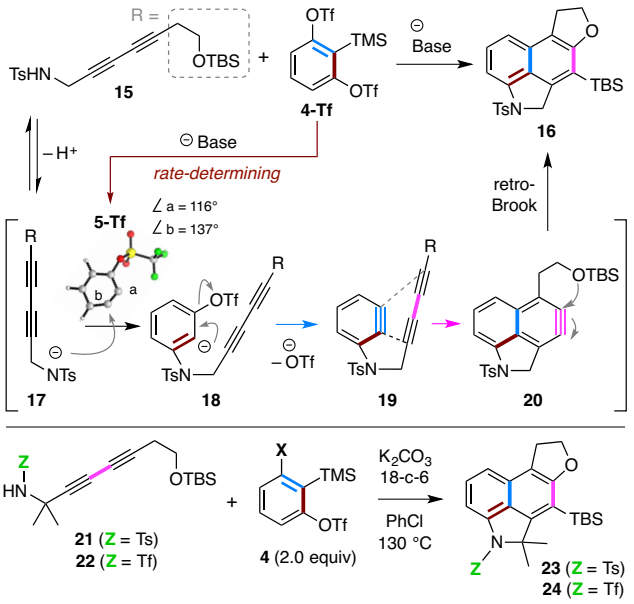


Figure 1. Marrying of classical and HDDA benzyne generation to produce naphthyne **13**. Ts = *p*-toluenesulfonyl. Tf = trifluoromethylsulfonyl. TMS = trimethylsilyl



entry	Z	X	time	conv. of 21/22	conv. of 4	isolated yield of 23/24
1	Ts	OTf	2 h	32%	100%	27% (84% brsm)
2	Ts	OTs	5 h	100%	100%	45%
3	**Tf**	OTf	2 h	100%	100%	**72%**
4	**Tf**	OTs	5 h	100%	100%	**76%**

Figure 2. Proposed mechanism and optimization of the sulfonamide substrate.

We opted to test the feasibility of this idea using **4-Tf** and diyne **15** bearing a sulfonamide functional group, a nucleophile demonstrated in Li's work to be an effective participant in the capture of the initial benzyne generated from this 1,2-benzdiyne equivalent (Figure 2).[5] Formation of benzyne **5-Tf** was expected to be the rate-limiting step due to the relatively short lifetime of arynes. The DFT optimized geometry for **5-Tf** [SMD(chlorobenzene)/B3LYP/6-31G**] indicated that the triflate group renders appreciable distortion (116° vs. 137°) of the two sp-hybridized benzyne carbons. As a result, the sulfonamide anion **17** should selectively add to carbon b to form the transient aryl anion **18**.[8] Elimination of the triflate anion would then produce a second benzyne **19** as long as protonation of the anionic carbon in **18** was sufficiently slow. In **19**, the 1,3-diyne moiety is separated by a three-atom tether from the proximal benzyne sp-carbon, so the intramolecular HDDA reaction was expected to proceed readily to give the naphthyne **20**.[3,9] The pendent silyl ether group should then capture the naphthyne faster than another external reagent (e.g., **17**) to arrive at the product naphthalene **16** via nucleophilic addition and retro-Brook rearrangement. To tolerate the silyl ether group, we screened several weak, non-fluoride bases. Unfortunately, diyne **15** was susceptible to decomposition under mildly basic conditions, perhaps initiated by deprotonation of a propargylic proton.[10] Therefore, we examined diyne **21,** having gem-dimethyl substitution to replace the labile propargylic C–H bonds. To our delight, desired naphthalene **23** was formed in 27% yield using readily available potassium carbonate/18-crown-6 ether as the base (entry 1, tabular insert in Figure 2). When **4-Ts** instead of **4-Tf** was used as the 1,2-benzdiyne equivalent, the formation of benzyne **5-Ts** was noticeably slower, and **23** was isolated in 45% yield (entry 2). Attempts to further optimize the yield of **23** (altering base, solvent, and/or temperature; Table S1) were not successful. However, we noticed that in the entry 1 result, we recovered 68% of diyne **21** (84% brsm), suggesting that the cascade following the initial trapping by **21** (cf. **18** to **16** via **19** and **20**) was efficient. We suspected that the *para*-toluenesulfonamide (TsNH) used in entries 1 and 2 was not a sufficiently efficient trap for benzyne **5**. Therefore, we explored modification of the pKa of the sulfonamide by changing to the trifluoromethylsulfonyl (Tf) group[11] to increase the concentration of the triflate stabilized analog of anion **17**. This should accelerate the rate of the initial benzyne trapping event. Indeed, under the same reaction conditions, triflamide **22** efficiently reacted with either **4-Tf** or **4-Ts** to afford naphthalene **24** in 72% or 76% yield, respectively (entries 3 and 4).

Encouraged by this result, we proceeded by examining this transformation with a series of diynes **25a-i**, each of which bears a different trapping functionality potentially capable of capturing naphthyne **26** intramolecularly (Figure 3). First, we tested several heteroatom-based nucleophiles, **25a-d**. Internal silyl ether traps with tethers different that in **21** and **22** gave good yields (**27a** and **27b**). Moreover, a free alcohol was accommodated, leading to **27c**. This reaction afforded a significant major by-product, namely **27c'** (the trimethylsilyl analog of **24**). We presume that the hydroxy group in diyne **25c** was being silylated either by the carbonate-TMS ester or, perhaps more likely, directly by the 1,2-benzdiyne equivalent **4**. Thus, the free alcohol **25c** or its corresponding TMS silyl ether gave **27c** and **27c'**, respectively. Quenching the reaction mixture directly with TBAF provided **27c** in 55% yield. The intramolecular sulfonamide trapping leading to **27d** also provided some mechanistic inferences. Consistent with our initial findings (Figure 2), the TfNHR nitrogen in **25d** is a faster trap than the TsNHR, which further supports the idea that the active nucleophile is indeed the deprotonated sulfonamide anion (cf. **17-Tf** vs. **17-Ts**).

Several additional classes of intramolecular trapping reactions were explored. An appropriately placed, pendant phenyl substituent efficiently gave the intramolecular Diels–Alder (IMDA) trapped adduct **27e** in 75% yield.[12] Formation of the aromatic ene reaction product **27f**[13] was accompanied, unexpectedly, by the formation of the 2:1 adduct **27f'**, which most likely arose from Diels–Alder reaction of benzyne **5-Tf** with the electron rich arene ring in **27f**. Once again, the regioselectivity of that second event can be explained by the distortion model (cf. **5-Tf**, Figure 2)—the more electron rich carbon (*para* to the oxygen) preferentially engaged the

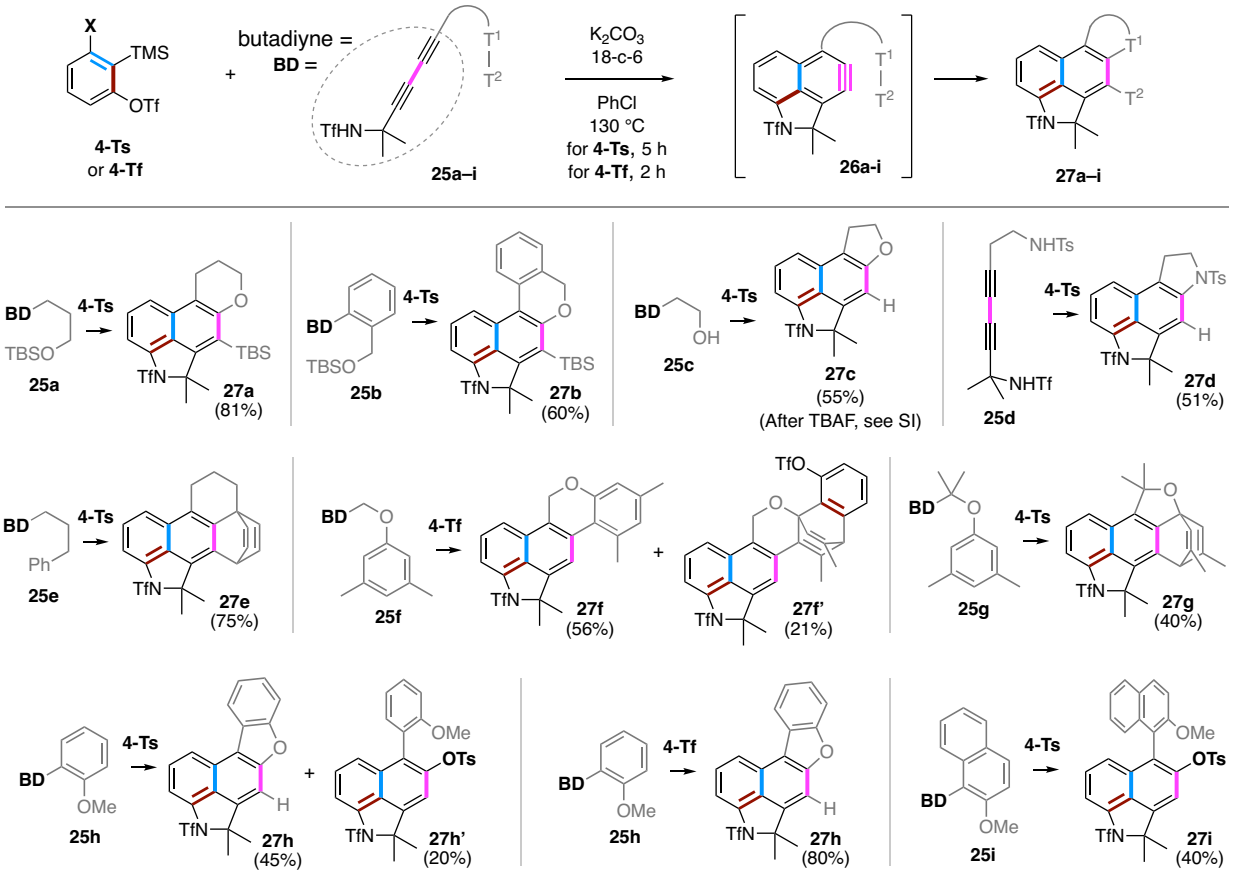


Figure 3. Examples of naphthyne formation followed by intramolecular trapping by appended T^1–T^2 groups; together, these demonstrate that a variety of electron rich species can capture the naphthyne intermediates.

more electrophilic benzyne carbon (*meta* to the triflate group) in an asynchronous, concerted cycloaddition. The *gem*-dimethylated analog **25g** led to a different outcome; the aromatic ene pathway was completely suppressed and the IMDA product **27g** was produced. These differences could be nicely accounted for by DFT calculations of the competing transition state geometries (see Figure S1). A dibenzofuran motif can be established by use of an *ortho*-methoxyphenyl substituent as a trapping group (cf. **27h**). When **4-Ts** was used as the bisbenzyne equivalent, the formation of **27h** was accompanied by the byproduct **27h'**, as a single constitutional isomer (see later discussion, accompanying Figure 4). This reveals a non-innocent role of the tosylate anion leaving group from the S_N2' process with **5-Ts**. When **4-Tf** was used as the precursor instead, **27h** was isolated in 80% yield due to the weaker nucleophilicity of triflate anion. Finally, if the rate of intramolecular *ortho*-methoxy trapping was further decreased, as exemplified by the case of **25i**, the steric repulsion caused by the additional ring fusion thwarted formation of the dibenzofuran product.; only the tosylate-trapped product **27i** was observed. This suggests that the transition state for methoxy attack at the proximal benzyne carbon requires a close to planar geometry to achieve effective orbital overlap. As a result, the naphthyne was primarily trapped by the external tosylate anion to provide binaphthol derivative **27i** as a single constitutional isomer in 40% yield plus a small amount of the isomeric products of DA reaction with a chlorobenzene solvent molecule (see Supporting Information).

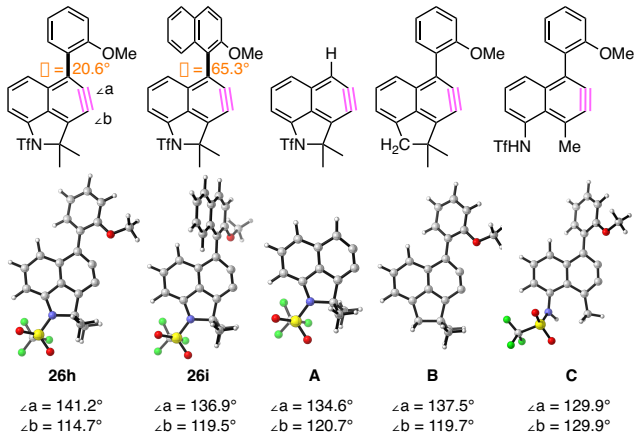


Figure 4. Calculated distortion angles of naphthynes **26h, 26i**, and **A-C**.

The unanticipated products **27h'** and **27i**, were formed with high regioselectivity during trapping by the external nucleophile. This was unexpected, because there are no obvious structural features (substituents, steric effect) that

might account for this selectivity. Nonetheless, we computed the [SMD(chlorobenzene)/B3LYP/6-31G**] geometries of naphthynes **26h** and **26i**, which lead to **27h'** and **27i**, respectively (Figure 4). The distortion of these two naphthynes is quite large and in a direction consistent with the observed nucleophilic attack by the tosylate anion at carbon a, the atom with the larger internal bond angle. To try to understand the contributing factor(s) for this distortion, we also computed the structures of several analogs. Removal of the aryl substituent (cf. **A**) has only a minor impact on the distortion ($\angle_a - \angle_b$). When the sulfonamide nitrogen was replaced by a methylene group (cf. **B**), again only a minor effect was seen. However, when the strain of the five membered ring that bridges the peri-positions on the naphthyne was removed (cf. **C**), the distortion essentially disappeared. Thus, it is the five-membered ring that is responsible for strongly perturbing the geometry of the naphthyne, thereby inducing attack by TsO^- at the more electrophilic carbon in **26h** and **26i**.

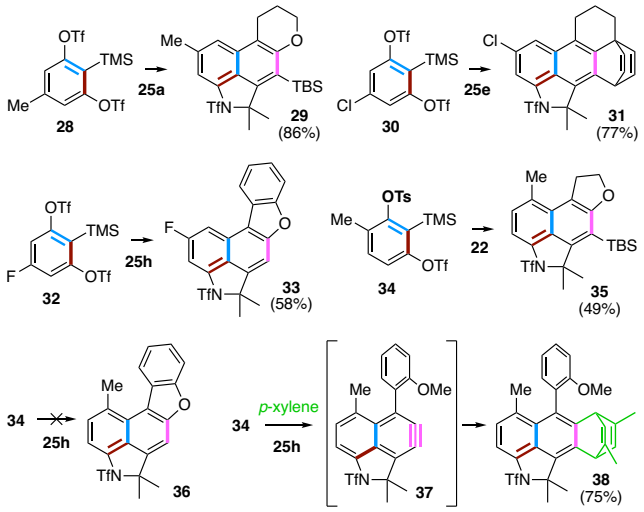


Figure 5. Reactions of other 1,2-benzdiyne equivalents. Chlorobenzene was the solvent for the first five examples; *p*-xylene was used for the formation of **38**.

To demonstrate a different element of modularity in the overall strategy, we prepared four different 1,2-benzdiyne equivalents (**28**, **30**, **32**, and **34**; Figure 5). Symmetrical 1,2-benzdiyne equivalents **28**, **30**, and **32**, when reacted with one of the diynylsulfonamides **25**, gave the corresponding naphthalene products **29**, **31**, and **33**, respectively, in good yields. The reaction of unsymmetrical precursor **34** and **22** afforded **35** as the only constitutional isomer, indicating faster initial benzyne generation through preferential loss of the triflate vs. tosylate.[5e] When **34** was paired with the diyne **25h**, no dibenzofuran product was seen, again likely reflecting the inability of the *o*-methoxyphenyl group to adopt a sufficiently planar geometry for good orbital overlap, now because of the presence of the methyl substituent at the naphthyne peri-position. On the other hand, a significant amount of chlorobenzene (solvent) trapped products (multiple isomers detected by NMR and MS analyses) of the naphthyne was observed. To reduce the number of possible regio- and diastereo- isomers, this reaction was carried out in *p*-xylene, which underwent a clean DA reaction with the naphthyne **37** to produce **38** in 75% yield. This result, along with the observed formation of **27i**, opens the possibility of using an external reagent for capturing naphthynes **26**. It is surprising that we did not detect products arising from addition of the diynylsulfonamide **25h** to the intermediate naphthyne **37.** Indeed, this type of 2:1 adduct was not observed for any of the reactions in our studies.

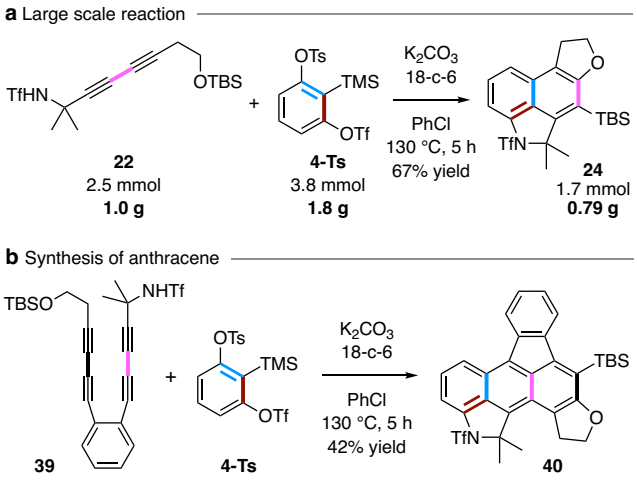


Figure 6. (**a**) Large scale reaction, and (**b**) synthesis of larger polycyclic arenes.

We show a practical aspect of this transformation in the gram-scale reaction depicted in Figure 6a. There, the loading of **4-Ts** was lowered to 1.5 equivalent, and slow addition of **4-Ts** was not crucial. The yield of **24** (67%) was comparable to that of the smaller scale outcome (76%, Figure 2). If an additional 1,3-diyne unit is present, as in, for example, sulfonamide **39**, an anthracyne intermediate can be formed by a second HDDA reaction of the naphthyne, which was then trapped by the tethered silyl ether to give the anthracene derivative **40** (Figure 6b).[7] This result demonstrates the potential of this tandem strategy for rapid construction of polycyclic arenes.

In summary, we have developed a one-pot cascade strategy for naphthyne formation using a 1,3-diyne containing a nucleophilic nitrogen atom and a 1,2-benzdiyne equivalent. This transformation requires only mildly basic conditions and allows rapid construction of various naphthalene products via three reactive aryne species (Figures 3 and 5). DFT calculations revealed that a five-membered ring that bridges the peri-positions on the naphthyne can induce significant distortion of the two sp-hybridized carbons in 2,3-naphthynes (Figure 4). Moreover, we have demonstrated the potential application of this process in the synthesis of polycyclic arenes (Figure 6b). Future studies will focus on the use of different nucleophiles and of different linkers[14] that connect the 1,3-diyne to the

benzyne for the final, HDDA step, as well as applications to the synthesis of extended π-systems.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures for all new reactions; spectroscopic characterization data for all new compounds; results of DFT calculations (3D structures, geometries, and energies); copies of NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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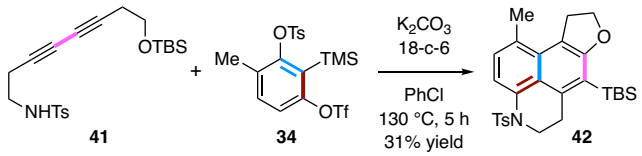
(14) One such linker is the sulfonamidoethyl moiety that connects the nucleophile and 1,3-diyne in **41**. This substrate, which lacks acidified propargylic protons, was able to capture the benzyne derived from **34** to produce the adduct **42**. This reaction is also notable because it represents a rare example of the HDDA reaction in which the diynophile and the 1,3-diyne are separated by a four-atom linker (cf. ref 9c).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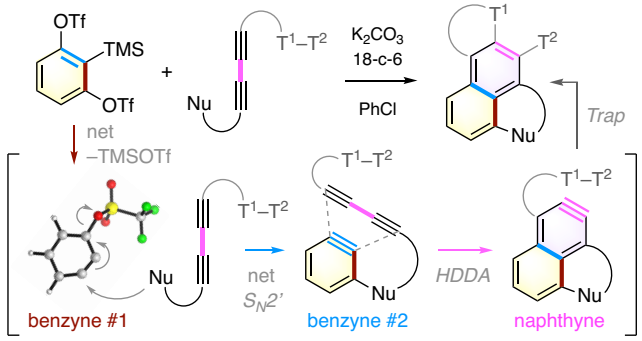
TOC Graphic: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