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Construction of Condensed Polycyclic Aromatic Frameworks through Intramolecular Cycloaddition Reactions Involving Arynes Bearing an Internal Alkyne Moiety

Suguru Yoshida,* Keita Shimizu, Keisuke Uchida, Yuki Hazama, Kazunobu Igawa, Katsuhiko Tomooka, and Takamitsu Hosoya*

Abstract: Facile synthetic methods for condensed polycyclic aromatic compounds via aryne intermediates are reported. The generation of arynes bearing a (3-arylpropargyl)oxy group from the corresponding *o*-iodoaryl triflate-type precursors efficiently afforded arene-fused oxaacenaphthene derivatives, which were formed through intramolecular [2+4] cycloaddition. Extending the method to the generation of arynes bearing a 1,3-diyne moiety led to a continuous generation of naphthalene intermediate through the hexadehydro Diels–Alder reaction involving the triple bond of aryne. This novel type of aryne-relay chemistry enabled the synthesis of a unique aminoarylated oxaacenaphthene derivative and highly ring-fused anthracene derivatives.

Condensed polycyclic aromatic compounds, such as phenanthrene and anthracene derivatives, are important scaffold structures that have wide applications in broad fields including materials science and natural product chemistry.^[1] Among the reported methods for constructing these complex skeletons,^[2] cycloaddition reactions of aryne intermediates are particularly useful.^[3–6] Nevertheless, condensed polycyclic aromatic compounds that are synthesizable by conventional methods are still limited. Herein, we report synthetic methods for constructing condensed polycyclic aromatic compounds that include strained 2*H*-naphtho[1,8-*bc*]furan (oxaacenaphthene) derivatives, which were formed through reactions involving arynes.

We previously reported a modular synthetic method for preparation of bis- and tris-1,2,3-triazoles via 3-(propargyloxy)benzyne (**1**) generated from *o*-iodoaryl triflate-type aryne precursor **1** by using (trimethylsilyl)methylmagnesium chloride as an activator (Figure 1A).^[5a] The cycloaddition of aryne **1** with azides and the subsequent copper-catalyzed cycloaddition of the remaining terminal alkyne moiety with another azides afforded diverse bis-1,2,3-triazoles. This

approach enabled the facile construction of a large chemical library that consists of a diverse range of compounds. To further diversify the synthesizable compounds based on this modular synthetic approach, we prepared *o*-iodoaryl triflate **3a** bearing (3-phenylpropargyl)oxy group and attempted the cycloaddition of aryne generated from **3a** with benzyl azide (**4**) (Figure 1B). As a result, treating the mixture of **3a** and **4** in THF with a silylmethyl Grignard reagent at -78 °C afforded the desired cycloadduct **5**, from which a variety of benzotriazoles could be prepared by the transformation of the internal alkyne moiety. From a careful examination of the byproducts, we identified a small amount of phenanthrene derivative, 5*H*-phenanthro[1,10-*bc*]furan (**6a**).^[7] The formation of tetracyclic compound **6a** indicates a possibility that two intramolecular C–C bond formations between the aryne carbons and the phenylethyne group has occurred.^[8] We were intrigued by this unexpected result and opted to delve into this transformation that would enable straightforward construction of condensed polycyclic aromatic frameworks.

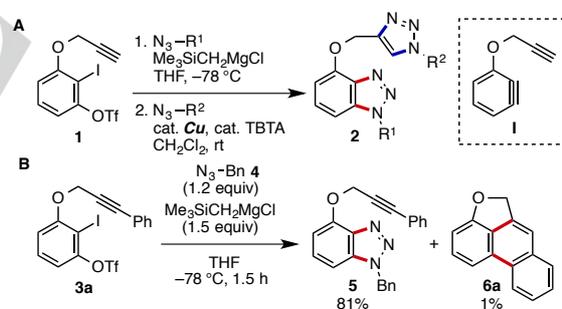


Figure 1. Cycloaddition of arynes bearing an alkyne moiety with azides. (A) Bis-1,2,3-triazole synthesis via 3-(propargyloxy)benzyne (**1**). (B) Reaction of aryne, generated from *o*-iodoaryl triflate **3a** by using a silylmethyl Grignard reagent, in the presence of azide **4**.

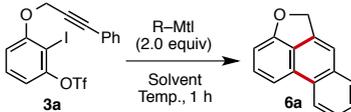
To achieve an efficient transformation from **3a** to **6a**, we screened the conditions by performing the reaction in the absence of an aryneophile (Table 1). Although only a low yield of the desired **6a** was obtained when the reaction was conducted at -78 °C (entry 1), remarkable improvements were observed when the reaction was conducted at higher temperatures (entries 2 and 3). The best result was obtained when the reaction was conducted at room temperature with diethyl ether as the solvent (entry 4). Using more nucleophilic activators instead of (trimethylsilyl)methylmagnesium chloride^[5] decreased the yield of **6a** (entries 5–7).

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Experimental procedures and characterization for new compounds including copies of NMR spectra (PDF). X-ray crystallographic data for **6c** (CCDC 1566709) (CIF).

Table 1: Optimization of the Reaction Conditions.


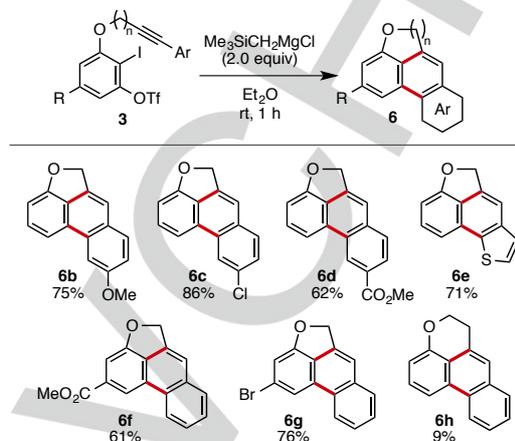
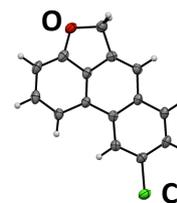
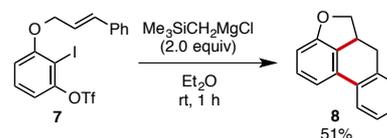
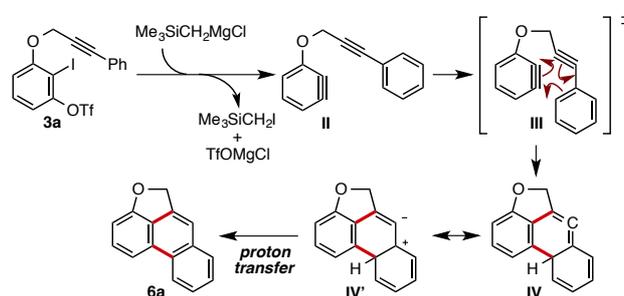
Entry	R-Mtl	Solvent	Temp.	Yield [%] ^[a]
1	Me ₃ SiCH ₂ MgCl	THF	-78 °C	20
2	Me ₃ SiCH ₂ MgCl	THF	-40 °C	51
3	Me ₃ SiCH ₂ MgCl	THF	rt	59
4	Me ₃ SiCH ₂ MgCl	Et ₂ O	rt	83 (82) ^[b]
5	<i>n</i> -BuLi	Et ₂ O	rt	35
6	<i>i</i> -PrMgCl·LiCl	Et ₂ O	rt	43
7	PhMgBr	Et ₂ O	rt	26

[a] Yields based on ¹H NMR analysis, unless otherwise noted. [b] Isolated yield in the parentheses.

Using the optimized conditions, various tetracyclic oxaacenaphthene derivatives **6b–g** were prepared from the corresponding *o*-iodoaryl triflates bearing an (3-arylpropargyl)oxy group, which were easily prepared from the corresponding 3-hydroxy-2-iodoaryl triflates and propargylalcohols by the Mitsunobu reaction^[9,10] (Figure 2). Substrates with 4-methoxy-, 4-chloro-, and 4-(methoxycarbonyl)phenyl groups on the alkyne moiety were transformed to condensed phenanthrene derivatives **6b–d**, leaving these groups untouched. The structure of chloro-substituted product **6c** was confirmed from the X-ray crystallographic analysis (Figure 3). Similarly, thiophene-fused oxaacenaphthene **6e** was obtained from 2-iodo-3-((3-(3-thienyl)propargyl)oxy)phenyl triflate. Substrates with a methoxycarbonyl and bromo groups on the benzene ring at the aryne-generating side also participated in this reaction to afford **6f** and **6g**, respectively. In contrast, the reaction of a substrate with one carbon-homologated tether afforded only a low yield of the desired phenanthrene **6h** fused with a 6-membered ring, suggesting the importance of the relative configuration of aryne-ethynyl moiety to the triple bond of aryne. In addition, the reaction of *o*-iodoaryl triflate **7**, wherein the alkyne moiety of **3a** was changed to *trans*-olefin, proceeded to afford tetracyclic 9,10-dihydrophenanthrene derivative **8** (Scheme 1).

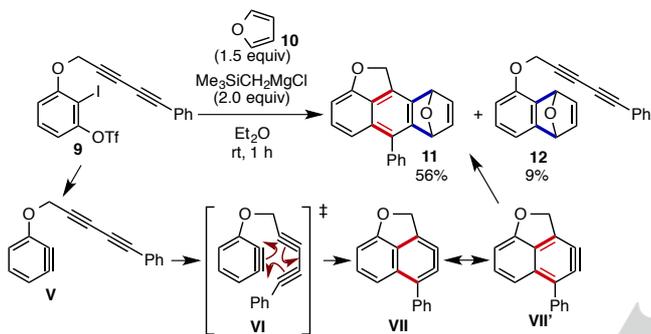
A plausible reaction mechanism is shown in Scheme 2. The formation of benzotriazole **5** from the reaction in the presence of azide **4** clearly indicates the generation of aryne **II** from *o*-iodoaryl triflate **3a**. Subsequent intramolecular [2+4] cycloaddition between the triple bond of aryne and the phenylethynyl group via distorted transition state **III** would provide allenic intermediate **IV**, which is a resonance form of zwitterionic intermediate **IV'**. Theoretical calculations (B3LYP/6-311+G(d,p)) indicate that the strained allenic intermediate **IV** is 31.9 kcal/mol more stable than the aryne intermediate **II**, suggesting that allene **IV** is justifiable as an intermediate

structure.^[10] Natural bond orbital analysis^[10] supports the contribution of the polarized resonance structure **IV'**, from which aromatization that involves proton transfer to the anionic carbon occurs to afford the phenanthrene derivative **6a**.

**Figure 2.** Synthesis of various tetracyclic aromatics.**Figure 3.** X-ray crystal structure of **6c**.**Scheme 1.** Reaction from 3-(Cinnamloxy)benzynes Precursor **7**.**Scheme 2.** Plausible Reaction Mechanism.

On the basis of the plausible reaction mechanism depicted in Scheme 2 and the reported hexadehydro Diels–Alder reaction,^[6]

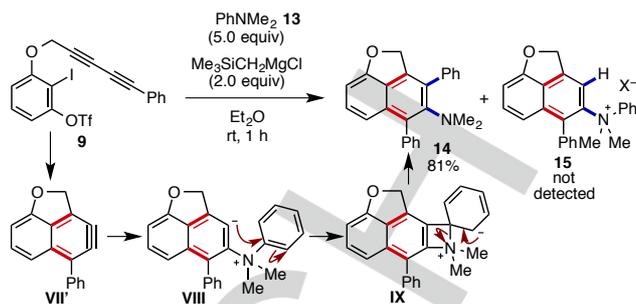
we conceived the idea of generating a strained naphthalene **VII'** through a similar type of intramolecular [2+4] cycloaddition reaction between the triple bond of aryne and the 1,3-diene moiety of **V** (Scheme 3). To test our hypothesis, we prepared *o*-iodoaryl triflate **9** bearing a 1,3-diyne moiety and treated it with a silylmethyl Grignard reagent in the presence of furan (**10**) at room temperature. As expected, anthracene derivative **11** was obtained as a major product along with a small amount of cycloadduct **12**, which was formed by the direct reaction between the initial aryne intermediate **V** and furan (**10**). This result demonstrates that naphthalene **VII'** was successfully generated as the second aryne species and trapped by furan (**10**) to afford an anthracene derivative **11**, suggesting that the intramolecular [2+4] cycloaddition proceeded faster than the intermolecular cycloaddition.^[11]



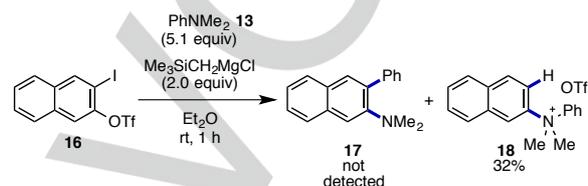
Scheme 3. Generation of Strained Naphthalene **VII'**.

After conducting an extensive survey on the reactivity of naphthalene **VII'**, we found that it reacted with *N,N*-dimethylaniline (**13**) in a unique fashion (Scheme 4). Treating aryne precursor **9** with a silylmethyl Grignard reagent in the presence of **13** at room temperature afforded an unexpected two *ortho*-phenyl groups-substituted (dimethylamino)naphthalene derivative **14** in high yield without the formation of anticipated ammonium salt **15**. The product **14** could be obtained through the addition of **13** to naphthalene **VII'** to form a zwitterionic intermediate **VIII**, followed by migratory *C*-phenylation via Meisenheimer complex **IX**. Because the reaction of simple 2,3-naphthalene with **13** afforded only ammonium salt **18**,^[12] and the formation of phenyl-migrated product **17** was not observed (Scheme 5), the formation of **14** through the migratory *C*-phenylation of **VIII**^[13] is likely to be facilitated by the highly strained five-membered ring-fused structure. Although the details on this unique aminoarylation of aryne is yet to be investigated, this approach would allow for the facile synthesis of highly functionalized sterically hindered aminonaphthalenes, which are difficult to prepare by conventional method.

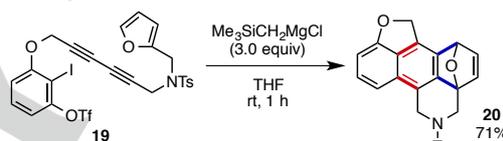
The generation of a naphthalene intermediate from a 1,3-diyne-armed aryne precursor bearing an additional arynophilic moiety resulted in the formation of a highly condensed polycyclic aromatic compound. For example, the sequential generation of two types of arynes from precursor **19** with an intramolecular furan moiety afforded a highly ring-fused hexacyclic anthracene derivative **20** in high yield (Scheme 6).



Scheme 4. Aminoarylation of Strained Naphthalene **VII'**.



Scheme 5. Reaction with Unstrained Naphthalene.



Scheme 6. Synthesis of Hexacyclic Anthracene Derivative **20**.

In summary, we have developed facile methods for constructing condensed polycyclic aromatic frameworks through the generation of arynes from *o*-iodoaryl triflates bearing an arylethynyl group or a 1,3-diyne moiety. In the case of arynes bearing a 1,3-diyne moiety, a naphthalene intermediate was generated through a novel type of aryne-relay chemistry, which is the first example of hexadehydro Diels–Alder reaction involving the triple bond of aryne. Since various 3-(propargyloxy)aryne precursors are easily synthesizable, a diverse range of highly condensed aromatic compounds could be prepared from simple modules using this method. Further studies, including the theoretical analysis of the intramolecular cycloaddition between the triple bond of aryne and an arylethynyl group or a 1,3-diyne moiety, are currently underway.

Acknowledgements

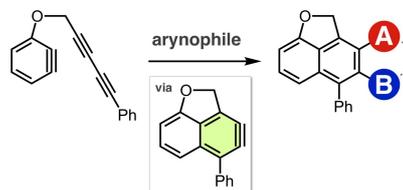
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Keywords: aryne • hexadehydro Diels–Alder reaction • naphthalene • oxaacenaphthene • aminoarylation

- [1] a) *Marine Biotechnology, Vol. 1, Pharmaceutical and Bioactive Natural Products* (D. H. Attaway, O. R. Zaborsky, Eds.) Springer: New York, **1993**; b) A. P. Krapcho, M. J. Maresch, M. P. Hacker, L. Hazelhurst, E. Menta, A. Oliva, S. Spinelli, G. Beggiolin, F. C. Giuliani, G. Pezzoni, S. Tognella, *Curr. Med. Chem.* **1995**, *2*, 803; c) *Bioactive Compounds in Foods* (J. Gilbert, H. Z. Şenyuva, Eds.) Wiley-Blackwell: Chichester, **2009**.
- [2] a) A. J. Floyd, S. F. Dyke, S. E. Ward, *Chem. Rev.* **1976**, *76*, 509; b) X. Feng, W. Pisula, K. Müllen, *Pure Appl. Chem.* **2009**, *81*, 2203; c) Y. Shen, C.-F. Chen, *Chem. Rev.* **2012**, *112*, 1463.
- [3] For some recent reviews on arynes, see: a) P. M. Tadross, B. M. Stoltz, *Chem. Rev.* **2012**, *112*, 3550; b) D. Pérez, D. Peña, E. Guitián, *Eur. J. Org. Chem.* **2013**, 5981; c) A. E. Goetz, T. K. Shah, N. K. Garg, *Chem. Commun.* **2015**, *51*, 34; d) H. Yoshida, Aryne-Based Multicomponent Reactions. In *Multicomponent Reactions in Organic Synthesis* (J. Zhu, Q. Wang, M. Wang, Eds.) Wiley-VCH: Weinheim, **2015**, pp. 39–71; e) S. Yoshida, T. Hosoya, *Chem. Lett.* **2015**, *44*, 1450; f) R. Karmakar, D. Lee, *Chem. Soc. Rev.* **2016**, *45*, 4459; g) S. S. Bhojgude, A. Bhunia, A. T. Biju, *Acc. Chem. Res.* **2016**, *49*, 1658; h) J.-A. García-López, M. F. Greaney, *Chem. Soc. Rev.* **2016**, *45*, 6766; i) J. Shi, Y. Li, Y. Li, *Chem. Soc. Rev.* **2017**, *46*, 1707.
- [4] For selected recent reports on arynes, see: a) J. Shi, D. Qiu, J. Wang, H. Xu, Y. Li, *J. Am. Chem. Soc.* **2015**, *137*, 5670; b) S. Yoshida, Y. Hazama, Y. Sumida, T. Yano, T. Hosoya, *Molecules* **2015**, *20*, 10131; c) S. Yoshida, K. Shimomori, T. Nonaka, T. Hosoya, *Chem. Lett.* **2015**, *44*, 1324; d) S. Yoshida, T. Yano, Y. Misawa, Y. Sugimura, K. Igawa, S. Shimizu, K. Tomooka, T. Hosoya, *J. Am. Chem. Soc.* **2015**, *137*, 14071; e) E. Demory, K. Devaraj, A. Orthaber, P. J. Gates, L. T. Pilarski, *Angew. Chem. Int. Ed.* **2015**, *54*, 11765; *Angew. Chem.* **2015**, *127*, 11931; f) C. M. Holden, S. M. A. Soheli, M. F. Greaney, *Angew. Chem. Int. Ed.* **2016**, *55*, 2450; *Angew. Chem.* **2016**, *128*, 2496; g) S. K. Sundalam, A. Nilova, T. L. Seidl, D. R. Stuart, *Angew. Chem. Int. Ed.* **2016**, *55*, 8431; *Angew. Chem.* **2016**, *128*, 8571; h) T. Ikawa, S. Masuda, A. Takagi, S. Akai, *Chem. Sci.* **2016**, *7*, 5206; i) N. F. F. Nathel, L. A. Morrill, H. Mayr, N. K. Garg, *J. Am. Chem. Soc.* **2016**, *138*, 10402; j) M. Pérez-Gómez, J.-A. García-López, *Angew. Chem.; Int. Ed.* **2016**, *55*, 14389; *Angew. Chem.* **2016**, *128*, 14601; k) Y. Li, C. Mück-Lichtenfeld, A. Studer, *Angew. Chem. Int. Ed.* **2016**, *55*, 14435; *Angew. Chem.* **2016**, *128*, 14649; l) Y. Sumida, T. Sumida, D. Hashizume, T. Hosoya, *Org. Lett.* **2016**, *18*, 5600; m) S. Umezumi, G. dos Passos Gomes, T. Yoshinaga, M. Sakae, K. Matsumoto, T. Iwata, I. Alabugin, M. Shindo, *Angew. Chem. Int. Ed.* **2017**, *56*, 1298; *Angew. Chem.* **2017**, *129*, 1318; n) J. Shi, H. Xu, D. Qiu, J. He, Y. Li, *J. Am. Chem. Soc.* **2017**, *139*, 623; o) S. Yoshida, H. Nakajima, K. Uchida, T. Yano, M. Kondo, T. Matsushita, T. Hosoya, *Chem. Lett.* **2017**, *46*, 77; p) K. Uchida, S. Yoshida, T. Hosoya, *Org. Lett.* **2017**, *19*, 1184; q) T. Kitamura, K. Gondo, J. Oyamada, *J. Am. Chem. Soc.* **2017**, *139*, 8416; r) J. B. Lin, T. K. Shah, A. E. Goetz, N. K. Garg, K. N. Houk, *J. Am. Chem. Soc.* **2017**, *139*, 10447.
- [5] For our reports on synthetic chemistry using a silylmethyl Grignard reagent, see: a) S. Yoshida, T. Nonaka, T. Morita, T. Hosoya, *Org. Biomol. Chem.* **2014**, *12*, 7489; b) S. Yoshida, K. Uchida, K. Igawa, K. Tomooka, T. Hosoya, *Chem. Commun.* **2014**, *50*, 15059; c) S. Yoshida, K. Uchida, T. Hosoya, *Chem. Lett.* **2015**, *44*, 691; d) S. Yoshida, F. Karaki, K. Uchida, T. Hosoya, *Chem. Commun.* **2015**, *51*, 8745; e) S. Yoshida, T. Morita, T. Hosoya, *Chem. Lett.* **2016**, *45*, 726; f) K. Uchida, S. Yoshida, T. Hosoya, *Synthesis* **2016**, *48*, 4099; g) S. Yoshida, T. Yano, Y. Nishiyama, Y. Misawa, M. Kondo, T. Matsushita, K. Igawa, K. Tomooka, T. Hosoya, *Chem. Commun.* **2016**, *52*, 11199; h) S. Yoshida, Y. Nakamura, K. Uchida, Y. Hazama, T. Hosoya, *Org. Lett.* **2016**, *18*, 6212; i) T. Morita, S. Yoshida, M. Kondo, T. Matsushita, T. Hosoya, *Chem. Lett.* **2017**, *46*, 81; j) T. Morita, Y. Nishiyama, S. Yoshida, T. Hosoya, *Chem. Lett.* **2017**, *46*, 118; k) S. Yoshida, A. Nagai, K. Uchida, T. Hosoya, *Chem. Lett.* **2017**, *46*, 733; l) Y. Nakamura, S. Yoshida, T. Hosoya, *Chem. Lett.* **2017**, *46*, 858.
- [6] For selected reports on hexadehydro Diels–Alder reaction, see: a) T. R. Hoye, B. Baire, D. Niu, P. H. Willoughby, B. P. Woods, *Nature* **2012**, *490*, 208; b) S. Y. Yun, K.-P. Wang, N.-K. Lee, P. Mamidipalli, D. Lee, *J. Am. Chem. Soc.* **2013**, *135*, 4668; c) D. Niu, P. H. Willoughby, B. P. Woods, B. Baire, T. R. Hoye, *Nature* **2013**, *501*, 531; d) D. Niu, T. R. Hoye, *Nat. Chem.* **2014**, *6*, 34; e) P. H. Willoughby, D. Niu, T. Wang, M. K. Haj, C. J. Cramer, T. R. Hoye, *J. Am. Chem. Soc.* **2014**, *136*, 13657; f) J. Chen, V. Palani, T. R. Hoye, *J. Am. Chem. Soc.* **2016**, *138*, 4318; g) T. Wang, R. R. Naredla, S. K. Thompson, T. R. Hoye, *Nature* **2016**, *532*, 484; h) T. Wang, D. Niu, T. R. Hoye, *J. Am. Chem. Soc.* **2016**, *138*, 7832; i) F. Xu, K. W. Hershey, R. J. Holmes, T. R. Hoye, *J. Am. Chem. Soc.* **2016**, *138*, 12739; j) T. Wang, T. R. Hoye, *J. Am. Chem. Soc.* **2016**, *138*, 13870; k) R. Karmakar, D. Lee, *Org. Lett.* **2016**, *18*, 6105; l) Y. Hu, Y. Hu, Q. Hu, J. Ma, S. Lv, B. Liu, S. Wang, *Chem. Eur. J.* **2017**, *23*, 4065; m) S. P. Ross, T. R. Hoye, *Nat. Chem.* **2017**, *9*, 523; n) F. Xu, X. Xiao, T. R. Hoye, *J. Am. Chem. Soc.* **2017**, *139*, 8400.
- [7] For synthetic methods for the construction of 2H-naphtho[1,8-bc]furan structures related to **6a**, see: a) J. Jauch, *Angew. Chem. Int. Ed.* **2008**, *47*, 34; *Angew. Chem.* **2008**, *120*, 34; b) K. C. Nicolaou, Y. H. Lim, J. Becker, *Angew. Chem. Int. Ed.* **2009**, *48*, 3444; *Angew. Chem.* **2009**, *121*, 3496; c) R. Kumar, Y. Hoshimoto, E. Tamai, M. Ohashi, S. Ogoshi, *Nat. Commun.* **2017**, *8*, 32.
- [8] For the pioneering work on the transformations through intramolecular [2+4] cycloadditions between arynes and enynes including arenynes, see: a) A. Cobas, E. Guitián, L. Castedo, *J. Org. Chem.* **1997**, *62*, 4896; b) M. E. Hayes, H. Shinokubo, R. L. Danheiser, *Org. Lett.* **2005**, *7*, 3917. For the intramolecular [2+4] cycloadditions between arynes and styrenes, see: c) S. S. Bhojgude, A. Bhunia, R. G. Gonnade, A. T. Biju, *Org. Lett.* **2014**, *16*, 676.
- [9] a) O. Mitsunobu, M. Yamada, T. Mukaiyama, *Bull. Chem. Soc. Jpn.* **1967**, *40*, 935; b) O. Mitsunobu, M. Yamada, *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2380. For selected reviews, see: c) O. Mitsunobu, *Synthesis* **1981**, *1*; d) D. L. Hughes, *Org. React.* **1992**, *42*, 335; e) K. C. K. Swamy, N. N. B. Kumar, E. Balaraman, K. V. P. P. Kumar, *Chem. Rev.* **2009**, *109*, 2551.
- [10] See Supporting Information for details.
- [11] Treatment of a mixture of *o*-iodoaryl triflate **9** with furan (**10**, 5.0 equiv) with Me₃SiCH₂MgCl (2.0 equiv) at room temperature afforded only 22% yield of **11** along with **12** (23%).
- [12] M. Hirsch, S. Dhara, C. E. Diesendruck, *Org. Lett.* **2016**, *18*, 980.
- [13] For the pioneering study on the reaction between benzyne and *N,N*-dialkylanilines, see: A. R. Lepley, A. G. Giumanini, A. B. Giumanini, W. A. Khan, *J. Org. Chem.* **1966**, *31*, 2051.

COMMUNICATION



Facile synthetic methods for condensed polycyclic aromatic compounds via aryne intermediates bearing an alkyne moiety are reported. In particular, the generation of arynes bearing a 1,3-diyne moiety led to a continuous generation of naphthalene intermediate through the hexadehydro Diels–Alder reaction involving the triple bond of aryne.

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