

## Synthetic Methods

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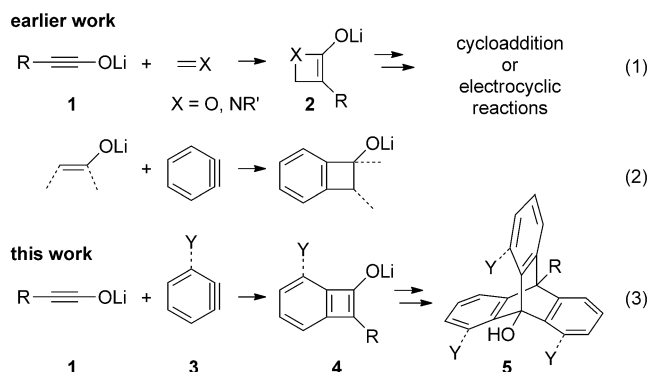
## Regioselective One-Pot Synthesis of Triptycenes via Triple-Cycloadditions of Arynes to Ynolates

Satoshi Umezu, Gabriel dos Passos Gomes, Tatsuro Yoshinaga, Mikei Sakae, Kenji Matsumoto, Takayuki Iwata, Igor Alabugin, and Mitsuru Shindo\*

**Abstract:** We developed the novel one-pot synthetic method of substituted triptycenes by the reaction of ynolates and arynes. This four-step process involves three cycloadditions and electrocyclic ring opening of the strained Dewar anthracene. Each of the three related but structurally distinct classes of nucleophiles (ynolate, enolate, and anthracenolate) reacts with *o*-benzyne in the same predictable manner controlled by chelation and negative hyperconjugation. The resulting functionalized  $C_3$ -symmetrical triptycenes hold promise in the design of functional materials.

Ynolates **1** are compact energy-rich nucleophiles with great potential in synthetic organic chemistry.<sup>[1]</sup> As dianion equivalents, ynolates are useful as nucleophilic initiators of one-pot sequences leading to rapid preparation of useful products.<sup>[2]</sup> Formal cycloaddition reactions of ynolates with polar  $C=X$  ( $X = O, N$ ) double bonds have been reported by us and others to yield unsaturated four-membered heterocycles **2** such as  $\beta$ -lactone or  $\beta$ -lactam enolates leading to various reactions and products (Scheme 1, Equation (1)).<sup>[2b,3]</sup> In comparison with cycloadditions to the polar bonds, examples of synthetic reactions with nonpolar multiple  $C-C$  bonds remain, to the best of our knowledge, relatively scarce.<sup>[4]</sup> Based on the high electrophilicity of the non-polar  $C-C$  triple bond of arynes,<sup>[5]</sup> these strained alkynes can be expected to readily participate in cycloadditions with nucleophilic ynolates. Herein, we report a one-pot sequence of three efficient and regioselective cycloadditions, initiated by the reaction between ynolates and arynes (Scheme 1, Equation (3)). This sequence provides substituted triptycenes **5** in a highly regioselective head-to-head manner.

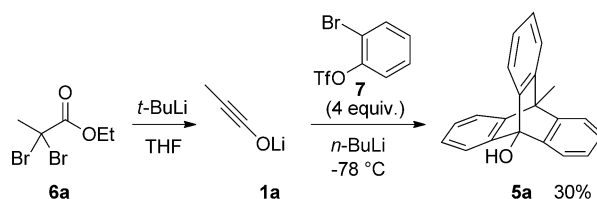
In analogy with the known reactions of enolates and arynes (Scheme 1, Equation (2)),<sup>[6]</sup> one could expect that reaction of ynolates **1** and arynes **3** will lead to the formation of benzocyclobutenone enolates **4**. Although these synthetic intermediates<sup>[7]</sup> would be destabilized by antiaromaticity, we



**Scheme 1.** Cycloadditions of ynolates to polar and non-polar multiple bonds.

will show that their electronic properties lead to new rich reactivity features.

We adopted 2-bromophenol triflate **7** as a precursor of benzyne.<sup>[8]</sup> Treatment of the precursor **7**, added to an in situ prepared ynolate solution in THF (Scheme 2),<sup>[9]</sup> with *n*-BuLi at  $-78^\circ\text{C}$ , led to the generation of the anticipated *o*-benzyne. As expected, the latter was trapped by the ynolate. Surprisingly, however, the reaction involved three moles of *o*-benzyne, leading to 9-hydroxy-10-methyltriptycene (**5a**) as the major product in 30% yield.



**Scheme 2.** Reaction of ynolate with benzyne to provide 9-hydroxy-10-methyltriptycene **5a**.

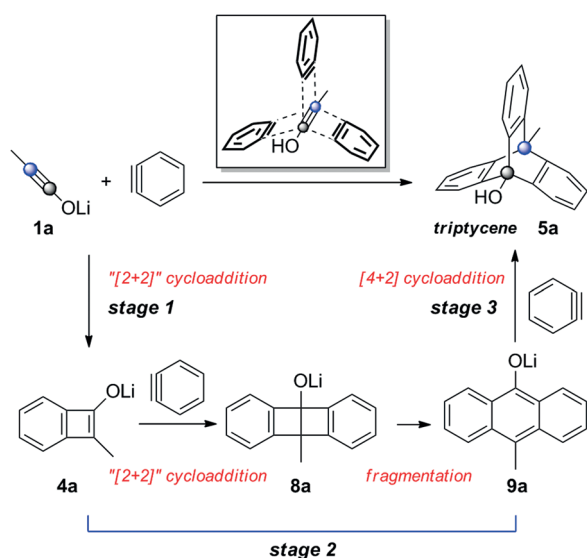
The suggested mechanism for the formation of this unexpected product is shown in Scheme 3. Ynolate **1a** adds to benzyne to give a benzocyclobutenone enolate **4a**, which is sufficiently nucleophilic to add to another benzyne to form the Dewar anthracene **8a**.<sup>[10]</sup> Relief of antiaromaticity is likely to contribute to the efficiency of this process. The fused [2.2.0] core of the product is highly strained and can undergo spontaneous ring-opening with the formation of electron-rich anthracene alkoxide **9a**.<sup>[11]</sup> This penultimate intermediate engages the third benzyne molecule in the final [4+2] cycloaddition step that furnishes the isolated triptycene

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**Scheme 3.** Triple cycloaddition of benzyne to ynoate leads to triptycene.

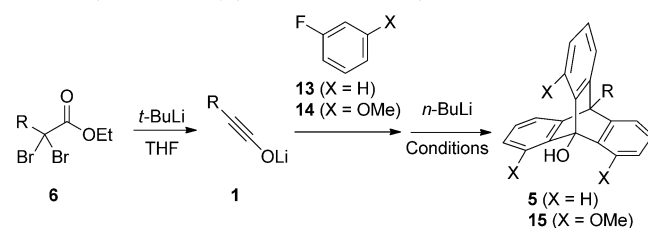
product **5a**. It is noteworthy that the overall cascade disassembles the triple bond into two one-carbon units that “glue” the three aromatic rings together. This is a conceptually unique application of alkynes in synthesis.

Triptycenes, which have three benzene rings fixed by a rigid barrelene skeleton, are useful structural units for the preparation of functional materials and supramolecular systems.<sup>[12]</sup> Generally, triptycenes are synthesized with the Diels–Alder reaction of benzyne with anthracene,<sup>[13]</sup> but this method often suffers from poor efficiency. Furthermore, access to substituted functionalized triptycenes is limited because of the relative scarcity and occasional instability of substituted anthracene precursors. These limitations prompted us to investigate the new reaction as a practical synthetic approach to the construction of triptycenes.

The low efficiency in the above reaction was due to generation of numerous side products. Several of the side products, detected by GC-MS analysis, provide mechanistic information; 10-methylanthracen-9-ol originates from the premature exit from the proposed reaction cascade,<sup>[14]</sup> whereas formation of butylbenzene and 10-methylphenanthren-9-ol is due to trapping of *o*-benzyne with species other than the ynoate (see Figure SI-1 in the Supporting Information). Benzyne reactions are usually conducted under the excess of the trapping reagent in order to suppress the side reactions. In our case, at least three equivalents of benzyne to ynoate are required to yield the triptycene; however, effective trapping of benzyne needs excess of ynoate. To solve this discrepancy, benzyne should be gradually generated in small amounts in the presence of ynoate.

By using the *ortho* lithiation as an aryne formation method, the yield was improved to 42% when butyllithium was added to fluorobenzene **13** at room temperature in one hour. Using this method, we synthesized triptycenes from several ynoates. Notably, even the sterically hindered ynoates provided produced the target polycyclic products (Table 1).

**Table 1:** Synthesis of triptycenes from several ynoates.<sup>[a]</sup>



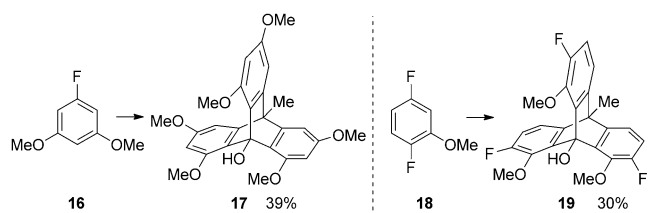
Entry	Ynoate	R	13/14	Conditions	Product	Yield [%]
1	<b>1a</b>	Me	<b>13</b>	<b>A</b>	<b>5a</b>	42
2	<b>1b</b>	<i>i</i> -Pr	<b>13</b>	<b>A</b>	<b>5b</b>	35
3	<b>1c</b>	<i>n</i> -Bu	<b>13</b>	<b>A</b>	<b>5c</b>	52
4	<b>1d</b>	<i>t</i> -Bu	<b>13</b>	<b>A</b>	<b>5d</b>	39
5	<b>1e</b>	Ph	<b>13</b>	<b>A</b>	<b>5e</b>	27
6	<b>1a</b>	Me	<b>14</b>	<b>B</b>	<b>15a</b>	69
7	<b>1b</b>	<i>i</i> -Pr	<b>14</b>	<b>A</b>	<b>15b</b>	39
8	<b>1c</b>	<i>n</i> -Bu	<b>14</b>	<b>B</b>	<b>15c</b>	48
9	<b>1f</b>	hexyl	<b>14</b>	<b>B</b>	<b>15f</b>	37
10	<b>1e</b>	Ph	<b>14</b>	<b>A</b>	<b>15e</b>	37

[a] Reaction conditions: **6** (0.5 mmol), *t*-BuLi (2.0 mmol), THF,  $-78^{\circ}\text{C}$  to  $0^{\circ}\text{C}$ ; then condition A: **13** or **14** (3.0 mmol), *n*-BuLi (2.5 mmol, addition for 1 h), RT, condition B: **14** (2.0 mmol), *n*-BuLi (2.0 mmol, addition for 5 min),  $-20^{\circ}\text{C}$ .

We then investigated reactivity of substituted benzynes. 3-Methoxybenzyne, derived from 3-fluoroanisole **14** and butyllithium, reacts with ynoate **1** at  $-20^{\circ}\text{C}$  to afford triptycene **15** in good yield. It is noteworthy that the major product had all oxygen functionalities, i.e., the three methoxy groups and one hydroxy group, at the same side of the triptycene.<sup>[15]</sup> This high regioselectivity of reaction is consistent with previous reports of selective nucleophilic attack at the C1 position of similar alkynes, rationalized via charge distribution, or distortion models.<sup>[5c,16]</sup> We will discuss the question of regioselectivity in the computational part of this paper.

Furthermore, disubstituted benzynes also react with ynoate **1a** regioselectively to provide the corresponding multisubstituted triptycenes (**17** and **19**) (Scheme 4). Reactions of aryl fluorides (**16** and **18**) with additional substituents gave products consistent with deprotonation of C–H bond activated by two adjacent  $\sigma$ -acceptors.

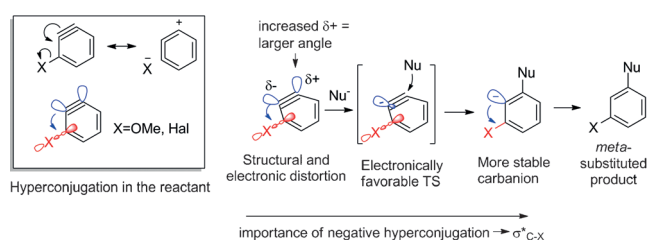
Calculations were used to gain insight into the origin of high regioselectivity observed in the three reactions of *o*-benzynes. We focused on the reactivity of the OMe-substituted benzyne. It is known that nucleophiles attack these species at the *meta*-position relative to the OMe group. This selectivity has been attributed to ground state polarization and distortion of the LUMO. Despite the previous success of



**Scheme 4.** Synthesis of triptycenes using several benzyne precursors.

such analysis, the ground state geometries have predictive power only when they point out to an emerging electronic effect that will be amplified in the TS. In a more precise analysis of benzyne reactivity, the regioselectivity is controlled by progressive evolution of negative hyperconjugation from a moderate  $\pi_{\text{in}} \rightarrow \sigma_{\text{C-O}}^*$  interaction in the reactant to a strong  $n_{\text{C}} \rightarrow \sigma_{\text{C-O}}^*$  interaction in the anionic product (see Figure SI-2). Trends in the ground state geometry correctly predict the observed reaction product only because the ground state structural distortion and the dominant force of TS stereoelectronic stabilization coincide.<sup>[17]</sup>

The observed structural distortion in the MeO-benzyne is consistent with the importance of hyperconjugative  $\pi_{\text{in}} \rightarrow \sigma_{\text{C-O}}^*$  interaction. In particular, the greater bending at the benzyne carbon adjacent to the OMe group reflects increased electron density at this carbon where it interacts with the vicinal  $\sigma_{\text{C-O}}^*$  acceptor (Scheme 5).



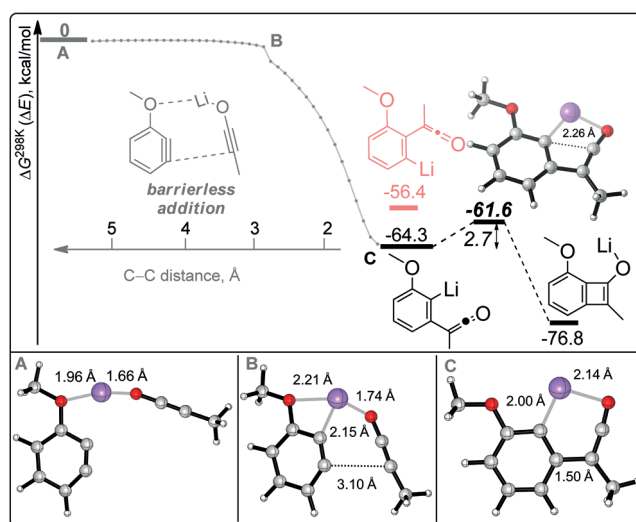
**Scheme 5.** The ground state structural distortion and dominant force of TS stereoelectronic stabilization are the same: ground state geometry predicts correct reaction product.

Interestingly, no TS could be located for the reaction of *o*-benzyne and lithium ynolate. Instead, the chelated O...LiO complex is transformed into the product without any transient penalty. This calculation paints a very different picture from the reaction of benzyne with less reactive nucleophiles. Addition of ynolate to benzyne is highly exergonic ( $> 60 \text{ kcal mol}^{-1}$ ) and, according to the Hammond–Leffler postulate, the TS is expected to be very early. Furthermore, large reaction exergonicity can lead to the disappearance of reaction barriers.<sup>[18]</sup>

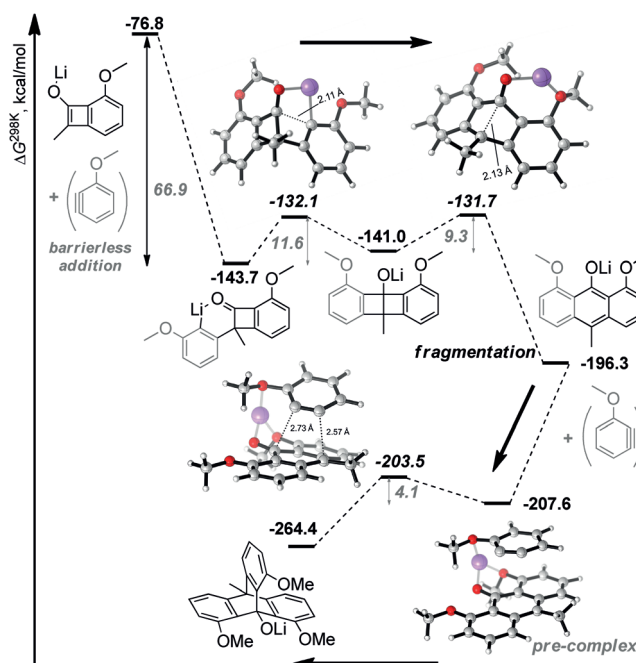
The key process at the barrierless stage is the change from O–Li to C–Li coordination that precedes the C–C bond formation (Figure 1B). Both O...Li interactions are maintained throughout this stage, and O...Li...O chelation is likely to play a substantial role in directing the initial stage of this process.<sup>[19]</sup> The overall “cycloaddition” is distinctly non-concerted: the barrierless C–C bond formation leads to an acyclic ketene intermediate that undergoes fast 4-*exo* closure in a separate step. Formation of the non-observed isomer is less favorable due to the lack of chelation and lower hyperconjugative stabilization.

Although formation of four-membered intermediate from the two high-energy alkyne reactants is exergonic, it gives a product that is destabilized by antiaromaticity as confirmed by a positive NICS(1)<sup>[20]</sup> value and the ACID<sup>[21]</sup> plots (SI part).

In many ways, the reactions of ynolate and enolate with *o*-benzyne are similar (Figure 2). In particular, the initial C–C



**Figure 1.** Top: Barrierless addition of ynolate to MeO-benzyne yields the more stable isomer. Bottom: Evolution of chelated geometries during addition of ynolate to MeO-benzyne.



**Figure 2.** Computed energetics of the enolate (top) and the Diels–Alder (bottom) stages of the cascade.

bond formation from the enolate is also barrierless (see the SI) and leads to the formation of an aryl anion that undergoes subsequent 4-*exo* cyclization. Again, the overall cycloaddition is non-concerted. Due to the relief of antiaromaticity, the first C–C bond formation with the *o*-benzyne is  $2.6 \text{ kcal mol}^{-1}$  more exergonic for the fused enolate in comparison to the ynolate. Because of accumulation of strain, the 4-*exo* cyclization barrier is considerably higher than the one in the ynolate addition ( $\approx 12$  vs.  $3 \text{ kcal mol}^{-1}$ ). Furthermore, the cyclization is mildly endergonic and, hence, should be reversible.

The fragmentation of the Dewar intermediate provides thermodynamic driving force for the overall enolate reaction

with *o*-benzyne. The relatively low barrier is a consequence of two factors: gain of aromaticity (the thermodynamic effect on kinetics)<sup>[18]</sup> and the effect of anionic oxygen on pericyclic reactions.<sup>[11]</sup>

The final Diels–Alder reaction is concerted (Figure 2, bottom) but highly asynchronous: “phenolate” attack at C3 of OMe-benzyne precedes formation of the second C–C bond (at C2). The calculated reaction barrier is remarkably low. Significant negative charge accumulation at C2 in the TS (NBO charge at C2 is  $-0.17e$  vs.  $+0.12e$  on C3) benefits strongly from the  $\pi \rightarrow \sigma_{C-O}^*$  hyperconjugative assistance.

Despite progressing through a panoply of unstable intermediates, the overall cascade is  $>260$  kcal mol<sup>-1</sup> exergonic. This large driving force highlights the power of alkynes as the high-energy entry point into unusual chemical cascades.<sup>[22]</sup>

In conclusion, we have developed a novel one-pot approach to substituted triptycenes by the reaction of ynolates and arynes. This process contains successive four reactions. Each of the three nucleophiles reacts with *o*-benzyne in the same predictable manner controlled by chelation and negative hyperconjugation. In every case, either the key intermediate or the transition state leading to the observed product display significant negative charge accumulation next to a  $\sigma$ -acceptor C–O bond. The overall cascade disassembles the triple bond in two one-carbon units that regioselectively connect three *o*-benzyne.<sup>[23]</sup> This is a conceptually unique application of alkynes in synthesis and the first example of the formal insertion of three arynes into a triple bond.<sup>[24]</sup> The resulting functionalized C<sub>3</sub>-symmetrical triptycenes hold promise in the design of functional materials.<sup>[25]</sup>

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## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** aryne · directing effect · hyperconjugation · triptycene · ynolate

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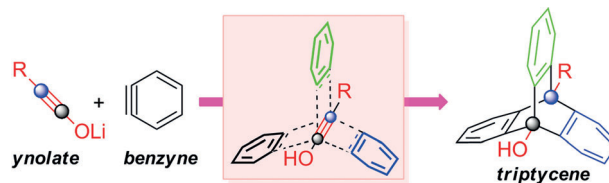
## Communications



## Synthetic Methods

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Regioselective One-Pot Synthesis of  
Triptycenes via Triple-Cycloadditions of  
Arynes to Ynolates



**Three alkynes and one triple bond:** The title reaction constitutes a four-step process involving three cycloadditions and electrocyclic ring opening of the strained Dewar anthracene. Each of the three related but structurally distinct classes of

nucleophiles (ynolate, enolate, and anthracenolate) reacts with *o*-benzyne in the same predictable manner controlled by chelation and negative hyperconjugation.