

Title	Copper-catalyzed site-selective direct arylation of triptycene
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Citation	Chemistry Letters. 2020, 49(6), p. 689-692
Version Type	AM
URL	<a href="https://hdl.handle.net/11094/92837">https://hdl.handle.net/11094/92837</a>
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# Copper-Catalyzed Site-Selective Direct Arylation of Triptycene

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1 A site-selective direct C–H arylation protocol for  
2 triptycene skeleton is developed using copper catalyst and  
3 diaryliodonium reagents. With the aid of directing groups,  
4 C<sub>3</sub>-symmetric trisubstituted triptycenes are selectively  
5 synthesized, and the structure was determined by the X-ray  
6 diffraction analysis. Further derivatization of the installed  
7 bromo functionalities are also described.

8 **Keywords:** Copper, C–H Activation, Triptycene

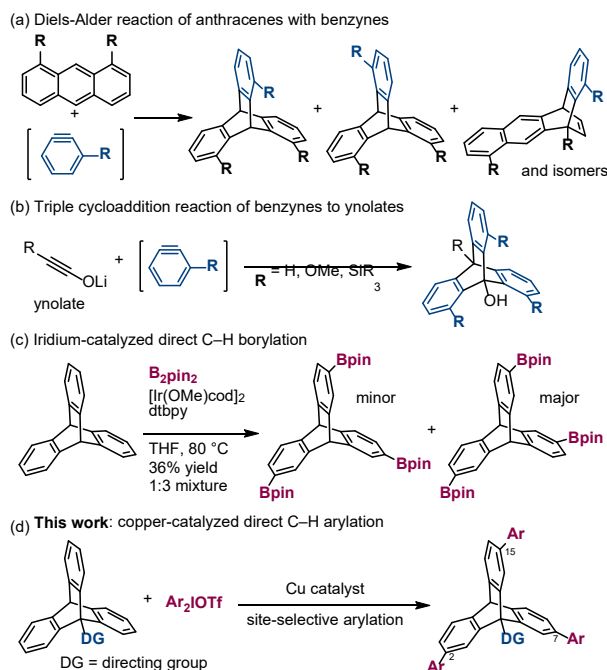
10 Triptycene is a paddle-wheel shaped aromatic  
11 hydrocarbon in which the three benzene rings are fused  
12 within a bicyclo[2.2.2]octatriene (barrelene) core.<sup>1</sup> Because  
13 of the unique three-dimensional rigid architecture, triptycene  
14 derivatives have found wide applications in many research  
15 fields involving supramolecular chemistry, molecular  
16 machine, host-guest chemistry, material science, etc.<sup>2,3</sup>  
17 Accordingly, there is a great demand for the development of  
18 efficient and controllable synthetic tools for manufacturing  
19 functionalized triptycenes.

20 A conventional synthetic method for the triptycene  
21 derivatives is the Diels-Alder reaction of anthracenes with  
22 benzenes (or quinones). It is hardly possible to control the  
23 regioselectivity of the cycloaddition event with any  
24 substituents on the periphery of the reactants, so that the  
25 target product needs to be separated from the complex  
26 mixture of isomers (Scheme 1a).<sup>4</sup> Moreover, the preparation  
27 of functionalized anthracenes suffers from cumbersome  
28 multi-step synthesis. As a potentially relevant transformation,  
29 Shindo *et al.* developed a sequential triple addition reaction  
30 of lithium ynoles to benzenes (Scheme 1b).<sup>5</sup> This excellent  
31 method offers an easy access to symmetrically-functionalized  
32 triptycenes with high regioselectivity, whereas the  
33 substitution pattern was rather limited. Electrophilic aromatic  
34 substitution<sup>6,7</sup> and iridium-catalyzed direct C–H borylation  
35 (Scheme 1c)<sup>8</sup> have also been adopted to functionalize the  
36 triptycene skeleton. The product distribution of these  
37 transformations is, however, totally governed by statistic  
38 factor, and the competing overreaction is usually inevitable.<sup>9</sup>

39 In order to address the synthetic limitation described  
40 above, we envisioned developing a site-selective direct  
41 functionalization protocol with the aid of transition-metal  
42 catalysis. Although the last few decades witnessed a  
43 tremendous achievement in the field of directing-group-  
44 assisted C–H activation chemistry,<sup>10</sup> there has been no report  
45 for the decoration of triptycene scaffolds upon this strategy.  
46 We assumed that the installation of appropriate functionality  
47 at the bridgehead position would facilitate the direct C–H  
48 transformation of the proximal three benzene rings. In this  
49 manuscript, we focused on a copper-catalyzed direct C–H

50 arylation using diaryliodonium salts as arylating reagents due  
51 to the enhanced electrophilic nature of the Cu(III)-aryl  
52 species and the high regioselectivity (Scheme 1d).<sup>11,12,13</sup> This  
53 reaction system produces a series of 2,7,15-trisubstituted C<sub>3</sub>-  
54 symmetric triptycenes, which are difficult to be assembled  
55 through the conventional synthetic methods.

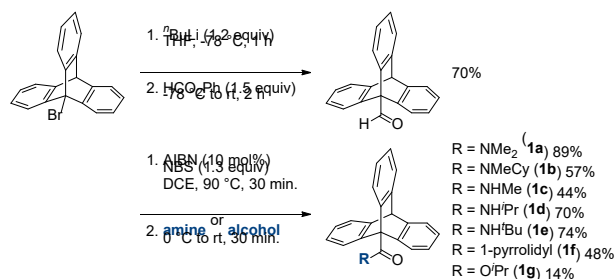
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57

58 **Scheme 1.** Representative Synthetic Methods for Functionalized  
59 Triptycenes.

60 At the outset of this study, we attempted to establish a  
61 synthetic method for introducing carbonyl-based directing  
62 groups at the bridgehead position (Scheme 2). A  
63 commercially available 9-bromotriptycene was treated with  
64 *n*-butyllithium, and the obtained lithium reagent was further  
65 reacted with phenylformate to give 9-formyltriptycene. This  
66 was converted to the corresponding acid bromide using NBS  
67 (*N*-bromosuccinimide) and a catalytic amount of AIBN  
68 (azodiisobutyronitrile).<sup>14</sup> Addition of any amine or alcohol  
69 produced the target amides **1a–1f** and ester **1g**. Direct  
70 transformation from the lithiated species to amides or esters  
71 using carbamoyl chlorides or chloroformate, respectively,  
72 was totally unsuccessful.



Scheme 2. Synthesis of 9-Substituted Triptycenes.

After the preliminary screening of the reaction conditions with these prepared substrates, the desired tri-arylated products were obtained using  $\text{Ph}_2\text{IOTf}$  as an arylating reagent in the presence of Cu complexes.<sup>15</sup> Consequently, optimization study was conducted using **1a** as a model substrate (Table 1). With 5.0 mol% of  $\text{Cu}(\text{OTf})\cdot 1/2\text{C}_6\text{H}_6$  catalyst and 4.0 equiv of  $\text{Ph}_2\text{IOTf}$  (**2a**), the target product **3aa** (tri-Ph) was obtained in 16% yield along with the di-Ph (52%) and the mono-Ph (29%) products (entry 1). The structure of **3aa** was unambiguously determined by the single crystal X-ray diffraction analysis.<sup>16</sup> Increased amount of the Cu catalyst (40 mol%) and **2a** (6.0 equiv) shifted the product distribution to the desired product up to 33% yield (entries 2 and 3), but further improvement was not achieved with the prolonged reaction time (entry 4). This was probably because decomposition of the hypervalent iodine reagent **2a** was competing under the conditions. To our

delight, **3aa** was obtained in 48% yield when **2a** was added portionwise in four parts during the course of reaction (entry 5). In order to trap an excess acid byproduct (TfOH), we examined the effect of base additives. The addition of  $\text{N}^i\text{Pr}_2\text{Et}$  in a portionwise manner (added in three parts, immediately before the addition of **2a**) improved the yield of **3aa** to 57% (entry 6). Increased amount of the base did not significantly affected the yield (entries 7 and 8). With 1.0 equiv of  $\text{N}^i\text{Pr}_2\text{Et}$  in total, the amount of  $\text{Cu}(\text{OTf})\cdot 1/2\text{C}_6\text{H}_6$  catalyst could be reduced to 10 mol% without significant drop of the productivity (entry 9). Other bases such as  $\text{NEt}_3$  (entry 10) and DBU (entry 11) were not effective.

Since the increased loading of Cu catalyst (up to 150 mol%) did not improve the reactivity even when added portionwise, the moderate yield was not likely due to the catalyst deactivation but rather to the inhibition by side-products. Actually, a higher 73% yield of **3aa** was obtained in a two-pot procedure, where the crude mixture was again subjected to the same reaction conditions after aqueous work up (Scheme 3).

According to the literature,<sup>17</sup> we assume that the present reaction proceeds via a Heck-like mechanism (Scheme 4).  $\text{Cu}(\text{OTf})_2$  was oxidized by the iodonium reagent to generate  $\text{Ph-Cu}(\text{OTf})_2$  species. With the assistance of carbonyl coordination, the aryl group is transferred to the “meta” position of the triptycene core through a four-membered-ring transition state. Subsequent deprotonation furnishes the arylated product and  $\text{CuOTf}$ , closing the catalytic cycle.

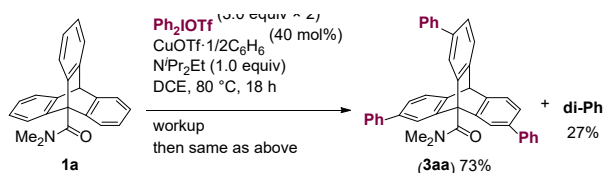
Table 1. Optimization Study. <sup>a)</sup>

entry	deviation from the standard conditions	time	tri-Ph <sup>b)</sup>	di-Ph <sup>b)</sup>	mono-Ph <sup>b)</sup>
1	$\text{Cu}(\text{OTf})\cdot 1/2\text{C}_6\text{H}_6$ (5.0 mol%), <b>2a</b> (4.0 equiv)	16 h	16%	52%	29%
2	<b>2a</b> (4.0 equiv)	16 h	26%	54%	19%
3	--	40 h	33%	54%	13%
4	--	70 h	33%	53%	13%
5	<b>2a</b> (1.5 equiv $\times$ 4)	22 h	48%	47%	6%
6	<b>2a</b> (1.5 equiv $\times$ 4), $\text{N}^i\text{Pr}_2\text{Et}$ (0.25 equiv $\times$ 3)	22 h	57%	41%	3%
7	<b>2a</b> (1.5 equiv $\times$ 4), $\text{N}^i\text{Pr}_2\text{Et}$ (0.33 equiv $\times$ 3)	22 h	58% (42%) <sup>c)</sup>	40%	2%
8	<b>2a</b> (1.5 equiv $\times$ 4), $\text{N}^i\text{Pr}_2\text{Et}$ (0.5 equiv $\times$ 3)	22 h	51%	45%	3%
9	$\text{Cu}(\text{OTf})\cdot 1/2\text{C}_6\text{H}_6$ (10 mol%) <b>2a</b> (1.5 equiv $\times$ 4), $\text{N}^i\text{Pr}_2\text{Et}$ (0.33 equiv $\times$ 3)	22 h	53%	44%	3%
10	<b>2a</b> (1.5 equiv $\times$ 4), $\text{NEt}_3$ (0.5 equiv $\times$ 3)	22 h	45%	50%	5%
11	<b>2a</b> (1.5 equiv $\times$ 4), DBU (0.5 equiv $\times$ 3)	22 h	19%	57%	23%

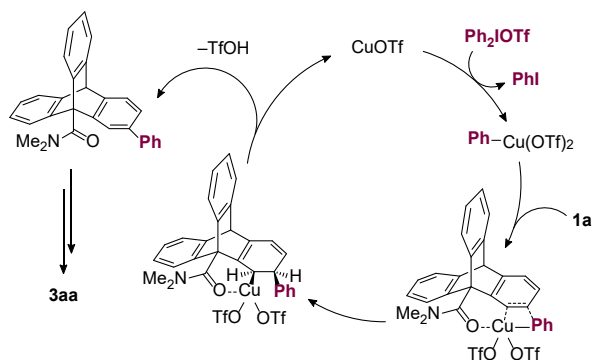
<sup>a)</sup> Standard conditions: **1a** (0.05 mmol), **2a** (0.3 mmol),  $\text{Cu}(\text{OTf})\cdot 1/2\text{C}_6\text{H}_6$  (0.02 mmol), DCE (2.0 mL).

<sup>b)</sup> The yield was determined by  $^1\text{H}$  NMR analysis. <sup>c)</sup> Isolated yield.

Tf = trifluoromethanesulfonyl, DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene



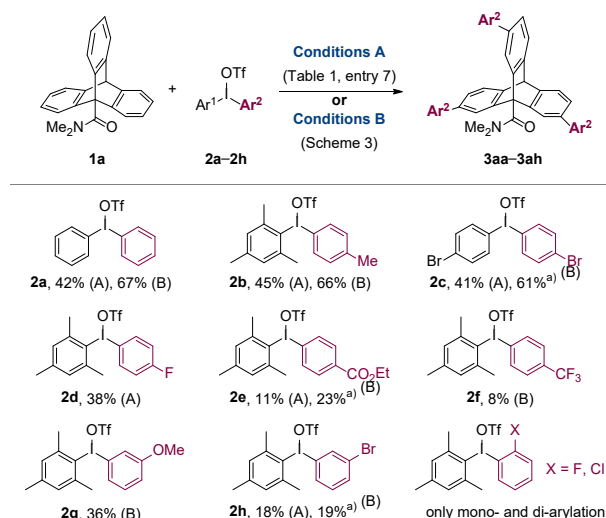
**Scheme 3.** Arylation of **1a** in a Two-pot Procedure. NMR yields are shown.



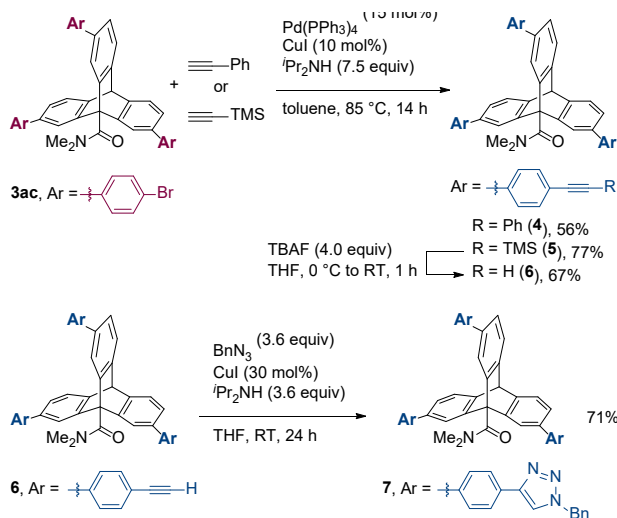
**Scheme 4.** Proposed Reaction Mechanism.

6 We next investigated the reaction efficiency of a series  
7 of substituted iodonium reagents under the reaction  
8 conditions of entry 7 in Table 1 (conditions A) and of Scheme  
9 3 (conditions B). The values in Scheme 5 represents the yield  
10 of tri-arylated products. For the reaction with *para*-Me (**2b**),  
11 *para*-Br (**2c**), and *para*-F (**2d**) substituents, the corresponding  
12 products were isolated in 38~45% yields, being comparable  
13 to that of reaction with **2a**. Higher yields of **3aa** (67%), **3ab**  
14 (66%), and **3ac** (61%) were obtained with the conditions B.  
15 Electron-withdrawing ester (**2e**) and trifluoromethyl (**2f**)  
16 groups considerably retarded the reaction to give the products  
17 in lower yields. The meta-substituted aryl groups (**2g**, **2h**)  
18 also could be transferred selectively to the triptycene benzene  
19 rings. On the other hand, ortho-substituted iodonium reagents  
20 only afforded mono- and di-arylated products, and the  
21 formation of tri-arylated products was negligible.

22 The bromo (**3ac**, **3ah**) and ester (**3ae**) functionalities  
23 offer numerous possible transformations afterward, so that  
24 these compounds would be potentially useful  $C_3$ -symmetric  
25 triptycene building blocks. As a particular example for the  
26 derivatization of the product, we performed alkylation of  
27 **3ac** (Scheme 6). The bromo groups were converted to the  
28 alkynyl groups under the standard Sonogashira coupling  
29 conditions to deliver **4** and **5** respectively in 56% and 77%  
30 yields. Deprotection of the TMS group on **5** was affected by  
31 TBAF (tetrabutylammonium fluoride) to afford the terminal  
32 alkyne **6**, which was further transformed into **7** via through  
33 the Huisgen cycloaddition reaction.



**Scheme 5.** Scope for the Arylating Reagents. Isolated yields for the tri-arylated products are shown. <sup>a</sup>) Determined by <sup>1</sup>H NMR analysis.



**Scheme 6.** Derivatization of the Products.

50 In summary, we have developed a copper-catalyzed  
51 site-selective arylation protocol with the aid of amide  
52 functionality placed at the bridgehead position. This report  
53 demonstrate the first example of directing-group-assisted C–  
54 H functionalization of the triptycene scaffold, producing  $C_3$ -  
55 symmetric tri-substituted triptycene derivatives exclusively.  
56 As exemplified in this study, the transition-metal-catalyzed  
57 direct C–H activation methodology would be a proper mean  
58 of decollating the triptycene periphery.

59 This work was supported by JSPS KAKENHI Grant No. JP  
60 19K15586 (Grant-in-Aid for Young Scientists) to Y.N. and  
61 JP 17H06092 (Grant-in-Aid for Specially Promoted  
62 Research) to M.M.

63 The authors declare no competing financial interest.

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1 Supporting Information is available on  
2 [http://dx.doi.org/10.1246/cl.\\*\\*\\*\\*\\*](http://dx.doi.org/10.1246/cl.*****).

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You are requested to put a brief abstract (50-60 words, one paragraph style) with the graphical abstract you provided, so that readers can easily understand what the graphic shows.

Graphical Abstract	
Textual Information	
A brief abstract	A site-selective direct C–H arylation protocol for triptycene skeleton is developed using copper catalyst and diaryliodonium reagents. With the aid of directing groups, $C_3$ -symmetric trisubstituted triptycenes are selectively synthesized, and the structure was determined by the X-ray diffraction analysis. Further derivatization of the installed bromo functionalities are also described.
Title	Copper-Catalyzed Site-Selective Direct Arylation of Triptycene
Authors' Names	Keisuke Ueno, Yuji Nishii, Masahiro Miura
Graphical Information	
<p>&lt;Please insert your Graphical Abstract: The size is limited within 100 mm width and 30 mm height, or 48 mm square&gt;</p> 