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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 C₃-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

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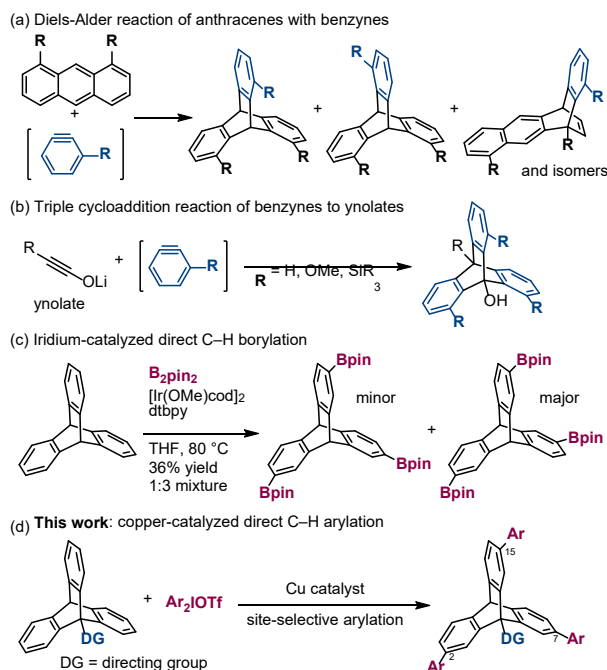
10 Triptycene is a paddle-wheel shaped aromatic
11 hydrocarbon in which the three benzene rings are fused
12 within a bicyclo[2.2.2]octatriene (barrelene) core.¹ Because
13 of the unique three-dimensional rigid architecture, triptycene
14 derivatives have found wide applications in many research
15 fields involving supramolecular chemistry, molecular
16 machine, host-guest chemistry, material science, etc.^{2,3}
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 benzyne (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).⁴ 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 ynolates to benzyne (Scheme 1b).⁵ 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^{6,7} and iridium-catalyzed direct C–H borylation
35 (Scheme 1c)⁸ 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.⁹

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,¹⁰ 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).^{11,12,13} This
53 reaction system produces a series of 2,7,15-trisubstituted C₃-
54 symmetric triptycenes, which are difficult to be assembled
55 through the conventional synthetic methods.

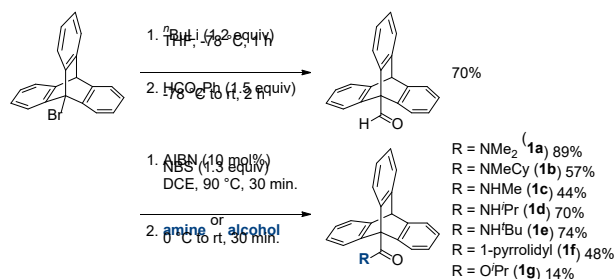
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58 **Scheme 1.** Representative Synthetic Methods for Functionalized
59 Triptycenes.

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).¹⁴ 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 Ph_2IOTf as an arylating reagent in the presence of Cu complexes.¹⁵ 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 Ph_2IOTf (**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.¹⁶ 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 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,¹⁷ 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 CuOTf , closing the catalytic cycle.

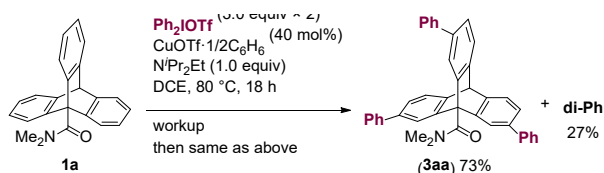
Table 1. Optimization Study. ^{a)}

| entry | deviation from the standard conditions | time | tri-Ph ^{b)} | di-Ph ^{b)} | mono-Ph ^{b)} |
|-------|--|------|-------------------------|---------------------|-----------------------|
| 1 | $\text{Cu}(\text{OTf})\cdot 1/2\text{C}_6\text{H}_6$ (5.0 mol%), 2a (4.0 equiv) | 16 h | 16% | 52% | 29% |
| 2 | 2a (4.0 equiv) | 16 h | 26% | 54% | 19% |
| 3 | -- | 40 h | 33% | 54% | 13% |
| 4 | -- | 70 h | 33% | 53% | 13% |
| 5 | 2a (1.5 equiv \times 4) | 22 h | 48% | 47% | 6% |
| 6 | 2a (1.5 equiv \times 4), $\text{N}^i\text{Pr}_2\text{Et}$ (0.25 equiv \times 3) | 22 h | 57% | 41% | 3% |
| 7 | 2a (1.5 equiv \times 4), $\text{N}^i\text{Pr}_2\text{Et}$ (0.33 equiv \times 3) | 22 h | 58% (42%) ^{c)} | 40% | 2% |
| 8 | 2a (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%) 2a (1.5 equiv \times 4), $\text{N}^i\text{Pr}_2\text{Et}$ (0.33 equiv \times 3) | 22 h | 53% | 44% | 3% |
| 10 | 2a (1.5 equiv \times 4), NEt_3 (0.5 equiv \times 3) | 22 h | 45% | 50% | 5% |
| 11 | 2a (1.5 equiv \times 4), DBU (0.5 equiv \times 3) | 22 h | 19% | 57% | 23% |

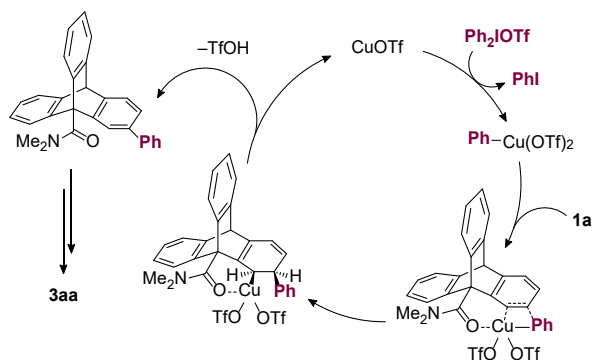
^{a)} Standard conditions: **1a** (0.05 mmol), **2a** (0.3 mmol), $\text{Cu}(\text{OTf})\cdot 1/2\text{C}_6\text{H}_6$ (0.02 mmol), DCE (2.0 mL).

^{b)} The yield was determined by ^1H NMR analysis. ^{c)} Isolated yield.

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



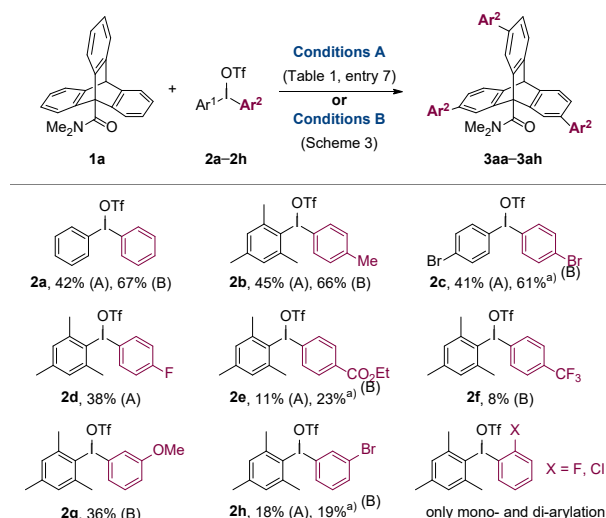
Scheme 3. Arylation of **1a** in a Two-pot Procedure. NMR yields are shown.



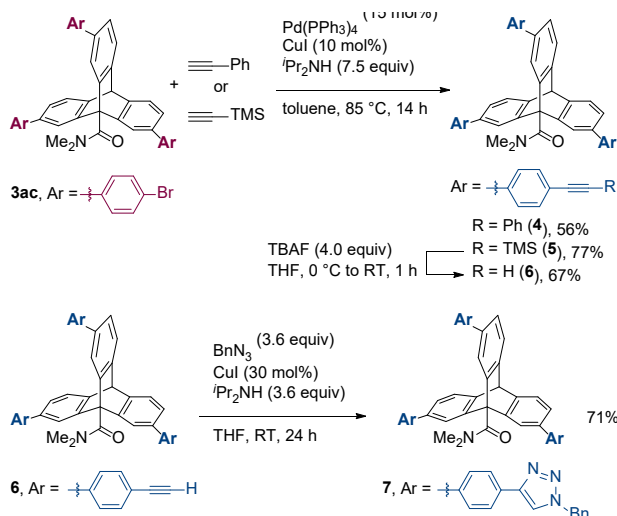
Scheme 4. Proposed Reaction Mechanism.

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 C₃-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. ^a) Determined by ¹H 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 C₃-
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.

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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.*****.

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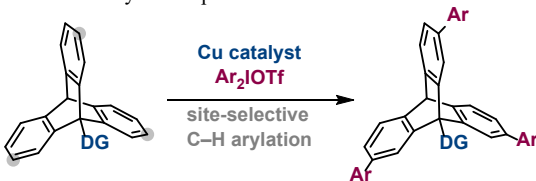
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| A brief abstract | A site-selective direct C–H arylation protocol for triptycene skeleton is developed using copper catalyst and diaryliodonium reagents. With the aid of directing groups, C_3 -symmetric trisubstituted triptycenes are selectively synthesized, and the structure was determined by the X-ray diffraction analysis. Further derivatization of the installed bromo functionalities are also described. |
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| Authors' Names | Keisuke Ueno, Yuji Nishii, Masahiro Miura |
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