A Meta-Selective Copper-Catalyzed C H Bond Arylation

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the silver nanoparticle concentration, size, and distribution, we have produced inks with high solids loading (≥70 wt %) that are ideally suited for direct-write assembly. We have shown that self-supporting microelectrodes in either planar or 3D forms of arbitrary complexity can be patterned on a wide variety of substrates. Using this technique, we have further demonstrated the feasibility of wire bonding to fragile devices and patterning complex interconnects for solar cell and LED arrays.

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Supporting Online Material

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Figs. S1 to S9
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A Meta-Selective Copper-Catalyzed C–H Bond Arylation

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For over a century, chemical transformations of benzene derivatives have been guided by the high selectivity for electrophilic attack at the ortho/para positions in electron-rich substrates and at the meta position in electron-deficient molecules. We have developed a copper-catalyzed arylation reaction that, in contrast, selectively substitutes phenyl electrophiles at the aromatic carbon–hydrogen sites meta to an amido substituent. This previously elusive class of transformation is applicable to a broad range of aromatic compounds.

Aromatic organic compounds are ubiquitous in modern society as medicines and functionalized materials (*1*). These molecules comprise cyclic aryl cores with an often complex array of substituents on the ring carbons, which in many cases are most straightforwardly appended by electrophilic substitution (*2*). Ever since the pioneering work of Friedel and Crafts (*3*), it has been widely established that electron-donating substituents direct incoming electrophiles to the ortho and para positions, whereas electron-withdrawing groups steer to the meta position (Fig. 1A). This fundamental reactivity pattern facilitates a predictable outcome in simple cases; however, a common problem encountered in synthesis is how to access the isomer that is not anticipated by these rules. Solutions to this problem often require numerous functional group additions or manipulations in order to tailor the directing electronic properties of the precursor to furnish the desired product. Furthermore, in complex systems, where there may be more than one electronic or sterically active substituent, the competition between these directing groups may lead to mixtures of products. Although there have been some reports that indirectly address these problems (*4*–*7*), circumventing the inherent ortho/para-selectivity of electron-rich aromatic systems to generate the meta product remains a largely elusive and unmet goal for chemical synthesis.

A central theme of our research has been the development of methods to obviate reliance on complex functional group manipulations through direct metal-catalyzed C–H bond transformations (*8*, *9*). A key aspect of this goal is the ability to control the site selectivity of these transformations under mild conditions; a challenge that is further complicated by the ubiquitous nature of the C–H bond in organic molecules (*10*–*15*). The three mechanisms that usually rationalize the majority of selective metal-catalyzed C–H bond activation methods involve electrophilic aromatic substitution with electron-rich, π-nucleophilic arenes (*16*), concerted metalation-deprotonation with simple and electron-deficient benzenes (*17*–*19*), and directed cyclometalation (*20*–*26*). These mechanistic pathways most commonly form the ortho-substitution product, and as a result there is a paucity of methods for metal-catalyzed C–H bond activation at the meta position of a substituted benzene ring (*27*, *28*).

Here we describe the development of a reactivity concept for a metal-catalyzed aromatic C–H bond functionalization strategy that selectively generates the elusive meta isomer. The outcome is not predicted by the conventional rules associated with electronic factors, directing groups, or steric effects, and provides direct access to the meta isomer on highly versatile electron-rich aromatic structures. The process is simple, proceeds under mild conditions, uses inexpensive copper catalysts, and forms valuable products that would be difficult to synthesize by other methods (Fig. 1B). Furthermore, the reactivity and selectivity of this process should be compatible with other arene and C–H bond transformations and will streamline synthetic strategy for the assembly of medicines, natural products, and industrially relevant aromatic molecules.

We previously identified a copper catalysis system, based on electrophilic metalation, that enables site-selective C–H bond arylation on the indole skeleton (Fig. 2A) (*10*). We speculated that a Cu(I) catalyst is oxidized to a Cu(III)-aryl intermediate (*29*), a highly electrophilic d^8-configured metal species, that undergoes Friedel-Crafts–type metalation and arylation at the C3 position of the indole (Fig. 2B). We see C3 arylation when using our copper catalyst, whereas an almost identical process using Pd(II)-salts delivers the C2 isomer (*30*). Although the origin of this dichotomy remains unclear, it led us to speculate that use of our copper catalyst might enable us to reverse the established selectivity of other electrophilic Pd(II)-catalyzed transformations. For example, many Pd(II)-catalyzed reactions are ortho-selective and have been routinely developed by virtue of the coordinat-

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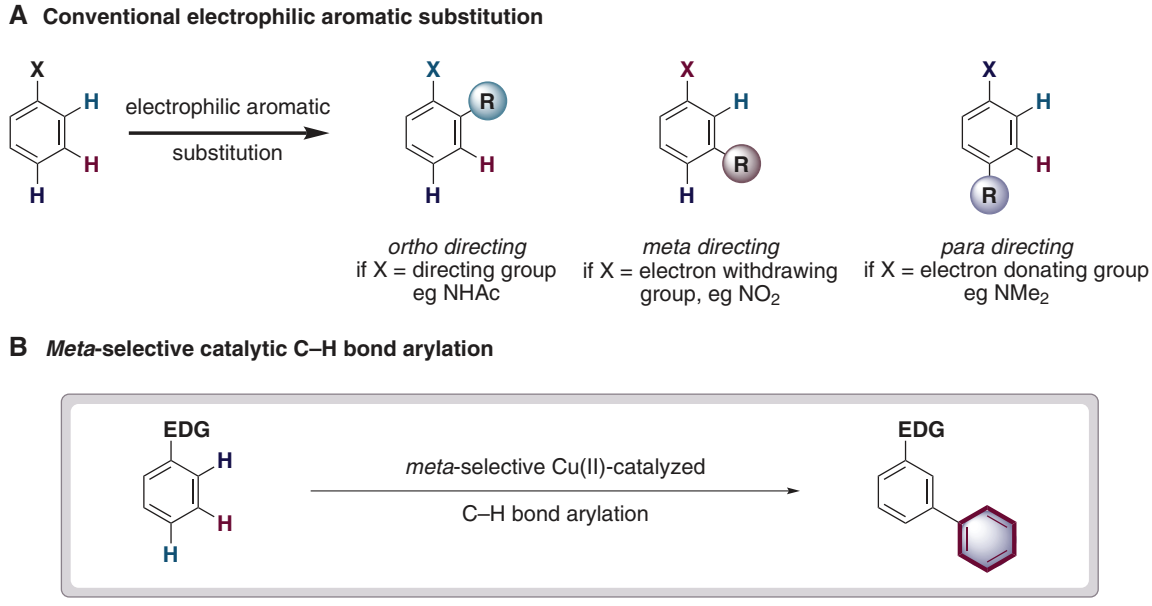


Fig. 1. (**A**) Conventional reactivity trends in electrophilic aromatic substitution. (**B**) Meta-selective catalytic C–H bond arylation. EDG, electron-donating group; Me, methyl; Ac, acetyl.

ing effect of directing groups (*20*–*26*). We reasoned that a highly electrophilic Cu(III)-aryl species could react through a different pathway with molecules such as acetanilides, potentially leading to a positional isomer not observed in conventional aromatic substitution reactions (Fig. 2C). The acetanilides are an important class of aromatic molecule that already undergoes a plethora of transformations leading to ortho/para products (*20*). Furthermore, the acetamide group is a versatile motif that can be readily transformed into a range of other functionalities through conventional synthetic procedures.

To test this hypothesis, we treated acetanilide **1a** with Ph_2IOTf (the arylating agent; Ph, phenyl; Tf, triflate) in the presence of 10 mole % $Cu(OTf)_2$ (catalyst) in 1,2-dichloroethane solvent at 70°C (*31*). Arylation occurred at the meta position to afford **2a**, albeit in low isolated yield (Table 1, entry 1); and in line with our blueprint, no products arising from monoarylation at the ortho or para position were observed (determined by ^1H nuclear magnetic resonance analysis, <5%). Furthermore, no arylation was observed with compounds that do not possess an amide group (*31*). The same exclusive meta-selectivity was observed with 2-methylacetanilide **1b**, to form the meta product **2b**, in improved 43% yield. These outcomes are in contrast to the similar Pd(II)-catalyzed C–H arylation of acetanilide that delivered the ortho-substituted product (*32*). Only the elegant iridium-catalyzed C–H borylation, developed independently by Smith-Maleczka and Hartwig-Miyuara-Ishiyama, can achieve such selectivity in certain cases (*27*, *28*). The C–H borylation reaction is mainly influenced by the steric effects on the aromatic molecule and leads to functionalization at a position that is not adjacent to any other group. In cases such as **1b**, however, the borylation reaction would be expected to afford a mixture of meta and para isomers.

Encouraged by these initial results, we next addressed reaction optimization with 2-methylanilides as our model system. We found that changing the nature of the acyl group had a large effect on the yield of the reaction without compromising the meta-selectivity (Table 1, entries 2 to 6). The reaction works with carbamate and urea groups (Table 1, entries 3 and 4), although the conversions are only moderate. However, benzamides and pivanilides (Table 1, entries 5 and 6) performed much better in the reaction, producing good yields of the desired biaryl products. In all cases, arylation is the result of reaction at the meta position to the amide, and no reaction occurs in the absence of the copper catalyst.

Although we cannot be certain of the precise mechanism of the reaction at this stage, a possible rationalization could involve the highly electrophilic Cu(III)-aryl species activating the aromatic ring sufficiently to permit an anti–oxy-cupration of the carbonyl group of an acetamide across the 2,3 positions on the arene ring (Fig. 2D, step 1). This dearomatizing transformation would place the Cu(III)-aryl species at the meta position, and rearomatizing deprotonation (step 2) followed by reductive elimination (step 3) would deliver the meta product (*33*).

Having identified a suitable amide moiety, we explored the substrate scope (Fig. 3A). The copper-catalyzed meta-arylation displays broad substrate capacity and is tolerant of a range of substituents in all positions of the aromatic ring (*34*). For example, ortho-substituted pivanilides readily produce the 1,2,5-trisubstituted arene system, in which arylation has taken place in the meta position to the amido group regardless of the electronic properties of the ortho substituent [**2f** to **2j** (**2f-j**)]. Although electron-deficient substrates suffer from poorer reactivity, it is notable that even in the presence of a competing meta-directing substituent (SO_2Me, **2k**), we observed exclusive arylation at the meta position to the amide group, in line with our hypothesis. When the pivanilide was substituted in the meta position, the C–H arylation afforded the 1,3,5 arene isomer, again with arylation taking place in the meta position to the nitrogen substituent (entries **2l-p**). Although the yields are a little lower than those of the corresponding ortho-substituted anilides, this is not the result of other isomeric products but of a slower reaction rate that leads to incomplete conversion of the starting material. Particularly noteworthy is the tolerance of halogen groups (**2m** and **2o**), which remain unaffected during the reaction; these examples demonstrate that the copper-catalyzed C–H arylation provides a complementary platform for further elaboration via conventional Pd(0)-catalyzed cross-coupling chemistry. The simple pivanilide system forms the meta-diarylation product (**2q**). The arylation process can also be extended to systems bearing a para substituent, and the arylation takes place in the sterically most demanding position, consistent with our meta-directing hypothesis, to form 1,3,4,5-tetrasubstituted anilides (**2r**). In these cases, the symmetrical diarylation predominates; however, it is possible to access the 1,3,4-trisubstituted monoarylated system (**2s**) by controlling the stoichiometry of the reaction.

More complex (tri- or tetrasubstituted) anilide starting materials are also compatible in this reaction, leading to highly functionalized products (**2t-u**) in reasonable to good yields. A hexasubstituted arene (**2v**) can be synthesized in moderate yield by this process, and versatile heterocyclic motifs such as the indoline system (**2w**) can be selectively arylated to form useful products that would be difficult to access by other methods. Moreover, the nature of the aryl coupling partner can be varied in the reaction, thereby extending the utility of this process. A range of steric, electronic,

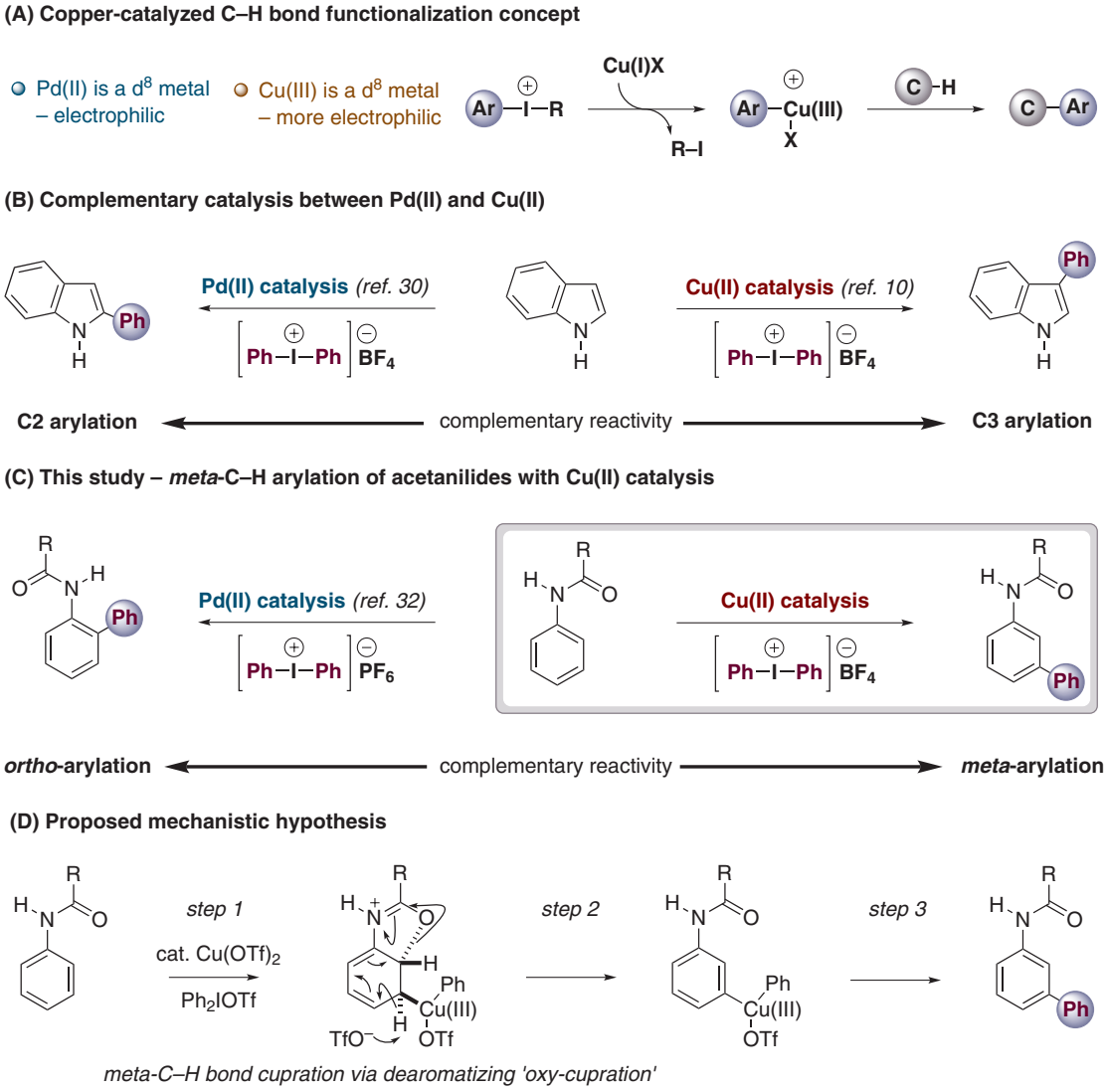
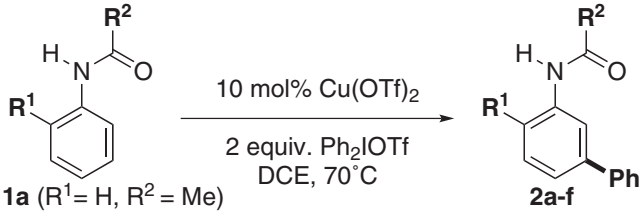


Fig. 2. Design blueprint for meta-selective copper-catalyzed C–H bond arylation (**A** to **D**). Ar, general aryl group; Ph, phenyl; Tf, triflate; R, general hydrocarbon group.

Table 1. Optimization studies for meta-selective Cu(II)-catalyzed C–H bond arylation. DCE, 1,2-dichloroethane.

Reaction optimization



1a (R^1 = H, R^2 = Me)
1b (R^1 = Me, R^2 = Me)

entry	R^1	R^2	product	yield %
1	H	Me	**2a**	14
2	Me	Me	**2b**	43
3	Me	OMe	**2c**	45
4	Me	NEt_2	**2d**	31
5	Me	Ph	**2e**	73
6	Me	CMe_3	**2f**	79

and functionally diverse aryl groups can be transferred via the unsymmetrical iodonium salts (*35*) in good yields (Fig. 3B). In these cases, the large size of the mesityl group precludes its transfer in the coupling step, facilitating the formation of a range of functionalized biaryl products (*10*, *30*).

The meta-selectivity of this arylating transformation can be controllably overridden in certain cases, providing further access to alternative isomeric products (Fig. 4). A 3-oxygenated pivanilide derivative can be tuned through simple and straightforward manipulation of the oxygen-protecting group to afford either the 1,3,5- or 1,3,6-trisubstituted arene product. For example, a moderately electron-withdrawing 3-OTs group (Ts, tosylate) facilitates reaction in the meta position to the amide motif, in line with our model, to afford the 1,3,5-functionalization pattern (**2x**). However, if the more electron-donating 3-OMe group is incorporated, then the arylation is steered to the 6-position (ortho to the amido group and para to the methoxy) to give **2y** in good yield. This controllable switch in regioselectivity is

indicative of potential versatility in this arylation method.

A broad range of substrates is compatible with this operationally simple and mild copper-catalyzed arylation process. The method is best suited to more electron-donating substitutents on the anilide ring, but still tolerates electron-withdrawing groups, producing the meta isomer with exquisite selectivity. In certain cases the meta-selectivity can be overridden by strongly electron-donating substituents that provide a further platform for exploring the reaction parameters.

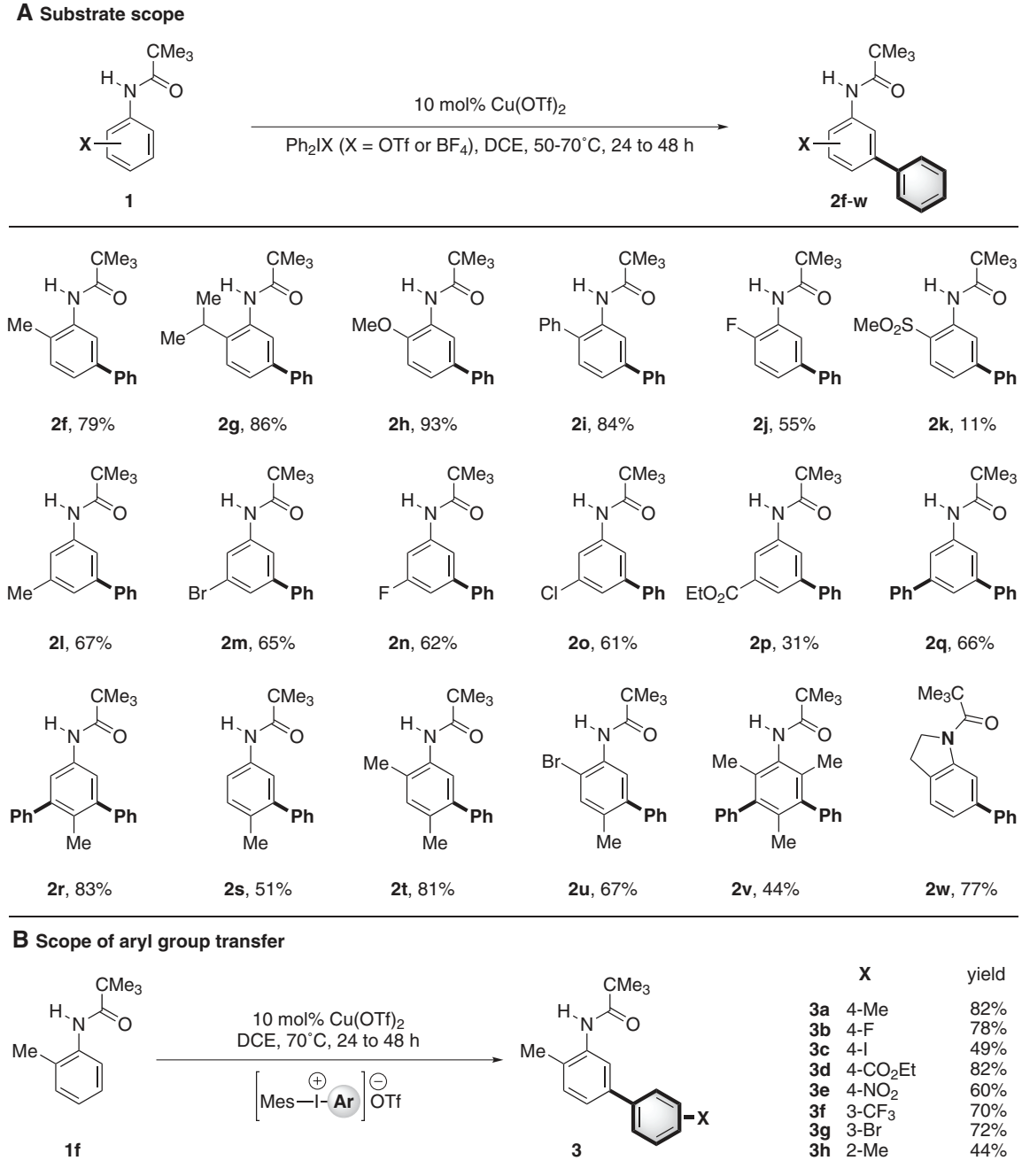


Fig. 3. Scope of anilide (**A**) and arylating (**B**) groups in the Cu(II)-catalyzed C–H bond arylation reaction; Mes, 2,4,6-trimethylphenyl; Et, ethyl. For **2s**, two equivalents of pivanilide were used.

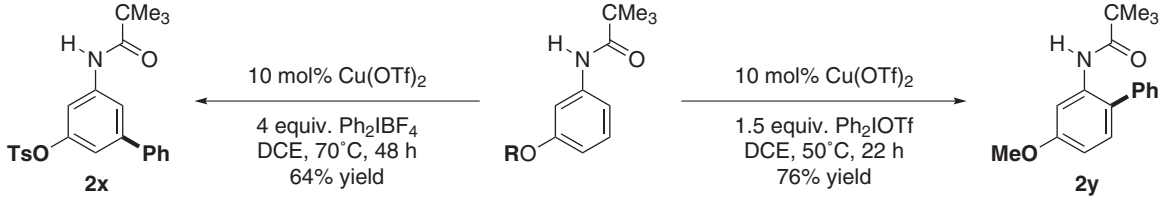


Fig. 4. Controlling the site selectivity of the C–H arylation reaction; Ts, tosylate.

We anticipate that this general copper-catalyzed meta-C–H bond functionalization reaction will provide direct access to the elusive positional isomers in aromatic chemistry and have a major impact on the way that complex molecules, pharmaceuticals, and functionalized materials are synthesized.

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Supporting Online Material

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Spectral Data

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The Burgess Shale Anomalocaridid *Hurdia* and Its Significance for Early Euarthropod Evolution

Allison C. Daley,[1]* Graham E. Budd,[1] Jean-Bernard Caron,[2] Gregory D. Edgecombe,[3] Desmond Collins[4]

As the largest predators of the Cambrian seas, the anomalocaridids had an important impact in structuring the first complex marine animal communities, but many aspects of anomalocaridid morphology, diversity, ecology, and affinity remain unclear owing to a paucity of specimens. Here we describe the anomalocaridid *Hurdia*, based on several hundred specimens from the Burgess Shale in Canada. *Hurdia* possesses a general body architecture similar to those of *Anomalocaris* and *Laggania*, including the presence of exceptionally well-preserved gills, but differs from those anomalocaridids by possessing a prominent anterior carapace structure. These features amplify and clarify the diversity of known anomalocaridid morphology and provide insight into the origins of important arthropod features, such as the head shield and respiratory exites.

Like other anomalocaridids (*1*), *Hurdia* has a complex history. The mouthparts (*2*), frontal appendages (*3*–*5*), body (*6*), and frontal carapaces (*7*, *8*) were all first described in isolation as separate animals with disparate affinities, including medusoids, holothurians, and various arthropods (*1*). When research in the 1980s revealed that many of these taxa were in fact different parts of the same animal, two anomalocaridid genera were defined (*9*), and several specimens here identified as *Hurdia* were assigned to either *Anomalocaris* or *Laggania*. These genera possess stalked eyes, frontal appendages, a circular toothed mouth structure, and a body bearing gills in association with lateral flaps. Later, Collins (*10*, *11*) informally recognized that a third undescribed anomalocaridid exhibits all these features, as well as a prominent anterior carapace composed of a triangular element, the *Hurdia* carapace (*7*), together with the purported phyllopod carapace *Proboscicaris* (*8*).

Access to important new material at the Royal Ontario Museum and restudy of older collections (*12*) identified parts of the *Hurdia* animal scattered through at least eight Cambrian taxa. This realization clarifies the systematics and complex morphology of Burgess Shale anomalocaridids, revealing that previous reconstructions of *Anomalocaris* and *Laggania* have been partially misled by the inclusion of *Hurdia* material. For clarity, generic names previously applied to anomalocaridid body parts are referred to as follows: "Hurdia" (*7*) is referred to as the H-element, "Proboscicaris" (*8*) as the P-element (with both together as the frontal carapace), "Peytoia" (*2*) as the mouthpart, and "appendage F" (*3*–*5*) as frontal appendage.

Systemic paleontology. Stem Euarthropoda, Class Dinocarida, Order Radiodonta, Genus *Hurdia* Walcott, 1912. **Synonymy and taphonomy.** See supporting online material (SOM) text. **Type species.** *Hurdia victoria* Walcott, 1912. **Revised diagnosis.** Anomalocaridid with body divided into two components of subequal length: anterior with a nonmineralized reticulated frontal carapace and posterior consisting of a trunk with seven to nine lightly cuticularized segments. The frontal carapace includes a triangular H-element attached dorsally and a pair of lateral P-elements.

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