

This is the peer reviewed version of the following article: W. C. Fu, Z. Wang, W. T. K. Chan, Z. Lin, F. Y. Kwong, Regioselective Synthesis of Polycyclic and Heptagon-embedded Aromatic Compounds through a Versatile π -Extension of Aryl Halides, *Angew. Chem. Int. Ed.* 2017, 56, 7166, which has been published in final form at <https://doi.org/10.1002/anie.201703551>. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Use of Self-Archived Versions. This article may not be enhanced, enriched or otherwise transformed into a derivative work, without express permission from Wiley or by statutory rights under applicable legislation. Copyright notices must not be removed, obscured or modified. The article must be linked to Wiley's version of record on Wiley Online Library and any embedding, framing or otherwise making available the article or pages thereof by third parties from platforms, services and websites other than Wiley Online Library must be prohibited.

Regioselective Synthesis of Polycyclic and Heptagon-embedded Aromatic Compounds through A Versatile π -Extension of Aryl Halides**

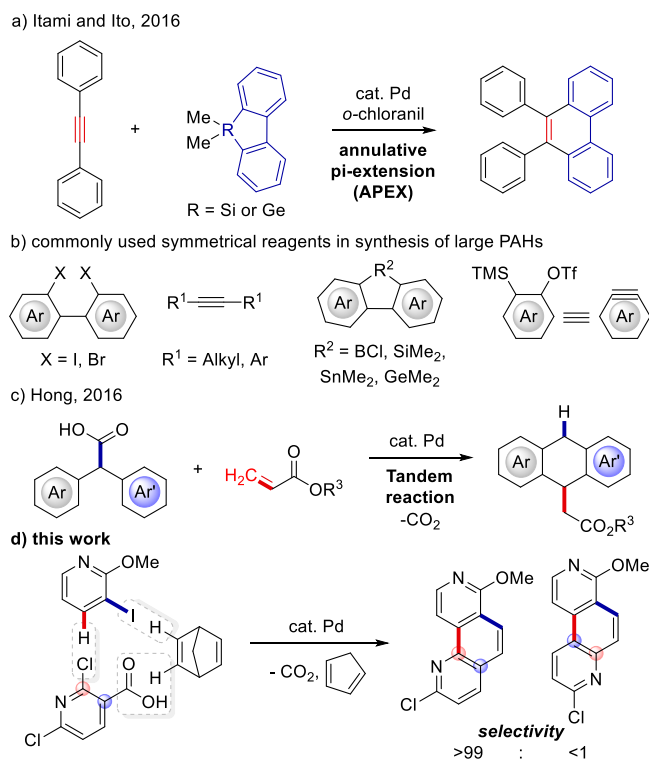
Wai Chung Fu, Zheng Wang, Wesley Ting Kwok Chan, Zhenyang Lin* and Fuk Yee Kwong*

Abstract: A versatile π -extension reaction is developed based on the three-component cross-coupling of aryl halides, 2-haloarylcarboxylic acids and norbornadiene. The transformation is driven by the direction and subsequent decarboxylation of the carboxyl group while norbornadiene serves as an ortho-C-H activator and ethylene synthon via a retro-Diels Alder reaction. A comprehensive DFT calculation is performed to account for the catalytic intermediates.

Polycyclic (hetero)aromatic compounds containing extended π -systems are core and important motifs in the construction of organic materials^[1] and they govern the properties and shapes of nanomaterials.^[2] Although many organic protocols as well as transition metal-catalyzed reactions^[3] were developed to access these compounds, they mostly suffered from limited scope because of the unavailability or compulsory pre-functionalization of coupling reagents. Moreover, heteroatom-incorporated substrates are not widely available and particular strategies were often devised to form only one specific class of compound. Whereas from a step-wise and economic perspective, the synthesis of extended π -systems mostly involved the assembly of multiple aromatic fragments by separate and sequential reactions such as Suzuki coupling, C-H arylations and oxidative Cross-Dehydrogenative Coupling (CDC).^[4] As a result, these limitations may offset the practicality and accessibility of these methods. Therefore, it represents a vital step in the field of material sciences to develop an efficient method that employs readily available building blocks and provides structurally diverse and regioselective polyaromatic hydrocarbons (PAHs).

Very recently, Itami and co-workers developed an elegant annulative π -extension (APEX) reaction for the one-pot aromatic extension of the PAHs' K-region^[5], alkynes^[6] and heteroarenes^[7] using dibenzosiloles or dibenzogermoles (Scheme 1A). However, symmetrical π -extension fragment or coupling partners were used and the regioselectivity was not fully demonstrated. Indeed, the regioselective synthesis of planar aromatic systems remained a long-standing challenge and most methods were prone to the use of symmetrical reagents^[5-8] such as alkynes^[8d,9] or *ortho*-TMS aryl triflate-generated arynes (Scheme 1B).^[10] Their unselective insertions to the metal center were difficult to control by an ancillary ligand and mostly gave isomeric mixtures that are inseparable. We are highly interested in the development of cross-coupling reactions^[11] toward material science and we realized that domino reactions^[12] such as norbornene(NBE)-mediated palladium cascades^[13] held great potential not only in tackling the sequential reactions in one-pot, but also provided access to the ubiquitous aryl halides. However, the homo-coupling of aryl halides might be facile while directing groups, which assisted in the controlled heterobiaryl coupling, might be difficult to be removed after reactions.^[12f] Recently, the use of carboxylic acid as traceless directing group has received significant attention^[14] and Hong 's group recently demonstrated this strategy with an impressive tandem synthesis of acenes (Scheme 1C).^[12b] Nonetheless, the employment of carboxyl-group for assisted direction in the NBE-mediated palladium cascades was not yet studied and we envisioned that it would be omitted during the course of such a reaction.

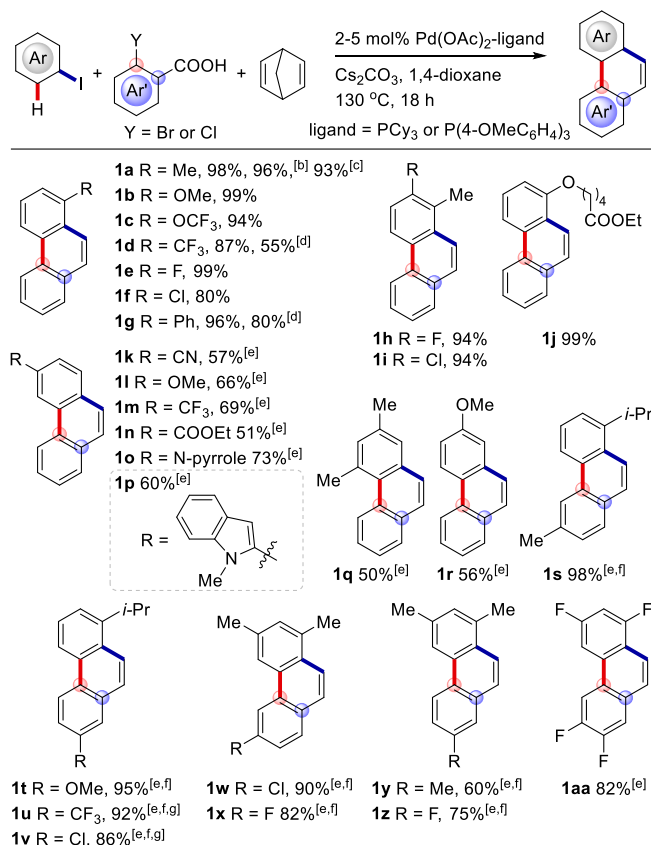
During our investigation, we found that the three-component reaction among 2-iodotoluene, 2-bromobenzoic acid and norbornadiene (NBDE) in the presence of a Pd(OAc)₂/PPh₃ catalyst gave **1a** in 75% product yield (Table S1). We postulated that a norbornadiene-fused intermediate underwent a *retro*-Diels-Alder reaction to afford the phenanthrene scaffold.^[15] In this context, we report a novel one-pot reaction to assemble three easily available fragments to generate regioselective polyaromatics. It allowed for the selective placement of heteroatoms and functional groups at desired positions in an extended π -system while unusual heptagon-embedded polyheteroaromatic compounds could be prepared easily.



Scheme 1. Palladium-catalyzed π -extension reactions.

An optimization was undertaken and the results were detailed in the supporting information (Table S1). The use of Cs₂CO₃ as base was crucial for the coupling reaction and PCy₃ proved to be the best ligand. With a promising condition in hand, we first studied the scope of aryl iodides (Scheme 2). In general, a series of electronically and sterically varied *ortho*-substituted aryl iodides reacted smoothly and afforded the desired products in excellent yields (**1a-1j**). *para*-Substituted aryl iodides were transformed to the corresponding phenanthrenes with moderate-to-good isolated yields (**1k-1p**). It is worth noting that product **1q** was successfully obtained in 50% yield, indicating *ortho*-C-H-activation was undertaken despite the steric hindrance of the *meta*-methyl groups. However, the C-H-activation did not take place at C2 position of 3-iodoanisole and only a single product was obtained (**1r**). By-product formations were generally not observed except for **1q** whereas a cyclization product was found.^[16] Next, the regioselectivity was examined by testing a series of *ortho*-halobenzoic acids. We found that the selective coupling was feasible by using P(4-OMeC₆H₄)₃ as ligand and completely selective products were formed for entries **1s-1aa** with good-to-excellent yields. Our reaction tolerated a variety of functionalities including trifluoromethyl ether (**1c**), ester (**1j**, **1n**), nitrile (**1m**) as well as heterocycles (**1o**, **1p**). Chloro group (**1f**, **1i**, **1v-1w**) remained intact and could be further coupled with π -fragments by means of Suzuki coupling or C-H arylations. Aryl bromides were also found to be applicable substrates (**1d**, **1g**). To further realize the amenability of this

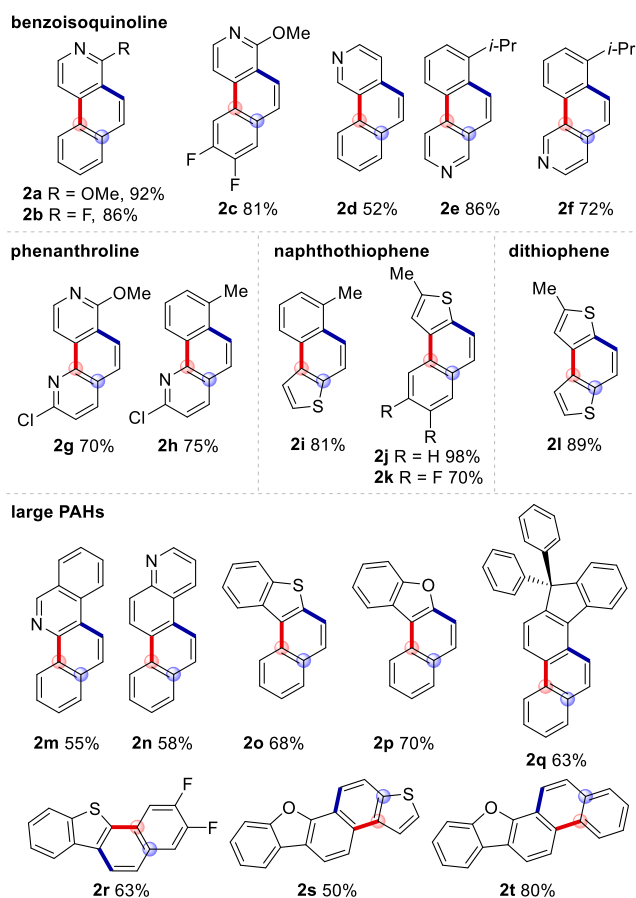
method, the reaction was conducted outside glovebox in a 7 mmol scale and 1.28 gram of **1a** was afforded (96% isolated yield). The catalyst loading could be further reduced to 1.0 mol% with only a slight drop in product yield to 93% (**1a**).



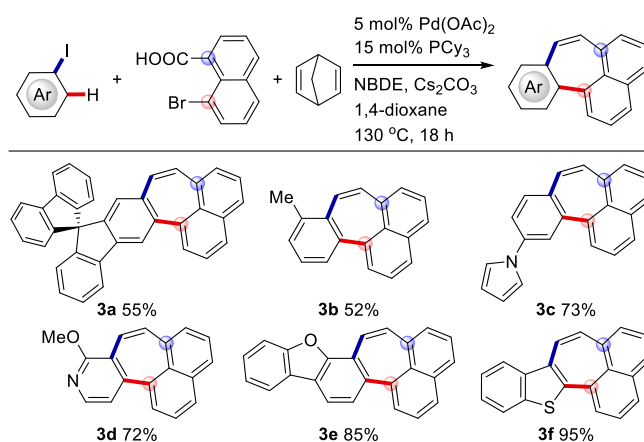
Scheme 2. Reaction scope for aryl halides and 2-halobenzoic acids.^[a] [a] Reaction conditions: Pd(OAc)₂ (2.0 mol%), PCy₃ (6.0 mol%), aryl halide (0.2 mmol), 2-bromoaryl carboxylic acid (0.4 mmol), norbornadiene (0.5 mmol), Cs₂CO₃ (0.6 mmol), 1,4-dioxane (0.1 M, 2 mL), 130 °C for 18 h under N₂. Isolated yields were reported. [b] 2-Iodotoluene (7 mmol). [c] 1.0 mol% Pd and 3.0 mol% PCy₃. [d] ArBr was used. [e] 5.0 mol% Pd and 15.0 mol% ligand. [f] P(4-OMeC₆H₄)₃ was used. [g] 2-Chloroaryl carboxylic acid was used (Y = Cl).

Normally, heteroatoms were rarely seen in an extended π -system because of their unavailability as particular coupling reagents such as arynes but our method provided access to the widely available heteroaryl halides or carboxylic acids to prepare different classes of polyheteroaromatics (**2a-2l**, Scheme 4). Compounds containing N, S, O heteroatoms were prepared efficiently under standard reaction conditions to give moderate-to-excellent yields (**2a-2l**, Scheme 4). Heteroatom-incorporated large PAHs containing four to five aromatic rings could also be synthesized by our methodology (**2m-2t**). Importantly, an extended aromatic system containing the subunits of thiophene and furan was successfully synthesized in 50% yield with complete regioselectivity (**2s**). On the one hand, these compounds are of great interest in optoelectronics^[17], molecular therapeutics^[18], and might be useful ligands in Pd-catalyzed sp³-C-H functionalizations.^[19] On the other hand, the large planar aromatic systems and controlled positions of heteroatoms could contribute beneficial properties in thin-film transistors.^[20]

Recently, heptagon-embedded compounds received much attention as they provided novel geometries in conjugated carbon-based nanomaterials and might alter their original properties significantly.^[21] Our preliminary results showed that 8-bromo-1-naphthoic acid was a viable secondary electrophile and transformed the aryl halides into heptagon-embedded aromatic compounds as depicted in Scheme 4. We successfully performed one-pot synthesis of unique heteroatom-fused heptagonal polyaromatics which could not be synthesized by traditional synthesis methods and were previously difficult to access due to unavailable heteroaryl reagents or requirement of multiple synthetic steps. Heptagon-containing compounds **3a** to **3d** gave green to yellow fluorescence under 365 nm UV irradiation, unlike the blue fluorescence given by their analogues (**1a**, **1o**, **2a** and **2q**). Crystals of **3e** and **3f** suitable for X-ray analysis were grown from solutions in dichloromethane by slow evaporation.^[22] The C₆-C₇-C₁₀ polycyclic framework of **3e** constituted a distorted molecule while **3f** was slightly bended with a C₅-C₇-C₁₀ polycyclic structure (Figure 1). The molecular packing in the crystal structures of **3e** and **3f** both showed columnar arrays and π - π interactions between stacking molecules (Figure S1). The π -to- π distances of the overlapping naphthyl and heterocyclic rings in the crystal structures of **3e** and **3f** respectively measure 3.45-3.60 Å and 3.50 Å. With the presense of π - π stacking interactions, we believe the compounds obtained herein are potential candidates for applications in solid-state organic semiconductors.^[21b,21c,21d] Bond lengths for the seven-membered ring and adjacent C-C bonds were detailed in Figure S2.



Scheme 3. Synthesis of polycyclic heteroaromatic compounds and large PAHs. See supporting information for detailed reaction conditions.



Scheme 4. Application of the π -extension reaction in the preparation of heptagon-embedded aromatic compounds.

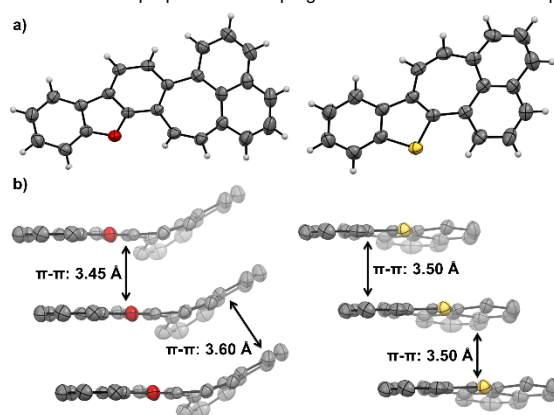
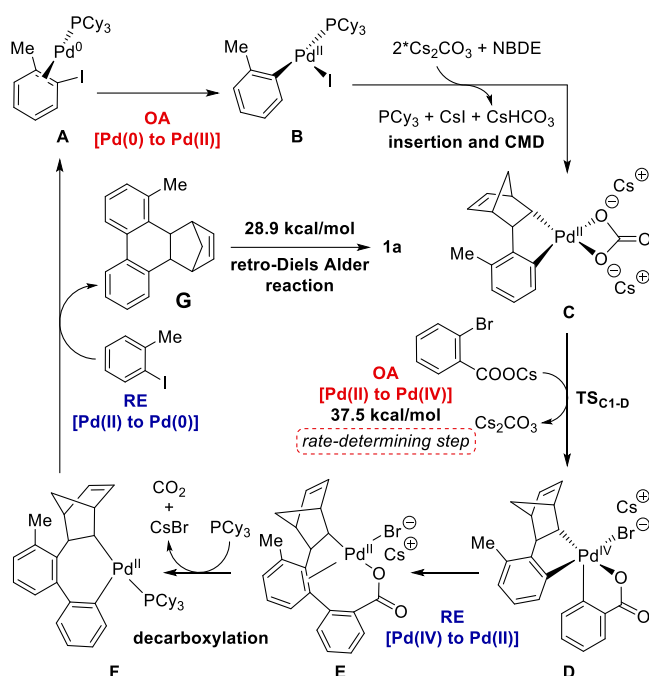


Figure 1. a) The top view of crystal structures for **3e** and **3f**. b) Molecular packing in the crystal structures of **3e** and **3f** featuring π - π interactions between molecules (hydrogens atoms omitted for clarity).

After establishing a new π -extension protocol with an ample reaction scope, we wished to shed light on the reaction mechanism by a comprehensive DFT calculation to account for the key intermediates in the catalytic cycle (Scheme 5). In general, the proposed cycle involves six major steps; 1) oxidative addition of aryl iodide to Pd(0) gives Pd(II); 2) insertion of NBDE followed by a concerted metalation-deprotonation process (CMD)^[23] leading to C-H bond cleavage; 3) oxidative addition [Pd(II) to Pd(IV)]: one molecule of cesium 2-bromobenzoate adds to Pd(II); 4) reductive elimination [Pd(IV) to Pd(II)]; 5) decarboxylation to release CO₂; 6) reductive elimination [Pd(II) to Pd(0)] to complete the cycle. In order to exemplify the catalytic process, we used the real PCy₃ in the computation and the most feasible overall energy profiles were illustrated in Figure S3 (supporting information). The oxidative addition of aryl iodide followed by CMD is facile while the same are true for reductive elimination of Pd(IV) to Pd(II) and the decarboxylation process followed by catalyst regeneration. The rate-determining step is the C-Br oxidative addition of 2-bromobenzoate to Pd(II) (from **C** + cesium 2-bromobenzoate \rightarrow **D** + Cs₂CO₃) with a free energy barrier of 35.7 kcal/mol. The mechanism involves the association/dissociation of phosphine ligands and therefore, higher concentration of phosphine is needed in order to facilitate the reaction.^[24] Species **G** is neither experimentally observed by GC analysis nor isolated. The free energy barrier for the retro-Diels Alder (rDA) reaction of species **G** \rightarrow **1a** was calculated to be 28.9 kcal/mol, which is lower than the abovementioned rate-determining step (35.7 kcal/mol). Thus, it is expected **G** will undergo rDA reaction instantaneously after the catalytic cycle to give the final product **1a** while releasing a cyclopentadiene.



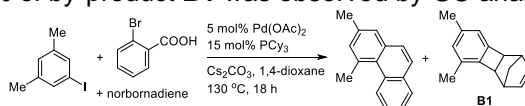
Scheme 5. Six major steps and key intermediates accounted for the π -extension reaction by means of DFT calculations, relative free energies of the representative catalytic pathway are given in kcal/mol. See Figure S3 for a detailed diagram with all transition states.

In conclusion, we have succeeded in showing a straightforward one-pot π -extension protocol using the easily available aryl halides and *ortho*-haloaryl carboxylic acids. This protocol features (i) broad substrate scope with respect to both coupling partners and heteroaromatic reagents; (ii) exceptional regioselectivity for manipulating non-symmetrical polyaromatics; (iii) the facile one-step preparation of non-planar aromatic heptagons with potential applications in solid-state organic semiconductors. Comprehensive DFT study indicated that the Pd(II) to Pd(IV) oxidative addition might be the possible rate-determining step in this decarboxylative norbornadiene-mediated palladium cascade. Our method excludes the prefunctionalization of coupling reagents and provides one-step access to universal PAHs, while also features selective placement of heteroatoms and functional groups at desired positions in an extended π -system. We believed this protocol will be widely adopted across material science (nanomaterials, optoelectronics, thin-film transistors), medicinal chemistry and organic chemistry.

Referneces

- [1] a) S. H. Strauss, O. V. Boltalina, I. V. Kuvychko, US9249071 B2, **2016**; b) M. Li, C. An, T. Marszalek, X. Guo, Y.-Z. Long, H. Yin, C. Gu, M. Baumgarten, W. Pisula, K. Müllen, *Chem. Mater.* **2015**, *27*, 2218; c) A. H. Parham, A. Buesing, H. Heil, P. Stoessel, US 9006503 B2, **2015**; d) Z. Sun, Q. Ye, C. Chi, J. Wu, *Chem. Soc. Rev.* **2012**, *41*, 7857.
- [2] Z. Sun, J. Wu, *J. Mater. Chem.* **2012**, *22*, 4151; b) Y. Segawa, H. Ito, K. Itami, *Nat. Rev. Mater.* **2016**, *1*, 15002; c) M. D. Watson, A. Fechtenkötter, K. Müllen, *Chem. Rev.* **2001**, *101*, 1267.
- [3] For reviews on the synthesis of PAHs by means of traditional organic synthesis or transition metal-catalyzed methods: a) Y. Segawa, T. Maekawa, K. Itami, *Angew. Chem. Int. Ed.* **2015**, *54*, 66, b) X. Feng, W. Pisula, K. Müllen, *Pure Appl. Chem.* **2009**, *81*, 2203; for some recent notable examples, see: c) V. Rajeshkumar, M. C. Stuparu, *Chem. Commun.* **2016**, *52*, 9957; d) M. Żyła-Karwowska, H. Zhylitskaya, J. Cybińska, T. Lis, P. J. Chmielewski, M. Stępień, *Angew. Chem. Int. Ed.* **2016**, *55*, 14658; e) K. Ozaki, H. Zhang, H. Ito, A. Lei, K. Itami, *Chem. Sci.* **2013**, *4*, 3416; f) M. Iwasaki, Y. Araki, S. Iino, Y. Nishihara, *J. Org. Chem.* **2015**, *80*, 9247.

- [4] a) J. Vollbrecht, H. Bock, C. Wiebeler, S. Schumacher, H. Kitzerow, *Chem. Eur. J.* **2014**, *20*, 12026; b) N.-h. Chang, X.-c. Chen, H. Nonobe, Y. Okuda, H. Mori, K. Nakajima, Y. Nishihara, *Org. Lett.* **2013**, *15*, 3558.
- [5] a) K. Ozaki, K. Kawasumi, M. Shibata, H. Ito, K. Itami, *Nat. Commun.* **2016**, *55*, 1; b) K. Kato, Y. Segawa, K. Itami, *Can. J. Chem.* **2017**, *95*, 329.
- [6] K. Ozaki, K. Murai, W. Matsuoka, K. Kawasumi, H. Ito, K. Itami, *Angew. Chem. Int. Ed.* **2017**, *56*, 1361.
- [7] K. Ozaki, W. Matsuoka, H. Ito, K. Itami, *Org. Lett.* **2017**, *19*, 1930.
- [8] Examples on use of symmetrical reagents, for 1,2-diborylalkenes: a) M. Shimizu, Y. Tomioka, I. Nagao, T. Kadowaki, T. Hiyama, *Chem. Asian. J.* **2012**, *7*, 1644; b) M. Shimizu, I. Nagao, Y. Tomioka, T. Kadowaki, T. Hiyama, *Tetrahedron* **2011**, *67*, 8014; for borofluorene: c) Y. Shoji, N. Tanaka, S. Muranaka, N. Shigeno, H. Sugiyama, K. Takenouchi, F. Hajjaj, T. Fukushima, *Nat. Commun.* **2016**, *7*, 12704; for 2,2'-dihalobiaryls: d) J. Ma, G. Li, Y. Qiao, J. Tu, S. Liu, F. Xu, *Synlett* **2015**, *26*, 1991; e) M. Shimizu, I. Nagao, Y. Tomioka, T. Hiyama, *Angew. Chem. Int. Ed.* **2012**, *47*, 8096; for 9-stannafluorenes: f) I. Nagao, M. Shimizu, T. Hiyama, *Angew. Chem. Int. Ed.* **2009**, *48*, 7573.
- [9] Selected examples: a) M. Catellani, E. Motti, S. Baratta, *Org. Lett.* **2001**, *3*, 3611; b) Y.-D. Lin, C.-L. Cho, C.-W. Ko, A. Pulte, Y.-T. Wu, *J. Org. Chem.* **2012**, *77*, 9979.
- [10] For a review on the use of arynes in synthesis of PAHs: a) D. Wu, H. Ge, S. H. Liu, J. Yin, *RSC Adv.* **2013**, *3*, 22727; for notable examples: b) E. Yoshikawa, Y. Yamamoto, *Angew. Chem. Int. Ed.* **2000**, *39*, 173; c) K. V. Radhakrishnan, E. Yoshikawa, Y. Yamamoto, *Tetrahedron Lett.* **1999**, *40*, 7533; d) S. Bhuvaneshwari, M. Jeganmohan, C.-H. Cheng, *Org. Lett.* **2006**, *8*, 5581; e) T. T. Jayanth, M. Jeganmohan, C.-H. Cheng, *J. Org. Chem.* **2004**, *69*, 8445.
- [11] a) W. C. Fu, Y. Wu, C. M. So, S. M. Wong, A. Lei, F. Y. Kwong, *Org. Lett.* **2016**, *18*, 5300; b) W. K. Chow, C. M. So, C. P. Lau, F. Y. Kwong, *Chem. Eur. J.* **2011**, *17*, 6913; c) P. Y. Choy, W. K. Chow, C. M. So, C. P. Lau, F. Y. Kwong, *Chem. Eur. J.* **2010**, *16*, 9982; d) K. H. Chung, C. M. So, S. M. Wong, C. H. Luk, Z. Zhou, C. P. Lau, F. Y. Kwong, *Chem. Commun.* **2012**, *48*, 1967;
- [12] For a book chapter on domino reactions: a) G. C. Tsui, M. Lautens, *C-H Activation Reactions in Domino Processes. In Domino Reactions*, Wiley-VCH Verlag GmbH & Co. KGaA, **2014**, 67-104. For recent notable examples, see: b) K. Kim, D. Vasu, H. Im, S. Hong, *Angew. Chem. Int. Ed.* **2016**, *128*, 8794; c) T. Jia, A. Bellomo, S. Montel, M. Zhang, K. EL Baina, B. Zheng, P. J. Walsh, *Angew. Chem. Int. Ed.* **2014**, *53*, 260; d) Z. Qureshi, J. Y. Kim, T. Bruun, H. Lam, M. Lautens, *ACS Catal.* **2016**, *6*, 4946; e) K. Yamamoto, T. Bruun J. Y., Kim, L. Zhang, M. Lautens, *Org. Lett.* **2016**, *18*, 2644; f) Y.-B. Zhao, B. Mariampillai, D. A. Candito, B. Laleu, M. Li, M. Lautens, *Angew. Chem. Int. Ed.* **2009**, *48*, 1849.
- [13] For reviews on norbornene-mediated or co-catalyzed and palladium-catalyzed reactions: a) J. Ye, M. Lautens, *Nat. Chem.* **2015**, *7*, 863; b) A. Martins, B. Mariampillai, M. Lautens, *Top. Curr. Chem.* **2009**, *292*, 1; c) N. Della Ca, M. Fontana, E. Motti, M. Catellani, *Acc. Chem. Res.* **2016**, *49*, 1389; for recent notable examples, see: d) B. Luo, J.-M. Gao, M. Lautens, *Org. Lett.* **2016**, *18*, 4166; e) P. Wang, G.-C. Li, P. Jain, M. E. Farmer, J. He, P.-X. Shen, J.-Q. Yu, *J. Am. Chem. Soc.* **2016**, *138*, 14092; f) Z. Dong, J. Wang, Z. Ren, G. Dong, *Angew. Chem. Int. Ed.* **2015**, *54*, 12664; g) H. Zhang, P. Chen, G. Liu, *Angew. Chem. Int. Ed.* **2014**, *53*, 10174; h) F. Sun, M. Li, C. He, B. Wang, B. Li, X. Sui, Z. Gu, *J. Am. Chem. Soc.* **2016**, *138*, 7456.
- [14] For selected examples regarding use of carboxylic acid as removable directing groups in transition-metal catalysis, see: ref. 8b, a) X. Qin, D. Sun, Q. You, Y. Cheng, J. Lan, J. You, *Org. Lett.* **2015**, *17*, 1762; b) J. Cornella, M. Rigbi, I. Larrosa, *Angew. Chem. Int. Ed.* **2011**, *50*, 9429; c) J. Luo, S. Preciado, I. Larrosa, *J. Am. Chem. Soc.* **2014**, *136*, 4109; d) Y. Zhang, H. Zhao, M. Zhang, W. Su, *Angew. Chem. Int. Ed.* **2015**, *54*, 3817; e) D. Lee, S. Chang, *Chem. Eur. J.* **2015**, *21*, 5364; f) J. Luo, S. Preciado, I. Larrosa, *Chem. Commun.* **2015**, *51*, 3127. For a recent review on decarboxylative coupling reactions, see: g) N. Rodríguez, L. J. Goossen, *Chem. Soc. Rev.* **2011**, *40*, 5030.
- [15] a) P. Thansandote, D. G. Hulcoop, M. Langer, M. Lautens, *J. Org. Chem.* **2008**, *74*, 1673; b) D. G. Hulcoop, M. Lautens, *Org. Lett.* **2007**, *9*, 1761; c) N. Della Ca, G. Maestri, M. Malacria, E. Derat, M. Catellani, *Angew. Chem. Int. Ed.* **2011**, *50*, 12257; d) M. Cheng, J. Yan, F. Hu, H. Chen, Y. Hu, *Chem. Sci.* **2013**, *4*, 526.
- [16] After reaction, ca. 20% of by-product **B1** was observed by GC analysis.



- [17] L. Ying, C.-L. Ho, H. Wu, Y. Cao, W.-Y. Wong, *Adv. Mater.* **2014**, *26*, 2459.
- [18] a) C. Bailly, *Chem. Soc. Rev.* **2012**, *112*, 3611; b) D.-L. Ma, H.-Z. He, K.-H. Leung, D. S.-H. Chan, C.-H. Leung, *Angew. Chem. Int. Ed.* **2013**, *52*, 7666.
- [19] J. He, H. Jiang, R. Takise, R.-Y. Zhu, G. Chen, H.-X. Dai, T. G. M. Dhar, J. Shi, H. Zhang, P. T. W. Cheng, J.-Q. Yu, *Angew. Chem. Int. Ed.* **2016**, *55*, 785.
- [20] a) Z. Liang, Q. Tang, R. Mao, D. Liu, J. Xu, Q. Miao, *Adv. Mater.* **2011**, *23*, 5514; b) Z. Liang, Q. Tang, J. Xu, Q. Miao, *Adv. Mater.* **2011**, *23*, 1535; c) Q. Miao, *Adv. Mater.* **2014**, *26*, 5541.
- [21] a) K. Kato, Y. Segawa, L. T. Scott, K. Itami, *Chem. Asian. J.* **2015**, *10*, 1635; b) K. Y. Cheung, X. Xu, Q. Miao, *J. Am. Chem. Soc.* **2015**, *137*, 3910; c) J. Luo, X. Xu, R. Mao, Q. Miao, *J. Am. Chem. Soc.* **2012**, *134*, 13796; X. Yang, D. Liu, Q. Miao, *Angew. Chem. Int. Ed.* **2014**, *53*, 6786.
- [22] The X-ray crystallographic data for **3e** (CCDC 1539219) and **3f** (CCDC 1539220) is available free of charge on the The Cambridge Crystallographic Data Centre at: www.ccdc.cam.ac.uk/data_request/cif.
- [23] For the initial reports on CMD, see: a) M. Lafrance, K. Fagnou, *J. Am. Chem. Soc.* **2006**, *128*, 16496; b) S. I. Gorelsky, D. Lapointe, K. Fagnou, *J. Am. Chem. Soc.* **2008**, *130*, 10848.
- [24] W.-J. Chen, Z. Lin, *Dalton Trans.* **2014**, *43*, 11138.