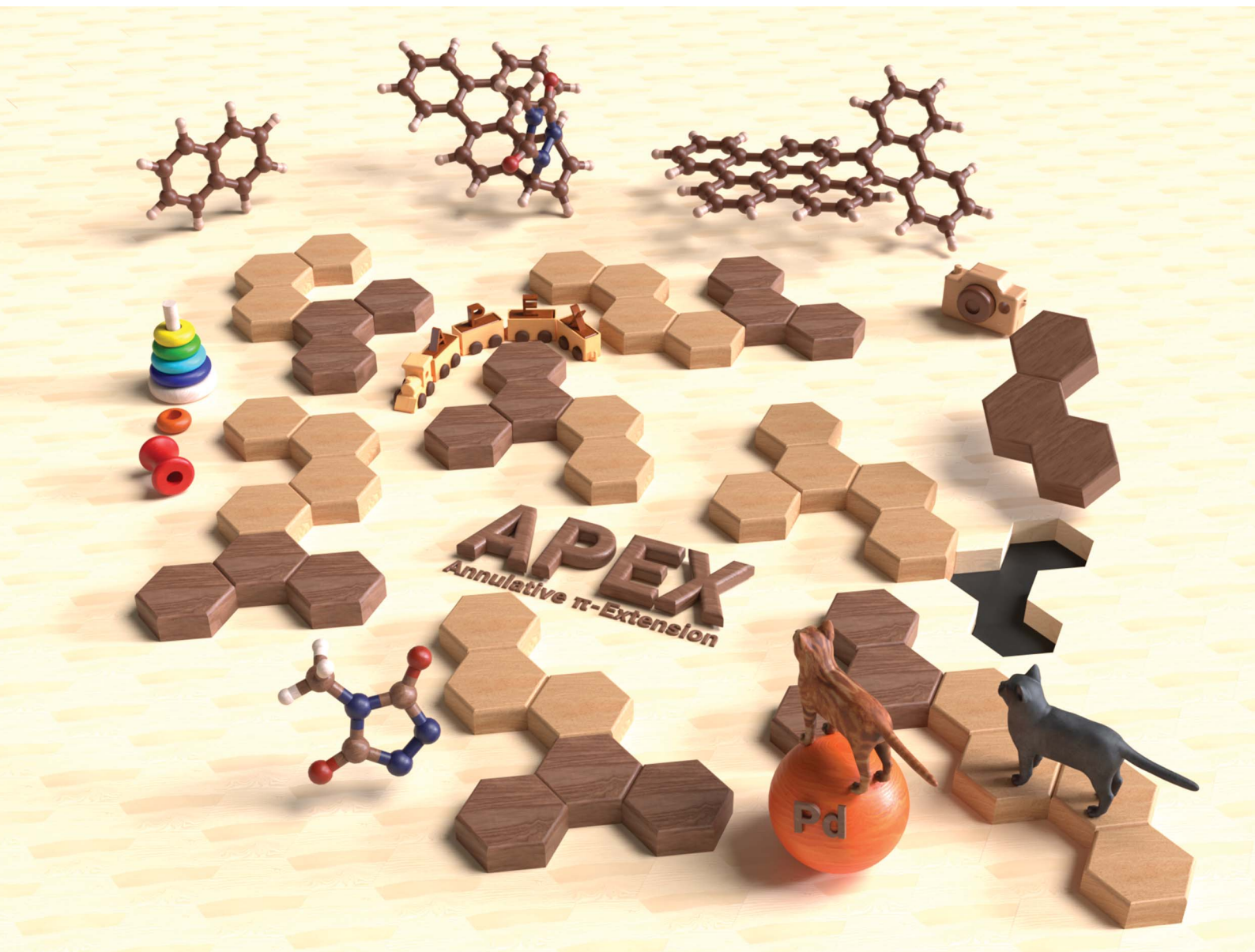


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L-region-selective annulative π -extension through dearomative activation of polycyclic aromatic hydrocarbons

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Annulative π -extension (APEX) reaction is a useful aromatic ring-fusion method for the synthesis of large polycyclic aromatic hydrocarbons (PAHs) from unfunctionalized small PAHs. While APEX reactions in the *K*-, *M*-, and *bay*-regions of PAHs have been developed, *L*-region selective APEX is yet to be achieved. Herein, we report a stepwise *L*-region selective APEX of unfunctionalized PAHs by dearomative activation with *N*-methyltriazoline dione, followed by Pd-catalyzed annulation with aryl Grignard reagents. Various difficult-to-synthesize core-expanded PAHs can be synthesized by *L*-APEX from unfunctionalized naphthalene, phenanthrene, chrysene, and [4]helicene.

Introduction

Annulative π -extension (APEX)¹ reaction, employed to extend a new fused aromatic ring(s) to unfunctionalized aromatics, has attracted attention in recent years as a powerful method for the precise synthesis of polycyclic aromatic compounds and nanographenes (Fig. 1a). The advantageous characteristics of APEX, such as unnecessary prefunctionalized aromatics and direct C–H bond transformations, enable late-stage modification, successive elongation, and diversity-oriented synthesis of nanographenes. In recent years, various research groups, including our group, have developed APEX reactions.^{2–7} In particular, with regard to the APEX reaction of polycyclic aromatic hydrocarbons (PAHs), the Diels–Alder reactions with alkenes, alkynes, and arynes for the *bay*-region (concave armchair edge) of perylene derivatives are well-known.² We have also developed the *K*-region selective APEX reaction of PAHs using a Pd catalyst,³ and the *M*-region APEX selective APEX using *N*-methyl-1,2,4-triazoline-3,5-dione (MTAD) and Fe-catalyzed diarylation.⁴ In addition, a limited example of *fissure*-region (zig-zag edge surrounded by two neighboring *peri*-carbon atoms in naphthalene) selective APEX reactions was recently achieved by a Li(0)-mediated mechanochemical Birch reductive arylation/cyclodehydrogenation sequence.⁵ However, no *L*-region (C1–C2 positions of naphthalene)-selective APEX (*L*-

APEX) reaction of PAHs has been developed to date. The development of this missing-piece *L*-APEX can facilitate a more comprehensive synthesis of a wider variety of nanographenes and will lead to a further step forward in nanographene synthetic chemistry.⁸

Taking *L*-APEX of naphthalene (**1a**) to benzo[*g*]chrysene as an example, the conventional stepwise π -extension seems to be applicable by C1-position selective bromination of **1a**, Suzuki–Miyaura coupling with (1,1'-biphenyl)-2-ylboronic acid, and cyclodehydrogenation, so-called Scholl reaction, of 1-([1,1-biphenyl]-2-yl)naphthalene (**A**) with triflic acid (TfOH) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (Fig. 1b). However, a synthetically fatal problem occurs in the final Scholl reaction step. The Scholl reaction of **A** with DDQ/TfOH is initiated by protonation, and the obtained arenium cation **B** predominantly undergoes a 1,2-aryl shift to afford the thermodynamically more stable cation species **C**. Aromatic electrophilic substitution does not give benzo[*g*]chrysene (*L*-APEX product), but its isomer *M*-APEX product, benzo[*f*]tetraphene, is the major product. This counterintuitive aromatic rearrangement often occurs in the synthesis of nanographenes when Scholl reactions are applied to sterically congested aromatics.^{9,10} Therefore, the development of *L*-APEX reactions is highly important in terms of not only filling in missing pieces in APEX chemistry but also providing a complementary method in synthetic chemistry for various nanographenes.

Results and discussion

To achieve the unprecedented *L*-APEX reaction, we considered that Sarlah's work on dearomative functionalization of arenes with MTAD would be valid.¹¹ Indeed, in 2021, he and our group jointly demonstrated the *M*-APEX reaction of PAHs through (i) regioselective dearomatization of PAHs **1** with MTAD, (ii) Fe-

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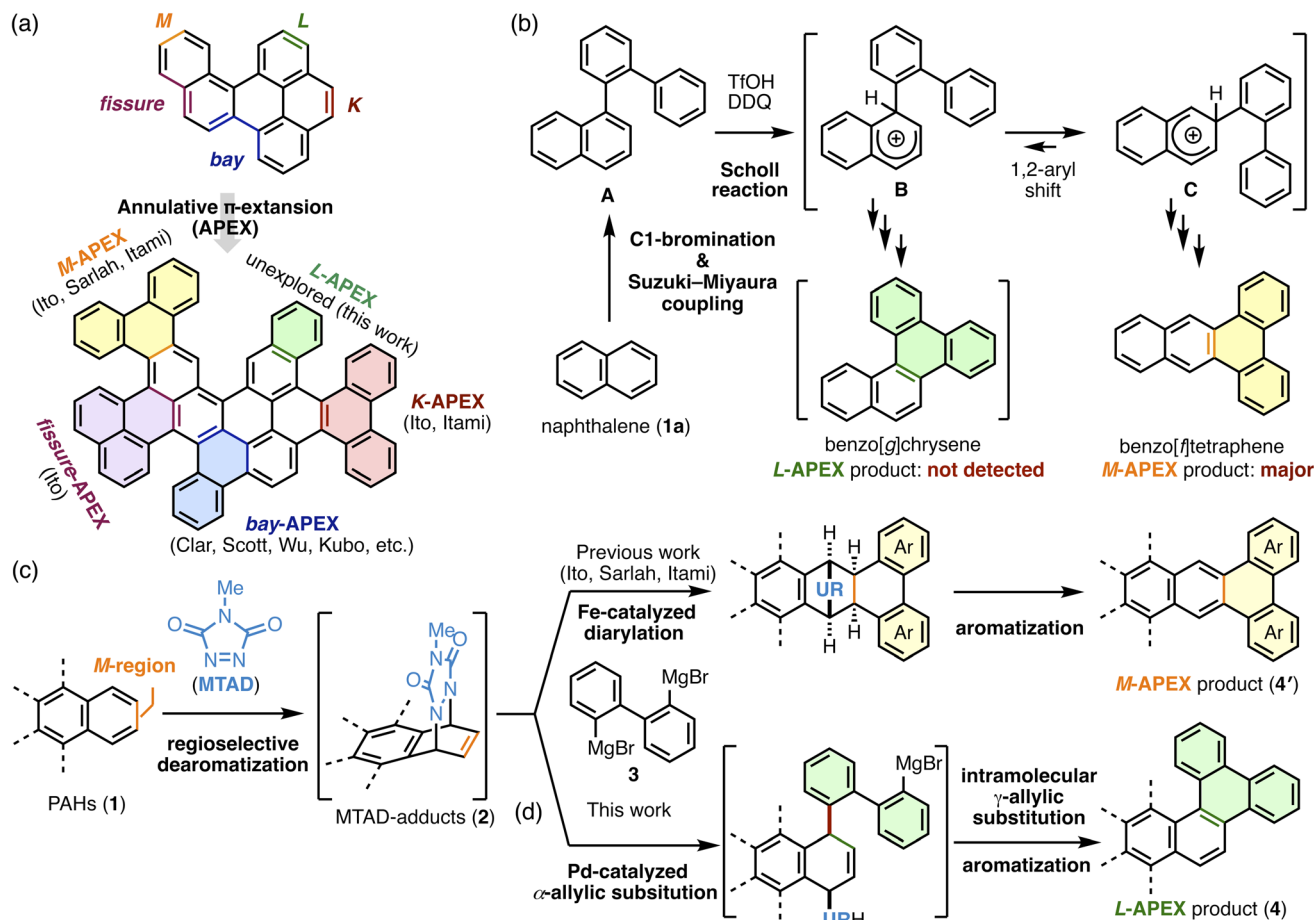


Fig. 1 (a) Peripheral regions of PAHs and annulative π -extension (APEX). (b) Classical stepwise π -extension route from naphthalene to benzo[*g*]chrysene/benzotetraphene. (c) Previous work on *M*-APEX via dearomative activation of PAHs followed by Fe-catalyzed di-annulation and aromatization. (d) This study.

catalyzed diarylation of MTAD-adducts **2** with bis-Grignard reagents **3**, and (iii) aromatization by elimination of a bridged urea moiety, affording *M*-APEX products **4'** (Fig. 1c).⁴ On one hand, MTAD-adducts **2** possess olefinic moieties, which are suitable for Fe-catalyzed arylation,¹² and on the other hand, they possess allylic urea moieties, which are active for various allylic substitution reactions as actively demonstrated by Sarlah and other groups.^{11,13} As a part of our continuous investigation into APEX chemistry, herein, we report the *L*-region selective APEX reaction of PAHs by dearomative activation with MTAD, followed by Pd-catalyzed stepwise allylic substitution and aromatization (Fig. 1d). The use of di-Grignard reagents and Pd catalysts enabled intermolecular and intramolecular allylic substitution, affording sterically congested *L*-region extended products **4**.

Our initial investigation toward *L*-APEX is intermolecular α -allylic substitution of naphthalene-MTAD adduct **2a**, which was easily obtained by the photoinduced cycloaddition of **1a** with MTAD (Fig. 2a). In the previous Sarlah's study, α -allylic substitution of **2a** with phenyl Grignard reagent (PhMgBr) was achieved by catalytic amounts of Pd₂(dba)₃ (dba: dibenzylideneacetone) and DPEphos, affording the *syn*-1,4-adduct.^{11a} Inspired by this result, we applied a similar catalytic

system using Pd₂(dba)₃, phosphine ligands and biphenyl Grignard reagent **3a**. Unlike our expectation to obtain *syn*-1,4-adduct **5** as a major product, *anti*-1,2-adduct **5'** was preferentially obtained via γ -allylic substitution even using various phosphine ligands such as XPhos and 1,4-bis(diphenylphosphino)butane (dppb) (see SI for the results using other phosphine ligands). The reaction with **3a** in the presence of Pd(dba)₂/XPhos gave **5'** in 53% yield, whose structure was elucidated by X-ray diffraction (XRD) analysis of its *N*-methylated derivative **5'-Me** (Fig. S1). Then, the bis-Grignard reagent **3b** was used to anticipate changes in the reaction profile and simultaneous cyclization. Interestingly, the use of dppb and 1,1'-bis(diphenylphosphino)ferrocene (dppf) afforded the desired 1,4-adduct **5** in 57% and 42% yields, respectively, through α -allylic substitution. In these reactions, the simultaneous cyclization to afford **7** (Fig. 2c) did not occur. The relative configuration and regioselectivity of **5** were also confirmed by XRD analysis (see Fig. S3). Next, we attempted simple oxidative/acidic cyclization of **5** or **5'** in the presence of DDQ and TfOH¹⁴ or FeCl₃ (ref. 15) (Fig. 2b). However, both reactions gave a mixture of *L*-APEX product **4a** and *M*-APEX product **4a'**, which implies a 1,2-aryl shift^{9,10} and undesired cyclization occur in those cationic intermediates. Other examinations of the one-pot



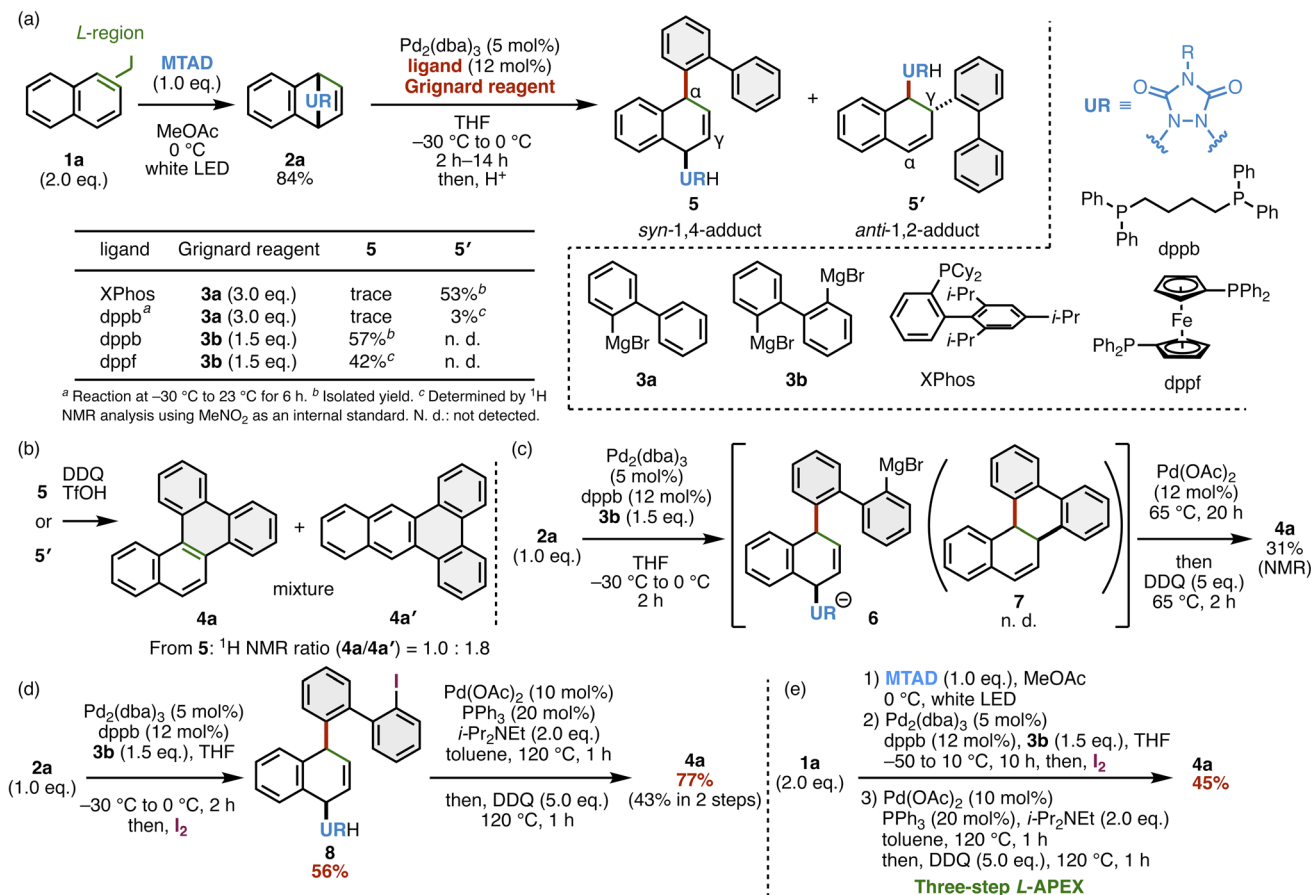


Fig. 2 (a) Initial investigation on L-APEX via Pd-catalyzed α -allylic substitution of 4 with bis-Grignard reagent 3, cationic cyclization and aromatization. (b) Two-step L-APEX via Pd-catalyzed one-pot α -allylic substitution and cyclization. (c) L-APEX via Pd-catalyzed one-pot α - and γ -allylic substitutions. (d and e) Stepwise L-APEX via Pd-catalyzed one-pot α - and γ -allylic substitutions.

annulation of 2a were performed by (i) Pd(0)-catalyzed α -allylic substitution with 3b, (ii) Pd(II)-catalyzed intramolecular γ -allylic substitution of 6 by the remaining aryl magnesium bromide moiety, and (iii) oxidation of the *in situ* generated precursor 7, yielding 4a in 31% NMR yield (Fig. 2c). While this one-pot procedure is attractive in terms of step economy, the reaction mixture contained various side products; thus, the isolation of 4a was expected to be difficult. To improve the yield of final product 4a, we further examined the reaction conditions and found a stepwise L-APEX via the preparation and isolation of iodoarene 8 by trapping aryl Grignard species 6 with iodine, (ii) Pd(OAc)₂/PPh₃-catalyzed intramolecular γ -allylic substitution of 8 in a S_N2' fashion, and (iii) oxidation by DDQ (Fig. 2d). This protocol enabled the isolation of 8 and 4a in 56% and 77% yields, respectively, and 43% of the overall yield from 2a was satisfactory. Finally, a one-pot three-step L-APEX sequence from 1a to 4a was demonstrated to afford 4a in 45% isolated yield (Fig. 2e), which is a reasonable result considering the result shown in Fig. 2d.

Using the optimized conditions for the three-step L-APEX from naphthalene, we examined the scope of PAHs in this reaction (Fig. 3). In the first step (step 1), the cycloaddition of phenanthrene (1b), benzo[*c*]phenanthrene (1c), and chrysene (1d) with MTAD gave cycloadducts 2b, 2c, and 2d selectively.

Using crude MTAD-adducts without purification, α -allylic arylation/iodination (step 2) and intramolecular γ -allylic arylation/oxidation were successively demonstrated, affording 4a in 45%, benzo[*f*]picene (4b)/dibenzo[*c,g*]chrysene (4b') in 10%/8%, dibenzo[*a,j*]picene (4c)/benzo[*g*]naphtho[2,1-*c*]chrysene (4c') in 13%/14% and dibenzo[*a,c*]picene (4d)/benzo[*g*]naphtho[1,2-*c*]chrysene (4d') in 6%/8% isolated yields. In the allylic arylation of 2b, 2c and 2d, nearly no regioselectivity was observed, although they had two sterically different positions. Interestingly, sterically congested helicenes 4b', 4c' and 4d' were also obtained.

Motivated by the presence of *K*- and *L*-regions in the L-APEX products 4a and 4b', we demonstrated further π -extension by APEX reactions. Previously, we achieved *M*-APEX of 4a to afford 9,^{4a} and *K*, *bay*-APEX of 4a to afford 10 (ref. 3e) (Fig. 4a). The newly developed L-APEX reaction was applied to 4a to afford tribenzo[*a,c,j*]picene (11) in 5% yield. In this reaction, 4a, which can reversibly form the corresponding MTAD-4a adduct, as well as uncyclized intermediates structurally related to 8 and its dehalogenated analogue, were observed during purification, leading to a decreased yield of 11. As another demonstration, pentabenzo[*a,c,f,g,i,j,rst*]pentaphene (13) was obtained in overall 10% yield by Pd-catalyzed *K*-APEX of 4b' with 2,2'-diiodo-1,1'-biphenyl (12). As often encountered in a previous study,^{3e} these



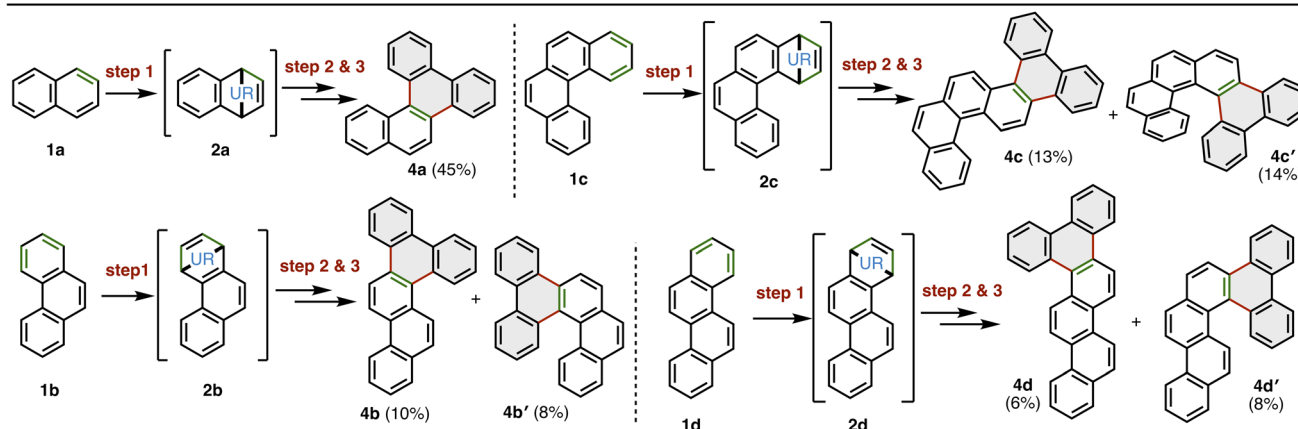
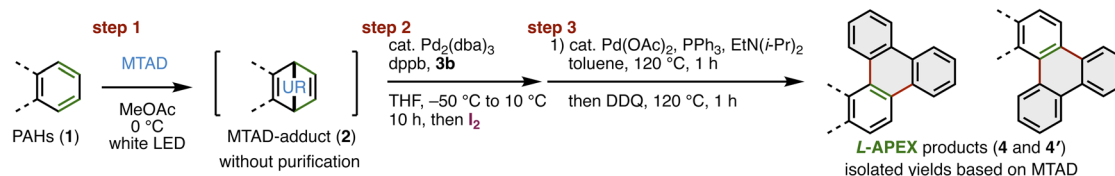


Fig. 3 Scope of PAHs in a three-step *L*-APEX reaction. Reaction conditions for step 1: MTAD (1.0 eq.) and PAHs (2.0–10 eq.) in MeOAc at 0 °C with white LED irradiation; step 2: Pd₂(dba)₃ (5 mol%), dppb (12 mol%) and **3b** (1.5 eq.) in THF at –50 °C to 10 °C for 10 h, then I₂ in THF; step 3: Pd(OAc)₂ (10 mol%), PPh₃ (20 mol%) and *i*-Pr₂NEt (2.0 eq.), toluene at 120 °C for 1 h, then DDQ (5.0 eq.) at 120 °C for 1 h.

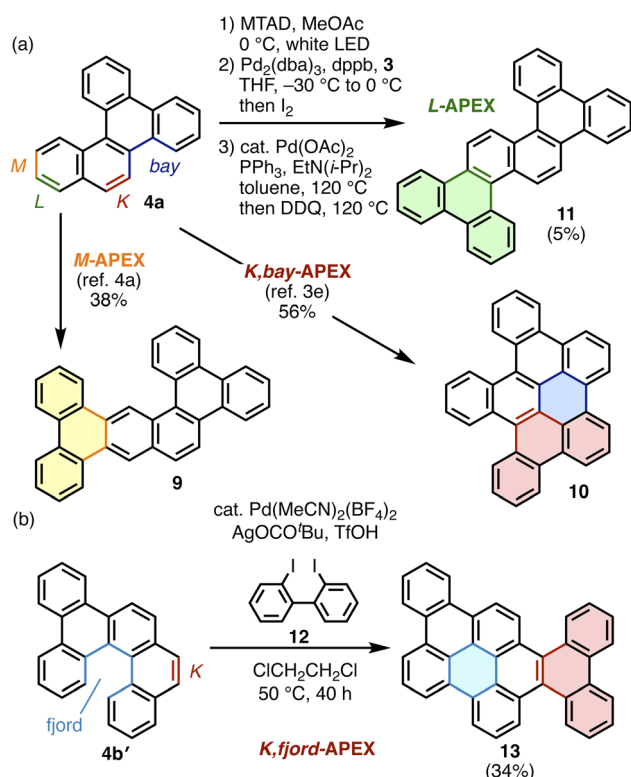


Fig. 4 (a) *K*, *L*, *M*, and *bay*-APEX of **4a**. (b) Further π -extension of **4b'** using Pd-catalyzed *K*-APEX with diiodobiphenyl **12** and simultaneous cyclodehydrogenation in the *fjord*-region.

oxidative reaction conditions induced simultaneous cyclodehydrogenation in the *fjord*-region, giving fully graphitized nanographene **13**.

Conclusions

In conclusion, we have developed an untapped *L*-APEX reaction of unfunctionalized PAHs by dearomative activation with MTAD, followed by Pd-catalyzed one-step or two-step annulation with aryl Grignard reagents. MTAD was selectively attached to the terminal benzo-fusion moieties of PAHs, and the generated allyl urea moieties were arylated by Pd-catalyzed α - and γ -allylic substitutions with bis-Grignard reagents. While the regioselectivity between different *L*-regions and the total yields was low, this represents the first example of an *L*-region APEX reaction, and difficult-to-synthesize PAH molecules can be obtained by this method.

Author contributions

K. N. mainly synthesized, analyzed, and characterized all the compounds and performed the theoretical calculations. W. M. developed the preliminary experimental results related to this study. H. I. and K. I. designed and directed the study and supervised the experiments. The manuscript was written by H. I., and all authors finalized the manuscript through proof-reading. All the authors approved the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

CCDC 2506075–2506078 (**5'**, **8**, **11** and **5**) contain the supplementary crystallographic data for this paper.^{16a–d}



Supplementary information (SI): experimental and characterization data, including crystallographic data, and NMR spectra. See DOI: <https://doi.org/10.1039/d5sc09309k>.

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