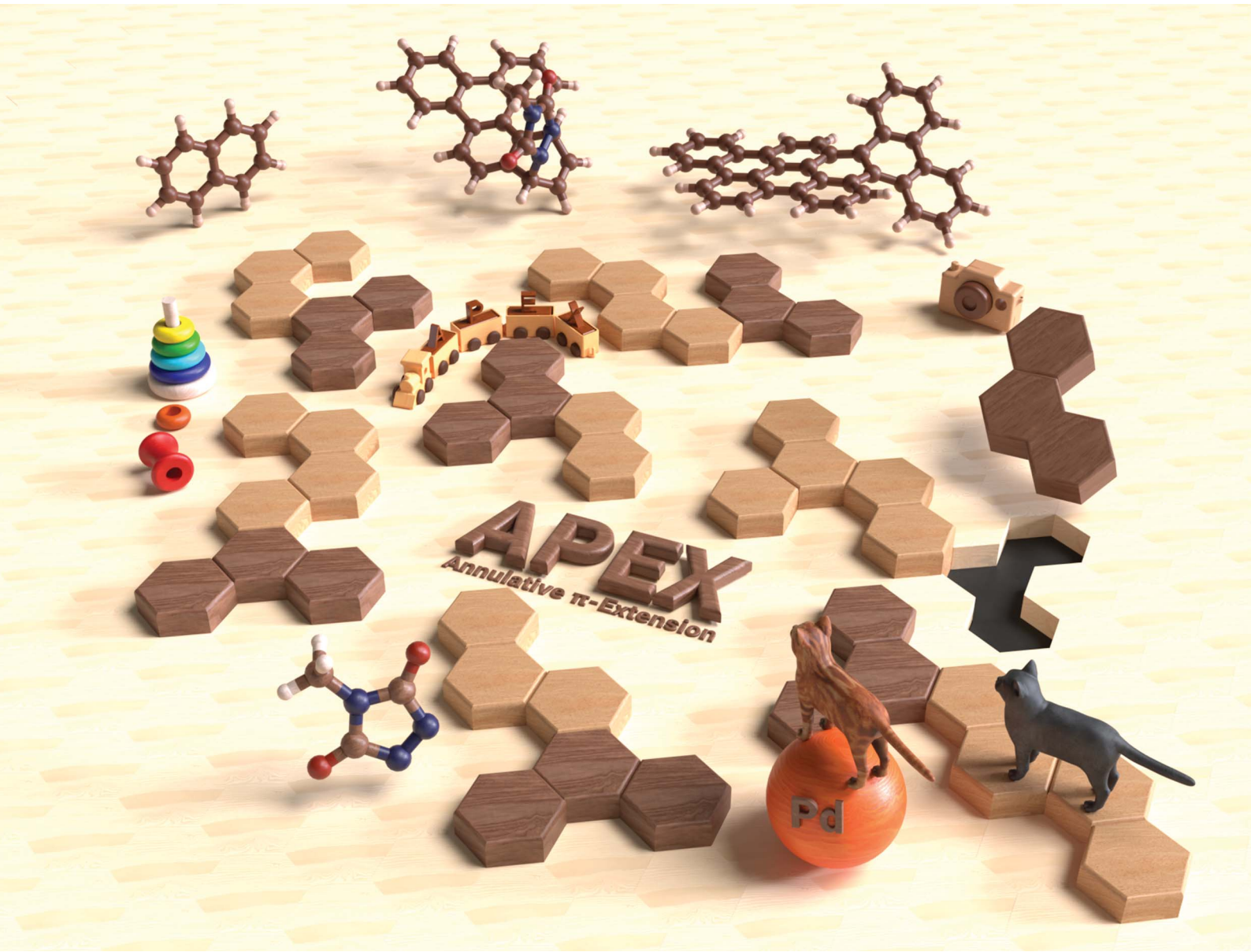
Volume 17
Number 8
25 February 2026
Pages 3861–4348

Chemical Science

rsc.li/chemical-science



ISSN 2041-6539

ROYAL SOCIETY OF CHEMISTRY

EDGE ARTICLE
Hideto Ito, Kenichiro Itami *et al.*
L-region-selective annulative π-extension through dearomative activation of polycyclic aromatic hydrocarbons

Chemical Science

ROYAL SOCIETY OF CHEMISTRY

EDGE ARTICLE

View Article Online
View Journal | View Issue

Cite this: *Chem. Sci.*, 2026, **17**, 3998

All publication charges for this article have been paid for by the Royal Society of Chemistry

Received 28th November 2025
Accepted 27th January 2026

DOI: 10.1039/d5sc09309k

rsc.li/chemical-science

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

Kanami Nakata,[a] Wataru Matsuoka,[a] Hideto Ito *[a] and Kenichiro Itami *[bcd]

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-

[a]*Department of Chemistry, Graduate School of Science, Nagoya University, Nagoya 464-8602, Japan. E-mail: ito.hideto.p4@f.mail.nagoya-u.ac.jp*

[b]*Molecule Creation Laboratory, Pioneering Research Institute (PRI), RIKEN, Wako, Saitama 351-0198, Japan. E-mail: kenichiro.itami@riken.jp*

[c]*Expanded Chemical Space Research Team, Center for Sustainable Resource Science (CSRS), RIKEN, Wako, Saitama 351-0198, Japan*

[d]*Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University, Nagoya 464-8602, Japan*

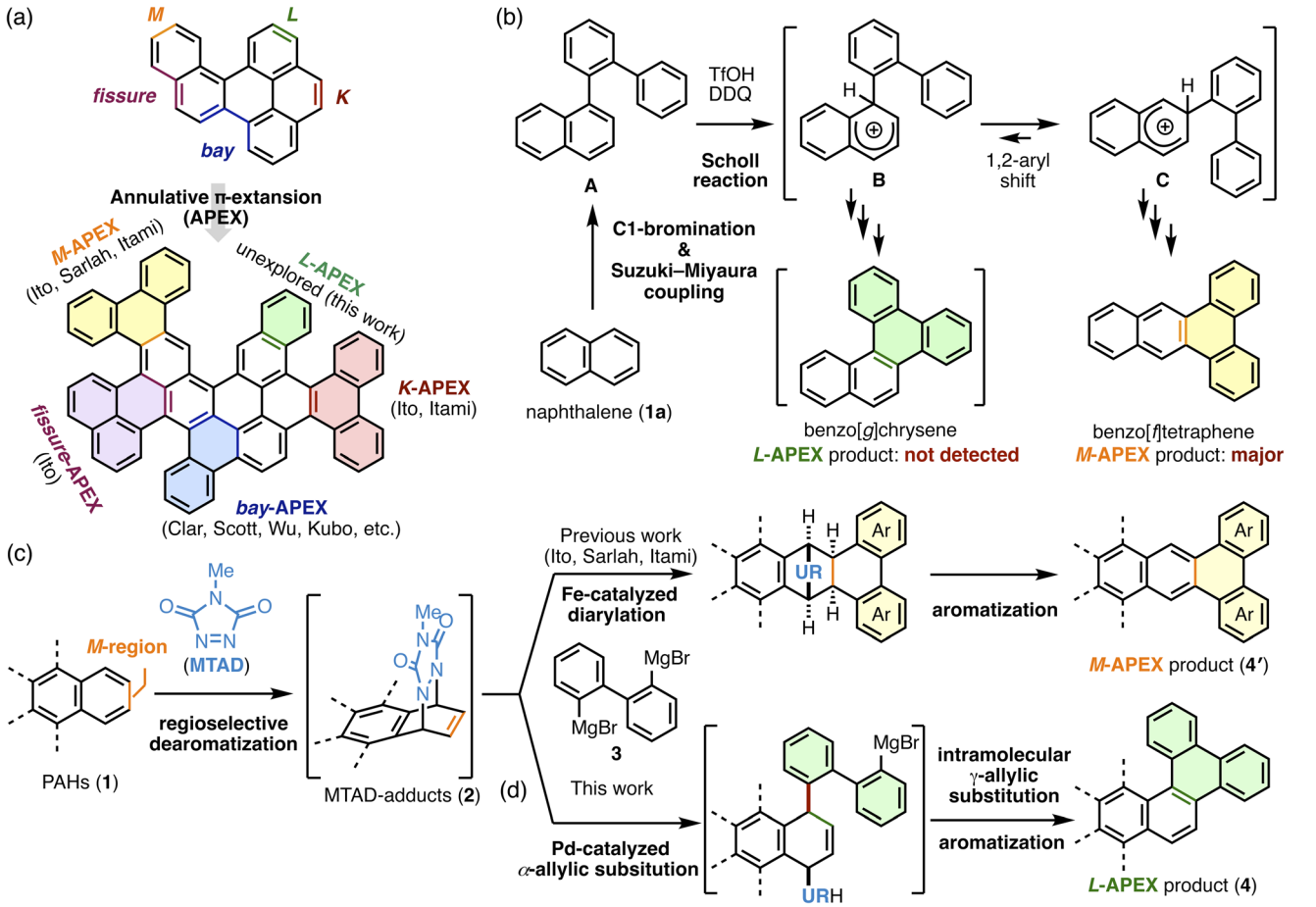


Fig. 1 (a) Peripheral regions of PAHs and annulative π-extension (APEX). (b) Classical stepwise π-extension route from naphthalene to benzochrysene/benzotetraphene. (c) Previous work on *M*-APEX *via* dearomative activation of PAHs followed by Fe-catalyzed di-annulation and aromatization. (d) This study.

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 $Pd_2(dba)_3$ (dba: dibenzylideneacetone) and DPEphos, affording the *syn*-1,4-adduct.[11a] Inspired by this result, we applied a similar catalytic system using $Pd_2(dba)_3$, 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 TfOH[14] or $FeCl_3$ (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

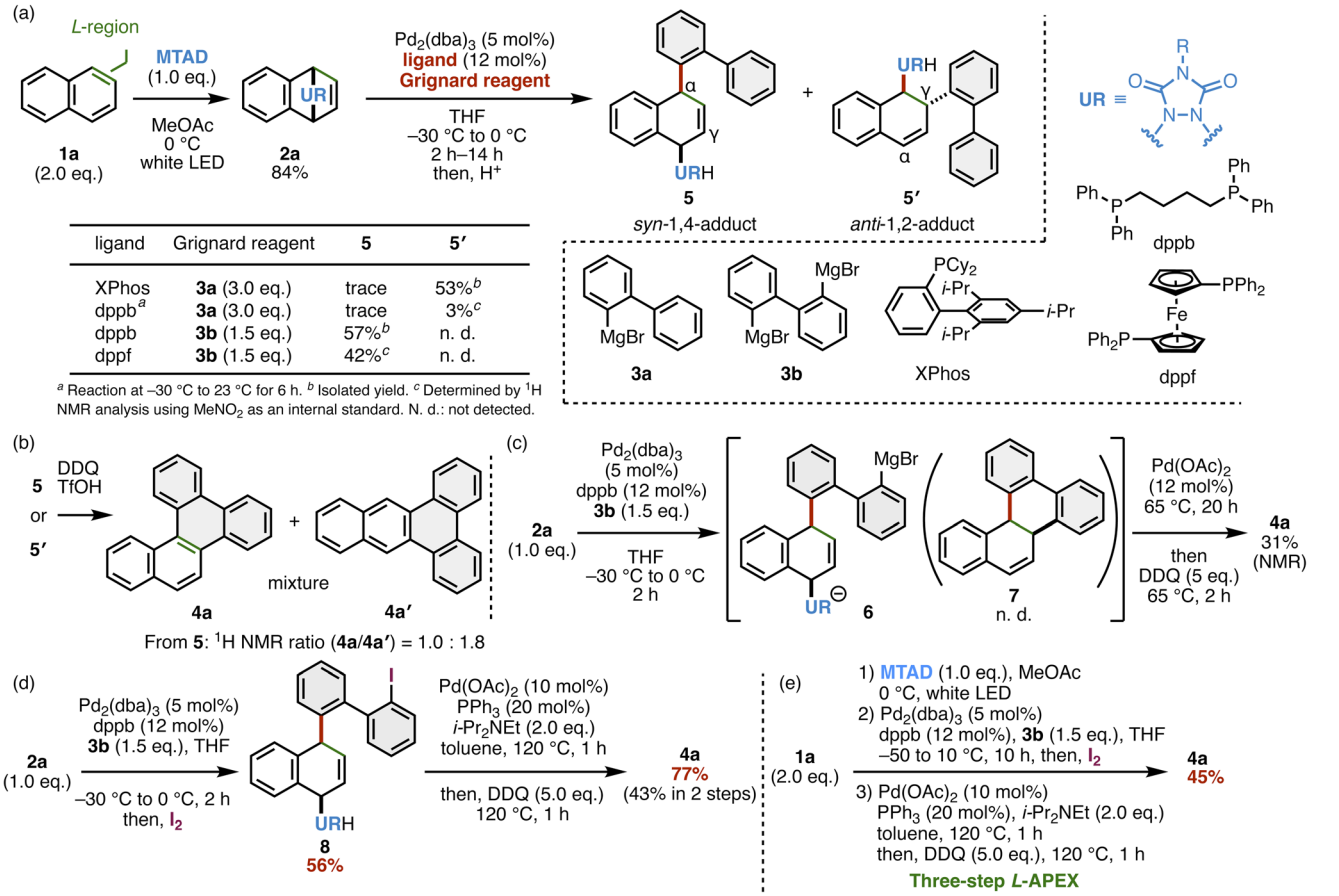


Fig. 2 (a) Initial investigation on *L*-APEX *via* Pd-catalyzed α-allylic substitution of **4** with bis-Grignard reagent **3**, cationic cyclization and aromatization. (b) Two-step *L*-APEX *via* Pd-catalyzed one-pot α-allylic substitution and cyclization. (c) *L*-APEX *via* Pd-catalyzed one-pot α- 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) $Pd(OAc)_2$/PPh_3-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. 3*e*) (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*,*fg*,*ij*,*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

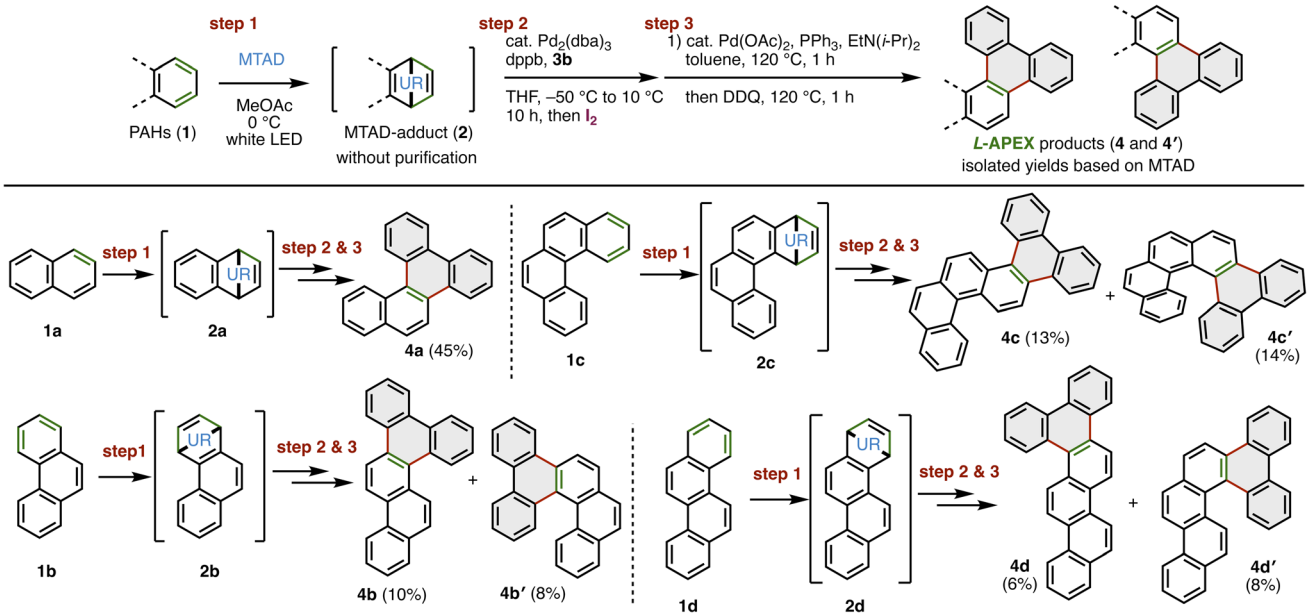


Fig. 3 Scope of PAHs in a three-step *L*-APEX reaction. Reaction conditions for step 1: MTAD (1.0 eq.) and PAHs (2.0–10 eq.) in MeOAc at 0 °C with white LED irradiation; step 2: $Pd_2(dba)_3$ (5 mol%), dppb (12 mol%) and **3b** (1.5 eq.) in THF at −50 °C to 10 °C for 10 h, then I_2 in THF; step 3: $Pd(OAc)_2$ (10 mol%), PPh_3 (20 mol%) and *i*-Pr_2NEt (2.0 eq.), toluene at 120 °C for 1 h, then DDQ (5.0 eq.) at 120 °C for 1 h.

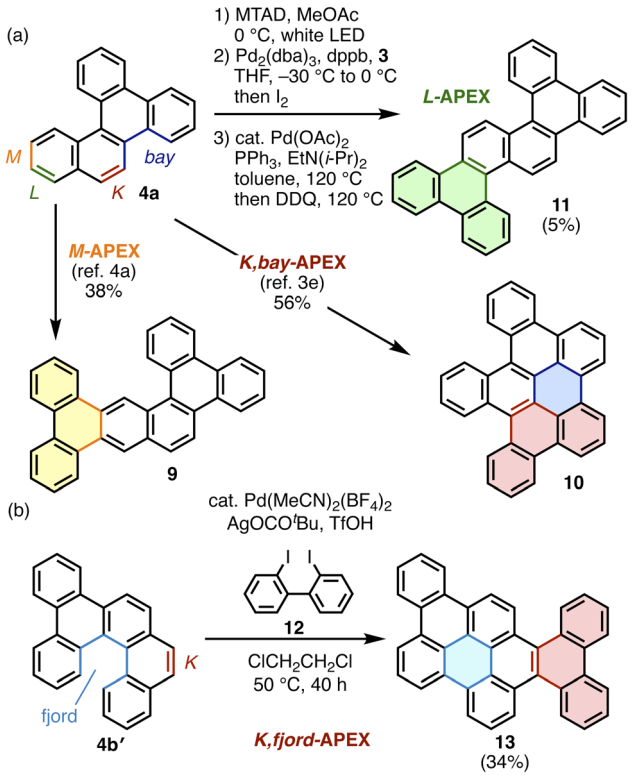


Fig. 4 (a) *K*, *L*, *M*, and *bay*-APEX of **4a**. (b) Further π-extension of **4b′** using Pd-catalyzed *K*-APEX with diiodobiphenyl **12** and simultaneous cyclodehydrogenation in the *fjord*-region.

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 proofreading. 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 crystallo-graphic data, and NMR spectra. See DOI: https://doi.org/10.1039/d5sc09309k.

Acknowledgements

This study was supported by the JST-ERATO program (JPMJER1302 to K. I.), JSPS KAKENHI (JP19H05463 and JP25H00429 to K. I., JP21H01931, JP25K01764 and JP25H01408 to H. I.), Tatematsu Foundation (22B025 to H. I.), and Kondo Memorial Foundation (2022-03 to H. I.). We thank Dr Keigo E. Yamada, Dr Hiroki Shudo, Mr Daiki Imoto, Dr Kou P. Kawahara, and Mr Takato Mori (Nagoya University) for their assistance with X-ray diffraction analysis, and Mr Kumpei Hasebe for assistance with MS analysis. The DART-MS measurements were conducted using resources from the Chemical Instrumentation Facility (CIF) of the Research Center for Materials Science (RCMS) at Nagoya University. The computations were performed at the Research Center for Computational Science, Okazaki, Japan (Project No. 23-IMS-C061, 24-IMS-C059, and 25-IMS-C061).

Notes and references

1 Reviews on APEX reactions: (*a*) H. Ito, K. Ozaki and K. Itami, *Angew. Chem., Int. Ed.*, 2017, **56**, 11144–11148; (*b*) H. Ito, Y. Segawa, K. Murakami and K. Itami, *J. Am. Chem. Soc.*, 2019, **141**, 3–10; (*c*) H. Ito, K. P. Kawahara and K. Itami, *Synthesis*, 2024, **2024**(56), 1335–1354.

2 *Bay*-region selective APEX reaction of PAHs: (*a*) E. Clar, *Ber. Dtsch. Chem. Ges.*, 1932, **65**, 846–853; (*b*) E. Clar and M. Zander, *J. Chem. Soc.*, 1957, 4616–4619; (*c*) E. Clar, *Nature*, 1948, **161**, 238–239; (*d*) E. H. Fort, P. M. Donovan and L. T. Scott, *J. Am. Chem. Soc.*, 2009, **131**, 16006–16007; (*e*) E. H. Fort and L. T. Scott, *Angew. Chem., Int. Ed.*, 2010, **49**, 6626–6628; (*f*) E. H. Fort and L. T. Scott, *J. Mater. Chem.*, 2011, **21**, 1373–1381; (*g*) E. H. Fort, M. S. Jeffreys and L. T. Scott, *Chem. Commun.*, 2012, **48**, 8102–8104; (*h*) E. H. Fort and L. T. Scott, *Tetrahedron Lett.*, 2011, **52**, 2051–2054; (*i*) H. Hopff and H. R. Schweizer, *Helv. Chim. Acta*, 1959, **42**, 2315–2333; (*j*) J. Li, C. Jiao, K.-W. Huang and J. Wu, *Chem.–Eur. J.*, 2011, **17**, 14672–14680; (*k*) A. Konishi, Y. Hirao, K. Matsumoto, H. Kurata and T. Kubo, *Chem. Lett.*, 2013, **42**, 592–594; (*l*) B. Schuler, S. Collazos, L. Gross, G. Meyer, D. Pérez, E. Guitián and D. Peña, *Angew. Chem., Int. Ed.*, 2014, **53**, 9004–9006; (*m*) T. Nakamuro, K. Kumazawa, H. Ito and K. Itami, *Synlett*, 2019, **30**, 423–428; (*n*) N. Zink-Lorre, A. Doncel-Giménez, E. Font-Sanchis, J. Calbo, Á. Sastre-Santos, E. Ortí and F. Fernández-Lázaro, *Org. Chem. Front.*, 2019, **6**, 2860–2871.

3 *K*-region selective APEX reaction of PAHs: (*a*) K. Ozaki, K. Kawasumi, M. Shibata, H. Ito and K. Itami, *Nat. Commun.*, 2015, **6**, 6251; (*b*) Y. Yano, H. Ito, Y. Segawa and K. Itami, *Synlett*, 2016, **27**, 2081–2084; (*c*) Y. Morinaka, H. Ito, K. J. Fujimoto, T. Yanai, Y. Ono, T. Tanaka and K. Itami, *Angew. Chem., Int. Ed.*, 2024, **63**, e202409619; (*d*) M. Shibata, H. Ito and K. Itami, *J. Am. Chem. Soc.*, 2018, **140**, 2196–2200; (*e*) W. Matsuoka, H. Ito and K. Itami, *Angew. Chem., Int. Ed.*, 2017, **56**, 12224–12228; (*f*) M. Kubo, K. Noguchi and K. Nakano, *ChemPlusChem*, 2121, **86**, 171–175; (*g*) A. Swain, K. Radacki, H. Braunschweig and P. Ravat, *Chem. Sci.*, 2024, **15**, 11737–11747; (*h*) K. Song, Y. Zhang, S. Wu, S. Yang, S. Wei, S. Chen, H. Ito, K. Itami and Y. Li, *Org. Chem. Front.*, 2025, **12**, 2225–2231; (*i*) Y. Nakashige, H. Nakatsuji, K. Matsushima, K. Murakami, H. Ito and K. Itami, *Precis. Chem.*, 2025, **3**, 535–540.

4 *M*-region selective APEX reaction of PAHs: (*a*) W. Matsuoka, H. Ito, D. Sarlah and K. Itami, *Nat. Commun.*, 2021, **12**, 3940; (*b*) W. Matsuoka, K. P. Kawahara, H. Ito, D. Sarlah and K. Itami, *J. Am. Chem. Soc.*, 2023, **145**, 658–664; (*c*) V. M. Pham and N. Cramer, *Angew. Chem., Int. Ed.*, 2014, **53**, 3484–3487.

5 *Fissure*-region selective APEX reaction of PAHs: (*a*) Y. Toyama, A. Yagi, K. Itami and H. Ito, *Nat. Commun.*, 2025, **16**, 5044; (*b*) M. Murata, M. Togo, D. Mishima, A. Harada and M. Muraoka, *Org. Lett.*, 2020, **22**, 4160–4163.

6 Other APEX reactions from our group: (*a*) H. Kitano, W. Matsuoka, H. Ito and K. Itami, *Chem. Sci.*, 2018, **9**, 7556–7560; (*b*) K. P. Kawahara, W. Matsuoka, H. Ito and K. Itami, *Angew. Chem., Int. Ed.*, 2020, **59**, 6383–6388; (*c*) K. P. Kawahara, H. Ito and K. Itami, *Chem. Commun.*, 2023, **59**, 1157–1160; (*d*) K. P. Kawahara, H. Ito and K. Itami, *Org. Chem. Front.*, 2023, **10**, 1880–1889.

7 Other related transition metal-catalyzed APEX reactions of simple aromatics: (*a*) T. Sakakibara, Y. Tanaka and S. Yamaki, *Chem. Lett.*, 1986, **15**, 797–800; (*b*) M. Yamashita, H. Horiguchi, K. Hirano, T. Satoh and M. Miura, *J. Org. Chem.*, 2009, **74**, 7481–7488; (*c*) S. Mochida, N. Umeda, K. Hirano, T. Satoh and M. Miura, *Chem. Lett.*, 2010, **39**, 744–746; (*d*) N. Umeda, H. Tsurugi, T. Satoh and M. Miura, *Angew. Chem., Int. Ed.*, 2008, **47**, 4019–4022; (*e*) Y.-T. Wu, K.-H. Huang, C.-C. Shin and T.-C. Wu, *Chem.–Eur. J.*, 2008, **14**, 6697–6703; (*f*) J. Wu, X. Cui, X. Mi, Y. Li and Y. Wu, *Chem. Commun.*, 2010, **46**, 6771–6773; (*g*) Z. Shi, C. Tang and N. Jiao, *Adv. Synth. Catal.*, 2012, **354**, 2695–2700; (*h*) E. Tomita, K. Yamada, Y. Shibata, K. Tanaka, M. Kojima, T. Yoshino and S. Matsunaga, *Angew. Chem., Int. Ed.*, 2020, **59**, 10474–10478; (*i*) Y. Wu, W. Zhang, Q. Peng, C.-K. Ran, B.-Q. Wang, P. Hu, K.-Q. Zhao, C. Feng and S.-K. Xiang, *Org. Lett.*, 2018, **20**, 2278–2281; (*j*) Q. Peng, W. Zhang, K. Zhao, Y. Du, C. Feng, B.-Q. Wang, D.-M. Fang, X.-Z. Chen, H.-L. Ni and S.-K. Xiang, *Adv. Synth. Catal.*, 2020, **362**, 206–212; (*k*) K. Zhao, Y. Du, Q. Peng, W.-H. Yu, B.-Q. Wang, C. Feng and S.-K. Xiang, *J. Org. Chem.*, 2021, **86**, 2986–2997; (*l*) H.-C. Hsiao, P. Annamalai, J. Jayakumar, S.-Y. Sun and S.-C. Chuang, *Adv. Synth. Catal.*, 2021, **363**, 1695–1701.

8 Reviews on the synthesis of nanographenes: (*a*) X. Feng, W. Pisula and K. Müllen, *Pure Appl. Chem.*, 2009, **81**, 2203–2224; (*b*) M. Grzybowski, B. Sadowski, H. Butenschön and D. T. Gryko, *Angew. Chem., Int. Ed.*, 2020, **59**, 2998–3027; (*c*) A. Narita, Z. Chen, Q. Chen and K. Müllen, *Chem. Sci.*, 2019, **10**, 964–975; (*d*) J. Wu, W. Pisula and K. Müllen,

Chem. Rev., 2007, **107**, 718–747; (*e*) M. D. Watson, A. Fechtenkötter and K. Müllen, *Chem. Rev.*, 2001, **101**, 1267–1300; (*f*) Z. Sun, Q. Ye, C. Chi and J. Wu, *Chem. Soc. Rev.*, 2012, **41**, 7857–7889; (*g*) C. Wang, H. Dong, W. Hu, Y. Liu and D. Zhu, *Chem. Rev.*, 2012, **112**, 2208–2267; (*h*) A. Facchetti, *Chem. Mater.*, 2011, **23**, 733–758; (*i*) R. Rieger and K. Müllen, *J. Phys. Org. Chem.*, 2010, **23**, 315–325; (*j*) Y. Segawa, H. Ito and K. Itami, *Nat. Rev. Mater.*, 2016, **1**, 15002.

9 S. L. Skraba-Joiner, E. C. Mclaughlin, A. Ajaz, R. Thamatam and R. P. Johnson, *J. Org. Chem.*, 2015, **80**, 9578–9583.

10 Review on rearrangements in the Scholl reaction: N. Ponugoti and V. Parthasarathy, *Chem.–Eur. J.*, 2022, **28**, e202103530.

11 (*a*) C. Tang, M. Okumura, Y. Zhu, A. R. Hooper, Y. Zhou, Y.-H. Lee and D. Sarlah, *Angew. Chem., Int. Ed.*, 2019, **58**, 10245–10249; (*b*) C. Tang, M. Okumura, H. Deng and D. Sarlah, *Angew. Chem., Int. Ed.*, 2019, **58**, 15762–15766; (*c*) W. C. Wertjes, M. Okumura and D. Sarlah, *J. Am. Chem. Soc.*, 2019, **141**, 163–167; (*d*) M. Okumura, A. S. Shved and D. Sarlah, *J. Am. Chem. Soc.*, 2017, **139**, 17787–17790.

12 (*a*) A. Matsumoto, L. Illies and E. Nakamura, *J. Am. Chem. Soc.*, 2011, **133**, 6557–6561; (*b*) Y. Sun, H. Tang, K. Chen, L. Hu, J. Yao, S. Shaik and H. Chen, *J. Am. Chem. Soc.*, 2016, **138**, 3715–3724.

13 Representative reviews and recent examples on palladium-catalyzed allylic substitutions: (*a*) B. M. Trost and D. L. Van Vranken, *Chem. Rev.*, 1996, **96**, 395–422; (*b*) O. Pàmies, J. Margalef, S. Cañellas, J. James, E. Judge, P. J. Guiry, C. Moberg, J.-E. Bäckvall, A. Pfaltz, M. A. Pericàs and M. Diéguez, *Chem. Rev.*, 2021, **121**, 4373–4505; (*c*) K. Ikeda, R. Kojima, K. Kawai, T. Murakami, T. Kikuchi, M. Kojima, T. Yoshino and S. Matsunaga, *J. Am. Chem. Soc.*, 2023, **145**, 9326–9333.

14 L. Zhai, R. Shukla and R. Rathore, *Org. Lett.*, 2009, **11**, 3474–3477.

15 (*a*) R. Dorel, C. Manzano, M. Grisolia, W. Soe, C. Joachim and A. M. Echavarren, *Chem. Commun.*, 2015, **51**, 6932–6935; (*b*) L. Zhai, R. Shukla, S. H. Wadumethrige and R. Rathore, *J. Org. Chem.*, 2010, **75**, 4748–4756.

16 (*a*) CCDC 2506075: Experimental Crystal Structure Determination, 2026, DOI: 10.5517/ccdc.csd.cc2q3s4s; (*b*) CCDC 2506076: Experimental Crystal Structure Determination, 2026, DOI: 10.5517/ccdc.csd.cc2q3s5t; (*c*) CCDC 2506077: Experimental Crystal Structure Determination, 2026, DOI: 10.5517/ccdc.csd.cc2q3s6v; (*d*) CCDC 2506078: Experimental Crystal Structure Determination, 2026, DOI: 10.5517/ccdc.csd.cc2q3s7w.