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Chiral Picene Synthesis and Unexpected Transformations Catalyzed by Brønsted Acid

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Abstract

We report the first synthesis of an axially chiral picene via sequential Sonogashira and Suzuki-Miyaura cross-couplings followed by Brønsted acid-catalyzed alkyne benzannulation. Unexpected reactivity during the final step led to the formation of additional products through aryl migration and subsequent acid-promoted transformations. Mechanistic investigations revealed the concurrent formation of chiral picene and benzo[4]helicene, while stronger acid promoted the further transformation of chiral picene through a dihydrodibenzopentaphene intermediate, ultimately yielding a planar polycyclic aromatic hydrocarbon through the elimination of anisole. These findings highlight competing reaction pathways in alkyne benzannulation and reveal unexpected reactivity in the synthesis of smaller chiral polycyclic aromatic hydrocarbons. Compared with our previously reported chiral peropyrene, chiral picene

exhibits an ~100 nm hypsochromic shift in absorption and emission, together with a reduced end-to-end twist angle of 20° versus 28° for chiral peropyrene. These differences reflect the reduced π -extension of the picene framework and its distinct steric constraints. X-ray crystallography unambiguously confirmed the chiral picene and additional product structures, revealing distinct molecular geometries and providing insight into the structural consequences of the competing reaction pathways.

Keywords

benzannulation; chirality; nanographene; phenacene; picene

Introduction

The development of inherently chiral, non-planar polycyclic aromatic hydrocarbons (PAHs)—including contorted and helically twisted frameworks such as twistacenes, helicenes, and irregular/nonalternant nanographenes—has emerged as a key area of research [1–4]. The field of chiral nanographene preparation is driven by their tunable π -electron delocalization, unique solid-state organization, and potential in chiral optoelectronic and materials applications. Phenacenes, like picene, are a nanographene subclass with unique properties for potential use in organic electronics such as organic field-effect transistors (OFETs), organic photovoltaics (OPVs), and organic light-emitting diodes (OLEDs) [5–11].

In 2017, the Chalifoux group reported the synthesis and characterization of chiral peropyrenes and their photophysical properties [12]. Like peropyrene, picene possesses a rigid backbone and is a flat, planar PAH when unsubstituted on the *bay*-regions [13]. Analogously, chiral picene may likewise exhibit interesting chiroptic properties as it was a key intermediate in the synthesis of chiral peropyrene [12].

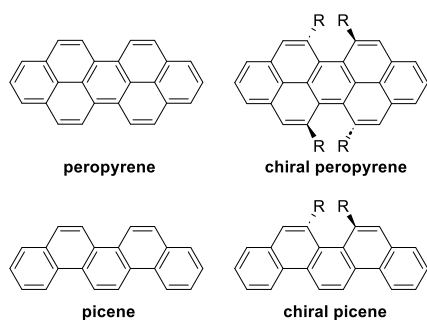
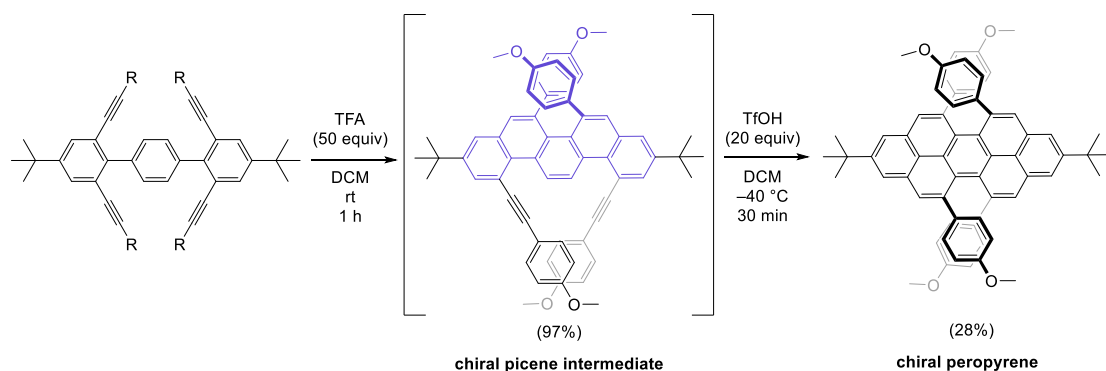


Figure 1: Comparison of peropyrene, chiral peropyrene, picene, and chiral picene structures.

In regards to the properties of picene, Okamoto, Yamaji, and co-workers in 2011 demonstrated that picene thin film OFETs could be used in applications such as gas sensors and other organic electronic devices [14]. In 2014, Okamoto et al. also showed that terminally alkylated picene produced a 4x greater field-effect mobility than unsubstituted picene [15]. Additional functionalized, and extended picene derivatives have since been explored as potential materials for organic electronic devices, including OFETs and OLEDs [16–19].

We have previously reported the use of alkyne benzannulation to access axially chiral peropyrene, teropyrene, and quateropyrene derivatives, in which steric repulsion between *bay*-region substituents induces twisting of the π -conjugated framework and gives rise to axial chirality [12,20–23]. The Chalifoux group has previously utilized Brønsted acid for alkyne benzannulations using trifluoroacetic acid (TFA) followed by triflic acid (TfOH) to promote a four-fold alkyne benzannulation for the synthesis of chiral peropyrenes (Scheme 1) [12]. While we have observed the use of Brønsted acids to facilitate the alkyne benzannulation reaction, the use of these acids is limited to electron-rich systems. To the best of our knowledge, we have not found any picenes that have been rendered chiral. By functionalizing the picene backbone and inducing chirality through alkyne benzannulation, the properties of this type of compound are now further investigated.



Scheme 1. Synthesis of chiral peropyrene derivatives, with chiral picene intermediate.

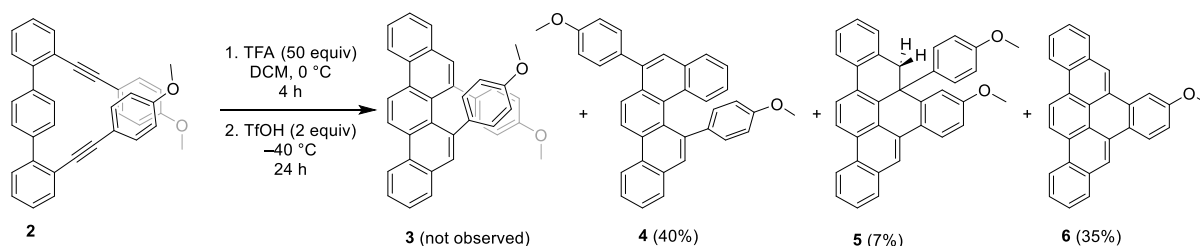
As observed in the previously synthesized chiral peropyrene (Scheme 1), the formation of the picene intermediate with two aryl substituents within the *bay*-region causes steric clashing that results in twisting of the backbone, leading to chirality. The thermodynamic driving force for this reaction is hypothesized to be the progression from a high-energy alkyne-containing precursors to lower-energy extended π -electron systems [23]. In addition to the π -system expansion, placing alkoxy-substituted aryl groups in the *bay*-region improves solubility and expands the scope of applications for these molecules.

Here we report the use of Brønsted acid to afford a chiral picene along with some unexpected and interesting side products. In addition, the progression of this synthesis afforded an electron-rich terphenyl species. The synthesis of the chiral picene in this work confirms that the double alkyne benzannulation preferentially occurs on the same side of the picene backbone, as seen in the synthesis of chiral peropyrene when the picene derivative is formed [12].

Results and Discussion

Synthesis of Chiral Picene

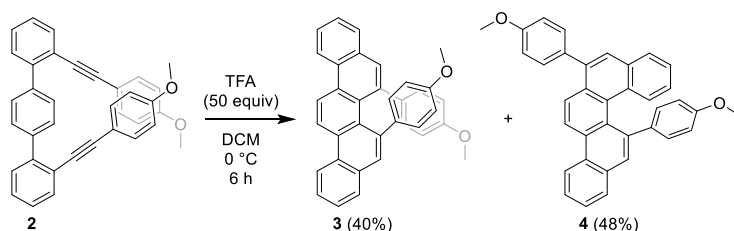
The initial synthesis of chiral picene was attempted using ethynyl terphenyl **2** following previously reported conditions [12]. The reaction was allowed to proceed for an extended period, and the desired chiral picene **3** was not detected in the final product mixture; instead, additional, unexpected products were isolated (Scheme 2). Based on the resulting products, it was hypothesized that the addition of TFA concurrently formed compounds **3** and **4**, with prolonged exposure to the acidic reaction conditions resulting in further transformation of **3**. Specifically, the addition of TfOH converted **3** to dihydrodibenzopentaphene **5**, which further transformed to compound **6** under the harsh acidic conditions.



Scheme 2: Alkyne benzannulation of compound **2** with a TFA/TfOH mixture to produce products **4**, **5**, and **6**.

To further investigate the formation and subsequent transformation of chiral picene **3**, the reaction was performed using TFA alone, following a previously reported procedure [12]. Under these conditions, compounds **3** and **4** were isolated, with no formation of compounds **5** or **6** observed (Scheme 3). These results support the formation of **3** and **4** as the initial products of the reaction and demonstrate that the stronger acidity of TfOH promotes subsequent transformations of **3** that are not observed with TFA. To further examine the formation of **3** and **4**, the reaction was monitored by NMR over time under the TFA conditions, which revealed their concurrent formation upon addition

of TFA (see Supporting Information File 1, Figures S1–S3). The reaction conditions also influence the subsequent fate of **3**: conducting the reaction at room temperature rather than 0 °C resulted in the formation of **5**, in addition to **3** and **4**, suggesting that further transformation of **3** is facilitated at higher temperature.



Scheme 3. TFA-promoted alkyne benzannulation of compound **2** to form a mixture of products **3** and **4**.

Following the initial alkyne benzannulation, compounds **3** and **4** are proposed to form through two competing mechanistic pathways (Figure 2). Both pathways begin with protonation of the alkyne in the monocyclized intermediate by Brønsted acid, generating a cationic intermediate. Compound **3** may form through the conventional alkyne benzannulation pathway, in which the π electrons attack the vinyl carbocation through a 6-*endo*-dig cyclization (blue carbon) to construct the picene backbone. Subsequent deprotonation restores aromaticity, affording **3** and regenerating the acid catalyst. Alternatively, a 5-*endo*-dig cyclization (red carbon) may produce a spirocyclic intermediate. Bond migration via the blue arrow, followed by rearomatization leads to compound **3**. The formation of compound **4** is proposed to proceed through the same spirocyclic intermediate followed by an alternative skeletal rearrangement. In this pathway, a different bond migration (red arrow) followed by rearomatization yields the [4]helicene derivative **4**.

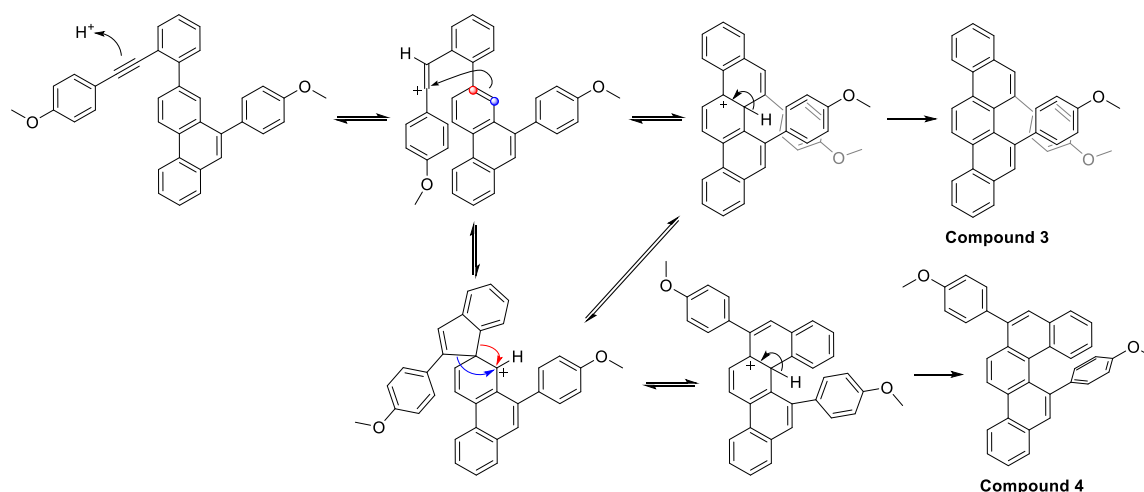


Figure 2. Proposed mechanistic pathways for the formation of compounds **3** and **4**.

Similar types of migrations in both proposed mechanisms have been reported in the synthesis of nanographenes [24–30]. A control experiment was performed to distinguish between the proposed pathways for the alkyne benzannulation leading to compounds **3** and **4**. Following a modified literature procedure [31], a model compound was synthesized and the results support the reaction proceeding through a competitive spirocyclic pathway for the formation of compound **4** (see Supporting Information File 1 for further details).

Compound **5** is proposed to form from chiral picene **3** through Brønsted acid-promoted activation of the K-region (Figure 3a). Similar transformations have been previously observed in sterically congested alkyne cyclizations and PAH systems under acidic conditions [25–27,29,32–34]. The proposed mechanism begins with protonation of the K-region of **3**, generating a benzylic carbocation that undergoes intramolecular attack by the neighboring *bay*-region aryl group. This cyclization forms a new C–C bond and a σ -complex intermediate, which subsequently undergoes deprotonation to restore aromaticity and yield the dihydrodibenzopentaphene backbone of **5**. This

transformation may partially relieve steric congestion within the chiral picene framework. Structurally, compound **5** features a quaternary carbon center bearing a pseudo-axial phenyl group, as well as diastereotopic methylene protons, which are assigned using HSQC spectroscopy (see Supporting Information File 1, Figure S22). As shown in Scheme 2, treatment of compound **5** with excess TfOH results in the elimination of the pendant anisole group to yield compound **6**. The proposed mechanism involves protonation of the anisole substituent, followed by the deprotonation and C–C bond fragmentation to eliminate the anisole group and form **6** (Figure 3b).

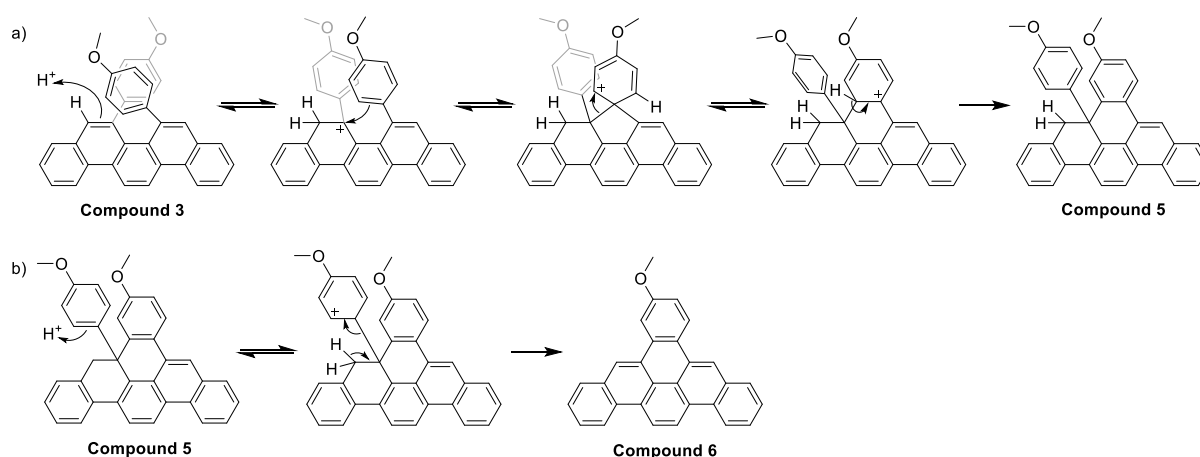


Figure 3. Brønsted acid promoted transformation of compound **3** to compound **5**.

The transformation of compound **3** to compound **5** may be rationalized in part by the relative aromaticity of the chiral picene backbone. Nucleus-Independent Chemical Shift (NICS) Z-scan calculations [35–37] were performed for each unique backbone ring to evaluate their relative aromatic character (Figure 4). Ring 2 of compound **3** exhibits more olefinic character than rings 1 and 3, consistent with its lower aromaticity. This difference may favor protonation at ring 2, facilitating the subsequent transformation to compound **5**.

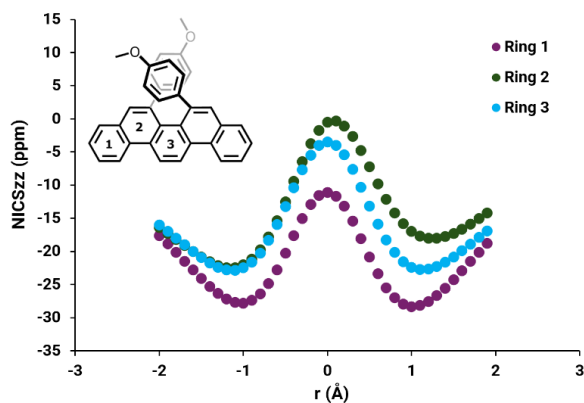


Figure 4. NICS_{zz} scans for chiral picene **3** modeled at M06-2X/6-311+G(d,p) [38].

X-Ray Crystallographic Analysis

Single crystals of compound **3** were crystallized from acetone. The X-ray crystal structure of **3** demonstrates the picene backbone is twisted as a result of steric overlap and repulsion between the two aryl substituents in the *bay*-region (Figure 5). Like chiral peropyrene, chiral picene forms as a racemic mixture of two axially chiral enantiomers. The unit cell contains two crystallographically independent *M* and two crystallographically independent *P* stereoisomers, confirming the formation of a racemic mixture. The structure packs in enantiomeric pairs in a herringbone-like motif (Figure 5b), however, intermolecular π – π stacking is not observed. The *bay*-region dihedral angle is 25.8°, demonstrating the axial chirality induced by the overlapping aryl substituents. For comparison, chiral peropyrenes exhibit *bay*-region dihedral angles up to 32° [22]. The steric repulsion between the overlapping aryl substituents also results in a twisted picene backbone, with an end-to-end twist angle of 20°, compared to 28° for the chiral peropyrene analog of **3** [12]. The closest distance between the two overlapping aryl substituents in the *bay*-region is 3.3–3.4 Å. The ¹H NMR spectrum of compound **3** also exhibits broadened resonances in the aromatic region, which is consistent with restricted free rotation of the overlapping aryl substituents at room temperature (see Supporting Information File 1, Figure S15).

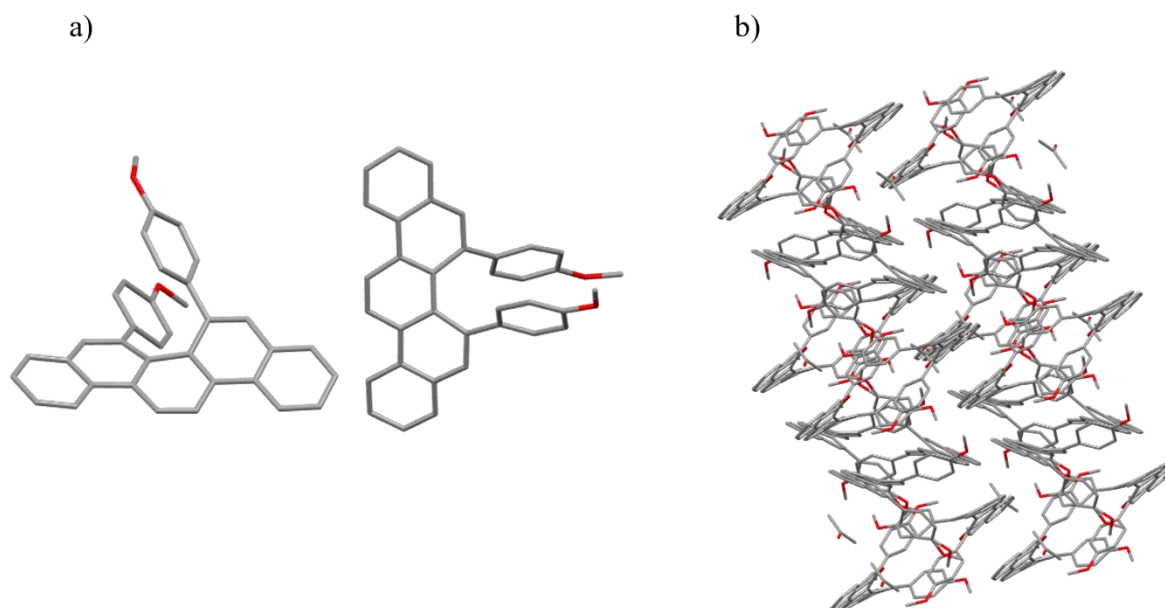


Figure 5. a) X-ray structures (capped sticks) of compound **3** (hydrogens removed for clarity) and b) enantiomeric herringbone-like packing arrangements (containing acetone within the crystal packing; hydrogens omitted for clarity).

Single crystals of compound **4** were grown by dissolving in hot hexanes, cooling of the saturated solution to room temperature, and allowing the crystals to grow slowly over time. The X-ray crystal structure of **4** reveals a helical conformation arising from twisting along the cove-region, with both *M* and *P* conformations present in the crystal (Figures 6a–b). Intramolecular π – π stacking is observed with distances varying from 3.59–3.71 Å (Figure 6c). The torsional angles along the cove-region of **4**, measured from C16 to C20, are $\phi = 18.7^\circ$, 30.2° , and 19.7° , respectively (Figure 6a). These torsional angles demonstrate the significant twisting of the cove-region required to accommodate the steric interactions within the helical framework and is consistent with the degree of twisting observed in related [4]helicene structures reported in the literature [39]. Restricted rotation of the pendant aryl within the cove-region of compound **4** is observed in ^1H NMR spectra with broadening of the expected signals. The broadened signals are resolved as apparent doublets or overlapped signals with

the use of VT NMR spectroscopy (see Supporting Information File 1, Figure S19). The crystal structure therefore provides structural evidence that **4** adopts a helical conformation in the solid state.

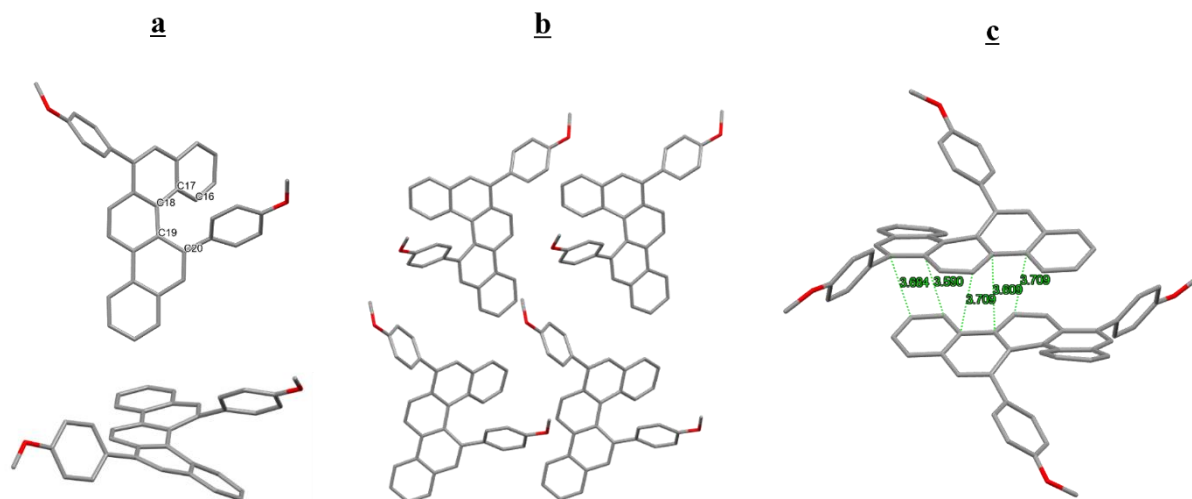


Figure 6. a) X-ray structures (capped sticks, select hydrogens removed for clarity) of **4**, b) crystal packing, and c) intermolecular π – π stacking.

Single crystals of compound **5** were grown by slow evaporation from DCM. The X-ray crystal structure confirms the formation of the new C–C bond and the resulting connectivity of the fused framework (Figures 7a–c). The anisole substituent at the quaternary carbon (C4) is oriented approximately perpendicular to the backbone. The C3–C4, C4–C27, C4–C5, and C5–C6 bond lengths range from 1.50 to 1.54 Å, consistent with C–C single-bond character in this portion of the structure (Figure 7b). The C2–C5 torsional angle is 40.6°, reflecting the nonplanar geometry introduced upon formation of the new C–C bond (Figure 7c). The crystal contains an enantiomeric pair of **5**, with minimum intermolecular distances of 3.5–3.8 Å between the paired molecules (Figure 7d).

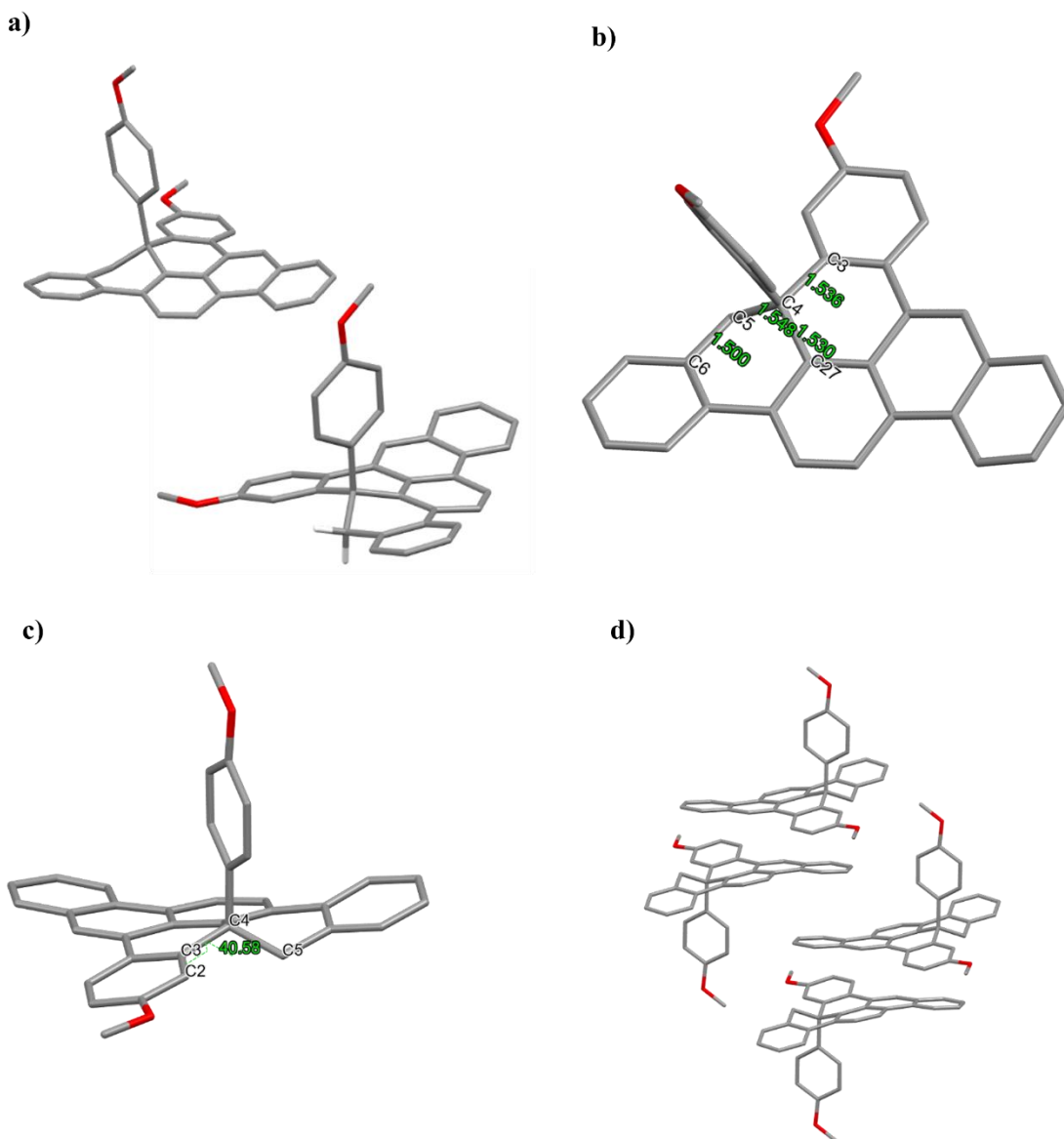


Figure 7. X-ray structures (capped sticks, select hydrogens removed for clarity) of **5** (a) bond distances (b), selected torsional angle (c), and crystal packing (d).

Single crystals of compound **6** were grown by slow evaporation from hexafluorobenzene (C_6F_6). The compound crystallized as a co-crystal with C_6F_6 . The crystal packing of compound **6** demonstrates slip-stack packing with π - π intermolecular distances varying from 3.4–3.6 Å (Figure 8). Compound **6** is only partially miscible with polar aprotic solvents and aromatic solvents, demonstrated by

the low solubility in the ^1H and ^{13}C NMR spectra (see Supporting Information Figures S23–25).

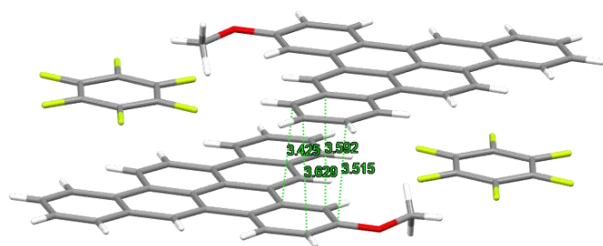


Figure 8. X-ray structures of compound **6** co-crystallized with C_6F_6 (π - π intermolecular distances shown for selected rings).

DFT Calculations

The conversion of terphenyl **2** to products **3-5** along with the corresponding monocyclized phenanthrene intermediate **2a** were investigated computationally to further examine the relative energies (Figure 9). Despite the inherent strain associated with the contorted π -frameworks of compounds **3-5**, the calculated intermediate and products are lower in energy than the corresponding starting materials, indicating that the overall transformations are thermodynamically favorable. This result showcases how the high energy of the alkyne-containing starting materials provides a thermodynamic driving force for the formation of new C-C bonds and the expansion of π -systems.

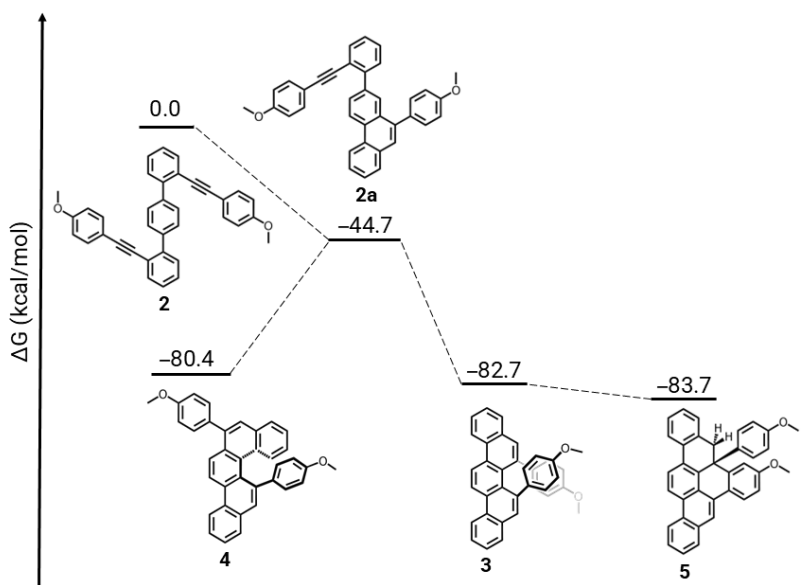


Figure 9. Calculated relative free energies of compounds **2-5**. Energies were calculated at the M06-2X/6-311+G(d,p) level of theory.

Photophysical Properties

Chiral peropyrene derivatives absorb and emit primarily in the green region of the UV–visible spectrum [12], whereas chiral picene **3** and the related products described herein absorb and emit in the violet-to-blue region (see Supporting Information File 1, Figures S9–S12 for spectra). The reduced π -extension of the picene framework relative to chiral peropyrene results in a blue shift of ~100 nm. Chiral picene **3** exhibits an optical gap ($E_{g(\text{opt})}$) of 3.17 eV compared to the analogous chiral peropyrene at 2.33 eV. The optical gap of **3** is slightly lower than the reported $E_{g(\text{opt})}$ of 3.3 eV for planar picene [8]. The absorption and emission profiles of compound **5** are consistent with those reported for related pentaphene-containing structures [40–42]. Similarly, the absorption and emission profiles of **6** are also in accordance with analogous compounds reported in the literature [43,44].

Conclusion

In summary, we reported the first synthesis of an axially chiral picene, achieved through Sonogashira cross-coupling to prepare the tolan precursor, followed by Suzuki–Miyaura cross-coupling and Brønsted acid-catalyzed alkyne benzannulation. Under the reaction conditions, compounds **3** and **4** form concurrently, with stronger acid promoting the subsequent transformation of **3** through **5** to **6**, providing insight into competing reaction pathways that can accompany the synthesis of smaller chiral PAHs. Crystallographic and photophysical characterization reveals clear structural and electronic differences between chiral picene and chiral peropyrene. Reducing the π -extension along the armchair edge by two C=C units, while removing the associated *bay*-region aryl substituents, results in a ~100 nm blue shift in absorption and emission and an increase in the optical gap from 2.33 to 3.17 eV. The chiral picene adopts an end-to-end twist angle of 20°, compared to 28° for chiral peropyrene [12]. The crystal structure of chiral picene reveals an enantiomeric packing arrangement with a more herringbone-like motif, in contrast to the face-to-face molecular packing observed for chiral peropyrene. Overall, this work highlights both the synthetic opportunities and challenges associated with utilizing alkyne benzannulation to access smaller chiral PAH systems. Ongoing studies are directed toward expanding the scope of this benzannulation strategy using Lewis acid catalysis and investigating the chiroptical and electronic properties of related systems.

Supporting Information

Supporting Information File 1:

File Name: Supporting_Information.pdf

File Format: PDF

Title: Details on synthesis, characterization, spectroscopy, and X-ray analysis for CCDC numbers 2591461-2591463, and 2595611.

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References

1. Pascal, R. A. *Chem. Rev.* **2006**, *106*, 4809–4819. <https://doi.org/10.1021/cr050550l>
2. Magiera, K. M.; Aryal, V.; Chalifoux, W. A. *Org. Biomol. Chem.* **2020**, *18*, 2372–2386. <https://doi.org/10.1039/D0OB00182A>
3. Anderson, H. V.; Gois, N. D.; Chalifoux, W. A. *Org. Chem. Front.* **2023**, *10*, 4167–4197. <https://doi.org/10.1039/D3QO00517H>
4. Kumar, V.; Páez, J. L.; Míguez-Lago, S.; Cuerva, J. M.; Cruz, C. M.; Campaña, A. *G. Chem. Soc. Rev.* **2025**, *54*, 4922–4947. <https://doi.org/10.1039/d4cs00745j>
5. Shimo, Y.; Mikami, T.; Hamao, S.; Goto, H.; Okamoto, H.; Eguchi, R.; Gohda, S.; Hayashi, Y.; Kubozono, Y. *Sci. Rep.* **2016**, *6*, 21008. <https://doi.org/10.1038/srep21008>
6. Moreira, T. S.; Ferreira, M.; Dall'armellina, A.; Cristiano, R.; Gallardo, H.; Hillard, E. A.; Bock, H.; Durola, F. *Eur. J. Org. Chem.* **2017**, *2017*, 4548–4551. <https://doi.org/10.1002/ejoc.201700893>
7. Okamoto, H.; Hamao, S.; Eguchi, R.; Goto, H.; Takabayashi, Y.; Yen, P. Y.-H.; Liang, L. U.; Chou, C.-W.; Hoffmann, G.; Gohda, S.; Sugino, H.; Liao, Y.-F.; Ishii, H.; Kubozono, Y. *Sci. Rep.* **2019**, *9*, 4009. <https://doi.org/10.1038/s41598-019-39899-4>

8. Okamoto, H. Organic Chemistry of π -Conjugated Polycyclic Aromatic Hydrocarbons: Acenes and Phenacenes. In *Physics and Chemistry of Carbon-Based Materials: Basics and Applications*; Kubozono, Y., Ed.; Springer Singapore: Singapore, 2019; pp 211–228. https://doi.org/10.1007/978-981-13-3417-7_7
9. Zhang, Y.; Eguchi, R.; Hamao, S.; Goto, K.; Tani, F.; Yamaji, M.; Kubozono, Y.; Okamoto, H. *Chem. Commun.* **2021**, 57, 4768–4771. <https://doi.org/10.1039/d1cc01294k>
10. Zhang, Y.; Eguchi, R.; Hamao, S.; Okamoto, H.; Goto, H.; Kubozono, Y. *ACS Omega* **2022**, 7, 5495–5501. <https://doi.org/10.1021/acsomega.1c06932>
11. Wang, Q.; Wang, W.-Z.; Zhang, R.; Zhai, Z.; Chen, X.; Li, M.; Jin, Y.; Zhu, L.; Li, Y.; Ye, K.-Y. *JACS Au* **2025**, 5, 4281–4287. <https://doi.org/10.1021/jacsau.5c00653>
12. Yang, W.; Longhi, G.; Abbate, S.; Lucotti, A.; Tommasini, M.; Villani, C.; Catalano, V. J.; Lykhin, A. O.; Varganov, S. A.; Chalifoux, W. A. *J. Am. Chem. Soc.* **2017**, 139, 13102–13109. <https://doi.org/10.1021/jacs.7b06848>
13. Clar, E. Part II Kata-Annellated Hydrocarbons. In *Polycyclic Hydrocarbons*; Springer-Verlag: Berlin, Hiedelberg, 1964; Vol. 1, pp 268–274. <https://doi.org/10.1007/978-3-662-01665-7>
14. Okamoto, H.; Yamaji, M.; Gohda, S.; Kubozono, Y.; Komura, N.; Sato, K.; Sugino, H.; Satake, K. *Org. Lett.* **2011**, 13, 2758–2761. <https://doi.org/10.1021/ol200874q>
15. Okamoto, H.; Hamao, S.; Goto, H.; Sakai, Y.; Izumi, M.; Gohda, S.; Kubozono, Y.; Eguchi, R. *Sci. Rep.* **2014**, 4, 5048. <https://doi.org/10.1038/srep05048>
16. Balambiga, B.; Dheepika, R.; Devibala, P.; Imran, P. M.; Nagarajan, S. *Sci. Rep.* **2020**, 10, 22029. <https://doi.org/10.1038/s41598-020-78356-5>
17. Wu, D.; Ge, H.; Chen, Z.; Liang, J.; Huang, J.; Zhang, Y.; Chen, X.; Meng, X.; Hua Liu, S.; Yin, J. *Org. Biomol. Chem.* **2014**, 12, 8902–8910. <https://doi.org/10.1039/C4OB01486C>

18. Wang, X.; Chen, L.; Li, N.; Wu, D.; Xia, J. *Chem. – Eur. J.* **2023**, *29*, e202300480. <https://doi.org/10.1002/chem.202300480>
19. Sahoo, S. R.; Baryshnikov, G. V.; Ågren, H. *J. Phys. Chem. A* **2025**, *129*, 2396–2410. <https://doi.org/10.1021/acs.jpca.4c07345>
20. Malone, R. J.; Soldner, S.; Fregoso, G. M.; Anhalt, O.; Stolte, M.; Würthner, F.; Chalifoux, W. A. *Org. Lett.* **2026**, *28*, 5532–5535. <https://doi.org/10.1021/acs.orglett.6c01154>
21. Yang, W.; Monteiro, J. H. S. K.; de Bettencourt-Dias, A.; Catalano, V. J.; Chalifoux, W. A. *Angew. Chem. Int. Ed.* **2016**, *55*, 10427–10430. <https://doi.org/10.1002/anie.201604741>
22. Yang, W.; Kazemi, R. R.; Karunathilake, N.; Catalano, V. J.; Alpuche-Aviles, M. A.; Chalifoux, W. A. *Org. Chem. Front.* **2018**, *5*, 2288–2295. <https://doi.org/10.1039/C8QO00389K>
23. Malone, R. J.; Chalifoux, W. A. *Acc. Chem. Res.* **2025**, *58*, 2379–2393. <https://doi.org/10.1021/acs.accounts.5c00211>
24. Liu, J.; Narita, A.; Osella, S.; Zhang, W.; Schollmeyer, D.; Beljonne, D.; Feng, X.; Müllen, K. *J. Am. Chem. Soc.* **2016**, *138*, 2602–2608. <https://doi.org/10.1021/jacs.5b10399>
25. He, M.; Swager, T. M. *J. Am. Chem. Soc.* **2020**, *142*, 17876–17880. <https://doi.org/10.1021/jacs.0c05965>
26. Ajaz, A.; McLaughlin, E. C.; Skraba, S. L.; Thammatam, R.; Johnson, R. P. *J. Org. Chem.* **2012**, *77*, 9487–9495. <https://doi.org/10.1021/jo301848g>
27. Nobusue, S.; Xie, C.; Patel, K.; Kojima, T.; Sakaguchi, H. *Chem. – Eur. J.* **2025**, *31*, e202501221. <https://doi.org/10.1002/chem.202501221>
28. Krzeszewski, M.; Sahara, K.; Poronik, Y. M.; Kubo, T.; Gryko, D. T. *Org. Lett.* **2018**, *20*, 1517–1520. <https://doi.org/10.1021/acs.orglett.8b00223>

29. Goldfinger, M. B.; Crawford, K. B.; Swager, T. M. *J. Am. Chem. Soc.* **1997**, *119*, 4578–4593. <https://doi.org/10.1021/ja9642673>
30. Bam, R.; Yang, W.; Longhi, G.; Abbate, S.; Lucotti, A.; Tommasini, M.; Franzini, R.; Villani, C.; Catalano, V. J.; Olmstead, M. M.; Chalifoux, W. A. *Org. Lett.* **2019**, *21*, 8652–8656. <https://doi.org/10.1021/acs.orglett.9b03273>
31. Gicquiaud, J.; Hacıhasanoğlu, A.; Hermange, P.; Sotiropoulos, J.-M.; Toullec, P. Y. *Adv. Synth. Catal.* **2019**, *361*, 2025–2030. <https://doi.org/10.1002/adsc.201801526>
32. Necula, A.; Racoveanu-Schiketanz, A.; Gheorghiu, M. D.; Scott, L. T. *J. Org. Chem.* **1995**, *60*, 3448–3451. <https://doi.org/10.1021/jo00116a035>
33. Goldfinger, M. B.; Crawford, K. B.; Swager, T. M. *J. Am. Chem. Soc.* **1997**, *119*, 4578–4593. <https://doi.org/10.1021/ja9642673>
34. Skraba-Joiner, S. L.; McLaughlin, E. C.; Ajaz, A.; Thamatham, R.; Johnson, R. P. *J. Org. Chem.* **2015**, *80*, 9578–9583. <https://doi.org/10.1021/acs.joc.5b01559>
35. Stanger, A. *J. Org. Chem.* **2010**, *75*, 2281–2288. <https://doi.org/10.1021/jo1000753>
36. Stanger, A. *J. Org. Chem.* **2006**, *71*, 883–893. <https://doi.org/10.1021/jo051746o>
37. Stanger, A.; Rahalkar, A. *Aroma*, 2014. <https://chemistry.technion.ac.il/en/team/amnon-stanger/>
38. Gaussian 16, Revision C.01; Gaussian, Inc.: Wallingford, CT, 2016.
39. Hartung, T.; Machleid, R.; Simon, M.; Golz, C.; Alcarazo, M. *Angew. Chem. Int. Ed.* **2020**, *59*, 5660–5664. <https://doi.org/10.1002/anie.201915870>
40. Lang, K. F.; Zander, M. *Chem. Ber.* **1965**, *98*, 597–600. <https://doi.org/10.1002/cber.19650980236>
41. Xu, X.; Haar, A. L. V.; Yoshioka, R.; Zhang, Q.; Vasylevskiy, S.; Musser, A. J.; Narita, A. *Chem. Commun.* **2023**, *59*, 720–723. <https://doi.org/10.1039/D2CC05369A>

42. Xu, X.; Gunasekaran, S.; Renken, S.; Ripani, L.; Schollmeyer, D.; Kim, W.; Marcaccio, M.; Musser, A.; Narita, A. *Adv. Sci.* **2022**, *9*, 2200004. <https://doi.org/10.1002/advs.202200004>
43. Marae, I. S.; Tan, J.; Yoshioka, R.; Ziadi, Z.; Khaskin, E.; Vasylevskyi, S.; Kabe, R.; Xu, X.; Narita, A. *Beilstein J. Org. Chem.* **2025**, *21*, 270–276. <https://doi.org/10.3762/bjoc.21.19>
44. Clar, E.; Mcandrew, B. A.; Stephen, J. F. *Tetrahedron* **1970**, *26*, 5465–5478. [https://doi.org/10.1016/S0040-4020\(01\)98757-5](https://doi.org/10.1016/S0040-4020(01)98757-5)