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Lithium-mediated mechanochemical annulative dimerization of diarylacetylenes for synthesis of 1,4-dihydrodinaphthopentalenes

Koya M. Hori,^a † Yoshifumi Toyama,^b † Takato Mori,^a Takumu Nakamura,^b Yohei Ono^b and Hideto Ito^{a*}

1,4-Dihydrodiarenopentalenes, the reduced derivatives of diarenopentalene, have attracted attention owing to their rigid planar π -conjugated ladder framework, photophysical properties, C_2 -chiral structure, and potential applications in physical organic chemistry and materials science. Unlike the established methods for parent diarenopentalenes, the synthetic method for 1,4-dihydrodiarenopentalenes is less established, and the constructed structures are highly limited to dihydrodibenzopentalenes with trialkylsilyl substituents. Herein, we report a novel method for synthesizing 1,4-dihydrodinaphthopentalene derivatives by mechanochemical annulative dimerization of 2-(arylethynyl)naphthalenes with a lithium(0) wire. This reaction is easy to handle—even in an ambient atmosphere at room temperature—and requires a minimum amount of tetrahydrofuran for efficient grinding, resulting in the formation of various 1,4-diaryl-1,4-dihydrodinaphthopentalenes within 15 min. Furthermore, structural and theoretical analyses, as well as photophysical and chiro-optical measurements, reveal untapped properties of chiral 1,4-dihydrodinaphthopentalene.

homologues of dibenzo[*a,e*]pentalenes, namely, dihydrodibenzopentalenes or dihydroindenoindene, have also garnered interest as π -conjugated ladder platforms.^{4,5} Dihydrodibenzopentalene possesses a fixed, rigid, and planar C_2 -symmetric stilbene structure. Depending on the substituents at the benzylic positions (*R* and *R'*), it possesses a planar chirality. This framework serves as a synthetic precursor for chiral dibenzocyclooctatetraene, a so-called “chiral diene” ligand, for asymmetric catalysis.^{6a,b} Incorporating the multi-aryldihydropentalene moiety into an oligo- or polyarylene is known as an effective strategy to elongate and kinetically stabilize the π -conjugated system in the design of organic electronic materials.⁷ Classical stepwise synthetic routes to dihydrodibenzopentalene include derivatization of the dihydropentalene-1,4-dione derivative,⁸ dimerizative annulation of ethyl phenylacetate,^{4,5} and transannulation of dibenzocyclooctatetraene derivatives.⁶ Tsuji *et al.* reported the synthesis of dihydrodibenzopentalenes and its oligomers through a tandem cyclization reaction in *ortho*-substituted diphenylacetylene derivatives.⁹ Saito and Kuwabara reported a one-step synthesis of disilylated dibenzo[*a,e*]pentalenes from 1-phenyl-2-(trialkylsilyl)acetylenes using bulk lithium or sodium dispersion in the solution state. Further transformation into tri- and tetra-substituted dihydrodibenzopentalenes *via* the stepwise addition of MeLi and electrophiles has also been demonstrated.^{10,11} Furthermore, Xi¹² also reported a one-pot synthesis of similar disilylated dihydrodibenzopentalene *via* dimerizative dilithiation of 1-phenyl-2-silylacetylenes with lithium,^{10,11} followed by reaction with Ba[N(SiMe₃)₂]₂ and quenching with H₂O (Fig. 1B). Although these alkyne dimerization methods are attractive in terms of step economy and availability of the starting alkynes, the scope of alkynes is highly limited to 1-phenyl-2-(trialkylsilyl)acetylenes, and alkyne dimerization using diarylacetylene or examples of diarenodihydropentalenes other than dibenzo-fused structures have not been reported to date. This could be due to the stability and reactivity of 1,4-dilithio-1,3-butadiene bearing α -silyl groups,^{10,12,13} which is easily generated *in situ* by the reaction of

Introduction

Dibenzo[*a,e*]pentalene or indenoindene is a distinctive example of a ladder-type polycyclic π -conjugated hydrocarbon, characterized by a fused 6-5-5-6-membered ring system (Fig. 1A).¹ This molecule and its derivatives have received marked interest owing to their narrow highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gaps² and anti-aromatic 8π -electron system stabilized by two benzenes. Therefore, various stoichiometric and catalytic preparation methods have been developed so far.³ The hydrogenated

^aGraduate School of Science, Nagoya University, Chikusa, Nagoya 464-8602, Japan. E-mail: ito.hideto.p4@f.mail.nagoya-u.ac.jp

^bTokyo Research Center, Advanced Materials Research Laboratory, Advanced Integration Research Center, Research Division, Tosoh Corporation, 2743-1 Hayakawa, Ayase, Kanagawa 252-1123, Japan

† Equal contribution.



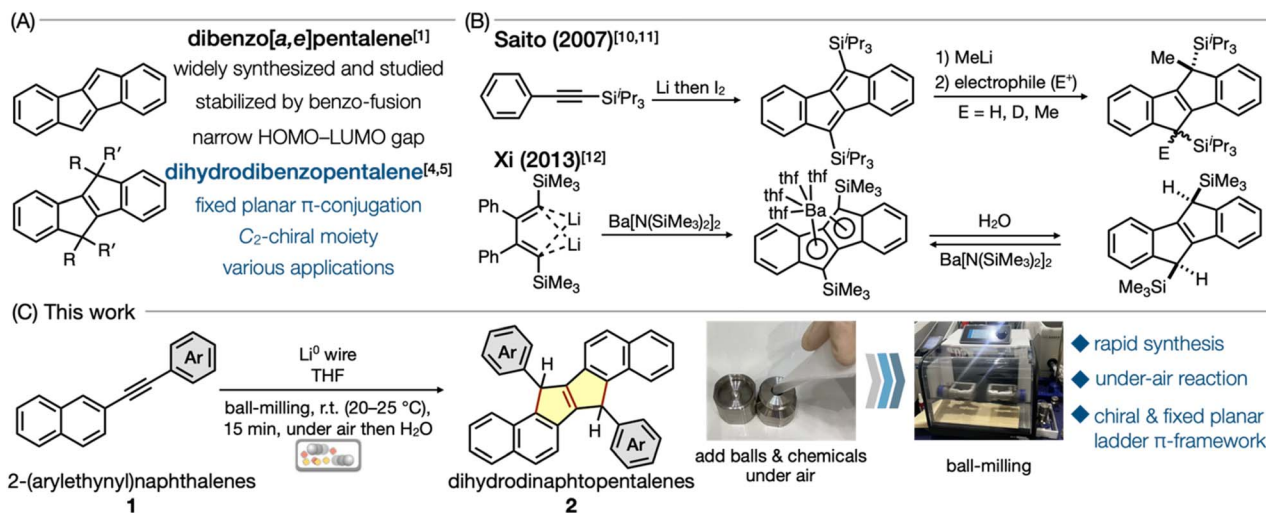


Fig. 1 (A) Dibenzo[*a,e*]pentalene and dihydrodibenzopentalene. (B) Previous reports on synthesis of dihydrodibenzopentalenes. (C) Mechanochemical synthesis of dihydroindaphthopentalenes (this work).

1-phenyl-2-silylacetylenes with lithium in tetrahydrofuran (THF). To expand the scope of the available diarenodihropentalenes, the development of alternative and/or more feasible methods is urgently required.

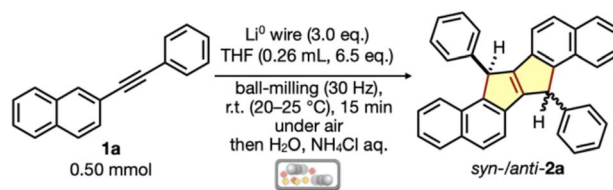
In this regard, we and the Ito/Kubota group have recently developed lithium-mediated mechanochemical transformations of aromatic compounds, such as anionic cyclo-dehydrogenation,^{13a} Birch reduction,^{14a} Birch reductive arylation,^{13a} and related transformations^{14b} using bulk lithium. Despite the fact that bulk lithium sources (*e.g.*, lithium wire) generally exhibit low reactivity in the solution state owing to their higher atomization enthalpy and melting point than those of sodium and potassium,^{13a} direct vigorous mixing by ball-milling pieces of lithium(0) wire and aromatic compounds with stoichiometric amounts of additives forms aromatic anionic species even in air, realizing highly efficient, quick transformations^{13a,14} and unprecedented reactions.^{13b} Over the course of our mechanochemistry investigation,^{15,16} we surprisingly found that mechanochemical grinding of 2-(arylethynyl)naphthalene **1** with lithium(0) wire and aqueous work-up resulted in unexpected formation of 1,4-diaryl-1,4-dihydroindaphthopentalene **2** (Fig. 1C). To the best of our knowledge, there is no example of annulative dimerization of bare diarylacetylene with alkali metals, whereas 1-phenyl-2-(trialkylsilyl)acetylenes can undergo annulation with lithium(0) or potassium(0) in the solution state using THF to afford dibenzo[*a,e*]pentalene.^{10–12} The dihydroindaphthopentalene core itself is unprecedented, and its fixed planar π -conjugation system, crystallographic packing, photophysical properties, and potential as a novel chiral platform are of interest to the physical organic chemistry community. Herein, we report the synthesis of dihydroindaphthopentalenes with two dangling aryl substituents *via* lithium(0)-mediated mechanochemical annulative dimerization of 2-(arylethynyl)naphthalenes. Unlike typical solution-state reactions using alkali metals, the developed mechanochemical reaction can be performed in air at room

temperature, without solvents for solubilizing the substrates. The prepared compounds exhibit novel dihydroindaphthopentalene skeletons, and their crystallographic structures, photophysical and chiroptical properties are characterized.

Results and discussion

Through exhaustive optimization of the reaction conditions, we found that mechanochemical annulative dimerization of 2-(phenylethynyl)naphthalene (**1a**) (0.50 mmol, 1.0 eq.) proceeded using liquid-assisted grinding (LAG)¹⁷ at room temperature (r.t.: 20–25 °C) under air by ball milling with lithium wire pieces (3 eq.), a small amount of THF (0.26 mL, 6.5 eq.) and a 7-millimeter-diameter stainless-steel ball in a 1.5 mL stainless-steel jar (Table 1, entry 1). After ball milling for 15 min, the jar was opened to air, and the deep-black slurry was quenched by adding H₂O. Aqueous workup using sat. NH₄Cl aq. afforded dihydroindaphthopentalene **2a** as the major product, with a 23% ¹H-NMR yield as a 7.5:1.0 *syn*-/*anti*-mixture. In this reaction, various side products, such as fully aromatized dinaphthopentalene and alkyne reduction products, appear to form, which lowers the yield and mass balance of the reaction. Purification by size-exclusion chromatography (SEC) enabled the isolation of *syn*-**2a** in 16% yield. The isolated yield of *syn*-**2a** was unsatisfactory, likely owing to the difficulty in separating it from other isomers and impurities during SEC purification. The relative configuration of *syn*-**2a** was determined by the X-ray diffraction (XRD) analysis of a single crystal (see Fig. 4A). The use of 4 eq. of lithium(0) also afforded **2a** in 21% NMR yield, with increased *syn*-selectivity (*syn*/*anti* = 22:1.0). Reducing the amount of lithium(0) from 3 equiv. to 2 or 1 eq. decreased the yield of **2a** and *syn*-selectivity (10% with *syn*/*anti* = 3.3:1.0; 6% with *syn*/*anti* = 3.0:1.0) (Table 1, entries 2 and 3). In controlled experiments, the use of other LAG additives, such as 1,4-dioxane, 1,2-dimethoxyethane (DME), cyclopentyl methyl ether (CPME), *N,N,N',N'*-tetramethylethylenediamine (TMEDA), and



Table 1 Optimized reaction conditions and effect of parameters for the lithium-mediated mechanochemical alkyne dimerization.^{a,d}

Entry	Deviation from the standard conditions	Yield of 2a ^b	Ratio of <i>syn/anti-2a</i>
1	None	23% (<i>syn-2a</i> : 16% ^c)	7.5 : 1.0
2	Li (4.0 eq.) instead of 3.0 eq.	21%	22 : 1.0
3	Li (2.0 eq.) instead of 3.0 eq.	10%	3.3 : 1.0
4	Li (1.0 eq.) instead of 3.0 eq.	6%	3.0 : 1.0
5	1,4-Dioxane was used instead of THF	3%	2.3 : 1.0
6	DME instead of THF	2%	1.4 : 1.0
7	CPME, TMEDA, or hexane instead of THF	0%	—
8	0.32 mL (8.0 eq.) of THF	22%	5.9 : 1.0
9	0.19 mL (4.6 eq.) of THF	0%	—
10	0.64 mL (16 eq.) of THF	5%	1.0 : 1.1
11	Li naphthalenide (4.0 eq.), THF (10 mL), 0 °C, N ₂ , 3 h	0%	—
12	Heating by heat gun at a preset temperature of 70 °C	20%	4.5 : 1.0
13	Reaction conducted in a 5.0 mL stainless-steel jar using a stainless-steel ball with a diameter of 10 mm	1%	1.8 : 1.0
14	Ball-milling was conducted at 20 Hz	9.7%	5.4 : 1.0
15	Reaction under Ar	23%	4.9 : 1.0

^a Reactions were conducted in a 1.5 mL stainless-steel jar using a stainless-steel ball with a diameter of 7 mm by ball milling using a Retsch MM400 ball mill machine. The reactions were conducted under air at r.t. (20–25 °C). ^b ¹H-NMR yield using Cl₂CHCHCl₂ as an internal standard. ^c Isolated yield of *syn-2a* by SEC. ^d The reaction was carried out in a two-neck round-bottom flask using a magnetic stirring bar and a stirrer under N₂.

hexane resulted in low yields or no formation of **2a** (Table 1, entries 5–7). The addition of 8.0 eq. of THF yielded **2a** in an amount comparable to that of the reaction under standard conditions (entry 8), whereas the reactions conducted with 4.6 or 16 eq. of THF were ineffective (entries 9 and 10). Compared with mechanochemical grinding, no reaction occurred when lithium naphthalenide (4.0 eq.) was added to THF (10 mL) at 0 °C (entry 11). Mechanochemical grinding and direct heating using a heat gun (70 °C preset temperature) did not improve the yield of **2a** (20%, *syn/anti* = 4.5 : 1) (Table 1, entry 12). By using a 5 mL stainless-steel jar and a 10-millimeter-diameter stainless-steel ball instead of a 1.5 mL jar and a 7 mm ball, the yield of **2a** dramatically dropped to 1% (entry 13). Although we tested lower-frequency ball-milling at 20 Hz to prevent overreaction and lowering the product yield (entry 14),¹⁹ the yield of **2a** rather decreased to 9.7% (*syn/anti* = 5.4 : 1) upon the full consumption of starting material. Notably, the reaction under argon atmosphere did not improve the yield of **2a** (entry 15). These results indicate that the mechanochemical reaction is highly specific in the solid or slurry state, and that the amount of THF additive, the size of the jar/ball and mixing frequencies greatly influence the reaction progress.

Next, we performed control experiments to elucidate the reaction profile of the mechanochemical alkyne dimerization. In the deuteration experiments, the addition of D₂O instead of H₂O followed by sat. NH₄Cl aq. in the quenching step produced a mixture of **2a** and deuterated product (**2a-D**) in 11% isolated

yield with a 97% deuteration ratio (Fig. 2A). In contrary, additional grinding for 60 min after adding D₂O alone resulted in dramatical drop of isolated yield (2.8%) along with almost completion of deuteration at the two benzylic positions (98%D). These indicates that the bis(cyclopentadienyl anion) species **E** (Fig. 2K) is relatively stable and remained intact even after the addition of D₂O, but is rapidly protonated with sat. NH₄Cl aq. In addition, extending the mixing time under basic conditions can induce significant degradation. Then we demonstrated trapping this dianion species by other electrophiles. The addition of iodomethane¹⁰ and extra grinding for 60 min afforded the dimethylated product **2a-Me** in 16% yield as a *syn*- and *anti*-mixture (Fig. 2B). Based on our previous findings of the Birch reductive arylation of polycyclic aromatic hydrocarbons with fluoroarenes,^{13b} we found that a similar arylation occurred in the presence of 2-fluoropyridine, affording pyridylated dihydrodinaphthopentalene (**2a-Py**) in 28% yield (Fig. 2C). Expecting that quenching with I₂/THF as an oxidant can afford dinaphthopentalene **3a** as well demonstrated in the synthesis of silyl-substituted dibenzo[*a,e*]pentalene,¹⁰ we tried the similar reaction as shown in Fig. 2D. Although the formation of **3a**, which was previously synthesized by Takimiya and Kawase²⁰ using an alternative synthetic method, was certainly detected by ¹H and ¹³C NMR spectra and EI-MS, it was obtained as an inseparable mixture of other side products (see Fig. S3 and S4 for details). Interestingly, 1-(phenylethynyl)naphthalene (**1b**) did not afford the corresponding dihydrodinaphthopentalene



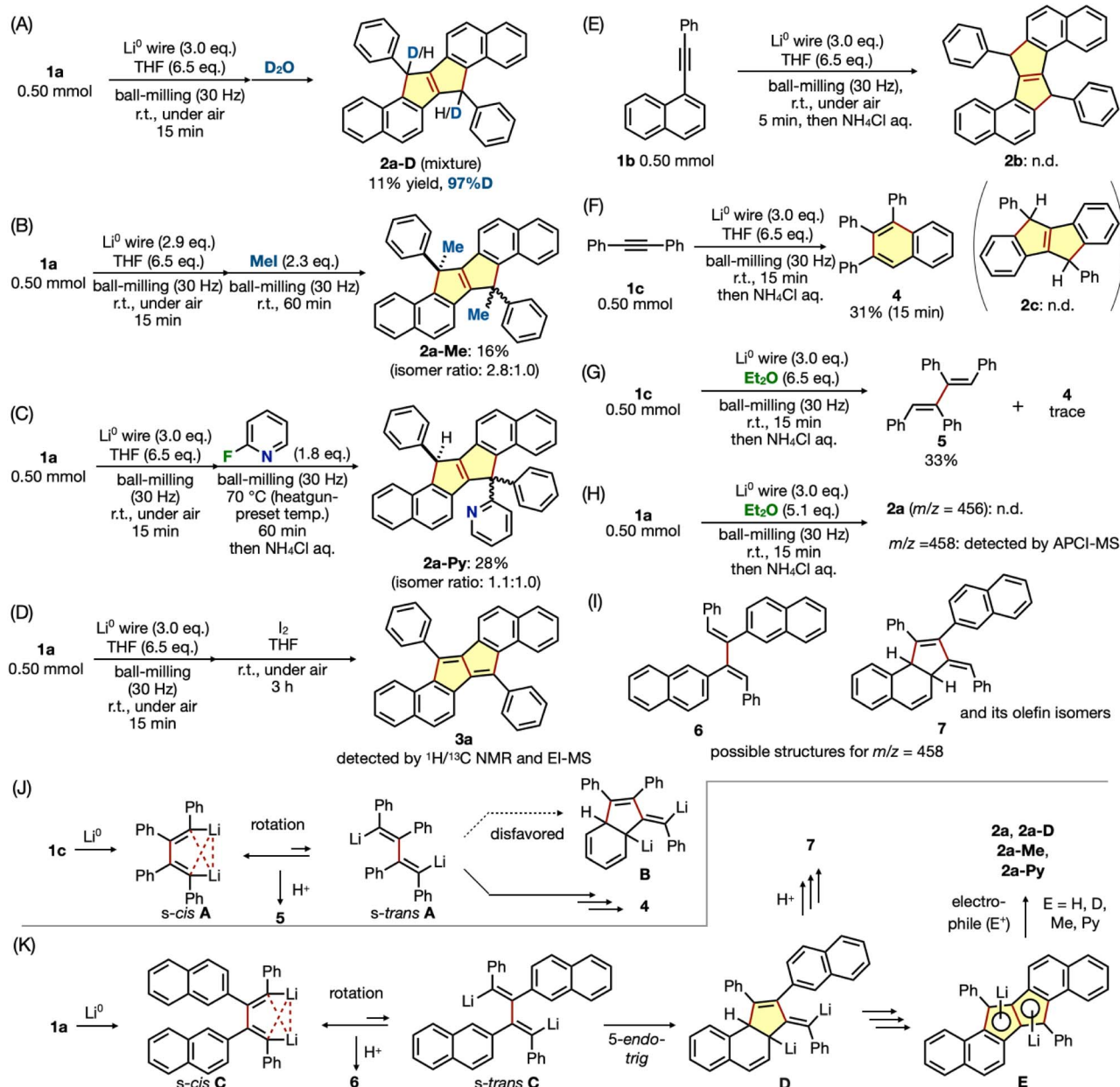


Fig. 2 (A–H) Control experiments for elucidation of reaction mechanism. (I) Plausible structures for $m/z = 458$. (J) Proposed reaction pathway to **4** from **1c** based on ref. 12b. (K) Proposed reaction pathway in the reaction of **1a** with lithium(0).

2b (Fig. 2E). Furthermore, the use of diphenylacetylene (**1c**) afforded a completely different product, 1,2,3-triphenyl-naphthalene (**4**), in 31% yield without any dihydropentalene derivative **2c** (Fig. 2F). The similar reaction was also recently reported by Kuwabara, who carried out the reaction in the solution state using lithium(0) and NaO^tBu in THF.^{11a} The further early report by Smith and Hoehn also clarified that the reaction of **1c** with a stoichiometric amount of lithium(0) in Et_2O affords 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene (**A** in Fig. 2J), and an excess amount of lithium(0) further promotes the cyclization to not the five-membered-ring intermediate **B**, but the six-membered-ring product **4**.^{11b} In fact, the mechanochemical reaction of **1c** with lithium(0) and Et_2O

for 15 min and aqueous work-up also gave (1*E*,3*E*)-1,2,3,4-tetraphenyl-1,3-butadiene (**5**) in 33% yield (Fig. 2G), which implies that dilithio intermediate **A** formed and the subsequent cyclization is slower with Et_2O than that with THF. To trap the similar intermediate, the mechanochemical reaction of **1a** was examined with Et_2O for 15 min, resulting in the formation of complex mixture including a major compound having 458 of m/z as a mass peak in APCI-MS analysis (Fig. 2H). While the isolation of the major compound was failed due to the complexity of crude mixture and the presence of various rotamers, two possible structures **6** and **7** can be considered by judging from ^1H NMR and MS analysis (Fig. 2I). Particularly, butadiene **6** seem to be contained because the singlet olefinic



proton peak in ^1H NMR at $\delta = 6.8$ ppm in $\text{ClCD}_2\text{CD}_2\text{Cl}$ is very resemble to that observed in compound **5** ($\delta = 6.75\text{--}6.73$ ppm in CDCl_3). This result would be indirect evidence for the initial formation of 1,4-dilithio-1,3-butadiene species derived from **1a**.

Based on these control experiments and our expectation, we summarized the proposed mechanism to afford **2c** and **4** from **1a** and **1c** in (Fig. 2J and K). In the reaction of **1c** with lithium(0), 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene (**A**) was preferentially forms as a *s-cis* form.^{10,12b} It is well known that there is an equilibrium between *s-cis* **A** and *s-trans* **A**, which via to the *s-cis* form.^{10,12} While the cyclization of *s-trans* **A** is expected difficult because it accompanies energetically unfavorable dearomatization of a benzene ring. In the case of the reaction of **1a**, the formation of similar 1,4-dilithio-1,3-butadiene **C** can initially form, and its *s-trans* form can be allowed to cyclize in a fashion of 5-*endo-trig* to afford allyl lithium species **D**. Then, the formation of bis(cyclopentadienyl) dilithium **E**¹⁰ via a second cyclization and elimination of benzylic hydrogen atoms followed by quenching with electrophiles affords dihydrodinaphthopentalene derivatives. We rationalize that **1b** and **1c** did not afford the corresponding dihydropentalenes because the stabilities of the anions corresponding to **B** were relatively low, that is, the π -benzyl-allyl anion **D** derived from **1a** is more stable than those generated from **1b** and **1c**. The low yield of **2a** could also be due to the lower stability of bis(cyclopentadienyl) dianion **E** than the corresponding disilylated anion derived from 2-trialkylsilylphenylacetylene,^{10,12} and the active anion species degraded much more easily in the present reaction.

Next, we explored the substrate scope of various 2-(arylethynyl)naphthalenes **1d–1j**. All experiments were performed on a 0.50 mmol scale under air at r.t. (Fig. 3). The use of 2-[[4-(*t*-butyl)phenyl]ethynyl]naphthalene (**1d**) afforded a mixture of

syn-/*anti*-**2d** in 79% yield, and *syn*-**2d** was isolated in 18% yield after purification by SEC. The reaction of 2-[[4-methoxyphenyl]ethynyl]naphthalene (**1e**) proceeded, affording the corresponding diarylated pentalenes *syn*-/*anti*-**2e** in 29% yield. However, isolation by SEC resulted in 4.6% (*syn*-**2e**) and 1.5% (*anti*-**2e**) yields owing to significant degradation of products in purification. In addition, the reaction of naphthylacetylene with *p*-(diphenylamino)phenyl group **1f** afforded a mixture of *syn*-/*anti*-**2f** in 33% yield, and *syn*-/*anti*-**2f** was isolated by SEC in 8.0% and 6.6% yields, respectively. On the other hand, phenylethynyl naphthalenes containing electron-withdrawing groups, such as 1-[[4-fluorophenyl]ethynyl]naphthalene (**1g**) and 1-[[3-cyanophenyl]ethynyl]naphthalene (**1h**), were found to be ineffective in this mechanochemical dimerization. The reaction of **1g** underwent to give trace amount of **2g** along with the major formation of defluorinated product **2a** which can be due to lithium-halogen exchanging.^{16f} In contrast, majority of **1h** remained intact after the reaction. Then, 1-(arylethynyl)naphthalenes bearing naphthalen-2-yl (**1i**) and triphenylene-2-yl (**1j**) moieties were transformed into a *syn*-/*anti*-mixture of **2i** (25%) and **2j** (14%), and SEC separation afforded *syn*-**2i** in 4.6% yields. While the final isolated yields of *syn* and/or *anti* isomers were unsatisfactory owing to the difficulties in SEC separation and the significant degradation in SEC, the combined yields of *syn*-/*anti*-**2** at the silica gel column chromatography were moderate. Notably, a series of compounds are relatively unstable under air and basic conditions probably due to the presence of reactive benzylic/allylic protons on cyclopentadiene structures, and the products having electro-donating aryl groups **2e** and **2f** show lower stabilities than others. This mechanochemical reaction protocol provides a rapid, simple one-pot synthesis of novel dihydrodinaphthopentalenes.

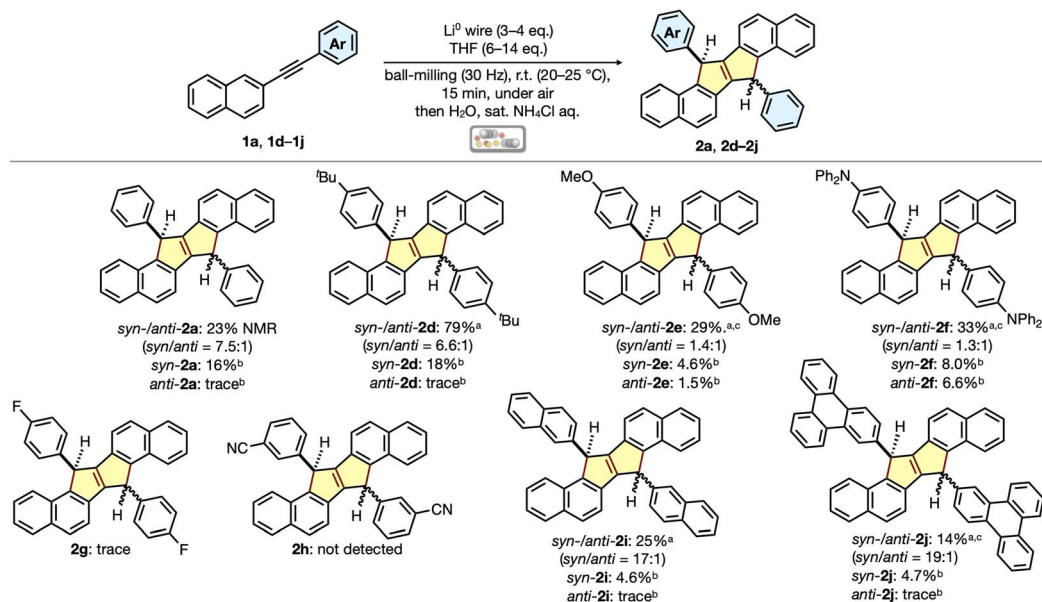


Fig. 3 Substrate scope in the lithium-mediated mechanochemical alkyne dimerization (reaction scale: 0.18–0.50 mmol). ^aCombined isolated yield of mixture of *syn*-/*anti*-**2** after silica gel column chromatography. ^bIsolated yield of each isomer after SEC. ^cReaction was carried out at 70 °C of heat-gun preset temperature for 99 min.



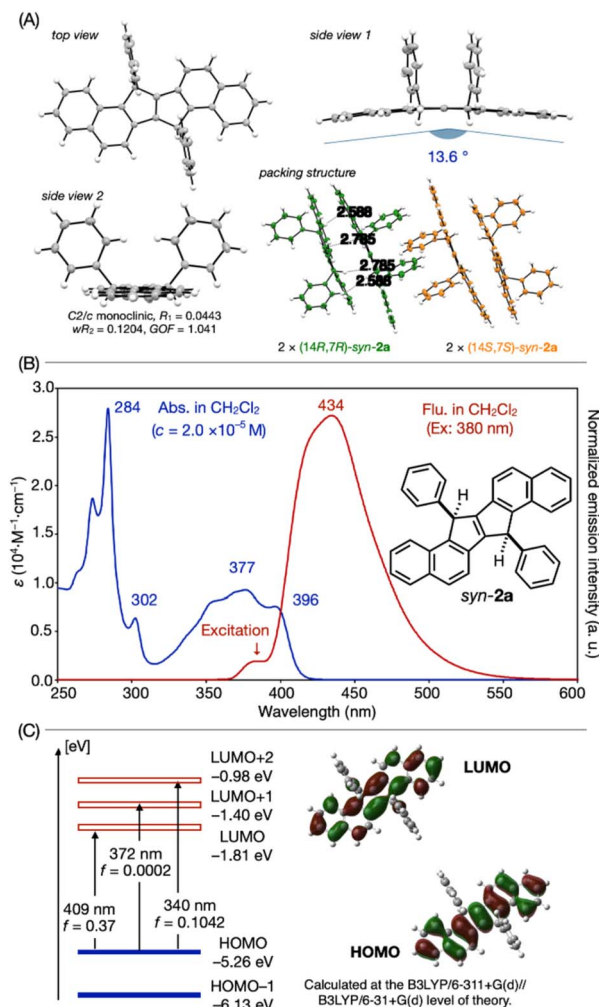


Fig. 4 (A) X-ray crystallographic structures of *syn-2a*. (B) UV-vis absorption (blue line) and emission (red line) spectra of *syn-2a* (c = 2.0 × 10⁻⁵ M) in CH₂Cl₂. Molar absorptivities of each peak: $\epsilon_{284} = 2.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, $\epsilon_{302} = 6.4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$, $\epsilon_{377} = 9.3 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$, and $\epsilon_{396} = 7.6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. Excitation wavelength for emission spectrum: 380 nm. (C) Possible transitions calculated using TD-DFT at the B3LYP/6-311 + G(d,p)//B3LYP/6-31G + (d) level of theory and depiction of frontier MOs.

Because the obtained dihydrodinaphthopentalene has a novel structural motif similar to that of dihydropentalene and can be regarded as a fixed planar stilbene derivative with a C₂-symmetric chiral structure, its structural, electronic, photo-physical, and chiro-optical properties are of interest. First, we obtained a single crystal of *syn-2a* and determined its X-ray crystallographic structure (Fig. 4A). It exhibited a slightly bent but almost planar bismethylene-bridged dinaphthylethene core with two dangling phenyl groups whose benzene rings were parallel to each other. In the packing structure, two identical enantiomers were paired and stacked on sterically less-hindered faces through weak CH- π interactions between benzylic protons and aromatic sp²-carbons. This pair (green molecules in Fig. 4A, bottom right) and the opposite enantiomeric pairs (orange molecules in Fig. 4A, bottom right) were

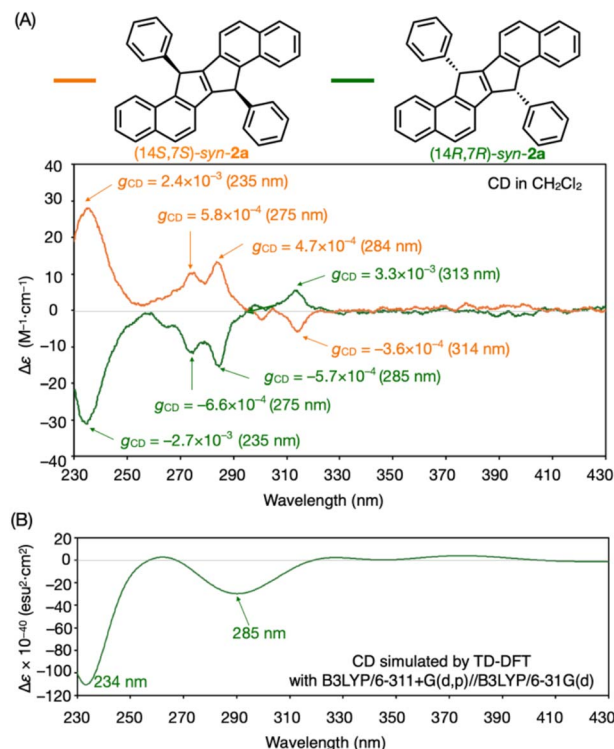


Fig. 5 (A) CD spectra of *(7S,14S)-syn-2a* (later-eluted fraction, orange line, c = 2.2 × 10⁻⁵ M) and *(7R,14R)-syn-2a* (earlier-eluted fraction, green line, c = 2.0 × 10⁻⁵ M) measured in CH₂Cl₂ at 0 °C. (B) Predicted CD spectrum of *(7R,14R)-syn-2a* calculated by TD-DFT at B3LYP/6-311G + (d,p)//B3LYP/6-31G + (d) level with N state = 100 and UV-vis peak half-width at half-height = 0.20 eV.

alternately aligned. In this packing structure, π - π stacking was not apparent between each molecule.

Next, we measured the UV-vis absorption spectrum of a solution of *syn-2a* in CH₂Cl₂ (c = 2.0 × 10⁻⁵ M) (Fig. 4B). A sharp absorption maximum at $\lambda_{\text{abs}} = 284$ nm and broad absorption bands containing absorption maxima at $\lambda_{\text{abs}} = 377$ and 396 nm were observed. Compared with a major absorption peak at 333 nm in the longest-wavelength region (300–390 nm) of the absorption spectrum of (*E*)-1,2-di(naphthalen-2-yl)ethene (**8**) (see ESI and ref. 18), which features a partial structural motif of *syn-2a*, the absorption band of *syn-2a* was red-shifted to 320–430 nm, with a maximum at 377 nm. The molar absorptivity (ϵ) at the peak maximum diminished from $8.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ (**8** in CH₂Cl₂; see ESI) to $9.3 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ (*syn-2a*). The red shift of the peak maximum can be attributed to the effect of π -extension derived from a fixed planarity by bis-methylene bridging. The decreased absorptivity was also rationalized by the suppressed allowed transitions caused by the breakdown of molecular symmetry by molecular vibrations and bond rotations.

In the frontier molecular orbitals (MOs) calculated at the B3LYP/6-31G+(d) level of theory, the HOMO and LUMO were mainly delocalized across the dihydrodinaphthopentalene core (Fig. 4C). Time-dependent density functional theory (TD-DFT) calculations at the B3LYP/6-311 + G(d,p)//B3LYP/6-31 + G(d) level also revealed that the experimental absorption maximum at



$\lambda_{\text{abs}} = 396 \text{ nm}$ is well reproduced by the allowed HOMO \rightarrow LUMO transition ($S_0 \rightarrow S_1$; $\lambda = 409 \text{ nm}$, oscillator strength (f) = 0.37). By contrast, the second transition, arising from HOMO \rightarrow LUMO+1 excitations ($S_0 \rightarrow S_2$; $\lambda = 372 \text{ nm}$, $f = 0.0002$) are essentially forbidden (see ESI for details of other transitions). Furthermore, *syn-2a* exhibited fluorescence upon excitation with 380 nm light, and a broad emission band from 390 to 570 nm with a maximum at $\lambda_{\text{em}} = 434 \text{ nm}$ was observed (Fig. 4B). The emission maximum was also significantly red-shifted compared with that of compound **5** ($\lambda_{\text{em}} = 384 \text{ nm}$; see ESI for details).

After optimizing the separation conditions, each enantiomer in racemic *syn-2a* was successfully resolved by high-performance liquid chromatography (HPLC) using a chiral column (DAICEL CHIRALPAK IF) and *n*-hexane/ CH_2Cl_2 (80 : 20) as the eluent. In the circular dichroism (CD) spectra, the earlier- and later-eluted fractions show *levo* (green line in Fig. 5A) and *dextro* (orange line in Fig. 5A) optical rotations in the 230–300 nm range, and the two spectra were almost mirror images. In addition, opposite-sign Cotton effects were observed at *ca.* 300 nm, which were attributed to the phenyl rings around the chiral carbon centers. However, significant optical rotations were not observed in the range of 330–400 nm, which corresponds to the absorption of the dihydrodibenzopentalene core. The CD spectrum of (7*R*,14*R*)-*syn-2a* simulated by TD-DFT (Fig. 5B) was identical to the experimentally obtained spectrum of the earlier-eluted fraction (green line in Fig. 5A).

Conclusions

In summary, we developed a novel mechanochemical dimerization of 2-(arylethynyl)naphthalenes and a synthetic method for dihydrodibenzopentalene analogs. By directly mixing lithium wires, diarylacetylenes, and a stoichiometric THF additive in air using a ball mill, diarylated dihydrodibenzopentalenes formed quickly, even in air. To clarify the potential of *syn-2a* as a novel scaffold for π -conjugated ladder molecules with face chirality and fixed planarity, we determined the structural features of *syn-2a* by XRD analysis, photophysical properties by UV-vis absorption/emission spectroscopy, electronic properties by DFT calculations, and chiroptical properties by CD measurements. Further studies using established methods and synthesized molecules are ongoing in our laboratory.

Author contributions

Y. T. preliminarily discovered the reaction, and K. M. H. mainly developed the reaction, synthesized, analyzed, and characterized all compounds and performed theoretical calculations with partial support from Y. T., T. N. and Y. O. T. M. conducted XRD analysis. H. I. directed the project, designed the target compounds, supervised the experiments, and supported the data analyses. The draft manuscript was written by Y. T. and H. I., and all authors finalized the manuscript through proof-reading. All authors approved the final version of the manuscript. K. M. H. and Y. T. equally contributed to this paper.

Conflicts of interest

There are no conflicts to declare.

Data availability

CCDC 2495836 (*syn-2a*) contains the supplementary crystallographic data for this paper²¹.

Experimental and characterization data, including crystallographic data, photophysical measurements, and NMR spectra, as well as computational investigations have been included as part of the electronic supplementary information (SI). Supplementary information: syntheses, NMR, UV-vis absorption, emission, CD spectra, DFT calculations, and crystallographic table. See DOI: <https://doi.org/10.1039/d5mr00145e>.

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