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Diversified Syntheses of Tetrathia[7]helicenes by Metal-Catalyzed Cross Coupling Reactions

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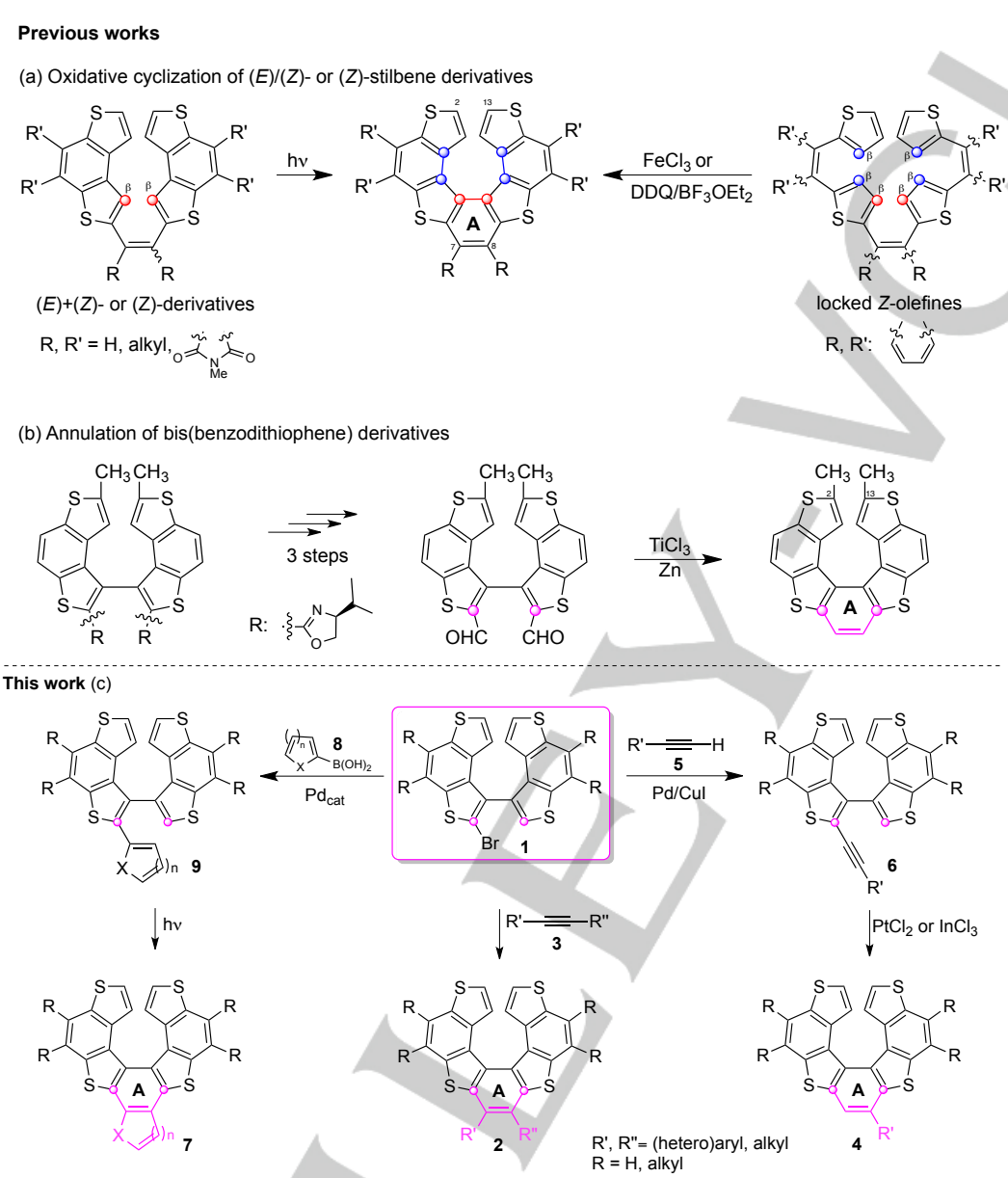
Abstract: Efficient and versatile synthetic routes of functionalized tetrathia[7]helicenes (7-THs) are described. The key intermediates of these methodologies are 2-bromo-3,3'-bibenzo[1,2-*b*:4,3-*b*']dithiophenes (**1**), synthesized through a palladium-catalyzed homocoupling reaction between two benzo[1,2-*b*:4,3-*b*']dithiophene units followed by a regioselective α-bromination. Direct palladium-catalyzed annulation of bromides **1** with internal alkynes provides a set of 7,8-disubstituted 7-THs **2** in moderate to good yields (46-80%). Otherwise, 7-monosubstituted 7-THs **4** have been prepared through Sonogashira coupling of **1** with terminal alkynes, followed by platinum- or indium-promoted cycloisomerization of alkynyl intermediates **6**. Finally, the versatility of bromides **1** has also been demonstrated by using them for the preparation of benzo (hetero) fused 7-TH derivatives **7** via Suzuki coupling with (hetero)arylboronic acids and the photocyclization of the obtained intermediates **9**.

Introduction

Helicenes are inherently chiral helical-shaped molecules, formed of *ortho*-fused benzene or other heteroaromatic rings.[1] The helical configuration joined with their extended π-conjugated system provide helicenes with exceptionally chiroptical properties, that have been extensively exploited in a variety of domains.[1,2] Thia[n]helicenes, in which benzene rings alternate with thiophene rings, are a subclass of heterohelicenes that have gained much attention due to their unique characteristics combining the electronic properties of oligothiophenes with the peculiar chiroptical features associated to the helical structure.[3]
Over several years we have been interested in the study of configurationally stable tetrathia[7]helicene (7-TH) derivatives, that are emerging as one of the most promising class of thiahelicenes for applications in nonlinear optics,[4] organic electronic devices,[5] catalysis,[6] electrochemical sensing,[7] biology.[8] The reliable and selective functionalization of 7-TH scaffold in the α-position of the terminal thiophene rings allows the insertion of different substituents,[9] that modulate structural features and electronic properties of the helical skeleton[10] and enable highly enantioselective optical resolution.[11]
In order to best exploit the potential of 7-TH derivatives, different synthetic methodologies have been described, and these mainly include oxidative photocyclization of stilbenes[9,12,13] besides a few non-photochemical procedures.[14] In particular, the central benzene ring A can be built through two main strategies: (a) the formation of C_β-C_β bonds by means of oxidative cyclization of the corresponding stilbene-like precursors (Scheme 1a); (b) the annulation of 3,3'-bis(benzo[1,2-*b*:4,3-*b*']dithiophene) derivatives (Scheme 1b).
The first strategy (Scheme 1a) is the most common procedure to prepare 7-TH systems in racemic form, and it involves the photocyclization of 1,2-bis(benzodithienyl)ethenes as a mixture of (*E*)- and (*Z*)-isomers in turn prepared *via* Wittig olefination[12] or reductive McMurry coupling.[9] As the first step of this photochemical reaction is the *E*/*Z* isomerization of the double bond, a further optimization of this methodology concerns the use of 1,2-bis(benzodithienyl)ethenes as *Z*-isomers,[13] that undergo faster and more efficient photocyclization. Alternatively, benzo fused 7-TH systems were also synthesized through non-photochemical procedures that make use of DDQ in combination with $BF_3{\cdot}OEt_2$[14a] or $FeCl_3$[14b] as oxidants to promote the oxidative cyclodehydrogenation of 1,2-bis(2-thienyl)benzene precursors. Overall, the oxidative cyclization of stilbene derivatives represents a direct and low-cost methodology to prepare the parent 7-TH or 7-TH systems, nevertheless a limited number of substituents in the 7- and 8- positions can be present due to the low compatibility of many functional groups under photochemical and/or oxidative conditions.[9c] The second strategy (Scheme 1b), that involves the formation of 3,3'-bis(benzodithiophene) species, is still much underdeveloped compared to the first one, and only two examples of cyclization of 3,3'-bis(benzo[1,2-*b*:4,3-*b*']dithiophene) have been reported for the synthesis of the enantiopure 2,13-dimethyltetrathia[7]helicene,[14c] and of a pentathia[7]helicene.[15] On the other hand, this approach represents the most suitable and promising way to achieve highly functionalized 7-TH systems, especially in enantioenriched form taking advantage of the potential axial chirality of bis(benzodithiophene) species. In this context, the design and development of more general and straightforward procedures, that exploit the versatility provided by metal-promoted cross-coupling reactions, would afford a significant synthetic advancement in thiahelicene chemistry.
In our continuing efforts aimed at finding efficient and more versatile syntheses of differently functionalized 7-TH framework, we looked for novel methodologies for the cyclization of bis(benzodithiophene) species that make use of transition metal-

catalyzed cross-coupling reactions, such as the annulation of 2-halobibenzodithienyl species **1** with alkynes **5** and the cycloisomerization of 2-alkynyl-3,3'-bibenzodithienyl systems **6** (Scheme 1c). Indeed, although the palladium catalyzed annulation of 2-halobiaryls with alkynes has been extensively used to prepare functionalized phenanthrene-like systems,[16] to the best of the authors' knowledge, this methodology has not been employed to prepare thiahelicenes.



Scheme 1. Synthesis of tetrathia[7]helicene derivatives: past and present works

Likewise, metal-catalyzed cycloaromatization of 2-ethynylbiaryls[17] is a convenient alternative by which enantioenriched 7-TH derivatives could be obtained performing the reaction in the presence of chiral ligands. Dienyne cycloisomerizations have been widely employed to prepare helicenes,[18] and some highly enantioselective syntheses of carbohelicenes[19] and azahelicenes[20] have been described by using chiral Au(I) catalysts. However, no example of cycloisomerization of 2-alkynyl-3,3'-bibenzodithienyls to prepare 7-TH has been so far reported.

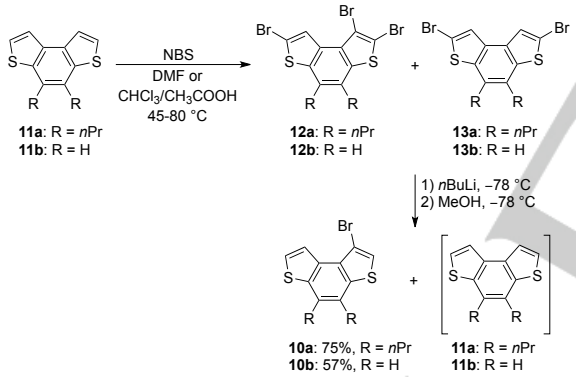
Herein, we report the study of three diverse methodologies for the synthesis of functionalized 7-TH frameworks using 2-bromo-3,3'-bibenzodithienyls **1** as key intermediates. According to Scheme 1c, a set of 7,8-disubstituted thiahelicenes **2** has been prepared through the Pd-catalyzed annulation of bromides **1** with internal alkynes **3**, while the synthesis of 7-monosubstituted compounds **4** has been realized via a two-step procedure involving a Sonogashira coupling of **1** with alkynes **5**, followed by the metal-promoted cycloisomerization of intermediates **6**. It is worth mentioning that these procedures provide a facile

access to 7-TH derivatives bearing (hetero)aryl substituents in 7- and/or 8-position. Finally, the synthesis of benzo fused 7-TH systems **7** has been also explored by means of a two-step procedure involving a Suzuki coupling of **1** with (hetero)aryl boronic acids **8**, followed by photochemical cyclization of intermediates **9**.

Results and Discussion

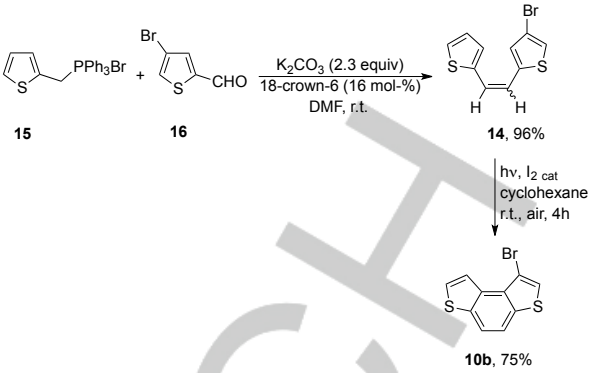
Synthesis of 2-bromo-3,3'-bibenzo[1,2-*b*:4,3-*b*']dithiophenes 1

Our approach for the synthesis of bromides **1** made use of 1-bromobenzo[1,2-*b*:4,3-*b*']dithiophenes **10**, which were synthesized according to a two-step procedure involving the electrophilic bromination of benzodithiophenes **11**, followed by the selective debromination of 1,2,7-tribromobenzodithiophene **12** through lithium-halogen exchange reaction with *n*BuLi and quenching with methanol[20] (Scheme 2). The bromination of **11a**[21] using NBS (3.3 equiv) in DMF at 80 °C provided the tribromide **12a** and dibromide **13a** that were isolated as mixture in 1:0.14 molar ratio (76% yield of **12a** in the mixture by NMR). Otherwise, the bromination of **11b**[22] was performed using a very large amount of NBS (6.5 equiv) in chloroform/acetic acid (1:1) at 45 °C. These conditions allowed to get the mixture of tribromide **12b** and dibromide **13b** in 24:1 molar ratio (71% yield of **12b** in the mixture by NMR).[23]



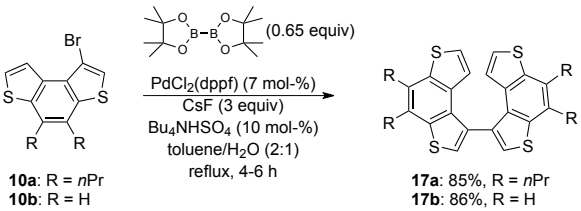
Scheme 2. Two-step synthesis of 1-bromobenzodithiophenes **10a**,**b**.

The treatment of these mixtures with *n*BuLi at –78 °C followed by the addition of MeOH afforded the required bromides **10a** and **10b** in 75% and 57% yield, respectively. Small amounts of benzodithiophenes **11a** and **11b** were also recovered (10-20%).
In the case of **10b**, obtained in moderate yield from this procedure, a convenient synthetic alternative was found by introducing bromine atom in the suitable position before the formation of benzodithiophene ring. As shown in Scheme 3, **10b** was prepared in 75% yield through the photochemical cyclization of 4-bromo-2-[2-(2-thienyl)-ethenyl]-thiophene (**14**), in turn obtained in 96% yield by Wittig reaction of (2-thienylmethyl)triphenyl phosphonium bromide[24] (**15**) and the commercially available 4-bromo-2-thiophencarbaldehyde (**16**).



Scheme 3. Alternative synthesis of **10b**

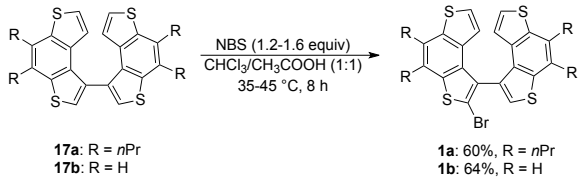
Next, we investigated the homocoupling reaction of bromides **10** to obtain the corresponding biaryls **17** following, at first, dimerization procedures described by Rajca *et al.*[15] for similar benzodithiophene-based dimers. Unfortunately, palladium-catalyzed reductive dimerization of bromide **10a** under different experimental conditions provided the desired biaryl **17a** in traces, and **10a** was generally recovered in almost quantitative yield. Similarly, Li/Br exchange reaction of **10a** followed by oxidation with $CuCl_2$ provided **17a** in unsatisfactory yields (20-30%). We then considered the one-pot Miyaura borylation/Suzuki coupling (MBSC) as the alternative procedure for the dimerization of **10**. The MBSC represents a convenient methodology to prepare symmetrical and unsymmetrical biaryl systems, that allows to avoid the isolation of arylboron intermediates.[25] Miura *et al.* reported that the palladium-catalyzed one-pot MBSC of aryl bromides, including thienyl bromides, could be efficiently promoted in the presence of bis(pinacolato)diboron (B_2Pin_2) under phase-transfer conditions, by the use of a catalytic amount of Bu_4NHSO_4 in a biphasic solvent system formed by toluene and water.[25m] We then examined similar conditions to synthesize **17** (for further details on the optimization of the reaction conditions see Table S1, ESI), and we found that one-pot MBSC of bromides **10a**,**b** with B_2Pin_2 (0.65 equiv) could be efficiently carried out in the presence of $PdCl_2$(dppf) (7 mol-%) as catalyst, Bu_4NHSO_4 (10 mol-%) and CsF (3 equiv) in a mixture of toluene and water at reflux (Scheme 4).



Scheme 4. One-pot MBSC homocoupling reaction of bromides **10a**,**b**

Dimers **17a** and **17b** were isolated in good yield (85-86%), and only traces (< 5%) of the parent benzodithiophenes **11a,b** were observed in the reaction mixture. It is noteworthy that these reactions could be scaled-up, allowing us to prepare up to 1 g of **17a** and **17b** in a single run.
Having secured good access to dimers **17**, we studied their selective bromination to obtain monobromides **1**. Although

dimers **17** display four terminal thiophene rings with free alpha and beta positions, which in principle could undergo electrophilic substitution, thiophenes involved in the C_β-C_β biaryl bond could be more reactive due to the presence of the electron-rich benzodithienyl moiety in the beta-position. A similar behavior has also been observed for the synthesis of 2-bromo-3,3'-dithiophene through the selective α-bromination of 3,3'-dithiophene with NBS.[26] To verify this hypothesis, we reacted **17a** with a small molar excess of NBS (1.2 equiv) in chloroform/acetic acid 1:1 mixture at 35 °C (Scheme 5).



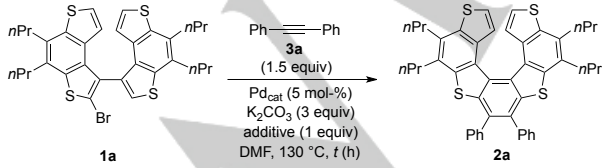
Scheme 5. Bromination of bi(benzodithiophene) compounds **17a**,**b**.

We were pleased to find that the mixture of this reaction contained the required bromide **1a** as major product after 8 h along with small amounts of the unreacted **17a**, and other brominated side-products. Chromatographic purification of this mixture allowed us to isolate **1a** in 60% yield. Similar reaction conditions were also used to synthesize bromide **1b**, which was isolated in 64% yield using 1.6 equiv of NBS at 45 °C (Scheme 5).

Synthesis of 7,8-disubstituted 7-TH derivatives 2

With key bromides **1** in place, we sought to take advantage of these intermediates for the synthesis of diverse classes of tetrathia[7]helicenes, such as 7,8-disubstituted derivatives **2** through the direct palladium-catalyzed C-H annulation of **1** with internal alkynes **3** (Scheme 1c). To this end, we initially studied the annulation of **1a** with diphenylacetylene (**3a**) under experimental conditions very similar to those described for the annulation of 2-bromo-3,3'-dithiophene to give the corresponding 4,5-disubstituted benzo[1,2-*b*:4,3-*b*']dithiophenes.[27] In particular, when **1a** was reacted with **3a** (1.5 equiv) in the presence of $Pd(PPh_3)Cl_2$ (5 mol-%), LiBr (1 equiv) and K_2CO_3 (3 equiv) in DMF at 130 °C, thiahelicene **2a** was isolated 60% yield (entry 1, Table 1).

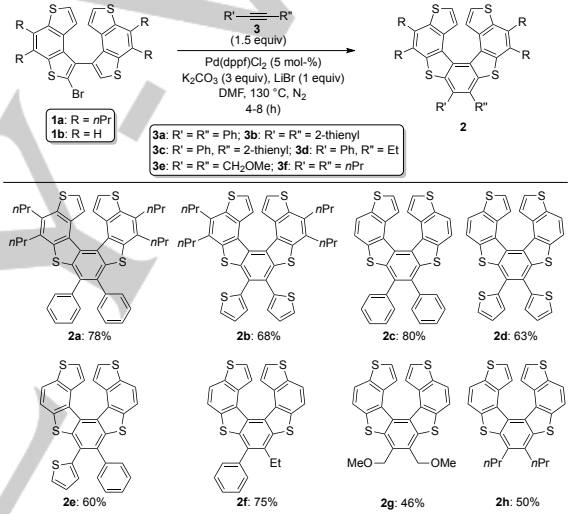
Table 1. Optimization of the Pd-catalyzed annulation of **1a** with alkyne **3a**



Entry[a]	$Pd_{cat.}$	Additive	*t* (h)[b]	Yield of **2a** (%)[c]
1	$Pd(PPh_3)_2Cl_2$	LiBr	8	60[d]
2	$Pd[P(tBu)_3]_2$	LiBr	8	62[d,e]
3	$Pd(dppf)Cl_2$	LiBr	6	78[e]
4	$Pd(dppf)Cl_2$	-	12	58[d]

[a] The reactions were run with 0.1 mmol of **1a** in DMF at 130 °C (oil bath). [b] The reactions were stopped when they did not further progress. [c] Isolated yield. [d] Small amounts of **1a** was recovered (5-10%). [e] Debrominated by-product **17a** was recovered (ca. 10%).

Encouraged by this result, a couple of different palladium catalysts were examined (entries 2-3, Table 1). A lower reactivity was observed when a Pd(0) catalyst such as $Pd([P(tBu)_3])_2$ was used (entry 2, Table 1), while the use of $Pd(dppf)Cl_2$ increased the yield of **2a** up to 78% (entry 3, Table 1), so this latter was selected as the best catalyst for this reaction. Finally, the presence of a stoichiometric amount of LiBr[28] was found to be beneficial for the reaction (compare entries 3 and 4, Table 1). As summarized in Scheme 6, the scope of this reaction was tested by using various (hetero)aryl- and alkyl-containing internal alkynes that underwent the cyclization with bromides **1** under the experimental conditions reported in entry 3 of Table 1, giving a series of 7,8-disubstituted 7-TH **2** in moderate to good yields.



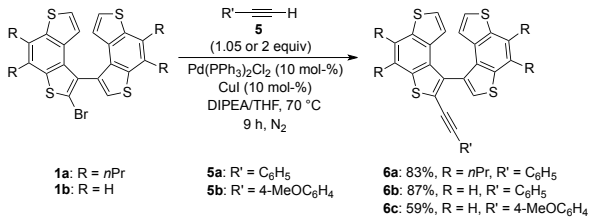
Scheme 6. Synthesis of 7,8-disubstituted 7-TH derivatives **2a**-**h**.

The reactions efficiently proceeded to give the desired cyclized products regardless of the electron density of bromides **1**, while the nature of the alkyne seemed to influence the outcome of this reaction. Alkyl and alkyloxy substituted alkynes gave the corresponding helicenes **2g** and **2h** in lower yields (46 and 50%, respectively) than those obtained using (hetero)aryl substituents (60-80%). Furthermore, no product was obtained using both terminal alkynes (e.g. phenylacetylene) and trialkysilylacetylenes (e.g. Me_3Si-C≡C$SiMe_3$). In the latter case, the desilylation of alkyne is presumably more favorite than the annulation reaction.
Of note, this procedure allows the synthesis of tetrathia[7]helicenes substituted in the 7 and 8 positions with aryl or heteroaryl groups that cannot be prepared through the photochemical cyclization of the corresponding alkene precursors. Indeed, several attempts to prepare 7,8-diphenyltetrathia[7]helicene (**2c**) through the photocyclization of the (*Z*)-1,2-bis(benzodithienyl)-1,2-diphenylethene failed, since the reaction provided complex reaction mixtures, from which we were not able to isolate the desired 7-TH **2c**.

Synthesis of 7-substituted 7-TH derivatives 4

To further expand the usefulness of bromides **1**, we considered a two-step procedure for the synthesis of 7-aryltetrathia[7]helicenes **4**, involving the Sonogashira coupling between bromides **1** and terminal acetylenes **5** followed by an intramolecular hydroarylation of the corresponding alkynes **6** (Scheme 1c). As previously mentioned, thiahelicenes **4** cannot be obtained by the direct Pd-catalyzed annulation of bromides **1** with terminal alkynes according to the procedure shown in Scheme 6.

Thus, we performed a preliminary study for the cyclization of three model alkynes **6a**–**c** by using transition metal salts. Alkynes **6a-c** were synthesized in good yields (59-87%) by reacting **1** with the terminal acetylenes **5a**,**b** in the presence of $Pd(PPh_3)_2Cl_2$ (10 mol-%) and CuI (10 mol-%) in DIPEA/THF at 70 °C (Scheme 7).



Scheme 7. Synthesis of alkynes **6a**–**c**.

Colorless needles of **6c** were obtained by layering hexane over a dichloromethane solution. The structure of the molecule has been confirmed by X-ray diffraction analysis. The ORTEP view of the molecule is reported in Figure 1, together with the atomic numbering scheme. A selection of the most important bond distances and angles is listed in the caption.

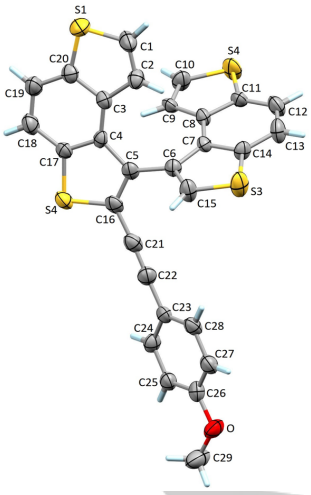
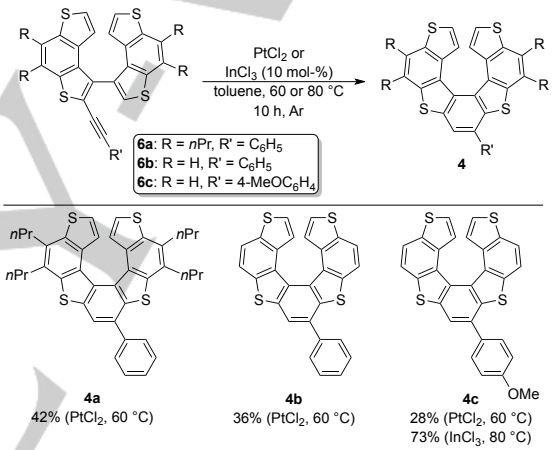


Figure 1. Ortep view of compound **6c**. Ellipsoids are drawn at their 50% level. Bond distances [Å] and angles [deg]: C2-C3 1.422(10), C3-C4 1.415(11), C4-C5 1.455(10), C18-C19 1.356(12), C5-C6 1.474(10), C6-C7 1.430(10), C7-C8 1.437(10), C8-C9 1.435(10), C12-C13 1.357(11), C16 C21 1.440(12), C21 C22 1.201(11), C22 C23 1.427(12); C16-C5-C4 110.9(6), C16-C5-C6 122.7(7), C4-C5-C6 126.4(7), C15-C6-C7 111.4(7), C15-C6-C5 121.8(7), C7-C6-C5 126.6(7), C5-C16-C21 128.4(7), C5-C16-S2 114.2(6), C21-C16-S2 117.3(6), C22-C21-C16 176.5(9), C21-C22-C23 177.6(10).

Each of the two benzodithienyl moieties are practically planar and they are connected via C5-C6 bond. The dihedral angle between the mean planes is 65.76°. It is interesting to note that in the benzene rings the C12-C13 and C18-C19 bond lengths are significantly shorter than the C3-C4 and C7-C8 ones, in agreement with parent systems and thiahelicene precursors reported in literature.[29] The mean plane of the methoxyphenyl substituent is twisted with respect to the benzodithienyl group, showing a dihedral angle of 27.49°. The carbon atoms involved in the triple bond are at a distance of 0.066 and 0.153 Å, respectively, for C21 and C22 from the mean plane of the substituted benzodithienyl moiety. In the crystals, a racemic mixture of the two atropoisomers is present.

Alkynes **6a-c** were then tested in the cycloisomerization promoted by $PtCl_2$, $InCl_3$ and $AuCl_3$, and the effect of some parameters such as the nature of the metal catalyst, the solvent and the temperature on the outcome of this reaction was evaluated (see Table S3, ESI). Scheme 8 reports the best results obtained in this study.



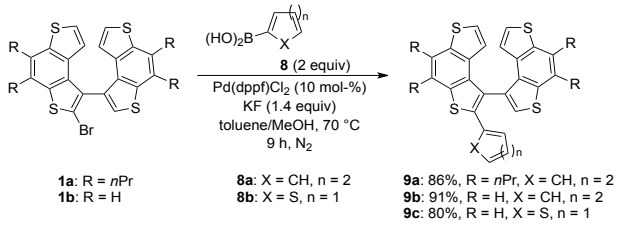
Scheme 8. Cycloisomerization of alkynes **6a-c**.

The $PtCl_2$-promoted cycloisomerization of **6a-c** provided the corresponding helicenes **4a-c** in moderate yields (28-42%), while $InCl_3$ efficiently catalyzed the reaction of the electron-rich substrate **6c** (73% yield of **4c**), but it did not provide any product with alkynes **6a** and **6b**. Conversely, no reaction occurred using $AuCl_3$ as catalyst, and the starting alkynes **6** were quantitatively recovered under different experimental conditions (see Table S3, ESI). These results clearly demonstrate that this reaction is strongly influenced by the nature of the catalyst and the electronic features of the alkynes, and further investigations, especially focused on the catalytic system, could improve the effectiveness of the process.

Synthesis of benzo fused 7-TH derivatives 7

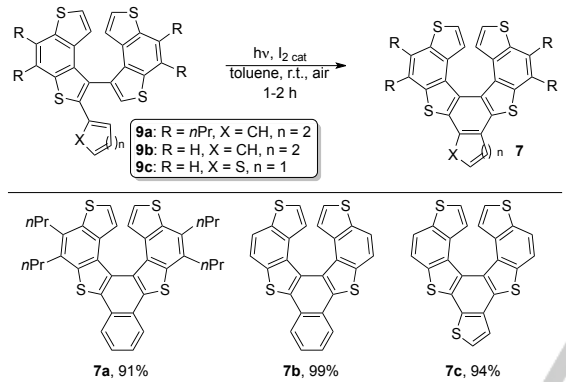
The utility of bromides **1** was also investigated for the synthesis of benzo fused 7-TH derivatives **7**, which were prepared according to the two-step sequence involving a Pd-catalyzed Suzuki reaction with (hetero)aryl boronic acids **8**, followed by the photochemical cyclization of intermediates **9** (Scheme 1c). Efficient Suzuki coupling reactions were performed using $Pd(dppf)Cl_2$ as catalyst and KF as base in toluene/MeOH at

70 °C, and **9a-c** were isolated in good to excellent yields (Scheme 9).



Scheme 9. Synthesis of intermediates **9** by Suzuki reaction between bromides **1** and (hetero)arylboronic acids **8**.

Finally, the photocyclization of **9** was carried out through the irradiation of a diluted solution of **9** in toluene by means of a medium-pressure Hg lamp in the presence of a catalytic amount of iodine at room temperature (Scheme 10).



Scheme 10. Synthesis of benzo fused thiahelicenes **7** by photocyclization of **9**.

The cyclization of both phenyl and thienyl pendant smoothly provided the corresponding helicenes **7a-c** in excellent yields (91-99%) in very short reaction time (1-2 h).

Conclusion

In this work, we have developed highly versatile procedures for the synthesis of functionalized 7-TH scaffolds through transition metal-promoted annulation reactions of bis(benzodithiophene) species. It is noteworthy that the direct annulation of bromides **1** with internal alkynes can be successful employed to synthesize 7-TH derivatives bearing in the 7- and 8-position various substituents, including (hetero)aryl groups. Alternatively, the introduction of alkynyl pendants via Sonogashira coupling or (hetero)aryl units using Suzuki chemistry were equally possible on bromides **1**, yielding 7-substituted helicenes **4** and benzo fused systems **7** through $PtCl_2$- or $InCl_3$-promoted cycloisomerization reaction of alkynes **6** and oxidative photocyclization of intermediates **9**, respectively. This study affords an important contribution to thiahelicene synthesis since the substrate scope of these protocols can be easily extended thanks to a wide range of readily and commercially available alkynes and (hetero)aryl boronic acids.

Finally, the possibility of using these synthetic routes in an asymmetric version to obtain enantioenriched 7-TH is currently under investigation. In this respect, a deep study on the stereochemical properties of chiral atropoisomeric biaryl derivatives **1**, **6**, **9** and **17** will be faced to elucidate their configurational stability.

Experimental Section

General Information. Unless otherwise stated, all reactions were performed in flame-dried glassware under a positive argon or nitrogen atmosphere using standard Schlenk and vacuum-line techniques. If not otherwise indicated, chemicals obtained from commercial sources were used as received. *N*-Bromosuccinimide (NBS) was recrystallized from water.[30] Solutions of *n*BuLi (1.6 M in hexane) were purchased from Aldrich and titrated prior to use. 4,5-Dipropylbenzo[1,2-*b*:4,3-*b*']dithiophene (**11a**),[21] benzo[1,2-*b*:4,3-*b*']dithiophene (**11b**),[22] 2-thienylmethyl)triphenyl phosphonium bromide (**15**)[24] and alkyne **3c**[31] were synthesized as previously reported. Thin-layer chromatography (TLC) was performed using Merck silica gel 60 F254 precoated plates. Column chromatography was carried out with Aldrich silica gel (70-230 mesh). Melting points were determined with a Büchi Melting Point B-540 apparatus and are uncorrected. The ^1H and ^{13}C NMR spectra were recorded at 25 °C on Bruker AC-300, AC-400, AC-500 and AC-600 spectrometers. Chemical shifts were reported relative to the residual $CDCl_3$ resonance (^1H: δ = 7.26 ppm, ^{13}C: δ = 77.0 for $CDCl_3$; ^1H: δ = 5.33 ppm for CD_2Cl_2). The chemical shifts are given in ppm and coupling constants in Hz. The IR spectra were recorded on powders using ATR Fourier Transform Infrared (FTIR) spectrometer (PerkinElmer spectrum 100). High Resolution Electron Ionization (HR EI) mass spectra were recorded on a FISONS - Vg Autospec- M246 spectrometer. Reverse-phase RP-HPLC analyses were performed on Agilent 1100 series system, equipped with DAD 300 analyzer, using Zorbax Eclipse XDB-C18 (150 mm x 4.6 mm, 5 µm) as analytical column.

Synthesis of the mixture 12a and 13a. To a solution of **11a** (6.19 mmol, 1.7 g) in dry DMF (15 mL) NBS (19.2 mmol, 3.42 g) was added at room temperature and the resulting mixture was stirred at 80 °C. The outcome of the reaction was monitored by RP-HPLC analysis (eluent: CH_3CN). After 6 h the reaction mixture was cooled to room temperature, diluted with CH_2Cl_2 and poured into water (70 mL). The aqueous phase was extracted with CH_2Cl_2 (4 × 40 mL), and the collected organic phases were washed with water (4 × 20 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane as the eluent to afford a mixture of bromides **12a** and **13a** (2.74 g, **12a**:**13a** = 1:0.14 NMR molar ratio): bromide **12a** (2.40 g, 76%), bromide **13a** (336 mg). ^1H NMR (300 MHz, mixture **12a** and **13a**, $CDCl_3$): δ = 8.61 (s, 1H, **12a**), 7.55 (s, 2H, **13a**), 2.90–2.83 (m, 4H, **12a** + **13a**), 1.77–1.68 (m, 4H, **12a** + **13a**), 1.10–1.04 (m, 6H, **12a** + **13a**). The assignment has been made taking into account NMR data reported in literature for **12a** and **13a**.[21]

Synthesis of the mixture 12b and 13b. To a mixture of **11b** (1.05 mmol, 200 mg) in $CHCl_3$ (6 mL) and AcOH (6 mL) NBS (6.8 mmol, 1.21 g) was added in portions and the resulting suspension was stirred at 45 °C. The outcome of the reaction was monitored by RP-HPLC analysis (acetonitrile as the eluent). After 8 h, the mixture was cooled to room temperature, and a saturated solution of $NaHCO_3$ was slowly added under vigorously stirring until neutralization. The aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL), and the collected organic phases were washed with H_2O (2 × 20 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane as the eluent to afford a mixture of bromides **12b** and **13b** (332 mg, **12b**:**13b** = 24:1 NMR molar

ratio): bromide **12b** (319 mg, 0.749 mmol, 71%), bromide **13b** (13 mg, 0.0312 mmol). ^{1}H NMR (300 MHz, mixture **12b** and **13b**, $CDCl_3$): δ = 8.64 (s, 1H, **12b**), 7.72 (d, J = 8.6 Hz, 1H, **12b**), 7.64 (d, J = 8.6 Hz, 1H, **12b**), 7.62 (s, 2H, **13b**), 7.59 (s, 2H, **13b**). The assignment has been made taking into account NMR data for **12b**[23] and **13b**.[32]

Synthesis of 1-bromo-4,5-dipropylbenzo[1,2-*b*:4,3-*b*']dithiophene 10a. To a stirring solution of **12a**:**13a** in 1:0.14 NMR molar ratio (1.5 g, 2.58 mmol of **12a** and 0.42 mmol of **13a**) in dry THF (22 mL) at – 78 °C a solution of *n*-BuLi (4.5 mL, 6.3 mmol, 1.4 M in hexane,) was added dropwise under an argon atmosphere, and the resulting mixture was stirred for 1 h at – 78 °C. MeOH (1 mL) was added dropwise to the mixture at – 78 °C, and after 15 min the mixture was warmed at room temperature. A saturated aqueous solution of NH_4Cl (20 mL) was slowly added, and the aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL). The collected organic phases were washed with H_2O (2 × 20 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane as the eluent to afford **10a** (658 mg, 75%) as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.66 (d, J = 5.6 Hz, 1H), 7.53 (d, J = 5.6 Hz, 1H), 7.47 (s, 1H), 3.03–2.95 (m, 4H), 1.85–1.69 (m, 4H), 1.12–1.06 (m, 6H). Spectroscopic data are in agreement with those reported in literature.[21] Compound **11a** was also recovered (123 mg).

Synthesis of 1-bromobenzo[1,2-*b*:4,3-*b*']dithiophene 10b. To a stirring solution of **12b**:**13b** in 24:1 NMR molar ratio (290 mg, 0.65 mmol of **12b** and 0.03 mmol of **13b**) in dry THF (10 mL) at – 78 °C a solution of *n*-BuLi (0.89 mL, 1.43 mmol, 1.6 M in hexane) was added dropwise under an argon atmosphere, and the resulting mixture was stirred for 1 h at – 78 °C. MeOH (1 mL) was added dropwise to the mixture at – 78 °C, and after 15 min the mixture was warmed at room temperature. A saturated aqueous solution of NH_4Cl (20 mL) was slowly added, and the aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL). The collected organic phases were washed with H_2O (2 × 20 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane as the eluent to afford **10b** (100 mg, 57%) as a colorless solid, m.p. (hexane) 122–124 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.69 (d, J = 5.5 Hz, 1H), 7.89 (d, J = 8.7 Hz, 1H), 7.79 (d, J = 8.6 Hz, 1H), 7.62 (d, J = 5.5 Hz, 1H), 7.54 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.3 (C_q), 136.2 (C_q), 133.9 (C_q), 131.4 (C_q), 126.1 (CH), 124.0 (CH), 121.5 (CH), 120.0 (CH), 118.8 (CH), 106.2 (C_q). IR (neat): $\tilde{\nu}$ = 2959, 2923, 2868, 2853, 1461, 1378, 1329, 1259, 1185, 1160, 1158, 1146, 1089, 967, 884, 851, 830, 790, 738, 703, 619, 555, 479, 460, 440 cm^{-1}; HRMS (EI): calcd for $C_{10}H_5BrS_2$ [M]$^+$: 267.9016, found 267.9016. Compound **11b** was also recovered (33 mg).

Synthesis of 4-bromo-2-[2-(2-thienyl)-ethenyl]-thiophene (14). A mixture of phosphonium salt **15** (9.4 g, 21.5 mmol), K_2CO_3 (6.8 g, 49.4 mmol), 18-crown-6 ether (0.9 g, 3.4 mmol) and aldehyde **16** (4.4 g, 23.1 mmol) in DMF (40 mL) was stirred at room temperature. After 48 h, the solvent was removed under reduced pressure, and the residue was poured into water (50 mL). The aqueous phase was extracted with CH_2Cl_2 (4 × 20 mL), and the collected organic phases were washed with H_2O (2 × 30 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane as the eluent to afford **14** (5.62 g, 96%) as a colorless solid as a mixture of *E*/*Z* isomers in 1:1 molar ratio. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.28 (d, J = 5.0 Hz, 1H, *Z*), 7.22 (d, J = 5.0 Hz, 1H, *E*), 6.99–7.15 (m, 7H, *E*+*Z*), 6.91–6.96 (d, J = 15.8 Hz, 1H, *E* + bs 2H), 6.66 (d, J = 11.7 Hz, 1H, *Z*), 6.49 (d, J = 11.7 Hz, 1H, *Z*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.2, 141.6, 140.2, 138.3, 130.2, 128.7, 127.7 (2C), 126.9, 126.7 (2C), 125.0, 124.5, 123.2, 122.6, 121.2, 121.1, 120.0, 110.2, 109.5. IR (neat): $\tilde{\nu}$ = 3109, 3076, 1618, 1523, 1492, 1459, 1435, 1365, 1325, 1269, 1183, 1162, 1078, 1042, 942, 867, 853, 828, 769, 727, 703, 592, 557, 527, 475, 431 cm^{-1}; HRMS (EI): calcd for $C_{10}H_7BrS_2$ [M]$^+$: 269.9172, found 269.9163.

Photocyclization of 4-bromo-2-[2-(2-thienyl)-ethenyl]-thiophene (14). A stirred solution of compound **14** (300 mg, 1.12 mmol) and a catalytic amount of iodine in cyclohexane (750 mL) was irradiated at room temperature with a 125 W unfiltered medium-pressure Hg lamp. The outcome of the reaction was monitored by HPLC analysis (eluent: H_2O/CH_3CN = 95:5). After completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel with hexane as eluent to give **10b** (225 mg, 75%) as colorless solid. Compound **11b** was also recovered (11 mg). Spectroscopic data are in agreement with those obtained for the preparation of **10b** following the procedure in Scheme 2.

General procedure for the synthesis of bis(benzodithiophene) derivatives 17a,b. A deaerated mixture of bromide **10** (1.5 mmol), bis(pinacolato)diboron (247.6 mg, 0.98 mmol), $Pd(dppf)Cl_2$ (76.8 mg, 0.105 mmol), CsF (683.5 mg, 4.5 mmol) and nBu$_4$NHSO$_4$ (50.9 mg, 0.15 mmol) in toluene (2 mL) and water (1 mL) was refluxed under nitrogen for 4-6 h. The outcome of the reaction was monitored by TLC analysis (hexane). After completion of the reaction, the mixture was cooled to room temperature and poured into water (10 mL). The aqueous phase was extracted with CH_2Cl_2 (4 × 5 mL), and the collected organic phases were dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to provide the required product **17**.

Bis(benzodithiophene) 17a. The crude product obtained from the Pd-catalyzed homocoupling reaction of bromide **10a** was purified by column chromatography on silica gel with hexane as the eluent to give **17a** (348 mg, 85%) as colorless solid, m.p. (pentane) 170–171 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44 (s, 2H), 7.02 (d, J = 5.5 Hz, 2H), 6.55 (d, J = 5.5 Hz, 2H), 3.12–2.95 (m, 8H, CH_2), 1.91–1.80 (m, 8H, CH_2), 1.20–1.09 (m, 6H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.8 (C_q), 139.0 (C_q), 133.7 (C_q), 132.8 (C_q), 132.1 (C_q), 130.7 (C_q), 130.2 (C_q), 124.5 (CH), 124.2 (CH), 122.3 (CH), 34.5 (CH_2), 34.2 (CH_2), 23.3 (CH_2), 23.1 (CH_2), 14.8 (CH_3), 14.7 (CH_3). IR (neat): $\tilde{\nu}$ = 2955, 2917, 2849, 1464, 1366, 1261, 1087, 1018, 1006, 854, 831, 817, 802, 766, 753, 709, 688, 645, 635, 423 cm^{-1}; HRMS (EI): calcd for $C_{32}H_{34}S_4$ [M]$^+$: 546.1543, found 546.1540.

Bis(benzodithiophene) 17b. The crude product obtained from the Pd-catalyzed homocoupling reaction of bromide **10b** was purified by column chromatography on silica gel with hexane as the eluent to give **17b** (243 mg, 86%) as colorless solid, m.p. (hexane) 178–180 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.93 (d, J = 8.7 Hz, 2H), 7.89 (d, J = 8.7 Hz, 2H), 7.58 (s, 2H), 7.09 (d, J = 5.5 Hz, 2H), 6.49 (d, J = 5.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.5 (C_q), 136.7 (C_q), 134.6 (C_q), 133.8 (C_q), 132.8 (C_q), 126.1 (CH), 125.7 (CH), 121.5 (CH), 119.5 (CH), 118.9 (CH). IR (neat): $\tilde{\nu}$ = 1382, 1269, 1260, 1153, 1090, 875, 855, 822, 813, 794, 784, 763, 741, 712, 462 cm^{-1}; HRMS (EI): calcd for $C_{20}H_{10}S_4$ [M]$^+$: 377.9665, found 377.9650.

General procedure for the synthesis of bromides 1a,b. To a mixture of **17** (0.20 mmol) in $CHCl_3$ (2 mL) and AcOH (2 mL) NBS (0.28-0.32 mmol, 50.0-56.6 mg) was added in portions and the resulting suspension was stirred at 35-45 °C. The outcome of the reaction was monitored by RP-HPLC analysis (eluent: CH_3CN). After 8 h, the mixture was cooled to room temperature, and a saturated solution of $NaHCO_3$ was slowly added under vigorously stirring until neutralization. The aqueous phase was extracted with CH_2Cl_2 (4 × 10 mL), and the collected organic phases were washed with H_2O (2 × 10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to provide the required product **1**.

2-Bromo-3,3'-bibenzo[1,2-*b*:4,3-*b*']dithiophene 1a. The crude product obtained from the bromination of **14a** was purified by column chromatography on silica gel with hexane as the eluent to give **1a** (76 mg, 60%) as colorless solid (RP-HPLC purity up to 92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46 (s, 1H), 7.09 (d, J = 5.5 Hz, 1H), 7.03 (d, J = 5.5 Hz, 1H), 6.62 (d, J = 5.6 Hz, 1H), 6.40 (d, J = 5.6 Hz, 1H), 3.12–2.95 (m, 8H, CH_2),

1.95–1.75 (m, 8H, CH_2), 1.21–1.07 (m, 12H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.1 (C_q), 139.8 (C_q), 139.3 (C_q), 138.5 (C_q), 134.1 (C_q), 132.5 (C_q), 132.2 (C_q), 131.8 (C_q), 131.7 (C_q), 131.3 (C_q), 131.1 (C_q), 130.8 (C_q), 130.2 (C_q), 129.3 (C_q), 125.0 (CH), 124.9 (CH), 124.8 (CH), 121.9 (CH), 121.8 (CH), 114.5 (C_q), 34.5 (CH_2), 34.4 (CH_2), 34.2 (CH_2), 34.1 (CH_2), 23.3 (CH_2), 23.2 (CH_2), 23.1 (CH_2), 23.0 (CH_2), 14.8 (CH_3), 14.7 (CH_3). IR (neat): $\tilde{\nu}$ = 2955, 2924, 2865, 2852, 1467, 1451, 1375, 1364, 1267, 1172, 1160, 1087, 854, 828, 817, 768, 753, 709, 644, 637, 422 cm^{-1}; HRMS (EI): calcd for $C_{32}H_{33}S_4Br$ $[M]^+$: 624.0649, found 624.0686.

2-Bromo-3,3'-bibenzo[1,2-*b*:4,3-*b*']dithiophene 1b. The crude product obtained from the bromination of **14b** was purified by column chromatography on silica gel with hexane as the eluent to give **1b** (58 mg, 64%) as colorless solid (RP-HPLC purity up to 90%). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.96–7.86 (m, 3H), 7.80–7.77 (m, 1H), 7.60 (s, 1H), 7.18 (d, *J* = 5.5 Hz, 1H), 7.12 (d, *J* = 5.5 Hz, 1H), 6.58 (d, *J* = 5.5 Hz, 1H), 6.38 (d, *J* = 5.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.0 (C_q), 137.6 (C_q), 137.1 (C_q), 136.2 (C_q), 134.3 (C_q), 133.9 (C_q), 133.5 (C_q), 133.2 (C_q), 133.1 (C_q), 130.9 (C_q), 126.6 (CH), 126.5 (2CH), 121.2 (CH), 121.0 (CH), 119.7 (CH), 119.6 (CH), 119.0 (CH), 117.9 (CH), 116.2 (C_q). IR (neat): $\tilde{\nu}$ = 1383, 1328, 1156, 1148, 1084, 866, 848, 822, 770, 756, 707, 679, 659, 633, 517, 462, 433, 423 cm^{-1}; HRMS (ESI): calcd for $C_{20}H_9BrS_4$ $[M]^+$: 455.8770, found 455.8794.

General procedure for the synthesis of 7,8-disubstituted helicenes 2. To a flame-dried reaction vessel bromide **1** (0.10 mmol), Pd(dppf)Cl_2 (3.7 mg, 0.005 mmol), LiBr (8.6 mg, 0.10 mmol), K_2CO_3 (41.5 mg, 0.30 mmol) and alkyne **3** (0.15 mmol), if a solid, were added. The reaction vessel was fitted with a silicon septum, evacuated and back-filled with nitrogen, and this sequence was repeated twice. Deaerated DMF (5 mL) and alkyne **3** (0.15 mmol), if a liquid, were then added successively under a stream of nitrogen at room temperature. The resulting mixture was stirred at reflux under nitrogen for 4-6 h. The outcome of the reaction was monitored by TLC analysis. After completion of the reaction, the mixture was cooled to room temperature and poured into water (20 mL). The aqueous phase was extracted with CH_2Cl_2 (4 × 10 mL), and the collected organic phases were washed with brine (2 × 20 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to provide the required product **2**.

7,8-Diphenyl-4,5,10,11-tetrapropyltetrathia[7]helicene (2a). The crude product obtained from the Pd-catalyzed annulation reaction between bromide **1a** and alkyne **3a** was purified by column chromatography on silica gel with hexane as the eluent to give **2a** (56 mg, 78%) as yellow solid, m.p. (heptane) 298–300 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.52–7.28 (m, 10H, phenyl), 6.82 (d, *J* = 5.6 Hz, 2H, thiophene-7TH), 6.80 (d, *J* = 5.6 Hz, 2H, thiophene-7TH), 3.14–3.01 (m, 8H, CH_2), 1.88–1.83 (m, 8H, CH_2), 1.16–1.09 (m, 12H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 139.3 (2C_q), 139.1 (C_q), 138.7 (C_q), 134.2 (C_q), 132.8 (C_q), 132.4 (C_q), 130.4 (2CH), 129.9 (C_q), 129.8 (C_q), 129.5 (C_q), 128.2 (2CH), 127.5 (CH), 125.9 (CH), 122.4 (CH), 34.6 (CH_2), 34.3 (CH_2), 23.3 (2CH_2), 14.7 (2CH_3). IR (neat): $\tilde{\nu}$ = 2956, 2922, 2866, 2863, 1741, 1599, 1555, 1462, 1455, 1441, 1376, 1346, 1327, 1263, 1234, 1207, 1105, 1089, 1028, 916, 886, 843, 832, 818, 768, 753, 741, 698, 666, 647, 633, 609, 542, 433 cm^{-1}; HRMS (EI): calcd for $C_{46}H_{42}S_4$ $[M]^+$: 722.2169, found 722.2155.

4,5,10,11-Tetrapropyl-7,8-di(2-thienyl)tetrathia[7]helicene (2b). The crude product obtained from the Pd-catalyzed annulation reaction between bromide **1a** and alkyne **3b** was purified by column chromatography on silica gel with the mixture of hexane/ CH_2Cl_2 (9:1) as the eluent to give **2b** (50 mg, 68%) as yellow solid, m.p. (heptane) 254–256 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.43 (dd, *J* = 5.1, 1.0 Hz, 2H, thienyl), 7.31 (dd, *J* = 3.5, 1.0 Hz, 2H, thienyl), 7.13 (dd, *J* = 5.1, 3.5 Hz, 2H, thienyl), 6.81 (d, *J* = 5.6 Hz, 2H, thiophene-7TH), 6.72 (d, *J* = 5.6 Hz, 2H, thiophene-7TH), 3.17–2.99 (m, 8H, CH_2), 1.92–1.81 (m, 8H, CH_2), 1.14 (t, *J* = 7.3 Hz, 12H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 140.1 (C_q), 139.7 (C_q), 139.5 (C_q), 138.8 (C_q), 134.2 (C_q), 133.2 (C_q), 130.3 (C_q), 129.7 (C_q), 129.2 (C_q), 129.1 (CH), 127.2 (CH), 126.8 (CH), 126.3 (C_q), 125.8 (CH), 122.6 (CH), 34.6 (CH_2), 34.3 (CH_2), 23.3 (2CH_2), 14.74 (CH_3), 14.67 (CH_3). IR (neat): $\tilde{\nu}$ = 2956, 2922, 2852, 1737, 1464, 1260, 1207, 1168, 1090, 1019, 851, 800, 696, 646 cm^{-1}; HRMS (EI): calcd for $C_{42}H_{38}S_6$ $[M]^+$: 734.1298, found 734.1300.

7,8-Diphenyltetrathia[7]helicene (2c). The crude product obtained from the Pd-catalyzed annulation reaction between bromide **1b** and alkyne **3a** was purified by column chromatography on silica gel with hexane as the eluent to give **2c** (44 mg, 80%) as yellow solid, m.p. (hexane/ CH_2Cl_2) 308–310 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.5 Hz, 2H, Ar-7TH), 7.89 (d, *J* = 8.3 Hz, 2H, Ar-7TH), 7.50–7.30 (m, 10H, phenyl), 6.95 (d, *J* = 5.6 Hz, 2H, thiophene-7TH), 6.84 (d, *J* = 5.5 Hz, 2H, thiophene-7TH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.5 (C_q), 138.7 (C_q), 137.4 (C_q), 136.7 (C_q), 136.1 (C_q), 133.0 (C_q), 131.2 (C_q), 130.3 (2CH), 129.2 (C_q), 128.3 (2CH), 127.7 (CH), 125.3 (CH), 124.4 (CH), 121.3 (CH), 118.5 (CH). IR (neat): $\tilde{\nu}$ = 3091, 3061, 2955, 2921, 2851, 1867, 1734, 1599, 1493, 1441, 1399, 1379, 1354, 1327, 1260, 1223, 1191, 1157, 1092, 1069, 1025, 913, 899, 887, 853, 842, 825, 809, 791, 771, 761, 743, 730, 712, 700, 680, 641, 612, 602, 594, 566, 552, 523, 490, 482, 464, 451, 429 cm^{-1}; HRMS (ESI): calcd for $C_{34}H_{18}S_4$ $[M]^+$: 554.0291, found 554.0291.

7,8-Di(2-thienyl)tetrathia[7]helicene (2d). The crude product obtained from the Pd-catalyzed annulation reaction between bromide **1b** and alkyne **3b** was purified by column chromatography on silica gel with the mixture of hexane/ CH_2Cl_2 (95:5) as the eluent to give **2d** (35 mg, 63%) as yellow solid, m.p. (heptane) 348–349 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 8.5 Hz, 2H, Ar-7TH), 7.92 (d, *J* = 8.5 Hz, 2H, Ar-7TH), 7.44 (dd, *J* = 5.1, 1.0 Hz, 2H, thienyl), 7.33 (dd, *J* = 3.5, 1.0 Hz, 2H, thienyl), 7.13 (dd, *J* = 5.1, 3.6 Hz, 2H, thienyl), 6.94 (d, *J* = 5.6 Hz, 2H, thiophene-7TH), 6.76 (d, *J* = 5.6 Hz, 2H, thiophene-7TH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.4 (C_q), 141.2 (C_q), 139.2 (C_q), 137.6 (C_q), 136.7 (C_q), 136.1 (C_q), 130.9 (C_q), 129.7 (C_q), 129.1 (CH), 127.4 (CH), 126.8 (CH), 125.2 (CH), 124.6 (CH), 121.6 (CH), 118.5 (CH). IR (neat): $\tilde{\nu}$ = 1381, 1325, 1293, 1212, 1194, 1181, 1159, 1091, 1078, 1046, 1024, 900, 890, 853, 827, 793, 770, 754, 698, 649, 596, 545, 492, 474, 454, 434, 421 cm^{-1}; HRMS (EI): calcd for $C_{30}H_{14}S_6$ $[M]^+$: 565.9420, found 565.9420.

7-Phenyl-8-(2-thienyl)tetrathia[7]helicene (2e). The crude product obtained from the Pd-catalyzed annulation reaction between bromide **1b** and alkyne **3c** was purified by column chromatography on silica gel with the mixture of hexane/ CH_2Cl_2 (95:5) as the eluent to give **2e** (33 mg, 60%) as yellow solid, m.p. (hexane/ CH_2Cl_2) 344–345 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.04–8.01 (m, 2H, Ar-7TH), 7.93 (d, *J* = 8.5 Hz, 1H, Ar-7TH), 7.88 (d, *J* = 8.6 Hz, 1H, Ar-7TH), 7.52–7.38 (m, 5H, phenyl), 7.36 (dd, *J* = 5.2, 1.1 Hz, 1H, thienyl), 7.23 (dd, *J* = 3.5, 1.1 Hz, 1H, thienyl), 7.06 (dd, *J* = 5.1, 3.6 Hz, 1H, thienyl), 6.95–6.93 (m, 2H, thiophene-7TH), 6.82–6.79 (m, 2H, thiophene-7TH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.2 (C_q), 140.4 (C_q), 139.3 (C_q), 138.8 (C_q), 137.8 (C_q), 137.3 (C_q), 136.7 (C_q), 136.2 (C_q), 136.1 (C_q), 134.1 (C_q), 131.6 (C_q), 131.1 (C_q), 131.0 (C_q), 130.1 (2CH), 129.6 (C_q), 129.2 (C_q), 128.9 (CH), 128.4 (2CH), 128.1 (CH), 127.1 (CH), 126.7 (CH), 125.8 (C_q), 125.2 (2CH), 124.5 (CH), 124.4 (CH), 121.5 (CH), 121.4 (CH), 118.5 (2CH). IR (neat): $\tilde{\nu}$ = 1382, 1327, 1288, 1189, 1158, 899, 887, 854, 833, 825, 792, 769, 752, 733, 713, 702, 646, 597, 593, 546, 490, 482, 451 cm^{-1}; HRMS (EI): calcd for $C_{32}H_{16}S_5$ $[M]^+$: 559.9856, found 559.9856.

7-Ethyl-8-phenyltetrathia[7]helicene (2f). The crude product obtained from the Pd-catalyzed annulation reaction between bromide **1b** and alkyne **3d** was purified by column chromatography on silica gel with the mixture of hexane/ CH_2Cl_2 (9:1) as the eluent to give **2f** (38 mg, 75%) as colorless solid, m.p. (heptane) 279–282 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.06–7.96 (m, 3H, Ar-7TH), 7.84 (d, *J* = 8.5 Hz, 1H, Ar-7TH), 7.61–7.49 (m, 5H, phenyl), 6.93-6.90 (m, 2H, thiophene-7TH), 6.82–6.78 (m, 2H, thiophene 7TH), 3.01 (q, *J* = 7.7 Hz, 2H, CH_2, Et), 1.32 (t, *J* = 7.5 Hz, 3H, CH_3, Et). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.7 (C_q), 139.0 (C_q), 138.8 (C_q), 137.1 (C_q), 136.7 (C_q), 136.5 (C_q), 136.4 (C_q), 136.2 (C_q), 136.0 (C_q),

133.7 (C_q), 133.3 (C_q), 131.4 (C_q), 131.2 (C_q), 129.8 (CH), 129.5(CH), 129.4 (C_q), 128.85 (CH), 128.78 (CH), 128.2 (CH), 127.9 (C_q), 125.3 (CH), 125.2 (CH), 124.3 (CH), 124.1 (CH), 121.2 (CH), 120.9 (CH), 118.6 (CH), 118.5 (CH), 25.9 (CH_2), 14.3 (CH_3). IR (neat): ν̃ = 2962, 2920, 2850, 1732, 1599, 1459, 1441, 1381, 1326, 1260, 1187, 1159, 1058, 1024, 901, 884, 856, 814, 790, 764, 700, 634, 594, 486, 470 cm^{-1}; HRMS (EI): calcd for $C_{30}H_{18}S_4$ $[M]^+$: 506.0291, found 506.0304.

7,8-Bis(methoxymethyl)tetrathia[7]helicene (2g). The crude product obtained from the Pd-catalyzed annulation reaction between bromide **1b** and alkyne **3e** was purified by column chromatography on silica gel with the mixture of hexane/ CH_2Cl_2 (1:1) as the eluent to give **2g** (22 mg, 46%) as yellow solid, m.p. (heptane) 167–168 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.04 (d, J = 8.5 Hz, 2H, Ar-7TH), 7.97 (d, J = 8.5 Hz, 2H, Ar-7TH), 6.89 (d, J = 5.5 Hz, 2H, thiophene-7TH), 6.68 (d, J = 5.5 Hz, 2H, thiophene 7-TH), 5.15 (d, J = 12.2 Hz, 2H, CH_2), 5.05 (d, J = 12.2 Hz, 2H, CH_2), 3.51 (s, 6H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.4 (C_q), 137.1 (C_q), 136.6 (C_q), 136.0 (C_q), 130.7 (C_q), 130.1 (C_q), 128.5 (C_q), 125.1 (CH), 124.4 (CH), 121.5 (CH), 118.5 (CH), 70.3 (CH_2), 58.3 (OCH_3). IR (neat): ν̃ = 3096, 2921, 2873, 2814, 1716, 1659, 1559, 1447, 1379, 1326, 1187, 1160, 1145, 1086, 997, 950, 885, 821, 788, 769, 704, 655, 540, 528, 469, 458 cm^{-1}; HRMS (EI): calcd for $C_{26}H_{18}O_2S_4$ $[M]^+$: 490.0190, found 490.0189.

7,8-Dipropyltetrathia[7]helicene (2h). The crude product obtained from the Pd-catalyzed annulation reaction between bromide **1b** and alkyne **3f** was purified by column chromatography on silica gel with hexane as the eluent to give **2h** (24 mg, 50%) as colorless solid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.99 (d, J = 8.6 Hz, 2H, Ar-7TH), 7.95 (d, J = 8.6 Hz, 2H, Ar-7TH), 6.88 (d, J = 5.6 Hz, 2H thiophene-7TH), 6.74 (d, J = 5.6 Hz, 2H, thiophene-7TH), 3.22–3.03 (m, 4H, CH_2), 1.92–1.85 (m, 4H, CH_2), 1.16 (t, J = 7.3 Hz, 6H, CH_3). Spectroscopic data are in agreement with those reported in literature.[9b]

General procedure for the synthesis of alkynes 6a-c. A deaerated mixture of bromide **1** (0.2 mmol), alkyne **5** (0.21-0.4 mmol), $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol), CuI (3.8 mg, 0.02 mmol) in dry THF (5 mL) and DIPEA (5 mL) was stirred at 70 °C for 9 h under a nitrogen atmosphere. The outcome of the reaction was monitored by TLC analysis. After completion of the reaction, the mixture was cooled to room temperature and poured into a saturated NH_4Cl solution (10 mL). The aqueous phase was extracted with CH_2Cl_2 (4 × 15 mL), and the collected organic phases were washed with water (2 × 15 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to provide the required product **6**.

Alkyne 6a. The crude product obtained from the Sonogashira reaction between bromide **1a** and alkyne **5a** (0.4 mmol) was purified by column chromatography on silica gel with the mixture of hexane/ CH_2Cl_2 (19:1) as the eluent to give **6a** (107 mg, 83%) as colorless solid, m.p. (heptane) 80–85 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.55 (s, 1H, thiophene), 7.20–7.12 (m, 3H, phenyl), 7.05 (d, J = 5.6 Hz, 2H, thiophene), 7.02–6.99 (m, 2H, phenyl), 6.71 (d, J = 5.6 Hz, 1H, thiophene), 6.63 (d, J = 5.6 Hz, 1H, thiophene), 3.14–2.95 (m, 8H, CH_2), 1.93–1.80 (m, 8H, CH_2), 1.18 (t, J = 7.3 Hz, 6H, CH_3), 1.12 (t, J = 7.3 Hz, 6H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.2 (C_q), 139.7 (C_q), 139.2 (C_q), 138.4 (C_q), 137.9 (C_q), 132.8 (C_q), 132.7 (C_q), 132.2 (C_q), 132.1 (C_q), 131.8 (C_q), 131.3 (2CH), 130.6 (C_q), 130.1 (C_q), 129.8 (C_q), 128.2 (CH), 128.1 (2CH), 124.9 (2CH), 124.4 (CH), 122.7 (C_q), 122.5 (CH), 122.4 (CH), 120.8 (C_q), 97.2 (C≡C), 83.2 (C≡C), 34.5 ($2CH_2$), 34.2 ($2CH_2$), 23.3 ($1CH_2$), 23.1 ($3CH_2$), 14.7 ($4CH_3$). IR (neat): ν̃ = 2956, 2927, 2868, 1454, 1444, 1087, 884, 851, 830, 818, 769, 752, 710, 687, 644, 525, 506 cm^{-1}; HRMS (EI): calcd for $C_{40}H_{38}S_4$ $[M]^+$: 646.1856, found 646.1858.

Alkyne 6b. The crude product obtained from the Sonogashira reaction between bromide **1b** and alkyne **5a** (0.4 mmol) was purified by column chromatography on silica gel with the mixture of hexane/ CH_2Cl_2 (9:1) as the eluent to give **6b** (83 mg, 87%) as colorless solid, m.p. (hexane/ CH_2Cl_2) 203–206 °C. ^1H NMR (300 MHz, CD_2Cl_2): δ = 8.01–7.87 (m, 4H, Ar), 7.75 (s, 1H, thiophene), 7.26–7.10 (m, 7H), 6.60 (d, J = 5.5 Hz, 1H, thiophene), 6.52 (d, J = 5.5 Hz, 1H, thiophene). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.9 (C_q), 137.5 (C_q), 137.0 (C_q), 136.8 (C_q), 136.2 (C_q), 134.6 (C_q), 134.5 (C_q), 133.60 (C_q), 133.59 (C_q), 131.43 (C_q), 131.35 (2CH), 128.5 (CH), 128.2 (2CH), 126.51 (CH), 126.48 (CH), 126.1 (CH), 122.5 (C_q), 122.4 (C_q), 121.7 (CH), 121.6 (CH), 120.6 (CH), 119.4 (CH), 119.0 (CH), 118.4 (CH), 97.8 (C≡C), 82.7 (C≡C). IR (neat): ν̃ = 1594, 1566, 1493, 1440, 1383, 1332, 1252, 1193, 1158, 1146, 1067, 1024, 962, 920, 887, 854, 835, 822, 807, 789, 770, 760, 743, 714, 704, 690, 666, 643, 555, 534, 516, 495, 482, 471, 456, 427 cm^{-1}; HRMS (EI): calcd for $C_{28}H_{14}S_4$ $[M]^+$: 477.9978, found 477.9987.

Alkyne 6c. The crude product obtained from the Sonogashira reaction between bromide **1b** and alkyne **5b** (0.21 mmol) was purified by column chromatography on silica gel with the mixture of hexane/ CH_2Cl_2 (7:3) as the eluent to give **6c** (60 mg, 59%) as colorless solid, m.p. (hexane/ CH_2Cl_2) 208–212 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.96–7.88 (m, 3H, Ar), 7.83 (d, J = 8.6 Hz, 1H, Ar), 7.68 (s, 1H, thiophene), 7.14–7.10 (m, 2H, thiophene), 7.03 (d, J = 8.7 Hz, 2H, phenyl), 6.72 (d, J = 8.8 Hz, 2H, phenyl), 6.66 (d, J = 5.5 Hz, 1H, thiophene), 6.53 (d, J = 5.5 Hz, 1H, thiophene), 3.75 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.8 (C_q), 137.9 (C_q), 137.4 (C_q), 136.9 (C_q), 136.1 (C_q), 135.9 (C_q), 134.6 (C_q), 134.4 (C_q), 133.7 ($2C_q$), 132.9 (2CH), 131.6 (C_q), 126.44 (CH), 126.39 (CH), 126.0 (CH), 122.9 (C_q), 121.7 (2CH), 120.4 (CH), 119.4 (CH), 119.0 (CH), 118.4 (CH), 114.5 (C_q), 113.9 (2CH), 98.0 (C≡C), 81.5 (C≡C), 55.2 (OCH_3). IR (neat): ν̃ = 2955, 2920, 2850, 1739, 1601, 1505, 1462, 1439, 1386, 1290, 1247, 1173, 1155, 1108, 1090, 1056, 1020, 973, 854, 826, 786, 761, 708, 671, 525, 473, 457 cm^{-1}; HRMS (EI): calcd for $C_{29}H_{16}OS_4$ [M]+: 508.0084, found 508.0080.

General procedure for the synthesis of 7-substituted 7-TH derivatives 4. To a flame-dried reaction vessel, alkynes **6** (0.20 mmol), $PtCl_2$ (5.3 mg, 0.02 mmol) or $InCl_3$ (4.4 mg, 0.02 mmol) were added. The reaction vessel was fitted with a silicon septum, evacuated and back-filled with argon, and this sequence was repeated twice. Deaerated toluene (1 mL) was added successively under a stream of argon at room temperature. The resulting mixture was stirred at 60 or 80 °C under argon for 10 h. The outcome of the reaction was monitored by TLC analysis. After completion of the reaction, the mixture was cooled to room temperature and the solvent was removed under reduced pressure. The crude mixture was purified by column chromatography on silica gel to provide the required product **4**.

4,5,10,11-Tetrapropyl-7-phenyltetrathia[7]helicene (4a). The crude product obtained from the cycloisomerization of **6a** in the presence of $PtCl_2$ (0.02 mmol) at 60 °C was purified by column chromatography on silica gel with the mixture of hexane/ CH_2Cl_2 (9:1) as the eluent to give **4a** (54 mg, 42%) as yellow solid, m.p. (heptane) 220–225 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.97 (s, 1H, Ar-7TH), 7.87–7.85 (m, 2H, phenyl), 7.62–7.58 (m, 2H, phenyl), 7.53–7.49 (m, 1H, phenyl), 6.82–6.79 (m, 2H, thiophene-7TH), 6.75 (d, J = 5.6 Hz, 2H, thiophene-7TH), 3.20–2.99 (m, 8H, CH_2), 1.92–1.84 (m, 8H, CH_2), 1.23–1.12 (m, 12H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.4 (C_q), 139.0 (C_q), 138.9 (C_q), 138.8 (C_q), 138.7 (C_q), 137.7 (C_q), 136.6 (C_q), 134.25 ($2C_q$), 134.16 (C_q), 132.93 (C_q), 132.88 (C_q), 131.0 (C_q), 129.8 (C_q), 129.7 (C_q), 129.6 (C_q), 129.4 (C_q), 129.1 (C_q), 128.9 (2CH), 128.7 (2CH), 128.1 (CH), 125.9 (2CH), 122.4 (2CH), 119.7 (CH), 34.64 ($2CH_2$), 34.57 (CH_2), 34.3 (CH_2), 23.3 ($4CH_2$), 14.81 (CH_3), 14.76 (CH_3), 14.69 ($2CH_3$). IR (neat): ν̃ = 2957, 2927, 2868, 1495, 1469, 1454, 1334, 1158, 1029, 1088, 930, 881, 826, 818, 763, 751, 699, 646, 591 cm^{-1}; HRMS (EI): calcd for $C_{40}H_{38}S_4$ $[M]^+$: 646.1856, found 646.1865.

7-Phenyltetrathia[7]helicene (4b). The crude product obtained from the cycloisomerization of **6b** in the presence of $PtCl_2$ (5.3 mg, 0.02 mmol) at 60 °C was purified by column chromatography on silica gel with the mixture of hexane/ CH_2Cl_2 (7:3) as the eluent to give **4b** (34 mg, 36%) as yellow solid, m.p. (hexane/ CH_2Cl_2) 301–308 °C. ^1H NMR (500 MHz,

$CDCl_3$): δ = 8.06–8.02 (m, 3H, Ar-7TH), 7.99 (d, *J* = 8.5 Hz, 1H, Ar-7TH), 7.94 (d, *J* = 8.5 Hz, 1H, Ar-7TH), 7.86–7.84 (m, 2H, phenyl), 7.60–7.57 (m, 2H, phenyl), 7.52–7.49 (m, 1H, phenyl), 6.94–6.91 (m, 2H, thiophene-7TH), 6.78–6.76 (m, 2H, thiophene-7TH). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.0 (C_q), 138.5 (C_q), 137.6 (C_q), 137.2 (C_q), 136.9 (C_q), 136.74 (C_q), 136.66 (C_q), 136.2 (C_q), 136.1 (C_q), 134.8 (C_q), 131.1 (C_q), 130.8 (C_q), 130.4 (C_q), 129.0 (C_q), 128.9 (2CH), 128.6 (2CH), 128.4 (CH), 125.2 (2CH), 124.4 (2CH), 121.4 (CH), 121.3 (CH), 120.2 (CH), 118.7 (CH), 118.5 (CH). IR (neat): ν̃ = 2953, 2921, 2852, 1564, 1444, 1382, 1327, 1260, 1196, 1152, 1086, 1027, 922, 895, 873, 821, 794, 788, 768, 745, 735, 697, 659, 622, 588, 578, 541, 519, 471, 455, 443 cm^{-1}; HRMS (EI) calcd for $C_{28}H_{14}S_4$ [M]$^+$: 477.9978, found 477.9986.

7-(*p*-Methoxy)phenyltetrathia[7]helicene (4c). The crude product obtained from the cycloisomerization of **6c** in the presence of $InCl_3$ (4.4 mg, 0.02 mmol) at 80 °C was purified by column chromatography on silica gel with the mixture of hexane/ CH_2Cl_2 (9:1) as the eluent to give **4c** (74 mg, 73%) as yellow solid, m.p. (hexane/ CH_2Cl_2) 245–248 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.05–7.92 (m, 5H), 7.78 (d, *J* = 8.6 Hz, 2H, phenyl), 7.12 (d, *J* = 8.6 Hz, 2H, phenyl), 6.93–6.91 (m, 2H, thiophene-7TH), 6.77 (d, *J* = 5.6 Hz, 2H, thiophene-7TH), 3.93 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.8 (C_q), 138.6 (C_q), 137.7 (C_q), 137.1 (C_q), 136.7 (2C_q), 136.6 (C_q), 136.1 (2C_q), 134.6 (C_q), 132.4 (C_q), 131.2 (C_q), 130.8 (C_q), 130.3 (C_q), 129.8 (2CH), 128.7 (C_q), 125.3 (2CH), 124.3 (2CH), 121.4 (CH), 121.2 (CH), 120.0 (CH), 118.7 (CH), 118.5 (CH), 114.4 (2CH), 55.4 (OCH_3). IR (neat): ν̃ = 3083, 3013, 2955, 2924, 2832, 1607, 1575, 1508, 1458, 1437, 1415, 1383, 1327, 1281, 1247, 1198, 1175, 1154, 1116, 1090, 1043, 1030, 923, 894, 884, 875, 831, 823, 809, 786, 768, 748, 737, 708, 695, 682, 658, 642, 602, 570, 556, 540, 512, 495, 474, 451, 420, 411, 407 cm^{-1}; HRMS (EI) calcd for $C_{29}H_{16}OS_4$ [M]+: 508.0084, found 508.0084.

General procedure for the synthesis of 2-aryl-bis(benzodithiophene) derivatives 9a-c. A deaerated mixture of bromide **1** (0.1 mmol), arylboronic acid **8** (0.2 mmol), Pd(dppf)Cl_2 (7.3 mg, 0.01 mmol), KF (17 mg, 0.3 mmol) in toluene (5 mL) and methanol (5 mL) was stirred at 70 °C for 9 h under a nitrogen atmosphere. The outcome of the reaction was monitored by TLC analysis. After completion of the reaction, the mixture was cooled to room temperature and the solvent was removed under reduced pressure. The residue was taken up with CH_2Cl_2 and poured into water (10 mL). The aqueous phase was extracted with CH_2Cl_2 (4 × 5 mL), and the collected organic phases were dried over Na_2SO_4, and concentrated under reduced pressure. The crude was purified by column chromatography on silica gel to provide the required product **9**.

2-Phenyl-bis(benzodithiophene) 9a. The crude product obtained from the Suzuki reaction between bromide **1a** and phenylboronic acid (**8a**) was purified by column chromatography on silica gel with hexane as the eluent to give **9a** (53 mg, 86%) as colorless solid, m.p. (hexane) 68–72 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36-7.33 (m, 2H, phenyl), 7.31 (s, 1H, thiophene), 7.14–7.11 (m, 3H, phenyl), 7.03 (d, *J* = 5.6 Hz, 1H, thiophene), 6.96 (d, *J* = 5.5 Hz, 1H, thiophene), 6.72 (d, *J* = 5.6 Hz, 1H, thiophene), 6.19 (d, *J* = 5.6 Hz, 1H, thiophene), 3.11–2.96 (m, 8H, CH_2), 1.94–1.77 (m, 8H, CH_2), 1.21–1.08 (m, 12H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.2 (C_q), 140.0 (C_q), 139.8 (C_q), 139.2 (C_q), 137.2 (C_q), 134.4 (C_q), 133.9 (C_q), 133.2 (C_q), 132.9 (C_q), 132.8 (C_q), 132.6 (C_q), 130.8 (C_q), 130.7 (C_q), 130.2 (C_q), 129.7 (C_q), 129.1 (C_q), 128.8 (2CH), 128.4 (2CH), 127.5 (CH), 124.7 (CH), 124.4 (CH), 124.3 (CH), 122.3 (CH), 122.0 (CH), 34.52 (CH_2), 34.49 (CH_2), 34.2 (2CH_2), 23.3 (CH_2), 23.2 (CH_2), 23.1 (2CH_2), 14.7 (4CH_3). IR (neat): ν̃ = 2958, 2933, 2865, 1464, 1443, 1165, 1088, 932, 888, 854, 833, 822, 774, 755, 724, 713, 690, 644, 620, 600, 571, 522, 496, 425 cm^{-1}; HRMS (EI) calcd for $C_{38}H_{38}S_4$ [M]$^+$: 622.1856, found 622.1858.

2-Phenyl-bis(benzodithiophene) 9b. The crude product obtained from the Suzuki reaction between bromide **1b** and phenylboronic acid (**8a**) was purified by column chromatography on silica gel with hexane as the eluent to give **9b** (41 mg, 91%) as colorless solid, m.p. (heptane) 240–242 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94–7.85 (m, 4H, Ar), 7.42 (s, 1H, thiophene), 7.33–7.30 (m, 2H, phenyl), 7.16–7.12 (m, 3H phenyl + 1H thiophene), 7.05 (d, *J* = 5.5 Hz, 2H, thiophene), 6.69 (d, *J* = 5.5 Hz, 1H, thiophene), 6.21 (d, *J* = 5.5 Hz, 1H, thiophene). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.9 (C_q), 137.8 (C_q), 137.6 (C_q), 136.9 (C_q), 135.6 (C_q), 135.1 (C_q), 134.6 (2C_q), 134.4 (C_q), 134.0 (C_q), 132.4 (C_q), 128.8 (2CH), 128.5 (2CH), 128.2 (C_q), 127.9 (CH), 126.5 (CH), 125.97 (CH), 125.95 (CH), 121.5 (CH), 121.2 (CH), 119.6 (CH), 119.4 (CH), 119.1 (CH), 118.4 (CH). IR (neat): ν̃ = 1463, 1386, 1335, 1193, 1160, 1144, 1085, 930, 884, 853, 819, 783, 775, 763, 744, 711, 702, 693, 671, 603, 534, 516, 495, 477, 461 cm^{-1}; HRMS (EI): calcd for $C_{26}H_{14}S_4$ [M]$^+$: 453.9978, found 453.9979.

2-(2-Thienyl)-bis(benzodithiophene) 9c. The crude product obtained from the Suzuki reaction between bromide **1b** and 2-thienylboronic acid (**8b**) was purified by column chromatography on silica gel with hexane as the eluent to give **9c** (37 mg, 80%) as colorless solid, m.p. (heptane) 232–235 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.7 Hz, 1H, Ar) 7.90 (d, *J* = 8.7 Hz, 1H, Ar), 7.87–7.82 (m, 2H, Ar), 7.61 (s, 1H, thiophene), 7.18 (dd, *J* = 3.7, 1.1 Hz, 1H, thienyl), 7.11 (d, *J* = 5.5 Hz, 1H, thiophene), 7.09 (d, *J* = 5.6 Hz, 1H, thiophene), 7.04 (dd, *J* = 5.1, 1.2 Hz, 1H, thienyl), 6.85 (dd, *J* = 5.1, 3.7 Hz, 1H, thienyl), 6.65 (dd, *J* = 5.6, 0.7 Hz, 1H, thiophene), 6.35 (dd, *J* = 5.6, 0.6 Hz, 1H, thiophene). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.0 (C_q), 137.5 (C_q), 137.4 (C_q), 136.1 (C_q), 135.7 (C_q), 135.4 (C_q), 134.59 (C_q), 134.55 (C_q), 134.2 (C_q), 133.6 (C_q), 131.7 (C_q), 127.5 (C_q), 127.1 (CH), 126.9 (CH), 126.8 (CH), 126.5 (CH), 126.4 (CH), 126.2 (CH), 121.4 (CH), 121.2 (CH), 119.69 (CH), 119.65 (CH), 119.0 (CH), 118.2 (CH). IR (neat): ν̃ = 1418, 1386, 1330, 1193, 1159, 1145, 1085, 880, 855, 823, 791, 773, 746, 694, 671, 645, 534, 463, 452 cm^{-1}; HRMS (EI): calcd for $C_{24}H_{12}S_5$ [M]$^+$: 459.9542, found 459.9549.

General procedure for the synthesis of benzo fused 7-TH derivatives 7a-c. A stirred solution of compound **9** (0.1 mmol) and a catalytic amount of iodine in toluene (750 mL) was irradiated at room temperature with a 125 W unfiltered medium-pressure Hg lamp. The outcome of the reaction was monitored by HPLC analysis (eluent: H_2O/CH_3CN = 95:5). After completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel to provide the required product **7**.

Benzo fused derivative 7a. The crude product obtained from the photocyclization of **9a** was purified by column chromatography on silica gel with the mixture hexane/ CH_2Cl_2 (9:1) as the eluent to give **7a** (56 mg, 91%) as colorless solid, m.p. (hexane) 244–247 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.35–8.31 (m, 2H, fused phenyl), 7.67–7.64 (m, 2H Ar-7TH), 6.81 (d, *J* = 5.7 Hz, 2H, thiophene-7TH), 6.78 (d, *J* = 5.5 Hz, 2H, thiophene-7TH), 3.20–3.00 (m, 8H, CH_2), 2.00–1.88 (m, 8H, CH_2), 1.24 (t, *J* = 7.3 Hz, 6H, CH_3), 1.16 (t, *J* = 7.3 Hz, 6H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.0 (C_q), 137.8 (C_q), 136.0 (C_q), 134.1 (C_q), 132.4 (C_q), 130.3 (C_q), 129.8 (C_q), 128.7 (C_q), 127.4 (C_q), 126.6 (CH), 125.8 (CH), 124.9 (CH), 122.2 (CH), 34.60 (CH_2), 34.58 (CH_2), 23.4 (2CH_2), 14.9 (CH_3), 14.7 (CH_3). IR (neat): ν̃ = 2956, 2927, 2868, 1468, 1453, 1376, 1329, 1246, 1158, 1109, 1086, 1026, 939, 882, 818, 761, 743, 702, 673, 646, 622, 492, 420 cm^{-1}; HRMS (EI): calcd for $C_{38}H_{36}S_4$ [M]$^+$: 620.1700, found 620.1703.

Benzo fused derivative 7b. The crude product obtained from the photocyclization of **9b** was purified by column chromatography on silica gel with the mixture hexane/CH_2Cl_2 (9:1) as the eluent to give **7b** (44 mg, 99%) as colorless solid, m.p. (hexane/CH_2Cl_2) 293–294 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.33–8.30 (m, 2H, fused phenyl), 8.03 (s, 4H, Ar-7TH), 7.71–7.68 (m, 2H, fused phenyl), 6.90 (d, *J* = 5.6 Hz, 2H, thiophene-7TH), 6.83 (d, *J* = 5.6 Hz, 2H, thiophene-7TH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.3 (C_q), 136.9 (C_q), 135.9 (C_q), 135.7 (C_q), 132.0 (C_q), 127.9 (C_q), 127.5 (C_q), 127.2 (CH), 125.14 (CH), 125.07 (CH), 124.1 (CH), 120.9 (CH), 118.7 (CH). IR (neat): ν̃ = 1414, 1382, 1372, 1330, 1300, 1282, 1226, 1190, 1157, 1095, 1033, 1015, 918, 897, 885, 827, 819, 787, 777,

766, 756, 740, 723, 702, 652, 620, 542, 466, 440 cm^{-1}; HRMS (EI): calcd for $C_{26}H_{12}S_4$ $[M]^+$: 451.9822, found 451.9822.

Benzo fused derivative 7c. The crude product obtained from the photocyclization of **9c** was purified by column chromatography on silica gel with the mixture hexane/CH_2Cl_2 (9:1) as the eluent to give **7c** (43 mg, 94%) as colorless solid, m.p. (heptane) 276–279 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.04–7.98 (m, 4H, Ar-7TH), 7.75 (d, *J* = 5.3 Hz, 1H, fused thiophene), 7.68 (d, *J* = 5.3 Hz, 1H, fused thiophene), 6.90 (d, *J* = 5.5 Hz, 1H, thiophene-7TH), 6.89 (d, *J* = 5.5 Hz, 1H, thiophene-7TH), 6.79 (dd, *J* = 5.6 Hz, 0.6 Hz, 1H, thiophene-7TH), 6.78 (dd, *J* = 5.6 Hz, 0.7 Hz, 1H, thiophene-7TH). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.0 (C_q), 136.9 (C_q), 136.1 (C_q), 136.0 (C_q), 135.4 (C_q), 135.2 (C_q), 133.5 (C_q), 132.7 (C_q), 132.3 (C_q), 132.1 (C_q), 131.7 (C_q), 131.6 (C_q), 127.4 ($2C_q$), 127.1 (CH), 125.2 (2CH), 124.2 (CH), 124.1 (CH), 122.7 (CH), 121.0 (CH), 120.9 (CH), 118.72 (CH), 118.69 (CH). IR (neat): $\bar{\nu}$ = 3096, 2964, 2922, 2822, 1461, 1386, 1343, 1325, 1300, 1260, 1194, 1156, 1125, 1095, 1067, 1016, 934, 915, 896, 882, 855, 826, 816, 789, 776, 767, 749, 721, 701, 688, 639, 627, 586, 541, 507, 490, 479, 472, 459, 421 cm^{-1}; HRMS (EI): calcd for $C_{24}H_{10}S_5$ $[M]^+$: 457.9386, found 457.9384.

CCDC 2033732 (for **6c**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

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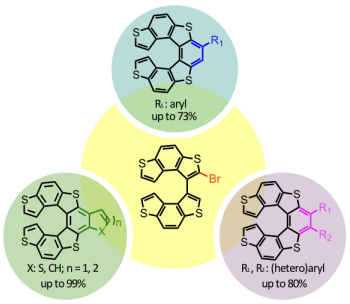
Table of Contents



Highly versatile procedures have been developed for the synthesis of functionalized tetrathia[7]helicenes, including benzo fused systems, through transition metal-promoted annulation reactions of bis(benzodithiophene) species, obtained from 2-bromo-3,3'-bibenzo[1,2-*b*:4,3-*b*']dithiophene as key intermediate.