Synthesis of macrocyclic heteroarylenes by consecutive inter- and intramolecular cycloadditions of thiophenylene-tethered triynes

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ABSTRACT

Consecutive inter- and intramolecular [2+2+2] cycloadditions of various thiophenylene-tethered triynes were comprehensively studied by using chiral Rh catalysts. When we started from 2,3- and 3,4-thiophenylene-tethered substrates, dimerization proceeded and chiral tetraheteroarylenes were obtained. In contrast, reactions of 2,5-thiophenylene-tethered substrates gave hexaheteroarylenes as trimers. When bis- and tris(2,5-thiophenylene)-tethered triynes were used, mixtures of dimers and trimers were obtained, which included macrocyclic systems that contained up to 12 aromatic rings, and their photophysical properties were measured.

Cycloaddition, Thiophene, Chirality, Heteroarylenes, Asymmetric Synthesis, Macrocycles, Rhodium

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1. Introduction

In organic functional materials, such as organic light emitting diodes and photovoltaic cells, a thiophene skeleton often plays a key role in π -conjugated systems, which can confer unique electronic and/or photophysical properties.¹ Various types of oligo- and polyheteroarylenes, in which several aromatic and heteroaromatic rings including thiophene(s) are linearly connected, have been prepared and evaluated.²

In contrast, cyclic heteroarylenes have also attracted considerable attention. For example, 3,4-tetrathiophenylene, in which four thiophene rings are connected at their 3- and 4-positions, was prepared in 1975 by the Cu-mediated homo-coupling of 4,4'-dibromo-3,3'-bithiophene.³ The Ni-mediated coupling of four molecules of 3,4-dibromothiophene was subsequently reported as a more facile protocol.⁴ 2,3-Tetrathiophenylene has also been synthesized by the Cu-mediated homo-coupling of 3,3'-dibromo-2,2'-bithiophene.⁵ Recently, 4,5-tetrathiazolene was prepared via Pd-catalyzed consecutive inter- and intramolecular C-H arylations.⁶ For macrocyclic polythiophenylenes that contain more than four thiophene rings, Bäuerle synthesized cyclic polythiophenylenes tethered by 1,3-diyne moieties, which formed a thiophene skeleton by the reaction with Na₂S.⁷ This protocol realized the construction of cyclic polythiophenylene with up to 16 thiophene rings. He further succeeded in the construction of from [10] to [35]thiophenylenes via the Pt complex-templated coupling of quinquethiophene distannane along with demetallation, albeit in low yield.⁸ Iyoda reported the synthesis

of heteroarylenes, in which a cyclic system was constructed by thiophene and naphthalene rings.^{9,10}

In contrast, we have developed consecutive inter- and intramolecular [2+2+2] cycloadditions for the synthesis of various types of cyclic polyphenylenes.¹¹ By choosing the appropriate *ortho*, *meta*, or *para*-phenylene-tethered triynes, we obtained

Scheme 1. Our previous work of consecutive inter- and intramolecular [2+2+2] cycloadditions of phenylene-tethered triynes

tetra- and/or hexaphenylenes, some of which have axial chiralities derived from restricted rotation about biaryl bonds (Scheme 1).

We next focused on the use of thiophene-tethered triynes: the reaction of the triynes gives cyclic heteroarylenes consisting of both thiophene and benzene rings, which are new cyclic π -conjugate systems. In this article, we report the Rh-catalyzed [2+2+2] cycloaddition of 2,3-, 3,4-, 2,5-thiophenylene-, and 2,3-benzothiophenylene-tethered triynes. The reaction of bis- and tris(2,5-thiophenylene)-tethered triynes is also disclosed.

2. Results and discussion

2.1. 2,3-Thiophenylene-tethered triynes

We chose 2-ethynyl-3-(nitrogen-tethered 1,6-diyne)-substituted thiophene **1a** as a model substrate and subjected it to the Rh-catalyzed reaction (Table 1). When a cationic Rh-achiral BIPHEP complex was used in 1,2-dichloroethane (DCE), the desired tetraheteroarylene **2a** was obtained as a dimer in moderate yield (entry 1). The induction of chirality was ascertained by HPLC analysis using a chiral column, which means that the rotation of single bonds between benzene and thiophene rings was restricted due to rigid cyclic π -system in compound **2a**. We next used the optimal chiral catalysts, which realized the highly enantioselective synthesis of tetraphenylenes from *ortho*-phenylene-tethered triynes.¹¹ Cy-BINAP gave the product in good yield, but almost no enantioinduction was observed (entry 2). QuinoxP*¹² achieved moderate yield and ee (entry 3). We further examined several diphosphines with an axially chiral biaryl skeleton (entries 4-6): DTBM-SEGPHOS gave the best yield of 84%, but the ee was low. Among DUPHOS ligands (entries 7 and 8), bulky *i*-Pr-DUPHOS gave the product in moderate yield, but the ee did not exceed that with QuinoxP*. In further investigations, we used BIPHEP for the preparation of racemic compounds, and mainly used Cy-BINAP and QuinoxP* for the enantioselective reaction.

Table 1. Screening of ligands for the reaction of triyne **1a**

Entry	Ligand ^a	Yield (%)	Ee (%)
1	BIPHEP	61	-
2	(<i>R</i>)-Cy-BINAP	70	3
3	(<i>R,R</i>)-QuinoxP*	45	52
4	(<i>R</i>)-BINAP	40	11
5	(<i>R</i>)-Cy-SEGPHOS	71	30
6	(<i>S</i>)-DTBM-SEGPHOS	84	7
7	(<i>R,R</i>)-Me-DUPHOS	52	17
8	(<i>R,R</i>)- <i>i</i> -Pr-DUPHOS	46	41

^a BIPHEP: bis(diphenylphosphino)-1,1'-biphenyl, Cy-BINAP: 2,2'-bis(dicyclohexylphosphino)-1,1'-binaphthyl, QuinoxP*: 2,3-bis(*tert*-butylmethylphosphino)quinoxaline, Cy-SEGPHOS: 5,5'-bis(dicyclohexylphosphino)-4,4'-bi-1,3-benzodioxole,

DTBM-SEGPHOS: 5,5'-bis[di(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphino]-4,4'-bi-1,3-benzodioxole, Me-DUPHOS: 1,2-bis(2,5-dimethylphospholano)benzene, *i*-Pr-DUPHOS: 1,2-bis(2,5-diisopropylphospholano)benzene.

We examined other 2,3-thiophenylene-tethered triynes (Table 2). The reaction of triyne **1b** possessing a carbon-tethered 1,6-diyne moiety gave the corresponding cycloadduct **2b** under achiral conditions (entry 1), and QuinoxP* realized moderate ee, albeit in low yield (entry 3). In the case of phenyl-substituted triyne **1c**, Cy-BINAP gave better enantioselectivity (entry 5) and QuinoxP* gave better yield (entry 6).

Table 2. Reaction of 2,3-thiophenylene-tethered triynes

Entry	R	Z	Triyne	Ligand ^b	Yield (%)	Ee (%)
1	Me	CE ₂ ^a	1b	BIPHEP	84 (2b)	-
2	Me	CE ₂ ^a	1b	Cy-BINAP	10 (2b)	14
3	Me	CE ₂ ^a	1b	QuinoxP*	38 (2b)	69
4	Ph	NTs	1c	BIPHEP	61 (2c)	-
5	Ph	NTs	1c	Cy-BINAP	36 (2c)	34
6	Ph	NTs	1c	QuinoxP*	72 (2c)	15

^a CE₂: C(CO₂Me).

^b (*R*)-Cy-BINAP and (*R,R*)-QuinoxP* were used.

The proposed scheme for the dimerization of 2,3-thiophenylene-tethered triynes **1** would be the same as that for *ortho*-phenylene-tethered triynes (Scheme 2).¹¹ An intermolecular reaction of the metallacyclopentadiene moiety of **A**, derived from the first triyne, with a terminal alkyne moiety of the second triyne gives intermediate **B**. Oxidative coupling of the remaining 1,6-diyne moiety of the second triyne gives metallacyclopentadiene **C**. The subsequent intramolecular reaction gives chiral tetraheterophenylene **2** as a dimer.

Scheme 2. Proposed scheme of inter- and intramolecular [2+2+2] cycloadditions of two molecules of triynes **1**

We considered that axial chirality is not induced in the *ortho*-dithienyl benzene intermediate **B**, in which two thiophene rings freely rotate at room temperature. This could explain the significant decrease in the ee of tetraheteroarylenes **2** compared with that of tetraphenylenes.¹¹ We checked this speculation by stepwise reactions: *ortho*-dithienyl benzene **3b** was prepared by using a chiral Rh catalyst at 0 °C and isolated,¹³ and then subjected to the intramolecular reaction in the presence of an achiral Rh catalyst (Scheme 3). The ee of the obtained cycloadduct **2b** was below 2%, as we expected.

Scheme 3. Stepwise synthesis of tetraheteroarylene **2b**

We anticipated that a 2,3-benzothiophenylene tether, in place of 2,3-thiophenylene, could induce axial chirality in intermediate **B** and that the corresponding cycloadducts could be obtained with an ee as high as those of tetraphenylenes. In fact, excellent to almost perfect enantioselectivity was achieved in the reaction of 2,3-benzothiophenylene-tethered triynes **4a** and **4b** when QuinoxP* was used as a chiral ligand (Table 3).

Table 3. Reaction of 2,3-benzothiophenylene-tethered triynes **4**

Entry	Z	Triyne	Ligand ^a	Yield (%)	Ee (%)
1	NTs	4a	BIPHEP	70 (5a)	-
2	NTs	4a	Cy-BINAP	22 (5a)	82
3	NTs	4a	QuinoxP*	47 (5a)	>99
4	C(CO ₂ Me) ₂	4b	BIPHEP	31 (5b)	-
5	C(CO ₂ Me) ₂	4b	Cy-BINAP	8 (5b)	87
6	C(CO ₂ Me) ₂	4b	QuinoxP*	19 (5b)	96

^a (*R*)-Cy-BINAP and (*R,R*)-QuinoxP* were used.

We ascertained the asymmetric induction by the stepwise reaction of benzothiophenylene-tethered triyne **4b** (Scheme 4). The *ortho*-bis(benzothiienyl)benzene **6b**, which corresponds to intermediate **B** in Scheme 2, was prepared with the chiral Rh catalyst and asymmetric induction with excellent enantioselectivity was determined by HPLC analysis using a chiral column.¹⁴ The subsequent intramolecular reaction using the achiral catalyst gave **5b** quantitatively with excellent ee.

Scheme 4. Stepwise synthesis of tetraheteroarylene **5b**

As an oxygen analogue of triynes **4**, we examined 2,3-benzofuranylen-tethered triynes **7** under the same reaction conditions (Table 4). All of the reaction gave many unidentified products and the yields of tetraheteroarylenes **8** containing two benzofuran moieties were generally low. However, good ee was achieved when QuinoxP* was used as a chiral ligand (entries 3 and 6).

Table 4. Reaction of 2,3-benzofuranylene-tethered triynes **7**

Entry	Z	Triyne	Ligand ^a	Yield (%)	Ee (%)
1	NTs	7a	BIPHEP	19 (8a)	-

2	NTs	7a	Cy-BINAP	9 (8a)	<2
3	NTs	7a	QuinoxP*	16 (8a)	81
4	C(CO ₂ Me) ₂	7b	BIPHEP	15 (8b)	-
5	C(CO ₂ Me) ₂	7b	Cy-BINAP	3 (8b)	12
6	C(CO ₂ Me) ₂	7b	QuinoxP*	6 (8b)	83

^a (*R*)-Cy-BINAP and (*R,R*)-QuinoxP* were used.

2.2. 3,4-Thiophenylene-tethered triynes

As different substituents on the thiophene ring, we next examined 3,4-thiophenylene-tethered triynes **9** (Table 5). In the reactions of both **9a** and **9b**, Cy-BINAP gave the desired tetraheteroarylenes **10a** and **10b** in high yield with low ee, while QuinoxP* gave a low yield with moderate ee.

Table 5. Reaction of 3,4-thiophenylene-tethered triynes **9**

Entry	Z	Triyne	Ligand ^a	Yield (%)	Ee (%)
1	NTs	9a	BIPHEP	17 (10a)	-
2	NTs	9a	Cy-BINAP	85 (10a)	37
3	NTs	9a	QuinoxP*	30 (10a)	64
4	C(CO ₂ Me) ₂	9b	BIPHEP	56 (10b)	-
5	C(CO ₂ Me) ₂	9b	Cy-BINAP	89 (10b)	15
6	C(CO ₂ Me) ₂	9b	QuinoxP*	28 (10b)	69

^a (*R*)-Cy-BINAP and (*R,R*)-QuinoxP* were used.

Racemic cycloadduct **10b**•CH₂Cl₂ became a single crystal and its structure was determined by X-ray analysis. The ORTEP diagram clearly shows a saddle-shaped molecule (Figure 1).

Figure 1. ORTEP diagram of **10b** (dichloromethane was omitted for clarity).

2.3. 2,5-Thiophenylene-tethered triynes

We further examined 2,5-thiophenylene-tethered triynes **11** under more dilute conditions (13 mM) than that used previously (0.1 M) (Table 6). The triynes were completely consumed at 60 °C in each reaction. While tetraheteroarylene as a dimer could

not be detected at all, C₃-symmetric hexaheteroarylenes **12** as trimers were the only isolable and characterized products. When Cy-BINAP was used as a ligand, moderate yield was achieved.

Table 6. Reaction of 2,5-thiophenylene-tethered triynes **11**

Entry	Z	Triyne	Ligand ^a	Yield (%)
1	NTs	11a	BIPHEP	28 (12a)
2	NTs	11a	Cy-BINAP	48 (12a)
3	NTs	11a	QuinoxP*	33 (12a)
4	C(CO ₂ Me) ₂	11b	Cy-BINAP	54 (12b)
5	C(CO ₂ Me) ₂	11b	QuinoxP*	26 (12b)

^a (*R*)-Cy-BINAP and (*R,R*)-QuinoxP* were used.

The proposed mechanism for the selective formation of trimers **12** from 2,5-thiophenylene-tethered triynes **11** would be different from that for the selective formation of hexaphenylenes from *para*-phenylene-tethered triynes (Scheme 5).¹¹ An intermolecular reaction of metallacycle **A'** derived from the first triyne and the terminal alkyne moiety of the second triyne gives a teraryl intermediate, and the subsequent oxidative coupling of the diyne moiety of the second triyne affords metallacycle **B'**. The terminal alkyne moiety of the first triyne could be close enough to react with **B'**, but does not react, since dimer **13** has severe ring-strain derived from the two facing thiophene rings. The second intermolecular reaction with the third triyne proceeds to give a quinque aryl intermediate, and subsequent oxidative coupling provides metallacycle **C'**, where the terminal alkyne moiety of the first triyne can react, since the intramolecular cycloadducts, hexaheteroarylenes **12**, have less ring-strain than **13**. The orientation of the terminal alkynes, which intermolecularly react with metallacycles **A'** and **B'**, is decisive for the selective formation of trimers **12** by the final intramolecular reaction. Other orientations lead to open-chain oligomers or polymers.

Scheme 5. Proposed scheme of inter- and intramolecular [2+2+2] cycloadditions of three molecules of triynes **11**

Based on the mechanism above, multi(2,5-thiophenylene)-tethered triynes can afford dimers due to the release of ring-strain. In fact, the reaction of bis(2,5-thiophenylene)-tethered triynes **14** gave hexaheteroarylenes **15** as dimers in addition to nonaheteroarylenes **16** as trimers under more dilute conditions (6.3 mM) (Table 7). In the case of carbon-tethered triyne **14b**, Cy-SEGPHOS selectively gave trimer **16b** in moderate yield (entry 5).

Table 7. Reaction of bis(2,5-thiophenylene)-tethered triynes **14**

Entry	Z	Triyne	Ligand ^a	Yield (%)	Yield (%)
1	NTs	14a	Cy-BINAP	20 (15a)	23 (16a)
2	NTs	14a	QuinoxP*	16 (15a)	27 (16a)
3	C(CO ₂ Me) ₂	14b	Cy-BINAP	9 (15b)	44 (16b)

4	C(CO ₂ Me) ₂	14b	QuinoxP*	16 (15b)	19 (16b)
5	C(CO ₂ Me) ₂	14b	Cy-SEGPHOS	4 (15b)	50 (16b)

^a (R)-Cy-BINAP, (R,R)-QuinoxP* and (R)-Cy-SEGPHOS were used.

We further examined the reaction of tris(2,5-thiophenylene)-tethered triynes **17** (Table 8). In all reactions, a mixture of dimer **18** and trimer **19** was obtained. Notably, dodecaheteroarylenes **19** were prepared in one pot from acyclic substrates, albeit in low yield.

Table 8. Reaction of tris(2,5-thiophenylene)-tethered triynes **17**

Entry	Z	Triyne	Ligand ^a	Yield (%)	Yield (%)
1	NTs	17a	Cy-BINAP	4 (18a)	23 (19a)
2	NTs	17a	QuinoxP*	12 (18a)	19 (19a)
3	C(CO ₂ Me) ₂	17b	Cy-BINAP	20 (18b)	3 (19b)
4	C(CO ₂ Me) ₂	17b	QuinoxP*	22 (18b)	10 (19b)

^a (R)-Cy-BINAP and (R,R)-QuinoxP* were used.

2.4. Photophysical properties of macrocyclic heteroarylenes

Finally we measured the absorption and emission spectra, as well as the absolute quantum yield of macrocyclic heteroarylenes derived from mono-, bis- and tris(2,5-thiophenylene)-tethered triynes (Table 9). In both the dimer series (**15** and **18**) and the trimer series (**12**, **16** and **19**), a red shift of the absorption maxima ($\lambda_{\text{max}}^{\text{kk}|\text{jk,abs}}$) was observed with an increase in the number of thiophene rings, as expected (**15** vs **18**, and **12** vs **16**, **19**). For macrocyclic systems with the same number of aromatic rings, the absorption maxima of more planar compounds **12** were more red-shifted than those of compounds **15**. In the fluorescence spectra of the trimer series of **16** and **19**, the emission maxima ($\lambda_{\text{max}}^{\text{em}}$) were almost the same regardless of

the number of thiophene rings, which suggests the ineffective elongation of π -conjugation in excited states. These cyclic molecules are characterized by large Stokes shifts (93–214 nm), probably due to their highly strained structure. A smaller, more strained ring system showed a greater Stokes shift than a larger ring system (**12,16** vs **19**).¹⁵ The quantum yield increased with an increase in the number of aromatic rings.

Table 9. Absorption and emission maxima, and quantum yields

compound	No. ^a	$\lambda_{\text{abs}}^{\text{max}}$ (nm) ^b	$\lambda_{\text{em}}^{\text{max}}$ (nm) ^{b,c}	Stokes shift (nm) ^b	$\Phi_F (10^{-2})^{b,c}$
15a	6	313	450	137	1.3
18a	8	365	493	128	4.0
12a	6	264	478	214	5.2
16a	9	344	492	148	6.8
19a	12	382	491	109	8.4
15b	6	312	449	136	1.5
18b	8	361	497	136	3.0
12b	6	287	462	175	5.1
16b	9	352	490	138	7.2
19b	12	383	486	93	11.5

^a The number of aromatic rings in macrocyclic system.

^b A dichloromethane solution.

^c Excitation at $\lambda_{\text{abs}}^{\text{max}}$.

3. Conclusions

We comprehensively studied Rh-catalyzed consecutive inter- and intramolecular [2+2+2] cycloadditions of various thiophenylene-tethered triynes. The present one-pot synthesis provided various macrocyclic heteroarylenes, which are composed of phenylene and thiophenylene moieties. The reaction of 2,3- and 3,4-thiophenylene-tethered triynes gave tetraheteroarylenes as dimers in moderate ee. When 2,3-benzothiophene-tethered triynes were used, excellent enantioselectivity was achieved. In contrast, 2,5-thiophenylene-tethered triynes afforded hexaheteroarylene as trimers and bis- and tris(2,5-thiophenylene)-tethered triynes gave mixtures of dimers and trimers. We created a series of compounds with a new cyclic π -conjugate system consisting of thiophene and benzene rings, and they showed unique photophysical properties based on their macrocyclic structures.

4. Experimental section

4.1. General

Anhydrous 1,2-dichloroethane was purchased and dried over activated molecular sieves 4A. Solvent was degassed by argon

bubbling prior to use. All reactions were carried out under an atmosphere of argon in oven-dried glassware with a magnetic stirring bar. Takasago International Corp. provided Cy-BINAP and Cy-SEPHOS, and Nippon Chemical Industrial Corp. did QuinoxP*. Other ligands were purchased from Strem Chemicals Inc.

IR spectra were recorded with a JASCO FT/IR-4100 spectrometer. NMR spectra were recorded with a JEOL AL-400 (400 MHz) using tetramethylsilane as an internal standard and CDCl₃ as a solvent except compound **15a**, which was measured in a DMSO-*d*₆ solution. High-resolution mass spectra (HRMS) were measured on a JEOL JMS-SX102A and JEOL SpiralTOF JMS-S3000 with FAB (Fast Atomic Bombardment) method or EI (electron impact) method at a JEOL GC-mate II or MALDI (Matrix Assisted Laser Desorption/Ionization) method at Bruker AutoflexIII. Optical rotations were measured on a JASCO DIP-1000 polarimeter. Ee was determined by HPLC analysis with detection at 254 nm using a chiral column (Daicel Chiralpak IA-3, 4.6 x 250 mm) at room temperature. UV-absorbance and emission were measured using JASCO V-570 and Hitachi F-2500, respectively. The absolute quantum yield was measured by Hamamatsu Photonics Quantaaurus-QY.

4.2. Typical experimental procedure (Tables 2–5)

[Rh(cod)₂]BF₄ (2.0 mg, 0.005 mmol) and diphosphine ligand (0.005 mmol), such as BIPHEP, Cy-BINAP, and QuinoxP*, were placed in a Schlenk tube, which was then evacuated and backfilled with argon (x5). To the reaction vessel was added dichloromethane (1.0 mL). Then it was filled with hydrogen, and the mixture was stirred at ambient temperature for 30 min under a hydrogen atmosphere. After removal of the solvent and hydrogen under the reduced pressure, the reaction vessel was filled with argon. 1,2-Dichloroethane (0.1 mL) was added to the flask and a red solution was prepared. Then, a 1,2-dichloroethane solution (0.4 mL) of triyne (0.05 mmol) was added to the solution and the mixture was stirred at room temperature for 1 h, then at 60 °C for 24 h. After the completion of the reaction, the volatiles were removed under reduced pressure, and the crude products were purified by thin-layer chromatography to give a chiral cycloadduct. The enantiomeric excess was determined by HPLC analysis using a chiral column.

4.2.1. *N*-[3-(2-Ethynylthiophen-3-yl)prop-2-ynyl]-*N*-tosylbut-2-yn-1-amine (**1a**).

Pale brown solid; mp 100 °C. IR (neat) 3255, 1352, 1163, 814 cm⁻¹. ¹H NMR δ 1.68 (t, *J* = 2.4 Hz, 3H), 2.33 (s, 3H), 3.52 (s, 1H), 4.15 (q, *J* = 2.4 Hz, 2H), 4.41 (s, 2H), 6.75 (d, *J* = 5.0 Hz, 1H), 7.13 (d, *J* = 5.0 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H). ¹³C NMR δ 3.4, 21.4, 36.9, 37.1, 71.5, 75.6, 79.6, 81.9, 85.1, 85.9, 125.2, 126.2, 126.9, 127.9, 129.3, 129.3, 135.3, 143.7. HRMS (FAB, positive) *m/z* Calcd. for C₂₀H₁₇NO₂S₂Na, 390.0598 ([M+Na]⁺); found, 390.0582 ([M+Na]⁺).

4.2.2. Dimethyl 2-(but-2-ynyl)-2-[3-(2-ethynylthiophen-3-yl)prop-2-ynyl]malonate (**1b**).

Yellow oil. IR (neat) 3269, 1739, 854 cm⁻¹. ¹H NMR δ 1.74 (s, 3H), 3.00 (s, 2H), 3.21 (s, 2H), 3.55 (s, 1H), 3.75 (s, 6H), 6.91 (d, *J* = 5.0 Hz, 1H), 7.11 (d, *J* = 5.0 Hz, 1H). ¹³C NMR δ 3.6, 23.3, 23.9, 53.1, 57.1, 73.1, 76.0, 77.6, 79.3, 85.1, 88.6, 124.8, 126.3, 127.8, 129.7, 169.5. HRMS (FAB, positive) *m/z* Calcd. for C₁₈H₁₆O₄SN₂, 351.0667 ([M+Na]⁺); found, 351.0654 ([M+Na]⁺).

4.2.3. *N*-(3-(2-Ethynylthiophen-3-yl)prop-2-ynyl)-*N*-tosyl-3-phenylprop-2-yn-1-amine (**1c**).

Brown solid; mp 80 °C. IR (neat) 3240, 1352, 1163, 758 cm⁻¹. ¹H NMR δ 2.29 (s, 3H), 3.52 (s, 1H), 4.47 (s, 4H), 6.77 (d, *J* = 5.4 Hz, 1H), 7.12 (d, *J* = 5.4 Hz, 1H), 7.20-7.27 (m, 7H), 7.77 (d, *J* = 8.4 Hz, 2H). ¹³C NMR δ 21.4, 37.3, 37.5, 75.6, 70.8, 81.5, 85.3, 85.7, 85.8, 122.1, 125.4, 126.3, 126.8, 127.9, 128.1, 128.5, 129.3, 129.5, 131.6, 135.0, 143.9. HRMS (FAB, positive) *m/z* Calcd. for C₂₅H₁₉NO₂S₂Na, 452.0755 ([M+Na]⁺); found, 452.0758 ([M+Na]⁺).

4.2.4. 8,16-Dimethyl-2,10-ditosyl-1,2,3,9,10,11-hexahydro-2,10-diazadiindenol[4',5':3,4;4'',5'':7,8]cycloocta[1,2-b:5,6-b']dithiophene (2a).

Pale yellow solid; mp 214 °C (decomp.) IR (neat) 1346, 1165, 814 cm⁻¹. ¹H NMR δ 2.18 (s, 6H), 2.39 (s, 6H), 4.22 (d, *J* = 13.8 Hz, 2H), 4.49 (d, *J* = 13.6 Hz, 2H), 4.54 (d, *J* = 13.6 Hz, 2H), 4.61 (d, *J* = 13.8 Hz, 2H), 6.74 (d, *J* = 4.8 Hz, 2H), 7.05 (s, 2H), 7.26-7.29 (m, 6H), 7.72 (d, *J* = 8.0 Hz, 4H). ¹³C NMR δ 18.3, 21.5, 53.2, 53.9, 125.5, 127.5, 128.1, 129.8, 129.8, 131.6, 131.7, 133.6, 133.9, 135.7, 136.5, 139.9, 143.7 (A pair of aromatic peaks was overlapped). HRMS (FAB, positive) *m/z* Calcd. for C₄₀H₃₄N₂O₄S₄Na, 757.1299 ([M+Na]⁺); found, 757.1282 ([M+Na]⁺). [α]_D²⁵ = 38.2 (c 0.125, CHCl₃, 52% ee). Ee was determined by HPLC analysis (eluent: 50% dichloromethane in hexane, flow rate: 0.3 mL/min, retention time: 17.7 min for minor isomer and 18.3 min for major isomer).

4.2.5. 8,16-Dimethyl-2,2,10,10-tetrakis(methoxycarbonyl)-1,2,3,9,10,11-hexahydrodiindenol[4',5':3,4;4'',5'':7,8]cycloocta[1,2-b:5,6-b']dithiophene (2b).

Pale yellow solid; mp 256 °C. IR (neat) 1756, 849 cm⁻¹. ¹H NMR δ 2.22 (s, 6H), 3.14 (d, *J* = 17.2 Hz, 2H), 3.53 (s, 4H), 3.68 (s, 6H), 3.72 (d, *J* = 17.2 Hz, 2H), 3.77 (s, 6H), 6.92 (d, *J* = 5.2 Hz, 2H), 7.03 (s, 2H), 7.23 (d, *J* = 5.2 Hz, 2H). ¹³C NMR δ 18.7, 39.5, 40.6, 52.9, 53.1, 59.7, 124.3, 129.0, 131.0, 131.2, 132.6, 133.4, 137.5, 139.1, 139.2, 140.3, 171.9, 172.3. HRMS (FAB, positive) *m/z* Calcd. for C₃₆H₃₂O₈S₂Na, 679.1436 ([M+Na]⁺); found, 679.1428 ([M+Na]⁺). [α]_D²⁵ = 41.6 (c 0.06, CHCl₃, 69% ee). Ee was determined by HPLC analysis (eluent: 50% dichloromethane in hexane, flow rate: 0.3 mL/min, retention time: 10.8 min for minor isomer and 11.3 min for major isomer).

4.2.6. 8,16-Diphenyl-2,10-ditosyl-1,2,3,9,10,11-hexahydro-2,10-diazadiindenol[4',5':3,4;4'',5'':7,8]cycloocta[1,2-b:5,6-b']dithiophene (2c).

Pale yellow solid; decomp. 293 °C. IR (neat) 1350, 1163, 771 cm⁻¹. ¹H NMR δ 2.37 (s, 6H), 4.32 (d, *J* = 14.2 Hz, 2H), 4.56 (d, *J* = 13.8 Hz, 2H), 4.66 (d, *J* = 14.2 Hz, 2H), 4.73 (d, *J* = 13.8 Hz, 2H), 6.83 (d, *J* = 5.2 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 4H), 7.32 (s, 4H), 7.33 (s, 4H), 7.40-7.45 (m, 6H), 7.67 (d, *J* = 8.0 Hz, 4H). ¹³C NMR δ 21.6, 53.8, 54.0, 126.1, 127.6, 128.1, 128.2, 128.4, 128.9, 129.9, 131.3, 131.4, 133.3, 134.4, 134.8, 136.6, 137.1, 138.6, 140.0, 143.9 (A pair of aromatic peaks was overlapped). HRMS (FAB, positive) *m/z* Calcd. for C₅₀H₃₈N₂O₄S₄Na, 881.1612 ([M+Na]⁺); found, 881.1574 ([M+Na]⁺). [α]_D²⁵ = 20.0 (c 0.1, CHCl₃, 34% ee). Ee was determined by HPLC analysis (eluent: 50% dichloromethane in hexane, flow rate: 0.3 mL/min, retention time: 19.1 min for major isomer and 19.9 min for minor isomer).

4.2.7. Dimethyl 5-{3-[4,4-bis(methoxycarbonyl)octa-1,6-dien-1-yl]thiophen-2-yl}-4-(2-ethynylthiophen-3-yl)-7-methyl-1H-indene-2,2(3H)-dicarboxylate (3b).

Pale yellow oil. IR (neat) 3276, 1738, 802 cm⁻¹. ¹H NMR δ 1.74 (s, 3H), 2.35 (s, 3H), 2.78 (s, 2H), 3.10 (s, 2H), 3.31 (s, 1H), 3.40 (s, 1H), 3.45 (s, 1H), 3.60 (s, 1H), 3.61 (s, 3H), 3.65 (s, 3H), 3.71 (s, 1H), 3.73 (s, 3H), 3.75 (s, 3H), 6.66 (d, *J* = 5.2 Hz, 1H), 6.87 (d, *J* = 5.2 Hz, 1H), 7.03 (d, *J* = 5.2 Hz, 1H), 7.08 (d, *J* = 5.2 Hz, 1H), 7.28 (s, 1H). ¹³C NMR δ 3.5, 18.8, 23.9, 39.7, 40.5, 52.7, 52.9, 57.1, 59.5, 59.6, 73.2, 79.0, 83.7, 83.8, 85.3, 85.8, 120.0, 124.0, 124.6, 125.8, 126.3, 128.9, 129.5, 129.9, 131.0, 131.2, 133.5, 139.8, 140.3, 144.5, 169.5, 172.2. HRMS (ESI, positive) *m/z* Calcd. for C₃₆H₃₂O₈S₂Na, 679.1436 ([M+Na]⁺); found, 679.1404 ([M+Na]⁺).

4.2.8. N-(But-2-ynyl)-N-[3-(2-ethynylbenzo[b]thiophen-3-yl)prop-2-ynyl]-4-methylbenzenesulfonamide (4a).

Pale brown solid; mp 91 °C. IR (neat) 3219, 1350, 1163, 930 cm⁻¹. ¹H NMR δ 1.71 (s, 3H), 2.15 (s, 3H), 3.67 (s, 1H), 4.22 (s, 2H), 4.55 (s, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.39 (dd, *J* = 7.1 Hz, 1H), 7.41 (dd, *J* = 7.1 Hz, 1H), 7.54 (d, *J* = 7.1 Hz, 1H), 7.71 (d, *J* = 7.1 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 2H). ¹³C NMR δ 3.5, 21.2, 37.0, 37.3, 71.6, 76.1, 78.6, 82.0, 87.1, 88.7, 122.0, 123.1, 123.3, 125.2, 126.5, 127.9, 129.4, 135.1, 138.0, 138.2, 143.8 (A pair of aromatic peaks was overlapped). HRMS (FAB, positive) *m/z* Calcd. for C₂₄H₁₉NO₂S₂Na, 440.0755 ([M+Na]⁺); found, 440.0762 ([M+Na]⁺).

4.2.9. Dimethyl 2-(but-2-ynyl)-2-[3-(2-ethynylbenzo[b]thiophen-3-yl)prop-2-ynyl]malonate (4b).

Brown solid; mp 102 °C. IR (neat) 3273, 1739, 758 cm⁻¹. ¹H NMR δ 1.78 (t, *J* = 2.5 Hz, 3H), 3.08 (q, *J* = 2.5 Hz, 2H), 3.36 (s, 2H), 3.70 (s, 1H), 3.79 (s, 6H), 7.40-7.44 (m, 2H), 7.71 (d, *J* = 6.6 Hz, 1H), 7.83 (d, *J* = 6.6 Hz, 1H). ¹³C NMR δ 3.5, 23.3, 24.1, 53.1, 57.1, 72.9, 76.3, 79.4, 79.4, 86.9, 91.5, 122.0, 123.5, 125.2, 126.4, 138.3, 138.5, 169.4 (Two pairs of aromatic peaks were overlapped). HRMS (FAB, positive) *m/z* Calcd. for C₂₂H₁₈O₄SNa, 401.0824 ([M+Na]⁺); found, 401.0805 ([M+Na]⁺).

4.2.10. 8,16-Dimethyl-2,10-ditosyl-1,2,3,9,10,11-hexahydro-2,10-diazadiindenol[4',5':3,4;4'',5'':7,8]cycloocta[1,2-b:5,6-b']bis(benzothiophene) (5a).

Pale yellow solid; mp 181 °C. IR (neat) 1384, 1165, 814 cm⁻¹. ¹H NMR δ 2.25 (s, 6H), 2.43 (s, 6H), 4.08 (d, *J* = 14.2 Hz, 2H), 4.40 (d, *J* = 14.2 Hz, 2H), 4.56 (s, 4H), 6.98 (d, *J* = 8.0 Hz, 2H), 7.18-7.22 (m, 4H), 7.28-7.30 (m, 6H), 7.64 (d, *J* = 8.4 Hz, 4H), 7.74 (d, *J* = 8.0 Hz, 2H). ¹³C NMR δ 18.5, 21.5, 53.3, 54.2, 121.0, 122.5, 124.5, 124.6, 127.6, 128.2, 129.8, 131.2, 131.5, 132.3, 133.4, 135.0, 136.2, 136.4, 137.8, 139.6, 140.3, 143.8. HRMS (FAB, positive) *m/z* Calcd. for C₄₈H₃₈N₂O₄S₄Na, 857.1612 ([M+Na]⁺); found, 857.1636 ([M+Na]⁺). [α]_D²⁵ = -79.0 (c 0.1, CHCl₃, >99% ee). Ee was determined by HPLC analysis (eluent: 50% dichloromethane in hexane, flow rate: 0.3 mL/min, retention time: 15.2 min for minor isomer and 15.5 min for major isomer).

4.2.11. Dimethyl-2,2,10,10-tetrakis(methoxycarbonyl)-1,2,3,9,10,11-hexahydrodiindenol[4',5':3,4;4'',5'':7,8]cycloocta[1,2-b:5,6-b']bis(benzothiophene) (5b).

Brown solid; mp 102 °C. IR (neat) 1732, 814, 764 cm⁻¹. ¹H NMR δ 2.31 (s, 6H), 3.06 (d, *J* = 17.2 Hz, 2H), 3.36 (d, *J* = 17.2 Hz, 2H), 3.44 (d, *J* = 16.8 Hz, 2H), 3.62-3.67 (m, 8H), 3.76 (s, 6H), 7.21-7.26 (m, 8H), 7.71-7.73 (m, 2H). ¹³C NMR δ 18.9, 39.5, 40.5, 52.9, 59.5, 122.1, 123.1, 124.1, 129.5, 130.5, 133.2, 138.5, 139.4, 139.8, 139.9, 171.8 (Four pairs of aromatic peaks were overlapped). HRMS (FAB, positive) *m/z* Calcd. for

$C_{44}H_{36}O_8S_2Na$, 779.1749 ([M+Na]⁺); found, 779.1757 ([M+Na]⁺). [α]_D²⁵ = -116.2 (c 0.05, CHCl₃, 96% ee). Ee was determined by HPLC analysis (eluent: 30% tetrahydrofuran in hexane, flow rate: 0.3 mL/min, retention time: 14.1 min for major isomer and 15.5 min for minor isomer).

4.2.12. 5-{3-[4,4-Bis(methoxycarbonyl)octa-1,6-diyn-1-yl]benzo[b]thiophen-2-yl}-4-(2-ethynylbenzo[b]thiophen-3-yl)-7-methyl-1H-indene-2,2(3H)-dicarboxylate (6b).

Pale yellow solid; mp 47 °C. IR (neat) 3269, 1738, 758 cm⁻¹. ¹H NMR δ 1.77 (t, *J* = 2.5 Hz, 3H), 2.43 (s, 3H), 2.96 (d, *J* = 3.4 Hz, 2H), 3.26 (d, *J* = 3.4 Hz, 2H), 3.44 (s, 1H), 3.64 (d, *J* = 3.4 Hz, 2H), 3.68 (s, 6H), 3.70-3.74 (m, 8H), 6.97 (s, 1H), 7.18 (t, *J* = 7.9 Hz, 1H), 7.27-7.34 (m, 3H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.52 (s, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.73 (d, *J* = 7.9 Hz, 1H). ¹³C NMR δ 3.6, 14.2, 19.1, 23.3, 24.2, 25.7, 29.8, 39.8, 40.3, 53.0, 57.2, 59.6, 68.1, 73.2, 79.3, 85.9, 88.3, 115.7, 121.8, 122.0, 123.0, 123.9, 124.2, 124.3, 124.6, 124.7, 124.9, 125.9, 127.2, 131.9, 133.3, 134.3, 138.3, 138.9, 139.1, 140.0, 140.0, 140.1, 140.7, 169.5, 169.6, 172.0, 172.2 (A pair of alkyne peaks was overlapped). HRMS (FAB, positive) *m/z* Calcd. for $C_{44}H_{36}O_8S_2Na$, 779.1716 ([M+Na]⁺); found, 779.1749 ([M+Na]⁺). [α]_D²⁵ = -49.0 (c 0.1, CHCl₃, >99% ee). Ee was determined by HPLC analysis (eluent: 10% ethanol in hexane, flow rate: 0.3 mL/min, retention time: 23.1 min for minor isomer and 23.7 min for major isomer).

4.2.13. N-(But-2-ynyl)-N-[3-(2-ethynylbenzofuran-3-yl)prop-2-ynyl]-4-methylbenzenesulfonamide (7a).

Brown oil. IR (neat) 3255, 1352, 1163, 816 cm⁻¹. ¹H NMR δ 1.71 (t, *J* = 2.4 Hz, 3H), 2.20 (s, 3H), 3.72 (s, 1H), 4.18 (q, *J* = 2.4 Hz, 2H), 4.51 (s, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 7.27-7.29 (m, 1H), 7.34-7.41 (m, 3H), 7.75 (d, *J* = 8.2 Hz, 2H). ¹³C NMR δ 3.5, 21.3, 37.1, 37.4, 71.6, 72.9, 75.1, 82.0, 87.2, 90.2, 111.5, 120.5, 123.8, 126.8, 127.1, 127.9, 128.0, 129.4, 129.5, 140.4, 143.8, 149.4. HRMS (FAB, positive) *m/z* Calcd. for $C_{24}H_{19}NO_3SNa$, 424.0983 ([M+Na]⁺); found, 424.0972 ([M+Na]⁺).

4.2.14. Dimethyl 2-(but-2-ynyl)-2-[3-(2-ethynylbenzofuran-3-yl)prop-2-ynyl]malonate (7b).

Brown oil. IR (neat) 3273, 1741, 748 cm⁻¹. ¹H NMR δ 1.78 (t, *J* = 2.5 Hz, 3H), 3.04 (q, *J* = 2.5 Hz, 2H), 3.32 (s, 2H), 3.75 (s, 1H), 3.79 (s, 6H), 7.26-7.32 (m, 1H), 7.35-7.43 (m, 2H), 7.59-7.61 (m, 1H). ¹³C NMR δ 3.5, 23.3, 24.1, 53.0, 57.1, 72.7, 72.9, 73.2, 79.4, 87.0, 92.9, 110.0, 111.4, 120.7, 123.8, 126.7, 127.6, 140.0, 153.9, 169.4. HRMS (FAB, positive) *m/z* Calcd. for $C_{22}H_{18}O_5$, 385.1052 ([M]⁺); found, 385.1063 ([M]⁺).

4.2.15. 8,16-Dimethyl-2,10-ditosyl-1,2,3,9,10,11-hexahydro-2,10-diazadiindeno[4',5':3,4;4'',5'':7,8]cycloocta[1,2-b:5,6-b']bis(benzofuran) (8a).

Pale yellow solid; mp 187 °C. IR (neat) 1348, 1165, 802 cm⁻¹. ¹H NMR δ 2.29 (s, 6H), 2.41 (s, 6H), 4.15 (d, *J* = 14.0 Hz, 2H), 4.54-4.67 (m, 6H), 6.97 (d, *J* = 8.4 Hz, 2H), 7.17 (dd, *J* = 7.4, 7.4 Hz, 2H), 7.28-7.32 (m, 6H), 7.38 (s, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 7.6 Hz, 4H). ¹³C NMR δ 18.5, 21.6, 53.4, 54.3, 111.9, 116.3, 120.2, 123.1, 125.1, 125.3, 127.3, 127.7, 129.9, 130.7, 131.3, 132.7, 133.5, 136.6, 137.6, 143.9, 152.0, 155.0. HRMS (FAB, positive) *m/z* Calcd. for $C_{48}H_{38}N_2O_6S_2Na$, 825.2069 ([M+Na]⁺); found, 825.2044 ([M+Na]⁺). [α]_D²⁵ = -96.8 (c 0.05, CHCl₃, 82% ee). Ee was determined by HPLC analysis (eluent: 30% tetrahydrofuran in hexane, flow rate: 0.3 mL/min, retention time: 21.8 min for major isomer and 23.2 min for minor isomer).

4.2.16. Dimethyl-2,2,10,10-tetrakis(methoxycarbonyl)-1,2,3,9,10,11-hexahydrodiindeno[4',5':3,4;4'',5'':7,8]cycloocta[1,2-b:5,6-b']bis(benzofuran) (8b).

Pale yellow solid; mp >300 °C. IR (neat) 1738, 750 cm⁻¹. ¹H NMR δ 2.34 (s, 6H), 3.14 (d, *J* = 17.2 Hz, 2H), 3.53 (d, *J* = 17.2 Hz, 2H), 3.63-3.72 (m, 10H), 3.80 (s, 6H), 7.21-7.34 (m, 8H), 7.45 (d, *J* = 7.8 Hz, 2H). ¹³C NMR δ 18.9, 39.7, 40.9, 53.0, 59.5, 111.5, 120.0, 122.7, 124.4, 125.6, 126.7, 130.9, 130.8, 133.6, 135.9, 140.1, 141.2, 152.7, 154.8, 171.9. HRMS (FAB, positive) *m/z* Calcd. for $C_{44}H_{36}O_{10}Na$, 747.2206 ([M+Na]⁺); found, 747.2207 ([M+Na]⁺). [α]_D²⁵ = -31.6 (c 0.05, CHCl₃, 83% ee). Ee was determined by HPLC analysis (eluent: 30% tetrahydrofuran in hexane, flow rate: 0.3 mL/min, retention time: 14.4 min for major isomer and 15.2 min for minor isomer).

4.2.17. N-[3-(4-Ethynylthiophen-3-yl)prop-2-ynyl]-N-tosylbut-2-yn-1-amine (9a).

Pale yellow solid; mp 65 °C. IR (neat) 3282, 1329, 1163, 899 cm⁻¹. ¹H NMR δ 1.68 (t, *J* = 1.6 Hz, 3H), 2.33 (s, 3H), 3.13 (s, 1H), 4.17 (brs, 2H), 4.40 (s, 2H), 7.18 (d, *J* = 3.2 Hz, 1H), 7.24 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 3.2 Hz, 1H), 7.74 (d, *J* = 8.6 Hz, 2H). ¹³C NMR δ 3.42, 21.4, 36.9, 37.1, 71.6, 77.1, 79.1, 79.4, 81.8, 84.1, 123.6, 124.2, 128.0, 128.5, 129.3, 129.6, 135.3, 143.6. HRMS (FAB, positive) *m/z* Calcd. for $C_{20}H_{17}NO_2S_2Na$, 390.0598 ([M+Na]⁺); found, 390.0602 ([M+Na]⁺).

4.2.18. Dimethyl 2-(but-2-ynyl)-2-[3-(4-ethynylthiophen-3-yl)prop-2-ynyl]malonate (9b).

Brown solid; mp 61 °C. IR (neat) 3276, 1738, 856 cm⁻¹. ¹H NMR δ 1.73 (t, *J* = 2.6 Hz, 3H), 2.94 (q, *J* = 2.6 Hz, 2H), 3.18 (s, 2H), 3.60 (s, 1H), 3.74 (s, 6H), 6.33 (d, *J* = 1.8 Hz, 1H), 7.24 (d, *J* = 1.8 Hz, 1H). ¹³C NMR δ 3.6, 23.2, 23.7, 53.1, 57.0, 73.1, 77.0, 77.4, 79.3, 79.7, 86.6, 123.8, 124.9, 128.3, 129.6, 169.4. HRMS (FAB, positive) *m/z* Calcd. for $C_{18}H_{16}O_4SNa$, 351.0667 ([M+Na]⁺); found, 351.0679 ([M+Na]⁺).

4.2.19. 8,16-Dimethyl-2,10-ditosyl-1,2,3,9,10,11-hexahydro-2,10-diazadiindeno[4',5':3,4;4'',5'':7,8]cycloocta[1,2-c:5,6-c']dithiophene (10a).

Pale yellow solid; mp 224 °C. IR (neat) 1346, 1163, 814 cm⁻¹. ¹H NMR δ 2.17 (s, 6H), 2.40 (s, 6H), 4.24 (d, *J* = 13.8 Hz, 2H), 4.52 (s, 4H), 4.62 (d, *J* = 13.8 Hz, 2H), 6.94 (s, 2H), 6.98 (s, 2H), 7.05 (s, 2H), 7.29 (d, *J* = 7.9 Hz, 4H), 7.72 (d, *J* = 7.9 Hz, 4H). ¹³C NMR δ 17.4, 20.6, 52.4, 53.1, 122.3, 122.4, 126.6, 127.7, 128.9, 129.8, 131.0, 132.6, 134.1, 134.7, 135.8, 137.7, 140.9, 142.8. HRMS (FAB, positive) *m/z* Calcd. for $C_{40}H_{34}N_2O_4S_4Na$, 757.1299 ([M+Na]⁺); found, 757.1277 ([M+Na]⁺). [α]_D²⁵ = 31.1 (c 0.12, CHCl₃, 64% ee). Ee was determined by HPLC analysis (eluent: 50% dichloromethane in hexane, flow rate: 0.3 mL/min, retention time: 21.6 min for minor isomer and 22.7 min for major isomer).

4.2.20. 8,16-Dimethyl-2,2,10,10-tetrakis(methoxycarbonyl)-1,2,3,9,10,11-hexahydrodiindeno[4',5':3,4;4'',5'':7,8]cycloocta[1,2-c:5,6-c']dithiophene (10b).

White solid; mp 260 °C. IR (neat) 1738, 862 cm⁻¹. ¹H NMR δ 2.19 (s, 6H), 3.13 (d, *J* = 6.3 Hz, 2H), 3.52 (s, 4H), 3.65 (s, 6H), 3.74 (d, *J* = 6.3 Hz, 2H), 3.75 (s, 6H), 6.93 (s, 2H), 7.03 (s, 4H). ¹³C NMR δ 18.8, 39.8, 40.8, 53.0, 53.2, 59.8, 122.6, 123.1, 130.0, 130.2, 132.9, 136.3, 138.4, 139.9, 140.0, 143.1, 172.0, 172.4. HRMS (FAB, positive) *m/z* Calcd. for $C_{36}H_{32}O_8S_2Na$, 679.1436 ([M+Na]⁺); found, 679.1423 ([M+Na]⁺). [α]_D²⁵ = 41.6 (c 0.06, CHCl₃, 68% ee). Ee was determined by HPLC analysis (eluent: 50% dichloromethane in hexane, flow rate: 0.3 mL/min, retention time: 11.4 min for minor isomer and 12.5 min for major isomer).

major isomer). The crystal data of racemic **10b**·CH₂Cl₂: C₃₇H₃₄Cl₂O₈S₂, M=741.40, triclinic, space group P-1 (#2), a = 11.6535(2) Å, b = 12.2849(3) Å, c = 13.6729(3) Å, α = 105.3788(8)°, β = 103.4915(8)°, γ = 103.6083(8)°, V = 1740.65(6) Å³, T=173 K, Z=2, μ(Cu-Kα) 32.3205 cm⁻¹; number of reflections measured: total 17833 and unique 6159, R1=0.0662, wR2=0.2313. CCDC 1020470.

4.3. Typical experimental procedure (Table 6)

[Rh(cod)₂]BF₄ (2.0 mg, 0.005 mmol) and diphosphine ligand (0.005 mmol), such as BIPHEP, Cy-BINAP, and QuinoxP*, were placed in a Schlenk tube, which was then evacuated and backfilled with argon (x5). To the reaction vessel was added dichloromethane (1.0 mL). Then it was filled with hydrogen, and the mixture was stirred at ambient temperature for 30 min under a hydrogen atmosphere. After removal of the solvent and hydrogen under the reduced pressure, the reaction vessel was filled with argon. 1,2-Dichloroethane (1.5 mL) was added to the flask and a red solution was prepared. Then, a 1,2-dichloroethane solution (2.5 mL) of triyne **11** (0.05 mmol) was added to the solution and the mixture was stirred at room temperature for 1 h, then at 60 °C for 24 h. After the completion of the reaction, the volatiles were removed under reduced pressure, and the crude products were purified by thin-layer chromatography to give chiral cycloadduct **12**.

4.3.1. *N*-[3-(5-Ethynylthiophen-2-yl)prop-2-ynyl]-*N*-tosylbut-2-yn-1-amine (**11a**).

Brown solid; mp 85 °C. IR (neat) 3273, 1350, 1163, 814 cm⁻¹. ¹H NMR δ 1.70 (s, 3H), 2.40 (s, 3H), 3.36 (s, 1H), 4.10 (s, 2H), 4.40 (s, 2H), 6.84 (d, *J* = 9.4 Hz, 1H), 7.05 (d, *J* = 9.4 Hz, 1H), 7.27 (s, 2H), 7.73 (s, 2H). ¹³C NMR δ 3.6, 21.6, 37.3, 71.6, 76.3, 78.2, 82.3, 86.9, 123.5, 123.9, 128.0, 129.6, 132.1, 132.7, 135.4, 143.9 (A pair of aliphatic peaks overlapped and a pair of alkyne peaks were overlapped). HRMS (FAB, positive) *m/z* Calcd. for C₂₀H₁₇NO₂S₂Na, 390.0598 ([M+Na]⁺); found, 390.0600 ([M+Na]⁺).

4.3.2. Dimethyl 2-(but-2-ynyl)-2-[3-(5-ethynylthiophen-2-yl)prop-2-ynyl]malonate (**11b**).

Pale brown solid; mp 83 °C. IR (neat) 3282, 1739, 808 cm⁻¹. ¹H NMR δ 1.77 (s, 3H), 2.94 (s, 2H), 3.20 (s, 2H), 3.34 (s, 1H), 3.77 (s, 6H), 6.96 (d, *J* = 3.6 Hz, 1H), 7.07 (d, *J* = 3.6 Hz, 1H). ¹³C NMR δ 4.1, 23.9, 24.5, 53.6, 57.6, 73.4, 76.7, 77.0, 80.1, 82.4, 90.0, 123.2, 125.4, 132.0, 133.3, 170.0. HRMS (FAB, positive) *m/z* Calcd. for C₁₈H₁₆O₄SNa, 351.0667 ([M+Na]⁺); found, 351.0661 ([M+Na]⁺).

4.3.3. Hexaheteroarylene **12a**.

Pale yellow solid; mp 256 °C (decomp.). IR (neat) 1352, 1169, 814 cm⁻¹. ¹H NMR δ 2.25 (s, 9H), 2.40 (s, 9H), 4.51 (s, 6H), 4.60 (s, 6H), 6.68 (d, *J* = 3.6 Hz, 3H), 6.75 (d, *J* = 3.6 Hz, 3H), 7.22 (s, 3H), 7.30 (d, *J* = 8.2 Hz, 6H), 7.73 (d, *J* = 8.2 Hz, 6H). ¹³C NMR δ 18.6, 21.6, 53.6, 54.4, 126.7, 127.0, 127.3, 127.6, 130.0, 131.1, 132.7, 133.7, 135.2, 135.3, 137.0, 140.0, 143.1, 143.8. HRMS (FAB, positive) *m/z* Calcd. for C₆₀H₅₁N₃O₆S₆Na, 1124.2000 ([M+Na]⁺); found, 1124.2056 ([M+Na]⁺).

4.3.4. Hexaheteroarylene **12b**.

Pale yellow solid; mp 173 °C (decomp.). IR (neat) 1739, 802 cm⁻¹. ¹H NMR δ 2.30 (s, 9H), 3.53 (s, 6H), 3.60 (s, 6H), 3.74 (s, 18H), 6.78 (s, 6H), 7.18 (s, 3H). ¹³C NMR δ 18.9, 39.8, 41.0, 53.1, 59.6, 126.5, 127.2, 128.1, 130.5, 133.5, 134.7, 138.7, 140.5, 140.6, 143.5, 172.2. HRMS (FAB, positive) *m/z* Calcd. for C₅₄H₄₈O₁₂S₃Na, 1007.2203 ([M+Na]⁺); found, 1007.2206 ([M+Na]⁺).

4.4. Typical experimental procedure (Tables 7 and 8)

[Rh(cod)₂]BF₄ (2.0 mg, 0.005 mmol) and diphosphine ligand (0.005 mmol), such as Cy-BINAP, QuinoxP*, and Cy-SEPHOS, were placed in a Schlenk tube, which was then evacuated and backfilled with argon (x5). To the reaction vessel was added dichloromethane (1.0 mL). Then it was filled with hydrogen, and the mixture was stirred at ambient temperature for 30 min under a hydrogen atmosphere. After removal of the solvent and hydrogen under the reduced pressure, the reaction vessel was filled with argon. 1,2-Dichloroethane (6.5 mL) was added to the flask and a red solution was prepared. Then, a 1,2-dichloroethane solution (1.5 mL) of triyne **14** or **17** (0.05 mmol) was added to the solution and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, the volatiles were removed under reduced pressure, and the crude products were purified by thin-layer chromatography to give cycloadducts **15** and **16**, **18** and **19**, respectively.

4.4.1. *N*-[3-[5-(5-Ethynylthiophen-2-yl)thiophen-2-yl]prop-2-ynyl]-*N*-tosylbut-2-yn-1-amine (**14a**).

Yellow solid; mp 105 °C. IR (neat) 3276, 1352, 1161 cm⁻¹. ¹H NMR δ 1.71 (t, *J* = 2.4 Hz, 3H), 2.40 (s, 3H), 3.42 (s, 1H), 4.11 (q, *J* = 2.4 Hz, 2H), 4.41 (s, 2H), 6.91 (d, *J* = 3.6 Hz, 1H), 6.98 (d, *J* = 4.0 Hz, 1H), 7.00 (d, *J* = 3.6 Hz, 1H), 7.17 (d, *J* = 4.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H). ¹³C NMR δ 3.5, 21.6, 37.2, 37.3, 71.5, 76.6, 78.5, 82.1, 82.7, 87.3, 121.4, 121.6, 123.7, 123.8, 127.9, 129.5, 133.3, 134.0, 135.3, 137.8, 143.8 (A pair of aromatic peaks was overlapped). HRMS (FAB, positive) *m/z* Calcd. for C₂₄H₂₀NO₂S₃Na, 450.0656 ([M+H]⁺); found, 450.0658 ([M+H]⁺).

4.4.2. Dimethyl 2-(but-2-ynyl)-2-[3-[5-(5-ethynylthiophen-2-yl)thiophen-2-yl]prop-2-ynyl]malonate (**14b**).

Yellow solid; mp 87 °C. IR (neat) 3208, 1739, 795 cm⁻¹. ¹H NMR δ 1.78 (t, *J* = 2.4 Hz, 3H), 2.96 (q, *J* = 2.4 Hz, 2H), 3.22 (s, 2H), 3.41 (s, 1H), 3.78 (s, 6H), 6.99-7.02 (m, 3H), 7.16 (d, *J* = 3.6 Hz, 1H). ¹³C NMR δ 3.5, 23.3, 24.0, 53.1, 57.1, 72.8, 76.4, 77.2, 79.4, 82.5, 89.8, 121.1, 122.7, 123.6, 123.9, 132.6, 133.9, 137.1, 169.4 (A pair of aromatic peaks was overlapped). HRMS (FAB, positive) *m/z* Calcd. for C₂₂H₁₉O₄S₂, 411.0725 ([M+H]⁺); found, 411.0745 ([M+H]⁺).

4.4.3. Hexaheteroarylene **15a**.

Pale yellow solid; mp 214 °C (decomp.). IR (neat) 1367, 1161, 795 cm⁻¹. ¹H NMR (DMSO) δ 2.28 (s, 6H), 2.39 (s, 6H), 4.62 (s, 4H), 4.65 (s, 4H), 6.86 (d, *J* = 3.4 Hz, 2H), 6.93 (d, *J* = 4.0 Hz, 2H), 6.99 (d, *J* = 3.4 Hz, 2H), 7.08 (d, *J* = 4.0 Hz, 2H), 7.33 (s, 2H), 7.43 (d, *J* = 8.2 Hz, 4H), 7.80 (d, *J* = 8.2 Hz, 4H). ¹³C NMR (DMSO) δ 18.6, 21.6, 53.6, 54.1, 123.4, 124.0, 127.1, 127.6, 127.7, 128.9, 129.1, 129.5, 129.8, 130.1, 133.3, 133.8, 135.4, 135.8, 135.9, 139.4, 143.9, 146.4. HRMS (FAB, positive) *m/z* Calcd. for C₄₈H₃₈N₂O₄S₆, 898.1156 ([M]⁺); found, 898.1153 ([M]⁺).

4.4.4. Nonaheteroarylene **16a**.

Yellow solid; mp 207 °C (decomp.). IR (neat) 1367, 1161, 795 cm⁻¹. ¹H NMR δ 2.27 (s, 9H), 2.42 (s, 9H), 4.56 (s, 6H), 4.63 (s, 6H), 6.72 (d, *J* = 3.4 Hz, 3H), 6.86 (d, *J* = 3.4 Hz, 3H), 6.95 (d, *J* = 1.3 Hz, 3H), 6.96 (d, *J* = 1.3 Hz, 3H), 7.24 (s, 3H), 7.33 (d, *J* = 8.6 Hz, 6H), 7.75 (d, *J* = 8.6 Hz, 6H). ¹³C NMR δ 14.2, 22.8, 53.6, 124.1, 125.7, 127.5, 127.7, 127.9, 129.6, 129.9, 130.3, 131.1, 133.1, 133.8, 134.4, 135.0, 135.3, 137.3, 138.7, 140.4, 143.8 (A pair of aliphatic peaks was overlapped). HRMS (FAB, positive) *m/z* Calcd. for C₇₂H₅₇N₃O₆S₉, 1347.1734 ([M]⁺); found, 1347.1688 ([M]⁺).

4.4.5. Hexaheteroarylene **15b**.

Pale yellow solid; mp 186 °C (decomp.). IR (neat) 1739, 802 cm^{-1} . ^1H NMR δ 2.34 (s, 6H), 3.64 (s, 4H), 3.72 (s, 4H), 3.77 (s, 12H), 6.76 (d, $J = 3.2$ Hz, 2H), 6.84 (d, $J = 3.2$ Hz, 2H), 6.86 (d, $J = 3.2$ Hz, 2H), 6.90 (d, $J = 3.2$ Hz, 2H), 7.23 (s, 2H). ^{13}C NMR δ 19.0, 39.9, 40.8, 53.1, 59.6, 122.9, 123.5, 128.3, 128.7, 129.3, 134.2, 135.0, 138.8, 139.2, 139.5, 139.8, 144.3, 147.2, 172.1 (A pair of aromatic peaks was overlapped). HRMS (FAB, positive) m/z Calcd. for $\text{C}_{44}\text{H}_{36}\text{O}_8\text{S}_4$, 820.1293 ($[\text{M}]^+$); found, 820.1278 ($[\text{M}]^+$).

4.4.6. Nonaheteroarylene **16b**.

Pale yellow solid; mp 168 °C. IR (neat) 1739, 795 cm^{-1} . ^1H NMR δ 2.31 (s, 9H), 3.57 (s, 6H), 3.61 (s, 6H), 3.75 (s, 18H), 6.79 (d, $J = 4.0$ Hz, 3H), 6.86 (d, $J = 3.6$ Hz, 3H), 6.95 (d, $J = 4.0$ Hz, 3H), 6.97 (d, $J = 3.6$ Hz, 3H), 7.19 (s, 3H). ^{13}C NMR δ 19.0, 39.8, 41.0, 53.3, 59.6, 123.2, 123.6, 127.0, 127.4, 129.3, 130.1, 130.5, 134.1, 134.3, 138.3, 138.5, 138.9, 140.8, 141.7, 172.1. HRMS (FAB, positive) m/z Calcd. for $\text{C}_{66}\text{H}_{54}\text{O}_{12}\text{S}_6$, 1230.1940 ($[\text{M}]^+$); found, 1230.1937 ($[\text{M}]^+$).

4.4.7. *N*-(3-{5-[5-(5-Ethynylthiophen-2-yl)thiophen-2-yl]thiophen-2-yl}prop-2-ynyl)-*N*-tosylbut-2-yn-1-amine (**17a**).

Pale brown solid; mp 138 °C. IR (neat) 3276, 1352, 1165 cm^{-1} . ^1H NMR δ 1.71 (t, $J = 2.6$ Hz, 3H), 2.41 (s, 3H), 3.42 (s, 1H), 4.11 (q, $J = 2.6$ Hz, 2H), 4.42 (s, 2H), 6.91 (d, $J = 4.0$ Hz, 1H), 6.97 (d, $J = 4.0$ Hz, 1H), 7.02 (d, $J = 4.0$ Hz, 1H), 7.05 (d, $J = 4.0$ Hz, 1H), 7.08 (d, $J = 4.0$ Hz, 1H), 7.18 (d, $J = 4.0$ Hz, 1H), 7.30 (d, $J = 8.0$ Hz, 2H), 7.75 (d, $J = 8.0$ Hz, 2H). ^{13}C NMR δ 3.5, 21.6, 37.2, 37.3, 71.5, 78.6, 82.1, 82.6, 87.2, 121.0, 121.1, 123.3, 123.4, 124.8, 125.0, 127.9, 129.5, 133.3, 134.0, 135.3, 135.9, 135.9, 138.2, 138.4, 143.7 (A pair of alkyne peaks was overlapped). HRMS (ESI, positive) m/z Calcd. for $\text{C}_{28}\text{H}_{21}\text{NO}_2\text{S}_4\text{Na}$, 554.0353 ($[\text{M}+\text{Na}]^+$); found, 554.0359 ($[\text{M}+\text{Na}]^+$).

4.4.8. Dimethyl 2-(but-2-ynyl)-2-(3-{5-[5-(5-Ethynylthiophen-2-yl)thiophen-2-yl]thiophen-2-yl}prop-2-ynyl)malonate (**17b**).

Pale brown solid; mp 104 °C. IR (neat) 3276, 1742, 795 cm^{-1} . ^1H NMR δ 1.78 (t, $J = 2.5$ Hz, 3H), 2.96 (q, $J = 2.5$ Hz, 2H), 3.23 (s, 2H), 3.42 (s, 1H), 6.99 (s, 6H), 6.99 (d, $J = 4.0$ Hz, 1H), 7.01-7.03 (m, 2H), 7.04 (d, $J = 3.6$ Hz, 1H), 7.07 (d, $J = 4.0$ Hz, 1H), 7.17 (d, $J = 4.0$ Hz, 1H). ^{13}C NMR δ 3.5, 23.3, 24.0, 53.1, 57.1, 72.8, 76.5, 76.8, 79.4, 82.5, 89.8, 120.8, 122.2, 123.3, 123.4, 124.7, 125.0, 132.7, 134.0, 135.6, 136.3, 137.5, 138.6, 169.4. HRMS (FAB, positive) m/z Calcd. for $\text{C}_{26}\text{H}_{20}\text{O}_4\text{S}_3\text{Na}$, 515.0421 ($[\text{M}+\text{Na}]^+$); found, 515.0401 ($[\text{M}+\text{Na}]^+$).

4.4.9. Nonaheteroarylene **18a**.

Yellow solid; mp 256 °C (decomp.). IR (neat) 1367, 1163 cm^{-1} . ^1H NMR δ 2.26 (s, 6H), 2.41 (s, 6H), 4.58 (s, 4H), 4.64 (s, 4H), 6.79 (d, $J = 3.4$ Hz, 2H), 6.82 (d, $J = 3.4$ Hz, 2H), 6.88 (d, $J = 3.4$ Hz, 2H), 6.91 (d, $J = 3.4$ Hz, 2H), 6.95 (d, $J = 3.7$ Hz, 2H), 7.04 (d, $J = 3.7$ Hz, 2H), 7.22 (s, 2H), 7.32 (d, $J = 7.9$ Hz, 4H), 7.75 (d, $J = 7.9$ Hz, 4H). ^{13}C NMR δ 19.5, 22.9, 53.5, 53.6, 110.0, 110.2, 111.6, 117.5, 123.7, 127.8, 128.7, 129.5, 130.1, 132.0, 133.8, 134.0, 138.9, 139.0, 142.9, 143.9 (Six pairs of aromatic peaks were overlapped). HRMS (MALDI, positive) m/z Calcd. for $\text{C}_{56}\text{H}_{42}\text{N}_2\text{O}_4\text{S}_8$, 1062.0905 ($[\text{M}]^+$); found, 1062.0904 ($[\text{M}]^+$).

4.4.10. Dodecaheteroarylene **19a**.

Yellow solid; mp 245 °C (decomp.). IR (neat) 1360, 1157, 798 cm^{-1} . ^1H NMR δ 2.27 (s, 9H), 2.42 (s, 9H), 4.58 (s, 6H), 4.64 (s, 6H), 6.81 (d, $J = 4.0$ Hz, 3H), 6.83 (d, $J = 4.0$ Hz, 3H), 6.89 (d, $J = 4.0$ Hz, 3H), 6.92 (d, $J = 4.0$ Hz, 3H), 6.96 (d, $J =$

4.0 Hz, 3H), 7.06 (d, $J = 4.0$ Hz, 3H), 7.33 (d, $J = 8.0$ Hz, 6H), 7.76 (d, $J = 8.0$ Hz, 6H). ^{13}C NMR δ 18.7, 21.6, 53.6, 54.3, 119.7, 120.2, 123.2, 123.3, 123.4, 124.0, 125.0, 125.5, 127.6, 127.8, 130.0, 133.1, 133.1, 134.4, 134.7, 135.4, 138.6, 139.0, 143.8, 144.8, 149.8, 151.9. HRMS (MALDI, positive) m/z Calcd. for $\text{C}_{84}\text{H}_{63}\text{N}_3\text{O}_6\text{S}_{12}$, 1593.1360 ($[\text{M}]^+$); found, 1593.1363 ($[\text{M}]^+$).

4.4.11. Nonaheteroarylene **18b**.

Orange solid; mp >300 °C. IR (neat) 1734, 798 cm^{-1} . ^1H NMR δ 2.34 (s, 6H), 3.64 (s, 8H), 3.77 (s, 12H), 6.83 (d, $J = 3.6$ Hz, 2H), 6.95 (d, $J = 3.6$ Hz, 2H), 7.00 (d, $J = 3.6$ Hz, 2H), 7.03 (d, $J = 3.6$ Hz, 2H), 7.05 (d, $J = 3.6$ Hz, 2H), 7.08 (d, $J = 3.6$ Hz, 2H), 7.36 (s, 2H). ^{13}C NMR δ 19.1, 39.9, 40.9, 53.3, 59.6, 121.7, 122.1, 123.1, 124.8, 125.3, 126.2, 126.8, 127.2, 128.4, 130.0, 134.4, 134.6, 135.9, 138.3, 138.6, 140.5, 140.8, 142.2, 172.1. HRMS (FAB, positive) m/z Calcd. for $\text{C}_{52}\text{H}_{40}\text{O}_8\text{S}_6$, 984.1047 ($[\text{M}]^+$); found, 984.1047 ($[\text{M}]^+$).

4.4.12. Dodecaheteroarylene **19b**.

Orange solid; mp 117 °C. IR (neat) 1734, 795 cm^{-1} . ^1H NMR δ 2.32 (s, 9H), 3.58 (s, 6H), 3.61 (s, 6H), 3.75 (s, 18H), 6.83 (d, $J = 4.0$ Hz, 3H), 6.86 (d, $J = 3.4$ Hz, 3H), 6.88 (d, $J = 3.4$ Hz, 3H), 6.91 (d, $J = 3.4$ Hz, 3H), 6.95 (d, $J = 4.0$ Hz, 3H), 7.06 (d, $J = 3.4$ Hz, 3H), 7.21 (s, 3H). ^{13}C NMR δ 19.0, 39.8, 41.0, 53.1, 59.6, 123.1, 123.2, 124.1, 124.1, 127.5, 128.9, 130.2, 133.8, 133.9, 134.2, 135.8, 136.0, 138.2, 138.6, 139.0, 140.8, 141.7, 172.1 (A pair of aromatic peaks was overlapped). HRMS (FAB, positive) m/z Calcd. for $\text{C}_{78}\text{H}_{60}\text{O}_{12}\text{S}_9$, 1476.1571 ($[\text{M}]^+$); found, 1476.1554 ($[\text{M}]^+$).

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Synthesis of macrocyclic heteroarylenes by consecutive inter- and intramolecular cycloadditions of thiophene-tethered triynes

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