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Iridium-catalyzed consecutive and enantioselective [2+2+2] cycloaddition of tetraynes and hexaynes for the construction of an axially chiral biaryl system

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Abstract

A chiral iridium complex catalyzed a consecutive and enantioselective [2+2+2] cycloaddition of polyynes to give axially chiral compounds. Intermolecular reaction of tetraynes, possessing aryl groups on their termini, with protected but-2-yne-1,4-diols gave C_2-symmetrical quateraryl compounds. Intramolecular reaction of hexaynes, possessing aryl or alkyl groups on their termini gave C_2-symmetrical biaryl compounds. The catalytic synthesis of a pentacene derivative with axial chiralities is also discussed.

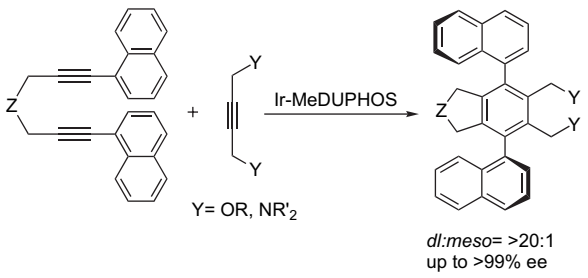
Keywords: Iridium; Enantioselective; Cycloaddition; Axial chirality; Biaryls

1. Introduction

In 2004, the transition metal-catalyzed [2+2+2] cycloaddition took a leap into a new dimension of organic synthesis: enantioselective [2+2+2] cycloaddition along with the generation of axial chirality was achieved by three groups, including ours, using chiral Co, Ir, and Rh catalysts, respectively.[1]

In 1948, Ni-mediated cyclooligomerization of acetylene was reported, where benzene was detected as a [2+2+2] cycloadduct.[2] In 1967, Co-mediated cyclotrimerization of diphenylacetylene was disclosed, which should be recognized as the first practical example of [2+2+2] cycloaddition for the synthesis of substituted benzenes.[3] Comprehensive research of Co-catalyzed reaction of various alkynes and nitriles drastically increased the synthetic value.[4] Today, [2+2+2] cycloaddition is the most atom-economical and reliable protocol for the synthesis of substituted aromatic rings using various transition metal catalysts.[5] However, the examples of enantioselective [2+2+2] cycloaddition of alkynes for the synthesis of chiral cyclic compounds have been limited: Ni-catalyzed enantiotopic-group-selective reaction of triynes with acetylene was reported in 1999, where a chiral center was generated at the benzylic position of the formed benzene ring.[6] Ni-catalyzed enantioselective intramolecular cycloaddition of triynes was another example, where a helically chiral compound was enantioselectively obtained.[7]

Against this background, we designed the enantioselective [2+2+2] cycloaddition of 1,6-diynes, having naphthyl groups on their termini, and a monoalkyne possessing heteroatoms at its propargylic positions, which give C_2-symmetrical teraryl compounds with two axial chiralities (Eq. 1). We found that Ir-Me-DUPHOS catalyst promoted the [2+2+2] cycloaddition



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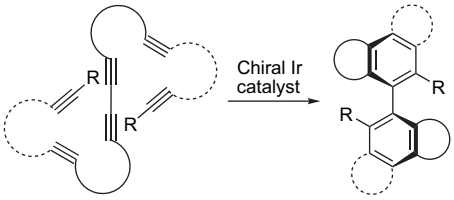
of highly congested substrates and that almost perfect diastereo- and enantioselectivities could be attained.[1b,8a]

We applied the reaction to sequential [2+2+2] cycloaddition of polyynes, which have two or four 1,6-diyne moieties with naphthalene spacer(s)[8b] and to intramolecular reaction of 1,6,11-triynes for the synthesis of *ortho*-diarylbenzene derivatives.[8c] In all these examples, axial chiralities were generated between aryl substituents on the alkyne termini of substrates and the formed benzene ring(s). This manuscript discloses Ir-catalyzed enantioselective inter- and intramolecular [2+2+2] cycloaddition of tetraynes and hexaynes, possessing a 1,3-diyne moiety, respectively, where an axial chirality is generated between the consecutively formed two benzene rings (Scheme 1).[9]



Scheme 1. Construction of axially chiral biaryls by consecutive [2+2+2] cycloaddition.

2. Results and discussion

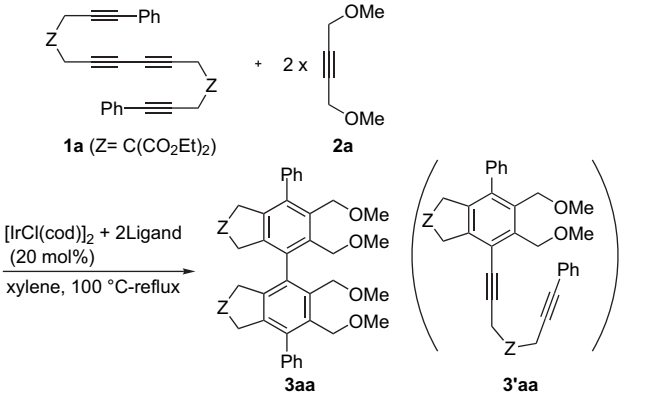
2.1. Intermolecular [2+2+2] cycloaddition of tetraynes and monoalkynes

We chose carbon-tethered tetrayne **1a** as a model substrate and examined the reaction with 1,4-dimethoxybut-2-yne (**2a**) using chiral iridium catalysts, which were in situ prepared from $[IrCl(cod)]_2$ and chiral diphosphine ligands (Table 1). When Me-DUPHOS was used, tetrayne **1a** was completely consumed at 100 °C and the desired quateraryl product **3aa** was obtained in moderate ee; however, mono-cyclized product **3′aa** remained even after a prolonged reaction time, and the yield of **3aa** was low (entry 1). Bulkier DUPHOS ligands did not improve yield nor ee in refluxed xylene (entries 2 and 3). In the case of BINAP, the formation of quateraryl product **3aa** could not be detected (entry 4). BDPP achieved moderate yield and ee in the reaction of a 1,6-diyne with monoalkyne **2a**,[1b] but it did not succeed in the consecutive [2+2+2] cycloaddition (entry 5). In contrast, CHIRAPHOS was a favorable ligand: the yield was good by complete consumption of diyne **3′aa**, and the ee was comparable with Me-DUPHOS (entry 6).

We next examined a protecting group of but-2-yne-1,4-diol as a monoalkyne: in place of methyl, a bulkier TBS (*tert*-butyldimethylsilyl) group apparently improved the enantioselectivity, and ee reached almost 90% (Eq. 2).[10]

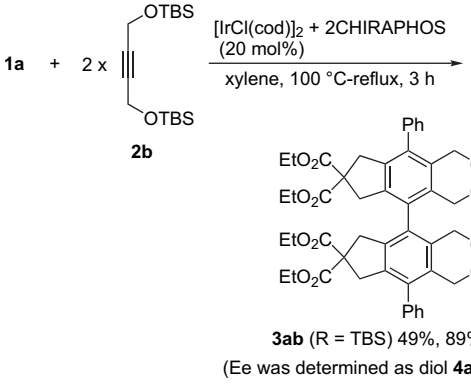
In the presence of in situ prepared Ir-CHIRAPHOS catalyst, nitrogen-tethered tetrayne **1b** was submitted to the consecutive [2+2+2] cycloaddition with TBS-protected diol **2b** in 1,2-dimethoxyethane because tetrayne **1b** was hardly soluble in xylene. The reaction proceeded even at room temperature and C_2-symmetrical quateraryl **3bb** was obtained in moderate yield along with the formation of mono-cyclized

Table 1
Screening of various chiral diphosphine ligands for the intermolecular consecutive [2+2+2] cycloaddition of tetrayne **1a**



Entry[a]	Ligand[b]	Time (h)	Yield of **3aa** (%)	ee (%)
1[c]	Me-DUPHOS	2	33	63
2	Et-DUPHOS	2	23	23
3	*i*-Pr-DUPHOS	3	24	7
4	BINAP	2	—	—
5	BDPP	6	14	<2
6	CHIRAPHOS	2	85	58

[a] Tetrayne **1a**/monoalkyne **2a**=1:6.
[b] (*S*)- and (*S*,*S*)-Isomers were used. Me-DUPHOS: 1,2-bis(2,5-dimethylphospholano)benzene, Et-DUPHOS: 1,2-bis(2,5-diethylphospholano)benzene, *i*-Pr-DUPHOS: 1,2-bis(2,5-diisopropylphospholano)benzene, BINAP: 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl, BDPP: 2,4-bis(diphenylphosphino)-pentane, CHIRAPHOS: 2,3-bis(diphenylphosphino)butane.
[c] The reaction was examined at 100 °C.



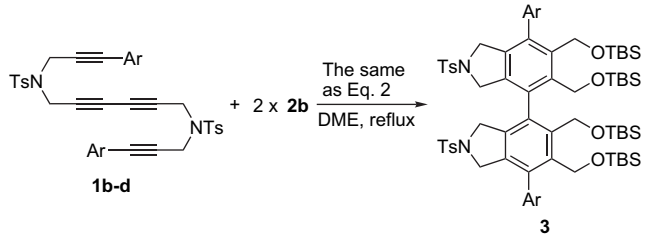
3ab (R = TBS) 49%, 89% ee
(Ee was determined as diol **4ab** (R = H))

(2)

product, but ee was low (Table 2, entry 1). When the reaction was examined under reflux conditions, both yield and ee were dramatically improved (entry 2). Tetraynes **1c** and **1d**, possessing electron-withdrawing and -donating groups on aryl substituents of alkyne termini, respectively, were also good substrates, and the corresponding axially chiral compounds **3cb** and **3db** were obtained with ee comparable with that of **3bb** (entries 3 and 4). Also in the case of nitrogen-tethered tetrayne, a bulky protecting group for the but-2-yne-1,4-diol is important for high enantioselectivity and the ee of cycloadduct of tetrayne **1d** with monoalkyne **2a** was moderate (entry 5).

In order to investigate the role of the bulky TBS group in the present enantioselective [2+2+2] cycloaddition, the reaction of two mono-cyclized diynes was examined under the

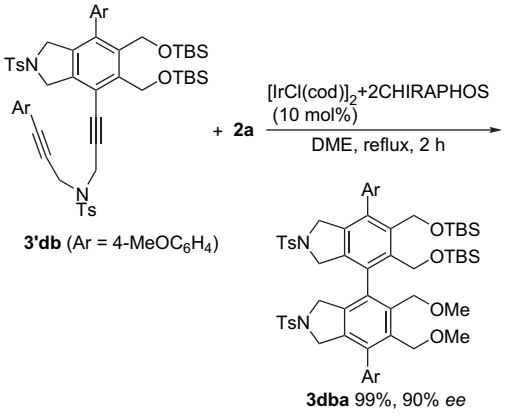
Table 2
Consecutive intermolecular [2+2+2] cycloaddition of nitrogen-tethered tetraynes



Entry[a]	Ar	Tetrayne	Time (h)	Yield (%)	ee (%)[b]
1[c]	C_6H_5	**1b**	2	41 (**3bb**)	37
2	C_6H_5	**1b**	1	76 (**3bb**)	86
3	4-BrC_6H_4	**1c**	1	89 (**3cb**)	82
4	4-$MeOC_6H_4$	**1d**	1	59 (**3db**)	86
5[d]	4-$MeOC_6H_4$	**1d**	1	86 (**3da**)	44

[a] Tetrayne **1a**/monoalkyne **2**=1:6.
[b] Except entry 5, the ee was determined as diols **4bb**–**db** after deprotection of TBS group.
[c] The reaction was examined at room temperature.
[d] Monoalkyne **2a** was used in place of **2b**.

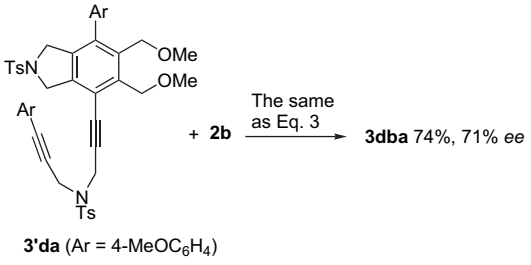
same reaction conditions: when mono-cyclized diyne **3′db**, which was prepared from tetrayne **1d** and TBS-protected diol **2b**, was submitted to the reaction with methoxy-protected diol **2a**, unsymmetrical quateraryl product **3dba** was obtained in high ee, which is almost comparable with that of **3db** (entry 4 in Table 2) (Eq. 3). On the other hand, the reaction of mono-cyclized diyne **3′da**, which was prepared from tetrayne **1d** and Me-protected diol **2a**, gave the same product **3dba** in lower ee, however, which is much higher than that of **3da** (entry 5 in Table 2) (Eq. 4). These results imply that the bulkiness of the first alkyne determined the asymmetric induction of axial chirality regardless of the second alkyne, but that the second alkyne also influenced it to some extent.



(3)

2.2. Intramolecular [2+2+2] cycloaddition of hexaynes

We next investigated the intramolecular [2+2+2] cycloaddition of hexaynes possessing a 1,3-diyne moiety. There are various types of cyclotrimerization of alkynes including inter- and intramolecular reaction; however, there is only one

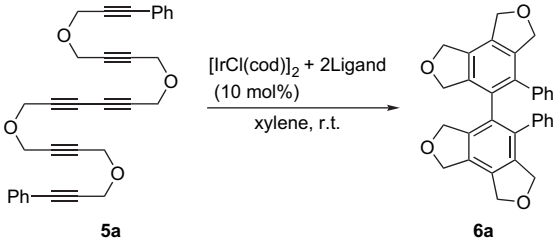


(4)

example of intramolecular consecutive cycloaddition of hexaynes for the construction of biaryl systems, as far as we know.[11] In the presence of in situ prepared chiral iridium catalyst, oxygen-tethered hexayne **5a** was examined (Table 3). Ir-Me-DUPHOS catalyst gave a complex mixture at room temperature (entry 1). In the case of Ir-CHIRAPHOS, hexayne **5a** was completely consumed within 15 min, and biaryl **6a** was obtained in low yield with low ee (entry 2). BDPP was a better ligand, and moderate yield and ee was achieved (entry 3). Different from intermolecular consecutive [2+2+2] cycloaddition of tetraynes, BINAP was a preferable ligand for the intramolecular reaction (entry 4). Bulkier BINAP derivatives gave better results and xylylBINAP induced excellent enantioselectivity (entries 5 and 6).

Under the best reaction conditions (Table 3, entry 6), we examined an intramolecular consecutive [2+2+2] cycloaddition of various hexaynes (Table 4). Electron-withdrawing and -donating groups on aryl substituents of alkyne termini were tolerated, and the corresponding doubly cyclized products **6b** and **6c** were obtained in excellent ee (entries 1 and 2). Nitrogen-tethered hexayne **5d** was also transformed into biaryl **6d** with excellent ee yet in moderate yield because of the formation of unidentified byproducts (entry 3). In the case of methyl-substituted hexayne **5e**, doubly cyclized product **6e** was formed but was difficult to be isolated from a complex mixture, and ee was very low. Introduction of an

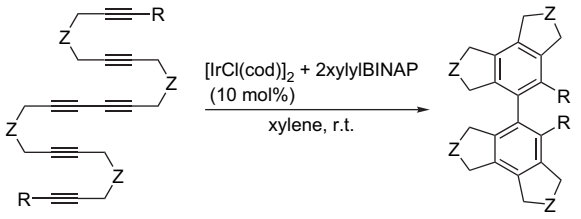
Table 3
Screening of various chiral diphosphine ligands for the consecutive intramolecular [2+2+2] cycloaddition of hexayne **5a**



Entry	Ligand[a]	Time (min)	Yield of **5a** (%)	ee (%)
1	Me-DUPHOS	120	—	—
2	CHIRAPHOS	15	17	32
3	BDPP	15	54	53
4	BINAP	15	53	85
5	tolBINAP	15	62	95
6	xylylBINAP	15	81	97

[a] (*S*)- and (*S*,*S*)-Isomers were used. tolBINAP: 2,2′-bis(di-*p*-tolylphosphino)-1,1′-binaphthyl, xylylBINAP: 2,2′-bis(di(3,5-xylyl)phosphino)-1,1′-binaphthyl.

Table 4
Consecutive intramolecular [2+2+2] cycloaddition of various hexaynes, possessing oxygen or nitrogen-tether



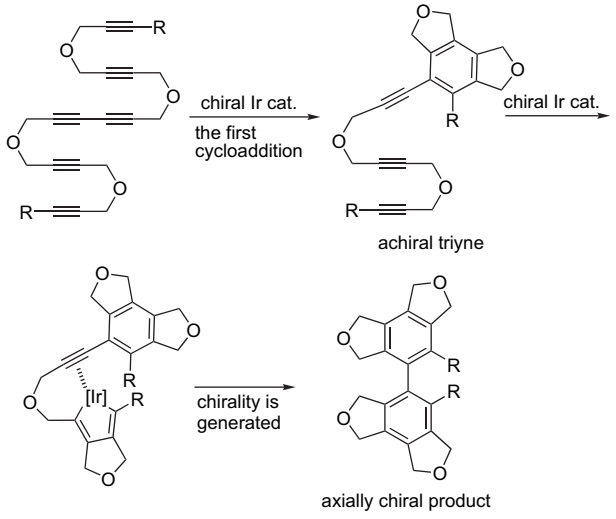
5 6

Entry	Z	R	Hexayne	Time (h)	Yield (%)	ee (%)
1	O	4-BrC_6H_4	**5b**	0.25	66 (**6b**)	98
2	O	4-$MeOC_6H_4$	**5c**	0.25	78 (**6c**)	97
3[a]	NTs	Ph	**5d**	24	52 (**6d**)	98
4	O	Me	**5e**	24	ca. 40 (**6e**)	<10
5	O	*i*-Pr	**5f**	3	69 (**6f**)	96

[a] The reaction was examined at 40 °C.

isopropyl group drastically improved the enantioselectivity, and biaryl **6f** was obtained in acceptable yield (entry 6).

A possible reaction scheme of hexaynes is depicted in Scheme 2. The first cycloaddition of the triyne moiety of the hexayne gives achiral triyne. The following oxidative coupling would occur at the less bulky diyne moiety, which is distant from the formed benzene ring. At the next step of intramolecular reaction of the metallacyclopentadiene and the alkyne moiety, the steric repulsion between substituents on alkyne termini of the hexayne and the chiral ligand on the metal center would be important for high enantioselectivity.



Scheme 2. Possible reaction scheme of the intramolecular consecutive [2+2+2] cycloaddition.

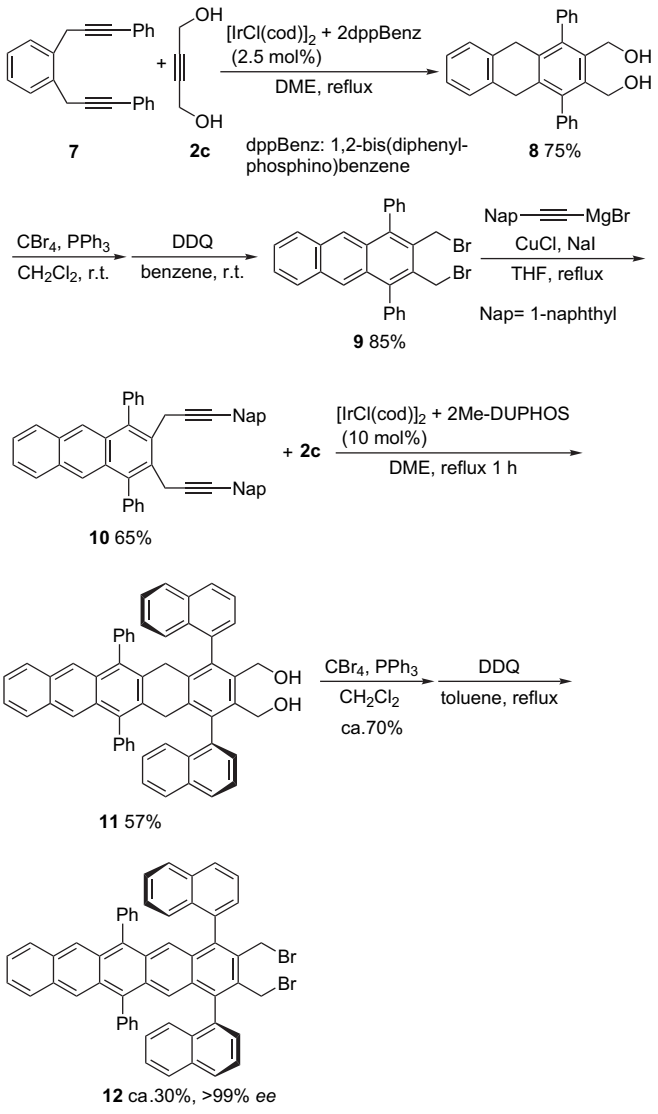
2.3. Ir-catalyzed [2+2+2] cycloaddition as a key step in the synthesis of a chiral pentacene derivative

Acenes are organic materials with high field effect mobility, and, in particular, pentacene is recognized as the most promising candidate for application on organic thin-film transistors.[12] Tahakashi has comprehensively studied the synthesis of substituted pentacenes by the homologation method, where Zr-mediated [2+2+2] cycloaddition of diynes and monoalkynes is a key step.[13]

In order to make the best use of Ir-catalyzed enantioselective [2+2+2] cycloaddition, we examined the asymmetric synthesis of a multi-substituted pentacene (Scheme 3). Ir-catalyzed [2+2+2] cycloaddition of diyne **7**[14] with diol **2c** proceeded efficiently, and the following dibromination and oxidation gave anthracene derivative **9**. Dialkynylation of dibromide **9** using (1-naphthyl)ethynylmagnesium bromide gave diyne **10** and enantioselective [2+2+2] cycloaddition with diol **2c** was examined by Ir-Me-DUPHOS catalyst.[1b] The following dibromination and aromatization gave axially chiral C_2-symmetrical pentacene **12** with excellent ee.

3. Conclusion

In summary, we have developed inter- and intramolecular consecutive [2+2+2] cycloaddition, where axial chirality



Scheme 3. The catalytic synthesis of an axially chiral pentacene derivative.

was enantiomerically generated between the newly formed benzene rings. Ir-CHIRAPHOS and -xylylBINAP were efficient catalyst for the reaction of tetraynes with monoalkyne and hexaynes, respectively. We also demonstrated the first asymmetric synthesis of a substituted pentacene using Ir-catalyzed enantioselective [2+2+2] cycloaddition.

4. Experimental

4.1. General

Anhydrous xylene and 1,2-dimethoxyethane are commercially available. They were dried over molecular sieves 4 Å (MS 4 Å) and degassed by argon bubbling before use. All reactions were examined under an argon atmosphere. IR spectra were recorded with Horiba FT730 spectrophotometer. NMR spectra were measured with JEOL AL-400 and Lambda500 spectrometers using tetramethylsilane as an internal standard and $CDCl_3$ as a solvent. Mass spectra were measured with JEOL JMS-SX102A and elemental analyses with Perkin–Elmer PE2400II. Optical rotation was measured with Jasco DIP-1000 polarimeter.

4.2. Typical experimental procedure for intermolecular reaction of tetraynes with monoalkyne (Eq. 2)

Preparation of tetraynes **1a**: the propargylation of diethyl 2-(3-phenylprop-2-ynyl)malonate using propargyl bromide gave diethyl 1-diphenylhepta-1,6-diyne-4,4-dicarboxylate. The oxidative homo-coupling of the diyne using a stoichiometric amount of CuCl–TMEDA complex in MeOH under the aerobic conditions at room temperature gave tetrayne **1a**.

$[IrCl(cod)]_2$ (6.7 mg, 0.01 mmol) and (*S*,*S*)-CHIRAPHOS (8.5 mg, 0.02 mmol) were stirred in xylene (1.0 mL) at room temperature to give a reddish solution. Tetrayne **1a** (31.1 mg, 0.05 mmol) and monoalkyne **2b** (94.4 mg, 0.30 mmol) in xylene (3.0 mL) were added to the solution, and the mixture was stirred at 100 °C for 1 h, then under reflux conditions for 2 h. The solvent was removed under reduced pressure, and the crude products were purified by thin layer chromatography to give pure quateraryl **3ab**.

4.2.1. Tetraethyl 1,14-diphenyltetradeca-1,6,8,13-tetrayne-4,4,11,11-tetracarboxylate (*1a*)

White solid; mp 66 °C; IR (CH_2Cl_2) 1738, 1207, 758 cm^{-1}; ^1H NMR δ=1.27 (t, *J*=7.2 Hz, 12H), 3.12 (s, 4H), 3.17 (s, 4H), 4.25 (q, *J*=7.2 Hz, 8H), 7.27–7.28 (m, 6H), 7.35–7.37 (m, 4H); ^{13}C NMR δ=14.0, 23.6, 23.7, 56.7, 62.1, 68.0, 72.4, 83.7, 83.8, 122.9, 128.0, 128.2, 131.6, 168.5; HRMS (FAB) for M+H found *m/z* 623.2638, calcd for $C_{38}H_{39}O_8$: 623.2645. Anal. Calcd for $C_{38}H_{38}O_8$: C, 73.29; H, 6.15. Found: C, 73.04; H, 5.86.

4.2.2. N^1,N^6-Ditosyl-N^1,N^6-bis(3-phenylprop-2-ynyl) hexa-2,4-diyne-1,6-diamine (*1b*)

Pale yellow solid; mp 127 °C (decomp.); IR (CH_2Cl_2) 1352, 1163, 756 cm^{-1}; ^1H NMR δ=2.36 (s, 6H), 4.25 (s, 4H), 4.34 (s, 4H), 7.16–7.18 (m, 4H), 7.27–7.28 (m, 10H), 7.72–7.74 (m, 4H); ^{13}C NMR δ=21.5, 37.2, 37.6, 69.5, 71.8, 80.9, 86.2, 121.9, 127.9, 128.2, 128.6, 129.6, 131.6, 134.9, 144.2; HRMS (FAB) for M–H found *m/z* 643.1753, calcd for $C_{38}H_{31}N_2O_4S_2$: 643.1725.

4.2.3. N^1,N^6-Bis(3-(4-bromophenyl)prop-2-ynyl)-N^1,N^6-ditosylhexa-2,4-diyne-1,6-diamine (*1c*)

White solid; mp 142 °C (decomp.); IR (CH_2Cl_2) 1352, 1163, 661 cm^{-1}; ^1H NMR δ=2.37 (s, 6H), 4.23 (s, 4H), 4.32 (s, 4H), 7.02 (d, *J*=8.2 Hz, 4H), 7.28 (d, *J*=8.2 Hz, 4H), 7.36–7.41 (m, 4H), 7.73 (d, *J*=8.4 Hz, 4H); ^{13}C NMR δ=21.5, 37.3, 37.5, 69.5, 71.8, 82.2, 85.1, 120.8, 122.9, 127.9, 129.6, 131.4, 133.0, 134.9, 144.2; HRMS (FAB) for M+H found *m/z* 801.0108, calcd for $C_{38}H_{31}N_2O_4S_2^{79}Br_2$: 801.0092.

4.2.4. N^1,N^6-Ditosyl-N^1,N^6-bis(3-(4-methoxyphenyl)prop-2-ynyl)hexa-2,4-diyne-1,6-diamine (*1d*)

Pale yellow solid; mp 132 °C (decomp.); IR (CH_2Cl_2) 1350, 1248, 1163, 669 cm^{-1}; ^1H NMR δ=2.37 (s, 6H), 3.79 (s, 6H), 4.24 (s, 4H), 4.32 (s, 4H), 6.78 (d, *J*=8.6 Hz, 4H), 7.12 (d, *J*=8.6 Hz, 4H), 7.28 (d, *J*=8.0 Hz, 4H), 7.73 (d, *J*=8.0 Hz, 4H); ^{13}C NMR δ=21.5, 37.2, 37.6, 55.3, 69.4, 71.8, 79.5, 86.2, 113.9, 127.9, 129.5, 129.6, 133.1, 134.9, 144.1, 159.8; HRMS (FAB) for M+H found *m/z* 705.2125, calcd for $C_{40}H_{37}N_2O_6S_2$: 705.2093.

4.2.5. 7,7′-Diphenyl-2,2,2′,2′-tetrakis(ethoxycarbonyl)-5,6,5′,6′-tetrakis(methoxymethyl)-2,3,2′,3′-tetrahydro-1H,1′H-4,4′-biindenyl (*3aa*)

Yellow oil; IR (neat) 2919, 1348, 1162, 906 cm^{-1}; ^1H NMR δ=1.16 (d, *J*=2.4 Hz, 4H), 1.18 (d, *J*=2.4 Hz, 4H), 1.20 (d, *J*=2.4 Hz, 4H), 3.13 (s, 6H), 3.19 (s, 6H), 3.32 (d, *J*=16.8 Hz, 4H), 3.42 (d, *J*=16.8 Hz, 4H), 4.08–4.20 (m, 12H), 4.24 (d, *J*=10.0 Hz, 2H), 4.33 (d, *J*=10.0 Hz, 2H), 7.26–7.45 (m, 10H); ^{13}C NMR δ=13.9, 40.4, 40.8, 58.0, 58.7, 59.6, 61.4, 69.0, 69.5, 127.0, 128.0, 129.3, 129.5, 134.2, 135.2, 135.7, 139.0, 139.3, 139.6, 171.5, 171.6 (two signals in the aliphatic region were overlapped); HRMS (FAB) for M+Na found *m/z* 873.3820, calcd for $C_{50}H_{58}O_{12}Na$: 873.3826. $[\alpha]_D^{29.0}$ 8.96 (*c* 0.71, $CHCl_3$, 58% ee). The enantiomeric excess was determined by HPLC analysis using a chiral column (Daicel Chiralpak IA: 4×250 mm, 254 nm UV detector, rt, eluent: 3%, 2-propanol in hexane, flow rate: 0.5 mL/min, retention time: 11 min for major isomer and 13 min for minor isomer).

4.2.6. 5,6,5′,6′-Tetrakis(tert-butyldimethylsilyloxymethyl)-7,7′-diphenyl-2,2,2′,2′-tetrakis(ethoxycarbonyl)-2,3,2′,3′-tetrahydro-1H,1′H-4,4′-biindenyl (*3ab*)

White solid; mp 195 °C; IR (CH_2Cl_2) 1734, 1255, 1068, 835 cm^{-1}; ^1H NMR δ=−0.21 (s, 12H), −0.18 (s, 6H), −0.14 (s, 6H), 0.78 (s, 18H), 0.82 (s, 18H), 1.16–1.19 (m, 12H), 3.21 (d, *J*=6.2 Hz, 2H), 3.26 (d, *J*=6.2 Hz, 2H), 3.35 (d, *J*=8.6 Hz, 2H), 3.39 (d, *J*=8.6 Hz, 2H), 4.06–4.14 (m, 8H), 4.40 (d, *J*=10.4 Hz, 2H), 4.51 (d, *J*=10.6 Hz, 2H), 4.56 (d, *J*=10.4 Hz, 2H), 4.61 (d, *J*=10.6 Hz, 2H), 7.25–7.26 (m, 2H), 7.35–7.41 (m, 8H); ^{13}C NMR δ=−6.0, −5.8, −5.7–5.6, 13.9, 14.0, 18.2,

18.2, 25.9, 26.0, 40.2, 40.7, 59.3, 59.6, 59.6, 61.3, 61.4, 126.9, 128.0, 128.1, 129.3, 129.8, 135.5, 136.6, 138.8, 139.0, 139.7, 171.4, 171.8; HRMS (FAB) for M−H found *m/z* 1249.6686, calcd for $C_{70}H_{105}O_{12}Si_4$: 1249.6683. $[\alpha]_D^{26}$ 34.3 (*c* 1.04, $CHCl_3$).

*4.2.7. 7,7′-Diphenyl-2,2,2′,2′-tetrakis(ethoxycarbonyl)-5,6,5′,6′-tetrakis(hydroxymethyl)-2,3,2′,3′-tetrahydro-1H,1′H-4,4′-biindenyl (**4ab**)*

Colorless oil; IR (neat) 2927, 1731, 1248, 706 cm^{-1}; ^1H NMR δ=1.16−1.22 (m, 12H), 3.26 (d, *J*=17.2 Hz, 2H), 3.53 (d, *J*=17.2 Hz, 2H), 3.65 (br s, 2H), 4.12−4.13 (m, 12H), 4.23 (d, *J*=14.0 Hz, 2H), 4.51 (d, *J*=11.6 Hz, 2H), 4.63 (d, *J*=14.0 Hz, 2H), 4.71 (d, *J*=11.6 Hz, 2H), 4.94 (br s, 2H), 7.27−7.30 (m, 2H), 7.41−7.49 (m, 8H); ^{13}C NMR δ=40.3, 40.8, 59.5, 60.0, 60.4, 61.7, 61.8, 127.4, 128.4, 128.6, 129.2, 129.2, 134.6, 137.7, 138.7, 139.0, 139.2, 171.2, 171.5; HRMS (FAB) for M+H found *m/z* 795.3350, calcd for $C_{46}H_{51}O_{12}$: 795.3381. $[\alpha]_D^{26}$ −45.4 (*c* 0.34, $CHCl_3$, 89% ee). The enantiomeric excess was determined by HPLC analysis using a chiral column (Daicel Chiralpak IA: 4×250 mm, 254 nm UV detector, rt, eluent: 15%, 2-propanol in hexane, flow rate: 1.0 mL/min, retention time: 15 min for minor isomer and 17 min for major isomer).

*4.2.8. 5,6,5′,6′-Tetrakis(tert-butyldimethylsilyloxymethyl)-7,7′-diphenyl-2,2′-ditosyl-4,4′-biisoindolinyl (**3bb**)*

Colorless oil; IR (neat) 1354, 1255, 1165, 1066, 837 cm^{-1}; ^1H NMR δ=−0.28 (s, 6H), −0.26 (s, 6H), −0.19 (s, 6H), −0.15 (s, 6H), 0.72 (s, 18H), 0.81 (s, 18H), 2.41 (s, 6H), 4.18 (d, *J*=13.2 Hz, 2H), 4.27−4.44 (m, 10H), 4.53 (d, *J*=10.4 Hz, 2H), 4.57 (d, *J*=10.4 Hz, 2H), 7.18 (s, 2H), 7.31 (d, *J*=8.0 Hz, 4H), 7.36−7.48 (m, 8H), 7.64 (d, *J*=8.0 Hz, 4H); ^{13}C NMR δ=−6.2, −5.9, −5.8, −5.6, 18.1, 18.2, 21.5, 25.8, 25.8, 54.1, 54.5, 58.8, 59.2, 127.3, 127.6, 128.5, 128.7, 129.2, 129.9, 133.2, 134.1, 134.7, 135.1, 137.6, 137.8, 138.2, 143.6; HRMS (FAB) for M−H found *m/z* 1271.5886, calcd for $C_{70}H_{99}N_2O_8Si_4S_2$: 1271.5920. $[\alpha]_D^{27}$ 17.8 (*c* 2.22, $CHCl_3$).

*4.2.9. 7,7′-Diphenyl-2,2′-ditosyl-5,6,5′,6′-tetrakis-(hydroxymethyl)-4,4′-biisoindolinyl (**4bb**)*

White solid; mp 225 °C (decomp.); IR (CH_2Cl_2) 3336, 1348, 1163, 1016, 667 cm^{-1}; ^1H NMR δ=2.42 (s, 6H), 3.53 (br s, 2H), 4.01−4.04 (m, 2H), 4.14 (d, *J*=13.8 Hz, 2H), 4.21 (d, *J*=13.8 Hz, 2H), 4.31 (d, *J*=14.0 Hz, 2H), 4.45−4.49 (m, 4H), 4.55−4.58 (m, 2H), 4.70 (d, *J*=11.2 Hz, 2H), 4.97 (br s, 2H), 7.22 (d, *J*=8.0 Hz, 2H), 7.32−7.37 (m, 6H), 7.43−7.51 (m, 6H), 7.62 (d, *J*=8.0 Hz, 4H); ^{13}C NMR δ=21.5, 54.2, 54.2, 57.0, 60.0, 127.2, 128.1, 128.5, 128.9, 130.0, 132.2, 133.5, 134.4, 136.0, 137.3, 138.5, 138.7, 138.8, 144.1; HRMS (FAB) for M+H found *m/z* 817.2609, calcd for $C_{46}H_{45}N_2O_8S_2$: 817.2617. $[\alpha]_D^{24}$ −37.1 (*c* 1.37, $CHCl_3$, 86% ee). The enantiomeric excess was determined by HPLC analysis using a chiral column (Daicel Chiralpak IB: 4×250 mm, 254 nm UV detector, rt, eluent: 40%, 2-propanol in hexane, flow rate: 1.0 mL/min, retention time: 8 min for minor isomer and 11 min for major isomer).

*4.2.10. 7,7′-Bis(4-bromophenyl)-5,6,5′,6′-tetrakis(tert-butyldimethylsilyloxymethyl)-2,2′-ditosyl-4,4′-biisoindolinyl (**3cb**)*

Pale yellow solid; mp 240 °C (decomp.); IR (CH_2Cl_2) 1354, 1255, 1165, 1068, 837 cm^{-1}; ^1H NMR δ=−0.29 (s, 6H), −0.27 (s, 6H), −0.15 (s, 6H), −0.11 (s, 6H), 0.71 (s, 18H), 0.82 (s, 18H), 2.41 (s, 6H), 4.16 (d, *J*=14.0 Hz, 2H), 4.25−4.41 (m, 10H), 4.49 (d, *J*=10.6 Hz, 2H), 4.55 (d, *J*=10.6 Hz, 2H), 7.07 (d, *J*=8.2 Hz, 2H), 7.26−7.33 (m, 6H), 7.57 (d, *J*=8.2 Hz, 2H), 7.63−7.65 (m, 6H); ^{13}C NMR δ=−6.2, −5.9, −5.7, −5.6, 18.0, 18.2, 21.5, 25.7, 25.8, 53.9, 54.4, 58.7, 59.1, 121.9, 127.3, 129.9, 130.4, 130.9, 131.7, 133.4, 133.9, 134.9, 135.1, 137.0, 137.6, 137.8, 143.7; HRMS (FAB) for M+H found *m/z* 1429.4292, calcd for $C_{70}H_{99}N_2O_8Si_4S_2^{79}Br_2$: 1429.4287. $[\alpha]_D^{23}$ 3.3 (*c* 1.28, $CHCl_3$).

*4.2.11. 7,7′-Bis(4-bromophenyl)-2,2′-ditosyl-5,6,5′,6′-tetrakis(hydroxymethyl)-4,4′-biisoindolinyl (**4cb**)*

White solid; mp 182 °C; IR (CH_2Cl_2) 3307, 1344, 1162, 669 cm^{-1}; ^1H NMR δ=2.42 (s, 6H), 3.69 (br s, 2H), 4.00 (d, *J*=12.4 Hz, 2H), 4.10−4.29 (m, 6H), 4.39−4.46 (m, 4H), 4.54 (d, *J*=12.0 Hz, 2H), 4.68 (d, *J*=12.0 Hz, 2H), 4.96 (br s, 2H), 7.10−7.12 (m, 2H), 7.24−7.26 (m, 2H), 7.32 (m, 4H), 7.61−7.65 (m, 8H); ^{13}C NMR δ=21.6, 54.0, 54.1, 58.9, 60.0, 122.5, 127.2, 128.3, 130.1, 130.2, 130.6, 132.0, 132.1, 132.4, 133.4, 134.6, 135.9, 136.1, 137.3, 138.7, 138.8, 144.2; HRMS (FAB) for M+H found *m/z* 973.0825, calcd for $C_{46}H_{43}N_2O_8S_2^{79}Br_2$: 973.0828. $[\alpha]_D^{23}$ −47.5 (*c* 1.39, $CHCl_3$, 82% ee). The enantiomeric excess was determined by HPLC analysis using a chiral column (Daicel Chiralpak IB: 4×250 mm, 254 nm UV detector, rt, eluent: 40%, 2-propanol in hexane, flow rate: 1.0 mL/min, retention time: 7 min for minor isomer and 10 min for major isomer).

*4.2.12. 5,6,5′,6′-Tetrakis(tert-butyldimethylsilyloxymethyl)-2,2′-ditosyl-7,7′-bis(4-methoxyphenyl)-4,4′-biisoindolinyl (**3db**)*

Dark yellow solid; mp 234 °C; IR (CH_2Cl_2) 1352, 1250, 1164, 1064, 836 cm^{-1}; ^1H NMR δ=−0.30 (s, 6H), −0.27 (s, 6H), −0.15 (s, 6H), −0.11 (s, 6H), 0.71 (s, 18H), 0.82 (s, 18H), 2.40 (s, 6H), 3.90 (s, 6H), 4.17 (d, *J*=12.4 Hz, 2H), 4.26−4.45 (m, 10H), 4.50−4.58 (m, 4H), 6.95 (d, *J*=8.4 Hz, 2H), 7.01 (d, *J*=8.0 Hz, 2H), 7.11 (d, *J*=8.4 Hz, 2H), 7.26−7.32 (m, 6H), 7.64 (d, *J*=8.4 Hz, 4H); ^{13}C NMR δ=−6.2, −5.9, −5.7, −5.5, 18.1, 18.2, 21.5, 25.8, 25.8, 54.2, 54.5, 55.4, 58.9, 59.2, 113.6, 114.0, 127.3, 129.9, 130.4, 133.1, 134.1, 134.6, 135.5, 137.6, 137.8, 138.1, 143.6, 159.0; HRMS (FAB) for M−H found *m/z* 1331.6147, calcd for $C_{72}H_{103}N_2O_{10}Si_4S_2$: 1331.6131. $[\alpha]_D^{23}$ 8.3 (*c* 0.78, $CHCl_3$).

*4.2.13. 2,2′-Ditosyl-5,6,5′,6′-tetrakis(hydroxymethyl)-7,7′-bis(4-methoxyphenyl)-4,4′-biisoindolinyl (**4db**)*

White solid; mp 174 °C; IR (CH_2Cl_2) 3311, 1346, 1248, 1161, 1016, 669 cm^{-1}; ^1H NMR δ=2.42 (s, 6H), 3.60 (br s, 2H), 3.89 (s, 6H), 4.00 (d, *J*=12.5 Hz, 2H), 4.12 (d, *J*=14.2 Hz, 2H), 4.20 (d, *J*=14.2 Hz, 2H), 4.32 (d, *J*=14.0 Hz, 2H), 4.47−4.55 (m, 6H), 4.68 (d, *J*=11.5 Hz, 2H), 5.05 (br

s, 2H), 7.00–7.02 (m, 4H), 7.13–7.15 (m, 2H), 7.26–7.39 (m, 6H), 7.62 (d, J=8.5 Hz, 4H); ^{13}C NMR δ=21.5, 54.3, 55.4, 59.0, 60.0, 114.3, 127.2, 128.3, 129.7, 130.0, 132.0, 133.6, 134.3, 136.3, 138.3, 138.7, 139.0, 144.1, 159.4; HRMS (FAB) for M−H found m/z 875.2682, calcd for $C_{48}H_{47}N_2O_{10}S_2$: 875.2672. $[\alpha]_D^{23}$ −47.7 (c 1.21, $CHCl_3$, 86% ee). The enantiomeric excess was determined by HPLC analysis using a chiral column (Daicel Chiralpak IB: 4×250 mm, 254 nm UV detector, rt, eluent: 40%, 2-propanol in hexane, flow rate: 1.0 mL/min, retention time: 10 min for minor isomer and 21 min for major isomer).

4.2.14. 2,2′-Ditosyl-5,6,5′,6′-tetrakis(methoxymethyl)-7,7′-bis(4-methoxyphenyl)-4,4′-biisoindolinyl (**3da**)

Yellow oil; IR (neat) 1247, 1162 cm^{-1}; ^{1}H NMR δ=1.68 (s, 6H), 2.41 (s, 6H), 2.29 (s, 6H), 3.21 (s, 6H), 3.90 (s, 6H), 3.98 (d, J=10.2 Hz, 2H), 4.10 (d, J=5.4 Hz, 2H), 4.12 (d, J=9.0 Hz, 2H), 4.14 (d, J=9.0 Hz, 2H), 4.32 (d, J=10.2 Hz, 4H), 4.34 (d, J=5.4 Hz, 2H), 4.44 (d, J=12.2 Hz, 2H), 4.47 (d, J=12.2 Hz, 2H), 6.98 (d, J=8.4 Hz, 2H), 7.01 (d, J=8.4 Hz, 2H), 7.20 (d, J=8.2 Hz, 2H), 7.25 (d, J=8.2 Hz, 2H), 7.31 (d, J=8.0 Hz, 4H), 7.64 (d, J=8.0 Hz, 4H); ^{13}C NMR δ=21.5, 54.2, 55.3, 58.2, 58.6, 68.5, 69.0, 113.7, 113.9, 127.4, 129.8, 129.9, 133.1, 133.7, 135.3, 135.7, 135.8, 136.1, 138.6, 143.6, 159.1; HRMS (FAB) for M−H found m/z 931.3270, calcd for $C_{52}H_{56}N_2O_{10}S_2$: 931.3298. $[\alpha]_D^{24}$ 2.94 (c 3.16, $CHCl_3$, 44% ee). The enantiomeric excess was determined by HPLC analysis using a chiral column (Daicel Chiralpak IA: 4×250 mm, 254 nm UV detector, rt, eluent: 20%, 2-propanol in hexane, flow rate: 0.5 mL/min, retention time: 18 min for minor isomer and 19 min for major isomer).

4.2.15. 5,6-Bis(tert-butyldimethylsilyloxymethyl)-7-(4-methoxyphenyl)-4-(7-(4-methoxyphenyl)-4-tosyl-4-azahept-1,6-diynyl)-2-tosylisoindoline (**3′db**)

Colorless oil; IR (neat) 1249, 1164, 835 cm^{-1}; ^{1}H NMR δ=−0.18 (s, 6H), 0.00 (s, 6H), 0.75 (s, 9H), 0.79 (s, 9H), 2.23 (s, 3H), 2.30 (s, 3H), 3.72 (s, 3H), 3.79 (s, 3H), 4.23 (s, 2H), 4.36 (s, 2H), 4.39 (s, 2H), 4.43 (s, 4H), 4.82 (s, 2H), 6.71 (d, J=8.6 Hz, 2H), 6.84 (d, J=8.6 Hz, 2H), 7.01 (d, J=8.6 Hz, 2H), 7.08 (d, J=8.6 Hz, 2H), 7.17 (d, J=7.6 Hz, 4H), 7.58 (d, J=8.0 Hz, 2H), 7.70 (d, J=8.0 Hz, 2H); ^{13}C NMR δ=−5.6, −5.1, 18.2, 21.4, 25.8, 37.4, 54.4, 55.4, 58.7, 60.5, 79.6, 81.5, 86.2, 89.6, 113.8, 114.1, 116.9, 127.5, 127.9, 129.7, 129.8, 129.9, 133.2, 133.6, 135.2, 135.3, 138.1, 138.5, 141.7, 143.7, 144.0, 159.2, 159.8 (four signals in the aliphatic region and three signals in the aromatic region were overlapped); HRMS (FAB) for M−H found m/z 1017.4001, calcd for $C_{56}H_{69}N_2O_8Si_2S_2$: 1017.4034.

4.2.16. 5,6-Bis(methoxymethyl)-7-(4-methoxyphenyl)-4-(7-(4-methoxyphenyl)-4-tosyl-4-azahept-1,6-diynyl)-2-tosylisoindoline (**3′da**)

Yellow oil; IR (neat) 1247, 1162 cm^{-1}; ^{1}H NMR δ=2.26 (s, 3H), 2.32 (s, 3H), 3.12 (s, 3H), 3.31 (s, 3H), 3.73 (s, 3H), 3.80 (s, 3H), 4.09 (s, 2H), 4.26 (s, 2H), 4.39 (s, 2H), 4.42 (s, 2H), 4.49 (s, 2H), 4.52 (s, 2H), 6.72 (d, J=8.9 Hz, 2H), 6.87 (d, J=8.9 Hz, 2H), 7.00 (d, J=8.9 Hz, 2H), 7.08 (d, J=8.9 Hz, 2H), 7.20 (d, J=7.8 Hz, 2H), 7.20 (d, J=7.8 Hz, 2H), 7.61 (d, J=8.3 Hz, 2H), 7.71 (d, J=8.3 Hz, 2H); ^{13}C NMR δ=21.5, 37.4, 54.4, 55.3, 58.3, 58.7, 68.1, 68.3, 79.6, 81.1, 86.5, 89.9, 113.9, 114.1, 117.8, 127.5, 127.9, 129.5, 129.7, 129.9, 133.2, 133.5, 135.1, 135.7, 135.8, 138.8, 139.0, 139.4, 143.8, 144.1, 159.2, 159.3, 159.8 (four signals in the aliphatic region and a signal in the aromatic region were overlapped); HRMS (FAB) for M+H found m/z 819.2775, calcd for $C_{46}H_{47}N_2O_8S_2$: 819.2774.

4.2.17. 5′,6′-Bis(tert-butyldimethylsilyloxymethyl)-2,2′-ditosyl-5,6-bis(methoxymethyl)-7,7′-bis(4-methoxyphenyl)-4,4′-biisoindolinyl (**3dba**)

Colorless oil; IR (neat) 1348, 1247, 1162, 1095, 835 cm^{-1}; ^{1}H NMR δ=−0.18 (s, 3H), −0.12 (s, 3H), −0.04 (s, 3H), 0.00 (s, 3H), 0.83 (s, 9H), 0.92 (s, 9H), 2.5 (d, J=6.3 Hz, 6H), 3.05 (s, 3H), 3.29 (s, 3H), 4.0 (s, 6H), 4.15–4.72 (m, 16H), 7.06–7.43 (m, 12H), 7.74 (d, J=8.3 Hz, 4H); ^{13}C NMR δ=−6.2, −6.0, −5.6, −5.5, 18.0, 18.2, 21.5, 25.8, 25.8, 54.2, 54.5, 55.3, 55.4, 58.2, 58.6, 59.2, 69.1, 113.7, 114.0, 127.2, 127.5, 129.8, 129.9, 130.2, 130.3, 130.5, 132.7, 133.5, 133.9, 134.4, 135.3, 135.8, 136.1, 137.9, 138.2, 138.4, 143.5, 143.8, 159.1 (five signals in the aliphatic region and six signals in the aromatic region were overlapped); HRMS (FAB) for M−H found m/z 1131.4725, calcd for $C_{62}H_{79}N_2O_{10}Si_2S_2$: 1131.4715. $[\alpha]_D^{31}$ 3.12 (c 0.81, C_6H_6, 90% ee). The enantiomeric excess was determined by HPLC analysis using a chiral column (Daicel Chiralpak IA: 4×250 mm, 254 nm UV detector, rt, eluent: 10% 2-propanol in hexane, flow rate: 1.0 mL/min, retention time: 9 min for minor isomer and 11 min for major isomer).

4.3. Typical experimental procedure for intramolecular reaction of hexaynes (Table 3, entry 6)

Preparation of hexayne **5a**: mono-etherification of but-2-yne-1,4-diol using 3-bromo-1-phenylprop-1-yne gave 4-(3-phenylprop-2-ynyloxy)but-2-yn-1-ol.[15] The following etherification using propargyl bromide gave 1-(3-phenylprop-2-ynyloxy)-4-(prop-2-ynyloxy)but-2-yne. The oxidative homo-coupling of the triyne using a stoichiometric amount of CuCl–TMEDA complex in MeOH under the aerobic conditions at room temperature gave hexayne **5a**.

[IrCl(cod)]$_2$ (10.8 mg, 0.016 mmol) and (*S*)-xylylBINAP (23.6 mg, 0.032 mmol) were stirred in xylene (1.7 mL) at room temperature to give a reddish solution. Hexayne **5a** (76.0 mg, 0.16 mmol) in xylene (4.8 mL) was added to the solution and the mixture was stirred at room temperature. The solvent was removed under reduced pressure, and the crude products were purified by column chromatography using Florisil to give pure cycloadduct **6a**.

4.3.1. 1,6-Bis(4-(3-phenylprop-2-ynyloxy)but-2-ynyloxy)-hexa-2,4-diyne (**5a**)

Yellow oil; IR (neat) 1070, 757 cm^{-1}; ^{1}H NMR δ=4.32 (s, 4H), 4.34 (s, 4H), 4.37 (s, 4H), 4.47 (s, 4H), 7.31–7.33 (m, 6H), 7.44–7.46 (m, 4H); ^{13}C NMR δ=56.7, 56.9, 57.0,

57.4, 70.8, 74.7, 81.7, 82.7, 84.1, 86.9, 122.4, 128.3, 128.6, 131.8; HRMS (FAB) for M+Na found *m/z* 497.1732, calcd for $C_{32}H_{26}O_4Na$: 497.1831.

*4.3.2. 1,6-Bis(4-(3-(4-bromophenyl)prop-2-ynyloxy)-but-2-ynyloxy)hexa-2,4-diyne (**5b**)*

Yellow oil; IR (neat) 1070, 823 cm^{-1}; ^1H NMR δ=4.31 (t, *J*=1.7 Hz, 4H), 4.34 (s, 4H), 4.36 (t, *J*=1.7 Hz, 4H), 4.45 (s, 4H), 7.31 (d, *J*=8.5 Hz, 4H), 7.45 (t, *J*=8.5 Hz, 4H); ^{13}C NMR δ=56.9, 56.9, 57.0, 57.3, 70.8, 74.7, 81.8, 82.5, 85.3, 85.8, 121.3, 122.9, 131.6, 133.2; HRMS (FAB) for M+Na found *m/z* 652.9933, calcd for $C_{32}H_{24}O_4Na^{79}Br_2$:652.9939.

*4.3.3. 1,6-Bis(4-(3-(4-methoxyphenyl)prop-2-ynyloxy)-but-2-ynyloxy)hexa-2,4-diyne (**5c**)*

Yellow oil; IR (neat) 2848, 1064, 831 cm^{-1}; ^1H NMR δ=3.81 (s, 6H), 4.32 (s, 4H), 4.34 (s, 4H), 4.36 (s, 4H), 4.46 (s, 4H), 6.84 (d, *J*=8.4 Hz, 4H), 7.39 (d, *J*=8.4 Hz, 4H); ^{13}C NMR δ=55.2, 56.6, 56.9, 56.9, 57.5, 70.7, 74.7, 81.6, 82.6, 82.7, 86.8, 113.9, 114.4, 133.2, 159.7; HRMS (FAB) for M+Na found *m/z* 557.1947, calcd for $C_{34}H_{30}O_6Na$: 557.1940.

*4.3.4. N^1,N^6-Bis(4-(N-(3-phenylprop-2-ynyl)-N-tosylamino)-but-2-ynyl)-N^1,N^6-ditosylhexa-2,4-diyne-1,6-diamine (**5d**)*

White solid; mp 69 °C, IR (CH_2Cl_2) 1350, 1163, 661 cm^{-1}; ^1H NMR δ=2.36 (s, 6H), 2.42 (s, 6H), 4.02 (s, 8H), 4.08 (s, 4H), 4.21 (s, 4H), 7.13 (d, *J*=6.8 Hz, 4H), 7.42–7.31 (m, 14H), 7.65 (d, *J*=8.3 Hz, 4H), 7.70 (d, *J*=8.3 Hz, 4H); ^{13}C NMR δ=21.5, 21.6, 36.5, 36.7, 36.9, 37.2, 69.4, 71.7, 76.7, 79.1, 81.0, 86.0, 127.7, 27.8, 128.2, 128.6, 129.6, 129.7, 129.7, 131.5, 134.8, 135.1, 144.1, 144.4; HRMS (FAB) for M+H found *m/z* 1087.2938, calcd for $C_{60}H_{55}N_4O_8S_4$: 1087.2903.

*4.3.5. 1,6-Bis(4-(but-2-ynyloxy)but-2-ynyloxy)-hexa-2,4-diyne (**5e**)*

Yellow oil; IR (neat) 2854, 1070 cm^{-1}; ^1H NMR δ=1.87 (s, 6H), 4.20 (s, 2H), 4.21 (s, 2H), 4.29 (s, 4H), 4.30 (s, 4H), 4.33 (s, 4H); ^{13}C NMR δ=3.6, 56.5, 56.9, 57.0, 57.2, 70.8, 74.2, 74.7, 81.4, 82.8, 83.3; HRMS (FAB) for M+H found *m/z* 351.1598, calcd for $C_{22}H_{23}O_4$: 351.1596.

*4.3.6. 1,6-Bis(4-(4-methylpent-2-ynyloxy)but-2-ynyloxy)hexa-2,4-diyne (**5f**)*

Yellow oil; IR (neat) 2854, 1074 cm^{-1}; ^1H NMR δ=1.18 (d, *J*=6.8 Hz, 12H), 2.58–2.61 (m, 2H), 4.22 (s, 4H), 4.28 (s, 4H), 4.30 (s, 4H), 4.33 (s, 4H); ^{13}C NMR δ=20.4, 22.7, 56.3, 56.8, 56.9, 57.1, 70.7, 74.0, 74.6, 81.3, 82.8, 93.1; HRMS (FAB) for M+H found *m/z* 407.2221, calcd for $C_{26}H_{31}O_4$: 407.2222.

*4.3.7. 5,5′-Diphenyl-1,3,6,8,1′,3′,6′,8′-octahydro-4,4′-bi(2,7-dioxa-as-indacenyl) (**6a**)*

Yellow oil; IR (neat) 1060, 752 cm^{-1}; ^1H NMR δ=4.61 (d, *J*=12.5 Hz, 2H), 4.89 (d, *J*=13.1 Hz, 2H), 4.92 (d, *J*=12.5 Hz, 2H), 4.97 (d, *J*=13.1 Hz, 2H), 5.03 (d, *J*=12.7 Hz, 2H), 5.08 (d, *J*=12.7 Hz, 2H), 5.12 (s, 4H), 6.49 (d, *J*=7.31 Hz, 4H), 7.07–7.18 (m, 6H); ^{13}C NMR δ=72.6, 72.8, 73.6, 74.0, 127.1, 127.7, 128.8, 130.0, 131.0, 132.0, 134.1, 137.6, 138.8, 139.1; HRMS (FAB) for M−H found *m/z* 473.1753, calcd for $C_{32}H_{25}O_4$: 473.1753. $[\alpha]_D^{26.7}$ −23.8 (*c* 1.58, $CHCl_3$, 97% ee). The enantiomeric excess was determined by HPLC analysis using a chiral column (Daicel Chiralpak AD: 4×250 mm, 254 nm UV detector, rt, eluent: 20%, 2-propanol in hexane, flow rate: 1.0 mL/min, retention time: 15 min for major isomer and 22 min for minor isomer).

*4.3.8. 5,5′-Bis(4-bromophenyl)-1,3,6,8,1′,3′,6′,8′-octahydro-4,4′-bi(2,7-dioxa-as-indacenyl) (**6b**)*

Yellow oil; IR (neat) 1047, 734 cm^{-1}; ^1H NMR δ=4.59 (d, *J*=12.7 Hz, 2H), 4.85 (d, *J*=12.7 Hz, 2H), 4.93 (d, *J*=12.5 Hz, 2H), 4.96 (d, *J*=12.5 Hz, 2H), 5.03 (d, *J*=13.3 Hz, 2H), 5.10 (d, *J*=13.3 Hz, 2H), 5.12 (s, 4H), 6.37 (d, *J*=8.2 Hz, 4H), 7.25 (d, *J*=8.2 Hz, 4H); ^{13}C NMR δ=72.6, 72.8, 73.3, 73.9, 121.4, 129.5, 130.4, 131.1, 131.6, 132.5, 132.7, 136.4, 138.9, 139.3; HRMS (FAB) for M−H found *m/z* 628.9969, calcd for $C_{32}H_{23}O_4^{79}Br_2$: 628.9963. $[\alpha]_D^{39.8}$ 26.4 (*c* 0.81, $CHCl_3$, 98% ee). The enantiomeric excess was determined by HPLC analysis using a chiral column (Daicel Chiralpak AD: 4×250 mm, 254 nm UV detector, rt, eluent: 20%, 2-propanol in hexane, flow rate: 1.0 mL/min, retention time: 12 min for major isomer and 16 min for minor isomer).

*4.3.9. 5,5′-Bis(4-methoxyphenyl)-1,3,6,8,1′,3′,6′,8′-octahydro-4,4′-bi(2,7-dioxa-as-indacenyl) (**6c**)*

Yellow oil; IR (neat) 2850, 1245, 734 cm^{-1}; ^1H NMR δ=3.78 (s, 6H), 4.66 (d, *J*=12.4 Hz, 2H), 4.83 (d, *J*=12.2 Hz, 2H), 4.93 (d, *J*=12.4 Hz, 2H), 4.93 (d, *J*=12.2 Hz, 2H), 5.03 (d, *J*=13.3 Hz, 2H), 5.08 (d, *J*=13.3 Hz, 2H), 5.10 (s, 4H), 6.47 (d, *J*=8.5 Hz, 4H), 6.64 (d, *J*=8.5 Hz, 4H); ^{13}C NMR δ=55.1, 72.7, 72.8, 73.6, 74.0, 113.1, 129.9, 129.9, 130.2, 130.6, 131.8, 133.8, 138.9, 139.0, 158.4; HRMS (FAB) for M found *m/z* 534.2020, calcd for $C_{34}H_{30}O_6$: 534.2042. $[\alpha]_D^{37.3}$ 13.3 (*c* 0.66, $CHCl_3$, 97% ee). The enantiomeric excess was determined by HPLC analysis using a chiral column (Daicel Chiralpak IB: 4×250 mm, 254 nm UV detector, rt, eluent: 20%, 2-propanol in hexane, flow rate: 1.0 mL/min, retention time: 13 min for minor isomer and 20 min for major isomer).

*4.3.10. 5,5′-Diphenyl-2,7-ditosyl-1,3,6,8,1′,3′,6′,8′-octahydro-4,4′-bi(2,7-diaza-as-indacenyl) (**6d**)*

White solid; mp 180 °C; IR (CH_2Cl_2) 1346, 1165, 667 cm^{-1}; ^1H NMR δ=2.41 (s, 6H), 2.47 (s, 6H), 3.91 (d, *J*=14.3 Hz, 2H), 4.13 (d, *J*=14.3 Hz, 2H), 4.20 (d, *J*=14.3 Hz, 2H), 4.34 (d, *J*=13.6 Hz, 2H), 4.37 (d, *J*=13.6 Hz, 2H), 4.49 (s, 4H), 4.53 (d, *J*=14.3 Hz, 2H), 6.20 (d, *J*=7.50 Hz, 4H), 6.98 (dd, *J*=7.5, 7.5 Hz, 4H), 7.15 (dd, *J*=7.5, 7.5 Hz, 2H), 7.31 (d, *J*=8.0 Hz, 4H), 7.39 (d, *J*=8.0 Hz, 4H), 7.66 (d, *J*=8.0 Hz, 4H), 7.70 (d, *J*=8.0 Hz, 4H); ^{13}C NMR δ=21.6, 52.4, 52.7, 53.3, 54.3, 127.4, 127.5, 127.7, 128.0, 128.4, 129.7, 130.0, 130.2, 130.9, 131.1, 133.0, 133.5, 135.7, 135.9, 136.1, 136.4, 143.9, 144.4 (a signal in the aliphatic region was overlapped); HRMS (FAB) for M+H found *m/z* 1087.2896, calcd for $C_{60}H_{55}N_4O_8S_4$: 1087.2903.

$[\alpha]_D^{22.6}$ −46.7 (*c* 1.04, $CHCl_3$, 98% ee). The enantiomeric excess was determined by HPLC analysis using a chiral column (Daicel Chiralpak IA: 4×250 mm, 254 nm UV detector, rt, eluent: 50%, CH_2Cl_2 in hexane, flow rate: 1.0 mL/min, retention time: 12 min for major isomer and 15 min for minor isomer).

*4.3.11. 5,5′-Dimethyl-1,3,6,8,1′,3′,6′,8′-octahydro-4,4′-bi(2,7-dioxa-as-indacenyl) (**6e**)*

White solid; mp 272 °C (decomp.); IR (CH_2Cl_2) 2844, 1045 cm^{-1}; ^1H NMR δ=1.89 (s, 6H), 4.67 (s, 4H), 5.08 (s, 4H), 5.11 (s, 4H), 5.13 (s, 4H); ^{13}C NMR δ=15.6, 72.8, 72.9, 73.3, 73.3, 128.1, 129.6, 130.7, 131.2, 137.9, 138.7; HRMS (FAB) for M+H found *m/z* 351.1581, calcd for $C_{22}H_{23}O_4$: 351.1596. The enantiomeric excess was approximately determined by HPLC analysis using a chiral column (Daicel Chiralpak AD-H: 4×250 mm, 254 nm UV detector, rt, eluent: 10%, 2-propanol in hexane, flow rate: 1.0 mL/min, retention time: 16 min for major isomer and 18 min for minor isomer).

*4.3.12. 5,5′-Diisopropyl-1,3,6,8,1′,3′,6′,8′-octahydro-4,4′-bi(2,7-dioxa-as-indacenyl) (**6f**)*

White solid; mp 240 °C (decomp.); IR (CH_2Cl_2) 1051 cm^{-1}; ^1H NMR δ=1.07 (d, *J*=7.1 Hz, 6H), 1.16 (d, *J*=7.1 Hz, 6H), 2.80 (m, 2H), 4.61 (d, *J*=12.5 Hz, 2H), 4.65 (d, *J*=12.5 Hz, 2H), 5.01 (s, 4H), 5.06 (s, 4H), 5.29 (s, 4H); ^{13}C NMR δ=21.0, 21.7, 29.8, 71.3, 72.7, 72.9, 73.8, 129.9, 130.6, 132.9, 137.1, 138.1, 139.2; HRMS (FAB) for M−H found *m/z* 405.2067, calcd for $C_{26}H_{29}O_4$: 405.2066. $[\alpha]_D^{25.3}$ 10.0 (*c* 0.29, $CHCl_3$, 96% ee). The enantiomeric excess was determined by HPLC analysis using a chiral column (Daicel Chiralpak IA: 4×250 mm, 254 nm UV detector, rt, eluent: 20%, 2-propanol in hexane, flow rate: 1.0 mL/min, retention time: 6 min for major isomer and 8 min for minor isomer).

*4.4. The synthesis of chiral pentacene **12***

Iridium-catalyzed [2+2+2] cycloaddition was examined according to our procedure.[8a] The other reactions in Scheme 3 were examined according to the literature procedure.[13b]

*4.4.1. 1,4-Diphenyl-2,3-bis(hydroxymethyl)-9,10-dihydroanthracene (**8**)*

Brown solid; mp 185 °C (decomp.); IR (CH_2Cl_2) 703, 732, 3432 cm^{-1}; ^1H NMR δ=2.89 (br s, 2H), 3.61 (s, 4H), 4.50 (s, 4H), 7.05−7.52 (m, 14H); ^{13}C NMR δ=34.8, 60.8, 126.0, 127.1, 127.3, 128.5, 129.5, 135.4, 135.8, 136.6, 139.7, 140.6; HRMS (FAB) for M−H found *m/z* 391.1668, calcd for $C_{28}H_{23}O_2$: 391.1698.

*4.4.2. 1,4-Diphenyl-bis(3-(naphthalen-1-yl)prop-2-ynyl)-2,3-dihydroanthracene (**10**)*

Yellow solid; mp 188 °C (decomp.); IR (CH_2Cl_2) 701, 732, 744, 773, 798 cm^{-1}; ^1H NMR δ=4.22 (s, 4H), 7.35−7.81 (m, 26H), 7.98 (s, 2H), 8.26 (d, *J*=7.8 Hz, 2H); ^{13}C NMR δ=22.7, 79.9, 93.5, 121.4, 125.2, 125.4, 125.8, 126.2, 126.5, 127.7, 128.2, 128.6, 130.2, 130.6, 131.1, 131.2, 131.4, 133.1, 133.5, 139.3, 139.5 (three signals in the aromatic region were overlapped); HRMS (FAB) for M found *m/z* 658.2623, calcd for $C_{52}H_{34}$: 658.2661.

*4.4.3. 6,13-Diphenyl-2,3-bis(hydroxymethyl)-1,4-bis(naphthalen-1-yl)-5,14-dihydropentacene (**11**)*

Yellow oil; IR (CH_2Cl_2) 701, 746, 777, 3681 cm^{-1}; ^1H NMR δ=2.65 (br s, 2H), 3.32 (d, *J*=16.7 Hz, 2H), 3.48 (d, *J*=16.7 Hz, 2H), 4.31 (d, *J*=12.2 Hz, 2H), 4.39 (d, *J*=12.2 Hz, 2H), 6.60 (d, *J*=7.3 Hz, 2H), 6.79 (dd, *J*=7.3, 7.3 Hz, 2H), 7.12−7.83 (m, 24H), 7.93 (d, *J*=8.0 Hz, 2H); ^{13}C NMR δ=33.1, 61.1, 124.9, 125.1, 125.4, 125.9, 126.2, 126.5, 127.4, 127.6, 127.9, 128.1, 128.5, 129.9, 130.0, 130.4, 130.8, 132.7, 133.4, 133.6, 135.6, 136.6, 136.9, 137.8, 138.1, 138.5; HRMS (FAB) for M found *m/z* 744.3021, calcd for $C_{56}H_{40}O_2$: 744.3028. $[\alpha]_D^{25.7}$ 117.7 (*c* 1.92, $CHCl_3$).

*4.4.4. 2,3-Bis(bromomethyl)-6,13-diphenyl-1,4-bis(naphthalen-1-yl)pentacene (**12**)*

Blue purple solid; mp 200 °C (decomp.); IR (CH_2Cl_2) 796, 777, 748, 701 cm^{-1}, ^1H NMR δ=4.25 (d, *J*=10.0 Hz, 2H), 4.61 (d, *J*=10.0 Hz, 2H), 6.72 (d, *J*=7.5 Hz, 2H), 6.80−7.88 (m, 26H), 7.96 (d, *J*=8.5 Hz, 2H), 8.24 (s, 2H); ^{13}C NMR δ=58.5, 125.0, 125.1, 125.5, 125.6, 125.8, 126.7, 126.9, 127.6, 127.6, 127.7, 128.1, 128.2, 128.3, 128.4, 130.8, 130.8, 130.9, 131.0, 132.8, 133.0, 133.4, 136.1, 136.9, 138.3, 139.7; HRMS (FAB) for M found *m/z* 866.1173, calcd for $C_{56}H_{36}^{78}Br_2$: 866.1184. The enantiomeric excess was determined by HPLC analysis using a chiral column (Daicel Chiralpak IA: 4×250 mm, 254 nm UV detector, rt, eluent: 5%, CH_2Cl_2 in hexane, flow rate: 0.5 mL/min, retention time: 19 min for minor isomer and 22 min for major isomer).

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