Asymmetric synthesis of multi-substituted triptycenes *via* enantioselective alkynylation of 1,5-dibromoanthracene-9,10-dione

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ABSTRACT

Enantioselective alkynylation of 1,5-dibromoanthracene-9,10-dione by alkynyllithium reagents prepared from alkynes, *n*-BuLi, and sparteine gave chiral *cis*-diols possessing two alkyne moieties with moderate ee. Subsequent Ru-catalyzed [2+2+2] cycloaddition of the diol with alkynes afforded chiral 1,5-dibromotriptycenes.

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1. Introduction

Iptycene is a group of compounds that possess a bicyclo[2.2.2]octa-2,5,7-triene skeleton, in which the bridge moieties are joined by aromatic rings. Among them, the simplest one is triptycene, which is composed of three phenyl rings. Bartlett first synthesized triptycene in 1942 by a multi-step protocol.¹ Wittig and Ludwig disclosed a one-step protocol of a [4+2] cycloaddition of anthracene with benzyne,² and this has been the most conventional procedure for the preparation of triptycene derivatives. The triptycene skeleton has a rigid, three-dimensional structure; therefore, it is fascinating as a key unit for making unique molecular architectures. Oki's work of triptycene-based molecular balances is a pioneering achievement, which elucidated upon non-covalent weak interactions.³ Since then, many applications of triptycene-containing molecules have been reported.⁴ Diphosphine ligands,⁵ a molecular compass and gyroscope,⁶ and supermolecular system in host-guest chemistry^{7,8} are representative examples. Swager comprehensively studied triptycene-based polymers, which offer a new avenue for material chemistry.⁹

Multi-substituted triptycenes can be chiral. While an asymmetric synthesis was reported in 1962 by using resolution of diastereomeric salts,¹⁰ to the best of our knowledge an enantioselective synthesis has not been reported on. In contrast, Swager reported on a new protocol for the synthesis of triptycene derivatives using consecutive 1,2-addition of alkynyllithiums to anthraquinone along with the [2+2+2]

cycloaddition with alkynes.¹¹ We considered that an enantioselective alkynylation of two carbonyl moieties of a 1,5-disubstituted anthraquinone can realize an asymmetric synthesis of triptycene derivatives (Scheme 1). Herein we report a sparteine-mediated enantioselective alkynylation for the construction of chiral triptycene skeletons, followed by stereospecific [2+2+2] cycloaddition.

Scheme 1. Enantioselective synthesis of chiral triptycenes

2. Results and discussion

We chose 1,5-dibromoanthracene-9,10-dione **1** as a model diketone for the preparation of useful chiral synthetic building blocks. The enantioselective alkynylation of **1** was examined by using a stoichiometric amount of chiral phenylethynyl lithium reagents in toluene at room temperature (Table 1).¹²⁻¹⁵ When a catalytic amount of BINOL **L1** was used as the chiral ligand in THF,^{12b} dialkynylated product *cis*-**2a** was obtained, but the ee was below 2% (entry 1). In contrast, when using more than stoichiometric amounts of (+)-sparteine **L2**, it induced a moderate ee of 58% (entry 2). The enantioselectivity from sparteine surrogate **L3** was lower than sparteine (entry 3). Chiral diamine **L4** derived from cyclohexane-1,2-diamine did not show enantioinduction but the related chiral diamine **L5**, which possessed bulky alkyl chains gave 35% ee (entries 4 and 5). Proline-derived **L6** and 2,2'-diamino-1,1'-binaphthyl-derived **L7** were not effective in this enantioselective alkynylation (entries 6 and 7). In each entry, the total yield of *cis*- and *trans*-**2a** was excellent, but the *cis*-isomer was the minor product.

Table 1. Screening of ligands in consecutive and enantioselective alkynylations of diketone **1**

Chiral ligands:

Entry	Ligand	Yield (%) ^a	Ee (%) ^a
1 ^b	L1	15	<2
2	L2	29	58
3	L3	26	36
4	L4	24	<2
5	L5	14	35
6	L6	15	16
7	L7	23	<2

^a Yield and ee of *cis*-**2a**.

^b **L1** (20 mol%) was used in THF.

We next studied the reaction conditions using sparteine as a chiral ligand (Table 2). It was found that *s*-BuLi and *t*-BuLi gave comparable ee to those of *n*-BuLi, but the *cis/trans* ratio was slightly different (entries 1-3).¹⁶ A sub-stoichiometric amount of sparteine also gave enantioinduction, albeit with lower selectivity (entry 4). The solvent effect was significant on the enantioselectivity and toluene was found to give the best (entries 5-7). After screening of the reaction temperatures, a slightly better enantioselectivity was achieved at lower temperature (entries 8-10).

Table 2. Screening of reaction conditions for the enantioselective dialkynylation

Entry	BuLi	Solvent	Temp. (°C)	Yield (%) ^a	<i>cis:trans</i>	Ee (%) ^b
1	<i>n</i> -BuLi	toluene	rt	97	1.0:3.3	58
2	<i>s</i> -BuLi	toluene	rt	94	1.0:4.9	58
3	<i>t</i> -BuLi	toluene	rt	97	1.0:2.7	58
4 ^c	<i>n</i> -BuLi	toluene	rt	66	1.0:3.1	40
5	<i>n</i> -BuLi	hexane	rt	95	1.0:2.6	50
6	<i>n</i> -BuLi	THF	rt	95	1.0:3.3	8
7	<i>n</i> -BuLi	ether	rt	>99	1.0:3.3	40
8	<i>n</i> -BuLi	toluene	0	57	1.0:3.5	63
9	<i>n</i> -BuLi	toluene	10	94	1.0:3.8	64
10	<i>n</i> -BuLi	toluene	40	96	1.0:4.6	54

^a Total yield of *cis*- and *trans*-isomers.

^b Enantiomeric excess of *cis*-**2a**.

^c Sparteine (0.5 equiv) was used.

The scope of the alkynes was investigated under the reaction conditions of entry 1 in Table 2 (Table 3). Both electron-donating and withdrawing group-substituted aryl alkynes could also be used (entries 1 and 2). In the case of 4-chloroethynylbenzene, the yield of dialkynylated product **2c** was moderate due to the formation of a mono-alkynylated product, but the ratio of the *cis*-isomer increased and the enantioselectivity was almost the same as that of phenylacetylene. 1-Hexyne also gave the corresponding product **2d** and the ee of *cis*-isomer was moderate (entry 3).

Table 3. Scope of alkynes in the enantioselective dialkynylation

Entry	R	Yield (%) ^a	<i>cis:trans</i>	Ee (%) ^b
1	4-MeOC ₆ H ₄	49 2b	1.0:0.3	55
2	4-ClC ₆ H ₄	68 2c	1.0:1.0	60
3	<i>n</i> -Bu	64 2d	1.0:1.1	50

^a Total yield of *cis*- and *trans*-isomers.

^b Enantiomeric excess of *cis*-**2a**.

Next we transformed the obtained *cis*-diol **2a** into chiral triptycenes **3** via a Ru-catalyzed [2+2+2] cycloaddition with alkynes (Table 4).¹¹ Excess amounts of alkynes were needed, but chiral triptycenes were obtained by the reaction with hex-1-yne, oct-1-yne and 1,4-dihydroxybut-2-yne. The retention of the enantiomeric excess of the obtained cycloadducts was determined for each entry.

Table 4. Ru-catalyzed stereospecific [2+2+2] cycloaddition of *cis*-**2a** with alkynes

Entry	R ¹	R ²	Yield (%)
1	<i>n</i> -C ₄ H ₉	H	59 3aa
2	<i>n</i> -C ₆ H ₁₃	H	53 3ab
3	CH ₂ OH	CH ₂ OH	51 3ac

Finally, we demonstrated the use of the obtained triptycene as a chiral building block. Consecutive Suzuki coupling of dibromide **3ac** proceeded in high yield and chiral diaryl-substituted triptycene **4** was obtained (Eq. 1).

3. Conclusion

We have developed the first example of an asymmetric synthesis of chiral triptycenes via an enantioselective protocol. Consecutive alkynylation of 1,5-dibromoanthracene-9,10-dione using sparteine-based chiral alkynyllithium reagents along with Ru-catalyzed [2+2+2] cycloaddition with alkynes gave chiral triptycenes with moderate enantiomeric excesses. The obtained dibromo products can be used as chiral building blocks for the construction of more complex molecules.

4. Experimental

4.1. General

Anhydrous toluene was purchased and dried over activated molecular sieves 4Å. All reactions were carried out under an argon atmosphere in oven-dried glassware with a magnetic stirring bar. 1,5-Dibromoanthracene-9,10-dione **1** was prepared by a literature method.¹⁷ NMR spectra were recorded with a JEOL AL-500 (500 MHz) using tetramethylsilane as an internal standard and CDCl₃ or acetone-*d*₆. High-resolution mass spectra (HRMS) were measured on a Thermo Scientific Exactive Plus orbitrap mass spectrometer. Optical rotations were measured on

a JASCO DIP-1000 polarimeter. Ee was determined by HPLC analysis with detection at 254 nm using Daicel chiral columns (4.6 x 250 mm) at room temperature.

4.2. Typical experimental procedure for the enantioselective alkynylation (entry 1 in Table 2)

A solution of *n*-butyllithium (1.6 M in hexane, 0.095 mL, 0.15 mmol) and (+)-sparteine (34.5 μL, 0.15 mmol) was added dropwise to a toluene solution (0.3 mL) of phenylacetylene (19.8 μL, 0.18 mmol) at 0 °C. The reaction mixture was stirred for one hour at room temperature. 1,5-Dibromoanthracene-9,10-dione **1** (18.3 mg, 0.05 mmol) was then added to the solution and the reaction mixture was stirred for 3 days. The reaction was quenched with saturated NH₄Cl aqueous solution, and the organic materials were extracted with ethyl acetate. The combined organic layer was washed with water and brine, then dried over Na₂SO₄. After the solvent was removed under reduced pressure, the resulting crude products were purified by preparative TLC, and analytically pure *cis*-**2a** (6.2 mg, 0.010 mmol) and *trans*-**2a** (21.3 mg, 0.037 mmol) were obtained.

4.2.1. *cis*-1,5-Dibromo-9,10-bis(phenylethynyl)-9,10-dihydroanthracene-9,10-diol *cis*-**2a**

Off-white solid; mp >150 °C (dec.); ¹H NMR (acetone-*d*₆) δ 5.93 (s, 2H), 7.25-7.37 (m, 10H), 7.44 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.80 (d, *J* = 7.8 Hz, 2H), 8.22 (d, *J* = 8.1 Hz, 2H); ¹³C NMR (acetone-*d*₆) δ 67.0, 86.4, 92.8, 123.2, 123.4, 129.3, 129.5, 129.9, 130.6, 132.2, 133.4, 136.1, 141.9; HRMS (ESI positive) *m/z* calcd for C₃₀H₁₈Br₂NaO₂ ([M+Na]⁺): 590.9566. Found: 590.9565. [α]_D²⁶ = -128 (c 0.7, CHCl₃) 58% ee. Ee was determined by HPLC analysis using Daicel Chiralpak IC (eluent: 10% ethyl acetate in hexane, flow rate: 1.0 mL/min, retention time: 22.0 min for major isomer and 27.8 min for minor isomer).

4.2.2. *trans*-1,5-Dibromo-9,10-bis(phenylethynyl)-9,10-dihydroanthracene-9,10-diol *trans*-**2a**

Off-white solid; mp >150 °C (dec.); ¹H NMR (acetone-*d*₆) δ 5.88 (s, 2H), 7.32-7.42 (m, 10H), 7.44 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.81 (d, *J* = 7.9 Hz, 2H), 8.25 (d, *J* = 8.2 Hz, 2H); ¹³C NMR (acetone-*d*₆) δ 67.7, 86.9, 93.8, 123.5, 123.7, 129.4, 129.6, 130.6, 130.7, 132.3, 133.8, 136.3, 142.4; HRMS (ESI positive) *m/z* calcd for C₃₀H₁₈Br₂NaO₂ ([M+Na]⁺): 590.9566. Found: 590.9567

4.2.3. *cis*-1,5-Dibromo-9,10-dihydro-9,10-bis[2-(4-methoxyphenyl)ethynyl]anthracene-9,10-diol *cis*-**2b**

Yellow solid; mp >150 °C (dec.); ¹H NMR (acetone-*d*₆) δ 3.77 (s, 6H), 5.82 (s, 2H), 6.84 (d, *J* = 9.0 Hz, 4H), 7.28 (d, *J* = 9.0 Hz, 4H), 7.42 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.78 (d, *J* = 7.9 Hz, 2H), 8.20 (d, *J* = 8.3 Hz, 2H); ¹³C NMR (acetone-*d*₆) δ 55.6, 67.0, 86.5, 91.4, 114.8, 115.4, 123.1, 129.9, 130.4, 133.5, 133.8, 136.0, 142.0, 160.9; HRMS (ESI positive) *m/z* calcd for C₃₂H₂₂Br₂NaO₄ ([M+Na]⁺): 650.9777. Found: 650.9772. [α]_D²⁶ = -112 (c 0.67, CHCl₃) 55% ee. Ee was determined by HPLC analysis using Daicel Chiralpak IE-3 (eluent: 20% ethyl acetate in hexane, flow rate: 1.0 mL/min, retention time: 20.2 min for major isomer and 16.9 min for minor isomer).

4.2.4. *trans*-1,5-Dibromo-9,10-dihydro-9,10-bis[2-(4-methoxyphenyl)ethynyl]anthracene-9,10-diol *trans*-**2b**

Pale orange solid; mp >150 °C (dec.); ¹H NMR (acetone-*d*₆) δ 3.80 (s, 6H), 5.78 (s, 2H), 6.90 (d, *J* = 9.1 Hz, 4H), 7.33 (d, *J* = 9.0 Hz, 4H), 7.42 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.79 (d, *J* = 7.8 Hz, 2H), 8.23 (d, *J* = 8.2 Hz, 2H); ¹³C NMR (acetone-*d*₆) δ 55.8,

67.7, 87.0, 92.5, 115.1, 115.7, 123.5, 130.6, 130.6, 133.9, 134.0, 136.2, 161.1; HRMS (ESI positive) m/z calcd for $C_{32}H_{22}Br_2NaO_2$ ($[M+Na]^+$): 650.9777. Found: 650.9772.

4.2.5. *cis*-1,5-Dibromo-9,10-bis[2-(4-chlorophenyl)ethynyl]-9,10-dihydroanthracene-9,10-diol *cis*-2c

Pale yellow solid; mp >150 °C (dec.); 1H NMR (acetone- d_6) δ 5.93 (s, 2H), 7.33-7.38 (m, 8H), 7.44 (dd, J = 8.0, 8.0 Hz, 2H), 7.81 (d, J = 7.8 Hz, 2H), 8.20 (d, J = 8.2 Hz, 2H); ^{13}C NMR (acetone- d_6) δ : 67.1, 85.4, 93.9, 122.3, 123.4, 129.7, 130.1, 130.9, 133.4, 134.0, 135.2, 136.4, 141.9; HRMS (ESI positive) m/z calcd for $C_{30}H_{16}Br_2Cl_2NaO_2$ ($[M+Na]^+$): 658.8786. Found: 658.8784. $[\alpha]_D^{26}$ = -119 (c 0.37, $CHCl_3$) 60% ee. Ee was determined by HPLC analysis using Daicel Chiralpak IF-3 (eluent: 20% ethyl acetate in hexane, flow rate: 1.0 mL/min, retention time: 16.2 min for major isomer and 14.3 min for minor isomer).

4.2.6. *trans*-1,5-Dibromo-9,10-bis[2-(4-chlorophenyl)ethynyl]-9,10-dihydroanthracene-9,10-diol *trans*-2c

Pale yellow solid; mp >150 °C (dec.); 1H NMR ($CDCl_3$) δ 4.61 (s, 2H), 7.25 (d, J = 8.8 Hz, 4H), 7.30 (d, J = 8.8 Hz, 4H), 7.39 (dd, J = 8.0, 8.0 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H), 8.17 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 67.4, 86.3, 92.8, 120.9, 121.9, 128.8, 130.1, 130.3, 132.6, 133.0, 135.0, 135.6, 139.2; HRMS (ESI positive) m/z calcd for $C_{30}H_{16}Br_2Cl_2NaO_2$ ($[M+Na]^+$): 658.8786. Found: 658.8779.

4.2.7. *cis*-1,5-Dibromo-9,10-di(hex-1-ynyl)-9,10-dihydroanthracene-9,10-diol *cis*-2d

Pale yellow solid; mp 75-78 °C; 1H NMR ($CDCl_3$) δ 0.84 (t, J = 7.4 Hz, 6H), 1.27-1.37 (m, 4H), 1.39-1.48 (m, 4H), 2.14 (t, J = 7.2, Hz, 4H), 4.53 (s, 2H), 7.30 (dd, J = 8.0, 8.0 Hz, 2H), 7.67 (d, J = 7.9 Hz, 2H), 8.05 (d, J = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.7, 18.8, 22.1, 30.4, 66.2, 82.4, 88.2, 121.4, 129.3, 129.7, 132.7, 135.1, 139.7; HRMS (ESI positive) m/z calcd for $C_{26}H_{26}Br_2NaO_2$ ($[M+Na]^+$): 551.0192. Found: 551.0195. $[\alpha]_D^{26}$ = -87.2 (c 0.62, $CHCl_3$) 50% ee. Ee was determined by HPLC analysis using Daicel Chiralpak IC (eluent: 10% ethyl acetate in hexane, flow rate: 1.0 mL/min, retention time: 14.8 min for major isomer and 17.5 min for minor isomer).

4.2.8. *trans*-1,5-Dibromo-9,10-di(hex-1-ynyl)-9,10-dihydroanthracene-9,10-diol *trans*-2d

Pale pink solid; mp 176-178 °C; 1H NMR ($CDCl_3$) δ 0.85 (t, J = 7.4 Hz, 6H), 1.28-1.38 (m, 4H), 1.39-1.48 (m, 4H), 2.14 (t, J = 7.1 Hz, 4H), 4.40 (s, 2H), 7.30 (dd, J = 8.0, 8.0 Hz, 2H), 7.68 (d, J = 7.9 Hz, 2H), 8.06 (d, J = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.7, 18.8, 22.1, 30.3, 67.0, 83.3, 88.9, 121.7, 129.7, 129.9, 133.0, 135.2, 139.9; HRMS (ESI positive) m/z calcd for $C_{26}H_{26}Br_2NaO_2$ ($[M+Na]^+$): 551.0192. Found: 551.0195.

4.3. Typical experimental procedure for the [2+2+2] cycloaddition (entry 1 in Table 4)

At first, $RuClCp(PPh_3)_2$ (3.6 mg, 0.005 mmol 10 mol%) and *cis*-2a (28.5 mg, 0.05 mmol) were placed in a Schlenk tube, which was then evacuated and backfilled with argon. 1-Hexyne (56.8 μ L, 0.5 mmol) and 1,4-dioxane (0.5 mL) were then added and the reaction vessel was immersed in an oil bath at 105 °C for one day. The solvent was removed under reduced pressure, and the crude products were purified by preparative TLC to give analytically pure **3aa** (14.7 mg, 0.029 mmol, 59%).

4.3.1. 5,13-Dibromo-2-butyl-1,4-diphenyl-9,10-dihydro-9,10-[1,2]benzenoanthracene **3aa**

Yellow foam; 1H NMR (acetone- d_6) δ 0.66 (t, J = 7.5 Hz, 3H), 0.82-0.97 (m, 2H), 1.03-1.12 (m, 2H), 2.15-2.31 (m, 2H), 3.49 (s, 1H), 4.05 (s, 1H), 6.86 (s, 1H), 6.97-7.10 (m, 2H), 7.30 (dd, J = 8.7, 8.7 Hz, 2H), 7.36 (d, J = 8.0 Hz, 1H), 7.38-7.67 (m, 11H); ^{13}C NMR (acetone- d_6) δ 14.0, 23.3, 33.0, 34.3, 82.0, 82.4, 114.7, 114.9, 121.8, 122.1, 128.3, 128.5, 128.8, 129.4, 129.6, 130.2, 131.0, 131.4, 133.7, 133.7, 136.2, 137.2, 140.3, 140.3, 140.4, 140.6, 143.0, 143.1, 150.3, 150.4 (a pair of peaks at aromatic region is overlapped); HRMS (ESI positive) m/z calcd for $C_{36}H_{28}Br_2NaO_2$ ($[M+Na]^+$): 673.0348. Found: 673.0345. $[\alpha]_D^{26}$ = -212 (c 0.20, $CHCl_3$) 58% ee. Ee was determined by HPLC analysis using Daicel Chiralpak IA (eluent: 2% dichloromethane in hexane, flow rate: 1.0 mL/min, retention time: 7.4 min for major isomer and 10.5 min for minor isomer).

4.3.2. 5,13-Dibromo-2-hexyl-1,4-diphenyl-9,10-dihydro-9,10-[1,2]benzenoanthracene **3ab**

Tan colored foam; 1H NMR (acetone- d_6) δ 0.75 (t, J = 7.3 Hz, 3H), 0.83-0.95 (m, 2H), 0.99-1.17 (m, 6H), 2.14-2.31 (m, 2H), 3.49 (s, 1H), 4.04 (s, 1H), 6.86 (s, 1H), 6.99-7.09 (m, 2H), 7.27-7.66 (m, 14H); ^{13}C NMR (acetone- d_6) δ 14.4, 23.1, 32.1, 32.1, 33.4, 82.0, 82.4, 114.7, 114.9, 121.8, 122.1, 128.3, 128.5, 128.8, 129.4, 129.6, 130.2, 131.0, 131.4, 133.7, 133.7, 136.2, 137.2, 140.3, 140.4, 140.4, 140.6, 140.6, 143.0, 143.1, 150.3, 150.4 (a pair of peaks at aliphatic region and a pair of peaks at aromatic region are overlapped); HRMS (ESI positive) m/z calcd for $C_{38}H_{32}Br_2NaO_2$ ($[M+Na]^+$): 701.0661. Found: 701.0657. $[\alpha]_D^{26}$ = -216 (c 0.21, $CHCl_3$) 58% ee. Ee was determined by HPLC analysis using Daicel Chiralpak IA (eluent: 2% dichloromethane in hexane, flow rate: 1.0 mL/min, retention time: 7.1 min for major isomer and 10.1 min for minor isomer).

4.3.3. 5,13-Dibromo-2,3-bis(hydroxymethyl)-1,4-diphenyl-9,10-dihydro-9,10-[1,2]benzenoanthracene-9,10-diol **3ac**

Pale yellow foam; 1H NMR (acetone- d_6) δ 3.49 (s, 2H), 4.08-4.13 (m, 2H), 4.23-4.31 (m, 2H), 4.38-4.45 (dd, J = 7.9, 7.9 Hz, 2H), 7.01-7.08 (m, 2H), 7.27-7.36 (m, 4H), 7.43-7.49 (m, 2H), 7.54-7.66 (m, 8H); ^{13}C NMR δ 59.4, 82.1, 114.8, 122.0, 128.4, 128.9, 129.3, 129.5, 130.0, 131.8, 133.7, 137.3, 139.0, 140.2, 140.3, 142.7, 150.0; HRMS (ESI positive) m/z calcd for $C_{34}H_{24}Br_2NaO_4$ ($[M+Na]^+$): 676.9934. Found: 676.9935. $[\alpha]_D^{26}$ = -17.0 (c 0.85, $CHCl_3$) 58% ee. Ee was determined by HPLC analysis using Daicel Chiralpak IA (eluent: 40% dichloromethane in hexane, flow rate: 1.0 mL/min, retention time: 18.1 min for major isomer and 20.8 min for minor isomer).

4.4. Suzuki coupling of **3ac** (Eq. 1)

To a THF solution (0.1 mL) of dibromo **3ac** (11.2 mg, 0.017 mmol), 4-methoxyphenylboronic acid (7.7 mg, 0.051 mmol), $PdCl_2(PPh_3)_2$ (1.0 mg, 0.0014 mmol, 8.3 mol%) and 0.5 M K_3PO_4 aq. (0.1 mL, 0.05 mmol) were added at room temperature. The mixture was stirred at 60 °C for 17 h and then filtered through a pad of silica gel with ethyl acetate. Purification by preparative TLC gave analytically pure product **4** (10.6 mg, 0.015 mmol, 88%).

4.4.1. 2,3-Bis(hydroxymethyl)-5,13-bis(4-methoxyphenyl)-1,4-diphenyl-9,10-dihydro-9,10-[1,2]benzenoanthracene-9,10-diol **4**

Pale yellow foam; 1H NMR ($CDCl_3$) δ 2.03 (s, 2H), 2.42 (s, 2H), 3.87 (s, 6H), 4.30 (s, 4H), 6.83 (d, J = 7.7 Hz, 4H), 6.92 (d, J = 8.7 Hz, 2H), 7.07 (dd, J = 7.6, 7.6 Hz, 2H), 7.11-7.17 (m, 4H), 7.20-7.25 (m, 4H), 7.27-7.34 (m, 4H), 7.35-7.39 (m, 2H), 7.54 (d, J = 7.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 55.4, 59.5, 81.9,

113.1, 113.4, 120.2, 124.9, 127.2, 128.1, 128.2, 129.9, 130.0, 130.3, 131.5, 133.0, 135.5, 136.1, 136.6, 139.6, 140.0, 143.6, 146.6, 158.8; HRMS (ESI positive) m/z calcd for $C_{48}H_{38}NaO_6$ ($[M+Na]^+$): 733.2561. Found: 733.2559. $[\alpha]_{D}^{26} = 23.4$ (c 0.49, $CHCl_3$).

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Graphical Abstract

Asymmetric synthesis of multi-substituted triptycenes via enantioselective alkynylation of 1,5-dibromoanthracene-9,10-dione

Takanori Shibata* and Yuri Kamimura

Stereochemistry Abstract

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$C_{30}H_{18}Br_2O_2$

cis-1,5-Dibromo-9,10-bis(phenylethynyl)-9,10-dihydroanthracene-9,10-diol

Ee = 58% from HPLC

$[\alpha]_D^{26} = -128$ (*c* 0.70, $CHCl_3$)

Source of chirality: (+)-sparteine

Absolute configuration: not determined

Takanori Shibata and Yuri Kamimura

$4-MeOC_6H_4$

$C_{32}H_{22}Br_2O_2$

cis-1,5-Dibromo-9,10-dihydro-9,10-bis[2-(4-methoxyphenyl)ethynyl]anthracene-9,10-diol

Ee = 55% from HPLC

$[\alpha]_D^{26} = -112$ (*c* 0.67, $CHCl_3$)

Source of chirality: (+)-sparteine

Absolute configuration: not determined

Takanori Shibata and Yuri Kamimura

$4-ClC_6H_4$

$C_{30}H_{16}Br_2Cl_2O_2$

cis-1,5-Dibromo-9,10-bis(2-(4-chlorophenyl)ethynyl)-9,10-dihydroanthracene-9,10-diol

Ee = 60% from HPLC

$[\alpha]_D^{26} = -119$ (*c* 0.37, $CHCl_3$)

Source of chirality: (+)-sparteine

Absolute configuration: not determined

Takanori Shibata and Yuri Kamimura

$C_{48}H_{38}O_6$

2,3-Bis(hydroxymethyl)-5,13-bis(4-methoxyphenyl)-1,4-diphenyl-9,10-dihydro-9,10-[1,2]benzenoanthracene-9,10-diol

$[\alpha]_{H_2O}^{26} = +23.4$ (c 0.49, $CHCl_3$)

Source of chirality: (+)-sparteine

Absolute configuration: not determined

Takanori Shibata and Yuri Kamimura

$C_{30}H_{16}Br_2Cl_2O_2$
cis-1,5-Dibromo-9,10-di(hex-1-ynyl)-9,10-dihydroanthracene-9,10-diol

Ee = 50% from HPLC
 $[\alpha]_D^{26} = -87.2$ (c 0.62, $CHCl_3$)
 Source of chirality: (+)-sparteine
 Absolute configuration: not determined

Takanori Shibata and Yuri Kamimura

$C_{36}H_{28}Br_2O_2$
 5,13-Dibromo-2-butyl-1,4-diphenyl-9,10-dihydro-9,10-[1,2]benzenoanthracene

Ee = 58% from HPLC
 $[\alpha]_{Hg435}^{26} = -212$ (c 0.20, $CHCl_3$)
 Source of chirality: (+)-sparteine
 Absolute configuration: not determined

Takanori Shibata and Yuri Kamimura

$C_{38}H_{32}Br_2O_2$
 5,13-Dibromo-2-hexyl-1,4-diphenyl-9,10-dihydro-9,10-[1,2]benzenoanthracene

Ee = 58% from HPLC
 $[\alpha]_{Hg435}^{26} = -216$ (c 0.21, $CHCl_3$)
 Source of chirality: (+)-sparteine
 Absolute configuration: not determined

Takanori Shibata and Yuri Kamimura

$C_{34}H_{24}Br_2O_4$
 5,13-Dibromo-2,3-bis(hydroxymethyl)-1,4-diphenyl-9,10-dihydro-9,10-[1,2]benzenoanthracene-9,10-diol

Ee = 58% from HPLC
 $[\alpha]_{Hg435}^{26} = -17.0$ (c 0.85, $CHCl_3$)
 Source of chirality: (+)-sparteine
 Absolute configuration: not determined