Synthesis of a Configurationally Locked [5]Helicene Derivative

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Abstract: The photochemical cyclisation–dehydrogenation of the bis-styrylbenzene **3**, where the terminal aryl moieties are connected by a suitable chiral tether derived from 1,3-pentanediol, led to a chiral, configurationally locked [5]helicene derivative. An X-ray diffraction study showed that an (*S*,*S*)-configuration of the chiral auxiliary induces a (*P*)-configuration of the helical framework.

Key words: helical structures, chiral auxiliaries, diols, photochemistry, stereoselectivity

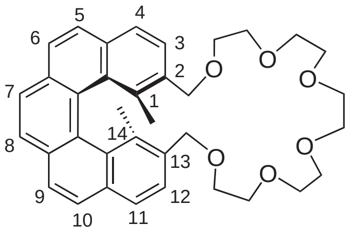
Since their discovery by Newman and Lednicer,[1] enantiomerically pure helicene derivatives have attracted attention because of their unique chiral structure and very high optical rotation values. To date, their potential as chiral ligands,[2] catalysts,[3] auxiliaries,[4] molecular recognition agents[5] and materials[6] is well established.[7]

A number of helicenes have been obtained in enantiomerically enriched form mainly by separation of racemic mixtures through crystallisation,[1] HPLC techniques[8] or chromatographic separation of the diastereoisomeric mixtures formed with stoichiometric chiral auxiliaries.[4a,9] Some studies have been also reported, where chirality transfer or retention from enantiomerically enriched starting materials are applied to helicene syntheses,[10] while enantioselective catalytic methods are at a very early stage and afford to date only moderate enantiomeric excesses.[11] Finally, some asymmetric syntheses have been performed which make use of chiral auxiliaries covalently bonded to the starting material, in the key, enantio-determining step.[12]

Concerning the application of helicenes in chiral technologies, a major issue is their configurational stability, which appeared to be surprising low. The easy racemization of helical frameworks is usually assigned to twisting distributed over a large number of aromatic bonds.

Among simple, unsubstituted carbohelicenes, a sequence of at least six aromatic rings is required to ensure configurational stability at room temperature.[13] Lower members are known to racemize quite easily. This is the case for the parent [5]helicene, which displays a $t_{1/2}$ of 62 min at 57 °C. Nevertheless, samples of optically enriched [5]helicene could be prepared by either crystallization from a racemic mixture by using (+)-TAPA [2-(2,4,5,7-tetranitro-9-fluorenylideneaminoxy)propionic acid] as the resolving agent, or starting from optically pure binaphthyl derivatives. The non-racemic samples of [5]helicenes were thus isolated at 0 °C and displayed $[\alpha]_{578}$ values of –1670° and +2270° (2430°) respectively.[14,10b]

An increased configurational stability can be attained by introducing substituents on the 1,14 positions of [5]helicene derivatives, which create higher steric hindrance. Thus, for instance, the optically pure 1,14-dimethyl substituted [5]helicene **I** (Figure 1) {$[\alpha]_D$ –754 (MeOH)} showed no optical rotation change after refluxing its ethanol solution for 24 h.[15]



I[15]

Figure 1

Here we report on the synthesis of a new [5]helicene derivative where the helical chirality has been set by means of a chiral tether connecting the 2,13 positions.

In this work, the configurationally locked [5]helicene **4** has been prepared by using a chiral tether derived from (*R*,*R*)-2,4-pentanediol, which is connected to the 2,13 positions of the final helicene through ether functions. The choice of the chiral tether was based on the known high efficiency of the 2,4-pentanediol bis-ether moiety as a chiral auxiliary in many diastereoselective intramolecular reactions.[16] Notably, the highly diastereoselective synthesis of atropoisomeric biaryls has been performed via the copper-promoted coupling of tethered bis-aryl derivatives.[17] Intramolecular carbene insertion reactions[18] and [2 + 2]-cycloaddition reactions have also been described.[19]

Our synthetic strategy is shown in Scheme 1.

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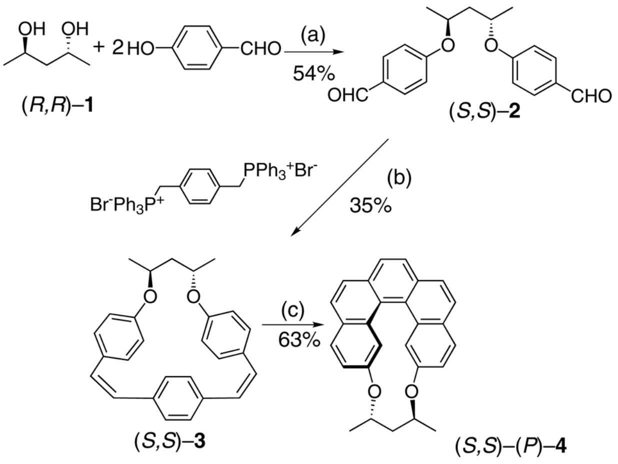

Scheme 1 *Reagents and conditions*: (a) Diethyl azodicarboxylate (DEAD), PPh_3, THF, 40 °C, 18 h; (b) EtOLi, EtOH, 50 °C, 18 h; (c) hν, I_2, propylene oxide, toluene, 15 min

The (*R*,*R*)-2,4-pentanediol was used as the enantiomerically pure starting material for the synthesis of the bis-ether derivative **2**, through a Mitsunobu reaction with two equivalents of *p*-hydroxybenzaldehyde.

The formyl groups of **2** were then involved in an inter–intramolecular bis-Wittig reaction with the bis-phosphonium salt of α,α′-dibromo-*p*-xylene.[20] The macrocyclic bis-ether **3** was obtained in moderate yield (35%), probably because of concurrent intermolecular reactions. It is assumed to have a Z,Z stereochemistry, based on the C_2-symmetric structure highlighted by the ^1H NMR spectrum.

The helicene moiety was formed then by the classical photochemical cyclisation–dehydrogenation reaction[21] of the bis-styryl derivative **3**, where the chiral bis-ether bridge links the terminal aromatic rings. Photolysis of the macrocyclic bis-ether (*S*,*S*)-**3** (Heraeus high-pressure mercury lamp, 150 Watt) was performed in toluene, for about 15 min, on a 700 mg scale, and afforded the corresponding [5]helicene **4**. Prolonged reaction times led to the formation of the substituted perylene **5** as the main product (Figure 2).[22]

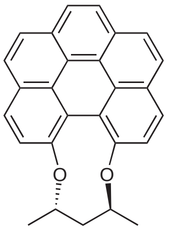
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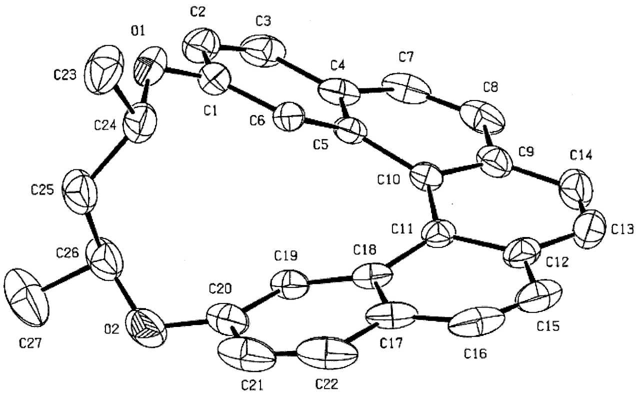
Figure 2

Based on the slow racemisation of [5]helicene at room temperature, the formation of a mixture of two diastereoisomers of **4** could be expected, which might equilibrate slowly at room temperature. The [5]helicene derivative **4** was obtained as a single isomer. The $[\alpha]_D$ value for this compound is +975 (*c* 0.5, $CHCl_3$), which suggests a (*P*)-configuration of the helical moiety.

The (*P*)-helicity of **4** was confirmed by an X-ray diffraction study [relative stereochemistry with respect to the known (*S*,*S*)-configuration of the diether moiety]. An ORTEP drawing of **4** is shown in Figure 3.



Bond distances of **4** (Å)

C(2)-C(3)	1.357(2)	C(9)-C-10)	1.453(2)
C(5)-C(6)	1.408(2)	C(13)-C(14)	1.348(3)
C(7)-C(8)	1.346(2)	C(10)-C(11)	1.450(2)

Dihedral angles of **4** (deg.)

C(19)-C(18)-C(11)-C(10)	17.7
C(18)-C(11)-C(10)-C(5)	22.9
C(11)-C(10)-C(5)-C(6)	19.0

Figure 3 Crystal structure of **4**: ORTEP drawing, selected bond distances and dihedral angles.

The helical twisting of **4** is defined by the dihedral angles given in Figure 3, with a mean value of about 20°. The outer bonds are shortened (mean value of 1.35 Å) with respect to the benzene ring (1.39 Å) whereas the inner bond distances are lengthened to about 1.45 Å.

NMR studies suggest that the bis-ether tether locks the configuration of the helical framework, at least in the temperature range from –40 °C to 80 °C. No epimerization was observed by heating **4** at about 80 °C for more than ten hours.

Substituents on the 2,13 positions are not expected to have a severe effect on the configurational stability of [5]helicene derivatives.[23] Thus the observed stabilization should be mainly assigned to the presence of the configurationally defined tether. The [5]helicene derivative shown in Figure 3 should represent the thermodynamically favored epimer of **4**.

In conclusion, we have disclosed here a stereoselective approach to the [5]helicene **4**, where the presence of the chiral tether prevents epimerization of the helical framework at room temperature. The broad range of potential uses of chiral helicenes in material science and catalysis, for instance, suggests interesting application fields for **4** in future work.

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Photo-cyclizations were performed in a water-cooled Quartz photoreactor using a high-pressure mercury immersion lamp (Heraeus TQ 150). NMR spectra were recorded on either a Bruker AM 200 or an AM 400 spectrometer. Silica gel 60 mesh was used for column chromatography. The *p*-xylylenebis(triphenylphosphonium) bromide was prepared from PPh_3 and α,α′-dibromoxylene in refluxing DMF, according to the usual procedure.[24]

(*S*,*S*)-2,4-Bis(4-formylphenyloxy)pentane (2)

A solution containing 4-hydroxybenzaldehyde (5.4 g, 44 mmol) and diethyl azodicarboxylate (DEAD, 6.4 mL, 41 mmol) in THF (40 mL) was prepared under argon. A solution of (*R*,*R*)-2,4-pentanediol (2.1 g, 20 mmol) and PPh_3 (10.5 g, 40 mmol) in THF (60 mL) was added dropwise, at r.t. The mixture was stirred overnight at 45 °C. After evaporation of the solvent, the residue was taken up in EtOAc, filtered and purified by chromatography (silica gel; cyclohexane–EtOAc, 90:10). (*S*,*S*)-**2** was isolated.

Yield: 3.4 g (54%); pale yellow oil; $R_f = 0.3$; $[\alpha]_D$ +114 (*c* 1, $CHCl_3$).

^1H NMR ($CDCl_3$): δ = 1.37 (d, *J* = 6.1 Hz, 6 H, Me), 2.05 (dd, *J* = 7.0, 5.5 Hz, 2 H, CH_2), 4.7 (m, 2 H, CHO), 6.88 (4 H), 7.71 (4 H), 9.83 (s, 2 H, CHO).

^{13}C NMR ($CDCl_3$): δ = 20.0 (Me), 44.4 (CH_2), 70.8 (OCH), 115.7 (CH), 129.8 (C), 132.0 (CH), 163.1 (OC), 190.6 (CHO).

EI MS: *m*/*z* (%) = 312 (M, 13), 149 (100), 121 (60).

(*S*,*S*)-3

Lithium ethoxide (0.25 M in EtOH, 80 mL, 20 mmol) was added to a solution of *p*-xylylenebis(triphenylphosphonium) bromide (7.1 g, 9 mmol) and (*S*,*S*)-2,4-bis(4-formylphenyloxy)pentane (2.8 g, 9 mmol) in EtOH (500 mL) at r.t. The mixture was heated at 50 °C for16 h. The reaction mixture was hydrolysed with H_2O. After evaporation of the EtOH and extraction of the aq phase with CH_2Cl_2, the crude product was purified by chromatography (cyclohexane–EtOAc, gradient from 100:0 to 90:10). (*S*,*S*)-**3** was obtained.

Yield: 1.2 g (35%); colorless solid; $[\alpha]_D$ +204 (*c* 0.5, $CHCl_3$).

^1H NMR ($CDCl_3$): δ = 1.36 (d, *J* = 6.2 Hz, 6 H, Me), 1.91 (dd, *J* = 7.2, 5.4 Hz, 2 H, CH_2), 4,60 (m, 2 H, CHO), 6.63 (AB, *J* = 11.4 Hz, 2 H), 6.70 (AB, *J* = 11.4 Hz, 2 H), 6.72 (4 H), 6.77 (s, 4 H), 6.87 (4 H).

^{13}C NMR ($CDCl_3$): δ = 21.0 (Me), 44.8 (CH_2), 71.3 (OCH), 115.5, 128.6, 130.2, (CH), 130.7(C), 130.8, 131.4 (CH), 135.9 (C), 157.4 (OC).

EI MS: *m*/*z* (%) = 382 (M, 65), 340 (40), 314 (100).

The [5]helicene (*S*,*S*)-(*P*)-4

Photolysis of **(*S*,*S*)-3** (700 mg, 1.8 mmol) was performed in toluene (1 L), in the presence of iodine (1 g, 3.9 mmol) and propylene oxide (12 mL) for 15 min. Evaporation of the solvent and column chromatography (cyclohexane–EtOAc, 95:5 mixture) and crystallisation (CH_2Cl_2–Et_2O–pentane, 1:1:1) yielded **4**.

Yield: 430 mg (63%); colorless solid; $[\alpha]_D$ +975 (*c* 0.5, $CHCl_3$).

^1H NMR ($CDCl_3$): δ = 1.28 (d, *J* = 6.3 Hz, 6 H, Me), 2.07 (dd, *J* = 6.2 Hz, 4.1 Hz, 2 H, CH_2), 4.86 (m, 2 H, CHO), 7.16 (dd, *J* = 8.7, 2.4 Hz, 2 H, CH-3 and 12), 7.82 (d, *J* = 8.5 Hz, 2 H), 7.85 (d, *J* = 8.7 Hz, 2 H), 7.88 (d, *J* = 8.5 Hz, 2 H), 7.92 (s, 2 H, CH-7 and 8), 8.18 (d, *J* = 2.4 Hz, 2 H, CH-1 and 14).

^{13}C NMR ($CDCl_3$): δ = 23.0 (Me), 49.1 (CH_2), 72.9 (OCH), 115.3 (CH-*o*-O), 120.0 (CH-*o*-O), 124.9 (CH), 126.2 (C), 126.8 (CH), 127.7 (CH), 128.4 (C), 129.6 (CH), 130.4 (C), 132.8 (C), 155.5 (C-O).

MS (CI, NH_3): *m*/*z* (%) = 379 (M + H, 100%).

HRMS (CI): *m*/*z* calcd for $C_{27}H_{23}O_2$: 379.1698; found: 379.1700.

The second epimer (*S*,*S*)-(*M*)-**4**, could not be identified in the reaction mixture or produced by thermal isomerization of (*S*,*S*)-(*P*)-**4**.

Perylene 5

Perylene **5** was obtained as the main product when **3** was photolysed for about 1 h, under the same experimental conditions as above. Its structure was assigned from the ^1H and ^{13}C NMR data.

^1H NMR ($CDCl_3$): δ = 1.64 (d, *J* = 6.4 Hz, 6 H, Me), 2.48 (t, *J* = 5.0 Hz, 2 H, CH_2), 5.25 (m, 2 H, CHO), 7.75 (d, *J* = 8.6 Hz, 2 H), 7.97 (d, *J* = 8.8 Hz, 2 H), 8.03 (d, *J* = 8.8 Hz, 2 H), 8.08 (d, *J* = 8.6 Hz, 2 H), 8.25 (s, 2 H).

^{13}C NMR ($CDCl_3$): δ = 23.4 (Me), 45.1 (CH_2), 73.7 (OCH), 116.9 (CH-*o*-O), 118.6 (C-*o*-O), 124.2 (C), 124.8, 125.5, 126.3 (CH), 126.6, 128.6, 128.7 (C), 156.3 (CO).

HRMS (CI): *m*/*z* calcd for $C_{27}H_{21}O_2$: 377.1542; found: 377.1538.

X-Ray Crystal Structure Determination of (*S*,*S*)-(*P*)-4

Single crystals of **4** were obtained by recrystallisation from Et_2O–pentane. X-ray data were recorded on a KappaCCD diffractometer. Chemical formula $C_{27}H_{22}O_2$, M = 378.45 crystal dimensions 0.22 × 0.20 × 0.20 mm, orthorhombic, $P2_12_12_1$, *a* = 6.268(5), *b* = 12.970(5), *c* = 24.185(5) Å, volume 1966.1(18) Å^3, Z = 4, ρ_{calcd} = 1.278 g/cm^3, X-ray source MoKα, λ = 0.71069 Å, T = 150.0(10) K, measured reflections = 4464, independent reflections = 4464, reflections used 3891, refinement type Fsqd, parameters refined 265, *R*1 = 0.0399, *wR*2 = 0.1085, Flack's parameter = 0.2(12).

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References

(1) (a) Newman, M. S.; Lutz, W. B.; Lednicer, D. *J. Am. Chem. Soc.* **1955**, *77*, 3420. (b) Newman, M. S.; Lednicer, D. *J. Am. Chem. Soc.* **1956**, *78*, 4765.

(2) (a) Dreher, S. D.; Katz, T. J.; Lam, K.-C.; Rheingold, A. L. *J. Org. Chem.* **2000**, *65*, 815. (b) Terfort, A.; Görls, H.; Brunner, H. *Synthesis* **1997**, 79. (c) Reetz, M. T.; Beuttenmüller, E. W.; Goddard, R. *Tetrahedron Lett.* **1997**, *38*, 3211. (d) Reetz, M. T.; Sostmann, S. *J. Organomet. Chem.* **2000**, *603*, 105.

(3) Sato, I.; Yamashima, R.; Kadowaki, K.; Yamamoto, J.; Shibata, T.; Soai, K. *Angew. Chem. Int. Ed.* **2001**, *40*, 1096.

(4) (a) Ben Hassine, B.; Gorsane, M.; Pecher, J.; Martin, R. H. *Bull. Soc. Chim. Belg.* **1986**, *95*, 547. (b) Ben Hassine, B.; Gorsane, M.; Pecher, J.; Martin, R. H. *Bull. Soc. Chim. Belg.* **1987**, *96*, 801. (c) Ben Hassine, B.; Gorsane, M.; Pecher, J.; Martin, R. H. *Bull. Soc. Chim. Belg.* **1985**, *994*, 597.
(d) Ben Hassine, B.; Gorsane, M.; Pecher, J.; Martin, R. H. *Bull. Soc. Chim. Belg.* **1985**, *94*, 759.

(5) (a) Yamamoto, K.; Ikeda, T.; Kitsuki, T.; Okamoto, Y.; Chikamatsu, H.; Nakazaki, M. *J. Chem. Soc., Perkin Trans. 1* **1990**, 271. (b) Tanaka, K.; Shogase, Y.; Osuga, H.; Suzuki, H.; Nakanishi, W.; Nakamura, K.; Kawai, Y. *J. Chem. Soc., Chem. Commun.* **1995**, 1873.

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(6) (a) Nuckolls, C.; Katz, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 9541. (b) Nuckolls, C.; Katz, T. J.; Verbiest, T.; Van Elshocht, S.; Kuball, H.-G.; Kiesewalter, S.; Lovinger, A. J.; Persoons, A. *J. Am. Chem. Soc.* **1998**, *120*, 8656. (c) Verbiest, T.; Sioncke, S.; Persoons, A.; Vyklicky, L.; Katz, T. J. *Angew. Chem. Int. Ed.* **2002**, *41*, 3882. (d) Fasel, R.; Parschau, M.; Ernst, K.-H. *Angew. Chem. Int. Ed.* **2003**, *42*, 5178.

(7) Urbano, A. *Angew. Chem. Int. Ed.* **2003**, *42*, 3986.

(8) Representative examples: (a) Mikes, F.; Boshart, G.; Gil-Av, E. *J. Chem. Soc., Chem. Commun.* **1976**, 99. (b) Nakazaki, M.; Yamamoto, K.; Ikeda, T.; Kitsuki, T.; Okamoto, Y. *J. Chem. Soc., Chem. Commun.* **1983**, 787. (c) Stammel, C.; Fröhlich, R.; Wolff, C.; Wenck, H.; de Meijere, A.; Mattay, J. *Eur. J. Org. Chem.* **1999**, 1709.

(9) Nuckolls, C.; Katz, T. J.; Katz, G.; Collings, P. J.; Castellanos, L. *J. Am. Chem. Soc.* **1999**, *121*, 79.

(10) (a) Bestmann, H. J.; Both, W. *Chem. Ber.* **1974**, *107*, 2923. (b) Stara, I. G.; Stary, I.; Tichy, M.; Zavada, J.; Hanus, V. *J. Am. Chem. Soc.* **1994**, *116*, 5084. (c) Tanaka, K.; Suzuki, H.; Osuga, H. *J. Org. Chem.* **1997**, *62*, 4465. (d) Gingras, M.; Dubois, F. *Tetrahedron Lett.* **1999**, *40*, 1309. (e) Ogawa, Y.; Toyama, M.; Karikomi, M.; Seki, K.; Haga, K.; Uyehara, T. *Tetrahedron Lett.* **2003**, *44*, 2167.

(11) Teply, F.; Stara, I. G.; Stary, I.; Kollarovic, A.; Saman, D.; Vyskocil, S.; Fiedler, P. *J. Org. Chem.* **2003**, *68*, 5193.

(12) (a) Cochez, Y.; Jespers, J.; Libert, V.; Mislow, K.; Martin, R. H. *Bull. Soc. Chim. Belg.* **1975**, *84*, 1033. (b) Tanaka, K.; Osuga, H.; Suzuki, H. *Tetrahedron: Asymmetry* **1993**, *4*, 1843. (c) Tanaka, K.; Osuga, H.; Shogase, Y.; Suzuki, H. *Tetrahedron Lett.* **1995**, *36*, 915. (d) Tanaka, K.; Kitahara, Y.; Suzuki, H.; Osuga, H.; Kawai, Y. *Tetrahedron Lett.* **1996**, *37*, 5925. (e) Carreño, M. C.; García-Cerrado, S.; Urbano, A. *J. Am. Chem. Soc.* **2001**, *123*, 7929. (f) Carreño, M. C.; García-Cerrado, S.; Urbano, A. *Chem. Commun.* **2002**, 1412. (g) Carreño, M. C.; García-Cerrado, S.; Urbano, A. *Chem.–Eur. J.* **2003**, *9*, 4118.

(13) (a) Martin, R. H.; Marchant, M. J. *Tetrahedron* **1974**, *30*, 347. (b) Martin, R. H. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 649. (c) Borkent, J. H.; Laarhoven, W. H. *Tetrahedron* **1978**, *34*, 2565.

(14) (a) Goedicke, Ch.; Stegmeyer, H. *Tetrahedron Lett.* **1970**, *12*, 937. (b) Bestmann, H. J.; Both, W. *Chem. Ber.* **1974**, *107*, 2923.

(15) (a) Nakazaki, M.; Yamamoto, K.; Ikeda, T.; Kitsuki, T.; Okamoto, Y. *J. Chem. Soc., Chem. Commun.* **1983**, 787. (b) Yamamoto, K.; Ikeda, T.; Kitsuki, T.; Okamoto, Y.; Chikamatsu, H.; Nakazaki, M. *J. Chem. Soc., Perkin Trans. 1* **1990**, 271.

(16) Sugimura, T. *Eur. J. Org. Chem.* **2004**, 1185.

(17) (a) Sugimura, T.; Yamada, H.; Inoue, S.; Tai, A. *Tetrahedron: Asymmetry* **1997**, *8*, 649. (b) Michaud, G.; Bulliard, M.; Ricard, L.; Genêt, J.-P.; Marinetti, A. *Chem.–Eur. J.* **2002**, *8*, 3327.

(18) Sugimura, T.; Hagiya, Y.; Sato, Y.; Tei, T.; Tai, A.; Okuyama, T. *Org. Lett.* **2001**, *3*, 37.

(19) (a) Sugimura, T.; Tei, T.; Mori, A.; Okuyama, T.; Tai, A. *J. Am. Chem. Soc.* **2000**, *122*, 2128. (b) Tei, T.; Sato, Y.; Hagiya, K.; Tai, A.; Okuyama, T.; Sugimura, T. *J. Org. Chem.* **2002**, *67*, 6593.

(20) An analogous bis-Wittig reaction has already been applied to an achiral substrate for the synthesis of [6]helicene derivatives: Reetz, M. T.; Sostmann, S. *Tetrahedron* **2001**, *57*, 2515.

(21) (a) Flammang-Barbieux, M.; Nasielski, J.; Martin, R. H. *Tetrahedron Lett.* **1967**, 743. (b) Liu, L.; Yang, B.; Katz, T. J.; Poindexter, M. K. *J. Org. Chem.* **1991**, *56*, 3769.

(22) Perylenes are the usual side-products of analogous photocyclisation reactions: Laarhoven, W. H.; Cuppen, T. J. H. M.; Nivard, R. J. F. *Tetrahedron* **1970**, *26*, 1069.

(23) Janke, R. H.; Haufe, G.; Würthwein, E.-U.; Borkent, J.-H. *J. Am. Chem. Soc.* **1996**, *118*, 6031.

(24) Maercker, A. *Org. React.* **1965**, *14*, 270.

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