Functionalized Heptahelicene Bidentate Ligands and Chiral Building Blocks

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Abstract: Syntheses of functionalized heptahelicenes **11**–**13** disubstituted at positions 3 and 16 by hydroxymethyl or bromomethyl functions are described as a new series of bidentate ligands or chiral building blocks. Those functions are flexible enough and properly positioned for a possible chelate effect onto a metal center. Photocyclodehydrogenation, phase-transfer-catalyzed Wittig reaction, and use of THP groups for increasing solubility and further functional group transformations were key elements in this synthetic route.

Key words: arenes, chirality, helical structures, chelates, supramolecular chemistry

The first carbohelicene, namely pentahelicene, was prepared in 1918.[2] However, it took almost 20 and 30 years, respectively, to report hexahelicene[3] and heptahelicene[4] (Figure 1). The first photocyclodehydrogenation reaction of stilbene-like derivatives leading to heptahelicene was shown in 1967 but one of us also reported a non-photochemical method in 1999.[4b] Helicenes are not only aesthetic and intriguing helicoidal polyaromatics, often studied in theoretical chemistry because of their distorted π-system, but they became the centerfold of newly expanding research in the fields of asymmetric catalysis,[5] advanced materials,[6] molecular electronics (dendrimers, conductors, polymers, liquid crystals, molecular monolayers and films, etc.), optics (OLED, chiroptical switches, NLO, etc.) and supramolecular helicoidal chemistry.[7]

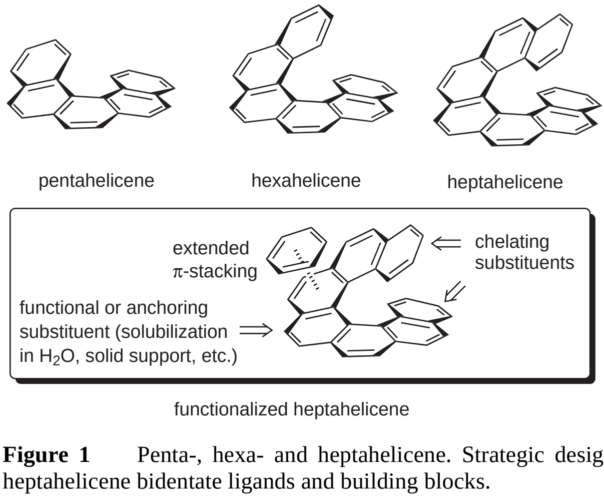

Figure 1 Penta-, hexa- and heptahelicene. Strategic design of heptahelicene bidentate ligands and building blocks.

In spite of some efforts and modest results in asymmetric catalysis, numerous applications and improvements are still sought in helicene chemistry. The heptahelicene series was particularly neglected, with only a few [7]carbohelicenes synthesized, but none of them as bidentate ligand.[8] As a consequence, our objective was to disclose the first synthesis of functionalized heptahelicenes as bidentate ligands and to describe new helicoidal chiral intermediates. Several reasons guided us toward those targets: a) in spite of early results as excellent chiral auxiliaries two decades ago, heptahelicenes were not put forward again in asymmetric synthesis until lately;[9] b) high optical rotation values ($[\alpha]_D$ ^{25} +6200 for heptahelicene)[10] would allow a better precision in evaluating enantio- and diastereopurities; c) good π-donor abilities helped in resolving hexahelicene with chiral TAPA[3b]; it was indicative that π-stacking could serve as a key binding element for pre-assembling aromatic substrates and catalysts prior to asymmetric reactions; d) because of distorded π-systems, the solubility of such compounds are usually better than their polyaromatic linear analogues (e.g. pentacene); e) heptahelicenes could be used at relatively high temperatures (<150 °C, $\Delta\Delta H^{\neq}_{rac}$ = 40.5 kcal/mol[11]) because of good stereochemical stability, compared to some binaphthyl counterparts; f) their helicoidal nature could serve as a large chiral template for helicoidal recognition, chiral induction and molecular assemblies in supramolecular chemistry and advanced materials.

As shown in Scheme 1, a preliminary study in the synthesis of functionalized heptahelicenes was achieved. After molecular modeling experiments (MM2 calculations), it appeared to us that a direct connection of a coordinating heteroatom ligand (O, N, P, etc.) to the terminal benzene rings, would not lead to a favorable geometry for a strong chelate effect on a metal center. Previous experiments in the hexahelicene series did not also lead to the best results using this approach. The use of benzylic-type functions at positions 3 and 16 would give enough degree of freedom to help in the adjustment of the ligand onto a metal center, as shown in Figure 2. Molecular mechanic calculations of **11** showed an approximative O–O distance of 3.9 Å, which was indicative of a possible chelate arrangement on a metal center. The closest distance between carbon atoms of terminal phenyl rings was about 3.5 Å, indicating a distorted and weak π-stacking.

As shown in the next paragraphs, short syntheses of 3,16- and 3,9,16-substituted heptahelicenes are presented. Starting from 2,6-naphthalene dicarboxylic acid (**4**), a

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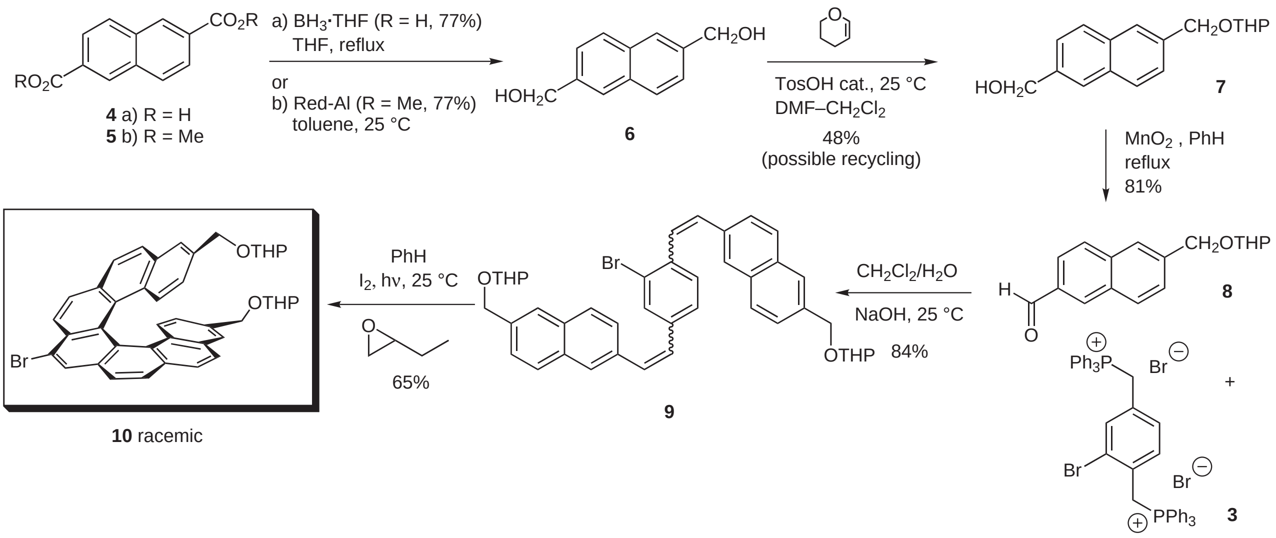


Scheme 1 Simple and efficient preparation of functionalized heptahelicene by photocyclodehydrogenation.

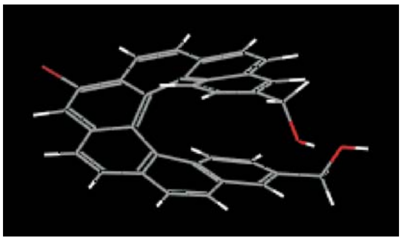
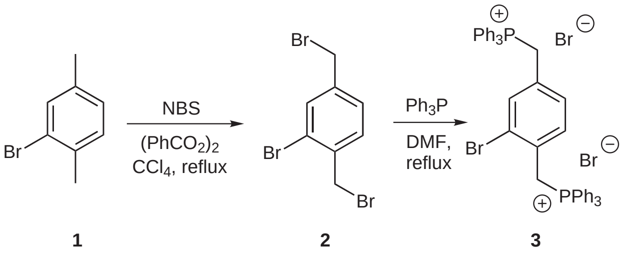


Figure 2 MM2-calculated structure of **11**.

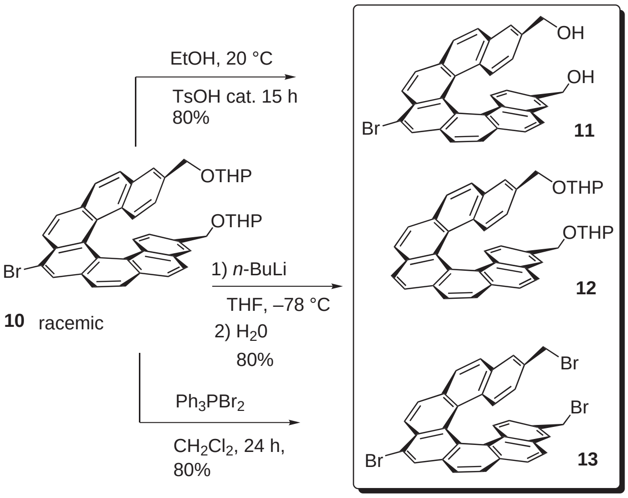
reduction with BH_3·THF (or generation in situ from $NaBH_4$ and BF_3·OEt_2) produced the corresponding 2,6-bis(hydroxymethyl) naphthalene (**6**)[12] in a 77% yield on a multiple gram scale. By analogy, 2,6-bis(carbomethoxy) naphthalene (**5**) was easily reduced to the same diol in a 82% yield (or 78% yield, 50 g scale) by using Red-Al® in toluene at room temperature for 30 minutes. A mono-selective THP protection of the diol was achieved with dihydropyran (0.5 equiv). In order to dissolve the substrate, a DMF–CH_2Cl_2 (3:2 v/v) solution was needed for better homogeneity at 20 °C. In the best case, a yield of 48% of **7** was obtained along with unreacted diol **6** and di-THP by-product. A trituration in chloroform allowed the isolation of insoluble diol **6** after filtration. Mono- and di-THP derivatives could easily be separated on silica gel (CH_2Cl_2–EtOAc, 80:20). Acidic methanolysis of the di-THP product provided diol **6** which could be combined to the first crop and recycled toward a mono-protection. Mono-protected diol **7** could be oxidized with activated MnO_2 in refluxing benzene for three hours. After filtration on silica gel, the corresponding aldehyde **8**[13] was produced on a gram scale as a sufficiently pure product (81% yield) for a double Wittig reaction with reagent **3** (Scheme 2). The latter was easily prepared on a large scale from a double benzylic bromination of 1-bromo-2,5-dimethylbenzene with NBS,[8m] followed by triphenylphosphine in refluxing DMF; the bis(triphenylphosphonium) salt **3** being smoothly produced by a double nucleophilic reaction. A double Wittig reaction generated the bis(stilbene)-type derivative **9**[14] in a 84% yield under phase-transfer conditions in an aqueous mixture. The 'bromine auxiliary' strategy[15] was used for a better regioselectivity and reactivity in the photocyclodehydrogenation reaction, but more interestingly, it also allowed anchoring groups for further chemical manipulations (Figure 1, such as an attachment to a solid support for heterogeneous enantiocatalysis or for introducing solubilizing groups in aqueous conditions). Compound **9** showed a greenish fluorescent aspect in solution. The use of THP protecting groups helped in two ways: to improve solubility of this intermediate before a double photocyclization and to prevent some adventitious side reactions. Concerning the key-step photochemical reaction, we used an epoxide to trap the acid formed, and iodine to ensure the oxidative aromatization.[6m] Doubly protected and brominated heptahelicene **10**[16] was thus produced as a yellow solid in a 65% yield.



Scheme 2 Preparation of bisphosphonium salt **3**.

Debromination of **10** was achieved by treatment with *n*-BuLi in THF at –78 °C, followed by quenching with H_2O. It provided a protected C_2-symmetric bifunctionalized chiral building block **12**. The choice and importance of THP in ensuring an adequate solubilization at low temperature played a major role in the polyarene anion formation through a bromine–lithium exchange reaction.

An acid-catalyzed ethanolic deprotection of **10** generated 9-bromo-3,16-bis(hydroxymethyl) heptahelicene **11**[17] in a 78% yield. This deprotection produced an interesting functionalized diol, which could eventually be tested for complexation with a metal center (Scheme 3).



Scheme 3 Synthesis of functionalized heptahelicene chiral bidentate ligands and building blocks.

A straightforward functionalization through an activation strategy leads us to convert both CH$_2$O–THP groups into benzylic bromide functions (CH$_2$Br) as in **13**. Triphenylphosphine dibromide smoothly achieved that reaction in a 80% yield, at room temperature for 24 hours. This transformation set up possibilities for introducing various metal-coordinating groups such as phosphine or amino groups. Additionally, it also opened up new opportunities for promoting C–C coupling reactions (Suzuki, Stille, Neghishi, etc.) or carbon–heteroatom bond formations (C–O, C–S, C–N, C–P, etc.). For instance, an Arbuzov reaction with diphenylethoxyphosphine in refluxing toluene followed by a deoxygenative reduction with HSiCl$_3$ might allow the formation of 3,16-bis(diphenylphosphino) groups.

In summary, new functionalized heptahelicenes were produced in a synthetic sequence involving gram-scale preparation of intermediates. They represent the first chiral bidentate ligands in the heptahelicene series, after careful positioning of coordinating substituents. Among the mentioned properties are possible π-stacking with aromatic substrates, a large chiral template, use as a building block for inducing chirality in supramolecular assemblies and use in the preparation of new helicoidal colored materials.

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Alcohol **7** (2.221 g, 8.16 mmol) was dissolved in distilled benzene (35 mL) at 20 °C and MnO_2 (3.60 g, 50.7 mmol) was added to the solution. The resulting black suspension was refluxed for 3 h. After filtration on a short column of silica gel and evaporation of solvent, compound **8** was recovered as a solid (1.789 g, 6.62 mmol, 81% yield). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.50–2.00$ (6 H, m, CH_2), 3.50–3.65 (1 H, m, CH_2O), 3.90–4.05 (1 H, m, CH_2O), 4.70 (1 H, d, *J* = 12.8 Hz, naphthyl-CH_2O), 4.77 (1 H, app t, *J* = 3.3 Hz, O–CH–O), 4.98 (1 H, d, *J* = 12.8 Hz, naphthyl-CH_2O), 7.58 (1 H, dd, *J* = 1.5 Hz, 8.4 Hz, H arom.), 7.85–8.00 (4 H, m, H arom.), 8.31 (1 H, s, H arom.), 10.14 (1 H, s, CHO). ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 19.4$ (CH_2), 25.5 (CH_2), 30.6 (CH_2), 62.2 (CH_2–O), 68.6 (CH_2–O), 98.1 (O–CH–O), 123.1 (CH arom.), 126.2 (CH arom.), 126.9 (CH arom.), 129.0 (CH arom.), 129.6 (CH arom.), 130.7 (C arom.), 132.1 (C arom.), 134.1 (CH arom.), 136.5 (C arom.), 139.7 (C arom.), 192.0 (CHO). MS (EI, 70 eV): *m/z* (%) = 270 (4.6) [M^+], 186 (8.5) [$M^+ - C_5H_8O$], 169 (100) [M^+ – OTHP], 141 (35) [M^+ – CHO – OTHP]. $R_f = 0.63$ (TLC, SiO_2, CH_2Cl_2–EtOAc, 95:5).

(14) **Synthesis of Bis(stilbene) 9.**
At 20 °C, aldehyde **8** (2.658 g, 9.84 mmol) was dissolved in CH_2Cl_2 (50 mL), followed by addition of phosphonium salt **3** (4.266 g, 4.92 mmol) and an aq solution of 5 M KOH (50 mL). After vigorous stirring for 15 h, the organic layer was separated and dried over anhyd $MgSO_4$. After filtration and evaporation of the solvent, the expected bis(stilbene) was purified on a SiO_2 flash chromatography column using CH_2Cl_2–MeOH (98:2) as eluent. Bis(stilbene) (**9**) was obtained as a solid (isomeric mixture, 2.85g. 4.13 mmol, 84% yield). ^1H NMR (250 MHz, $CDCl_2CDCl_2$, isomeric mixture): $\delta = 1.40–2.00$ (m, 12 H, CH_2), 3.40–3.60 (m, 2 H, CH_2–O), 3.85–4.00 (m, 2 H, CH_2–O), 4.50–4.75 (m, 4 H, naphthyl-CH_2, O–CH–O), 4.85–5.00 (m, 2 H,), 6.90–7.30 (m, 2 H, CH=CH), 7.40–8.00 (m, 16 H, H arom.), 8.26 (s, 1 H, H arom. CH=CBr). ^{13}C NMR (62.9 MHz, $CDCl_2CDCl_2$, isomeric mixture): $\delta = 19.4$ (CH_2), 25.4 (CH_2), 30.6 (CH_2), 62.2 (CH_2–O), 68.7 (CH_2–O), 97.9 (O–CH–O), 123.0 (CH arom.), 123.70–139.83 (multiple signals from an isomeric mixture). MS (EI, 70 eV): *m/z* (%) = 690 (3.4) [M^+ (^{81}Br)], 688 (3.2) [M^+ (^{79}Br)], 606 (13) [$M^+ (^{81}Br) - C_5H_8O$], 604 (14) [$M^+ (^{79}Br) - C_5H_8O$], 522 (88) [$M^+ (^{81}Br) - C_{10}H_{16}O_2$], 520 (100) [$M^+ (^{79}Br) - C_{10}H_{16}O_2$]. HRMS (EI, 70 eV): *m/z* (%) = 690.2193 [M^+ (^{81}Br), exp.; 690.2168 calcd], 688.2192 [M^+ (^{79}Br), exp.; 688.2188 calcd], 522.1004 [$M^+ (^{81}Br) - C_{10}H_{16}O_2$, exp.; 522.1017 calcd], 520.0999 [$M^+ (^{79}Br) - C_{10}H_{16}O_2$, exp.; 520.1038 calcd].

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(16) **Photocyclodehydrogenation Procedure to 10.**
In a photochemical reactor equipped with a water cooling jacket and a stir bar, compound **9** (0.420 g, 0.609 mmol), iodine (309 mg, 1.22 mmol) and 1,2-epoxybutane (8.0 mL) were dissolved in high purity grade benzene (700 mL). Nitrogen gas was bubbled through the solution within 30 min while stirring vigorously for removing oxygen prior to irradiation with a high-pressure mercury lamp for 3 h. When the reaction was complete, excess of iodine was reduced with a 15% aqueous solution of $Na_2S_2O_3$ (20 mL). The aqueous phase was separated and the organic layer dried over $MgSO_4$. After filtration and evaporation of solvent, the crude was purified by flash chromatography on silica gel with CH_2Cl_2–EtOAc (98:2) and then (95:5). Helicene **10** was obtained as a yellow solid (0.270 g, 0.393 mmol, 65% yield). ^1H NMR (250 MHz, $CDCl_2CDCl_2$): $\delta = 1.40–2.00$ (m, 12 H, CH_2), 3.50 (m, 2 H, CH_2–O), 3.85 (m, 2 H, CH_2–O), 4.36 (d, *J* = 12.4 Hz, 2 H, naphthyl-CH_2), 4.52 (m, 4 H, O–CH–O, naphthyl-CH_2), 6.39 (d, *J* = 7.0 Hz, 1 H, H arom.), 6.42 (d, *J* = 7.7 Hz, 1 H, H arom.), 6.98 (d, *J* = 7.3 Hz, 2 H, H arom.), 7.22 (s, 1 H, H arom.), 7.24 (s, 1 H, H arom), 7.70 (d, *J* = 8.8 Hz, 1 H, H arom.), 7.74 (d, *J* = 8.8 Hz, 1 H, H arom.), 7.40–7.50 (m, 2 H, H arom.), 7.87 (d, *J* = 8.0 Hz, 1 H, H arom.), 7.92 (d, *J* = 8.0 Hz, 1 H, H arom.), 7.99 (d, *J* = 8.8 Hz, 1 H, H arom.), 8.32 (s, 1 H, H arom. CH=CBr), 8.42 (d, *J* = 8.4 Hz, 1 H, H arom.). ^{13}C NMR (62.9 MHz, $CDCl_2CDCl_2$, DEPT): $\delta = 19.3$ (CH_2), 25.5 (CH_2), 30.6 (CH_2), 62.0 (CH_2O), 67.7 (CH_2O), 96.9 (OCHO), 121.1 (C arom.), 123.7 (CH arom.), 123.9 (CH arom.), 124.0 (CH arom.), 124.3 (CH arom.), 124.6 (C arom.), 125.2 (CH arom.), 125.3 (CH arom.), 125.4 (CH arom.), 125.6 (CH arom.), 125.9 (CH arom.), 126.9 (C arom.), 127.4 (CH arom.), 127.6 (C arom.), 127.9 (CH arom.), 128.3 (CH arom.), 128.4 (C arom.), 128.6 (C arom.), 129.9 (CH arom.), 130.2 (C arom.), 130.8 (C

arom.), 131.4 (C arom.), 131.5 (C arom.), 131.9 (C arom.), 135.1 (C arom.). MS (EI, 70 eV): *m/z* (%) = 686 (45) [M^+ (^{81}Br)], 684 (43) [M^+ (^{79}Br)], 602 (41) [M^+ (^{81}Br) – C_5H_8O], 600(39) [M^+ (^{79}Br) – C_5H_8O], 520 (25) [M^+ (^{81}Br) – 2OTHP], 518 (30) [M^+ (^{79}Br) – 2OTHP]. R_f = 0.42 (TLC, SiO_2, CH_2Cl_2–EtOAc, 98:2).

(17) **9-Bromo-3,16-bis(hydroxymethyl)heptahelicene (11).** Compound **10** (83.2 mg, 0.121 mmol) was added to EtOH (25 mL) as a suspension at 20 °C, followed by *p*-toluenesulfonic acid hydrate as catalyst (5.0 mg, 0.0026 mmol). After vigorous stirring for 15 h, the solvent was evaporated and crude diol **11** was purified by flash chromatography on SiO_2 with CH_2Cl_2–EtOAc (80:20) and then pure EtOAc as eluent. Pure diol **11** was obtained (50.1 mg, 0.097 mmol, 80% yield). ^1H NMR (250 MHz, DMSO-d_6): δ = 4.35 (4 H, CH_2OH), 5.10 (2 H, large, OH), 6.36 (dd, *J* = 1.1 Hz, *J* = 8.8 Hz, 2 H, CH), 6.86 (dd, *J* = 2.2 Hz, *J* = 8.8 Hz, 2 H, CH), 7.34 (2 H, app. s, CH arom.), 7.61 (1 H, d, *J* = 8.0 Hz, CH), 7.64 (d, 1 H, *J* = 8.0 Hz, CH), 7.84 (d, 1 H, *J* = 8.9 Hz, CH), 7.88 (d, 1 H, *J* = 9.1 Hz, CH), 8.10 (s, 2 H, CH arom.), 8.18 (d, 1 H, *J* = 8.4 Hz, CH), 8.35 (d, 1 H, *J* = 8.4 Hz, CH), 8.57 (s, 1 H, CH arom.). ^{13}C NMR (62.9 MHz, DMSO-d_6, DEPT): δ = 62.4 (CH_2OH), 120.3 (C), 122.6 (CH), 123.1 (CH), 123.5 (CH), 124.1 (C), 124.6 (CH), 125.4 (CH arom.), 125.6 (CH), 125.7 (CH), 126.5 (C), 127.5 (C), 127.7 (C), 127.9 (CH), 128.4 (CH), 128.7 (CH), 128.8 (CH), 129.4 (C), 129.9 (CH), 130.5 (C), 130.6 (C), 131.6 (C), 131.7 (C), 139.5 (C), 139.6 (C). MS (EI, 70 eV): *m/z* (%) = 518 (66) [M^+ (^{81}Br)], 516 (100) [M^+ (^{79}Br)], 374 (60) [M^+ – HBr – CH_2OH –CH_2OH], 187 (51) [$C_{30}H_{14}^{++}$]. R_f = 0.05 (TLC, SiO_2, CH_2Cl_2–EtOAc, 4:1).