JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

Synthesis and Structural Elucidation of Diversely Functionalized 5,10-Diaza[5]Helicenes

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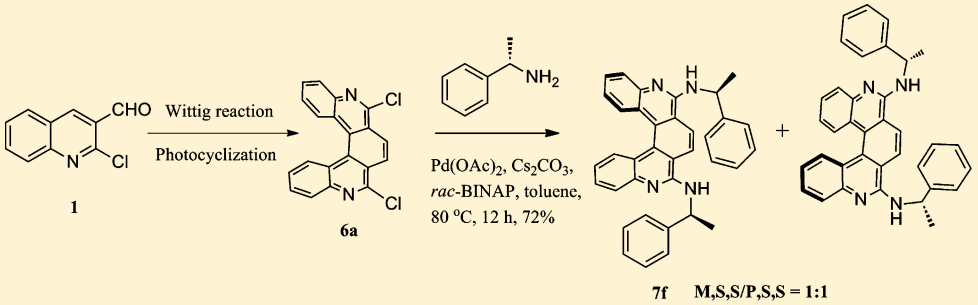
Supporting Information



ABSTRACT: Diversely functionalized diaza[5]helicenes have been synthesized starting from 6,9-dichloro-5,10-diaza[5]helicene, which was prepared from a readily available quinoline building block via Wittig reaction followed by photochemical electrocyclization. The helicene skeleton was substituted by a variety of O-, S-, N-, and C-centered nucleophiles using nucleophilic aromatic substitution reactions and palladium-catalyzed reactions like Suzuki coupling and Buchwald–Hartwig aminations. We have determined, using X-ray single-crystal diffraction, the crystal structures of the chloro- and methoxy-substituted diaza[5]helicenes. A resolution strategy based on diastereomeric separation by substitution of the dichloro derivative with a chiral amine has been shown.

INTRODUCTION

Helicene chemistry has emerged to be a field of great interest because of the fascinating properties of helicenes. These *ortho*-annulated polycyclic aromatic or heteroaromatic compounds are endowed with a inherently chiral π-conjugated system and thus show intriguing interactions with circularly polarized light while lacking a stereogenic center.[1] The inherent chirality originates from the steric repulsion between the *ortho*-condensed aromatic rings, which locks the system in either the *P*- or *M*-configuration.[2] Helicenes have been extensively studied due to their excellent self-assembly in the solid state,[3] their ability to behave as organic conductors,[4] and their use in optical resolutions[5] and molecular recognition.[6] Furthermore, enantiomerically pure helicenes form supramolecular architectures and exhibit second-order nonlinear optical and chiroptical properties,[7] which allows for one of their potential applications.[8] To exploit these properties, helicene chemistry is currently developing from fundamental science to applications. Previous work has focused on the experimental and also theoretical points of view.[9]

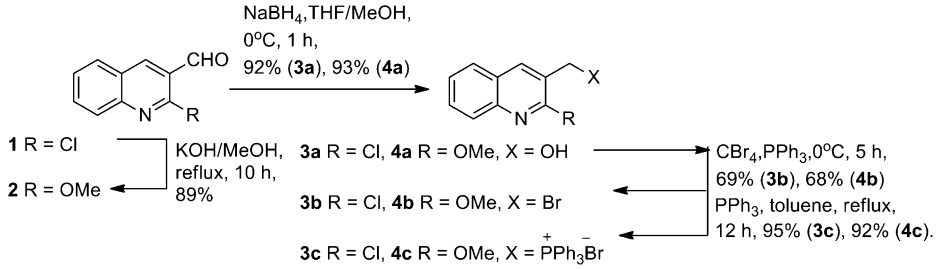
Azahelicenes constitute a subgroup of the heterahelicenes and have been intensively studied due to their prospective applications in fields such as light-emitting devices and chemosensors.[2,10] Indeed, nitrogen-containing heterahelicenes have gained interest because their complexes with transition-metal ions show interesting properties in harvesting visible light.[11] Furthermore, if the helicene backbone has more than one nitrogen atom, interesting supramolecular complexes can be formed. These molecules have a tendency toward $\pi-\pi^*$ stacking and the building of columnar systems, which can form the basis of materials for optoelectronic applications.[12] Applications of azahelicene derivatives have been reported in the field of asymmetric catalysis,[13,14] self-assembly,[15] and metal coordination complexes.[16]

In the past few years, various methods have been described for the synthesis of aza[5]helicenes, methods that include the classical photochemical procedure by Caronna et al.[17] and its expansion by Ben Hassine et al.,[18,19] and a versatile synthetic method based on Bu_3SnH-mediated coupling was developed by Harrowven and co-workers.[20] Furthermore, the [2 + 2 + 2] cycloisomerization of triynes,[21−23] the Stille–Kelly reaction of dihalogenated *cis*-stilbene type precursors,[14] and palladium-catalyzed arylations[24] are a few reported metal-catalyzed cyclizations. Examples of the synthesis of aza[5]helicenes and diaza[5]helicenes are known in the literature, but to the best of

Received: August 24, 2012
Published: October 24, 2012

   dx.doi.org/10.1021/jo301814m | J. Org. Chem. 2012, 77, 10176−10183

Scheme 1. Synthesis of Phosphonium Salts 3c and 4c



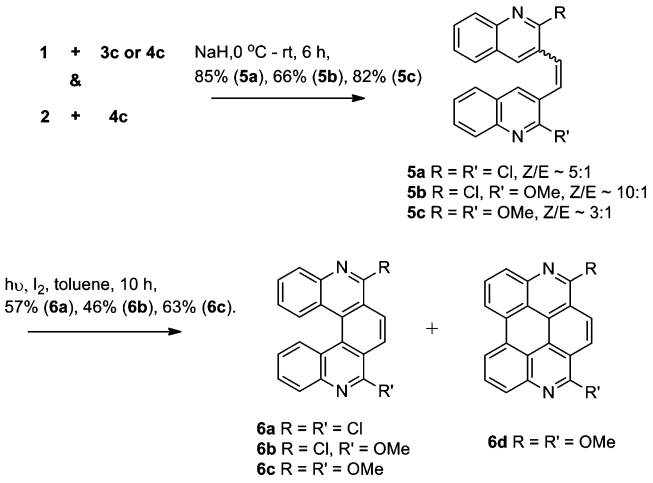
our knowledge, diaza[5]helicenes with flexibility toward functionalization, especially with S_NAr reactions, are not very well-known. Herein, we report the synthesis of symmetric and asymmetric diaza[5]helicenes with chloro or methoxy groups at the 6 and/or 9 position (numbering with respect to the parent diazahelicenes) of the helicene skeleton, which provides an opportunity for functionalization with a variety of oxygen-, sulfur-, nitrogen-, and carbon-centered nucleophiles by S_NAr reactions,[25] Suzuki coupling,[26] and Buchwald–Hartwig amination.[27]

RESULTS AND DISCUSSION

Our approach makes use of easily accessible 2-chloroquinoline-3-carboxaldehyde[28] **1** as a versatile building block. We employ the Wittig reaction and photochemical cyclization strategy. The cooperative *ortho* effect[20] of the halo and alkoxy groups controls the stereochemical course of the Wittig reaction leading to *Z*-selectivity, which in turn increases the yield of the photocyclization reactions. 2-chloroquinoline-3-carboxaldehyde **1** was prepared from acetanilide according to a literature procedure[28] and was converted to **2** by refluxing with a solution of KOH in MeOH to give 2-methoxyquinoline-3-carboxaldehyde in 89% yield. Aldehydes **1** and **2** were reduced to the corresponding alcohols **3a** and **4a** using sodium borohydride in THF/MeOH. The alcohols thus obtained were subsequently converted via the Appel reaction to the bromo derivatives (**3b** and **4b**), which were converted to their phosphonium salts by reaction with triphenylphosphine in refluxing toluene for 12 h in 95% (**3c**) and 92% (**4c**) yield (Scheme 1).

Wittig olefination[29] of the phosphonium salts **3c** and **4c** with 2-chloroquinoline-3-carboxaldehyde **1** and 2-methoxyquinoline-3-carboxaldehyde **2**, respectively, using NaH as base in CH_2Cl_2 gave the symmetric azastilbene derivatives **5a** (85%, *cis*/*trans* ~5:1) and **5c** (82%, *cis*/*trans* ~3:1) (Scheme 2). The alkenes were obtained with a high degree of *Z* selectivity. The effect of halo and alkoxy substituents to control the stereochemical outcome of the Wittig reaction is evident. Similarly, the reaction of 2-chloroquinoline-3-carboxaldehyde **1** with phosphonium salt **4c** gave the asymmetric diazastilbene derivative **5b** (*cis*/*trans* ~10:1) in 66% yield. Compounds **5a–c** were fully characterized by ^1H and ^{13}C NMR spectroscopy and HRMS. The ratio of the isomers was determined by integration of the ^1H NMR spectrum. Since *E–Z* isomerization occurs during the irradiation process, no specific configuration of the alkene precursor was required, but a high ratio of *cis*-isomer is beneficial because of the increased solubility as compared to the corresponding *trans*-isomer. The bis(quinolyl)ethene derivatives **5a–c** obtained were subjected to oxidative photocyclization[30] using a stoichiometric amount of iodine and toluene as the solvent (1.0 mM). The reaction mixture was irradiated at room temperature using a photochemical reactor

Scheme 2. Wittig Reaction and Photocyclization



(wavelength used is 350 nm) to obtain the diaza[5]helicenes **6a–c** in good yields. These compounds were fully characterized by NMR spectroscopy and HRMS and show good solubility in a variety of medium-polarity solvents such as CH_2Cl_2, EtOAc, and THF. A typical side product, diazabenzo[*ghi*]perylene, was obtained each time during the photocyclization step, its yield depending on the reaction time. We observed at most 8% of the perylene (isolated only in the case of **6d**) in each reaction run for 10 h, sufficient for the complete conversion of the starting material.

Increasing the reaction time also significantly increased the amount of diazabenzo[*ghi*]perylene **6d** formed. Nevertheless, complete conversion of **5c** to diazabenzo[*ghi*]perylene **6d** was not observed even after irradiation for 3 days. Each time, a significant amount of diaza[5]helicene **6c** remained unreacted (~25%). Complete spectroscopic characterization of diazabenzo[*ghi*]perylene **6d** was not possible due to its low solubility in various organic solvents, and it was characterized by HRMS.

Solid-State Structural Elucidation. Crystals of **6c** were obtained by diffusing pentane into a chloroform solution of the compound. The racemic compound crystallizes into the centrosymmetric triclinic space group *P*-1 with one molecule in the asymmetric unit (Figure 1). The distortion of the molecular structure (65.22°), defined by the sum of the three dihedral angles C17–C14–C4–C5, C14–C4–C5–C8, and C4–C5–C8–C13, is comparable to the value of a non-substituted diaza[5]helicene (61.34°).[17,31] Viewed down the *b*-axis, the molecules form columns of alternating opposite enantiomers, held together with different kinds of weak interactions (Figure 2). π–π stacking inside the columns occurs between pyridine rings, with centroid–centroid

dx.doi.org/10.1021/jo301814m | J. Org. Chem. 2012, 77, 10176–10183

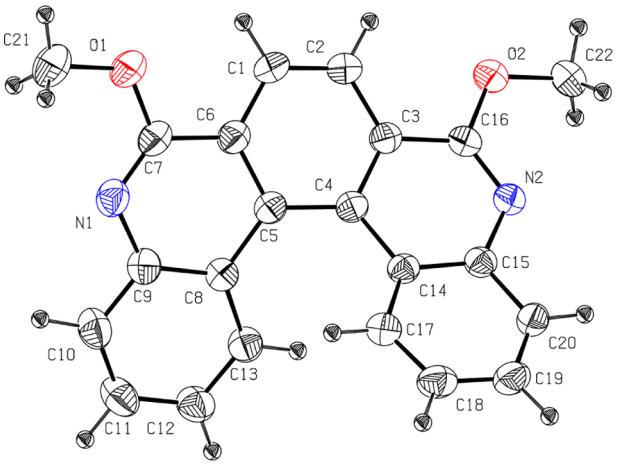


Figure 1. ORTEP view of molecular structure of **6c**, thermal ellipsoids drawn at 50% probability.

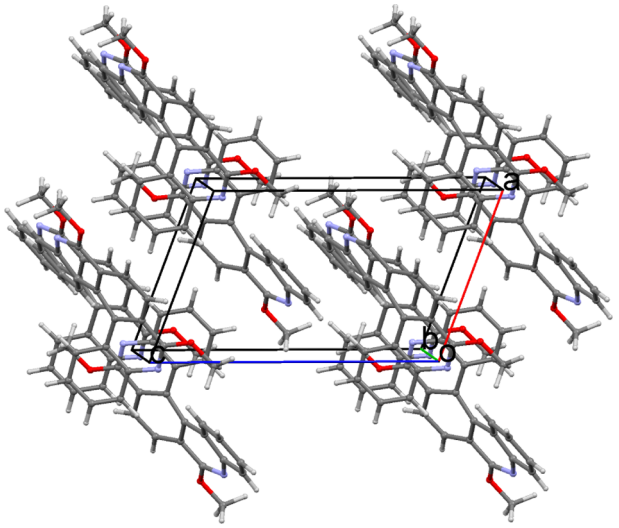


Figure 2. Packing in the crystals structure of **6c**, viewed along the *b*-axis.

distances of 4.528(2) and 4.685(2) Å. The different columns interlink with each other by several $\pi-\pi$ interactions starting from the benzene ring C(8)−C(13), with centroid−centroid distances ranging from 4.4469(19) Å to 5.425(2) Å. Additionally, a C−H···π interaction occurs between the hydrogen on C(12) and one of the pyridine rings (C12−H12···Cg1; with Cg1 the centroid of the pyridine ring containing N2, C12···Cg1 = 3.448(2) Å).

Crystals of **6a** were obtained by diffusing pentane into a chloroform solution of the compound. In comparison to **6c**, the methoxy groups are exchanged with chlorine atoms. The racemic compound crystallizes into the centrosymmetric triclinic space group *P*-1 with two molecules in the asymmetric unit (Figure 3). The distortion of the molecular structures (60.52° and 61.23°), defined by the sum of the three dihedral angles, C20−C16−C1−C6, C16−C1−C6−C9, C1−C6−C9−C13, C33−C29−C26−C21, C29−C26−C21−C36, and C26−C21−C36−C40 is again comparable to the value of a nonsubstituted diaza[5]helicene (61.34°).[17,31]

In comparison to the previous structure, the crystal structure now forms layers inside the crystal packing that are easily visible when looking down the *a*-axis (Figure 4). The layers are kept together by the nonclassical hydrogen bonds C(17)−H(17)···N(3) and C(30)−H(30)···N(2) with D···A distances of respectively 3.511(2) and 3.508(2) Å. Several $\pi-\pi$ interactions are seen between the different layers, mainly between the pyridine and outer benzene rings, with distances ranging from 3.7100(10) to 4.0898(10) Å. Remarkably, none of the chlorine atoms is involved in intermolecular (nonclassical) hydrogen bonding. Cl(1), however, is involved in a halogen−π interaction with the benzene ring C(15)−C(20) with a distance to the centroid of this ring of 3.9885(9) Å.

Functionalization of the Diaza[5]helicenes. Helicenes **6a−c** were obtained using the Wittig reaction-plus-photocyclization strategy in good yield and opened a new area for further functionalization. Though postcyclization functionalization is known for carbohelicenes,[32] it is an underexplored area for diaza[5]helicenes. Here, we report the easy functionalization via S_NAr reactions and palladium-catalyzed coupling reactions. In this way, a variety of O-, S-, N-, and C-centered nucleophiles can be bound to the diazahelicene platform (Scheme 3).

In the first set of reactions, some S_NAr reactions with O-, S-, and N-nucleophiles were tested (Scheme 3). Initially, 6,9-dichloro-5,10-diaza[5]helicene **6a** was reacted with NaSMe (2.5 equiv) in DMF, and the reaction mixture was stirred at 80 °C for 12 h. After column chromatographic purification, the desired diaza[5]helicene **7a** was obtained in 58% yield. S_NAr of thiophenol (2.5 equiv) on **6a** could be performed using K_2CO_3

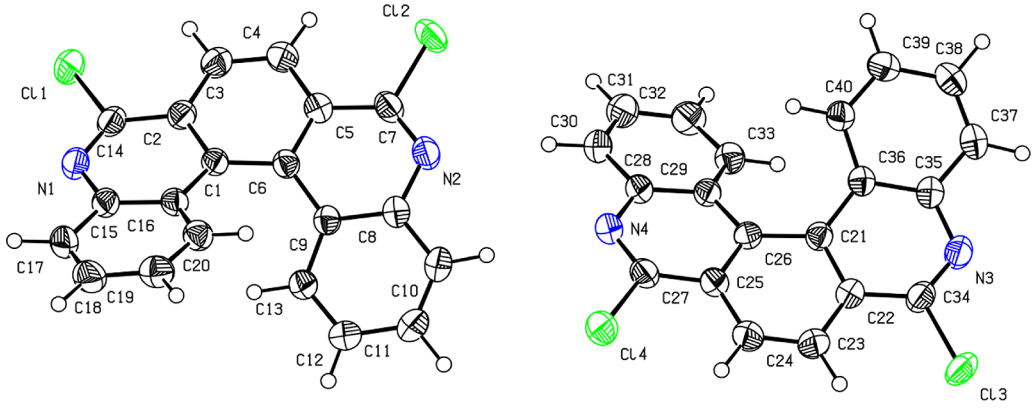


Figure 3. ORTEP view of the molecular structure of **6a**, showing two molecules in the asymmetric unit. Thermal ellipsoids are drawn at 50% propability.

dx.doi.org/10.1021/jo301814m | J. Org. Chem. 2012, 77, 10176−10183

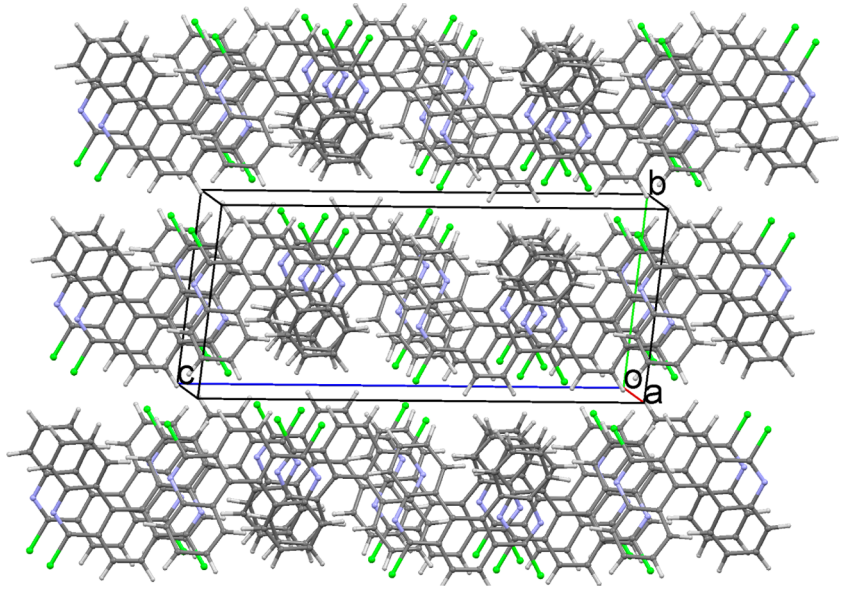
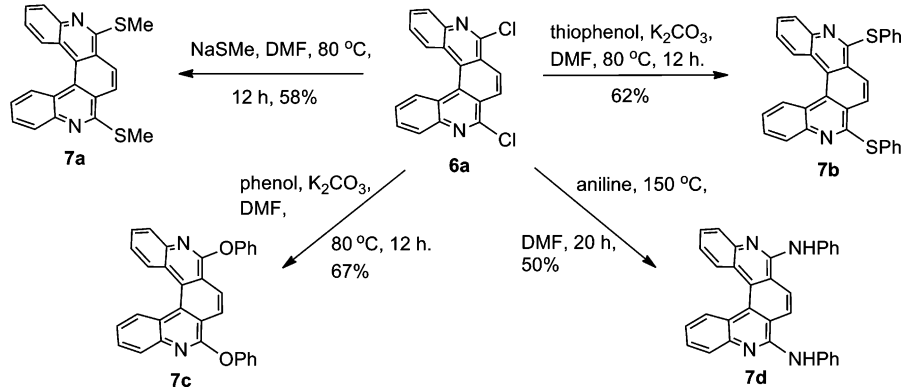
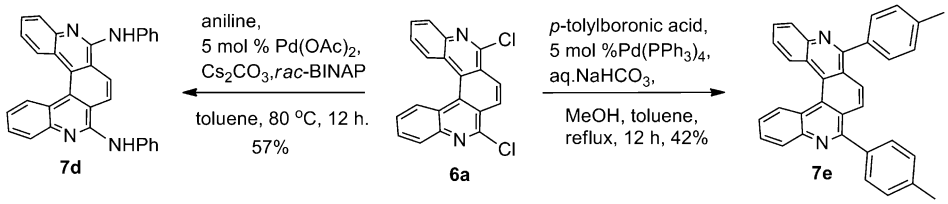


Figure 4. Packing in the crystal structure of **6a**, viewed along the *a*-axis.

Scheme 3. Functionalized Diaza[5]helicene Synthesized via S_NAr Reaction



Scheme 4. Functionalized Diaza[5]helicene Synthesized via Palladium-Catalyzed Suzuki Coupling and Buchwald–Hartwig Amination Reactions



as base and DMF as solvent, and the reaction mixture was stirred at 80 °C for 12 h to furnish product **7b** in 62% yield after column purification.

We opted for phenol as an O-nucleophile. S_NAr of phenolate (2.5 equiv) on **6a** could be performed using the conditions optimized for thiophenol affording compound **7c** in 67% yield. The introduction of N-nucleophiles appeared to be more challenging. Using different conditions with temperatures up to 100 °C, no satisfying results were obtained for the substitution of aniline. Only at 150 °C was a reaction between helicene **6a** and aniline observed. When an excess (5 equiv) of aniline was added to **6a** in DMF, and the reaction was kept at 150 °C for 20 h, diaza[5]helicene **7d** was obtained in 50% yield. All compounds obtained were characterized by NMR spectroscopy and HRMS.

In the second set, we explored the Suzuki and Buchwald–Hartwig amination reactions (Scheme 4). The substitution of both chloro groups at the 6 and 9 positions of the diaza[5]helicene were done by Suzuki cross-coupling reactions. An aryl group was introduced on the helicene skeleton using *p*-tolylboronic acid (2.5 equiv), $Pd(PPh_3)_4$, aqueous $NaHCO_3$, MeOH, and toluene. The reaction mixture was stirred for 12 h in refluxing toluene, yielding 42% of the desired product **7e**.

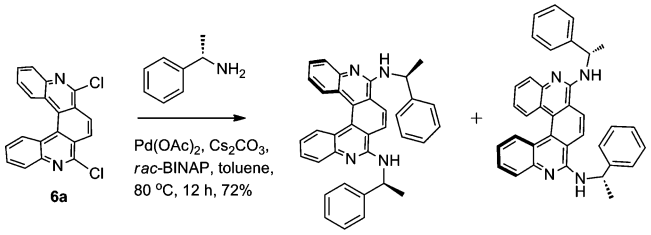
Next, we attempted to substitute with aniline via Buchwald amination conditions, which we expected to be more efficient than the previously attempted S_NAr reaction. 6,9-Dichloro-5,10-diaza[5]helicene was reacted with aniline using Cs_2CO_3, 5

dx.doi.org/10.1021/jo301814m | J. Org. Chem. 2012, 77, 10176–10183

mol % of $Pd(OAc)_2$, *rac*-BINAP, and toluene as the solvent. The reaction was run at 80 °C for 12 h to furnish the desired product **7d** in 57% yield. We indeed observed a significant decrease in the reaction time and an increase in yield with these conditions.

Resolution via Diastereomeric Separation. Expanding on the Buchwald−Hartwig amination, we envisaged that a chiral amine upon substitution to the racemic helicene skeleton would result in the formation of diastereomers of the helicene, which then could easily be separated via column chromatography. Thus, palladium-mediated amination of **6a** with L-(−)-α-methylbenzylamine using Cs_2CO_3, 5 mol % of $Pd(OAc)_2$, *rac*-BINAP, and toluene as the solvent furnished the desired product **7f** in 72% yield as a 1:1 mixture of diastereomers (M,S,S/P,S,S = 1:1; the ratio of isomers was determined by integration of the NMR spectra) (Scheme 5).

Scheme 5. Resolution via Diastereomeric Separation



The diastereomers formed were readily separated by silica gel column chromatography. It was interesting to see that the pure diastereomeric forms separated by column chromatography racemize/revert back to a 1:1 mixture at room temperature (~25 °C). HPLC of the diaza[5]helicenes at room temperature shows the presence of two helical isomers, but the separation was never up to the baseline, probably indicating their dynamic behavior (see the Supporting Information). To confirm this, flash column chromatography was performed at low temperatures (−10 to 0 °C) using a precooled solvent system, with the fractions being stored at −10 °C as soon as they were collected from the column. The solvent was removed under vacuum, the flasks being kept cold during evaporation. The fractions were kept at −10 °C before performing the racemization studies using temperature-dependent ^{1}H NMR spectroscopy. We determined the $t_{1/2}$ at 25 °C to be 26 min and the free energy barrier for racemization to be 22.4 kcal mol^{-1}. Analogously, we obtained a $t_{1/2}$ of 4.2 h at 10 °C (see the Supporting Information). The results obtained could be compared with the studies of Caronna et al.[33] on the monoaza[5]helicenes, which describe experimental and calculated CD measurements of a series of monoaza[5]helicenes and their half-lives ($t_{1/2}$) and energy barriers. Comparing our own observations with these literature values, it is clear that the insertion of one or more nitrogen atom decreases the enantiomeric stability of the helicene compared to the carbo[5]helicenes, which have a $t_{1/2}$ of 62.7 min at 57 °C.[33] Thus, the resolution strategy employed was indeed useful for the separation of the racemic diazahelicene, but due to a very low racemization barrier, the chiral forms cannot be handled easily at room temperature. From the 1:1 ratio that is the convergence point of the isomerization, it can be concluded that there is no significant energy difference between the two diastereomers, and the chiral group is too far removed from the helicene to have an influence.

CONCLUSION

In the present study, we have developed an efficient and flexible method for functionalization of the helicene skeleton with a variety of O-, S-, N-, and C-centered nucleophiles via straightforward methods. This strategy has also opened an opportunity for substitution of chiral groups leading to the resolution of the racemic helicene and exploration of various applications of azahelicenes. Though the rapid racemization at room temperature of the diaza[5]helicene derivatives employed in the present study is inevitable, the ease of elaboration of the substitution pattern introduces a platform for exploring this strategy in future work for synthesis and substitution of higher helicenes, thus illustrating the wide and unprecedented scope of the procedures.

EXPERIMENTAL SECTION

General Experimental Methods. NMR spectra were acquired on commercial instruments (300 and 400 MHz), and chemical shifts (δ) are reported in parts per million (ppm) referenced to tetramethylsilane (^{1}H) or the internal (NMR) solvent signal (^{13}C). Mass spectra were acquired using EI (70 eV ionization energy). Exact mass measurements were performed in the EI mode at a resolution of 10000 and also on a quadrupole orthogonal acceleration time-of-flight mass spectrometer. Samples were infused at 3 μL/min, and spectra were obtained in positive (or negative) ionization mode with a resolution of 15000 (fwhm). For column chromatography, 70−230 mesh silica 60 was used as the stationary phase. Chemicals received from commercial sources were used without further purification. K_2CO_3 (anhydrous, granulated) was finely ground (with mortar and pestle) prior to use. All solvents were used as received from commercial sources and not explicitly dried prior to use ($H_2O \leq 0.1\%$). All photochemical reactions were performed in the photochemical reactor equipped with interchangeable light sources (250 nm, 300 nm, 350 nm lamps).

Experimental and Characterization Data. *Synthesis of 2-Chloroquinoline-3-carboxaldehyde (**1**).* This compound has been prepared according to the literature procedure[28] from acetanilide. Material identity was confirmed by mp, MS, and ^{1}H and ^{13}C NMR.

*Synthesis of 2-Methoxyquinoline-3-carboxaldehyde (**2**).* 2-Chloroquinoline-3-carboxaldehyde **1** (5.0 g, 26.1 mmol) was added to a solution of KOH (2.12 g, 39.0 mmol) in MeOH (250 mL), and the reaction mixture was refluxed for 10 h. The solution was then cooled to room temperature and water (200 mL) was added to obtain a precipitate which was filtered, washed with water and Et_2O, and dried under vacuum to obtain **2** (4.30 g, 89%) as an off-white solid: mp 112−113 °C; MS (EI) m/z = 188 $[MH]^+$; HRMS (EI) calcd for $C_{11}H_9NO_2$ 187.0633, found m/z = 187.0609; ^{1}HNMR (300 MHz, $CDCl_3$, 25 °C, TMS) δ 10.45 (s, 1H; CHO), 8.56 (s, 1H; ArH), 7.87−7.81 (m, 2H; ArH), 7.72 (t, 1H, J = 6.9 Hz; ArH), 7.42 (t, 1H, J = 6.9 Hz; ArH), 4.18 (s, 3H; OMe); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS) δ 189.5 (CHO), 161.3, 149.1, 140.1, 132.7, 129.8, 127.4, 125.1 (C, CH), 53.9 (OCH_3).

*Synthesis of (2-Chloroquinolin-3-yl)methanol (**3a**). General Procedure.* To a stirred solution of aldehyde **1** (3.0 g, 15.6 mmol) in THF (50 mL) and MeOH (50 mL) was added sodium borohydride (0.888 g, 23.4 mmol), and the reaction mixture was stirred at 0 °C for 30 min. The reaction mixture was quenched with water and diluted with Et_2O, the organic layer was separated, washed with brine, dried over anhydrous $MgSO_4$, and evaporated to dryness to give **3a** (2.76 g, 92%) as a white solid. The compound obtained was used without further purification: mp 167−168 °C; MS (EI) m/z = 194 $[MH]^+$; HRMS (EI) calcd for $C_{10}H_8NOCl$ 193.0294, found m/z 193.0290; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.47 (s, 1H, ArH), 8.09 (d, 1H, J = 7.7 Hz, ArH), 7.96 (d, 1H, J = 8.4 Hz, ArH), 7.78 (t, 1H, J = 7.1 Hz, ArH), 7.65 (t, 1H, J = 7.5 Hz, ArH), 5.72 (s, 1H, OH), 4.70 (d, 2H, J = 4.6 Hz, CH_2OH); ^{13}C NMR (75 MHz, DMSO-d_6, 25 °C, TMS) δ 148.4,

dx.doi.org/10.1021/jo301814m | J. Org. Chem. 2012, 77, 10176−10183

146.0, 135.9, 133.9, 130.2, 127.9, 127.5, 127.3, 127.2 (C, CH), 59.9 (CH_2OH).

*Synthesis of 3-(Bromomethyl)-2-chloroquinoline (**3b**).* To a solution of (2-chloroquinolin-3-yl)methanol **3a** (2.50 g, 12.9 mmol) in dichloromethane was added tetrabromomethane (6.46 g, 19.35 mmol) and the reaction mixture cooled to 0 °C. Then a solution of triphenylphosphine (5.03 g, 19.35 mmol) in dichloromethane was added dropwise. The reaction mixture was stirred at room temperature for 5 h and then quenched with water. The organic layer was separated, washed with brine, dried over anhydrous $MgSO_4$, and evaporated to dryness and purified by column chromatography using EtOAc/petroleum ether (20:80) as eluent to furnish compound **3b** (2.34 g, 69%) as a white solid: mp 125−126 °C; MS (EI) m/z = 255 $[MH]^+$; HRMS (EI) calcd for $C_{10}H_7NBrCl$ 254.9450, found m/z 254.9469; ^1H NMR (300 MHz, $CDCl_3$) δ 8.24 (s, 1H, ArH), 8.02 (d, 1H, J = 8.1 Hz, ArH), 7.82 (d, 1H, J = 8.1 Hz, ArH), 7.75 (t, 1H, J = 7.5 Hz, ArH), 7.58 (t, 1H, J = 7.3 Hz, ArH), 4.72 (s, 2H, OH), 4.70 (d, 2H, CH_2Br); ^{13}C NMR (75 MHz,$CDCl_3$, 25 °C, TMS) δ 150.1, 147.4, 139.4, 138.7, 131.2, 129.6, 128.5, 127.6, 127.2 (C, CH), 29.9 (CH_2Br).

*(2-Chloroquinolin-3-yl)methyltriphenylphosphonium Bromide (**3c**).* To a solution of compound **3b** (2.0 g, 7.84 mmol) in toluene was added triphenylphosphine (5.8 g, 23.5 mmol), the reaction mixture was refluxed for 12 h and cooled to room temperature, and the solid obtained was filtered, washed with pentane, and dried under vacuum to furnish the phosphonium salt **3c** (3.8 g, 95%) as a white solid: mp 256−257 °C; MS (ESI+) m/z = 518 $[MH]^+$ (observed 518 − Br = 438); HRMS (EI) calcd for $C_{28}H_{22}NClP$ 438.1178 [M − Br], found m/z 438.1168 [M − Br]; ^1H NMR (300 MHz, $CDCl_3$) δ 8.70 (s, 1H, ArH), 7.91 (d, 1H, J = 8.1 Hz, ArH), 7.66−7.84 (m, 17H, ArH), 7.54 (t, 1H, J = 7.1 Hz, ArH), 5.98 (d, 2H, J = 14 Hz, CH_2P); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS) δ 150.9, 147.0, 147.9, 142.8, 142.7, 135.4, 134.3, 134.1, 131.4, 130.5, 130.3, 128.1, 127.6, 126.9, 120.1, 117.6, 116.4 (C, CH), 28.5, 27.84 (CH_2).

*Synthesis of (2-Methoxyquinolin-3-yl)methanol (**4a**).* Synthesis according to the general procedure leading to **3a**; 2-methoxyquinoline-3-carboxaldehyde **2** (3.0 g, 16.0 mmol), $NaBH_4$ (1.03 g, 27.2 mmol), THF/MeOH (1:1, 50 mL). Compound **4a** (2.8 g, 93%) was obtained as a white solid: mp 78−80 °C; MS (EI) m/z = 190 $[MH]^+$; HRMS (EI) calcd for $C_{11}H_{11}NO_2$ 189.0790, found m/z 189.0793; ^1H NMR (300 MHz, $CDCl_3$) δ 7.95 (s, 1H, ArH), 7.84 (d, 1H, J = 8.2 Hz, ArH), 7.71 (d, 1H, J = 7.5 Hz, ArH), 7.62 (t, 1H, J = 7.1 Hz, ArH), 7.32 (t, 1H, J = 7.8 Hz, ArH), 4.76 (d, 2H, J = 5.8 Hz, CH_2), 4.11 (s, 3H, OCH_3), 2.43 (t, 1H, J = 6.2 Hz, OH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS) δ 160.3, 146.0, 135.7, 129.3, 127.5, 125.3, 124.9, 124.3(C, CH), 61.4 (CH_2OH), 53.6 (OCH_3).

*Synthesis of 3-(Bromomethyl)-2-methoxyquinoline (**4b**).* Synthesis according to the general procedure leading to **3b**, (2-methoxyquinolin-3-yl)methanol **4a** (2.8 g, 14.7 mmol), tetrabromomethane (4.9 g, 14.7 mmol), triphenylphosphine (3.8 g, 14.7 mmol), and dichloromethane. Compound **4b** (2.5 g, 68%) was obtained as a white solid: mp 105−107 °C; MS (EI) m/z = 251 $[MH]^+$; HRMS (EI) calcd for $C_{11}H_{10}NBrO$ 250.9946, found m/z 250.9948; ^1H NMR (300 MHz, $CDCl_3$) δ 8.02 (s, 1H, ArH), 7.84 (d, 1H, J = 8.2 Hz, ArH), 7.70 (d, 1H, J = 7.9 Hz, ArH), 7.62 (t, 1H, J = 8.1 Hz, ArH), 7.38 (t, 1H, J = 7.7 Hz, ArH), 4.61 (s, 2H, CH_2Br), 4.14 (s, 1H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS) δ 159.9, 146.7, 138.8, 130.1, 127.6, 127.1, 124.5 (C, CH), 53.9 (OCH_3), 28.3 (CH_2Br).

*Synthesis of (2-Methoxyquinolin-3-yl)methyltriphenylphosphonium Bromide (**4c**).* Synthesis according to the general procedure leading to **3c**, 3-(bromomethyl)-2-methoxyquinoline **4b** (2.0 g, 7.9 mmol), triphenylphosphine (6.1 g, 23.8 mmol), and toluene. Phosphonium salt **4c** (3.7 g, 92%) was obtained as a white solid: mp 202−204 °C; MS (ESI+) m/z = 514 $[MH]^+$(obsd 514 − Br = 434); HRMS (EI) calcd for $C_{29}H_{25}NOP$ 434.1674 [M − Br], found m/z 434.1667 [M − Br]; ^1H NMR (300 MHz, $CDCl_3$) δ 8.42 (s, 1H, ArH), 7.83−7.56 (m, 18H, ArH), 7.33 (t, 1H, J = 7.7 Hz, ArH), 5.63 (d, 2H, J = 14.4 Hz, CH_2P), 3.45 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ 159.4, 146.2, 142.3, 135.0, 134.3, 134.1, 130.2, 130.1, 127.9, 126.8, 124.9, 124.5, 118.5, 117.4, 112.0, 111.9 (C, CH), 53.2 (OCH_3), 25.5, 24.8 (CH_2).

*Synthesis of 1,2-bis(2′-Chloroquinolin-3-yl)ethene (**5a**). General Procedure.* A solution of 2-chloroquinoline-3-carboxaldehyde **1** (0.50 g, 2.6 mmol) was added dropwise to a stirred solution of phosphonium salt **3c** (1.6 g, 3.1 mmol) and sodium hydride (0.187 g, 7.8 mmol) in dichloromethane at 0 °C, after which the reaction mixture was stirred for 6 h. The crude product was purified by silica gel column chromatography using EtOAc/petroleum ether (15:85) as eluent to obtain compound **5a** (0.780 g, 85%, Z/E ∼5:1) as a yellow solid: mp 216−217 °C; MS (ESI+) m/z = 351 $[MH]^+$; HRMS (EI) calcd for $C_{20}H_{12}N_2Cl_2$ 350.0378, found m/z 350.0385; ^1H NMR (300 MHz, $CDCl_3$, mixture of *cis* and *trans* isomers) δ 8.50 (s, 2H, vinylic protons of *trans* isomer), 8.05−7.91 (m, 4H, ArH), 7.80 (s, 4H, ArH), 7.80−7.60 (m, 4H, ArH), 7.47- 7.38 (m, 4H, ArH), 7.06 (s, 2H, vinylic protons of *cis* isomer); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.4, 130.8, 129.1, 128.3, 127.7, 127.3 (C, CH).

*Synthesis of 2-Chloro-3-(2-(2-methoxyquinolin-3-yl)vinyl)-quinoline (**5b**).* Synthesis according to the general procedure leading to **5a**, 2-chloroquinoline-3-carboxaldehyde **1** (0.50 g, 2.6 mmol), phosphonium salt **4c** (1.6 g, 3.1 mmol), and sodium hydride (0.187 g, 7.8 mmol) in dichloromethane. Purified by column chromatography using EtOAc/petroleum ether (20:80) to obtain **5b** (0.625 g, 66%, Z/E ∼10:1) as a yellow solid: mp 171−172 °C; MS (ESI+) m/z = 347 $[MH]^+$; HRMS (EI) calcd for $C_{21}H_{15}N_2ClO$ 346.0873, found m/z 346.0874; ^1H NMR (300 MHz, $CDCl_3$, mixture of *cis*−*trans* isomers) δ 8.47 (s, 1H, ArH), 8.28 (s, 1H, ArH), 8.00−7.97 (m, 2H, ArH), 7.89 (s, 2H, ArH), 7.80−7.77 (m, 2H, ArH), 7.70−7.66 (m, 2H, ArH), 7.63−7.62 (m, 2H, ArH), 7.57−7.54 (m, 2H, ArH), 7.48−7.45 (m, 2H, ArH), 7.40−7.36 (m, 2H, ArH), 7.23−7.21 (m, 2H, ArH), 7.01−6.91 (m, 4H, ArH), 4.19 (s, 3H, CH_3-*trans* isomer), 4.05 (s, 3H, CH_3-*cis* isomer); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.1, 150.6, 146.9, 146.1, 137.9, 137.7, 130.5, 129.9, 129.7, 128.3, 127.8, 127.6, 127.1, 127.0, 126.9, 124.9, 124.3, 120.7, (C,CH), 53.8 (CH_3).

*Synthesis of 1,2-Bis(2′-methoxyquinolin-3-yl)ethene (**5c**).* Synthesis according to the general procedure leading to **5a**, 2-methoxyquinoline-3-carboxaldehyde **2** (0.50 g, 2.67 mmol), phosphonium salt **4c** (1.69 g, 3.2 mmol), and sodium hydride (0.192 g, 8.0 mmol) in dichloromethane. Purified by column chromatography using EtOAc/petroleum ether (20:80) to obtain **5c** (0.750 g, 82%, Z/E ∼3:1) as a yellow solid: mp 149−150 °C; MS (ESI+) m/z = 343 $[MH]^+$; HRMS (EI) calcd for $C_{22}H_{18}N_2O_2$ 342.1368, found m/z 342.1355; ^1H NMR (300 MHz, $CDCl_3$) δ 8.25 (s, 2H, vinylic protons of *trans* isomer), 7.81−7.75 (m, 4H, ArH), 7.61−7.51 (m, 4H, ArH), 7.40−7.37 (m, 4H, ArH), 7.25−7.20 (m, 4H, ArH), 6.88 (s, 2H, vinylic protons of *cis* isomer), 4.18 (s, 6H, CH_3 of *trans* isomer), 4.08 (s, 6H, CH_3 of *cis* isomer); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.3, 145.9, 137.1, 134.1, 129.5, 127.6, 127.5, 127.0, 126.9, 126.5, 125.4, 125.0, 124.4, 124.1, 121.7 (C, CH), 53.88, 53.83 (CH_3).

*Synthesis of 6,9-Dichloro-5,10-diaza[5]helicene (**6a**). General Procedure.* To a solution of compound **5a** (0.15 g, 0.42 mmol, mixture of two isomers) in toluene (425 mL) was added iodine (0.108 g, 0.42 mmol). Argon was bubbled through the solution for 30 min, and then excess propylene oxide was added to the solution. The reaction mixture was irradiated using a Rayonet photochemical reactor (wavelength used is 350 nm) for 10 h, after which it was washed with aqueous $Na_2S_2O_3$, water, and brine, dried over anhydrous $MgSO_4$, and evaporated to afford a dark yellow residue. Purification by column chromatography using EtOAc/petroleum ether (10:90) as eluent gave the racemic diaza[5]helicene **6a** (0.085 g, 57%) as a light yellow solid: mp 247−249 °C; MS (ESI+) m/z = 349 $[MH]^+$; HRMS (EI) calcd for $C_{20}H_{10}N_2Cl_2$ 348.0221, found m/z 348.0227; ^1H NMR (300 MHz, $CDCl_3$) δ 8.57 (s, 2H, ArH), 8.42 (d, 2H, J = 8.4 Hz, ArH), 8.16 (d, 2H, J = 8.1 Hz, ArH), 7.73 (t, 2H, J = 7.3, ArH), 7.37 (t, 2H, J = 8.1 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS) δ 150.9, 144.5, 131.9, 130.4, 128.9, 127.6, 127.1, 126.5, 126.1, 124.0 (C, CH).

*Synthesis of 6-Chloro,9-methoxy-5,10-diaza[5]helicene (**6b**).* Synthesis according to the general procedure leading to **6a**, compound **5b** (0.15 g, 0.43 mmol), and I_2 (0.109 g, 0.43 mmol) in toluene. Purification by column chromatography using EtOAc/petroleum ether

dx.doi.org/10.1021/jo301814m | J. Org. Chem. 2012, 77, 10176−10183

(20:80) as eluent gave the racemic diaza[5]helicene **6b** (0.069 g, 46%) as a light yellow solid: mp 217−219 °C; MS (ESI+) m/z = 345 $[MH]^+$; HRMS (EI) calcd for $C_{21}H_{13}N_2ClO$ 344.0716, found m/z 344.0694; ^1H NMR (300 MHz, $CDCl_3$) δ 8.54 (d, 1H, J = 8.4 Hz, ArH), 8.47 (s, 1H, ArH), 8.35 (d, 1H, J = 8.2 Hz, ArH), 8.12 (d, 1H, J = 8.2 Hz, ArH), 7.95 (d, 1H, J = 8.1 Hz, ArH), 7.69 (t, 1H, J = 8.1 Hz, ArH), 7.60 (t, 1H, J = 8.1 Hz, ArH), 7.35 (t, 1H, J = 8.1 Hz, ArH), 7.18 (t, 1H, J = 8.1 Hz, ArH), 4.32 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS) δ 159.0, 151.2, 144.4, 144.2, 131.9, 129.9, 129.7, 128.7, 127.8, 127.6, 127.0, 125.7, 125.6, 124.4, 124.3, 123.0, 122.7, 122.4 (C,CH), 54.3 (OCH_3).

*Synthesis of 6,9-Dimethoxy-5,10-diaza[5]helicene (**6c**).* Synthesis according to the general procedure leading to **6a**, compound **5c** (0.20 g, 0.58 mmol), and I_2 (0.148 g, 0.58 mmol) in toluene. Purification by column chromatography using EtOAc/petroleum ether (20:80) as eluent gave the racemic diaza[5]helicene **6c** (0.125 g, 63%) as a light yellow solid: mp 198−202 °C; MS (ESI+) m/z = 341 $[MH]^+$; HRMS (EI) calcd for $C_{22}H_{16}N_2O_2$ 340.1212, found m/z 340.1185; ^1H NMR (300 MHz, $CDCl_3$) δ 8.48 (d, 2H, J = 8.4 Hz, ArH), 8.39 (s, 2H, ArH), 7.93 (d, 2H, J = 8.1 Hz, ArH), 7.57 (t, 2H, J = 7.7 Hz, ArH), 7.17 (t, 2H, J = 7.7 Hz, ArH), 4.29 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS) δ 159.3, 144.1, 131.9, 129.2, 127.9, 127.4, 123.3, 122.7, 122.5 (C,CH), 54.2 (OCH_3). During the synthesis of diaza[5]helicene, the typical side product diazabenzo[*ghi*]perylene was formed in low yield.

*Synthesis of 5,8-Dimethoxy-4,9-diazabenzoperylene (**6d**).* Synthesis according to the general procedure leading to **6a**, compound **5c** (0.05 g, 0.146 mmol), and I_2 (0.074 g, 0.292 mmol) in toluene. The reaction mixture was irradiated for 3 days. Purification by column chromatography using EtOAc/petroleum ether (20:80) to CH_2Cl_2/toluene (50:50) as eluent gave first the racemic diaza[5]helicene **6c** (0.012 g, 25%) as a light yellow solid and **6d** (0.031 g, 63%) as a silver-white solid. Material identity of the first fraction was confirmed by mp, MS, and ^1H and ^{13}C NMR of **6c**. For **6d**: mp 305−310 °C; MS (EI) m/z = 338 $[MH]^+$; HRMS (EI) calcd for $C_{22}H_{14}N_2O_2$ 338.1055, found m/z 338.1051.

Nucleophilic Substitution Reactions. *Synthesis of 6,9-Bis-(thiomethoxy)-5,10-diaza[5]helicene (**7a**).* To a solution of **6a** (20 mg, 0.05 mmol) in DMF (10 mL) was added sodium thiomethoxide (10 mg, 0.14 mmol),d and the reaction was stirred at 80 °C for 12 h. Subsequently, the mixture was diluted with EtOAc (20 mL) and washed with distilled water (3 × 20 mL). The organic fraction was dried over $MgSO_4$ and filtered, and the solvent was removed under vacuum. After column chromatographic purification using EtOAc/petroleum ether (20:80) as eluent, the substituted diaza[5]helicene **7a** (12.5 mg, 58%) was obtained as a light yellow solid: mp 250−253 °C; MS (ESI+) m/z = 373 $[MH]^+$; HRMS (EI) calcd for $C_{22}H_{16}N_2S_2$ 372.0755, found m/z 372.0766; ^1H NMR (300 MHz, $CDCl_3$) δ 8.41 (d, 2H, J = 8.0 Hz, ArH), 8.35 (s, 2H, ArH), 8.05 (d, 2H, J = 8.2 Hz, ArH), 7.61(t, 2H, J = 8.1 Hz, ArH), 7.22 (t, 2H, J = 8.3 Hz, ArH), 2.86 (s, 6H, SCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ 159.7, 145.3, 129.6, 129.4, 128.1, 127.6, 124.0, 123.7, 123.2(C, CH), 13.5 (SCH_3).

*Synthesis of 6,9-Bis(thiophenoxy)-5,10-diaza[5]helicene(**7b**).* To a solution of **6a** (20 mg, 0.05 mmol) in DMF (10 mL) were added K_2CO_3 (19.8 mg, 0.14 mmol) and thiophenol (14 μL, 0.14 mmol), and the reaction was stirred at 80 °C for 12 h. Subsequently, the mixture was diluted with ethyl acetate (20 mL) and washed with distilled water (3 × 20 mL). The organic fraction was dried over $MgSO_4$ and filtered, and the solvent was removed under vacuum. After column chromatographic purification using EtOAc/petroleum ether (30:70) as eluent the substituted diaza[5]helicene **7b** (18 mg, 62%) was obtained as a light yellow solid: mp 227−229 °C; MS (ESI+) m/z = 497 $[MH]^+$; HRMS (EI) calcd for $C_{32}H_{20}N_2S_2$ 496.1068, found m/z 496.1071; ^1H NMR (300 MHz, $CDCl_3$) δ 8.53 (s, 2H, ArH), 8.39 (d, 2H, J = 8.1 Hz, ArH), 7.84 (d, 2H, J = 8.1 Hz, ArH), 7.82−7.69 (m, 4H, ArH), 7.53 (t, 2H, J = 6.9 Hz, ArH), 7.49−7.45 (m, 6H, ArH), 7.23 (t, 2H, J = 7.1 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS) δ158.8, 145.1, 135.0, 130.3, 129.4, 129.2, 128.8, 128.7, 127.6, 127.4, 124.6, 124.4, 123.7 (C, CH).

*Synthesis of 6,9-Bis(phenoxy)-5,10-diaza[5]helicene (**7c**).* To a solution of **6a** (20 mg, 0.057 mmol) in DMF (10 mL) were added K_2CO_3 (19.8 mg, 0.14 mmol) and phenol (13.4 mg, 0.14 mmol), and the reaction was stirred at 80 °C for 12 h. Subsequently, the mixture was diluted with ethyl acetate (20 mL) and washed with distilled water (3 × 20 mL). The organic fraction was dried over $MgSO_4$ and filtered, and the solvent was removed under vacuum. After column chromatographic purification using EtOAc/petroleum ether (20:80) as eluent the substituted diaza[5]helicene **7d** (18 mg, 67%) was obtained as a yellow solid: mp 256−258 °C; MS (ESI+) m/z = 465 $[MH]^+$; HRMS (EI) calcd for $C_{32}H_{20}N_2O_2$ 464.1525, found m/z 464.1525; ^1H NMR (300 MHz, $CDCl_3$) δ 8.68 (s, 2H, ArH), 8.54 (d, 2H, J = 8.1 Hz, ArH), 7.83 (d, 2H, J = 8.2 Hz, ArH), 7.58−7.49 (m, 6H, ArH), 7.43−7.41 (m, 4H, ArH), 7.32 (t, 2H, J = 7.1 Hz, ArH), 7.21 (t, 2H, J = 6.9 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS) δ158.7, 153.8, 143.7, 132.6, 129.6, 129.4, 128.1, 127.7, 125.1, 123.7, 123.5, 123.2, 122.6, 122.1 (C, CH).

*Synthesis of 6,9-Bis(phenylamino)-5,10-diaza[5]helicene (**7d**).* To a solution **6a** (20 mg, 0.057 mmol) in DMF (10 mL) was added aniline (26 μL, 0.28 mmol, 5 equiv), and the reaction mixture was stirred at 150 °C for 20 h. Subsequently, the mixture was diluted with ethyl acetate (20 mL) and washed with distilled water (3 × 20 mL). The organic fraction was dried over $MgSO_4$ and filtered, and the solvent was removed under vacuum. After column chromatographic purification using EtOAc/petroleum ether (40:60) as eluent, the substituted diaza[5]helicene **7d** (13 mg, 50%) was obtained as a yellow solid: mp 288−290 °C; MS (ESI+) m/z = 463 $[MH]^+$; HRMS (EI) calcd for $C_{32}H_{22}N_4$ 462.1844, found m/z 462.1840; ^1H NMR (300 MHz, DMSO-d_6) δ 9.54 (s, 2H, NH), 8.73 (s, 2H, ArH), 8.27 (d, 2H, J = 8.4 Hz, ArH), 8.10−8.07 (m, 4H, ArH), 7.75 (d, 2H, J = 8.1 Hz, ArH), 7.55 (t, 2H, J = 7.7 Hz, ArH), 7.45−7.40 (m, 4H, ArH), 7.14−7.07 (m, 4H, ArH); ^{13}C NMR (75 MHz, DMSO-d_6, 25 °C, TMS) δ 150.9, 144.5, 141.2, 131.1, 129.5, 128.5, 127.3, 126.8, 122.7, 122.3, 121.8, 121.7, 121.4, 120.8.

Palladium-Catalyzed Reactions. *Suzuki Coupling. Synthesis of 6,9-Bis(4-methylphenyl)-5,10-diaza[5]helicene (**7e**).* To a solution of **6a** (20 mg, 0.057 mmol) in toluene (20 mL) was added $Pd(PPh_3)_4$ (3 mg, 5 mol %), and to this a solution of *p*-tolylboronic acid (24 mg, 0.171 mmol) in aqueous $NaHCO_3$ (19 mg, 0.228 mmol) and MeOH (0.5 mL) was added. The reaction mixture was refluxed for 12 h. Subsequently, the mixture was washed with distilled water (3 × 20 mL). The organic fraction was dried over $MgSO_4$ and filtered, and the solvent was removed under vacuum. After column chromatographic purification using EtOAc/petroleum ether (20:80) as eluent the substituted diaza[5]helicene **7e** (11.2 mg, 42%) was obtained as an off-white solid: mp 286−287 °C; MS (ESI+) m/z = 461 $[MH]^+$; HRMS (EI) calcd for $C_{34}H_{24}N_2$ 460.1939, found m/z 460.1926; ^1H NMR (300 MHz, $CDCl_3$) δ 8.63 (d, 2H, J = 8.2 Hz, ArH), 8.30 (d, 2H, J = 8.1 Hz, ArH), 8.05 (s, 2H, ArH), 7.76−7.68 (m, 6H, ArH), 7.42−7.36 (m, 6H, ArH), 2.48 (s, 6H, $PhCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS) δ 160.1, 145.0, 139.2, 136.7, 131.0, 130.4, 129.8, 129.4, 129.3, 127.4, 126.7, 126.6, 125.4, 124.5 (C, CH), 21.5 (CH_3).

Buchwald−Hartwig Amination. *Synthesis of 6,9-Bis-(phenylamino)-5,10-diaza[5]helicene (**7d**).* To a solution **6a** (20 mg, 0.057 mmol) in toluene (10 mL) were added aniline (13.3 mg, 0.143 mmol), Cs_2CO_3 (370 mg, 1.14 mmol), *rac*-BINAP (1.7 mg, 0.0028 mmol), and $Pd(OAc)_2$ (1.2 mg, 0.0057 mmol), and the reaction mixture was stirred at 80 °C for 12 h. Subsequently, the mixture was diluted with ethyl acetate (20 mL) and washed with distilled water (3 × 20 mL). The organic fraction was dried over $MgSO_4$ and filtered and the solvent was removed under vacuum. After column chromatographic purification using EtOAc/petroleum ether (40:60) as eluent the substituted diaza[5]helicene **7d** (15.2 mg, 57%) was obtained as a yellow solid. The material's identity was compared with **7d** prepared via S_NAr reaction and confirmed by mp, MS, and ^1H and ^{13}C NMR.

*Synthesis of 6,9-Bis[(S)-α-(methylbenzylamino)]-5,10-diaza[5]-helicene (**7f**).* To a solution of **6a** (50 mg, 0.143 mmol) in toluene (20 mL) were added (*S*)-α-methyl benzylamine (43 μL, 0.358 mmol), Cs_2CO_3 (931 mg, 2.86 mmol), *rac*-BINAP (4.4 mg, 5 mol %), and

$Pd(OAc)_2$ (3.2 mg, 10 mol %), and the reaction mixture was stirred at 80 °C for 12 h. Subsequently, the mixture was diluted with ethyl acetate (20 mL) and washed with distilled water (3 × 20 mL). The organic fraction was dried over $MgSO_4$ and filtered, and the solvent was removed under vacuum. After column chromatographic purification using EtOAc/petroleum ether (20:80) as eluent, the diaza[5]helicene **7f** (54 mg, 72% 1:1 mixture of diastereomers) was obtained as a yellow solid: mp 205−207 °C; MS (ESI+) m/z = 519 $[MH]^+$; HRMS (EI) calcd for $C_{36}H_{30}N_4$ 519.2549 $[M + H]^+$, found m/z 519.2552; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33−8.29 (m, 4H, ArH), 7.83 (s, 2H, ArH), 7.81 (s, 2H, ArH), 7.77 (d, 2H, J = 7.6 Hz, ArH), 7.72 (d, 2H, J = 8.2 Hz, ArH), 7.58−7.55 (m, 8H, ArH), 7.47−7.42 (m, 4H, ArH), 7.39−7.36 (m, 8H, ArH), 7.29−7.25 (m, 4H, ArH), 6.99−6.96 (m, 8H, ArH), 5.80−5.78 (m, 2H, CH of one diastereomer), 5.75−5.73 (m, 2H, CH of second diastereomers), 5.51−5.48 (m, 4H, NH), 1.78−1.74 (m, 12H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ 152.1, 152.0, 145.7, 145.0, 144.8, 132.2, 132.1, 129.3, 128.8, 128.6, 128.0, 127.3, 127.2, 126.9, 126.8, 126.7 (C, CH), 50.8, 50.4 (CHNH), 22.4, 22.3 (CH_3).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra of the novel precursors and diaza[5]helicenes **6a−c** and substituted derivatives. Temperature-dependent ^{1}HNMR spectra and racemization studies related analysis and HPLC of compound **7f**. UV−vis and CD spectra of compound **7f**. X-ray data for compounds **6a** and **6c**. This material is available free of charge via the Internet at http://pubs.acs.org

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the FWO (Fund for Scientific Research - Flanders), the K.U. Leuven, and the Ministerie voor Wetenschapsbeleid (IAP-IV-27) for continuing financial support, the Hercules Foundation of the Flemish Government (Grant No. 20100225-7) for mass spectrometry, and the Ministry of Science Education and Sports of the Republic of Croatia (Grant No. 098-0982933-2911).

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