

Synthesis, Structures, and Optical Properties of Aza[4]helicenes

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A series of aza[4]helicenes have been conveniently synthesized in yields of 71–92 % by a one-pot procedure involving the Pictet–Spengler reaction. The structures of the aza[4]helicenes were characterized by ¹H and ¹³C NMR spectroscopy, mass spectrometry, and X-ray crystallography. Moreover, it was found that the aza[4]helicenes self-assemble into 2D layers or herringbone-like structures in the solid state. In addition, the optical properties were investigated by UV and fluorescence spectroscopic methods.

Introduction

Helicenes^[1] are a class of molecules with many intriguing features such as extended aromaticity, chirality, and the ability to self-assemble into columnar solid-state architectures as well as to behave as organic conductors. Since Newman and Lednicer reported the synthesis and resolution of hexahelicene in 1956.^[2] a great deal of work has been carried out on helicenes and heterohelicenes with the backbone composed of carbon atoms only and selected heteroatoms, respectively.^[1,3] So far, various synthetic strategies for the synthesis of carbo- and heterohelicenes have been developed, including photocyclization reactions,^[4] Diels-Alder cycloadditions,^[5] cyclotrimerizations of acetylenes,^[6] carbenoid couplings,^[7] electrophilic aromatic cyclizations,^[8] radical cyclizations,^[9] olefin metathesis,^[10] cycloisomerizations,^[11] and Friedel-Crafts-type cyclizations.^[12] However, limited substrate scope, multistep reactions, air-sensitive organometallic reagents, or metal catalysis have usually restricted the usefulness and generality of these strategies for affording helicenes or heterohelicenes. Thus, developing new methodologies for their synthesis remains very important in this area of research.

Recently, owing to their interesting properties, azahelicenes have attracted considerable attention in the development of asymmetric catalysis,^[13] chemosensors,^[14] dye materials,^[15] and supramolecular assemblies,^[16] In addition, examples of the synthesis and applications of [4]helicenes have been described.^[17] However, few studies on aza[4]-

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helicenes have been reported, which has also limited their practical applications.^[18]

The Pictet–Spengler reaction^[19] remains one of the most widely used methods for the synthesis of isoquinolines and β -carbolines by C–C and C–N bond formation.^[20] Recently, Kundu and co-workers employed the reaction to afford various nitrogen-substituted heteroaromatic molecules.^[21] Moreover, Youn and Bihn successfully synthesized a series of 6-substituted phenanthridines by the Pictet–Spengler reaction.^[22] Herein we report the synthesis of aza[4]helicenes by a one-pot Pictet–Spengler reaction. In this way, a series of aza[4]helicenes with different functional groups have been conveniently obtained in good yields, and their structures were characterized by ¹H and ¹³C NMR spectroscopy, MS, and X-ray diffraction. In addition, the optical properties of the azahelicenes were investigated by UV and fluorescence spectroscopic methods.

Results and Discussion

Synthesis of Aza[4]helicenes

We first prepared the arylamine **4**, the key precursor for the Pictet–Spengler reaction.^[23] As shown in Scheme 1, the Suzuki coupling reaction between naphthylboronic acid (1)



Scheme 1. Synthesis of arylamine 4.



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and 1-bromo-2-nitrobenzene (2) gave compound 3 in 95% yield, which was then reduced by H₂ in the presence of Pd/ C to produce the arylamine 4 in 98% yield.

With compound **4** in hand, we first tested the Pictet– Spengler reaction between **4** and the commercially available 4-methoxybenzaldehyde (Scheme 2). It was found that when both of the reactants were dissolved in toluene containing



Scheme 2. Synthesis of aza[4]helicenes 5.

2% trifluoroacetic acid (TFA) and the mixture was heated at reflux in a round-bottomed flask for even 72 h, aza[4]helicene **5c** was only obtained in <5% yield. However, when the mixture was heated with stirring at 140 °C in a sealed tube for 48 h, the target product was isolated in 56% yield. We next investigated the effect of solvent on the condensation reaction (Table 1) and found that under the same

Table 1. Effect of solvent on the synthesis of aza[4]helicene 5c.

Entry	Solvent	Yield [%]
1	toluene	56
2	chlorobenzene	50
3	xylene	40
4	N,N-dimethylformamide	35
5	acetonitrile	10
6	TFA	92

Table 2. Synthesis of aza[4]helicenes 5 by the Pictet–Spengler reaction.^[a]

Entry	Aldehyde	Product	Yield (%)	Entry	Aldehyde	Product	Yield (%)
1	PhCHO	C	90	8	2-NO ₂ C ₆ H ₄ CHO	Sh	74
2	4-MeC₀H₄CHO		89	9	4-BrC ₆ H₄CHO	Br Br Si	71
3	4-MeOC₀H₄CHO	CCH3 CCH3 Sc	92	10	4-CF ₃ C ₆ H ₄ CHO		73
4	3-MeOC ₆ H ₄ CHO	CCCH3 CCCH3 5d	90	11	thiophene-2- carbaldehyde		84
5	2-MeOC ₆ H ₄ CHO		85	12	pyridine-2- carbaldehyde		80
6	4-NO ₂ C ₆ H ₄ CHO	Sf	83	13	paraformaldehyde	N 5m	85
7	3-NO ₂ C ₆ H ₄ CHO		78	14	propylaldehyde		82

[a] Performed under the optimized experimental conditions: 4 (1 equiv.), aldehyde (2 equiv.), TFA (2 mL), 140 °C, 48 h in an autoclave.

reaction conditions with chlorobenzene, xylene, N,N-dimethylformamide, or acetonitrile as solvent, product **5c** was isolated in lower yields than in toluene. However, when TFA was used as solvent, aza[4]helicene **5c** was obtained in 92% yield (Table 1, entry 6).

The Pictet-Spengler reactions between amine 4 and other commercially available aryl aldehydes were then carried out under the optimized reaction conditions and the results are summarized in Table 2. It was found that both electron-rich and -deficient aryl aldehydes gave the corresponding aza[4]helicenes in good yields. In addition, the positions of the substituents in the aryl aldehyde showed no obvious effects on the reaction (Table 2, entries 3-5). The Pictet-Spengler reactions of thiophene-2- and pyridine-2-carbaldehyde with 4 also worked well in TFA in an autoclave over 48 h, giving the aza[4]helicenes 5k and 5l (Table 2, entries 11 and 12) in yields of 84 and 80%, respectively. The aza[4]helicenes 5m and 5n (Table 2, entries 13 and 14) were also obtained in good yields by the reaction of 4 with paraformaldehyde or propanal, respectively, under the same conditions. In addition, we also obtained aza[4]helicene 50 in 98% yield by the demethylation of compound 5e with boron tribromide in dichloromethane (Scheme 3). The structures of the new aza[4]helicenes were all characterized by ¹H and ¹³C NMR spectroscopy, MS, and elementary analyses.



Scheme 3. Synthesis of aza[4]helicene 50.

Crystal Structures of Aza[4]helicenes

To further investigate the structures of the aza[4]helicenes and their self-assembling behavior in the solid state, we obtained single crystals of 5a-5f, 5h, and 5o suitable for X-ray diffraction analysis by vapor diffusion of petroleum ether into their solutions in ethyl acetate. As shown in Figure 1 (a), the distortion^[24] of the molecular structure of **5a**, which is defined by the sum of the two torsion angles of C5-C6-C7-C8 and C6-C7-C8-C9, is 40.0°, which is consistent with a helical structure. Moreover, we noted a dihedral angle of 46.1° between the aromatic rings A and B. We also found that by virtue of CH ... N hydrogen bonding between the nitrogen atom of one azahelicene molecule and an aromatic proton of an adjacent molecule, or vice versa, with a distance of 2.59 Å (a), and a pair of CH··· π interactions between an aromatic proton and an adjacent aromatic ring of the azahelicene, with a distance of 2.85 (b) or 2.86 Å (c), respectively, molecule 5a self-assembles into a 2D layer structure (Figure 1, c,d).

Similar to the case of **5a**, molecule **5b** also shows a helical structure with a distortion of 39.2° and a dihedral angle between the aromatic rings A and B of 48.8°. Moreover, by



Figure 1. Top views of the crystal structures of (a) 5a and (b) 5b. (c) View of the noncovalent interactions (dashed lines) between adjacent molecules of 5a. (d) Crystal packing of 5a viewed along the *c* axis. (e) Crystal packing of 5b viewed along the *c* axis. Hydrogen atoms not involved in interactions have been omitted for clarity.

virtue of CH···N hydrogen bonding and CH··· π interactions between adjacent molecules, molecule **5b** also self-assembles into a 2D layer structure (Figure 1, e).

For the azahelicenes **5c–e** with a methoxyphenyl group (Figure 2, a–c), the corresponding distortion angles are 30.3, 38.5, and 35.8°, respectively, which are all smaller than



Figure 2. Crystal structures of (a) **5c**, (b) **5d**, (c) **5e**, and (d) **5o**. Hydrogen atoms have been omitted for clarity.



Figure 3. (a) View of the noncovalent interactions (dashed lines) between adjacent molecules of **5c**. (b) Crystal packing of **5c**. Hydrogen atoms not involved in the interaction have been omitted for clarity.

that of **5a**, but they are also consistent with helical structures. The dihedral angles between the substituted benzene ring and the pyridine ring of the azahelicene skeleton are 63.0 (**5c**), 51.5 (**5d**), and 57.5° (**5e**), respectively, which are larger than that of **5a**. Moreover, we also obtained the crystal structure of **5o**, the demethylated product of **5e**. As shown in Figure 2 (d), molecule **5o** also shows a helical structure, but the distortion of 34.6° is smaller than that of its precursor **5e**. In addition, the dihedral angle between the two adjacent aromatic rings (67.4°) is greater than that of **5e** and no intramolecular OH····N hydrogen bonding was found.

The self-assembling behavior of **5c** in the solid state was also investigated. As shown in Figure 3, it was found that by virtue of a pair of CH···O hydrogen bonds (a, 2.59 Å) and a pair of CH···N hydrogen bonds (b, 2.66 Å) between the aromatic protons of molecule A and the oxygen and nitrogen atoms of molecule B, and the aromatic protons of molecule B and the oxygen and nitrogen atoms of the adjacent molecule C, molecule **5c** self-assembles into a wave-like layer structure (Figure 3b). The layers can further pack into a 3D microporous architecture through a pair of CH··· π interactions (c) between two adjacent helicene molecules with a distance of 2.87 Å. Similarly, by virtue of multiple CH···O and CH···N hydrogen bonds and CH··· π and π ··· π interactions between adjacent molecules, **5d** and **5e** also self-assemble into 2D layer or wave-like layer structures



Figure 4. (a) Packing of **5d**. (b) Packing of **5e**. (c) Packing of **5o**. Hydrogen atoms have been omitted for clarity.



Figure 5. Crystal structures of (a) **5f** and (b) **5h**. Packing of (c) **5f** and (d) **5h**. Hydrogen atoms have been omitted for clarity.

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(Figure 4, a,b). The azahelicene **50** was found to adopt a 2D herringbone-like layer structure (Figure 4, c) and these layers can further pack into a 3D microporous architecture in the solid state.

In the case of azahelicenes 5f and 5h, the distortion of the helical structure of 5f containing a *p*-nitrophenyl moiety (38.6°) is clearly larger than that of **5h** (27.7°) with an onitrophenyl group. However, the dihedral angle of 5f (47.2°) between the substituted benzene ring and the pyridine ring of the azahelicene skeleton is significantly smaller than that of **5h** (69.4°) in which the *o*-nitro group exerts steric strain (Figure 5, a,b). In addition, it was found that azahelicene 5f can also pack into a wave-like layer structure (Figure 5, c) through multiple CH···O hydrogen bonds and π ··· π interactions between adjacent molecules. However, for azahelicene 5h, a microporous network structure (Figure 5, d) is formed instead of a layer-by-layer structure through multiple noncovalent interactions, including CH···N and CH···O hydrogen bonds and CH··· π and π ··· π interactions between adjacent molecules. This is in contrast to 5h, which might be due to the different dihedral angles of azahelicenes 5f and 5h.

Optical Properties of the Aza[4]helicenes

The optical properties of the aza[4]helicenes were also studied by UV and fluorescent spectroscopy, and the results are summarized in Table 3. The UV/Vis spectra of aza[4]helicenes 5a-o in CH₂Cl₂ exhibit absorption bands with maxima at 274–307 nm, with the azahelicenes with electronwithdrawing groups appearing at longer wavelengths than those with electron-donating groups. However, the positions of the substituents had no obvious effect on the maximum of the absorption peak (entries 3–5). In the fluorescent spectra, the emission maxima for the helicene skeleton were observed at about 400 nm, and the substituent groups and their positions had no obvious effect on the emission, probably due to the indirect connection of the substituent groups to the helicene skeleton. In addition, the fluorescence intensities of the aza[4]helicenes were weak, which

Table 3. Optical properties of aza[4]helicenes 5 in CH₂Cl₂.^[a]

Entry	Aza[4]helicene	$\lambda_{\rm abs}$ [nm]	$\lambda_{\rm em}$ [nm]
1	5a	284	413
2	5b	281	414
3	5c	283	403
4	5d	286	411
5	5e	278	406
6	5f	306	398
7	5g	307	397
8	5h	307	400
9	5i	281	414
10	5j	287	410
11	5k	300	410
12	51	281	422
13	5m	274	402
14	5n	275	400

[a] [5] = 1.0×10^{-5} M.

might be due to the lone-pair electrons on the nitrogen causing fluorescence quenching.

Conclusions

We have shown a simple and convenient one-pot procedure for the synthesis of a series of aza[4]helicenes by using the Pictet–Spengler reaction. The structures of the aza[4]helicenes were characterized by ¹H and ¹³C NMR spectroscopy, MS, and X-ray diffraction analyses. It was found that the aza[4]helicenes self-assemble into 2D layer or herringbone-like structures in the solid state. The optical properties of the aza[4]helicenes were also investigated. We believe that this method could also be used for the synthesis of other azahelicenes, including those with more rings, and that these new azahelicenes could find widespread applications in materials science and supramolecular chemistry.

Experimental Section

General: Melting points were taken with an electrothermal melting point apparatus and are uncorrected. ¹H and ¹³C NMR spectra were recorded with a Bruker AV 300 NMR spectrometer. EI mass spectra were obtained with an FTICR mass spectrometer. Elemental analyses were carried out with an Elemental FLASH EA1112 instrument. Materials obtained commercially were used without further purification.

General Procedure for the Synthesis of Aza[4]helicenes: An aldehyde (2 equiv., 0.20 mmol) was added to a solution of arylaniline **4** (1 equiv., 0.10 mmol) in TFA (2 mL). The resulting mixture, in a 5 mL tube, was placed in an autoclave and then heated with stirring at 140 °C for 48 h. The reaction mixture was diluted with ethyl acetate, neutralized with sat. NaHCO₃, extracted with ethyl acetate (3×10 mL), and washed with brine. The organic layer was dried with MgSO₄ and concentrated in vacuo to give a residue, which was purified by column chromatography on silica gel with ethyl acetate and petroleum ether (1:1–1:10) as eluent to provide the corresponding product.

The spectral data for compounds 5a, 5b, and 5m are consistent with the data reported in the literature.^[22,25]

Compound 5a: $R_f = 0.50$ (ethyl acetate/petroleum ether, 1:10), yield 90%, yellow solid; m.p. 136–138 °C. ¹H NMR (300 MHz, CDCl₃): $\delta = 9.28-9.01$ (m, 2 H), 8.37 (d, J = 7.1 Hz,1 H), 8.13–7.93 (m, 2 H), 7.93–7.68 (m, 7 H), 7.55 (s, 3 H) ppm. MS (EI): m/z = 305 [M]⁺.

Compound 5b: $R_{\rm f} = 0.65$ (ethyl acetate/petroleum ether, 1:5), yield 89%, yellow solid; m.p. 128–129 °C. ¹H NMR (300 MHz, CDCl₃): $\delta = 8.98$ (d, J = 8.0 Hz, 1 H), 8.85 (d, J = 8.3 Hz, 1 H), 8.23 (d, J = 8.0 Hz, 1 H), 7.84 (d, J = 8.7 Hz, 2 H), 7.72–7.58 (m, 2 H), 7.56–7.44 (m, 5 H), 7.22 (d, J = 7.5 Hz, 2 H), 2.34 (s, 3 H) ppm. MS (EI): m/z = 319 [M]⁺.

Compound 5c: $R_{\rm f} = 0.40$ (ethyl acetate/petroleum ether, 1:5), yield 92%, yellow solid; m.p. 189–191 °C. ¹H NMR (300 MHz, CDCl₃): $\delta = 9.20$ –9.15 (m, 1 H), 9.04 (d, J = 8.4 Hz, 1 H), 8.35 (d, J = 7.2 Hz, 1 H), 8.06–8.02 (m, 2 H), 7.88 (d, J = 8.9 Hz, 1 H), 7.83–7.67 (m, 6 H), 7.10 (d, J = 8.6 Hz, 2 H), 3.92 (s, 3 H) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 160.1$, 160.0, 145.9, 134.8, 132.8, 132.6, 131.6, 130.9, 130.2, 129.0, 128.9, 128.5, 128.4, 128.9, 127.7, 127.0, 126.8, 126.4, 125.1, 124.0, 123.9, 113.9, 55.5 ppm. MS (EI):

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 $m/z = 335 \text{ [M]}^+$. C₂₄H₁₇NO (335.40): calcd. C 85.94, H 5.11, N 4.18; found C 85.90, H 5.13, N 4.19.

Compound 5d: $R_{\rm f} = 0.32$ (ethyl acetate/petroleum ether, 1:10), yield 90%, yellow solid; m.p. 135–137 °C. ¹H NMR (300 MHz, CDCl₃): $\delta = 9.17$ (d, J = 8.0 Hz, 1 H), 9.05 (d, J = 8.2 Hz, 1 H), 8.37 (d, J = 8.0 Hz, 1 H), 8.16–7.94 (m, 2 H), 7.92–7.66 (m, 5 H), 7.47 (t, J = 7.9 Hz, 1 H), 7.26 (d, J = 13.4 Hz, 2 H), 7.08 (d, J = 7.9 Hz, 1 H), 3.88 (s, 3 H) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 160.2$, 159.7, 145.7, 141.4, 134.75, 132.7, 130.3, 129.5, 129.0, 128.6, 128.6, 128.5, 128.0, 127.8, 127.0, 126.8, 126.6, 125.0, 124.1, 123.8, 122.6, 115.3, 114.7, 55.4 ppm. MS (EI): m/z = 335 [M]⁺. C₂₄H₁₇NO (335.40): calcd. C 85.94, H 5.11, N 4.18; found C 85.96, H 5.10, N 4.19.

Compound 5e: $R_{\rm f} = 0.33$ (ethyl acetate/petroleum ether, 1:5), yield 85%, yellow solid; m.p. 136–139 °C. ¹H NMR (300 MHz, CDCl₃): $\delta = 9.21$ (d, J = 7.9 Hz, 1 H), 9.09 (d, J = 8.0 Hz, 1 H), 8.38 (d, J = 7.9 Hz, 1 H), 8.02 (d, J = 6.8 Hz, 1 H), 7.88–7.62 (m, 6 H), 7.51 (t, J = 7.5 Hz, 2 H), 7.17 (t, J = 7.4 Hz, 1 H), 7.08 (d, J = 8.1 Hz, 1 H), 3.67 (s, 3 H) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 158.9$, 157.3, 146.0, 134.8, 131.7, 131.1, 130.4, 130.2, 129.4, 129.1, 128.6, 128.6, 128.2, 127.8, 127.7, 127.1, 126.6, 126.5, 125.2, 125.0, 124.3, 121.1, 111.1, 55.6 ppm. MS (EI): m/z = 335 [M]⁺. C₂₄H₁₇NO (335.40): calcd. C 85.94, H 5.11, N 4.18; found C 85.93, H 5.12, N 4.17.

Compound 5f: $R_{\rm f} = 0.26$ (ethyl acetate/petroleum ether, 1:5), yield 83%, pale-yellow solid; m.p. 185–187 °C. ¹H NMR (300 MHz, CDCl₃): $\delta = 9.20$ (d, J = 8.2 Hz, 1 H), 9.09 (d, J = 7.9 Hz, 1 H), 8.28 (ddd, J = 7.7, 4.8, 1.1 Hz, 2 H), 8.09–7.97 (m, 1 H), 7.87–7.62 (m, 8 H), 7.52 (d, J = 8.8 Hz, 1 H) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 157.5$, 148.7, 145.6, 135.6, 134.8, 133.6, 132.3, 132.2, 130.2, 129.7, 129.1, 128.8, 128.7, 128.6, 128.6, 128.1, 127.2, 127.1, 127.1, 124.9, 124.3, 124.0, 123.2 ppm. MS (EI): m/z = 350 [M]⁺. C₂₃H₁₄N₂O₂ (350.38): calcd. C 78.84, H 4.03, N 8.00; found C 78.83, H 4.02, N 8.02.

Compound 5g: $R_{\rm f} = 0.20$ (ethyl acetate/petroleum ether, 1:5), yield 78%, pale-yellow solid; m.p. 173–175 °C. ¹H NMR (300 MHz, CDCl₃): $\delta = 9.22$ –9.17 (m, 1 H), 9.09 (d, J = 8.2 Hz, 1 H), 8.67 (d, J = 1.7 Hz, 1 H), 8.48–8.30 (m, 2 H), 8.15–8.01 (m, 2 H), 7.95–7.66 (m, 7 H) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 157.5$, 148.4, 145.6, 141.8, 136.2, 134.8, 133.1, 130.3, 129.5, 129.0, 128.8, 128.7, 128.5, 128.3, 127.2, 127.2, 127.1, 125.3, 124.3, 123.8, 123.2 ppm. MS (EI): m/z = 350 [M]⁺. C₂₃H₁₄N₂O₂ (350.38): calcd. C 78.84, H 4.03, N 8.00; found C 78.80, H 4.04, N 8.01.

Compound 5h: $R_{\rm f} = 0.24$ (ethyl acetate/petroleum ether, 1:5), yield 74%, pale-yellow solid; m.p. 163–165 °C. ¹H NMR (300 MHz, CDCl₃): $\delta = 9.21-9.13$ (m, 1 H), 9.05 (d, J = 8.3 Hz, 1 H), 8.34 (dd, J = 8.1, 1.2 Hz, 1 H), 8.10–8.02 (m, 1 H), 7.89 (q, J = 8.9 Hz, 2 H), 7.84–7.69 (m, 6 H), 7.66–7.60 (m, 2 H) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 159.1, 145.7, 139.0, 134.7, 132.8, 131.8, 131.7, 130.3, 129.0, 128.6, 128.6, 128.1, 128.0, 127.1, 127.0, 126.8, 124.5, 124.1, 123.5, 123.2 ppm. MS (EI): <math>m/z = 350$ [M]⁺. C₂₃H₁₄N₂O₂ (350.38): calcd. C 78.84, H 4.03, N 8.00; found C 78.91, H 4.04, N 7.92.

Compound 5i: $R_{\rm f} = 0.40$ (ethyl acetate/petroleum ether, 1:5), yield 71%, white solid; m.p. 121–123 °C. ¹H NMR (300 MHz, CDCl₃): $\delta = 9.20-9.14$ (m, 1 H), 9.06 (d, J = 8.3 Hz, 1 H), 8.35 (d, J = 8.1 Hz, 1 H), 8.08–8.02 (m, 1 H), 7.95–7.86 (m, 2 H), 7.85–7.69 (m, 6 H), 7.63 (d, J = 8.4 Hz, 2 H) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 167.7$, 159.1, 145.7, 139.0, 134.7, 132.8, 132.3, 131.8, 131.7, 130.9, 130.3, 129.0, 128.9, 128.6, 128.1, 128.0, 127.1, 126.9, 126.7, 124.5, 124.1, 123.5, 123.2 ppm. MS (EI): m/z = 383 [M]⁺.

 $\rm C_{23}H_{14}BrN$ (384.27): calcd. C 71.89, H 3.67, N 3.65; found C 71.92, H 3.66, N 3.64.

Compound 5j: $R_f = 0.70$ (ethyl acetate/petroleum ether, 1:5), yield 73%, white solid; m.p. 177–179 °C. ¹H NMR (300 MHz, [D₆]acetone): $\delta = 9.28-9.21$ (m, 1 H), 9.20–9.11 (m, 1 H), 8.29 (dd, J = 8.0, 1.5 Hz, 1 H), 8.20 (dd, J = 6.9, 2.5 Hz, 1 H), 8.08 (d, J = 8.9 Hz, 1 H), 7.99 (dd, J = 13.5, 8.4 Hz, 5 H), 7.93–7.83 (m, 4 H) ppm. ¹³C NMR (75 MHz, [D₆]acetone): $\delta = 159.4, 155.1, 146.6, 145.1, 135.7, 133.2, 132.0, 131.8, 131.2, 129.7, 129.7, 129.6, 129.4, 129.3, 129.2, 128.2, 128.1, 127.9, 126.1, 126.1, 125.0, 124.8, 124.2 ppm. MS (EI): <math>m/z = 373$ [M]⁺. C₂₄H₁₄F₃N (373.38): calcd. C 77.20, H 3.78, N 3.75; found C 77.23, H 3.76, N 3.77.

Compound 5k: $R_{\rm f} = 0.66$ (ethyl acetate/petroleum ether, 1:10), yield 84%, pale-yellow solid; m.p. 110–113 °C. ¹H NMR (300 MHz, [D₆]acetone): $\delta = 9.17$ (s, 1 H), 9.05 (s, 1 H), 8.50 (d, J = 6.7 Hz, 1 H), 8.30–8.05 (m, 3 H), 7.90–7.67 (m, 6 H), 7.31 (s, 1 H) ppm. ¹³C NMR (75 MHz, [D₆]acetone): $\delta = 153.6$, 146.6, 144.1, 135.7, 133.6, 130.8, 130.7, 129.7, 129.6, 129.4, 129.3, 129.2, 129.1, 128.4, 128.1, 127.9, 127.8, 124.69, 124.5, 123.9 ppm. MS (EI): m/z = 311 [M]⁺. C₂₁H₁₃NS (311.40): calcd. C 81.00, H 4.21, N 4.50; found C 80.99, H 4.22, N 4.51.

Compound 51: $R_{\rm f} = 0.50$ (ethyl acetate/petroleum ether, 1:1), yield 80%, pale-yellow solid; m.p. 146–148 °C. ¹H NMR (300 MHz, CDCl₃): $\delta = 9.17$ (d, J = 5.2 Hz, 1 H), 9.08 (d, J = 8.2 Hz, 1 H), 8.83 (s, 1 H), 8.38 (d, J = 8.1 Hz, 1 H), 8.27 (d, J = 8.9 Hz, 1 H), 8.07–7.88 (m, 4 H), 7.80 (dd, J = 18.1, 9.9 Hz, 4 H), 7.53–7.43 (m, 1 H) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 158.6$, 157.7, 148.9, 145.5, 137.1, 134.8, 133.0, 130.4, 129.01, 128.6, 128.5, 128.5, 128.1, 128.0, 127.1, 127.0, 126.7, 125.5, 124.7, 124.5, 123.6, 123.3 ppm. MS (EI): m/z = 306 [M]⁺. C₂₂H₁₄N₂ (306.37): calcd. C 86.25, H 4.61, N 9.14; found C 86.29, H 4.60, N 9.13.

Compound 5m: $R_{\rm f} = 0.20$ (ethyl acetate/petroleum ether, 1:10), yield 85%, yellow solid; m.p. 189–191 °C. ¹H NMR (300 MHz, CDCl₃): $\delta = 9.36$ (s, 1 H), 9.20 (d, J = 9.1 Hz, 1 H), 9.11 (d, J = 8.2 Hz, 1 H), 8.39–8.23 (m, 1 H), 8.08 (dd, J = 6.3, 3.0 Hz, 1 H), 8.02 (d, J = 8.5 Hz, 1 H), 7.95 (d, J = 8.5 Hz, 1 H), 7.87–7.70 (m, 4 H) ppm. MS (EI): m/z = 229 [M]⁺.

Compound 5n: $R_f = 0.70$ (ethyl acetate/petroleum ether, 1:10), yield 82%, pale-yellow solid; m.p. 78–79 °C. ¹H NMR (300 MHz, CDCl₃): $\delta = 9.19-9.07$ (m, 1 H), 8.96 (d, J = 8.3 Hz, 1 H), 8.24 (d, J = 8.2 Hz, 1 H), 8.15 (d, J = 8.9 Hz, 1 H), 8.04 (dd, J = 6.5, 2.9 Hz, 1 H), 7.97 (d, J = 8.8 Hz, 1 H), 7.79–7.68 (m, 3 H), 7.68–7.61 (m, 1 H), 3.48 (q, J = 7.5 Hz, 2 H), 1.54 (t, J = 7.5 Hz, 3 H) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 162.3$, 145.7, 134.6, 132.0, 129.5, 129.3, 128.6, 128.5, 128.2, 128.2, 127.7, 127.1, 126.7, 125.9, 123.9, 123.7, 122.6, 29.8, 13.9 ppm. MS (EI): m/z = 257 [M]⁺. C₁₉H₁₅N (257.33): calcd. C 88.68, H 5.88, N 5.44; found C 88.65, H 5.87, N 5.45.

Compound 50: Boron bromide in dichloromethane (2.0 mL, 1 M) was added to a solution of **5e** (34 mg, 0.1 mmol) in dry dichloromethane (10 mL) in an ice bath. After stirring the reaction mixture at room temp. for 1 h, it was hydrolyzed with hydrochloric acid (0.1 M, 3 mL). The aqueous layer was extracted twice with dichloromethane (2×10 mL) and the organic layers were combined, washed with water, dried with anhydrous Na₂SO₄, and evaporated under reduced pressure. The crude product was purified by column chromatography over silica gel (eluent: 1:5 ethyl acetate/petroleum ether) to afford 33 mg of **50**. $R_{\rm f} = 0.70$ (ethyl acetate/petroleum ether, 1:5), yield 98%, yellow solid; m.p. 201–203 °C. ¹H NMR (300 MHz, CDCl₃): $\delta = 9.13$ (dd, J = 6.0, 3.5 Hz, 1 H), 9.03 (d, J = 8.3 Hz, 1 H), 8.32 (d, J = 8.9 Hz, 1 H), 8.23 (dd, J = 8.1, 1.1 Hz,

1 H), 8.07 (dd, J = 6.1, 3.3 Hz, 1 H), 7.93 (d, J = 8.9 Hz, 1 H), 7.84–7.64 (m, 5 H), 7.41 (dd, J = 11.2, 4.2 Hz, 1 H), 7.27–7.21 (m, 2 H), 7.02 (t, J = 7.5 Hz, 1 H) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 158.2$, 158.0, 143.5, 134.9, 134.4, 132.4, 131.1, 128.9, 128.8, 128.8, 128.4, 127.6, 127.2, 127.0, 126.9, 124.9, 123.8, 123.1, 121.6, 118.9, 118.2 ppm. MS (ESI): m/z = 321 [M]⁺. C₂₃H₁₅NO (321.38): calcd. C 85.96, H 4.70, N 4.36; found C 88.90, H 4.72, N 4.38.

X-ray Crystallographic Study: X-ray crystallographic data were collected by using a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite-monochromated Mo- K_{α} ($\lambda = 0.71073$ Å) radiation. The data were corrected for Lorentzian, polarization, and absorption effects. Structures were solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were placed in calculated positions and refined by using a riding model.

CCDC-915879 (for **5a**), -915880 (for **5b**), -915874 (for **5c**), -915875 (for **5d**), -915876 (for **5e**), -915877 (for **5f**), -915878 (for **5h**), and -915986 (for **5o**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

Compound 5a: $C_{23}H_{15}N$, *M* 305.36, crystal dimensions $0.80 \times 0.50 \times 0.10$ mm³, monoclinic, space group P2(1)/n, a = 10.376(6), b = 7.317(4), c = 20.485(11) Å, V = 1527.4(14) Å³, $D_c = 1.328$ Mg/ m³, Z = 4, 8691 reflections collected, 2671 independent [*R*(int) = 0.1679], giving $R_1 = 0.1638$ for observed unique reflections [$F^2 > 2\sigma(F^2)$] and $wR_2 = 0.3931$ for all data.

Compound 5b: $C_{24}H_{17}N$, *M* 319.39, crystal dimensions $0.27 \times 0.24 \times 0.18$ mm³, monoclinic, space group P2(1)/c, a = 10.896(2), b = 7.289(15), c = 21.401(4) Å, V = 1663.2(6) Å³, $D_c = 1.276$ Mg/ m³, Z = 4, 8691 reflections collected, 2671 independent [*R*(int) = 0.1679], giving $R_1 = 0.0770$ for observed unique reflections [$F^2 > 2\sigma(F^2)$] and $wR_2 = 0.1493$ for all data.

Compound 5c: $C_{24}H_{17}NO$, *M* 335.39, crystal dimensions $0.20 \times 0.12 \times 0.08$ mm³, monoclinic, space group *P*2(1)/*c*, *a* = 5.596(2), *b* = 18.632(7), *c* = 16.056(6) Å, *V* = 1672.8(11) Å³, *D_c* = 1.332 Mg/m³, *Z* = 4, 9130 reflections collected, 2928 independent [*R*(int) = 0.0568], giving *R*₁ = 0.0660 for observed unique reflections [*F*² > 2 σ (*F*²] and *wR*₂ = 0.1406 for all data.

Compound 5d: $C_{24}H_{17}NO$, *M* 335.39, crystal dimensions $0.20 \times 0.12 \times 0.08 \text{ mm}^3$, triclinic, space group $P\bar{1}$, a = 8.232(16), b = 10.227(2), c = 10.877(2) Å, V = 826.7(3) Å³, $D_c = 1.347$ Mg/m³, Z = 2, 9369 reflections collected, 3766 independent [*R*(int) = 0.0777], giving $R_1 = 0.0614$ for observed unique reflections [$F^2 > 2\sigma(F^2)$] and $wR_2 = 0.1437$ for all data.

Compound 5e: $C_{24}H_{17}NO$, *M* 335.39, crystal dimensions $0.30 \times 0.28 \times 0.26$ mm³, monoclinic, space group P2(1)/c, a = 11.349(2), b = 12.782(3), c = 11.772(2) Å, V = 1656.2(6) Å³, $D_c = 1.345$ Mg/ m³, Z = 4, 11357 reflections collected, 3772 independent [*R*(int) = 0.0436], giving $R_1 = 0.0630$ for observed unique reflections [$F^2 > 2\sigma(F^2)$] and $wR_2 = 0.1328$ for all data.

Compound 5f: $C_{23}H_{14}N_2O_2$, *M* 350.36, crystal dimensions $0.18 \times 0.13 \times 0.07 \text{ mm}^3$, monoclinic, space group P2(1)/c, a = 10.305(2), b = 12.782(3), c = 11.772(2) Å, V = 1656.2(6) Å³, $D_c = 1.345$ Mg/ m³, Z = 4, 11357 reflections collected, 3772 independent [*R*(int) = 0.0436], giving $R_1 = 0.0630$ for observed unique reflections [$F^2 > 2\sigma(F^2)$] and $wR_2 = 0.1328$ for all data.

Compound 5h: $C_{23}H_{14}N_2O_2$, *M* 350.36, crystal dimensions $0.18 \times 0.13 \times 0.07$ mm³, orthorhombic, space group *Pbca*, *a* = 13.323(3),

b = 13.347(3), c = 18.983(4) Å, V = 3375.6(12) Å³, $D_c = 1.379$ Mg/m³, Z = 8, 17109 reflections collected, 3855 independent [R(int) = 0.0656], giving $R_1 = 0.1043$ for observed unique reflections [$F^2 > 2\sigma(F^2)$] and $wR_2 = 0.2094$ for all data.

Compound 5o: $C_{23}H_{15}NO$, *M* 321.36, crystal dimensions $0.45 \times 0.21 \times 0.05 \text{ mm}^3$, monoclinic, space group P2(1)/c, a = 11.245(3), b = 13.306(3), c = 11.013(2) Å, V = 1605.2(8) Å³, $D_c = 1.330$ Mg/ m³, Z = 4, 10713 reflections collected, 3641 independent [*R*(int) = 0.0507], giving $R_1 = 0.0818$ for observed unique reflections [$F^2 > 2\sigma(F^2)$] and $wR_2 = 0.1544$ for all data.

Supporting Information (see footnote on the first page of this article): ¹H and ¹³C NMR spectra of aza[4]helicenes **5a–o** and crystal data of aza[4]helicenes **5a–f**, **5h**, and **5o**.

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