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Monoaza[5]helicenes. Part 2: Synthesis, characterisation and theoretical calculations

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Abstract—The synthesis of four different monoaza[5]helicenes is reported, to complete the whole series of these compounds, so that systematic studies on their properties can be carried out. They were fully characterised via NMR. A theoretical approach to explain why ring closure occurs to give the most crowded compound is reported, in comparison with earlier calculation methods.

1. Introduction

Photochemical cyclisation of stilbene derivatives is a well known method to obtain polycyclic molecules. In a previous paper,[1] which is part 1 of this work, we described the cyclisation of some ethylenic derivatives that allowed us to obtain a number of monoaza and diaza[5]helicenes. These molecules showed interesting properties depending on the position of the nitrogen in the helicene framework, like, for example, varying characteristic triplet lifetime or rate of racemisation.[1,2] Unfortunately, for different reasons, this synthetic approach appeared not to be of general application. In addition, among all possible products from ring closure reactions, helicene, the most crowded system, was obtained in all the cases we studied. Consequently, we were interested both in finding a way to obtain those aza[5]-helicenes that could not be synthesized with the route reported previously,[1] and also in applying theoretical considerations for the starting materials we used, to justify the photochemical cyclisation to give the helicene. In an earlier paper, we reported several different reasons why a single approach appeared not to be of general application,[3] and did not allow the formation of all the desired monoaza and diazahelicenes. We were interested in obtaining all the possible isomers because few aza[5]helicenes are known in the literature,[4–13] and there is no systematic study of their properties. This is despite the potential applications of helicenes that can be found, for example, in the fields of non-linear optics (NLO)[14] and circularly polarised luminescence.[15]

Indeed, the study we carried out on the already synthesized helicenes, showed a very long lifetime of the triplet state and a tendency to π–π stacking both in the solid state and for the azahelicenes by themselves or even for some metal complexes, allowing the build up of columnar system arranged in the space with a particular geometry, and with a control over chirality that may be valuable in designing new materials for optoelectronic applications.[16–20]

2. Results and discussion

2.1. Synthetic studies

The synthetic route we followed to obtain the azahelicenes was very simple and started from the synthesis of 1,2-disubstituted ethylenes (obtained through Wittig reaction from the appropriate aldehyde with the suitable phosphonium salt) that were afterwards cyclised photochemically to the desired helicenes as first described by Martin for the carbohelicene[21] and described in Scheme 1 for the synthesis of 4-aza[5]helicene.

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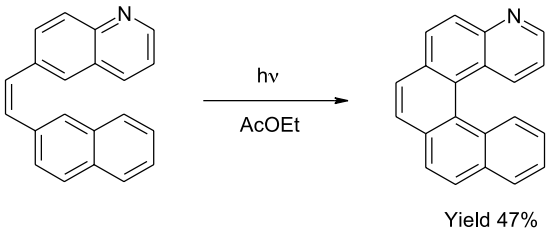
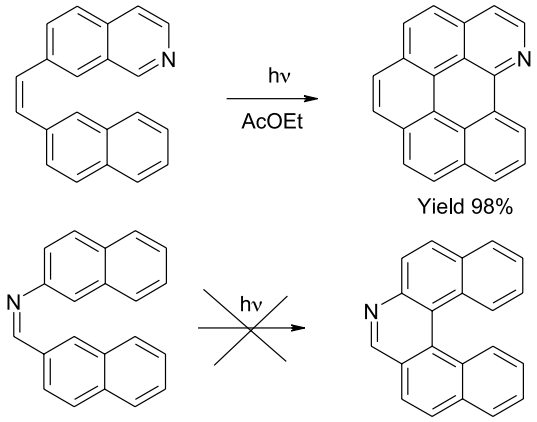


Scheme 1.



Scheme 2.

Following this synthetic approach, it was possible to synthesize nine different azahelicenes, namely 4-, 5-, 6-aza and 4,11-, 5,10-, 6,9-, 4,9-, 4,10- and 5,9-diaza[5]-helicenes. Other synthetic approaches were envisioned for the synthesis of carbo- and heterohelicenes,[22–26] but, in our opinion, when it is possible to apply the above route, this is the shortest, simplest and highest yielding. This approach, for different reasons, was not useful for obtaining the 2- and 7-aza derivatives (see Scheme 2), as well as for the preparation of the other monoazahelicenes. For example, we were not able to prepare 1-(2-naphthyl),2-(6-isoquinolyl) ethylene, the precursor for the 3-aza[5]-helicene, because 6-carboxaldehydeisoquinoline, to the best of our knowledge, is not reported in the literature, nor is 6-bromomethylisoquinoline, and we could not develop a synthetic strategy to obtain them. Also the preparation of 7-aza[5]helicene showed some difficulties, and attempts to repeat a published synthesis were unsuccessful.[12]

For these reasons, we decided to find a different approach to their synthesis, looking also to the possibility that it may open the route to obtain other diazahelicenes.

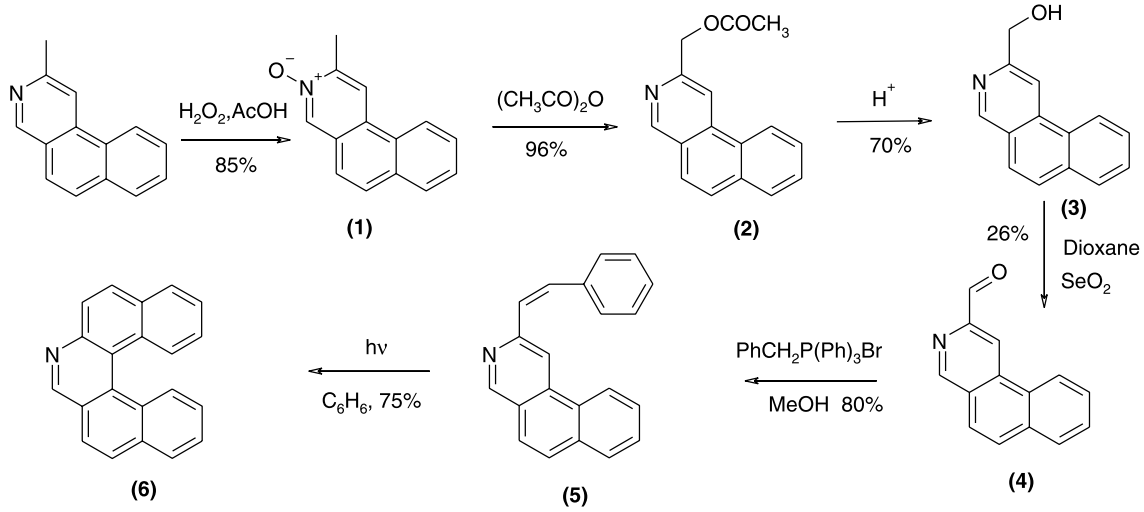
Since the photochemical ring closure had proven to be one of the simplest ways to obtain these compounds, we decided to study the photochemical ring closure of different ethylenic compounds, namely the compound carrying three *ortho*-condensed rings on one side of the ethene and one ring on the other side. The synthesis of these derivatives easily gave the desired helicenes, and eventually opened the route for the formation of some diaza[5]helicenes or of larger azahelicenes. We can anticipate that ring closure on the other side of the phenanthrene (or phenanthridine), giving a completely flat molecule with less strain, does not occur, at least in the case we studied.

The synthesis of the 2-methyl-benzo[*f*]isoquinoline[27] allowed to obtain the 7-aza[5]helicene (**6**) with a fair overall yield in few steps (Scheme 3).

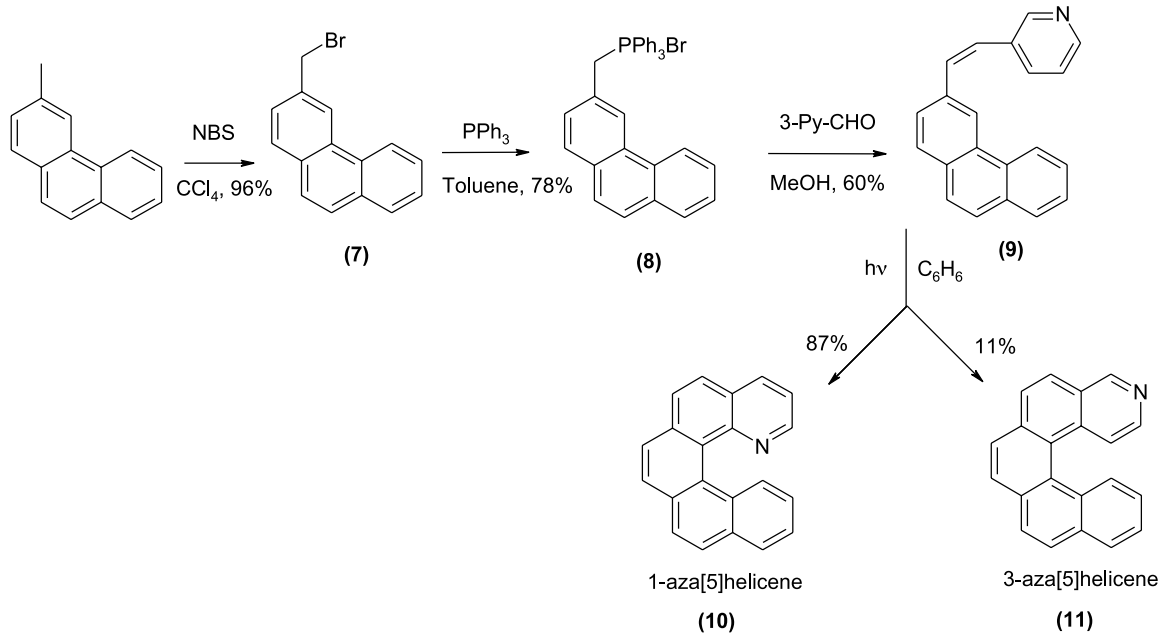
Despite the fact that generally the methyl group α to the heteroaromatic nitrogen is easily functionalised, in this phenanthridine it appeared to be rather unreactive. Transformation into the *N*-oxide allowed instead facile functionalisation through a rearrangement reaction. The other steps were rather obvious.

For the synthesis of 1- and 3-aza[5]helicenes two approaches are possible. The first starts by building an ethene derivative with a phenanthrene on one side and a 3-pyridine on the other. Its photochemical ring closure yielded two desired azahelicenes (**10**) and (**11**) in 9:1 ratio (Scheme 4).

The second synthetic approach may appear longer, because it was necessary to synthesize a starting phenanthridine



Scheme 3.



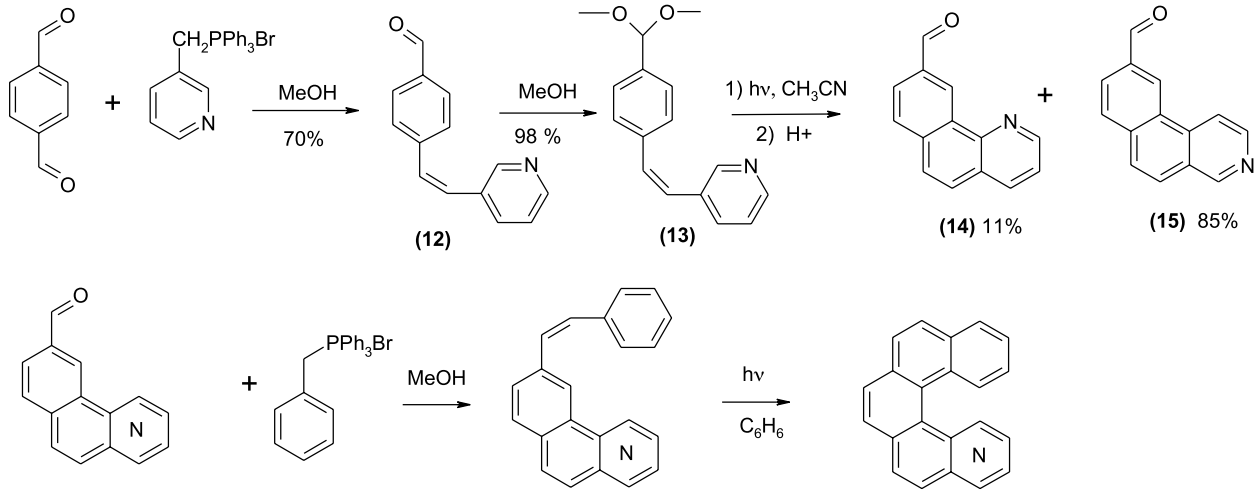
Scheme 4.

derivative. This was achieved through a Wittig reaction between terephthalaldehyde and the phosphonium salt of 3-bromomethylpyridine. With the use of an excess of terephthalaldehyde, it was possible to obtain the substitution of one aldehydic group only. Interestingly, the direct photolysis of this derivative did not give any ring closure, possibly because the $n\rightarrow\pi^*$ transition is lower in energy respect to the $\pi\rightarrow\pi^*$ transition. Confirmation of this hypothesis came from the transformation of the aldehyde to the corresponding dimethylketal. Irradiation of this derivative gave the two phenanthridines in very high overall yield (95%). Hydrolysis to their corresponding aldehydes was quantitative, and their separation was easily achieved (with an isomeric ratio of (**14**):(**15**) 1:8). The subsequent synthetic sequences to give (**10**) or (**11**) are illustrated in Scheme 5.

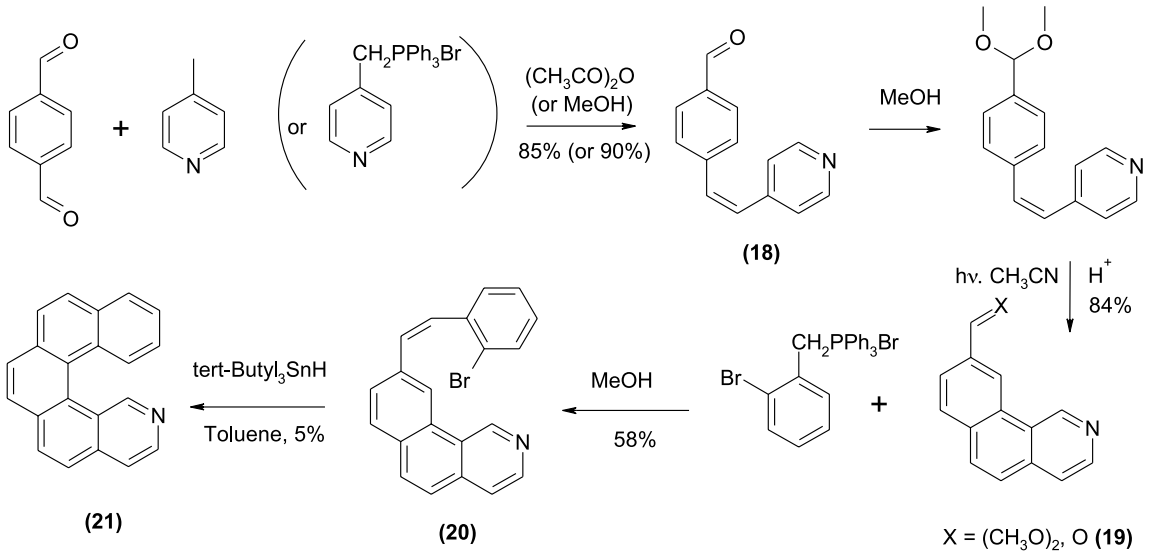
Since the yields were high in both cases, but the final amount of the two helicenes were different, one can choose the method depending on the helicene desired.

The synthesis of 2-aza[5]helicene was different, because, as we already stated, the photochemical ring closure of 7-(2-naphthalen-2-yl-vinyl)-isoquinoline yielded to the corresponding perylene, and the photochemical approach starting from either 4-(2-phenathrene-3-yl-vinyl)-pyridine or 9-styryl-benzo[*h*]isoquinoline gave the same result.

Since the last step cannot be a photochemical one, we designed another way to obtain the ring closure. This was obtained starting from benzo[*h*]isoquinoline-9-carbaldehyde (synthesised as illustrated in Scheme 6) and the 2-methylphosphonium salt of 1-bromobenzene. The



Scheme 5.



Scheme 6.

treatment of this derivative with (*tert*-butyl)$_3$SnH yielded the desired 2-aza[5]helicene (**21**). (Scheme 6).

2.2. Calculations

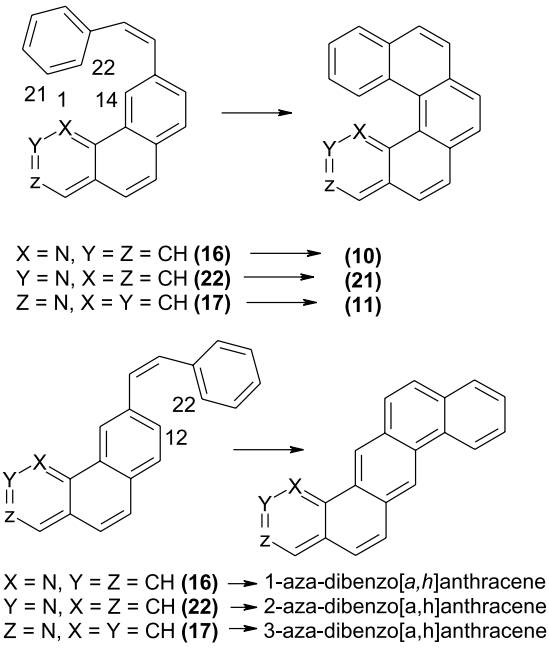
As pointed out in the first part of the paper, the photochemical cyclisation of these derivatives gave rise to the most crowded azahelicene rather that to the corresponding less strained dibenzo[*a*,*h*]anthracene (only the positions involved in the ring closure are highlighted in the scheme below for the sake of clarity).

Theoretical considerations and calculations on these mechanisms are already present in the literature. Some authors,[28,29] working in the context of the Hückel model, proposed a 'free valence' atomic index to characterize the reactivity of atoms in molecules, but generally they did not work together with experimental photochemists providing them with fresh experimental data. For these reasons, we decided to perform some calculations regarding the formation of the azahelicenes reported in this paper. Compounds (**16**), 9-styryl-benzo[*h*]isoquinoline (**22**) and (**17**) have been analysed by means of ab initio calculations using the package GAUSSIAN03.[30]

The ground-state geometry was determined by means of a DFT calculation with B3LYP functional and 6-31G basis set. Excited states have then been computed using the CIS method with the same basis set and geometry optimization has been carried out for the first excited state.

For each molecule two equilibrium configurations have been considered, the first one with a cis-geometry, close to the helicene structure (upper part in Scheme 7), while the second one with a trans-geometry close to the corresponding dibenzo[*a*,*h*]anthracene (lower part in Scheme 7).

In order to find an explanation for the different behaviour of the experiments for the production of helicenes with respect to other possible products, such as perilenes, (See Scheme 2) the value of an atomic index has been calculated by means



Scheme 7.

of the Natural Bond Orbital program included in the package GAUSSIAN03.[31]

In the present study, we have to take into account that the computational approach is different from a mere Hückel method and we need to define an atomic quantity F_A that mimics the 'free valence' atomic index. We introduce:

$$F_A = V_A - \sum_{B \neq A} b_{AB}^{(w)} \quad (1)$$

where V_A is the atomic valence returned by the NBO program as the sum of occupation numbers of the valence orbitals (as opposed to core orbitals) of atom A, $b_{AB}^{(w)}$ is the Wiberg bond index[32] of atoms A and B, and the sum is made over all the atoms B other than A.

Table 1. Differences of the '*F*' atomic indices in the excited state over the atoms of the scheme for the three structures (**16**), (**22**) and (**17**) (see Eq. 1 and discussion in the text)

	$F^*_{21}-F^*_1$	$F^*_{22}-F^*_{14}$	$F^*_{22}-F^*_{12}$
(**16**)	—	0.02078	0.01026
(**22**)	0.30355	0.01551	−0.00775
(**17**)	−0.03046	0.03432	0.00445

Table 2. Sums of the '*F*' atomic indices in the excited state over the atoms of the Scheme 7 for the three structures (**16**), (**22**) and (**17**) (see Eq. 1 and text)

	$(F^*_{21}+F^*_1)$	$(F^*_{22}+F^*_{14})$	$(F^*_{22}+F^*_{12})$
(**16**)	—	0.46762	0.50340
(**22**)	0.27981	0.48835	0.51153
(**17**)	0.61301	0.47542	0.50255

The above index has been calculated both in the ground state (F_A) and in the first excited state (F_A*).

In Table 1, we report the values of the differences $F^*_x-F^*_y$ for the positions considered in the above scheme; x and y indicate the reacting atoms, which have somewhat arbitrarily been chosen in the following order: x is on the benzene ring, y is on the phenanthridine system.

In Table 2, we report the sum $F^*_x+F^*_y$ for the reacting atoms x and y, as suggested in Ref. 29.

For compounds (**16**) and (**17**) the closure that yields the helicene is favoured with respect to the formation of the anthracene, and in accord to Table 1, this corresponds to the highest (positive) values for $F^*_x-F^*_y$. In the case of (**22**) however, the highest value for $F^*_x-F^*_y$ regards the closure between positions 21 and 1 suggesting that the perylene is formed first with this closure; the second highest value is calculated for positions 14 and 22. As matter of fact, even working at very low conversion, we were not able to detect any trace of the 2-aza[5]helicene that may close later to the perilene.

The calculations reported are for the cis conformers; we notice that the trans conformers have lower values for $F^*_x-F^*_y$, despite the fact that their ground state energies are slightly lower with the choice of the 6-31G basis set. Similar trends are found in Table 2, but the correlation with the observed reactivities of the studied molecules is not so immediate. Our obvious conclusion is that the first method seems to give better results for these indices.

Of course, more theoretical work should probably be done and further examples need to be considered to reach a definite conclusion; we also expect further support will

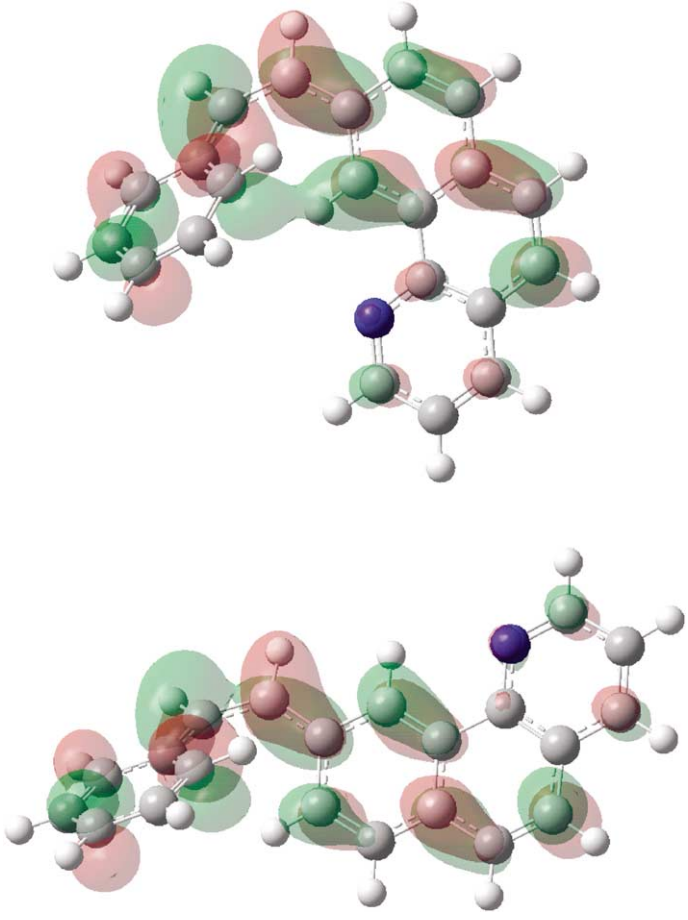


Figure 1. Isovalue surfaces of LUMO of the two conformers of (**16**) in the first excited state optimised geometries. The two colours refer to the two phases of the wavefunction.

come from future synthetic work. Also, due comparison with previous theoretical approaches in the literature[28,29] will be made in forthcoming work.

Further insight into this problem may be achieved by looking at the isovalue surface of LUMO orbital constructed with the aid of Gaussview package.[30] In Figure 1, we present the case of (**16**). A considerable superposition of the wavefunction for atoms 22 and 14 is observed, preparing compound (**16**) to react to helicene. In the single configuration interaction approach, the lower energy transition of both conformers has a fairly dominant contribution from HOMO–UMO, as expected, and its calculated dipole strength is higher than the dipole strength calculated for the two following transitions.

2.3. NMR

The assignment of the NMR spectra of the final helicenes was achieved by the combined use of spin–spin coupling constants in aromatic and heteroaromatic systems and H–H NOE, according to a general strategy already outlined in previous papers.[1,3]

In particular, we took advantage of the *J* coupling patterns within heteroaromatic bases to assign the signals in the N-containing part of the helicene. This approach can be conveniently used for the structural assessment of compounds (**10**), (**11**) and (**21**). Nevertheless, the assignment of the NMR spectrum of (**6**) deserves mention. Indeed, the position of the nitrogen atom in the molecular framework is such that the two naphthalene residues (C1–1 and C9–94) are in very similar chemical environments, making the discrimination of their ^{1}H NMR signals difficult. In this case, the assignment of H8 was the starting point, due to its diagnostic chemical shift. Selective irradiation of H8 gave 9.1% steady state NOE on H9. The large ^{3}J(H9–90) value (8.8 Hz) provided the assignment of the coupling partner H10. The signal assigned to H10 showed, by suitable resolution enhancement, a doublet of doublets multiplicity, with very small splitting (0.8 Hz) due to long range coupling with H14. The latter coupling is reported as 'zig zag' coupling in naphthalene derivatives.[33] This interpretation was confirmed by selective decoupling experiments. The unambiguous assignment of H14 (8.67 ppm) allowed us to assign the structurally related H1 (8.59 ppm). Steady state NOE difference spectra obtained after selective saturation of H1 and H14 allowed the assignment of the partially overlapped signals of H2 and H13. NOESY experiments allowed the assignment of H3 and H12, due to their dipolar contacts with already attributed H2 and H13. In turn, H3 and H12 gave cross peaks with the strongly overlapped H4 and H11 (8.01 and 8.02 ppm, respectively). The assignment of H5 was achieved via NOE with H4 and ^{5}J(H5–5)=0.8 Hz. The remaining doublet at 8.16 ppm was eventually assigned to H6.

3. Conclusions

The synthesis of four aza[5]helicenes is presented in order to complete the preparation of all the monoaza derivative of this class of molecules. The combined use of spin–spin coupling constants in aromatic and heteroaromatic systems and H–H NOE proved to be a general strategy for the elucidation of these structures. The Wiberg bond indexes seem to explain why the photochemical reactions bring to the most crowded of the two possible final molecules.

4. Experimental

All the solvents were distilled and dried before use. Benzaldehyde, terephthalaldeyde, bromomethylbenzene, 3-picoline, 3-pyridine aldehyde, 1-bromo,2-bromomethylbenzene, 2,2-dimethoxypropane, triphenylphosphine, azobisisobutyronitrile (AIBN),(*tert*-butyl)$_3$ tin hydride, acetic anhydride, SeO_2 and 1-bromo-pyrrolidine-2,5-dione (*N*-bromosuccinimide) are commercial products and were used without further purification. SeO_2 and Se (as product of the reactions) are poisonous and particular care must be used (well aerated hood and heavy gloves) when handled. NMR spectra were run either on Bruker ARX 400 or Bruker Avance 500 spectrometers operating at proton resonance frequencies of 400 and 500 MHz, respectively. The products were dissolved in $CDCl_3$ and tetramethylsilane (TMS) was added as reference. ^{1}H{^{1}H} NOE difference spectra and two-dimensional NOESY were carried out by using standard literature pulse sequences. Electron ionization mass spectra were recorded on a Finnigan MAT TSQ 70 instrument (70 ev, EI); the samples were introduced in the spectrometer source by direct probe insertion. Irradiations were carried out on a Rayonet RPR-100 photochemical reactor equipped with 16 interchangeable lamps irradiating either at 254, 300, or 350 nm as well in the visible range, dissolving the substance in the appropriate solvent. The ATR FT-IR spectra were recorded on a Avatar 370-Thermo.

4.1. Wittig reactions

General procedure. In a typical procedure in a flask containing a mixture of the aldehyde (1 mmol) and triphenyl-phosphonium bromide derivative (1 mmol) in methanol (15 mL), MeONa (0.065 g, 1.2 mmol) was added under stirring. The mixture was gently boiled for 3 h. After cooling, water was added, and the solution extracted many times with a large volume of CH_2Cl_2. After drying and solvent evacuation, the residue was chromatographed on silica gel. (Solvents), yield%, mp and physical properties are reported for each case.

4.2. Photochemical reactions

General procedure. The appropriate ethene derivative (1.0 mmol) was dissolved in benzene (150 mL) in a Pyrex vessel open to the air. The vessel was irradiated at 350 nm for a time ranging between 24 and 36 h. The irradiation was stopped when, and if, some tar begun to form. The solvent was removed under vacuum, and the residue was chromatographed on silica gel. R_f,(Solvents), yield%, mp, MS and NMR are reported for each case.

4.2.1. 2-Methylbenzo[*f*]isoquinoline. This compound was obtained as reported in the literature in 15% overall yield, mp 91–93 °C (lit. 93–95).[9]

4.2.2. 2-Methylbenzoisoquinoline *N*-oxide (1). The procedure used was adapted from the literature for the *N*-oxidation of the heterocyclic bases.[34] 2-Methylbenzoisoquinoline (1.00 g, 5.2 mmol) was dissolved in acetic acid (3 mL) and hydrogen peroxide 30% (5 mL) was added. The solution was warmed at 70 °C for 72 h. The solvent was evaporated and the residue was basified with a solution of $NaHCO_3$ and extracted with $CHCl_3$. After drying of the organic phase, the solvent was evacuated and the residue was triturated with diethyl ether to give (**1**) as a white solid in 85% yield, mp 145–147 °C, MS *m/z* 209 (M^+, 100%), 208 (78%), IR (cm^{-1}): 3384, 3038, 2918, 1600, 1454, 1317, 1237, 1180, 1162, 1000, 877, 803, 745, 618, ^1H NMR 2.75 (s, 3H, $1CH_3$), 7.52 (d, 1H, $J=9.0$ Hz, 1CH), 7.68 (m, 2H, 2CH), 7.78 (d, 1H, $J=9.0$ Hz, 1CH), 7.88 (dd, 1H, $J=7.0$, 2.0 Hz, 1CH), 8.36 (s, 1H, CH), 8.48 (dd, 1H, $J=7.0$, 2.0 Hz, 1CH), 8.84 (s, 1H, CH), Elemental analysis calcd(%) for $C_{14}H_{11}NO$ (209.2): C 80.36, H 5.30, N 6.69, found C 80.50, H 5.30, N 6.67.

4.2.3. Acetic acid benzo[*f*]isoquinolin-2-ylmethyl ester (2). Compound (**1**) (0.50 g, 2.4 mmol) was dissolved in acetic anhydride (8 mL) and refluxed for 24 h.[35] After cooling off the solution, the excess of acetic anhydride was eliminated under vacuum leaving an almost pure product. Compound (**2**) was obtained as brown oil in 96% yield, MS *m/z* 251 (M^+, 100%), IR (cm^{-1}): 2922, 1716, 1229, 1031, 877, 814, 743, ^1H NMR 2.22 (s, 3H, CH_3), 5.43 (s, 2H, CH_2), 7.72 (m, 2H, 2CH), 7.78 (d, 1H, $J=8.8$ Hz, 1CH), 7.82 (d, 1H, $J=8.8$ Hz, 1CH), 7.93 (m, 1H, 1CH), 8.43 (s, 1H, CH), 8.65 (m, 1H, 1CH), 9.22 (s, 1H, 1CH), elemental analysis calcd(%) for $C_{16}H_{13}NO_2$ (251.3): C 76.48, H 5.22, N 5.57, found C 76.66, H 5.23, N 5.56.

4.2.4. 2-Methylolbenzo[*f*]isoquinoline (3). Compound (**2**) (0.50 g, 1.99 mmol) was dissolved in concentrated hydrochloric acid, and the solution boiled for 18 h.[35] The solution was then cooled in an ice bath and basified with a solution of NaOH 2 M. The solution was extracted with diethyl ether. The organic layer was dried and the residue was chromatographed on silica gel, to give (**3**) (hexane/ethyl acetate 2:3) in 70% yield as a yellow solid, mp 106–108 °C, MS *m/z* 209 (M^+, 55%), 181 (100%), 152 (M^+, 53%), IR (cm^{-1}): 3031, 2938, 1740, 1457, 1375, 1228, 1098, 1054, 900, 823, 755, ^1H NMR 5.03 (s, 2H, CH_2), 7.71 (m, 2H, 2CH), 7.80 (d, 1H, $J=9.2$ Hz, 1CH), 7.83 (d, 1H, $J=9.2$ Hz, 1CH), 7.94 (dd, 1H, $J=9.1$, 1.9 Hz, 1CH), 8.43 (s, 1H, CH), 8.70 (dd, 1H, $J=9.1$, 1.9 Hz, 1CH), 9.22 (s, 1H, 1CH), elemental analysis calcd(%) for $C_{14}H_{11}NO$ (209.2): C 80.36, H 5.30, N 6.69, found C 80.09, H 5.32, N 6.67.

4.2.5. 2-Benzo[*f*]isoquinolinecarbaldehyde (4). The procedure used was adapted from the literature[36] for the oxidation of the heterocyclic alcohols. Compound (**3**) (0.50 g, 2.4 mmol) was dissolved in dioxane (15 mL) and SeO_2 (0.27 g, 2.4 mmol) was added. The resulting mixture was boiled for 3 h. After cooling, Se was filtered off, the solvent evacuated and the residue chromatographed on silica gel (hexane/ethyl acetate 2:3)to give (**4**) in 26% yield, and recovering unreacted (**3**) quantitatively. (**4**) is a yellow solid, mp 127–129 °C, MS *m/z* 207 (M^+, 52%), 179 (100%), 152 (46%), IR (cm^{-1}): 2843, 1691, 1402, 1116, 897, 821, 798, 734, 703, 600, elemental analysis calcd(%) for $C_{14}H_9NO$ (207.2): C 81.14, H 4.38, N 6.76, found C 81.35, H 4.37, N 6.79.

4.2.6. 2-Styrylbenzo[*f*]isoquinoline (5). For the preparation see the general procedure. Compound (**5**)(ethyl acetate) was obtained as a yellow solid in 80% yield, mp 147–149, MS *m/z* 281 (M^+, 39%), 280 (100%), IR (cm^{-1}): 2926, 1736, 1594, 1453, 1295, 974, 878, 825, 761, 600, ^1H NMR 7.30 (m, 2H, 2CH), 7.40 (m, 3H, 3CH), 7.43 (d, 1H, $J=16.1$ Hz, 1H), 7.66 (d, 2H, $J=7.0$ Hz, 2CH), 7.72 (m, 2H, 2CH), 7.88 (d, 1H, $J=16.1$ Hz, 1H),7.93 (m, 1H, 1CH), 8.42 (s, 1H, CH), 8.72 (m, 1H, CH), 9.23 (s, 1H, CH), elemental analysis calcd(%) for $C_{21}H_{15}N$ (281.4): C 89.65, H 5.37, N 4.98, found C 89.38, H 5.37, N 4.96.

4.2.7. 7-Aza[5]helicene (6). For the preparation see the general procedure.(**6**) was obtained as a yellow solid in yield 75%, mp 142–145 °C, MS *m/z* 279 (M^+, 54%), 278 (100%), IR (cm^{-1}): 2920, 818, 745, 715, 660, 614, 607, elemental analysis calcd(%) for $C_{21}H_{13}N$ (279.3): C 90.30, H 4.69, N 5.01, found C 90.08, H 4.70, N 5.02. NMR is reported in Table 3.

Table 3. NMR data for the aza[5]helicenes (**10**), (**21**), (**11**) and (**6**)

	(**10**)	(**21**)	(**11**)	(**6**)
H1	—	9.89s	8.28br d, $J=6.0$ Hz	8.59ddd, $J=0.8$, 1.2, 8.5 Hz
H2	8.70dd, $J=1.8$, 4.2 Hz	—	8.38br d, $J=6.0$ Hz	7.35ddd, $J=1.4$, 6.9, 8.5 Hz
H3	7.50dd, $J=4.2$, 8.1 Hz	8.56d, $J=5.6$ Hz	—	7.59ddd, $J=1.2$, 6.9, 8.0 Hz
H4	8.26dd, $J=1.8$, 8.1 Hz	7.70d, $J=5.6$ Hz	9.35br s	8.01dd, $J=1.4$, 8.0 Hz
H5	7.88d, $J=8.5$ Hz	8.08d, $J=8.6$ Hz	8.02m	8.10dd, $J=0.8$, 8.8 Hz
H6	7.98d, $J=8.5$ Hz	[a]	8.02m	8.10d, $J=8.8$ Hz
H7	7.99d, $J=8.3$ Hz[b]	[a]	7.99d, $J=8.3$ Hz[d]	—
H8	7.91d, $J=8.3$ Hz[b]	[a]	7.92d, $J=8.3$ Hz[d]	9.33s
H9	7.96d, $J=8.5$ Hz[c]	[a]	7.90d, $J=8.6$ Hz	7.99d, $J=8.8$ Hz
H10	7.86d, $J=8.5$ Hz[c]	[a]	7.90dd, $J=0.8$, 8.6 Hz	8.04dd, $J=0.8$, 8.8 Hz
H11	7.93dd, $J=1.6$, 8.0 Hz	7.97d, $J=8.2$ Hz	7.99d, $J=8.1$ Hz	8.02dd, $J=1.4$, 8.0 Hz
H12	7.54ddd, $J=1.5$, 6.8, 8.0 Hz	7.54t, $J=7.3$ Hz	7.58ddd, $J=1.2$, 6.9, 8.1 Hz	7.66ddd, $J=1.2$, 6.9, 8.0 Hz
H13	7.27ddd, $J=1.6$, 6.8, 8.3 Hz	7.36t, $J=7.3$ Hz	7.35ddd, $J=1.4$, 6.9, 8.4 Hz	7.39ddd, $J=1.6$, 6.9, 8.5 Hz
H14	8.05d, $J=8.3$ Hz	8.58d, $J=8.2$ Hz	8.46ddd, $J=0.8$, 1.2, 8.4 Hz	8.67ddd, $J=0.8$, 1.2, 8.5 Hz

[a] 7.97–7.84 ppm, m, H6+H7+H8+H9+H10.
[b,c,d] The assignment can be reversed.

4.2.8. 3-Bromomethylphenanthrene (7). The compound was prepared similarly to the procedure reported to obtain 9-bromomethylphenanthrene[37] by boiling 3-methylphenanthrene (1.0 g, 5.2 mmol) with *N*-bromosuccinimide (0.93 g, 5.2 mmol) and a few crystals of benzoylperoxide in CCl_4 for 4 h. (**7**) Was obtained as a white solid in 96% yield, mp 95–96 °C, MS *m/z* 271 (M^+, 8%), 270 (9%), 191 (100%), Elemental analysis calcd(%) for $C_{15}H_{11}Br$ (271.3): C 66.44, H 4.09, Br 29.47, found C 66.49, H 4.09, Br 29.51

4.2.9. 3-Phenanthrylmethyl-triphenyl-phosphonium-bromide (8). The compound was prepared from (**7**) (1.35 g, 5.0 mmol) and triphenylphosphine (1.31 g, 5.0 mmol) in boiling toluene (35 mL). The phosphonium salt precipitated and was filtered off at the end of the reaction. Compound (**8**) was obtained as a white solid in 78% yield, mp 270–272 °C dec, and was used directly without further characterisation.

4.2.10. 3-(2-Phenanthren-3-yl-vinyl)-pyridine (9). For the preparation see the general procedure. Compound (**9**) was obtained as orange solid in 60% yield, mp 110–112, MS *m/z* 281 (M^+, 71%), 280 (100%), ^{1}H NMR 7.15 (d, 2H, J=8.8 Hz, 2CH), 7.22 (d, 2H, J=8.6 Hz, 2CH), 7.40 (m, 4H, 4CH), 7.45 (m, 2H, 2CH), 7.65 (d, 1H, J=8.8 Hz, 1CH), 7.71 (d, 1H, J=8.8 Hz, 1CH), 8.42 (dd, 1H, J=7.8, 1.6 Hz, 1CH), 8.44 (s, 1H, 1CH), 8.48 (s, 1H, 1CH), elemental analysis calcd(%) for $C_{21}H_{15}N$ (281.4): C 89.65, H 5.37, N 4.98, found C 89.76, H 5.37, N 4.99.

4.2.11. 1-Aza[5]helicene (10) and 3-aza[5]helicene (11). For the preparation see the general procedure. Compound (**10**) (hexane/ethyl acetate 5:1) was obtained as a yellow solid in 87% yield, mp 164–165 °C, MS *m/z*: 279 (M^+, 30%), 278 (100%), IR (cm^{-1}): 2900, 2839, 1619, 1563, 1256, 842, 723, 686, 643, 615, elemental analysis calcd(%) for $C_{21}H_{13}N$ (279.3): C 90.30, H 4.69, N 5.01, found C 90.47, H 4.68, N 5.02 (**11**) (hexane/ethyl acetate 1:2) was obtained as yellow solid in 11% yield, mp 178–179 °C, MS *m/z* 279 (M^+, 52%), 278 (100%), IR (cm^{-1}): 3069, 2970, 2931, 2861, 1730, 1632, 1592, 1261, 1284, 846, 746, 654, 615, elemental analysis calcd(%) for $C_{21}H_{13}N$ (279.3): C 90.30, H 4.69, N 5.01, found C 89.97, H 4.69, N 5.00. NMR are reported in Table 3.

4.2.12. 4-(2-Pyridin-3-yl-vinyl)-benzaldehyde (12). For the preparation see the general procedure, the only difference was that the molar ratio terephthaldehyde/3-pyridinylphosphonium bromide was 5:1.[38,39] (**12**) (hexane/ethyl acetate 1:2) was obtained as orange oil in 70% yield, MS *m/z* 209 (M^+, 100%), 208 (51%), 180 (92%), 152 (43%), IR (cm^{-1}): 1759, 1577, 1398, 1238, 1200, 1064, 977, 829, ^{1}H NMR 6.69 (d, 1H, J=12.0 Hz, CH), 6.79 (d, 1H, J=12.0 Hz, CH), 7.16 (dd, 1H, J=7.8, 5.1 Hz, 1CH), 7.35 (d, 2H, J=8.2 Hz, 2CH), 7.49 (d, 1H, J=7.8 Hz, 1CH), 7.75 (d, 2H, J=8.2 Hz, 2CH), 8.43 (s and d, 2H, J=5.1 Hz, 2CH), 9.95 (s, 1H, 1CHO), elemental analysis calcd(%) for $C_{14}H_{11}NO$ (209.2): C 80.36, H 5.30, N 6.69, found C 80.64, H 5.31, N 6.72.

4.2.13. 4-(2-Pyridin-3-yl-vinyl)-benzaldehyde dimethoxy-acetal (13). Compound (**12**) (1.0 g, 4.8 mmol) and 2,2-dimethoxyacetone (10 mL, 80 mmol) were dissolved in MeOH (10 mL) and a few crystals of *p*-toluenesulfonic acid were added. The solution was boiled, distilling off the azeotrope of MeOH–acetone.[40] At the end of the reaction MeONa was added and the solvent evaporated. The residue was dissolved in CH_2Cl_2, washed with water and dried on Na_2SO_4. Compound (**13**) was obtained as a yellow oil in 98% yield and MS *m/z* 255 (M^+, 8%), 224 (100%); the product was used without further characterisation.

4.2.14. Benzo[*h*]quinoline-9-carbaldehyde (14) and benzo[*f*]isoquinoline-9-carbaldehyde (15). The irradiation was carried out in acetonitrile (200 mL) for 48 h at 254 nm. At the end of the irradiation, the solution was stirred with HCl 1 M for 2 h to hydrolyse the ketals. The organic layer was washed with water, dried and the solvent removed. The residue was chromatographed on silica gel obtaining (**14**) and (**15**). Compound (**14**) (hexane/ethyl acetate 1:1) was obtained as yellow solid in 11% yield, mp 110–112 °C, MS *m/z*: 207 (M^+, 100%), 206 (62%), 178 (91%), 150 (18%), IR (cm^{-1}): 2880, 2792, 1689, 1579, 1278, 1233, 1180, 1165, 880, 776, 702, 595, ^{1}H NMR 7.61 (dd, 1H, J=8.0, 4.6 Hz, 1CH), 7.87 (d not resolved, 2H, 2CH), 8.01 (d, 1H, J=8.3 Hz, 1CH), 8.21 (dd, 1H, J=8.3, 1.7 Hz, 1CH), 8.24 (dd, 1H, J=8.0, 1.7 Hz, 1CH), 9.08 (dd, 1H, J=4.6, 1.7 Hz, 1CH), 9.80 (s, 1H, 1CH), 10.34 (s, 1H, CHO), elemental analysis calcd(%) for $C_{14}H_9NO$ (207.2): C 81.14, H 4.38, N 6.76, found C 80.86, H 4.39, N 6.74. Compound (**15**) (hexane/ethyl acetate 1:1) was obtained as yellow solid in 85% yield, mp 154–157 °C, MS *m/z*: 207 (M^+, 100%), 206 (72%), 178 (23%), 151 (57%), IR (cm^{-1}): 3005, 1739, 1695, 1515, 1373, 1289, 1223, 1207, 1193, 844, 775, 745, 707, 615, 601, ^{1}H NMR 7.92 (d, 1H, J=8.9 Hz, 1CH), 7.99 (d, 1H, J=8.9 Hz, 1CH), 8.08 (d, 1H, J=8.3 Hz, 1CH), 8.21 (d, 1H, J=8.3 Hz, 1CH), 8.52 (d, 1H, J=5.8 Hz, 1CH), 8.86 (d, 1H, J=5.8 Hz, 1CH), 9.18 (s, 1H, 1CH), 9.32 (s, 1H, 1CH), 10.31 (s, 1H, CHO), elemental analysis calcd(%) for $C_{14}H_9NO$ (207.2) C 81.14, H 4.38, N 6.76, found C 81.43, H 4.38, N 6.70.

4.2.15. 9-Styryl-benzo[*h*]quinoline (16) and 9-styryl-benzo[*f*]isoquinoline (17). For the preparation see the general procedure. Compound (**16**) (hexane/ethyl acetate 2:3) was obtained as yellow solid in 69% yield, mp 92–95 °C, MS *m/z* 281 (M^+, 80%), 280 (100%), IR (cm^{-1}): 2992, 2900, 2725, 1485, 1427, 1377, 980, 962, 831, 761, 693, 615, ^{1}H NMR 7.29 (m, 1H, 1CH), 7.40 (m, 4H, 4CH), 7.53 (dd, 2H, J=8.0, 4.4 Hz, 2CH), 7.59 (dd, 2H, J=8.0, 1.8 Hz, 2CH), 7.66 (dd, 1H, J=8.8, 6.2 Hz, 1CH), 7.79 (d, 1H, J=8.8 Hz, 1CH), 7.90 (m, 2H, 2CH), 8.18 (dd, 1CH, J=8.0, 1.8 Hz, 1CH), 9.02 (dd, 1H, J=4.4, 1.8 Hz, 1CH), 9.38 (s, 1H, 1CH), elemental analysis calcd(%) for $C_{21}H_{15}N$ (281.4): C 89.65, H 5.37, N 4.98, found C 89.64, H 5.38, N 5.00. For the preparation see the general procedure. Compound (**17**) (hexane/ethyl acetate 1:3) was obtained as yellow solid in 92% yield, mp 180–182 °C, MS *m/z* 281 (M^+, 100%), 280 (64%), IR (cm^{-1}): 3077, 3054, 2954, 1562, 1430, 969, 835, 737, 696, 629, ^{1}H NMR 7.36 (d, 1H, J=7.3 Hz, 1CH), 7.42 (m, 2H, 2CH), 7.44 (d, 2H, J=7.3 Hz, 2CH), 7.61 (d, 2H, J=7.3 Hz, 2CH), 7.95 (d, 1H, J=8.8 Hz, 1CH), 8.06 (d, 1H, J=8.2 Hz, 1CH), 8.11 (d, 1H, J=8.8 Hz, 1CH), 8.15 (d, 1H, J=8.2 Hz, 1CH), 8.78 (s and d, J=6.4 Hz, 2H, 2CH), 8.94 (d, 1H, J=6.4 Hz, 1CH), 9.41 (s, 1H, CH), elemental analysis calcd(%) for $C_{21}H_{15}N$

(281.4): C 89.65, H 5.37, N 4.98, found C 89.45, H 5.36, N 4.96.

4.2.16. 1-Aza[5]helicene (10) and 3-aza[5]helicene (11). For the preparation see the general procedure. Compound (**10**) yield 80%, (**11**) yield 95%.

4.2.17. 1-(2-Pyridin-4-yl-vinyl)benzaldehyde (18). This compound may be synthesised in two equivalent ways: the first started from the phosphonium salt of 4-bromomethylpyridine with terephthalaldehyde under the same experimental conditions as (**12**) yield 90%, or by direct condensation of 4-methylpyridine (1.9 mL, 20 mmol) with terephthalaldehyde (5.4 g, 40 mmol) in acetic anhydride (20 mL) and boiling for 5 h (Yield 85%).[41] (**18**)(CH_2Cl_2/ethyl acetate 4:1) was obtained as yellow solid, mp 110–112 °C (lit. 113.5–115 °C), MS *m/z* 209 (M^+, 80%), 180 (100%), 152 (61%), IR (cm^{-1}): 1749, 1694, 1497, 1232, 1200, 965, 824, ^1H NMR 7.04 (d, 1H, $J=16.5$ Hz, 1CH), 7.29 (d, 1H, $J=16$, 5 Hz, 1CH), 7.37 (dd, 2H, $J=4.4$, 1.5 Hz, 2CH), 7.55 (m, 4H, 4CH), 8.58 (dd, 2H, $J=4.4$, 1.5 Hz, 2CH), 10.10 (s, 1H, CHO), elemental analysis calcd(%) for $C_{14}H_{11}NO$ (209.2): C 80.36, H 5.30, N 6.69, found C 80.17, H 5.31, N 6.72.

4.2.18. Benzo[*h*]isoquinoline-9-carbaldehyde (19). After transformation of compound (**18**) in the corresponding ketal, (for the procedure see compound (**13**)), the irradiation was carried out in acetonitrile (200 mL) for 48 h at 254 nm. At the end of the irradiation, the solution was stirred with HCl 1 M for 2 h to hydrolyse the ketal. The organic layer was washed with water, dried and the solvent removed. The residue was chromatographed on silica gel (hexane/ethyl acetate 1:3) obtaining (**19**) as a deliquescent yellow solid in 84% yield, mp 135–137 °C, MS *m/z* 207 (M^+, 100%), 178 (44%), 151 (33%), IR (cm^{-1}): 3360, 2903, 2835, 1684, 1602, 1423, 1387, 1298, 1206, 1168, 1046, 1006, 814, 785, ^1H NMR 7.90 (m, 2H, 2CH), 8.10 (m, 2H, 2CH), 8.21 (dd, 1H, $J=8.1$, 1.5 Hz, 1CH), 8.80 (d, 1H, $J=5.6$ Hz, 1CH), 9.31 (s, 1H, CH), 10.21 (s, 1H, 1CH), 10.33 (s, 1H, CHO), elemental analysis calcd(%) for $C_{14}H_9NO$ (207.2): C 81.14, H 4.38, N 6.76, found C 81.45, H 4.38, N 6.75.

4.2.19. 9-[2(2-Bromo-phenyl)vinyl]-benzo[*h*]isoquinoline (20). For the preparation see the general procedure, (**20**) (hexane/ethyl acetate 1:3) was obtained as yellow oil in 58% yield, mp>250 °C, MS *m/z* 361 ($M^+ + 1$, 40%), 360 (M^+, 38%), 280 (100%), 252 (24%), IR (cm^{-1}): 3073, 3029, 2900, 1573, 1428, 1243, 1015, 842, 761, 734, 661, ^1H NMR 6.80 (d, 1H, $J=11.9$ Hz, 1CH), 6.94 (d, 1H, $J=11.9$ Hz, 1CH), 7.15 (m, 4H, 4CH),7.74 (d, 1H, $J=8.2$ Hz, 1CH), 7.65 (d, 1H, $J=5.4$ Hz, 1CH), 7.71 (d, 1H, $J=8.8$ Hz, 1CH), 7.72 (d, 1H, $J=8.2$ Hz, 1CH),7.83 (d, 1H, $J=8.8$ Hz, 1CH), 8.55 (s, 1H, 1CH), 8.66 (d, 1H, $J=5.4$ Hz, 1CH), 9.62 (s, 1H, CH), elemental analysis calcd(%) for $C_{21}H_{14}BrN$ (360.3): C 70.02, H 3.92, Br 22.18, N 3.89, found C 70.14, H 3.90, Br 22.26, N 3.89.

4.2.20. 2-Aza[5]helicene (21). Compound (**20**) (0.25 g, 0.7 mol) (*tert*-butyl)$_3$SnH (0.23 mL, 0.85 mmol) and AIBN (0.10 g, 0.6 mmol) were dissolved in toluene (80 mL) and boiled for 18 h.[42] After cooling, an aqueous solution of KF was added and the two phases were stirred vigorously for an additional 8 h. The organic phase was separated, dried and evaporated. Compound (**19**) (hexane/ethyl acetate 2:3) was obtained as yellow solid in 5% yield, mp 152–154 °C, MS *m/z* 279 (M^+, 35%), 278 (100%), IR (cm^{-1}): 3197, 1633, 1600, 1454, 1085, 1039, 880, 802, 745, 639, elemental analysis calcd(%) for $C_{21}H_{13}N$ (279.3): C 90.30, H 4.69, N 5.01, found C 90.11, H 4.70, N 5.01. NMR is reported in Table 3.

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