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New [4]helicene derivatives : Synthesis, characterization and photophysical properties

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ABSTRACT

The design and synthesis of new [4]helicene derivatives were carried out by incorporating well-defined electron donor and acceptor groups at selected positions of the aromatic nuclei, aiming to use them in optical applications. Helicenes have been obtained in good overall yields through a five-step sequence involving mild experimental conditions and easy purification. Photophysical properties of these tetracyclic systems have been evaluated by UV-visible absorption and fluorescence spectroscopies and an emission in the visible region was observed.

Keywords: Helicenes; Photolysis; Cyclization; Photooxidation; Optical properties.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) represent an important class of organic compounds which have two or more fused benzene rings. These compounds have received considerable attention due to their fascinating chemistry [1] and unique physical properties [2-3].

Owing to their specific structure and photoelectric properties, polycyclic aromatic hydrocarbons (PAHs) have led also to applications in electronic devices. They have proven to be one of the most important semiconductors [4-7]. Acenes, for example, represent highly attractive compounds with good performance as semiconductors and good emission properties, and they have been widely used in various fields, such as inorganic field-effect transistors [8-9], organic light-emitting diodes (OLEDs) [10] and organic photovoltaics [11-12].

Pyrene molecules, such as pyrene-cored [4]helicene derivatives **1** and **2** (Fig. 1) have excellent fluorescence features [13-14], which make them promising candidates for several important applications in modern electronic and optoelectronic devices.

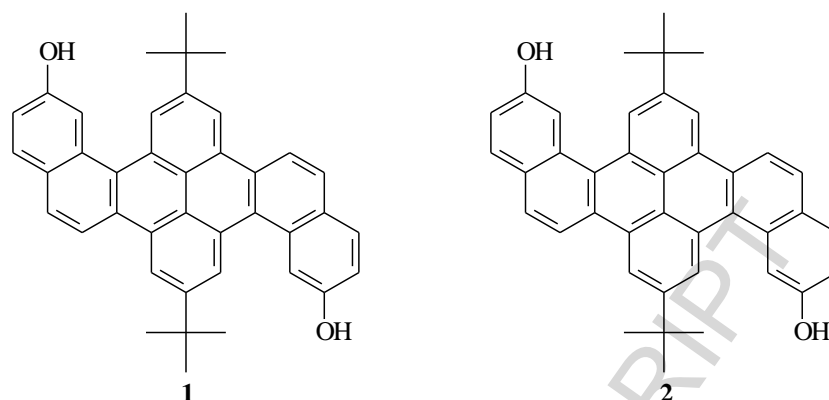


Figure 1. Chemical structures of pyrene-cored [4]helicenes **1** and **2**.

[4]helicene **3** is the smallest PAH that has showed biological activities such as carcinogenic [15], mutagenic [16] and antiproliferative activity [17]. 3,4-dihydrodiol **4** and the corresponding diepoxide **5** (Fig. 2) are highly potent carcinogenic metabolites [18-20]. Their photophysical and chiroptical properties have been also investigated [21-25].

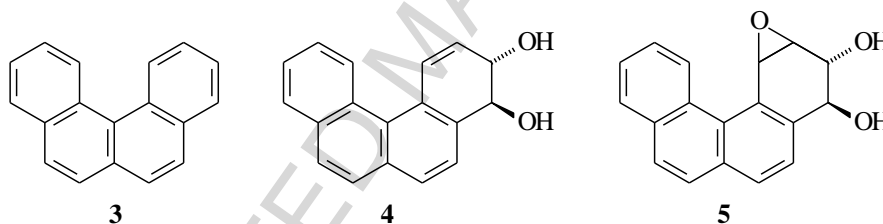


Figure 2. Representative examples of [4]helicene metabolites.

The [4]helicene skeleton demonstrate various applications such as molecular motor, building blocks for highly conjugated structures as well as larger [*n*]helicenes that have proved successful as chiral catalysts and ligands in asymmetric synthesis [26-33] and as blue emitters in OLEDs [34-35].

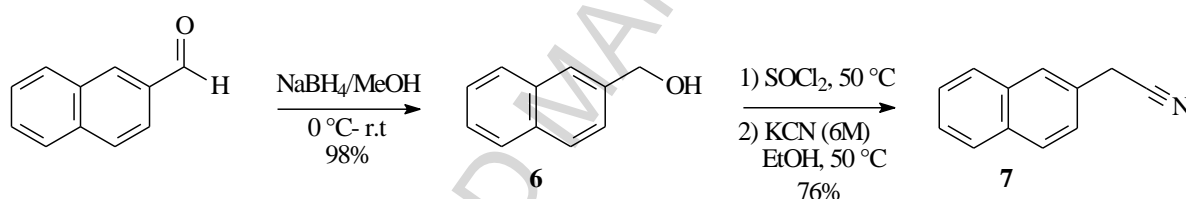
Numerous approaches to the synthesis of [4]helicene and its analogs have been developed in order to explore the particular properties of these molecules. A convenient synthetic strategy based on a cross-coupling reaction, 3-methoxy[4]helicene has been prepared [36]. Lakshman and co-workers have demonstrated the applicability of Pt-catalyzed cycloisomerization reactions of 1-(2-ethynylphenyl)naphthalenes to yield benzo[*c*]phenanthrene analogues that are otherwise not easy to access [37]. B. Zajc have described a photochemical procedure to yield regioselectively substituted monofluoro PAHs from 1,2-diarylfluoroethenes, which were synthesized *via* Julia-Kocienski olefination [38]. More

recently, Schindler and co-workers developed a synthetic strategy based on iron(III)-catalyzed carbonyl-olefin metathesis reactions toward benzo[*c*]phenanthrenes [39].

In this work, we report the synthesis and characterization of new [4]helicene derivatives bearing different reactive functional groups. Our synthetic approach is based the use of suitable α,β -unsaturated nitriles which undergo oxidative photocyclization to achieve the target helicenes.

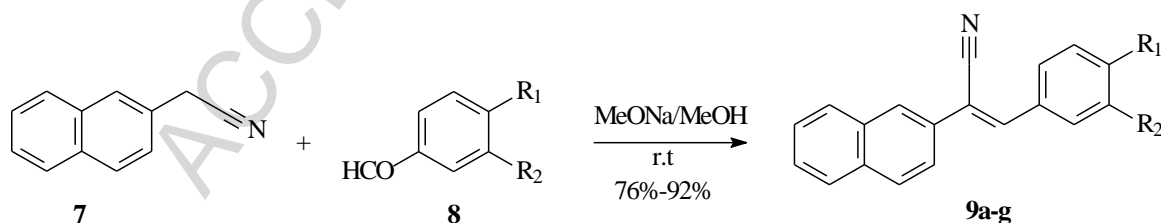
2. Results and discussion

2-naphthylacetonitrile (**7**) was available in three steps as shown in scheme 1. In the first step, we have prepared 2-naphthylmethanol (**6**) in 98% yield by reduction of 2-naphthaldehyde using sodium borohydride (NaBH_4) in anhydrous methanol. Reaction of alcohol **6** with thionyl chloride then treatment with an aqueous solution of potassium cyanide (6M) under heating at 50 °C in ethanol provided 2-naphthylacetonitrile (**7**), as a white solid, in 76% yield.



Scheme 1. Synthetic pathway for the synthesis of 2-naphthylacetonitrile (**7**).

Knoevenagel reaction between 2-naphthylacetonitrile (**7**) and various aromatic aldehydes **8** in the presence of sodium methoxide in methanol gave the corresponding α,β -unsaturated nitriles **9a-g** in 76%-92% yield (Scheme 2, Table 1).



Scheme 2. Synthetic strategy to obtain α,β -unsaturated nitriles **9a-g**.

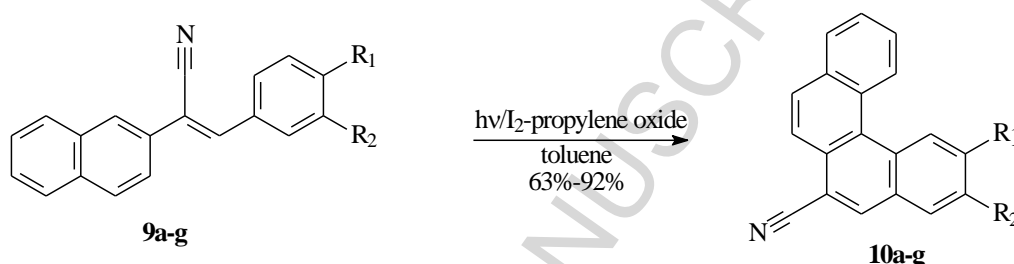
Table 1. Chemical yields of α,β -unsaturated nitriles **9a-g**.

α,β -unsaturated nitrile	R_1	R_2	yield (%) ^a
9a	F	H	85
9b	CF_3	H	76
9c	CO_2CH_3	H	91
9d	OCH_3	H	92

9e	CN	H	84
9f	SCH ₃	H	87
9g	OCH ₃	OCH ₃	90

^a Isolated yields.

Finally, the desired benzo[*c*]phenanthrenes were obtained through oxidative photocyclization of 1,2-diarylethenes **9a-g** using a 500 W high-pressure mercury immersion lamp. In fact, each resulting diarylethylene has been subjected to photocyclization on a 500 mg scale per 1 liter of toluene, in the presence of stoichiometric amount of iodine as oxidizing agent and an excess of propylene oxide as hydrogen iodide scavenger, to produce the corresponding benzo[*c*]phenanthrene derivative. This allowed us to obtain benzo[*c*]phenanthrenes **10a-g** in 63%-92% yield (Scheme 3, Table 2).



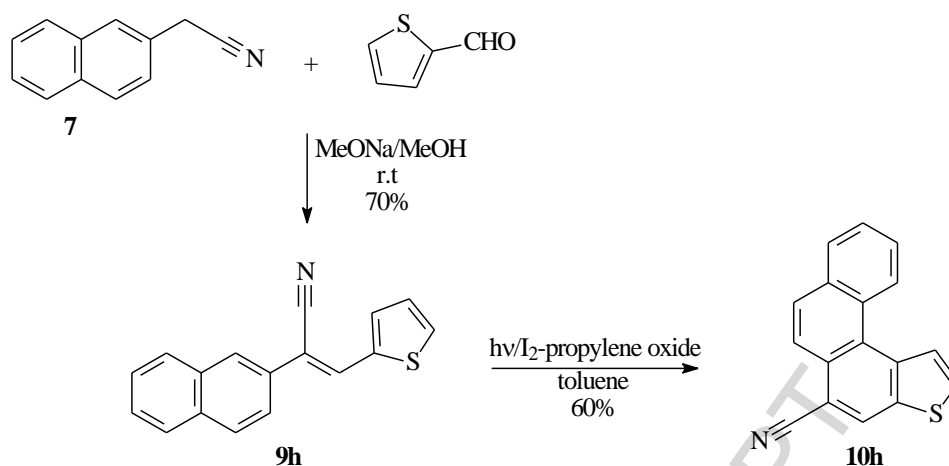
Scheme 3. Photocyclization of α,β -unsaturated nitriles **9a-g** into [4]helicenes **10a-g**.

Table 2. Chemical yields of benzo[*c*]phenanthrene derivatives **10a-g**.

Compound	R ₁	R ₂	Yield (%) ^a
10a	F	H	92
10b	CF ₃	H	75
10c	CO ₂ Me	H	86
10d	OCH ₃	H	78
10e	CN	H	63
10f	SCH ₃	H	77
10g	OCH ₃	OCH ₃	80

^a Isolated yields.

In order to extend the scope of these reactions, we have also prepared the benzo[*c*]phenanthrene like system **10h**, containing a thiophene ring, according to the same synthetic approach. Our procedure uses 2-naphthylacetonitrile (**7**) and thiophene-2-carbaldehyde as key building blocks for the synthesis of olefin **9h**, which is then converted into phenanthro[2,1-*b*]thiophene-5-carbonitrile (**10h**) by photolysis in 60% yield and 42% overall yield (Scheme 4).



Scheme 4. Synthetic route to phenanthro[2,1-*b*]thiophene-5-carbonitrile (**10h**).

X-ray analysis confirmed the structure of compound **10h**. Suitable crystals of this compound were obtained as orange plates by slow evaporation of a dichloromethane solution. The product was highly stable in air and to light. The X-ray analysis was carried out on a single crystal obtained from **10h** (Fig. 3). The torsion angles at the inner helical rim represented by C2-C3-C4-C5 and C3-C4-C5-C6, showed unequal and relatively small angles of -11° and -10° , respectively.

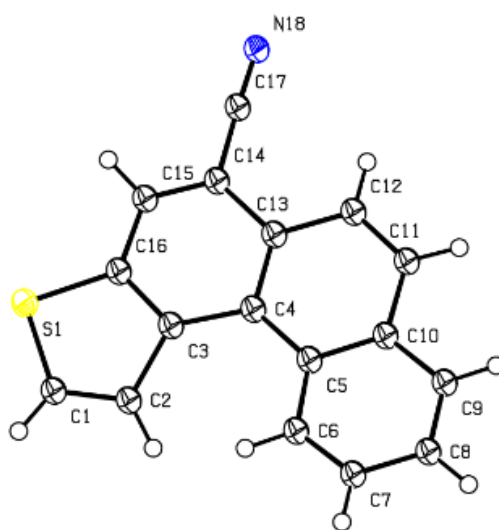


Figure 3. X-ray crystal structure of the tetracyclic system **10h**: ORTEP drawing.

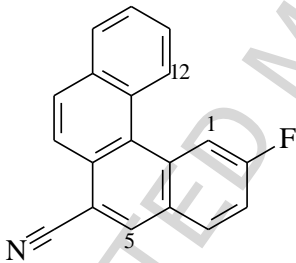
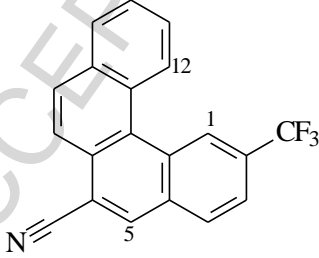
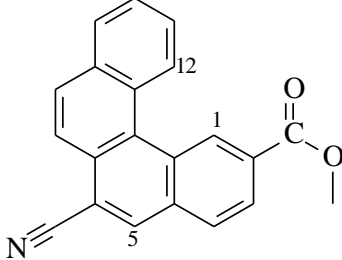
Selected ¹H NMR data for the tetracyclic compounds **10a-h** are gathered respectively in tables 3 and 4. Protons H₁ and H₁₂ in compounds **10a-g** are the most deshielded compared to the other aromatic protons owing to the magnetic anisotropic effect in the vicinity of the terminal benzene rings. This series of compound was examined to investigate the deshielding effect produced by the close approach of cyano group. Proton H₅ in each of the compounds **10a-g** is more deshielded than the rest of the aromatic protons with the exception of H₁ and

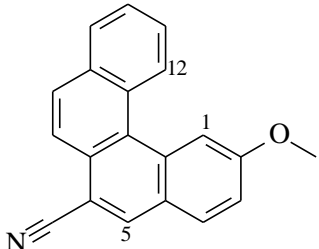
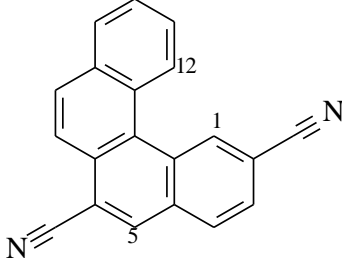
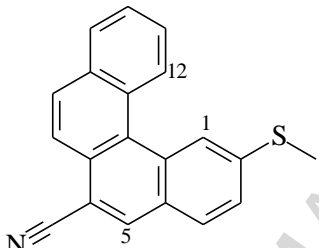
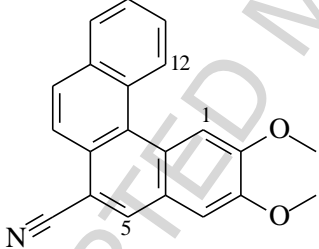
H₁₂ which are inside the crown. This deshielding is mainly attributed to the electron-withdrawing effect of the nitrile group. This deshielding appears to be more important in compounds **10a-c,e** which are still substituted with electron-withdrawing groups at position 2 of the tetracyclic skeleton.

Chemical shift of proton H₁ changes according to the substitutions at positions 2 and 3. In fact, this proton is more deshielded under the effect of electron-withdrawing groups (CF₃, CO₂Me, and CN) and is decreased under the effect of electron-donating groups (SCH₃ and OCH₃). In the case of 2-fluorobenzo[*c*]phenanthrene-6-carbonitrile **10a**, the signal for proton H₁ appears as a doublet of doublet ($J_{\text{H-H}} = 2.4$ Hz, $J_{\text{H-F}} = 12$ Hz) and not a singlet which proves that it couples with fluorine and proton H₃.

For compound **10h**, signals of protons H₁ and H₁₁ appear with characteristic downfield shifts at $\delta = 8.61$ ppm ($J = 5.4$ Hz) and $\delta = 9.03$ ppm ($J = 8.1$ Hz), respectively. The singlet assigned to proton H₄ is more deshielded than that of H₅ in compounds **10a-g** ($\delta = 8.44$ ppm).

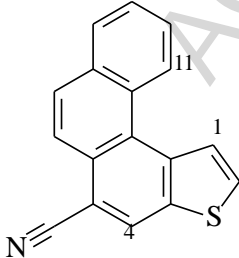
Table 3. Selected characteristic ¹H NMR (300 MHz) data (δ in ppm) for compounds **10a-g**.

Compound	Structure	δ (H ₁)	δ (H ₅)	δ (H ₁₂)
10a		8.70 (dd)	8.33 (s)	8.93 (d)
10b		9.36 (s)	8.41 (s)	8.89 (d)
10c		9.77 (s)	8.36 (s)	8.96 (d)

10d		8.51 (s)	8.27 (s)	9.07 (d)
10e		9.43 (s)	8.40 (s)	8.89 (d)
10f		8.83 (s)	8.27 (s)	8.98-9.01 (m)
10g		8.47 (s)	8.21 (s)	9.02-9.05 (m)

s: singlet, d: doublet, dd: doublet of doublet, m: multiplet

Table 4. Selected characteristic ^1H NMR (300 MHz) data (δ in ppm) for compound **10h**.

Compound	δ (H ₁)	δ (H ₁₁)	δ (H ₄)
	8.61 (d)	9.03 (d)	8.44 (s)

UV-Vis and fluorescence spectra of **10a-h** were measured in dilute chloroform solutions ($ca = 1.5 \times 10^{-5}$ M) at room temperature, and the results are summarized in Table 5. As shown in Fig.4, all compounds exhibited similar main absorbance bands in the range of 275-450 nm

with maxima at 289-320 nm that could be assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transitions. The optical band gap values of these systems appear to be lower than optical gap of 2-methyl-8,9-diaza[4]helicene ($E_{g-op} = 3.25$ eV) [40] and comparable to that of pyrene-cored [4]helicenes which might be promising candidates in organic light-emitting devices (OLEDs) [14]. Methyl-6-cyanobenzo[*c*]phenanthrene-2-carboxylate (**10c**) shows an optical band gap of 2.91 eV which was found to be much lower than that of 2-acetylbenzo[*c*]phenanthrene (3.05 eV) [41].

The tetracyclic systems **10a-h** show a typical emission of organic π -conjugated molecules. Photoluminescence (PL) of each dilute solution of compounds **10a-g** in chloroform, at room temperature, exhibits two main emissions in the range of 394-450 nm with shoulder peaks (Fig. 4). The phenanthro[2,1-*b*]thiophene-5-carbonitrile **10h** exhibits four emissions at 381 nm, 388 nm, 400 nm and 408 nm with a shoulder peak at 424 nm.

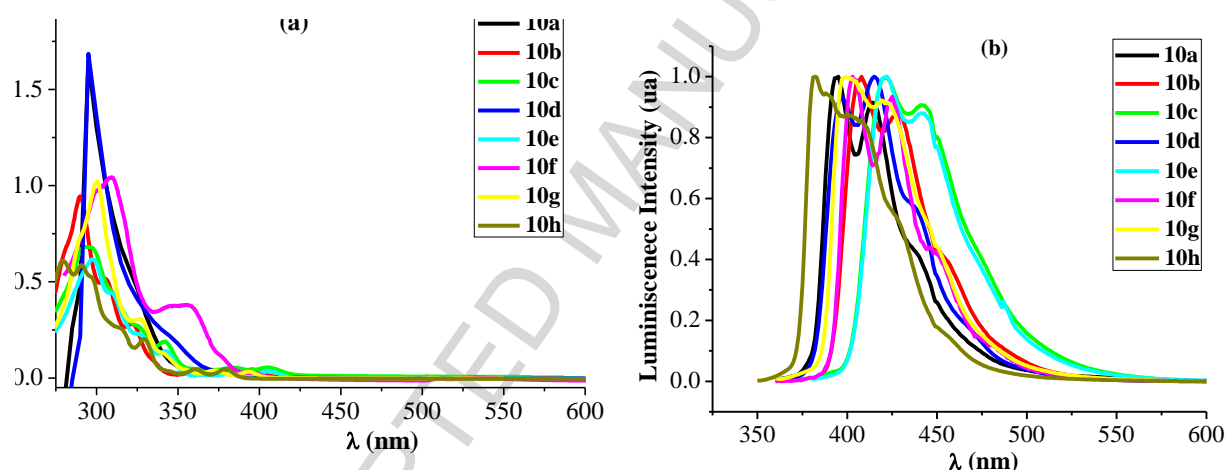


Figure 4. (a) UV-Vis and (b) normalized emission spectra of **10a-h** in dilute chloroform solutions ($c = 1.5 \times 10^{-5}$ M) at room temperature.

Table 5. Photophysical properties of [4]helicenes **10a-h**.

Compound	Absorption			Photoluminescence	
	λ_{max}^{abs} ^a (nm)	λ_{onset} (nm)	E_{g-op} ^b (eV)	λ_{max}^{ems} ^c (λ_{ex}) (nm)	FWHM ^d (nm)
10a	291	406	3.05	394 (340)	42
10b	290	408	3.03	408 (360)	47
10c	292	425	2.91	422 (350)	56
10d	300	400	3.10	415 (350)	54
10e	298	419	2.95	420 (360)	53
10f	309	408	3.03	403 (340)	42
10g	300	404	3.06	399 (350)	54
10h	291	389	3.17	382 (330)	53

^a Absorption maxima, measured in chloroform solutions (1.5×10^{-5} mol.L⁻¹) at room temperature.

^b The optical gap (E_{g-op}) was estimated from the onset point of the absorption spectra: $E_{g-op} = 1240/\lambda_{onset}$.

^c Emission maxima, measured in chloroform solutions (1.5×10^{-5} mol.L⁻¹) at room temperature.

^d Spectrum full width at half maximum.

3. Conclusion

In summary, we have developed a facile and moderately functional-group-tolerant method which allow the synthesis of a wide range of new tetracyclic π -conjugated systems with 39%-58% overall yields. The procedure offers several advantages, such as a simple synthetic procedure with an easy work-up and ready access to highly functionalized compounds in a low number of steps. In addition, the obtained compounds allow further modification reactions. These compounds could be used as building blocks for multifunctional larger [*n*]helicenes and supramolecular architectures as they could serve as convenient materials for optoelectronic applications.

Acknowledgements

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4. Experimental section

4.1. General

All reactions that were carried out under anhydrous conditions were performed under an inert nitrogen atmosphere. All reagents and solvents used in this work were purchased from Sigma-Aldrich unless otherwise noted. Isolated yields reflect the mass obtained through filtration or following flash column silica gel chromatography. Organic compounds were purified using silica gel obtained from Silicycle Chemical division (40-63 μ m; 230-240 mesh). The reactions were monitored by thin-layer chromatography using commercial silica-gel plate 60 coated with a fluorescence indicator (Silicycle Chemical division, 0.25 mm, F254.). Visualization of TLC plate was performed by UV (254 nm). All mixed solvent eluents are reported as v/v solutions. Melting points were measured on a Bibby Scientific Stuart Digital, Advanced, SMP30. All reported compounds were homogeneous by thin layer chromatography (TLC) and by ¹H NMR. NMR spectra were taken in CDCl₃ as solvent with tetramethylsilane as the internal reference using Bruker AC-300 instruments unless otherwise noted. Signals due to the solvent served as the internal standard (CHCl₃: δ 7.26 for ¹H, δ

77.16 for ^{13}C). The acquisition parameters are shown on all spectra. The ^1H NMR chemical shifts and coupling constants were determined assuming first-order behaviour. Multiplicity is indicated by one or more of the following: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad); the list of coupling constants (J) corresponds to the order of the multiplicity assignment. UV-Vis spectra were recorded on a spectrophotometer UV-1600PC.

4.2. Experimental procedure and spectroscopic data for 2-naphthylmethanol (**6**)

Sodium borohydride (500 mg, 13.1 mmol) was added in small portions to a stirred solution of 2-naphthaldehyde (1 g, 6.4 mmol) in dry methanol (25 mL) at 0 °C. The resulting mixture was allowed to come to room temperature and then stirred for 1h. The solvent was removed under vacuum and the resulting solid was washed with water and dried to give 950 mg of pure 2-naphthylmethanol (**6**) as a white solid in 98% yield. m.p = 79-81 °C; ^1H NMR (300 MHz, CDCl_3): δ (ppm): 1.81 (s, 1H, OH); 4.85 (s, 2H, CH_2); 7.48 (m, 3H); 7.82 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3): δ (ppm): 64.94 (CH_2); 124.61 (CH); 124.91 (CH); 125.34 (CH); 125.63 (CH); 127.18 (CH); 127.36 (CH); 127.79 (CH); 132.53 (C); 132.97 (C); 137.90 (C).

4.3. Experimental procedure and spectroscopic data for 2-naphthylacetonitrile (**8**)

A mixture of 2-naphthylmethanol **6** (1 g, 6.3 mmol) and SOCl_2 (15 mL) was stirred overnight at 50 °C. After removing the excess of SOCl_2 under vacuum, 10 mL of ethanol were added and the mixture was stirred for 15 min at room temperature. Then, 6 mL of a potassium cyanide solution (6 M) were added and the mixture was stirred vigorously at 50 °C for 3h and then poured into 50 mL of water and stirred for 30 min. The precipitate formed was recovered by filtration on fritted glass to give 0.8 g (76%) of the desired product **8** as a white solid. m.p = 82-84 °C; ^1H NMR (300 MHz, CDCl_3): δ (ppm): 3.91 (s, 2H, CH_2); 7.38 (dd, $J_1 = 1.5$ Hz, $J_2 = 8.4$ Hz, 1H); 7.53-7.55 (m, 2H); 7.84-7.89 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3): δ (ppm): 23.26 (CH_2); 117.14 (CN); 124.90 (C-H); 125.97 (C-H); 126.25 (C-H); 126.36 (C-H); 126.79 (C-H); 127.19 (C); 127.22 (CH); 128.54 (C-H); 132.31 (C); 132.93 (C).

4.4. General procedure for the preparation of unsaturated α,β -nitriles (**9a-h**)

A mixture of 1 molar equivalent of 2-naphthylacetonitrile (**7**) and 1 molar equivalent of aldehyde in dry methanol (30 mL) was stirred at 0 °C for 10 min. Then, sodium methoxide (2

equiv.) was added in small portions and the mixture was stirred for 30 min at 0 °C, and then for 6 hours at room temperature. The resulting precipitate was collected by filtration on a fritted glass, washed with water and dried.

4.4.1. (Z)-3-(p-Fluorophenyl)-2-(naphthalen-2-yl)acrylonitrile (**9a**)

White powder, 85%, m.p = 143-145 °C; ¹H NMR (300 MHz, CDCl₃): δ (ppm): 7.54-7.58 (m, 2H); 7.64 (s, 1H); 7.70-7.78 (m, 3H); 7.86-7.89 (m, 1H), 7.91 (d, J = 8.1 Hz, 2H); 8.00 (d, J = 8.4 Hz, 2H); 8.21 (s, 1H, H_{vinyl}); ¹³C NMR (75 MHz, CDCl₃): δ(ppm): 114.02 (C); 116.96 (CN); 121.78 (CH); 125.41 (CH); 125.46 (CH); 126.34 (CH); 126.68 (CH); 126.95 (CH); 127.25 (CH); 128.11 (CH); 128.62 (CH); 128.94 (2CH); 130.45 (C); 131.12 (C); 132.71 (C); 133.17 (C); 136.61 (C); 139.46 (CH); ¹⁹F NMR (282 MHz, CDCl₃): δ(ppm): -109.84.

4.4.2. (Z)-3-(p-Trifluoromethylphenyl)-2-(naphthalen-2-yl)acrylonitrile (**9b**)

White powder, 76%, m.p = 170-172 °C; ¹H NMR (300 MHz, CDCl₃): δ (ppm): 7.15 (t, J = 8.4 Hz, 2H); 7.53-7.56 (m, 2H); 7.63 (s, 1H); 7.75 (dd, J₁ = 8.7 Hz, J₂ = 1.5 Hz); 7.85-7.97 (m, 5H); 8.16 (s, 1H, H_{vinyl}); ¹³C NMR (75 MHz, CDCl₃): δ (ppm): 110.51 (C); 111.08 (C); 115.56 (CH); 115.85 (CH); 117.48 (CN); 121.90 (CH); 125.78 (CH); 126.53 (CH); 126.62 (CH); 127.21 (CH); 127.99 (C); 128.47 (C); 129.57 (CH); 129.64 (CH); 130.87 (CH); 130.98 (CH); 132.78 (C); 132.92 (C); 140.26 (CH); 143.37 (C).

4.4.3. (Z)-1-Methyl-p-[2-cyano-2-(naphthalen-2-yl)]vinylbenzoate (**9c**)

Yellow solid, 91%, m.p = 144-146 °C; ¹H NMR (300 MHz, CDCl₃): δ (ppm): 3.96 (s, 3H, OCH₃); 7.54-7.57 (m, 2H); 7.70 (s, 1H); 7.75 (d, J = 8.7 Hz, 1H); 7.85-7.93 (m, 3H); 7.97 (d, J = 8.1 Hz, 2H); 8.13 (d, J = 8.1 Hz, 2H); 8.20 (s, 1H, H_{vinyl}); ¹³C NMR (75 MHz, CDCl₃): δ (ppm): 51.87 (CH₃); 113.56 (C); 117.10 (CN); 121.84 (CH); 126.27 (CH); 126.63 (CH); 126.87 (CH); 127.24 (CH); 128.11 (CH); 128.58 (CH); 128.68 (2CH); 129.64 (2CH); 130.67 (C); 130.94 (C); 132.73 (C); 133.12 (C); 137.37 (C); 140.02 (CH); 165.82 (C=O).

4.4.4. (Z)-3-(p-Methoxyphenyl)-2-(naphthalen-2-yl)acrylonitrile (**9d**)

Yellow solid, 92%, m.p = 129-131 °C; ¹H NMR (300 MHz, CDCl₃): δ (ppm): 3.91 (s, 3H, OCH₃); 7.01 (d, J = 8.4 Hz, 2H); 7.52-7.55 (m, 2H), 7.62 (s, 1H); 7.75 (d, J = 7,8 Hz, 1H); 7.86-7.97 (m, 5H); 8.16 (s, 1H, H_{vinyl}); ¹³C NMR (75 MHz, CDCl₃): δ (ppm): 54.90 (OCH₃); 108.43 (C); 113.97 (2CH and CN); 122.08 (CH); 125.26 (CH); 126.19 (C); 126.26 (CH); 126.33 (CH); 127.13 (CH); 127.86 (CH); 128.27 (CH); 130.70 (2CH); 131.66 (C); 132.76 (C); 132.91 (C); 141.32 (CH); 161.03 (C).

4.4.5. (Z)-3-(p-Cyanophenyl)-2-(naphthalen-2-yl)acrylonitrile (**9e**)

Yellow solid, 84%, m.p = 205-207 °C; ¹H NMR (300 MHz, CDCl₃): δ (ppm): 7.57-7.60 (m, 2H); 7.67 (s, 1H); 7.76-7.79 (m, 3H); 7.88-7.89 (m, 1H); 7.94 (d, J = 9 Hz, 2H); 8.01 (d, J = 6 Hz, 2H); 8.22 (s, 1H, H_{vinyl}); ¹³C NMR (75 MHz, CDCl₃): δ (ppm): 113.11 (C); 115.06 (C); 116.62 (CN); 117.60 (CN); 121.73 (CH); 126.5 (CH); 126.71 (CH); 127.40 (CH); 127.24 (CH); 128.12 (CH); 128.68 (CH); 129.08 (2CH); 130.32 (CH); 132.09 (2CH); 132.74 (C); 133.33 (C); 137.45 (C); 138.64 (C).

4.4.6. (Z)-3-(p-(Methylthio)phenyl)-2-(naphthalen-2-yl)acrylonitrile (**9f**)

Yellow solid, 87%, m.p = 142-144 °C; ¹H NMR (300 MHz, CDCl₃): δ (ppm): 2.54 (s, 3H, CH₃); 7.32 (d, J = 8.4 Hz, 2H); 7.51-7.59 (m, 2H); 7.60 (s, 1H); 7.73 (d, J = 8.4 Hz, 1H); 7.83-7.92 (m, 4H); 8.15 (s, 1H, H_{vinyl}); ¹³C NMR (75 MHz, CDCl₃): δ (ppm): 14.52 (CH₃); 109.81 (C); 117.81 (CN); 121.96 (CH); 125.31 (2CH); 125.57 (CH); 126.46 (CH); 127.20 (CH); 127.96 (CH); 128.38 (CH); 129.18 (2CH); 129.69 (C); 131.29 (C); 132.82 (2C); 140.98 (2CH); 142.16 (C).

4.4.7. (Z)-3-(3',4'-Dimethoxyphenyl)-2-(naphthalen-2-yl)acrylonitrile (**9g**)

Yellow solid, 90%, m.p = 119-121 °C; ¹H NMR (300 MHz, CDCl₃): δ (ppm): 3.97 (s, 3H, OCH₃); 4.02 (s, 3H, OCH₃); 6.95 (d, J = 8.4 Hz, 1H); 7.41 (dd, J₁ = 8.4 Hz, J₂ = 2.1 Hz, 1H); 7.53-7.56 (m, 2H); 7.61 (s, 1H); 7.75-7.78 (m, 2H); 7.85-7.94 (m, 3H); 8.31 (s, 1H, H_{vinyl}); ¹³C NMR (75 MHz, CDCl₃): δ (ppm): 55.53 (2OCH₃); 108.23 (C); 110.89 (CH); 110.98 (CH); 118.24 (CN); 122.53 (CH); 124.47 (CH); 125.79 (CH); 126.85 (CH); 126.91 (CH); 127.68 (CH); 128.40 (CH); 128.83 (CH); 131.92 (C); 132.70 (2C); 132.85 (C); 142.09 (CH); 148.59 (C-O); 150.70 (C-O).

4.4.8. (Z)-2-(Naphthalen-2-yl)-3-(thiophen-2-yl)acrylonitrile (**9h**)

Yellow solid, 70%, m.p = 121-123 °C; ¹H NMR (300 MHz, CDCl₃): δ (ppm): 7.18-7.21 (m, 1H); 7.51-7.59 (m, 3H); 7.73-7.76 (m, 2H); 7.82 (s, 1H); 7.85-7.93 (3H); 8.15 (s, 1H, H_{vinyl}); ¹³C NMR (75 MHz, CDCl₃): δ (ppm): 107.85 (C); 117.74 (CN); 121.68 (CH); 125.46 (CH); 126.50 (2CH); 127.20 (CH); 127.42 (CH); 127.92 (2CH); 128.45 (CH); 129.61 (CH); 130.62 (C); 132.76 (C); 132.84 (C); 133.61 (CH); 137.57 (C).

4.5. General procedure for the photocyclization of α,β-unsaturated nitriles into [4]helicenes

To a solution of olefin **9** (2 mmol) in toluene (1 L) was added iodine (56 mg, 1.1 equiv). The solution was degassed for 15-20 min, and then propylene oxide (50 equiv) was added. Irradiation was performed using a falling-film photoreactor and a high-pressure Hg-vapor lamp (500 W, Hanovia). A flow of argon was maintained throughout the irradiation. The reaction was monitored by thin-layer chromatography (TLC). After completion, the solvent was removed under reduced pressure and the crude residue was purified by flash silica gel column chromatography (cyclohexane/EtOAc: 90/10) to yield the pure compound **10**. Spectroscopic data of the benzo[*c*]phenanthrene derivatives are given subsequently.

4.5.1. 2-Fluorobenzo[*c*]phenanthrene-6-carbonitrile (**10a**)

Brown powder, 92%, m.p = 218-220 °C; ¹H NMR (300 MHz, CDCl₃): δ (ppm): 7.47 (ddd, J₁ = 9 Hz, J₂ = 8.7 Hz, J₃ = 2.4 Hz, 1H); 7.69-7.77 (m, 2H); 8.02-8.08 (m, 3H); 8.19 (d, J = 9 Hz, 1H); 8.33 (s, 1H, H₅); 8.70 (dd, J_{H-F} = 12 Hz, J_{H-H} = 2.4 Hz, 1H, H₁); 8.93 (d, J = 9 Hz, 1H, H₁₂); ¹³C NMR (75 MHz, CDCl₃): δ (ppm): 108.63 (d, J_{F-C} = 2.62 Hz, C); 112.94 (d, J_{F-C} = 23.85 Hz, CH); 116.45 (d, J_{F-C} = 24.45 Hz, CH); 117.99 (CN); 123.03 (CH); 127.10 (CH); 127.18 (CH); 127.24 (C); 127.31 (CH); 128.25 (C); 128.84 (C); 128.95 (CH); 129.65 (C); 129.93 (CH); 131.62 (d, J_{F-C} = 9.52 Hz, CH); 133.11 (d, J_{F-C} = 9.37 Hz, C); 133.57 (C); 134.59 (CH); 161.48 (d, J_{F-C} = 284.4 Hz, C-F); ¹⁹F NMR (282 MHz, CDCl₃): δ (ppm): -108.29 (s).

4.5.2. 2-(Trifluoromethyl)benzo[*c*]phenanthrene-6-carbonitrile (**10b**)

White solid, 75%, m.p = 144-146 °C; ¹H NMR (300 MHz, CDCl₃): δ (ppm): 7.25-7.83 (m, 2H); 7.90 (d, J = 8.7 Hz, 1H); 8.10-8.13 (m, 2H); 8.17 (d, J = 8.4 Hz, 1H); 8.25 (d, J = 9 Hz, 1H); 8.41 (s, 1H, H₅); 8.89 (d, J = 8.1 Hz, 1H, H₁₂); 9.36 (s, 1H, H₁); ¹³C NMR (75 MHz, CDCl₃): δ(ppm): 111.56 (C); 117.50 (CN); 122.33 (C); 122.83 (CH); 122.89 (CH); 125.50 (CH); 127.39 (CH); 127.60 (CH); 127.68 (CH); 128.16 (C); 128.82 (C); 129.03 (CH); 130.09 (CH); 130.21 (CH); 130.41 (C); 130.84 (C); 130.90 (C); 132.71 (C); 133.86 (C); 134.09 (CH); ¹⁹F NMR (282 MHz, CDCl₃) : δ (ppm) : - 62.22 (s)

4.5.3. Methyl-6-cyanobenzo[*c*]phenanthrene-2-carboxylate (**10c**)

Yellow solid, 86%, m.p = 218-220 °C; ¹H NMR (300 MHz, CDCl₃): δ (ppm): 4.04 (s, 3H, CH₃); 7.71-7.78 (m, 2H); 8.06-8.09 (m, 3H); 8.22-8.29 (m, 2H); 8.36 (s, 1H, H₅); 8.96 (d, J = 8.1 Hz, 1H, H₁₂); 9.77 (s, 1H, H₁); ¹³C NMR (75 MHz, CDCl₃): δ(ppm): 52.66 (OCH₃); 111.46 (C); 117.71 (CN); 122.90 (CH); 126.65 (CH); 127.44 (CH); 127.54 (CH); 127.87 (CH); 128.23 (C); 128.58 (C); 128.88 (CH); 129.33 (CH); 129.46 (C); 129.90 (CH); 130.20 (C); 130.54 (CH); 131 (C); 133.55 (C); 133.86 (C); 134.22 (CH); 166.81 (C=O).

4.5.4. 2-Methoxybenzo[*c*]phenanthrene-6-carbonitrile (**10d**)

Yellow solid, 78%, m.p = 162-164 °C; ¹H NMR (300 MHz, CDCl₃): δ (ppm): 4.02 (s, 3H, CH₃); 7.32 (dd, J₁ = 9 Hz, J₂ = 2.4 Hz, 1H, H₃); 7.67-7.70 (m, 2H); 7.92 (d, J = 8.7 Hz, 1H); 7.99-8.06 (m, 2H); 8.19 (d, J = 8.7 Hz); 8.27 (s, 1H, H₅); 8.51 (s, 1H, H₁); 9.07 (d, J = 9.3 Hz, 1H, H₁₂); ¹³C NMR (75 MHz, CDCl₃): δ(ppm): 55.64 (OCH₃); 106.55 (C); 109.49 (CH); 117.56 (CH); 118.48 (CN); 123.26 (CH); 126.45 (C); 126.72 (2CH); 127.02 (CH); 127.11 (C); 128.89 (CH); 129.02 (C); 129.25 (CH); 130.01 (C); 130.81 (CH); 133.48 (C); 133.55 (C); 134.77 (CH); 160.64 (C-O).

4.5.5. 2-Cyanobenzo[*c*]phenanthrene-6-carbonitrile (**10e**)

Yellow solid, 63%, m.p = 259-261 °C; ¹H NMR (300 MHz, CDCl₃): δ (ppm): 7.77-7.89 (m, 3H); 8.12-8.18 (m, 3H); 8.28 (d, J = 8.7 Hz, 1H); 8.40 (s, 1H, H₅); 8.89 (d, J = 8.1 Hz, 1H, H₁₂); 9.43 (s, 1H, H₁); ¹³C NMR (75 MHz, CDCl₃): δ(ppm): 112.59 (2C); 117.19 (CN); 118.74 (CN); 122.85 (CH); 127.45 (CH); 127.67 (C); 127.90 (CH); 128 (CH); 129.06 (C);

129.13 (CH); 130.19 (CH); 130.64 (CH); 131.01 (C); 132.94 (C); 133.48 (CH); 133.86 (CH); 134 (C).

4.5.6 2-(Methylthio)benzo[*c*]phenanthrene-6-carbonitrile (**10f**)

White solid, 77%, m.p = 143-145 °C; ¹H NMR (300 MHz, CDCl₃): δ (ppm): 2.68 (s, 3H, CH₃); 7.54 (dd, J₁ = 8.4 Hz, J₂ = 1.5 Hz, 1H, H₃); 7.68-7.75 (m, 2H); 8.22-8.29 (m, 2H); 7.90 (d, J = 8.4 Hz, 1H); 8.02 (d, J = 8.7 Hz, 1H); 8.05-8.09 (m, 1H); 8.19 (d, J = 8.7 Hz, 1H); 8.27 (s, 1H, H₅); 8.83 (s, 1H, H₁); 8.98-9.01 (m, 1H, H₁₂); ¹³C NMR (75 MHz, CDCl₃): δ(ppm): 14.96 (CH₃); 107.47 (C); 117.78 (CN); 122.62 (CH); 123.13 (CH); 124.97 (CH); 126.35 (CH); 126.44 (CH); 126.40 (C); 126.84 (CH); 128.35 (C); 128.39 (CH); 128.50 (C); 128.75 (CH); 128.91 (CH); 129.21 (C); 131.59 (C); 133.13 (C); 134.16 (CH); 140.83 (C).

4.5.7. 2,3-Dimethoxybenzo[*c*]phenanthrene-6-carbonitrile (**10g**)

Beige powder, 80%, m.p = 209-211 °C; ¹H NMR (300 MHz, CDCl₃): δ (ppm): 4.09 (s, 6H, 2OCH₃); 7.31 (s, 1H, H₄); 7.66-7.69 (m, 2H); 7.93 (d, J = 8.7 Hz, 1H); 8.03 (dd, J₁ = 6 Hz, J₂ = 2.4 Hz, 1H); 8.16 (d, J = 8.7 Hz, 1H); 8.21 (s, 1H, H₅); 8.47 (s, 1H, H₁); 9.02-9.05 (m, 1H, H₁₂); ¹³C NMR (75 MHz, CDCl₃): δ(ppm): 55.60 (OCH₃); 55.67 (OCH₃); 106.42 (C); 107.53 (CH); 107.91 (CH); 118.11 (CN); 122.85 (CH); 126.01 (CH); 126.25 (CH); 126.40 (CH); 126.67 (C); 126.76 (C); 127.01 (C); 127.48 (C); 127.77 (CH); 128.43 (CH); 129.22 (C); 132.98 (CH); 133.10 (C); 149.10 (C-O); 151.07 (C-O).

4.5.8. Phenanthro[2,1-*b*]thiophene-5-carbonitrile (**10h**)

Brown solid, 60%, m.p = 150-152 °C; ¹H NMR (300 MHz, CDCl₃): δ (ppm): 7.70-7.80 (m, 2H); 7.95-7.99 (m, 2H); 8.02-8.09 (m, 1H); 8.25 (d, J = 9Hz, 1H); 8.47 (s, 1H, H₄); 8.61 (d, J = 5.4 Hz, 1H, H₁); 9.03 (d, J = 8.1 Hz, 1H, H₁₁); ¹³C NMR (75 MHz, CDCl₃): δ(ppm): 107.15 (C); 118.48 (CN); 123.57 (CH); 125.93 (CH); 126.35 (CH); 126.85 (C); 127.22 (2CH); 127.74 (CH); 128.78 (CH); 129.01 (CH); 129.33 (C); 129.85 (C); 131.11 (CH); 133.01 (C); 138.19 (C); 138.30 (C).

Crystal data for compound **10h** (C₁₇H₉NS) were recorded on a D8 VENTURE Bruker AXS diffractometer, M = 259.31, monoclinic, space group *P* 21. a = 3.8867(14) Å, b = 17.900(6)Å, c = 16.609(6)Å, V = 1153.8(7)Å³, Z = 4, ρ_{calcd} = 1.493 g.cm⁻³, X-ray source Mo-

$K\alpha$, $\lambda = 0.71073 \text{ \AA}$, $T = 150(2) \text{ K}$; observed reflections 2098; refinement method Full-matrix Least-squares on F^2 ; parameters refined 140; $R(F) = 0.1305$, $wR(F^2) = 0.3105$. Crystallographic data for the structure in this Letter have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1588231. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 (0) 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or via www.ccdc.cam.ac.uk/data_request/cif.

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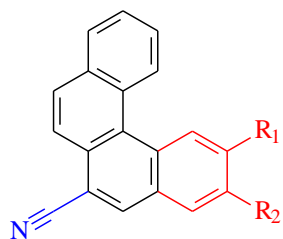
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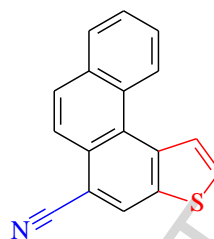
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Graphical abstract



R₁ = F, CF₃, CO₂Me, OMe, CN, SMe
R₂ = H, OMe



ACCEPTED MANUSCRIPT

Highlights

Facile method was developed for [4]helicenes preparation from 2-naphthaldehyde.

Photophysical properties of [4]helicenes were studied in solutions.

Optical gap values of [4]helicenes were found to be less than 3.2 eV.

ACCEPTED MANUSCRIPT