ARTICLE

Aza-aromatic polycycles based on triphenylene and acridine or acridone: synthesis and properties

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Salima Bouarfa,[a,b] Philippe Jéhan,[c] William Erb,[a] Olivier Mongin,[a] François-Hugues Porée,[a] Thierry Roisnel,[a] Ghenia Bentabed-Ababsa,[b] Nicolas Le Yondre*[c] and Florence Mongin*[c]

Acridine- and acridone-based polycyclic aromatics were prepared by using as the key steps a copper-catalysed *N*-arylation of 2-aminobenzaldehyde, 2-aminophenones, or ethyl 2-aminobenzoate with 2-iodotriphenylene, and an acid-mediated cyclization. The regioselectivity of this intramolecular S_EAr reaction was studied by performing Hückel theory calculations on the precursors. Due to their structural similarity with some MALDI-MS matrices, two acridine-based polycycles were evaluated for this purpose. Finally, in view of structure-properties relationships, preliminary studies of the photophysical properties of the synthesized acridine- and acridone-based polycycles were performed.

1. Introduction

Acridines and acridones are planar skeletons that play an important role in biologically active molecules, but also in organic materials for various applications.[1-3] For example, both acridine and acridone patterns have been found in fluorescent sensors[4, 5] and in hole transporting materials.[6, 7]

Polyaromatic hydrocarbons (PAHs) are also structural units playing an important role in compounds endowed with biological and physicochemical (e.g. electronic and photophysical) properties.[8] Furthermore, the incorporation of one or more nitrogen atoms into PAHs has attracted the attention of chemists due to the impact of this heteroatom on the properties of these organic scaffolds.[9-12] However, the development of materials based on nitrogen-containing PAHs depends on the availability of synthetic methods that can be used to access them. For example, few studies have been dedicated to the synthesis of acridine- and acridone-based PAHs with more than five rings.[13]

In pioneered studies, Buu-Hoï and co-workers obtained benzo[*c*]- and benzo[*a*]naphth[2,1-*j*]acridines from α- and β-naphthol, respectively, by regioselective Ullmann-Fetvadjian reaction with 2-aminophenanthrene in the presence of paraformaldehyde (Figure 1, top).[14] Similarly, benzo[*c*]- and benzo[*a*]naphth[2,3-*h*]acridines were respectively prepared from α- and β-naphthol by reaction with 1-aminoanthracene while using 2-aminoanthracene furnished benzo[*c*]- and benzo[*a*]naphth[2,3-*j*]acridines, respectively (Figure 1, middle and bottom).[15]

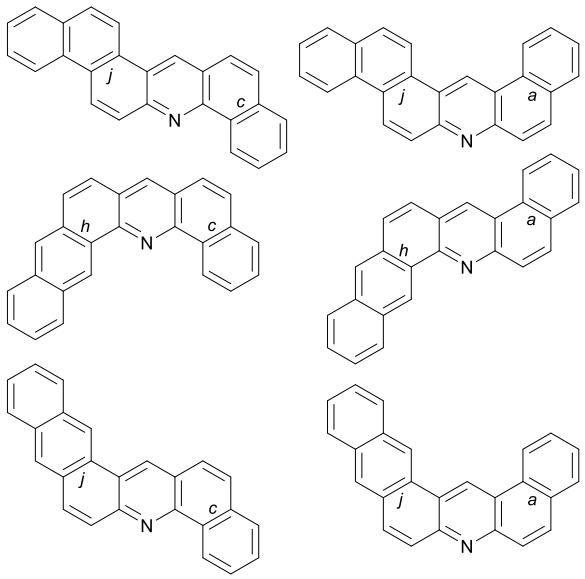


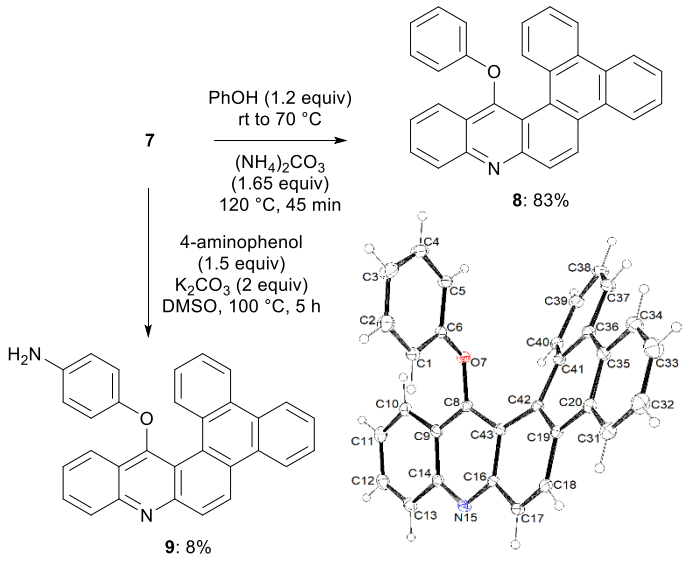
Figure 1 Benzo[*c*]- and benzo[*a*]naphth[2,1-*j*]acridines, benzo[*c*]- and benzo[*a*]naphth[2,3-*h*]acridines, and benzo[*c*]- and benzo[*a*]naphth[2,3-*j*]acridines already prepared.[14, 15]

As evidenced by recent studies, accessing acridine-based PAHs is always a challenge. For example, Hashmi and co-workers reported in 2018 a π-extending strategy towards dibenzo[*a*,*c*]acridines using gold-catalysis for C-H annulation of 2-ethynylbiaryls with anthranils.[16] We can also cite the modified iron-catalysed Povarov reaction involving 2-(2'-alkynylaryl)benzaldehydes and arylamines documented by Jana and co-workers in 2020 to access the same scaffolds[17] (Figure 2).

[a] *Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) - UMR 6226, F-35000 Rennes, France. E-mail: florence.mongin@univ-rennes1.fr*
[b] *Laboratoire de Synthèse Organique Appliquée, Faculté des Sciences Exactes et Appliquées, Université d'Oran 1 Ahmed Ben Bella, BP 1524 El M'Naouer, 31000 Oran, Algeria. E-mail: bentabedg@gmail.com*
[c] *Univ Rennes, CNRS, ScanMat - UMS 2001, Centre Régional de Mesures Physiques de l'Ouest - CRMPO, F-35000, Rennes, France. E-mail: nicolas.leyondre@univ-rennes1.fr*

† Electronic Supplementary Information (ESI) available: General information and crystallographic details; Experimental procedures and analyses of intermediate compounds; NMR spectra of the new compounds as well as numbering used in the experimental section; Highest occupied Hückel molecular orbitals (HOMO); Qualitative evaluation of two polycycles as matrices for MALDI-MS. CCDC 2085922, 2085923. For ESI and crystallographic data in CIF, see DOI: 10.1039/x0xx00000x

(methanesulfonic acid and palladium on charcoal in ethanol under reflux) did not allowed the expected amino derivative to be isolated.



Scheme 6 Conversion of 16-chlorophenanthro[9,10-*a*]acridine (**7**) and ORTEP diagram (30% probability) of 16-phenoxyphenanthro[9,10-*a*]acridine (**9**).

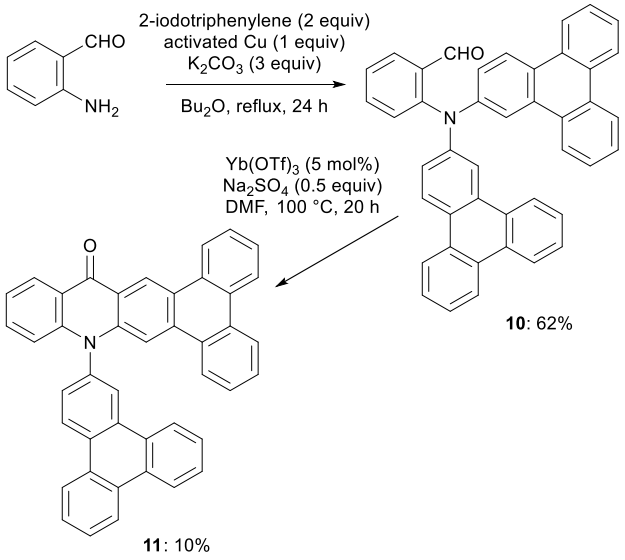
Finally, because the aryl ether **8** was easily obtained, we attempted the reaction of 4-aminophenol with the chloride **7** in the presence of a base. By performing the reaction in dimethylsulfoxide at 100 °C,[39] the aminoether **9** was formed. However, due to difficult purification, it was isolated in a low 8% yield (Scheme 6, bottom).

To prepare polycyclic aza-aromatics based on triphenylene and NH-free acridone, we first examined the mono-*N*-arylation of anthranilic acid with 2-iodotriphenylene, and the subsequent cyclization using polyphosphoric acid as described in similar cyclizations,[40] but we failed in isolating a triphenylene-based acridone by following this approach. Because Zhou and co-workers succeeded in cyclizing 2-(phenylamino)acetophenone into NH-free acridone by using copper(I) iodide (0.2 equiv) in dimethylsulfoxide at 140 °C under air atmosphere,[41] we attempted a similar reaction from the ketone **3c**. However, after 36 h, a complex mixture was obtained from which a NH-free acridone could not be detected.

These failures led us to rather turn to the synthesis of *N*-substituted triphenylene-based acridones. To this goal, we first attempted the cyclization of the ketones **3a** and **3b** in the presence of copper(I) iodide (0.2 equiv) in dimethylsulfoxide at 120 °C under air since these conditions were employed by Zhou and Deng to convert 2-(phenylamino)benzophenone into *N*-phenylacridone.[42] However, these conditions failed in delivering the expected products.

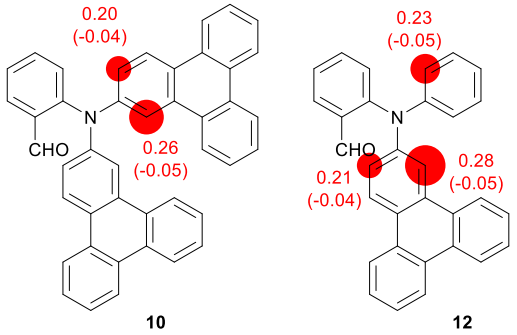
Consequently, we capitalized on the possible double copper-catalysed *N*-arylation of 2-aminobenzaldehyde we recently reported.[18] By reaction with 2-iodotriphenylene (2 equiv) in the presence of an excess of base (3 equiv) in refluxing diethyl ether for 24 h, the aldehyde **10** was obtained in 62% yield (Scheme 7, top). Next, we studied its cyclization, and first tested the acidic conditions employed to convert the compounds **3** into **4**; however, degradation took place, and no acridone could be isolated.

In 2013, Yang and co-workers cyclized *N*-methyl-*N*-phenyl-2-aminobenzaldehydes into *N*-methylacridones by recourse to catalytic ytterbium(III) triflate or scandium(III) triflate in the presence of sodium sulfate in dimethylformamide at 100 °C.[43] Inspired by this work, we applied the protocol using ytterbium(III) triflate, and observed the formation of the *N*-triphenylated triphenylene-based acridone **11**. However, it proved difficult to purify this compound which was only isolated in a low 10% yield by recrystallization from ethyl acetate (Scheme 7, bottom).



Scheme 7 Synthesis of *N*-(2-triphenylenyl)phenanthro[9,10-*b*]-15-acridone (**11**).

To rationalize the regioselectivity of the reaction, which probably takes place by intramolecular S_EAr reaction followed by oxidation,[43] we calculated as above both amplitudes of the HOMO coefficients and charges on the aldehyde **10** (see ESI and Scheme 8, left). Albeit in favour of the most hindered position, the difference between both cyclization sites on the triphenylene ring is not very marked and steric effects might become predominant. This is probably why a helicene-like acridone was not formed in this case.

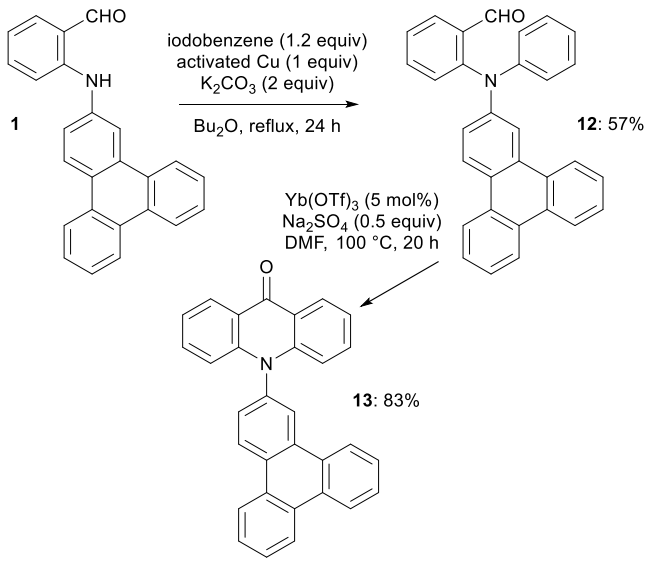


Scheme 8 Amplitudes of the highest occupied molecular orbital (HOMO) coefficients and charges (in brackets) obtained by using the HuLiS calculator[27] to rationalize the regioselective formation of the acridones **11** and **13**.

Similar calculations performed on the aldehyde **12** show a not very marked difference between the phenyl and the less hindered 2-triphenylenyl possible cyclization sites (see ESI and Scheme 8, right). Since there is also no peculiar difference between both sides regarding steric hindrance, a cyclization involving the phenyl ring might be expected. We therefore decided to synthesize the aldehyde **12**.

To attain compound **12**, it is possible to successively *N*-arylate 2-aminobenzaldehyde by using iodobenzene and 2-iodotriphenylene. In our hands, the first *N*-arylation under the conditions used in Scheme 3 to prepare **1** afforded 2-(phenylamino)benzaldehyde[18] in 86% yield; however, the second *N*-arylation using 2-iodotriphenylene proceeded in a low 22% yield (not shown).

When we reversed the step order, and thus involved **1** and iodobenzene, we could obtain **12** more satisfactorily (Scheme 9, top). Then, the cyclization of **12** was performed as before, by using either ytterbium(III) triflate or scandium(III) triflate, and the predicted acridone **13** was isolated in 83% yield (Scheme 9, bottom) and 64% yield (not shown), respectively. It is worth noting that *N*-arylation of acridone by using 2-iodotriphenylene (1.5 equiv) in the presence of potassium carbonate (2 equiv), copper(I) iodide (0.20 equiv) and 2,2,6,6-tetramethyl-3,5-heptanedione (0.40 equiv) in dimethylformamide at reflux for 24 h, as reported to access nitrogen-embedded quinoidal pentacenes,[44] only allowed us to isolate **13** in 8% yield (not shown).



Scheme 9 Synthesis of *N*-(2-triphenylenyl)-9-acridone (**13**).

2.2. Qualitative evaluation of acridine-based polycyclic aza-aromatics as matrices for MALDI-MS

With the structural similarity of **8** and **9** with 9-aminoacridine (9AA), the gold standard matrix for negative mode in MALDI-MS,[20] and azahelicenes which were described as potential candidates for MALDI or MAILD matrices,[45] we compared the ability of **8** and **9** to ionize a group of nine target compounds (mainly drugs, see ESI). Therefore, we designed a quick MALDI-MS method with the idea to focus on qualitative detection. We performed the experiments in both positive and negative mode, with the five different matrices DCTB, HCCA, 9-AA, **8** and **9**, with two solvents for a two-layer spotting[46] (90 spots and 180 experiments). Each experiment aimed to reach 500 counts on the base peak by increasing gradually the laser power. A better quality of MALDI mass spectra in term of resolution and exact mass precision is achieved within the little power as possible, this phenomenon is called irradiance or fluence.[47] We scaled this factor [Laser(+) or Laser(-)] from zero (upper than 66% of laser power) up to six (less than 15%). The goal was to obtain target compounds as base peaks, but if not possible, the relative intensity was exported. We scaled this factor [Target.in(+) or Target.in(-)] from zero (not seen) up to five (seen as base peak). A product factor [Product.LT] representing both the laser power applied and the presence of target compounds was calculated. We scaled specifically a factor [Target.BP(+), Target.BP(-) or Target.BP] representing the number of target compounds obtained as a base peak, in positive, negative or in both, without redundancy. The solvent influence was not relevant.

At the first sight, the Kiviat's diagram of average values of the factors for the five matrices shows that DCTB was surprisingly the best matrix in both ionization modes. 9-AA has slightly higher result in term of overall ionization of target compounds in negative mode but the ionization efficiency is bad (Figure 3).

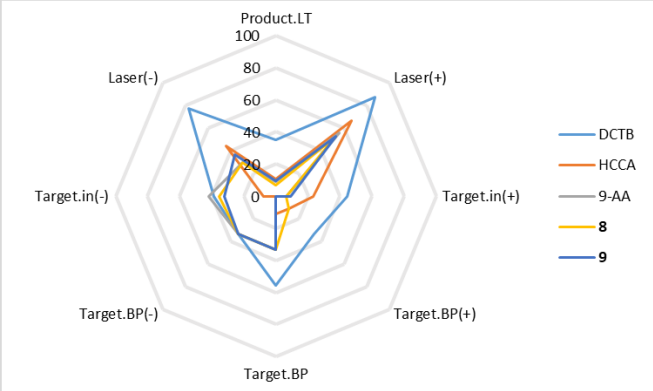


Figure 3 Qualitative analysis of the five matrices.

For more details, HCCA is a matrix mainly applied for positive mode in MALDI-MS. The Kiviat's diagram of average values for DCTB vs. HCCA matrices shows that HCCA ionized one target compound only in positive mode as expected, in comparison DCTB is the best in positive mode with three target compounds as base peak (see Figure 4). In a matter of fact, in this experiment DCTB is better than HCCA in positive ionization.

9-AA is the gold standard matrix for negative mode in MALDI-MS.[20] The Kiviat's diagram of average values for DCTB vs. 9-AA matrices shows that 9-AA was suitable to ionize three target compounds only in negative mode as expected, in comparison DCTB has also three target compounds as base peak (see ESI and Figure 5). 9-AA has slightly higher result in term of overall ionization of target compounds in negative mode (Target.in(-): 9-AA (42.2%) and DCTB (38.8%)). But DCTB ionization efficiency is really better (Laser(-): DCTB (76.8%) and 9-AA (29.5%)). In this work, DCTB is a better matrix than 9-AA in negative ionization.

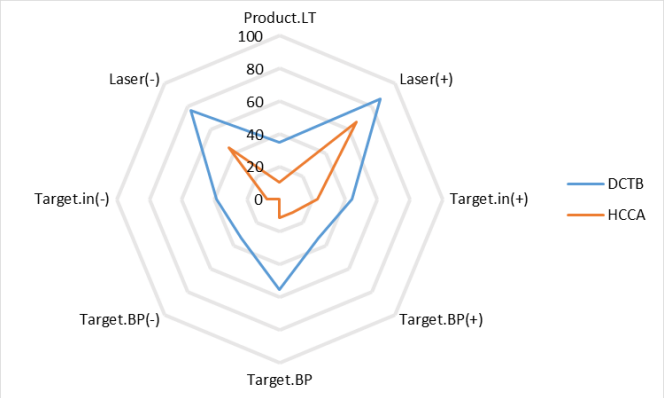


Figure 4 Qualitative analysis of DCTB vs. HCCA.

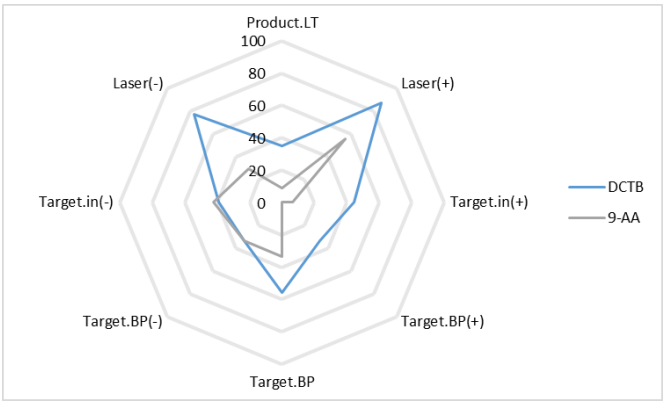


Figure 5 Qualitative analysis of DCTB vs. 9-AA.

For the comparison between 9-AA, **8** and **9**, the Kiviat's diagram shows that the three matrices were suitable to ionize three target compounds in negative mode as expected (see ESI and Figure 6). Although 9-AA gave the best result in term of overall ionization of target compounds in negative mode (Target.in(-) 9-AA (42.2%), **8** (35.6%) and **9** (32.2%)), the ionization efficiency of **9** is promising (Laser(-) **9** (36.2%) vs. **8** (29.7%) and 9-AA (29.5%)).

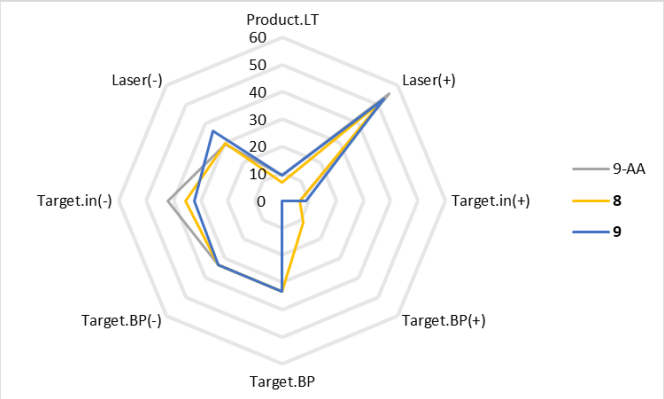


Figure 6 Qualitative analysis of 9-AA, **8** and **9**.

2.3. Photophysical properties of the synthesized acridine- and acridone-based aza-polycycles

Both acridine and acridone derivatives can display interesting fluorescence properties, in particular when substituted by electron-donating groups.[18, 48] Thus, to establish structure-properties relationships, preliminary studies of the photophysical properties of most of the nitrogen-containing polycycles were performed. Their UV-visible absorption and emission properties were investigated in toluene, and the results are gathered in Table 1.

Table 1 Absorption and emission properties of phenanthroacridines **2**, **4**, **7**, **8** and acridones **11**, **13** in toluene at 25°C.

Compound	λ_{abs} (nm)	ε_{max} (M^{-1} cm^{-1})	λ_{em} (nm)	Φ_F
2	392	9480	447	0.06
4a	414	14300	465, 495	0.30
4b	419	8700	469, 499	0.30
4c	412	12000	456, 485, 520	0.14
7	406	11500	467	0.02
8	399	11000	463	0.05
11	436	4760	445, 473	0.08
13	391	8940	398, 420	0.03

The three phenanthrol[9,10-*a*]acridines **2**, **7** and **8** exhibit similar absorption and emission properties, i.e. a lowest energy absorption band in the 350-450 nm range, with molar extinction coefficients of ~ 10^4 M^{-1} cm^{-1}, and an unresolved emission band in the violet-blue part of the visible (Figure 7). Substitution at 16-position leads to bathochromic shifts in both absorption and emission, with larger shifts with chloro (**7**) than with phenoxy (**8**). Their fluorescence quantum yields are rather low (2-6%), probably in relation with their non-planar helicene-like shape.

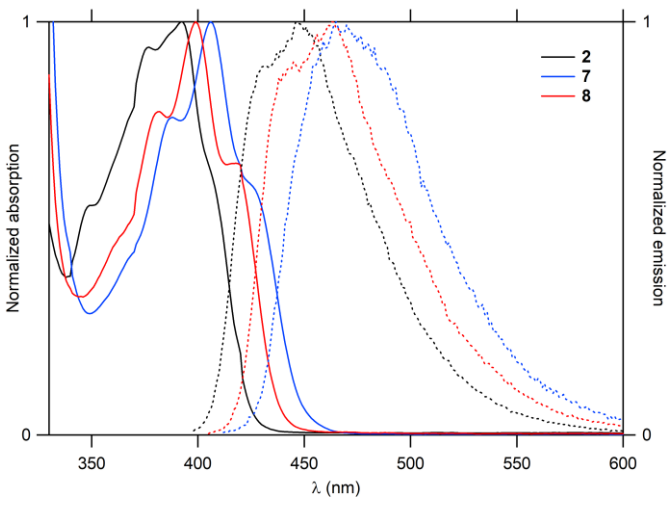


Figure 7 Absorption (solid line) and emission (dotted line) of phenanthrol[9,10-*a*]acridines **2**, **7** and **8** in toluene.

The three phenanthrol[9,10-*b*]acridines **4a-c** exhibit a structured absorption band with a maximum at around 415 nm and a structured emission band in the blue-green part of the visible (Figure 8). Introduction of a chlorine atom at the 13-position leads to small red-

shifts of the absorption (5 nm) and emission (4 nm) bands, whereas replacement of a phenyl ring by a weaker donor methyl group at the 15-position has almost no effect on the absorption but leads to a 10 nm blue-shift of the emission band. The fluorescence quantum yields of **4a-c** range between 14 and 30%. These compounds are therefore clearly more emissive than the helicene-like compounds **2**, **7** and **8**, in relation with their better planarity.

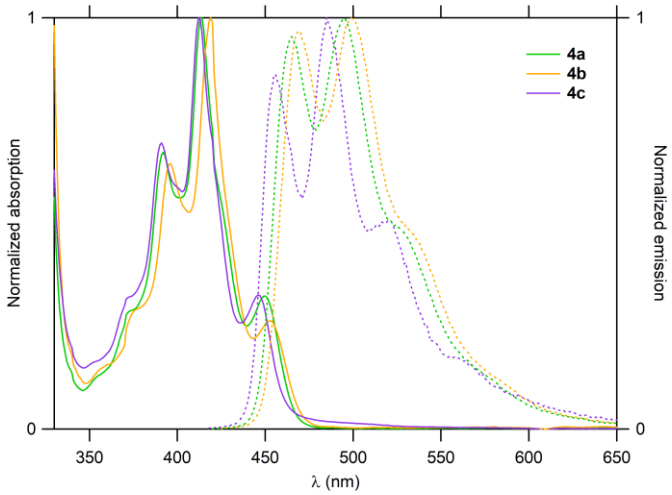


Figure 8 Absorption (solid line) and emission (dotted line) of phenanthrol[9,10-*b*]acridines **4a-c** in toluene.

Phenanthrol[9,10-*b*]acridone **11** and acridone **13** exhibit similar fine-structured lowest energy absorption and emission bands, but those of compound **11** are strongly red-shifted (45 nm in absorption and 47 nm in emission), in relation with the extended π-electron system of **11** in comparison with that of **13** (Figure 9). This extension also leads to a significant increase of the fluorescence quantum yield from 3% for **13** to 8% for **11**.

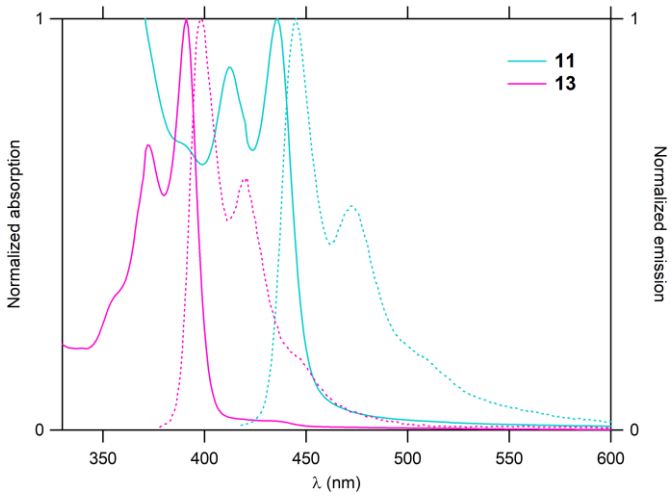


Figure 9 Absorption (solid line) and emission (dotted line) of acridones **11** and **13** in toluene.

3. Conclusions

Thus, in the present study, we evidenced the value of copper-catalysed *N*-arylation of anilines bearing an adjacent carbonylated function to access nitrogen-containing polyaromatic hydrocarbons (PAHs). Interestingly, the cyclization to PAHs occurred regioselectively; while formation of helicene-like scaffolds was observed in some cases (which corresponds to both orbital and charge controls), more linear polycycles prevailed from bulkier precursors.

Regarding the unexpected results obtained with DCTB as a MALDI-MS matrix, the introduction of a *trans*-2-[2-methyl-2-propenyliden-3-yl]malononitrile group (R-CH=C(CH_3)-CH=C($CN)_2$) on our original PAHs could be a promising strategy to reach more efficient matrices. Besides, other applications for the prepared aza-polycycles could be expected. Indeed, the introduction of heteroatoms, and in particular nitrogen, in nanographenes (which behave as graphene segments) can have a great impact on their properties (e.g. resistance to oxidation and dimerization, ability to molecular packing, optical and electrochemical behaviours, etc.), and can be used to tune them.[49] Therefore, as our strategy is able to easily deliver aza-polycycles, further development could be expected. Efforts are actually ongoing and will be reported in due course.

4. Experimental

The general information, synthetic procedures and analyses of the intermediates can be found in the ESI.†

Synthesis of the compounds 2 and 4 (General procedure).

They were prepared by adapting a literature procedure.[28] To 2-(2-triphenylenyl)aminobenzaldehyde (**1**; 0.37 g, 1.0 mmol), or the required 2-(2-triphenylenyl)aminophenone (1.0 mmol), in CH_3CO_2H (3 mL) was added 96% H_2SO_4 (2.8 mmol, 0.15 mL). The mixture was stirred at 110 °C for 2 h. After cooling to room temperature, water (5 mL) was added and the mixture was basified using 25% NH_4OH before extraction using AcOEt (3x20 mL), drying over $MgSO_4$, and removal of the solvent. The crude was purified as specified in the product description.

Phenanthro[9,10-*a*]acridine (2). It was prepared according to the general procedure by starting from 2-(2-triphenylenyl)aminobenzaldehyde (**1**). Purification by column chromatography on silica gel (eluent: petroleum ether-AcOEt 80:20; R_f = 0.375) gave **2** in 97% yield (0.34 g) as a yellow solid: mp 224 °C; IR (ATR): 723, 747, 766, 828, 856, 929, 965, 1144, 1244, 1373, 1418, 1433, 1477, 1495, 1523, 1539, 1610, 1717, 1965, 2850, 2919, 3059 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.59 (t, 1H, *J* = 7.45 Hz, H14), 7.69 and 7.71-7.75 (t, 1H, *J* = 7.0 Hz and m, 3H, H2, H3, H6 and H7), 7.85 (t, 1H, *J* = 7.6 Hz, H13), 8.05 (d, 1H, *J* = 8.3 Hz, H15), 8.31 (t, 2H, *J* = 8.6 Hz, H10 and H12), 8.62-8.64 (m, 1H, H8), 8.71-8.73 and 8.77 (m, 1H and t, 2H, *J* = 8.1 Hz; H1, H4 and H5), 8.83 (d, 1H, *J* = 9.4 Hz, H9), 9.66 (s, 1H, H16); ^{13}C NMR ($CDCl_3$) δ 123.3 (CH), 123.8 (C), 123.8 (CH), 123.9 (CH), 126.0 (CH, C14), 126.2 (C), 126.3 (CH, C9), 126.8 (CH), 127.0 (C), 127.1 (CH), 127.3 (C), 127.7 (CH), 127.8 (CH), 128.7 (CH, C15), 128.9

(CH), 129.0 (CH), 129.1 (CH), 129.2 (C), 129.4 (C), 130.3 (C), 130.7 (CH), 131.3 (C), 137.0 (CH, C16), 148.0 (C), 149.5 (C); HRMS (MALDI, DCTB matrix), *m/z*: 330.127 (2 ppm) found (calcd for $C_{25}H_{16}N$, $[M+H]^+$, requires 330.1277). **Crystal data for 2.** $C_{25}H_{15}N$, M = 329.38, monoclinic, $P\,2_1/c$, a = 12.054(2), b = 10.6413(10), c = 13.5706(19) Å, β = 114.096(9) °, V = 1589.1(4) Å^3, Z = 4, d = 1.377 g cm^{-3}, μ = 0.080 mm^{-1}. A final refinement on F^2 with 3521 unique intensities and 235 parameters converged at $\omega R(F^2)$ = 0.2049 ($R(F)$ = 0.0563) for 2798 observed reflections with $I > 2\sigma(I)$. CCDC 2085922.

15-Phenylphenanthro[9,10-*b*]acridine (4a). It was prepared according to the general procedure by starting from phenyl 2-(2-triphenylenyl)aminophenyl ketone (**3a**; 0.44 g). Purification by column chromatography on silica gel (eluent: petroleum ether-AcOEt 80:20; R_f = 0.40) gave **4a** in 57% yield (0.23 g) as an orange solid: mp 254 °C; IR (ATR): 702, 718, 757, 782, 873, 923, 1075, 1262, 1424, 1491, 1509, 1534, 1552, 1626, 2186, 3064 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.44-7.63 (m, 5H), 7.65-7.74 (m, 5H), 7.82 (t, *J* = 8.5 Hz, 2H), 8.23 (d, 1H, *J* = 6.3 Hz), 8.34 (d, 1H, *J* = 7.2 Hz), 8.48 (br s, 2H), 8.87 (br s, 1H), 8.91 (s, 1H), 9.50 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 121.2 (CH), 122.9 (CH), 123.6 (CH), 123.7 (CH), 124.0 (CH), 124.3 (C), 124.8 (CH), 125.3 (C), 125.7 (CH), 127.1 (CH), 127.8 (CH), 128.1 (CH), 128.3 (CH), 128.8 (C), 128.8 (2CH), 128.8 (CH), 128.9 (CH), 129.5 (CH), 129.8 (C), 129.9 (C), 130.4 (C), 130.5 (CH), 130.8 (C), 130.9 (2CH), 132.9 (C), 136.0 (C), 147.0 (C), 147.7 (C), 149.6 (C); HRMS (MALDI, DCTB matrix), *m/z*: 406.159 (0 ppm) found (calcd for $C_{31}H_{20}N$, $[M+H]^+$, requires 406.1590).

13-Chloro-15-phenylphenanthro[9,10-*b*]acridine (4b). It was prepared according to the general procedure by starting from 5-chloro-2-(2-triphenylenyl)aminophenyl phenyl ketone (**3b**; 0.48 g). Purification by column chromatography on silica gel (eluent: petroleum ether-AcOEt 80:20; R_f = 0.525) gave **4b** in 95% yield (0.42 g) as a yellow solid: mp > 260 °C; IR (ATR): 717, 754, 787, 821, 869, 878, 949, 970, 1029, 1067, 1135, 1164, 1256, 1307, 1404, 1421, 1441, 1487, 1507, 1599, 1952, 3064 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.47 (ddd, 1H, *J* = 8.2, 7.6 and 0.95 Hz), 7.53-7.57 (m, 3H), 7.61-7.66 (m, 3H), 7.70-7.74 (m, 4H), 8.16 (d, 1H, *J* = 7.0 Hz, H1), 8.23 (d, 1H, *J* = 9.1 Hz, H11), 8.40-8.44 (m, 2H, H4 and H5), 8.76 (dd, 1H, *J* = 6.0 and 3.6 Hz, H8), 8.82 (s, 1H, H16), 9.38 (s, 1H, H9); ^{13}C NMR ($CDCl_3$) δ 121.0 (CH), 122.6 (CH), 123.6 (CH), 123.7 (CH), 124.0 (CH), 124.3 (C), 129.2 (CH), 124.8 (CH), 125.2 (CH), 125.3 (C), 127.8 (CH), 128.1 (CH), 128.5 (CH), 129.0 (2CH), 129.1 (CH), 129.3 (C), 129.5 (C), 129.6 (C), 130.4 (C), 130.8 (C), 130.8 (2CH), 130.9 (CH), 131.6 (C), 131.8 (CH), 133.2 (C), 135.3 (C), 146.5 (C), 147.1 (C), 147.3 (C); HRMS (MALDI, DCTB matrix), *m/z*: 440.120 (0 ppm) found (calcd for $C_{31}H_{19}{}^{35}ClN$, $[M+H]^+$, requires 440.1200).

15-Methylphenanthro[9,10-*b*]acridine (4c). It was prepared according to the general procedure by starting from 2-(2-triphenylenyl)aminoacetophenone (**3c**; 0.36 g). Purification by recrystallization from AcOEt gave **4c** in 90% yield (0.31 g) as an orange solid: mp > 260 °C; IR (ATR): 717, 751, 857, 947, 1052, 1261, 1424, 1509, 1551, 1664, 2166, 2921 cm^{-1}; ^{1}H NMR ($CDCl_3$) at a lower concentration (about 1 mg in 0.5 mL) δ 3.35 (s, 3H, Me), 7.56 (t, 1H, *J* = 7.6 Hz), 7.63-7.68 (m, 4H), 7.79 (t, 1H, *J* = 7.5 Hz), 8.27 (d, 1H, *J* = 8.7 Hz), 8.30 (d, 1H, *J* = 8.8 Hz), 8.52-8.53 (m, 2H), 8.77 (d, 1H, *J* = 7.5 Hz), 8.84-8.86 (m, 1H), 9.44 (s, 2H); ^{1}H NMR ($CDCl_3$) at higher concentration (about 2 mg in 0.5 mL) δ 3.21 (s, 3H, Me), 7.49 (t, 1H, *J* = 7.6 Hz), 7.58-7.63 (m, 4H), 7.74 (t, 1H, *J* = 7.5 Hz), 8.20 (t, 2H, *J* = 8.7 Hz), 8.43 (d, 2H, *J* = 6.8 Hz), 8.63 (d, 1H, *J* = 6.8 Hz), 8.76 (d, 1H, *J* = 4.9 Hz), 9.25 (s, 1H), 9.31 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.0 (CH_3), 118.6 (CH), 123.5 (CH), 123.7 (CH), 123.8 (CH), 124.5 (C), 124.6 (CH), 124.8 (CH), 125.3 (CH), 125.5 (C), 127.8 (CH), 128.0 (CH), 128.2 (CH), 128.2 (C), 128.7 (CH), 129.8 (C), 130.0 (C), 130.2 (CH), 130.4 (C), 130.6 (C), 132.4 (C), 3C not seen, 3CH not seen; HRMS (MALDI, DCTB matrix), *m/z*: 344.144 (2 ppm) found (calcd for $C_{26}H_{18}N$, $[M+H]^+$, requires 344.1434).

16-Chlorophenanthro[9,10-*a*]acridine (7). It was prepared by adapting a literature procedure.[37] To 2-(2-triphenylenyl)aminobenzoic acid (**6**; 0.36 g, 1.0 mmol) was added a large excess of $POCl_3$ (4.0 mL). The solution was stirred at reflux under argon for 72 h and then concentrated to dryness. The residue was dissolved in CH_2Cl_2 and the solution slowly poured onto ice-cooled 15% aqueous NH_4OH solution. After decantation, the organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by column chromatography on silica gel (eluent: petroleum ether-AcOEt 80:20; R_f = 0.475) gave **7** in 84% yield (0.31 g) as a yellow solid: IR (ATR): 719, 741, 750, 819, 839, 909, 955, 1016, 1197, 1246, 1260, 1344, 1383, 1415, 1462, 1494, 1533, 1597, 1721, 2917 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.55 (td, 1H, *J* = 7.6 and 1.0 Hz), 7.64-7.76 (m, 4H), 7.89 (td, 1H, *J* = 7.7 and 1.2 Hz), 7.95 (d, 1H, *J* = 8.2 Hz), 8.18 (d, 1H, *J* = 9.2 Hz), 8.34 (d, 1H, *J* = 8.6 Hz), 8.55 (d, 1H, *J* = 8.7 Hz), 8.57-8.60 (m, 1H), 8.68 (d, 1H, *J* = 8.4 Hz), 8.72 (d, 1H, *J* = 9.2 Hz), 8.73-8.76 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 121.4 (C), 123.3 (CH), 123.4 (CH), 123.9 (CH), 125.0 (C), 125.1 (CH), 125.7 (CH), 125.7 (C), 126.6 (CH), 126.9 (CH), 127.3 (CH), 127.6 (CH), 127.9 (CH), 128.7 (CH), 128.7 (C), 128.9 (C), 129.3 (CH), 129.6 (C), 130.0 (C), 130.7 (CH), 131.1 (C), 131.5 (CH), 141.2 (C), 148.1 (C), 149.9 (C); HRMS (MALDI, DCTB matrix), *m/z*: 364.089 (1 ppm) found (calcd for $C_{25}H_{15}N^{35}Cl$, $[M+H]^+$, requires 364.0888).

16-Phenoxyphenanthro[9,10-*a*]acridine (8). It was obtained by adapting a literature procedure.[38] A mixture of 16-chlorophenanthro[9,10-*a*]acridine (**7**; 0.36 g, 1.0 mmol) and phenol (0.11 g, 1.2 mmol) was stirred and heated at 70 °C before addition of ammonium carbonate (0.13 g, 1.65 mmol). The internal temperature was raised to 120 °C and the reaction mixture was stirred at this temperature for 45 min. It was next cooled to 30 °C and poured into acetone (3 mL) cooled at 0 °C. A precipitate took form which was collected and washed with acetone. This solid was treated by sodium hydroxide (0.26 g) in water (6 mL), and the mixture extracted by CH_2Cl_2 (3 x 20 mL). The organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by column chromatography on silica gel (eluent: petroleum ether-AcOEt

80:20; R_f = 0.30) gave **8** in 83% yield (0.35 g) as a yellow solid: mp 206-210 °C; IR (ATR): 720, 745, 753, 765, 783, 804, 826, 1019, 1069, 1106, 1163, 1211, 1250, 1300, 1347, 1363, 1396, 1417, 1467, 1488, 1538, 1559, 1590, 2167, 2850, 2919, 3053 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.83 (d, 2H, *J* = 7.8 Hz), 6.48 (t, 1H, *J* = 7.3 Hz), 6.61 (t, 2H, *J* = 7.8 Hz), 7.58-7.67 (m, 5H), 7.90 (dd, 1H, *J* = 8.4 and 6.9 Hz), 8.24 (dq, 1H, *J* = 6.8 and 3.2 Hz), 8.31 (d, 1H, *J* = 9.3 Hz), 8.43 (t, 2H, *J* = 8.2 Hz), 8.48-8.57 (m, 3H), 8.72 (d, 1H, *J* = 9.4 Hz); ^{13}C NMR ($CDCl_3$) δ 114.7 (C), 115.1 (2CH), 121.4 (C), 122.0 (CH), 122.5 (CH), 123.0 (CH), 123.1 (CH), 123.6 (CH), 125.3 (C), 125.4 (CH), 126.2 (CH), 126.5 (CH), 126.8 (CH), 127.2 (CH), 127.3 (CH), 128.2 (C), 128.6 (C), 128.6 (2CH), 128.7 (C), 129.0 (CH), 129.1 (CH), 129.7 (C), 130.7 (C), 130.8 (CH), 131.2 (CH), 149.6 (C), 151.3 (C), 155.6 (C), 156.8 (C); HRMS (MALDI, DCTB matrix), *m/z*: 422.154 (0 ppm) found (calcd for $C_{31}H_{20}NO$, $[M+H]^+$, requires 422.1539). **Crystal data for 8.** $C_{31}H_{19}NO$, *M* = 421.47, triclinic, *P*-1, *a* = 9.6301(9), *b* = 10.5930(9), *c* = 10.6467(11) Å, *α* = 100.520(4), *β* = 91.593(4), *γ* = 95.892(3) °, *V* = 1060.99(17) $Å^3$, *Z* = 2, *d* = 1.319 g cm^{-3}, *μ* = 0.079 mm^{-1}. A final refinement on F^2 with 4864 unique intensities and 298 parameters converged at $\omega R(F^2)$ = 0.1270 ($R(F)$ = 0.0485) for 3977 observed reflections with $I > 2\sigma(I)$. CCDC 2085923.

16-(4-Aminophenoxy)phenanthro[9,10-*a*]acridine (9). It was prepared by adapting a literature procedure.[39] 16-Chlorophenanthro[9,10-*a*]acridine (**7**; 0.36 g, 1.0 mmol) and 4-aminophenol (0.16 g, 1.5 mmol) were dissolved in dimethylsulfoxide (DMSO; 2 mL). Potassium carbonate (0.28 g, 2.0 mmol) was next added, and the reaction mixture was stirred at 100 °C for 5 h. After cooling to room temperature, the reaction was poured onto ice water before extraction with AcOEt (3 x 20 mL). The organic phase was washed with brine and dried over $MgSO_4$ before concentration under reduced pressure. Purification by column chromatography on silica gel (eluent: AcOEt-petroleum ether 60:40; R_f = 0.575) followed by recrystallization from AcOEt gave **9** in 8% yield (35 mg) as an orange solid: mp > 260 °C; IR (ATR): 722, 755, 822, 890, 956, 1013, 1075, 1149, 1195, 1244, 1354, 1413, 1504, 1571, 3193 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.05 (s, 2H, NH_2), 5.61 (d, 2H, *J* = 8.5 Hz), 5.93 (d, 2H, *J* = 8.5 Hz), 7.61 (ddd, 1H, *J* = 7.6, 6.7 and 0.82 Hz), 7.63-7.73 (m, 4H), 7.89 (ddd, 1H, *J* = 7.7, 6.7 and 1.3 Hz), 8.23-8.25 (m, 1H), 8.27 (d, 1H, *J* = 9.3 Hz), 8.36 (d, 1H, *J* = 8.7 Hz), 8.45 (d, 1H, *J* = 8.2 Hz), 8.55-8.60 (m, 2H), 8.63-8.66 (m, 1H), 8.75 (d, 1H, *J* = 9.4 Hz); ^{13}C NMR ($CDCl_3$) δ 114.8 (C), 115.4 (2CH), 116.1 (2CH), 121.8 (C), 122.6 (CH), 123.3 (CH), 123.3 (CH), 123.7 (CH), 125.5 (CH), 125.6 (C), 126.1 (CH), 126.4 (CH), 126.8 (CH), 127.3 (CH), 127.4 (CH), 128.2 (C), 128.9 (C), 129.0 (CH), 129.3 (CH), 129.8 (C), 130.8 (CH), 130.8 (C), 131.4 (CH), 140.8 (C), 149.7 (C), 150.4 (C), 151.5 (C), 156.6 (C), 1C not seen; HRMS (MALDI, DCTB matrix), *m/z*: 437.168 (7 ppm) found (calcd for $C_{31}H_{21}N_2O$, $[M+H]^+$, requires 437.1648).

***N*,*N*-Bis(2-triphenylenyl)-2-aminobenzaldehyde (10).** It was prepared under an argon atmosphere by adapting a procedure reported previously.[30] To 2-aminobenzaldehyde (0.12 g, 1.0 mmol) and 2-iodotriphenylene[50] (0.35 g, 2.0 mmol) in degassed Bu_2O (1 mL) were successively added activated Cu[51] (13 mg, 0.20 mmol) and K_2CO_3 (0.43 g, 3.0 mmol). The mixture was degassed and refluxed under argon for 24 h. During this time, activated Cu[51] (4 x 13 mg, 4 x 0.20 mmol) was added after 2, 4, 6 and 8 h of heating. After cooling to room temperature, the mixture was concentrated. Purification by column chromatography on silica gel (eluent: petroleum ether-AcOEt 90:10; R_f = 0.325) gave **10** in 62% yield (0.36 g) as a yellow solid: mp 224 °C; IR (ATR): 718, 750, 816, 857, 872, 943, 1051, 1117, 1156, 1191, 1236, 1265, 1306, 1346, 1384, 1435, 1475, 1503, 1581, 1604, 1649, 1689, 1948, 2746, 2849, 2924, 3051, 3309 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.39 (d, 1H, *J* = 7.8 Hz, H3), 7.43 (t, 1H, *J* = 7.6 Hz, H5), 7.48 (dd, 2H, *J* = 8.8 and 2.3 Hz, H3'), 7.49-7.52 (m, 2H), 7.60-7.69 (m, 7H, H4), 8.04 (dd, 1H, *J* = 7.8 and 1.6 Hz, H6), 8.24 (d, 2H, *J* = 8.0 Hz), 8.38 (d, 2H, *J* = 2.3 Hz, H1'), 8.55-8.57 (m, 2H), 8.59 (d, 2H, *J* = 9.0 Hz, H4'), 8.63-8.64 (m, 4H), 10.42 (s, 1H, CHO); ^{13}C NMR ($CDCl_3$) δ 116.8 (2CH), 123.0 (2CH), 123.2 (2CH), 123.4 (2CH), 123.5 (2CH), 123.5 (2CH), 125.3 (2CH), 125.7 (2C), 126.2 (CH), 127.0 (2CH), 127.3 (2CH), 127.6 (2CH), 127.7 (2CH), 129.3 (2C), 129.4 (CH), 129.5 (2C), 129.7 (2C), 129.9 (CH), 130.4 (2C), 131.4 (2C), 132.2 (C, C2), 135.9 (CH), 148.0 (2C), 150.1 (C, C1), 190.6 (CH, CHO); HRMS (MALDI, DCTB matrix), *m/z*: 573.209 (0 ppm) found (calcd for $C_{43}H_{27}NO$, $M^{+\bullet}$, requires 573.2087).

***N*-(2-Triphenylenyl)phenanthro[9,10-*b*]-15-acridone (11).** It was prepared under an argon atmosphere by adapting a procedure reported previously.[43] A mixture of 2-(bis(2-triphenylenyl))aminobenzaldehyde (**10**; 0.57 g, 1.0 mmol), ytterbium triflate (31 mg, 50 μmol) and sodium sulfate (71 mg, 0.50 mmol) in dimethylformamide (DMF; 5 mL) was heated at 100 °C for 20 h. After cooling to room temperature, diethyl ether (250 mL) was added, and the organic phase was washed with water (100 mL). After drying the organic phase over sodium sulfate, the solvent was evaporated under vacuum. Purification by recrystallization from AcOEt gave **11** in 10% yield (57 mg) as a beige greenish solid: mp > 260 °C; IR (ATR): 716, 748, 821, 851, 909, 964, 1033, 1149, 1240, 1303, 1331, 1431, 1470, 1499, 1600, 1642, 3077 cm^{-1}; ^1H NMR ($CDCl_3$) at a lower concentration (about 0.5 mg in 0.5 mL) δ 6.92 (d, 1H, *J* = 8.6 Hz, H11), 7.30-7.35 (m, 2H), 7.51-7.56 (m, 2H), 7.64, 7.70-7.76 and 7.83-7.85 (t, 2H, *J* = 7.6 Hz, m, 2H and m, 2H), 7.81 (dd, 1H, *J* = 8.6 and 1.8 Hz, H3'), 7.89 (d, 1H, *J* = 8.1 Hz), 8.05 (s, 1H), 8.53-8.56 (m, 2H), 8.58 (d, 1H, *J* = 8.4 Hz), 8.72 (d, 1H, *J* = 7.9 Hz), 8.78 (d, 1H, *J* = 8.4 Hz), 8.80-8.82 (m, 1H), 8.84 (d, 1H, *J* = 1.8 Hz, H1'), 8.85-8.87 (m, 1H), 8.93 (d, 1H, *J* = 8.1 Hz), 9.12 (d, 1H, *J* = 8.6 Hz), 9.93 (s, 1H, H16); ^1H NMR ($CDCl_3$) at a higher concentration (about 1 mg in 0.5 mL) δ 6.92 (d, 1H, *J* = 8.6 Hz, H11), 7.30 (d, 1H, *J* = 8.3 Hz), 7.33 (d, 1H, *J* = 7.4 Hz), 7.62-7.65 (m, 2H), 7.69 (t, 1H, *J* = 7.8 Hz), 7.75 (t, 1H, *J* = 7.5 Hz), 7.80-7.84 (m, 3H), 7.88 (d, 1H, *J* = 8.1 Hz), 8.04 (s, 1H), 8.53 (dd, *J* = 7.4 and 2.8 Hz, 2H), 8.58 (d, 1H, *J* = 8.0 Hz), 8.71 (d, 1H, *J* = 7.8 Hz), 8.77 (d, 1H, *J* = 8.3 Hz), 8.80-8.82 (m, 1H), 8.84-8.86 (m, 2H), 8.91 (d, 1H, *J* = 8.1 Hz), 9.12 (d, 1H, *J* = 8.6 Hz), 9.91 (s, 1H, H16); ^{13}C NMR ($CDCl_3$) δ 110.3 (CH), 117.0 (CH), 121.5 (C), 121.7 (CH), 121.7 (C), 123.3

(CH), 123.4 (CH), 123.6 (CH), 123.7 (CH), 123.8 (CH), 123.9 (CH), 124.0 (CH), 124.0 (CH), 124.1 (CH), 124.8 (C), 125.4 (CH), 127.0 (CH), 127.4 (CH), 127.4 (CH), 127.8 (CH), 127.9 (CH), 128.0 (CH), 128.0 (CH), 128.5 (CH), 128.5 (CH), 128.6 (CH), 128.7 (CH), 128.8 (C), 129.1 (C), 129.2 (C), 129.3 (C), 130.0 (C), 130.4 (C), 130.6 (C), 130.9 (C), 131.3 (C), 132.7 (C), 133.9 (CH), 134.6 (C), 138.0 (C), 142.1 (C), 144.1 (C), 178.8 (C, C=O); HRMS (ASAP), *m/z*: 572.2012 (0 ppm) found (calcd for $C_{43}H_{26}NO$, $[M+H]^+$, requires 572.2009).

***N*-Phenyl-*N*-(2-triphenylenyl)-2-aminobenzaldehyde (12).** It was prepared under an argon atmosphere by adapting a procedure reported previously.[30] To 2-(2-triphenylenyl)aminobenzaldehyde (**1**; 0.35 g, 1.0 mmol) and iodobenzene (0.24 g, 0.13 mL, 1.2 mmol) in degassed Bu_2O (1 mL) were successively added activated Cu[51] (0.20 equiv, 13 mg, 0.20 mmol) and K_2CO_3 (2 equiv, 0.29 g, 2.0 mmol). The mixture was degassed and refluxed under argon for 24 h. During this time, activated Cu[51] (4 x 13 mg, 4 x 0.20 mmol) was added after 2, 4, 6 and 8 h of heating. After cooling to room temperature, the mixture was concentrated. Purification by column chromatography on silica gel (eluent: petroleum ether-AcOEt 90:10; R_f = 0.21) gave **12** in 57% yield (0.24 g) as a yellow solid: mp 126-132 °C; IR (ATR): 696, 721, 752, 821, 906, 1051, 1097, 1155, 1191, 1241, 1265, 1305, 1348, 1390, 1436, 1453, 1476, 1490, 1592, 1613, 1685, 1947, 2251, 2748, 2849, 3061 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.09 (t, 1H, *J* = 7.3 Hz), 7.15-7.17 (m, 2H), 7.27-7.37 (m, 5H), 7.54 (ddd, 1H, *J* = 8.2, 7.5 and 1.2 Hz), 7.59-7.64 (m, 3H), 7.98 (dd, 1H, *J* = 7.8 and 1.6 Hz), 8.24 (d, 1H, *J* = 8.2 Hz), 8.26 (d, 1H, *J* = 2.3 Hz, H1'), 8.51-8.53 (m, 2H), 8.61-8.63 (m, 2H), 10.33 (s, 1H, CHO); ^{13}C NMR ($CDCl_3$) δ 116.4 (CH), 122.8 (CH), 123.1 (CH), 123.3 (2CH), 123.4 (CH), 123.45 (CH), 123.45 (CH), 123.5 (CH), 125.0 (CH), 125.4 (C), 125.9 (CH), 126.8 (CH), 127.2 (CH), 127.5 (CH), 127.6 (CH), 129.3 (CH), 129.3 (C), 129.3 (C), 129.6 (CH), 129.7 (C), 129.9 (2CH), 130.3 (C), 131.3 (C), 132.1 (C), 135.7 (CH), 148.0 (C), 148.9 (C), 150.3 (C, C1), 190.8 (CH, CHO); HRMS (MALDI, DCTB matrix), *m/z*: 423.167 (12 ppm) found (calcd for $C_{31}H_{21}NO$, $M^{+\bullet}$, requires 423.1618).

***N*-(2-Triphenylenyl)-9-acridone (13).** It was prepared under an argon atmosphere by adapting a procedure reported previously.[43] A mixture of *N*-phenyl-*N*-(2-triphenylenyl)-2-aminobenzaldehyde (**12**; 0.44 g, 1.0 mmol), ytterbium triflate (31 mg, 50 μmol) and sodium sulfate (71 mg, 0.50 mmol) in DMF (5 mL) was heated at 100 °C for 20 h. After cooling to room temperature, diethyl ether (0.40 L) was added, and the organic phase was washed with water (100 mL). After drying the organic phase over sodium sulfate, the solvent was evaporated under vacuum. Purification by column chromatography on silica gel (eluent: petroleum ether-AcOEt 80:20; R_f = 0.325) gave **13** in 83% yield (0.36 g) as a beige solid: mp > 260 °C; IR (ATR): 722, 751, 801, 818, 864, 912, 938, 1027, 1076, 1160, 1258, 1306, 1361, 1449, 1458, 1486, 1507, 1597, 1631, 2962, 3068 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.89 (d, 2H, *J* = 8.6 Hz, H4 and H5), 7.31 (t, 2H, *J* = 7.4 Hz, H2 and H7), 7.49 (t, 2H, *J* = 7.6 Hz, H3 and H6), 7.62-7.66, 7.73 and 7.77-7.79 (m, 2H, t, 1H, *J* = 7.6 Hz and m, 2H; H3', H6', H7', H10' and H11'), 8.52 (d, 1H, *J* = 8.1 Hz, H12'), 8.65 (d, 2H, *J* = 7.9 Hz, H1 and H8), 8.68 (s, 1H, H1'), 8.71-8.79 (m, 3H), 9.00 (d, 1H, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 117.1 (2CH), 121.8 (2CH), 122.1 (C), 123.7 (CH), 123.7 (CH), 123.8 (CH), 123.8 (CH), 125.2 (CH), 126.7 (CH), 127.6 (2CH), 127.8 (CH), 127.9 (CH), 128.4 (CH), 128.4 (CH), 128.4 (CH), 128.9 (C), 129.1 (C), 130.4 (C), 130.5 (C), 130.8 (C), 132.4 (C), 133.5 (2CH), 137.9 (C), 143.5 (C), 178.4 (C, C=O); HRMS (ASAP), *m/z*: 422.1538 (0 ppm) found (calcd for $C_{31}H_{20}NO$, $[M+H]^+$, requires 422.1539).

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank the Université de Rennes 1 and the Centre National de la Recherche Scientifique (F. M.). We acknowledge the Fonds Européen de Développement Régional (FEDER; D8 VENTURE Bruker AXS diffractometer). We thank Joshua M. Sims for helpful discussions, H. T. Huynh for providing paracetamol, and F. Lassagne for his help all along the study.

Notes and references

1 A. Schmidt and M. Liu, *Adv. Heterocycl. Chem.*, 2015, **115**, 287-353.
2 M. Gensicka-Kowalewska, G. Cholewiński and K. Dzierzbicka, *RSC Adv.*, 2017, **7**, 15776-15804.
3 K. Durka, M. Urban, M. Dąbrowski, P. Jankowski, T. Kliś and S. Luliński, *ACS Omega*, 2019, **4**, 2482-2492.
4 M. Wu, W. Wu, X. Gao, X. Lin and Z. Xie, *Talanta*, 2008, **75**, 995-1001.
5 J. Kaur and P. Singh, *Chem. Commun.*, 2011, **47**, 4472-4474.
6 A.-N. Cho, N. Chakravarthi, K. Kranthiraja, S. S. Reddy, H.-S. Kim, S.-H. Jin and N.-G. Park, *J. Mater. Chem. A*, 2017, **5**, 7603-7611.
7 Y.-y. Jin and Q. Fang, *J. Org. Chem.*, 2019, **84**, 3832-3842.
8 R. G. Harvey, *Polycyclic Aromatic Hydrocarbons*, Wiley-VCH, Weinheim, 2002, pp. 20-31.
9 U. H. F. Bunz, J. U. Engelhart, B. D. Lindner and M. Schaffroth, *Angew. Chem., Int. Ed.*, 2013, **52**, 3810-3821.
10 Q. Miao, *Polycyclic Arenes and Heteroarenes*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2015.
11 M. Stępień, E. Gońka, M. Żyła and N. Sprutta, *Chem. Rev.*, 2017, **117**, 3479-3716.
12 Y. Lin, Z. Liu, Y. Niu, B. Zhang, Q. Lu, S. Wu, G. Centi, S. Perathoner, S. Heumann, L. Yu and D. S. Su, *ACS Nano*, 2019, **13**, 13995-14004.
13 R. M. Acheson, *Chemistry of Heterocyclic Compounds: Acridines*, John Wiley & Sons, Wiley–Blackwell, Second Edition, Volume 9, 1973, Chapter 7.
14 T. Do Cao, E. K. Weisburger, P. Mabille and N. P. Buu-Hoï, *J. Chem. Soc. C*, 1967, 665-668.
15 N. P. Buu-Hoï, M. Dufour and P. Jacquignon, *J. Chem. Soc. C*, 1969, 1337-1338.
16 Z. Zeng, H. Jin, K. Sekine, M. Rudolph, F. Rominger and A. S. K. Hashmi, *Angew. Chem., Int. Ed.*, 2018, **57**, 6935-6939.
17 B. Chakraborty, A. Kar, R. Chanda and U. Jana, *J. Org. Chem.*, 2020, **85**, 9281-9289.

18 S. Zeghada, G. Bentabed-Ababsa, O. Mongin, W. Erb, L. Picot, V. Thiery, T. Roisnel, V. Dorcet and F. Mongin, *Tetrahedron*, 2020, **76**, 131435.
19 N. Mokhtari Brikci-Nigassa, G. Bentabed-Ababsa, W. Erb, F. Chevallier, L. Picot, L. Vitek, A. Fleury, V. Thiéry, M. Souab, T. Robert, S. Ruchaud, S. Bach, T. Roisnel and F. Mongin, *Tetrahedron*, 2018, **74**, 1785-1801.
20 R. L. Vermillion-Salsbury and D. M. Hercules, *Rapid Commun. Mass Spectrom.*, 2002, **16**, 1575-1581.
21 Y. Kuninobu, T. Tatsuzaki, T. Matsuki and K. Takai, *J. Org. Chem.*, 2011, **76**, 7005-7009.
22 Q. Su, P. Li, M. He, Q. Wu, L. Ye and Y. Mu, *Org. Lett.*, 2014, **16**, 18-21.
23 R. S. Begunov, A. A. Sokolov, V. O. Belova and M. E. Solov'ev, *Russ. Chem. Bull.*, 2016, **65**, 644-647.
24 K. Fukui, T. Yonezawa, C. Nagata and H. Shingu, *J. Chem. Phys.*, 1954, **22**, 1433-1442.
25 Y. Carissan, D. Hagebaum-Reignier, N. Goudard and S. Humbel, *J. Phys. Chem. A*, 2008, **112**, 13256-13262.
26 Y. Shen and C.-F. Chen, *Chem. Rev.*, 2012, **112**, 1463-1535.
27 N. Goudard, Y. Carissan, D. Hagebaum-Reignier and S. Humbel, *HuLiS 3.3.4*, http://ism2.univ-amu.fr/hulis.
28 Y. Kitahara, T. Mizuno and A. Kubo, *Tetrahedron*, 2004, **60**, 4283-4288.
29 E. Berliner, *J. Am. Chem. Soc.*, 1942, **64**, 2894-2898.
30 S. Bouarfa, G. Bentabed-Ababsa, W. Erb, L. Picot, V. Thiery, T. Roisnel, V. Dorcet and F. Mongin, *Synthesis*, 2021, **53**, 1271-1284.
31 T. Fujita, I. Takahashi, M. Hayashi, J. Wang, K. Fuchibe and J. Ichikawa, *Eur. J. Org. Chem.*, 2017, **2017**, 262-265.
32 I. V. Borovlev, O. P. Demidov, G. A. Amangasieva and E. K. Avakyan, *Tetrahedron Lett.*, 2016, **57**, 3608-3611.
33 P. Huszthy, Z. Kontos, B. Vermes and A. Pinter, *Tetrahedron*, 2001, **57**, 4967-4975.
34 S. Yamada, D. Morizono and K. Yamamoto, *Tetrahedron Lett.*, 1992, **33**, 4329-4332.
35 P. Di Fruscia, K.-K. Ho, S. Laohasinnarong, M. Khongkow, S. H. B. Kroll, S. A. Islam, M. J. E. Sternberg, K. Schmidtkunz, M. Jung, E. W. F. Lam and M. J. Fuchter, *MedChemComm*, 2012, **3**, 373-378.
36 D. Hellwinkel and P. Ittemann, *Chem. Ber.*, 1986, **119**, 3165-3197.
37 H. Bertrand, R. Guillot, M.-P. Teulade-Fichou and D. Fichou, *Chem. Eur. J.*, 2013, **19**, 14654-14664.
38 A. Albert and B. Ritchie, *Org. Synth.*, 1942, **22**, 5-8.
39 S. Figueroa-Perez, S. Bennabi, H. Schirok and M. Thutewohl, *Tetrahedron Lett.*, 2006, **47**, 2069-2072.
40 T. L. Su, B. Kohler, T. C. Chou, M. W. Chun and K. A. Watanabe, *J. Med. Chem.*, 1992, **35**, 2703-2710.
41 W. Zhou, Y. Yang, Y. Liu and G.-J. Deng, *Green Chem.*, 2013, **15**, 76-80.
42 W. Zhou, Y. Liu, Y. Yang and G.-J. Deng, *Chem. Commun.*, 2012, **48**, 10678-10680.
43 X.-A. Li, H.-L. Wang and S.-D. Yang, *Org. Lett.*, 2013, **15**, 1794-1797.
44 G. Xie, V. Brosius, J. Han, F. Rominger, A. Dreuw, J. Freudenberg and U. H. F. Bunz, *Chem. Eur. J.*, 2020, **26**, 160-164.
45 M. Napagoda, L. Rulíšek, A. Jančařík, J. Klívar, M. Šámal, I. G. Stará, I. Starý, V. Šolínová, V. Kašička and A. Svatoš, *ChemPlusChem*, 2013, **78**, 937-942.
46 X. Fan and R. C. Beavis, *Rapid Commun. Mass Spectrom.*, 1994, **8**, 199-204.
47 A. Ingendoh, M. Karas, F. Hillenkamp and U. Giessmann, *Int. J. Mass Spectrom. Ion Processes*, 1994, **131**, 345-354.
48 See for example: R. Liu, G. Zhu and G. Zhang, *RSC Adv.*, 2020, **10**, 7092-7098.
49 See for example: C.-F. Liu, C. Cheng, Y. Jiang, W.-Y. Lai and W. Huang, *New J. Chem.*, 2017, **41**, 13619-13624.
50 R. Nandy and S. Sankararaman, *Org. Biomol. Chem.*, 2010, **8**, 2260-2266.
51 A. I. Vogel, A. R. Tatchell, B. S. Furnis, A. J. Hannaford and P. W. G. Smith, *Vogel's textbook of practical organic chemistry, 5th edn, Prentice Hall*, 1996.