The Photochemical Cyclodehydrogenation Route to Polycyclic Azaarenes

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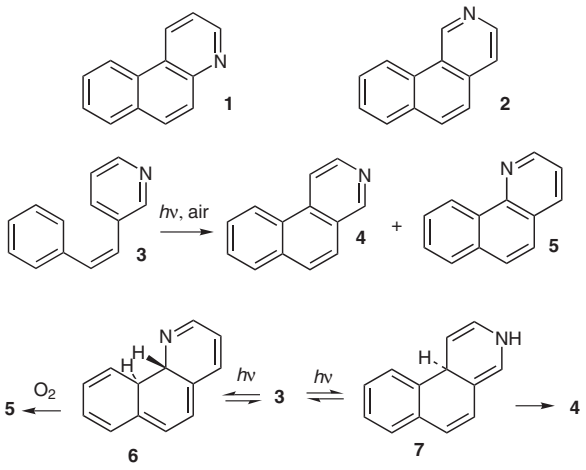
Abstract: This paper reports an investigation of photochemical cyclodehydrogenation for the preparation of polycyclic azaarenes. Various naphthoquinolines and naphthoisoquinolines were obtained from 2-, 3-, and 4-[2-(1- and 2-naphthyl)vinyl]pyridine. 4-[2-(3-Phenanthryl)vinyl]pyridine gave pyreno[1,10-*hij*]isoquinoline. An efficient preparation of (2-arylvinyl)pyridines is described.

Key words: polycycles, photochemistry, cyclizations, naphthoquinolines, naphthoisoquinolines

The first paper of this series[1] explained the need for general and efficient preparative methods for polycyclic azaarenes, and discussed one approach to such systems. This paper describes the use of photochemical cyclodehydrogenation.

It is well known that (*Z*)-stilbene undergoes photocyclization followed by dehydrogenation in the presence of a suitable oxidant (commonly air or iodine) to give phenanthrene, and similar behavior is shown by aza-substituted analogues.[2] Since *E*/*Z* isomerism occurs photochemically, it is possible in principle to use either isomer as starting material. Loader and Timmons reported that (*E*)-2-styrylpyridine and (*E*)-4-styrylpyridine led to benzo[*f*]quinoline (**1**) and benzo[*h*]isoquinoline (**2**) respectively, and (*Z*)-3-styrylpyridine (**3**) gave benzo[*f*]isoquinoline (**4**)[3](Scheme 1). At about the same time, Galiazzo et al. reported that (*Z*)-3-styrylpyridine also gave **5**, in lower yield.[4] Derivatives of styrylpyridines also give substituted benzoquinolines and benzisoquinolines.[4–7] Recent work has shown that 4-styrylpyridine gives predominantly benzo[*h*]isoquinoline (**2**) in Nafion-H$^+$ resin at low occupancy, but that substituted cyclobutanes are dominant at high occupancy.[8] Other recent work showed that the product isomer distribution from 3-styrylpyridine depends on the degree of oxygenation.[7] Photocyclization gives reversibly the intermediates **6** (by electrocyclization) and **7** (by electrocyclization and 1,7-H shift); isomer **6** can be dehydrogenated by oxygen (to give **5**) but its isomer **7** is stable to oxygen and gives rise to **4** by a different process, possibly involving disproportionation (Scheme 1).

These processes have been applied to some more extended ring systems. Loader and Timmons reported reactions of some styrylquinolines and styrylisoquinolines to give tetracyclic products,[9] and Aloisi et al. reported cyclization of some (phenanthrylvinyl)pyridines to pentacyclic products.[10] The photophysics of (naphthylvinyl)pyridines has been studied in detail,[11–13] and it has been shown that 3-[2-(1-naphthyl)vinyl]pyridine and 3-[2-(2-naphthyl)vinyl]pyridine each give two photocyclodehydrogenation products although full characterization data were not reported.[12] These observations are considered in more detail below. Further examples of this approach to azaarenes include cyclization of the Schiff's base derived from benzaldehyde and 2-naphthylamine,[14] and the application to form 4-aza[6]helicene,[15] and several aza- and diaza[5]helicenes.[16] In this paper, we report our investigations into the scope and limitations of the photocyclodehydrogenation of (2-arylvinyl)pyridines.



Scheme 1 Photocyclodehydrogenation products of styrylpyridines[3,4,7]

Aromatic aldehydes react with 2- and 4-picolines in hot acetic anhydride to give (2-arylvinyl)pyridines.[11,17] Galiazzo et al.[11] used this method to obtain n-[2-(m-naphthyl)vinyl]pyridines (m = 1,2; n = 2,4), for convenience referred to below as 'm,n-NVP'. We followed this procedure using 2- and 4-picoline, reacting each with 1-naphthaldehyde in acetic anhydride under reflux. Two products were obtained in each case, the isomeric pairs **8** and **9**, and **16** and **17** (Figure 1), with the *E*-forms being predominant. We obtained some improvement in yields by use of the higher boiling propionic anhydride as solvent and catalyst. When 2- and 4-picoline reacted similarly with 2-naphthaldehyde, the *E*-isomers **10** and **18** were obtained almost exclusively. Irradiation of these *E*-isomers with long wavelength (365 nm) UV radiation in deaerated solutions in toluene gave good conversions to the corresponding *Z*-isomers **11** and **19**. The methyl group of

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3-picoline is less acidic than that of 2- or 4-picoline, but the more reactive pyridine-3-acetic acid can be used for the preparation of the corresponding 3-pyridine isomers.[11] Treatment of 1- and 2-naphthaldehydes each with sodium pyridine-3-acetate in hot acetic anhydride, followed by decarboxylation, gave the isomeric pairs, **12/13** and **14/15**, in good yields.

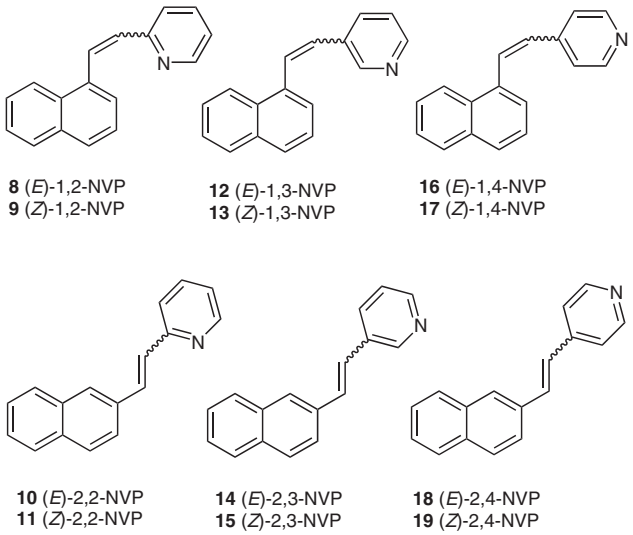
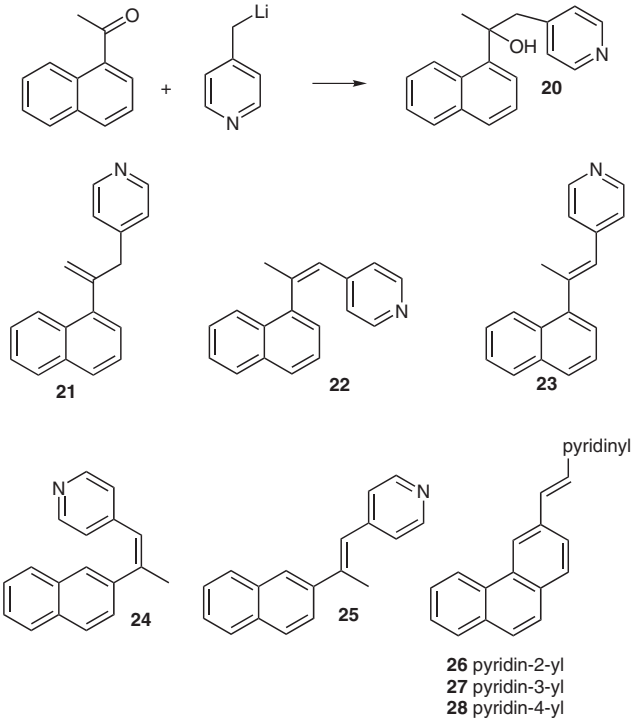


Figure 1 Isomers of n-[2-(m-naphthyl)vinyl]pyridine, 'm,n-NVP'

As the yields obtained from the condensations between picolines and naphthaldehydes were disappointing, especially in the 4-picoline cases, we subsequently sought an alternative procedure. Reaction between 1-naphthaldehyde and the anion of 4-picoline, generated from butyllithium, gave 1-(1-napththyl)-2-pyridin-4-ylethanol which could be dehydrated by treatment with acid to give (*E*)-1,4-NVP **16** in 66% overall yield in a short time. This is a significant improvement.

We then examined two methylated cases. Loader and Timmons had shown that several methylated styrylpyridines undergo photocyclodehydrogenation to give methylated tricyclic products, though with much concomitant polymerization,[3] and other authors have successfully cyclized styrylpyridines with a variety of substituents.[4–6] Developing the present new route to (naphthylvinyl)pyridines, we allowed 1-acetylnaphthalene to react with the lithiated anion of 4-picoline to give the alcohol **20**, which was dehydrated by acid at room temperature to give a mixture of the three alkenes **21**–**23**. At higher temperature, only alkene isomers **22** and **23** were obtained. A similar procedure starting from 2-acetylnaphthalene gave the isomeric alkenes **24** and **25** (Scheme 2).

Aloisi et al. described the preparation and photochemistry of several [(9-phenanthryl)vinyl]pyridines.[10] We have now prepared the corresponding isomers with substituents at the 3-position of phenanthrene. When phenanthrene-3-carbaldehyde and 4-picoline were heated in acetic anhydride, the expected isomeric (*E*)- and (*Z*)-4-[2-(3-phenanthryl)vinyl]pyridines were obtained, but in poor yield.



Scheme 2 4-[2-(Naphthyl)propenyl]pyridines and [2-(3-phenanthryl)vinyl]pyridines

However, the lithiated anions of 2-picoline and 4-picoline reacted readily with phenanthrene-3-carbaldehyde, each to give an alcohol which on dehydration gave a good yield of the *E*-alkene **26** or **28** respectively. The same procedure also worked for 3-picoline, so that the three isomeric alkenes were obtained exclusively as *E*-isomers **26**–**28**.

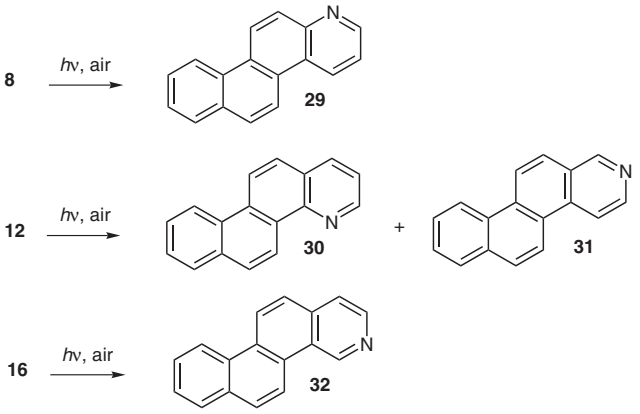
Masetti et al. reported that photochemical irradiation of (*Z*)-1,3-NVP **13** and (*Z*)-2,3-NVP **15** each gave two tetracyclic products, though characterization data were not given.[12] We have examined the series of (naphthylvinyl)pyridine isomers under a set of standard conditions. The compound 1,4-NVP **16** was chosen as the model to establish standard conditions, as this isomer can give only one tetracyclic product. Various solvents have been used in previous studies of photocyclodehydrogenation, including cyclohexane,[3,6,9] hexane,[4,10] hexane–benzene,[12] benzene,[18] ethyl acetate,[16] methanol,[7] *tert*-butyl alcohol,[6] and sulfuric acid;[5,19] a major criterion being adequate solubility. For this study mixtures of toluene and hexane were used. Dilute solutions are essential, to prevent near complete absorption of radiation, and concentrations of 10^{-2} mol dm^{-3} were used. Polymeric material built up on the vessel walls, causing further reduction in available radiation. It was found convenient to use 10-hour irradiation times, interrupted once to remove polymer. Air was bubbled through the solution for 30 minutes before and then throughout the reaction time, and in one case iodine was used as oxidant. Table 1 shows the yields of naphtho[1,2-*h*]isoquinoline (**32**) obtained under a variety of conditions, the optimum being formed in neat toluene without iodine. The remaining NVP isomers were subjected to the same

Table 1 Photocyclodehydrogenation of **16** in 10^{-2} mol dm^{-3} solutions

Solvent toluene–hexane	Oxidant	Yield of **32** (%) after 10 h
1:9	air	28
1:1	air	44
1:0	air	55
1:0	I_2	50

optimized conditions. Since all pairs of *E*-and *Z*-isomers are interconverted under the irradiation, the *E*-isomers were used as precursors.

(*E*)-1,2-NVP **8** gave naphtho[2,1-*f*]quinoline (**29**) (13%), and (*E*)-1,3-NVP **12** gave naphtho[1,2-*h*]quinoline (**30**) (4%) and naphtho[2,1-*f*]isoquinoline (**31**) (51%) (Scheme 3). The isomeric products **29–31** were identified by NMR spectra, and melting-points were in accord with literature values from alternative preparations.[20–22] (*E*)-1,4-NVP **16** gave a 55% yield of naphtho[1,2-*h*]isoquinoline (**32**), not previously described and identified from its NMR spectrum.

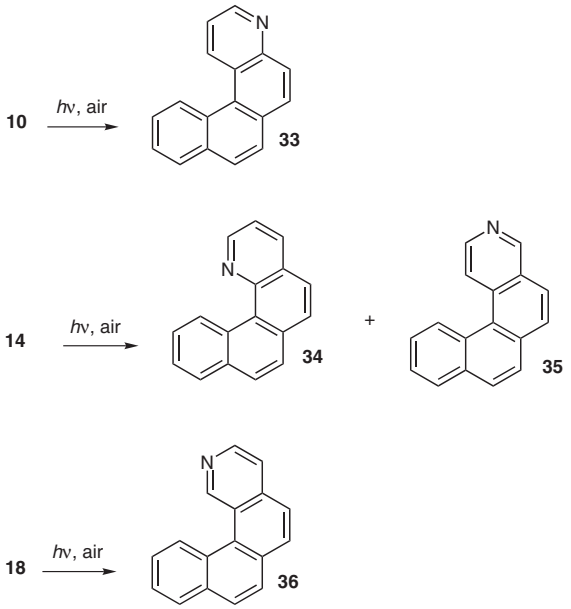


Scheme 3 Photocyclodehydrogenation of 1-napththyl compounds

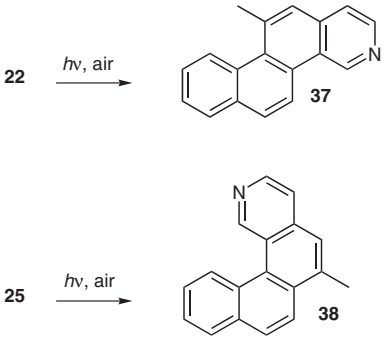
The 2-naphthyl series behaved similarly. (*E*)-2,2-NVP **10** gave naphtho[1,2-*f*]quinoline (**33**) (10%), and (*E*)-2,3-NVP **14** gave naphtho[2,1-*h*]quinoline (**34**) (2%) and naphtho[1,2-*f*]isoquinoline (**35**) (28%), all previously prepared by other routes.[11,20,21,23] 2,4-NVP **18** gave a 20% yield of naphtho[2,1-*h*]isoquinoline (**36**), not previously described (Scheme 4). All cases also gave insoluble polymeric material of unknown structure, in line with observations in previous related work,[3,6,9] as well as a number of by-products without the UV absorption indicative of tetracyclic aromatics.

Irradiation of the naphthylpropenylpyridines **22** and **25** proceeded similarly. Methyl derivatives **37** and **38** of the expected tetracycles were obtained, but in lower yields and were more difficult to purify (Scheme 5).

Each of the (naphthylvinyl)pyridines can exist as a number of rotamers which could give rise to different cyclization products, although it should not be expected that



Scheme 4 Photocyclodehydrogenation of 2-napththyl compounds

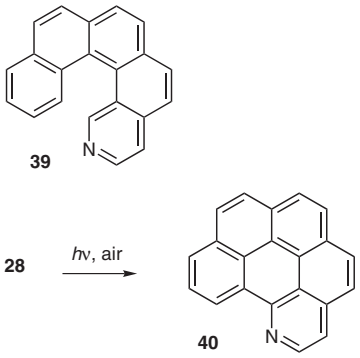


Scheme 5 Methylated photocyclodehydrogenation products

ground-state rotamer proportions correlate directly with product yields[12] which will depend on the initial electrocyclization and also on subsequent processes, for example those studied by Lewis et al. for 3-styrylpyridine.[7] Electrocyclization in the stilbene series occurs in the first excited singlet state and depends on the sums of the free valency indices at the linking positions.[24] Bazzini et al. have shown the value of *ab initio* calculations in related systems.[16] Without access to detailed calculations on the present cases, some general observations can be made about the results. Each of the 1,2- and 1,4-NVP isomers **8** and **16** could give only one azaarene, and this was observed, with a particularly good yield from **16** where cyclization is between the naphthalene 2-position and pyridine 3-position from either rotamer. Only one rotamer of **8** could cyclize because of the nitrogen location, and a poor yield was obtained. 1,3-NVP **12** gave the two products formally derived from the two rotamers around the C-pyridine bond; the highest yield was **31**, with cyclization to the pyridine 4-position rather than 2-position. This parallels the tendency of 3-styrylpyridine to give predominantly benzo[*h*]isoquinoline (**4**) rather than the isomer

5.[3,4,7] The 2-naphthyl series has additional possibilities because cyclization could be to the naphthalene 1-position forming 'bent' annulated products, or to the 3-position leading to 'linear' annulation. In practice, only the former was observed, and the results followed the pattern seen for the 1-naphthyl series, namely that cyclization of the 2,4-NVP **18** was more effective than for 2,2-NVP **10**, and the 2,3-NVP gave predominantly **35**, cyclized on to the pyridine 4-position rather than the 2-position. Cyclization adjacent to the nitrogen atom appears to be generally disfavored.

Irradiation of the 2- and 3-pyridine isomers of (*E*)-[2-(3-phenanthryl)vinyl]pyridine **26** and **27** in toluene or benzene as for the naphthyl compounds gave complete conversion to polymeric material of unknown structure. Noting that some arylvinylpyrenes cyclize in presence of iodine, but not oxygen,[25] an attempt was made with the present phenanthryl compounds **26** and **27**, but no pentacyclic product was identified. The analogous 4-pyridine compound **28** behaved quite differently, rapidly giving new UV absorption which was not as expected for the aza[5]helicene **39** (Scheme 6). The product was characterized as the fully dehydrogenated pyreno[1,10,9-*hij*]isoquinoline (**40**), presumably derived from an initial azahelicene which then undergoes a subsequent cyclization despite the final bond formation adjacent to nitrogen. An easy formation of **39** would accord with the observations in the naphthalene series where cyclization of the 4-pyridine compounds is relatively easy. Since our work was competed, Bazzini et al. have reported formation of **40** from 7-[2-(2-naphthyl)vinyl]isoquinoline, though several other isomers of this gave the expected azahelicenes.[16] The same authors have very recently reported the cyclization of 3-[(2-(3-phenanthryl)vinyl]pyridine using benzene as solvent,[18] so our failure with this may be due to interfering reactions involving the toluene solvent.



Scheme 6 Photocyclodehydrogenation of **28**

This work has confirmed that photocyclodehydrogenation can lead to a range of naphthoquinolines and naphthoisoquinolines. Yields are generally acceptable, though limited by concomitant polymerization, and quantities are limited by the nature of the photochemistry. The method generally gives better yields of fused isoquinolines than quinolines. Closure on to a position adjacent to nitrogen appears to be disfavored, and 'bent' annulated products are formed rather than the 'linear' isomers, complementary to a thermal route which appears to be controlled by steric considerations leading to 'linear' annulation.[1] Some of the azaarenes prepared have not to our knowledge been characterized previously and we have recorded ^{1}H and ^{13}C spectra for all under standard conditions as reference information, with assignments established by 2D methods and NOE where appropriate.

The efficient preparation of (2-arylvinyl)pyridines from methylated starting materials is expected to be generally applicable to other compounds. It may be advantageous over the Wittig reaction used by others[16,18] as that requires a halomethyl starting material.

Caution: Where information is available, aza-arenes in general are less potent as mutagens and carcinogens than the isosteric parent carbocycles. Nevertheless, precautions should be taken with these compounds. The experiments described were carried out on small scales in a well ventilated fume cupboard and all residues and waste disposed of as potentially hazardous material. Benzene was used in some cases where toluene failed, requiring appropriate precautions for use and disposal.

Melting points were determined on a Reichert hot stage apparatus. IR spectra were recorded in Nujol mulls on a PerkinElmer 1600 FTIR spectrometer. UV spectra were determined in Analar (AR) EtOH on a PerkinElmer Lambda 2 spectrophotometer. Microanalyses were performed on a PerkinElmer 240C Elemental Analyzer. Mass spectra at low resolution were measured with a Varian CH5-D or a Fisons VG Platform II spectrometer using electron impact ionization. Accurate mass values were determined by the EPSRC Mass spectrometry service (Swansea) on a VG ZAB spectrometer. NMR spectra were recorded at 20 °C on Bruker WM360 and AMX360 instruments at 360 MHz for ^{1}H and 90 MHz for ^{13}C (with Waltz-16 ^{1}H decoupling or by DEPT-135), using sample concentrations of approximately 0.06 M. Chemical shifts are quoted relative to TMS ($\delta = 0$). Correlations were determined from COSY-45, HETCOR and HMQC using 256 sets of 1024 data points. Nuclear Overhauser enhancements (NOE) were determined by the difference method using 12 repetitions of 8 'irradiated' and 8 'blank' pulses, the summed FIDs subtracted and Fourier-transformed after line-broadening of 1 Hz. Bruker DISNMR and UXNMR software was used throughout. TLC was carried out on Merck silica gel 60 F_{254}. Flash chromatography was carried out using Fisons matrix silica gel 60, 35–70 micron.

PE refers to petroleum ether of boiling range 40–60 °C. Et_2O was dried over sodium wire. Toluene was dried by azeotropic distillation. N_2 was passed through $CaCl_2$ and silica gel. 1-Naphthaldehyde, 2-naphthaldehyde, 1-acetylnaphthalene, and pyridine-3-acetic acid were commercially available (Aldrich). Phenanthrene-3-carbaldehyde was prepared as previously described.[1]

Photoreactions were carried out in a Photophysics RQ400 immersion-well reactor model 3140, using UV radiation (λ = 365–366 nm) from a Photophysics 400 W medium pressure mercury lamp with a borosilicate filter. The Pyrex vessel was water-cooled, and equipped with gas inlet and outlet.

2-(2-Arylvinyl)pyridines and 4-(2-Arylvinyl)pyridines; General Procedure A

The following procedure was modified from literature,[11] and shows typical quantities.

The naphthaldehyde (7.80 g, 0.05 mol) and 2- or 4-picoline (4.65 g, 0.05 mol) were refluxed in propionic anhydride (45.5 g, 0.35 mol)

for 48 h. The black mixture was quenched with H_2O (90 mL) and neutralized with NaOH soln. The tar-like mixture was extracted with $CHCl_3$ (3×50 mL), the extract washed with aq sat. soln of $NaHSO_3$ (2×150 mL), dried (K_2CO_3), the solvent removed by evaporation, and the black crude product purified as detailed below.

(*E*)- and (*Z*)-2-[2-(1-Naphthyl)vinyl]pyridines (8 and 9)
From 1-naphthaldehyde and 2-picoline. Distillation (bp 128–184 °C/0.02 mm Hg) and dry flash column chromatography (PE–EtOAc) gave **8** and **9**.

(i) (*E*)-2-[2-(1-Naphthyl)vinyl]pyridine (8)
Off-white solid; yield: 3.23 g (28%); mp 38–40 °C (Lit.[11] mp 39–40 °C).

^{1}H NMR ($CDCl_3$): δ = 8.68 (dt, *J* = 5, 1 Hz, 1 H, H-6), 8.43 (d, *J* = 16 Hz, 1 H, H-2′), 8.32 (d, *J* = 8 Hz, 1 H, H-8″), 7.87 (dd, *J* = 7.5, 2 Hz, 1 H, H-5″), 7.84–7.82 (2 d, each *J* = 8 Hz, each 1 H, H-2″,4″), 7.71 (td, *J* = 8, 2 Hz, 1 H, H-4), 7.58–7.47 (m, 4 H, H-3,3″,6″,7″), 7.24 (d, *J* = 16 Hz, 1 H, H-1′), 7.20 (dd, *J* = 8, 5 Hz, 1 H, H-5).

MS (EI): *m*/*z* (%) = 232 (10, [M + 1]$^+$), 231, 230 (100), 229, 152, 115, 78.

Anal. Calcd for $C_{17}H_{13}N$: C, 88.28; H, 5.67; N, 6.06. Found: C, 88.09; H, 5.49; N, 5.78.

(ii) (*Z*)-2-[2-(1-Naphthyl)vinyl]pyridine (9)
Colorless oil; yield: 0.17 g (1%).

^{1}H NMR ($CDCl_3$): δ = 8.54 (d, *J* = 5 Hz, 1 H, H-6), 8.06 (dd, *J* = 8, 1 Hz, 1 H, H-8″), 7.87 (dd, *J* = 8, 1 Hz, 1 H, H-5″), 7.79 (dd, *J* = 8, 3 Hz, 1 H, H-4″), 7.49 (m, 2 H, H-6″,7″), 7.35 (t, *J* = 8 Hz, 1 H, H-3″), 7.35 (d, *J* = 8 Hz, 1 H, H-2″), 7.30 (d, *J* = 12 Hz, 1 H, H-2′), 7.18 (td, *J* = 8, 1 Hz, 1 H, H-4), 6.99 (d, *J* = 12 Hz, 1 H, H-1′), 6.97 (dd, *J* = 8, 5 Hz, 1 H, H-5), 6.79 (d, *J* = 8 Hz, 1 H, H-3).

MS (EI): *m*/*z* (%) = 232 (25, [M + 1]$^+$), 231, 230 (100), 202, 152, 115, 78.

Anal. Calcd for $C_{17}H_{13}N$: C, 88.28; H, 5.67; N, 6.06. Found: C, 87.99; H, 5.97; N, 6.31.

(*E*)-2-[2-(2-Naphthyl)vinyl]pyridine (10)
From 2-naphthaldehyde (9.90 g, 0.063 mol) and 2-picoline (5.90 g, 0.063 mol) in propionic anhydride (57 g, 0.441 mol). Distillation (bp 119–210 °C/0.001 mm Hg) followed by dry flash column chromatography (PE–EtOAc) gave 2-naphthaldehyde followed by **10**; crude yield: 4.35 g (30%); pure as off-white crystals (toluene–PE, 1:3); mp 127–128 °C (Lit.[11] mp 123–124 °C).

^{1}H NMR ($CDCl_3$): δ = 8.64 (dd, *J* = 5, 2 Hz, 1 H, H-6), 7.95 (br s, 1 H, H-1″), 7.87– 7.78 (m, 4 H, H-3″,4″,5″,8″), 7.80 (d, *J* = 16 Hz, 1 H, H-2′), 7.69 (td, *J* = 8, 2 Hz, 1 H, H-4), 7.48 (m, 2 H, H-6″,7″), 7.44 (d, *J* = 8 Hz, 1 H, H-3), 7.17 (d, *J* = 16 Hz, 1 H, H-1′), 7.17 (ddd, *J* = 8, 5,1 Hz, 1 H, H-5).

MS (EI): *m*/*z* (%) = 232 (12, [M + 1]$^+$), 231, 230 (100), 79, 78, 52, 51.

Anal. Calcd for $C_{17}H_{13}N$: C, 88.28; H, 5.66; N, 6.06. Found: C, 88.12; H, 5.88; N, 5.88.

(*E*)- and (*Z*)-4-[2-(1-Naphthyl)vinyl]pyridines (16 and 17)
From 1-naphthaldehyde (15.6 g, 0.1 mol) and 4-picoline (9.5 g, 0.1 mol) in Ac_2O (72 g, 0.7 mol). Distillation (bp 180–238 °C/0.08 mm Hg) followed by column chromatography (PE–EtOAc) gave **16** and **17**.

(i) (*Z*)-4-[2-(1-Naphthyl)vinyl]pyridine (17)
Colorless oil; yield: 2.80 g (12%).

^{1}H NMR ($CDCl_3$): δ = 8.32 (d, *J* = 5 Hz, 2 H, H-2,6), 8.01 (dd, *J* = 8, 2 Hz, 1 H, H-8″), 7.89 (dd, *J* = 8, 1 Hz, 1 H, H-5″), 7.82 (d, *J* = 8 Hz, 1 H, H-4″), 7.52 (m, 2 H, H-6″,7″), 7.35 (t, *J* = 8 Hz, 1 H, H-3″), 7.29 (dd, *J* = 8, 2 Hz, 1 H, H-2″), 7.29 (d, *J* = 12 Hz, 1 H, H-2′), 6.92 (d, *J* = 5 Hz, 2 H, H-3,5), 6.77 (d, *J* = 12 Hz, 1 H, H-1′).

MS (EI): *m*/*z* (%) = 231 (27, [M$^+$]), 152, 115 (100), 101, 88, 75.

Anal. Calcd for $C_{17}H_{13}N$: C, 88.28; H, 5.66; N, 6.06. Found: C, 88.28; H, 5.76; N, 6.13.

(ii) (*E*)-4-[2-(1-Naphthyl)vinyl]pyridine (16)
Crude solid; yield: 6.42 g (28%); off-white crystals (toluene–PE, 1:1); mp 83–84 °C (Lit.[11] mp 82–83 °C).

^{1}H NMR ($CDCl_3$): δ = 8.62 (d, *J* = 5 Hz, 2 H, H-2,6), 8.18 (dd, *J* = 8, 1 Hz, 1 H, H-8″), 8.09 (d, *J* = 16 Hz, 1 H, H-2′), 7.88 (dd, *J* = 8, 1 Hz, 1 H, H-5″), 7.85 (d, *J* = 8 Hz, 1 H, H-4″), 7.76 (d, *J* = 8 Hz, 1 H, H-2″), 7.57 (td, *J* = 8, 1 Hz, 1 H, H-7″), 7.52 (td, *J* = 8, 1 Hz, 1 H, H-6″), 7.50 (t, *J* = 8 Hz, 1 H, H-3″), 7.43 (d, *J* = 5 Hz, 2 H, H-3,5), 7.06 (d, *J* = 16 Hz, 1 H, H-1′).

MS (EI): *m*/*z* (%) = 232 (44, [M + 1]$^+$), 231, 230 (100), 202, 153, 101, 88.

Anal. Calcd for $C_{17}H_{13}N$: C, 88.28; H, 5.66; N, 6.06. Found: C, 88.42; H, 5.84; N, 6.16.

(*E*)-4-[2-(2-Naphthyl)vinyl]pyridine (18)
From 2-naphthaldehyde (15.6 g, 0.1 mol) and 4-picoline (9.5 g, 0.1 mol) in Ac_2O (72 g, 0.7 mol). Distillation (bp 200–210 °C/0.01 mm Hg) gave a yellow solid consisting of **18** (8.90 g, 39%) with a trace of its *Z*-isomer **19**. Recrystallization (toluene–PE, 1:1) gave pure **18**; light yellow solid; mp 164–166 °C (Lit.[11] mp 158–160 °C).

^{1}H NMR ($CDCl_3$): δ = 8.60 (d, *J* = 6 Hz, 2 H, H-2,6), 7.91 (s, 1 H, H-1″), 7.86–7.82 (m, 3 H, H-4″,5″,8″), 7.75 (dd, *J* = 9, 2 Hz, 1 H, H-3″), 7.52–7.46 (m, 2 H, H-6″,7″), 7.47 (d, *J* = 16 Hz, 1 H, H-2′), 7.41 (d, *J* = 6 Hz, 2 H, H-3,5), 7.14 (d, *J* = 16 Hz, 1 H, H-1″).

MS (EI): *m*/*z* (%) = 232 (44, [M + 1]$^+$), 231, 230, 202, 101, 63, 51 (100).

Anal. Calcd for $C_{17}H_{13}N$: C, 88.28; H, 5.66; N, 6.06. Found: C, 88.13; H, 5.83; N, 6.02.

(*Z*)- and (*E*)-4-[2-(3-Phenanthryl)vinyl]pyridine (28)
From phenanthrene-3-carbaldehyde (2.32 g, 0.0113 mol) and 4-picoline (1.05 g, 0.0113 mol) in Ac_2O (8.04 g, 0.079 mol). Distillation (bp 240 °C/0.1 mm Hg), followed by dry flash column chromatography (PE–EtOAc) separated the *E*- and *Z*-products.

(i) (*Z*)-4-[2-(3-Phenanthryl)vinyl]pyridine
Oily solid; yield: 0.04 g (1%).

^{1}H NMR ($CDCl_3$): δ = 8.58 (br s, 1 H, H-4″), 8.47 (br s, 2 H, H-2,6), 8.41 (dd, *J* = 7, 2 Hz, 1 H, H-5″), 7.86 (dd, *J* = 7, 2 Hz, 1 H, H-8″), 7.74 (d, *J* = 8 Hz, 1 H, H-1″), 7.71 (AB system, *J* = 5 Hz, 2 H, H-9″,10″), 7.63–7.56 (m, 2 H, H-6″,7″), 7.42 (dd, *J* = 8, 1 Hz, 1 H, H-2″), 7.20 (d, *J* = 5.5 Hz, 2 H, H-3,5), 7.04 (d, *J* = 12 Hz, 1 H, H-2′), 6.63 (d, *J* = 12 Hz, 1 H, H-1′).

(ii) (*E*)-4-[2-(3-Phenanthryl)vinyl]pyridine (28)
Yellow solid; yield: 0.42 g (13%); mp 138–141 °C.

^{1}H NMR ($CDCl_3$): δ = 8.74 (br s, 1 H, H-4″), 8.73 (d, *J* = 8 Hz, 1 H, H-5″), 8.61 (d, *J* = 6 Hz, 2 H, H-2,6), 7.90 (dd, *J* = 8, 1 Hz, 1 H, H-8″), 7.89 (d, *J* = 8 Hz, 1 H, H-1″), 7.83 (dd, *J* = 8, 2 Hz, 1 H, H-2″), 7.74 (AB system, *J* = 5 Hz, 2 H, H-9″,10″), 7.69 (td, *J* = 8, 1 Hz, 1 H, H-6″), 7.62 (td, *J* = 8, 1 Hz, 1 H, H-7″), 7.56 (d, *J* = 16 Hz, 1 H, H-2″), 7.43 (d, *J* = 6 Hz, 2 H, H-3,5), 7.19 (d, *J* = 16 Hz, 1 H, H-1″).

3-(2-Arylvinyl)pyridines; General Procedure B
This procedure was modified from the literature.[11]

Sodium pyridine-3-acetate (4.15 g, 0.026 mol) and the naphthaldehyde (4.10 g, 0.026 mol) were heated under reflux in Ac_2O (19.5 g, 0.184 mol) for 24 h. The black tar-like mixture was poured into H_2O (50 mL) and the two immiscible phases left for 72 h. The H_2O-immiscible material was refluxed in NaOH soln (3 M, 50 mL) for 2 h, cooled, neutralized with HCl (3 M) and the resulting brown solid was collected by filtration and dried (P_2O_5). This crude substituted acrylic acid was added in small portions to a preheated (230 °C) suspension of copper chromite (1 g) in quinoline (50 mL) maintaining the temperature above 225 °C. The mixture was refluxed for a further 2 h, and then distilled under reduced pressure.

(*E*)- and (*Z*)-3-[2-(1-Naphthyl)vinyl]pyridines (12 and 13)
From sodium pyridine-3-acetate (4.15 g, 0.026 mol) and 1-naphthaldehyde (4.10 g, 0.026 mol) in Ac_2O (19.5 g, 0.184 mol). Distillation gave 1-naphthaldehyde, followed by quinoline, then a fraction (bp 160–190 °C/0.005 mm Hg) which was separated by column chromatography (PE–EtOAc).

(i) (*Z*)-3-[2-(1-Naphthyl)vinyl]pyridine (13)
Colorless oil; yield: 1.04 g (17%).

^{1}H NMR ($CDCl_3$): δ = 8.38 (d, *J* = 2 Hz, 1 H, H-2), 8.32 (dd, *J* = 5, 2 Hz, 1 H, H-6), 8.04 (dd, *J* = 8, 1 Hz, 1 H, H-8″), 7.89 (dd, *J* = 8, 1 Hz, 1 H, H-5″), 7.80 (d, *J* = 8 Hz, 1 H, H-4″), 7.50 (m, 2 H, H-6″,7″), 7.36 (t, *J* = 8 Hz, 1 H, H-3″), 7.31 (dd, *J* = 8, 1 Hz, 1 H, H-2″), 7.25 (dt, *J* = 8, 2 Hz, 1 H, H-4), 7.21 (d, *J* = 12 Hz, 1 H, H-2′), 6.94 (dd, *J* = 8, 5 Hz, 1 H, H-5), 6.82 (d, *J* = 12 Hz, 1 H, H-1′).

MS (EI): *m*/*z* (%) = 232 (45, [M + 1]$^+$), 231, 230, 99 (100), 75, 62, 51.

Anal. Calcd for $C_{17}H_{13}N$: C, 88.28; H, 5.66; N, 6.06. Found: C, 88.44; H, 5.88; N, 6.31.

(ii) (*E*)-3-[2-(1-Naphthyl)vinyl]pyridine (12)
Colorless oil; yield: 1.52 g (25%).

^{1}H NMR ($CDCl_3$): δ = 8.77 (d, *J* = 2 Hz, 1 H, H-2), 8.49 (dd, *J* = 5, 2 Hz, 1 H, H-6), 8.16 (br d, *J* = ca. 9 Hz, 1 H, H-8″), 7.89 (d, *J* = 16 Hz, 1 H, H-2′), 7.84 (dd, *J* = 8, 2 Hz, 1 H, H-4), 7.84 (dd, *J* = 8, 2 Hz, 1 H, H-5″), 7.80 (d, *J* = 8 Hz, 1 H, H-2″), 7.71 (d, *J* = 8 Hz, 1 H, H-4″), 7.52 (td, *J* = 8, 2 Hz, 1 H, H-7″), 7.51 (td, *J* = 8, 2 Hz, 1 H, H-6″), 7.46 (t, *J* = 8 Hz, 1 H, H-3″), 7.26 (dd, *J* = 8, 5 Hz, 1 H, H-5), 7.05 (d, *J* = 16 Hz, 1 H, H-1′).

MS (EI): *m*/*z* (%) = 232 (18, [M + 1]$^+$), 231, 230 (100), 115, 102, 101, 88.

Anal. Calcd for $C_{17}H_{13}N$: C, 88.28; H, 5.66; N, 6.06. Found: C, 88.04; H, 5.62; N, 5.94.

(*E*)- and (*Z*)-3-[2-(2-Naphthyl)vinyl]pyridines (14 and 15)
From sodium pyridine-3-acetate (4.92 g, 0.031 mol) and 2-naphthaldehyde (4.84 g, 0.031 mol) in Ac_2O (22.13 g, 0.217 mol). Distillation gave quinoline, followed by 2-naphthaldehyde, then a fraction (bp 110–180 °C/0.005 mm Hg) which was separated by column chromatography (EtOAc–PE).

(i) (*Z*)-3-[2-(2-Naphthyl)vinyl]pyridine (15)
Colorless oil; yield: 1.60 g (22%).

^{1}H NMR ($CDCl_3$): δ = 8.52 (d, *J* = 2 Hz, 1 H, H-2), 8.42 (dd, *J* = 5, 2 Hz, 1 H, H-6), 7.78 (dd, *J* = 8, 2 Hz, 1 H, H-8″), 7.71 (dd, *J* = 8, 2 Hz, 1 H, H-5″), 7.71 (br s, 1 H, H-1″), 7.68 (d, *J* = 8 Hz, 1 H, H-4″), 7.53 (dt, *J* = 8, 1 Hz, 1 H, H-4), 7.47–7.42 (m, 2 H, H-6″,7″), 7.29 (dd, *J* = 8, 1 Hz, 1 H, H-3″), 7.09 (dd, *J* = 8, 5 Hz, 1 H, H-5), 6.91 (d, *J* = 12 Hz, 1 H, H-2′), 6.63 (d, *J* = 12 Hz, 1 H, H-1′).

MS (EI): *m*/*z* (%) = 232 (26, [M + 1]$^+$), 231, 114, 100, 75, 62, 51 (100).

Anal. Calcd for $C_{17}H_{13}N$: C, 88.28; H, 5.66; N, 6.06. Found: C, 88.10; H, 5.60; N, 6.23.

(ii) (*E*)-3-[2-(2-Naphthyl)vinyl]pyridine (14)
White solid; crude yield: 0.48 g (7%); white crystals (toluene–PE, 1:2); mp 114–116 °C (Lit.[11] mp 118–119 °C).

^{1}H NMR ($CDCl_3$): δ = 8.79 (br s, 1 H, H-2), 8.52 (d, *J* = 5 Hz, 1 H, H-6), 7.90–7.81 (m, 4 H, H-4,4″,5″,8″), 7.84 (br s, 1 H, H-1″), 7.74 (dd, *J* = 8, 1 Hz, 1 H, H-3″), 7.52–7.45 (m, 2 H, H-6″,7″), 7.33 (d, *J* = 16 Hz, 1 H, H-2′), 7.31 (dd, *J* = 8, 5 Hz, 1 H, H-5), 7.19 (d, *J* = 16 Hz, 1 H, H-1′).

MS (EI): *m*/*z* (%) = 232 (22, [M + 1]$^+$), 231, 230, 114, 100, 87, 75 (100), 62.

Anal. Calcd for $C_{17}H_{13}N$: C, 88.28; H, 5.66; N, 6.06. Found: C, 88.42; H, 5.62; N, 6.22.

(2-Arylvinyl)pyridines via Alcohols; General Procedure C
a) *n*-BuLi in hexane (2.5 M, 5.72 mL, 0.0143 mol) was added to a stirred soln of freshly distilled diisopropylamine (1.70 mL, 0.013 mol) in anhyd THF (20 mL) at –5 °C under N_2. After 30 min, the soln was cooled to –78 °C and picoline (1.27 mL, 0.013 mol) was added. The orange soln was warmed to –5 °C, maintained at this temperature for 30 min, cooled to –78 °C and the aldehyde or ketone (2.03 g, 0.013 mol) added. The mixture was warmed to r.t., stirred for 30 min, cooled to –5 °C and quenched with a 20% molar excess of NH_4Cl, resulting in two yellow layers. The THF layer was separated and the solvent evaporated. The aqueous layer was extracted with $CHCl_3$ (2 × 20 mL) and the combined extracts added to the residue from the THF layer and the solvent removed. The resulting oil was dissolved in hot $CHCl_3$ (20 mL) and the alcohol left to crystallize overnight.

b) This alcohol (0.008 mol) was added to a soln of concd H_2SO_4 (10 mL) in glacial AcOH (40 mL) and stirred for 12 h at r.t., or for 3 h at reflux. The resulting yellow soln was poured into H_2O (200 mL), neutralized with NaOH soln and extracted into $CHCl_3$ (3 × 100 mL). The combined extracts were dried (K_2CO_3), filtered, and the solvent removed to leave a yellow oily-solid which was purified by wet-flash column chromatography eluting with mixtures of PE and EtOAc.

(*E*)-4-[2-(1-Naphthyl)vinyl]pyridine (16)
a) From 4-picoline and 1-naphthaldehyde. The intermediate white solid was filtered off and washed (PE), affording 1-(1-naphthyl)-2-pyridin-4-ylethanol; colorless crystals; yield: 2.57 g (79%); mp 167–169 °C.

IR (Nujol): 3186 (OH), 1610 (CN) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 8.45 (d, *J* = 6 Hz, 2 H, H-2″,6″), 8.12 (d, *J* = 8 Hz, 1 H, H-8′), 7.91 (dd, *J* = 8, 1 Hz, 1 H, H-5′), 7.81 (d, *J* = 8 Hz, 1 H, H-2′), 7.62 (d, *J* = 8 Hz, 1 H, H-4′), 7.53 (2 td, *J* = 8, 1 Hz, 2 H, H-6′,7′), 7.47 (t, *J* = 8 Hz, 1 H, H-3′), 7.17 (d, *J* = 6 Hz, 2 H, H-3″,5″), 5.72 (dd, *J* = 8.5, 3.9 Hz, 1 H, C*H*CH_2), 3.24 and 3.12 (AB of ABX system, J_{AB} = 13.6, J_{AX} = 3.9, J_{BX} = 8.5 Hz, 2 H, CHCH_2).

MS (EI): *m*/*z* (%) = 250 (5, [M + 1]$^+$), 249, 157, 129, 128, 127, 93 (100).

Anal. Calcd for $C_{17}H_{15}NO$: C, 81.89; H, 6.07; N, 5.62. Found: C, 81.70; H, 5.82; N, 5.51.

b) Dehydration of this alcohol (2 g, 0.008 mol) at r.t. gave exclusively **16** as an off-white solid (1.54 g, 83%), identical to the material prepared by the previous procedure.

(*Z*)- and (*E*)-4-[2-(1-Naphthyl)prop-1-en-1-yl]pyridine (22 and 23)

a) From 1-acetylnaphthalene (2.21 g, 1.98 mL, 0.013 mol) and 4-picoline (1.27 mL, 0.013 mol). The intermediate white solid was filtered off and washed with cold Et_2O (2 × 5 mL), affording 2-(1-naphthyl)-1-pyridin-4-ylpropan-2-ol (**20**); white solid; yield: 2.91 g (91%); mp 165–167 °C.

IR (Nujol): 3226 (OH), 1603 (CN) cm^{-1}.

^1H NMR ($CDCl_3$): δ = 8.89 (d, *J* = 9 Hz, 1 H, H-2″), 8.33 (d, *J* = 6 Hz, 2 H, H-2′,6′), 7.91 (dd, *J* = 8, 2 Hz, 1 H, H-8″), 7.79 (dd, *J* = 7, 2 Hz, 1 H, H-5″), 7.57 (td, *J* = 8, 2 Hz, 1 H, H-6″), 7.52 (td, *J* = 8, 2 Hz, 1 H, H-7″), 7.36–7.30 (m, 2 H, H-3″,4″), 6.81 (d, *J* = 6 Hz, 2 H, H-3′,5′), 3.52 (d, *J* = 13 Hz, 1 H, C$H_A$$H_B$), 3.40 (d, *J* = 13 Hz, 1 H, CH$_A$$H_B$), 2.43 (s, 1 H, OH), 1.79 (s, 3 H, CH_3).

MS (EI): *m*/*z* (%) = 263 (4, [M^+]), 171, 127, 93, 65, 43 (100).

Anal. Calcd for $C_{18}H_{17}NO$: C, 82.09; H, 6.51; N, 5.32. Found: C, 81.76; H, 6.60; N, 5.30.

b) The alcohol **20** (2.10 g, 0.008 mol) was dehydrated by treatment with acid for 3 h at reflux and the product was purified by chromatography.

(i) (*Z*)-4-[2-(1-Naphthyl)prop-1-en-1-yl]pyridine (22)

Colorless solid; yield: 0.32 g (16%); mp 56.5–58 °C.

^1H NMR ($CDCl_3$): δ = 8.16 (d, *J* = 6 Hz, 2 H, H-2,6), 7.89 (dd, *J* = 8, 1 Hz, 1 H, H-5″), 7.83 (2 dd superimposed, each *J* = 8, 1 Hz, each 1 H, H-4″,8″), 7.49 (td, *J* = 8, 1 Hz, 1 H, H-6″), 7.46 (t obsc, 1 H, H-3″), 7.42 (td, *J* = 8, 1 Hz, 1 H, H-7″), 7.22 (dd, *J* = 7, 1 Hz, 1 H, H-2″), 6.66 (d, *J* = 1.5 Hz, 1 H, H-1′), 6.60 (d, *J* = 6 Hz, 2 H, H-3,5), 2.33 (d, *J* = 1.5 Hz, 3 H, CH_3).

MS (EI): *m*/*z* (%) = 246 (30, [M + 1]$^+$), 245 (100), 230, 152, 63, 51.

UV (EtOH): λ_{max} (ε) = 314 (1150), 295 (5870), 283 (9170), 272 (11920), 259 (14670), 223 nm (64190).

Anal. Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71. Found: C, 87.96; H, 6.34; N, 5.55.

(ii) This was followed by a mixture of **22** and the *E*-isomer **23** (0.87g, 45%) but a pure sample of **23** could not be obtained due to very similar R_f values.

(*Z*)- and (*E*)-4-[2-(2-Naphthyl)prop-1-en-1-yl]pyridine (24 and 25)

a) From 2-acetylnaphthalene (2.21 g, 0.013 mol) and 4-picoline (1.27 mL, 0.013 mol). The intermediate white solid was filtered off and washed with cold Et_2O (2 × 5 mL) to give 2-(2-naphthyl)-1-pyridin-4-ylpropan-2-ol; white solid; yield: 2.10 g (61%); mp 161–163 °C.

IR (Nujol): 3159 (OH), 1606 (CN) cm^{-1}.

^1H NMR ($CDCl_3$): δ = 8.35 (d, *J* = 6 Hz, 2 H, H-2′,6′), 7.82 (m, 2 H, H-8″ and ArH), 7.79–7.77 (m, 2 H, H-1″ and ArH), 7.52 (dd, *J* = 9, 2 Hz, 1 H, H-3″), 7.49–7.46 (m, 2 H, H-6″, 7″), 6.91 (d, *J* = 6 Hz, 2 H, H-3′,5′), 3.20 (d, *J* = 13.1 Hz, 1 H, C$H_A$$H_B$), 3.11 (d, *J* = 13.1 Hz, 1 H, CH$_A$$H_B$), 2.29 (br s, 1 H, OH), 1.68 (s, 3 H, CH_3).

MS (EI): *m*/*z* (%) = 264 (50, [M + 1]$^+$), 263, 171, 127, 93, 43 (100).

Anal. Calcd for $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32. Found: C, 82.29; H, 6.79; N, 5.23.

b) This alcohol (2.0 g, 0.0076 mol) was dehydrated by treatment with acid for 3 h at reflux. Chromatography gave **24** and **25**.

(i) (*Z*)-4-[2-(2-Naphthyl)prop-1-en-1-yl]pyridine (24)

Crude white solid; yield: 0.18 g (10%); pure as white crystals (toluene–hexane); mp 93–95 °C.

^1H NMR ($CDCl_3$): δ = 8.27 (br s, 2 H, H-2,6), 7.83 (m, 1 H, H-8″), 7.77 (d, *J* = 9 Hz, 1 H, H-4″), 7.76 (m, 1 H, H-5″), 7.67 (br s, 1 H, H-1″), 7.50–7.46 (m, 2 H, H-6″, 7″), 7.24 (dd, *J* = 9, 2 Hz, 1 H, H-3″), 6.82 (d, *J* = 5.5 Hz, 2 H, H-3,5), 6.48 (d, *J* = 1.2 Hz, 1 H, H-1′), 2.33 (d, *J* = 1.2 Hz, 3 H, CH_3).

MS (EI): *m*/*z* (%) = 246 (30, [M + 1]$^+$), 245 (100), 244, 230, 128, 115.

UV (EtOH): λ_{max} (ε) = 302 (7550), 267 (15650), 223 nm (52020).

Anal. Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71. Found: C, 87.91; H, 6.26; N, 5.60.

(ii) (*E*)-4-[2-(2-Naphthyl)prop-1-en-1-yl]pyridine (25)

Crude white solid; yield: 0.77 g (41%); pure as white crystals (toluene–PE, 1:3); mp 132–134 °C.

^1H NMR ($CDCl_3$): δ = 8.62 (d, *J* = 6 Hz, 2 H, H-2,6), 7.95 (d, *J* = 2 Hz, 1 H, H-1″), 7.89–7.84 (m, 3 H, H-4″,5″,8″), 7.61 (dd, *J* = 9, 2 Hz, 1 H, H-3″), 7.50 (m, 2 H, H-6″, 7″), 7.30 (d, *J* = 6 Hz, 2 H, H-3,5), 6.88 (s, 1 H, H-1′), 2.42 (s, 3 H, CH_3).

MS (EI): *m*/*z* (%) = 246 (22, [M + 1]$^+$), 245 (100), 244, 230, 128,51.

UV (EtOH) : λ_{max} (ε) = 305 (20450), 276 (24490), 246 (13530), 227 nm (27430).

Anal. Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71. Found: C, 88.33; H, 6.02; N, 5.55.

(*E*)-2-[2-(3-Phenanthryl)vinyl]pyridine (26)

a) From 2-picoline (1.27 mL, 0.013 mol) and phenanthrene-3-carbaldehyde (2.68 g, 0.013 mol). Removal of the solvent afforded almost pure 1-(3-phenanthryl)-2-pyridin-2-ylethanol; viscous yellow oil; yield: 3.84 g (99%).

^1H NMR ($CDCl_3$): δ = 8.75 (s, 1 H, H-4′), 8.72 (d, *J* = 8 Hz, 1 H, H-5′), 8.58 (d, *J* = 5 Hz, 1 H, H-6″), 7.88 (dd, *J* = 8, 1 Hz, 1 H, H-8″), 7.87 (d, *J* = 8 Hz, 1 H, H-1′), 7.72 (app s, 2 H, H-9′, 10′), 7.65 (dd, *J* = 8, 1 Hz, 1 H, H-2′), 7.65–7.55 (m, 3 H, H-6′,7′,4′), 7.19 (dd, *J* = 7, 5 Hz, 1 H, H-5″), 7.13 (d, *J* = 7 Hz, 1 H, H-3″), 5.99 (br s, 1 H, OH), 5.45 (dd, *J* = 7.5, 4.6 Hz, 1 H, C*H*CH$_2$), 3.27 (AB of ABX system, 2 H, CHCH_2).

MS (EI): *m*/*z* (%) = 300 (35, [M + 1]$^+$), 299, 178, 93 (100), 80, 65.

b) This alcohol (1.90 g, 0.0064 mol) was dehydrated by treatment with acid at r.t. for 12 h to give exclusively **26**; crude yellow solid; yield: 1.13 g (63%); pure as bright yellow crystals (benzene, HAZARD); mp 118–120 °C.

^1H NMR ($CDCl_3$): δ = 8.82 (s, 1 H, H-4″), 8.72 (d, *J* = 8 Hz, 1 H, H-5″), 8.65 (dd, *J* = 5, 1 Hz, 1 H, H-6), 7.92 (d, *J* = 16 Hz, 1 H, H-2″), 7.89 (dd, *J* = 8, 1 Hz, 1 H, H-8″), 7.88 (m, 2 H, H-1″,2″), 7.73 (app s, 2 H, H-9″,10″), 7.69 (td, *J* = 8, 2 Hz, 1 H, H-4), 7.68 (td, *J* = 8, 1 Hz, 1 H, H-6″), 7.61 (td, *J* = 8, 1 Hz, 1 H, H-7″), 7.46 (d, *J* = 8 Hz, 1 H, H-3), 7.37 (d, *J* = 16 Hz, 1 H, H-1′), 7.18 (ddd, *J* = 8, 5, 1 Hz, 1 H, H-5).

MS (EI): *m*/*z* (%) = 282 (21, [M + 1]$^+$), 281, 280 (100), 140, 79, 78, 52.

UV (EtOH) : λ_{max} (ε) = 367 (12670), 350 (30920), 338 (38340), 269 (31430), 249 (33240), 241 (25340), 221 (13940), 203 nm (24840).

Anal. Calcd for $C_{21}H_{15}N$: C, 89.65; H, 5.37; N, 4.98. Found: C, 89.77; H, 5.42; N, 4.78.

(*E*)-3-[2-(3-Phenanthryl)vinyl]pyridine (27)

a) From 3-picoline (1.27 mL, 0.013 mol) and phenanthrene-3-carbaldehyde (2.68 g, 0.013 mol). Removal of the solvent followed by wet flash column chromatography (EtOAc–PE afforded 1-(3-phenanthryl)-2-pyridin-3-ylethanol: yellow solid; yield: 1.90 g (49%).

IR (Nujol): 3272 (OH), 1602 (CN) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 8.63 (d, *J* = 8 Hz, 1 H, H-5′), 8.58 (br s, 1 H, H-4′), 8.40 (d, *J* = 2 Hz, 1 H, H-2″), 8.38 (dd, *J* = 5, 2 Hz, 1 H, H-6″), 7.88 (dd, *J* = 8, 1 Hz, 1 H, H-8′), 7.85 (d, *J* = 8 Hz, 1 H, H-1′), 7.72 (app s, 2 H, H-9′,10′), 7.64 (td, *J* = 8, 1 Hz, 1 H, H-6′), 7.59 (td, *J* = 8, 1 Hz, 1 H, H-7′), 7.51 (dd, *J* = 8, 2 Hz, 1 H, H-2′), 7.45 (dt, *J* = 8, 2 Hz, 1 H, H-4″), 7.13 (dd, *J* = 8, 5 Hz, 1 H, H-5″), 5.11 (dd, *J* = 7.2, 5.8 Hz, 1 H, C*H*CH_2), 3.11 (AB of ABX, 2 H, CHCH_2), 3.03 (br s, 1 H, OH).

MS (EI): *m*/*z* (%) = 299 (11, $[M]^+$), 280, 207, 177, 93 (100), 65.

b) This alcohol (1.50 g, 0.005 mol) was dehydrated by treatment with acid for 12 h at r.t. followed by wet flash column chromatography (PE–EtOAc) to give **27**; yellow oily solid; yield: 0.82 g (58%); one spot R_f = 0.39 (EtOAc–PE, 1:1).

^{1}H NMR ($CDCl_3$): δ = 8.81 (d, *J* = 2 Hz, 1 H, H-2), 8.74 (d, *J* = 8 Hz, 1 H, H-5″), 8.73 (br s, 1 H, H-4″), 8.52 (dd, *J* = 5, 1.5 Hz, 1 H, H-6), 7.92 (dd, *J* = 8, 2 Hz, 1 H, H-4), 7.90 (dd, *J* = 8, 1 Hz, 1 H, H-8″), 7.89 (d, *J* = 8 Hz, 1 H, H-1″), 7.84 (dd, *J* = 8, 2 Hz, 1 H, H-2″), 7.74 (app s, 2 H, H-9″,10″), 7.69 (td, *J* = 8, 1 Hz, 1 H, H-6″), 7.62 (td, *J* = 8, 1 Hz, 1 H, H-7″), 7.44 (d, *J* = 16 Hz, 1 H, H-2′), 7.33 (dd, *J* = 8, 5 Hz, 1 H, H-5′), 7.27 (d, *J* = 16 Hz, 1 H, H-1′).

MS (EI): *m*/*z* (%) = 282 (8, $[M + 1]^+$), 281, 280 (100), 278, 202, 140, 79.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{21}H_{15}N$: 281.1204; found: 281.1204.

(*E*)-4-[2-(3-Phenanthryl)vinyl]pyridine (28)

a) From 4-picoline (1.27 mL, 0.013 mol) and phenanthrene-3-carbaldehyde (2.68 g, 0.013 mol). Removal of the solvent afforded crude 1-(3-phenanthryl)-2-pyridin-4-ylethanol; yellow oil: yield: 3.80 g (98%).

IR (Nujol): 3285 (OH), 1605 (CN) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 8.65 (d, *J* = 8 Hz, 1 H, H-5′), 8.61 (br s, 1 H, H-4′), 8.42 (d, *J* = 6 Hz, 2 H, H-2″,6″), 7.89 (dd, *J* = 8, 1.5 Hz, 1 H, H-8′), 7.86 (d, *J* = 8 Hz, 1 H, H-1′), 7.74 (app s, 2 H, H-9′,10′), 7.65 (td, *J* = 8, 1.5 Hz, 1 H, H-6′), 7.61 (td, *J* = 8, 1.5 Hz, 1 H, H-7′), 7.54 (dd, *J* = 8, 1.5 Hz, 1 H, H-2′), 7.13 (d, *J* = 6 Hz, 2 H, H-3″,5″), 5.19 (dd, *J* = 7.6, 5.4 Hz, 1 H, C*H*CH_2), 3.14 (AB of ABX system, 2 H, CHCH_2).

MS (EI): *m*/*z* (%) = 300 (5, $[M + 1]^+$), 299, 179, 178, 93 (100), 65.

b) This alcohol (3.50 g, 0.012 mol) was dehydrated by treatment with acid at r.t. for 12 h to give after wet flash column chromatography (PE–EtOAc) exclusively **28**; light-yellow solid; yield: 2.24 g (68%); recrystallized as light-yellow powder (benzene, HAZARD); mp 141.5–142.5 °C.

NMR as reported for **28** under General Procedure A.

MS (EI): *m*/*z* (%) = 282 (22, $[M + 1]^+$), 281 (100), 280, 140, 126, 51.

UV (EtOH): λ_{max} (ε) = 368 (6860), 351 (28590), 339 (35030), 281 (28370), 273 (30740), 250 (41900), 242 (32220), 204 nm (48210).

Anal. Calcd for $C_{21}H_{15}N$: C, 89.65; H, 5.37; N, 4.98. Found: C, 89.98; H, 5.42; N, 4.89.

Isomerization of *E*- to *Z*-Isomer; General Procedure D

A soln of *E*-isomer **10** or **18** (300 mg) in toluene (110 mL), deaerated by bubbling N_2 through for 30 min before and throughout the reaction, was irradiated (λ = 366 nm) at 19 °C for 1 h. Solvent was removed in vacuo and the resultant yellow oil purified by wet-flash column chromatography eluting with mixtures of PE and EtOAc.

(*Z*)-2-[2-(2-Naphthyl)vinyl]pyridine (11)[11]

From **10**. Chromatography gave unchanged *E*-isomer **10** followed by a fraction which was distilled (bp 250 °C/0.5 mm Hg) to give **11**; colorless oil; yield: 70%.

^{1}H NMR ($CDCl_3$): δ = 8.60 (dt, *J* = 5, 2 Hz, 1 H, H-6), 7.78 (dd, *J* = 8, 2 Hz, 1 H, H-8″), 7.76 (br s, 1 H, H-1″), 7.72 (dd, *J* = 8, 2 Hz, 1 H, H-5″), 7.67 (d, *J* = 9 Hz, 1H, H-4″), 7.47–7.42 (m, 2 H, H-6″,7′), 7.39 (td, *J* = 8, 2 Hz, 1 H, H-4), 7.33 (dd, *J* = 9, 2 Hz, 1 H, H-3″), 7.17 (d, *J* = 8 Hz, 1 H, H-3), 7.08 (ddd, *J* = 8, 5, 1 Hz, 1 H, H-5), 6.99 (d, *J* = 12 Hz, 1 H, H-2′), 6.78 (d, *J* = 12 Hz, 1 H, H-1′).

MS (EI): *m*/*z* (%) = 232 (14, $[M + 1]^+$), 231, 230, 115, 78, 51 (100).

Anal. Calcd for $C_{17}H_{13}N$: C, 88.28; H, 5.67; N, 6.06. Found: C, 88.25; H, 5.60; N, 6.31.

(*Z*)-4-[2-(2-Naphthyl)vinylpyridine (19)

From **18**. Chromatography gave **19** (188 mg, 63%) as a colorless oil followed by unchanged starting material. Distillation (bp 190 °C/0.6 mm Hg) gave pure **19**.

^{1}H NMR ($CDCl_3$): δ = 8.45 (d, *J* = 5 Hz, 2 H, H-2,6), 7.79 (dd, *J* = 8, 2 Hz, 1 H, H-8″), 7.72 (dd, *J* = 8, 2 Hz, 1 H, H-5″), 7.70 (s, 1 H, H-1″), 7.68 (d, *J* = 9 Hz, 1 H, H-4″), 7.49–7.43 (m, 2 H, H-6″,7″), 7.23 (dd, *J* = 9, 2 Hz, 1 H, H-3″), 7.14 (d, *J* = 5 Hz, 2 H, H-3,5), 6.95 (d, *J* = 12 Hz, 1 H, H-2′), 6.58 (d, *J* = 12 Hz, 1 H, H-1′).

MS (EI): *m*/*z* (%) = 231 (32, $[M^+]$), 230, 114, 99, 63 (100), 51.

Anal. Calcd for $C_{17}H_{13}N$: C, 88.28; H, 5.66; N, 6.06. Found: C, 88.21; H, 5.90; N, 6.01.

Photocyclodehydrogenation; General Procedure E

A soln of the arylvinylpyridine (231 mg, 1.0 mmol) in toluene (100 mL), aerated by bubbling air for 30 min before and throughout the reaction, was irradiated (λ = 366 nm) at 19 °C for 10 h, with one interruption to remove polymer from the vessel wall. The resulting soln was filtered and the filtrate evaporated to leave a brown oily solid which was purified by wet-flash column chromatography eluting with mixtures of PE and EtOAc.

Photocyclization of (*E*)-1,2-NVP (8); Naphtho[2,1-*f*]quinoline (29)

Chromatography gave three unidentified by-products, followed by naphtho[2,1-*f*]quinoline (**29**); crude yield: 31 mg (13%); pure as light yellow crystals (toluene); mp 225–227 °C (Lit.[21] mp 226–227 °C).

^{1}H NMR ($CDCl_3$): δ = 9.09 (br d, *J* = ca. 8.6 Hz, 1 H, H-4), 9.04 (dd, *J* = 4.3, 1.6 Hz, 1 H, H-2), 8.98 (d, *J* = 9.3 Hz, 1 H, H-11), 8.80 (br d, *J* = 8.3 Hz, 1 H, H-10), 8.64 (d, *J* = 9.0 Hz, 1 H, H-5), 8.28 (d, *J* = 9.3 Hz, 1 H, H-12), 8.07 (d, *J* = 9.0 Hz, 1 H, H-6), 8.02 (dd, *J* = 7.9, 1.4 Hz, 1 H, H-7), 7.76 (td, *J* = 7.9,1.4 Hz, 1 H, H-9), 7.68 (td, *J* = 7.9, 1.4 Hz, 1 H, H-8), 7.64 (dd, *J* = 8.5, 4.3 Hz, 1 H, H-3); NOE 8.64 → 9.09 (18%) and 8.07 (7%).

^{13}C NMR ($CDCl_3$): δ = 149.6 (C-2), 147.5 (C-12a), 132.35, 131.6 (C-4), 130.3, 128.6 (C-7), 128.2 (C-6), 128.0 (C-12), 127.8, 127.2 (C-9), 126.9 (C-8), 125.6, 125.3 (C-11), 123.2 (C-10), 121.4 (C-3), 120.5 (C-5).

MS (EI): *m*/*z* (%) = 230 (21, $[M + 1]^+$), 229 (100), 228, 101, 100, 88.

Anal. Calcd for $C_{17}H_{11}N$: C, 89.06; H, 4.84; N, 6.11. Found: C, 89.26; H, 4.77; N, 6.04.

Photocyclization of (*E*)-1,3-NVP (12)

Chromatography gave five components. The first unidentified material was followed by:

(i) Naphtho[1,2-*h*]quinoline (30)

White solid; yield: 9 mg (4%); mp 113–115 °C (Lit.[12] mp 118–119 °C).

^{1}H NMR ($CDCl_3$): δ = 9.37 (d, *J* = 9.0 Hz, 1 H, H-5), 9.07 (dd, *J* = 4.3, 1.7 Hz, 1 H, H-3), 8.76 (br d, *J* = ca. 8.1 Hz, 1 H, H-10), 8.75 (d, *J* = 9.0 Hz, 1 H, H-11), 8.25 (dd, *J* = 8.1, 1.7 Hz, 1 H, H-1),

8.08 (d, *J* = 9.0 Hz, 1 H, H-6), 8.03 (dd, *J* = 7.4, 1.4 Hz, 1 H, H-7), 7.92 (d, *J* = 9.0 Hz, 1 H, H-12), 7.72 (td, *J* = 7.4, 1.4 Hz, 1 H, H-9), 7.67 (td, *J* = 7.4, 1.4 Hz, 1 H, H-8), 7.55 (dd, *J* = 8.1, 4.3 Hz, 1 H, H-2); NOE 8.25 → 7.92 (6%) and 7.55 (5%).

^{13}C NMR ($CDCl_3$): δ = 149.3 (C-3), 146.2 (C-4a), 135.8 (C-1), 133.1, 130.3, 130.0, 129.75, 128.8 (C-7), 127.7 (C-6), 126.8 (C-8), 126.6 (C-9), 126.45, 125.8 (C-12), 123.1 (C-10), 122.3 (C-5), 122.1 (C-11), 121.6 (C-2).

MS (EI): *m*/*z* (%) = 230 (21, $[M + 1]^+$), 229 (100), 228, 200, 114, 100.

UV (EtOH): λ_{max} (ε) = 361 (2510), 343 (2510), 296 (18460), 265 (67350), 235 (18070), 215 nm (28900).

Anal. Calcd for $C_{17}H_{11}N$: C, 89.05; H, 4.84; N, 6.11. Found: C, 89.09; H, 4.45; N, 5.71.

(ii) Two further by-products, followed by:

Naphtho[2,1-*f*]isoquinoline (31)
Crude yield: 120 mg (51%); sublimed (160 °C/0.03 mm Hg) as a pure white solid; mp 238–240 °C (Lit.[22] mp 224–226 °C).

^{1}H NMR ($CDCl_3$): δ = 9.36 (s, 1 H, H-1), 8.83 (d, *J* = 9.1 Hz, 1 H, H-11), 8.80 (br d, *J* = ca. 8 Hz, 1 H, H-10), 8.78 (d, *J* = 5.9 Hz, 1 H, H-3), 8.64 (d, *J* = 9.0 Hz, 1 H, H-5), 8.49 (d, *J* = 5.9 Hz, 1 H, H-4), 8.09 (d, *J* = 9.1 Hz, 1 H, H-12), 8.06 (d, *J* = 9.0 Hz, 1 H, H-6), 8.03 (dd, *J* = 7.8, 1.5 Hz, 1 H, H-7), 7.76 (td, *J* = 7.8, 1.5 Hz, 1 H, H-9), 7.71 (td, *J* = 7.8, 1.5 Hz, 1 H, H-8); NOE 9.36 → 8.09 (8%).

^{13}C NMR ($CDCl_3$): δ = 152.1 (C-1), 144.7 (C-3), 134.5, 133.0, 130.6, 130.1, 128.7 (C-7), 128.1 (C-6), 127.3 (C-8), 127.1 (C-9), 126.5, 125.5 (C-12), 123.4 (C-10), 122.7 (C-11), 120.7 (C-5), 116.3 (C-4).

MS (EI): *m*/*z* (%) = 230 (20, $[M + 1]^+$), 229 (100), 228, 200, 114, 100, 57.

Anal. Calcd for $C_{17}H_{11}N$: C, 89.06; H, 4.84; N, 6.11. Found: C, 89.16; H, 5.11; N, 6.58.

Photocyclization of (*E*)-1,4-NVP (16); Naphtho[1,2-*h*]isoquinoline (32)
Chromatography gave a small amount of the *Z*-isomer **17** followed by **32**; crude yield: 126 mg (55%); sublimed (160 °C/0.03 mm Hg) as a pure white solid; mp 193–195 °C.

^{1}H NMR ($CDCl_3$): δ = 10.13 (s, 1 H, H-4), 8.87 (d, *J* = 9.1, 1 H, H-11), 8.76 (d, *J* = 9.1 Hz, 1 H, H-5), 8.72 (br d, *J* = ca. 8.4 Hz, 1 H, H-10), 8.71 (d, *J* = 5.4 Hz, 1 H, H-2), 8.06 (d, *J* = 9.1 Hz, 1 H, H-6), 8.00 (dd, *J* = 7.8, 1.2 Hz, 1 H, H-7), 7.91 (d, *J* = 9.1 Hz, 1 H, H-12), 7.77 (d, *J* = 5.4 Hz, 1 H, H-1), 7.73 (td, *J* = 7.8, 1.2 Hz, 1 H, H-9), 7.66 (td, *J* = 7.8, 1.2 Hz, 1 H, H-8); NOE 10.13 → 8.76 (23%).

^{13}C NMR ($CDCl_3$): δ = 147.6 (C-4), 144.3 (C-2), 135.4, 132.3, 130.2, 128.8 (C-6), 128.7 (C-7), 128.6, 127.7, 127.1 (C-9), 126.8 (C-8), 125.8 (C-11), 125.2, 125.2 (C-12), 122.8 (C-10), 120.8 (C-1), 119.9 (C-5).

MS (EI): *m*/*z* (%) = 230 (40, $[M + 1]^+$, 229 (100), 228, 200, 114, 100.

UV (EtOH): λ_{max} (ε) = 359 (4000), 350 (3180), 342 (5180), 321 (9000), 286 (14990), 264 (72720), 256 (54980), 239 (25630), 220 nm (24990).

Anal. Calcd for $C_{17}H_{11}N$: C, 89.06; H, 4.84; N, 6.11. Found: C, 89.20; H, 4.70; N, 6.17.

Photocyclization of (*E*)-2,2-NVP (10)
Chromatography gave three unidentified by-products followed by:

Naphtho[1,2-*f*]quinoline (33)
Off-white solid; yield: 24 mg (10%); mp 104–107 °C (Lit.[21,23]mp 106–107 °C); one spot R_f = 0.49 (EtOAc–PE, 1:1).

^{1}H NMR ($CDCl_3$): δ = 9.40 (br d, *J* = ca. 8.6 Hz, 1 H, H-1), 9.00 (dd, *J* = 4.2, 1.6 Hz, 1 H, H-3), 8.93 (br d, *J* = ca. 8.3 Hz, 1 H, H-12), 8.17 (d, *J* = 8.7 Hz, 1 H, H-5), 8.08 (d, *J* = 8.7 Hz, 1 H, H-6), 8.06 (dd, *J* = 7.7, 1.7 Hz, 1 H, H-9), 7.96 (d, *J* = 8.5 Hz, 1 H, H-8), 7.87 (d, *J* = 8.5 Hz, 1 H, H-7), 7.72 (td, *J* = 7.7, 1.7 Hz, 1 H, H-11), 7.66 (td, *J* = 7.7, 1.7 Hz, 1 H, H-10), 7.58 (dd, *J* = 8.6, 4.2 Hz, 1 H, H-2).

^{13}C NMR ($CDCl_3$): δ = 148.9 (C-3), 148.8 (C-4a), 135.6 (C-1), 133.5, 130.85, 130.7 (C-6), 130.0, 128.8 (C-9), 128.6 (C-5), 128.25 (C-8), 127.3 (C-12), 126.8, 126.6 (C-11 and C-7 superimposed), 126.3 (C-10), 125.4, 120.35 (C-2).

MS (EI): *m*/*z* (%) = 230 (47, $[M + 1]^+$), 229 (100), 228, 201, 114, 100.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{11}N$: 229.0891; found: 229.0891.

Photocyclization of (*E*)-2,3-NVP (14)
Chromatography gave five components.

(i) Naphtho[2,1-*h*]quinoline (34)
White solid; yield: 4 mg (2%); mp 89–94 °C (Lit.[20] mp 95–96 °C); one spot R_f = 0.80 (EtOAc–PE, 1:3).

^{1}H NMR ($CDCl_3$): δ = 11.21 (br d, *J* = ca. 8.9 Hz, 1 H, H-12), 9.21 (dd, *J* = 4.2, 2.0 Hz, 1 H, H-2), 8.28 (dd, *J* = 8.1, 1.9 Hz, 1 H, H-4), 8.02 (d, *J* = 8.6 Hz, 1 H, H-8), 8.01 (dd, *J* = 7.8, 1.2 Hz, 1 H, H-9), 7.94 (d, *J* = 8.5 Hz, 1 H, H-6), 7.88 (d, *J* = 8.6 Hz, 1 H, H-7), 7.85 (d, *J* = 8.5 Hz, 1 H, H-5), 7.83 (td, *J* = 7.8, 1.2 Hz, 1 H, H-11), 7.67 (td, *J* = 7.8, 1.2 Hz, 1 H, H-10), 7.55 (dd, *J* = 8.1, 4.2 Hz, 1 H, H-3); NOE 8.28 → 7.85 (4%) and 7.55 (3%).

^{13}C NMR ($CDCl_3$): δ = 148.4 (C-12c), 148.3 (C-2), 136.4 (C-4), 133.9, 133.6, 131.7, 130.7 (C-12), 129.8 (C-8), 128.6 (C-6), 126.85 (C-7), 128.4 (C-9), 127.8, 127.3 (C-11), 126.55 (C-5), 126.4, 126.2 (C-10), 120.5 (C-3).

MS (EI): *m*/*z* (%) = 230 (71, $[M + 1]^+$), 229 (100), 228, 114, 100, 83, 74, 50.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{11}N$: 229.0891; found: 229.0891.

(ii) three by-products, followed by:

Naphtho[1,2-*f*]isoquinoline (35)
Colorless crystals; yield: 65 mg (28%); mp 82–84 °C (Lit.[12] mp 79–80 °C); one spot R_f = 0.32 (EtOAc–PE, 1:1).

^{1}H NMR ($CDCl_3$): δ = 9.38 (s, 1 H, H-4), 9.08 (br d, *J* = ca. 8.4 Hz, 1 H, H-12), 8.91 (br d, *J* = ca. 6.1 Hz, 1 H, H-1), 8.74 (d, *J* = 6.1 Hz, 1 H, H-2), 8.05 (dd, *J* = 7.8, 1.3 Hz, 1 H, H-9), 8.00 (d, *J* = 8.5 Hz, 1 H, H-8), 7.98 (d, *J* = 8.5 Hz, 1 H, H-5), 7.93 (d, *J* = 8.5 Hz, 1 H, H-6), 7.84 (d, *J* = 8.5 Hz, 1 H, H-7), 7.74 (td, *J* = 7.8, 1.3 Hz, 1 H, H-11), 7.67 (td, *J* = 7.8, 1.3 Hz, 1 H, H-10); NOE 9.38 → 7.98 (7%).

^{13}C NMR ($CDCl_3$): δ = 152.2 (C-4), 144.1 (C-2), 134.1, 133.4, 133.4, 130.3, 129.7 (C-8), 128.9 (C-9), 128.5 (C-6), 128.2, 127.1 (C-12), 126.95 (C-11), 126.7 (C-7), 126.45 (C-10), 126.00 (C-5), 125.45, 120.5 (C-1).

MS (EI): *m*/*z* (%) = 230 (21, $[M + 1]^+$), 229 (100), 228, 200, 100, 87, 74, 63.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{11}N$: 229.0891; found: 229.0891.

Photocyclization of (*E*)-2,4-NVP (18); Naphtho[2,1-*h*]isoquinoline (36)

Chromatography gave two by-products followed by **36**; light-yellow crystals; yield: 45 mg (20%); mp 85–87 °C; one spot R_f = 0.46 (EtOAc–PE, 1:1).

^{1}H NMR ($CDCl_3$): δ = 10.41 (s, 1 H, H-1), 9.09 (br d, *J* = ca. 8.4 Hz, 1 H, H-12), 8.70 (d, *J* = 5.5 Hz, 1 H, H-3), 8.06 (dd, *J* = 7.5, 1.3 Hz, 1 H, H-9), 8.04 (d, *J* = 8.5 Hz, 1 H, H-6), 7.97 (d, *J* = 8.5 Hz, 1 H, H-8), 7.85 (2 d, each *J* = 8.5 Hz, 2 H, H-5,7), 7.83 (d, *J* = 5.5 Hz, 1 H, H-4), 7.76 (td, *J* = 7.5, 1.3 Hz, 1 H, H-11), 7.69 (td, *J* = 7.5, 1.3 Hz, 1 H, H-10).

^{13}C NMR ($CDCl_3$): δ = 150.7 (C-1), 143.4 (C-3), 136.6, 133.75, 131.5 (C-6), 131.4, 129.3, 128.7 (C-9), 128.4 (C-8), 128.1 (C-12), 126.95 (C-11), 126.8, 126.7 (C-10), 126.5 and 125.4 (C-5 and C-7), 125.5, 120.9 (C-4).

MS (EI): *m*/*z* (%) = 230 (30, $[M + 1]^+$), 229 (100), 227, 200, 114, 100.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{11}N$: 229.0891; found: 229.0891.

UV (EtOH): λ_{max} (ε) = 375 (1320), 356 (1800), 316 (11380), 294 (33100), 280 (49990), 242 (22030), 216 (42500), 201 nm (32650).

Photocyclization of (*Z*)-4-[2-(1-Naphthyl)prop-1-en-1-yl]pyridine (22); 11-Methylnaphtho[1,2-*h*]isoquinoline (37)

From **22** (245 mg, 1 mmol) in anhyd toluene (250 mL) irradiating for 24 h. Chromatography gave two minor by-products, followed by starting material and its *E*-isomer, and then **37**; cream-colored waxy solid; yield: 25 mg (10%); one spot R_f = 0.32 (EtOAc–PE, 1:1). Repeated attempts at purification by column chromatography did not give a sharp-melting-point material.

^{1}H NMR ($CDCl_3$): δ = 10.07 (s, 1 H, H-4), 8.91 (m, 1 H, H-10), 8.78 (d, *J* = 9.0 Hz, 1 H, H-5), 8.66 (d, *J* = 5.5 Hz, 1 H, H-2), 8.04 (d, *J* = 9.0 Hz, 1 H, H-6), 8.02 (m, 1 H, H-7), 7.75 (s, 1 H, H-12), 7.68 (d, *J* = 5.5 Hz, 1 H, H-1), 7.67–7.65 (m, 2 H, H-8 and H-9), 3.22 (s, 3 H, CH_3).

^{13}C NMR ($CDCl_3$): δ = 147.3 (C-4), 143.7 (C-2), 138.9, 134.8, 133.5, 131.3, 129.45, 129.1 and 128.8 (C-6 and C-7), 128.3 (C-12), 128.2, 127.4 (C-10), 126.3 and 125.9 (C-8 and C-9), 124.5, 120.4 (C-5), 119.9 (C-1), 28.0 (CH_3).

MS (EI): *m*/*z* (%) = 244 (25, $[M + 1]^+$), 243 (100), 242, 241, 213, 189, 121.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{13}N$: 243.1048; found: 243.1048.

UV (EtOH): λ_{max} (ε) = 365 (100), 347 (470), 326 (1130), 267 (27270), 260 (22290), 221 nm (12110).

Photocyclization of (*E*)-4-[2-(2-Naphthyl)prop-1-en-1-yl]pyridine (25); 6-Methylnaphtho[2,1-*h*]isoquinoline (38)

From **25** (245 mg, 1.0 mmol) in anhyd benzene (HAZARD, 110 mL) irradiating for 48 h. Chromatography gave first an unidentified colorless oil (1.84 g). Gradual elution (to EtOAc–PE, 1:4) gave pure *Z*-isomer of the starting material followed by a mixture of this and **38**, followed by **38**; colorless oily solid; yield after a second column chromatography: 47 mg (19%); pure by ^{1}H NMR, although repeated attempts at crystallization did not afford sharp-melting-point material; one spot R_f = 0.39 (EtOAc–PE, 1:1).

^{1}H NMR ($CDCl_3$): δ = 10.28 (s, 1 H, H-1), 9.06 (br d, *J* = ca. 8.3 Hz, 1 H, H-12), 8.64 (d, *J* = 5.5 Hz, 1 H, H-3), 8.08 (d, *J* = 8.8 Hz, 1 H, H-7), 8.07 (dd, *J* = 7.7, 1.4 Hz, 1 H, H-9), 8.02 (d, *J* = 8.8 Hz, 1 H, H-8), 7.74 (td, *J* = 7.7, 1.4 Hz, 1 H, H-11), 7.72 (d, *J* = 5.5 Hz, 1 H, H-4), 7.70 (s, 1 H, H-5), 7.69 (td, *J* = 7.7, 1.4 Hz, 1 H, H-10), 2.87 (s, 3 H, CH_3); NOE 2.87 → 7.70 (3%) and 8.08 (5%).

^{13}C NMR ($CDCl_3$): δ = 150.8 (C-1), 143.6 (C-3), 137.7, 136.4, 133.3, 131.1, 129.4, 128.6 (C-12), 128.4 (C-9), 128.1 (C-8), 127.1, 126.7 (C-11), 126.6 (C-10), 125.4 (C-5), 124.7, 122.2 (C-7), 120.0 (C-4), 20.7 (CH_3).

MS (EI): *m*/*z* (%) = 244 (56, $[M + 1]^+$), 243 (100), 228, 215, 121, 114.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{13}N$: 243.1048; found: 243.1048.

UV (EtOH): λ_{max} (ε) = 376 (1150), 356 (1250), 318 (8250), 294 (23690), 283 (38050), 250 (14600), 220 nm (34910).

The next component eluted was unreacted starting material followed by polymeric 'baseline' material.

Attempted Photocyclizations of (*E*)-2- and (*E*)-3-[2-(3-Phenanthryl)vinyl]pyridines (26 and 27)

From **26** or **27** (281 mg, 1.0 mmol) in toluene (450 mL) irradiating for 18 h. The solvent was removed from the yellow soln affording a brown oily solid for which TLC revealed one 'baseline spot' of high molecular weight, and which gave an envelope of broadened signals in the ^{1}H NMR spectrum. Similar results were found with I_2 in place of aeration.

Photocyclization of (*E*)-4-[2-(3-Phenanthryl)vinyl]pyridine (28); Pyreno[1,10,9-*hij*]isoquinoline (40)

From **28** (253 mg, 0.9 mmol) in toluene (450 mL) irradiating for 2 h. The yellow precipitate was filtered off, the filtrate evaporated and the resulting brown oily solid was purified by wet flash column chromatography (PE–EtOAc) to give the photocyclized product **40** as a bright yellow solid followed by starting material, its *Z*-isomer, and 'baseline' polymeric material; yellow needles (toluene); yield: 110 mg (44%); mp 291–292 °C; one spot R_f = 0.79 (EtOAc–PE, 1:1).

^{1}H NMR ($CDCl_3$): δ = 9.50 (d, *J* = 7.8 Hz, 1 H, H-8), 9.08 (d, *J* = 5.3 Hz, 1 H, H-6), 8.25 (dd, *J* = 7.7, 1.0 Hz, 1 H, H-10), 8.16 and 8.18 (AB system, *J* = 8.3 Hz, 2 H, H-1,2), 8.11 (d, *J* = 8.8 Hz, 1 H, H-3), 8.05 (t, *J* = 7.8 Hz, 1 H, H-9), 8.03 and 7.98 (2d, *J* = 8.8 Hz, 2 H, H-11,12), 7.85 (d, *J* = 8.8 Hz, 1 H, H-4), 7.85 (d, *J* = 5.3 Hz, 1 H, H-5); NOE 7.85 → 8.11 (2%) and 9.08 (4%).

^{13}C NMR ($CDCl_3$): δ = 149.1 (C-7a), 145.3 (C-6), 136.2, 131.5 (C-3), 131.2, 130.45, 130.1, 128.5 (C-10), 128.1 and 126.7 (C-12 and C-11), 126.5 (C-9), 126.0, 125.85 (C-1 and C-2), 124.8 (C-4), 123.6 (C-8), 122.95, 122.35, 120.2, 118.8 (C-5).

MS (EI): *m*/*z* (%) = 278 (36, $[M + 1]^+$), 277, 248, 83, 71, 69, 57 (100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{21}H_{11}N$: 277.0891; found: 277.0891.

UV (EtOH): λ_{max} (ε) = 409 (11680), 388 (12140), 376 (15510), 370 (14360), 357 (10400), 323 (5530), 300 (39030), 288 (32060), 277 (22060), 255 (21820), 219 (33990), 203 nm (47730).

Anal. Calcd for $C_{21}H_{11}N$: C, 90.95; H, 4.00; N, 5.05. Found: C, 90.45; H, 4.54; N, 4.50.

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