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Synthesis and Photoluminescent Properties of New Ceramidine Derivatives

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ABSTRACT: *A series of new ceramidine derivatives* **8a–f** *has been synthesized in 4–5 steps involving a Wittig reaction of ceramidonine with various triphenylphosphonium bromides. Their UV and photoluminescence (PL) properties are reported. The compounds showed medium to strong PL between 502 and 522 nm at a concentration of* 1×10^{-5} *M* CH_2Cl_2. © 2011 Wiley Periodicals, Inc. Heteroatom Chem 23:66–73, 2012; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.20753

INTRODUCTION

Ceramidonine, ceramidine, and their derivatives have been used in yellow to brown dyes of superior light-fastness [1], and studies on their photophysical properties, such as electronic absorption, emission, and fluorescence, have been published in the literature [2] (see Fig. 1).

Nowadays, organic light emitting diodes (OLED) are being studied by many researchers [3]. A typical OLED consists of a layer of organic or polymeric materials situated between two electrodes, the anode and cathode. It is necessary to have a set of red [4], green [5], and blue emitting materials [6] with excellent luminous efficiency, proper chromaticity, and the photochemical stability of emitters for an emitting layer for OLED. Though many organic, polymeric, and inorganic emitting materials have been reported on, many breakthroughs have yet to be achieved in the field of materials used for excellent efficiency of OLEDs. Although the possibility of good emitting properties for OLED, the emitting properties of ceramidine derivatives have not much been reported on in the literature.

Yoon et al. synthesized substituted ceramidonine by reacting of 1-aminoanthraquinone with a benzyne precursor derived from arylthianthrenium cation radical perchlorate salt (a highly explosive salt) in LDA, and their yields were good, but the harsh reaction condition was necessary [7]. Rogness and Larock used a method in which 1-aminoanthraquinone reacted with a benzyne derived from *o*-(trimethylsilyl)phenyl triflate in CsF to obtain ceramidonine in a 70% yield [8]. For convenience of reaction, we synthesized ceramidonine **7** in two steps by reacting 1-aminoanthraquinone with iodobenzene, following Friedel-Crafts arylation [9].

For the synthesis of target compounds **8a–f**, the Wittig reaction was adopted to incorporate the ceramidonine with various phosphonium salts to form the olefin structure. In this paper, we will report on

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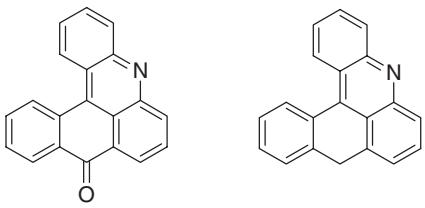


ceramidonine 7 ceramidine

FIGURE 1 Structure of ceramidine derivatives.

the synthesis of new ceramidine derivatives and their photoluminescent properties.

RESULTS AND DISCUSSION

Ceramidonine **7** was synthesized first for the synthesis of target compounds **8a–f** as in Scheme 1. 1-Aminoanthraquinone reacts with iodobenzene in the presence of copper powder, 18-crown-6, and potassium carbonate to give phenylamino anthraquinone in excellent yields of 98%. Cyclodehydration of phenylamino anthraquinone with anhydrous $AlCl_3$-NaCl yields the key intermediate ceramidonine **7** in a 80% yield [9].

Scheme 2 presents the route for synthesizing the target compound **8a–f**. The commercially available bromodiphenylmethane was combined with triphenylphosphine to give phenyl phosphonium salt **6a**. Compound **8a** was obtained by a Wittig reaction of phenyl phosphonium salt **6a** with ceramidonine **7** in the presence of potassium *tert*-butoxide as a base in dry THF. Synthesis of the target compounds **8b–d** was started with the preparation of diaryl alcohols according to the patent procedure [10]. A Grignard reaction of aryl bromide with ethyl formate gave the alcohols **1b–d**, following treatment of alcohols **1b–d** with the 10 molar equiv of acetyl bromide at reflux for 3 h to give the corresponding bromides **5b–d**. The reaction of the resulting compounds **5b–d** with triphenylphosphine in toluene produced phosphonium salts **6b–d**. The target compounds **8b–d** were obtained by a Wittig reaction of phosphonium salts **6b–d** with ceramidonine **7** in the presence of potassium *tert*-butoxide as a base in dry THF. The target compound **8e** was prepared by a different synthetic pathway. 2-Fluoropyridine underwent a nucleophilic attack following the making of an activated methylene anion of 2-methylpyridine [11] by a dropwise addition of *n*-butyllithium to give dipyridin-2-ylmethane **2** in a 77% yield. Compound **2** was heated with *N*-bromosuccinimide in CCl_4 for 45 min to give the bromide **5e**, which was taken to the next step without further purification. The bromide was refluxed with triphenylphosphine in toluene to give the phosphonium salt **6e**, following a Wittig reaction of phosphonium salts **6e** with ceramidonine **7** to form the target compound **8e**. 3-Bromopyridine reacts with *n*-butyllithium in an exchange reaction to form the organolithium pyridine, following a nucleophilic attack with methyl nicotinate to give ketone **3** [12]. A Wolff–Kishner reduction of ketone **3** using potassium hydroxide and hydrazine hydrate gave dipyridin-3-ylmethane **4** in an excellent yield of 96% [13]. Compound **8f** was prepared according to the same phosphonium formation procedure and Wittig reaction described with regard to compound **8a**.

The absorption spectra and photoluminescence (PL) spectra of the synthesized compounds **8a–f** were recorded using a UV/–vis spectrometer and fluorescence spectrometer at a concentration of 1×10^{-5} M CH_2Cl_2 solution. The UV and PL data are shown in Table 1 and Fig. 2.

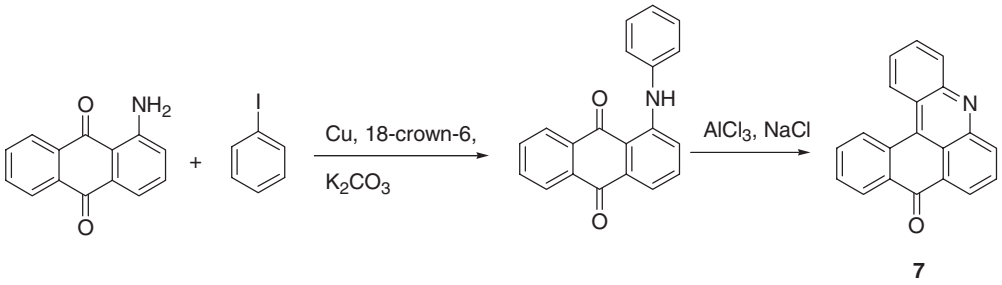
The UV spectra of all the recorded compounds showed maximum absorption in a range between 256 nm and 262 nm. All compounds **8a–f** showed an intense emission at a short range between 502 nm and 522 nm under the excitation of 365 nm. The PL λ maximum of compounds **8a–f** was similarly observed without the influence of an R_1 substituent of the compounds, but the emission intensity of the compounds showed a difference between the compounds at the same concentration of 1×10^{-5} M CH_2Cl_2 solution. Compound **8b** with the 4-biphenyl group as a substituent of R_1 showed the strongest emission maximum at 518 nm with a full width at the half maximum (FWHM) of 56 nm, and compounds **8d** with a naphthyl group and compound **8f** with a 3-pyridyl group as the substituent of R_1 showed a weak emissions maximum at 502 nm and 514 nm at a concentration of 1×10^{-5} M CH_2Cl_2 solution, respectively.

In summary, several new ceramidine derivatives were synthesized in 4–5 steps and UV/PL

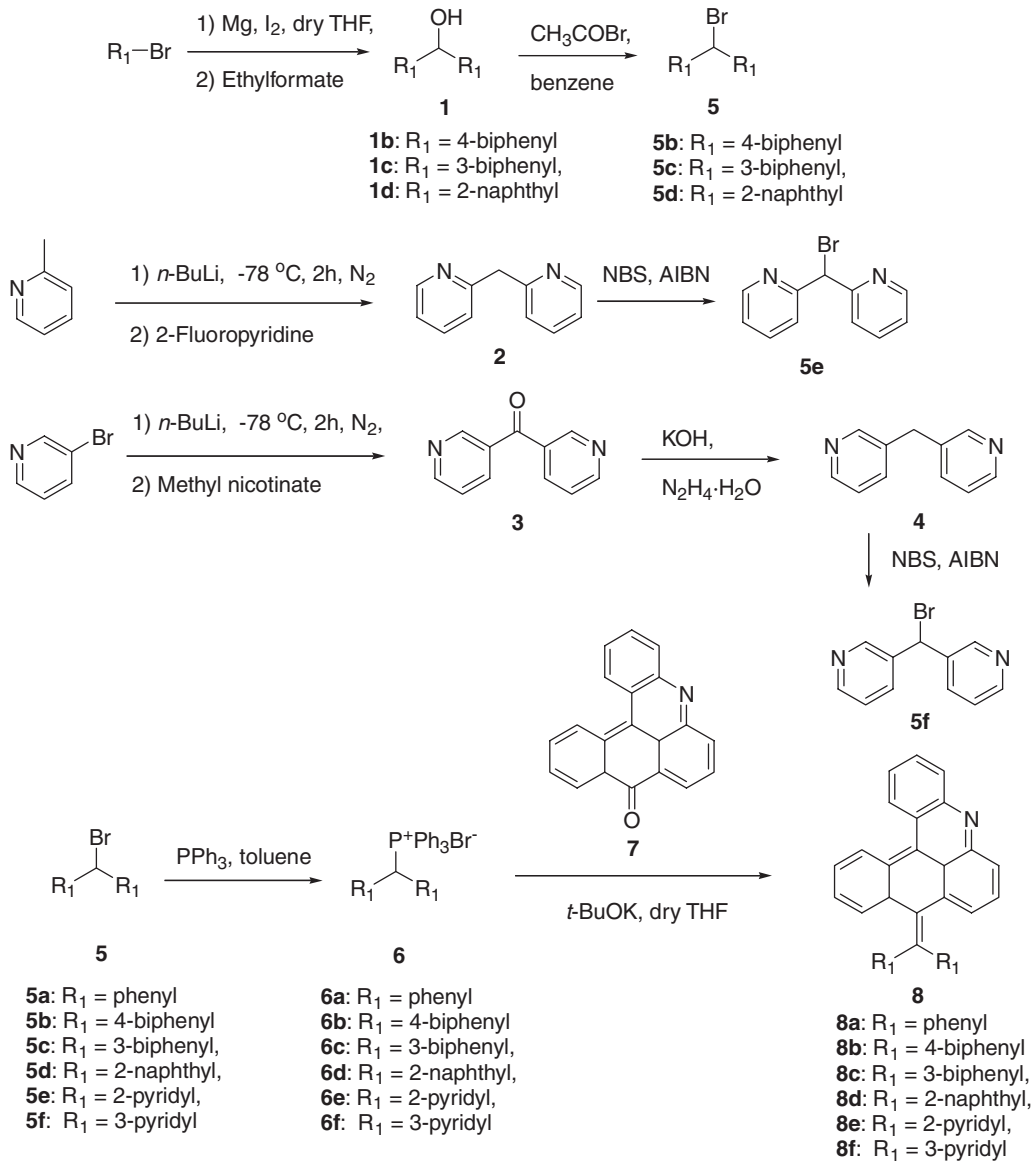
TABLE 1 The UV and PL Data of Compounds **8a–f**

	λ_{max} (nm)[a]		
Compound No.	UV	PL[b]	FWHM (nm)[c]
8a	260	522	75
8b	256	518	56
8c	258	514	41
8d	262	502	60
8e	257	513	50
8f	257	514	95

[a]Measured at a concentration of 1×10^{-5} M CH_2Cl_2 solution.
[b]PL spectra recorded by single beam excitation at UV λ_{max}.
[c]The full widths at half maximum value.



SCHEME 1 Synthesis of ceramidonine **7**.



SCHEME 2 Synthesis of target compounds **8a–f**.

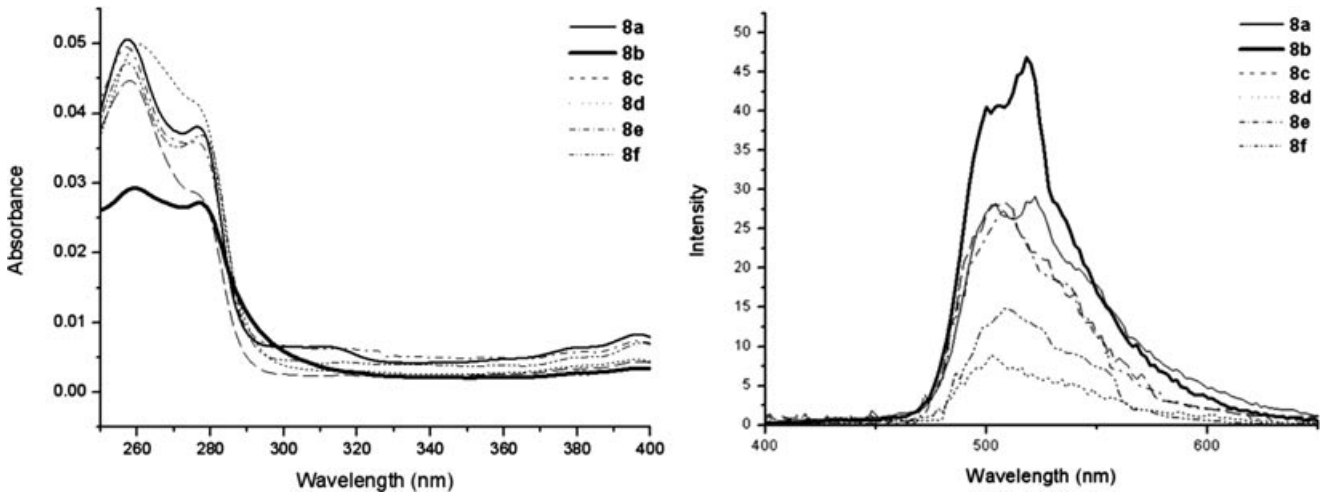


FIGURE 2 UV (left) and PL (right) spectra of compounds **8a–f** in a concentration of 1×10^{-5} M CH_2Cl_2 solution.

experiments showed them to have potential as green emitting materials for OLED or fluorescence dye. Further studies on the electroluminescence properties of the synthesized ceramidine derivatives **8a–f** are currently underway and will be presented elsewhere.

EXPERIMENTAL

General

The NMR spectra were recorded with a Bruker spectrometer operating at 300 MHz or 400 MHz for ^{1}H NMR and 75 MHz or 100 MHz for ^{13}C NMR. The multiplicities are abbreviated as s: singlet, d: doublet, t: triplet, m: multiplet, q: quartet, bs: broad singlet. The coupling constant *J* was recorded in Hertz (Hz) and it's subject to a little difference because the intact values measured by a spectrometer were used. The relative shift values of peak were recorded with a ppm unit using tetramethylsilane (TMS) as standard material. Melting points were determined on a SRS OPTIMELT. The FT-IR spectra were obtained on a Perkin Elmer 16E PC FT-IR spectrometer. UV spectra and PL spectra were recorded on a Perkin-Elmer Lambda25 UV/–vis spectrometer and Hitachi F-4500 fluorescence spectrometer, respectively. Thin layer chromatography (TLC) was performed using precoated plates (0.25 mm, Merck) of silica gel 60 F_{254} (230 ~ 400 mesh) for monitoring all reactions. Column chromatography separations were performed using silica gel (230 ~ 400 mesh, Merck). All the commercially available reagent chemicals were obtained from Aldrich, TCI, Wako Pure Chemical, Acros, and Dae-Jung Chemicals and generally used without further purification. All the reactions were performed in a nitrogen atmosphere.

Synthesis of Ceramidonine Derivatives **8a–f1**-*(Phenylamino)anthracene-9,10-dione*

1-aminoanthraquinone (29 g, 0.13 mol), iodobenzene (53 g, 0.26 mol), copper (12.4 g, 0.2 mol), 18-crown-6 (1.7 g, 0.007 mol), and potassium carbonate (27 g, 0.2 mol) were mixed in DMF (300 mL) and refluxed with N_2 for 24 h. After cooling, the reaction mixture was filtered to remove solids and the solvent was evaporated. The residue was dissolved in dichloromethane and washed with water, dried over $MgSO_4$, and concentrated in vacuo. The residue solid was washed with hot hexane and filtered to collect the solid to give the pure product as a purple solid. Yield: 38.1 g (98%). mp: 149 (mp: 147°C. lit. [14]).

Ceramidonine **7**

A mixture of $AlCl_3$ (83.4 g, 0.63 mol) and NaCl (20.3 g, 0.35 mol) was stirred at 110°C ~ 120°C for 10 min, then added to 1-(phenylamino)anthracene-9,10-dione (10.4 g, 0.04 mol) and stirred at 150°C ~ 160°C for 15 min. The reaction mixture was cooled to room temperature, and then an aqueous HCl solution (1:3, 1600 mL) was added and refluxed for 30 min. After cooling, the reaction mixture was filtered to remove solids and the filtrate was treated with a saturated a $NaHCO_3$ aqueous solution. Then the precipitate of product **7** was filtered, washed with water, and dried. Yield: 7.9 g (80%). mp: 210°C (mp: 202°C, lit. [8]).

Benzhydryltriphenylphosphonium Bromide **6a**

(Bromomethylene)dibenzene (47.5 g, 0.19 mmol) and triphenylphosphine (60.5 g, 0.23 mmol) were dissolved in toluene (100 mL), and the reaction mixture was refluxed with vigorous stirring for 12 h, during which time a white solid was precipitated from the solution. The reaction mixture was placed in the freezer at −10°C for 4 h and then filtered to collect the solid which was washed with hot ethyl acetate to give a pure product **6a** as a white solid. Yield: 95.8 g (99%). mp: 233°C (230°C, lit. [15]). IR (KBr) 3432, 3057, 2842, 1590, 1493, 1436, 1106, 756, 694 cm^{-1}. ^1H NMR (300 MHz, CD_3OD): δ (ppm) 7.10 (d, J = 17.71 Hz, 1H), 7.28–7.35 (m, 6H), 7.40 (d, J = 7.2 Hz, 4H), 7.52–7.72 (m, 12H), 7.83–7.85 (m, 3H); ^{13}C NMR (75 MHz, CD_3OD): δ (ppm) 128.6, 128.8, 128.9, 129.0, 129.1, 129.9, 130.1, 130.5, 130.6, 131.6, 131.8, 132.5, 133.2, 133.2, 134.8, 134.9, 135.1, 135.1.

9-(Diphenylmethylene) - 9H - naphtho[3,2,1 - kl] acridine **8a**

Compound **7** (15 g, 53 mmol) and **6a** (32.6 g, 64 mmol) were dissolved in dry THF (150 mL) and potassium *tert*-butoxide (7.2 g, 64 mmol, dissolved in methanol) was added dropwise. The reaction mixture was refluxed for 12 h, and then the solvent was evaporated. The residue was dissolved in dichloromethane and washed with water and brine. The combined organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography using a mixture solvent of hexane and ethyl acetate to give the title compound **8a** as an orange solid. Yield: 3.2 g (12%). mp: 218°C. IR (KBr): 3437, 1651, 1307, 767, 704 cm^{-1}. Elemental analyses ($C_{33}H_{21}N$) calcd: C, 91.85; H, 4.91; N, 3.25. Found: C, 91.35; H, 5.09; N, 3.55. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.08–7.12 (m, 2H), 7.18 (d, J = 4.1 Hz, 8H), 7.34 (t, J = 10.8 Hz, 2H), 7.40–7.53 (m, 6H), 8.07 (d, J = 8.6 Hz, 1H), 8.18 (d, J = 7.7 Hz, 1H), 8.32 (d, J = 6.7 Hz, 1H), 8.40 (d, J = 8.9 Hz, 1H), 8.45 (d, J = 7.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 51.1, 121.2, 123.0, 125.7, 126.4, 127.0, 127.6, 128.4, 128.5, 129.6, 129.7, 130.0, 130.5, 131.4, 132.5, 133.2, 133.5, 135.4, 143.6, 145.1, 149.8, 151.2, 182.9.

Dibiphenyl-4-ylmethanol **1b**

To a stirred suspension of magnesium (2.3 g, 94 mmol) in dry THF (150 mL) was added a small portion of iodine, and the resulting mixture was refluxed with N_2. To this refluxing solution, 4-bromobiphenyl (20 g, 86 mmol, dissolved in dry THF) was added and the heating was continued for 2 h. The oil bath was removed, and ethyl formate (3.2 g, 43 mmol) was added dropwise over 5 min to the hot reaction mixture and stirred for 2 h at room temperature. The reaction mixture was poured into a saturated NH_4Cl aqueous solution. After 30 min, the biphasic mixture was extracted with ethyl acetate. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography using the mixture solvent of hexane and ethyl acetate to give a pure product **1b**. Yield: 12.3 g (85%). mp: 150°C. IR (KBr): 3425, 1487, 763, 742, 694 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 2.84 (s, 1H), 5.95 (s, 1H), 7.42–7.57 (m, 10H), 7.66–7.69 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 75.9, 127.1, 127.2, 127.3, 127.4, 128.9, 140.6, 140.8, 143.0.

4,4′-(Bromomethylene)dibiphenyl **5b**

Acetyl bromide (40.2 g, 330 mmol) was added to a solution of compound **1b** (11 g, 33 mmol) in dry benzene (100 mL) and the resulting mixture refluxed for 4 h, then cooled to room temperature. The reaction mixture was removed by using a rotary evaporator and the resulting solid was washed with hexane to give a pure product **5b** as a gray solid. Yield: 11.8 g (90%). mp: 145°C. IR (KBr): 3429, 1484, 764, 740, 694 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.45 (s, 1H), 7.40–7.44 (m, 2H), 7.51 (t, J = 5.6 Hz, 4H), 7.64–7.67 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 55.2, 127.2, 127.4, 127.7, 128.9, 129.0, 140.0, 140.4, 141.1.

(Dibiphenyl-4-ylmethyl)triphenylphosphonium Bromide **6b**

Compound **6b** was synthesized as with compound **6a**. Yield: 18.7 g (88%). mp: 208°C. IR (KBr): 3428, 3053, 2814, 1620, 1486, 1437, 1106, 757, 722, 692 cm^{-1}. ^1H NMR (400 MHz, CD_3OD): δ (ppm) 7.00 (d, J = 17.7 Hz, 1H), 7.33 (d, J = 6.5 Hz, 2H), 7.56 (d, J = 5.8 Hz, 8H), 7.67–7.72 (m, 12H), 7.86 – 7.88 (m, 3H). ^{13}C NMR (100 MHz, CD_3OD): δ (ppm) 117.7, 118.5, 126.6, 127.3, 127.7, 127.8, 128.7, 129.9, 130.0, 131.1, 131.0, 132.0, 134.8, 134.8, 135.1, 139.3, 141.9.

9-(Dibiphenyl-4-ylmethylene)-9H-naphtho[3,2, 1-kl]acridine **8b**

Compound **8b** was synthesized as with compound **8a**. Yield: 5.85 g (28%). mp: 262°C. IR (KBr): 3436, 1655, 1307, 1072, 764, 699 cm^{-1}. Elemental analyses ($C_{45}H_{29}N$) calcd: C, 92.59; H, 5.01; N, 2.40. Found: C, 92.19; H, 5.23; N, 2.71. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.17–7.21 (m, 2H), 7.27–7.30 (m, 8H),

7.43–7.53 (m, 11H), 7.59–7.64 (m, 3H), 8.17 (d, J = 6.5 Hz, 1H), 8.34 (d, J = 6.0 Hz, 1H), 8.42 (d, J = 5.6 Hz, 1H), 8.53–8.58 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 50.4, 121.3, 123.1, 125.8, 127.0, 127.2, 127.7, 128.6, 128.8, 129.6, 129.8, 130.0, 130.2, 130.6, 131.6, 132.6, 133.2, 133.6, 135.5, 139.3, 140.8, 142.7, 150.0, 151.1, 183.0.

Dibiphenyl-3-ylmethanol **1c**

Compound **1c** was synthesized as with compound **1b**. Pale yellow oil. Yield: 11.3 g (78%). IR (KBr): 3408, 1598, 1479, 1453, 1423, 1168, 1032, 898, 758, 699 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 2.58 (s, 1H), 5.99 (s, 1H), 7.39–7.43 (m, 2H), 7.45–7.51 (m, 8H), 7.55–7.58 (m, 2H), 7.63–7.66 (m, 4H), 7.73 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 76.4, 125.4, 125.6, 126.5, 127.3, 127.4, 128.8, 129.1, 141.1, 141.6, 141.3.

(Dibiphenyl-3-ylmethyl)triphenylphosphonium Bromide **6c**

To a solution of compound **1c** (11 g, 33 mmol) in dry benzene (100 mL) was added acetyl bromide (40.2 g, 330 mmol) and the resulting mixture was refluxed for 4 h, then cooled to room temperature. The solvent and excess acetyl bromide were removed by using a rotary evaporator. The resulting crude mixture and triphenylphosphine (11.3 g, 43 mmol) were dissolved in toluene (30 mL), and the reaction mixture was refluxed with vigorous stirring for 12 h, during which time a white solid was precipitated from the solution. The reaction mixture was placed in the freezer at −10°C for 4 h and then filtered to collect the solid, which was washed with hot ethyl acetate to give a pure product **6c** as a white solid. Yield: 11.4 g (52%). mp: 238°C. IR (KBr): 3430, 3054, 2801, 1597, 1482, 1436, 1105, 755, 697 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.30–7.32 (m, 12H), 7.50–7.85 (m, 22H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 45.3, 45.8, 118.2, 119.3, 126.8, 127.2, 127.6, 128.8, 129.4, 129.5, 129.6, 129.9, 130.1, 130.2, 130.3, 133.6, 133.7, 134.8, 135.2, 135.3, 139.7, 141.4.

9-(Dibiphenyl-3-ylmethylene)-9H-naphtho[3,2,1-kl]acridine **8c**

Compound **8c** was synthesized as with compound **8a**. Yield: 1.2 g (11%). mp: 130°C. IR (KBr): 3435, 1655, 1597, 1522, 1306, 760, 700 cm^{-1}. Elemental analyses ($C_{45}H_{29}N$) calcd: C, 92.59; H, 5.01; N, 2.40. Found: C, 92.00; H, 5.45; N, 2.99. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.31–7.70 (m, 21H), 7.76–7.81 (m, 3H), 8.32 (d, J = 8.6 Hz, 1H), 8.55 (d, J = 9.1 Hz, 2H), 8.68 (d, J = 7.3 Hz, 1H), 8.76 (d, J = 8.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 51.2, 121.3, 123.2, 125.3, 125.8, 127.1, 127.2, 127.6, 128.6, 128.7, 128.8, 129.6, 129.8, 130.1, 130.6, 131.6, 132.5, 133.3, 133.6, 135.6, 141.2, 141.3, 144.0, 145.3, 150.0, 151.1, 183.1.

Dinaphthalen-2-ylmethanol **5d**

Compound **5d** was synthesized as with compound **6b**. Yield: 2.3 g (79%). mp: 113°C. IR (KBr): 3325, 1599, 1507, 1362, 1272, 1162, 1119, 1028, 859, 824, 789, 756 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 2.61 (s, 1H), 6.16 (s, 1H), 7.48–7.53 (m, 6H), 7.81–7.86 (m, 6H), 7.96 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 76.5, 124.9, 125.3, 126.1, 126.3, 127.7, 128.1, 128.4, 133.0, 133.3, 141.0.

2,2′-(Bromomethylene)dinaphthalene **1d**

Compound **1d** was synthesized as with compound **1b**. Yield: 2.6 g (98%). mp: 168°C. IR (KBr): 3429, 1507, 865, 778, 754, 688 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.68 (s, 1H), 7.42 (s, 1H), 7.54 (s, 3H), 7.69 (d, J = 8.2 Hz, 2H), 7.87–7.95 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 56.3, 126.58, 126.7, 127.4, 127.7, 128.3, 128.4, 128.6, 133.0, 133.0, 138.2.

(Dinaphthalen - 2 - ylmethyl)triphenylphosphonium Bromide **6d**

Compound **6d** was synthesized as with compound **6a**. Yield: 2.8 g (78%). mp: 240°C. IR (KBr): 3433, 3055, 2754, 1504, 1436, 1104, 737, 690 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.27–7.34 (m, 4H), 7.47 (s, 8H), 7.55–7.62 (m, 7H), 7.73–7.80 (m, 8H), 7.88 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 126.5, 126.9, 127.5, 128.2, 128.3, 128.3, 128.8, 129.9, 130.1, 130.6, 130.7, 130.8, 130.9, 132.7, 132.8, 135.0, 135.1, 135.2.

9-(Dinaphthalen-2-ylmethylene)-9H-naphtho [3,2,1-kl]acridine **8d**

Compound **8d** was synthesized as with compound **8a.** Yield: 123 mg (43%). mp: 190°C. IR (KBr): 3436, 1652, 1522, 1306, 769, 703 cm^{-1}. Elemental analyses ($C_{41}H_{25}N$) calcd: C, 92.63; H, 4.74; N, 2.63. Found: C, 92.21; H, 4.91; N, 2.22. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.44–7.45 (m, 4H), 7.56–7.61 (m, 3H), 7.66–7.85 (m, 13H), 8.28 (d, J = 8.3 Hz, 1H), 8.52 (d, J = 7.5 Hz, 1H), 8.57 (d, J = 7.5 Hz, 1H), 8.67 (d, J = 7.2 Hz, 1H), 8.73 (d, J = 8.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 51.3, 121.3, 123.1, 125.7, 125.8, 126.0, 127.2, 127.6, 127.6, 127.9, 128.1, 128.2, 128.5, 128.7, 129.6, 129.8, 130.4, 130.6, 131.6, 132.3,

132.6, 133.3, 133.5, 133.6, 135.6, 140.8, 141.2, 145.3, 150.0, 150.8, 183.1.

Dipyridin-2-ylmethane **2**

To a dry THF (40 mL) of 2-methylpyridine (3.72 g, 20 mmol) was added dropwise *n*-butyllithium (25 mL, 40 mmol, 1.6 M solution in THF) at −78°C in an N_2 atmosphere. After being stirred for 45 min and then warmed up to −20°C, 2-fluoropyridine (1.94 g, 20 mmol) was added dropwise and the reaction mixture was refluxed for 25 min, and ice (40 g) was added. The aqueous layer was extracted with dichloromethane, and the combined organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by distillation to give a pure product **2** as a slightly yellow oil. Yield: 2.6 g (77%). IR (KBr): 3432, 1589, 1473, 1433, 752 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 4.25 (s, 2H), 7.01–7.05 (m, 2H), 7.17 (d, $J = 7.8$ Hz, 2H), 7.50 (td, $J = 7.7$ Hz and 1.9 Hz, 2H), 8.45–8.47 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 47.3, 121.5, 123.6, 136.6, 149.4, 159.4.

(Dipyridin-2-ylmethyl)triphenylphosphonium Bromide **6e**

A mixture of compound **2** (2 g, 11.8 mmol), *N*-bromosuccinimide (2.3 g, 12.9 mmol), and a catalytic amount of 2,2′-azobis(isobutyronitrile) (58.0 mg, 0.36 mmol) in CCl_4 (40 mL) was refluxed during 10 h with N_2. The mixture was allowed to cool, and the precipitate was removed by suction filtration and washed with dichloromethane. The combined organic layer was washed with water, dried over $MgSO_4$ and concentrated in vacuo. The resulting crude bromide **5e** and triphenylphosphine (4.02 g, 15.34 mmol) were dissolved in toluene (4 mL), and the reaction mixture was refluxed with vigorous stirring for 12 h, during which time a brown solid was precipitated from the solution. The reaction mixture was placed in the freezer at −10°C for 4 h and then filtered to collect the solid, which was washed with hexane to give a product **6e** as a brown solid. Yield: 4.65 g (77%). mp: 230°C. IR (KBr): 3431, 3056, 2722, 1585, 1435, 1106, 693 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.26 (s, 2H), 6.64 (s, 6H), 6.74 (d, $J = 5.6$ Hz, 5H), 6.93 (d, $J = 5.6$ Hz, 2H), 7.03–7.08 (m, 6H), 7.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 53.1, 53.6, 119.7, 120.6, 123.0, 126.4, 126.5, 129.1, 129.2, 133.7, 135.0, 135.1, 137.5, 148.5, 153.8.

9-(Dipyridin-2-ylmethylene)-9H-naphtho[3,2,1-kl]acridine **8e**

Compound **8e** was synthesized as with compound **8a**. Yield: 35 mg (15%). mp: 270°C. IR (KBr): 3434, 1652, 1587, 1307, 769 cm^{-1}. Elemental analyses ($C_{31}H_{19}N_3$) calcd: C, 85.89; H, 4.42; N, 9.69. Found: C, 85.45; H, 4.19; N, 9.99. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.16 (d, $J = 5.0$ Hz, 2H), 7.47 (d, $J = 7.4$ Hz, 2H), 7.62–7.70 (m, 7H), 7.89 (d, $J = 7.2$ Hz, 1H), 8.25 (d, $J = 8.4$ Hz, 1H), 8.45–8.52 (m, 2H), 8.63–8.67 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 55.7, 121.2, 121.6, 123.0, 124.5, 125.7, 127.2, 127.5, 128.6, 129.5, 129.7, 129.9, 130.3, 130.5, 131.5, 132.5, 133.2, 133.5, 135.5, 136.5, 145.3, 148.5, 149.6, 149.9, 162.0, 183.0.

Dipyridin-3-ylmethanone **3**

n-Butyllithium (14.2 mL, 23 mmol, 1.6 M solution in THF) was added dropwise to a solution of 3-bromopyridine (3 g, 19 mmol) in dry diethylether (40 mL) at −78°C and stirred for 15 min. A solution of methyl nicotinate (2.6 g, 19 mmol) in dry diethylether (10 mL) was added dropwise to the reaction mixture at −78°C and stirred for another 2 h at the same temperature. Then the reaction was quenched with saturated an NH_4Cl aqueous solution and extracted with ethyl acetate. The combined organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography using a mixed solvent of hexane and ethyl acetate to give a pure product **3** as a yellow solid. Yield: 1.1 g (32%). mp: 103°C (mp: 106°C, lit. [16]).

Dipyridin-3-ylmethane **4**

Compound **3** (0.89 g, 4.83 mmol) was suspended in ethylene glycol (10 mL). Potassium hydroxide (0.57 g, 9.66 mmol) was added and the reaction was stirred at room temperature for 1 h. Then hydrazine hydrate (0.56 g, 11.12 mmol) was added and the reaction mixture was heated to 185°C. After 1 hr 45 min, the reaction was cooled to room temperature, diluted with water, and extracted with dichloromethane. The combined organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo to give a pure product **4** as a brown oil. Yield: 0.79 g (96%). IR (KBr): 3215, 1570, 1476, 1422, 1028, 779, 717 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 3.88 (s, 2H), 7.10–7.14 (m, 2H), 7.35–7.38 (m, 2H), 8.36–8.39 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 36.1, 123.5, 135.2, 136.2, 147.9, 149.9.

(Dipyridin-3-ylmethyl)triphenylphosphonium Bromide **6f**

Compound **6f** was prepared according to the procedure described with regard to compound **6e**. Yield: 0.23 g (11%). mp: 210°C. IR (KBr): 3431, 3038, 1630, 1437, 1108, 695cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.17–7.22 (m, 2H), 7.44–7.49 (m, 1H), 7.64–7.67 (m, 2H), 7.72–7.79 (m, 10H) 7.88–7.99 (m, 3H) 8.59–8.60 (m, 3H), 8.74–8.77 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 116.1, 117.3, 124.6, 124.9, 130.3, 130.5, 134.6, 134.8, 135.7, 138.8, 149.6, 150.2.

9-(Dipyridin-3-ylmethylene)-9H-naphtho[3,2,1-kl]acridine **8f**

Compound **8f** was synthesized as with compound **8a**. Yield: 15 mg (10%). mp: 180°C. IR (KBr): 3437, 1653, 1415, 1308, 771, 715 cm^{-1}. Elemental analyses ($C_{31}H_{19}N_3$) calcd: C, 85.89; H, 4.42; N, 9.69. Found: C, 85.98; H, 4.43; N, 9.68. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.29 (s, 3H), 7.42–7.81 (m, 7H), 8.24 (d, J = 8.3 Hz, 1H), 8.52–8.86 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 46.7, 121.3, 123.4, 125.8, 127.8, 127.9, 128.8, 129.2, 129.6, 130.0, 130.7, 131.3, 132.8, 133.5, 133.7, 133.8, 135.4, 136.2, 136.7, 138.0, 144.7, 148.1, 148.5, 150.1, 151.0.

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