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Fluorescent Tricyclic β-Azavinamidine–BF_2 Complexes

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ABSTRACT

*Boron trifluoride reacted with dipyrid-2-ylamine **6**, its N-methyl and 6,6'-dimethyl derivatives **8** and **10**, and 3,3',5,5'-tetraphenyl-6-azapyrromethene **13** to give fluorescent β-azavinamidine (1,3,5-triazapenta-1,3-diene) dyes: 10-azapyridomethene–BF_2 complex **5** (λ_f 422 nm, λ_{las} 426 nm), its quaternary 10-methyl tetrafluoroborate and 4,6-dimethyl derivatives **9** (λ_f 362 nm) and **11** (λ_f 416 nm), and 1,3,5,7-tetraphenyl-8-azapyrromethene–BF_2 complex **17** (λ_f 696 nm). Treating 3,3',4,4'-tetraphenyl-5,5',6-trimethylpyrromethene (prepared in situ from ethyl 3,4-diphenyl-5-methylpyrrole-2-carboxylate in a reaction with acetyl chloride) with boron trifluoride gave 1,2,6,7-tetraphenyl-3,5,8-trimethylpyrromethene–BF_2 complex **21**. Absorption for the vinamidine chromophore differed from that for the β-azavinamidine chromophore by a hypsochromic shift of 86 nm in a comparison of pyridomethene–BF_2 complex **3** with its 10-aza derivative **5** and by a bathochromic shift of 105 nm in a comparison of the pyrromethene–BF_2 complex **20** with the 8-azapyrromethene–BF_2 complex **17**.*

INTRODUCTION

By color and fluorescence, boron chelates generally resembled the open ligands [1]. When extended by conjugation the 1,4-diazabutadiene and vinamidine (1,5-diazapenta-1,3-diene), ligands were found in 5,5,5-, 6,5,6-, 6,6,6-, and 5,6,5-tricyclic BF_2 complexes. Typical examples included tetramethylbiimidazol-2-yl–BF_2 complex **1** (λ_{max} 334 nm) [2], dipyrid-2-yl–BF_2 complex hexafluorophosphate **2** (λ_{max} 422 nm) [3], and pyridomethene–BF_2 complex **3** (λ_{max} 468 nm) [4]. Fluorescence was strong in dye **1** (λ_f 377 nm, Φ 0.93) and in other biimidazol-2-yl–BF_2 complexes [2] and was not detected in dyes **2** and **3**. The truly outstanding 5,6,5-tricyclic pyrromethene–BF_2 complexes (P–BF_2) were solid dyes ranging from orange to deep blue in color (λ_{max} 493–580 nm); many showed strong fluorescence (λ_f 519–620 nm, $\Phi > 0.7$) and laser activity [5,6]. The photostable P–BF_2 laser dye 1,3,5,7,8-pentamethyl-2,6-diethylpyrromethene–BF_2 complex **4** (λ_{max} 517 nm, λ_f 546 nm, λ_{laser} 570 nm) [5,6] became the new undisputed champion in laser activity by doubling the power efficiency obtained from Rhodamine–6G (R–6G), the laser dye that was unsurpassed for over a quarter of a century [7–9]. Other P–BF_2 dyes became fluorescent probes for medical and biological research [10] and were highly successful photodynamic therapeutic agents for cancer [11,12]. Similar BF_2 complexes of 1-aza-4-oxabutadiene and 1,5-dioxapenta-1,3-diene ligands were cited for fluorescence and laser activity [6].

In a continuing search for fluorescent heterocycle–BF_2 complex dyes, λ_f 300–800 nm ($\Phi > 0.8$), the structures selected for this investigation were limited to 6,6,6- and 5,6,5-tricyclic β-azavinamidine (1,3,5-triazapenta-1,3-diene) derivatives and included a re-examination of a "boratriazinium salt" (λ_{las} 420 nm) that was presented with a 10-azapyridomethene–BF_2 complex structure **5** without the support of a synthesis procedure and characterization data [13].

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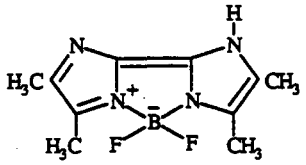

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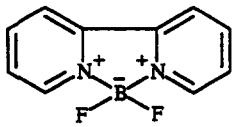

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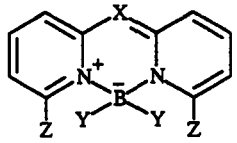
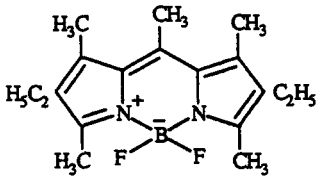


3 X = CH, Y = F, Z = H

5 X = N, Y = F, Z = H

7 X = N, Y = C_2H_5, Z = H

11 X = N, Y = F, Z = CH_3



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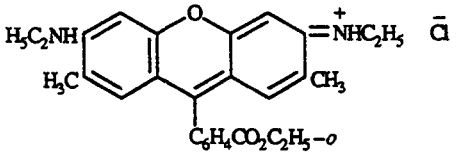


R–6G

RESULTS AND DISCUSSION

A condensation between dipyrid-2-ylamine **6** and boron trifluoride to give the complex **5** was patterned after a similar preparation of 10-azapyridomethene–$B(C_2H_5)_2$ complex **7** from the amine **6** and triethylboron [14]. Although the presence of an added tertiary amine was beneficial in the chelation of a pyrromethene salt by treatment with boron trifluoride [5,6], its presence in the treatment of the amine **6** with boron trifluoride led to an intractable mixture. An examination of complex **5** (λ_{max} 382 nm, λ_f 422 nm, λ_{las} 426 nm) confirmed the earlier report for the "boratriazinium salt" [13]. The structure of the BF_2 complex **5** was confirmed by an X-ray crystallographic analysis and is shown by the Ortep plot in Figure 1 [15]. A hypsochromic shift (86 nm) from λ_{max} 468 nm for pyridomethene–BF_2 complex **3** to λ_{max} 382 nm for its 10-aza derivative **5** was attributed to the replacement of a vinamidine with a β-azavinamidine chromophore.

After it was obtained from the amine **6** by treatment with methyl iodide in the presence of *n*-butyllithium methyldipyrid-2-ylamine, **8** was converted to the tetrafluoroborate salt **9** (λ_{max} 325 nm, λ_f 362 nm) of quaternary 10-methyl-10-azapyridomethene–BF_2 complex. Although methylation introduced a hypsochromic shift of 60 nm in both absorption and fluorescence, the protonated dye in its salts **5** · $HClO_4$ and **5** · HI showed no shift in absorption and a smaller hypsochromic shift of 25 nm in fluorescence. The laser activity characteristic of the lumophor in complex **5** was not found in any of its three salts.

A condensation between 2-amino-6-methylpyridine and 2-chloro-6-methylpyridine gave 6,6′-dimethyldipyrid-2-ylamine **10**, and the latter was converted by treatment with boron trifluoride to 4,6-dimethyl-10-azapyridomethene–BF_2 complex **11** (λ_{max} 396 nm, λ_f 416 nm). The undetected laser activity in complex **11** was apparently the result of alkyl substitution. This result was in contrast with laser activity enhancement by alkyl substitution in pyrromethenes [5,6].

By known procedures, 5,5′-diphenyl- and 3,3′,5,5′-tetraphenyl-6-aza-pyrromethenes **12** (λ_{max} 595 nm) [16–18] and **13** [17] were obtained from reactions between β-benzoylpropionitrile **14** and hydroxylamine in one instance [18] and between γ-nitro-β-phenylbutyrophenone **15** and ammonium formate in the other [17]. Although pyrro-

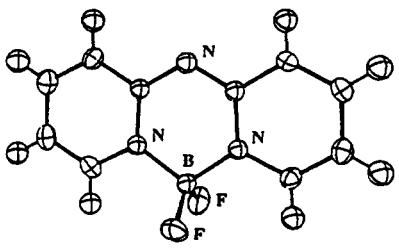
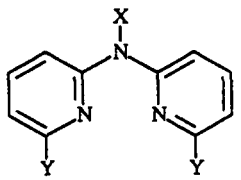


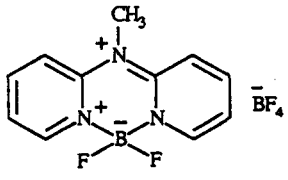
FIGURE 1 Ortep plot **5**.



6 X = Y = H

8 X = CH_3, Y = H

10 X = H, Y = CH_3



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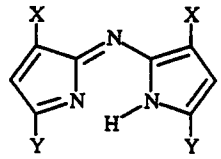


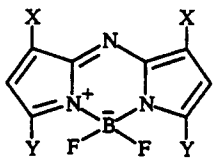
12 X = H, Y = C_6H_5

13 X = Y = C_6H_5

$C_6H_5COCH_2X$

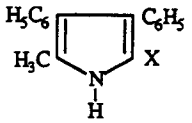
14 X = CH_2CN

15 X = $CHCH_2NO_2$ (C_6H_5)



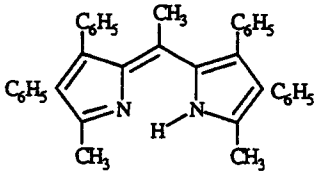
16 X = H, Y = C_6H_5

17 X = Y = C_6H_5



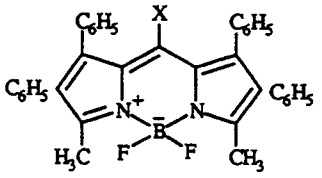
18 X = $CO_2C_2H_5$

22 X = H



•HCl

19



20 X = H

21 X = CH_3

methene–BF_2 complexes were efficiently produced (40 to 50%) from aryl derivatives of pyrromethene [5,6], similar treatment with boron trifluoride converted 5,5'-diphenyl-6-azapyrromethene **12** to an intractable mixture in which 3,5-diphenyl-8-azapyrromethene–BF_2 complex **16** was not detected and converted 3,3',5,5'-tetraphenyl-6-azapyrromethene **13** to 1,3,5,7-tetraphenyl-8-azapyrromethene–BF_2 complex **17** (λ_{max} 653 nm, λ_f 696 nm) in low yield.

Boron trifluoride converted 3,3',4,4'-tetraphenyl-5,5',6-trimethylpyrromethene hydrochloride **19** (prepared *in situ* from ethyl 3,4-diphenyl-5-methylpyrrole-2-carboxylate **18** in a reaction with acetyl chloride) to 1,2,6,7-tetraphenyl-3,5,8-trimethylpyrromethene–BF_2 complex **21** (λ_{max} 542 nm, λ_f 581 nm). Similar properties were reported for 1,2,6,7-tetraphenyl-3,5-dimethylpyrromethene–BF_2 complex dye **20** (λ_{max} 552 nm, λ_f 590 nm) [5]. A bathochromic shift of 105 nm in absorption and 110 nm in fluorescence described the replacement of a vinamidine chromophore in dyes **20** and **21** with a β-azavinamidine chromophore in dye **17**.

EXPERIMENTAL

Spectral data were obtained from the following instruments: Sargent-Welch 3-200 IR, Varian EM 360A, Varian Gemini-300, Varian Unity 400 NMR, Hewlett-Packard 5985 (70 eV) GC-MS, Cary 17 UV, Perkin-Elmer LS-5B Luminescence Spectrometer, Perkin-Elmer 1600 FT-IR, and Perkin-Elmer Lambda 6 (UV/VIS) Spectrometer. Elemental analyses were obtained from Galbraith Laboratories, Inc., Knoxville, TN, and Midwest Micro Lab, Indianapolis, IN. Melting points were obtained from a Laboratory Devices Mel-Temp II and were uncorrected. Except where noted otherwise, ^1H NMR spectra were run in $CDCl_3$ with $(CH_3)_4Si$ as an internal standard and ^{13}C NMR spectra were run in $CDCl_3$.

10-Azapyridomethene-BF_2 Complex **5**

Boron trifluoride etherate (3.55 g, 25 mmol) was slowly added at room temperature to a stirred solution of dipyrid-2-ylamine **6** (4.25 g, 25 mmol). The reaction mixture was heated at 80°C for 3 hours, cooled to room temperature, diluted with chloroform (100 mL), washed with water (50 mL), dried over magnesium sulfate, and concentrated to give a yellow residue. Recrystallization from a mixture of dichloromethane and hexane gave the complex **5** as a yellow crystalline solid (2.16 g, 40%) mp 142–145°C. ^1H NMR: δ 8.01 (s, 2H), 7.67 (t, 2H), 7.14 (d, 2H), 6.85 (t, 2H). ^{13}C NMR: δ 153.16, 140.02, 136.20, 122.27, 113.85. EI-MS, (*m/z*) (%): 219 (87, M), 218 (100), 217 (23), 170 (22). Anal. calcd for $C_{10}H_8N_3BF_2$: C, 54.79; H, 3.65; N, 19.18; F, 17.35. Found: C, 54.59; H, 3.71; N, 18.96; F, 17.58. UV absorption (ethanol): λ_{max} 382 nm, log ε 4.47. Fluorescence (ethanol): λ_{max} 422 nm, Φ 0.81 [excitation at 360 nm with LD 423 (1,2,3,8-tetrahydro-1,2,3,3,5-pentamethyl-7*H*-pyrrolo [3,2,*g*] quinolin-7-one) [19] as a standard]. Laser activity (methanol): λ_{max} 426 nm with output power efficiency at 40% relative to the output from stilbene 420 [20].

Methyldipyrid-2-ylamine **8**

A solution of *n*-butyllithium (0.42 g, 6.5 mmol) in hexane (2.6 mL) was added under nitrogen to a solution of di-2-pyridylamine **6** (1.0 g, 6 mmol) in dry tetrahydrofuran (100 mL) cooled to −78°C (Dry Ice, acetone). Stirring was continued as the temperature rose to room temperature. After 10 minutes, iodomethane (0.93 g, 6.4 mmol) was added. The reaction mixture was stirred at room temperature for 30 minutes and heated at 80–90°C for 20 minutes. The hot solution was filtered, concentrated, and combined with hydrochloric acid (5%, 100 mL). The solution was treated with ammonium hydroxide, extracted with dichloromethane (3 × 50 mL), dried over potassium carbonate, and concentrated to a brown oil. Chromatographic separation (acetone) gave the amine **8** as a light yellow oil (0.8 g, 75%). ^{1}H NMR: δ 8.3 (d, 2H), 7.5 (t, 2H), 7.16 (d, 2H), 6.85 (t, 2H), 3.63 (s, 3H). ^{13}C NMR: δ 157.7, 148.1, 137.1, 116.9, 114.3, 36.0. Anal. calcd for $C_{11}H_{11}N_3$: C, 71.34; H, 5.99; N, 22.69. Found: C, 71.28; H, 6.06; N, 22.43.

10-Methyl-10-azapyridomethene-BF_2 Complex Tetrafluoroborate **9**

Boron trifluoride etherate (1.1. mL, 9 mmol) was added to a stirred solution of methyldi-2-pyridylamine **8** (0.76 g, 4 mmol) in 1,2-dichloroethane (100 mL). The solution was heated at 80°C for 1 hour. The reaction mixture was cooled to room temperature and filtered to afford 0.98 g of a brown solid. The filtrate was concentrated and the residue was slurried in ether and filtered to give an additional 0.21 g of a brown solid. The combined solids were recrystallized from ethanol (50 mL, 95%) to give the salt **9** as a beige crystalline solid (0.67 g, 50%), mp 206–210°C. ^{1}H NMR (DMSO-d_6): δ 8.76 (s, 2H), 8.60 (t, 2H), 8.05 (d, 2H), 7.77 (t, 2H), 3.88 (s, 3H). ^{13}C NMR (DMSO-d_6): δ 148.7, 146.6, 138.5, 120.8, 115.7, 36.7. EI-MS (*m/z*) (%): 184 (11), 169 (6), 107 (28), 97 (25), 83 (33), 69 (57), 43 (100). Anal. calcd for $C_{11}H_{11}N_3B_2F_6$: C, 41.18; H, 3.46; N, 13.10. Found: C, 41.23; H, 3.40; N, 12.99. UV absorption (ethanol): λ_{max} 325 nm, log ϵ 4.22. Fluorescence (ethanol): λ_{max} 362 nm, Φ 0.36 (excitation at 360 nm with LD 423 [19] as a standard). No lasing activity was detected.

Di-6-methylpyrid-2-ylamine **10**

A mixture of 2-chloro-6-methylpyridine (19 g, 0.15 mol), 2-amino-6-methylpyridine (15 g, 0.14 mol), and zinc chloride (20 g, 0.15 mol) was heated under nitrogen (200°C, 10 hours). After cooling, the dark solution solidified and was treated with chloroform (200 mL) and then with water (200 mL) to give a yellow solid. The isolated solid was treated with aqueous sodium hydroxide (10%, 150 mL), heated at 100°C for 5 hours, and extracted with ether (3 × 100 mL). The solvent was removed by evaporation to give the amine **10** as a pale yellow amorphous solid (4.07 g, 22.4%), mp 89–91°C. ^{1}H NMR: δ 7.48 (s, 1H), 7.47 (t, 1H), 7.35 (d, 1H), 6.68 (d, 1H), 2.46 (s, 3H). ^{13}C NMR: δ 156.62, 153.46, 137.89, 115.41, 108.25, 24.23. EI-MS (*m/z*) (%): 199 (88, M^+), 198 (100). Anal. calcd for $C_{12}H_{13}N_3$: C, 72.36; H, 6.53; N, 21.11. Found: C, 72.38; H, 6.48; N, 21.23.

4,6-Dimethyl-10-azapyridomethene-BF_2 Complex **11**

Boron trifluoride etherate (8.9 g, 0.063 mol) was slowly added at room temperature to a stirred solution of the amine **10** (5.0 g, 0.025 mol) in toluene (50 mL). The reaction mixture was heated at 80°C for 3 hours, cooled to room temperature, diluted with chloroform (100 mL), washed with water (50 mL), dried over magnesium sulfate, and concentrated to give a yellow solid. Chromatographic purification (silica gel, 150 g, 230–400 mesh, 60 Å, ethyl acetate) followed by concentration of the blue fluorescent fraction gave complex **11** as a yellow crystalline solid (1.32 g, 21.4%), mp 234–236°C. ^{1}H NMR: δ 7.52 (dd, 2H), 6.99 (d, 2H), 6.61 (d, 2H), 2.72 (s, 6H). ^{13}C NMR: δ 154.11, 149.28, 139.47, 120.26, 115.72, 21.31. EI-MS (*m/z*) (%): 247 (86, M^+), 246 (100). Anal. calcd for $C_{12}H_{12}N_3BF_2$: C, 58.34; H, 4.86; N, 17.01. Found: C, 58.64; H, 4.84; N, 16.87. UV absorption (ethanol): λ_{max} 396 nm, log ϵ 4.50. Fluorescence (ethanol): λ_{max} 416 nm, Φ 0.40 (excitation at 370 nm) with Coumarin 503 as a standard. No lasing activity was observed.

γ-Nitro-β-phenylbutyrophenone **15**

A solution of sodium methoxide [from sodium (3.0 g, 0.130 mol) and methanol] in methanol (30 mL) was added rapidly with stirring to a solution of benzalacetophenone (20.0 g, 0.096 mol) and nitromethane (7.2 g, 0.118 mol) in methanol (50 mL) at 40°C and stirred for 15 minutes. The yellow solution was cooled and acidified with glacial acetic acid. A light yellow precipitate was collected and recrystallized from methanol to give the ketone **15** as a colorless amorphous solid, 16.5 g (64%), mp 102–103°C (lit. mp 103°C [21]). ^{1}H NMR: δ 7.90 (dd, 2H), 7.58 (t, 1H), 7.45 (t, 2H), 7.29 (M, 5H), 4.82 (dd, 1H), 4.68 (dd, 1H), 4.22 (M, 1H), 3.45 (dd, 1H), 3.44 (dd, 1H). ^{13}C NMR: δ 196.54, 138.98, 136.23, 133.36, 128.87, 128.55, 127.85, 127.66, 127.30, 79.52, 41.59, 39.36.

3,3',5,5'-Tetraphenyl-6-azapyrromethene **13**

A mixture of γ-nitro-β-phenylbutyrophenone (15.0 g, 0.056 mol) and ammonium formate (43.0 g, 0.68 mol) was heated at 180–190°C for 30 minutes, cooled to 70°C, and stirred overnight with methanol (350 mL). A blue precipitate was collected, washed with

cold methanol, and recrystallized from nitrobenzene to give the tetraphenylpyrroazamethene **13** as copper-green needles, 5.02 g (40%), mp 286–288°C (lit. mp 287–288°C [17]). ^{1}H NMR: δ 11.35 (s, 1H), 8.08 (m, 6H), 7.93 (s, 1H), 7.91 (s, 1H), 7.50 (m, 14H). UV (ethanol, dioxane): λ_{max} 592 nm, log ε 4.45; λ_{max} 594 nm, log ε 4.67.

1,3,5,7-Tetraphenyl-8-azapyrromethene–BF_2 Complex **17**

Diisopropylethylamine (8.53 g, 0.066 mol) was added with stirring to a solution of the tetraphenylpyrroazamethene **13** (5.02 g, 0.011 mol) in toluene (200 mL) and stirred for 15 minutes. After boron trifluoride etherate (7.93 g, 0.056 mol) was added dropwise, the solution was heated at 80°C for 1 hour. Water (100 mL) was added to the reaction mixture, and the organic layer was separated and dried (magnesium sulfate). After concentration, the residue was purified chromatographically [silica gel 150 g, 230–400 mesh, 60 Å, toluene/hexane (3/2)]. Concentration of a red fluorescent fraction gave the tetraphenylpyrroazamethene–BF_2 complex **17** as a copper-red amorphous solid 0.66 g (12%), mp 234–235°C. IR (KBr): ν 3465, 3062, 2357, 1648, 1515, 1476, 1456, 1398, 1302, 1226, 1123, 1037, 1022, 762, 693. ^{1}H NMR: δ 8.06 (m, 8H), 7.48 (m, 12H), 7.05 (s, 2H). ^{13}C NMR: δ 159.55, 145.58, 144.19, 132.29, 131.58, 130.88, 129.58, 129.49, 129.37, 128.62, 128.58, 119.09. EI-MS, *m/z* (%): 497 (100, M^+). Anal. calcd for $C_{32}H_{22}N_3BF_2$: C, 77.28; H, 4.43; N, 8.45. Found: C, 77.36; H, 4.48; N, 8.62. UV (ethanol, dioxane, *o*-xylene): λ_{max} 641, 644, 653 nm, log ε 4.78. Fluorescence (*o*-xylene): λ_f 696 nm, Φ 0.77 (excitation at 620 nm), Nile Blue A Perchlorate reference standard. Laser activity was not determined.

1,2,6,7-Tetraphenyl-3,5,8-trimethylpyrromethene–BF_2 Complex **21**

To a stirred mixture of 2-methyl-3,4-diphenyl pyrrole **22** [22] (2.33 g, 10 mmol) in dichloromethane (5 mL), acetyl chloride (1.58 g, 20 mmol) was added dropwise. The reaction mixture was heated at 40°C for 1 hour, cooled to room temperature, and triturated with hexane (300 mL) to bring about the separation of 3,3′,4,4′-tetraphenyl -5,5′,6-trimethylpyrromethene hydrochloride **19** as a brown solid (2.1 g, 89%). Triethylamine (2.42 g, 24 mmol) was added at room temperature to a suspension of the salt **19** (2.1 g, 4 mmol) in toluene (300 mL). The mixture was stirred for 20 minutes, boron trifluoride etherate (3.95 g, 28 mmol) was added dropwise, and the mixture was heated at 80°C for 1 hour. The reaction mixture was cooled to room temperature, washed with water (2 × 150 mL), and dried (magnesium sulfate). Concentration and purification of the crude mass by silica gel column chromatography (toluene) gave 1,2,6,7-tetraphenyl-3,5,8-trimethyl pyrromethene–BF_2 complex **21** as a red solid (1.2 g, 58%), mp 280–282°C (dec). IR (KBr): ν 2939, 1594, 1514, 1415, 1250, 978, 873, 773, 668. ^{1}H NMR: δ 7.3 (m, 20H), 2.69 (s, 6H), 2.37 (s, 3H). ^{13}C NMR: δ 131.18, 130.10, 130.01, 129.70, 129.01, 128.63, 128.42, 128.17, 127.87, 127.46, 127.04, 126.90, 126.69, 18.57, 13.52. Anal. calcd for $C_{36}H_{29}N_2BF_2$: C, 80.30; H, 5.39; N, 5.20. Found: C, 80.75; H, 5.46; N, 5.15. UV absorption (ethanol, dioxane): λ_{max} 540 and 542 nm, log ε 4.83. Fluorescence (dioxane) λ_{max} 581 nm, Φ 0.73 (excitation at 460 nm), acridine orange reference standard. No lasing activity was found.

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