Supporting Information

Bright, Color-Tunable Fluorescent Dyes in the VIS-NIR Region

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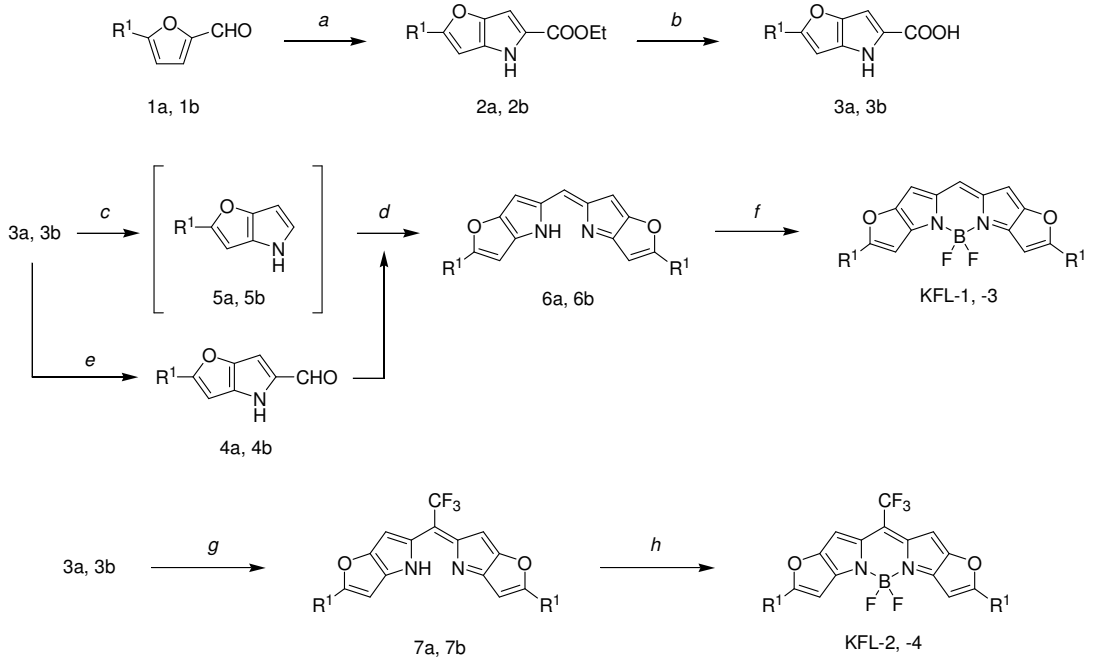
1. Synthesis

General

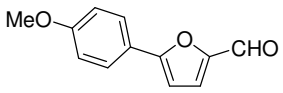
All chemical reagents and solvents for synthesis were purchased from commercial suppliers (Wako Pure Chemical, Tokyo Kasei Industry and Aldrich Chemical) and were used without further purification. All moisture-sensitive reactions were carried out under an atmosphere of argon. The composition of mixed solvents is given by the volume ratio (v/v). ^{1}H-NMR and ^{19}F-NMR spectra were recorded on a JEOL JNM-LA 300 (JEOL Ltd., Tokyo, Japan) or Varian MVX-300 (Varian Inc. Palo Alto, CA) spectrometer at room temperature. The measurements were performed at 300 MHz (for ^{1}H) and 282 MHz (for ^{19}F). All chemical shifts are relative to an internal standard of tetramethylsilane (δ = 0.0 ppm, for ^{1}H) or α,α,α-trifluorotoluene (TFT, δ = –62.9 ppm, for ^{19}F), respectively, and coupling constants are given in Hz. Flash chromatography separation was undertaken using a YFLC-Al-560 chromatograph (Yamazen Co., Osaka, Japan). MALDI-TOF (matrix-assisted laser desorption ionization - time of flight) mass spectra were recorded on an Ultraflex TOF/TOF spectrometer (Bruker) with α-cyano-4-hydroxycinnamic acid (CHCA) as matrix.

Scheme



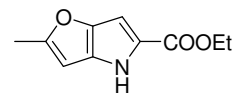
Reagents and conditions: a) N_3CH_2COOEt, 20% NaOEt, EtOH, 0°C to r.t., 2 h; toluene, reflux, 1−1.5 h; b) NaOH, EtOH/H_2O, reflux, 0.5−1 h; c) TFA, 50°C, 10 min; d) TFA, $POCl_3$, 5a or 5b, 50°C, 10 min; e) TFA, $CH(OEt)_3$, 50°C, 10 min; f) BF_3–Et_2O complex, TEA, halogenated solvent, reflux, 15 min; g) TFA/TFA anhydride, 80°C, 1 h; h) BF_3–Et_2O complex, TEA, toluene, reflux, 0.5-1 h.

5-(4-Methoxyphenyl)-furan-2-carbaldehyde 1b



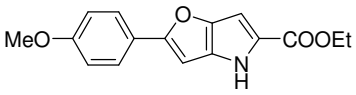
4-Methoxyphenylboronic acid (2.99 g, 19.7 mmol, 1.0 eq.) and 5-bromo-2-furaldehyde (3.46 g, 19.7 mmol, 1.0 eq.) were dissolved in toluene (120 ml), ethanol (30 ml) and 2 M Na_2CO_3 aqueous solution (20 ml), and degassed *in vacuo*. [1,1'-Bis(diphenylphosphino)-ferrocene]palladium(II) dichloride dichloromethane complex (1:1) (100 mg) was added into the mixture and heated at 80°C for 14 h. After cooling, the organic phase was washed with water and brine, dried over Na_2SO_4 and evaporated. The resulting residue was purified by flash chromatography (silica gel, eluent: *n*-hexane/ethyl acetate = 95/5 to 75/25) to obtain 5-(4-methoxyphenyl)-furan-2-carbaldehyde 1b as a yellow liquid (3.39 g, 84.8%). ^{1}H-NMR ($CDCl_3$): δ 9.60 (s, 1H), 7.77 (d, 2H, J = 9.0 Hz), 7.30 (d, 1H, J = 3.9 Hz), 6.96 (d, 2H, J = 9.0 Hz), 6.72 (d, 1H, J = 3.6 Hz), 3.86 (s, 3H)

2-Methyl-4*H*-furo[3,2-*b*]pyrrole-5-carboxylic acid ethyl ester 2a



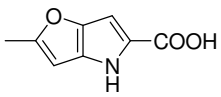
5-Methyl-furan-2-carbaldehyde 1a (1.80 g, 16.3 mmol, 1.0 eq.) and ethyl azidoacetate (2.80 g, 32.7 mmol, 2.0 eq.) were dissolved in anhydrous ethanol (90 ml) and stirred at 0°C. A solution of sodium ethoxide (20 wt% in ethanol, 11.1 g, 32.7 mmol, 2.0 eq.) was diluted with ethanol (30 ml) and added dropwise into the mixture, and stirring was continued for 2 h. Excess saturated aqueous NH_4Cl solution was added to form a yellow precipitate, which was collected by filtration. The precipitate was washed with water and dried *in vacuo*. The yellow solid was purified by chromatography (silica gel, eluent: *n*-hexane/ethyl acetate = 90/10) to obtain a yellow solid. The resulting solid was dissolved in toluene (30 ml) and heated to reflux for 1 h. After cooling, the solvent was evaporated. The residue was purified by chromatography (silica gel, *n*-hexane/ethyl acetate = 90/10) to obtain 2-methyl-4*H*-furo[3,2-*b*]pyrrole-5-carboxylic acid ethyl ester 2a as a pale yellow solid (0.980 g, 31.1%). ^{1}H-NMR ($CDCl_3$): δ 8.59 (br s, 1H), 6.73 (s, 1H), 6.08 (s, 1H), 4.33 (q, 2H, J = 7.1 Hz), 2.42 (s, 3H), 1.36 (t, 3H, J = 7.1 Hz)

2-(4-Methoxyphenyl)-4*H*-furo[3,2-*b*]pyrrole-5-carboxylic acid ethyl ester 2b



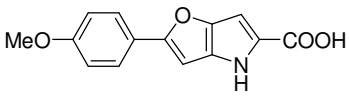
5-(4-Methoxyphenyl)-furan-2-carbaldehyde 1b (3.39 g, 16.8 mmol, 1.0 eq.) and ethyl azidoacetate (8.65 g, 67.0 mmol, 4.0 eq.) were dissolved in anhydrous ethanol (300 ml) and stirred at 0°C. A solution of sodium ethoxide (20 wt% in ethanol, 22.8 g, 67.0 mmol, 4.0 eq.) was added dropwise into the mixture, and stirred for 2 h. Excess saturated aqueous NH_4Cl solution was added to form a yellow precipitate, which was collected by filtration. The precipitate was washed with water and dried *in vacuo*. The resulting brown residue was dissolved in toluene (60 ml) and heated to reflux for 1.5 h. After cooling, the solvent was evaporated. The residue was recrystallized from *n*-hexane/ethyl acetate mixture to obtain the target compound (1.93 g). The mother liquor was concentrated and purified by flash chromatography (silica gel, eluent: *n*-hexane/chloroform = 10/90 to 0/100) to obtain further target compound (0.39 g). These compounds were combined and 2-(4-methoxyphenyl)-4*H*-furo[3,2-*b*]pyrrole-5-carboxylic acid ethyl ester 2b was obtained as a brown solid (2.32 g, 48.6%). ^{1}H-NMR ($CDCl_3$): δ 8.72 (s, 1H), 7.67 (d, 2H, J = 9.0 Hz), 6.94 (d, 2H, J = 9.0 Hz), 6.80 (s, 1H), 6.58 (s, 1H), 4.35 (q, 2H, J = 7.1 Hz), 3.85 (s, 3H), 1.38 (t, 3H)

2-Methyl-4*H*-furo[3,2-*b*]pyrrole-5-carboxylic acid 3a



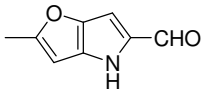
To a solution of 2-methyl-4*H*-furo[3,2-*b*]pyrrole-5-carboxylic acid ethyl ester 2a (287 mg, 1.49 mmol, 1.0 eq.) in ethanol (10 ml) was added NaOH (868 mg, 21.7 mmol, 14.6 eq.) in water (5 ml) and the mixture was refluxed for 30 min. After cooling, concentrated aqueous HCl solution was added to acidify the mixture and it was filtered. The resulting precipitate was washed with water and dried *in vacuo* to give a gray solid (149.5 mg). The filtrate was extracted with ethyl acetate, and the combined organic phase was washed with water and brine, then dried over Na_2SO_4 and evaporated to obtain a gray solid (55.6 mg). These solids were combined, and 2-methyl-4*H*-furo[3,2-*b*]pyrrole-5-carboxylic acid 3a was obtained as a gray solid (205 mg, 83.7%). ^{1}H-NMR (DMSO-d_6): δ 12.18 (s, 1H), 11.34 (s, 1H), 6.60 (s, 1H), 6.23 (s, 1H), 2.36 (s, 3H)

2-(4-Methoxyphenyl)-4*H*-furo[3,2-*b*]pyrrole-5-carboxylic acid 3b



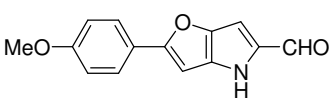
To a solution of 2-(4-methoxyphenyl)-4*H*-furo[3,2-*b*]pyrrole-5-carboxylic acid ethyl ester 2b (1.90 g, 6.66 mmol, 1.0 eq.) in ethanol (60 ml) was added NaOH (4.00 g, 100.0 mmol, 15.0 eq.) in water (30 ml) and the mixture was refluxed for 1 h. After cooling, concentrated aqueous HCl solution was added to acidify the mixture and it was filtered. The resulting precipitate was washed with water and dried *in vacuo* to obtain 2-(4-methoxyphenyl)-4*H*-furo[3,2-*b*]pyrrole-5-carboxylic acid 3b as a gray solid (1.56 g, 91.0%). ^{1}H-NMR (DMSO-d_6): δ 12.34 (s, 1H), 11.57 (s, 1H), 7.74 (d, 2H, J = 8.7 Hz), 7.01 (d, 2H, J = 8.7 Hz), 6.97 (s, 1H), 6.71 (s, 1H), 3.80 (s, 3H)

2-Methyl-4*H*-furo[3,2-*b*]pyrrole-5-carbaldehyde 4a



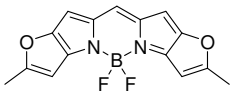
2-Methyl-4*H*-furo[3,2-*b*]pyrrole-5-carboxylic acid 3a (88.5 mg, 0.536 mmol) was dissolved in trifluoroacetic acid (2 ml) and stirred at 50°C for 10 min. Triethylorthoformate (1 ml) was added into the reaction mixture, and stirring continued for further 10 min. After cooling, the reaction mixture was poured into saturated aqueous $NaHCO_3$ solution to neutralize. The formed precipitate was filtered, washed with water and dried *in vacuo*. The precipitate was purified by flash chromatography (silica gel, eluent: *n*-hexane/ethyl acetate = 80/20 to 60/40) to obtain 2-methyl-4*H*-furo[3,2-*b*]pyrrole-5-carbaldehyde 4a as a yellow solid (71.2 mg, 89.1%). ^{1}H-NMR ($CDCl_3$): δ9.47 (bs, 1H), 9.38 (s, 1H), 6.68 (s, 1H), 6.13 (s, 1H), 2.44 (s, 3H)

2-(4-Methoxyphenyl)-4*H*-furo[3,2-*b*]pyrrole-5-carbaldehyde 4b



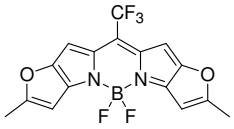
2-(4-Methoxyphenyl)-4*H*-furo[3,2-*b*]pyrrole-5-carboxylic acid 3b (28.6 mg, 0.111 mmol) was dissolved in trifluoroacetic acid (1 ml) and stirred at 50°C for 10 min. Triethylorthoformate (0.5 ml) was added into the reaction mixture, and stirring continued for further 10 min. After cooling, the reaction mixture was poured into saturated aqueous $NaHCO_3$ solution to neutralize. The formed precipitate was filtered, washed with water and dried *in vacuo*. The precipitate was purified by flash chromatography (silica gel, eluent: chloroform/ethyl acetate = 100/0 to 80/20) to obtain 2-(methoxypheny)-4*H*-furo[3,2-*b*]pyrrole-5-carbaldehyde 4b as a yellow solid (26.2 mg, 97.8%). ^{1}H-NMR ($CDCl_3$): δ9.42 (s, 1H), 9.02 (bs, 1H), 7.70 (d, 2H, J = 9.0 Hz), 6.96 (d, 2H, J = 8.7 Hz), 6.76 (s, 1H), 6.61 (s, 1H), 3.86 (s, 3H)

2,8-Dimethyl-difuro[2,3-*b*]-[3,2-*g*]-5,5-difluoro-5-bora-3a,4a-diaza-*s*-indacene (KFL-1)



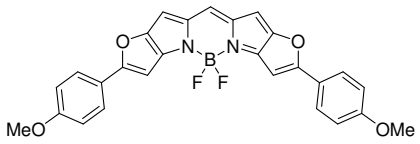
2-Methyl-4*H*-furo[3,2-*b*]pyrrole-5-carboxylic acid 3a (44.8 mg, 0.271 mmol, 1 eq.) was dissolved in trifluoroacetic acid (2 ml) and stirred at 50°C for 10 min. (2-Methyl-4*H*-furo[3,2-*b*]pyrrole 5a was obtained, and used for the next reaction without further purification.) 2-Methyl-4*H*-furo[3,2-*b*]pyrrole-5-carbaldehyde 4a (40.5 mg, 0.271 mmol, 1 eq.) and phosphoryl chloride (1.5 ml) was added into the reaction mixture, stirred further 10 min until an intense purple color was formed. After cooling, the reaction mixture was poured into saturated aqueous $NaHCO_3$ solution to neutralize. The formed precipitate was filtered, washed with water and dried *in vacuo*. The resulting compound was dissolved in chloroform (10 ml), before boron trifluoride diethyl ether complex (0.5 ml) and triethylamine (0.4 ml) were added and the mixture was refluxed for 10 min. After cooling, the reaction mixture was diluted with chloroform and washed with saturated aqueous $NaHCO_3$ solution and brine, dried over Na_2SO_4 and evaporated. The residue was purified by chromatography (silica gel, eluent: *n*-hexane/chloroform = 5/95) to obtain 2,8-dimethyl-difuro[2,3-*b*]-[3,2-*g*]-5,5-difluoro-5-bora-3a,4a-diaza-*s*-indacene (KFL-1) as a gold metallic solid (56.8 mg, 69.4%). ^{1}H-NMR ($CDCl_3$): δ 7.07 (s, 1H), 6.40 (s, 2H), 6.31 (s, 2H), 2.47 (s, 6H). MALDI-TOF (*m*/*z*): calculated for $C_{15}H_{11}BF_2N_2O_2$: 300.068; found: 299.931 $[M]^+$

2,8-Dimethyl-11-trifluoromethyl-difuro[2,3-*b*]-[3,2-*g*]-5,5-difluoro-5-bora-3a,4a-diaza-*s*-indacene (KFL-2)



2-Methyl-4*H*-furo[3,2-*b*]pyrrole-5-carboxylic acid 3a (61.0 mg, 0.370 mmol) was dissolved in trifluoroacetic acid (4 ml) and stirred at 40°C for 10 min. Trifluoroacetic anhydride (1 ml) was added into the reaction solution and stirring was continued at 80°C for 1 h (an intense blue color appeared). After cooling, the reaction solution was diluted with toluene and washed with saturated aqueous $NaHCO_3$ solution, water and brine, dried over Na_2SO_4, filtered and evaporated. The crude compound was dissolved in toluene (4 ml) and stirred at room temperature. Boron trifluoride diethyl ether complex (0.4 ml) and triethylamine (0.3 ml) were added into the reaction solution and stirring continued at 80°C for 30 min. After cooling, the reaction solution was diluted with toluene and washed with saturated aqueous $NaHCO_3$ solution, water and brine, dried over Na_2SO_4, filtered and evaporated. The crude product was purified by column chromatography (silica gel, eluent: toluene/ethyl acetate = 95/5) to obtain 2,8-dimethyl-11-trifluoromethyl-difuro[2,3-*b*]-[3,2-*g*]-5,5-difluoro-5-bora-3a,4a-diaza-*s*-indacene (KFL-2) as a gold metallic solid (27.1 mg, 39.9%). ^{1}H-NMR ($CDCl_3$): δ 6.68 (s, 2H), 6.32 (s, 2H), 2.50 (s, 6H). ^{19}F-NMR ($CDCl_3$): δ –54.7 (s, 3F), –149.4 (q, J = 28 Hz, 2F). MALDI-TOF (*m*/*z*): calculated for $C_{16}H_{10}BF_5N_2O_2$: 368.068; found: 368.095 $[M]^+$

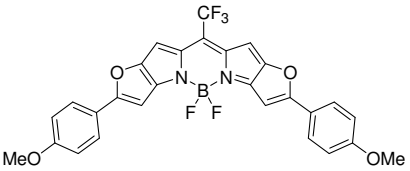
2,8-Di(4-methoxyphenyl)-difuro[2,3-*b*]-[3,2-*g*]-5,5-difluoro-5-bora-3a,4a-diaza-*s*-indacene (KFL-3)



2-(4-Methoxyphenyl)-4*H*-furo[3,2-*b*]pyrrole-5-carboxylic acid 3b (18.6 mg, 0.072 mmol, 1 eq.) was dissolved in trifluoroacetic acid (1 ml) and stirred at 50°C for 10 min. (2-(4-Methoxyphenyl)-4*H*-furo[3,2-*b*]pyrrole 5b was obtained, and used for the next reaction without further purification.) 2-(4-Methoxyphenyl)-4*H*-furo[3,2-*b*]pyrrole-5-carbaldehyde 4b (17.5 mg, 0.072 mmol, 1 eq.) and phosphoryl chloride (0.8 ml) was added into the reaction mixture, stirred further 10 min until an intense blue color was formed. After cooling, the reaction mixture was poured into saturated aqueous $NaHCO_3$ solution to neutralize. The formed precipitate was filtered, washed with water and dried *in vacuo*. The resulting compound was dissolved in 1,1,2-trichloroethane (10 ml), before boron trifluoride diethyl ether complex (0.20 ml) and triethylamine (0.15 ml) were added and the mixture was stirred at 100°C for 10 min. After cooling, the reaction mixture was diluted with chloroform and washed with saturated aqueous $NaHCO_3$ solution and brine, dried over Na_2SO_4 and evaporated. The residue was purified by chromatography (silica gel, eluent: chloroform/ethyl acetate = 95/5) to obtain 2,8-di(4-methoxyphenyl)-difuro[2,3-*b*]-[3,2-*g*]-5,5-difluoro-5-bora-3a,4a-diaza-*s*-indacene (KFL-3) as a gold metallic solid (22.5 mg,

64.3%). ^{1}H-NMR ($CDCl_3$): δ 7.78 (d, 4H, J = 9.0 Hz), 7.04 (s , 1H), 6.99 (d, 4H, J = 8.7 Hz), 6.83 (s, 2H), 6.47 (s, 2H), 3.89 (s, 6H). MALDI-TOF (*m*/*z*): calculated for $C_{27}H_{19}BF_2N_2O_4$: 484.141; found: 484.059 $[M]^+$

2,8-Di(4-methoxyphenyl)-11-trifluoromethyl-difuro[2,3-*b*]-[3,2-*g*]-5,5-difluoro-5-bora-3a,4a-diaza-*s*-indacene (KFL-4)



2-(4-Methoxyphenyl)-4*H*-furo[3,2-*b*]pyrrole-5-carboxylic acid 3a (298 mg, 11.7 mmol) was dissolved in trifluoroacetic acid (15 ml) and stirred at 40 ^{o}C for 15 min. Trifluoroacetic anhydride (3 ml) was added into the reaction solution and stirring continued at 80^{o}C for 30 min (an intense green color appeared). After cooling, the reaction solution was poured into aqueous $NaHCO_3$ solution containing crushed ice. The precipitate was filtered, washed with water and dried *in vacuo*. The crude compound was dissolved in toluene (70 ml) and stirred at room temperature. Boron trifluoride diethyl ether complex (1.2 ml) and triethylamine (0.8 ml) were added into the reaction solution and stirring continued at 80^{o}C for 15 min. After cooling, the reaction solution was diluted with toluene and washed with saturated aqueous $NaHCO_3$ solution, water and brine, dried over Na_2SO_4, filtered and evaporated. The crude compound was purified by chromatography (silica gel, eluent: toluene/ethyl acetate = 95/5) to obtain 2,8-di(4-methoxyphenyl)-11-trifluoromethyl-difuro[2,3-*b*]-[3,2-*g*]-5,5-difluoro-5-bora-3a,4a-diaza-*s*-indacene (KFL-4) as a green metallic solid (188 mg, 58.4%). ^{1}H-NMR ($CDCl_3$): δ 7.80 (d, 4H, J = 9.0 Hz), 7.00 (d, 4H, J = 8.8 Hz), 6.82 (s, 2H), 6.73 (s, 2H), 3.90 (s, 6H). ^{19}F-NMR ($CDCl_3$): δ –54.3 (s, 3F), –149.0 (q, J = 28 Hz, 2F). MALDI-TOF (*m*/*z*): calculated for $C_{28}H_{18}BF_5N_2O_4$: 552.128, found: 552.058 $[M]^+$

2. Measurement

All solvents for spectrometry were purchased from Kanto Chemical. Absorption spectra were recorded on a Hitachi U-2001 double beam spectrophotometer (Hitachi Co. Ltd., Tokyo, Japan). Measurements for the extinction coefficients were performed according to the following protocol. Around 1 mg of dye was weighed using a digital scale (Δw = 0.01 mg), and dissolved into 100 ml of chloroform. A number of further diluted solutions with different dye concentrations (C: 10^{-7} to 10^{-6} M) were prepared from this stock solution. The absorption spectra of these diluted solutions were measured, and the absorbance (A) and the concentration (C) were plotted on a graph of A versus C to determine the extinction coefficient (from the gradient). This protocol was performed 7 – 8 times for each dye, and the average value of the extinction coefficient, the standard deviation (s.d.), and the coefficient of variance (C.V.) were calculated. Each value of C.V. was found to be less than 5%, which confirmed the reliability of the value of each extinction coefficient (Table S1).

Fluorescence emission spectra and photostabilities were recorded on a F-4500 fluorophotometer (Hitachi Co., Tokyo, Japan) at 25°C. Quantum yields were recorded on a SREX Fluorolog-3 (Model FL-3-11, Horiba Jobin Yvon Co., Kyoto, Japan) at 25 °C. The instrument was equipped with a R2658P photomultiplier tube (Hamamatsu Photonics Co., Shizuoka, Japan) as a fluorescence detector. Measurements of quantum yields were performed by following the method recommended by Horiba Jobin Yvon (see: http://www.jp.jobinyvon.horiba.com/product_j/spex/quantum_yield/img/ quantum_yields.pdf). A number of diluted solutions of different dye concentrations (A < 0.10, to prevent reabsorption) were prepared and the absorbance (A) and the integrated fluorescence intensity (F) at each concentration was recorded at the following excitation wavelengths (575 nm, 610 nm, 670 nm and 710 nm, for KFL-1, -2, -3 and -4, respectively). Then a graph of F versus A was plotted to determine the gradient (G). Quantum yields ϕ were calculated using the following equation:

$$\phi_S = \phi_R \left(\frac{G_R}{G_S} \right) \left(\frac{n_R}{n_S} \right)^2$$

The subscripts R and S denote the reference dye and the sample, respectively. n is the refractive index of the solvent. The following reference dyes were used: cresyl violet (ϕ = 0.54±0.03 in methanol)[1] for KFL-1 and -2, boron-azadipyrromethene compound aza-BDP (ϕ = 0.36 in chloroform)[2] for KFL-3 and -4.

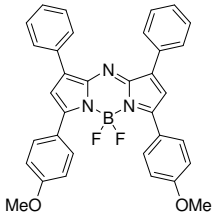


Chart S1. Chemical structure of the boron-azadipyrromethene compound aza-BDP

This protocol was performed 4 times for each dye, and the average value of the quantum yield, the standard deviation, and the coefficient of variance (C.V.) were calculated.

In order to estimate the total errors, including the systematical errors, a cross-check using other reference dyes was performed. For example, the quantum yield of cresyl violet (a reference dye for KFL-1 and -2) was independently measured using sulforhodamine 101 hydride as a reference dye (ϕ = 0.95±0.02 in ethanol)[3], and this measurement resulted in a quantum yield of cresyl violet (ϕ = 0.53±0.01, C.V.: 2.1%, n = 4), which is well corresponding to the reported value in the literature (0.54±0.03 in methanol) within 1.6% error. A similar measurement concerning aza-BDP (a reference dye for KFL-3 and -4) was undertaken. In this case, 3,3'-diethyl-thiadicarbocyanine (ϕ = 0.35±0.01 in methanol)[4] was used as a cross-check reference dye, and this measurement resulted in a quantum yield of aza-BDP (0.38±0.01, C.V.: 4.0%, n = 4), which is well corresponding to the reported value in the literature (ϕ = 0.36 in chloroform) within 6.1% error.

Table S1. Values of extinction coefficients and quantum yields of KFL-1 – -4 in chloroform.

Dye	Extinction coefficient			Quantum yield		
	ε ($M^{-1}cm^{-1}$)	C.V. (%)	n^a	ϕ	C.V. (%)	n
KFL-1	202,000 ± 8,300	4.11	7	0.96 ± 0.04	4.1	4
KFL-2	185,000 ± 7,050	3.81	7	0.98 ± 0.03	3.1	4
KFL-3	288,000 ± 4,910	1.71	7	0.86 ± 0.02	2.3	4
KFL-4	253,000 ± 10,200	4.03	8	0.56 ± 0.03	4.7	4

a number of measurements

Table S2. Values of quantum yields of KFL-1 – -4 in various solvents.

	toluene	$CHCl_3$	THF	MeCN	EtOH	MeOH
KFL-1	0.94	0.96	0.93	0.95	0.97	0.96
KFL-2	0.97	0.98	0.92	0.84	0.87	0.70
KFL-3	0.87	0.86	0.83	0.85	0.77	0.77
KFL-4	0.58	0.56	0.49	0.45	0.37	0.32

The photostability measurements of KFL-1, -2, -3, and -4 in ethanol were conducted by continuous irradiation with a Xe lamp (150 W), both with white light (without passing the monochromator), and at the optimum excitation wavelengths (570 nm, 600 nm, 640 nm and 720 nm, for KFL-1, -2, -3 and -4, respectively) with 10 nm slit width. The temperature was kept at 25 ^{o}C at all times. The samples were dissolved in ethanol in concentration resulting in absorbance at the absorption maximum of A = 0.10. Each emission intensity at the fluorescence maximum was recorded on the fluorometer with 2.5 nm slit width.

3. X-ray single-crystal structure analysis of KFL-4

Preparation and measurement

KFL-4 was dissolved in a minimal amount of chloroform and the solution was filtered to remove the insoluble dye. This filterated saturated solution was transferred into a flask, and the solvent was allowed to evaporate slowly at room temperature to afford a single crystal. The resulting green block crystal of KFL-4 having approximate dimensions of 0.30 × 0.20 × 0.20 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo-Kα radiation and a rotating anode generator.

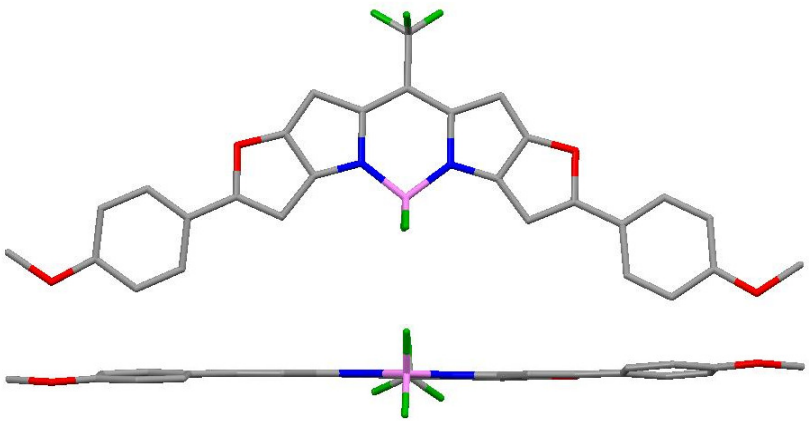


Figure S1. Front view (top) and side view (bottom) of the molecular structure of KFL-4.

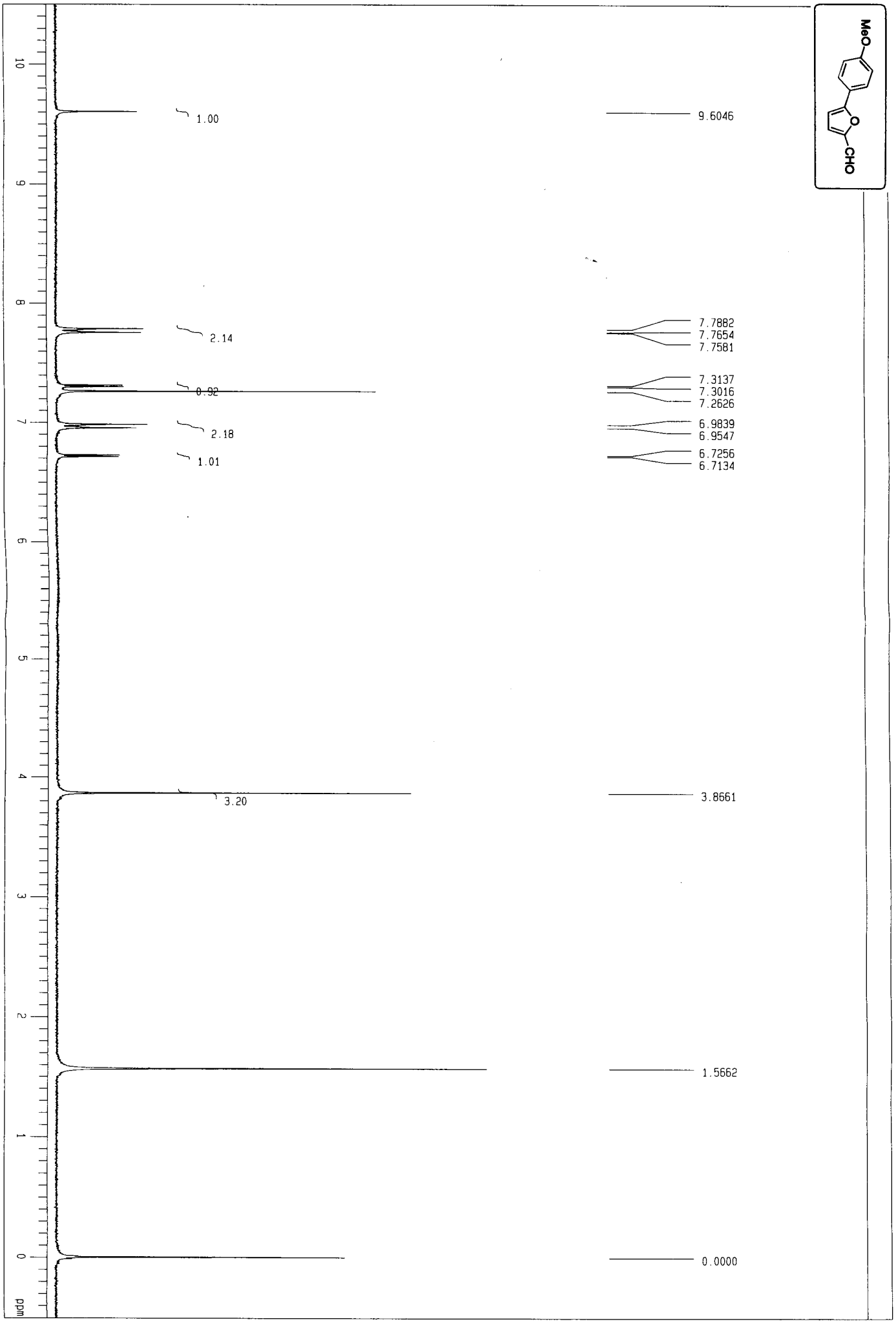
4. References

1. Magde, D.; Brannon, J. H.; Cremers, T. L.; Olmsted, J. *J. Phys. Chem.* **1979**, *83*, 696-699.

2. Gorman, A.; Killoran, J.; O'Shea, C.; Kenna, T.; Gallagher, W. M.; O'Shea, D. F. *J. Am. Chem. Soc.* **2004**, *126*, 10619-10631.

3. Velapoldi, R. A.; Tonnesen, H. H. *J. Fluorescence* **2004**, *14*, 465-472.

4. Dempster, D. N.; Morro, T.; Rankin, R.; Thompson, G. F. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 1479-1496.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7.2626
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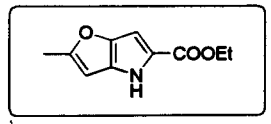

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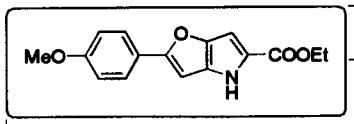

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6.5753
4.3892
4.3657
4.3413
4.3177
3.8490
1.6337
1.4078
1.3835
1.3599
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0.89
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2.02
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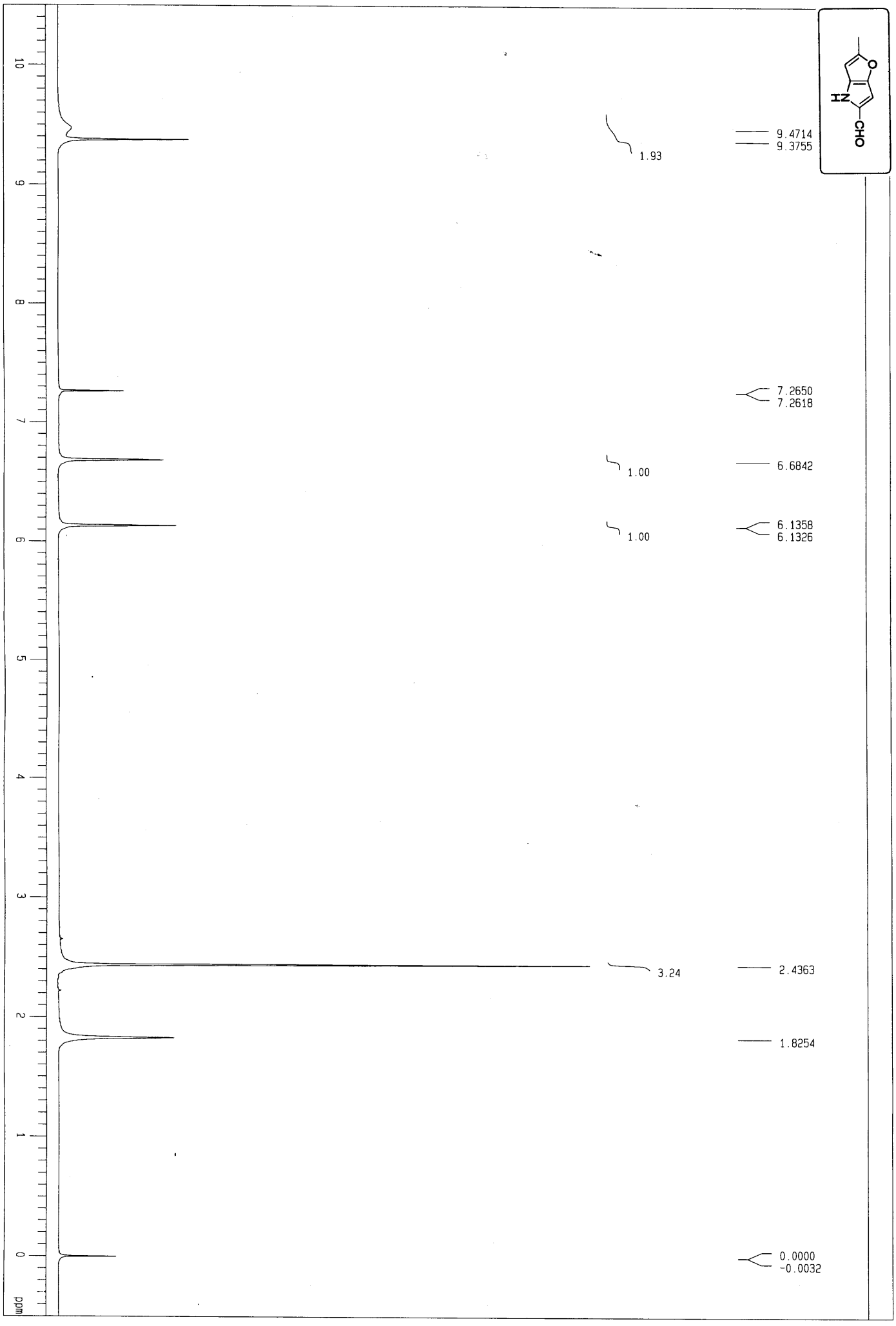
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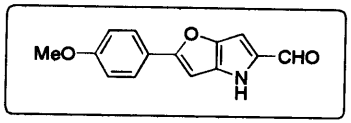

grease

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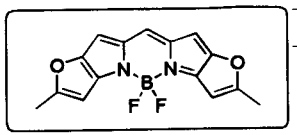

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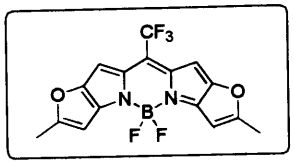
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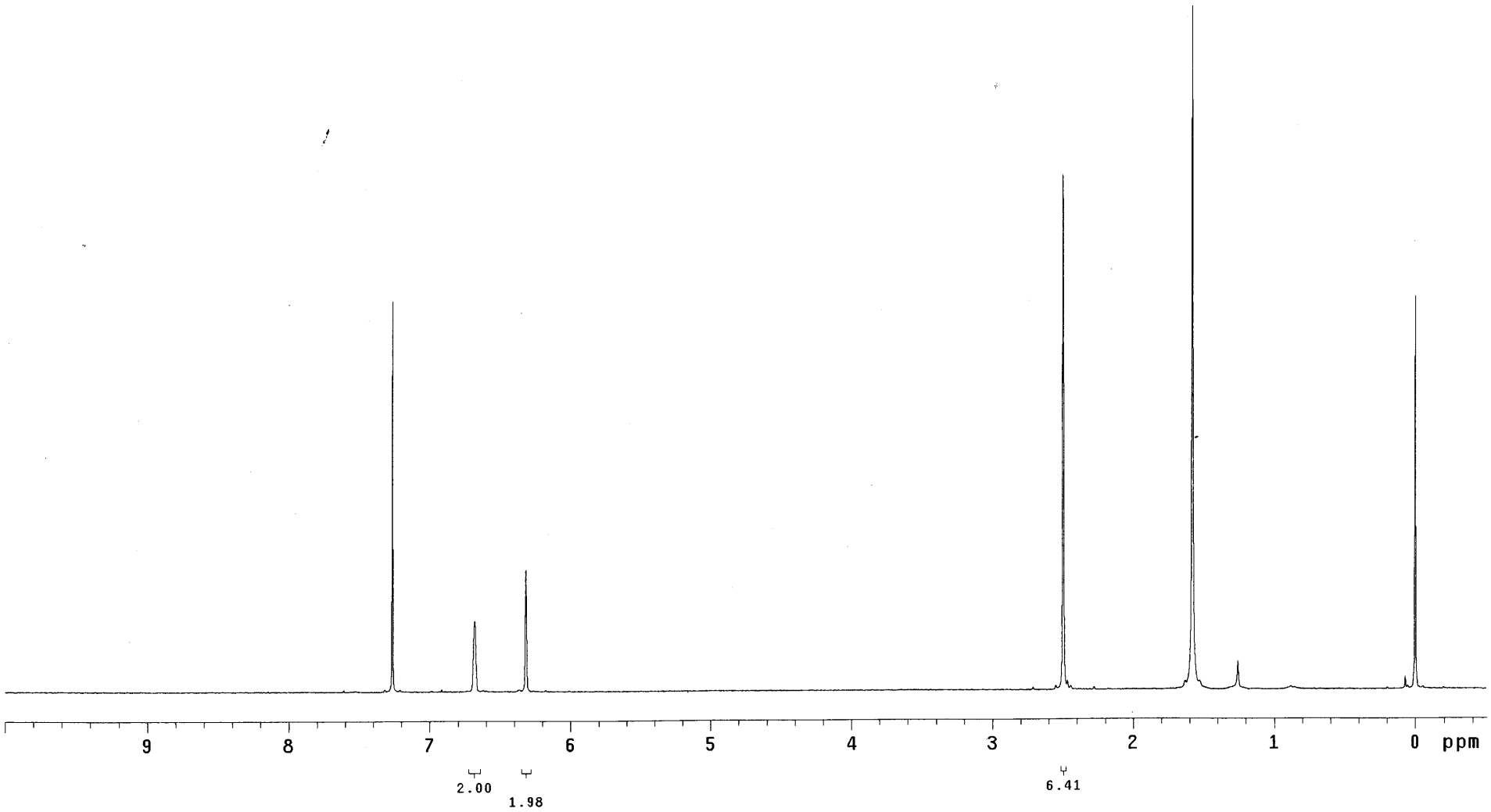
B
N
O
F
F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4
3
2
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ppm
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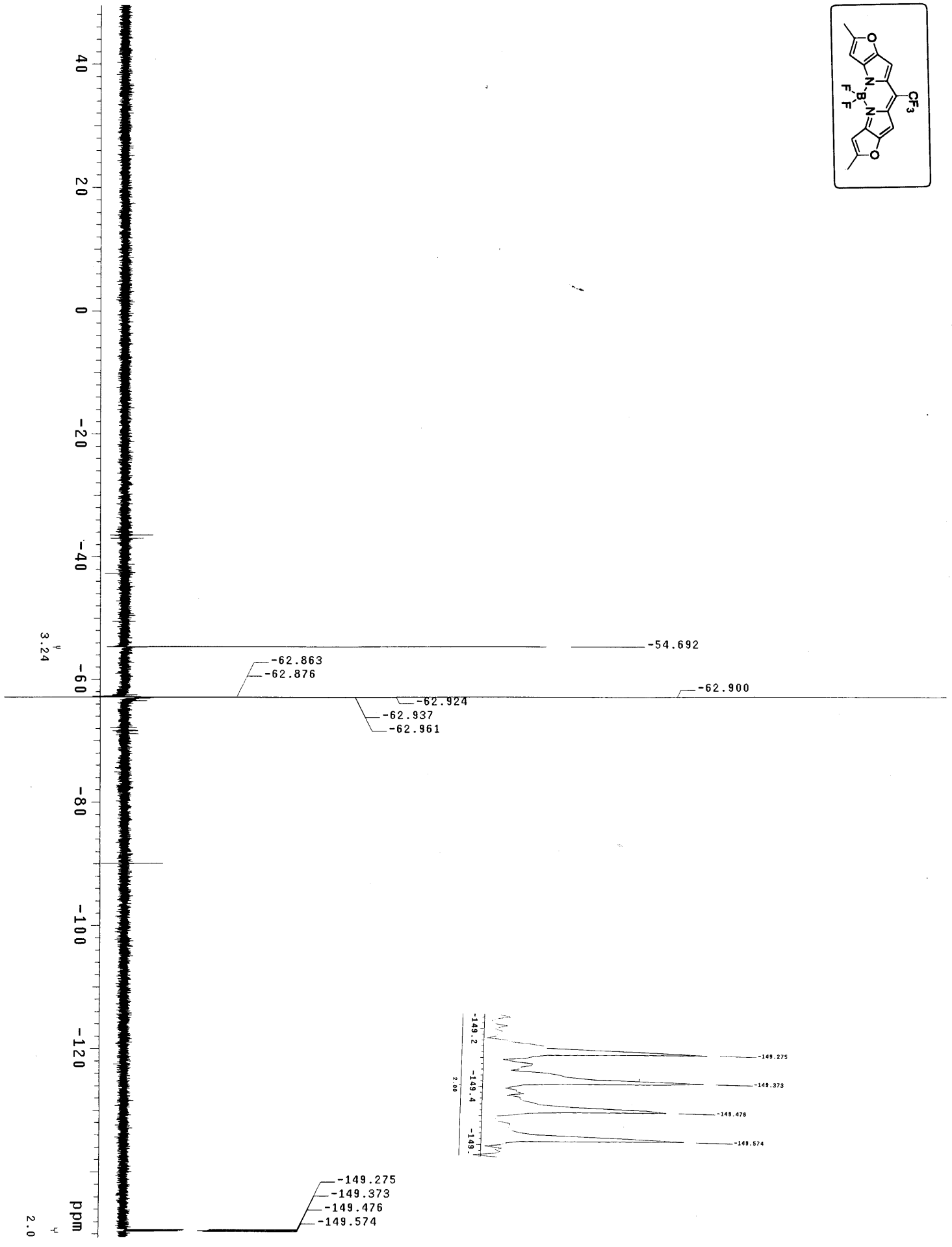
1.98
6.41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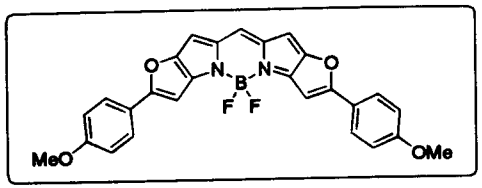
F
F
CF3


O
N
B
F F
N
O
MeO
OMe

9
8
7
6
5
4
3
2
1
0 ppm
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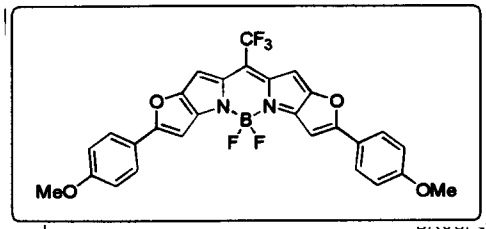
4.12
1.02
2.00
1.92
6.33



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MeO
OMe
CF3
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B
F
F
O

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