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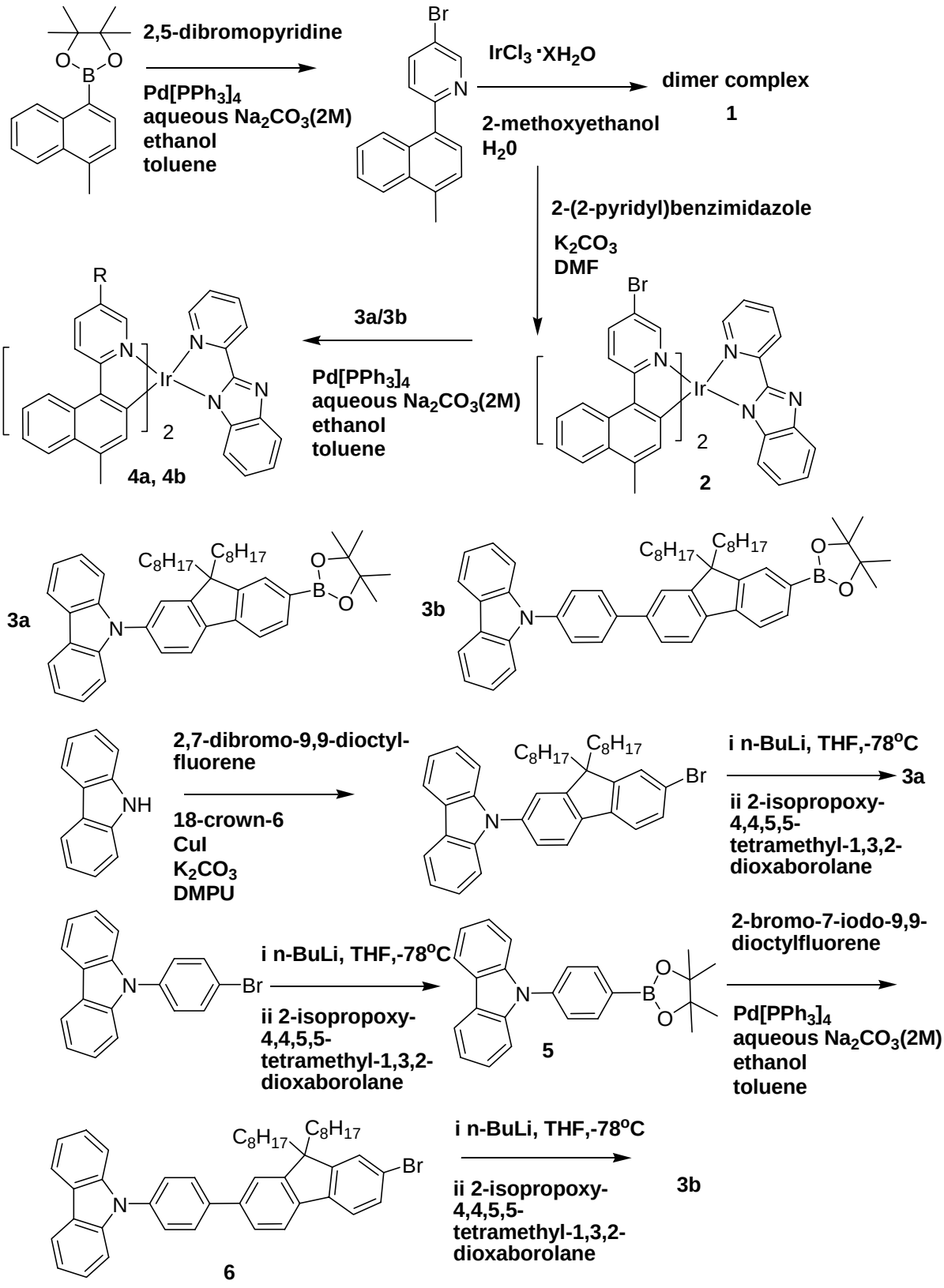
Experimental Section

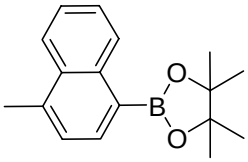
Materials and Instruments. All manipulations involving air-sensitive reagents were performed under an inert atmosphere of dry nitrogen. Tetrahydrofuran (THF) was dried over Na/benzophenone and distilled prior to use. 2,7-dibromofluorene, 2,7-dibromo-9,9-dioctylfuorene,[1] 9-(4-bromo-phenyl)-9*H*-carbazole[2] and 2-bromo-7-iodo-dioctyl-fluorene[3] were synthesized according to literature methods. The starting chemicals, unless otherwise specified, were used as received. *All the intermediates were isolated, analyzed by TLC (thin layer chromatography) on silica gel and ^1H NMR to ensure a clean incoming reaction.*

All the ^1H spectra were recorded in $CDCl_3$ with deuterated solvent as the internal reference. Time-of-flight mass spectrometry (TOF-MS) was performed in the positive ion mode with matrix of dithranol. The experimentally determined and calculated masses agree within the range of accuracy of the instrument and the mass peaks with the lowest isotopic mass are reported. The absolute solid emission quantum efficiency of **4a** and **4b** were obtained by excitation at 325 nm in an integrating sphere. Thermogravimetric analysis (TGA) was carried out under nitrogen purging at a heating rate of 20°C from 30 to 500 °C. DSC analyses were performed at a heating rate of 10 °C from -30 to 300 °C under nitrogen purging.

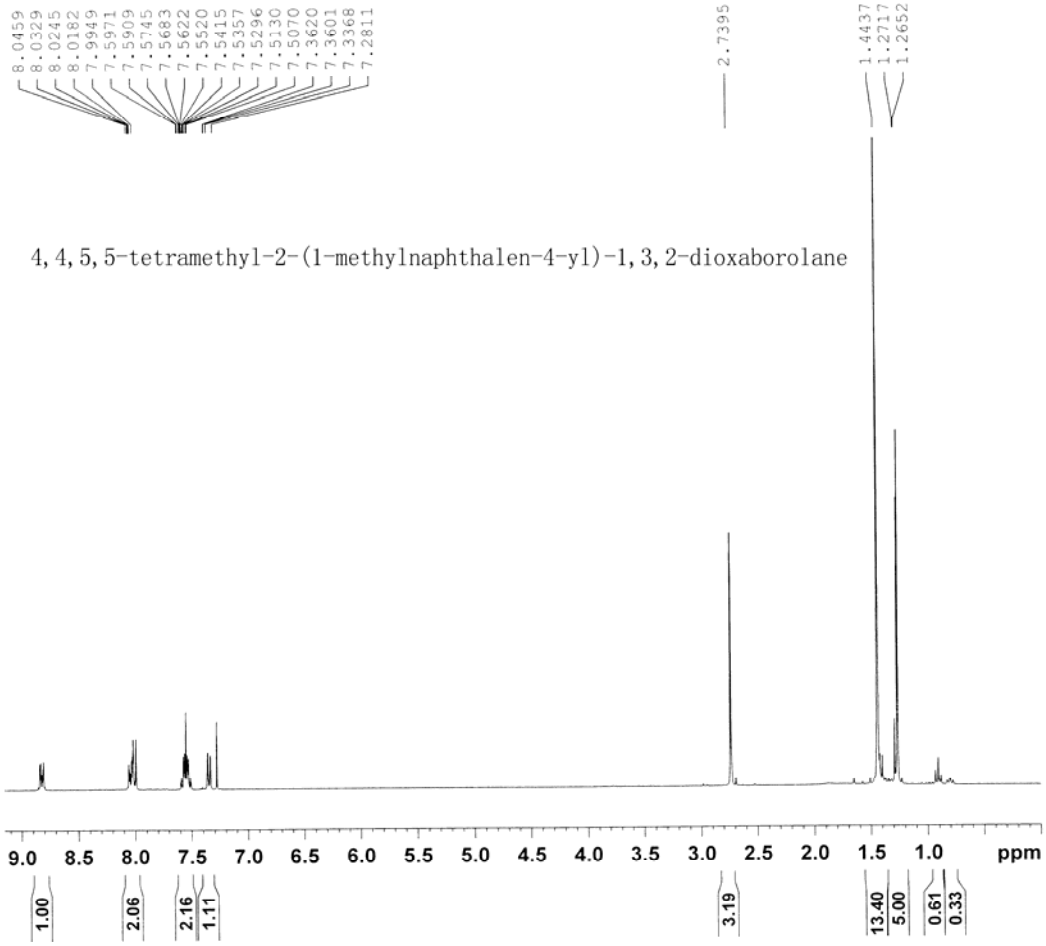


Scheme 1: Synthetic routes to soluble red-emitting complexes **4a** and **4b**.

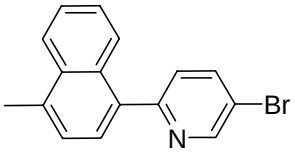
4,4,5,5-tetramethyl-2-(1-methylnaphthalen-4-yl)-1,3,2-dioxaborolane



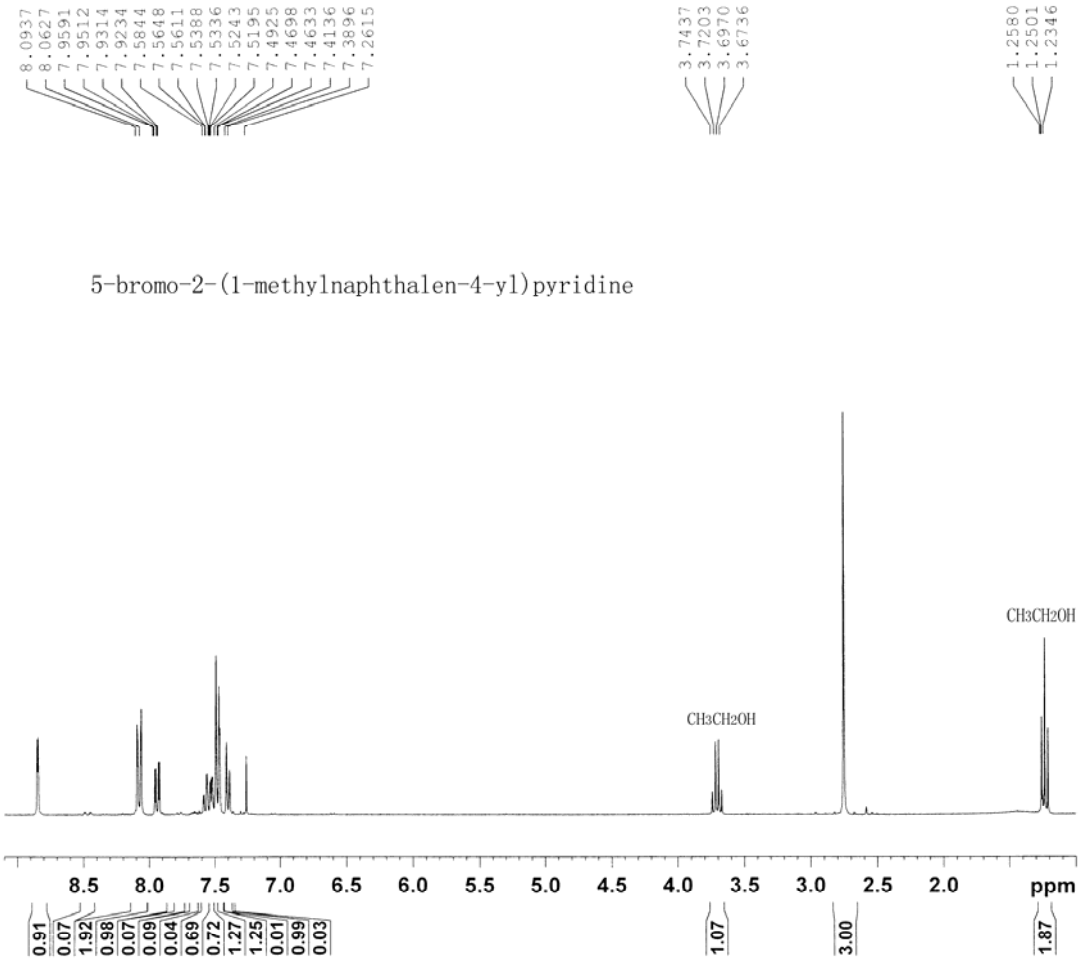
A solution of n-BuLi in hexanes (2.5 M, 19.8 ml, 49.4 mmol) was slowly added to a solution of 1-bromo-4-methylnaphthalene (5.7 ml, 35.9 mmol) in dry THF (100 ml) at –78°C under nitrogen. The mixture was stirred for 30 min at this temperature, and then 2-isopropoxy-4,4,5,5-tetramethyl- 1,3,2-dioxaborolane (10.3 ml, 49.4 mmol) was added. The mixture was stirred for 24 h under nitrogen whilst gradually warming to room temperature. The mixture was then poured into a large amount of distilled water. Organic products were extracted into dichloromethane. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residual was purified by silica chromatography using petroleum ether/dichloromethane (2:1 v/v) as the eluent to afford a white solid. Yield: 9.1 g **(**95%). TLC R_f: 0.82. mp 77-79 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.44 (s, 12H), 2.74 (s, 3H), 7.35 (d, 1H, J = 7.3 Hz), 7.50-7.60 (m, 2H), 7.99-8.06 (m, 2H), 8.81-8.84(m, 1H).



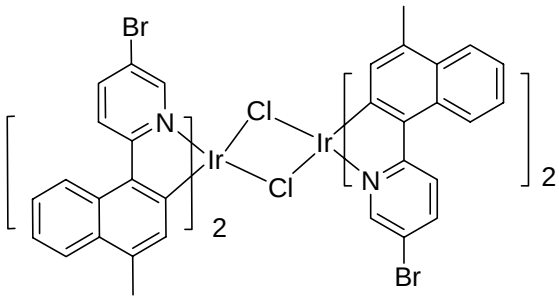
5-bromo-2-(1-methylnaphthalen-4-yl)pyridine



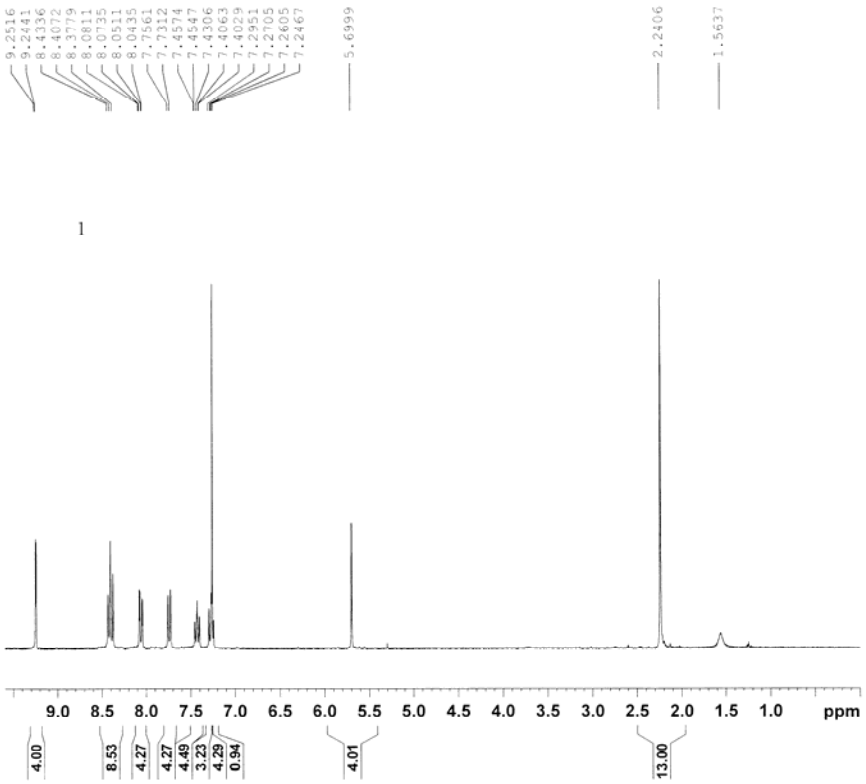
$Pd(PPh_3)_4$ (0.55 g, 0.47 mmol) was added to a mixture of 4,4,5,5-tetramethyl-2-(1-methylnaphthalen-4-yl)-1,3,2-dioxaborol ane (5 g, 18.6 mmol), 2,5-dibromopyridine (6.6 g, 28.1 mmol) in toluene (80 ml), aqueous Na_2CO_3 (2 M, 40 ml) and ethanol (20 ml) under a nitrogen atmosphere. The reaction was heated to reflux at 90°C for 24 h. After being cooled to room temperature, the mixture was diluted with distilled water. The organic layer was separated, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residual was purified by column chromatography using gradient elution with petroleum ether and dichloromethane to afford a white solid. Yield: 4.5 g (81%). TLC R_f (2:1 petroleum ether/dichloromethane v/v): 0.39. mp 107-109 °C. ^{1}H NMR (300 MHz,$CDCl_3$) δ (ppm): 2.75 (s, 3H), 7.40 (d, 1H, J = 7.2 Hz), 7.49-7.58(m, 4H), 7.94 (dd, 1H, J_1 = 2.4, J_2 = 8.4 Hz), 8.08 (d, 2H, J = 9.3 Hz), 8.84 (d, 1H, J = 2.4 Hz).



bis[5-bromo-2-(1-methylnaphthalen-4-yl)pyridine]$_4$Ir$_2$(μ-Cl)$_2$ 1

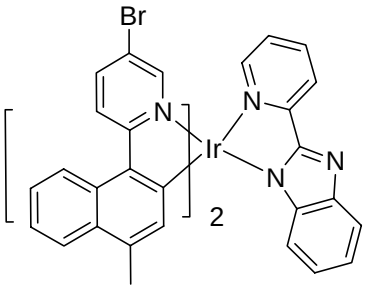


A mixture of 5-bromo-2-(1-methylnaphthalen-4-yl)pyridine (1.5 g, 5 mmol) and $IrCl_3 \cdot xH_2O$ (0.70 g, 2 mmol) in 3:1 2-methoxyethanol (30 ml)and water (10 ml) was refluxed for 24 h under nitrogen. After being cooled to room temperature, a small quantity of water was added to precipitate an orange solid. The precipitates were collected by filtration, washed with distilled water and re-dissolved in dichloromethane. The insoluble impurities were filtered off. The filtrate was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was washed with ethanol and dried under vacuum to afford a yellow solid. Yield: 1.2 g (75%). TLC R_f (1:1 petroleum ether/ dichloromethane v/v): 0.68. ^{1}H NMR (300 MHz,$CDCl_3$) δ (ppm): 2.24 (s, 12H), 5.70 (s, 4H), 7.27 (t, 4H, J = 7.2 Hz), 7.43 (t, 4H, J = 7.5 Hz), 7.75 (d, 4H, J = 7.8 Hz), 8.06 (dd, 4H, J_1 = 2.3 Hz, J_2 = 9.0 Hz), 8.41 (t, 8H, J = 7.9 Hz), 9.25 (d, 4H, J = 2.3 Hz).[1]

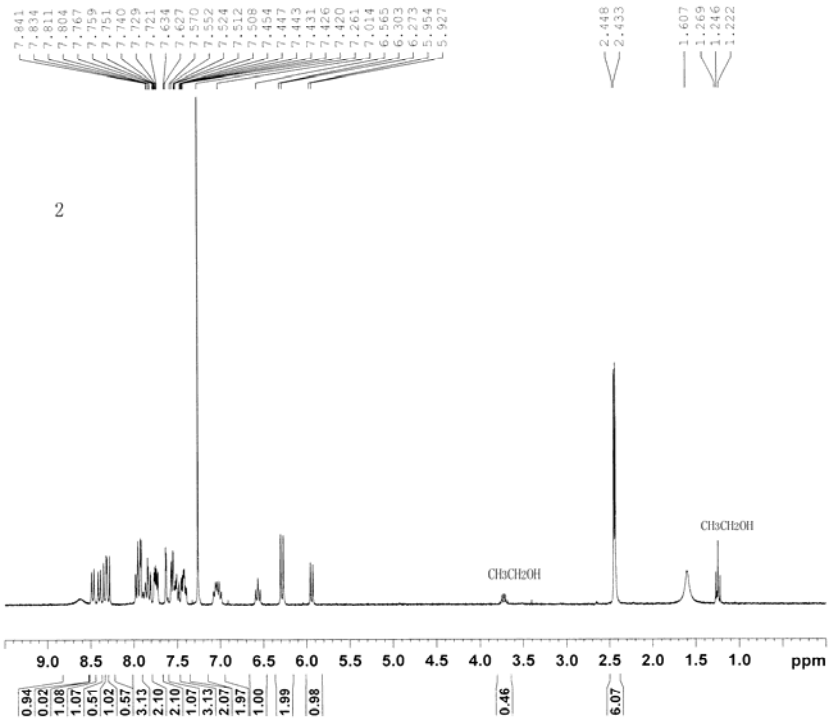


[1] The integral of 4.29 is related to the proton of $CHCl_3$.

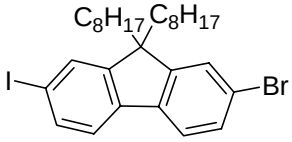
bis[5-bromo-2-(1-methylnaphthalen-4-yl)pyridine]Ir[2-(2-pyridyl)benzimidazolate] 2



A mixture of the chloro-bridged dimer complex **1** (0.60 g, 0.36 mmol), 2-(2-pyridyl)benzimidazole (0.11 g, 0.55 mmol) and K_2CO_3 (0.21 g, 1.46 mmol) in DMF (40 ml) was degassed several times and refluxed for 24 h under nitrogen, then cooled to room temperature. Upon addition of water, the precipitate obtained was filtered, washed with distilled water and re-dissolved in dichloromethane. The insoluble impurities were filtered off. The filtrate was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was washed with ethanol and dried under vacuum to afford **2** as a yellow solid. Yield: 0.51 g (72.8%). TLC R_f (4:1 dichloromethane/ ethyl acetate v/v): 0.5. ^{1}H NMR (300 MHz,$CDCl_3$) δ (ppm): 2.4484 (s, 3H), 2.4333(s, 3H), 5.94 (d, 1H, J = 8.0 Hz), 6.27 (s, 1H), 6.30 (s, 1H), 6.56 (t, 1H, J = 7.8 Hz), 6.99-7.08 (m, 2H), 7.40-7.63 (m, 6H), 7.72-7.77 (m, 2H), 7.72-7.98 (m, 5H), 8.28-8.34 (m, 2H), 8.40 (d, 1H, J = 8.1 Hz), 8.48 (d, 1H, J = 8.5 Hz), 8.63 (s, 1H). Elemental analysis (%) calcd for $C_{44}H_{30}Br_2IrN_5$: C, 53.88; H, 3.08; N, 7.14. found: C, 53.80; H, 3.09; N, 7.02. ESI MS: m/z 982(100%) MH^+ (Calcd. 980).

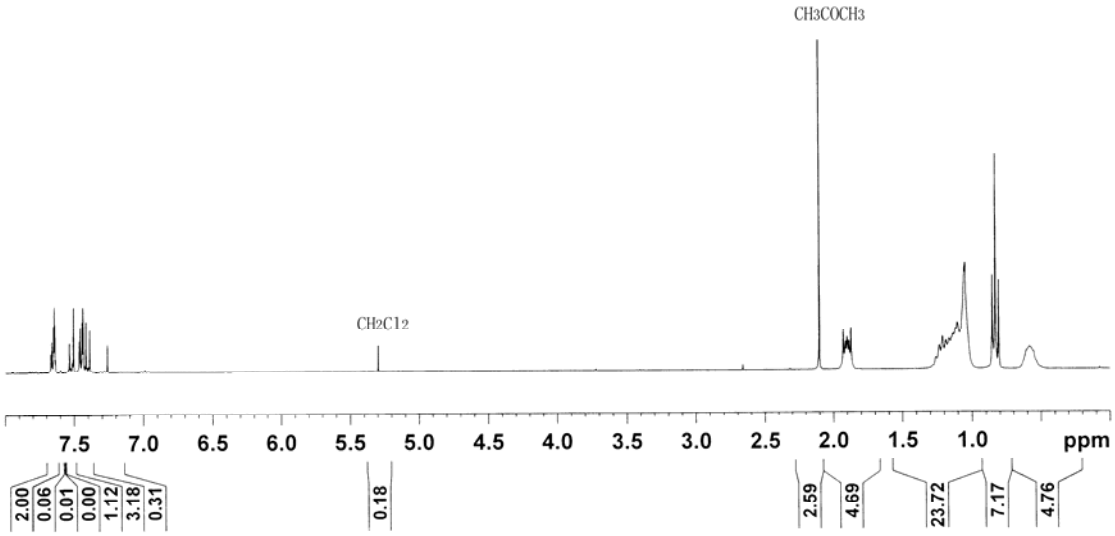


2-bromo-7-iodo-9,9-dioctylfluorene



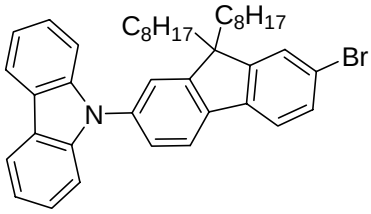
This compound[2] was prepared following the published procedure from 2-bromofluorene using *n*-octyl bromide. ^{1}H NMR (300 MHz,$CDCl_3$) δ (ppm): 0.58-0.62 (m, 4H), 0.84 (t, 6H, J = 9.0 Hz), 1.06-1.28 (m, 20H), 1.92 (t, 4H, J = 9.0 Hz), 7.41-7.55 (m, 4H), 7.66-7.69 (m, 2H).

2-bromo-7-iodo-9,9-dioctylfluorene



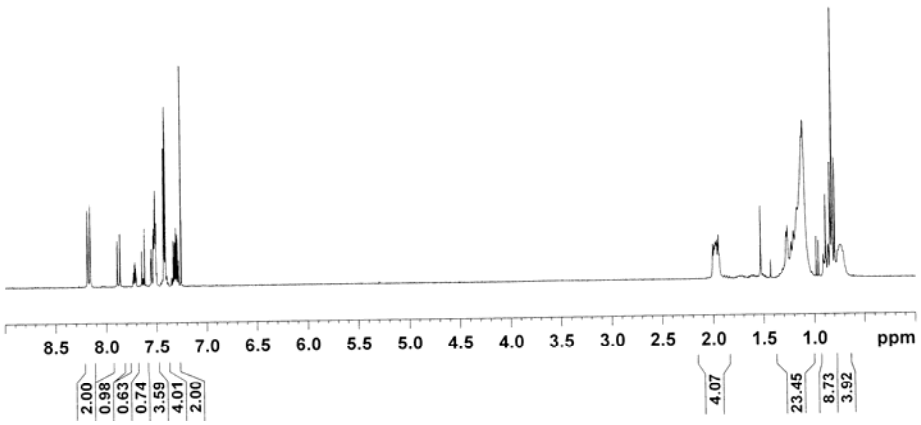
[2] First isolated as a colorless oil; gradual/partial solidification was observed with time.

9-(2-bromo-9,9-dioctylfluoren-7-yl)-9*H*-carbazole



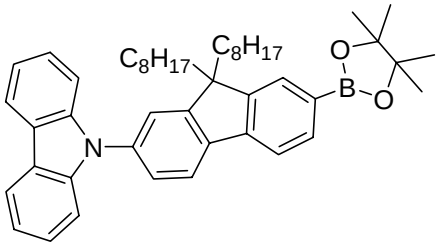
A mixture of CuI (0.35 g, 1.82 mmol), 18-Crown-6 (0.16 g, 0.62 mmol), K_2CO_3 (5.0 g, 36.4 mmol), 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) (1 ml), 2,7-dibromo-9,9-dioctylfluorene (12 g, 21.9 mmol) and carbazole (3.0 g, 18.2 mmol) was heated at 170 °C for 24 h under nitrogen. After being cooled to room temperature, the mixture was quenched with 1 *N* HCl and extracted with dichloromethane. The combined organic phase was washed with water, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified on a silica gel column by gradient elution with petroleum ether/dichloromethane to afford a colorless oil. Yield: 5.82 g (51%). TLC R_f (10:1 petroleum ether/dichloromethane v/v): 0.47. ^{1}H NMR (300 MHz,$CDCl_3$) δ (ppm): 0.73 (m, 4H), 0.82 (t, 6H, J = 7.0 Hz), 1.10 (m, 20H), 1.93-2.00 (m, 4H), 7.28-7.33 (m, 2H), 7.42 (d, 4H, J = 3.0 Hz), 7.49-7.73 (m, 5H), 7.87 (d, 1H, J = 7.9 Hz), 8.17 (d, 2H, J = 7.7 Hz).

9-(2-bromo-9,9-dioctylfluoren-7-yl)-9H-carbazole

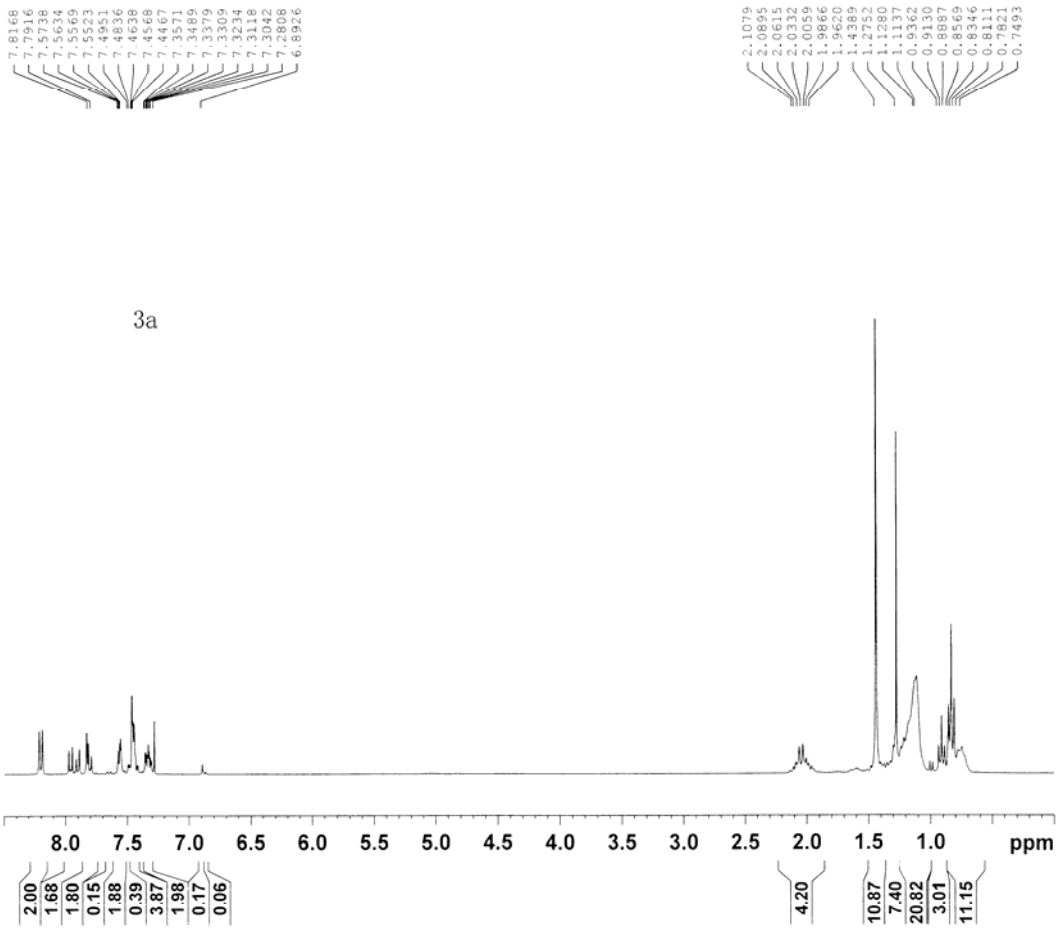


9-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluoren-7-yl)-9*H*-carbazole

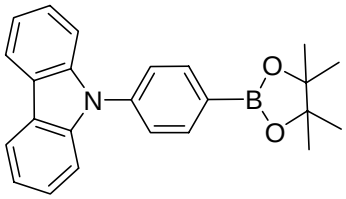
3a



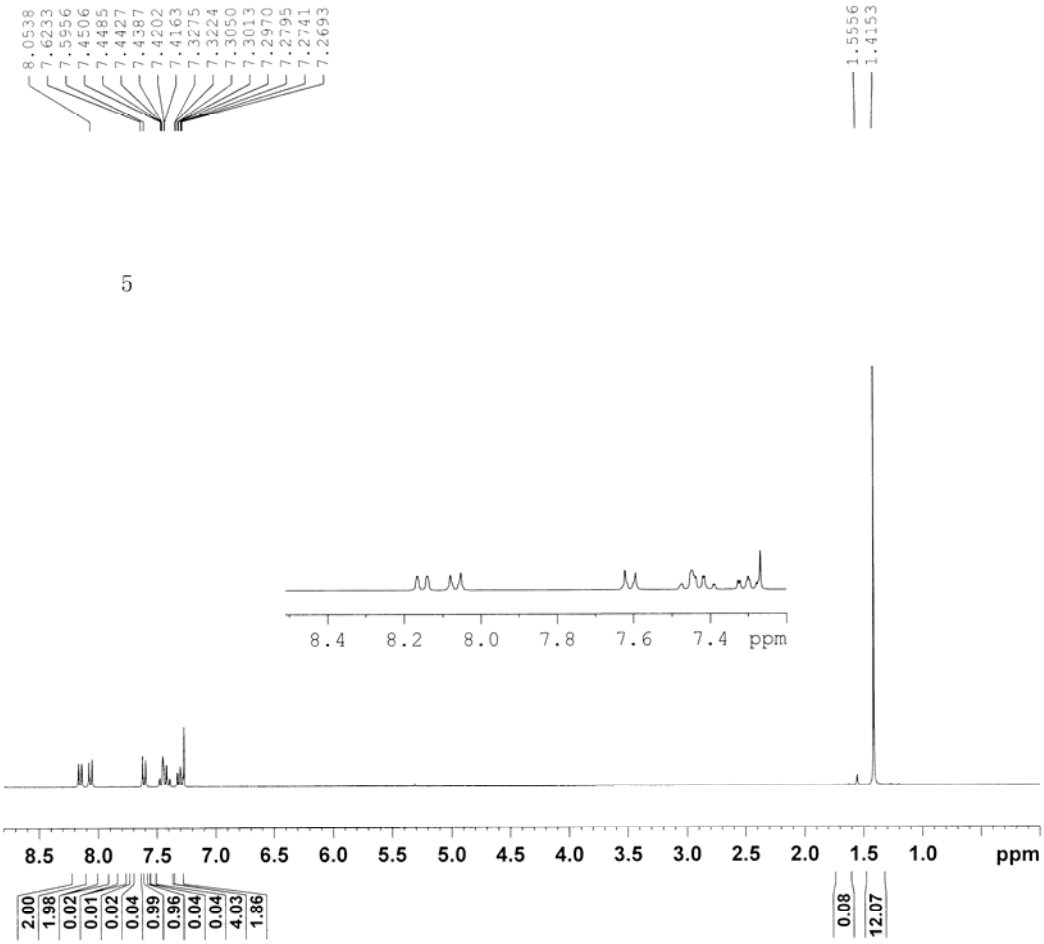
This compound was synthesized as a colorless oil by a similar method for 4,4,5,5-tetramethyl-2-(1-methyl-naphthalen-4-yl)-1,3,2-dioxa-borolane using 9-(2-bromo-9,9-dioctyl-fluoren-7-yl)-9*H*-carbazole. Yield: 75%. TLC R_f (3:1 petroleum ether/ dichloromethane v/v): 0.55. ^{1}H NMR (300 MHz,$CDCl_3$) δ (ppm): 0.75 (m, 4H), 0.83 (t, 6H, J = 7.5 Hz), 1.11 (m, 20H), 1.44 (s, 12H), 1.96-2.11 (m, 4H), 7.28-7.35 (m, 2H), 7.44-7.50 (m, 4H), 7.55-7.57 (m, 2H), 7.79-7.83 (m, 2H), 7.89-7.97 (m, 2H), 8.20 (d, 2H, J = 8.1 Hz).



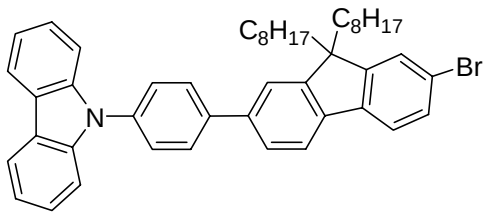
9-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9*H*-carbazole 5



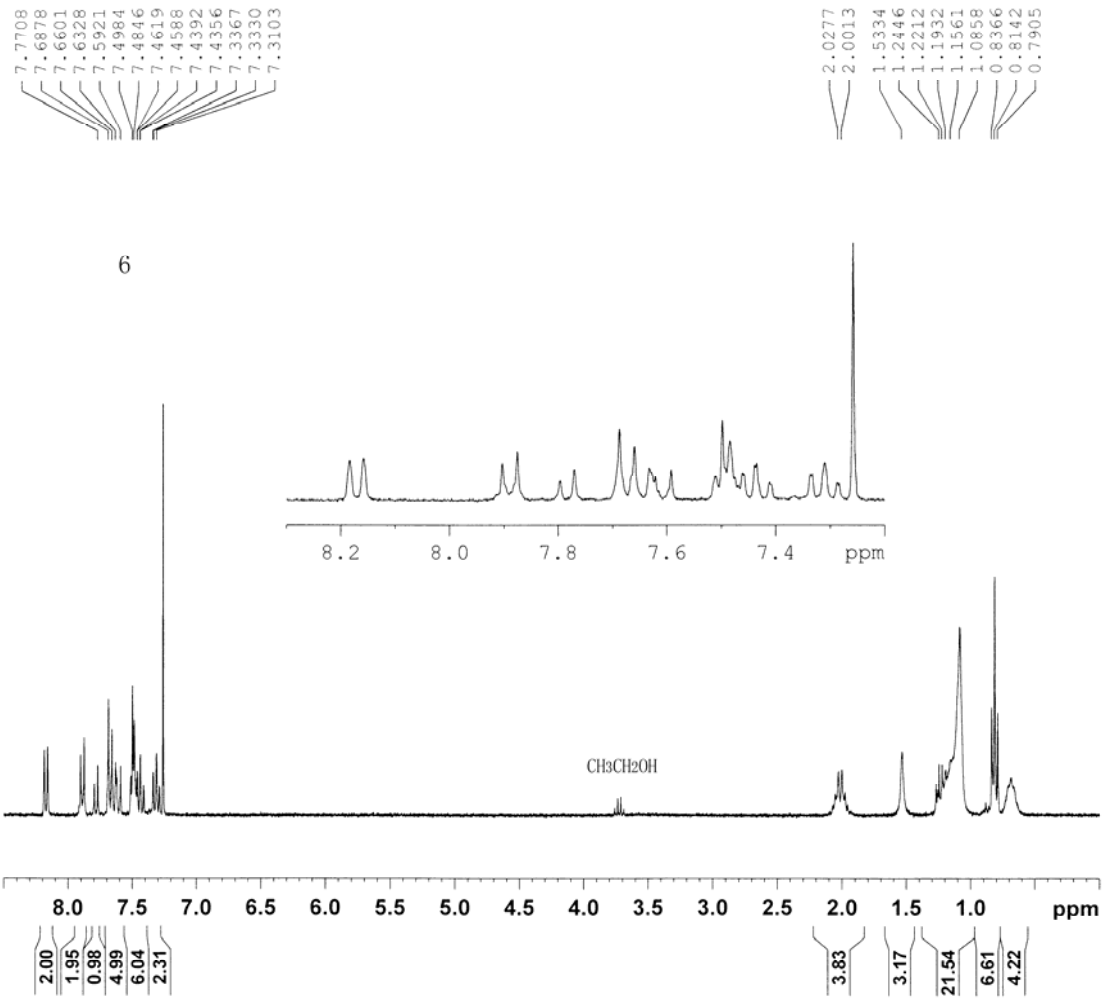
This compound was synthesized by a similar method for 4,4,5,5-tetramethyl-2-(1-methylnaphthalen-4-yl)-1,3,2-dioxaborolane as a white solid using 9-(4-bromophenyl)-9*H*-carbazole. Yield: 86%. TLC R_f (2:1 petroleum ether/ dichloromethane v/v): 0.47. mp 83-84 °C.^{1}H NMR (300 MHz,$CDCl_3$) δ (ppm): 1.42 (s, 12H), 7.27-7.32 (m, 2H), 7.41-7.45 (m, 4H), 7.61 (d, 2H, J = 8.1 Hz), 8.06 (d, 2H, J = 8.1 Hz), 8.15 (d, 2H, J = 7.7 Hz).



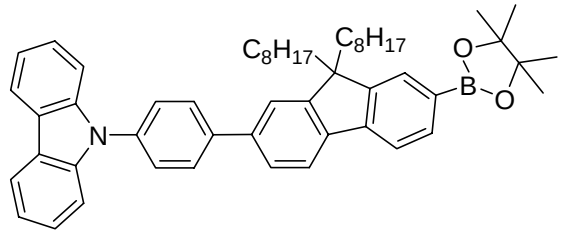
9-(4-(2-bromo-9,9-dioctylfluoren-7-yl)phenyl)-9*H*-carbazole 6



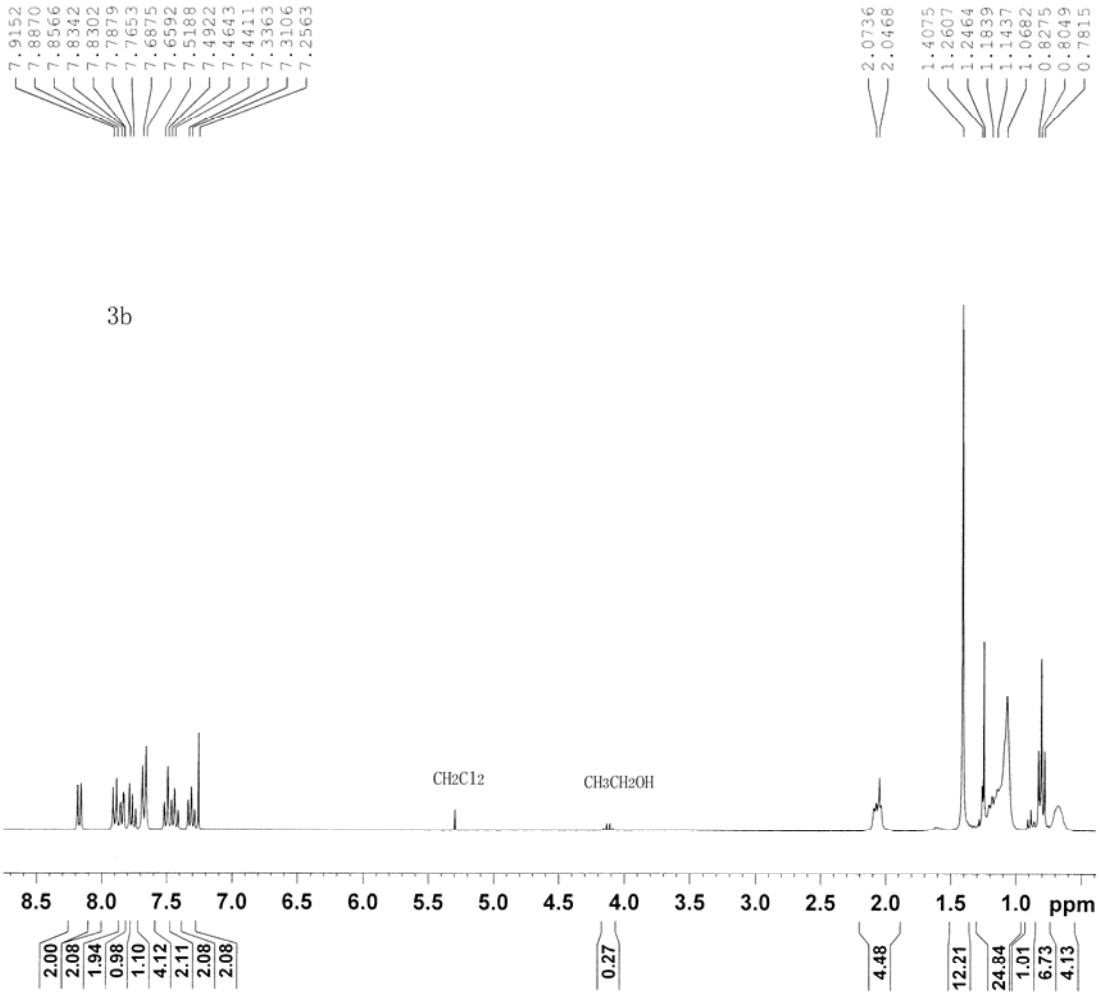
This compound was synthesized as a white solid by a similar method for 5-bromo-2-(1-methylnaphthalen-4-yl)pyridine using 2-bromo-7-iodo-9,9-dioctyl-fluorene and **5**. Yield: 54%. TLC R_f (petroleum ether):0.46. mp 125-127 °C. ^{1}H NMR (300 MHz,$CDCl_3$) δ (ppm): 0.68 (m, 4H), 0.81 (t, 6H, J = 7.1 Hz), 1.13-1.24 (m, 20H), 1.93-2.09 (m, 4H), 7.31 (td, 2H, J_1 = 7.4 Hz, J_2 = 0.99 Hz), 7.41-7.51 (m, 6H), 7.59-7.69 (m, 5H), 7.78 (d, 1H, J = 7.7 Hz), 7.89 (d, 2H, J = 8.3 Hz), 8.17 (d, 2H, J = 7.6 Hz). Elemental analysis (%) calcd for $C_{47}H_{52}BrN$: C, 79.42; H, 7.37; N, 1.97. found: C, 79.27; H, 7.04; N, 1.86. MALDI-TOF MS: m/z 709.7(100%) M^+ (Calcd.709.3).



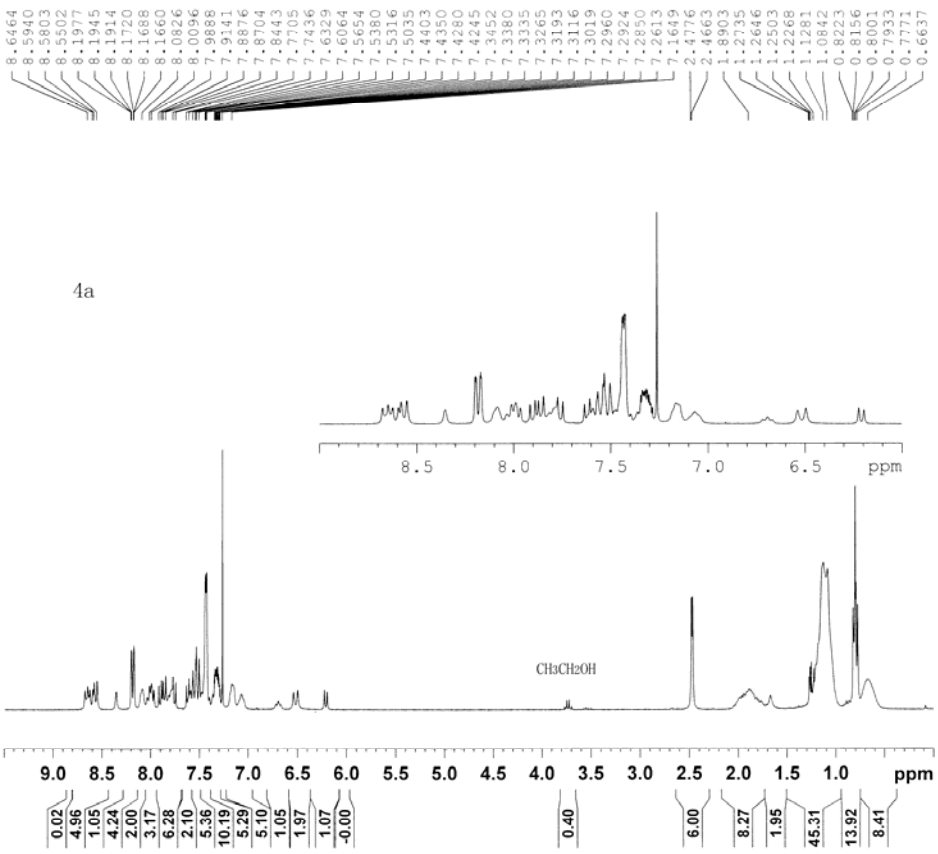
9-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluoren-7-yl)phenyl)-9*H*-carbazole 3b



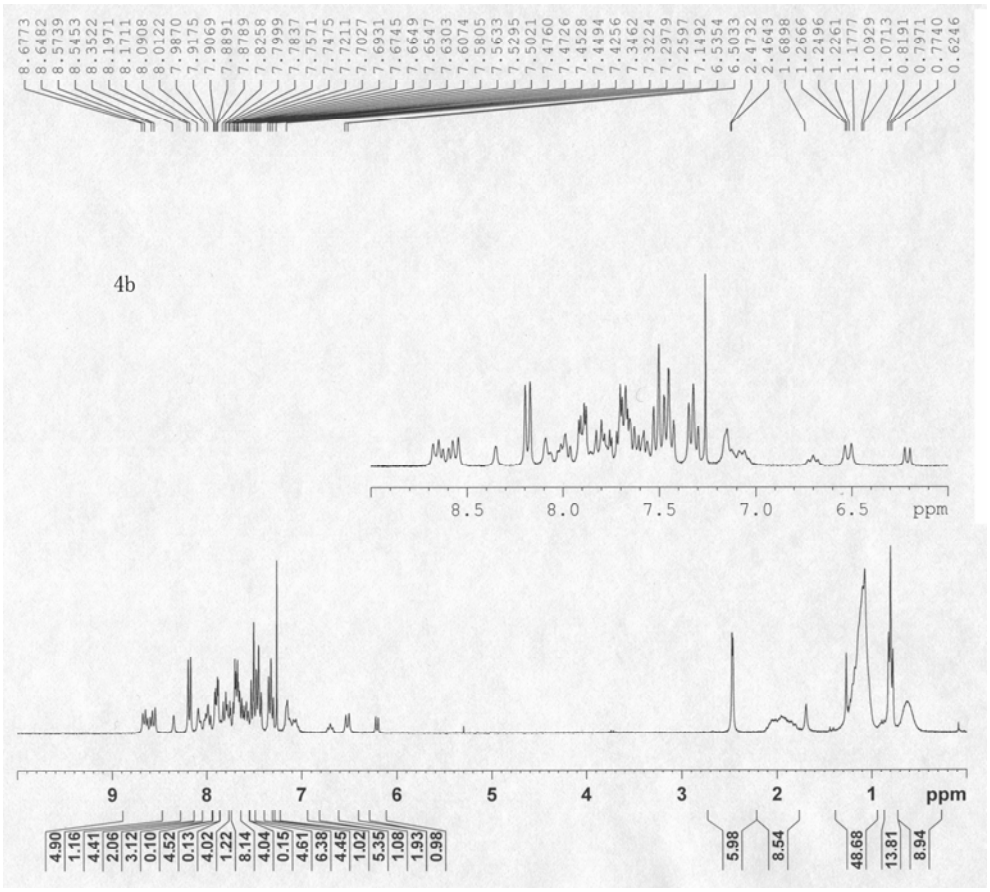
This compound was synthesized as a white solid by a similar method for 4,4,5,5-tetramethyl-2-(1-methylnaphthalen-4-yl)-1,3,2-dioxaborolane using **6**. Yield: 90%. TLC R_f (4:1 petroleum ether/ dichloromethane v/v):0.63. ^{1}H NMR (300 MHz,$CDCl_3$) δ (ppm): 0.65 (m, 4H), 0.80 (t, 6H, J = 7.2 Hz), 1.07-1.26 (m, 20H), 1.41(s, 12H), 2.05-2.07 (m, 4H), 7.31 (t, 2H, J = 7.5 Hz), 7.44 (t, 2H, J = 8.1 Hz), 7.50 (d, 2H, J = 7.9 Hz), 7.67 (d, 4H, J = 8.5 Hz), 7.76 (d, 1H, J = 7.5 Hz), 7.78 (s, 1H), 7.84 (d, 2H, J = 7.5 Hz), 7.90 (d, 2H, J = 8.4 Hz), 8.17 (d, 2H, J = 7.7 Hz).



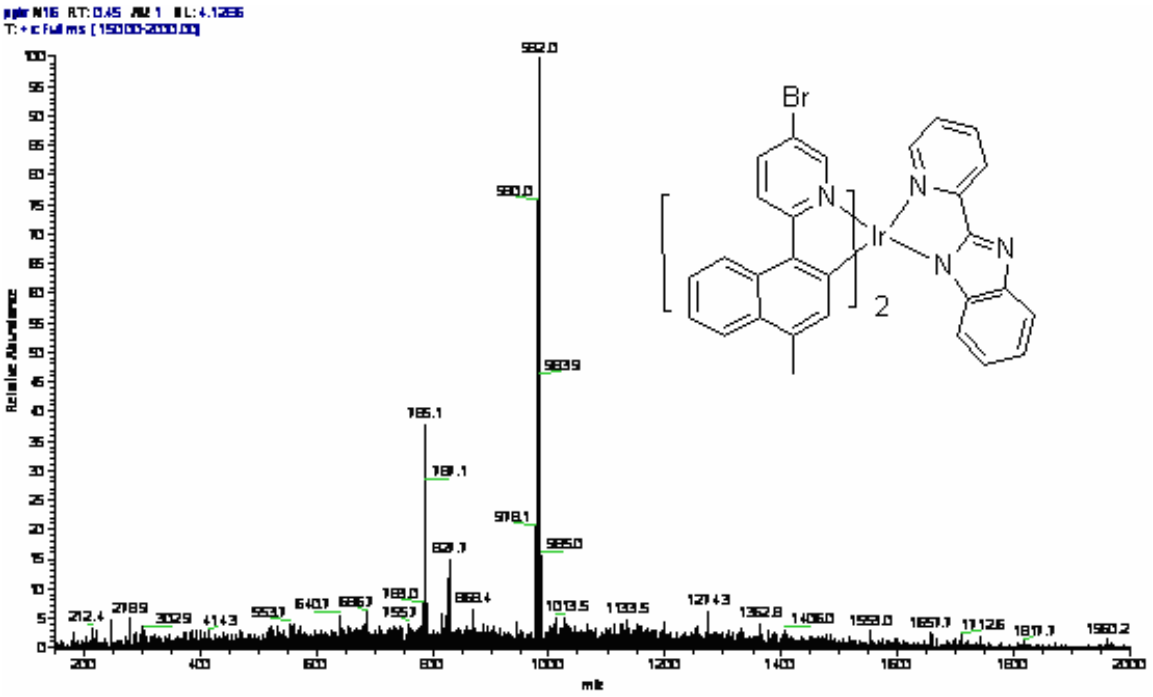
H NMR spectrum of **4a**



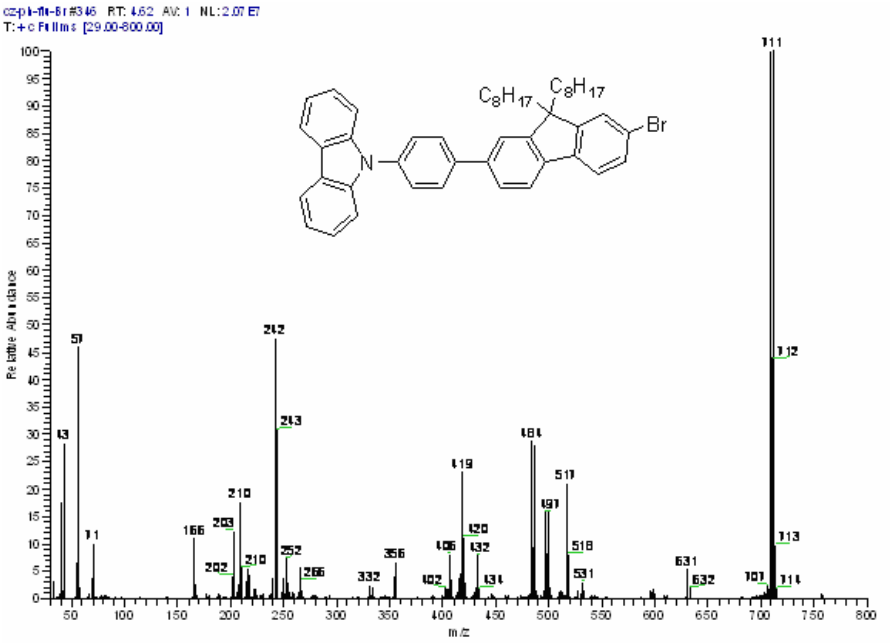
^{1}H NMR spectrum of **4b**



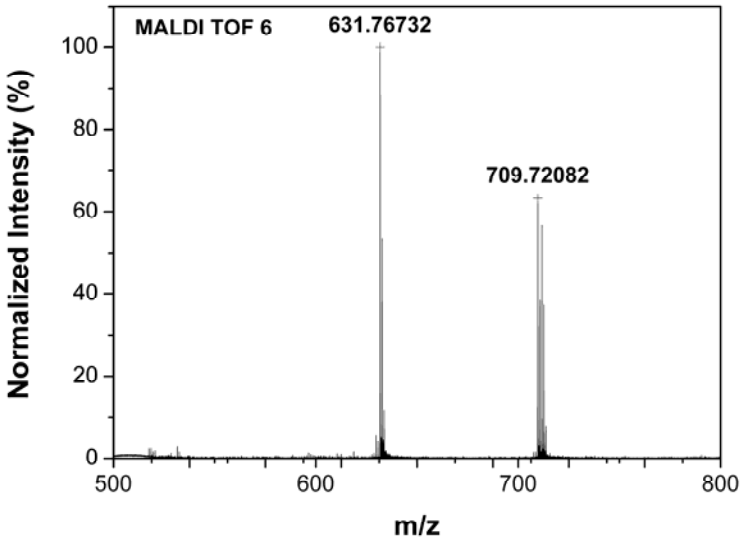
ESI MS of 2



The fragment m/z 785.1 corresponding to $[M\text{-}2\text{-}(2\text{-pyridyl})\text{benzimidazolate}]^+$



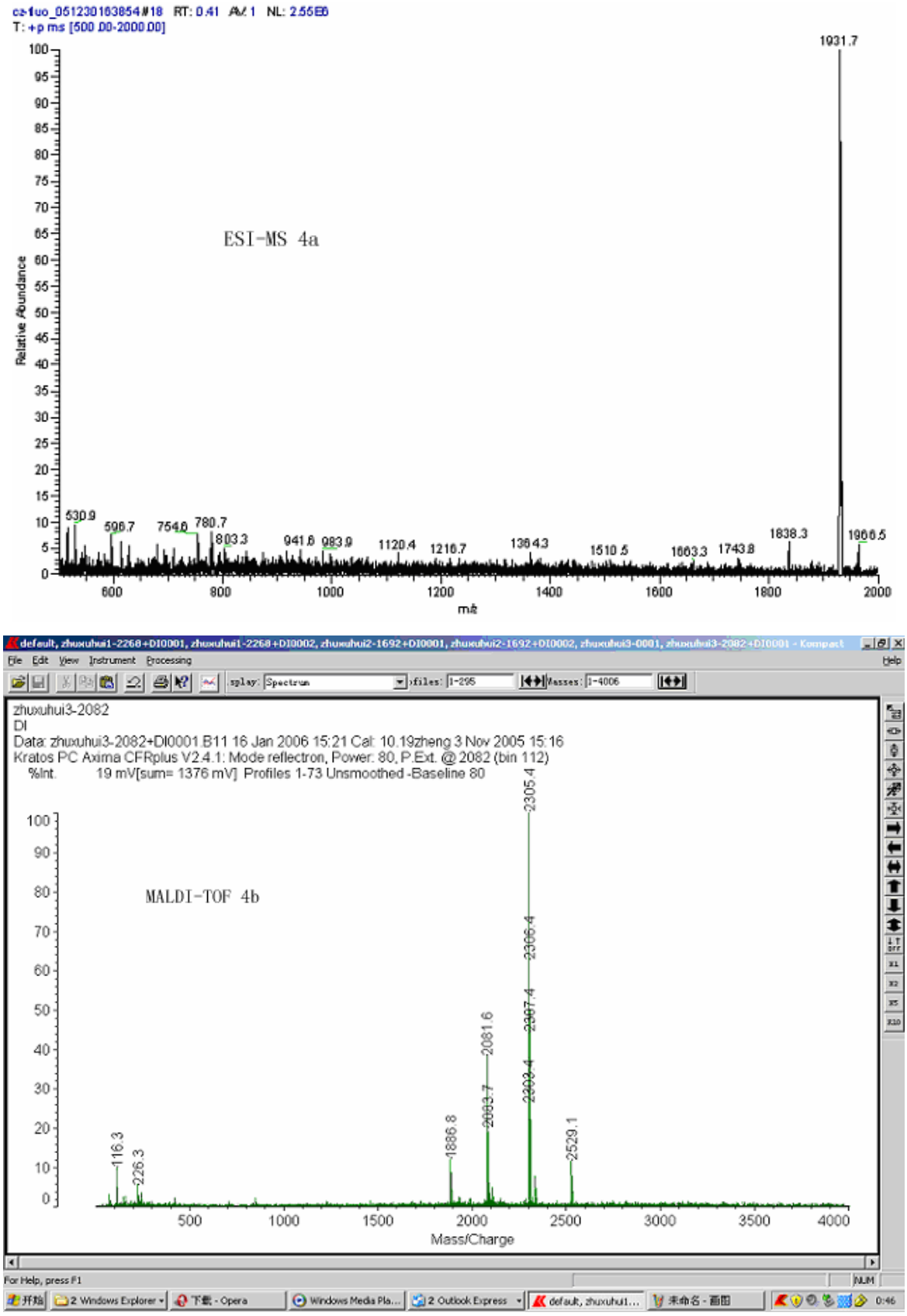
(a)



(b)[3]

MS of **6**: EI (a); MALDI-TOF (b)

[3] Upon increasing the laser energy, the intensity ratio I[M^+(637.8)]/I[M^+(709)] is enlarged. Additionally, based on the EI mass spectrum (**a**), H NMR and microanalysis of **6**, the fragment m/z 631.8(100%) in MALDI-TOF mass spectrum resulted from loss of the bromo atom by the parent bromide **6**.



ESI-MS of **4a** and MALDI-TOF mass spectrum of **4b**

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1. (a) Woo, E. P.; Inbasekaran, M.; Shiang, W.; Roof, G. R. *WO97/05184*, 1997. (b) Lee, J. I.; Klaerner, G.; Miller, R. D. *Chem. Mater.* **1999**, *11*, 1083.

2. Zhang, Q.; Chen, J. S.; Cheng, Y. X.; Wang, L. X.; Ma, D. G.; Jing, X. B.; Wang, F. S. *J. Mater. Chem.* **2004**, *14*, 895.

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