

Blue light-emitting and hole-transporting amorphous molecular materials based on diarylaminobiphenyl-functionalized bimesitylenes

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Experimental Section

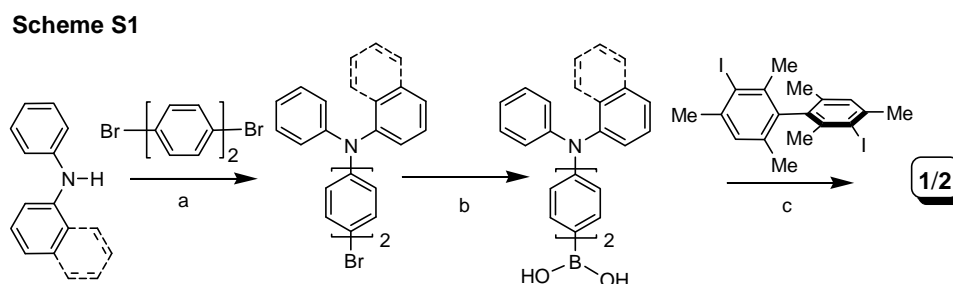
General Aspects. All the Pd-mediated cross-coupling reactions were performed under a nitrogen gas atmosphere in oven-dried pressure tubes. ^1H and ^{13}C NMR spectra were recorded on JOEL (400 MHz) spectrometer or Bruker AMX (400 MHz) in CDCl_3 as a solvent. Chemical shifts are reported in δ -scale downfield from tetramethylsilane. The FAB-Mass spectra were recorded on Jeol SX-102 mass system using argon/xenon as the FAB gas in a linear mode with *m*-nitrobenzyl alcohol as the matrix. The TGA and DSC measurements were carried out using a Perkin-Elmer instrument (Pyris-6 or DSC-7) at 10 °C/min under a nitrogen or argon gas atmosphere. UV-vis absorption spectra were recorded using a Jasco-550 spectrophotometer. Photoluminescence spectra were recorded using Spex Fluolog-2/Hitachi F-4500 spectrofluorimeter. The photoluminescence spectra of solutions were recorded in spectral grade solvents using 90° angle of detection, and those of the thin solid films by front-face detection. The PL quantum yields of the vacuum deposited films (1000 Å) were determined using the integrating sphere method. The ionization potentials were determined using photoelectron spectroscopy (Reiken Keiki AC-2) with UV intensity 5-30 nW. The current voltage (*I-V*) characteristics were recorded by Keithley model 2400 electrometer. The EL spectra were recorded using Hitachi F-4500 Spectrofluorimeter by blocking the incident radiation. The Commission Internationale de L'Eclairage (CIE) coordinates of the devices were determined by a PR650 spectroscan spectrometer.

Dry tetrahydrofuran (THF) and toluene were freshly distilled over sodium prior to use. All reactions were monitored by analytical thin layer chromatography (TLC) using commercial

aluminum sheets pre-coated with silica gel. Chromatography was conducted on silica gel (Acme, Mumbai, 60-120 mesh). All commercial chemicals were used as received.

The starting material bimesitylene¹ was synthesized according to the earlier reported procedure established from our laboratories. 4-Bromo-4'-diphenylaminobiphenyl,² 4-bromo-4'-(1-naphthylphenylamino)biphenyl,^{2b} 4-(diphenylamino)biphenyl-4'-boronic acid,^{2a} and 4-(1-naphthylphenylamino)biphenyl-4'-boronic acid³ were prepared following the literature-reported procedures; ¹H and ¹³C NMR were found to match with the reported ones.

General Scheme for the Synthesis of Triarylamine-anchored Bimesitylene Scaffolds 1 and 2.



^a Reagents and conditions: (a) Pd(OAc)₂, dppf, *t*-BuONa, 1,4-dibromobenzene or 4,4'-dibromobiphenyl (excess, 3-4 equiv), dry toluene, 110 °C, 36 h, 70-74%; (b) *n*-BuLi, THF, -78 °C, 30 min, B(*Oi*-Pr)₃, -78 °C-rt, 90 min, 58-74%; (c) Pd(PPh₃)₄, 2M K₂CO₃, toluene:THF (8:2), 90 °C, 24-48 h, 58-69%.

The triarylamine-anchored molecular systems based on bimesitylene were conveniently synthesized by 2-fold Suzuki coupling procedure using 3,3'-diiodobimesityl and the corresponding diarylamino-biphenylboronic acids as coupling partners.

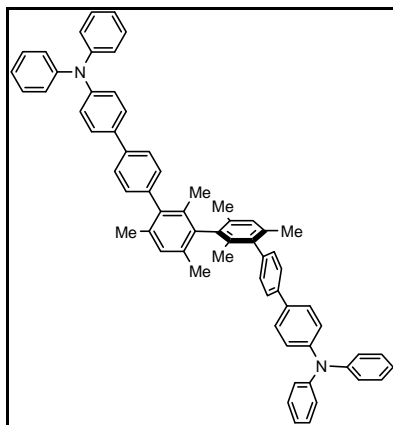
3,3'-Diiodobimesityl. In a two-necked round bottom flask, bimesityl (0.40 g, 1.68 mmol) was dissolved in 8 mL of CH₃CN. To this, 0.83 g (3.69 mmol) of NIS was added followed by 0.08 mL of TFA (catalytic amount) under ice-cold conditions. The reaction mixture was allowed to stir for 8 h. Subsequently, the reaction mixture was concentrated and the organic matter was extracted with CHCl₃. The combined organic extract was washed with NaHCO₃ solution followed by brine, dried over anhyd Na₂SO₄, filtered and evaporated to dryness. A careful silica-gel column chromatography using CHCl₃ and pet. ether afforded the diiodobimesityl as a colorless compound, 0.68 g (83% yield). IR (KBr) cm⁻¹ 2970, 2947, 2915, 1449, 1375; ¹H NMR (CDCl₃, 400 MHz) δ 1.78 (s, 6H), 2.07 (s, 6H), 2.48 (s, 6H), 7.03 (s, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 19.6, 26.7, 29.9, 106.2, 129.0, 135.2, 138.3, 138.8, 140.7.

General Procedure for the Synthesis of Triarylamine-Functionalized Bimesitylenes via Two-fold Suzuki Coupling.

The following is a representative procedure for the two-fold Suzuki coupling.

Preparation of 3,3'-Bis(4'-diphenylaminobiphenyl-4-yl)bimesityl 1. 3,3'-diiodobimesityl (0.80 g, 1.63 mmol), 4-(diphenylamino)biphenyl-4'-boronic acid (1.78 g, 4.89 mmol) and Pd(PPh₃)₄ (0.15 g, 8 mol%) were introduced into an oven-dried pressure tube under N₂. To this mixture, a mixture of dry THF and toluene (5 and 10 mL, respectively) and 2M K₂CO₃ solution (6 mL) were added. The reaction mixture was heated slowly from 60 to 90 °C, and maintained at this temperature for 24 h with constant stirring. After this period, the reaction

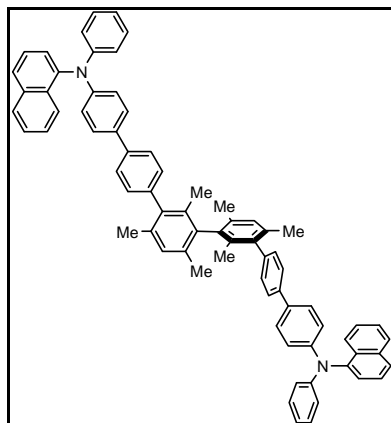
mixture was cooled and the contents were extracted with CHCl_3 . The pure compound was obtained as a colorless solid material after a column chromatography over silica gel.



1. Yield 69%. Colorless powder; IR (KBr) cm^{-1} 3027, 2916, 1590, 1491; ^1H NMR (500 MHz, CDCl_3) δ 1.68 (s, 6H), 1.97 (s, 6H), 2.09 (s, 6H), 7.04 (t, $J = 7.5$ Hz, 4H), 7.08 (s, 2H), 7.12-7.18 (m, 12H), 7.20-7.24 (m, 4H), 7.28 (t, $J = 7.5$ Hz, 8H), 7.56 (d, $J = 8.5$ Hz, 4H), 7.63 (t, $J = 10.0$ Hz, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 17.9 (q), 20.0 (q), 21.0 (q), 122.8 (d), 124.0 (d), 124.3 (d), 126.4 (d), 127.6 (d), 128.8 (d), 129.2 (d), 129.9 (d), 133.6 (s), 134.2 (s), 134.3 (s), 134.9 (s), 138.1 (s), 138.4 (s), 139.6 (s), 140.4 (s), 147.0 (s), 147.7 (s); FAB-MS 876 (M^+). Elemental analysis Calcd for $\text{C}_{66}\text{H}_{56}\text{N}_2$: C, 90.37; H, 6.43; N, 3.19; found C, 90.00; H, 6.21; N, 3.82.

Preparation of 3,3'-Bis(4'-(1-naphthylphenylamino)biphenyl-4-yl)bimesityl 2. This compound was prepared by following the general procedure described above. 3,3'-

Diiodobimesityl and 4-(1-naphthylphenylamino)biphenyl-4'-boronic acid were used as the Suzuki-coupling partners.



2. Yield 58%. Colorless powder; IR (KBr) cm^{-1} 3028, 2917, 2855, 1591, 1492, 1290, 1269; ^1H NMR (500 MHz, CDCl_3) δ 1.68 (s, 6H), 1.96 (s, 6H), 2.07 (s, 6H), 6.96 (dt, $J_t = 7.5$ Hz, $J_d = 1.0$ Hz, 2H), 7.06 (s, 2H), 7.09 (d, $J = 8.5$ Hz, 8H) 7.14-7.25 (m, 8H), 7.34-7.39 (m, 4H), 7.45-7.52 (m, 8H), 7.60 (t, $J = 8.5$ Hz, 4H), 7.79 (d, $J = 8.0$ Hz, 2H), 7.90 (d, $J = 8.0$ Hz, 2H), 7.97 (d, $J = 8.5$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 17.9 (q), 20.0 (q), 20.9 (q), 121.8 (d), 121.9 (d), 122.1 (d), 124.2 (d), 126.2 (d), 126.1 (d), 126.36 (d), 126.41 (d), 126.5 (d), 127.2 (d), 127.5 (d), 128.4 (d), 128.8 (d), 129.1 (d), 129.8 (d), 131.2 (s), 133.6 (s), 133.8 (s), 134.2 (s), 134.3 (s), 135.3 (s), 138.1 (s), 138.5 (s), 139.6 (s), 140.3 (s), 143.4 (s), 147.7 (s), 148.2 (s); FAB-MS 976 (M^+). Elemental analysis Calcd for $\text{C}_{74}\text{H}_{60}\text{N}_2$: C, 90.95; H, 6.19; N, 2.87; found C, 90.19; H, 6.70; N, 3.06.

PL Quantum Yield Measurements

An Integrating-sphere method⁴ was employed for determination of the quantum yields of **1** and **2** in dichloromethane solutions and in vacuum-deposited thin films. For the latter, the films of compounds **1** and **2** of thickness ca. 1000 Å were prepared on quartz plates (1 mm x 2 cm) by vacuum deposition.

In this protocol, the He-Cd laser beam (325 or 442 nm) interacts with a liquid or solid sample located inside an integrating sphere with internal diffuse white reflectance coating. Through a baffle-blocked opening, the uniformly scattered radiation is coupled to a fused-silica fiber and is detected by a spectrally-calibrated spectrometer-CCD system. The error associated with Φ_f was determined by repeated measurements on several dyes of known Φ_f values. Nile Red (1,4-dioxane) was one of the fluorescent dyes that was employed, for which the Φ_f was determined to be 67±5%. This value is close to the literature value of 68%.⁵

Electrochemical Measurements

The cyclicvoltammetry experiments were performed on a BAS-100 B electrochemical analyzer. Data were collected and analyzed using the electrochemical analysis software. All experiments were carried out in a three electrode compartment cell with a Pt wire counter electrode, a glassy carbon working electrode and Ag/AgNO₃ (0.1 M) reference electrode at varying scan rates. The supporting electrolyte used was 0.1 M tetrabutylammoniumhexafluoro phosphate solution in dry dichloromethane. The cell containing the solution of the sample (1mM) and the supporting electrolyte was purged with a nitrogen gas thoroughly before

scanning for its oxidation and reduction properties. The oxidation and reduction potentials were determined by taking the average of the anodic and cathodic peak potentials. The HOMO and LUMO values were estimated by using the following general equation: $E_{\text{HOMO}} = E_{\text{ox}} + 4.8 \text{ eV}$; $E_{\text{LUMO}} = E_{\text{HOMO}} - E_{\text{g}}^{\text{opt}}$.

Fabrication and Performance Characteristics of OLEDs

The multilayer OLEDs were fabricated by employing the triarylamine-anchored bimesitylenes as emitting/hole-transporting materials. The ITO coated glass substrates with a sheet resistance of $<50 \text{ } \Omega/\text{sq}$ were cleaned sequentially in an ultrasonicator using acetone, detergent solution, deionized water, ethanol, 2-propanol and subjected to oxygen plasma and UV treatments.

Vacuum Deposition. Vacuum deposition of the organic materials such as NPB, **1** or **2**, TPBI, LiF and Al was sequentially carried out under a pressure of 10^{-6} torr on top of etched ITO glass substrates. The rate of deposition for organic materials was maintained in the range of 0.1-0.5 Å/s. The evaporation rate and thickness of the organic layers were monitored by a quartz oscillator. After the vacuum deposition, the devices were sealed in an inert atmosphere glove box. EL spectra of the devices were obtained using a diode-array rapid analyzer system.

Electroluminescence Measurements. Current voltage and light intensity measurements were done on a Keithley 2400 source meter and a Newport 1835C optical meter equipped with a Newport 818-ST silicon photodiode.

References

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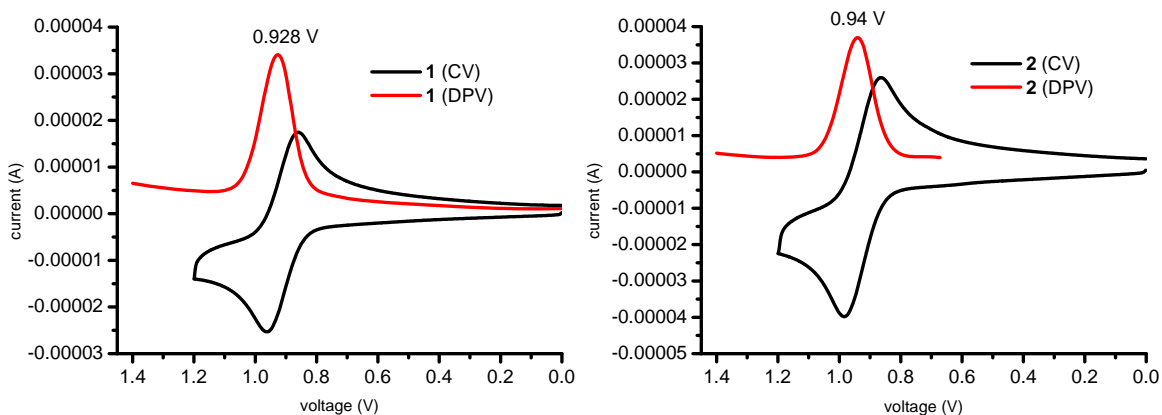


Figure S1. Cyclic voltammograms (black) and differential pulse voltammograms (red) for amines **1** (left) and **2** (right) using tetrabutylammonium hexafluorophosphate as a supporting electrolyte (0.1 M) in dichloromethane; the concentrations the solutions of **1** and **2** were 0.1 mM.

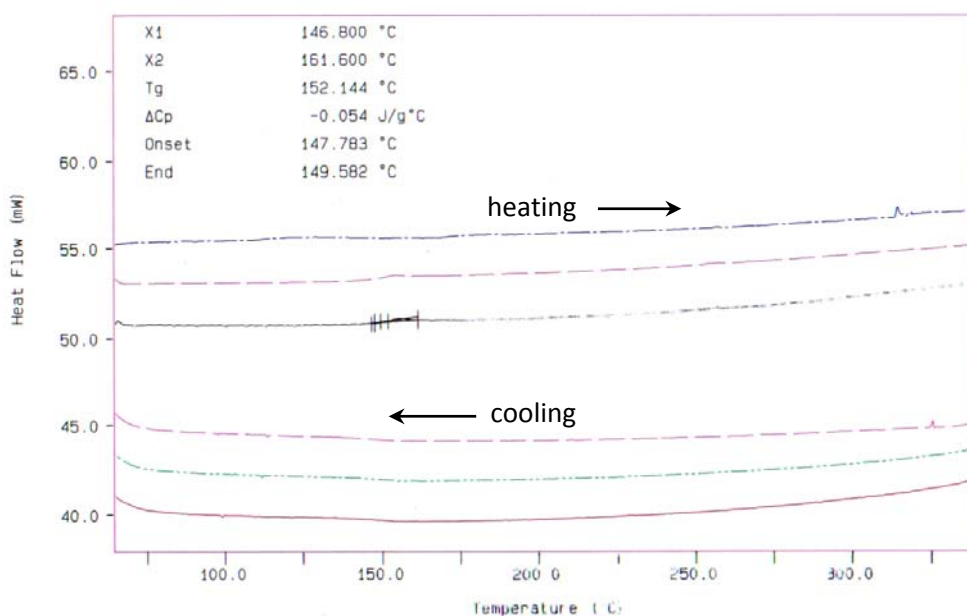


Figure S2. The typical DSC scans of **2** on three heating and cooling cycles.

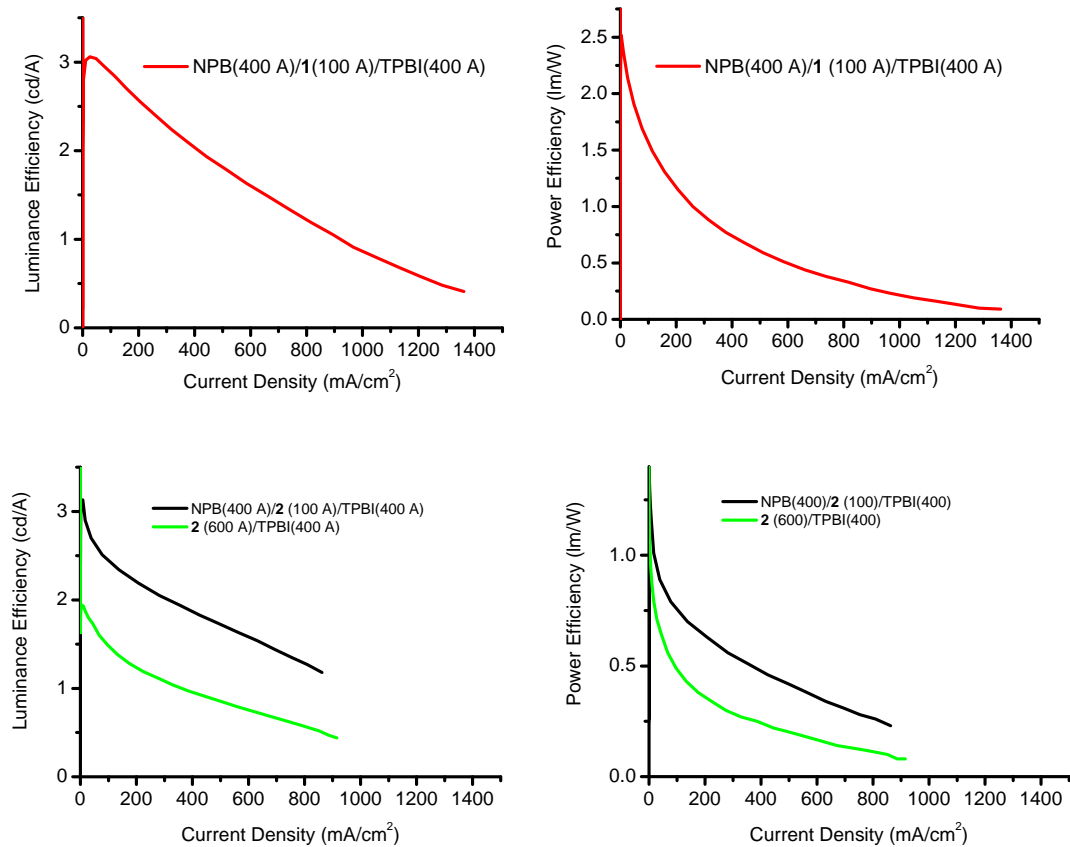


Figure S3. The luminance and power efficiencies for devices **1** and **2**.

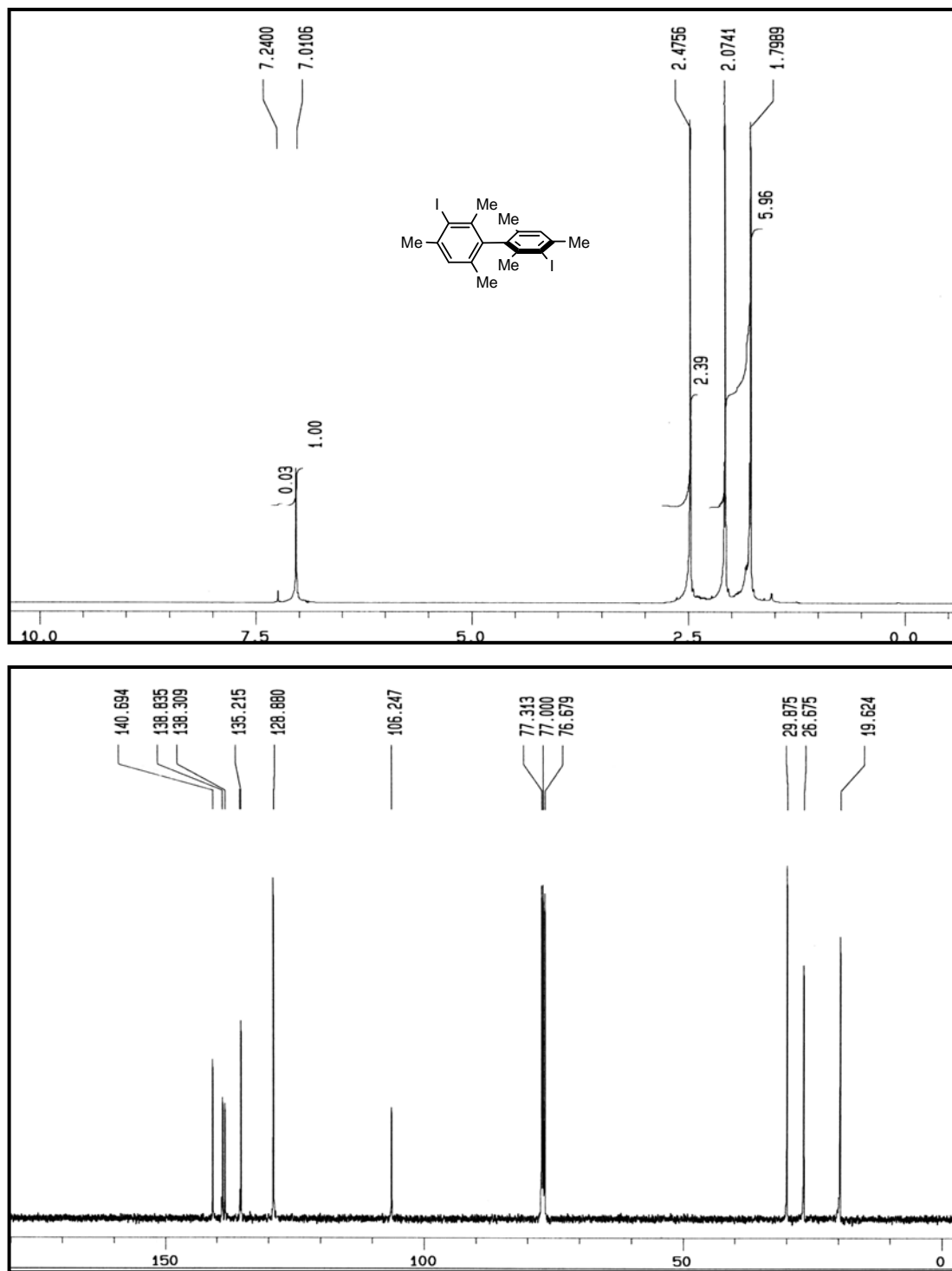


Figure S4. ^1H and ^{13}C NMR spectra of 3,3'-diiodobimesityl.

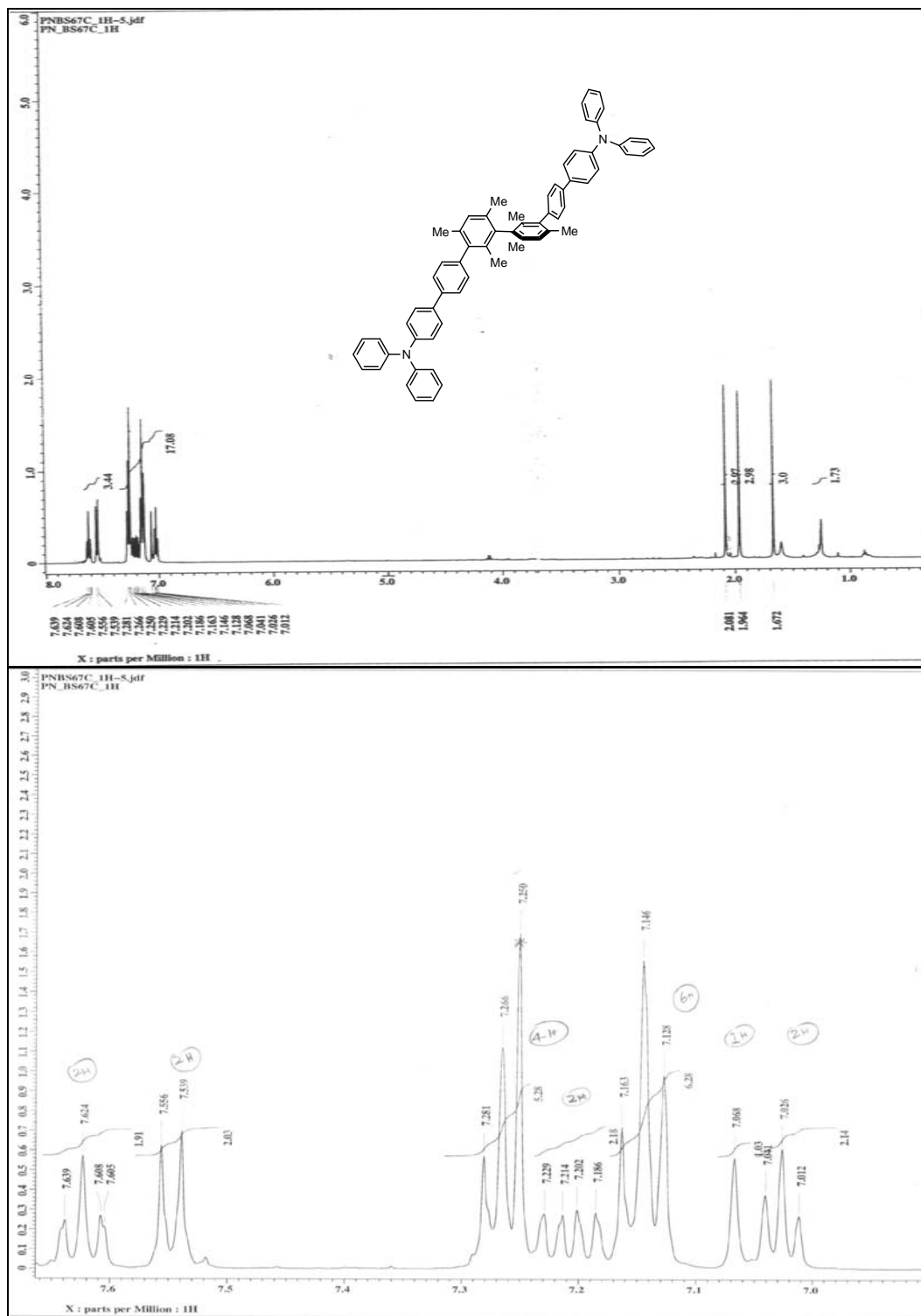


Figure S5. ¹H NMR (500 MHz) spectrum of amine 1 in CDCl₃. The bottom spectrum is an expansion of the aromatic region.

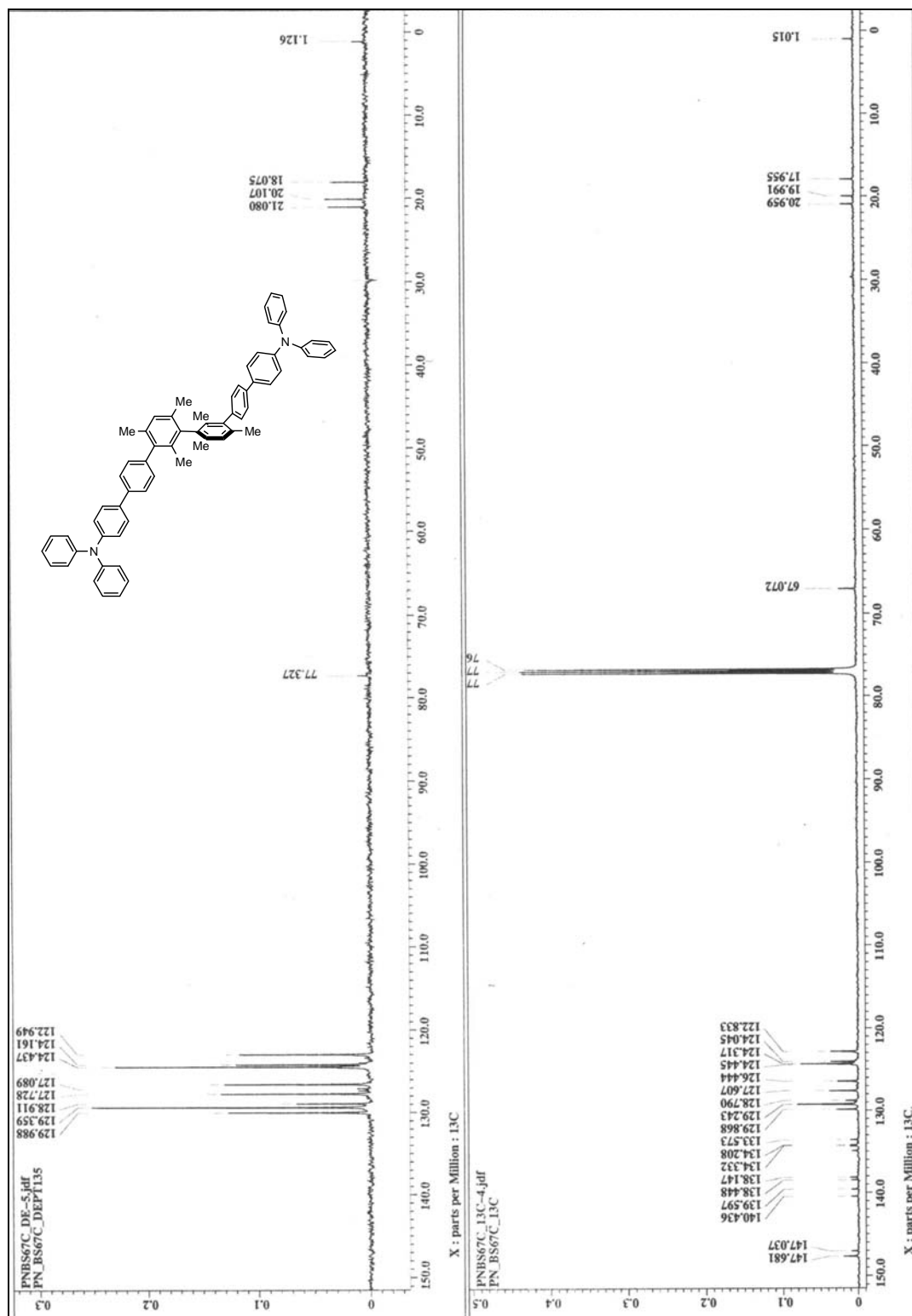


Figure S6. ^1H decoupled ^{13}C NMR spectrum of the amine **1** (bottom) and DEPT 135 (top).

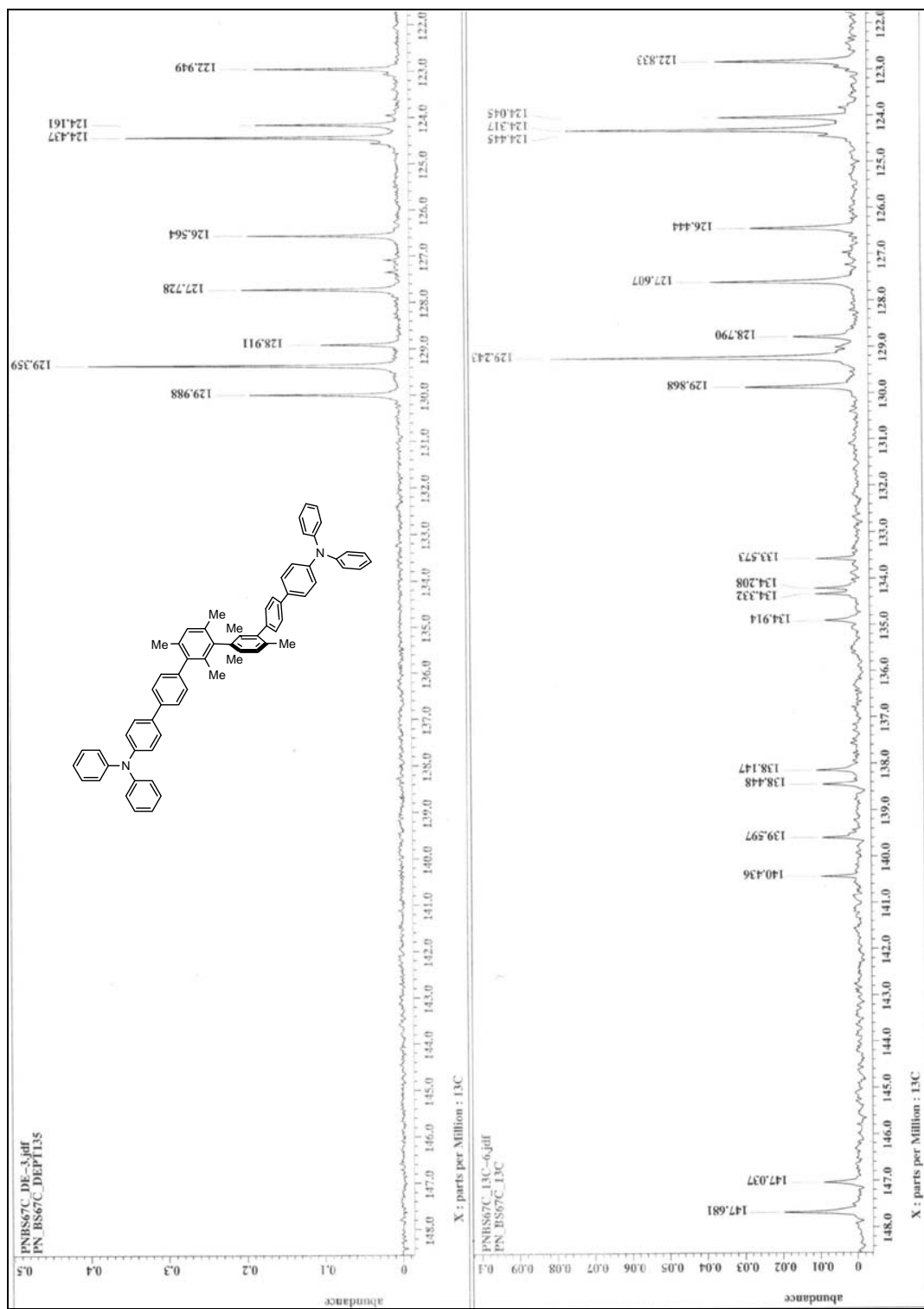


Figure S7. ^1H decoupled ^{13}C NMR spectrum of the amine **1** (bottom) and DEPT 135 (top).

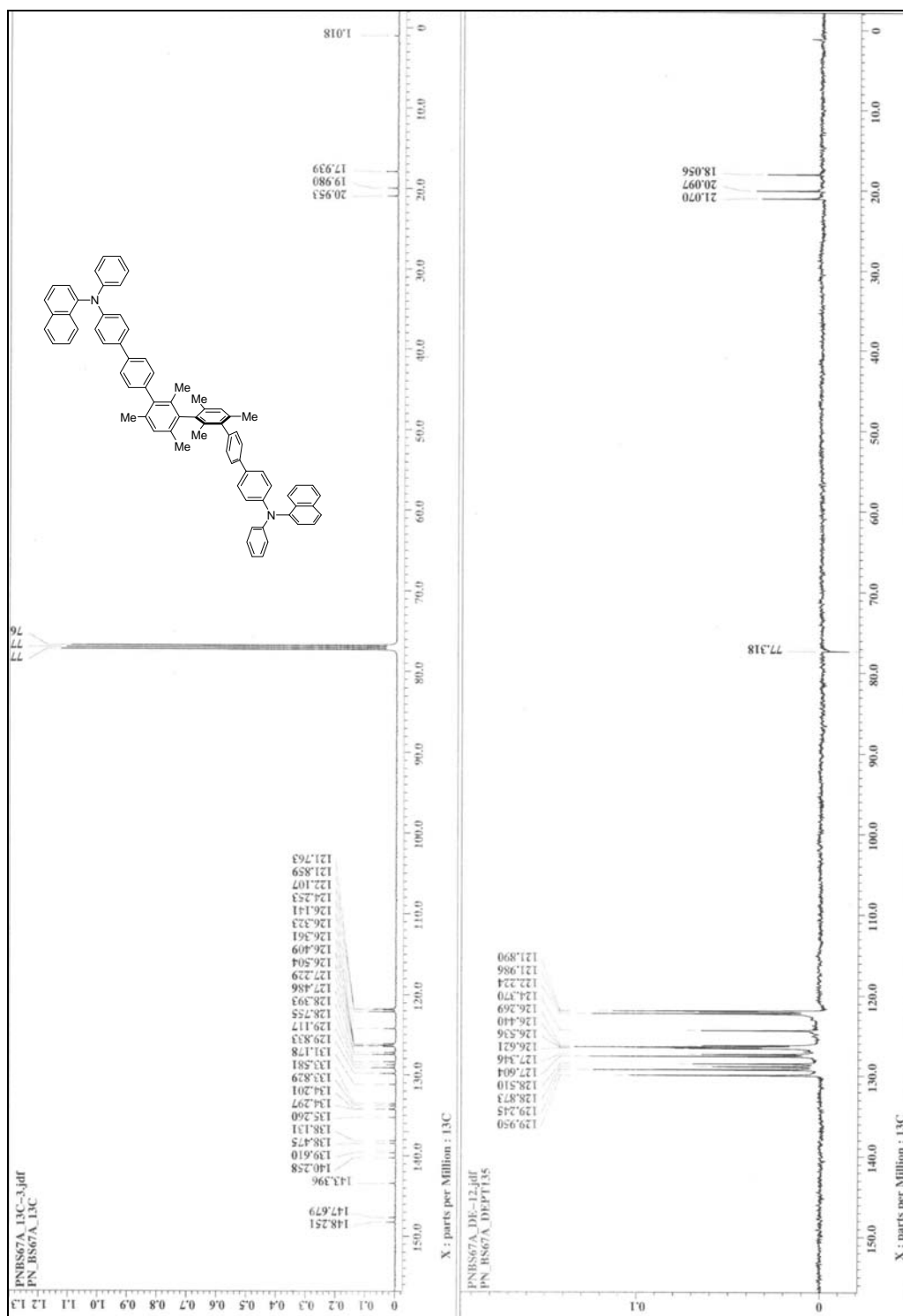


Figure S9. ^1H decoupled ^{13}C NMR of amine 2 (top) and DEPT 135 (bottom).

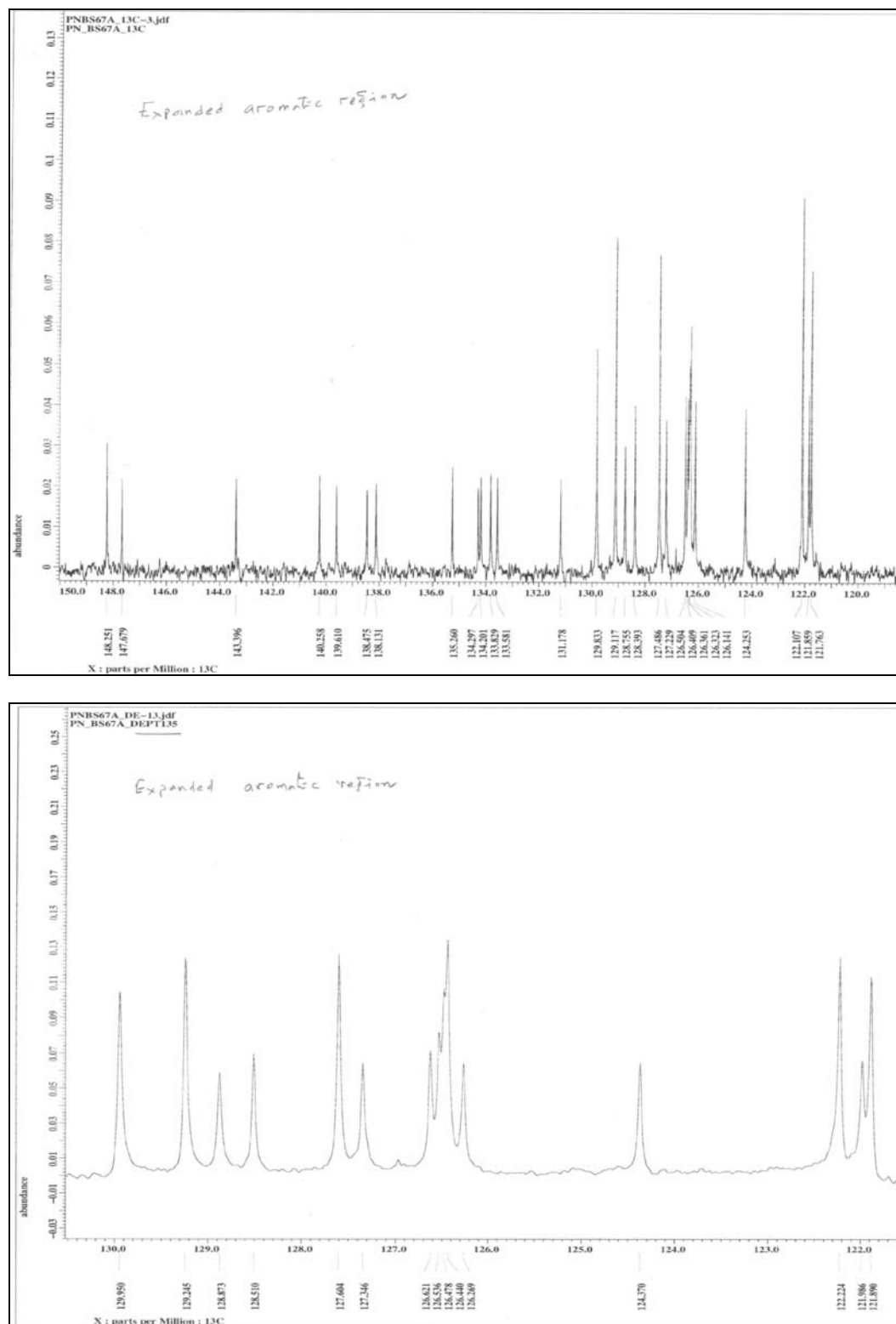


Figure S10. Expansions of ^1H decoupled ^{13}C NMR of amine **2** (top) and DEPT 135 (bottom).

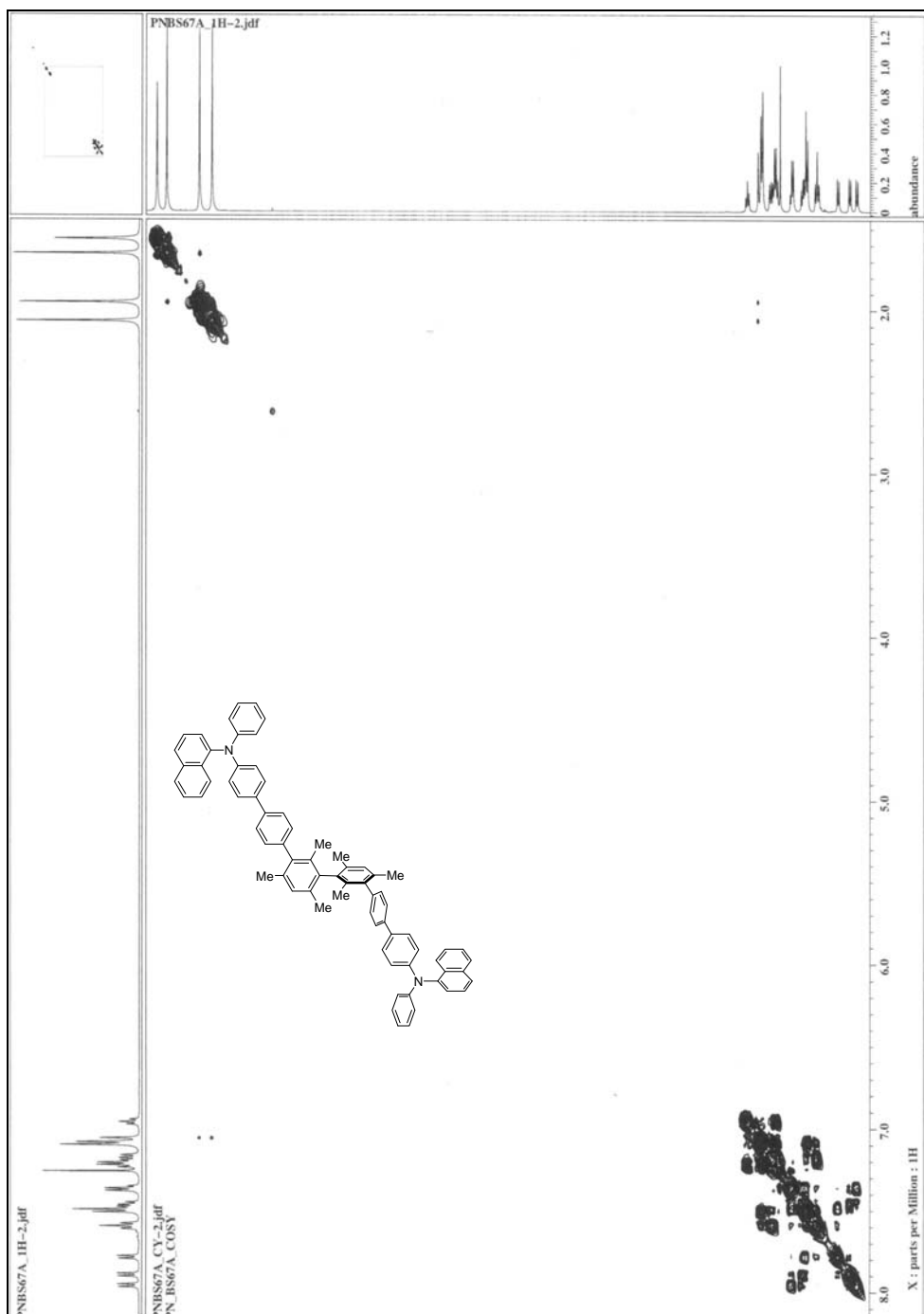


Figure S11. 2-Dimensional COSY spectrum of the amine **2**.

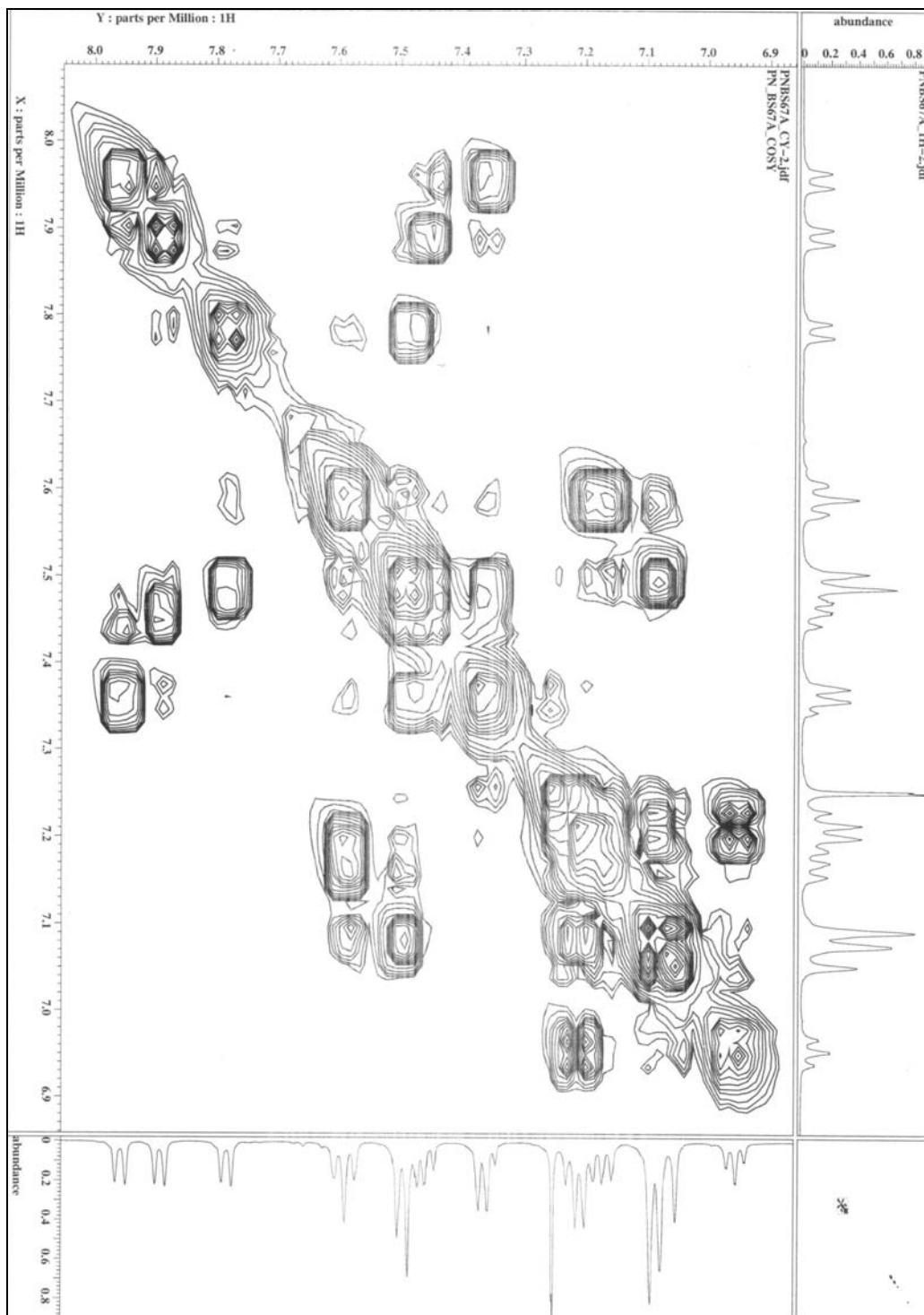


Figure S12. 2-Dimensional COSY spectrum of the diamine **2**.