Electronic Supplementary Information (ESI)

Largely Blue-shifted Emission through Minor Structural Modifications: Molecular Design, Synthesis, Aggregation-Induced Emission and Deep-blue OLED Application

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Experimental Section

Characterization

^{1}H and ^{13}C NMR spectra were measured on a MECUYRVX300 spectrometer. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a CARLOERBA-1106 microanalyzer. Mass spectra were measured on a ZAB 3F-HF mass spectrometer. MALDI-TOF mass spectra were recorded on a GCT premier CAB048 mass spectrometer. High-resolution mass spectra (HR-MS) were recorded on a JEOL LMS-HX-110 spectrometer with 3-nitrobenzyl alcohol (NBA) as a matrix. UV-vis absorption spectra were recorded on a Shimadzu UV-2500 recording spectrometer. Photoluminescence spectra were recorded on a Hitachi F-4500 fluorescence spectrometer. Differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC 822e at a heating and cooling rate of 15 ^{o}C min^{-1} from room temperature to 180 ^{o}C under argon. The glass transition temperature (T_g) was determined from the second heating scan. Thermogravimetric analysis (TGA) was undertaken with a NETZSCH STA 449C instrument. The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their weight loss while heating at a rate of 10 ^{o}C min^{-1} from 25 to 600 ^{o}C. Cyclic voltammetry (CV) was carried out on a CHI voltammetric analyzer in a three-electrode cell with a Pt counter electrode, a Ag/AgCl reference electrode, and a glassy carbon working electrode at a scan rate of 100 mVs^{-1} with 0.1 M tetrabutylammonium perchlorate (purchased from Alfa Aesar) as the supporting electrolyte, in anhydrous dichloromethane solution purged with nitrogen. The potential values obtained in reference to the Ag/Ag^{+} electrode were converted to values versus the saturated calomel electrode (SCE) by means of an internal ferrocenium/ferrocene (Fc^{+}/Fc) standard.

Computational details

The geometrical and electronic properties were optimized at B3LYP/6-31g(d) level using Gaussian 09 program. The molecular orbitals were obtained at the same level of theory.

Preparation of nanoaggregates

Stock THF solutions of the fluorophores were prepared with a concentration of 10^{-3} mol/L. Aliquots of the stock solution were transferred to 10 mL colorimetric cylinders. Then appropriate amounts of THF and water were added successively under vigorous shaking to furnish 10^{-5} M solutions with different water fractions (0-99.9 vol%). The PL measurements of the resultant solutions were then performed immediately.

OLED device fabrication and measurement

The hole-transporting material NPB (1,4-bis(1-naphthylphenylamino)-biphenyl) and electron-transporting material 1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene (TPBI) were obtained from a commercial source. The EL devices were fabricated by vacuum deposition of the materials at a base pressure of 10^{-6} Torr onto glass precoated with a layer of indium tin oxide (ITO) with a sheet resistance of 25Ω/square. Before deposition of an organic layer, the clear ITO substrates were treated with oxgen plasma for 2 min. The deposition rate of organic compounds was 1-2 Å s^{-1}. Finally, a cathode composed of lithium fluoride (1 nm) and aluminium (100 nm) was sequentially deposited onto the substrate in the vacuum of 10^{-6} Torr. The *L-V-J* of the devices was measured with a Keithey 2400 Source meter and a Keithey 2000 Source multimeter equipped with a calibrated silicon photodiode. The EL spectra were measured by JY SPEX CCD3000 spectrometer. All measurements were carried out at room temperature under ambient conditions.

Preparation of compounds

All other chemicals and reagents were obtained from commercial sources and used as received without further purification. Solvents for chemical synthesis were purified according to the standard procedures.

Synthesis of 3,6-Di-*tert*-butyl-9*H*-carbazole

9-*H*-carbazole (3.3 g, 20 mmol), 100 mL of nitromethane, and $ZnCl_2$ (8.1 g, 60 mmol) were added to a three-neck flask under a nitrogen atmosphere. 2-Chloro-2-methylpropane (6.5 ml, 60 mmol) was added dropwise under stirring. The mixture was stirred at room temperature for 5 h and then hydrolyzed with 100 mL of water. The product was extracted with CH_2Cl_2 (3 x 60 mL). The organic layer was washed with H_2O (2 x 150 mL), dried with Na_2SO_4, and evaporated under vacuum to yield 4.5 g (81%) of off-white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): δ 8.08 (d, J = 1.92 Hz, 2H), 7.83 (s b, 1H), 7.49 (dd, J = 8.46, 1.93 Hz, 2H), 7.33 (dd, J = 5.56, 0.49 Hz, 2H), 1.45 (s, 18H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 142.5, 138.3, 123.8, 123.5, 116.4, 110.3, 77.6, 77.3, 77.0, 35.0, 32.3. HRMS (ESI, *m/z*): $[M+H]^+$ for $C_{20}H_{25}N$, 280.2065; found, 280.2061.

General procedures for the synthesis of 1a-1d

All the compounds were synthesized by a similar procedure shown below. Aryl amine (60 mmol), $NaHCO_3$ (90 mmol) and 150 mL water were added into a 250 mL round-bottom flask under vigorous stirring, and iodine powder (12.7 g, 50 mmol) was added with several portions in 0.5 h. The reaction mixture was stirred for an additional hour at room temperature until the color of iodine disappeared. The crude product (1a-1d) was obtained by vacuum filtration and used for next step without purification.

General procedures for the synthesis of 2a-2d

All the compounds were synthesized by a similar procedure shown below. Compound 1a-1d (30 mmol) and $CuBr_2$ (37.5 mmol) were dissolved in 150 mL acetonitrile, and then BuONO (3.87 g, 37.5 mmol) was added dropwise. The mixture was stirred at 65 ^{o}C overnight. After filtration, the organic fraction was concentrated in vacuo. The crude product was purified by flash chromatography using petroleum ether as eluent to yield a colorless oil or solid in the yields of 50-60%. **2a.** ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.57 (s, 1H), 7.35 (d, J = 9 Hz, 1H), 7.22 (d, J = 10.2 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 139.5, 136.3, 133.9, 133.7, 133.6, 130.4, 22.7. MS (EI), m/z: 296.04 [M^+], calcd for C_7H_6BrI, 295.87.

2b. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.56 (s, 1H), 7.33-7.23 (m, 2H), 3.32-3.23 (m, 1H), 1.24-1.21 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 149.9, 136.5, 136.1, 134.7, 134.4, 130.2, 33.2, 23.0. MS (EI), m/z: 324.06 [M^+], calcd for $C_9H_{10}BrI$, 323.90.

2c. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.67 (s, 1H), 7.52-7.49 (m, 2H), 7.42-7.37 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 144.7, 139.9, 137.7, 134.8, 129.3, 128.2, 122.7, 122.6. MS (EI), m/z: 358.08 [M^+], calcd for $C_{12}H_8BrI$, 357.89.

2d. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.48-7.46 (m, 1H), 7.37-7.35 (m, 1H), 7.29-7.26 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 141.8, 138.2, 136.1, 118.8, 118.5. MS (EI), m/z: 300.04 [M^+], calcd for C_6H_3BrFI, 299.84.

General procedures for the synthesis of 3a-3d.

All the compounds were synthesized by a similar procedure shown below. A solution of *i*-PrMgCl (14.9 mmol) in THF (7.5 mL) was added dropwise to compound 2a-2d (2.5 mmol) in THF (40 mL) under N_2 at -78 ^{o}C. The mixture was stirred at -78 ^{o}C for 3 h. A solution of CuCN·2LiCl (2.71 mmol) in THF (10 mL) and benzoyl chloride (2.3 g, 16.24 mmol) were added successively at -78 ^{o}C. The mixture was warmed to room temperature overnight. After hydrolysis with saturated NH_4Cl, the mixture was extracted with CH_2Cl_2 (3×50 mL). The combined organic layers were dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by flash chromatography using petroleum ether/dichloromethane as eluent to yield a white solid in the yields of 60-90%.

3a. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.79-7.77 (m, 2H), 7.69-7.59 (m, 3H), 7.52-7.45 (m, 3H), 2.47 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 196.0, 138.5, 137.5, 136.8, 132.8, 132.5, 132.2, 130.1, 129.0, 128.5, 23.2. HRMS (ESI, *m/z*): $[M+H]^+$ for $C_{14}H_{11}BrO$, 275.0072; found, 275.0077.

3b. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.79-7.76 (m, 3H), 7.66-7.58 (m, 2H), 7.52-7.42 (m, 3H), 3.46-3.41 (m, 1H), 1.29-1.26 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 196.1, 147.9, 137.5, 137.1, 132.8, 130.2, 129.4, 129.0, 128.5, 33.1, 22.9. HRMS (ESI, *m/z*): $[M+H]^+$ for $C_{16}H_{15}BrO$, 303.0385; found, 303.0387.

3c. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.82-7.77 (m, 4H), 7.64-7.61 (m, 3H), 7.52-7.44 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 195.8, 143.0, 140.3, 137.3, 137.0, 133.5, 133.0, 132.7, 130.11, 129.6, 129.1, 128.6, 128.3, 127.8. HRMS (ESI, *m/z*): $[M+H]^+$ for $C_{19}H_{13}BrO$, 337.0228; found, 337.0233.

3d. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.82-7.77 (m, 2H), 7.71-7.59 (m, 2H), 7.55-7.46 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 194.5, 160.3, 157.8, 138.7, 136.8, 133.8, 133.2, 130.1, 129.7, 128.8, 128.5, 126.9. HRMS (ESI, *m/z*): $[M+H]^+$ for $C_{13}H_8BrFO$, 278.9821; found, 278.9813.

General procedures for the synthesis of 4a-4d

All the compounds were synthesized by a similar procedure shown below. A 2.2 M solution of *n*-butyllithium in hexane (14.5 mmol, 6.6 mL) was added to a solution of diphenylmethane (3.05 g, 18.11mmol) in anhydrous tetrahydrofuran (30 mL) at 0 ^{o}C under an N_2 atmosphere. After stirring for 1 h at this temperature, benzophenone derivative (3a-3d) (12 mmol) was added. After 2 h, the mixture was slowly warmed to room temperature. Then, the reaction was quenched with an aqueous solution of ammonium chloride and the mixture was extracted with dichloromethane. The organic layer was evaporated after drying with anhydrous sodium sulfate and the resultant crude product was dissolved in toluene (50 mL). The *p*-toluenesulfonic acid (0.42 g, 2.4 mmol) was added, and the mixture was refluxed overnight and cooled to room temperature. The mixture was evaporated and the crude product was purified by silica gel column chromatography using petroleum ether as eluent to obtain a white powder (4a-4d) in the yields of 56-65%.

4a. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.48-7.45 (m, 1H), 7.08-7.01 (m, 15H), 6.82-6.81 (m, 2H), 1.31 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 143.8, 143.5, 143.1, 141.6, 140.0, 137.3, 133.9, 131.8, 131.5, 131.4, 130.6, 128.1, 128.0, 127.9, 126.8, 123.2, 23.0. MS (EI), m/z: 424.31 [M^+], calcd for $C_{27}H_{21}Br$, 424.08.

4b. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.29-7.26 (m, 2H), 7.11-6.94 (m, 15H), 6.66-6.64 (m, 1H), 3.13-3.11 (m, 1H), 0.90-0.88 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 146.4, 144.0, 143.8, 143.4, 143.2, 141.6, 140.4, 132.3, 131.8, 131.3, 130.8, 130.2, 128.2, 127.9, 127.1, 126.7, 122.4, 32.6, 22.8. HRMS (ESI, *m/z*): [M^+] for $C_{29}H_{25}Br$, 454.1119; found, 454.1134.

4c. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.41-7.38 (m, 1H), 7.29-7.28 (m, 2H), 7.19-7.18 (m, 3H), 7.19-7.00 (m, 16H), 6.84-6.81 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 143.9, 143.6, 143.2, 142.1, 141.7, 141.0, 139.8, 134.9, 132.7, 131.6, 129.6, 128.3, 128.2, 127.8, 127.7, 127.2, 126.7, 120.7. HRMS (ESI, *m/z*): $[M+H]^+$ for $C_{32}H_{23}Br$, 487.1061; found, 487.1060.

4d. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.12-7.10 (m, 9H), 7.02-6.91 (m, 8H), 6.79-6.70 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 145.5, 144.4, 143.6, 143.1, 142.9, 142.7, 142.1, 138.9, 134.2, 133.6, 132.8, 131.4, 130.8,

129.2, 128.9, 128.6, 128.1, 127.7, 126.8, 121.2, 119.5. MS (EI), m/z: 428.28 [M^+], calcd for $C_{26}H_{18}BrF$, 428.06.

Synthesis of Cz-4d

3,6-Di-*tert*-butyl-9*H*-carbazole (2.18 g, 7.8 mmol) was dissolved in anhydrous DMF (25 mL) in a flask fixed with a magnetic stirrer and condenser. Potassium *tert*-butoxide (1.25 g, 11.2 mmol) was added and the mixture was heated at 100 ^oC for 10 min and compound 4d (3.19 g, 7.44 mmol) was added, then the resultant mixture was stirred at 100 ^oC for 12 h. The mixture was cooled to room temperature and the solvent was evaporated. The crude product was purified by silica gel column chromatography using petroleum ether/dichloromethane as eluent. A white powder was obtained in the yield of 49% (2.5 g). ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.12-8.11 (m, 2H), 7.48-7.43 (m, 4H), 7.22-7.08 (m, 16H), 7.08-6.92 (m, 2H), 1.46 (s, 18H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 145.01 142.86, 139.08, 136.59, 135.36, 133.99, 133.67, 133.26, 132.62, 132.34, 131.33, 128.27, 128.02, 125.93, 123.47, 123.04, 121.21, 116.12, 109.55, 34.74, 32.08. MS (EI), m/z: 689.28 [M^+], calcd for $C_{46}H_{42}BrN$, 688.74). HRMS (ESI, *m/z*): $[M+H]^+$ for $C_{46}H_{42}BrN$, 690.2558; found, 690.2534.

General procedures for the synthesis of 5a-5d

All the compounds were synthesized by a similar procedure shown below. A 2.2 M solution of *n*-butyllithium in hexane (3 mmol, 1.5mL) was added to a solution of aryl bromide (4a-4c, Cz-4d) (2 mmol) in anhydrous tetrahydrofuran (15 mL) at -78 ^oC under an N_2 atmosphere. After stirring for 4 h, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.80g, 4.2 mmol) was added. After 2 h, the mixture was slowly warmed to room temperature. After stirring overnight, the reaction was terminated by the added brine. The mixture was extracted with dichloromethane and the organic layer was combined, and dried with anhydrous sodium sulfate. After filtration and solvent evaporation, the crude product was purified by silica gel column chromatography using petroleum ether/dichloromethane as eluent. White powders of 5a-5d were obtained in the yield of 32-60%. **5a.** ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.48-7.45 (m, 1H), 7.08-7.01 (m, 15H), 6.82-6.81 (m, 2H), 1.31 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 146.4, 144.4, 143.8, 141.4, 141.1, 135.4, 132.9, 131.9, 131.4, 127.9, 126.6, 83.6, 25.2, 22.3. HRMS (ESI, *m/z*): $[M+H]^+$ for $C_{33}H_{33}BO_2$, 473.2652; found, 473.2654.

5b. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.50-7.48 (m, 1H), 7.08-6.97 (m, 16H), 6.79-6.76 (m, 1H), 3.47-3.42 (m, 1H), 1.31 (s, 12H), 0.89-0.88 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 154.4, 146.0, 143.9, 143.8, 143.5, 141.3, 141.0, 135.0, 131.4, 131.3, 131.2, 128.4, 127.7, 127.6, 126.3, 83.3, 31.1, 24.8, 24.0. HRMS (ESI, *m/z*): $[M+H]^+$ for $C_{35}H_{37}BO_2$, 501.2965; found, 501.2967.

5c. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.48-7.45 (m, 1H), 7.26-7.24 (m, 3H), 7.14-7.07 (m, 13H), 7.03-6.97 (m, 6H), 1.20 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 146.9, 145.7, 144.0, 143.7, 143.2, 141.7, 140.9, 134.2, 132.7, 131.9, 131.3, 129.4, 128.2, 128.1, 127.5, 126.8, 84.0, 24.9. HRMS (ESI, *m/z*): $[M+H]^+$ for $C_{38}H_{35}BO_2$, 535.2808; found, 535.2806.

5d. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.03-8.02 (m, 2H), 7.69-7.66 (m, 1H), 7.31-7.26 (m, 7H), 7.10-7.02 (m, 12H), 6.71-6.68 (m, 2H), 1.43 (s, 18H), 0.77 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 148.1, 143.5, 143.1, 142.3, 141.7, 140.4, 140.1, 135.7, 131.9, 131.7, 131.3, 129.8, 128.2, 127.7, 126.7, 123.1, 115.7, 109.1, 83.4, 34.7, 32.1, 24.3. HRMS (ESI, *m/z*): $[M+H]^+$ for $C_{52}H_{54}BNO_2$, 736.4326; found, 736.4330.

General procedures for the synthesis of Methyl-BTPE, Isopro-BTPE, Ph-BTPE and Cz-BTPE

All the compounds were synthesized by a similar procedure shown below in 60-84% yields. A mixture of aryl bromide (4a-4c, Cz-4d) (1 mmol), aryl boronic ester (5a-5d) (1 mmol), $Pd(PPh_3)_4$ (30 mg) and potassium hydroxide (5 mmol) in 15 mL of THF and 5 mL of distilled water in a 50 ml Schlenk tube was refluxed for 2 days under N_2. The mixture was extracted with dichloromethane. The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated by rotary evaporation. The crude product was purified by column chromatography on silica gel using petroleum ether/dichloromethane as eluent.

Methyl-BTPE. White powder. Yield: 61.9%. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.11-7.06 (m, 36H), 6.87-6.79

(m, 6H), 1.77 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 144.1, 144.0, 143.8, 142.6, 141.3, 141.0, 139.9, 135.2, 132.8, 131.6, 128.7, 127.9, 127.7, 126.6, 19.7. MS (EI), m/z: 690.35 [M^+], calcd for $C_{54}H_{42}$, 690.91). HRMS (ESI, *m/z*): $[M+H]^+$ for $C_{54}H_{42}$, 691.3365; found, 691.3370. Anal. Calcd for $C_{54}H_{42}$: C, 93.87; H, 6.13. Found: C, 93.53; H, 6.18.

Isopro-BTPE. White powder. Yield: 71%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.13-6.97 (m, 32H), 6.84-6.75 (m, 4H), 2.40-2.33 (m, 2H), 0.78-0.76 (m, 6H), 0.70-0.68 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 146.0, 144.5, 144.0, 143.6, 142.7, 141.8, 141.1, 138.4, 131.6, 129.2, 129.1, 127.9, 126.6, 126.4, 29.4, 24.7, 22.7. MS (EI), m/z: 746.38 [M^+], calcd for $C_{58}H_{50}$, 747.02). HRMS (ESI, *m/z*): [M^+] for $C_{58}H_{50}$, 746.3913; found, 746.3943. Anal. Calcd for $C_{58}H_{50}$: C, 93.25; H, 6.75. Found: C, 92.77; H, 6.84.

Ph-BTPE. White solid. Yield: 83.6%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.19-6.98 (m, 35H), 6.96-6.81 (m, 7H), 6.21-6.19 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 144.1, 143.8, 142.8, 141.3, 140.9, 140.3, 138.2, 133.3, 132.0, 131.4, 131.1, 130.4, 129.4, 128.1, 127.9, 127.4, 126.7, 125.9. MS (EI), m/z: 814.36 [M^+], calcd for $C_{64}H_{46}$, 814.25). HRMS (ESI, *m/z*): [M^+] for $C_{64}H_{46}$, 814.3600; found, 814.3611. Anal. Calcd for $C_{64}H_{46}$: C, 94.31; H, 5.69. Found: C, 94.06; H, 5.55.

Cz-BTPE. Light-green solid. Yield: 31.5%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.79-7.77 (m, 4H), 7.50-7.47 (m, 2H), 7.00-6.95 (m, 20H), 6.85-6.68 (m, 22H), 1.44 (s, 36H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 144.9, 143.6, 143.2, 141.9, 140.4, 136.6, 135.9, 132.3, 131.6, 131.5, 130.7, 128.0, 127.9, 126.7, 123.8, 123.0, 115.6, 110.4, 34.8, 32.4. MS (MALDI-TOF), m/z: 1217.37 [M^+], calcd for $C_{92}H_{84}N_2$, 1217.66). HRMS (ESI, *m/z*): $[M+H]^+$ for $C_{92}H_{84}N_2$, 1217.6713; found, 1217.6718. Anal. Calcd for $C_{92}H_{84}N_2$: C, 90.75; H, 6.95; N, 2.30. Found: C, 90.66; H, 6.52; N, 1.93.

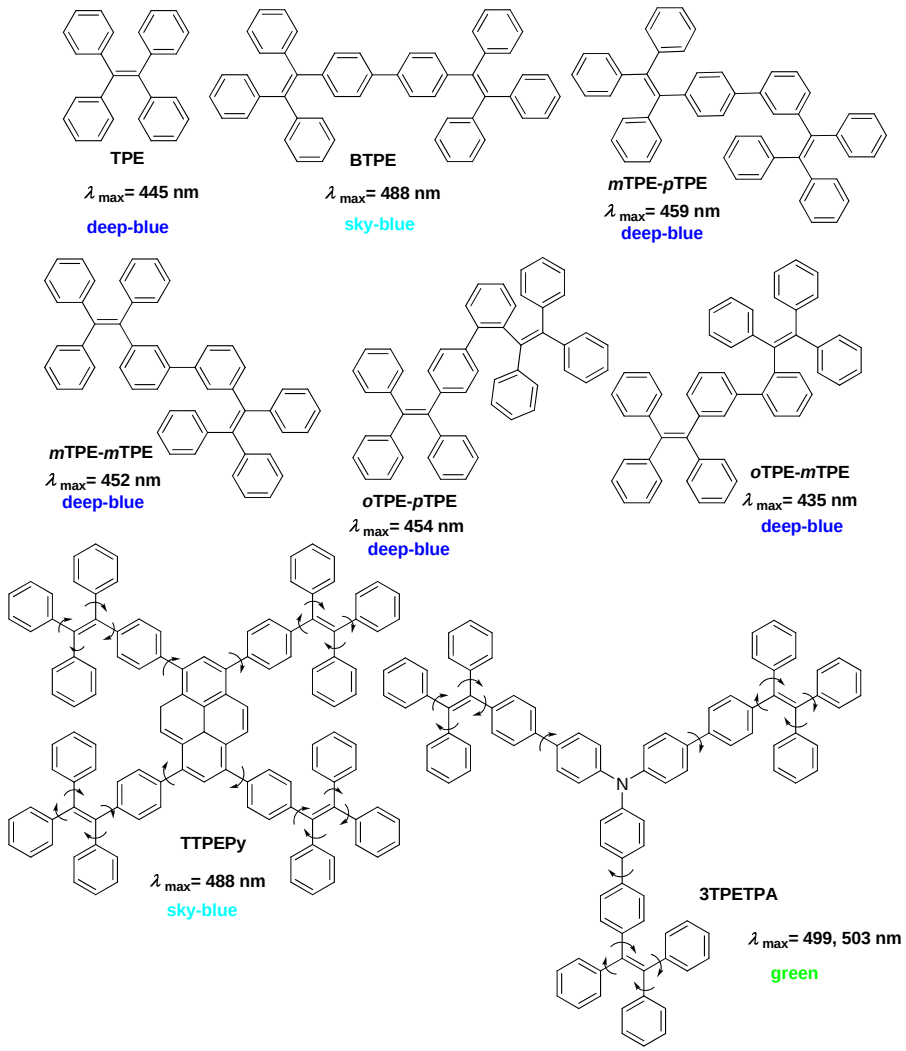
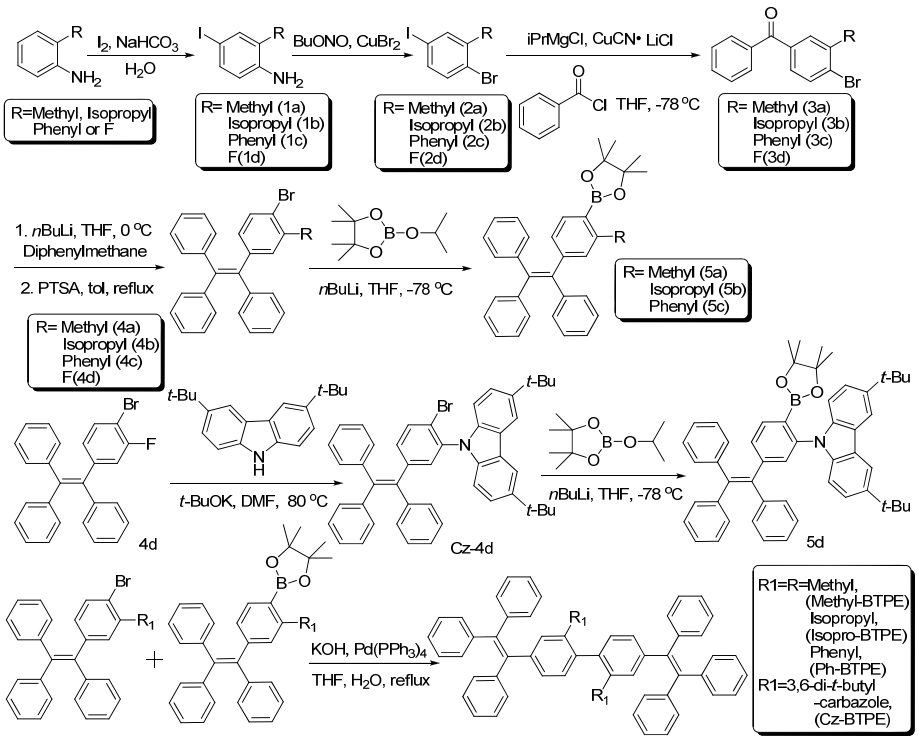


Chart S1. Chemical structures and EL peaks of TPE and some of its derivatives.



Scheme S1. Synthetic routes to Methyl-BTPE, Isopro-BTPE, Ph-BTPE and Cz-BTPE.

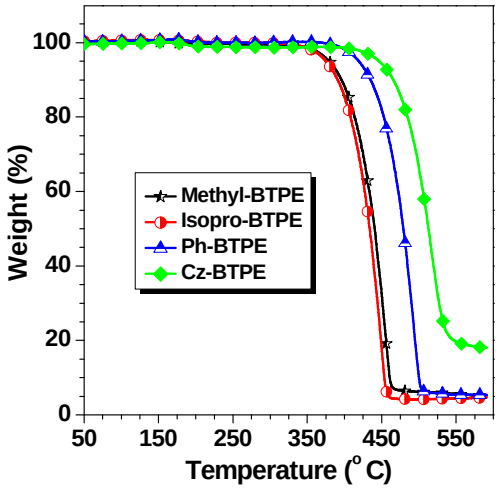


Figure S1. TGA curves of Methyl-BTPE, Isopro-BTPE, Ph-BTPE and Cz-BTPE recorded under N_2 at a heating rate of 10 °C/min.

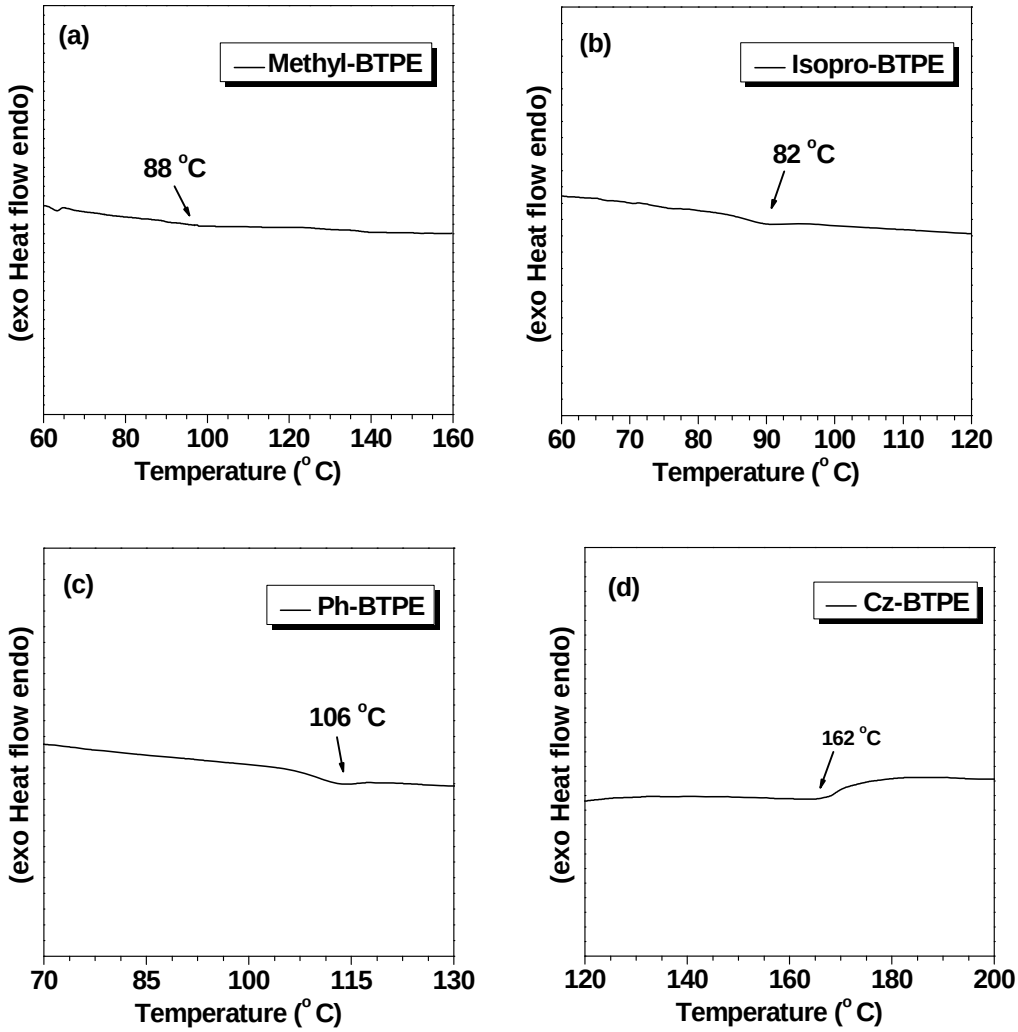


Figure S2 DSC (second heating cycle) thermograms of Methyl-BTPE, Isopro-BTPE, Ph-BTPE and Cz-BTPE recorded under N2 at a heating rate of 15 °C/min.

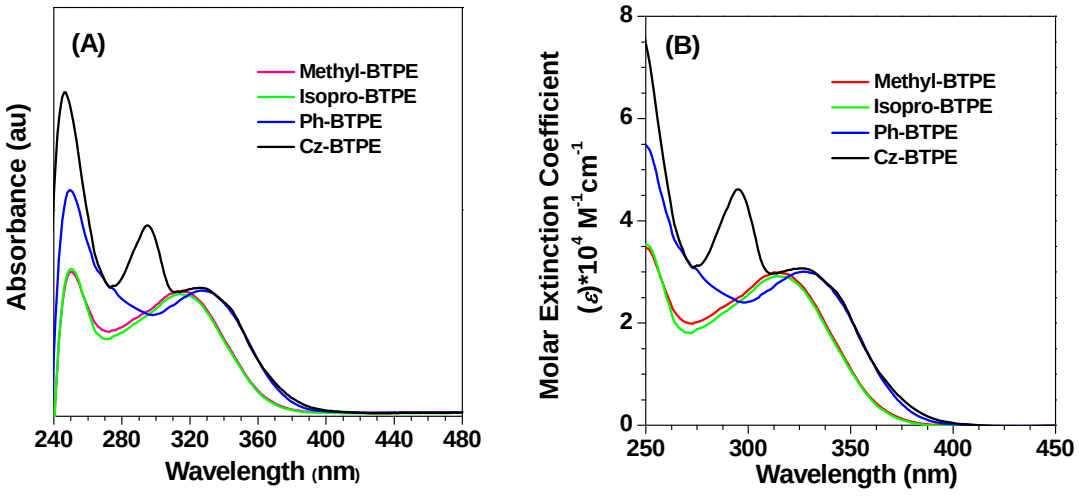


Figure S3. UV-vis spectra and of Methyl-BTPE, Isopro-BTPE, Ph-BTPE and Cz-BTPE in THF solution. Concentration (μM): 10.1, 10.6, 11.2 and 11.0.

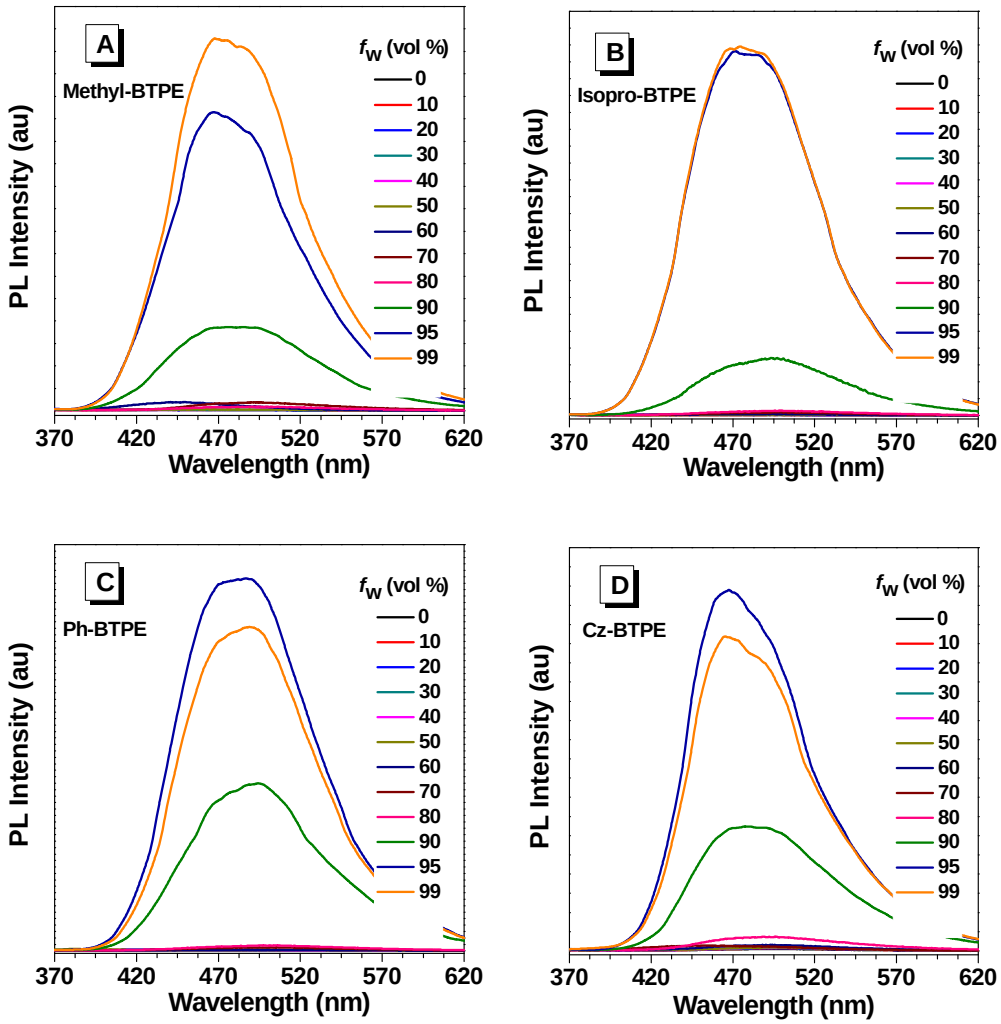


Figure S4. PL spectra of Methyl-BTPE (A), Isopro-BTPE (B), Ph-BTPE (C) and Cz-BTPE (D) in THF/H_2O mixtures with different water fractions. Concentration (μM): 10.1, 10.6, 11.2 and 11.0; excitation wavelength (nm): 330.

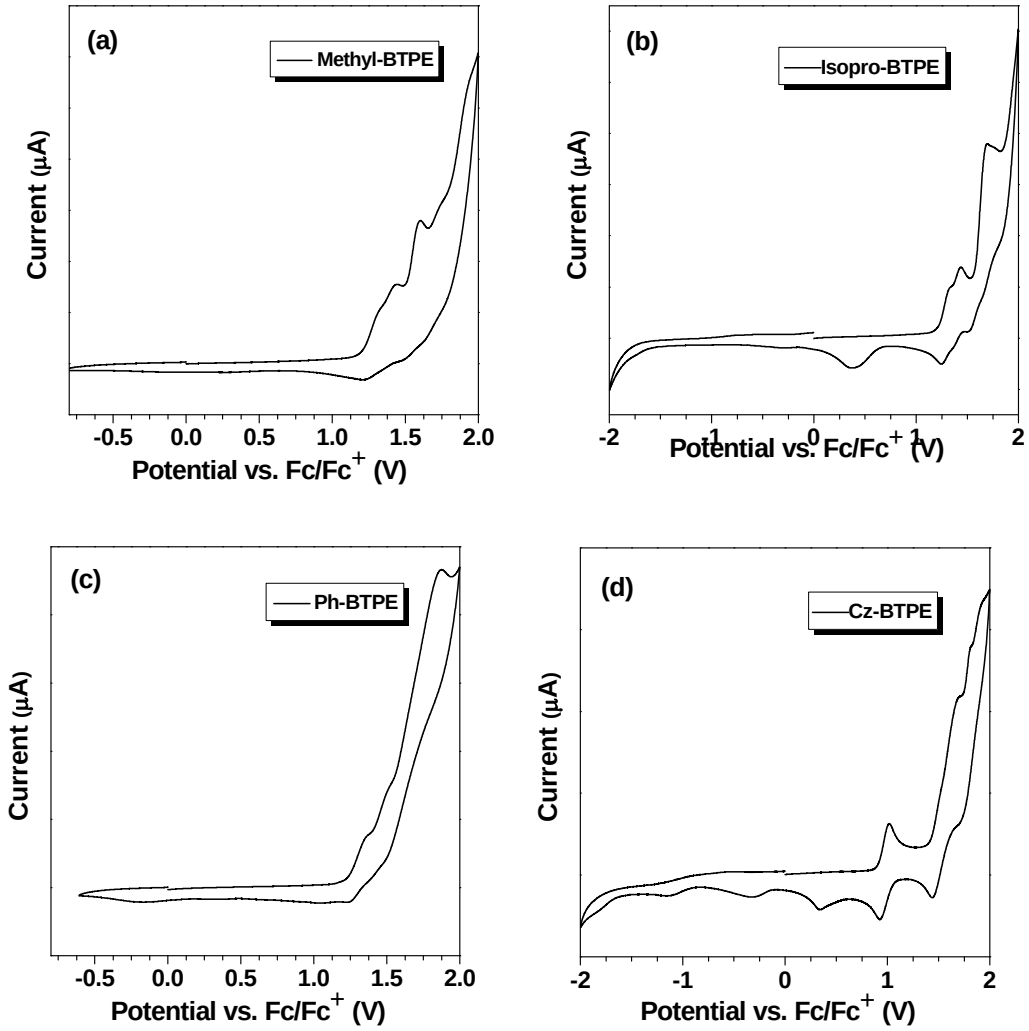


Figure S5. CV curves of Methyl-BTPE, Isopro-BTPE, Ph-BTPE and Cz-BTPE in CH_2Cl_2.

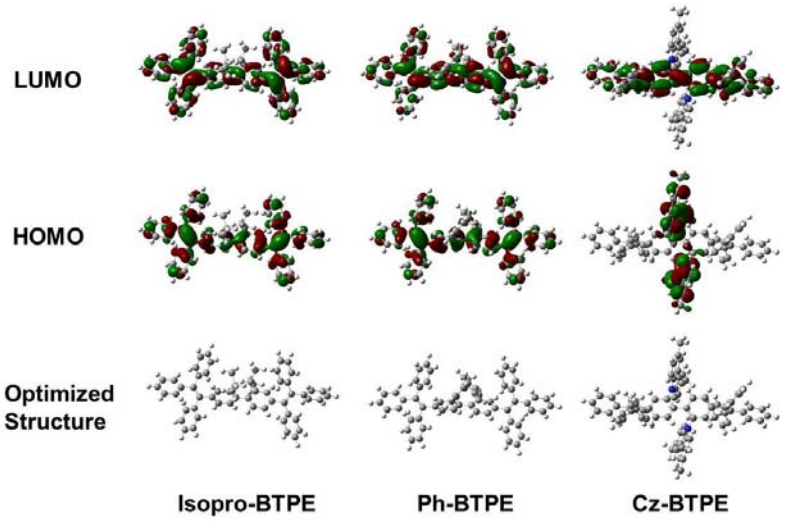


Figure S6. Calculated molecular orbital amplitude plots of HOMO and LUMO levels and optimized molecular structures of Isopro-BTPE, Ph-BTPE and Cz-BTPE.

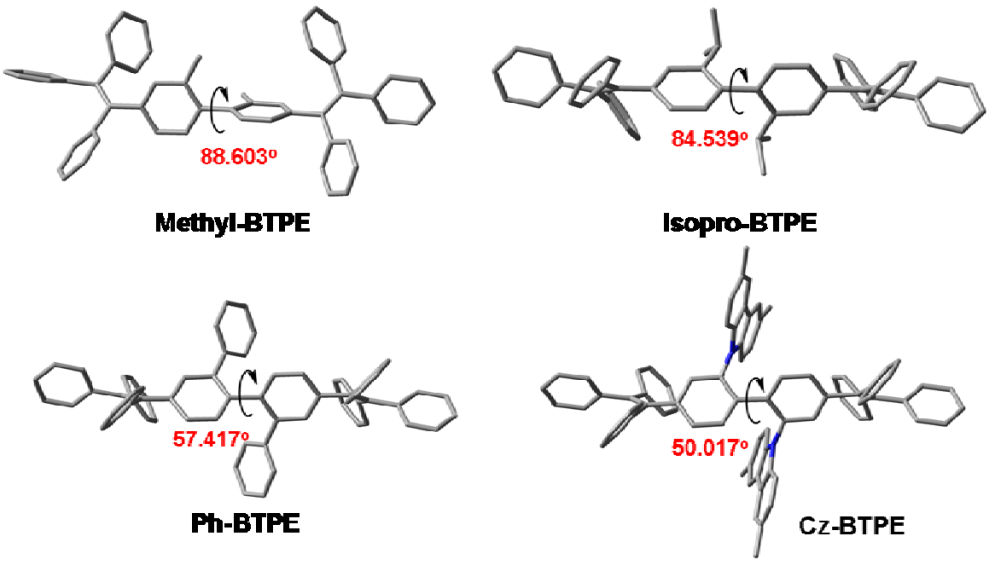


Figure S7. The dihedral angles and single bond lengths between the two TPE moieties according to the optimized structures of Methyl-BTPE, Isopro-BTPE, Ph-BTPE and Cz-BTPE.

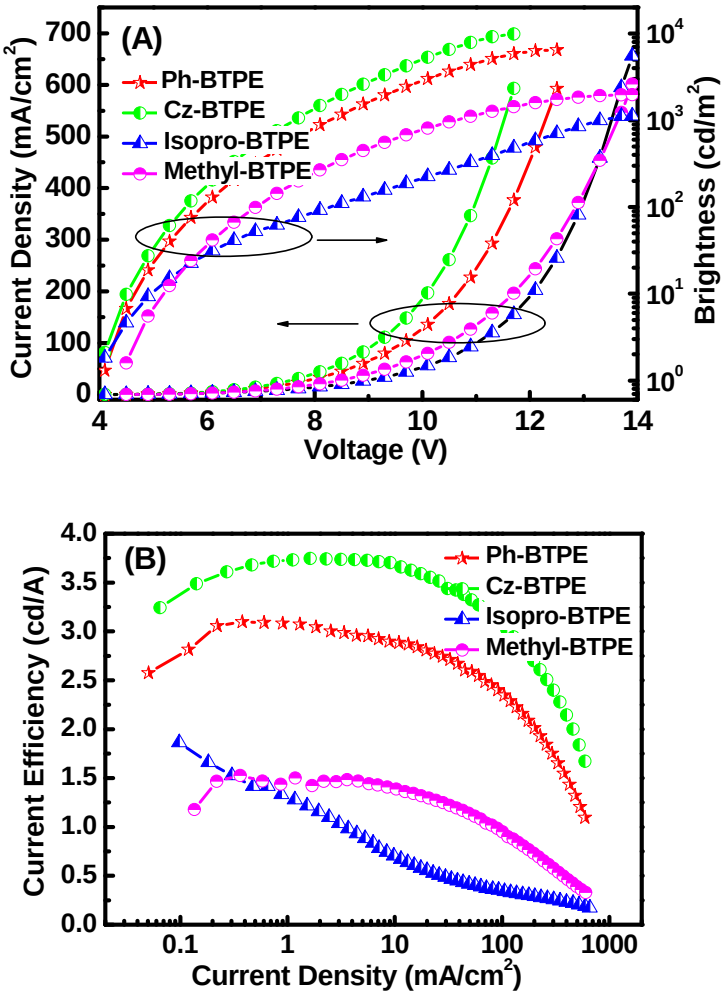
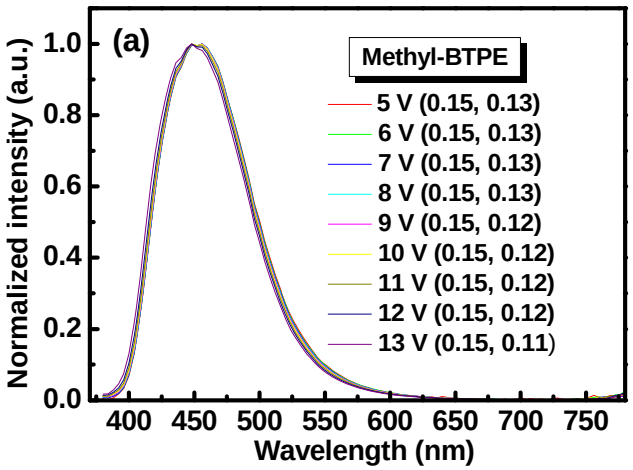
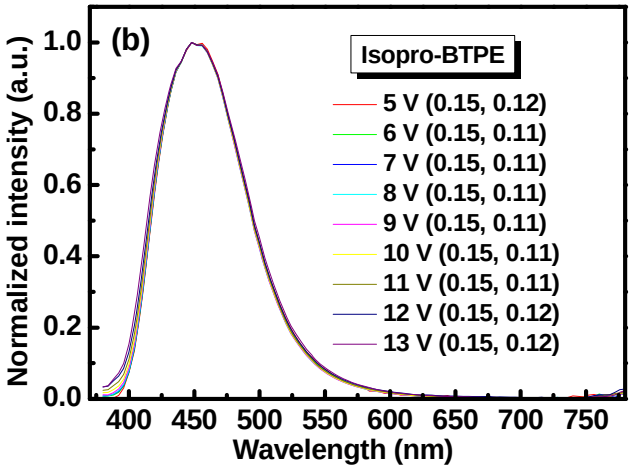
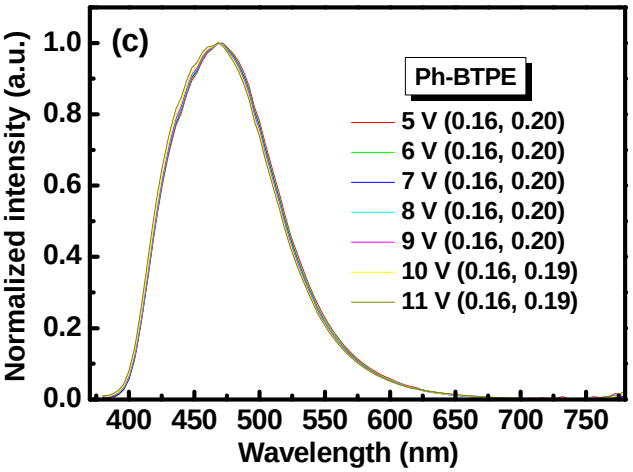


Figure S8. (A) Current density-voltage-luminance characteristics and (B) changes in current efficiency with the current density of the OLEDs based on Methyl-BTPE, Isopro-BTPE, Ph-BTPE and Cz-BTPE. Device configurations: ITO/MoO_3(10 nm)/NPB(60 nm)/EML(15 nm)/TPBi(35 nm)/LiF(1 nm)/Al.







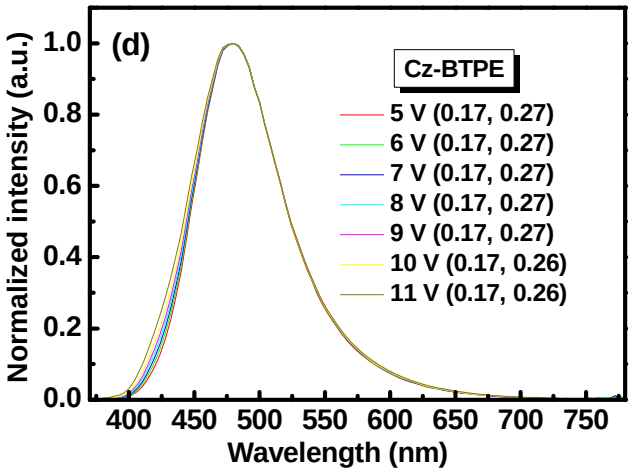


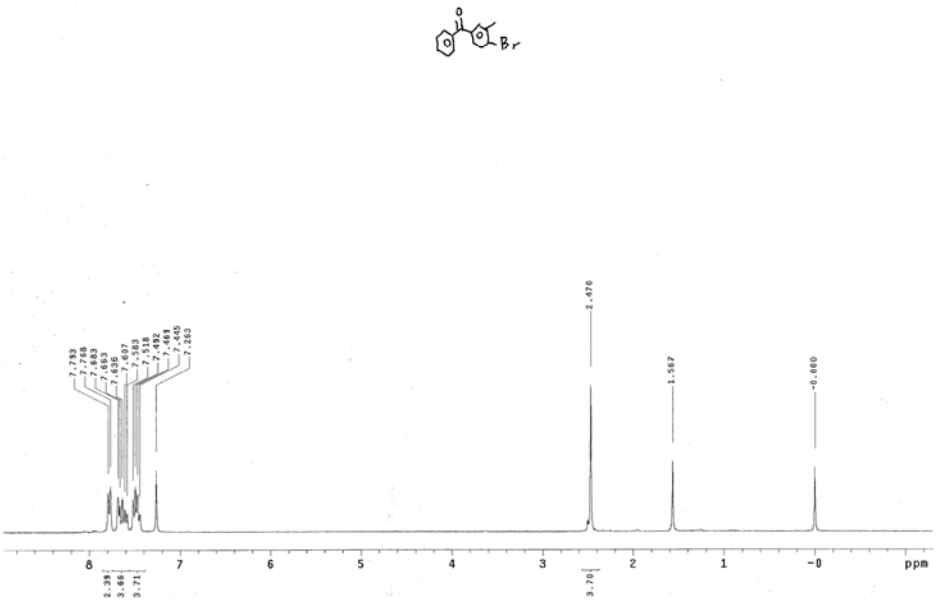
Figure S9. EL spectra and CIE Coordinates of (a) Methyl-BTPE (b) Isopro-BTPE (c) Ph-BTPE and (d) Cz-BTPE with different voltages.

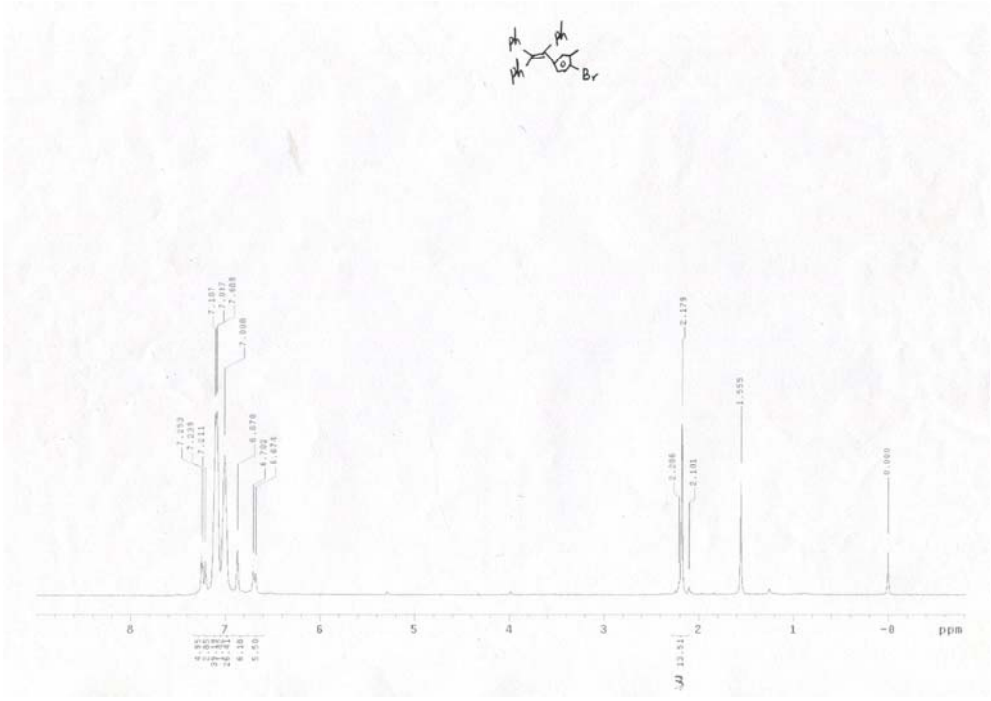
Table S1. The thermal, electrochemical and photophysical data of Methyl-BTPE, Isopro-BTPE, Ph-BTPE and Cz-BTPE.

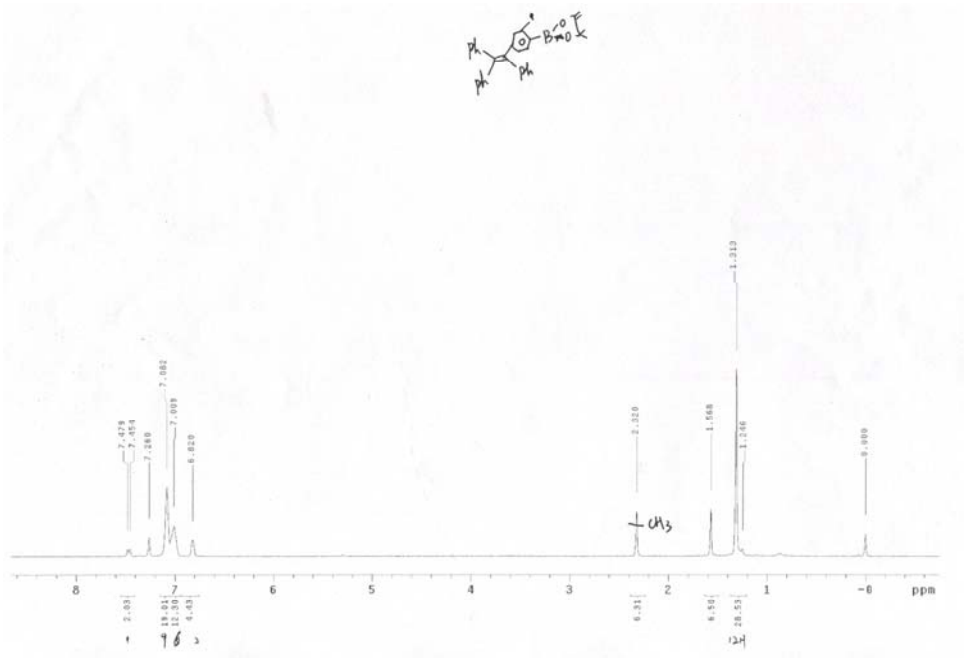
						PL λ_{max}		Φ_F (%)	$\lambda_{max,abs}$
	T_d[a]	Tg[b]	E_g[c]	E_{HOMO}[d]	E_{LUMO}[e]	aggr[f]	film	aggr[f]	soln[g]
	°C	°C	eV	eV	eV	nm	nm		nm
Methyl-BTPE	378	88	3.38	-5.53	-2.15	470	455	21.9	315
Isopro-BTPE	374	82	3.37	-5.54	-2.17	474	468	42.7	315
Ph-BTPE	418	106	3.25	-5.54	-2.29	484	459	49.9	328
Cz-BTPE	447	162	3.24	-5.21	-1.97	468	469	25.4	328

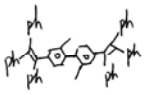
[a] 5% weight loss temperature measured by TGA under N_2. [b] Glass-transition temperature measured by DSC under N_2. [c] Band gap estimated from optical absorption band edge of the solution. [d] Calculated from the onset oxidation potentials of the compounds. [e]Estimated using empirical equations $E_{LUMO}=E_{HOMO}+E_g$. [f]Determined in THF:H_2O=1:99 solution. [g]Observed from absorption spectra in dilute THF solution, 10 μM.

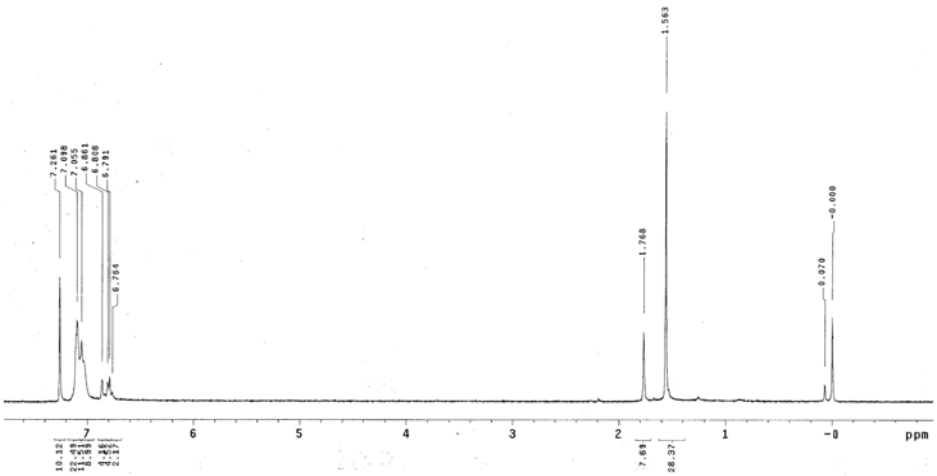
(A) ^{1}H NMR







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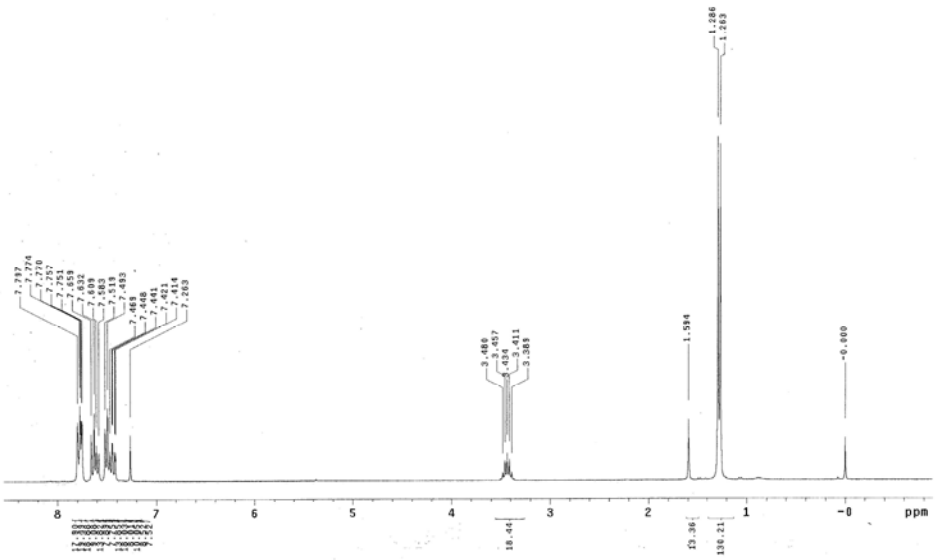
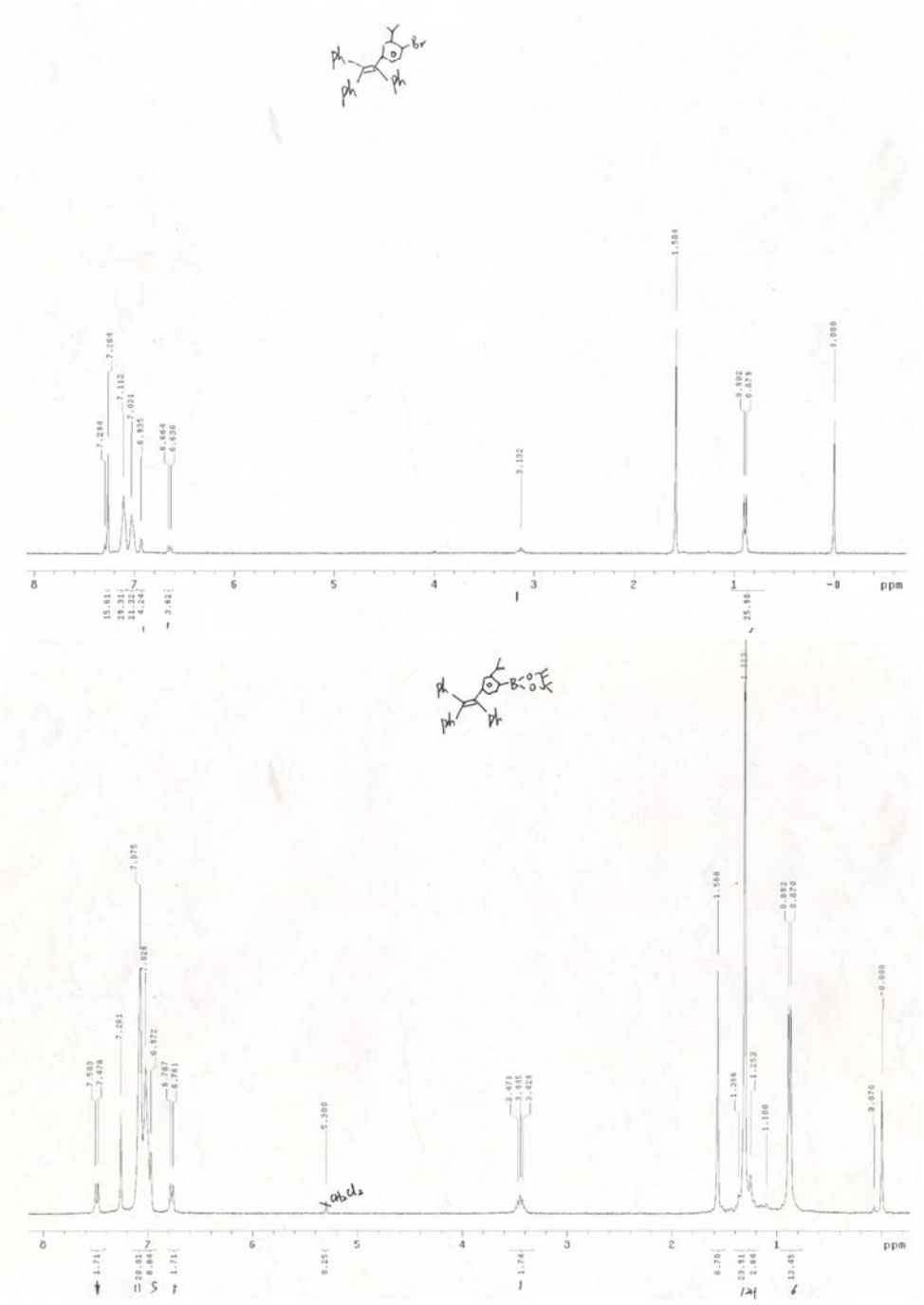
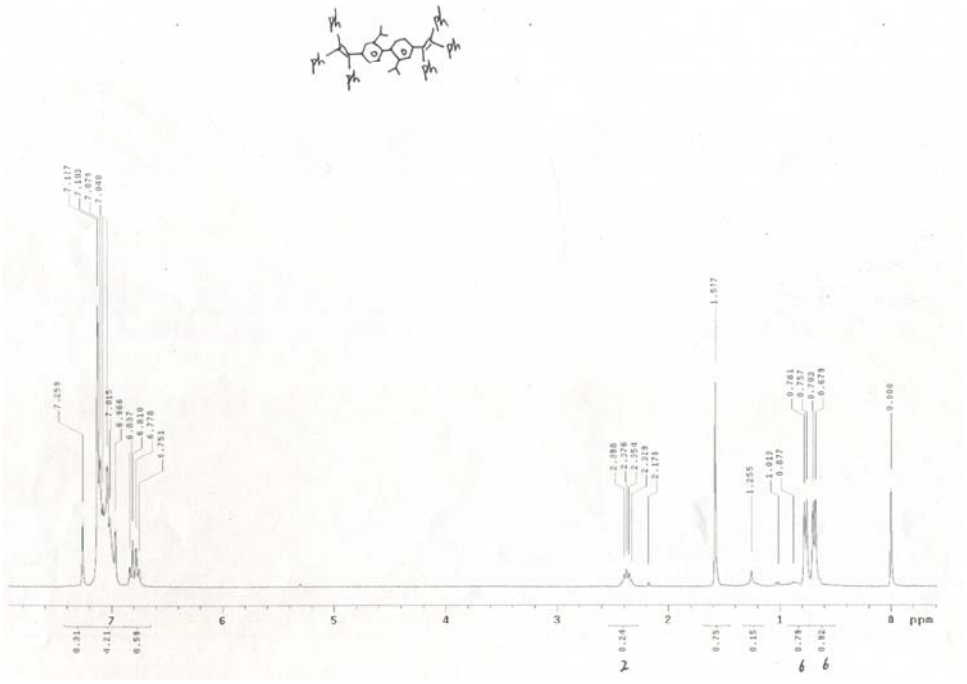
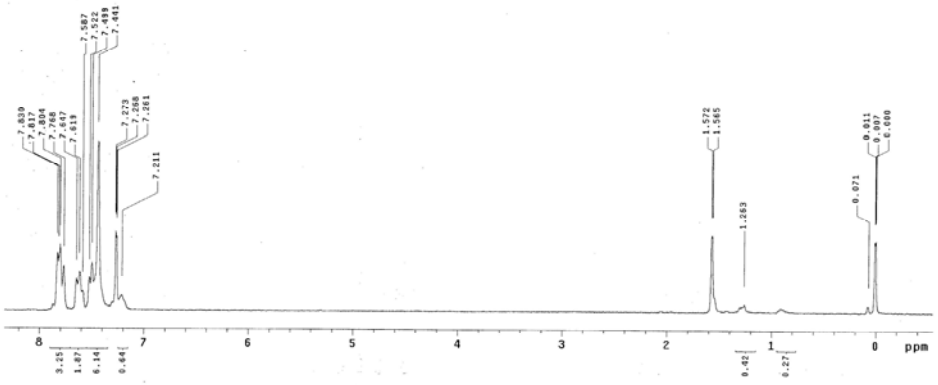
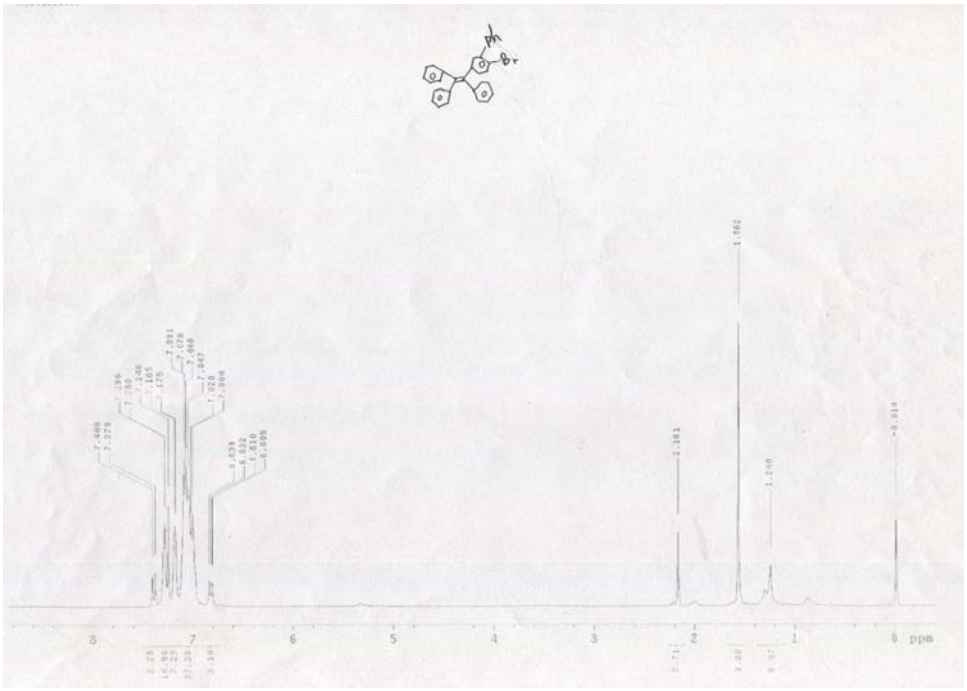
7.098
7.055
6.808
6.791
6.764
1.768
1.563
0.970
0.000
ppm

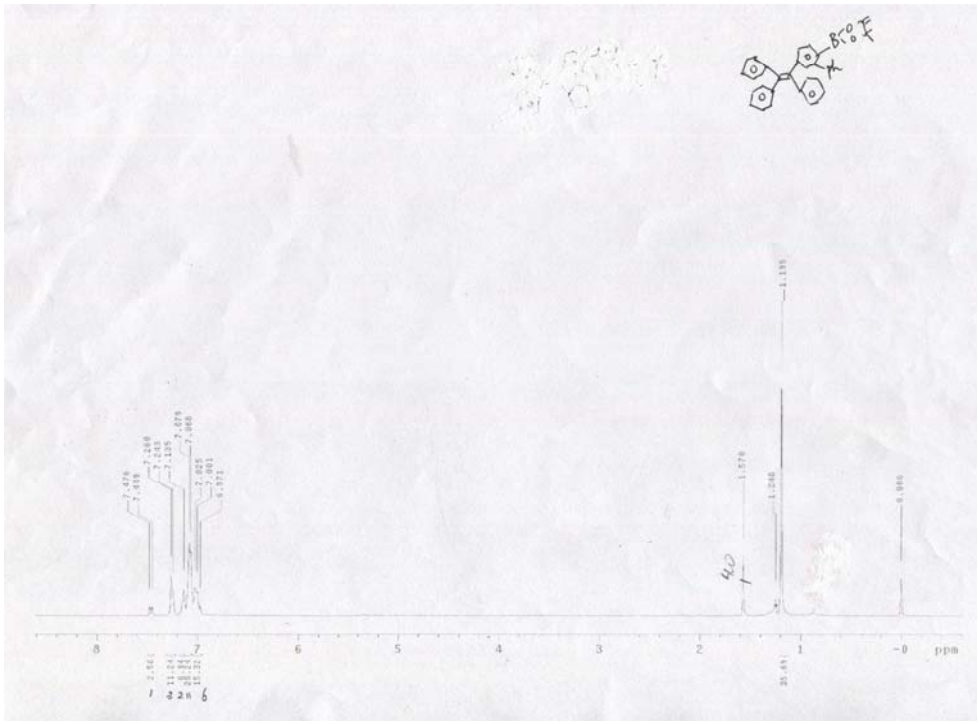

7.797
7.774
7.770
7.757
7.751
7.655
7.632
7.609
7.595
7.519
7.493
7.469
7.441
7.421
7.414
7.263
3.466
3.457
3.436
3.411
3.388
1.594
1.286
1.263
0.000
ppm

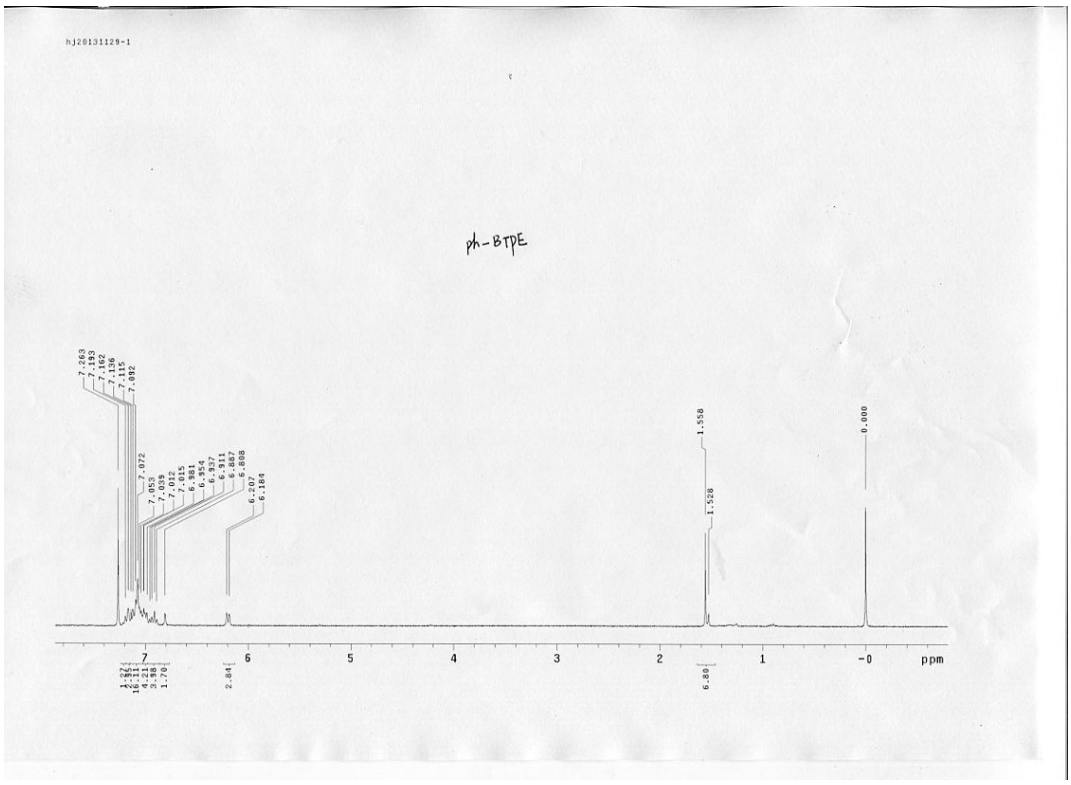


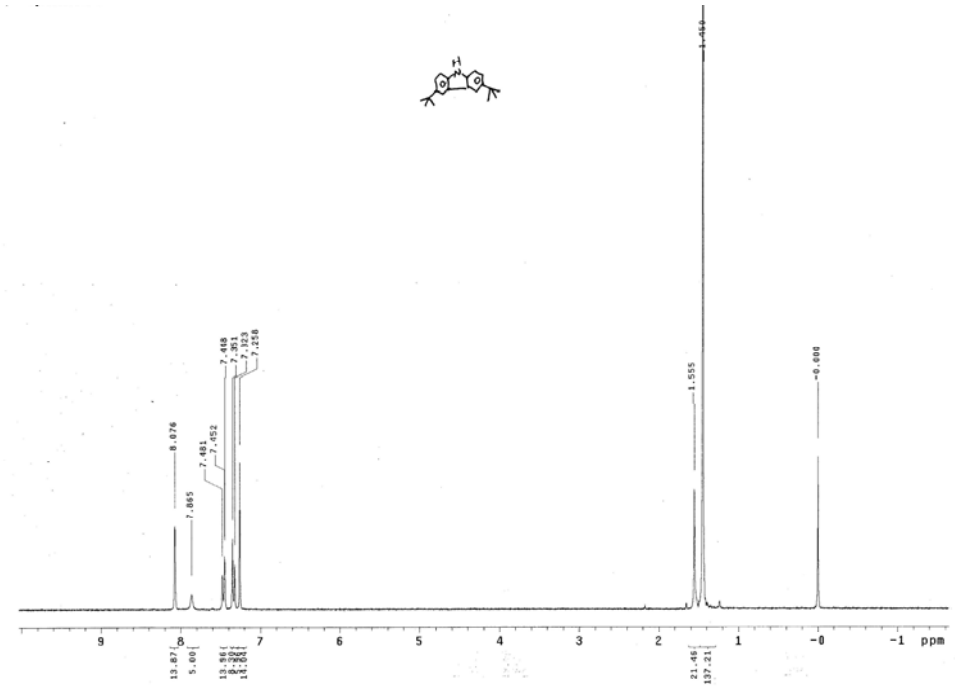









hj20131129-1
ph-BTPE
7.163
7.153
7.162
7.136
7.115
7.092
7.072
7.053
7.033
7.012
7.015
6.984
6.965
6.937
6.911
6.887
6.888
6.207
6.184
1.558
1.528
0.000
ppm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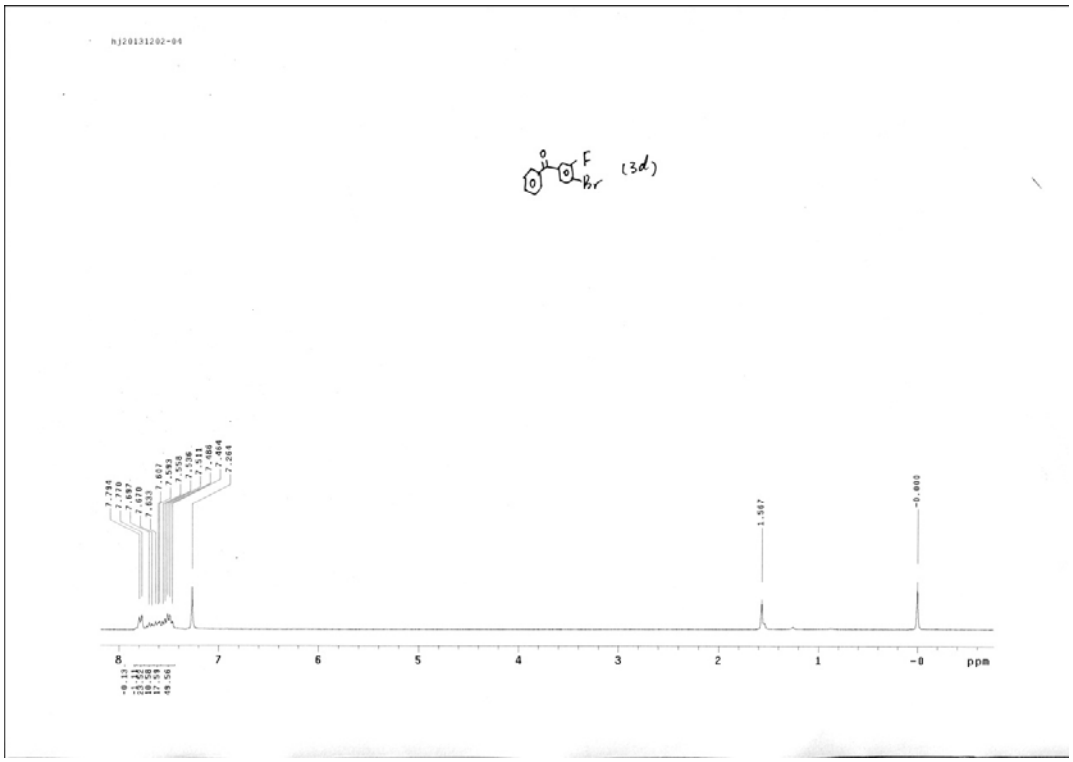
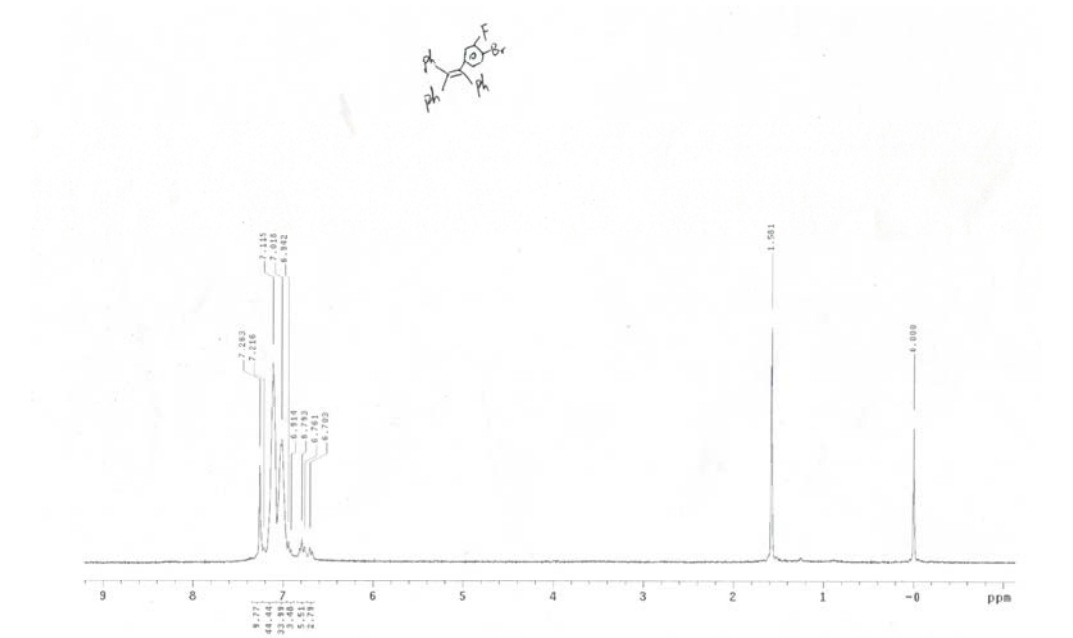
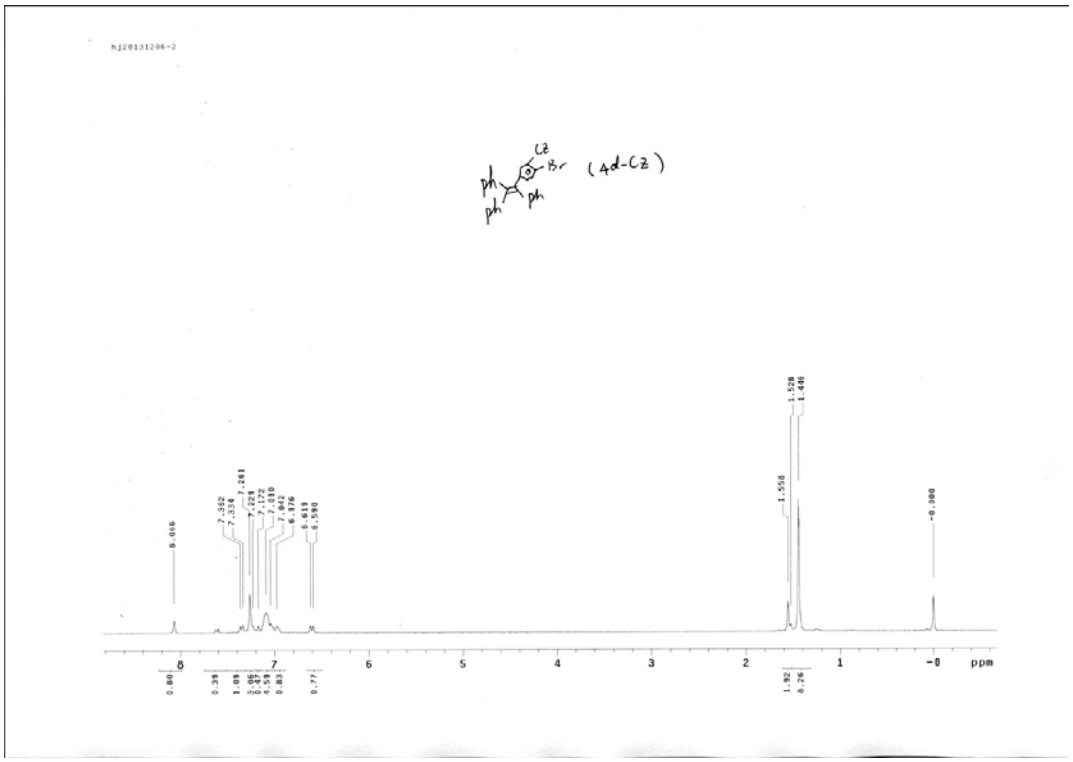
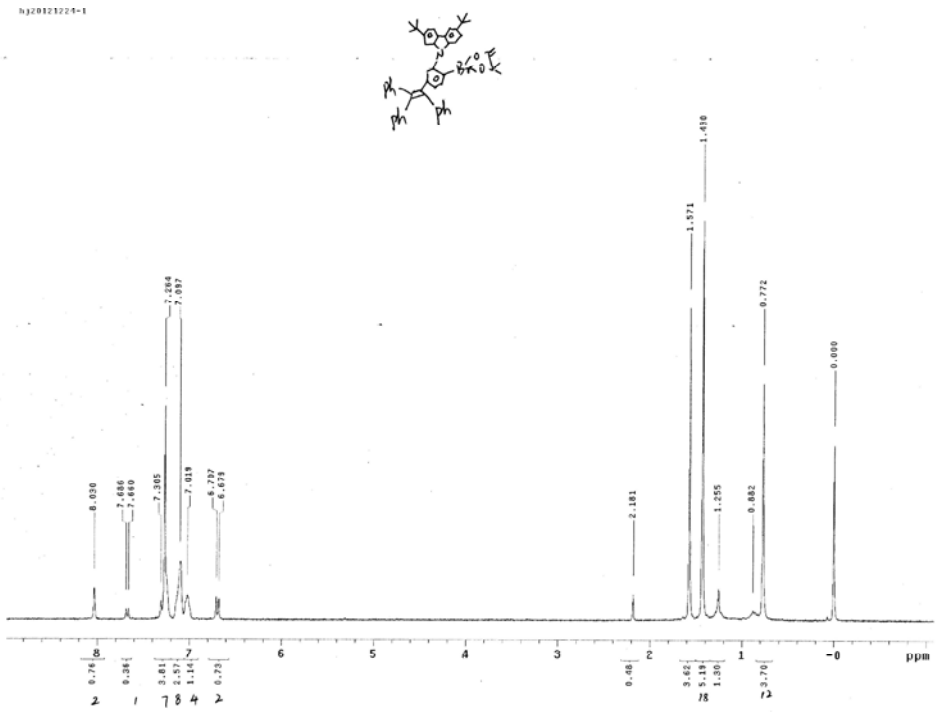
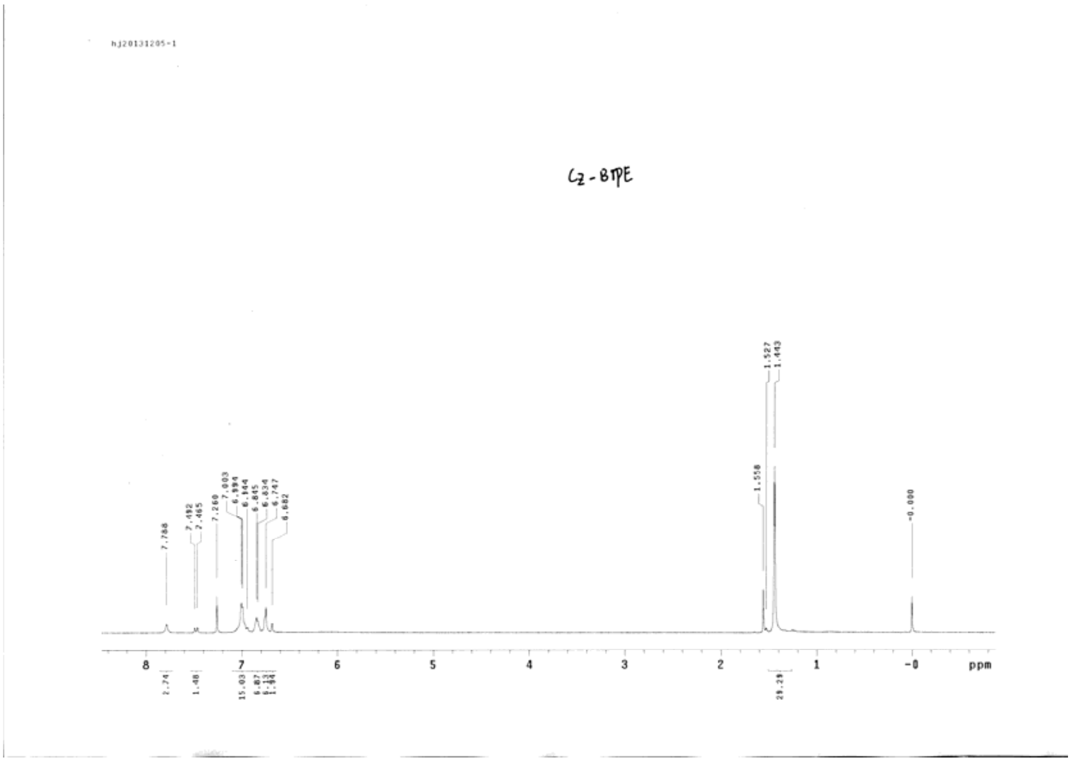
7.256
1.555
-0.000
ppm


(3d)
ppm

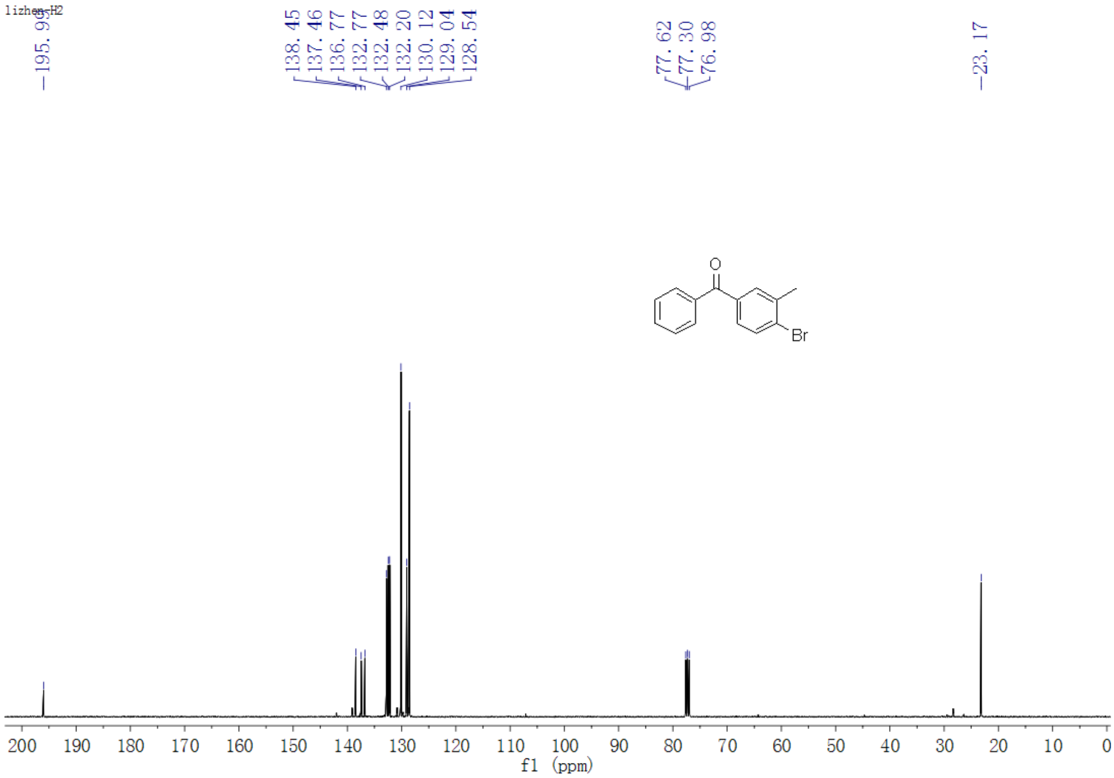

ppm

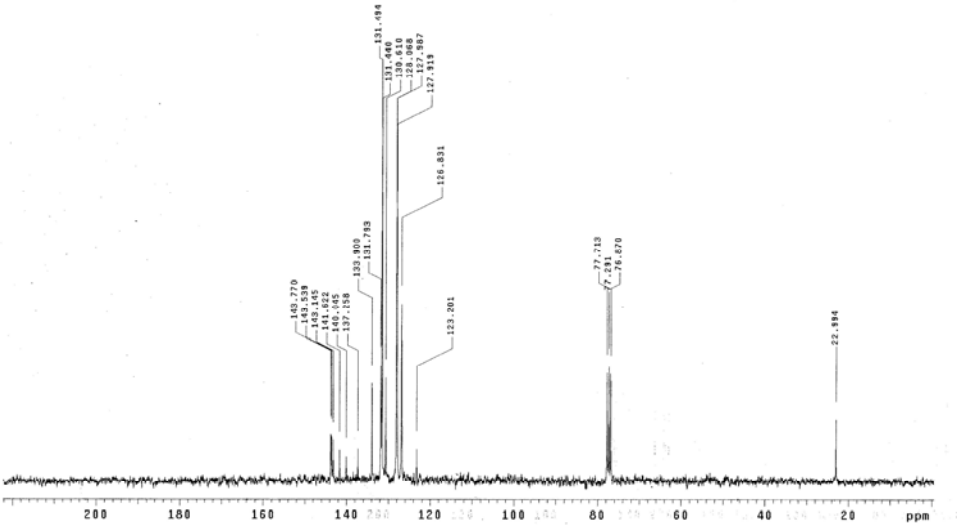

(4d-Cz)
ppm


ppm



(B) ^{13}C NMR


lizhen-H2
195.95
138.45
137.46
136.77
132.77
132.48
132.20
130.12
129.04
128.54
77.62
77.30
76.98
23.17
O
Br
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

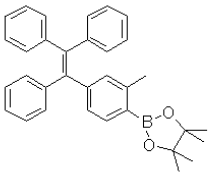


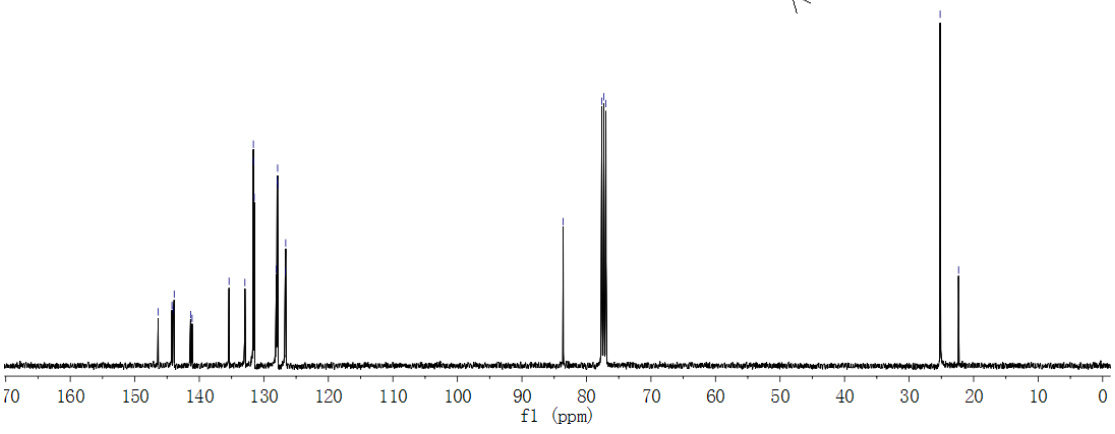
lizheng-H1

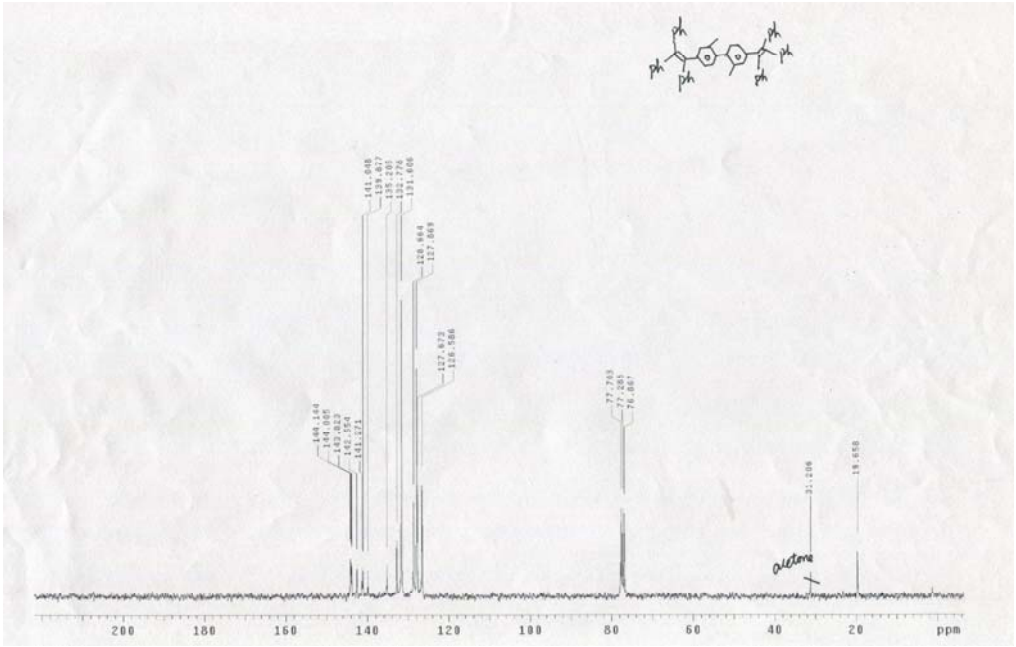
146.38
144.24
144.06
143.89
141.35
141.12
135.39
132.93
131.62
131.60
131.49
128.06
127.94
127.86
127.83
126.69
126.61

83.61
77.62
77.30
76.98

25.19
22.33

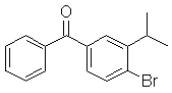


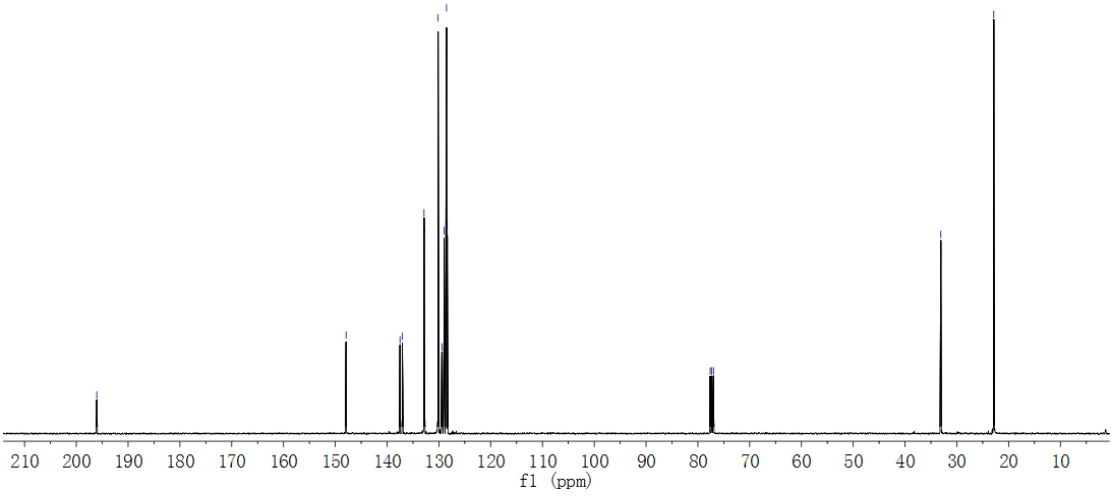


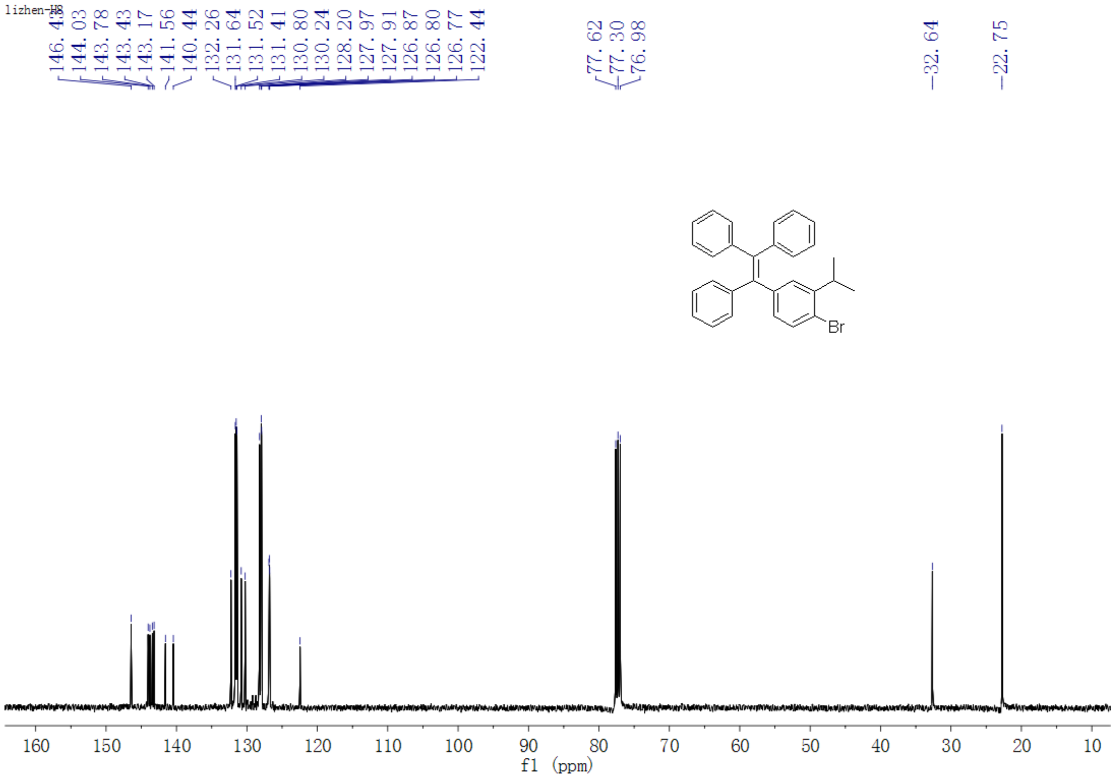


lizhen-H7

196.06
147.91
137.50
137.06
132.86
132.76
130.15
129.42
129.01
128.53
128.38
77.62
77.30
76.98
33.08
22.87






lizhen-HB
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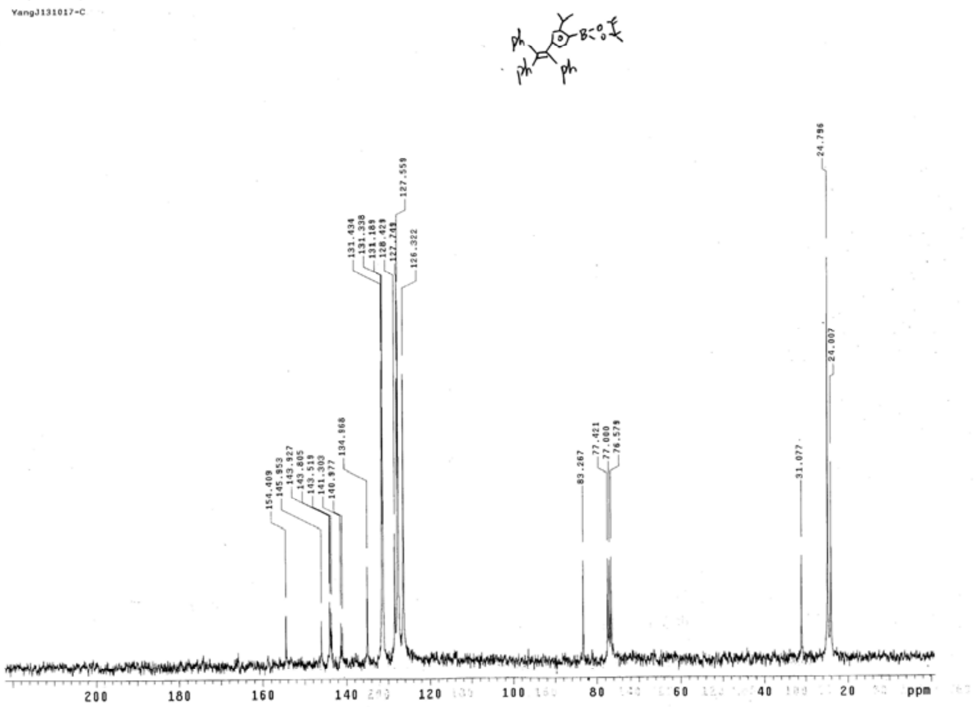
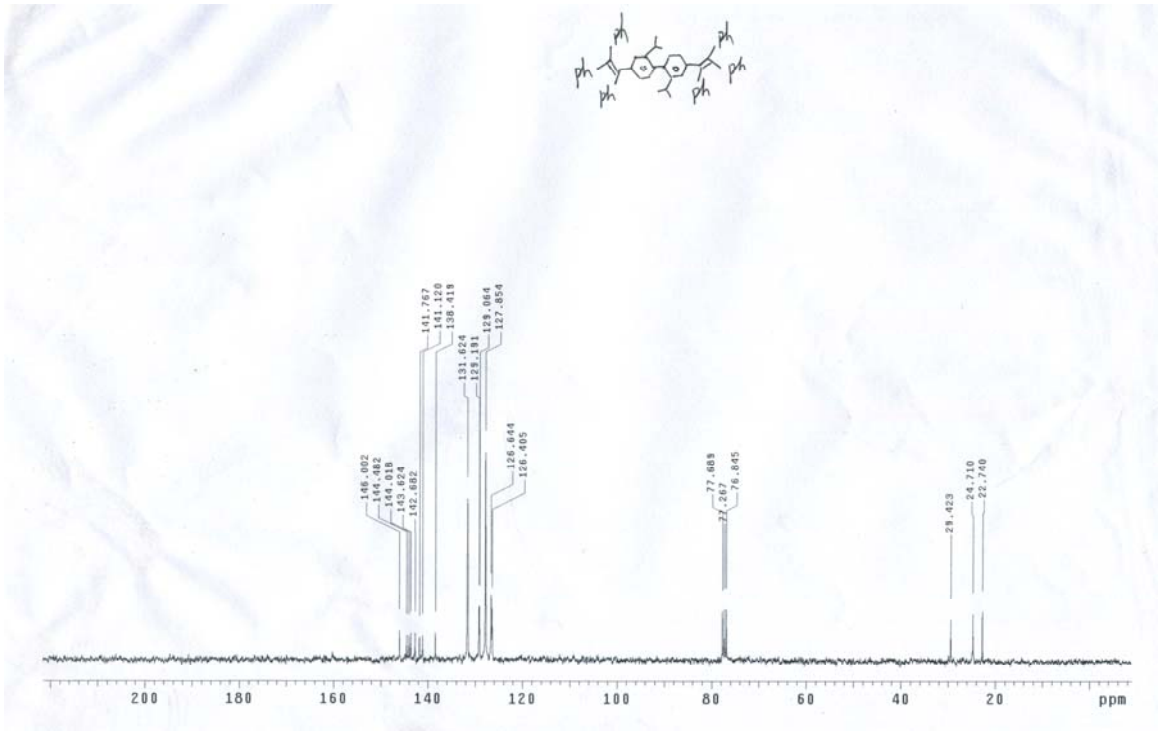
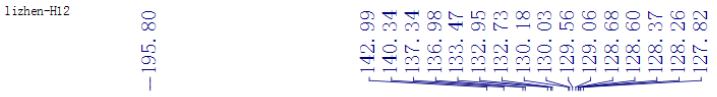
144.03
143.78
143.43
143.17
141.56
140.44
132.26
131.64
131.52
131.41
130.80
130.24
128.20
127.97
127.91
126.87
126.80
126.77
122.44
77.62
77.30
76.98
32.64
22.75
Br
f1 (ppm)


YangJ131017-C
ppm


Ph
Ph
Ph
Ph
Ph
O
O
146.002
144.632
144.016
143.624
142.682
141.767
141.120
138.419
131.624
129.181
129.064
127.854
126.644
126.405
77.689
77.267
76.845
29.423
24.710
22.740
200
180
160
140
120
100
80
60
40
20
ppm


lizhen-H12
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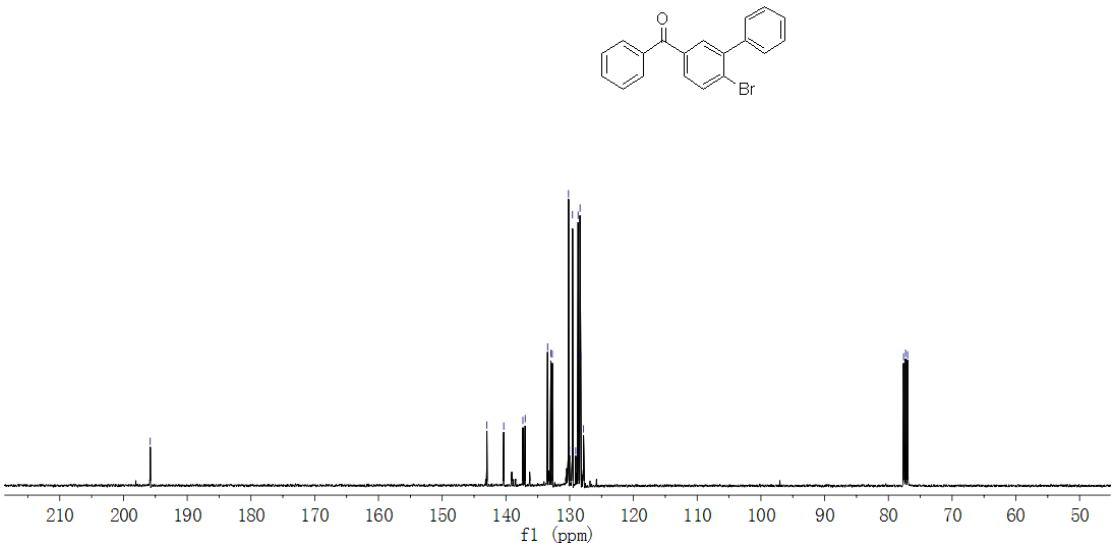
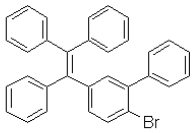
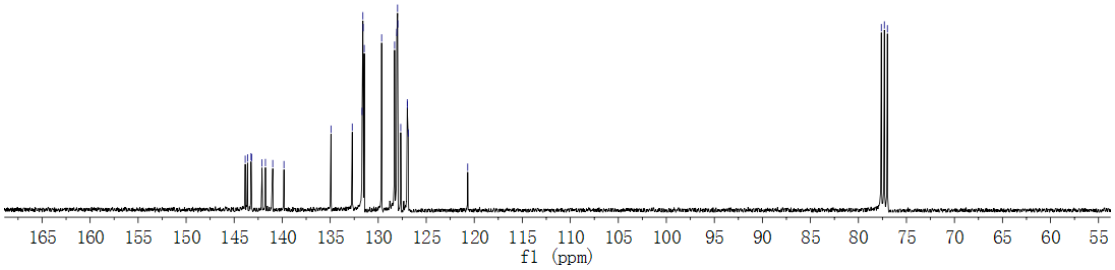
142.99
140.34
137.34
136.98
133.47
132.95
132.73
130.18
130.03
129.56
129.06
128.68
128.60
128.37
128.26
127.82
77.62
77.30
76.98


O
Br
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
f1 (ppm)

lizhen-H13

143.85
143.60
143.24
143.19
142.10
141.74
140.98
139.82
131.60
131.57
129.64
128.07
127.99
127.96
120.68
77.62
77.30
76.98





lizhen-H14

146.94
145.68
143.96
143.68
143.17
141.69
140.91
134.24
132.65
131.71
131.59
131.56
129.46
129.35
128.16
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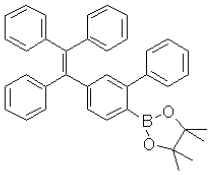
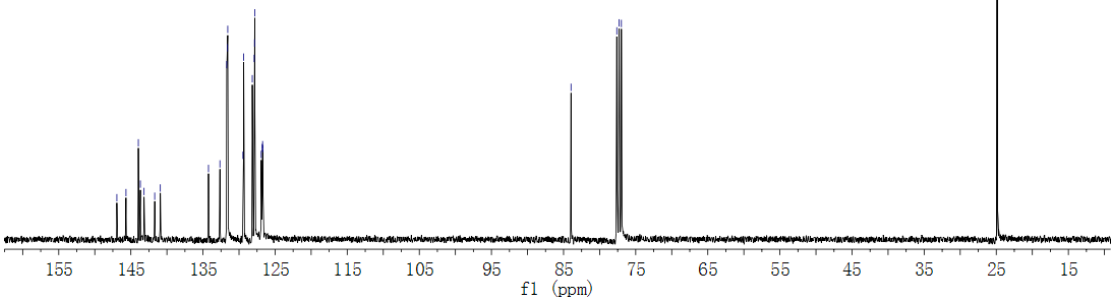
126.70
83.97
77.62
77.30
76.98
24.87





lizhen-H15

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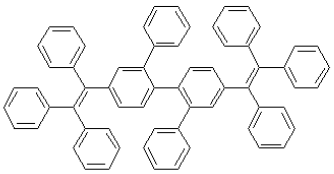
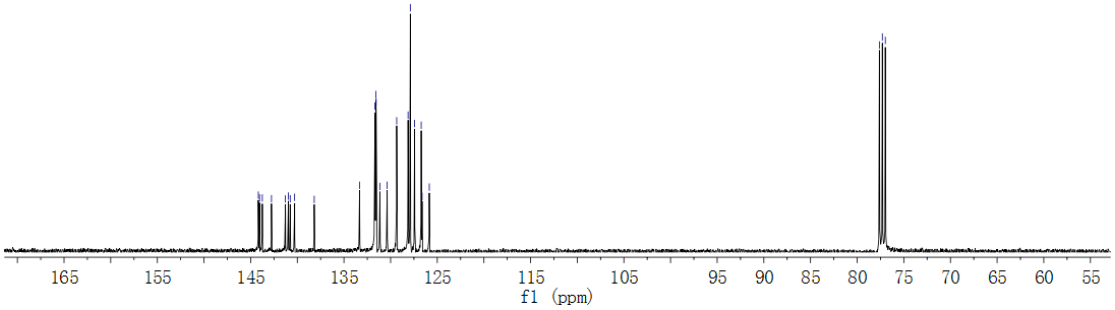
144.05
143.75
142.77
141.27
140.95
140.76
140.29
138.18
133.32
131.67
131.58
131.55
131.14
130.37
129.35
128.13
127.89
127.43
126.72
126.62
125.85

77.62
77.30
76.98



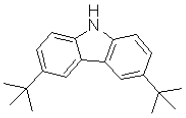


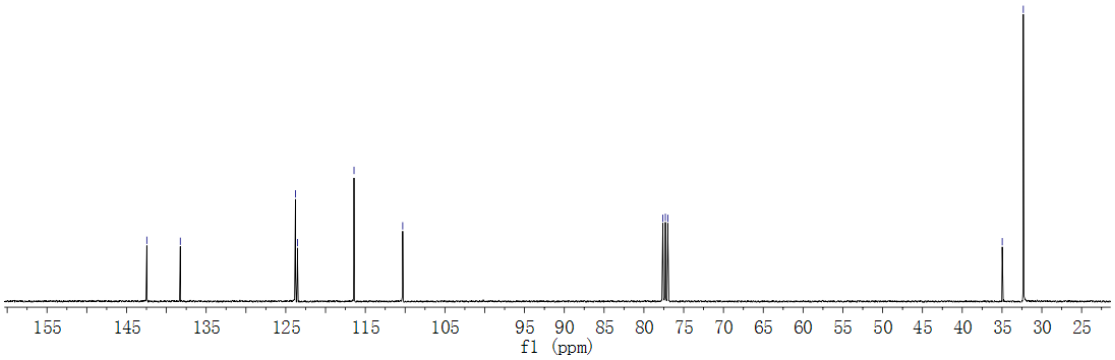
lizhen-H22

142.46
138.25
123.78
123.51
116.42
110.30

77.62
77.30
76.98

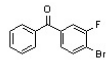
34.97
32.33





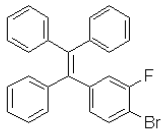
h17-c

194.53
160.30
157.82
138.70
136.82
133.82
133.21
130.13
129.70
128.75
128.47
126.94
126.90



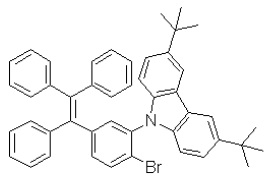
lizhen-H18

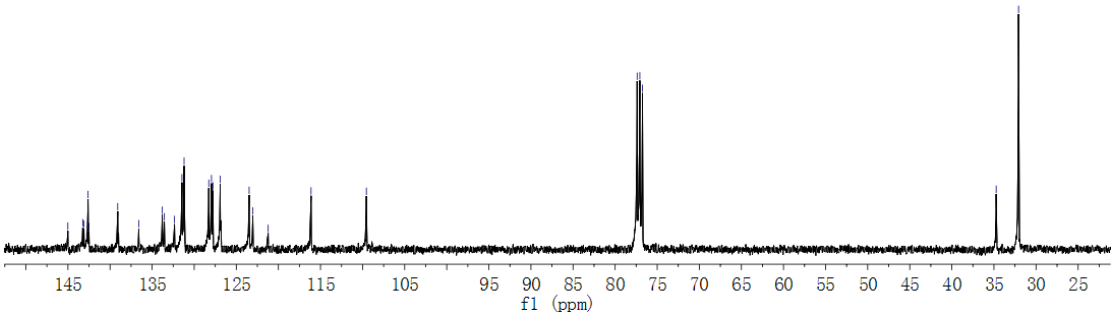
161.50
159.00
157.57
145.56
145.49
144.36
143.30
143.25
143.18
142.94
142.66
142.11
138.90
131.47
131.42
131.35
130.71
130.64
128.28
128.17
128.06
128.02
127.28
127.26
127.17
121.27
121.18
119.61
119.53
119.36
119.31



lizhen-H19

143.27
142.69
139.08
133.79
133.55
132.34
131.46
131.20
128.27
127.95
127.78
126.91
123.47
123.04
116.42
109.55
77.38
77.07
76.75
34.74
32.08





lizhen-H20

143.47
141.80
140.44
135.72
131.55
131.32
131.30
128.17
127.75
127.72
126.72
126.68
123.10
123.00
115.66
109.11
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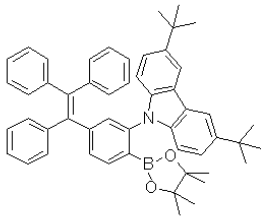
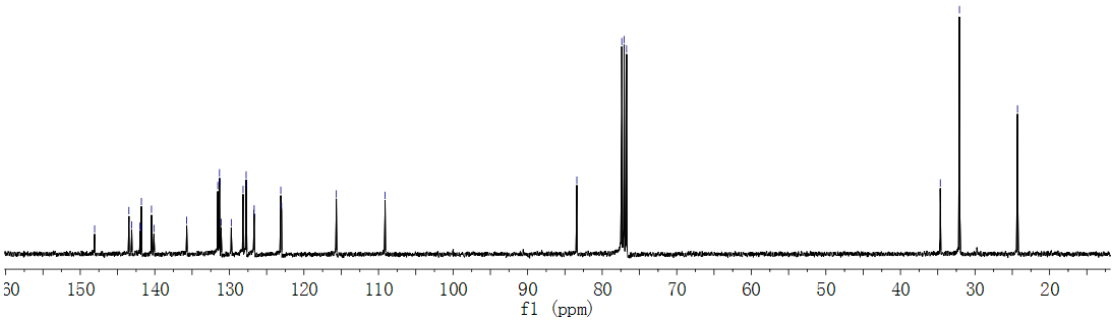
77.37
77.05
76.73
34.65
32.09
24.30





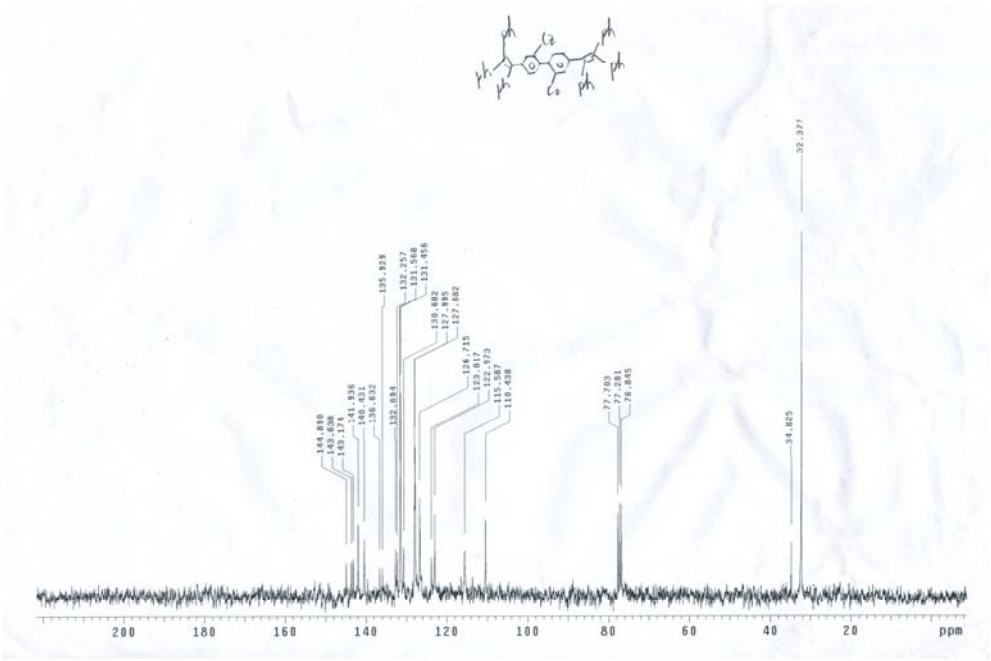


Figure S10 (A) ^{1}H NMR and (B) ^{13}C NMR spectra of the synthetic intermediates and final products.