Electronic Supplementary Information (ESI) for

Blue-light-emitting multifunctional triphenylamine-centered starburst quinolines: synthesis, electrochemical and photophysical properties

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I. General Methods.

All reagents were of analytical reagent grade or were chemically pure. All solvents were dried by standard methods and distilled before use. Melting points were measured on an X-4 microscope electrothermal apparatus (Taike China) and were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV spectrometer (500 MHz 400 MHz or 300 MHz for ^{1}H and 125 MHz 100 MHz or 75 MHz for ^{13}C). Mass spectra were recorded on a Agilent 1100 mass spectrometer. Fourier transformation infrared (FTIR) spectra were recorded in KBr pellets using an AVATAR 370 FTIR spectrometer (Thermo Nicolet). The elemental analyses were performed with a Vario El III elemental analyzer. Thermogravimetric analysis (TGA) of the molecules and differential scanning calorimetry (DSC) were conducted on NETZSCH STA 409 PC/PG ((heating rate of 10°C min^{-1}). Optical absorption spectra were obtained by using a HP-8453 UV/vis/near-IR Spectrophotometer (Agilent). Photoluminescence spectra were carried out on a LS-55 spectrofluorometer (Perkine-Elmer). The electrochemical experiments were carried out using a CHI 660C electrochemistry workstation (CHI USA). A standard one-compartment three-electrode cell was used with a Pt electrode as the working electrode, a Pt wire as the counter electrode and a Ag/Ag+ electrode (Ag in 0.1M $AgNO_3$ solution, from CHI, Inc.) as the reference electrode. TBAP (0.1 M) was used as the supporting electrolyte. The scan rate was 50 mV s^{-1}.

Measurements of fluorescence quantum yields. The fluorescence quantum yields ($\mathbf{\Phi_u}$) of compounds **1a-1g** were determined in chromatographic grade solvents. The optical density of the dilute solution of all compounds (the reference and compounds **1a-1g**) was less than 0.1 at the excitation wavelength, using quinine sulfate ($\mathbf{\Phi r}$ = 0.546 in 0.1N H_2SO_4)[1] as a references at excitation wavelengths of 365 nm. The quantum yield is calculated using equation. [1]

$$\Phi_u = \Phi_s (A_s F_u / A_u F_s) (\eta_u/\eta_s)^2 \quad (1)$$

Where: the u subscript refers to the unknown and s to the standard and other symbols have the following meanings: Φ is quantum yield, A is absorbance at the excitation wavelength, F the integrated emission area across the band η is the refractive index of the solvent.

Calculation methods and results. To understand electronic structures of starburst molecules **1a-1g**, the ground-state geometry of the molecules were first optimized at AM1 level and then their frontier molecular orbitals were calculated at the B3LYP/6-31G* level of theory with Gaussian 09.[2]

Table S1. DSC thermograms of **1c-1g** under a nitrogen atmosphere at a heating rate of 10℃ min^{-1}.

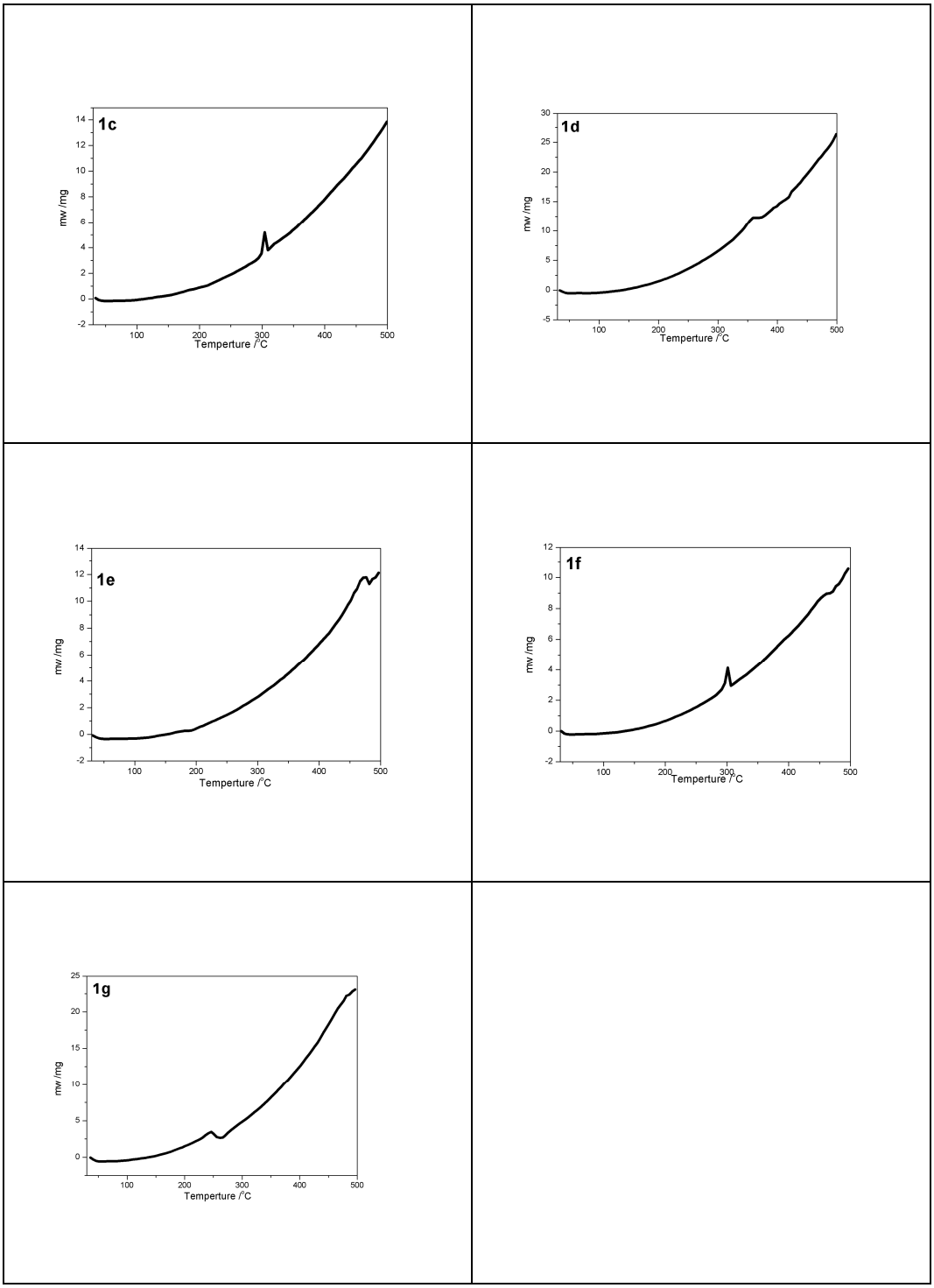
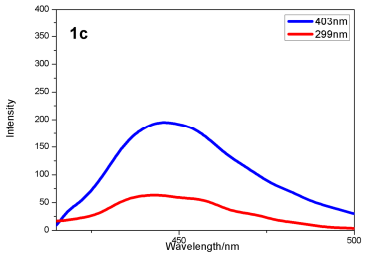
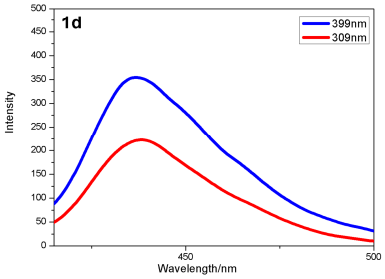
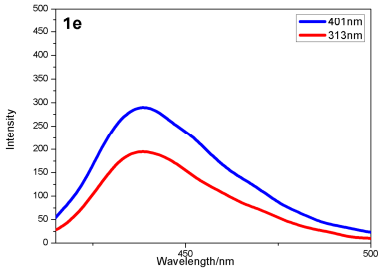
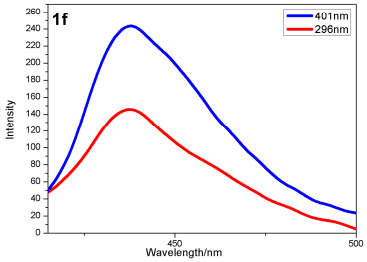


Table S2. Fluorescence spectra of **1c-1g** in toluene solutions at different excitation wavelength.









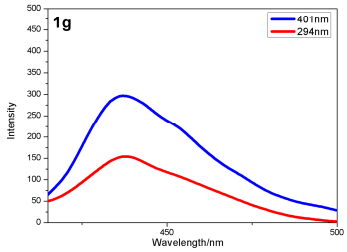


Table S3. Reduction cyclic voltammograms and Oxidation cyclic voltammograms of compounds **1a,1c,1d,1f,1g**.

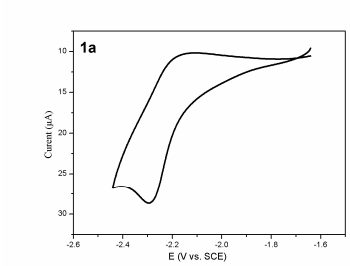
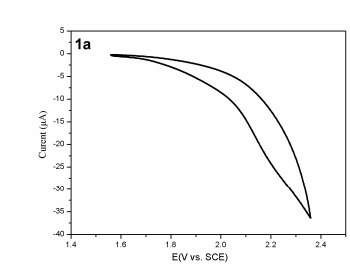
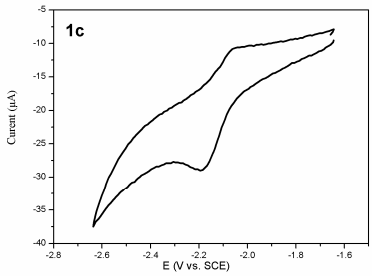
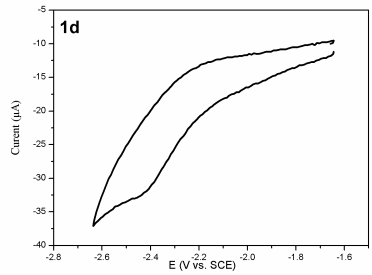
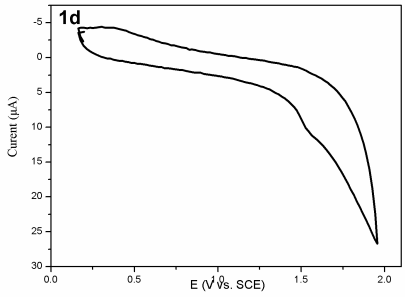
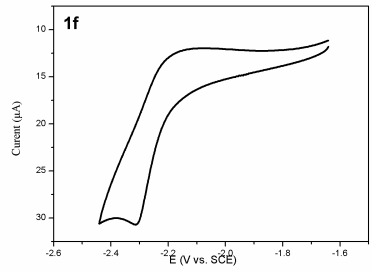
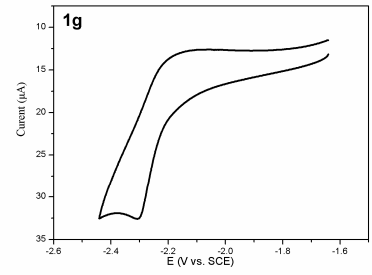
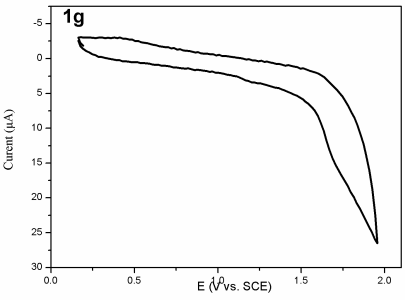
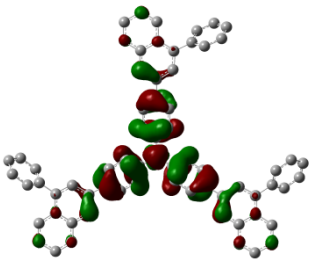
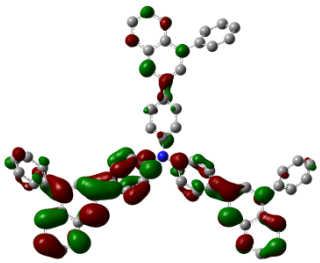
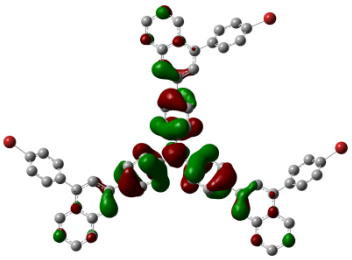
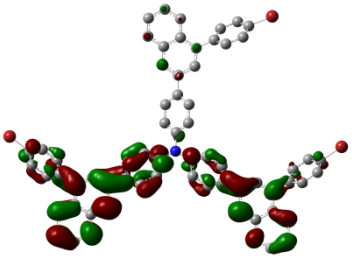
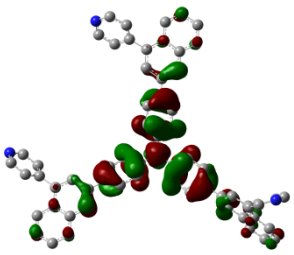
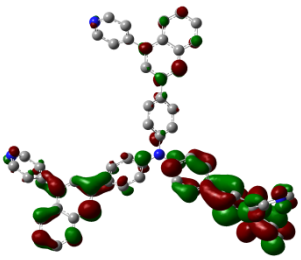
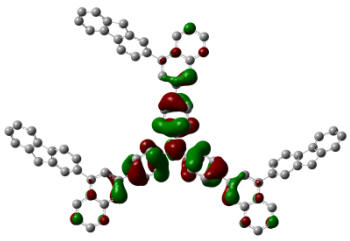
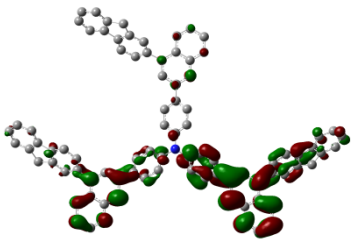
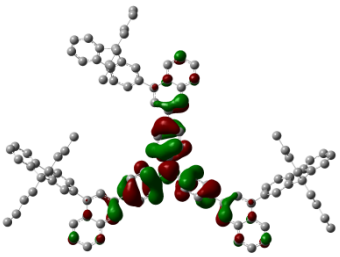
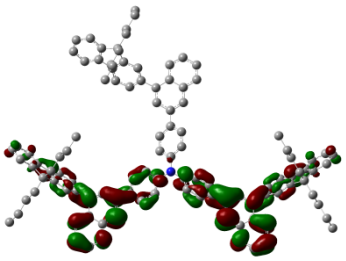
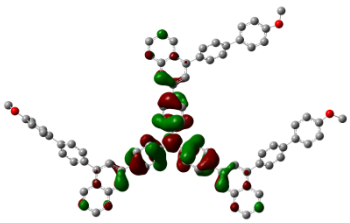
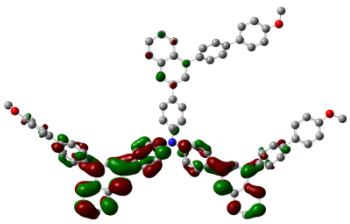
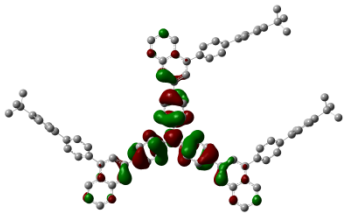
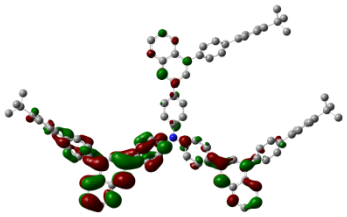
	reduction cyclic voltammograms	**oxidation cyclic voltammograms**
1a		
1c		--
1d		
1f		--
1g		

Table S4. Frontier molecular orbital plots of optimized structures of compounds **1a-1g**.

	HOMO	LUMO
1a		
1b		
1c		
1d		
1e		

1f		
1g		

II. Characterization Data of New Compounds

General procedure for synthesis of 3a-3e

To a stirred solution of boron trichloride (1 M solution in 1, 1, 2, 2-tetrachloroethane, 1.1 equiv based on an aniline) was added a solution of aniline in 1, 1, 2, 2-tetrachloroethane dropwise under ice cooling. To the resulting solution were added a nitrile (l.2 equiv based on an aniline) and Within 30 to 40 min, the complex dissolved during stirring at room temperature. The solution was then refluxed for 20-48 h, then cooled in ice and 2 N HCl was added dropwise under stirring. The resulting mixure was warmed to 80°C for 1 h, then cooled to room temperture and extracted with dichloromethane. The combined organic extracts were washed with brine and dried then the solvent was removed in vacuo. The residue was purified by column chromatography to afford compounds **3a-3e**.[3]

(2-Aminophenyl)phenylmethanone (3a). Yield was 54.6% as yellow crystals; mp 108-109℃.(lit 107-108℃[3]).

(2-Aminophenyl)(4-bromophenyl)methanone (3b). Yield was 53% as yellow solid; mp 106-107℃. (lit 107-108℃[4]).

(2-Aminophenyl)(4-pyridinyl)methanone (3c). Yield was35.3% as yellow solid; mp 160-162℃. (lit 163℃[5]).

(2-Aminophenyl)(9H-fluoren-2-yl)methanone (3d). Yield was 39.5% as yellow solid; mp 142-144℃. (lit140-150℃[6]).

(2-Aminophenyl)(9,9-dibutyl-9H-fluoren-2-yl)methanone (3e). Yield was 39% as yellow glutinous fluid. ^{1}H NMR (DMSO, 500 MHz): δ= 0.55-0.49(m 2H), 0.63(t 3H J=7.35Hz CH_2-CH_3), 1.06-1.00(m 2H), 2.05-1.95(m 2H), 3.37(s 1H NH_2), 6.48(t 0.5H J=7.3Hz and J=7.5Hz), 6.90(d 0.5H J=8.65Hz), 7.31-7.28(q 1H), 7.38(t 1H J=3.35Hz and J=5.2Hz), 7.47(t 0.5H J=3.35Hz and J=5.1Hz), 7.58(d 0.5H J=7.75Hz), 7.62(d 0.5H J=17.25Hz), 7.90-7.88(q 0.5H), 7.93(d 0.5H J=7.8Hz Ar-H); ^{13}C NMR (DMSO, 125 MHz): δ=197.81, 151.66, 150.93, 149.58, 143.31, 139.48, 138.38, 133.92, 133.51, 128.04, 127.98, 127.00, 123.32, 122.88, 120.50, 119.47, 116.86, 113.83, 54.60, 38.88, 25.66, 22.24, 13.57; TOFMS (EI) calcd for (M+) $C_{28}H_{31}NO$: 398.24, found 398.2 ; Elemental analysis calcd (%) for $C_{28}H_{31}NO$: C 84.59, H 7.86, N 3.52, O 4.02; found C 84.83, H 7.78, N 3.44, O 3.95; IR (KBr): nu(tilde) (cm^{-1}) =2955.8, 2926.53, 2856.8, 1624.3, 1583.3, 1247.8, 742.3.

General procedure for synthesis of 3f-3g[7]

A mixture of Na_2CO_3 (3.18 g, 30 mmol), $Pd(OAc)_2$ (15 mg, 0.5 mol%;), aryl halides (15mmol), arylboronic acid (22.5mmol), distilled water (52.5mL) and DMF (45mL) was stirred for the 20h. Afterward, the reaction solution was extracted four times with dichloromethane and dried over anhydrous sodium sulfate. The precipitate was purified by column chromatography.

(2-Aminophenyl)(4'-methoxy-[1,1'-biphenyl]-4-yl)methanone (3f). Yield was 80.5% as yellow solid; mp 136-138℃. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=3.84(s 3H –CH_3), 6.03(s 2H NH_2), 6.61(t 1H J=7.35Hz and J=7.7Hz), 6.73(d 1H J=8.25Hz), 6.99(d 2H J=8.55Hz), 7.28(t 1H J=7.5Hz and J=7.8Hz), 7.51(d 1H J=7.95Hz), 7.58(d 2H J=8.55Hz), 7.62(d 2H J=8.1Hz), 7.70(d 2H J=8.05Hz Ar-H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ=198.50, 159.70, 150.75, 143.55, 138.08, 134.32, 134.02, 132.58, 129.87, 128.26, 126.17, 118.45, 116.97, 115.51, 114.36, 55.32; TOFMS (EI) calcd for (M+) $C_{20}H_{17}NO_2$: 304.13, found 304.1 ;Elemental analysis calcd (%) for $C_{20}H_{17}NO_2$: C 79.19, H 5.65, N 4.62, O 10.55; found C 79.15, H 5.62, N 4.58, O 10.65; IR (KBr): nu(tilde) (cm^{-1}) =3057.6, 3031.6, 2832.2, 1588.9, 1540.1, 1509.5, 1492.8, 1287.6, 1247.6, 1178.7, 1040.0, 821.9, 763.4.

(2-Aminophenyl)(4'-(tert-butyl)-[1,1'-biphenyl]-4-yl)methanone (3g). Yield was 79.3% as yellow solid; mp 159-160℃. ^{1}H NMR ($CDCl^3$, 500 MHz): δ=1.37(s 9H –CH_3), 5.98(s 2H -NH2), 6.62(t 1H J=7.6Hz and J=7.45Hz), 6.73(d 1H J=8.25Hz), 7.28(t 1H J=7.55Hz and J=7.75Hz), 7.53~7.48(q 3H), 7.58(d 2H

J=7.85Hz), 7.66(d 2H J=7.85Hz), 7.71(d 2H J=7.85Hz Ar-H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ=198.55, 151.07, 150.74, 143.80, 138.45, 137.21, 134.36, 134.06, 129.81, 126.86, 126.53, 125.84, 118.44, 116.99, 115.54, 34.57, 31.29; TOFMS (EI) calcd for (M+) $C_{23}H_{23}NO$: 330.18, found 330.2; Elemental analysis calcd (%) for $C_{23}H_{23}NO$: C 83.85; H 7.04, N 4.25, O 4.86; found C 83.79, H 7.04, N 4.27, O 4.90; IR (KBr): nu(tilde) (cm^{-1}) =3059.7, 3029.9, 2959.0, 1589.4, 1541.7, 1511.3, 1493.1, 1359.1, 1287.3, 1269.8, 823.5, 765.4.

General procedure for synthesis of 1a-1g

A flask was charged with a mixture of 4,4',4''-triacetyltriphenylamine (1.0 mmol), 2-aminophenyl ketone compound (3a-3g) (3.2 mmol), acetic acid glacial (15 mL), and sulfuric acid (0.1 mL). It was stirred and refluxed under N2 for 18 h. After cooling, the mixture was slowly added to a stirred mixture of crushed ice and 25% ammonia solution in water to give a precipitate. This was filtered off, washed thoroughly with water. The precipitate was passed through a silica gel column via flash chromatography to remove impurities. The resulting product was then recrystallized from tetrahydrofuran/methanol solutions ranging from 30% to 50% methanol. Each was recrystallized twice.[8]

Tris(4-phenylquinolin-2-yl)-triphenylamine (1a). Yield was 35.8% as yellow crystals. ^{1}H NMR ($CDCl_3$ and TFA, 500 MHz): δ =7.50(d 2H J=8.6Hz),7.66~7.72(m 5H), 7.91(t 1H J=7.8Hz), 8.06(d 2H J=8.6Hz), 8.11(s 1H), 8.15(t 1H J=7.75Hz), 8.27(d 1H J=8.5Hz), 8.33(d 1H J=8.55Hz); ^{13}C NMR ($CDCl_3$ and TFA ,125 MHz): δ =152.86, 150.61, 138.82, 135.95, 134.95, 131.51, 130.63, 130.43, 129.68, 129.45, 128.11, 126.52, 126.39, 125.86, 120.93, 120.56; Elemental analysis calcd (%) for $C_{63}H_{42}N_4$: C 88.50, H 4.95, N 6.55; found C 88.45, H 5.04, N 6.51; IR (KBr): nu(tilde) (cm^{-1}) =3056.8, 3028.7, 1588.4, 1541.2, 1507.2, 1488.1, 1455.6, 1317.4, 1285.4, 837.4, 772.9, 700.4.

Tris(4-bromophenylquinolin-2-yl)-triphenylamine (1b). Yield was 41% as yellow crystals. ^{1}H NMR ($CDCl_3$ and TFA, 500 MHz): δ =7.49(d 2H J=8.3Hz), 7.55(d 2H J=8Hz), 7.85(d 2H J=8Hz), 7.91(t 1H J=7.65Hz), 8.06(t 3H J=8.3Hz and J=10.7Hz), 8.19~8.13(m 2H), 8.36(d 1H); ^{13}C NMR ($CDCl_3$ and TFA, 125 MHz): δ =159.18, 152.98, 150.47, 138.72, 135.81, 133.67, 132.91, 130.81, 130.62, 130.39, 127.42, 126.23, 125.91, 125.72, 120.77; Elemental analysis calcd (%) for $C_{63}H_{39}Br_3N_4$: C 69.31, H 3.60, Br 21.96, N 5.13; found C 69.50, H 3.67, Br 21.79, N 5.04; IR (KBr): nu(tilde) (cm^{-1}) =3059.3, 3033.4, 1592.4, 1540.1, 1504.3, 1484.5, 1316.6, 1283.4, 827.1, 762.5.

Tris(4-(4-(pyridin-4-yl)quinolin-2-yl)-triphenylamine (1c). Yield was 37.4% as yellow crystals. ^{1}H NMR (CDC_{l3}, 400 MHz): δ=7.36(d 2H J=10.5Hz), 7.51(s 3H), 7.78(t 3H J=14.05Hz), 8.14(d 2H J=10.5Hz), 8.25(d 1H J=10.45Hz), 8.82(s 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=156.25, 150.14, 148.80, 148.34, 146.30, 146.21, 134.24, 130.23, 129.99, 128.72, 126.74, 124.81, 124.60, 124.32, 118.63;Elemental analysis calcd (%) for $C_{60}H_{39}N_7$: C 83.99, H 4.58, N 11.43; found C 84.03, H 4.49, N 11.48;IR (KBr): nu(tilde) (cm^{-1}) =3053.9, 3034.1, 2956.0, 2927.0, 1586.8, 1538.4, 1508.0, 1490.3, 1412.7, 1358.4, 1318.9, 1282.1, 828.4, 765.7, 617.2.

Tris(4-(4-(9H-fluoren-2-yl)quinolin-2-yl)-triphenylamine (1d). Yield was 36.5% as yellow crystals. ^{1}H NMR ($CDCl_3$ and TFA, 500 MHz): δ=4.02(s 2H), 7.39-8.22(m 15H), 8.56(s 2H); ^{13}C NMR ($CDCl_3$ and TFA, 125 MHz): δ=159.34, 152.92,149.94, 144.58, 144.38, 143.76, 140.15, 139.31, 134.65, 133.20, 130.89, 139.40, 128.63, 128.06, 127.30, 127.14, 126.41, 126.16, 125.81, 125.28, 121.48, 36.92;Elemental analysis calcd (%) for $C_{84}H_{54}N_4$: C 90.13, H 4.86,N, 5.01; found C 90.16, H 4.90, N 4.94; IR (KBr): nu(tilde) (cm^{-1}) =3054.0, 3036.3, 1590.2, 1541.8, 1503.9, 1275.6, 1178.3, 833.0, 770.7, 734.1.

Tris((4-(9,9-dibutyl-9H-fluoren-2-yl)quinolin-2-yl)-triphenylamine (1e). Yield was 34.7% as yellow crystals. ^{1}H NMR ($CDCl_3$ and TFA, 500 MHz): δ=0.72(d 10H J=7.28Hz CH_2-CH_3), 1.14~1.11(q 4H 1-CH_2-), 2.10~2.07(q 4H -CH_2-), 7.44(d 3H J=9.05Hz), 7.50(d 2H J=8.55Hz), 7.63(s 1H), 7.67(d 1H J=7.75Hz), 7.88~7.85(q 2H), 8.01(d 1H J=7.8Hz), 8.07(d 2H J=8.5Hz), 8.13(t 2H J=7.95Hz and J=9.95Hz), 8.29(d 1H J=8.5Hz), 8.34(d 1H J=8.6Hz Ar-H); ^{13}C NMR ($CDCl_3$ and TFA, 125 MHz): δ=152.64, 152.14, 151.40, 150.38, 144.80, 139.48, 138.89, 135.51, 133.14, 130.54, 129.91, 128.83, 128.76, 127.87, 127.42, 126.47, 126.24, 125.69, 124.27, 123.28, 120.86, 120.76, 120.58, 55.60, 39.92, 26.15, 22.90, 13.62; Elemental analysis calcd (%) for $C_{108}H_{102}N_4$: C 89.09, H 7.06, N, 3.85; found C 89.14, H 7.07, N 3.79; IR (KBr): nu(tilde) (cm^{-1}) =3061.5, 3038.9, 2953.7, 2927.3, 2857.2, 1590.2, 1542.7, 1511.0, 1453.4, 1355.6, 1317.2, 1284.1, 1181.0, 834.1, 763.1, 741.7.

Tris((4-(4'-methoxy-[1,1'-biphenyl]-4-yl)quinolin-2-yl)-triphenylamine (1f). Yield was 33.2% as yellow crystals. ^{1}H NMR ($CDCl_3$ and TFA, 500 MHz): δ=4.00(s 3H -CH_3), 7.14(d 2H J=8.7Hz), 7.51(d 2H J=8.25Hz), 7.71(d 2H J=8.7Hz), 7.75(d 2H J=8.1Hz), 7.95~7.89(q 3H), 8.07(d 2H J=8.2Hz), 8.16(t 2H J=6.05Hz and J=7.95Hz), 8.38~8.33(q 2H Ar-H); ^{13}C NMR ($CDCl_3$ and TFA, 125 MHz): δ=158.99, 152.74,

150.55, 144.01, 138.85, 135.88, 133.37, 133.29, 130.59, 130.36, 130.18, 128.71, 128.08, 127.88, 126.53, 126.24, 125.83, 120.72, 120.61, 115.19, 56.06; Elemental analysis calcd (%) for $C_{84}H_{60}N_4O_3$: C 85.98, H 5.15, N 4.77, O 4.09; found C 85.90, H 5.25, N 4.79, O 4.06; IR (KBr): nu(tilde) (cm^{-1}) =3057.6, 3031.6, 2832.2, 1588.9, 1509.5, 1492.8, 1287.6, 1247.6, 1178.7, 1040.0, 821.9, 763.4.

Tris(4-(4'-(tert-butyl)-[1,1'-biphenyl]-4-yl)quinolin-2-yl)-triphenylamine(1g). Yield was 35% as yellow crystals. ^{1}H NMR ($CDCl_3$ and TFA, 500 MHz): δ=1.41(s 9H -CH_3), 7.49(d 2H J=8.35Hz), 7.55(d 2H J=8.2Hz), 7.68(d 2H J=8.15Hz), 7.75(d 2H J=8Hz), 7.92(t 3H J=7.95Hz and J=9.45Hz), 8.06(d 2H J=8.35Hz), 8.14(t 2H J=5.9Hz and J=7.7Hz), 8.35(t 2H J=9.15Hz and J=9.85Hz); ^{13}C NMR ($CDCl_3$ and TFA, 125 MHz): δ=152.73, 151.96, 150.38, 144.40, 138.80, 136.49, 135.63, 133.32, 130.56, 130.14, 140.04, 128.01, 127.91, 126.96, 126.38, 126.21, 126.07, 125.68, 120.71, 117.79, 115.52, 113.26, 111.00, 34.72, 31.25;Elemental analysis calcd (%) for $C_{93}H_{78}N_4$: C 89.24, H 6.28, N 4.48; found C 89.30, H 6.33, N 4.37; IR (KBr): nu(tilde) (cm–1) =3059.7, 3029.9, 2959.0, 1589.4, 1511.3, 1493.1, 1359.1, 1287.3, 1269.8, 823.5, 765.4.

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Ⅲ Mass spectrum of 3d, 3e and 3f

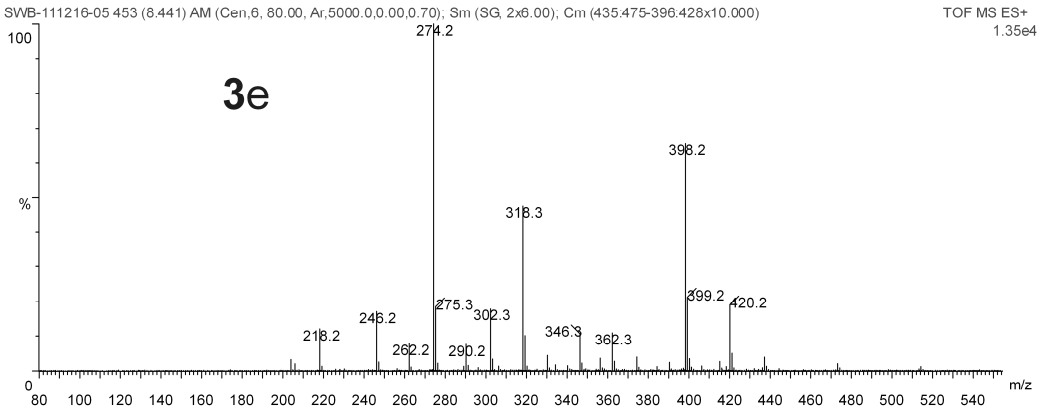

Figure S1. Mass spectrum of compound **3e**

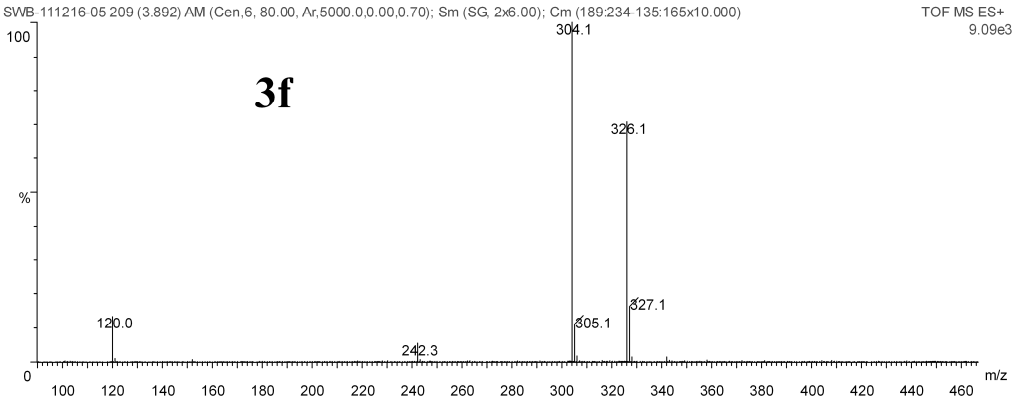

Figure S2. Mass spectrum of compound **3f**

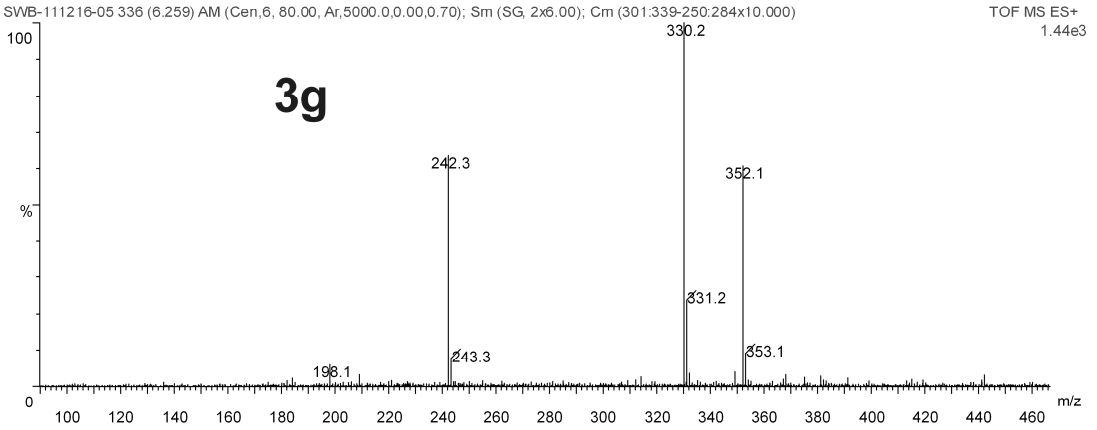

Figure S3. Mass spectrum of compound **3g**

Ⅳ Copies of ^{1}H and ^{13}C NMR Spectra of New Compounds

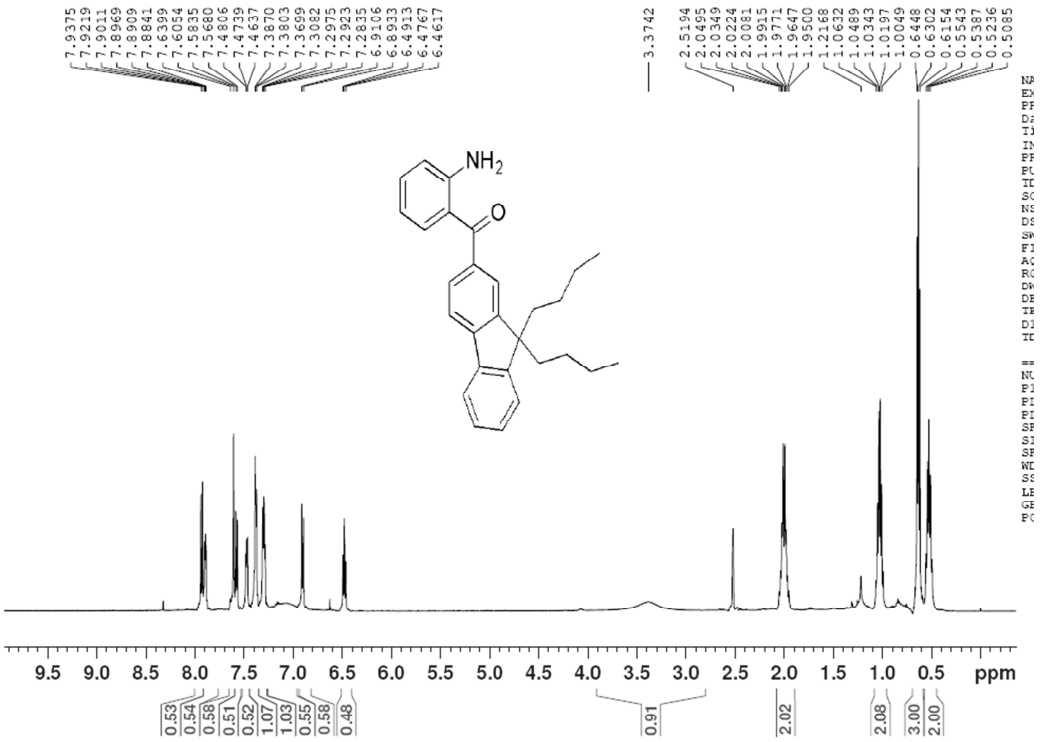

Figure S4.^{1}H NMR spectrum of **3e** in DMSO.

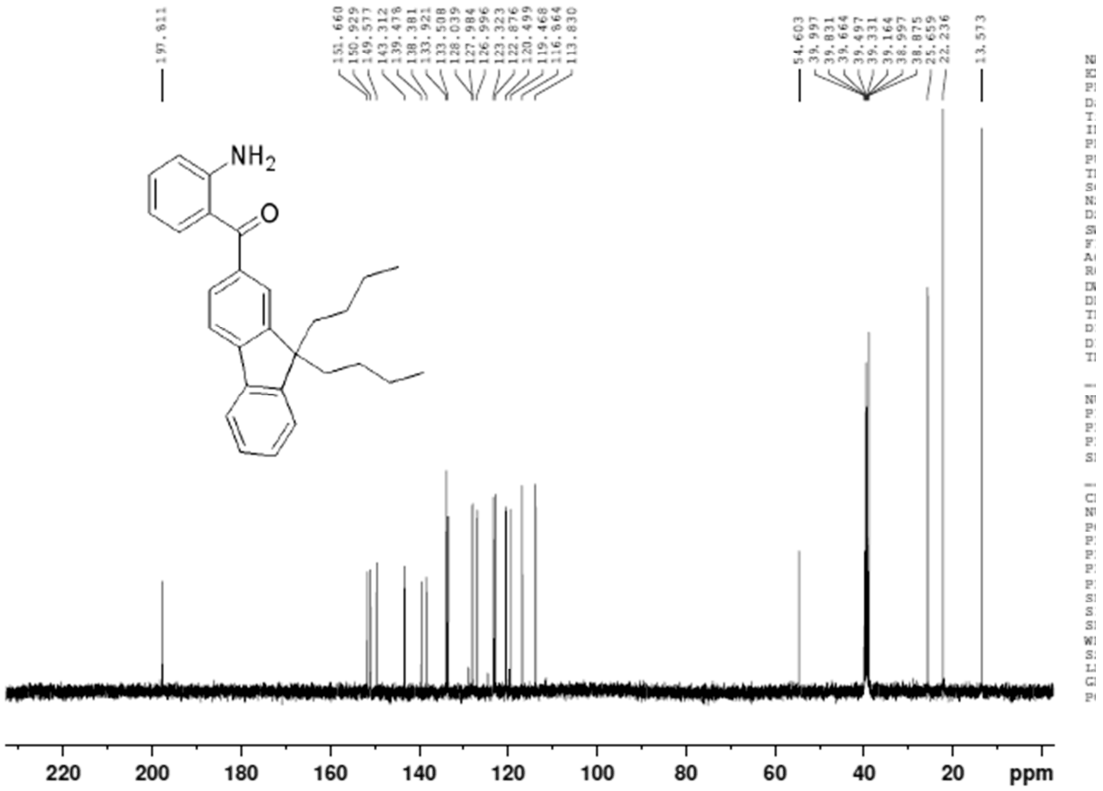

Figure S5.[13]C NMR spectrum of **3e** in DMSO.

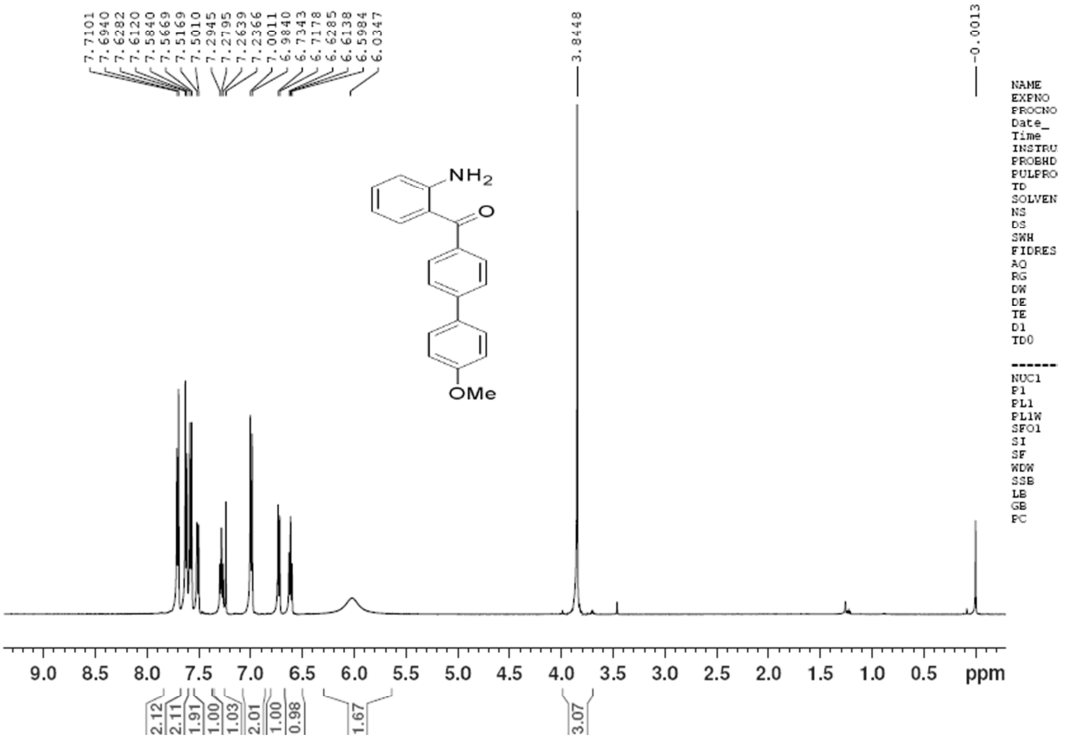

Figure S6.[1]H NMR spectrum of **3f** in $CDCl_3$.

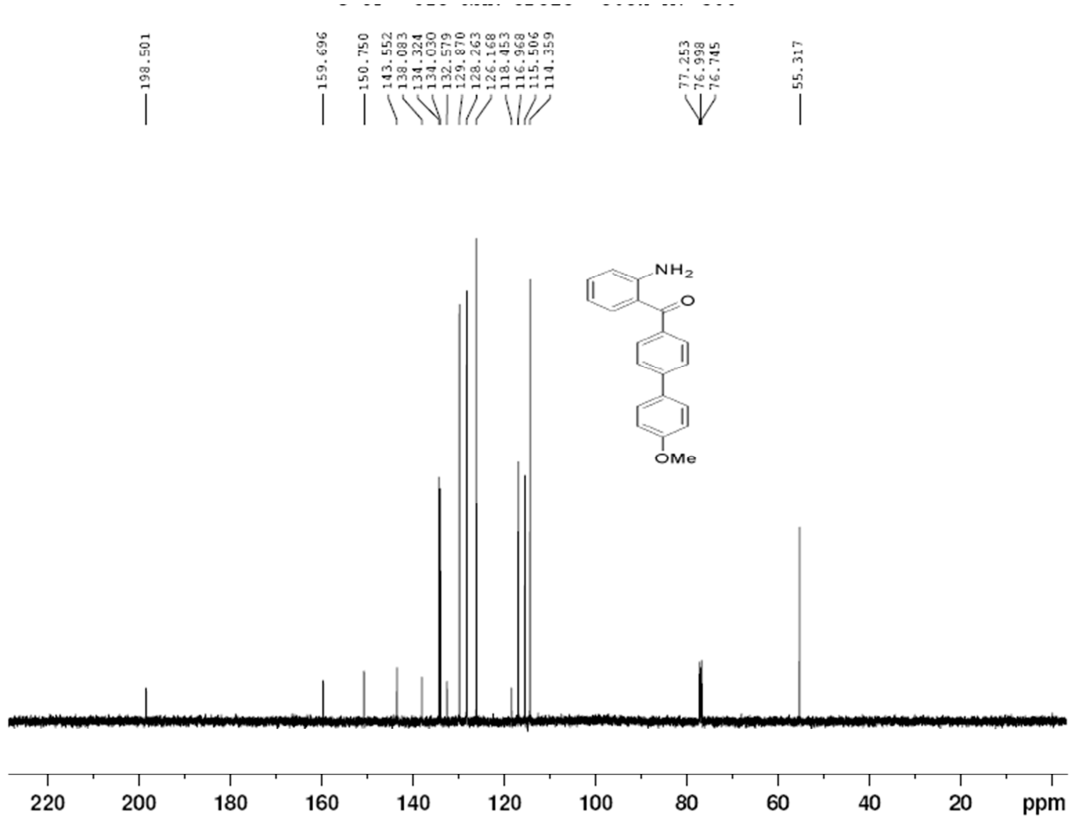

Figure S7.[13]C NMR spectrum of **3f** in $CDCl_3$.

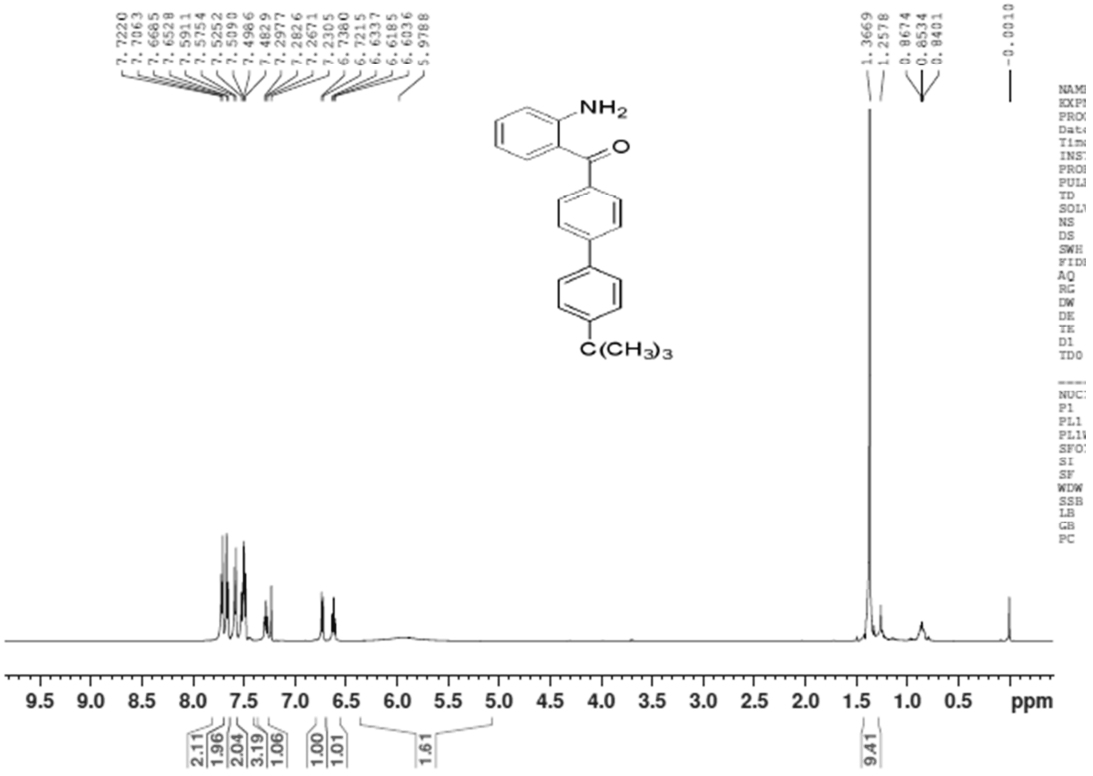

Figure S8.[1]H NMR spectrum of **3g** in $CDCl_3$

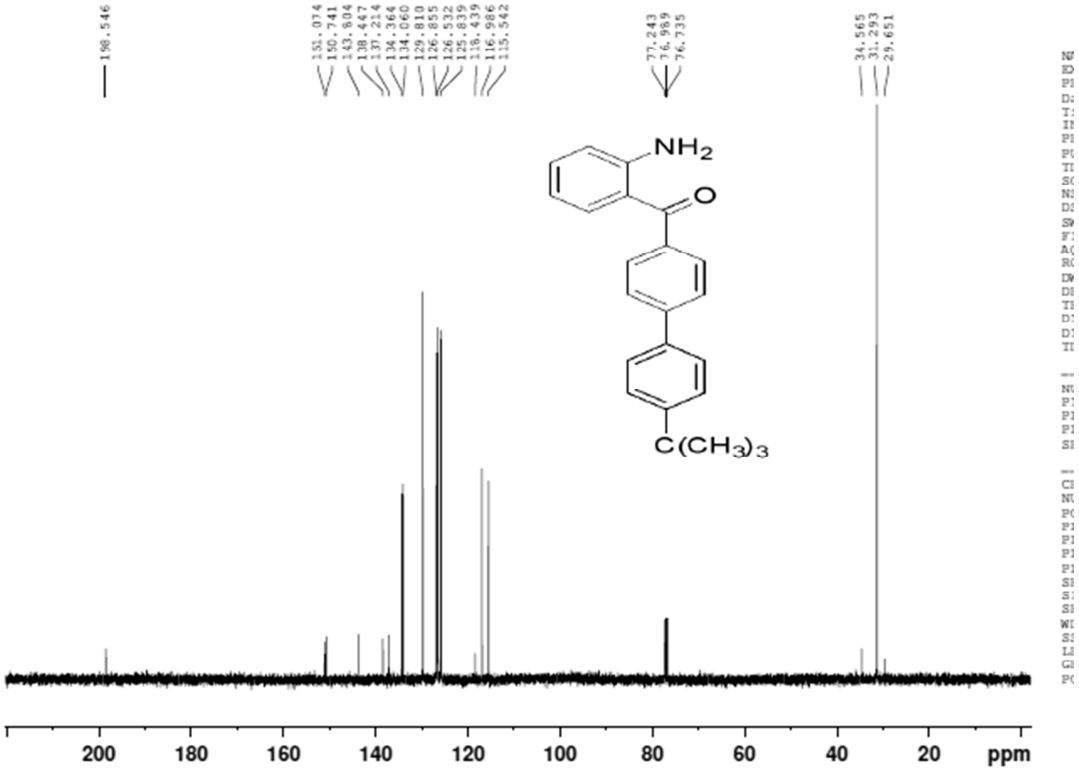

Figure S9.[13]C NMR spectrum of **3g** in $CDCl_3$

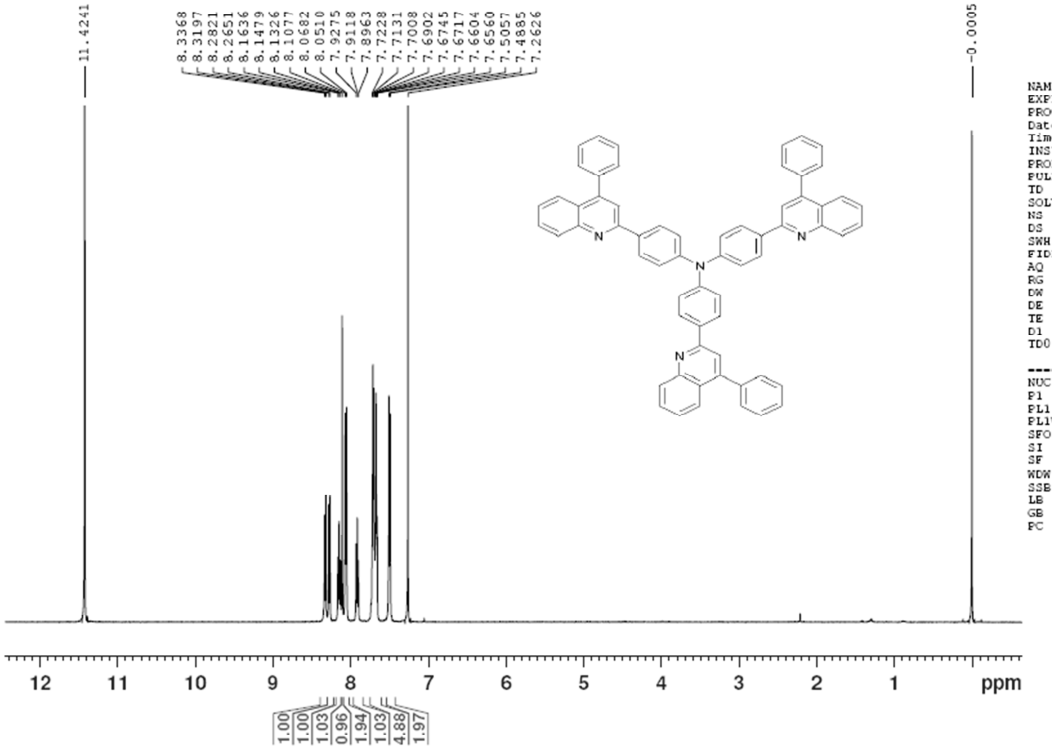

Figure S10.[1]H NMR spectrum of **1a** in $CDCl_3$ + TFA

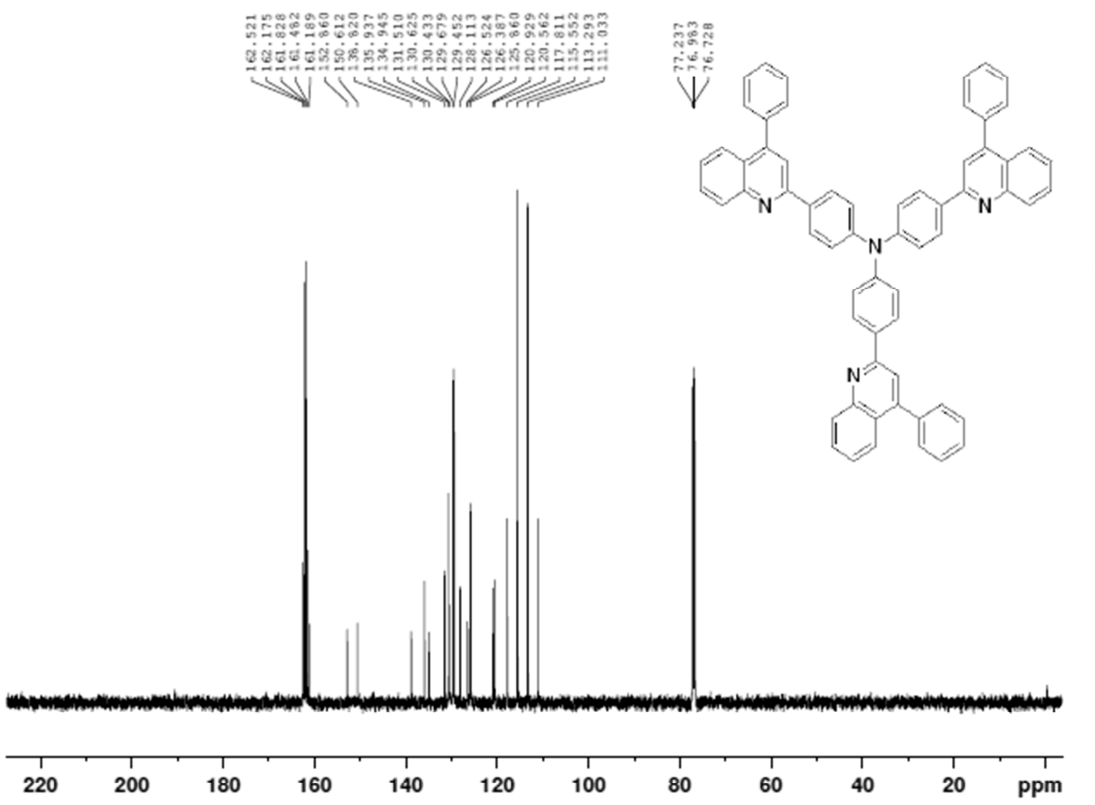

Figure S11.[13]C NMR spectrum of **1a** in $CDCl_3$ + TFA

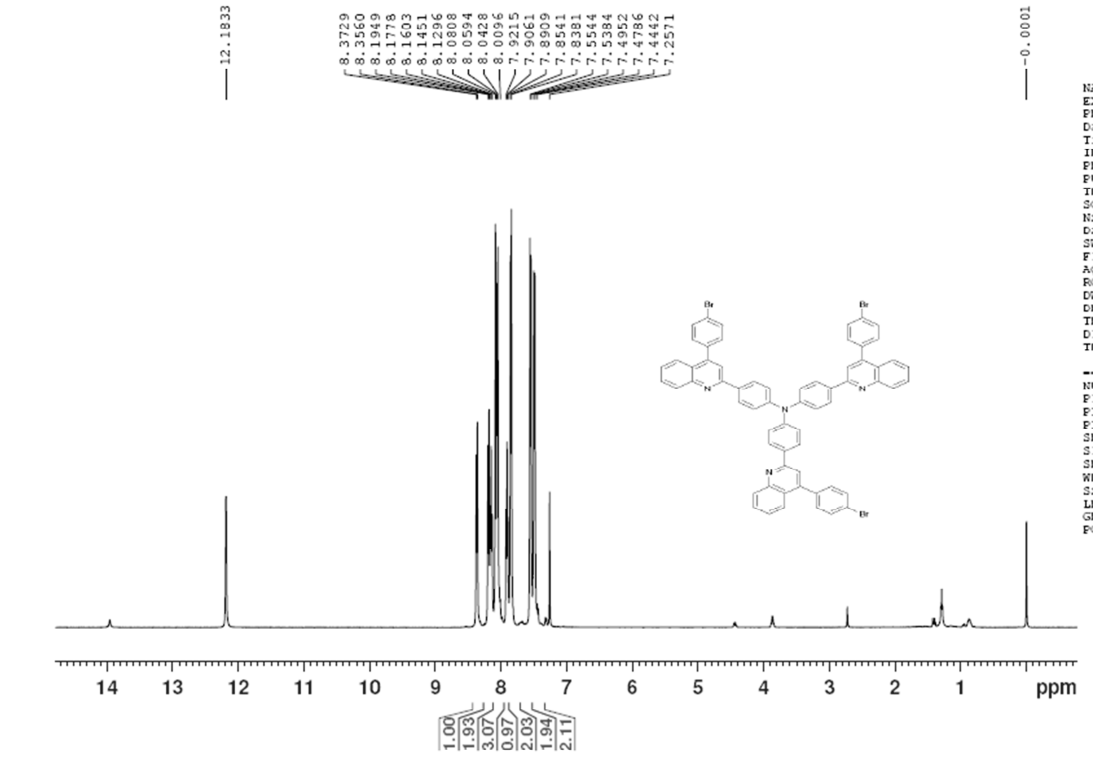

Figure S12.[1]H NMR spectrum of **1b** in $CDCl_3$ + TFA

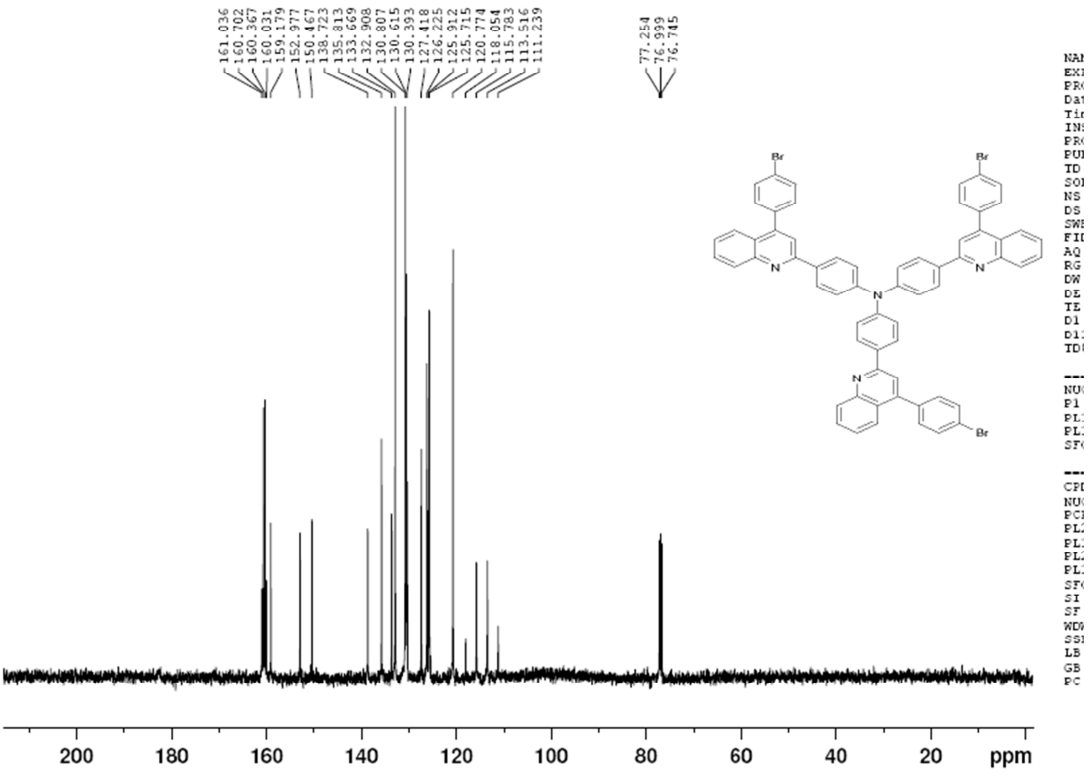

Figure S13.[13]C NMR spectrum of **1b** in $CDCl_3$ + TFA

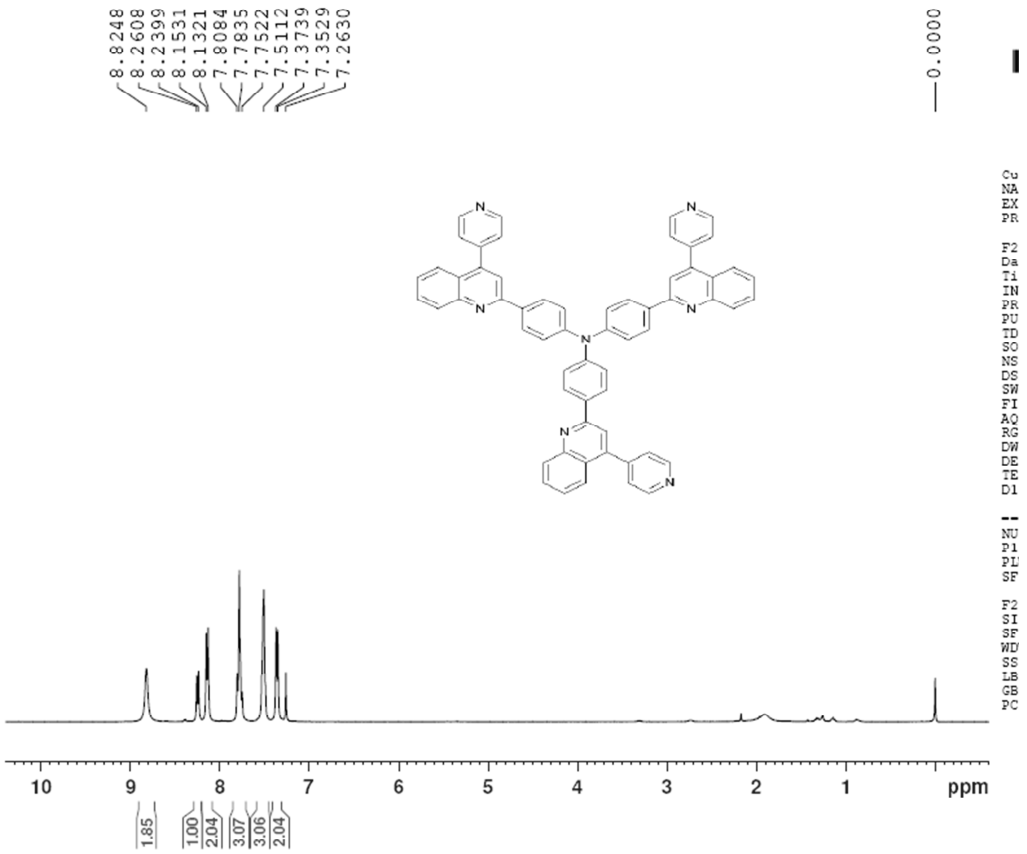

Figure S14.[1]H NMR spectrum of **1c** in $CDCl_3$

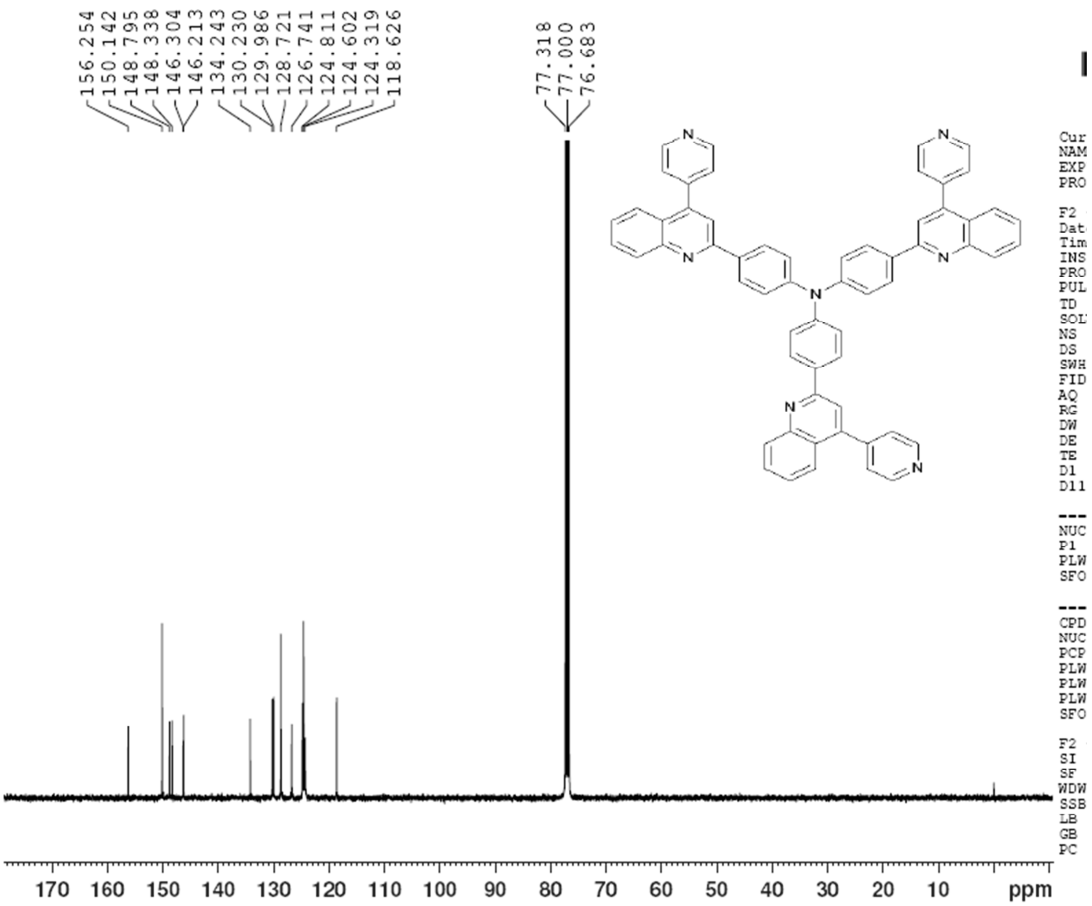

Figure S15. ^{13}C NMR spectrum of **1c** in $CDCl_3$

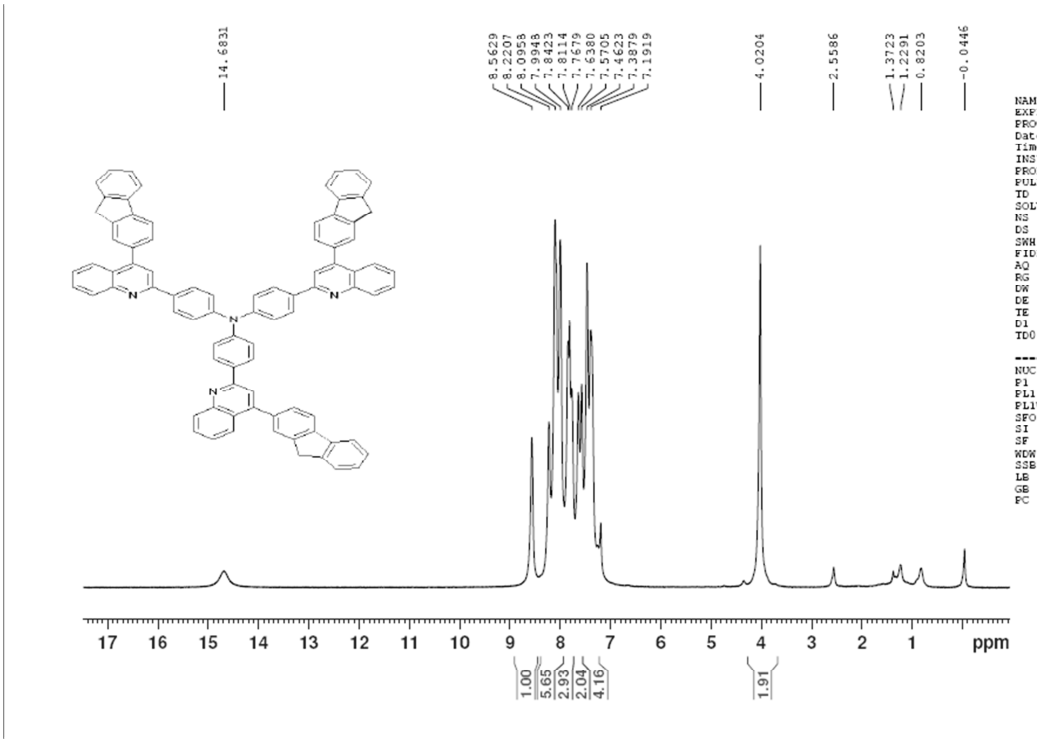

Figure S16. ^{1}H NMR spectrum of **1d** in $CDCl_3$ + TFA

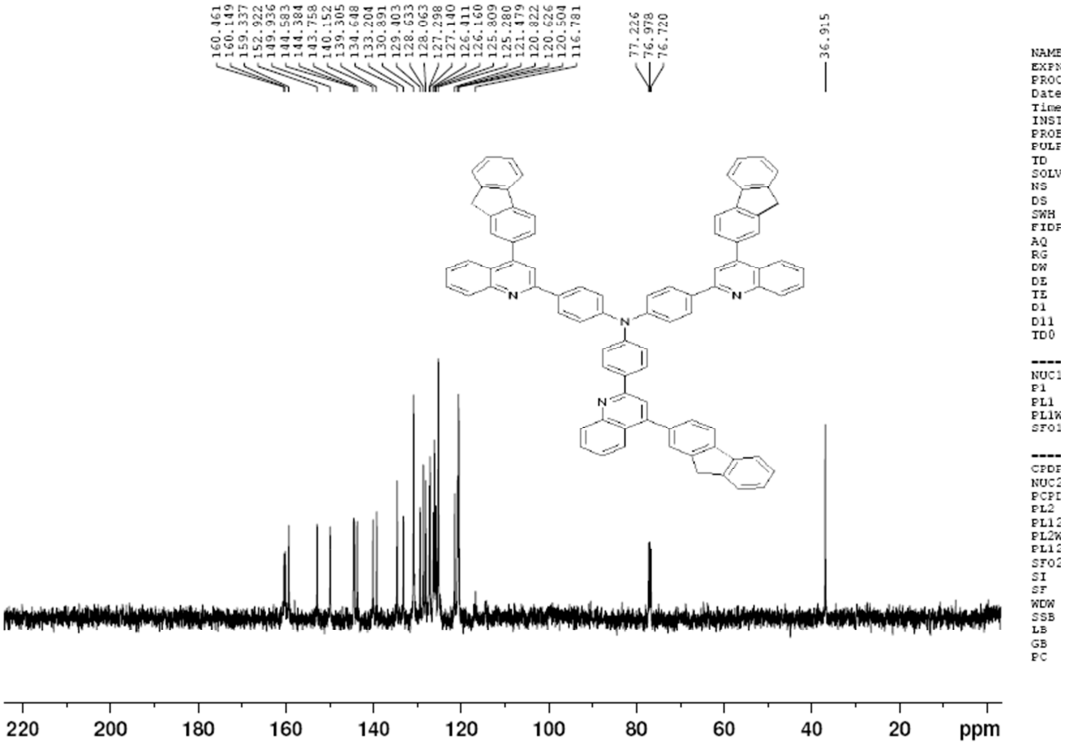

Figure S17. ^{13}C NMR spectrum of **1d** in $CDCl_3$ + TFA

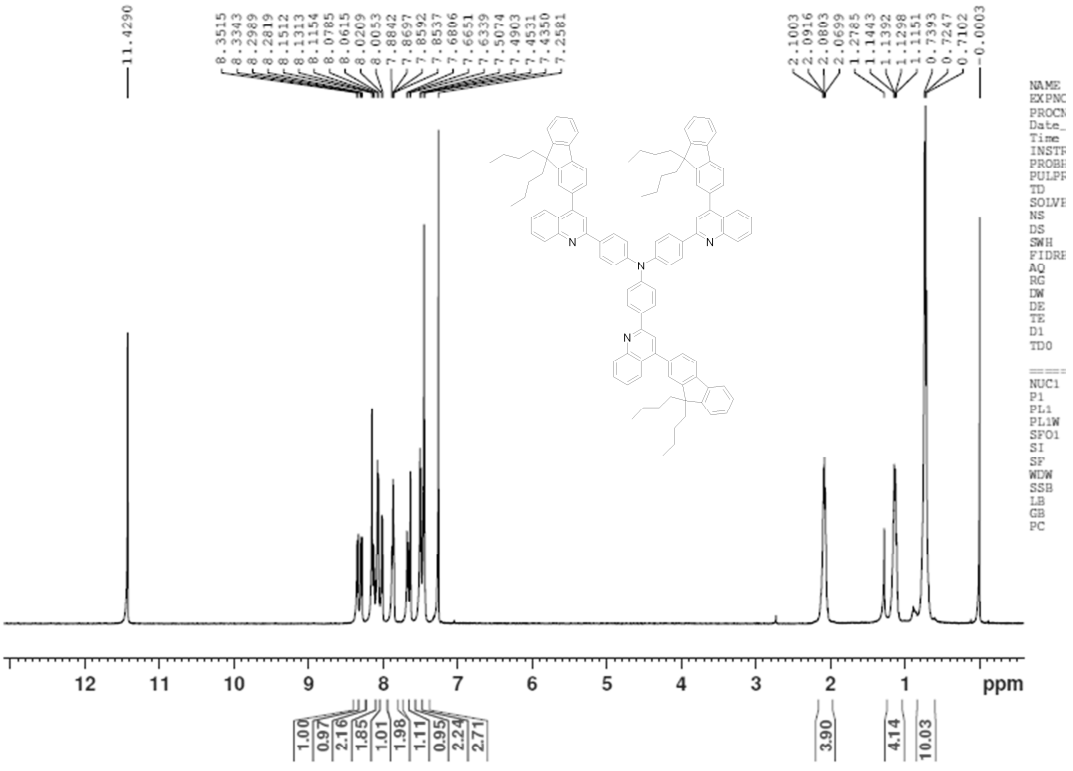

Figure S18. ^{1}H NMR spectrum of **1e** in $CDCl_3$ + TFA

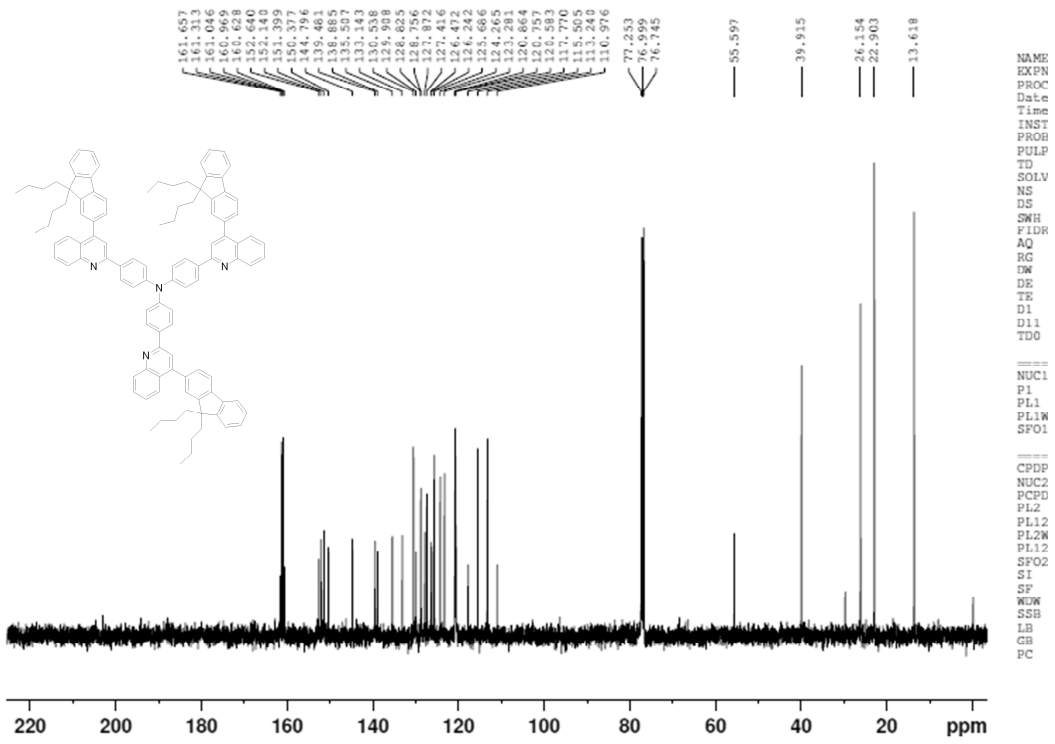

Figure S19. ^{13}C NMR spectrum of **1e** in $CDCl_3$ + TFA

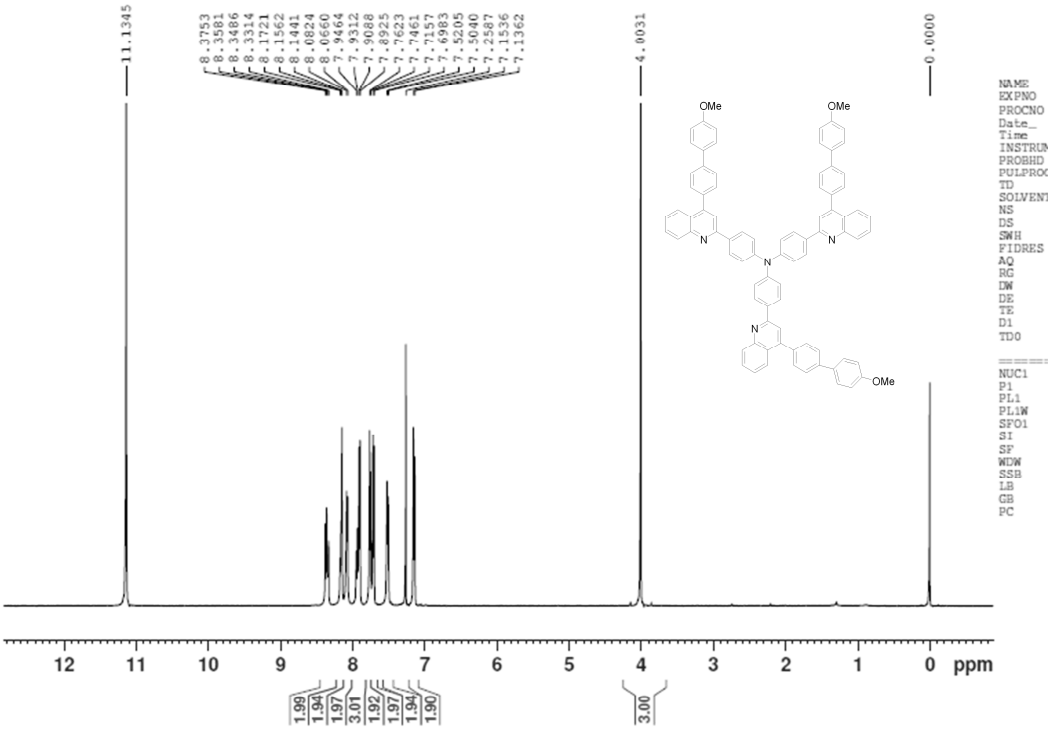

Figure S20. ^{1}H NMR spectrum of **1f** in $CDCl_3$ + TFA

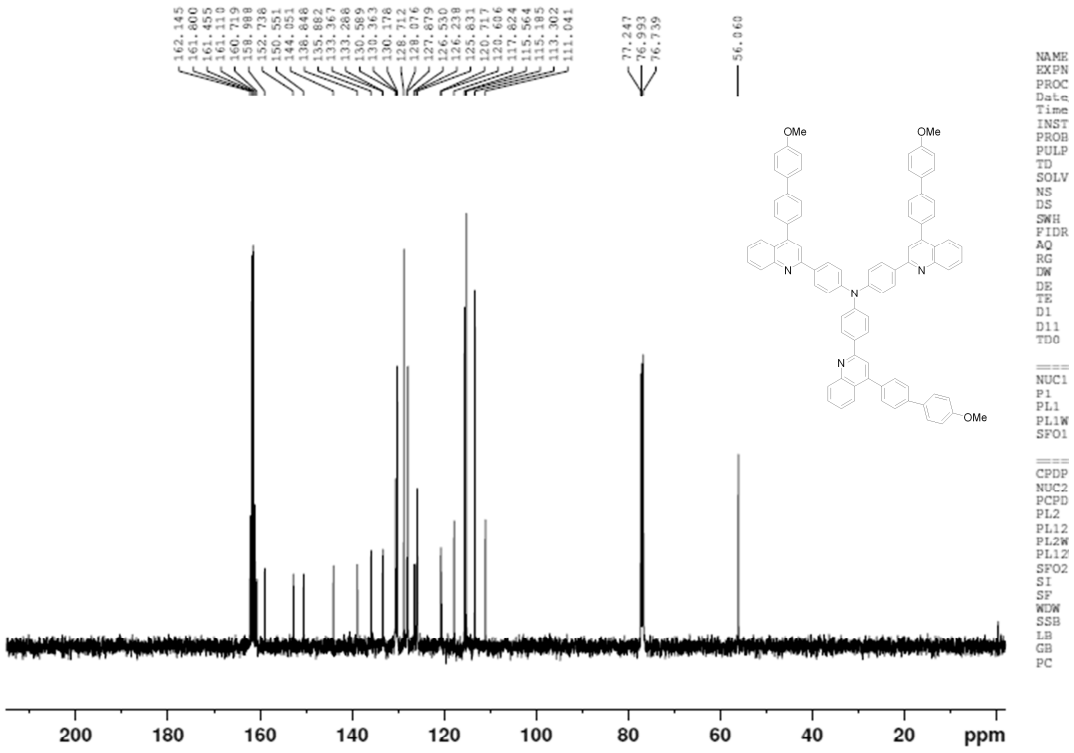

Figure S21. ^{13}C NMR spectrum of **1f** in $CDCl_3$ + TFA

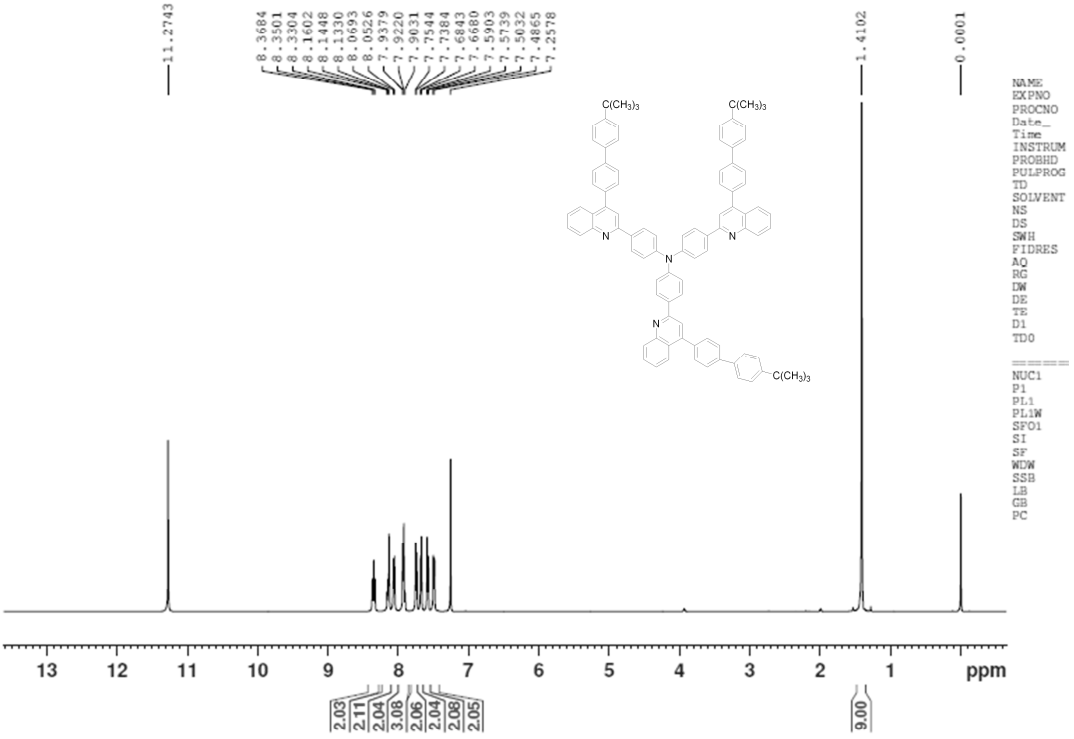

Figure S22. ^{1}H NMR spectrum of **1g** in $CDCl_3$ + TFA

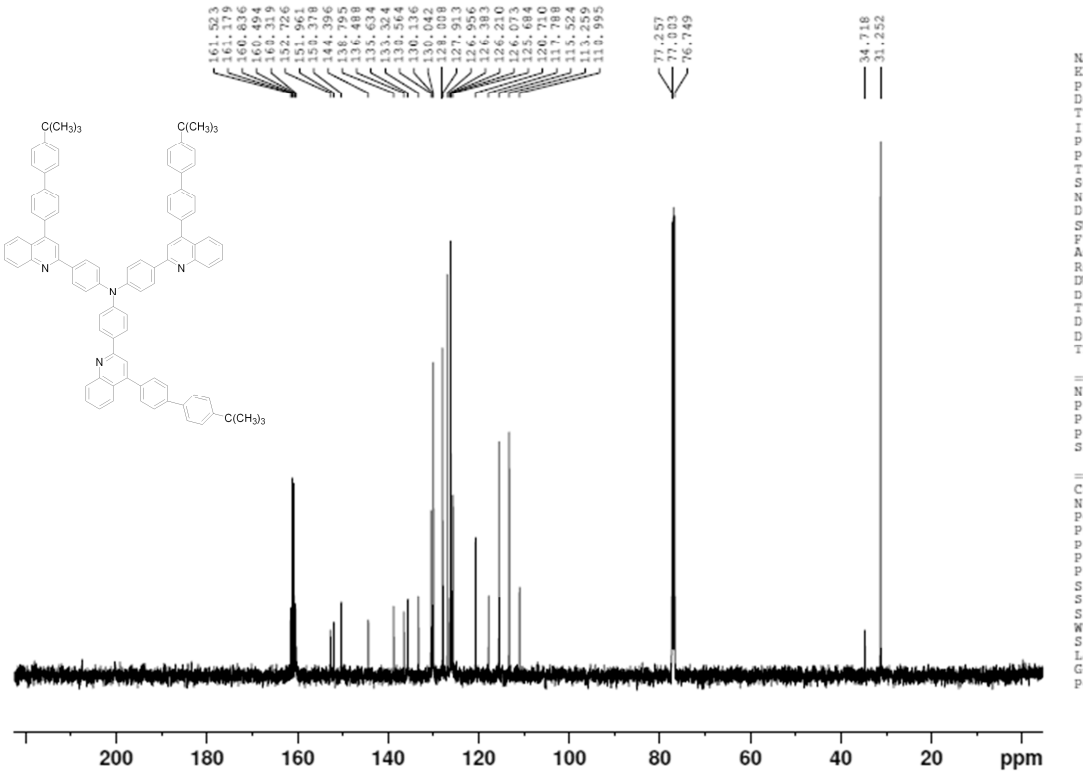

Figure S23. ^{13}C NMR spectrum of **1g** in $CDCl_3$ + TFA