Supplementary Material (ESI) for Chemical Communications

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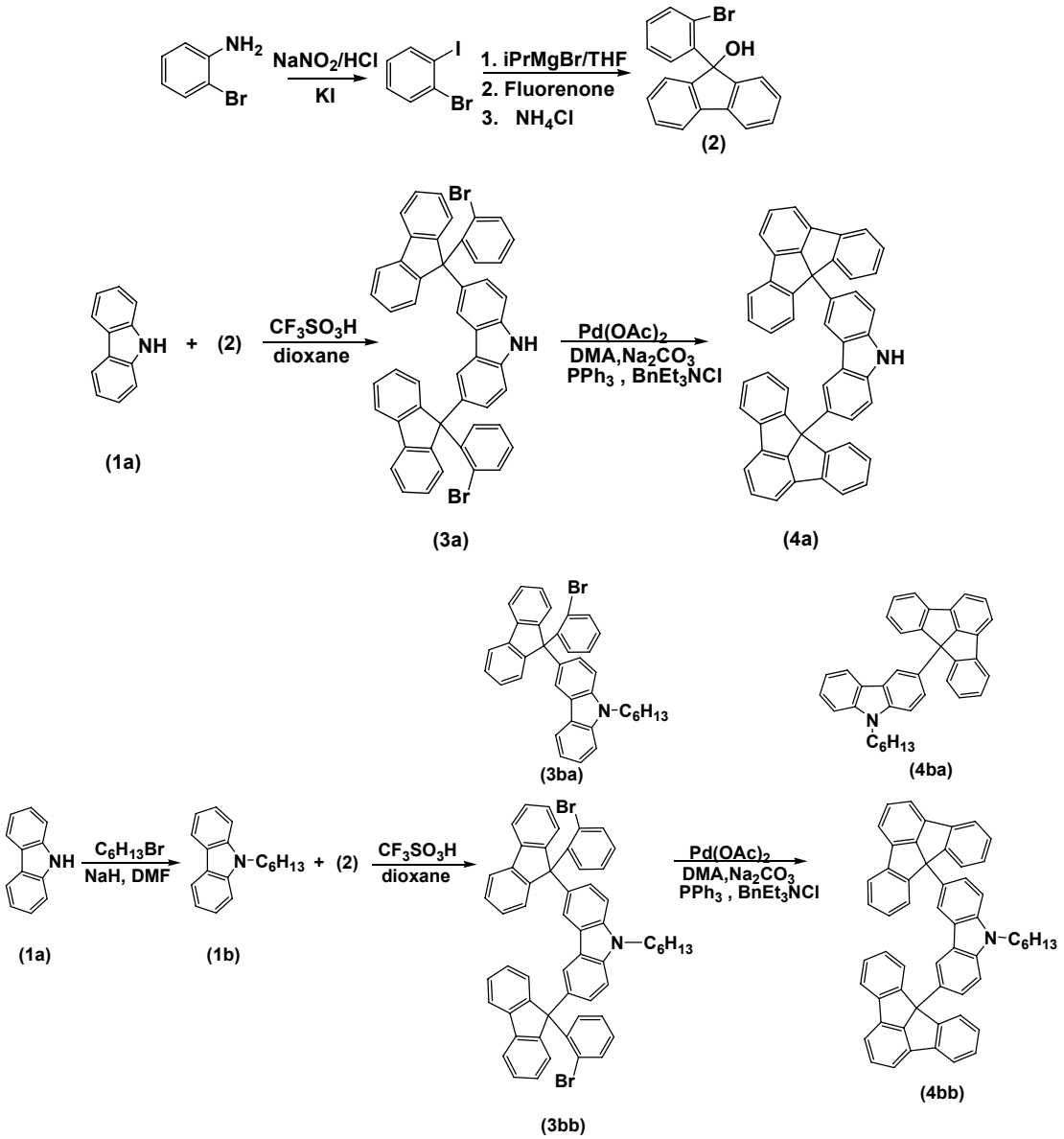
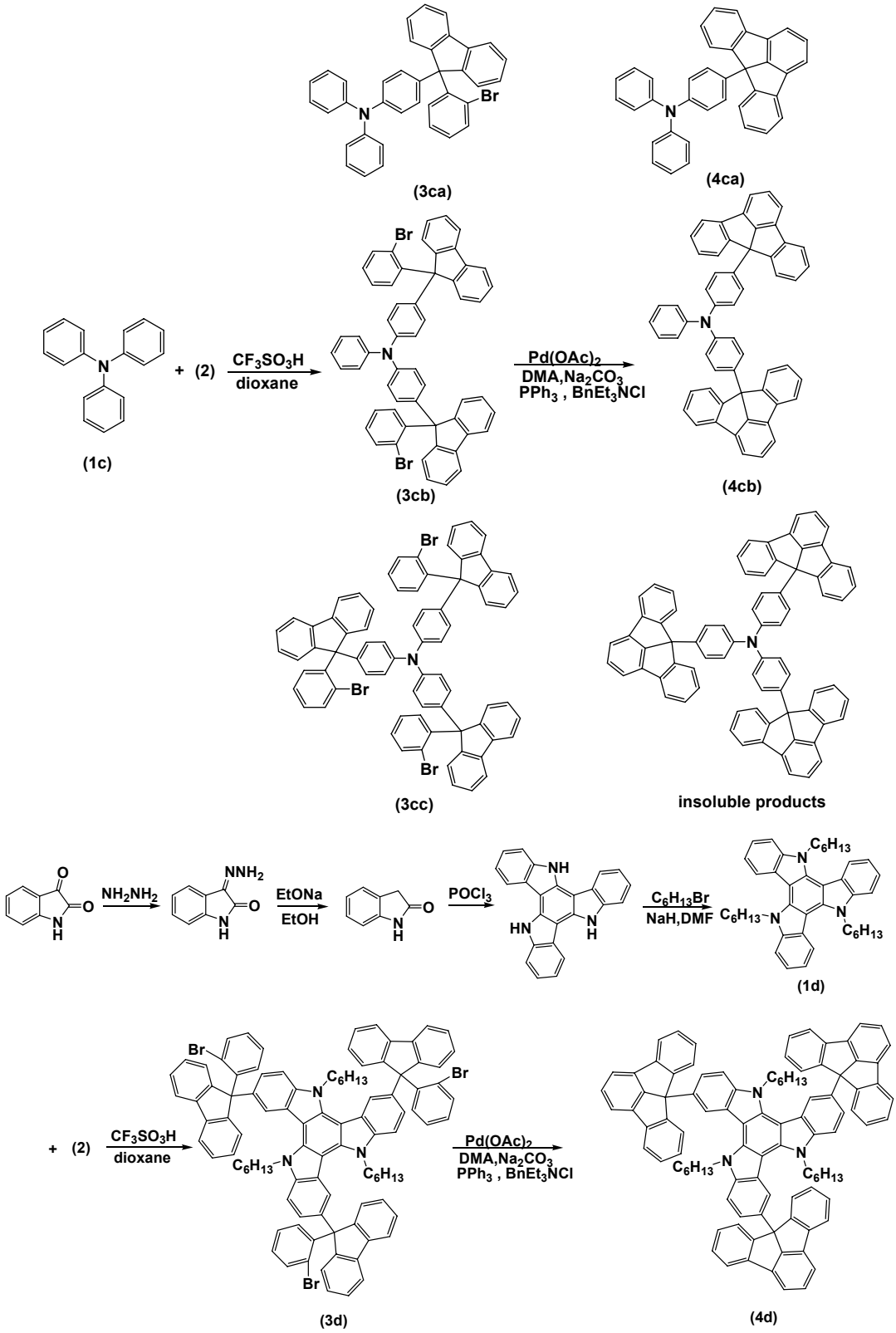
General remarks

All manipulations were performed by standard Schlenk techniques. Melting point was measured on X-4 micrographic measuring apparatus. THF was distilled over sodium-benzophenone. Other chemical reagents and solvents were obtained from commercial sources and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker DR×500 spectrometer (^{1}H NMR 500 MHz, ^{13}C NMR 125 Hz). Element analyses were measured on Vario EL element analysis instrument. UV-Vis absorption spectra were measured on VNICAM Helios (carry 50). Molecular fluorescence spectra were measured on HITACHI FL-4500. Data for X-ray structure analysis were collected at room temperature on a Bruker-AXS, detector with Mo $K\alpha$ radiation (λ= 0.71073 Å). Structures were solved by direct methods with SHELXTL (version 6.10). TGA and DSC were obtained on a Mettler Toledo TGA851e/SF/1100 thermogramm analyzer. Mass spectra (EI) were measured on a microOTOF II spectrometers, high resolution mass spectra (HRMS) were recorded on the GCT Premier TM.

Scheme I Synthetic routes to fluoradenes





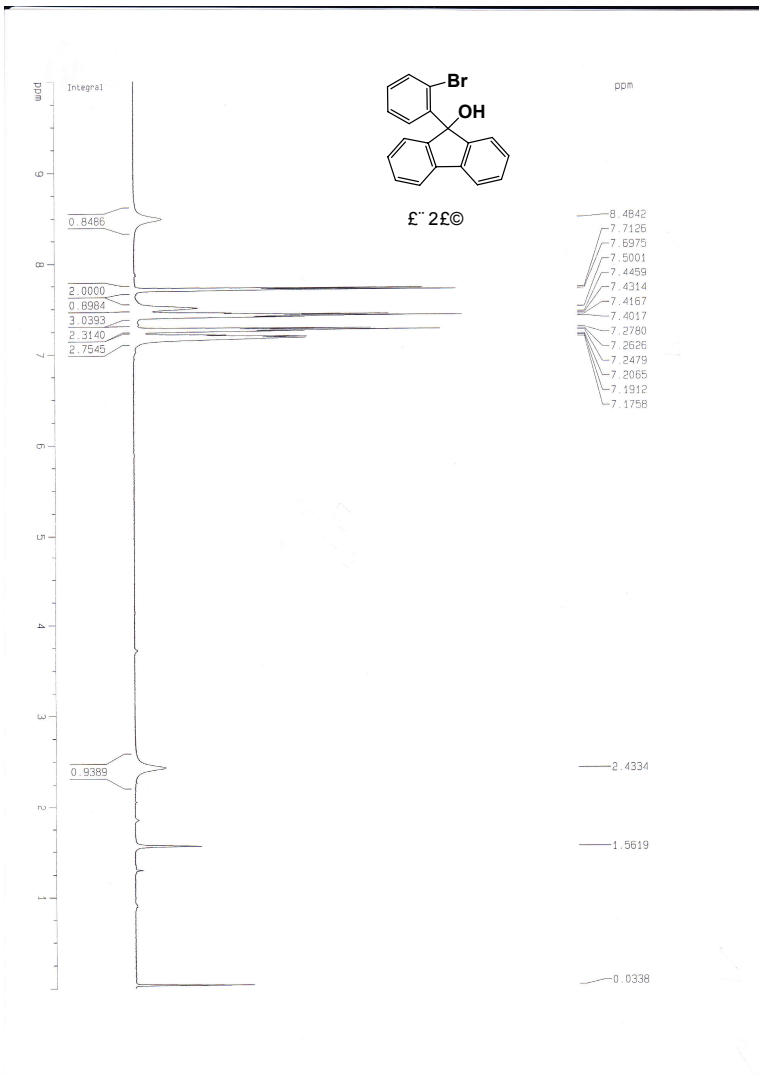
1-bromo-2-iodobenzene [1] The mixture of 2-bromoaniline (5g, 29.06 mmol) and aq. HCl (37 %, 15 mL) in H_2O (50 mL) was cooled to 0°C, then a solution of $NaNO_2$ (2.41 g, 34.87

mmol) in H_2O (50 mL) was added slowly to above solution of KI (7.23g, 43.59 mmol) in H_2O (11 mL) was added dropwise after the solid was dissolved completed, the color of solution turned to blood-red. After addition, the mixture was stirred for 30 minutes at room temperature, then heated at 70°C for another half hour. After cooling, the solution was neutralized by slow addition the solution of Na_2SO_3(0.43 mol/L, 20 mL), then extracted with CH_2Cl_2 (100 mL), the organic phase was washed with H_2O and dried over anhydrous $MgSO_4$, After filtration, the solvents was removed under reduced pressure and the residue was distilled to afford product as a pale-yellow liquid (3.85 g, yield: 77 %). ^{1}H NMR ($CDCl_3$, 500MHz): δ 7.88-7.86(dd, J=8.0Hz, J=1.4Hz 1H); 7.64-7.62(dd, J=8.0Hz, J=1.4Hz, 1H); 7.30-7.20(td, J=7.9Hz, J=1.4Hz 1H); 7.02-6.99(td, J=7.8Hz ,J=1.4Hz ,1H).

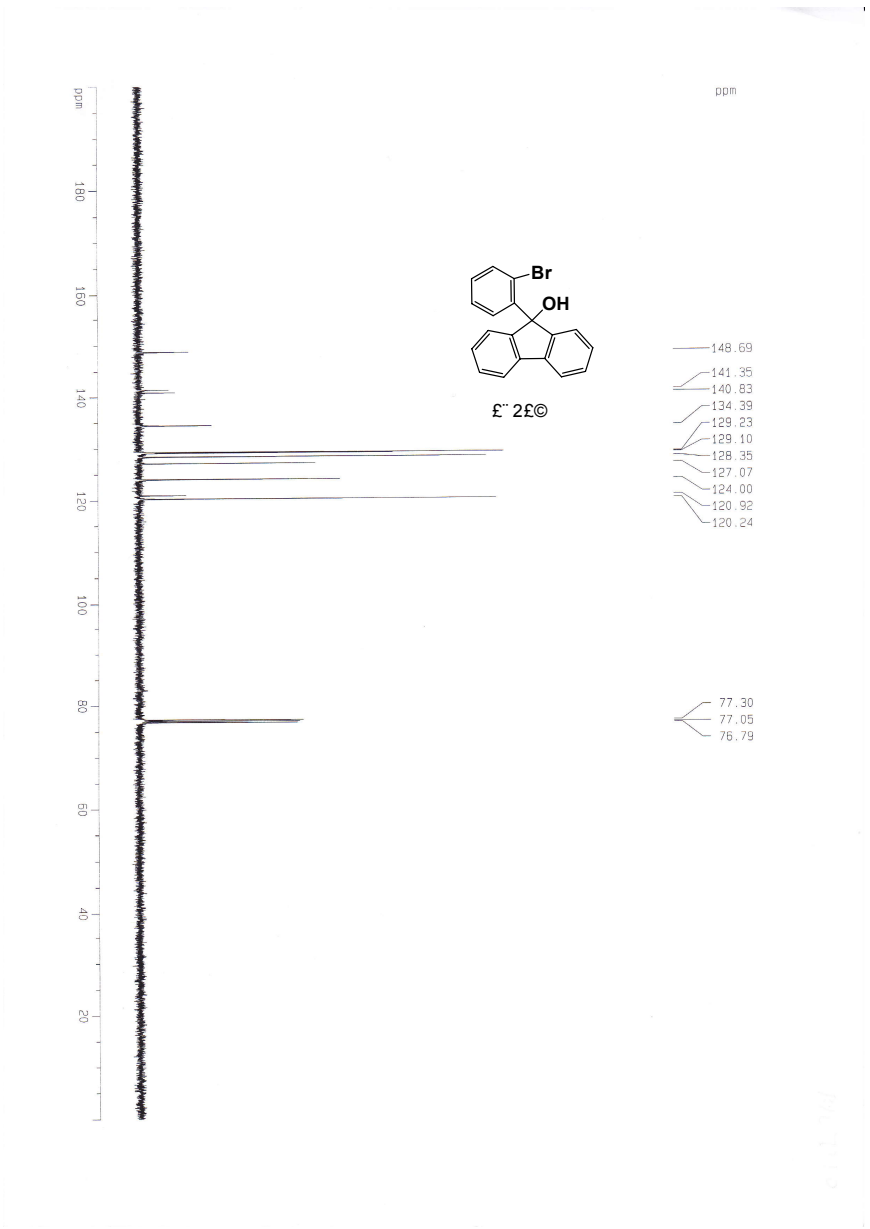
9-(2-bromophenyl)fluoren-9-ol (2) [2]

To the solution of compound 2-bromoiodobenzene (6.98 g, 24.67 mmol) in THF (25 mL) at -40°C was added slowly a solution of *i*PrMgBr in THF (1.0 M, 24 mL), and the stirring was continued for 3 hours, then the solution of fluorenone (2.88 g, 16 mmol) in THF (15mL) was added dropwise. After addition was completed, the mixture was stirred for further half hour, the stirring was continued at room temperature for another 12 hours. Subsequently the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with EtOAc (3×50mL). After separation, the organic phase was dried over anhydrous $MgSO_4$. After workup, the residue was recrystallized from EtOAc-PE to afford compound **2** as a white solid (3.51 g, yield 65 %). M. p. 142-144°C; ^{1}H NMR ($CDCl_3$, 500MHz): δ 8.48(br, 1H); 7.56(d, J=7.6Hz, 2H); 7.50(s, 1H); 7.45-7.40(m, 3H); 7.26(t, J=7.7Hz, 2H); 7.19(t,

J=7.7Hz, 3H); 2.43(br, 1H). ^{13}C NMR ($CDCl_3$, 125MHz): δ:120.24, 120.92, 124.00, 127.07, 128.35, 129.10, 129.23, 134.39, 140.83, 141.35, 148.69.



^{1}H NMR of compound **2** in $CDCl_3$.



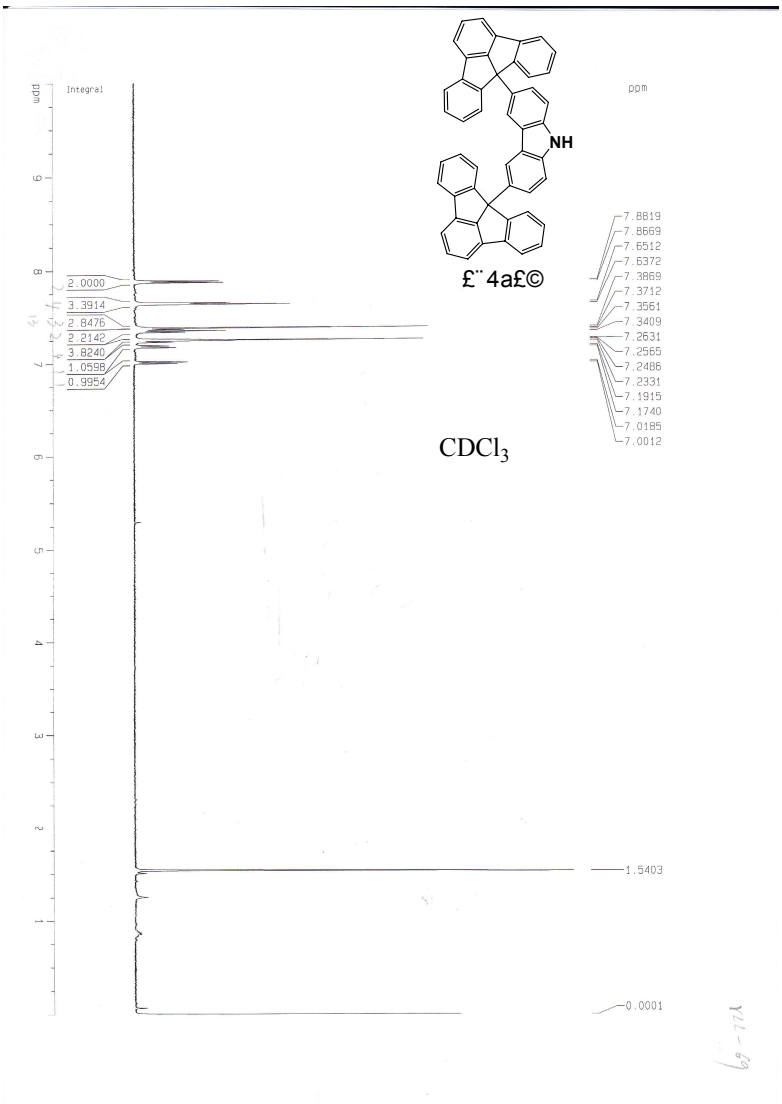
^{13}C NMR of compound **2** in $CDCl_3$.

3,6-bis(9-(2-bromophenyl)-9H-fluoren-9-yl)-9H-carbazole (3a)

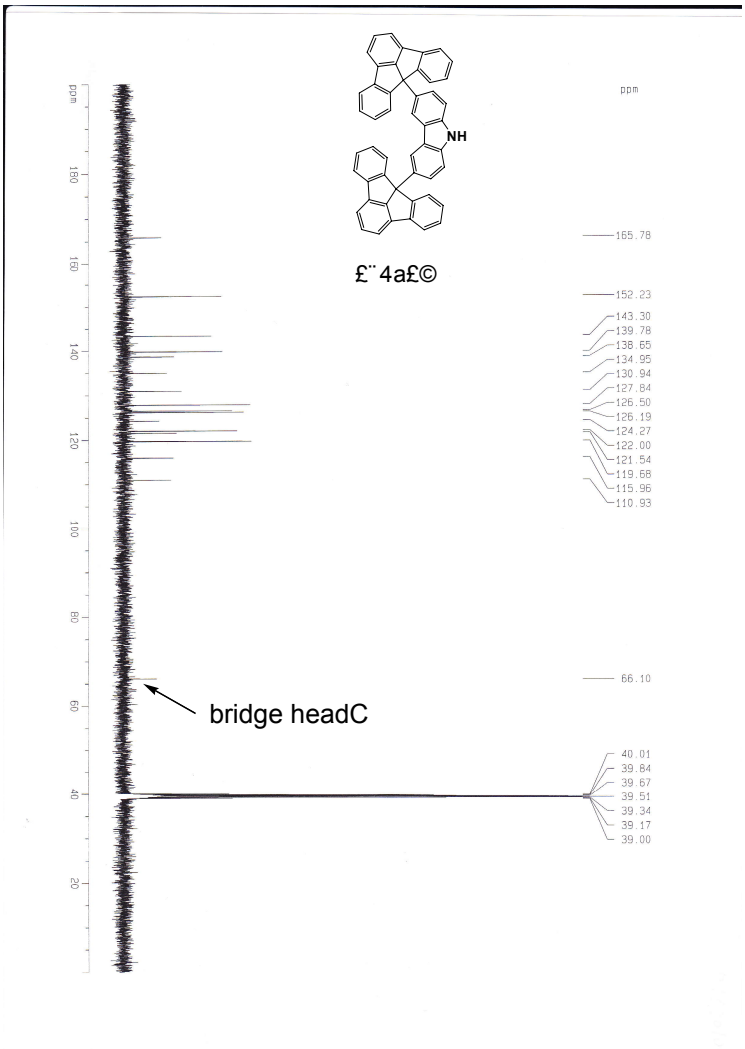
To the solution of carbazole (**1a**) (0.50 g, 2.97 mmol) and 9-(2-bromophenyl)fluorenol (2.0 g, 5.93 mmol) in dioxane(25 mL) was added very slowly CF_3SO_3H (0.89g, 5.93mmol), then the mixture was heated at 80 °C for 7 h, then cooled and poured into H_2O, the solid was filtered, dried. The residue was purified by column chromatography (PE: EtOAc = 5:1, R_f = 0.61) to form crude product **3a** (0.36 g, yield 15 %) which was used directly.

3,6-bis(7*b*-fluoradenyl)carbazole (4a)

The mixture of above mentioned crude 3,6-bis(9-(2-bromophenyl)fluorenyl)carbazole (**3a**) (0.36 g , 0.45 mmol), $Pd(OAc)_2$ (0.13 mmol, 30mg) , PPh_3 (70 mg, 0.29 mmol)和 Na_2CO_3 (240 mg, 2.25 mmol), $BnEt_3NCl$ (100 mg, 0.45mmol) in DMA (20 mL) was heated at 140°C for 5 h. After cooling, the mixture was poured into H_2O and extracted with CH_2Cl_2(3×30ml), the separated organic phase was dried over $MgSO_4$. After workup, the residue was purified by column chromatography (PE:EtOAc = 1:1, R_f = 0.75) to afford **4a** as a white solid (0.16 g, yield 55 %). M. p. > 350 °C. ^{1}H NMR ($CDCl_3$, 500MHz): δ 11.01(s, 1H); 8.25(d, J=7.5Hz, 4H); 7.74(d, J=7.5Hz, 4H); 7.69(s, 2H); 7.56(d, J=7.5Hz, 4H); 7.48(d, J=7.5Hz, 2H); 7.38-7.34(m, 6H); 7.28(t, J=7.5Hz, 4H); 7.17(d, J=7.5Hz, 2H). ^{13}C NMR (recorded in DMSO-d_6 due to solubility, 125MHz): δ 66.10, 110.93, 115.96, 119.68, 121.54, 122.00, 124.27, 126.19, 126.50, 127.84, 130.94, 134.95, 138.65, 139.78, 143.30, 152.23, 165.78. Anal. Calcd for $C_{50}H_{29}N$ (643.8): C, 93.28; H, 4.54; N, 2.18; Found: C, 92.94; H, 4.657 N, 1.966. HRMS: Calcd for $C_{50}H_{29}N+Na^+$ 666.220; found 666.2189.



^{1}H NMR of compound **4a** in $CDCl_3$.



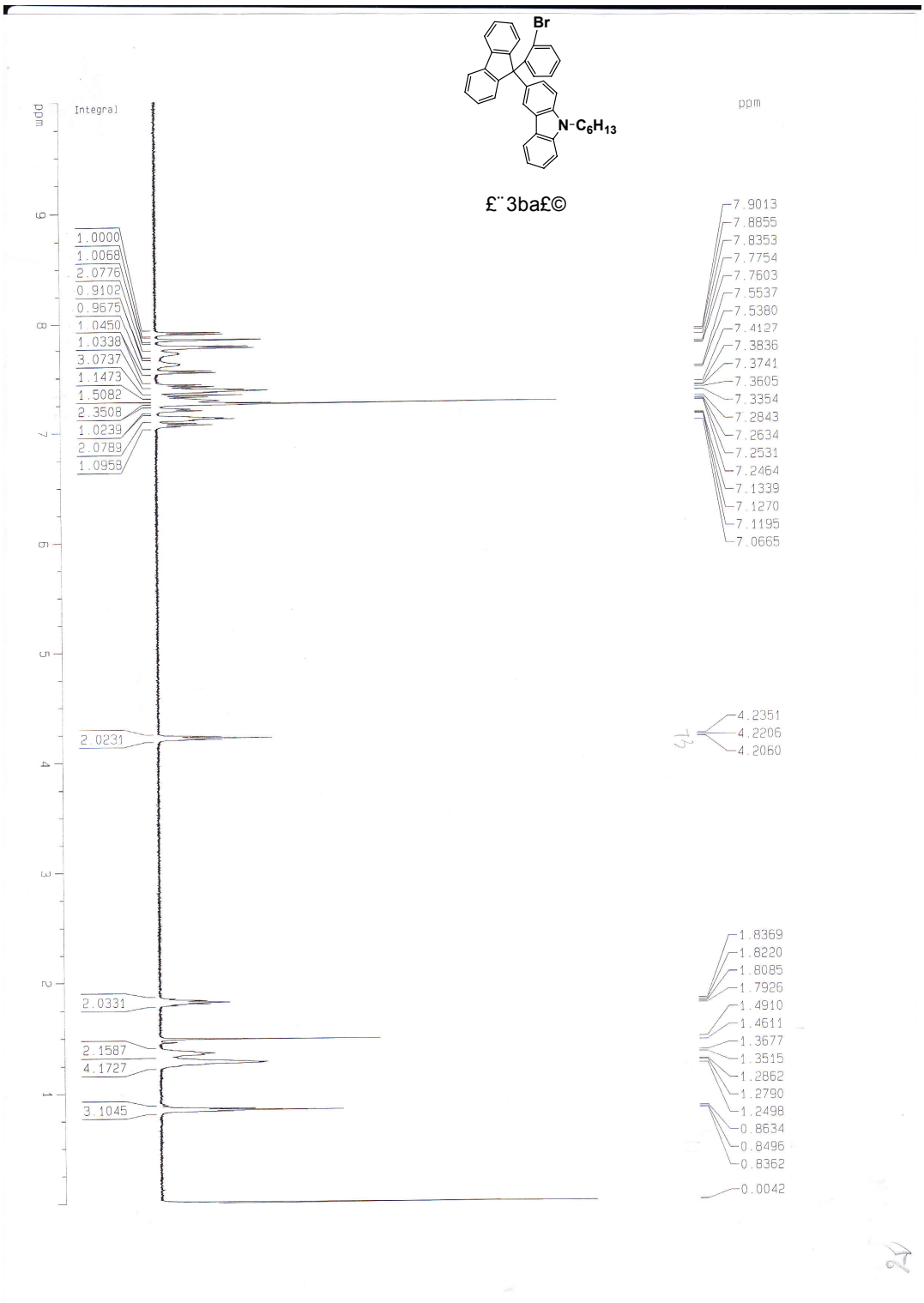
^{13}C NMR of compound **4a** in DMSO-d_6.

9-hexylcarbazole (1b) [3]

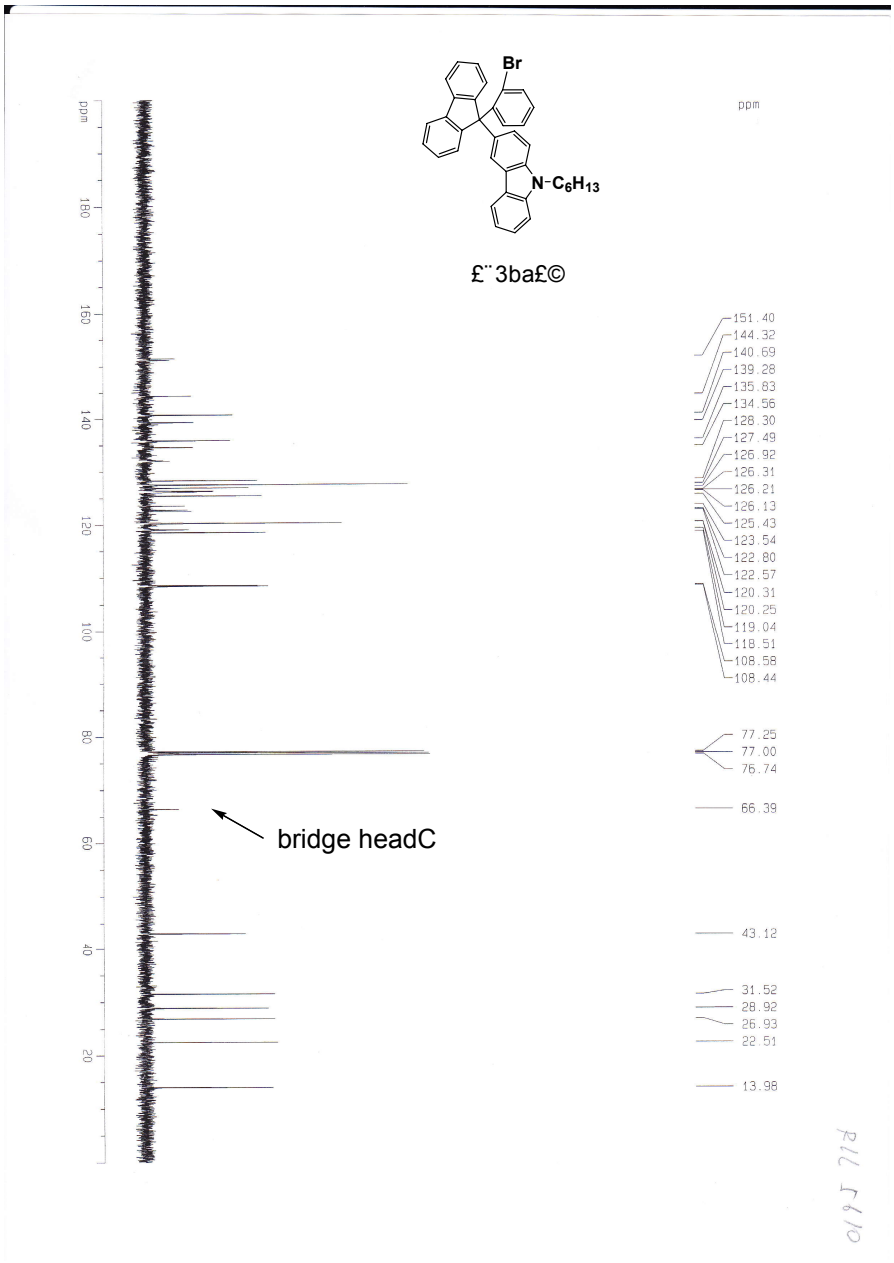
To a suspension of NaH (1.74 g, 60 % w/w dispersion in mineral oil, 44.0 mmol) in DMF (20 mL) was added a solution of carbazole (5.52 g, 33 mmol) in DMF (60 mL), the stirring continued for half hour, then n-hexyl bromide (6.54 g. 39.6 mmol) was added slowly, the reaction mixture was heated to reflux for 5 hours. After cooling, the mixture was poured into H_2O and extracted with CH_2Cl_2 (3×50mL), the organic phase was dried over anhydrous $MgSO_4$. After workup, the residue was recrystallized from EtOH to afford 9-hexylcarbazole (**1b**) as a white solid (6.39 g, yield 77 %). M. p. 64-66°C (Lit.[3] 62-63°C)

3-(9-(2-bromophenyl)fluoren-9-yl)-9-hexylcarbazole (3ba)

To the solution of 9-hexylcarbazole (2.80 g, 11.12 mmol) and CF_3SO_3H (0.67 g, 4.45 mmol) in dioxane (10 mL), was slowly added a solution of 9-(2-bromophenyl)fluoren-9-ol **(2)** (1.5 g, 4.45 mmol) in dioxane (10 mL), then the mixture was heated at 90 °C for 5 h. After cooling, the mixture was poured into H_2O, and extracted with CH_2Cl_2 (3×100ml), the separated organic phase was dried over $MgSO_4$. After workup, the residue was purified by column chromatography (PE:EtOAc = 40:1, R_f =0.5) to afford compound **3ba** as a white solid (2.8 g, yield 51%). M. p. 181-183°C; ^{1}H NMR ($CDCl_3$ 500 MHz): δ 7.89 (d, J = 7.9Hz, 1H); 7.84(s, 1H); 7.77(d, J=6.2Hz, 2H); 7.71(br, 1H); 7.62(br, 1H); 7.55(d, J=7.9Hz, 1H); 7.42(d, J = 8.8Hz, 1H); 7.40-7.36(m, 3H); 7.33(d, J=8.3Hz, 1H); 7.28(br, 1H); 7.25(t, J= 4.3 Hz, 2H); 7.20(d, J=7.7Hz,1H); 7.13-7.10(m, 2H); 7.08-7.05(m, 1H); 4.22(t, J=7.3Hz, 2H); 1.84-1.79(m, 2H); 1.37-1.35(m, 2H); 1.29-1.25(m, 4H); 0.85(t, J=6.8Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 13.98, 22.51, 26.93, 28.92, 31.52, 43.12, 66.39, 108.44, 108.58, 118.51, 119.04, 120.25, 120.31,122.57, 122.80, 123.54,,125.43, 126.13, 126.21, 126.31, 126.92, 127.49, 128.30, 134.56, 135.83, 139.28, 140.69, 144.32, 151.40; Anal. Calcd for $C_{37}H_{32}BrN$ (569): C,77.89; H,5.65; N,2.45; Found: C, 77.62; H, 5.827; N,2.642.



^{1}H NMR of compound **3ba** in $CDCl_3$.

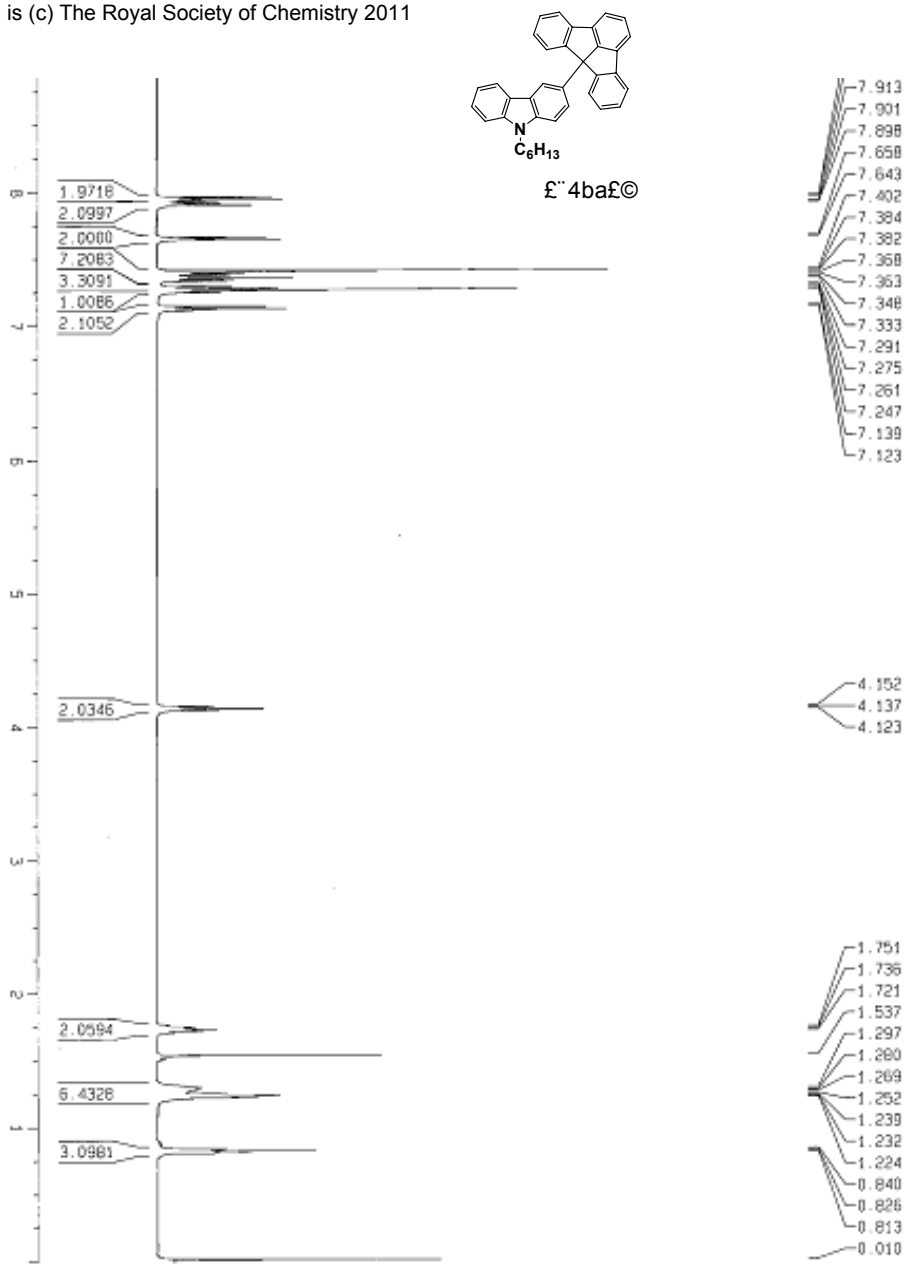


^{13}C NMR of compound **3ba** in $CDCl_3$.

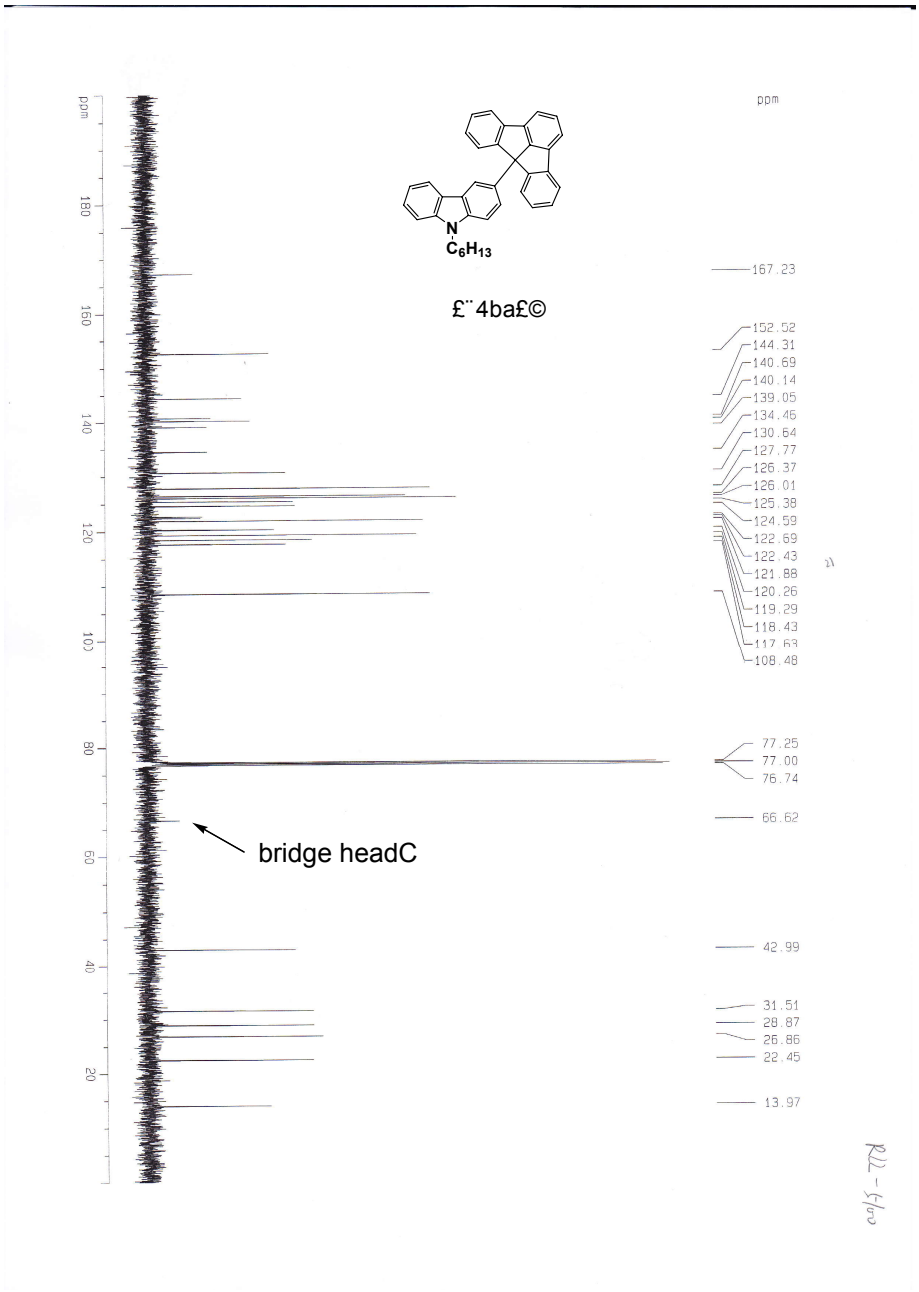
3-(7*b*-fluoradenyl)-9-hexylcarbazole (4ba)

A mixture of 3-(9-(2-bromophenyl)fluorenyl)-9-hexylcarbazole (0.57 g, 1.00 mmol), Pd(OAc)2 (50 mg, 0.20 mmol), PPh_3(120 mg, 0.44 mmol), Na_2CO_3(530 mg, 5 mmol) and $BnEt_3NCl$ (110 mg, 0.5 mmol) in DMA (20 mL) was heated at 140°C for 5 h. After cooling, the mixture was poured into H2O and extracted with CH_2Cl_2 (3×30mL), the separated organic phase was dried over $MgSO_4$. After workup, the residue was purified by column

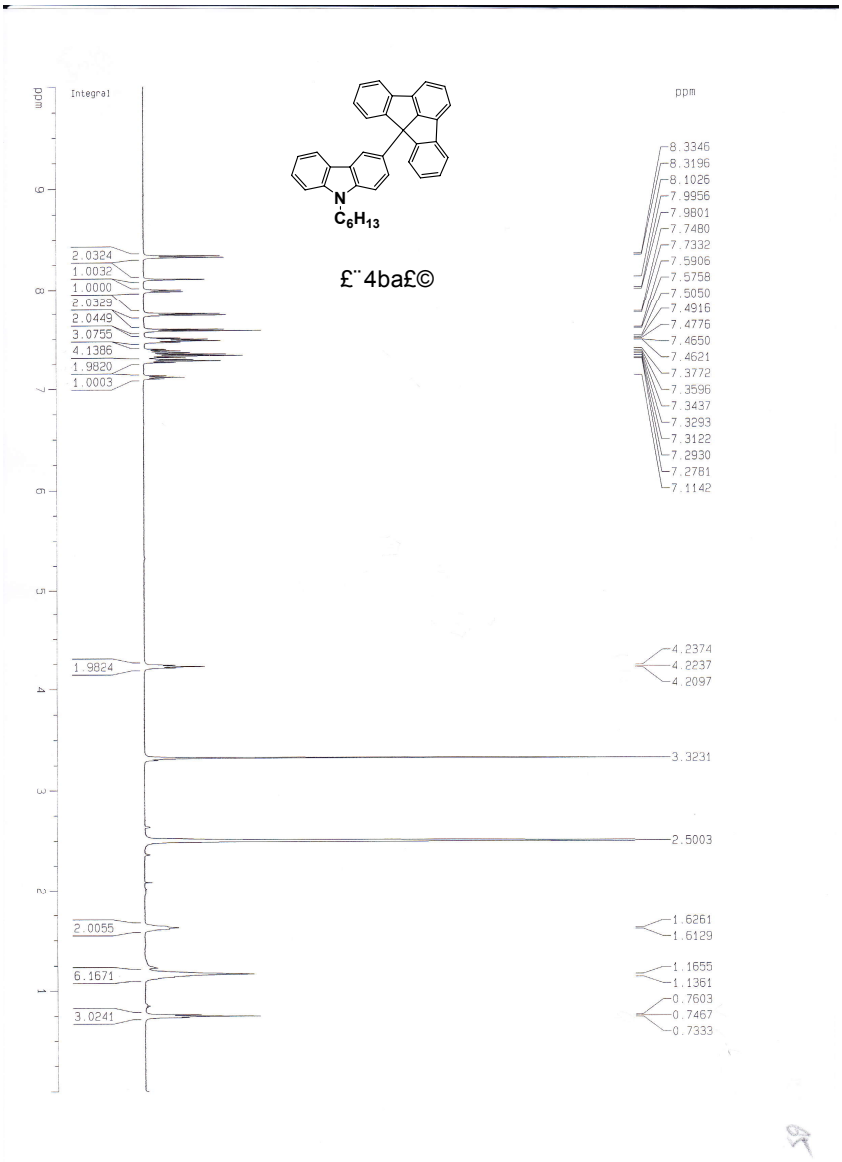
chromatography (PE:AcOEt = 20:1; R_f = 0.57) to afford compound **4ba** as a white solid (0.4 g, yield 82 %). M. p. 206-208°C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.95(d, J=7.5Hz, 2H); 7.93-7.90(m, 2H); 7.65(d, J=7.5Hz, 2H); 7.40-7.33(m, 7H); 7.28(t, J=7.5Hz, 3H, $CDCl_3$ overlap); 7.25(s, 1H); 7.12(t, J=7.5Hz, 2H); 4.14(t, J=7.3Hz, 2H); 1.75-1.72(m, 2H); 1.30-1.22(m, 6H); 0.83(t, J=6.8Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ: 13.97, 22.45, 26.86, 28.87, 31.51, 42.99, 66.62, 108.48, 117.63, 118.43, 119.29, 120.26, 121.88, 122.43, 122.69, 124.59, 125.38, 126.01, 126.37, 127.77, 130.64, 134.46, 139.05, 140.14, 140.69, 144.31, 152.52, 167.23; ^{1}H NMR (DMSO, 500 MHz): δ 8.33(d, J=7.5Hz, 2H); 8.10(s,1H); 7.99(d, J=7.8Hz, 1H); 7.74(d, J=7.4Hz, 2H); 7.58(d, J=7.4Hz, 2H);7.51-7.46(m, 3H); 7.39-7.31(m, 4H); 7.28(t, J=7.4Hz, 2H); 7.11(t, J=7.4Hz, 1H); 4.22(t, J=7.0Hz, 2H); 1.63-1.61(m, 2H); 1.17-1.14(m, 6H); 0.75(t, J =6.8Hz, 3H). Anal. Calcd for $C_{37}H_{31}N$(489): C, 90.76; H,6.38; N, 2.86; Found: C, 90.76; H,6.399 N, 2.757 ; m/z=489(M^+).



^{1}H NMR of compound **4ba** in $CDCl_3$



^{13}C NMR of compound **4ba** in $CDCl_3$

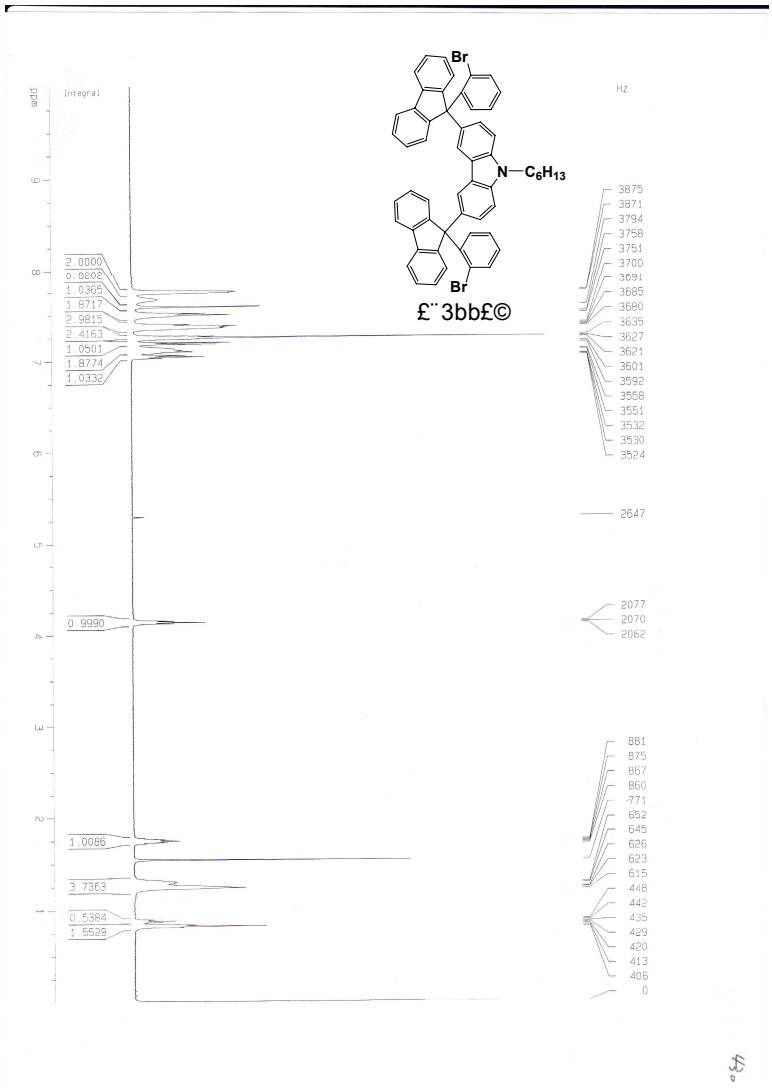


^{1}H NMR of compound **4ba** in DMSO-d_6.

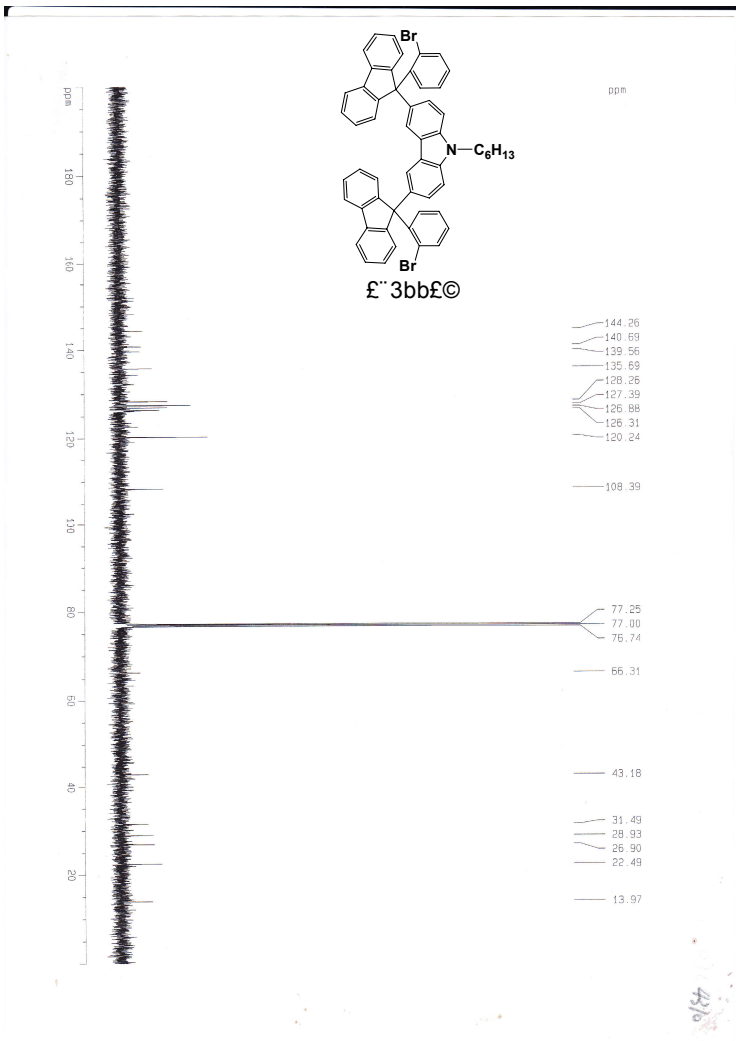
3,6-bis[9-(2-bromophenyl)fluoren-9-yl]-N-hexylcarbazole (3bb)

To the solution of N-hexylcarbazole (1.29 g, 5.19 mmol) and 9-(2-bromophenyl)-fluoren-9-ol **(2)** (3.5 g, 9.86 mmol) in dioxane (50 mL) was added slowly CF_3SO_3H (1.48 g, 9.86 mmol), then the mixture was heated at 80 °C for 5 h. After cooling, the mixture was poured into H_2O, and the solid was filtered and dried under vaccum, then purified by column chromatography (PE:EtOAc = 4:1, R_f = 0.67) to afford compound **3bb** as a white solid (2.0

g, yield 43 %). M. p.:156°C(collapsed); ^{1}H NMR ($CDCl_3$ 500MHz): δ7.75(s, 4H); 7.69(br, 2H); 7.59(s, 2H); 7.51(d, J=7.0Hz, 4H); 7.40-7.36(m, 6H); 7.25(t, J=7.5Hz, 4H); 7.19(d, J=9.0Hz, 2H); 7.12-7.08(m, 4H); 7.06-7.03(m, 2H); 4.14(t, J=7.5Hz, 2H); 1.76-1.72(m, 2H); 1.30-1.23(m, 6H); 0.83(t, J=7.0Hz, 3H). ^{13}C NMR ($CDCl_3$, 125MHz): δ 13.97, 22.49, 26.90, 28.93, 31.49, 43.18, 66.31, 108.39, 119.15, 120.24, 122.60, 126.31, 126.88, 127.39, 128.26, 132.14, 134.27, 135.69, 139.56, 140.69, 144.26, 148.08, 151.17, 151.79; Anal. Calcd for $C_{56}H_{43}Br_2N$ (889.8): C, 75.59; H, 4.87; N,1.57; Found: C, 75.51; H, 5.482; N, 1.903.



^{1} H NMR of compound **3bb** in $CDCl_3$.

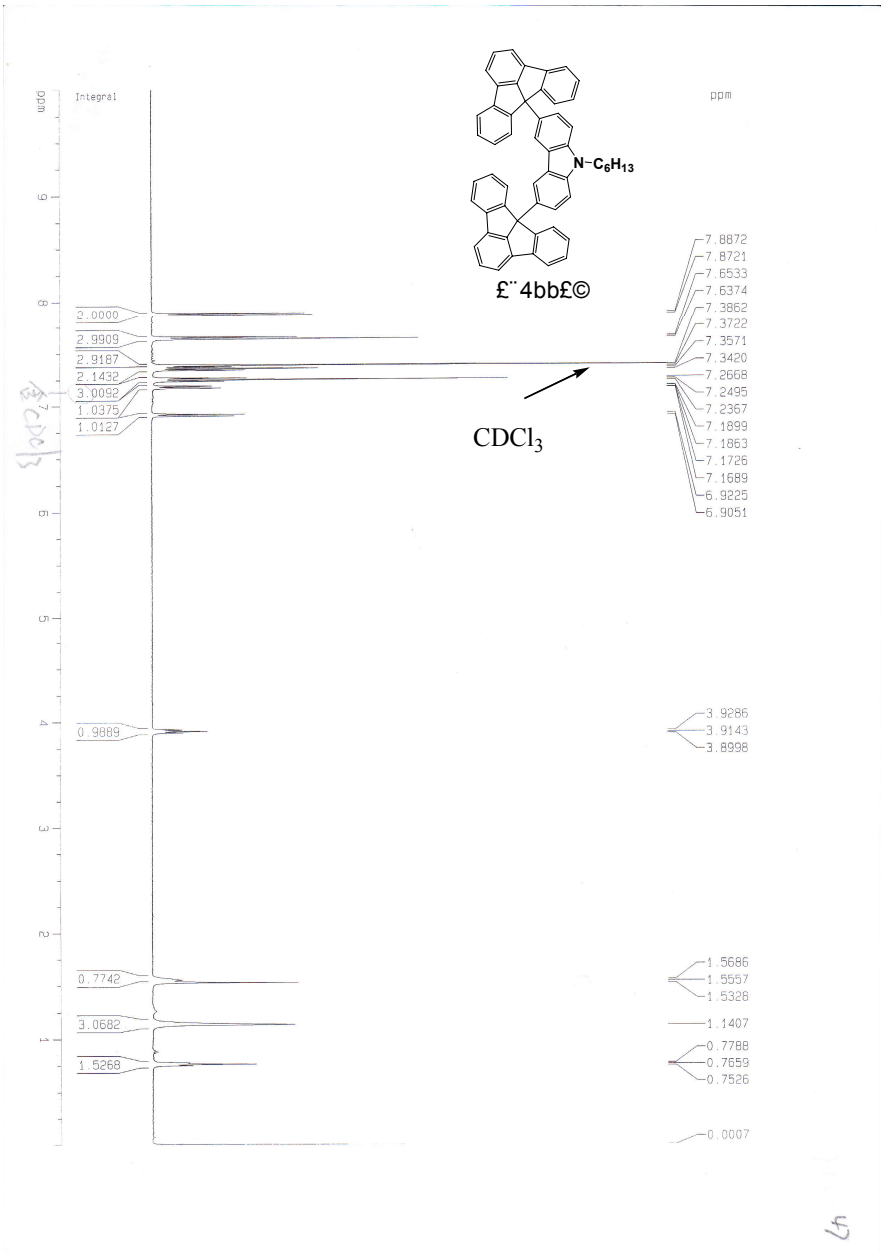


^{13}C NMR of compound **3bb** in $CDCl_3$.

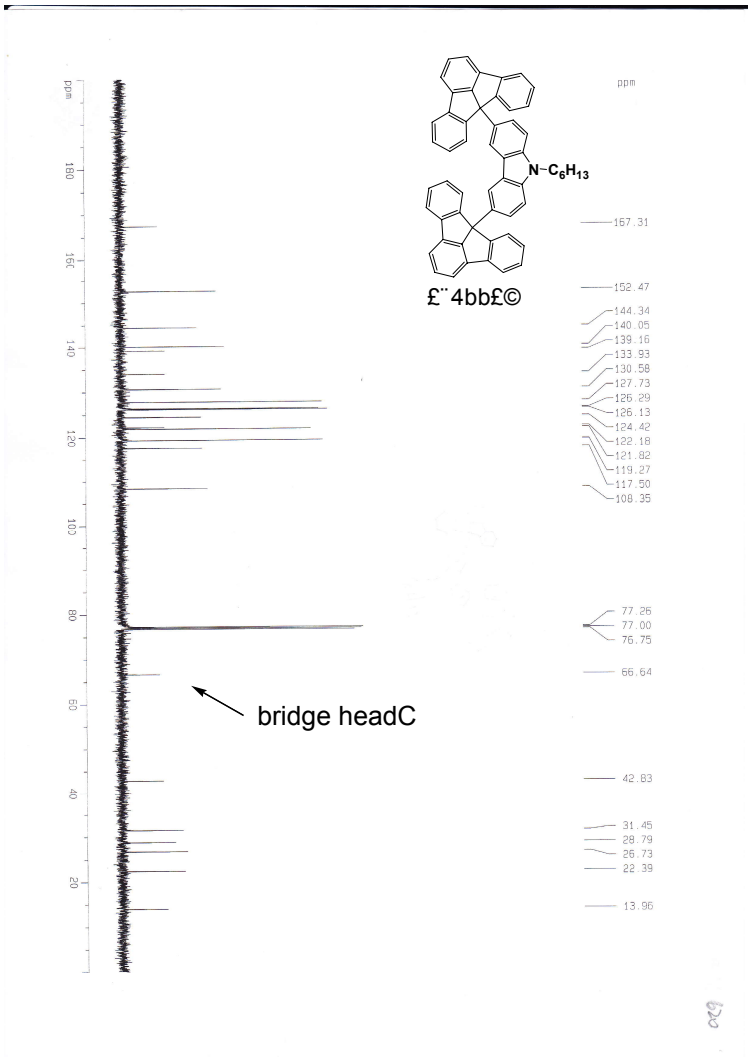
3,6-di(7*b*-fluoradenyl)-N-hexylcarbazole (4bb)

A mixture of 3,6-bis(9-(2-bromophenyl)fluorenyl)-N-hexylcarbazole(**3bb**)(0.50 g, 0.56 mmol), Pd(OAc)2 (40 mg, 0.17 mmol), PPh_3(100 mg, 0.37 mmol), Na_2CO_3(240 mg, 2.24 mmol) and $BnEt_3NCl$ (130 mg, 0.56 mmol) in DMA (20 mL) was heated at 140°C for 5 h. After cooling, the mixture was poured into H_2O and extracted with CH_2Cl_2(3×30 ml), the separated organic phase was dried over $MgSO_4$. After workup, the residue was purified by column chromatography (PE:EtOAc=2:1, R_f = 0.75) to afford compound **4bb** as a white solid (0.29 g, yield 71 %). M. p. 325°C (dec.). ^{1}H NMR ($CDCl_3$, 500MHz): δ 7.88(d, J =

7.6Hz, 4H); 7.65(d, J=8.0Hz, 6H); 7.39(s, 6H); 7.36(t, J=7.6Hz, 4H); 7.25(t, J=7.5Hz, 4H, $CDCl_3$ overlap); 7.19-7.17(dd, J=1.8Hz, J=8.7Hz, 2H); 6.91(d, J=8.7Hz, 2H); 3.91(t, J=7.2Hz, 2H); 1.56(m, 2H); 1.14(s, 6H); 0.77(t, J=6.6Hz, 3H). ^{13}C NMR ($CDCl_3$, 125MHz): δ 13.96, 22.39, 26.73, 28.79, 31.45, 42.83, 66.64, 108.35, 117.50, 119.27, 121.82, 122.18, 124.42, 126.13, 126.29, 127.73, 130.58, 133.93, 139.16, 140.05, 144.34, 152.47, 167.31; Anal. Calcd for $C_{56}H_{41}N$ (727.9): C, 92.40; H,5.68; N, 1.92; Found: C,92.20; H,5.796 N, 1.748 ; m/z=727(M^+).



^{1}H NMR of compound **4bb** in $CDCl_3$.



^{13}C NMR of compound **4bb** in $CDCl_3$.

[4-(9-(2-bromophenyl)fluoren-9-yl)phenyl]diphenylamine (3ca)

To a solution of triphenylamine (**1c**) (1.60 g, 6.51 mmol) and CF_3SO_3H (0.44 g, 2.96 mmol) in dioxane (10 mL) was added a solution of 9-(2-bromophenyl)fluorenol(1.0 g, 2.96 mmol) in dioxane (10 mL).The mixture was heated at 90°C and kept for 5h.After cooling, the mixture was poured into H_2O and extracted with CH_2Cl_2(3×50ml), the separated organic phase was dried over $MgSO_4$. After workup, the residue was purified by column chromatography (PE:EtOAc = 40:1, R_f = 0.5) to afford compound **3ca** as a white solid

(1.01g, yield 61 %). M. p.: 177°C (collapsed); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.75(d, J= 7.5Hz, 2H); 7.56(d, J=7.1Hz, 2H); 7.54(d, J=7.6Hz, 1H); 7.37(t, J=7.4Hz, 2H); 7.27(d, J=7.7Hz, 3H); 7.20(t, J=7.7Hz, 4H); 7.14(s, 2H); 7.07(dd, J=8.5Hz, J=7.7Hz, 6H); 6.97(t, J=7.4Hz, 2H); 6.90(d, J=8.6Hz, 2H). ^{13}C NMR ($CDCl_3$, 125MHz): δ 119.28, 121.84, 122.65, 123.21, 124.26, 126.00, 126.40, 127.13, 127.86, 129.07, 120.68, 137.75, 140.00, 144.38, 146.00, 147.57, 151.86; Anal. Calcd for $C_{37}H_{26}BrN$ (564.5): C,78.72; H,4.64; N,2.48; Found: C,79.10; H,5.369; N, 2.554.

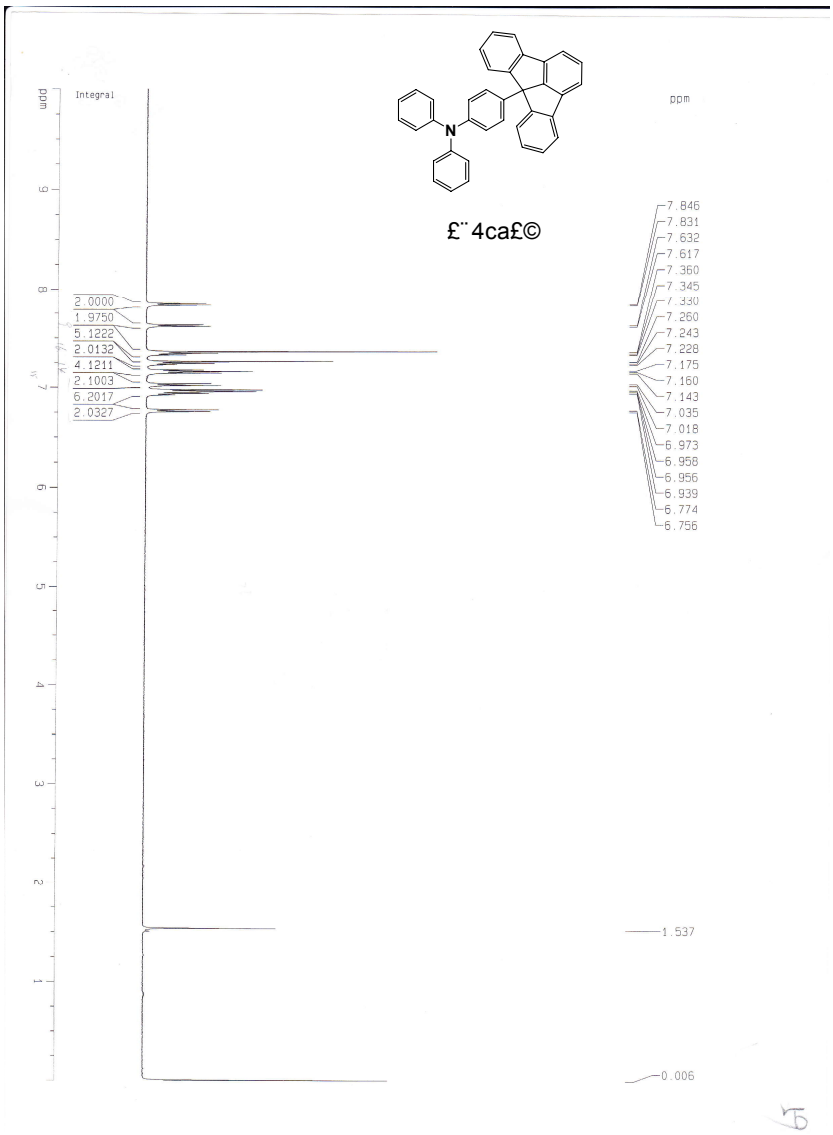
^{1} H NMR of compound **3ca** in $CDCl_3$.

^{13}C NMR of compound **3ca** in $CDCl_3$.

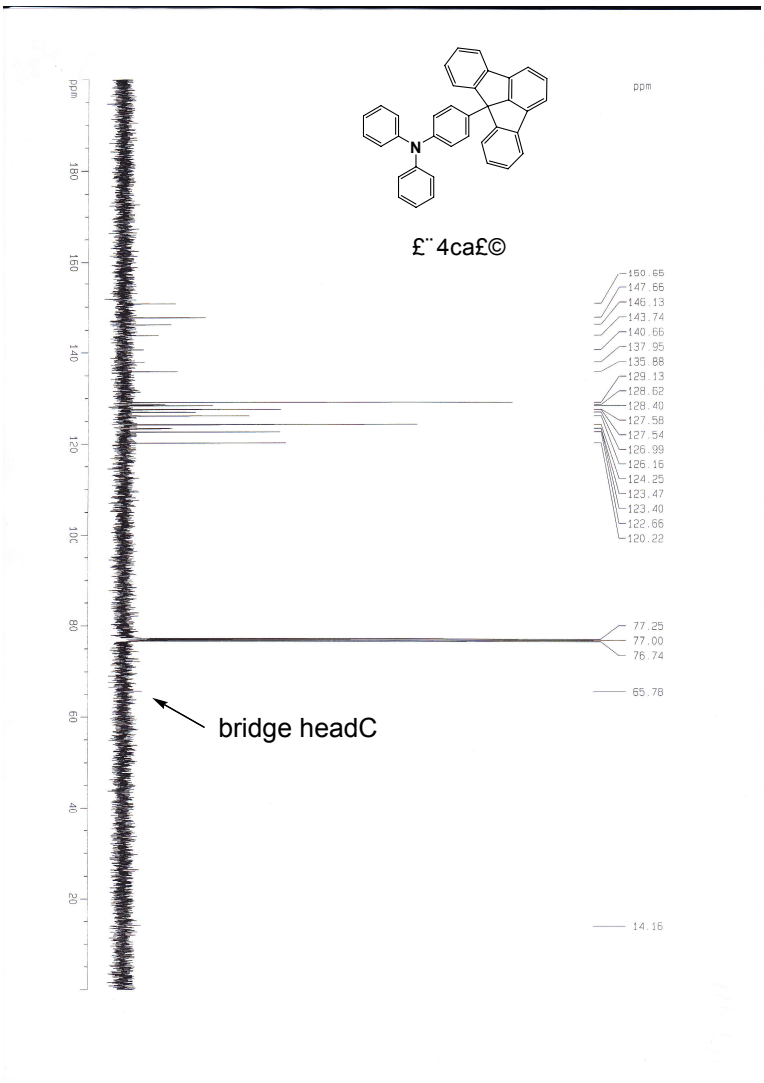
(4-(7*b*-fluoradenyl)diphenylamine (4ca)

A mixture of [4-(9-(2-bromophenyl)fluoren-9-yl)phenyl]diphenylamine (**3ca**) (0.56 g, 1.0 mmol), $Pd(OAc)_2$ (50 mg, 0.2 mmol), PPh_3 (120 mg, 0.44 mmol), Na_2CO_3(530 mg,5.0 mmol) and $BnEt_3NCl$ (130 mg, 0.56 mmol) in DMA (20 mL) was heated at 140°C for 4 h. After cooling, the mixture was poured into H_2O and extracted with CH_2Cl_2(3×30ml), the separated organic phase was dried over $MgSO_4$. After workup, the residue was purified by column chromatography (PE:EtOA = 20:1, R_f = 0.57) to afford compound **4ca** as a white solid (0.18 g, yield 37 %). M. p. 256-259 °C. ^{1}H NMR ($CDCl_3$ 500MHz): δ 7.84(d, J=7.5Hz,

2H); 7.50(d, J=7.5Hz, 2H); 7.35(t, J=7.5Hz, 5H); 7.24(d, J=7.5Hz, 2H); 7.16(t, J=8.0Hz, 4H); 7.03(d, J=4.3Hz, 2H); 6.97-6.92(m, 6H); 6.77(d, J=9.0Hz, 2H). ^{13}C NMR ($CDCl_3$, 125MHz): δ 65.78, 120.22, 122.66, 123.40, 123.47, 124.25, 126.16, 126.99, 127.54, 127.58, 128.40, 128.62, 129.13, 135.88, 137.95, 140.66, 143.74, 146.13, 147.66, 150.65; Anal. Calcd for $C_{37}H_{25}N.0.25H_2O$ (488.1): C, 91.05; H, 5.27; N, 2.87; Found: C, 90.93; H, 5.244 N,2.765 ; Calcd for $C_{37}H_{25}N+Na^+$ 506.19; found 506.1879.



^{1}H NMR of compound **4ca** in $CDCl_3$.

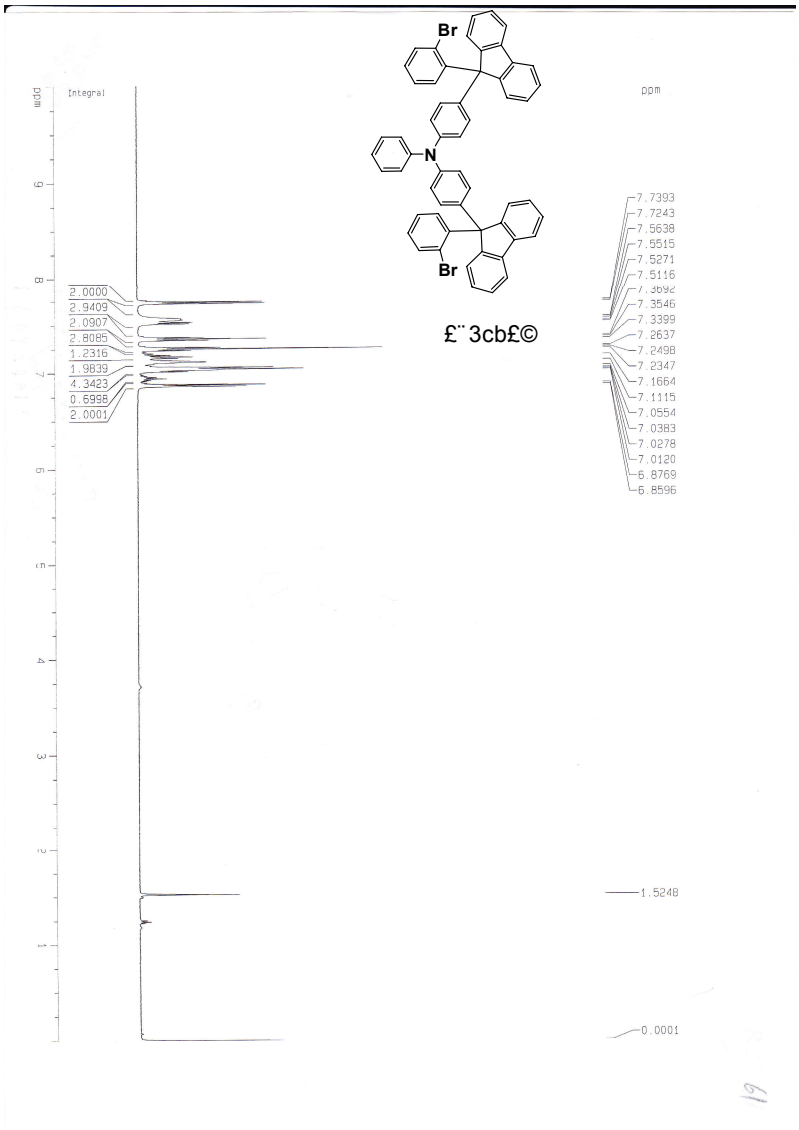


^{13}C NMR of compound **4ca** in $CDCl_3$.

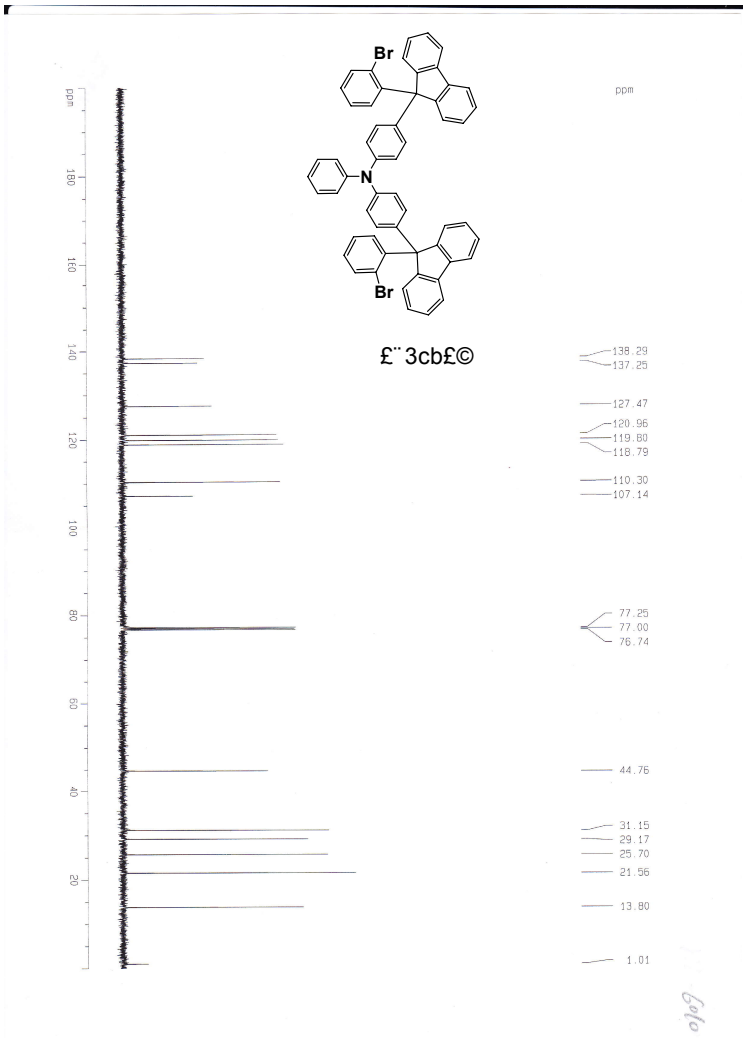
[4,4'-bis(9-(2-bromophenyl)fluoren-9-yl)phenyl]aniline (3cb)

To a solution of triphenylamine (**1c**) (0.5 g, 2.04 mmol) and CF_3SO_3H (0.44 g, 2.96 mmol) in dioxane (10 mL) was added a solution of 9-(2-bromophenyl)fluorenol (**2**) (0.67 g, 4.48 mmol) in dioxane (10 mL).The mixture was heated at 90°C and kept for 5h. After cooling, the mixture was poured into H_2O and extracted with CH_2Cl_2(3×50ml), the separated organic phase was dried over $MgSO_4$. After workup, the residue was purified by column chromatography (PE:EtOAc = 3:1, R_f = 0.8) to afford compound **3cb** as a white solid

(0.62 g, yield 34 %). M.p.:291°C(collapsed) ^{1}H NMR ($CDCl_3$, 500MHz): δ 7.73(d, J=7.5Hz, 4H); 7.56-7.51(m, 6H); 7.35(t, J=7.3Hz, 4H); 7.25(d, J=7.0Hz, 2H); 7.17(t, J=8.2Hz, 2H); 7.11-7.07(m, 4H); 7.06-7.01(m, 8H); 6.93(t, J=7.2Hz, 1H); 6.87(d, J=8.7Hz, 4H);^{13}C NMR ($CDCl_3$, 125MHz): δ: 65.74, 120.19, 122.77, 123.39, 123.44, 124.23, 124.53, 126.13, 126.97, 127.52, 127.55, 128.37, 128.54, 129.08, 129.12, 131.73, 135.85, 137.89, 140.61, 143.71, 145.93, 147.41, 150.62; Anal. Calcd for $C_{56}H_{31}Br_2N$ (883.7): C, 76.11; H,4.22; N,1.58; Found: C, 76.54; H,4.680; N,1.769.



^{1}H NMR of compound **3cb** in $CDCl_3$.

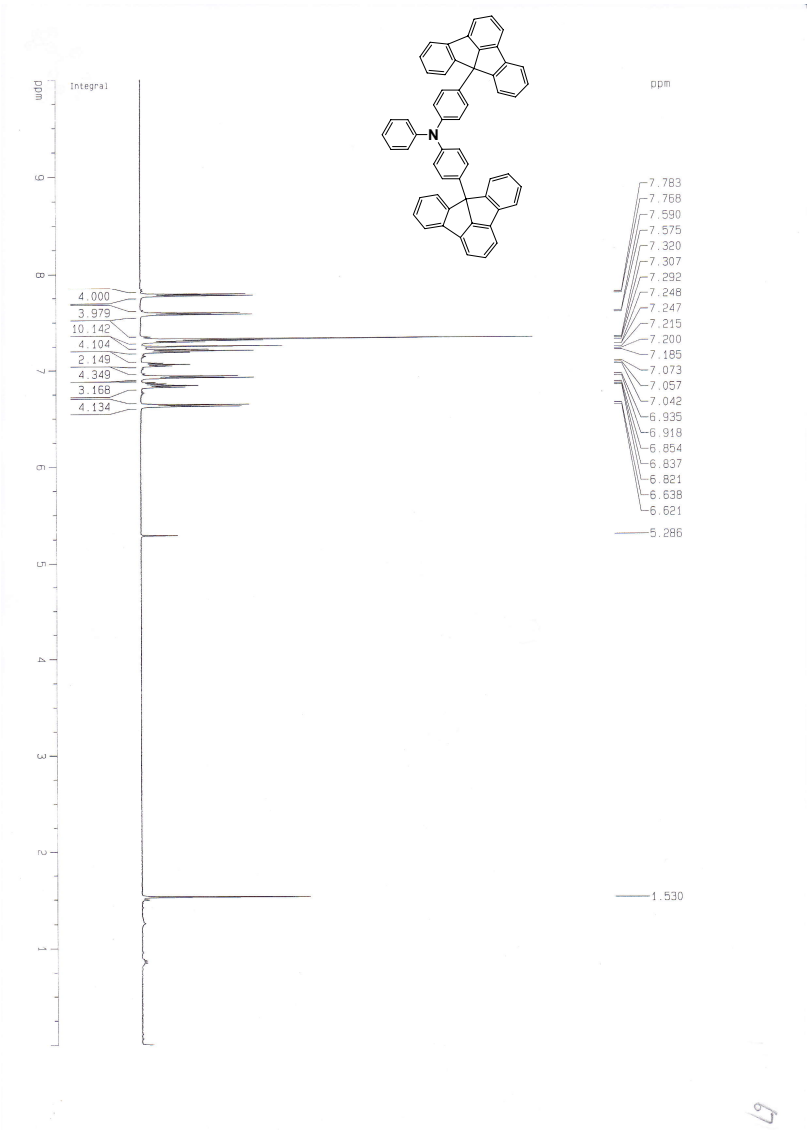


^{13}C NMR of compound **3cb** in $CDCl_3$.

4,4'-di(7b-fluoradenyl)phenyl)aniline (4cb)

A mixture of compound **3cb** (0.50 g, 0.57mmol), $Pd(OAc)_2$ (40 mg, 0.17 mmol), PPh_3 (100 mg, 0.37 mmol), Na_2CO_3(240 mg, 2.26 mmol) and $BnEt_3NCl$ (130 mg, 0.57 mmol) in DMA (20 mL) was heated at 140°C for 5 h. After cooling, the mixture was poured into H_2O and extracted with CH_2Cl_2(3×30ml), the separated organic phase was dried over $MgSO_4$. After workup, the residue was purified by column chromatography (PE:DCM = 1:1, R_f = 0.75) to afford compound **4cb** as a white solid (0.29 g, yield 71 %). M. p. 346-349°C; ^{1}H NMR

($CDCl_3$, 500 MHz): δ 7.78(d, J=7.5Hz, 4H); 7.58(d, J=7.5Hz, 4H); 7.31(t, J=6.5Hz, 10H); 7.20(t, J=7.5Hz, 4H); 7.06(t, J=8.0Hz, 2H);6.93(d, J=8.5Hz, 4H);6.87-6.83(m, 3H); 6.63(d, J=8.5Hz, 4H). 13 C NMR could not be obtained due to the low solubility in $CDCl_3$ or DMSO-d_6. Anal. Calcd for $C_{56}H_{35}N.H_2O$(739.9): C, 90.90; H, 5.04; N, 1.89; Found: C, 90.72; H, 5.153 N, 1.878 ; HRMS Calcd for C56H35N+H$^+$: 722.30; found 722.2825.

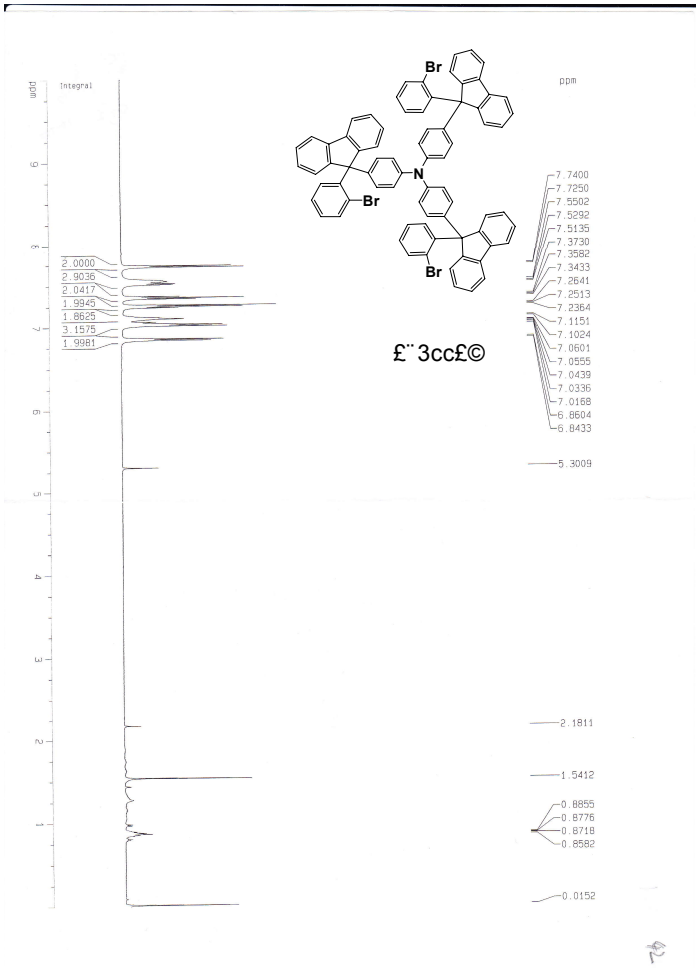


^{1}H NMR of compound **4cb** in $CDCl_3$.

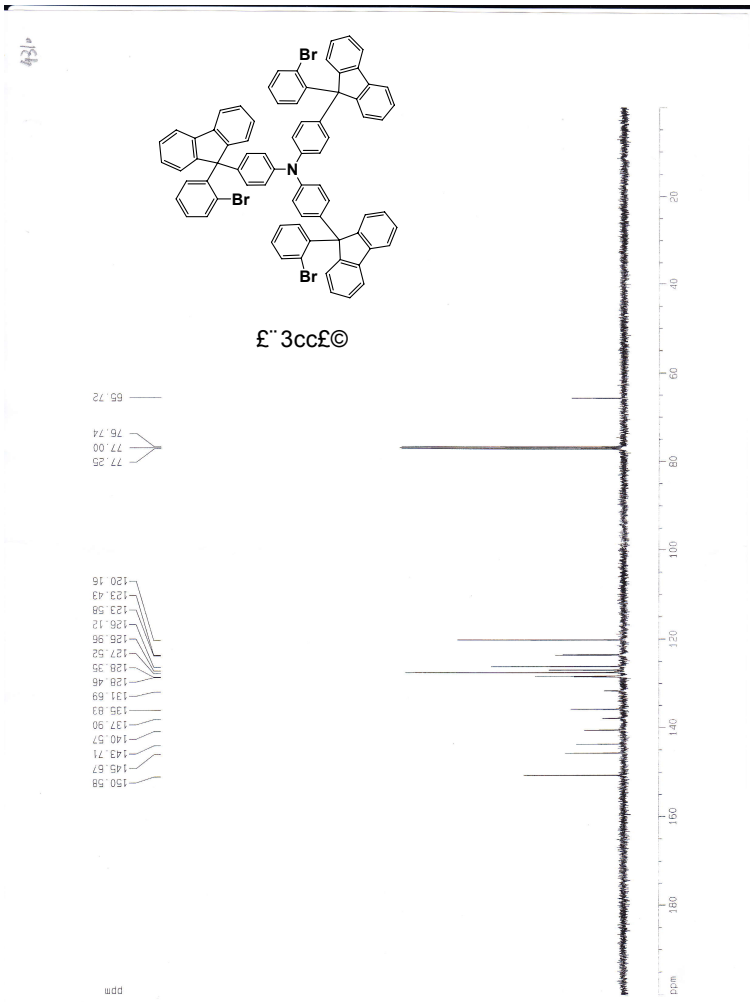
Tris[4,4',4"-(9-(2-bromophenyl)fluorenyl)phenyl]amine (**3cc**)

To a solution of triphenylamine (**1c**) (0.78g, 3.16mmol)and 9-(2-bromophenyl)-9-fluorenol (**2**) (3.2g, 9.49 mmol) in dioxane (50 ml) was added slowly CF_3SO_3H (1.33g, 8.85 mmol),

and the mixture was then heated at 90 °C for 3 hours. After cooling, it was poured into ice water and extracted with CH_2Cl_2(3×100ml), the organic phase was dried over $MgSO_4$. After workup, the residue was purified by column separation (PE: DCM = 2:1, R_f = 0.43) to afford **3cc** as a white solid (3.14g, yield 83%)。M.p.: 230°C (collapsed); ^{1}H NMR ($CDCl_3$, 500MHz): δ 7.73(d, J=7.5Hz, 6H); 7.55-7.51(m, 9H); 7.36(t, J=7.4Hz, 6H); 7.24(d, J=6.9Hz, 6H);7.11(d, J=6.4Hz, 6H);7.06-7.02(m, 9H);6.85(m, 3H); 6.63(d, J=8.6Hz, 6H).^{13}C NMR ($CDCl_3$, 125MHz): δ 150.58, 145.67, 143.71, 140.57, 137.90, 135.83, 131.69, 128.46, 128.35, 127.52, 126.96, 123.58, 123.43, 120.16; Anal. Calcd for $C_{75}H_{48}Br_3N$ (1199.1): C,74.89; H, 4.02; N,1.16; Found: C,74.85; H,4.471; N,1.162.



^{1} H NMR of compound **3cc** in $CDCl_3$.



^{13}C NMR of compound **3cc** in $CDCl_3$.

Attempt to synthesize Tris[4,4',4"-fluoradenylphenyl]amine 4cc:

Tris[4,4',4"-(9-(2-bromophenyl)fluorenyl)phenyl]amine(**3cc**) (0.50 g, 0.42 mmol) ,$Pd(OAc)_2$ (30 mg, 0.13 mmol), PPh_3 (70 mg, 0.27 mmol), Na_2CO_3(220 mg, 2.1 mmol) and $BnEt_3NCl$ (100 mg, 0.44 mmol) in DMA (20 mL) was heated at 150°C for 5 h. After cooling, the reaction mixture was poured into ice-cold water, the precipitate could not be extracted by common organic solvents. The solid with palladium impurity was filtered and could not be further purified due to its solubility.

Isatin-3-hydrazone [4]

Isatin (3.75 g, 25.4mmol) was suspended in 30mL of anhydrous methanol and 2.91g of hydrazine hydrate (85 %) is added in one portion. The solution is heated to a gentle reflux for one hour. The solution is then cooled in an ice bath. The yellow crystals are filtered after 0.5 h. Yield 3.68 g, yield 89.5%; M. p.:225°C (dec.).

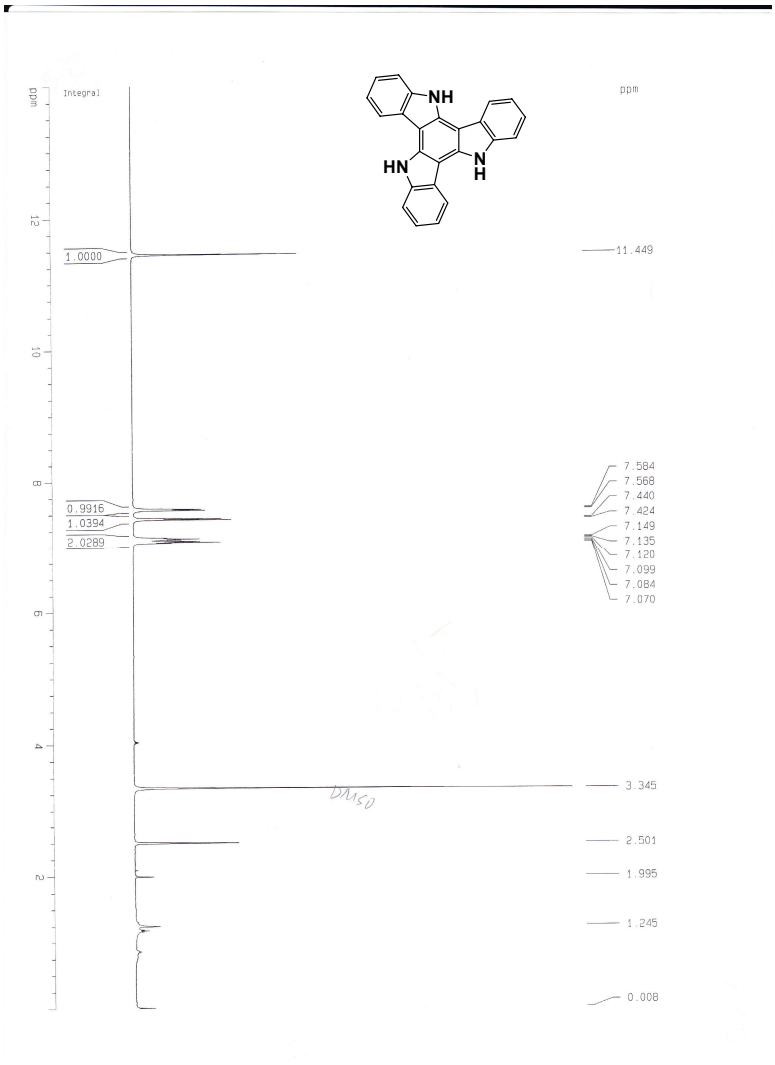
2-Indoline [4]

Small pieces of sodium metal (1.2 g, 50 mmol) was gradually dissolved in EtOH(30mLwith stirring. The above sodium ethoxide solution was added slowly to a solution of isatin-3-hydrazone (3 g, 18.6 mmol). After addition, the mixture was heated to reflux until no nitrogen gas evlolved. Then it was cooled down and 10% HCl was added to adjust pH = 1 and extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$. After workup, the residue was recrystallized from CH_2Cl_2-PE to form compound **15** as a pale-yellow solid (2.08 g, yield 69%). Mp:125-128°C

10,15-dihydro-5H-diindolo[3,2-a;3',2'-c]carbazole (triindole) [5]

The solution of oxo?indole (1.0 g, 7.5mmol) in $POCl_3$ (4 mL) was heated to 120°C for 15h. The extra $POCl_3$ was distilled, and the residue was poured into water and neutralized with aqueous Na_2CO_3 and extracted with EtOAc (3×50mL) , the organic phase was dried over $MgSO_4$. after workup, triindole was obtained by chromatopgarphy (PE:EtOAc=4:1, R_f = 0.67) as a yellow solid (70 mg, yield 8.1%). M. p. > 350°C; ^{1}H NMR (DMSO-d_6, 500 MHz):

δ 11.45(s, 1H); 7.58(d, J=8.0Hz, 1H); 7.43(d, J=8.0Hz, 1H); 7.15-7.07(m,2H).

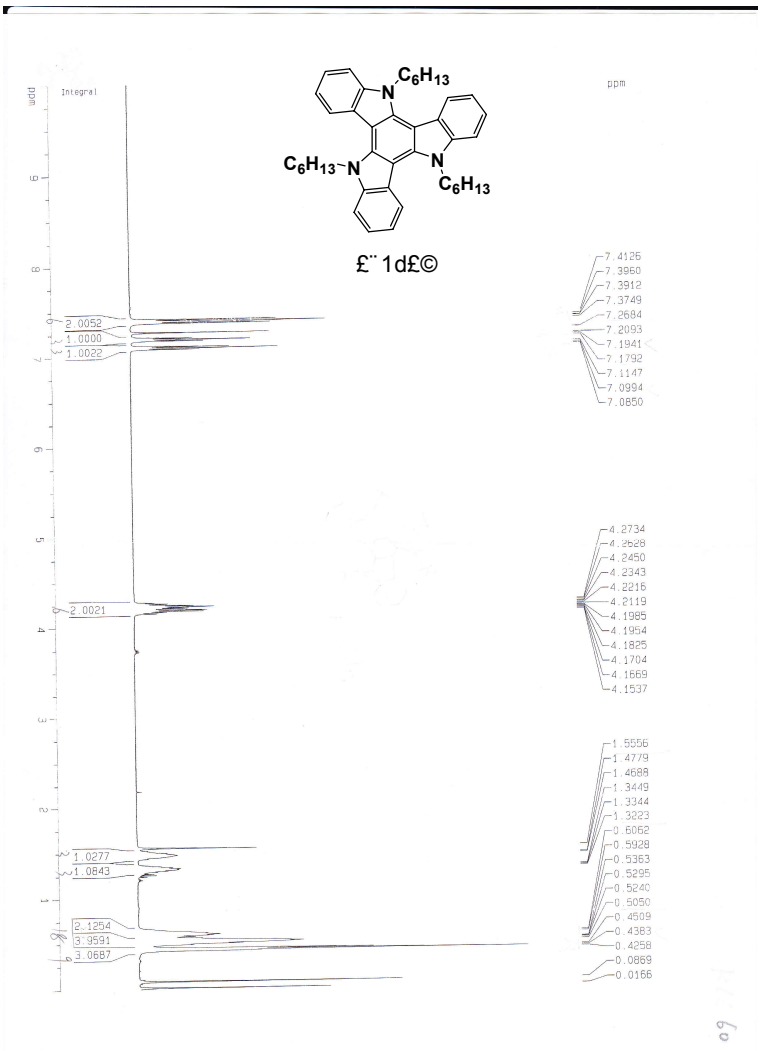


^{1}H NMR of triindole in DMSO–d_6.

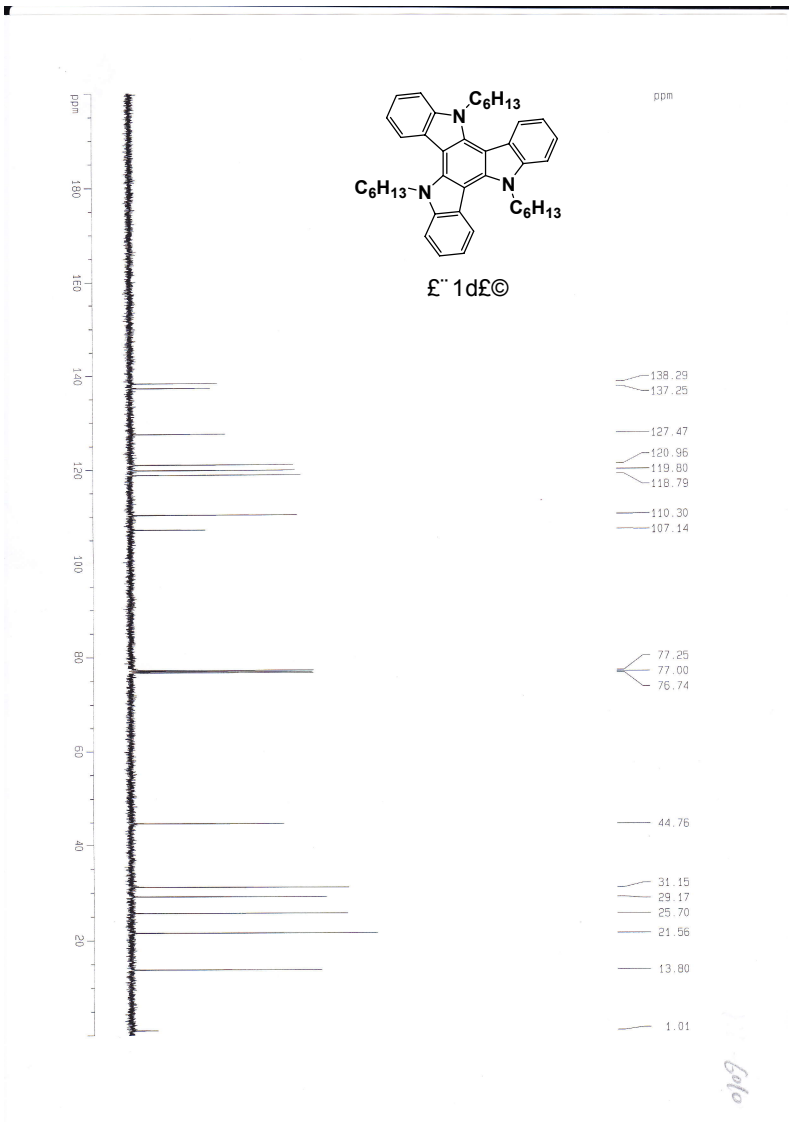
5,10,15-trihexyl-10,15-dihydro-5H-diindolo[3,2-a;3',2'-c]carbazole (1d) [3]

To a suspension of NaH (0.16 g 60 %w/w dispersion in mineral oil, 4.06mmol) in DMF (5 mL) was added a solution of triindole (0.4 g, 1.16 mmol) and the stirring was continued for half hour, then n-hexyl bromide (0.76 g, 4.63mmol) was added via syringe and the mixture was then refluxed for 1h. The cooled mixture was poured into water and extracted with CH_2Cl_2 (3×50mL). The organic phase was dried over $MgSO_4$. After workup, the residue

was recrystallized from EtOH to obtain compound **1d** as a yellow solid (0.67g, yield 97.1 %). Mp: 131-133°C. ^{1}H NMR ($CDCl_3$, 500MHz): δ 7.41-7.37(m, 6H); 7.19(t, J=7.6Hz, 3H); 7.10(t, J=7.2Hz, 3H); 4.27-4.15(m, 6H); 1.48-1.47(m, 3H); 1.34-1.32(m, 3H); 0.61-0.51(m, 18H); 0.44(t, J=6.3Hz, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 13.80, 21.56, 25.70, 29.17, 31.15, 44.76, 107.14, 110.30, 118.79, 119.80, 120.96, 127.47, 137.25, 138.29.



^{1} H NMR of compound **1d** in $CDCl_3$.



^{13}C NMR of compound **1d** in in $CDCl_3$.

5,10,15-trihexyl-2,7,12-tris[9-(2-bromophenyl)fluoren-9-yl]-10,15-dihydro-5H-diindolo[3,2-a;3',2'-c]carbazole (3d)

To a solution of 5,10,15-trihexyl-10,15-dihydro-5H-diindolo[3,2-a;3',2'-c]carbazole (**1d**) (0.6 g, 1.0 mmol) and 9-(2-bromophenyl)fluorenol (**2**) (1.18 g, 3.5 mmol) in dioxane (20 mL) was added CF_3SO_3H (0.53g, 3.5 mmol) via syringe, the mixture was then refluxed for 5h. After it was cooled down, poured into water and extracted with CH_2Cl_2(3×100mL), the organic phase was dried over $MgSO_4$. After workup, the residue was purified by column

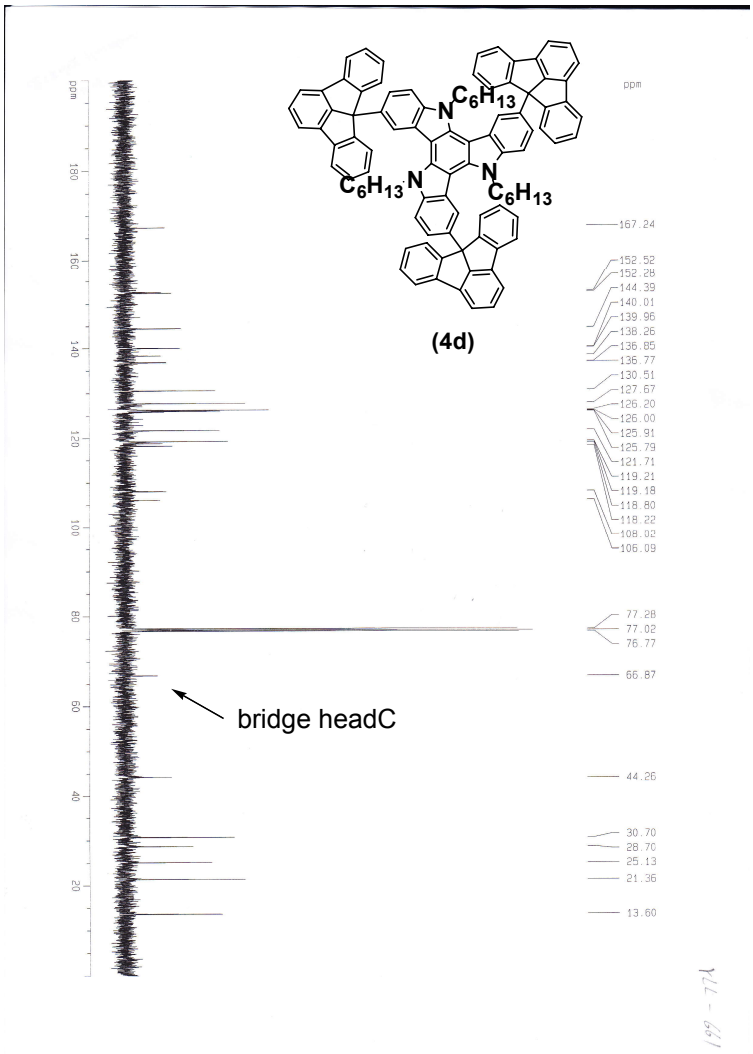
chromatography (PE:EtOAc = 3:1, R_f = 0.75) to afford crude product **3d** (0.72 g, yield 46 %), which was difficult to purify and used in next step without further purification.

5,10,15-trihexyl-2,7,12-trifluoradenyl-10,15-dihydro-5H-diindolo[3,2-a;3',2'-c]carbazole (4d)

The mixture of crude **3d** (0.50 g, 0.32 mmol), $Pd(OAc)_2$ (30 mg, 0.15 mmol) , PPh_3(80 mg, 0.32mmol), Na_2CO_3(140 mg, 1.28 mmol) , $BnEt_3NCl$ (70 mg, 0.32 mmol) in DMA (20 mL) was heated at 140°C for 5 h.. After cooling, the mixture was poured into H_2O and extracted with CH_2Cl_2(3×50mL), the separated organic phase was dried over $MgSO_4$. After workup, the residue was purified by column chromatography (PE:DCM = 20:1, R_f = 0.8) to afford **4d** as a yellow solid (0.35 g, yield 83 %).

^{1}H NMR ($CDCl_3$, 500MHz): δ 7.81-7.77(m, 6H); 7.57(d, J=7.0Hz, 6H); 7.34-7.25(m, 48H,$CDCl_3$ overlap); 7.16(t, J=7.0Hz, 18H); 6.99(s, 3H) ; 6.80(s, 6H); 3.74-3.67(m, 6H); 0.97-0.95(m, 6H); 0.45-0.24(m, 27H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 13.60, 21.36, 25.13, 28.70, 30.70, 44.2, 66.87, 106.09, 108.02, 118.22, 118.80, 119.18, 119.21, 121.71, 125.79, 125.91, 126.00, 126.20, 127.67, 130.51, 136.77, 136.85, 138.26, 139.96, 140.01, 144.39, 152.52, 167.24. Anal. Calcd for $C_{99}H_{81}N_3$(1312): C, 90.58; H,6.22; N, 3.20; Found: C, 90.32; H, 6.136; N,3.125. HRMS was not obtained due to its solubility.

^{1}H NMR of compound **4d** in $CDCl_3$.



^{13}C NMR of compound **4d** in $CDCl_3$.

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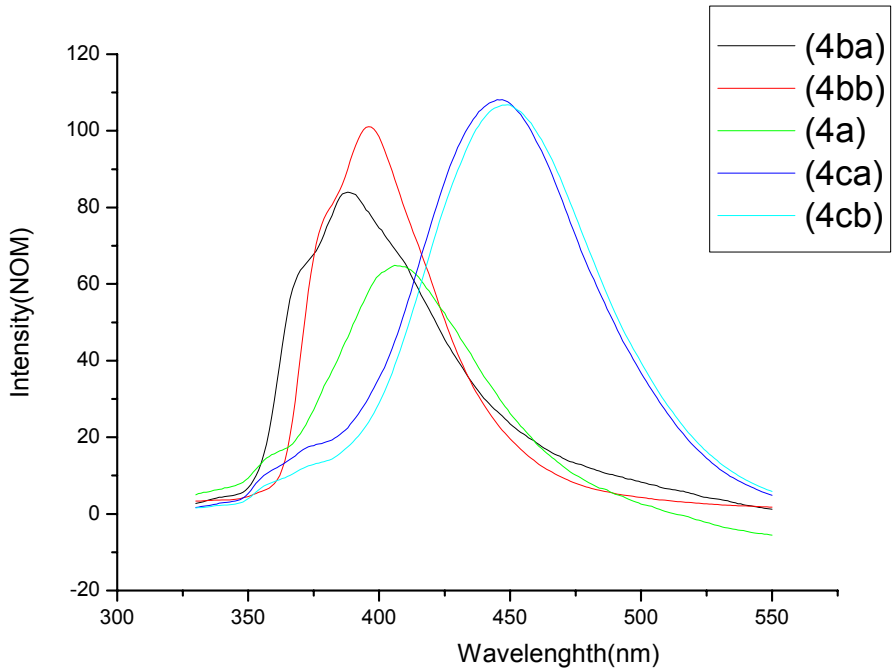

Fig.1. The fluorescence emission spectra of 4a, 4ba, 4bc, 4ca and 4cb

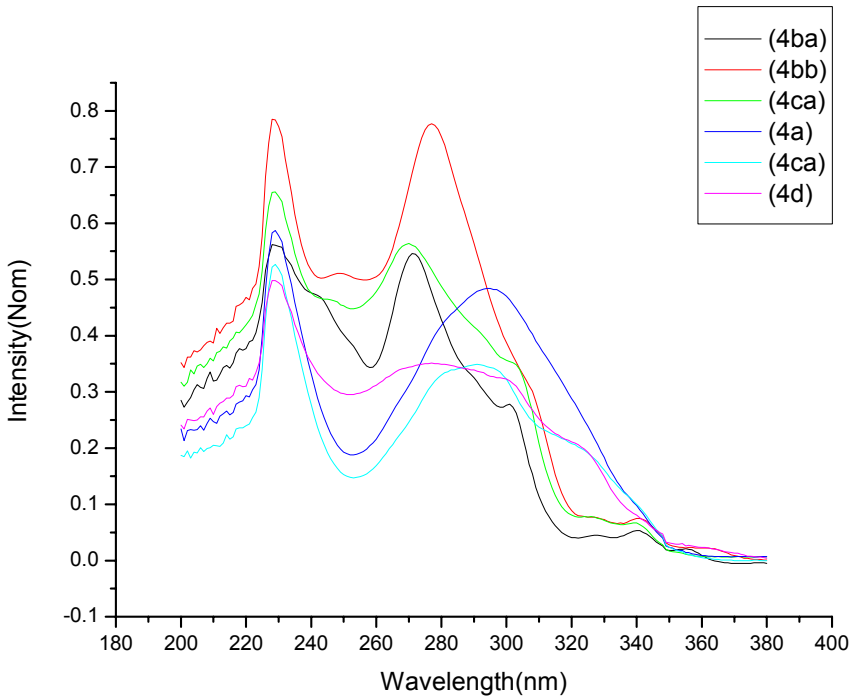

Fig. 2.The UV-vis absorption spectra of 4a, 4ba, 4bc, 4ca, 4cb and 4d

Table 1. The absorption and emission data of 4a, 4ba, 4bc, 4ca, 4cb and 4d (10^{-6}mol/L in CH_2Cl_2)

Compound	λ_{max} (nm/Abs)[a]	λ_{max} (nm/Em, liquid)[b]
4a	**270**	**406**
4ba	**340, 271**	**388**
4bb	**277**	**396**
4ca	**294**	**446**
4cb	**291**	**449**
4d	**277**	**-**

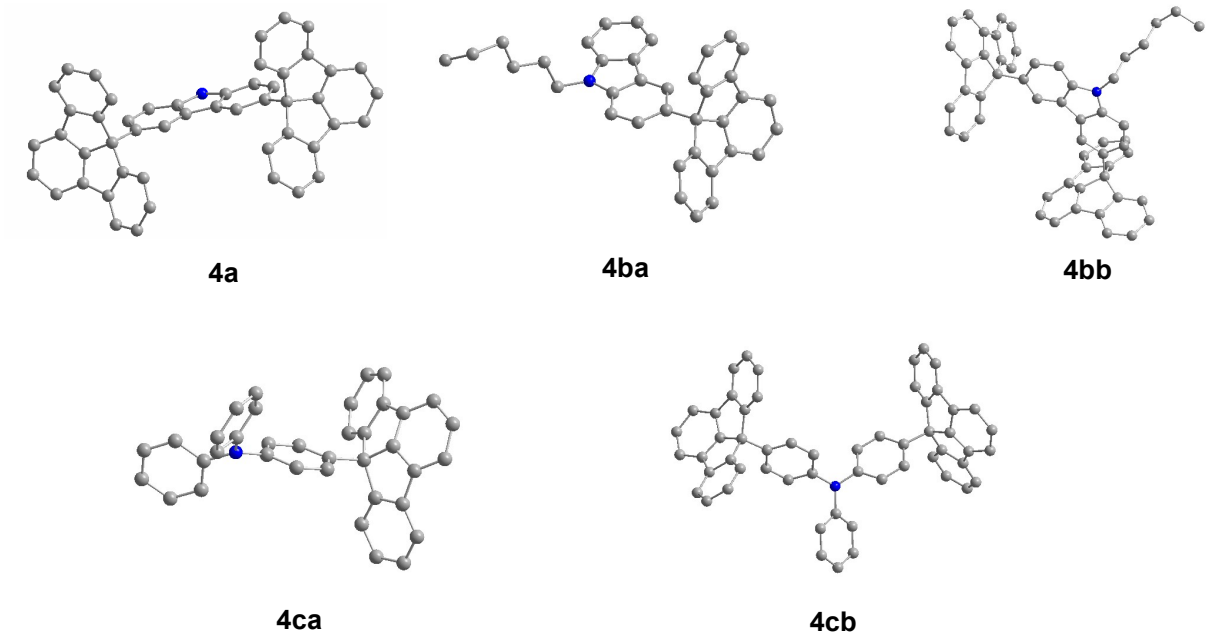

Fig. 3. Crystal structures of 4a, 4ba, 4bc, 4ca and 4cb

Table 2. Crystal data for 4a, 4ba, 4bc, 4ca and 4cb

Compund	**4a**	**4ba**	**4bb**	**4ca**	**4cb**
Empirical formula	$C_{54}H_{29}NO_2$	$C_{37}H_{31}N$	$C_{56}H_{41}N$	$C_{37}H_{25}N$	$C_{56}H_{35}N$
Molecular weight	723.78	489.63	727.90	483.58	721.85
Description	Colorless diamond	Colorless diamond	Colorless diamond	Colorless diamond	Colorless diamond
Size, mm^3	0.45 x 0.32 x 0.30	0.46 x 0.44 x 0.32	0.48 x 0.36 x 0.22	0.52 x 0.36 x 0.14	0.38 x 0.32 x 0.26
Temperature, K	296(2)	173(2)	173(2)	173(2)	296(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	P2(1)/m	C2/c	P2(1)	P2(1)/c	P-1

a, Å	8.3866(3)	28.2705(10)	13.3928(5)	8.2045(4)	8.1129(3)
b, Å	28.4107(9)	12.8474(5)	15.7368(5)	28.7349(14)	9.2093(3)
c, Å	8.9081(4)	15.7041(6)	19.3999(7)	10.9365(5)	27.8672(10)
α, degrees	90.00	90.00	90.00	90.00	88.7640(10)
β, degrees	117.9350(10)	112.2090(10)	107.3490(10)	96.475(2)	83.5200(10)
γ, degrees	90.00	90.00	90.00	90.00	65.0790(10)
V, $Å^3$	1875.21(12)	5280.6(3)	3902.7(2)	2561.9(2)	1875.37(11)
Z	2	8	4	4	2
Calculated density, Mg m^{-3}	1.282	1.232	1.239	1.254	1.278
Scan mode	φ- and ω-scans	φ- and ω-scans	φ- and ω-scans	φ- and ω-scans	φ- and ω-scans
F(000)	752	2080	1536	1016	2080
Absorption coefficient, mm^{-1}	0.077	0.070	0.071	0.072	0.073
θ range, degrees	2.69 to 25.01	1.77 to 25.01	1.59 to 25.01	2.00 to 25.01	1.47 to 25.00
Index ranges	$-9 \le h \le 8$ $-33 \le k \le 33$ $-10 \le l \le 10$	$-33 \le h \le 33$ $-15 \le k \le 15$ $-18 \le l \le 17$	$-15 \le h \le 15$ $-18 \le k \le 18$ $-23 \le l \le 23$	$-9 \le h \le 9$ $-34 \le k \le 34$ $-13 \le l \le 12$	$-9 \le h \le 9$ $-10 \le k \le 10$ $-33 \le l \le 33$
Reflections collected	21727	30006	44922	29335	22085
Independent reflections	3362 [R(int) = 0.0212]	4640 [R(int) = 0.0283]	6868 [R(int) = 0.0493]	4506 [R(int) = 0.1344]	6577 [R(int) = 0.0339]
Data/restraints /parameters	3362 / 204 / 319	4640 / 0 / 343	6868 / 0 / 514	4506 / 0 / 343	6577 / 0 / 514
GOF on F^2 (all)	1.084	1.045	1.029	0.998	1.018
Final R (I > 2σ(I))	R1 = 0.0439, wR2 = 0.1180	R1 = 0.0808, wR2 = 0.2111	R1=0.0594, wR2 =0.1526	R1 = 0.0509, wR2 = 0.0956	R1 = 0.0405, wR2 = 0.0917
R indices (all data)	R1 = 0.0490, wR2 = 0.1222	R1 = 0.0987, wR2 = 0.2323	R1=0.0855, wR2=0.1749	R1 = 0.1211, wR2 = 0.1184	R1 = 0.0644, wR2 = 0.1050
Max and min transmission	0.9772 and 0.9661	0.9778 and 0.9684	0.9846and 0.9669	0.9900 and 0.9636	0.9812 and 0.9728
Largest diff. peak, e/ $Å^3$	0.287	0.737	0.597	0.158	0.166
Largest diff. hole, e/ $Å^3$	-0.161	-0.545	-0.343	-0.204	-0.159

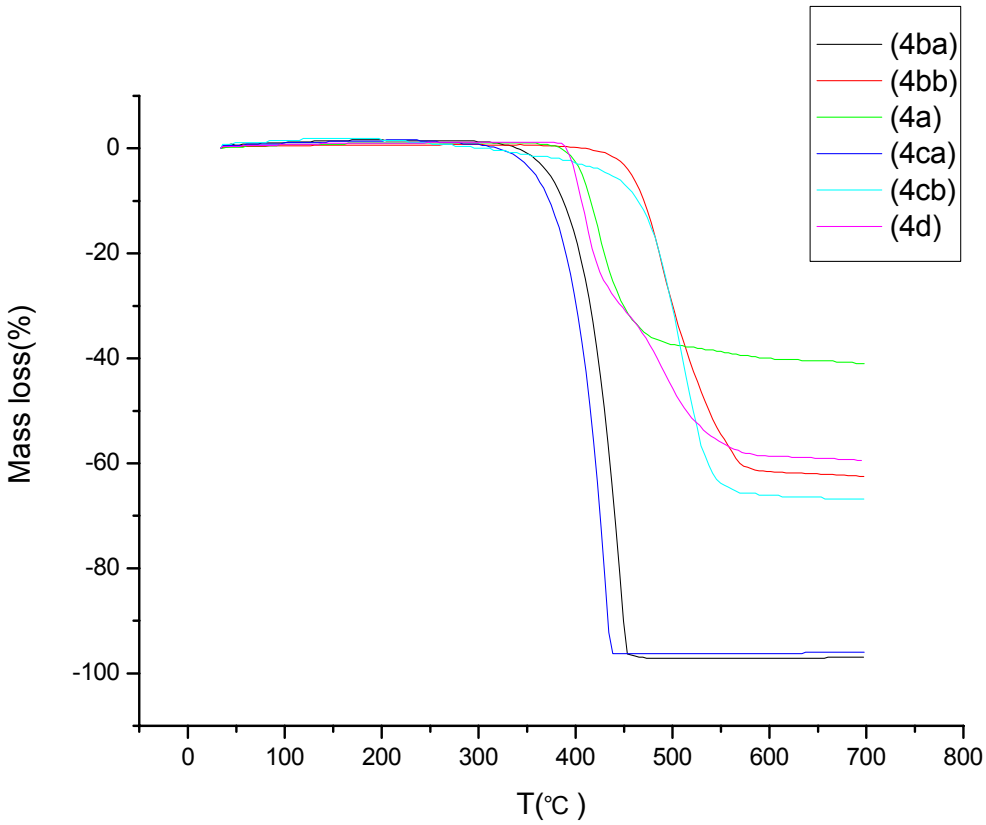

Figure 4. TGA curves of 4a, 4ba, 4bc, 4ca, 4cb and 4d

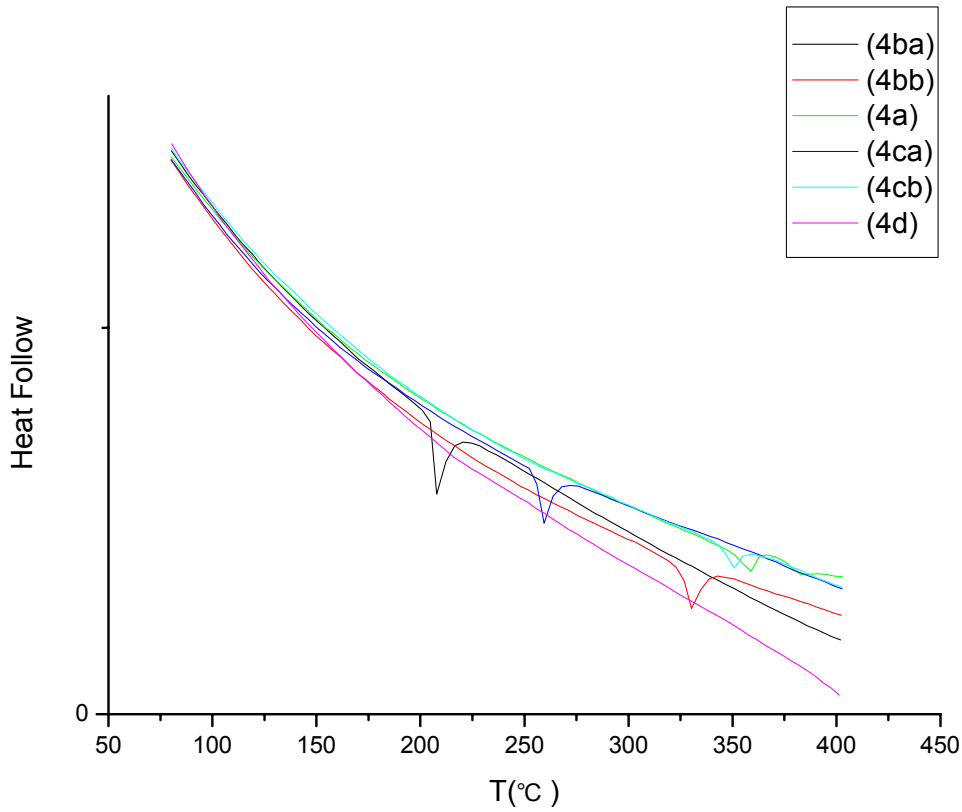

Figure 5. DSC curves of 4a, 4ba, 4bc, 4ca, 4cb and 4d

Table 3. Thermoanalysis data for 4a, 4ba, 4bc, 4ca, 4cb and 4d

	Td(°C)	Tm(°C)
4a	406	358
4ba	374	208
4bb	458	330
4ca	359	259
4cb	434	351
4d	401	-