Supporting information:

Facile C-H alkylation in water: Enabling defect free materials for optoelectronic devices

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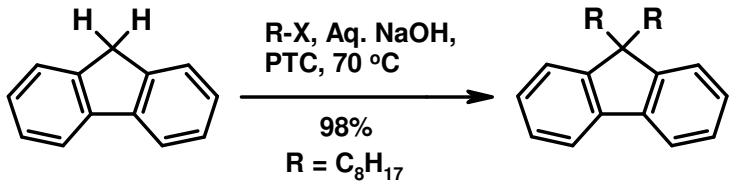
General Scheme for alkylation of fluorene: (**1a-4b**).



Scheme: 1

(1a) 9,9-Dihexyl-9H-fluorene: [1] $C_{25}H_{34}$, (0.405 g, 96%).

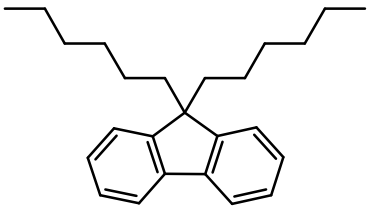


Figure 1: 1a

(1b) 9,9-Dioctyl-9H-fluorene:[2] $C_{29}H_{42}$, (0.48 g, 98%).

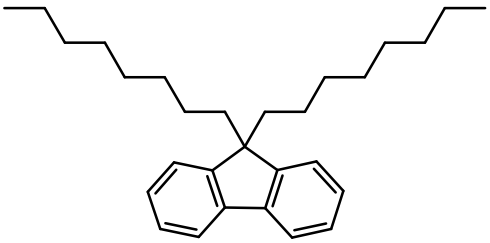


Figure 2: 1b

(1c) 9,9-Bis-(2-ethylhexyl)-9H-fluorene: $C_{29}H_{42}$. (0.43 g, 88%).

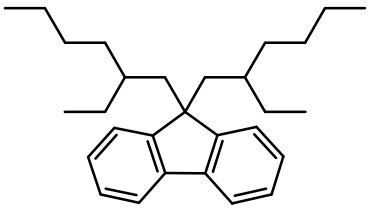


Figure 3: 1c

^{1}H NMR (400 MHz, $CDCl_3$): 7.68(d, 2H), 7.30(m, 6H), 1.97 (m, 4H), 0.75 (m, 26H), 0.50(m, 4H).

^{13}CNMR (100 MHz, $CDCl_3$): 150.5, 141.5, 126.8, 126.5, 124.2, 119.7, 55.0, 44.7, 34.7, 34.7, 33.8, 28.2, 27.0, 22.8, 14.2, 10.4.

Exact Mass: 390.3287, HR MS: 390.3253.

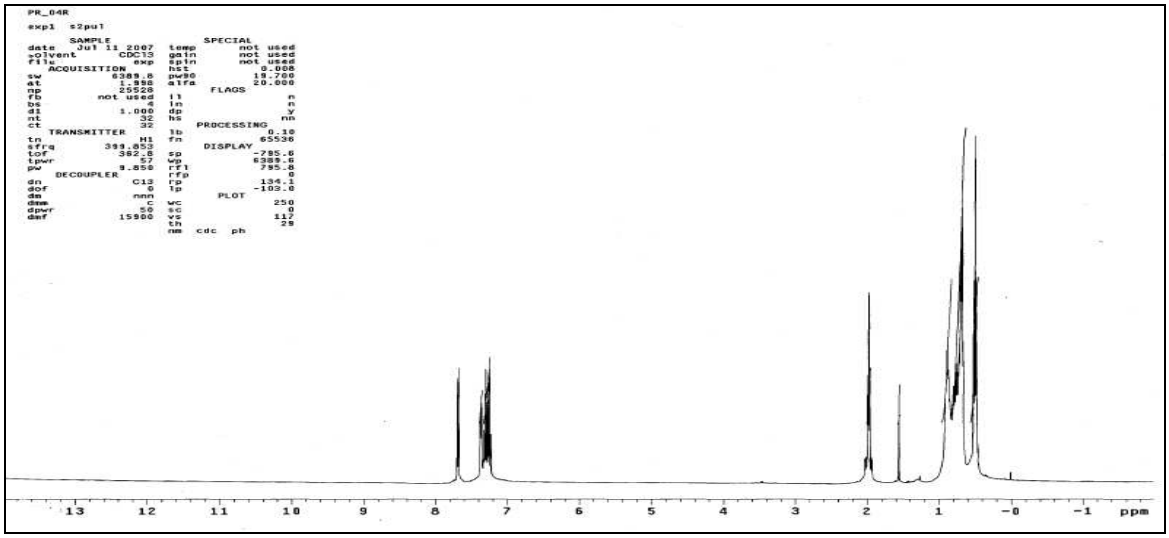


Figure 4: ^{1}H NMR (400 MHz, $CDCl_3$) of **1c.**

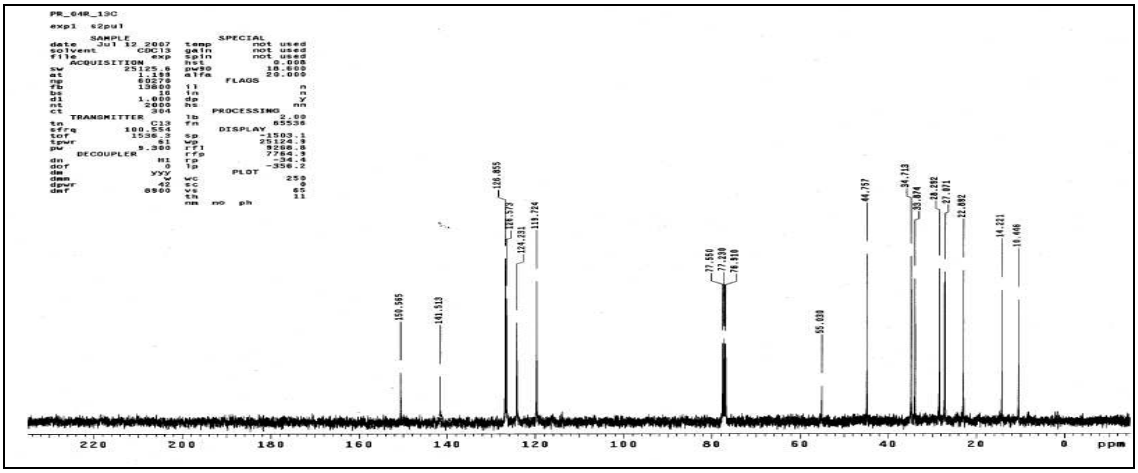


Figure 5: ^{13}CNMR (100 MHz, $CDCl_3$) of **1c.**

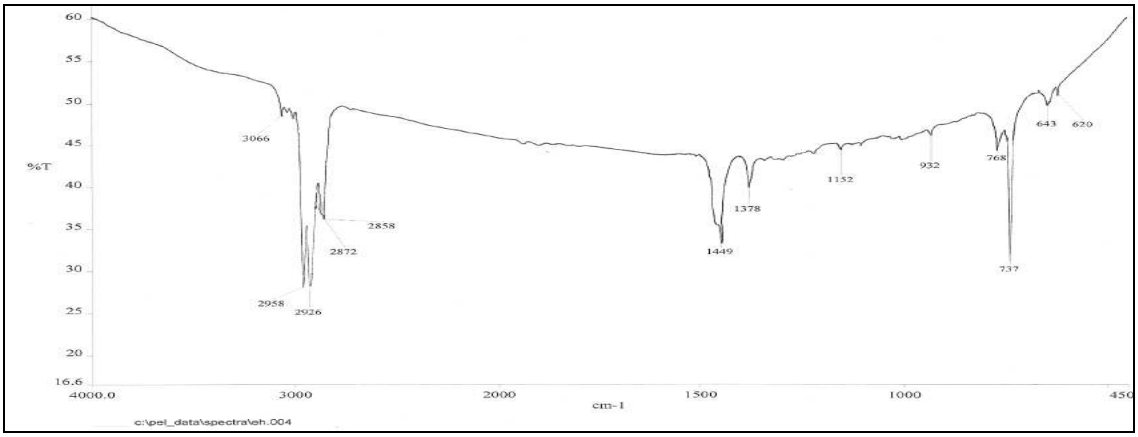


Figure 6: FTIR spectra of **1c**

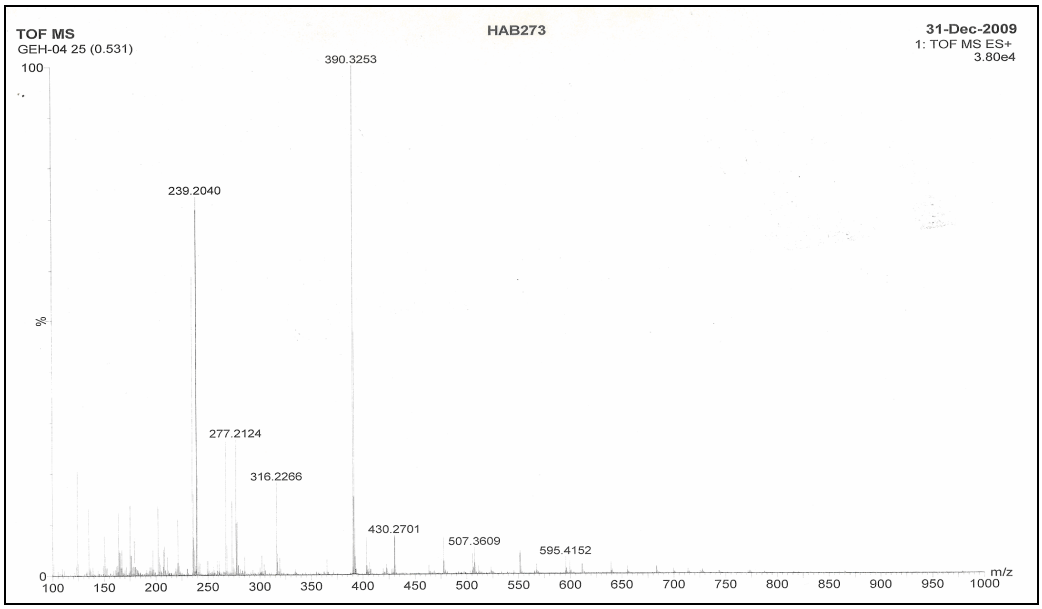
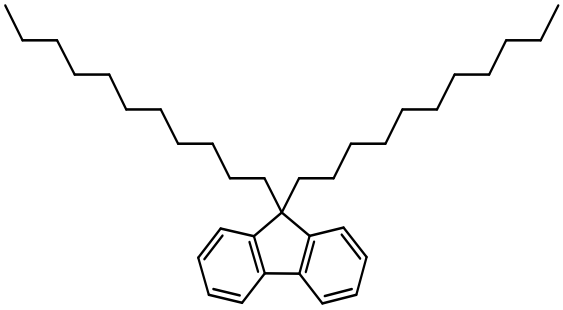


Figure 7: Mass spectra of **1c.**

(1d) 9,9-Diundecyl-9H-fluorene: $C_{35}H_{54,}$ (0.52 g, 88%).



^{1}H NMR (400 MHz, $CDCl_3$): 7.65(d, 2H), 7.28(m, 6H), 1.91(m, 4H), 1.38(m, 4H), 1.15(m, 22H), 0.99(s, 6H), 0.82(m, 6H), 0.56(m, 4H).

^{13}CNMR (100 MHz, $CDCl_3$): 150.8, 141.2, 127.2, 126.8, 122.9, 119.8, 55.1, 40.6, 34.1, 33.1, 32.1, 30.3, 29.5, 29.0, 28.4, 23.9, 22.9, 14.3.

Exact Mass: 474.4226, HR MS: 474.4257.

Figure 8: 1d

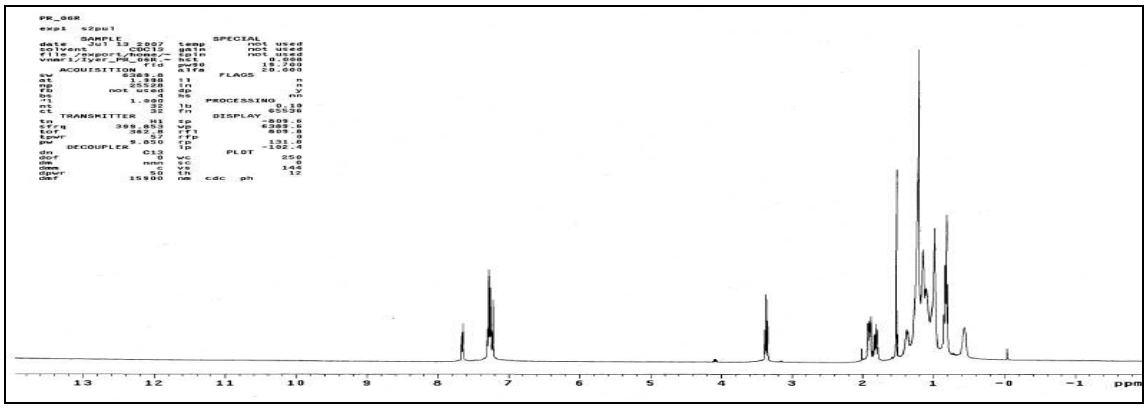


Figure 9: ^{1}H NMR (400 MHz, $CDCl_3$) of **1d.**

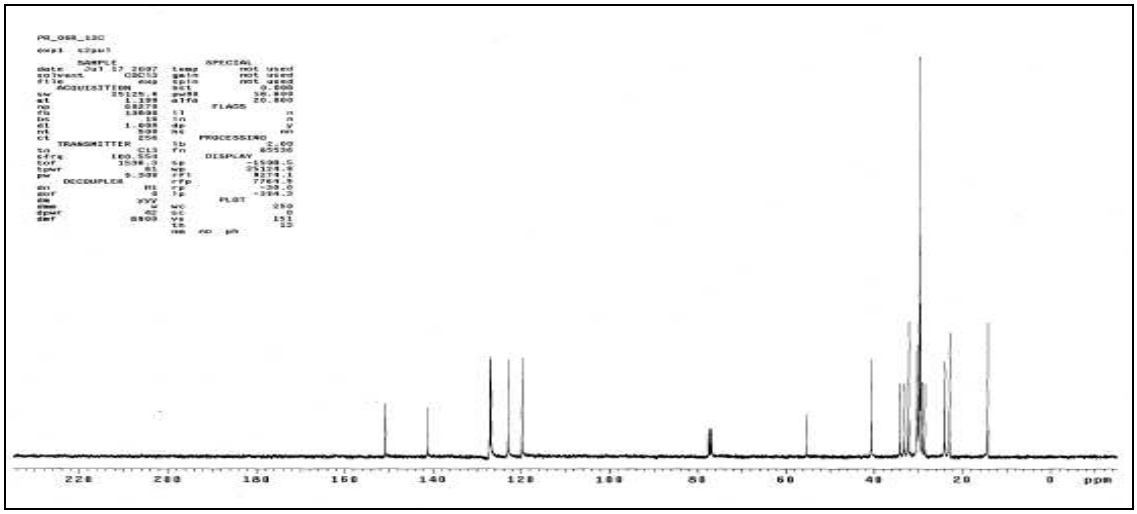


Figure 10: ^{13}CNMR (100 MHz, $CDCl_3$) of **1d.**

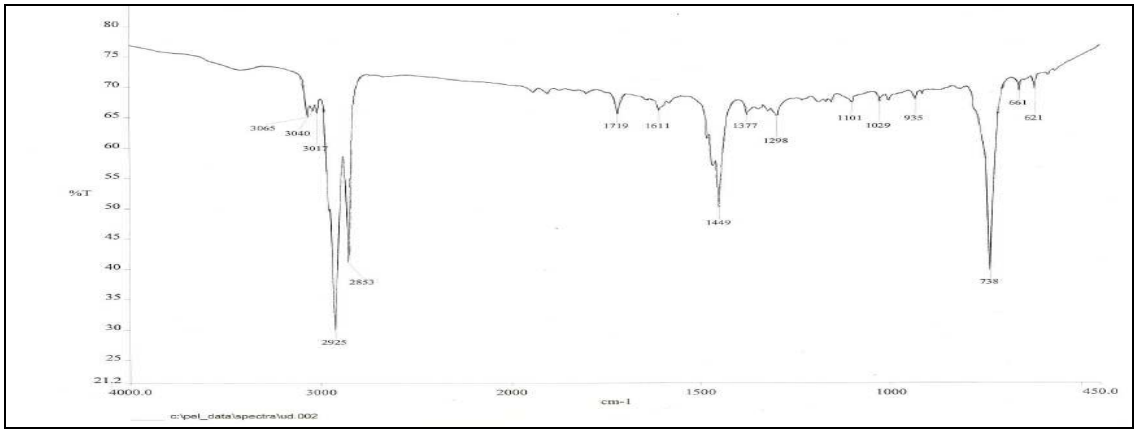


Figure 11: FTIR spectra of **1d**

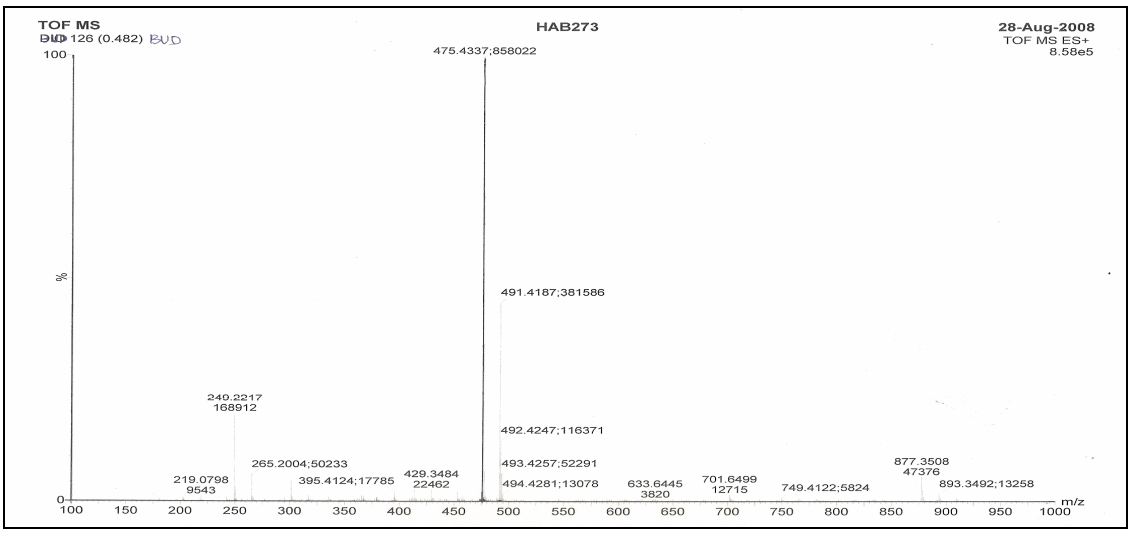


Figure 12: Mass spectra of **1d.**

(1e) 9,9-Bis-(6-bromohexyl)-9H-fluorene: $C_{25}H_{32}Br_2$, (0.58 g, 95%).

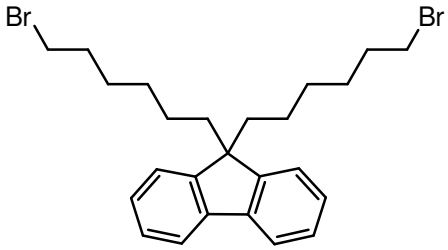


Figure 13: 1e

^{1}H NMR (400 MHz, $CDCl_3$): 7.68(m,2H), 7.28(m, 6H), 3.25(t, 4H), 1.95(m, 4H), 1.61(m, 4H), 1.15(m, 4H), 1.05(m, 4H), 0.60(m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): 150.8, 141.2, 127.2, 126.9, 122.8, 119.8, 54.9, 40.3, 34.1, 32.7, 29.2, 27.8, 23.6.

Exact Mass: 490.0871, HR MS: 490.0870.

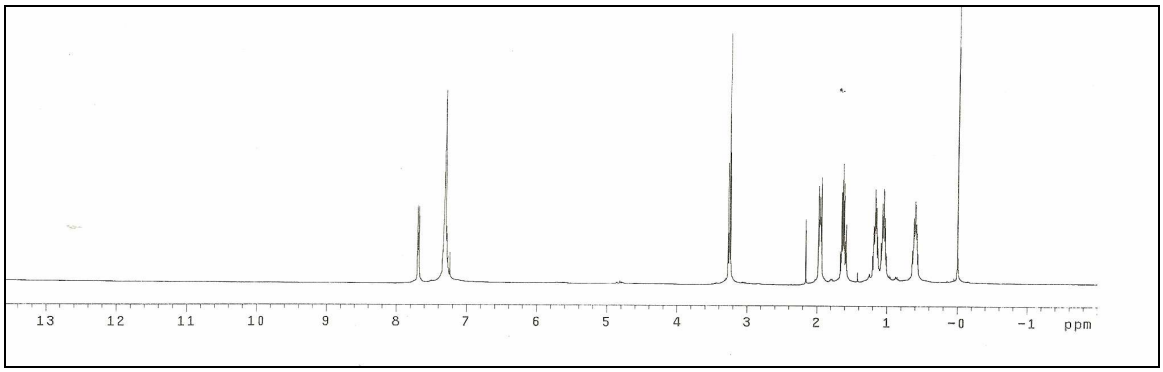


Figure 14: ^{1}H NMR (400 MHz, $CDCl_3$) of **1e.**

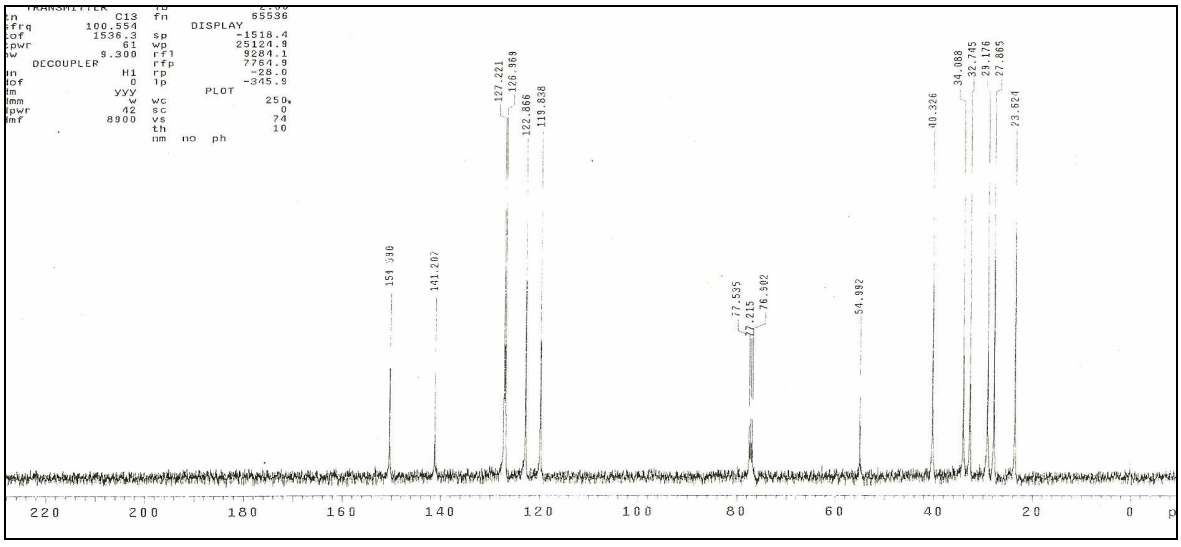


Figure 15: ^{13}CNMR (100 MHz, $CDCl_3$) of **1e.**

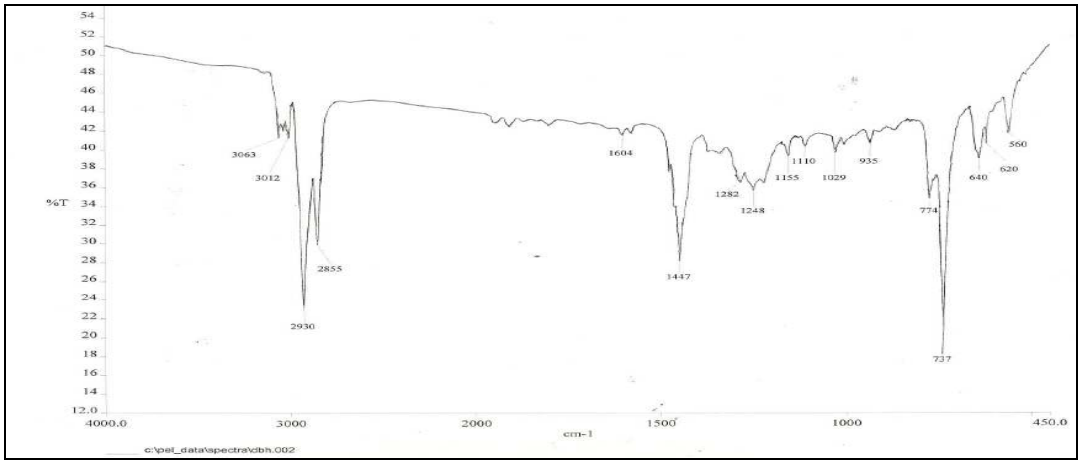


Figure 16: FTIR spectra of **1e**

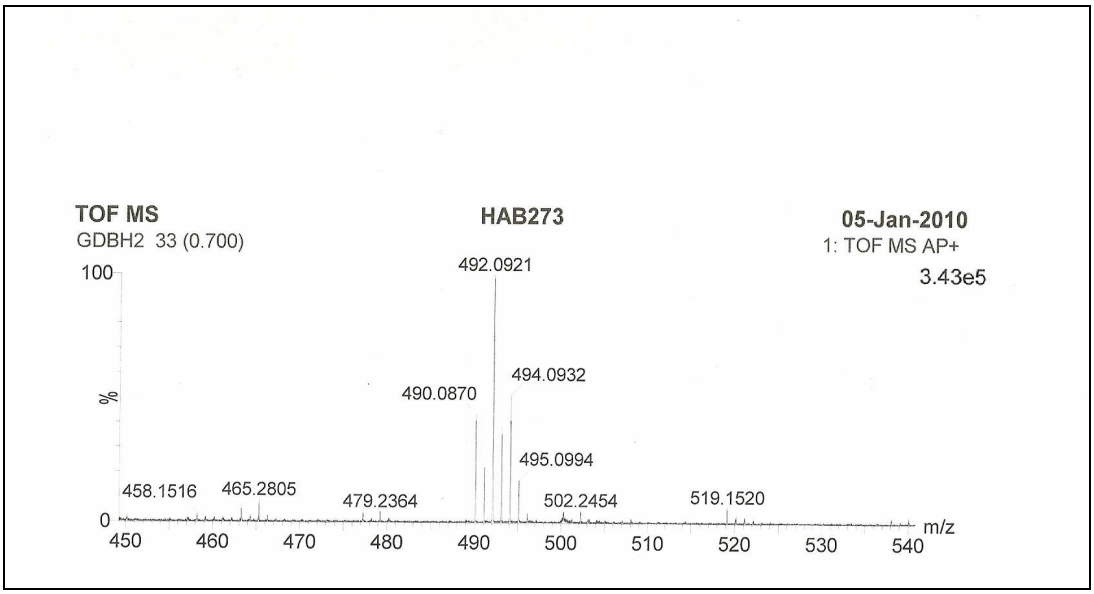


Figure 17: Mass spectra of **1e.**

(1f) 9,9-Bis-(8-bromooctyl)-9H-fluorene: $C_{29}H_{40}Br_2$, (0.62 g, 90%).

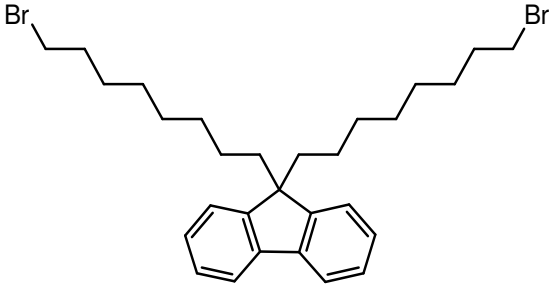


Figure 18: 1f

^{1}H NMR (400MHz, $CDCl_3$): 7.69(m,2H), 7.31(m, 6H), 3.33(t, 4H), 1.94(m, 4H), 1.74(m, 4H), 1.25(m, 4H), 1.05(m,12H), 0.58(m,4H).

^{13}C NMR (100 MHz, $CDCl_3$): 150.6, 141.2, 127.1, 126.8, 122.8, 119.7, 55.0, 40.4, 34.1, 32.8, 29.94, 29.1, 28.6, 28.1, 23.7.

Exact Mass: 546.1497, HR MS: 546.1489.

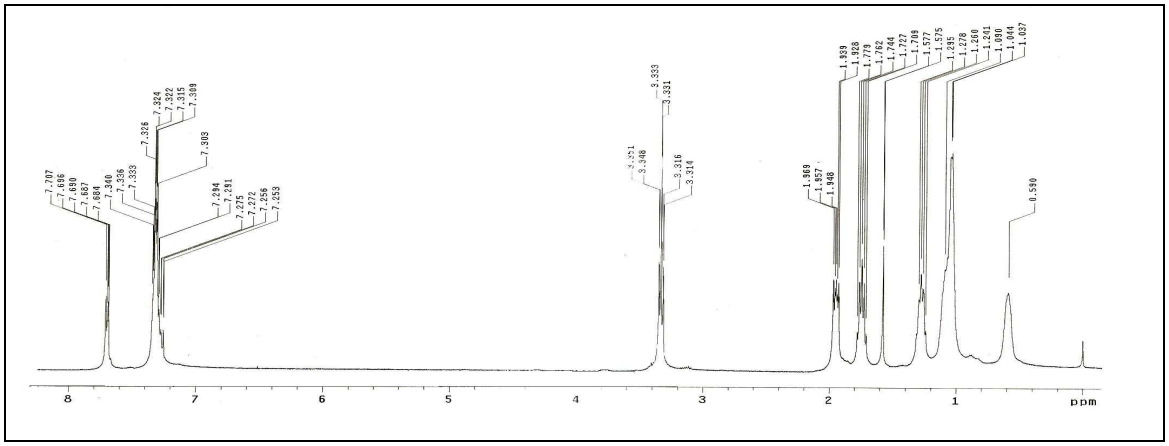


Figure 19: ^{1}H NMR (400MHz, $CDCl_3$) of **1f.**

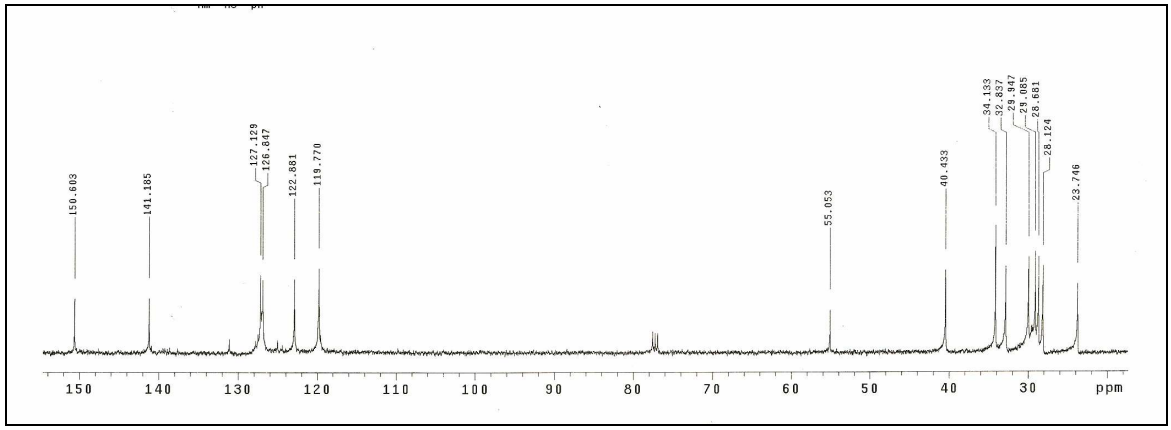


Figure 20: ^{13}CNMR (100 MHz, $CDCl_3$) of **1f.**

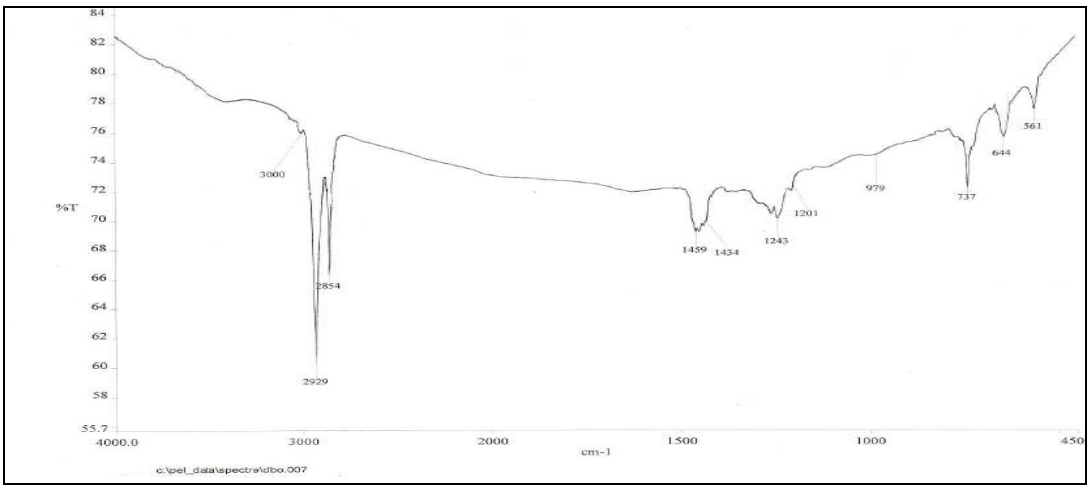


Figure 21: FTIR spectra of **1f**

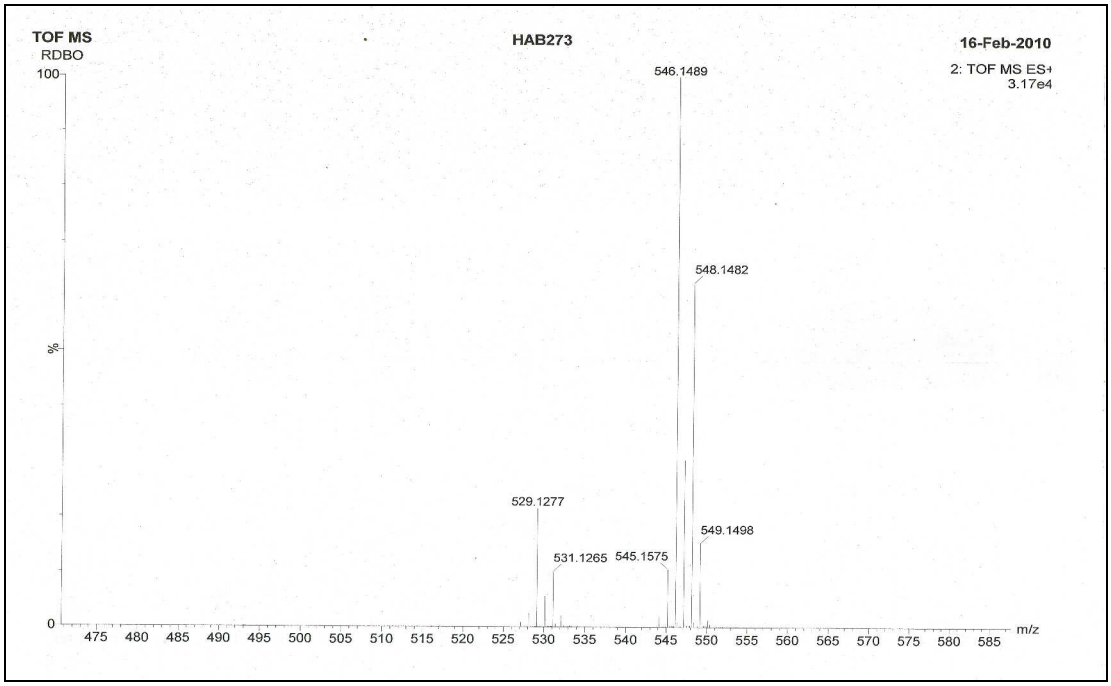


Figure 22: Mass spectra of **1f.**

(1g) 9,9-Bis-(6-iodohexyl)-9H-fluorene: $C_{25}H_{32}I_2$, (0.66 g, 90%).

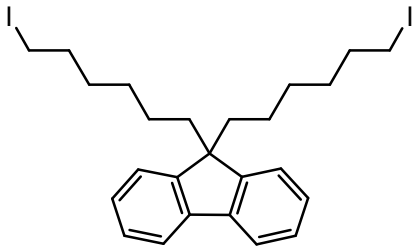


Figure 31: 1g

^{1}H NMR (400 MHz, $CDCl_3$): 7.69(d, 2H), 7.31(m, 6H), 3.04(t, 4H), 1.95(m, 4H), 1.60(m, 4H), 1.13(m, 4H), 1.04(m, 4H), 0.59(m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): 147.5, 141.3, 127.1, 127.0, 124.4, 119.9, 47.5, 33.5, 32.9, 30.4, 29.0, 25.4, 7.8.

Exact mass: 586.0593, HR MS: 586.0589.

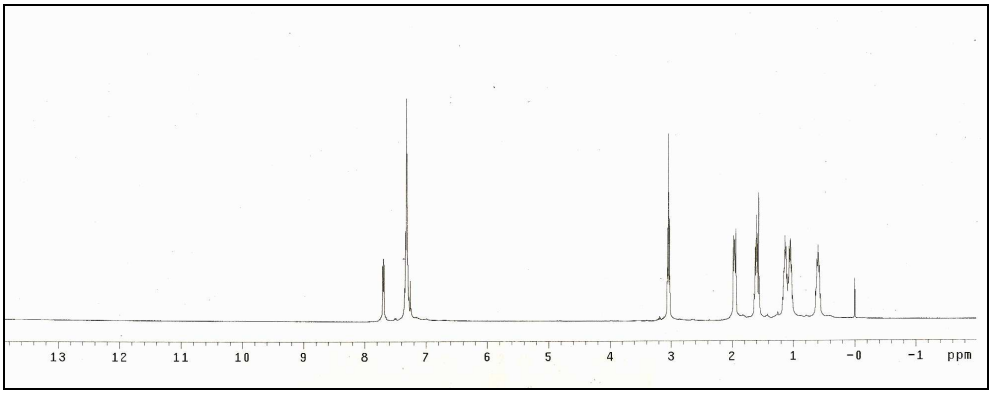


Figure 23: ^{1}H NMR (400 MHz, $CDCl_3$) of **1g.**

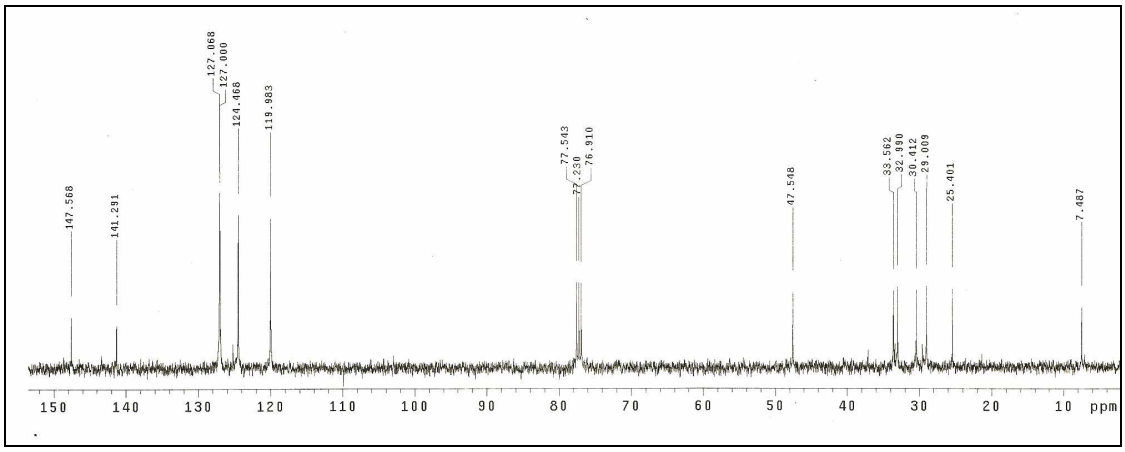


Figure 24: ^{13}C NMR (100 MHz, $CDCl_3$) of **1g.**

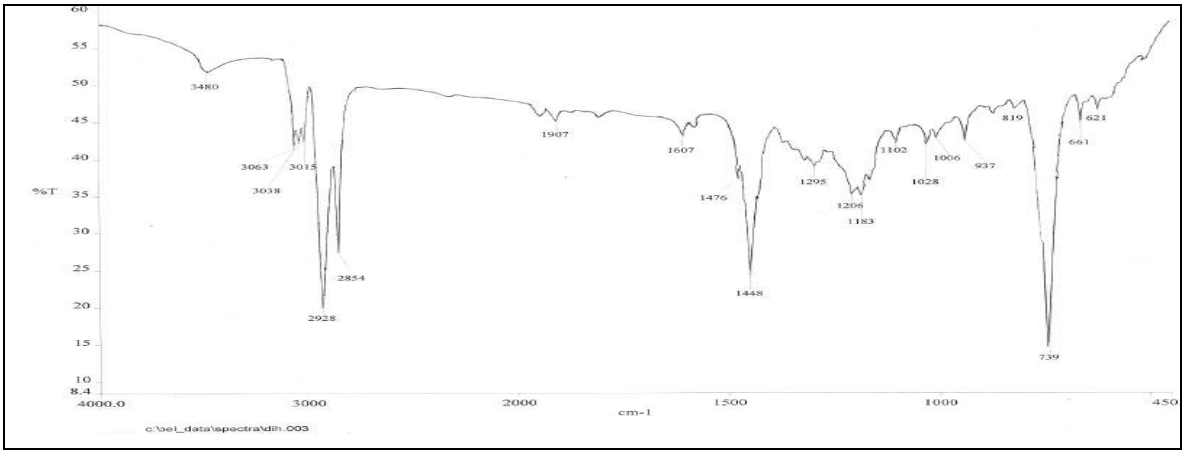


Figure 25: FTIR spectra of **1g**

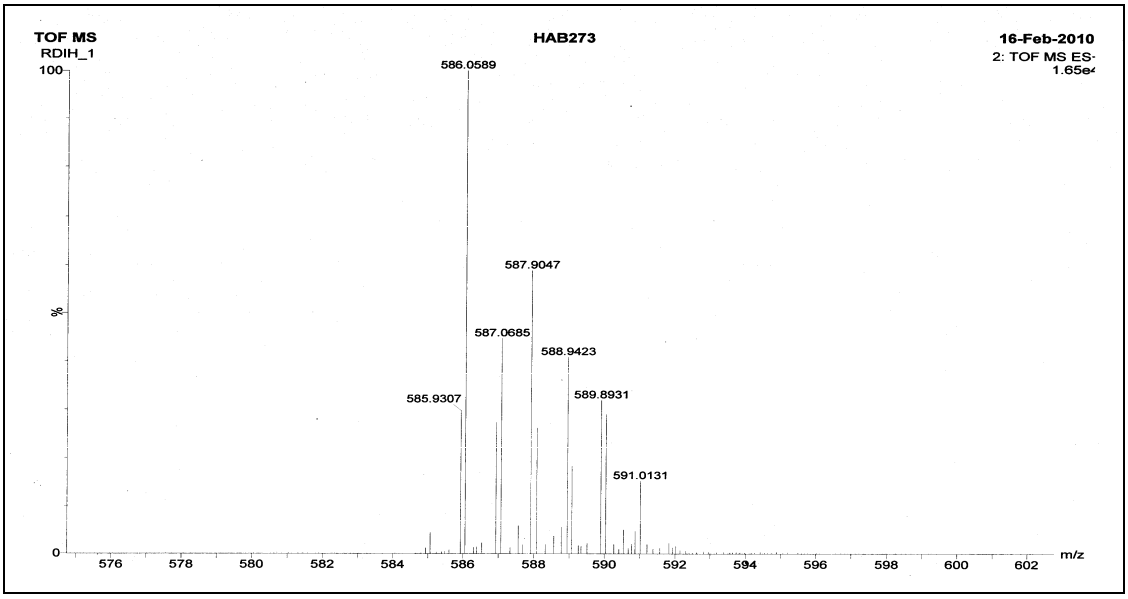


Figure 26: Mass spectra of **1g.**

(1h) 9,9-Bis-(8-iodooctyl)-9H-fluorene: $C_{29}H_{40}I_2$, (0.71 g, 88%).

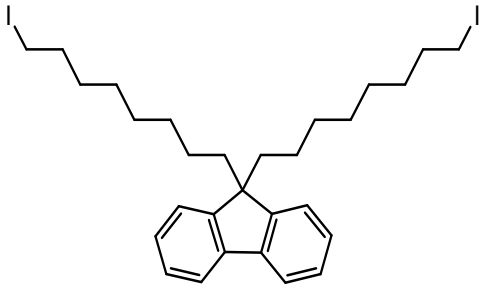


Figure 27: 1h

^{1}H NMR (400 MHz, $CDCl_3$): 7.69(d, 2H), 7.31(m, 6H), 3.26(t, 4H), 1.96(m, 4H), 1.62(m, 4H), 1.17(m, 4H), 1.05(m, 8H), 0.60(m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): 150.7, 141.3, 127.2, 126.8, 123.0, 119.8, 55.1, 40.5, 34.3, 32.9, 30.1, 29.2, 28.8, 28, 23.8.

Exact Mass: 642.1219, HR MS: 642.1216.

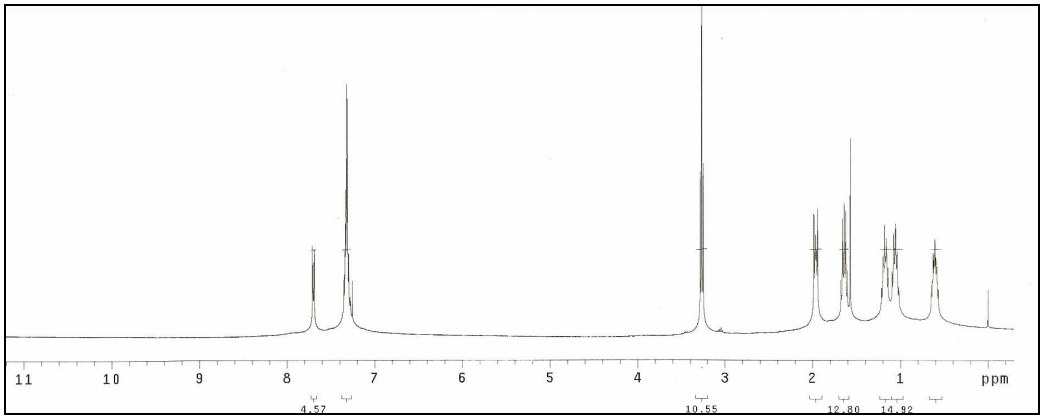


Figure 28: ^{1}H NMR (400 MHz, $CDCl_3$) of **1h.**

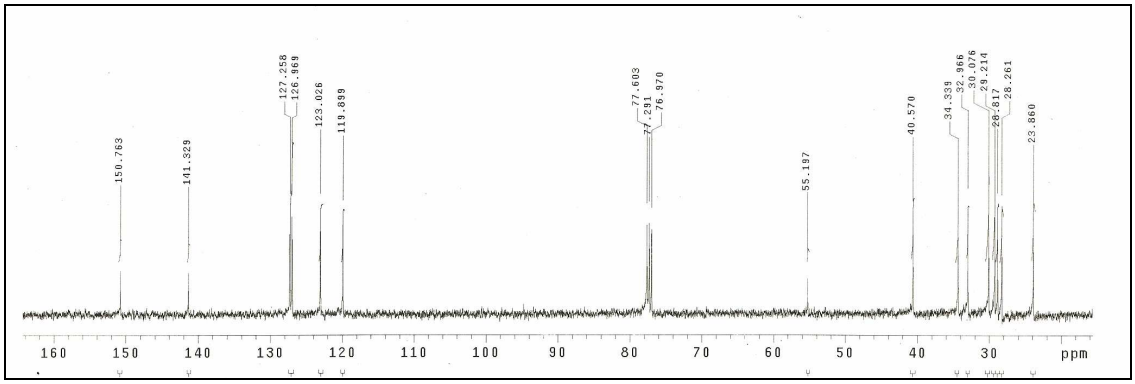


Figure 29: ^{13}C NMR (100 MHz, $CDCl_3$) of **1h.**

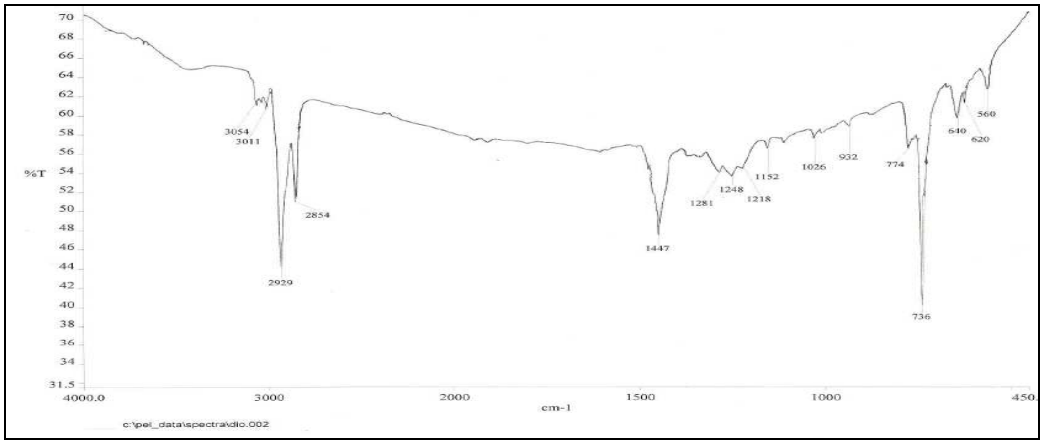


Figure 30: FTIR spectra of **1h**

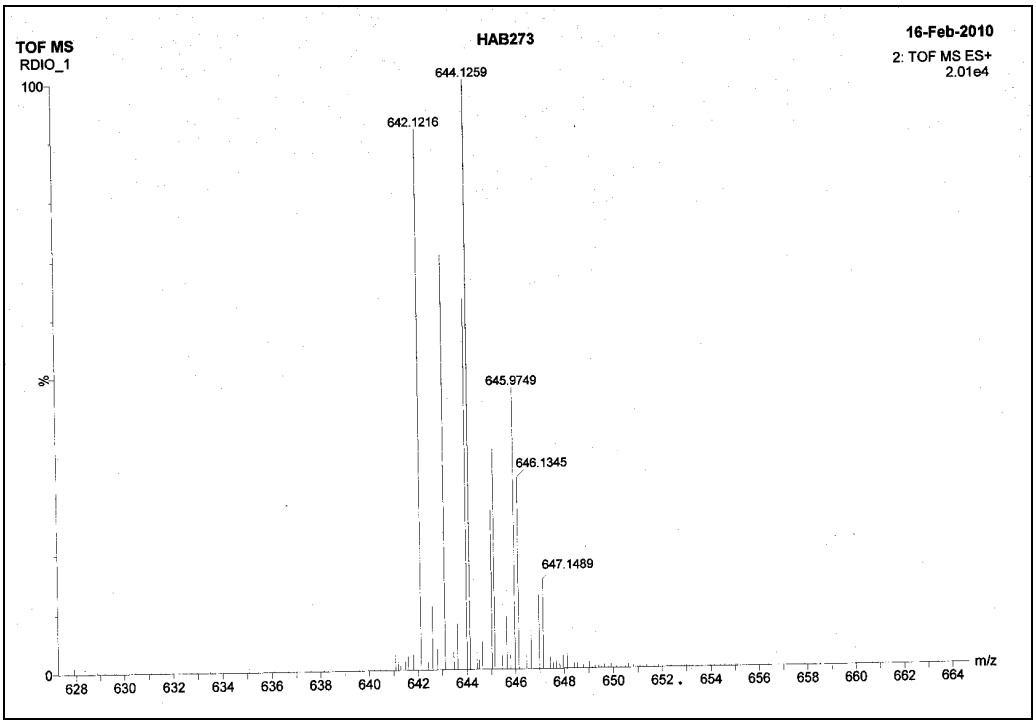


Figure 31: Mass spectra of **1h.**

(1i) 9,9-Dihexyl-9H-fluorene: $C_{25}H_{34}$. Product same as compound **1a.** (0.36 g, 85%).

(1j) 9,9-Dioctyl-9H-fluorene: $C_{29}H_{42}$. Product same as compound **1b.** (0.43 g, 87%).

(4a) 2,7-dibromo-9,9-dihexylfluorene:[2(a)] (0.31 g, 99%).

(4b) 2-bromo-9,9-dihexylfluorene:[3] (0.347 g, 98%).

Alkylation of carbazole and diphenylamine:

General: Carbazole (0.21 g, 1.25 mmol), haloalkane (bromo-hexane) (0.82 g, 5.02 mmol), 50% aq. NaOH and catalytic amount of tetrabutylammonium iodide (0.046 g. 10 mol %) was taken in a flask. The flask was heated at 70 ^{o}C continuously for 8 hrs. The reaction mixture was cooled to room temperature, and extracted with chloroform. The organic layer was washed with water and dried over anhydrous sodium sulphate. The solvent was removed under vacuum and the crude was

purified by column chromatography over silica gel with 10% chloroform in hexane as the eluent to give the desired product.

(4c) 9-Hexyl-9H-carbazole:[4] (0.28 g, 91%).

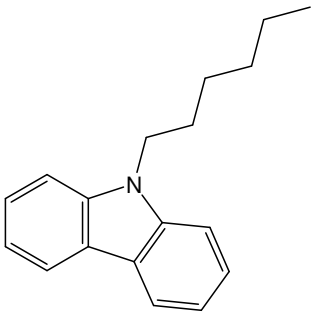


Figure 32: 4c

(4d) N-hexyl-diphenylamine: Same procedure as above was adopted for the alkylation of N-hexyl-diphenylamine. (0.235 g, 75%).

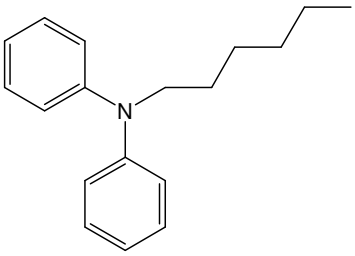


Figure 33: 4d

^{1}H NMR (400 MHz, $CDCl_3$): 7.26(t, 4H), 7.08(d, 4H), 6.92(t, 2H), 3.36(t, 2H), 1.68(m, 2h), 1.46(m, 2H), 1.09 (m, 7H).

^{13}C NMR (100MHz, $CDCl_3$): 143.1, 128.9, 120.3, 117.3, 52.4, 25.1, 23.9, 19.9, 19.5, 13.5.

Exact Mass: 253.1830, MS: 253.1800.

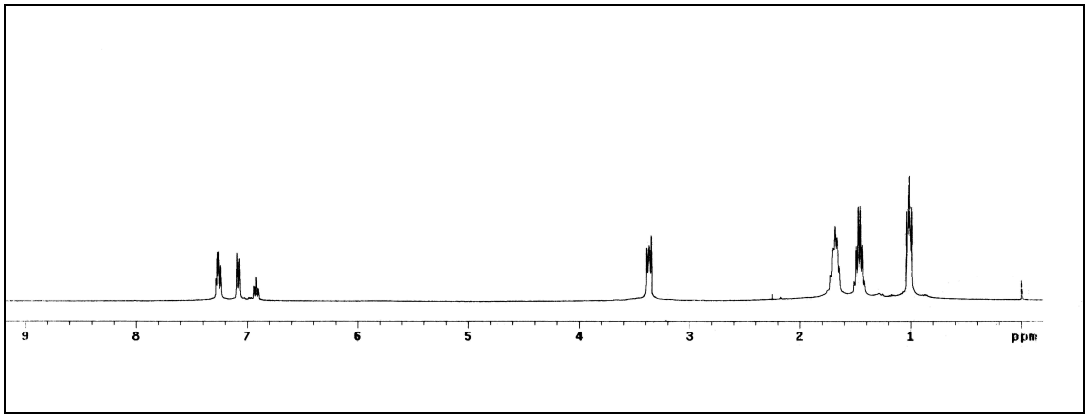


Figure 34: ^{1}H NMR (400 MHz, $CDCl_3$) of **4d.**

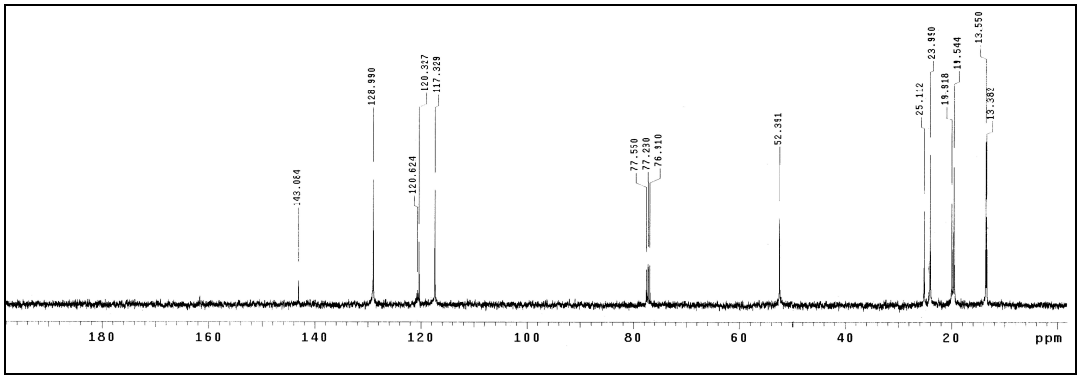


Figure 35: ^{13}C NMR (100MHz, $CDCl_3$) of **4d.**

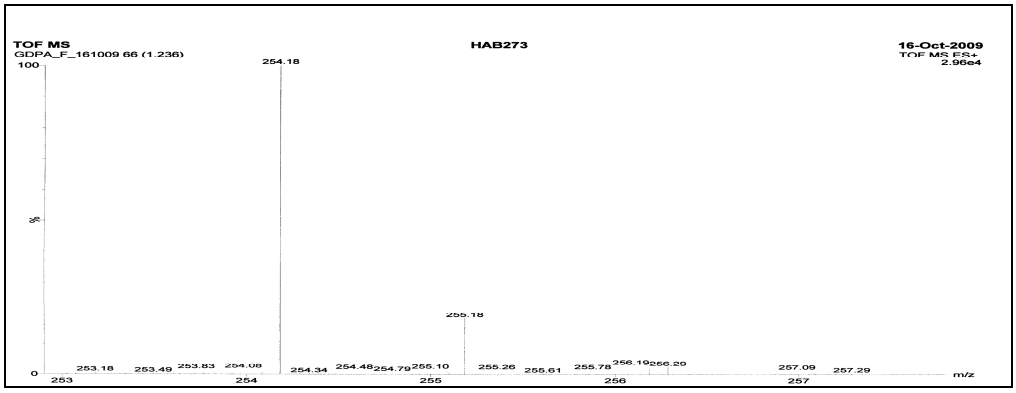


Figure 36: Mass spectra of **4d.**

(4e) N,N-Di-n-hexylaniline:[5] Same procedure as above was adopted for dialkylation of aniline with the quantity of haloalkane increased to 8.78mmol. (0.23 g, 72%).

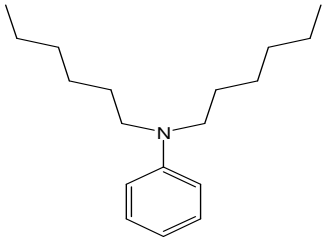


Figure 37: 4e

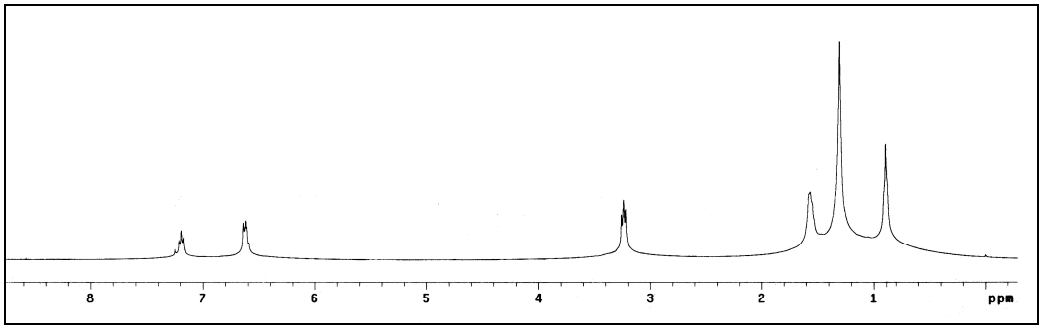


Figure 38: ^{1}H NMR (400 MHz, $CDCl_3$) of **4e**

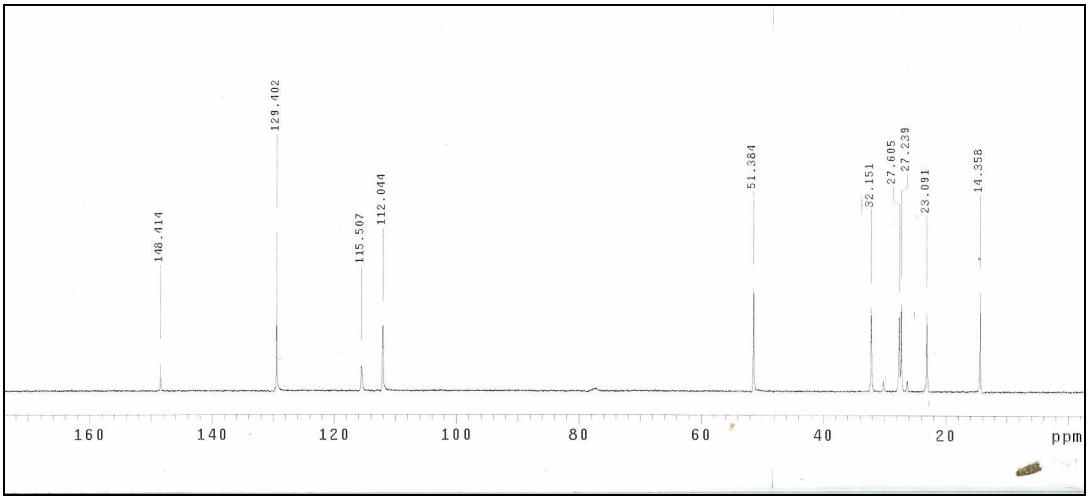


Figure 39: ^{13}C NMR (100MHz, $CDCl_3$) of **4e**

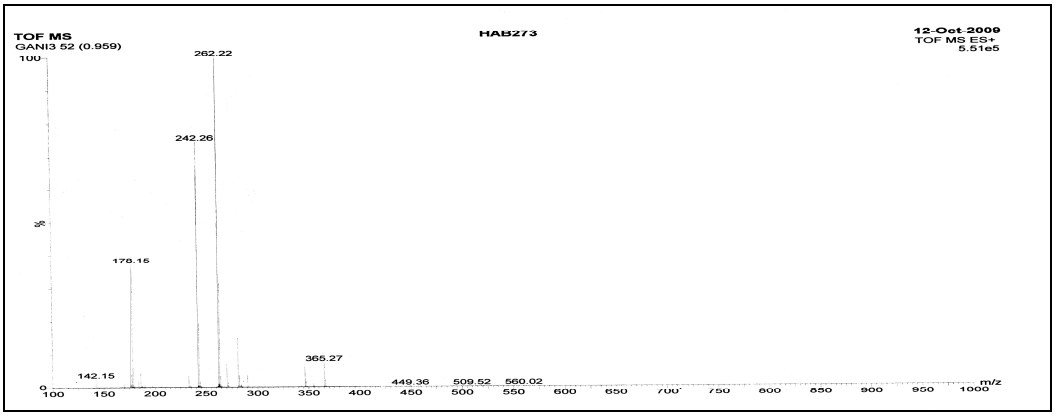


Figure 40: Mass spectra of **4e**

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