Supplementary Material (ESI)

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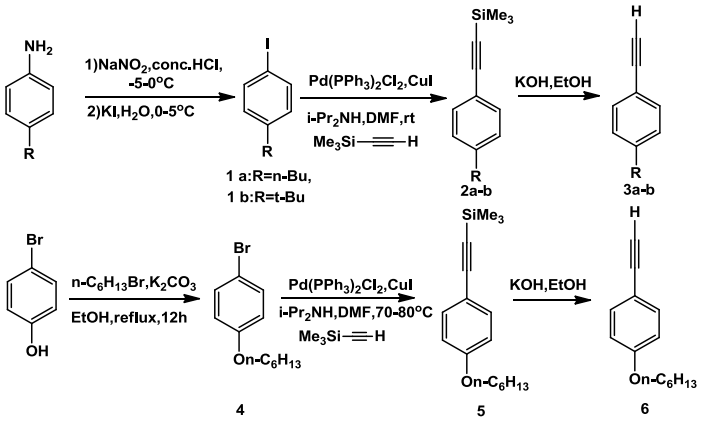
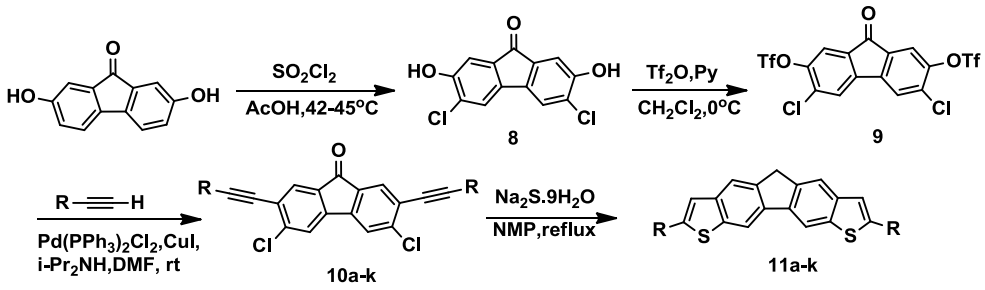
General remarks

All manipulations were performed by standard Schlenk techniques. Melting point was measured on X-4 micrographic measuring apparatus. All 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 400 M NMR (^{1}H NMR 400 MHz, ^{13}C NMR 100 MHz) and a Varian 300M NMR(^{1}H NMR 300 MHz, ^{13}C NMR 75 MHz), Data for X-ray structure analysis were collected on a Bruker Smart Apex II**,** detector with Mo *K*α radiation (λ= 0.71073 Å). Structures were solved by direct methods with SHELXTL-97. Mass spectra (EI) were measured on a Agilent 5973N. High resolution mass spectra (HRMS) were recorded on a Waters GCT Premier.

Scheme I Synthetic routes to target molecules and the related precursors





R a-k=H($SiMe_3$)(a), n-Pr_9b), Bu(c), t-Bu(d), i-pentyl(3-methyl-butyl)(e), n-pentyl(f), hexyl(g), phenyl(h), 4-butylphenyl(i), 4-t-butylphenyl(j), 4-hexyloxylphenyl(k)

Synthesis of 4-n-butyl-iodobenzene(1a). [1] To a stirred mixture of 4-n-butylaniline (2.980 g, 20 mmol) and conc. HCl (12 mL) was added dropwise a solution of $NaNO_2$ (1.656 g, 24 mmol) in water (7 mL) at -5°C. The resulting mixture was stirred for another 30 min, and then a solution of KI(6.640 g, 40 mmol) in water (7 mL) was added dropwise while maintaining the temperature between 0-5°C, then it was stirred overnight at room temperature, followed by being poured into a solution of sodium pyrosulfite (20 M, 20 mL) and extracted with dichloromethane three times. The combined organic layer was consecutively washed with 5 % NaOH solution, water and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel eluted with petroleum ether, to give 4-n-butyl-iodobenzene as an colorless oily liquid (3.638 g, 70 %). R_f = 0.78 (PE), which was used directly for next step.

Synthesis of trimethylsilyl (4-n-butylphenyl)acetylene(2a) [S1] To a degassed solution of 4-n-butyl-iodobenzene(10.720 g, 41.23 mmol) in triethylamine (100 mL) were added trimethylsilylethyne (4.200 g, 42.86 mmol), $Pd(PPh_3)_2Cl_2$ (0.648 g, 0.923 mmol, 2.2 mol%) and CuI (0.142 g, 0.745 mmol, 1.8 mol%). It was heated to 50 °C for 4h and poured into aq. HCl (5 %). The resulting mixture was extracted with dichloromethane for three times. The combined organic layer was dried over $MgSO_4$ and concentrated in vacuo. The

residue was purified by column chromatography on silica gel eluted with petroleum ether to give trimethylsilyl (4-n-butylphenyl)acetylene as a pale yellow oily liquid(8.525 g, 90 %), R_f = 0.62(PE), which was used directly.

Synthesis of 4-n-butylphenylacetylene(3a) [s1] The mixture of trimethylsilyl-(4-n-butylphenyl)acetylene (6.485 g, 28.2 mmol), and sodium hydroxide (3.000 g, 60 mmol) in methanol(100 mL) was stirred overnight at the room temperature. Then it was concentrated in vacuo and poured into water, followed by extracted with dichloromethane for three times. The combined organic phase was dried over $MgSO_4$ and concentrated in vacuo to give 4-n-butylphenylacetylene(4.786 g, 79 %)as a colorless oily liquid. R_f = 0.72 (PE). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 7.45 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 8.3 Hz, 2H), 3.06 (s, 1H), 2.64 (t, J = 7.7 Hz, 2H), 1.72 – 1.54 (m, 2H), 1.38 (dq, J = 14.4, 7.3 Hz, 2H), 0.97 (t, J = 7.3 Hz, 3H).

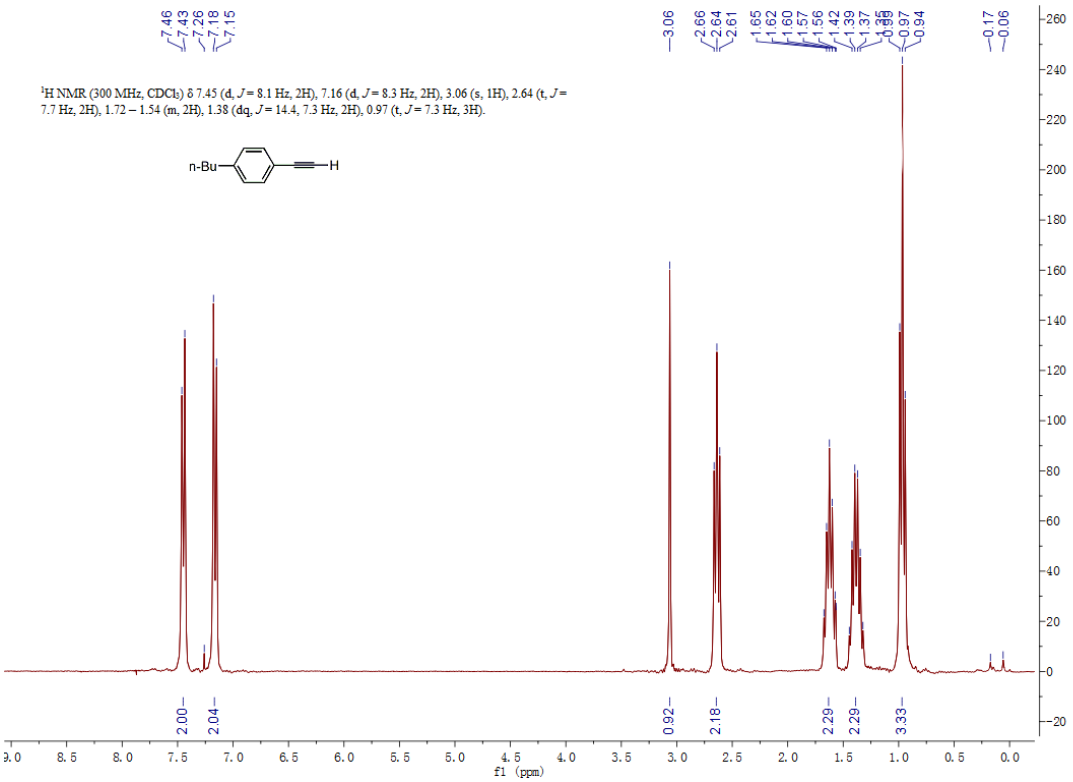


Fig. 1. The ^{1}H NMR of 4-n-butylphenylacetylene(3a)

Synthesis of 4-tert-butyl-iodobenzene(1b) [s1] A similar procedure as described for 4-n-butyl-iodobenzene was used by employing. 4-tert-butylaniline (7.450 g, 50 mmol), conc. HCl (30 mL), $NaNO_2$(4.140 g, 60 mmol) in water (17 mL) and KI(12.450 g, 75 mmol) in water(17 mL) to afford 4-tert-butyl-iodobenzene (7.557 g, 58 %), R_f = 0.68(hexane), which was used directly.

Synthesis of trimethylsilyl(4-tert-butylphenyl)acetylene(2b) To a degassed solution of 4-tert-butyl-iodobenzene(7.557 g, 29 mmol) and diisopropylamine (6 mL) in DMF(50 mL) were added subsequently trimethylsilylacetylene (3.475 g, 35.5 mmol), $Pd(PPh_3)_2Cl_2$(0.268 g, 0.38 mmol, 1.3 mol%) and CuI (0.157 g, 0.824 mmol,2.8 mol%). The mixture was stirred for 9h at the room temperature before poured into 5 % HCl (200 ml). It was extracted with dichloromethane for three times. The combined organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel eluted with petroleum ether to give trimethylsilyl(4-tert-butylphenyl)acetylene as a pale yellow oily liquid (6.02 g, 87 %), R_f = 0.64 (PE).

Synthesis of 4-tert-butylphenylacetylene(3b) A similar procedure as the synthesis of 4-butylphenylacetylene. The 1-tert-butyl-4- [2-(trimethylsilyl)ethynyl]benzene(6.02 g, 26.2 mmol), NaOH (2.62 g, 52.4 mmol) in methanol (50 mL) to give 4-tert-butylphenyl acetylene (2.350 g, 82 %).R_f = 0.69 (hexane). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ :7.46 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.3 Hz, 2H), 3.05 (s, 1H), 1.33 (s, 9H).

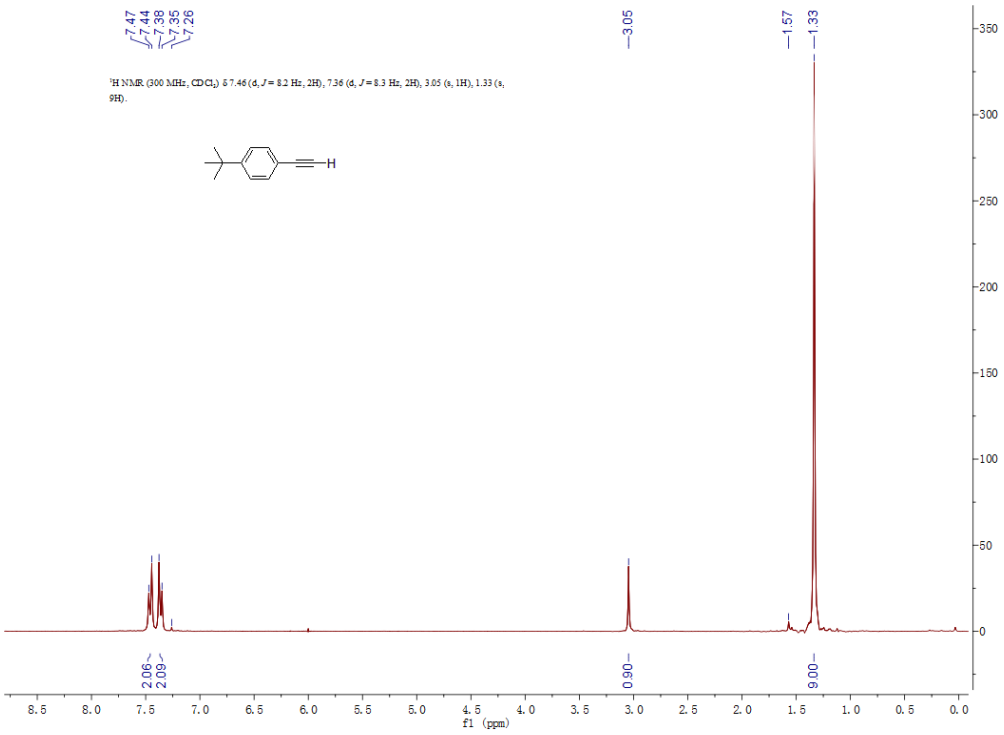


Fig. 2. The ^{1}HNMR of 4-tert-butylphenylacetylene(3b)

Synthesis of 4-hexoxylbromobenzene (4) [s2] The mixture of 4-bromophenol (5.21 g, 30.1 mmol), potassium carbonate(5.190 g, 45 mmol) and 1-bromohexane(7.425 g, 45 mmol) in ethanol(25 mL) was heated under reflux for 12 h. The solid was removed by filtration, and the solvent was evaporated to give the crude product, which was purified by column chromatography on silica gel to obtain a colorless oil (7.665 g, 99 %). R_f = 0.65 (PE : EA = 20 : 1, V/V).

Synthesis of 1-ethynyl-4-hexyloxybenzene(6) To a degassed solution of 4-hexyloxy bromobenzene(3.598 g, 14 mmol) and diisopropylamine(8 mL) in DMF(50 mL) were added trimethylsilylethyne(1.869 g, 21 mmol), $Pd(PPh_3)_2Cl_2$(0.196 g, 0.28 mmol, 2 mol%) and CuI (0.054 g, 0.028 mmol, 2 mol%). The mixture was heated to 70-80 °C for 12 h. then poured it into the 5 % HCl solution, and was extracted with dichloromethane for three times. The combined organic was dried over $MgSO_4$. The solvent was removed

under vacuo. The crude product**(5)** without further purified. A mixture of the whole crude product **(5)** and potassium carbonate(11.592 g, 84 mmol) in methanol (60 mL) was stirred overnight at room temperature, which was then poured into 5 % HCl solution and extracted with dichloromethane for three times. The combined organic layer was dried with $MgSO_4$. The crude product was purified by column chromatography on silica gel to give pale yellow oil (2.000 g, 71 %). R_f = 0.25 (PE:DCM=20:1,V/V). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 7.51 - 7.34 (m, 2H), 6.91 – 6.69 (m, 2H), 3.93 (t, J = 6.6 Hz, 2H), 2.98 (s, 1H), 1.82-1.69 (m, 2H), 1.50 – 1.37 (m, 2H), 1.32 (dd, J = 8.7, 5.6 Hz, 4H), 0.90 (t, J = 6.9 Hz, 3H).

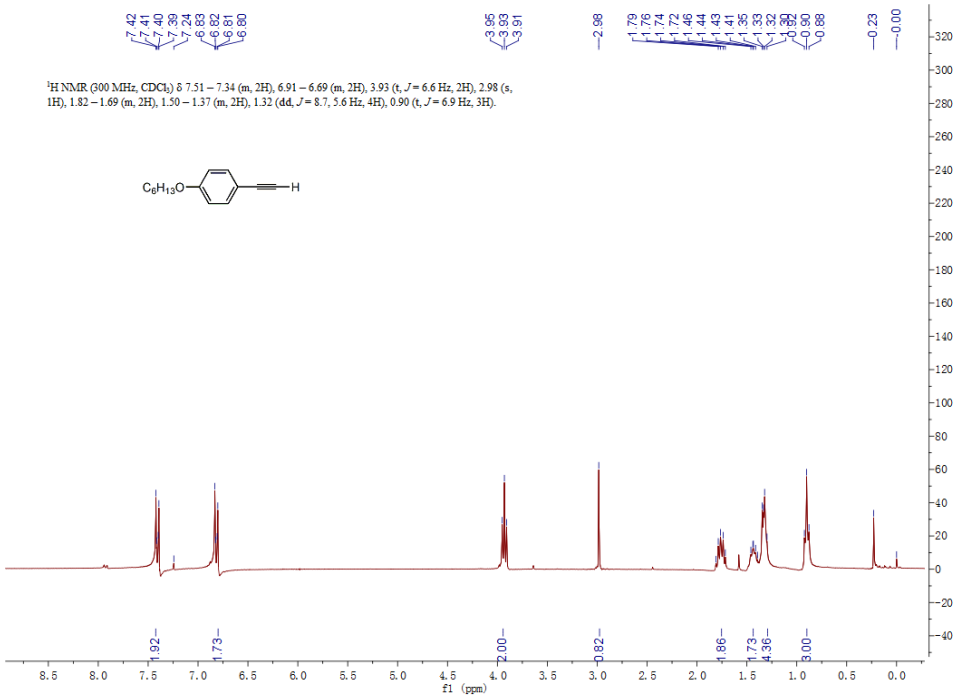
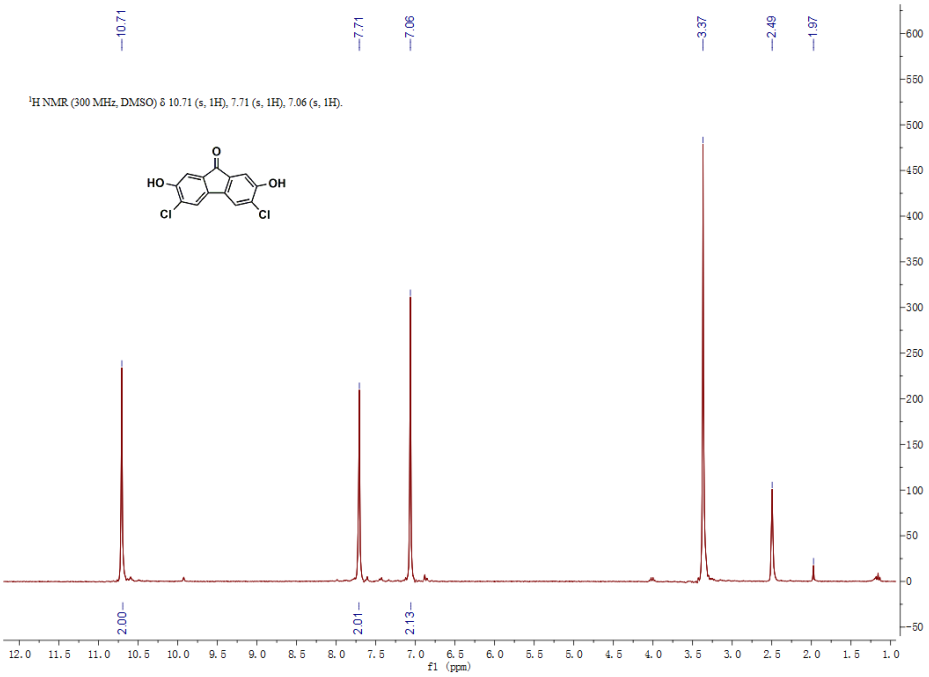


Fig. 3. The ^{1}HNMR of 4-hexyloxylphenylacetylene(6)

Synthesis of 3,6-dichloro-2,7-dihydroxy-9-fluorenone (8) [s3]

To a preheated to 42^{o}C and stirred suspension of 2,7-dihydroxy-9-fluorenone (10.490 g, 49.5 mmol) in glacial acetic acid(250 mL) was added SO_2Cl_2(20 mL, 247.4 mmol) dropwise under nitrogen while keeping the temperature below 45 °C. The color of

suspension changed from dark-red to orange gradually. The stirring was continued for 40 min before cooling. The solid was filtered and washed sequently with water and acetone before it was subjected to be dried under vacuum to afford an orange solid (12.541 g, 90 %). R_f = 0.83 (PE:AcOEt =1/1 (V/V)). M.p. 319-320°C. ^{1}H NMR (300 MHz, DMSO-d_6, ppm) δ: 10.71 (s, 2H), 7.71 (s, 2H), 7.06 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ: 191.82, 153.81, 135.68, 133.76, 126.36, 122.78, 112.25.



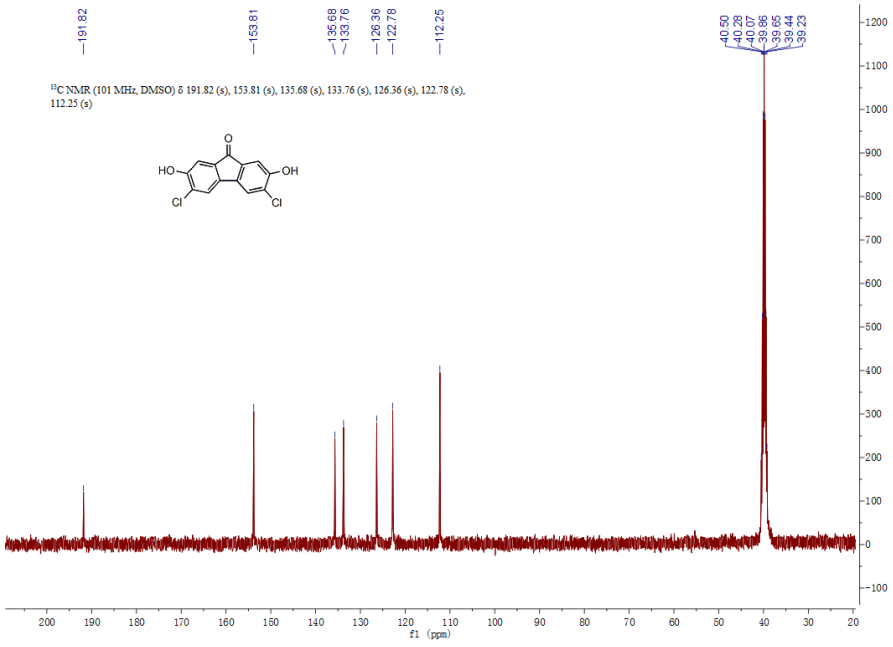
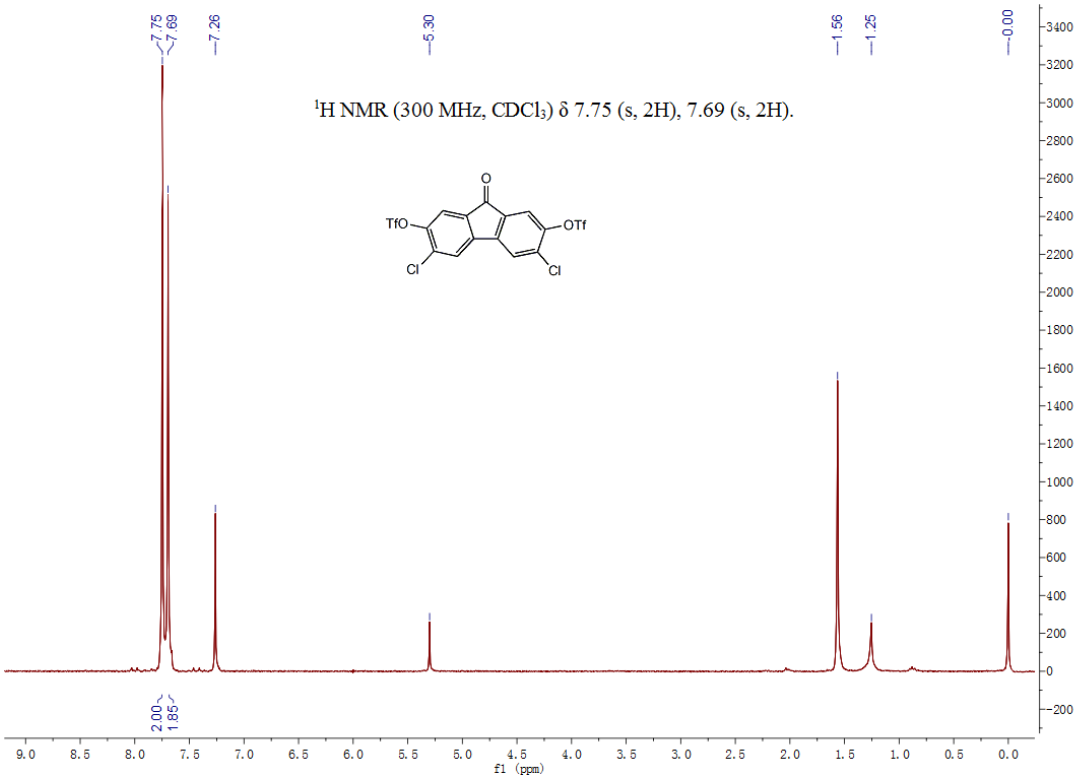


Fig. 4. ^{1}H NMR and ^{13}C NMR of compound 8

3,6-dichloro-2,7-bis(trifluoromethanesulfonyloxy)-9-fluorenone (9)[s4a-b]

To a solution of 3,6-dichloro-2,7-dihydroxy-9-fluorenone(3.829 g, 13.6 mmol) and pyridine (4 mL) in dichloromethane (100 mL) was added Tf_2O (8.0 mL，47.6 mmol) at 0 °C. The sturring was continued overnight at room temperature before it was poured into water, which was then extracted with dichloromethane. The combined organic phase was dried over $MgSO_4$. After filtered, the filtration was evaporated and the residue was recrystallized from the mixture of AcOEt and Petroether (2:1, V/V) to afford a yellow solid(6.878 g, 93 %); R_f = 0.57 (PE:EtOAc = 10:1). M.p. 185-186°C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 7.75 (s, 2H), 7.69 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 187.27, 146.88, 142.01, 134.83, 134.07, 123.91, 119.60, 29.73.



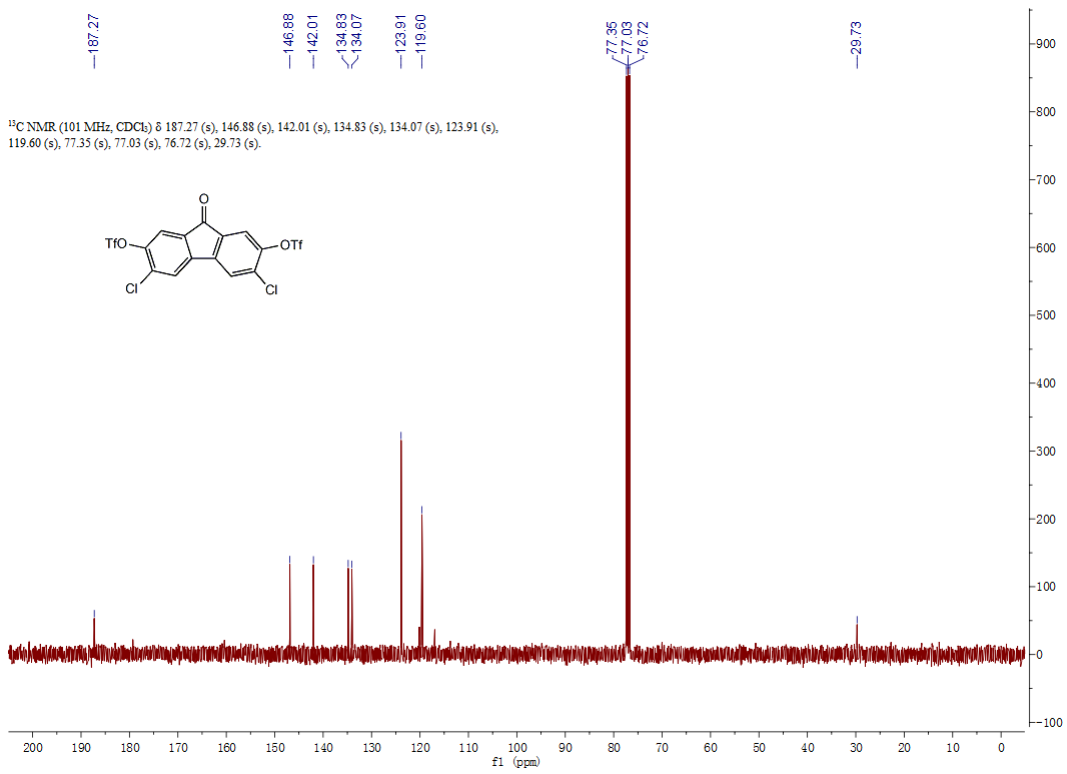


Fig. 5. ^{1}H NMR and ^{13}C NMR of compound 9

General procedure for preparation of 2,7-di(substituted-ethynyl)-3,6-dichloro-9-fluorenones ©by Sonogashira couplingre reaction (10a as example)[4sa-b]

(1)2,7-di(trimethylsilylethynyl)-3,6-dichloro-9-fluorenone (10a)

Under N_2, a mixture of **9**(0.218 g,0.4 mmol), $Pd(PPh_3)_2Cl_2$(0.014 g, 0.02 mmol, 5 mol%), CuI (0.019 g, 0.1 mmol, 10 mol%), *i*-Pr_2NH(1 mL), trimethylsilylacetylene (0.098 g, 1 mmol) in DMF (10 mL) was stirred at room temperature for 9 h before it was poured into diluted HCl (5 %). The mixture was extracted with CH_2Cl_2. The combined organic phase was washed with water for three times before it was dried over $MgSO_4$. The filtration was evaporated and washed with EtOH to afford a yellow solid (0.154 g, 88 %). M.p. 294-296°C; R_f = 0.73 (PE:EtOAc = 20:1); ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 7.77 (s, 2H), 7.53 (s, 2H), 0.28 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 189.93, 143.27, 143.21, 132.83, 129.49, 124.72, 122.19, 103.79, 100.57, 0.00.

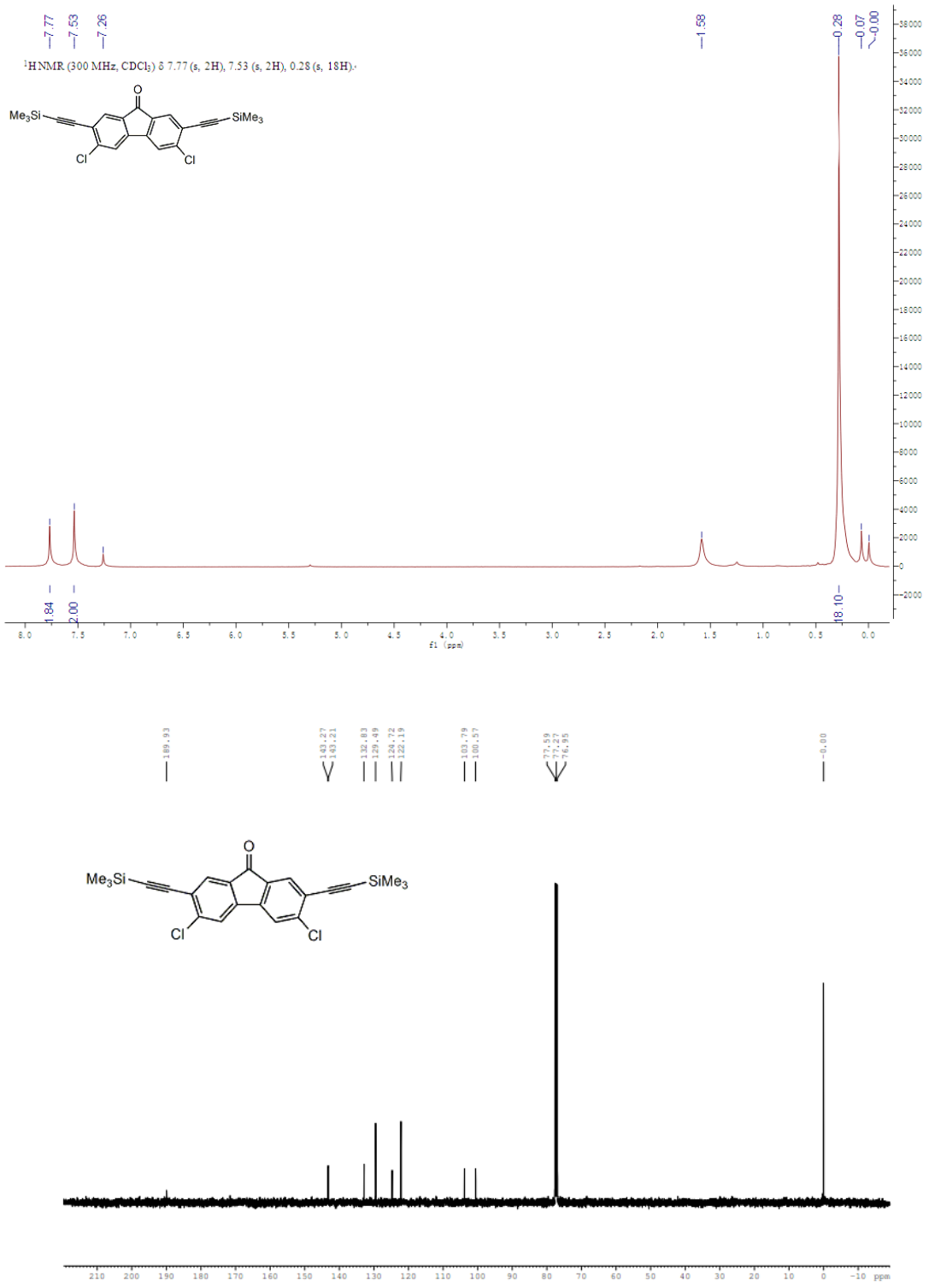
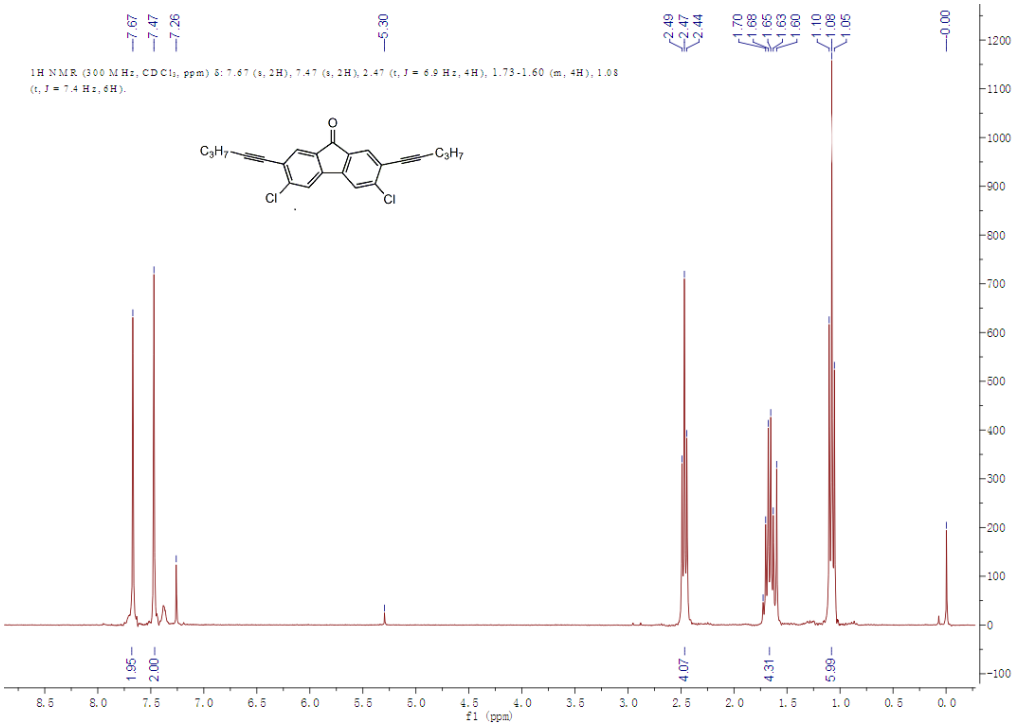


Fig.6. ^{1}H NMR and ^{13}C NMR of compound 10a

(2) 2,7-di(1-pentynyl)-3,6-dichloro-9-fluorenone (10b)

It is obtained the same as 10a by employing 9 (11.400 g, 21 mmol), $Pd(PPh_3)_2Cl_2$ (0.737 g, 1.05 mmol, 5 mol%), CuI(0.400 g, 2.1 mmol, 10 mol%), *i*-Pr_2NH(15 mL),

1-pentyne (5.000 g, 73.5 mmol) in DMF (300 mL) to afford a yellow solid (6.180 g, 88 %). M.p. 217-218°C; R_f = 0.6 (PE:EtOAc = 20:1). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 7.67 (s, 2H), 7.47 (s, 2H), 2.47 (t, J = 6.9 Hz, 4H), 1.73-1.60 (m, 4H), 1.08 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 190.09, 142.43, 142.23, 132.47, 128.76, 125.05, 121.61, 98.92, 77.26, 21.95, 21.68, 13.54.



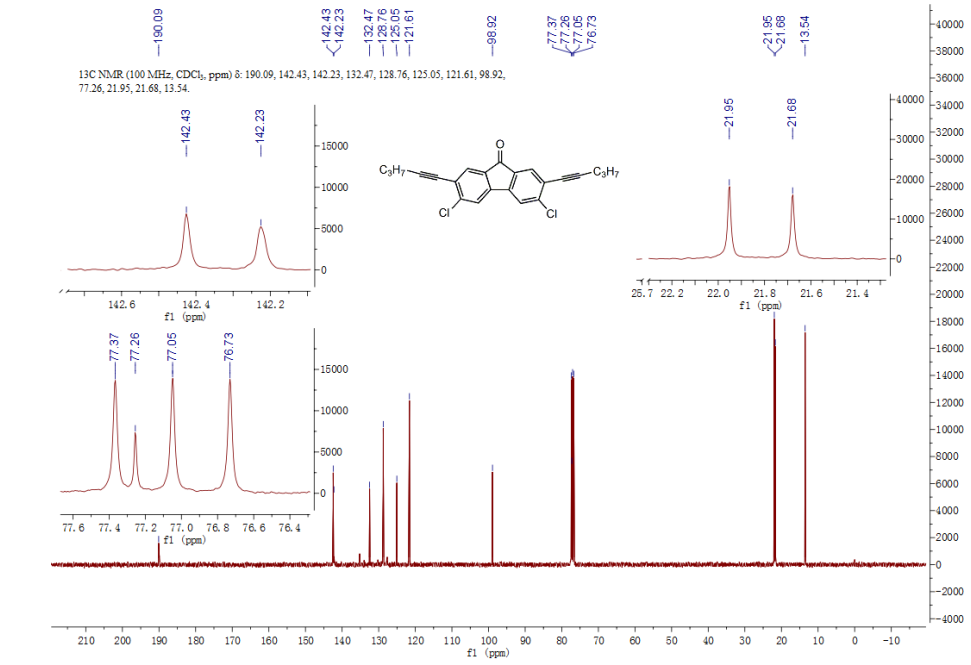
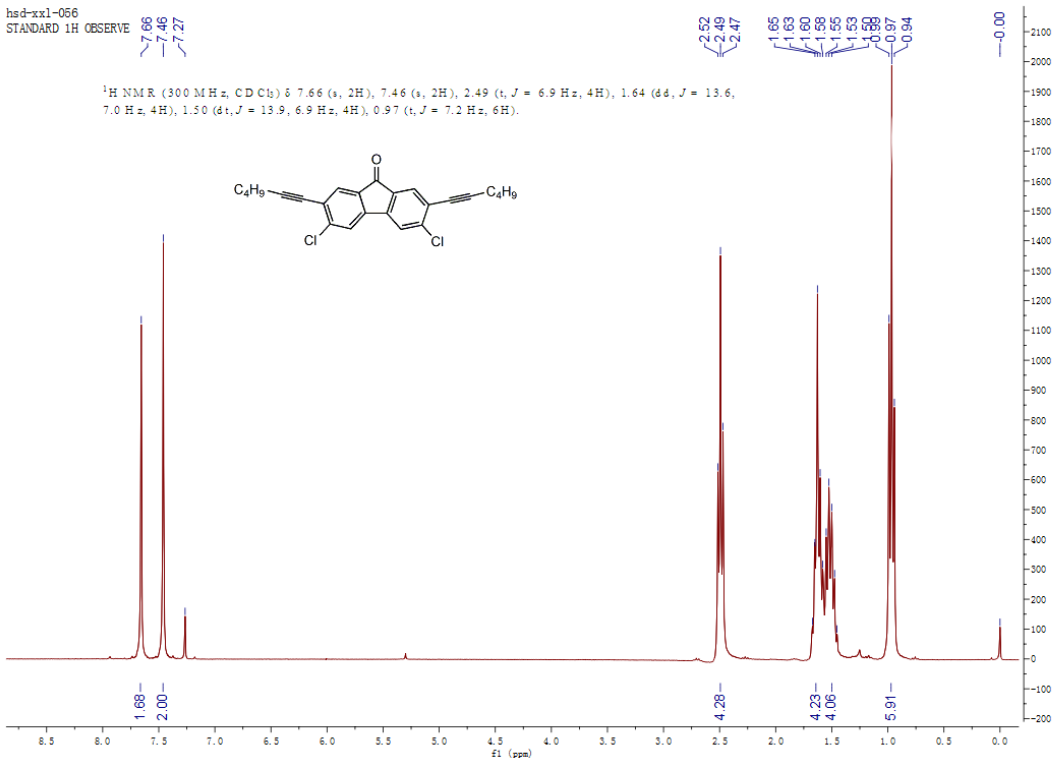


Fig. 7. ^{1}H NMR and ^{13}C NMR of compound 10b

(3) 2,7-di(1-hexynyl)- 3,6-dichloro-9-fluorenone (10c)

It is obtained the same as 10a by employing **9** (5.45 g,10 mmol)，$Pd(PPh_3)_2Cl_2$(0.351 g, 0.5 mmol, 5 mol%), CuI(0.191 g, 1 mmol, 10 mol%), *i*-Pr_2NH(8 mL), 1-hexyne(2.000 g, 25 mmol) in DMF (140 mL) to afford a yellow solid(3.250 g, 79 %). M.p. 212-214°C; R_f = 0.57 (PE:EtOAc = 20:1). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 7.66 (s, 2H), 7.46 (s, 2H), 2.49 (t, J = 6.9 Hz, 4H), 1.64 (dd, J = 13.6, 7.0 Hz, 4H), 1.50 (dt, J = 13.9, 6.9 Hz, 4H), 0.97 (t, J = 7.2 Hz, 6H).^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 190.31, 142.56, 142.39, 132.64, 128.94, 125.21, 121.76, 99.21, 77.23, 30.62, 22.09, 19.53, 13.75.



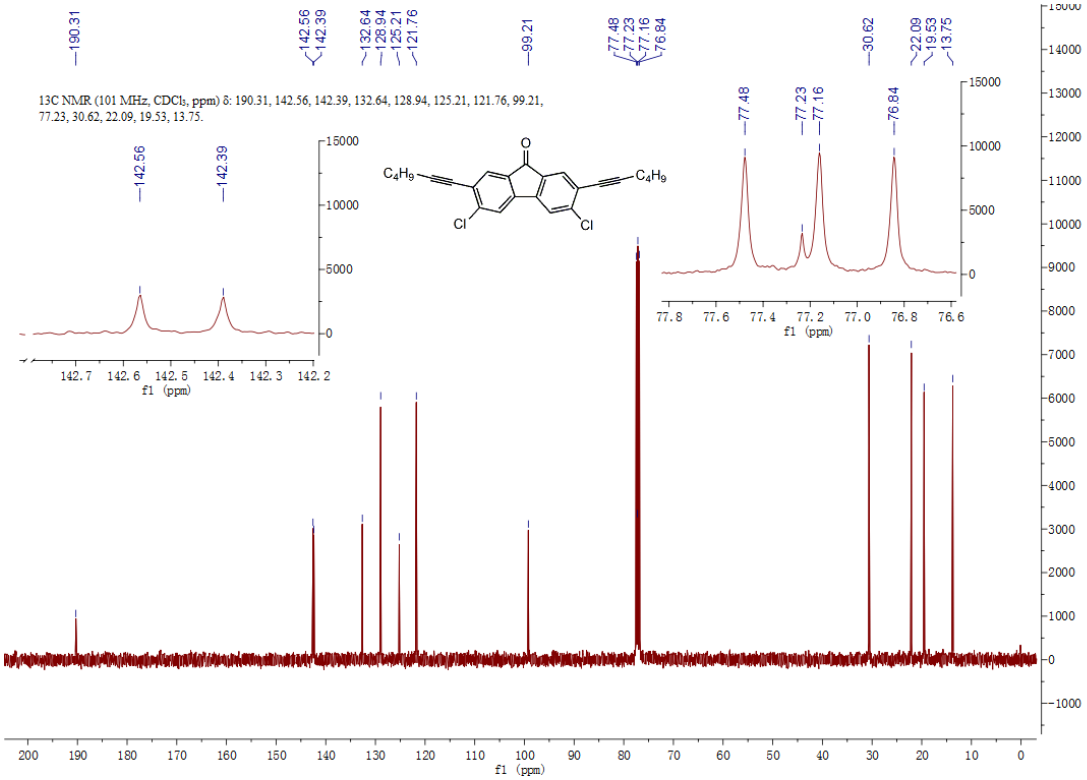


Fig. 8. ^{1}H NMR and ^{13}C NMR of compound 10c

(4) 2,7-di(3,3-dimethyl-1-butynyl)-3,6-dichloro-9-fluorenone (10d)

It is essentially obtained the same as 10a by employing 9(10.780 g,19.8 mmol), $Pd(PPh_3)_2Cl_2$ (0.702 g, 1 mmol, 5 mol%),CuI(0.387 g, 2 mmol, 10 mol%),i-Pr_2NH(15 mL) and 3,3-dimethyl-1-butyne (5.000 g, 60.97 mmol) in DMF (180 mL) to afford a yellow solid(6.54 g, 81 %). M.p. 294-295°C; R_f = 0.74 (PE:EtOAc = 20:1). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 7.67 (s, 2H), 7.48 (s, 2H), 1.35 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 190.29, 142.54, 142.30, 132.51, 128.71, 125.06, 121.64, 106.98, 75.73, 30.74, 28.42.

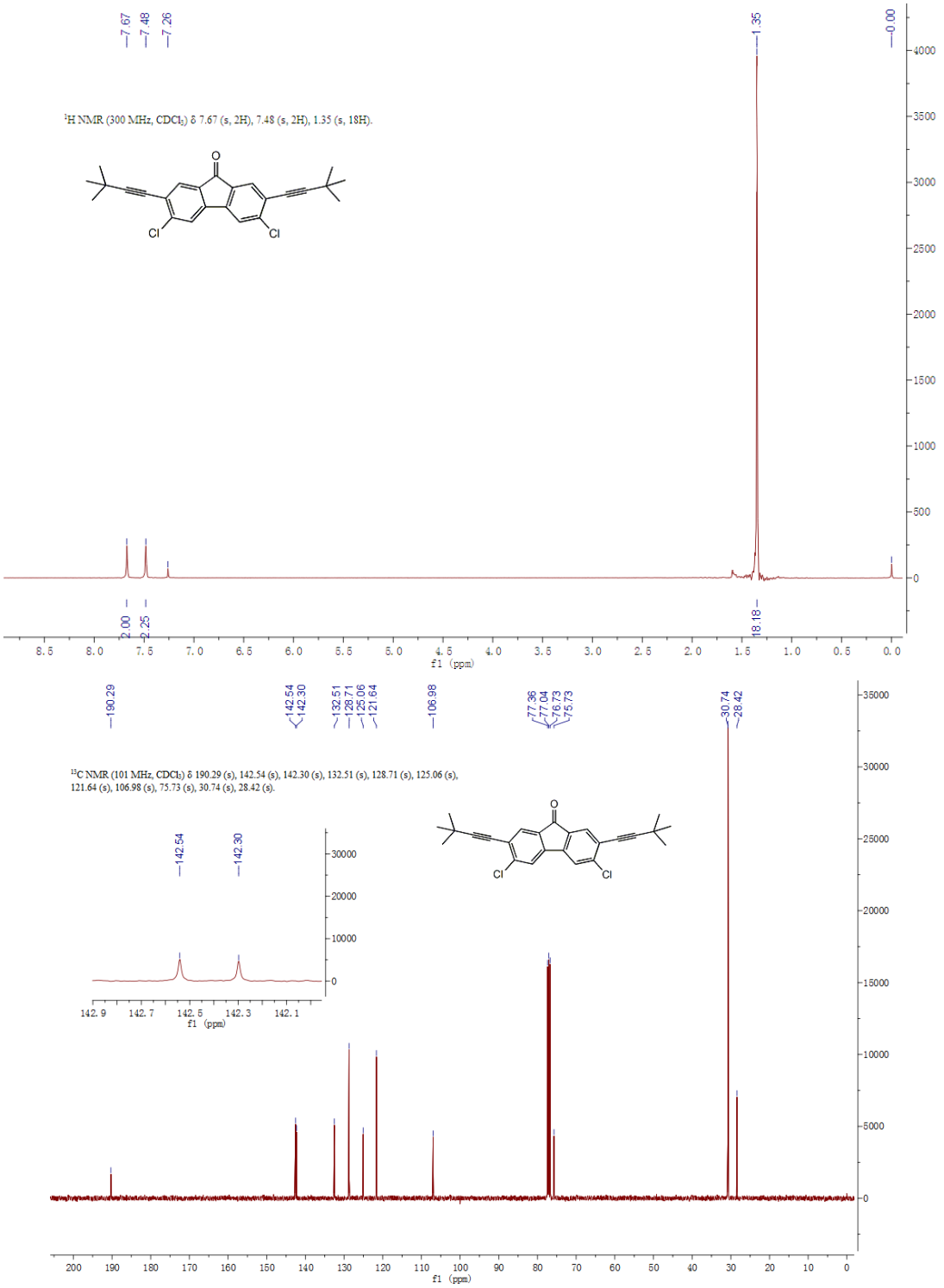
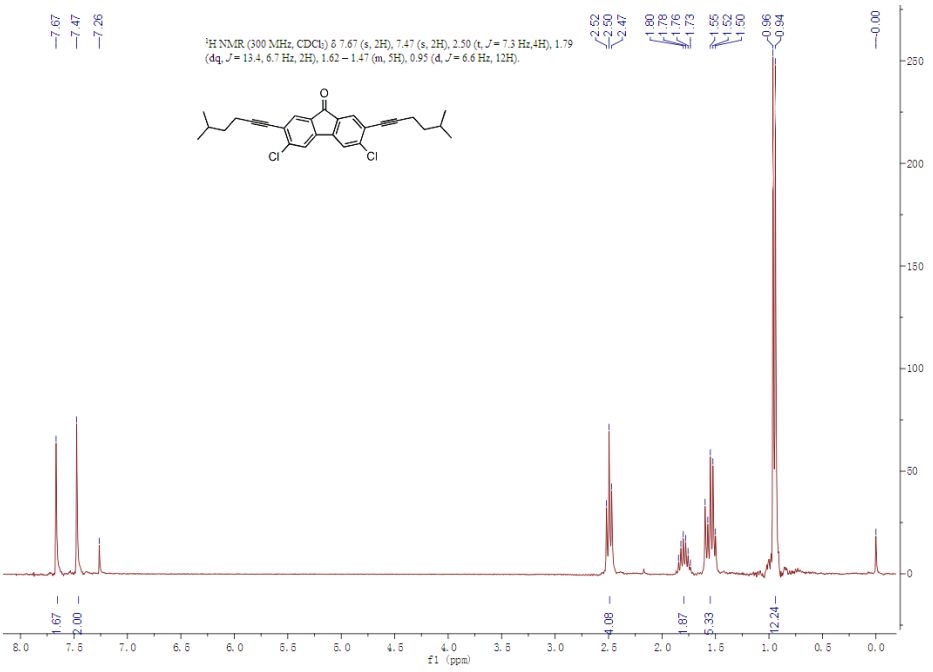


Fig. 9. ^{1}H NMR and ^{13}C NMR of compound 10d

(5) 2,7-di(5-methyl-1-hexynyl)-3,6-dichloro-9-fluorenone (10e)

It is obtained the same as 10a by employing 9 (0.545 g, 1 mmol)，$Pd(PPh_3)_2Cl_2$ (0.035 g, 0.05 mmol, 5 mol%), CuI(0.019 g, 0.1 mmol, 10 mol%), i-Pr_2NH(1 mL) and

5-methyl- 1-hexyne (0.264 g, 2.4 mmol) in DMF (20 mL) to afford a yellow solid (0.305 g, 72 %). M.p. 192-195°C; R_f = 0.33 (PE:EtOAc = 20:1). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 7.67 (s, 2H), 7.47 (s, 2H), 2.50 (t, J = 7.3 Hz, 4H), 1.79 (dq, J = 13.4, 6.7 Hz, 2H), 1.62 – 1.47 (m, 4H), 0.95 (d, J = 6.6 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 193.02, 148.37, 145.54, 140.14, 139.08, 132.90, 121.59, 119.00, 113.58, 39.95, 28.74, 27.57, 22.40.



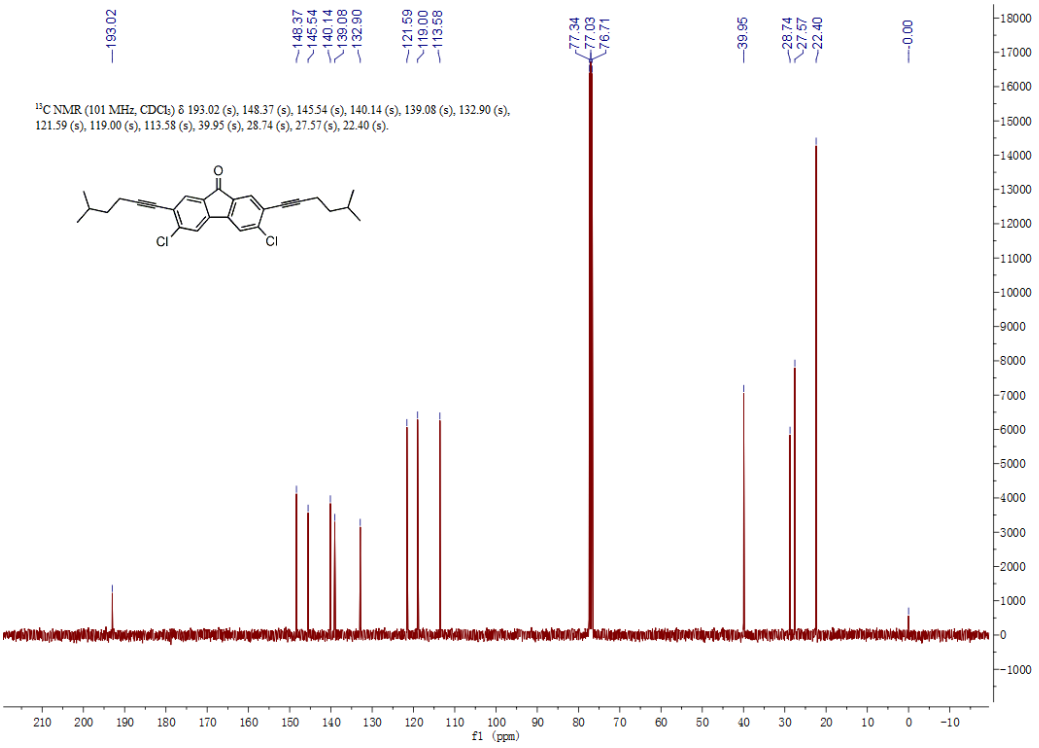


Fig. 10. ^{1}H NMR and ^{13}C NMR of compound 10e

(6) 2,7-di(1-heptynyl）-3,6-dichloro-9-fluorenone (10f)

It is essentially obtained the same as 10a by employing 9(3.720 g, 6 mmol), $Pd(PPh_3)_2Cl_2$ (0.211 g, 0.3 mmol, 5 mol%), CuI(0.114 g, 0.06 mmol, 10 mol%), i-Pr_2NH(6 mL), 1-heptyne (1.382 g, 14.4 mmol) in DMF(100 mL)to form a yellow solid (1.953 g, 78 %). M.p. 184- 188°C ; R_f = 0.71 (PE:EtOAc = 20:1). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 7.66 (s, 2H), 7.46 (s, 2H), 2.48 (t, *J* = 6.9 Hz, 4H), 1.64 (dt, *J* = 13.9, 6.7 Hz, 4H), 1.53 – 1.30 (m, 8H), 0.91 (t, J = 6.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 190.29, 142.49, 142.32, 132.56, 128.87, 125.11, 121.68, 99.17, 77.12, 31.02, 28.12, 22.20, 19.67, 14.02.

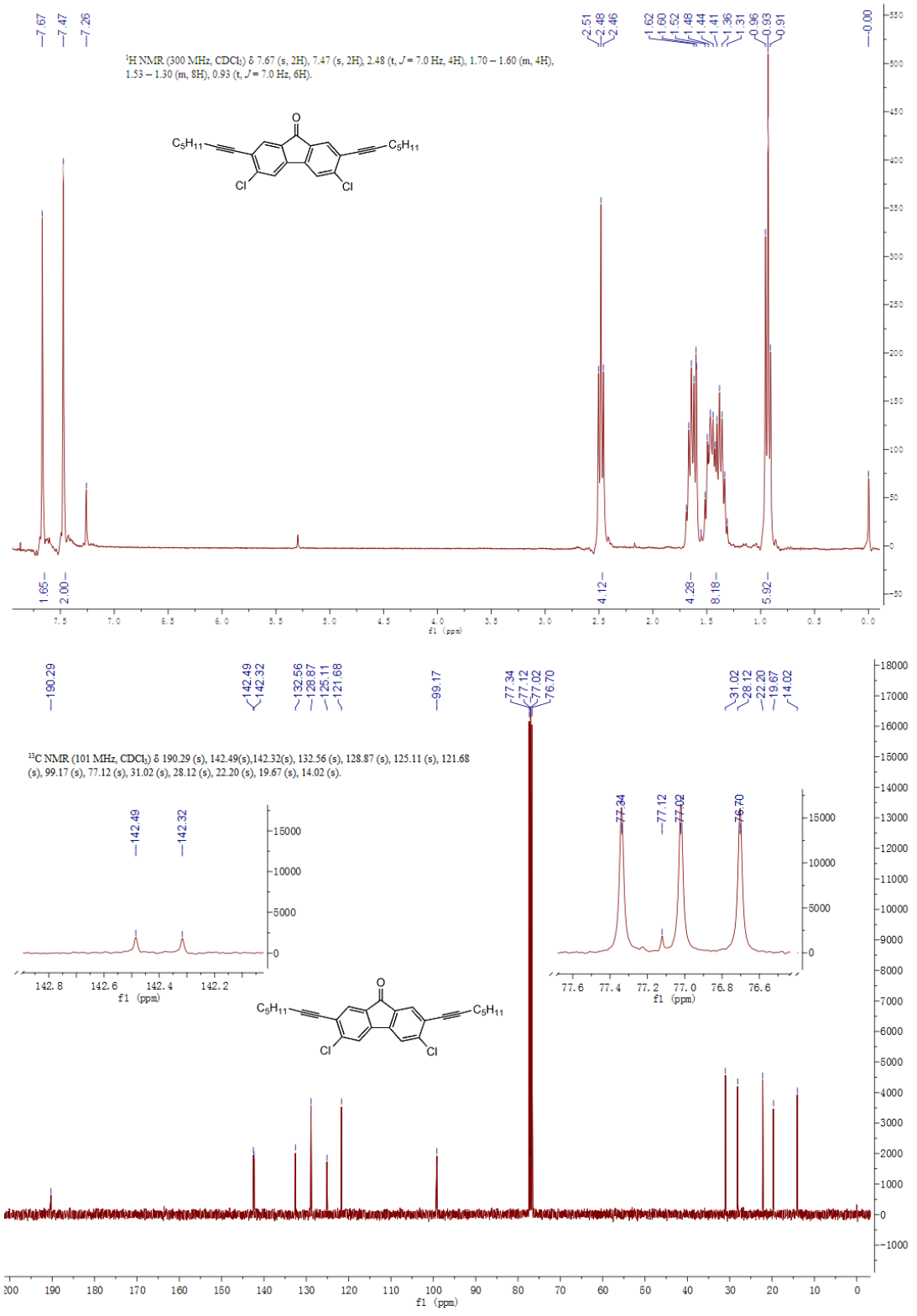
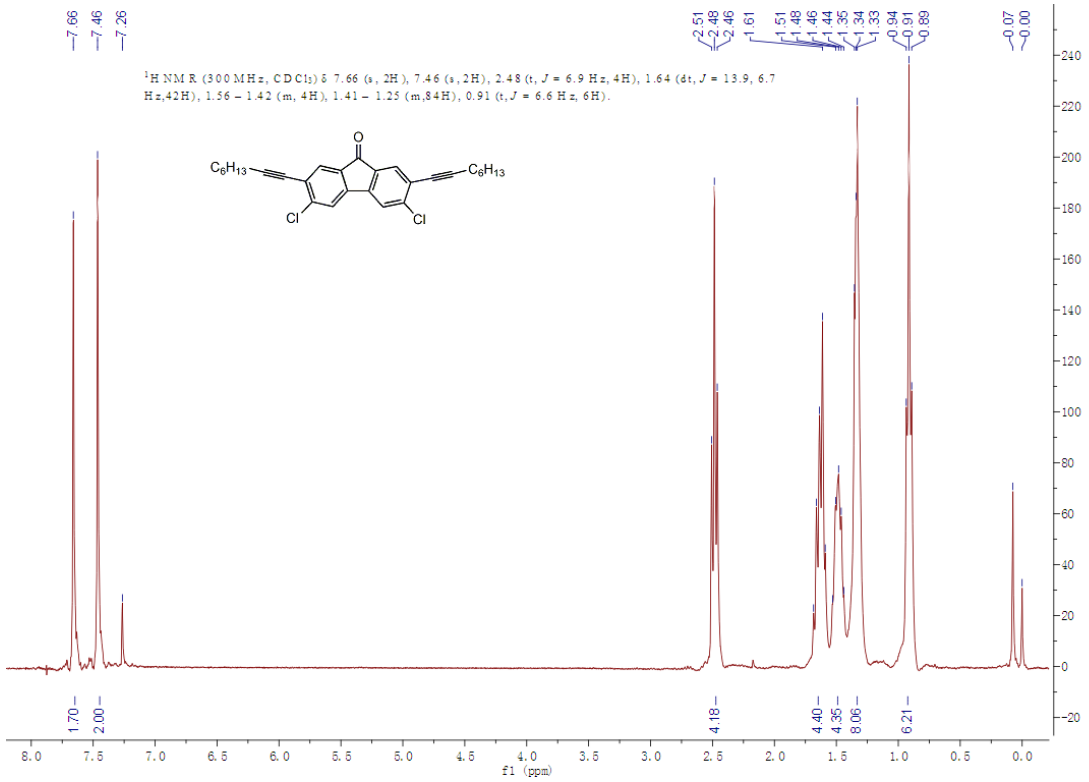


Fig. 11. ^{1}H NMR and ^{13}C NMR of compound 10f

(7) 2,7-di(1-octynyl)-3,6-dichloro-9-fluorenone (10g)

It is essentially obtained the same as 10a by employing 9(0.621 g,1.1 mmol),

$Pd(PPh_3)_2Cl_2$ (0.035 g, 0.05 mmol, 5 mol%), CuI(0.019 g, 0.1 mmol, 10 mol%), i-Pr_2NH(1 mL) and 1-octyne (0.264 g, 2.4 mmol) in DMF (20 mL) to lead to a yellow solid (0.352 g, 74 %). M.p. 167-168°C; R_f = 0.58 (PE:EtOAc = 20:1). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 7.66 (s, 2H), 7.46 (s, 2H), 2.48 (t, J = 6.9 Hz, 4H), 1.64 (dt, J = 13.9, 6.7 Hz, 4H), 1.56-1.42(m, 4H), 1.41 – 1.25 (m, 8H), 0.91 (t, J = 6.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 189.21, 141.44, 141.25, 131.50, 127.80, 124.06, 120.63, 98.13, 76.09, 30.30, 27.52, 27.38, 21.55, 18.69, 13.07.



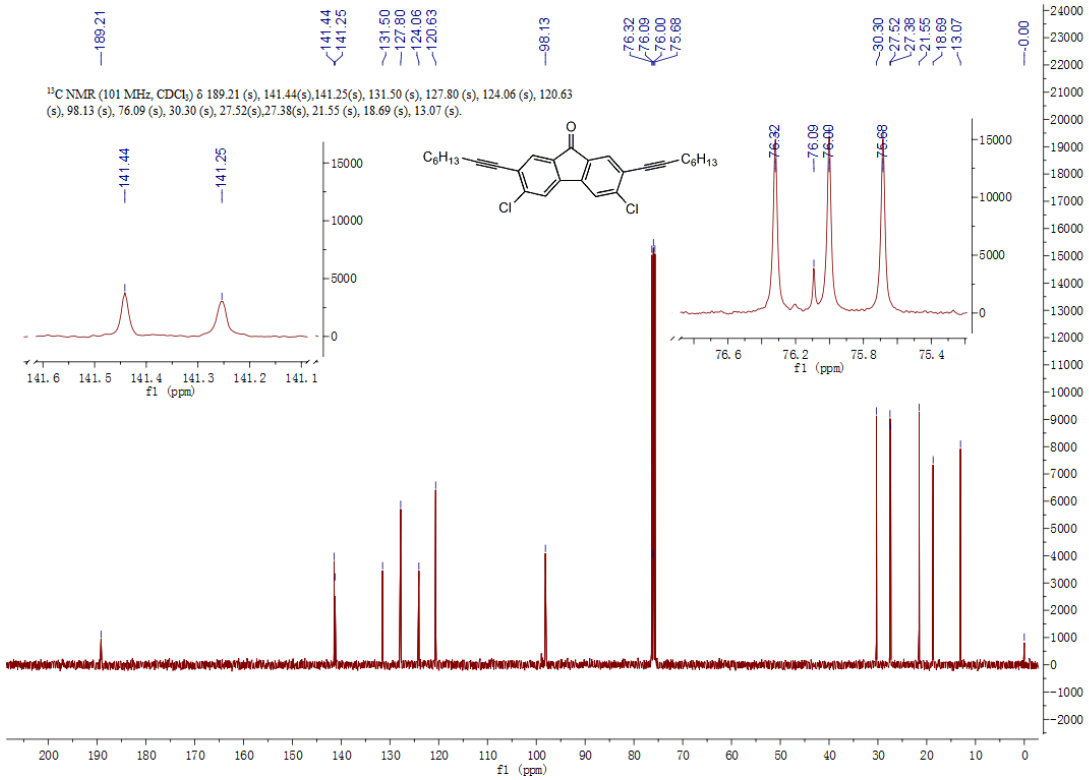


Fig. 12. ^{1}H NMR and ^{13}C NMR of compound 10g

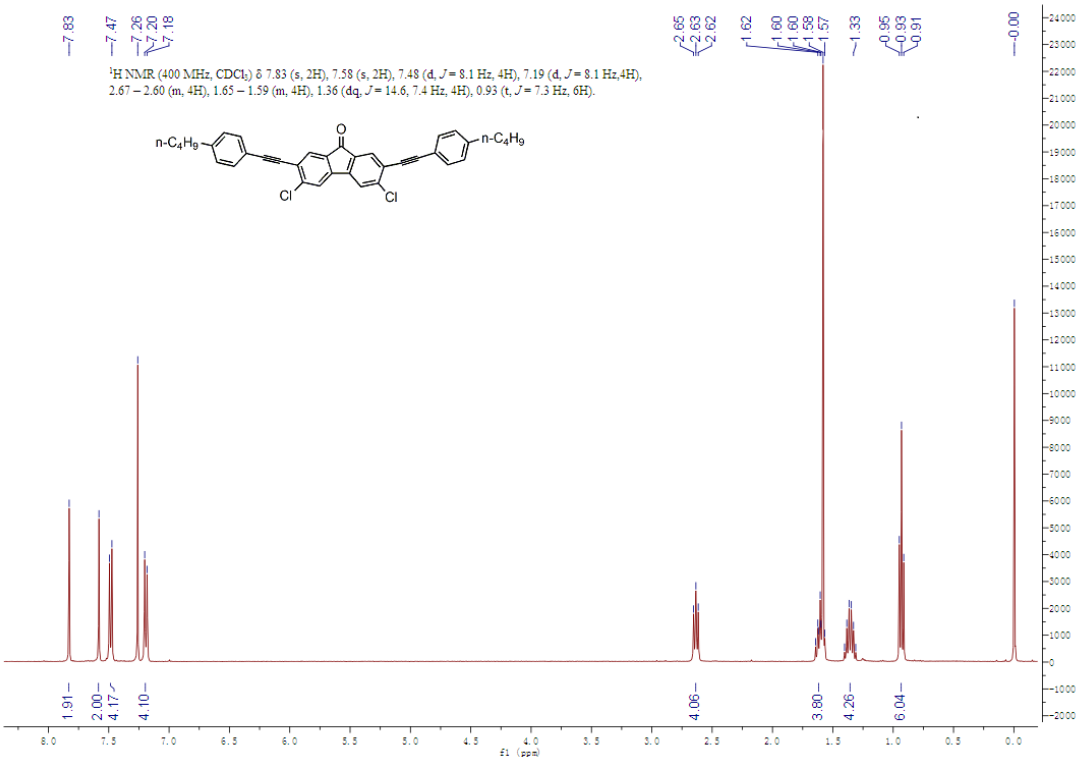
(8) 2,7-di(phenylethynyl)-3,6-dichloro-9-fluorenone (10h)

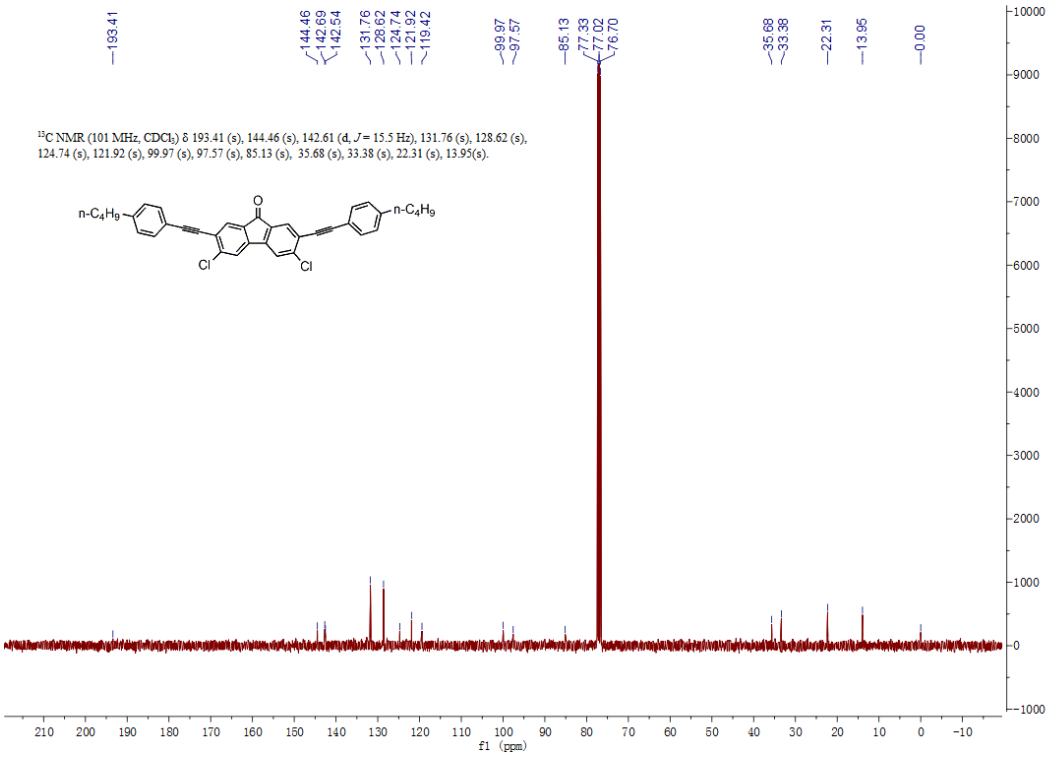
It is essentially obtained the same as 10a by employing 9 (1.09 g, 2.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.070 g, 0.1 mmol, 5 mol%), CuI(0.038 g, 0.2 mmol, 10 mol%), i-Pr_2NH(5 mL) and phenyl- acetylene (0.51 g, 5.0 mmol) in DMF (50 mL) to form a red solid(0.352 g, 74%). M.p. 327-330°C. This solid is insoluble in common solvents which prevents its further characterization.

(9) 2,7-di(4-butylphenylethynyl)-3,6-dichloro-9-fluorenone (10i)

It is essentially obtained the same as 10a by employing 9(4.360 g, 8.0 mmol), $Pd(PPh_3)_2Cl_2$(0.280 g，0.4 mmol, 5 mol%), CuI (0.152 g, 0.8 mmol, 10 mol%), i-Pr_2NH (8 mL) and 4-butylphenylacetylene (3.16 g, 20 mmol) in DMF (150 mL) to afford a yellow solid (3.72 g, 82%). M.p. 277-284°C; R_f = 0.45 (PE:EtOAc = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.83 (s, 2H), 7.58 (s, 2H), 7.498(d, J = 8.1 Hz, 4H), 7.19 (d, J = 8.1 Hz, 4H),

2.67 – 2.60 (m, 4H), 1.65 – 1.59 (m, 4H), 1.36 (dq, J = 14.6, 7.4 Hz, 4H), 0.93 (t, J = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 193.41, 144.46, 142.61, 131.76, 128.65, 124.74, 121.92, 99.97, 97.57, 85.13, 35.68, 33.38, 22.31, 13.95. MS: m/z = 560 (M^+)





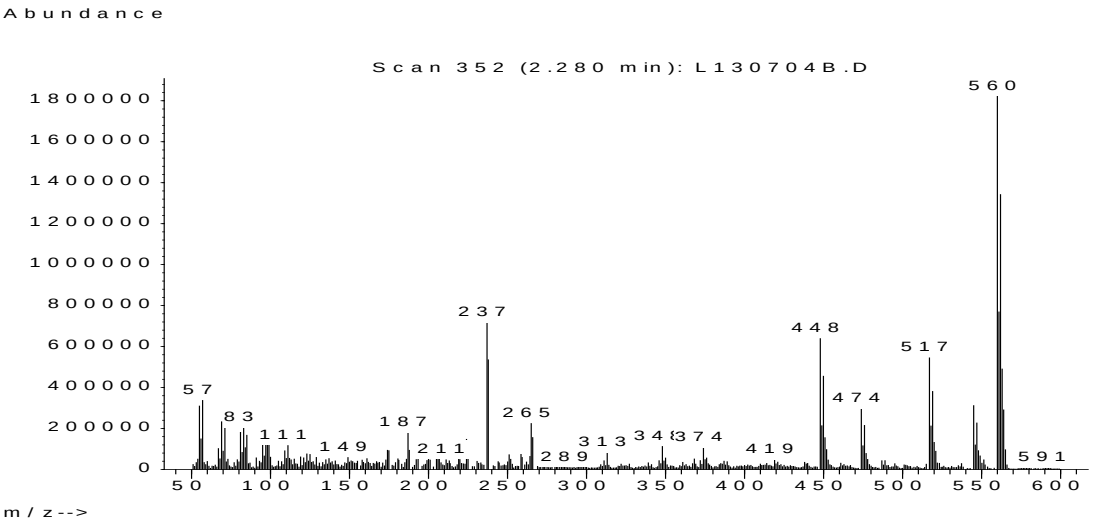


Fig. 13. ^{1}H NMR , ^{13}C NMR and MS of compound 10i

(10) 2,7-di(4-tert-butylphenylethynyl)-3,6-dichloro-9-fluorenone (10j)

It is essentially obtained the same as 10a by employing 9 (2.000 g, 3.67 mmol), $Pd(PPh_3)_2Cl_2$ (0.129 g, 0.18 mmol, 5 mol%), CuI(0.070 g, 0.36 mmol, 10 mol%), i-Pr_2NH (3 mL) and 4-tert-butylpenylacetylene(1.45 g, 9.18 mmol) in DMF (100 mL) to form a yellow solid(1.683 g, 82 %); M.p. 360-361°C; R_f = 0.45 (PE:EtOAc = 20:1). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 7.85 (s, 2H), 7.60 (s, 2H), 7.52 (d, J = 7.8 Hz, 4H), 7.41 (d, J = 8.2 Hz, 4H), 1.34 (s, 18H). Good carbon NMR could not be obtained due to its low solubility. MS: m/z =560 (M^+).

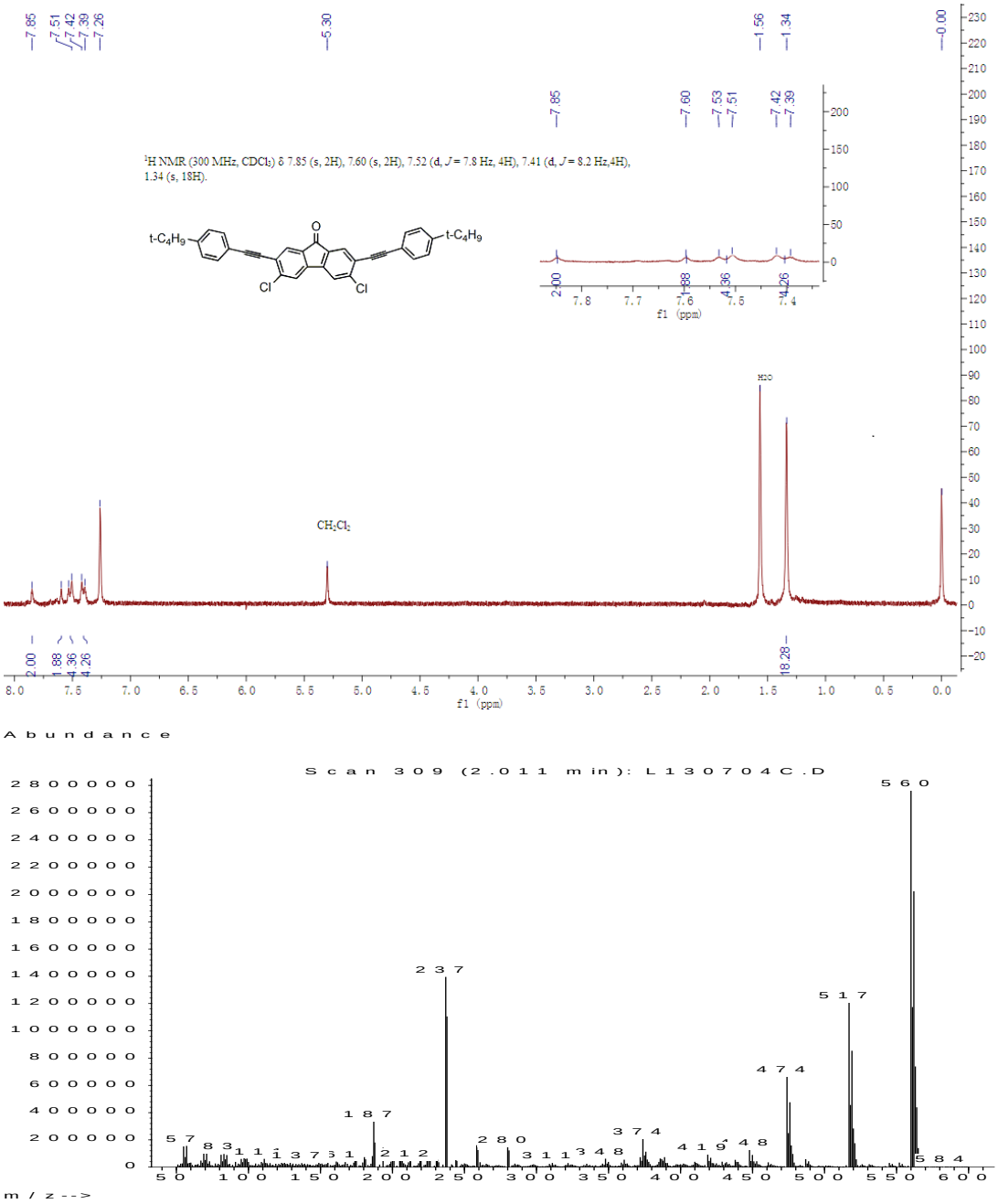


Fig.14. ^{1}H NMR and MS of compound 10j

(11) 2,7-di(4-hexyloxyphenylethynyl)-3,6-dichloro-9-fluorenone (10k)

It is essentially obtained the same as 1c by employing 9 (1.090 g, 2 mmol), $Pd(PPh_3)_2Cl_2$ (0.070 g, 0.1 mmol, 5 mol%), CuI (0.038 g, 0.2 mmol, 10 mol%), i-Pr_2NH (3 mL) and 4-hexyloxyl phenyleacetylene (1.212 g, 6 mmol) in DMF (20 mL) to form an organe-red (1.022 g, 79 %); M.p. 268-270°C; R_f = 0.15 (PE:DCM = 2:1). ^{1}H NMR (300

MHz, $CDCl_3$, ppm) δ: 7.82 (s, 2H), 7.57 (s, 2H), 7.50 (d, J = 8.7 Hz, 4H), 6.89 (d, J = 8.8 Hz, 4H), 3.98 (t, J = 6.6 Hz, 4H), 1.84-1.74 (m, 4H), 1.51 – 1.42 (m, 4H), 1.34 (d, J=7.2, 3.4Hz, 8H), 0.90 (dd,J=120, 4.9Hz, 6H). High qualified carbon NMR could not be obtained due to its low solubility. MS: m/z = 648 (M^+)

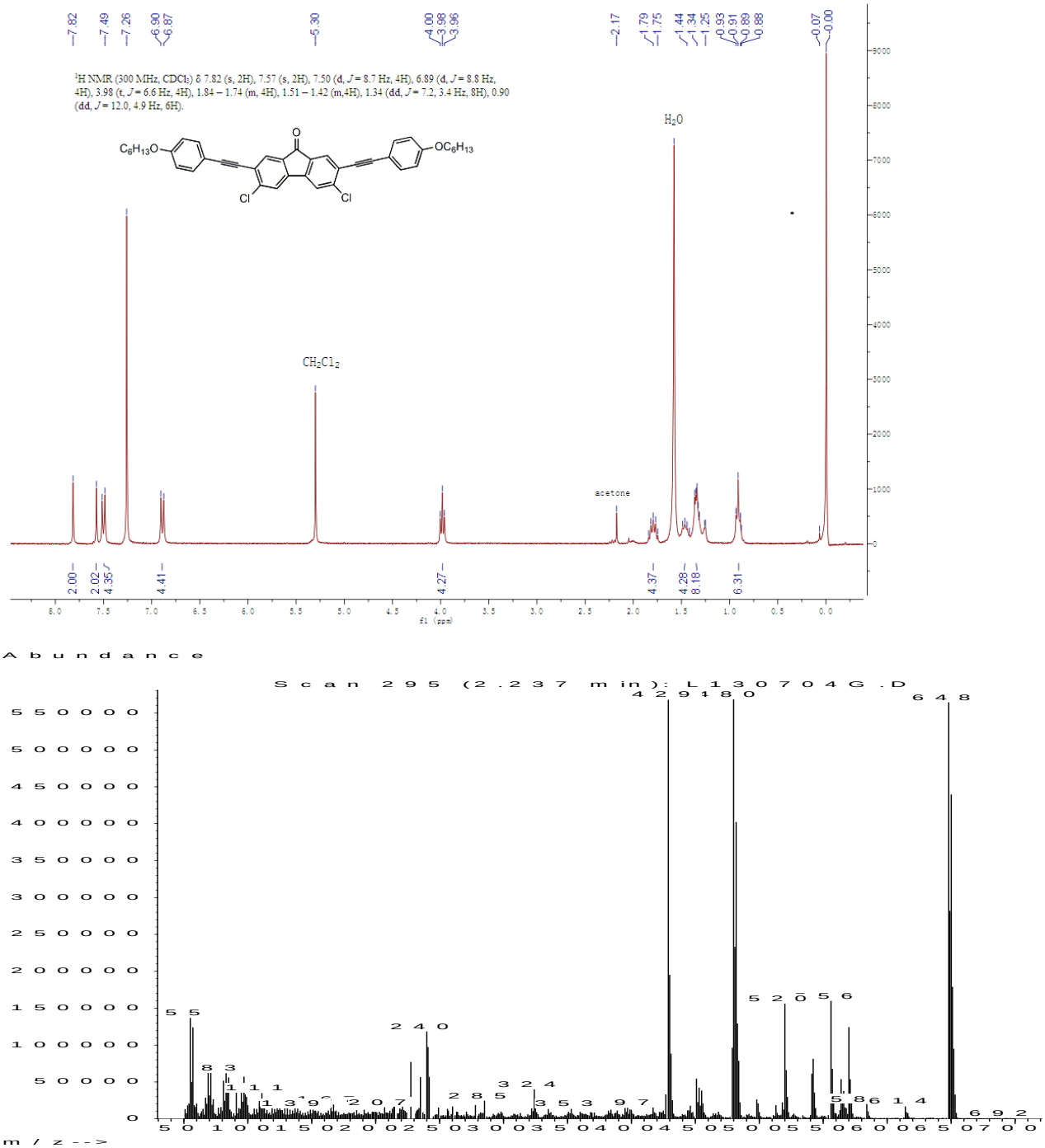
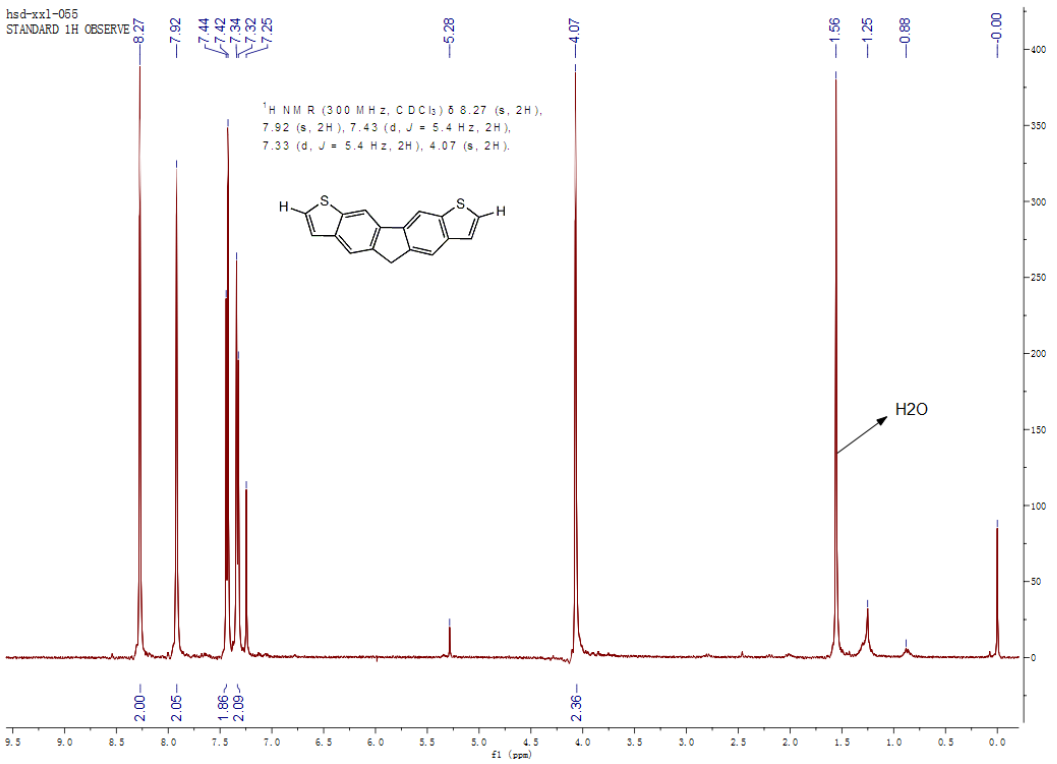


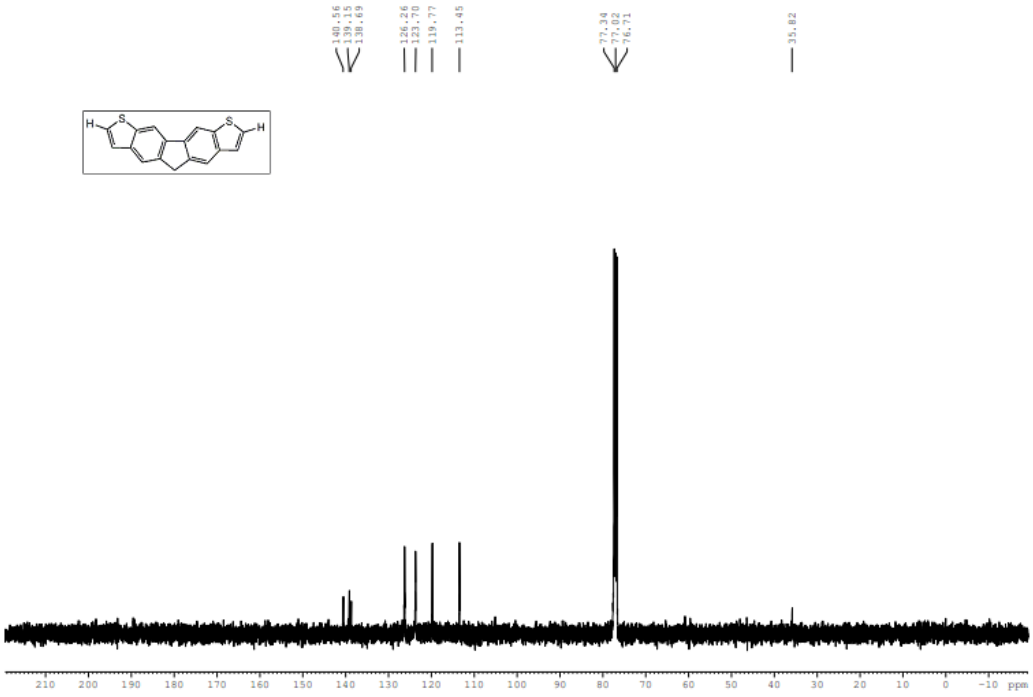
Fig.15. ^{1}H NMR and MS of compound 10k

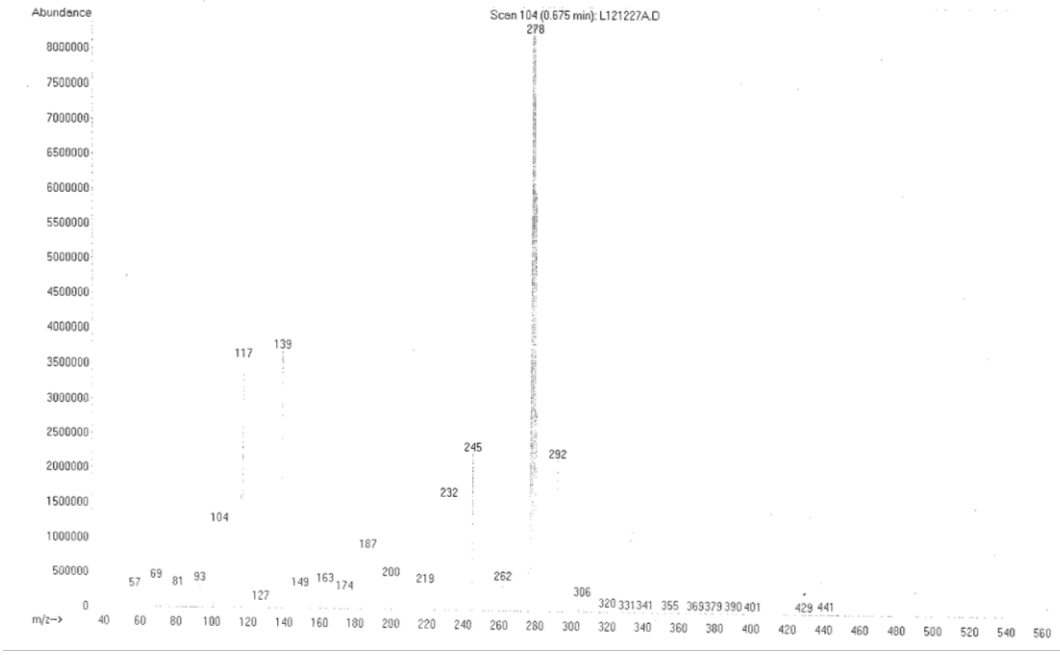
General procedure for the preparation of 2,8-disubstituted-dithieno[3,2-b：6,7-b']fluorenes (11) (11a as example) [4sa-b]

(1) dithieno[3, 2-b: 6, 7-b']fluorene (11a)

A suspension of $Na_2S.9H_2O$ (6.530 g, 27 mmol) in N-methylpyrrolinone (NMP)(50 mL) was stirred for 15 min under N_2 before the addition of 2,7-di(trimethylsilylethynyl)-3,6-dichloro-9-fluorenone (10a)(2.000 g, 4.5 mmol) as solid. The mixture was refluxed for 12 h before it was poured into a saturated NH_4Cl solution. It was extracted by DCM. The combined organic phase was washed by water for three times and then dried over MgSO4. After filtered and the filtration was dried and subjected to column separation (PE) to afford a white solid (0.315 g, 25 %); M.p. 214-215°C; R_f = 0.22 (PE). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 8.27 (s, 2H), 7.92 (s, 2H), 7.43 (d, J = 5.4 Hz, 2H), 7.33 (d, J = 5.4 Hz, 2H), 4.07 (s, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ:140.56, 139.15, 138.69, 126.26, 123.70, 119.77, 113.45, 35.82.; MS: m/z = 278 (M^+); HRMS for $C_{17}H_{10}S_2$: required: 278.0224; Found:278.0223.







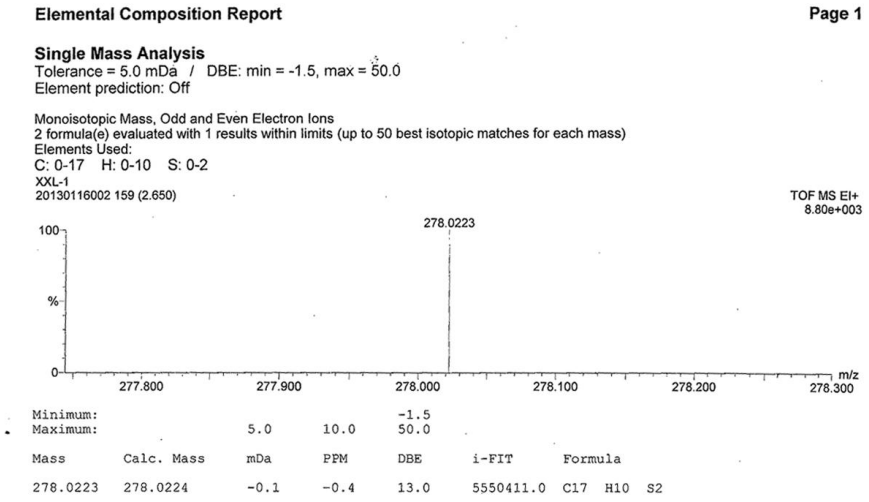
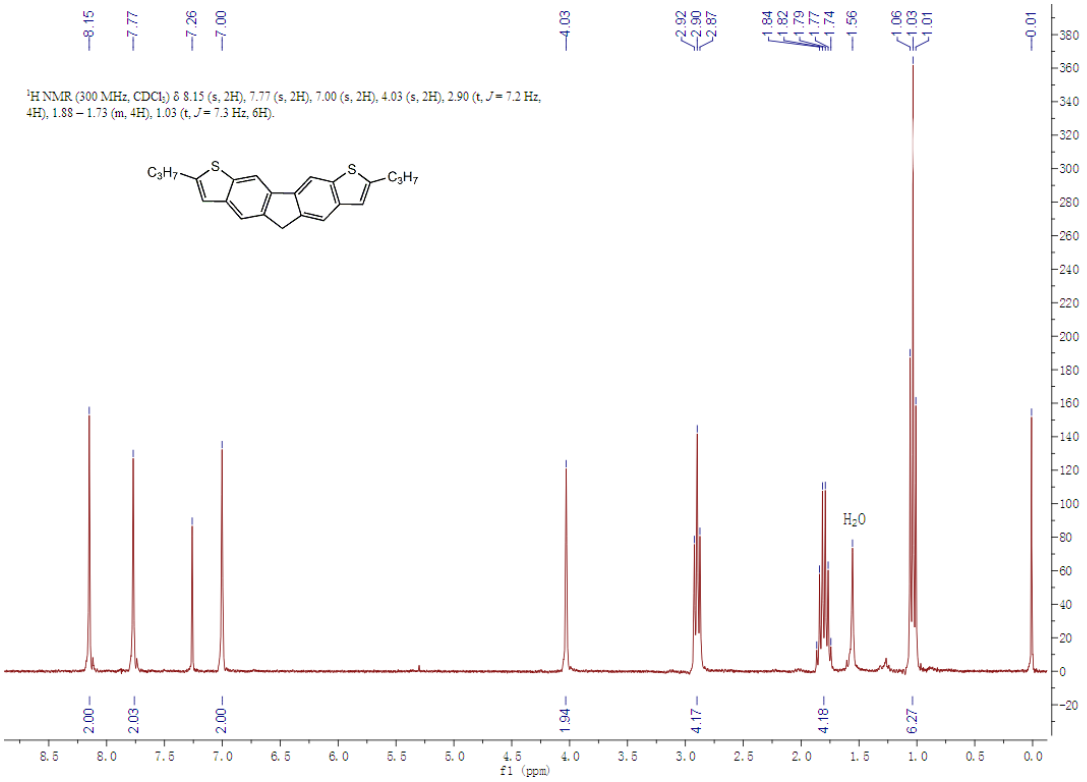


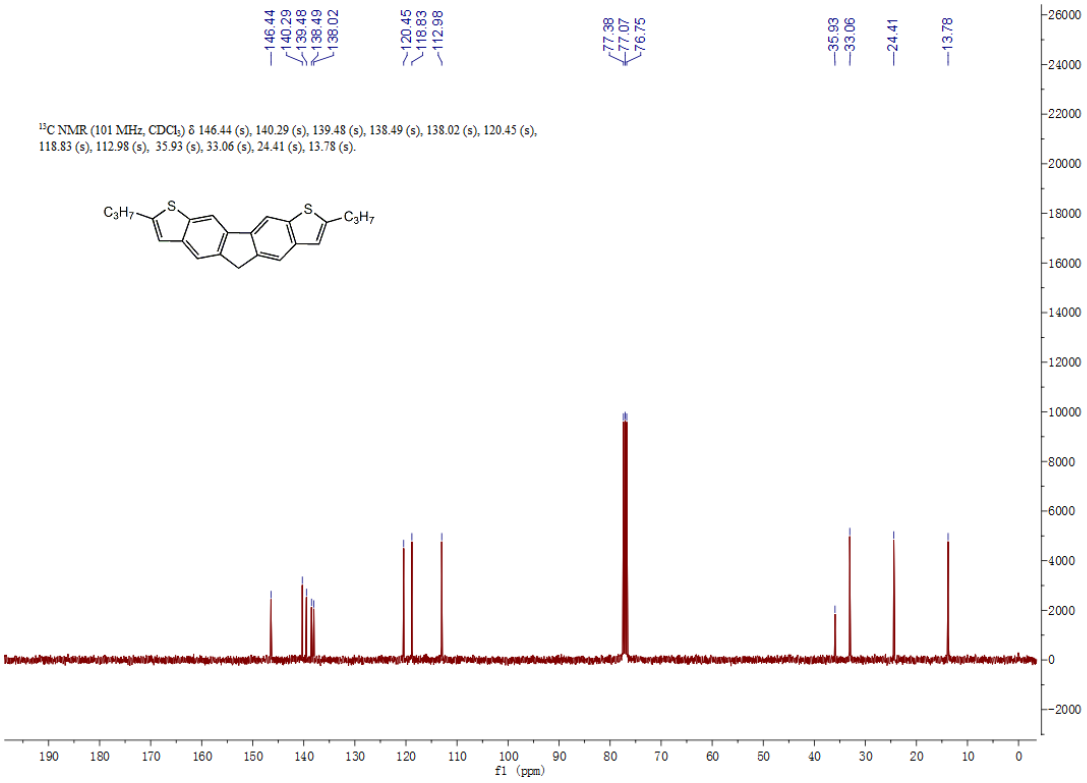
Fig. 16. ^{1}H NMR , ^{13}C NMR, MS and HRMS of compound 11a

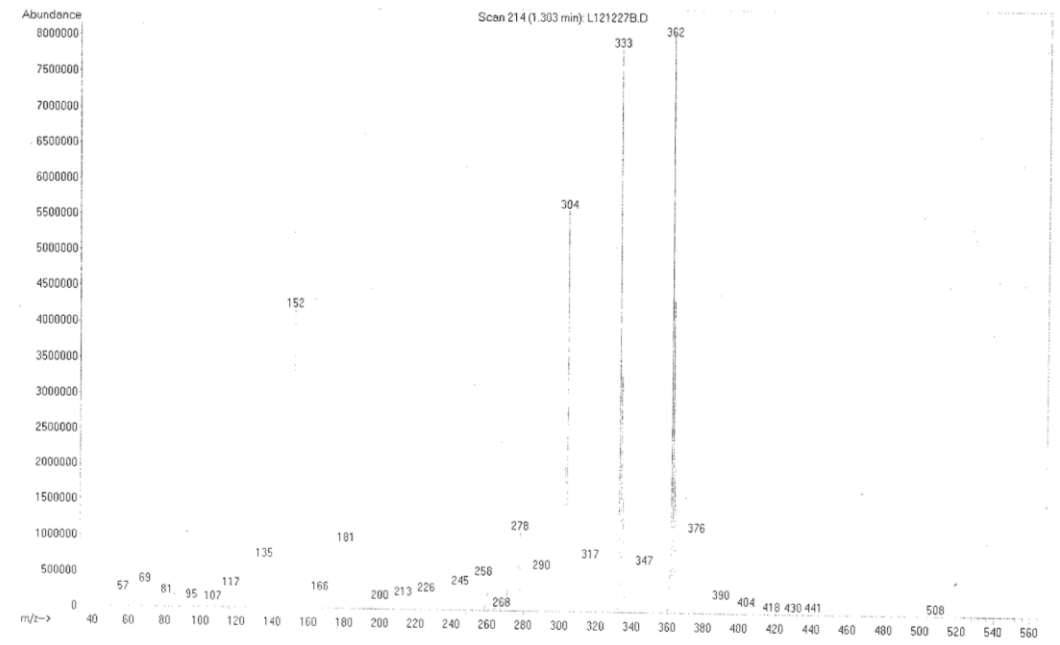
(2) 2,8-di-*n*-propyl-dithieno[3, 2-b: 6, 7-b']fluorene (11b)

This is prepared essentially the same as **11a** by employing $Na_2S.9H_2O$ (4.320 g, 18 mmol), NMP(30 mL) and **10b** (1.143 g, 3 mmol) to form a white solid(0.429 g, 40 %). M.p. 158-159°C; R_f = 0.24 (PE). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 8.15 (s, 2H), 7.77 (s, 2H), 7.00 (s, 2H), 4.03 (s, 2H), 2.90 (t, J = 7.2 Hz, 4H), 1.88 -1.73 (m, 4H), 1.03 (t, J = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 146.44, 140.29, 139.48, 138.49, 138.02, 120.45, 118.83, 112.98, 35.93, 33.06, 24.41, 13.78.; MS: m/z = 362(M^+); HRMS for $C_{23}H_{22}S_2$

required: 362.1163; Found: 362.1162.







Elemental Composition Report **Page 1**

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Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
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XXL-2
20130116003 327 (5.451)

TOF MS EI+
1.99e+002

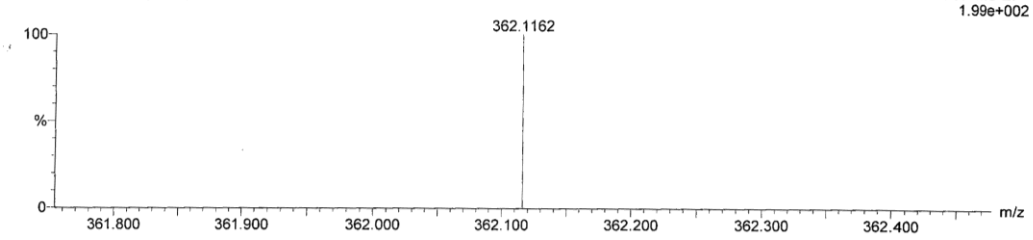

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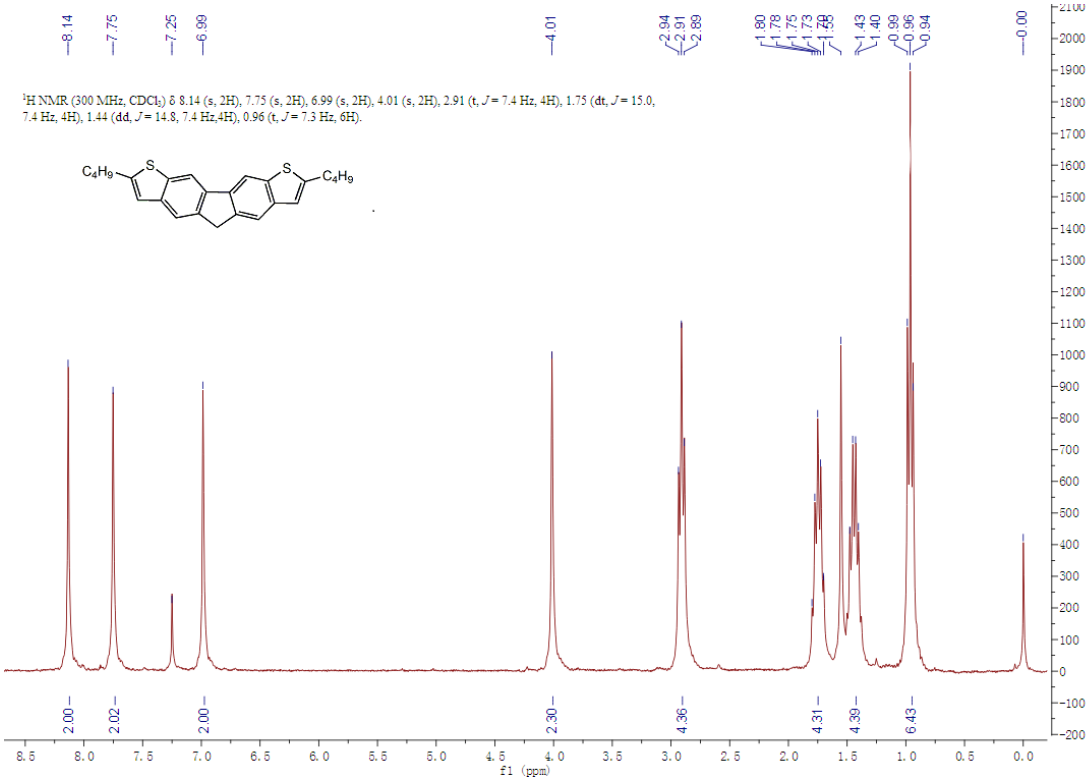
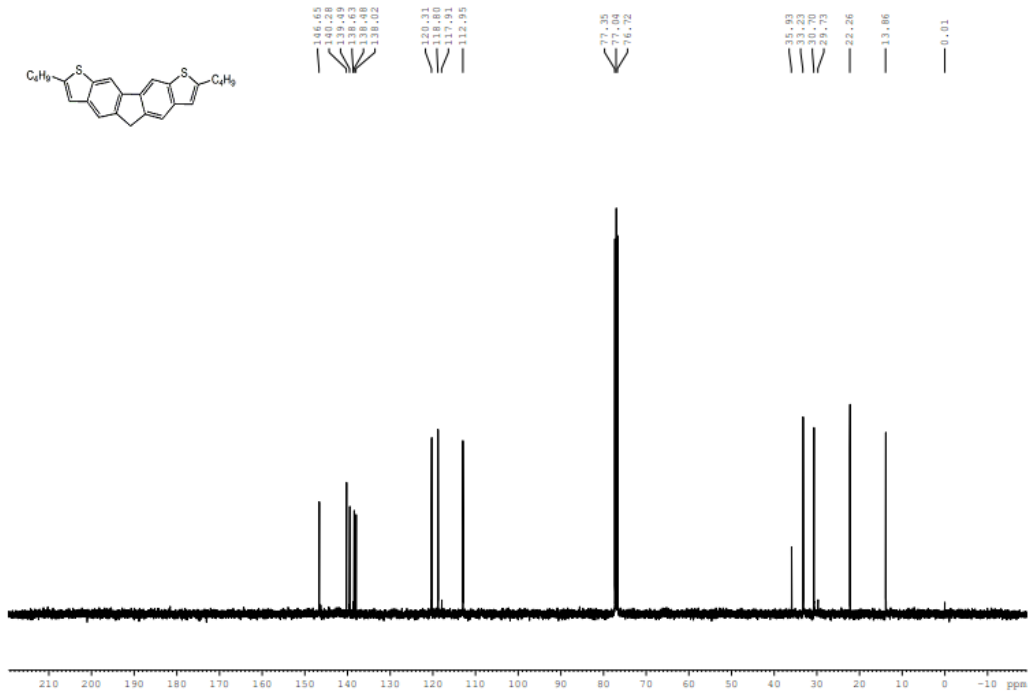
Fig. 17. ^{1}H NMR , ^{13}C NMR, MS and HRMS of compound 11b

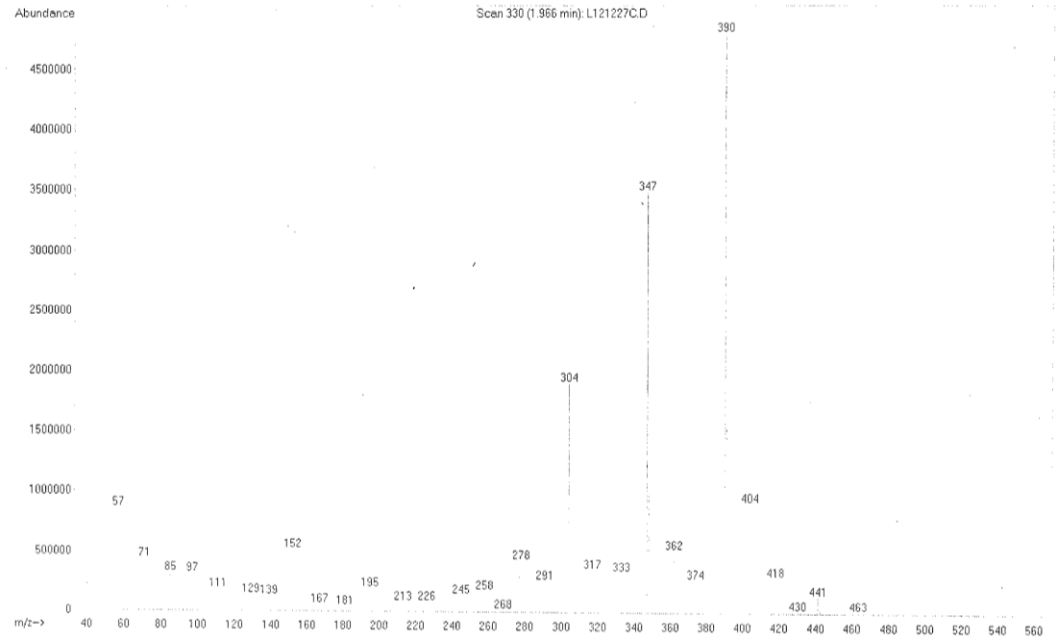
(3) 2,8-di-n-butyl-dithieno[3, 2-b: 6, 7-b']fluorene (11c)

This is prepared essentially the same as **11a** by employing $Na_2S.9H_2O$ (2.020 g, 8.4 mmol), NMP(20 mL) and **10c**(0.829 g, 2 mmol) to form a white solid(0.341 g, 43 %). M.p. 146- 148°C; R_f = 0.24 (PE). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 8.14 (s, 2H), 7.75 (s, 2H), 6.99 (s, 2H), 4.01 (s, 2H), 2.91 (t, J = 7.4 Hz, 4H), 1.75 (dt, J = 15.0, 7.4 Hz, 4H), 1.44 (dd, J = 14.8, 7.4 Hz, 4H), 0.96 (t, J = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 146.65,

140.28, 139.49, 138.48, 138.02, 120.31, 118.80, 112.95, 35.93, 33.23, 22.26, 13.86.; MS: m/z=390(M^+); HRMS for $C_{25}H_{26}S_2$ required: 390.1476. Found: 390.1474.







Elemental Composition Report **Page 1**

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Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
2 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
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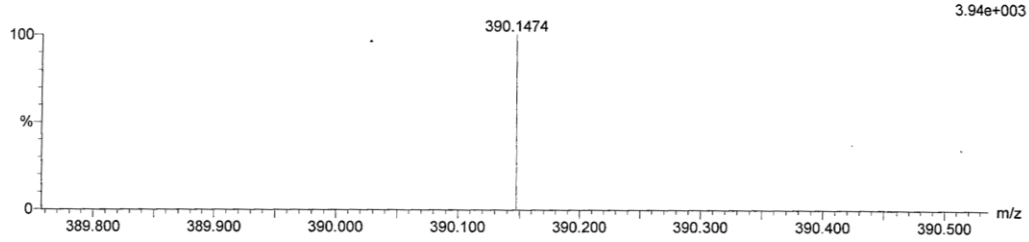
XXL-3
20130116004 456 (7.601)

TOF MS EI+
3.94e+003



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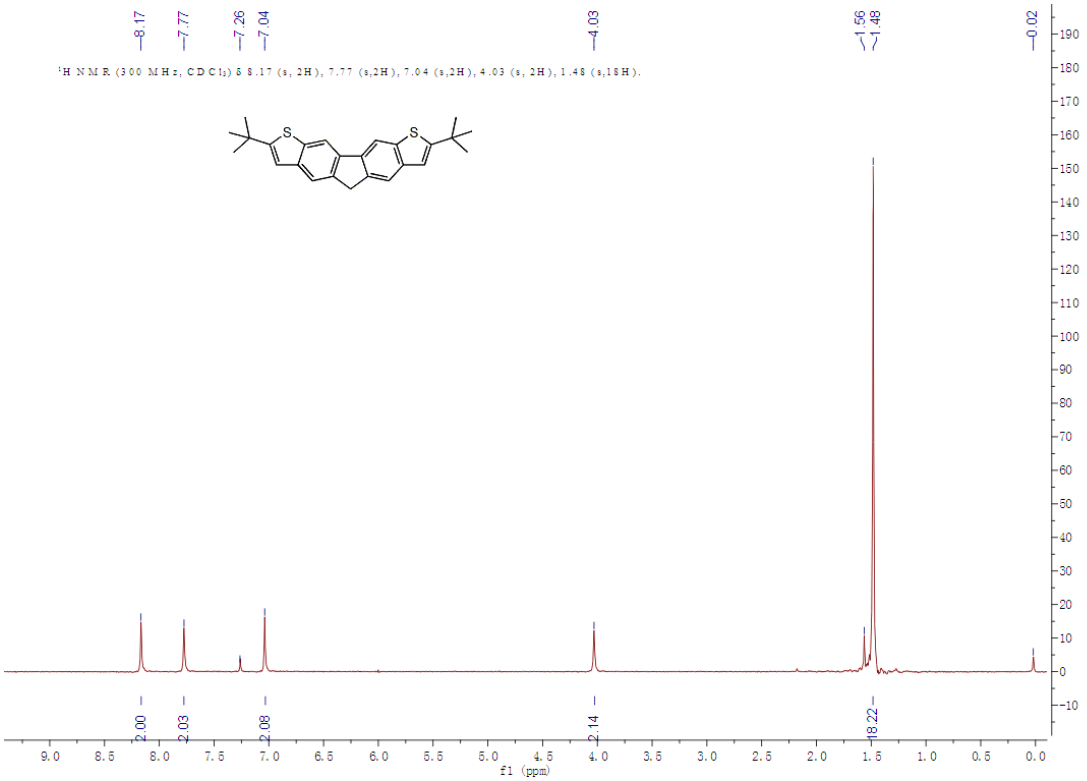
390.1474	390.1476	-0.2	-0.5	13.0	5547985.5	C25 H26 S2

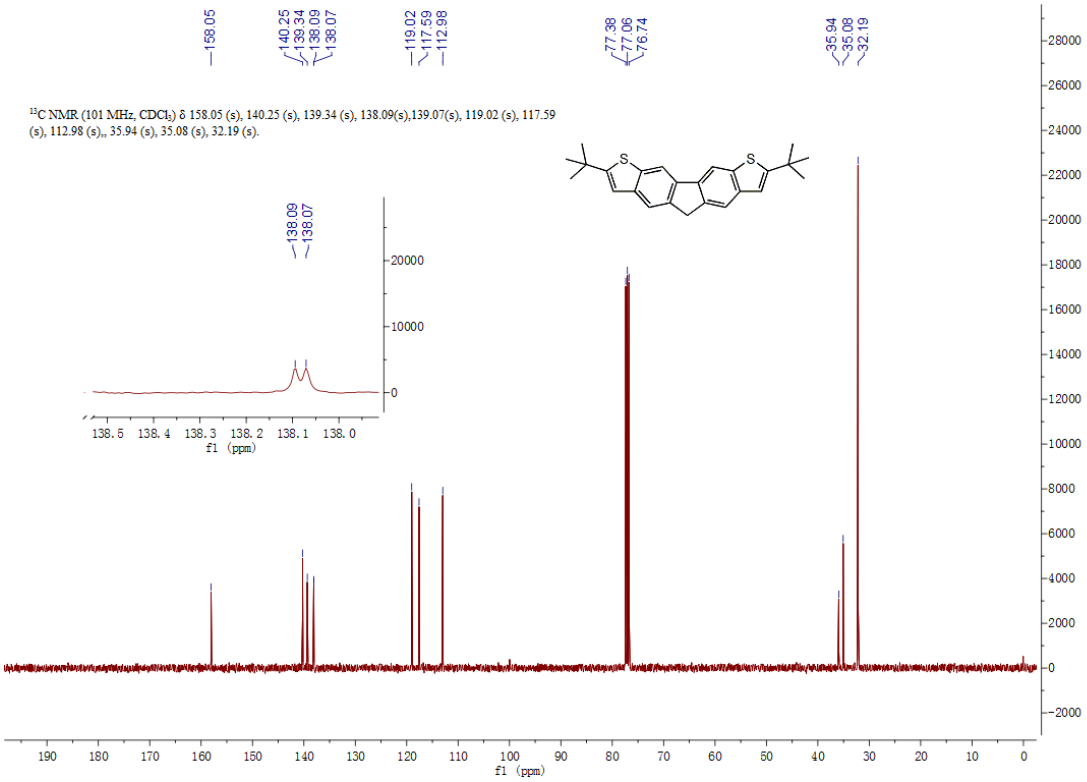
Fig.18. ^{1}H NMR, ^{13}C NMR, MS and HRMS of compound 11c

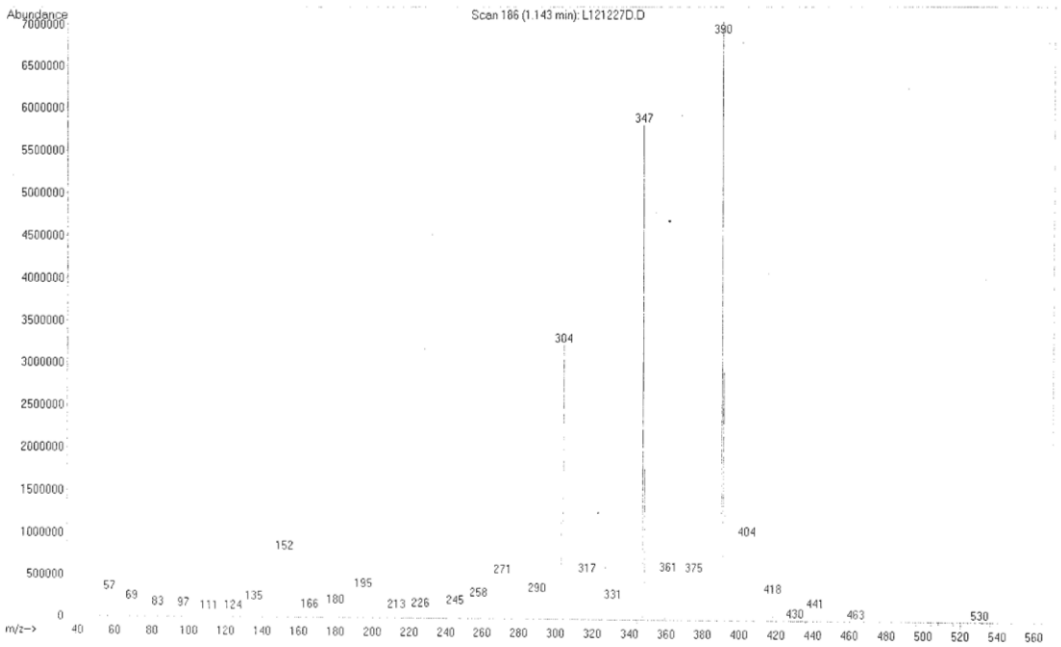
(4) 2,8-di-tert-butyl-dithieno[3, 2-b: 6, 7-b']fluorene (11d)

This is prepared essentially the same as **11a** by employing $Na_2S.9H_2O$ (4.320 g, 18 mmol), NMP (30 mL) and **10d** (1.227 g, 3 mmol) to form a white solid (0.319 g, 27 %). M.p. 254-257°C; R_f = 0.28 (PE). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 8.17 (s, 2H), 7.77 (s, 2H), 7.04 (s, 2H), 4.03 (s, 2H), 1.48 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 158.05,

140.25, 139.34, 138.09, 139.07, 119.02, 117.59, 112.98, 35.94, 35.08, 32.19.; MS: m/z = 390 (M^+); HRMS for $C_{25}H_{26}S_2$ required: 390.1476; Found: 390.1477.







Elemental Composition Report **Page 1**

Single Mass Analysis
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Monoisotopic Mass, Odd and Even Electron Ions
2 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
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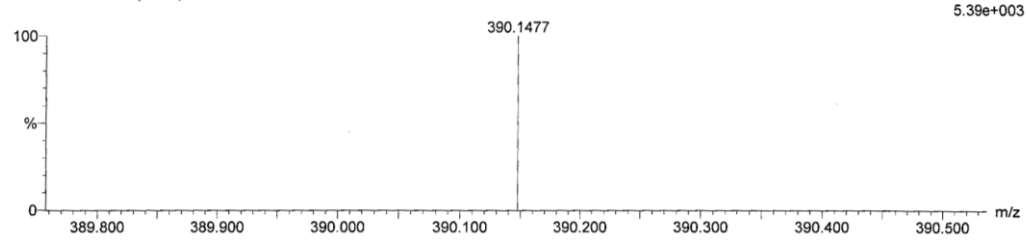
XXL-4
20130116005 543 (9.051)

TOF MS EI+
5.39e+003



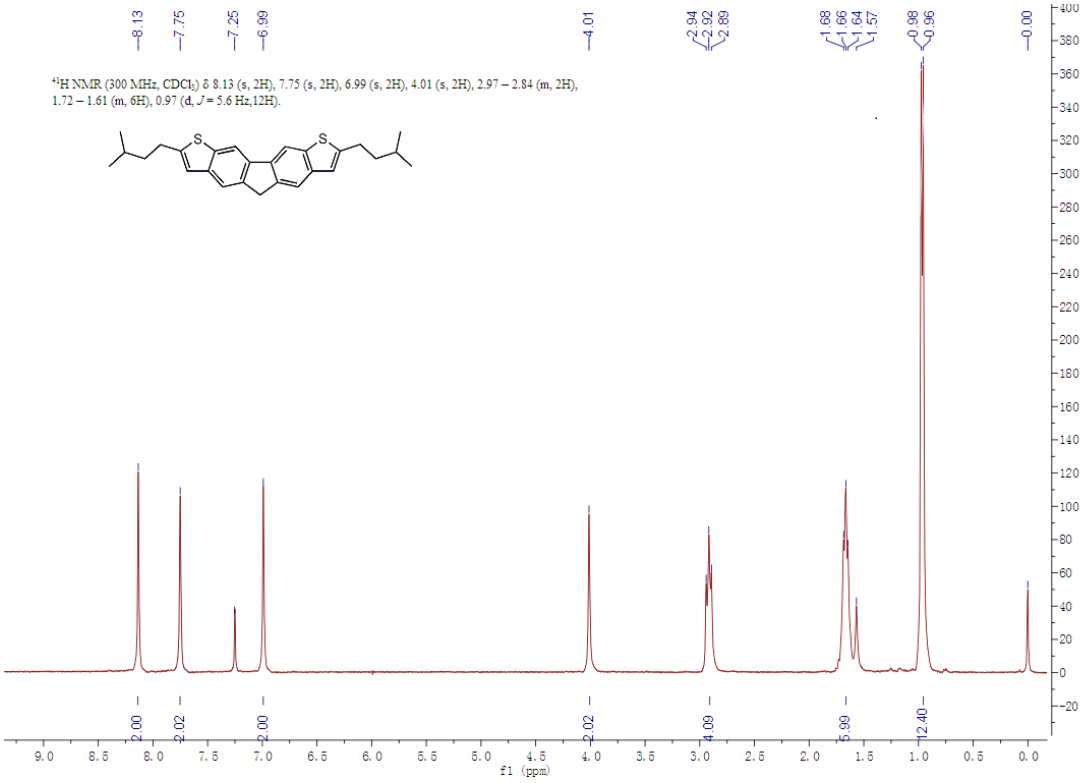
Minimum:		5.0	10.0	-1.5		
Maximum:				50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
390.1477	390.1476	0.1	0.3	13.0	5548713.5	C25 H26 S2

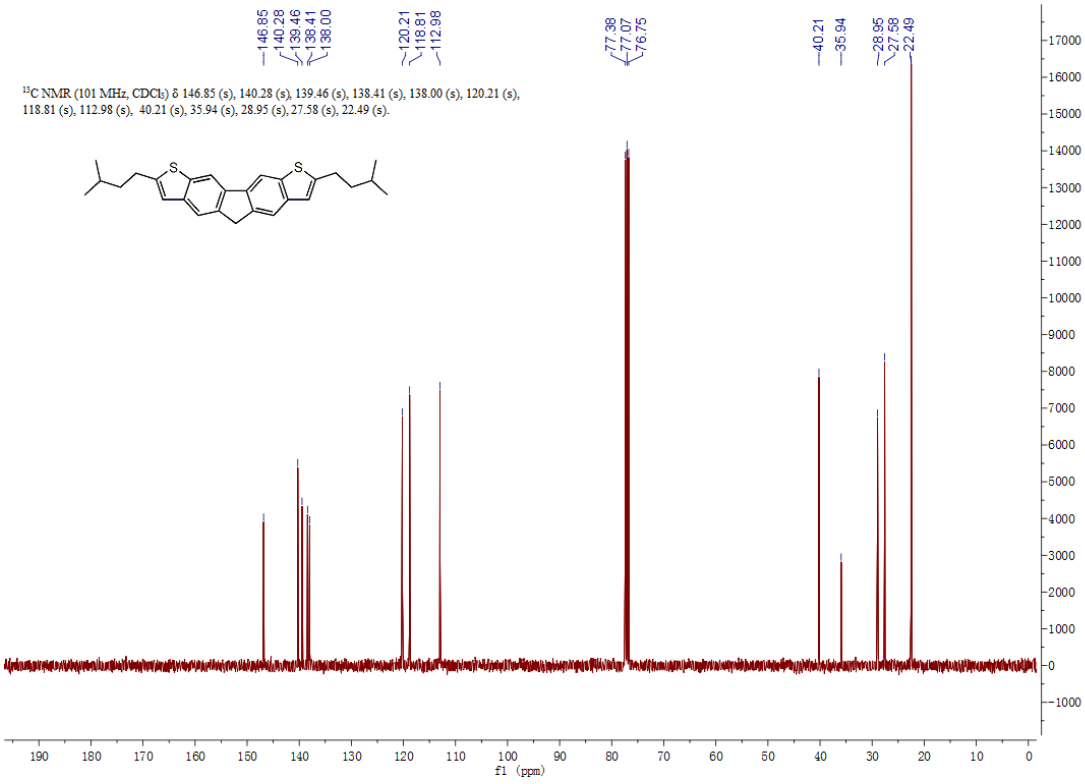
Fig.19. ^{1}H NMR , ^{13}C NMR, MS and HRMS of compound 11d

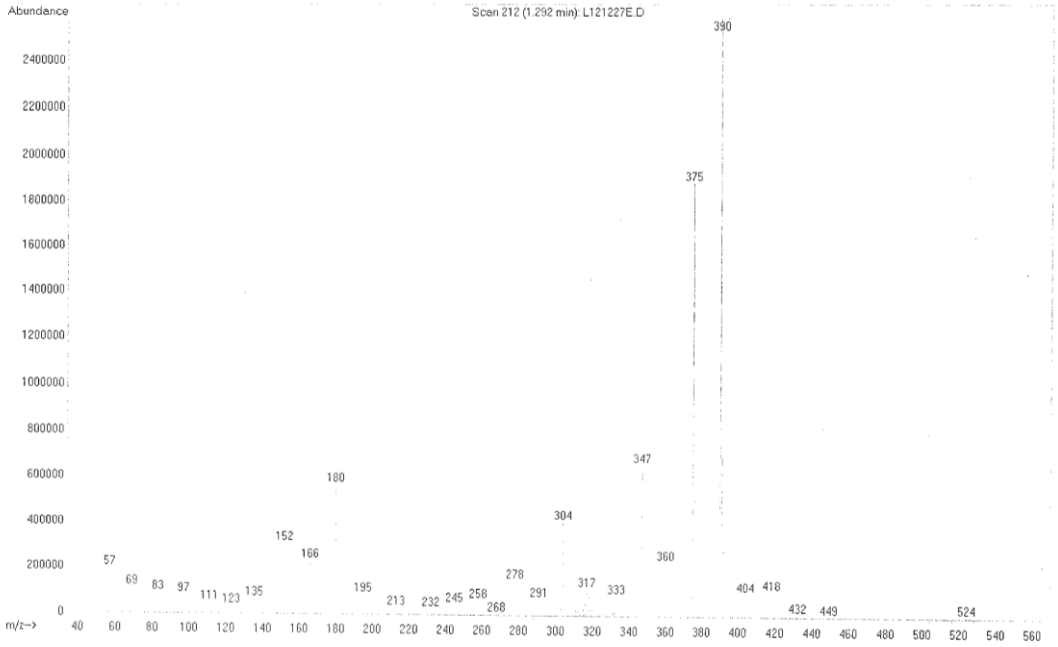
(5) 2,8-di-*iso*-pentyl-dithieno[3, 2-b: 6, 7-b']fluorene (11e)

This is prepared essentially the same as **11a** by employing $Na_2S.9H_2O$ (0.576 g, 2.4 mmol), NMP(10 mL) and **10e** (0.169 g, 0.4 mmol) to form a white solid (0.055 g, 36 %); M.p. 221-224°C; R_f = 0.29 (PE). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 8.13 (s, 2H), 7.75 (s, 2H), 6.99 (s, 2H), 4.01 (s, 2H), 2.97 - 2.84 (m, 2H), 1.72 - 1.61 (m, 6H), 0.97 (d, *J* = 5.6 Hz,

12H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 146.85, 140.28, 139.46, 138.41, 138.00, 120.21, 118.81, 112.98, 40.21, 35.94, 28.95, 27.58, 22.49.; MS: m/z=418(M^+); HRMS for $C_{27}H_{30}S_2$ required: 418.1789; Found: 418.1790.







Elemental Composition Report **Page 1**

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Monoisotopic Mass, Odd and Even Electron Ions
2 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
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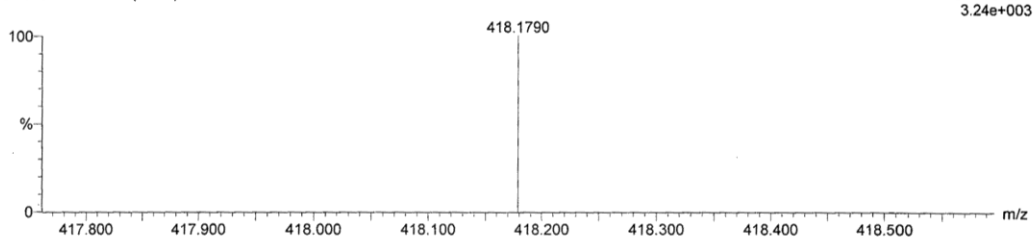
XXL-5
20130117001 176 (2.934)

TOF MS EI+
3.24e+003



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Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
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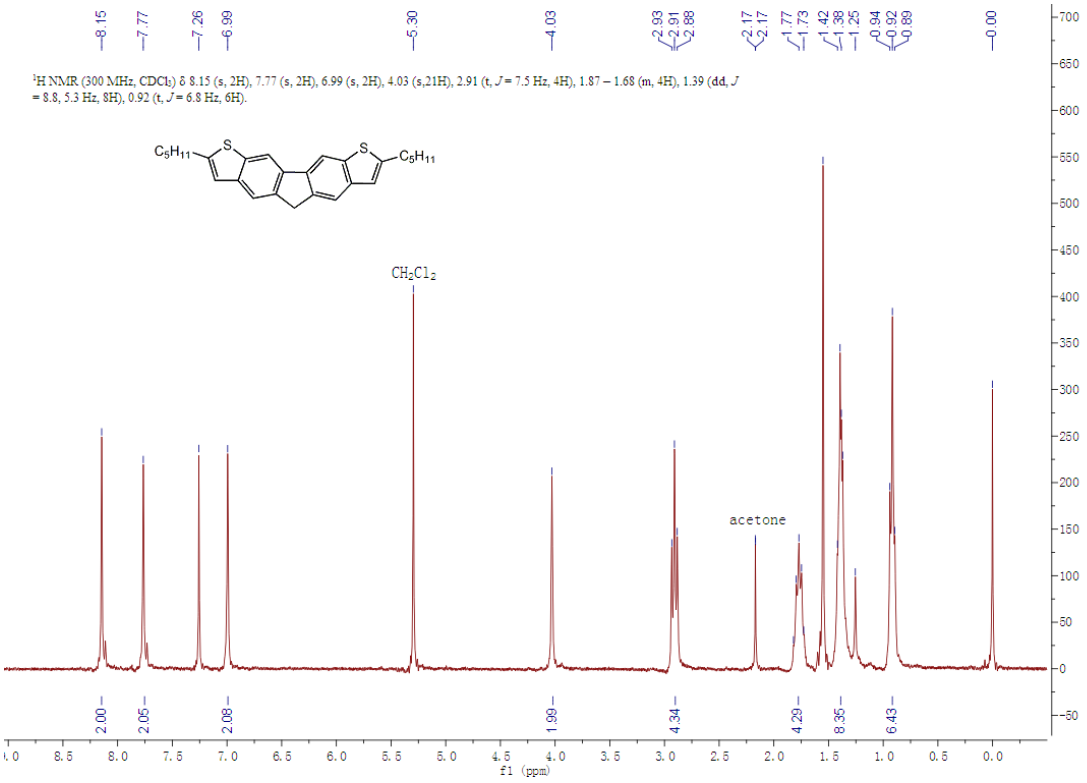
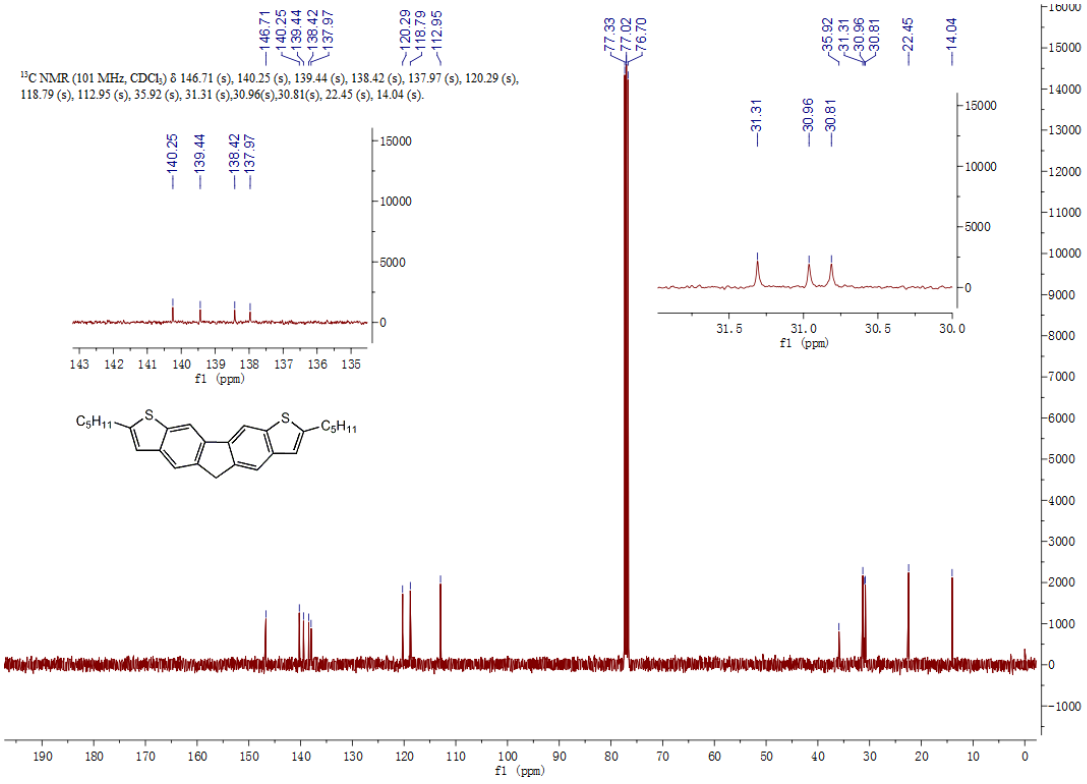
Fig. 20. ^{1}H NMR, ^{13}C NMR, MS and HRMS of compound 11e

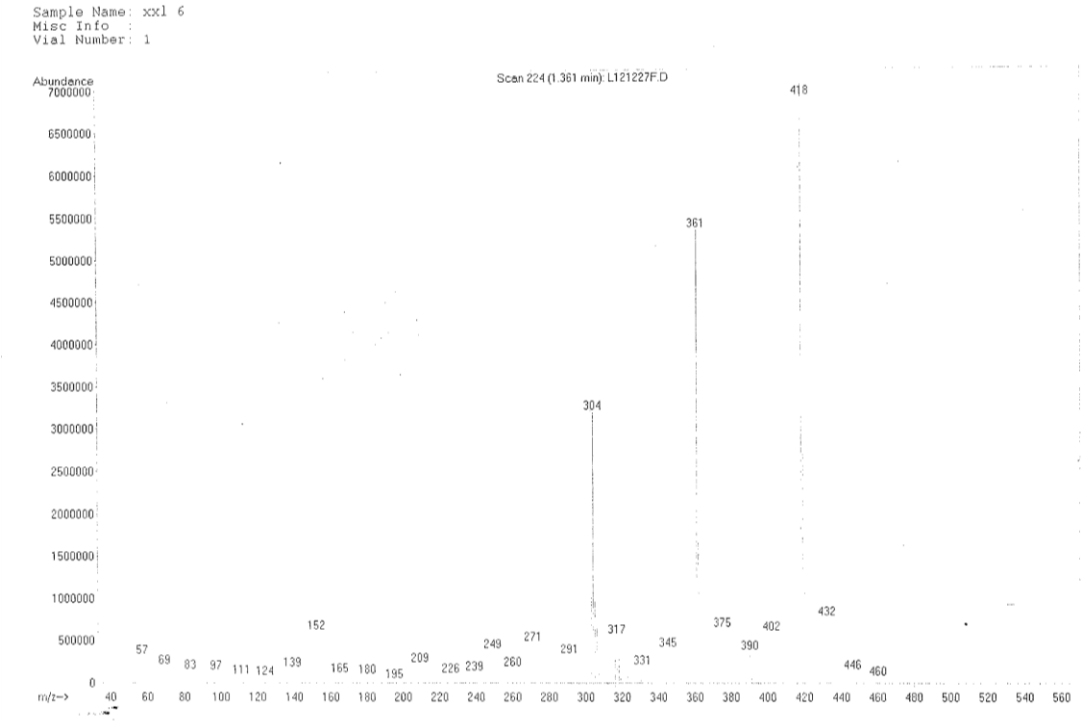
(6) 2,8-di-*n*-pentyl-dithieno[3, 2-b: 6, 7-b']fluorene(11f)

This is prepared essentially the same as **11a** by employing $Na_2S.9H_2O$ (2.88 g, 12 mmol), NMP(20 mL) and **10f** (0.874 g, 2 mmol) to form a white solid (0.263 g, 32 %). M.p. 150-151°C; R_f = 0.29 (PE). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 8.15 (s, 2H), 7.77 (s, 2H), 6.99 (s, 2H), 4.03 (s, 2H), 2.91 (t, J = 7.5 Hz, 4H), 1.87 - 1.68 (m, 4H), 1.39 (dd, J = 8.8,

5.3 Hz, 8H), 0.92 (t, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 146.71, 140.25, 139.44, 138.42, 137.97, 120.29, 118.79, 112.95, 35.92, 31.31, 30.96, 30.81, 22.45, 14.04.; MS:m/z=418(M^+); HRMS for $C_{27}H_{30}S_2$ required: 418.1789; Found: 418.1787.





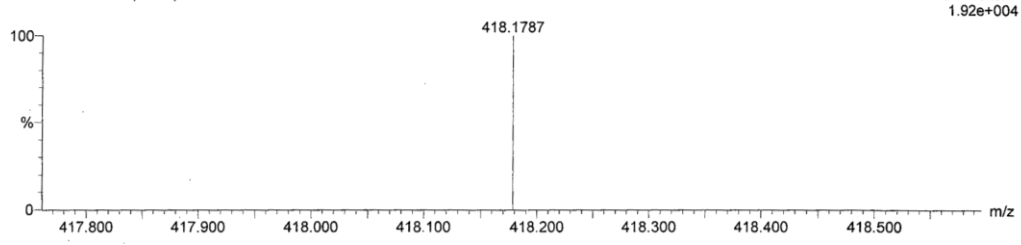


Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
2 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-27 H: 0-30 S: 0-2
XXL-6
20130117002 123 (2.050)

TOF MS EI+
1.92e+004



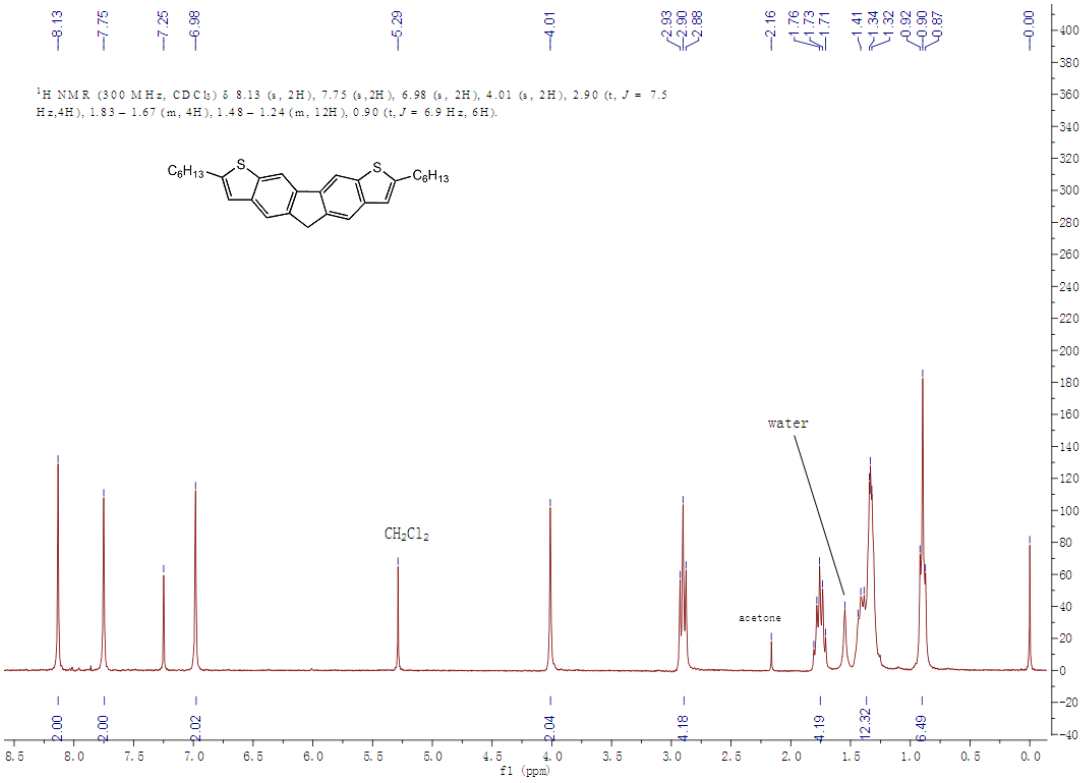
Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
418.1787	418.1789	-0.2	-0.5	13.0	5555597.5	C27 H30 S2

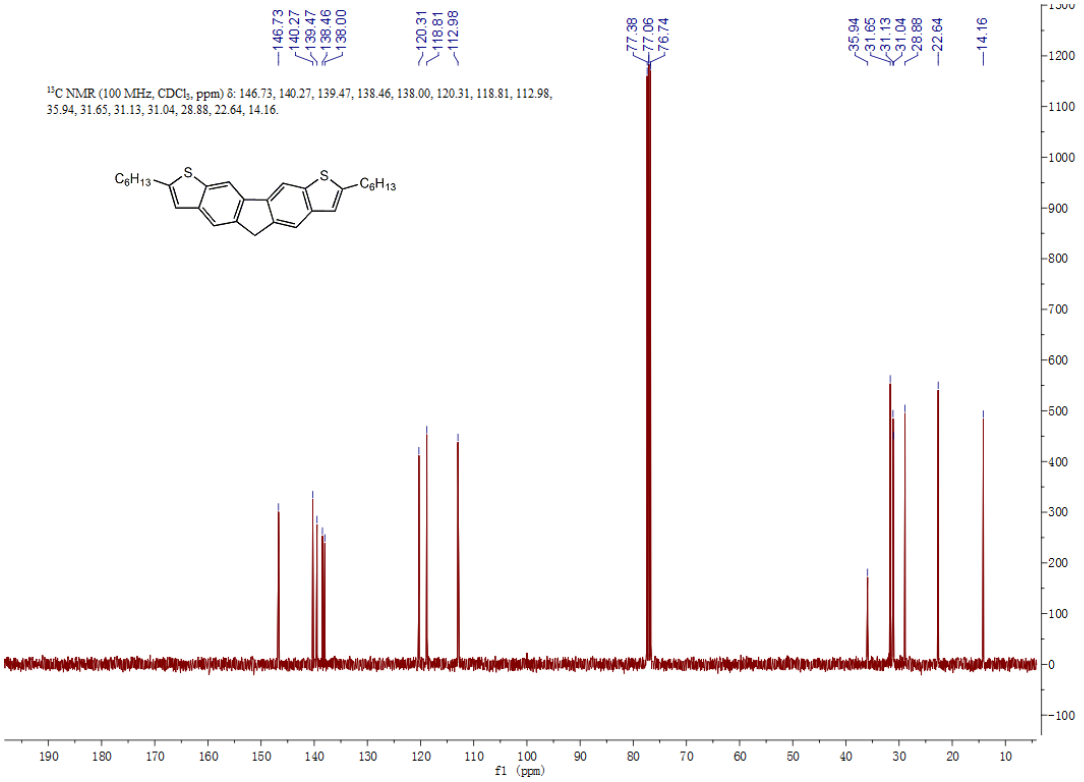
Fig. 21. ^{1}H NMR , ^{13}C NMR, MS and HRMS of compound 11f

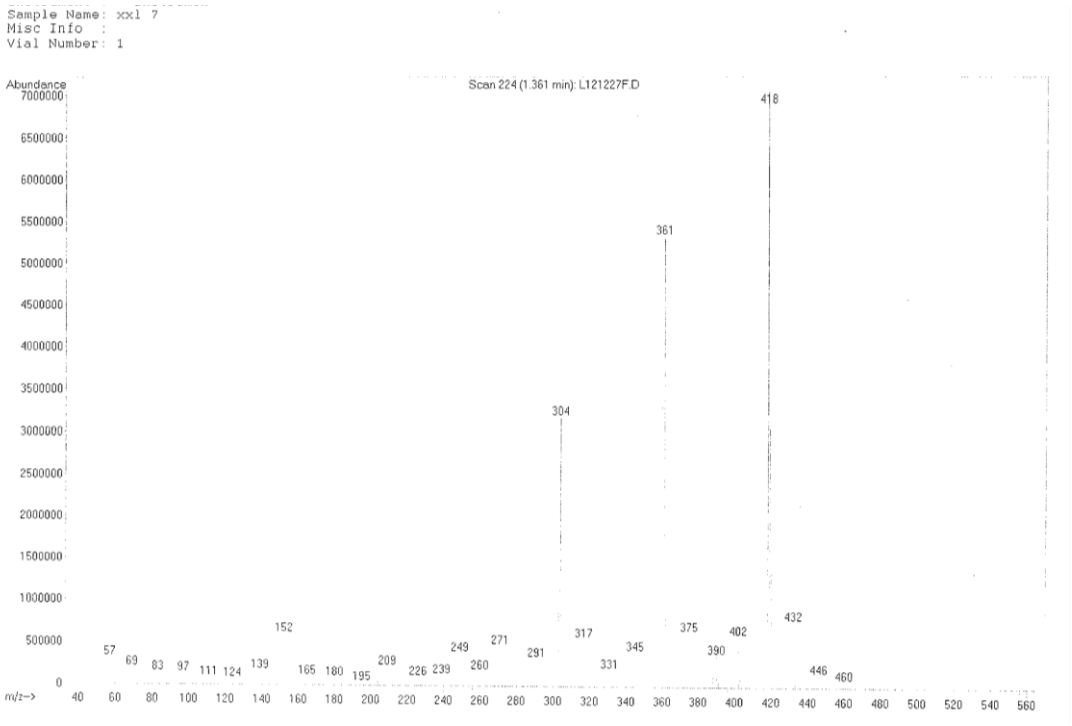
(7) 2,8-di-*n*-hexyl-dithieno[3, 2-b: 6, 7-b']fluorene (11g)

This is prepared essentially the same as **11a** by employing $Na_2S.9H_2O$ (0.910 g,3.8 mmol), NMP(20 mL) and **10g**(0.200 g,0.43 mmol) to form a white solid (0.080 g, 42 %). M.p. 107-108°C; R_f = 0.29 (PE). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 8.13 (s, 2H), 7.75 (s, 2H), 6.98 (s, 2H), 4.01 (s, 2H), 2.90 (t, J = 7.5 Hz, 4H), 1.83-1.67 (m, 4H), 1.48 - 1.24 (m, 12H), 0.90

(t, J = 6.9 Hz, 6H).^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 146.73, 140.27, 139.47, 138.46, 138.00, 120.31, 118.81, 112.98, 35.94, 31.65, 31.13, 31.04, 28.88, 22.64, 14.16.; MS: m / z = 446 (M^+); HRMS for $C_{29}H_{34}S_2$ required 446.2102; Found: 446.2104.





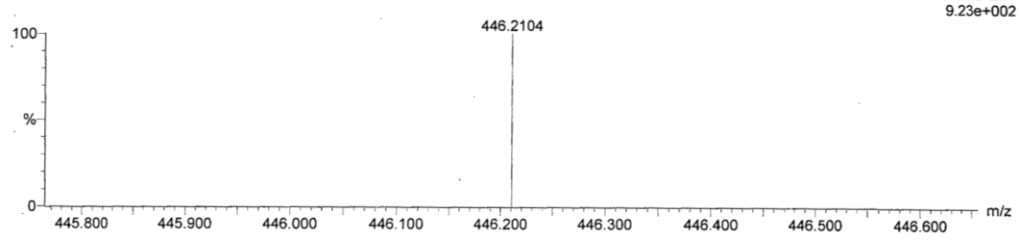


Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
3 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-30 H: 0-35 S: 0-2
XXL-7
20130117003 552 (9.201)

TOF MS EI+
9.23e+002



Minimum:		5.0	10.0	-1.5		
Maximum:				50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
446.2104	446.2102	0.2	0.4	13.0	5546480.0	C29 H34 S2

Fig. 22. ^{1}H NMR, ^{13}C NMR, MS and HRMS of compound 11g

(8)2,8-diphenyl-dithieno[3, 2-b: 6,7-b']fluorene (11h)

This is prepared essentially the same as **11a** by employing $Na_2S.9H_2O$ (2.4 g, 10 mmol), NMP(10 mL) and **10h** (0.449 g, 1 mmol) to form a white solid (0.105 g, 24 %). M.p. 221-224°C; (R_f = 0.4, PE:DCM=4:1). ^{1}HNMR: (300 MHz, $CDCl_3$, ppm) δ:8.21 (s, 2H), 7.86

(s, 2H), 7.74 (s, 4H), 7.57 (s, 2H), 7.40 (d, *J* = 24.7 Hz, 4H), 4.11 (s, 2H). High qualified carbon NMR could not be obtained due to its low solubility. MS: m / z = 429 (M-1)

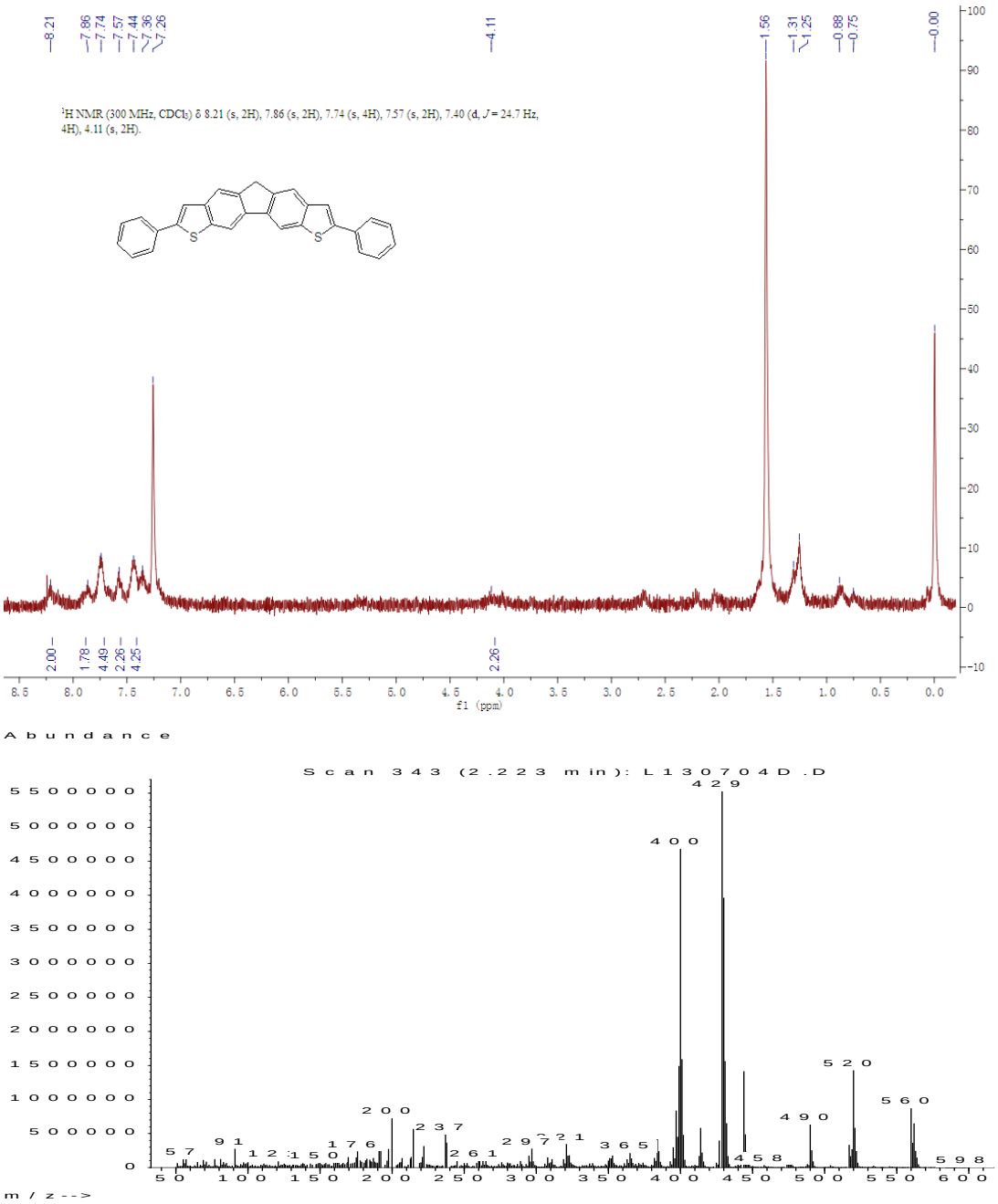
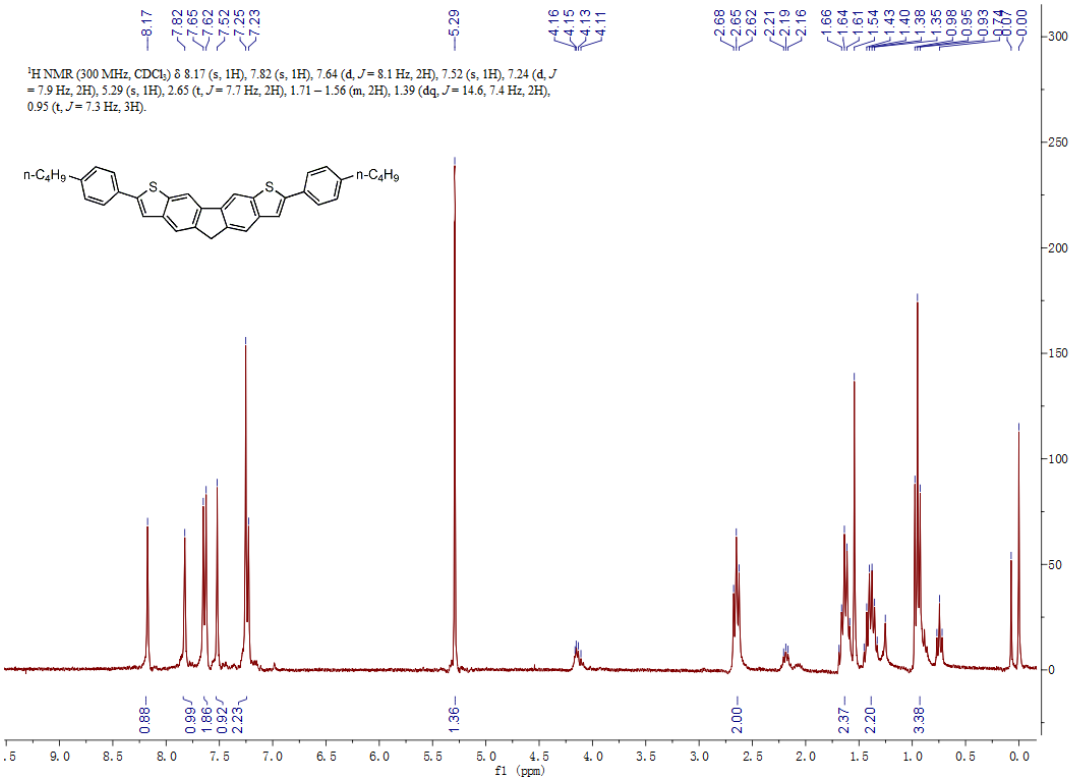


Fig. 23. ^{1}H NMR , MS of compound 11h

(9) 2,8-di-(4-n-butylphenyl)dithieno [3, 2-b: 6, 7-b']fluorene (11i)

This is prepared essentially the same as **11a** by employing $Na_2S.9H_2O$ (4.320 g,18 mmol), NMP (40 mL) and **10i** (1.683 g, 3 mmol) and separated by column chromatography

(PE:EtOAc = 20:1, V/V) to afford a pale-yellow solid (1.098 g, 23 %). M.p. 190-195°C; R_f = 0.74(PE:DCM = 2:1, V/V). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 8.17 (s, 1H), 7.82 (s, 1H), 7.64 (d, J = 8.1 Hz, 2H), 7.52 (s, 1H), 7.24 (d, J = 7.9 Hz, 2H), 2.65 (t, J = 7.7 Hz, 2H), 1.71 – 1.56 (m, 2H), 1.39 (dq, J = 14.6, 7.4 Hz, 2H), 0.95 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 151.38, 151.34, 146.73, 131.67, 131.65, 126.04, 125.90, 118.94 , 118.91, 118.68, 113.16 , 113.07, 100.47, 34.70, 31.26 .



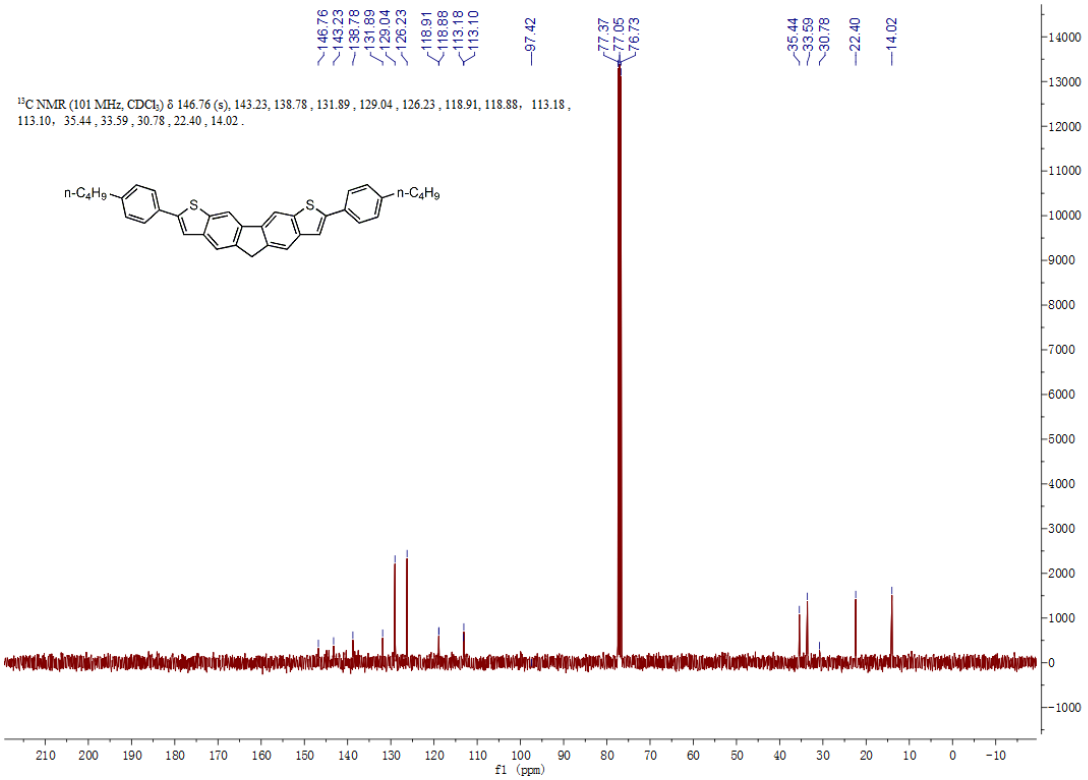


Fig.24. ^{1}H NMR and ^{13}C NMR of compound 11i

(10) 2,8-di-(4-tert-butylphenyl)dithieno [3, 2-b: 6, 7-b']fluorene (11j)

This is prepared the same as **11a** by employing $Na_2S.9H_2O$ (0.200 g, 0.36 mmol), NMP(10 mL) and **10j** (0.538 g, 2.23 mmol) and separated by column chromatography (PE:EtOAc = 20:1) to afford a pale-yellow solid(0.052 g, 27 %). M.p. 311-315°C, R_f = 0.74 (PE:DCM = 2:1).^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 7.85 (s, 1H), 7.60 (s, 1H), 7.52 (d, J = 7.8 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 151.38, 151.34，146.73 , 131.67, 131.65, 126.04, 125.90, 118.94 , 118.91, 118.68, 113.16 , 113.07, 100.47, 34.70, 31.26. MS: m / z = 542 (M^+).

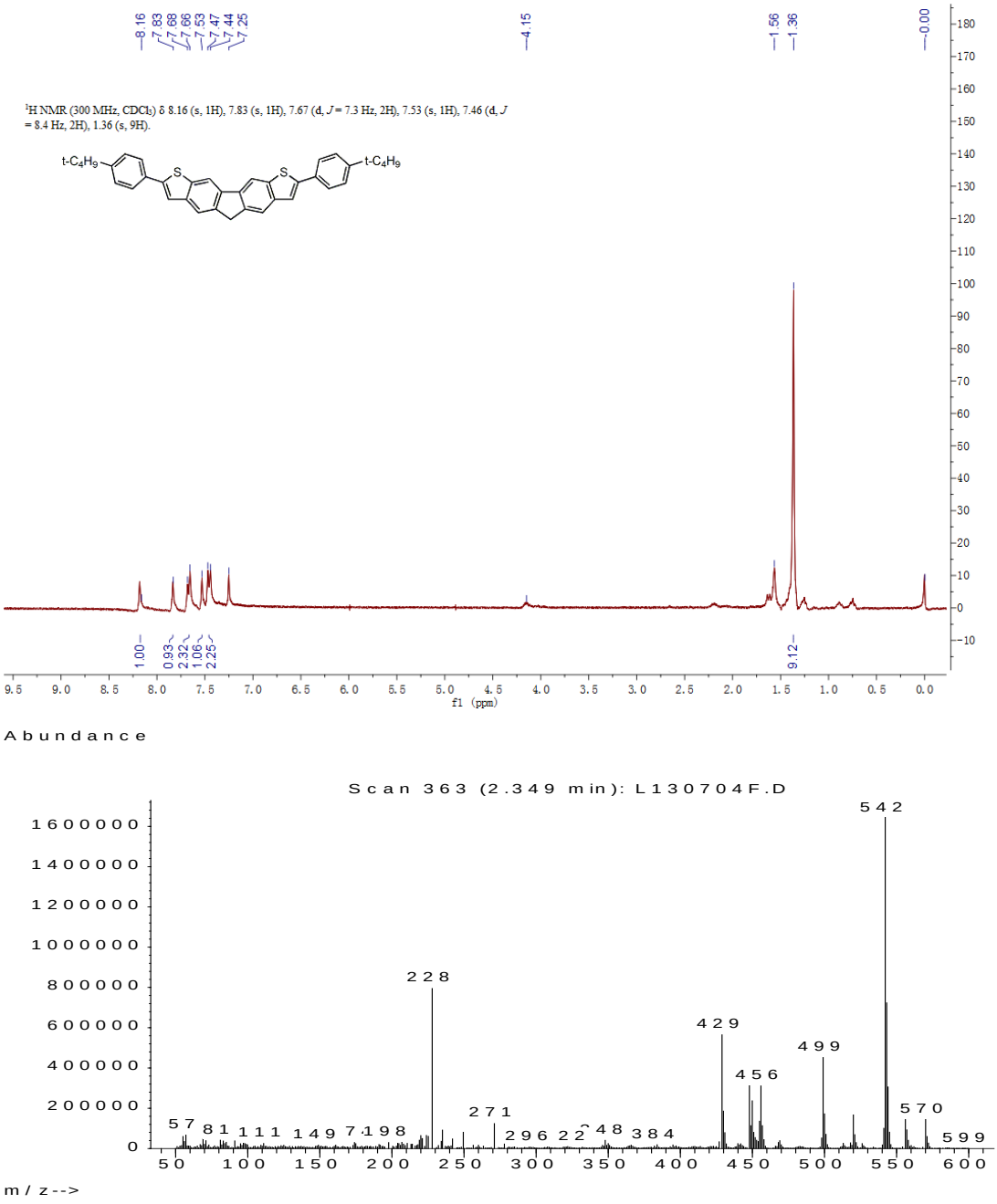


Fig. 25. ^{1}H NMR and MS of compound 11j

（11）2,8-di(4-hexyloxyphenyl)-dithieno[3, 2-b: 6,7-b']fluorene (11k)

This is prepared essentially the same as **11a** by employing $Na_2S.9H_2O$ (0.606 g, 3 mmol), NMP(10 mL) and **10k** (0.202 g, 0.3 mmol) and separated by column chromatography (PE:DCM = 1:1) to afford a white solid(0.050 g, 28 %), M.p. 160-162°C; R_f = 0.5(PE:DCM = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.83 (s, 1H), 7.59 (s, 1H), 7.49 (d, *J* = 8.1 Hz,

2H), 7.20 (d, *J* = 8.1 Hz, 2H), 2.68 - 2.60 (m, 2H), 1.66 - 1.56 (m, 6H), 1.36 (dq, *J* = 14.6, 7.4 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). High qualified carbon NMR could not be obtained due to its low solubility.

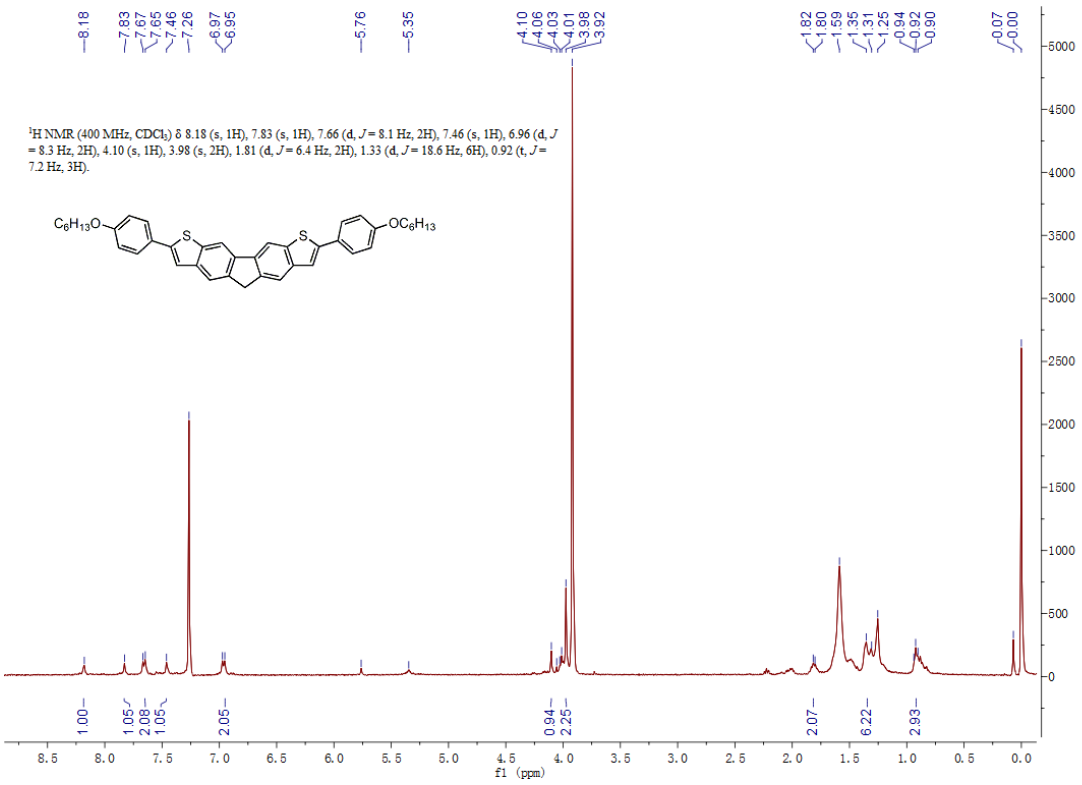
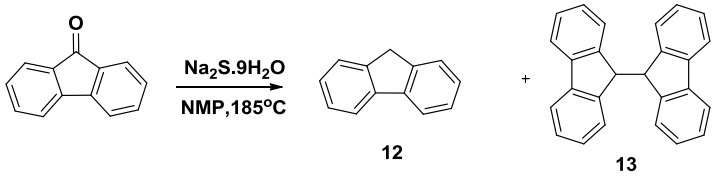


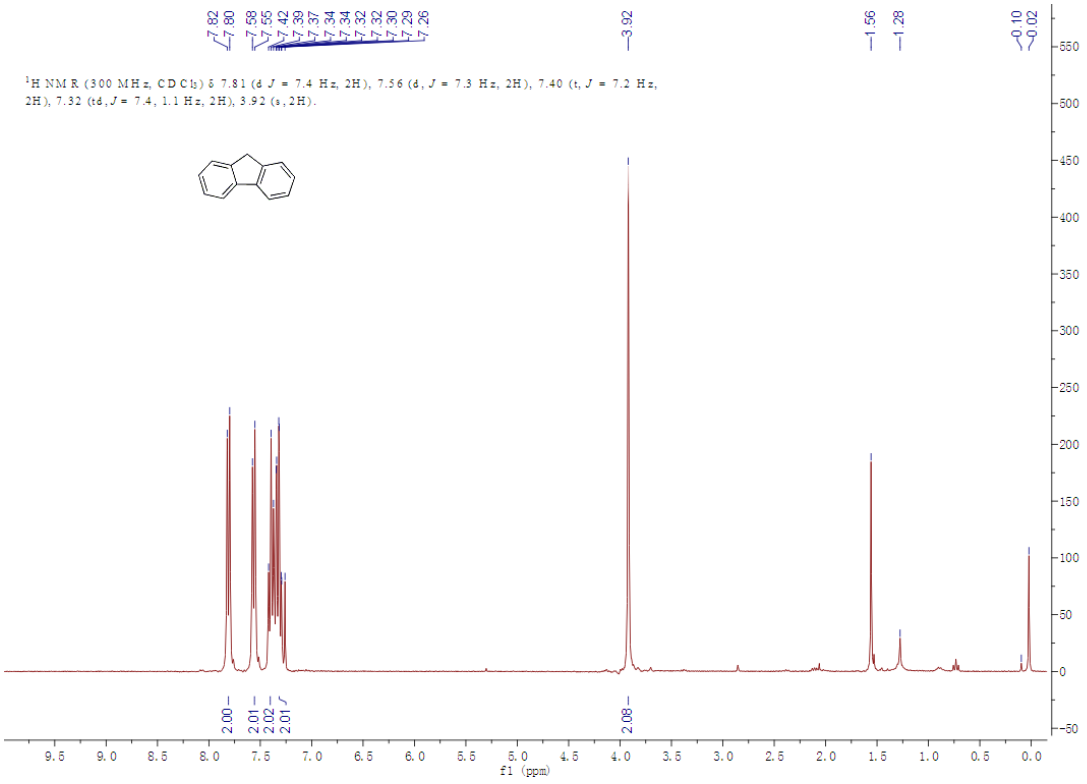
Fig. 26. ^{1}H NMR of compound 11k

Reduction of fluorenone to fluorene:



A 25mLRD flask was charged fluorenone(0.900 g, 5 mmol), $Na_2S.9H_2O$(6.000 g, 25 mmol), NMP (50 mL) and the mixture was refluxed for 12 h under N_2 before cooling. Then it was poured into saturated NH_4Cl and extracted with CH_2Cl_2 (3 x 50 ml). And the combined organic phase was washed with water for three times before dried over $MgSO_4$.

After workup, the residue was purified by column chromatography to afford a white solid **12** (0.385 g, 46 %). R_f= 0.58 (PE), M.p. 101-104°C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 7.81 (d, *J* = 7.4 Hz, 2H), 7.56 (d, *J* = 7.3 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.32 (td, *J* = 7.4, 1.1 Hz, 2H), 3.92 (s, 2H). And the second fraction was obtained as a white solid **13** (0.180 g, 22 %); R_f = 0.2(PE). M.p. 245-247°C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ:7.64 (d, *J* = 7.5 Hz, 4H), 7.27 (t, *J* = 7.7 Hz, 4H), 7.08 (t, *J* = 7.4 Hz, 4H), 6.95 (d, *J* = 7.0 Hz, 4H), 4.83 (s, 2H).



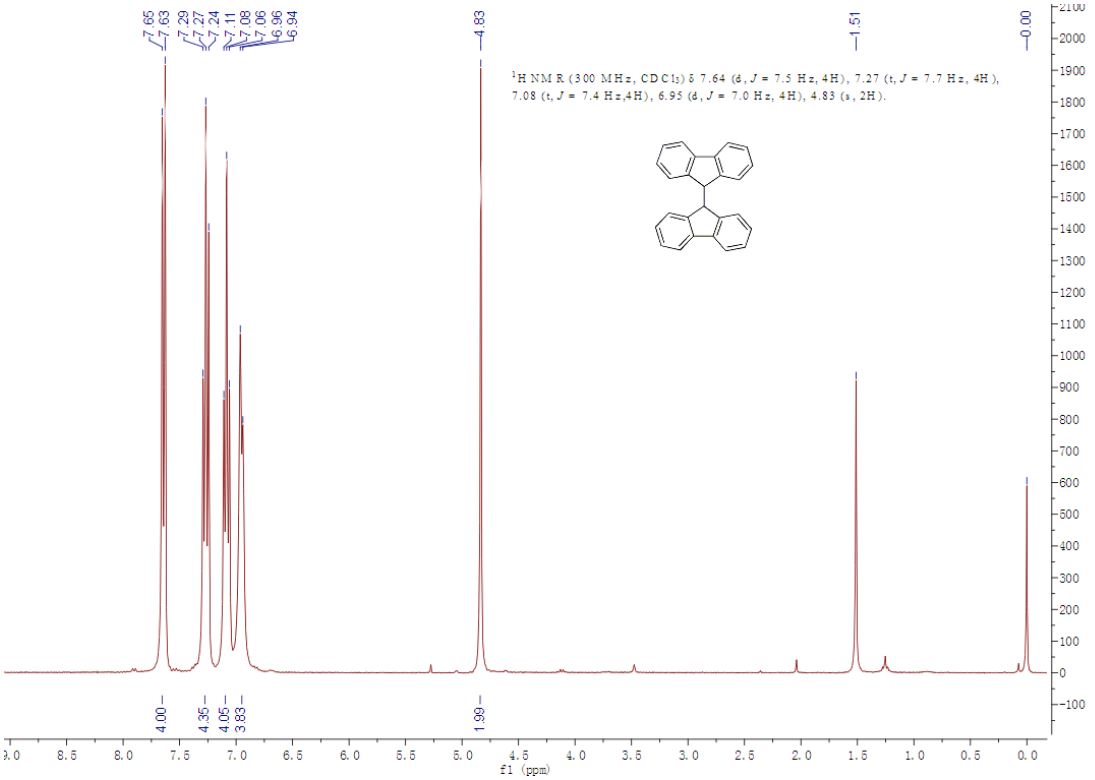
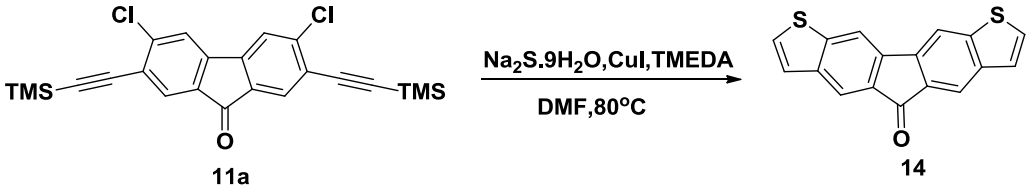


Fig. 27. ^{1}H NMR of compound 12 and 13

CuI-catalyzed ring close reaction of 11a to dithieno[3, 2-b: 6,7-b']fluorenone (14). [s5]



Under N_2, a mixture of 2,7-di(trimethylsilylethynyl)-3,6-dichloro-9-fluorenone (**11a**) (0.221 g, 0.5 mmol), Na2S.9 H2O (0.606 g, 2.5 mmol), CuI(0.019 g, 0.1 mmol) and TMEDA (0.3 mL) in DMF (5 mL) was heated to 80 °C for 24 h. Then it was cooled and poured into aq. HCl and extracted with CH_2Cl_2(3 x 100 ml). The combined organic phase was washed with water and dried over $MgSO_4$. The column chromatography (PE:AcOEt=20:1) was applied to purify to afford an orange solid(0.096 g, 66 %); R_f = 0.27 (PE:AcOEt =20:1,V/V). M.p. 284-287°C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 8.11 (s, 2H), 8.00 (s, 2H), 7.46 (d, *J* = 3 Hz, 2H), 7.38 (d, *J* = 3 Hz, 2H). ^{13}C NMR (75 MHz, DMSO-d6, ppm) δ: 191.68, 145.80, 139.81, 139.02, 132.43, 129.19, 125.50, 119.81, 115.19.

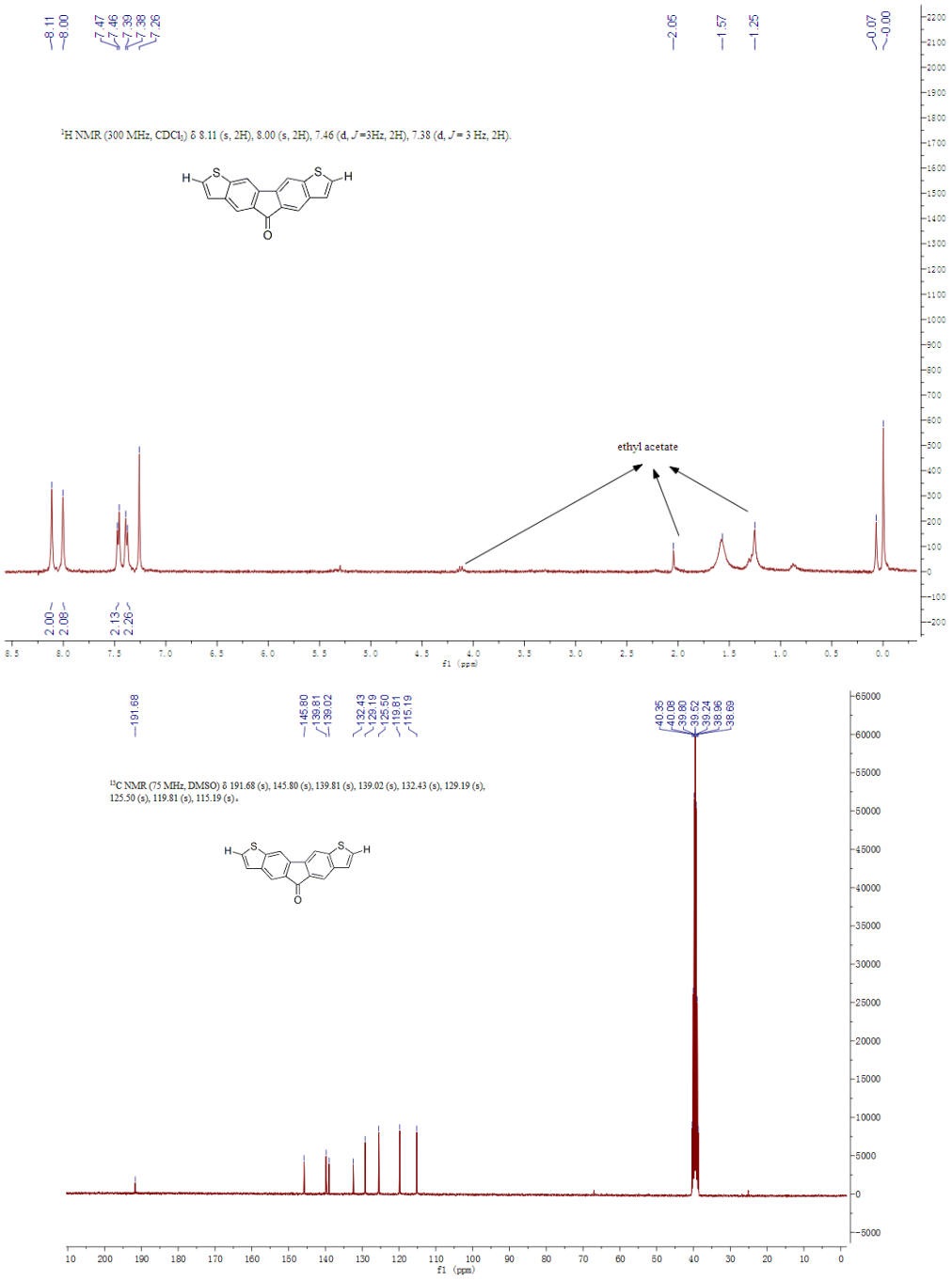


Fig. 28. ^{1}H NMR and ^{13}CNMR of compound 14

References:

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S4. (a)S. Shinamura, E. Miyazaki, K. Takimiya. *J. Org. Chem.*, 2010, **75**, 1228-1234.; (b)S. Shinamura, I. Osaka, E. Miyazaki. *J. Am. Chem. Soc.*, 2011, **133**, 5024-5035.

S5. L. L. Sun, C. L. Deng, R. Y. Tang, X. G. Zhang. *J. Org. Chem.*, 2011, **76**, 7546-7550.

Table 1. Crystal data for 11f (deposited Number CCDC 919150)

Compound	**11f**
Empirical formula	$C_{27}H_{30}S_2$
Molecular weight	418.63
Description	Colorless; block
Size, mm^3	0.36 x 0.28 x 0.22
Temperature, K	296(2)
Crystal system	triclinic
Space group	p-1
a, Å	7.6535(9)
b, Å	11.5648(14)
c, Å	13.8466(17)
α, degrees	67.639(3)
β, degrees	84.037(4)
γ, degrees	81.169(4)
V, Å^3	1118.6(2)
Z	2
Calculated density, Mg m^{-3}	1.243
Scan mode	multi-scan
F(000)	448
Absorption coefficient, mm^{-1}	0.249
θ range, degrees	1.59 to 25.01
Index ranges	-9≤h≤9; -12≤k≤13; -16≤l≤15
Reflections collected	13113
Independent reflections	3920[R(int) = 0.025]
Data/restraints/parameters	3920/0/262
GOF on F^2 (all)	1.027
Final R (I > 2σ(I))	R1 = 0.0492, wR2 = 0.1006
R indices (all data)	R1 = 0.0357 wR2 = 1.027
Max and min transmission	0.9472 and 0.9157
Largest diff. peak and hole, e/ Å^3	0.237 and -0.137