Supporting Information

Unexpectedly Superior Efficiency of Chloride-directed Double Suzuki-Miyaura Cross-coupling Reaction to That of Bromide for the Synthesis of Sterically Hindered 2,7-Diaryl Fluorenes

Yu-Qing Peng, Yong-Qing Li,* Miao-Miao Liu, Chen Ni and Yu-Cai Cao*

State Key Laboratory of Polyolefins and Catalysis, Shanghai Key Laboratory of Catalysis Technology for Polyolefins, Shanghai Research Institute of Chemical Industry Co. Ltd., Shanghai 200062, P. R. China
E-mail: liyongqing@srici.cn, caoyc@srici.cn.

CONTENTS

1. General Considerations. S1
2. General procedures for Suzuki-Miyaura cross-coupling reaction S1
3. Characterization Data of Double Suzuki-Miyaura coupling products. S2
4. Crystallographic data for **7** S6
5. NMR Spectra S10
6. HRMS analysis reports for the compounds S25
7. References S32

1. General Considerations.

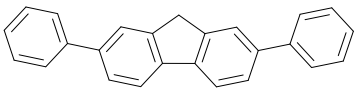
All reactions were carried out under a nitrogen atmosphere unless otherwise specified. Unless otherwise noted, commercialized reagents were used without further purification. HPLC yield was determined on Shimadzu LC-20A. Elemental analysis was determined on Elementar vario micro cubo automatic element analyzer. HRMS was measured on Thermo Scientific Q Exactive HF Orbitrap-FTMS. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-ECZR 500 MHz spectrometer at ambient temperature unless otherwise indicated. ^{1}H chemical shifts were referenced to $CDCl_3$ (7.26 ppm) and Tetrachloroethane (6.0 ppm), ^{13}C chemical shifts were referenced to $CDCl_3$ (77.16 ppm) and Tetrachloroethane (73.78 ppm).[1] Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet-doublet (dd), quintet (quint), septet (sept), multiplet (m), and broad (br). NMR reaction controls for the optimization experiments were usually measured by diluting 25 mg of the crude reaction mixture with 0.5 mL of $CDCl_3$, mixed in the NMR tubes.

2. General procedures for Suzuki-Miyaura cross-coupling reaction

A mixture of 2,7-diaryl fluorenes (2.5 mmol), arylboronic acid (6.25~7.5 mmol), Pd complex catalyst (0.5~1.0 mol% of Pd loading), and base (5.0~10 mmol) was charged in a solvent (20 mL). The mixture was pumped and refilled with nitrogen three times. The resulting mixture was stirred at 80~100℃ under nitrogen for 2 h and then cooled to room temperature, washed with water (200 mL), and EtOH (2× 50 mL). The filtrate was concentrated in *vacuo*, dissolved in dichloromethane (50 mL), dried over sodium sulfate, and purified by crystallization at -20℃ to obtain the coupling product.

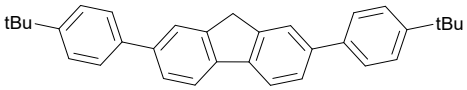
3. Characterization Data of Double Suzuki-Miyaura coupling products.

2,7-diphenylfluorene (1)



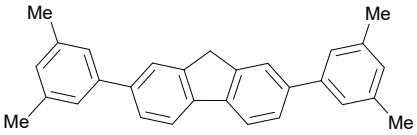
Brown solid (0.66 g, 83%); ^{1}H NMR (500 MHz, Tetrachloroethane) δ 8.00 – 7.84 (m, 4H), 7.84 – 7.64 (m, 6H), 7.64 – 7.33 (m, 6H), 4.09 (s, 2H); ^{13}C NMR (126 MHz, Tetrachloroethane) δ 144.01, 141.35, 140.52, 139.91, 128.51, 126.94, 126.91, 125.91, 123.55, 119.92, 36.97. HRMS (ESI) *m*/*z* calcd for $C_{25}H_{18}Na^{+}$ $[M+Na]^{+}$: 341.1306, found 341.1312. The NMR spectroscopic data matches previously reported data.[2]

2,7-bis(4-*tert*-butylbutylphenyl)fluorene (2)



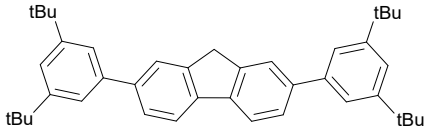
White solid (0.61 g, 57%); ^{1}H NMR (500 MHz, Chloroform-d) δ 7.84 (d, J = 7.9 Hz, 2H), 7.78 (s, 2H), 7.63 (d, J = 5.4 Hz, 4H), 7.61 (s, 2H), 7.49 (d, J = 8.4 Hz, 4H), 4.02 (s, 2H), 1.38 (s, 18H); ^{13}C NMR (126 MHz, Tetrachloroethane) δ 150.18, 143.96, 140.33, 139.65, 138.19, 126.59, 125.67, 125.41, 123.31, 119.82, 37.02, 34.24, 31.25.; HRMS (ESI) *m*/*z* calcd for $C_{33}H_{35}$ $[M]^{+}$: 431.2739, found 431.2738.

2,7-bis(3,5-dimethylphenyl)fluorene (3)



White solid (0.81 g, 87%); ^{1}H NMR (500 MHz, Chloroform) δ 7.86 – 7.76 (m, 4H), 7.62 (dd, J = 7.9, 1.7 Hz, 2H), 7.29 (s, 4H), 7.01 (s, 2H), 4.01 (s, 2H), 2.41 (s, 12H). ^{13}C NMR (126 MHz, Tetrachloroethane) δ 143.97, 141.05, 140.27, 139.71, 138.25, 128.94, 128.75, 125.99, 125.15, 125.06, 124.92, 123.73, 120.04, 36.98, 21.50, 21.41; HRMS (ESI) *m*/*z* calcd for $C_{29}H_{26}Na^{+}$ $[M+Na]^{+}$: 397.1932, found 397.1925. The NMR spectroscopic data matches previously reported data.[3]

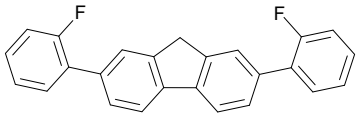
2,7-bis(3,5-di-*tert*-butylphenyl)fluorene (4)



Brown solid (0.80 g, 59%); ^{1}H NMR (500 MHz, Chloroform-d) δ 7.86 (d, J = 7.9 Hz, 2H), 7.78 (d, J = 0.9 Hz, 2H), 7.63 (dd, J = 7.9, 1.7 Hz, 2H), 7.50 (d, J = 1.8 Hz, 4H), 7.45 (t, J = 1.8 Hz, 2H), 4.04 (s, 2H), 1.41 (s, 36H); ^{13}C NMR (126 MHz, Chloroform-d) δ 151.24, 144.16, 141.20, 141.05, 140.58, 126.49, 124.23, 121.88,

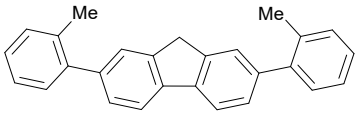
121.44, 120.18, 77.40, 77.15, 76.89, 37.22, 35.15, 31.72; HRMS (ESI) *m*/*z* calcd for $C_{41}H_{50}Na^+$ $[M+Na]^+$: 565.3810, found 565.3795.

2,7-bis(2-fluorophenyl)fluorene (5)



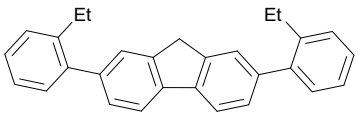
White solid (0.65 g, 73%); ^{1}H NMR (500 MHz, Chloroform-d) δ 7.89 (d, J = 7.9 Hz, 2H), 7.77 (d, J = 1.7 Hz, 2H), 7.61 (dt, J = 7.9, 1.7 Hz, 2H), 7.56 – 7.51 (m, 2H), 7.38 – 7.31 (m, 2H), 7.26 (d, J = 1.3 Hz, 1H), 7.25 (d, J = 1.3 Hz, 1H), 7.22 (d, J = 1.2 Hz, 1H), 7.20 (dd, J = 2.7, 1.2 Hz, 1H), 4.02 (s, 2H); ^{13}C NMR (126 MHz, Chloroform-d) δ 160.99, 159.02, 143.89, 141.01, 134.57, 131.00, 129.01, 128.06, 125.89, 124.54, 120.13, 116.38, 116.20, 77.41, 77.16, 76.91, 37.19; HRMS (ESI) *m*/*z* calcd for $C_{25}H_{17}F_2$ $[M]^+$:355.1298, found 355.1295.

2,7-bis(2-methylphenyl)fluorene (6)



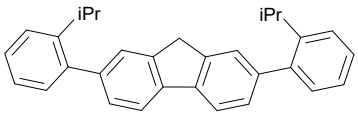
White solid(0.82 g, 95%); ^{1}H NMR (500 MHz, Chloroform-d) δ 7.81 (d, J = 7.8 Hz, 2H), 7.49 (s, 2H), 7.34 (d, J = 7.8 Hz, 2H), 7.31 – 7.27 (m, 4H), 7.25 (d, J = 3.9 Hz, 2H), 3.94 (s, 2H), 2.31 (s, 6H); ^{13}C NMR (126 MHz, Chloroform-d) δ 143.53, 142.41, 140.71, 140.36, 135.65, 130.59, 130.35, 130.13, 128.25, 127.40, 126.10, 126.02, 119.65, 77.53, 77.27, 77.02, 37.20, 20.85; HRMS (ESI) *m*/*z* calcd for $C_{27}H_{22}$[M]$^+$: 346.1716, found 346.1713. The NMR spectroscopic data matches previously reported data.[4]

2,7-bis(2-ethylphenyl)fluorene (7)



Yellow solid (0.45 g, 48%); ^{1}H NMR (500 MHz, Chloroform-d) δ 7.82 – 7.26 (m, 8H), 7.25 – 7.07 (m, 6H), 3.87 (s, 2H), 2.61 (q, J = 7.6 Hz, 4H), 1.07 (t, J = 7.5 Hz, 6H); ^{13}C NMR (126 MHz, Tetrachloroethane) δ 143.18, 141.69, 141.66, 140.41, 139.76, 130.03, 128.56, 127.97, 127.38, 125.92, 125.53, 119.32, 36.97, 26.18, 15.67; HRMS (ESI) *m*/*z* calcd for $C_{29}H_{26}$[M]$^+$: 374.2029, found 374.2028.

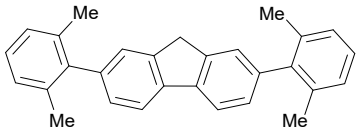
2,7-bis(2-*iso*-propylphenyl)fluorene (8)



Yellow solid (0.73 g, 73%); ^{1}H NMR (500 MHz, Chloroform-d) δ 7.85 (d, J = 7.7 Hz, 2H), 7.50 (s, 2H), 7.43 (dd, J = 7.8, 1.3 Hz, 2H), 7.39 – 7.33 (m, 4H), 7.27 (d, J = 5.5 Hz, 2H), 7.26 – 7.21 (m, 2H), 4.00 (s, 2H), 3.20 – 3.13 (m, 2H), 1.20 (d, J = 6.9 Hz, 12H); ^{13}C NMR (126 MHz, Chloroform-d) δ 146.61, 143.33, 141.50, 140.74,

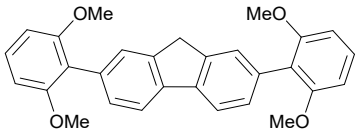
140.22, 130.17, 128.24, 127.75, 126.12, 125.67, 119.42, 77.41, 77.16, 76.91, 37.16, 29.56, 24.44; HRMS (ESI) *m*/*z* calcd for $C_{31}H_{30}[M]^+$: 402.2342, found 402.2343.

2,7-bis(2,6-dimethylphenyl)fluorene (9)



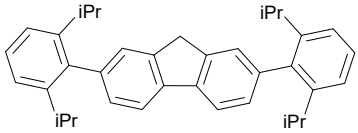
White solid (0.8 g, 85%); ^{1}H NMR (500 MHz, Chloroform) δ 7.91 (d, J = 7.8 Hz, 2H), 7.37 (s, 2H), 7.23 – 7.16 (m, 8H), 4.03 (s, 2H), 2.12 (s, 12H); ^{13}C NMR (126 MHz, Chloroform-d) δ 143.69, 142.25, 140.18, 139.74, 136.33, 127.83, 127.42, 127.11, 125.81, 119.91, 37.14, 21.05; HRMS (ESI) *m*/*z* calcd. for $C_{29}H_{26}[M]^+$: 374.2029, found 374.2027. The NMR spectroscopic data matches previously reported data.[4]

2,7-bis(2,6-dimethoxyphenyl)fluorene (10)



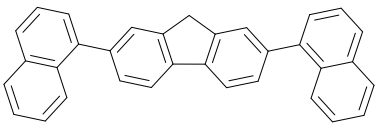
White solid (0.65 g, 59%); ^{1}H NMR (500 MHz, Chloroform-d) δ 7.85 (d, J = 7.8 Hz, 2H), 7.54 (s, 2H), 7.42 – 7.28 (m, 4H), 6.71 (d, J = 8.4 Hz, 4H), 4.00 (s, 2H), 3.77 (s, 12H); ^{13}C NMR (126 MHz, Chloroform-d) δ 157.95, 143.08, 140.72, 132.29, 129.48, 128.59, 127.54, 120.12, 119.22, 104.41, 56.11, 37.18; HRMS (ESI) *m*/*z* calcd for $C_{29}H_{27}O_4$ $[M]^+$: 439.1909, found 439.1910.

2,7-bis(2,6-di-*iso*-propylphenyl)fluorene (11)



White solid (0.45 g, 37%); ^{1}H NMR (500 MHz, Chloroform-d) δ 7.86 (d, J = 7.6 Hz, 2H), 7.36 (s, 4H), 7.21 (dd, J = 14.7, 7.4 Hz, 6H), 4.03 (s, 2H), 2.69 (s, 4H), 1.09 (d, J = 6.9 Hz, 24H); ^{13}C NMR (126 MHz, Chloroform-d) δ 147.11, 143.26, 140.12, 139.36, 128.71, 127.58, 126.58, 125.98, 123.04, 119.43, 37.21, 30.76, 24.30; HRMS (ESI) *m*/*z* calcd for $C_{37}H_{43}Na^+$ $[M+Na]^+$: 487.3365, found 487.3358.

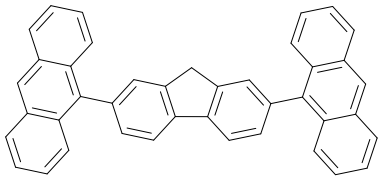
2,7-di(naphthalen-1-yl)fluorene (12)



White solid (0.88 g, 85%); ^{1}H NMR (500 MHz, Chloroform-d) δ 8.03 (d, J = 8.4 Hz, 2H), 7.97 (dd, J = 13.7, 7.9 Hz, 4H), 7.91 (d, J = 8.1 Hz, 2H), 7.73 (s, 2H), 7.60 – 7.52 (m, 8H), 7.48 (t, J = 7.7 Hz, 2H), 4.09 (s, 2H); ^{13}C NMR (126 MHz, Chloroform-d) δ 143.72, 140.75, 140.67, 139.52, 134.00, 131.92, 129.13, 128.46, 127.73, 127.16, 126.94, 126.27, 126.18, 125.93, 125.57, 119.85, 37.20. The NMR spectroscopic data

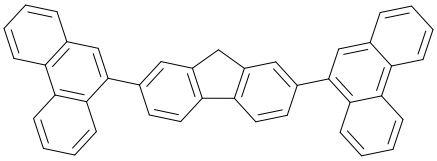
match previously reported data.[2] HRMS (ESI) *m/z* calcd for $C_{33}H_{22}Na^+$ $[M+Na]^+$: 441.1619, found 441.1621.

2,7-bis(9-anthracenyl)fluorene (13)



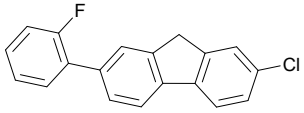
White solid (1.05 g, 81%); ^{1}H NMR (500 MHz, Tetrachloroethane-d_2) δ 8.56 (s, 2H), 8.15 (dd, J = 24.9, 7.8 Hz, 6H), 8.00 – 7.84 (m, 4H), 7.76 (s, 2H), 7.68 – 7.38 (m, 10H), 4.24 (s, 2H); ^{13}C NMR (126 MHz, Tetrachloroethane) δ 143.58, 140.75, 137.56, 137.23, 131.51, 130.43, 130.10, 128.14, 127.99, 126.79, 126.27, 125.12, 124.90, 119.65, 37.04; HRMS (ESI) *m/z* calcd for $C_{41}H_{26}Na^+$ $[M+Na]^+$: 541.1932, found 541.1926.

2,7-bis(9-phenanthrenyl)fluorene (14)



Yellow solid (0.94 g, 73%); ^{1}H NMR (500 MHz, Tetrachloroethane-d_2) δ 8.83 (d, J = 8.0 Hz, 2H), 8.77 (d, J = 7.8 Hz, 2H), 8.05 (t, J = 9.2 Hz, 4H), 7.97 (d, J = 7.3 Hz, 2H), 7.82 (d, J = 8.0 Hz, 4H), 7.74 (s, 4H), 7.69 (d, J = 7.4 Hz, 2H), 7.63 (dd, J = 18.3, 7.7 Hz, 4H), 4.15 (s, 2H).; ^{13}C NMR (126 MHz, Tetrachloroethane) δ 143.54, 140.66, 139.52, 139.03, 131.66, 131.41, 130.72, 130.00, 128.84, 128.48, 127.27, 126.90, 126.65, 126.60, 126.36, 126.33, 126.26, 122.76, 122.40, 119.57, 37.05; HRMS (ESI) *m/z* calcd for $C_{41}H_{26}Na^+$ [M+Na]: 541.1932, found 541.1935.

2-Chloro-7-(2-fluorophenyl)-fluorene (15)



Yellow solid (0.60 g, 80%); ^{1}H NMR (500 MHz, Chloroform-d) δ 7.82 (d, J = 7.9 Hz, 1H), 7.76 – 7.69 (m, 2H), 7.58 (dt, J = 7.9, 1.7 Hz, 1H), 7.54 (d, J = 1.8 Hz, 1H), 7.49 (td, J = 7.8, 1.8 Hz, 1H), 7.39 – 7.31 (m, 2H), 7.25 – 7.15 (m, 2H), 3.95 (s, 2H); ^{13}C NMR (126 MHz, Tetrachloroethane) δ 158.92, 145.25, 143.29, 140.30, 139.99, 134.68, 132.69, 130.91, 130.89, 129.08, 129.01, 128.12, 127.29, 125.87, 125.84, 125.50, 124.52, 124.50, 121.00, 119.98, 116.35, 116.17, 36.94.

4. Crystallographic data for 7

Single crystal for X-ray diffraction analysis was isolated for **7** (CCDC: 2327221) by diffusing n-hexane into a solution of the compound in dichloromethane at -20℃. The crystal structure and the characteristic bond lengths and angles of **7** were determined.

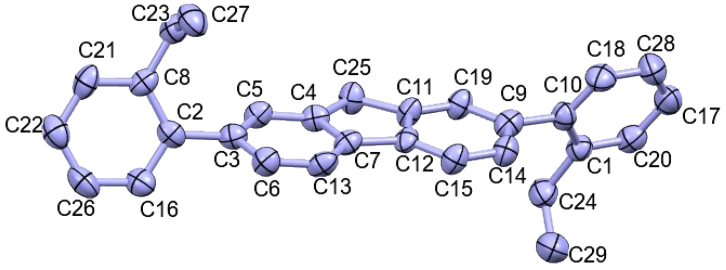


Figure S-1 Molecular structure of **7** drawn with 50% probability elliposoids. Hydrogen aroms are omitted for clarity.

Table S-1 Crystal data and structural refinements parameters of **7**

Chemical formula	$C_{29}H_{26}$
Mr (g / mol)	374.50
Crystal System	Triclinic
Space-Group	P
Temperature (K)	193(2)
a (Å)	7.944(2)
b (Å)	11.109(3)
c (Å)	13.450(4)
α (°)	70.038(14)
β (°)	75.929(15)
γ (°)	76.156(14)
V (Å^3)	1066.16
Z	2
Radiation type	Ga *K*a
μ (mm^{-1})	0.314
Crystal size (mm^3)	0.20 × 0.14× 0.12
F(000)	400
No. of measured	9993
No. of independent	2261
No. of observed [$I > 2\sigma(I)$] reflections	1725
R_{int}	0.0729
R[$F^2 > 2\sigma(F^2)$]	0.1416
wR(F^2)	0.3521
S/*GooF*/*GoF*	1.563
No. of reflections	2261
No. of paramenters	265
No. of restrains	0
H-atom treatment	Constr
$\Delta\rho_{max}$ (*e* Å^{-3})	0.774
$\Delta\rho_{min}$ (*e* Å^{-3})	-0.381

Table S-2 The bond length of single crystal structure

Number	Atom1	Atom2	Length
1	C1	C10	1.391(8)
2	C1	C20	1.40(1)
3	C1	C24	1.50(1)
4	C2	C3	1.496(8)
5	C2	C8	1.421(9)
6	C2	C16	1.37(1)
7	C3	C5	1.38(1)
8	C3	C6	1.40(1)
9	C4	C5	1.386(8)
10	C4	C7	1.397(9)
11	C4	C25	1.50(1)
12	C5	H5	0.951
13	C6	H6	0.95
14	C6	C13	1.369(9)
15	C7	C12	1.472(9)
16	C7	C13	1.39(1)
17	C8	C21	1.392(9)
18	C8	C23	1.49(1)
19	C9	C10	1.490(9)
20	C9	C14	1.40(1)
21	C9	C19	1.398(8)
22	C10	C18	1.385(9)
23	C11	C12	1.40(1)
24	C11	C19	1.370(9)
25	C11	C25	1.496(8)
26	C12	C15	1.394(8)
27	C13	H13	0.95
28	C14	H14	0.95
29	C14	C15	1.388(9)
30	C15	H15	0.95
31	C16	H16	0.95
32	C16	C26	1.38(1)
33	C17	H17	0.95
34	C17	C20	1.38(1)
35	C17	C28	1.37(1)
36	C18	H18	0.95
37	C18	C28	1.38(1)
38	C19	H19	0.949
39	C20	H20	0.95
40	C21	H21	0.949
41	C21	C22	1.40(1)
42	C22	H22	0.95
43	C22	C26	1.38(1)
44	C23	H23A	0.99
45	C23	H23B	0.99
46	C23	C27	1.499(9)
47	C24	H24A	0.99
48	C24	H24B	0.99
49	C24	C29	1.49(1)
50	C25	H25A	0.99
51	C25	H25B	0.99
52	C26	H26	0.95
53	C27	H27A	0.98

54	C27	H27B	0.98
55	C27	H27C	0.979
56	C28	H28	0.95
57	C29	H29A	0.98
58	C29	H29B	0.98
59	C29	H29C	0.98

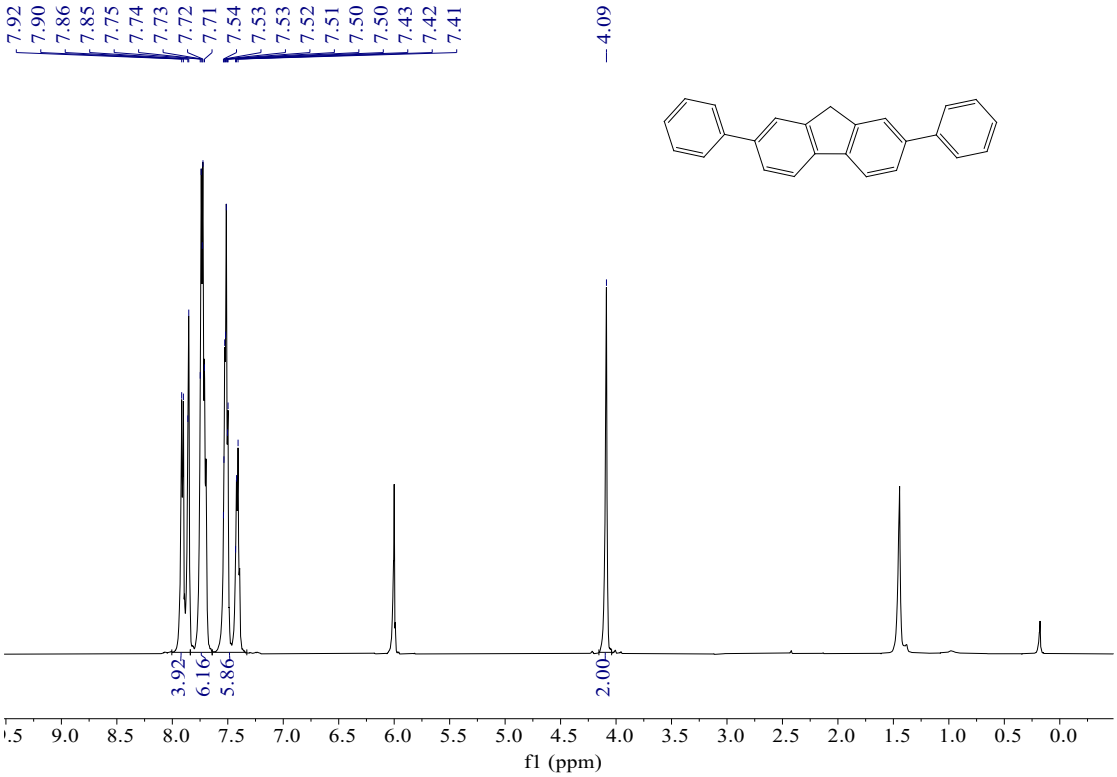
Table S-3 The bond Angle of the single crystal structure

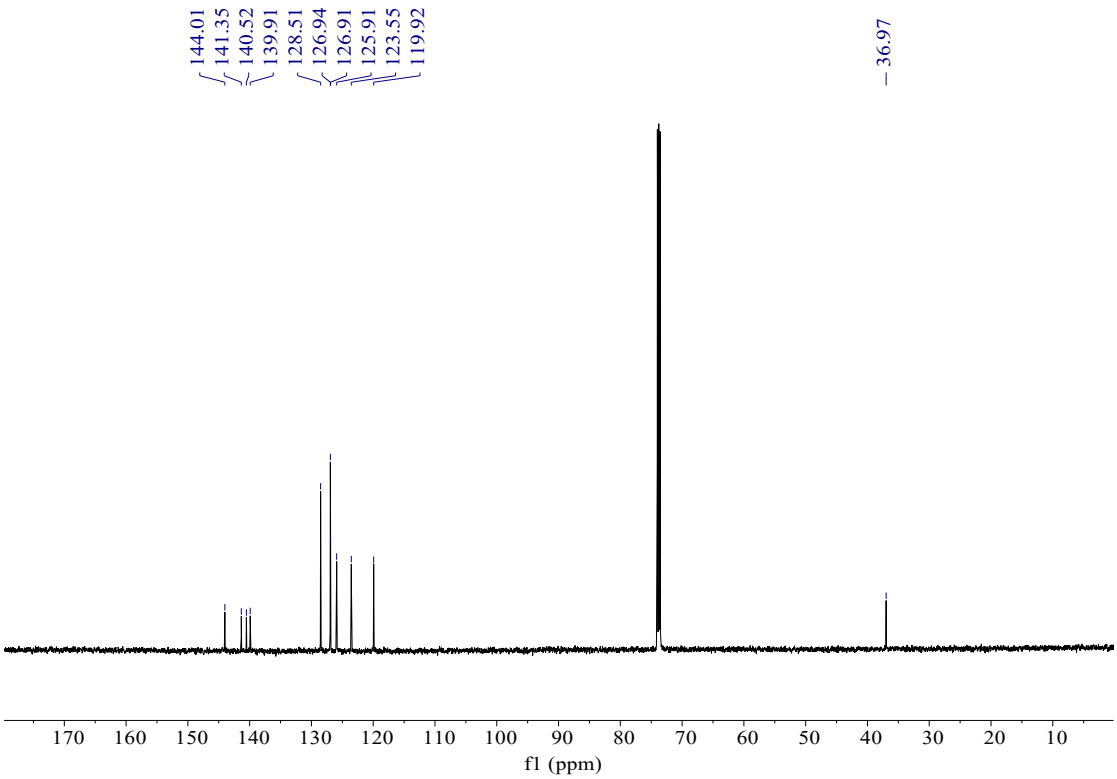
Number	Atom1	Atom2	Atom3	Angle
1	C10	C1	C20	118.2(6)
2	C10	C1	C24	122.9(6)
3	C20	C1	C24	118.8(6)
4	C3	C2	C8	120.5(6)
5	C3	C2	C16	119.9(6)
6	C8	C2	C16	119.7(6)
7	C2	C3	C5	120.7(6)
8	C2	C3	C6	120.4(6)
9	C5	C3	C6	118.9(6)
10	C5	C4	C7	120.0(6)
11	C5	C4	C25	130.2(6)
12	C7	C4	C25	109.7(5)
13	C3	C5	C4	120.4(6)
14	C3	C5	H5	119.9
15	C4	C5	H5	119.8
16	C3	C6	H6	119.4
17	C3	C6	C13	121.2(6)
18	H6	C6	C13	119.4
19	C4	C7	C12	108.4(6)
20	C4	C7	C13	119.7(6)
21	C12	C7	C13	131.9(6)
22	C2	C8	C21	118.3(6)
23	C2	C8	C23	122.5(6)
24	C21	C8	C23	118.9(6)
25	C10	C9	C14	119.7(6)
26	C10	C9	C19	121.8(6)
27	C14	C9	C19	118.5(6)
28	C1	C10	C9	121.4(6)
29	C1	C10	C18	119.2(6)
30	C9	C10	C18	119.4(6)
31	C12	C11	C19	119.5(6)
32	C12	C11	C25	109.8(6)
33	C19	C11	C25	130.6(6)
34	C7	C12	C11	108.4(6)
35	C7	C12	C15	131.1(6)
36	C11	C12	C15	120.5(6)
37	C6	C13	C7	119.8(6)
38	C6	C13	H13	120.1
39	C7	C13	H13	120.1
40	C9	C14	H14	119.5
41	C9	C14	C15	120.9(6)
42	H14	C14	C15	119.6
43	C12	C15	C14	119.1(6)
44	C12	C15	H15	120.5
45	C14	C15	H15	120.4

46	C2	C16	H16	119
47	C2	C16	C26	121.9(7)
48	H16	C16	C26	119.1
49	H17	C17	C20	120.4
50	H17	C17	C28	120.3
51	C20	C17	C28	119.3(7)
52	C10	C18	H18	119.2
53	C10	C18	C28	121.6(7)
54	H18	C18	C28	119.2
55	C9	C19	C11	121.4(6)
56	C9	C19	H19	119.3
57	C11	C19	H19	119.3
58	C1	C20	C17	121.9(7)
59	C1	C20	H20	119
60	C17	C20	H20	119
61	C8	C21	H21	119.6
62	C8	C21	C22	120.8(6)
63	H21	C21	C22	119.6
64	C21	C22	H22	120.1
65	C21	C22	C26	119.8(7)
66	H22	C22	C26	120.1
67	C8	C23	H23A	109.1
68	C8	C23	H23B	109
69	C8	C23	C27	112.7(6)
70	H23A	C23	H23B	107.8
71	H23A	C23	C27	109.1
72	H23B	C23	C27	109
73	C1	C24	H24A	109.3
74	C1	C24	H24B	109.2
75	C1	C24	C29	112.0(6)
76	H24A	C24	H24B	107.9
77	H24A	C24	C29	109.2
78	H24B	C24	C29	109.2
79	C4	C25	C11	103.5(5)
80	C4	C25	H25A	111
81	C4	C25	H25B	111.1
82	C11	C25	H25A	111.1
83	C11	C25	H25B	111.1
84	H25A	C25	H25B	109
85	C16	C26	C22	119.5(7)
86	C16	C26	H26	120.3
87	C22	C26	H26	120.2
88	C23	C27	H27A	109.4
89	C23	C27	H27B	109.4
90	C23	C27	H27C	109.5
91	H27A	C27	H27B	109.5
92	H27A	C27	H27C	109.5
93	H27B	C27	H27C	109.5
94	C17	C28	C18	119.8(7)
95	C17	C28	H28	120.1
96	C18	C28	H28	120.1
97	C24	C29	H29A	109.5
98	C24	C29	H29B	109.5
99	C24	C29	H29C	109.5
100	H29A	C29	H29B	109.5

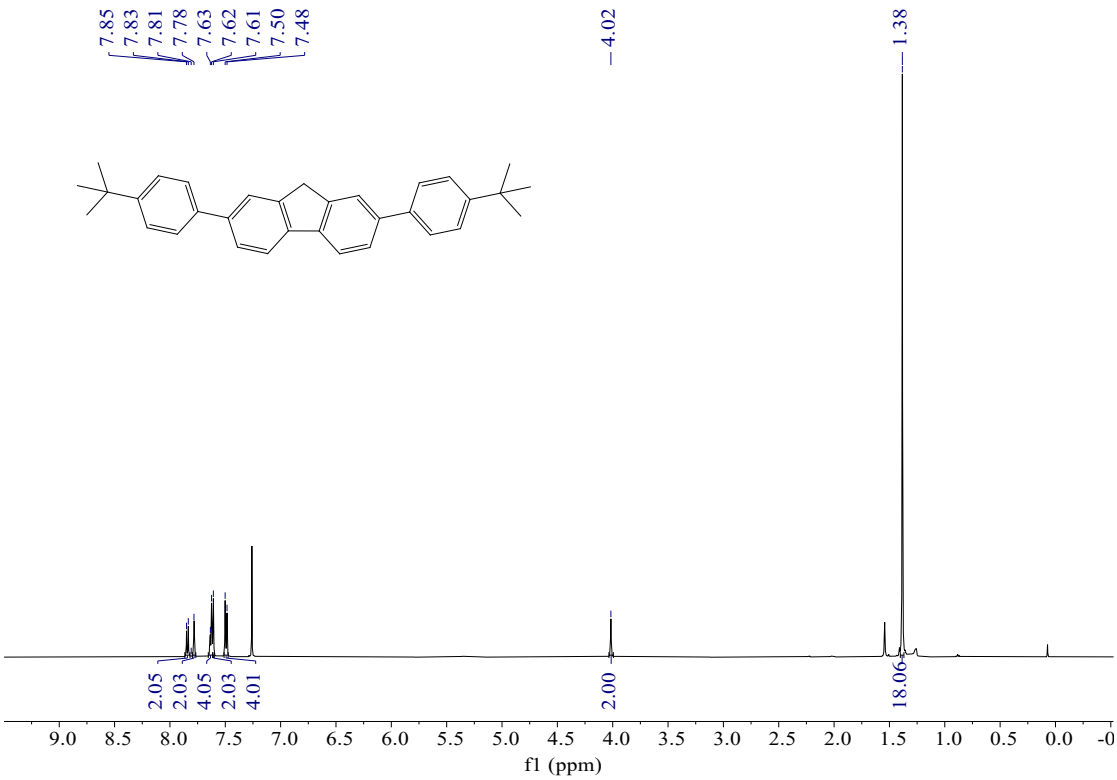
101	H29A	C29	H29C	109.5
102	H29B	C29	H29C	109.5

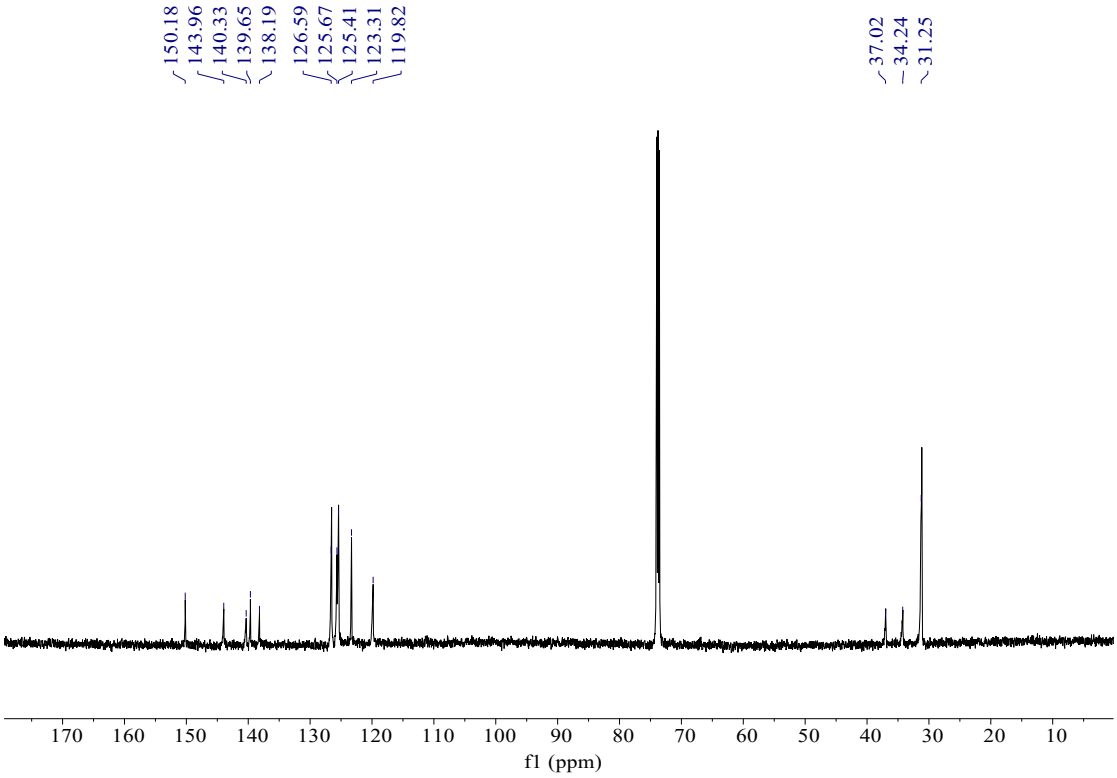
5. NMR Spectra



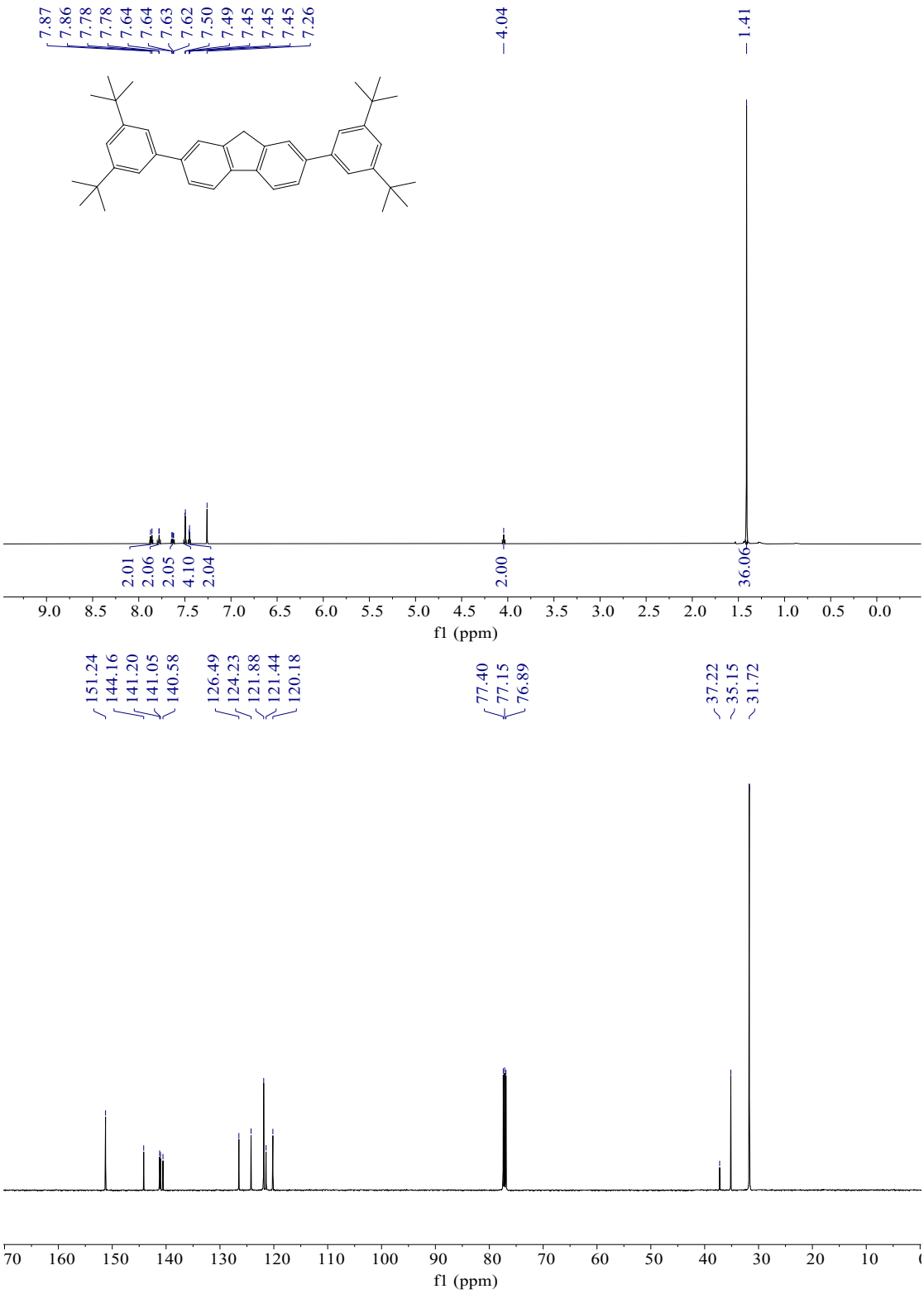


^{1}H and ^{13}C NMR of 2,7-diphenylfluorene (1)

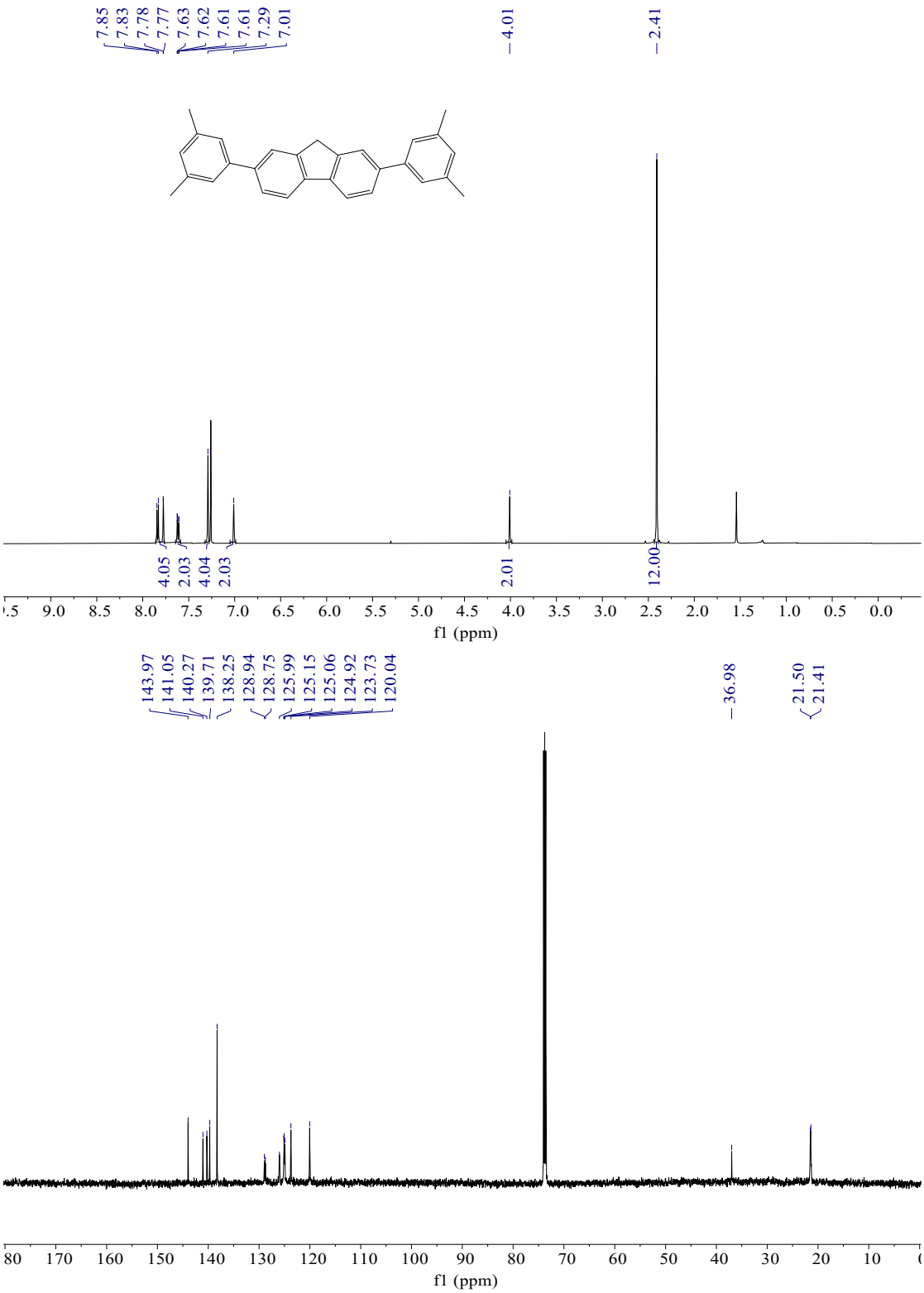




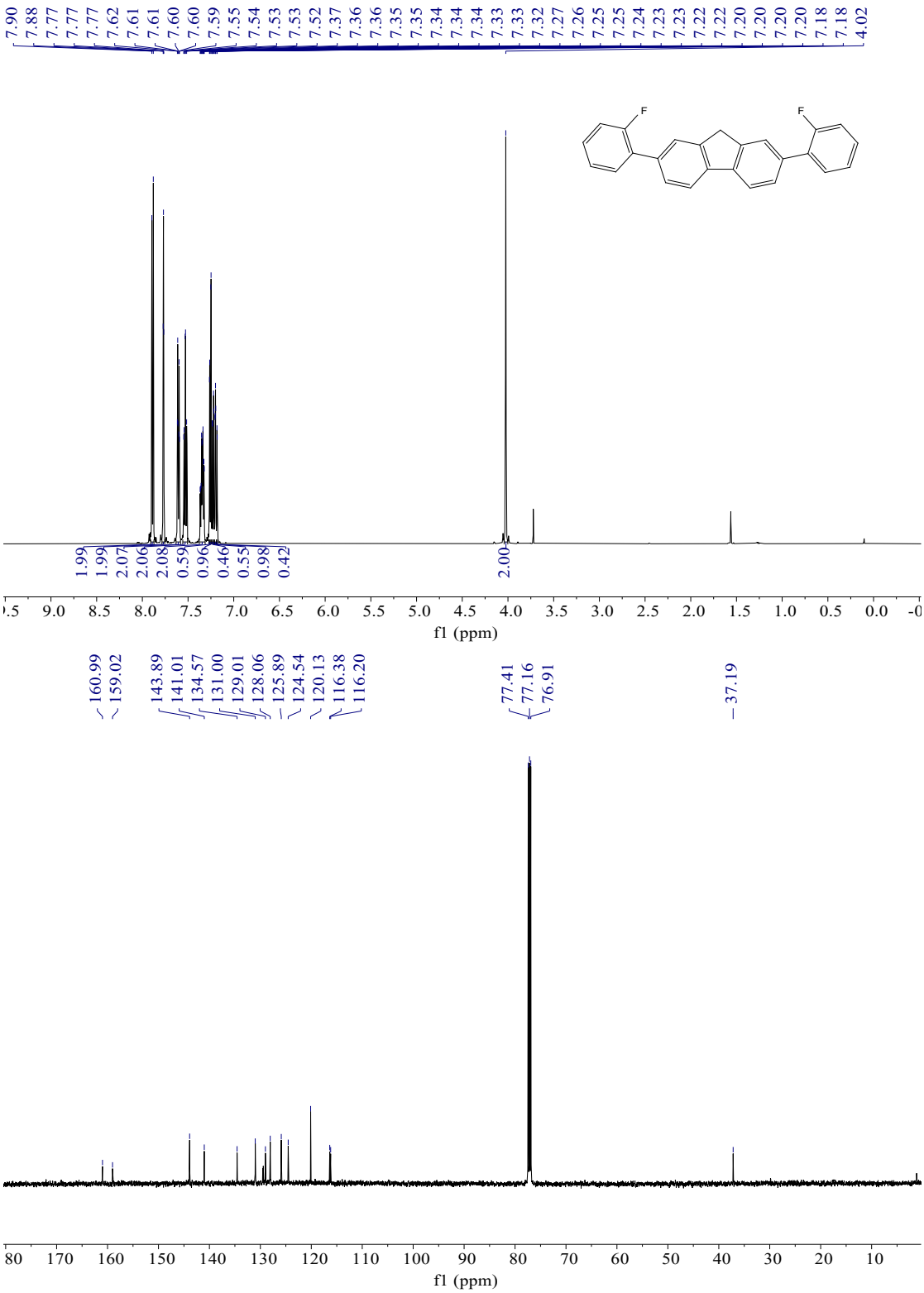
^{1}H and ^{13}C NMR of 2,7-bis(4-^{t}butylphenyl)fluorene (2)



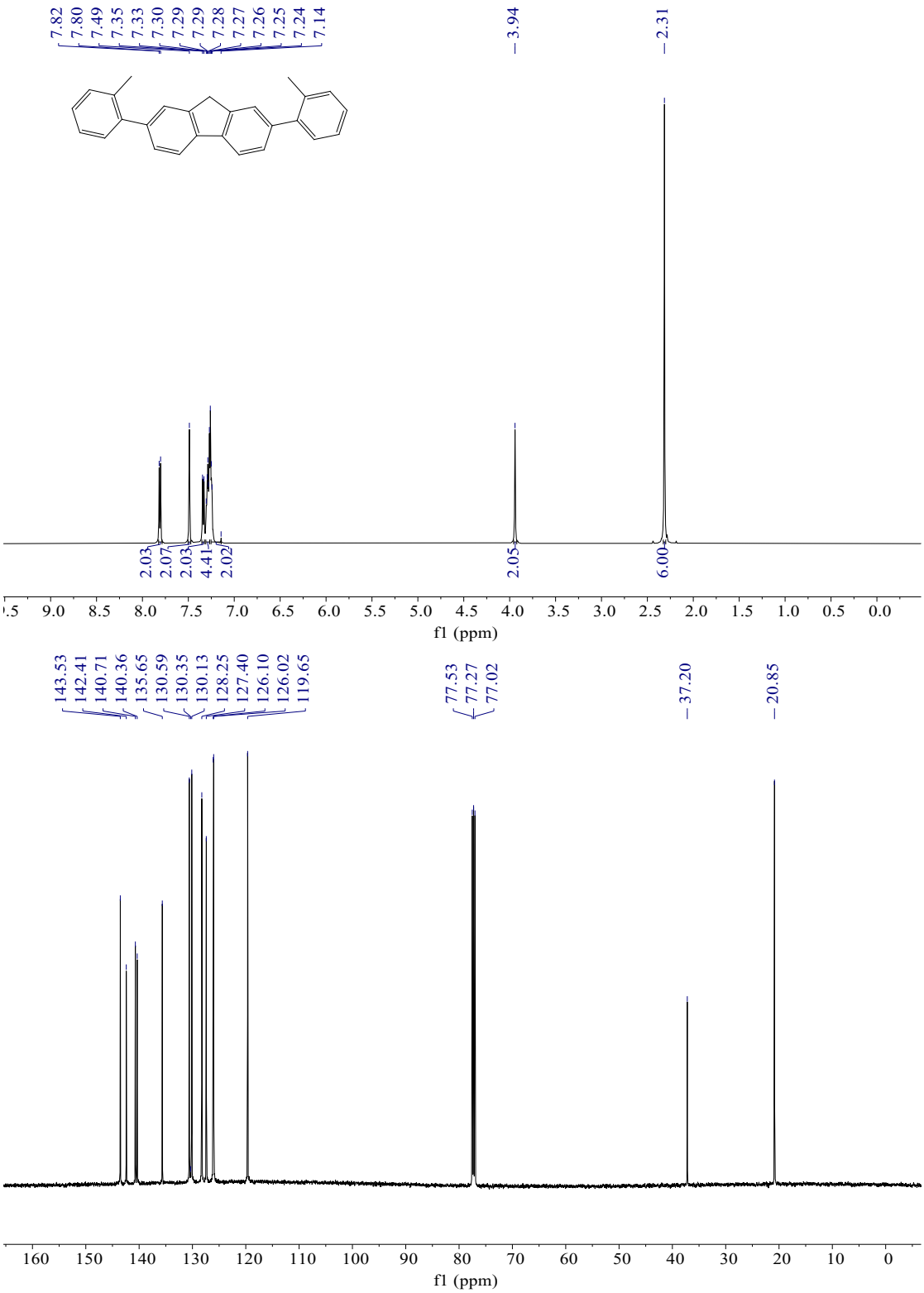
^{1}H and ^{13}C NMR of 2,7-bis(3,5-di^{t}butylphenyl)fluorene (3)



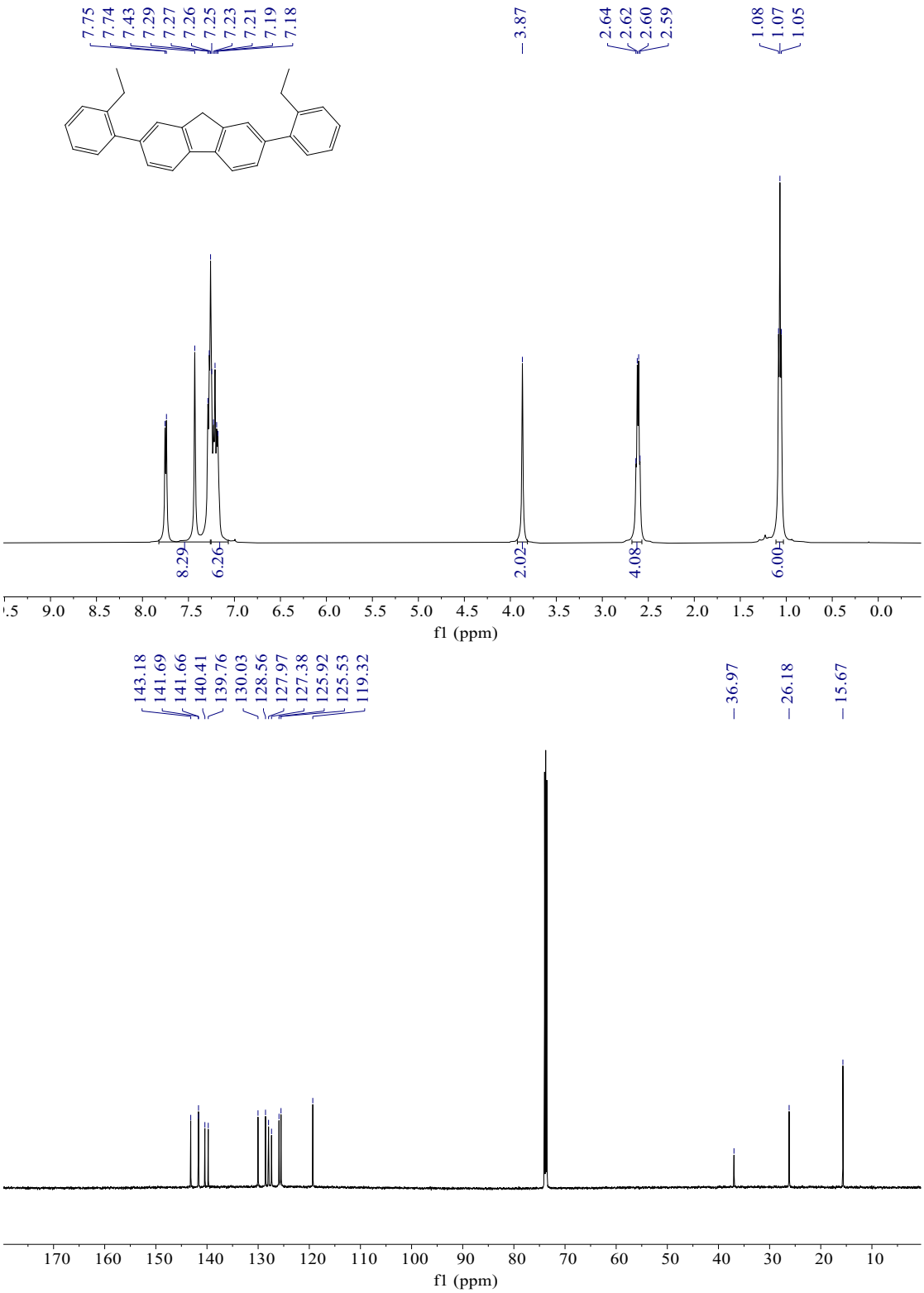
^{1}H and ^{13}C NMR of 2,7-bis(3,5-dimethylphenyl)fluorene (4)



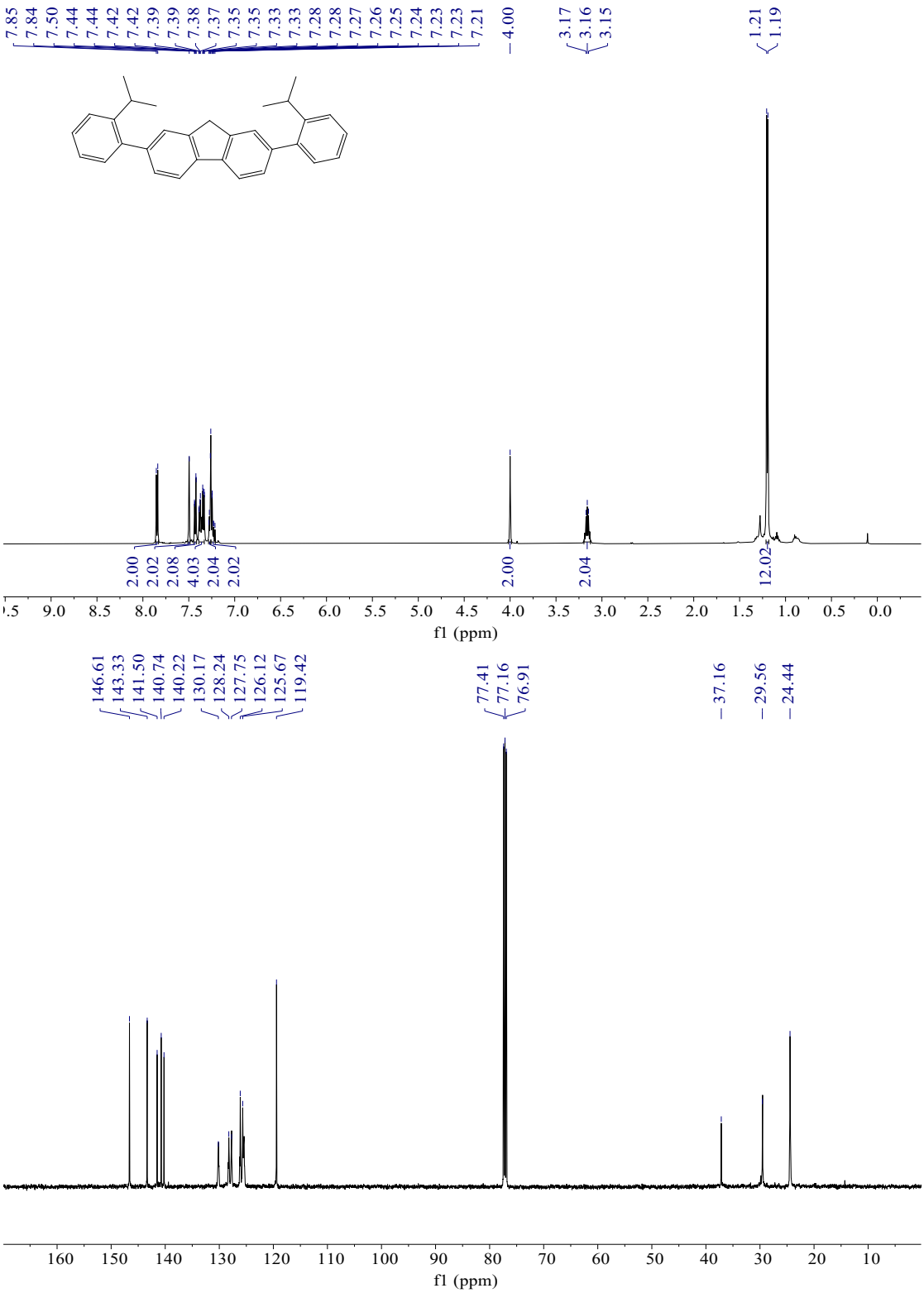
^{1}H and ^{13}C NMR of 2,7-bis(2-fluorophenyl)fluorene (5)



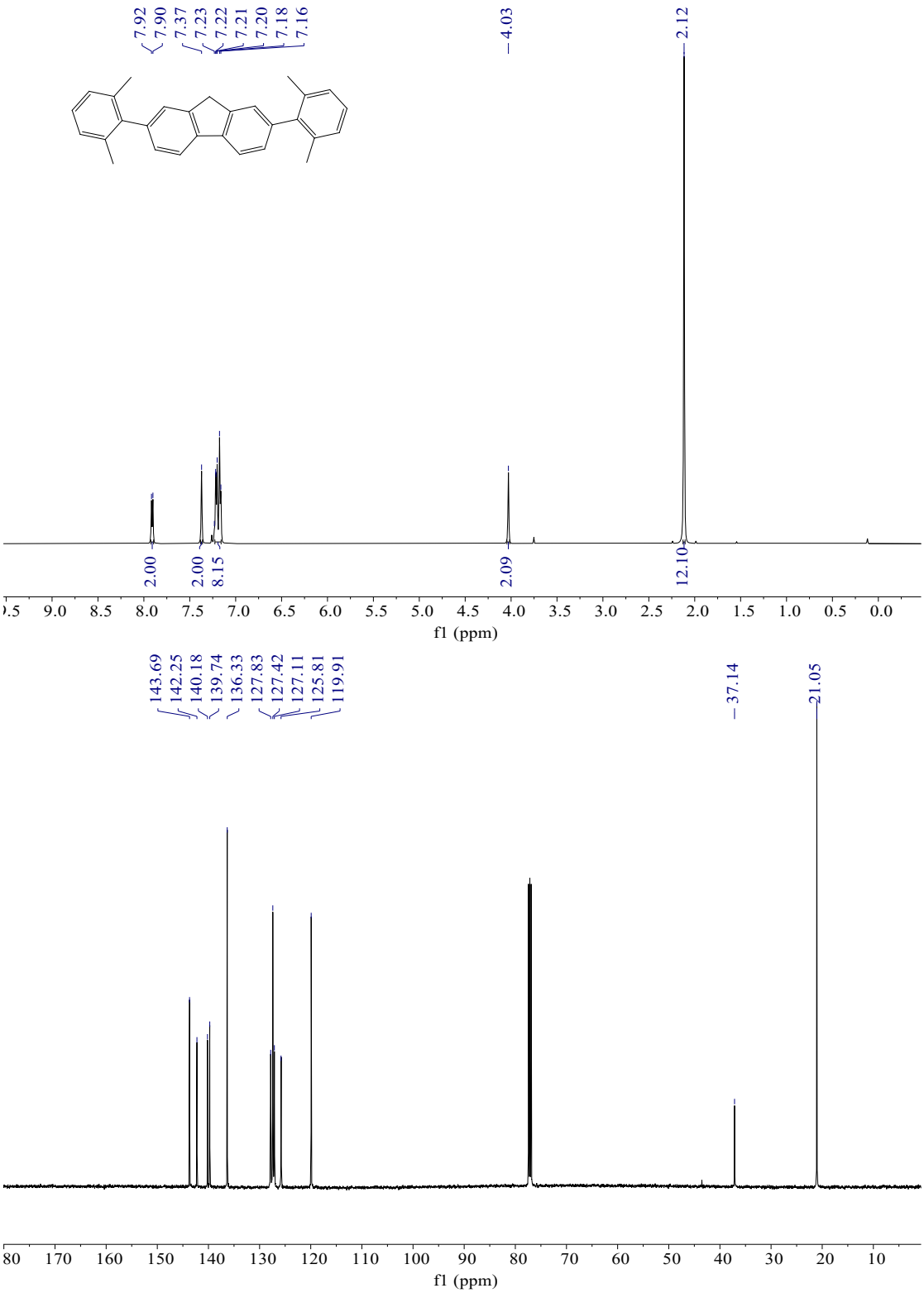
^{1}H and ^{13}C NMR of 2,7-bis(2-methylphenyl)fluorene (6)



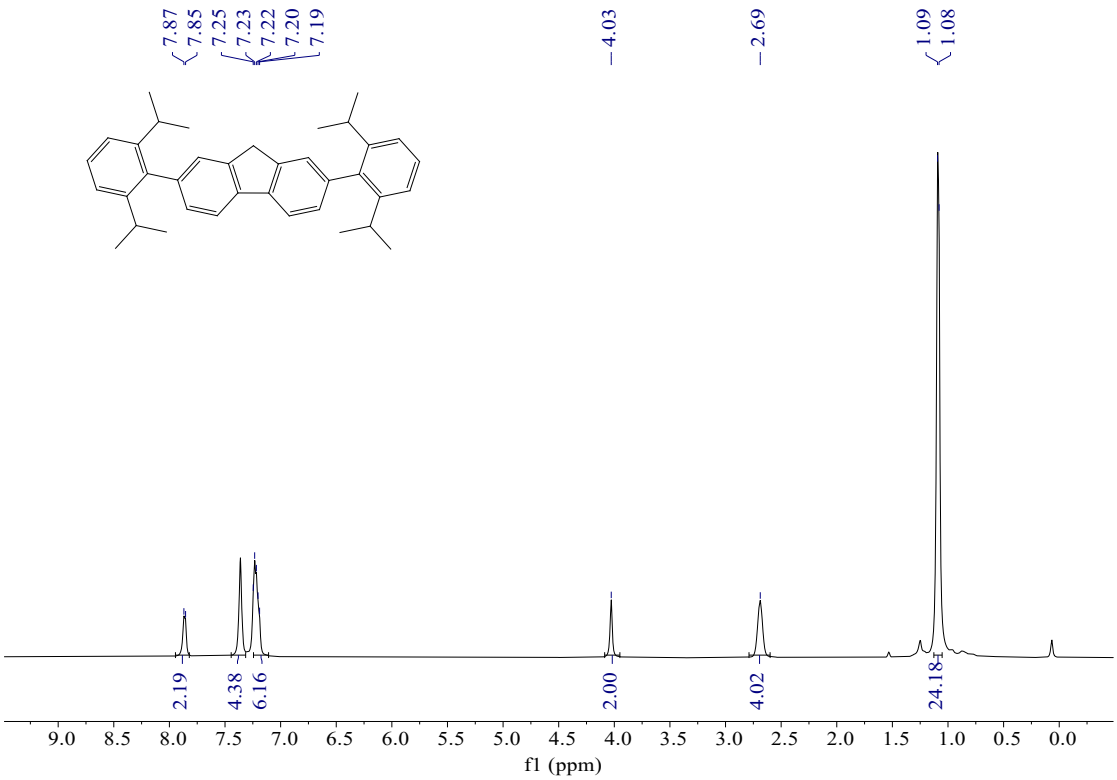
^{1}H and ^{13}C NMR of 2,7-bis(2-ethylphenyl)fluorene (7)

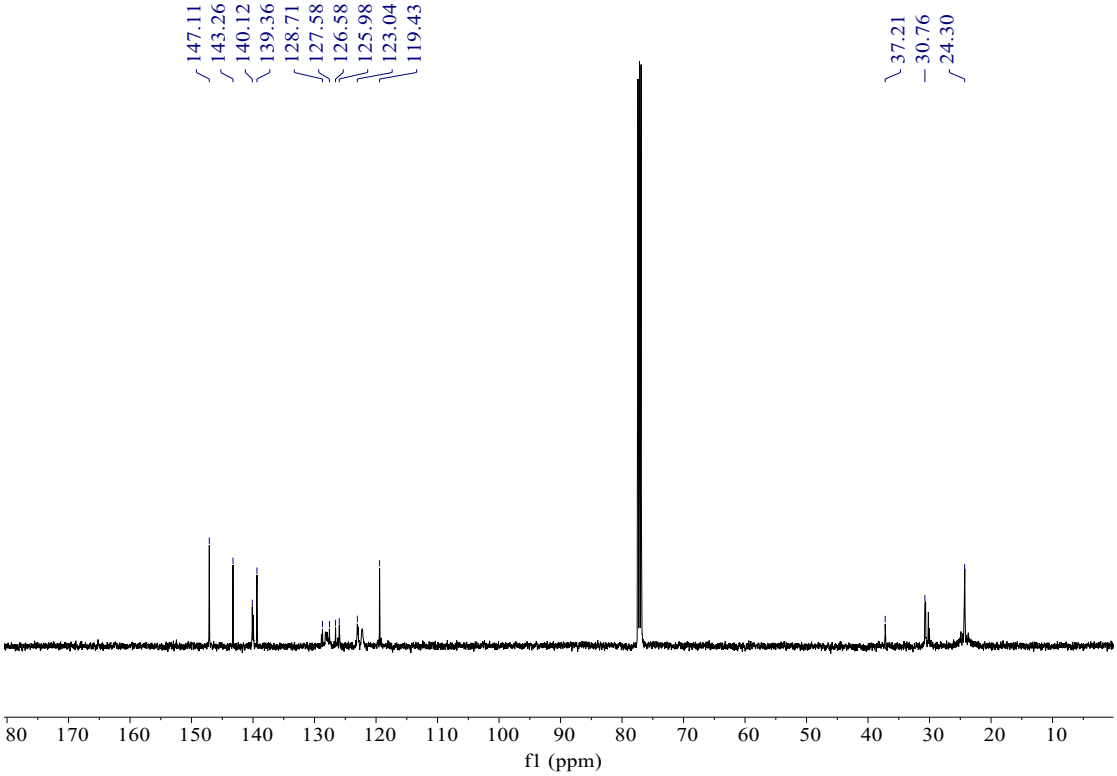


^{1}H and ^{13}C NMR of 2,7-bis(2-^{iso}propylphenyl)fluorene (8)

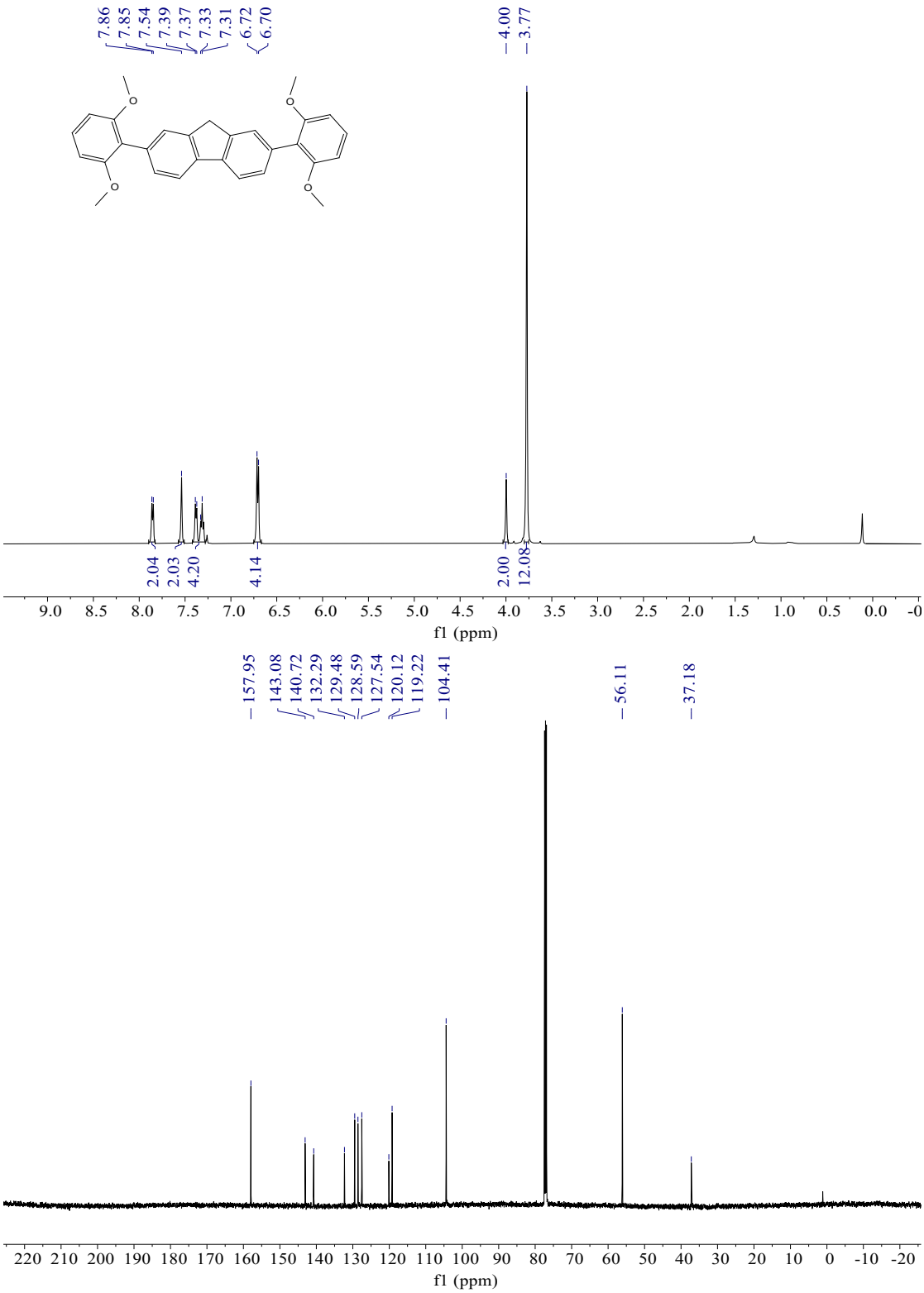


^{1}H and ^{13}C NMR of 2,7-bis(2,6-dimethylphenyl)fluorene (9)

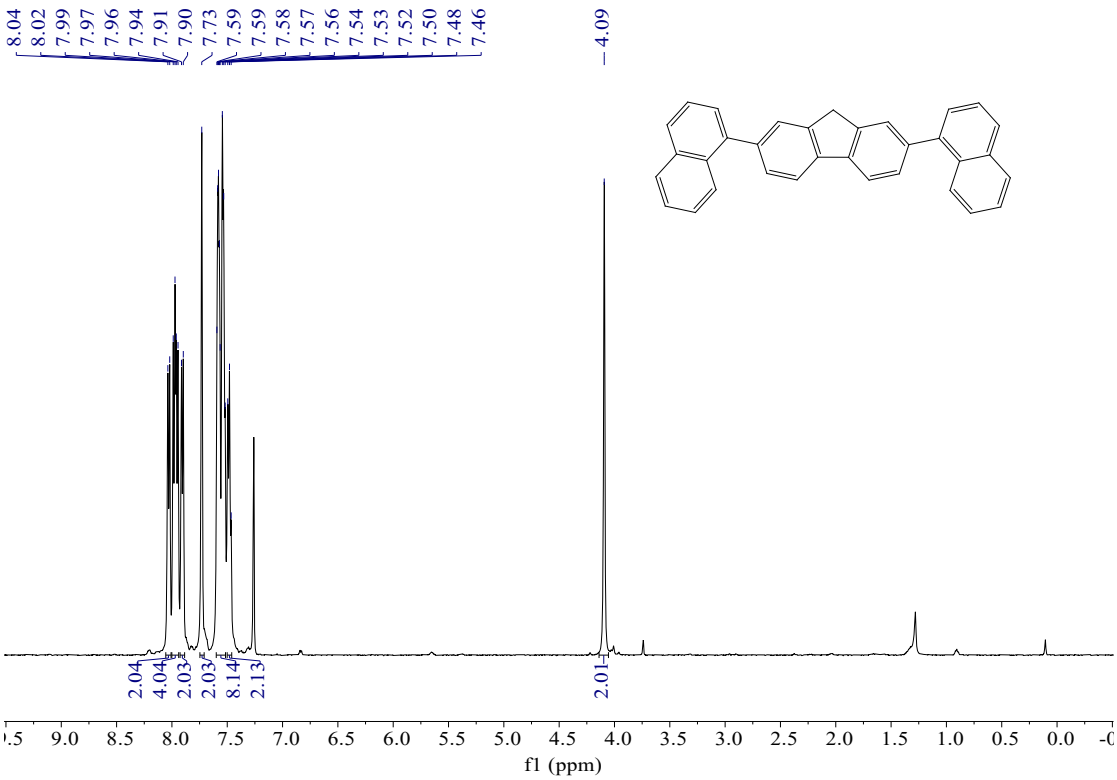


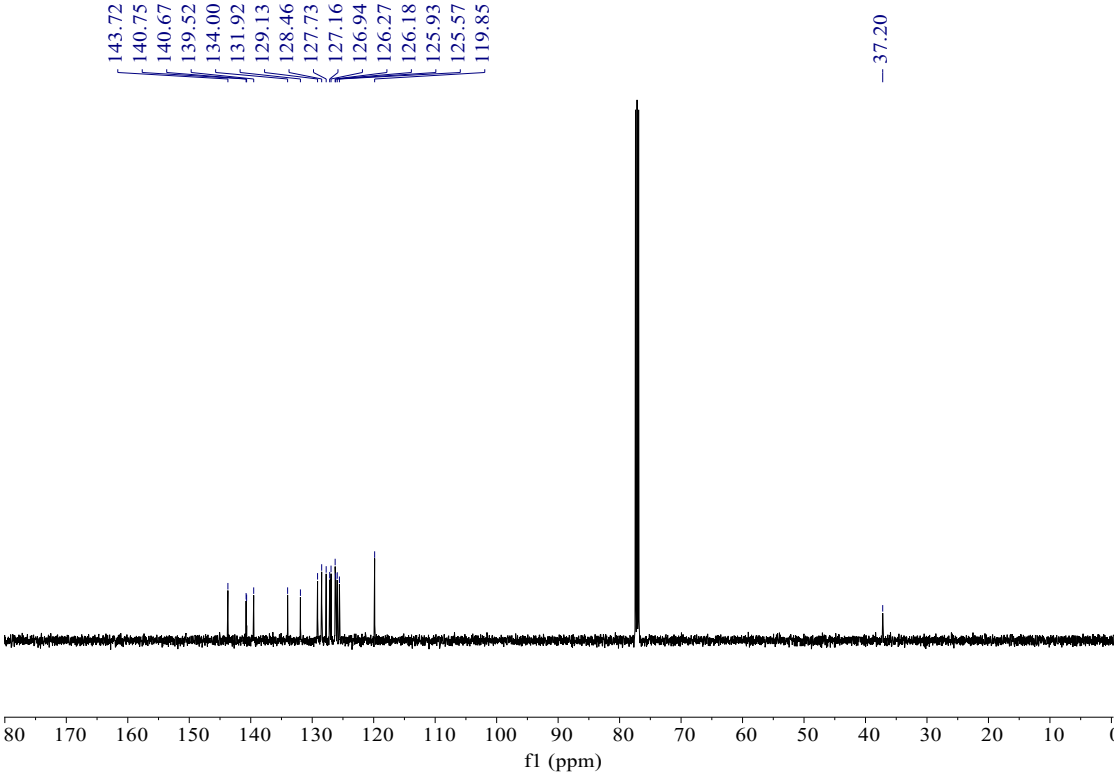


^{1}H and ^{13}C NMR of 2,7-bis(2,6-di^{iso}propylphenyl)fluorene (10)

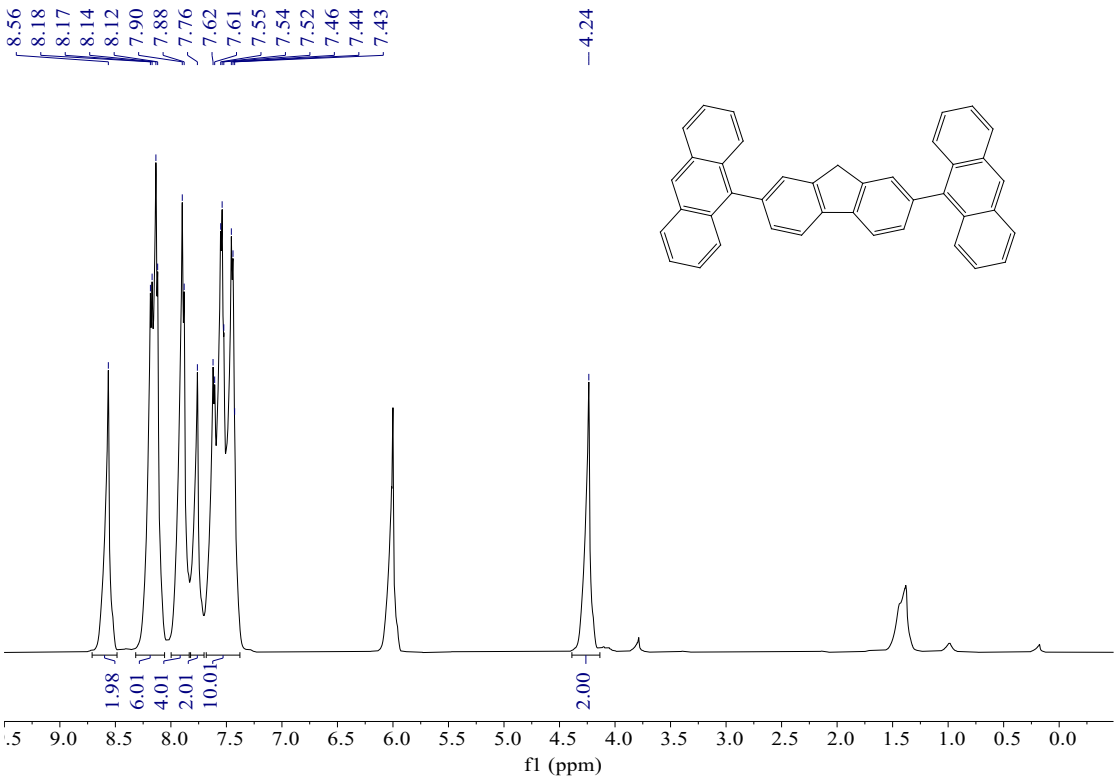


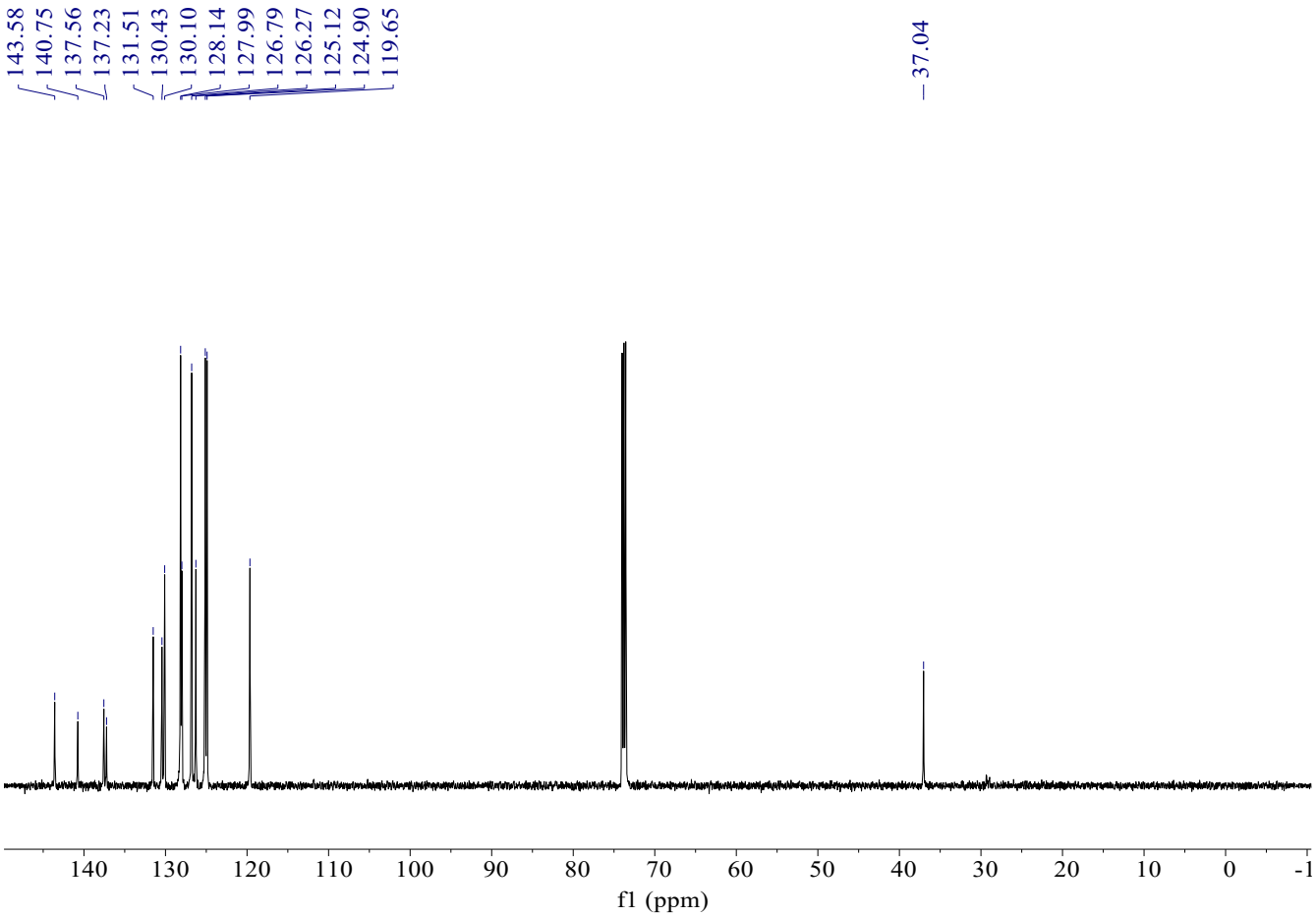
^{1}H and ^{13}C NMR of 2,7-bis(2,6-dimethoxyphenyl)fluorene (11)



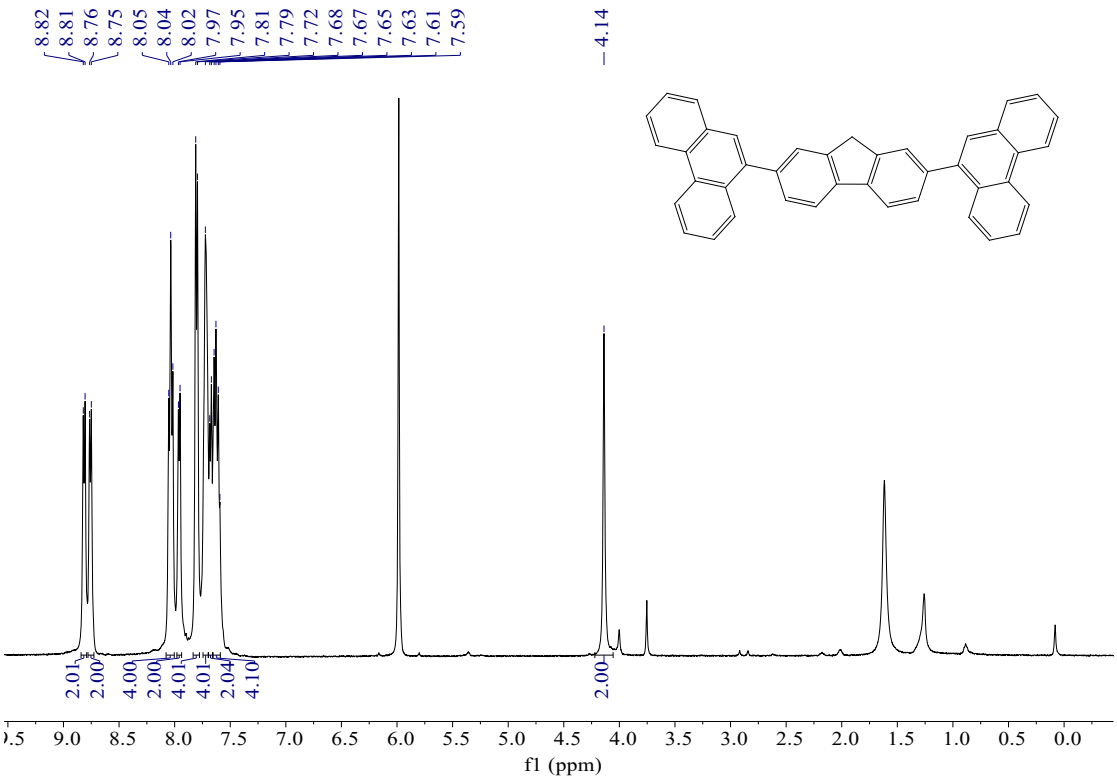


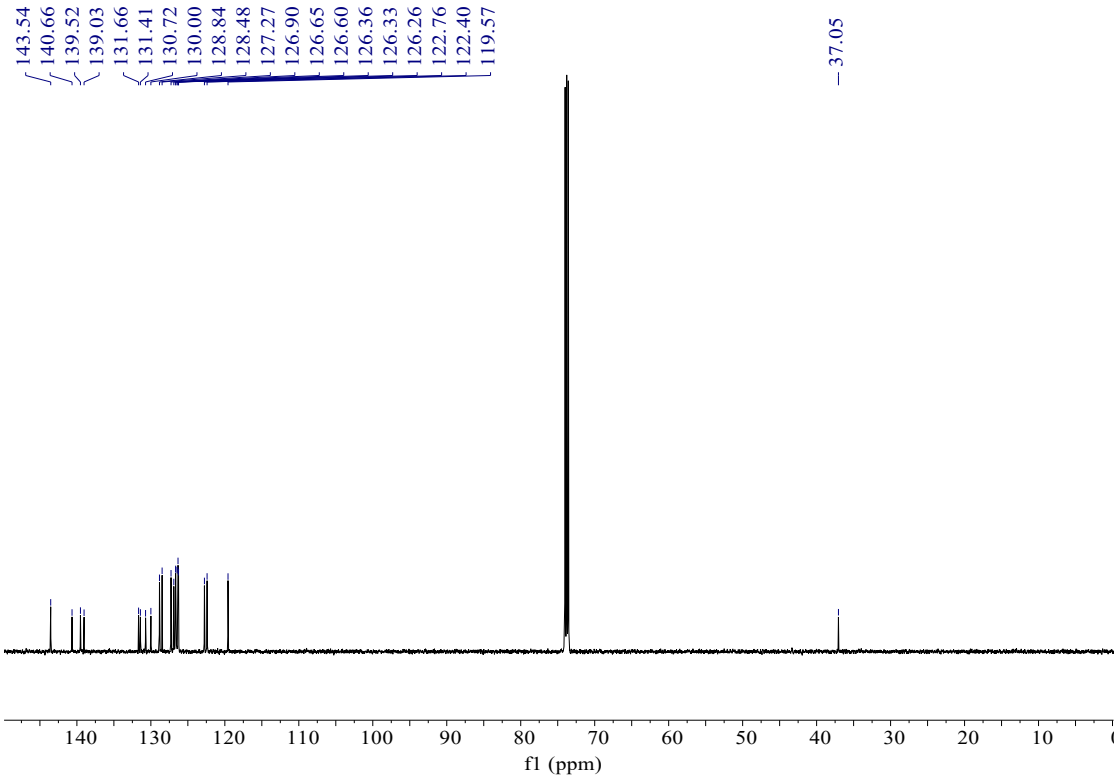
^{1}H and ^{13}C NMR of 2,7-di(naphthalen-1-yl)fluorene (12)



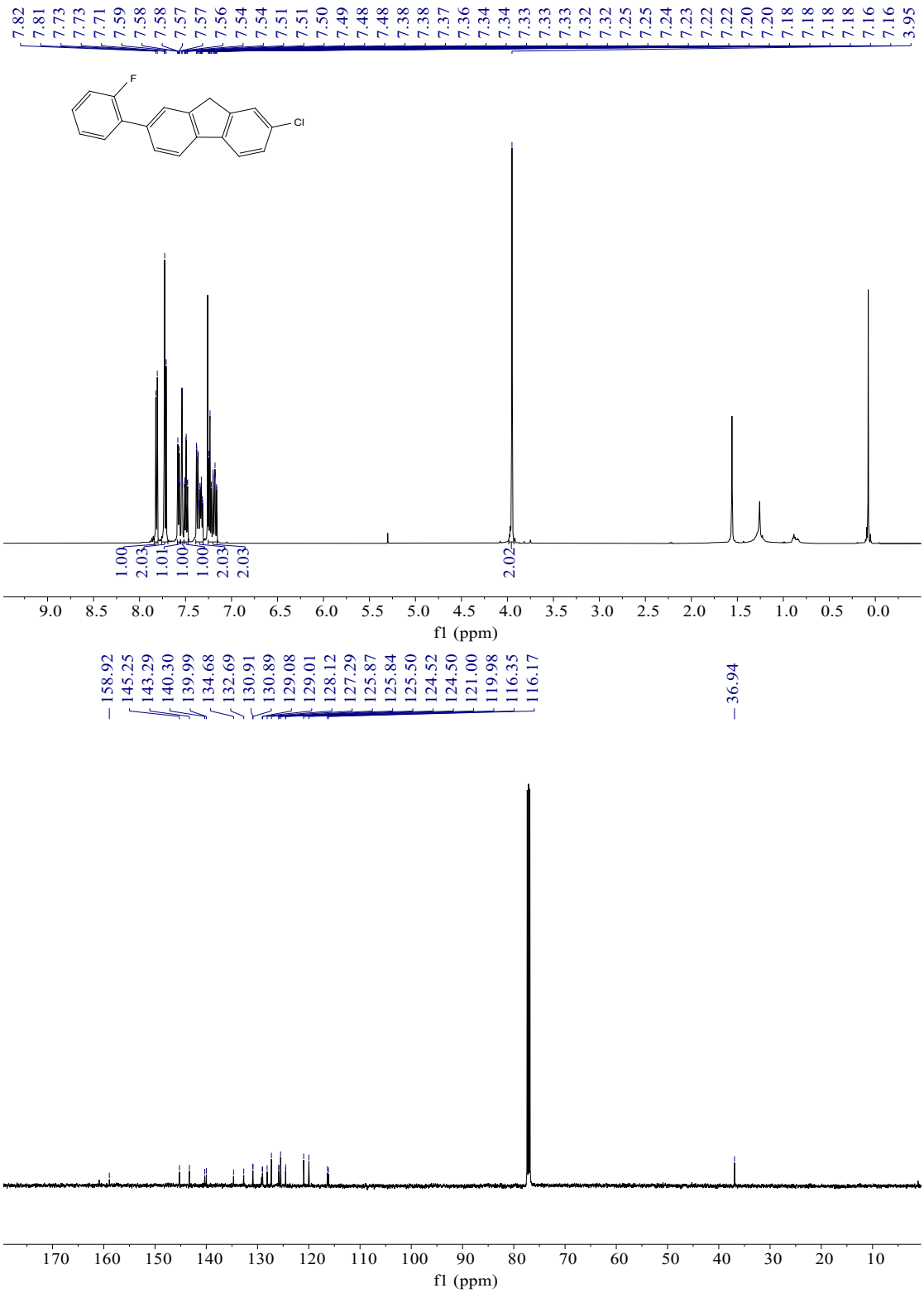


^{1}H and ^{13}C NMR of 2,7-bis(9-anthracenyl)fluorene (13)





^{1}H and ^{13}C NMR of 2,7-bis(9-phenanthrenyl)fluorene (14)



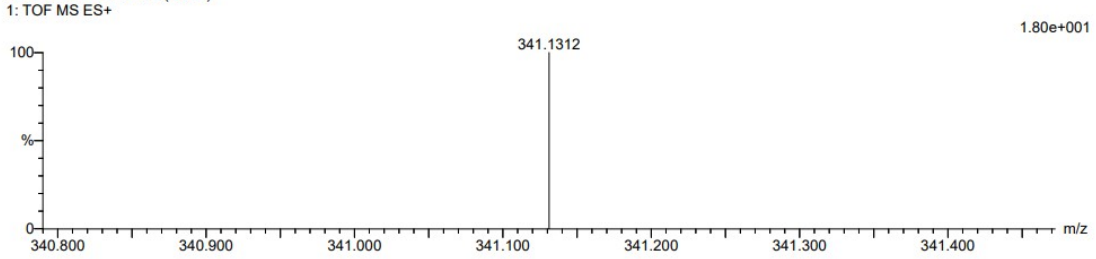
^{1}H and ^{13}C NMR of 2-Chloro-7-(2-fluorophenyl)-fluorene (15)

6. HRMS analysis reports for the compounds

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
3 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-25 H: 0-19 B: 0-1 Na: 0-1
20240120-1-4-Pos 130 (0.529)
1: TOF MS ES+



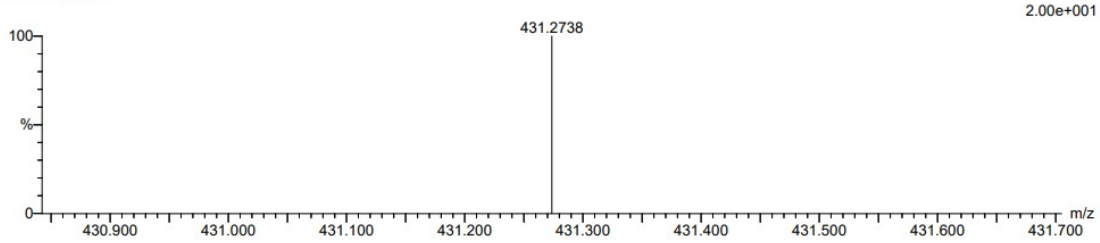
Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
341.1312	341.1306	0.6	1.8	16.5	12.8	n/a	n/a	C25 H18 Na

HRMS (ESI) spectra of 1

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
7 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-33 H: 0-35 B: 0-1 Na: 0-1
20240120-1-8-Pos 125 (0.505)
1: TOF MS ES+



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
431.2738	431.2739	-0.1	-0.2	16.5	14.1	n/a	n/a	C33 H35

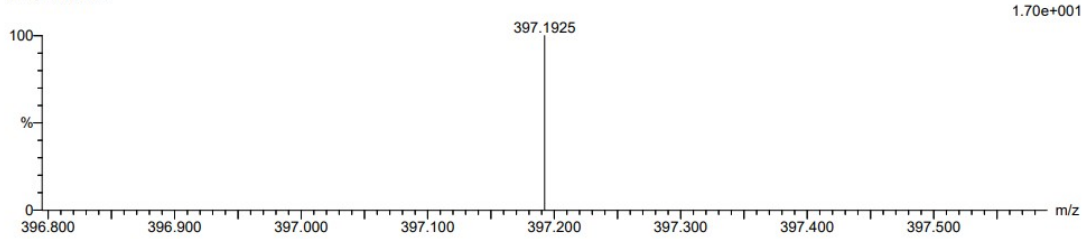
HRMS (ESI) spectra of 2

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
3 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-29 H: 0-27 B: 0-1 Na: 0-1

20240120-1-1-Pos 102 (0.418)
1: TOF MS ES+



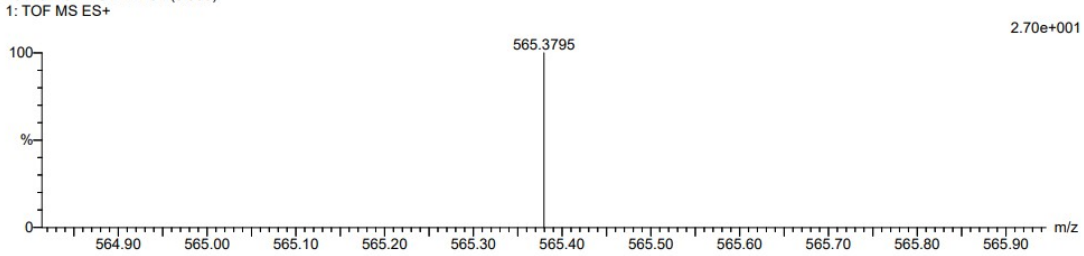
Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
397.1925	397.1932	-0.7	-1.8	16.5	13.2	n/a	n/a	C29 H26 Na

HRMS (ESI) spectra of 3

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
3 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-41 H: 0-55 B: 0-1 Na: 0-1
20240120-1-10-Pos 251 (0.999)
1: TOF MS ES+



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
565.3795	565.3810	-1.5	-2.7	16.5	15.8	n/a	n/a	C41 H50 Na

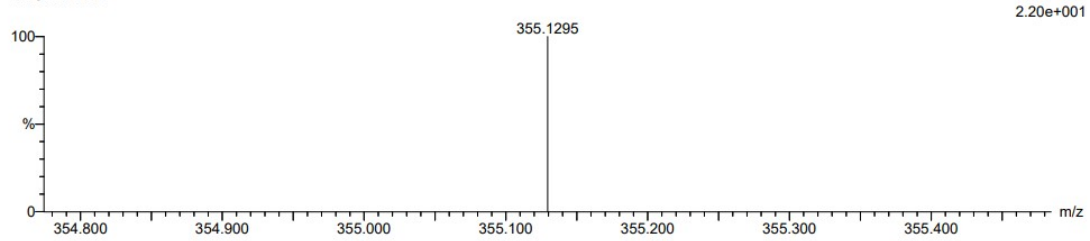
HRMS (ESI) spectra of 4

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
7 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-25 H: 0-17 B: 0-1 Na: 0-1 F: 0-2

20240120-1-9-Pos 107 (0.437)
1: TOF MS ES+



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
355.1295	355.1298	-0.3	-0.8	16.5	13.4	n/a	n/a	C25 H17 F2

HRMS (ESI) spectra of 5

National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution ESI-MS REPORT

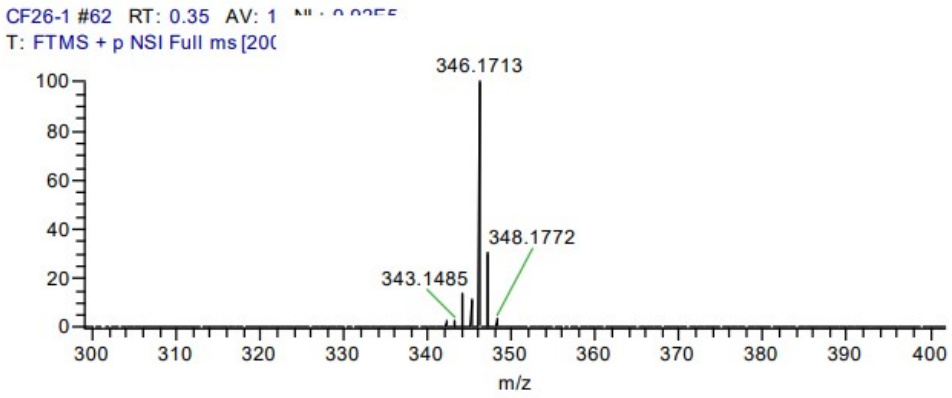
Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS

Card Serial Number: E-W2024011504

Sample Serial Number: CF26-1

Operator: Wang HY Date: 2024/01/15

Operation Mode: AP-MALDI Positive Ion Mode



Elemental composition search on mass 346.1713

m/z= 341.1713-351.1713

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
346.1713	346.1716	-0.99	17.0	$C_{27}H_{22}$

HRMS (ESI) spectra of 6

National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution ESI-MS REPORT

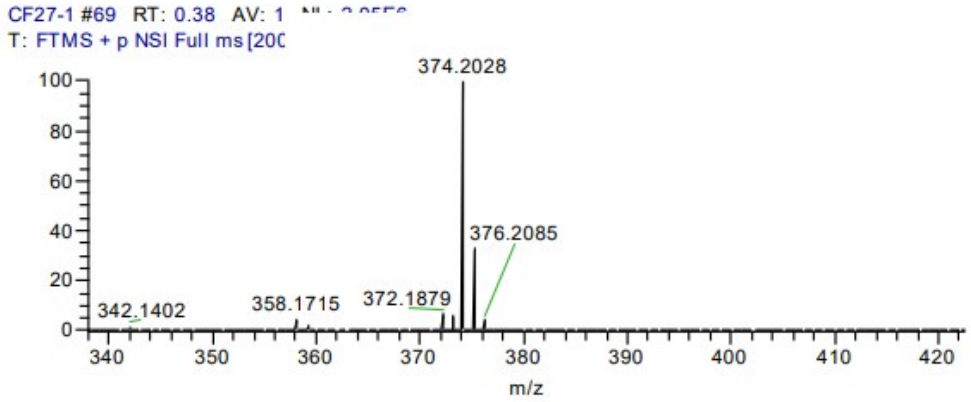
Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS

Card Serial Number: E-W2024011503

Sample Serial Number: CF27-1

Operator: Wang HY Date: 2024/01/15

Operation Mode: AP-MALDI Positive Ion Mode



Elemental composition search on mass 374.2028

m/z= 369.2028-379.2028

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
374.2028	374.2029	-0.38	17.0	$C_{29}H_{26}$

HRMS (ESI) spectra of 7

National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution ESI-MS REPORT

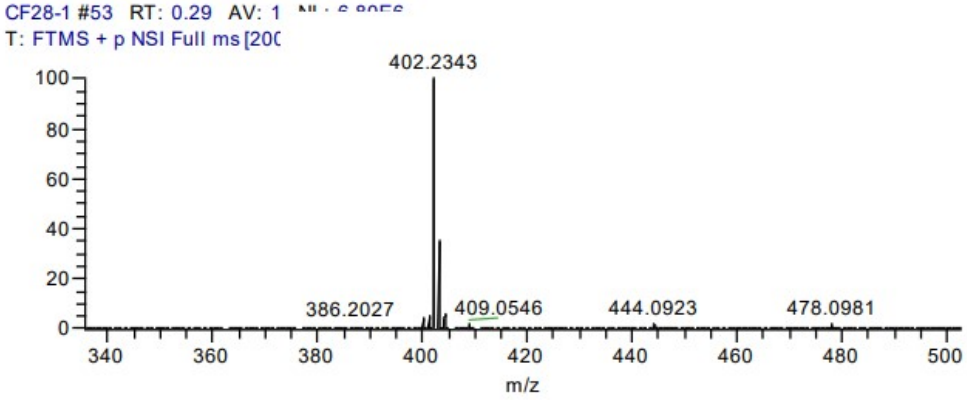
Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS

Card Serial Number: E-W2024011502

Sample Serial Number: CF28-1

Operator: Wang HY Date: 2024/01/15

Operation Mode: AP-MALDI Positive Ion Mode



Elemental composition search on mass 402.2343

m/z= 397.2343-407.2343

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
402.2343	402.2342	0.27	17.0	$C_{31}H_{30}$

HRMS (ESI) spectra of 8

National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution ESI-MS REPORT

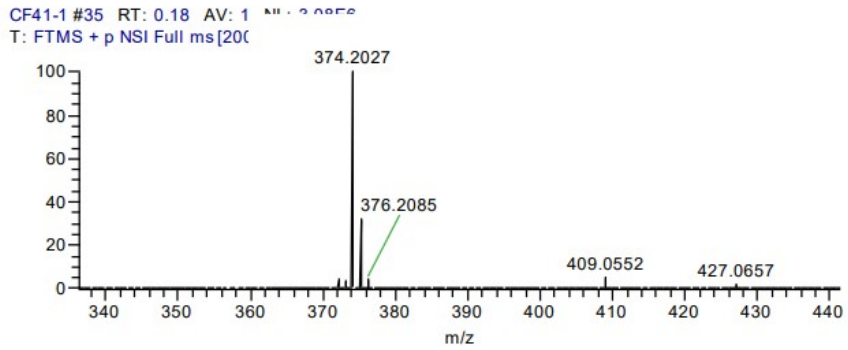
Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS

Card Serial Number: E-W2024011501

Sample Serial Number: CF41-1

Operator: Wang HY Date: 2024/01/15

Operation Mode: AP-MALDI Positive Ion Mode



Elemental composition search on mass 374.2027

m/z= 369.2027-379.2027

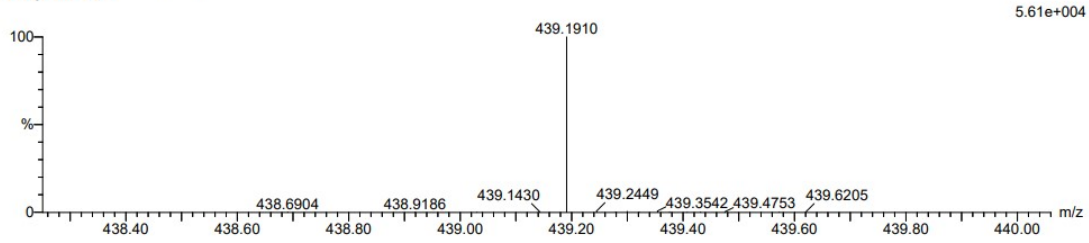
m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
374.2027	374.2029	-0.46	17.0	$C_{29}H_{26}$

HRMS (ESI) spectra of 9

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
13 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-29 H: 0-27 B: 0-1 O: 0-4 Na: 0-1
20240120-1-6-Pos 93 (0.384)
1: TOF MS ES+



Minimum:			-1.5	
Maximum:	5.0	10.0	50.0	

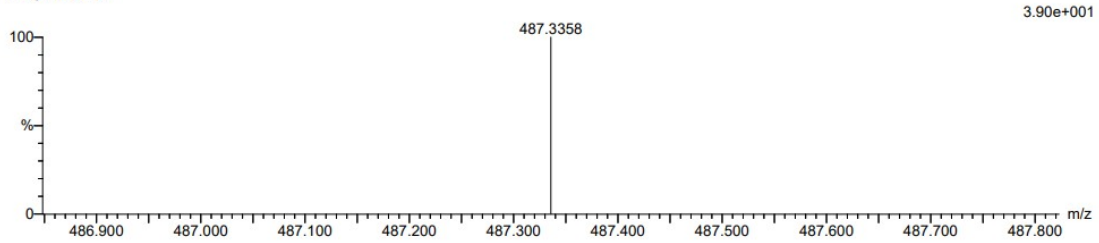
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
439.1910	439.1909	0.1	0.2	16.5	129.7	n/a	n/a	C29 H27 O4

HRMS (ESI) spectra of 10

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
7 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-37 H: 0-43 B: 0-1 Na: 0-1
20240120-1-5-Pos 331 (1.314)
1: TOF MS ES+



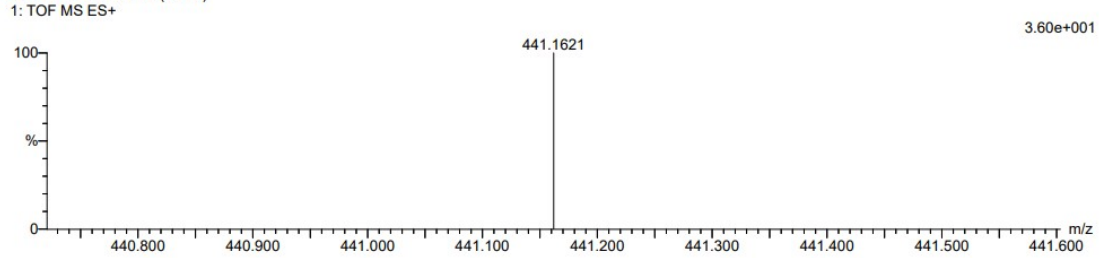
Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
487.3358	487.3365	-0.7	-1.4	16.5	16.4	n/a	n/a	C37 H43

HRMS (ESI) spectra of 11

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
3 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-33 H: 0-23 B: 0-1 Na: 0-1
20240120-1-3-Pos 75 (0.310)
1: TOF MS ES+



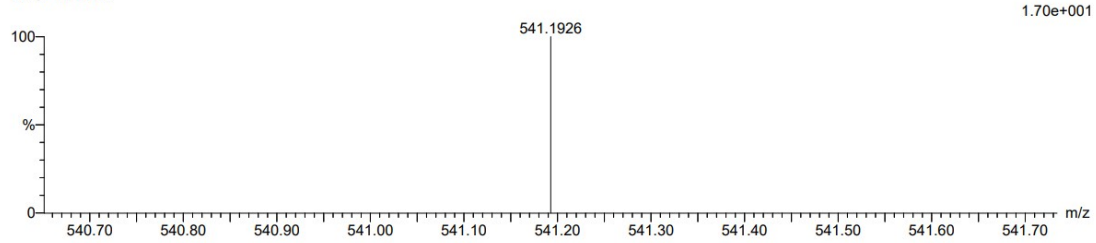
Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
441.1621	441.1619	0.2	0.5	22.5	15.8	n/a	n/a	C33 H22 Na

HRMS (ESI) spectra of 12

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
3 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-41 H: 0-27 B: 0-1 Na: 0-1
20240120-1-11-Pos 60 (0.253)
1: TOF MS ES+



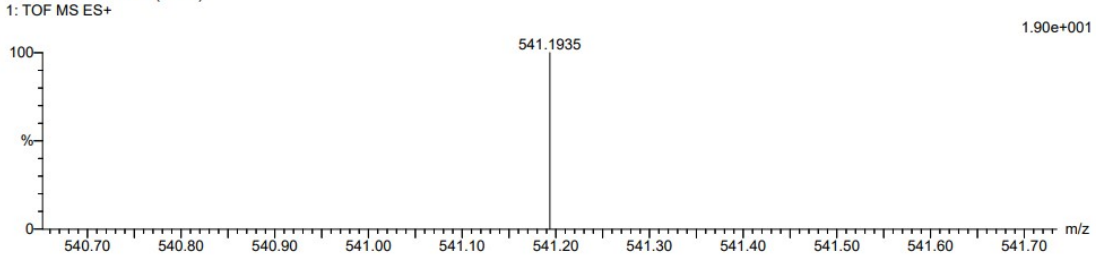
Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
541.1926	541.1932	-0.6	-1.1	28.5	14.4	n/a	n/a	C41 H26 Na

HRMS (ESI) spectra of 13

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
3 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-41 H: 0-27 B: 0-1 Na: 0-1
20240120-1-2-Pos 92 (0.380)
1: TOF MS ES+



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
541.1935	541.1932	0.3	0.6	28.5	14.7	n/a	n/a	C41 H26 Na

HRMS (ESI) spectra of 14

7. References

1. H. E. Gottlieb, V. Kotlyar and A. Nudelman, NMR Chemical Shifts of Common Laboratory Solvents as Trace Impurities, *J Org Chem*, 1997, **62**, 7512-7515.
2. H. G. Alt and R. Zenk, Syndiospezifische polymerisation von propylen: 2- und 2,7-substituierte metallocenkomplex des typs ($C_{13}H_{8-n}R_nCR'_2C_5H_4$)$MCl_2$ (n = 1,2; R = alkoxy, alkyl, aryl, hal; R′=Me, Ph; M = Zr, Hf), *J.Organomet*, 1996,

522, 39-54.
3. Z. Zhou, Y. Zhao, H. Zhen, Z. Lin and Q. J. A. O. C. Ling, Poly(ethylene glycol)- and glucopyranoside-substituted N-heterocyclic carbene precursors for the synthesis of arylfluorene derivatives using efficient palladium-catalyzed aqueous Suzuki reaction, *Appl. Organomet. Chem.* 2016, **30**, 924-931.
4. J. J. Esteb, M. Bergeron, C. N. Dormady, J. C. W. Chien and M. D. Rausch, Novel C1 symmetric zirconocenes containing substituted fluorenyl moieties for the polymerization of olefins, *J. Organomet*, 2003, **675**, 97-104.