Supporting Information

Chelation-assisted Pd-catalysed *ortho*-selective oxidative C–H/C–H cross-coupling of aromatic carboxylic acids with arenes and intramolecular Friedel-Crafts acylation: one-pot formation of fluorenones

Denan Sun, Bijin Li, Jingbo Lan,* Quan Huang and Jingsong You*

Key Laboratory of Green Chemistry and Technology of Ministry of Education, College of Chemistry, and State Key Laboratory of Biotherapy, West China Medical School, Sichuan University, 29 Wangjiang Road, Chengdu 610064, PR China

Fax: 86-28-85412203; E-mail: jingbolan@scu.edu.cn; jsyou@scu.edu.cn

Table of Contents

I. General remarks.....S3

II. Optimization of the synthesis of fluorenones.....S3

III. General procedure for the synthesis of flureones S6

IV. Mechanistic study.....S6

V. UV-Vis absorption and Emission spectra of **6**.....S8

VI. Experimental data for the described substances.....S8

VII. References.....S19

VIII. Copies of ^{1}H and ^{13}C NMR spectra.....S20

I. General Remarks

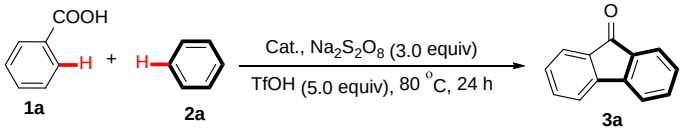
NMR spectra were obtained on a Bruker AV II-400 MHz spectrometer. The ^{1}H NMR (400 MHz) chemical shifts were measured relative to $CDCl_3$, TMS or DMSO-d_6 as the internal reference ($CDCl_3$: δ = 7.26 ppm; TMS: δ = 0.00 ppm; DMSO-d_6: δ = 2.50 ppm). The ^{13}C NMR (100 MHz) chemical shifts were given using $CDCl_3$ or DMSO-d_6 as the internal standard ($CDCl_3$: δ = 77.16 ppm; DMSO-d_6: δ = 39.52 ppm). High-resolution mass spectra (HRMS) were obtained with a Waters-Q-TOF-Premier (ESI). Melting points were determined with XRC-1 and are uncorrected. Absorption spectra were obtained on HITACHI U-2910 spectrometer. Fluorescence spectra and absolute quantum yields were collected on a Horiba Jobin Yvon-Edison Fluoromax-4 fluorescence spectrometer with a calibrated integrating sphere system.

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. $Pd(OAc)_2$ was purchased from Shanxi Kaida Chemical Engineering (China) CO., Ltd. All syntheses and manipulations were carried out under air atmosphere. Biphenyl-2-carboxylic acid was prepared according to the literature procedures.[1] 2,3,4,5,6-Pentadeuteriobenzoic acid (benzoic-d_5 acid) was prepared according to the known procedure.[2]

II. Optimization of the synthesis of fluorenone

A flame-dried Schlenk test tube with a magnetic stirring bar was charged with benzoic acid **1a** (0.2-0.4 mmol), benzene **2a** (0.8-10 mmol), catalyst (10 mol%), oxidant (3.0 equiv), ligand and acid under an air atmosphere. The resulting mixture was stirred for 5 min at room temperature, and then heated at 30-100 ^{o}C for 24 h. The resulting solution was cooled to ambient temperature, diluted with 20 mL of CH_2Cl_2, filtered through a celite pad, and washed with 10-20 mL of CH_2Cl_2. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) to provide the desired product **3a**.

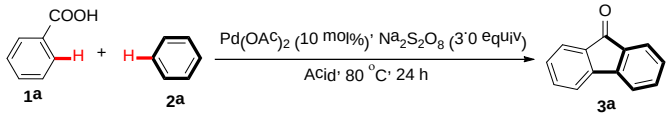
***Table S1*. Screening Catalyst**[a]



Entry	Catalyst	Yield (%)[b]
1	$Cu(OAc)_2.H_2O$	n.d.
2	$PdCl_2$	n.d.
3	$Pd(Ph_3)_4$	trace
4	$Pd(Ph_3)_2Cl_2$	n.d.
5	$Pd(OAc)_2$	45
6	$[Cp^*RhCl_2]_2$	n.d.
7	$Pd(TFA)_2$	40
8	$Pd_2(dba)_3$	trace

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (10 mmol), catalyst (10 mol%), $Na_2S_2O_8$ (3.0 equiv), TfOH (5.0 equiv) at 80 °C under an air atmosphere for 24 h. [b]Yield of isolated product. TfOH = trifluoromethanesulfonic acid. TFA = trifluoroacetic acid. dba = dibenzylideneacetone.

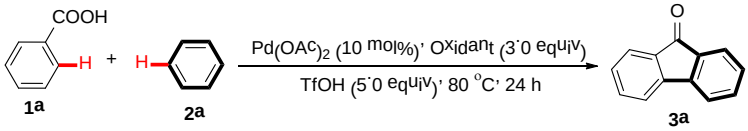
***Table S2*. Screening Acid**[a]



Entry	Acid	Yield (%)[b]
1	HOAc	nd
2	TFA	nd
3	PivOH	nd
4	MSA	nd
5	$TsOH.H_2O$	20
6	TfOH	45
7[c]	TfOH	38

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (10 mmol), $Pd(OAc)_2$ (10 mol%), $Na_2S_2O_8$ (3.0 equiv), acid (5.0 equiv) at 80 °C under an air atmosphere for 24 h. [b]Yield of isolated product. [c]TfOH (4.0 equiv). MSA = methanesulfonic acid. TsOH = *p*-toluenesulfonic acid. PivOH = trimethylacetic acid.

***Table S3*. Screening Oxidant**[a]

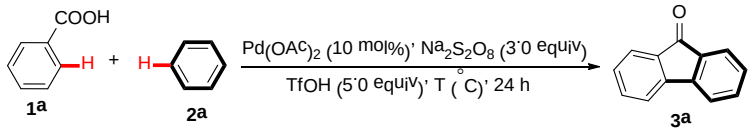


Entry	Oxidant	Yield (%)[b]
1	$K_2S_2O_8$	40
2	$Na_2S_2O_8$	45
3	$(NH_4)_2S_2O_8$	35

4	AgOAc	20
5	Ag_2CO_3	trace.
6	Ag_2O	30
7	$Cu(OAc)_2$	n.d.
8	$PhI(OAc)_2$	n.d.
9	BQ	n.d.
10	$CuCl_2$	n.d.

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (10 mmol), $Pd(OAc)_2$ (10 mol%), oxidant (3.0 equiv), TfOH (5.0 equiv) at 80 °C under an air atmosphere for 24 h. [b]Yield of isolated product. BQ = benzoquinone.

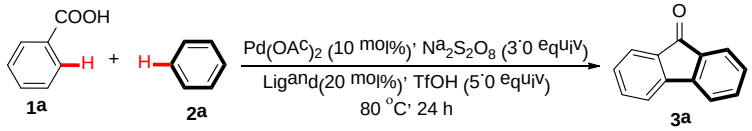
Table S4 **Screening Temperature**[a]



Entry	T (°C)	Yield (%)[b]
1	30	nd
2	60	trace
3	70	35
4	80	45
5	90	40
6	100	trace

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (10 mmol), $Pd(OAc)_2$ (10 mol%), $Na_2S_2O_8$ (3.0 equiv), TfOH (5.0 equiv) under an air atmosphere for 24 h. [b]Yield of isolated product.

Table S5. **Screening Ligand**[a]

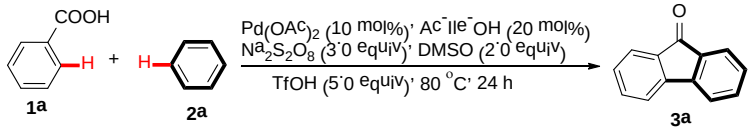


Entry	Ligand	Yield (%)[b]
1	Ac-Gly-OH	40
2	Ac-Ile-OH	45
3	Ac-Val-OH	35
4	Boc-Ile-OH	trace
5	Boc-Gly-OH	trace.
6	Ac-Leu-OH	30
7	PPh_3	n.d.
8[c]	DMSO	60
9	MeCN	n.d.
10[d]	Ac-Ile-OH/DMSO	78

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (10 mmol), $Pd(OAc)_2$ (10 mol%), $Na_2S_2O_8$ (3.0 equiv), TfOH (5.0 equiv), ligand at 80 °C under an air atmosphere for 24 h. [b]Yield of isolated product.

[c]DMSO (2.0 equiv). [d]Ac-Ile-OH (20mol%), DMSO (2.0 equiv). Ac-Gly-OH = 2-acetamidoacetic acid. Ac-Ile-OH = 2-acetamido-3-methylpentanoic acid. Ac-Leu-OH = 2-acetamido-4-methylpentanoic acid. Ac-Val-OH = 2-acetamido-3-methylbutanoic acid. Boc-Gly-OH = 2-((tert-butoxycarbonyl)amino)acetic acid. Boc-Ile-OH = 2-((tert-butoxycarbonyl)amino)-3-methylpentanoic acid. DMSO = dimethyl sulfoxide.

***Table S6*. Screening the Amount of Benzene**[a]



Entry	**1a** (mmol)	**2a** (mmol)	Yield (%)[b]
1	0.2	~10.0 (1.0 ml)	78
2	0.2	~5.0 (0.5 ml)	79
3	0.2	~2.0 (0.2 ml)	75
4	0.2	~1.0 (0.1 ml)	75
5	0.4	1.6 (0.15 ml)	82

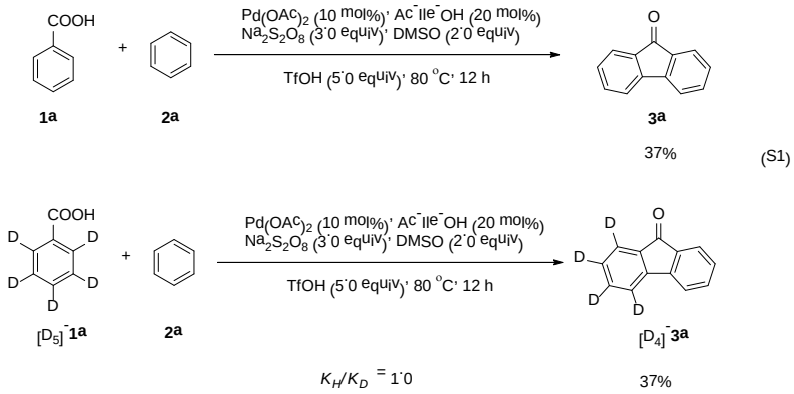
[a]Reaction conditions: **1a** (0.2~0.4 mmol), **2a** (1.0~10.0 mmol), $Pd(OAc)_2$ (10 mol%), Ac-Ile-OH (20 mol%), $Na_2S_2O_8$ (3.0 equiv), TfOH (5.0 equiv) under an air atmosphere for 24 h. [b]Yield of isolated product.

III. General procedure for the synthesis of fluorenones

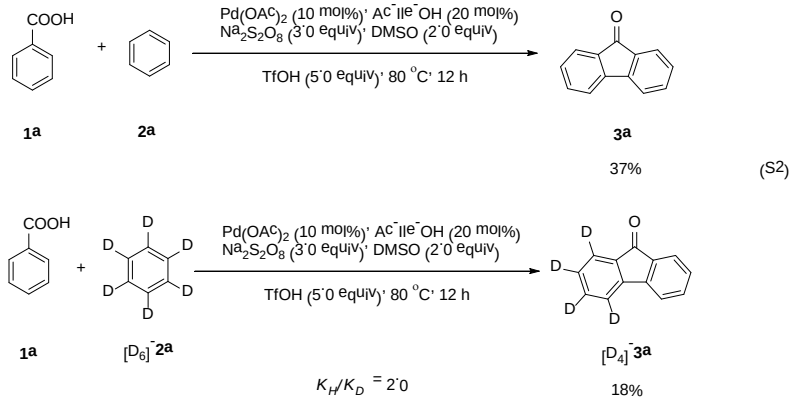
A flame-dried Schlenk test tube with a magnetic stirring bar was charged with benzoic acids (0.4 mmol), arenes (1.6 mmol, 4.0 equiv), $Pd(OAc)_2$ (10 mol%), $Na_2S_2O_8$ (3.0 equiv), Ac-Ile-OH (0.2 equiv), DMSO (2.0 equiv) and HOTf (2.0 mmol, 5 equiv) under an air atmosphere. The resulting mixture was stirred for 5 min at room temperature, and then heated at 80 ºC for 24 h. The resulting solution was cooled to ambient temperature, diluted with 20 mL of CH_2Cl_2, filtered through a celite pad, and washed with 10-20 mL of CH_2Cl_2. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product.

IV. Mechanism study

1. Kinetic isotope experiments



Two sets of reactions were carried out in a parallel manner. In each case benzene was allowed to react with benzoic acid and 2,3,4,5,6-pentadeuteriobenzoic acid (benzoic-d_5 acid), respectively. The sealed tubes were screw-capped and heated to 80 ºC (oil bath). After being stirred for 12 h, the resulting solution was cooled to ambient temperature, diluted with 20 mL of CH_2Cl_2, filtered through a celite pad, and washed with 10-20 mL of CH_2Cl_2. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired **3a** and [D_4]-**3a** as yellow solid.



Two sets of reactions were carried out in a parallel manner. In each case benzoic acid was allowed to react with benzene and benzene-d_6, respectively. The sealed tubes were screw-capped and heated to 80 °C (oil bath). After being stirred for 12 h, the resulting solution was cooled to ambient temperature, diluted with 20 mL of CH_2Cl_2, filtered through a celite pad, and washed with 10-20 mL of CH_2Cl_2. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product **3a** and [D_4]-**3a** as yellow solid.

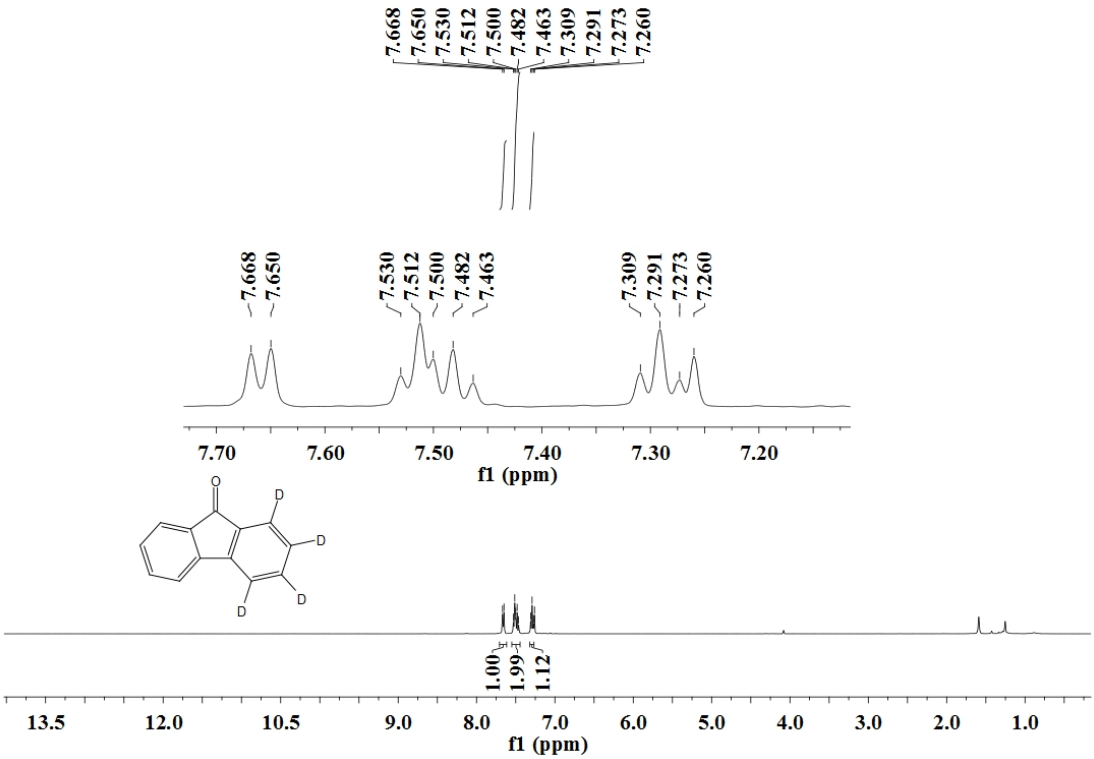


Figure. S1. Copy of ^{1}H NMR spectra of [D_4]-**3a**.

V. UV-Vis absorption and emission spectra of 6.

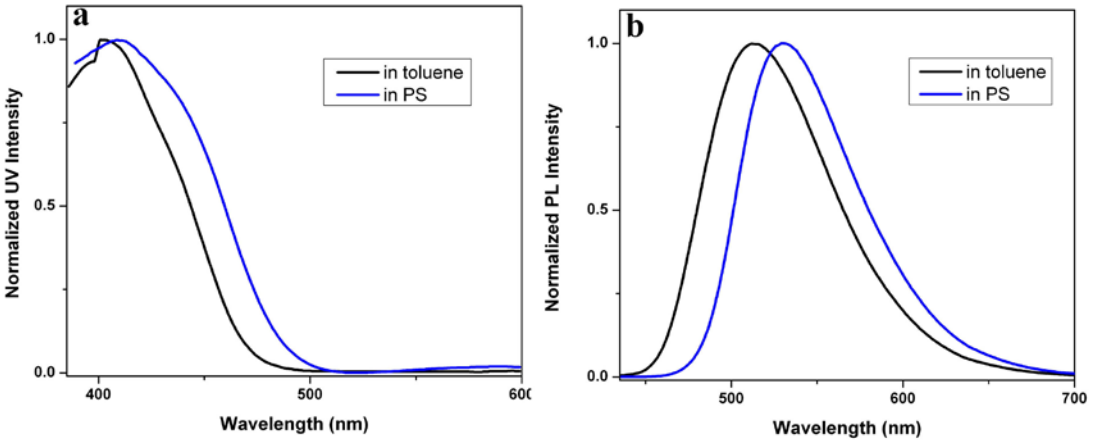
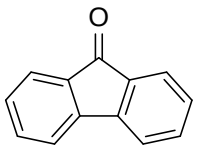


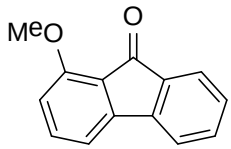
Figure S2. (a) UV-Vis absorption spectra of **6** in toluene (5.0×10^{-5} M) and in PS film (5.0 wt%); (b) Emission spectra of **6** in toluene (5.0×10^{-5} M) and in PS film (5.0 wt%).

VI. Experimental data for the described substances.



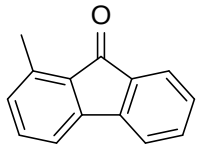
9*H*-Fluoren-9-one (3a)

Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 50/1, v/v) afforded the desired product as a yellow solid (59.0 mg, 82%). M.p.: 83-85 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (t, J = 7.2 Hz, 2H), 7.48 (t, J = 7.2 Hz, 2H), 7.52 (d, J = 7.2 Hz, 2H), 7.66 (d, J = 7.2 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 120.4, 124.4, 129.2, 134.2, 134.8, 144.5, 194.1 ppm. HRMS (ESI^+): calcd for $C_{13}H_8NaO$ $[M+Na]^+$ 203.0473, found 203.0469.



1-Methoxy-9*H*-fluoren-9-one (3b)

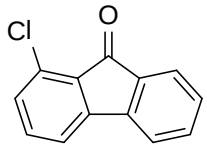
Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 20/1, v/v) afforded the desired product as a yellow solid (67.2 mg, 80%). M.p.: 138-139 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.98 (s, 3H), 6.82 (d, J = 8.4 Hz, 1H), 7.12 (d, J = 7.2 Hz, 1H), 7.28 (t, J = 7.2 Hz, 1H), 7.42-7.49 (m, 3H), 7.64 (d, J = 7.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 56.1, 113.0, 113.1, 120.2, 120.3, 124.0, 129.3, 134.0, 134.6, 136.9, 143.3, 146.6, 158.4, 192.1 ppm. HRMS (ESI^+): calcd for $C_{14}H_{10}NaO_2$ $[M+Na]^+$ 233.0578, found 233.0576.



1-Methyl-9*H*-fluoren-9-one (3c)

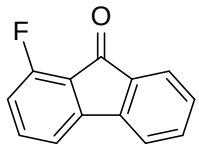
Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 20/1, v/v) afforded the desired product as a yellow solid (59.0 mg, 76%). M.p.: 98-100 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.63 (s, 3H), 7.04 (d, J = 6.4 Hz, 1H), 7.28 (td, J = 7.2 Hz, J = 0.8 Hz, 1H), 7.31-7.36 (m, 2H), 7.46 (t, J = 7.6 Hz, 1H), 7.50 (d, J = 7.2 Hz, 1H), 7.62 (d, J = 7.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.0, 118.0, 120.2, 124.0, 129.0, 131.0, 132.0, 134.1, 134.5, 139.6, 144.0, 144.9, 195.3 ppm.

HRMS (ESI$^+$): calcd for $C_{14}H_{10}NaO$ $[M+Na]^+$ 217.0629, found 217.0625.



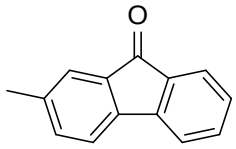
1-Chloro-9*H*-fluoren-9-one (3d)

Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 20/1, v/v) afforded the desired product as a yellow solid (69.5 mg, 81%). M.p.: 138-140 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22 (d, J = 7.6 Hz, 1H), 7.34 (t, J = 7.2 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.44 (d, J = 7.2 Hz, 1H), 7.49-7.55 (m, 2H), 7.69 (d, J = 7.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 118.8, 120.5, 124.6, 129.6, 129.8, 131.1, 132.8, 134.0, 134.9, 135.4, 142.7, 146.6, 191.0 ppm. HRMS (ESI$^+$): calcd for $C_{13}H_7ClNaO$ $[M+Na]^+$ 237.0083, found 237.0089.



1-Fluoro-9*H*-fluoren-9-one (3e)

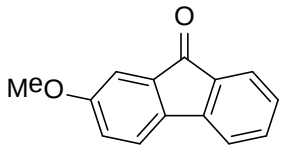
Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 20/1, v/v) afforded the desired product as a yellow solid (64.2 mg, 81%). M.p.: 112-114 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.95 (t, J = 8.4 Hz, 1H), 7.32-7.36 (m, 2H), 7.46-7.56 (m, 3H), 7.69 (d, J = 7.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 116.52, 116.55, 117.6, 117.8, 120.8, 124.7, 129.8, 134.1, 134.8, 137.1, 137.2, 143.5, 143.6, 146.51, 146.55, 158.2, 160.8, 190.3 ppm. HRMS (ESI$^+$): calcd for $C_{13}H_8FO$ $[M+H]^+$ 199.0559, found 199.0556.



2-Methyl-9*H*-fluoren-9-one (3f)

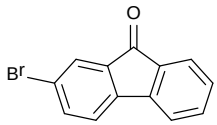
Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h.

Purification via silica gel column chromatography (petroleum ether/EtOAc = 20/1, v/v) afforded the desired product as a yellow solid (58.2 mg, 75%). M.p.: 93-95 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.38 (s, 3H), 7.24-7.26 (m, 1H), 7.28 (d, J = 8.0 Hz, 1H), 7.40 (d, J = 7.6 Hz, 1H), 7.44-7.47 (m, 3H), 7.63 (d, J = 7.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5, 120.1, 120.3, 124.4, 125.2, 128.7, 134.4, 134.6, 134.8, 135.3, 139.4, 142.0, 144.8, 194.4 ppm. HRMS (ESI^+): calcd for $C_{14}H_{11}O$ $[M+H]^+$ 195.0810, found 195.0808.



2-Methoxy-9*H*-fluoren-9-one (3g)

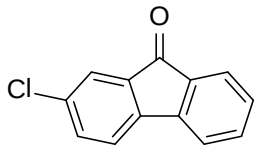
Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 20/1, v/v) afforded the desired product as a yellow solid (61.3 mg, 73%). M.p.:78-80 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.92 (s, 3H), 7.04 (d, J = 8.0 Hz, 1H), 7.24-7.32 (m, 2H), 7.45-7.51 (m, 3H), 7.66 (d, J = 7.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.9, 109.5, 119.7, 120.4, 121.5, 124.5, 128.0, 134.5, 135.0, 136.1, 137.1, 145.0, 161.0, 194.0 ppm. HRMS (ESI^+): calcd for $C_{14}H_{10}NaO_2$ $[M+Na]^+$ 233.0578, found 233.0581.



2-Bromo-9*H*-fluoren-9-one (3h)

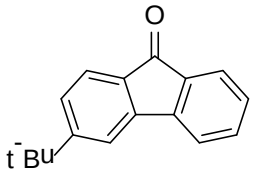
Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 20/1, v/v) afforded the desired product as a yellow solid (81.9 mg, 79%). M.p.: 138-140 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31-7.35 (m, 1H), 7.40 (d, J = 8.0 Hz, 1H), 7.50-7.51 (m, 2H), 7.61 (d, J = 7.6 Hz, 1H), 7.66 (d, J = 7.6 Hz, 1H), 7.77 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 120.6, 121.9, 123.0, 124.7, 127.7, 129.6, 133.8, 135.2, 135.9, 137.2, 143.1, 143.8, 192.5 ppm. HRMS (ESI^+): calcd for

$C_{13}H_7BrNaO$ $[M+Na]^+$ 280.9578, found 280.9584.



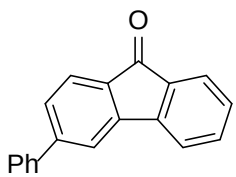
2-Chloro-9*H*-fluoren-9-one (3i)

Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 20/1, v/v) afforded the desired product as a yellow solid (64.2 mg, 75%). M.p.: 122-124 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29-7.32 (m, 1H), 7.45 (s, 2H), 7.50 (d, J = 4.0 Hz, 2H), 7.62 (s, 1H), 7.66 (d, J = 7.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 120.6, 121.5, 124.8, 124.9, 129.5, 134.1, 134.3, 135.19, 135.24, 135.8, 142.7, 143.8, 192.6 ppm. HRMS (ESI^+): calcd for $C_{13}H_7ClNaO$ $[M+Na]^+$ 237.0083, found 237.0087.



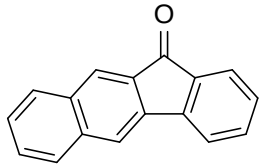
3-Tert-butyl-9*H*-fluoren-9-one (3j)

Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 20/1, v/v) afforded the desired product as a yellow liquid (68.9 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.38 (s, 9 H), 7.28 (t, J = 7.2 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.54-7.55 (m, 2H), 7.59 (d, J = 8.0 Hz, 1H), 7.64 (d, J = 7.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.3, 35.7, 117.7, 120.2, 124.3, 126.2, 129.0, 132.0, 134.6, 134.9, 144.71, 144.72, 159.2, 193.9 ppm. HRMS (ESI^+): calcd for $C_{17}H_{17}O$ $[M+H]^+$ 237.1279, found 237.1254.



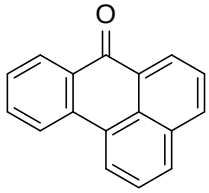
3-Phenyl-9*H*-fluoren-9-one (3k)

Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 40/1, v/v) afforded the desired product as a yellow solid (59.4 mg, 58%). M.p.: 99-101 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (t, J = 7.2 Hz, 1H), 7.43 (t, J = 7.2 Hz, 1H), 7.48-7.53 (m, 4H), 7.58 (d, J = 7.2 Hz, 1H), 7.65-7.69 (m, 3H), 7.72-7.74 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 119.4, 120.4, 124.4, 124.9, 127.3, 128.1, 128.6, 129.1, 129.4, 133.1, 134.8, 140.3, 144.2, 145.3, 148.0, 193.7 ppm. HRMS (ESI$^+$): calcd for $C_{19}H_{13}O$ $[M+H]^+$ 257.0966, found 257.0962.



11*H*-Benzo[*b*]fluoren-11-one (3l)

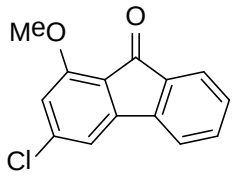
Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 20/1, v/v) afforded the desired product as a yellow solid (48.7mg, 53%). M.p.: 143-145 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (t, J = 7.2 Hz, 1H), 7.47 (t, J = 7.2 Hz, 1H), 7.53-7.58 (m, 2H), 7.71 (d, J = 7.6 Hz, 1H), 7.75 (d, J = 7.2 Hz, 1H), 7.82 (d, J = 8.4 Hz, 1H), 7.86 (s, 1H), 7.89 (d, J = 8.0 Hz, 1H), 8.17(s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 119.2, 121.1, 124.6, 125.8, 127.1, 128.9, 129.1, 129.3, 131.0, 133.0, 133.8, 135.2, 136.3, 137.1, 138.5, 145.0, 193.3 ppm. HRMS (ESI$^+$): calcd for $C_{17}H_{10}NaO$ $[M+Na]^+$ 253.0629, found 253.0627.



7*H*-Benzo[*de*]anthracen-7-one (3m)

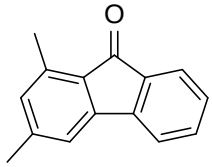
Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 20/1, v/v) afforded the desired product as a yellow solid (50.6 mg, 55%). M.p.: 165-167 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (t, J = 7.6 Hz, 1H), 7.71 (t, J = 8.0 Hz, 1H),

7.74-7.82 (m, 2H), 8.03 (d, *J* = 8.0 Hz, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 8.37 (d, *J* = 8.0 Hz, 1H), 8.49 (d, *J* = 7.6 Hz, 1H), 8.53 (d, *J* = 8.0 Hz, 1H), 8.78 (d, *J* = 7.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 123.2, 124.3, 126.7, 126.8, 127.1, 128.1, 128.3, 128.5, 128.7, 130.0, 130.4, 131.3, 133.2, 133.5, 135.3, 136.4, 184.1 ppm. HRMS (ESI$^+$): calcd for $C_{17}H_{10}NaO$ $[M+Na]^+$ 253.0629, found 253.0632.



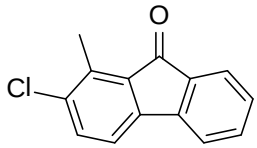
1-Methoxy-3-chloro -9*H*-fluoren-9-one (3n)

Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 10/1, v/v) afforded the desired product as a yellow solid (51.9 mg, 55%). M.p.: 145-147 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.98 (s, 3H), 6.84 (s, 1H), 7.14 (s, 1H), 7.32-7.36 (m, 1H), 7.48 (d, *J* = 4.0 Hz, 2H), 7.66 (d, *J* = 7.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 56.4, 113.5, 113.9, 118.8, 120.5, 124.2, 130.0, 134.1, 134.8, 142.2, 142.7, 147.9, 158.6, 190.8 ppm. HRMS (ESI$^+$): calcd for $C_{14}H_9ClNaO_2$ $[M+Na]^+$ 267.0189, found 267.0186.



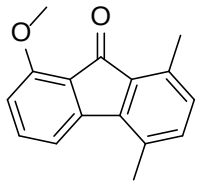
1,3-Dimethyl-9*H*-fluoren-9-one (3o)

Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 20/1, v/v) afforded the desired product as a yellow solid (49.9 mg, 60%). M.p.: 108-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.37 (s, 3H), 2.58 (s, 3H), 6.84 (s, 1H), 7.16 (s, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.42-7.47 (m, 2H), 7.60 (d, *J* = 6.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.9, 22.1, 119.0, 119.9, 123.8, 128.8, 128.9, 132.4, 134.1, 135.0, 139.5, 143.8, 145.1, 145.3, 194.8 ppm. HRMS (ESI$^+$): calcd for $C_{15}H_{13}O$ $[M+H]^+$ 209.0966, found 209.0963.



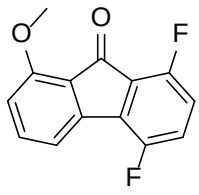
1-Methyl-2-chloro-9*H*-fluoren-9-one (3p)

Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 20/1, v/v) afforded the desired product as a yellow solid (64.0 mg, 70%). M.p.: 140-142 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.69 (s, 3H), 7.29 (d, J = 7.6 Hz, 2H), 7.43 (d, J = 7.6 Hz, 1H), 7.47-7.50 (m, 2H), 7.63 (d, J = 7.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 118.7, 120.1, 124.3, 129.2, 132.3, 134.18, 134.21, 134.8, 136.5, 137.9, 143.0, 143.4, 194.1 ppm. HRMS (ESI^+): calcd for $C_{15}H_9ClNaO$ $[M+Na]^+$ 251.0240, found 251.0219.



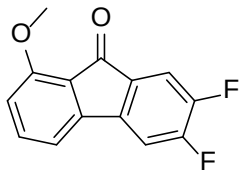
8-Methoxy-1,4-dimethyl-9*H*-fluoren-9-one (4a)

Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 10/1, v/v) afforded the desired product **4a** as a yellow solid (68.5 mg, 72%). M.p.: 113-115 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.54 (s, 3H), 2.59 (s, 3H), 3.98 (s, 3H), 6.84 (d, J = 8.8 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 7.09 (d, J = 8.0 Hz, 1H), 7.24(d, J = 7.6 Hz, 1H), 7.43 (t, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.7, 20.4, 56.0, 112.5, 116.2, 120.6, 131.1, 131.4, 132.0, 136.31, 136.32, 136.8, 141.3, 147.1, 158.3, 193.9 ppm. HRMS (ESI^+): calcd for $C_{16}H_{14}NaO_2$ $[M+Na]^+$ 261.0891, found 261.0893.



1,4-Difluoro-8-methoxy-9*H*-fluoren-9-one (4b)

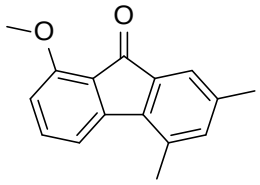
A flame-dried Schlenk test tube with a magnetic stirring bar was charged with **1b** (60.8 mg, 0.4 mmol), arene **2c** (4.0 equiv, 1.6 mmol), $Pd(OAc)_2$ (0.04 mmol, 10 mol%), $Na_2S_2O_8$ (3.0 equiv), Ac-Ile-OH (0.2 equiv), MeCN (2.0 equiv) and TfOH (2.0 mmol, 5.0 equiv) under an air atmosphere (the order is very important, arene **2c** should be added last). The resulting mixture was stirred for 5 min at room temperature, and then heated at 80 ºC for the indicated time. The resulting solution was cooled to ambient temperature, diluted with 20 mL of CH_2Cl_2, filtered through a celite pad, and washed with 10-20 mL of CH_2Cl_2. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) to provide the desired product **4b** as a yellow solid (64.2 mg, 65%). M.p.: 163-165 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.99 (s, 3H), 6.85-6.92 (m, 1H), 7.05 (d, J = 6.8 Hz, 1H), 7.28-7.34 (m, 1H), 7.43-7.53 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 56.1, 109.9, 110.1, 113.1, 113.56, 113.58, 113.7, 113.8, 114.0, 117.0, 117.1, 117.3, 117.5, 120.27, 120.29, 120.48, 120.52, 120.56, 120.60, 130.89, 130.92, 130.94, 130.97, 137.3, 137.4, 140.11, 140.14, 140.19, 140.22, 144.59, 144.61, 144.63, 150.0, 150.1, 152.5, 152.6, 153.0 153.2, 155.6, 155.7, 158.5, 189.4 ppm. HRMS (ESI$^+$): calcd for $C_{14}H_9F_2O_2$ $[M+H]^+$ 247.0571, found 247.0575.



6,7-Difluoro-1-methoxy-9*H*-fluoren-9-one (4c)

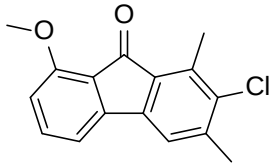
A flame-dried Schlenk test tube with a magnetic stirring bar was charged with **1b** (60.8 mg, 0.4 mmol), arene **2d** (4.0 equiv, 1.6 mmol), $Pd(OAc)_2$ (0.04 mmol, 10 mol%), $Na_2S_2O_8$ (3.0 equiv), Ac-Ile-OH (0.1 equiv), MeCN (2.0 equiv) and TfOH (2.0 mmol, 5.0 equiv) under an air atmosphere (the order is very important, arene should be added last). The resulting mixture was stirred for 5 min at room temperature, and then heated at 80 ºC for the indicated time. The resulting solution was cooled to

ambient temperature, diluted with 20 mL of CH_2Cl_2, filtered through a celite pad, and washed with 10-20 mL of CH_2Cl_2. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) to provide the desired product **4c** as a yellow solid (61.3 mg, 62%). M.p.: 163-165 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.99 (s, 3H), 6.86 (d, *J* = 8.8 Hz, 1H), 7.05 (d, *J* = 7.2 Hz, 1H), 7.26-7.31 (m, 1H), 7.44 (d, *J* = 6.8 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 56.1, 109.9, 110.1, 113.1, 113.53, 113.55, 113.6, 113.72, 113.74, 120.2, 120.3, 130.87, 130.91, 130.93, 130.96, 137.3, 140.10, 140.13, 140.17, 140.21, 144.6, 150.0, 150.1, 152.5, 152.6, 153.0, 153.2, 155.6, 155.7, 158.5, 189.3 ppm. HRMS (ESI$^+$): calcd for $C_{14}H_8F_2NaO_2$ $[M+Na]^+$ 269.0390, found 269.0392.



8-Methoxy-1,3-dimethyl-9*H*-fluoren-9-one (4d)

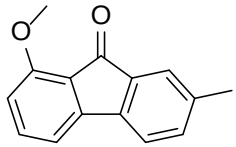
Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 10/1, v/v) afforded the desired product **4d** as a yellow solid (58.1 mg, 61%). M.p.: 148-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.33 (s, 3H), 2.53 (s, 3H), 3.98 (s, 3H), 6.81 (d, *J* = 8.4 Hz, 1H), 7.04 (s, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.34 (s, 1H), 7.43(t, *J* = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.3, 21.2, 56.0, 112.3, 116.0, 120.5, 122.5, 133.3, 135.4, 136.8, 137.4, 138.3, 139.2, 147.9, 158.4, 192.7 ppm. HRMS (ESI$^+$): calcd for $C_{16}H_{14}NaO_2$ $[M+Na]^+$ 261.0891, found 261.0890.



2-Chloro-8-methoxy-1,3-dimethyl-9*H*-fluoren-9-one (4e)

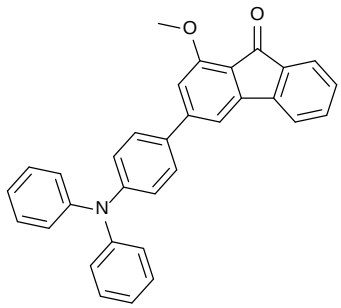
A flame-dried Schlenk test tube with a magnetic stirring bar was charged with **1b** (60.8 mg, 0.4 mmol), arene **2f** (4.0 equiv, 1.6 mmol), $Pd(OAc)_2$ (0.04 mmol, 10

mol%), $Na_2S_2O_8$ (3.0 equiv), Ac-Ile-OH (0.2 equiv), MeCN (2.0 equiv) and TfOH (2.0 mmol, 5.0 equiv) under an air atmosphere (the order is very important, arene should be added last). The resulting mixture was stirred for 5 min at room temperature, and then heated at 80 ºC for the indicated time. The resulting solution was cooled to ambient temperature, diluted with 20 mL of CH_2Cl_2, filtered through a celite pad, and washed with 10-20 mL of CH_2Cl_2. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) to provide the desired product **4e** as a yellow solid (76.2 mg, 70%). M.p.: 118-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.42 (s, 3H), 2.68 (s, 3H), 3.97 (s, 3H), 6.81 (d, J = 8.4 Hz, 1H), 7.06 (d, J = 7.2 Hz, 1H), 7.22 (s, 1H), 7.42 (t, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.0, 56.0, 112.6, 113.0, 120.3, 120.6, 130.3, 136.6, 136.7, 137.8, 141.7, 141.8, 145.2, 158.3, 192.3 ppm. HRMS (ESI$^+$): calcd for $C_{16}H_{14}ClO_2$ $[M+H]^+$ 273.0682, found 273.0678.



1-Methoxy-7-methyl-9*H*-fluoren-9-one (4f)

Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 10/1, v/v) afforded the desired product **4f** as a yellow solid (50.2 mg, 56%). M.p.: 128-130 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.37 (s, 3H), 3.98 (s, 3H), 6.80 (d, J = 8.4 Hz, 1H), 7.09 (d, J = 7.2 Hz, 1H), 7.25 (d, J = 8.8 Hz, 1 H), 7.37 (d, J = 7.2 Hz, 1H), 7.43 (t, J = 8.0 Hz, 1H), 7.47 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5, 56.1, 112.7, 112.8, 120.2, 120.3, 124.8, 134.5, 134.9, 136.9, 139.6, 140.7, 146.9, 158.4, 192.4 ppm. HRMS (ESI$^+$): calcd for $C_{15}H_{12}NaO_2$ $[M+Na]^+$ 247.0735, found 247.0742.



3-(4-(Diphenylamino)phenyl)-1-methoxy-9*H*-fluoren-9-one (6)

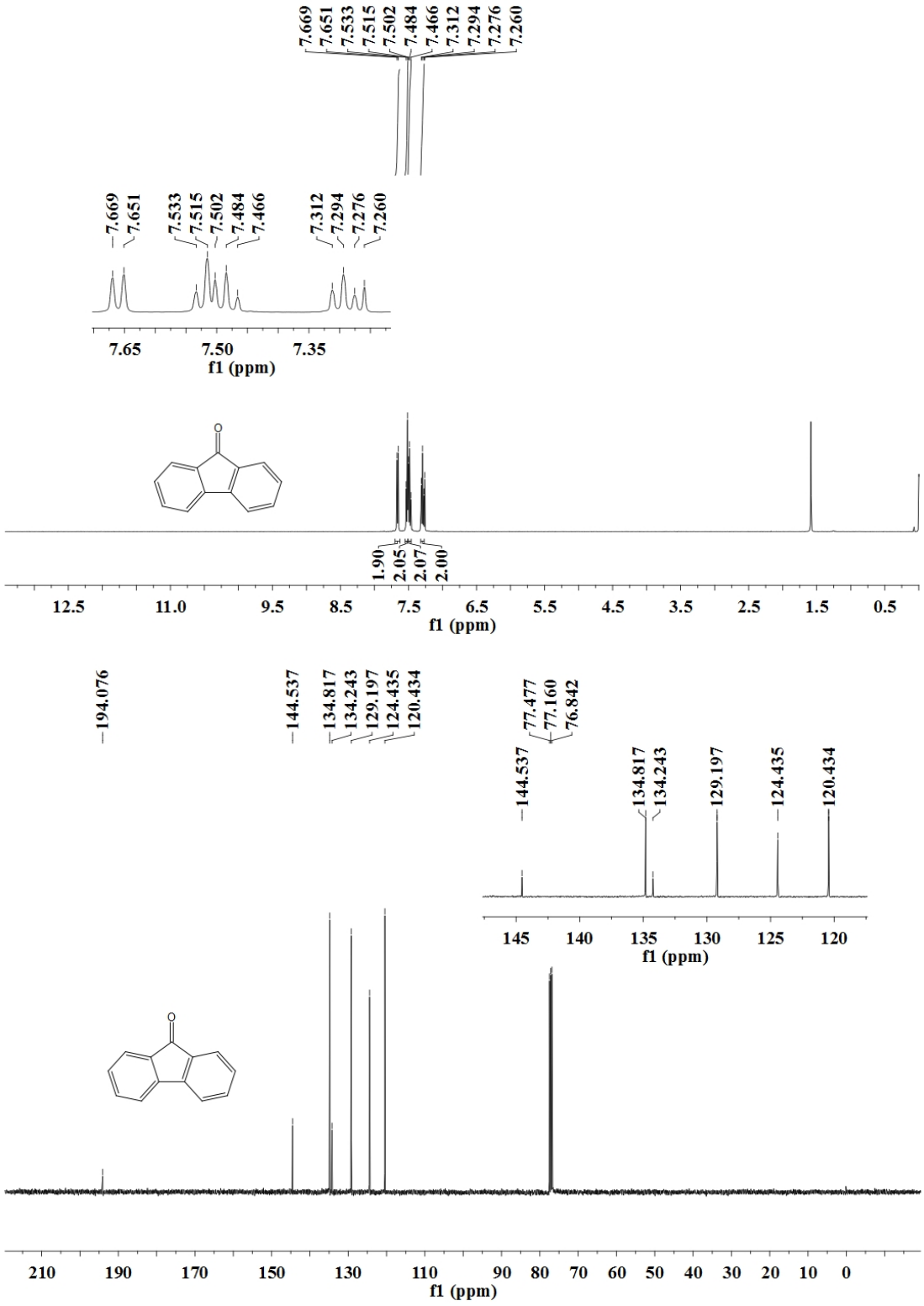
A flame-dried Schlenk test tube with a magnetic stirring bar was charged with **3n** (73.4 mg, 0.3 mmol), 4-(diphenylamino)phenylboronic acid (171.6 mg, 0.6 mmol), $Pd(OAc)_2$ (10 mol%), XPhos (20 mol%), K_3PO_4 (3.0 equiv) and THF (4 ml) under an N_2 atmosphere. The reaction mixture was stirred at 100 ºC for 24 h. The reaction mixture was then cooled to ambient temperature, diluted with 10-20 mL of EtOAc, filtered through a celite pad, and washed with 10-20 mL of EtOAc. Organic solvent was removed under reduced pressure. The residue was purified by flash column chromatography (petroleum ether/EtOAc = 5/1, v/v) to afford the desired product **6** as a yellow solid (70.7 mg, 52%). M.p.: 78-80 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.05 (s, 3H), 6.96 (s, 1H), 7.08 (t, *J* = 7.2 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 5H), 7.28-7.34 (m, 6H), 7.45-7.56 (m, 5H), 7.67 (d, *J* = 7.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 56.1, 111.0, 111.8, 120.2, 123.2, 123.7, 124.0, 124.5, 125.0, 128.1, 129.4, 129.6, 133.5, 133.9, 135.3, 143.1, 147.2, 147.4, 148.7, 149.9, 158.7, 191.6 ppm. HRMS (ESI^+): calcd for $C_{32}H_{23}NNaO_2$ $[M+Na]^+$ 476.1626, found 476.1632.

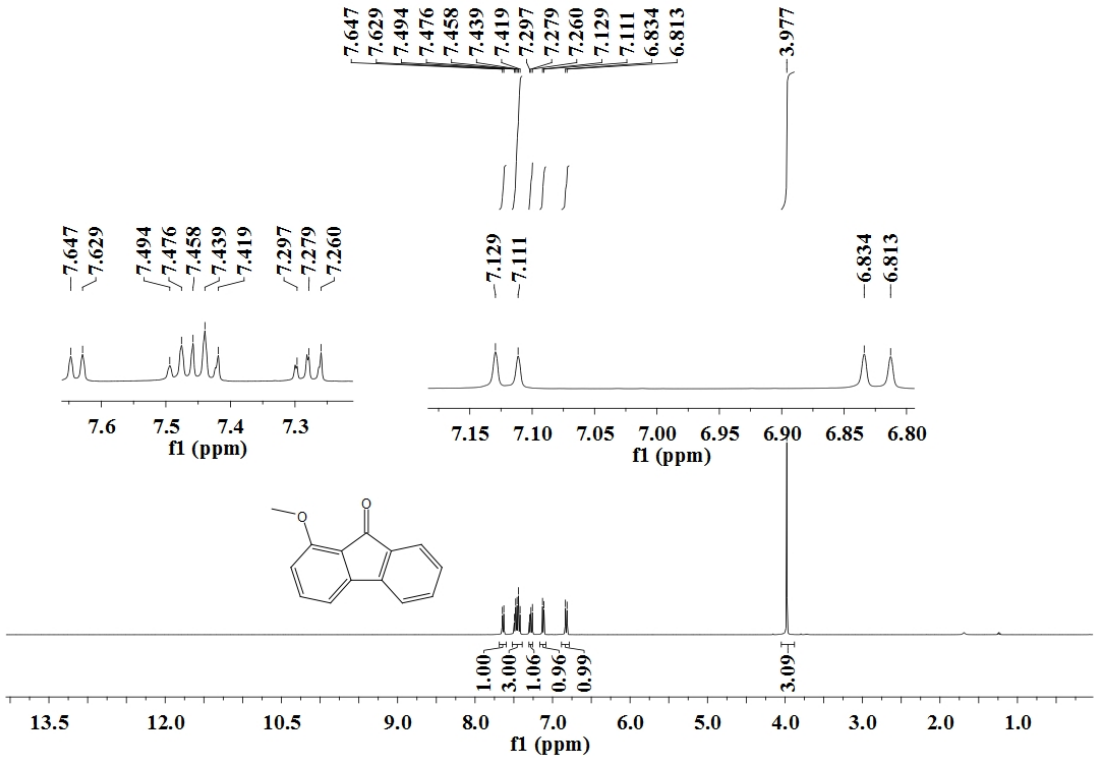
VII. References

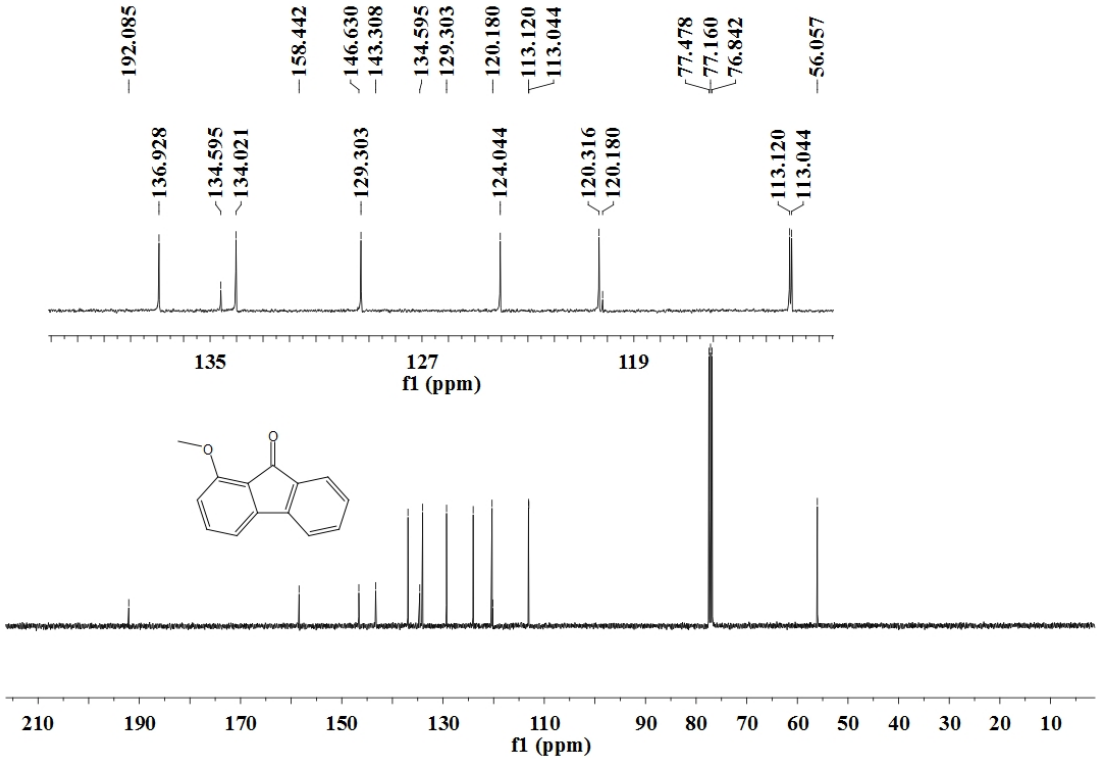
[1] N.P. Ramirez, I. Bosque, J. C. Gonzalez-Gomez, *Org. Lett.*, 2015, **17**, 4550.

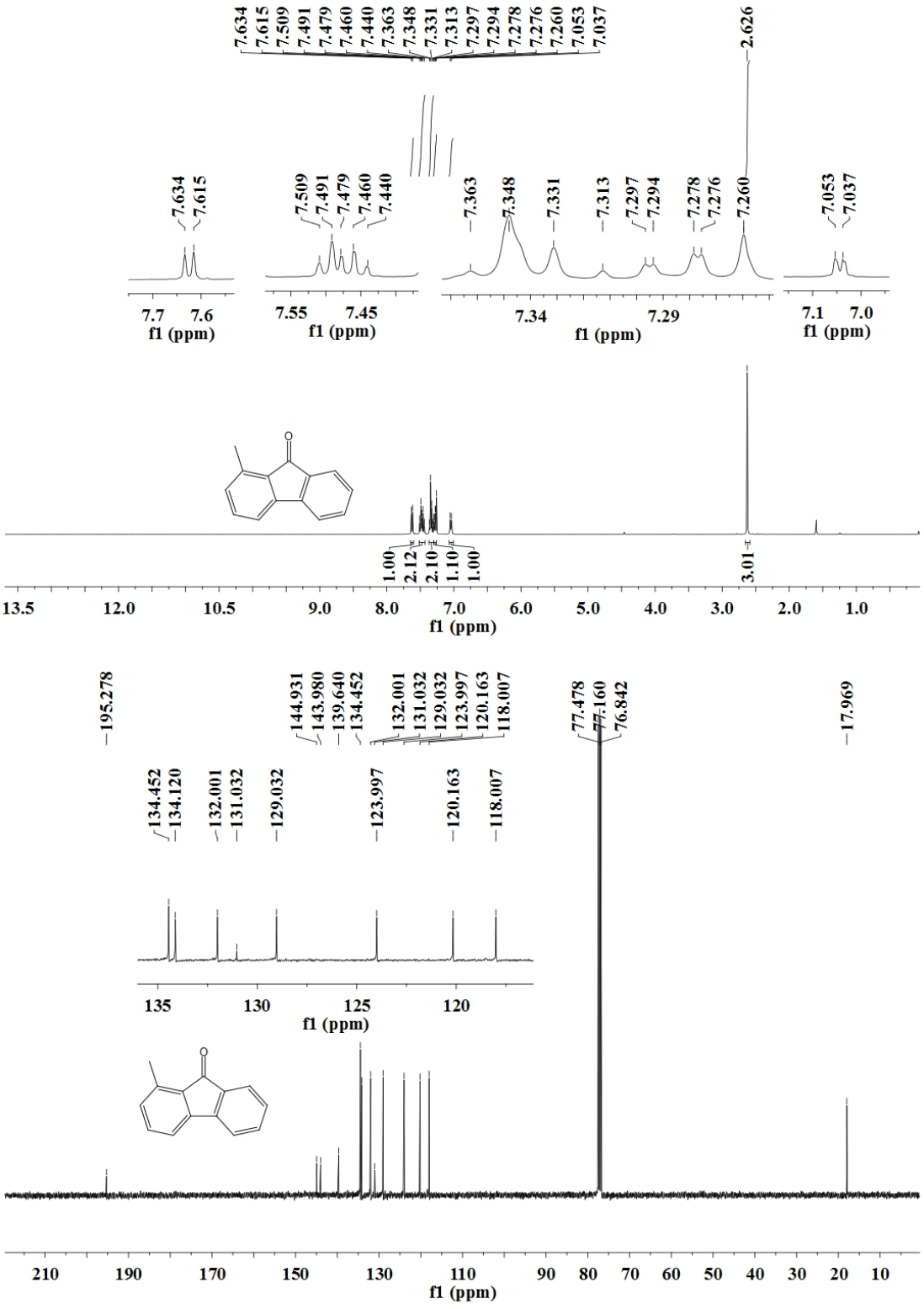
[2] L. Ackermann, A.V. Lygin, N. Hofmann, *Angew. Chem. Int. Ed.*, 2011, **50**, 6379.

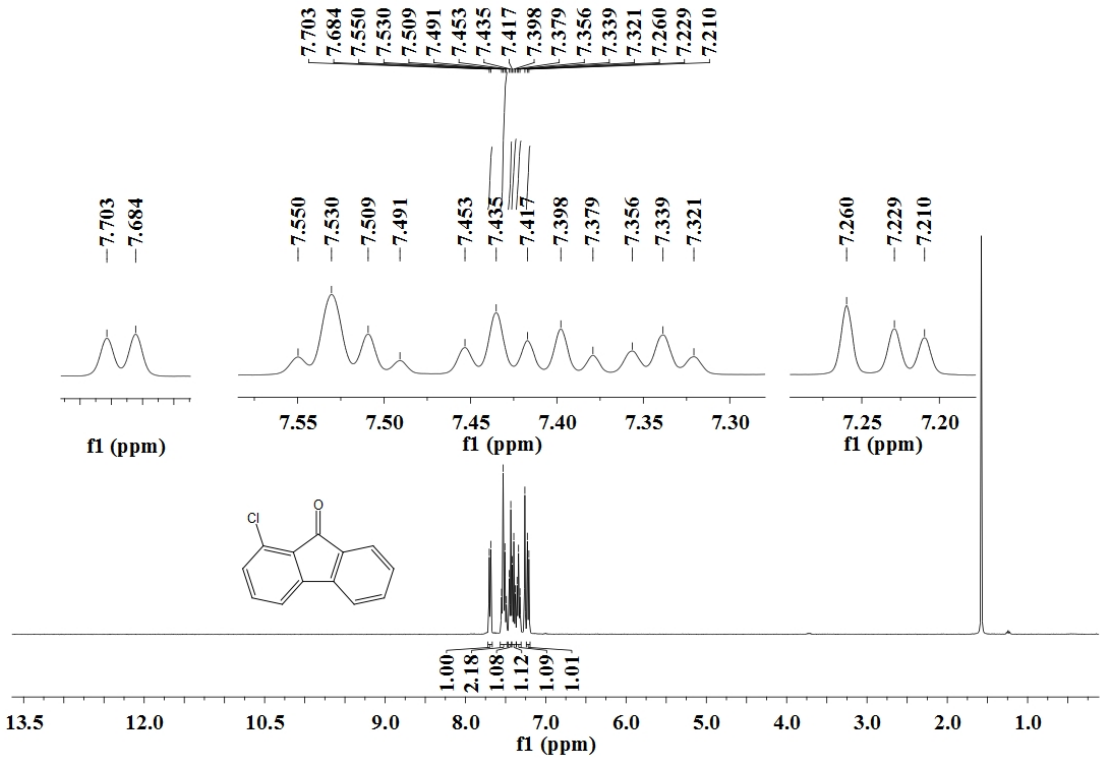
VIII. Copies of ^{1}H and ^{13}C NMR spectra.

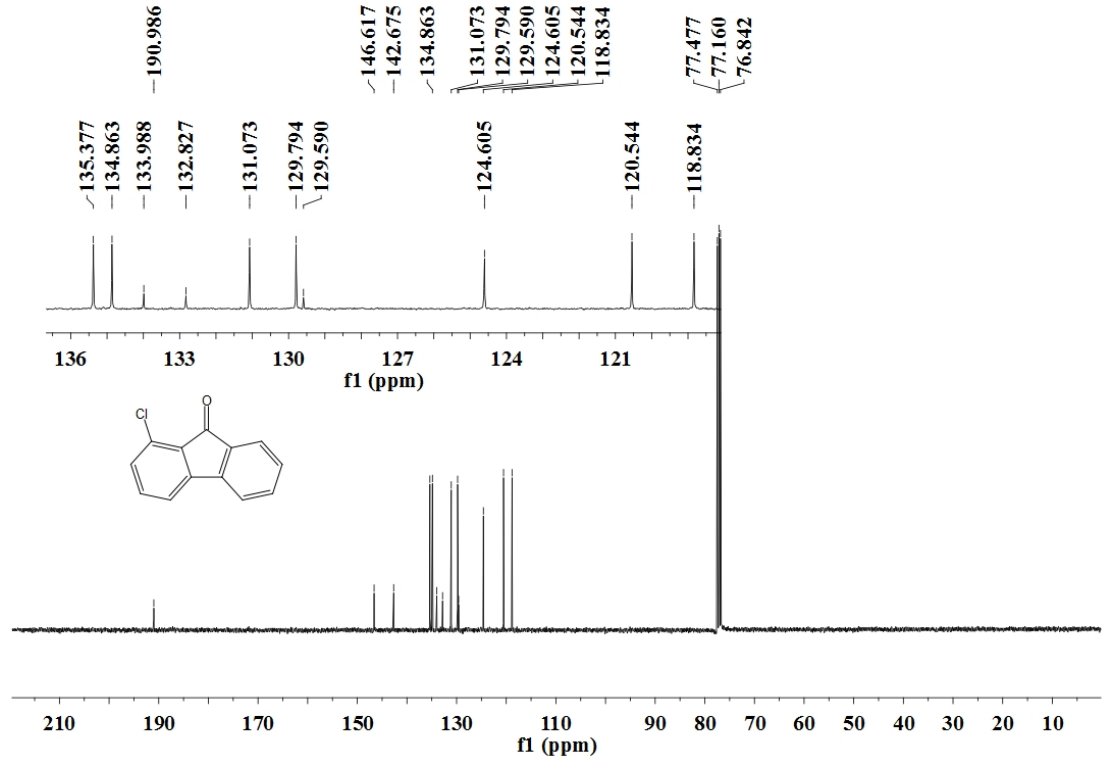


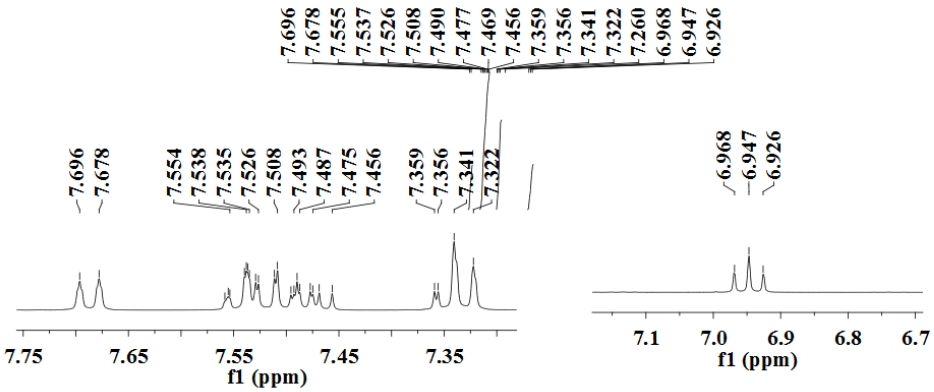

7.647
7.629
7.494
7.476
7.458
7.439
7.419
7.297
7.279
7.260
7.129
7.111
6.834
6.813
3.977
f1 (ppm)
1.00
3.00
1.06
0.96
0.99
3.09

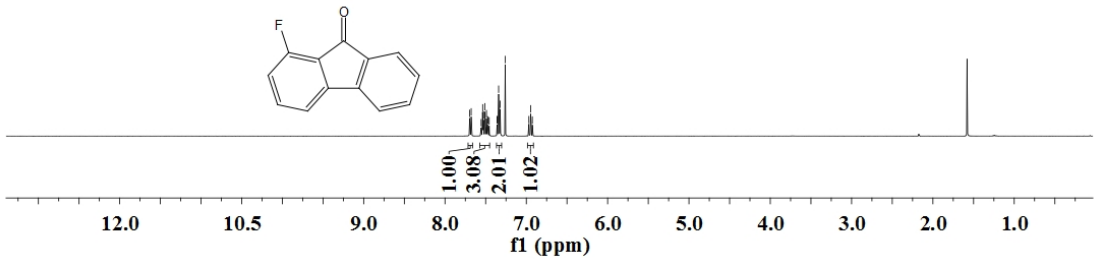

192.085
158.442
146.630
143.308
134.595
129.303
120.180
113.120
113.044
77.478
77.160
76.842
56.057
136.928
134.595
134.021
129.303
124.044
120.316
120.180
113.120
113.044
f1 (ppm)

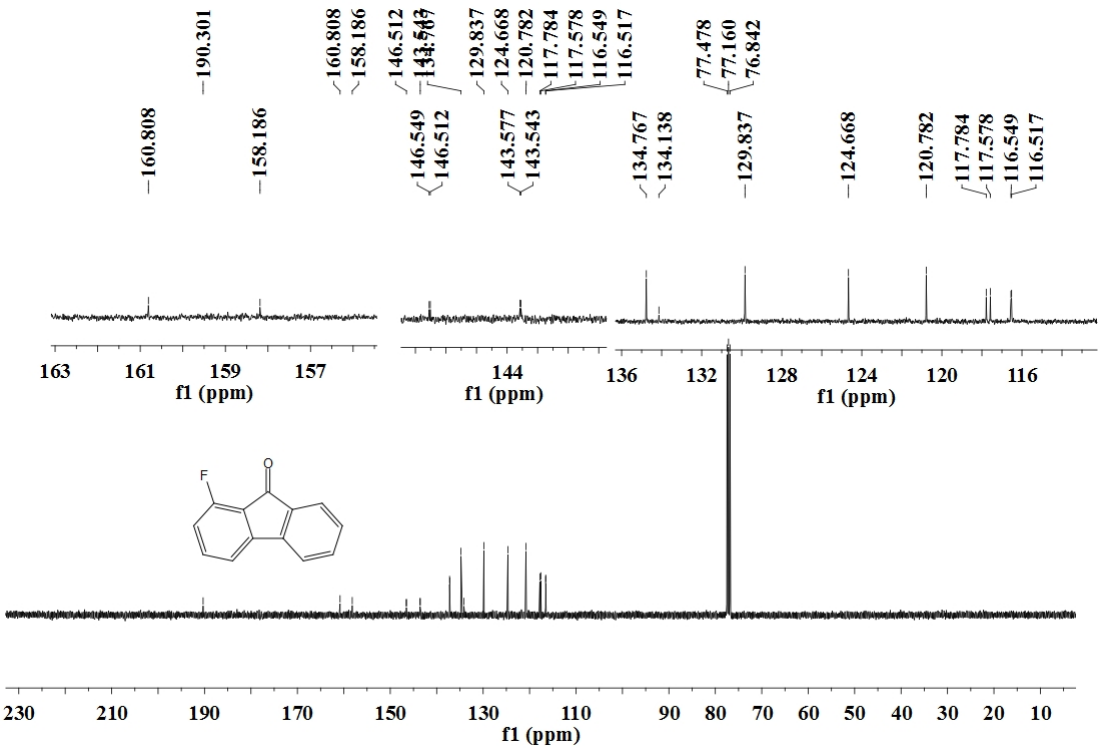

7.634
7.615
7.509
7.491
7.479
7.460
7.440
7.363
7.348
7.331
7.313
7.297
7.294
7.278
7.276
7.260
7.053
7.037
2.626
f1 (ppm)
1.00
2.12
2.10
1.10
1.00
3.01
195.278
144.931
143.980
139.640
134.452
132.001
131.032
129.032
123.997
120.163
118.007
77.478
77.160
76.842
17.969
134.452
134.120
132.001
131.032
129.032
123.997
120.163
118.007
f1 (ppm)

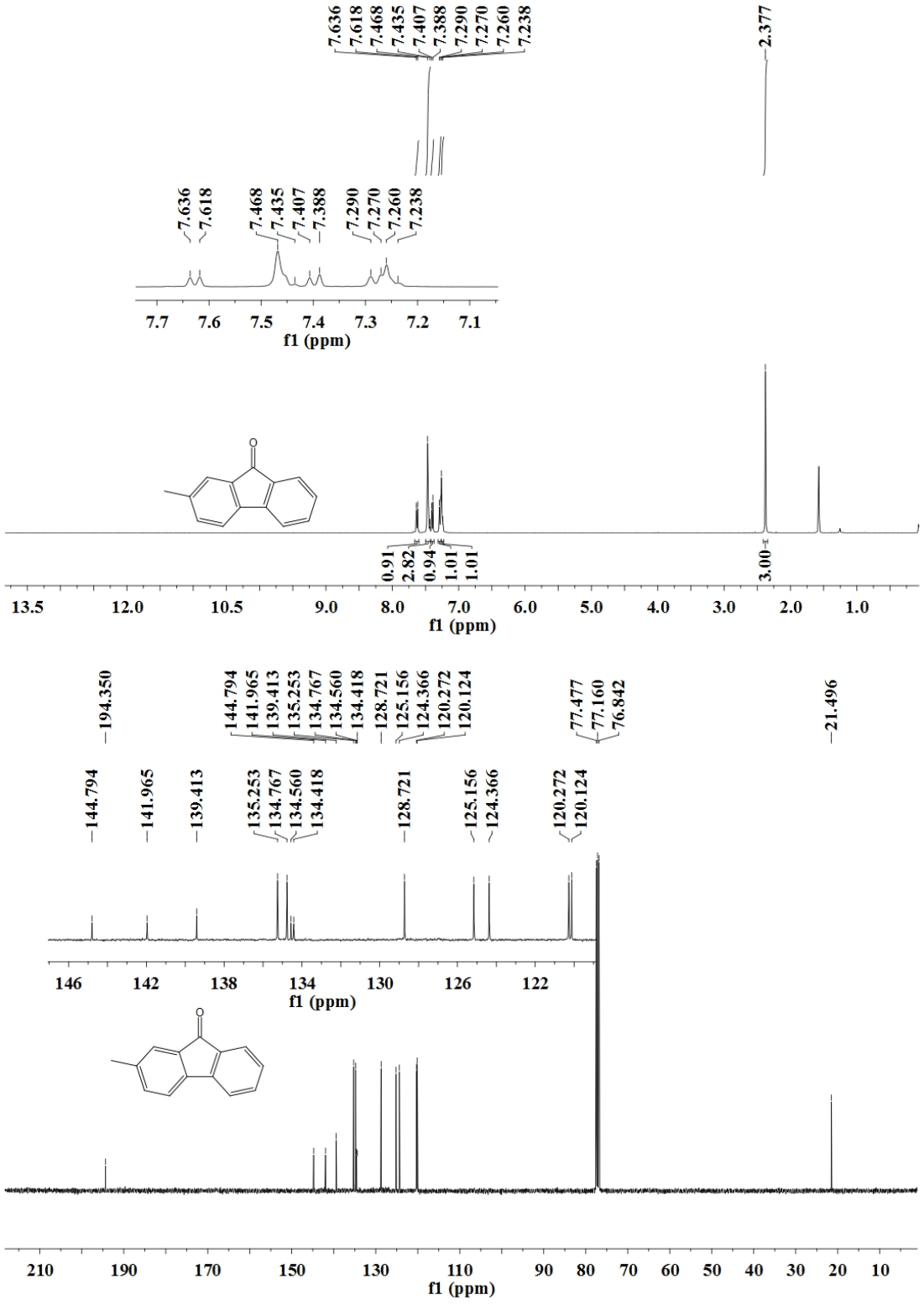

7.703
7.684
7.550
7.530
7.509
7.491
7.453
7.435
7.417
7.398
7.379
7.356
7.339
7.321
7.260
7.229
7.210
f1 (ppm)
Cl
O
1.00
2.18
1.08
1.12
1.09
1.01

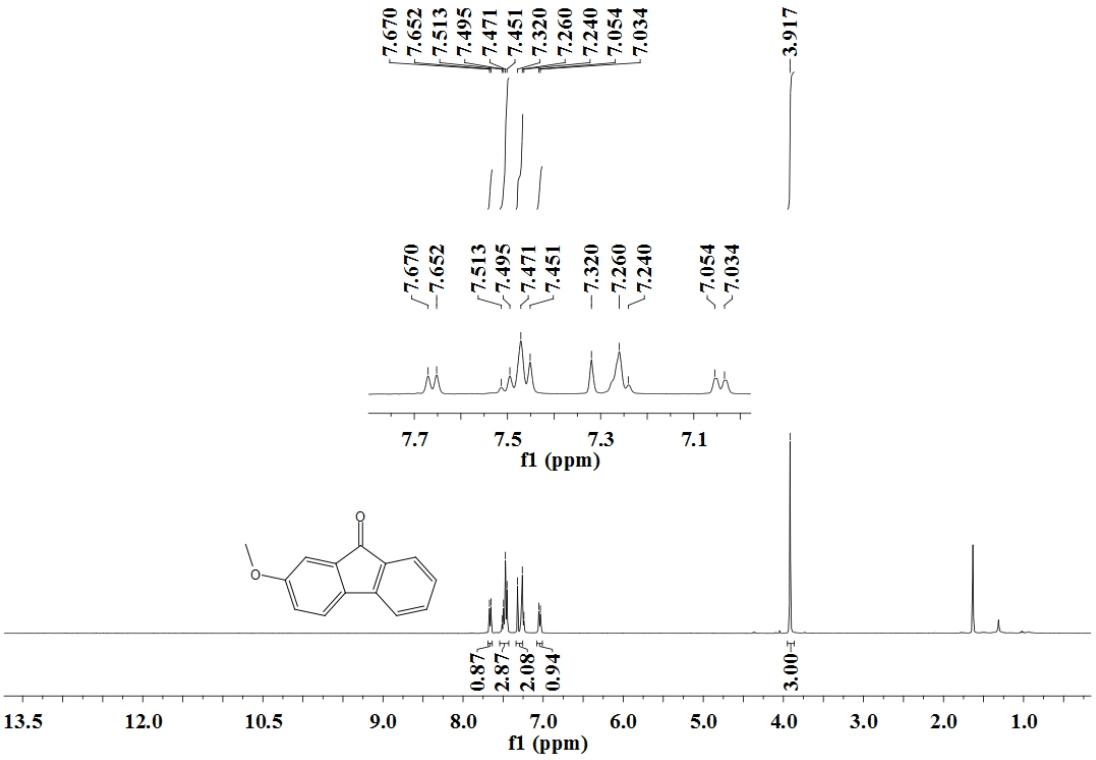

190.986
146.617
142.675
134.863
131.073
129.794
129.590
124.605
120.544
118.834
77.477
77.160
76.842
135.377
134.863
133.988
132.827
131.073
129.794
129.590
124.605
120.544
118.834
f1 (ppm)
Cl
O

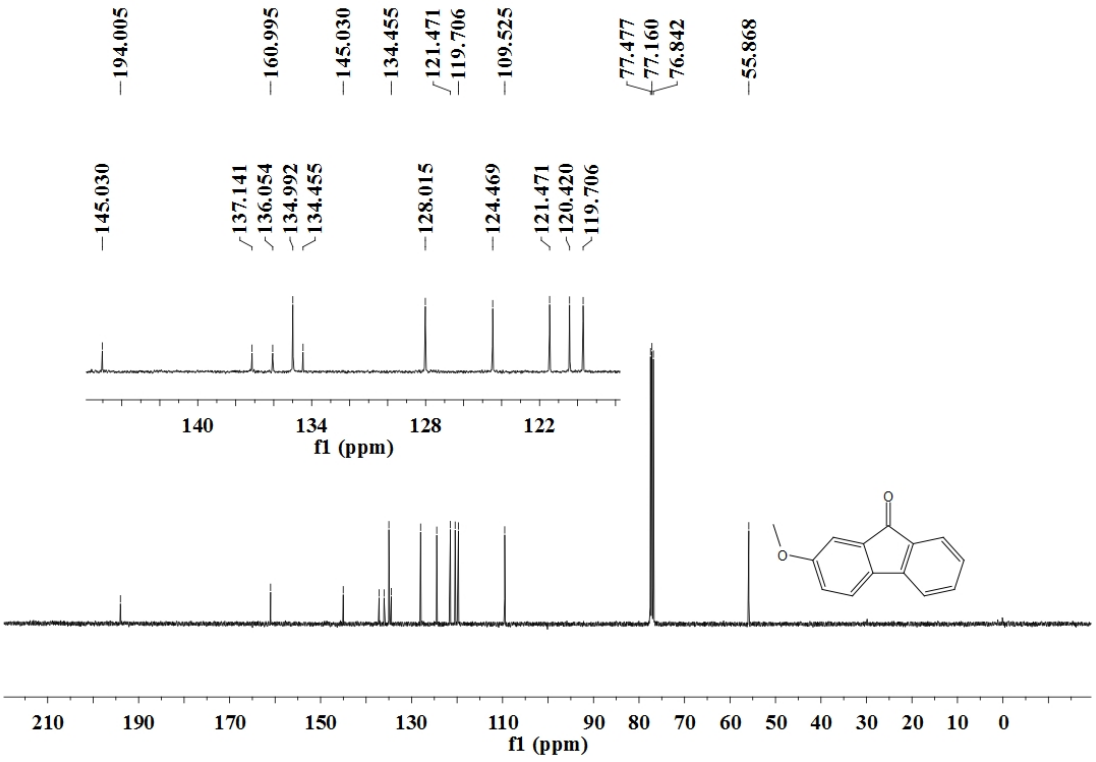

7.696
7.678
7.555
7.537
7.526
7.508
7.490
7.477
7.469
7.456
7.359
7.356
7.341
7.322
7.260
6.968
6.947
6.926
7.554
7.538
7.535
7.526
7.508
7.493
7.487
7.475
7.456
7.75
7.65
7.55
7.45
7.35
f1 (ppm)
7.1
7.0
6.9
6.8
6.7
f1 (ppm)

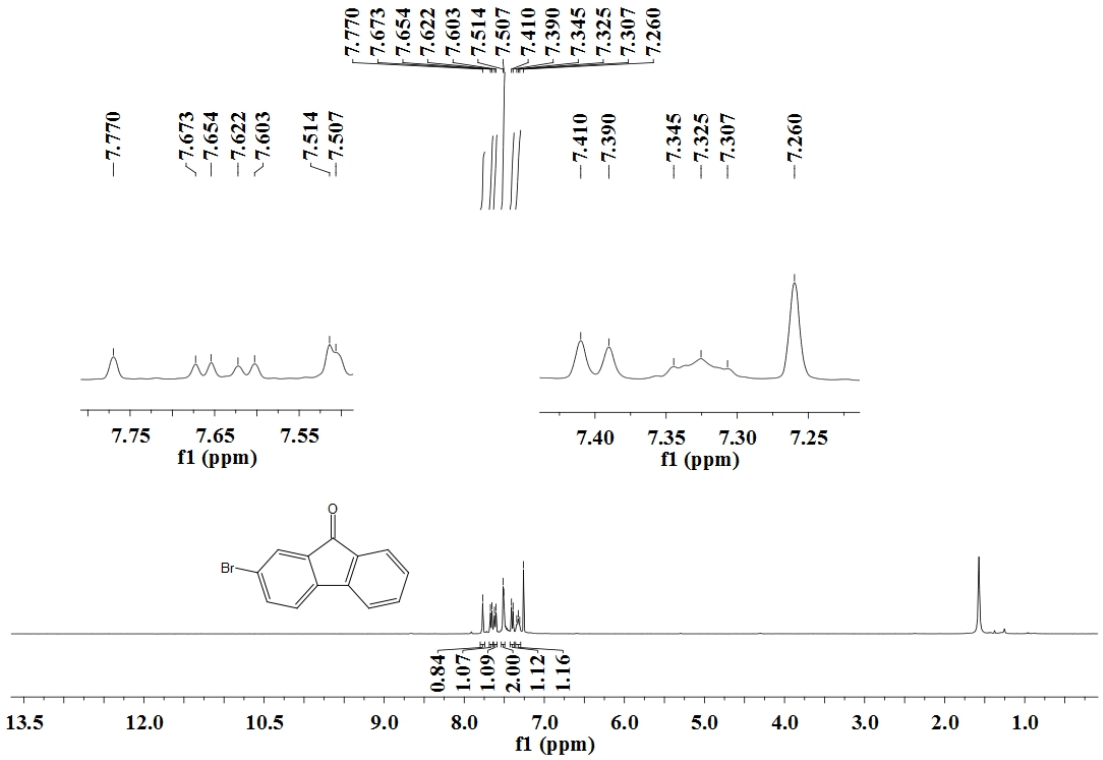

F
O
1.00
3.08
2.01
1.02
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
f1 (ppm)

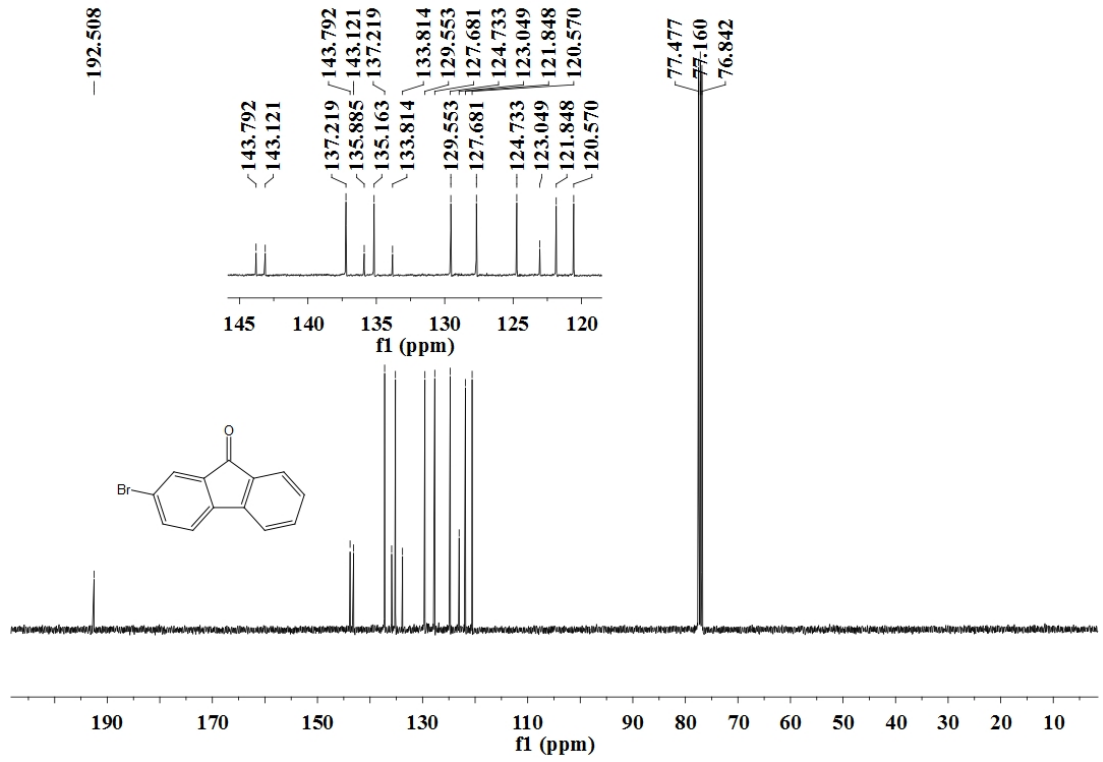

190.301
160.808
158.186
146.512
129.837
124.668
120.782
117.784
117.578
116.549
116.517
77.478
77.160
76.842
134.767
134.138
143.577
143.543
163
161
159
157
f1 (ppm)
144
f1 (ppm)
136
132
128
124
120
116
f1 (ppm)
F
O
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)

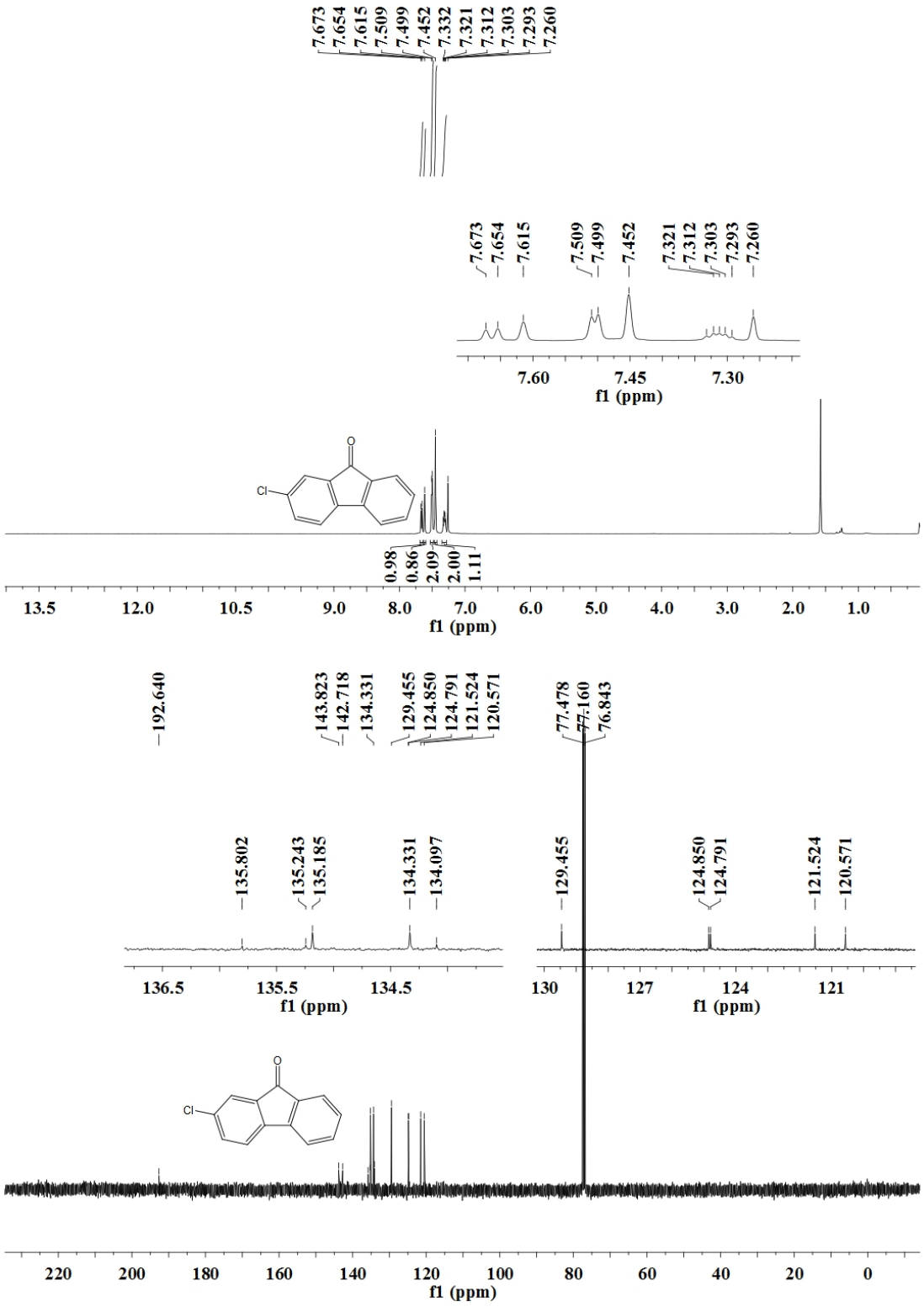

7.636
7.618
7.468
7.435
7.407
7.388
7.290
7.270
7.260
7.238
2.377
f1 (ppm)
0.91
2.82
0.94
1.01
1.01
3.00
f1 (ppm)
194.350
144.794
141.965
139.413
135.253
134.767
134.560
134.418
128.721
125.156
124.366
120.272
120.124
77.477
77.160
76.842
21.496
f1 (ppm)
f1 (ppm)

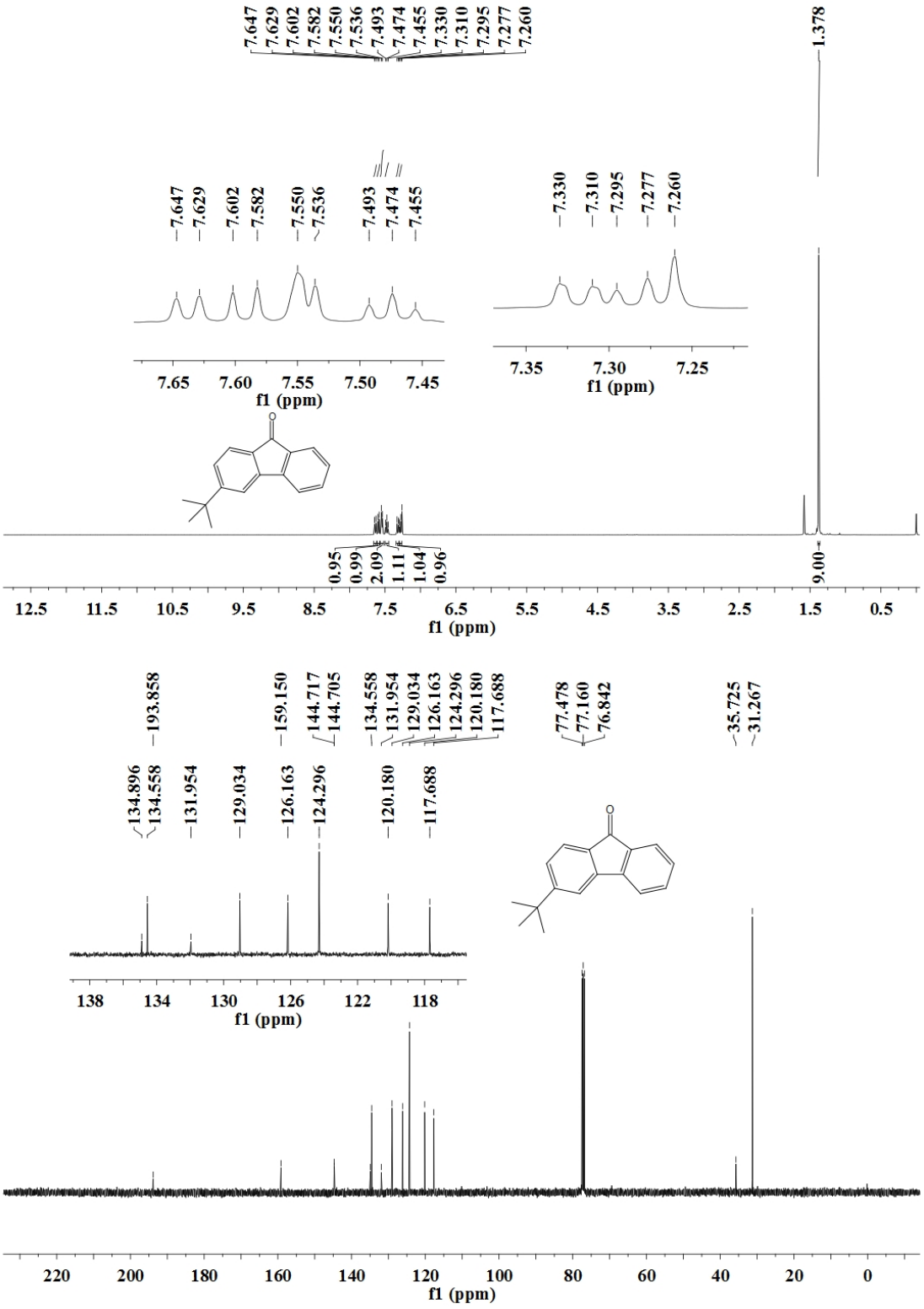

7.670
7.652
7.513
7.495
7.471
7.451
7.320
7.260
7.240
7.054
7.034
3.917
7.7
7.5
7.3
7.1
f1 (ppm)
0.87
2.87
2.08
0.94
3.00
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
f1 (ppm)

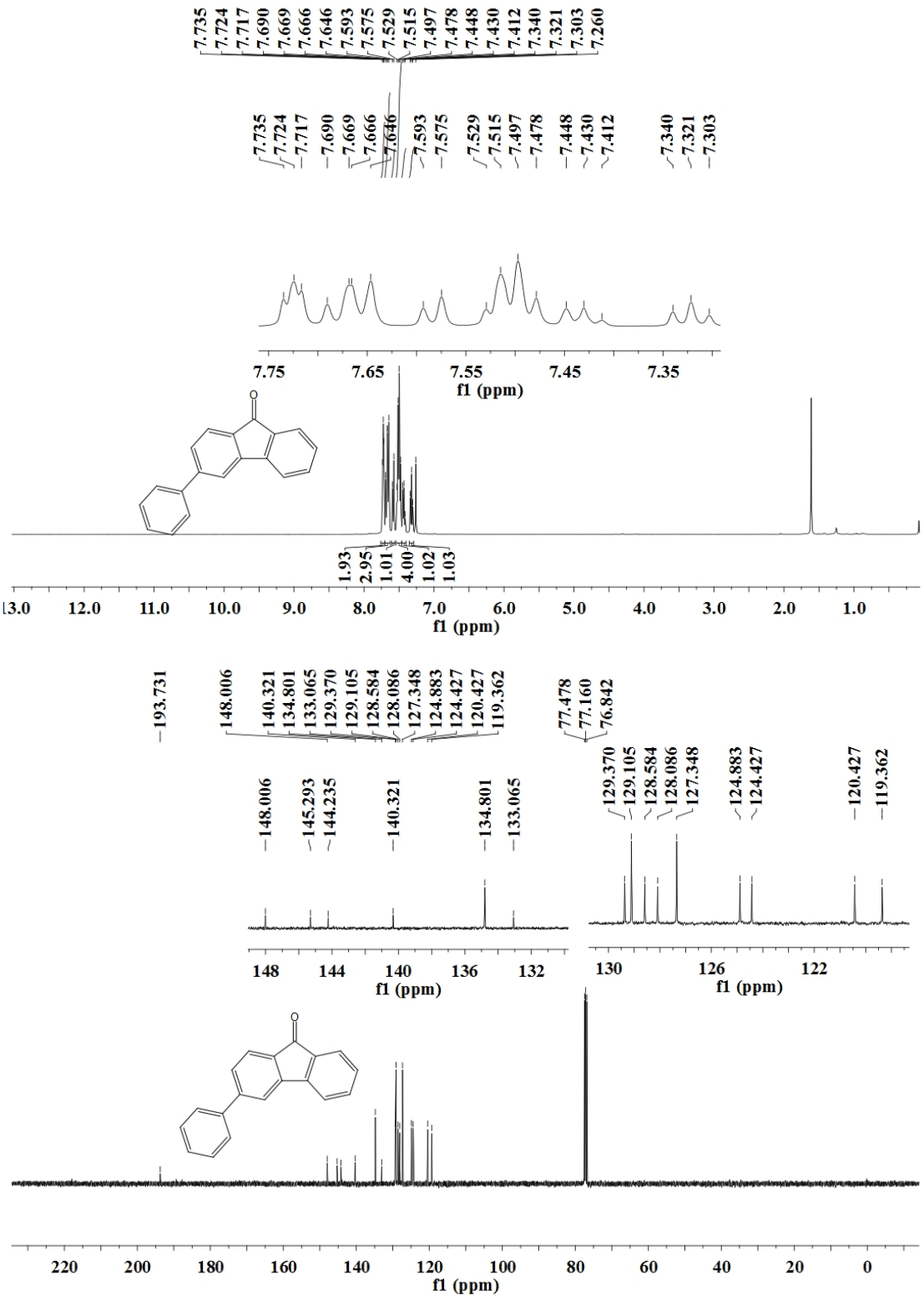

194.005
160.995
145.030
134.455
121.471
119.706
109.525
77.477
77.160
76.842
55.868
145.030
137.141
136.054
134.992
134.455
128.015
124.469
121.471
120.420
119.706
140
134
128
122
f1 (ppm)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

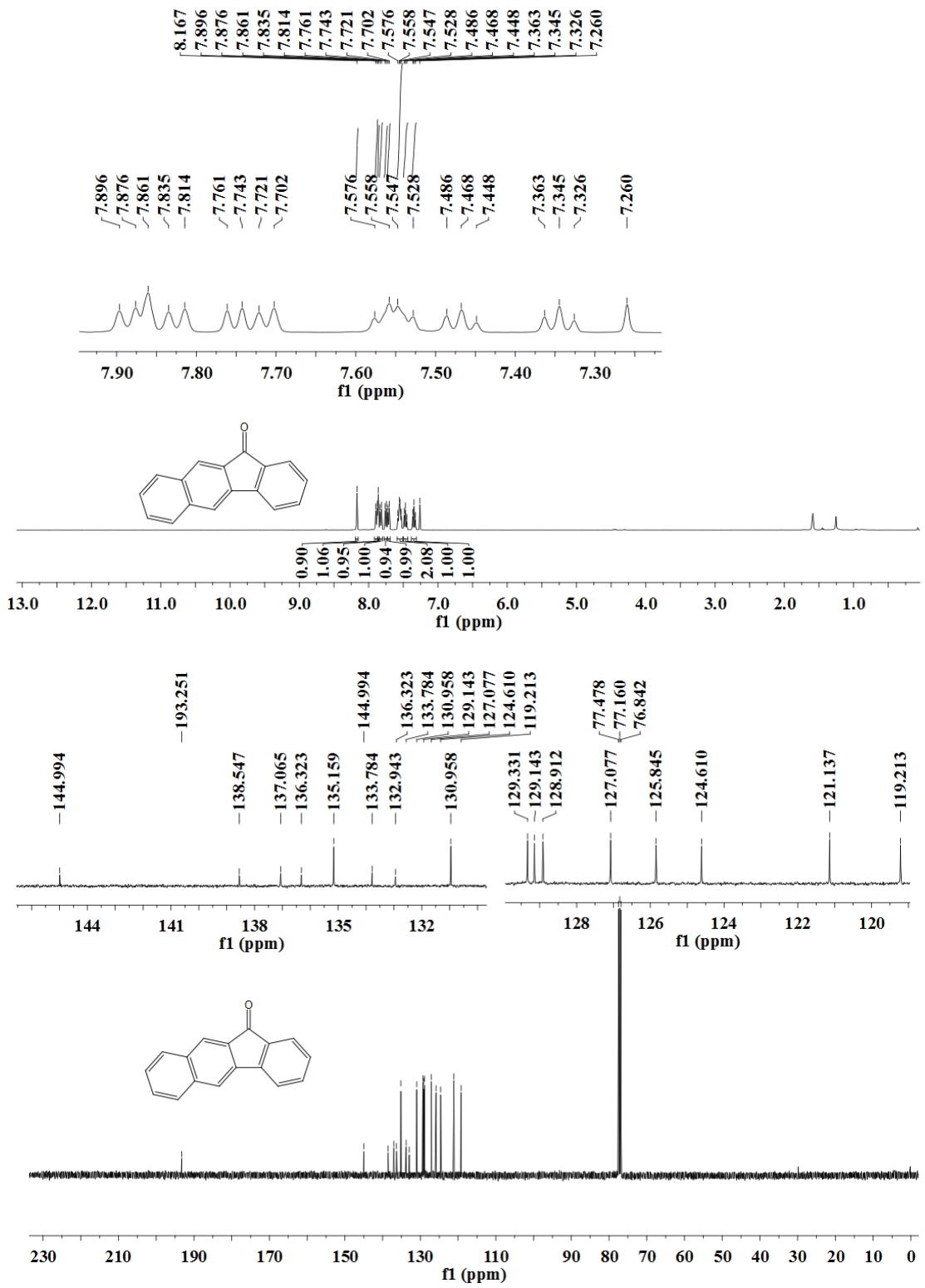

7.770
7.673
7.654
7.622
7.603
7.514
7.507
7.410
7.390
7.345
7.325
7.307
7.260
7.75
7.65
7.55
7.40
7.35
7.30
7.25
f1 (ppm)
Br
O
0.84
1.07
1.09
2.00
1.12
1.16
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
f1 (ppm)

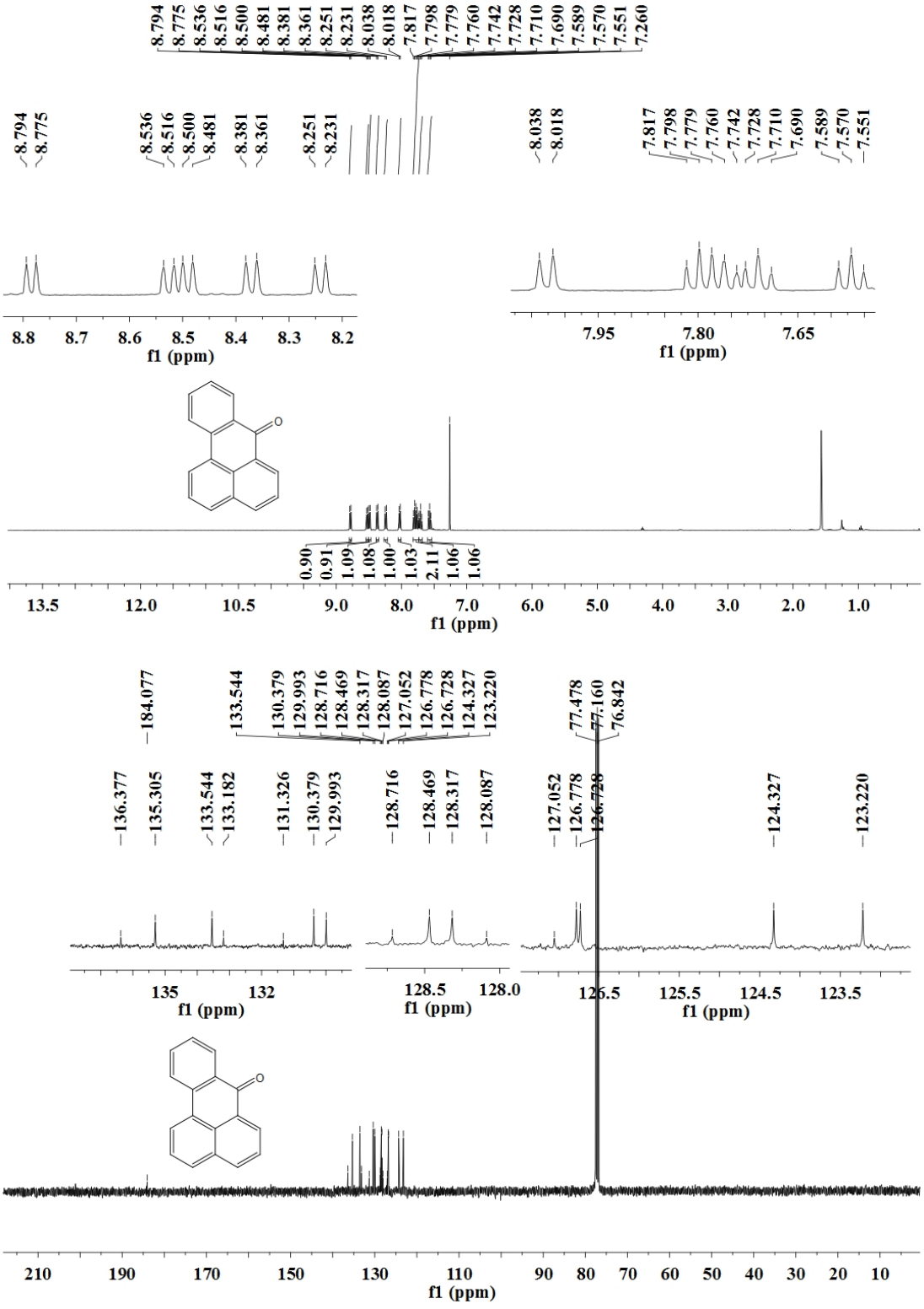

192.508
143.792
143.121
137.219
135.885
135.163
133.814
129.553
127.681
124.733
123.049
121.848
120.570
77.477
77.160
76.842
145
140
135
130
125
120
f1 (ppm)
Br
O
190
170
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)

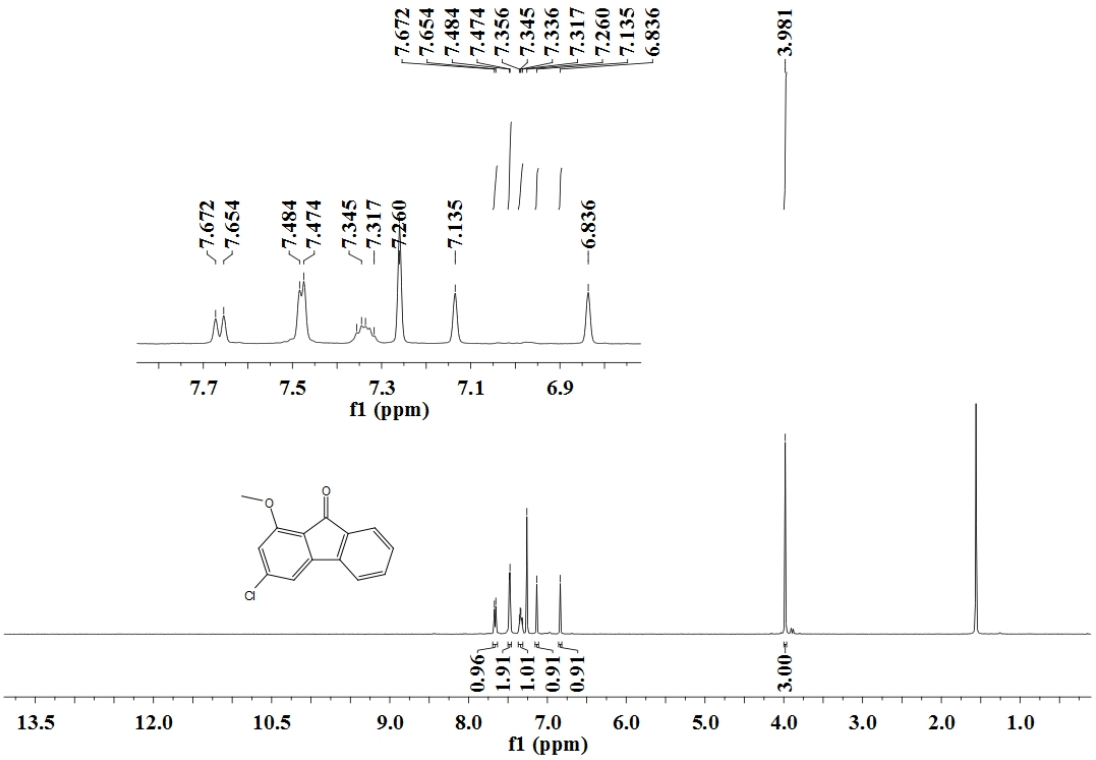

7.673
7.654
7.615
7.509
7.499
7.452
7.332
7.321
7.312
7.303
7.293
7.260
7.60
7.45
7.30
f1 (ppm)
O
Cl
0.98
0.86
2.09
2.00
1.11
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
f1 (ppm)
192.640
143.823
142.718
134.331
129.455
124.850
124.791
121.524
120.571
77.478
77.160
76.843
135.802
135.243
135.185
134.331
134.097
129.455
124.850
124.791
121.524
120.571
136.5
135.5
134.5
f1 (ppm)
130
127
124
121
f1 (ppm)
O
Cl
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

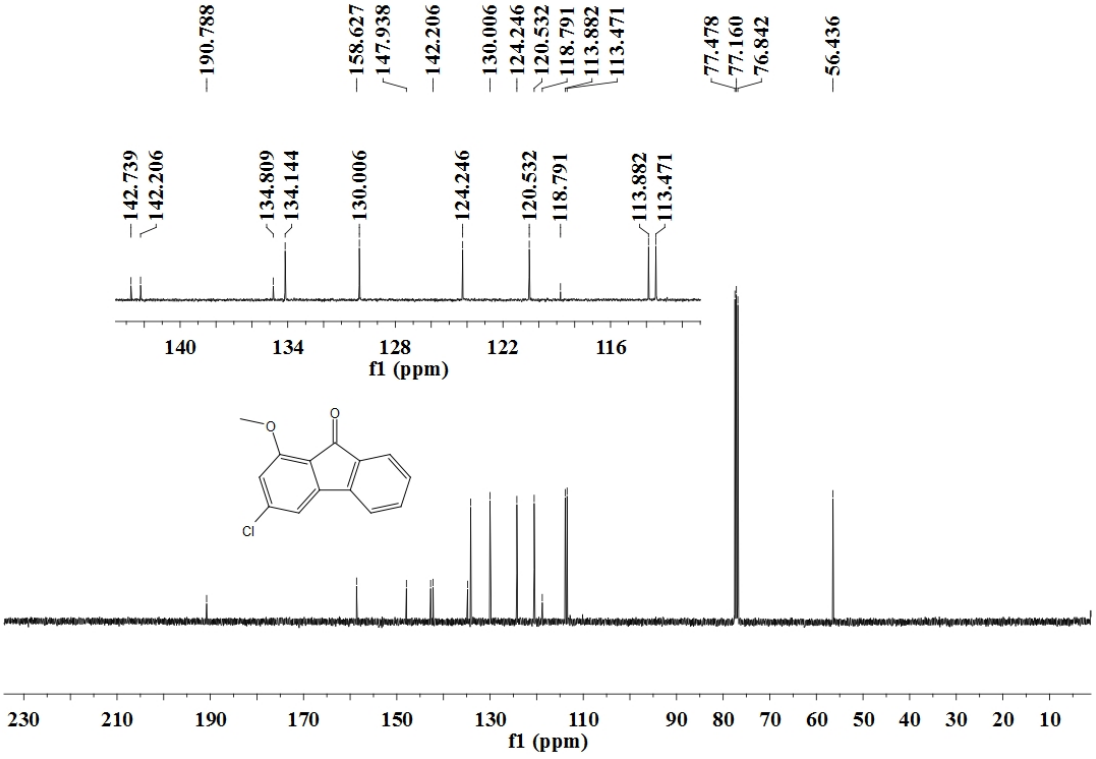

7.647
7.629
7.602
7.582
7.550
7.536
7.493
7.474
7.455
7.330
7.310
7.295
7.277
7.260
1.378
f1 (ppm)
0.95
0.99
2.09
1.11
1.04
0.96
9.00
193.858
159.150
144.717
144.705
134.558
131.954
129.034
126.163
124.296
120.180
117.688
77.478
77.160
76.842
35.725
31.267
134.896
f1 (ppm)

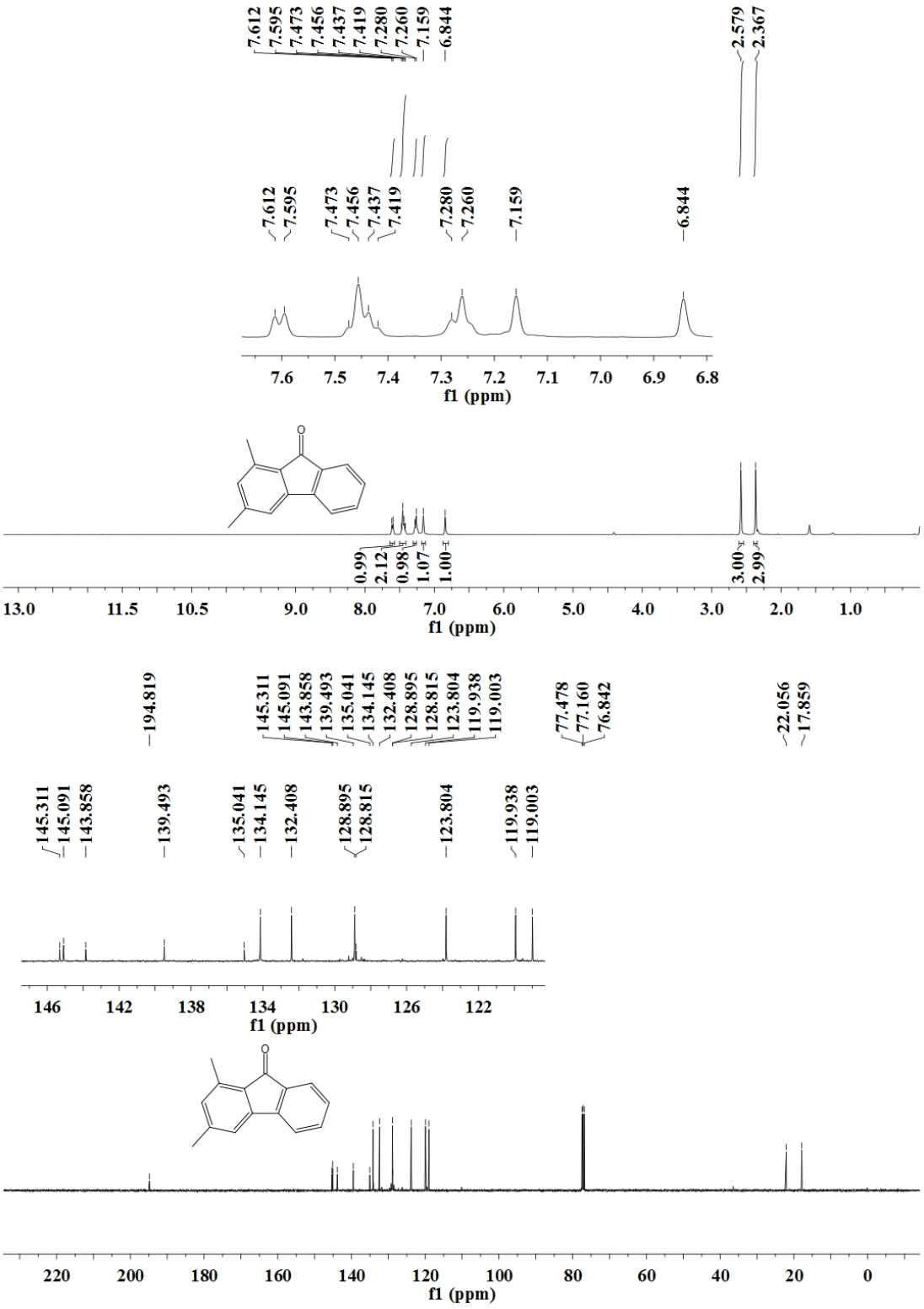

7.735
7.724
7.717
7.690
7.669
7.666
7.646
7.593
7.575
7.529
7.515
7.497
7.478
7.448
7.430
7.412
7.340
7.321
7.303
7.260
7.75
7.65
7.55
7.45
7.35
f1 (ppm)
1.93
2.95
1.01
4.00
1.02
1.03
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
f1 (ppm)
193.731
148.006
140.321
134.801
133.065
129.370
129.105
128.584
128.086
127.348
124.883
124.427
120.427
119.362
77.478
77.160
76.842
148.006
145.293
144.235
140.321
134.801
133.065
129.370
129.105
128.584
128.086
127.348
124.883
124.427
120.427
119.362
148
144
140
136
132
f1 (ppm)
130
126
122
f1 (ppm)
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

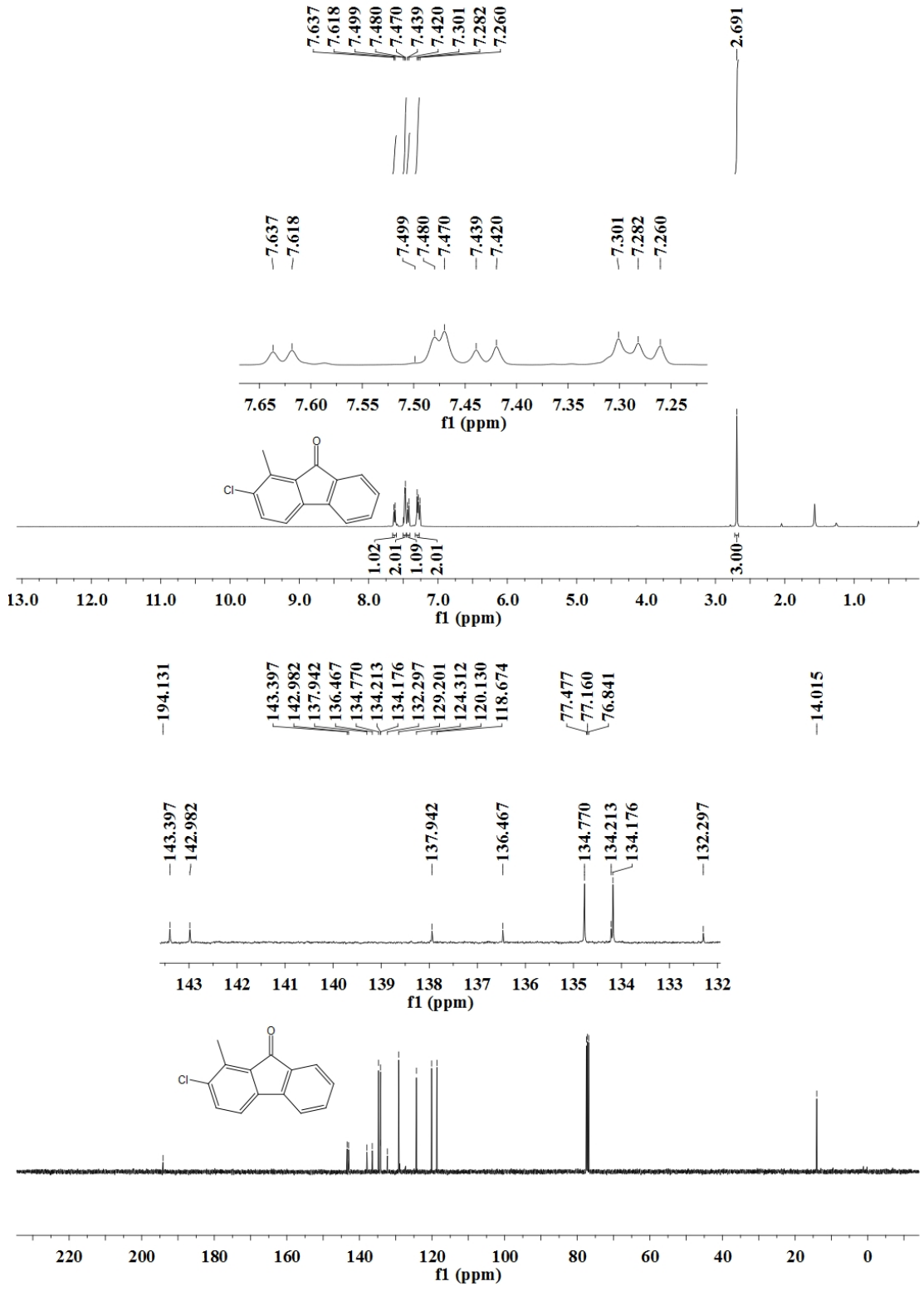

8.167
7.896
7.876
7.861
7.835
7.814
7.761
7.743
7.721
7.702
7.576
7.558
7.547
7.528
7.486
7.468
7.448
7.363
7.345
7.326
7.260
f1 (ppm)
O
0.90
1.06
0.95
1.00
0.94
0.99
2.08
1.00
1.00
f1 (ppm)
193.251
144.994
136.323
133.784
130.958
129.143
127.077
124.610
119.213
77.478
77.160
76.842
144.994
138.547
137.065
136.323
135.159
133.784
132.943
130.958
129.331
129.143
128.912
127.077
125.845
124.610
121.137
119.213
f1 (ppm)
f1 (ppm)
O
f1 (ppm)

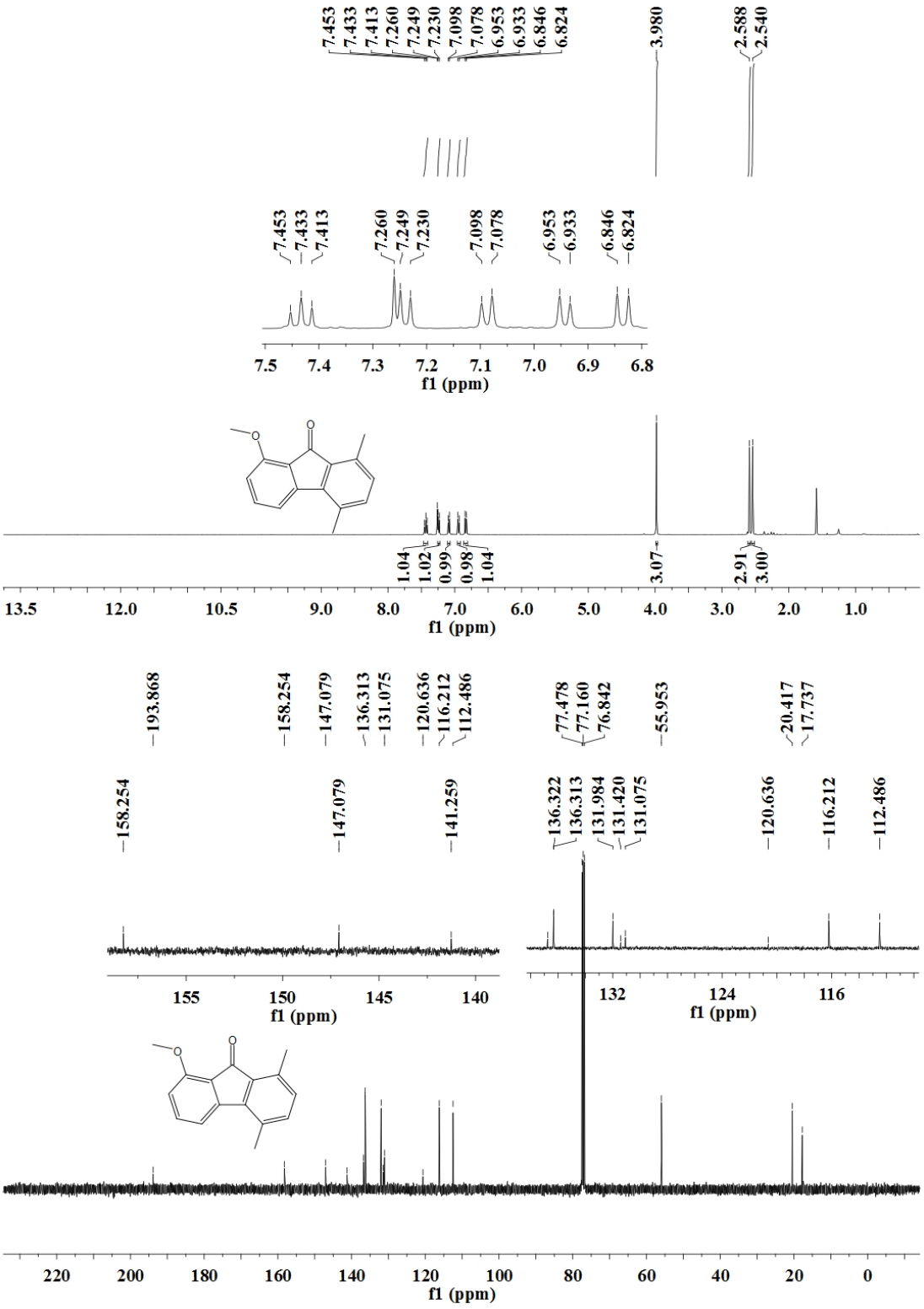

8.794
8.775
8.536
8.516
8.500
8.481
8.381
8.361
8.251
8.231
8.038
8.018
7.817
7.798
7.779
7.760
7.742
7.728
7.710
7.690
7.589
7.570
7.551
7.260
f1 (ppm)
0.90
0.91
1.09
1.08
1.00
1.03
2.11
1.06
1.06
184.077
136.377
135.305
133.544
133.182
131.326
130.379
129.993
128.716
128.469
128.317
128.087
127.052
126.778
126.728
124.327
123.220
77.478
77.160
76.842

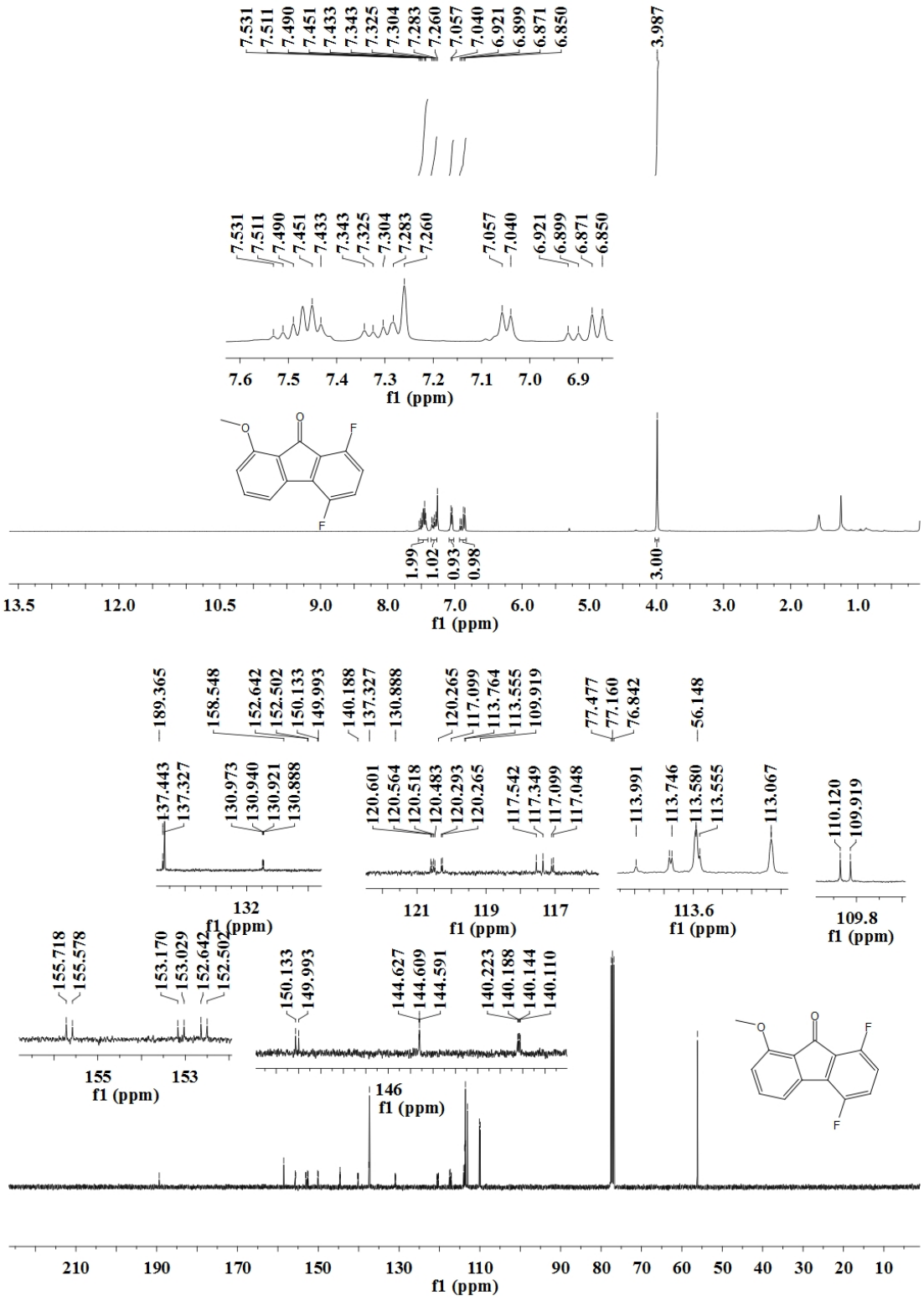

7.672
7.654
7.484
7.474
7.356
7.345
7.336
7.317
7.260
7.135
6.836
3.981
7.7
7.5
7.3
7.1
6.9
f1 (ppm)
0.96
1.91
1.01
0.91
0.91
3.00
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
f1 (ppm)

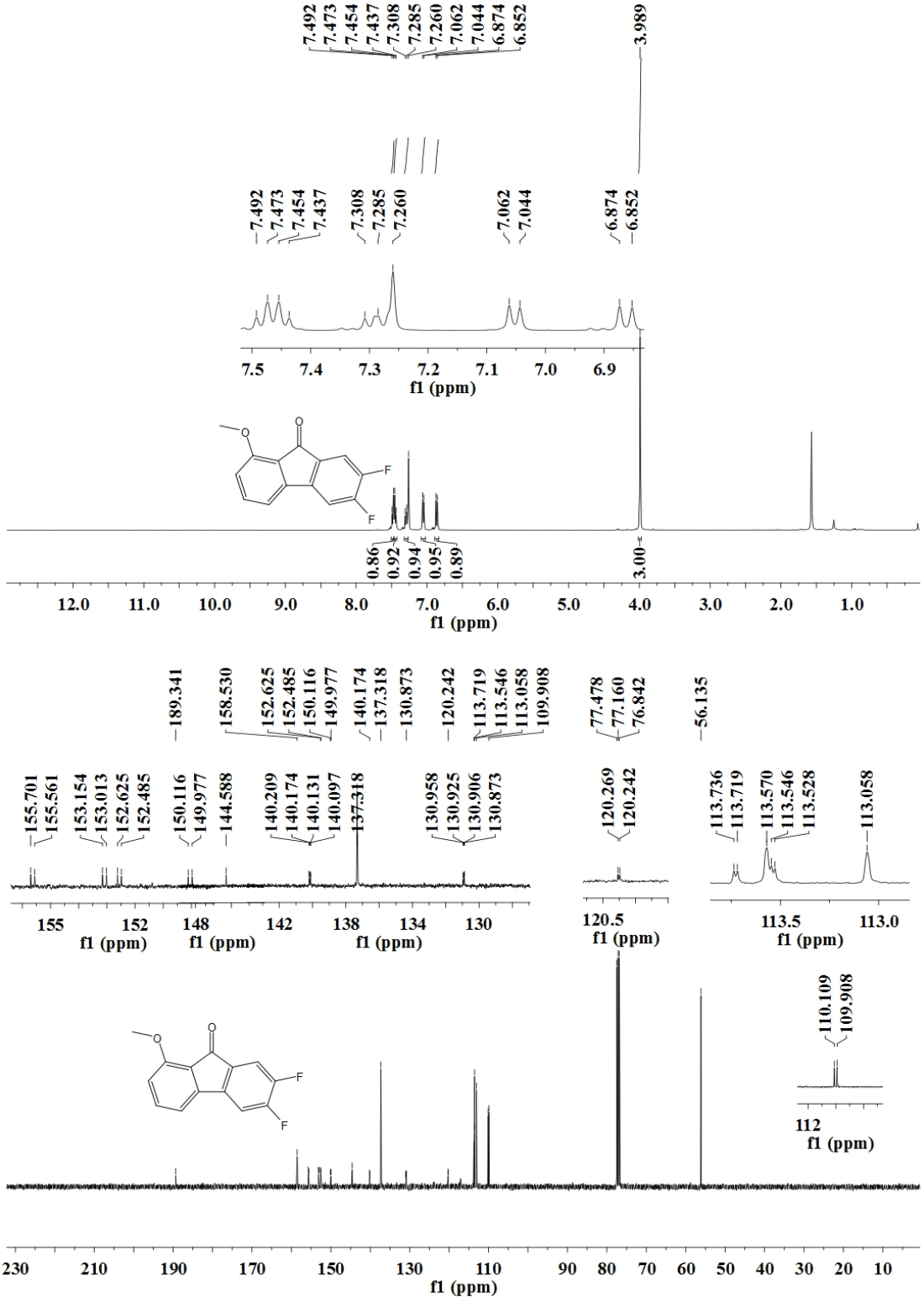

190.788
158.627
147.938
142.206
130.006
124.246
120.532
118.791
113.882
113.471
77.478
77.160
76.842
56.436
142.739
142.206
134.809
134.144
130.006
124.246
120.532
118.791
113.882
113.471
140
134
128
122
116
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)

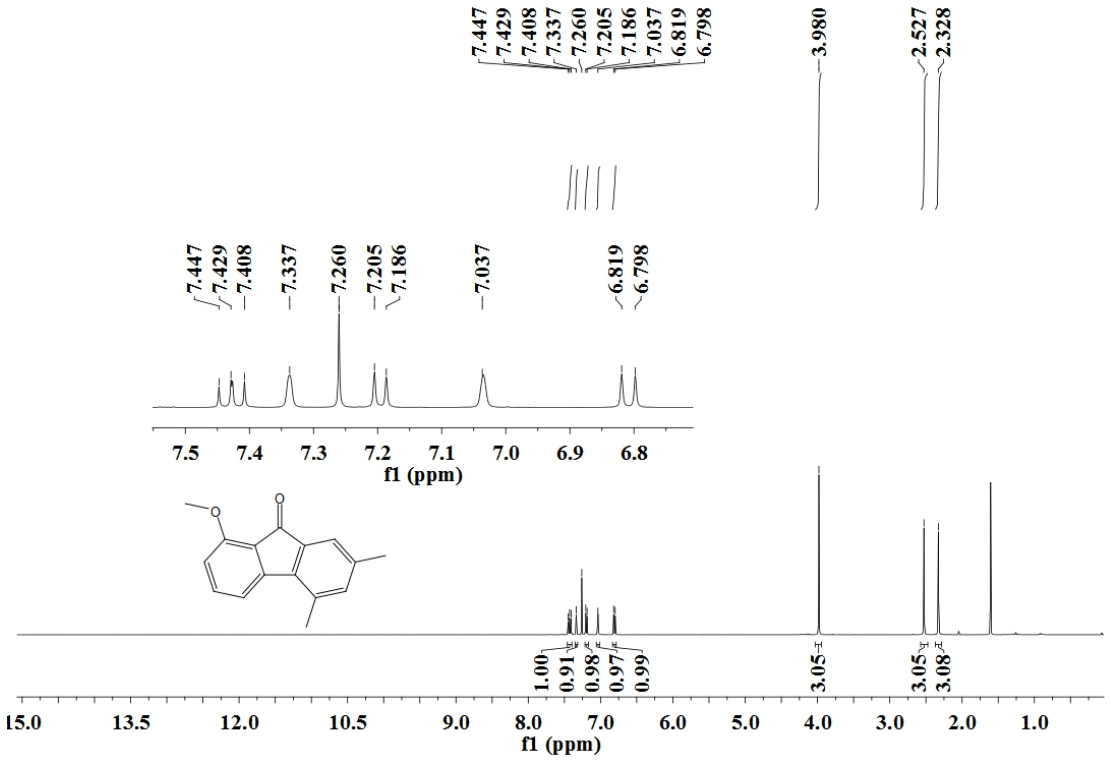

7.612
7.595
7.473
7.456
7.437
7.419
7.280
7.260
7.159
6.844
2.579
2.367
f1 (ppm)
0.99
2.12
0.98
1.07
1.00
3.00
2.99
f1 (ppm)
194.819
145.311
145.091
143.858
139.493
135.041
134.145
132.408
128.895
128.815
123.804
119.938
119.003
77.478
77.160
76.842
22.056
17.859
f1 (ppm)
f1 (ppm)

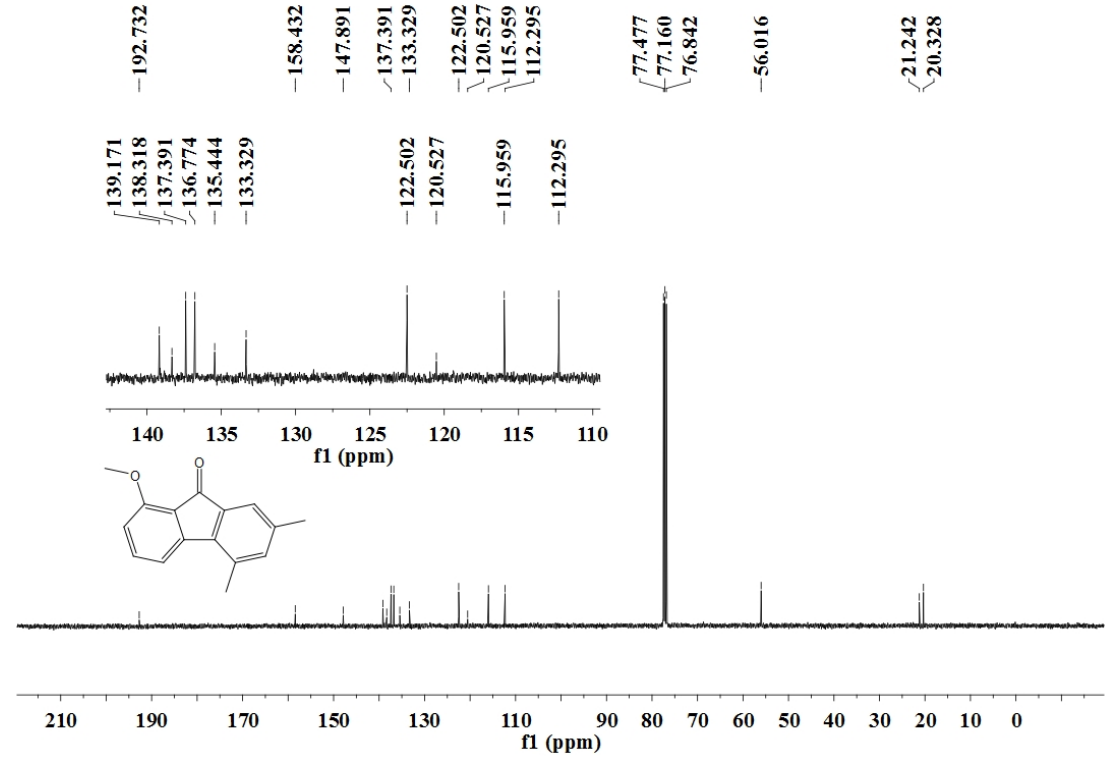

7.637
7.618
7.499
7.480
7.470
7.439
7.420
7.301
7.282
7.260
2.691
7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25
f1 (ppm)
O
Cl
1.02
2.01
1.09
2.01
3.00
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
f1 (ppm)
194.131
143.397
142.982
137.942
136.467
134.770
134.213
134.176
132.297
129.201
124.312
120.130
118.674
77.477
77.160
76.841
14.015
143 142 141 140 139 138 137 136 135 134 133 132
f1 (ppm)
220 200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

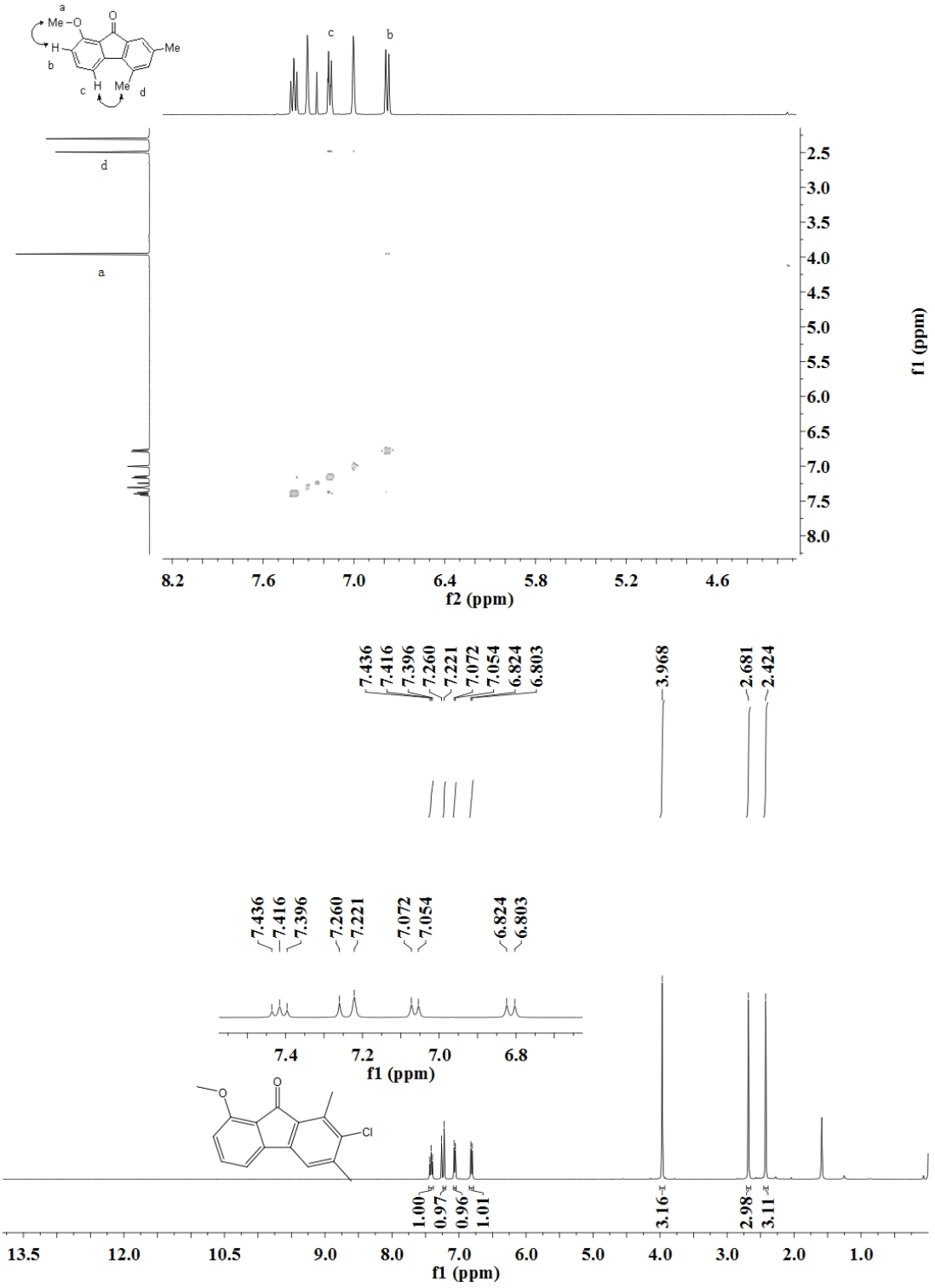

7.453
7.433
7.413
7.260
7.249
7.230
7.098
7.078
6.953
6.933
6.846
6.824
3.980
2.588
2.540
f1 (ppm)
1.04
1.02
0.99
0.98
1.04
3.07
2.91
3.00
193.868
158.254
147.079
136.313
131.075
120.636
116.212
112.486
77.478
77.160
76.842
55.953
20.417
17.737
136.322
131.984
131.420
141.259
f1 (ppm)

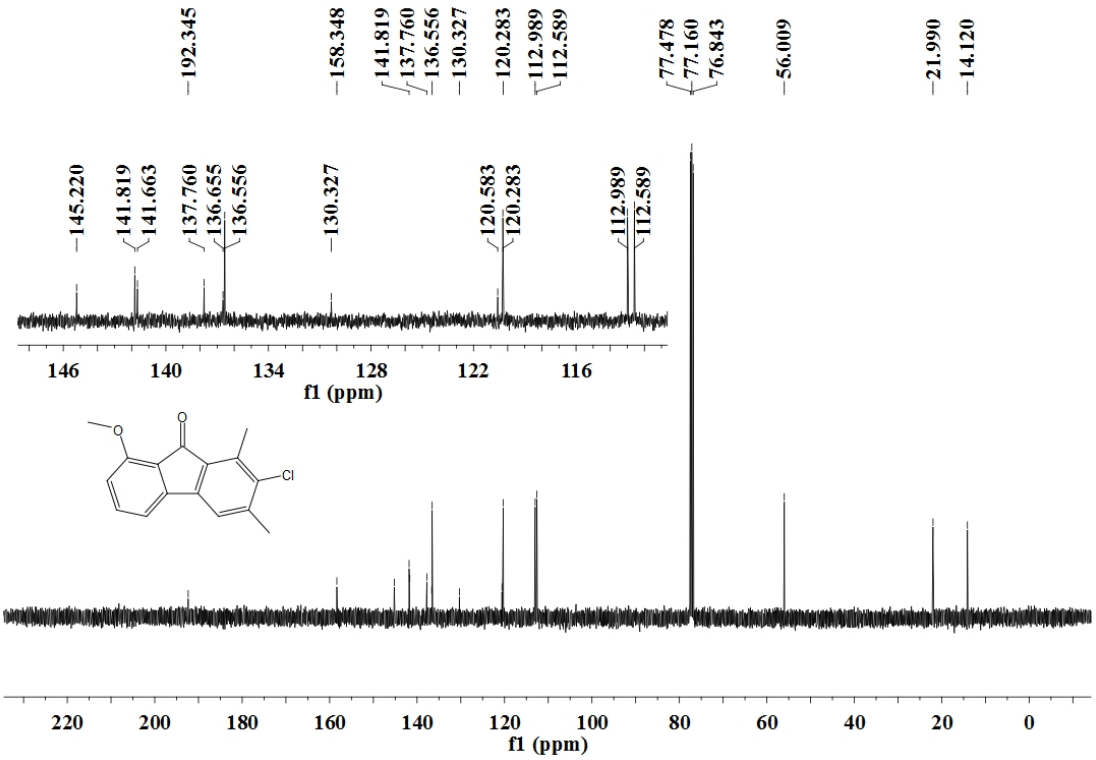

7.531
7.511
7.490
7.451
7.433
7.343
7.325
7.304
7.283
7.260
7.057
7.040
6.921
6.899
6.871
6.850
3.987
f1 (ppm)
1.99
1.02
0.93
0.98
3.00
189.365
158.548
152.642
152.502
150.133
149.993
140.188
137.327
130.888
120.265
117.099
113.764
113.555
109.919
77.477
77.160
76.842
56.148
155.718
155.578
153.170
153.029
152.642
152.502
150.133
149.993
144.627
144.609
144.591
140.223
140.188
140.144
140.110
137.443
137.327
130.973
130.940
130.921
130.888
120.601
120.564
120.518
120.483
120.293
120.265
117.542
117.349
117.099
117.048
113.991
113.746
113.580
113.555
113.067
110.120
109.919

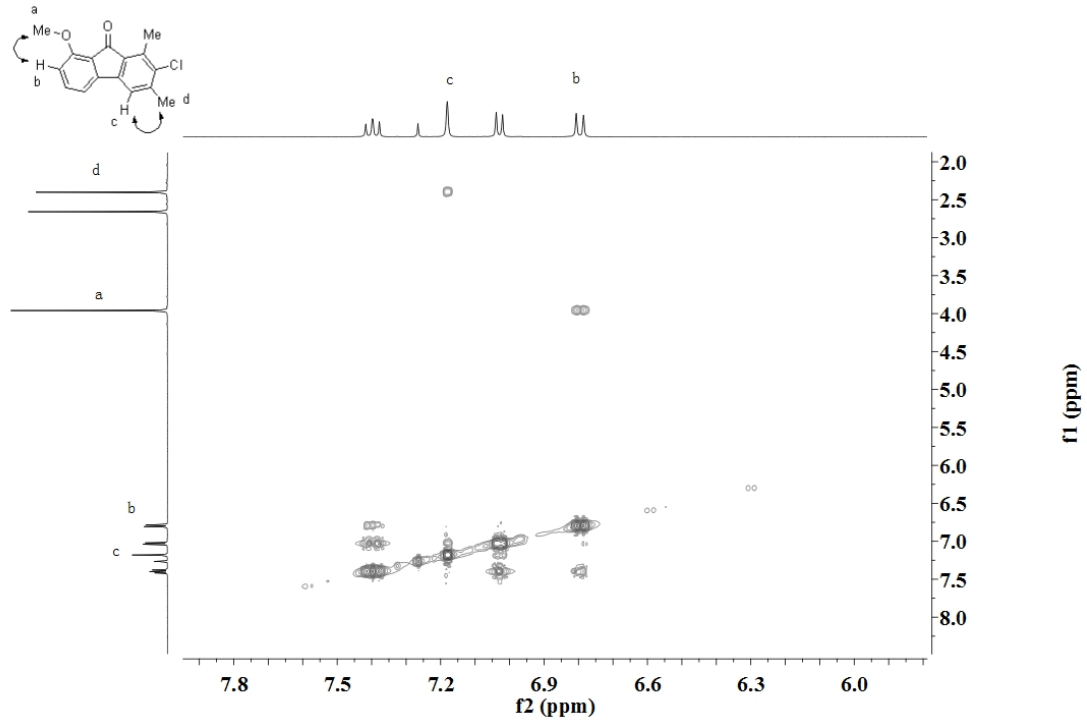

7.492
7.473
7.454
7.437
7.308
7.285
7.260
7.062
7.044
6.874
6.852
3.989
f1 (ppm)
0.86
0.92
0.94
0.95
0.89
3.00
189.341
158.530
152.625
152.485
150.116
149.977
140.174
137.318
130.873
120.242
113.719
113.546
113.058
109.908
77.478
77.160
76.842
56.135
155.701
155.561
153.154
153.013
152.625
152.485
150.116
149.977
144.588
140.209
140.174
140.131
140.097
137.318
130.958
130.925
130.906
130.873
120.269
120.242
113.736
113.719
113.570
113.546
113.528
113.058
110.109
109.908
O
F

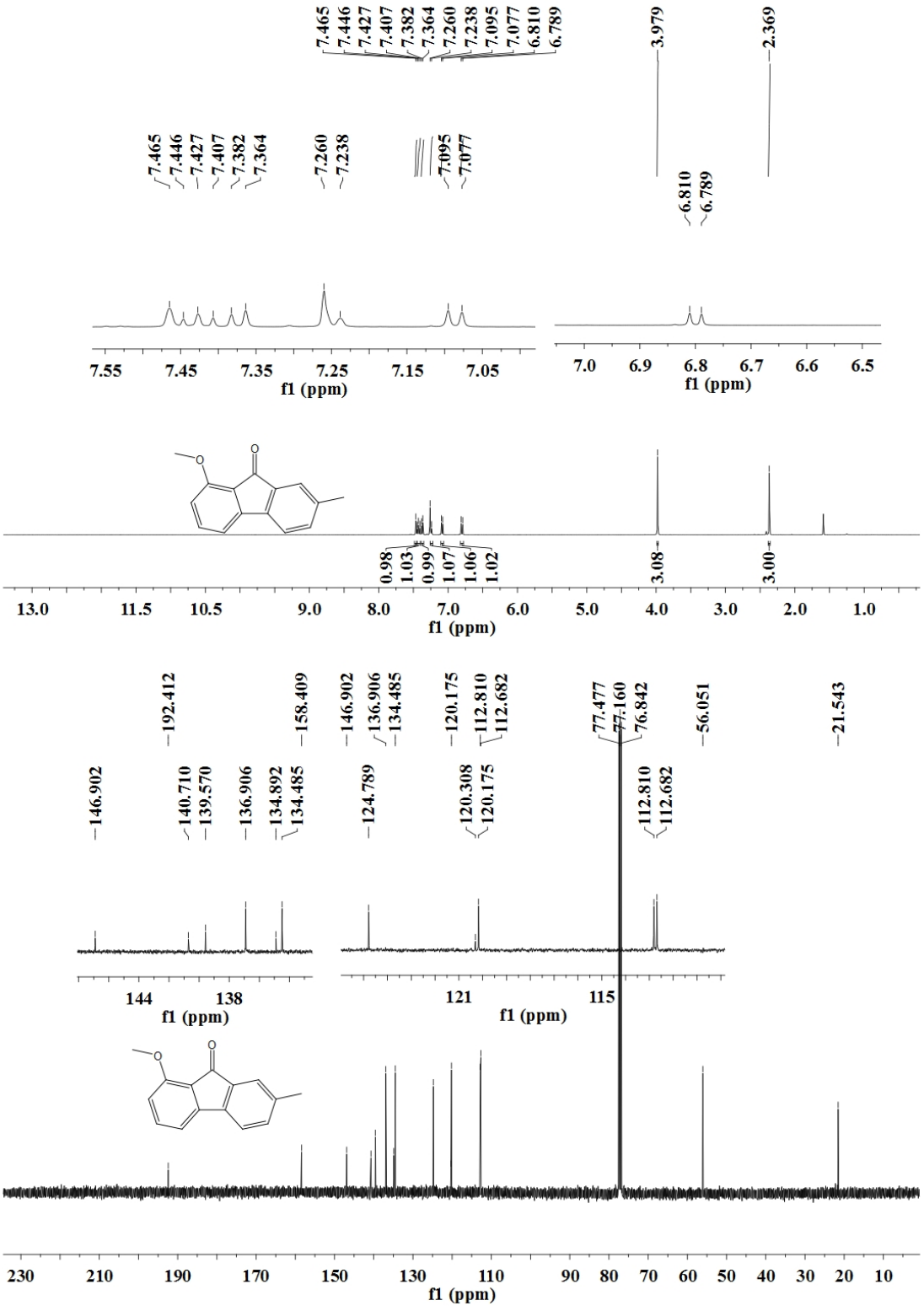

7.447
7.429
7.408
7.337
7.260
7.205
7.186
7.037
6.819
6.798
3.980
2.527
2.328
1.00
0.91
0.98
0.97
0.99
3.05
3.05
3.08
f1 (ppm)

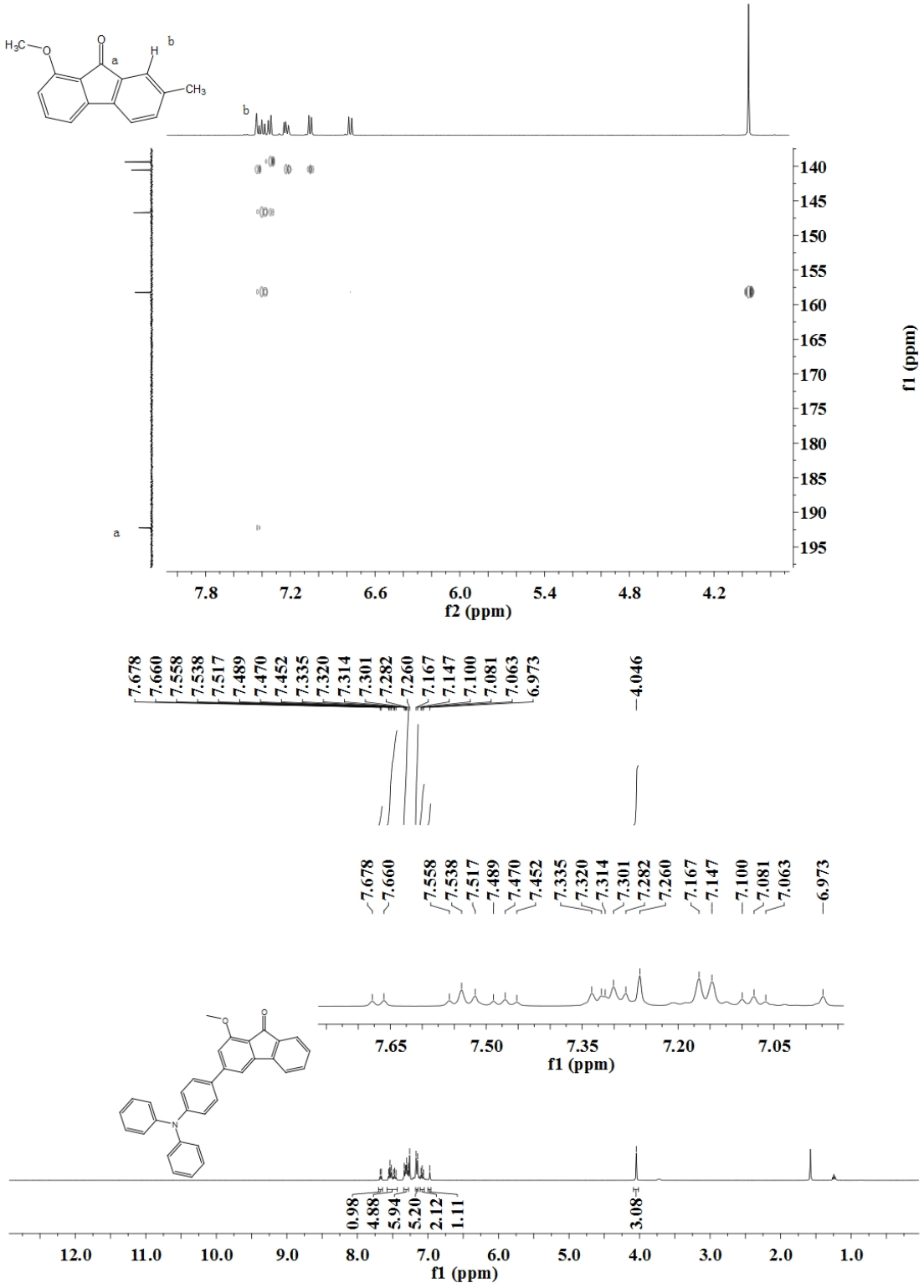

192.732
158.432
147.891
137.391
133.329
122.502
120.527
115.959
112.295
77.477
77.160
76.842
56.016
21.242
20.328
139.171
138.318
137.391
136.774
135.444
133.329
122.502
120.527
115.959
112.295
f1 (ppm)

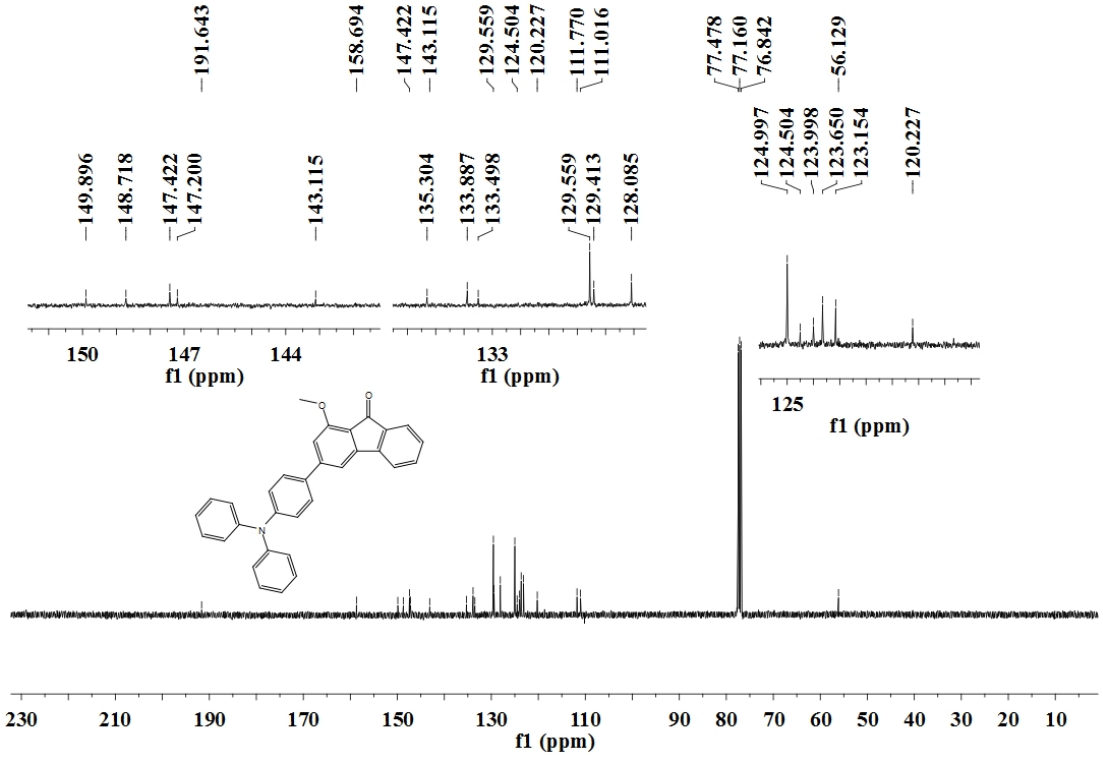

a
Me–O
O
H
b
Me
c
H
Me
d
c
b
d
a
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
f1 (ppm)
8.2
7.6
7.0
6.4
5.8
5.2
4.6
f2 (ppm)
7.436
7.416
7.396
7.260
7.221
7.072
7.054
6.824
6.803
3.968
2.681
2.424
7.4
7.2
7.0
6.8
f1 (ppm)
O
O
Cl
1.00
0.97
0.96
1.01
3.16
2.98
3.11
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
f1 (ppm)


192.345
158.348
141.819
137.760
136.556
130.327
120.283
112.989
112.589
77.478
77.160
76.843
56.009
21.990
14.120
145.220
141.819
141.663
137.760
136.655
136.556
130.327
120.583
120.283
112.989
112.589
146
140
134
128
122
116
f1 (ppm)
O
O
Cl
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


a
Me
O
Me
H
b
Cl
Me
d
H
c
c
b
d
a
b
c
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
f1 (ppm)
7.8
7.5
7.2
6.9
6.6
6.3
6.0
f2 (ppm)


7.465
7.446
7.427
7.407
7.382
7.364
7.260
7.238
7.095
7.077
6.810
6.789
3.979
2.369
f1 (ppm)
0.98
1.03
0.99
1.07
1.06
1.02
3.08
3.00
192.412
158.409
146.902
136.906
134.485
120.175
112.810
112.682
77.477
77.160
76.842
56.051
21.543
140.710
139.570
134.892
124.789
120.308
144
138
121
115


H3C
O
a
H
b
CH3
b
a
140
145
150
155
160
165
170
175
180
185
190
195
f1 (ppm)
7.8
7.2
6.6
6.0
5.4
4.8
4.2
f2 (ppm)
7.678
7.660
7.558
7.538
7.517
7.489
7.470
7.452
7.335
7.320
7.314
7.301
7.282
7.260
7.167
7.147
7.100
7.081
7.063
6.973
4.046
7.65
7.50
7.35
7.20
7.05
f1 (ppm)
0.98
4.88
5.94
5.20
2.12
1.11
3.08
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
f1 (ppm)


191.643
158.694
147.422
143.115
129.559
124.504
120.227
111.770
111.016
77.478
77.160
76.842
56.129
149.896
148.718
147.422
147.200
143.115
135.304
133.887
133.498
129.559
129.413
128.085
124.997
124.504
123.998
123.650
123.154
120.227
150
147
144
f1 (ppm)
133
f1 (ppm)
125
f1 (ppm)
O
O
N
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)