Supplementary Information

Synthesis of Fluorenes and Their Related Compounds from Biaryls and Meldrum's Acid Derivatives

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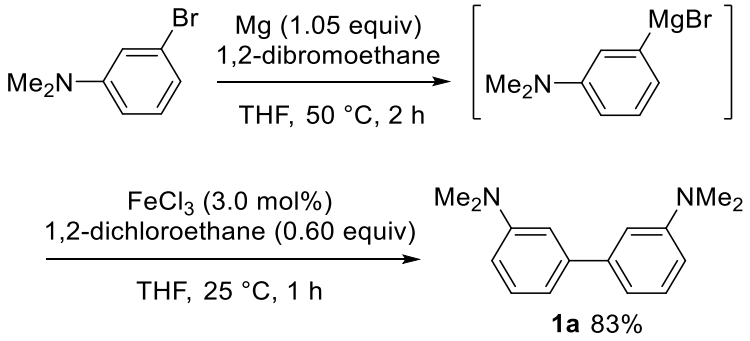
Contents

1. General

All reactions were carried out using standard Schlenk techniques under an inert atmosphere. All reagents were purchased from commercial sources and used without further purification unless otherwise noted. NMR spectra were recorded on JEOL ECZ-400 (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR) and JEOL JNM-ECA600 (600 MHz for ^{1}H NMR, 150 MHz for ^{13}C NMR). Proton and carbon chemical shifts are reported relative to the residual solvent ($CDCl_3$ (δ 7.26 for ^{1}H NMR or δ 77.16 for ^{13}C NMR), CD_2Cl_2 (δ 5.32 for ^{1}H NMR or δ 53.84 for ^{13}C NMR), Acetone-d_6 (δ 2.05 for ^{1}H NMR or δ 29.84, 206.26 for ^{13}C NMR)) used as an internal reference. HRMS were measured on a JEOL JMS-700 spectrometer. UV/vis absorption spectra was measured with a V650 spectrophotometer (JASCO). Fluorescent spectra and quantum yield were measured with C9920-02 absolute quantum yield spectrometer (Hamamatsu Photonics).

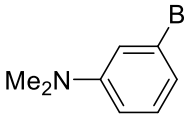
2. Synthesis and Characterization of Substrates

Synthesis of 1a



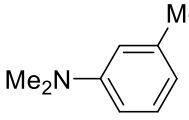
Scheme S1. Synthesis of Compound **1a**

3-Bromo-*N*,*N*-dimethylaniline



3-Bromo-*N*,*N*-dimethylaniline was synthesized according to the reported method:[1] A mixture of 3-bromoaniline (17.2 g, 100 mmol, 1.00 equiv), iodomethane (31.2 g, 220 mmol, 2.20 equiv), and K_2CO_3 (30.4 g, 220 mmol, 2.20 equiv) in dehydrated DMF (150 mL) was stirred at 75 °C for 24 h. After completion of the reaction monitored by TLC, the reaction mixture was poured into aq. $NaHCO_3$ solution and extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The mixture was purified by column chromatography on silica gel (hexane) to give 3-bromo-*N*,*N*-dimethylaniline as a pale yellow oil (19.1 g, 95.7 mmol, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (dd, *J* = 8.1, 8.1 Hz, 1H), 6.85-6.79 (m, 2H), 6.62 (ddd, *J* = 8.4, 2.4, 1.0 Hz, 1H), 2.94 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.8, 130.4, 123.5, 119.2, 115.2, 111.0, 40.5. The analytical data is in accordance with the previous report.[2]

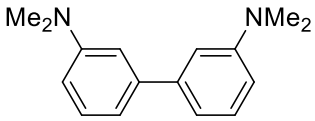
(3-(Dimethylamino)phenyl)magnesium bromide



The Grignard reagent (3-(dimethylamino)phenyl)magnesium bromide) was prepared according to the reported method:[3] A 200 mL two-necked round bottom flask was equipped with a magnetic stirrer bar and a constant-pressure dropping funnel. All equipments were dried over by a heat gun or an oven, and activated magnesium turnings (2.37 g, 97.7 mmol, 1.05 equiv) was added. The equipment was sealed with rubber septum, evacuated, and back filled with nitrogen. 1.0 M solution of 3-bromo-*N*,*N*-dimethylaniline (18.6 g, 93.0 mmol, 1.00 equiv)

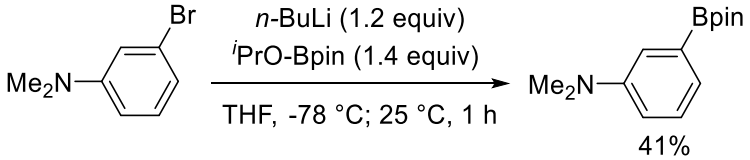
in dehydrated THF (93 mL) was dropwise via the constant-pressure dropping funnel at rt within 30 min. A few drops (1 drop per 1 mL of the solution) of 1,2-dibromoethane was added via a syringe to initiate the reaction. Upon the addition, the flask was immersed in a preheated oil-bath at 50 °C for 2 h. The prepared 3-(*N*,*N*-dimethylamino)phenyl magnesium bromide (1.0 M in THF) was stored in nitrogen atmosphere and used in the next step.

N^3,N^3,$N^{3'}$,$N^{3'}$-Tetramethyl-[1,1'-biphenyl]-3,3'-diamine (1a)

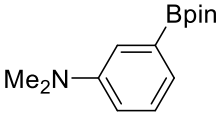


Compound **1a** was synthesized according to the reported method:[4] Dried 100 mL two-necked flask equipped with a constant-pressure dropping funnel and a magnetic stirrer bar was charged under nitrogen with a 0.10 M solution of $FeCl_3$ (122 mg, 0.750 mmol, 3.0 mol%) in dehydrated THF (7.5 mL) and 1,2-dichloroethane (1.48 g, 15.0 mmol, 0.60 equiv). A solution of 3-(*N*,*N*-dimethylamino)phenyl magnesium bromide in THF (1.0 M, 25.0 mmol) was added dropwise via the constant-pressure dropping funnel. The color immediately changed to dark brown and the temperature of the reaction mixture increased. The resulting mixture was stirred at room temperature for 1 h, and then quenched with H_2O (30 mL). After extraction with CH_2Cl_2 (3 × 50 mL), the combined organic layer was dried over anhydrous Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure. The residue was purified via column chromatography on silica gel (hexane: ethyl acetate = 100: 1 to 19:1 with 1% NEt_3) to give compound **1a** as a brown oil (2.50 g, 10.4 mmol, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (dd, *J* = 8.1, 8.1 Hz, 2H), 6.96-6.94 (m, 4H), 6.78-6.70 (m, 2H), 3.00 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.0, 143.5, 129.4, 116.3, 112.1, 111.7, 40.9.

Synthesis of 3-(dimethylamino)phenylboronic acid pinacol ester



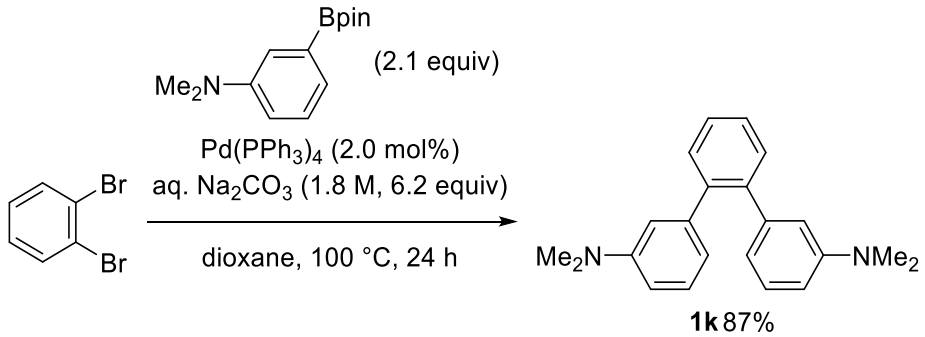
Scheme S2. Synthesis of 3-(dimethylamino)phenylboronic acid pinacol ester



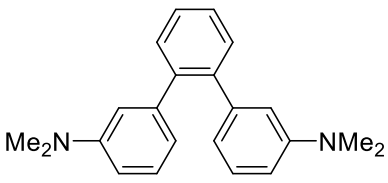
3-(Dimethylamino)phenylboronic acid pinacol ester was synthesized according to the reported method (Scheme S2):[5] A solution of 3-bromo-*N*,*N*-dimethylaniline (18.0 g, 90.0 mmol, 1.0 equiv) and

dehydrated THF (180 mL) was added into a 500 mL three-necked flask with a magnetic stirrer bar and a constant-pressure dropping funnel. All equipments were dried over by a heat gun or an oven, and charged with nitrogen. ^{n}BuLi (1.6 M in hexane; 67.5 mL, 106 mmol, 1.20 equiv) was added dropwise at -78 °C. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (23.4 g, 126 mmol, 1.4 equiv) was added to the mixture and the mixture was stirred for 2 h at -78 °C. After warmed to room temperature slowly, the reaction mixture was quenched with water and extracted with diethyl ether. The combined organic phase was dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 50:1) to give 3-(dimethylamino)phenylboronic acid pinacol ester as a colorless oil (9.10 g, 36.8 mmol, 41%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.22-7.16 (m, 2H), 6.86 (ddd, *J* = 8.2, 2.7, 1.2 Hz, 1H), 2.97 (s, 6H), 1.34 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.3, 128.6, 123.4, 118.8, 115.9, 83.7, 40.9, 25.0 (The boron-bound carbon was not detected due to quadrupolar relaxation.) The analytical data is in accordance with the previous report.[6]

Synthesis of $N^3,N^3,N^{3''},N^{3''}$-Tetramethyl-[1,1':2',1''-terphenyl]-3,3''-diamine (1k)



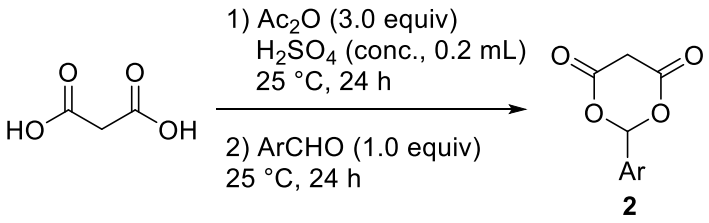
Scheme S3. Synthesis of **1k**



Compound **1k** was synthesized according to the reported method (Scheme S3):[7] 1,2-Dibromobenzene (3.61 g, 15.3 mmol, 1.00 equiv), 3-(dimethylamino)phenylboronic acid pinacol ester (7.96 g, 32.0 mmol, 2.1 equiv), tetrakis(triphenylphosphine)palladium (354 mg, 0.306 mmol, 2.0 mol%), and dioxane (50 mL) were added into a 300 mL three-necked flask which was

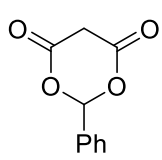
dried over by a heat gun or an oven. Aq. Na_2CO_3 (1.78 M , 94.9 mmol, 10.1 g, 53.3 mL, 6.2 equiv) was added into the flask via syringe. After bubbling of nitrogen gas for 10 min, the mixture was stirred under nitrogen at 100 °C for 24 h, and the reaction mixture was extracted with toluene. The organic layer was washed with brine and dried with Na_2SO_4. After filtration and removal of the solvent, the residue was purified by chromatography on silica gel (hexane/ethyl acetate = 30:1) to give **1k** as a yellow solid (4.21 g, 13.3 mmol, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52−7.46 (m, 2H), 7.44-7.37 (m, 2H), 7.12 (dd, *J* = 7.9, 7.9 Hz, 2H), 6.65-6.58 (m, 4H), 6.55 (dd, *J* = 2.4, 1.6 Hz, 2H), 2.78 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4, 142.5, 141.5, 130.5, 128.6, 127.3, 118.7, 115.4, 111.2, 40.9. HRMS (EI^+) Calcd for $C_{22}H_{24}N_2$ ($[M]^+$) 316.1939, Found 316.1940.

Procedures for the synthesis of Meldrum's acid derivatives



Scheme S4. Synthesis of Meldrum's acid derivatives **2**

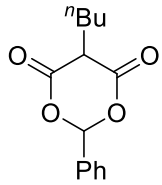
2-Phenyl-1,3-dioxane-4,6-dione (2a)



2-Phenyl-1,3-dioxane-4,6-dione (**2a**) was synthesized by the modified procedure of af reported method.[8] A suspension of malonic acid (10.4 g, 100 mmol, 1.00 equiv) and Ac_2O (30.6 g, 300 mmol, 3.00 equiv) was added into a 300 mL three-necked flask which was dried over by a heat gun, and charged with nitrogen gas. Conc. H_2SO_4 (0.20 mL) was added dropwise to the suspension and the mixture was stirred at 25 °C for 24 h. Benzaldehyde (10.6 g, 100 mmol, 1.00 equiv) was added dropwise into the mixture. After the reaction at 25 °C overnight, toluene (30 mL) was added and excess AcOH and Ac_2O were removed under reduced pressure below 40 °C to give the crude product as an orange suspension. The solid was separated by filtering the suspension and washed with H_2O (200 mL) and Et_2O (10 mL). After dissolving the solid into acetone (100 mL), hexane (400 mL) was added and the mixture was stirred for 15 min. The precipitates were separated by filtration, and dried to give 2-phenyl-1,3-dioxane-4,6-dione (**2a**) as a white powder (12.9 g, 67.1 mmol, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.46 (m, 5H), 6.80 (s, 1H), 3.83 (d, *J* = 18.8 Hz, 1H),

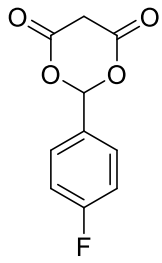
3.65 (d, J = 18.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.2, 132.3, 131.2, 129.2, 126.5, 98.1, 39.2. The analytical data is in accordance with the previous report.[8]

5-Butyl-2-phenyl-1,3-dioxane-4,6-dione (2a-Bu)



The synthesis method of 5-butyl-2-phenyl-1,3-dioxane-4,6-dione (**2a-Bu**) is similar as compound **2a**. A suspension of 2-butylmalonic acid (5.00 g, 31.2 mmol, 1.00 equiv) and Ac_2O (9.60 g, 93.6 mmol, 3.00 equiv) was added into a 50 mL two-necked flask which was dried over by a heat gun, and charged with nitrogen gas. Conc. H_2SO_4 (1 drop) was added to the suspension and the mixture was stirred at 25 °C for 24 h. Benzaldehyde (3.30 g, 31.2 mmol, 1.00 equiv) was added dropwise into the mixture. After the reaction at 25 °C overnight, toluene (10 mL) was added and excess AcOH and Ac_2O were removed under reduced pressure below 40 °C to give a crude product as an orange suspension. The solid was separated by filteration and washed with H_2O (30 mL) and Et_2O (3 mL). After dissolving the solid into acetone (15 mL), ice water (60 mL) was added and the mixture was stirred for 15 min. The precipitate was separated by filtration, washed with H_2O and dried over to give 5-butyl-2-phenyl-1,3-dioxane-4,6-dione (**2a-Bu**) as a white powder (361 mg, 1.50 mmol, 5%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61-7.55 (m, 2H), 7.53-7.44 (m, 3H), 6.79 (s, 1H), 3.68 (t, J = 5.5 Hz, 1H), 2.10 (dd, J = 15.9, 5.6 Hz, 2H), 1.56 (p, J = 7.7 Hz, 2H), 1.43 (sept, J = 7.3, 2H), 0.96 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 131.9, 131.2, 129.0, 126.7, 96.7, 48.6, 29.1, 24.2, 22.8, 13.9; HRMS (EI^+) Calcd for $C_{14}H_{16}O_4$ ($[M]^+$) 248.1049, Found 248.1047.

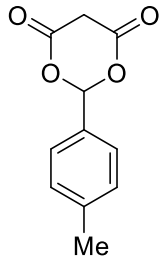
2-(4-Fluorophenyl)-1,3-dioxane-4,6-dione (2b)



The synthetic method of 2-(4-Fluorophenyl)-1,3-dioxane-4,6-dione (**2b**) is similar as compound **2a**. A suspension of malonic acid (2.08 g, 20.0 mmol, 1.00 equiv) and Ac_2O (6.13 g, 60.0 mmol, 3.00 equiv) was added into a 50 mL two-necked flask which was dried over by a heat gun, and charged with nitrogen gas. Conc. H_2SO_4 (1 drop) was added to the suspension and the mixture was stirred at 25 °C for 24 h. 4-Fluorobenzaldehyde (2.48 g, 20.0 mmol, 1.00 equiv) was added dropwise into the mixture. After the reaction at 25 °C overnight, toluene (6.0 mL) was added and excess AcOH and Ac_2O were removed under reduced pressure below 40 °C to give a crude product as an orange suspension. The solid was separated by filteration and washed with H_2O (20 mL) and Et_2O (2.0 mL). After dissolving the solid into acetone (10 mL), ice water (40 mL) was added and the mixture was stirred for 15 min. The precipitates were separated by filtration, washed with H_2O

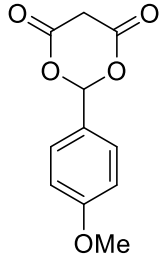
and dried over to give 2-(4-fluorophenyl)-1,3-dioxane-4,6-dione (**2b**) as a white powder (2.01 g, 9.50 mmol, 48%). ^{1}H NMR (400 MHz, Acetone-d_6): δ 7.79-7.64 (m, 2H), 7.36-7.27 (m, 2H), 7.22 (s, 1H), 4.48 (d, J = 18.7 Hz, 1H), 3.64 (d, J = 18.7 Hz, 1H); ^{13}C NMR (100 MHz, Acetone-d_6): δ 165.0, 164.6 (d, $J_{C\text{-}F}$ = 247 Hz), 130.6 (d, $J_{C\text{-}F}$ = 3.2 Hz), 130.1 (d, $J_{C\text{-}F}$ = 9.1 Hz), 116.7 (d, $J_{C\text{-}F}$ = 22.1 Hz), 97.9, 39.9; ^{19}F NMR (378 MHz, Acetone-d_6): δ -111.48. The analytical data is in accordance with the previous report.[9]

2-(*p*-Tolyl)-1,3-dioxane-4,6-dione (2c)



The synthesis method of 2-(*p*-tolyl)-1,3-dioxane-4,6-dione (**2d**) is the same as compound **2a**. A suspension of malonic acid (2.08 g, 20.0 mmol, 1.00 equiv) and Ac_2O (6.13 g, 60.0 mmol, 3.00 equiv) were added into a 50 mL two-necked flask which was dried over by a heat gun, and charged with nitrogen gas. Conc. H_2SO_4 (1 drop) was added to the suspension and the mixture was stirred at 25 °C for 24 h. 4-Methylbenzaldehyde (2.40 g, 20.0 mmol, 1.00 equiv) was added dropwise into the reaction mixture. After the reaction at 25 °C overnight, toluene (6.0 mL) was added and excess AcOH and Ac_2O were removed under reduced pressure below 40 °C to give a crude product as an orange suspension. The solid was separated by filteration and washed with H_2O (20 mL) and Et_2O (2.0 mL). After dissolving the solid into acetone (10 mL), ice water (40 mL) was added and the mixture was stirred for 15 min. The precipitates were separated by filtration, washed with H_2O and dried over to give 2-(*p*-tolyl)-1,3-dioxane-4,6-dione (**2d**) as a white powder (2.14 g, 10.38 mmol, 52%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 8.1 Hz, 2H), 6.76 (s, 1H), 3.89-3.56 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 141.5, 129.8, 129.4, 126.4, 98.3, 39.2, 21.5. The analytical data is in accordance with the previous report.[9]

2-(4-Methoxyphenyl)-1,3-dioxane-4,6-dione (2d)



The synthetic method of 2-(4-methoxyphenyl)-1,3-dioxane-4,6-dione (**2c**) is the same as compound **2a**. A suspension of malonic acid (2.08 g, 20.0 mmol, 1.00 equiv) and Ac_2O (6.13 g, 60.0 mmol, 3.00 equiv) was added into a 50 mL two-necked flask which was dried over by a heat gun, and charged with nitrogen gas. Conc. H_2SO_4 (1 drop) was added to the suspension and the mixture was stirred at 25 °C for 24 h. 4-Methoxybenzaldehyde (2.72 g, 20.0 mmol, 1.00 equiv) was added dropwise into the

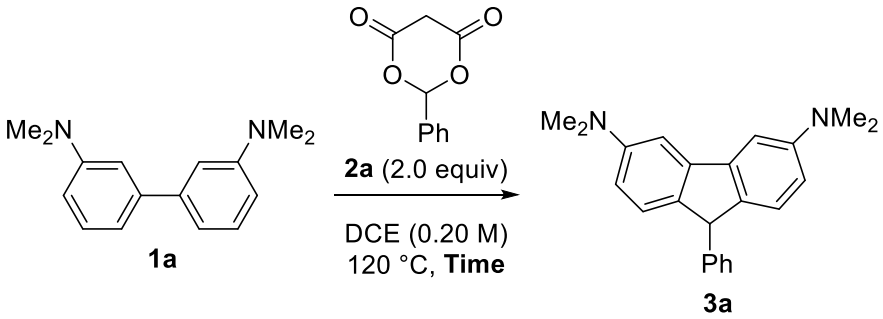
mixture. After the reaction at 25 °C overnight, toluene (6.0 mL) was added and excess AcOH and Ac_2O were removed under reduced pressure below 40 °C to give a crude product as an orange suspension. The solid was separated by filteration and washed with H_2O (20 mL) and Et_2O (2.0 mL). After dissolving the solid into acetone (10 mL), ice water (40 mL) was added and the mixture was stirred for 15 min. The precipitates were separated by filtration, washed with H_2O and dried over to give 2-(4-methoxyphenyl)-1,3-dioxane-4,6-dione (**2c**) as a pale yellow powder (1.27 g, 5.70 mmol, 29%). ^{1}H NMR (400 MHz, Acetone-d_6): δ 7.55 (d, J = 8.9 Hz, 2H), 7.13 (s, 1H), 7.06 (d, J = 8.9 Hz, 2H), 4.46 (d, J = 18.5 Hz, 1H), 3.85 (s, 3H), 3.60 (d, J = 18.5 Hz, 1H); ^{13}C NMR (100 MHz, Acetone-d_6) δ 165.3, 162.4, 129.2, 126.2, 115.0, 98.6, 55.8, 39.8. The analytical data is in accordance with the previous report.[9]

3. Optimization of Reaction Conditions

In the optimization of reaction conditions, the yield of product and the conversion of the starting material compound **1a** were determined by ^{1}H NMR with 1,1,2,2-tetrachloroethane (TCE) as an internal standard unless otherwise noted.

The reaction time was optimized by screening 0.5 h, 1 h, 2 h, 3 h, and 24 h (**Table S1**). The highest yield was obtained for 3 h (44%).

Table S1. Screening of reaction time

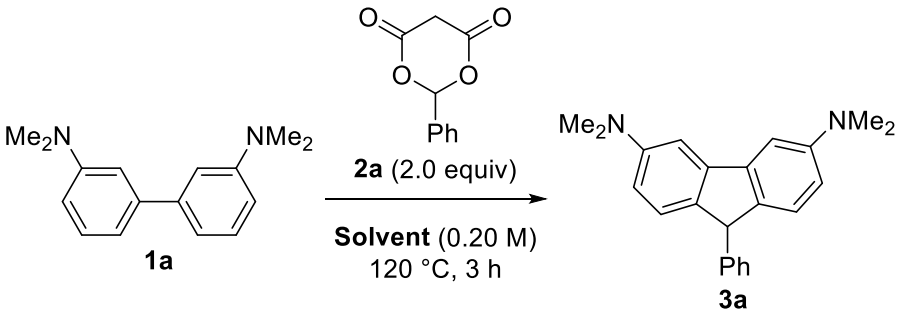


entry	time (h)	conv. (%)[a]	yield (%)[a]
1	0.5	39	25
2	1	51	37
3	2	58	43
4	3	56	44
5	24	73	40

[a] ^{1}H NMR yield using 1,1,2,2-tetrachloroethane as an internal standard.

Several solvents were screened (**Table S2**). The best yield was obtained in 1,2-dichloroethane (DCE, entry 1, 44%). The reaction did not proceed in acetone (entry 2). The yields of **3a** in ethers, such as 1,4-dioxane, tetrahydrofuran (THF), cyclopentyl methyl ether (CPME), and diphenyl ether, were lower than that in DCE (entries 3-6). Nitroethane and acetonitrile gave **3a** in low yields (entries 7 and 8). Because the reaction in DCE gave good yield, halogenated solvents, such as chloroform, tetrachloroethane, and 1,2-dichlorobenzene, were screened (entries 10-12). As a result, DCE was still the best solvent and **3a** was obtained in 58% yield in 0.10 M for 9 h.

Table S2. Screening of several solvents

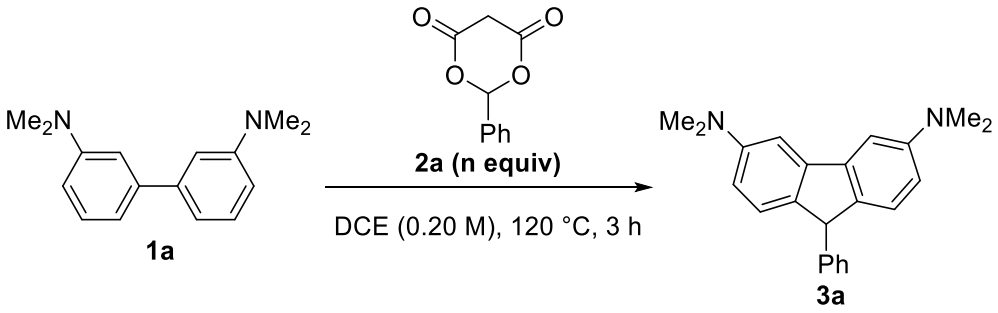


entry	solvent	conv. (%)[a]	yield (%)[a]
1	DCE	56	44
2	acetone	7	0
3	1,4-dioxane	46	23
4	THF	51	22
5	CPME	31	11
6	diphenyl ether	35	0
7	nitroethane	38	15
8	CH_3CN	16	4
9[b]	DCE	78	58
10[b]	$CHCl_3$	70	53
11[b]	tetrachloroethane	81	47
12[b]	1,2-dichlorobenzene	72	43

[a] ^{1}H NMR yield using 1,1,2,2-tetrachloroethane as an internal standard. [b] 0.10 M, 9 h.

The equivalents of Meldrum's acid derivative **2a** were screened from 1 to 4 equivalents (**Table S3**). The yield of **3a** was improved by increasing the amount of **2a** from 1 equivalent to 2 equivalents (entries 1 and 2). However, the yields of **2a** in entries 3 and 4 were almost the same as that in entry 2. Therefore, 2 equivalents of **2a** was selected as the best reaction conditions (entry 2).

Table S3. Screening of equivalents of Meldrum's acid derivative **2a**

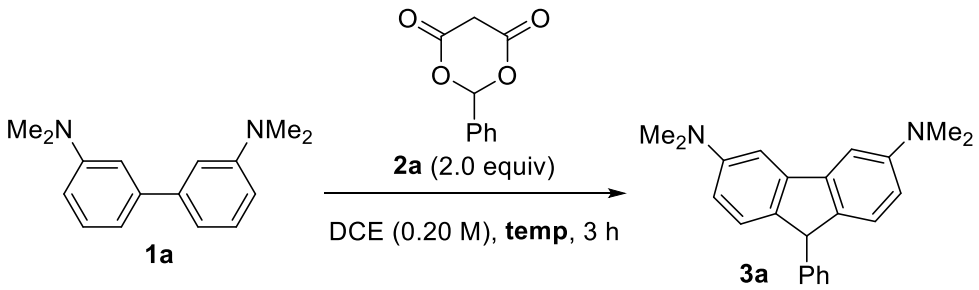


entry	equiv of **2a**	conv. (%)[a]	yield (%)[a]
1	1	55	35
2	2	56	44
3	3	69	46
4	4	74	46

[a] ^{1}H NMR yield using 1,1,2,2-tetrachloroethane as an internal standard.

The reaction temperature was tested at 100 °C, 120 °C, and 140 °C (**Table S4**). Compared with the reaction at 100 °C (entry 1), the yield of **3a** increased (entry 2). When the temperature was raised to 140 °C, the yield of **3a** was not improved (entry 3). Therefore, 120 °C was selected as the best reaction temperature.

Table S4. Screening of temperature

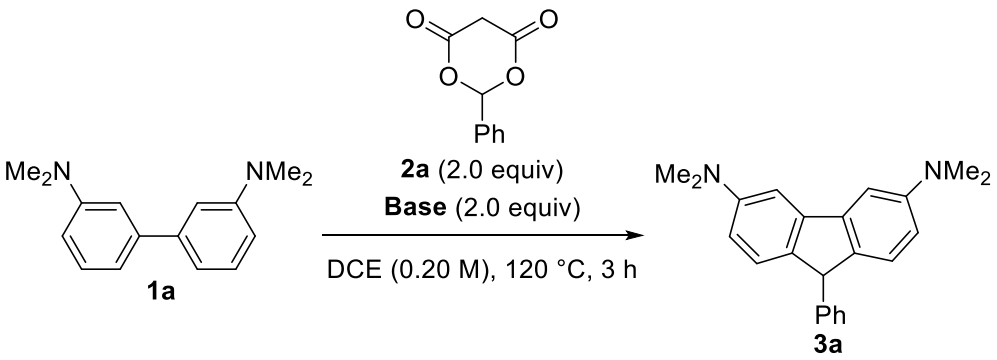


entry	temp (°C)	conv. (%)[a]	yield (%)[a]
1	100	31	14
2	120	56	44
3	140	80	45

[a] ^{1}H NMR yield using 1,1,2,2-tetrachloroethane as an internal standard.

When the reaction tube was opened after the reaction, the smell of acetic acid was detected. It is known that Meldrum's acid decomposes to acetic acid under high temperature.[10] Because there is a possibility that acetic acid would influence the reaction, several bases were screened to neutralize acetic acid (**Table S5**). Although inorganic bases, Na_2CO_3, K_2CO_3, and Cs_2CO_3 (entries 2-4), and organic bases, Et_3N and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (entries 5 and 6), were tested, the yield of **3a** was not improved.

Table S5. Screening of several bases

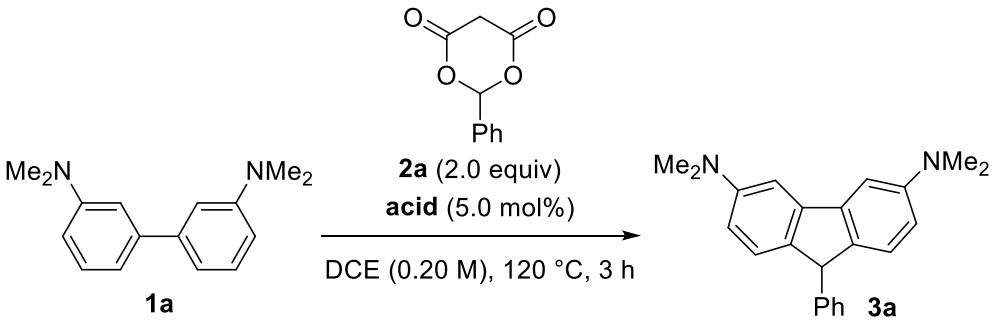


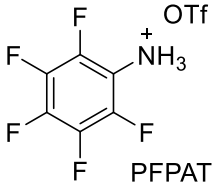
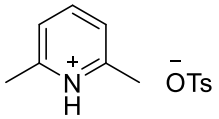
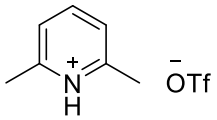
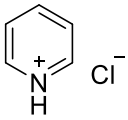
entry	base	conv. (%)[a]	yield (%)[a]
1	none	56	44
2	Na_2CO_3	28	12
3	K_2CO_3	15	11
4	Cs_2CO_3	18	4
5	Et_3N	16	10
6	DBU	13	9

[a] ^{1}H NMR yield using 1,1,2,2-tetrachloroethane as an internal standard.

Several Lewis and Brønsted acids were screened to improve the yield of **3a** (**Table S6**). Several Lewis acids (entries 2-4) and Brønsted acids (entries 5 and 6) did not improve the yield of **3a**. Pentafluorophenylammonium triflate (PFPAT) is more stable than convenient Lewis acids and it could catalyze double Friedel-Crafts reaction in high yield.[11] Therefore, catalytic amounts of four kinds of Brønsted acids including PFPAT were tested. However, the yield of **3a** was not improved (entries 7-10).

Table S6. Screening of several acids

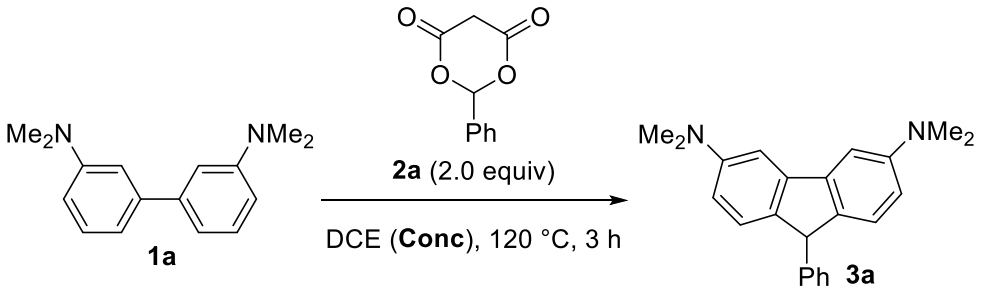


entry	acid	conv. (%)[a]	yield (%)[a]
1	none	56	44
2	$FeCl_3$	62	27
3	$AlCl_3$	60	34
4	$B(C_6F_5)_3$	62	38
5	CF_3COOH	68	44
6	$TsOH{\cdot}H_2O$	67	42
7	 PFPAT	68	44
8		53	36
9		58	37
10		63	35

[a] ^1H NMR yield using 1,1,2,2-tetrachloroethane as an internal standard.

The concentration may influence the yield of **3a** because this reaction is annulation. By changing the concentrations from 0.025 M to 1.0 M (**Table S7**, entries 1–6), the reaction in 0.10 M gave the best result and afforded **3a** in 51% yield (entry 3).

Table S7. Screening of several concentrations

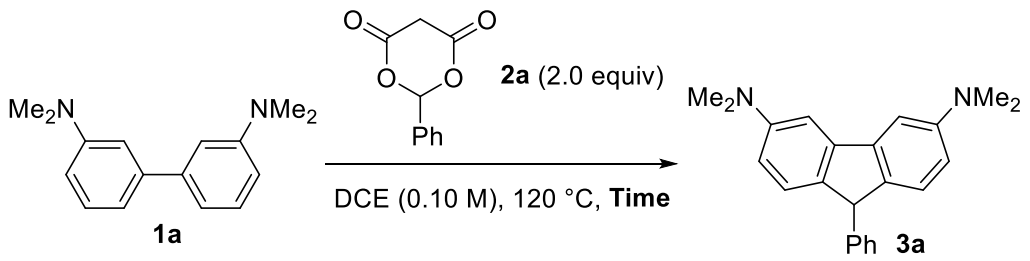


entry	conc. (M)	conv. (%)[a]	yield (%)[a]
1	0.025	22	2
2	0.05	38	23
3	0.10	68	51
4	0.20	56	44
5	0.50	54	28
6	1.0	46	24

[a] ^{1}H NMR yield using 1,1,2,2-tetrachloroethane as an internal standard.

Under the preliminary optimization of the reaction time (**Table S1**), it was found that the yield of **3a** was not changed when the reaction time was extended from 3 h to 24 h, but the conversion increased from 56% to 73%. I screened the reaction time again between 3 h and 24 h under the best reaction conditions (**Table S8**). The yield of **3a** reached 58% after 6 h (entry 6), and the significant increase of the yield was not observed in longer time (entries 7–16). Therefore, the reaction conditions of entry 6 was selected as the optimized reaction conditions.

Table S8. Screening of reaction time at low concentration (0.10 M)

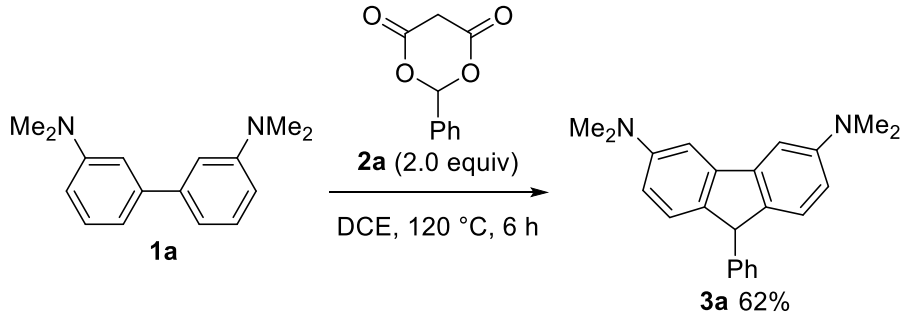


entry	time (h)	conv. (%)[a]	yield (%)[a]	entry	time (h)	conv. (%)[a]	yield (%)[a]
1	1	57	43	9	9	78	58
2	2	68	47	10	10	80	59
3	3	68	51	11	11	80	58
4	4	73	53	12	12	81	59
5	5	73	57	13	15	84	56
6	6	73	58	14	18	83	59
7	7	79	59	15	21	84	59
8	8	78	61	16	24	85	58

[a] ^{1}H NMR yield using 1,1,2,2-tetrachloroethane as an internal standard.

4. Substrate Scope

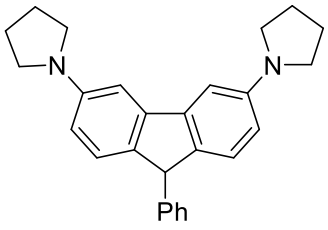
Typical Procedure for the Synthesis of Fluorene Derivatives 3 (Scheme S5)



Scheme S5. Synthesis of N^3,N^3,N^6,N^6-tetramethyl-9-phenyl-9*H*-fluorene-3,6-diamine (**3a**)

A 5 mL reaction tube sealed with a screw cap and a magnetic stirrer bar was charged with nitrogen gas. Compound **1a** (48.1 mg, 0.200 mmol, 1.0 equiv), 2-phenyl-1,3-dioxane-4,6-dione (**2a**, 76.9 mg, 0.400 mmol, 2.0 equiv) and dehydrated 1,2-dichloroethane (DCE, 2.0 mL) were added under nitrogen atmosphere. The reaction mixture was stirred at 120 ℃ (oil bath) for 6 h. After the reaction completed, the mixture was concentrated in vacuo. The mixture was purified by column chromatography on silica gel (hexane/ethyl acetate = 30:1 to 15:1) to afford **3a** as a pale yellow solid (40.7 mg, 0.124 mmol, 62%, conversion yield: 94%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.26-7.20 (m, 2H), 7.20-7.15 (m, 1H), 7.14 (d, *J* = 2.5 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.06-7.01 (m, 2H), 6.65 (dd, *J* = 8.4, 2.5 Hz, 2H), 4.90 (s, 1H), 3.02 (s, 12H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 151.1, 144.1, 142.6, 137.9, 128.8, 128.3, 126.7, 125.7, 112.6, 103.9, 53.0, 41.3; HRMS (EI$^+$) Calcd for $C_{23}H_{24}N_2$ ([M]$^+$) 328.1939, Found 328.1939.

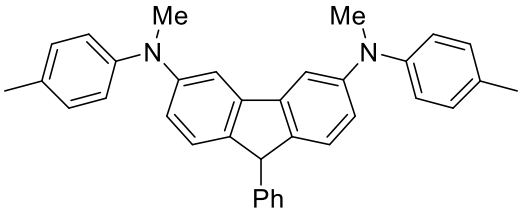
1,1'-(9-Phenyl-9*H*-fluorene-3,6-diyl)dipyrrolidine (3b)



A 5 mL reaction tube equipped with a screw cap and a magnetic stirrer bar was charged with nitrogen gas. Compound **1b** (58.5 mg, 0.200 mmol, 1.0 equiv), 2-phenyl-1,3-dioxane-4,6-dione (**2a**, 76.9 mg, 0.400 mmol, 2.0 equiv) and dehydrated 1,2-dichloroethane (2.0 mL) were added under nitrogen atmosphere. The reaction mixture was stirred at 120 ℃ for 6 h. After the reaction completed, the mixture was concentrated in vacuo. The mixture was purified by column chromatography on silica gel (hexane/ethyl acetate = 40:1) to afford **3b** as a white

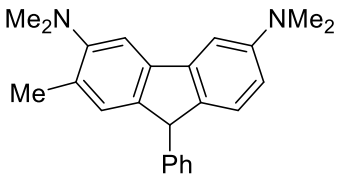
solid (15.0 mg, 0.0800 mmol, 42%, conversion yield: 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ7.27-7.20 (m, 2H), 7.20-7.13 (m, 1H), 7.09-7.01 (m, 4H), 6.97 (s, 2H), 6.49 (d, *J* = 7.5 Hz, 2H), 4.89 (s, 1H), 3.36 (t, *J* = 6.3 Hz, 8H), 2.04 (t, *J* = 6.3 Hz, 8H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ148.2, 144.4, 142.7, 136.8, 128.8, 128.3, 126.6, 125.7, 111.6, 102.8, 53.0, 48.5, 25.9; HRMS (EI^+) Calcd for $C_{27}H_{28}N_2$ ($[M]^+$) 380.2252, Found 380.2250.

N^3,N^6-Dimethyl-9-phenyl-N^3,N^6-di-*p*-tolyl-9*H*-fluorene-3,6-diamine (3c)



A 5 mL reaction tube equipped with a screw cap and a magnetic stirrer bar was charged with nitrogen gas. Compound **1c** (78.5 mg, 0.200 mmol, 1.0 equiv), 2-phenyl-1,3-dioxane-4,6-dione (**2a**, 76.9 mg, 0.400 mmol, 2.0 equiv) and dehydrated 1,2-dichloroethane (2.0 mL) were added under nitrogen atmosphere. The mixture was stirred at 120 ℃ for 6 h. After the reaction completed, the reaction mixture was concentrated in vacuo. The mixture was purified by column chromatography on silica gel (hexane/DCM = 4:1 to 1:1) to afford **3c** as a white solid (59.2 mg, 0.123 mmol, 61%, conversion yield: 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 2.0 Hz, 2H), 7.32-7.26 (m, 2H), 7.26-7.20 (m, 1H), 7.18-7.13 (m, 4H), 7.11 (d, *J* = 8.2 Hz, 4H), 6.99 (d, *J* = 8.4 Hz, 4H), 6.88 (dd, *J* = 8.2, 2.0 Hz, 2H), 4.97 (s, 1H), 3.35 (s, 6H), 2.33 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.0, 147.1, 142.5, 142.2, 141.4, 131.2, 130.0, 128.7, 128.3, 126.8, 125.7, 121.1, 119.7, 111.1, 53.4, 41.0, 20.8; HRMS (EI^+) Calcd for $C_{35}H_{32}N_2$ ($[M]^+$) 480.2565, Found 480.2565.

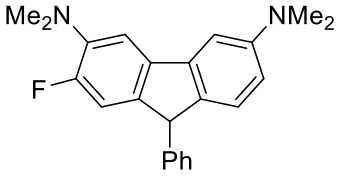
N^3,N^3,N^6,N^6,2-Pentamethyl-9-phenyl-9*H*-fluorene-3,6-diamine (3d)



A 5 mL reaction tube equipped with a screw cap and a magnetic stirrer bar was charged with nitrogen gas. Compound **1d** (25.4 mg, 0.100 mmol, 1.0 equiv), 2-phenyl-1,3-dioxane-4,6-dione (**2a**, 38.4 mg, 0.200 mmol, 2.0 equiv) and dehydrated 1,2-dichloroethane (1.0 mL) were added under nitrogen atmosphere. The mixture was stirred at 120 ℃ for 6 h. After the reaction completed, the reaction mixture was concentrated in vacuo. The mixture was purified by column chromatography on silica gel (hexane/ethyl acetate = 20:1) to afford **3d** as a yellow solid (8.0 mg, 0.023 mmol, 23%, conversion yield: 47%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.47 (s, 1H), 7.29-7.22 (m, 2H), 7.22-7.16 (m, 1H), 7.12 (d, *J* = 2.3 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 7.06-7.02 (m, 3H), 6.64 (dd, *J* = 8.4, 2.3 Hz, 1H), 4.89 (s, 1H), 3.02 (s, 6H), 2.77 (s, 6H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 151.0, 143.9, 143.5, 142.6, 140.2, 137.2, 131.9, 131.3, 128.9,

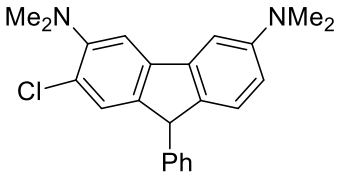
128.4, 127.8, 126.8, 125.7, 112.4, 110.0, 103.8, 53.3, 44.8, 41.4, 18.8; HRMS (EI^+) Calcd for $C_{24}H_{26}N_2$ ($[M]^+$) 342.2096, Found 342.2095.

2-Fluoro-*N*^{3},*N*^{3},*N*^{6},*N*^{6}-tetramethyl-9-phenyl-9*H*-fluorene-3,6-diamine (3e)



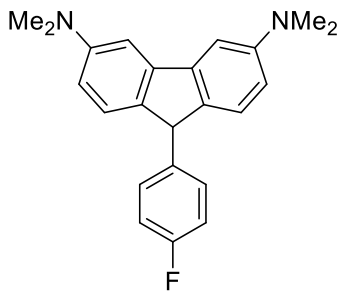
A 5 mL reaction tube equipped with a screw cap and a magnetic stirrer bar was charged with nitrogen gas. Compound **1e** (51.7 mg, 0.200 mmol, 1.0 equiv), 2-phenyl-1,3-dioxane-4,6-dione (**2a**, 76.9 mg, 0.400 mmol, 2.0 equiv) and dehydrated 1,2-dichloroethane (2.0 mL) were added under nitrogen atmosphere. The mixture was stirred at 120 ℃ for 6 h. After the reaction completed, the reaction mixture was concentrated in vacuo. The mixture was purified by column chromatography on silica gel (hexane/ethyl acetate = 40:1) to afford **3e** as a pale yellow solid (37.0 mg, 0.110 mmol, 53%, conversion yield: 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (d, *J* = 8.2 Hz, 1H), 7.30-7.19 (m, 3H), 7.15 (d, *J* = 8.4 Hz, 1H), 7.13-7.04 (m, 3H), 6.95 (d, *J* = 12.4 Hz, 1H), 6.68 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.90 (s, 1H), 3.05 (s, 6H), 2.93 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.5 (d, $J_{C\text{-}F}$ = 244 Hz), 150.6, 142.5 (d, $J_{C\text{-}F}$ = 8.8 Hz), 142.3, 141.7, 140.5 (d, $J_{C\text{-}F}$ = 9.9 Hz), 137.3 (d, $J_{C\text{-}F}$ = 2.0 Hz), 131.1, 128.8, 128.2, 126.8, 125.6, 113.1 (d, $J_{C\text{-}F}$ = 22.5 Hz), 112.2, 109.4 (d, $J_{C\text{-}F}$ = 3.4 Hz), 103.6, 53.3, 43.5, 41.4; ^{19}F NMR (378 MHz, $CDCl_3$): δ-122.9 (s); HRMS (EI^+) Calcd for $C_{23}H_{23}FN_2$ ($[M]^+$) 346.1845, Found 348.1847.

2-Chloro-*N*^{3},*N*^{3},*N*^{6},*N*^{6}-tetramethyl-9-phenyl-9*H*-fluorene-3,6-diamine (3f)



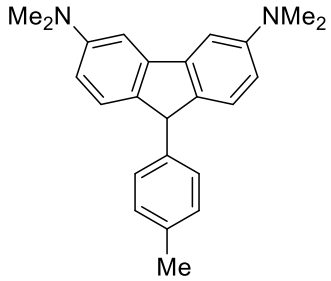
A 5 mL reaction tube equipped with a screw cap and a magnetic stirrer bar was charged with nitrogen gas. Compound **1f** (55.0 mg, 0.200 mmol, 1.0 equiv), 2-phenyl-1,3-dioxane-4,6-dione (**2a**, 76.9 mg, 0.400 mmol, 2.0 equiv) and dehydrated 1,2-dichloroethane (2.0 mL) were added under nitrogen atmosphere. The mixture was stirred at 120 ℃ for 6 h. After the reaction completed, the reaction mixture was concentrated in vacuo. The mixture was purified by column chromatography on silica gel (hexane/ethyl acetate = 40:1) to afford **3f** as a yellow solid (29.9 mg, 0.0820 mmol, 41%, conversion yield: 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (s, 1H), 7.32-7.20 (m, 4H), 7.18-7.05 (m, 4H), 6.70 (dd, *J* = 8.3, 2.2 Hz, 1H), 4.92 (s, 1H), 3.05 (s, 6H), 2.91 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.6, 149.9, 144.2, 142.0, 141.4, 140.9, 131.1, 128.8, 128.2, 127.4, 127.3, 126.9, 125.8, 112.9, 111.0, 103.6, 53.1, 44.4, 41.3; HRMS (EI^+) Calcd for $C_{23}H_{23}ClN_2$ ($[M]^+$) 362.1550, Found 362.1550.

9-(4-Fluorophenyl)-*N*^{3},*N*^{3},*N*^{6},*N*^{6}-tetramethyl-9*H*-fluorene-3,6-diamine (3g)



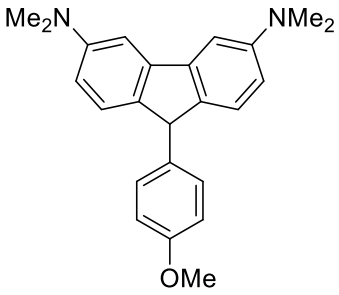
A 5 mL reaction tube equipped with a screw cap and a magnetic stirrer bar was charged with nitrogen gas. Compound **1a** (48.0 mg, 0.200 mmol, 1.0 equiv), 2-(4-fluorophenyl)-1,3-dioxane-4,6-dione (**2b**, 84.1 mg, 0.400 mmol, 2.0 equiv) and dehydrated 1,2-dichloroethane (2.0 mL) were added under nitrogen atmosphere. The reaction mixture was stirred at 120 ℃ for 6 h. After the reaction completed, the mixture was concentrated in vacuo. The mixture was purified by column chromatography on silica gel (hexane/ethyl acetate = 40:1) to afford **3g** as a red solid (38.0 mg, 0.110 mmol, 55%, conversion yield: 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19-7.10 (m, 4H), 7.06 (dd, *J* = 8.5, 5.6 Hz, 2H), 6.93 (dd, *J* = 8.6, 8.6 Hz, 2H), 6.69 (dd, *J* = 8.3, 2.4 Hz, 2H), 4.90 (s, 1H), 3.05 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.7 (d, $J_{C\text{-}F}$ = 242 Hz), 150.6, 142.4, 139.1 (d, $J_{C\text{-}F}$ = 3.2 Hz), 137.8, 129.6 (d, $J_{C\text{-}F}$ = 7.7 Hz), 125.5, 115.4 (d, $J_{C\text{-}F}$ = 21.1 Hz), 112.6, 103.8, 52.1, 41.4; ^{19}F NMR (378 MHz, $CDCl_3$): δ -117.0 (s, F); HRMS (EI$^+$) Calcd for $C_{23}H_{23}FN_2$ ([M]$^+$) 346.1845, Found 346.1845.

***N*^{3},*N*^{3},*N*^{6},*N*^{6}-Tetramethyl-9-(*p*-tolyl)-9*H*-fluorene-3,6-diamine (3h)**



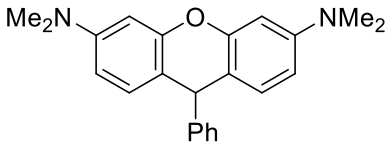
A 5 mL reaction tube equipped with a screw cap and a magnetic stirrer bar was charged with nitrogen gas. Compound **1a** (48.0 mg, 0.200 mmol, 1.0 equiv), 2-(*p*-tolyl)-1,3-dioxane-4,6-dione (**2c**, 82.5 mg, 0.400 mmol, 2.0 equiv) and dehydrated 1,2-dichloroethane (2.0 mL) were added under nitrogen atmosphere. The mixture was stirred at 120 ℃ for 6 h. After the reaction completed, the reaction mixture was concentrated in vacuo. The mixture was purified by column chromatography on silica gel (hexane/ethyl acetate = 10:1 to 5:1) to afford **3h** as a white solid (33.0 mg, 0.0960 mmol, 48%, conversion yield: 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (d, *J* = 8.6 Hz, 4H), 7.09-6.94 (m, 4H), 6.77-6.59 (m, 2H), 4.89 (s, 1H), 3.04 (s, 12H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 142.4, 140.3, 138.2, 135.9, 129.3, 128.1, 125.5, 112.6, 103.9, 52.5, 41.5, 21.2; HRMS (EI$^+$) Calcd for $C_{24}H_{26}N_2$ ([M]$^+$) 342.2096, Found 342.2096.

9-(4-Methoxyphenyl)-*N*^{3},*N*^{3},*N*^{6},*N*^{6}-tetramethyl-9*H*-fluorene-3,6-diamine (3i)



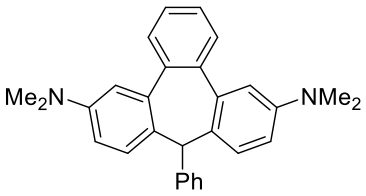
A 5 mL reaction tube equipped with a screw cap and a magnetic stirrer bar was charged with nitrogen gas. Compound **1a** (48.0 mg, 0.200 mmol, 1.0 equiv), 2-(4-methoxyphenyl)-1,3-dioxane-4,6-dione (**2d**, 88.9 mg, 0.400 mmol, 2.0 equiv) and dehydrated 1,2-dichloroethane (2.0 mL) were added under nitrogen atmosphere. The mixture was stirred at 120 ℃ for 6 h. After the reaction completed, the reaction mixture was concentrated in vacuo. The mixture was purified by column chromatography on silica gel (hexane/ethyl acetate = 40:1) to afford **3i** as a red solid (29.0 mg, 0.0800 mmol, 40%, conversion yield: 71%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.15 (d, *J* = 2.2 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 6.66 (dd, *J* = 8.3, 2.2 Hz, 2H), 4.86 (s, 1H), 3.75 (s, 3H), 3.02 (s, 12H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 158.7, 150.9, 142.5, 138.2, 135.8, 129.2, 125.6, 114.2, 112.7, 103.9, 55.5, 52.2, 41.4; HRMS (EI$^+$) Calcd for $C_{24}H_{26}N_2O$ ([M]$^+$) 358.2045, Found 358.2045.

***N*^{3},*N*^{3},*N*^{6},*N*^{6}-Tetramethyl-9-phenyl-9*H*-xanthene-3,6-diamine (3j)**



A 5 mL reaction tube equipped with a screw cap and a magnetic stirrer bar was charged with nitrogen gas. 3,3'-Oxybis(*N*,*N*-dimethylaniline) (51.3 mg, 0.200 mmol, 1.0 equiv), 2-phenyl-1,3-dioxane-4,6-dione (**2a**, 76.9 mg, 0.400 mmol, 2.0 equiv) and dehydrated 1,2-dichloroethane (2.0 mL) were added under nitrogen atmosphere. The mixture was stirred at 120 ℃ for 6 h. After the reaction completed, the reaction mixture was concentrated in vacuo. The mixture was purified by column chromatography on silica gel (hexane/ethyl acetate = 30:1) to afford **3j** as a white solid (30.0 mg, 0.0871 mmol, 44%,, conversion yield: 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.23 (m, 2H), 7.21-7.12 (m, 3H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.47 (d, *J* = 2.1 Hz, 2H), 6.40 (dd, *J* = 8.5, 2.4 Hz, 2H), 5.09 (s, 1H), 2.94 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.8, 150.4, 148.0, 130.3, 128.6, 128.6, 126.3, 113.2, 108.5, 99.92, 42.9, 40.8; HRMS (EI$^+$) Calcd for $C_{23}H_{24}N_2O$ ([M]$^+$) 344.1889, Found 344.1889.

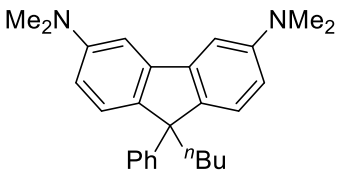
N^6,N^6,N^{12},N^{12}-Tetramethyl-9-phenyl-9*H*-tribenzo[*a*,*c*,*e*][7]annulene-6,12-diamine (3k)



A 5 mL reaction tube equipped with a screw cap and a magnetic stirrer bar was charged with nitrogen gas. Compound **1l** (63.3 mg, 0.200 mmol, 1.0 equiv), 2-phenyl-1,3-dioxane-4,6-dione (**2a**, 76.9 mg, 0.400 mmol, 2.0 equiv) and dehydrated 1,2-dichloroethane (2.0 mL) were added under nitrogen atmosphere. The mixture was stirred at 120 ℃ for 6 h. After the reaction completed, the reaction mixture was concentrated in vacuo. The mixture was purified by column chromatography on silica gel (hexane/ethyl acetate = 50:1) to afford **3l** as a white solid (30.0 mg, 0.0700 mmol, 37%, conversion yield: 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (dd, *J* = 5.8, 3.4 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.13 (dd, *J* = 5.8, 3.4 Hz, 2H), 6.98-6.66 (m, 9H), 5.12 (s, 1H), 2.97 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.5, 142.6, 139.7, 138.5, 135.0, 129.7, 129.3, 127.2, 127.0, 126.9, 125.1, 115.6, 112.5, 55.5, 41.2; HRMS (EI^+) Calcd for $C_{29}H_{28}N_2$ ($[M]^+$) 404.2252, Found 404.2252.

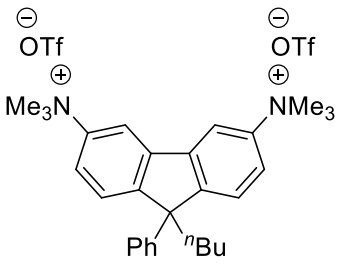
5. Extension of π-Conjugated System Using Amino Groups

9-Butyl-*N*^{3},*N*^{3},*N*^{6},*N*^{6}-tetramethyl-9-phenyl-9*H*-fluorene-3,6-diamine (4)



Compound **4** was synthesized according to the reported method.[12.]A solution of **3a** (65.7 mg, 0.200 mmol, 1.0 equiv) in 0.40 mL anhydrous tetrahydrofuran was stirred at 0 ℃ in a 5 mL Schlenk flask under nitogen gas. *n*BuLi (1.6 M hexane solution, 0.13 mL, 0.21 mmol, 1.05 equiv) was added dropwise to the reaction mixture and the mixture was stirred at 20 ℃ for 90 min. Then, the mixture was cooled to 0 ℃ and 1-chlorobutane (20.4 mg, 0.220 mmol, 1.1 equiv) was added followed by further stirring for 2 h (TLC was used to detect the reaction process). After the reaction mixture was cooled to room temperature, the mixture was hydrolyzed with a mixture of water and diethyl ether. The organic layer was separated and dried over $MgSO_4$ and filtration followed by evaporation to give the crude product. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 5:1) to afford **4** as a yellow solid (73.0 mg, 0.190 mmol, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.20 (m, 4H), 7.18-7.09 (m, 5H), 6.72 (dd, *J* = 8.4, 2.4 Hz, 2H), 3.07 (s, 12H), 2.43 (t, *J* = 8.3 Hz, 2H), 1.26 (tt, *J* = 8.3, 7.8 Hz, 2H), 0.89 (tt, *J* = 7.8, 7.6 Hz, 2H), 0.80 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.2, 146.8, 142.0, 141.7, 128.2, 126.7, 125.9, 124.6, 112.6, 103.7, 57.2, 41.3, 38.1, 26.5, 23.4, 14.1. HRMS (EI^+) Calcd for $C_{29}H_{28}N_2$ ($[M]^+$) 404.2252, Found 404.2252.

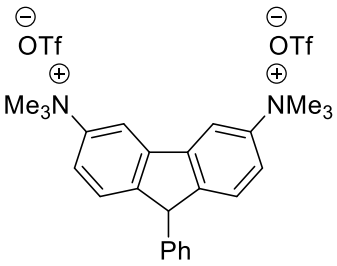
9-Butyl-*N*^{3},*N*^{3},*N*^{3},*N*^{6},*N*^{6},*N*^{6}-hexamethyl-9-phenyl-9*H*-fluorene-3,6-diaminium trifluoromethanesulfonate (5)



Compound **5** was synthesized according to the reported method.[13] A solution of **4** (122 mg, 0.320 mmol, 1.0 equiv) and anhydrous dichloromethane (2.1 mL) was added in a dry Schlenk flask with a stirrer bar. To the stirring solution, methyl trifluoromethanesulfonate (115 mg, 0.700 mmol, 2.2 equiv) was added dropwise and the mixture was stirring at 25 ℃ for 2 h. The reaction mixture was concentrated and treated with diethyl ether (2 mL). The solid was filtered and washed with diethyl ether and hexane followed by drying to give the final product **5** as an orange solid (225 mg, 0.316 mmol, 99%). ^{1}H NMR (400 MHz, Acetone-d_6): δ 8.92 (d, *J* = 2.7 Hz, 2H), 8.07 (dd, *J* = 8.6, 2.7 Hz, 2H), 7.66 (d, *J* = 8.6 Hz, 2H), 7.30-7.19 (m, 5H), 3.94 (s, 18H), 2.66 (t, *J* = 8.3 Hz, 2H), 1.24 (tt, *J* = 8.3, 7.4 Hz, 2H), 0.77- 0.69 (m, 5H); ^{13}C NMR (100 MHz, Acetone-d_6): δ 154.7, 148.3, 143.7,

142.2, 129.6, 128.0, 127.3, 126.9, 122.1 (q, J = 329 Hz), 121.3, 114.8, 59.9, 58.0, 37.5, 26.9, 23.4, 14.0; HRMS (FAB$^+$) Calcd for $C_{30}H_{38}F_3N_2O_3S^+$ ([M-TfO$^-$]$^+$) 563.2555, Found 563.2554.

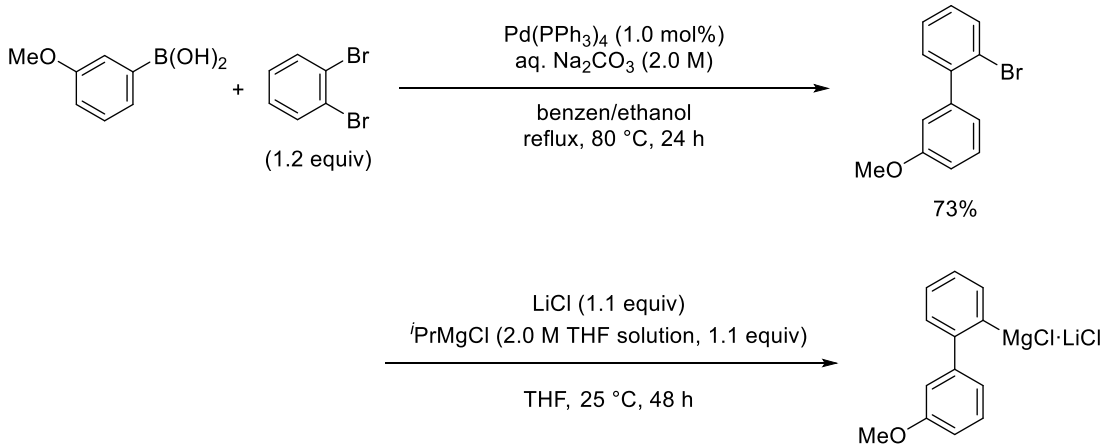
N^3,N^3,N^3,N^6,N^6,N^6-Hexamethyl-9-phenyl-9*H*-fluorene-3,6-diaminium trifluoromethanesulfonate (8)



The synthetic method of **8** was the same as **5**. A solution of **3a** (197 mg, 0.600 mmol, 1.0 equiv) and anhydrous dichloromethane (4.0 mL) was added in a dry Schlenk flask with a stirrer bar. To the stirring solution, methyl trifluoromethanesulfonate (217 mg, 1.32 mmol, 2.2 equiv) was added dropwise followed by stirring at 25 ℃ for 2 h. The reaction mixture was concentrated and treated with diethyl ether (4 mL). The solid was filtered and washed with diethyl ether and hexane followed by drying to give the final product **8** as a pale yellow solid (390 mg, 0.594 mmol, 99%). ^{1}H NMR (400 MHz, Acetone-d_6): δ 9.02 (s, 2H), 8.06 (dd, J = 8.6, 2.7 Hz, 2H), 7.64 (d, J = 8.6 Hz, 2H), 7.39 -7.28 (m, 3H), 7.18-7.12 (m, 2H), 5.49 (s, 1H), 3.97 (s, 18H); ^{13}C NMR (100 MHz, Acetone-d_6): δ 150.9, 148.4, 142.4, 140.2, 129.8, 128.9, 128.3, 127.7, 121.9 (q, J = 319 Hz), 121.1, 114.6, 57.9, 54.1, HRMS (FAB$^+$) Calcd for $C_{26}H_{30}F_3N_2O_3S^+$ ([M-TfO$^-$]$^+$) 507.1929, Found 507.1930.

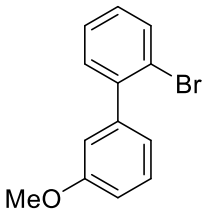
20-Butyl-3,16-dimethoxy-20-phenyl-20*H*-cyclopenta[1,2-*b*:3,4-*b*']ditriphenylene (7)

(1) Preparation of turbo Grignard reagent (Scheme S6)

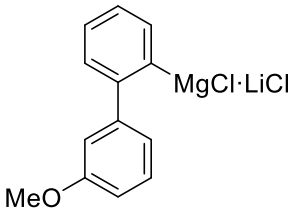


Scheme S6. Preparation of Turbo Grignard reagent

2-Bromo-3'-methoxy-1,1'-biphenyl

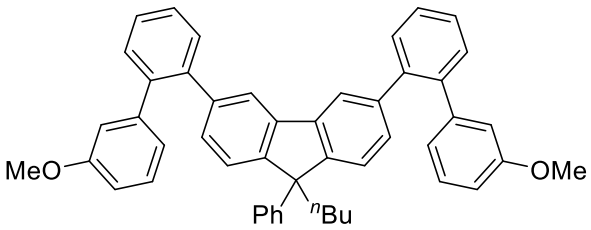


The synthesis method was according to the reported procedure.[14] (3-Methoxyphenyl)boronic acid (1.52 g, 10.0 mmol, 1.0 equiv), 1,2-dibromobenzene (2.83 g, 12.0 mmol, 1.2 equiv), benzene (80 mL), ethanol (24 mL), and aq. Na_2CO_3 (2.0 M, 15 mL, 30 mmol, 3.0 equiv) were charged into a three-neck flask with a stirrer bar and a condensor. The solution was bubbled by nitrogen to remove the oxygen for 15 min followed by the addition of $Pd(PPh_3)_4$ (116 mg, 0.100 mmol, 1.0 mol%) into the reaction mixture. The reaction mixture was heated at 80 ℃ for 24 h. After cooling the reaction mixture to room temperature, the mixture was diluted with water (60 mL). The mixture was extracted with ethyl acetate (3 x 50 mL) and the organic layer was washed with brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (hexane/dichloromethane = 20:1) to afford product as colorless liquid (1.93 g, 5.13 mmol, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.0 Hz, 1H), 7.38-7.33 (m, 3H), 7.25-7.18 (m, 1H), 7.03-6.92 (m, 3H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 142.6, 133.3, 131.3, 129.2, 128.9, 127.5, 122.7, 122.0, 115.2, 113.4, 55.4 (One signal was not detected). The analytical data is in accordance with the previous report.[14]



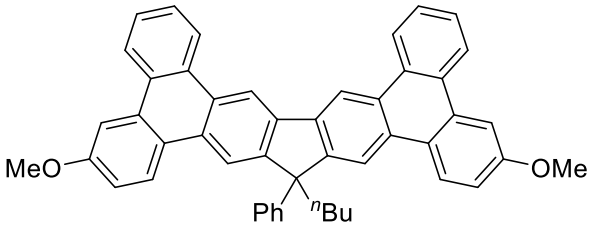
The synthesis of Turbo Grignard reagent was according to the reported procedure.[15] A dry 5 mL Schlenk flask was charged with LiCl (44.1 mg, 1.04 mmol, 1.3 equiv) and a stirrer bar. The mixture was heated at 125 ℃ under vacuum for 1 h to remove the water from LiCl. After cooling to room temperature, the flask was charged with nitrogen gas and isopropylmagnesium chloride in tetrahydrofuran (2.0 M, 1.13 mL, 2.25 mmol, 1.2 equiv) was added dropwise and the mixture was stirred at 25 ℃ for 2 h to prepare isopropylmagnesium chloride-lithium chloride (^{i}PrMgCl·LiCl) solution. A solution of 2-bromo-3'-methoxy-1,1'-biphenyl (493 mg, 1.88 mmol, 1.0 equiv) in 1.13 mL anhydrous tetrahydrofuran was added into the reaction mixture and the mixture was stirred for 24 h to prepare 1.0 M Turbo Grignard reagent. The reagent was used directly in the next step.

(2) Synthesis of compound 6



A dry 5 mL Schlenk flask was charged with a solution of compound **5** (493 mg, 0.750 mmol, 1.0 equiv) and $PdCl_2(PPh_3)_2$ (10.5 mg, 0.0150 mmol, 2.0 mol%) in anhydrous tetrahydrofuran (1.5 mL) under nitrogen gas. The Turbo Grignard reagent (1.0 M, 1.88 mL, 1.88 mmol, 2.5 equiv) was added dropwise into the solution and stirred at 25 ℃ for 1 h. The reaction was quenched by sat. aq. NH_4Cl and extracted with dichloromethane（3 x 10 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 40:1) to afford **6** as a white solid (47.5 mg, 0.0700 mmol, 22%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.40 (m, 10H), 7.23-7.18 (m, 2H), 7.17-7.12 (m, 3H), 7.10 (d, *J* = 7.8 Hz, 2H), 7.01 (d, *J* = 7.4 Hz, 2H), 6.93 (dd, *J* = 7.8, 1.6 Hz, 2H), 6.82 (ddd, *J* = 7.6, 1.5, 1.0 Hz, 2H), 6.70 (ddd, *J* = 8.2, 2.6, 0.9 Hz, 2H), 6.64 (dd, *J* = 2.5, 1.6 Hz, 2H), 3.49 (s, 6H), 2.40 (t, *J* = 8.2 Hz, 2H), 1.19 (quint, *J* = 7.3 Hz, 2H), 0.77 (t, *J* = 7.4 Hz, 3H), 0.67 (dt, *J* = 7.7, 3.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 150.5, 145.4, 142.9, 141.0, 140.8, 140.7, 140.6, 130.6, 130.4, 129.6, 128.9, 128.4, 127.6, 126.7, 126.4, 123.7, 122.4, 121.1, 115.3, 113.0, 58.4, 55.1, 37.5, 26.1, 23.2, 14.0 (One signal was not detected); HRMS (EI^+) Calcd for $C_{49}H_{42}O_2$ ($[M]^+$) 662.3185, Found 662.3183.

(3) Synthesis of compound 7 by the Scholl reaction

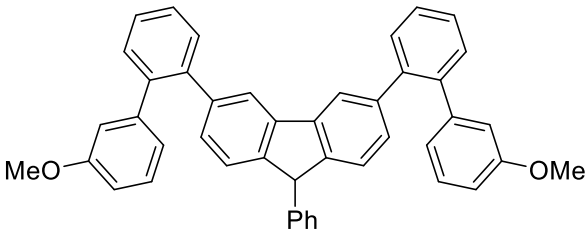


The synthesis method was according to the reported procedure.[16] A dry Schlenk flask was charged with **6** (13.3 mg, 0.0200 mmol, 1.0 equiv) in anhydrous dichloromethane (1.0 mL). A solution of $FeCl_3$ (64.9 mg, 0.400 mmol, 20.0 equiv) in nitromethane (0.20 mL) was added and the mixture was stirred at 25 ℃ for 24 h. The reaction mixture was concentrated under reduced pressure and purified by column chromatography on silica gel (hexane/dichloromethane = 4:1) and reprecipitation (dichloromethane/hexane) to afford **7** as a white solid (6.0 mg, 0.00900 mmol, 45%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.29 (s, 2H), 8.98 (d, *J* = 8.4 Hz, 2H), 8.64 (d, *J* = 8.3 Hz, 2H), 8.54 (d, *J* = 9.2 Hz, 2H), 8.43 (s, 2H), 8.07 (d, *J* = 2.2 Hz, 2H), 7.80 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.72 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.42 (d, *J* = 7.3 Hz, 2H), 7.33-7.17 (m, 5H), 4.03 (s, 6H), 2.83 (t, *J* = 8.2 Hz, 2H), 1.25 (tt, *J* = 8.2, 7.6 Hz, 2H), 0.85 (tt, *J* = 7.6, 7.3 Hz, 2H), 0.67 (t, *J* = 7.3 Hz, 3H); ^{13}C

NMR (100 MHz, CD_2Cl_2): δ 159.5, 152.5, 139.8, 131.6, 130.9, 130.7, 129.8, 129.0, 128.9, 128.0, 127.5, 127.4, 126.9, 125.6, 124.4, 124.0, 123.9, 118.8, 116.4, 116.3, 114.9, 106.1, 59.5, 55.9, 38.9, 26.9, 23.6, 14.1; HRMS (EI^+) Calcd for $C_{49}H_{38}O_2$ ($[M]^+$) 658.2872, Found 658.2870.

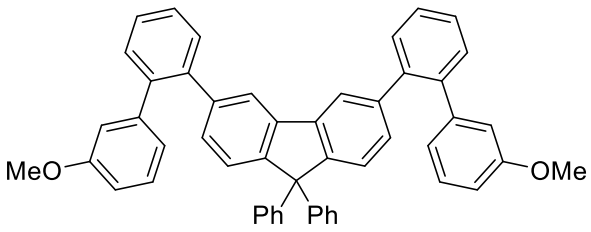
3,16-Dimethoxy-20,20-diphenyl-20*H*-cyclopenta[1,2-*b*:3,4-*b*']ditriphenylene (11)

(1) Synthesis of compound 9



A dry 5 mL Schlenk flask was charged with a solution of **8** (328 mg, 0.500 mmol, 1.0 equiv) and $PdCl_2(PPh_3)_2$ (7.0 mg, 0.010 mmol, 2.0 mol%) in anhydrous tetrahydrofuran (1.0 mL) under nitrogen gas. The Turbo Grignard reagent (1.0 M, 1.25 mL, 1.25 mmol, 2.5 equiv) was added dropwise into the solution and stirred at 25 ℃ for 1 h. The reaction was quenched with sat. aq. NH_4Cl and extracted with dichloromethane（3 x 10 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 40:1) to afford **8** as a white solid (37.5 mg, 0.0620 mmol, 12%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 1.2 Hz, 2H), 7.53-7.43 (m, 8H), 7.30-7.27 (m, 1H), 7.26-7.21 (m, 2H), 7.18-7.11 (m, 4H), 7.08-7.04 (m, 2H), 6.98 (dd, *J* = 7.8, 1.6 Hz, 2H), 6.84 (ddd, *J* = 7.6, 1.6, 1.0 Hz, 2H), 6.73 (ddd, *J* = 8.2, 2.6, 0.9 Hz, 2H), 6.68 (dd, *J* = 2.5, 1.4 Hz, 2H), 5.00 (s, 1H), 3.55 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 146.6, 142.9, 141.8, 141.1, 140.9, 140.6, 132.5, 130.7, 130.5, 129.4, 129.0, 128.8, 128.4, 128.1, 127.7, 126.9, 124.7, 122.5, 121.1, 115.4, 112.9, 55.2, 54.0; HRMS (EI^+) Calcd for $C_{45}H_{34}O_2$ ($[M]^+$) 606.2559, Found 606.2556.

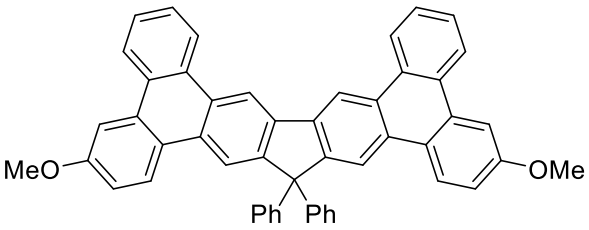
(2) Synthesis of compound 10



Compound **10** was synthesized according to the reported procedure.[17] A dry 5 mL Schlenk tube was charged with a solution of **9** (48.5 mg, 0.0800 mmol, 1.0 equiv), bromobenzene (15.1 mg, 0.0960 mmol, 1.2 equiv), $Pd(dba)_2$ (2.3 mg, 0.0040 mmol, 0.050 equiv), PPh_3 (2.1 mg, 0.0080 mmol, 0.10 equiv) and KO^{t}Bu (10.8 mg, 0.0960 mmol, 1.2 equiv) in toluene (0.60 mL) under nitrogen gas. The mixture was stirred at 100 ℃ for 12 h. After cooling to room temperature, the reaction mixture was quenched with water and extracted with

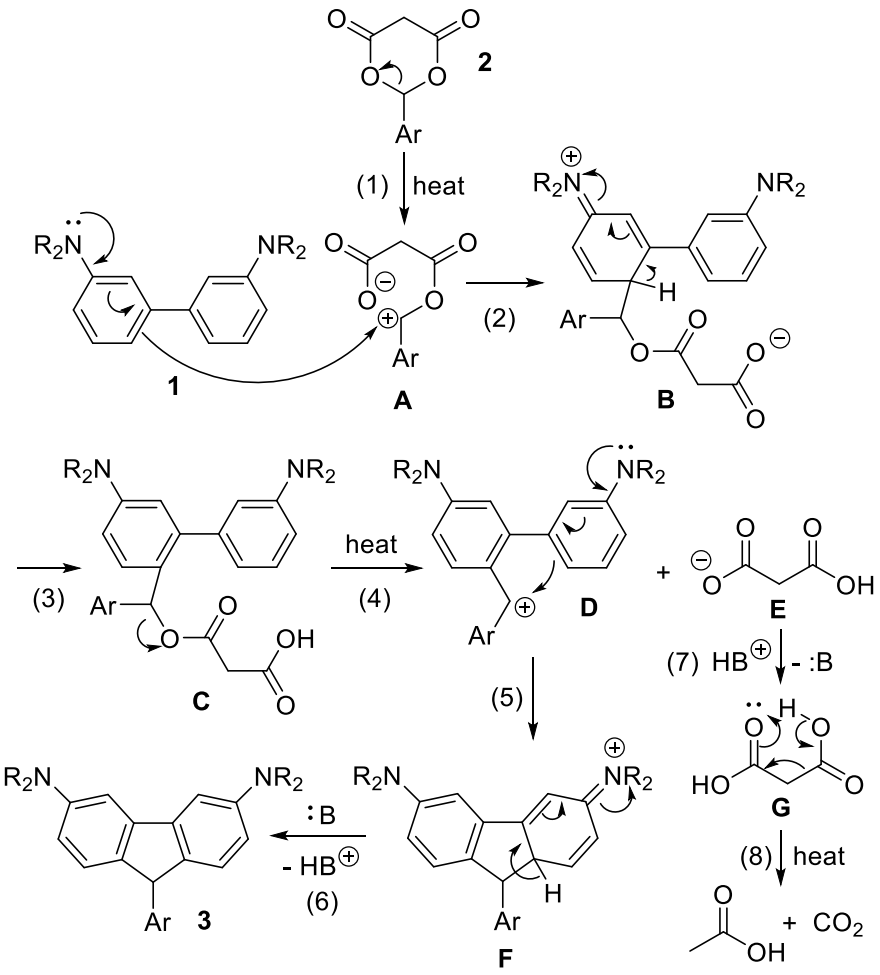
dichloromethane (3 x 10 mL). The organic layer was dried over $MgSO_4$ followed by filtration and concentration under reduced pressure. Because substrate **9** still remained, the residue, other reactants, and a solvent [bromobenzene (15.1 mg, 0.0960 mmol, 1.2 equiv), $Pd(dba)_2$ (2.3 mg, 0.0040 mmol, 0.050 equiv), PPh_3 (2.1 mg, 0.0080 mmol, 0.10 equiv), KO^tBu (10.8 mg, 0.0960 mmol, 1.2 equiv), toluene (0.60 mL)] were added into a dry 5 mL Schlenk tube and the mixture was stirred at 100 ℃ for 12 h to consume starting substance **9** completely. Then, the reaction mixture was after-treated as the same method as described above. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20:1) to afford **10** as a white solid (34.0 mg, 0.0500 mmol, 62%).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.42 (m, 10H), 7.26-7.20 (m, 8H), 7.19-7.13 (m, 6H), 6.98 (dd, *J* = 7.9, 1.7 Hz, 2H), 6.89 (d, *J* = 7.8 Hz, 2H), 6.74 (ddd, *J* = 8.3, 2.6, 0.9 Hz, 2H), 6.61 (dd, *J* = 2.5, 1.6 Hz, 2H), 3.41 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0, 149.8, 145.9, 142.8, 141.2, 140.75, 140.67, 139.9, 131.0, 130.7, 130.44, 130.37, 129.8, 129.0, 128.3, 128.2, 127.7, 127.6, 126.7, 125.6, 122.3, 121.4, 115.3, 113.2, 65.0, 55.1.

(3) Synthesis of 11 by the Scholl reaction



Synthesis method of **11** was the same as **7**. A dry Schlenk flask was charged with compound **10** (34.0 mg, 0.0500 mmol, 1.0 equiv) in anhydrous dichloromethane (2.5 mL). A solution of $FeCl_3$ (162 mg, 1.00 mmol, 20.0 equiv) in nitromethane (0.60 mL) was added and the mixture was stirred at 25 ℃ for 24 h. The reaction mixture was concentrated under reduced pressure and purified by column chromatography on silica gel (hexane/dichloromethane = 4:1) and reprecipitation (dichloromethane/hexane) to afford **11** as a yellow solid (8.0 mg, 0.012 mmol, 24%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.31 (s, 2H), 8.98 (d, *J* = 7.2 Hz, 2H), 8.67-8.59 (m, 4H), 8.49 (d, *J* = 9.2 Hz, 2H), 8.07 (s, 2H), 7.85-7.69 (m, 4H), 7.47 (d, *J* = 6.6 Hz, 4H), 7.34-7.22 (m, 8H), 4.03 (s, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2, CD_2Cl_2/CS_2 = 5:1): δ 159.5, 151.5, 146.7, 139.0, 131.7, 130.9, 130.8, 130.1, 129.0, 128.9, 128.0, 127.7, 127.3, 125.7, 124.4, 124.2, 124.0, 121.0, 116.4, 115.2, 106.2, 97.0, 59.2, 55.6; HRMS (EI^+) Calcd for $C_{51}H_{34}O_2$ ($[M]^+$) 678.2559, Found 678.2561.

6. Reaction Mechanism Verification Experiment



Scheme S7. Proposed mechanism

As described in the main text, acetic acid and CO_2 were proposed to generate as side products in the proposed mechanism (Scheme S7). Here are the verification experiment details of the acetic acid and CO_2 generation.

Verification experiment of acetic acid

The experiment is similar to typical procedure for the synthesis of fluorene derivatives 3 (Scheme S5). A 5 mL reaction tube equipped with a screw cap and a magnetic stirrer bar was charged with nitrogen gas. Compound **1a** (48.1 mg, 0.200 mmol, 1.0 equiv), 2-phenyl-1,3-dioxane-4,6-dione (**2a**, 76.9 mg, 0.400 mmol, 2.0 equiv) and deuterated chloroform ($CDCl_3$, 2.0 mL) were added under nitrogen atmosphere. After freezing degassing, the reaction mixture was stirred at 120 ℃ for 6 h. After the reaction completed,

1,1,2,2-tetrachloroethane (16.1 mg, 0.0950 mmol) was added as an internal standard into the mixture and the ^{1}H NMR (Figure S1) and ^{13}C NMR (Figure S2) of the mixture were measured immediately. Acetic acid was detected in 75% yield (0.150 mmol) (**3a** was obtained in 52% yield (0.105 mmol, 60% conversion based on **1a**).

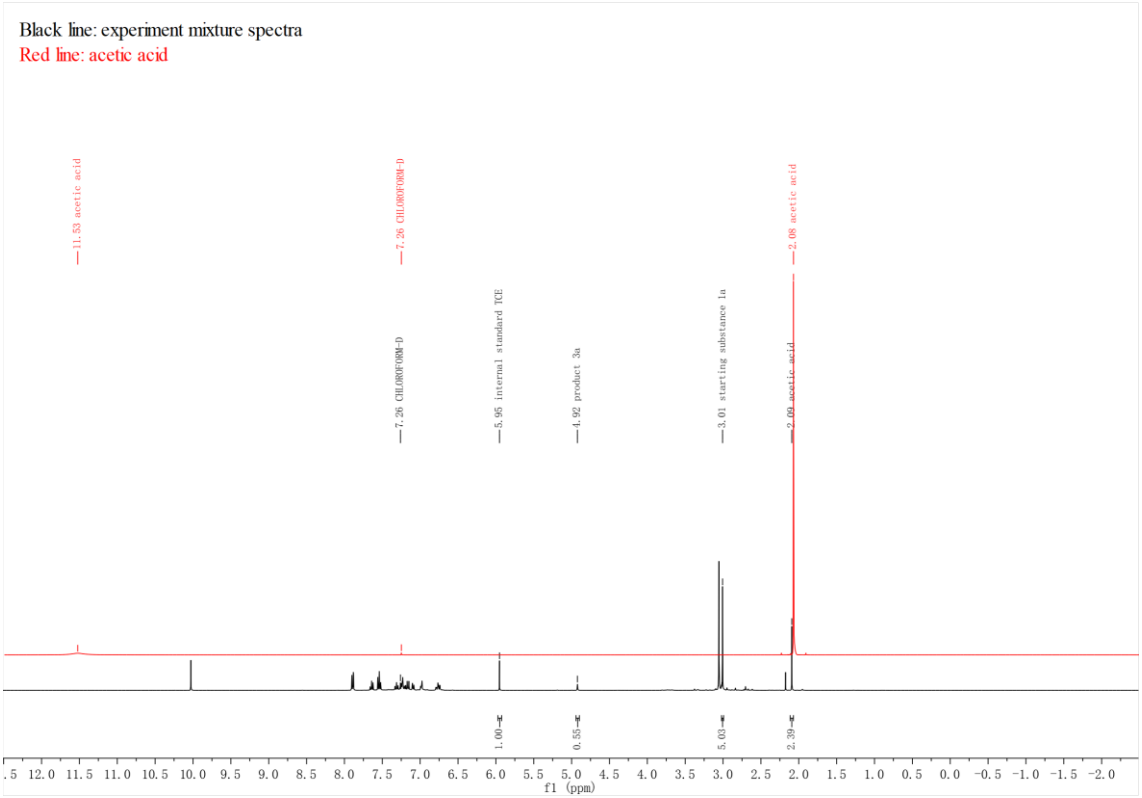


Figure S1. ^{1}H NMR ($CDCl_3$, 400 MHz): verification experiment of acetic acid

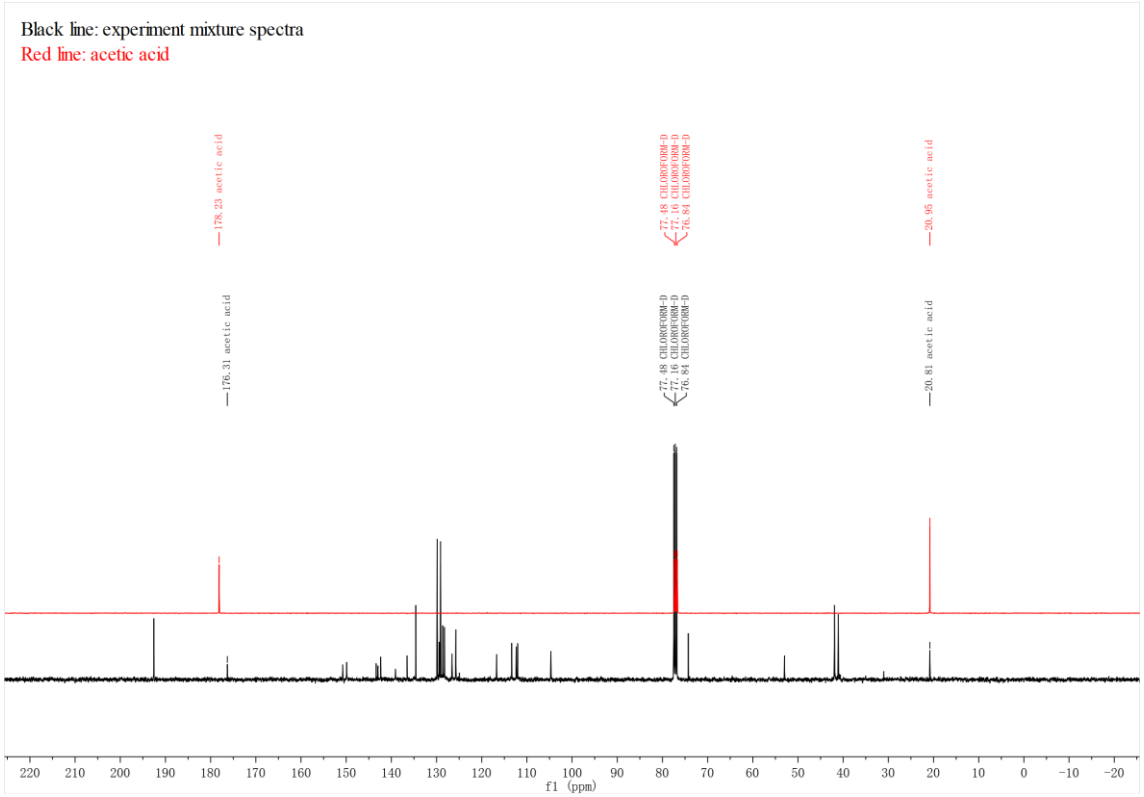
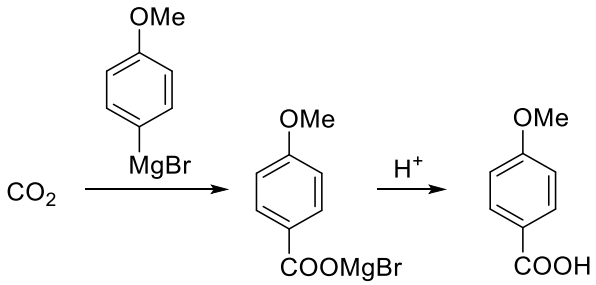


Figure S2. ^{13}C NMR ($CDCl_3$, 100 MHz): verification experiment of acetic acid

Verification experiment of CO_2

CO_2 gas was detected by a reaction with the Grignard reagent to produce the corresponding benzoic acid (Scheme S8).



Scheme S8. Detection of CO_2

(1) Synthesis of (4-methoxyphenyl)magnesium bromide (1.6 M solution in tetrahydrofuran)

A two neck flask equipped with a magnetic stirrer, a condenser, and a dropping funnel was dried by a heat gun and filled with nitrogen gas. Mg-turnings (778 mg, 32.0 mmol,

2.5 equiv) was added into the flask and heated with a heat gun under vacuum for 5 min and keep stirring to burnish the Mg for 15 min. After cooling to room temperature, the flask was filled with nitrogen gas again and dehydrated and degassed THF (6.0 mL) was added into the flask. 4-Bromoanisole (2.40 g, 12.8 mmol, 1.0 equiv) in THF (2.0 mL) was added into the flask dropwise with the dropping funnel and the reaction mixture was stirred at 25 ℃ for 1 h.

(2) Detection of CO_2 by the reaction with (4-methoxyphenyl)magnesium bromide

The reaction device was constructed as shown in Figure S3. Two dried and nitrogen flushed 5 mL Schlenk flask equipped with magnetic stirrer were connected with rubber tube. Biphenyl **1a** (96.1mg, 0.400 mmol, 1.0 equiv), Meldrum's acid derivative **2a** (154 mg, 0.800 mmol, 2.0 equiv), and dehydrated and degassed 1,2-dichlorobenzene (2.0 mL) were added into the left Schlenk flask and (4-methoxyphenyl)magnesium bromide in tetrahydrofuran (2.0 mL) was added into the right flask under nitrogen atmosphere. The left flask was heated by oil bath at 120 ℃ for 9 h. After cooling to room temperature, 1,1,2,2-tetrachloroethane was added as an internal standard into the left flask and the yield and conversion of the reaction was calculated by 1H NMR measurement (**3a**: 45% yield, conversion yield based on **1a**: 69%). After cooling the right Schlenk tube to 0 ℃, the reaction mixture was diluted with diethyl ether (10 mL) followed by addition of 1 M HCl (5.0 mL) to the mixture dropwise for quenching the reaction. The reaction mixture was extracted with dichloromethane（3 x 10 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. 1,1,2,2-Tetrachloroethane (69.5 mg, 0.414 mmol) was added as the internal standard into the mixture, and the ^{1}H NMR (Figure S4) and ^{13}C NMR (Figure S5) of the mixture were measured immediately. the yield of *p*-anisic acid was formed in 107% yield (0.426 mmol) based on **1a**.

Figure S3. The device of CO_2 verfication experiment

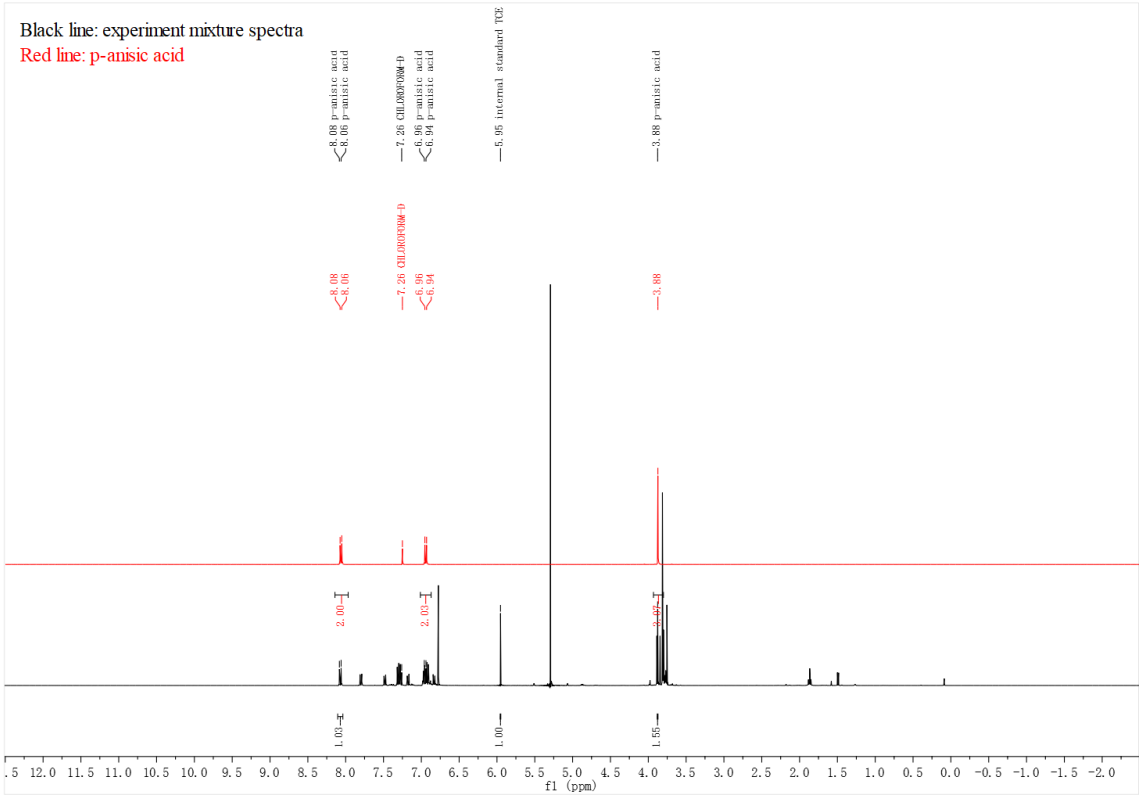


Figure S4. ^{1}H NMR ($CDCl_3$, 400 MHz): verification experiment of CO_2

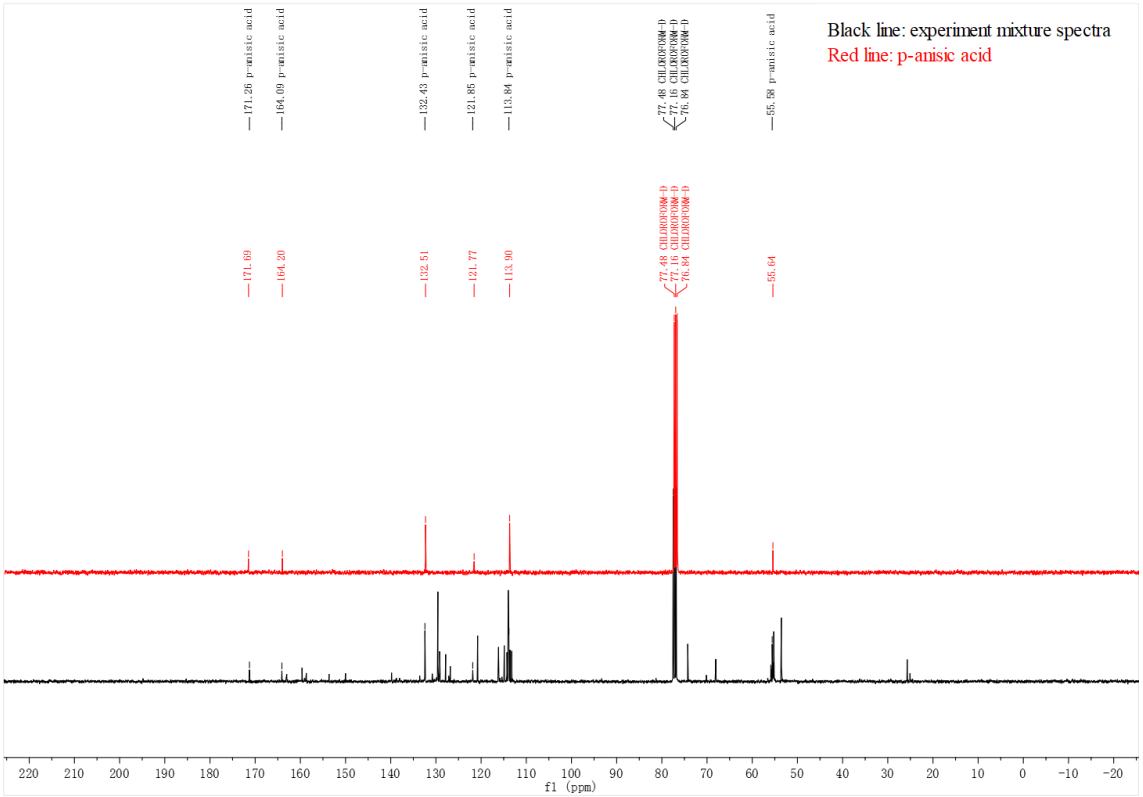


Figure S5. ^{13}C NMR ($CDCl_3$, 100 MHz): verification experiment of CO_2

7. Photophysical Properties of π-Conjugated Molecules

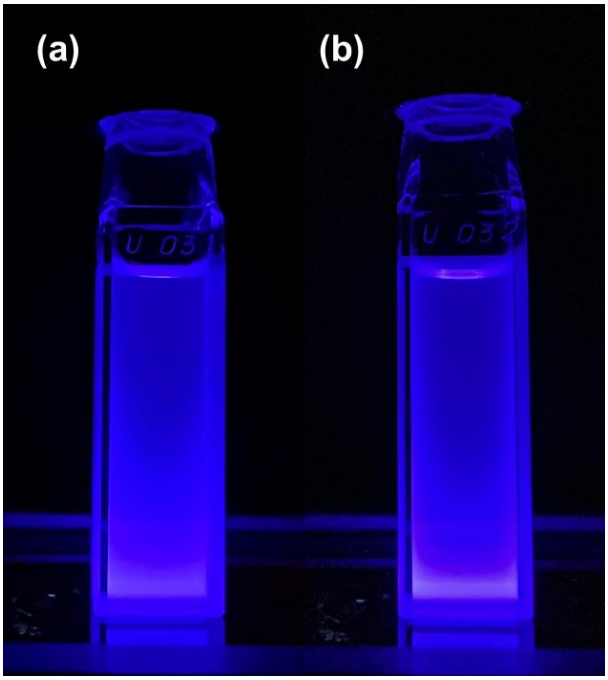
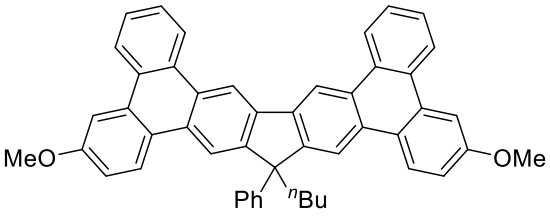
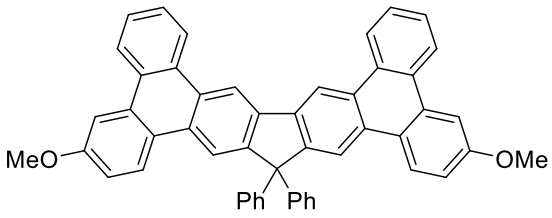


Figure S6. Fluorescence of 0.10 mM dichloromethane solution of (a) π-conjugated molecule **7** and (b) π-conjugated molecule **11** under UV irradiation (λ_{ex} = 365 nm)

Table S8. Photophysical properties of π-conjugated molecules **7** and **11**



7



11

compound	conditions	λ_{ab} (nm)	λ_{ex} (nm)	λ_{em} (nm)	Φ_F	FWHM (nm)
7	0.1 mM in dichloromethane	282	282	412	0.63	29
		348	348	412	0.65	29
		382	382	412	0.69	29
11	0.1 mM in dichloromethane	284	284	414	0.73	28
		350	350	414	0.68	28
		382	382	414	0.66	28

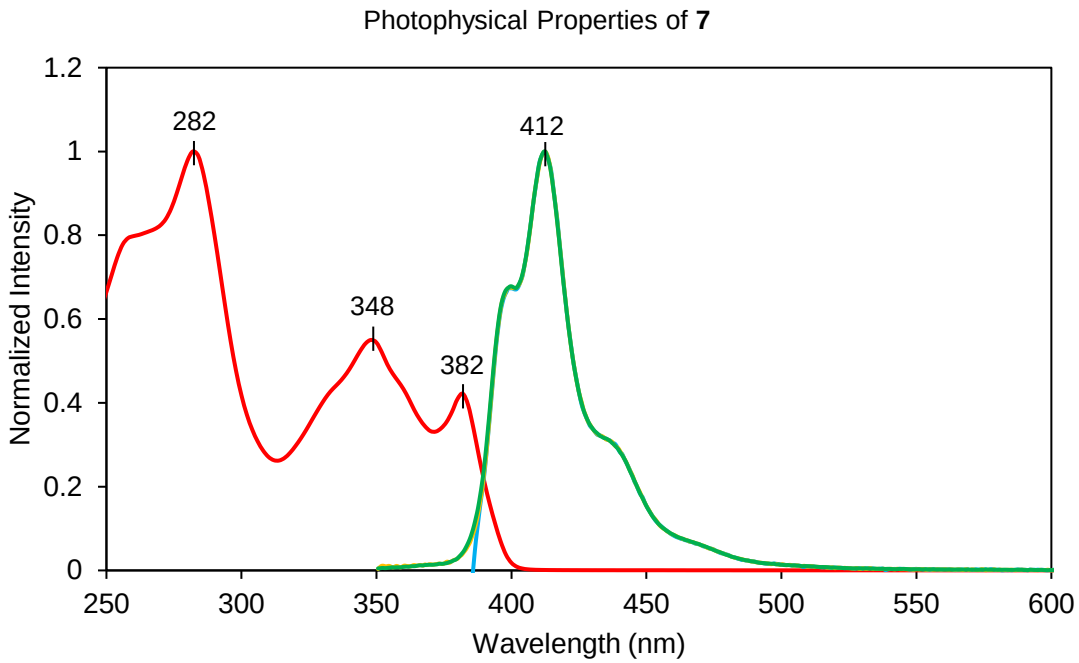


Figure S7. UV/Vis spectrum (red line) and fluorescence spectrum of compound **7** (green line: λ_{ex} = 282 nm; yellow line: λ_{ex} = 348 nm; blue line: λ_{ex} = 382 nm)

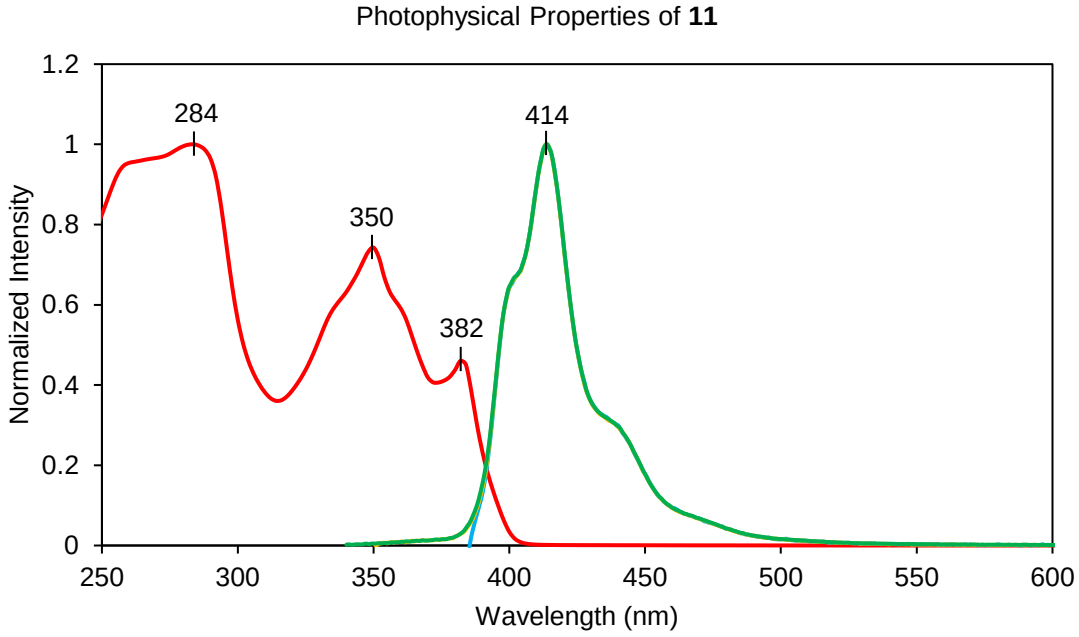


Figure S8. UV/Vis spectrum (red line) and fluorescence spectrum of compound **11** (green line: λ_{ex} = 284 nm; yellow line: λ_{ex} = 350 nm; blue line: λ_{ex} = 382 nm)

8. NMR Spectra

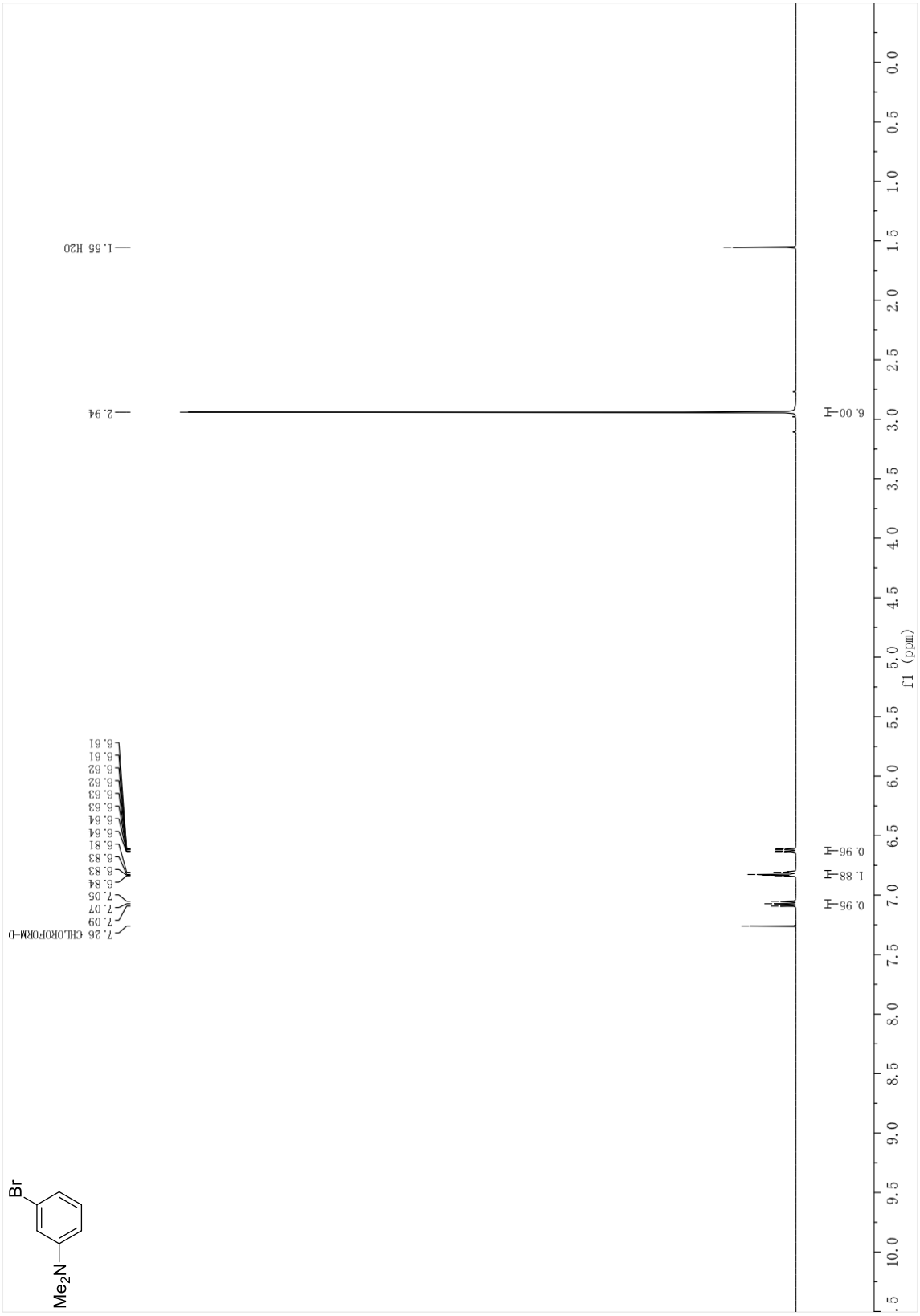


Figure S9. ^{1}H NMR ($CDCl_3$, 400 MHz): 3-Bromo-*N*,*N*-dimethylaniline

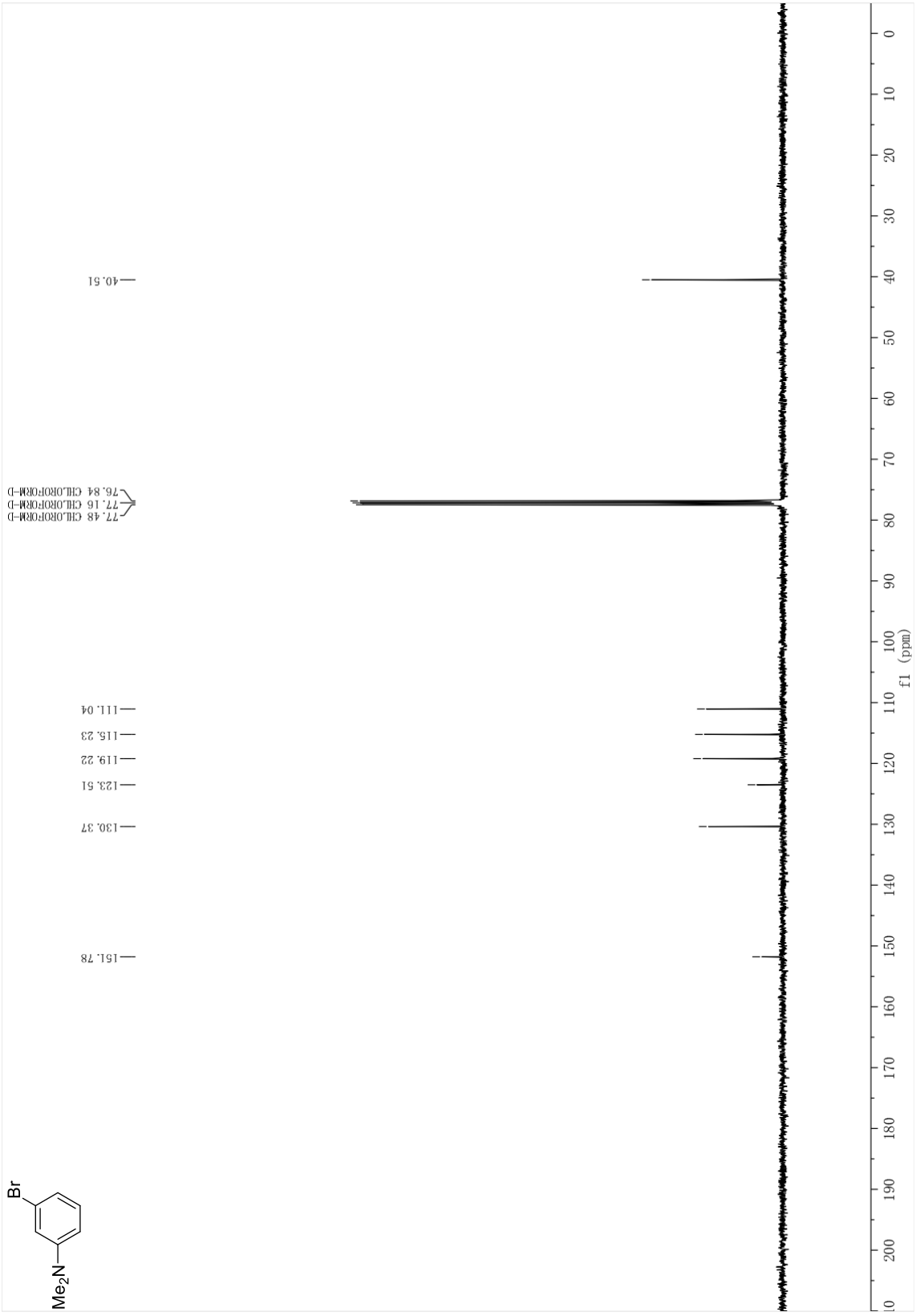


Figure S10. ^{13}C NMR ($CDCl_3$, 100 MHz): 3-Bromo-*N*,*N*-dimethylaniline

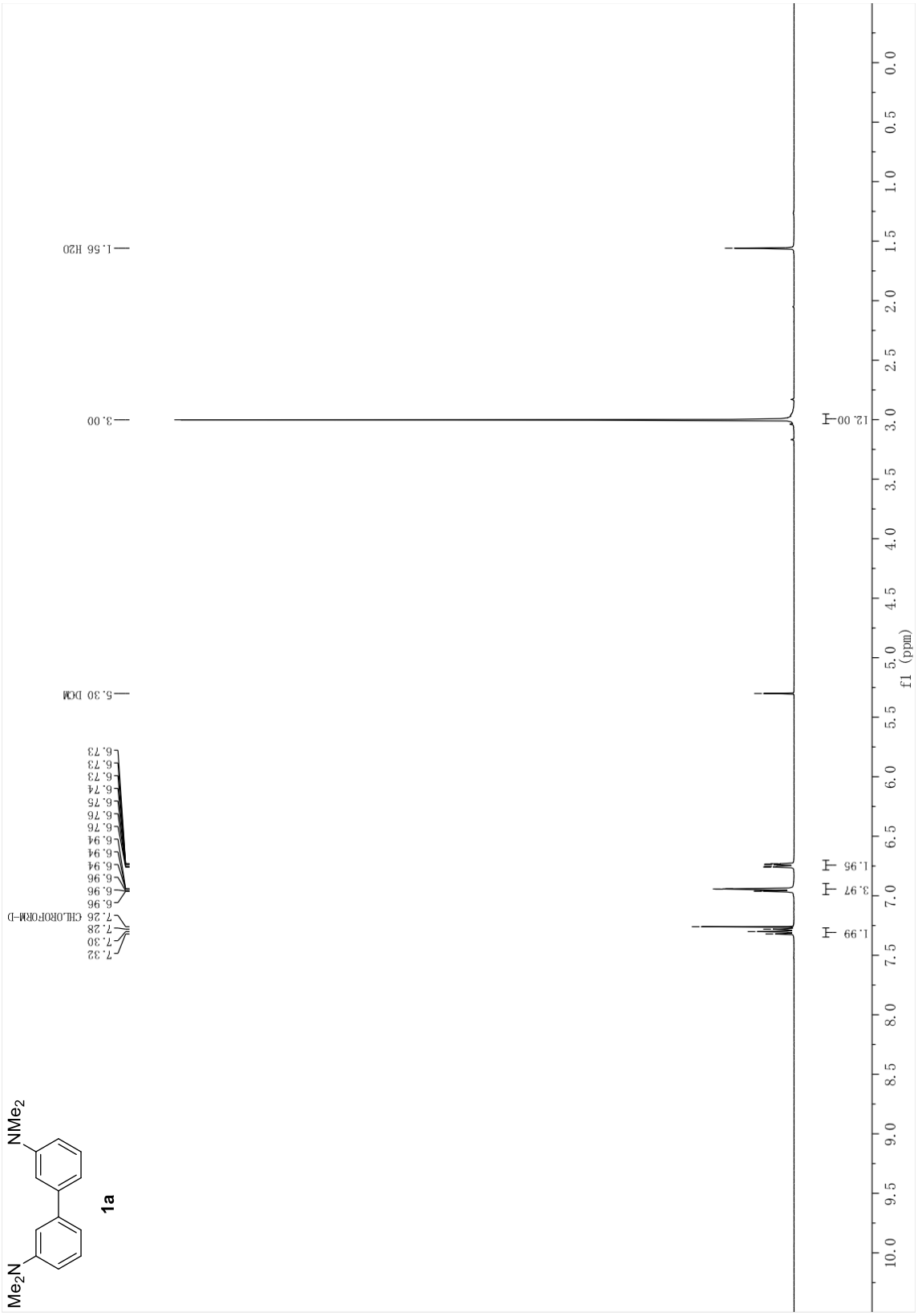


Figure S11. ^{1}H NMR ($CDCl_3$, 400 MHz): **1a**

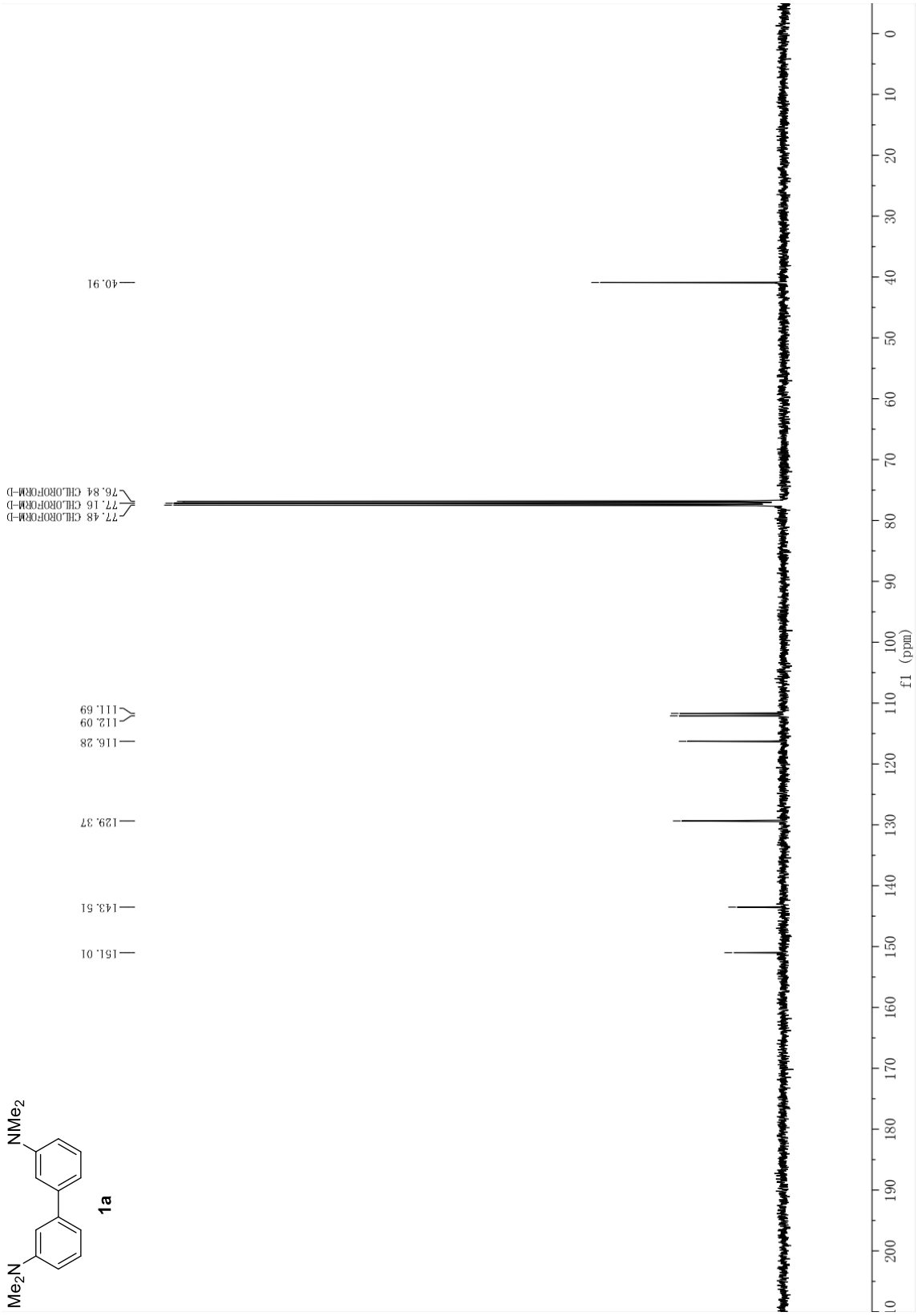


Figure S12. ^{13}C NMR ($CDCl_3$, 100 MHz): **1a**

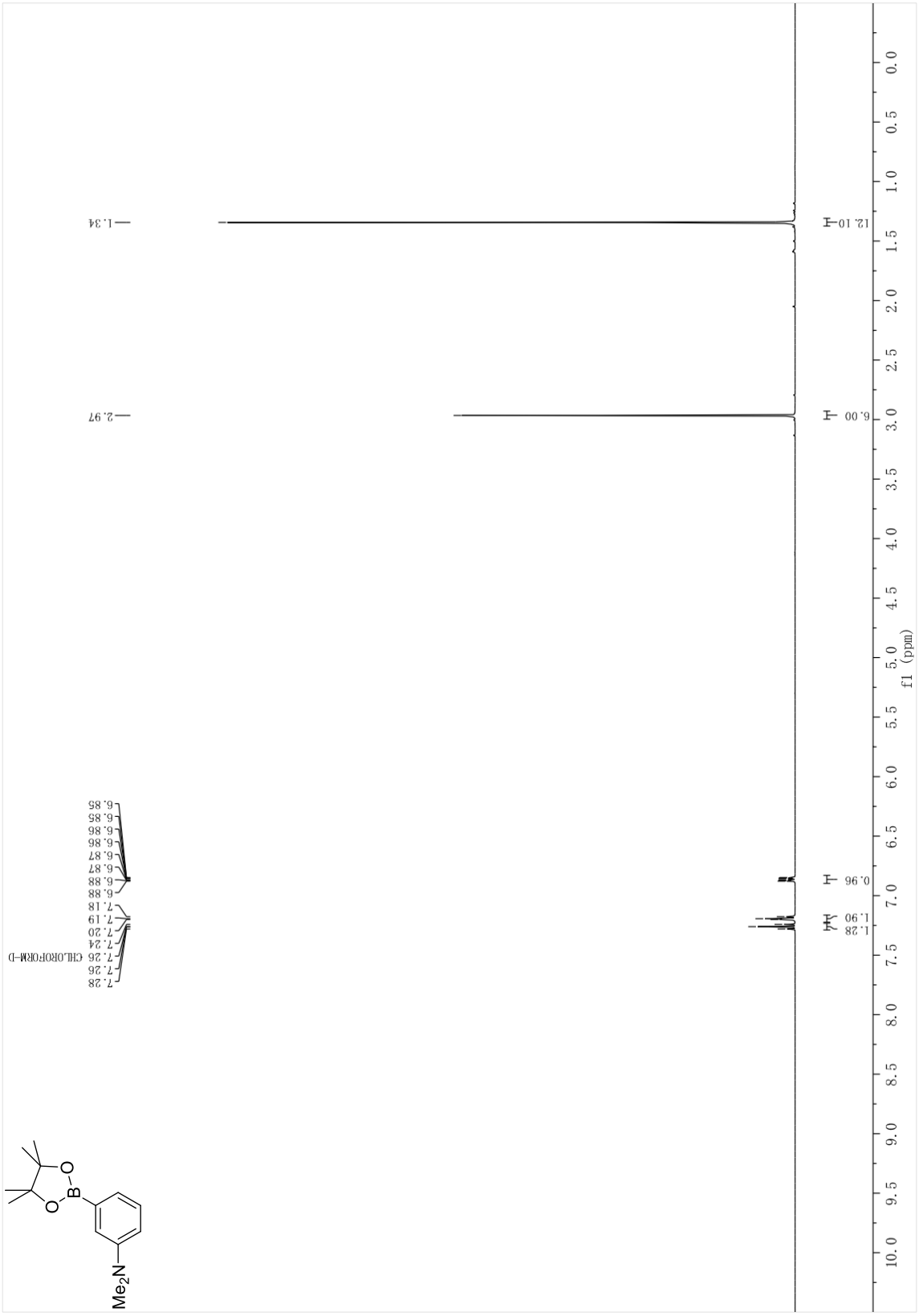


Figure S13. ^{1}H NMR ($CDCl_3$, 400 MHz): 3-(Dimethylamino)phenylboronic Acid Pinacol Ester

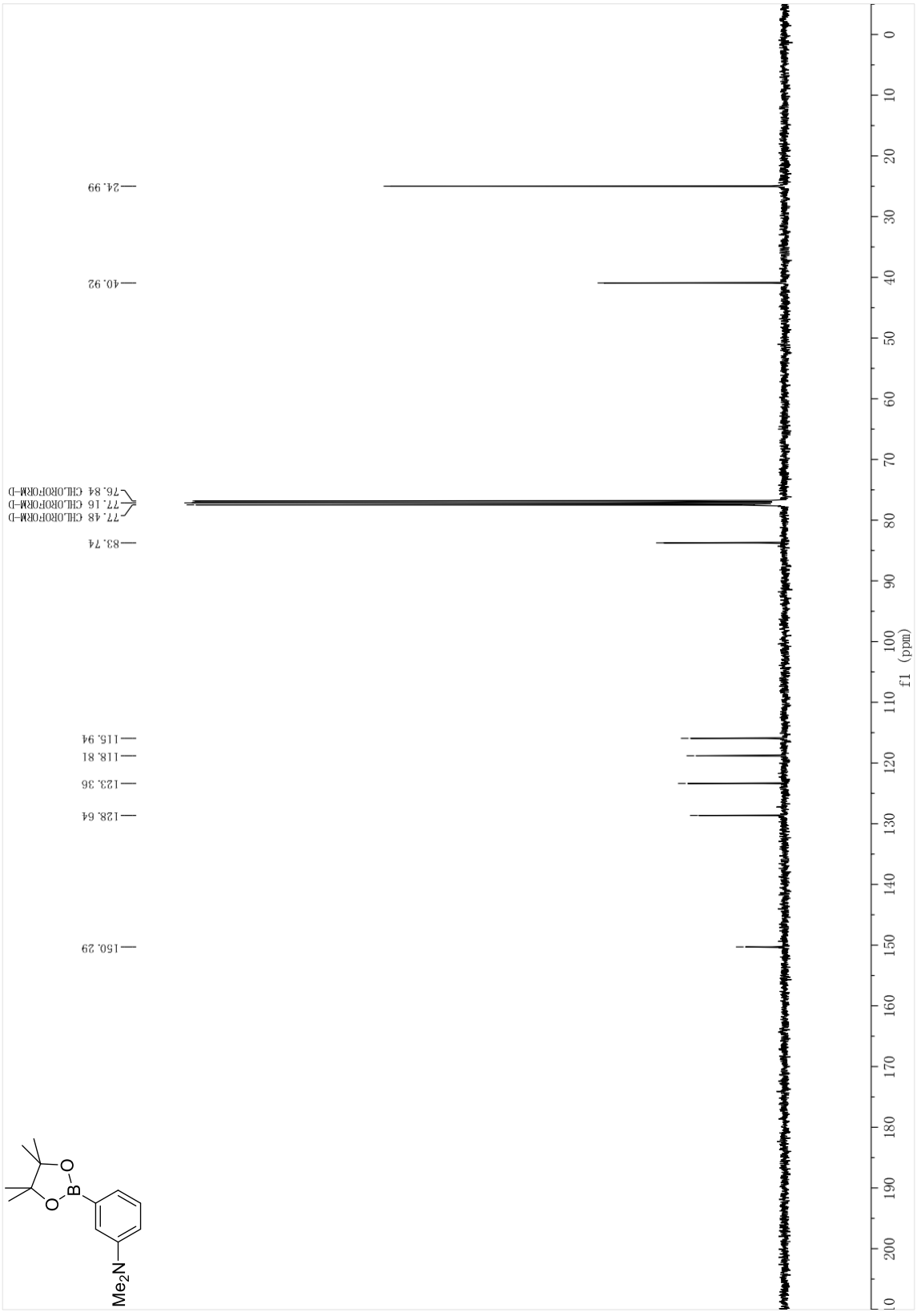


Figure S14. ^{13}C NMR ($CDCl_3$, 100 MHz): 3-(Dimethylamino)phenylboronic Acid Pinacol Ester

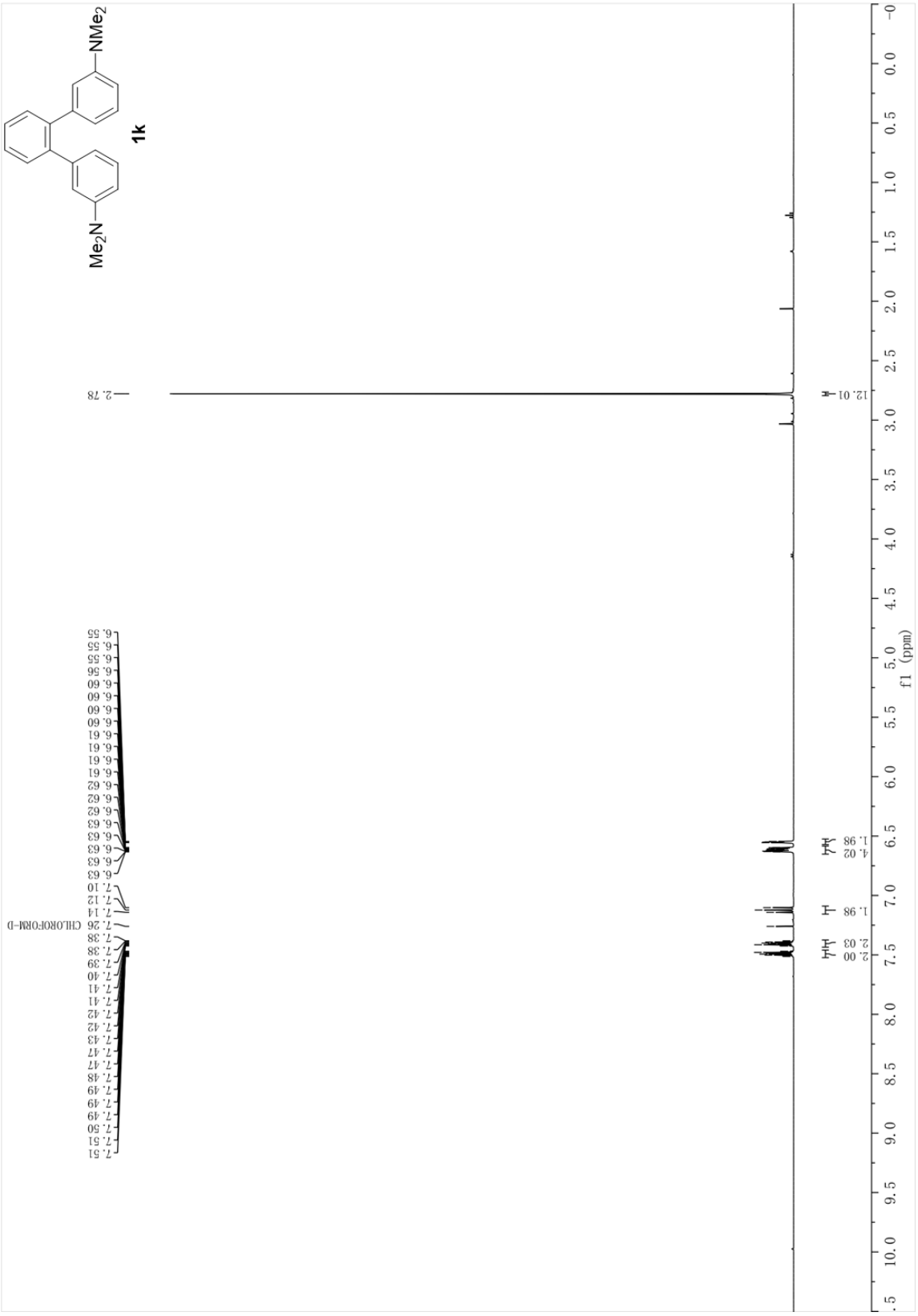


Figure S15. ^{1}H NMR ($CDCl_3$, 400 MHz): **1k**

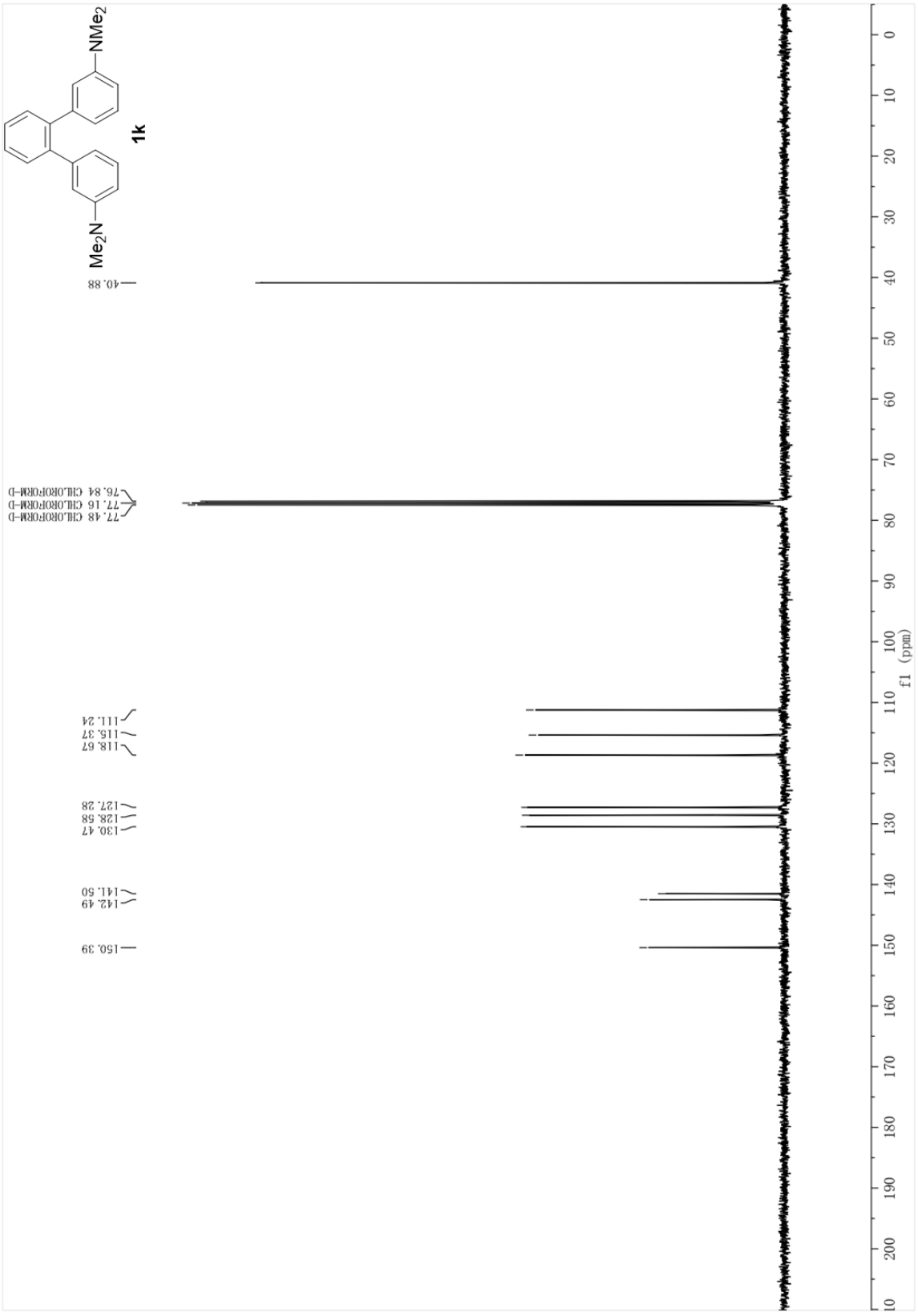


Figure S16. ^{13}C NMR ($CDCl_3$, 100 MHz): **1k**

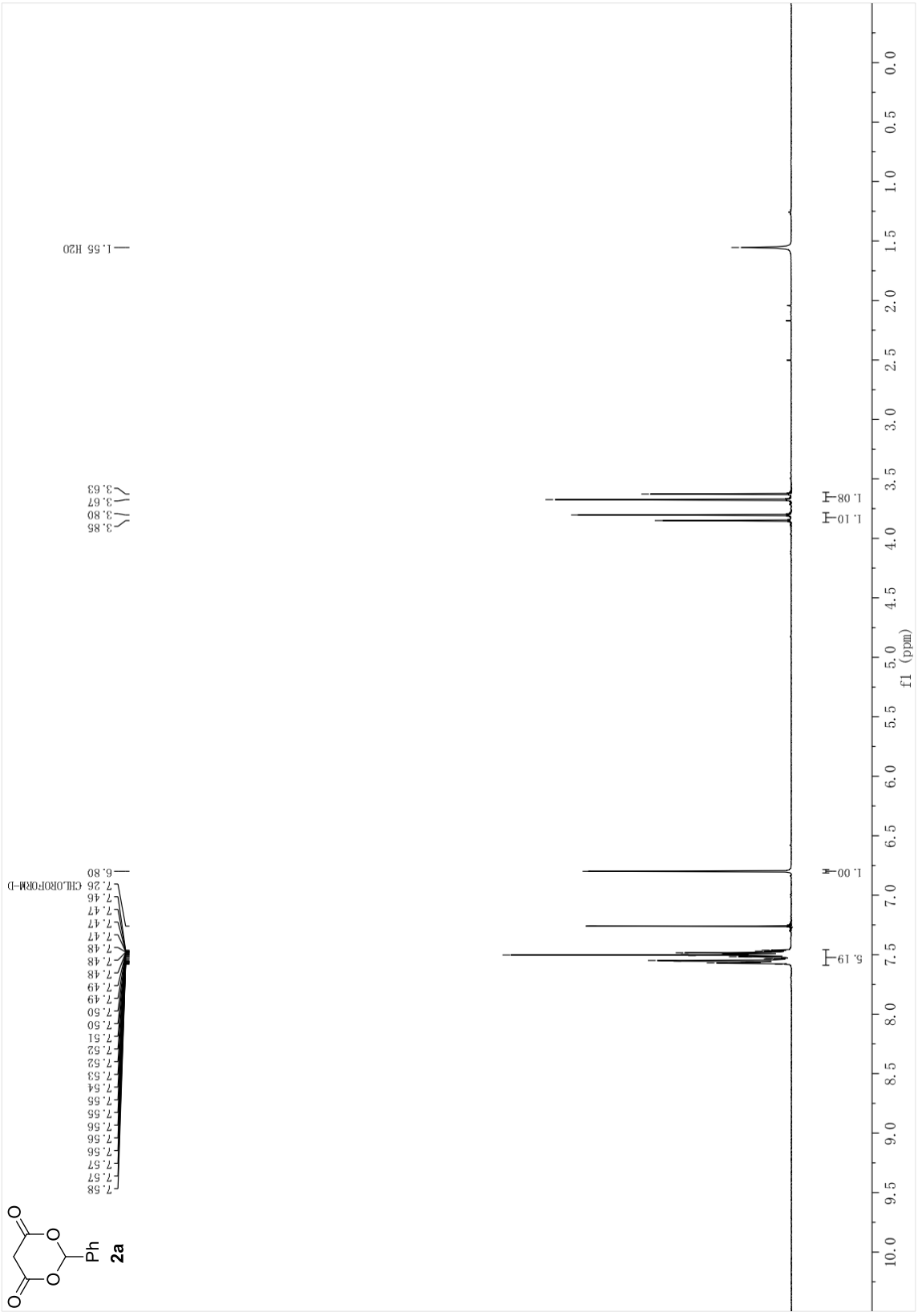


Figure S17. ^{1}H NMR ($CDCl_3$, 400 MHz): 2-Phenyl-1,3-dioxane-4,6-dione (**2a**)

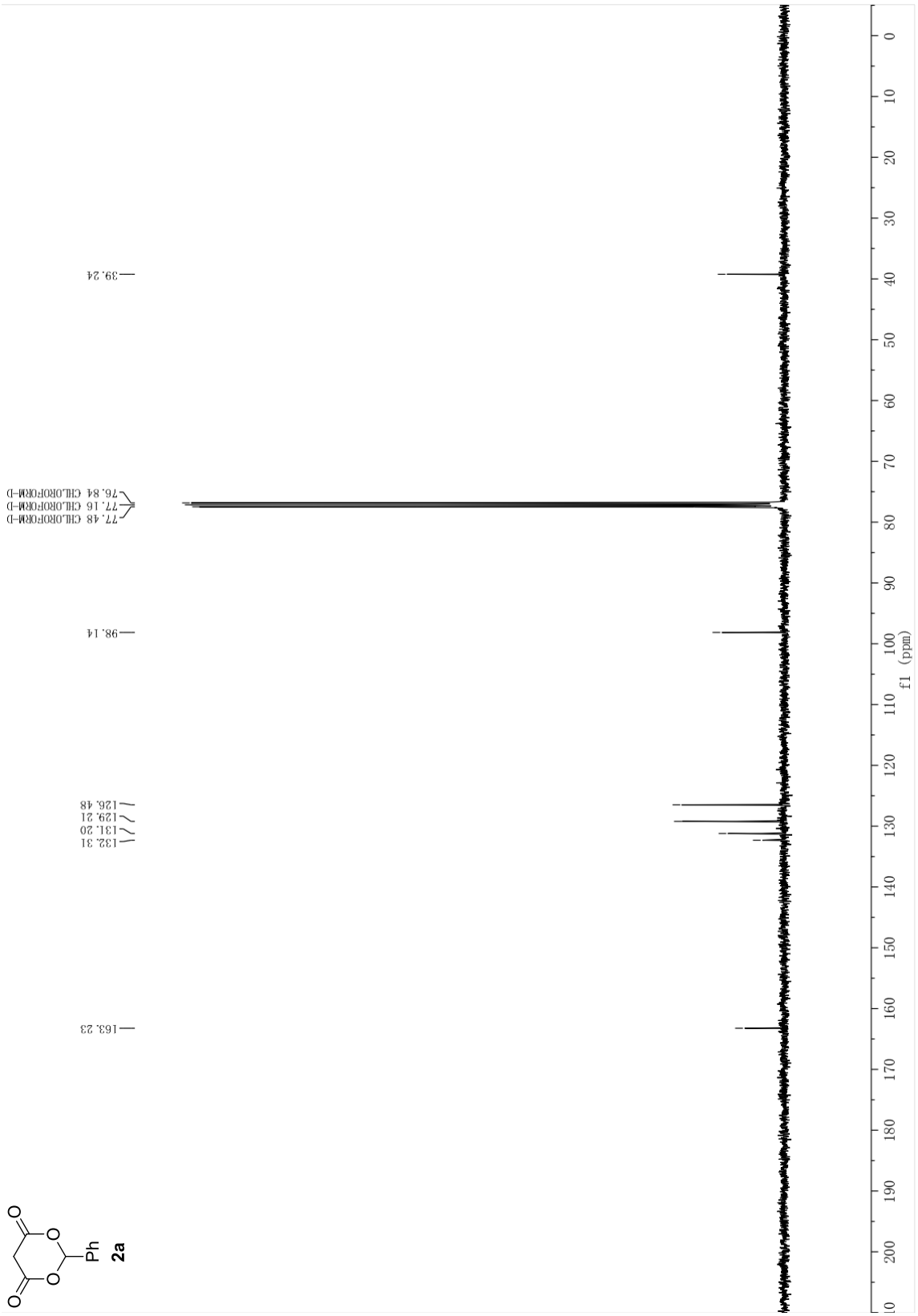


Figure S18. ^{13}C NMR ($CDCl_3$, 100 MHz): 2-Phenyl-1,3-dioxane-4,6-dione (**2a**)

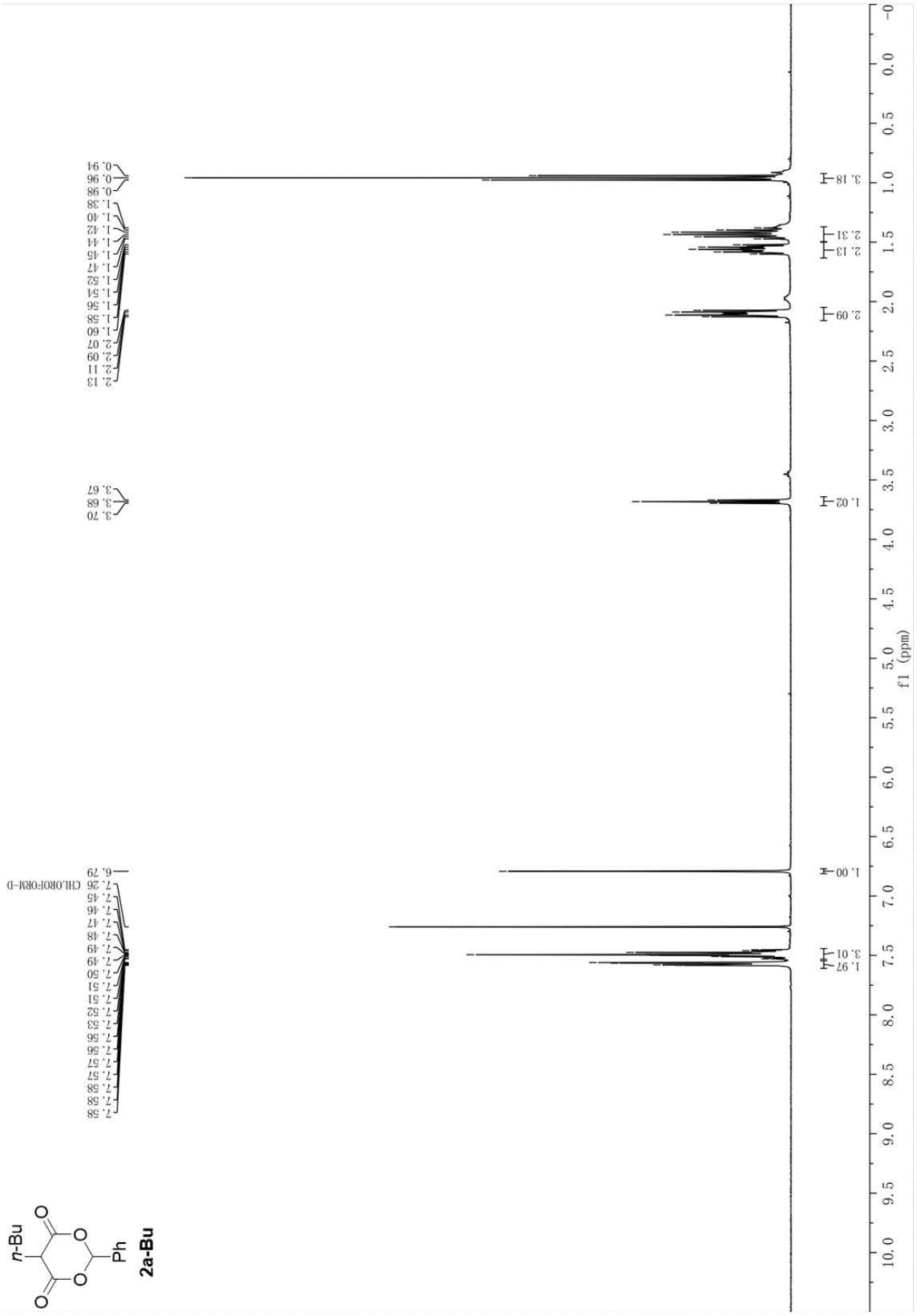


Figure S19. ^{1}H NMR ($CDCl_3$, 400 MHz): 5-Butyl-2-phenyl-1,3-dioxane-4,6-dione (**2a-Bu**)

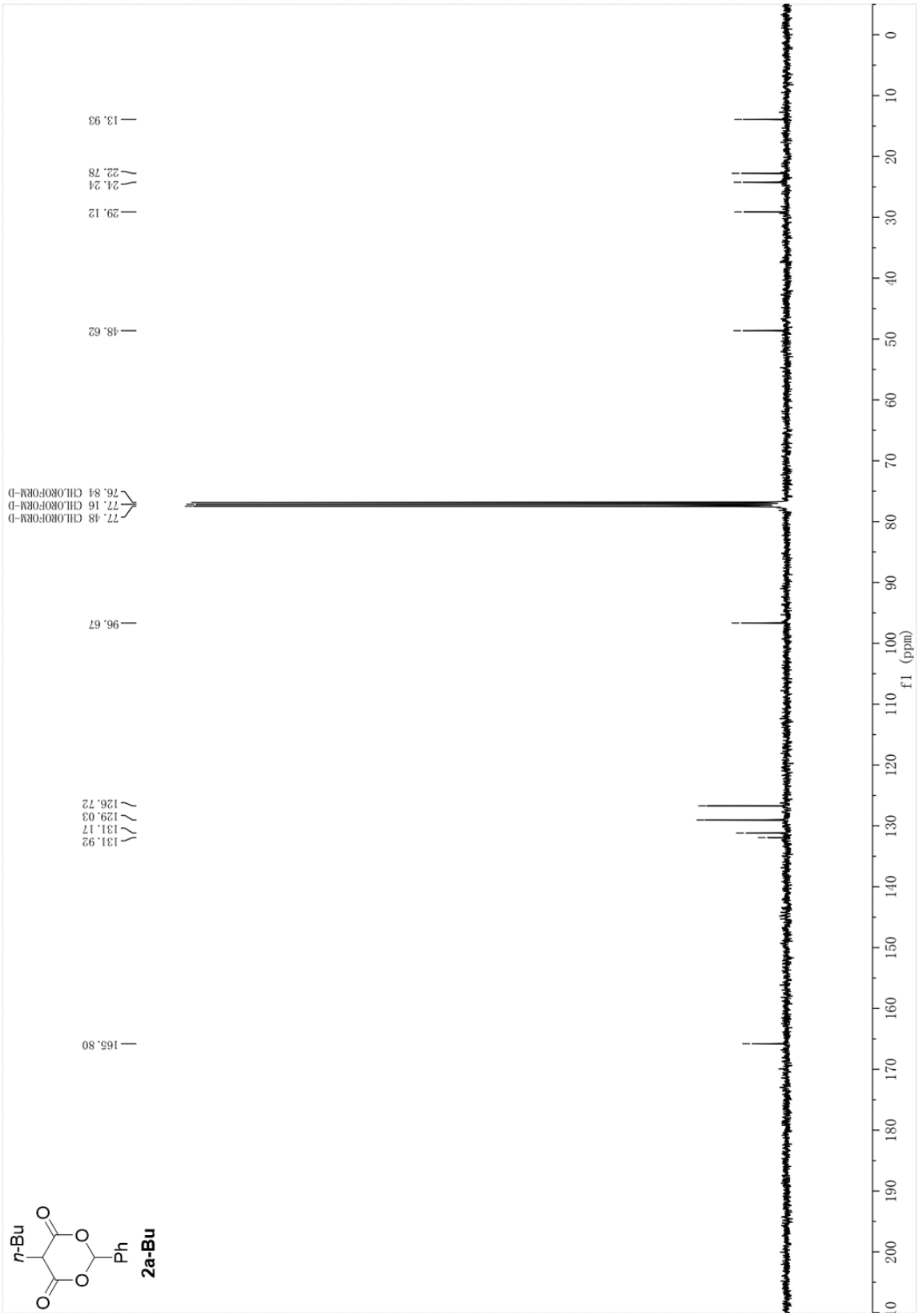


Figure S20. ^{13}C NMR ($CDCl_3$, 100 MHz): 5-Butyl-2-phenyl-1,3-dioxane-4,6-dione (**2a-Bu**)

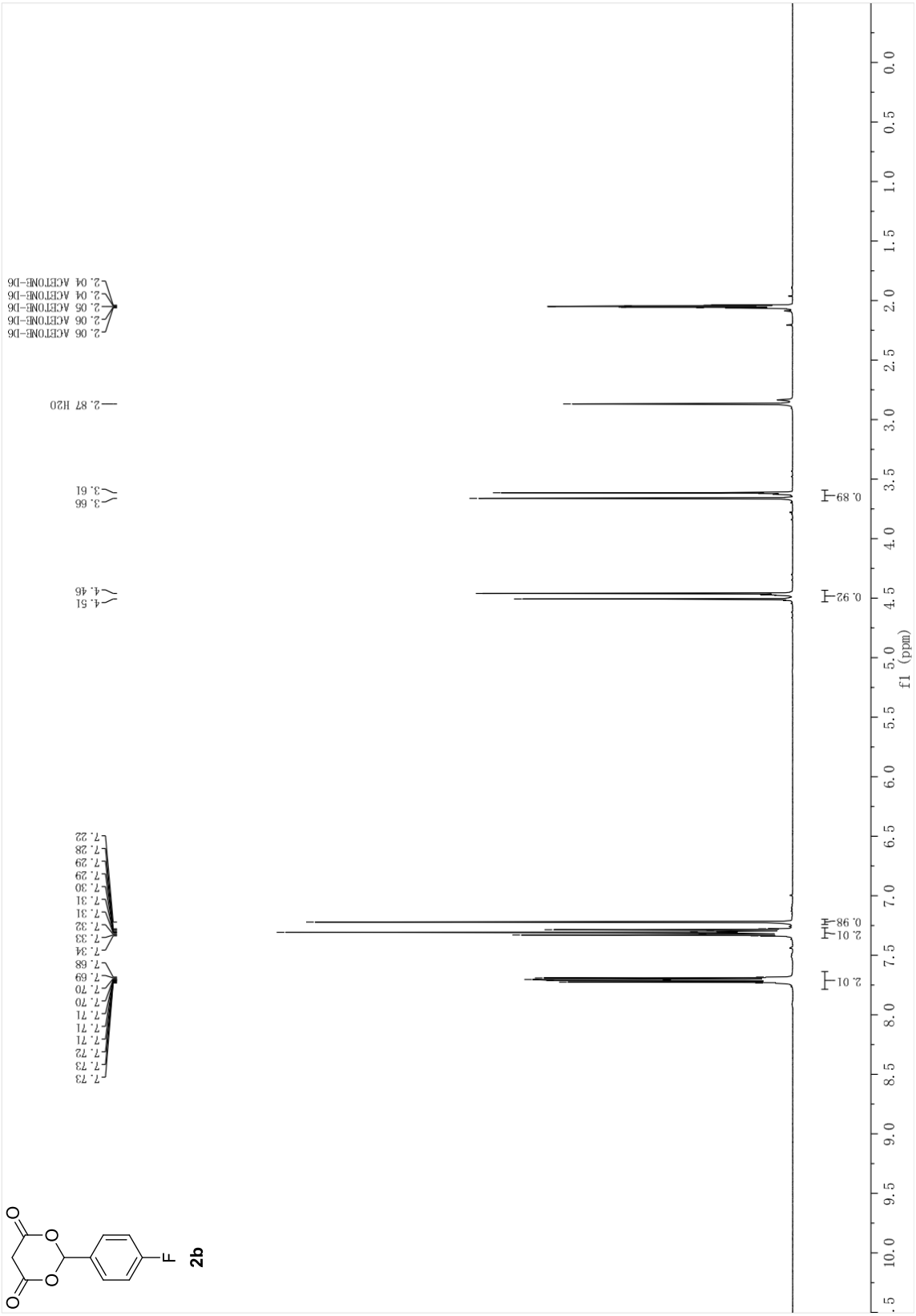


Figure S21. ^{1}H NMR (Acetone-d_6, 400 MHz): 2-(4-Fluorophenyl)-1,3-dioxane-4,6-dione (**2b**)

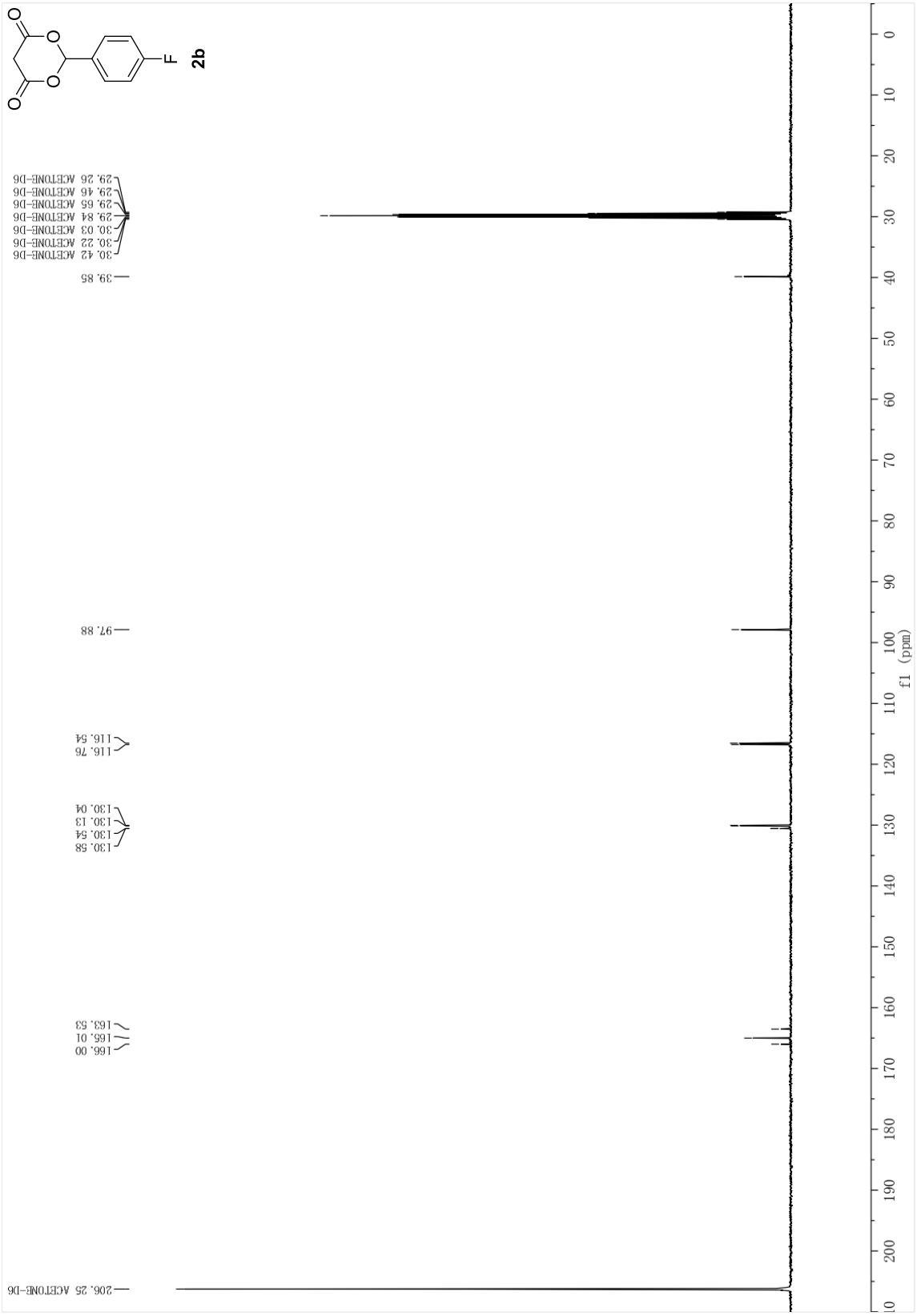


Figure S22. ^{13}C NMR (100 MHz, Acetone-d_6): 2-(4-Fluorophenyl)-1,3-dioxane-4,6-dione (**2b**)

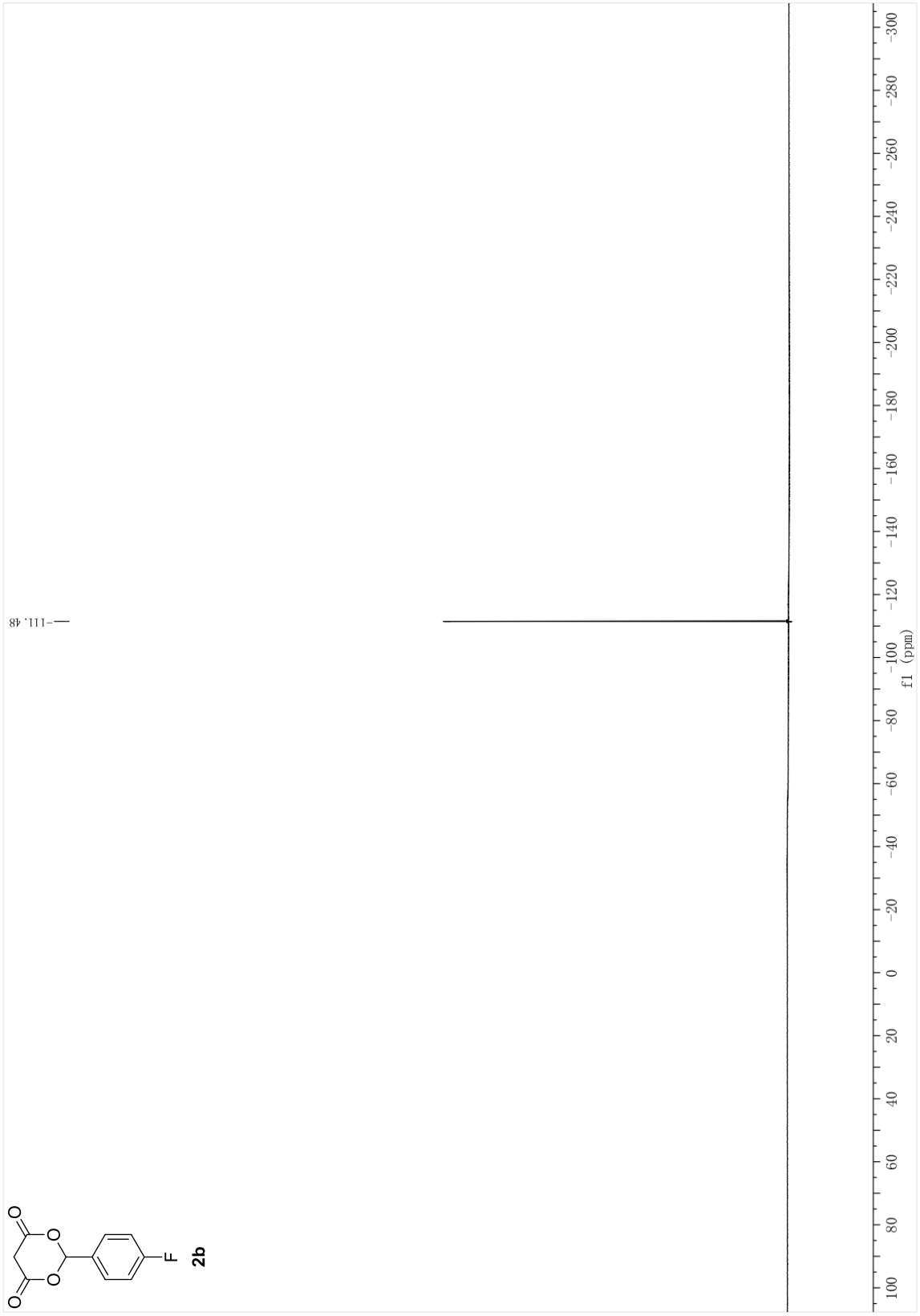


Figure S23. ^{19}F NMR (378 MHz, Acetone-d_6): 2-(4-Fluorophenyl)-1,3-dioxane-4,6-dione (**2b**)

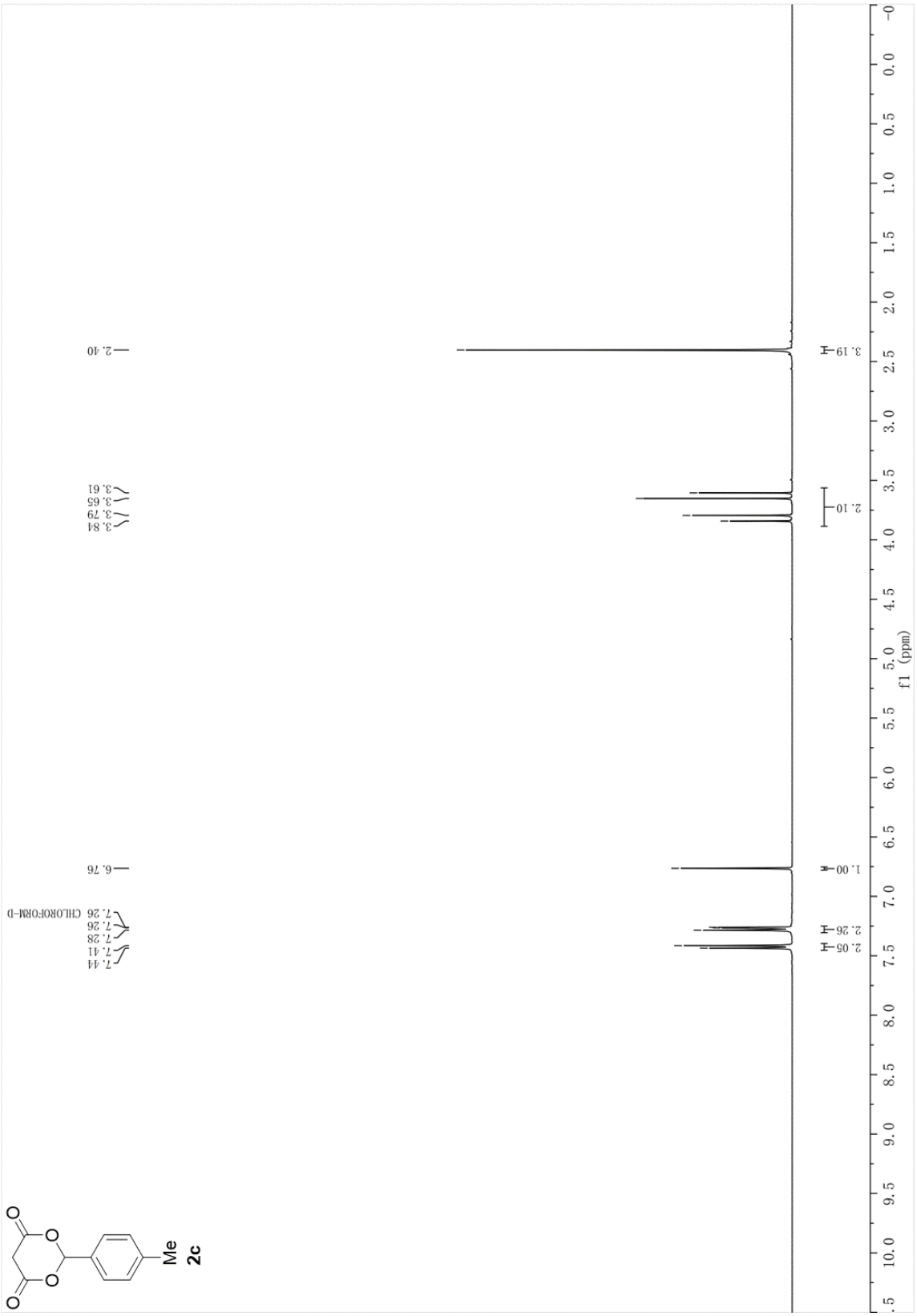


Figure S24. ^{1}H NMR (400 MHz, $CDCl_3$): 2-(*p*-Tolyl)-1,3-dioxane-4,6-dione (**2c**)

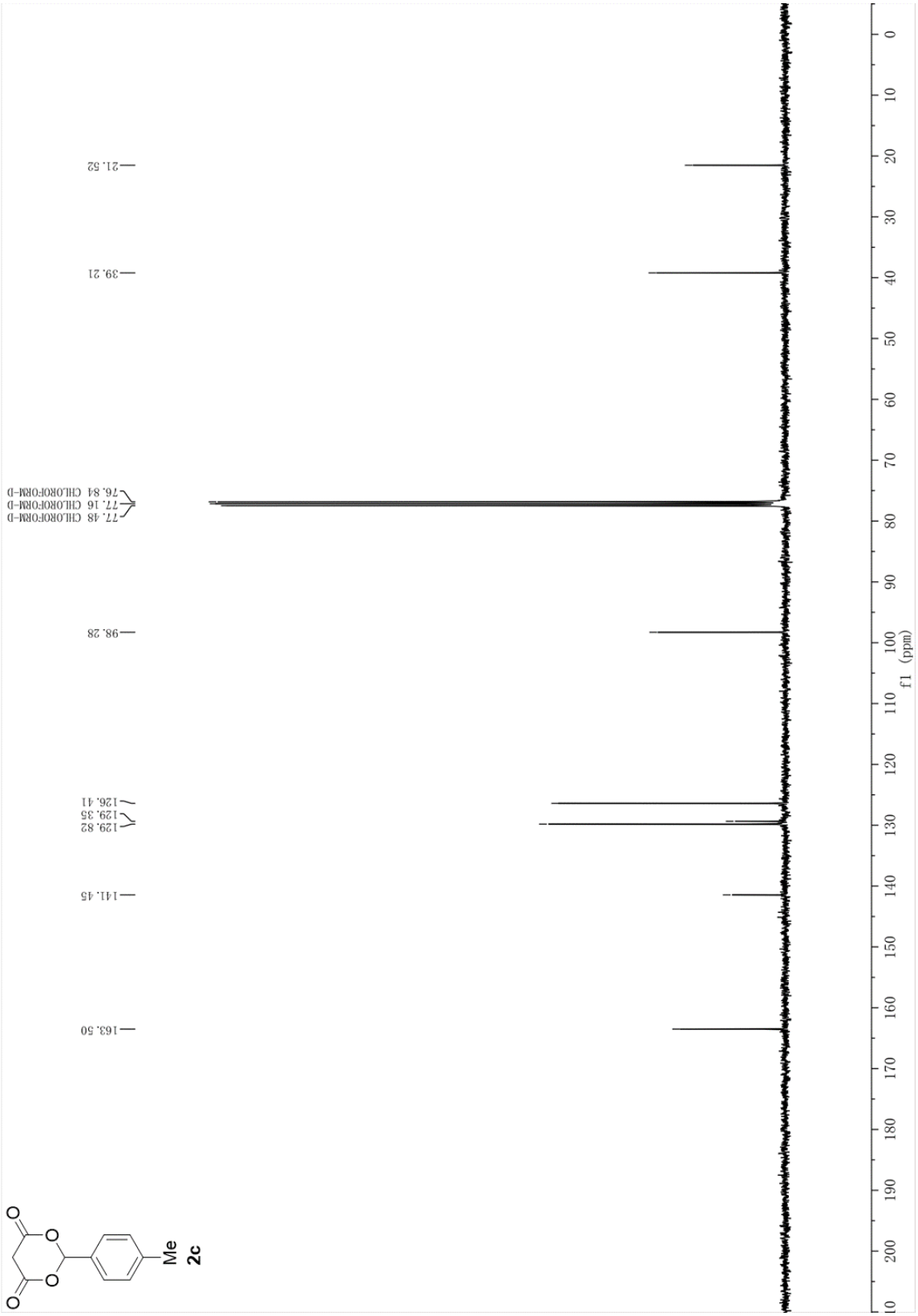


Figure S25. ^{13}C NMR (100 MHz, $CDCl_3$): 2-(*p*-Tolyl)-1,3-dioxane-4,6-dione (**2c**)

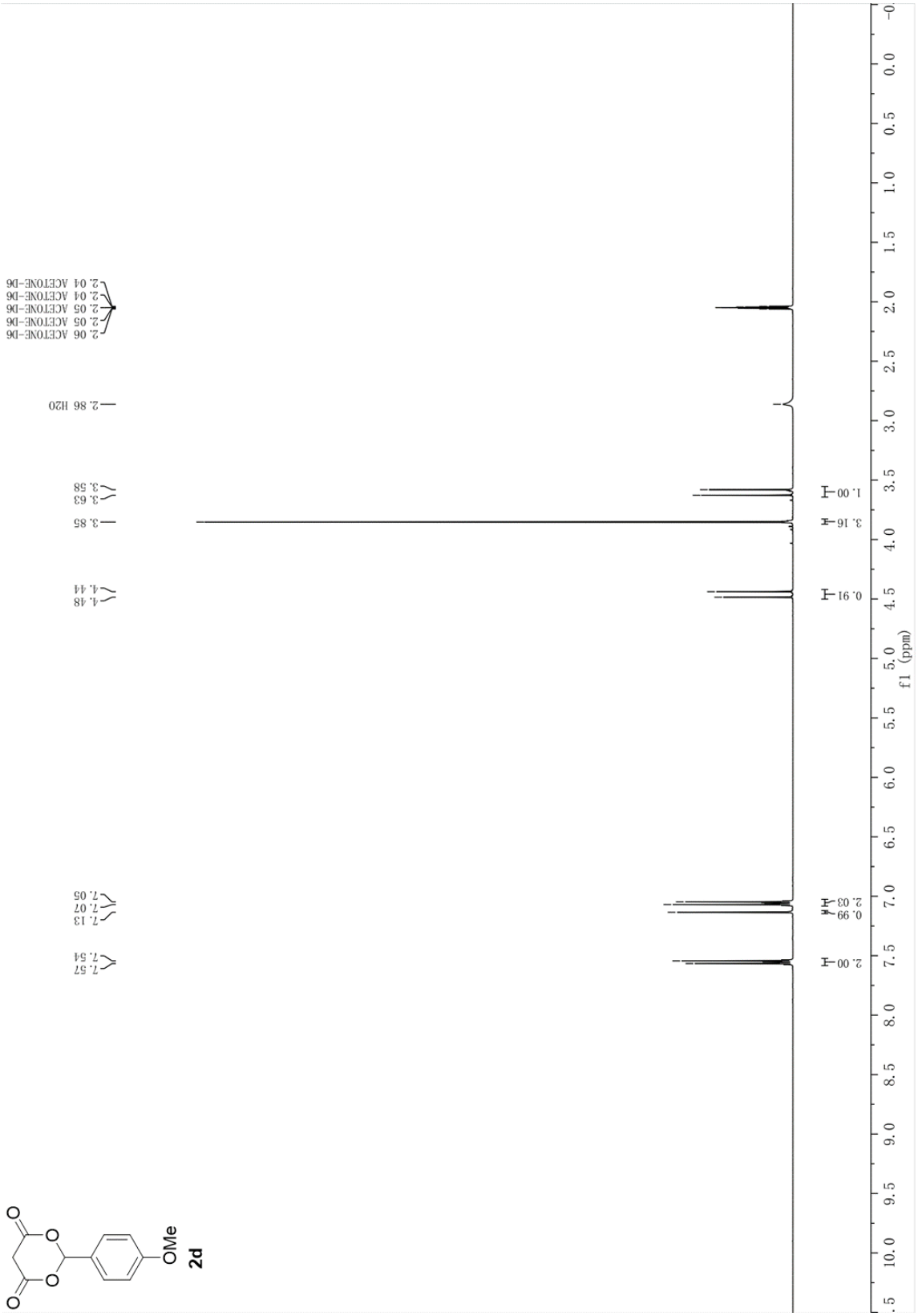


Figure S26. ^{1}H NMR (Acetone-d_6, 400 MHz): 2-(4-Methoxyphenyl)-1,3-dioxane-4,6-dione (**2d**)

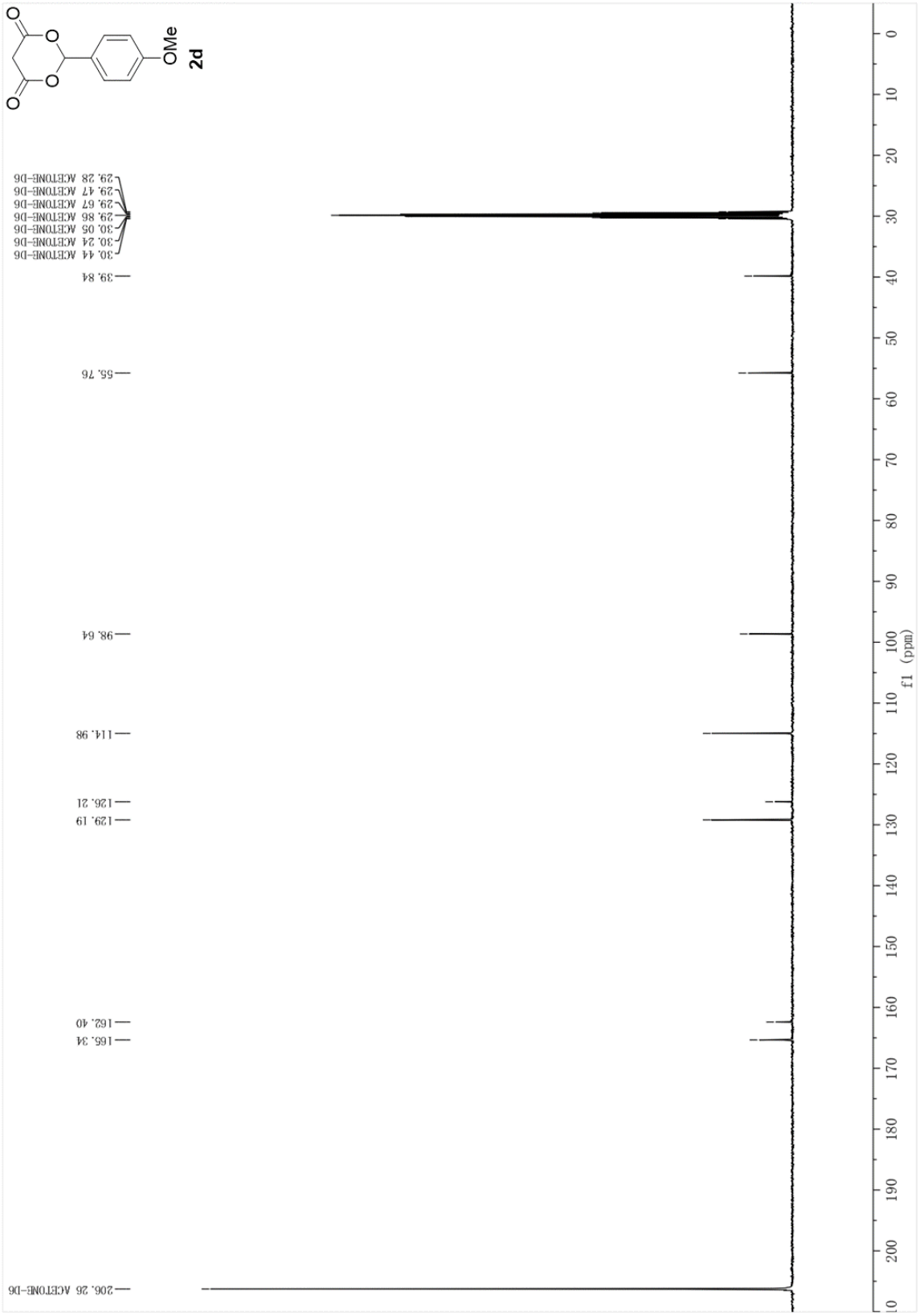


Figure S27. ^{13}C NMR (100 MHz, Acetone-d_6): 2-(4-Methoxyphenyl)-1,3-dioxane-4,6-dione (**2d**)

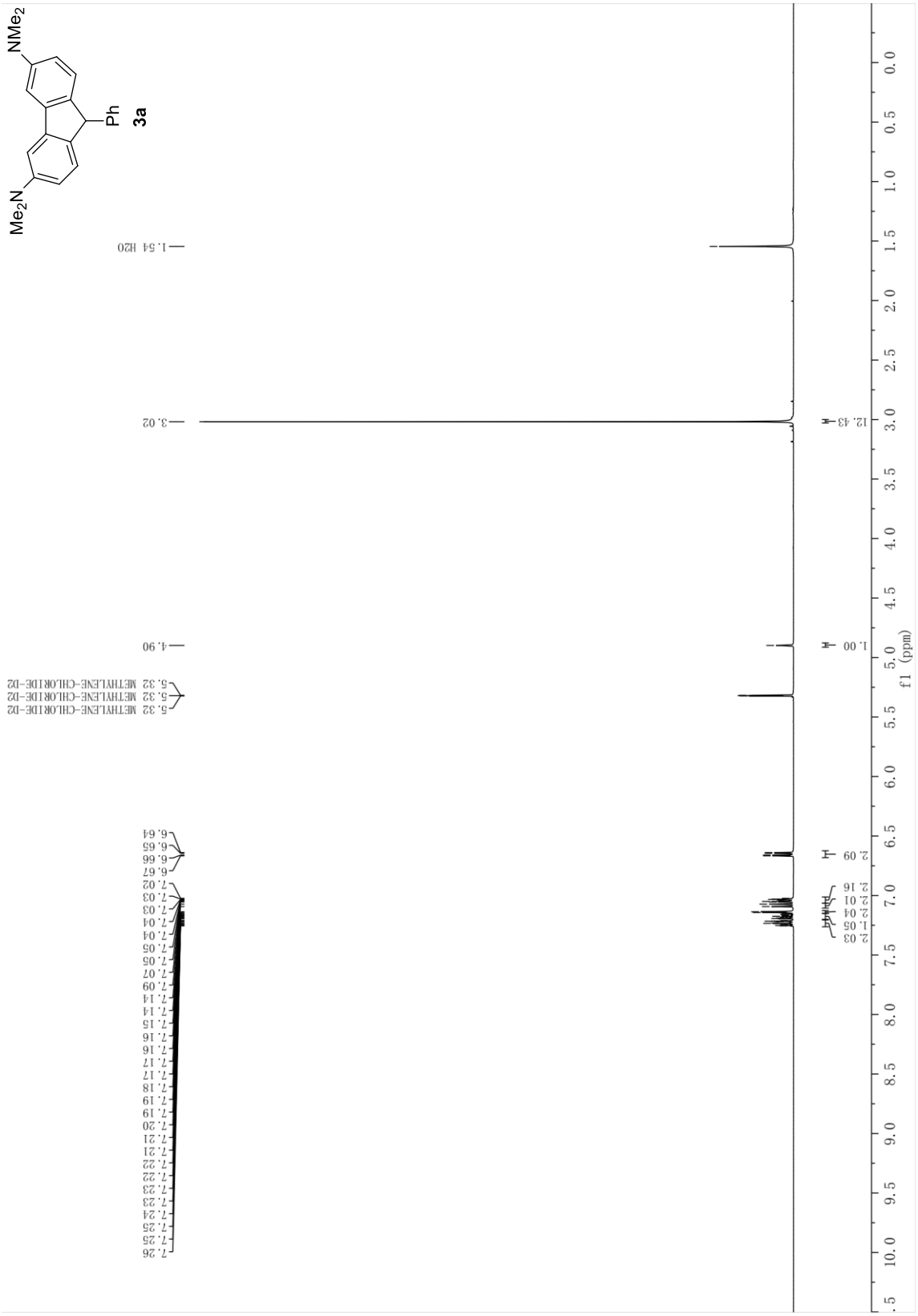


Figure S28. ^{1}H NMR (400 MHz, CD_2Cl_2): **3a**

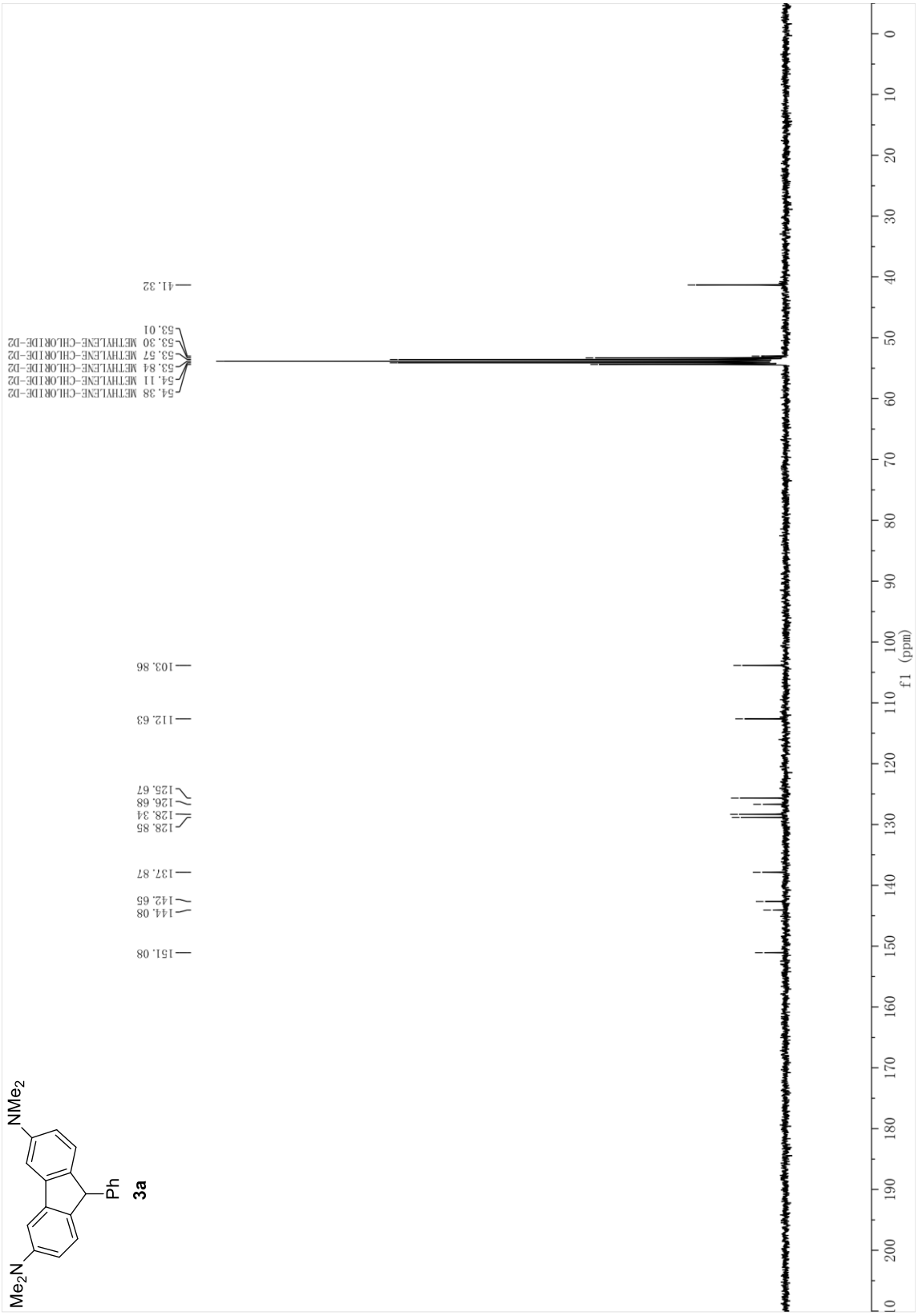


Figure S29. ^{13}C NMR (100 MHz, CD_2Cl_2): **3a**

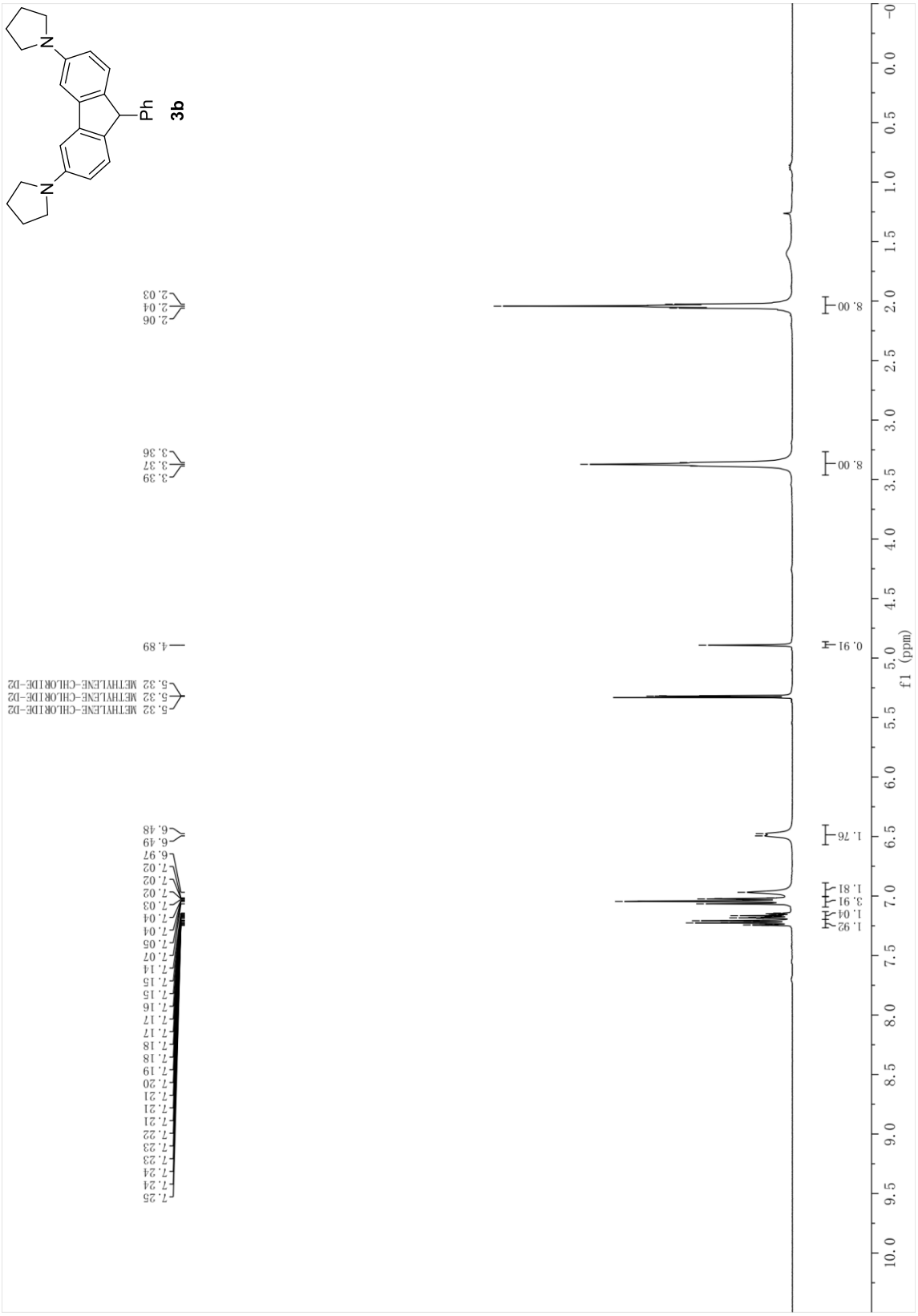


Figure S30. ^{1}H NMR (CD_2Cl_2, 400 MHz): **3b**

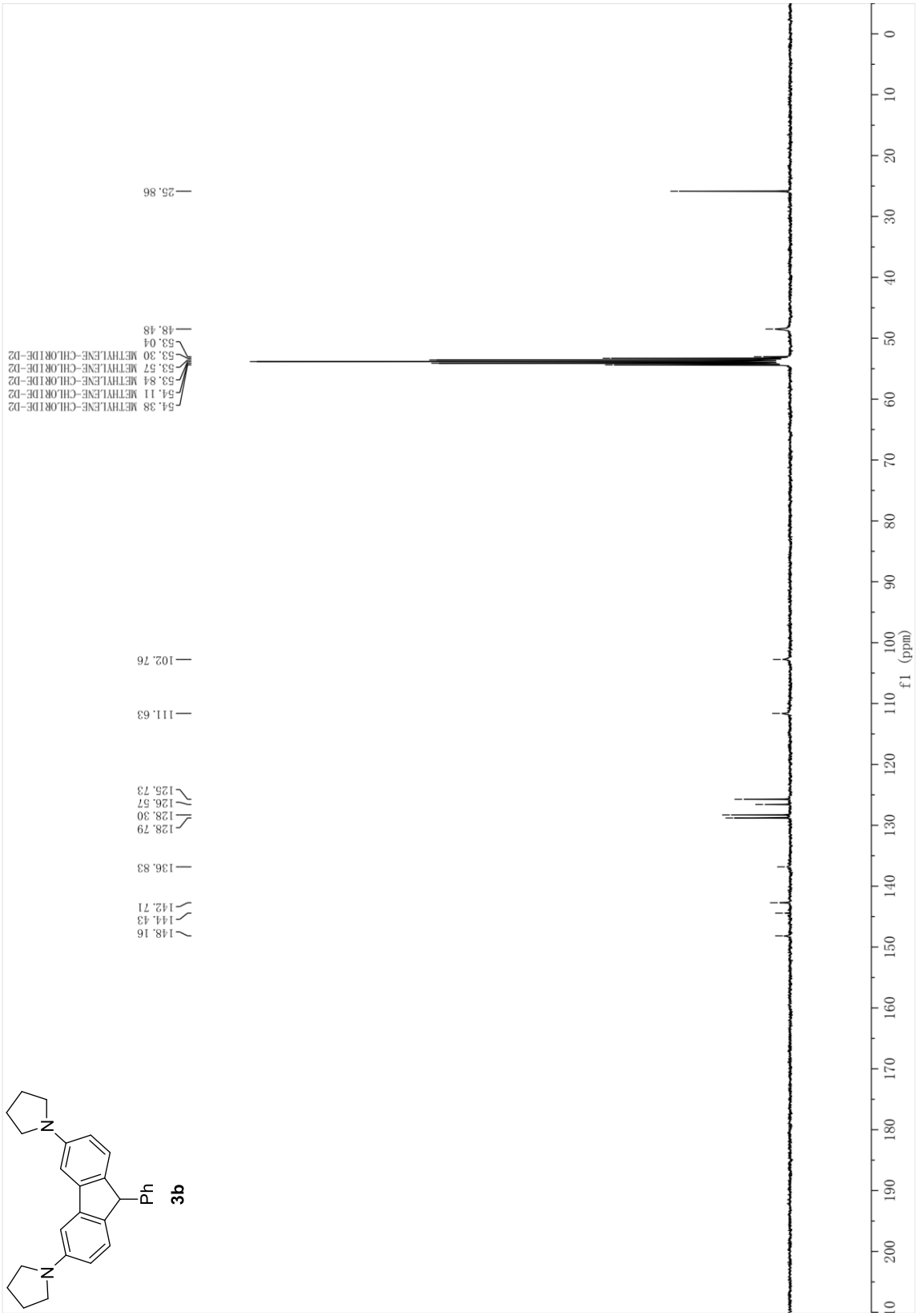


Figure S31. ^{13}C NMR (CD_2Cl_2, 100 MHz): **3b**

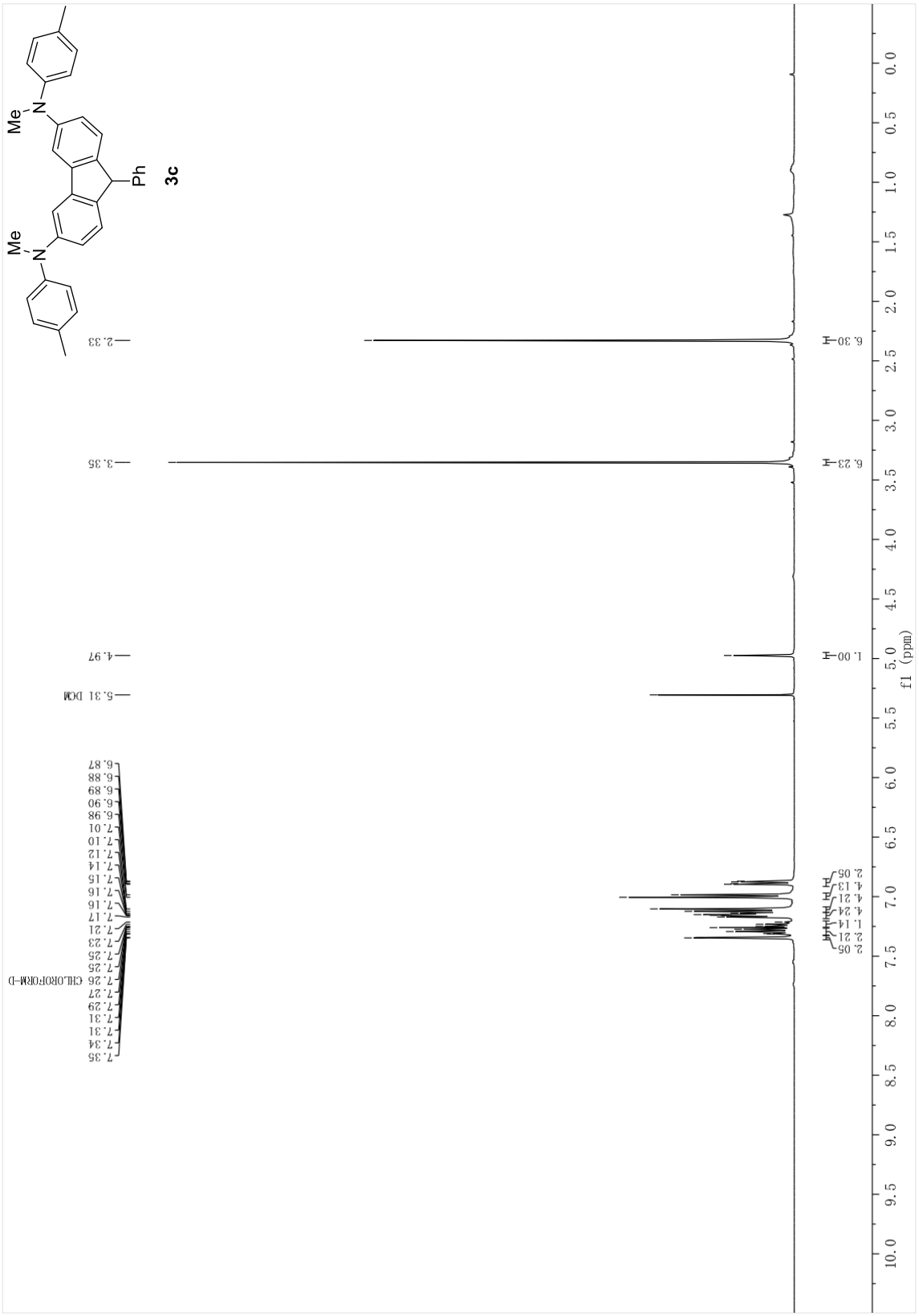


Figure S32. ^{1}H NMR ($CDCl_3$, 400 MHz): **3c**

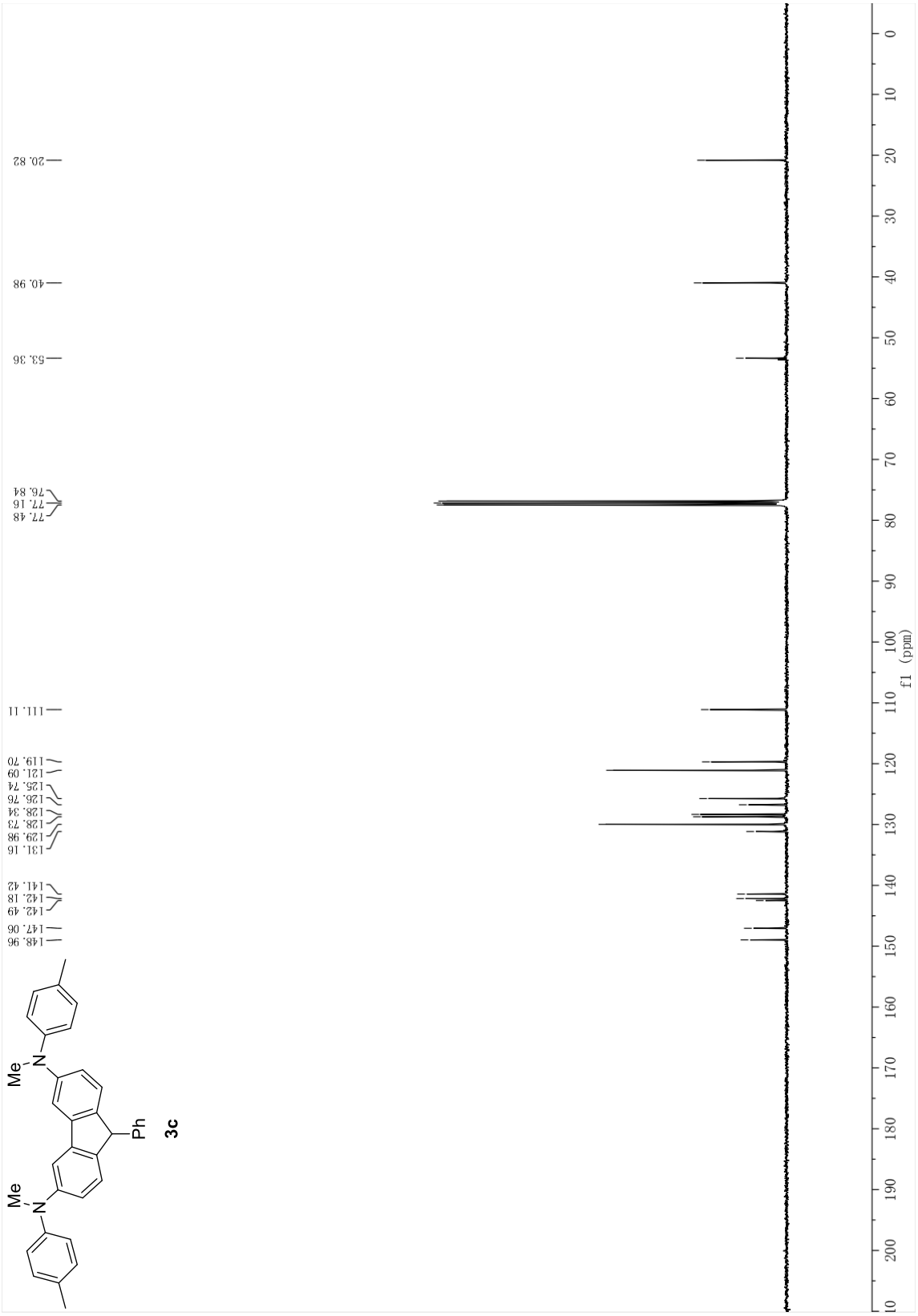


Figure S33. ^{13}C NMR ($CDCl_3$, 100 MHz): **3c**

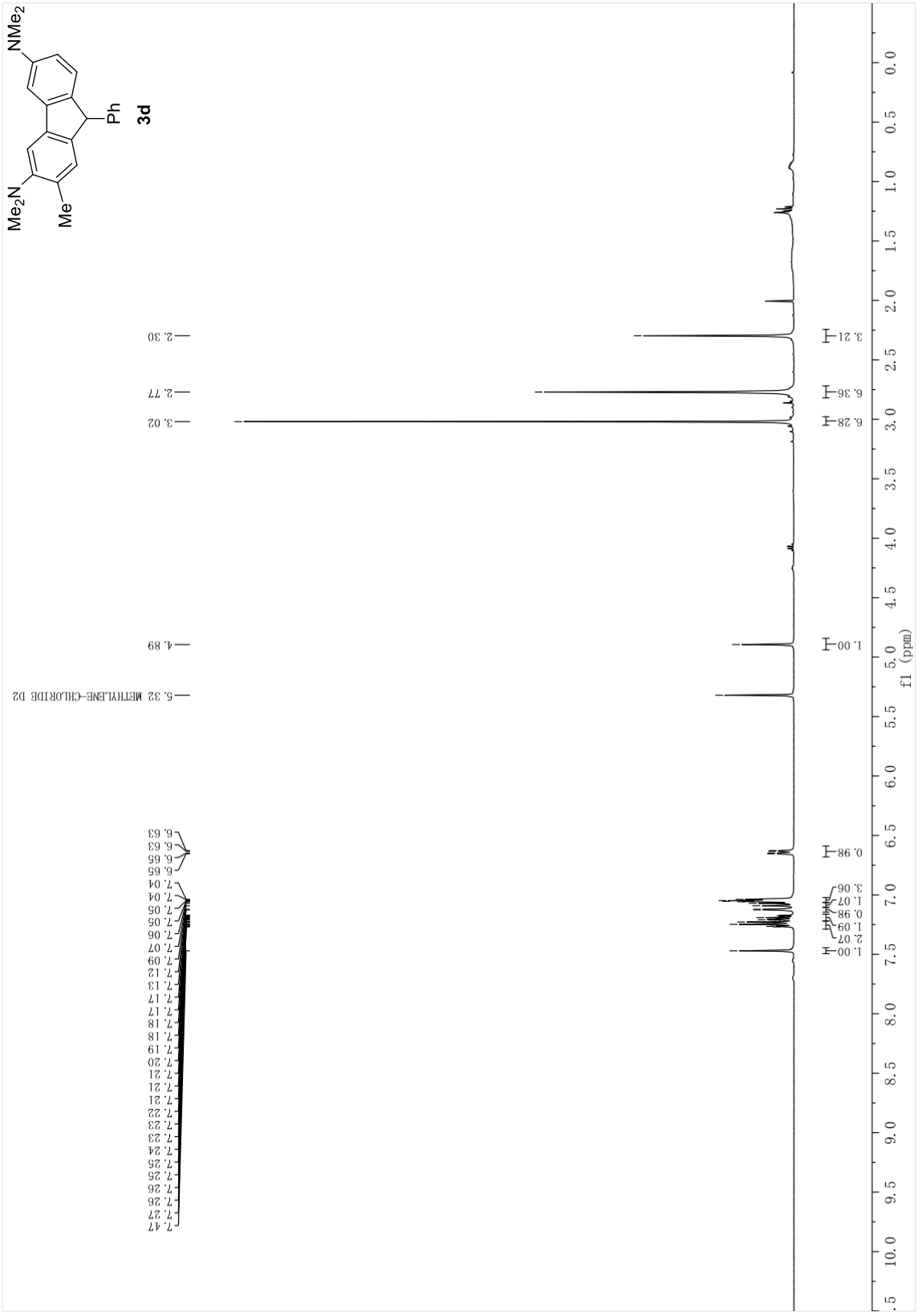


Figure S34. ^{1}H NMR (CD_2Cl_2, 400 MHz): **3d**

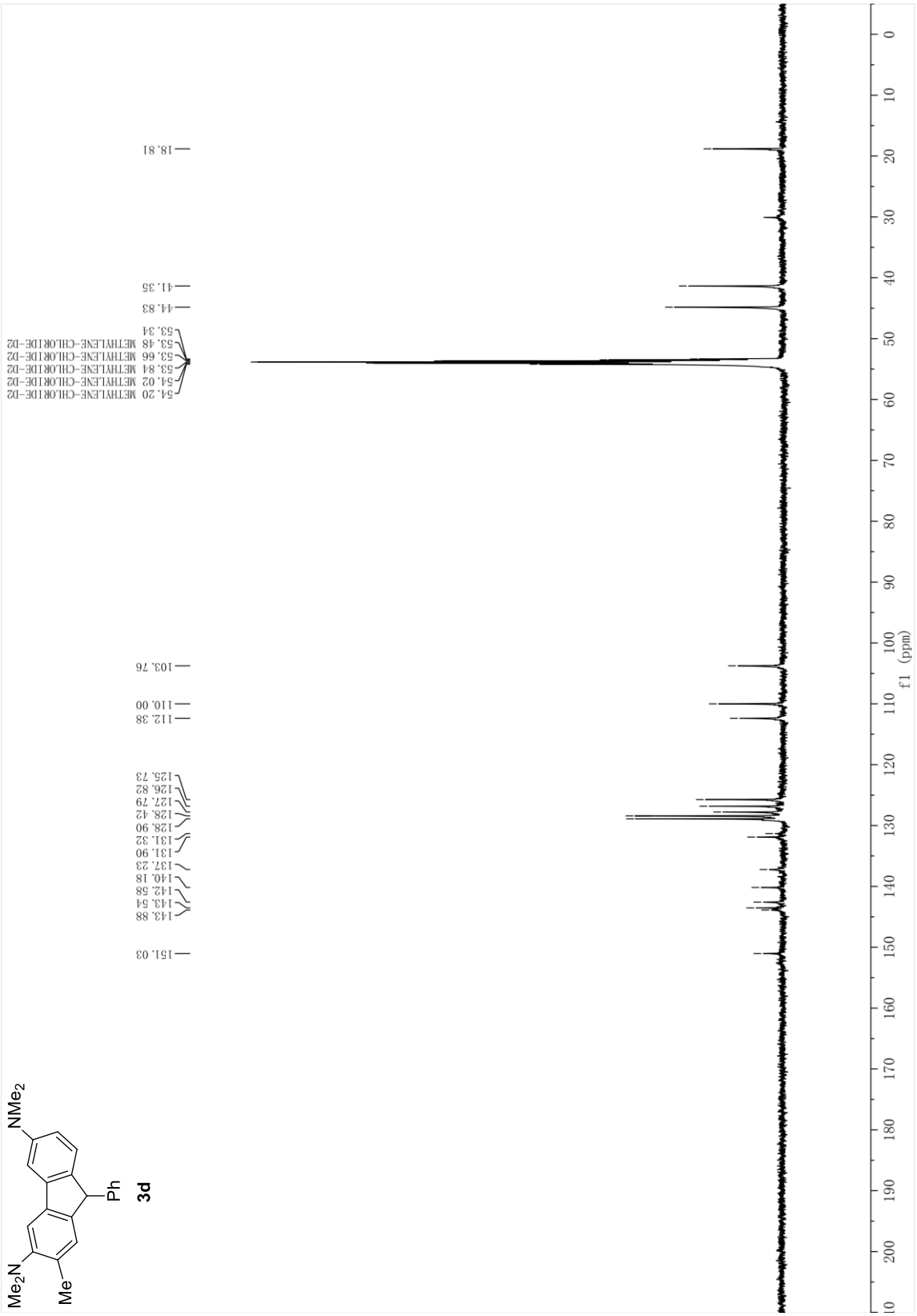


Figure S35. ^{13}C NMR (150 MHz, CD_2Cl_2): **3d**

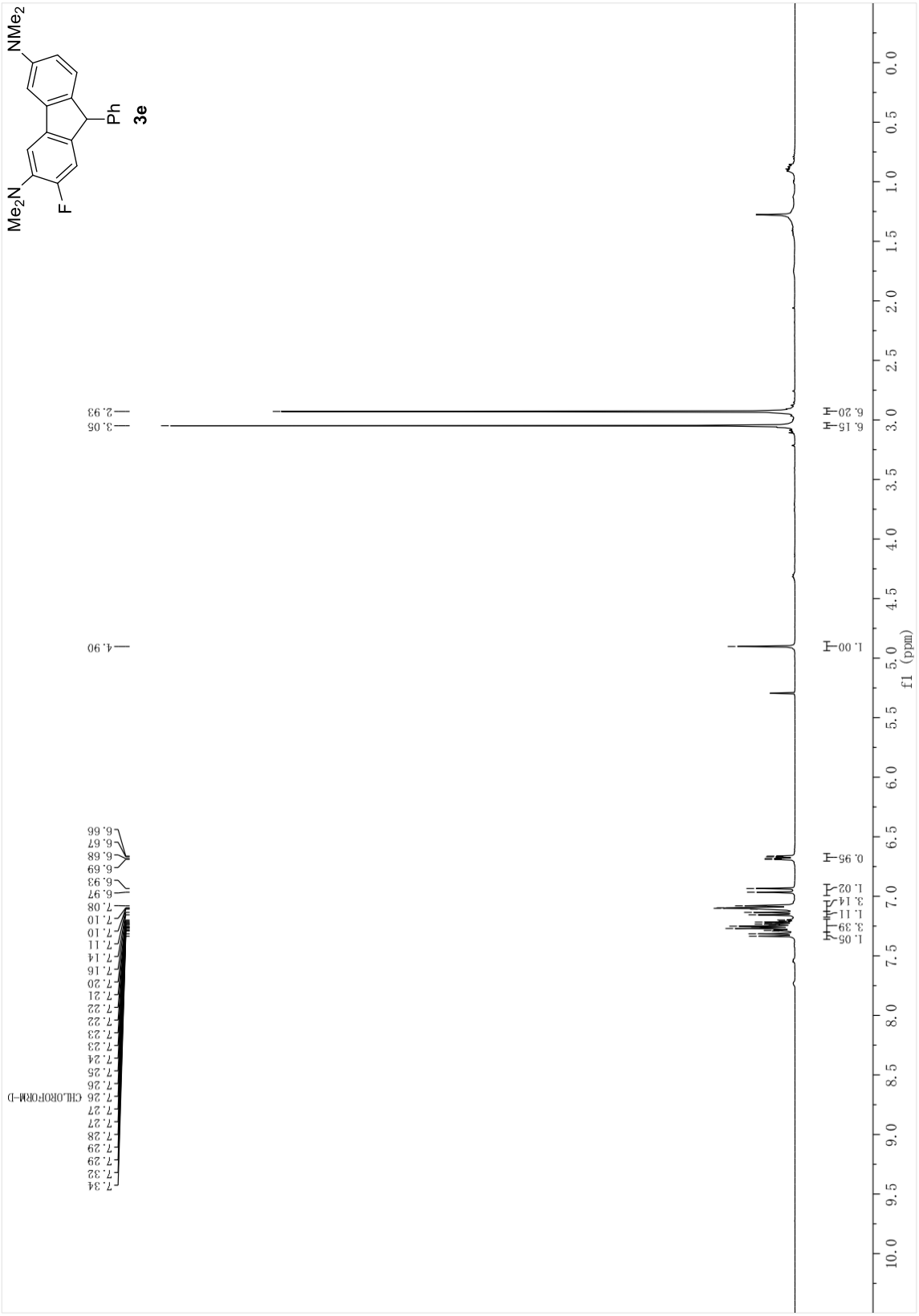


Figure S36. ^{1}H NMR ($CDCl_3$, 400 MHz): **3e**

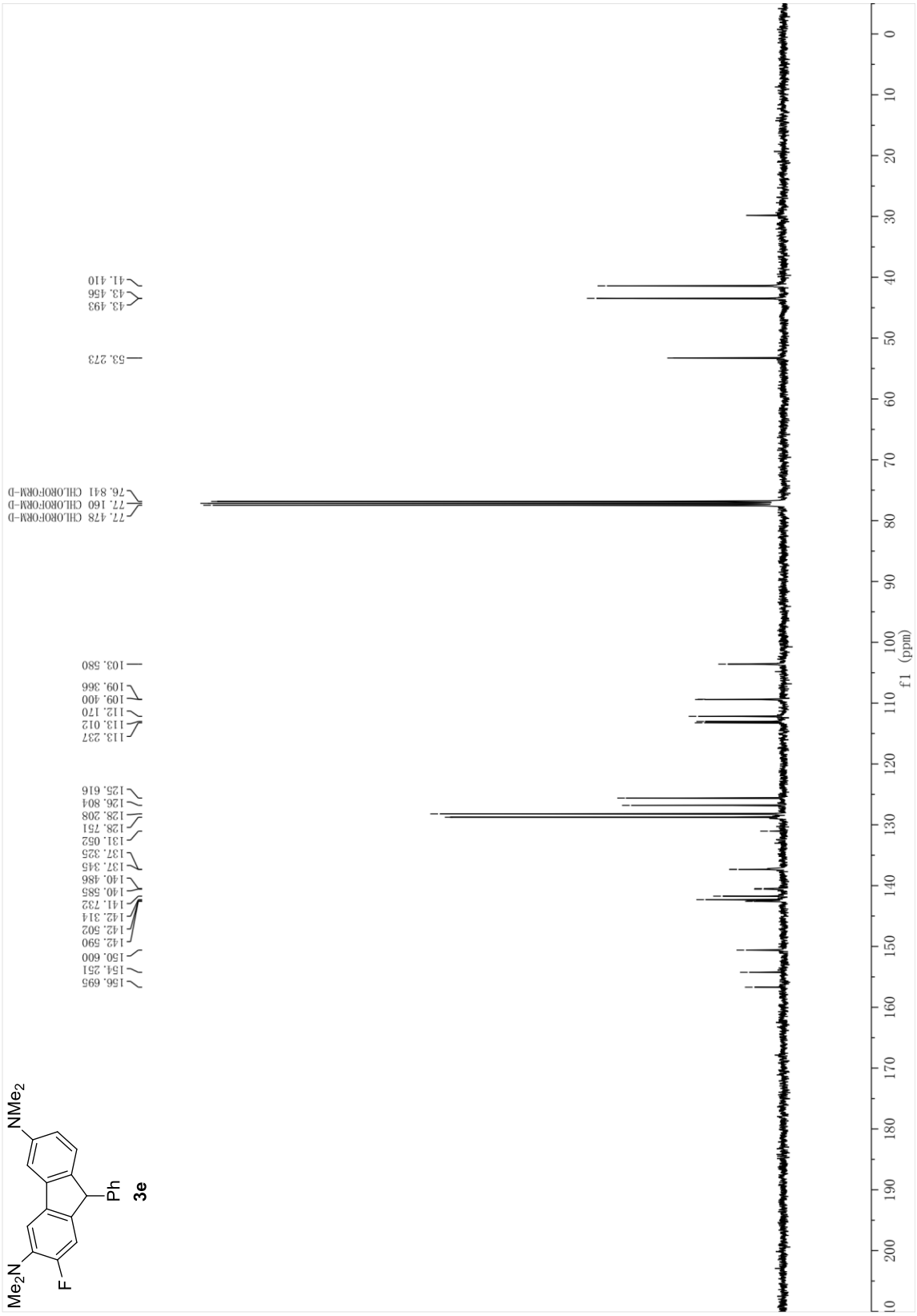


Figure S37. ^{13}C NMR ($CDCl_3$, 100 MHz): **3e**

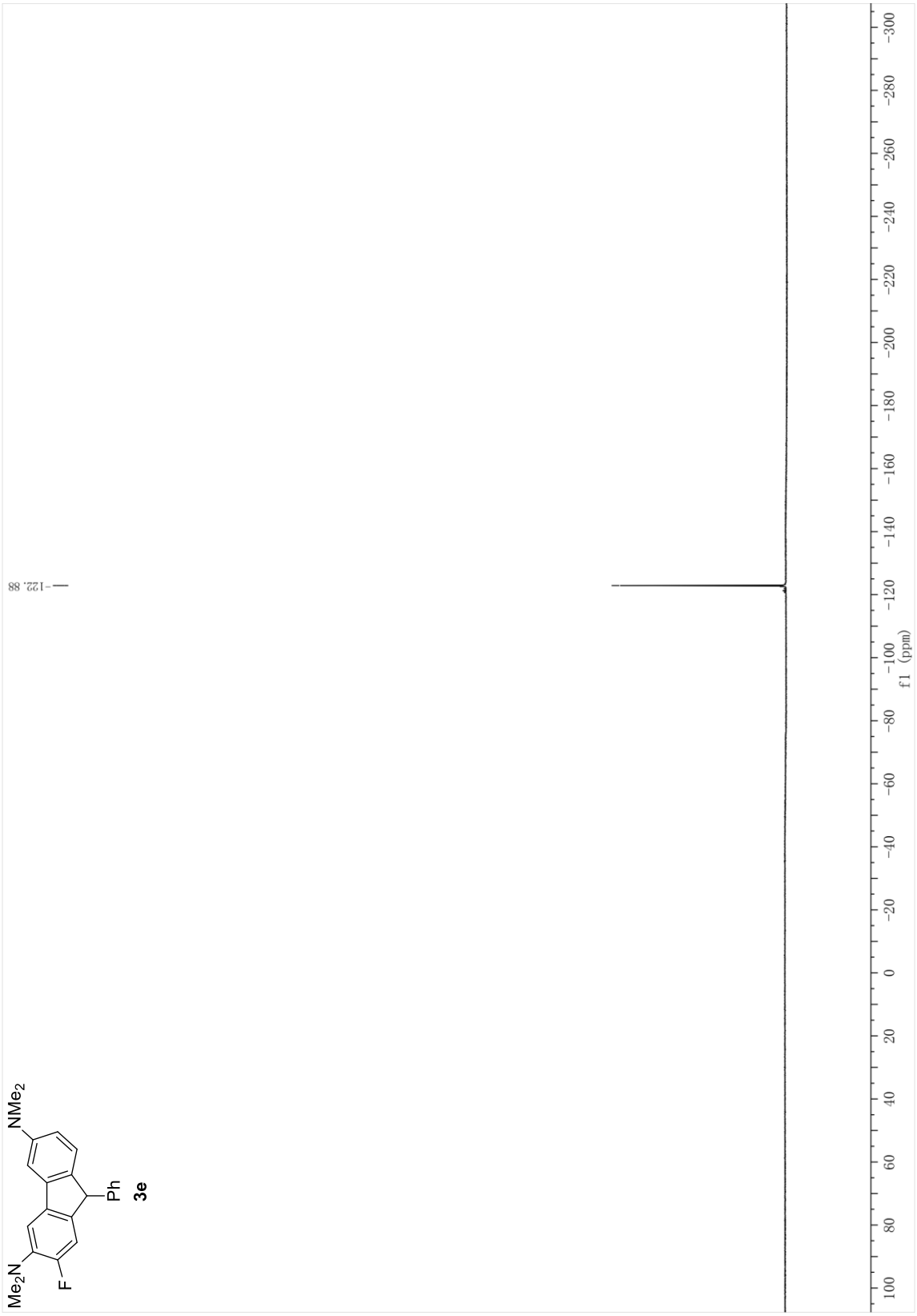


Figure S38. ^{19}F NMR (378 MHz, $CDCl_3$): **3e**

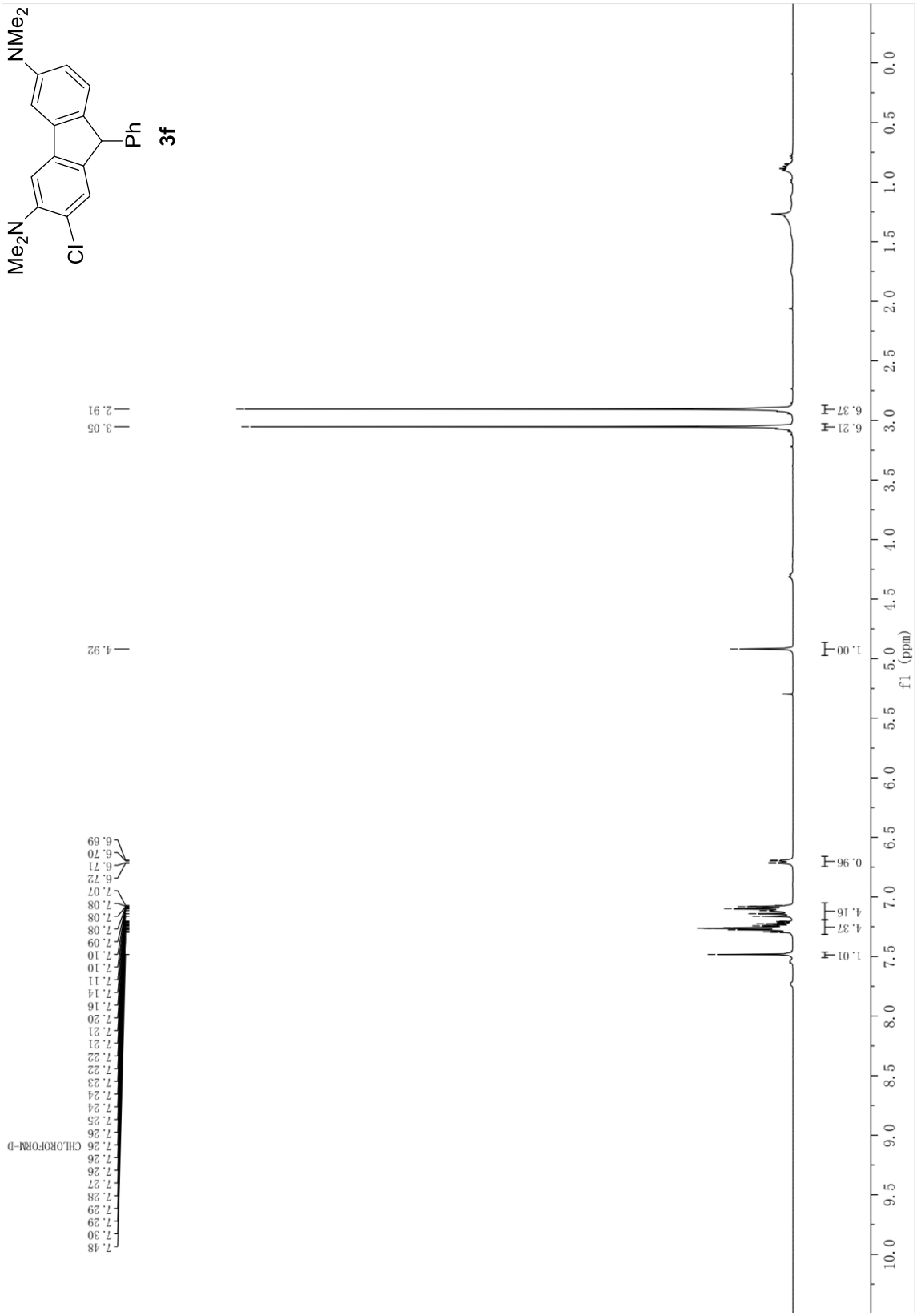


Figure S39. ^{1}H NMR ($CDCl_3$, 400 MHz): **3f**

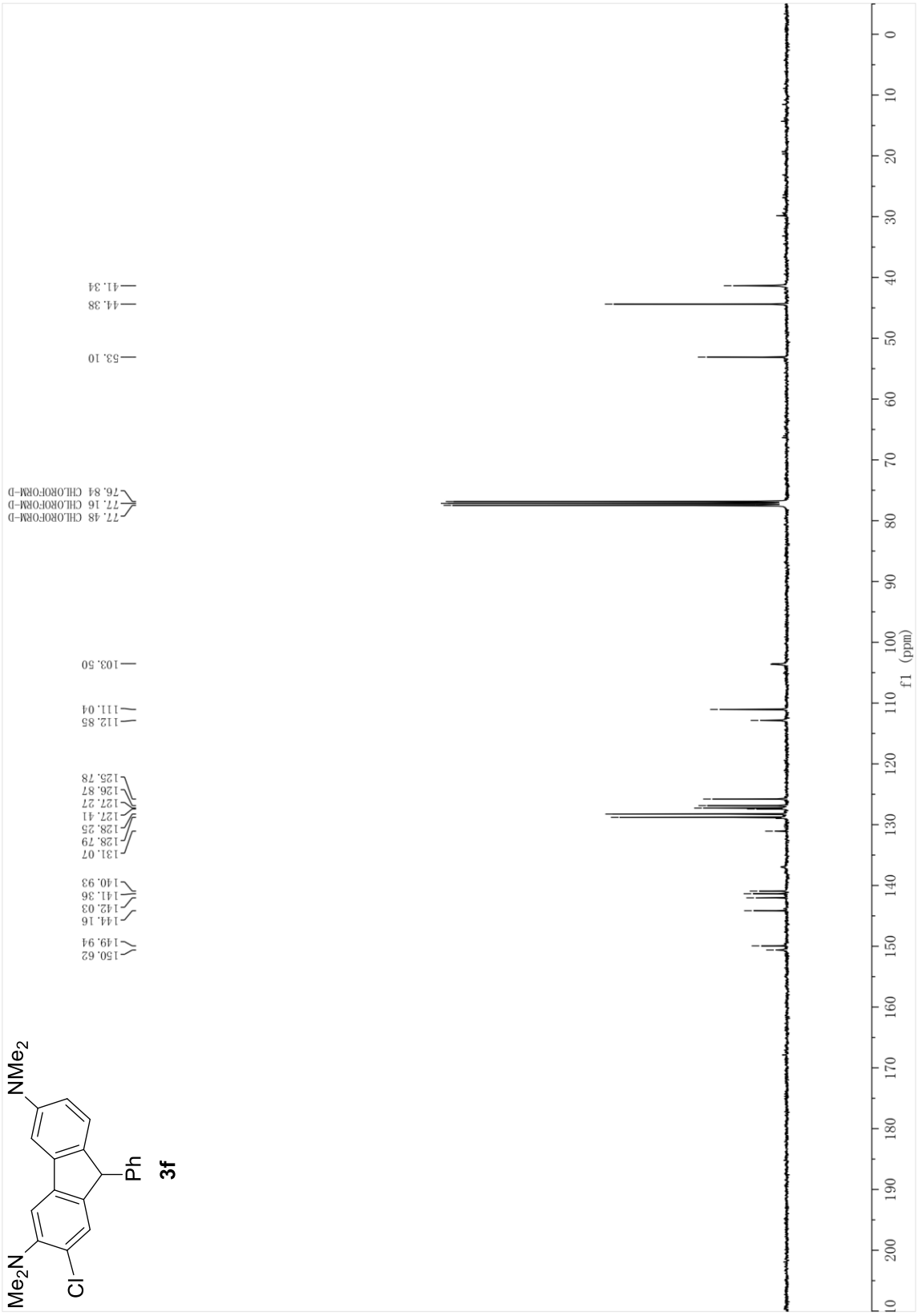


Figure S40. ^{13}C NMR ($CDCl_3$, 100 MHz): **3f**

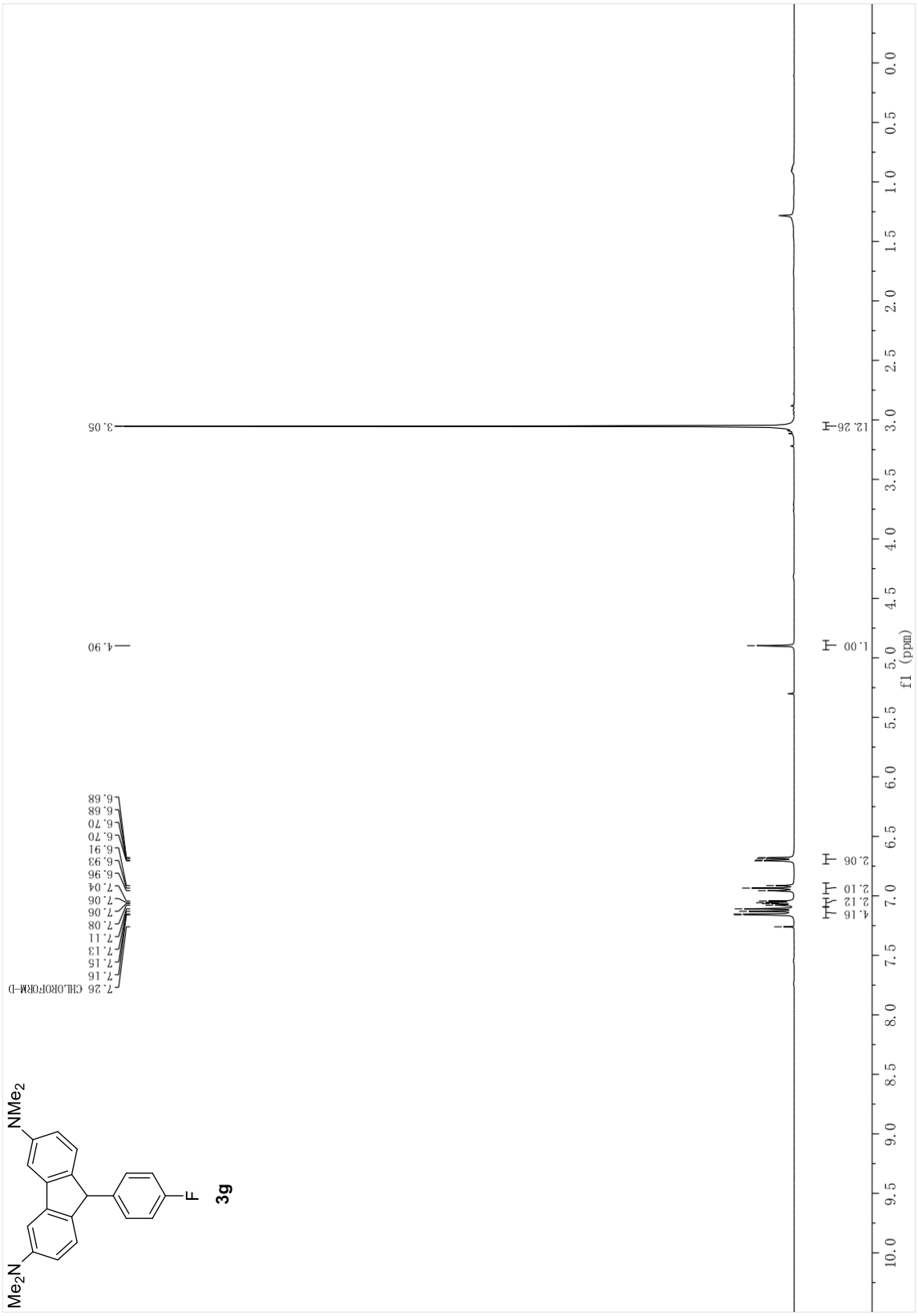


Figure S41. ^{1}H NMR ($CDCl_3$, 400 MHz): **3g**

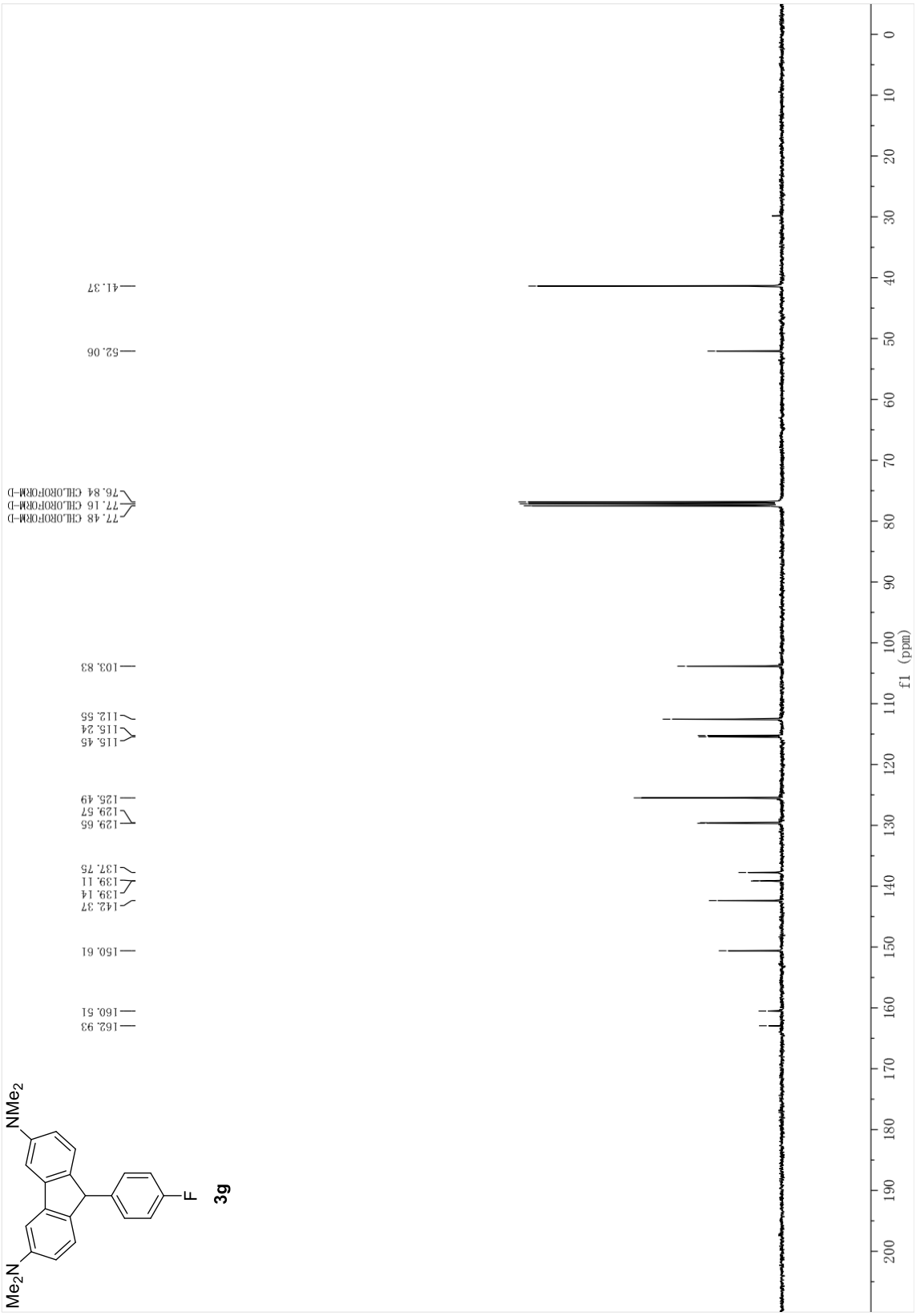


Figure S42. ^{13}C NMR (100 MHz, $CDCl_3$): **3g**

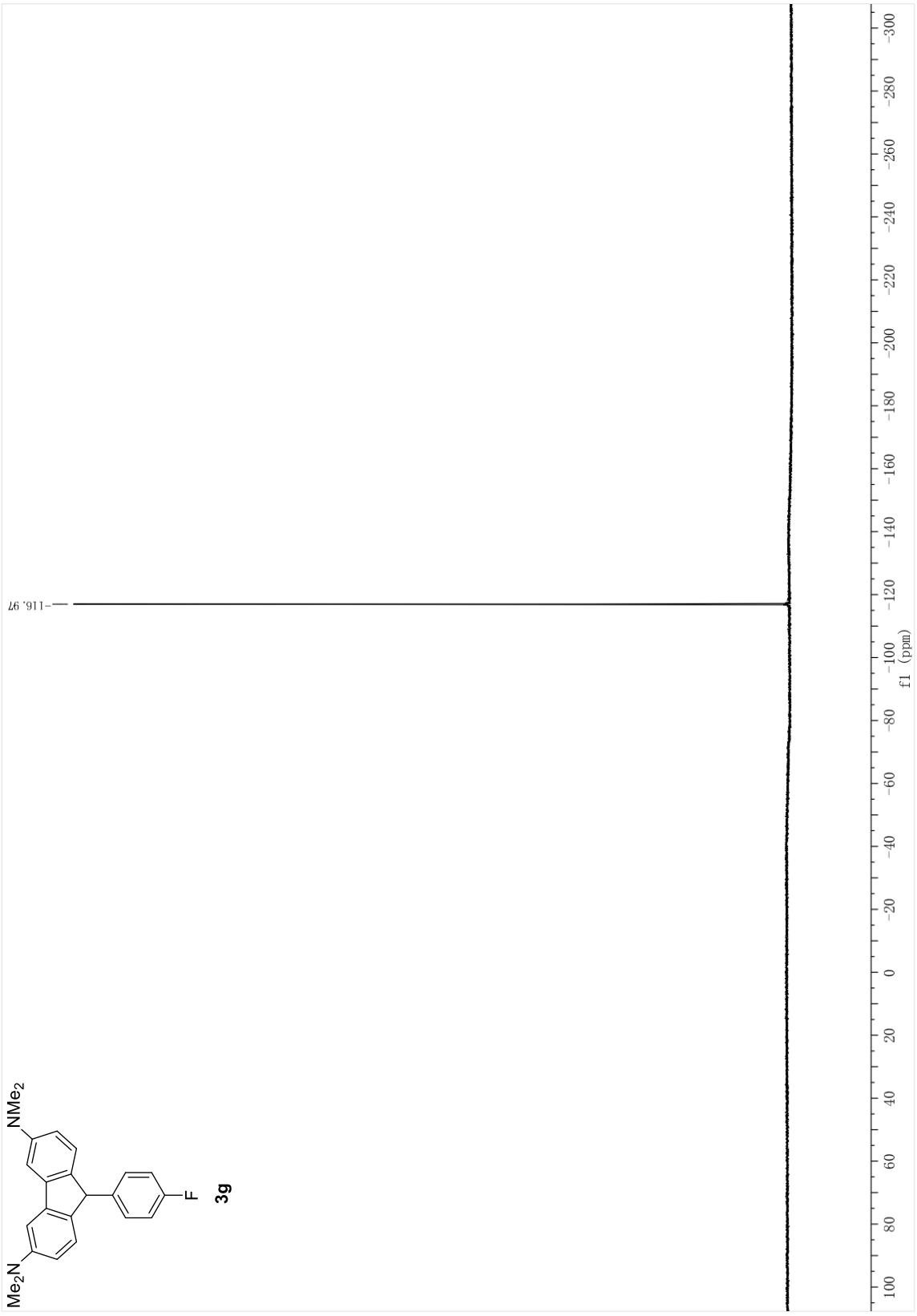


Figure S43. ^{19}F NMR (378 MHz, $CDCl_3$): **3g**

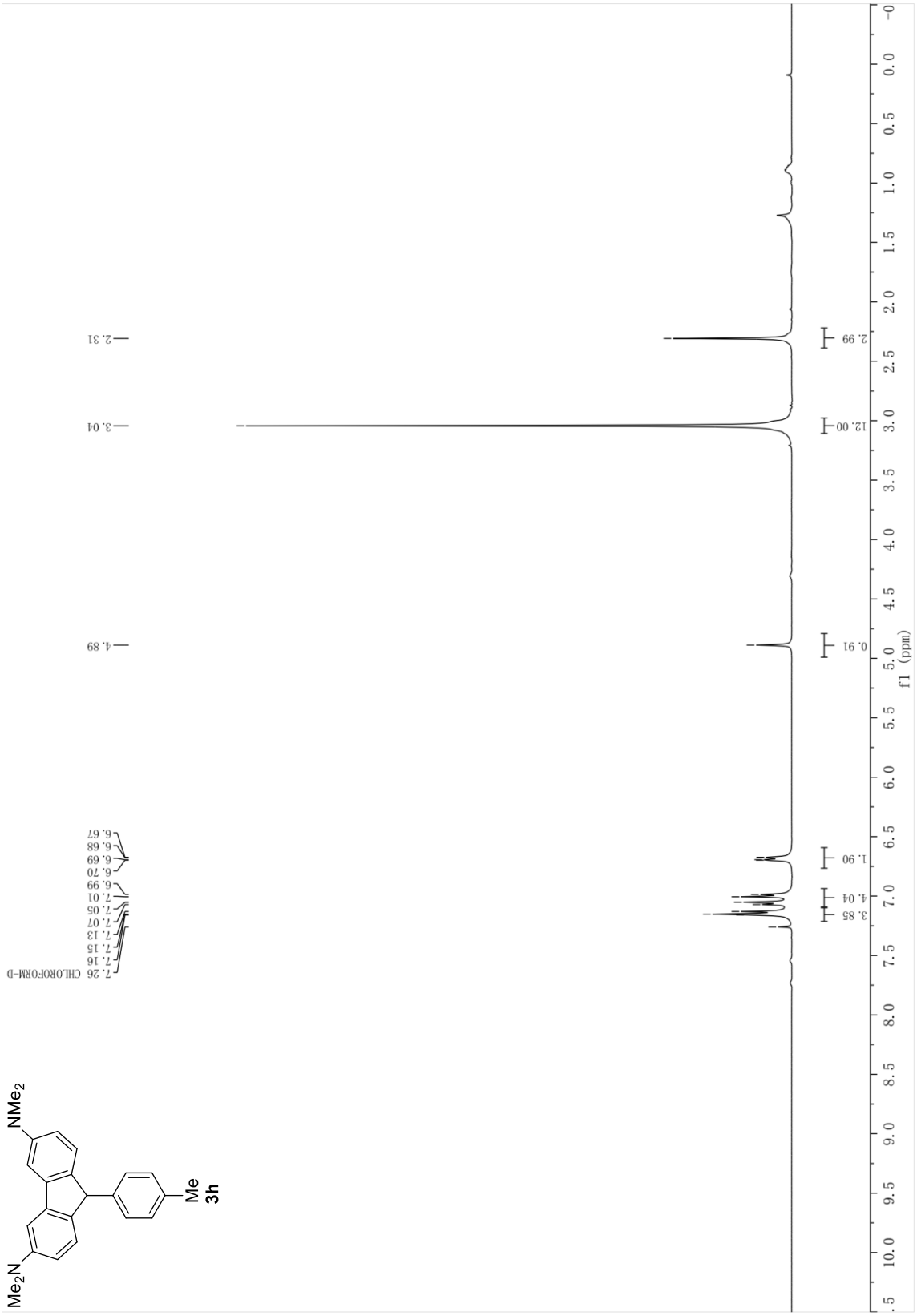


Figure S44. ^{1}H NMR ($CDCl_3$, 400 MHz): **3h**

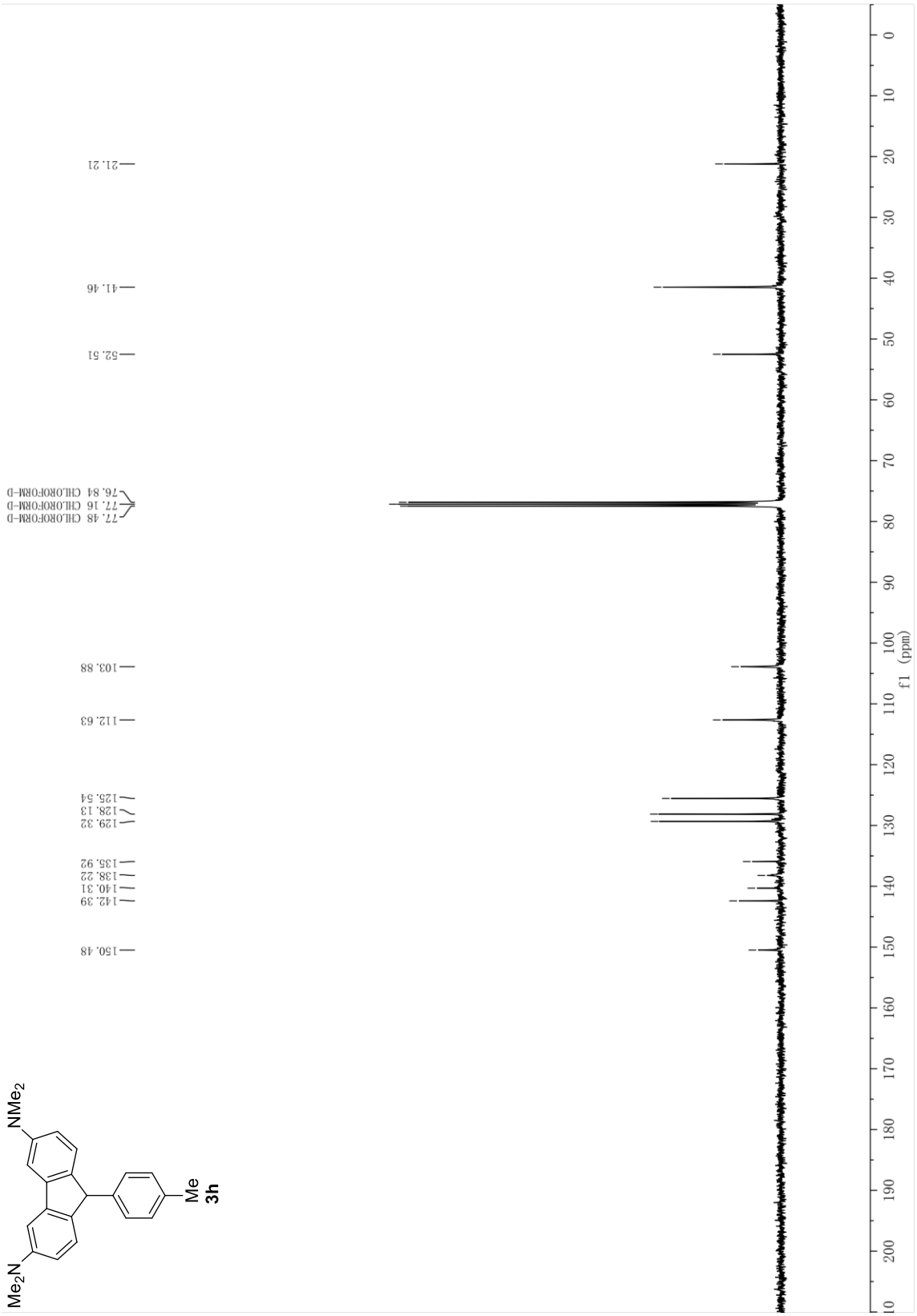


Figure S45. ^{13}C NMR ($CDCl_3$, 100 MHz): **3h**

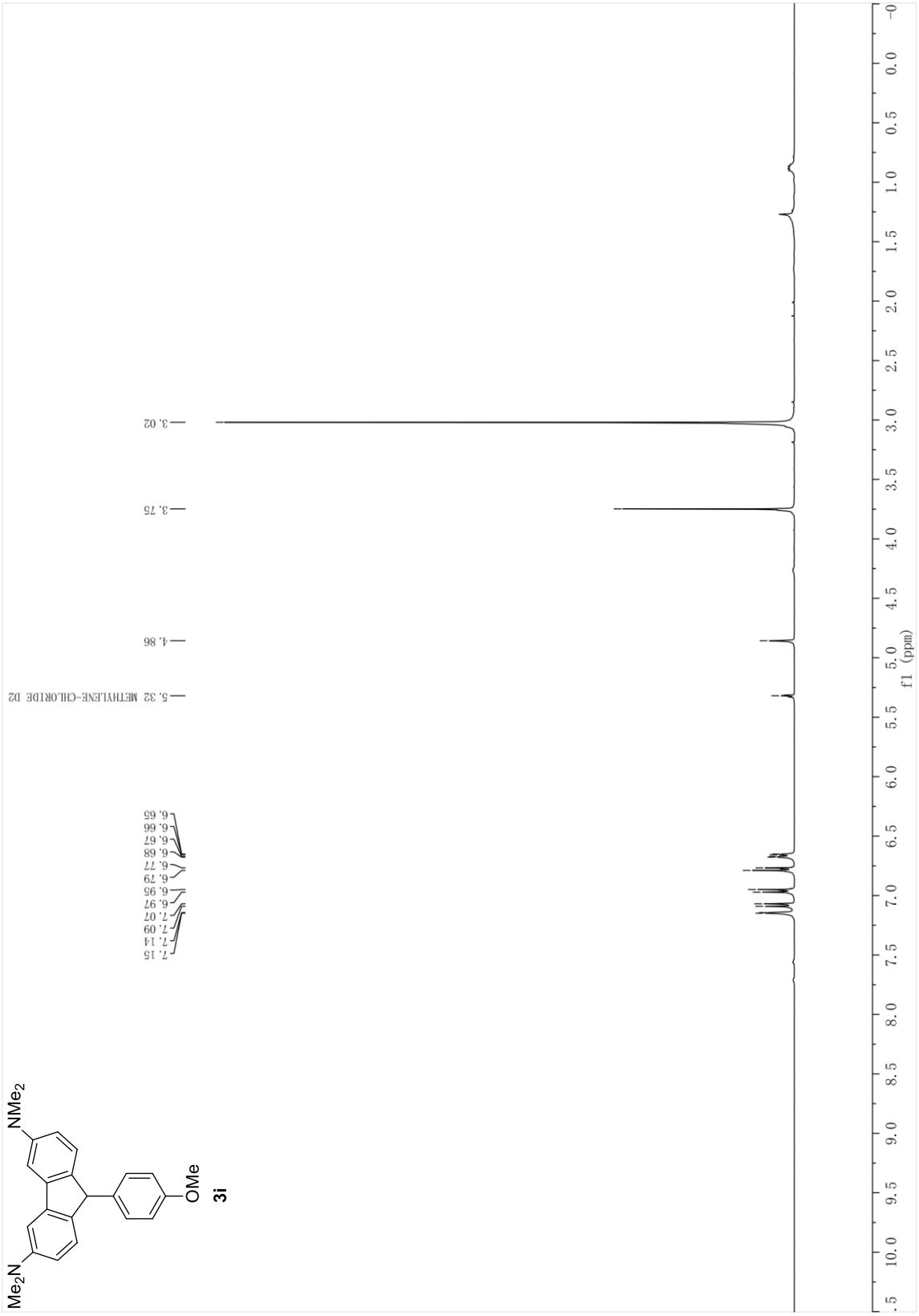


Figure S46. ^{1}H NMR (CD_2Cl_2, 400 MHz): **3i**

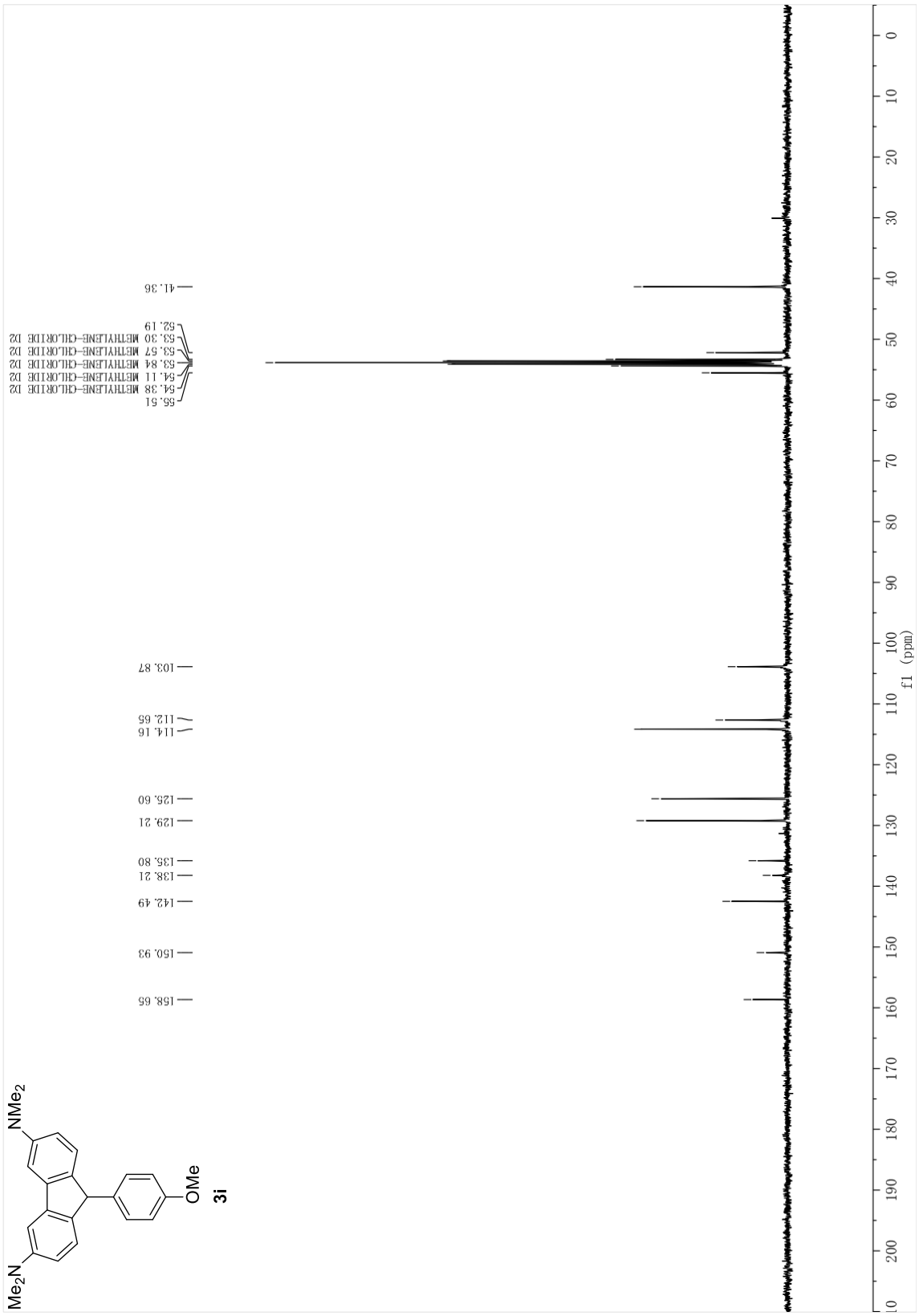


Figure S47. ^{13}C NMR (100 MHz, CD_2Cl_2): **3i**

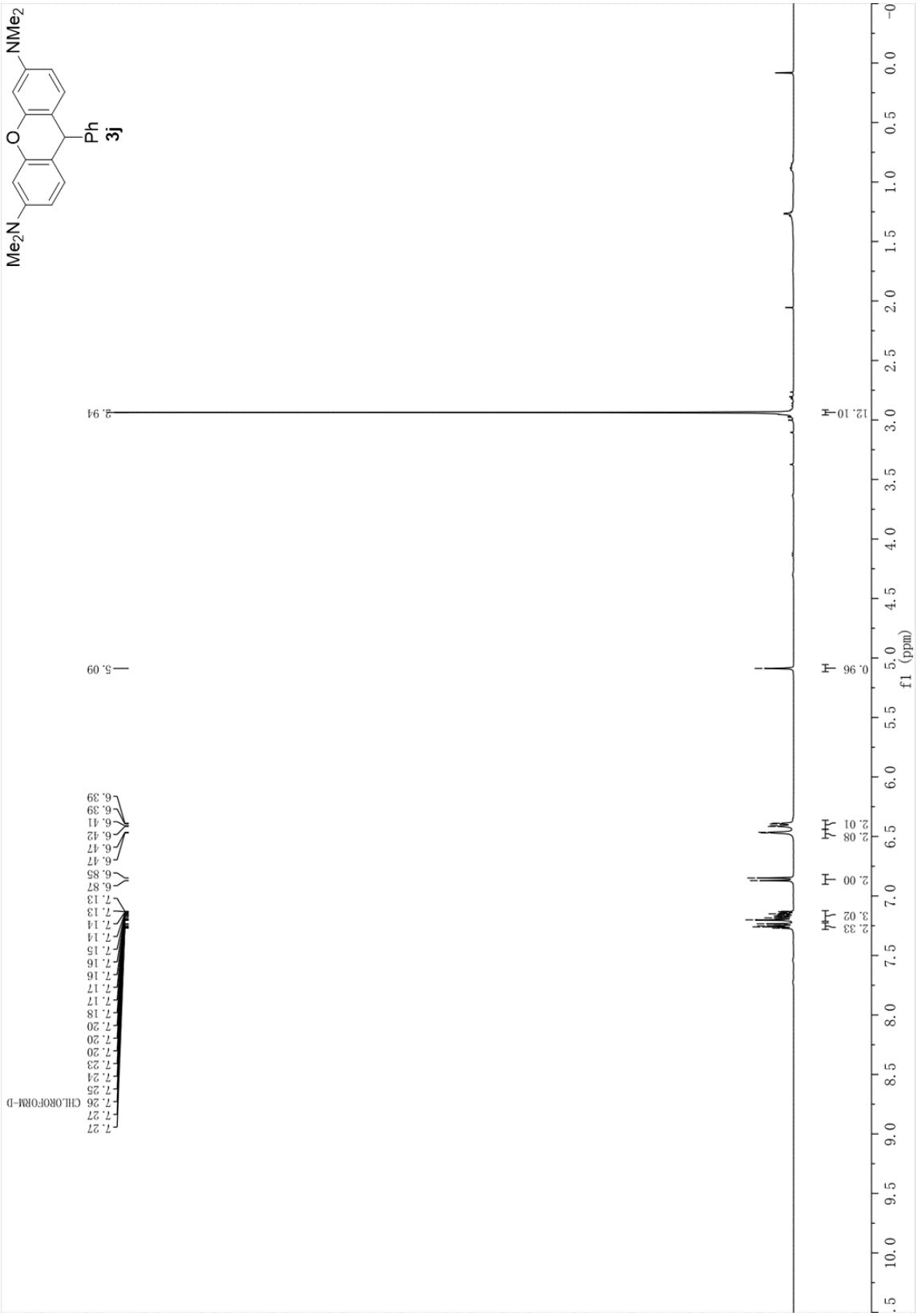


Figure S48. ^{1}H NMR ($CDCl_3$, 400 MHz): **3j**

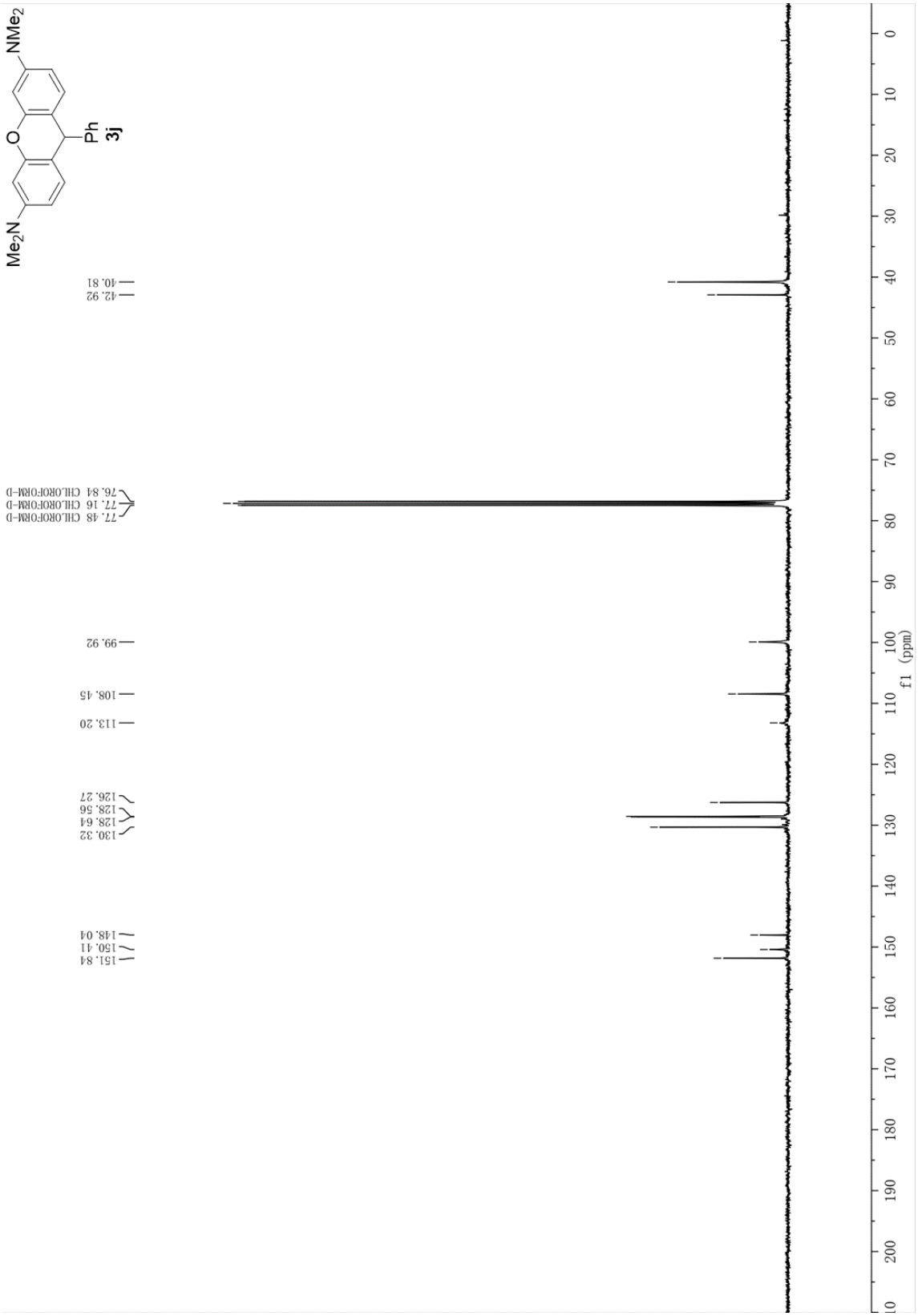


Figure S49. ^{13}C NMR (100 MHz, $CDCl_3$): **3j**

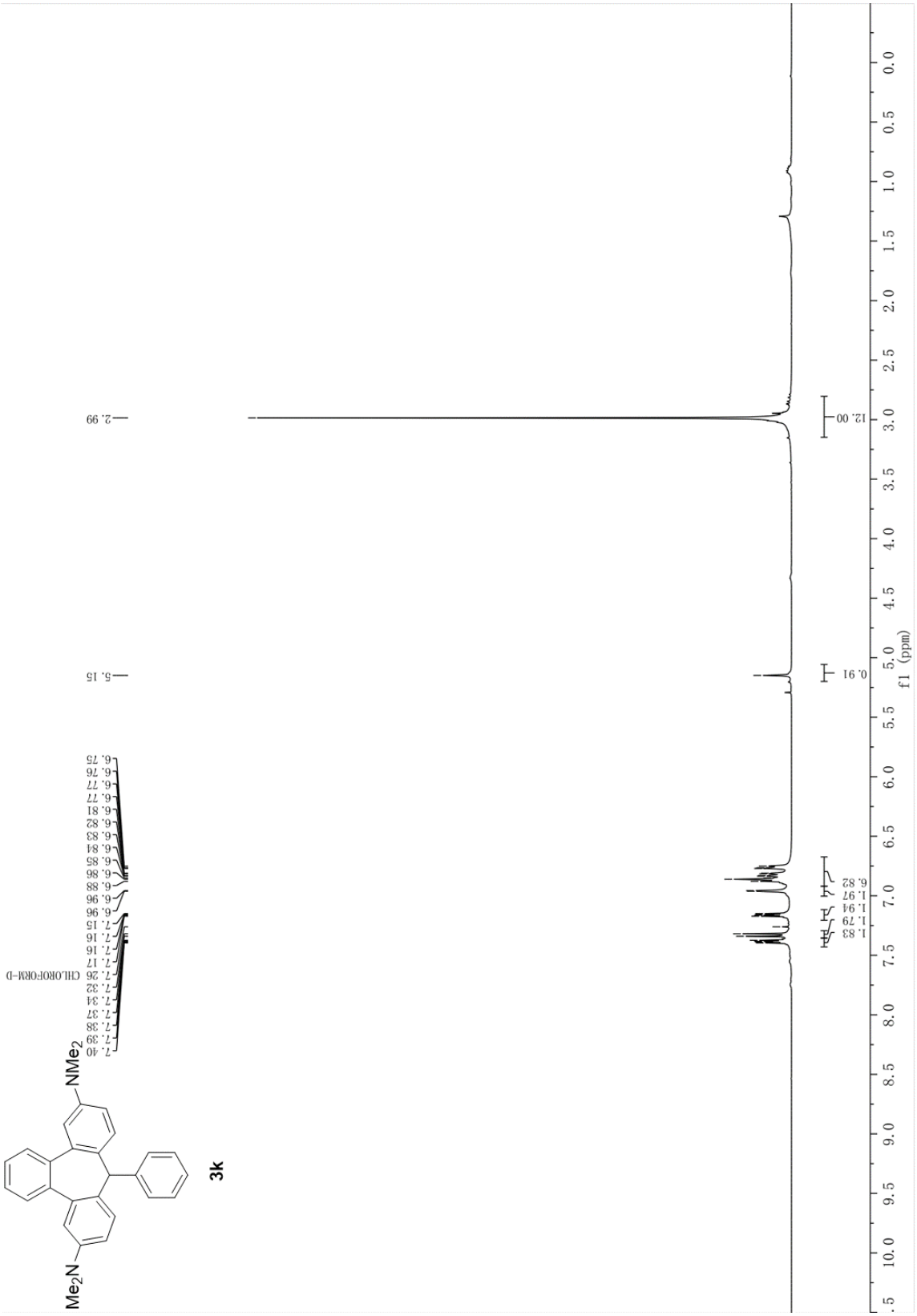


Figure S50. ^{1}H NMR ($CDCl_3$, 400 MHz): **3k**

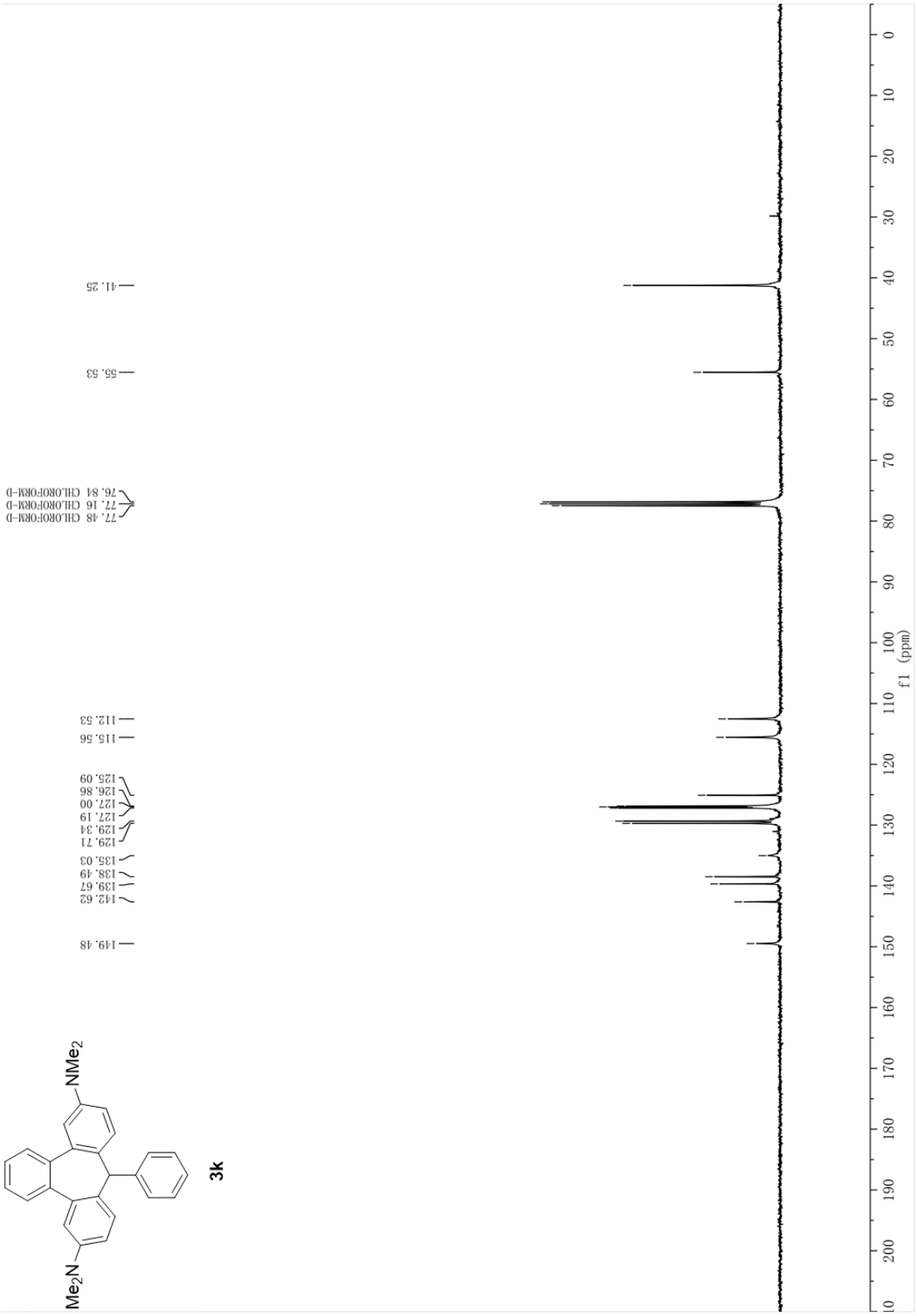


Figure S51. ^{13}C NMR ($CDCl_3$, 100 MHz): **3k**

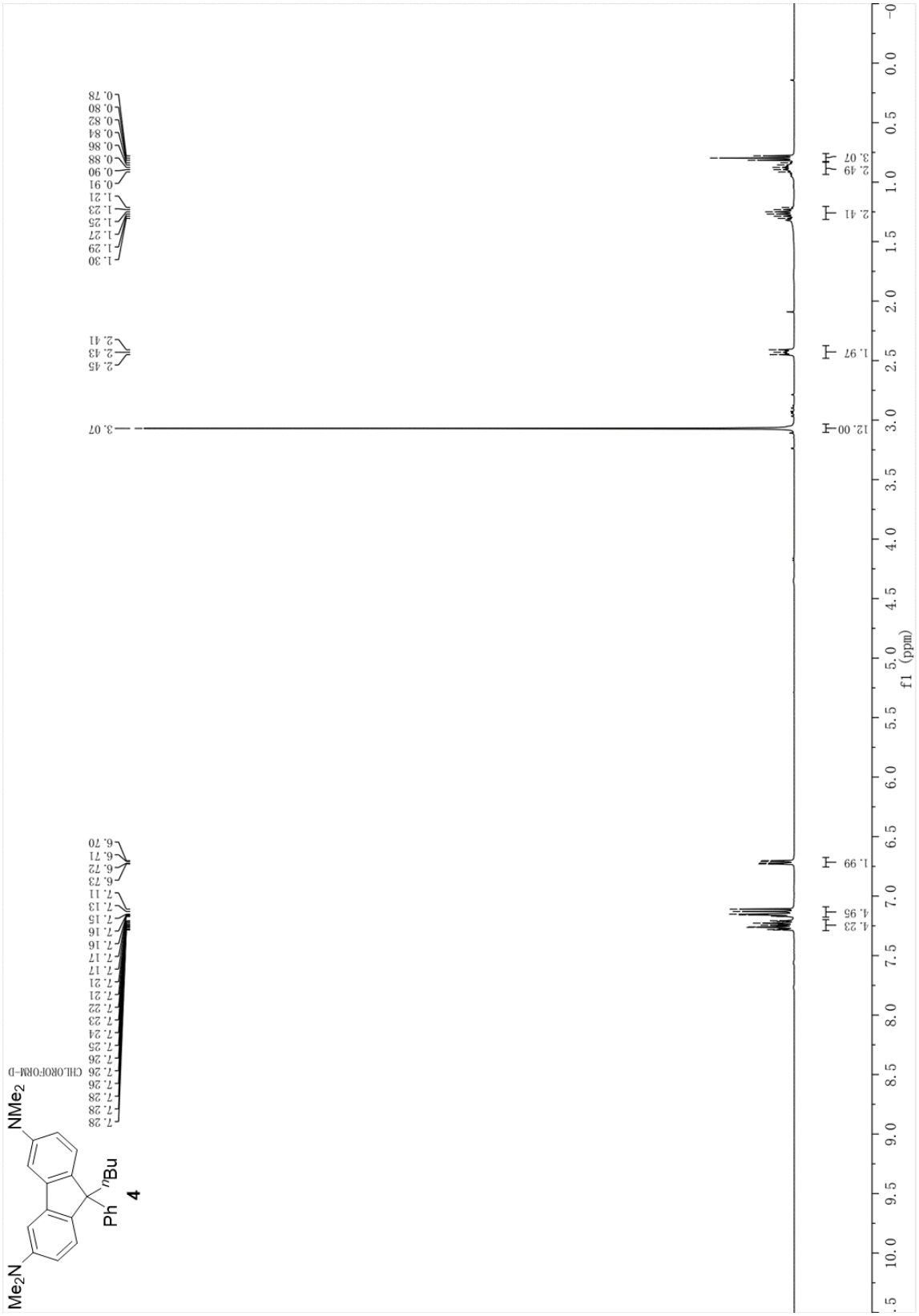


Figure S52. ^{1}H NMR ($CDCl_3$, 400 MHz): **4**

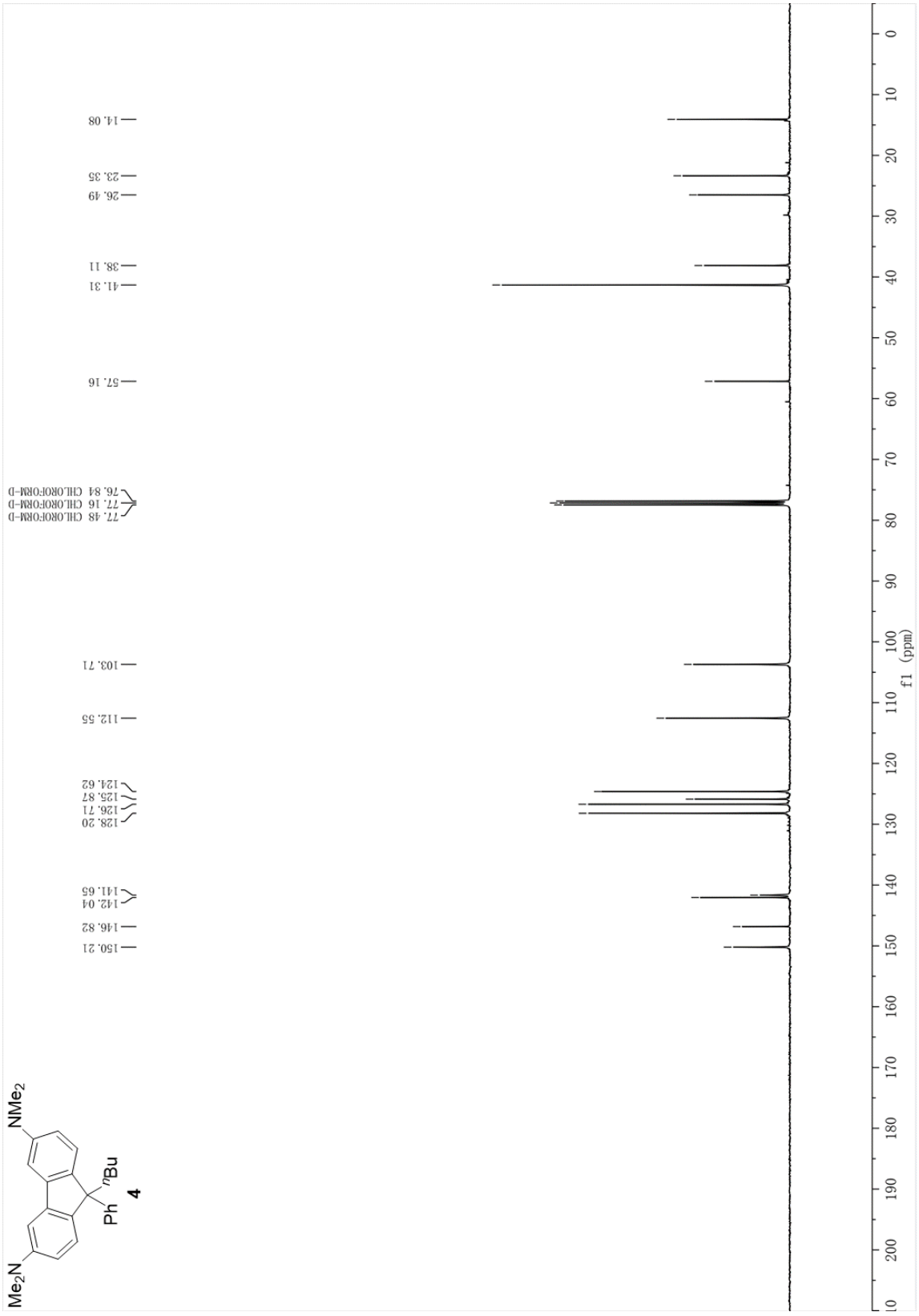


Figure S53. ^{13}C NMR ($CDCl_3$, 100 MHz): **4**

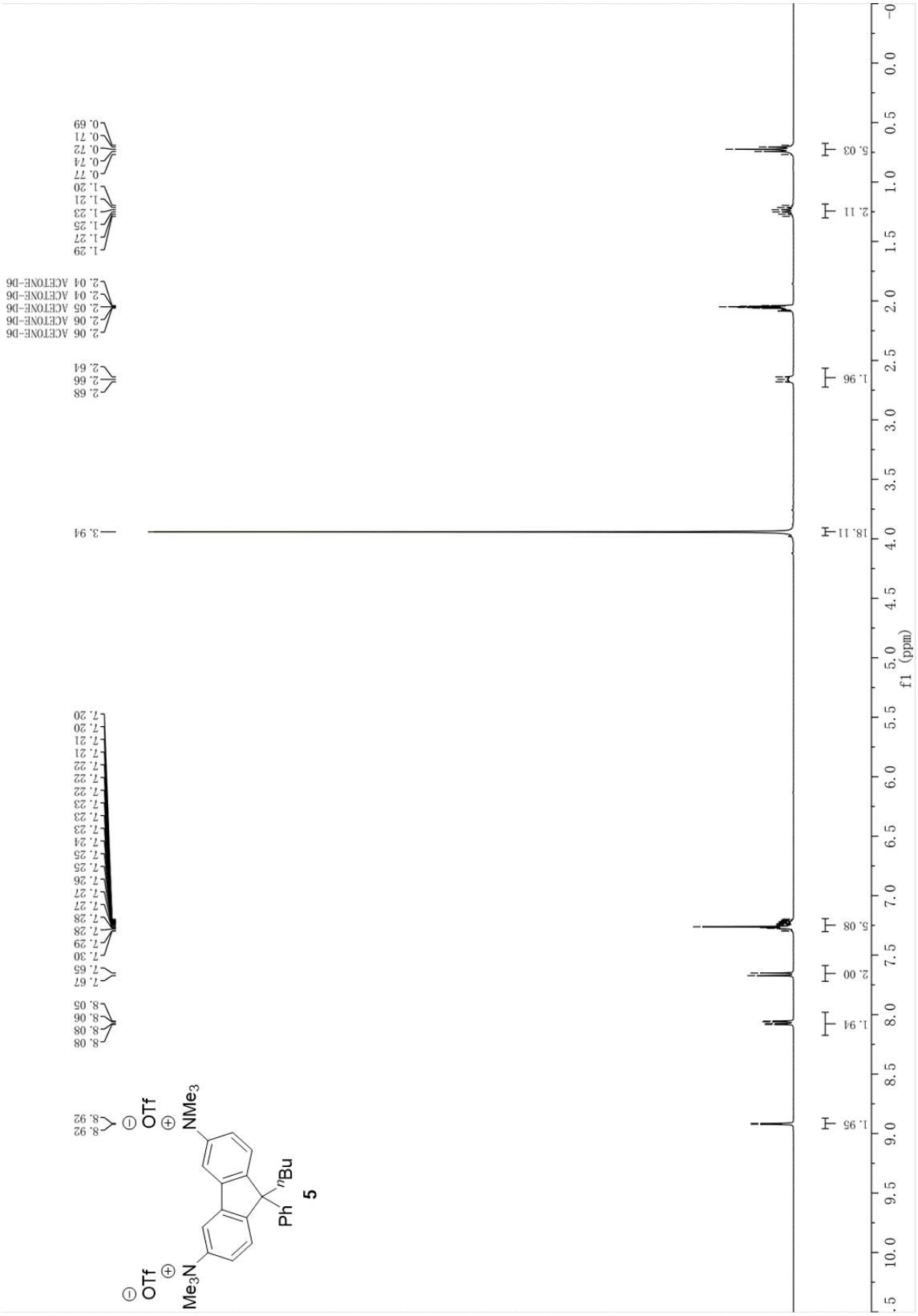


Figure S54. ^{1}H NMR (Acetone-d_6, 400 MHz): **5**

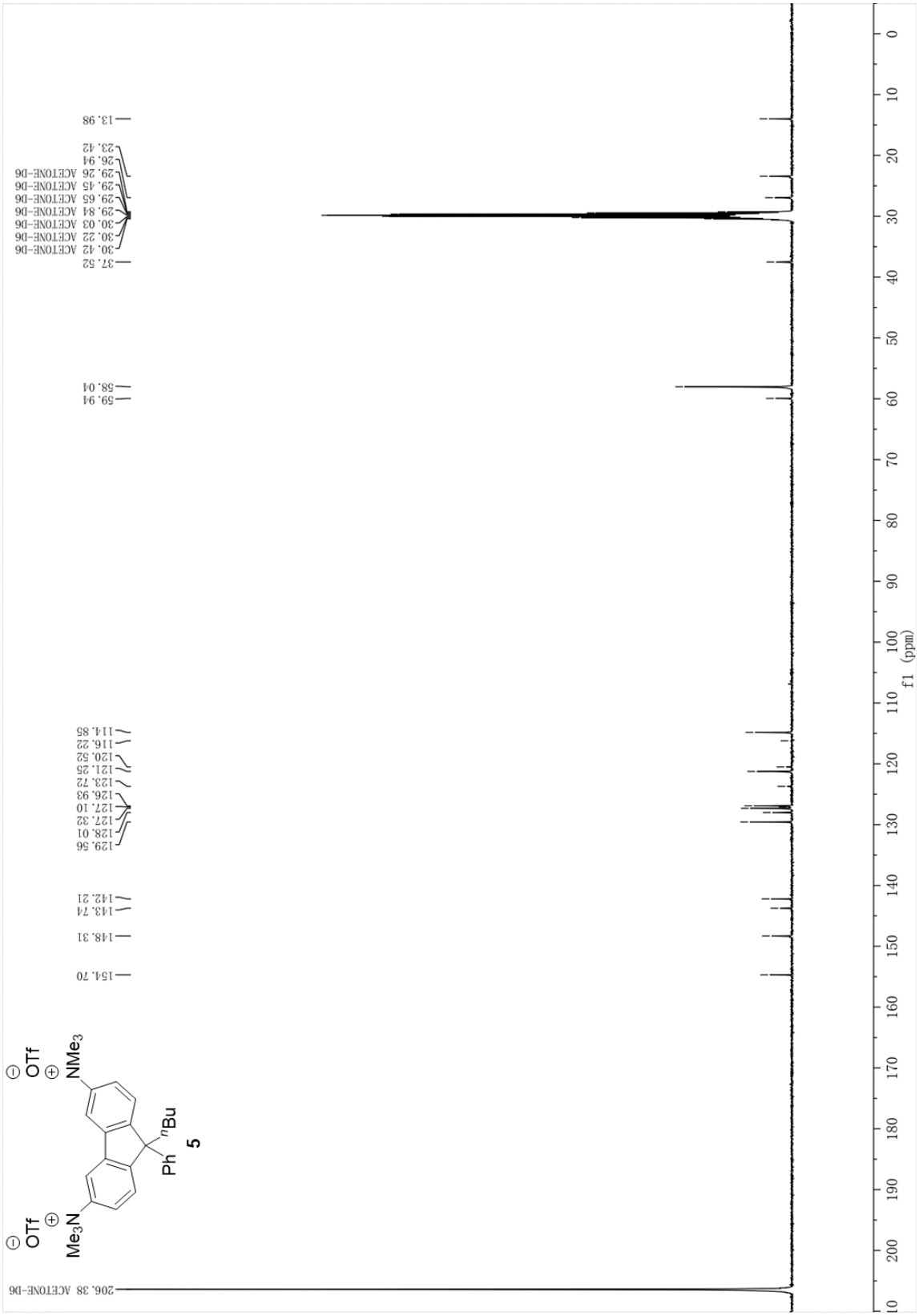


Figure S55. ^{13}C NMR (Acetone-d_6, 100 MHz): **5**

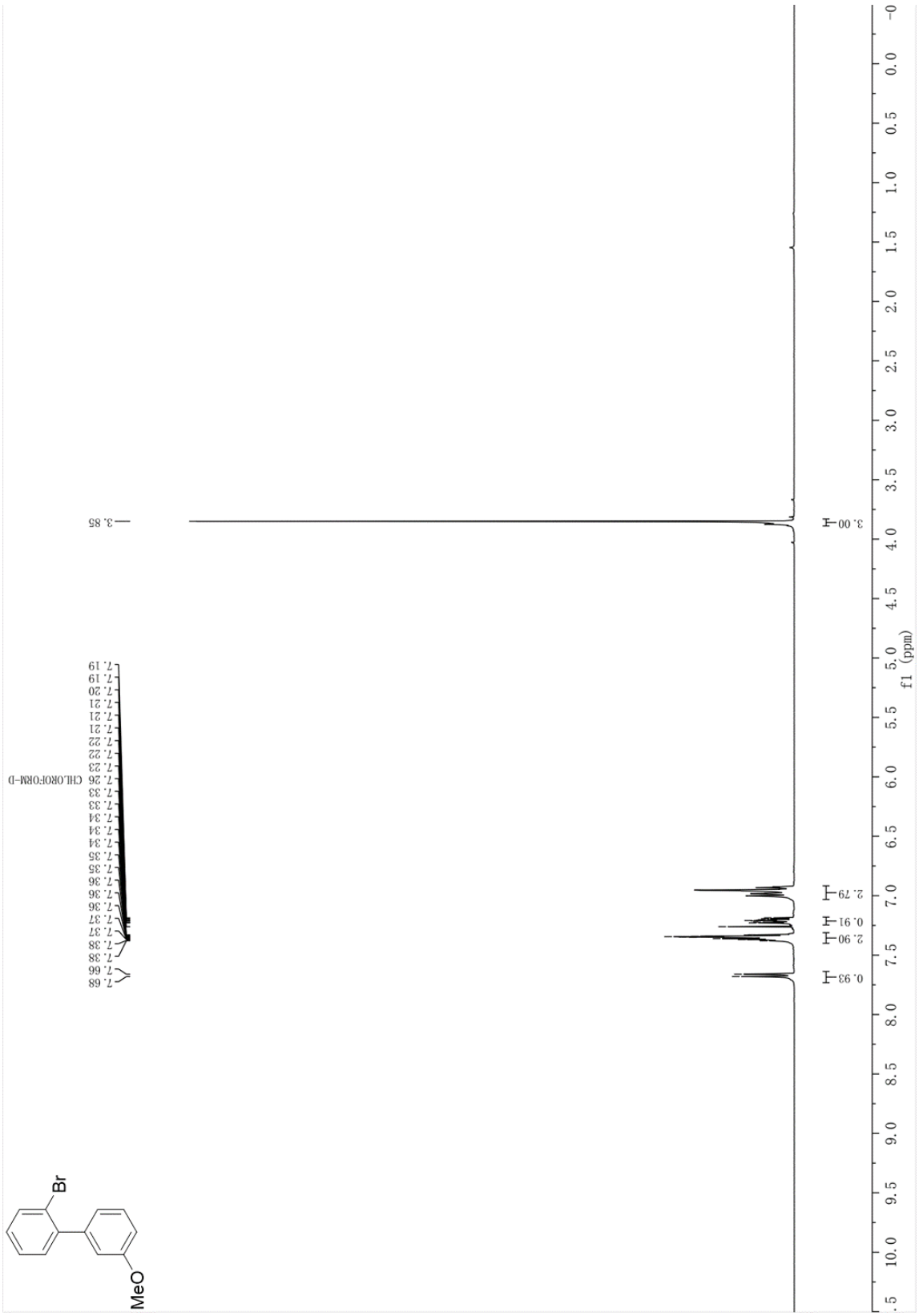


Figure S56. ^{1}H NMR ($CDCl_3$, 400 MHz): 2-Bromo-3'-methoxy-1,1'-biphenyl

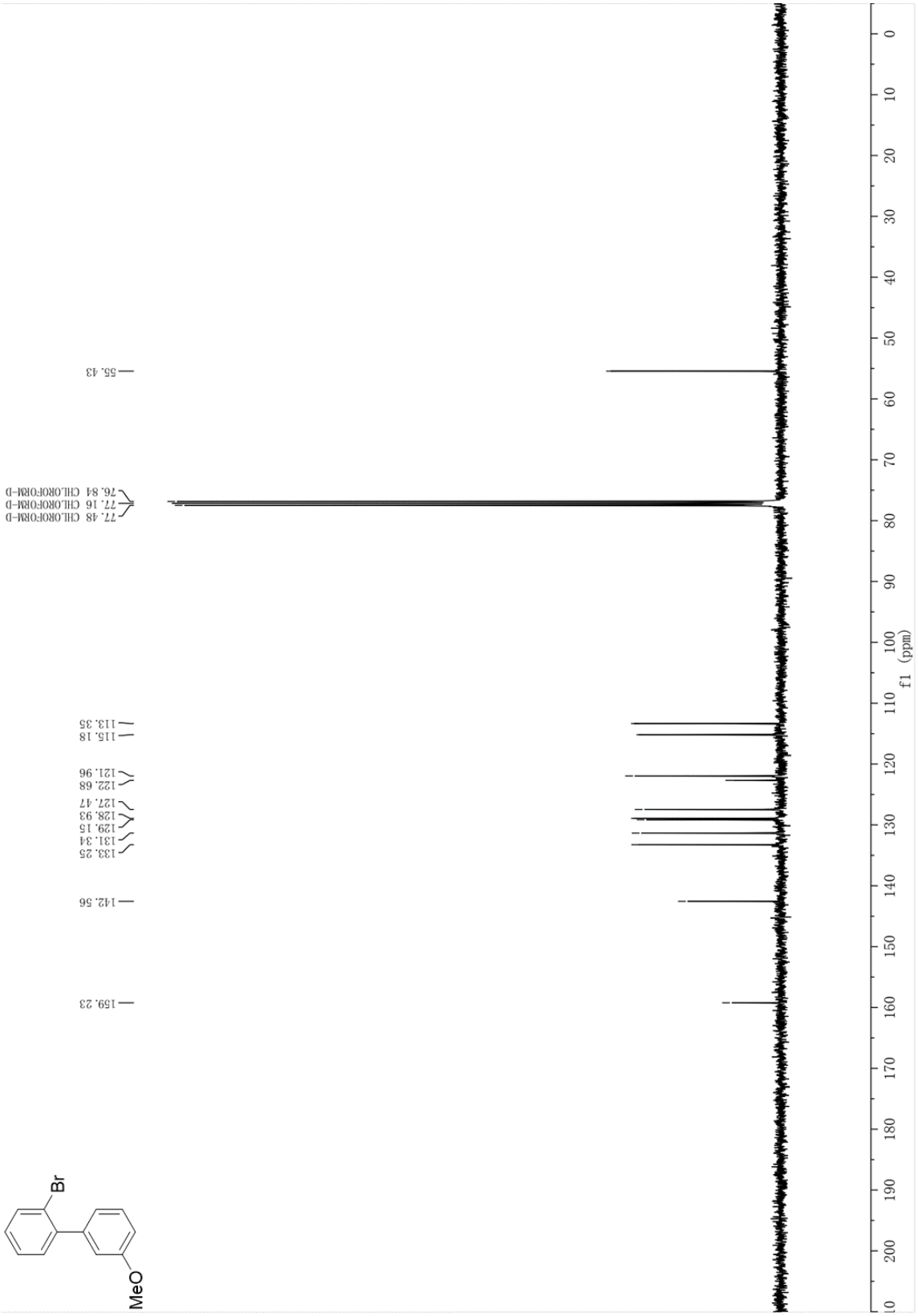


Figure S57. ^{13}C NMR ($CDCl_3$, 100 MHz): 2-Bromo-3'-methoxy-1,1'-biphenyl

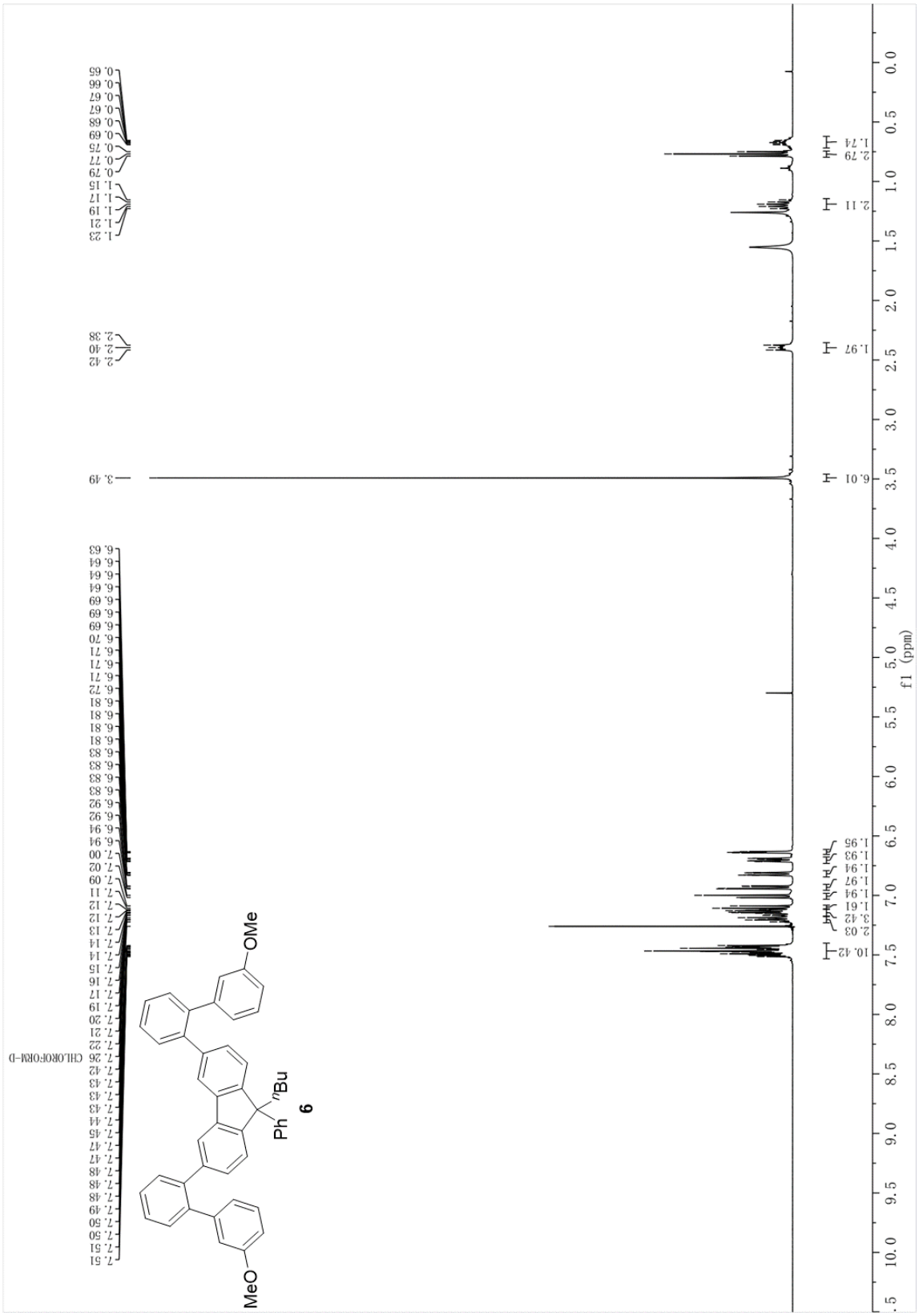


Figure S58. ^{1}H NMR ($CDCl_3$, 400 MHz): **6**

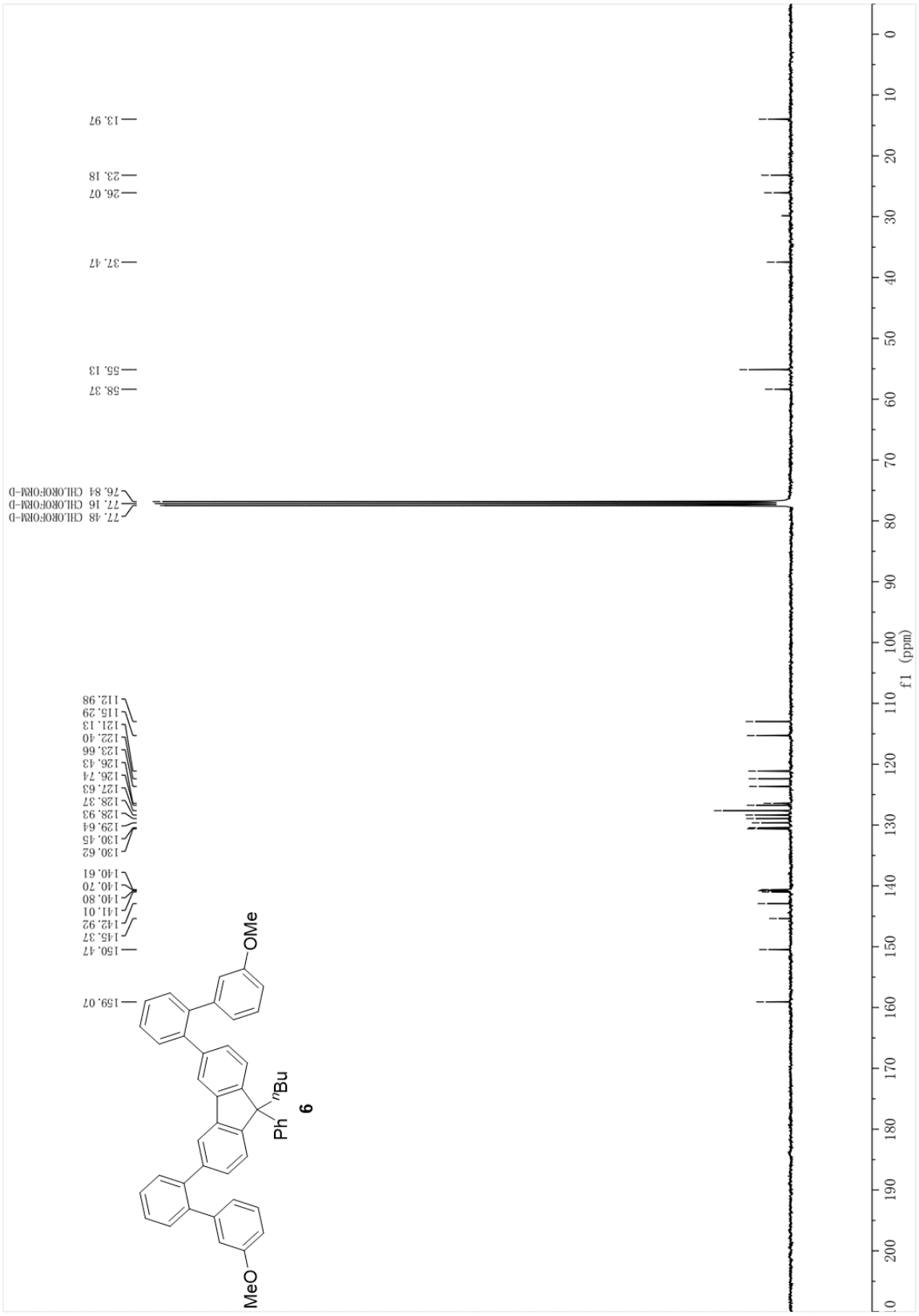


Figure S59. ^{13}C NMR ($CDCl_3$, 100 MHz): **6**

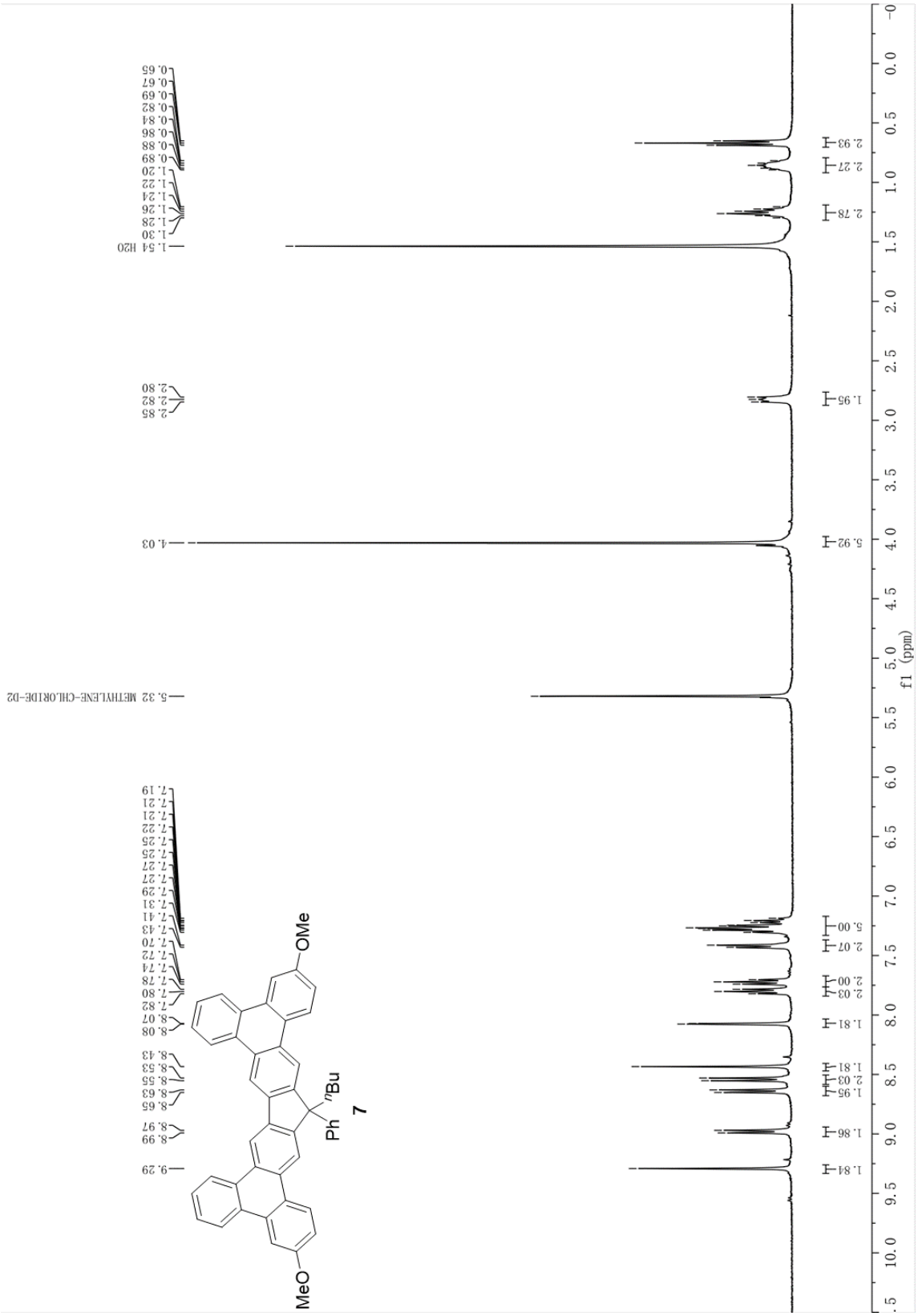


Figure S60. ^{1}H NMR ($CDCl_3$, 400 MHz): **7**

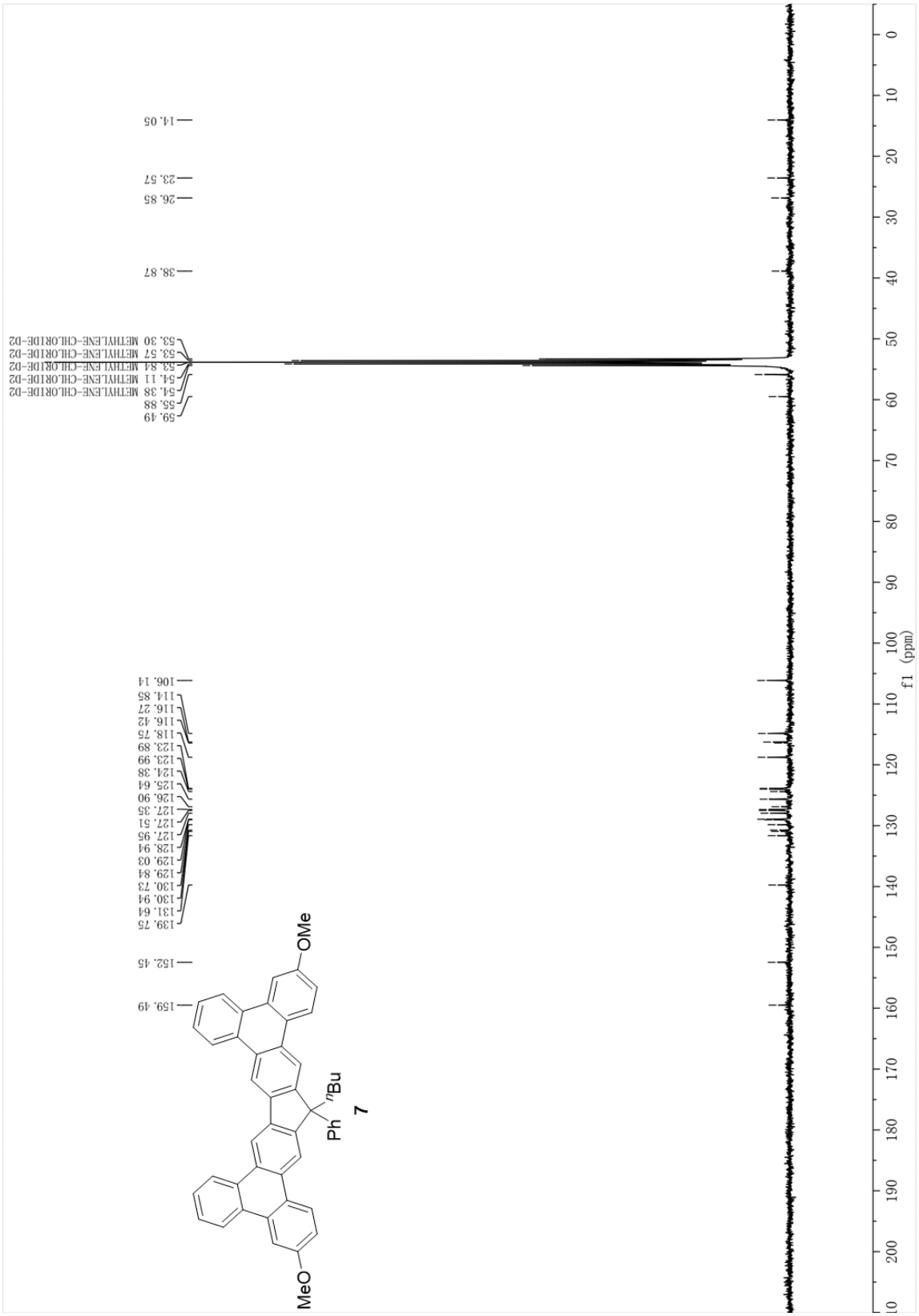


Figure S61. ^{13}C NMR ($CDCl_3$, 100 MHz): **7**

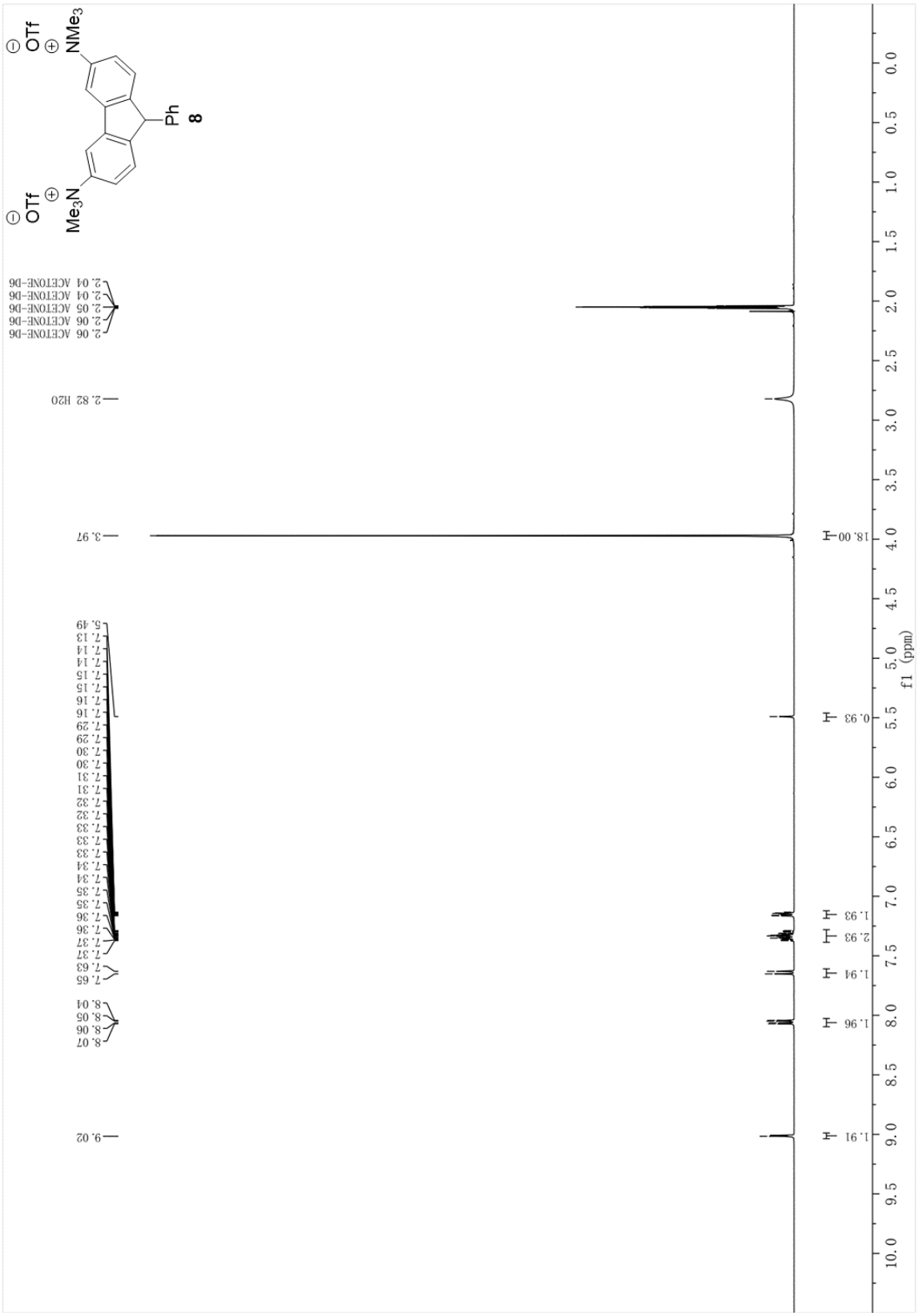


Figure S62. ^{1}H NMR (Acetone-d_6, 400 MHz): **8**

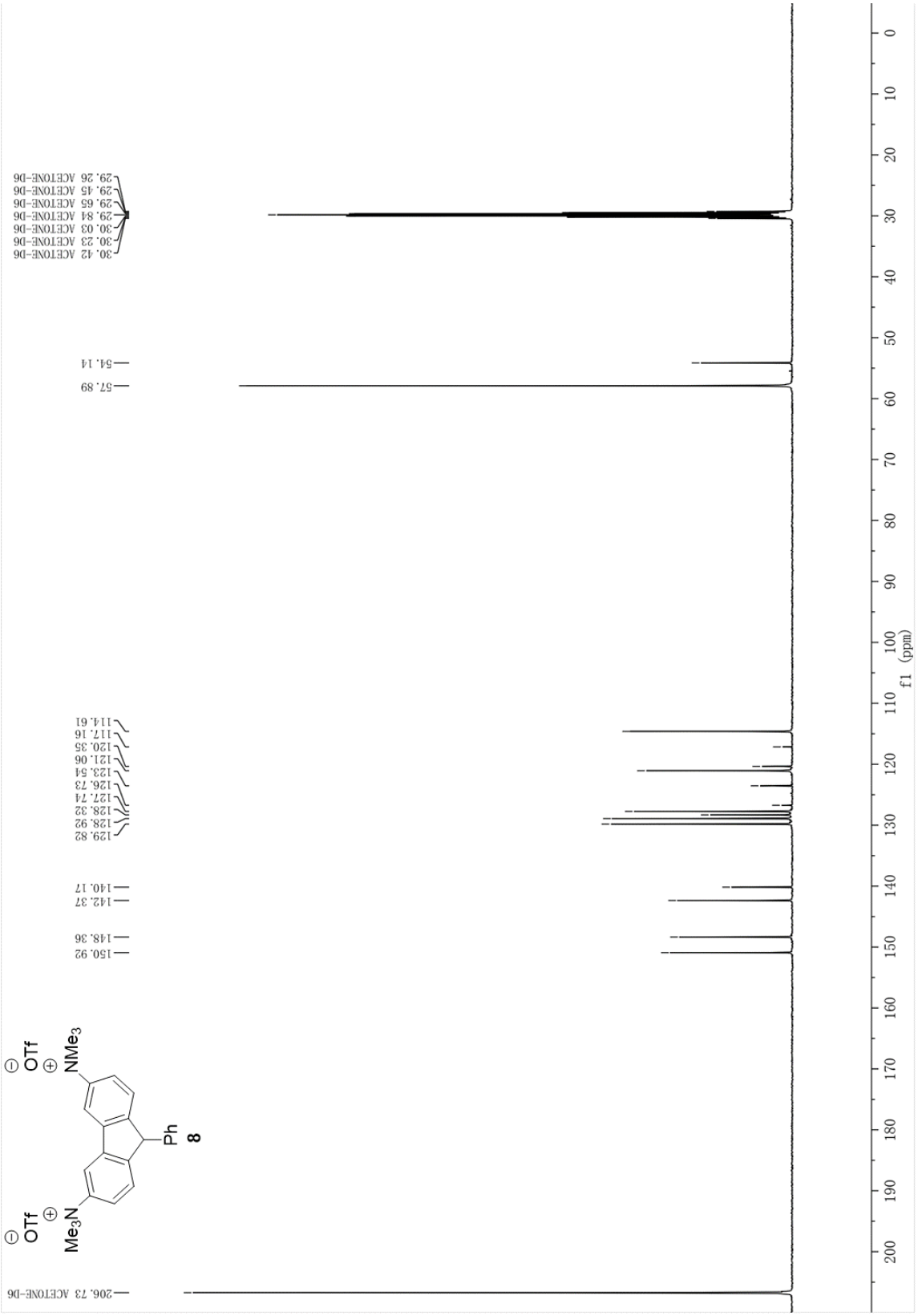


Figure S63. ^{13}C NMR (Acetone-d_6, 100 MHz): **8**

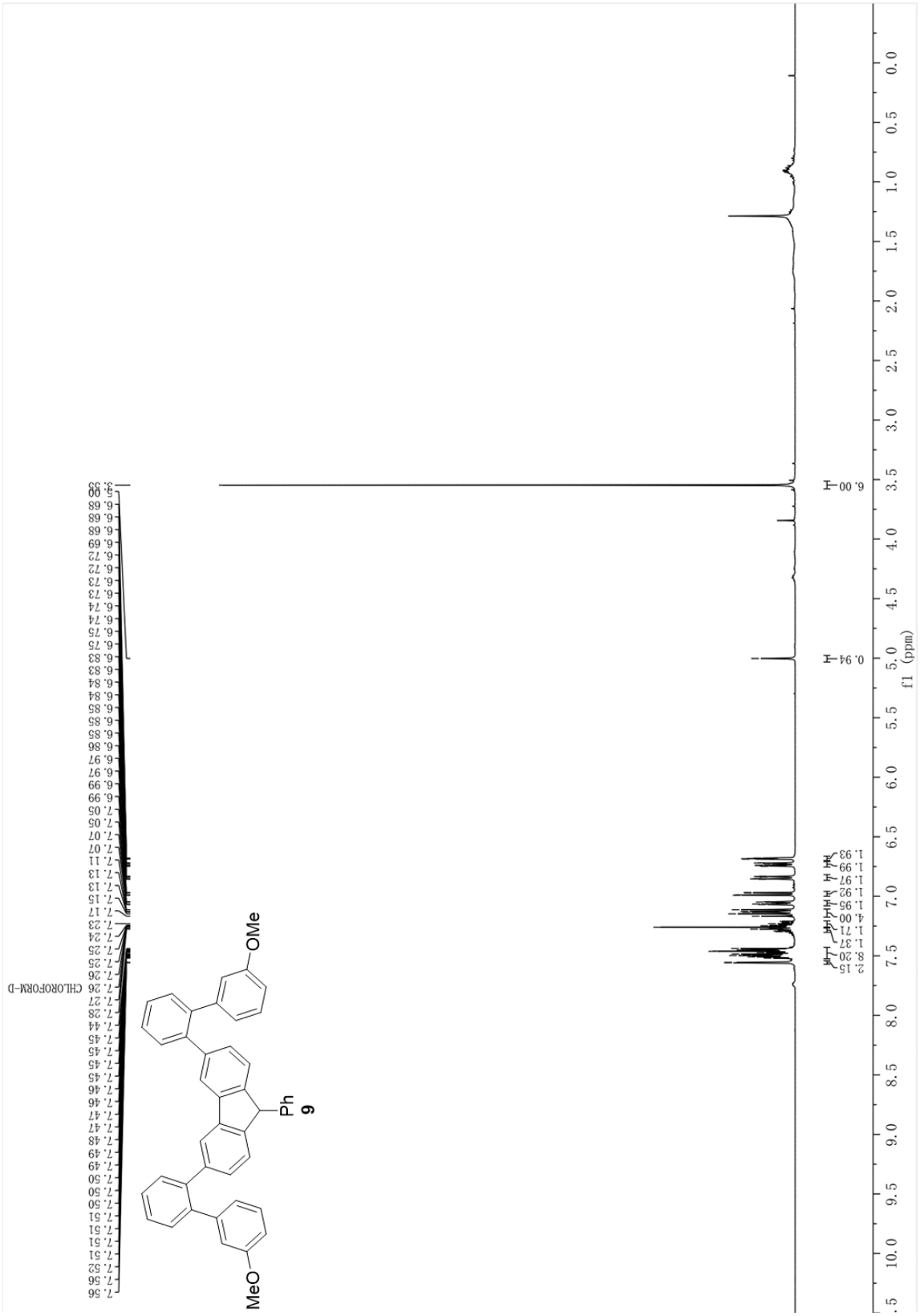


Figure S64. ^{1}H NMR ($CDCl_3$, 400 MHz): **9**

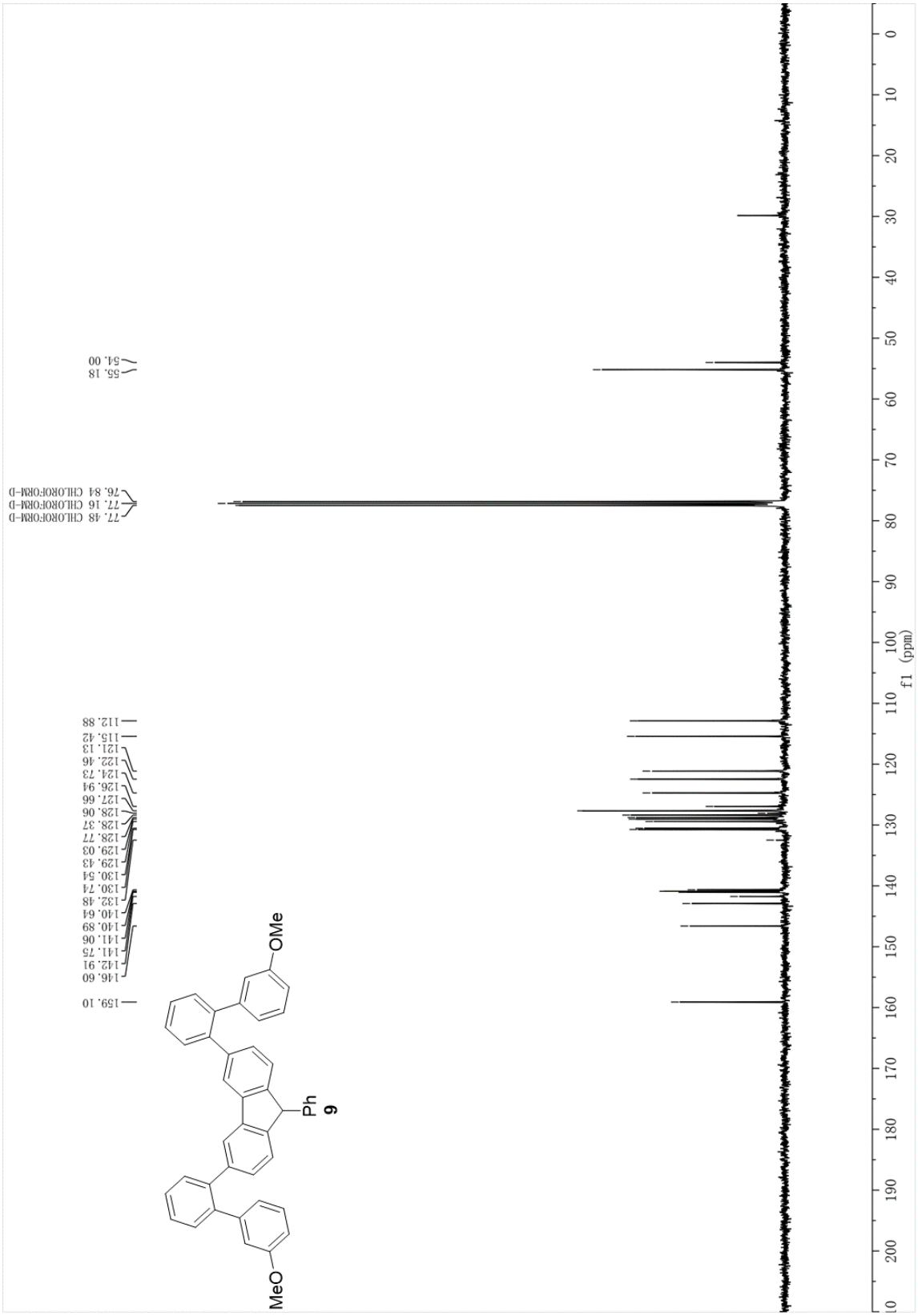


Figure S65. ^{13}C NMR ($CDCl_3$, 100 MHz): **9**

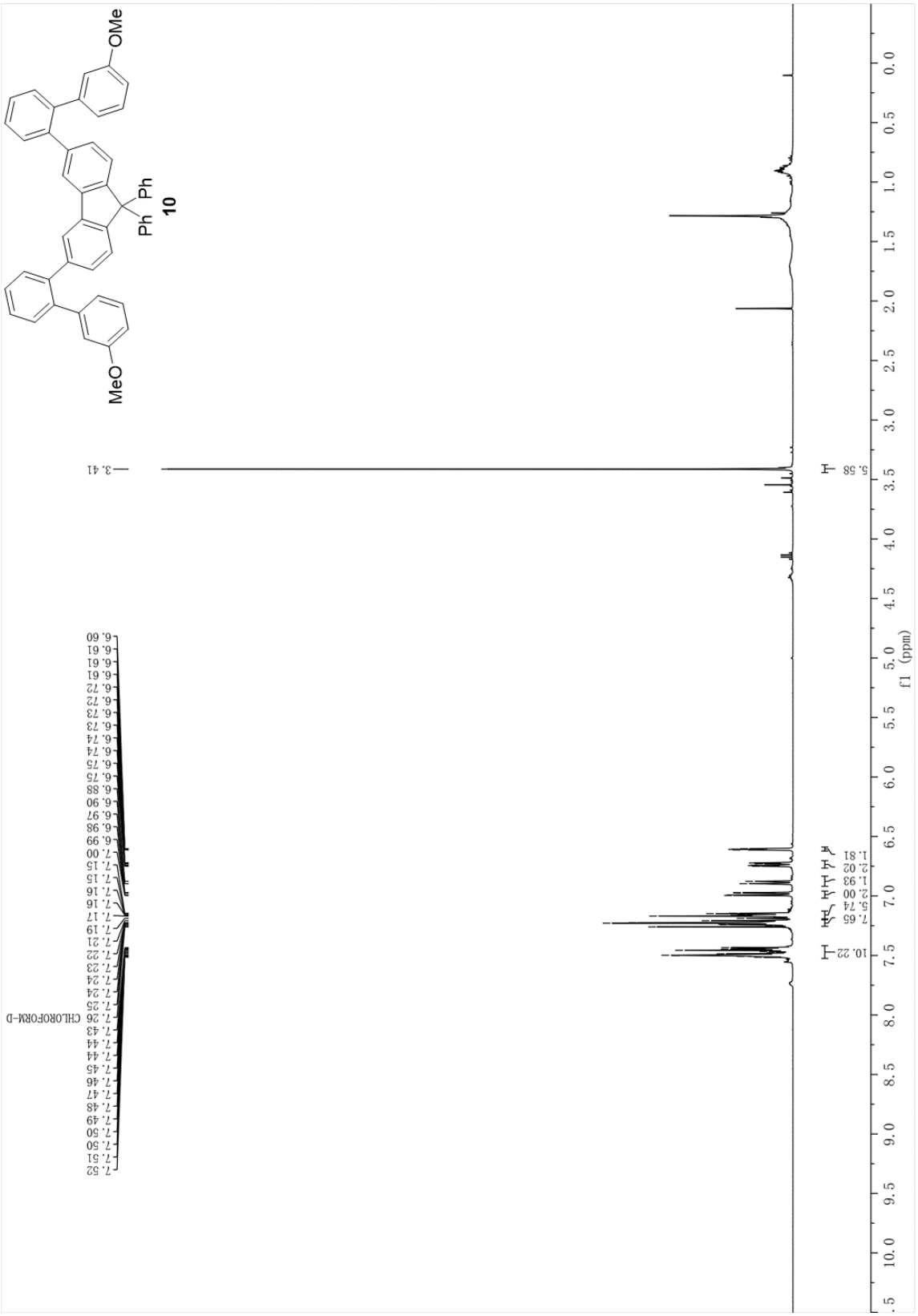


Figure S66. ^{1}H NMR ($CDCl_3$, 400 MHz): **10**

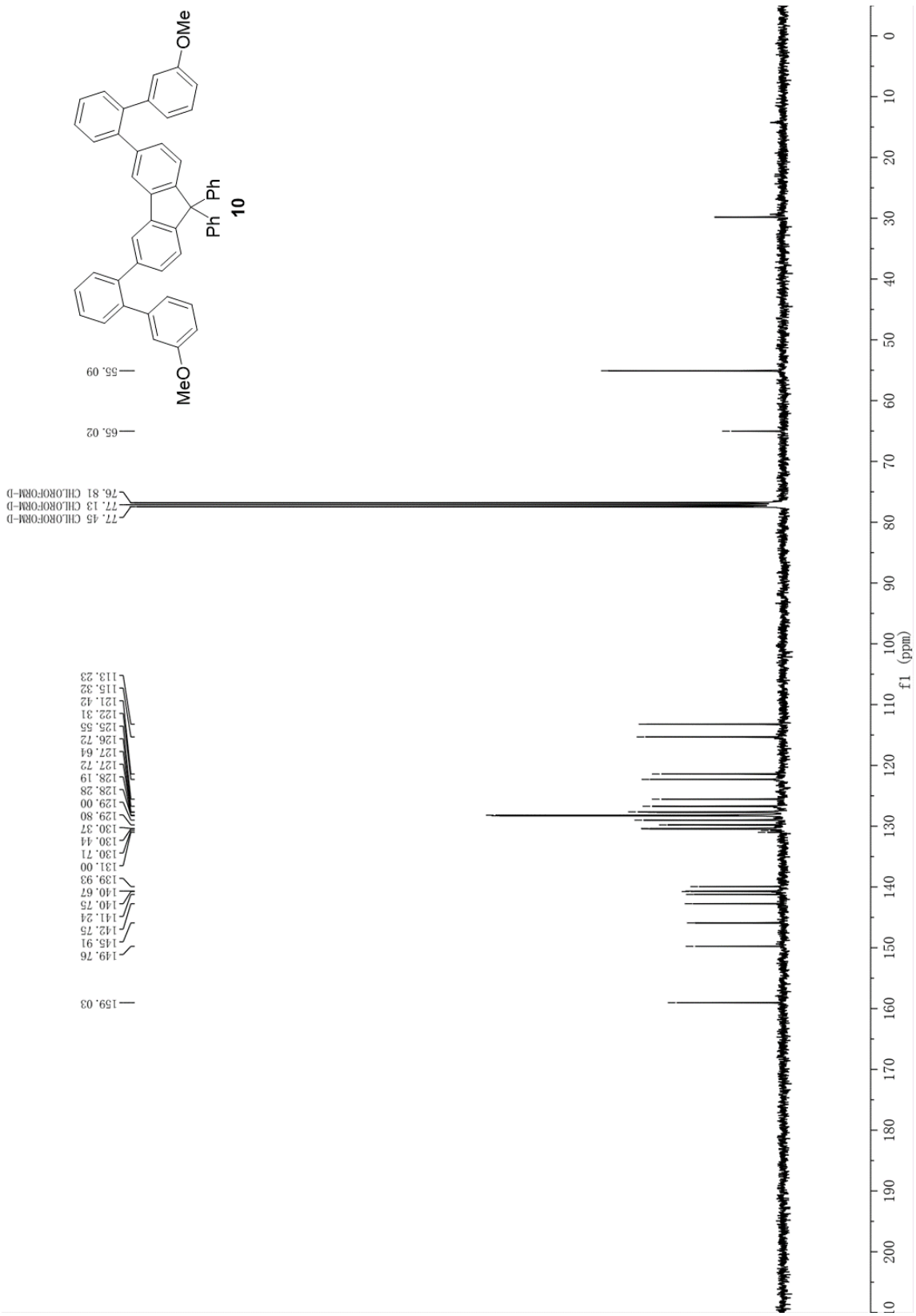


Figure S67. ^{13}C NMR ($CDCl_3$, 100 MHz): **10**

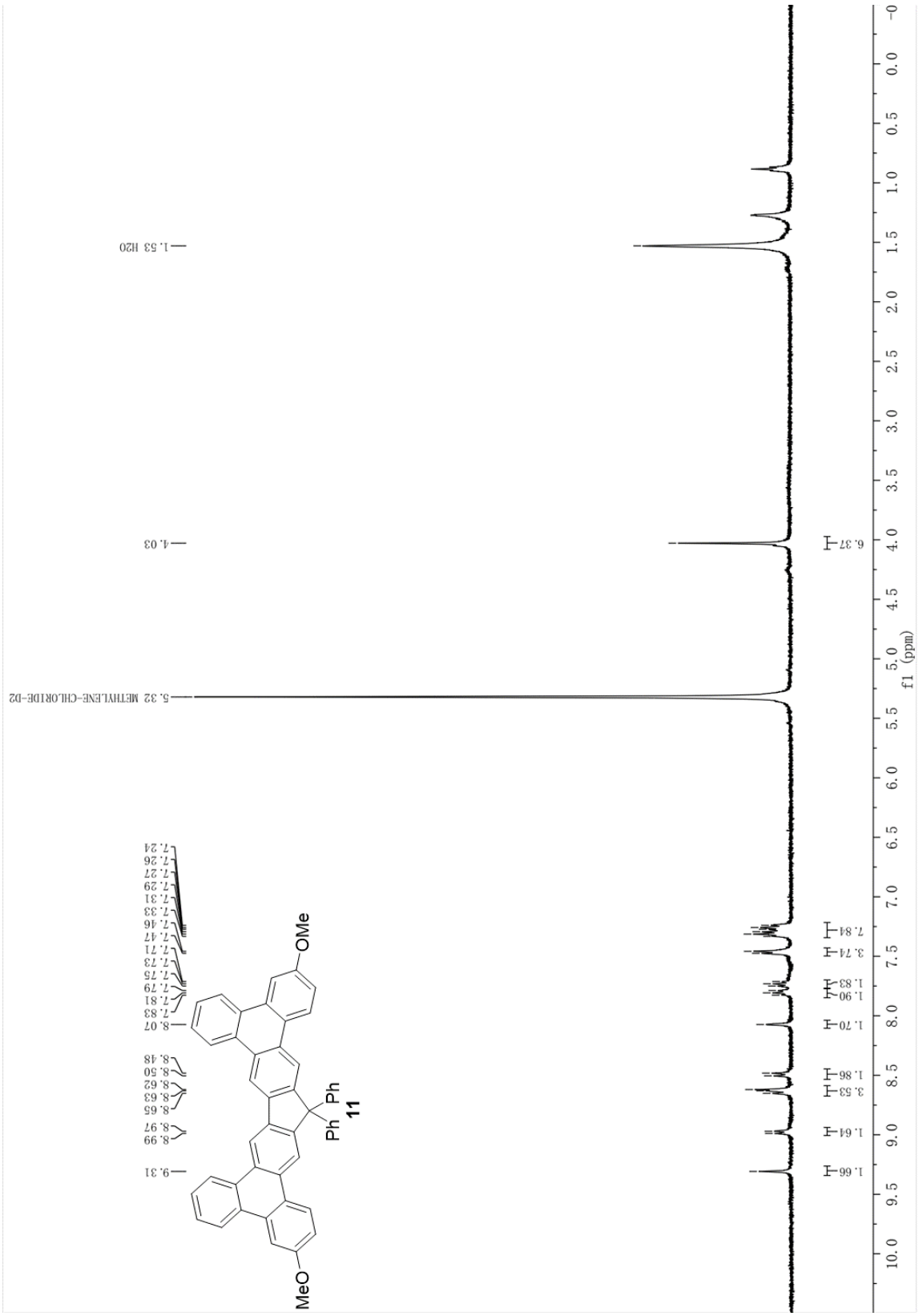


Figure S68. ^{1}H NMR (CD_2Cl_2, 400 MHz): **11**

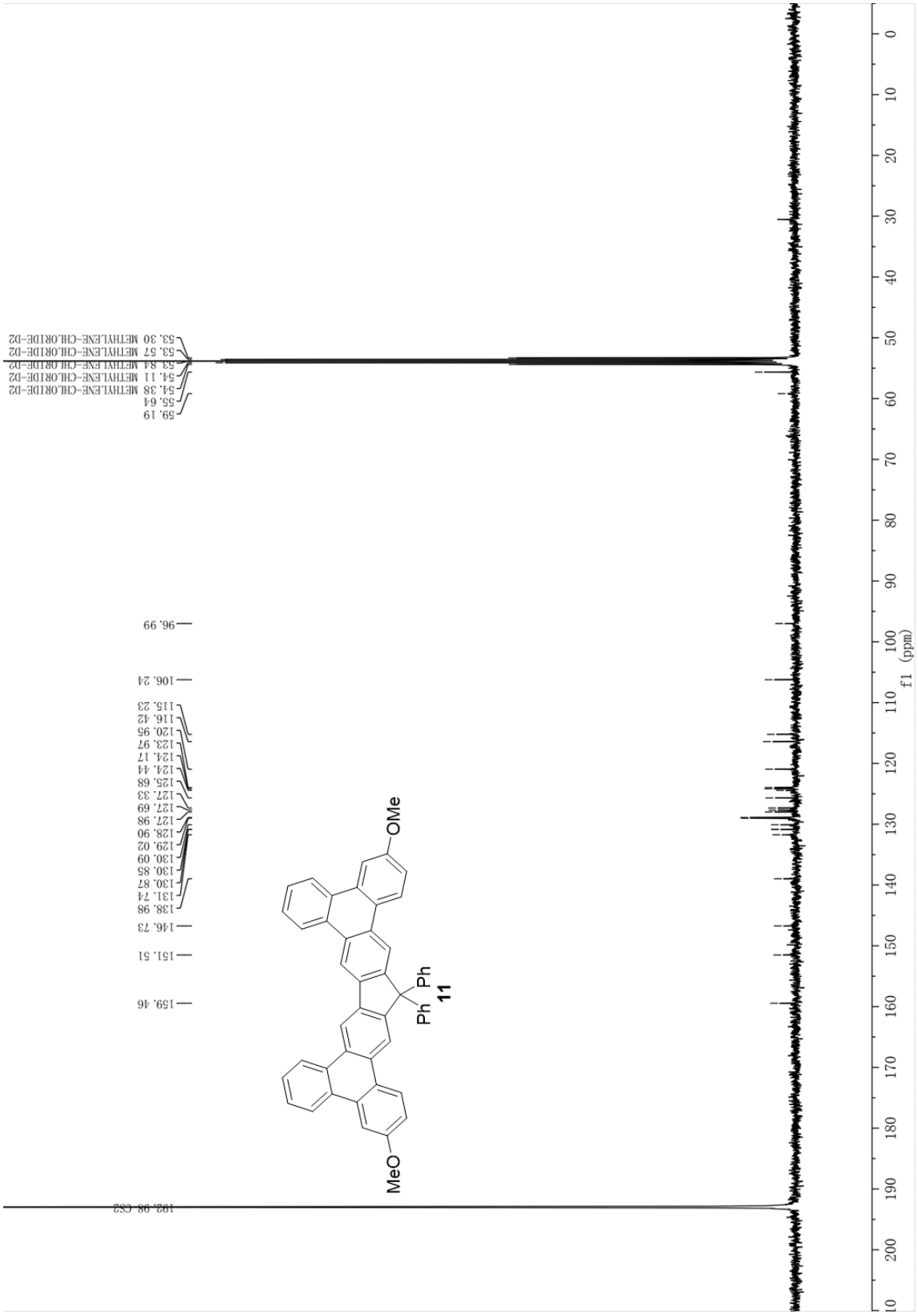


Figure S69. ^{13}C NMR (CD_2Cl_2, 100 MHz): **11**

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