Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Synthesis of Multi-donor Dyes and Influence of Molecular Design on Dye-sensitized Solar Cells

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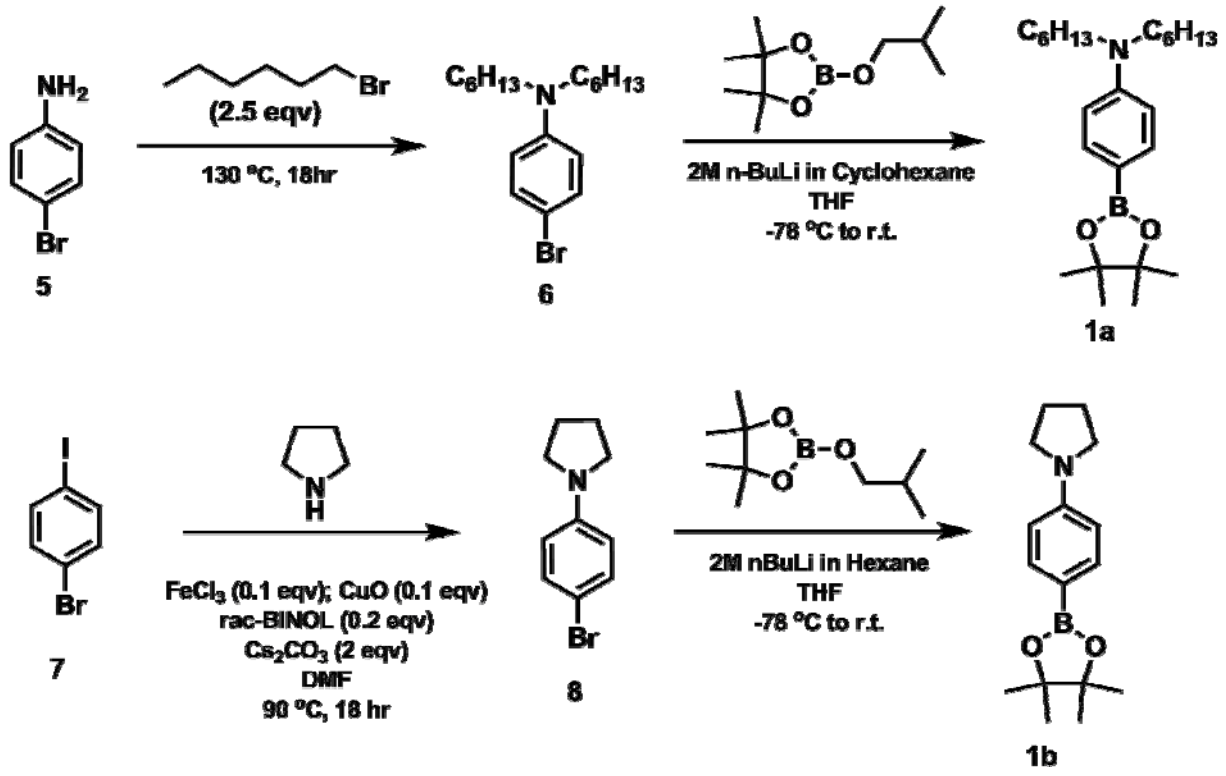


Scheme S1: Synthesis of intermediate compounds **1a** and **1b**.

Synthesis of 4-bromo-N,N-dihexylaniline (6)

4-Bromoaniline (5 g, 29 mmol) and 1-bromohexane (10.2 mL, 73 mmol) were heated to 130 °C and stirred for 18 hours. The reaction mixture was cooled to room temperature and 2M NaOH (50 mL) was added. The aqueous layer was extracted with diethyl ether (2 x 100 mL), the combined organic layers were dried with anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure to obtain a black crude product, which was purified using column chromatography on silica gel with hexane as eluent to isolate pale yellow oil (3.62 g, yield 36.7%). MS (EI) m/z = 339.3 (M^+), 340.3 (calcd.). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ = 7.26 – 7.29 (d, 2H), 6.51 – 6.54 (d, 2H), 3.22 – 3.27 (t, 4H,), 1.56 – 1.58 (broad, 4H), 1.34 (s, 12H), 0.94 (s, 6H). Elem. Anal. Calcd. for $C_{18}H_{30}BrN$: C, 63.52%; H, 8.88%; Br, 23.48, N, 4.12%; found: C, 63.14%; H, 8.58%; Br, 23.70, N, 4.19%.

Synthesis of 4-dihexylamino-phenylboronic acid pinacol ester (1a)

Compound **6** (3.80 g, 11.18 mmol) was dissolved in anhydrous THF (50 mL) under nitrogen atmosphere and cooled to -78 °C in dry ice / acetone bath. n-BuLi in cyclohexane (15 mL, 30 mmol) was added drop wise and stirred at -78 °C for 1 hr. To this mixture, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5 mL, 22.8 mmol) was added slowly, stirred and gradually

warmed to room temperature. The mixture was added to ice water (50 mL, 0 °C), extracted with diethyl ether (2 x 50 mL), dried over anhydrous Na_2SO_4 and filtered. The organic solvent was removed under reduced pressure to obtain brown oil. The crude product was purified over silica gel column using dichloromethane (DCM)/hexane (1:4) mixture as eluent to yield orange oil (2.72 g, 63 %). MS (EI) m/z = 387.4 (M^+), 387.4 (calcd.). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.66 – 7.69 (d, 4H), 6.61 – 6.64 (d, 4H), 3.27 – 3.32 (t, 4H), 1.60 (quintet, 4H), 1.33 (s, 24H), 0.91 – 0.94 (t, 6H, $–CH_3$). Elem. Anal. Calcd. for $C_{24}H_{42}BNO_2$: C, 74.41%; H, 10.93%; N, 3.62%; found: C, 74.26%; H, 10.65%; N, 3.79%.

Synthesis of 4-pyrrolidino-1-bromobenzene (8)

1-Bromo-4-iodobenzene (5 g, 17.75 mmol), iron(III) chloride (0.29 g, 1.79 mmol), copper(II) oxide (0.14 g, 1.76 mmol), rac-BINOL (1.02 g, 3.56 mmol) and cesium carbonate (12 g, 36.83 mmol) were taken into 250 mL round bottom flask, connected to vacuum for removing the air and backfilled with nitrogen gas. A solution of pyrrolidine (1.75 mL, 21.32 mmol) in DMF (35 mL) was added and the reaction mixture was stirred at 90 °C for 18 hours. After cooling to room temperature, the mixture was diluted with DCM (100 mL) and filtered to remove insoluble solids. The insoluble residue was rinsed with DCM, filtrate was washed with 1M NaOH (200 mL) followed by water (100 mL), combined organic layer was dried over anhydrous Na_2SO_4, filtered, concentrated under reduced pressure and the crude product was purified using column chromatography with DCM : Hexane (1:10) mixture as eluent to get a white solid (3.41 g, yield 85%). MS (EI) m/z = 224.1 (M^+), 226.1 (calcd.). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.26 – 7.30 (d, 2H), 6.44 – 6.47 (d, 2H), 3.23 – 3.27 (t, 4H), 1.99 – 2.03 (quintet, 4H). ^{13}C NMR (δ, 75.4 MHz, $CDCl_3$) ppm: δ = 146.69, 131.66, 113.27, 47.77, 25.43. Elem. Anal. Calcd. for $C_{10}H_{12}BrN$: C, 53.12%; H, 5.35%; Br, 35.34, N, 6.19%; found: C, 53.24%; H, 5.33%; Br, 35.80, N, 6.27%.

Synthesis of 4-pyrrolidino-phenylboronic acid pinacol ester (1b)

Compound **8** (3.41 g, 15.1 mmol) dissolved in anhydrous THF (80 mL) was cooled to -78 °C under nitrogen atmosphere. To this, 2M n-BuLi in cyclohexane (16 mL, 32 mmol) was added slowly and stirred at -78 °C for 1 hr. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6.2 mL, 30.4 mmol) was added slowly to the mixture, stirred and allowed to warm up to room temperature. The reaction mixture was added to ice water (50 mL), extracted with diethyl ether (3 x 50 mL), combined organic extracts were dried on anhydrous Na_2SO_4, filtered and the excess solvent was removed under reduced pressure to obtain a dark brown oil. The crude product was dissolved in minimum amount of diethyl ether, cooled to 0 °C for crystallization of the compound as pale pink crystals and collected by filtration (2.95 g, yield 71%). MS (EI) m/z = 273.2 (M^+), 273.2 (calcd.). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.66 – 7.69 (d, 2H), 6.54 – 6.57 (d, 2H), 3.30 – 3.34 (t, 4H), 1.98 – 2.03 (quintet, 4H), 1.32 (s, 12H). Elem. Anal. Calcd. for $C_{16}H_{24}BNO_2$: C, 70.35%; H, 8.86%; N, 5.13%; found: C, 70.47%; H, 9.01%; N, 5.21%.

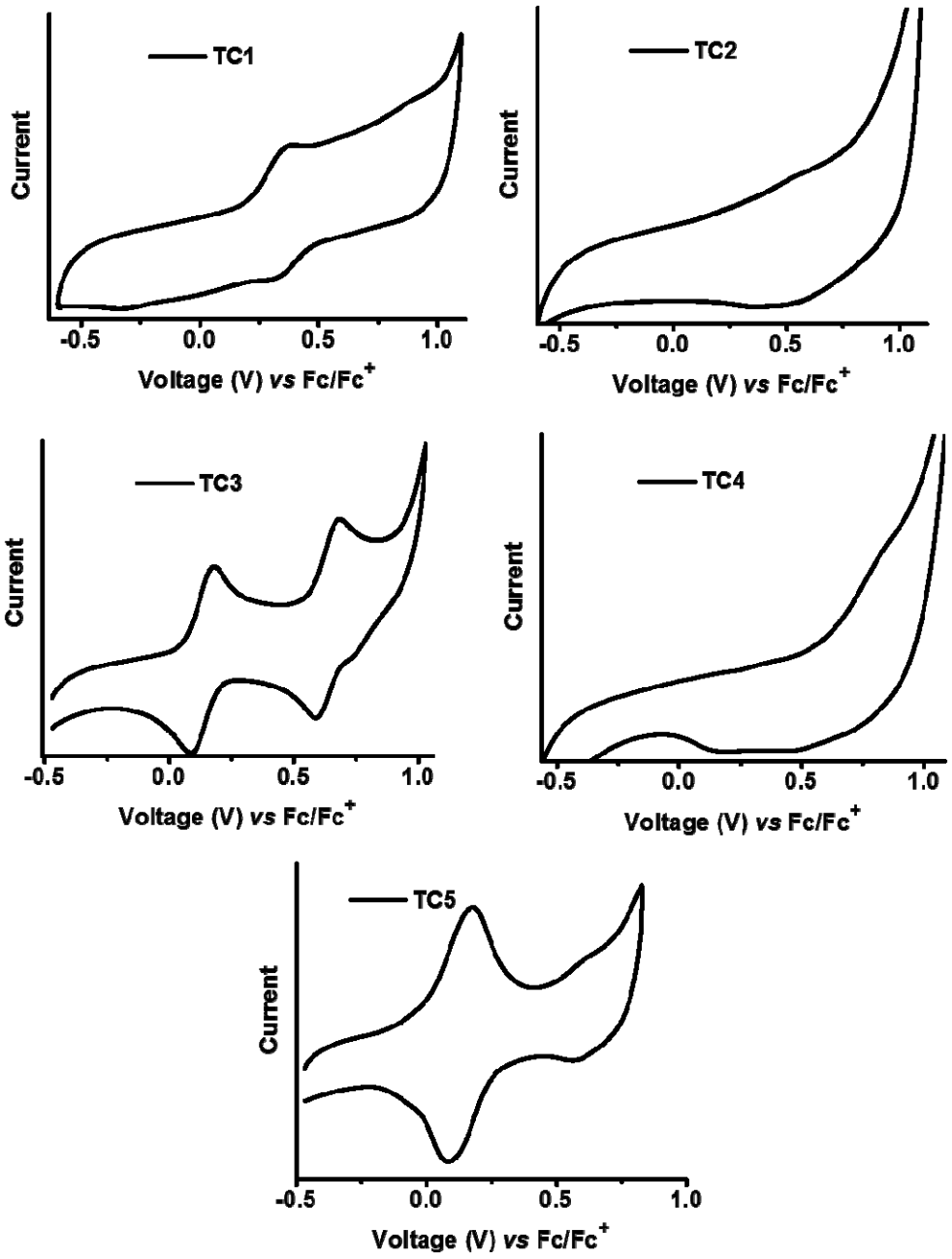


Figure S1. Enlarged cyclic voltammetry scans of dyes **TC1 – TC5** at a scan rate of 100 mV/s in THF solution. Potentials reported with respect to ferrocene.

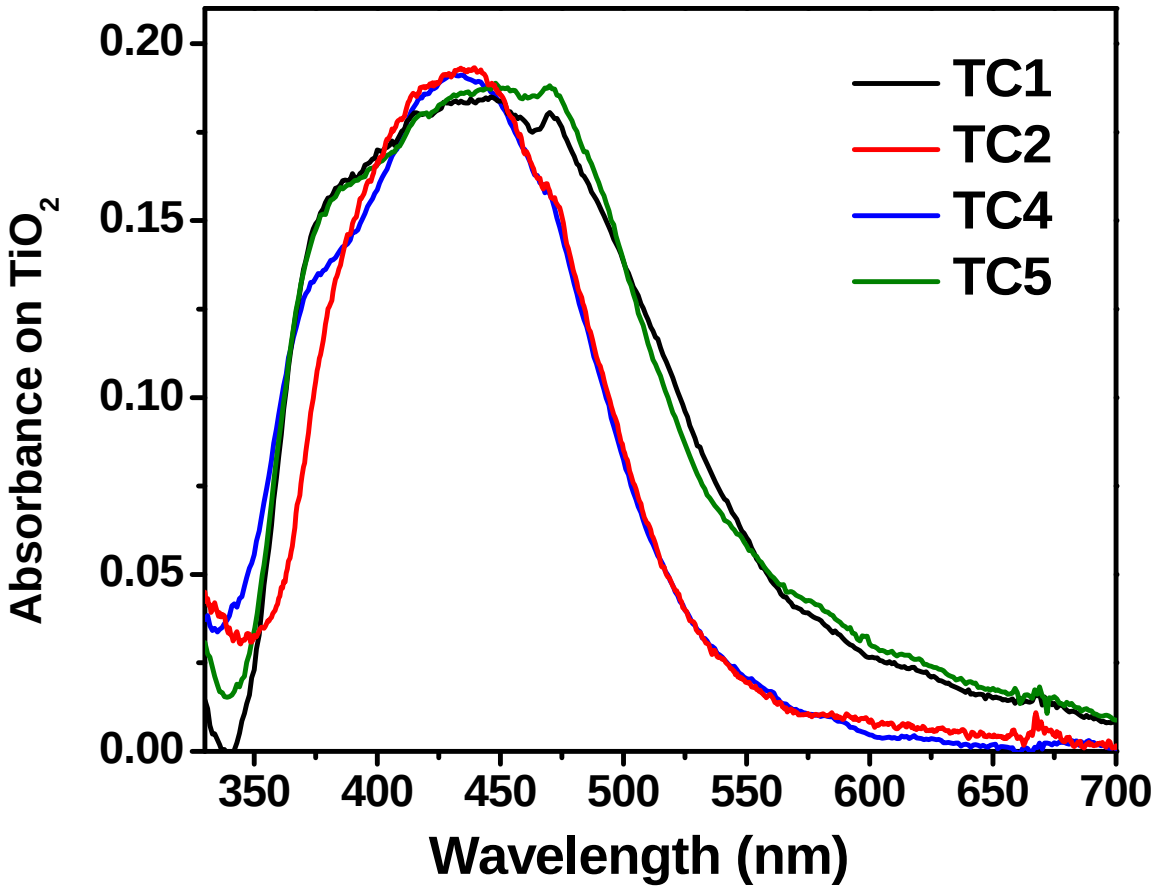


Figure S2. UV-vis absorption spectra of dyes (TC1, TC2, TC4 and TC5) on TiO_2 coated quartz plates. The plates were immersed in 0.25 mM dye solutions in THF for 24 hours and rinsed several times using fresh THF solvent.

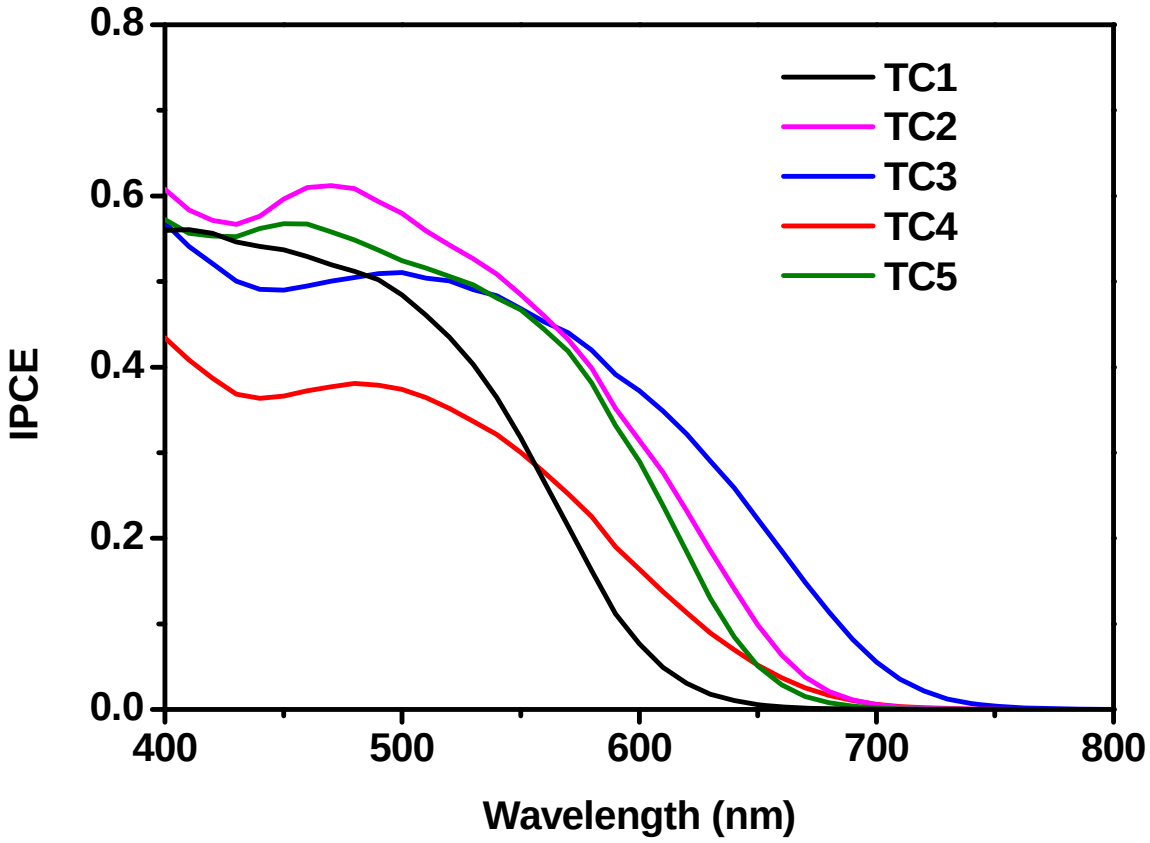
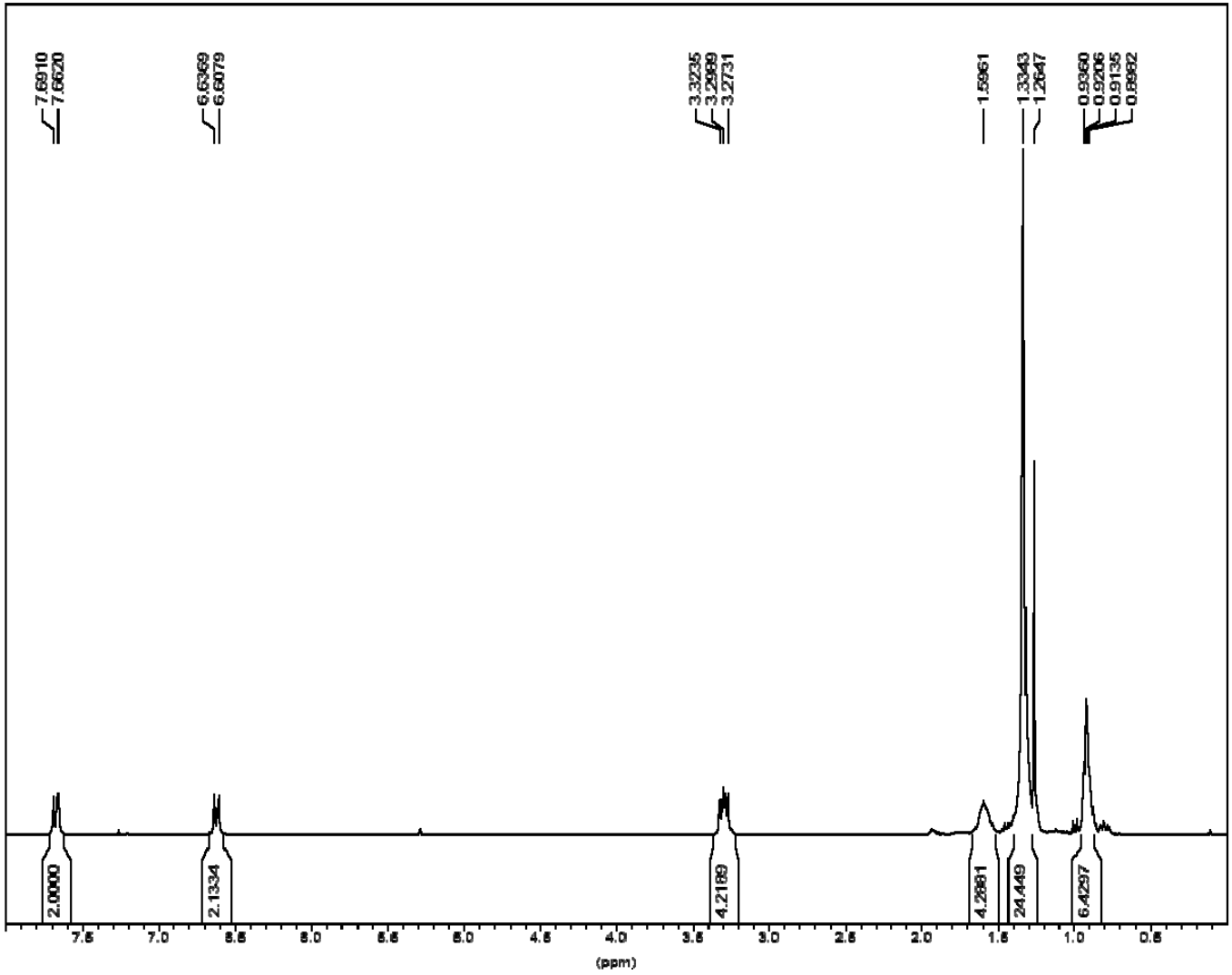


Figure S3. IPCE (Incident photon-to-current efficiency) curves of **TC1** - **TC5** dyes. The electrodes were immersed into a 0.25 mM solution of sensitizer in THF solution.

1H NMR and MS spectra of compound **1a**

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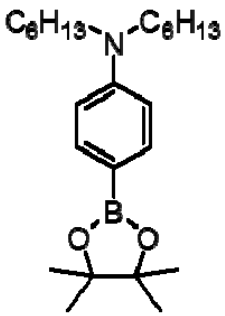

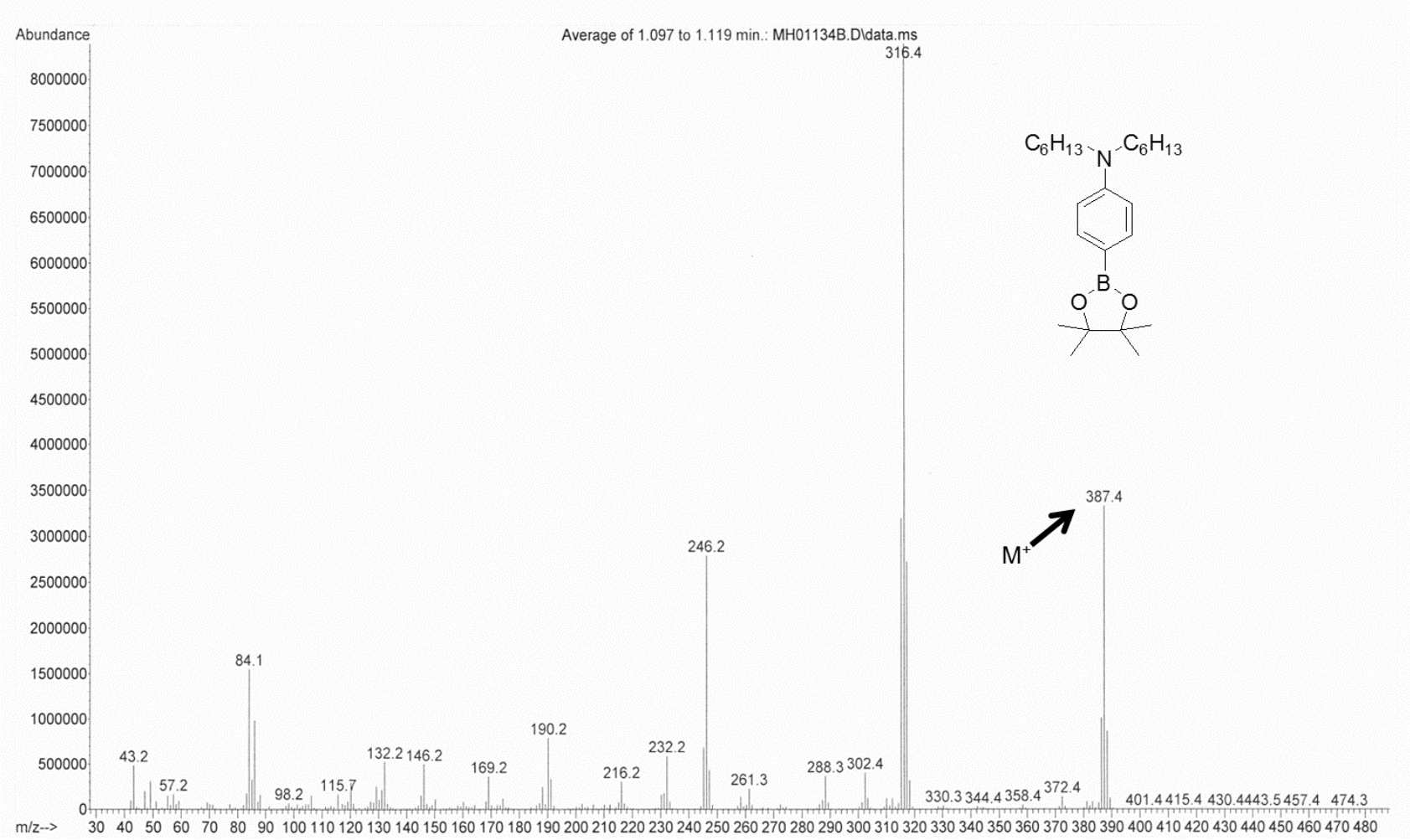
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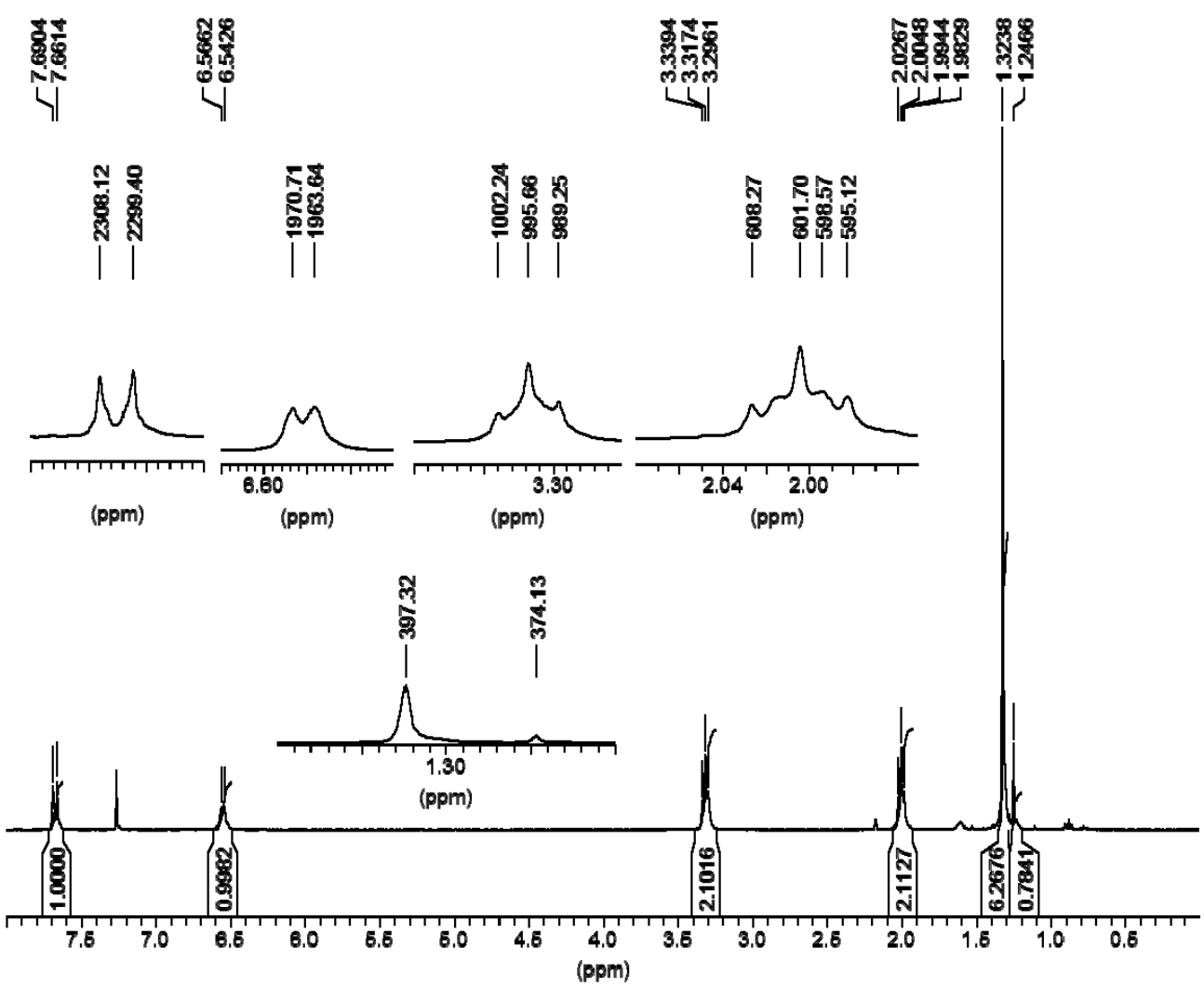
m/z-->

1H NMR and MS spectra of compound **1b**

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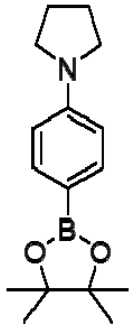

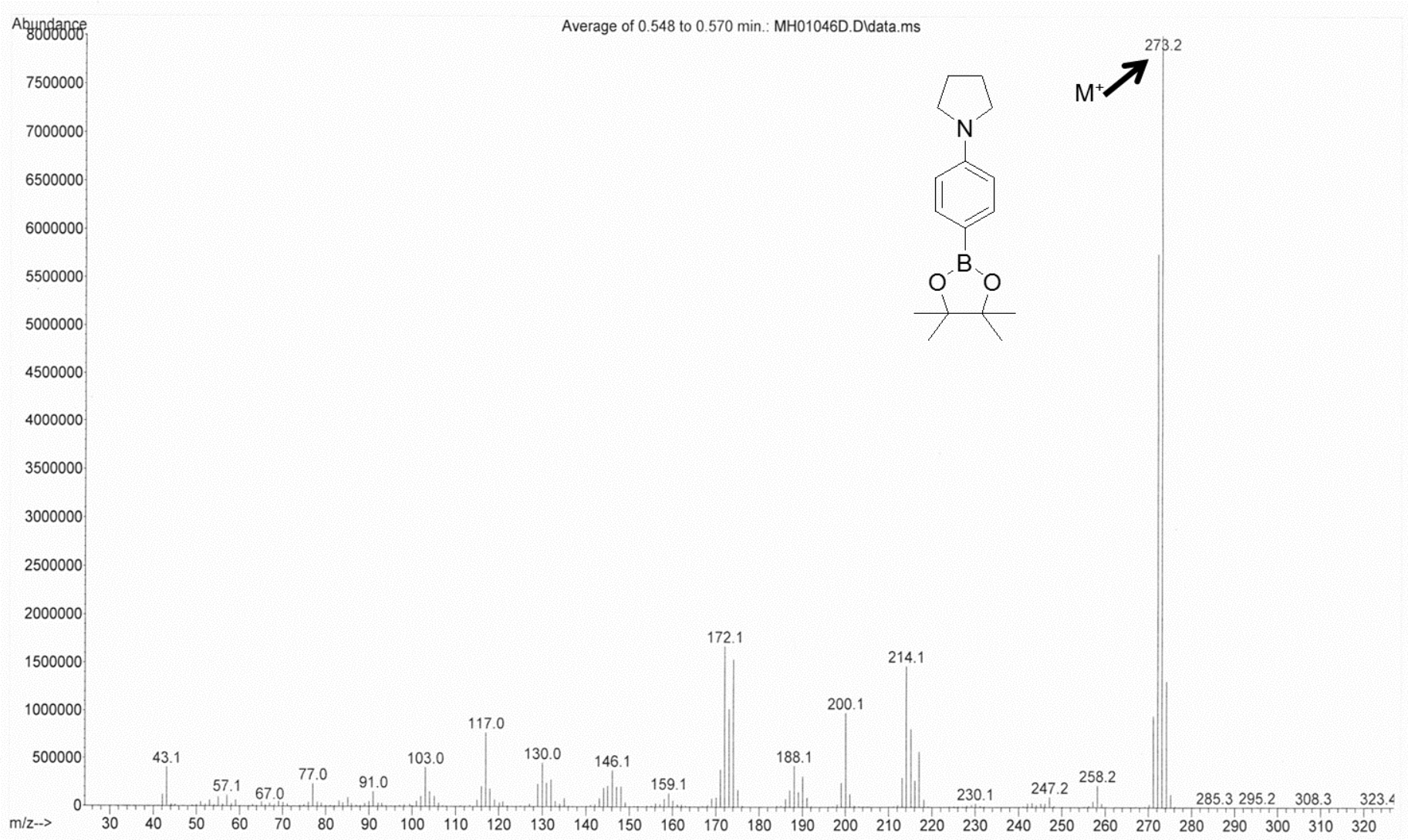
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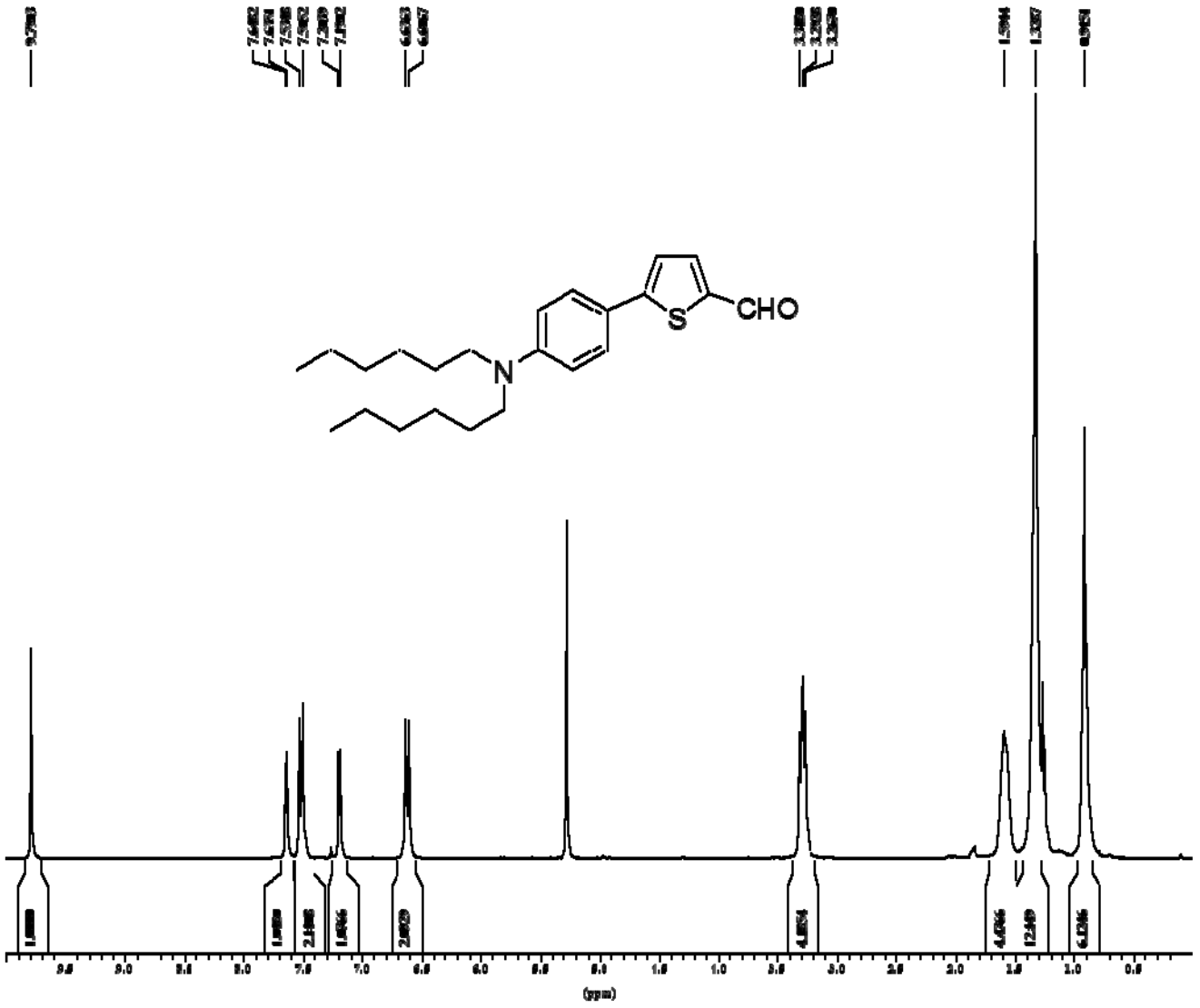
1H & 13C NMR of compound **2a**



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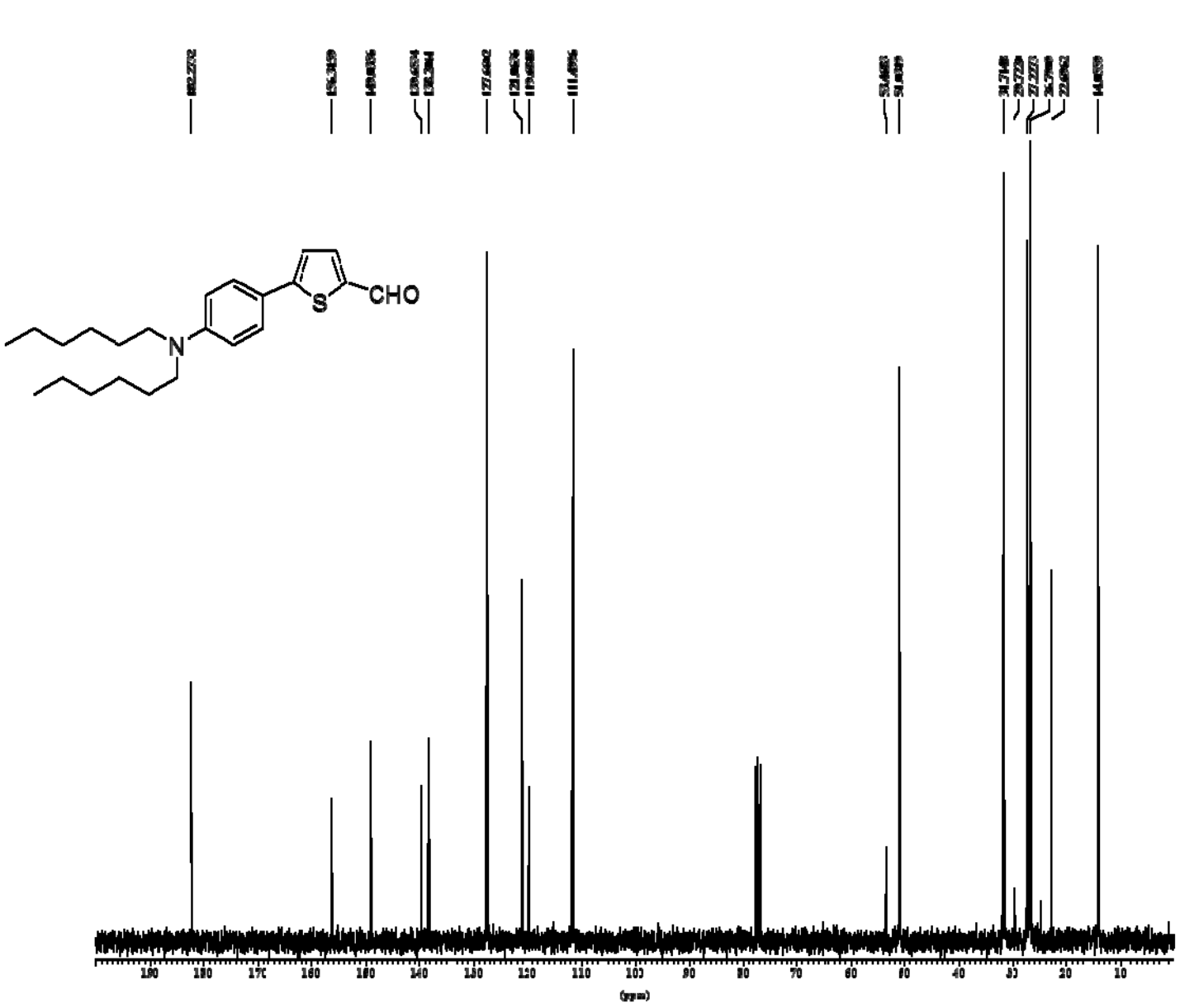

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SOLVENT : CDCl3

SW : 238.1968 ppm

TD : 32768

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*** Processing Parameters ***

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*** 1D NMR Plot Parameters ***

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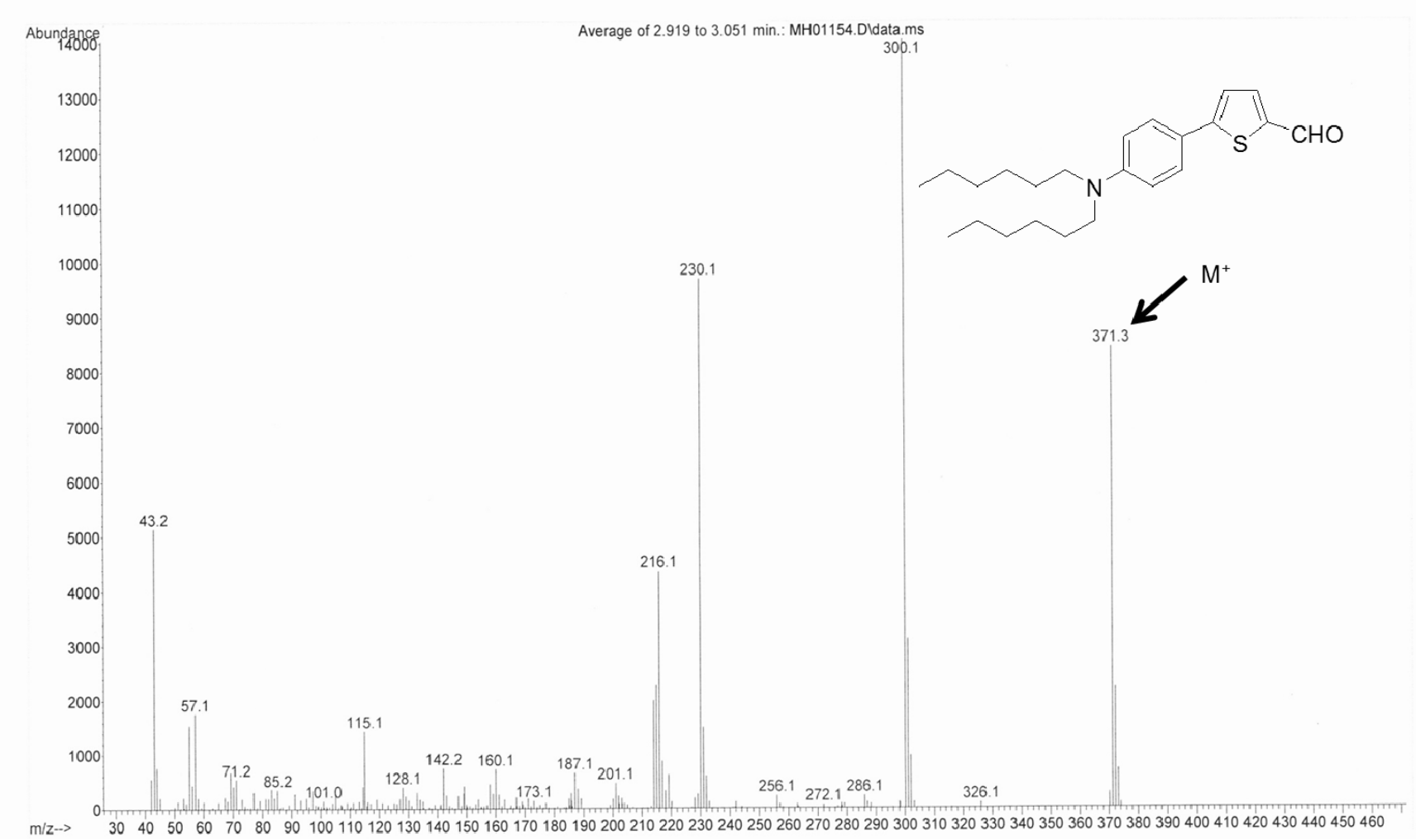
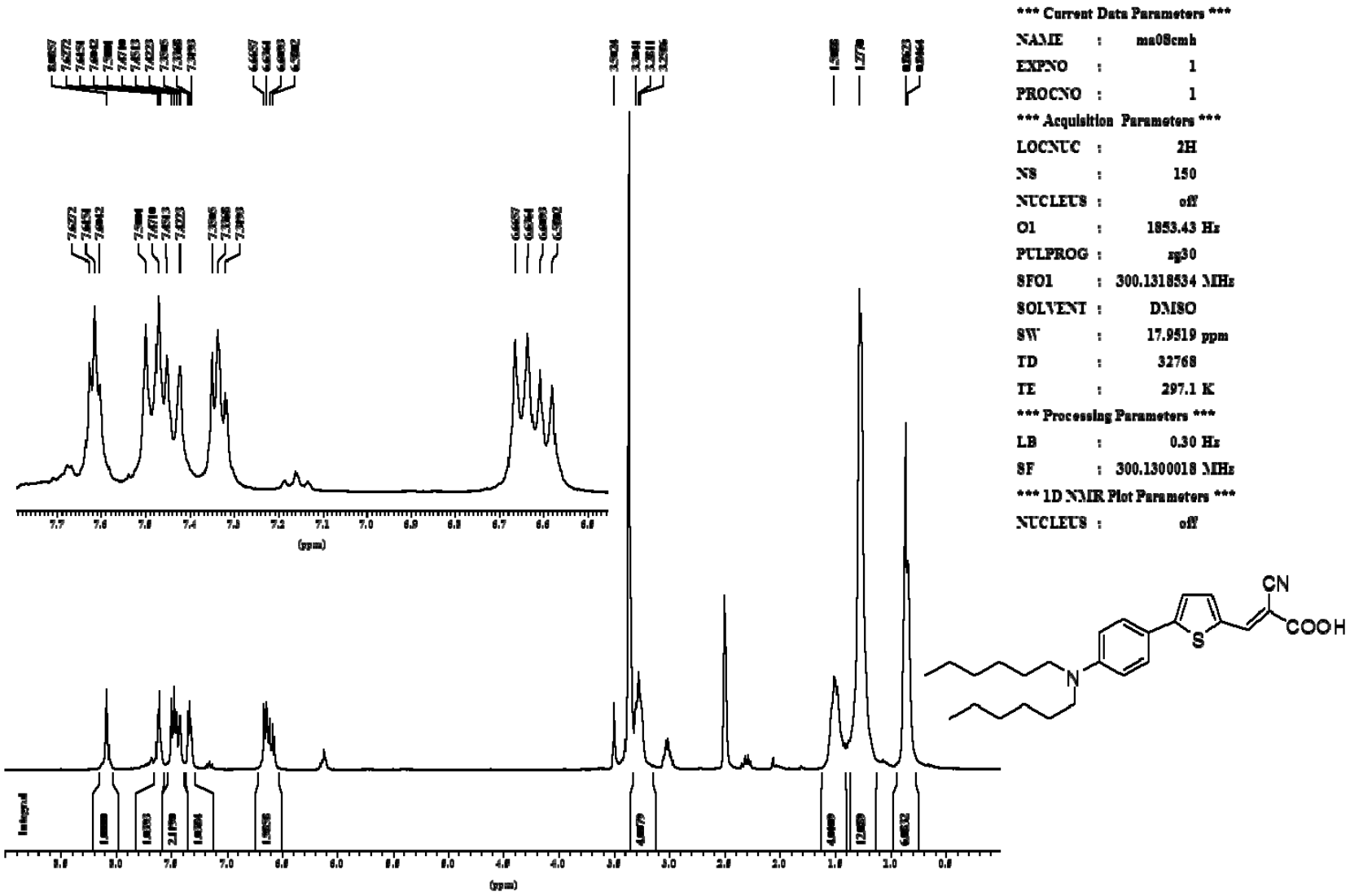
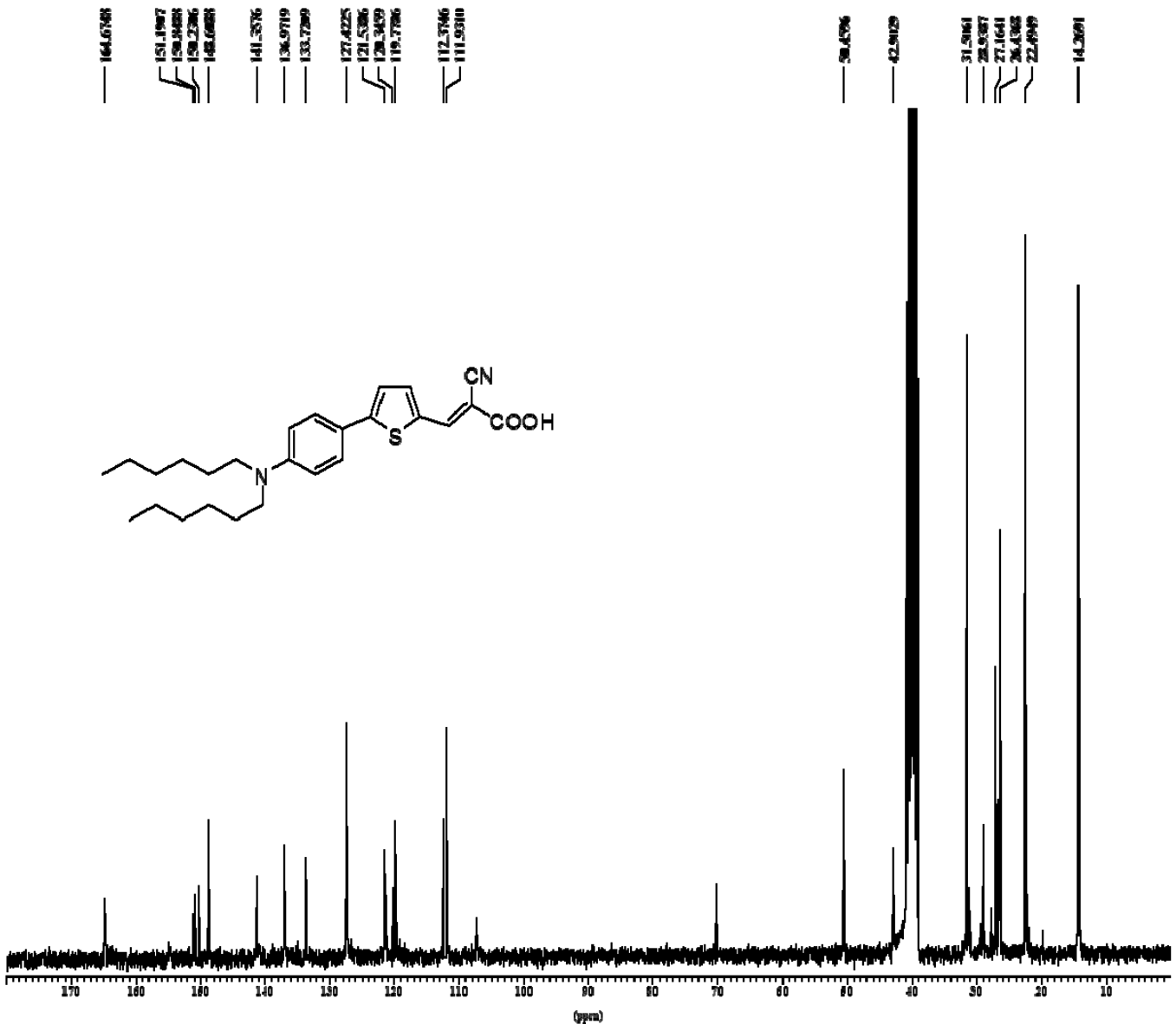
MS spectra of compound **2a**



1H & 13C NMR of compound **TC1**





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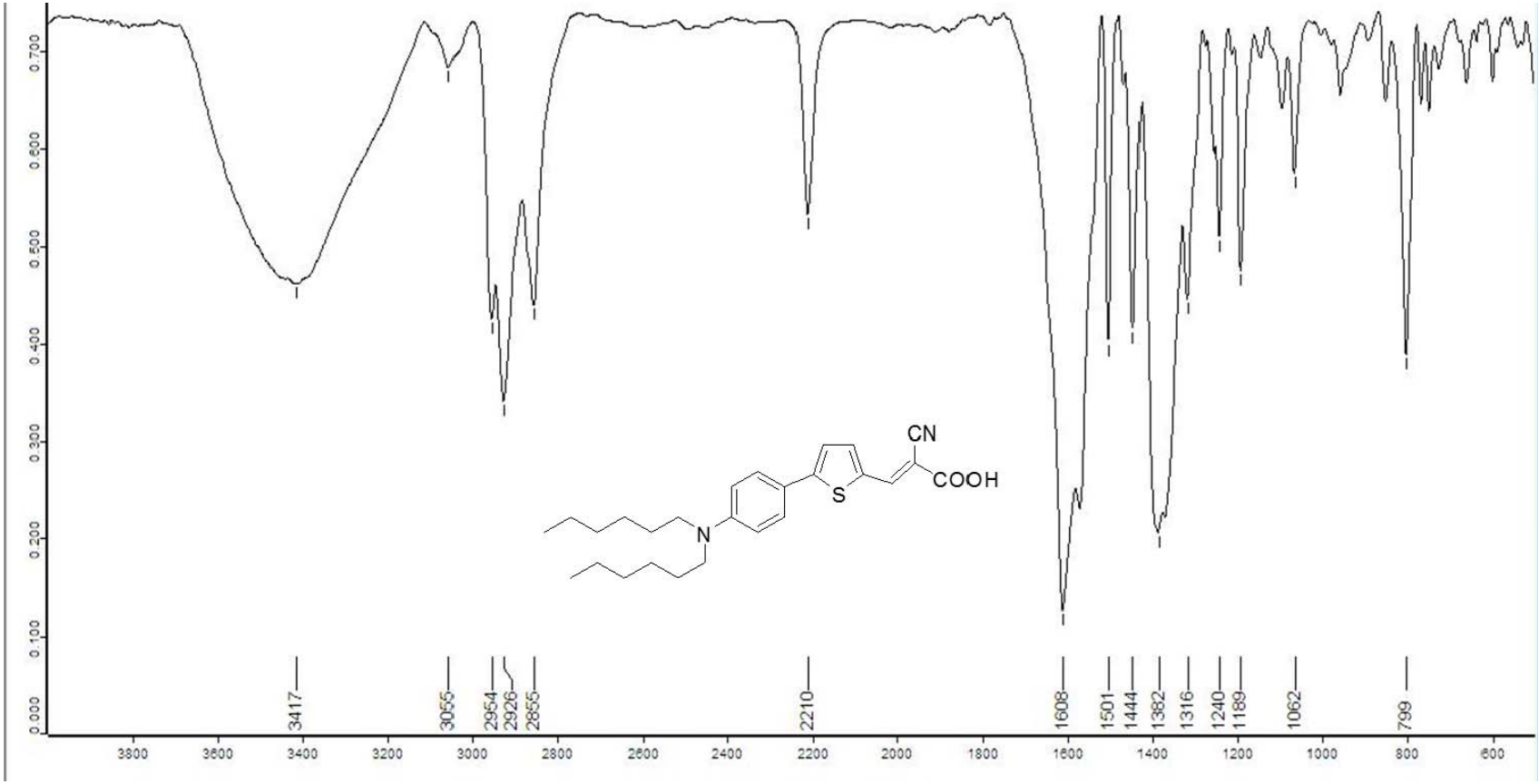
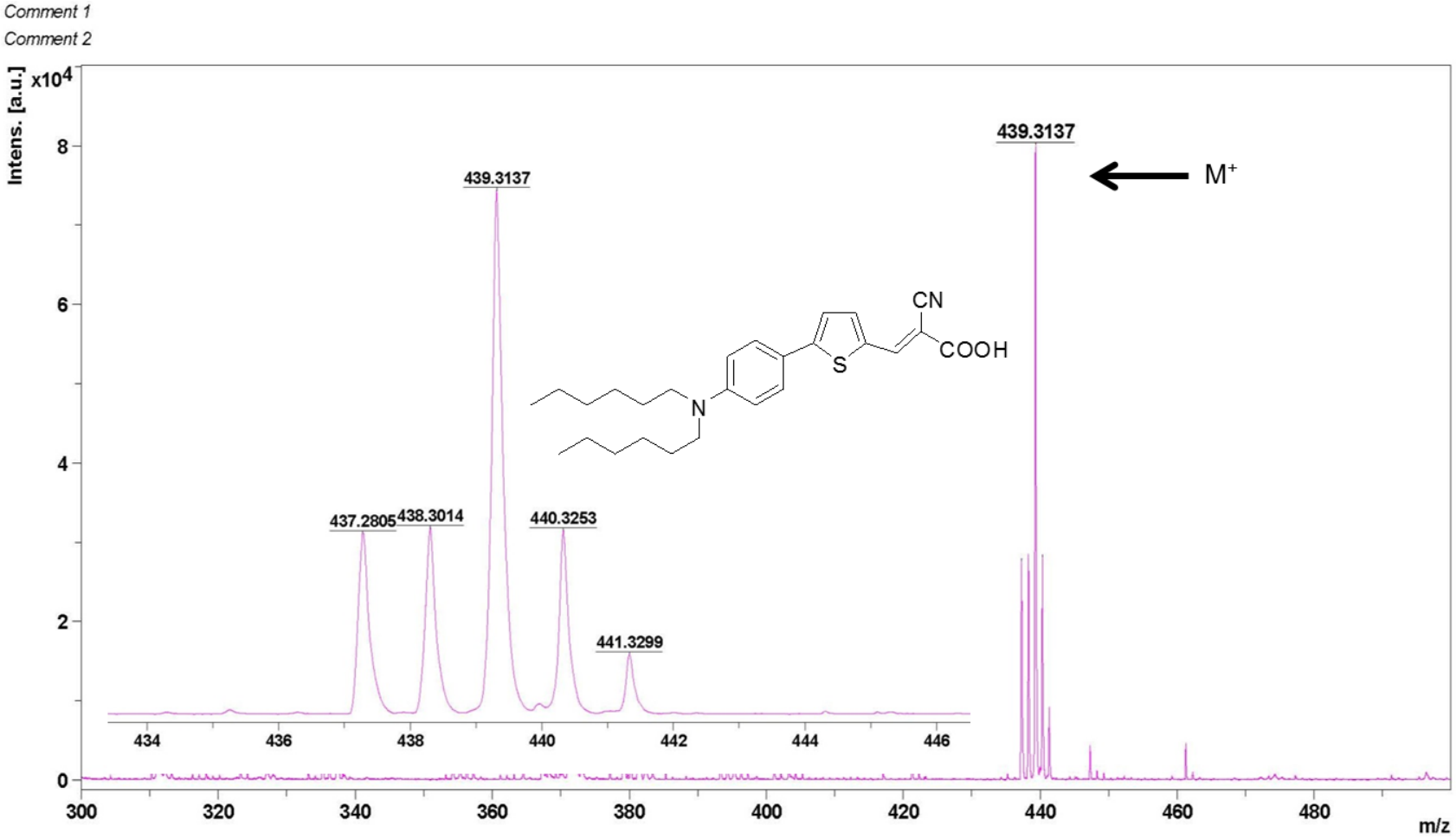
FT-IR & MALDI-TOF of compound **TC1**

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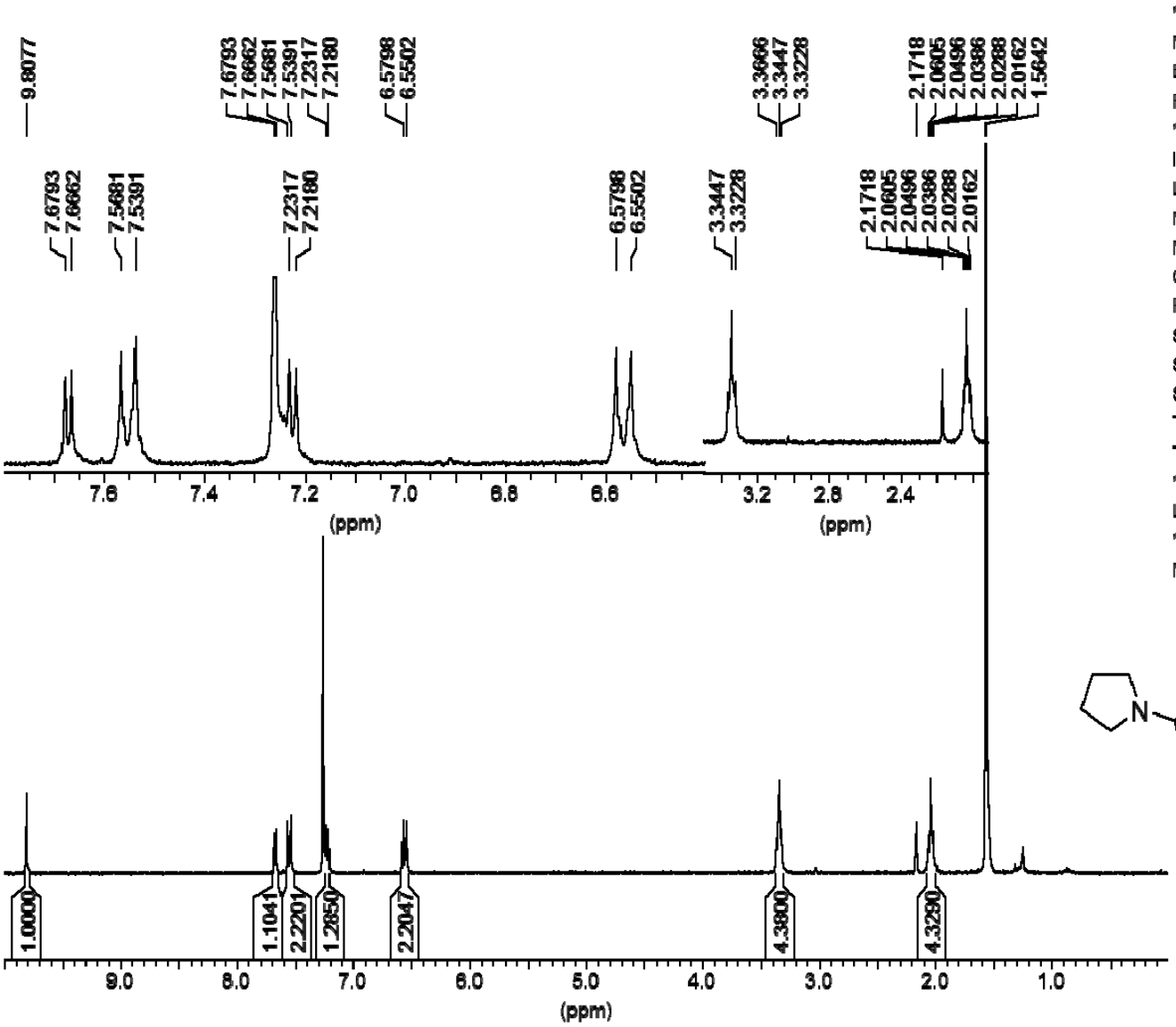
1H & 13C NMR of compound **2b**

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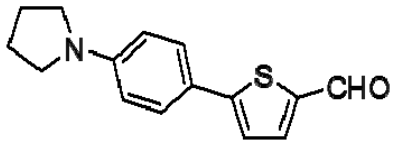

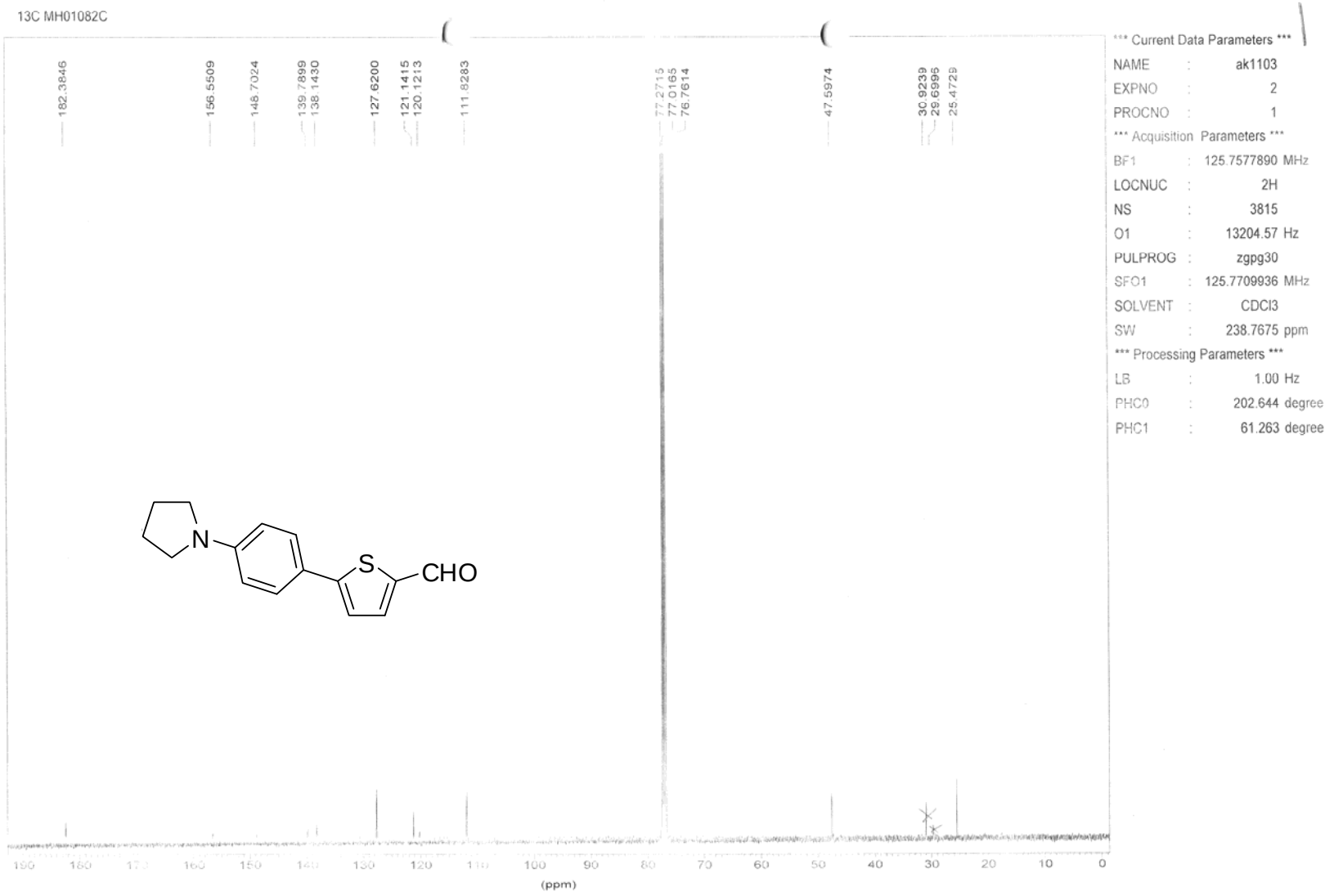
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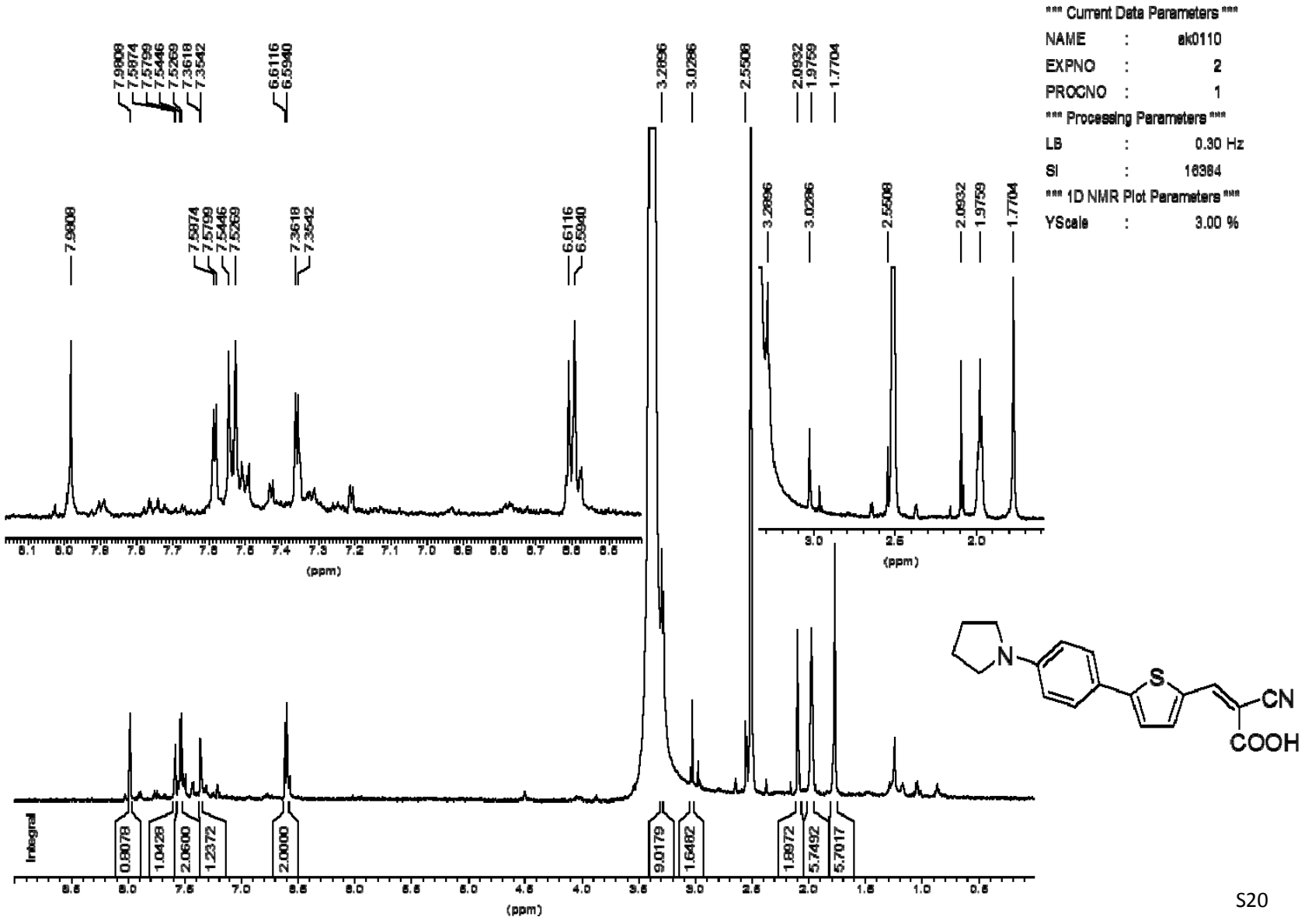
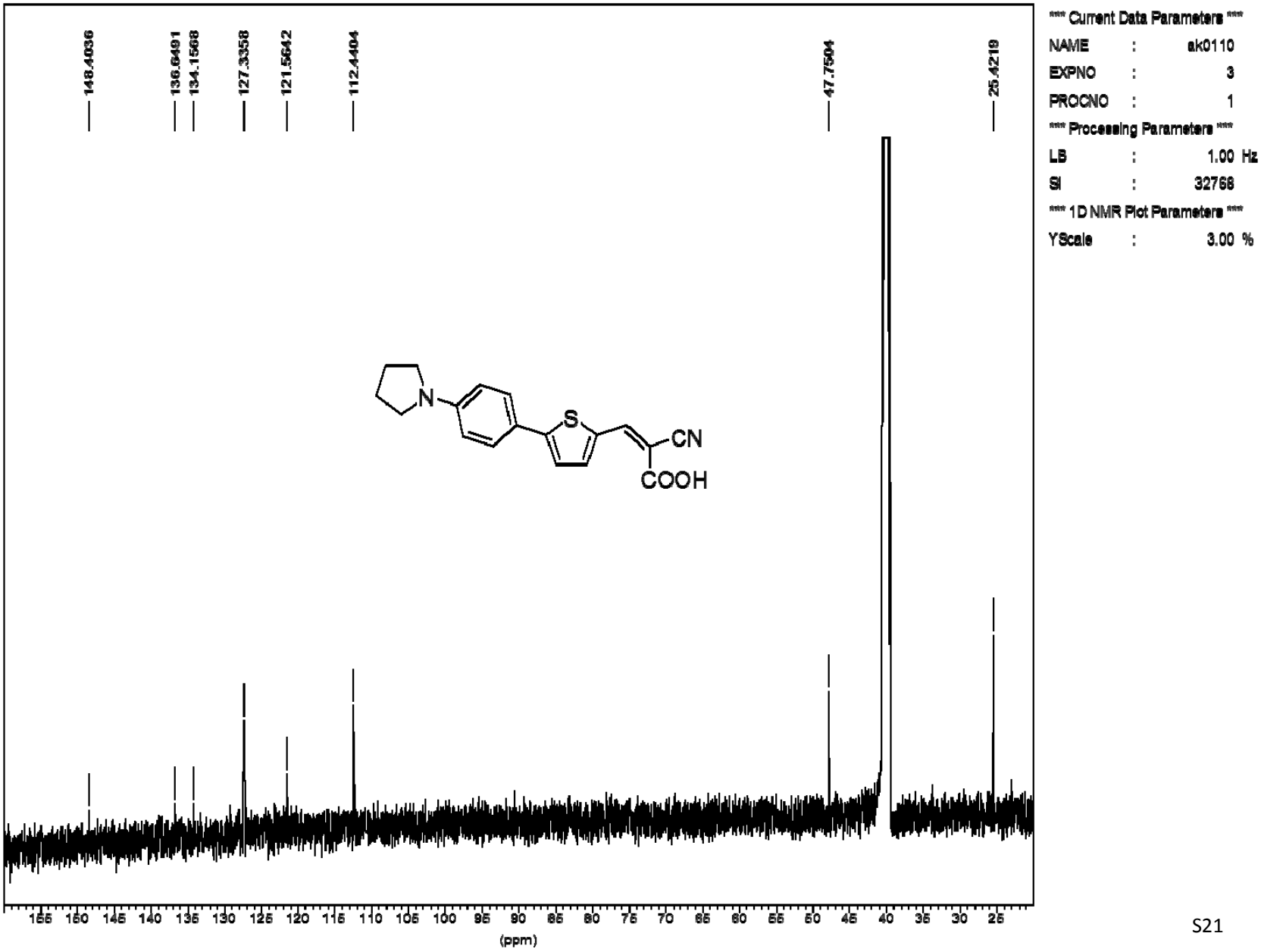
1H & 13C NMR of compound **TC2**

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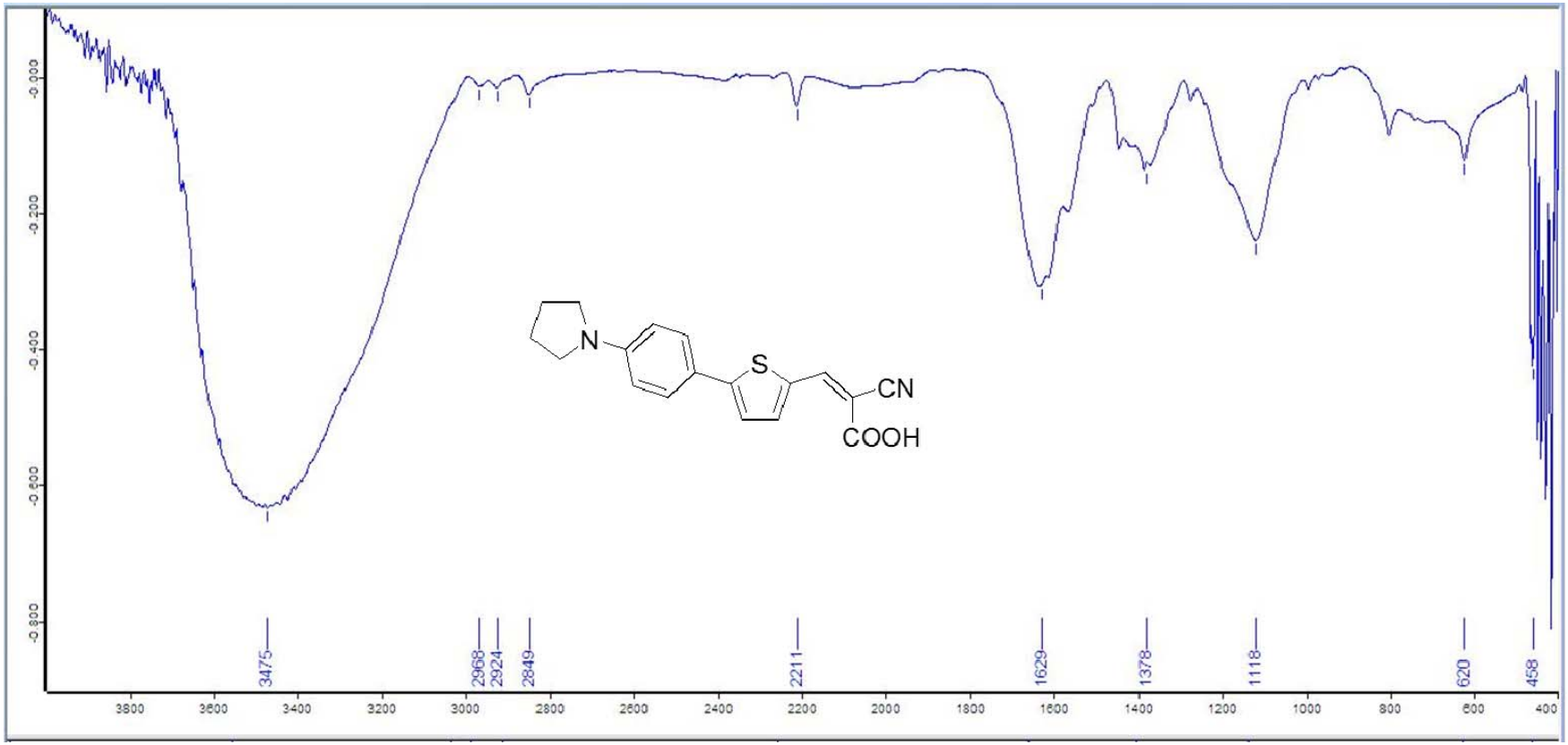

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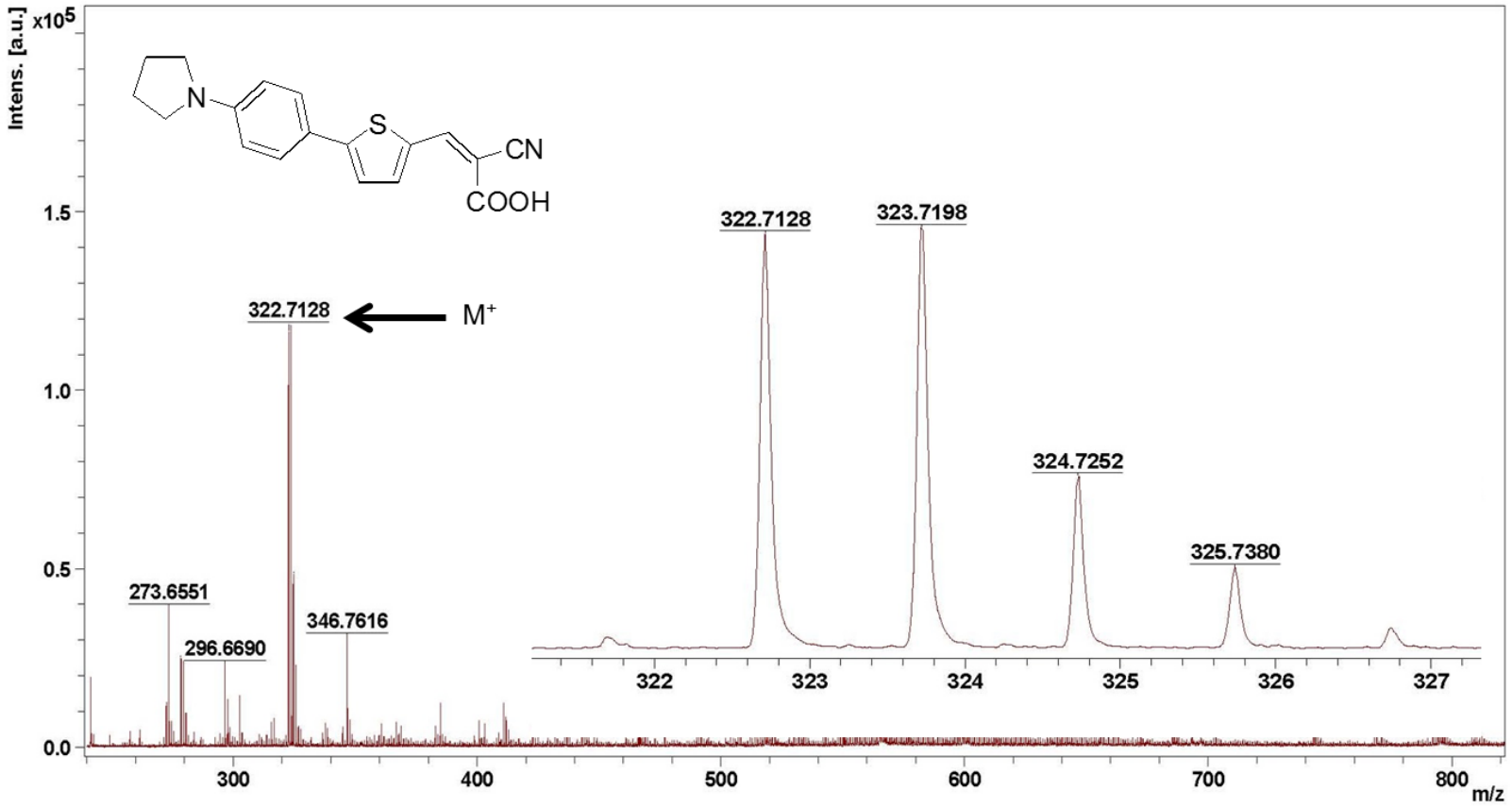

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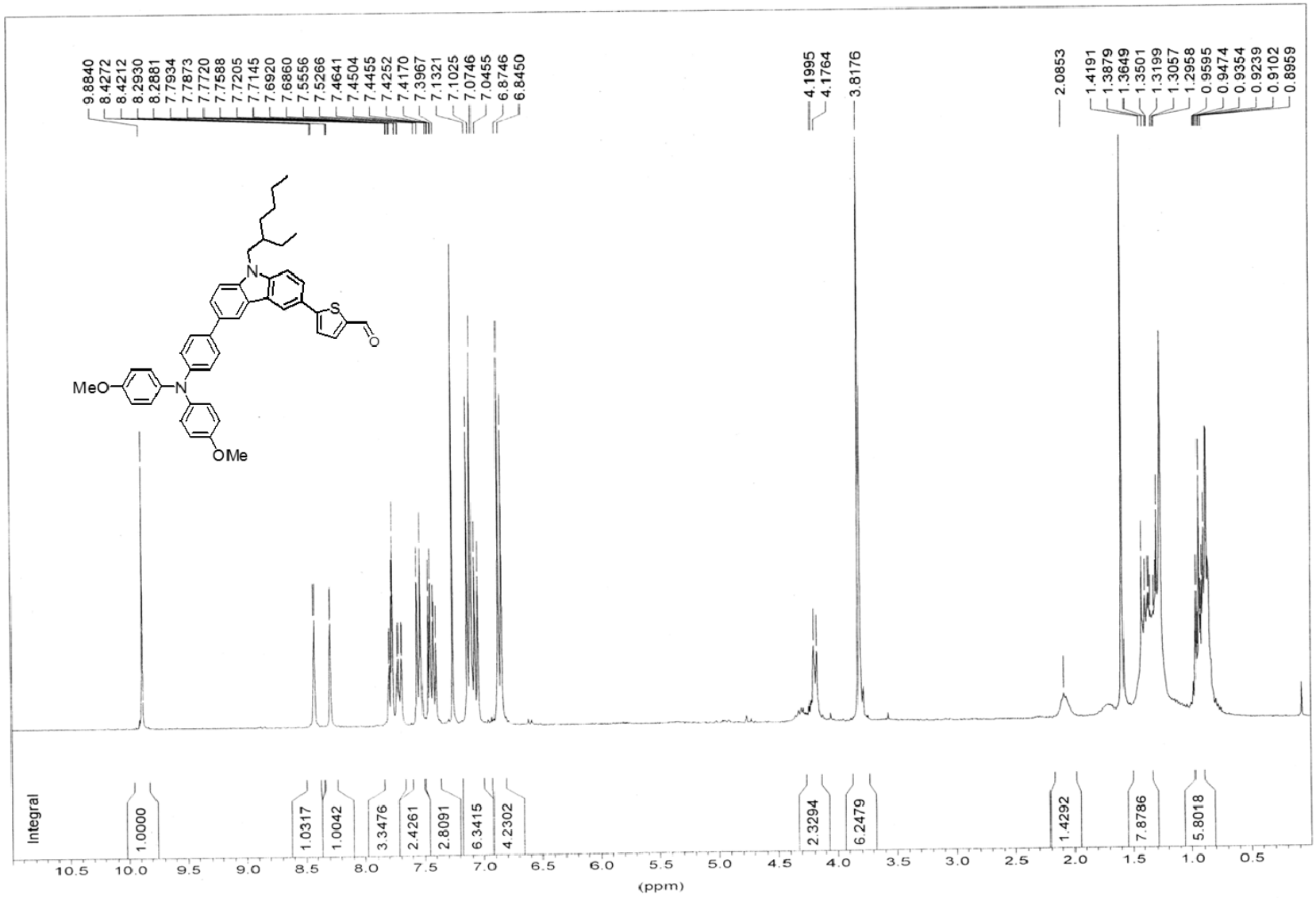

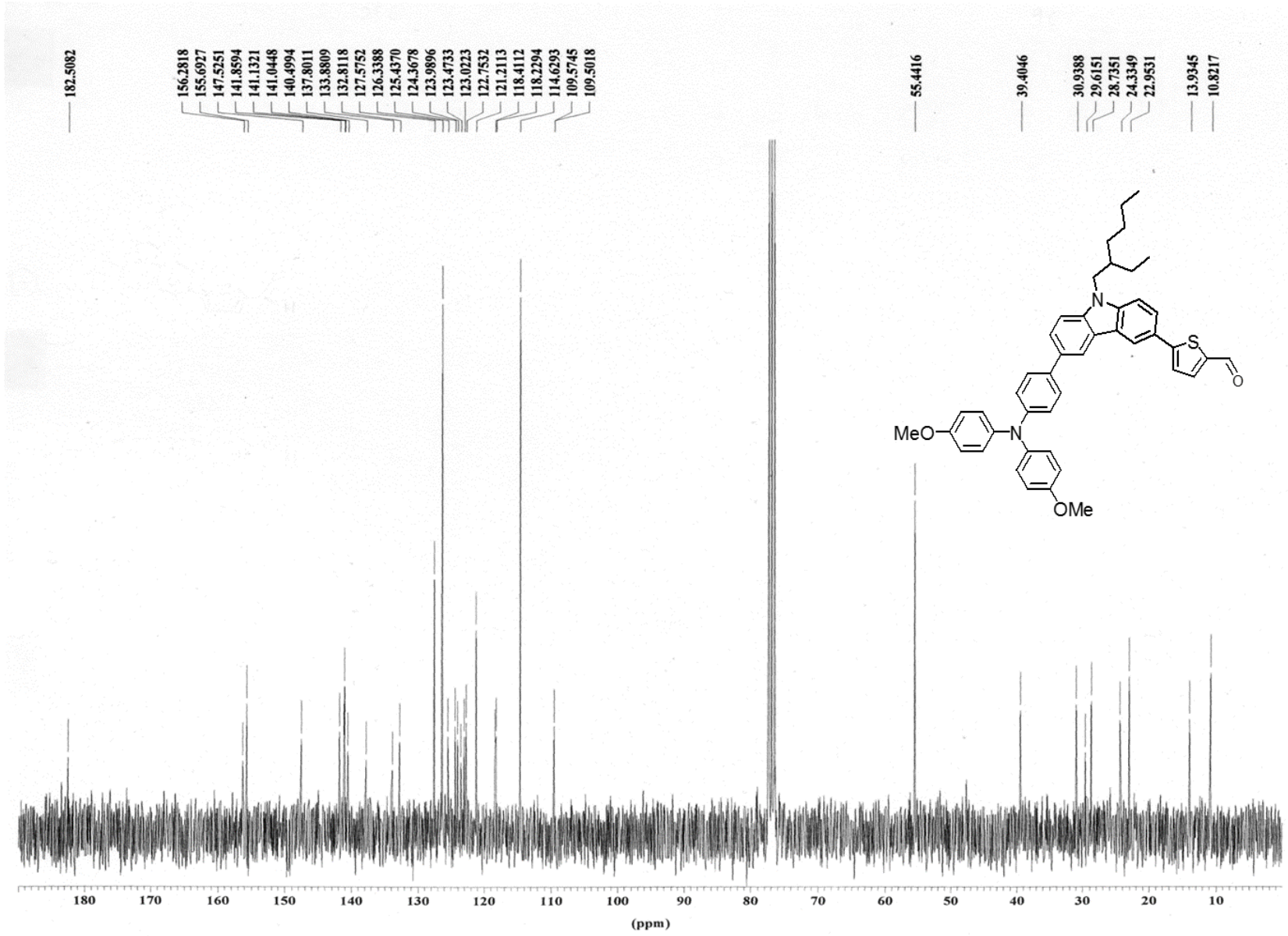
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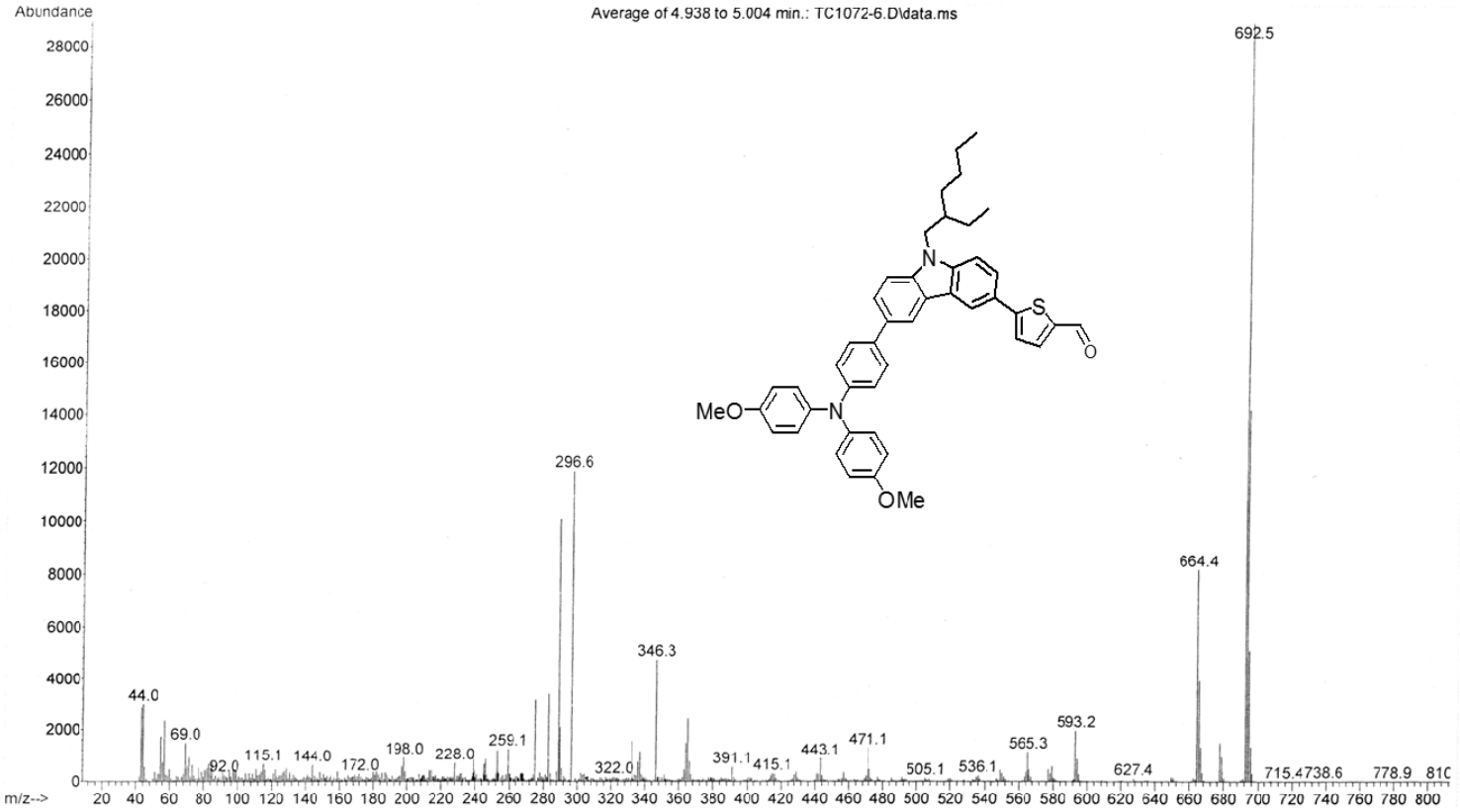
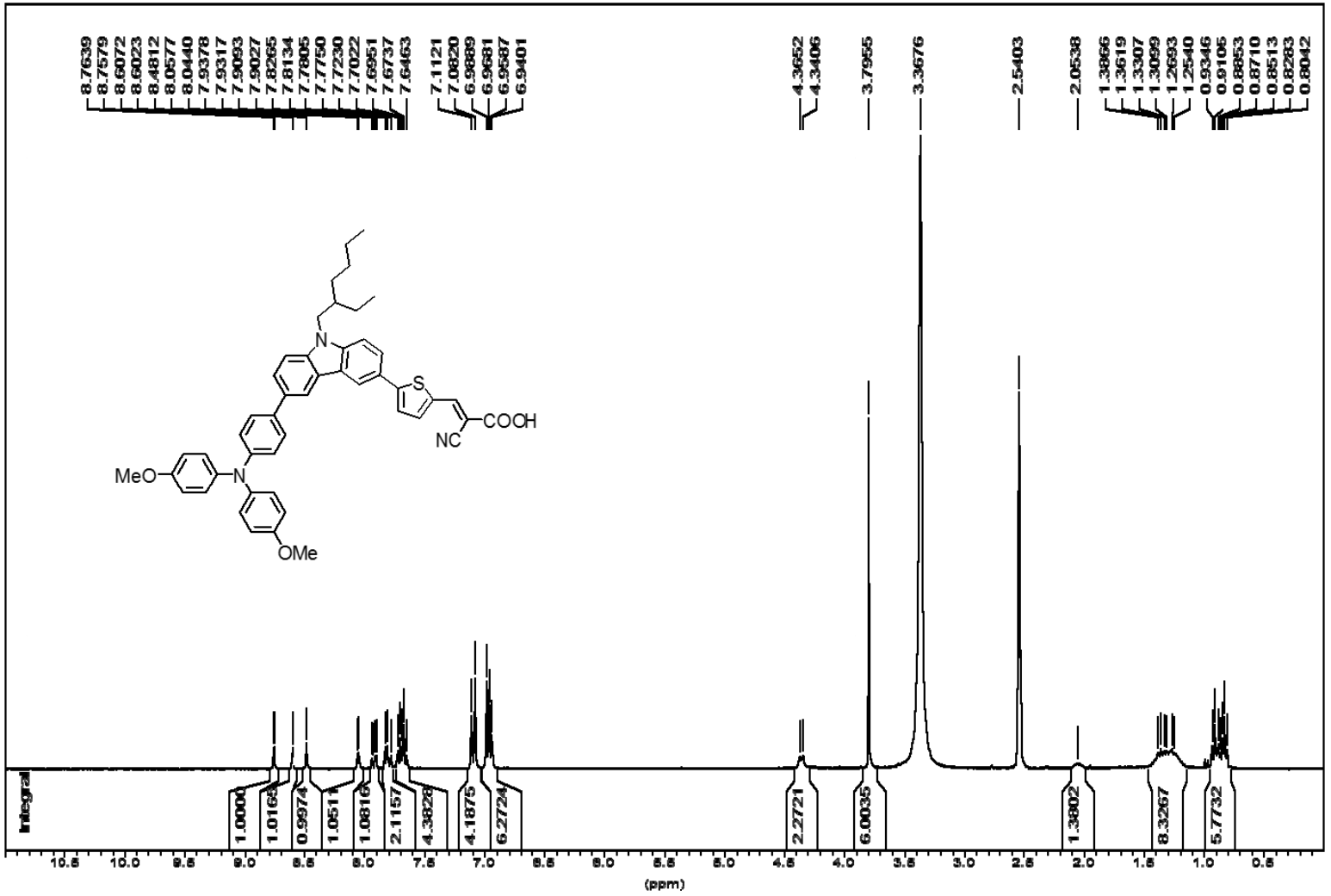
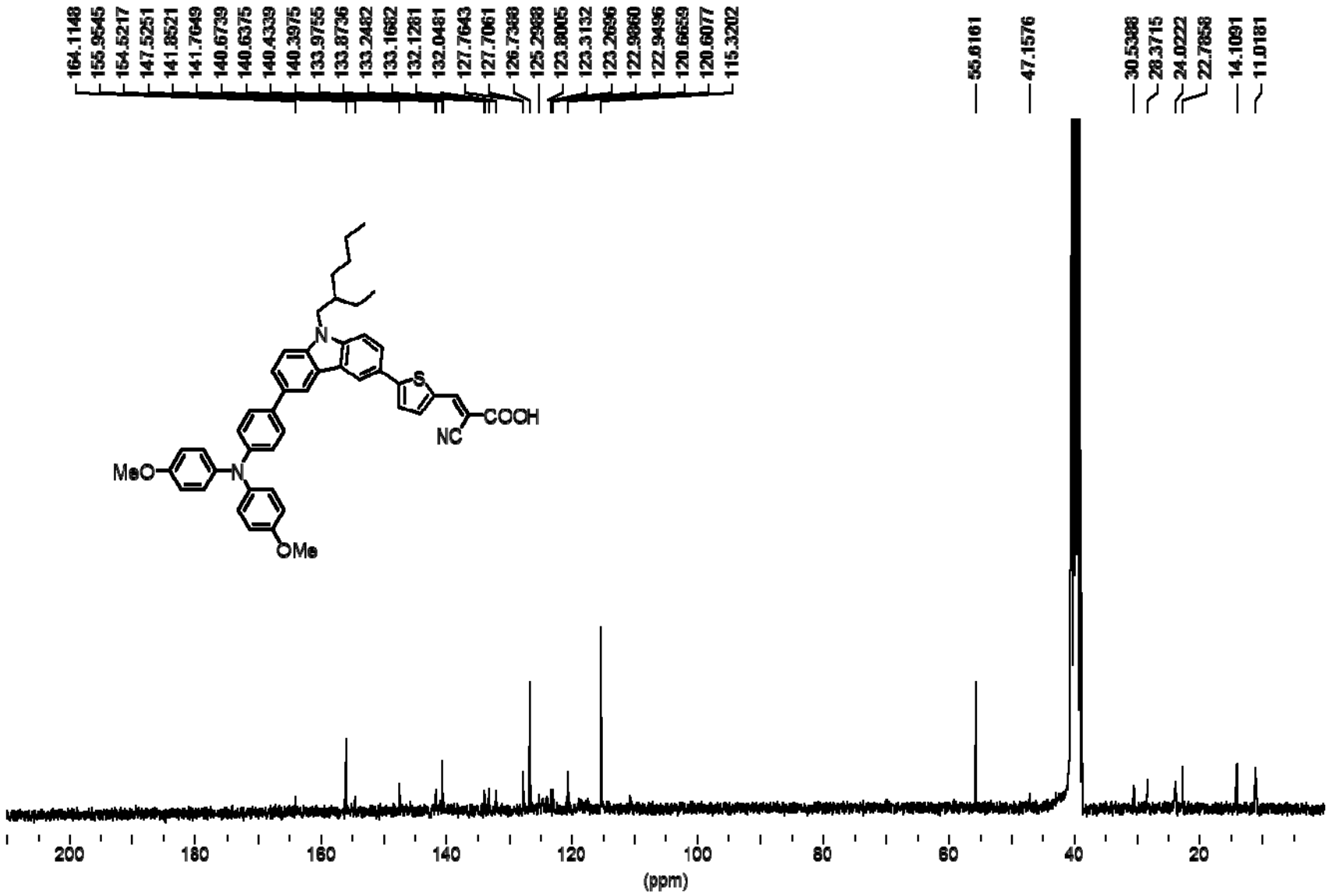
Mass spectra of compound **3c**

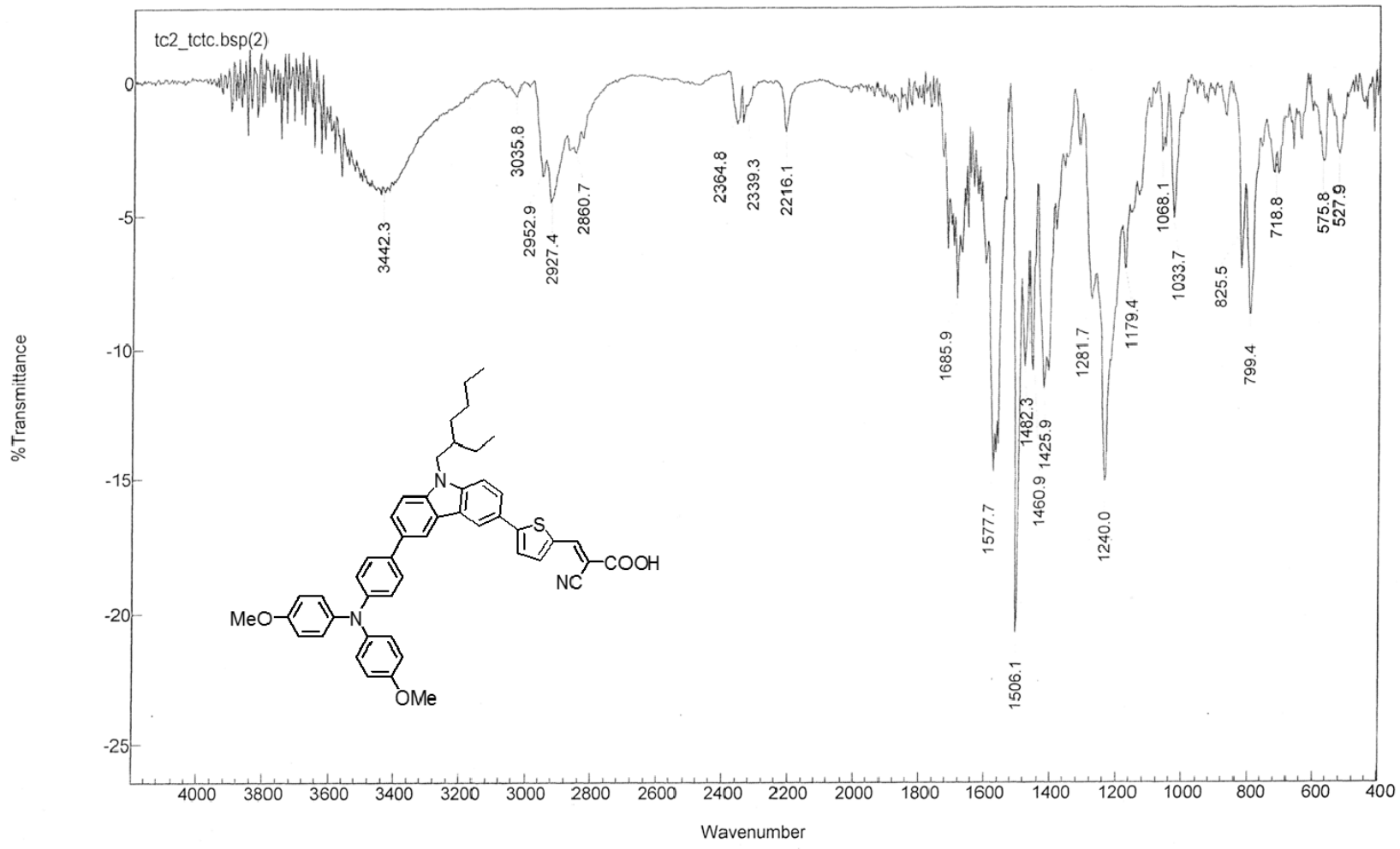


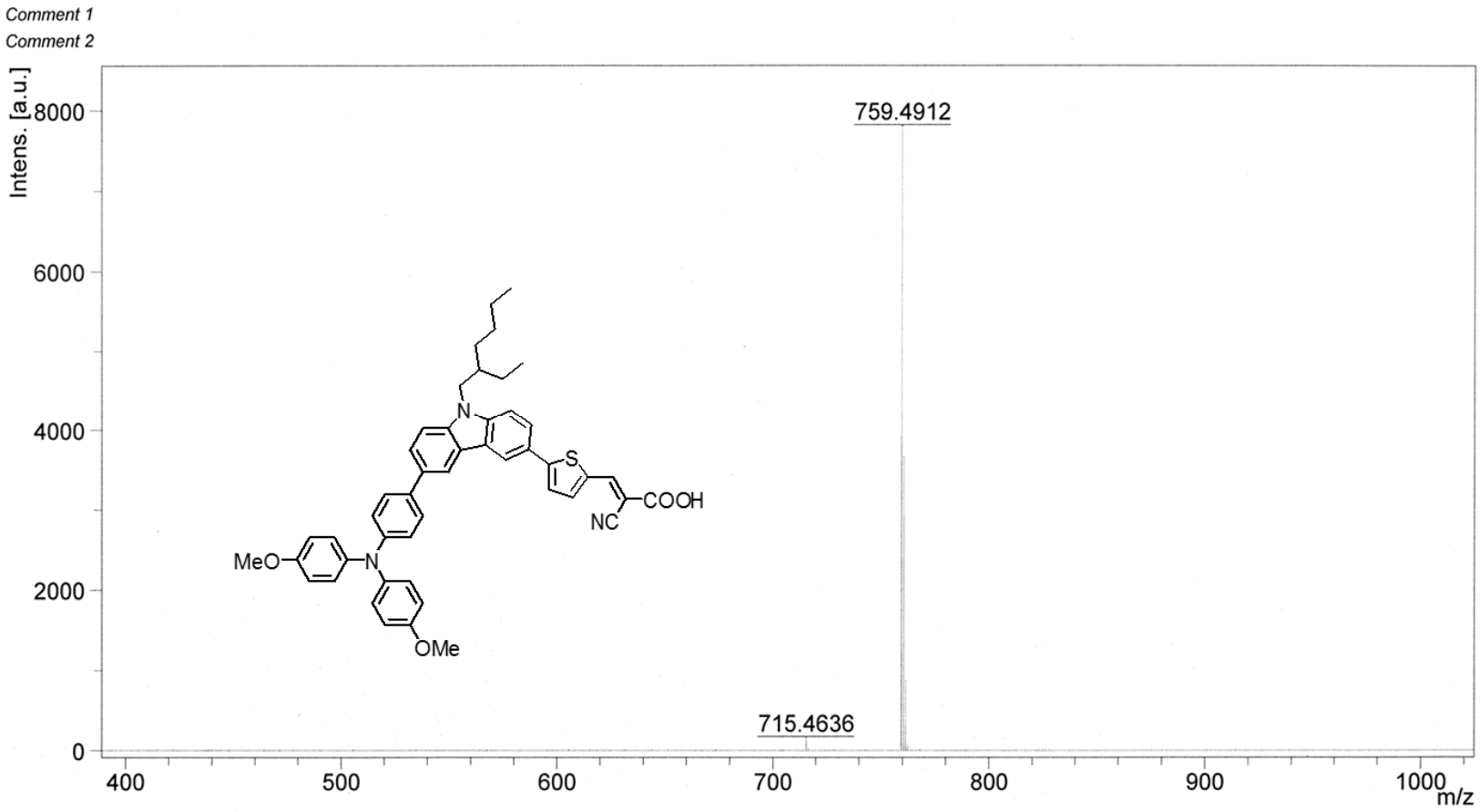
1H & 13C NMR of compound **TC3**



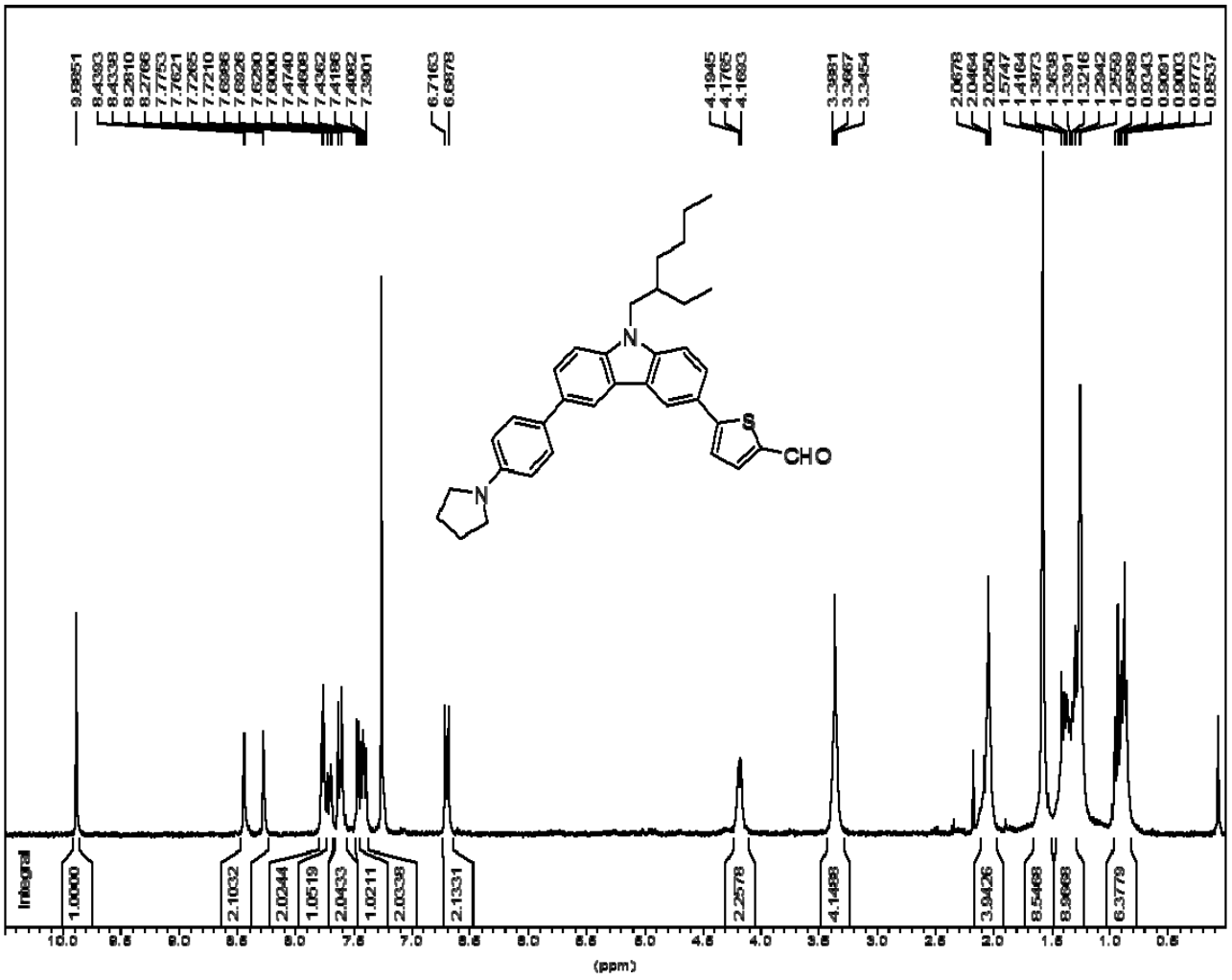

164.1148
155.9545
154.5217
147.5251
141.8521
141.7649
140.6739
140.6375
140.4339
140.3975
133.9755
133.8736
133.2482
133.1682
132.1281
132.0481
127.7643
127.7061
126.7368
125.2968
123.8805
123.3132
123.2696
122.9860
122.9496
120.6659
120.6077
115.3202
55.6161
47.1576
30.5388
28.3715
24.0222
22.7858
14.1091
11.0181
N
S
COOH
NC
MeO
N
OMe
200
180
160
140
120
100
80
60
40
20
(ppm)

FT-IR & MALDI-TOF of compound **TC3**




Comment 1
Comment 2
Intens. [a.u.]
8000
6000
4000
2000
0
759.4912
715.4636
400
500
600
700
800
900
1000
m/z
N
S
COOH
NC
MeO
N
OMe

1H & 13C NMR of compound **3b**



*** Current Data Parameters ***

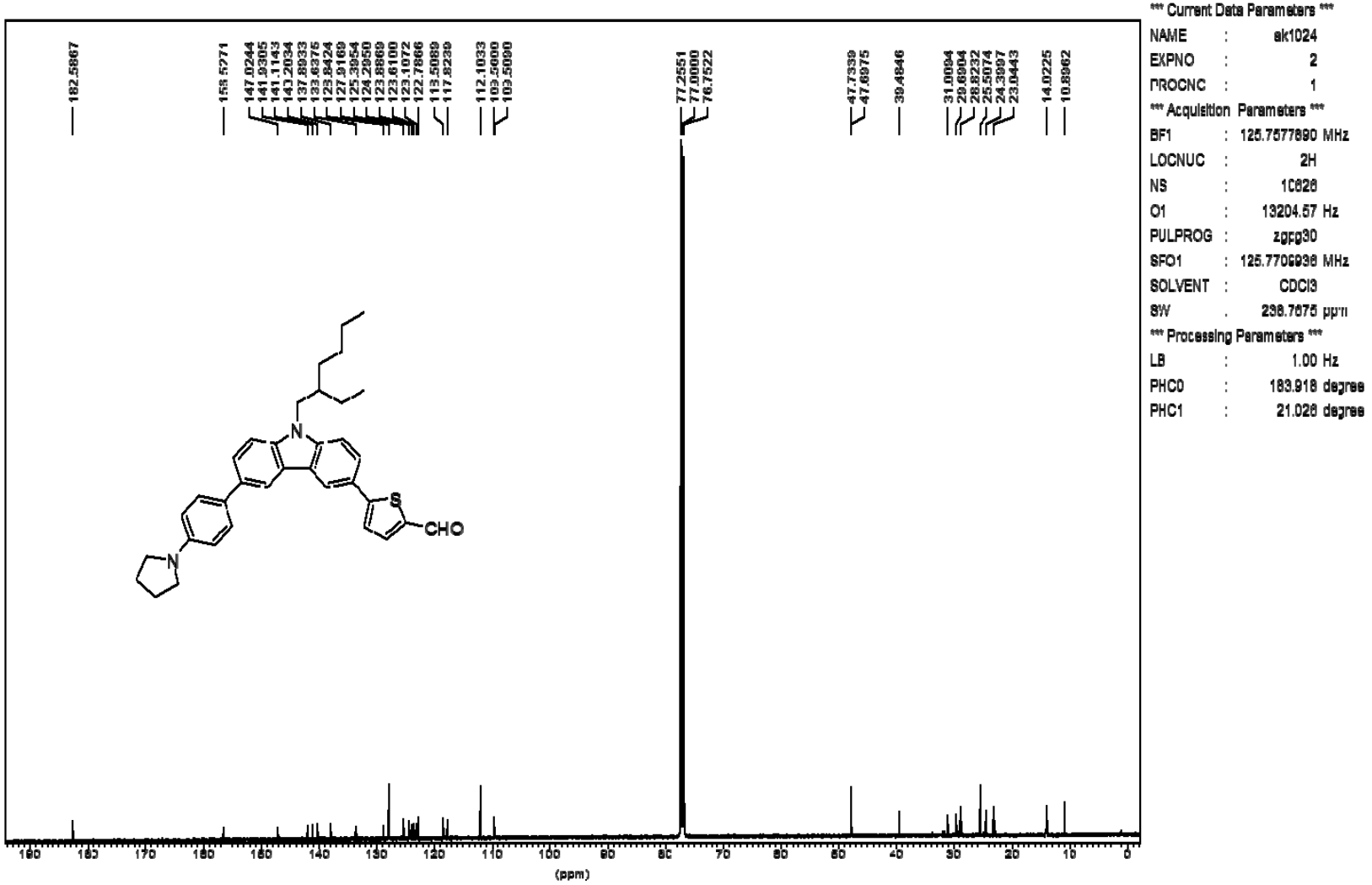
NAME	:	oc24cmh
EXPNO	:	3
PROCNO	:	1

*** Acquisition Parameters ***

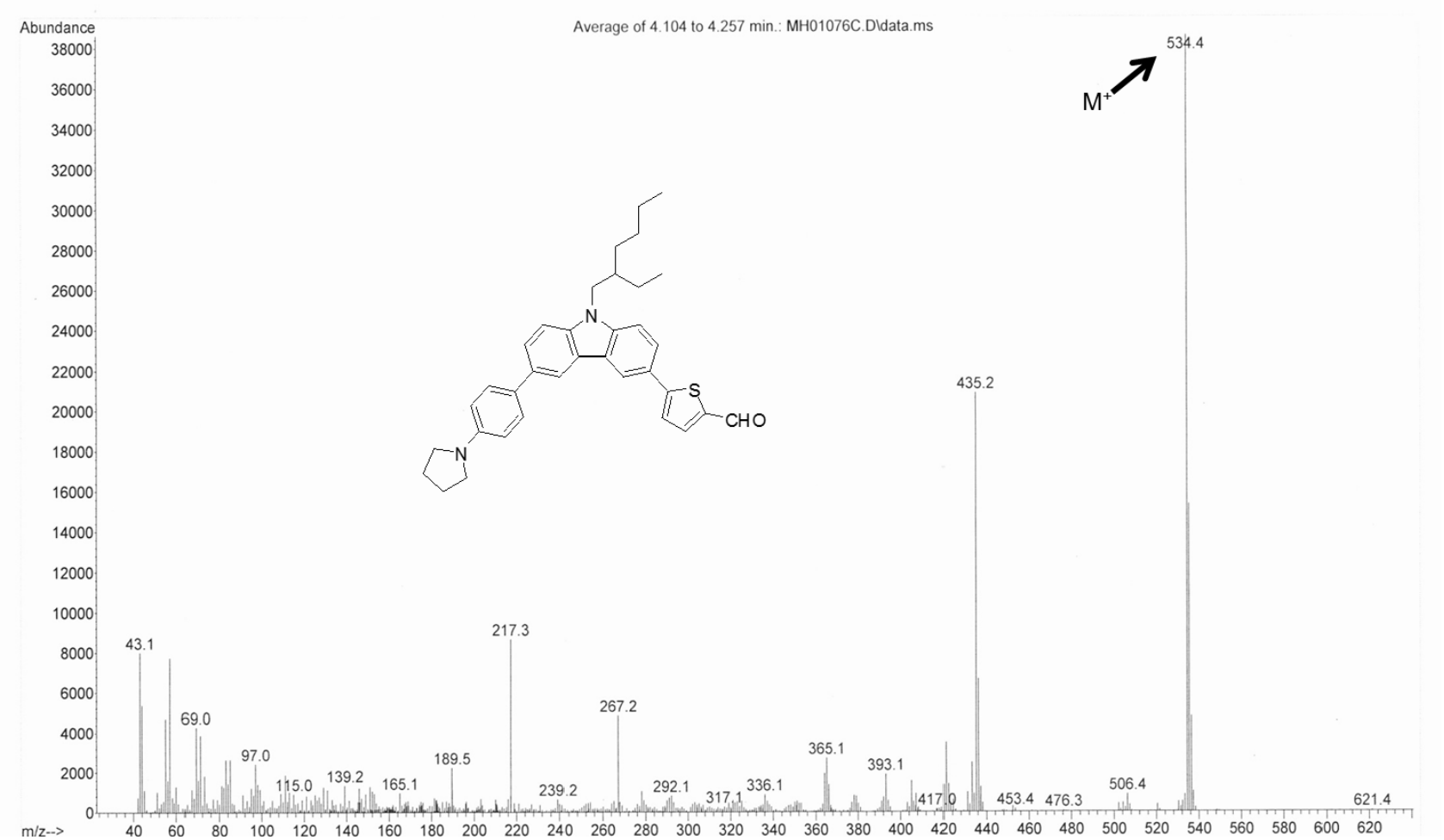
BF1	:	300.1300000 MHz
LOCNUC	:	2H
NS	:	8
O1	:	1853.43 Hz
PULPROG	:	zg30
SFO1	:	300.1318534 MHz
SOLVENT	:	CDCl3
SW	:	17.9519 ppm

*** Processing Parameters ***

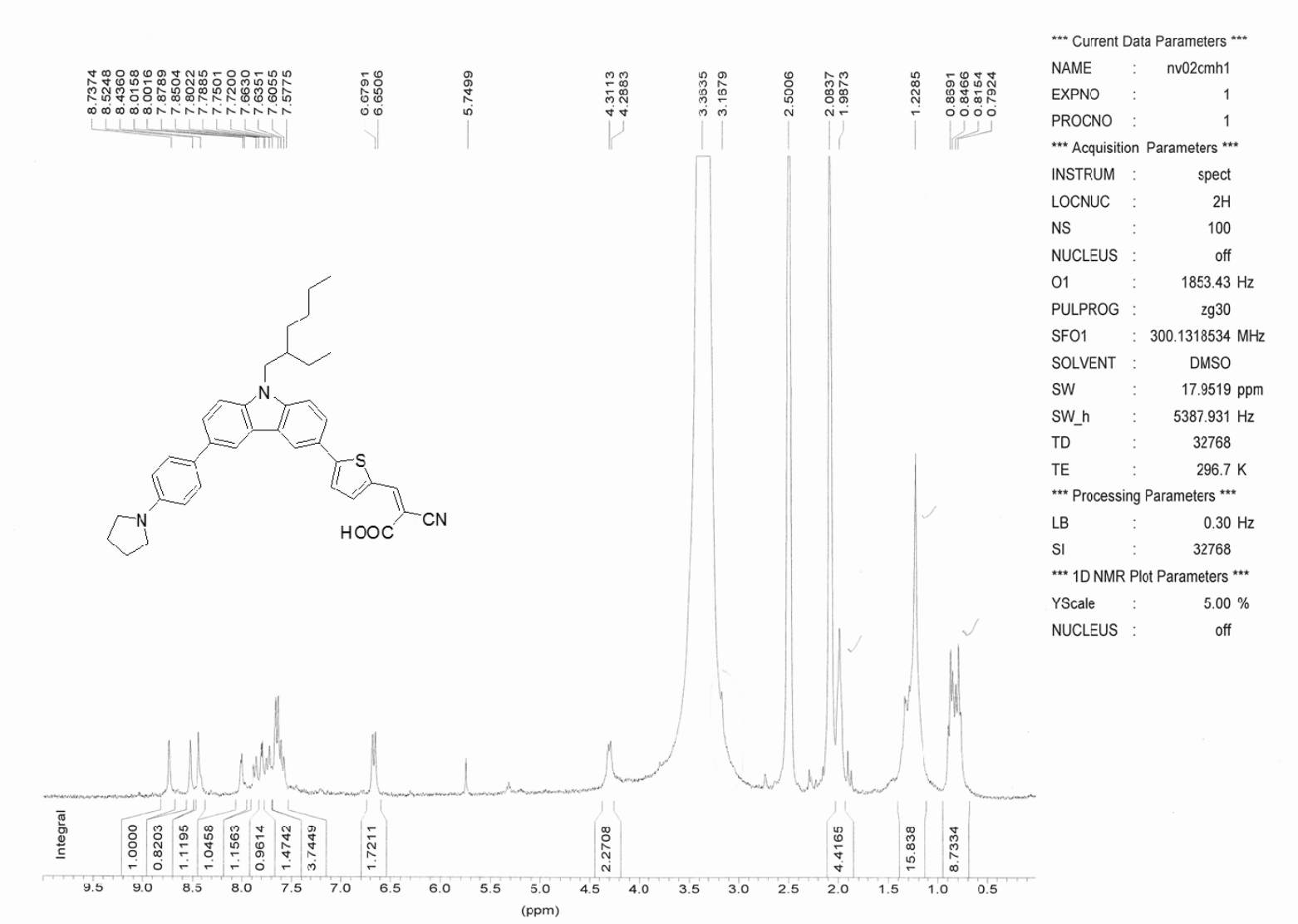
LB	:	0.30 Hz
PHC0	:	303.400 degree
PHC1	:	-0.157 degree


13C AMX500 MH01073C
182.5867
158.5771
147.0244
141.9305
141.1143
140.2034
137.8933
133.6375
129.8424
127.9169
125.3954
124.2950
123.8869
123.6100
123.1072
122.7866
113.5089
117.8239
112.1033
109.5000
109.5090
77.2551
77.0000
76.7522
47.7339
47.6975
39.4846
31.0094
29.6904
28.8232
25.5074
24.3997
23.0443
14.0225
10.8962
S
N
N
CHO
(ppm)
*** Current Data Parameters ***
NAME : ak1024
EXPNO : 2
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 125.7577890 MHz
LOCNUC : 2H
NS : 10628
O1 : 13204.57 Hz
PULPROG : zgpg30
SFO1 : 125.7706936 MHz
SOLVENT : CDCl3
SW : 238.7675 ppm
*** Processing Parameters ***
LB : 1.00 Hz
PHC0 : 183.918 degree
PHC1 : 21.028 degree

Mass spectra of compound **3b**



1H NMR & FT-IR of compound **TC4**



*** Current Data Parameters ***

NAME	:	nv02cmh1
EXPNO	:	1
PROCNO	:	1

*** Acquisition Parameters ***

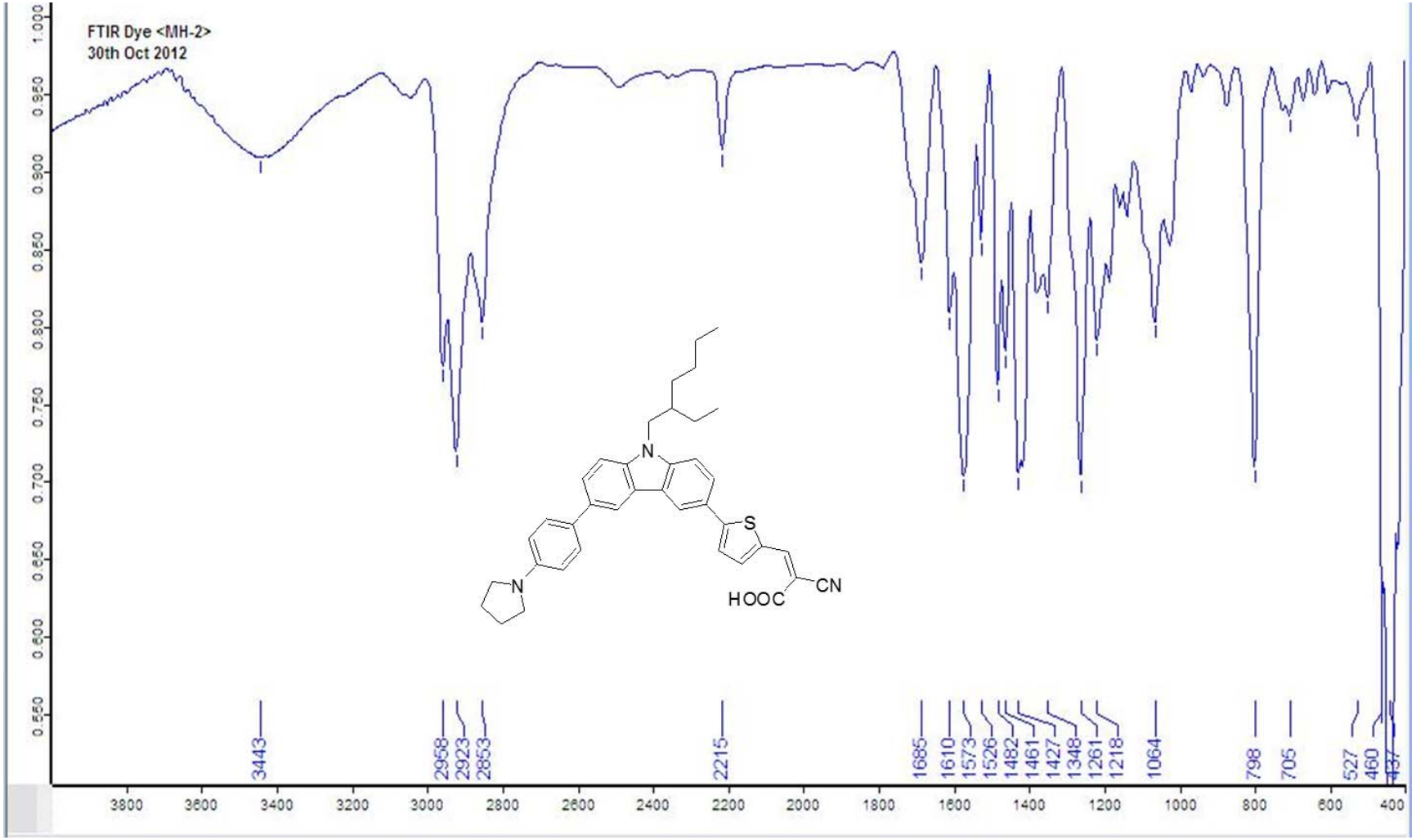
INSTRUM	:	spect
LOCNUC	:	2H
NS	:	100
NUCLEUS	:	off
O1	:	1853.43 Hz
PULPROG	:	zg30
SFO1	:	300.1318534 MHz
SOLVENT	:	DMSO
SW	:	17.9519 ppm
SW_h	:	5387.931 Hz
TD	:	32768
TE	:	296.7 K

*** Processing Parameters ***

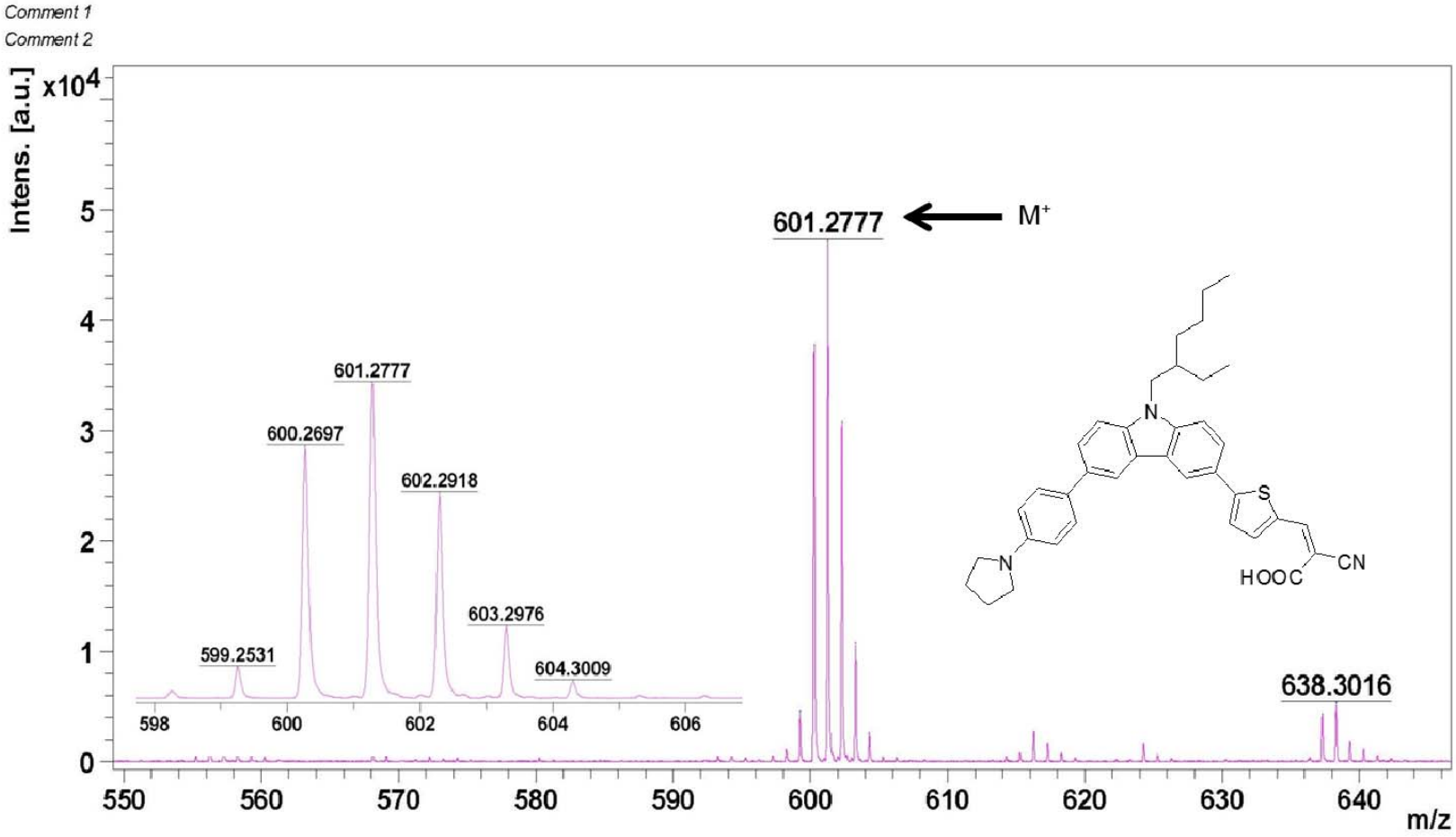
LB	:	0.30 Hz
SI	:	32768

*** 1D NMR Plot Parameters ***

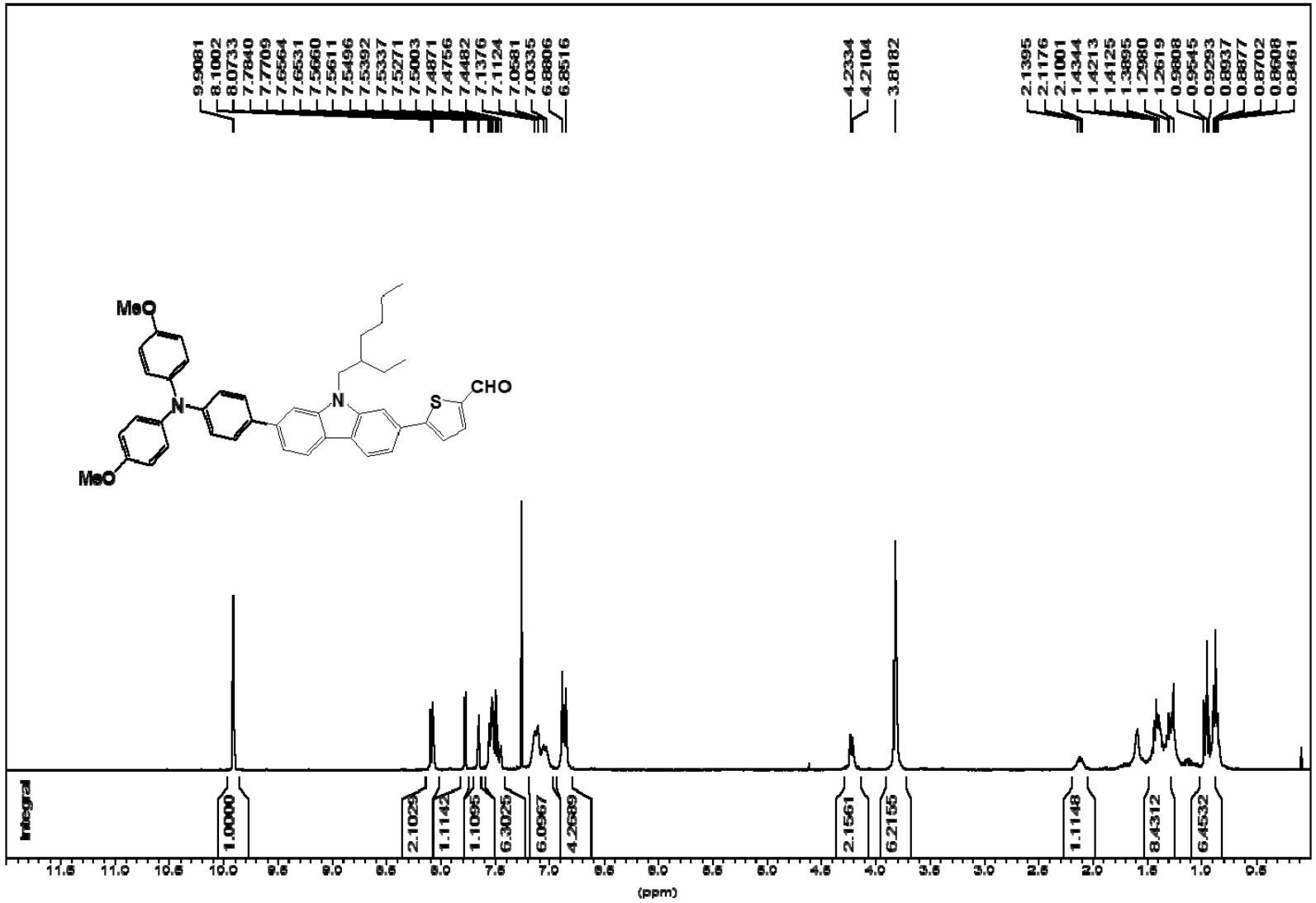
YScale	:	5.00 %
NUCLEUS	:	off

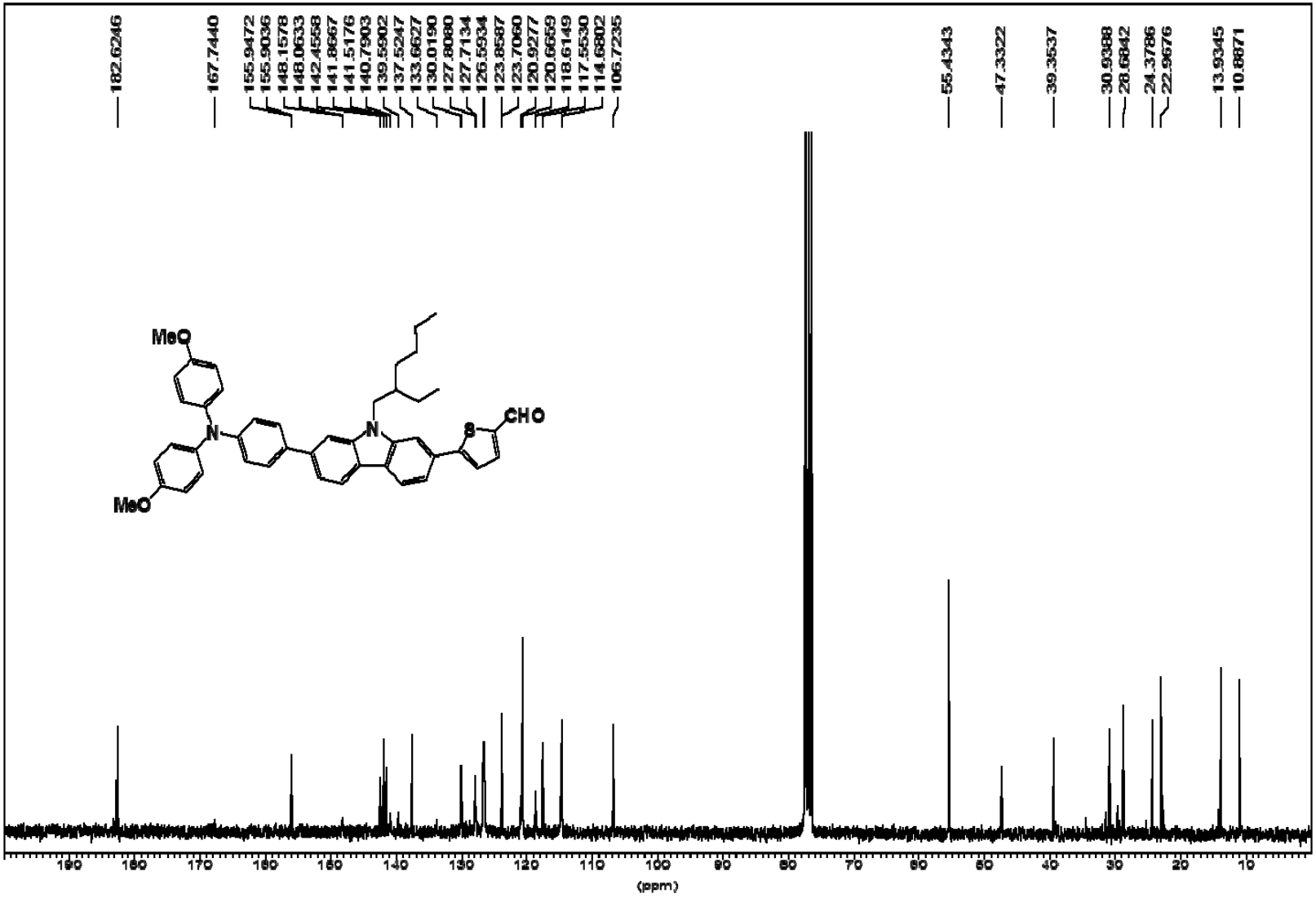

FTIR Dye <MH-2>
30th Oct 2012
1.000
0.950
0.900
0.850
0.800
0.750
0.700
0.650
0.600
0.550
3443
2958
2923
2853
2215
1685
1610
1573
1526
1482
1461
1427
1348
1261
1218
1064
798
705
527
460
437
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
N
S
N
HOOC
CN

MALDI-TOF of compound **TC4**

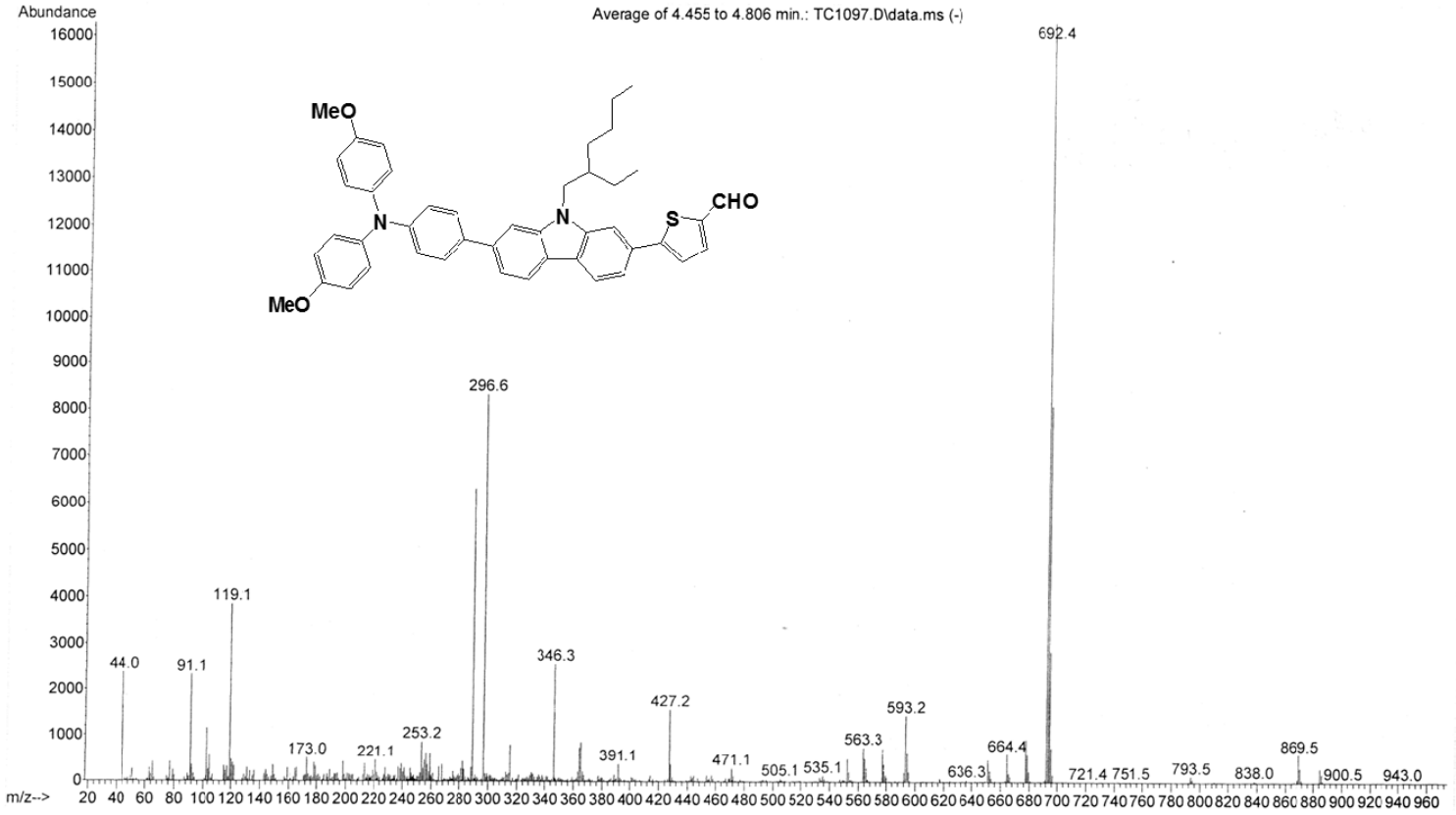


1H & 13C NMR of compound **4**

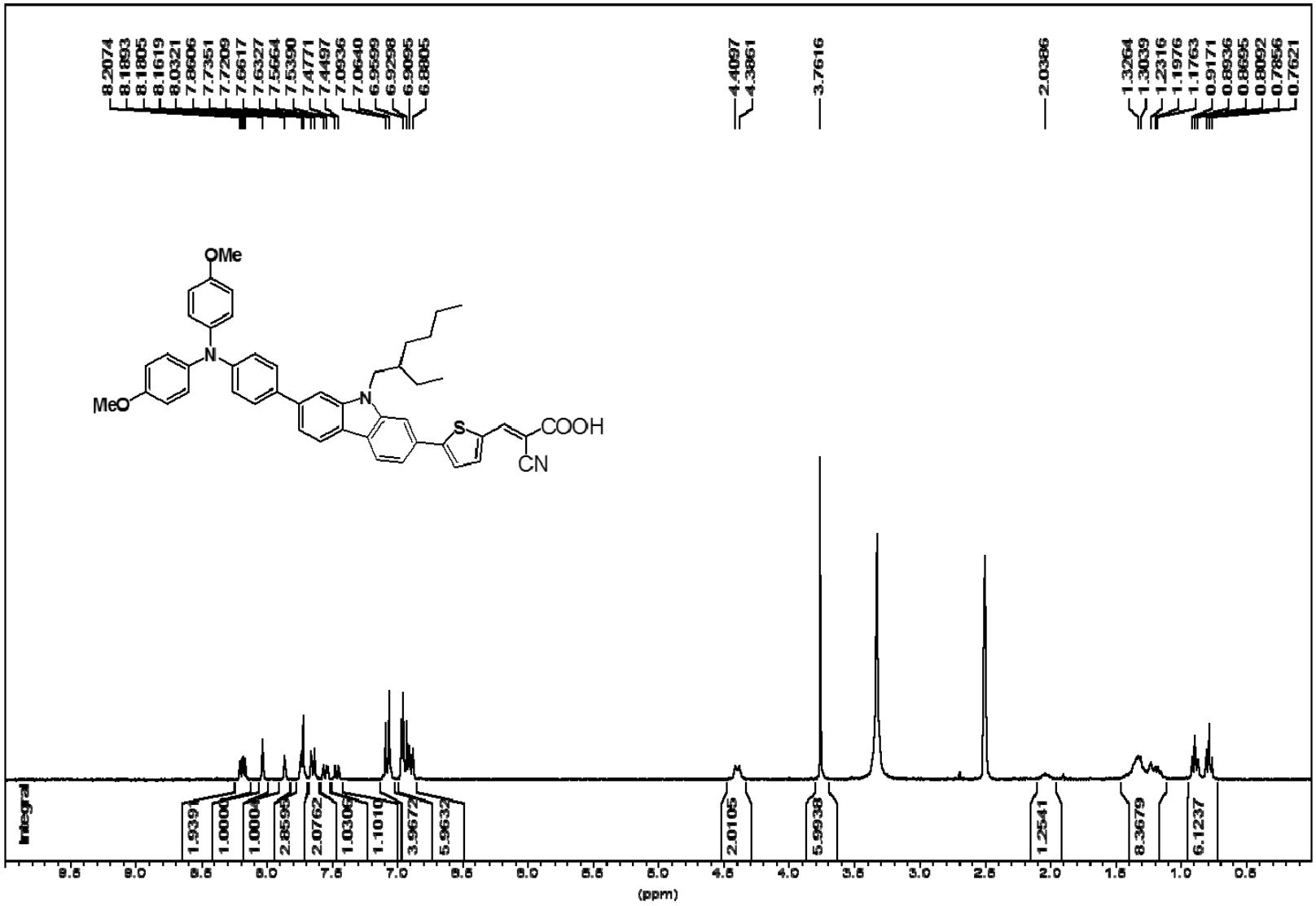


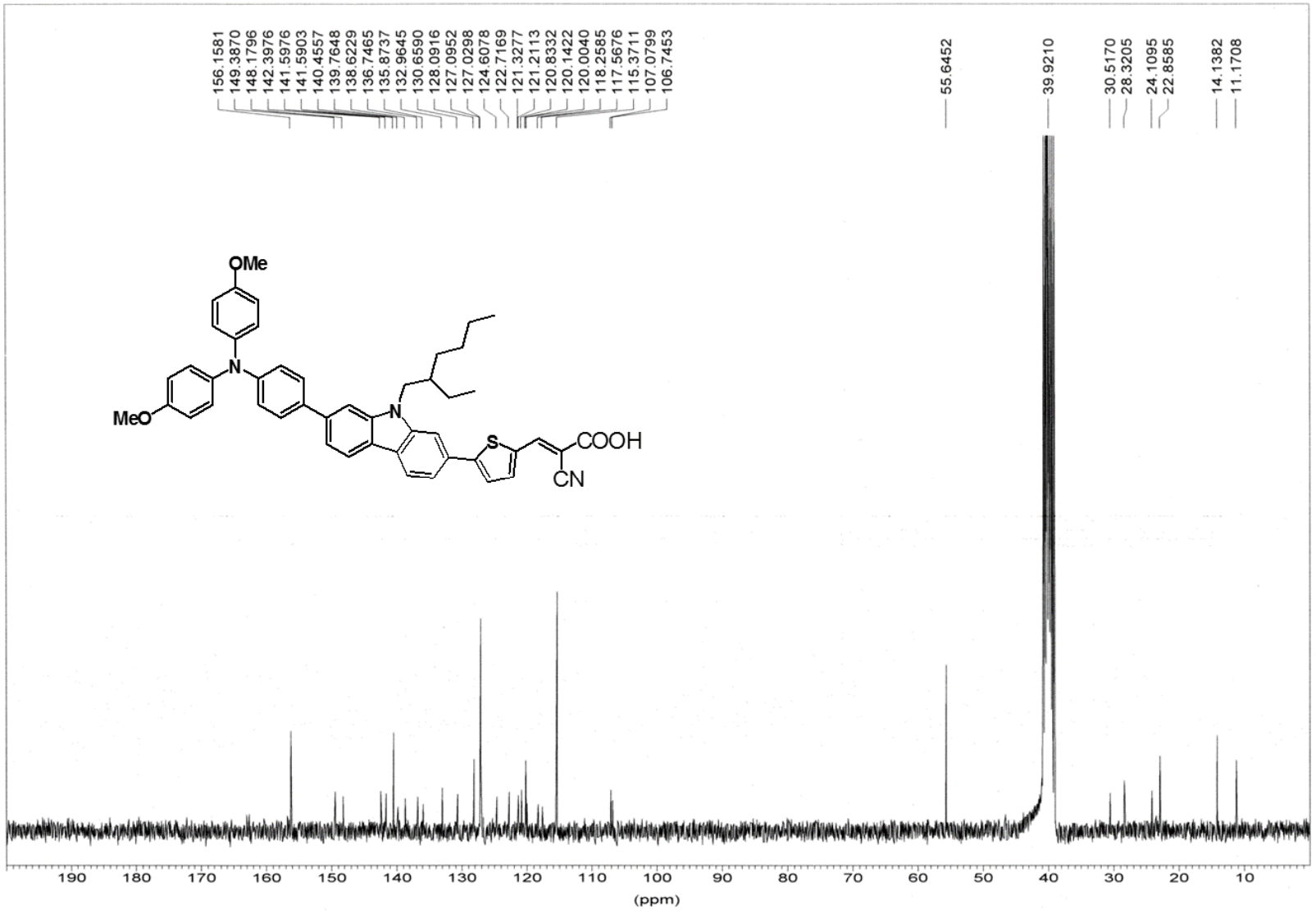

182.6246
167.7440
155.9472
155.9036
148.1578
148.0633
142.4558
141.8667
141.5176
140.7903
139.5902
137.5247
133.6627
130.0190
127.8080
127.7134
126.5934
123.8587
123.7060
120.9277
120.6659
118.6149
117.5530
114.6802
106.7235
55.4343
47.3322
39.3537
30.9388
28.6842
24.3786
22.9676
13.9345
10.8871
MeO
MeO
N
N
S
CHO
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

Mass spectra of compound **4**

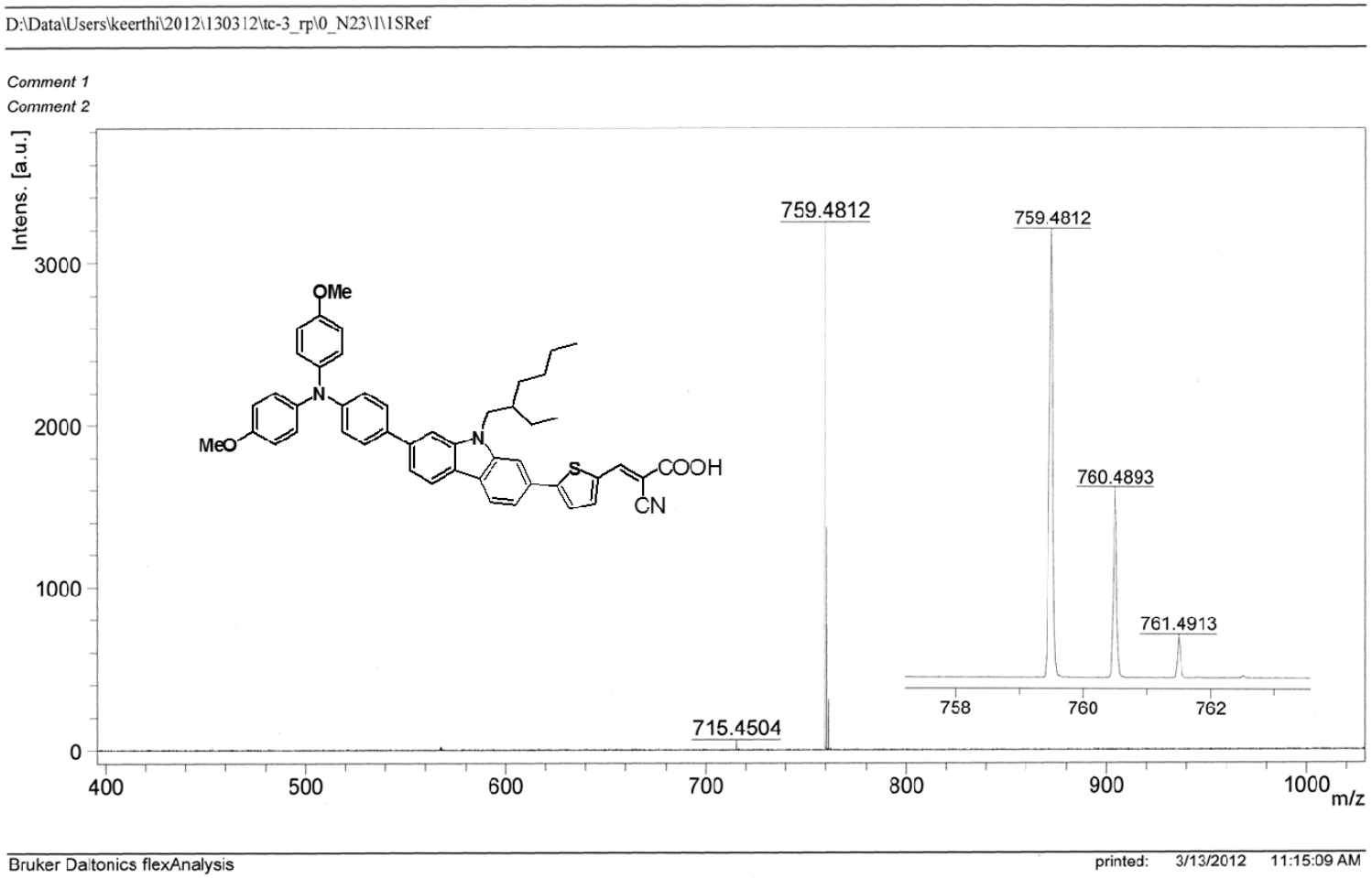


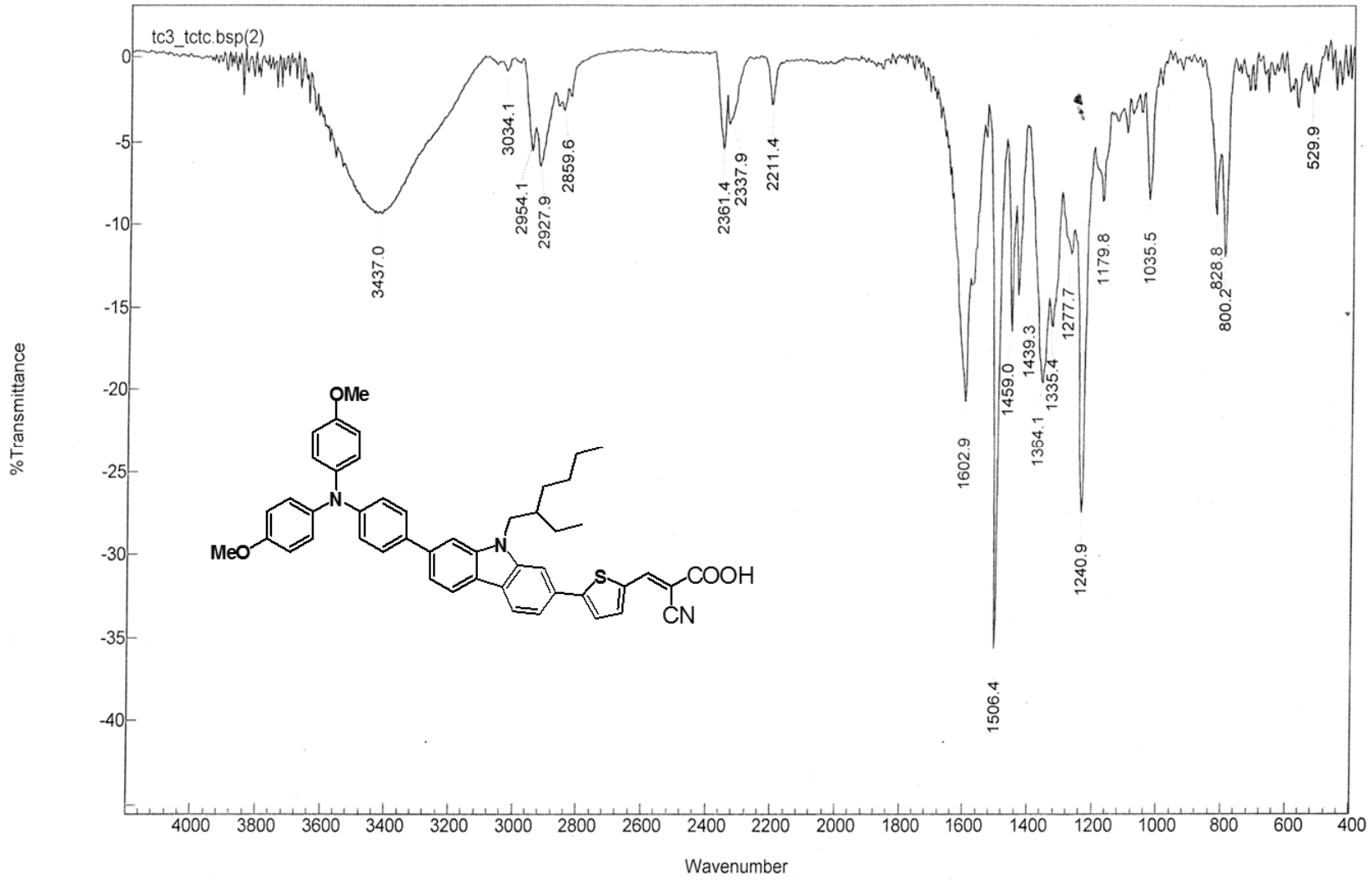
1H & 13C NMR of compound **TC5**




156.1581
149.3870
148.1796
142.3976
141.5976
141.5903
140.4557
139.7648
138.6229
136.7465
135.8737
132.9645
130.6590
128.0916
127.0952
127.0298
124.6078
122.7169
121.3277
121.2113
120.8332
120.1422
120.0040
118.2585
117.5676
115.3711
107.0799
106.7453
55.6452
39.9210
30.5170
28.3205
24.1095
22.8585
14.1382
11.1708
OMe
MeO
N
N
S
COOH
CN
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

FT-IR and MALDI-TOF of compound **TC5**




tc3_tctc.bsp(2)
%Transmittance
Wavenumber
3437.0
3034.1
2954.1
2927.9
2859.6
2361.4
2337.9
2211.4
1602.9
1506.4
1459.0
1439.3
1364.1
1335.4
1277.7
1240.9
1179.8
1035.5
828.8
800.2
529.9
OMe
MeO
N
N
S
COOH
CN