

L-Proline catalyzed synthesis of 2-aryl-2*H*,5*H*-thiopyrano[2,3-*b*]thiochromen-5-ones from 4-hydroxydithiocoumarins and cinnamaldehyde derivatives

Electronic Supporting Information

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1. General information and methods

Starting material 4-Hydroxydithiocoumarin and 4-hydroxythiocoumarin was synthesized in our laboratory via previously reported methods. While cinnamaldehyde derivatives were all Sigma Aldrich. Melting points were recorded using the melting point apparatus (Stuart company). ¹H and ¹³C NMR spectra were recorded on 400 and 500 MHz and 100, 125 MHz (Bruker) NMR spectrometers, respectively. TMS is used as an internal reference; chemical shifts (δ scale) are reported in parts per million (ppm). ¹H NMR spectra are reported in the order of multiplicity, coupling constant (J value) in Hertz (Hz), and the number of protons; signals were characterized as s (singlet), d (doublet), t (triplet), m (multiplet) and bs (broad). IR spectra were recorded on an IR spectrophotometer. HRMS spectra were recorded on a TOF mass analyser. The structure was also determined using a single XRD diffractometer.

2. X-ray crystallographic data of compound 3e

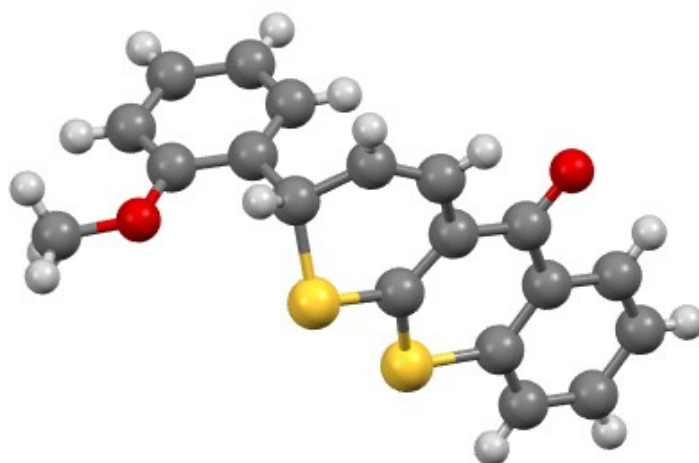


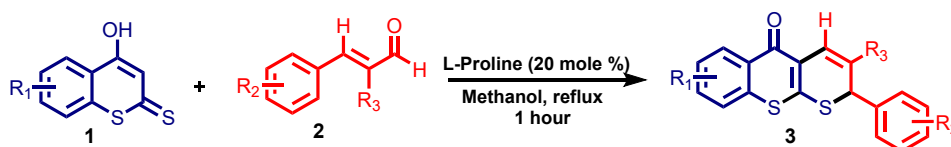
Figure. ORTEP Diagram of compound **3e**

Table S1. Crystal data and structure refinement for compound (**3e**)

Entry	Identification Code	Compound 3e
01	Empirical formula	<u>C₁₉H₁₄O₂S₂</u>
02	Formula weight	338.42
03	Temperature	<u>297</u> K
04	Wavelength	0.71073
05	Radiation type	Mo K α
06	Radiation system	Fine-focus sealed tube
07	Crystal system	<u>Triclinic</u>
08	Space group	P-1
09	Cell length(Å)	(a) <u>7.6579 (10)</u> , (b) <u>13.8840(19)</u> (c) <u>14.998 (2)</u>
10	Cell angle (°)	α <u>87.216 (3)</u> , β <u>89.610 (4)</u> , γ <u>83.982 (3)</u>
11	Cell volume (Å ³)	1584.0 (4)

12	Density	1.419
13	Absorption correction	multi-scan
14	Reflection number	6867
15	Cell formula units Z	2
16	CCDC no	2311036

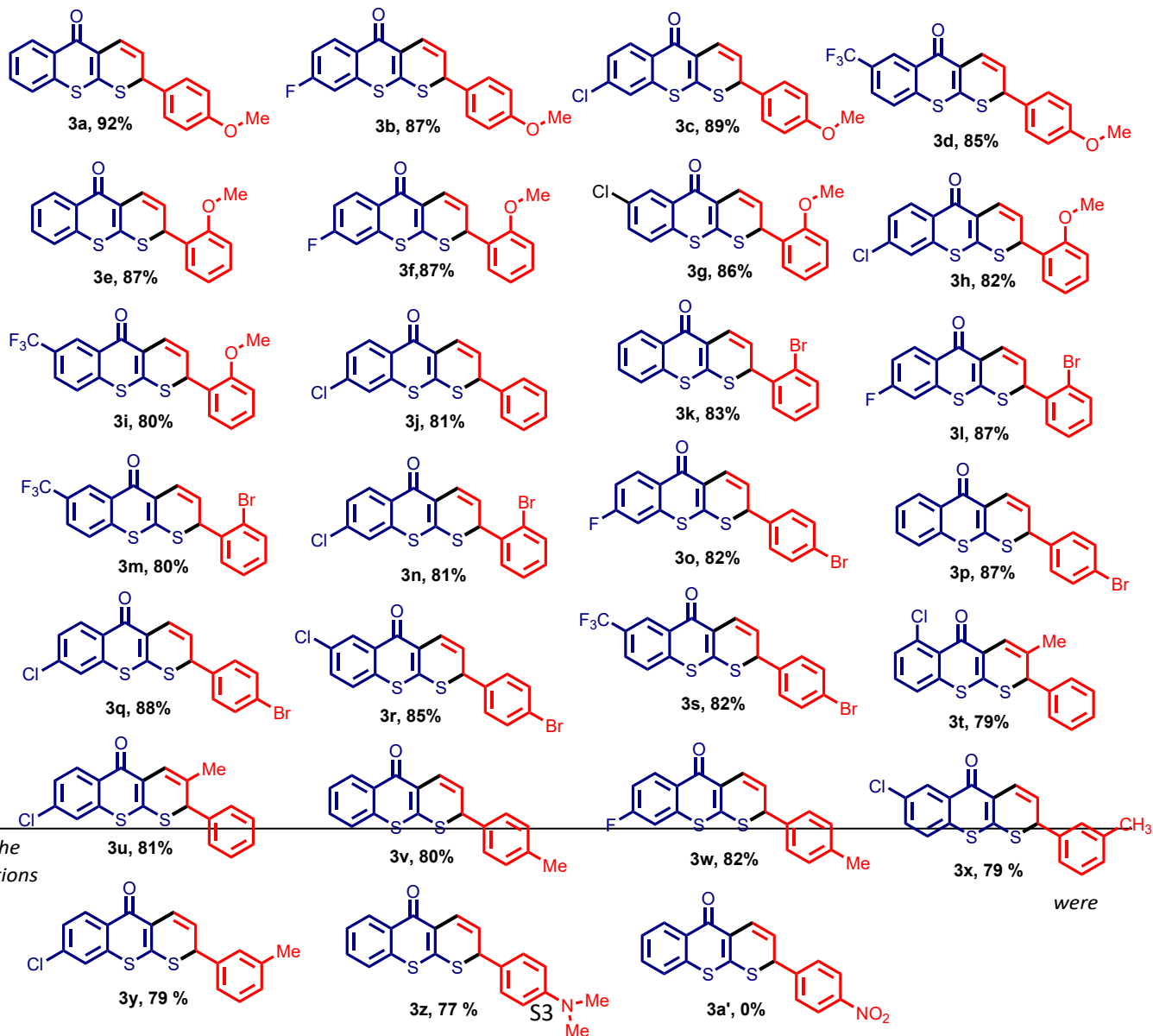
3. Substrate scope^{a,b}



$R_1 = 5\text{Cl}, 6\text{Cl}, 7\text{Cl}, 7\text{F}, 6\text{CF}_3$

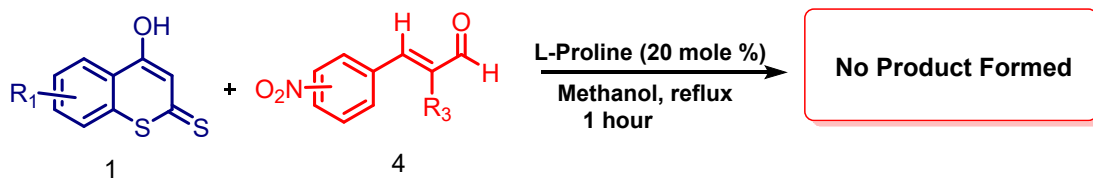
$R_2 = \text{Br}, -\text{CH}_3, -\text{OMe}, \text{NO}_2, -\text{NMe}_2$

$R_3 = -\text{CH}_3$



carried out using 4-hydroxydithiocoumarin (**1**, 0.2 mmol), cinnamaldehyde (**2**, 0.2 mmol) in the presence of 20 mol% catalyst, 1 mL of methanol Solvent at reflux temperature. ^bIsolated yield.

4. Unsuccessful results^a



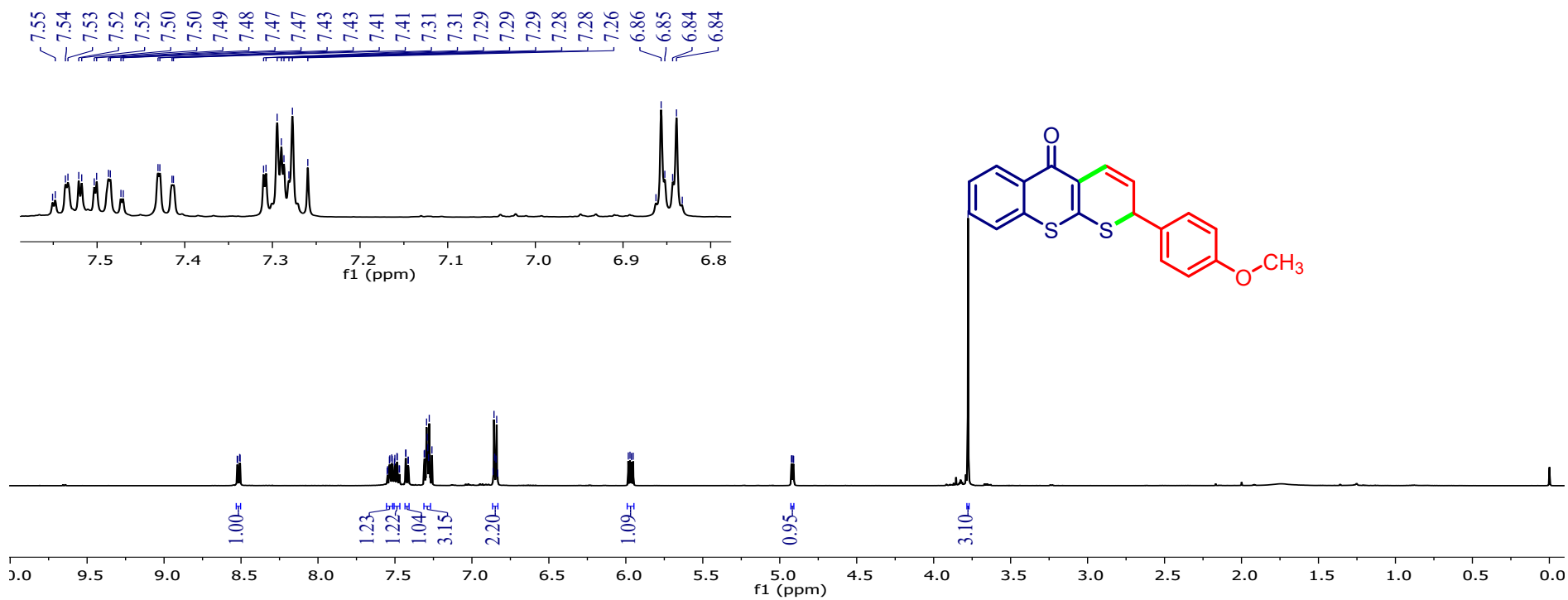
The reactions were carried out using 4-hydroxydithiocoumarin (**1**, 0.2 mmol), Nitrocinnamaldehyde (**4**, 0.2 mmol) in the presence of 20 mol% catalyst, 1 mL of methanol Solvent at reflux temperature.

5. ^1H , ^{13}C spectrum and HRMS of all compounds

^1H NMR Compound (3a)

ATK-AA-1-1H.24.fid
ATK-AA-1-1H

8.52 8.52 8.51 8.51 7.55 7.55 7.54 7.53 7.52 7.52 7.50 7.50 7.49 7.48 7.47 7.47 7.43 7.43 7.41 7.41 7.31 7.31 7.29 7.29 7.29 7.28 7.28 7.26 7.26 6.86 6.86 6.85 6.84 6.84 6.83 5.98 5.97 5.96 5.95 4.92 4.92 4.91 4.91 3.78

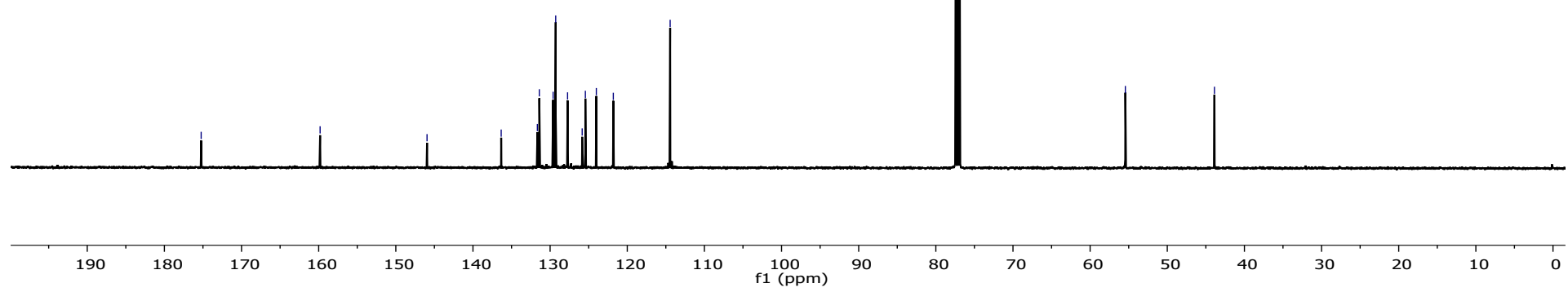
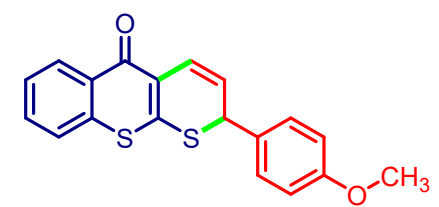
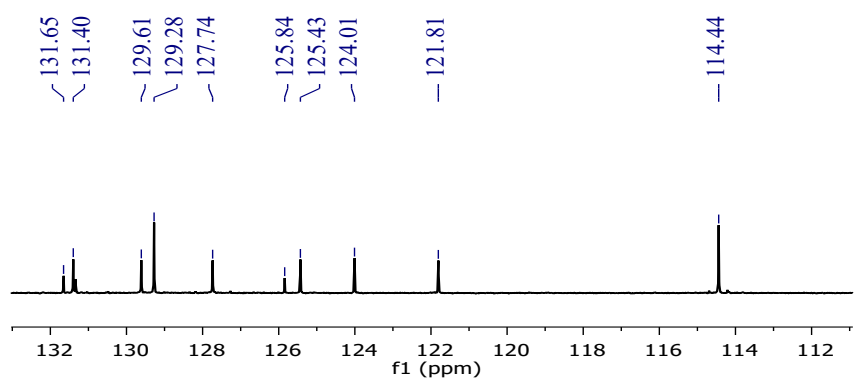


¹³C NMR Compound (3a)

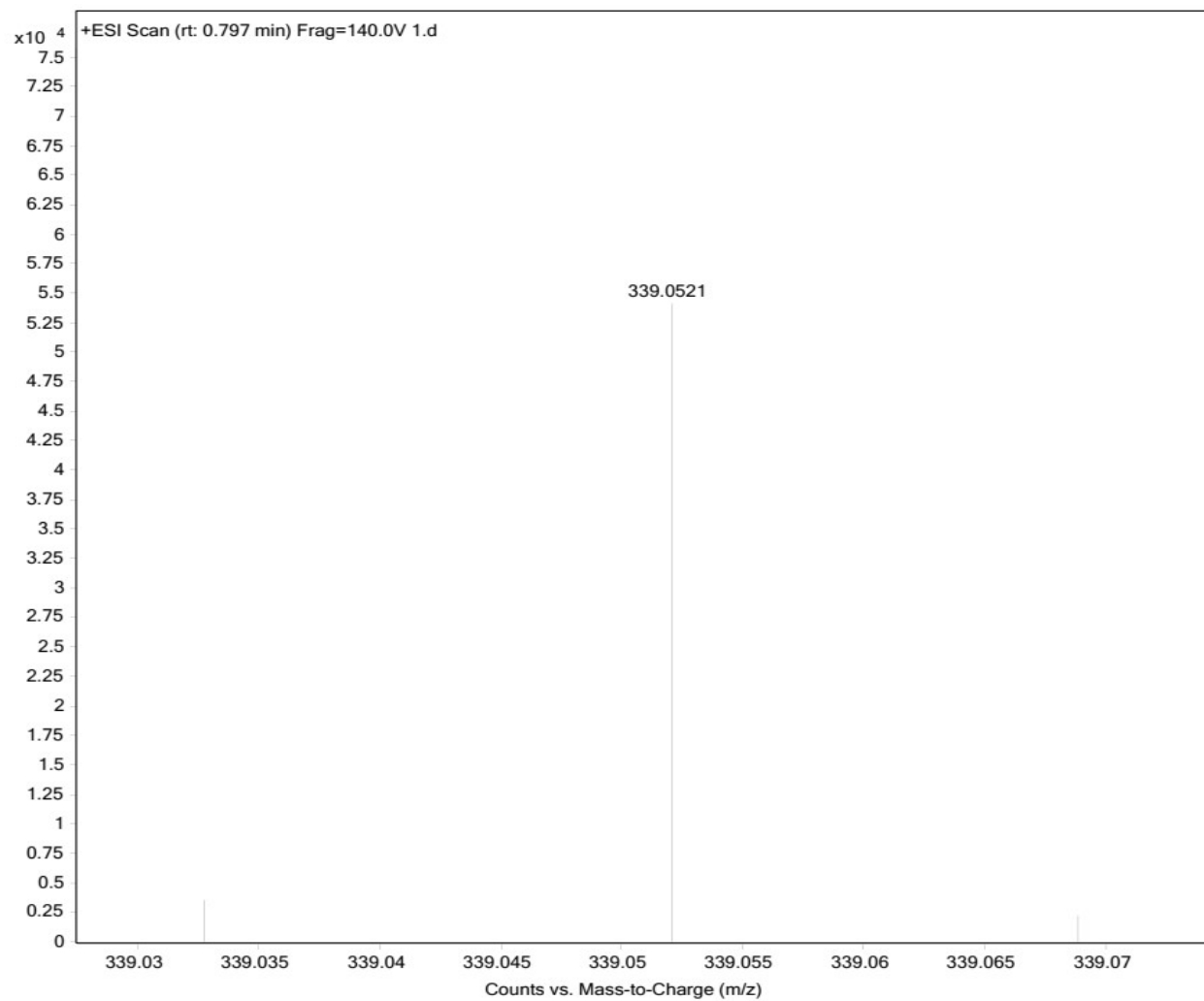
ATK-AA-1-13C.26.fid
ATK-AA-1-13C

175.23
159.81
145.95
136.34
131.65
131.40
129.61
129.28
127.74
125.84
125.43
124.01
121.81
114.44

77.41
77.16
76.91
55.43
43.88

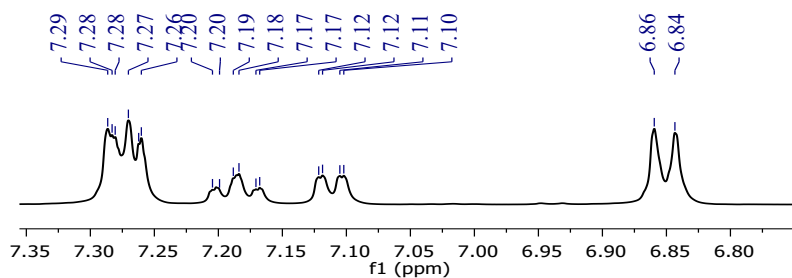


HRMS 3a

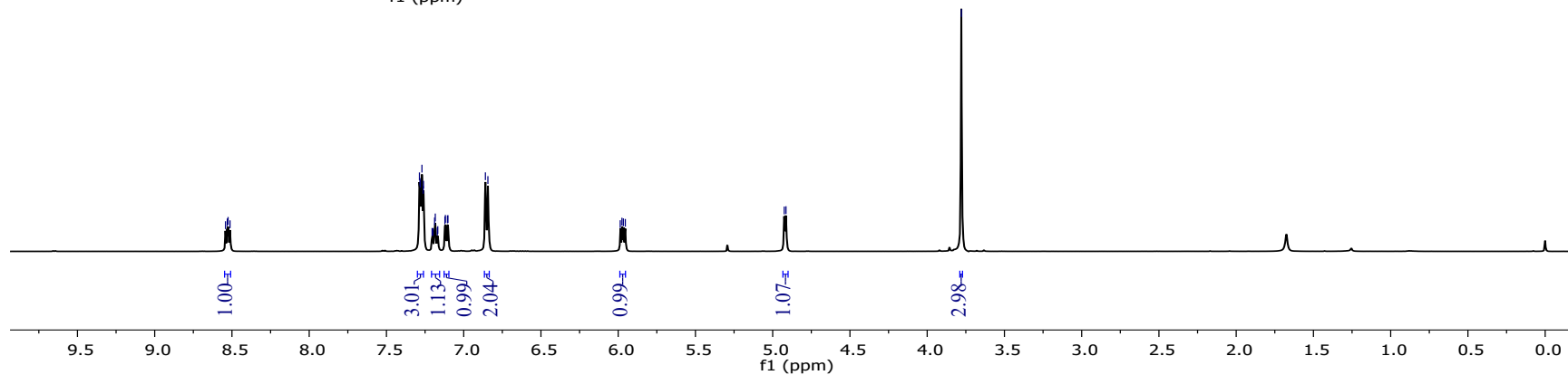
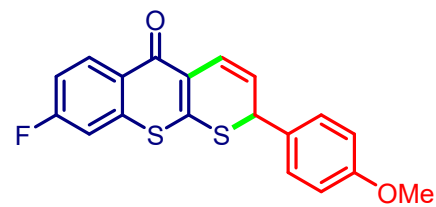


^1H NMR Compound (3b)

ATK-AA-72-FH-3-01
 ATK-AA-72-FH-3-01



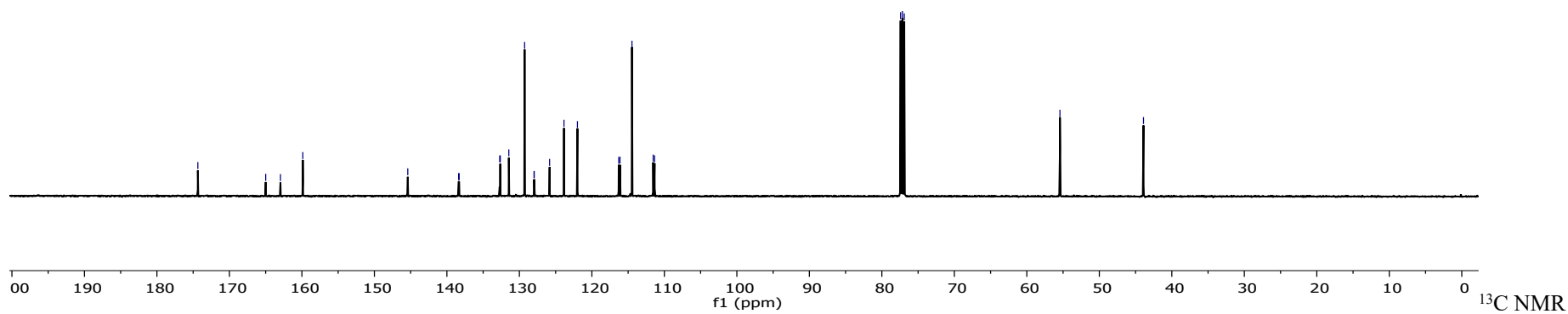
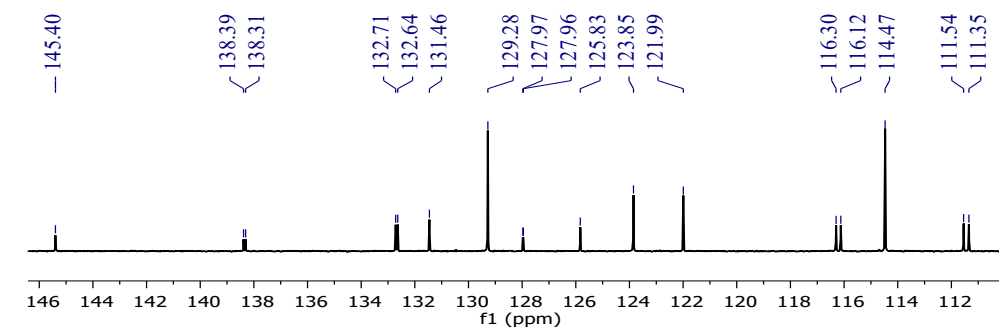
— 3.78



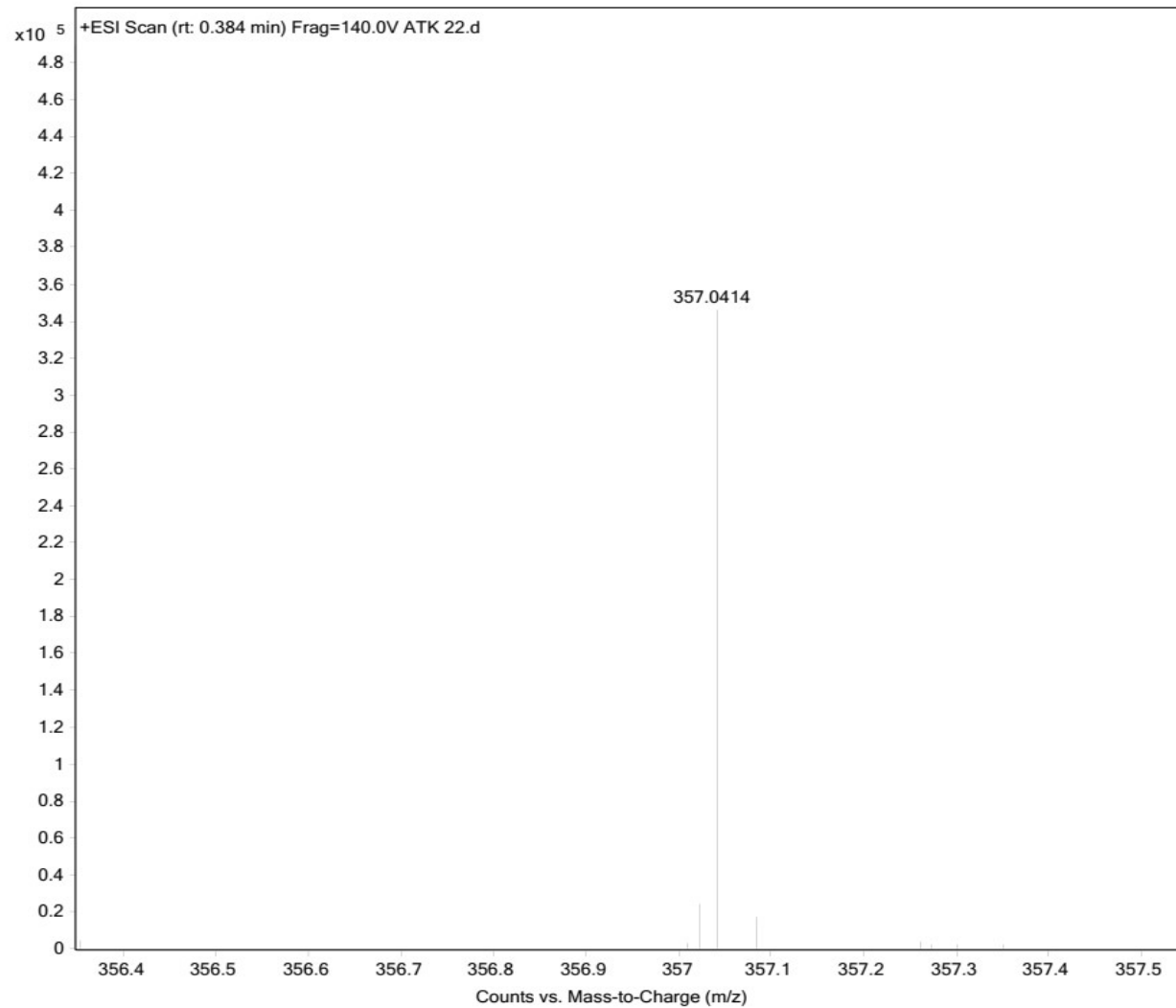
¹³C NMR Compound (3b)

ATK-AA-22-13C.1.fid
ATK-AA-22-13C

174.36
164.99
162.96
159.87
145.40
138.39
138.31
132.71
132.64
131.46
129.28
127.97
127.96
125.83
123.85
121.99
116.30
116.12
114.47
111.54
111.35
77.41
77.16
76.91
55.43
43.91

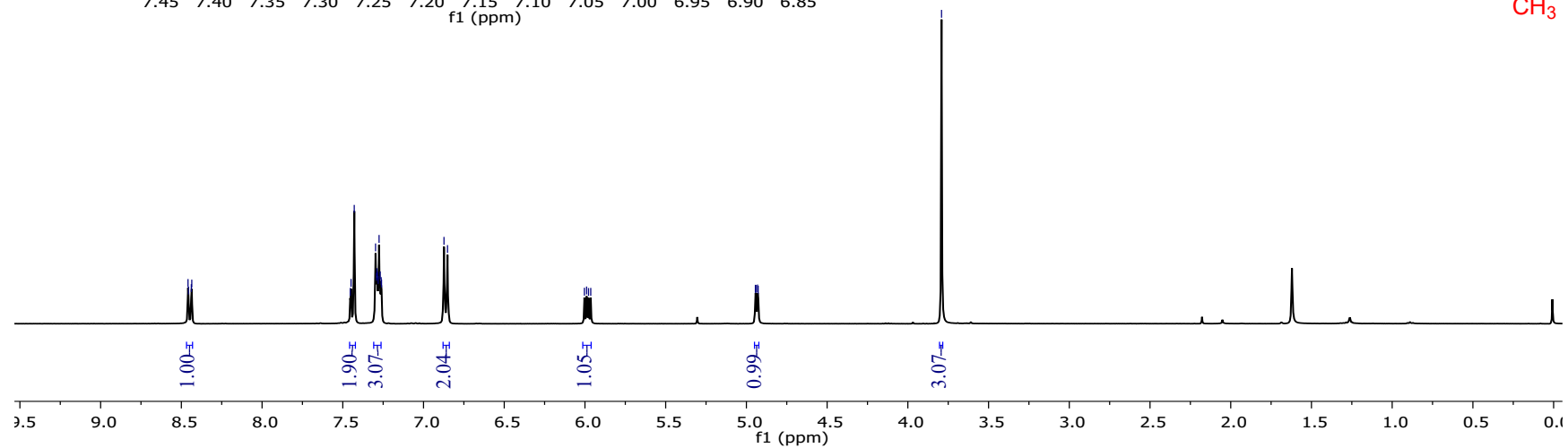
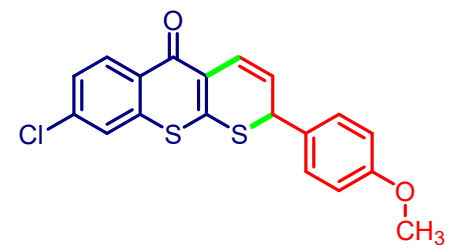
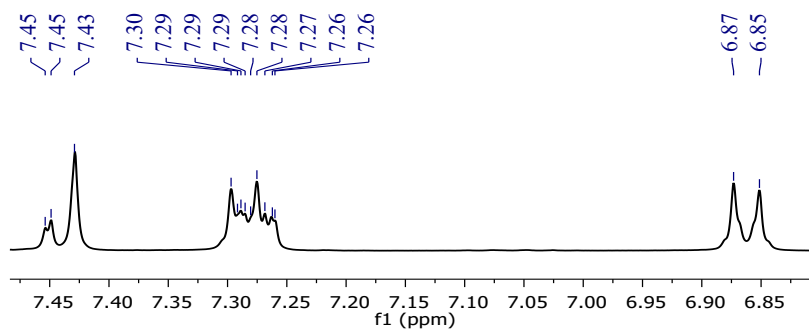


HRMS of compound 3b



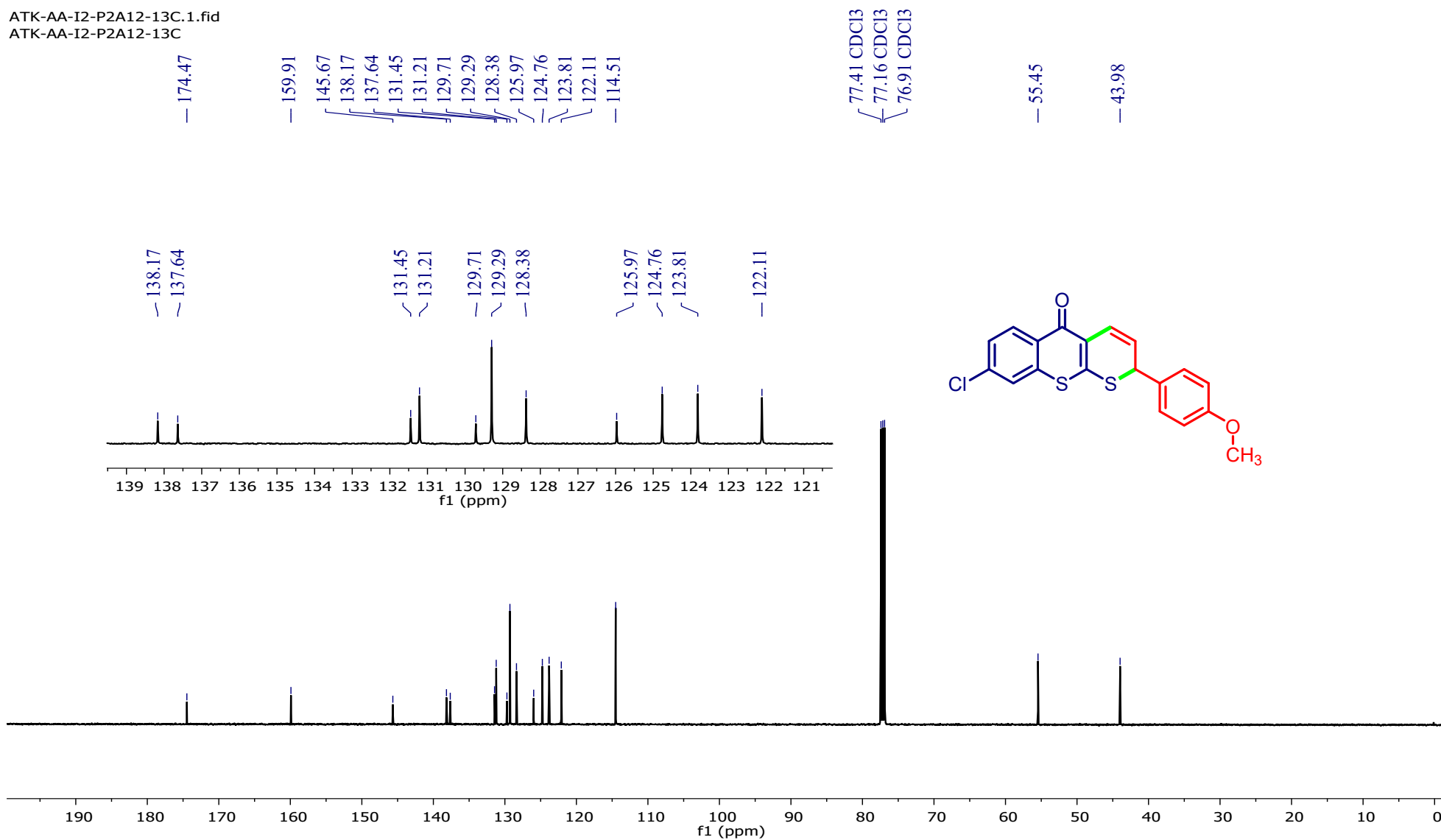
¹H NMR Compound (3c)

ATK-AA-12-P2A12-1H.1.fid — ATK-AA-12-P2A12-1H

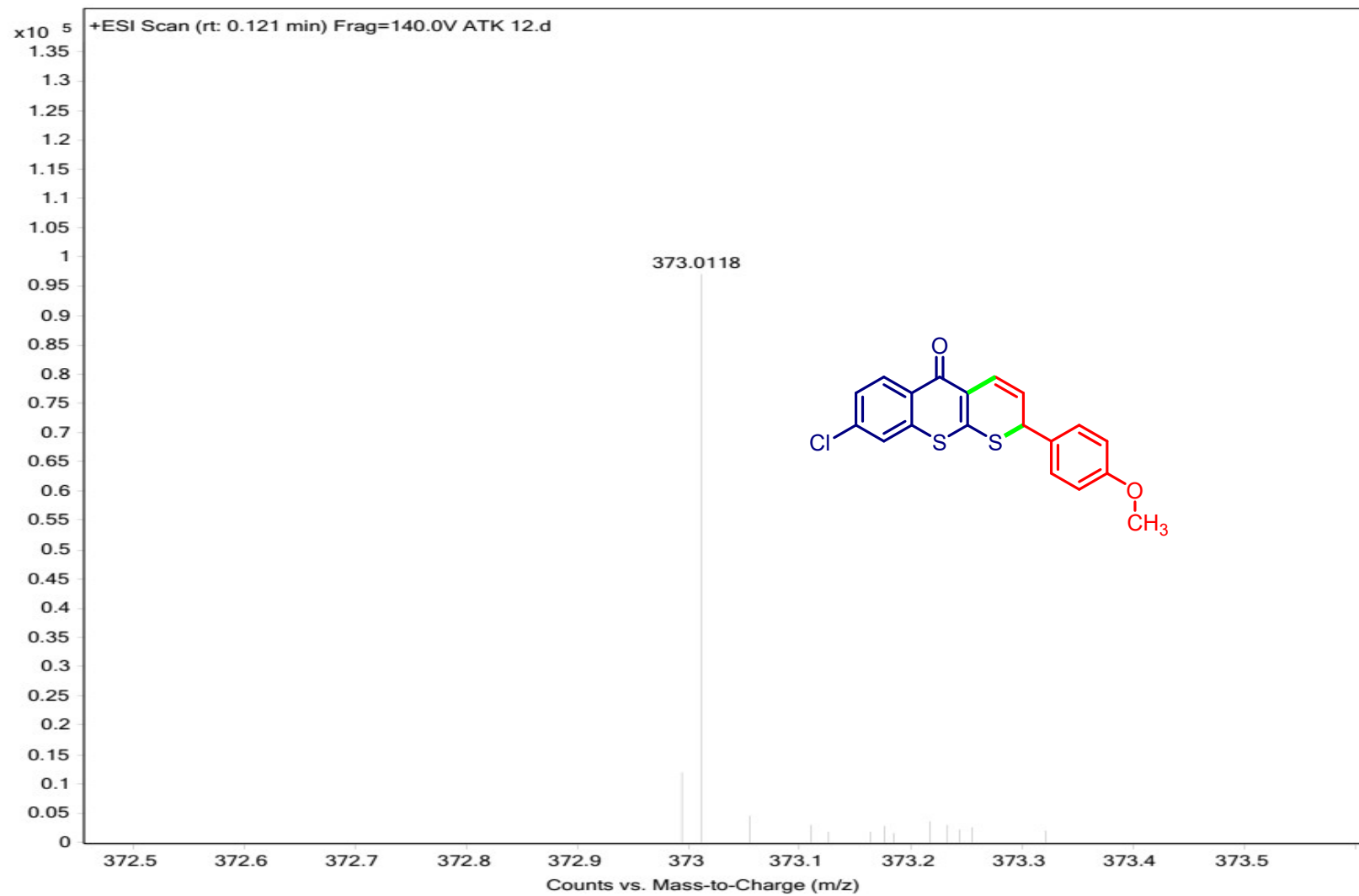


¹³C NMR Compound (3c)

ATK-AA-I2-P2A12-13C.1.fid
ATK-AA-I2-P2A12-13C



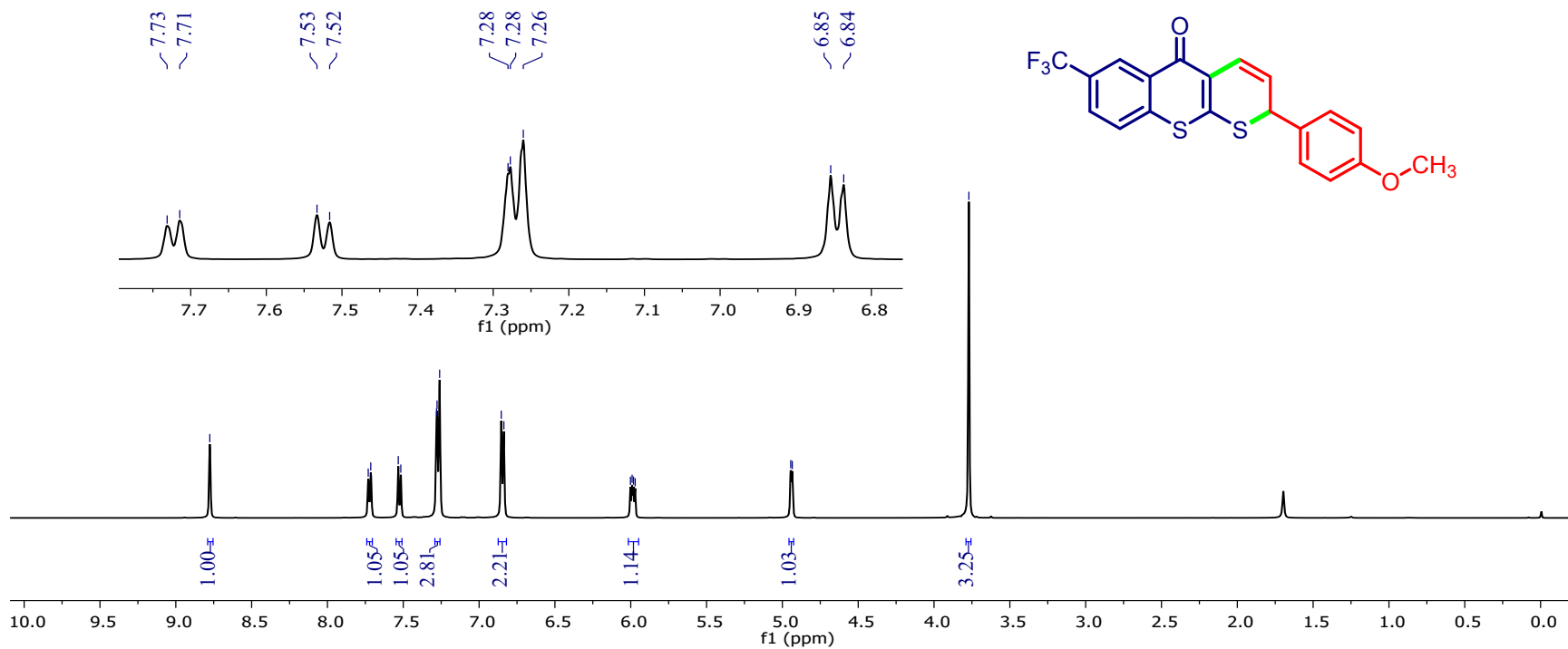
HRMS compound (3c)



¹H NMR of compound (3d)

MPO-AA-31-1H.5.fid
MPO-AA-31-1H

8.78
7.73
7.71
7.53
7.52
7.28
7.28
7.26
6.85
6.84
6.00
5.99
5.98
5.97
4.95
4.93
3.77

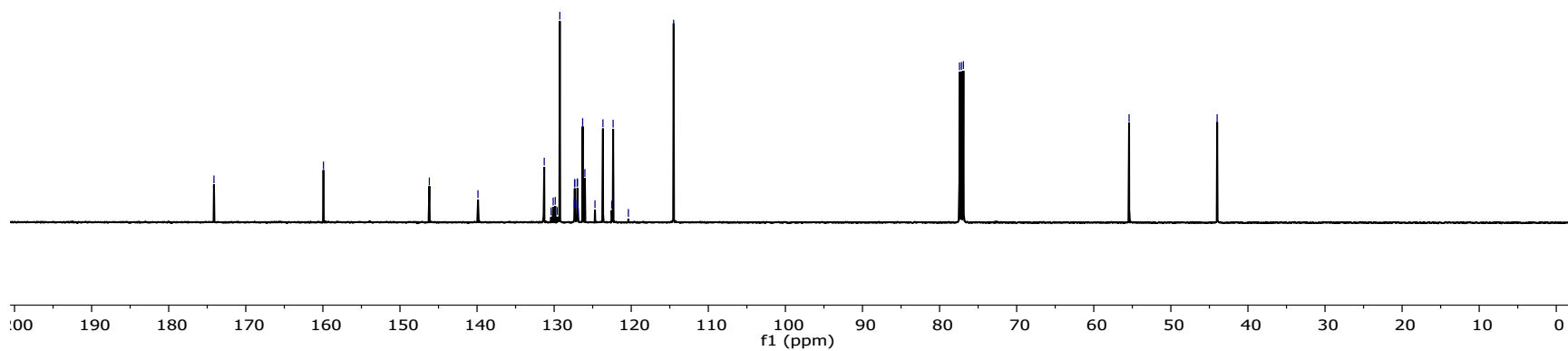
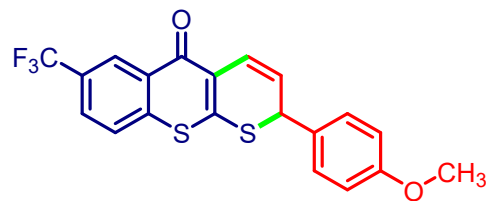
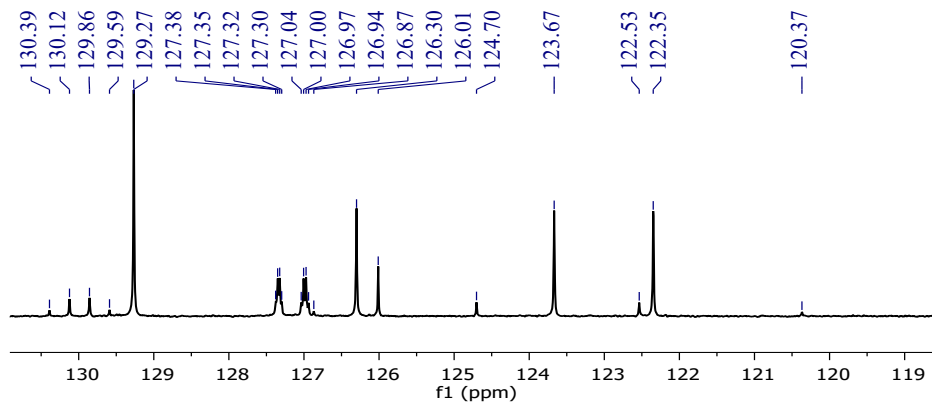


(500 MHz, DMSO-*d*₆) δ 8.78 (s, 1H), 7.72 (d, *J* = 8.3 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.29 – 7.26 (m, 3H), 6.85 (d, *J* = 8.6 Hz, 2H), 5.99 (dd, *J* = 10.2, 5.5 Hz, 1H), 4.94 (d, *J* = 5.1 Hz, 1H), 3.77 (s, 3H).

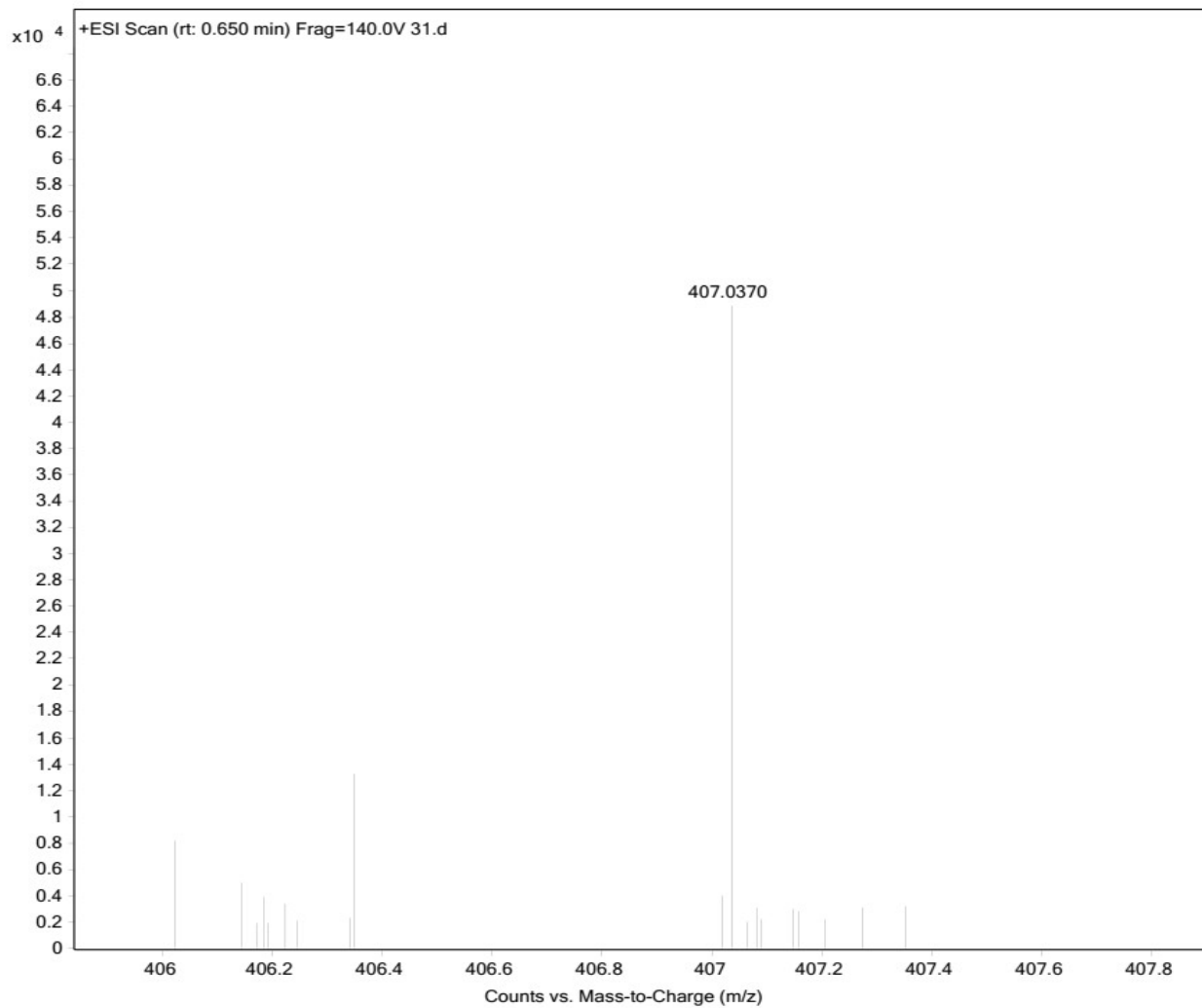
¹³C NMR of compound (3d)

MPO-AA-31-13C.1.fid
MPO-AA-31-13C

174.13
159.92
146.19
139.88
131.35
131.28
130.39
130.12
129.86
129.59
129.27
129.27
127.38
127.35
127.32
127.30
127.04
127.00
126.97
126.94
126.87
126.30
126.01
124.70
123.67
122.53
122.35
120.37
114.50
77.41
77.16
76.91
55.42
43.99

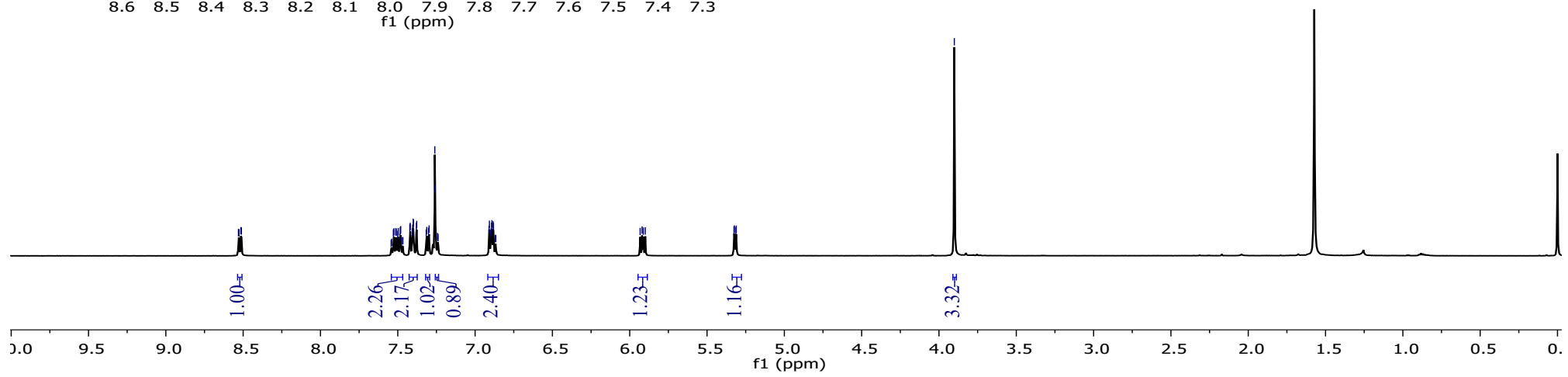
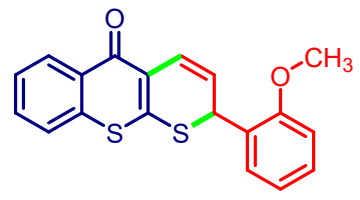
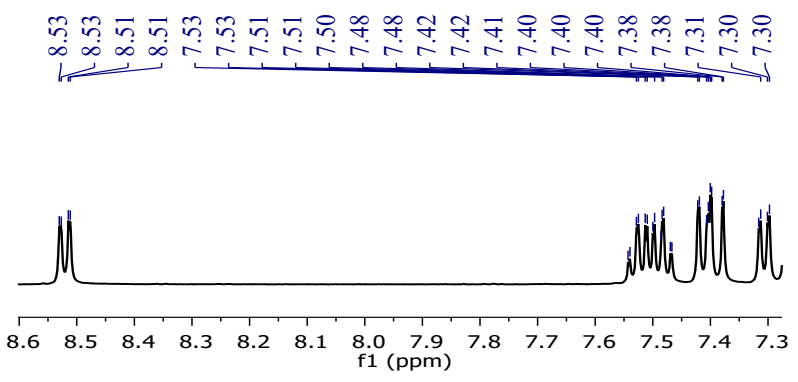


Hrms 3d



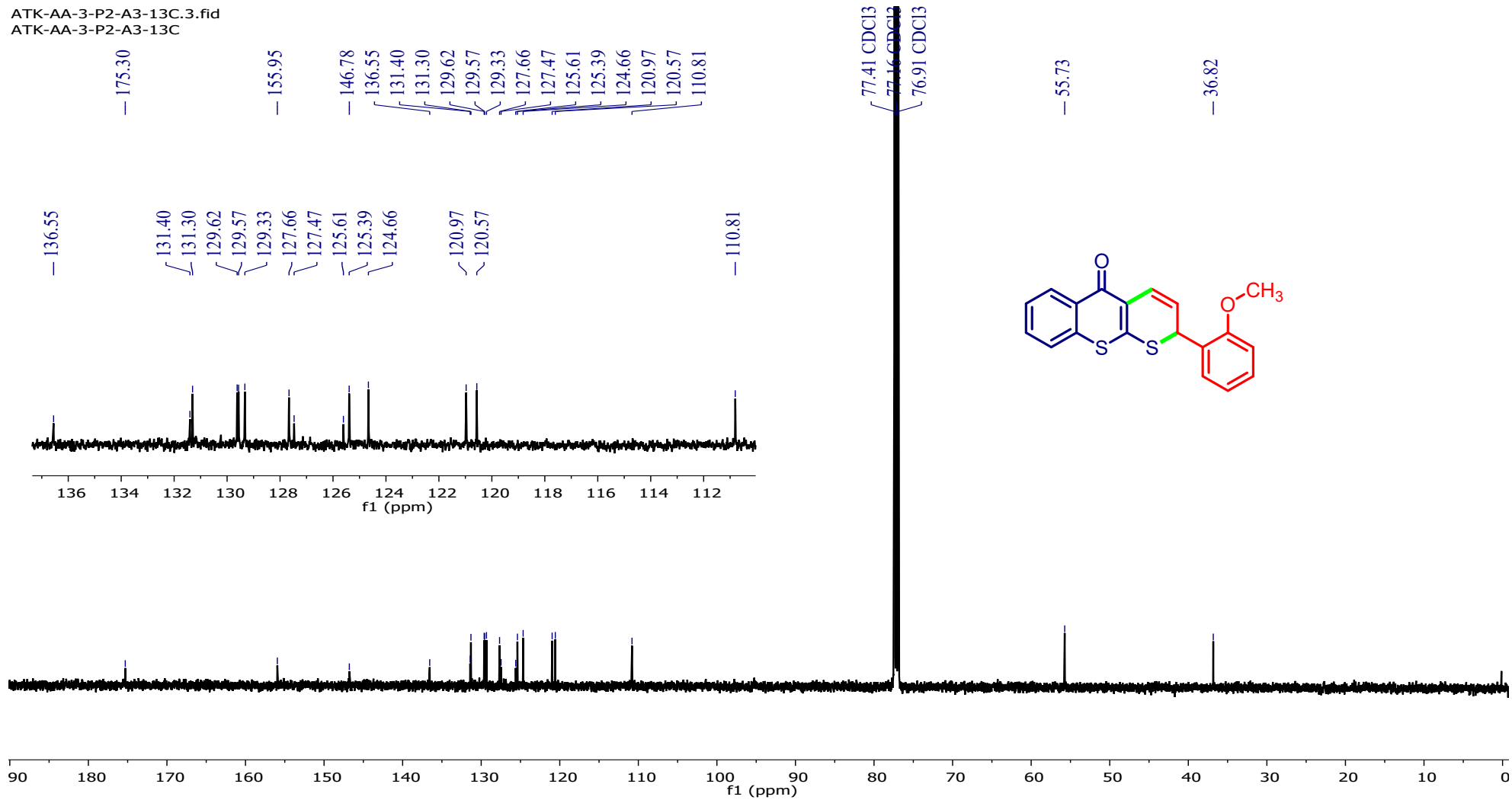
¹H NMR Compound (3e)

ATK-AA-3-P2-A3-1H-101d
 ATK-AA-3-P2-A3-1H

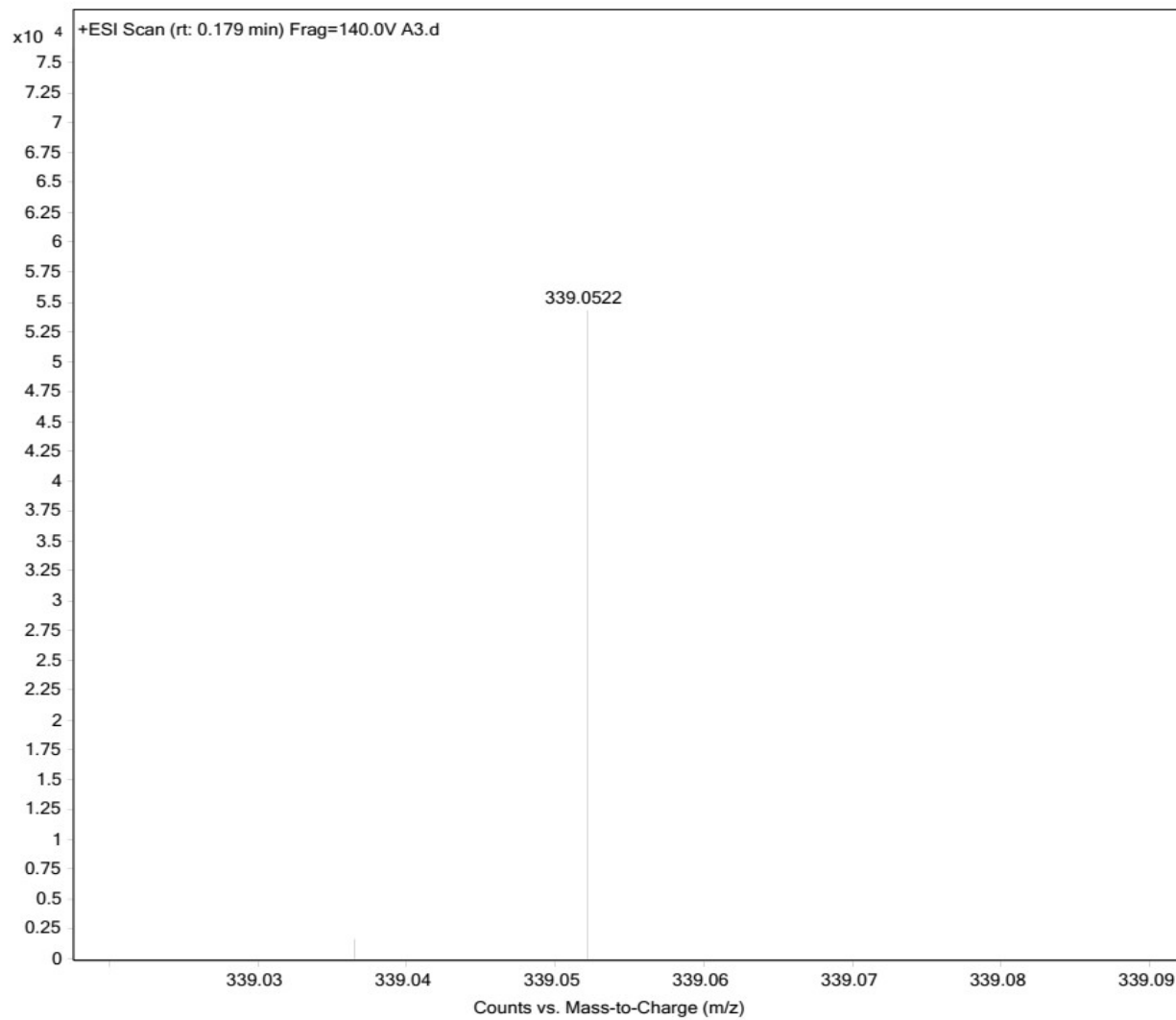


¹³C NMR Compound (3e)

ATK-AA-3-P2-A3-13C.3.fid
ATK-AA-3-P2-A3-13C



HRMS (3e)

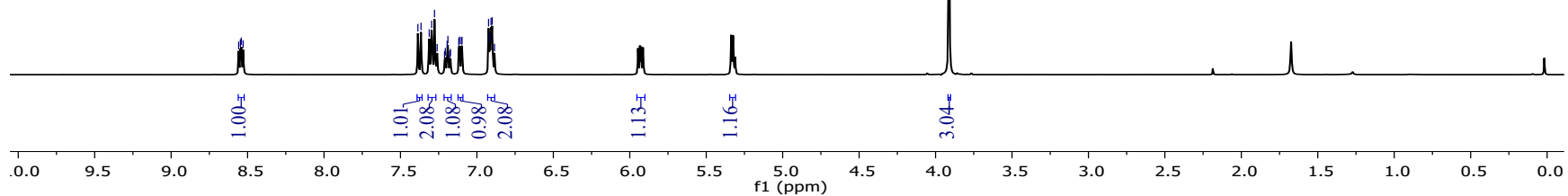
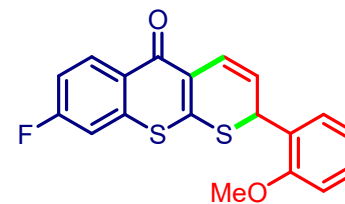
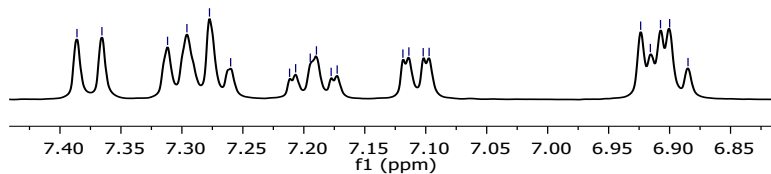


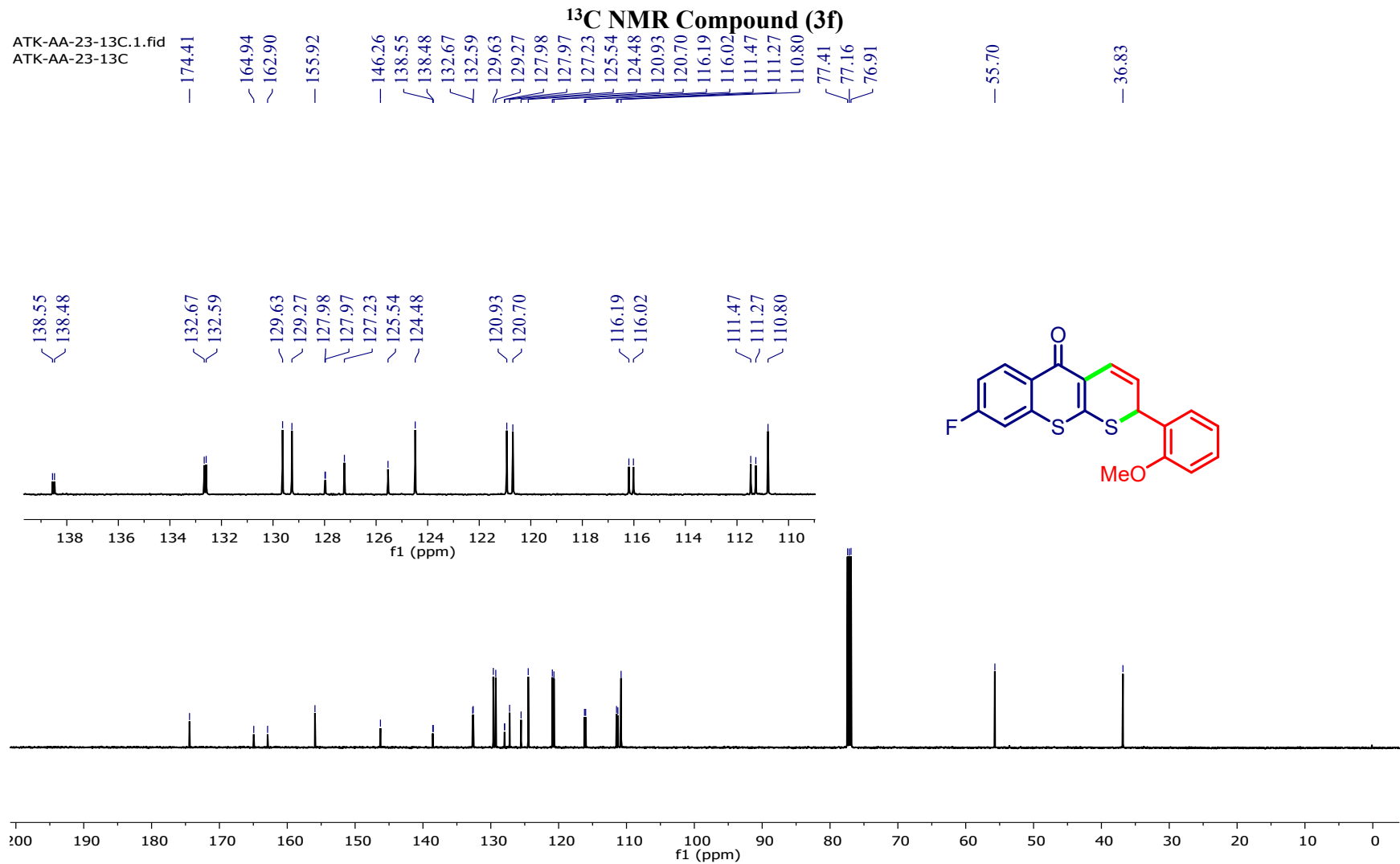
¹H NMR Compound (3f)

ATK-AA-23-1H.5.fid
ATK-AA-23-1H

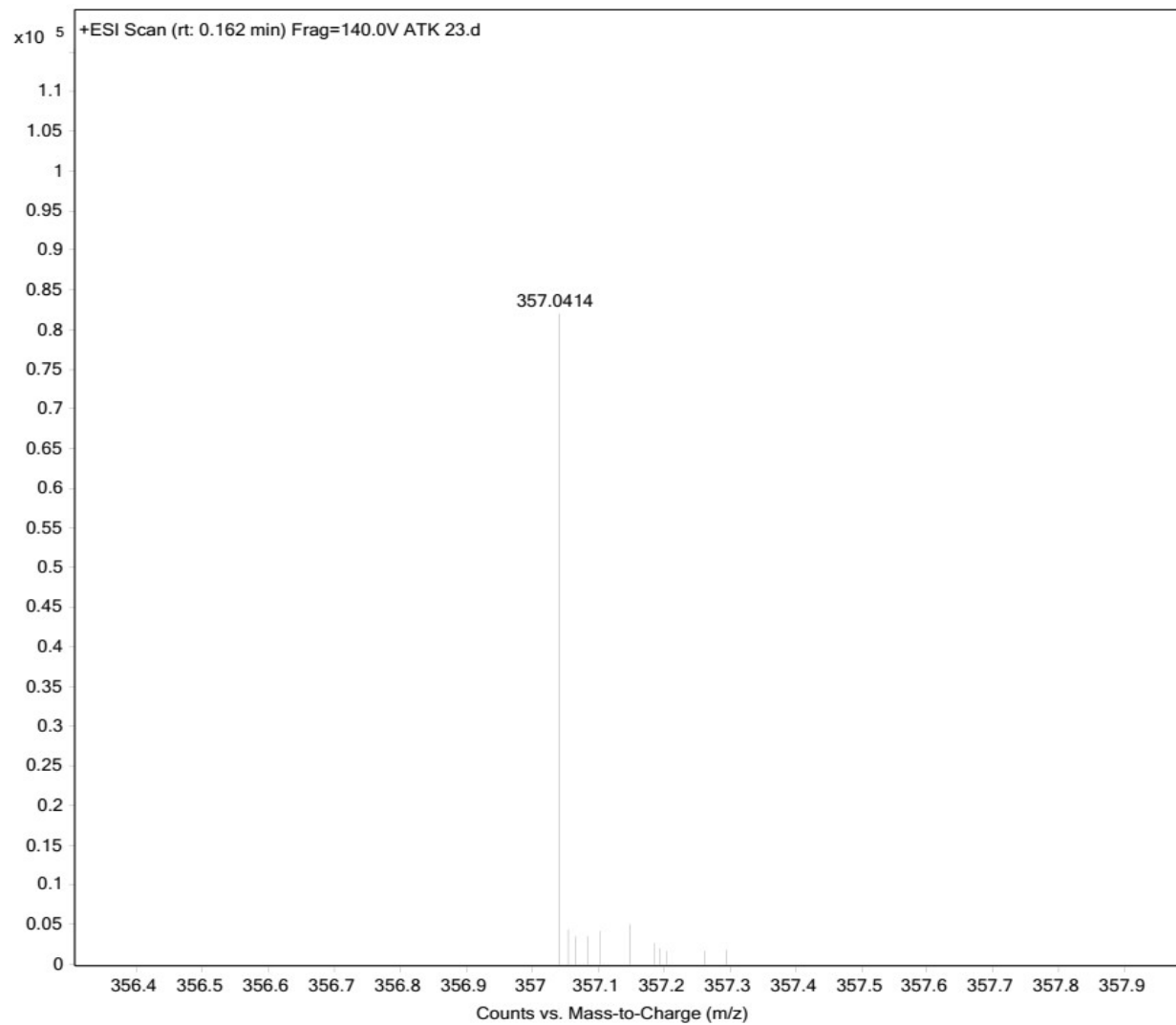
8.56
8.55
8.54
8.53
7.39
7.37
7.31
7.30
7.28
7.26
7.21
7.21
7.21
7.19
7.19
7.18
7.17
7.12
7.11
7.10
7.10
6.92
6.92
6.91
6.90
6.88
3.91

7.39
7.37
7.31
7.30
7.28
7.26
7.21
7.21
7.19
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7.10
7.10
6.92
6.92
6.91
6.90
6.88





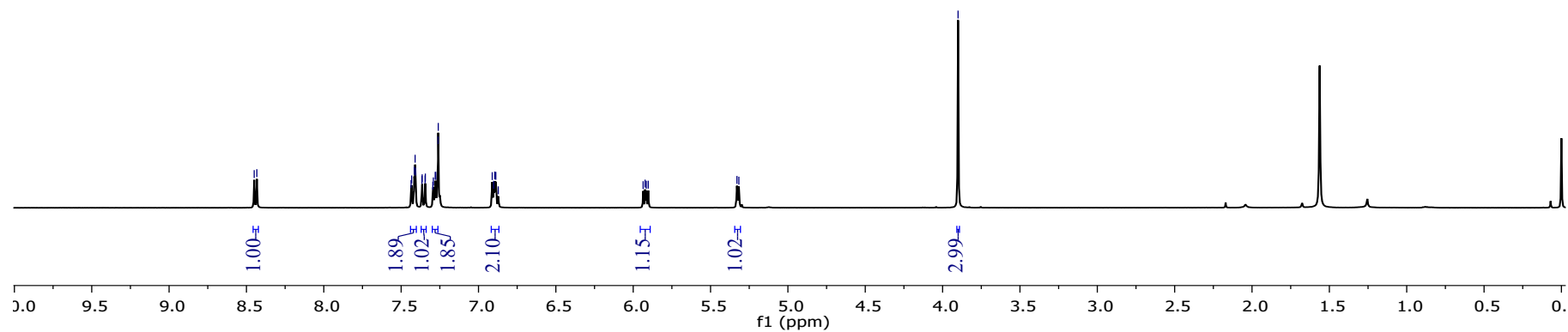
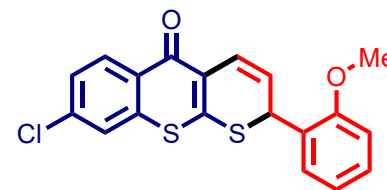
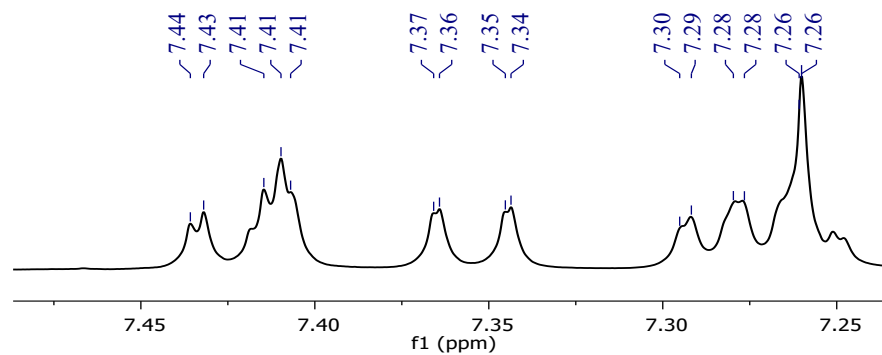
HRMS 3f



¹H NMR Compound (3g)

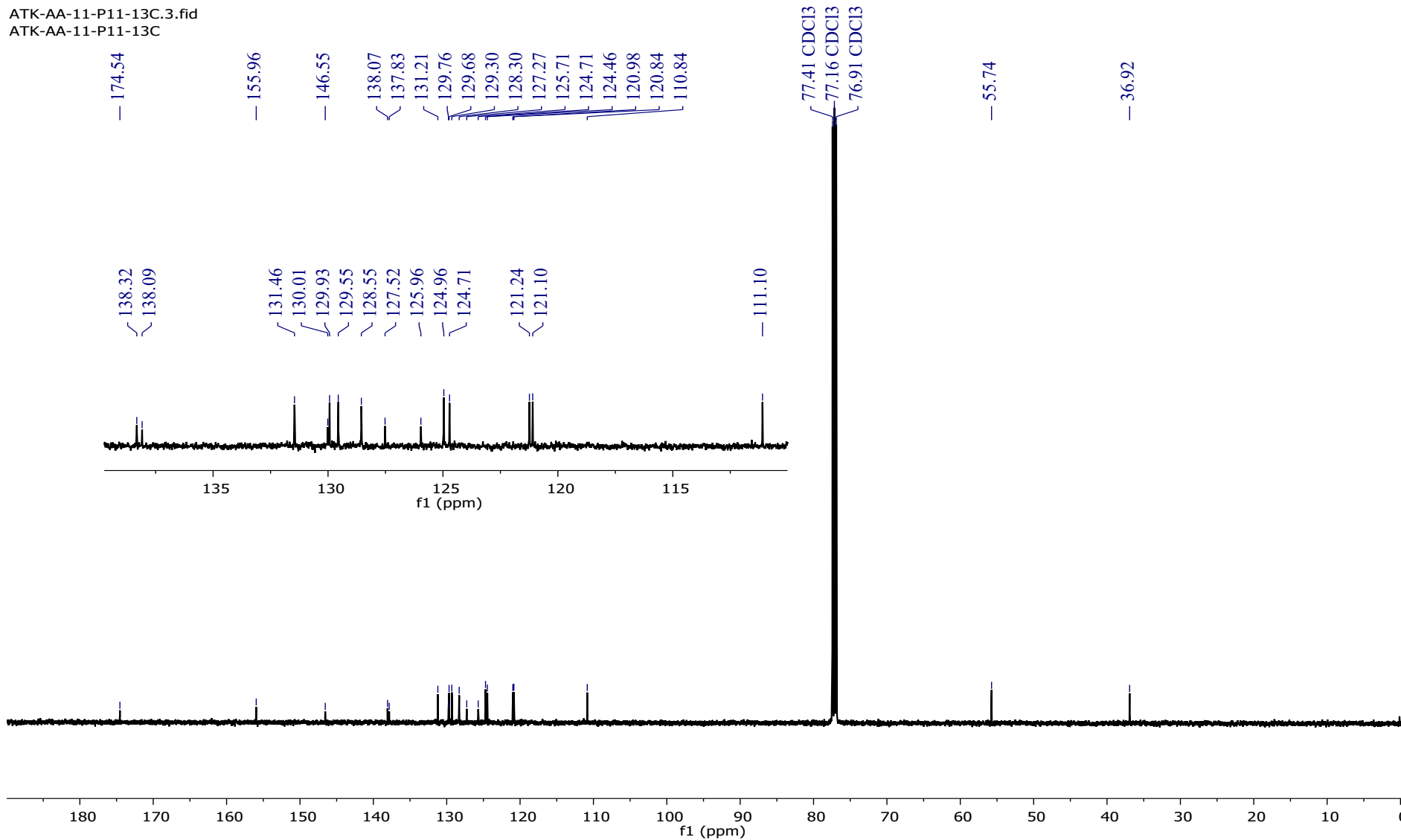
ATK-AA-11-P11-1H.1.fid — ATK-AA-11-P11-1H

8.45
8.43
7.44
7.43
7.41
7.41
7.41
7.37
7.36
7.35
7.34
7.30
7.29
7.28
7.28
7.26
7.26
6.91
6.90
6.89
6.89
6.87
5.94
5.92
5.92
5.90
5.33
5.32
— 3.90

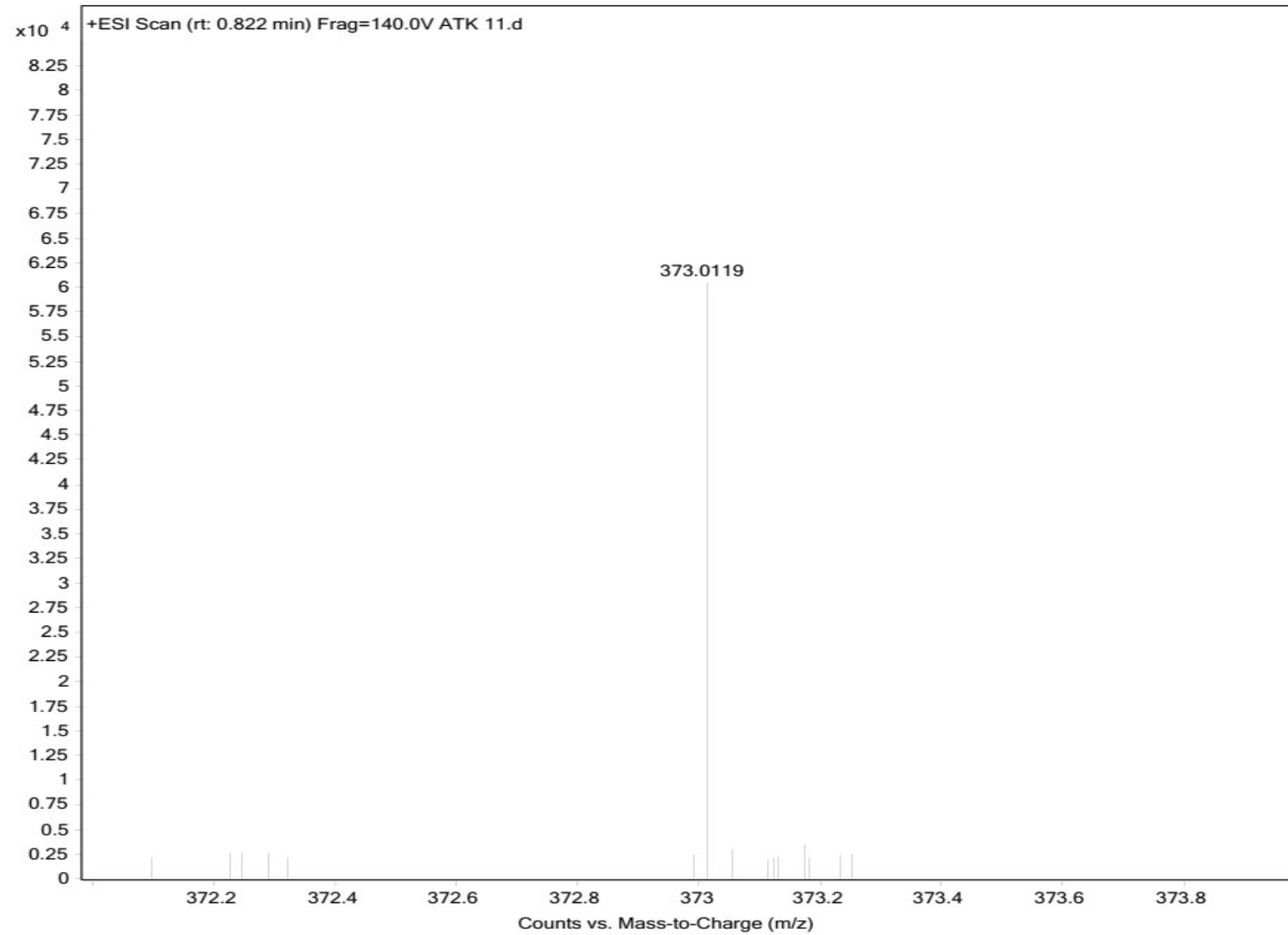


^{13}C NMR Compound (3g)

ATK-AA-11-P11-13C.3.fid
ATK-AA-11-P11-13C



HRMS compound (3g)

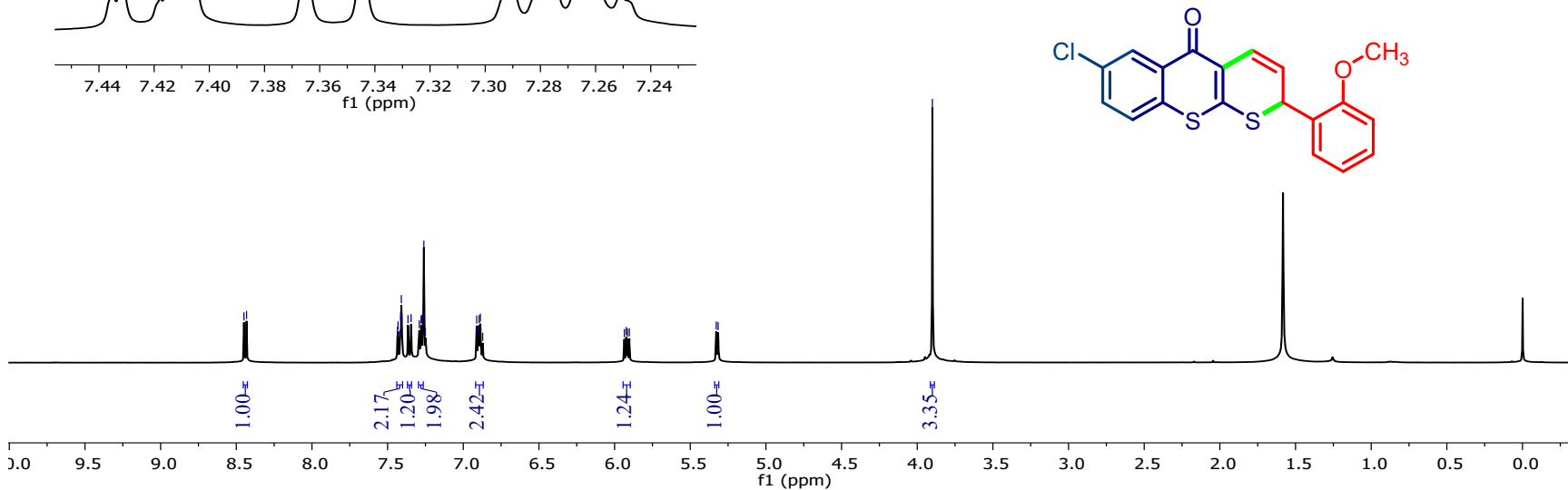
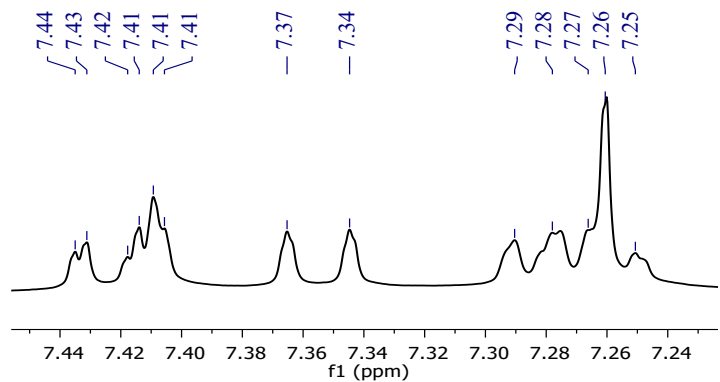


¹H NMR of compound (3h)

ATK-AA-17-1H.4.fid — ATK-AA-17-1H

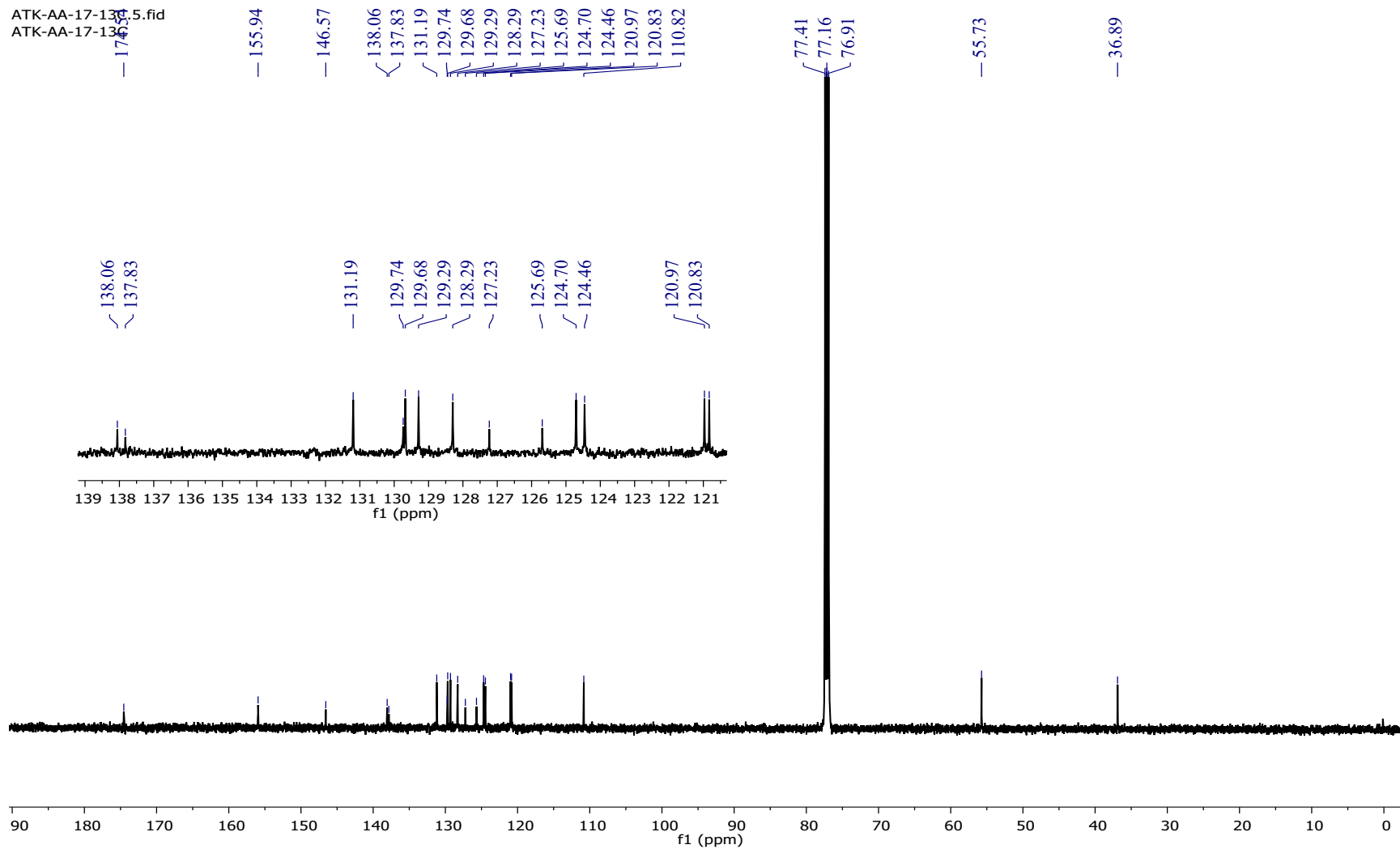
8.45
8.43
7.44
7.43
7.42
7.41
7.41
7.41
7.37
7.34
7.34
7.29
7.28
7.28
7.27
7.26
7.25
6.91
6.90
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5.94
5.92
5.92
5.90
5.33
5.32

— 3.90

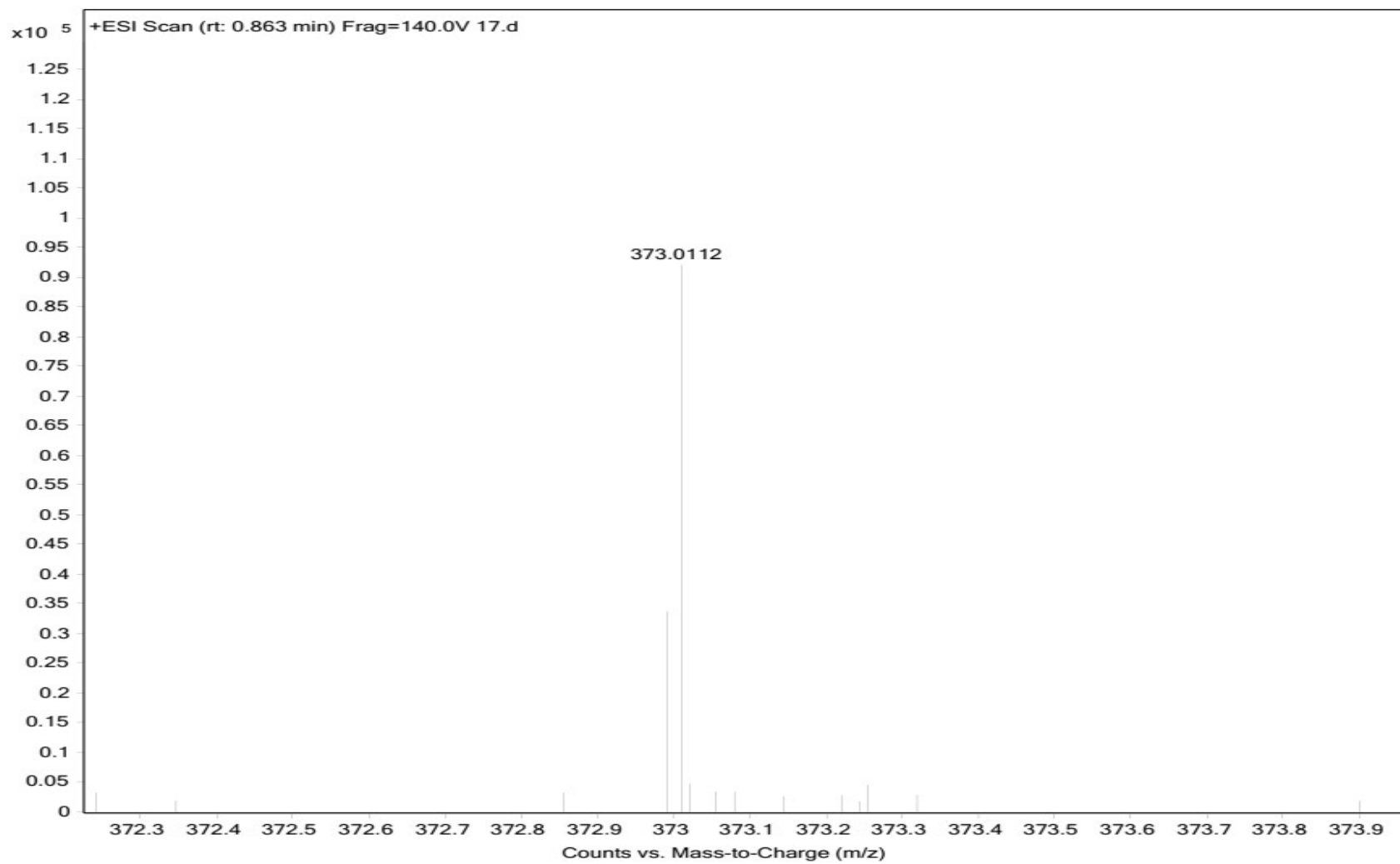


¹³C NMR Compound (3h)

ATK-AA-17-1339_5.fid
ATK-AA-17-1339

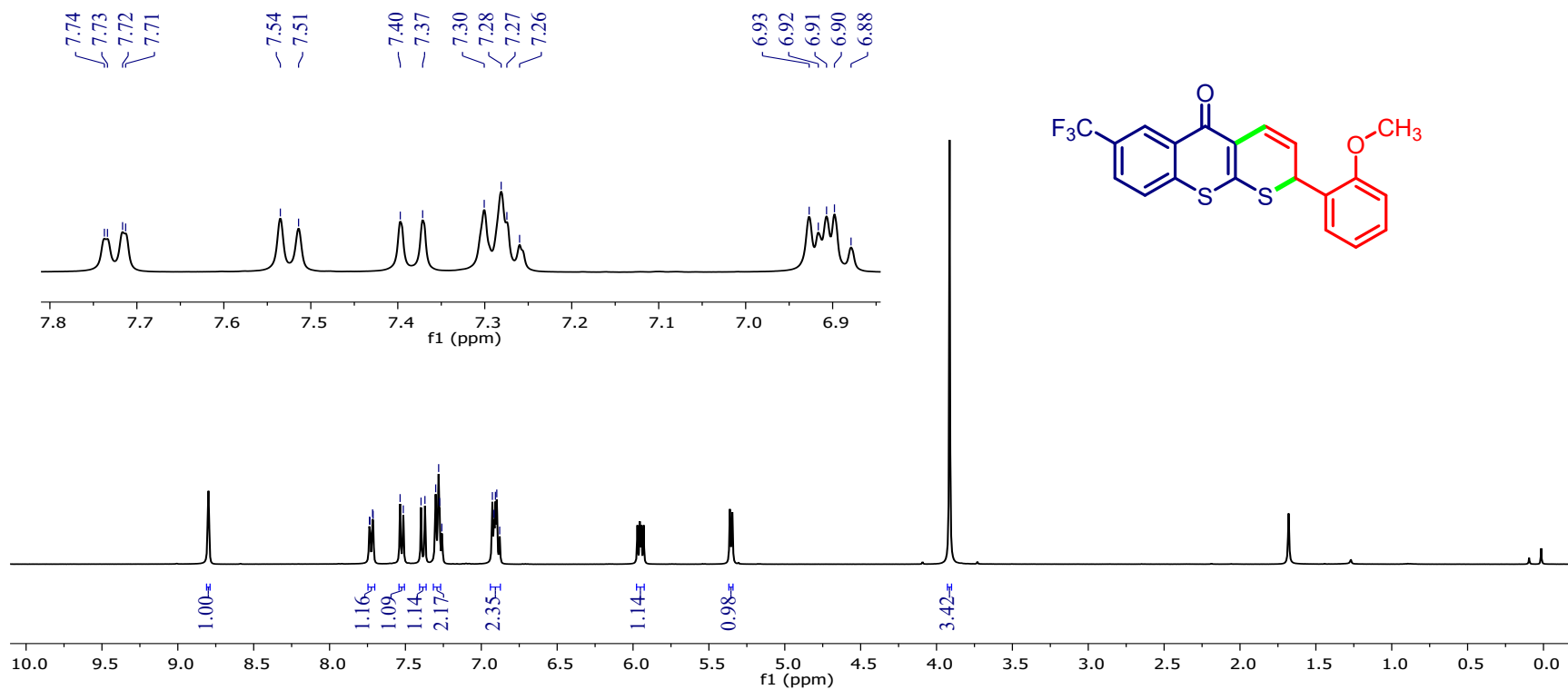
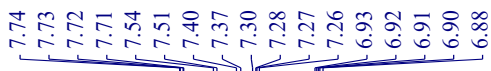


HRMS of compound (3h)

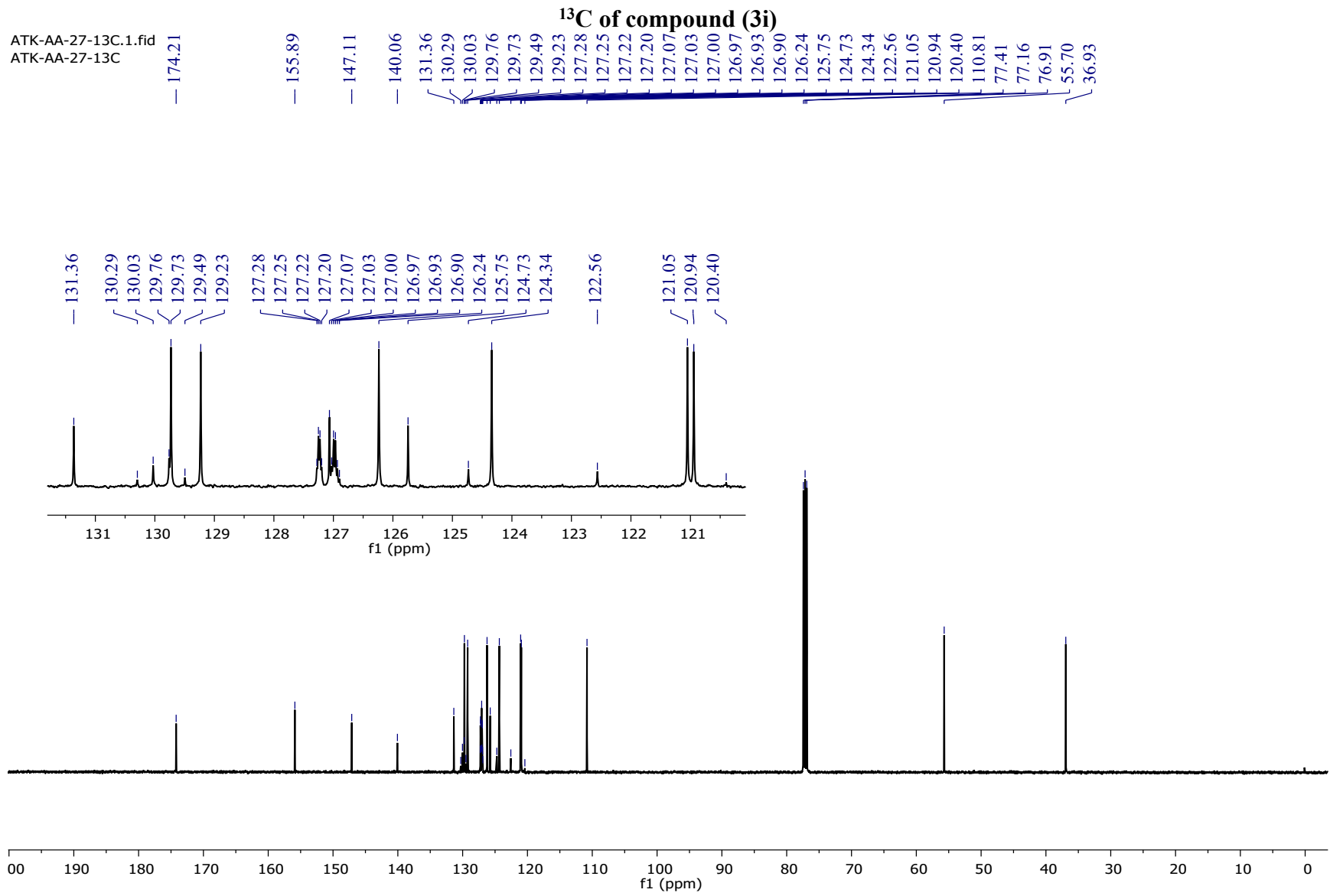


¹H NMR of compound (3i)

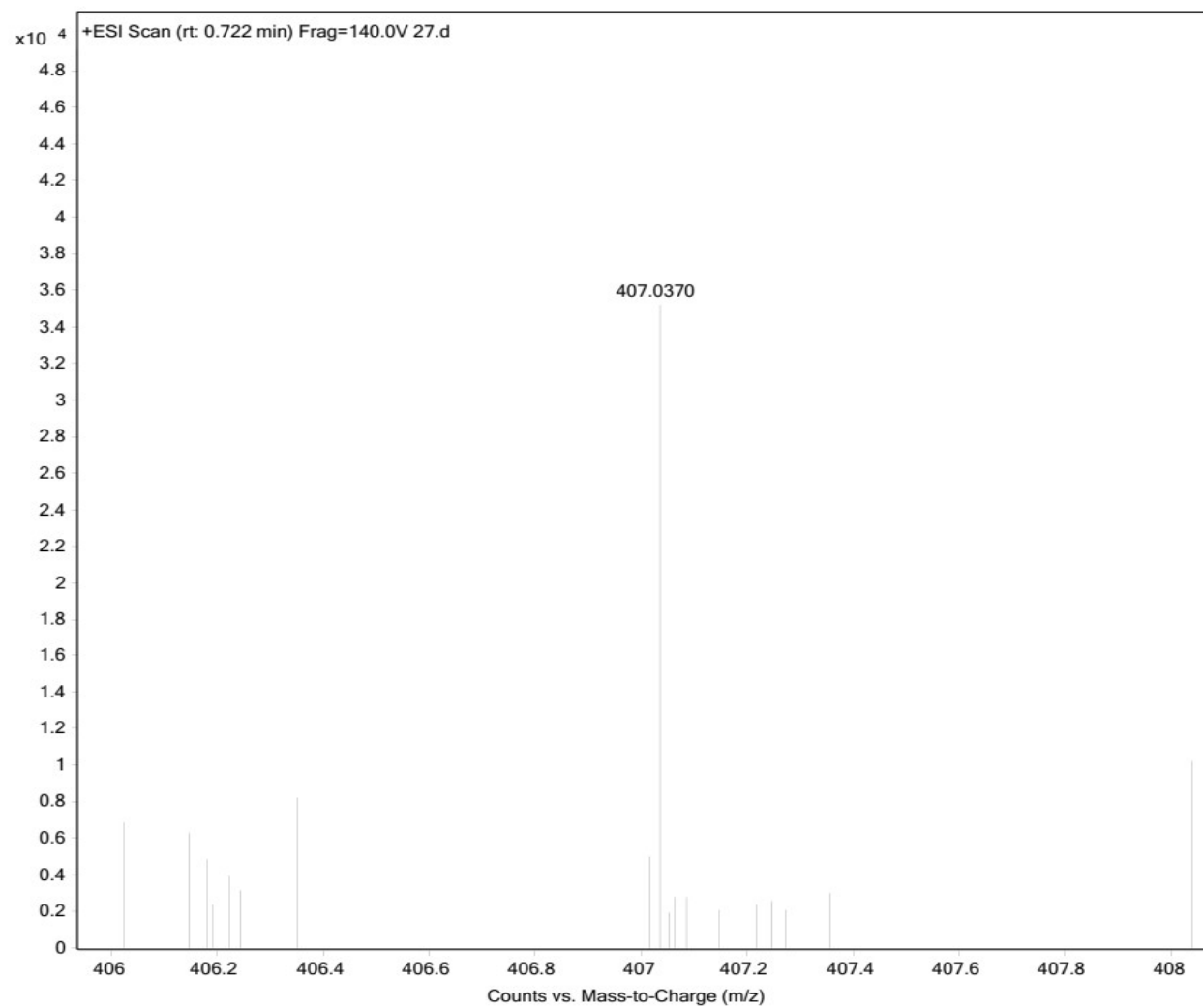
ATK-AA-127-1H.1.fid
ATK-AA-127-1H



(400 MHz, Chloroform-*d*) δ 8.81 – 8.79 (m, 1H), 7.75 – 7.70 (m, 1H), 7.52 (d, $J = 8.4$ Hz, 1H), 7.38 (d, $J = 10.3$ Hz, 1H), 7.32 – 7.27 (m, 2H), 6.94 – 6.87 (m, 2H), 5.95 (dd, $J = 10.3, 6.3$ Hz, 1H), 5.35 (d, $J = 6.2$ Hz, 1H), 3.91 (s, 3H).



HRMS 3i

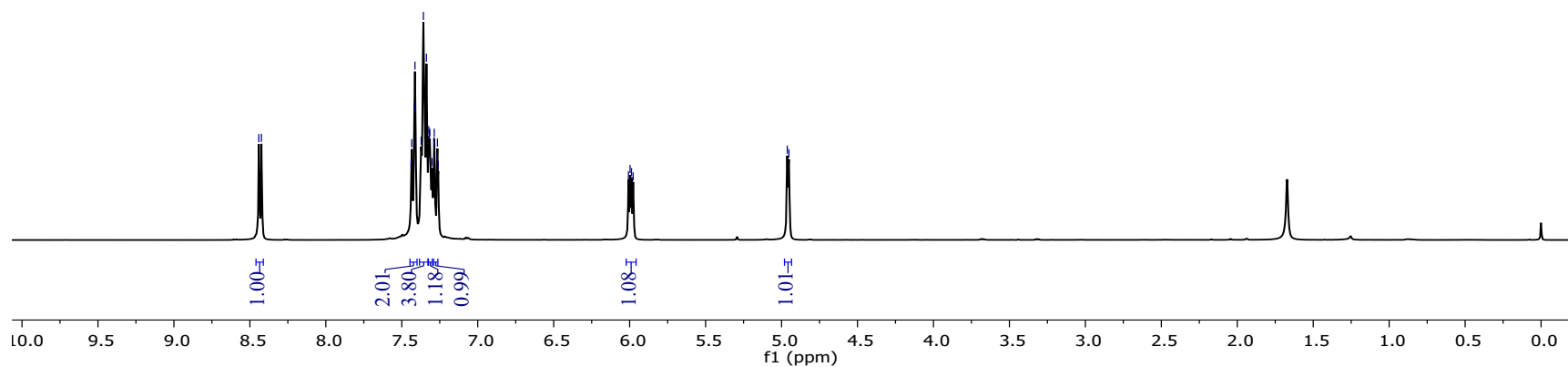
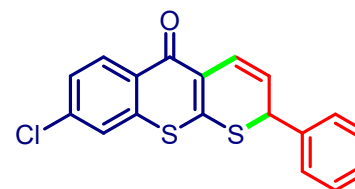
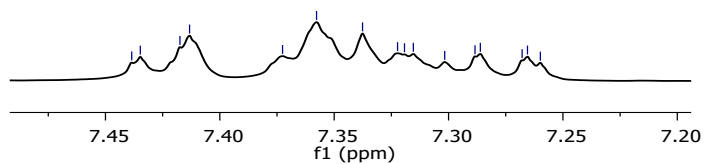


¹H NMR Compound (3j)

ATK-AA-8-1H.3.fid — ATK-AA-8-1H

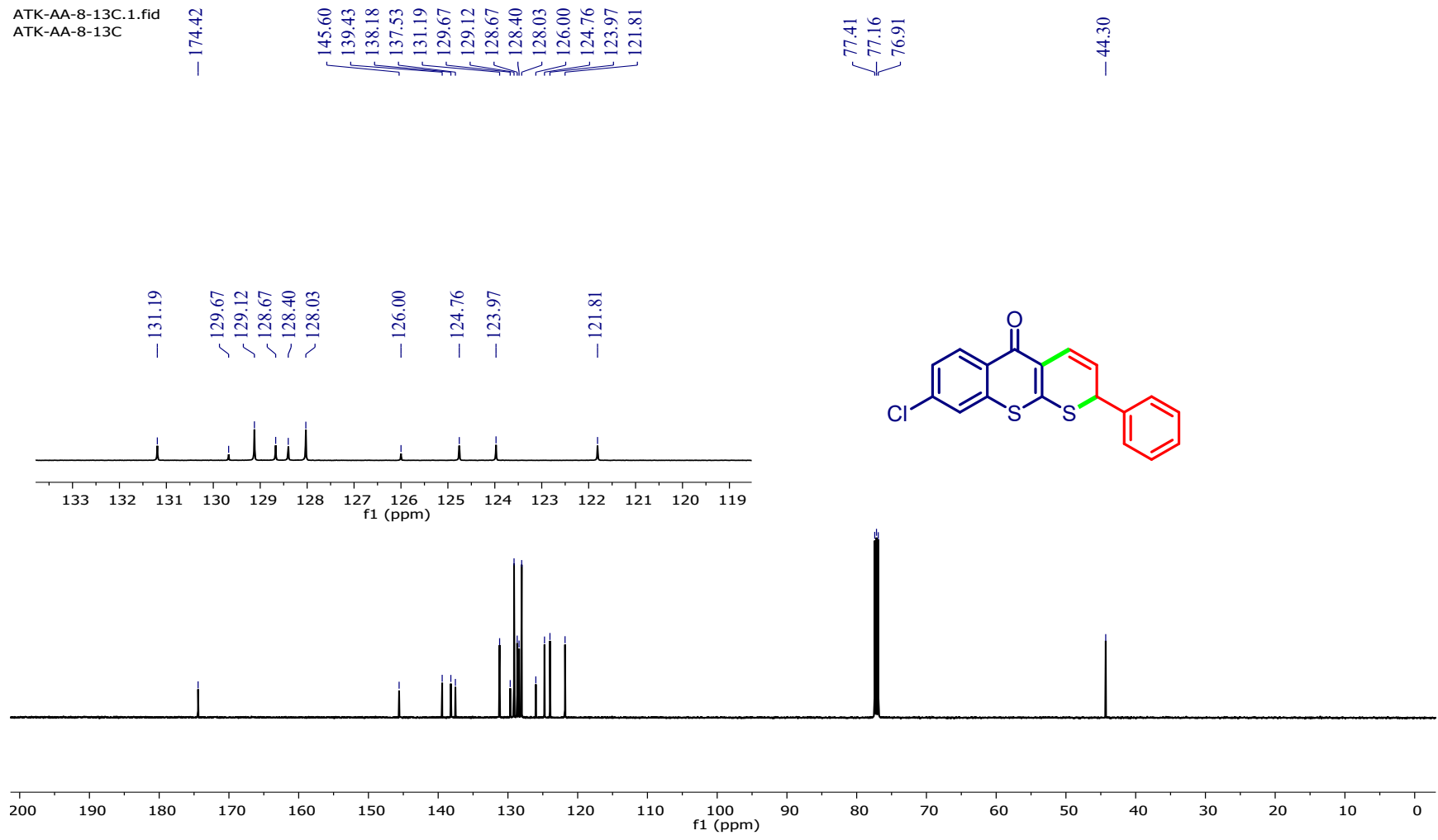
8.44
8.42
7.44
7.43
7.42
7.41
7.37
7.36
7.34
7.32
7.32
7.32
7.30
7.29
7.29
7.27
7.27
7.26
6.01
6.00
5.99
5.98
4.96
4.95

7.44
7.43
7.42
7.41
7.37
7.36
7.34
7.32
7.32
7.32
7.30
7.29
7.29
7.27
7.27
7.26

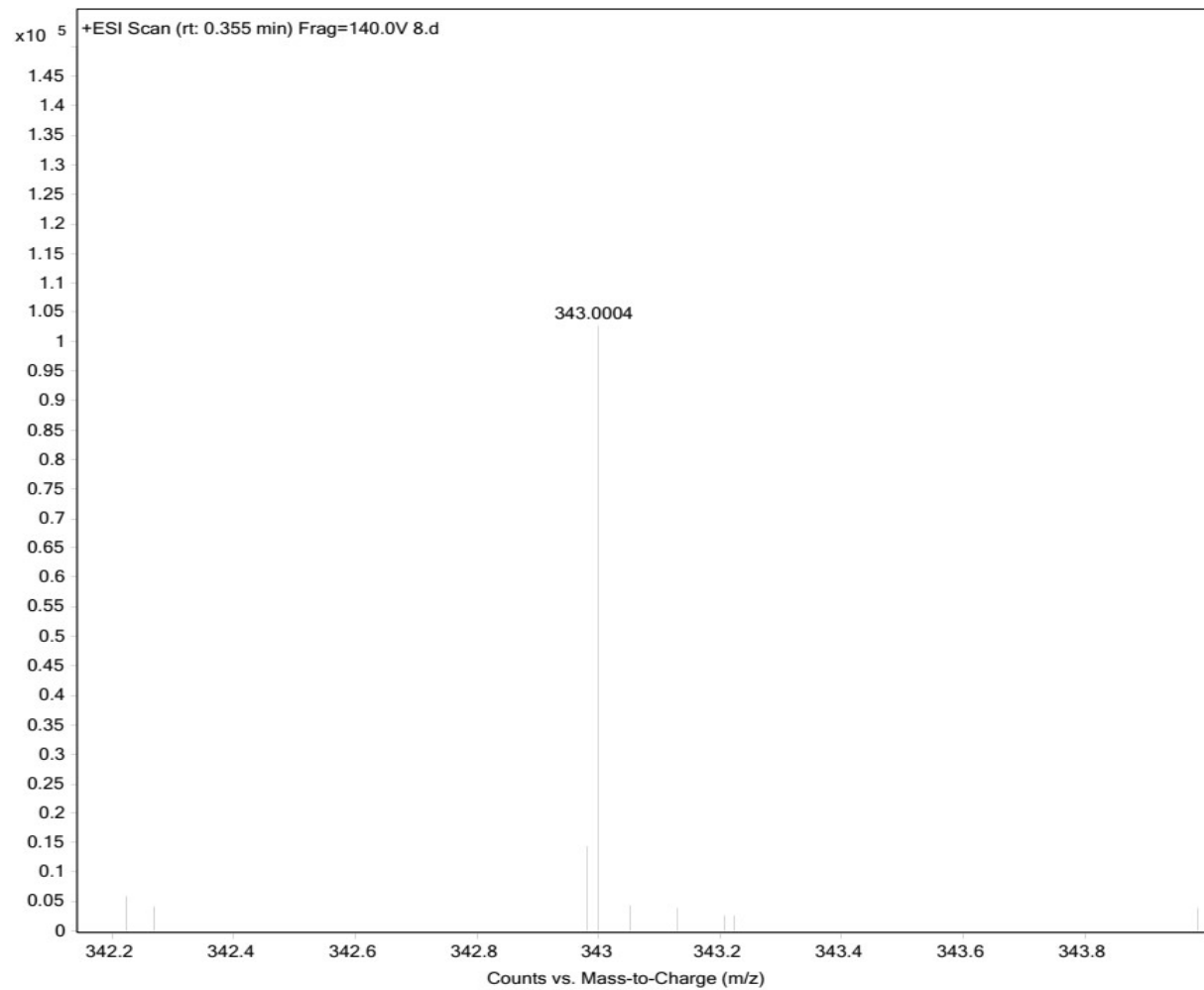


¹³C NMR Compound (a3j)

ATK-AA-8-13C.1.fid
ATK-AA-8-13C

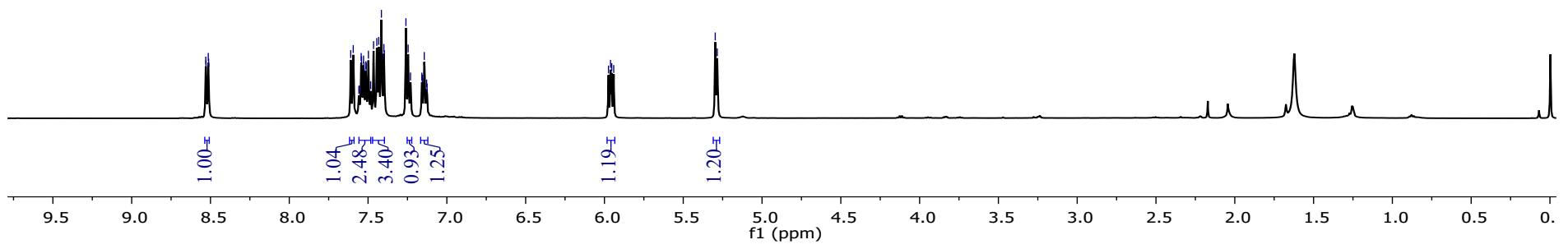
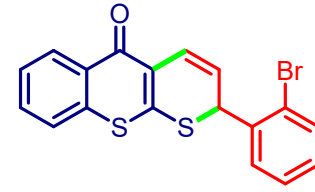
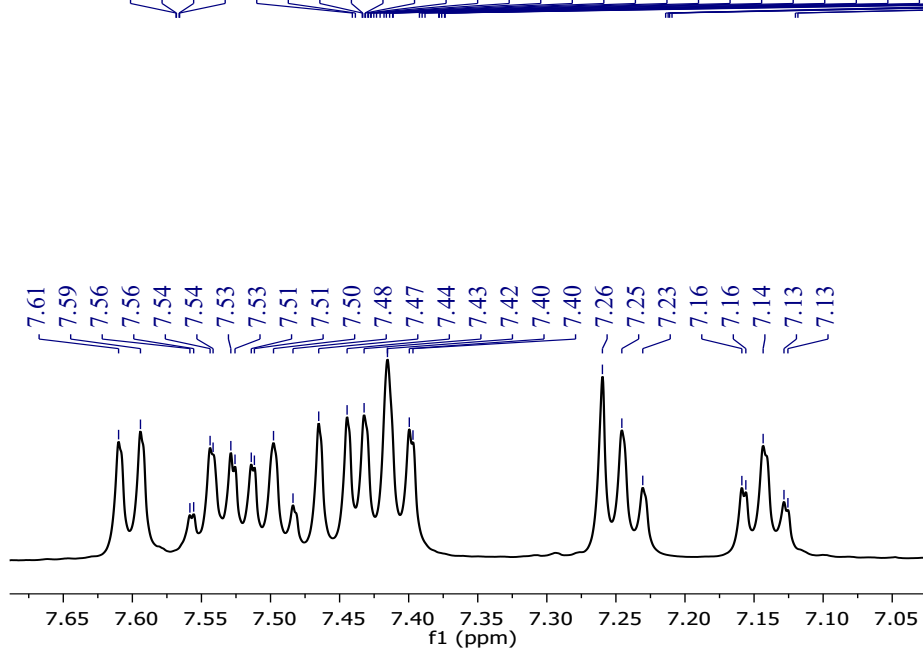


HRMS of 3j



¹H NMR Compound (3k)

ATK-AA-13-P2A13
ATK-AA-13-P2A13

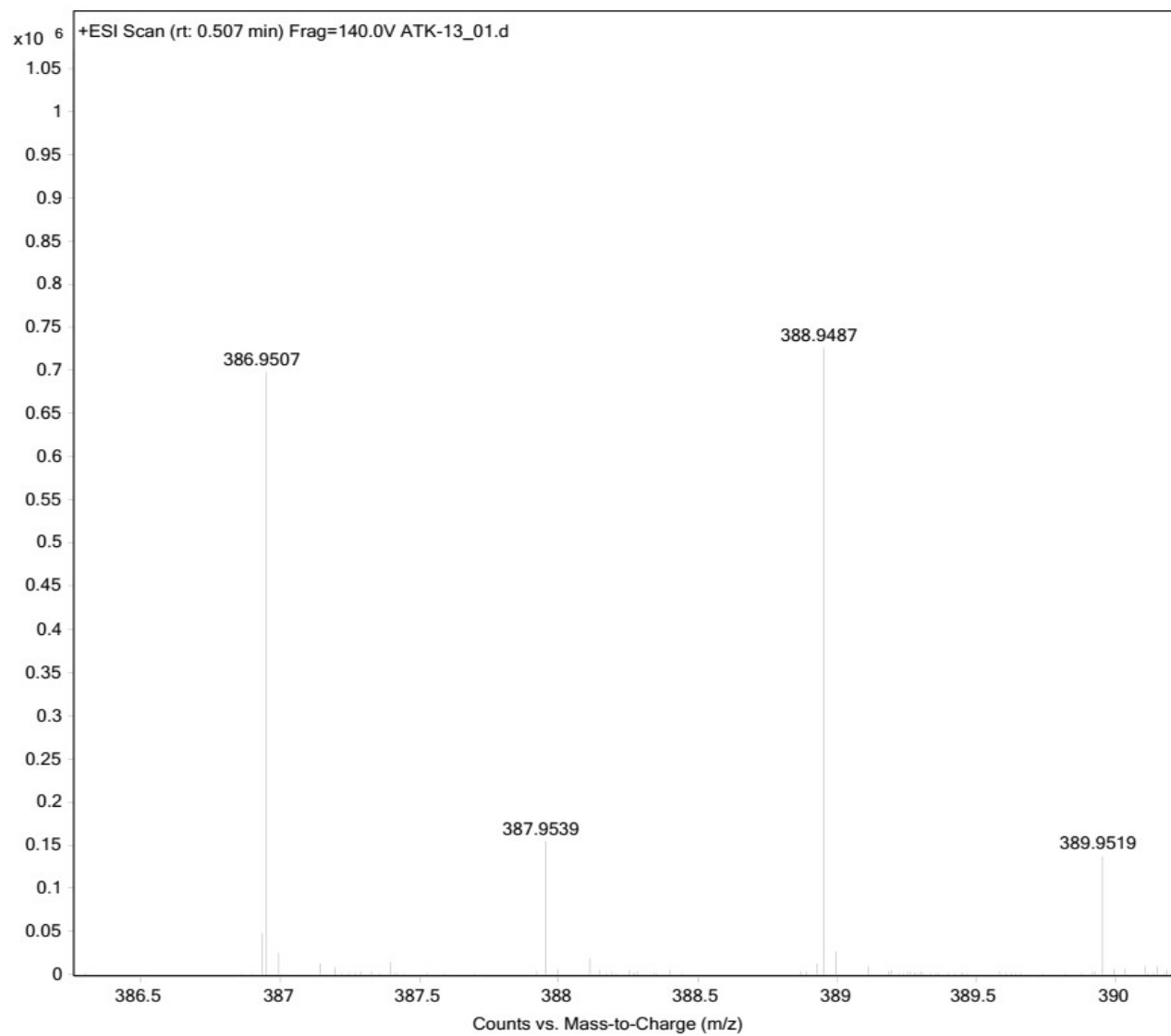


¹H NMR Compound (3k)

ATK-AA-13-P2A13-13C.3.fid
ATK-AA-13-P2A13-13C

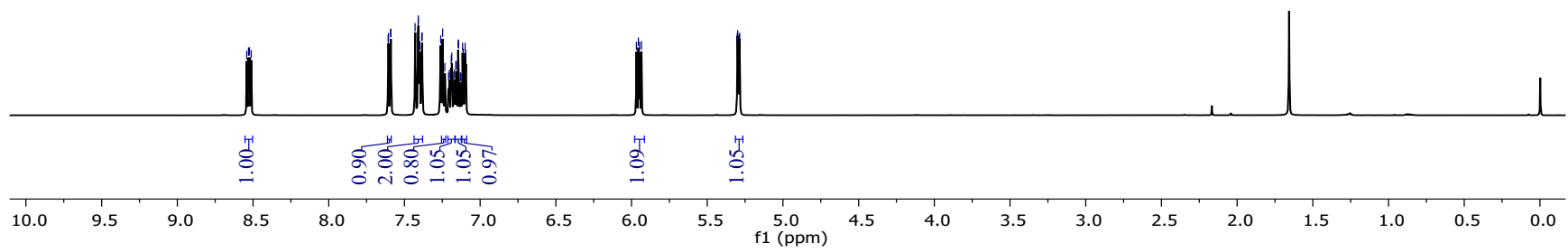
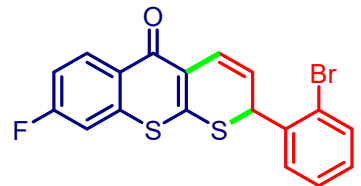
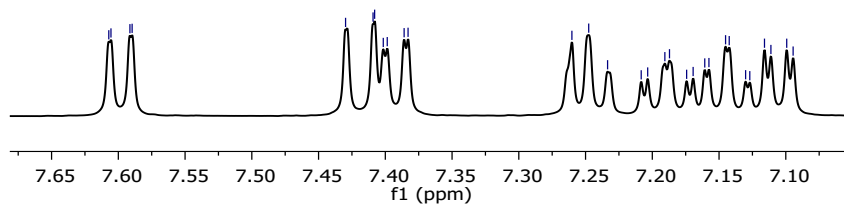


HRMS Compound (3k)



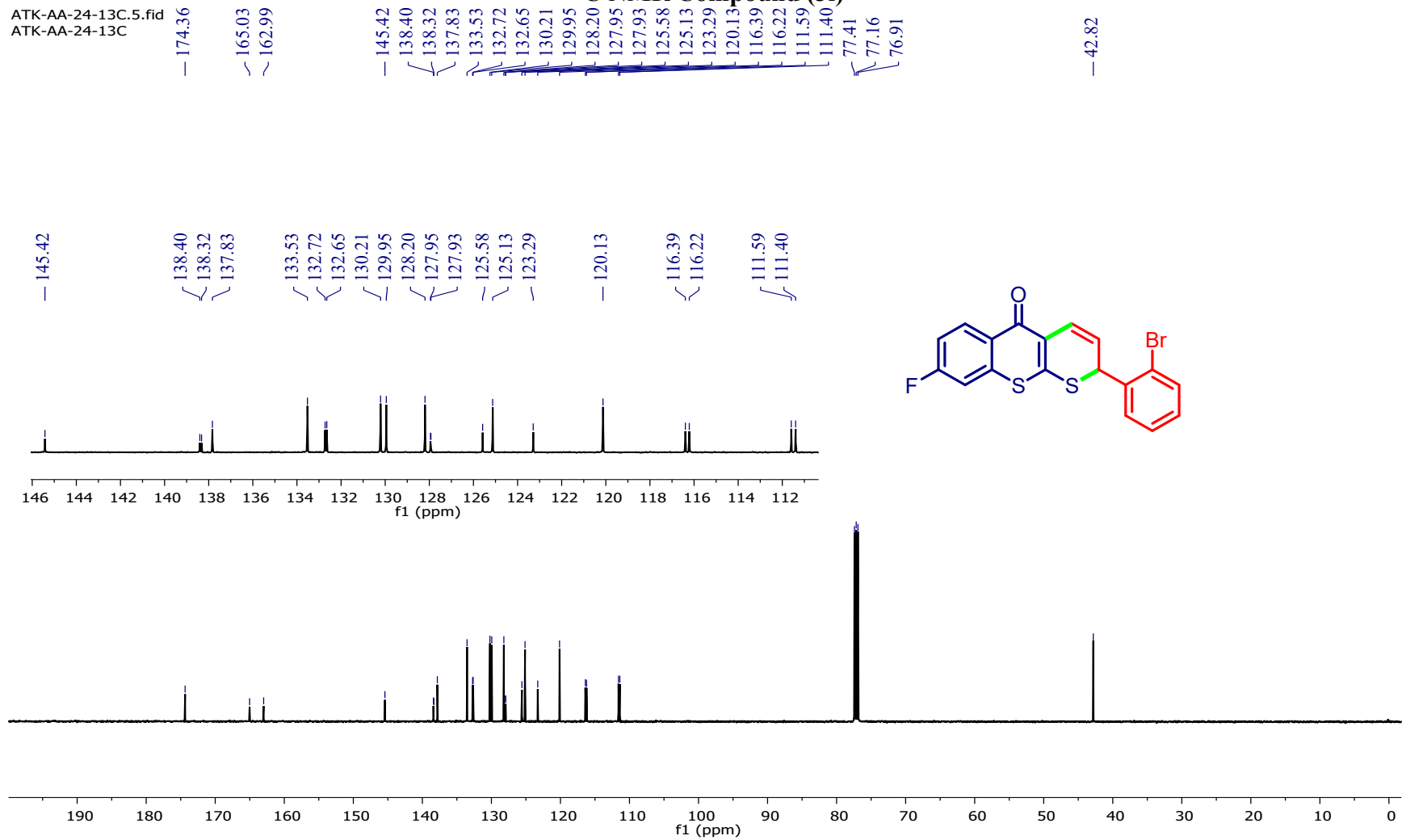
¹H NMR Compound (3l)

ATK-AA-24-1H.1.fid
ATK-AA-24-1H

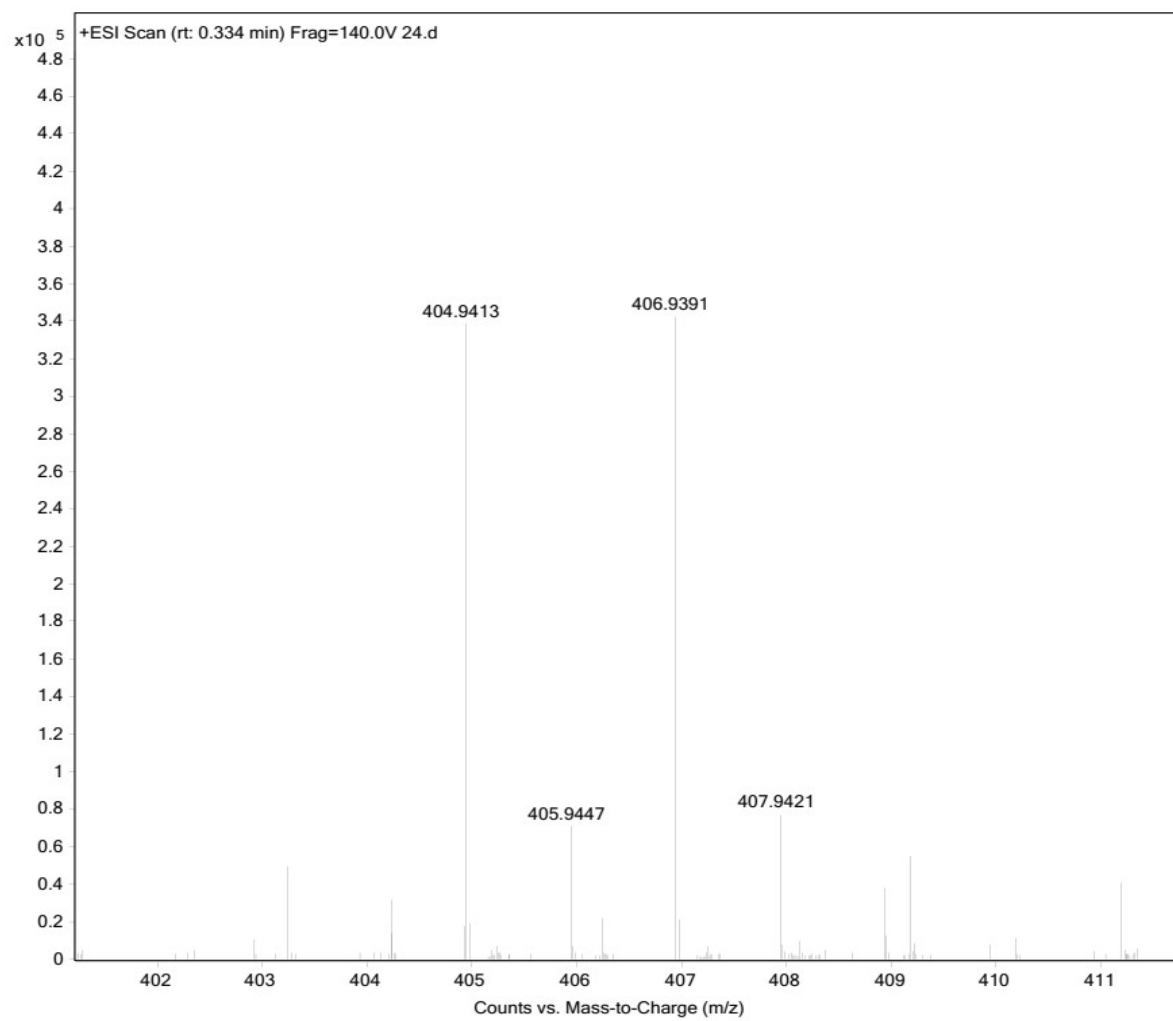


ATK-AA-24-13C.5.fid
ATK-AA-24-13C

¹³C NMR Compound (3l)

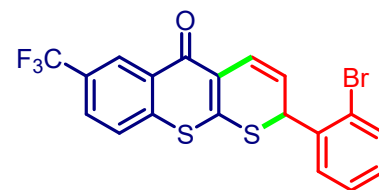


HRMS (31)

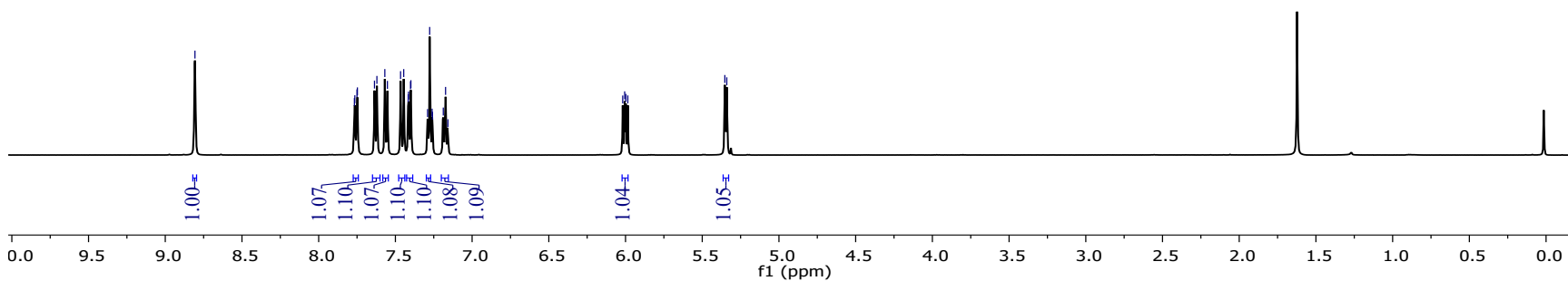
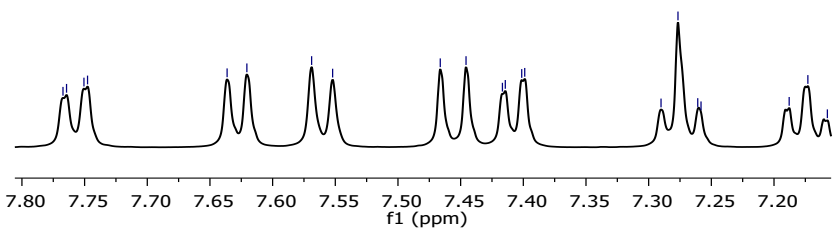


¹H NMR of compound (3m)

MPO-AA-30-11-15-110
MPO-AA-30-11-15-110
7.77
7.76
7.75
7.75
7.64
7.62
7.57
7.55
7.47
7.45
7.42
7.41
7.40
7.40
7.29
7.28
7.26
7.26
7.19
7.17
7.16
6.02
6.01
6.00
5.99
5.35
5.34

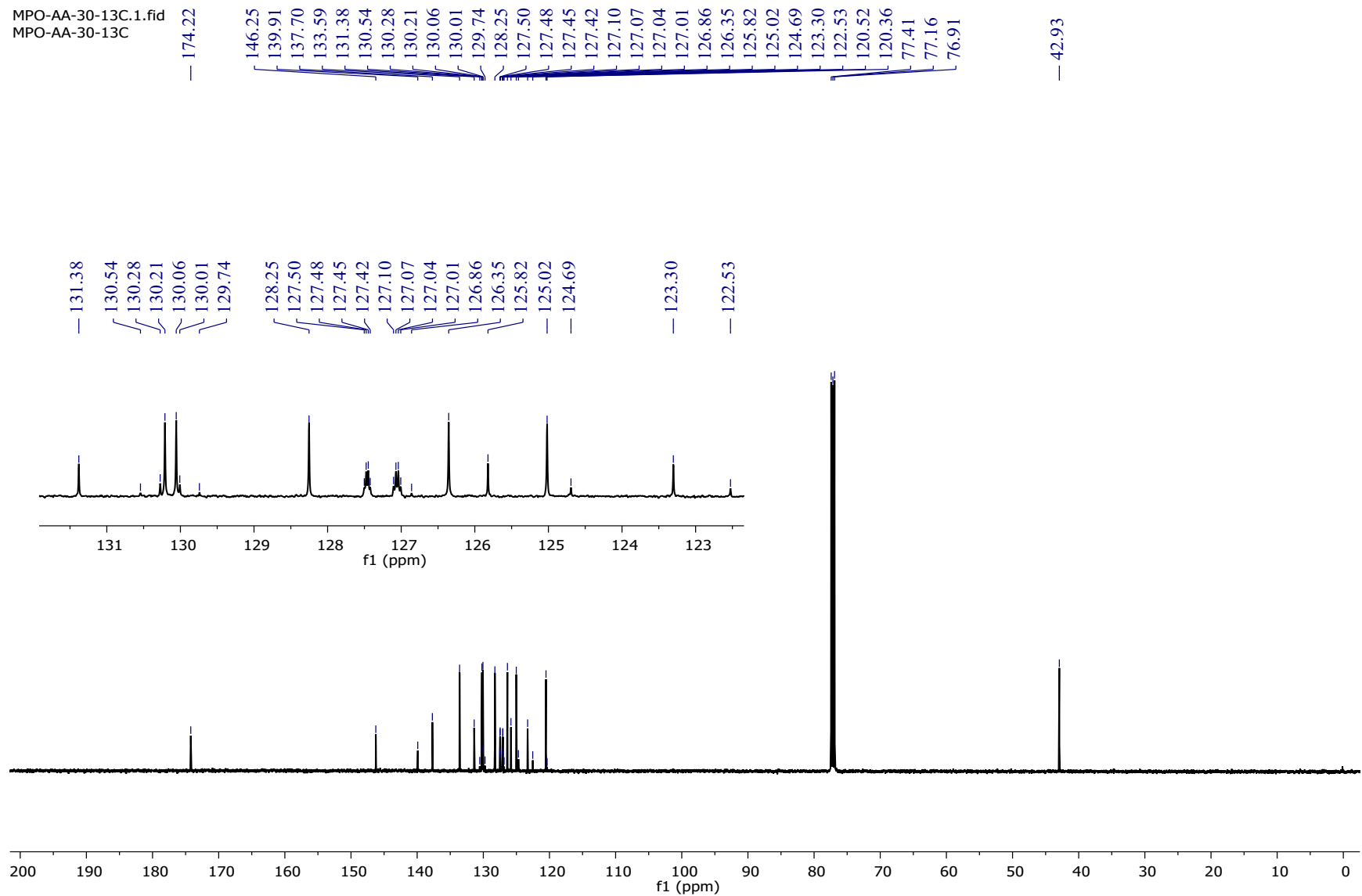


7.77
7.76
7.75
7.75
7.64
7.62
7.57
7.55
7.47
7.45
7.42
7.41
7.40
7.40
7.29
7.28
7.26
7.26
7.19
7.17
7.16

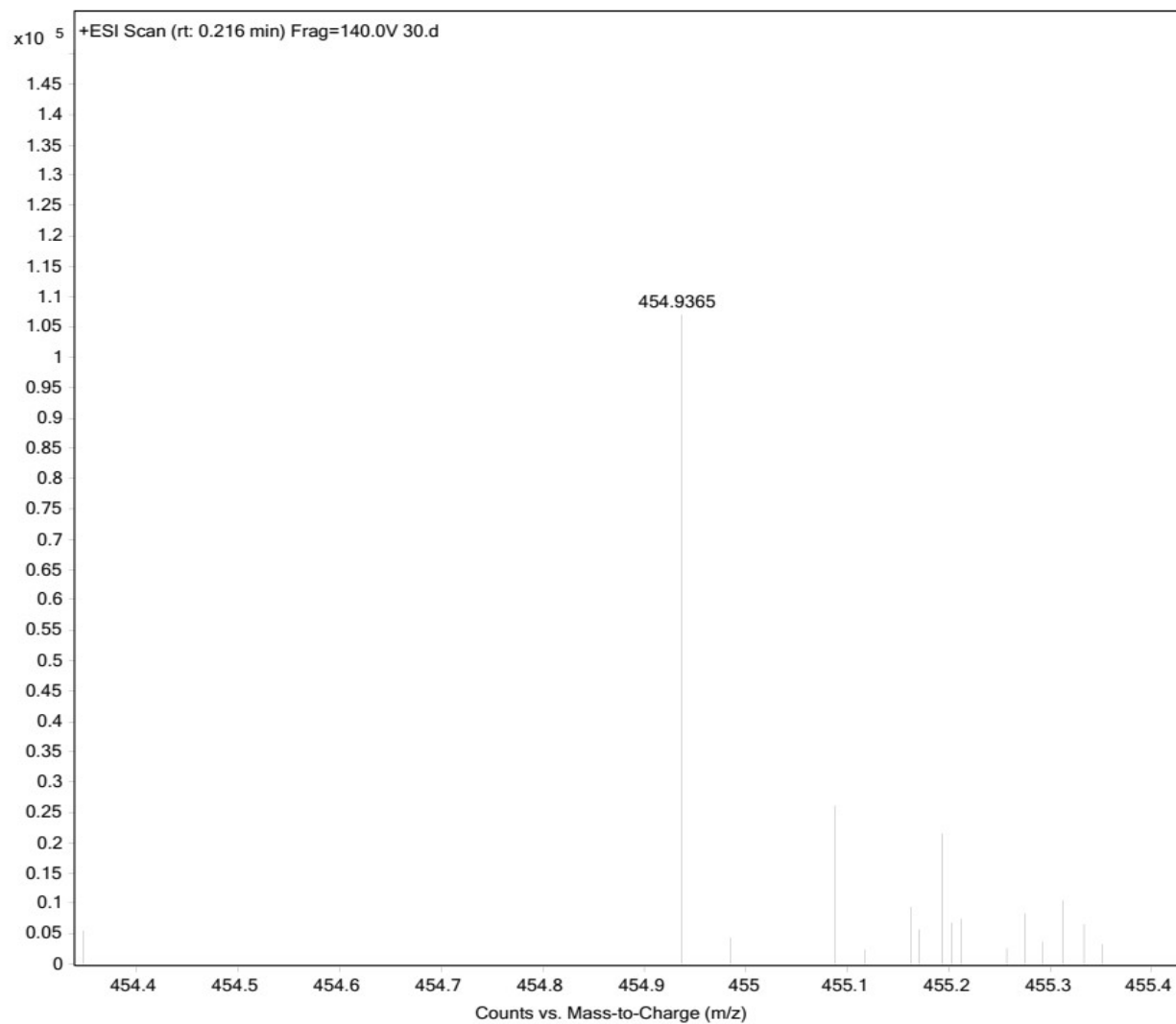


¹³C of compound (3m)

MPO-AA-30-13C.1.fid
MPO-AA-30-13C



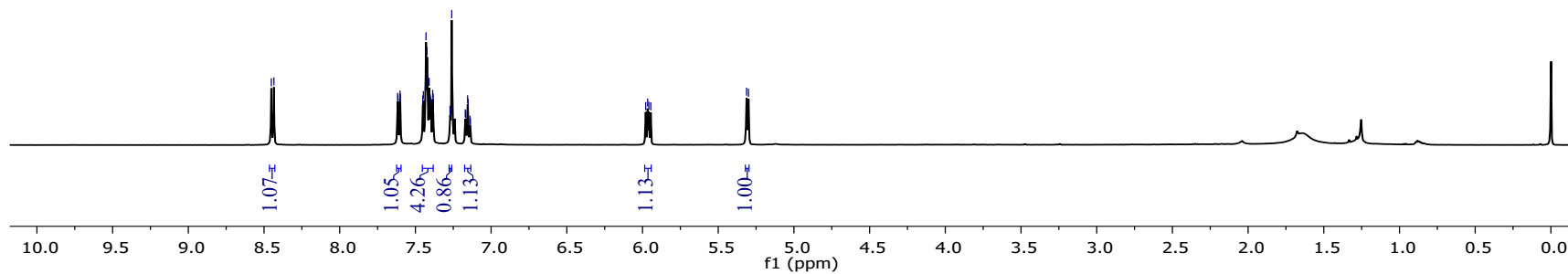
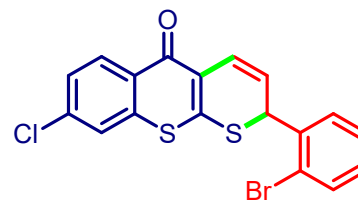
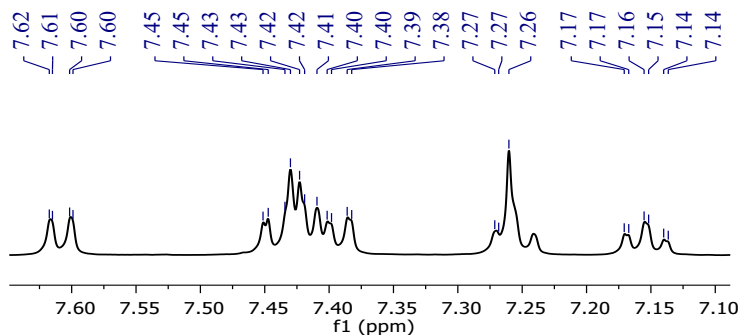
HRMS of 3m



¹H NMR Compound (n)

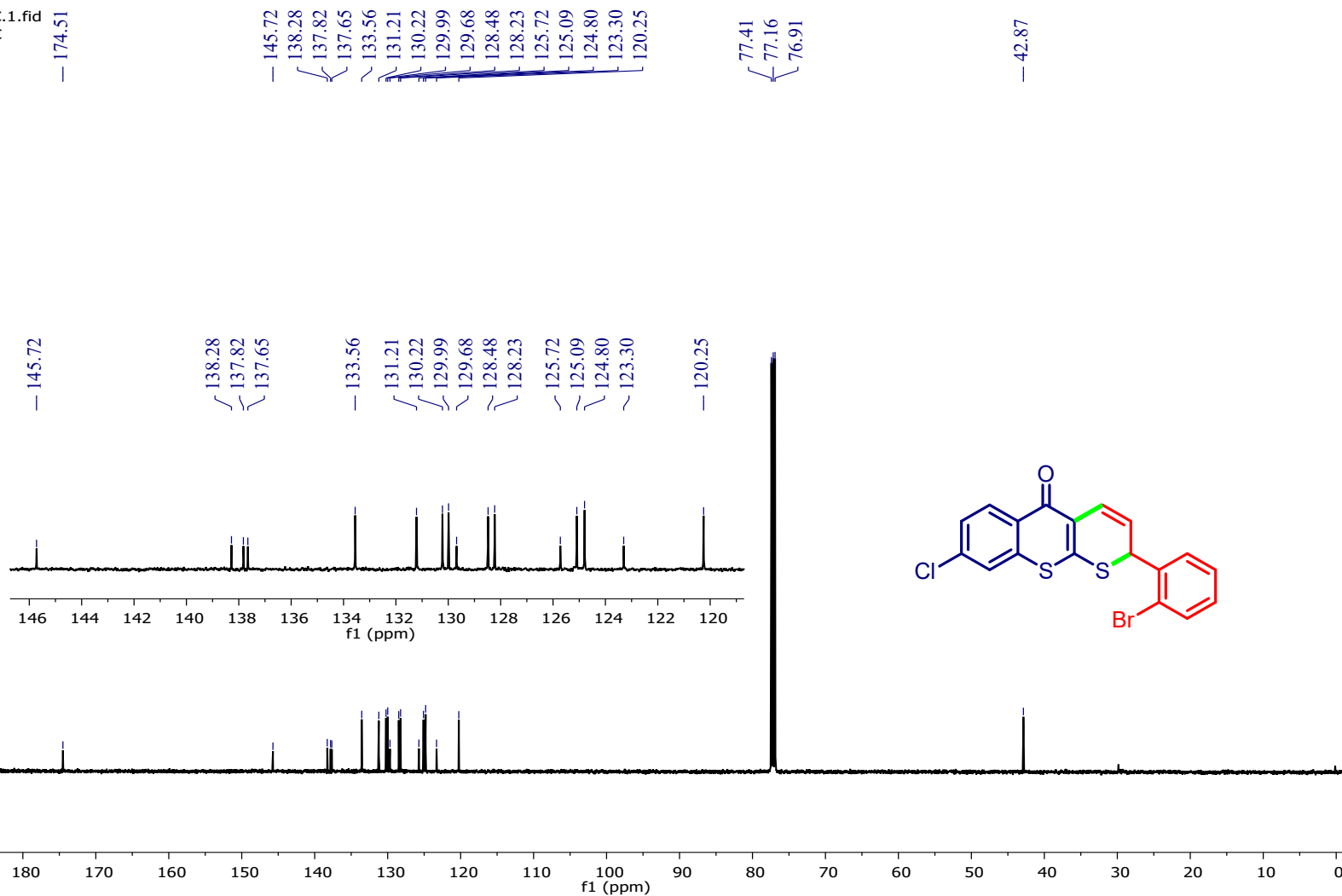
ATK-AA-18-1H.1.fid
ATK-AA-18-1H

8.45
8.43
7.62
7.61
7.60
7.60
7.45
7.45
7.43
7.43
7.42
7.42
7.41
7.40
7.40
7.39
7.38
7.27
7.27
7.26
7.17
7.17
7.16
7.15
7.14
7.14
5.98
5.96
5.95
5.31
5.30



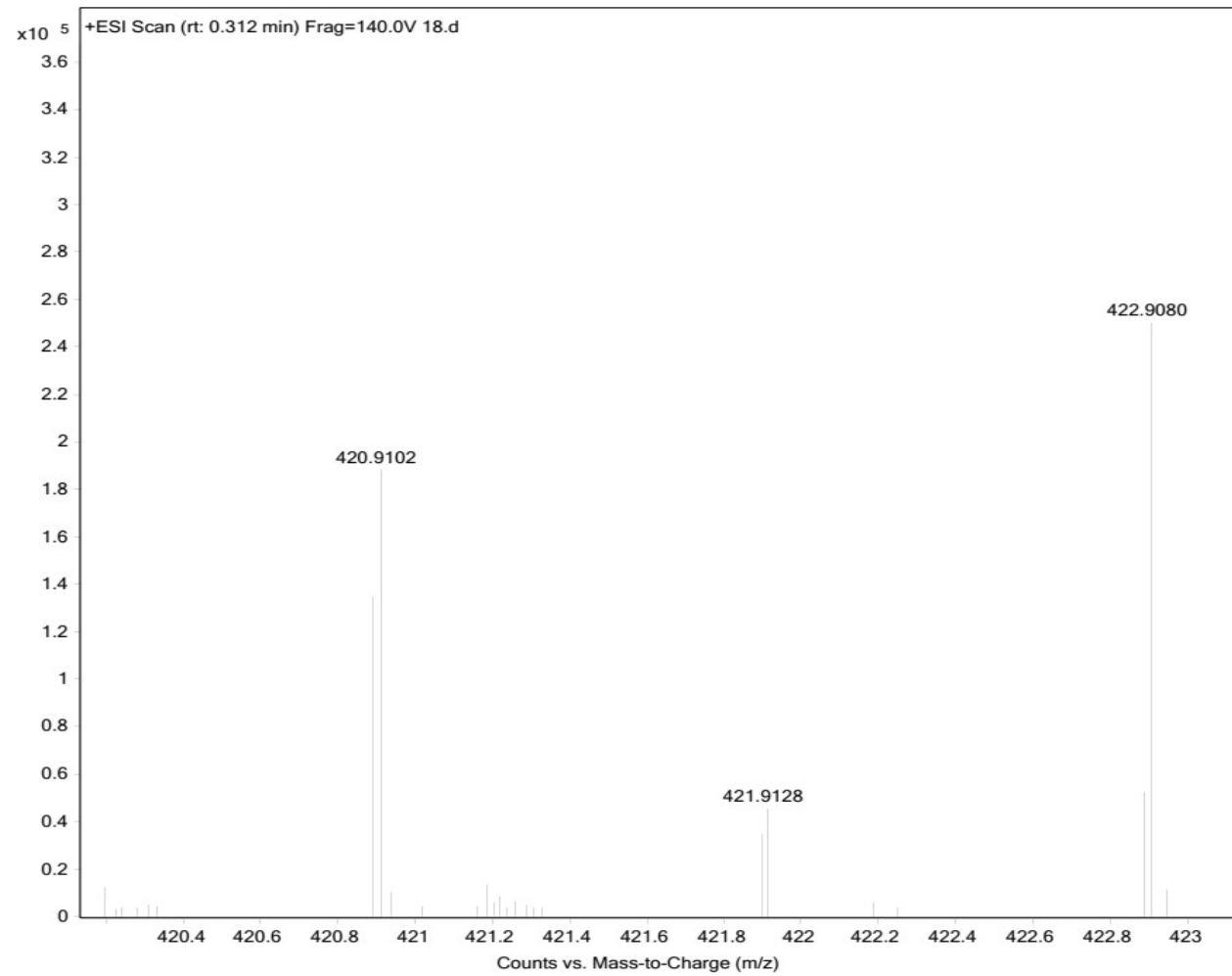
¹³C NMR Compound (3n)

ATK-AA-18-13C.1.fid
ATK-AA-18-13C



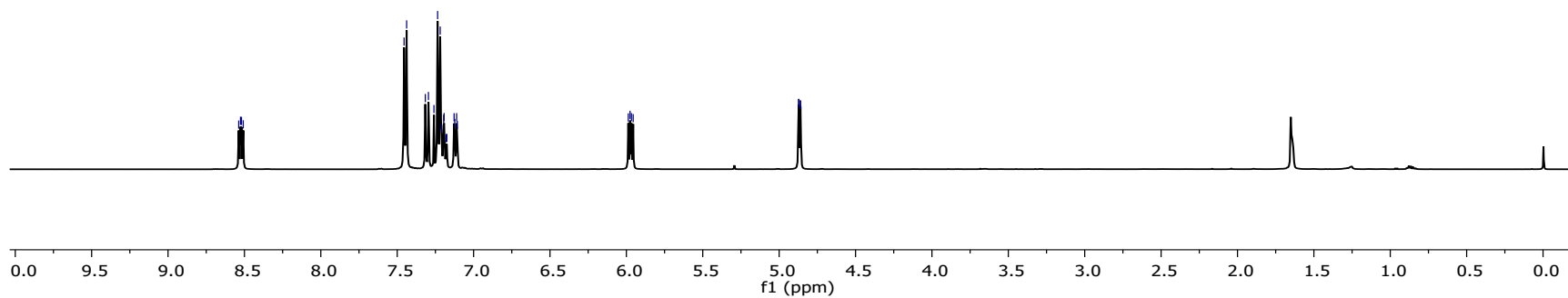
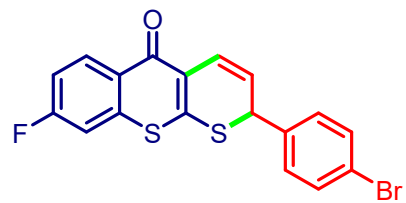
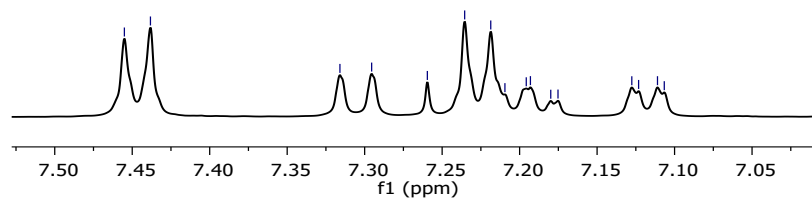
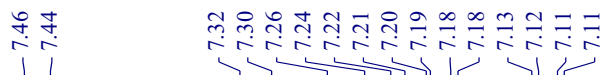
(125 MHz, Chloroform-*d*) δ 174.5, 145.7, 138.2, 137.8, 137.6, 133.5, 131.2, 130.2, 129.9, 129.6, 128.4, 128.2, 125.7, 125.0, 124.8, 123.3, 120.2, 42.8.

HRMS of 3n



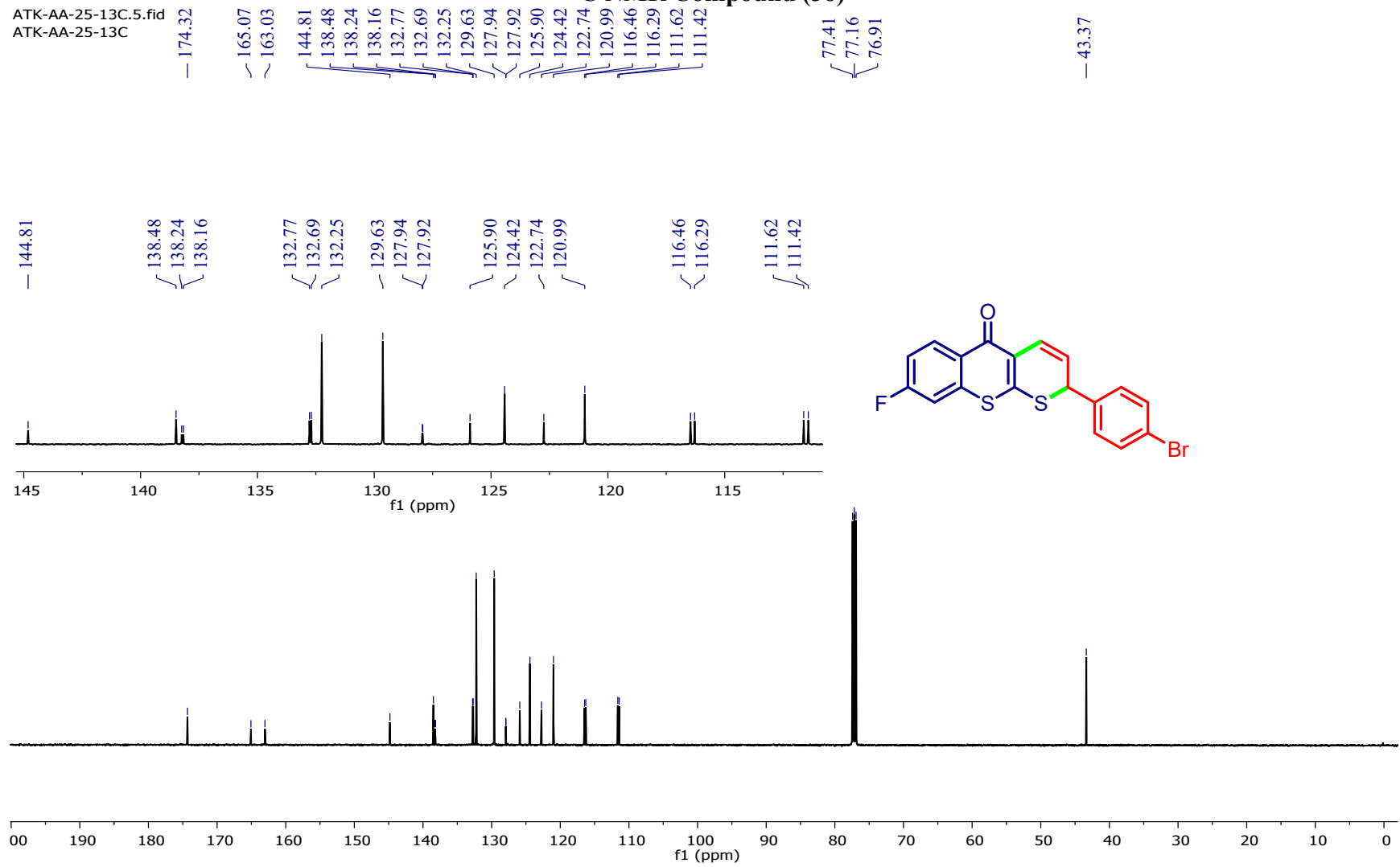
¹H NMR Compound (3o)

ATK-AA-25-1H.1.fid — ATK-AA-25-1H

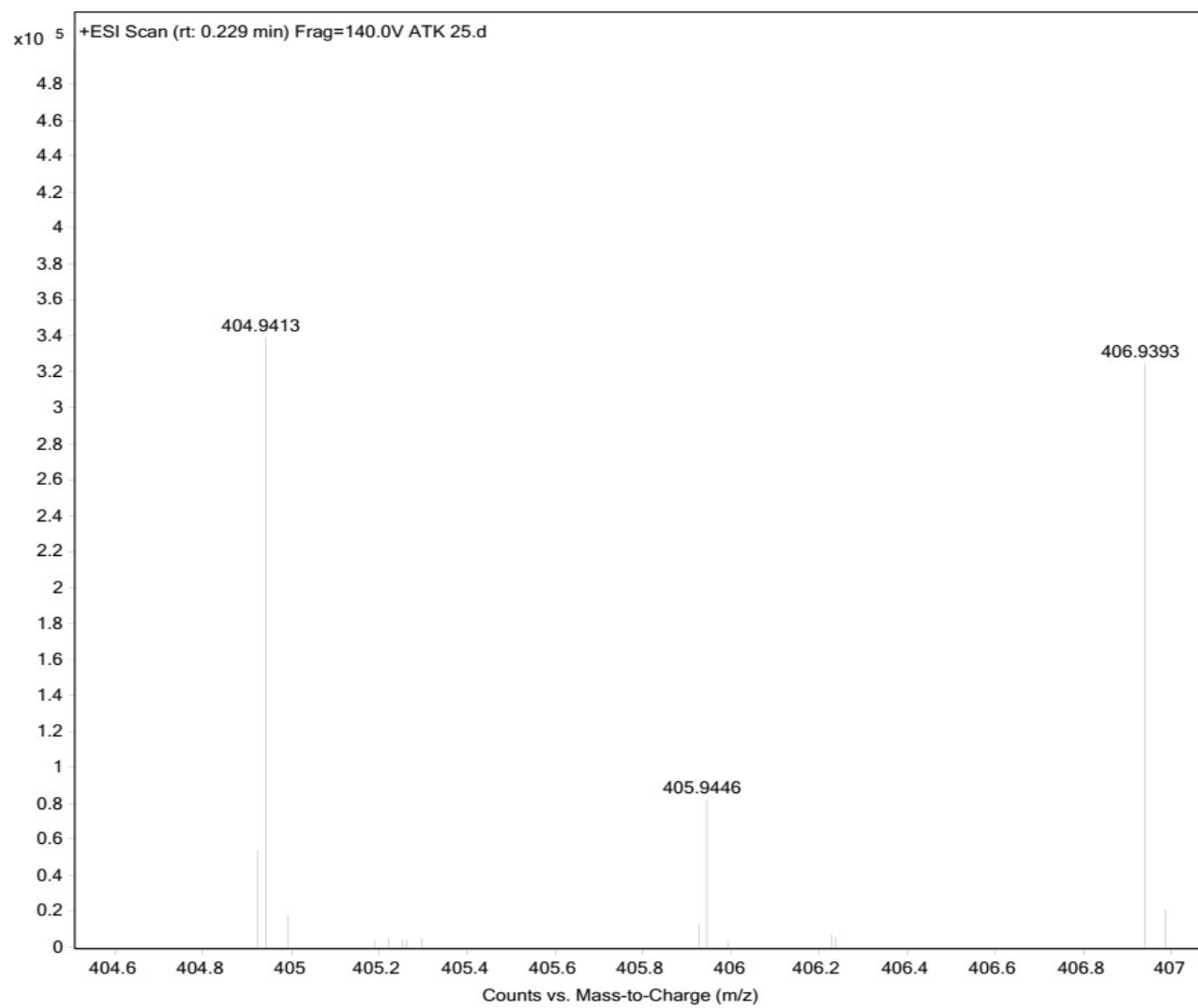


¹³C NMR Compound (3o)

ATK-AA-25-13C.5.fid
ATK-AA-25-13C



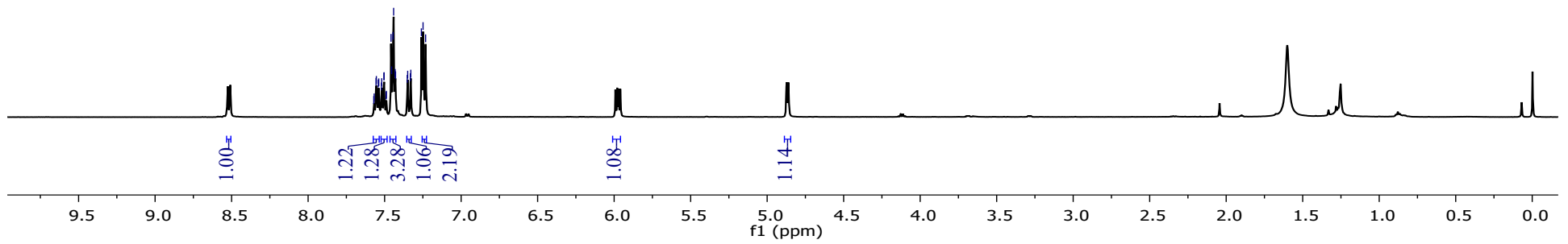
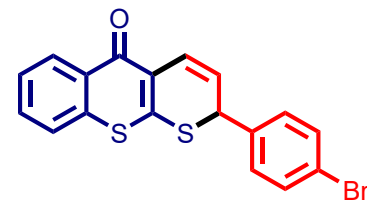
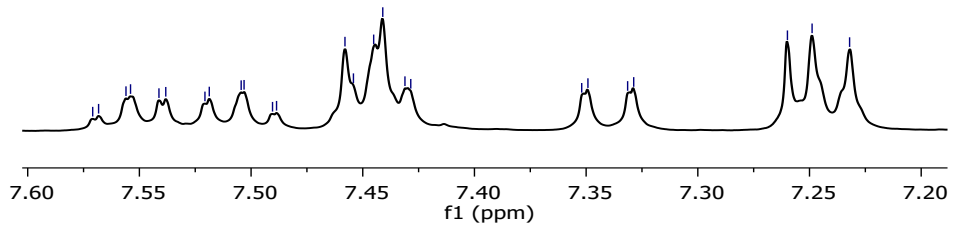
HRMS 3o



^1H NMR Compound (3p)

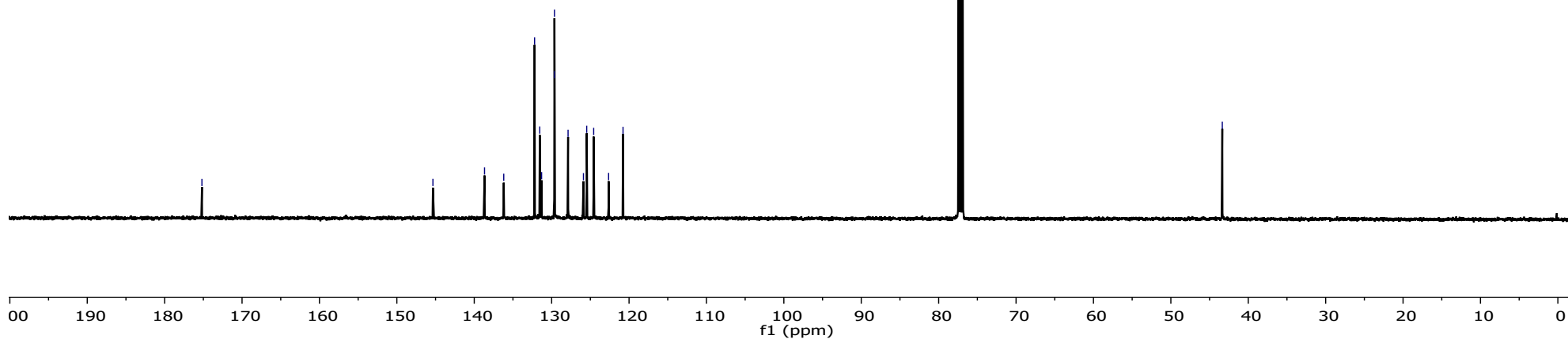
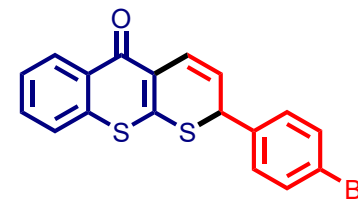
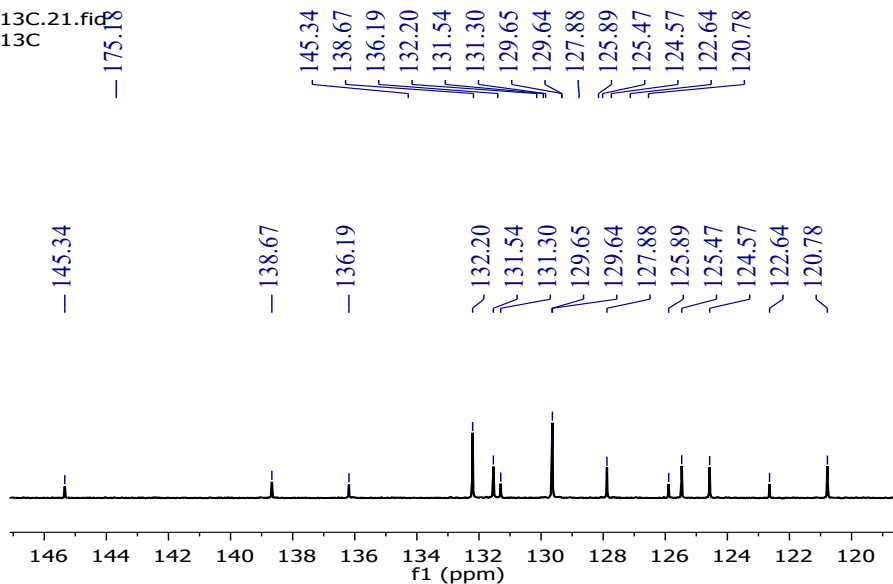
ATK-AA-14-PA14-H 7.57
ATK-AA-14-PA14-H 7.57
ATK-AA-14-PA14-H 7.56
ATK-AA-14-PA14-H 7.55
ATK-AA-14-PA14-H 7.54
ATK-AA-14-PA14-H 7.54
ATK-AA-14-PA14-H 7.52
ATK-AA-14-PA14-H 7.52
ATK-AA-14-PA14-H 7.50
ATK-AA-14-PA14-H 7.50
ATK-AA-14-PA14-H 7.49
ATK-AA-14-PA14-H 7.49
ATK-AA-14-PA14-H 7.46
ATK-AA-14-PA14-H 7.45
ATK-AA-14-PA14-H 7.45
ATK-AA-14-PA14-H 7.44
ATK-AA-14-PA14-H 7.43
ATK-AA-14-PA14-H 7.43
ATK-AA-14-PA14-H 7.35
ATK-AA-14-PA14-H 7.35
ATK-AA-14-PA14-H 7.33
ATK-AA-14-PA14-H 7.33
ATK-AA-14-PA14-H 7.26
ATK-AA-14-PA14-H 7.25
ATK-AA-14-PA14-H 7.23

7.57
7.57
7.56
7.55
7.54
7.54
7.52
7.52
7.50
7.50
7.49
7.49
7.46
7.45
7.45
7.44
7.43
7.43
7.35
7.35
7.33
7.33
7.26
7.25
7.23



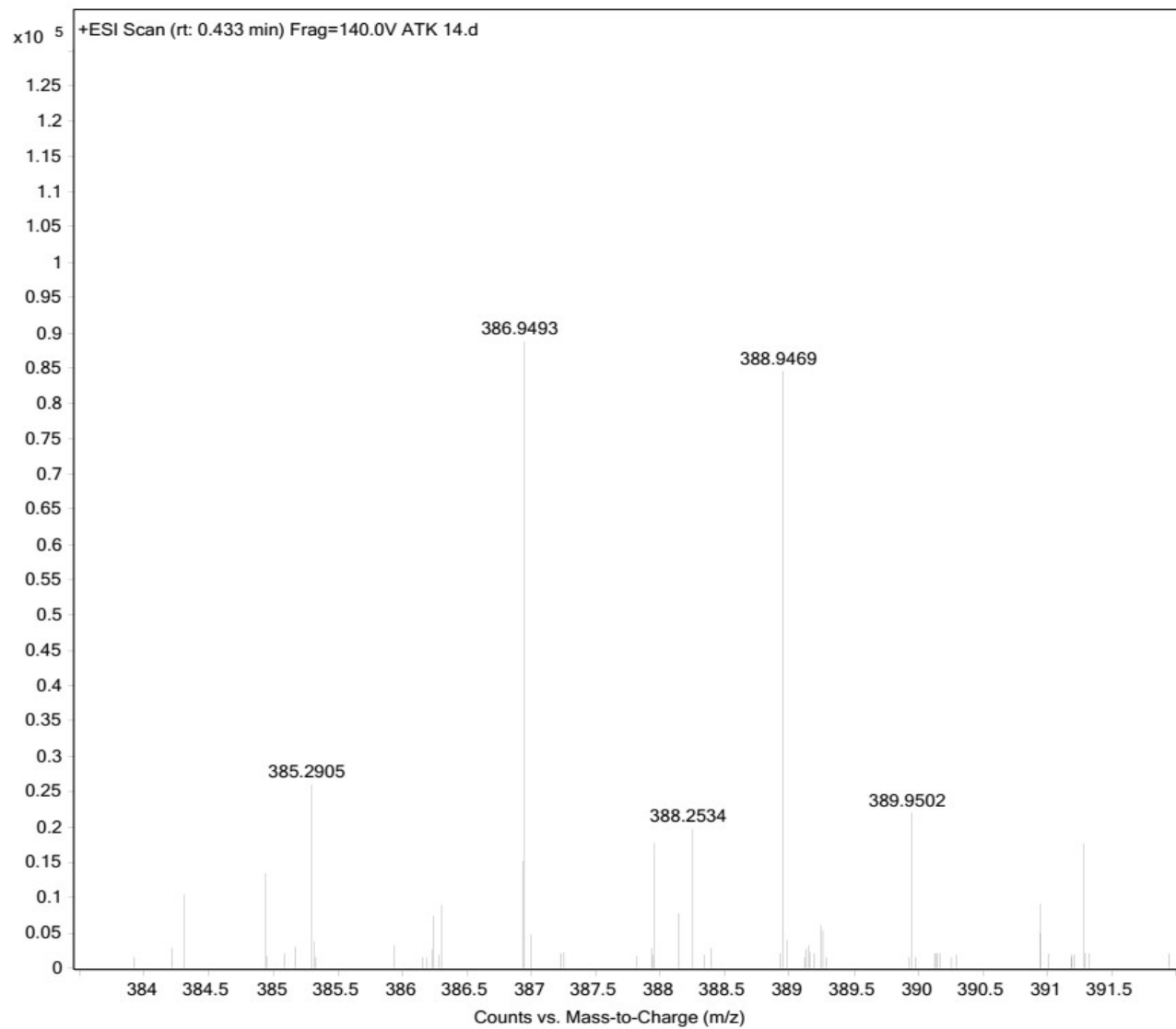
¹³C NMR Compound (3p)

ATK-AA-14-13C.21.fid
ATK-AA-14-13C



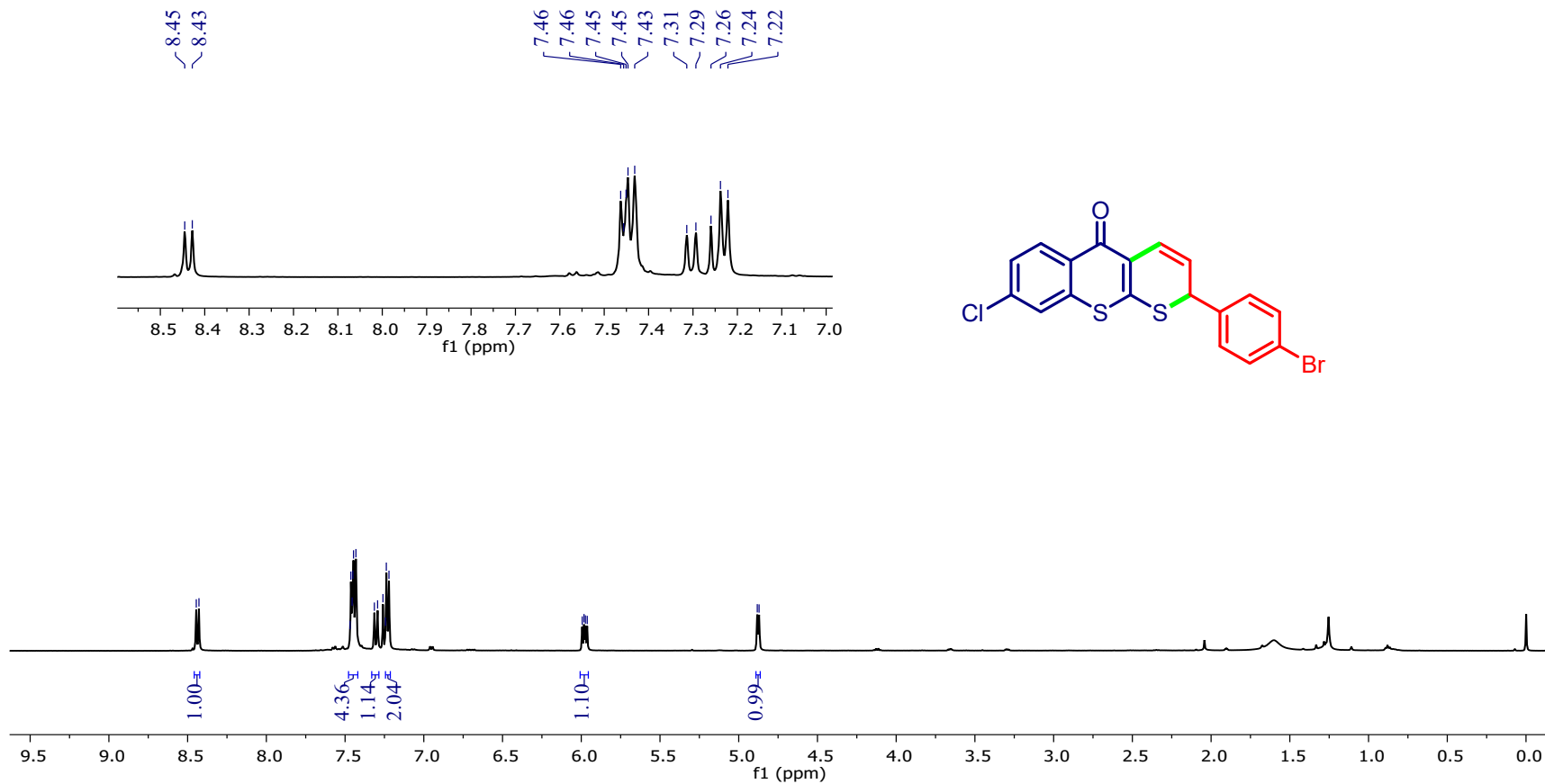
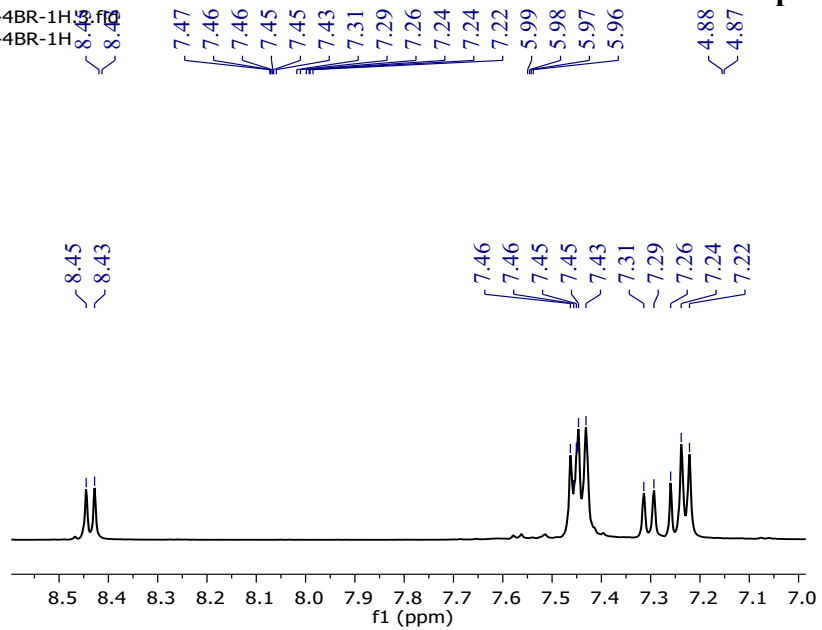
¹³C NMR (126 MHz, Chloroform-*d*) δ 175.1, 145.3, 138.6, 136.1, 132.2 (2C), 131.5, 131.3, 129.6, 129.6 (2C), 127.8, 125.8, 125.4, 124.5, 122.6, 120.7, 43.3.

HRMS 3p



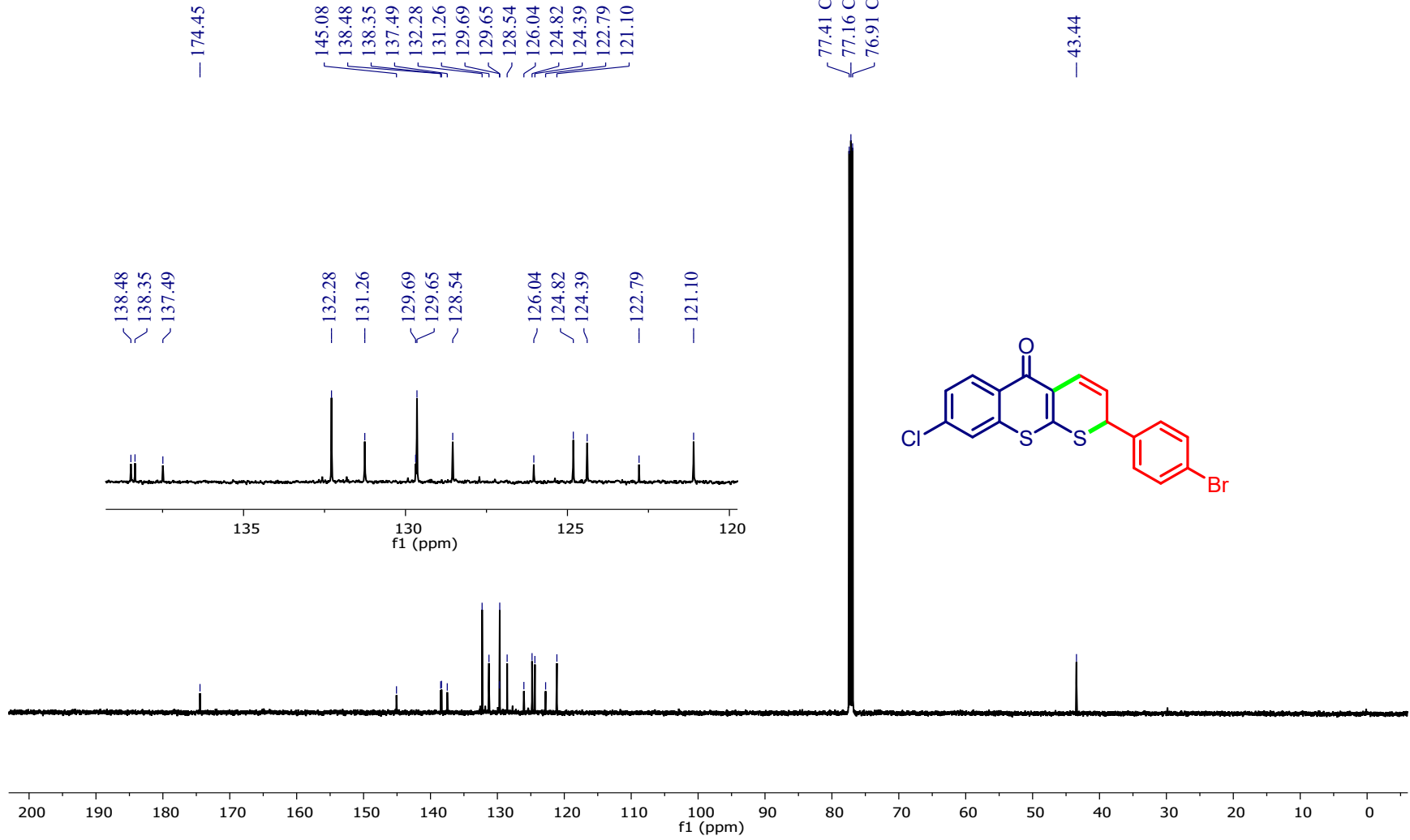
¹H NMR Compound (3q)

ATK-AA-19-4BR-1H
ATK-AA-19-4BR-1H

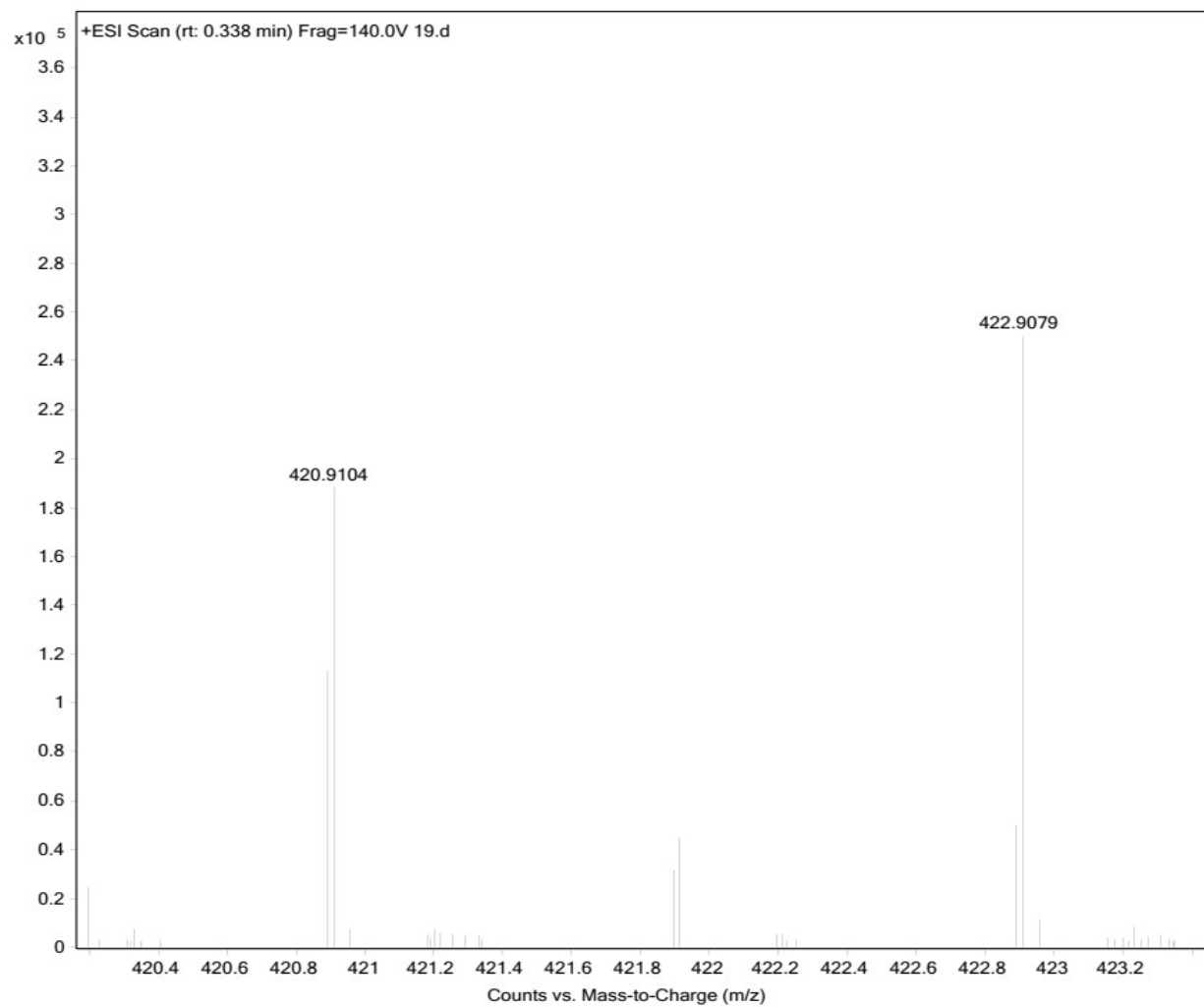


¹³C NMR Compound (3q)

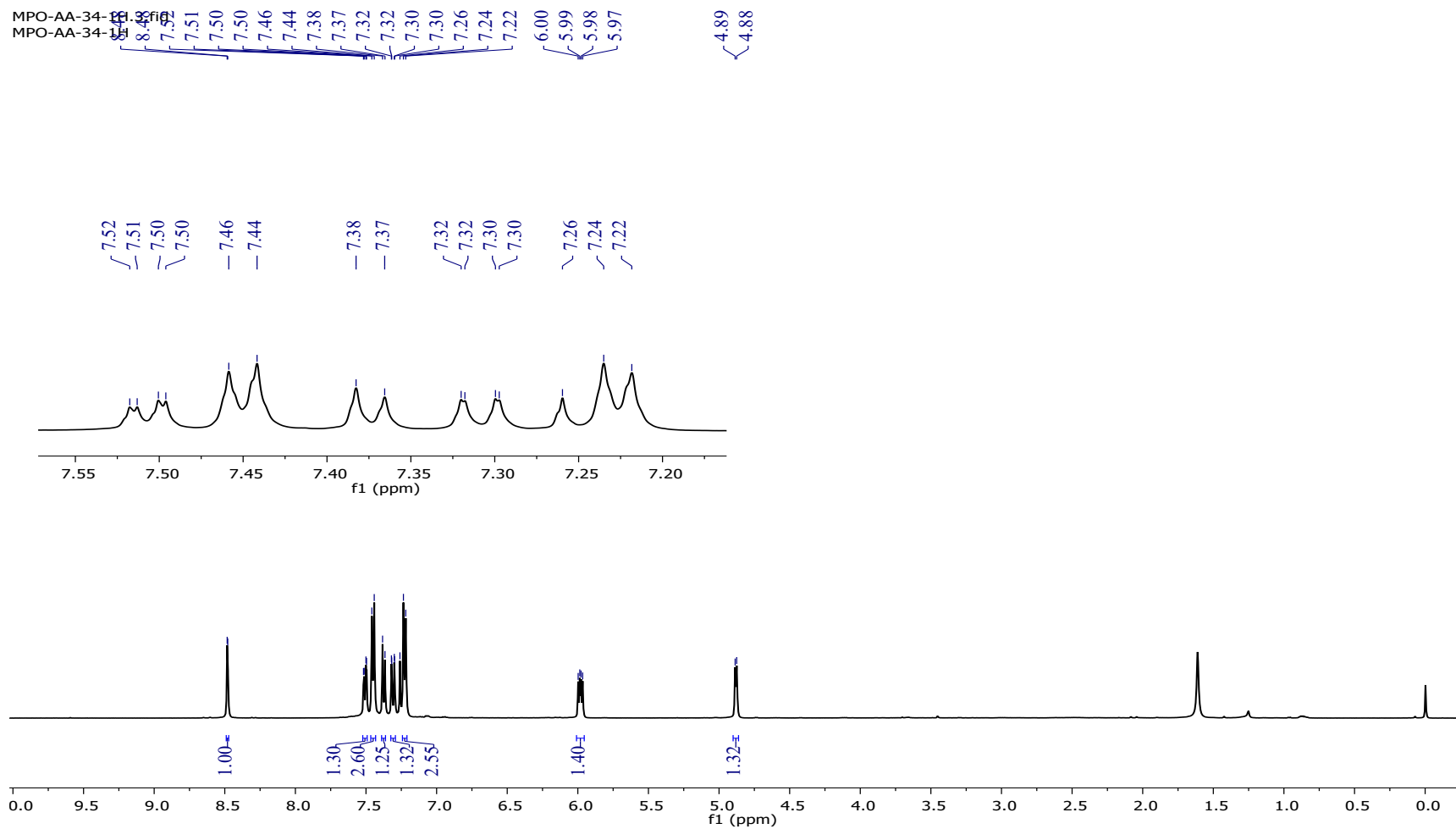
ATK-AA-19-4BR-13C.1.fid
ATK-AA-19-4BR-13C



HRMS 3q

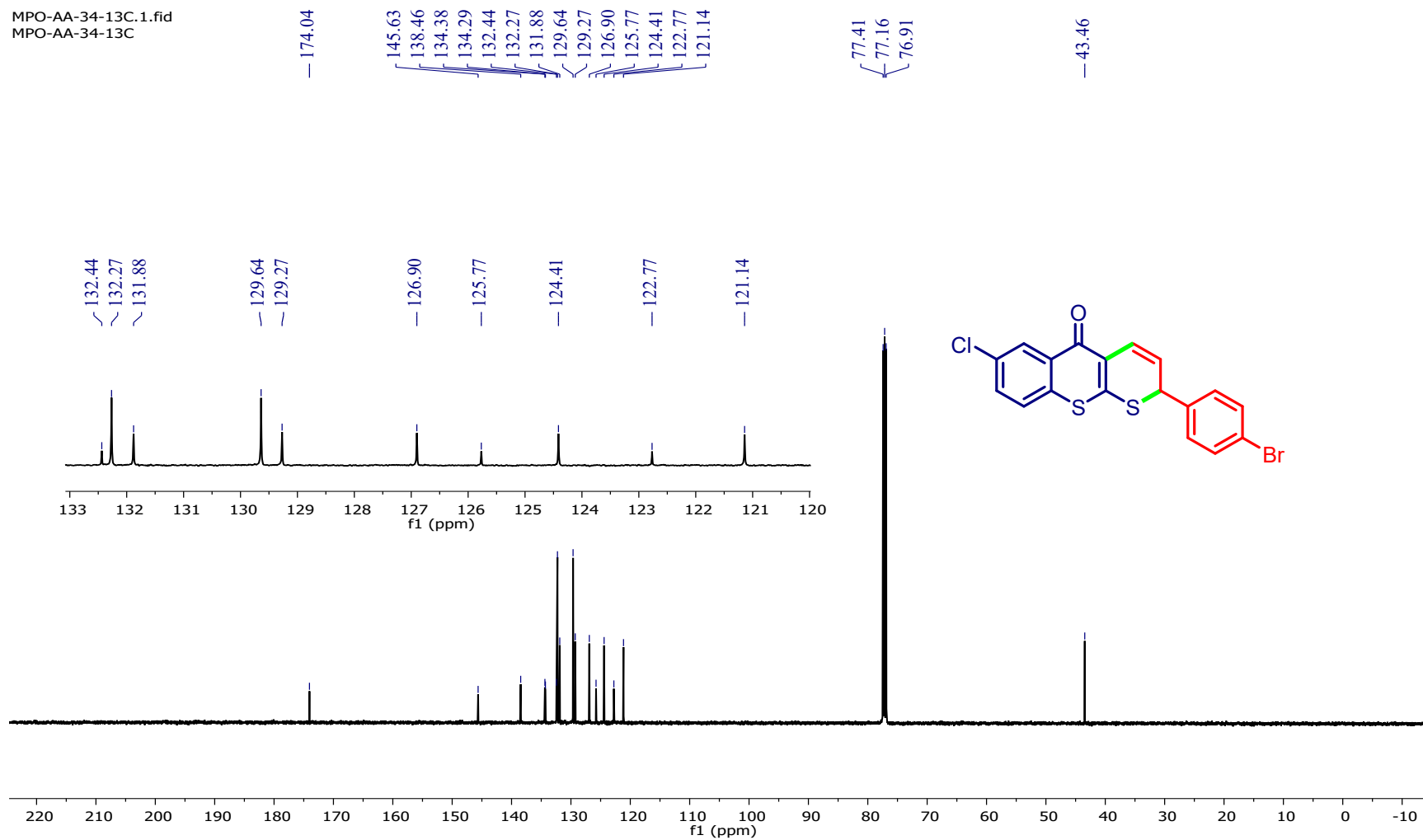


¹H NMR of compound (3r)

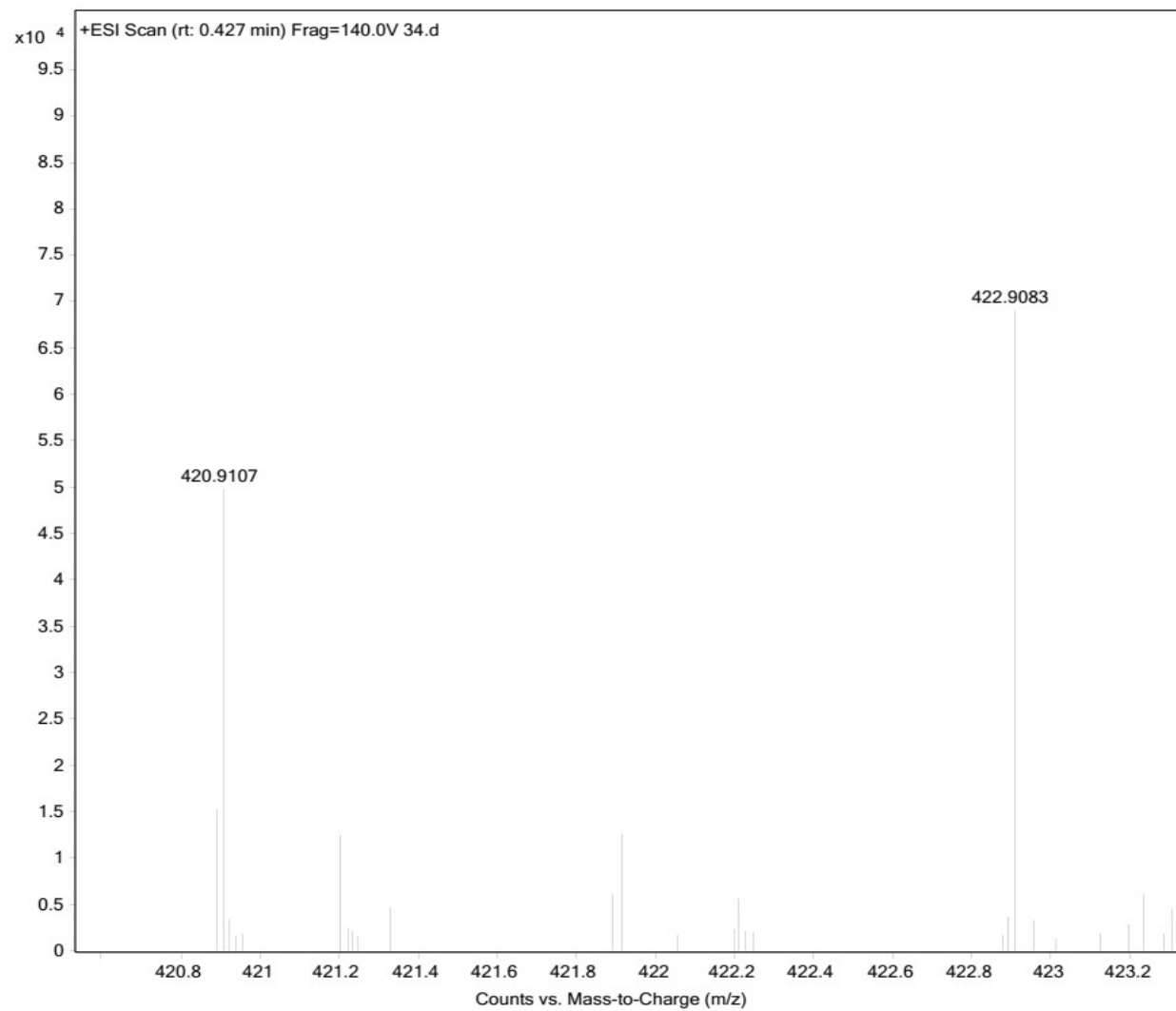


¹³C NMR of compound (3r)

MPO-AA-34-13C.1.fid
MPO-AA-34-13C



HRMS of 3r



¹H NMR of compound (3s)

ATK-AA-29-1H.1.f1
ATK-AA-29-1H

8.81
8.81

7.77
7.76
7.75
7.75
7.57
7.56

7.31
7.31
7.29
7.29
7.28
7.26

6.04
6.03
6.02
6.01

4.98
4.98
4.97
4.97

2.35

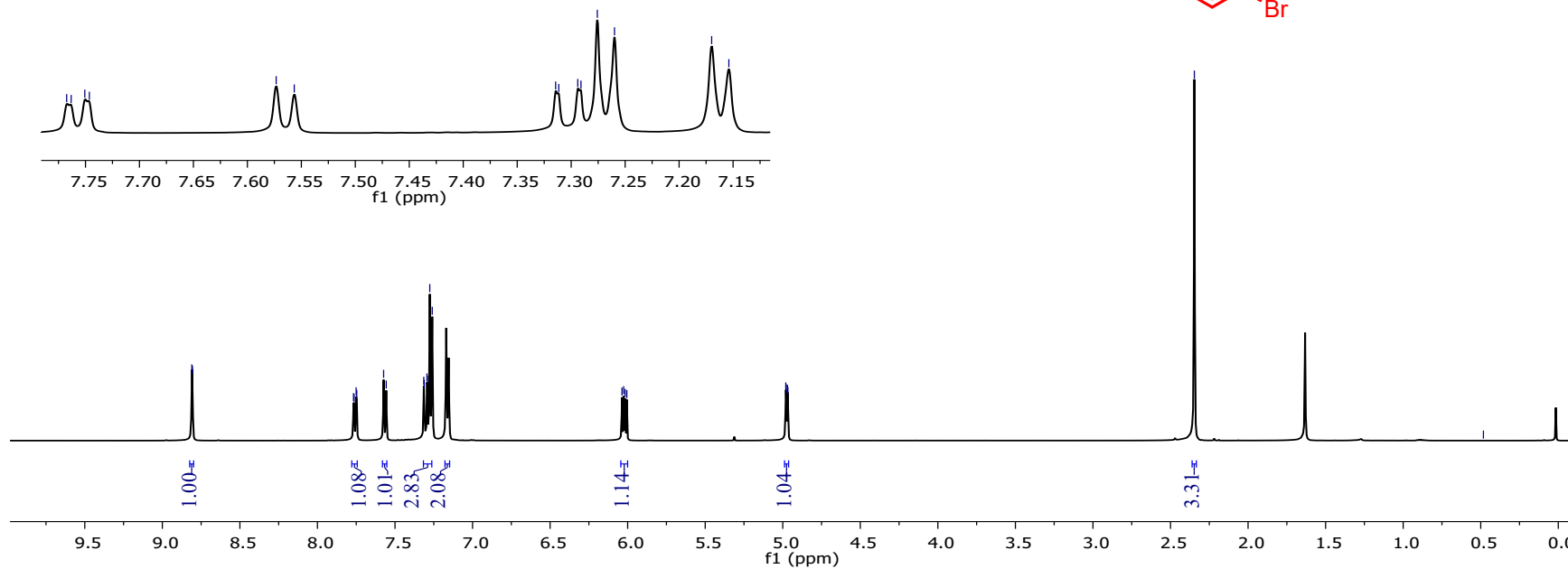
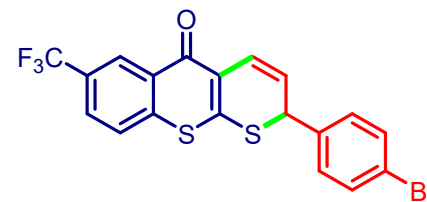
0.48

7.77
7.76
7.75

7.57
7.56

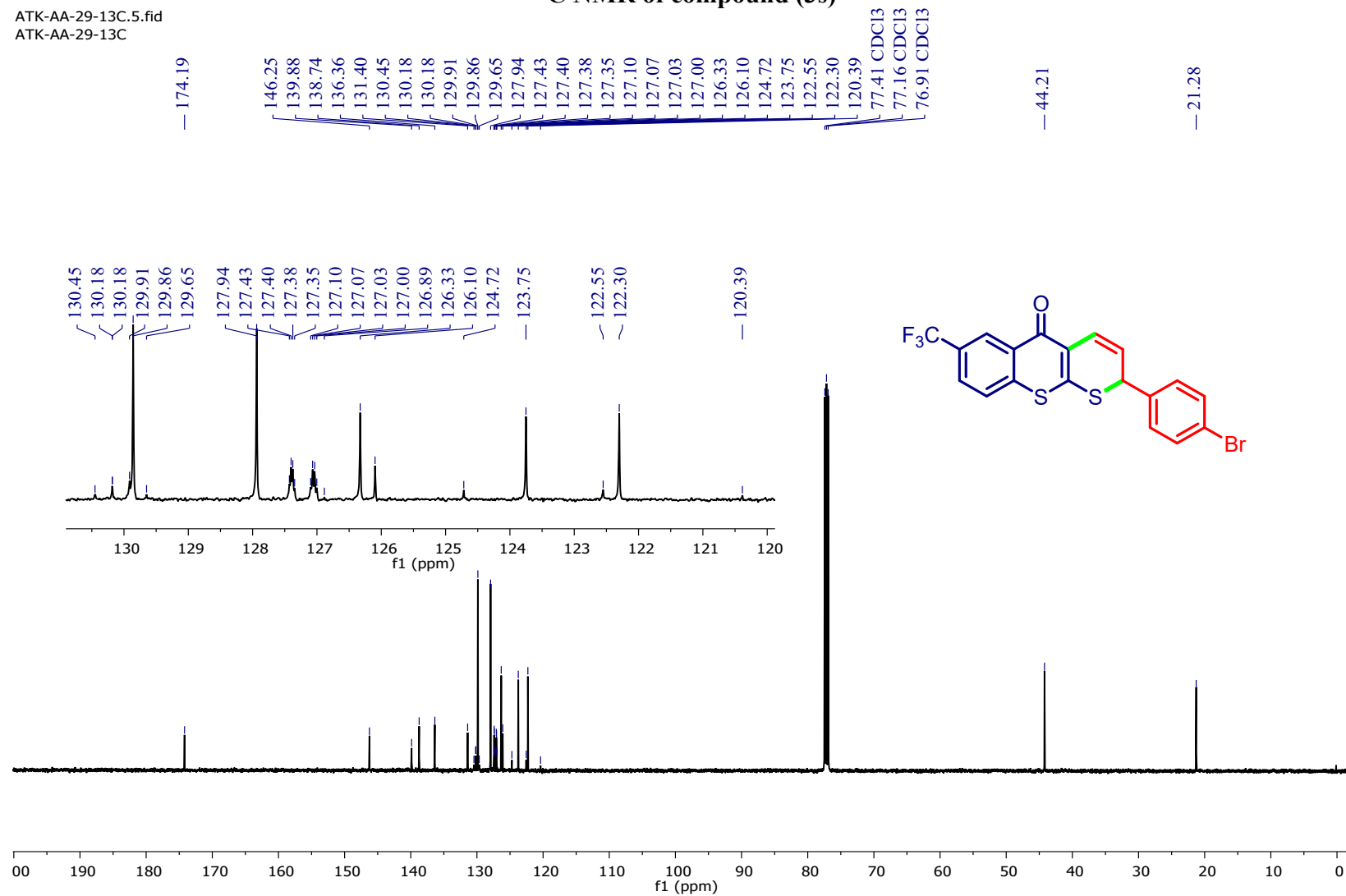
7.31
7.31
7.29
7.29
7.28
7.26

7.17
7.15

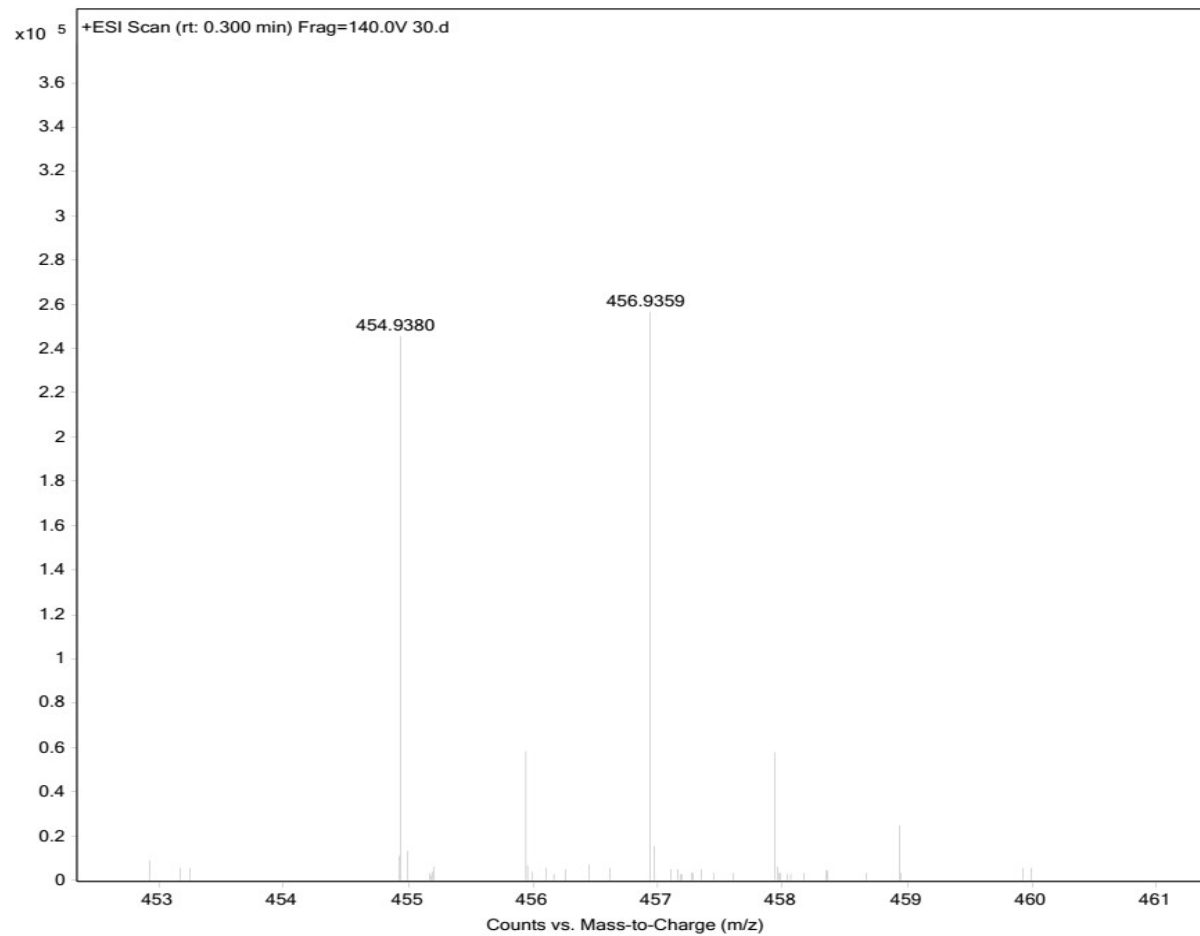


¹³C NMR of compound (3s)

ATK-AA-29-13C.5.fid
ATK-AA-29-13C



HRMS a(3s)



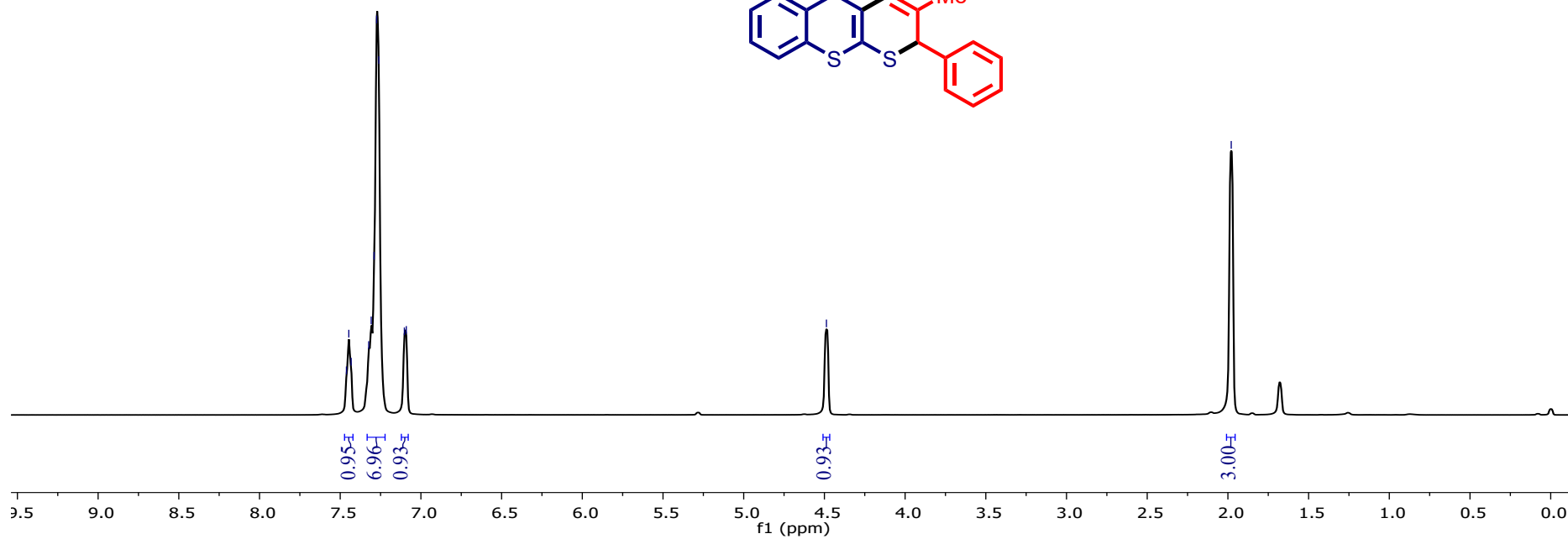
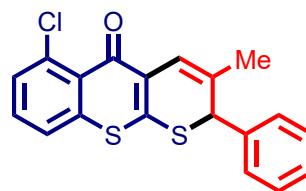
ATK-AA-35-1H.1.fid
ATK-AA-35-1H

¹H NMR Compound (3t)

7.46
7.45
7.43
7.32
7.31
7.29
7.27
7.26
7.10
7.09

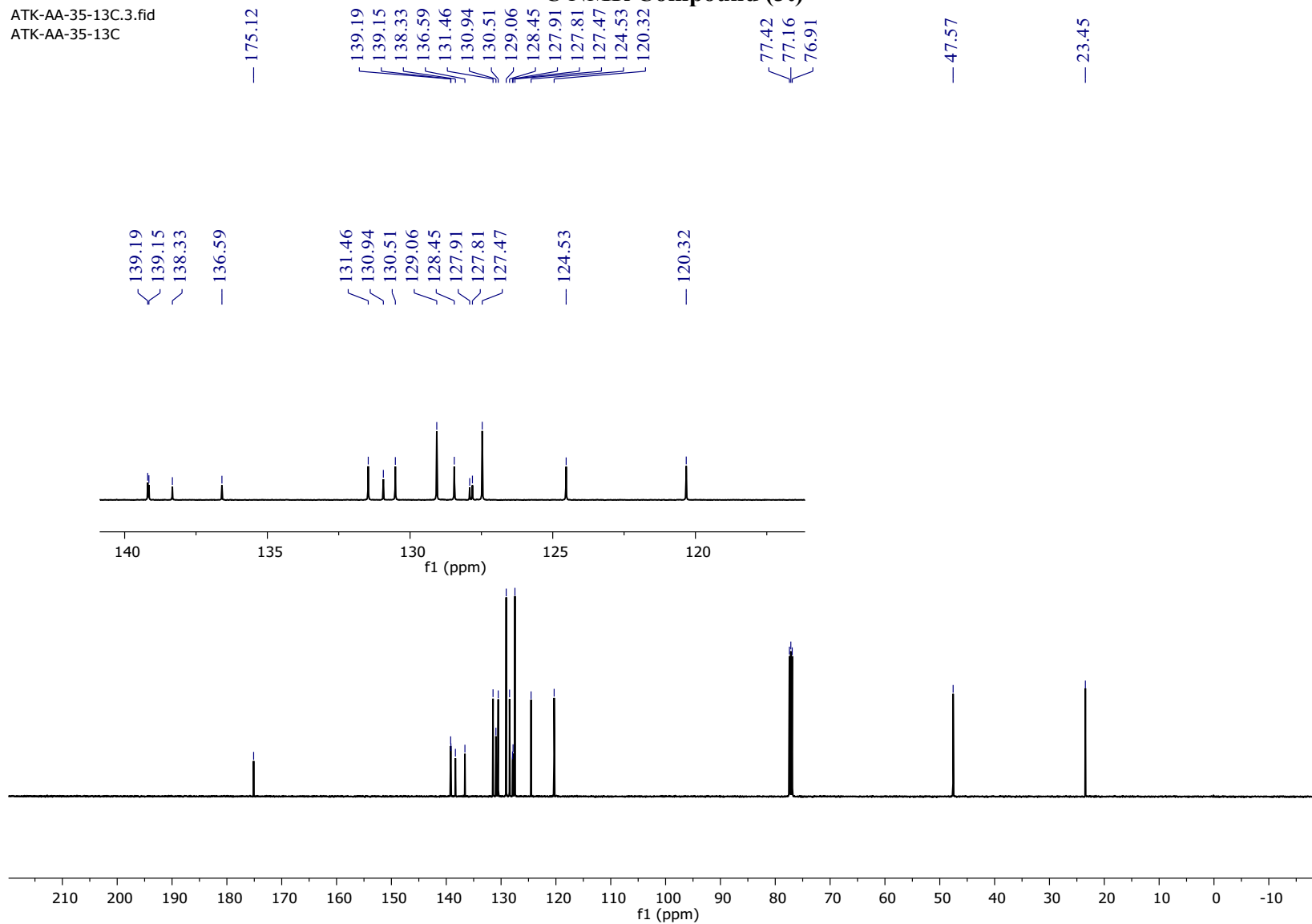
4.49

1.98

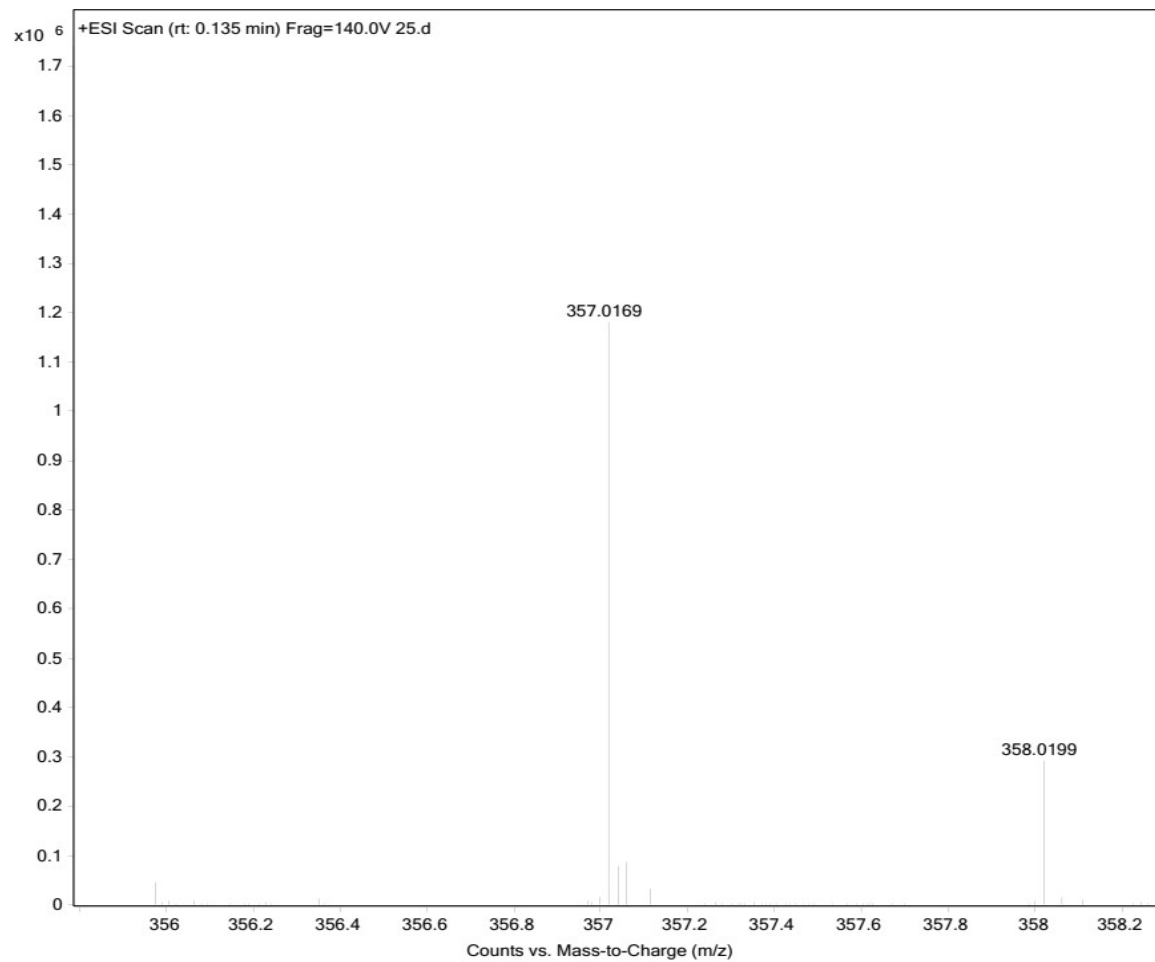


ATK-AA-35-13C.3.fid
ATK-AA-35-13C

¹³C NMR Compound (3t)



HRMS (3t)



¹H NMR (3u)

ATK-AA-28-1H.1
ATK-AA-28-1H

8.45
8.44
7.44
7.43
7.41
7.41
7.29
7.28
7.27
7.26
7.19
7.19

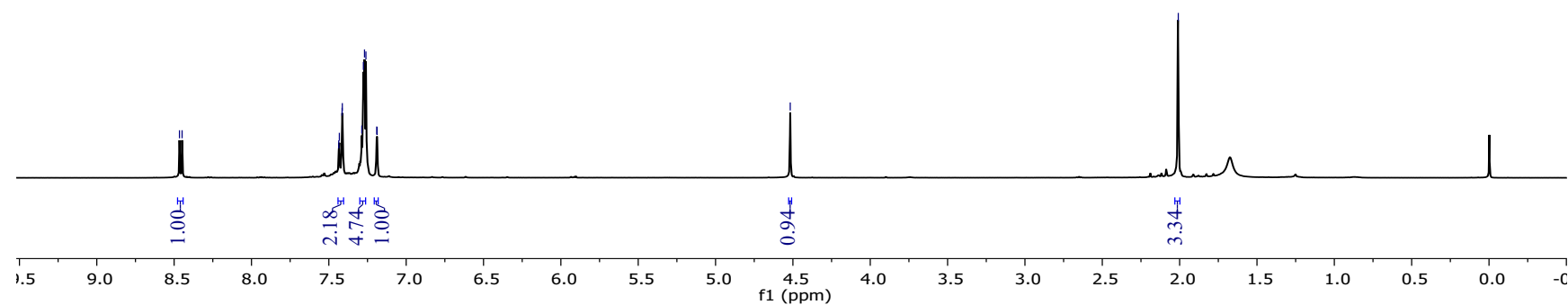
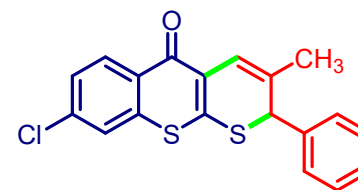
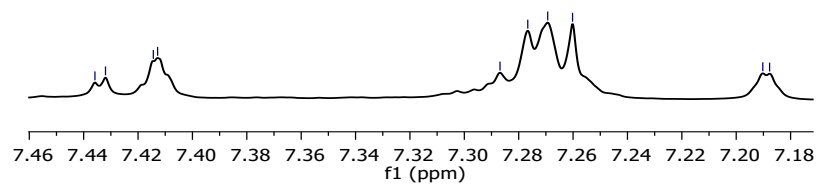
4.52

2.01

7.44
7.43
7.41
7.41

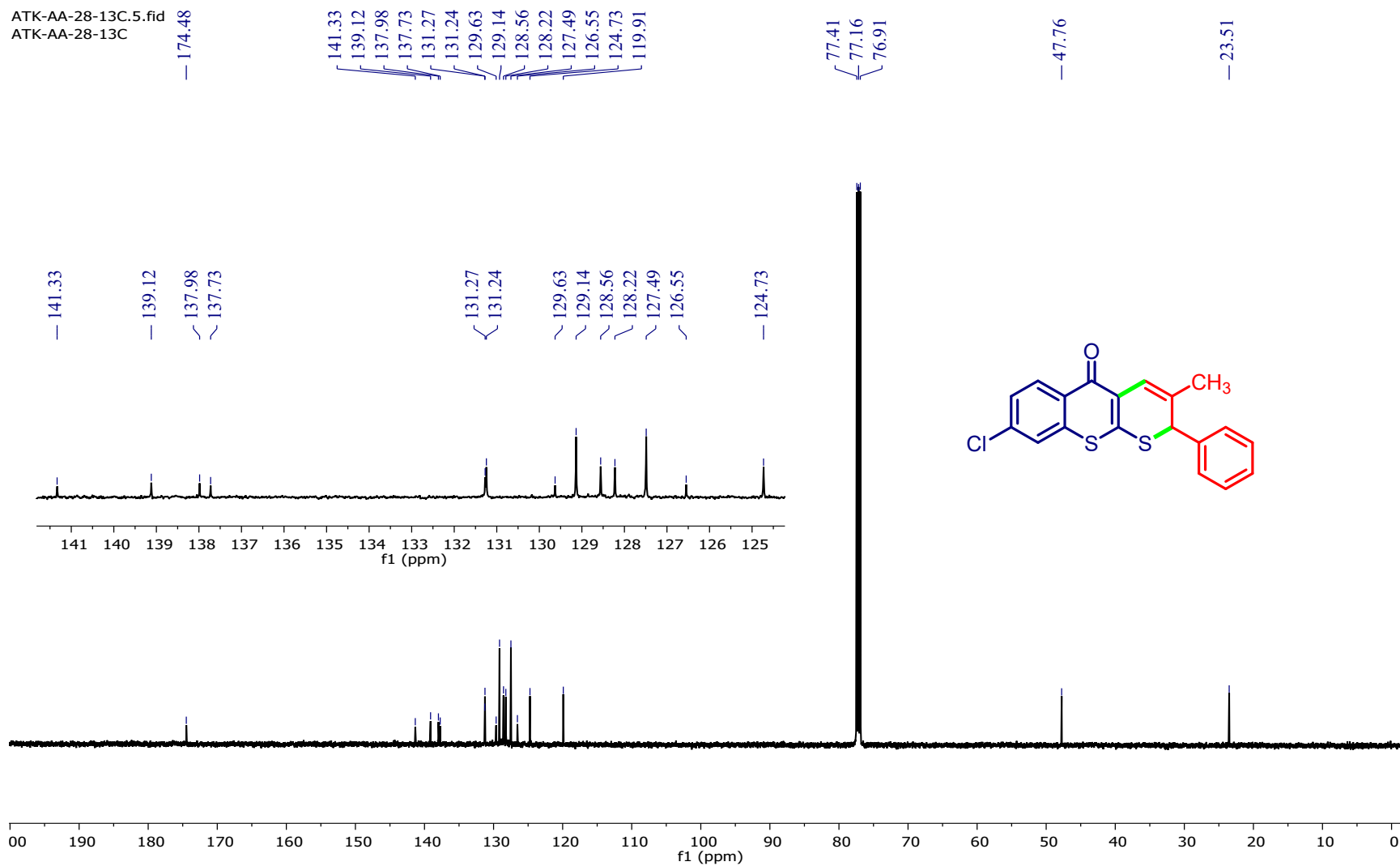
7.29
7.28
7.27
7.26

7.19
7.19



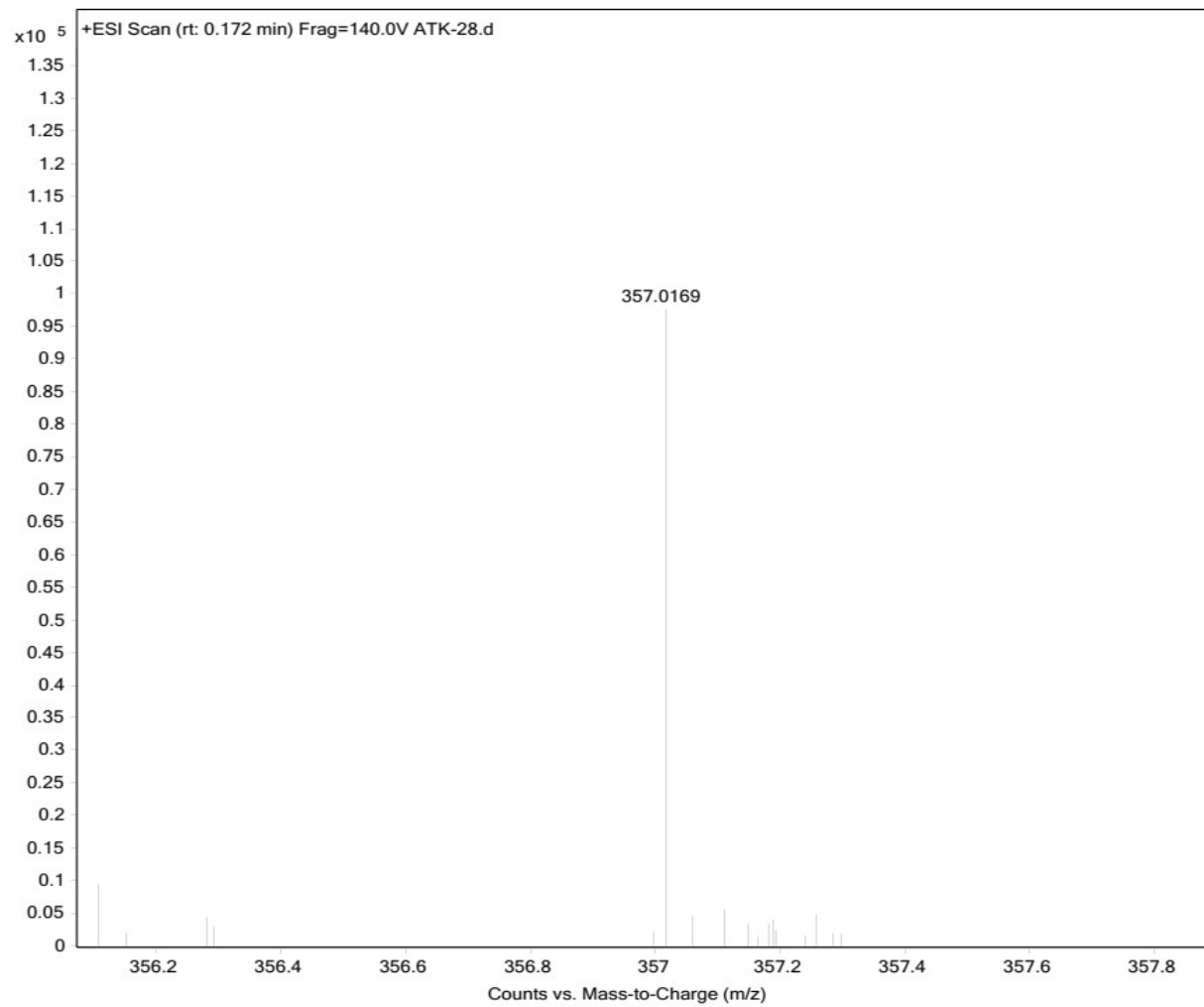
¹³C NMR of compound (3u)

ATK-AA-28-13C.5.fid
ATK-AA-28-13C



(126 MHz, Chloroform-*d*) δ 174.48, 141.33, 139.12, 137.98, 137.73, 131.27, 131.24, 129.63, 129.14, 128.56, 128.22, 127.49, 126.55, 124.73, 119.91, 47.76, 23.51. ¹³C NMR

HRMS 3u

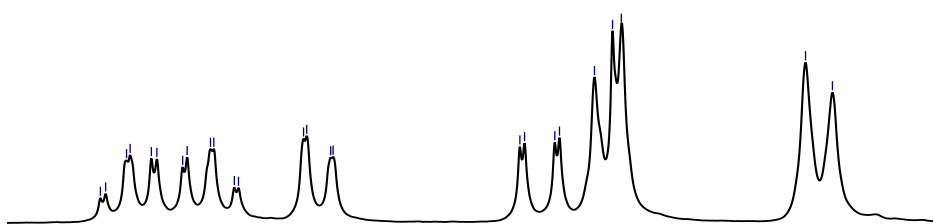


¹H NMR Compound (3v)

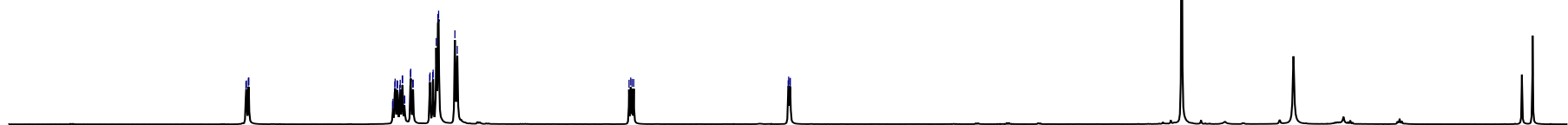
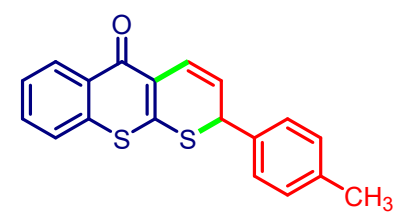
ATK-AA-15-P2P-1H.1.f1
ATK-AA-15-P2P-1H

8.53
8.52
8.52
7.57
7.56
7.55
7.55
7.54
7.53
7.52
7.52
7.50
7.50
7.49
7.48
7.48
7.45
7.44
7.43
7.43
7.32
7.32
7.30
7.30
7.28
7.27
7.26
7.15
7.14
6.00
5.99
5.98
5.97
4.94
4.94
4.93
4.93
2.33

7.57
7.56
7.55
7.55
7.54
7.53
7.52
7.52
7.50
7.50
7.49
7.48
7.45
7.44
7.43
7.43
7.32
7.32
7.30
7.30
7.28
7.27
7.26
7.15
7.14



7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10

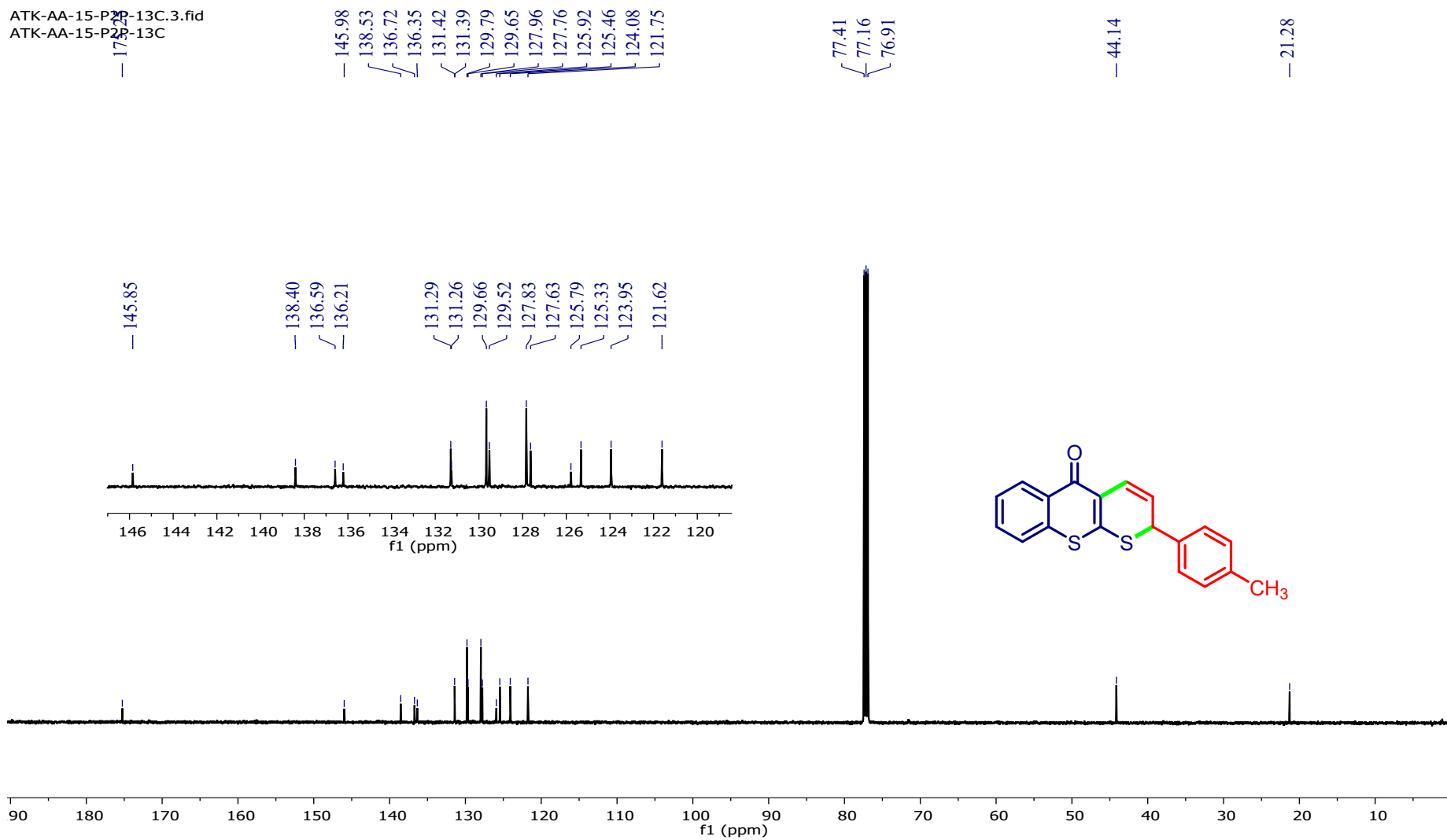


1.00
2.39
0.95
3.03
1.98
1.14
1.06
3.48

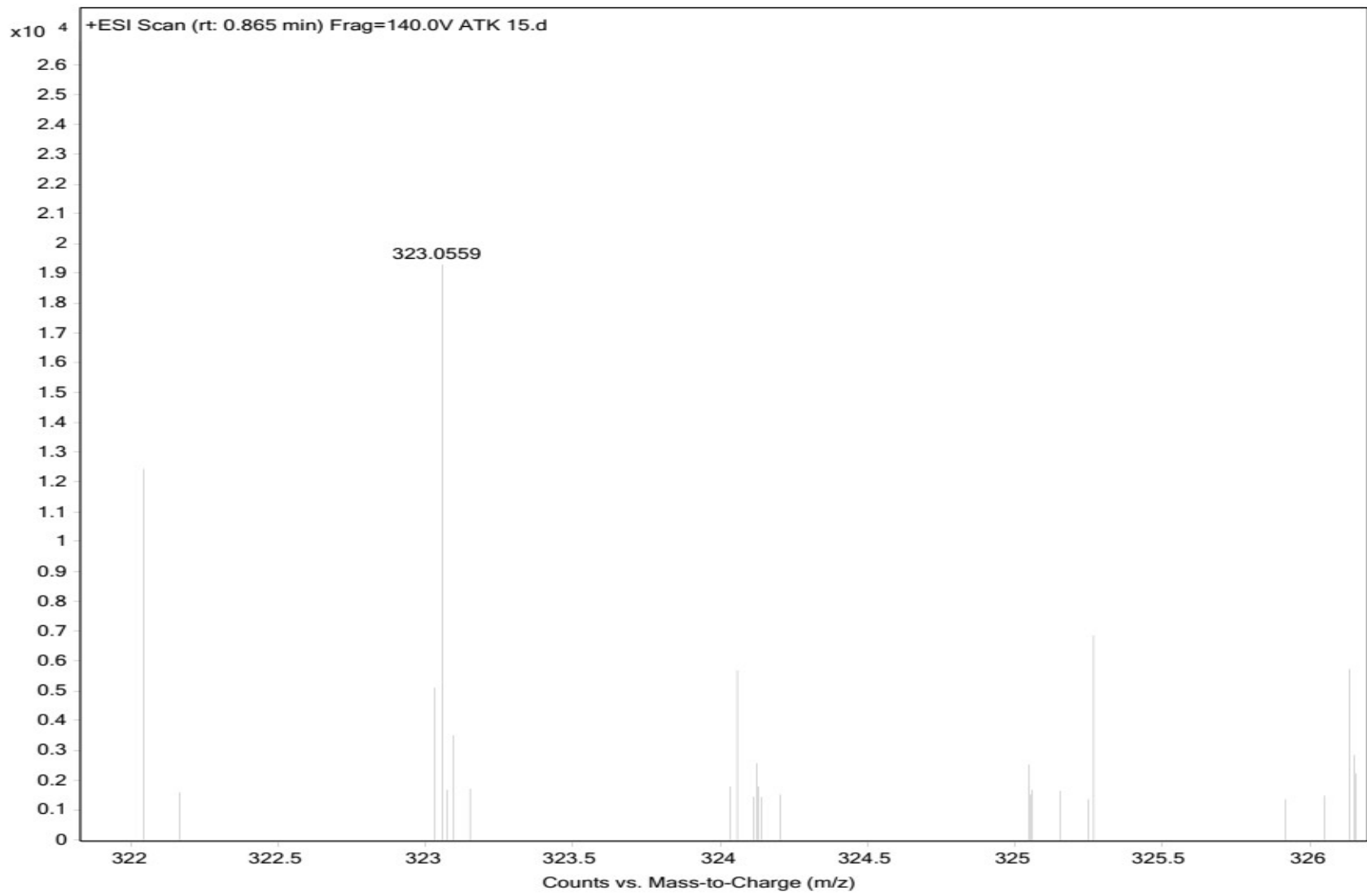
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

¹³C NMR Compound (3v)

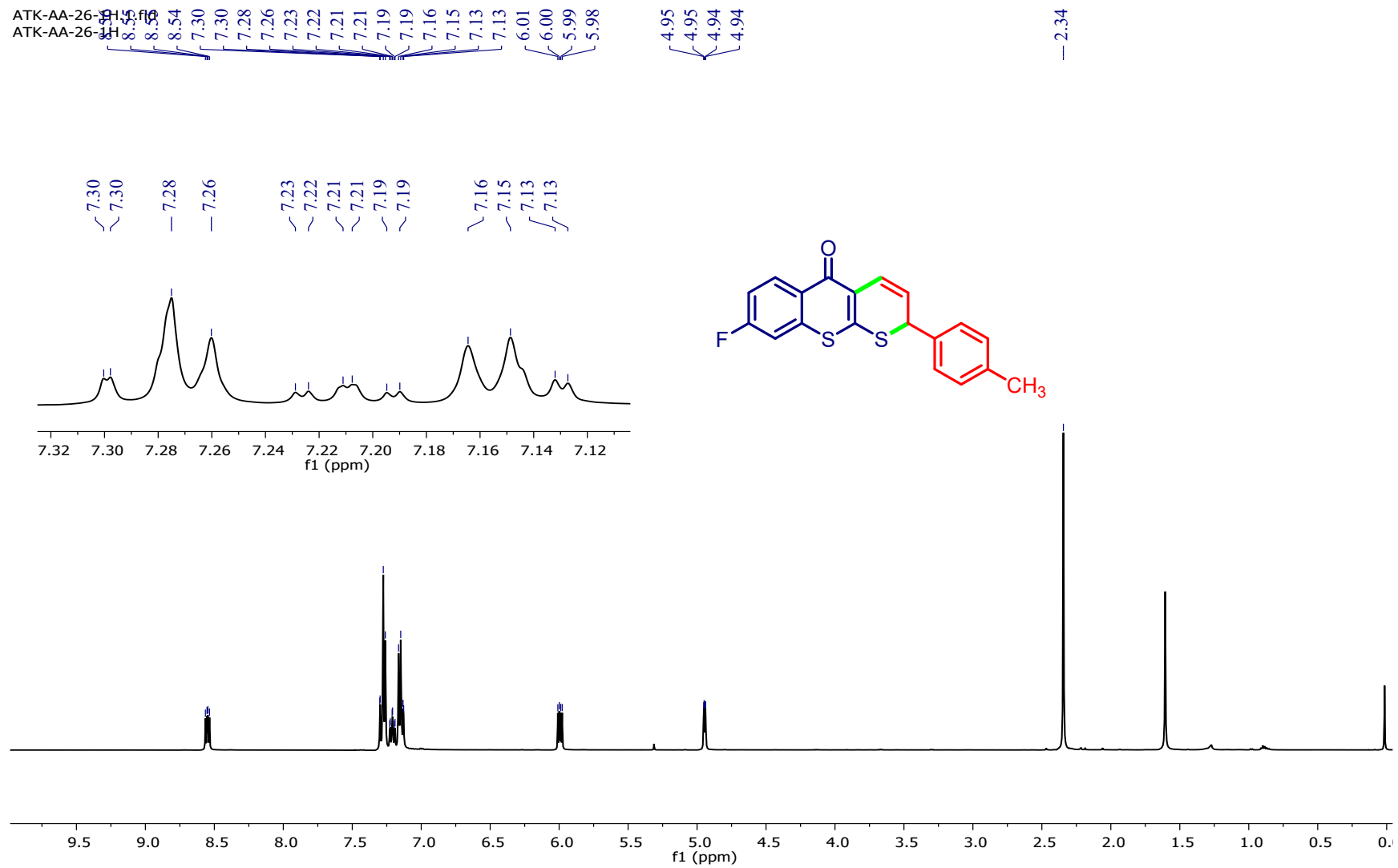
ATK-AA-15-P29-13C.3.fid
ATK-AA-15-P29-13C



HRMS (3v)



¹H NMR of compound (3w)



¹³C NMR of compound (3w)

ATK-AA-26-1303.fid
ATK-AA-26-1303

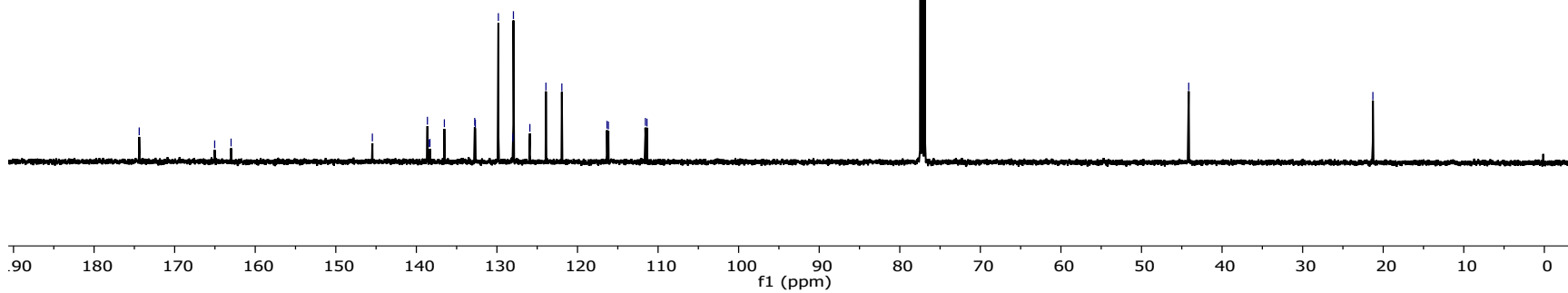
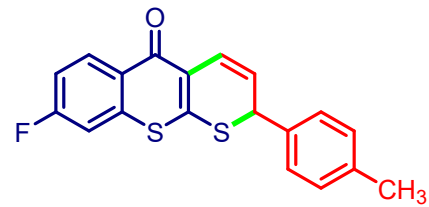
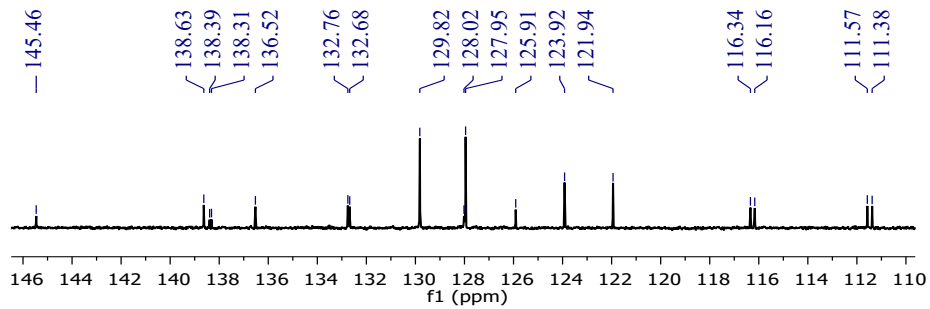
174.40
165.03
163.00

145.46
138.63
138.39
138.31
136.52
132.76
132.68
129.82
128.02
127.95
125.91
123.92
121.94
116.34
116.16
111.57
111.38

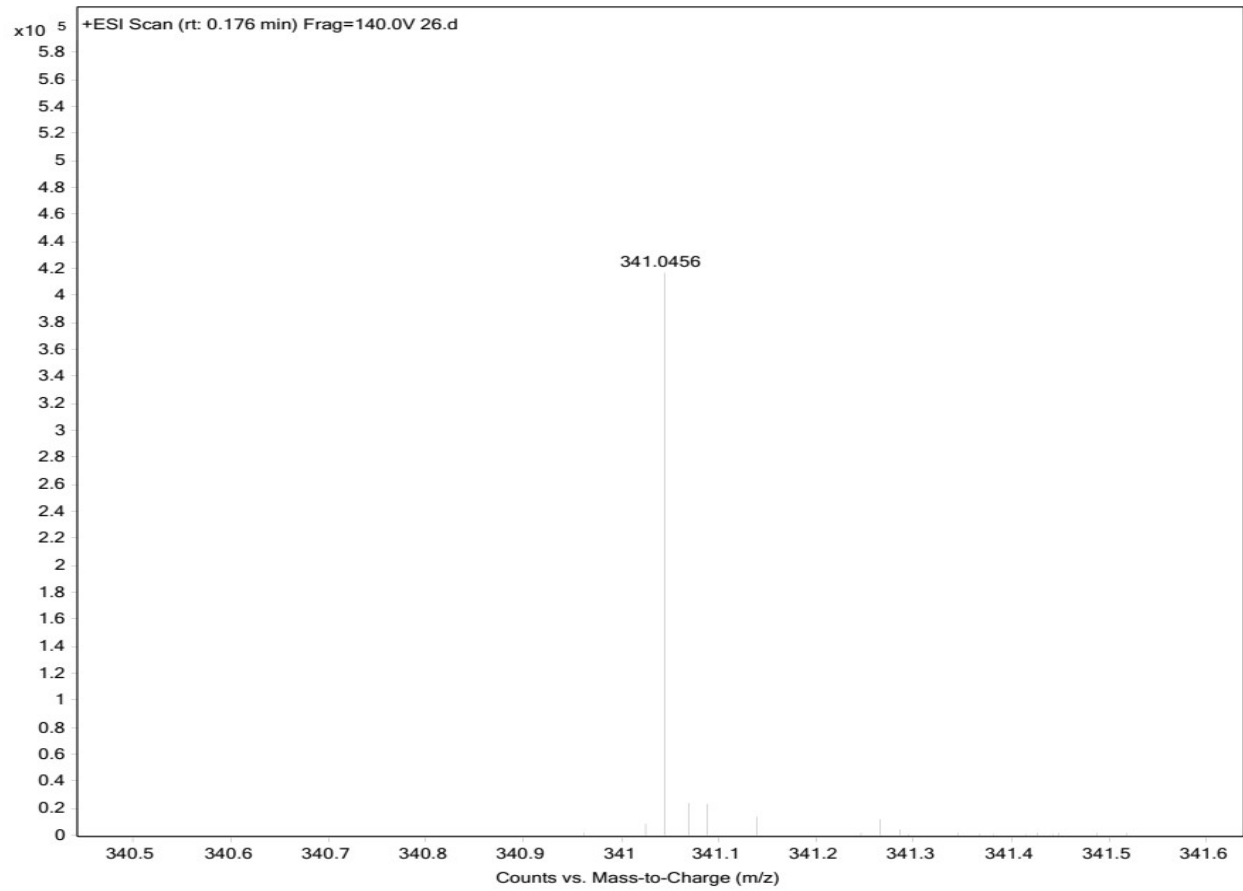
77.41
77.16
76.91

44.14

21.28



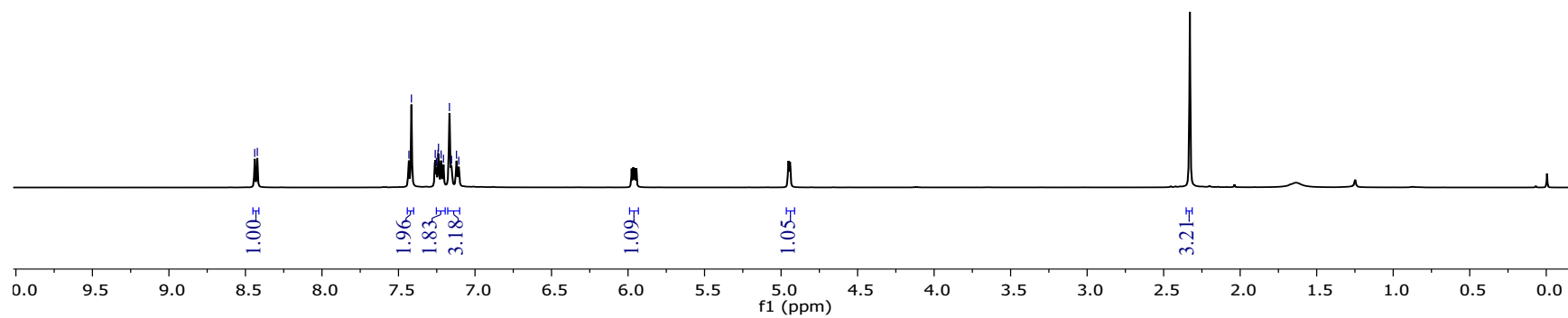
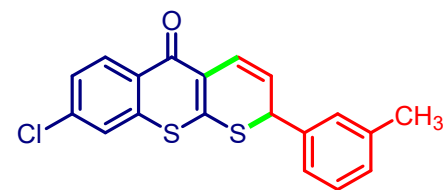
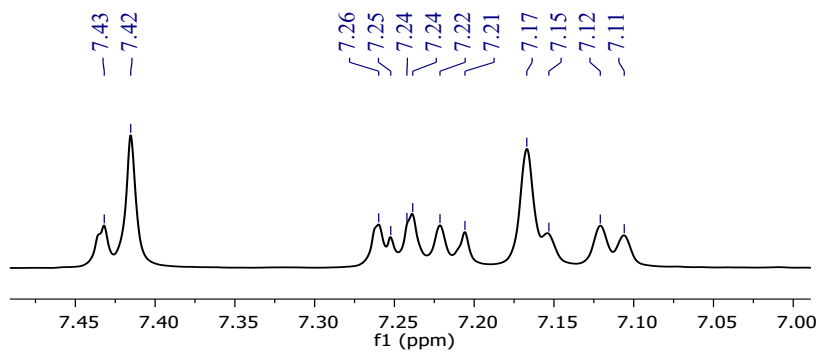
HRMS 3w

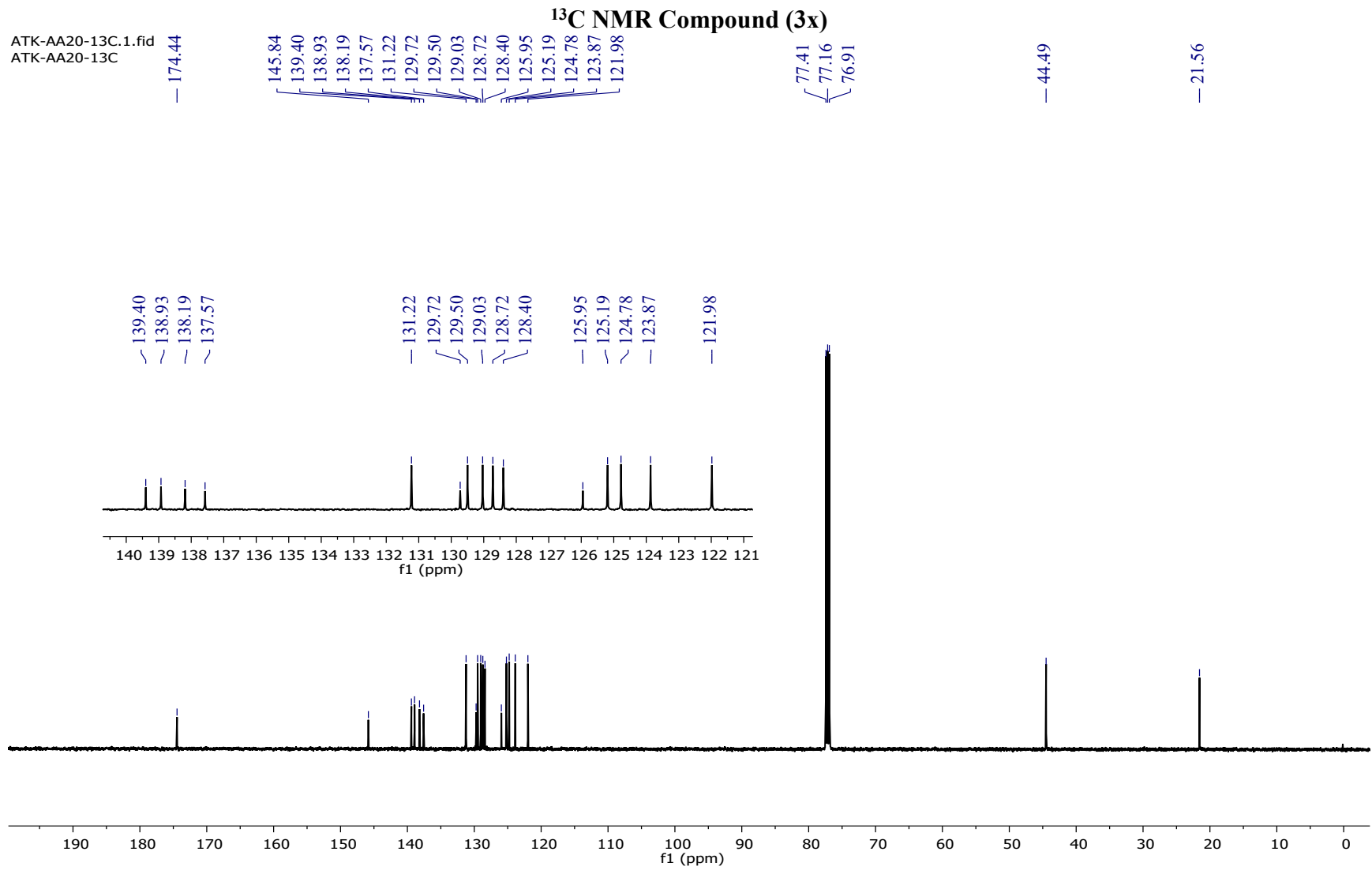


ATK-AA20-1H.3.fid
ATK-AA20-1H

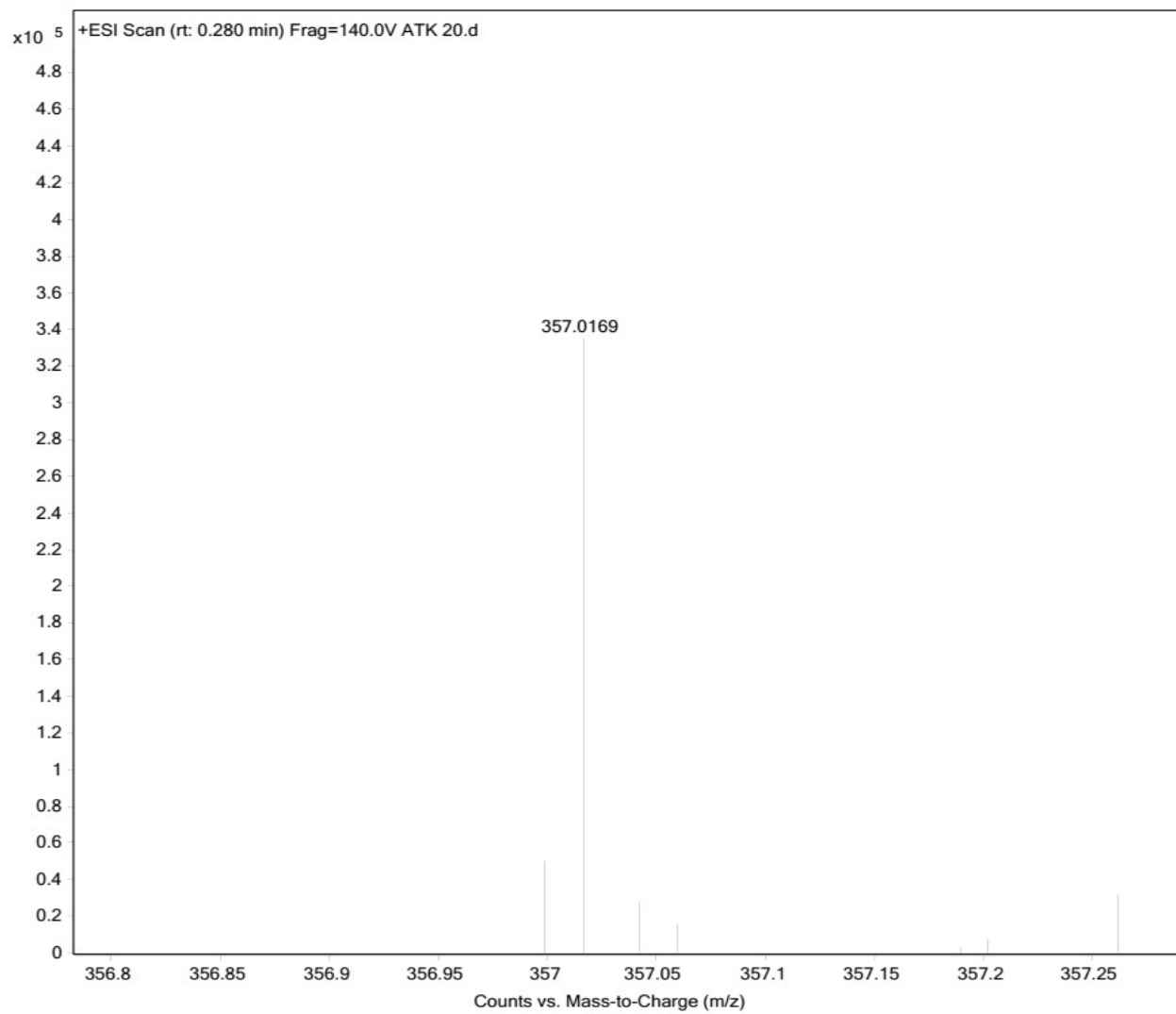
¹H NMR Compound (3x)

8.44
8.42
7.43
7.42
7.26
7.25
7.24
7.24
7.22
7.21
7.17
7.15
7.12
7.11



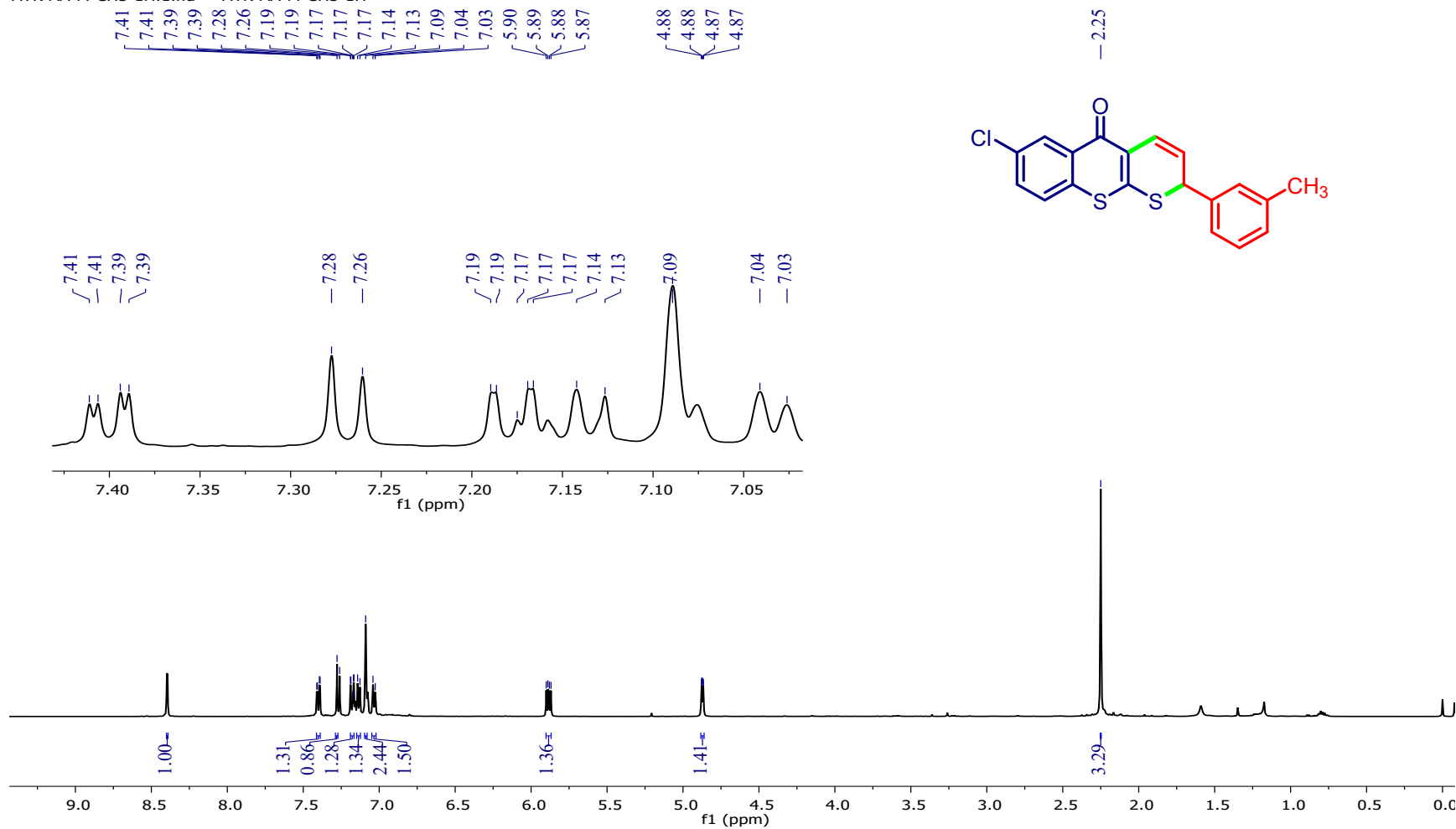


HRMS of compound (3x)



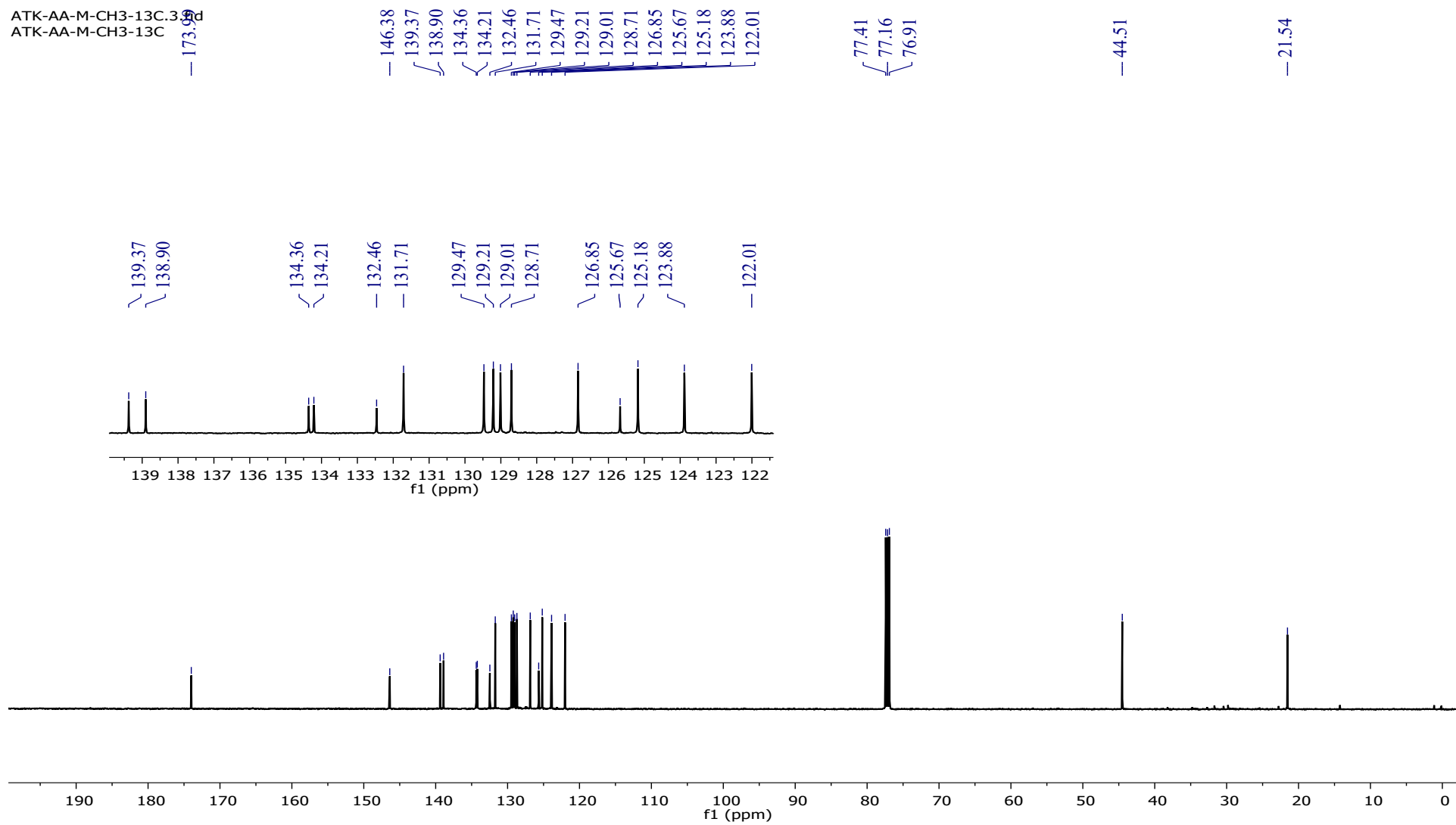
¹H NMR of compound (3y)

ATK-AA-M-CH3-1H.1.fid — ATK-AA-M-CH3-1H

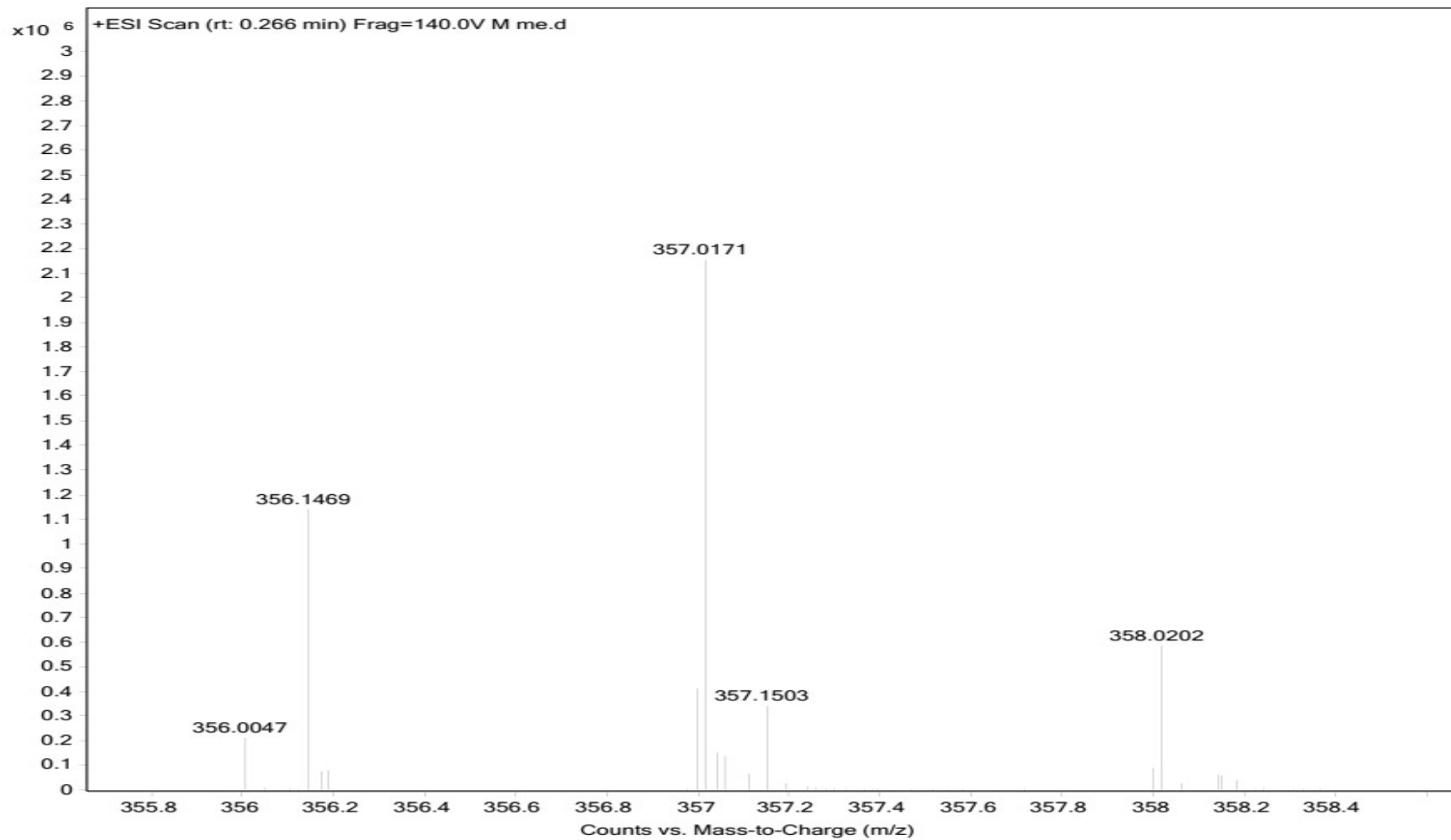


¹³C NMR of compound (3y)

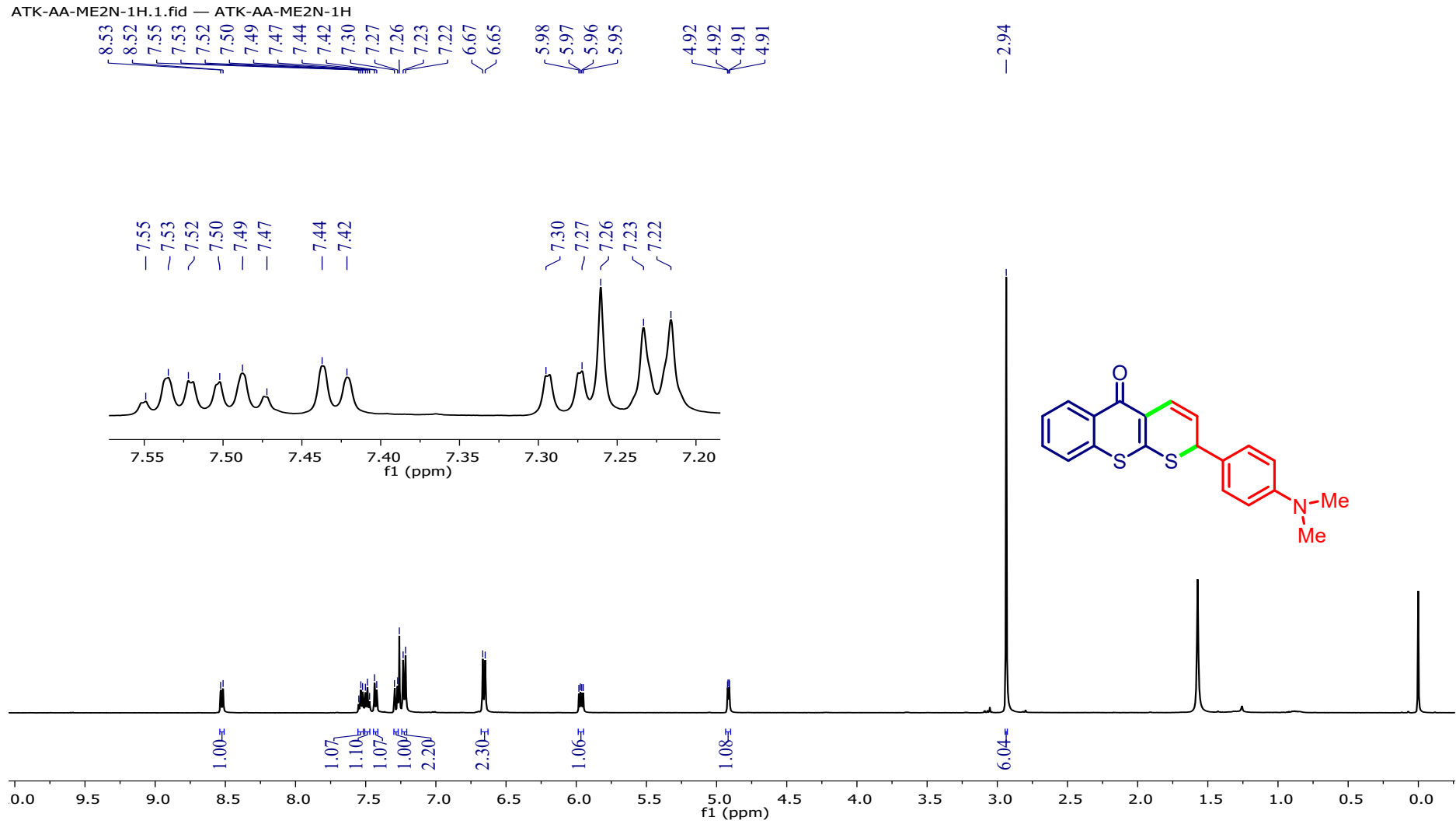
ATK-AA-M-CH3-13C.39d
ATK-AA-M-CH3-13C



HRMS of compound (3y)

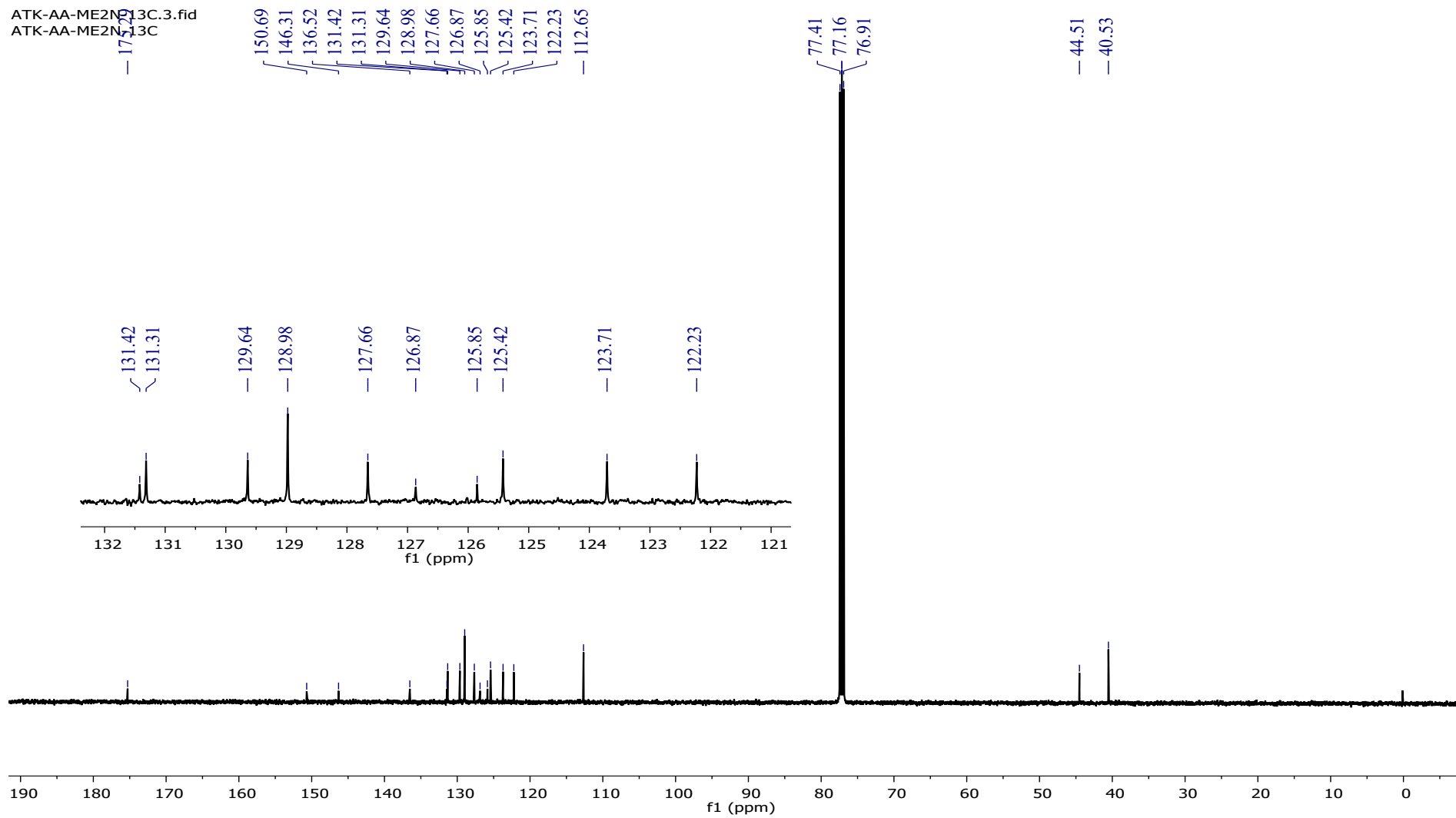


¹H NMR of compound (3z)

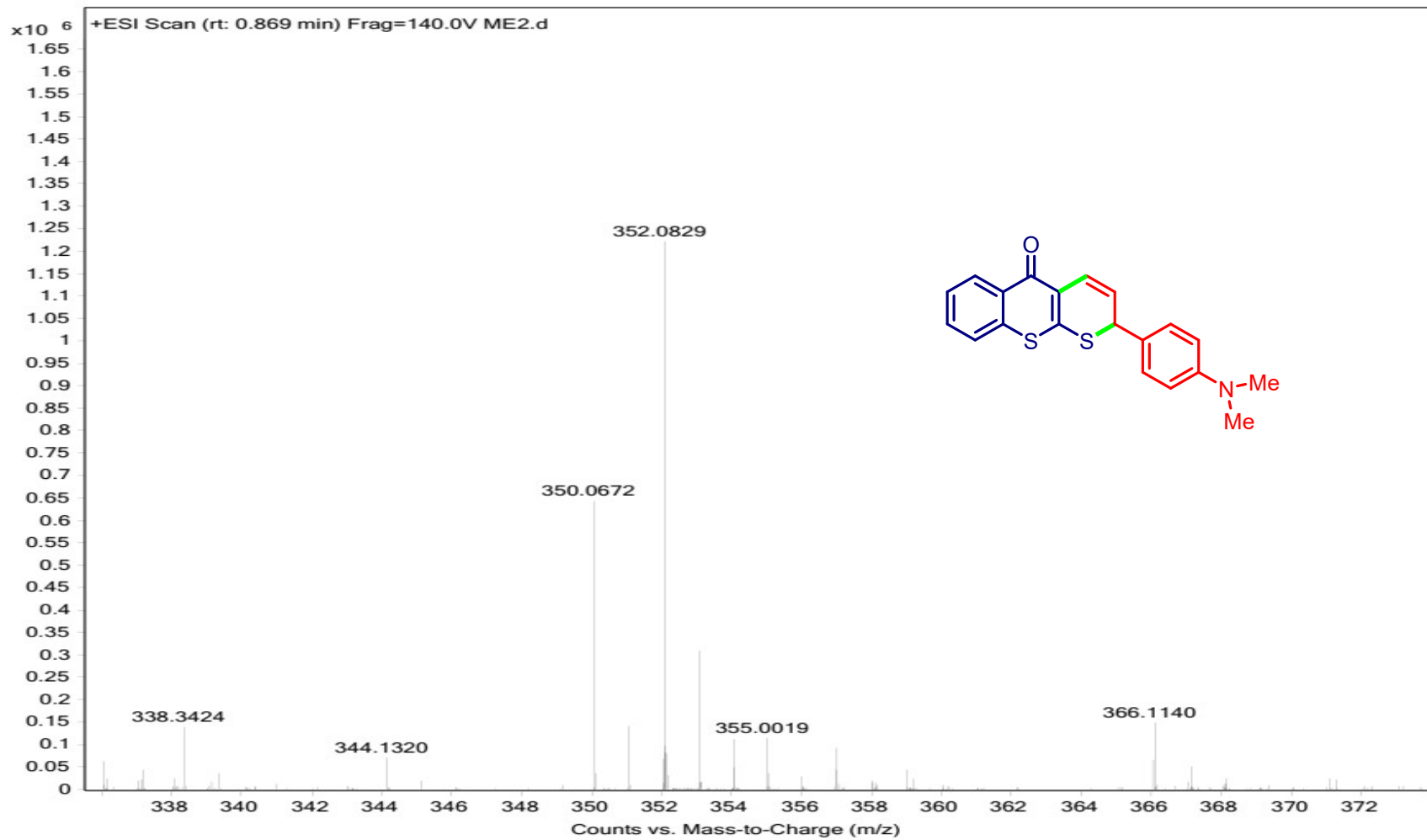


¹³C NMR of compound (3z)

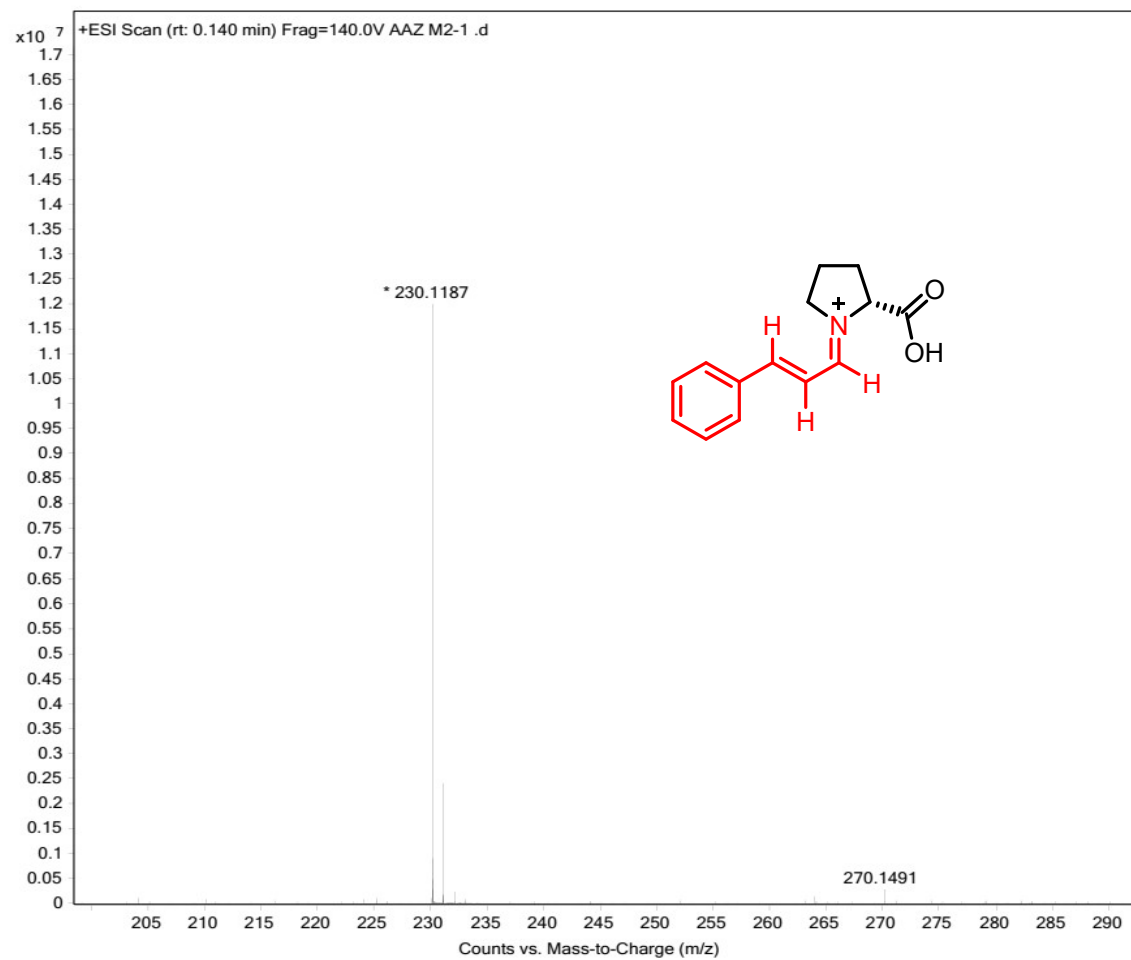
ATK-AA-ME2N13C.3.fid
ATK-AA-ME2N13C



HRMS of compound (3z)



6. HRMS of intermediate (A1)



Expected m/z calculated for $C_{14}H_{16}NO_2$ 230.1176($M + H^+$); **Found** 230.1187.

