New Journal of Chemistry

Supporting Information To:

Efficient and selective azidation of *per-O*-acetylated sugars using ultrasound activation: Application to the one-pot synthesis of 1,2,3-triazole glycosides

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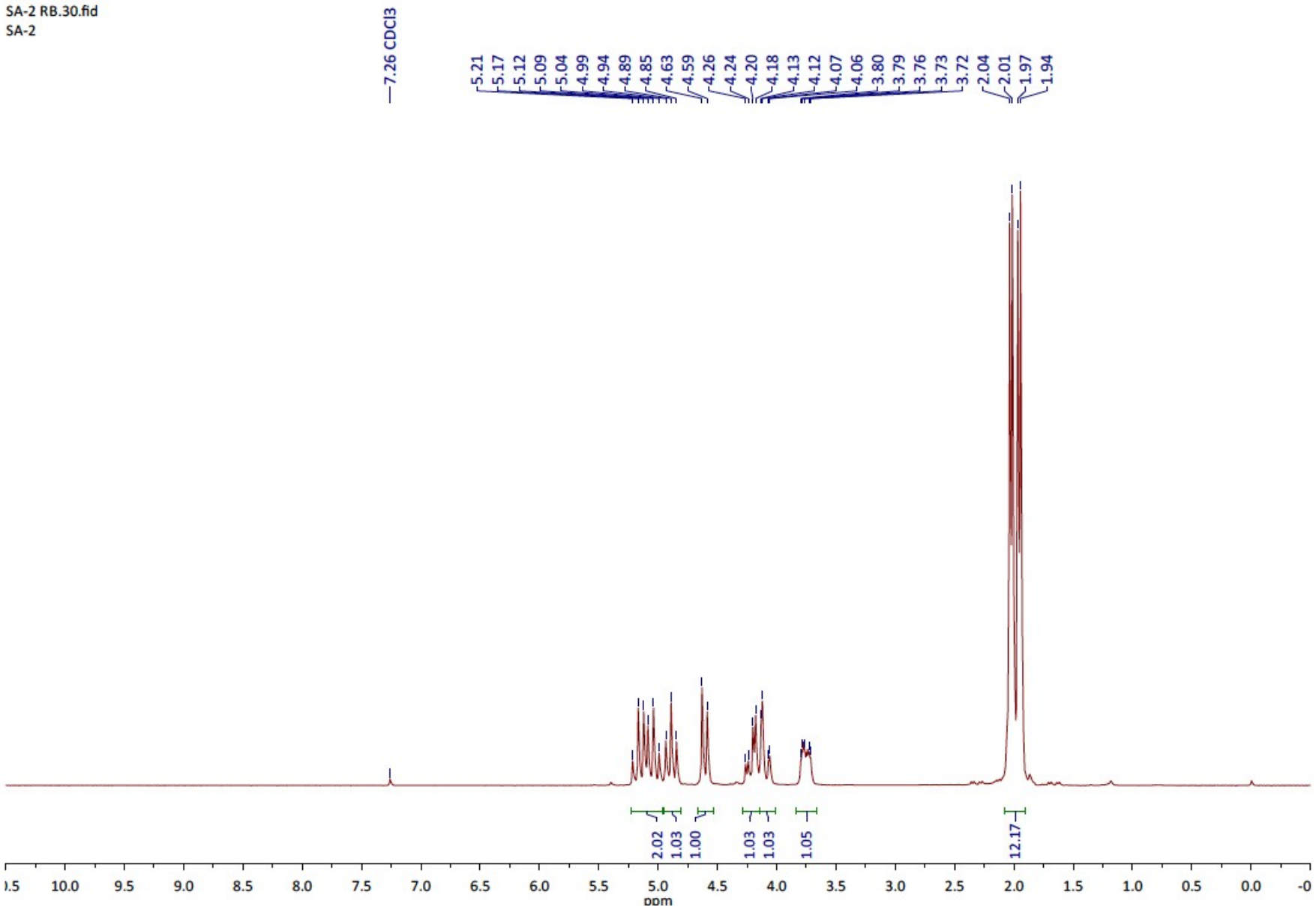
Experimental section

General. All organic solvents were purchased from commercial sources and used as received or dried using standard procedures, unless otherwise stated. All chemicals were purchased from Aldrich, Merck or Alfa Aesar and used without further purification; thin layer chromatography (TLC) was performed on precoated Merck 60 GF254 silica gel plates and revealed by spraying (p-anisaldehyde or H_2SO_4/EtOH), and detection by means of UV light at 254 and 360 nm. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 200 MHz spectrometer. Mass spectra (ESI MS) were recorded on a Brucker (Daltonics Esquire 3000+). HRMS spectra were carried out on a ThermoFisher Q Exactive plus in ESI mode positive and negative depending on the compounds to identify. We use a pump syringe at a flow of 3ul/mn and with the mass spectrometer at a resolution of 140 000 at m/z 200 for best accuracy. The purity of compounds was further verified to be >95% by HPLC analysis using analytical columns Hypersil (C18 (ELITE), 4.6 mm x 250 mm) or Nucleosil (120-5C8 (HICHROM), 4.6 mm x 250 mm) with an isocratic elution of CH_3CN/H_2O, 90/10. The ultrasound-assisted reactions were carried out in a "Branson Bransonic® 5510 DTH UltraSonic Bath Cleaner", with a frequency of 40 kHz. The ultrasonic cleaner has a power consumption of 185W (399 × 371 × 401 mm) with liquid holding capacity of 9.5 L.

General procedure for the synthesis of azidoglycoside (2a-e). To a cold suspension of sodium azide (2 mmol) in dichloromethane (5 mL), sulfuryl chloride (1mmol) is added drop wise. After the completion of the addition the mixture is sonicated for few minutes, and then the acetylated sugar **1a-e** (2 mmol) and Lewis acid catalyst (20 mol %) are added to the mixture. The reaction mixture is sonicated during 45 min. After the completion of the reaction (TLC monitoring), the mixture was diluted with dichloromethane and washed with a saturated aqueous solution of $NaHCO_3$. The organic layer was washed with water (2×10 mL), dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The residue was subjected to purification by silica gel column chromatography [Cyclohexane-EtOAc (9:1)] to give the pure azidoglycoside **2a-e**.

General procedure for one-pot synthesis of 1,2,3-triazolyl glycosides. To a cooled suspension of sodium azide (2 mmol) in dichloromethane (5 ml), sulfuryl chloride (1 mmol) is added drop wise. After the completion of the addition the mixture was sonicated at room temperature. The sugar derivative (2 mmol) and anhydrous $FeCl_3$ catalyst (20 mol %) were added and sonication continued. After reaction completion (TLC monitoring), the alkyne (4 mmol), CuI (4 mmol) and diisopropylethylamine (4 mmol) were added to the mixture and then left under sonication. After completion of the reaction (TLC monitoring), the mixture was diluted with dichloromethane and successively washed with a saturated solution of NH_4Cl and water (2×10 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (Cyclohexane-EtOAc 8:2 to 5:5) to afford the triazolyl glycosides **3**.

Figure S1. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) and HRMS spectra for compound **2c.**



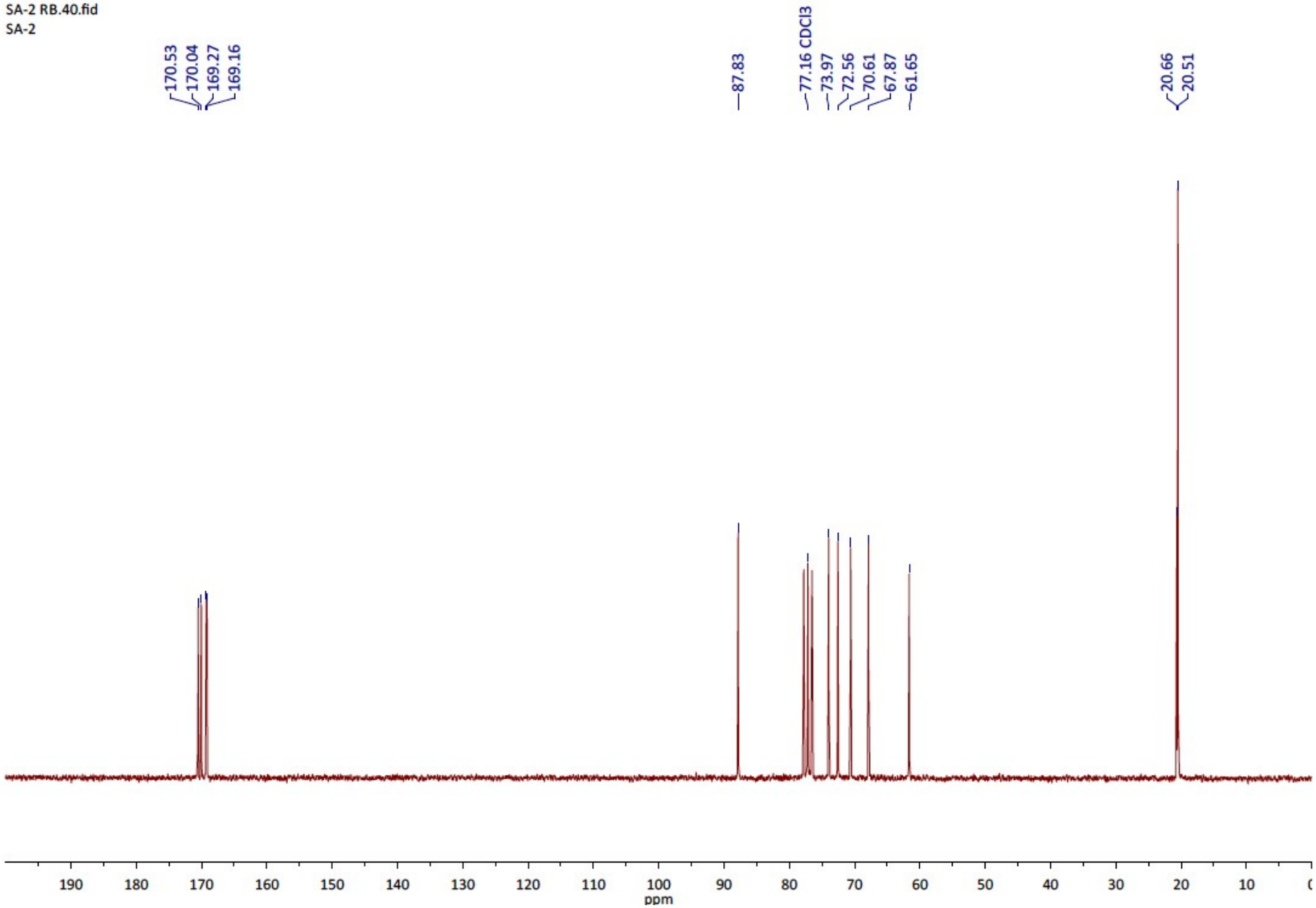
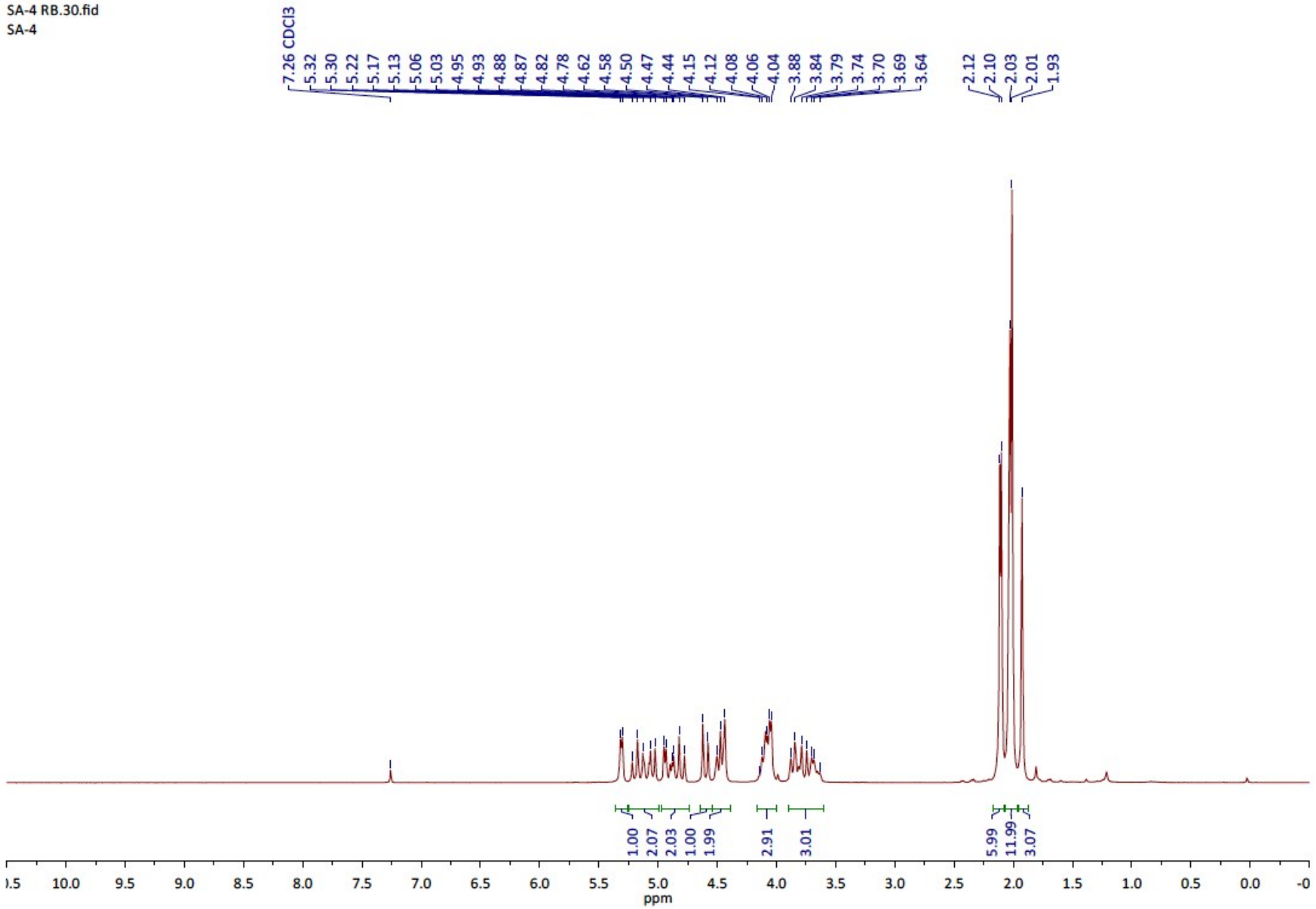

SA-2 RB.40.fid
SA-2
170.53
170.04
169.27
169.16
87.83
77.16 CDCl3
73.97
72.56
70.61
67.87
61.65
20.66
20.51
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Figure S2. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) and HRMS spectra for compound **2d.**



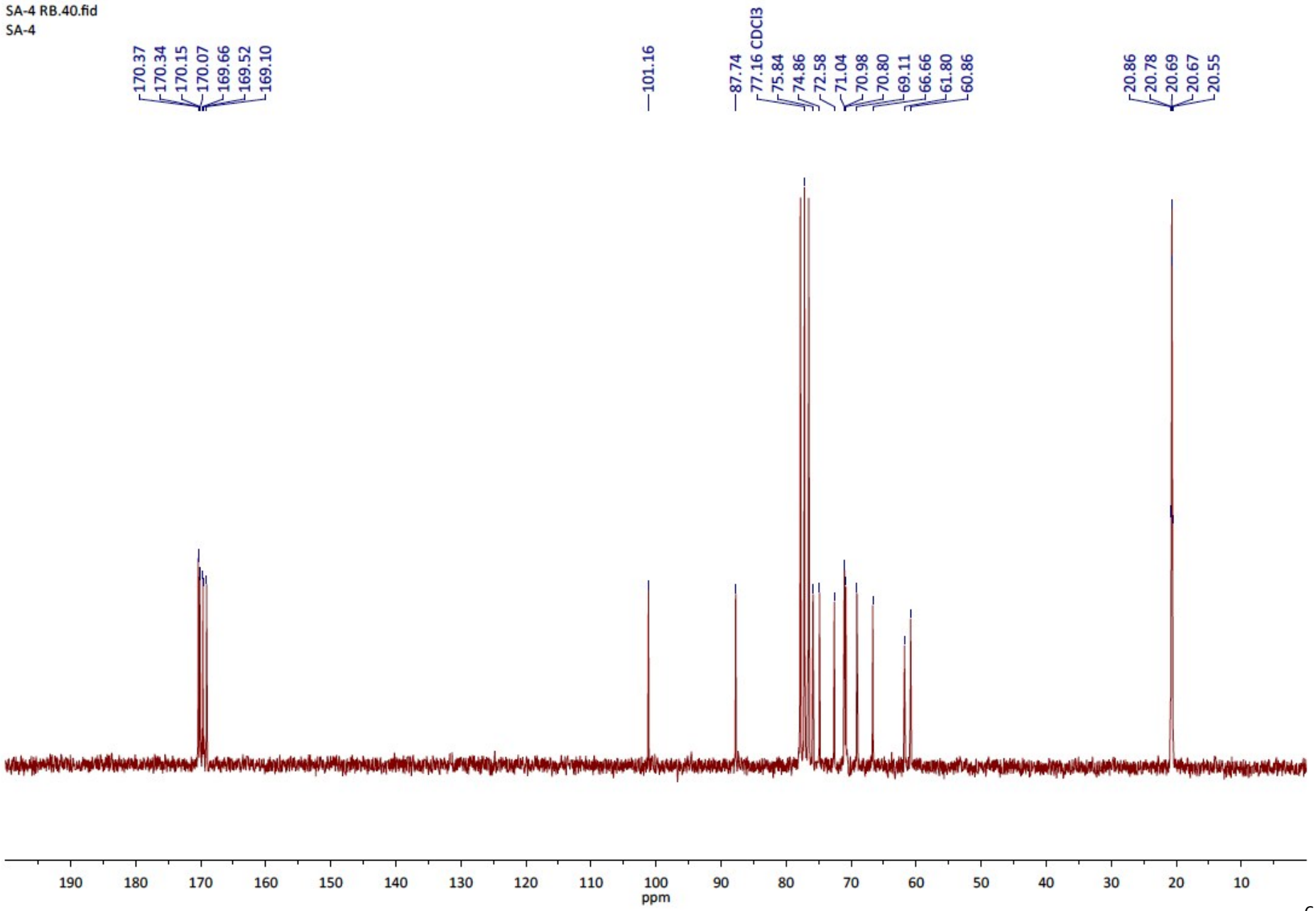
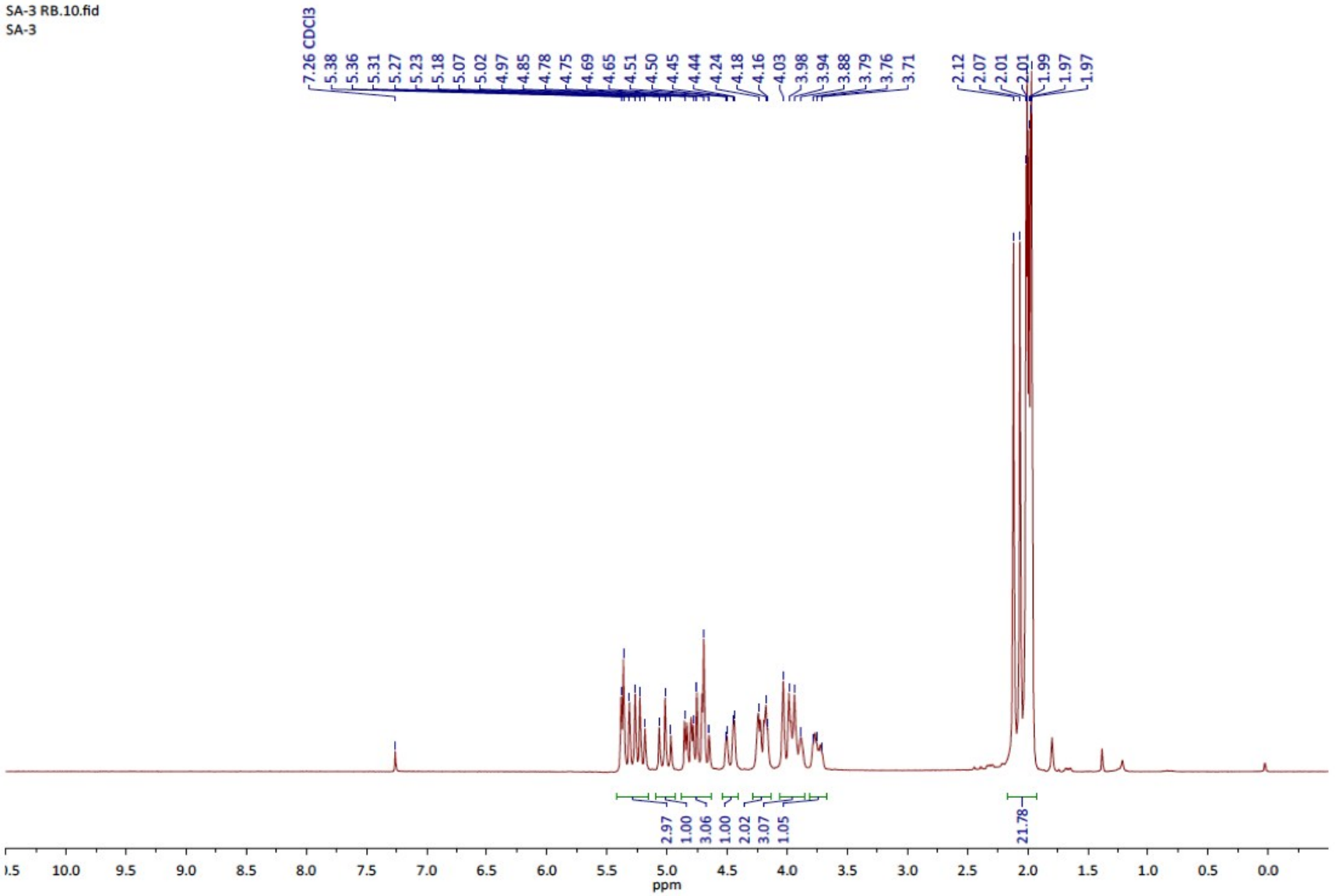

SA-4 RB.40.fid
SA-4
170.37
170.34
170.15
170.07
169.66
169.52
169.10
101.16
87.74
77.16 CDCl3
75.84
74.86
72.58
71.04
70.98
70.80
69.11
66.66
61.80
60.86
20.86
20.78
20.69
20.67
20.55
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Figure S3. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) and HRMS spectra for compound **2e.**



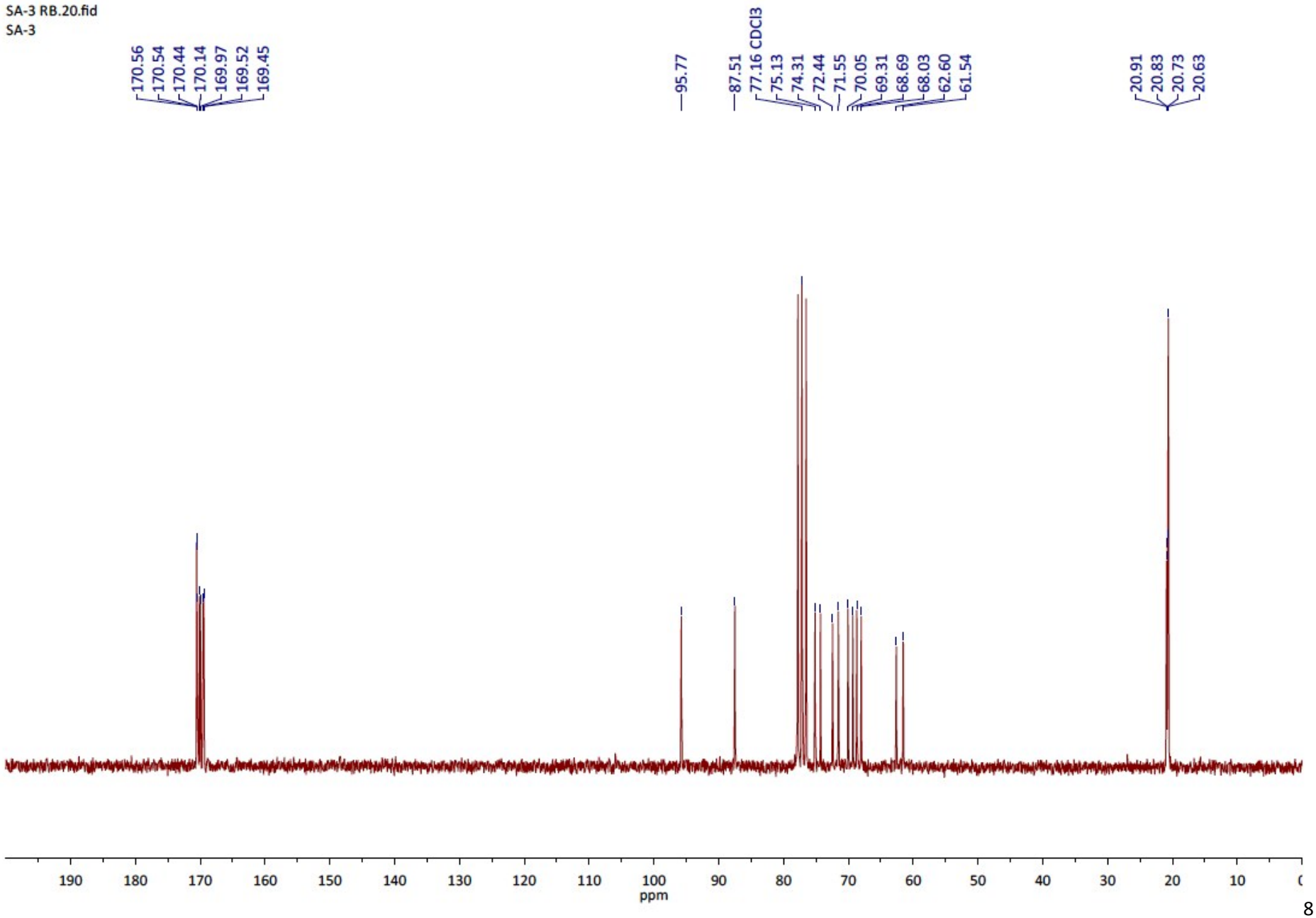
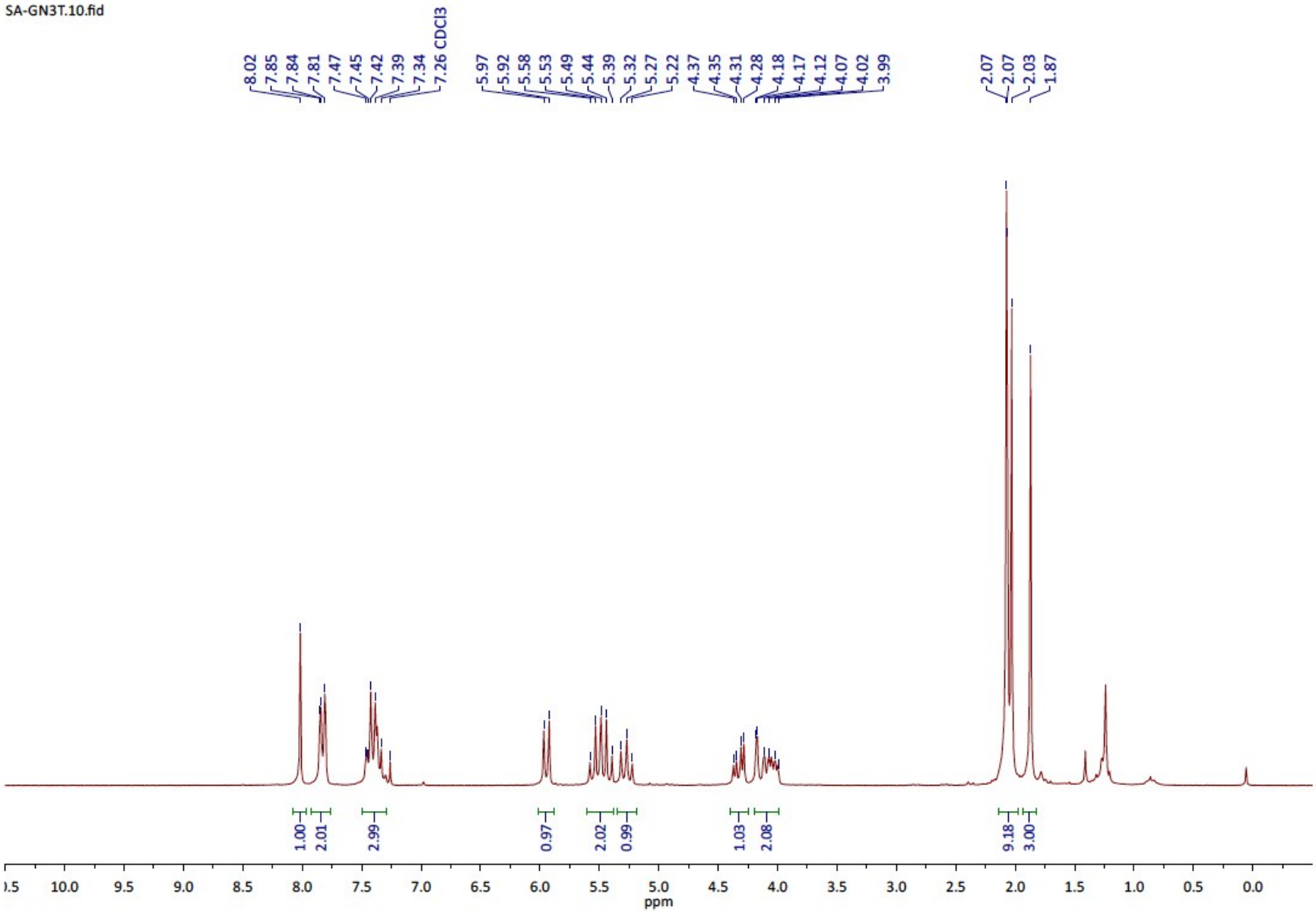

SA-3 RB.20.fid
SA-3
170.56
170.54
170.44
170.14
169.97
169.52
169.45
95.77
87.51
77.16 CDCl3
75.13
74.31
72.44
71.55
70.05
69.31
68.69
68.03
62.60
61.54
20.91
20.83
20.73
20.63
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Figure S4. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) and HRMS spectra for compound **3b.**



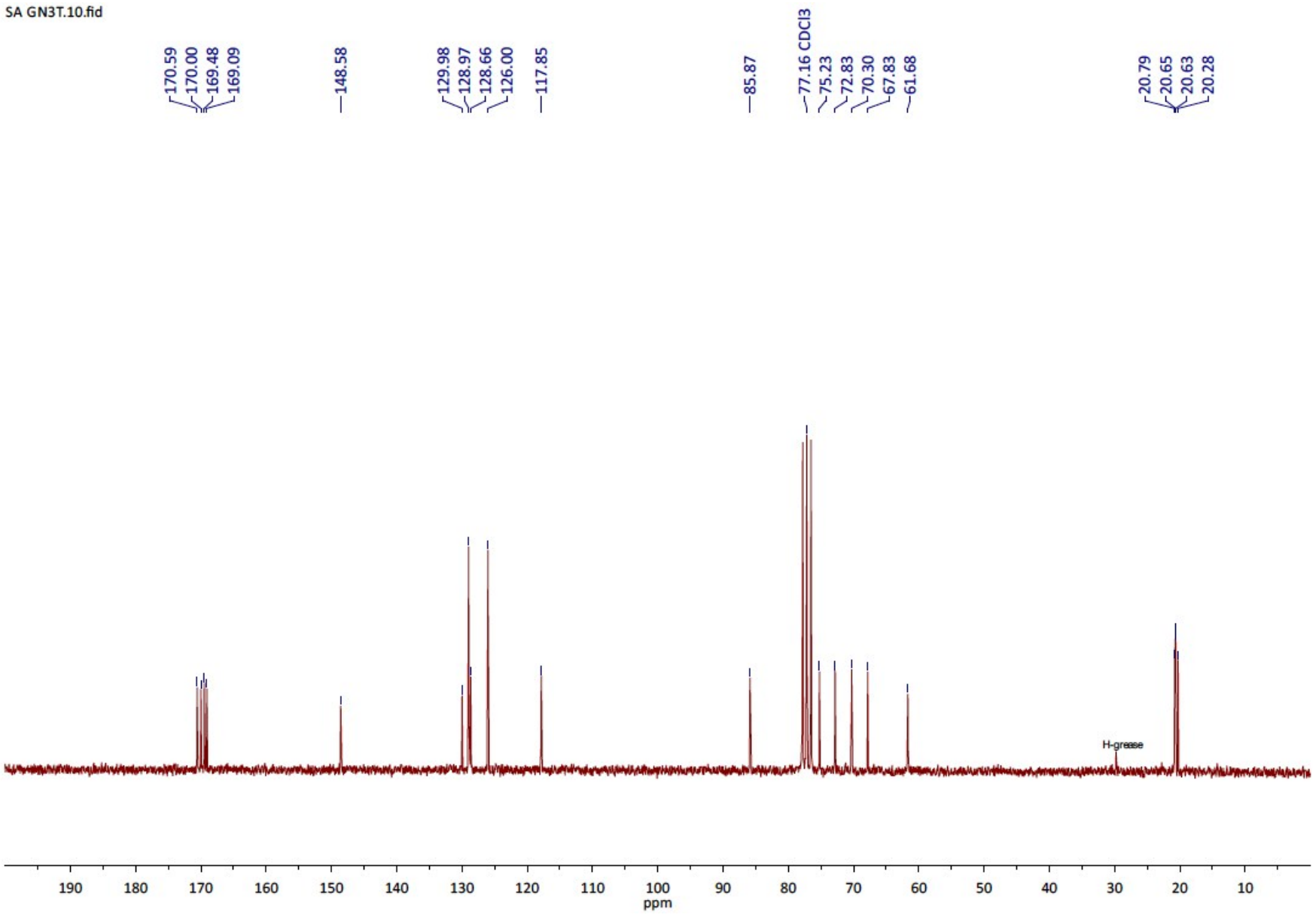
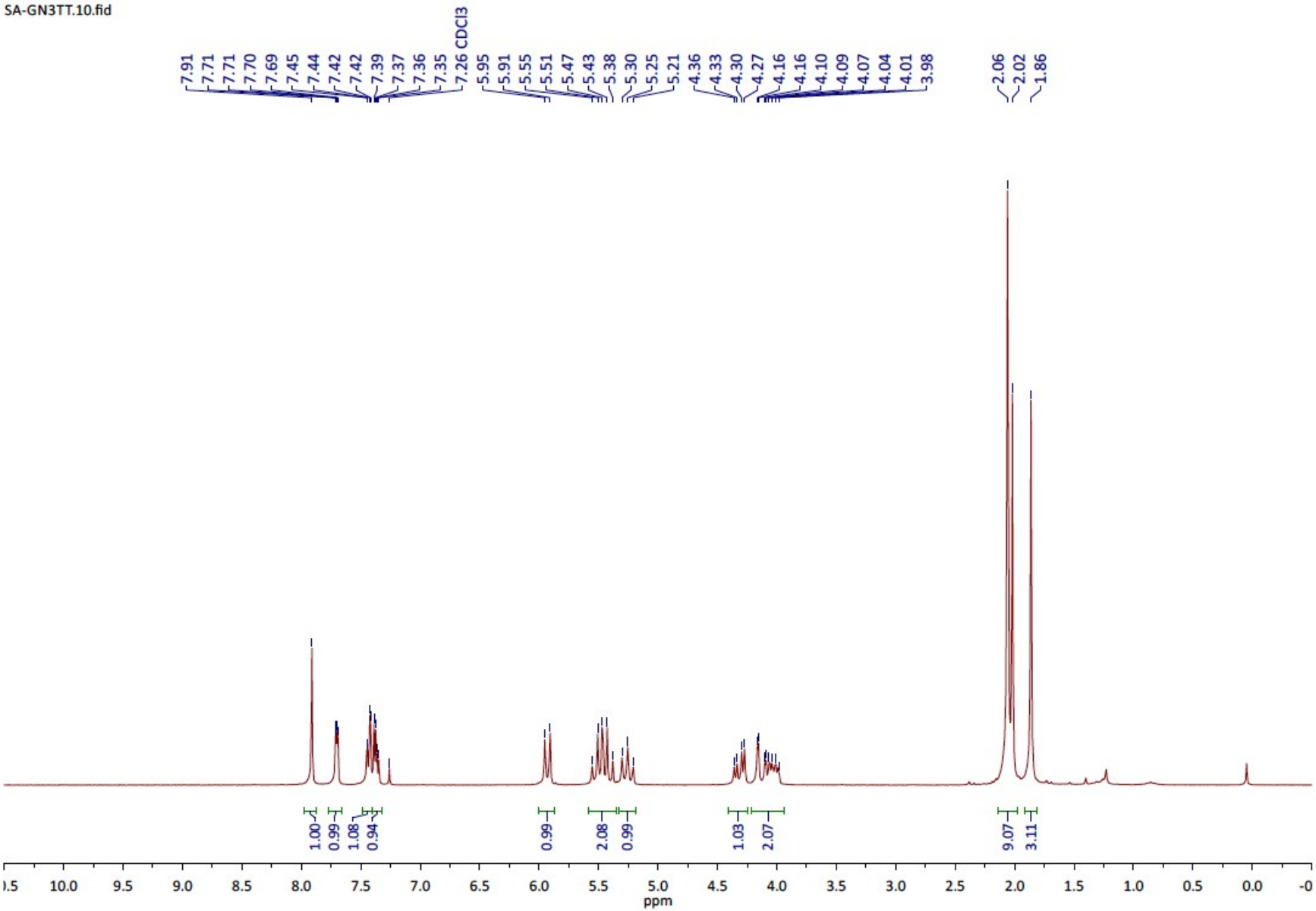

SA GN3T.10.fid
170.59
170.00
169.48
169.09
148.58
129.98
128.97
128.66
126.00
117.85
85.87
77.16 CDCl3
75.23
72.83
70.30
67.83
61.68
20.79
20.65
20.63
20.28
H-grease
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Figure S5. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) and HRMS spectra for compound **3c.**



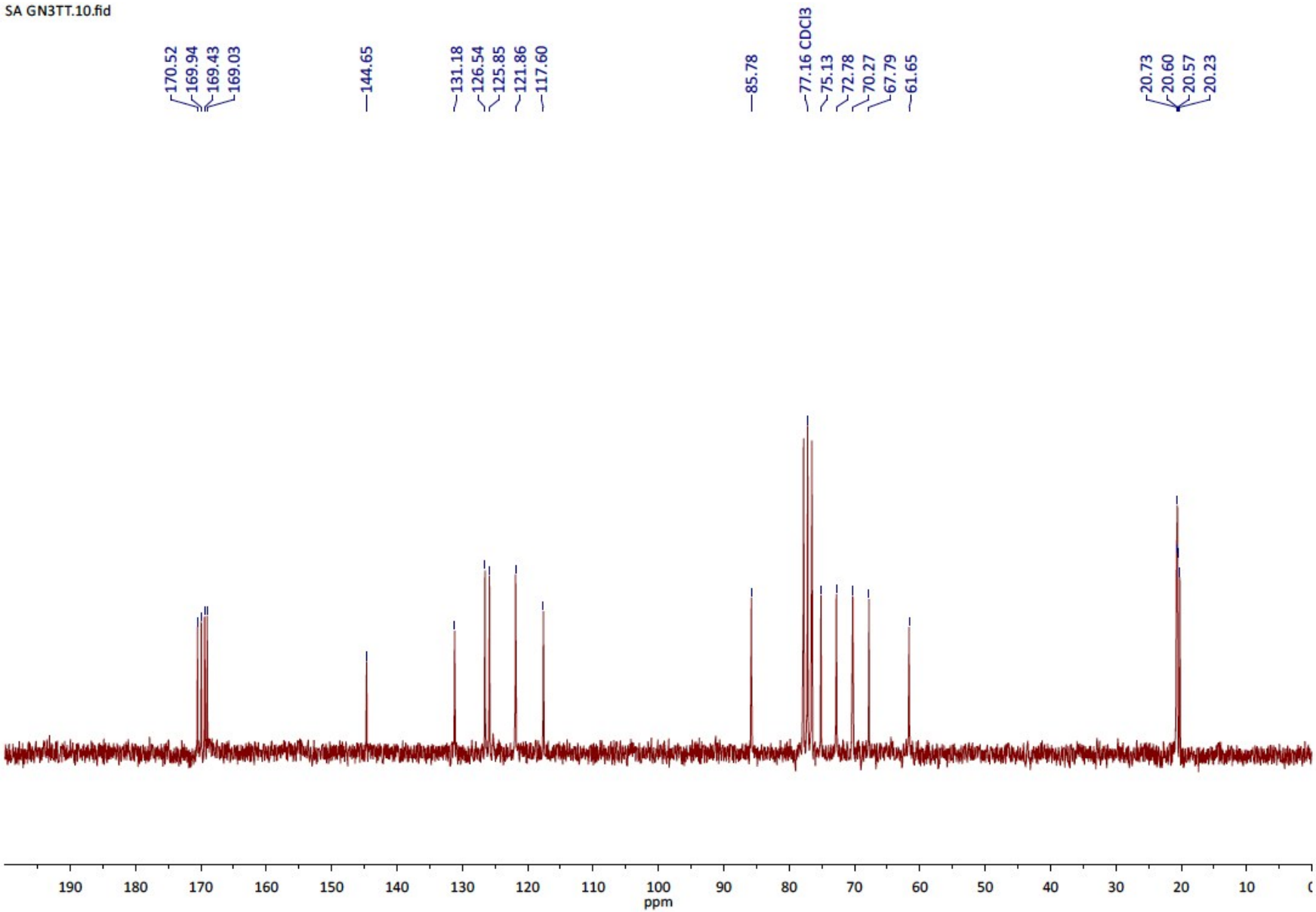
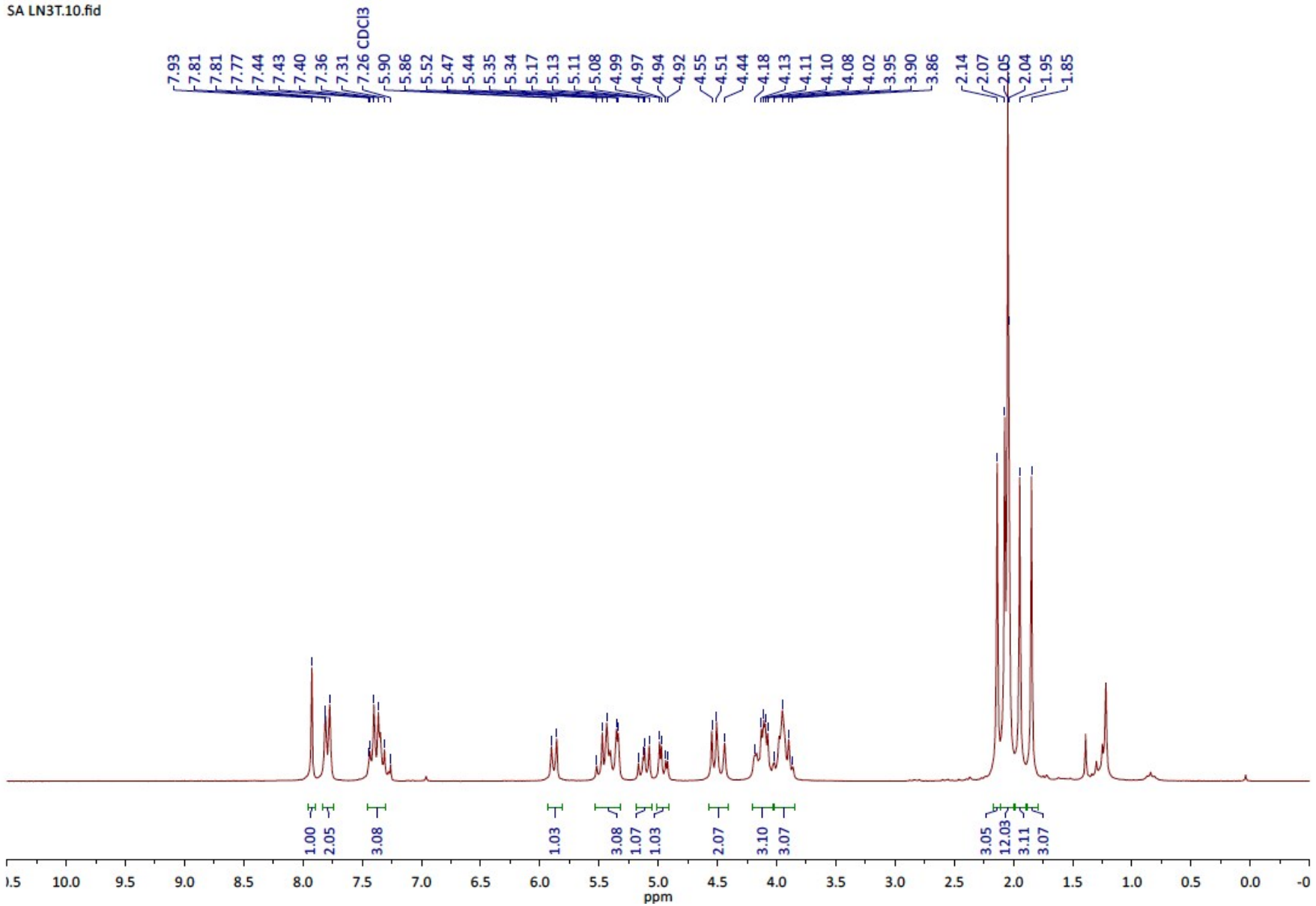

SA GN3TT.10.fid
170.52
169.94
169.43
169.03
144.65
131.18
126.54
125.85
121.86
117.60
85.78
77.16 CDCl3
75.13
72.78
70.27
67.79
61.65
20.73
20.60
20.57
20.23
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Figure S6. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) and HRMS spectra for compound **3d.**



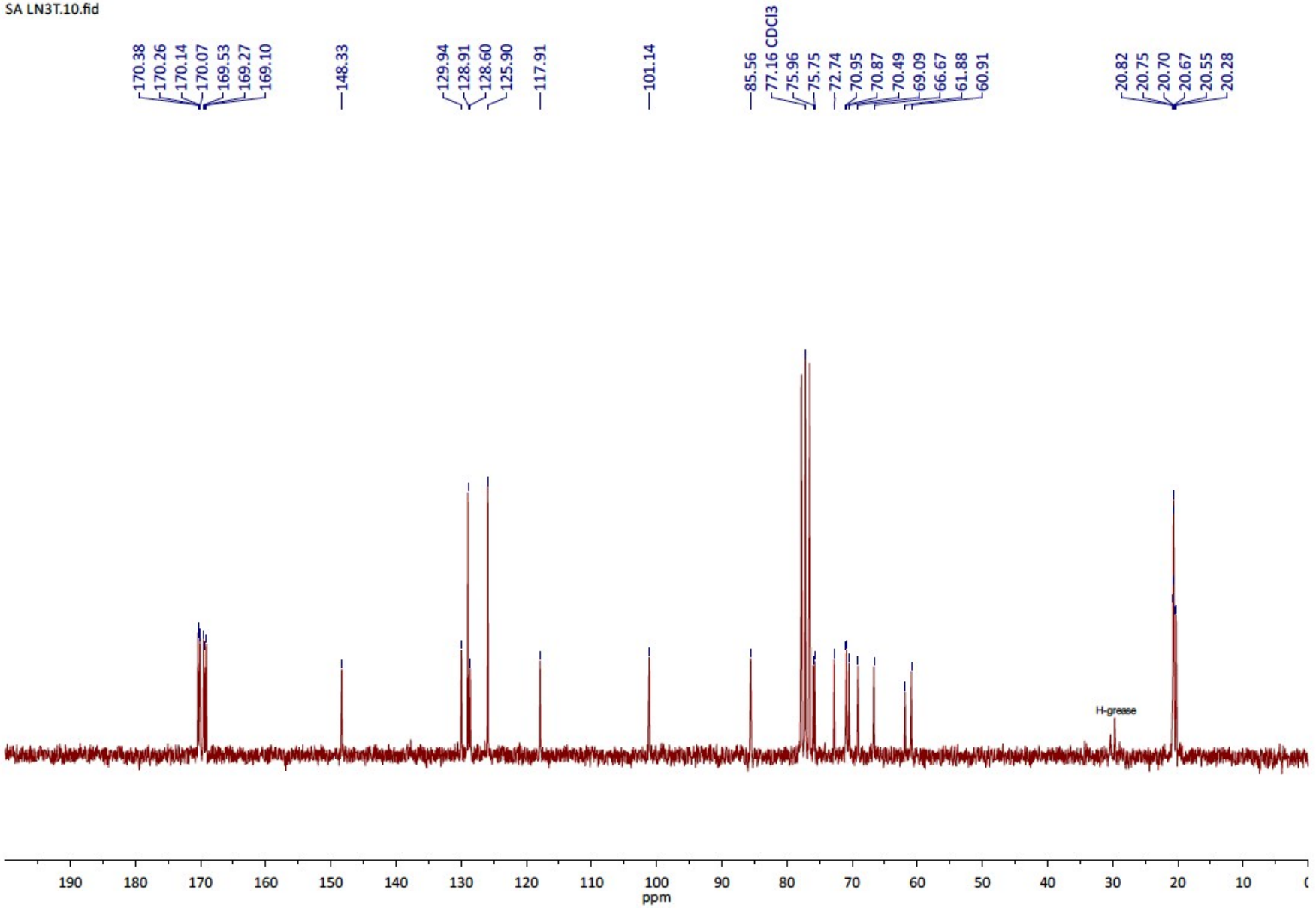
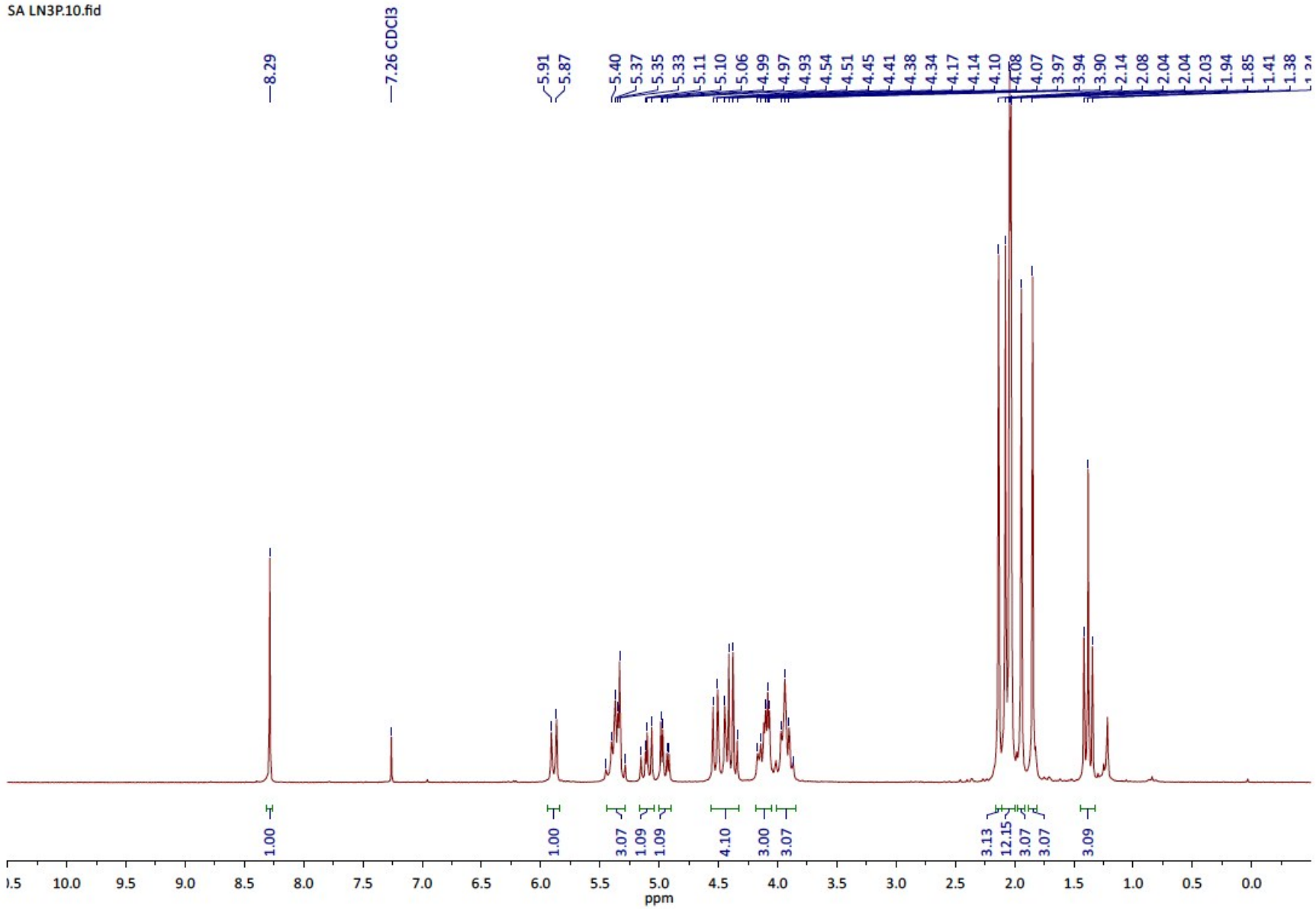

SA LN3T.10.fid
170.38
170.26
170.14
170.07
169.53
169.27
169.10
148.33
129.94
128.91
128.60
125.90
117.91
101.14
85.56
77.16 CDCl3
75.96
75.75
72.74
70.95
70.87
70.49
69.09
66.67
61.88
60.91
20.82
20.75
20.70
20.67
20.55
20.28
H-grease
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Figure S7. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) and HRMS spectra for compound **3e.**



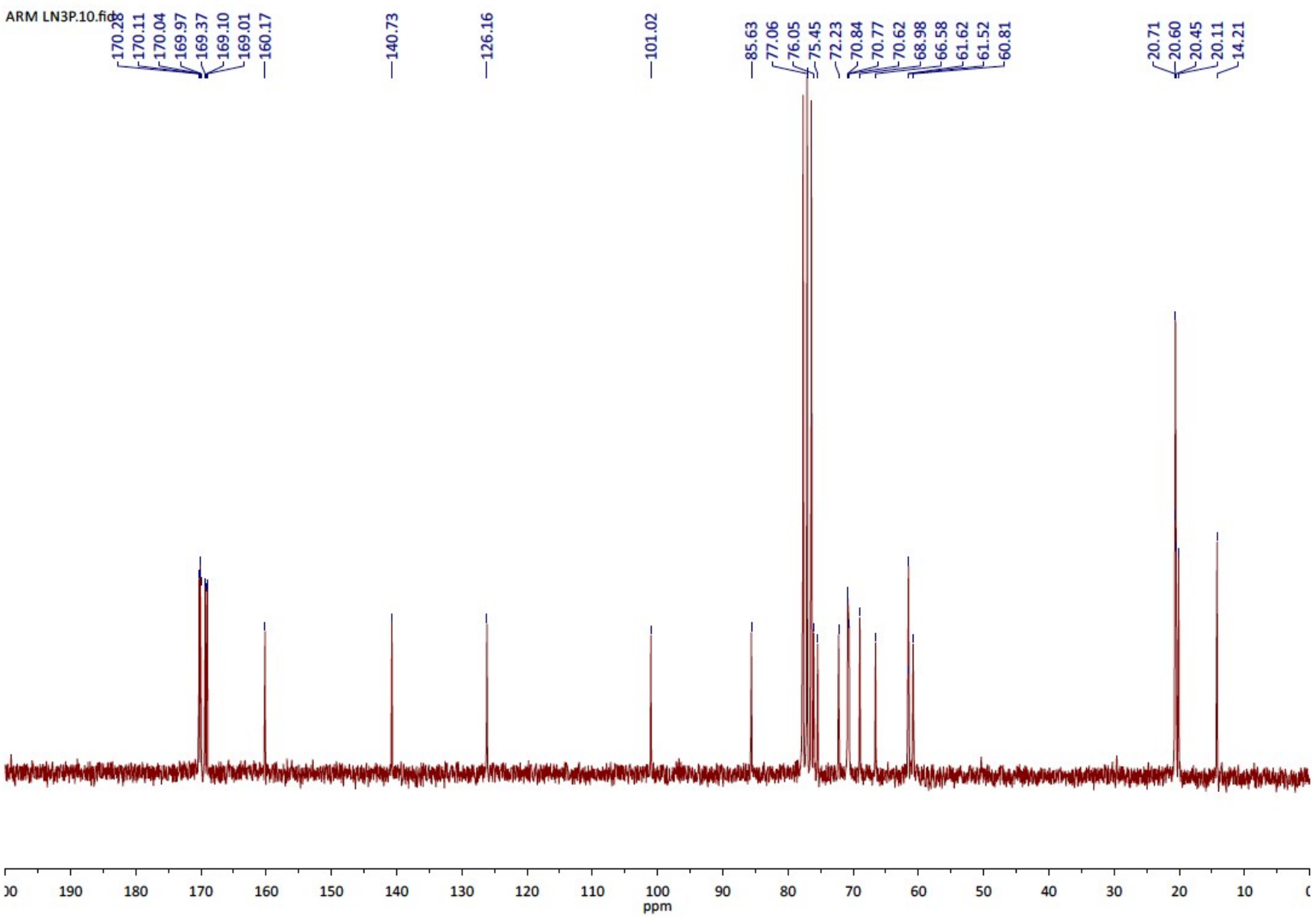
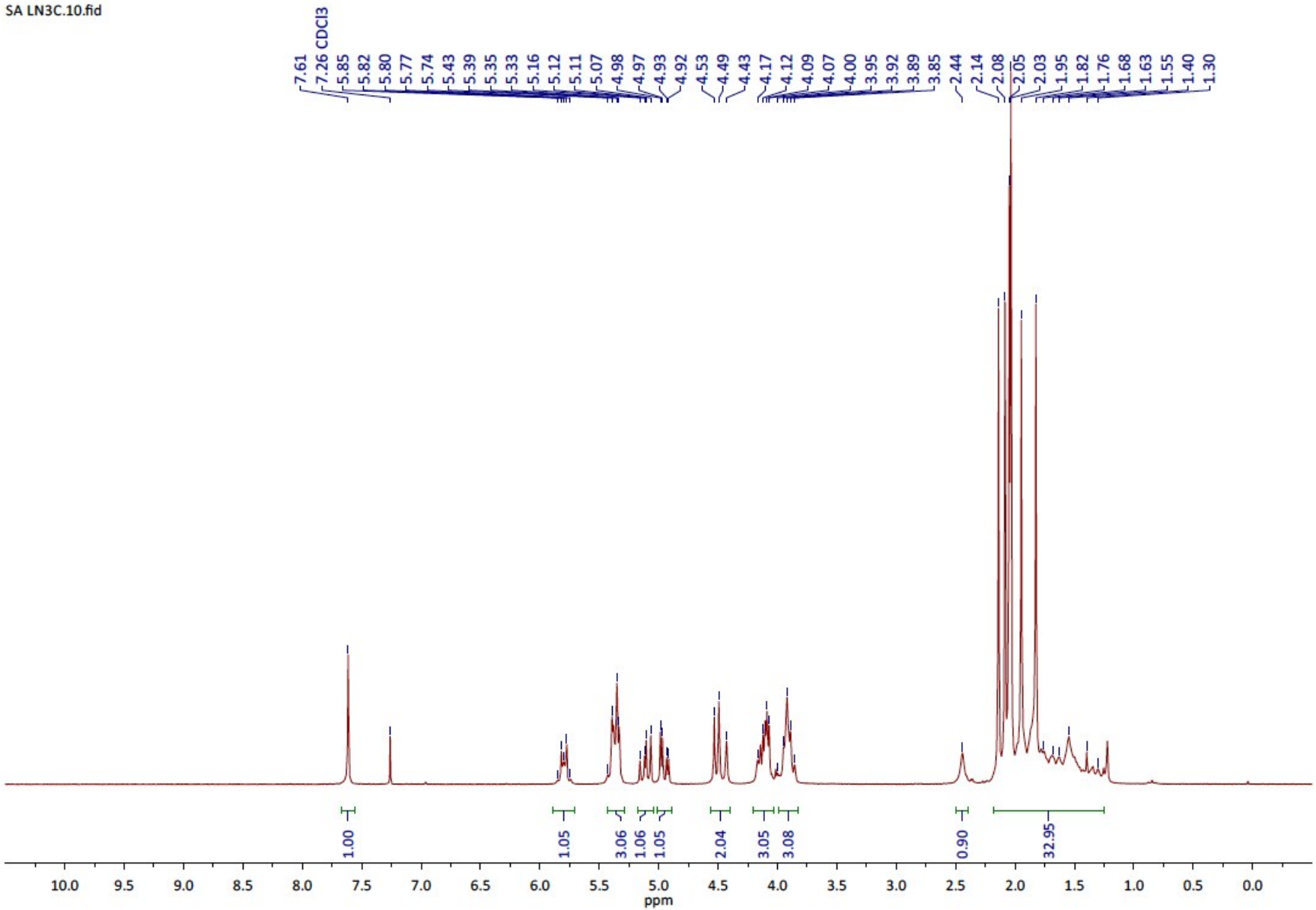

ARM LN3P.10.fid
170.28
170.11
170.04
169.97
169.37
169.10
169.01
160.17
140.73
126.16
101.02
85.63
77.06
76.05
75.45
72.23
70.84
70.77
70.62
68.98
66.58
61.62
61.52
60.81
20.71
20.60
20.45
20.11
14.21
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Figure S8. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) and HRMS spectra for compound **3f.**



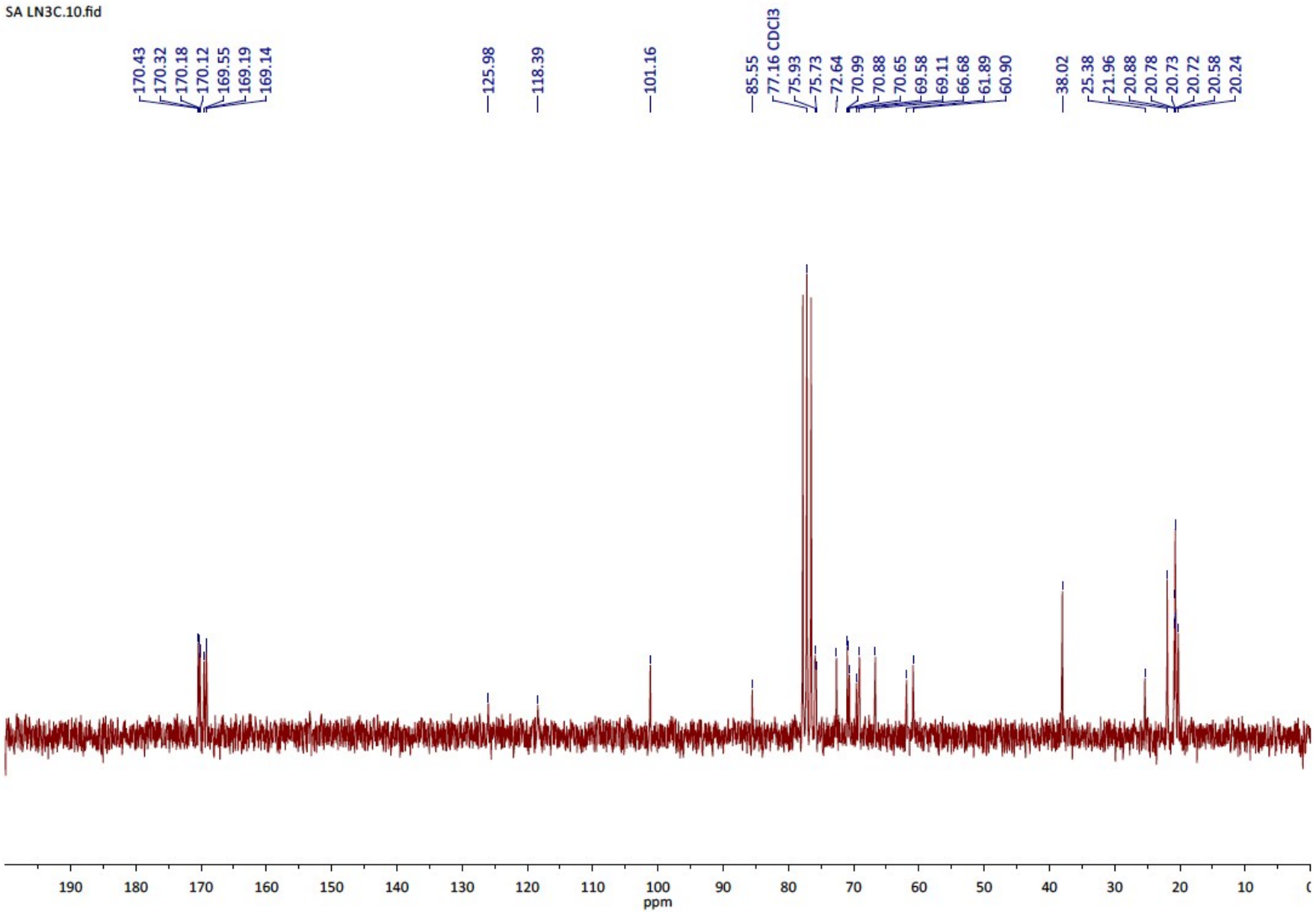
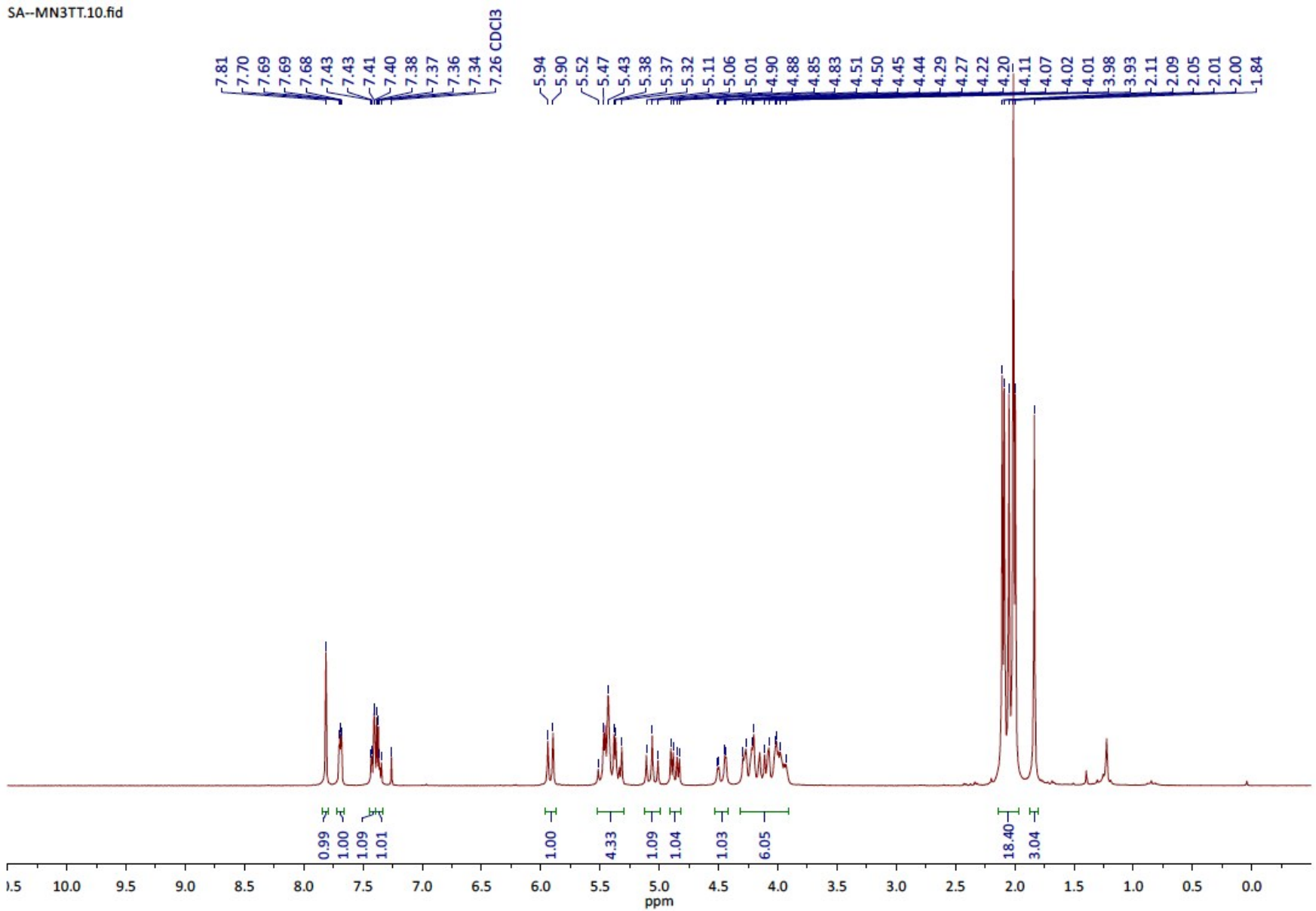

SA LN3C.10.fid
170.43
170.32
170.18
170.12
169.55
169.19
169.14
125.98
118.39
101.16
85.55
77.16 CDCl3
75.93
75.73
72.64
70.99
70.88
70.65
69.58
69.11
66.68
61.89
60.90
38.02
25.38
21.96
20.88
20.78
20.73
20.72
20.58
20.24
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Figure S9. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) and HRMS spectra for compound **3g.**



SA MN3TT.10.fid

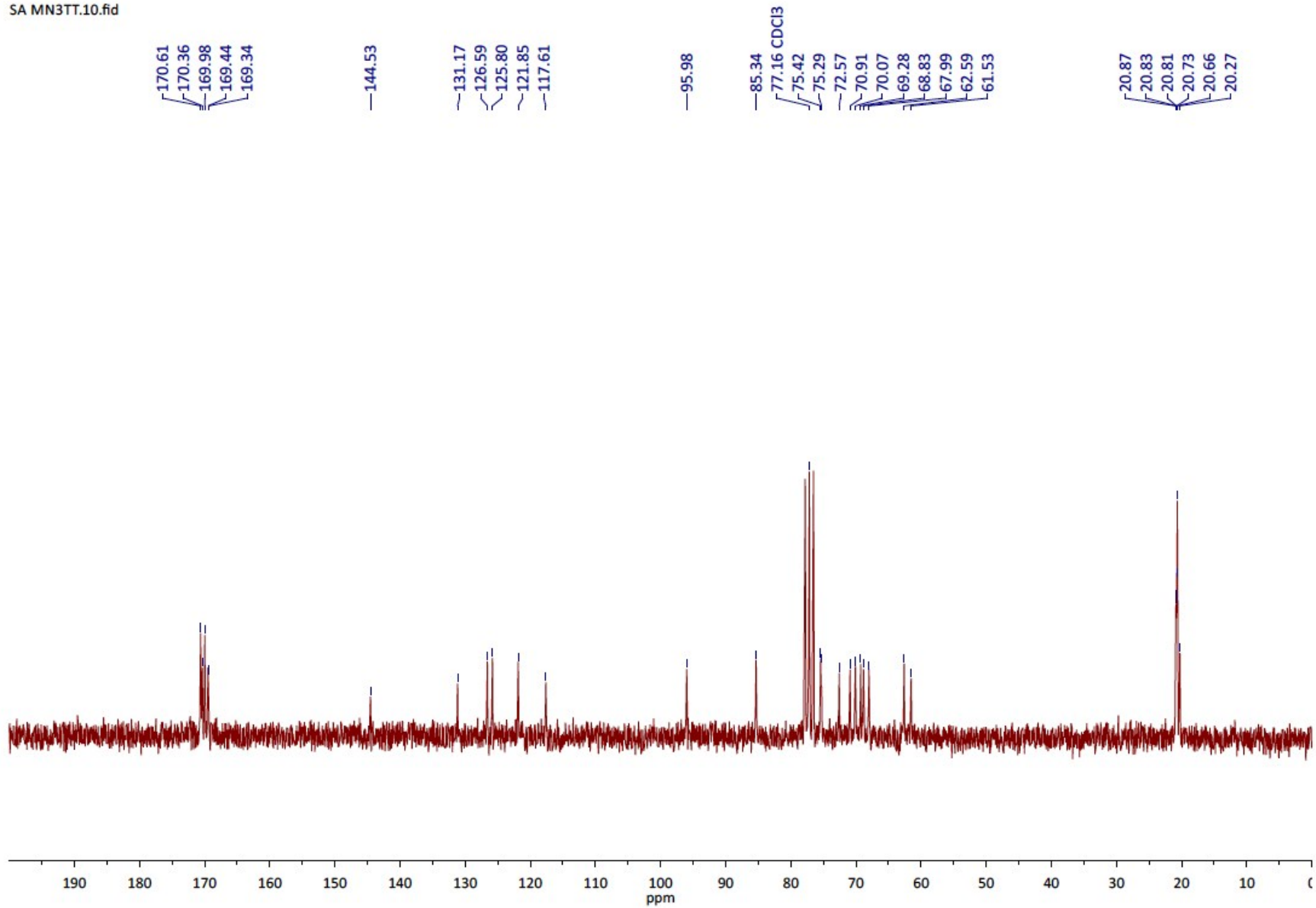
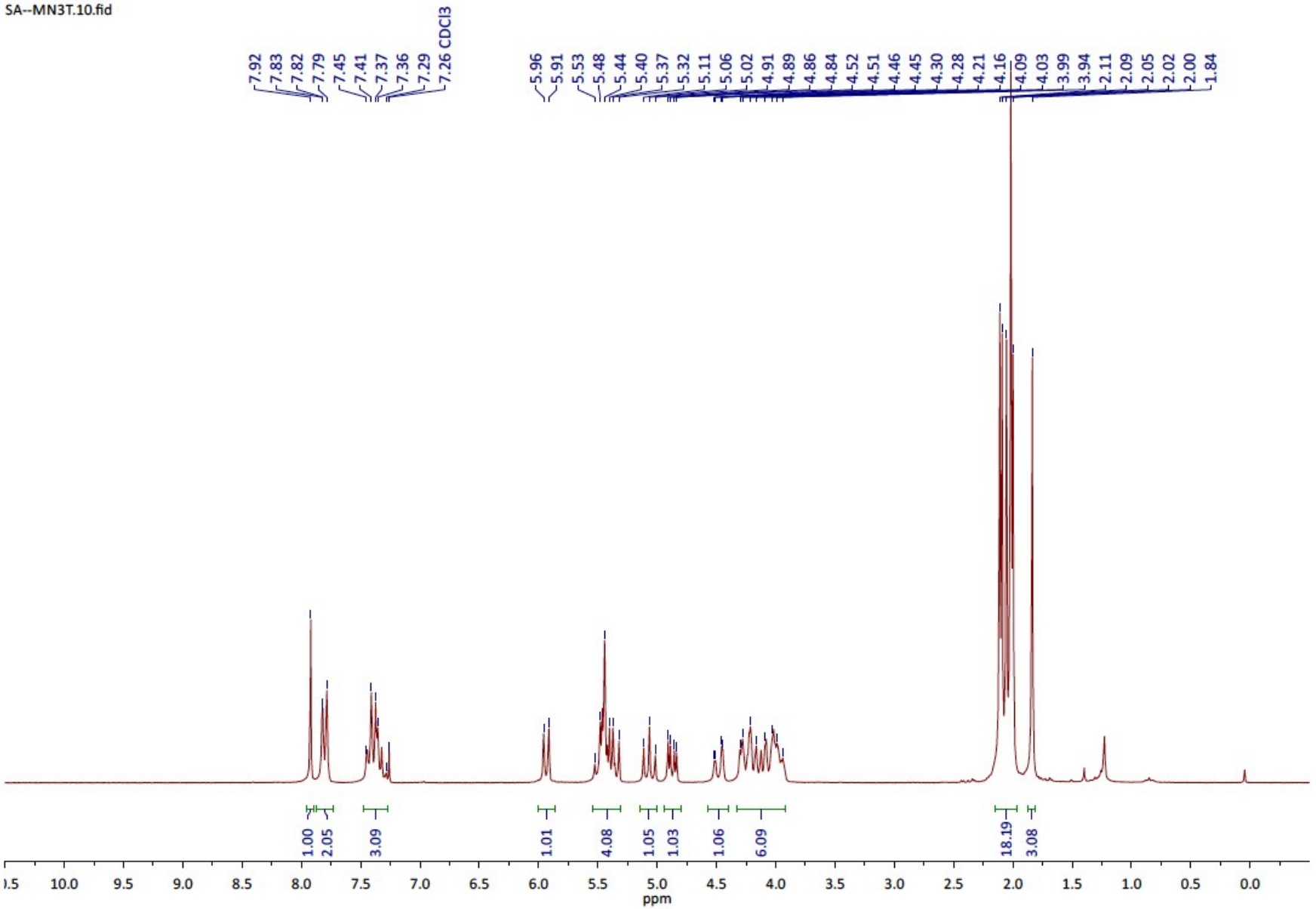


Figure S10. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) and HRMS spectra for compound **3h.**



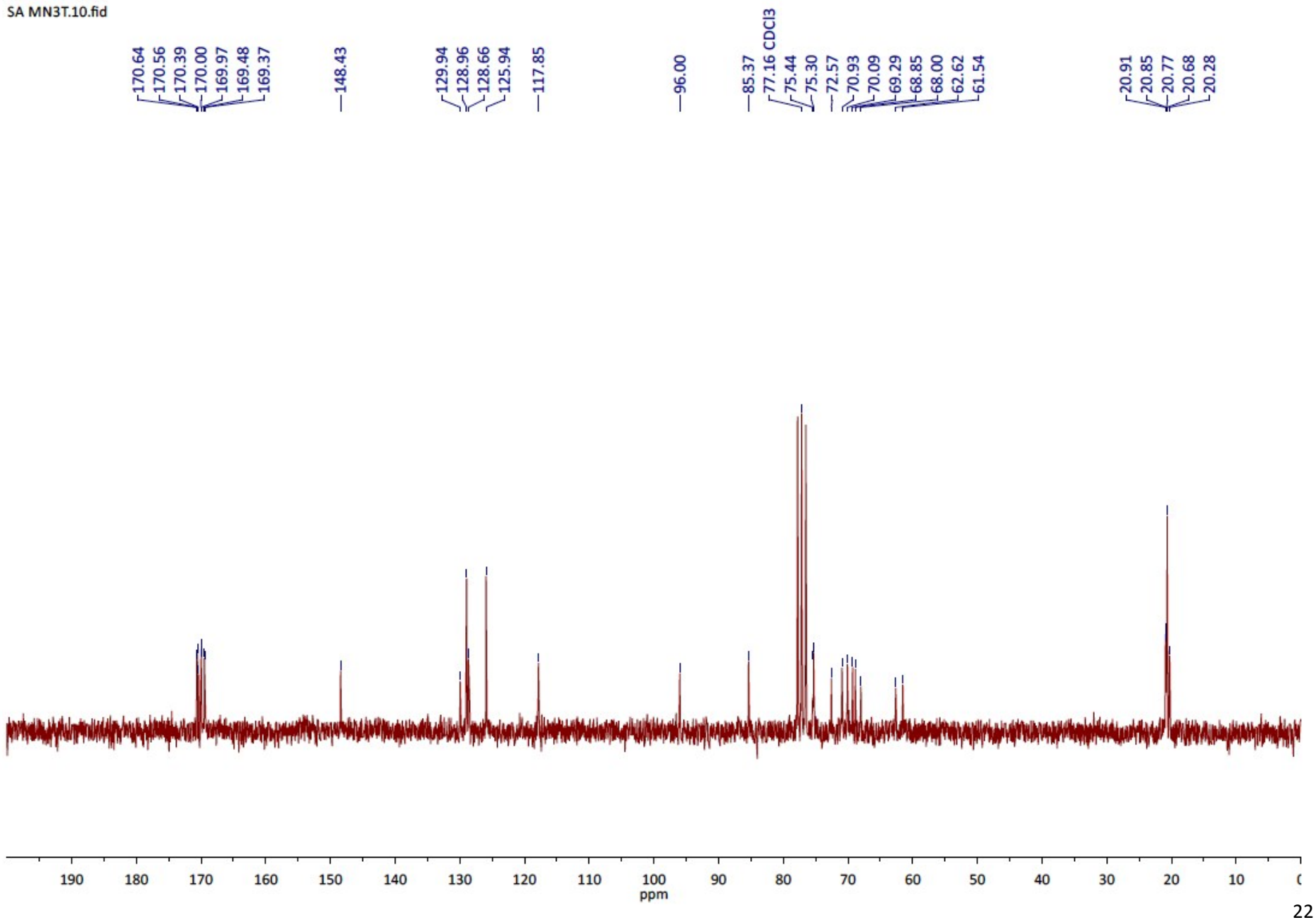
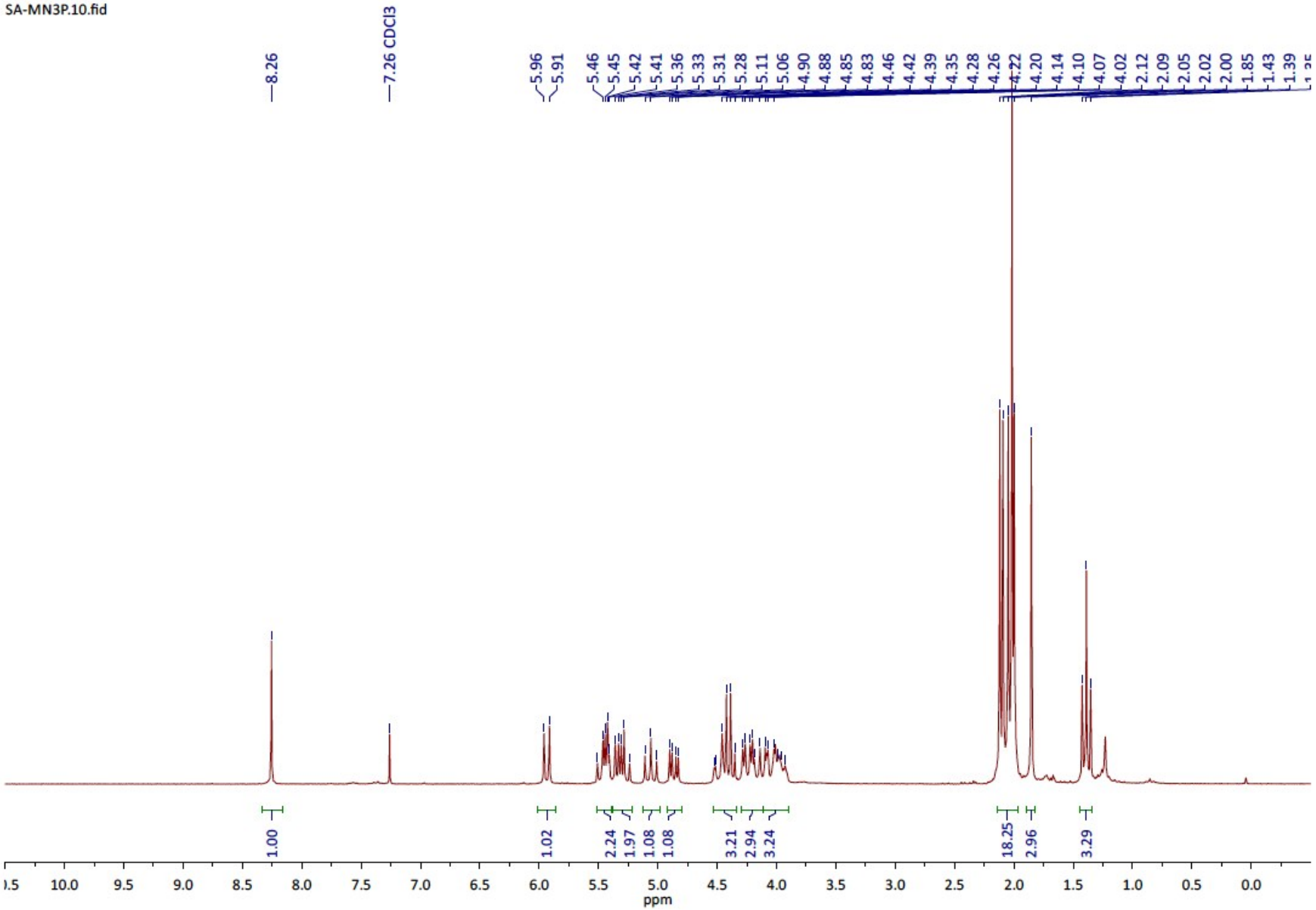

SA MN3T.10.fid
170.64
170.56
170.39
170.00
169.97
169.48
169.37
148.43
129.94
128.96
128.66
125.94
117.85
96.00
85.37
77.16 CDCl3
75.44
75.30
72.57
70.93
70.09
69.29
68.85
68.00
62.62
61.54
20.91
20.85
20.77
20.68
20.28
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Figure S11. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) and HRMS spectra for compound **3i.**



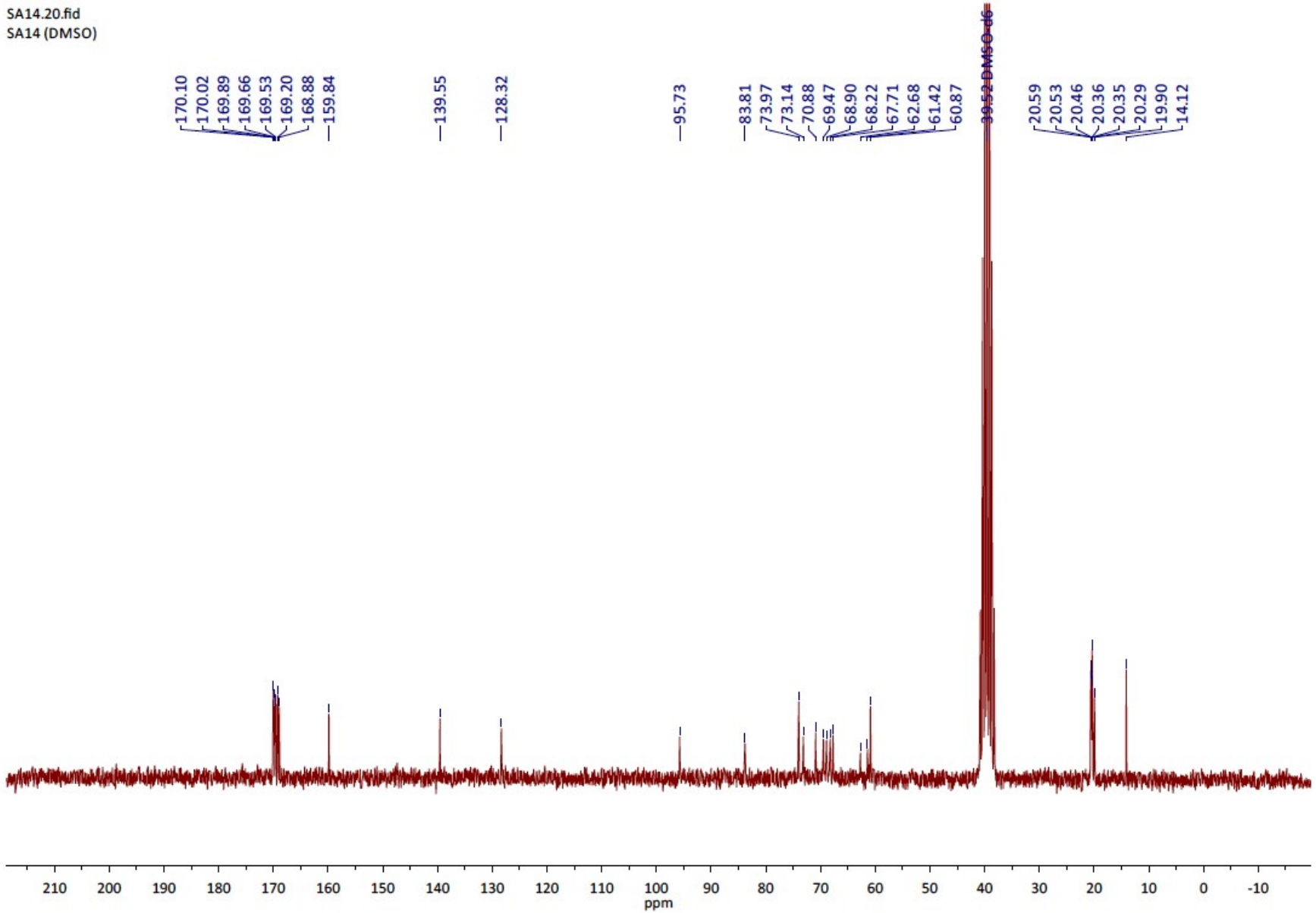
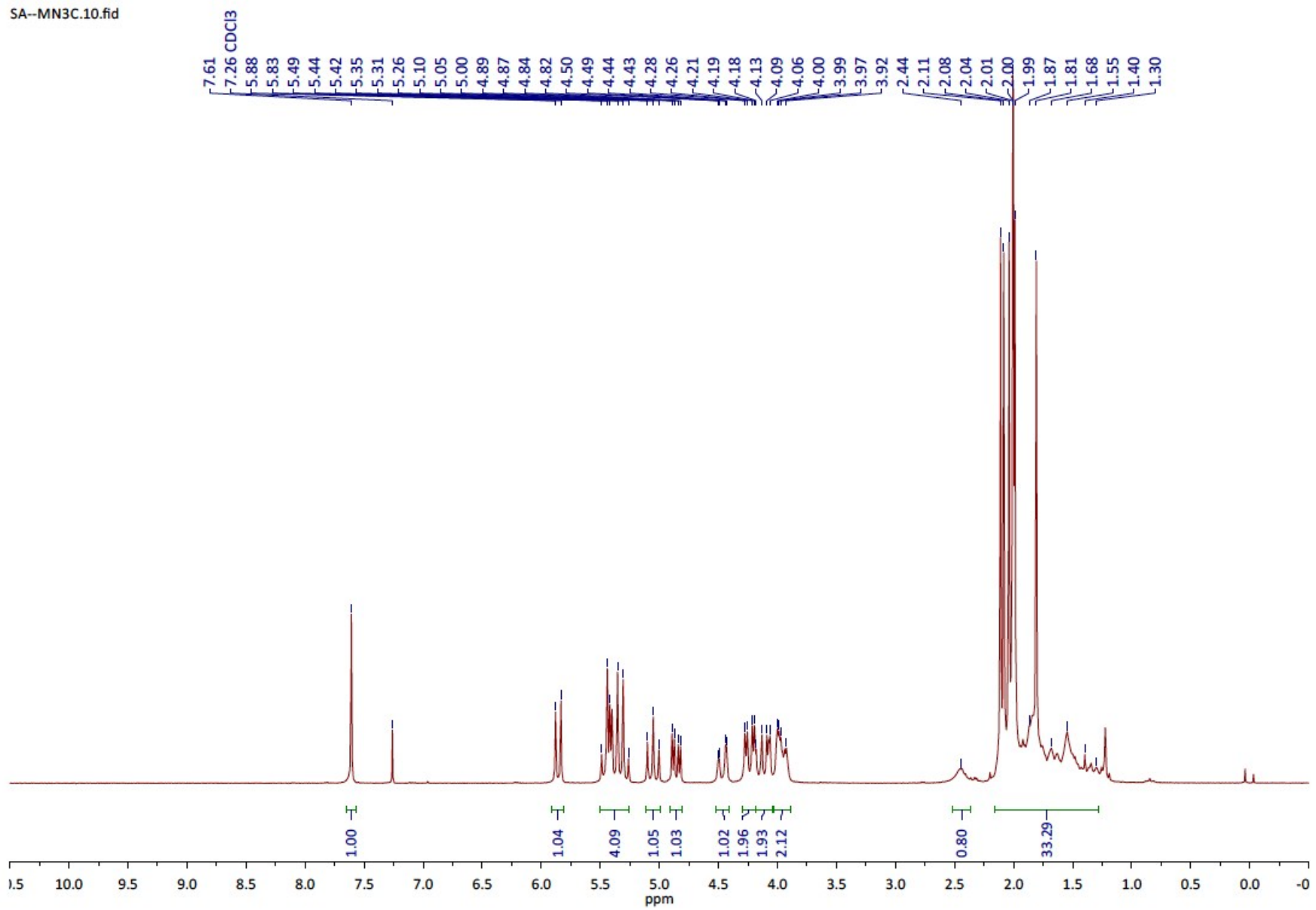

SA14.20.fid
SA14 (DMSO)
170.10
170.02
169.89
169.66
169.53
169.20
168.88
159.84
139.55
128.32
95.73
83.81
73.97
73.14
70.88
69.47
68.90
68.22
67.71
62.68
61.42
60.87
39.52 DMSO-d6
20.59
20.53
20.46
20.36
20.35
20.29
19.90
14.12
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

Figure S12. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) and HRMS spectra for compound **3j.**



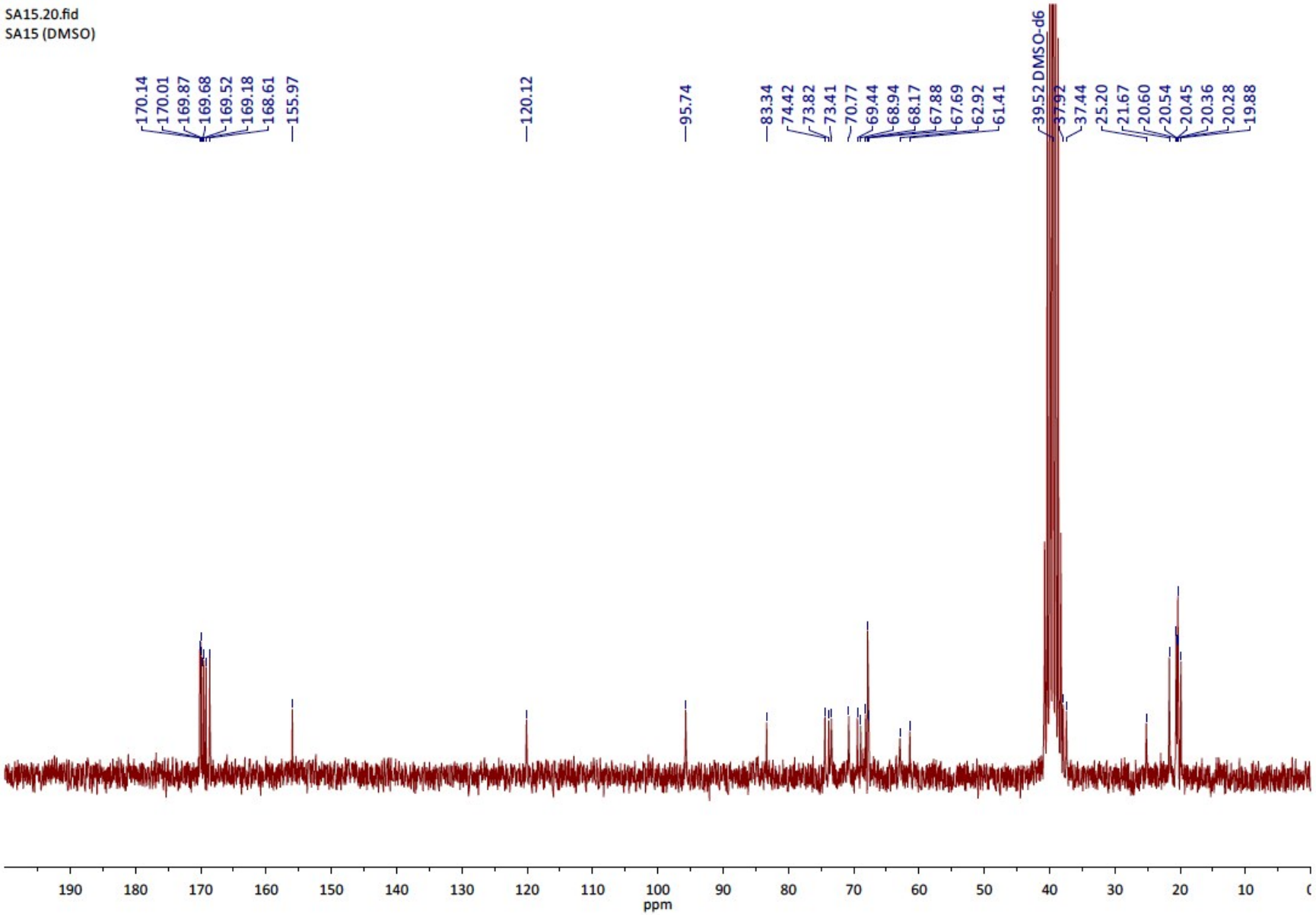
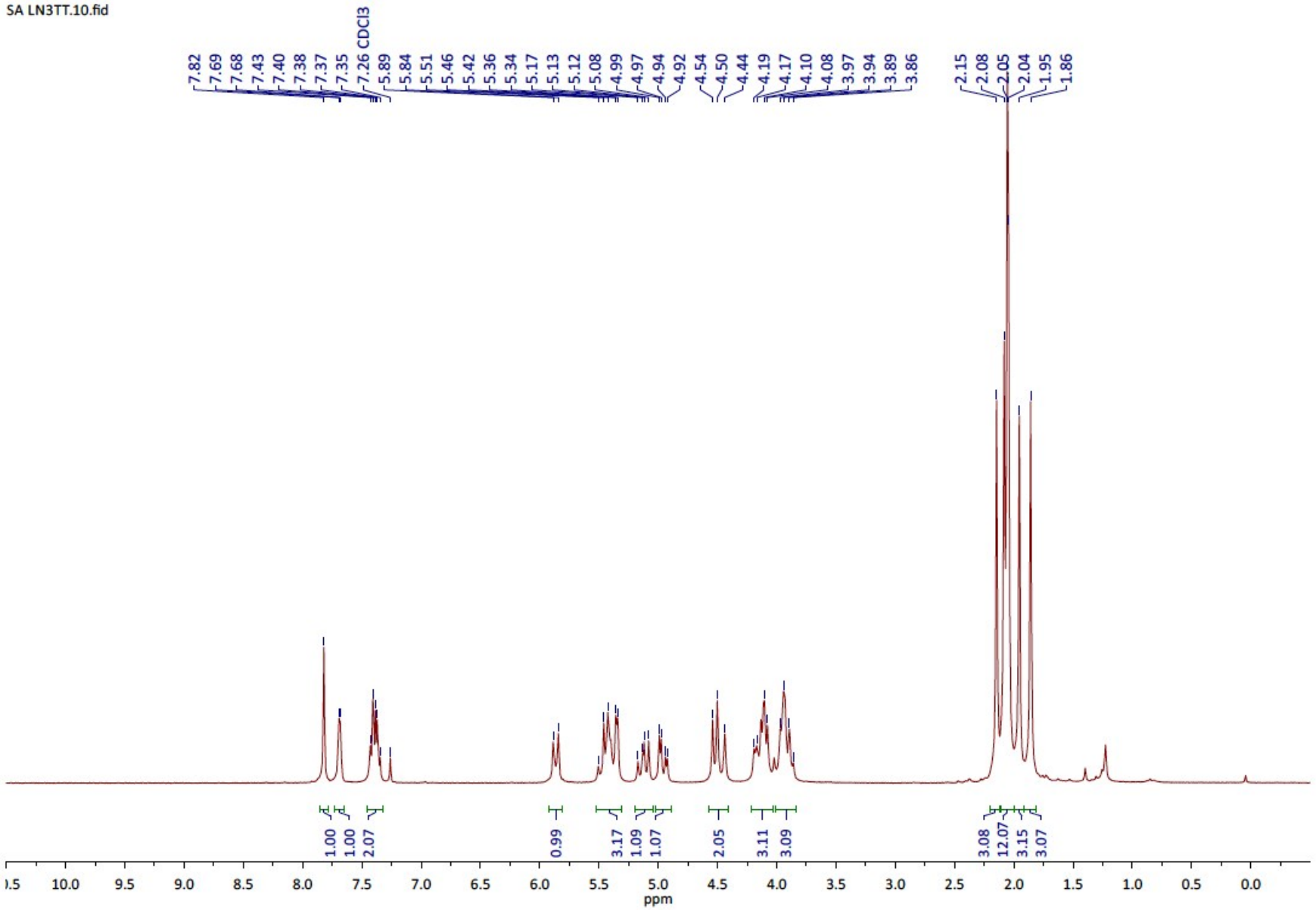
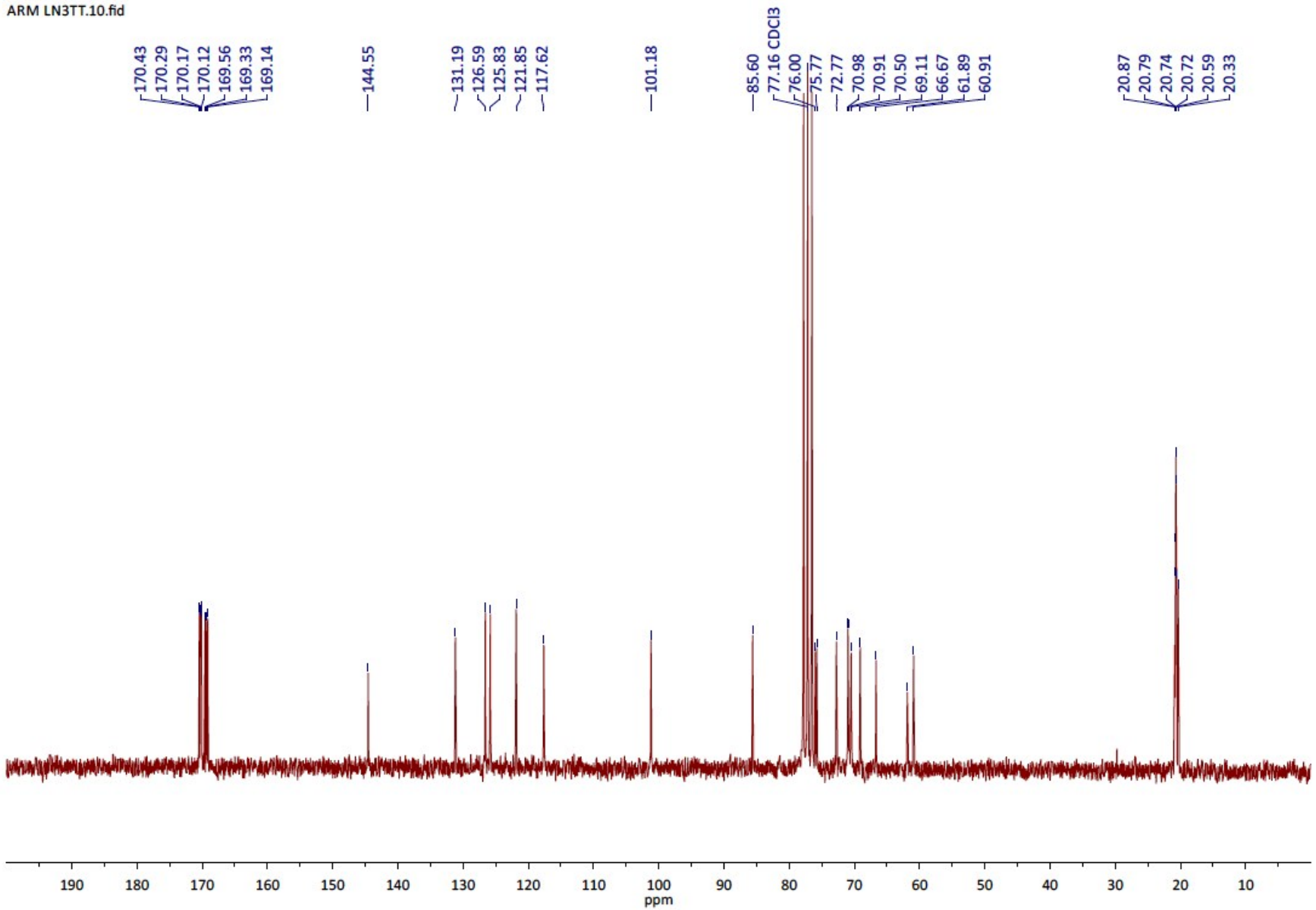
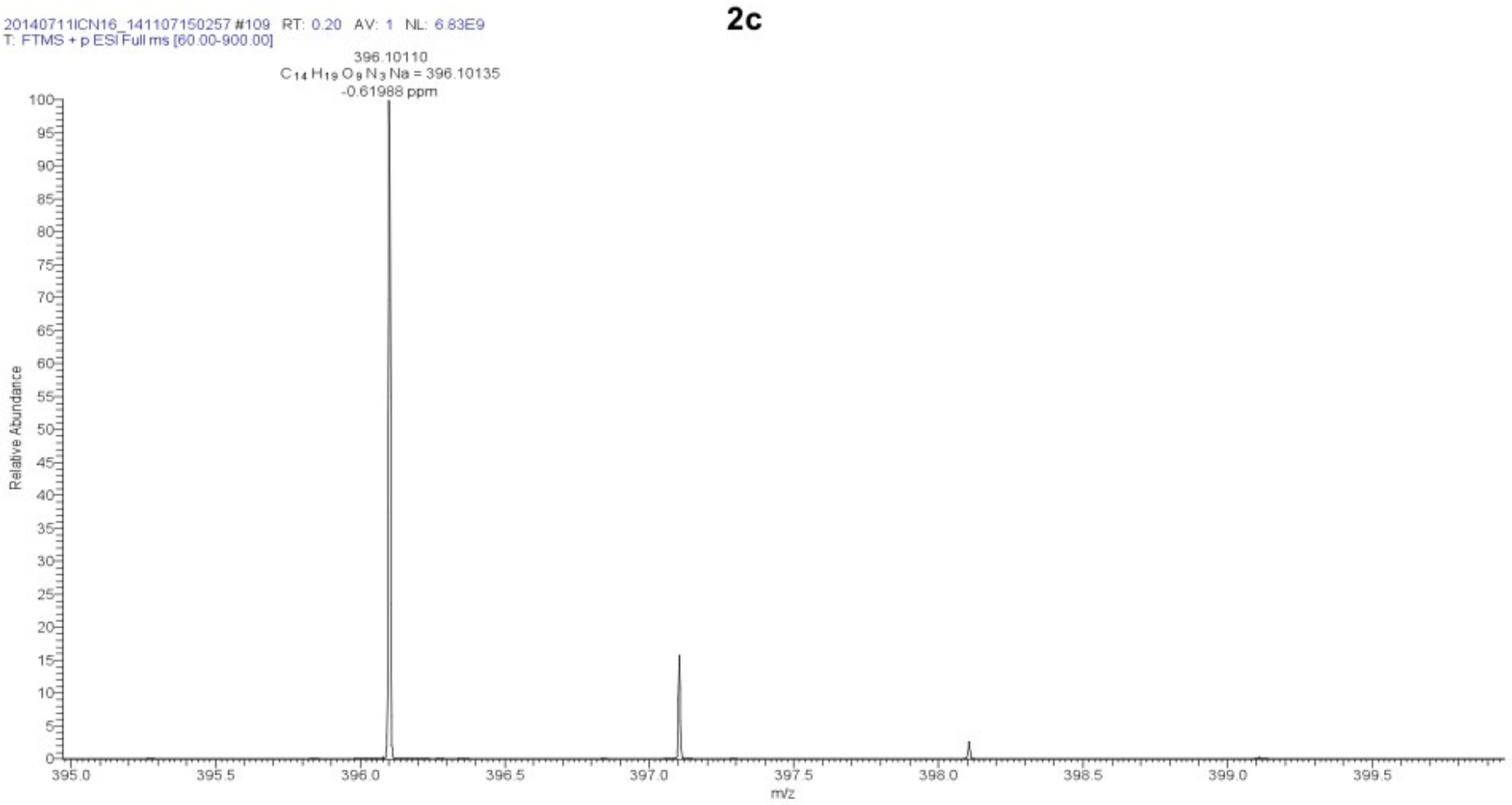

SA15.20.fid
SA15 (DMSO)
170.14
170.01
169.87
169.68
169.52
169.18
168.61
155.97
120.12
95.74
83.34
74.42
73.82
73.41
70.77
69.44
68.94
68.17
67.88
67.69
62.92
61.41
39.52 DMSO-d6
37.92
37.44
25.20
21.67
20.60
20.54
20.45
20.36
20.28
19.88
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Figure S12. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) and HRMS spectra for compound **3k.**

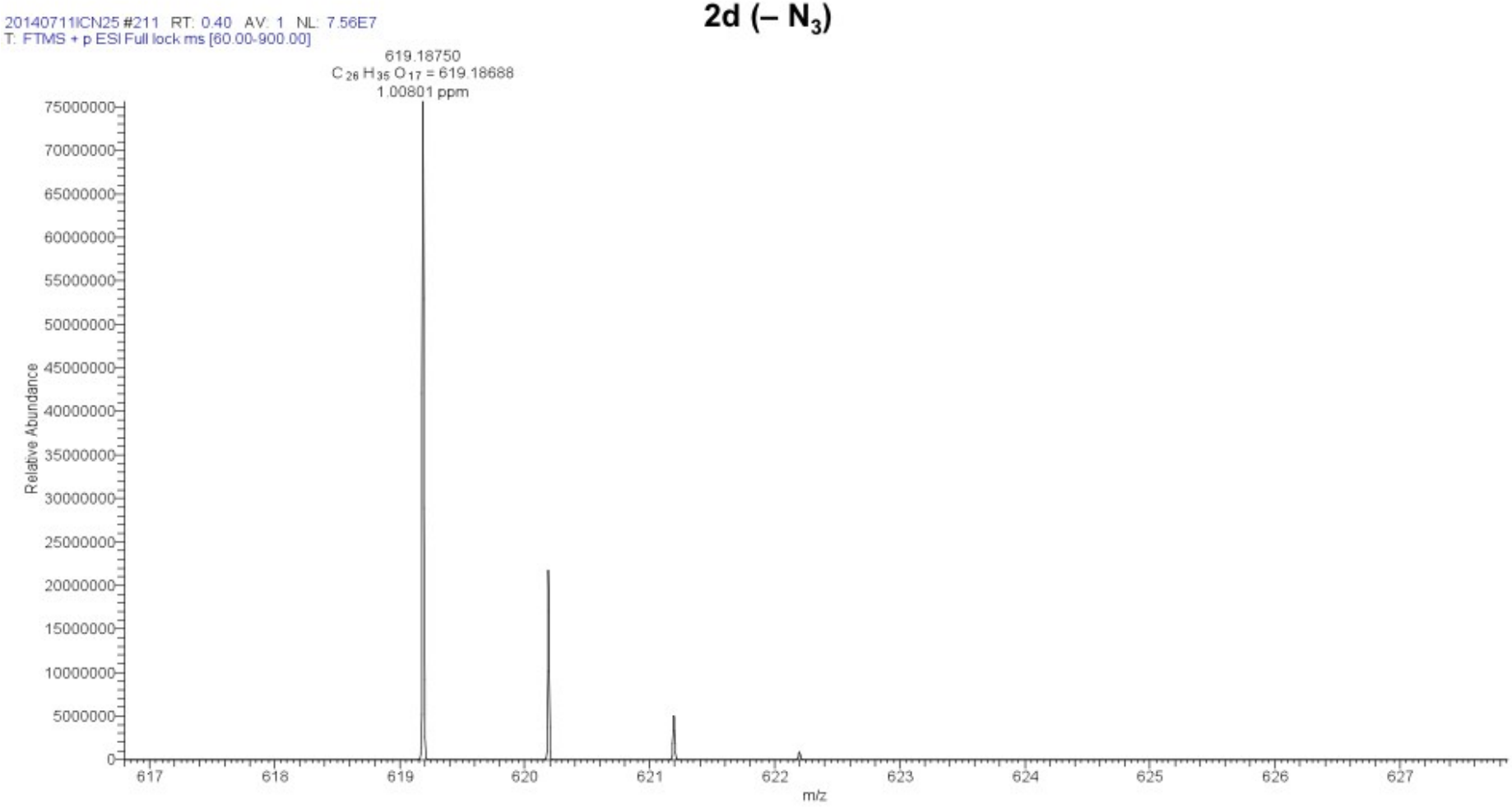



ARM LN3TT.10.fid
170.43
170.29
170.17
170.12
169.56
169.33
169.14
144.55
131.19
126.59
125.83
121.85
117.62
101.18
85.60
77.16 CDCl3
76.00
75.77
72.77
70.98
70.91
70.50
69.11
66.67
61.89
60.91
20.87
20.79
20.74
20.72
20.59
20.33
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

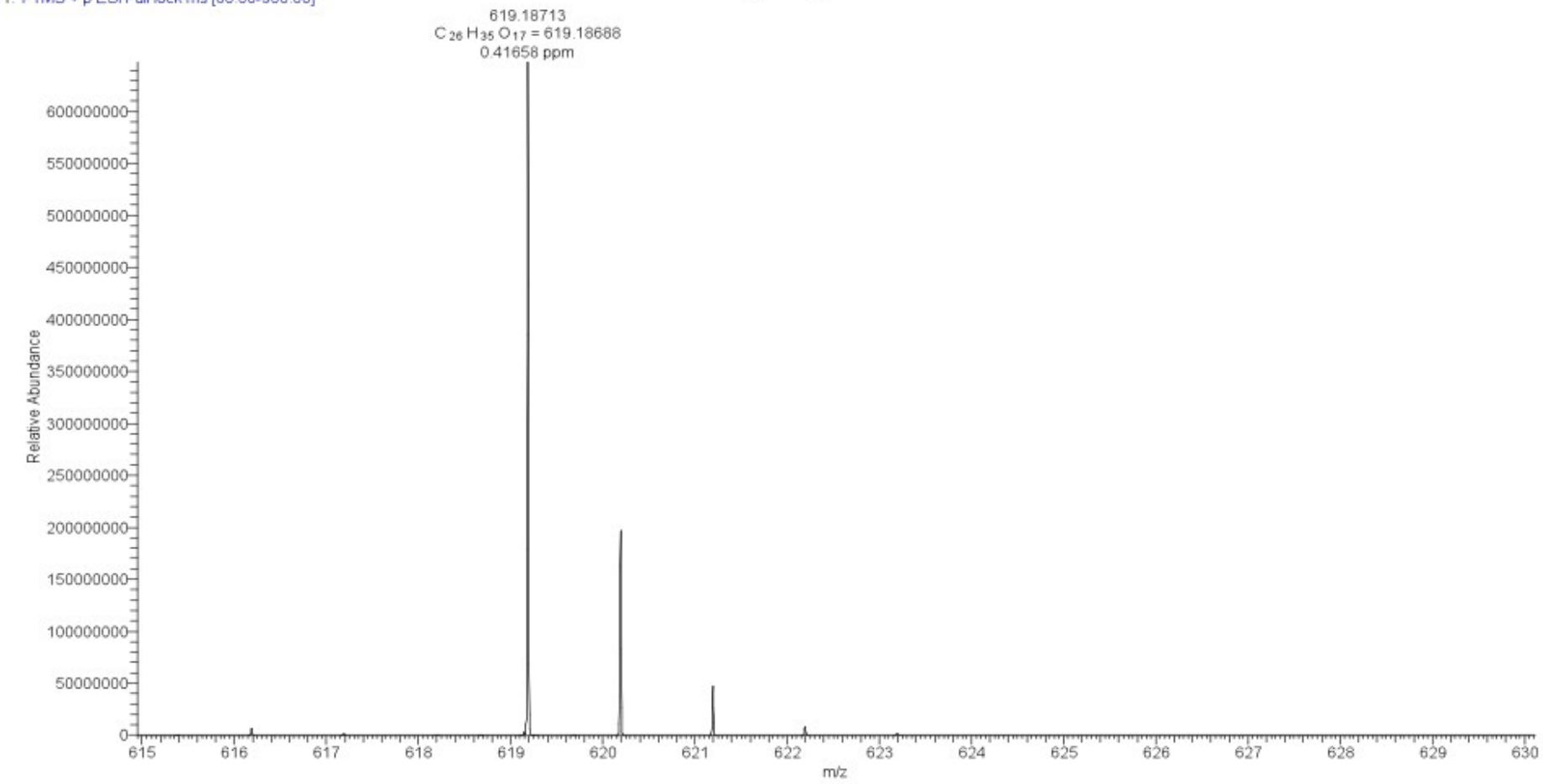
HRMS data


2c
20140711ICN16_141107150257 #109 RT: 0.20 AV: 1 NL: 6.83E9
T: FTMS + p ESI Full ms [60.00-900.00]
396.10110
C14 H19 O8 N3 Na = 396.10135
-0.61988 ppm
Relative Abundance
m/z
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
395.0
395.5
396.0
396.5
397.0
397.5
398.0
398.5
399.0
399.5

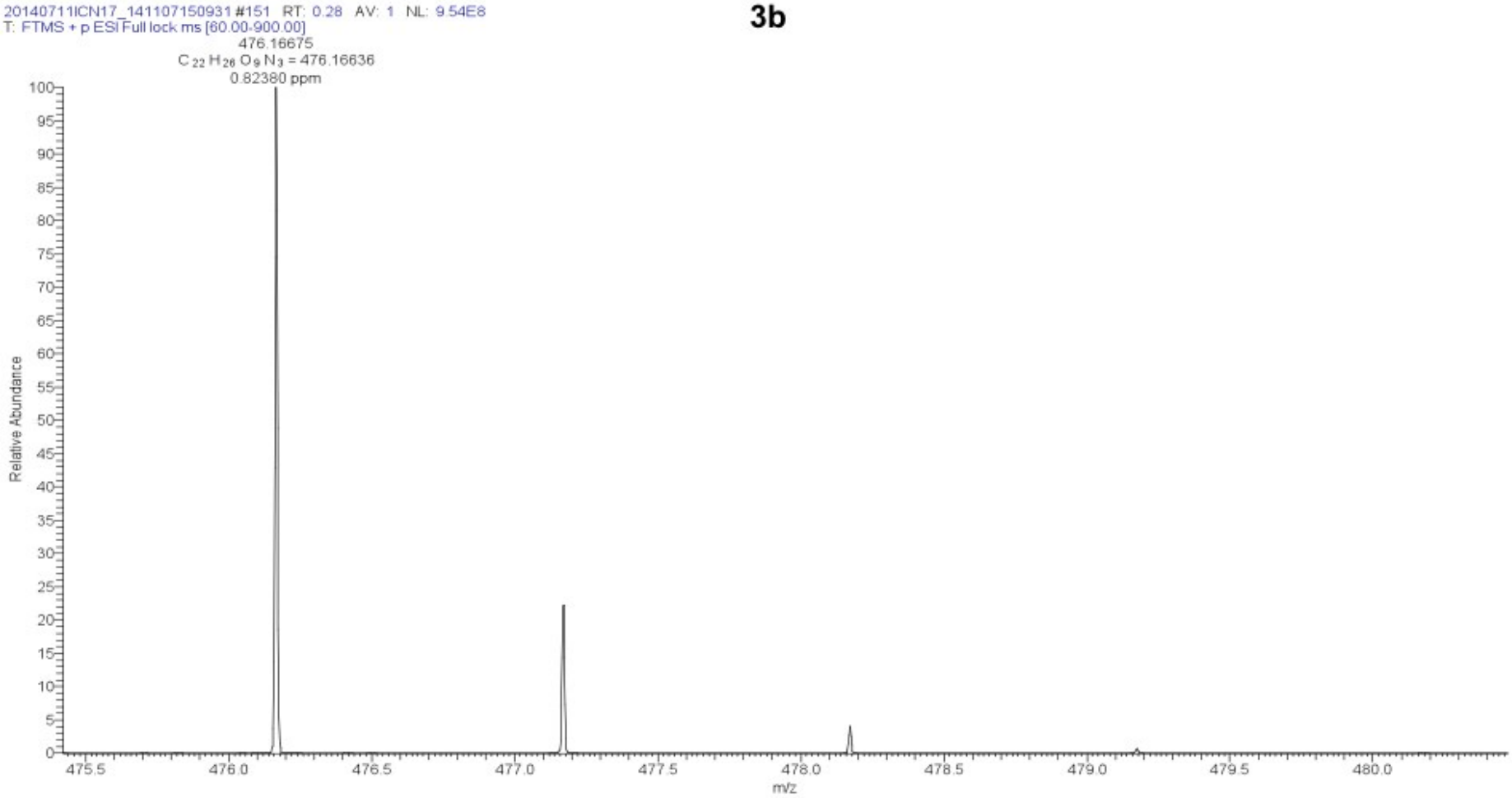
2d (– N_3)


20140711ICN25 #211 RT: 0.40 AV: 1 NL: 7.56E7
T: FTMS + p ESI Full lock ms [60.00-900.00]
619.18750
C 26 H 35 O 17 = 619.18688
1.00801 ppm
Relative Abundance
m/z
75000000
70000000
65000000
60000000
55000000
50000000
45000000
40000000
35000000
30000000
25000000
20000000
15000000
10000000
5000000
0
617
618
619
620
621
622
623
624
625
626
627

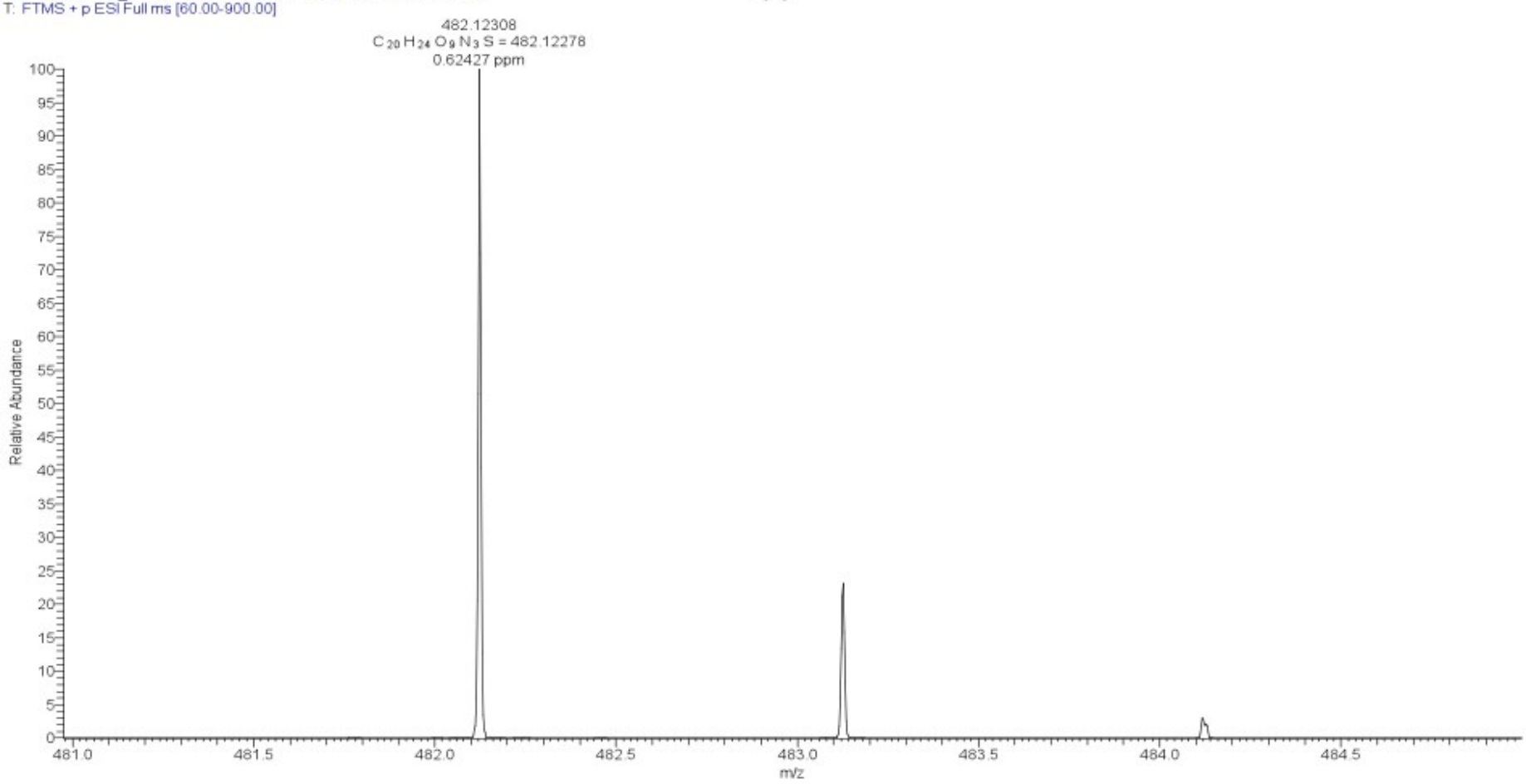
2e (– N_3)


20140711ICN20 #169 RT: 0.32 AV: 1 NL: 6.47E8
T: FTMS + p ESI Full lock ms [60.00-900.00]
619.18713
C 26 H 35 O 17 = 619.18688
0.41658 ppm
Relative Abundance
600000000
550000000
500000000
450000000
400000000
350000000
300000000
250000000
200000000
150000000
100000000
50000000
0
615
616
617
618
619
620
621
622
623
624
625
626
627
628
629
630
m/z

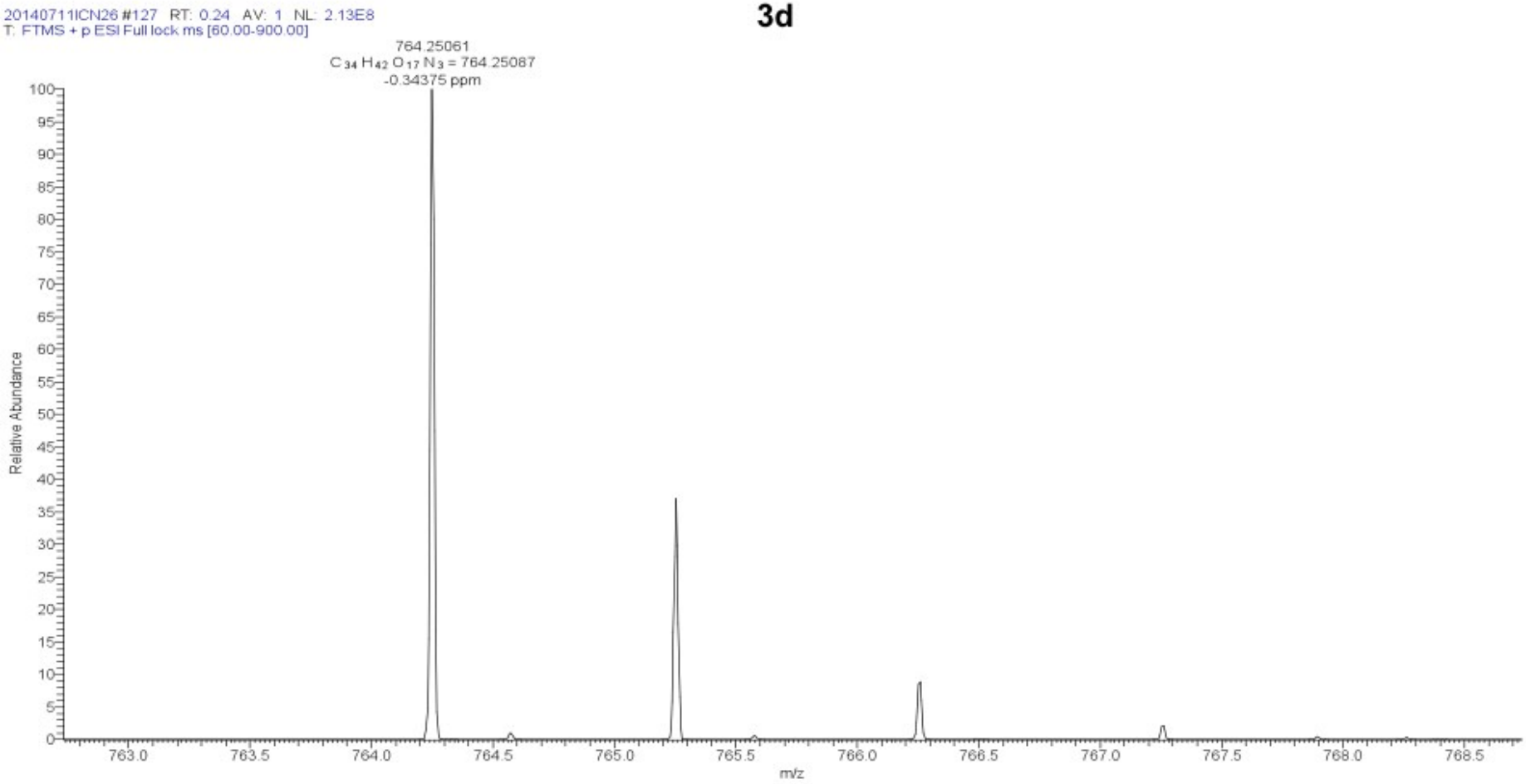
3b


20140711ICN17_141107150931 #151 RT: 0.28 AV: 1 NL: 9.54E8
T: FTMS + p ESI Full lock ms [60.00-900.00]
476.16675
C 22 H 26 O 9 N 3 = 476.16636
0.82380 ppm
Relative Abundance
m/z
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
475.5
476.0
476.5
477.0
477.5
478.0
478.5
479.0
479.5
480.0

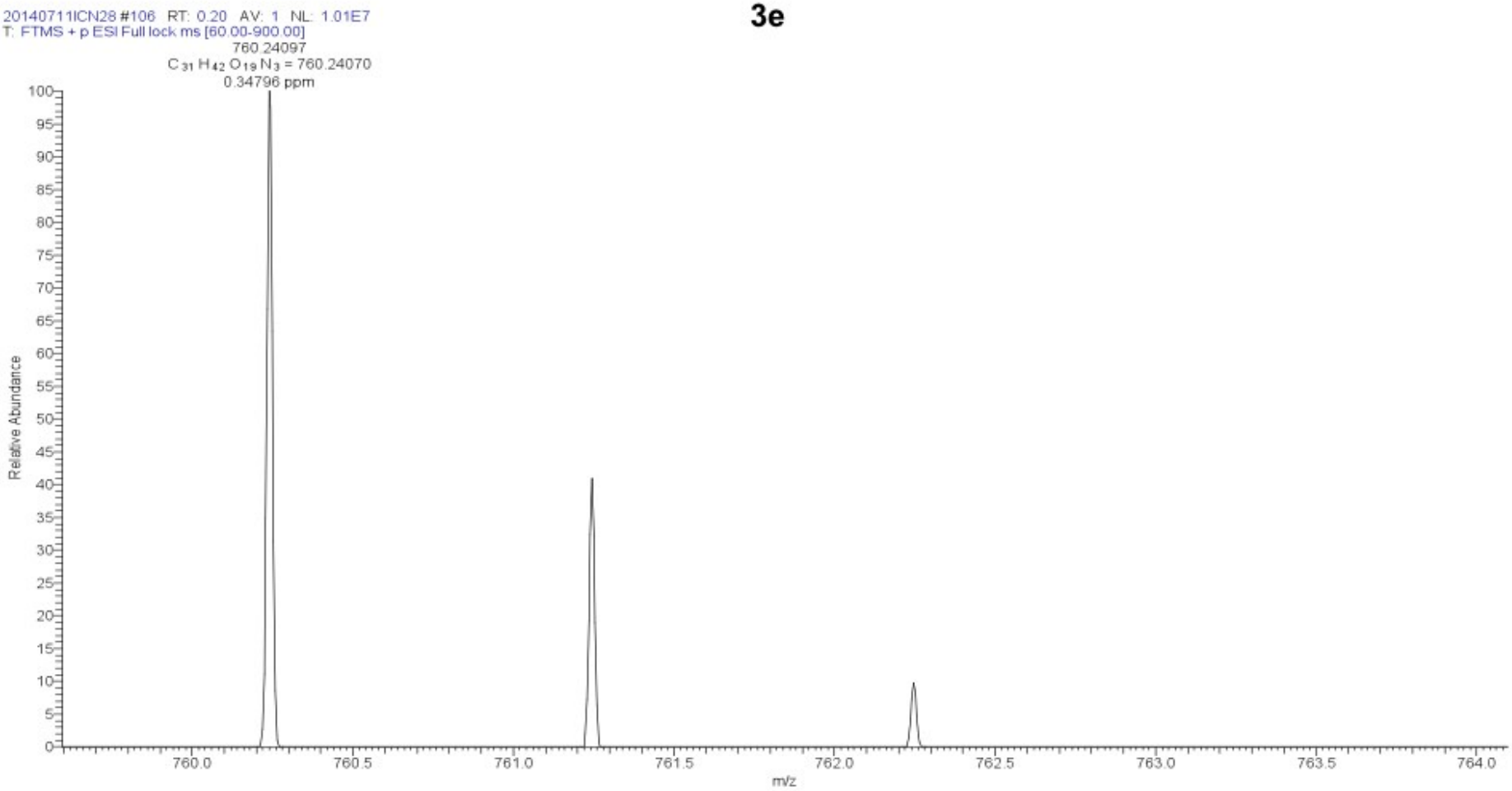
3c


20140711ICN18_141107151605 #151 RT: 0.28 AV: 1 NL: 1.80E9
T: FTMS + p ESI Full ms [60.00-900.00]
482.12308
C 20 H 24 O 9 N 3 S = 482.12278
0.62427 ppm
Relative Abundance
m/z
481.0
481.5
482.0
482.5
483.0
483.5
484.0
484.5

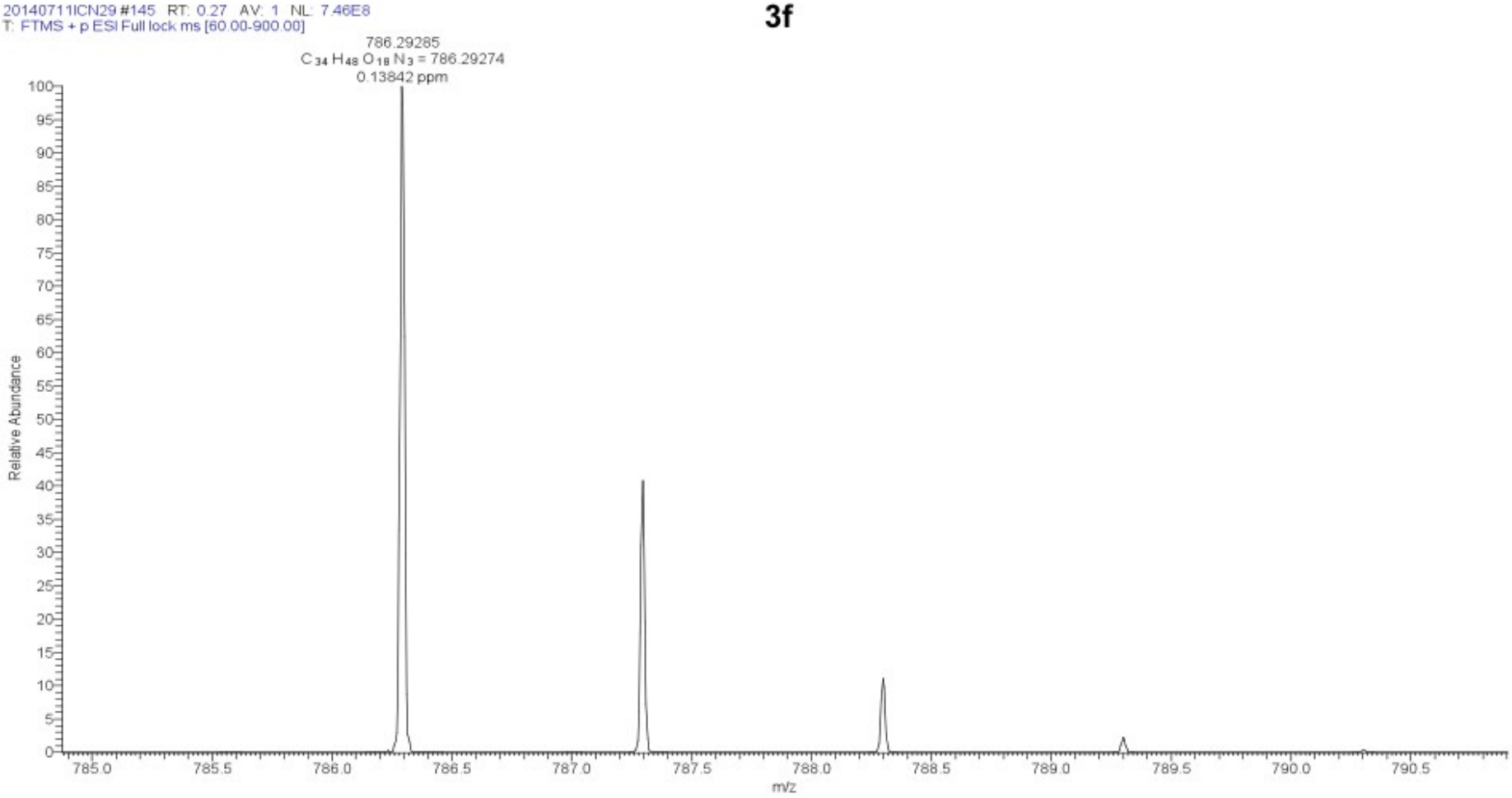
3d


20140711ICN26 #127 RT: 0.24 AV: 1 NL: 2.13E8
T: FTMS + p ESI Full lock ms [60.00-900.00]
764.25061
C 34 H 42 O 17 N 3 = 764.25087
-0.34375 ppm
Relative Abundance
m/z
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
763.0
763.5
764.0
764.5
765.0
765.5
766.0
766.5
767.0
767.5
768.0
768.5

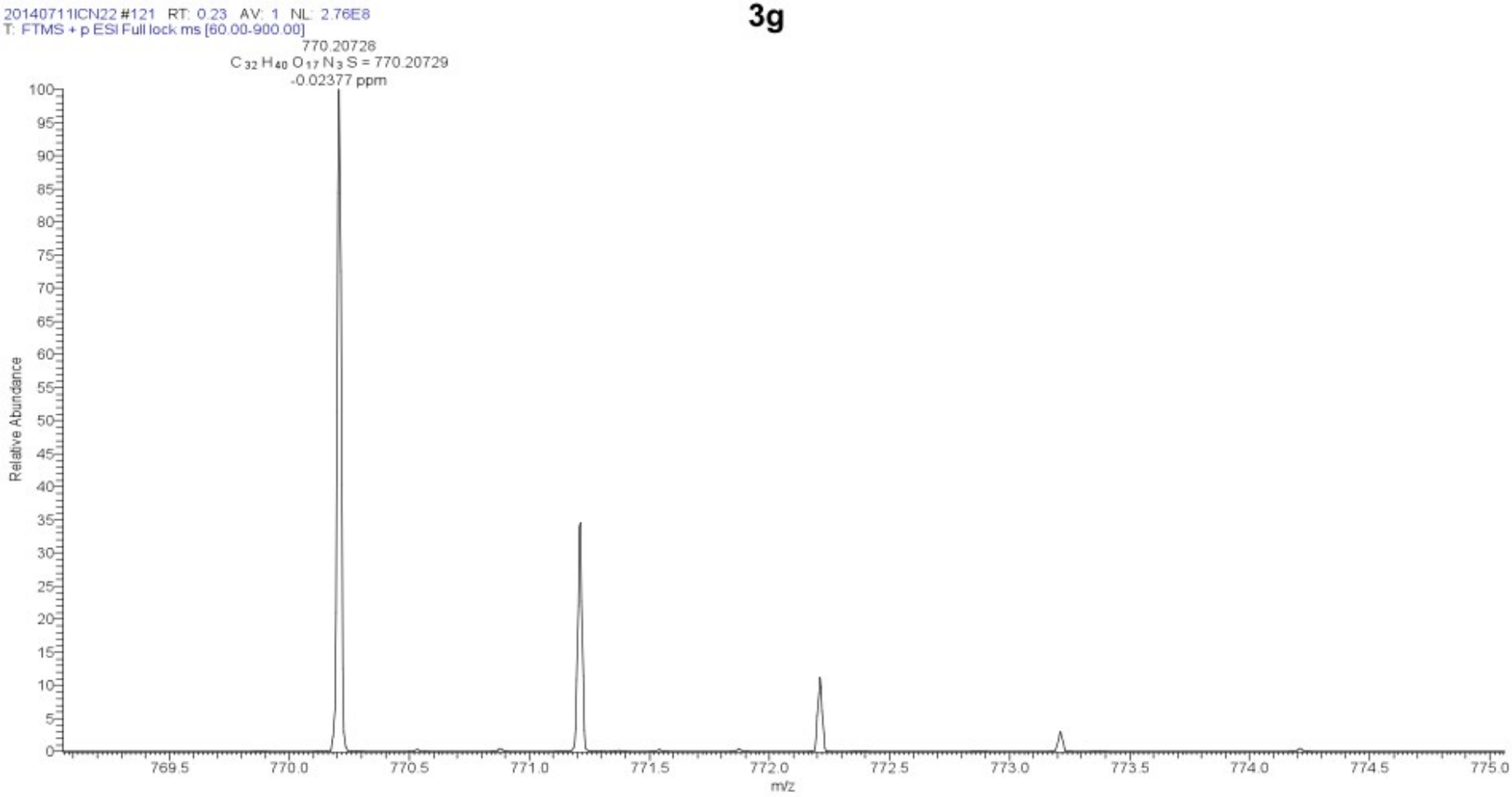
3e


20140711ICN28 #106 RT: 0.20 AV: 1 NL: 1.01E7
T: FTMS + p ESI Full lock ms [60.00-900.00]
760.24097
C31 H42 O19 N3 = 760.24070
0.34796 ppm
Relative Abundance
m/z
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
760.0
760.5
761.0
761.5
762.0
762.5
763.0
763.5
764.0

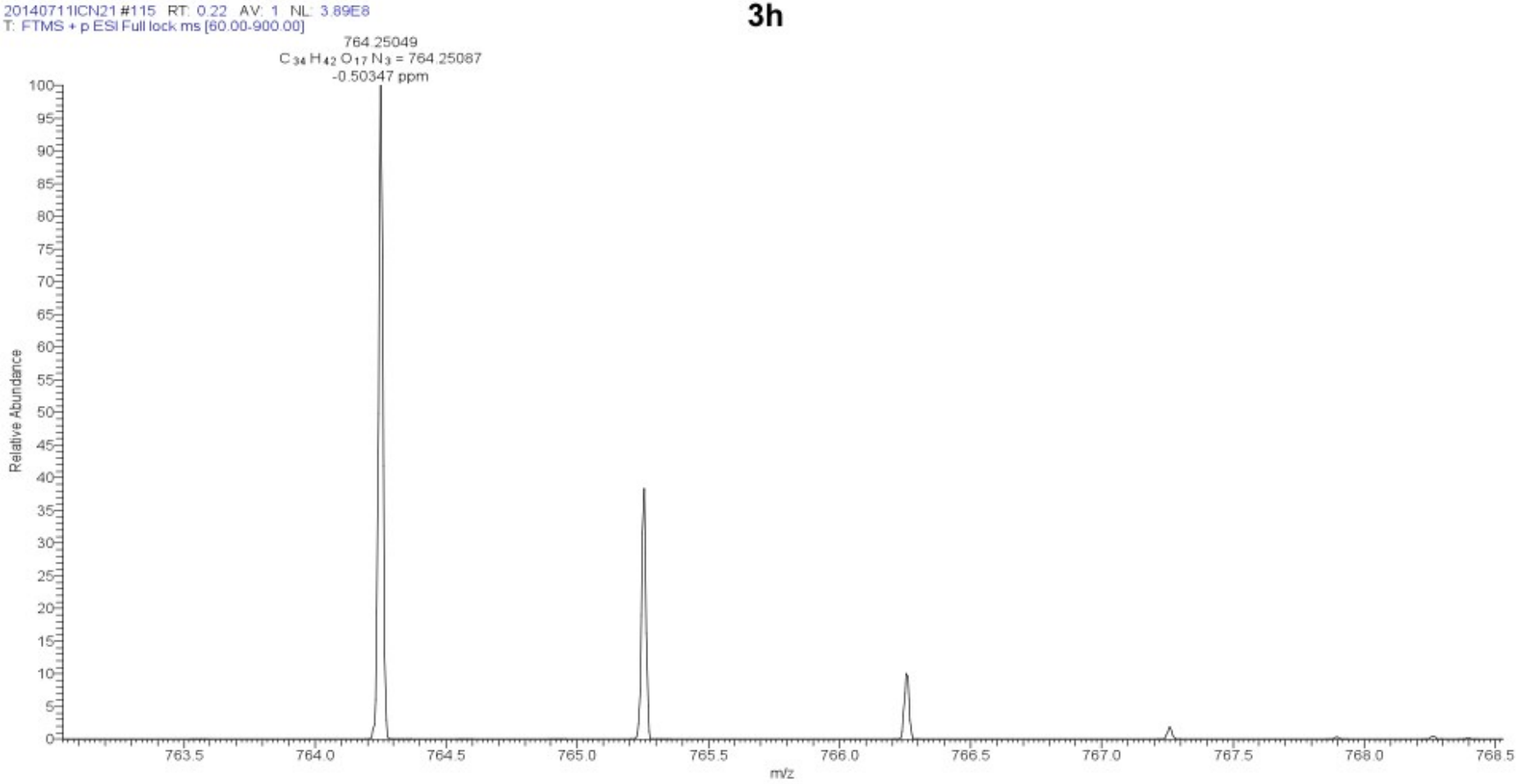
3f


20140711ICN29 #145 RT: 0.27 AV: 1 NL: 7.46E8
T: FTMS + p ESI Full lock ms [60.00-900.00]
786.29285
C 34 H 48 O 18 N 3 = 786.29274
0.13842 ppm
Relative Abundance
m/z
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
785.0
785.5
786.0
786.5
787.0
787.5
788.0
788.5
789.0
789.5
790.0
790.5

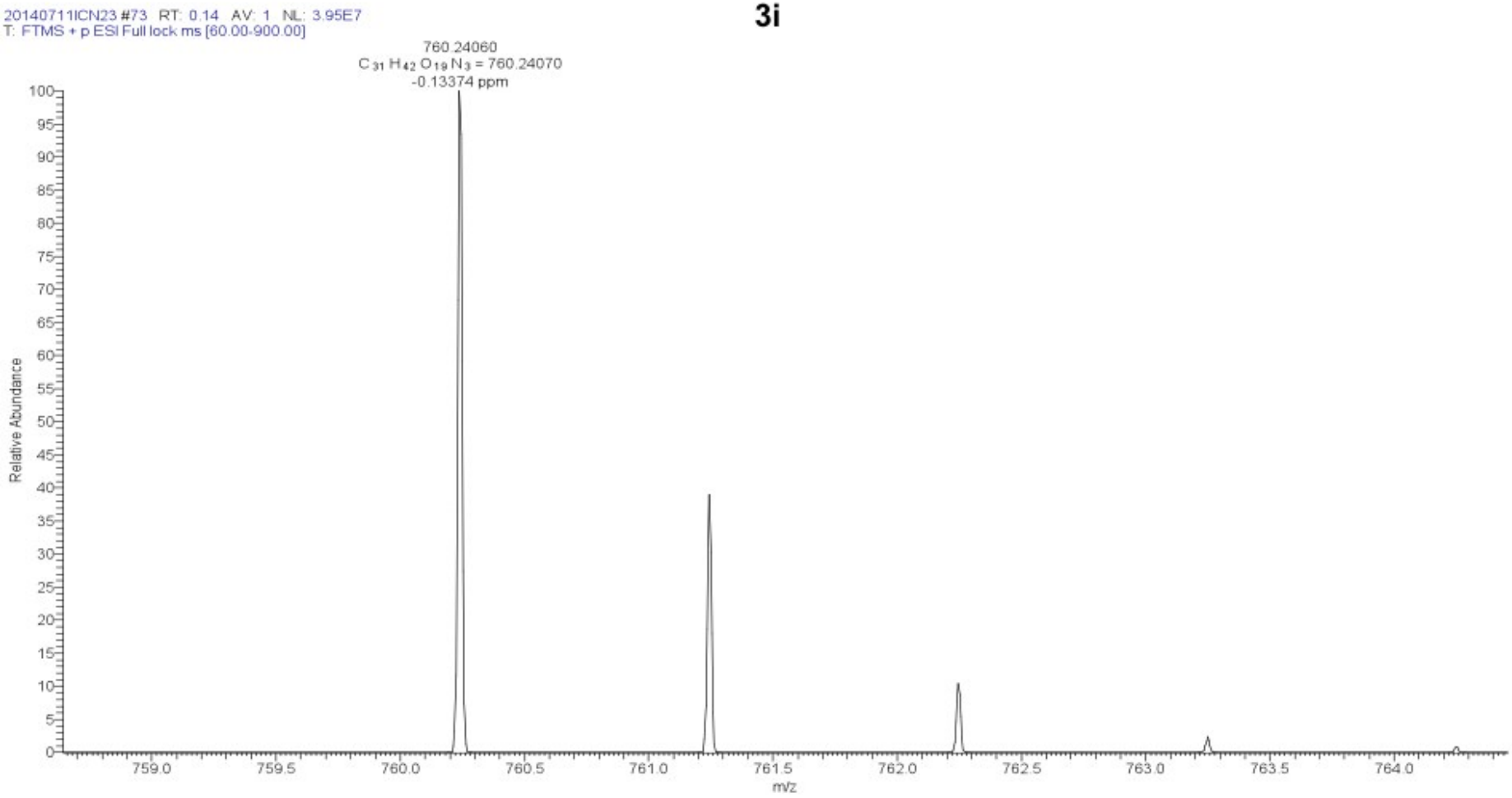
3g


20140711ICN22 #121 RT: 0.23 AV: 1 NL: 2.76E8
T: FTMS + p ESI Full lock ms [60.00-900.00]
770.20726
C 32 H 40 O 17 N 3 S = 770.20729
-0.02377 ppm
Relative Abundance
m/z
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
769.5
770.0
770.5
771.0
771.5
772.0
772.5
773.0
773.5
774.0
774.5
775.0

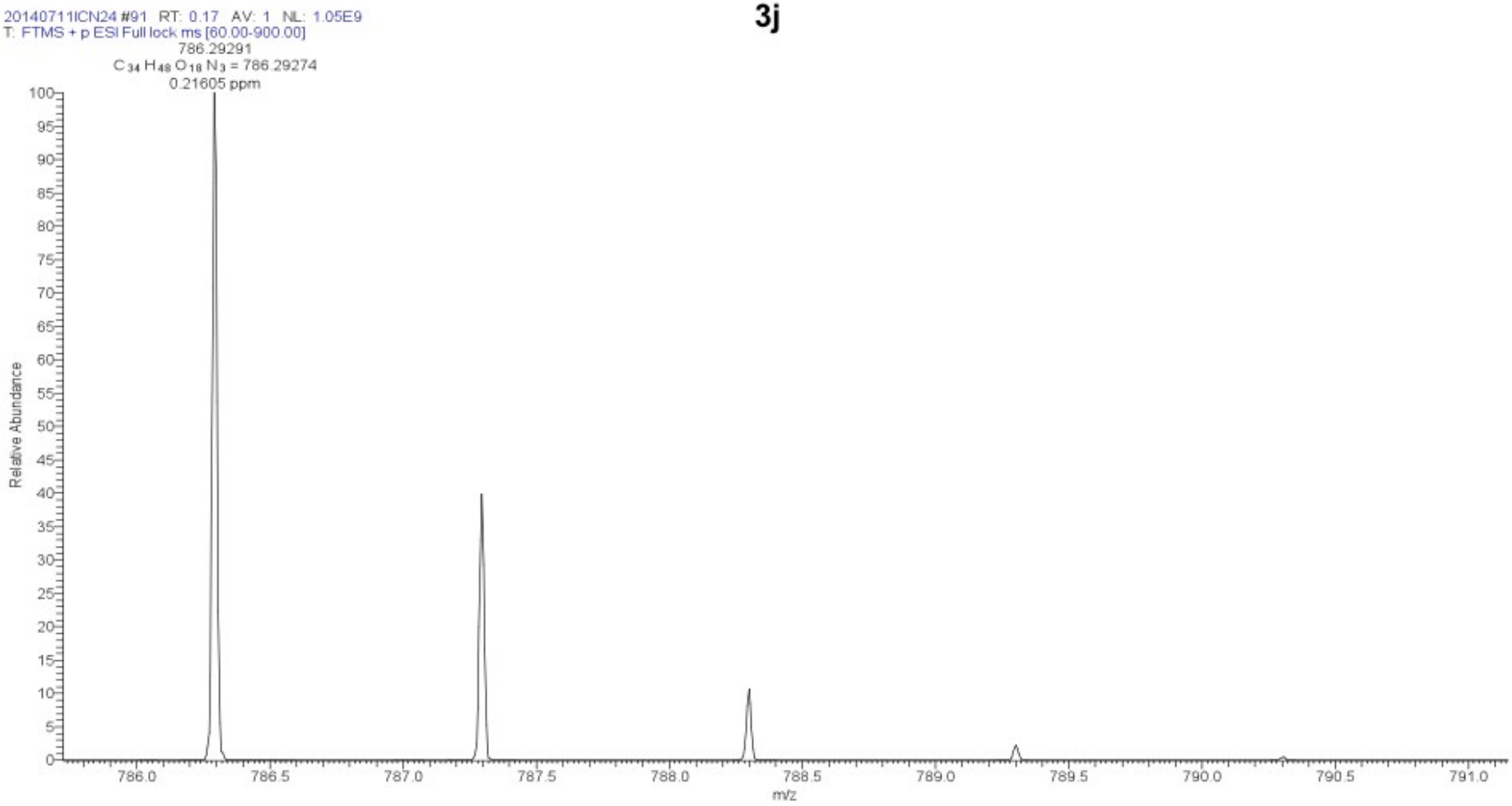
3h


20140711ICN21 #115 RT: 0.22 AV: 1 NL: 3.89E8
T: FTMS + p ESI Full lock ms [60.00-900.00]
764.25049
C34 H42 O17 N3 = 764.25087
-0.50347 ppm
Relative Abundance
m/z
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
763.5
764.0
764.5
765.0
765.5
766.0
766.5
767.0
767.5
768.0
768.5

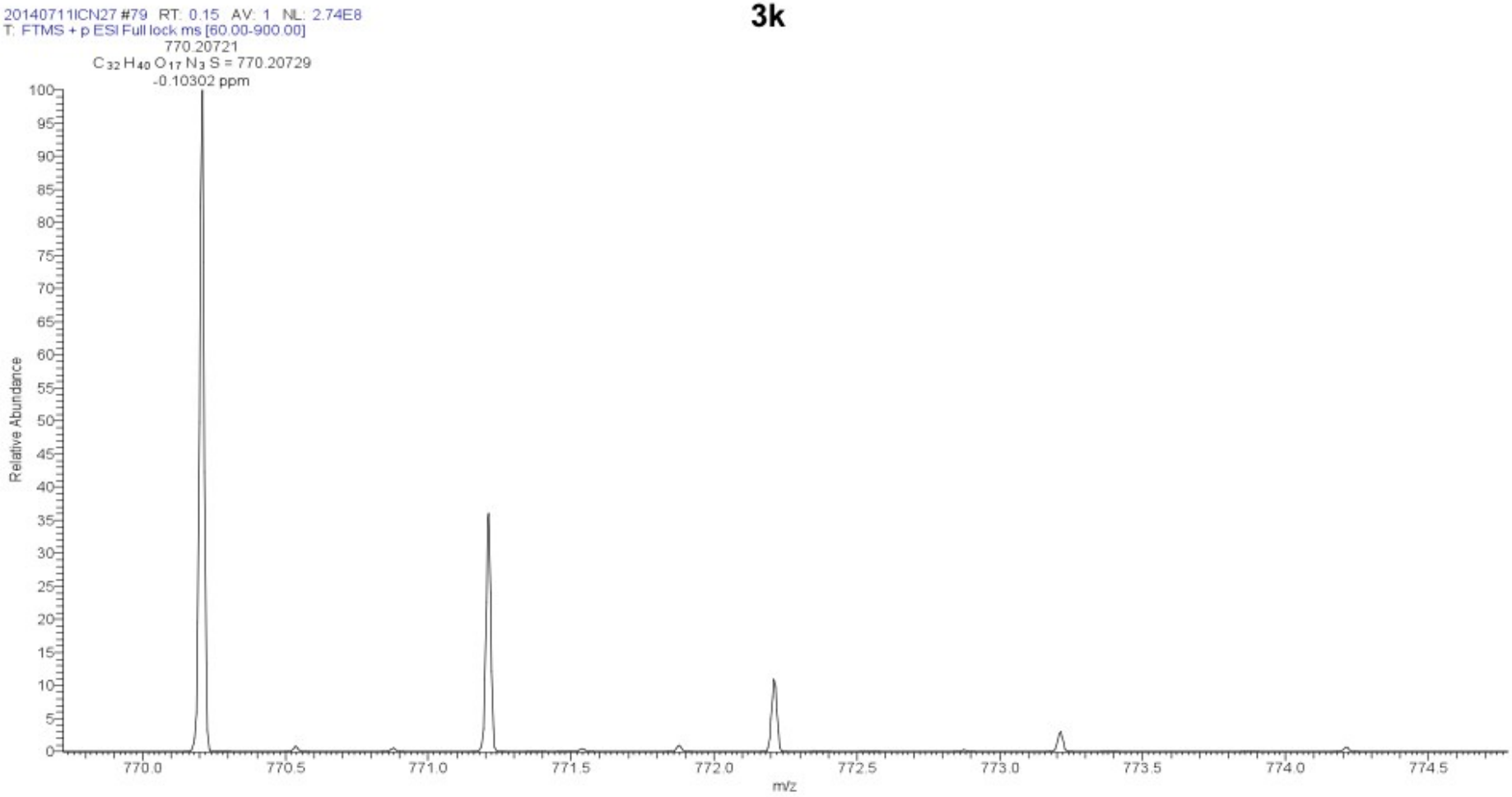
3i


20140711ICN23 #73 RT: 0.14 AV: 1 NL: 3.95E7
T: FTMS + p ESI Full lock ms [60.00-900.00]
760.24060
C 31 H 42 O 19 N 3 = 760.24070
-0.13374 ppm
Relative Abundance
m/z
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
759.0
759.5
760.0
760.5
761.0
761.5
762.0
762.5
763.0
763.5
764.0

3j


20140711ICN24 #91 RT: 0.17 AV: 1 NL: 1.05E9
T: FTMS + p ESI Full lock ms [60.00-900.00]
786.29291
C34 H48 O18 N3 = 786.29274
0.21605 ppm
Relative Abundance
m/z
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
786.0
786.5
787.0
787.5
788.0
788.5
789.0
789.5
790.0
790.5
791.0

3k


20140711ICN27 #79 RT: 0.15 AV: 1 NL: 2.74E8
T: FTMS + p ESI Full lock ms [60.00-900.00]
770.20721
C 32 H 40 O 17 N 3 S = 770.20729
-0.10302 ppm
Relative Abundance
m/z
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
770.0
770.5
771.0
771.5
772.0
772.5
773.0
773.5
774.0
774.5