# Experimental Supporting Information

## Organic Dye Catalyzed, Visible-Light Photoredox Bromination of Arenes and Heteroarenes using N-Bromosuccinimide

David A. Rogers, Roxanne G. Brown, Zachary C. Brandeburg, Eric Y. Ko, Megan D. Hopkins, Gabriel LeBlanc and Angus A. Lamar*

Department of Chemistry and Biochemistry, The University of Tulsa, 800 S. Tucker Dr., Tulsa, OK 74104, USA.

angus-lamar@utulsa.edu

Index



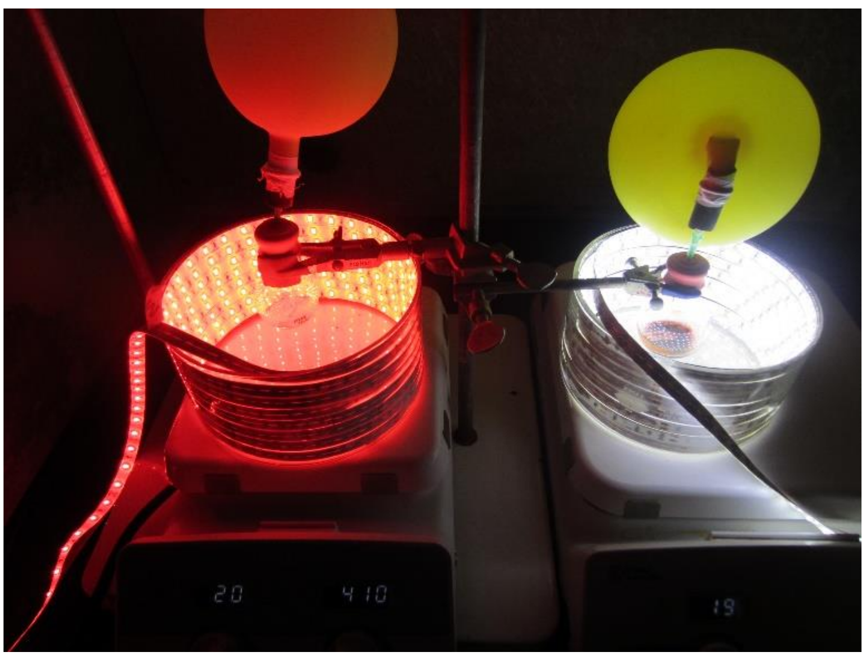


**Figure S1.** On the left – A red LED strip (620 nm) light bath reaction vessel

On the right – A white LED strip (cool white) light bath reaction vessel

Photocatalytic reactions were performed in a light bath which was constructed in our laboratory similar to our previous reports as follows.[1-3] Waterproof 5050 LED strips (12V with power adapter, 18 LEDs/foot, approximately 0.24 Watt per LED – 72 Watt per strip) are coiled around the interior of evaporating dish (170mm x 90mm) using the adhesive backing of the LED strip. A Petri dish (150 x 20 mm) is placed upside down at the bottom of the dish to serve as an elevated glass "floor" to ensure that a round-bottom flask receives maximum light exposure. The temperature inside the dish is monitored and is generally maintained (air-cooled) between 19-22 $^{o}C$ (the temperature has not been observed above 25 $^{o}C$).

## Methods for electrochemical experiments

Electrochemical experiments were performed using a BioLogic SP-200 Potentiostat using a platinum disk working electrode, a platinum mesh counter electrode, and a silver wire as the quasi-reference electrode. The electrolyte consisted of 0.25 mM erythrosine B and 100 mM tetrabutylammonium hexafluorophosphate in acetonitrile. In some experiments, 1 mM ferrocene was used as an internal standard, as well as for calibration of the quasi-reference electrode. The ferrocene formal potential was found to be 0.477 V vs the silver wire quasi-reference electrode. Cyclic voltammetry was performed using a scan rate of 500 mV/s.

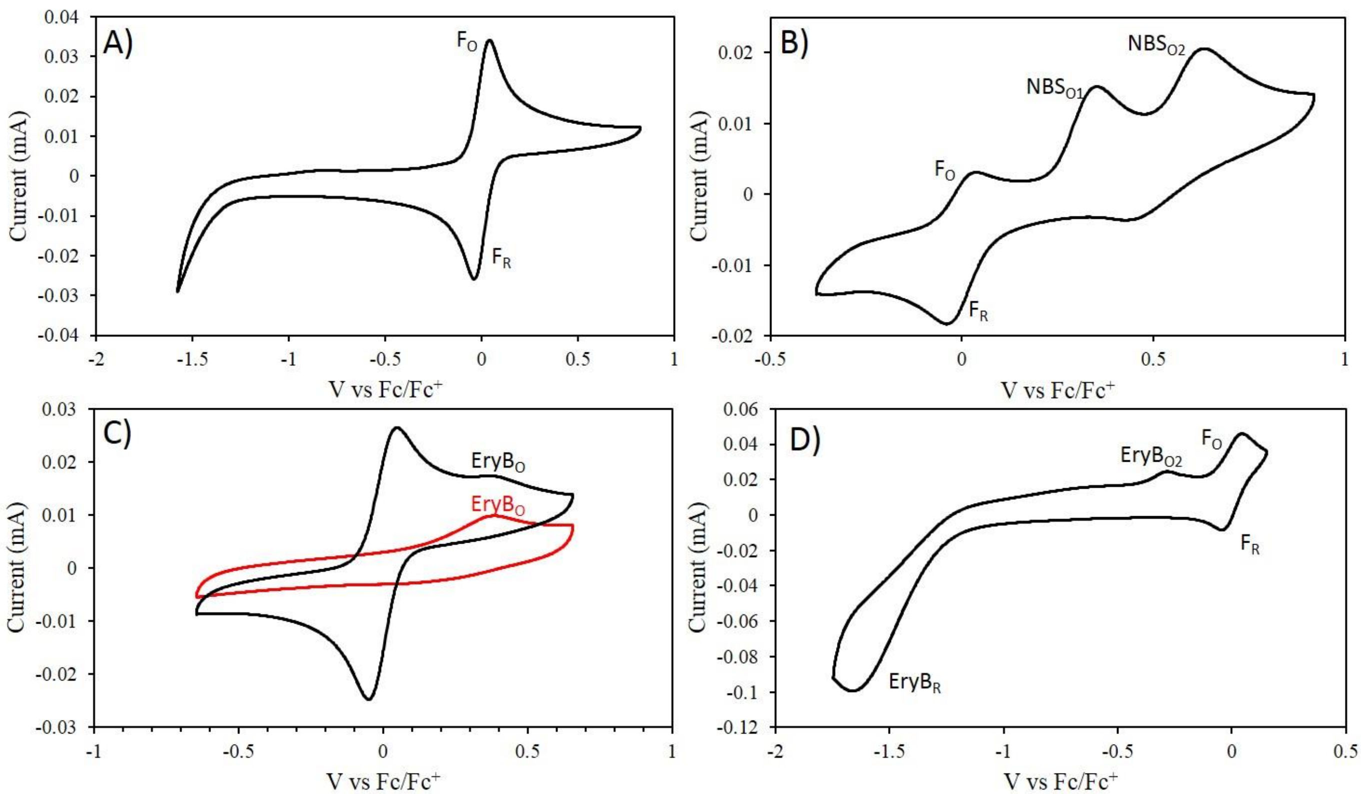



**Figure S2.** Cyclic voltammograms of (A) ferrocene, (B) NBS with ferrocene, (C) Ery B with (black) and without (red) ferrocene, and (D) Ery B with ferrocene using a platinum disk working electrode. Major redox peaks have been labeled as oxidation ($_O$) or reduction ($_R$) along with an abbreviation for the chemical entity. Formal potentials for irreversible electrochemical behavior were estimated using the half-wave potential. Note that the oxidation peak observed in (D), labeled EryB$_{O2}$, only appears after a reducing potential (below -1V vs Fc/Fc$^+$) has been reached and is therefore not an oxidation of the ground state Ery B.

*1-Bromonaphthalene* (**3**)

The title compound was quantified using gas chromatography with adamantane as an internal standard. A standard curve of 1-bromonaphthalene (Figure S3) was prepared in 5 separate reaction vessels by adding varying amounts of 1-bromonaphthalene (between 0 and 0.25 mmol) to 3 mL of acetonitrile. To each of the 3 mL acetonitrile solutions was added 8 mL of hexanes and 0.156 mmol (20 mg) of adamantane. The acetonitrile solution was extracted with the hexanes, and 1 mL of the hexanes portion was removed for gas chromatography injection. Gas chromatography was performed using a Shimadzu GC-2010 Plus with GCMS-QP2010 with a Restek Rtx-5MS capillary column (30m; 0.25 mmID; 0.25 um df; Crossbond – 5% diphenyl/95% dimethyl pilosiloxane). The GC method was as follows: 40 °C for 5 minutes, then increase at 10 °C/minute for 16 minutes (up to 200 °C). 200 °C is maintained for 10 additional minutes. As seen in Figure S4, 1-Bromonaphthalene is observed at 16.8 minutes, and confirmed by MS (EI) *m/z* 206 and 208 ($M^+$ 1:1 ratio; 50% rel. intensity) 127 (100% rel. intensity) 63 (90% rel. intensity).

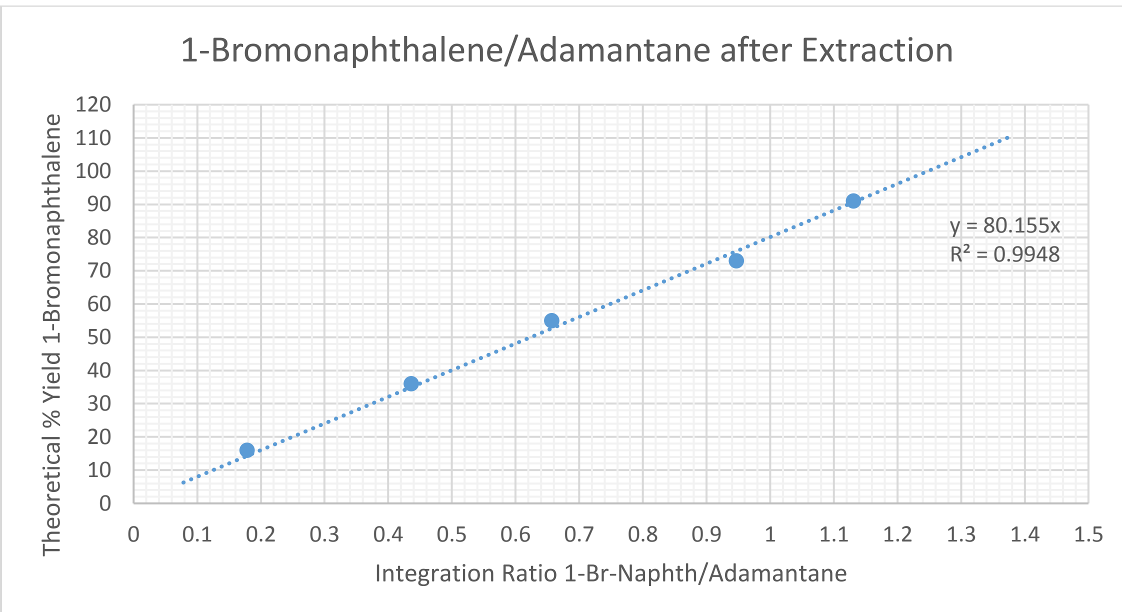



**Figure S3.** Standard curve of 1-bromonaphthalene versus internal standard (adamantane)

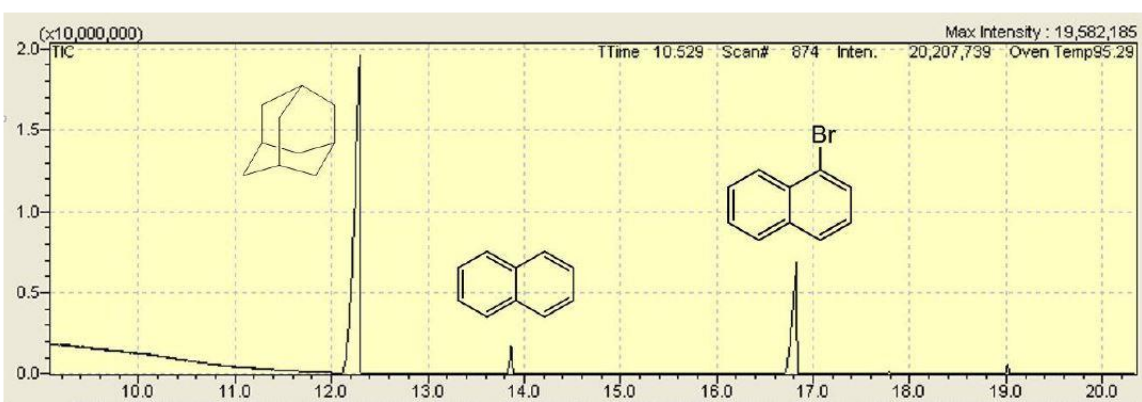


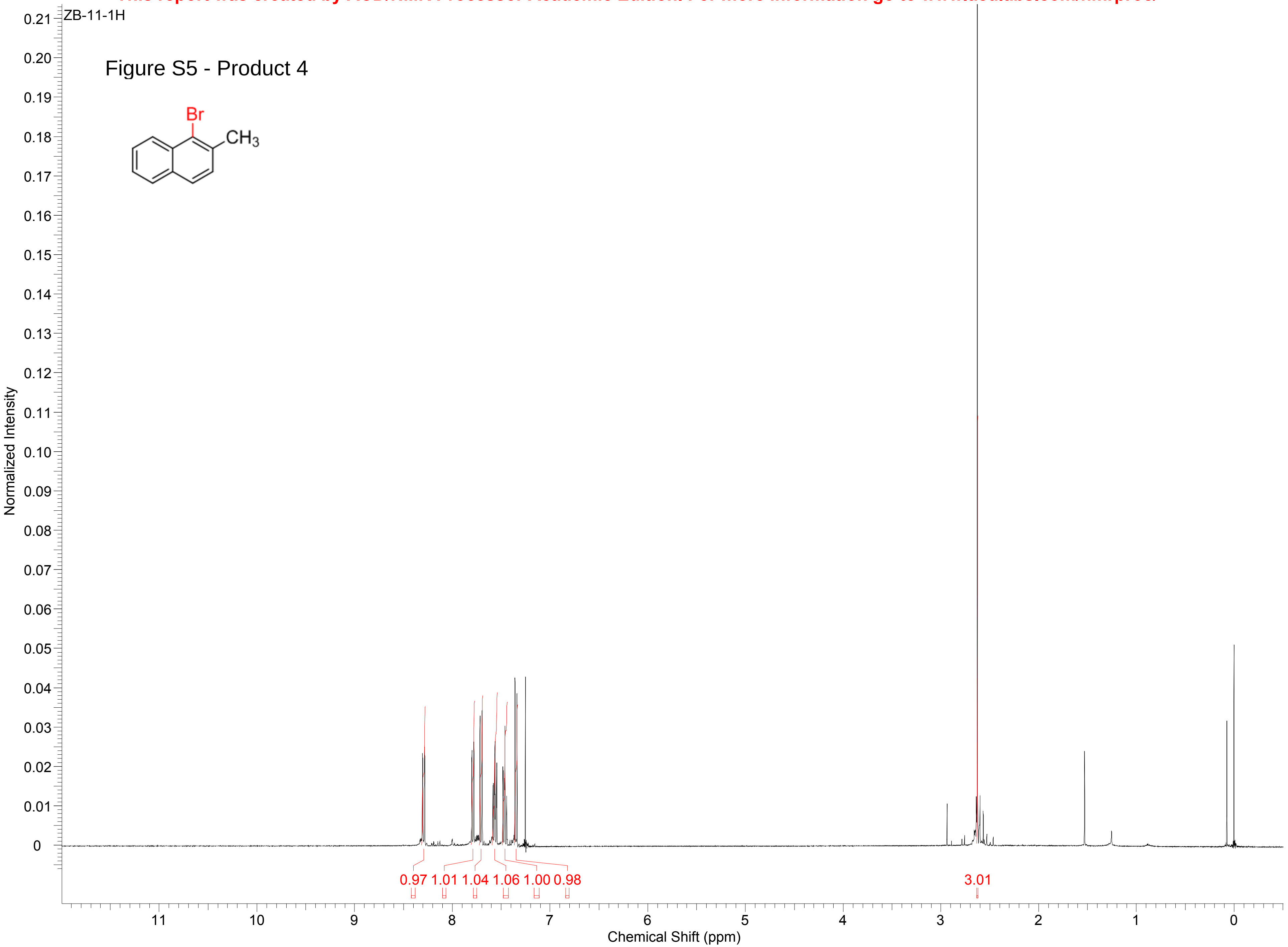

**Figure S4.** Expanded view of a typical GCMS chromatogram.

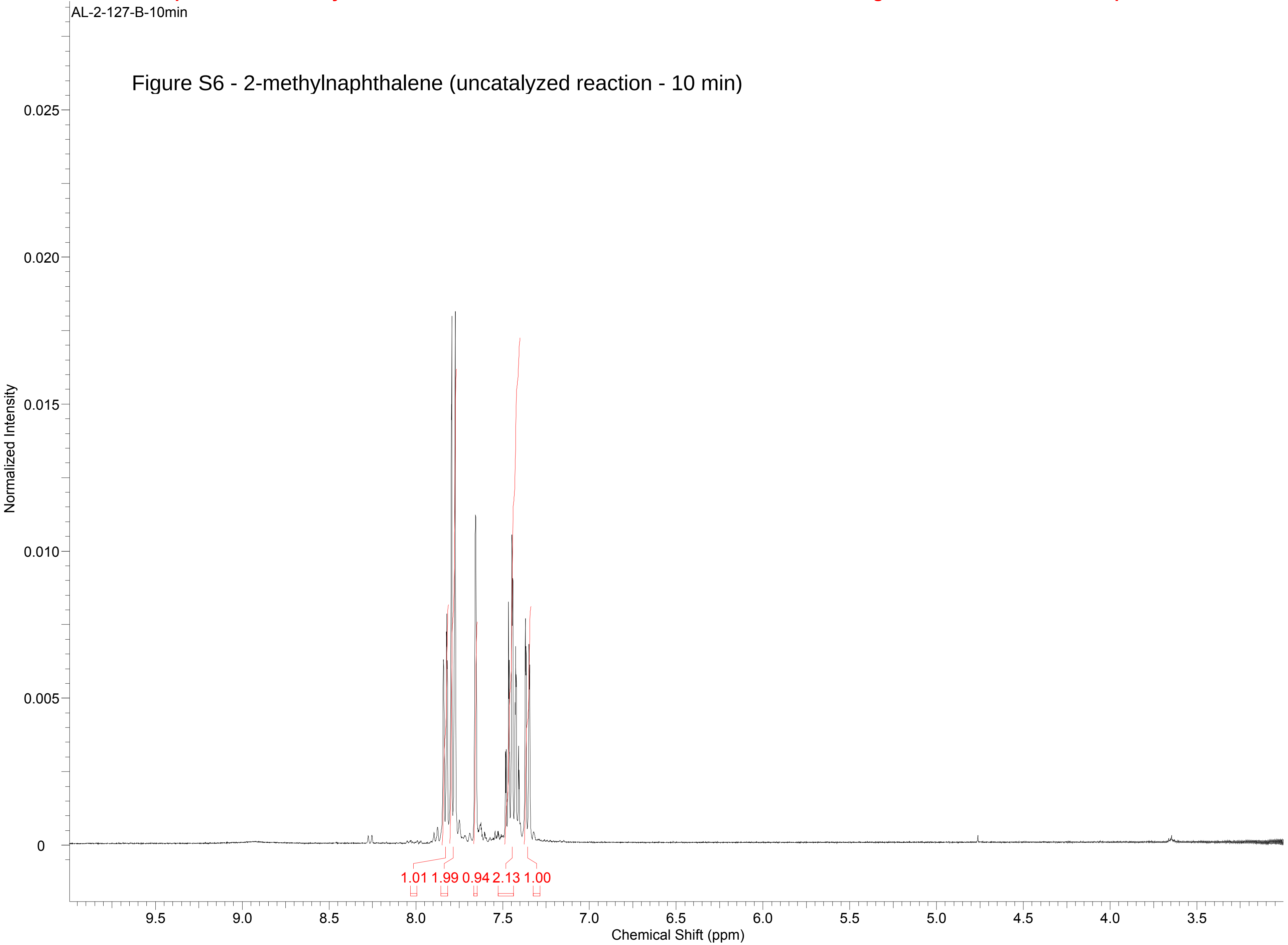
### *1-Bromo-4-methoxybenzene* (**5**)

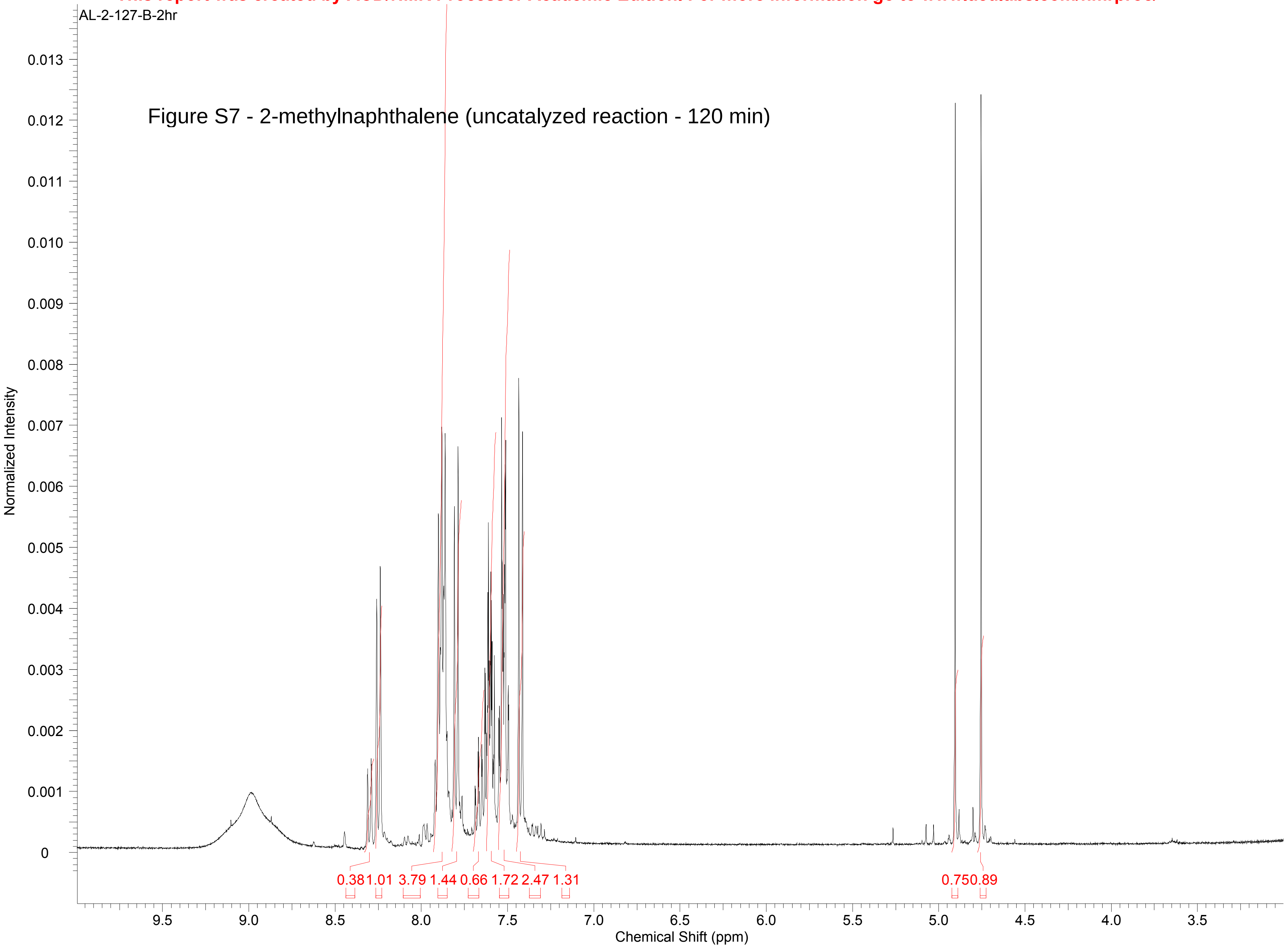
The title compound was observed by $^{1}$H NMR and compared to a reported spectrum.[4] One equivalent of nitrobenzene was added as internal standard at the conclusion of the reaction time period. The $^{1}$H NMR spectrum is included within this supporting information document (Figure S10).

References:

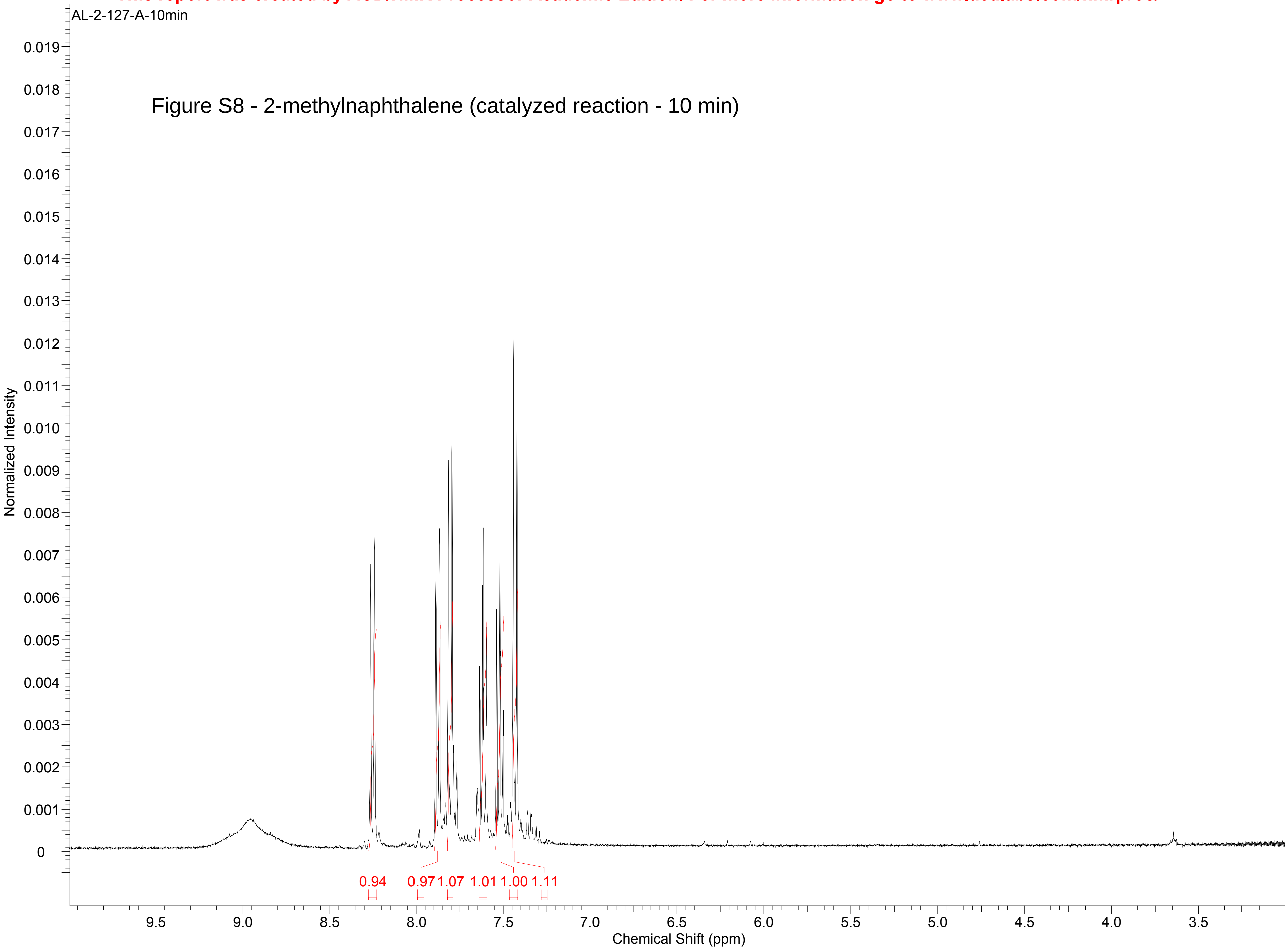

1. Brueckner, A. C.; Hancock, E. N.; Anders, E. J.; Tierney, M. M.; Morgan, H. R.; Scott, K. A.; Lamar, A. A., Visible-light-mediated, nitrogen-centered radical amination of tertiary alkyl halides under metal-free conditions to form [α]-tertiary amines. *Organic & biomolecular chemistry* **2016,** *14* (19), 4387-4392.
2. Hopkins, M. D.; Scott, K. A.; DeMier, B. C.; Morgan, H. R.; Macgruder, J. A.; Lamar, A. A., Formation of N-sulfonyl imines from iminoiodinanes by iodine-promoted, N-centered radical sulfonamidation of aldehydes. *Organic & biomolecular chemistry* **2017,** *15* (43), 9209-9216.
3. Hopkins, M.; Brandeburg, Z.; Hanson, A.; Lamar, A., Visible-Light, Iodine-Promoted Formation of N-Sulfonyl Imines and N-Alkylsulfonamides from Aldehydes and Hypervalent Iodine Reagents. *Molecules* **2018,** *23* (8), 1838.
4. Braddock, D. C.; Cansell, G.; Hermitage, S. A., (Diacetoxyiodo)benzene-Lithium Bromide as a Convenient Electrophilic Br+ Source. *Synlett* **2004,** 461-464.

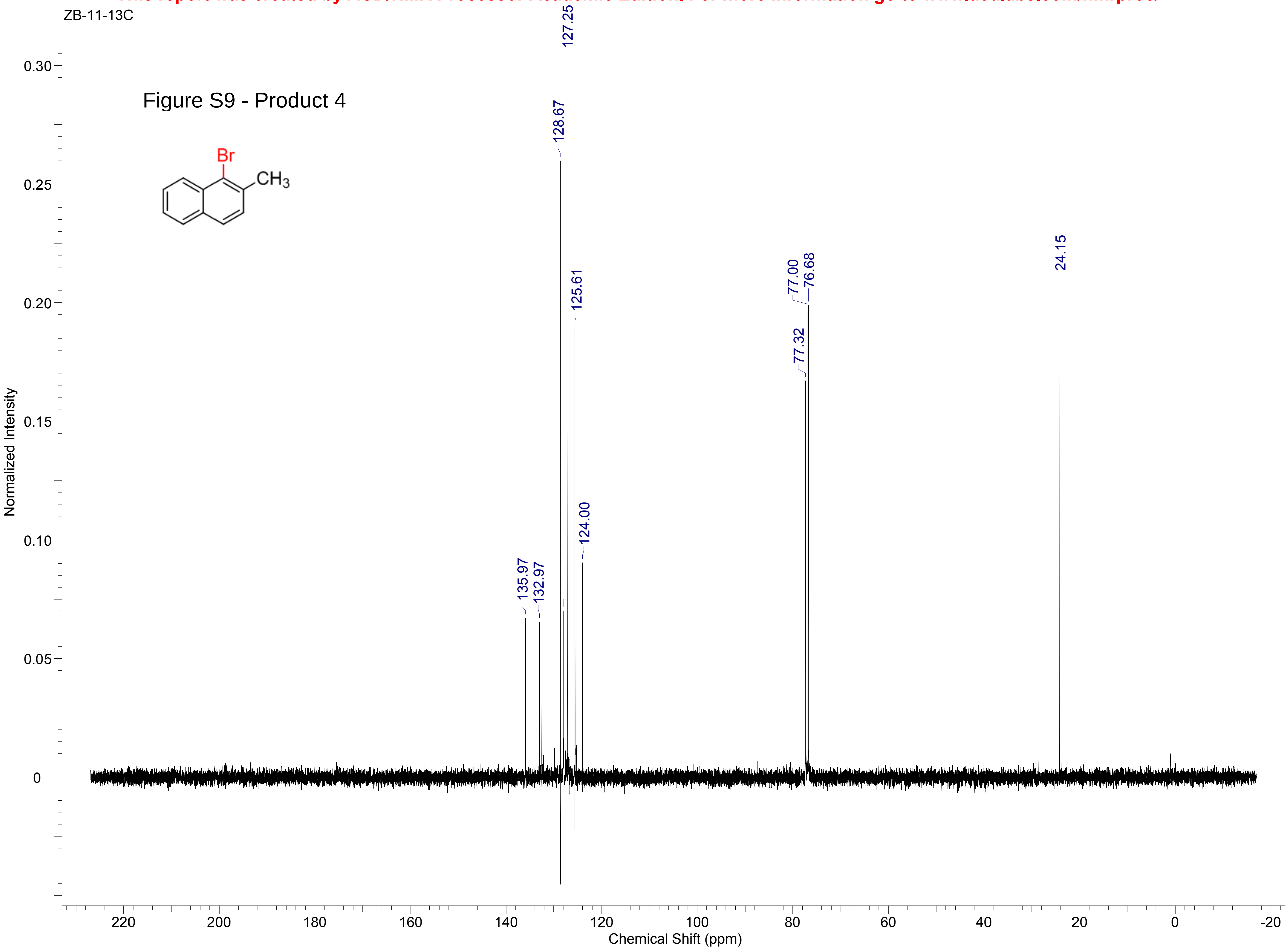

ZB-11-1H
Figure S5 - Product 4
Br
CH3
Normalized Intensity
Chemical Shift (ppm)
0.97 1.01 1.04 1.06 1.00 0.98
3.01

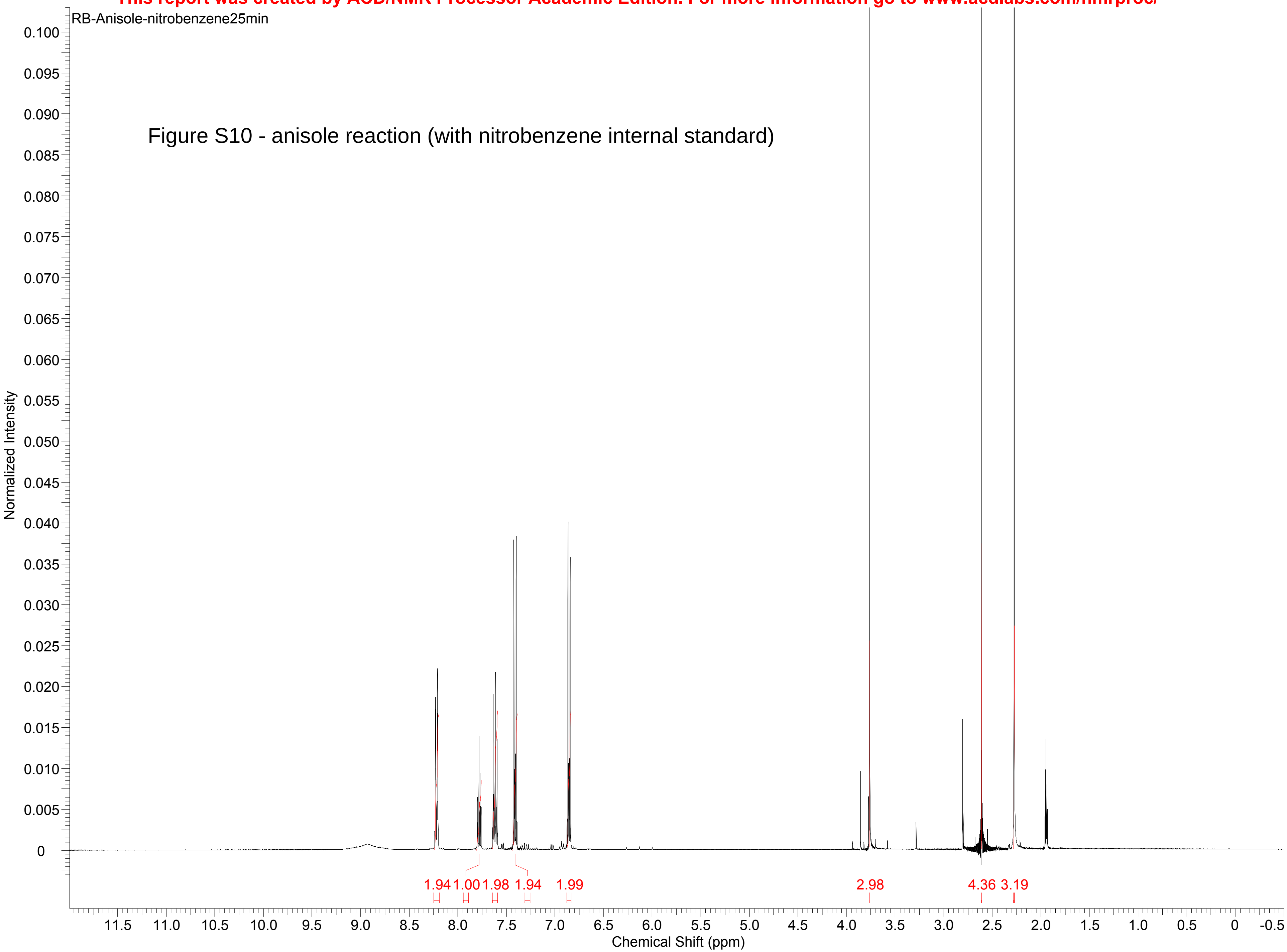

AL-2-127-B-10min
Figure S6 - 2-methylnaphthalene (uncatalyzed reaction - 10 min)
Normalized Intensity
0.025
0.020
0.015
0.010
0.005
0
1.01 1.99 0.94 2.13 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5
Chemical Shift (ppm)

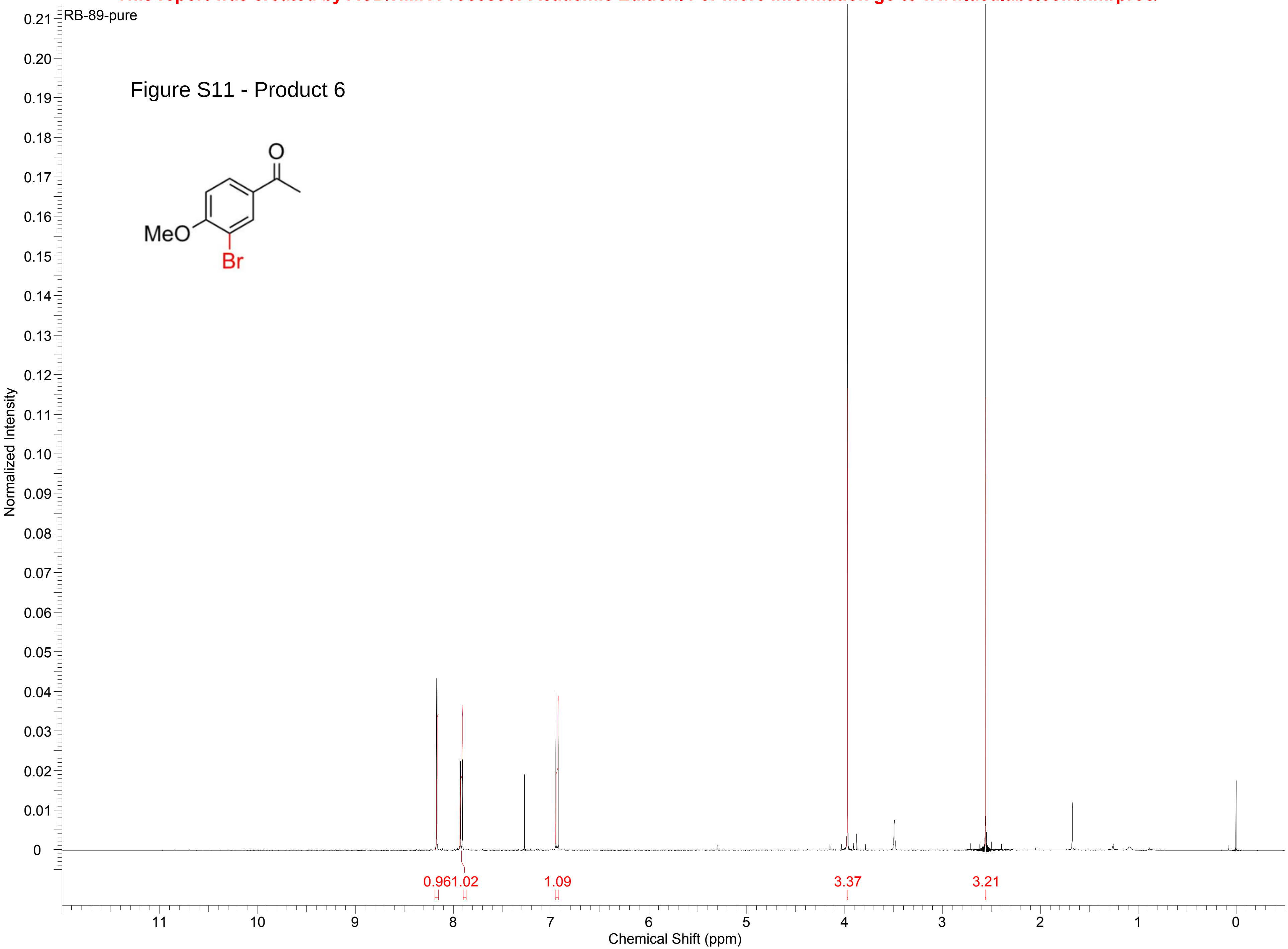


AL-2-127-B-2hr
Figure S7 - 2-methylnaphthalene (uncatalyzed reaction - 120 min)
Normalized Intensity
0.013
0.012
0.011
0.010
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
0.38
1.01
3.79
1.44
0.66
1.72
2.47
1.31
0.75
0.89
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
Chemical Shift (ppm)

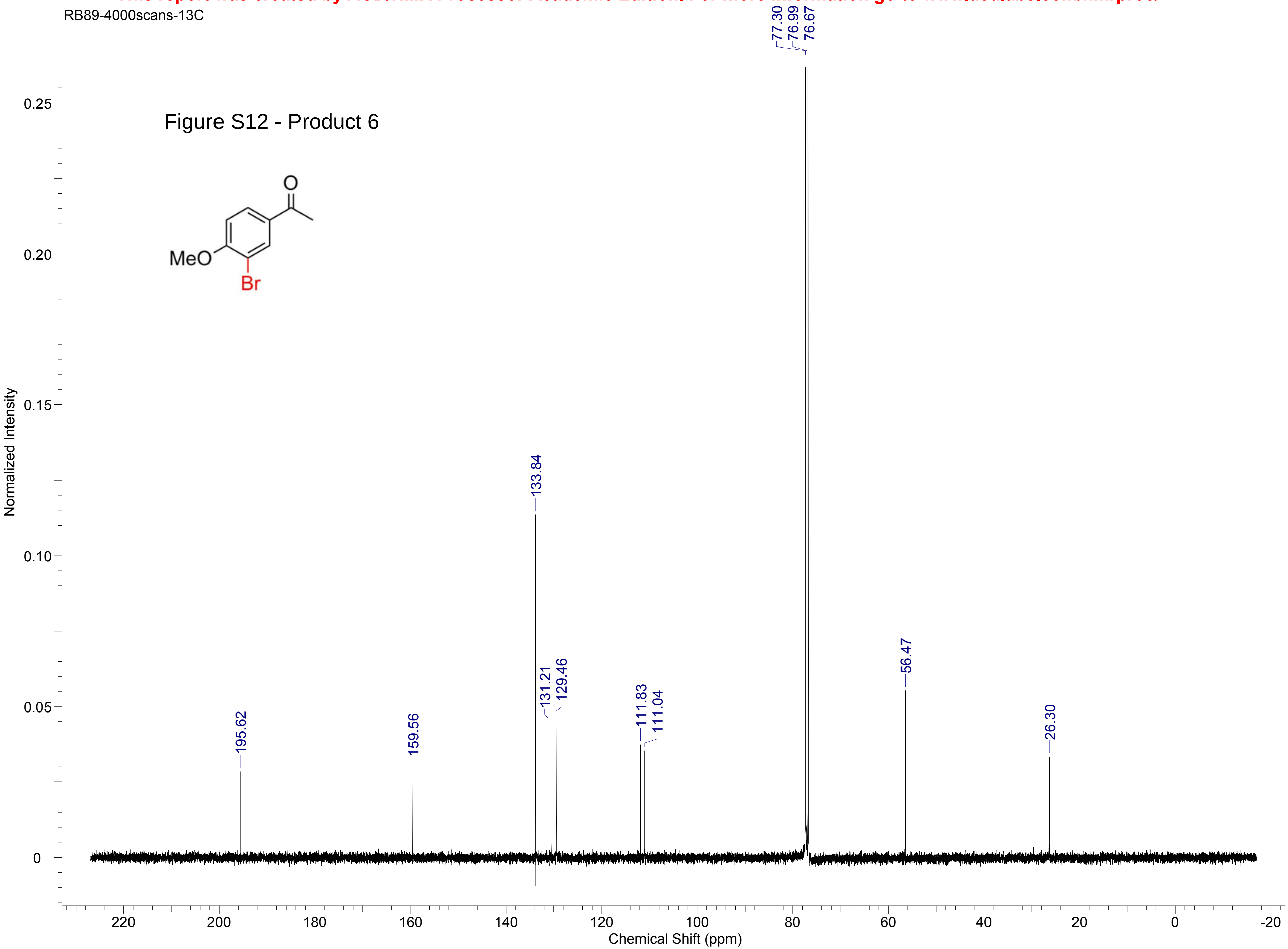

AL-2-127-A-10min
Figure S8 - 2-methylnaphthalene (catalyzed reaction - 10 min)
Normalized Intensity
0.019
0.018
0.017
0.016
0.015
0.014
0.013
0.012
0.011
0.010
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
0.94
0.97
1.07
1.01
1.00
1.11
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
Chemical Shift (ppm)

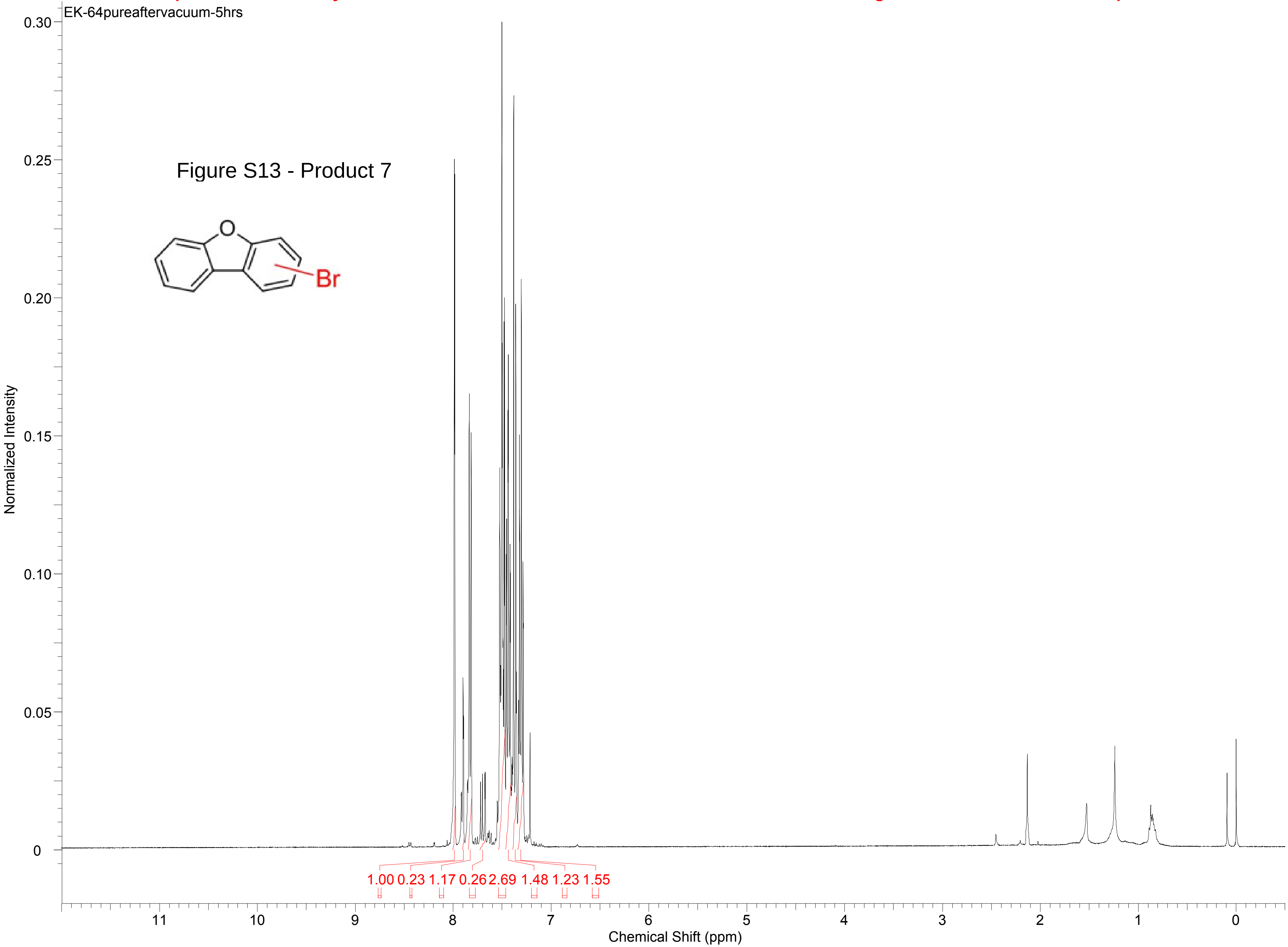

ZB-11-13C
Figure S9 - Product 4
Br
CH3
127.25
128.67
125.61
124.00
135.97
132.97
77.00
76.68
77.32
24.15
Normalized Intensity
0.30
0.25
0.20
0.15
0.10
0.05
0
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

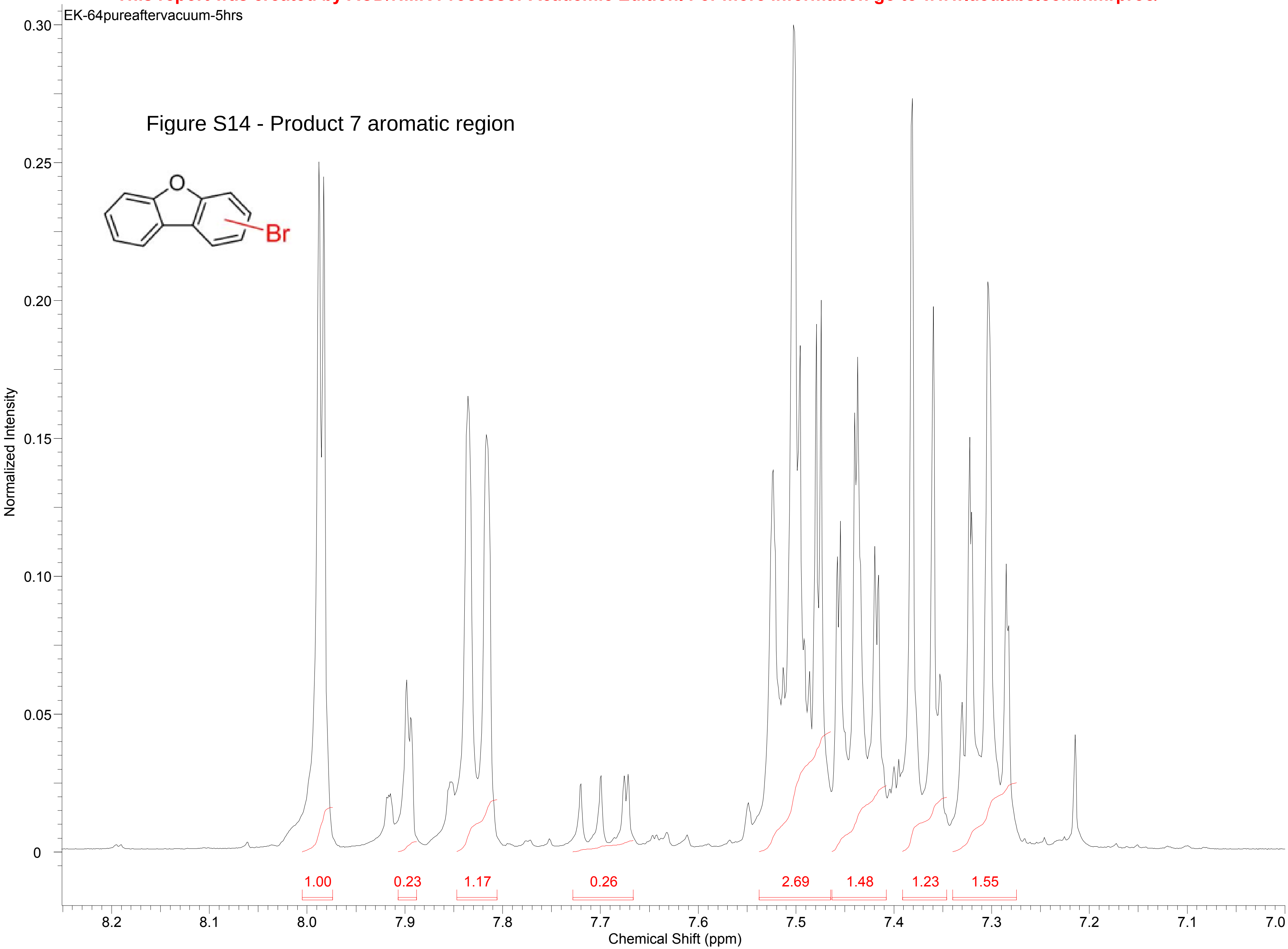

RB-Anisole-nitrobenzene25min
Figure S10 - anisole reaction (with nitrobenzene internal standard)
Normalized Intensity
Chemical Shift (ppm)
1.94 1.00 1.98 1.94 1.99
2.98
4.36 3.19

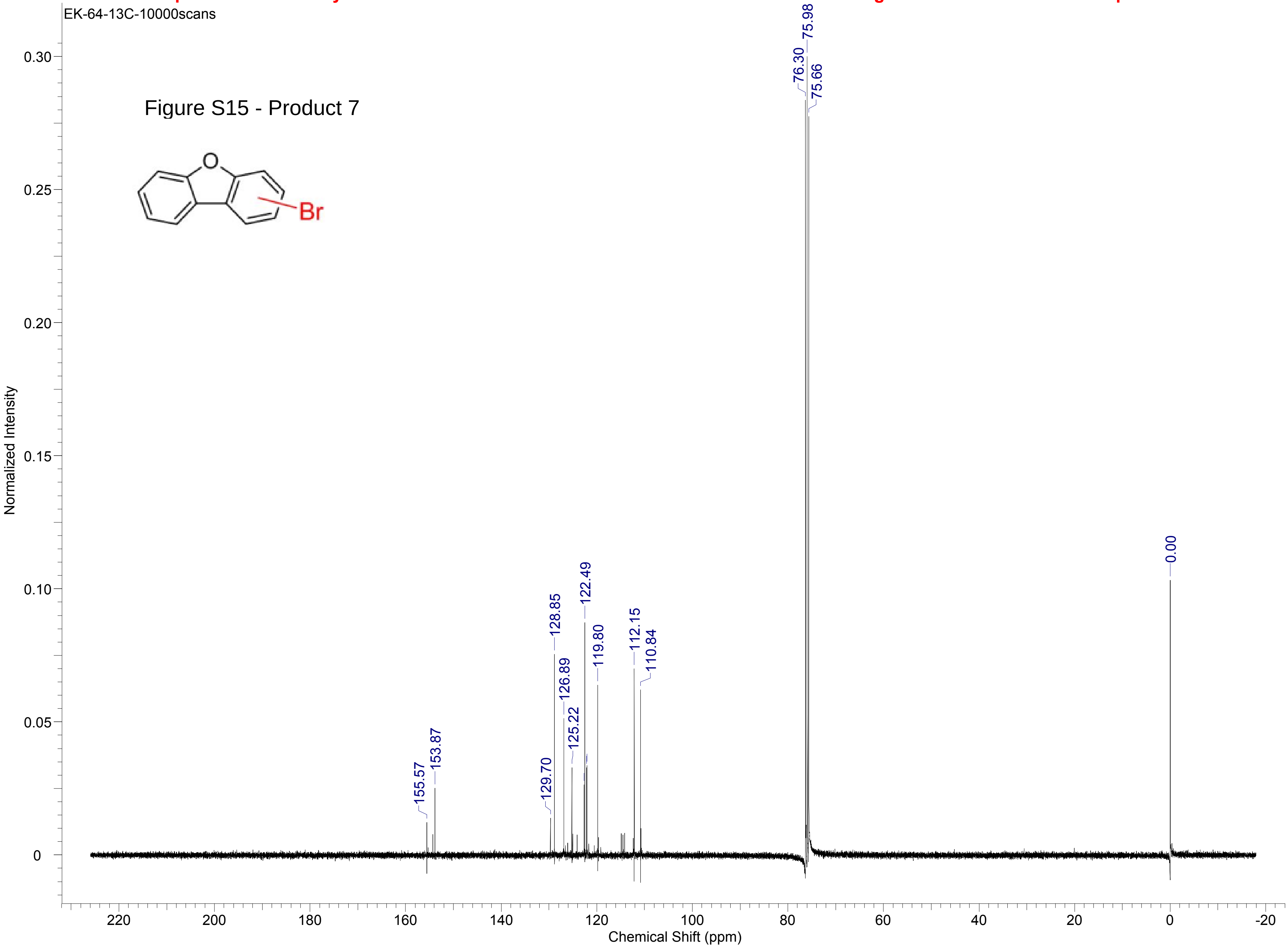

RB-89-pure
Figure S11 - Product 6
O
MeO
Br
Normalized Intensity
0.21
0.20
0.19
0.18
0.17
0.16
0.15
0.14
0.13
0.12
0.11
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0.96
1.02
1.09
3.37
3.21
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

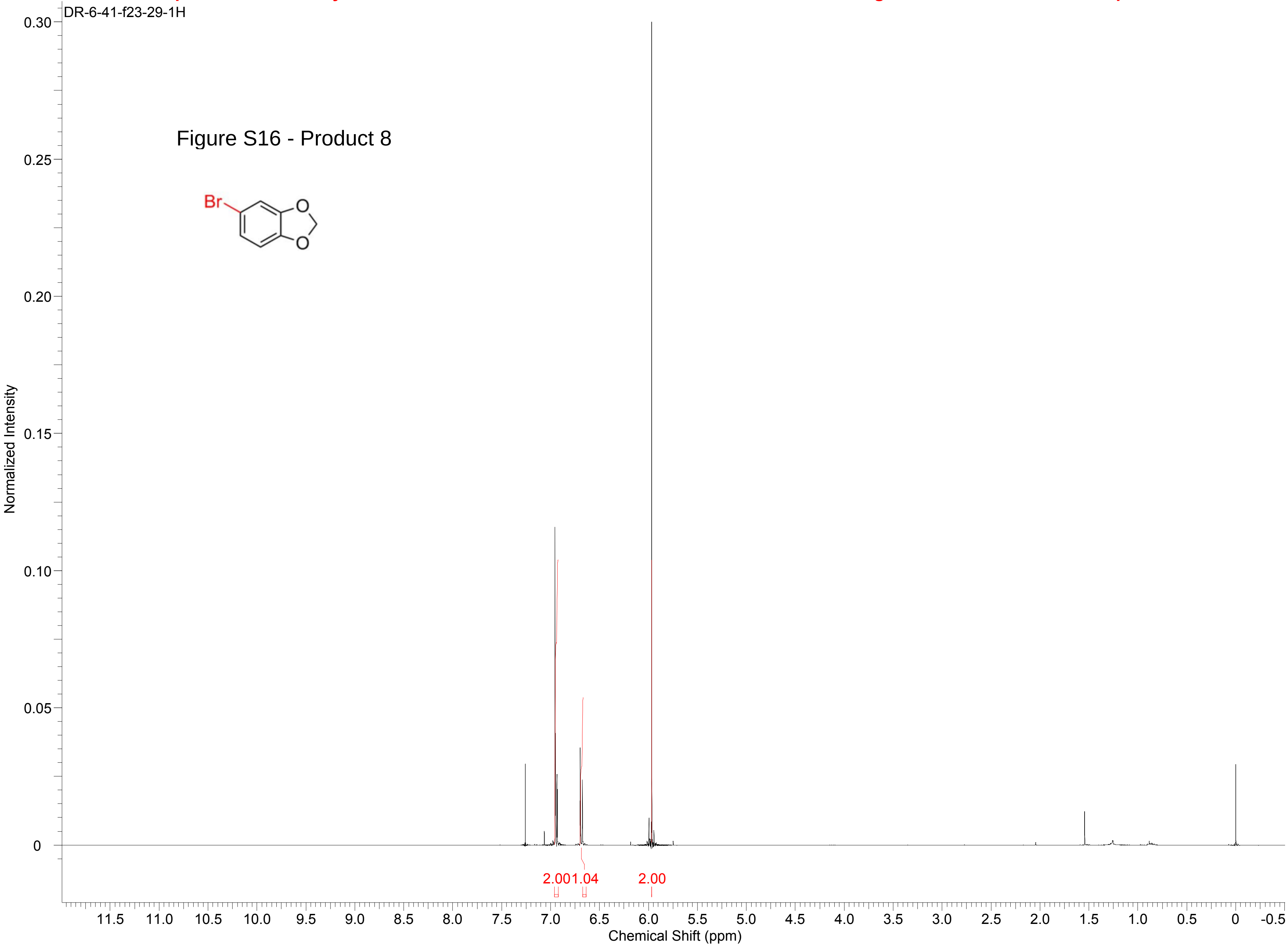
This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

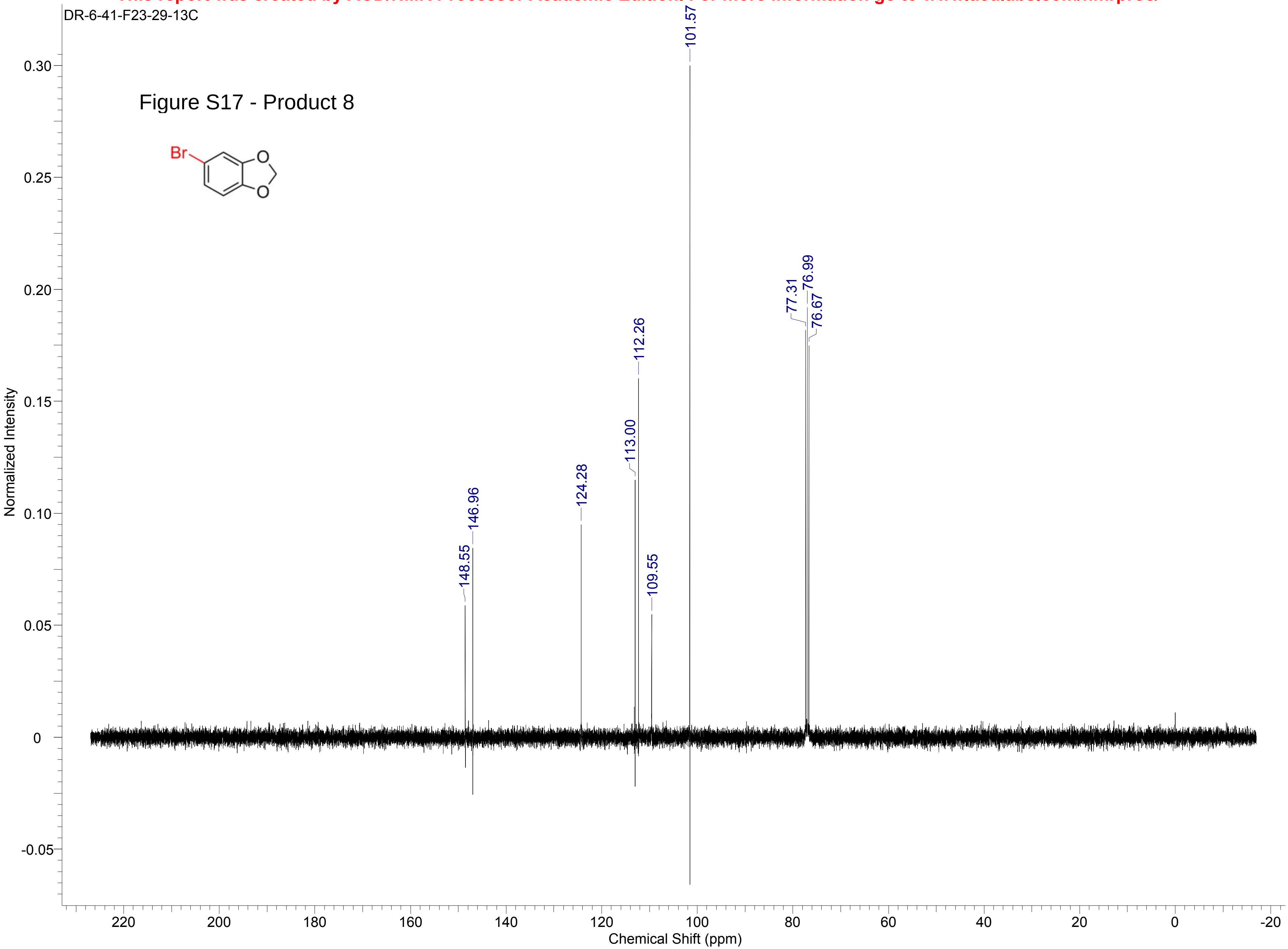


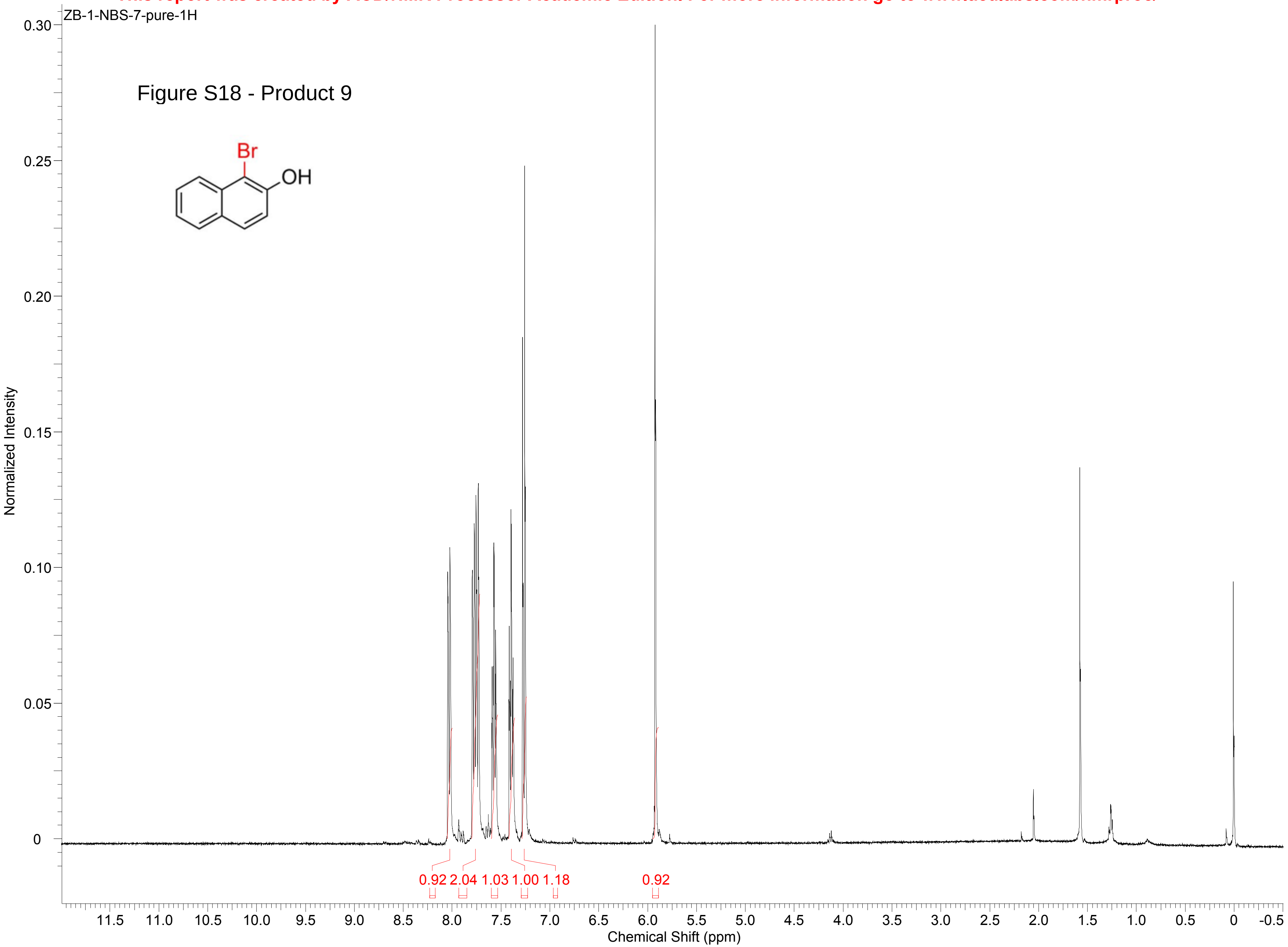

EK-64pureaftervacuum-5hrs
Figure S13 - Product 7
O
Br
Normalized Intensity
0.30
0.25
0.20
0.15
0.10
0.05
0
1.00 0.23 1.17 0.26 2.69 1.48 1.23 1.55
11 10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)

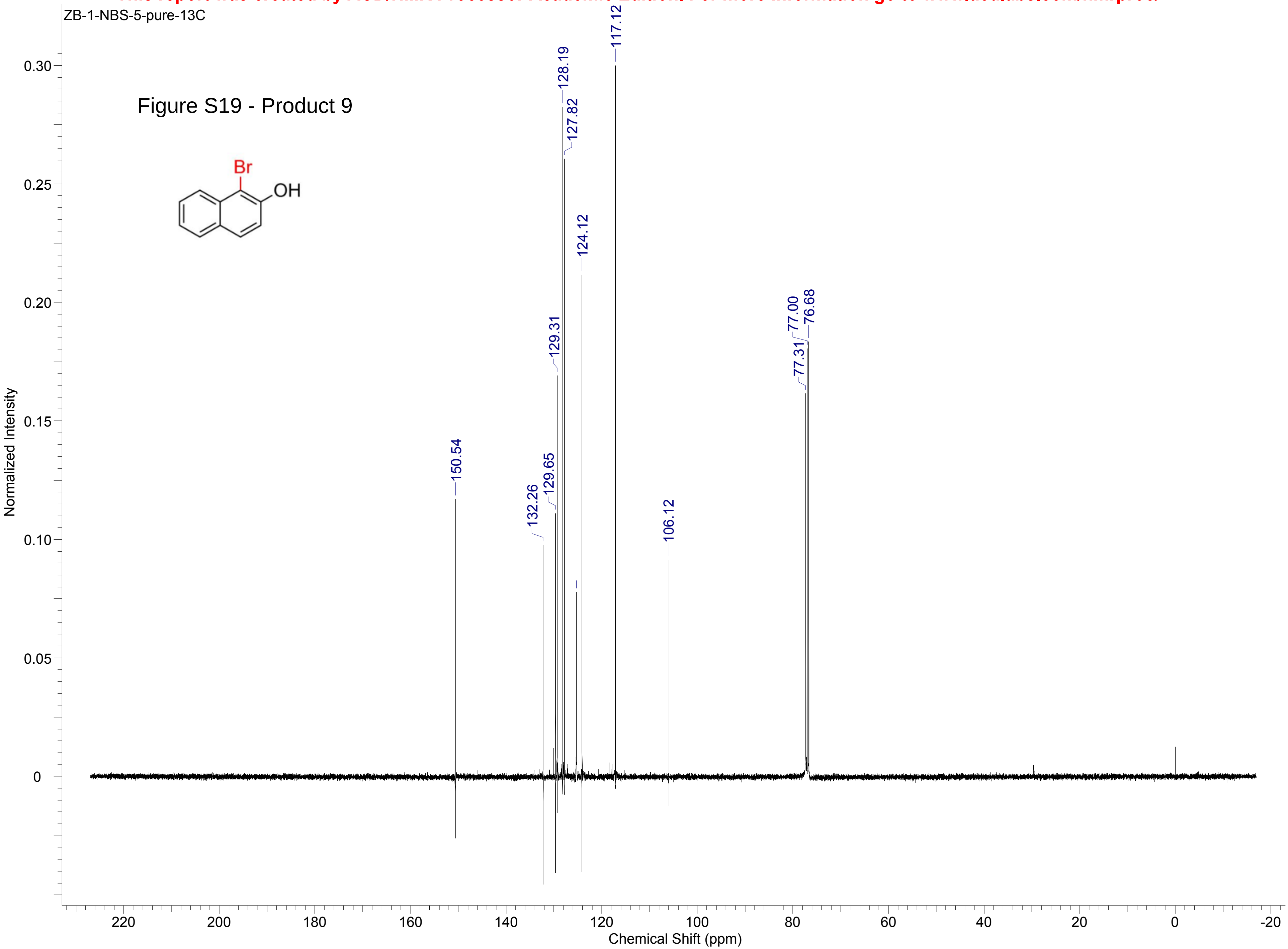

EK-64pureaftervacuum-5hrs
Figure S14 - Product 7 aromatic region
O
Br
Normalized Intensity
0.30
0.25
0.20
0.15
0.10
0.05
0
1.00
0.23
1.17
0.26
2.69
1.48
1.23
1.55
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
Chemical Shift (ppm)

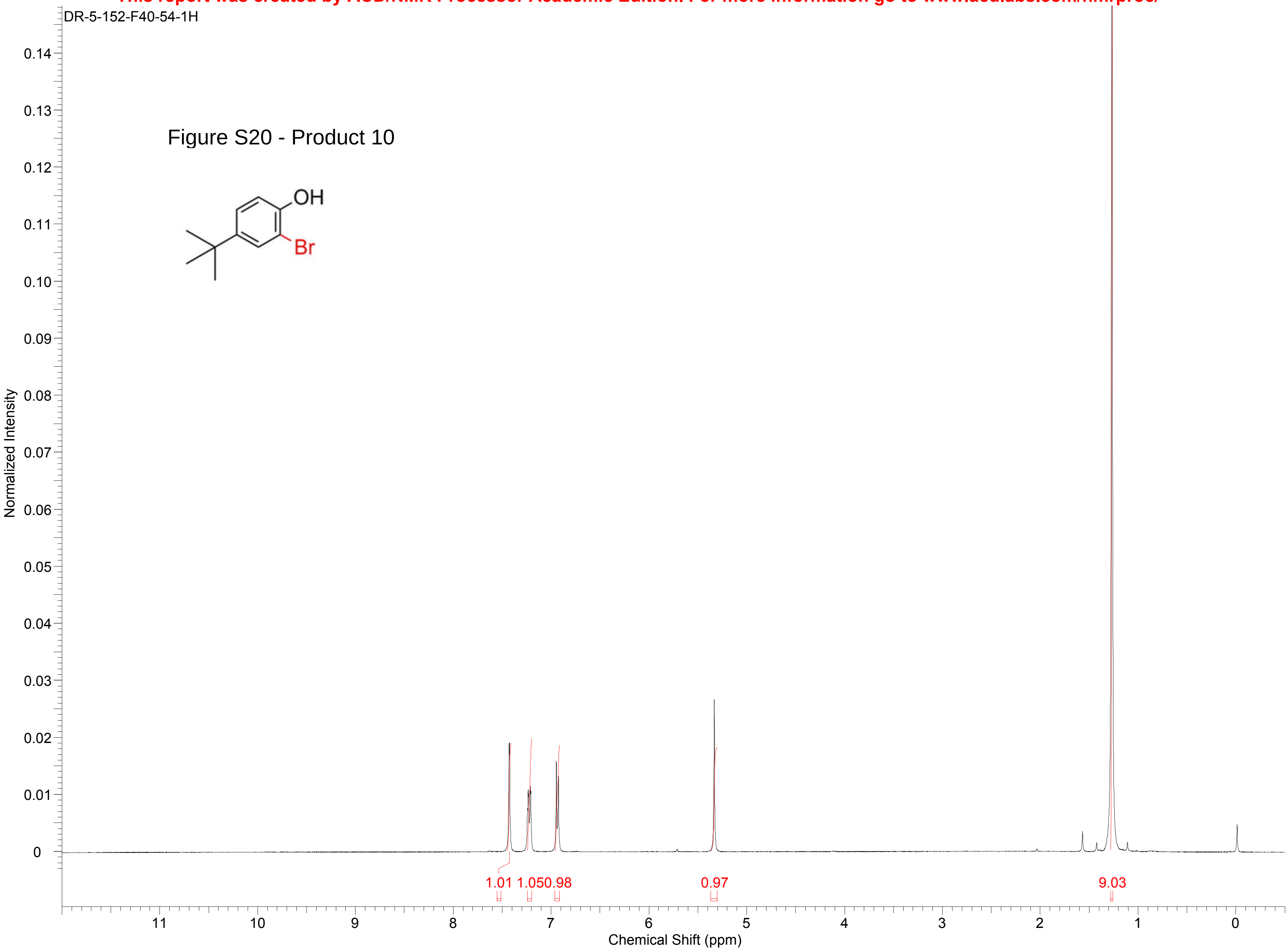

EK-64-13C-10000scans
Figure S15 - Product 7
O
Br
75.98
76.30
75.66
0.00
122.49
128.85
119.80
112.15
110.84
126.89
125.22
129.70
153.87
155.57
Normalized Intensity
Chemical Shift (ppm)


DR-6-41-f23-29-1H
Figure S16 - Product 8
Br
O
O
2.00
1.04
2.00
Normalized Intensity
Chemical Shift (ppm)

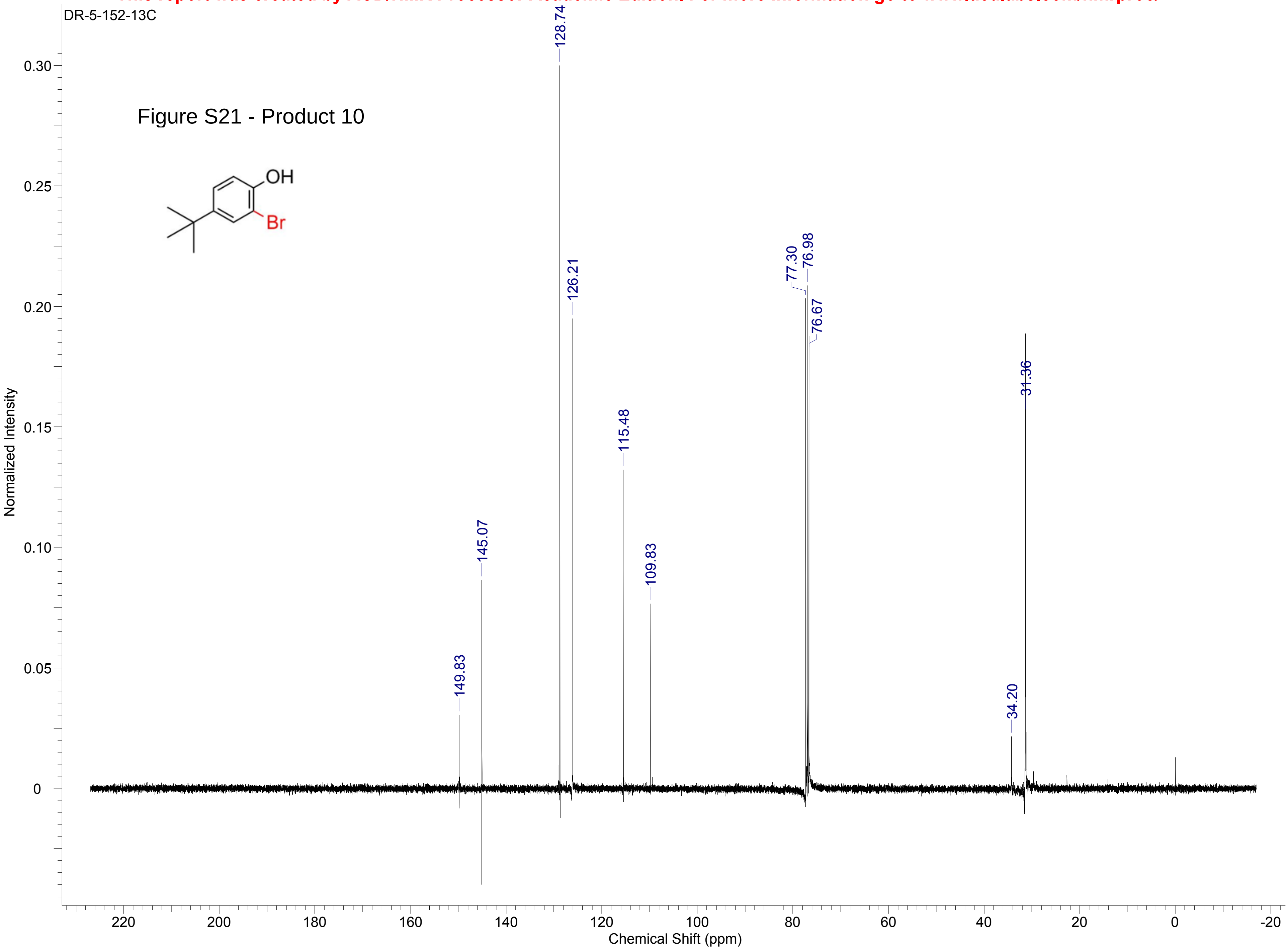

DR-6-41-F23-29-13C
Figure S17 - Product 8
Br
O
O
101.57
77.31
76.99
76.67
112.26
113.00
124.28
146.96
148.55
109.55
Normalized Intensity
Chemical Shift (ppm)
0.30
0.25
0.20
0.15
0.10
0.05
0
-0.05
220
200
180
160
140
120
100
80
60
40
20
0
-20


ZB-1-NBS-7-pure-1H
Figure S18 - Product 9
Br
OH
Normalized Intensity
0.30
0.25
0.20
0.15
0.10
0.05
0
0.92 2.04 1.03 1.00 1.18
0.92
11.5 11.0 10.5 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 -0.5
Chemical Shift (ppm)


ZB-1-NBS-5-pure-13C
Figure S19 - Product 9
Br
OH
117.12
128.19
127.82
124.12
129.31
150.54
132.26
129.65
106.12
77.00
76.68
77.31
Normalized Intensity
0.30
0.25
0.20
0.15
0.10
0.05
0
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

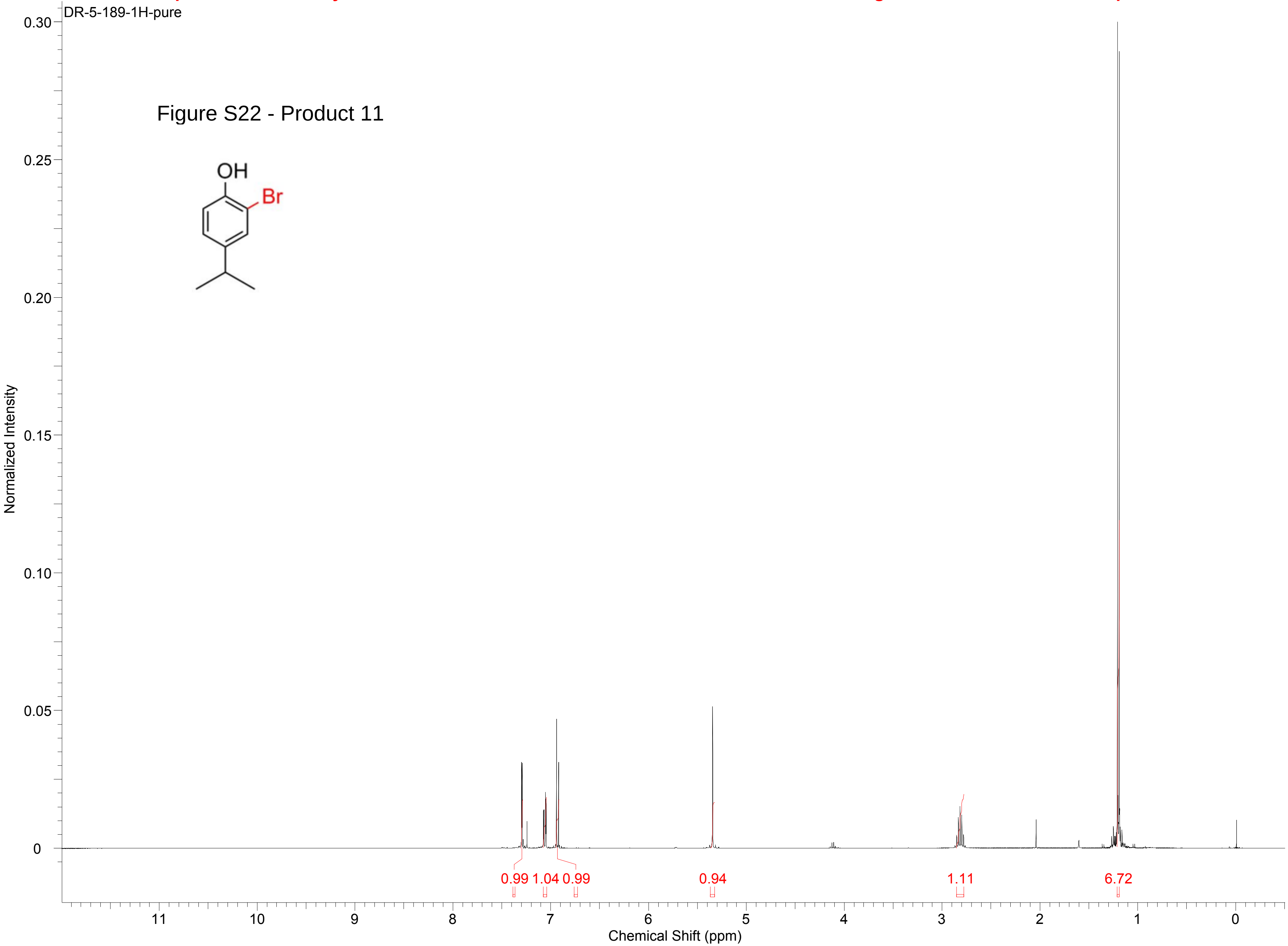


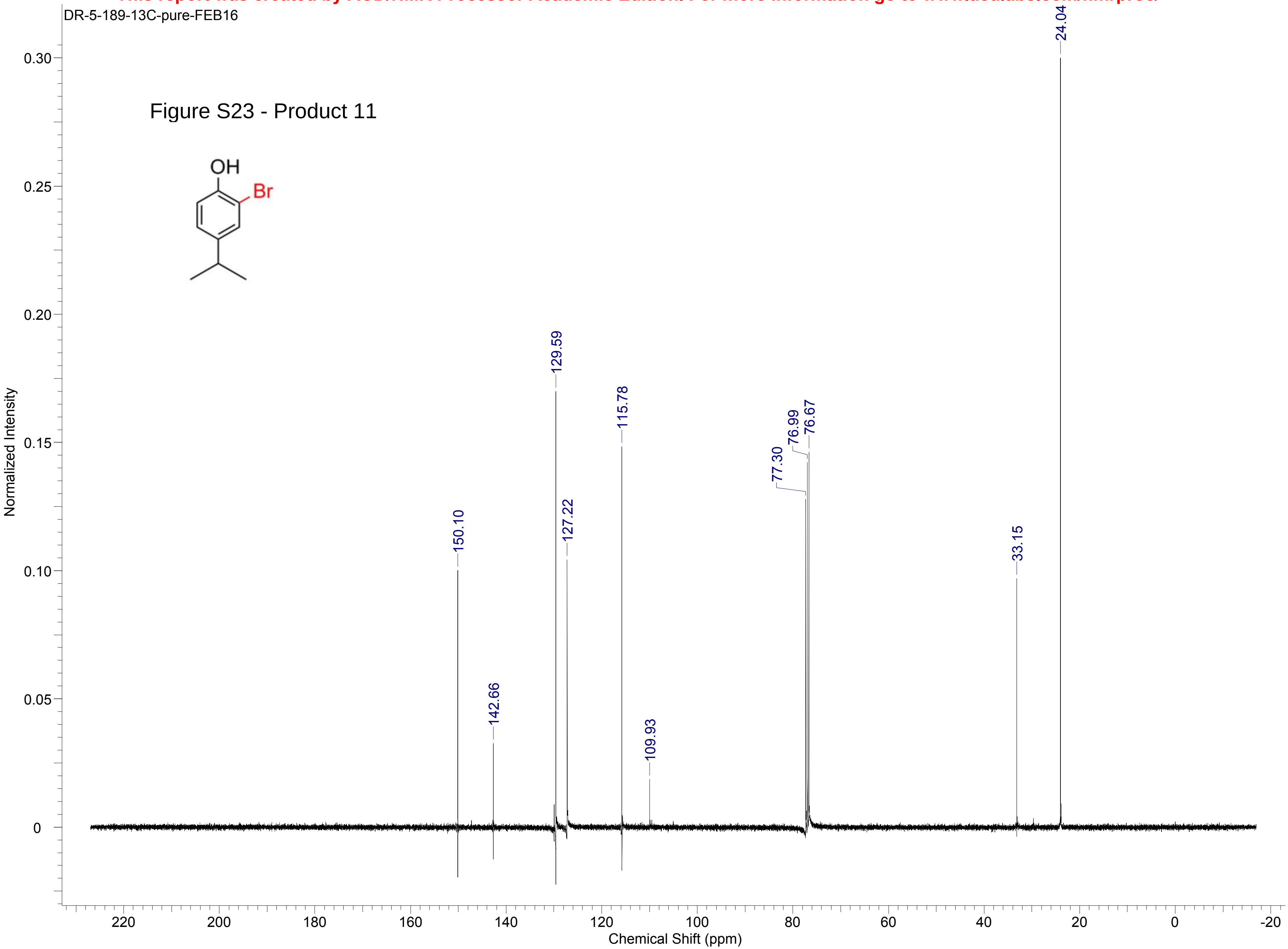
DR-5-152-F40-54-1H
Figure S20 - Product 10
OH
Br
Normalized Intensity
0.14
0.13
0.12
0.11
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
1.01
1.05
0.98
0.97
9.03
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

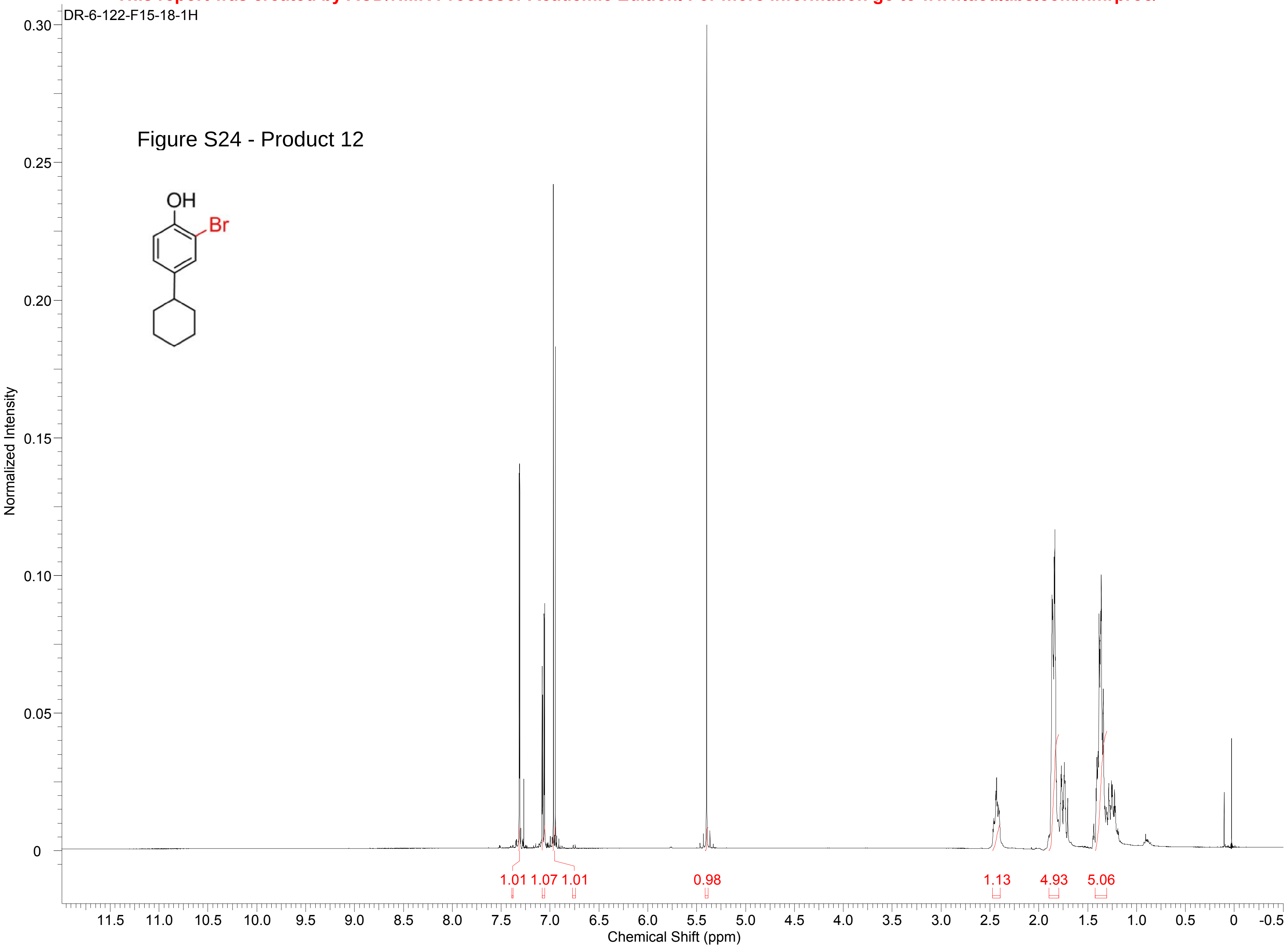

DR-5-152-13C
Figure S21 - Product 10
OH
Br
128.74
126.21
115.48
109.83
145.07
149.83
77.30
76.98
76.67
31.36
34.20
Normalized Intensity
Chemical Shift (ppm)

This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Figure S22 - Product 11




DR-5-189-13C-pure-FEB16
Figure S23 - Product 11
OH
Br
24.04
129.59
115.78
76.99
76.67
77.30
127.22
150.10
33.15
142.66
109.93
Normalized Intensity
0.30
0.25
0.20
0.15
0.10
0.05
0
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)


DR-6-122-F15-18-1H
Figure S24 - Product 12
OH
Br
Normalized Intensity
0.30
0.25
0.20
0.15
0.10
0.05
0
1.01 1.07 1.01
0.98
1.13
4.93
5.06
11.5 11.0 10.5 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 -0.5
Chemical Shift (ppm)

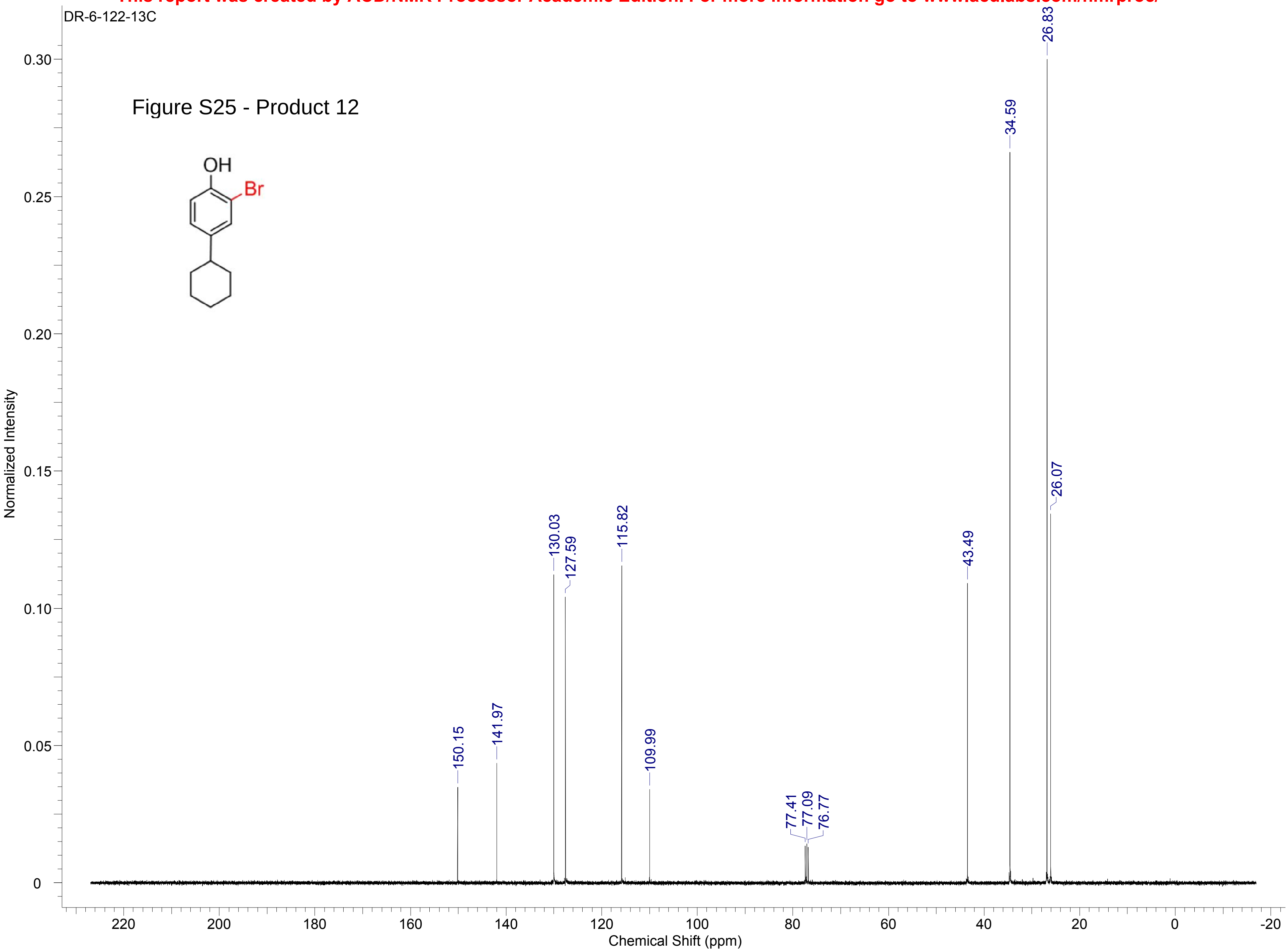



Figure S25 - Product 12

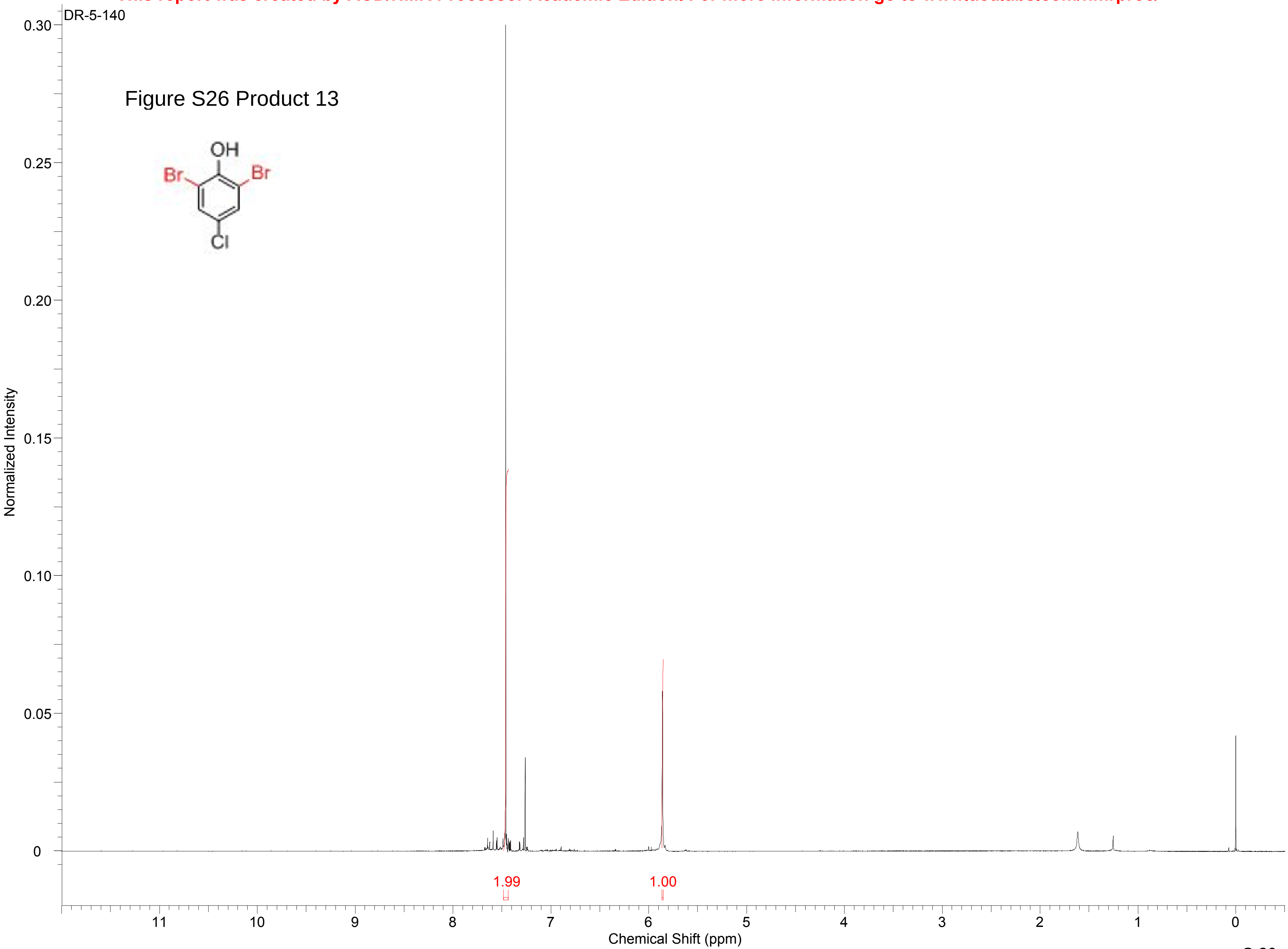
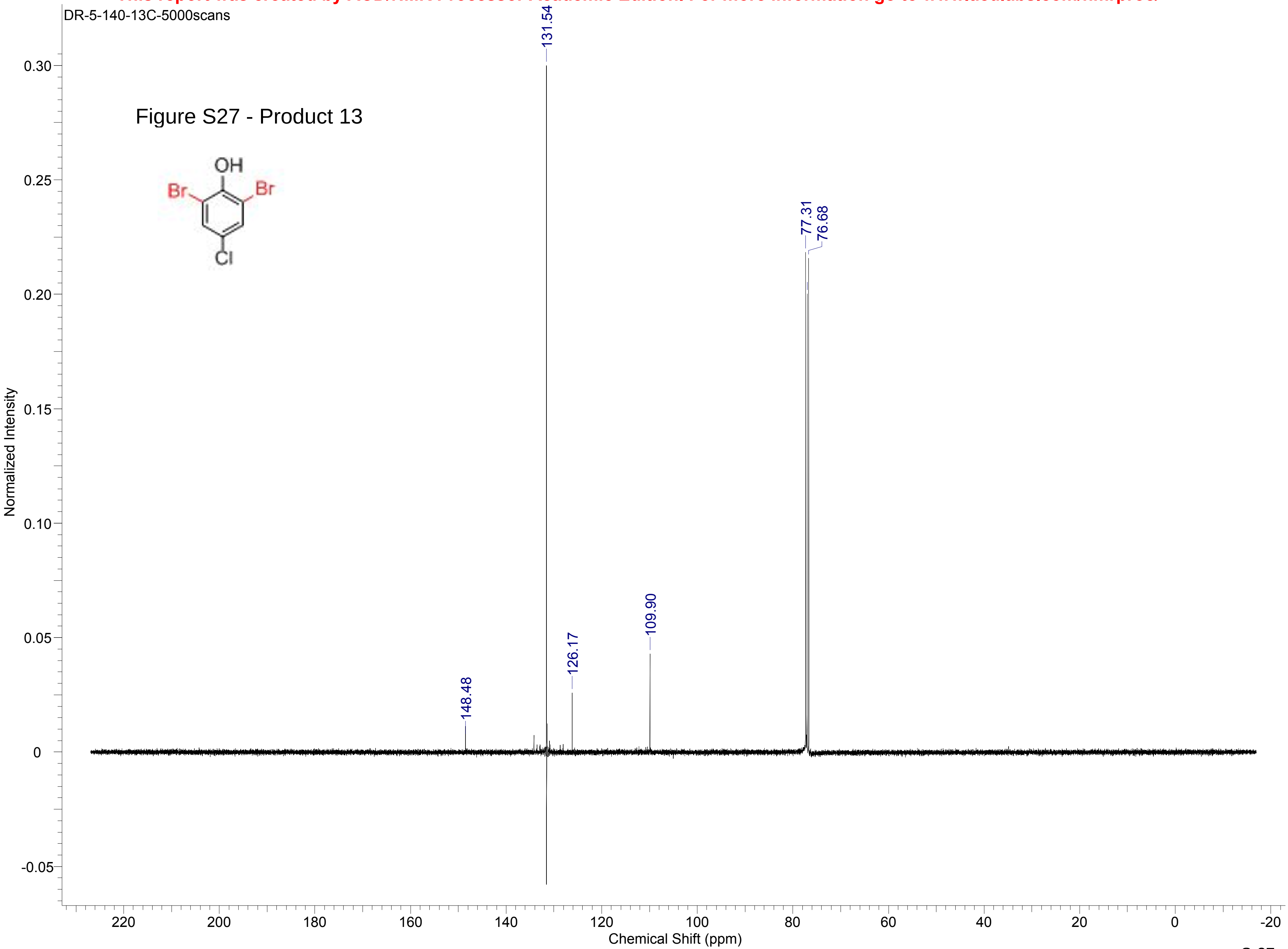
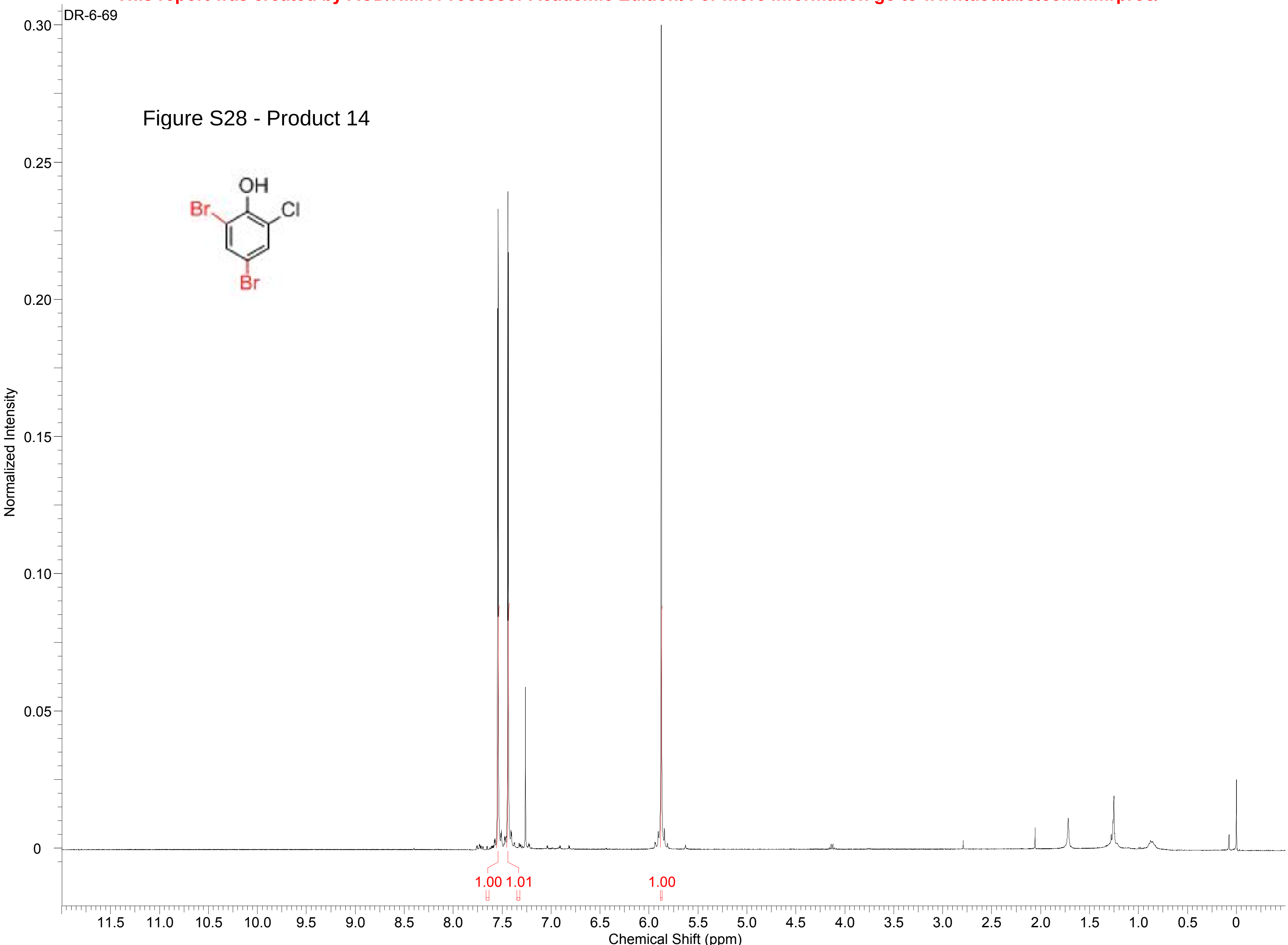



Figure S26 Product 13


DR-5-140-13C-5000scans
Figure S27 - Product 13
OH
Br
Br
Cl
131.54
77.31
76.68
148.48
126.17
109.90
Normalized Intensity
0.30
0.25
0.20
0.15
0.10
0.05
0
-0.05
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)


DR-6-69
Figure S28 - Product 14
OH
Br
Cl
Br
Normalized Intensity
0.30
0.25
0.20
0.15
0.10
0.05
0
1.00 1.01
1.00
11.5 11.0 10.5 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
Chemical Shift (ppm)

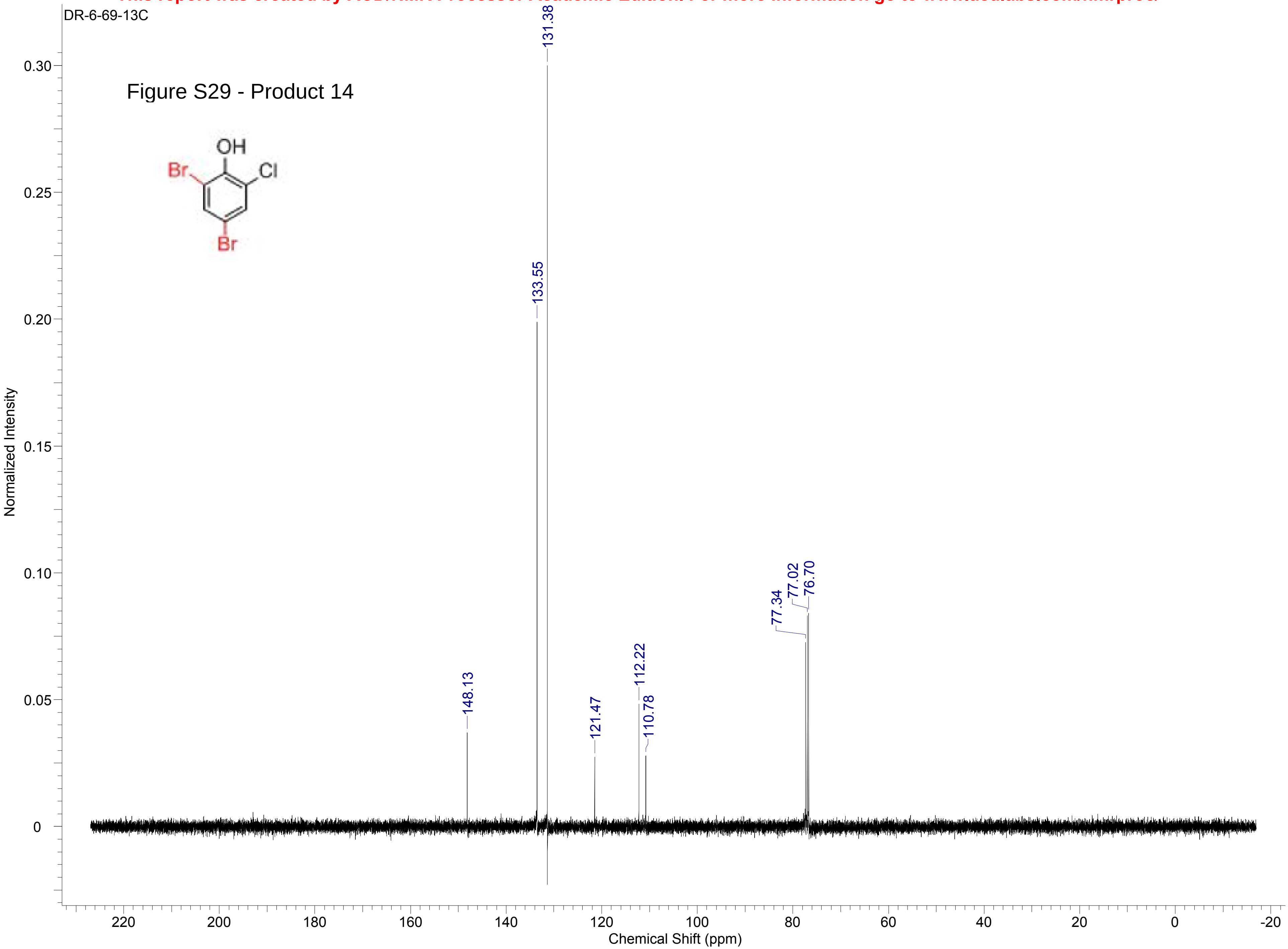
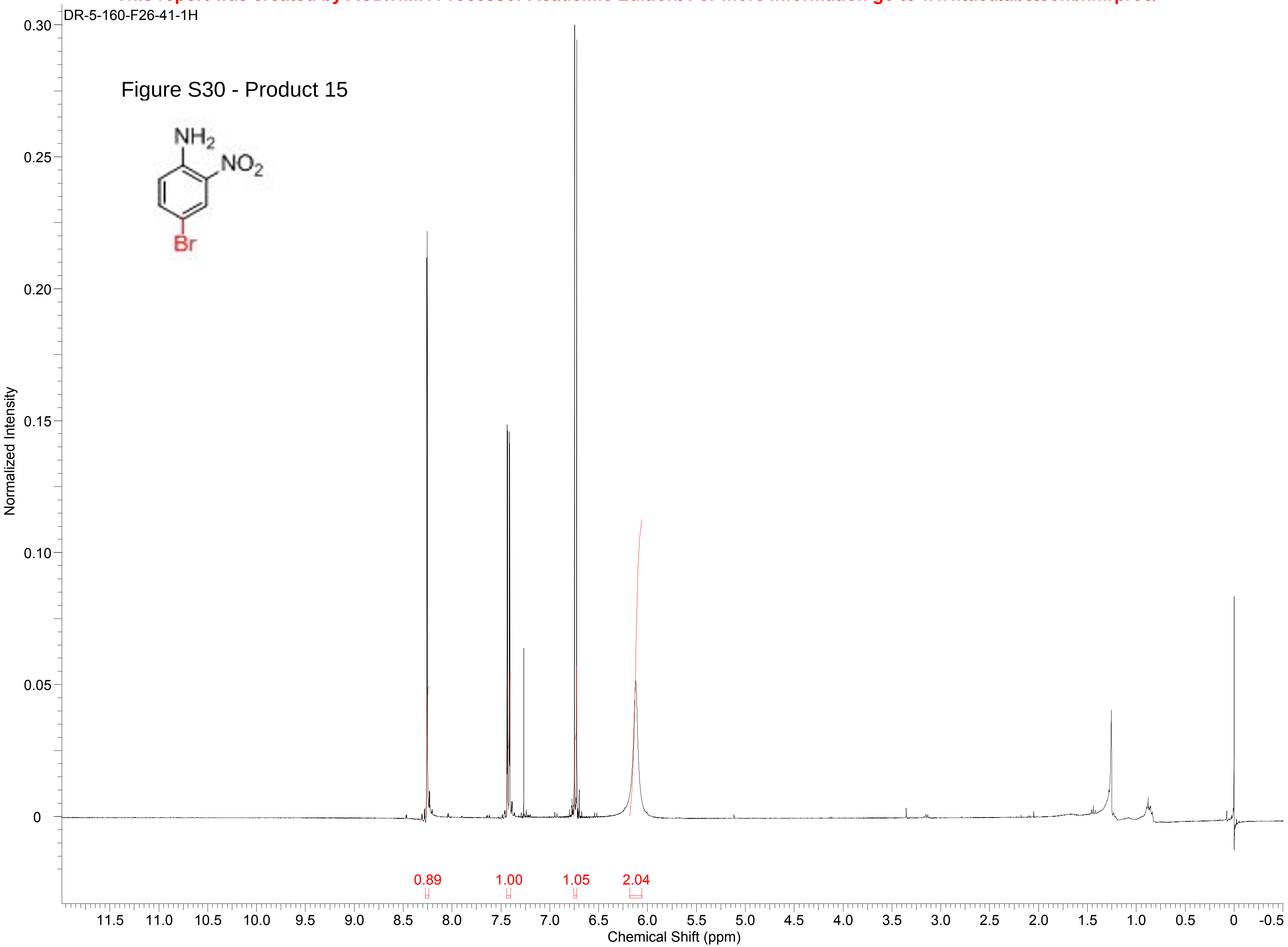
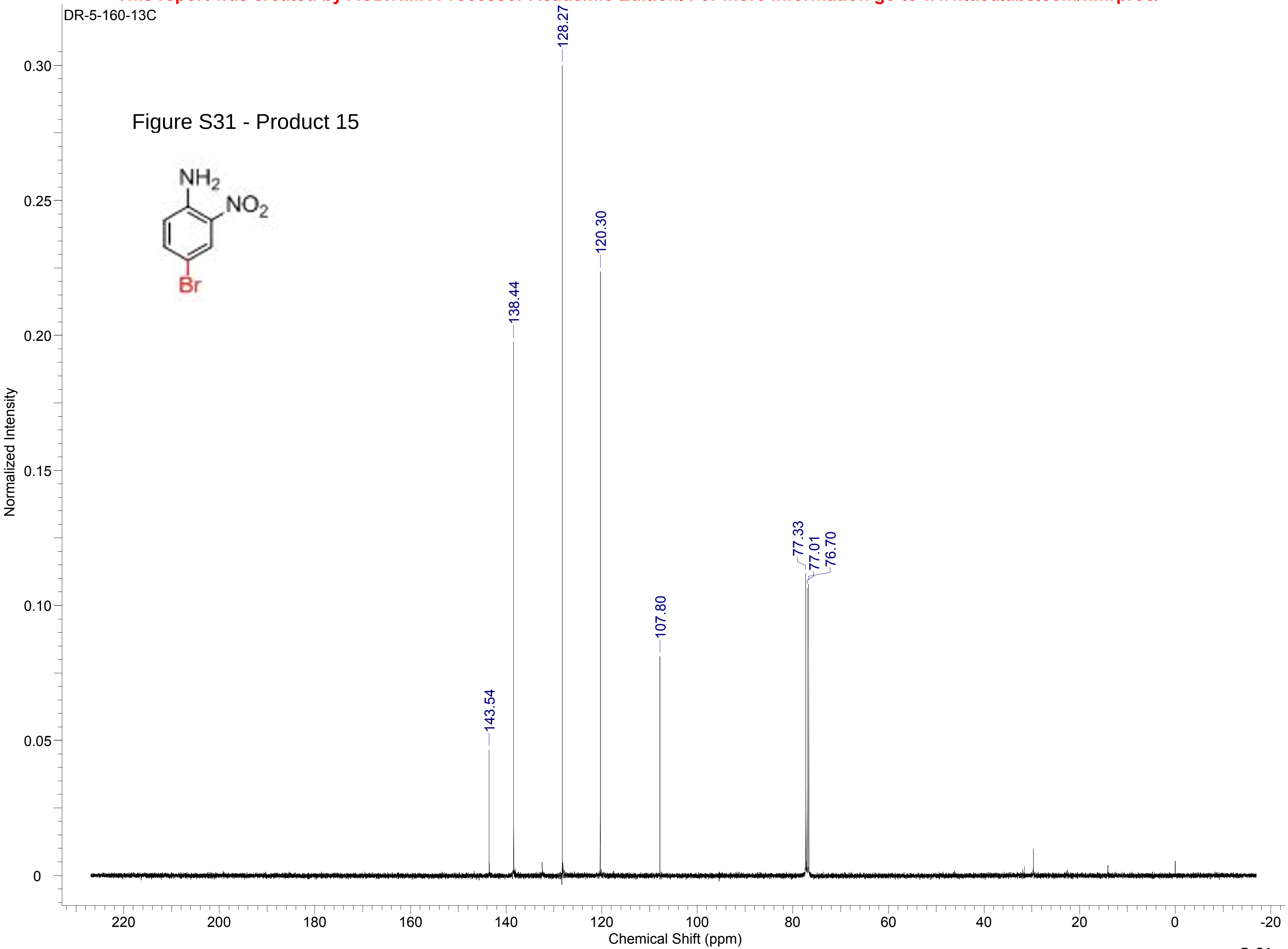



Figure S29 - Product 14


DR-5-160-F26-41-1H
Figure S30 - Product 15
NH2
NO2
Br
0.30
0.25
0.20
0.15
0.10
0.05
0
Normalized Intensity
0.89
1.00
1.05
2.04
11.5
11.0
10.5
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
-0.5
Chemical Shift (ppm)


DR-5-160-13C
Figure S31 - Product 15
NH2
NO2
Br
143.54
138.44
128.27
120.30
107.80
77.33
77.01
76.70
Normalized Intensity
Chemical Shift (ppm)

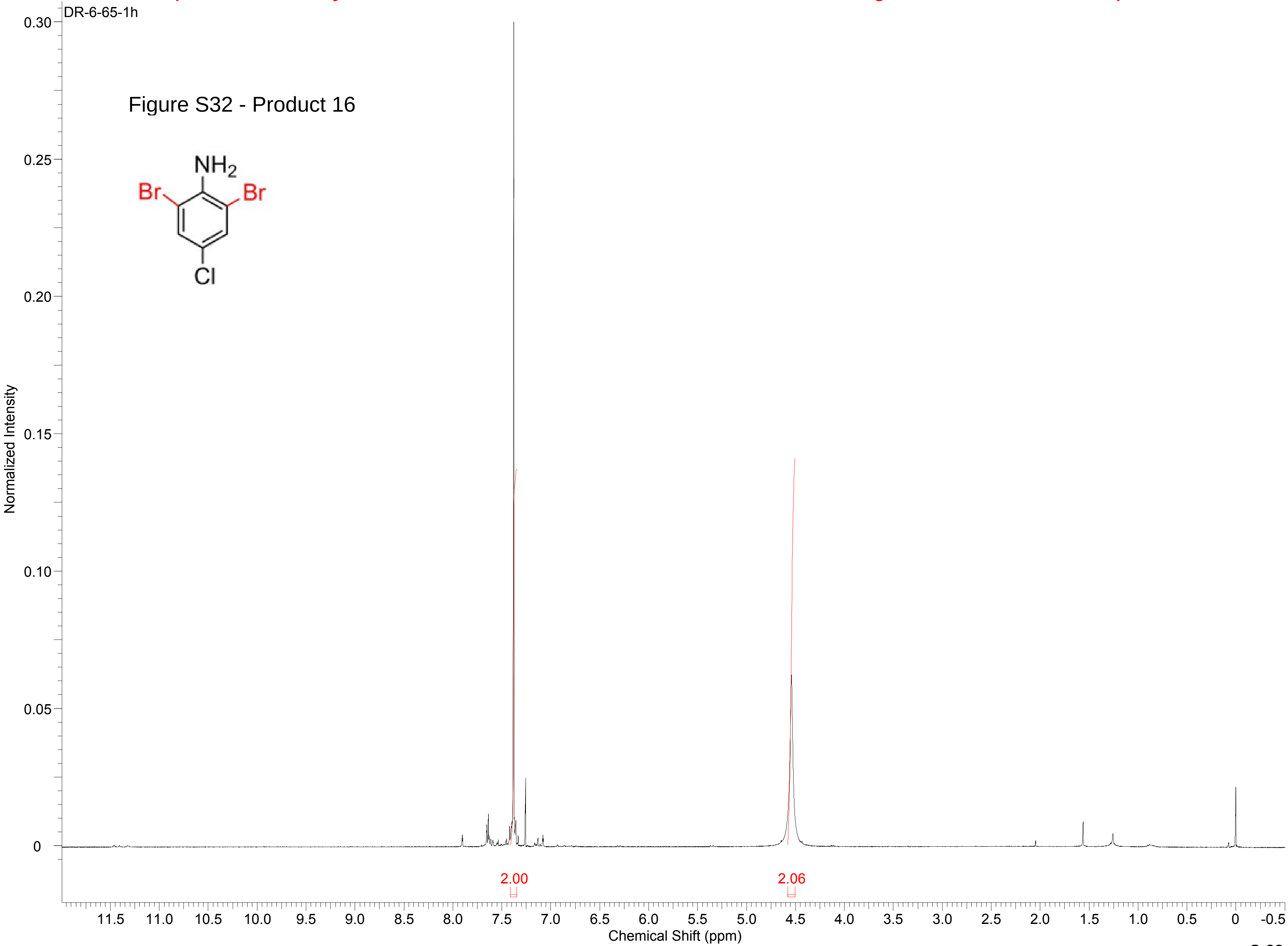



Figure S32 - Product 16

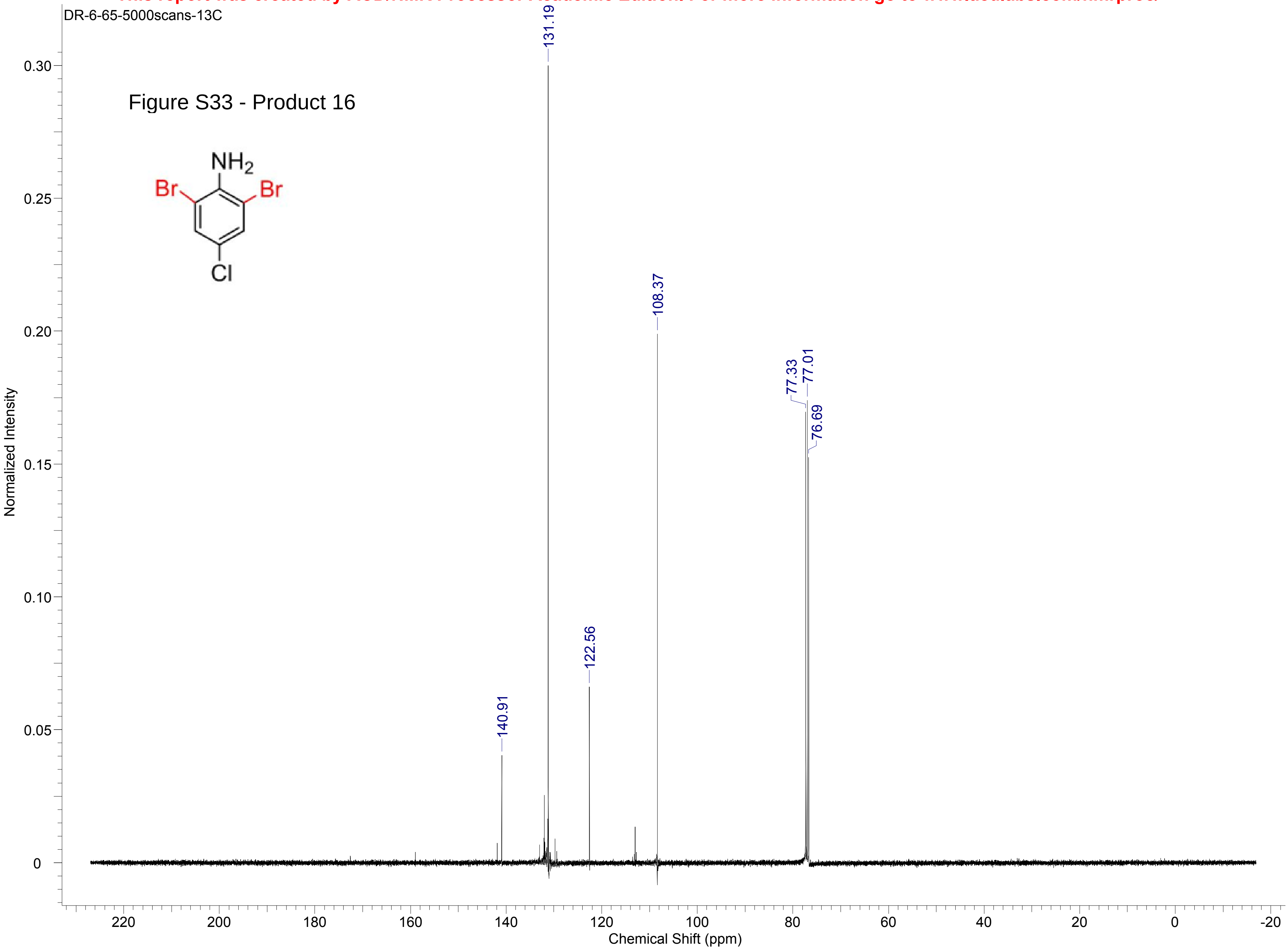
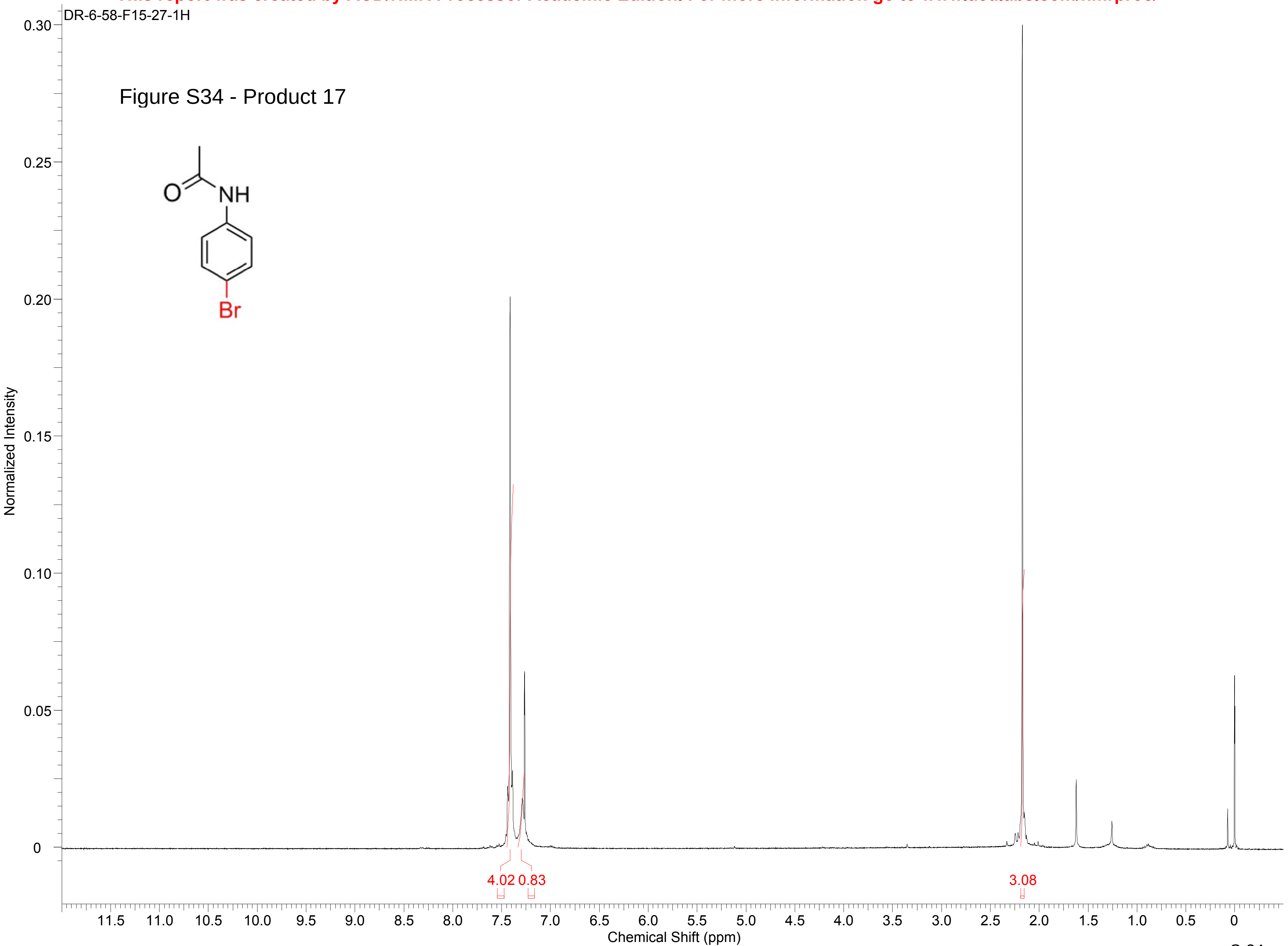



Figure S33 - Product 16


DR-6-58-F15-27-1H
Figure S34 - Product 17
O
NH
Br
Normalized Intensity
0.30
0.25
0.20
0.15
0.10
0.05
0
4.02
0.83
3.08
11.5
11.0
10.5
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
Chemical Shift (ppm)

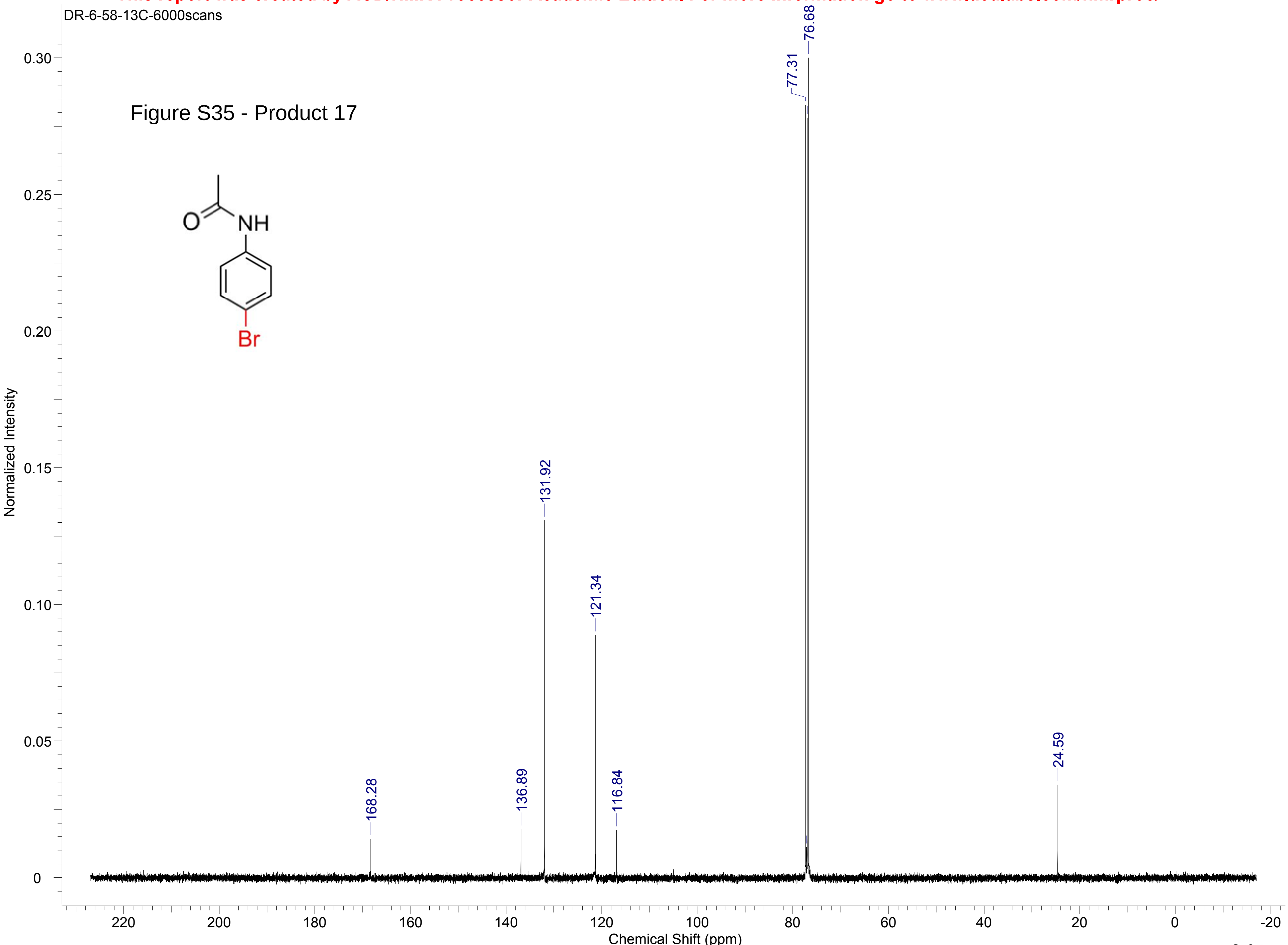
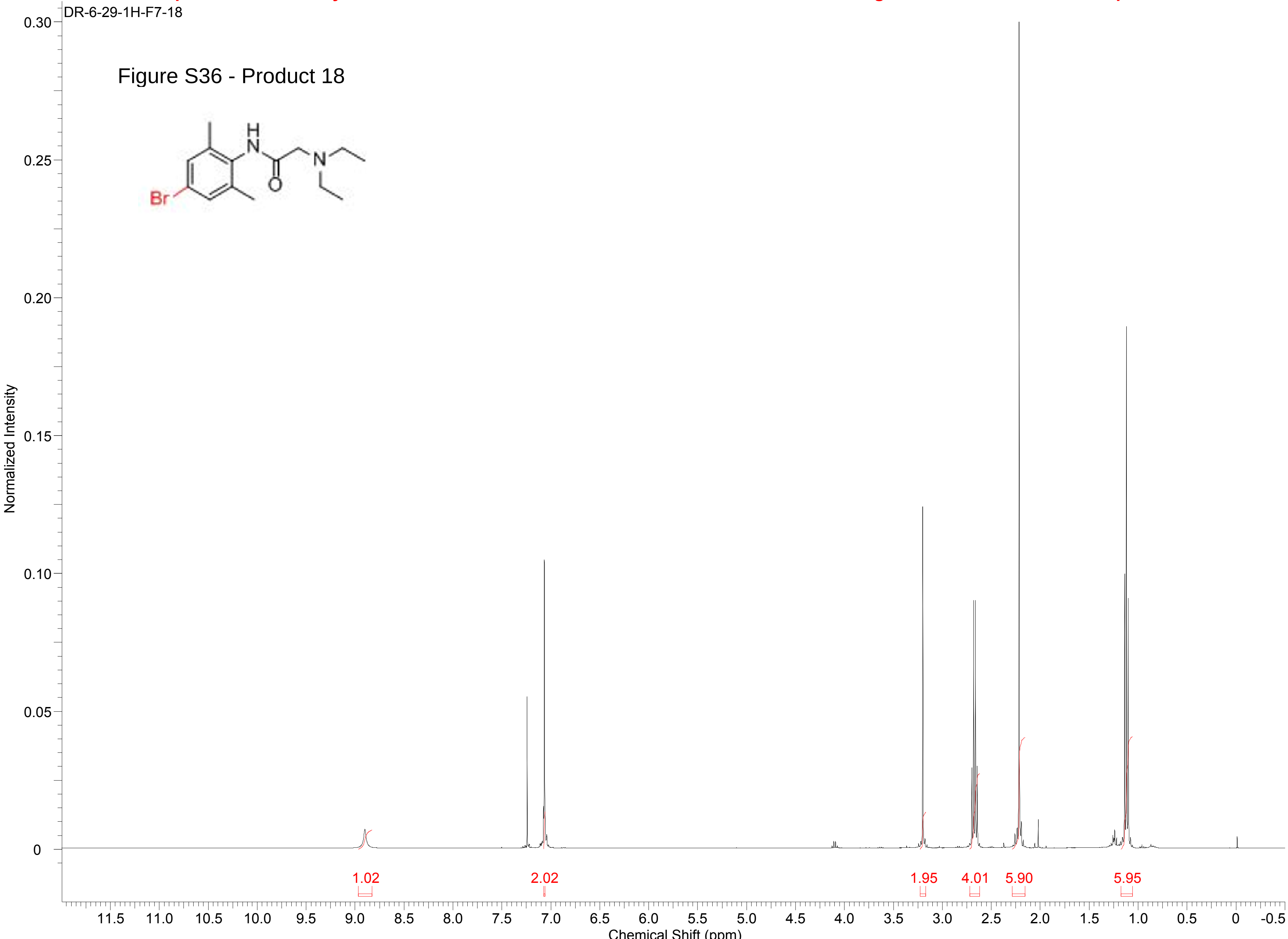
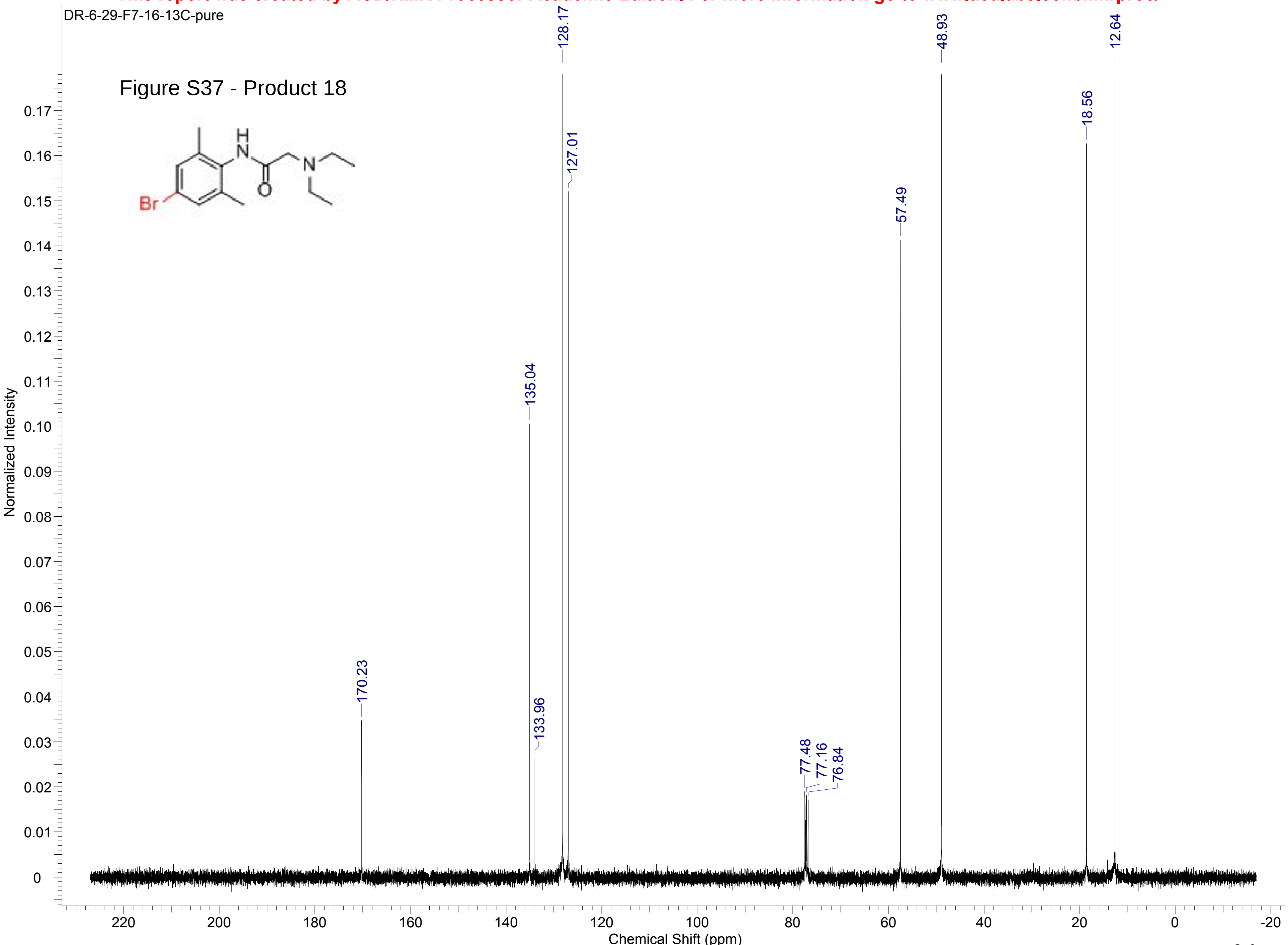
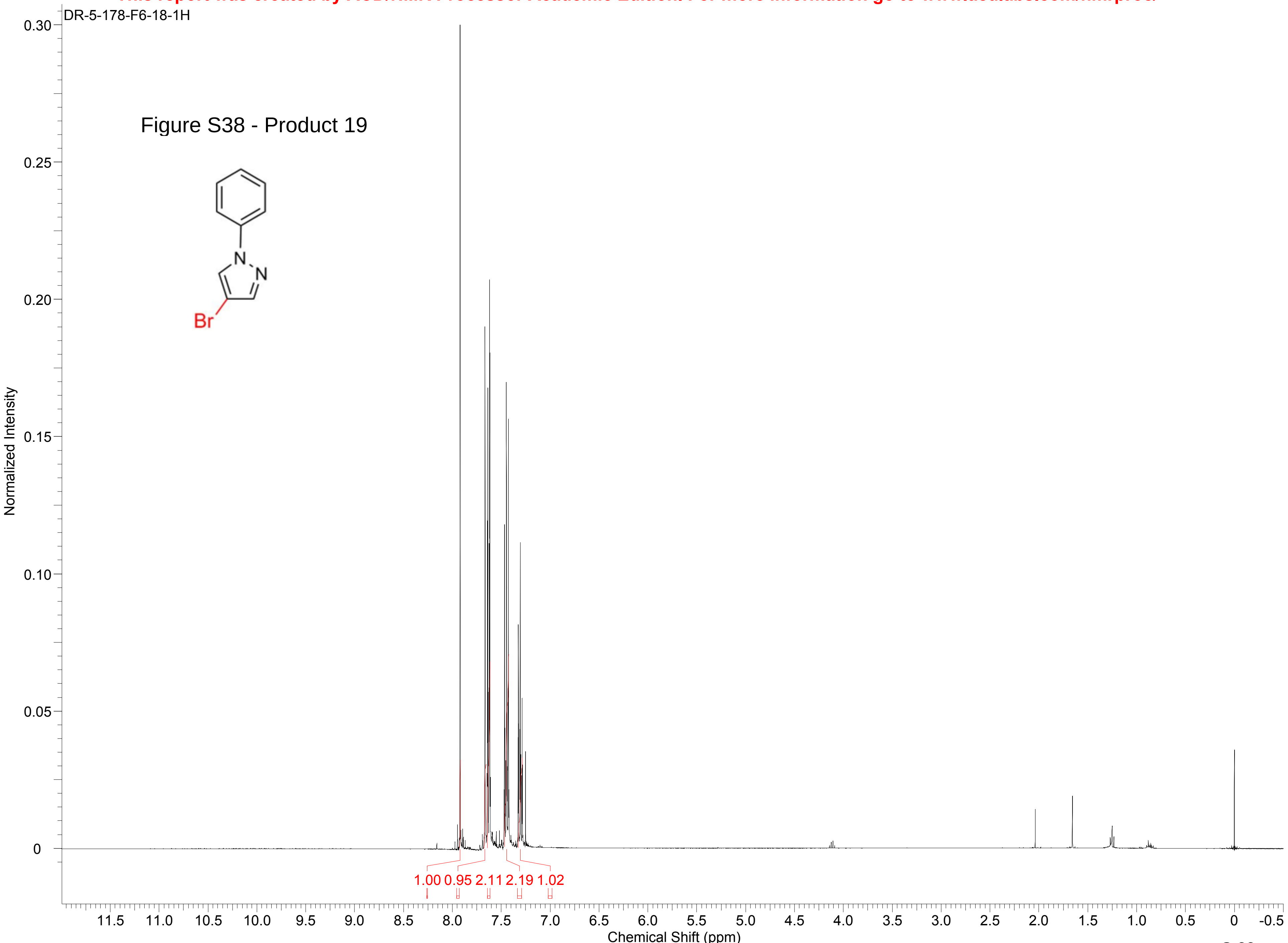

DR-6-58-13C-6000scans
Figure S35 - Product 17
O
NH
Br
Normalized Intensity
0.30
0.25
0.20
0.15
0.10
0.05
0
168.28
136.89
131.92
121.34
116.84
77.31
76.68
24.59
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

Figure S36 - Product 18




DR-6-29-F7-16-13C-pure
Figure S37 - Product 18
Br
H
N
N
O
128.17
48.93
12.64
127.01
18.56
57.49
135.04
170.23
133.96
77.48
77.16
76.84
Normalized Intensity
Chemical Shift (ppm)



DR-5-178-F6-18-1H
Figure S38 - Product 19
N
N
Br
Normalized Intensity
0.30
0.25
0.20
0.15
0.10
0.05
0
1.00 0.95 2.11 2.19 1.02
11.5 11.0 10.5 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 -0.5
Chemical Shift (ppm)

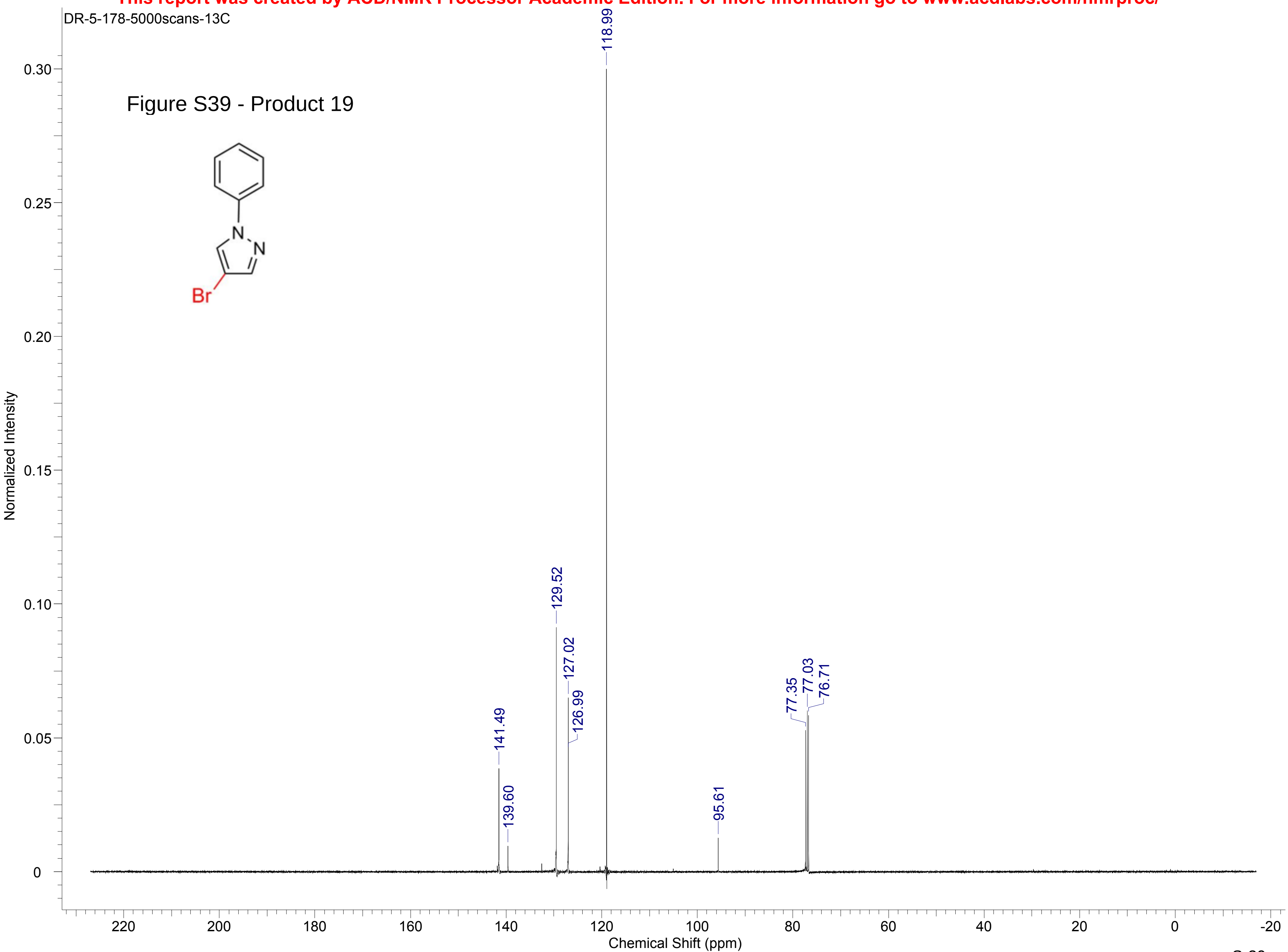
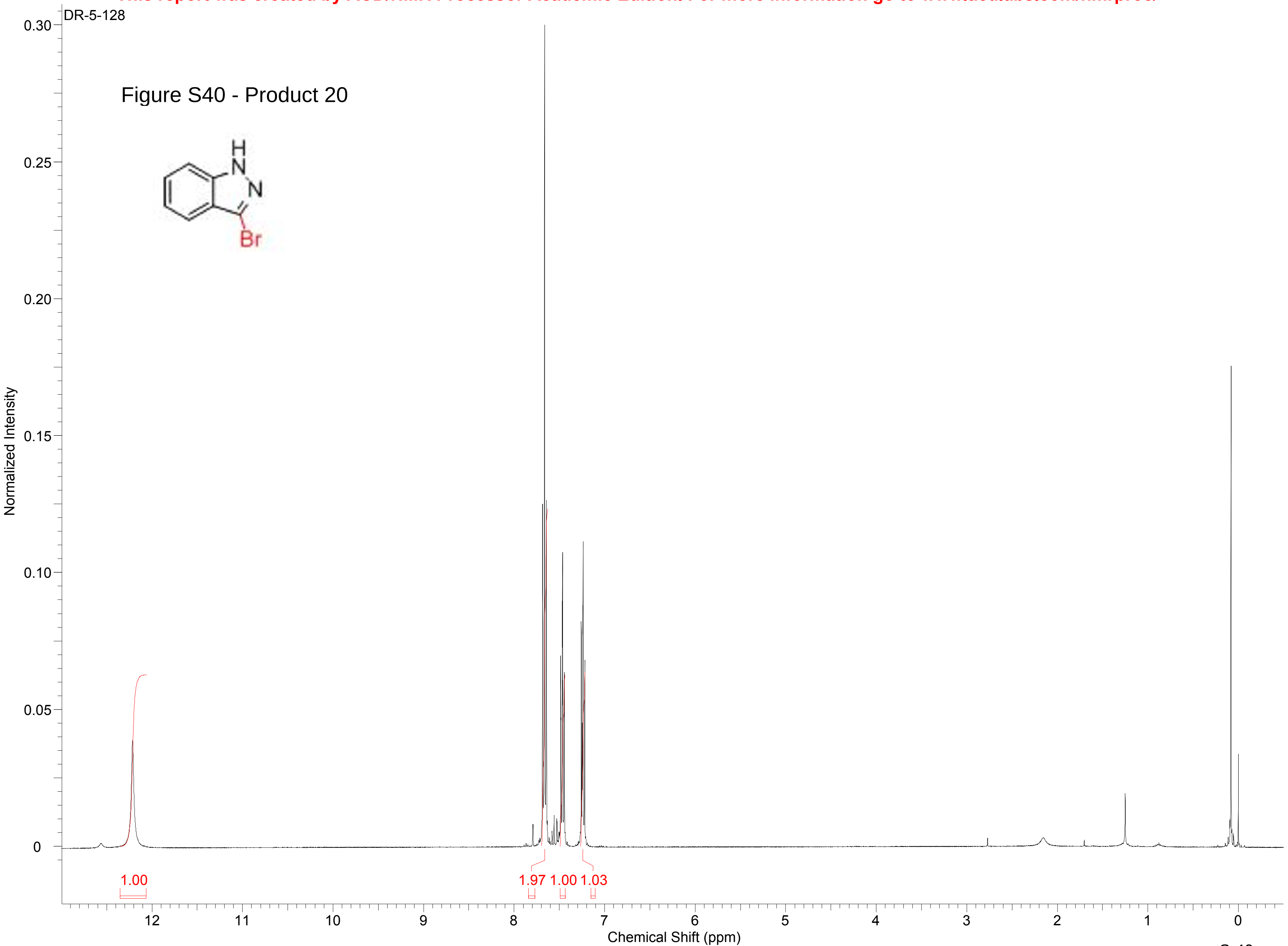
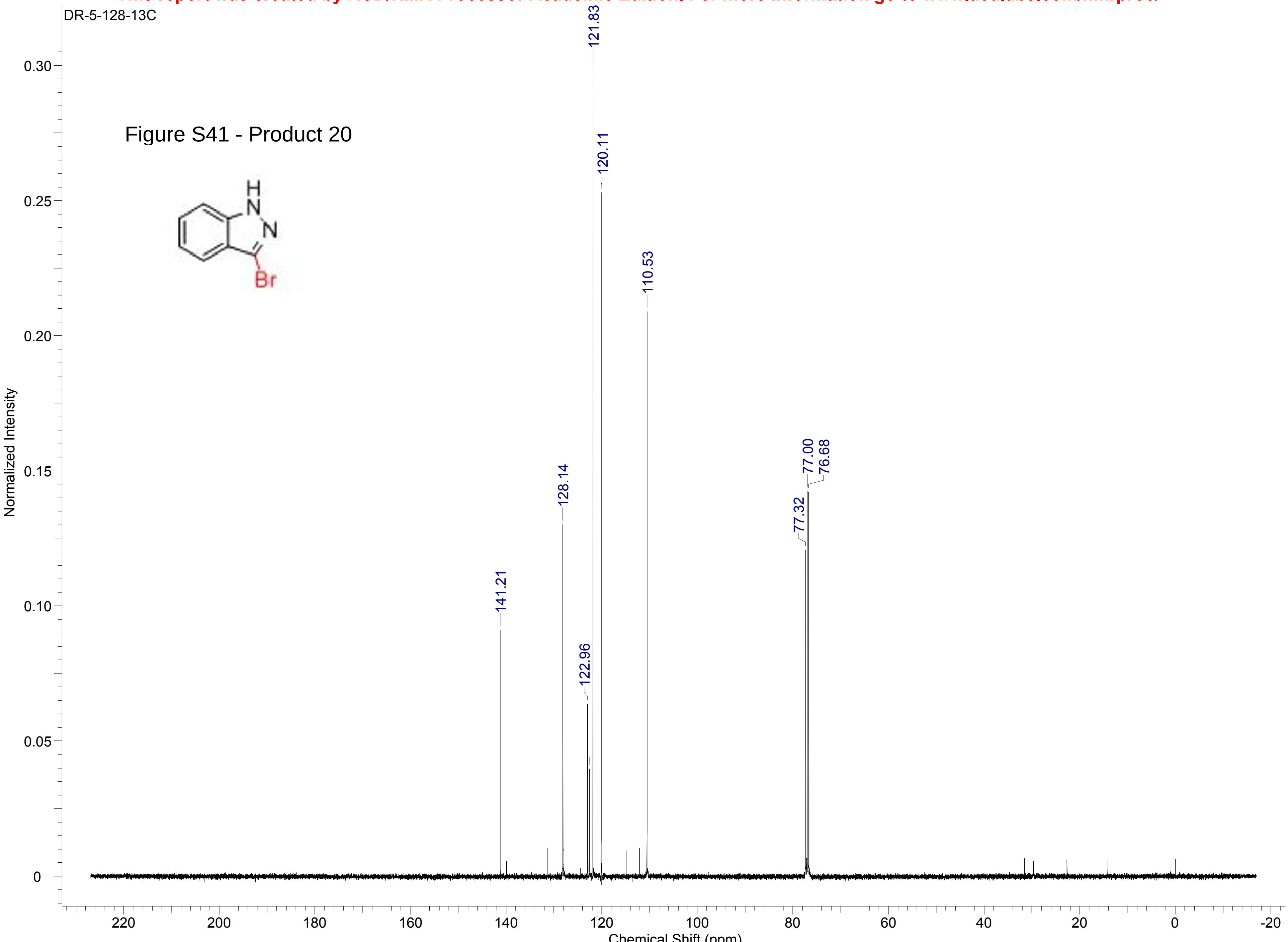
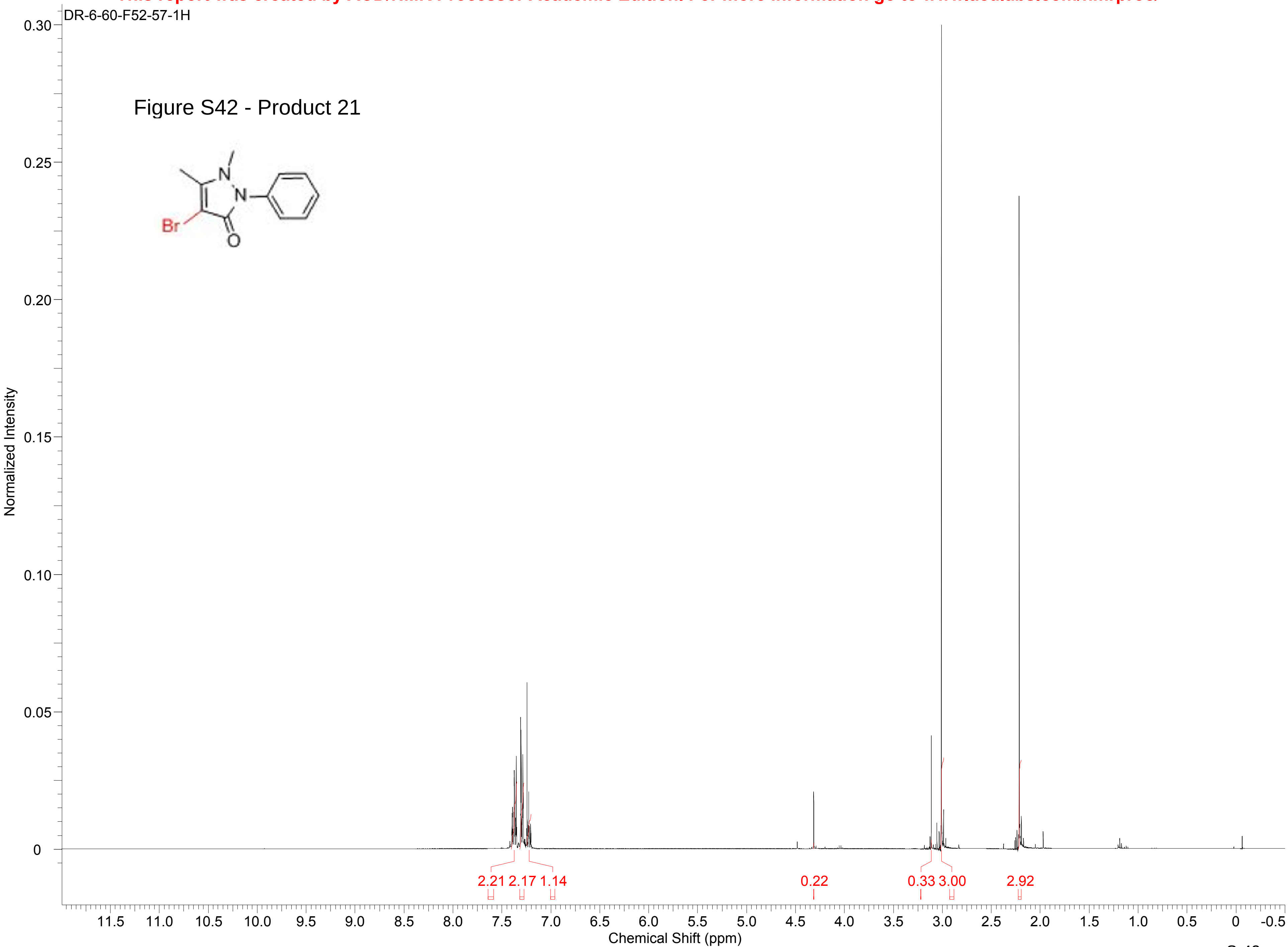
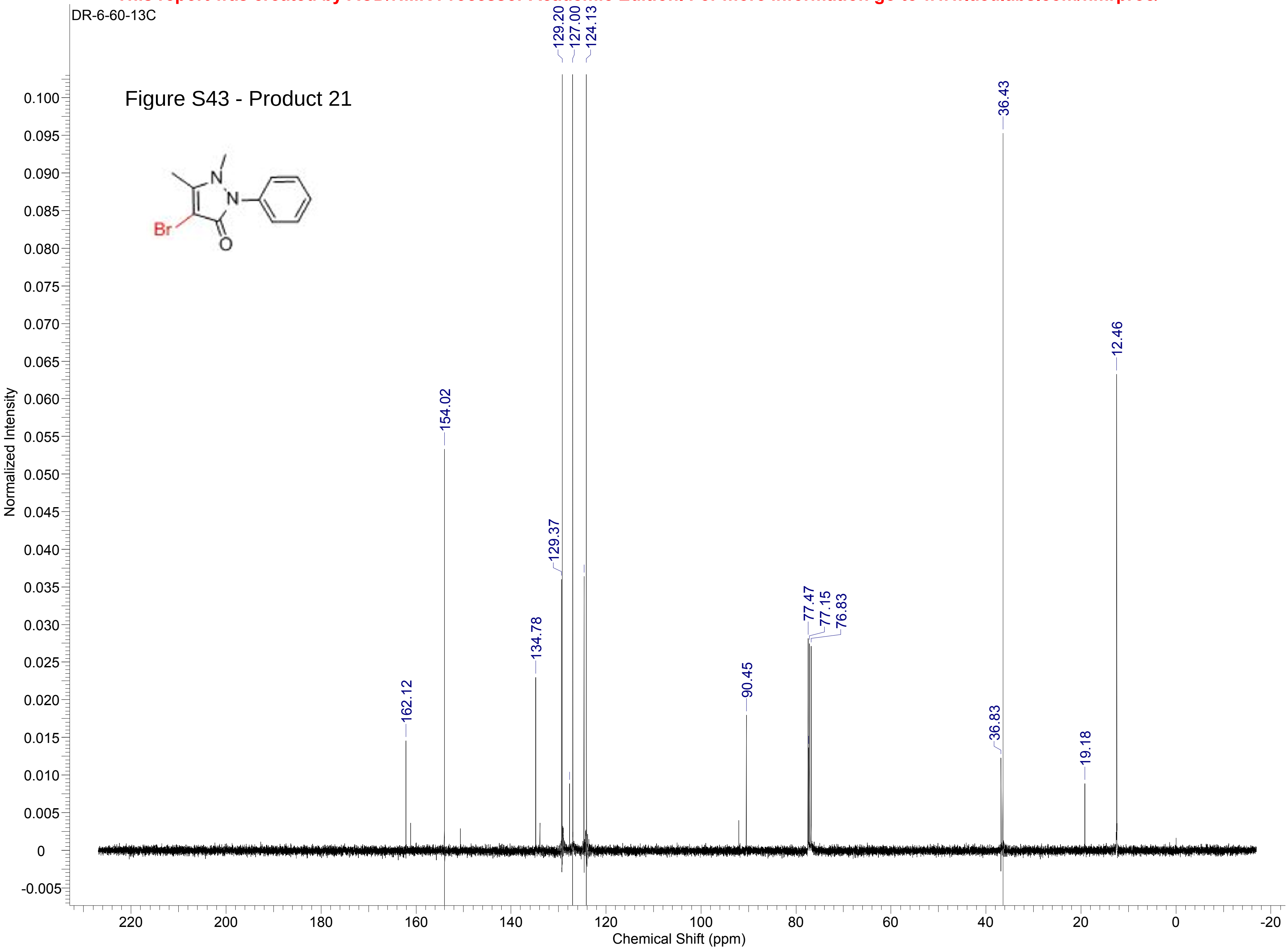

DR-5-178-5000scans-13C
Figure S39 - Product 19
N
N
Br
118.99
129.52
127.02
126.99
141.49
139.60
95.61
77.35
77.03
76.71
Normalized Intensity
0.30
0.25
0.20
0.15
0.10
0.05
0
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

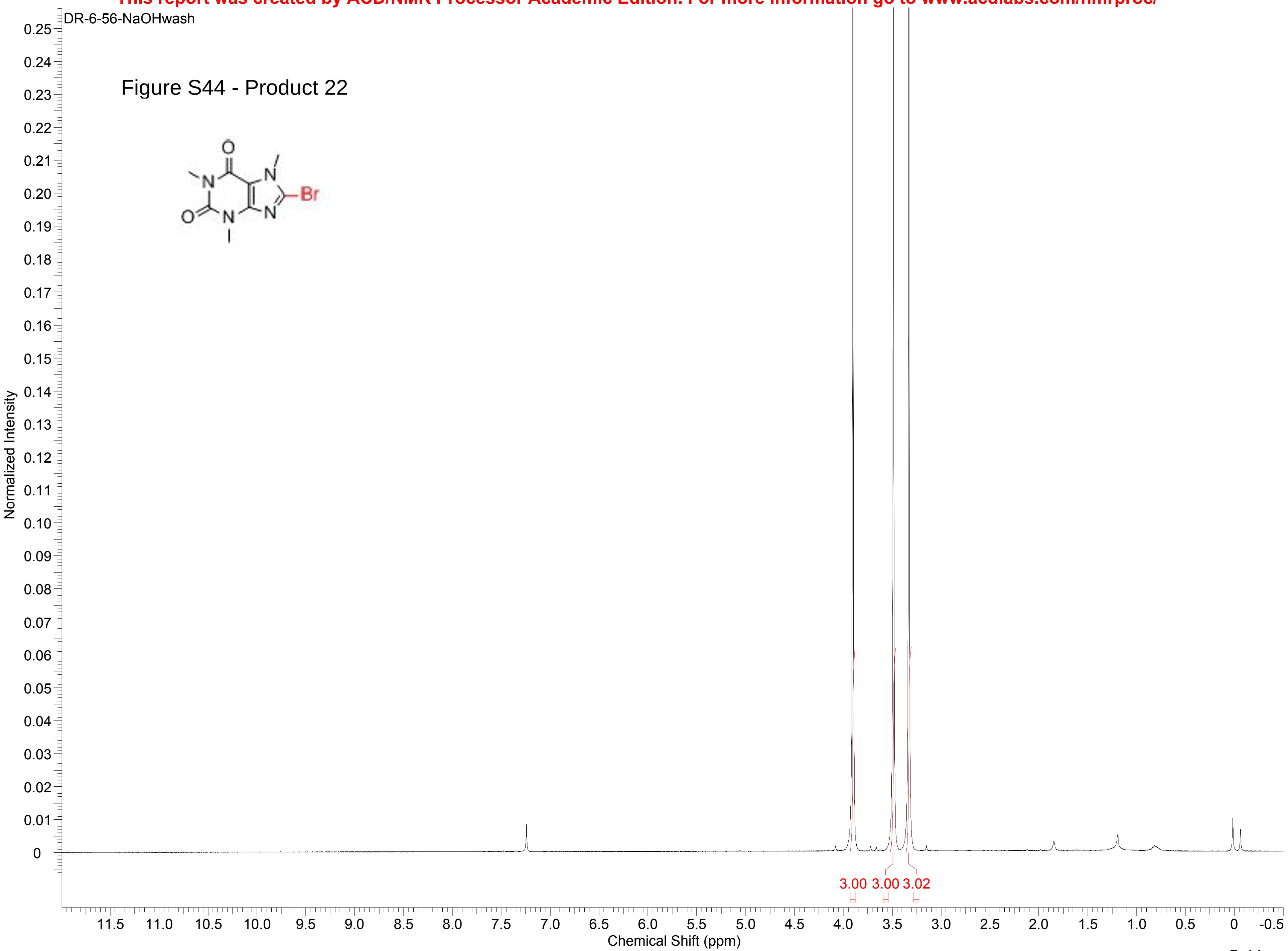
Figure S40 - Product 20




DR-5-128-13C
Figure S41 - Product 20
H
N
N
Br
121.83
120.11
110.53
128.14
141.21
122.96
77.32
77.00
76.68
Normalized Intensity
0.30
0.25
0.20
0.15
0.10
0.05
0
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)


DR-6-60-F52-57-1H
Figure S42 - Product 21
Br
N
N
O
Normalized Intensity
0.30
0.25
0.20
0.15
0.10
0.05
0
2.21 2.17 1.14
0.22
0.33 3.00
2.92
11.5 11.0 10.5 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 -0.5
Chemical Shift (ppm)


DR-6-60-13C
Figure S43 - Product 21
Br
N
N
O
129.20
127.00
124.13
36.43
12.46
154.02
129.37
134.78
77.47
77.15
76.83
90.45
162.12
36.83
19.18
Normalized Intensity
Chemical Shift (ppm)


DR-6-56-NaOHwash
Figure S44 - Product 22
O
N
N
Br
O
N
N
Normalized Intensity
0.25
0.24
0.23
0.22
0.21
0.20
0.19
0.18
0.17
0.16
0.15
0.14
0.13
0.12
0.11
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
3.00
3.00
3.02
11.5
11.0
10.5
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
-0.5
Chemical Shift (ppm)

**This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/**

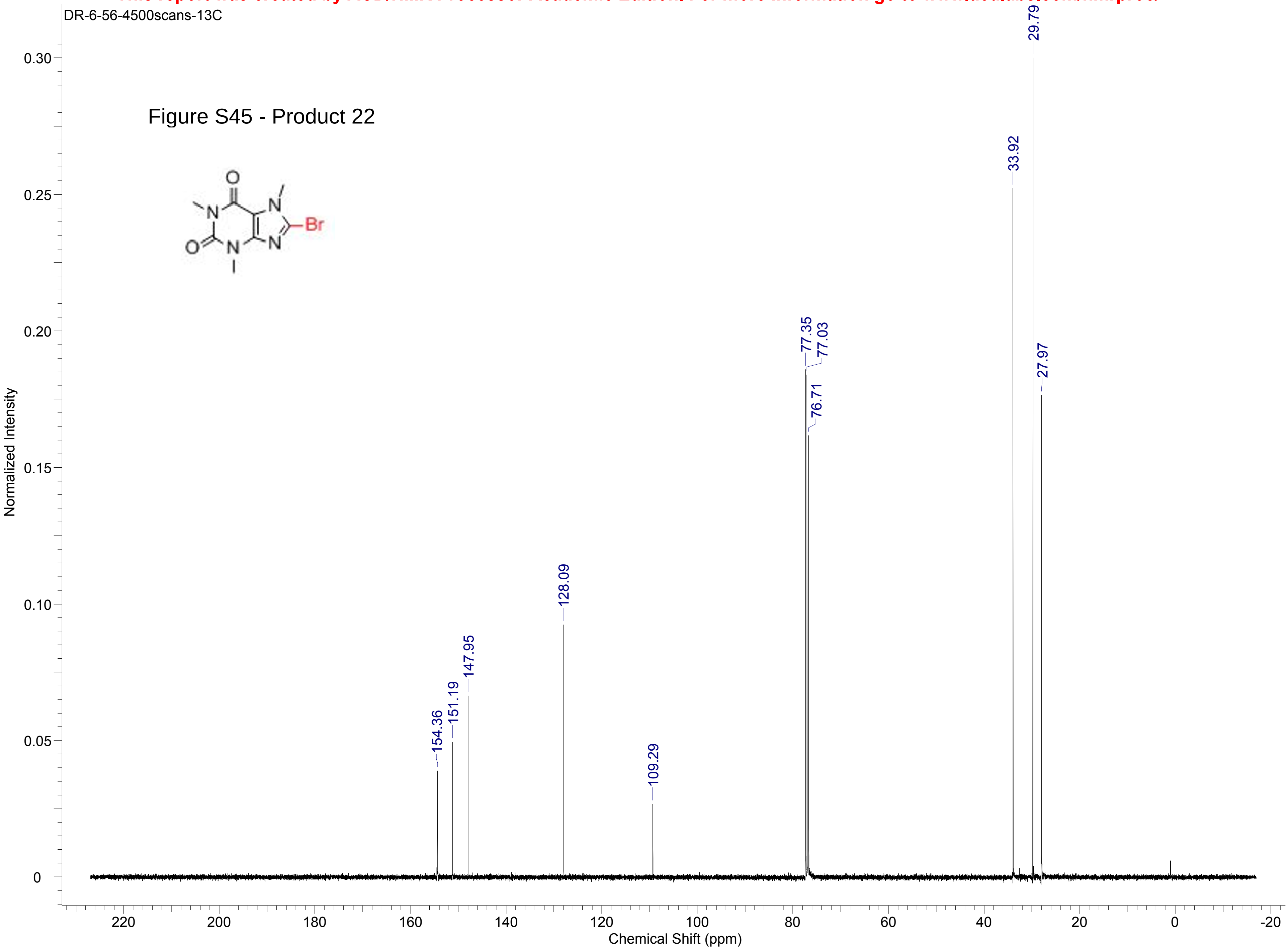



Figure S45 - Product 22

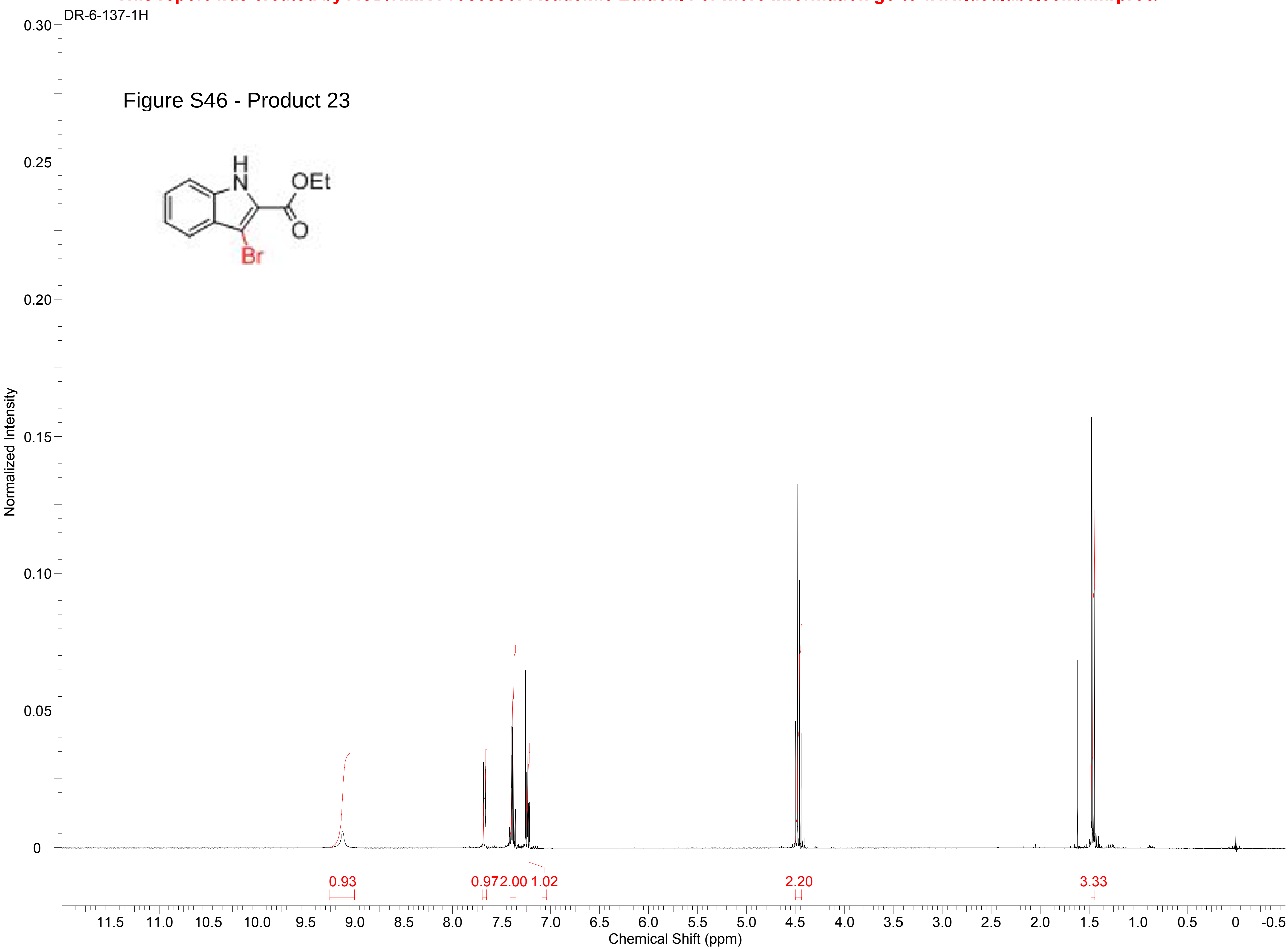
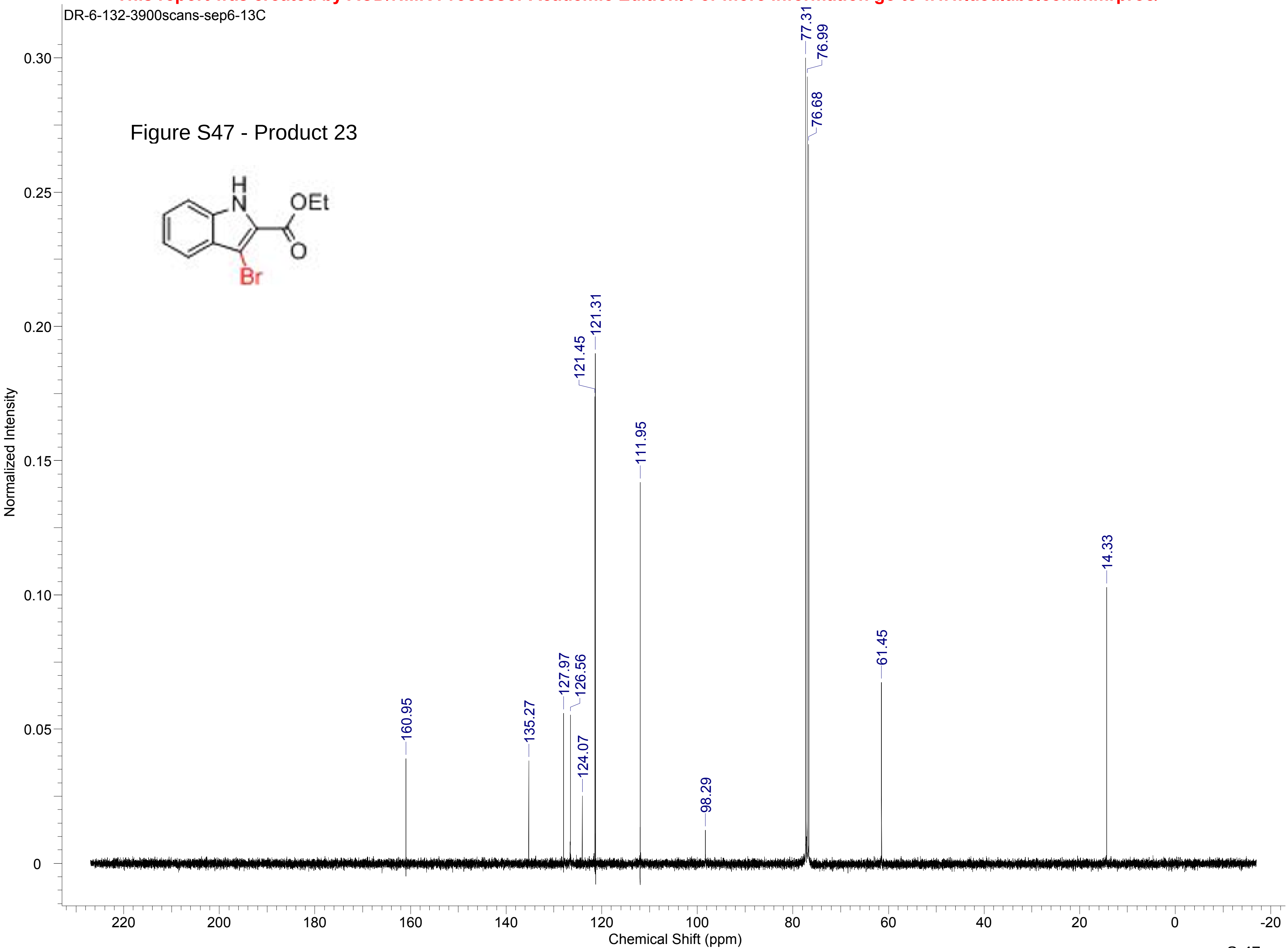
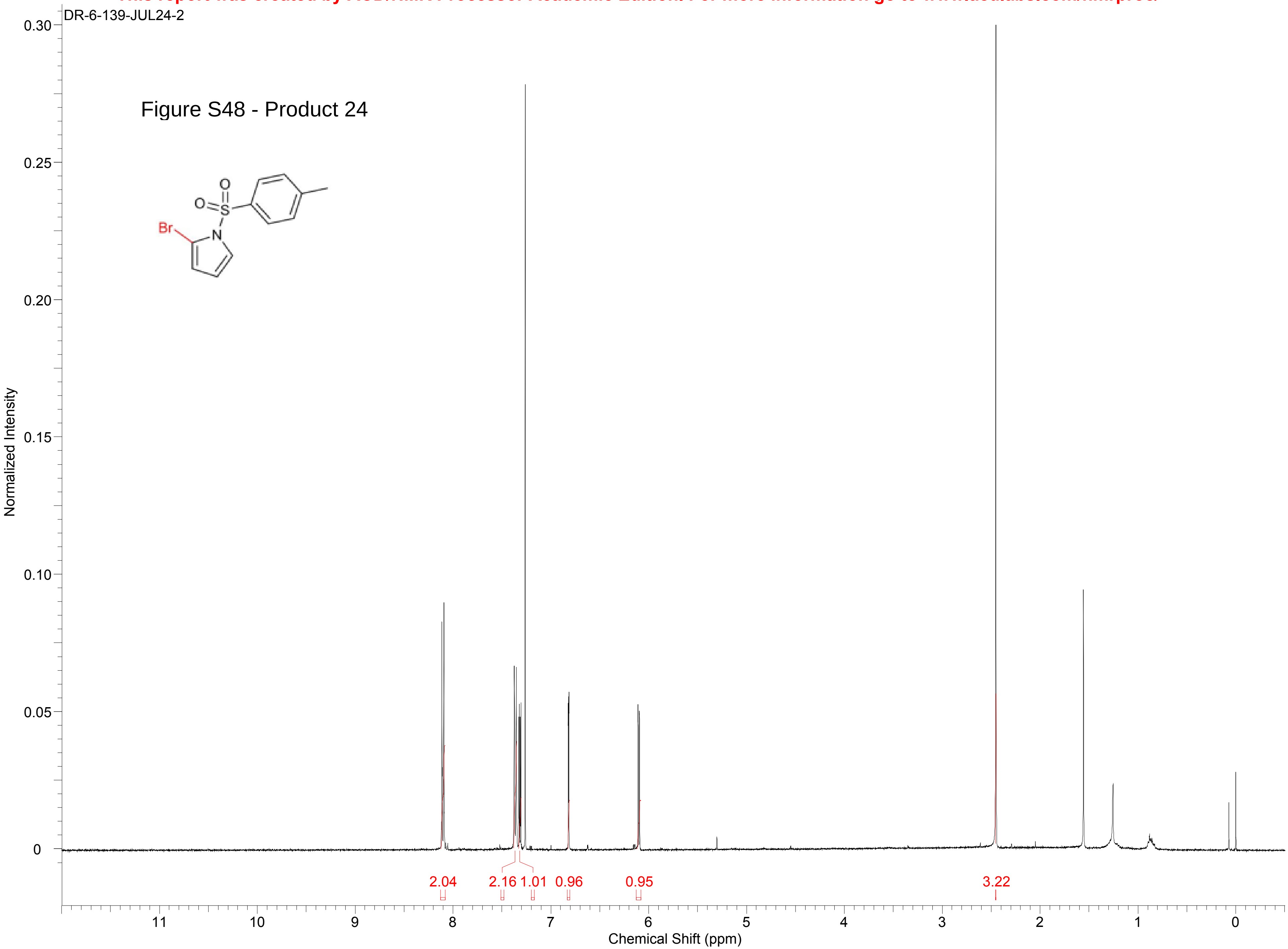
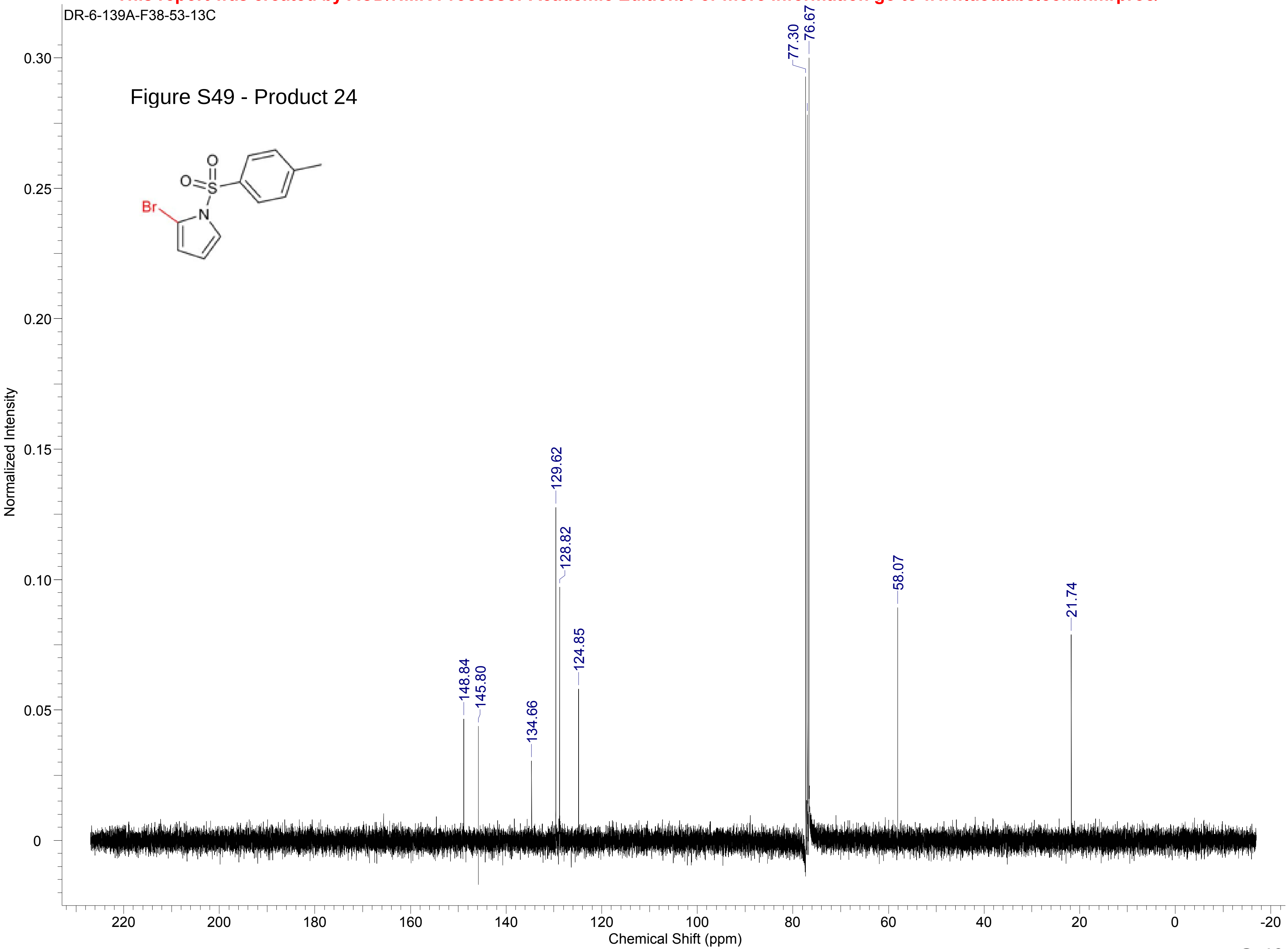

DR-6-137-1H
Figure S46 - Product 23
H
N
OEt
O
Br
Normalized Intensity
0.30
0.25
0.20
0.15
0.10
0.05
0
0.93
0.97
2.00
1.02
2.20
3.33
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
-0.5
Chemical Shift (ppm)

Figure S47 - Product 23




DR-6-139-JUL24-2
Figure S48 - Product 24
O
O
S
Br
N
Normalized Intensity
0.30
0.25
0.20
0.15
0.10
0.05
0
2.04
2.16
1.01
0.96
0.95
3.22
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


DR-6-139A-F38-53-13C
Figure S49 - Product 24
O
O
S
N
Br
77.30
76.67
129.62
128.82
124.85
148.84
145.80
134.66
58.07
21.74
Normalized Intensity
0.30
0.25
0.20
0.15
0.10
0.05
0
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)