

Supporting Information

Diastereoselective Synthesis of Glycopyrans 1,2-Annulated with Dioxazinanes from Anhydrosugars and N-substituted Nitrones

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HSQC Correlation of 3a

	¹ H	¹³ C
H-1	4.97 (d, <i>J</i> = 7.8 Hz, 1H)	97.8
H-2	3.50 (dd, <i>J</i> = 10.2, 7.8 Hz, 1H)	76.7
H-3	5.34 (t, <i>J</i> = 9.6 Hz, 1H)	71.4
H-4	5.11 (t, <i>J</i> = 9.6 Hz, 1H)	68.9
H-5	3.96 – 3.91 (m, 1H)	74.0
H-6a	4.26 (dd, <i>J</i> = 12.4, 4.7 Hz, 1H)	61.9
H-6b	4.19 (dd, <i>J</i> = 12.5, 2.1 Hz, 1H)	61.9
H-7	3.63 (s, 1H)	97.4

COSY Correlation of 3a

	¹ H	¹ H
H-1	4.97 (d, <i>J</i> = 7.8 Hz, 1H)	3.50 (dd, <i>J</i> = 10.2, 7.8 Hz, 1H)
H-2	3.50 (dd, <i>J</i> = 10.2, 7.8 Hz, 1H)	5.34 (t, <i>J</i> = 9.6 Hz, 1H), 3.50 (dd, <i>J</i> = 10.2, 7.8 Hz, 1H)
H-3	5.34 (t, <i>J</i> = 9.6 Hz, 1H)	3.50 (dd, <i>J</i> = 10.2, 7.8 Hz, 1H), 5.11 (t, <i>J</i> = 9.6 Hz, 1H)
H-4	5.11 (t, <i>J</i> = 9.6 Hz, 1H)	5.34 (t, <i>J</i> = 9.6 Hz, 1H), 3.96 – 3.91 (m, 1H)
H-5	3.96 – 3.91 (m, 1H)	5.11 (t, <i>J</i> = 9.6 Hz, 1H), 4.26 (dd, <i>J</i> = 12.4, 4.7 Hz, 1H)
H-6a	4.26 (dd, <i>J</i> = 12.4, 4.7 Hz, 1H)	3.96 – 3.91 (m, 1H)

NOESY Correlation of 3a

	¹ H	¹ H
H-1	4.97 (d, <i>J</i> = 7.8 Hz, 1H)	3.96 – 3.91 (m, 1H), 3.50 (dd, <i>J</i> = 10.2, 7.8 Hz, 1H), 5.34 (t, <i>J</i> = 9.6 Hz, 1H)

H-2	3.50 (dd, $J = 10.2, 7.8$ Hz, 1H)	3.63 (s, 1H)
H-3	5.34 (t, $J = 9.6$ Hz, 1H)	3.50 (dd, $J = 10.2, 7.8$ Hz, 1H), 4.97 (d, $J = 7.8$ Hz, 1H), 3.96 – 3.91 (m, 1H)
H-4	5.11 (t, $J = 9.6$ Hz, 1H)	3.50 (dd, $J = 10.2, 7.8$ Hz, 1H), 3.96 – 3.91 (m, 1H), 4.26 (dd, $J = 12.4, 4.7$ Hz, 1H), 5.34 (t, $J = 9.6$ Hz, 1H)
H-5	3.96 – 3.91 (m, 1H)	4.26 (dd, $J = 12.4, 4.7$ Hz, 1H), 4.97 (d, $J = 7.8$ Hz, 1H), 5.11 (t, $J = 9.6$ Hz, 1H)
H-6a	4.26 (dd, $J = 12.4, 4.7$ Hz, 1H)	3.96 – 3.91 (m, 1H)
H-7	3.63 (s, 1H)	3.50 (dd, $J = 10.2, 7.8$ Hz, 1H),

HSQC Correlation of compound 4b

	^1H	^{13}C
H-1, CH ₂ of OBn	4.89 – 4.81 (m, 3H)	99.3, 76.8
H-7	4.79 (s, 1H)	98.6
CH ₂ of OBn	4.66 (dd, $J = 28.6, 11.8$ Hz, 2H)	76.0, 75.1
CH ₂ of OBn	4.52 (dd, $J = 11.2, 9.1$ Hz, 2H)	76.8, 75.1
H-3, H-4, H-6a, H-6b	3.85 – 3.72 (m, 4H)	82.6, 78.9, 70.0
H-5	3.68 (d, $J = 9.4$ Hz, 1H)	78.7
H-2	3.49 (t, $J = 8.5$ Hz, 1H)	81.8
N-CH ₃	2.40 (s, 3H)	42.3

COSY Correlation of 4b

	^1H	^1H
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H-1	4.89 – 4.81 (m, 3H)	3.49 (t, $J = 8.5$ Hz, 1H)
H-2	3.49 (t, $J = 8.5$ Hz, 1H)	3.49 (t, $J = 8.5$ Hz, 1H), 4.89 – 4.81 (m, 3H),
H-3	3.85 – 3.72 (m, 4H)	3.49 (t, $J = 8.5$ Hz, 1H), 3.85 – 3.72 (m, 4H)
H-4	3.85 – 3.72 (m, 4H)	3.85 – 3.72 (m, 4H), 3.68 (d, $J = 9.4$ Hz, 1H)
H-5	3.68 (d, $J = 9.4$ Hz, 1H)	3.85 – 3.72 (m, 4H)
H-6a,b	3.85 – 3.72 (m, 4H)	3.85 – 3.72 (m, 4H)

NOESY Correlation of 4b

	¹ H	¹ H
H-1	4.89 – 4.81 (m, 3H)	3.85 – 3.72 (m, 4H), 3.68 (d, $J = 9.4$ Hz, 1H)
H-2	3.49 (t, $J = 8.5$ Hz, 1H)	3.85 – 3.72 (m, 4H), 4.79 (s, 1H)
H-3	3.85 – 3.72 (m, 4H)	3.68 (d, $J = 9.4$ Hz, 1H), 4.89 – 4.81 (m, 3H)
H-4	3.85 – 3.72 (m, 4H)	3.49 (t, $J = 8.5$ Hz, 1H)
H-5	3.68 (d, $J = 9.4$ Hz, 1H)	3.85 – 3.72 (m, 4H), 4.89 – 4.81 (m, 3H)
H-7	4.79 (s, 1H)	2.40 (s, 1H), 3.49 (t, $J = 8.5$ Hz, 1H)

HSQC Correlation of 4j

	¹ H	¹³ C
H-1	4.80 (d, $J = 7.6$ Hz, 1H)	99.0

H-2	4.01 (dd, $J = 10.3, 7.7$ Hz, 1H)	77.7
H-3	3.78 (t, $J = 6.4$ Hz, 1H)	75.9
H-4	3.70 – 3.63 (m, 3H)	78.1
H-5	3.97 (d, $J = 2.1$ Hz, 1H)	74.6
H-6a,b	3.70 – 3.63 (m, 3H)	68.2
H-7	4.83 (s, 1H)	97.8

COSY Correlation of 4j

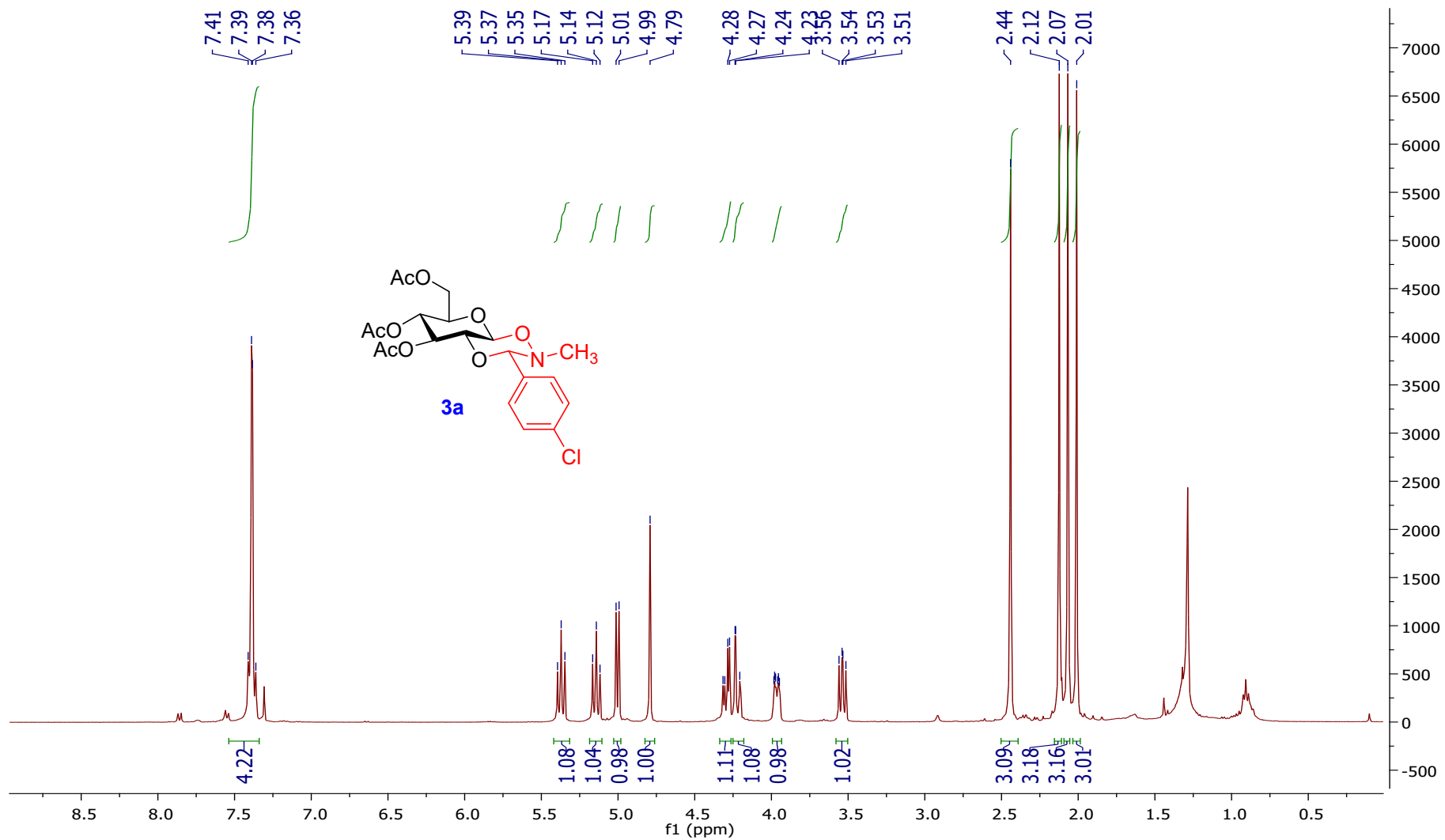
	¹ H	¹ H
H-1	4.80 (d, $J = 7.6$ Hz, 1H)	4.01 (dd, $J = 10.3, 7.7$ Hz, 1H)
H-2	4.01 (dd, $J = 10.3, 7.7$ Hz, 1H)	3.78 (t, $J = 6.4$ Hz, 1H)
H-3	3.78 (t, $J = 6.4$ Hz, 1H)	3.70 – 3.63 (m, 3H)
H-4	3.70 – 3.63 (m, 3H)	3.97 (d, $J = 2.1$ Hz, 1H)
H-5	3.97 (d, $J = 2.1$ Hz, 1H)	3.70 – 3.63 (m, 3H)
H-6a,b	3.70 – 3.63 (m, 3H)	3.97 (d, $J = 2.1$ Hz, 1H)

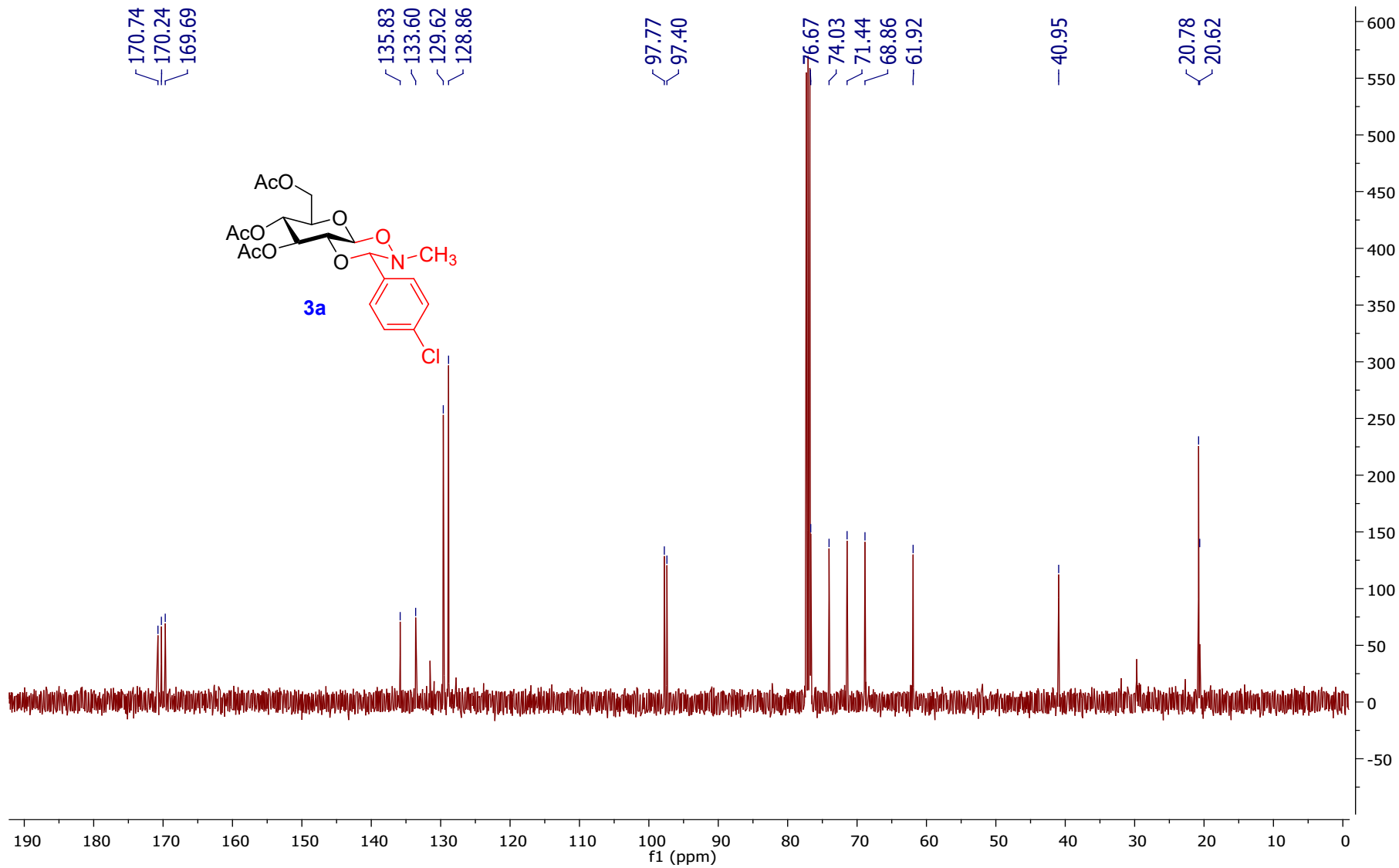
NOESY Correlation of 4j

	¹ H	¹ H
H-1	4.80 (d, $J = 7.6$ Hz, 1H)	5.34 (t, $J = 9.6$ Hz, 1H), 3.96 – 3.91 (m, 1H)

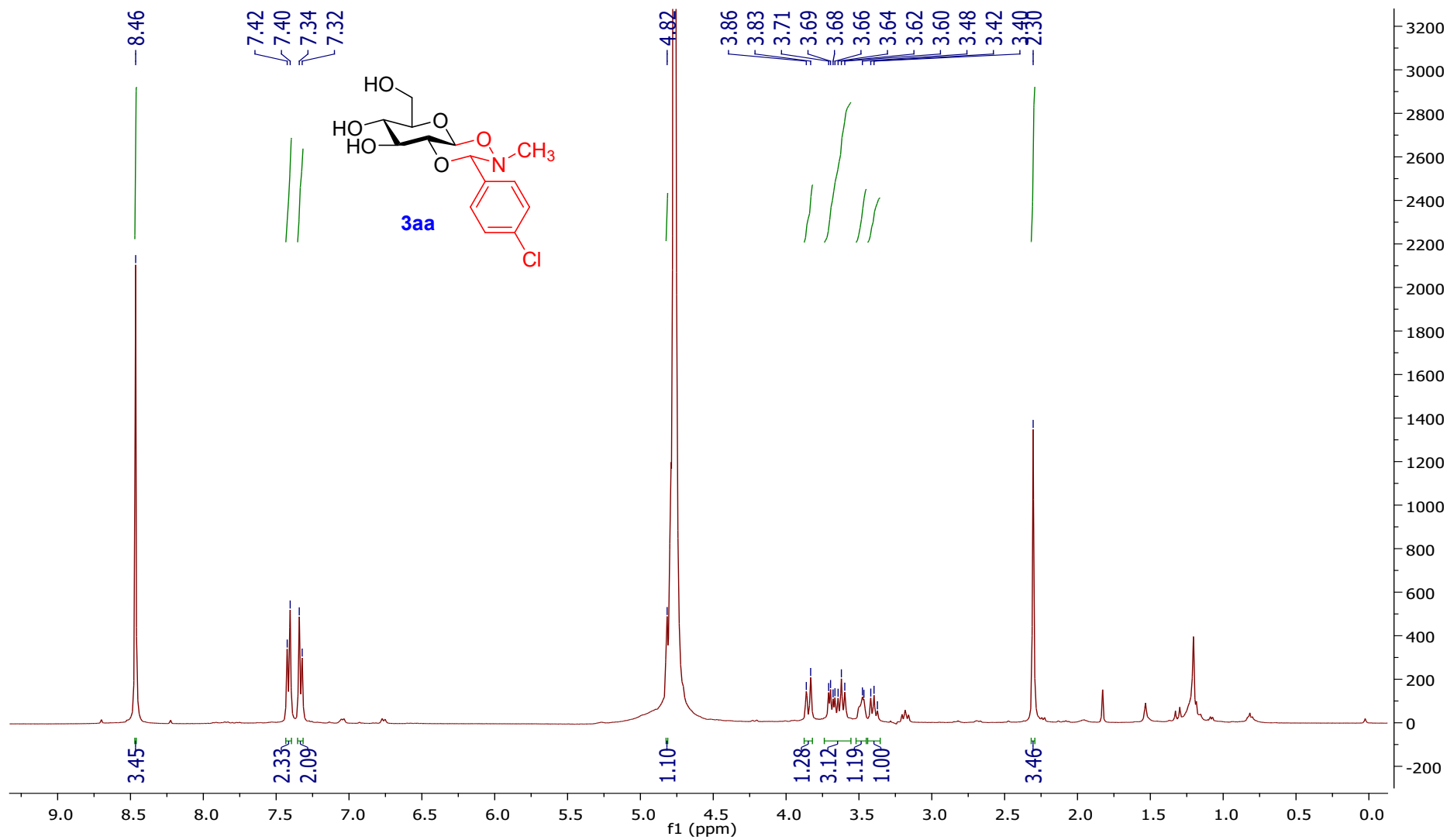
H-2	4.01 (dd, $J = 10.3, 7.7$ Hz, 1H)	4.83 (s, 1H)
H-3	3.78 (t, $J = 6.4$ Hz, 1H)	4.80 (d, $J = 7.6$ Hz, 1H), 3.97 (d, $J = 2.1$ Hz, 1H)
H-4	3.70 – 3.63 (m, 3H)	-----
H-5	3.97 (d, $J = 2.1$ Hz, 1H)	3.78 (t, $J = 6.4$ Hz, 1H), 4.80 (d, $J = 7.6$ Hz, 1H)
H-7	4.83 (s, 1H)	4.01 (dd, $J = 10.3, 7.7$ Hz, 1H)

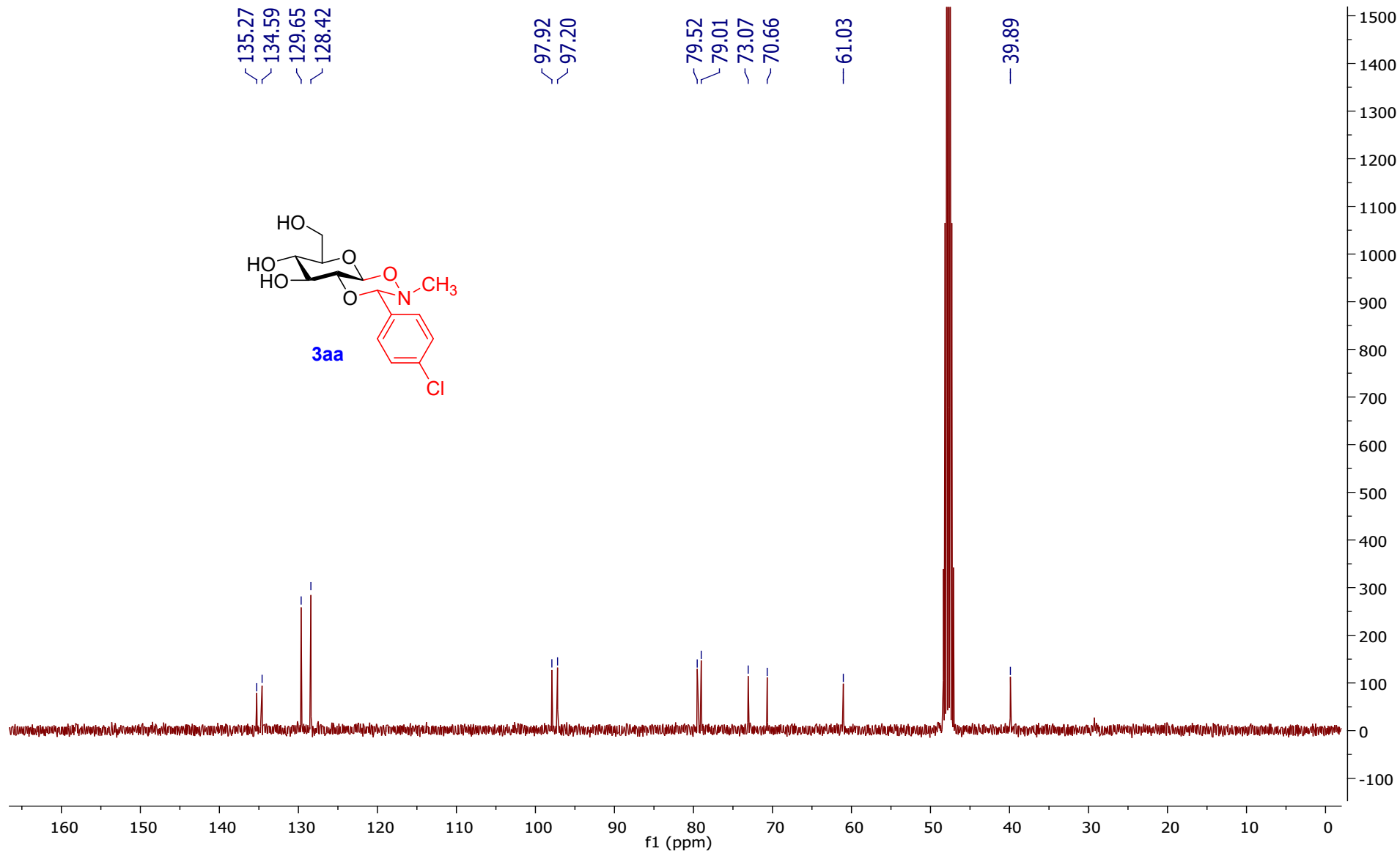
¹H NMR (400 MHz) and ¹³C NMR (126 MHz) of compound 3a



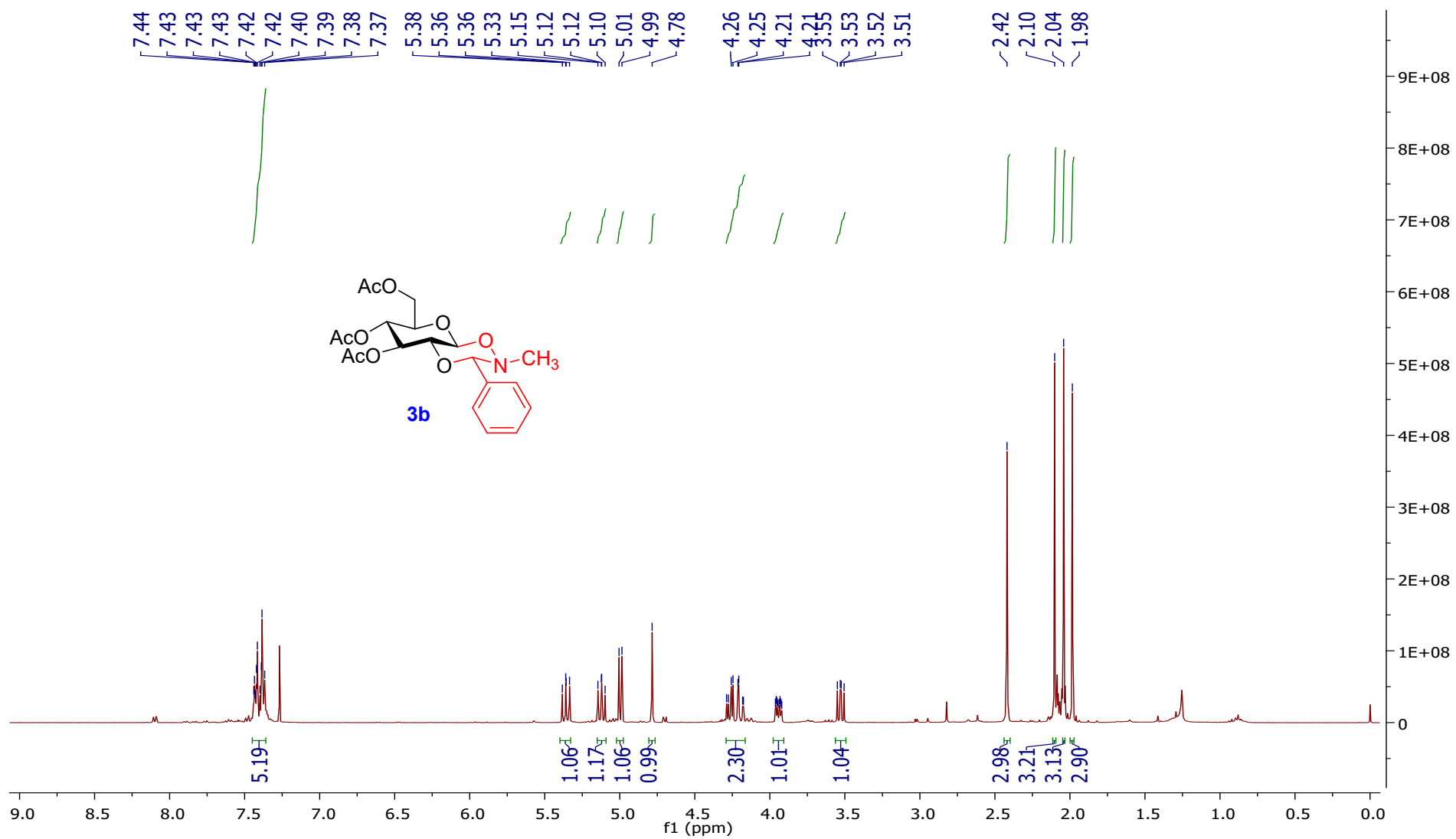


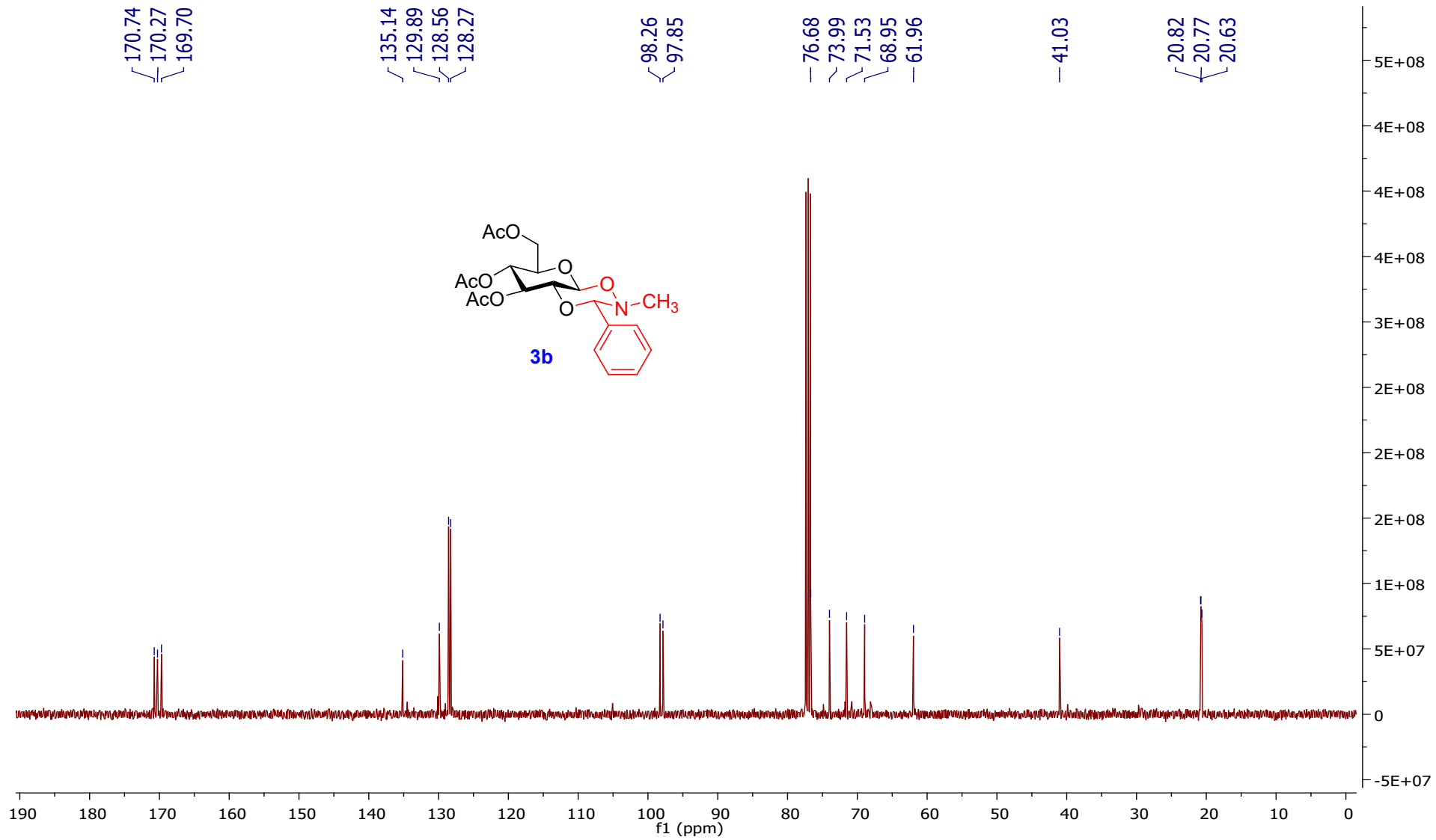
¹H NMR (400 MHz) and ¹³C NMR (101 MHz) of compound 3aa



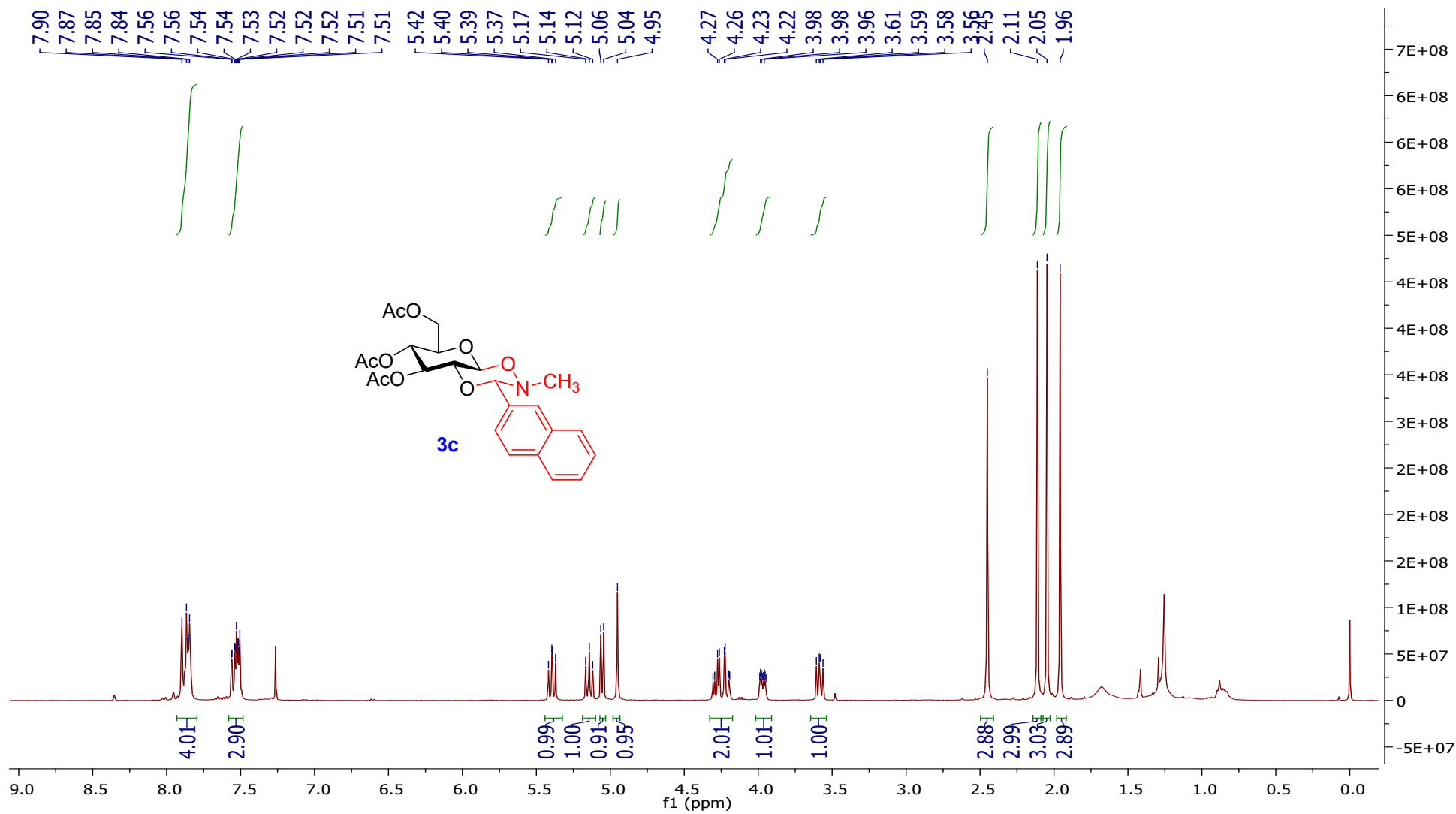


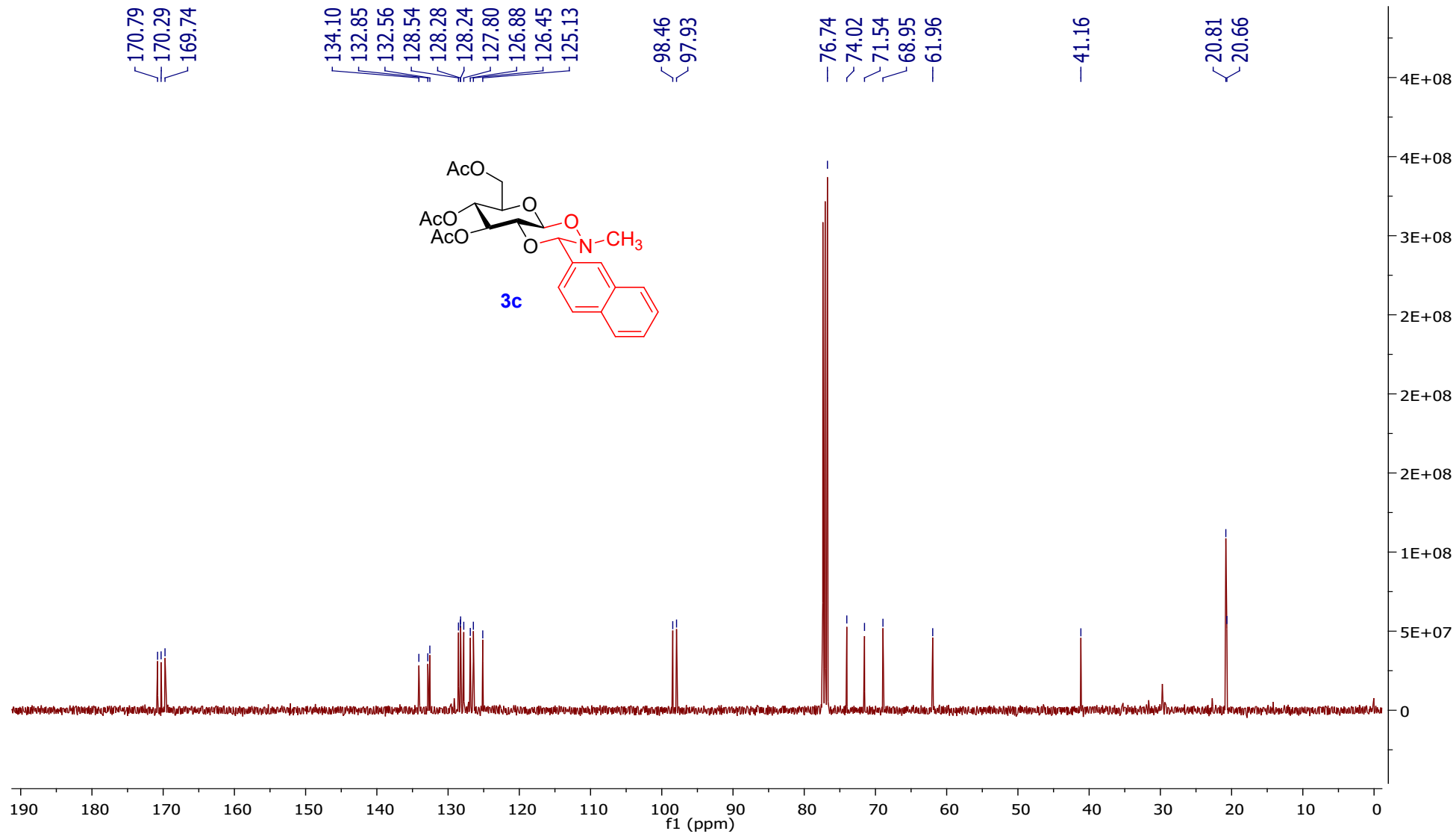
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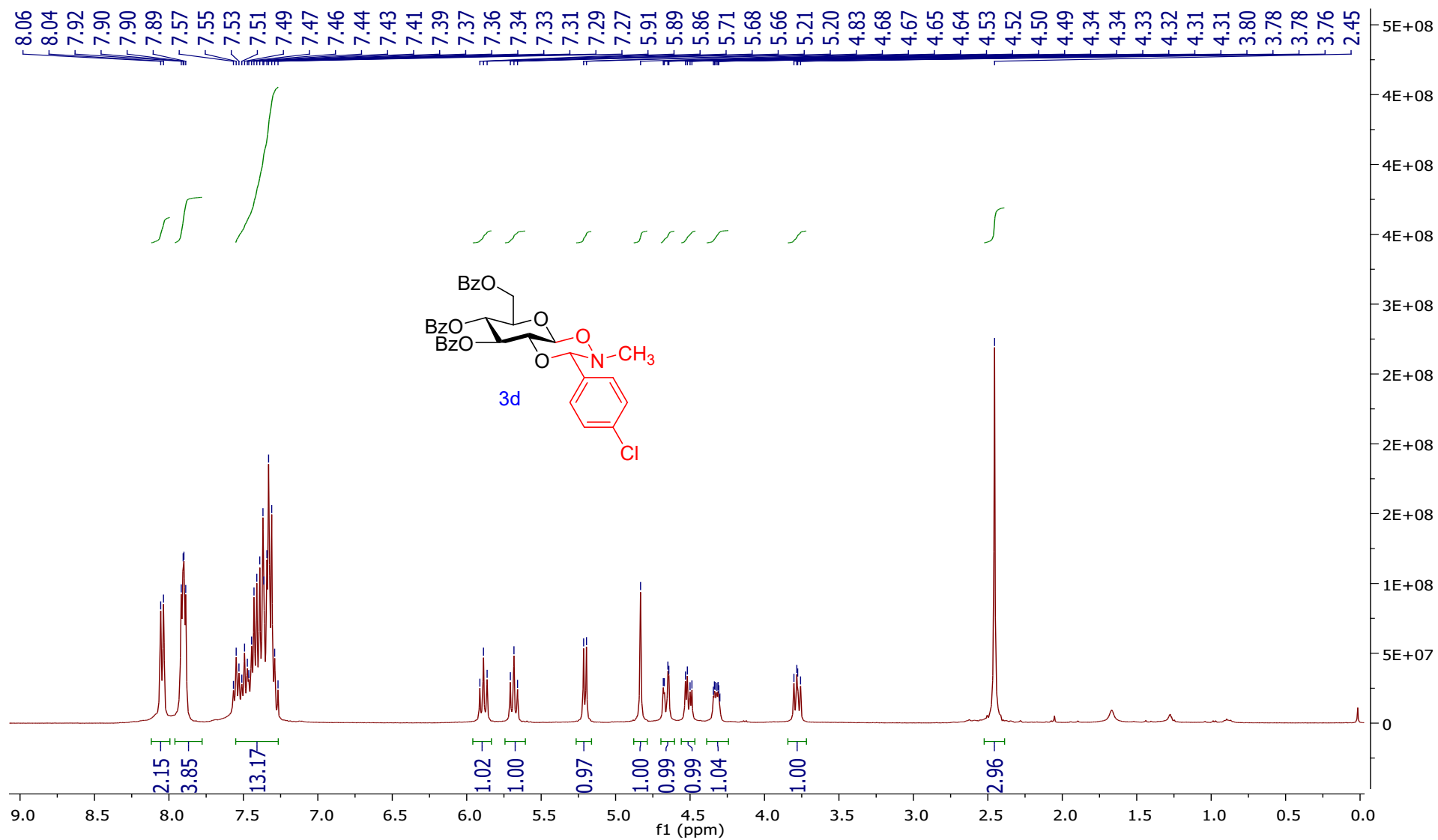


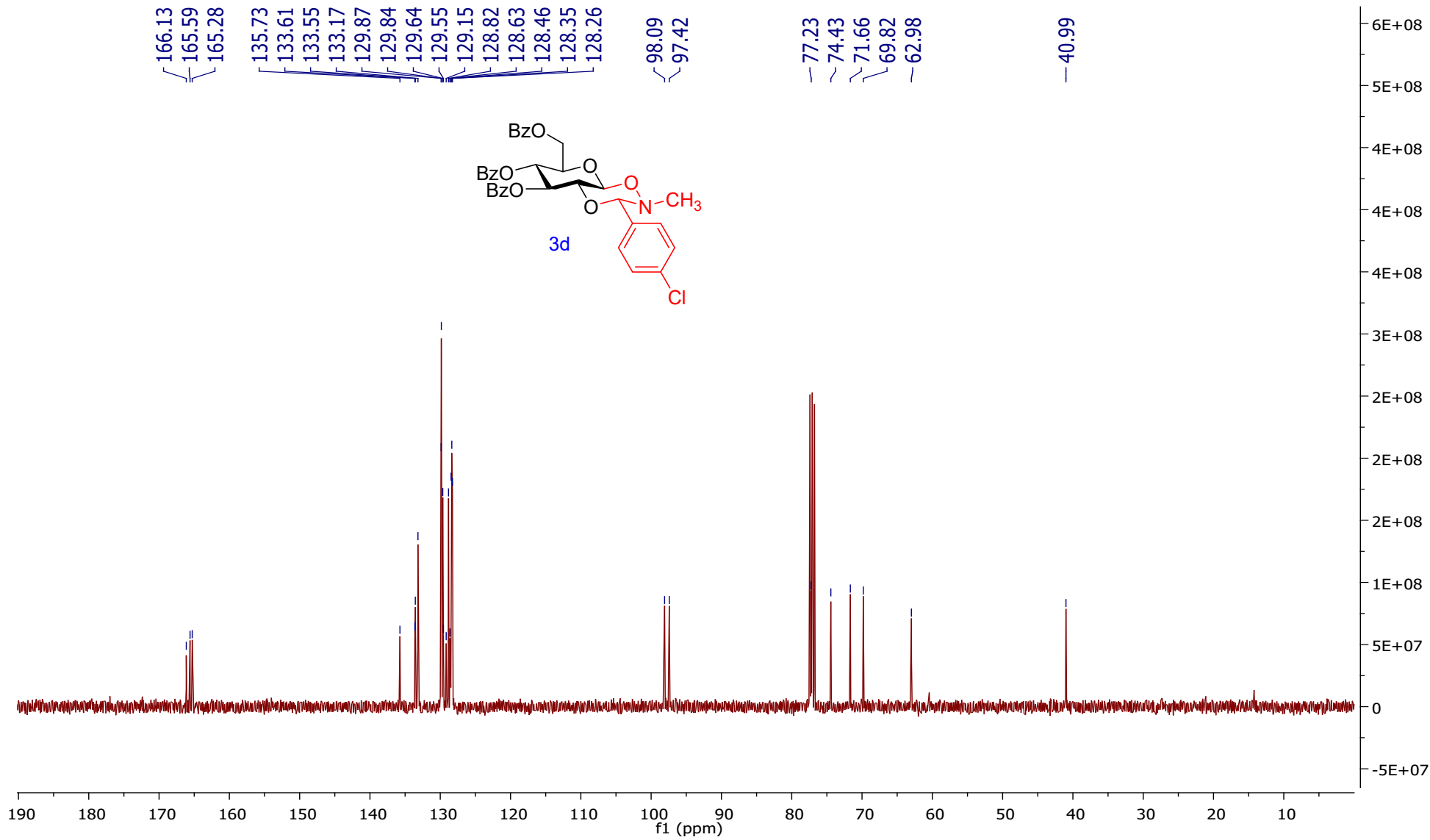
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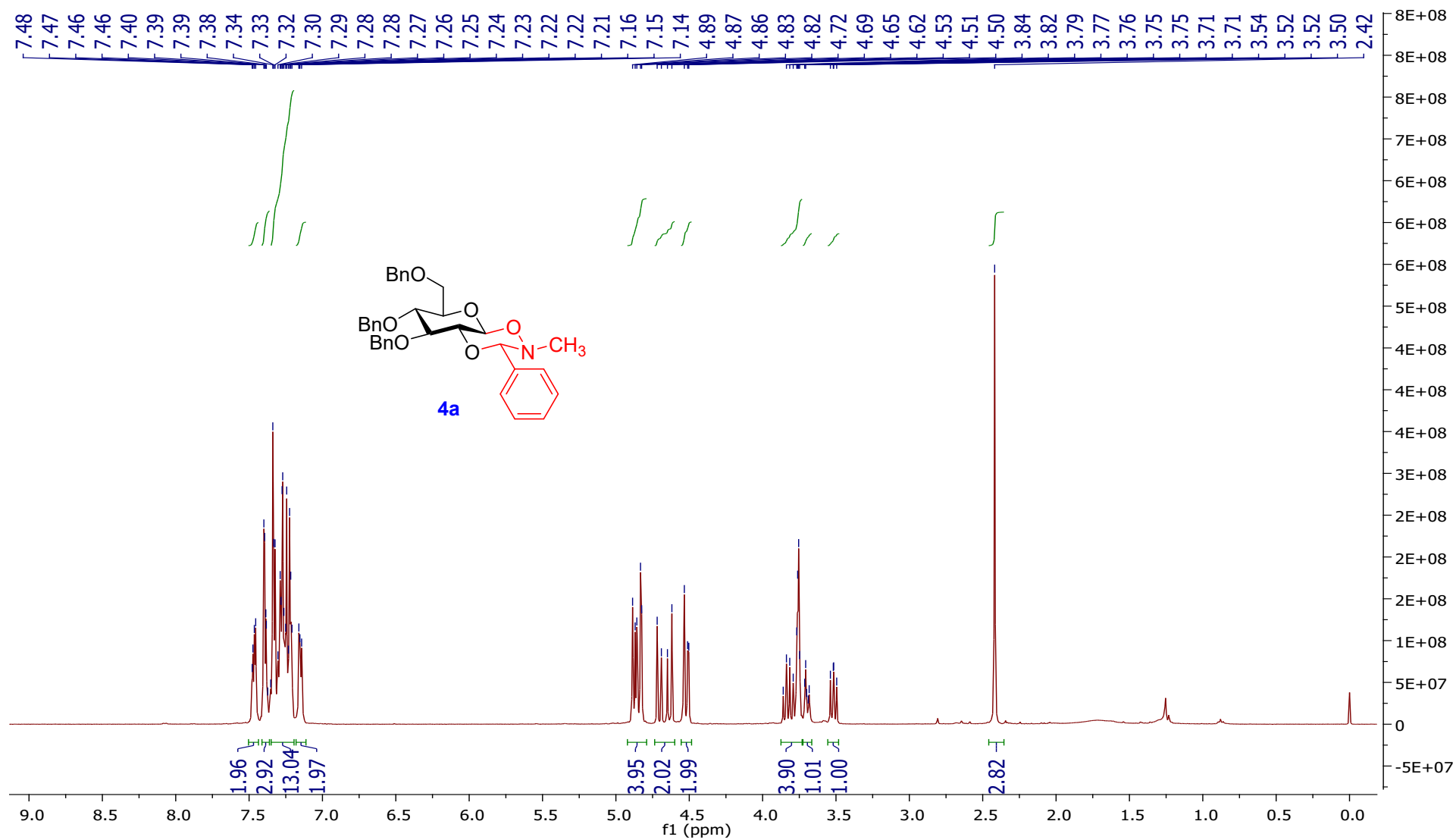


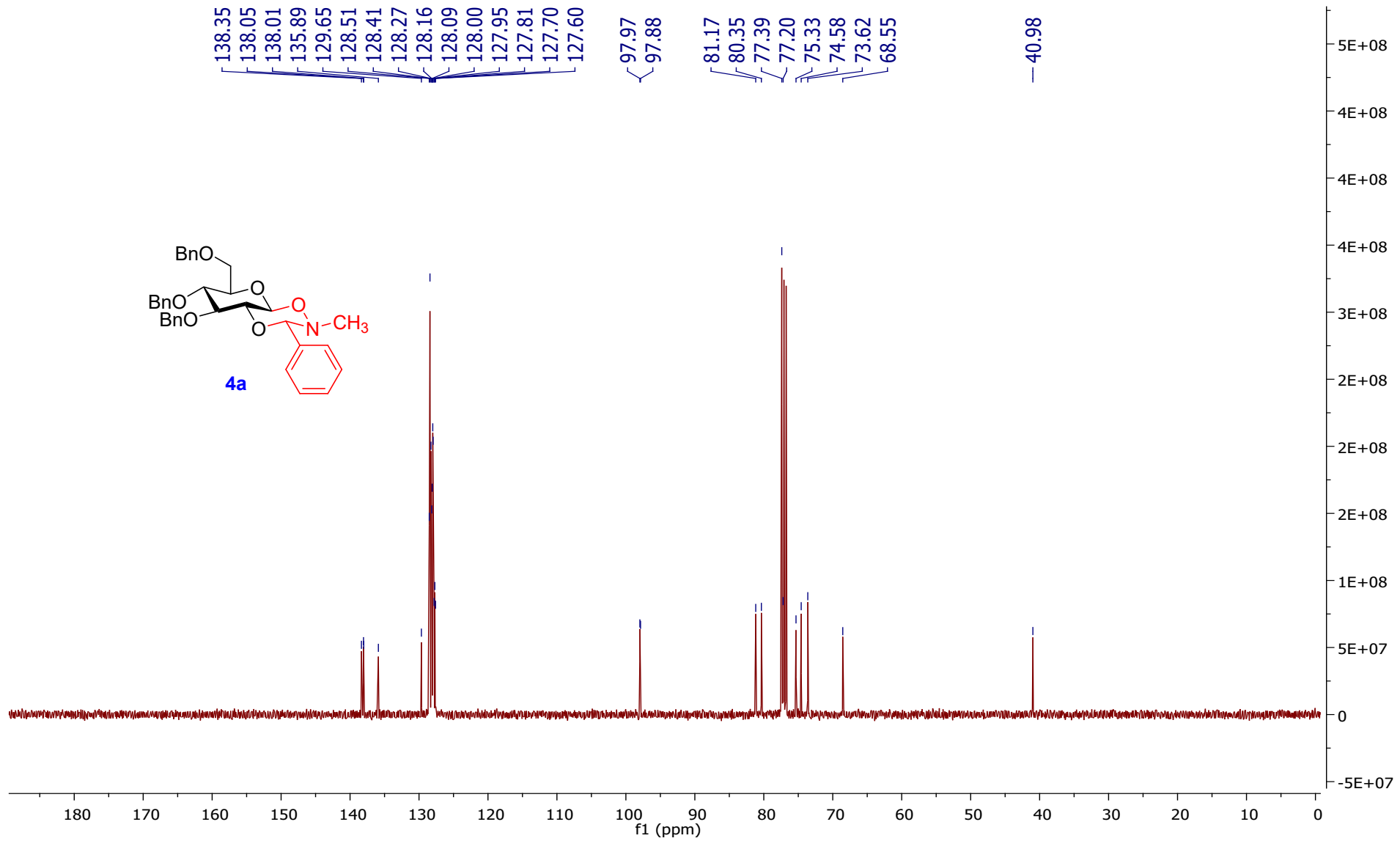
¹H NMR (400 MHz) and ¹³C NMR (101 MHz) of compound 3d



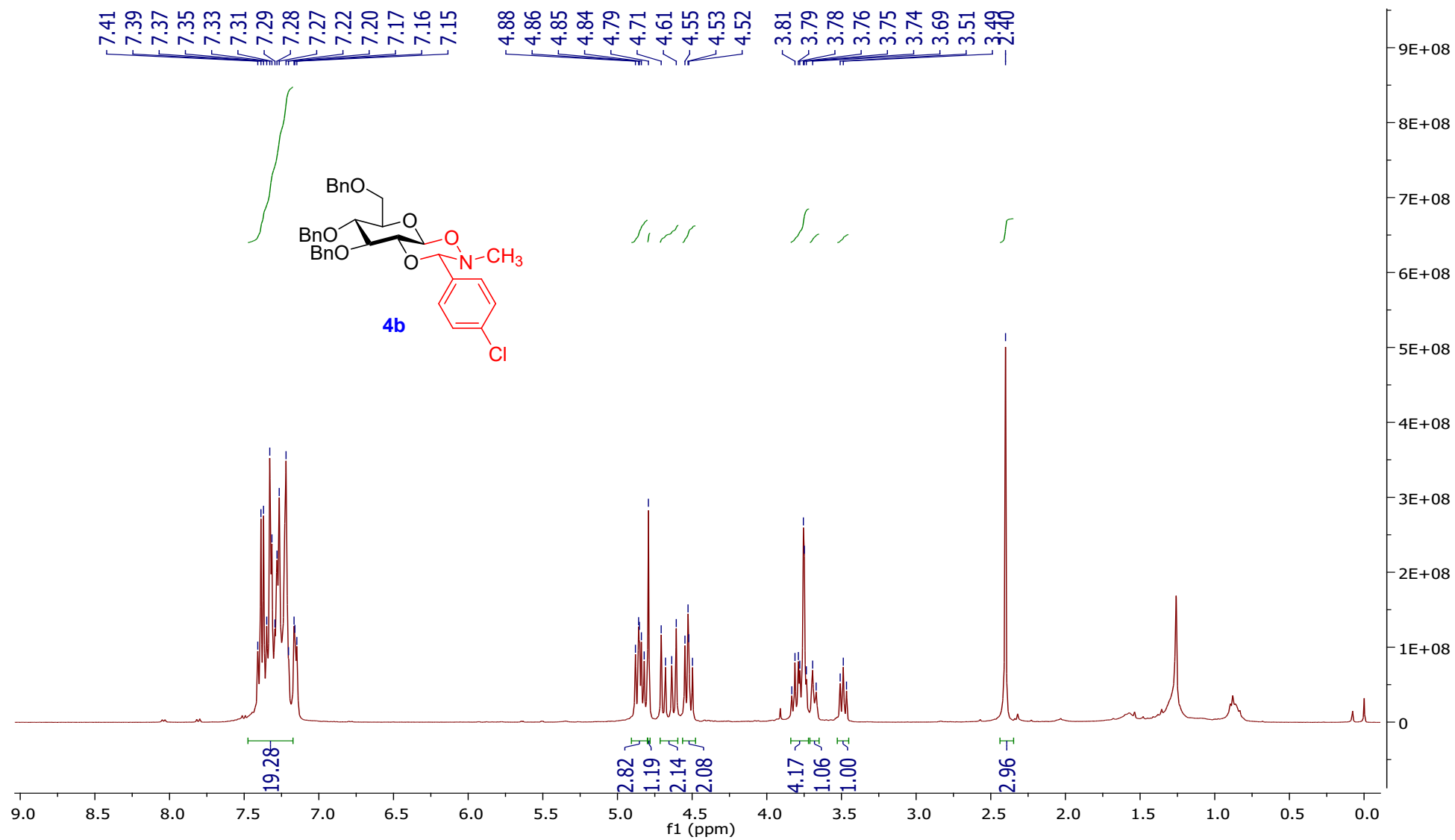


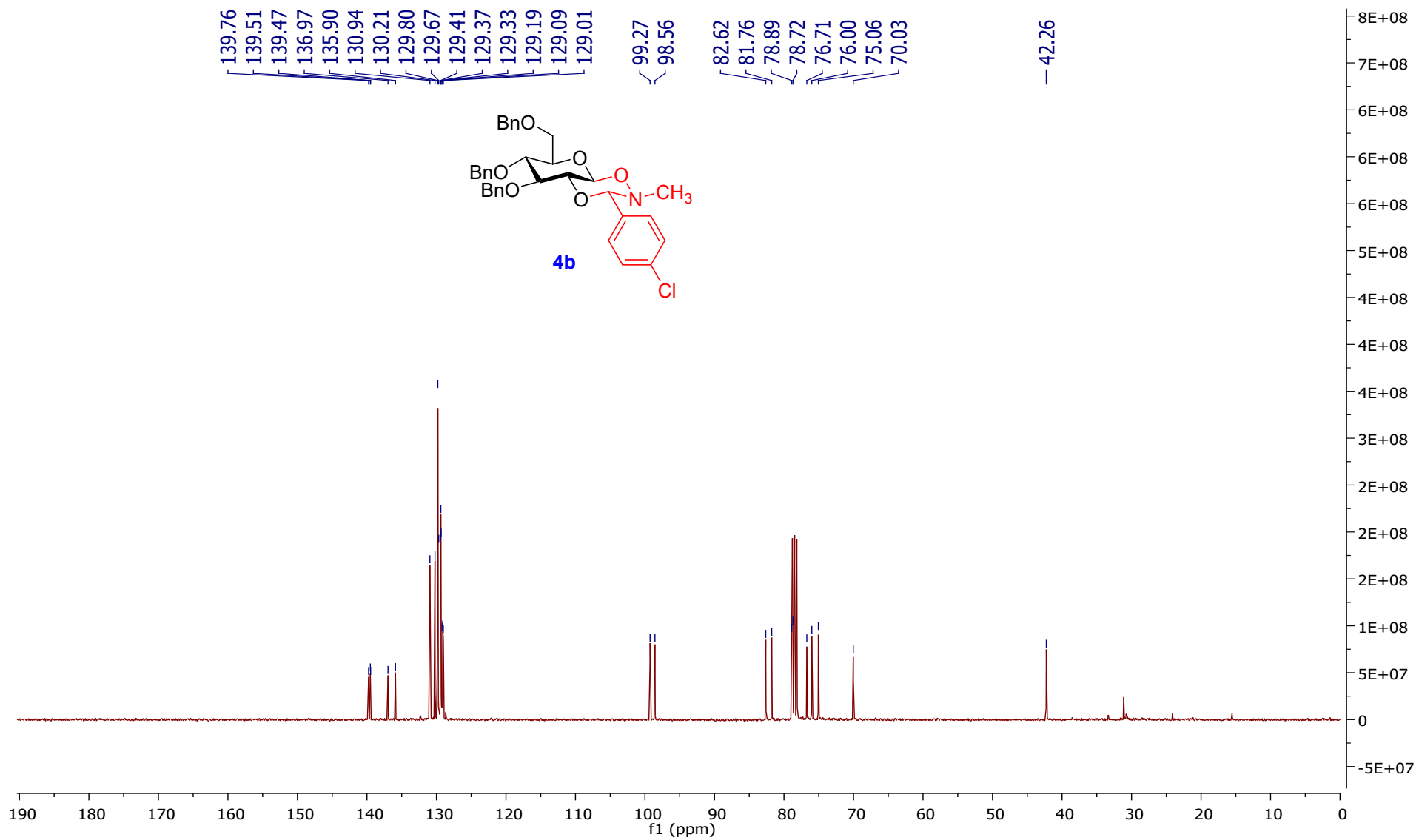
^1H NMR (400 MHz) and ^{13}C NMR (101 MHz) of compound 4a



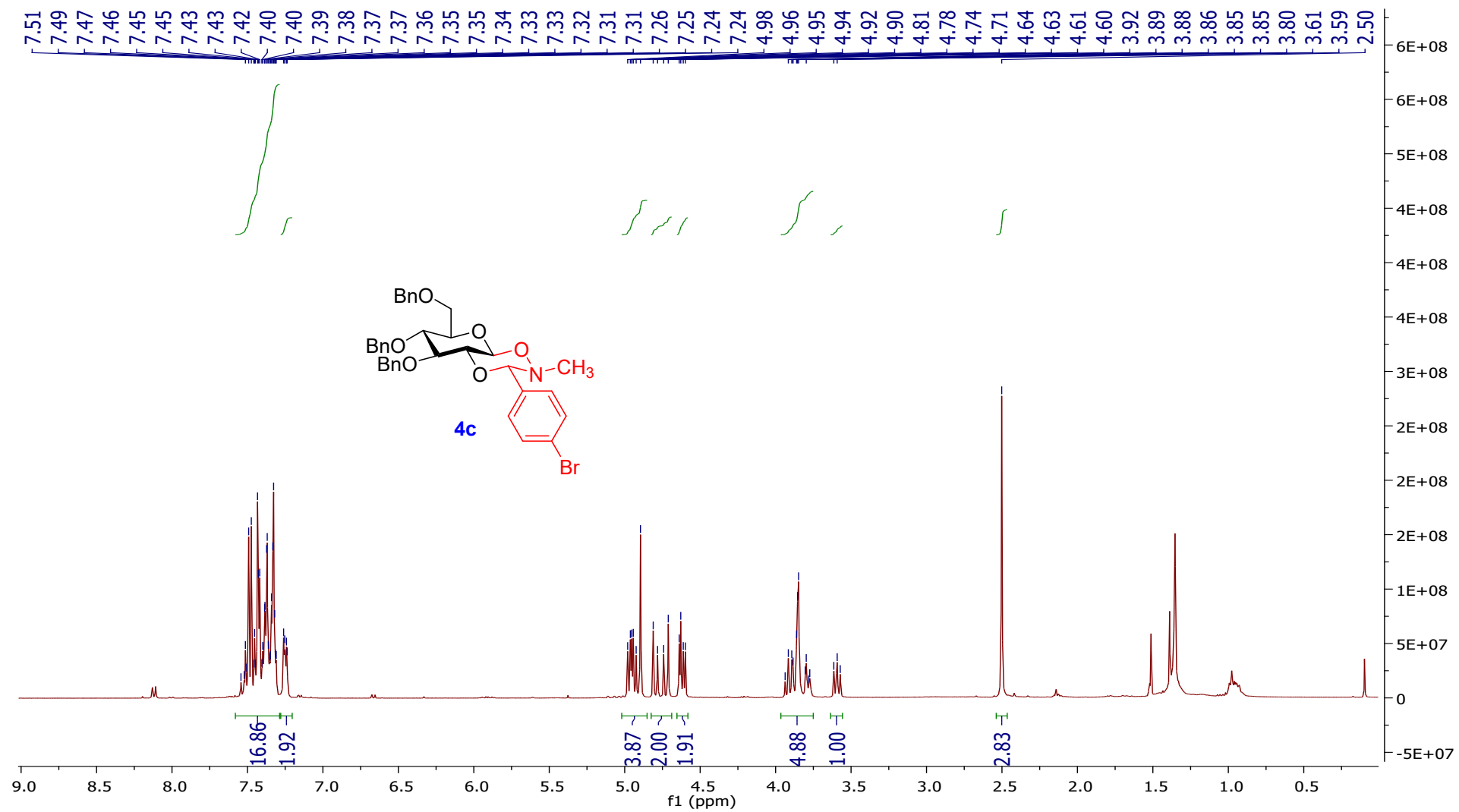


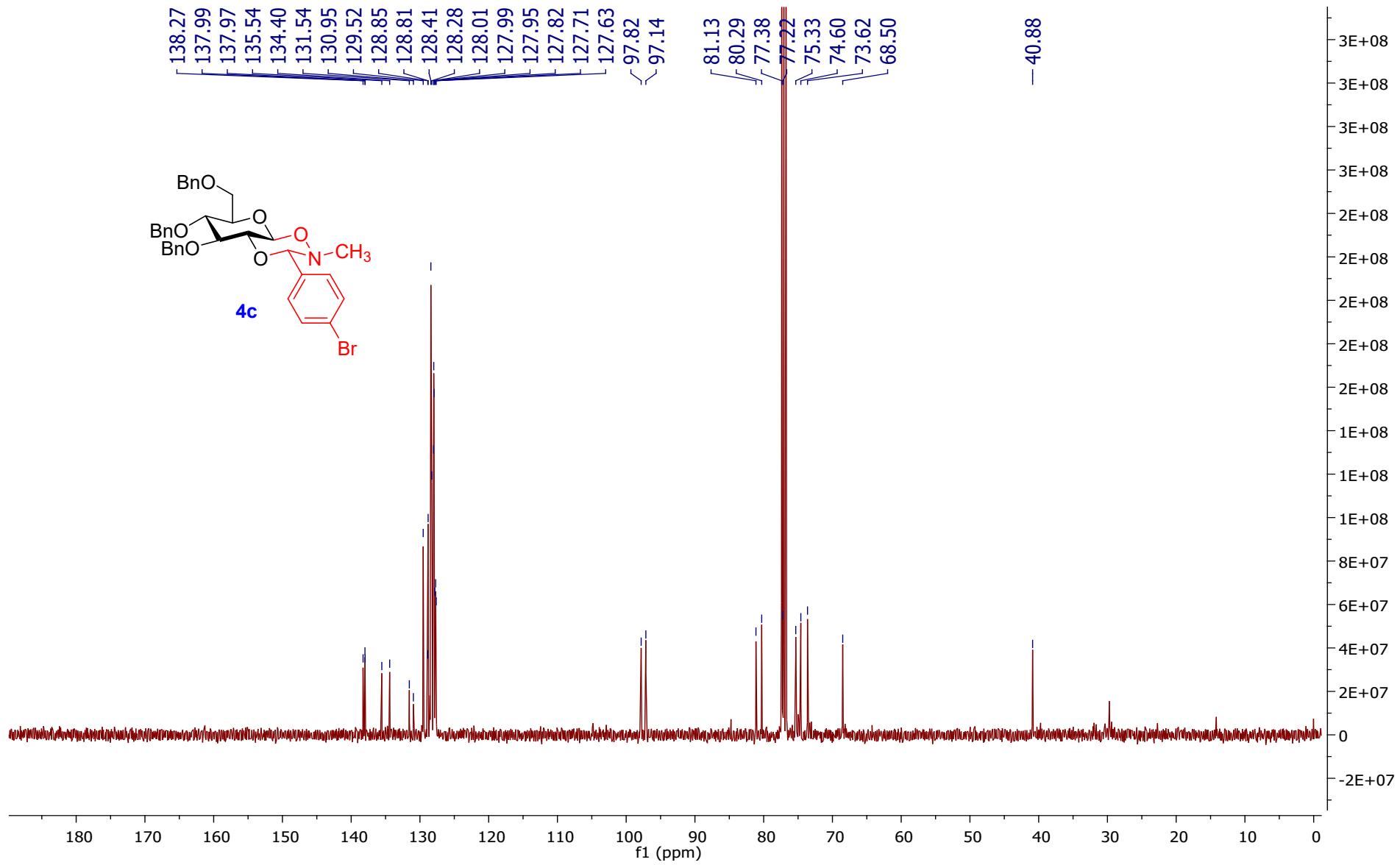
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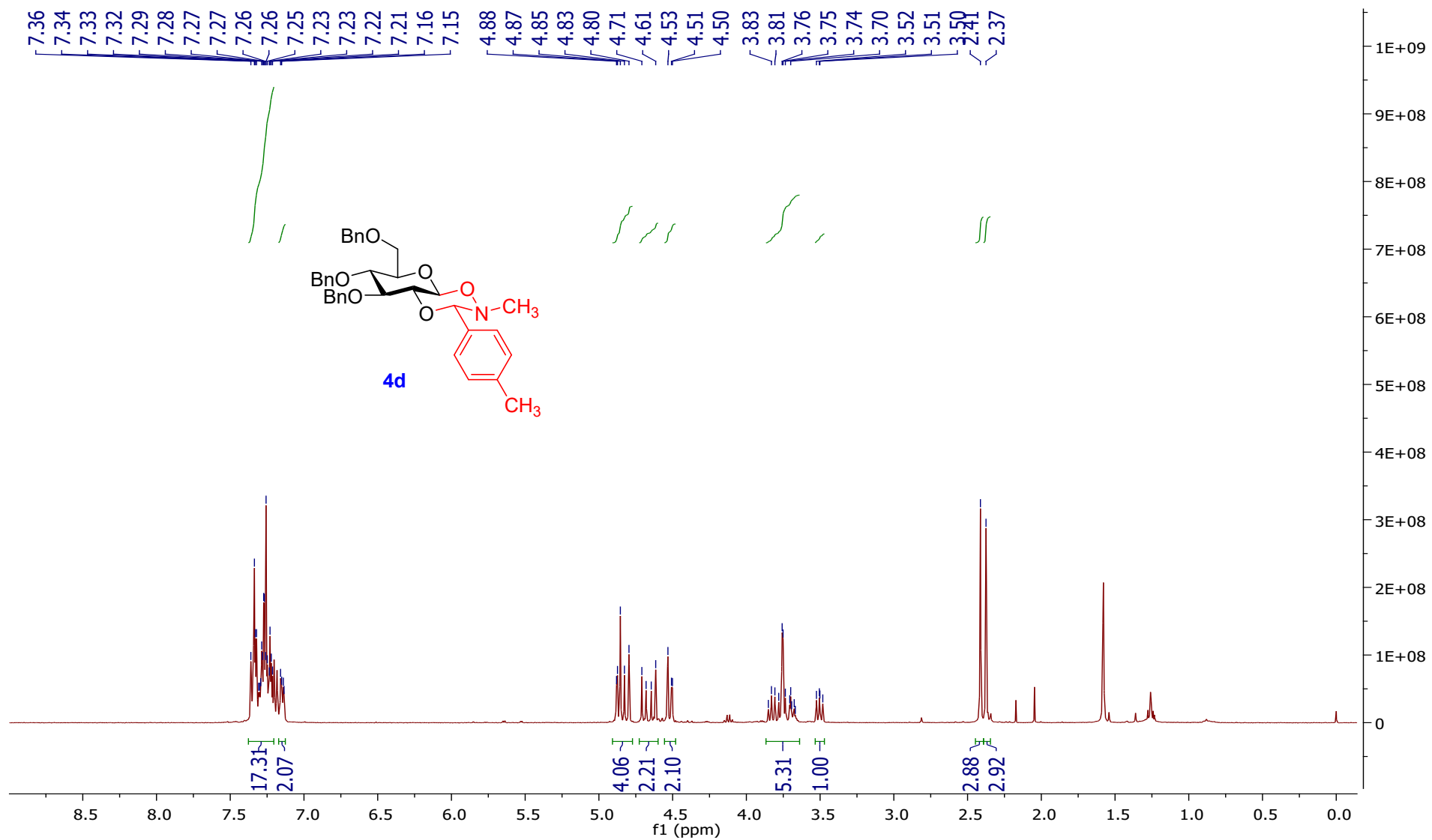


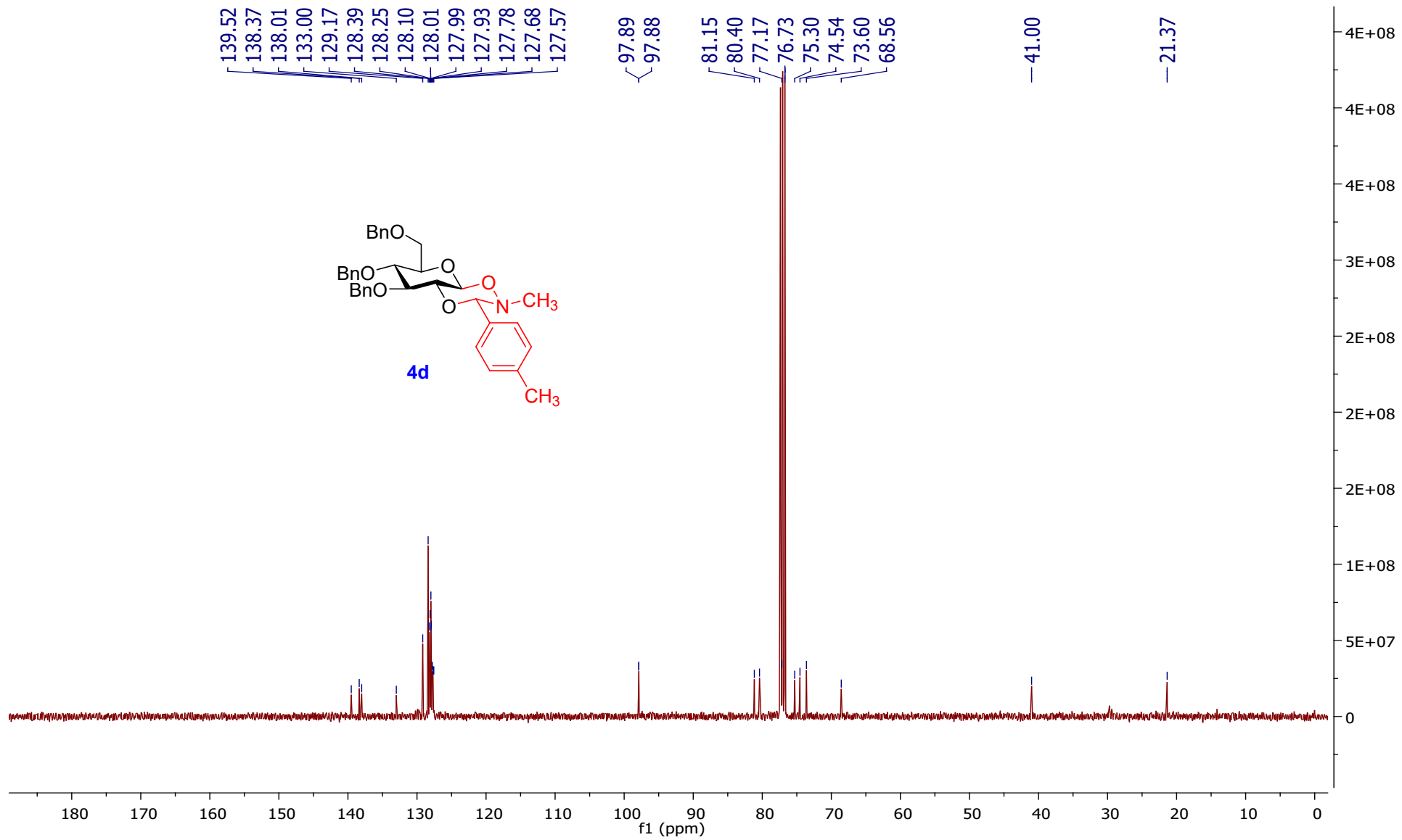
¹H NMR (400 MHz) and ¹³C NMR (101 MHz) of compound 4c



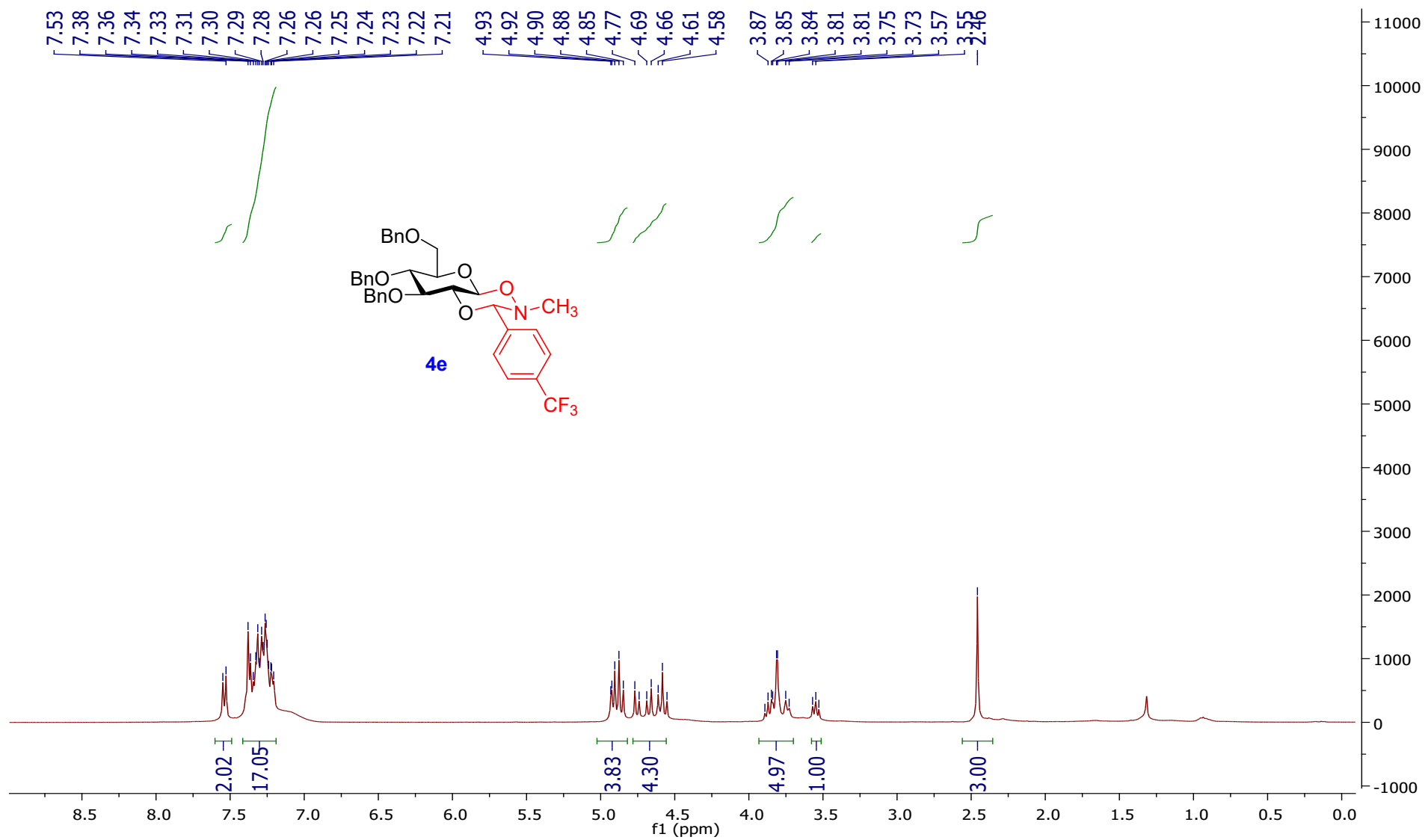


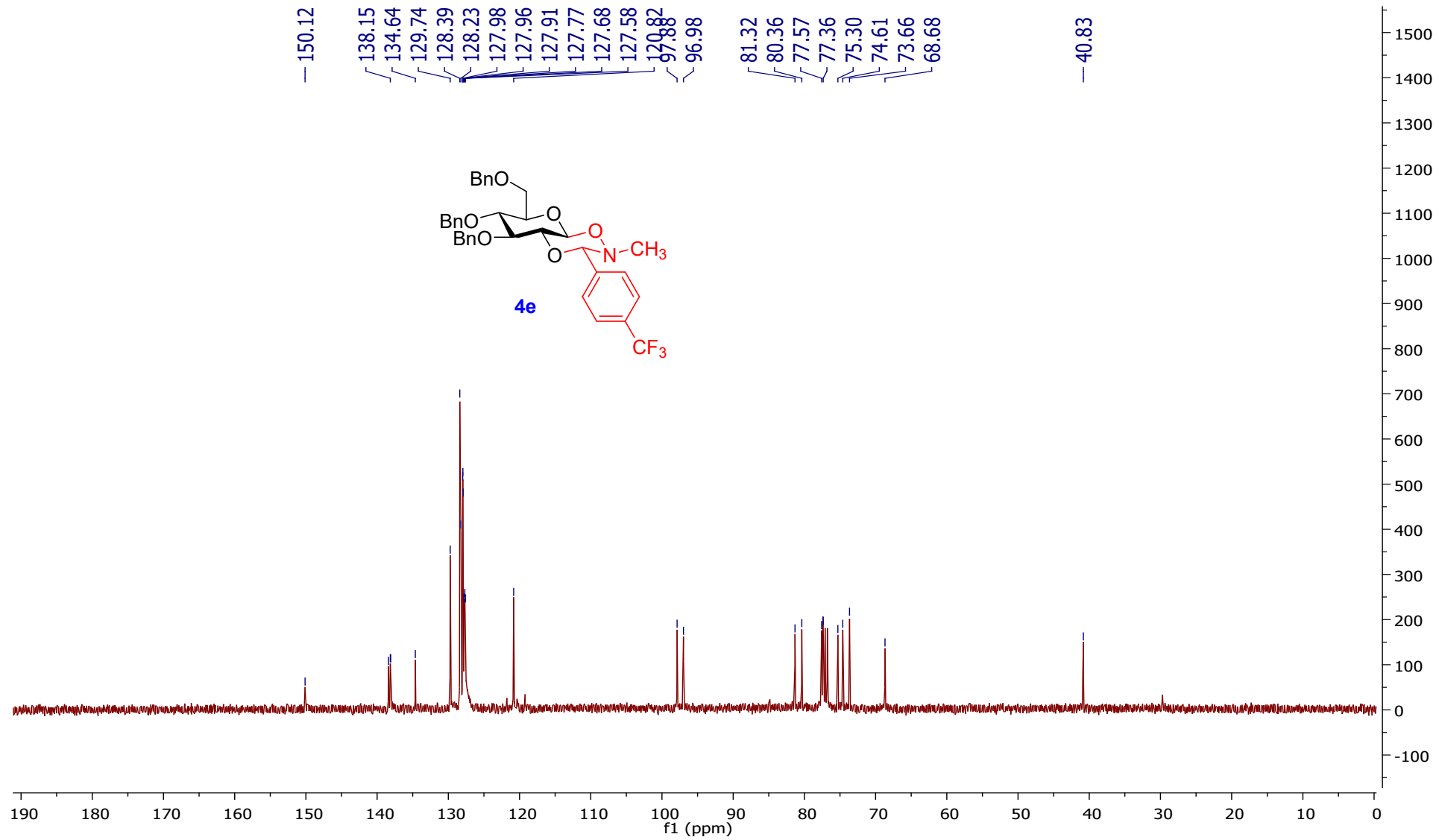
¹H NMR (400 MHz) and ¹³C NMR (101 MHz) of compound 4d



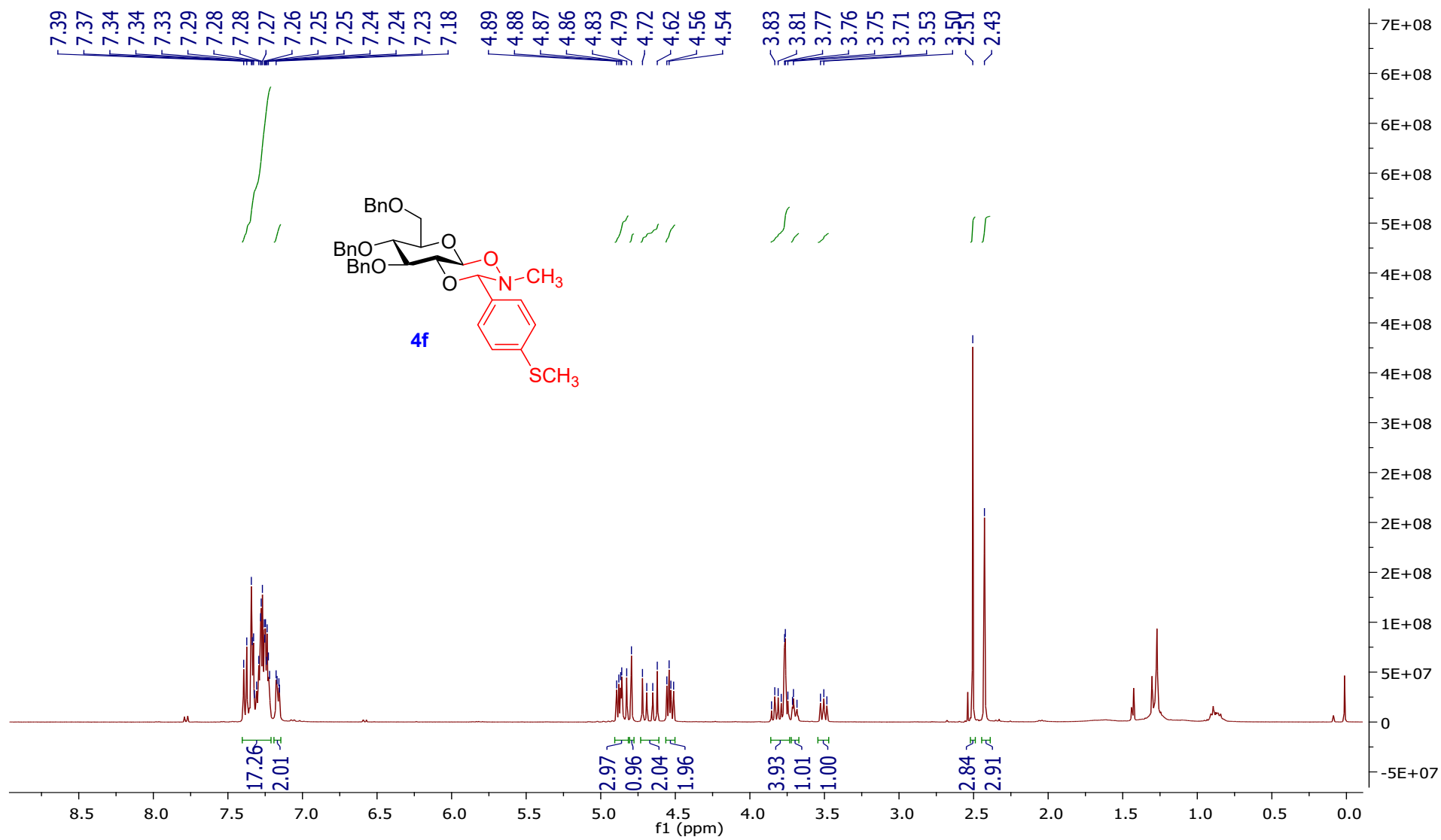


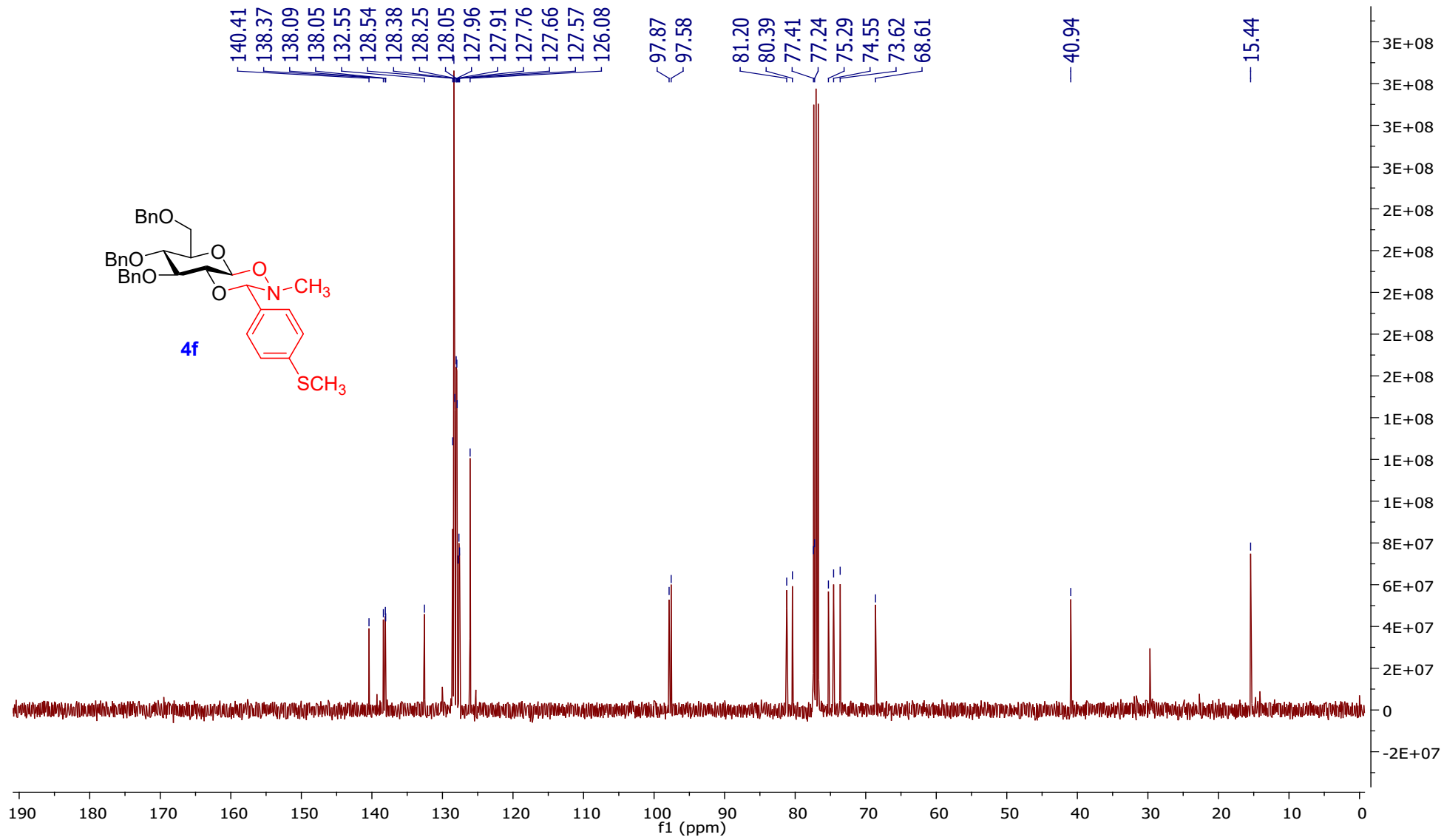
¹H NMR (400 MHz) and ¹³C NMR (101 MHz) of compound 4e



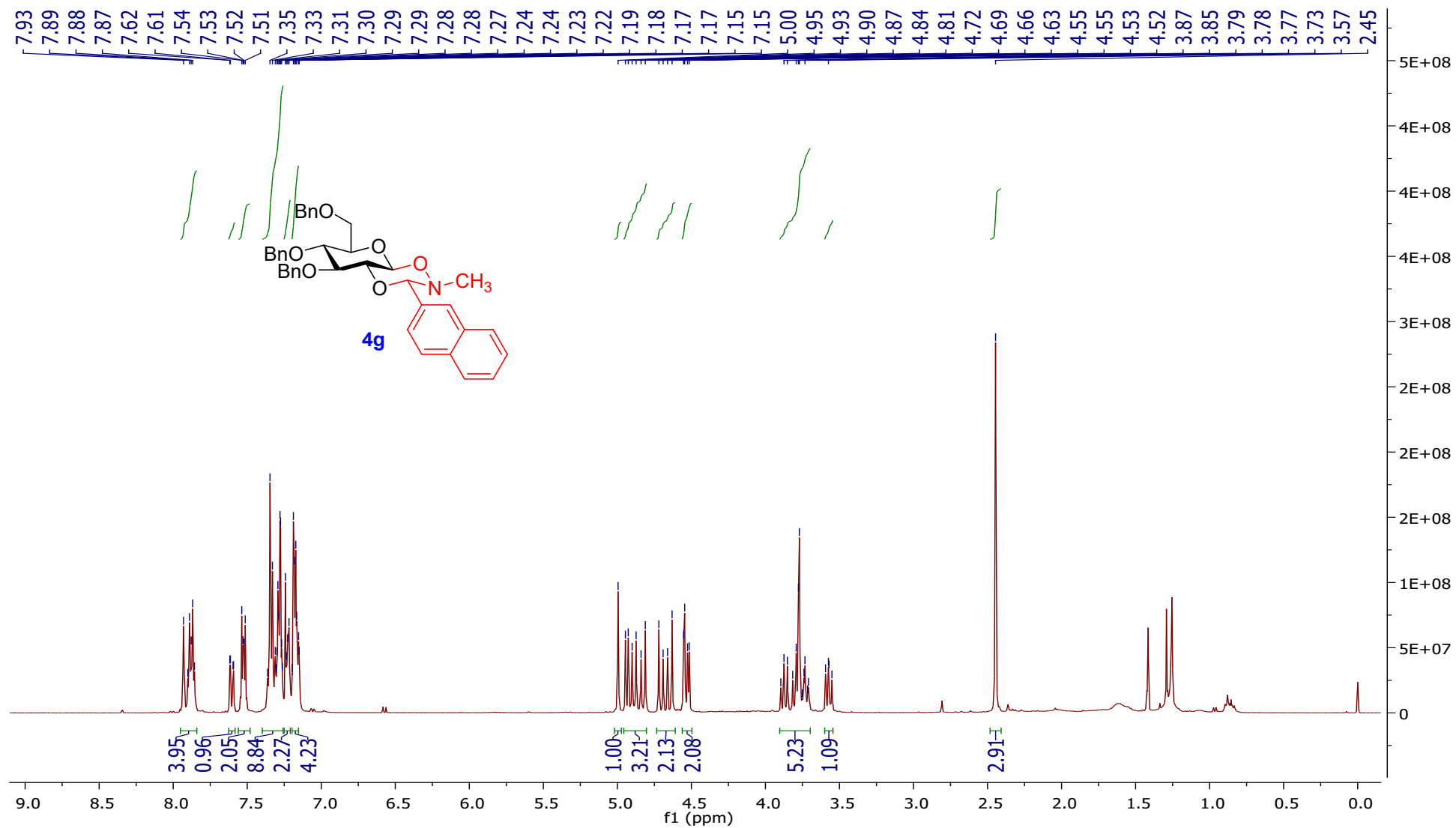


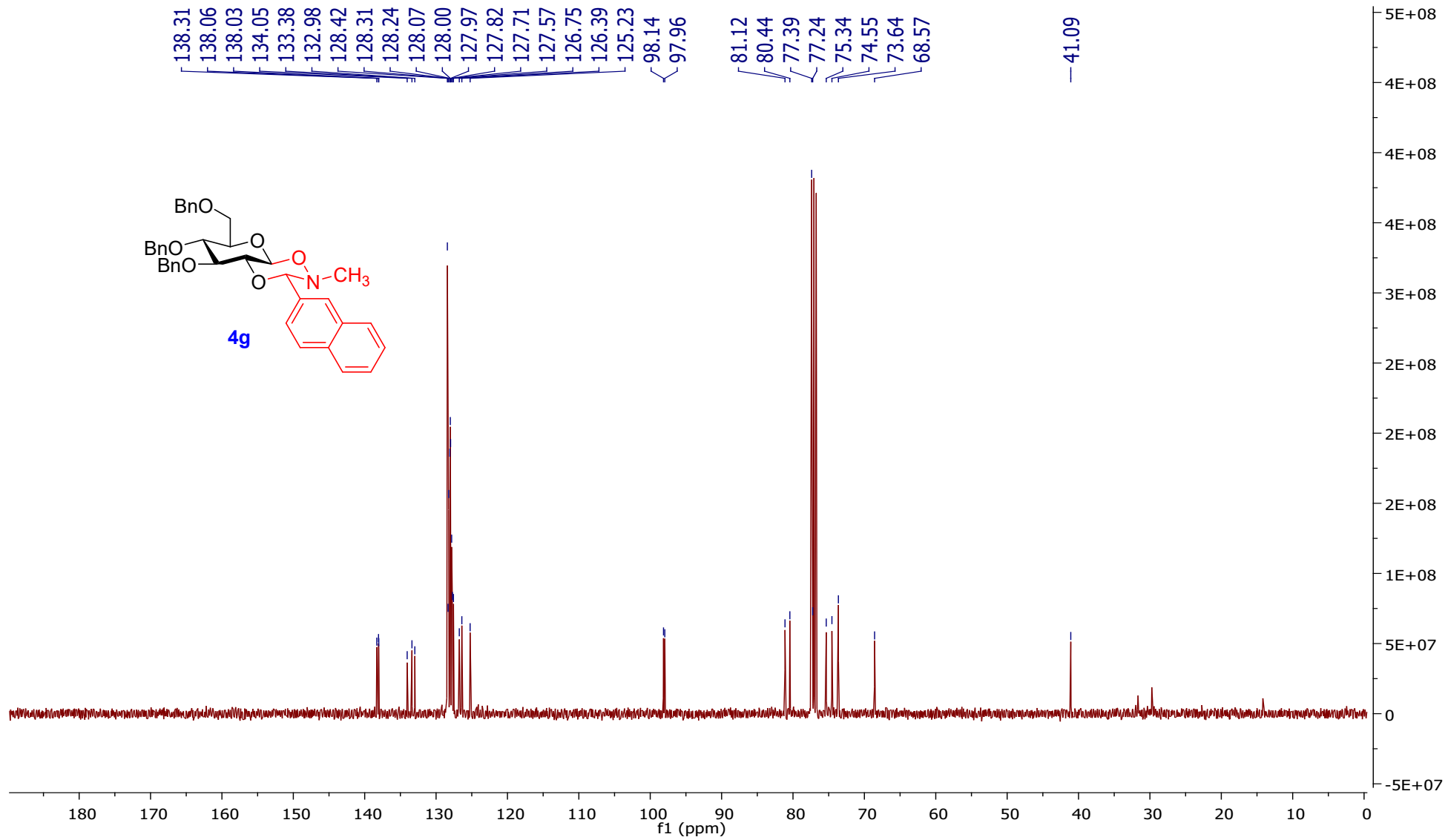
¹H NMR (400 MHz) and ¹³C NMR (101 MHz) of compound 4f



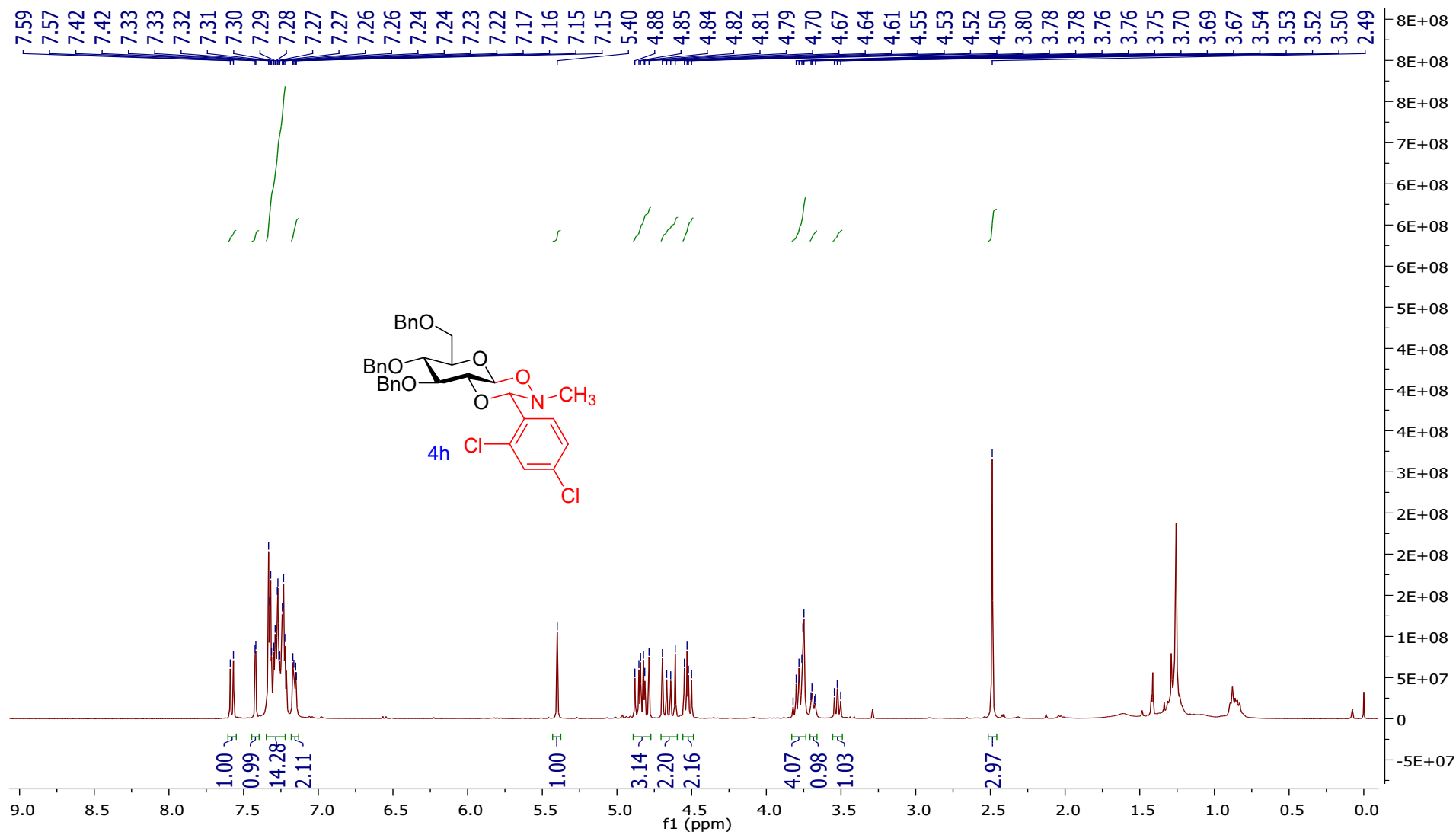


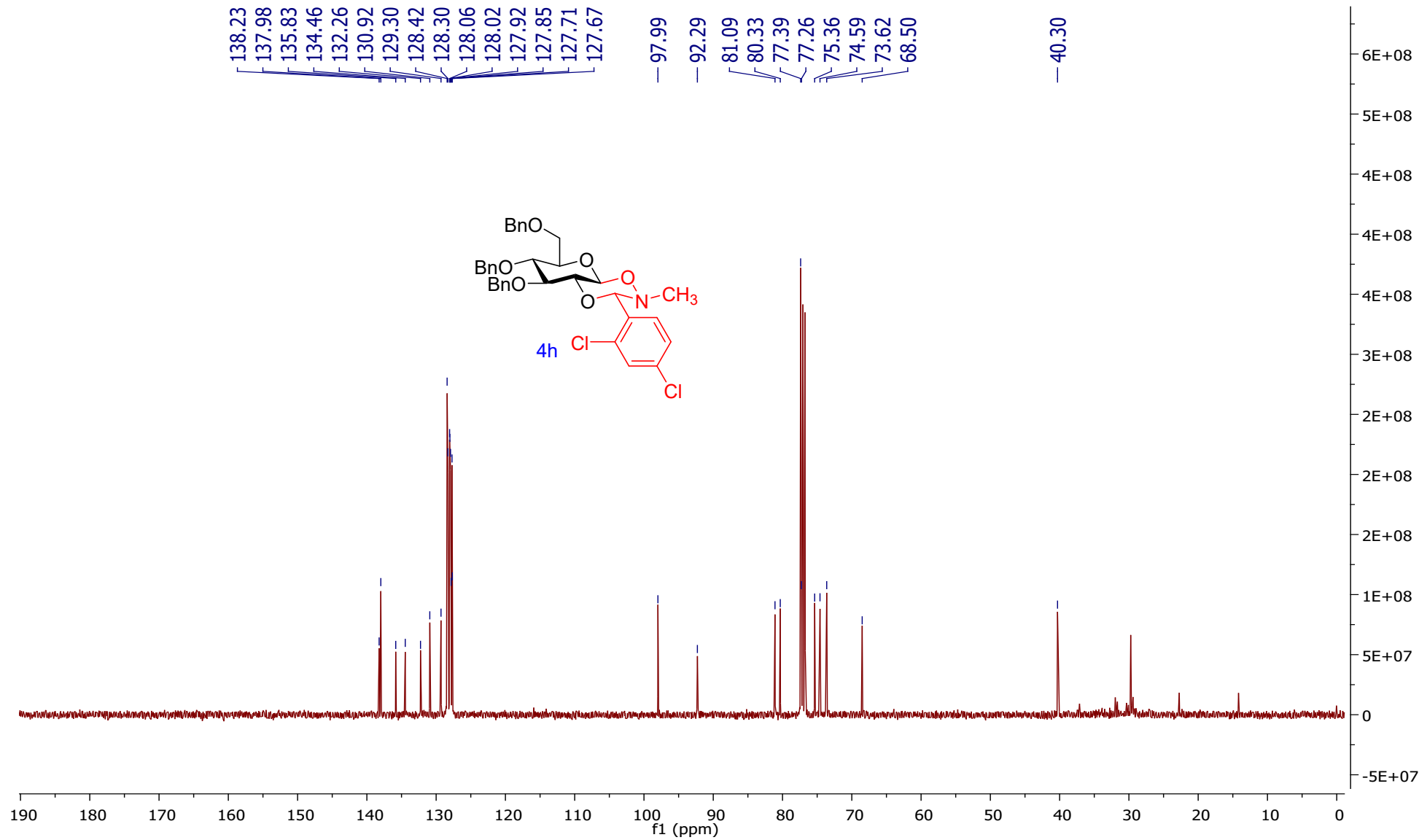
¹H NMR (400 MHz) and ¹³C NMR (126 MHz) of compound 4g



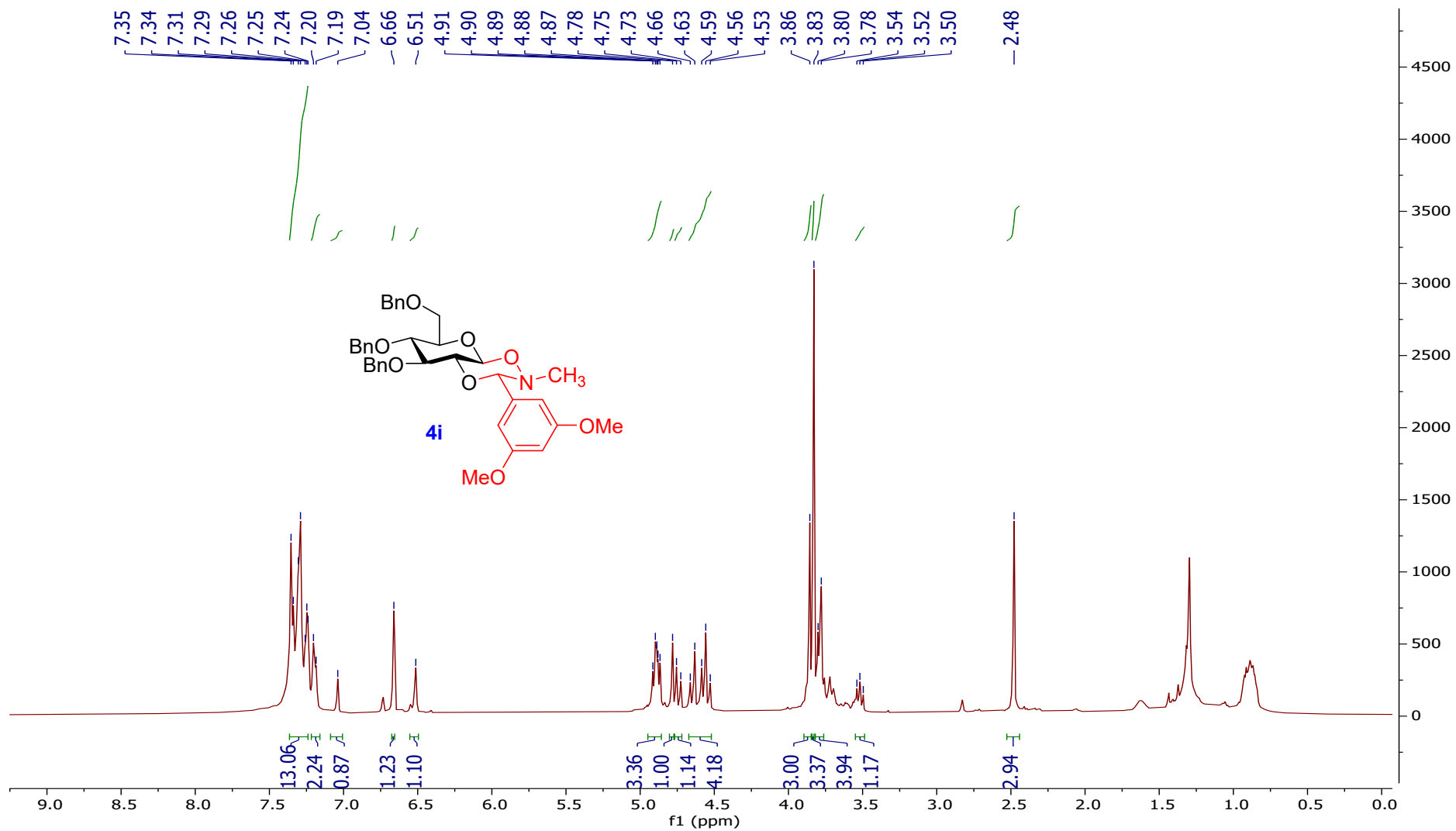


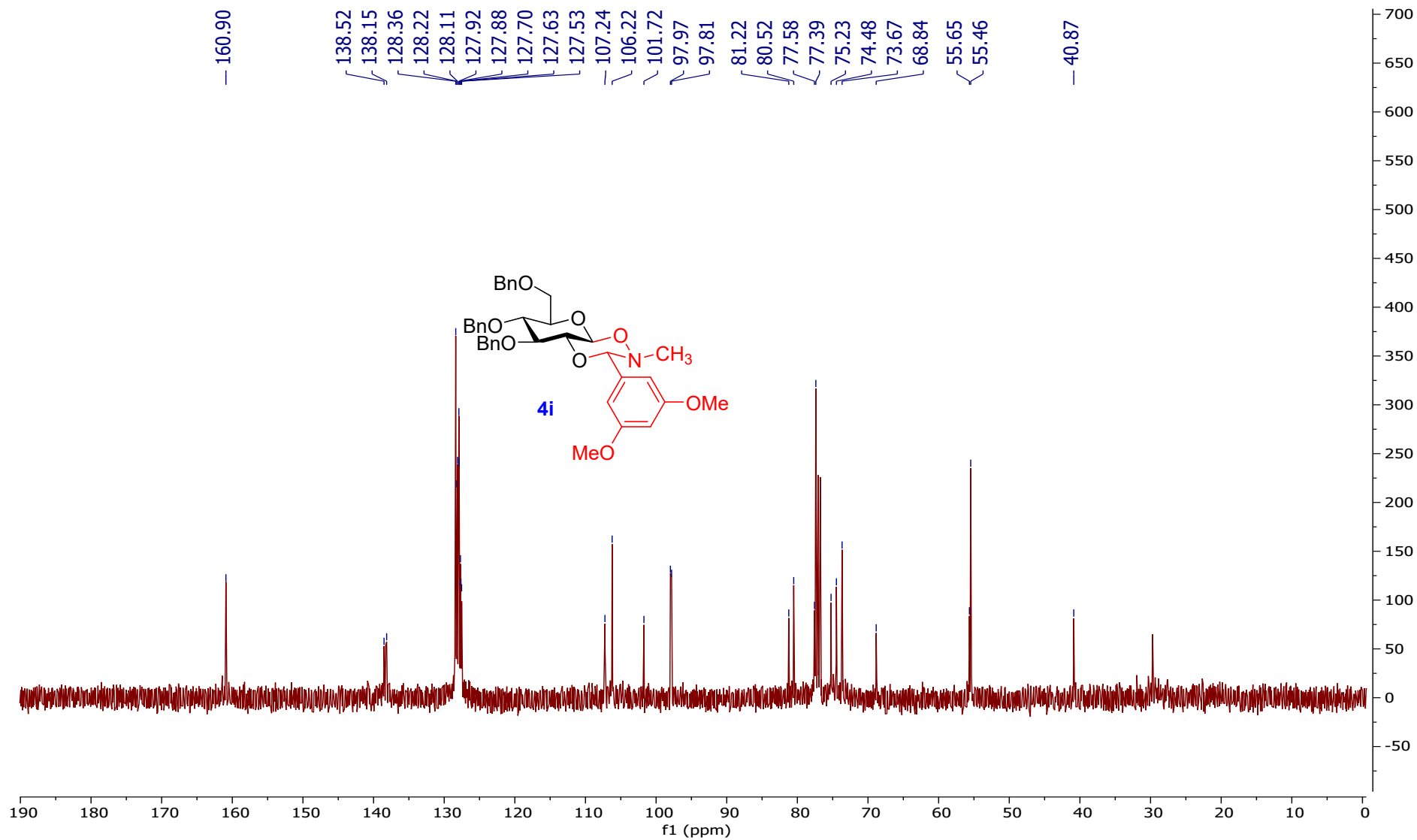
¹H NMR (400 MHz) and ¹³C NMR (101 MHz) of compound 4h



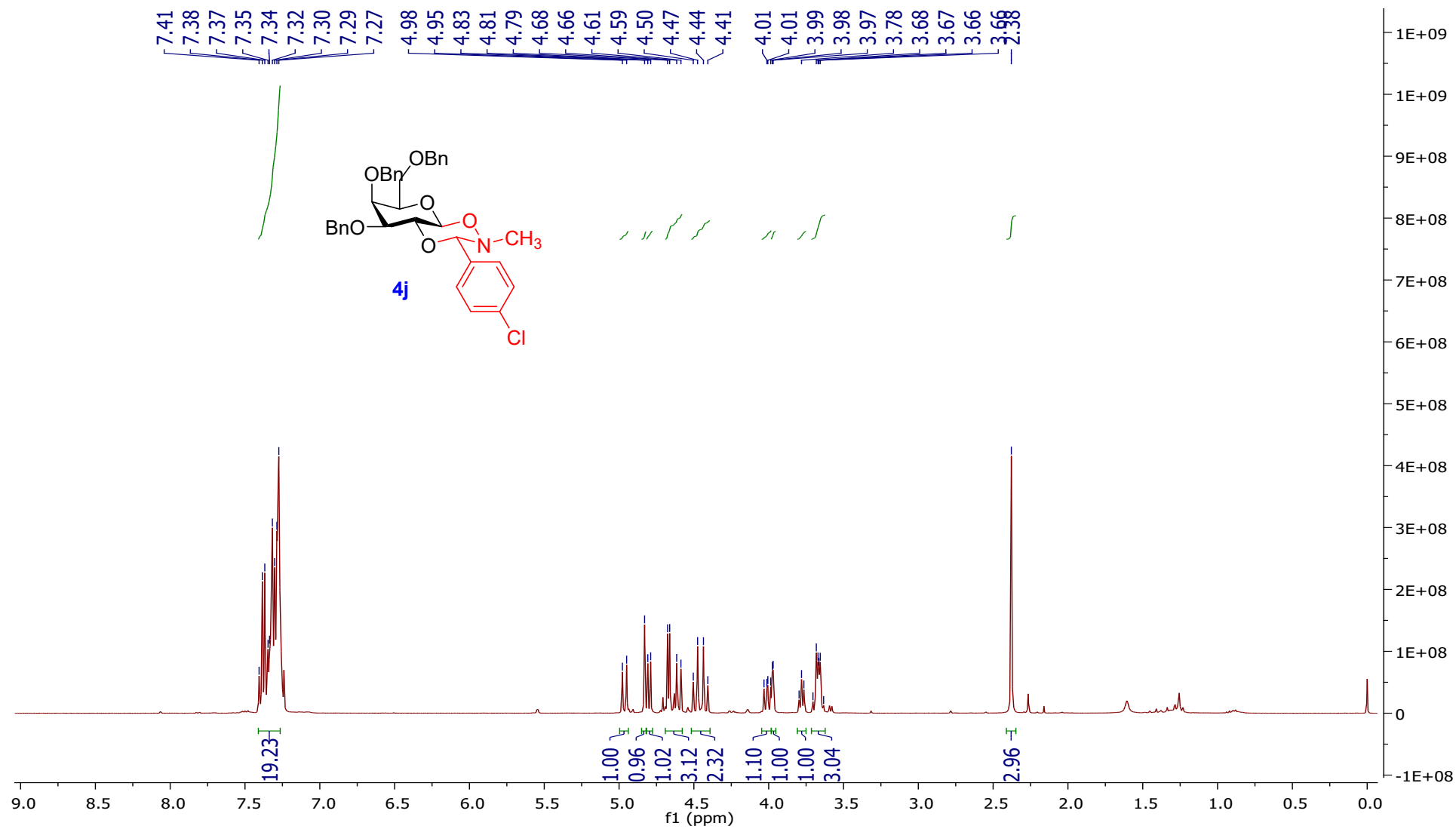


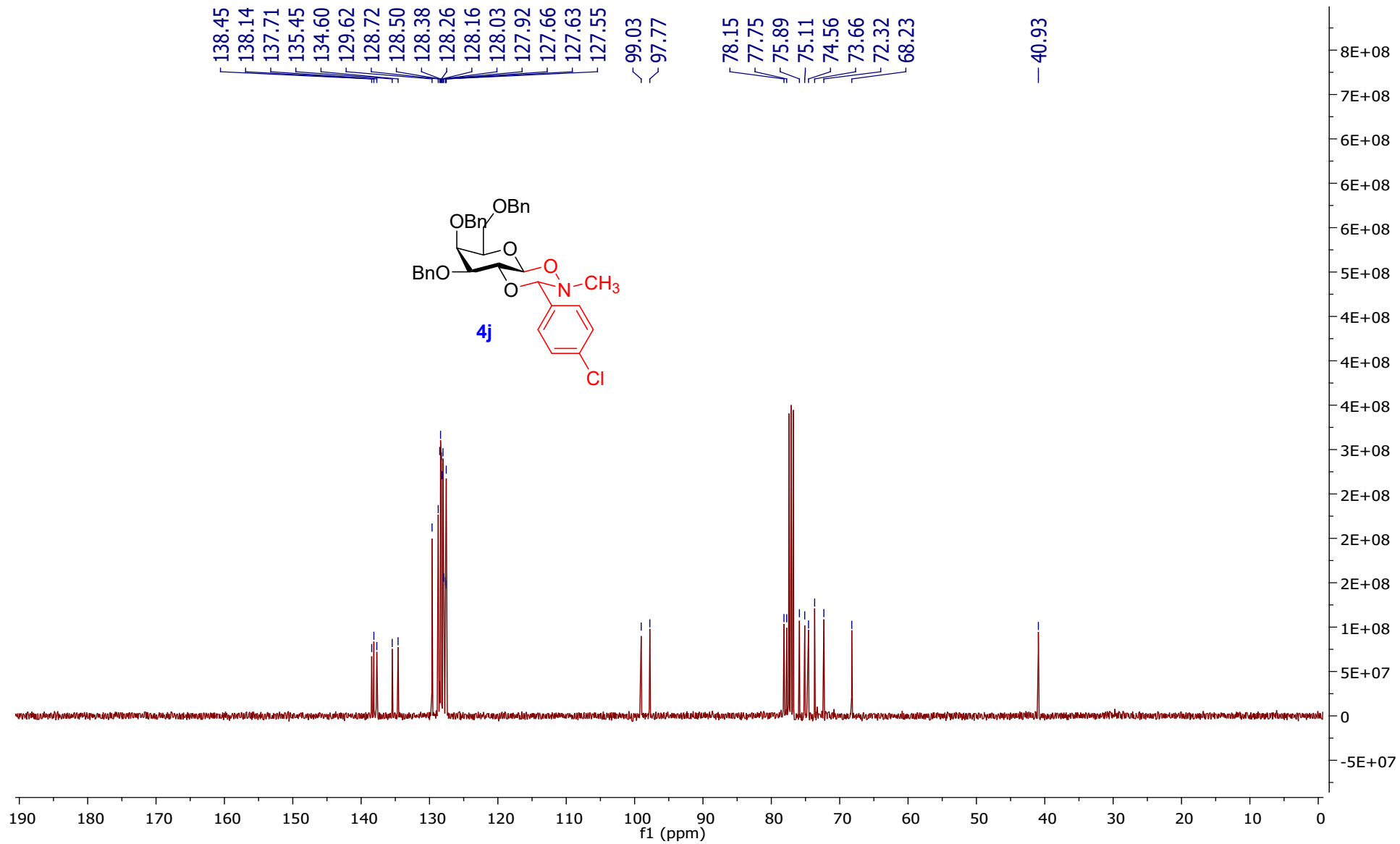
¹H NMR (400 MHz) and ¹³C NMR (101 MHz) of compound 4i



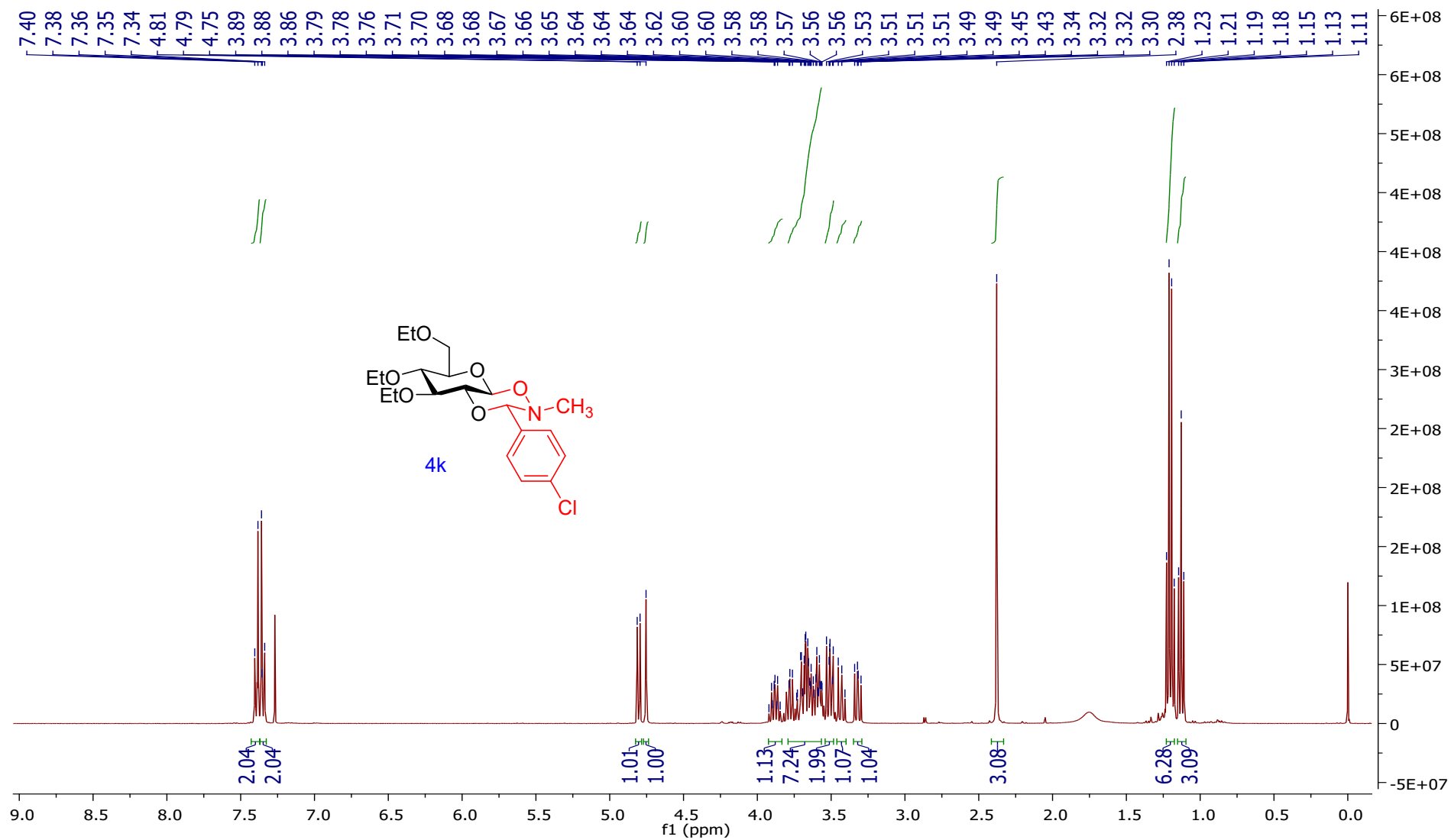


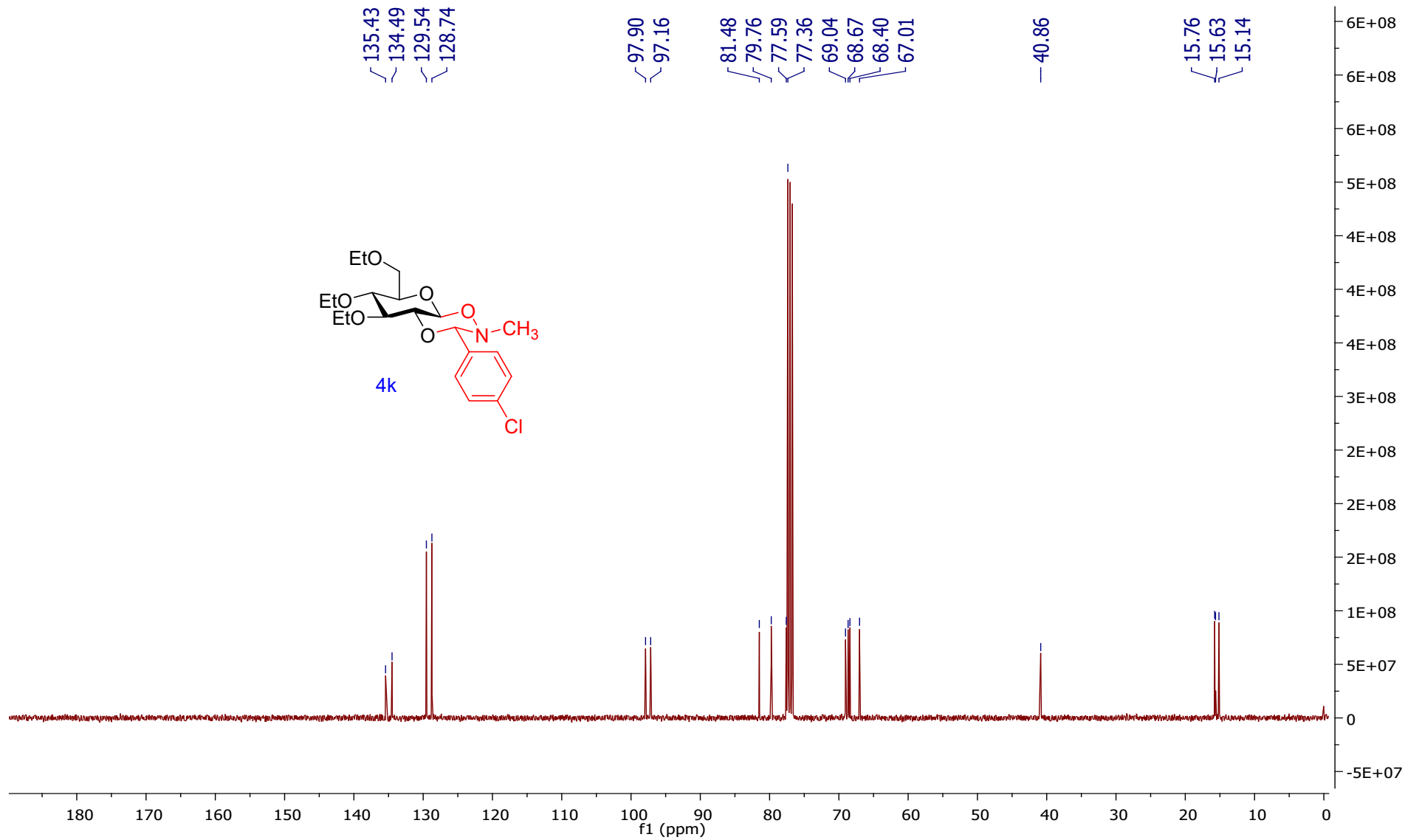
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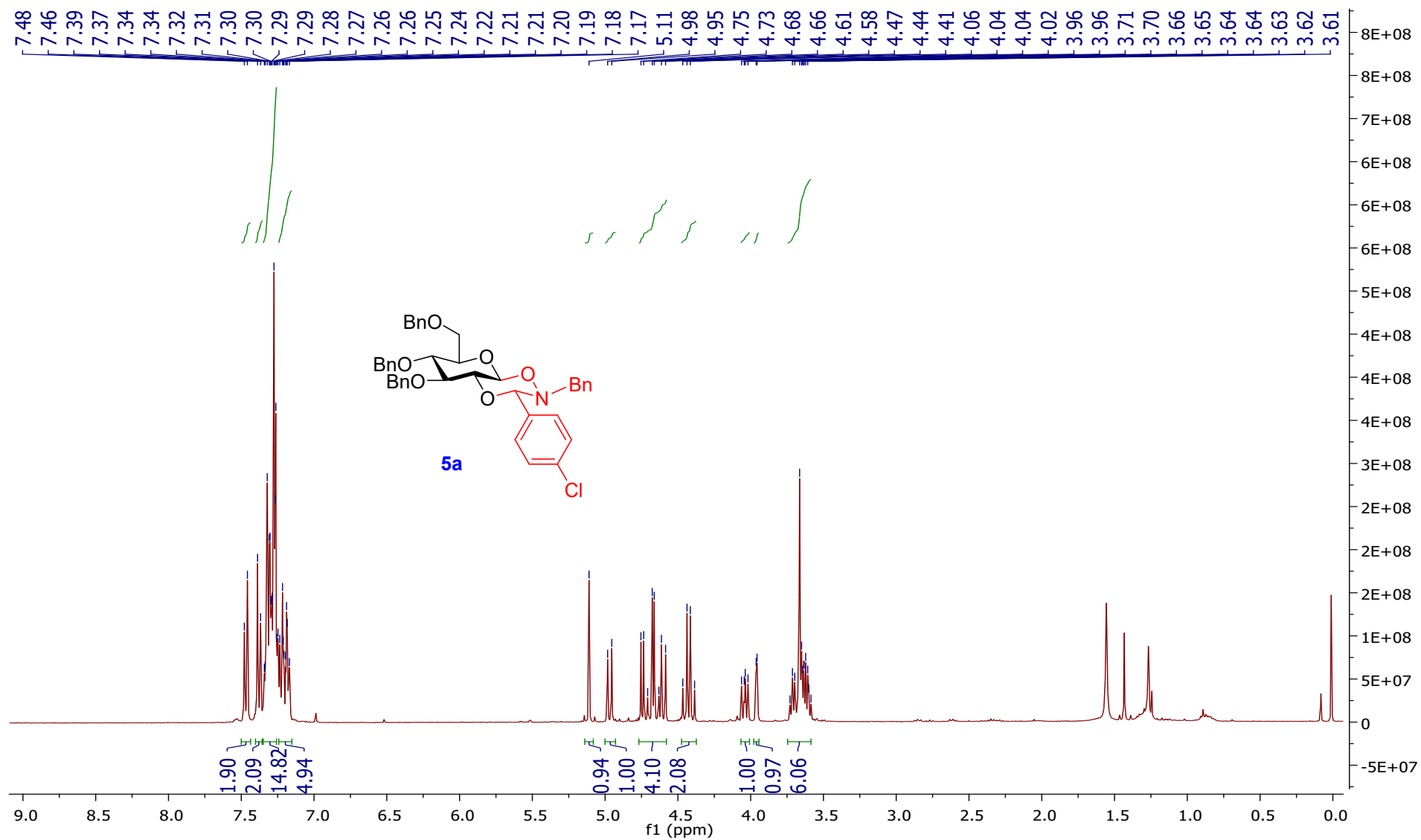


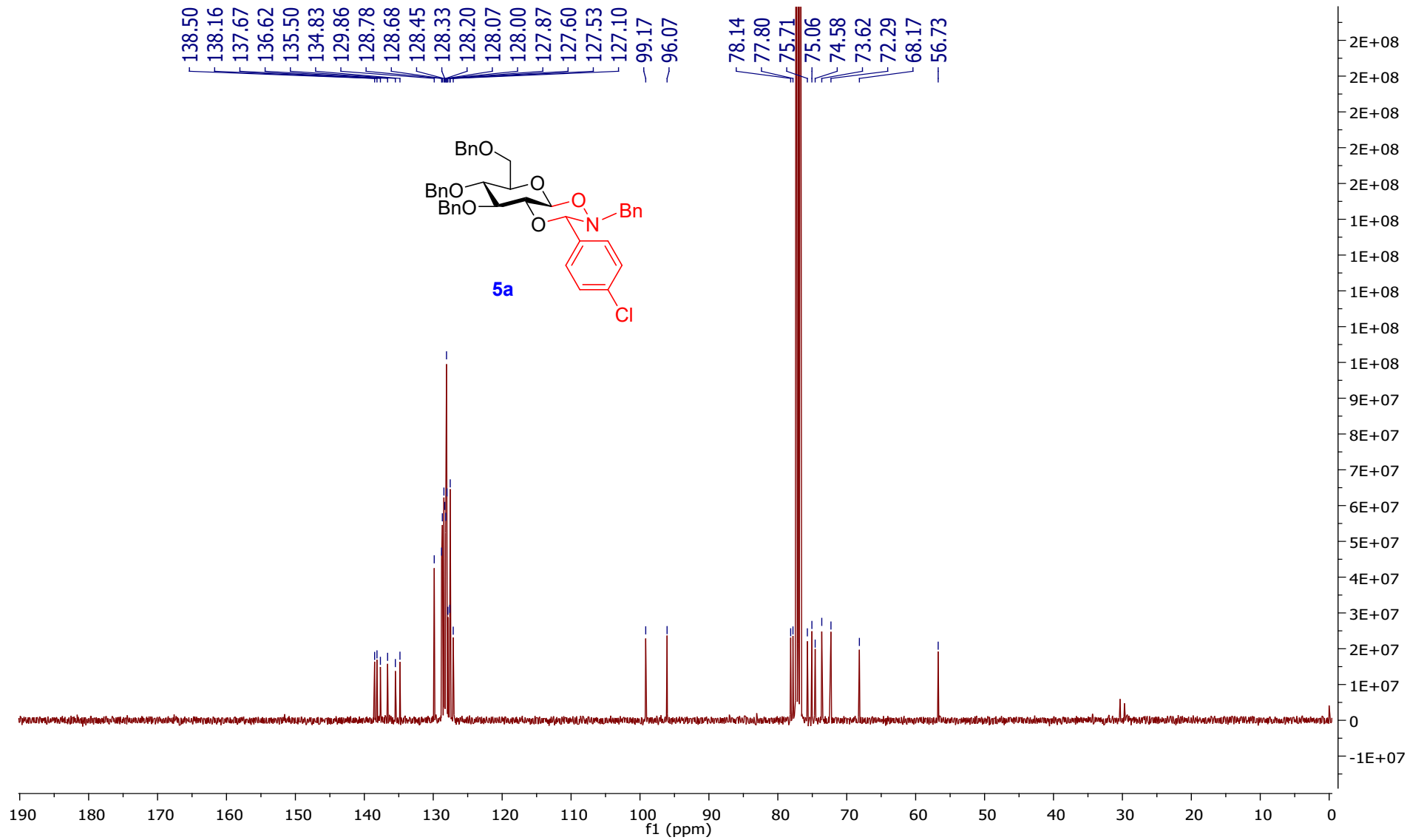
¹H NMR (400 MHz) and ¹³C NMR (101 MHz) of compound 4k



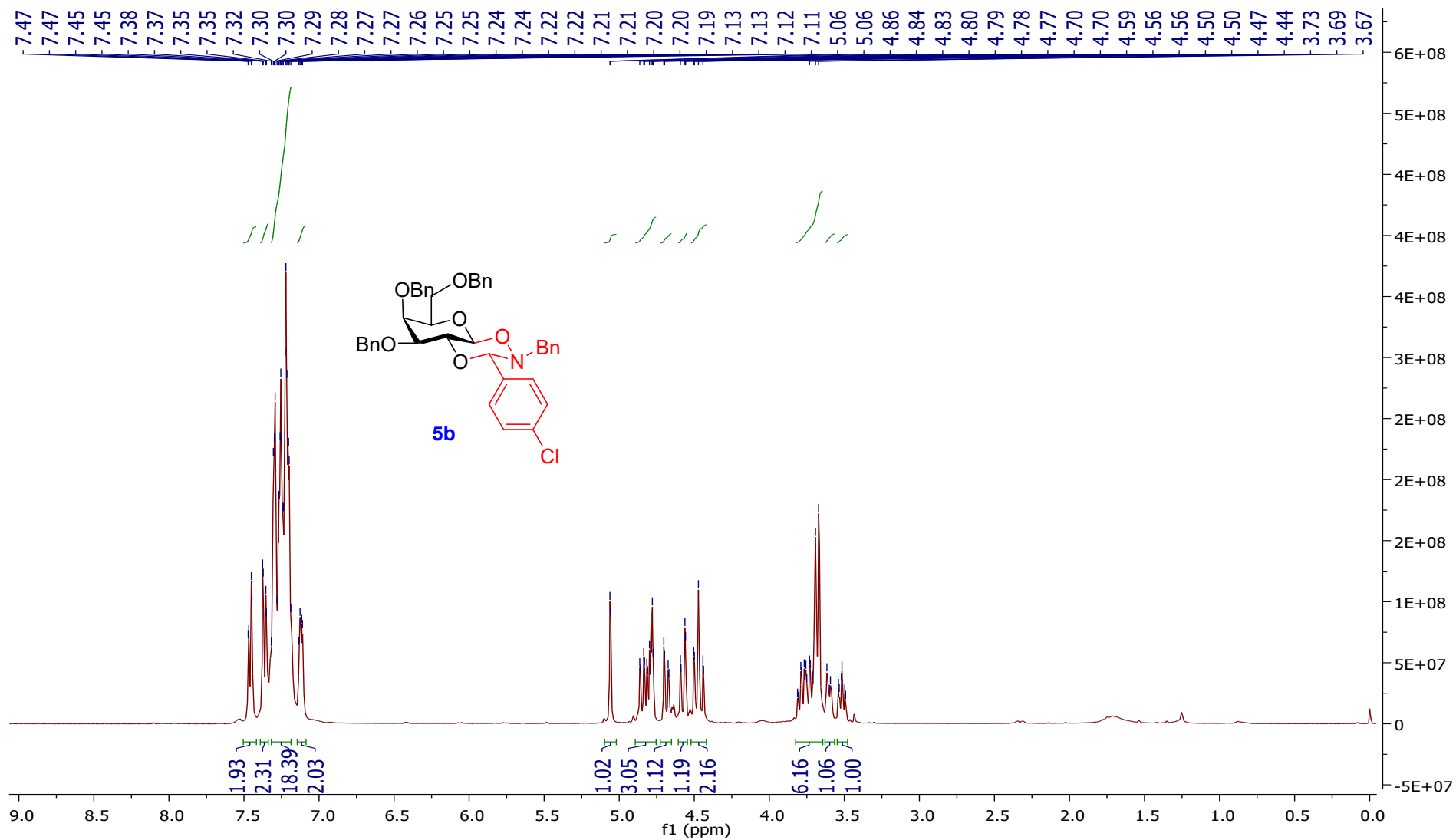


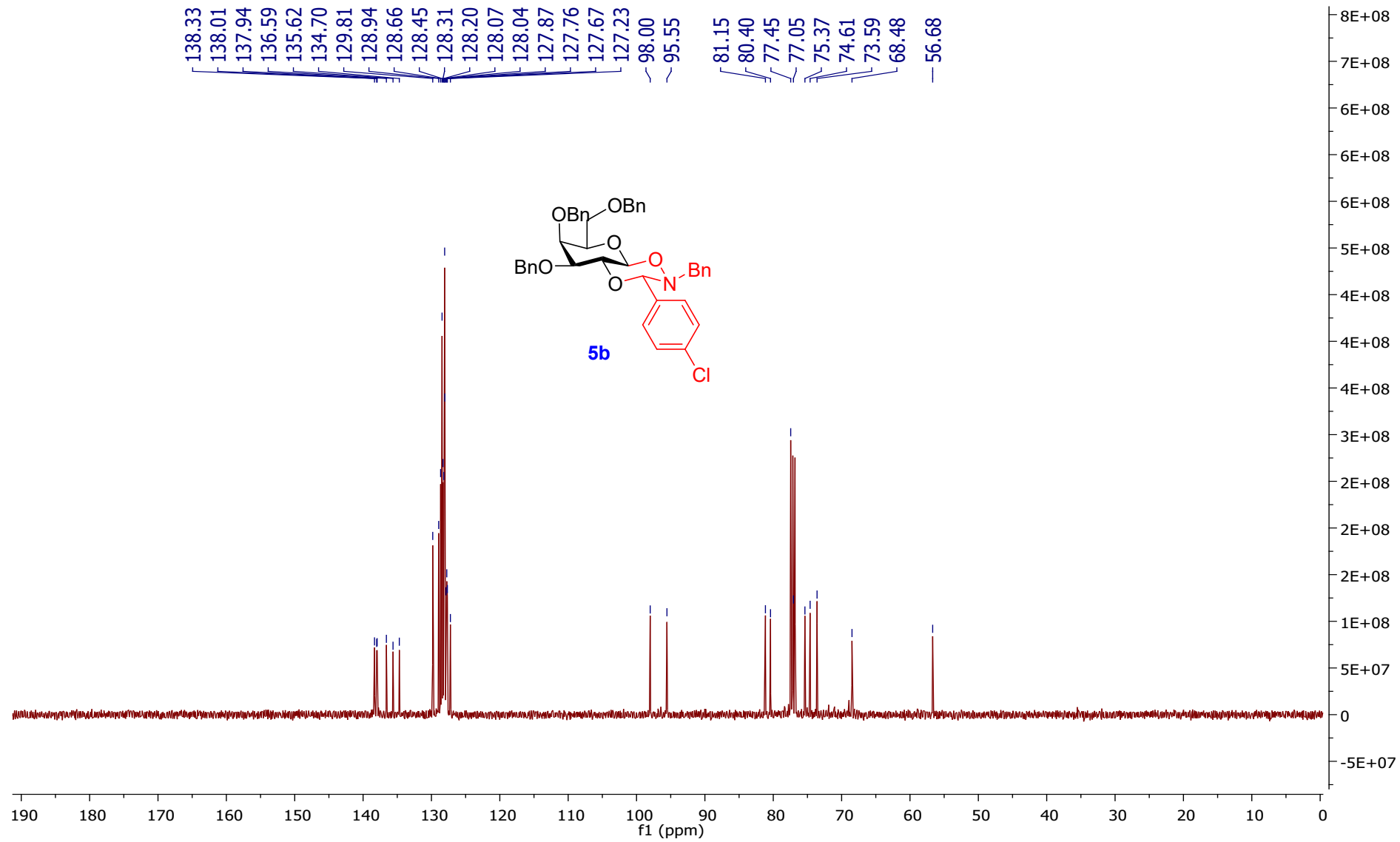
¹H NMR (400 MHz) and ¹³C NMR (101 MHz) of compound 5a



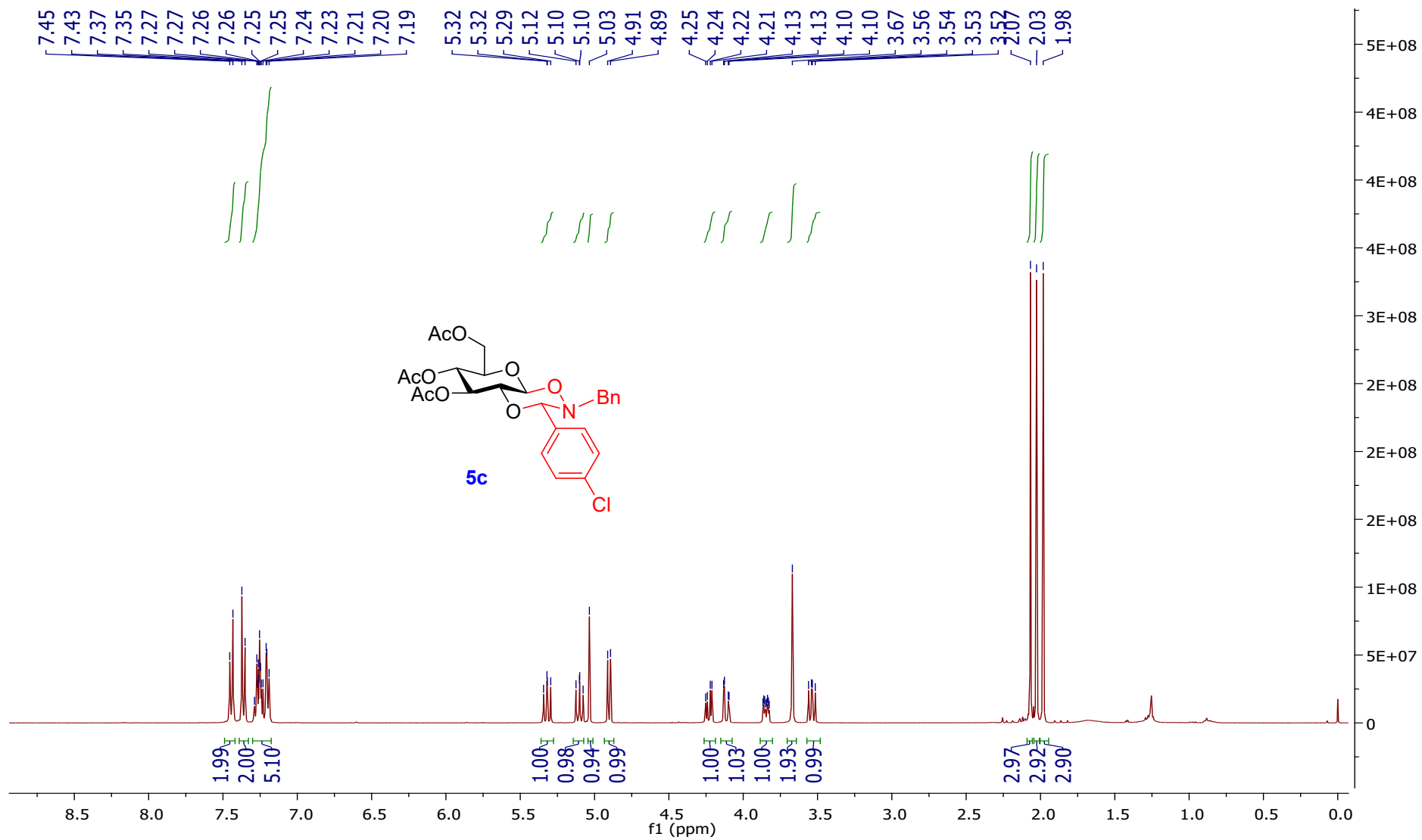


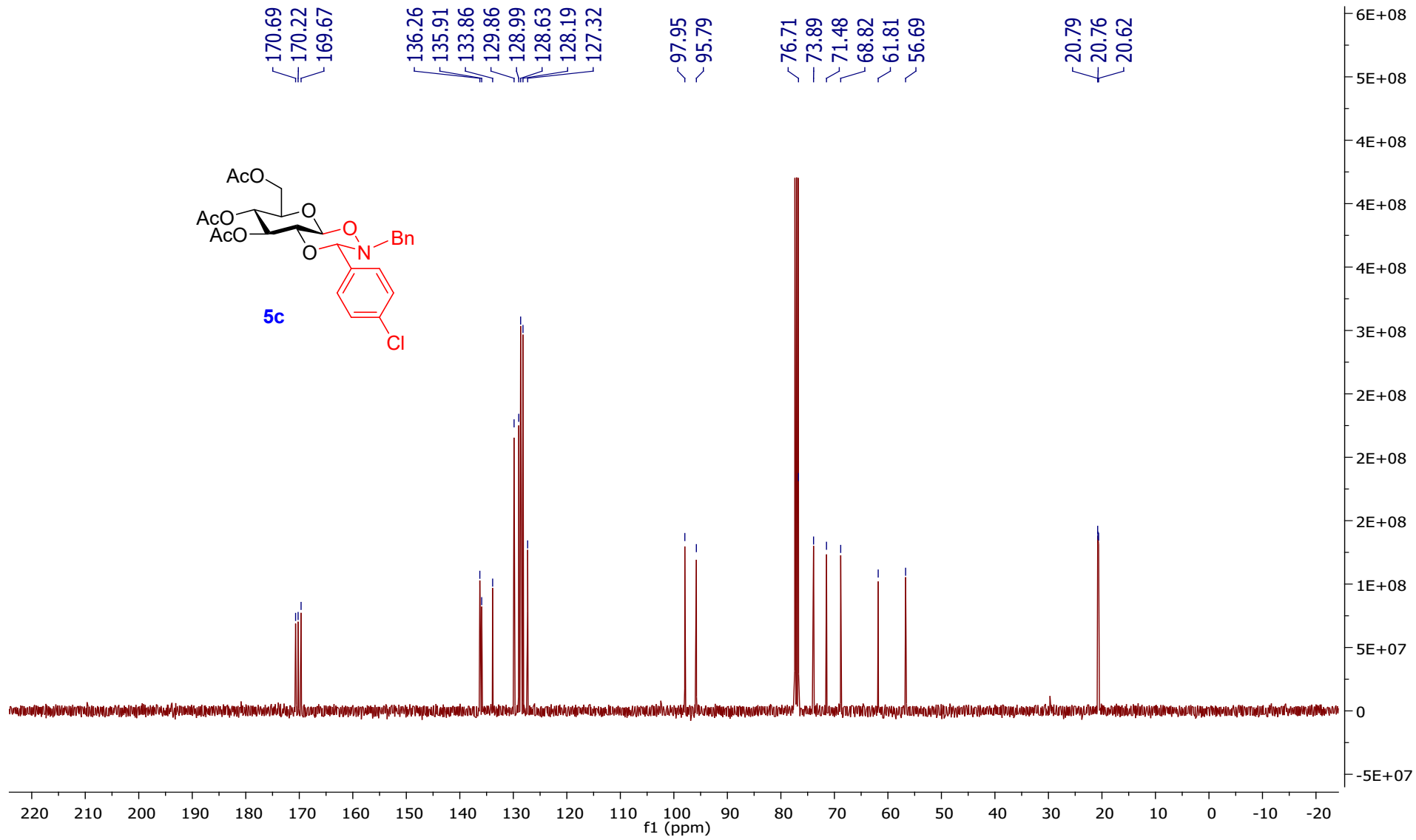
¹H NMR (400 MHz) and ¹³C NMR (101 MHz) of compound 5b



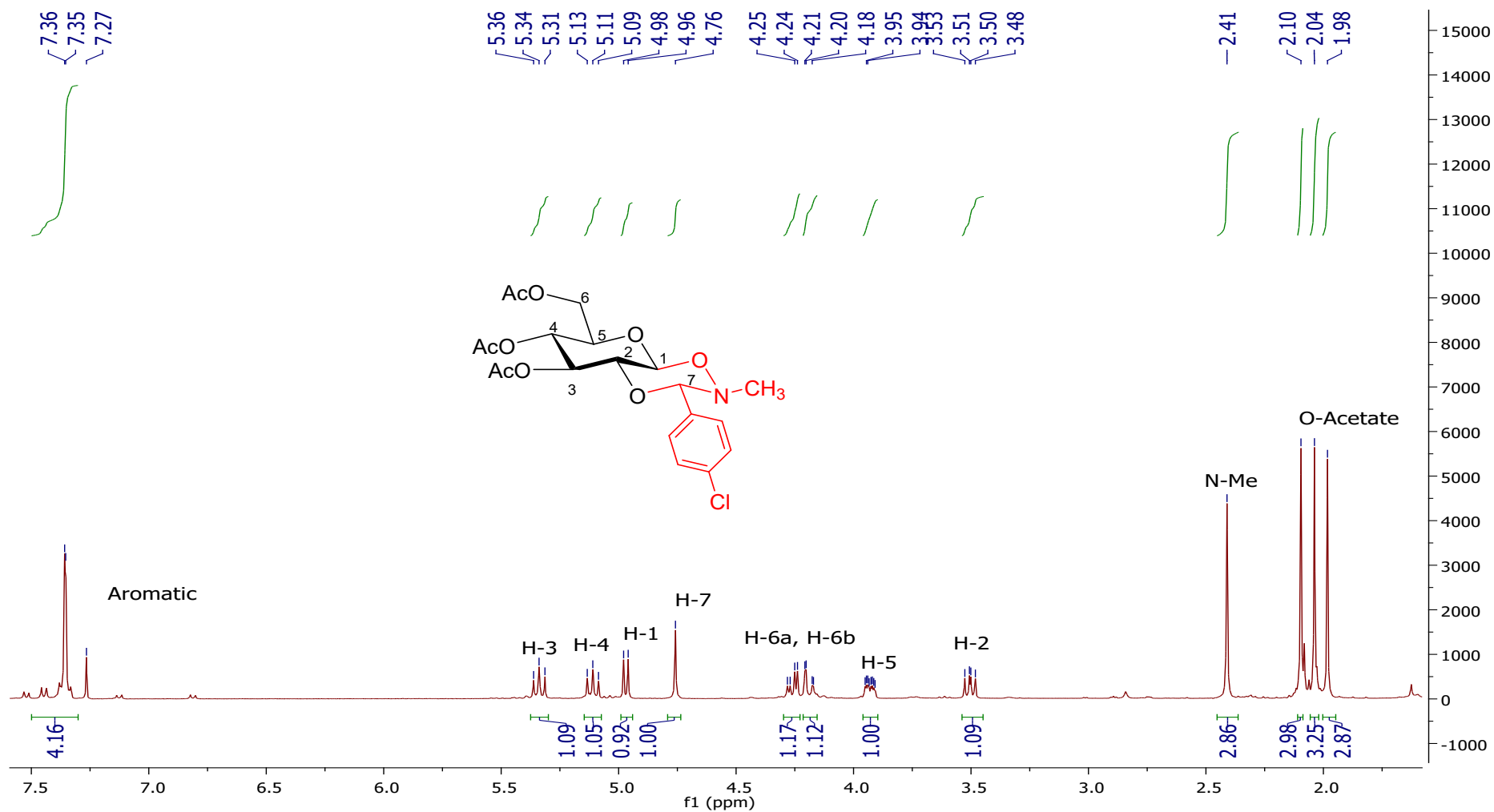


¹H NMR (400 MHz) and ¹³C NMR (101 MHz) of compound 5c

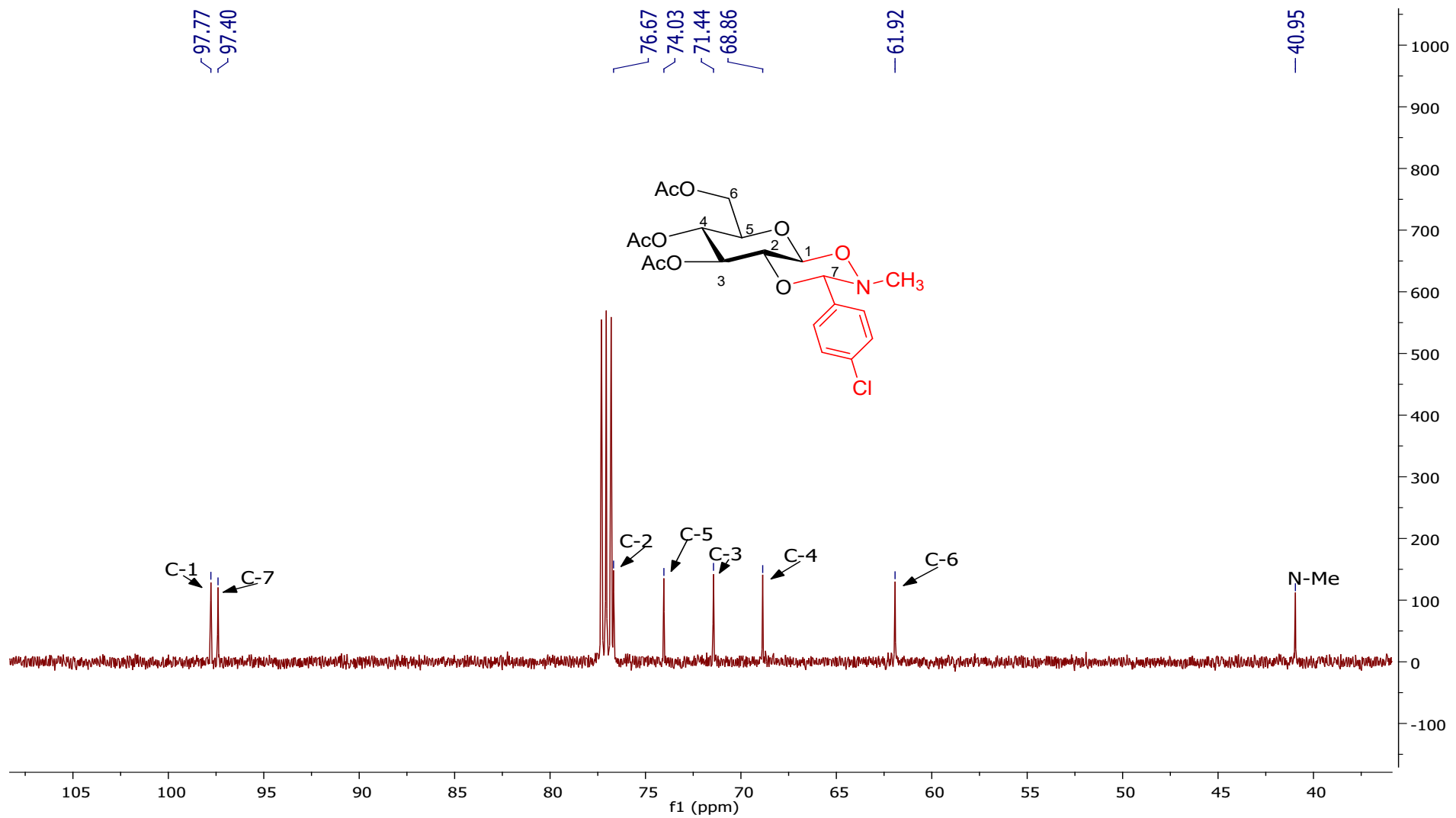




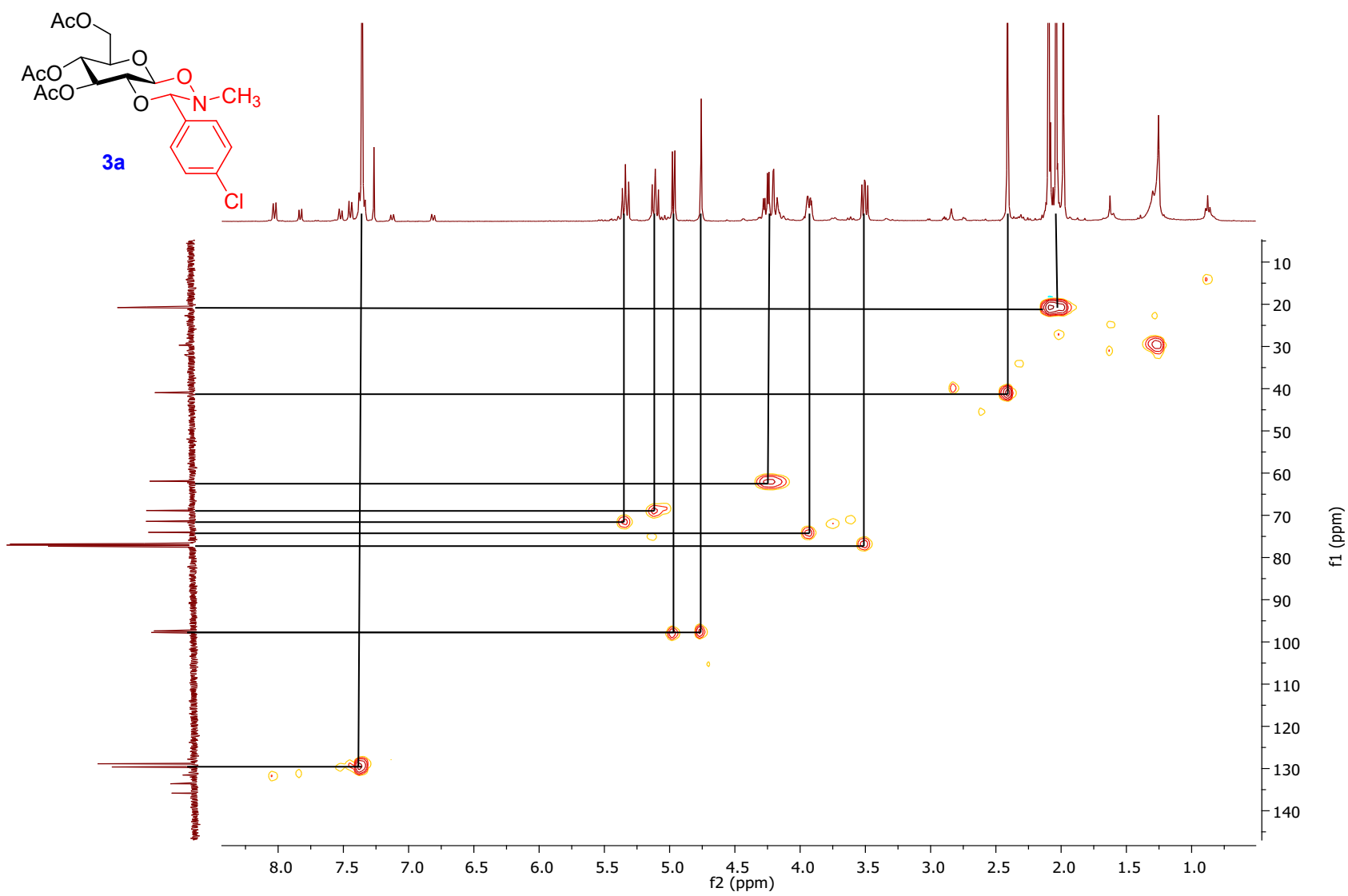
¹H NMR (400 MHz) of compound 3a



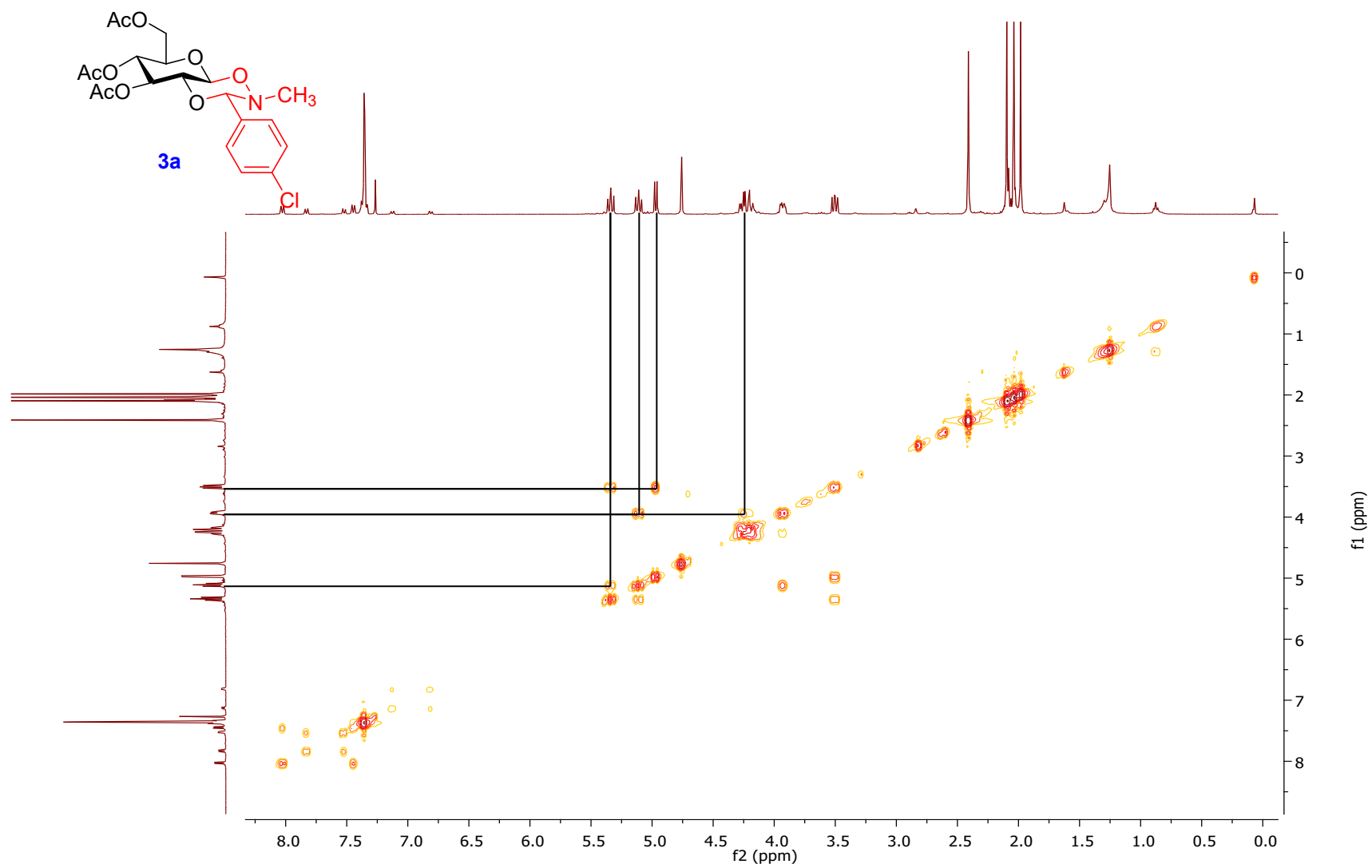
¹³C NMR (101 MHz) of compound 3a



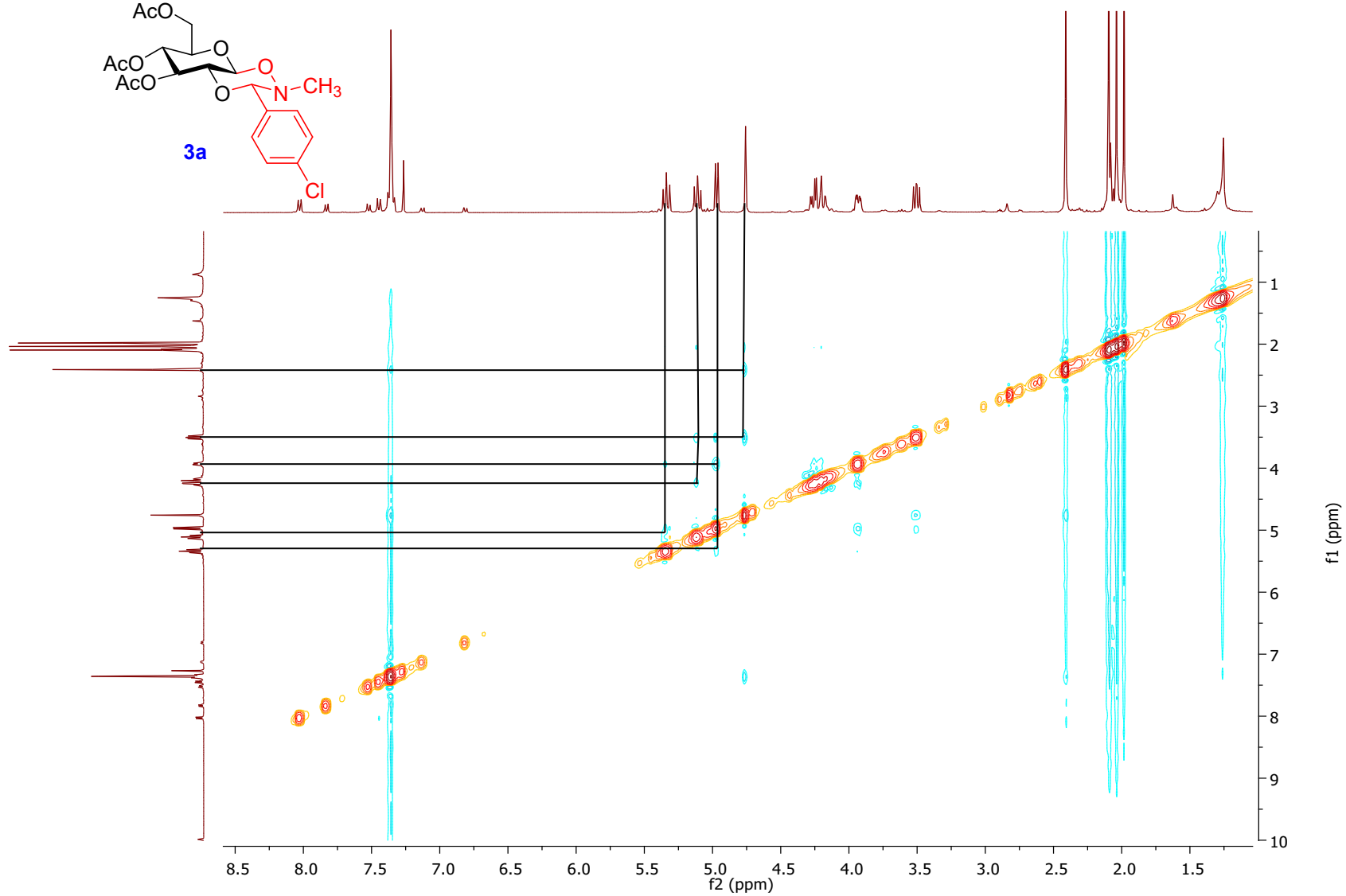
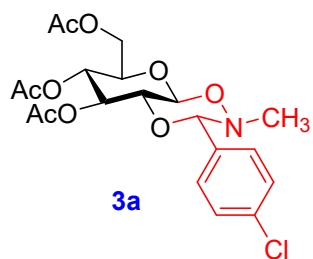
HSQC of compound **3a**



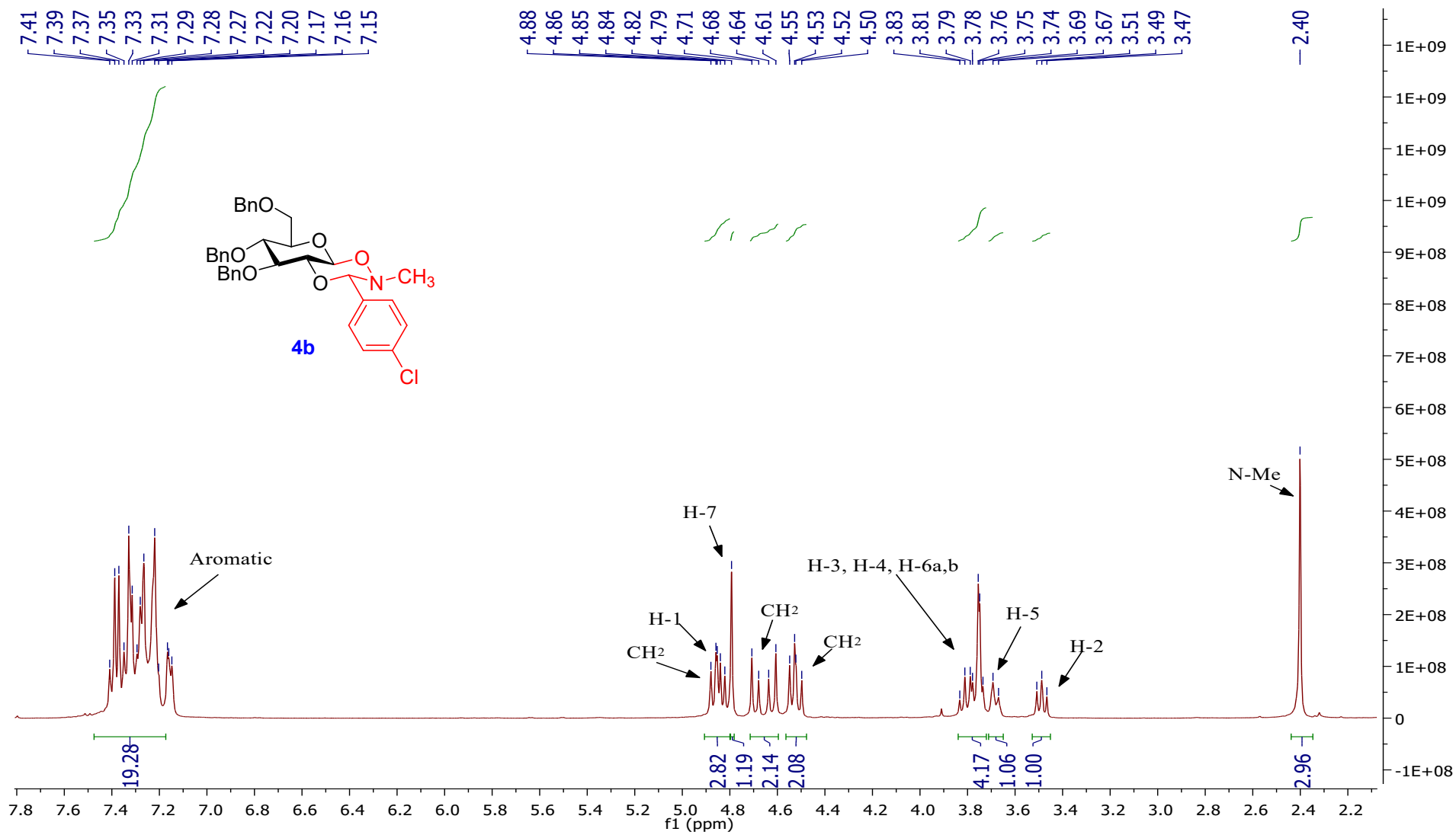
COSY of compound **3a**



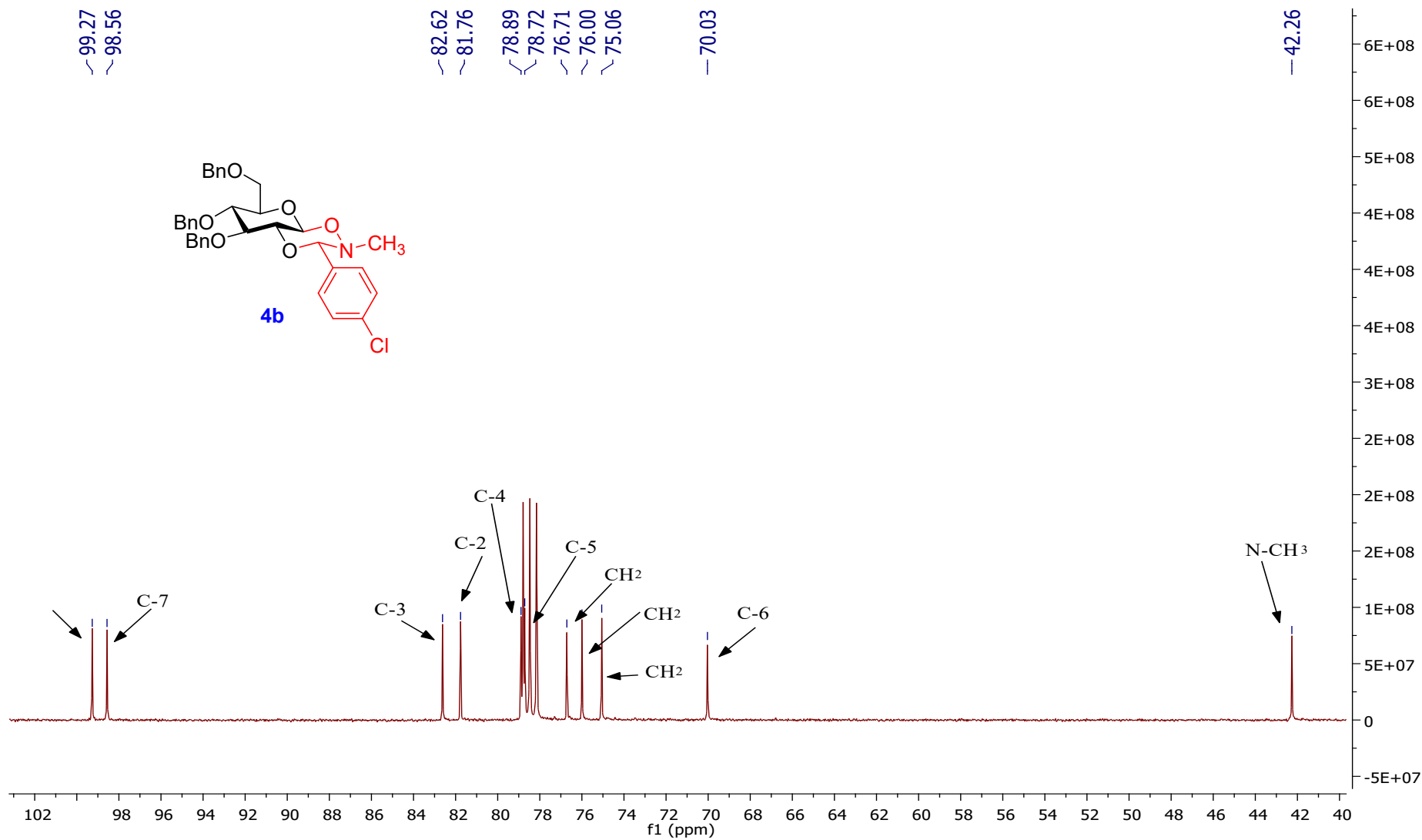
NOESY of compound **3a**



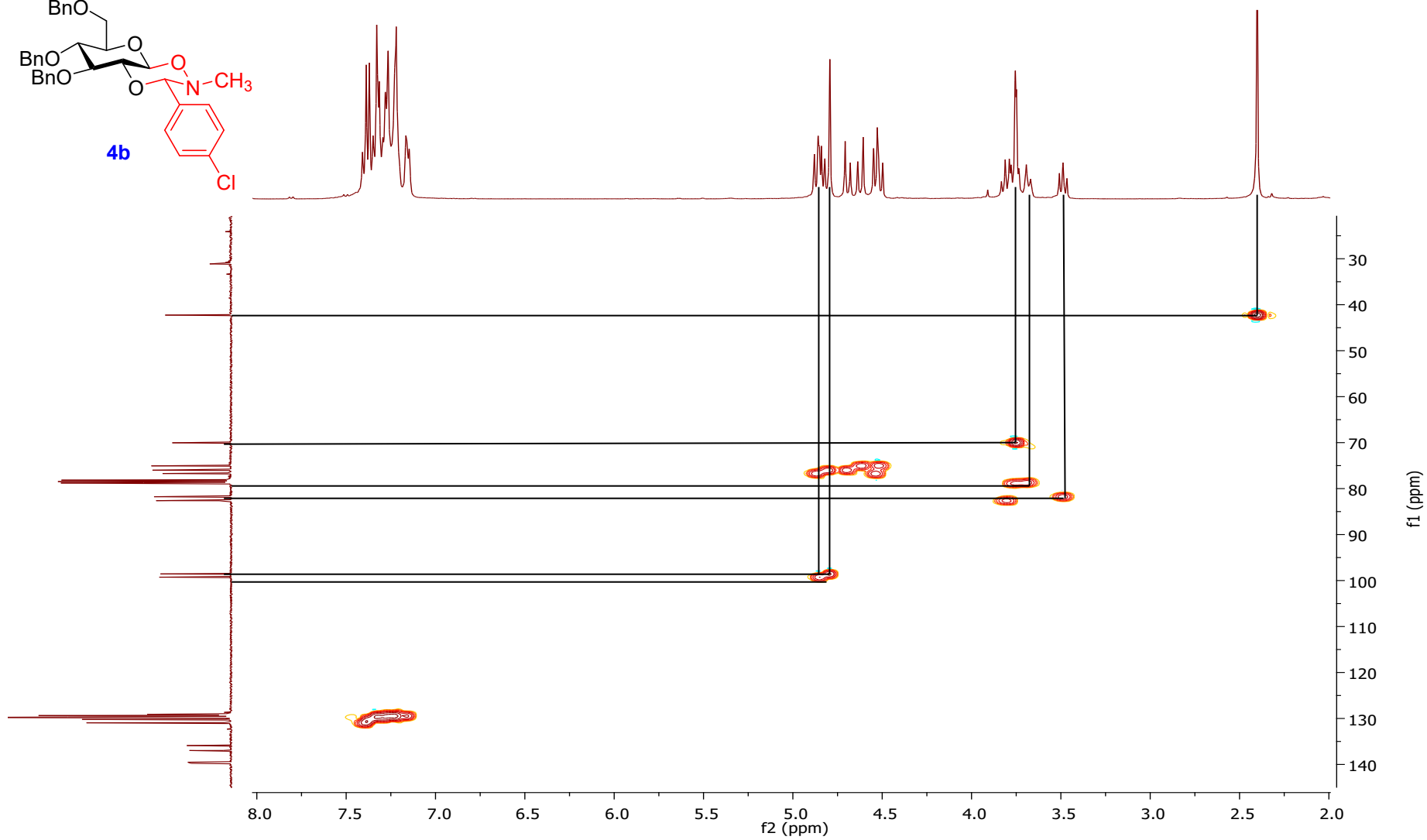
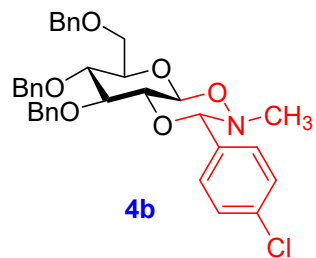
Labeled ¹H of compound 4b



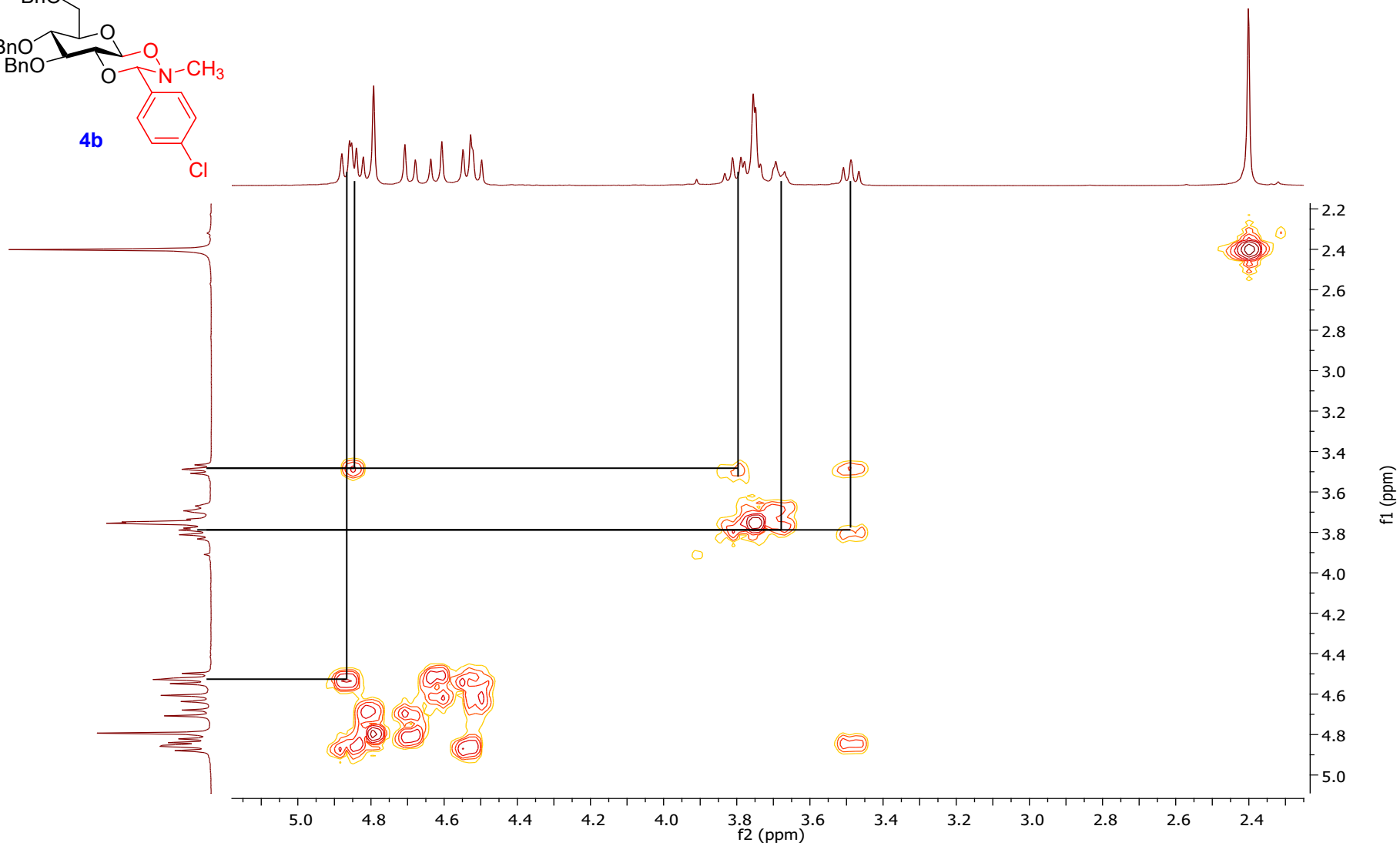
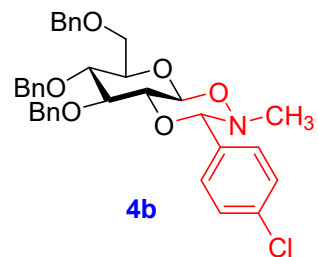
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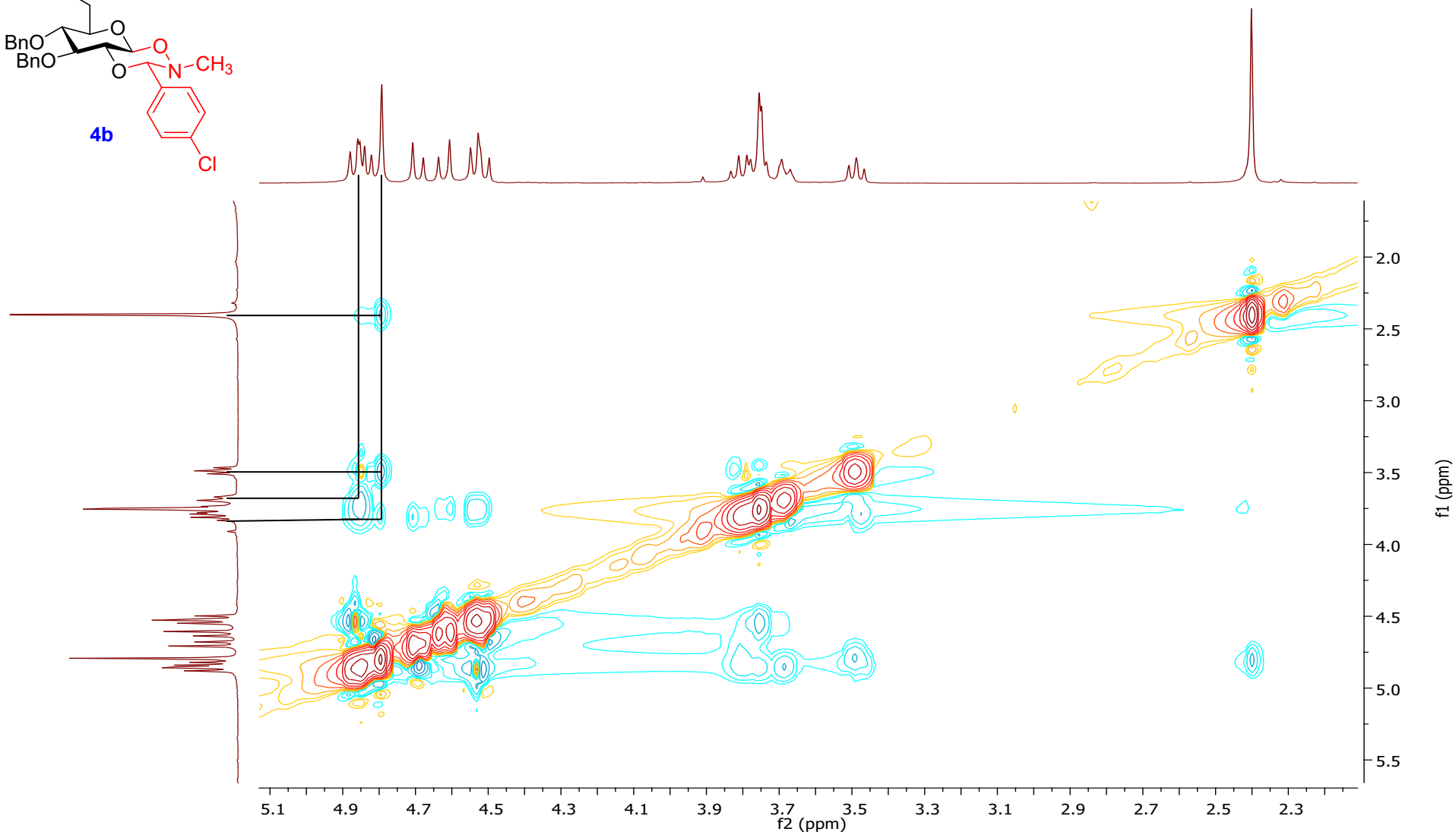
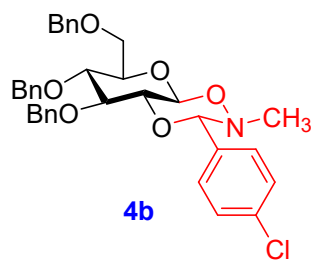
HSQC of compound 4b



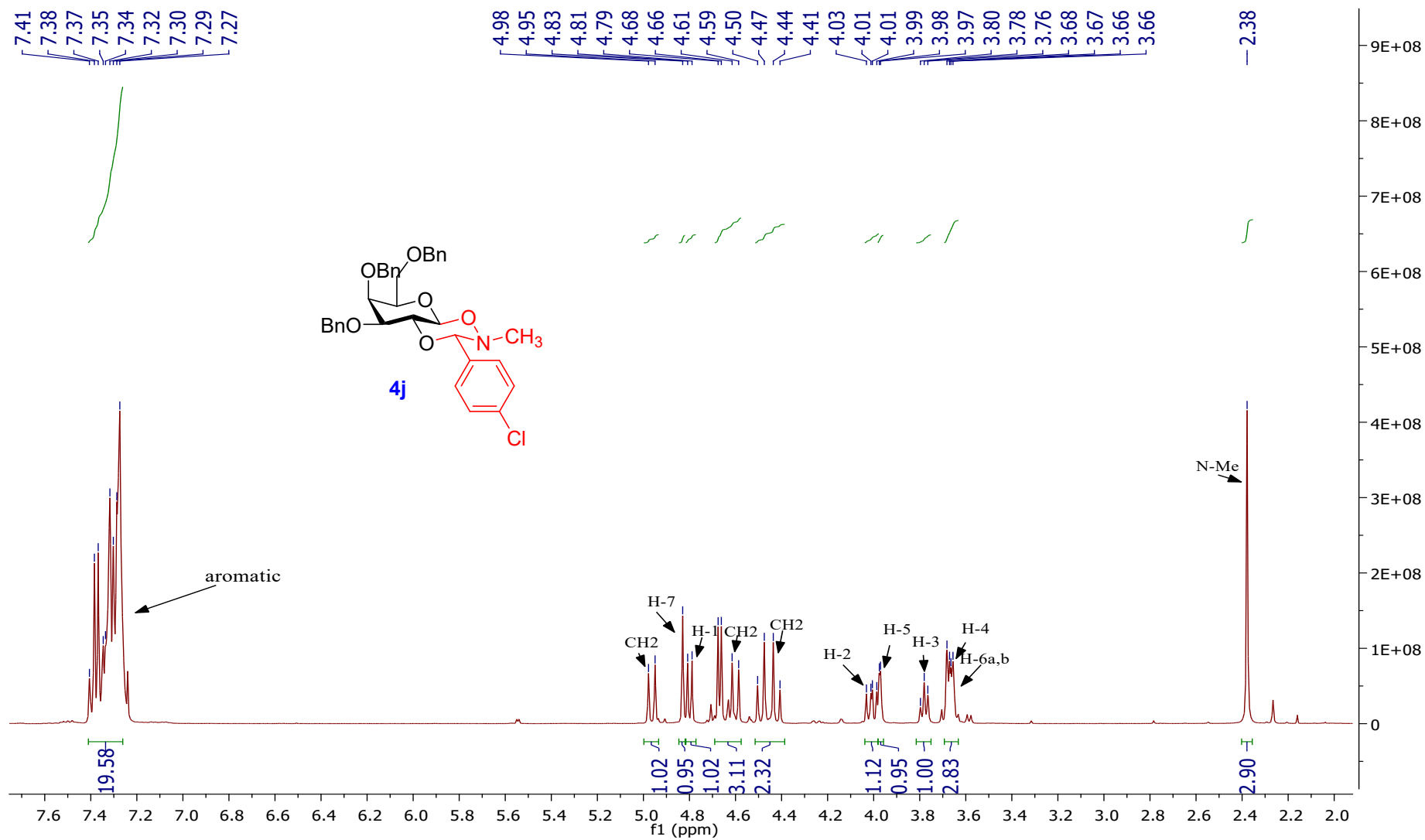
COSY of Compound 4b



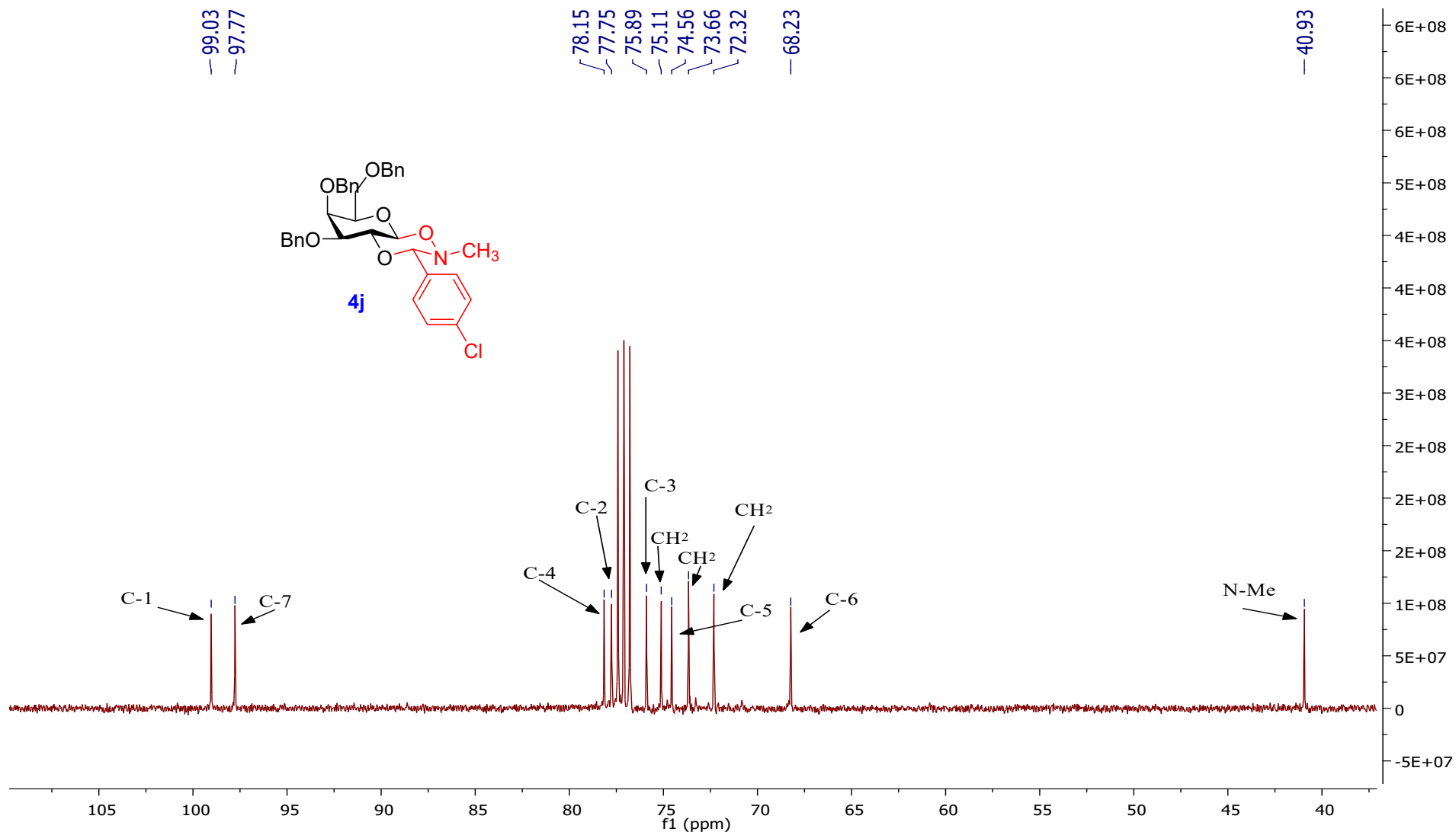
NOESY of compound 4b



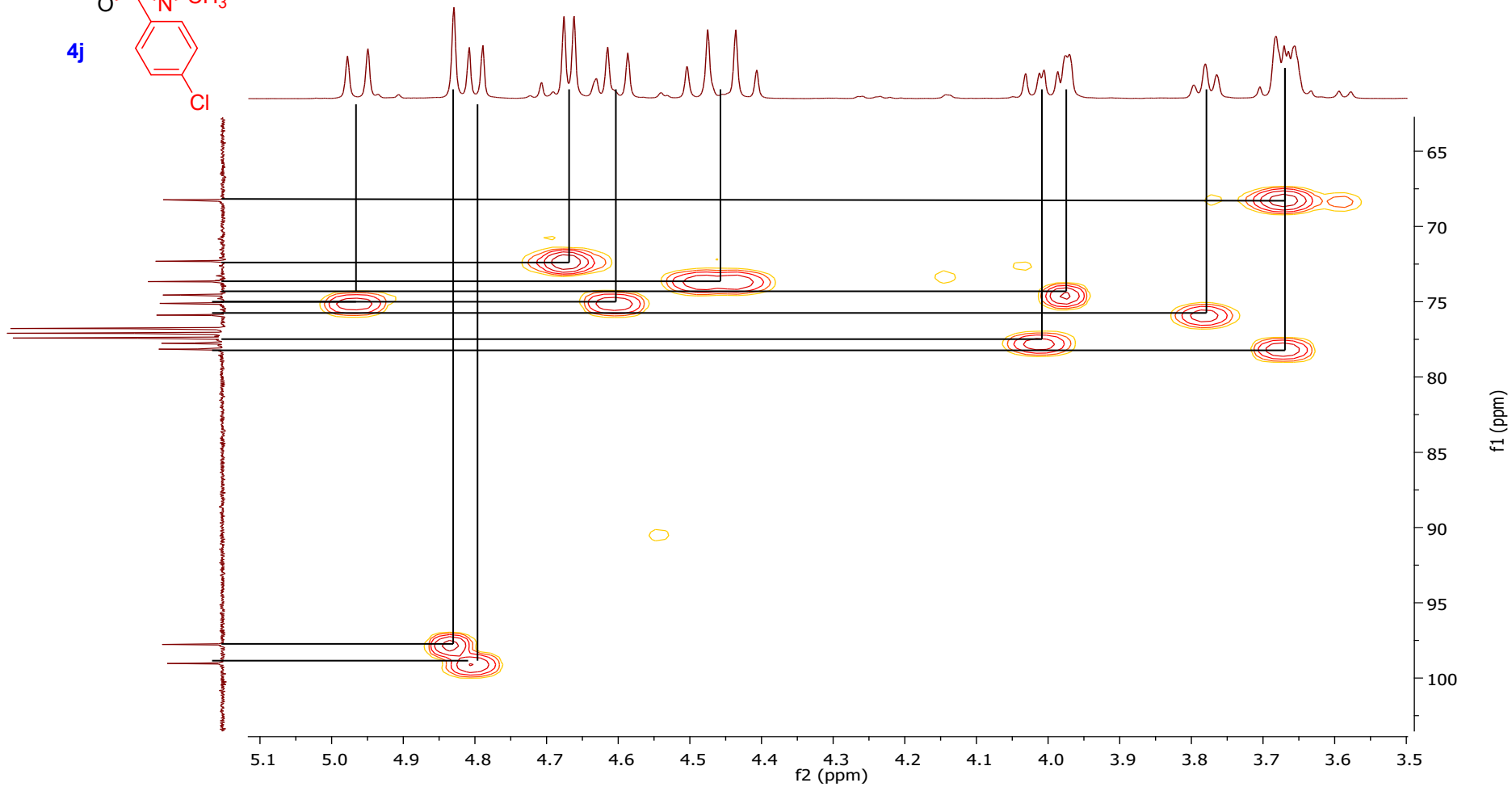
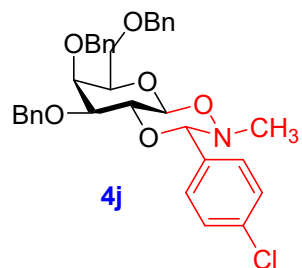
Labeled ¹H of compound 4j



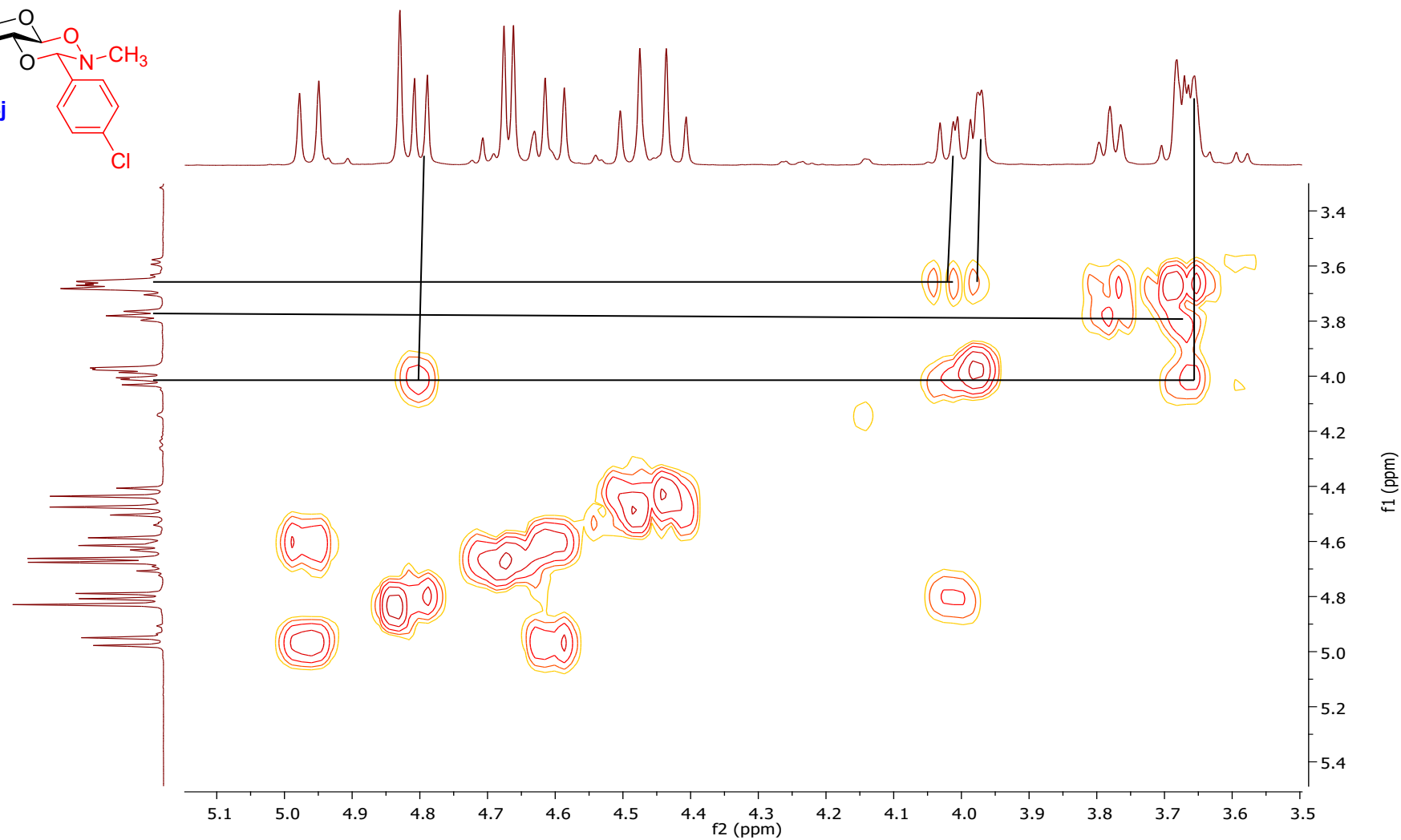
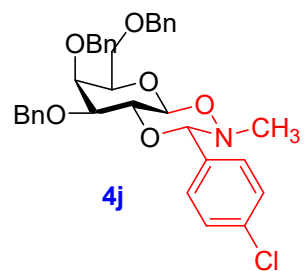
Labeled ¹³C of compound 4j



HSQC correlation of 4j



COSY correlation of 4j



NOESY correlation of 4j

