Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Chirality Extension of an Oxazine Building Block En Route to Total Syntheses of (+)-Hyacinthacine A_2 and Sphingofungin B

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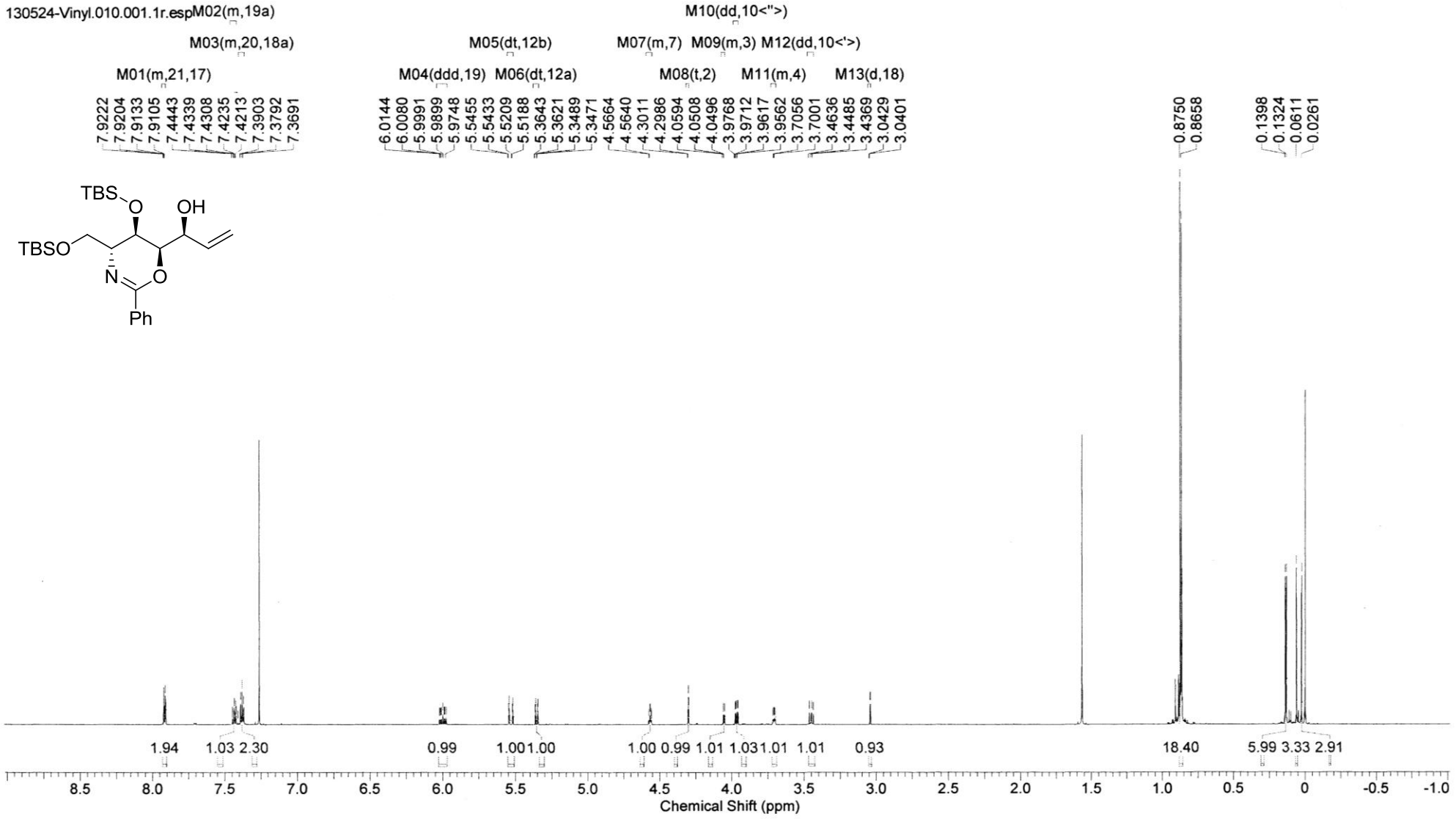
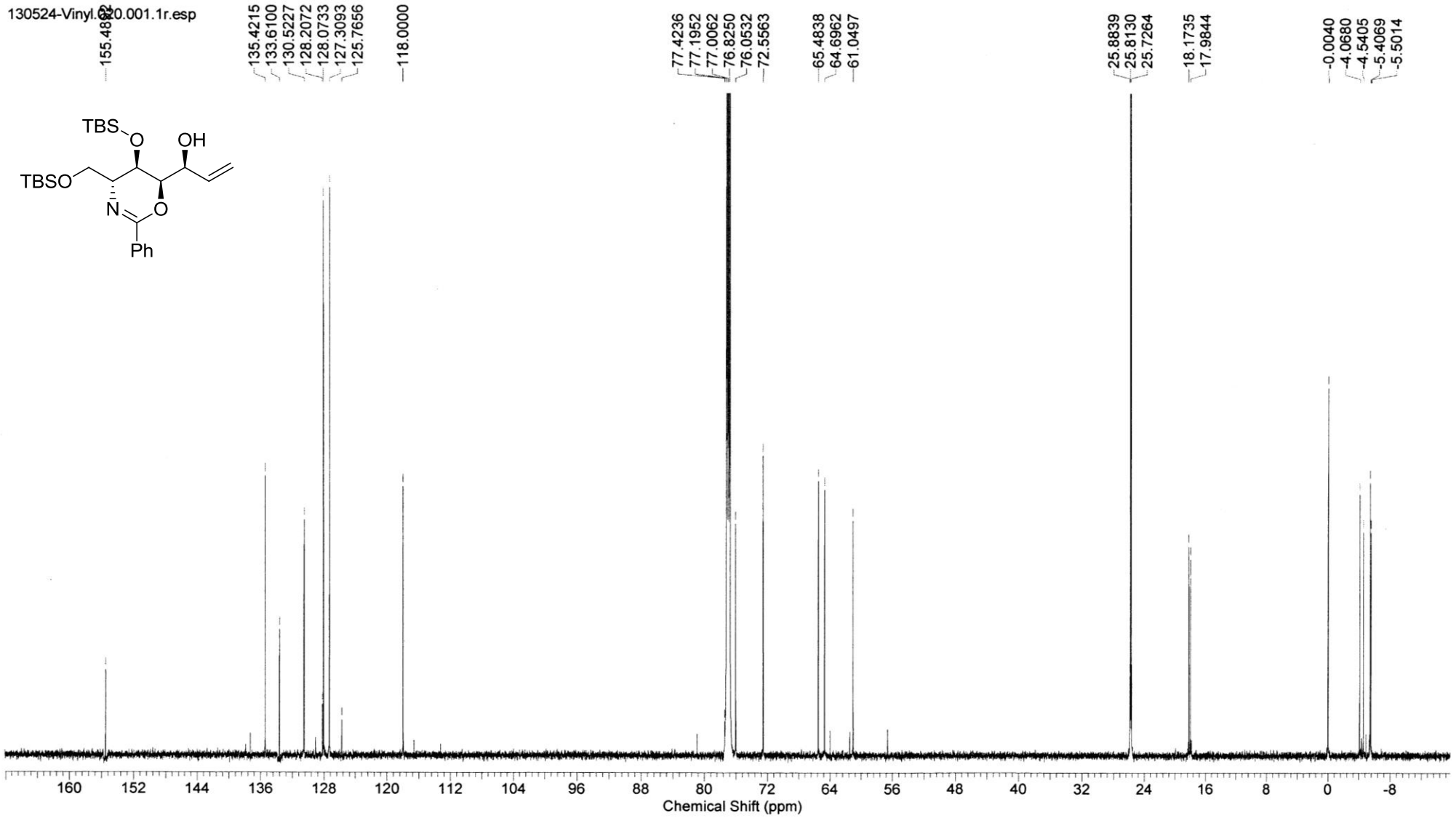
[b] Yonsung Fine Chemicals Co., Ltd., Hwaseong 445-944, Republic of Korea
whham@skku.edu

Supporting information

syn-**5a** (700 MHz, $CDCl_3$)



syn-**5a** (175 MHz, $CDCl_3$)



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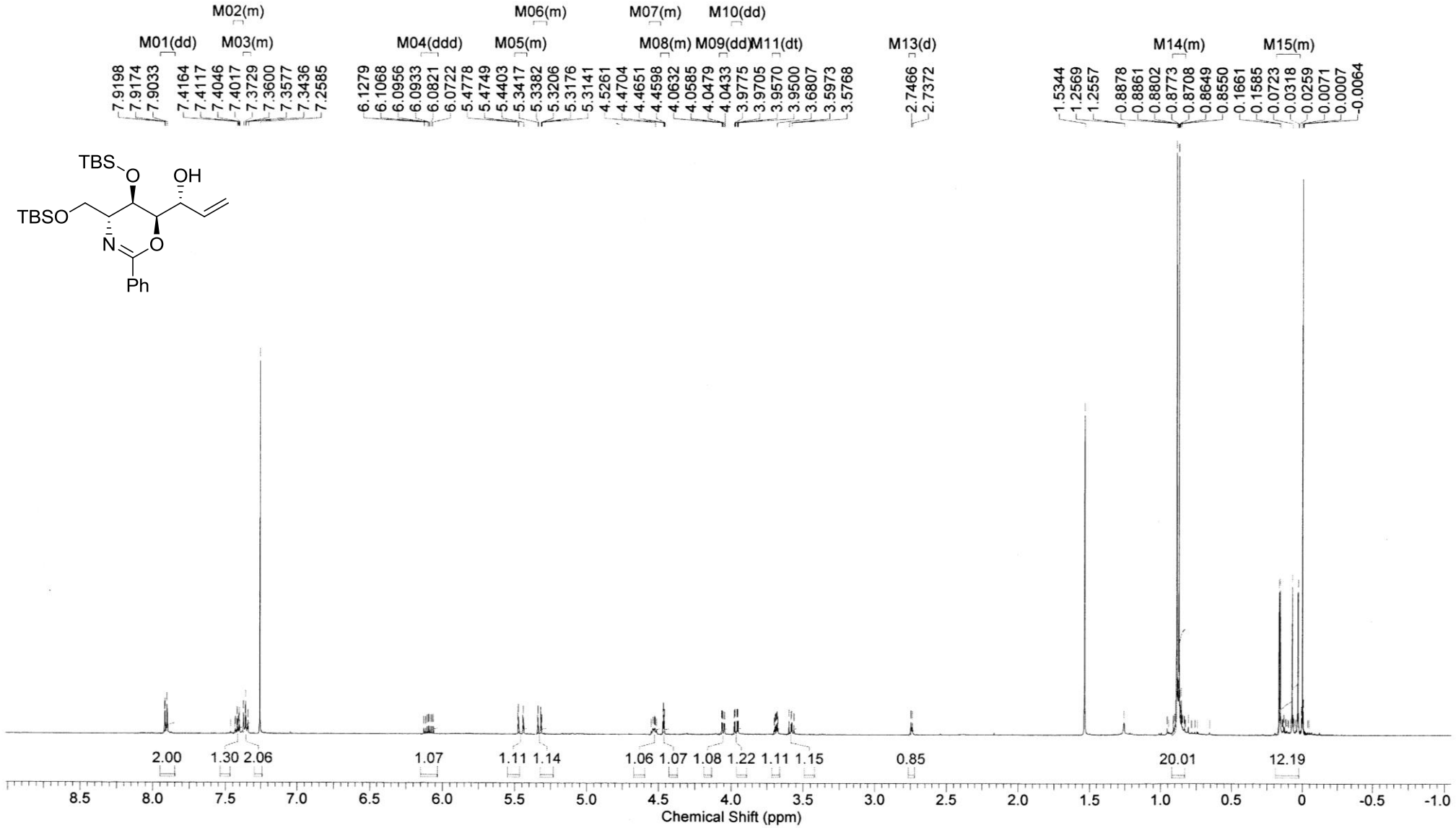

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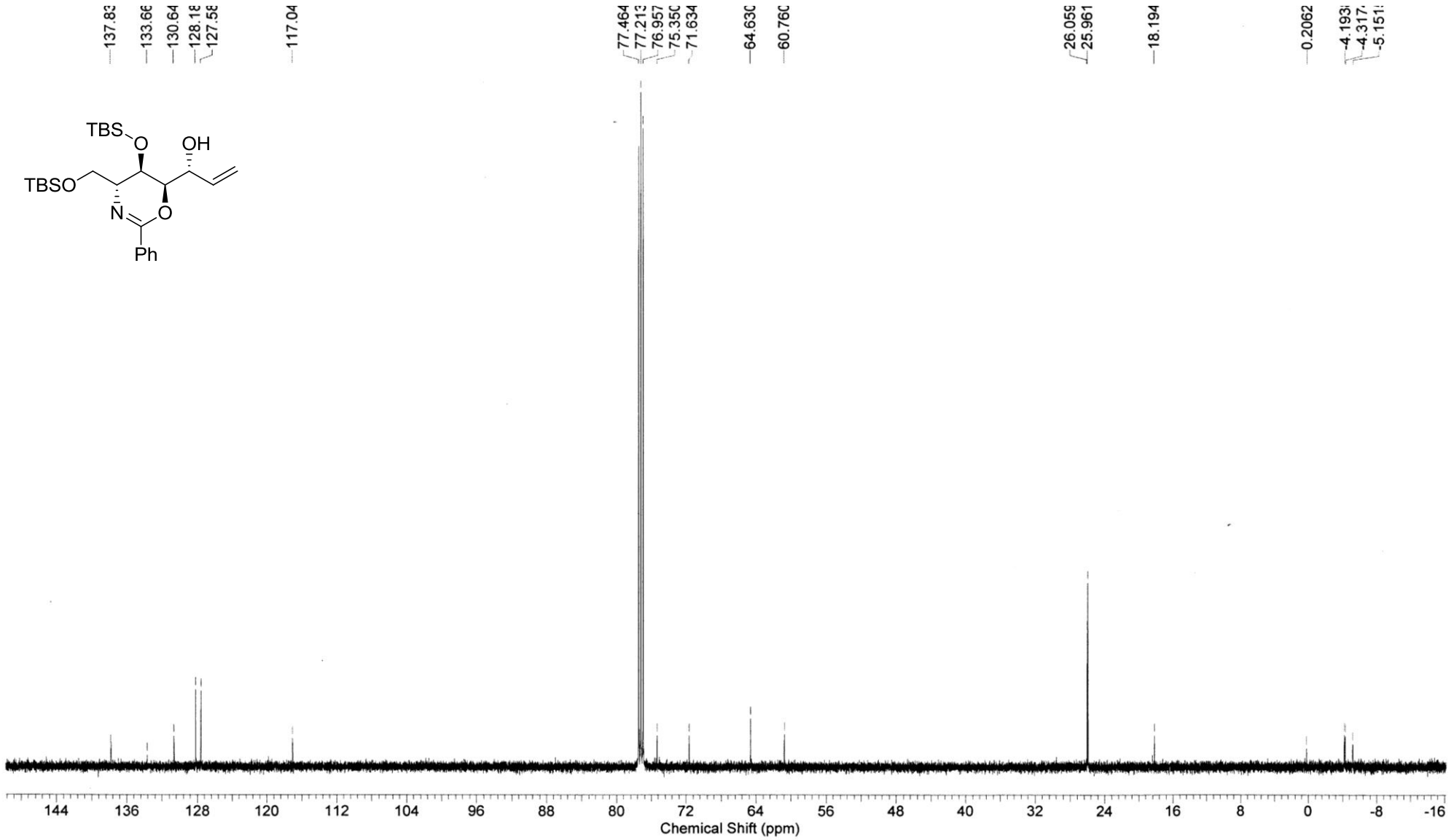

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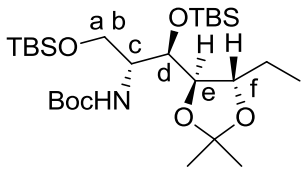

cis-**6** (NOESY)

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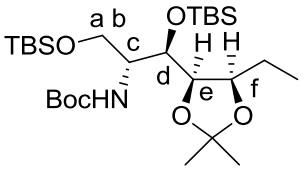
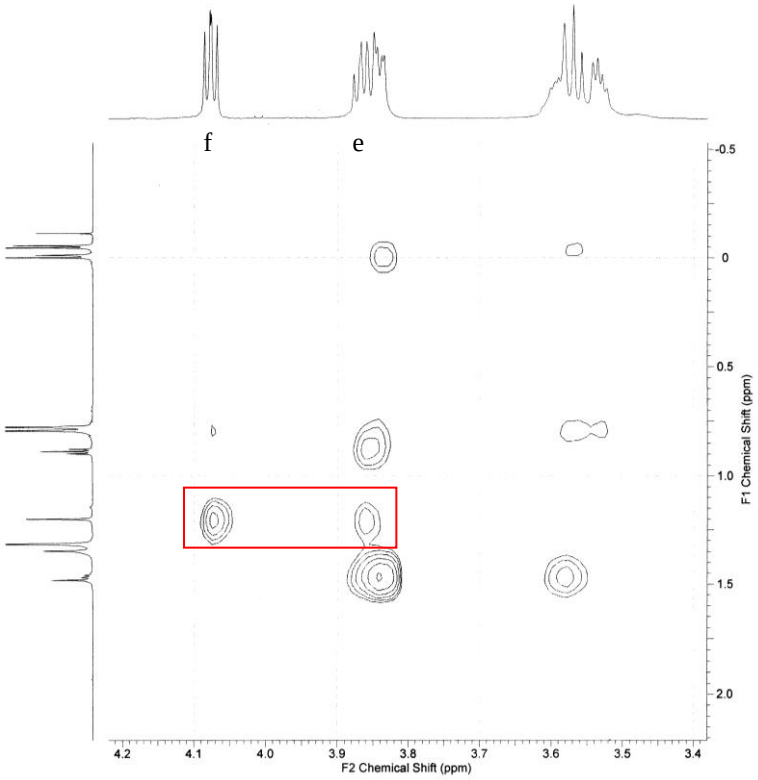
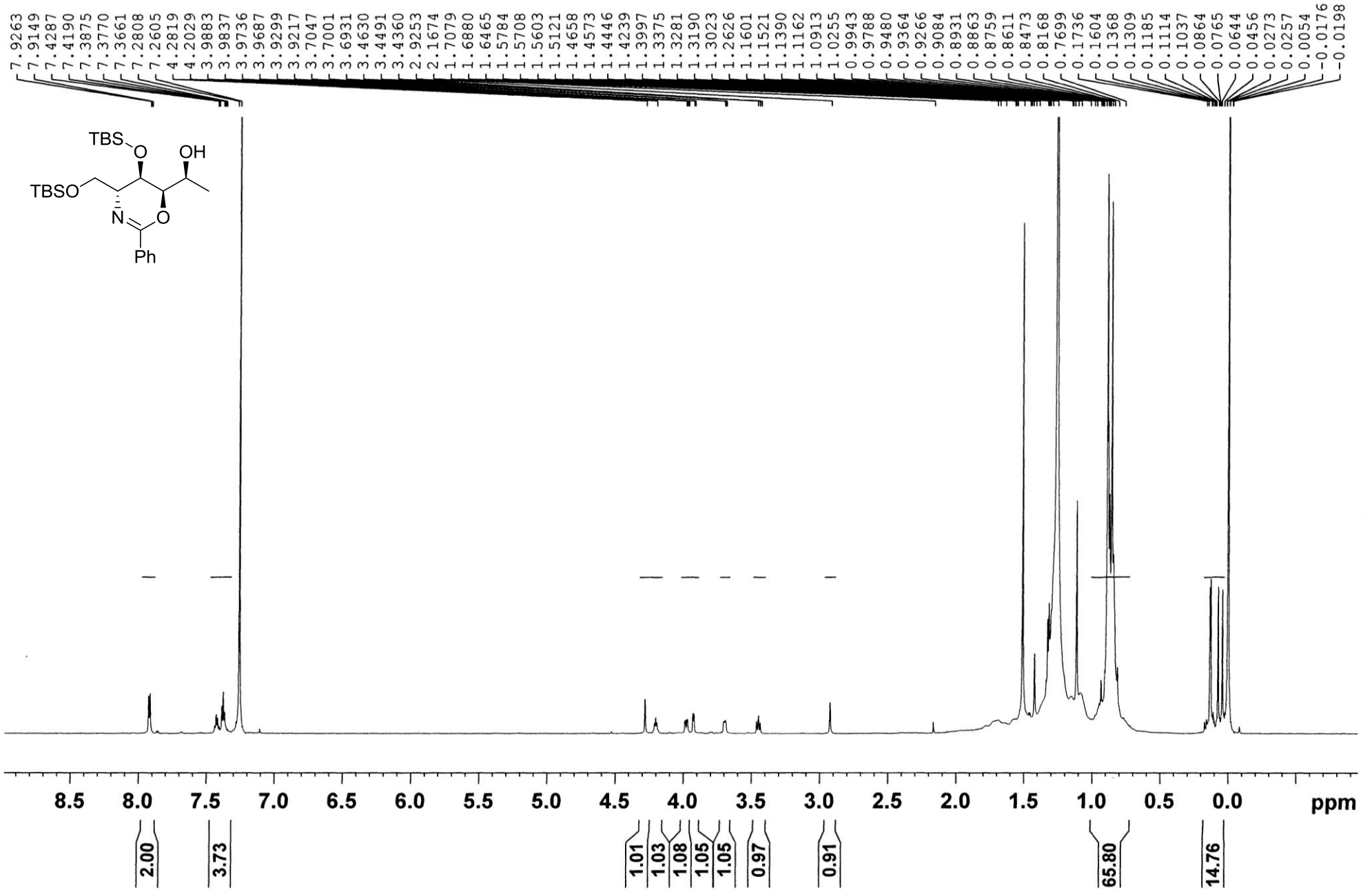




syn-**5b** (700 MHz, $CDCl_3$)



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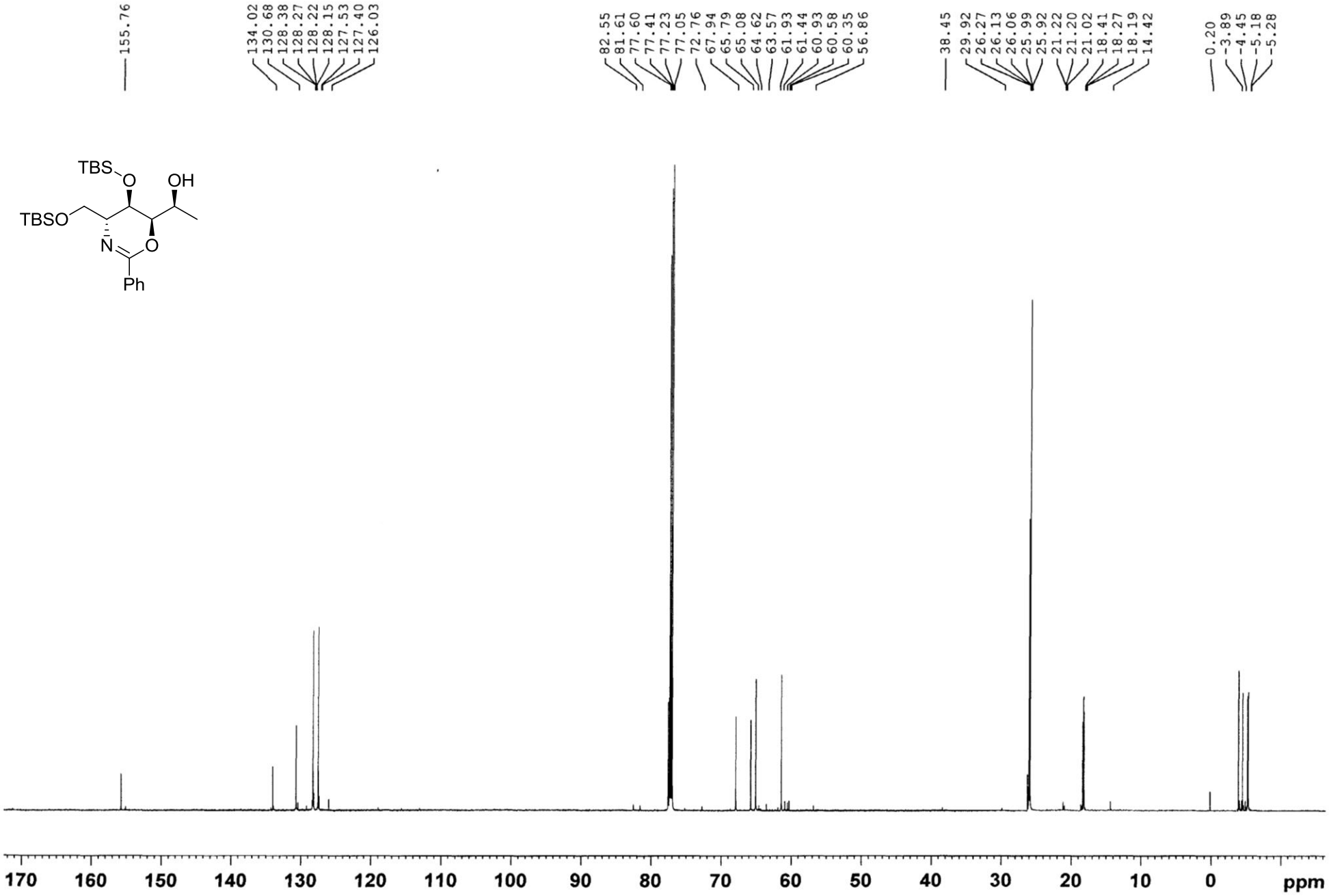

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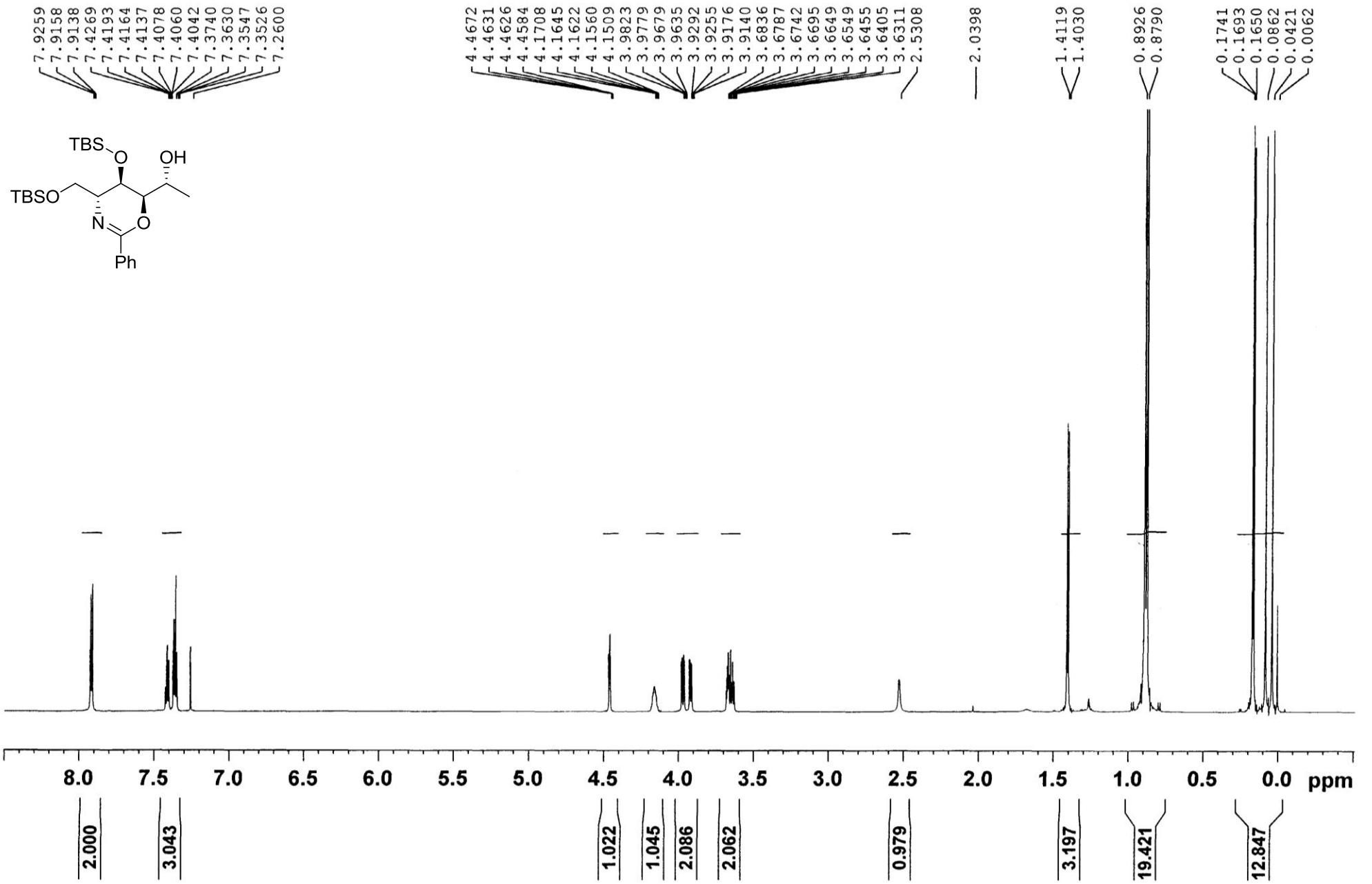

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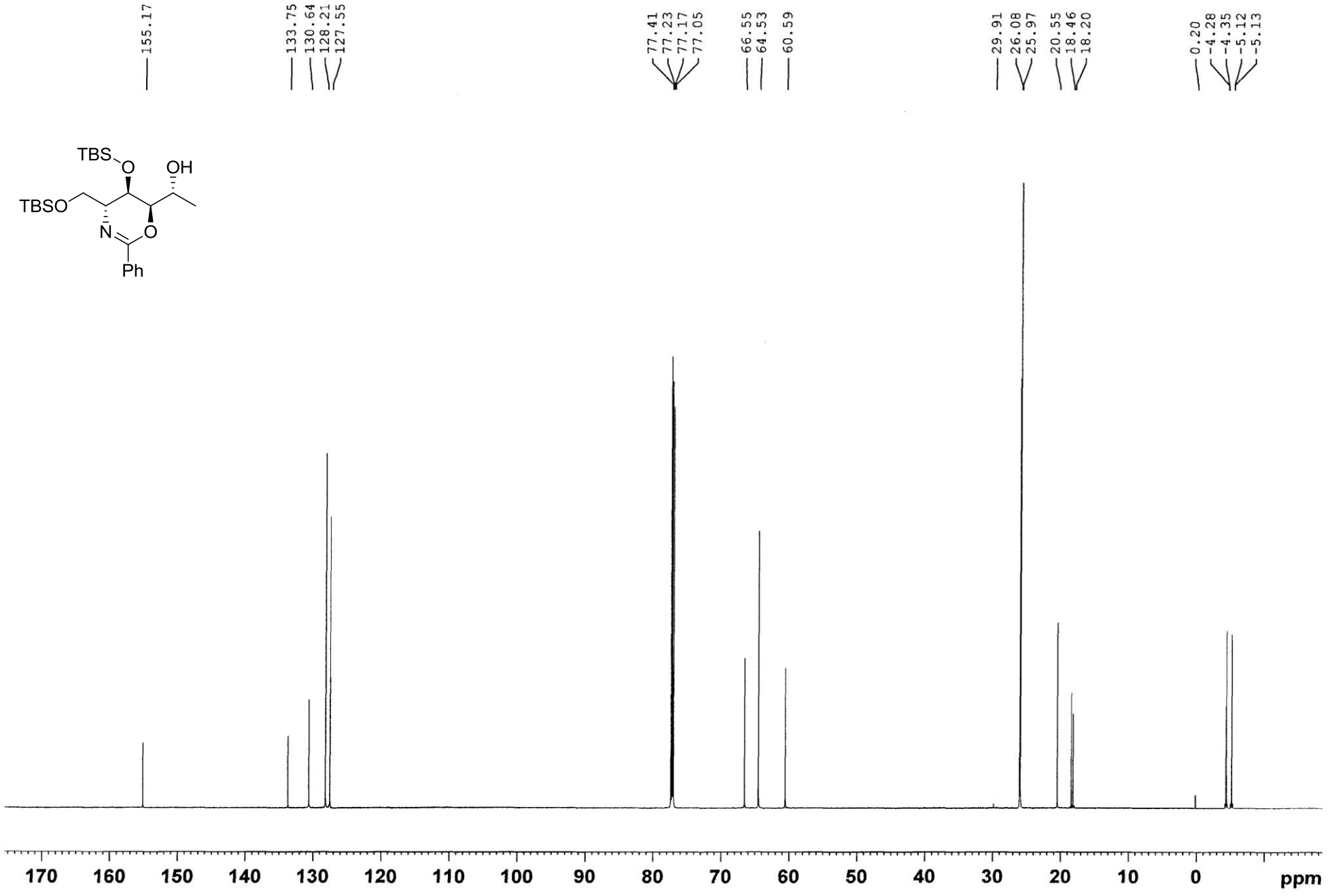

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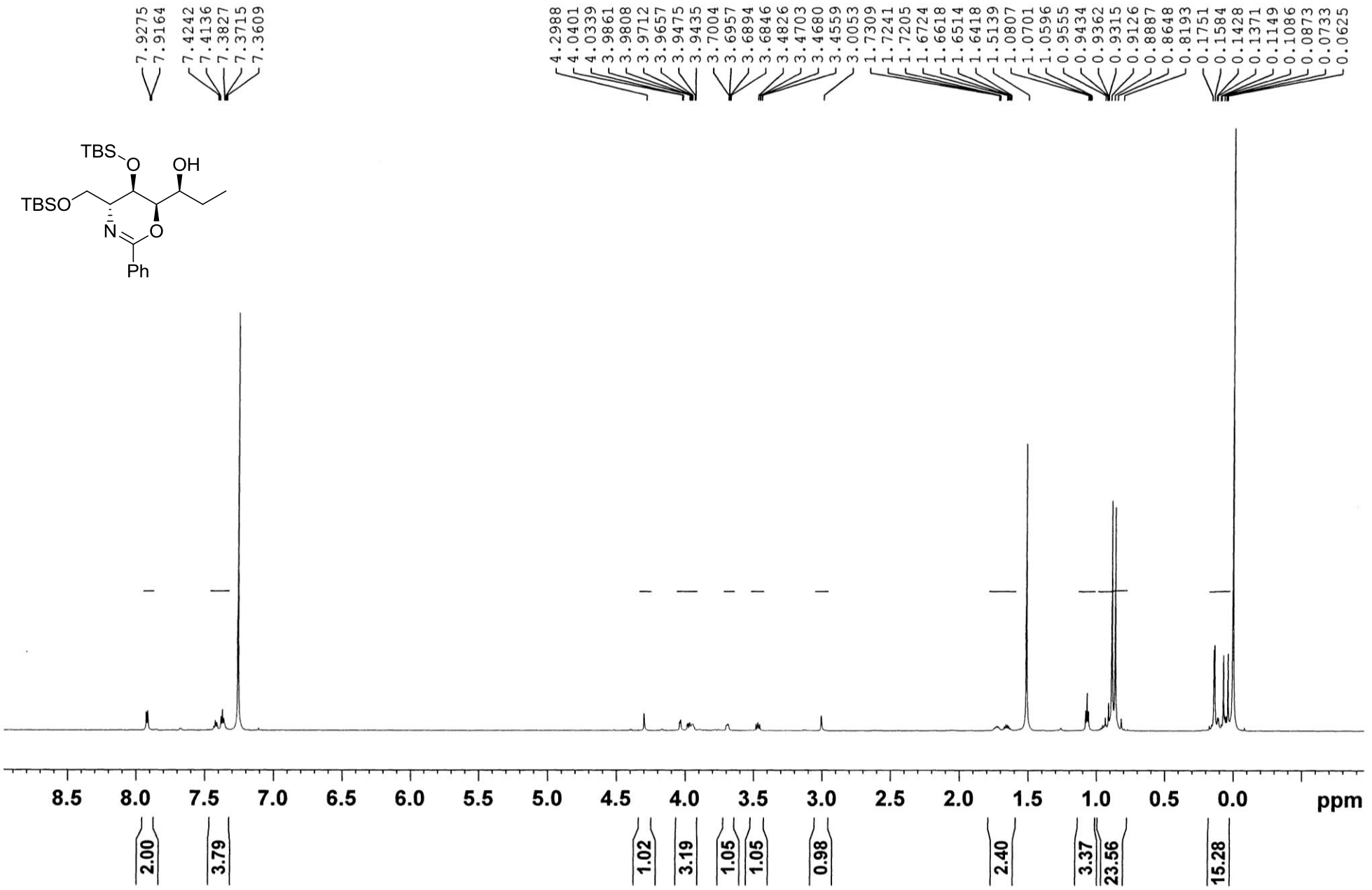

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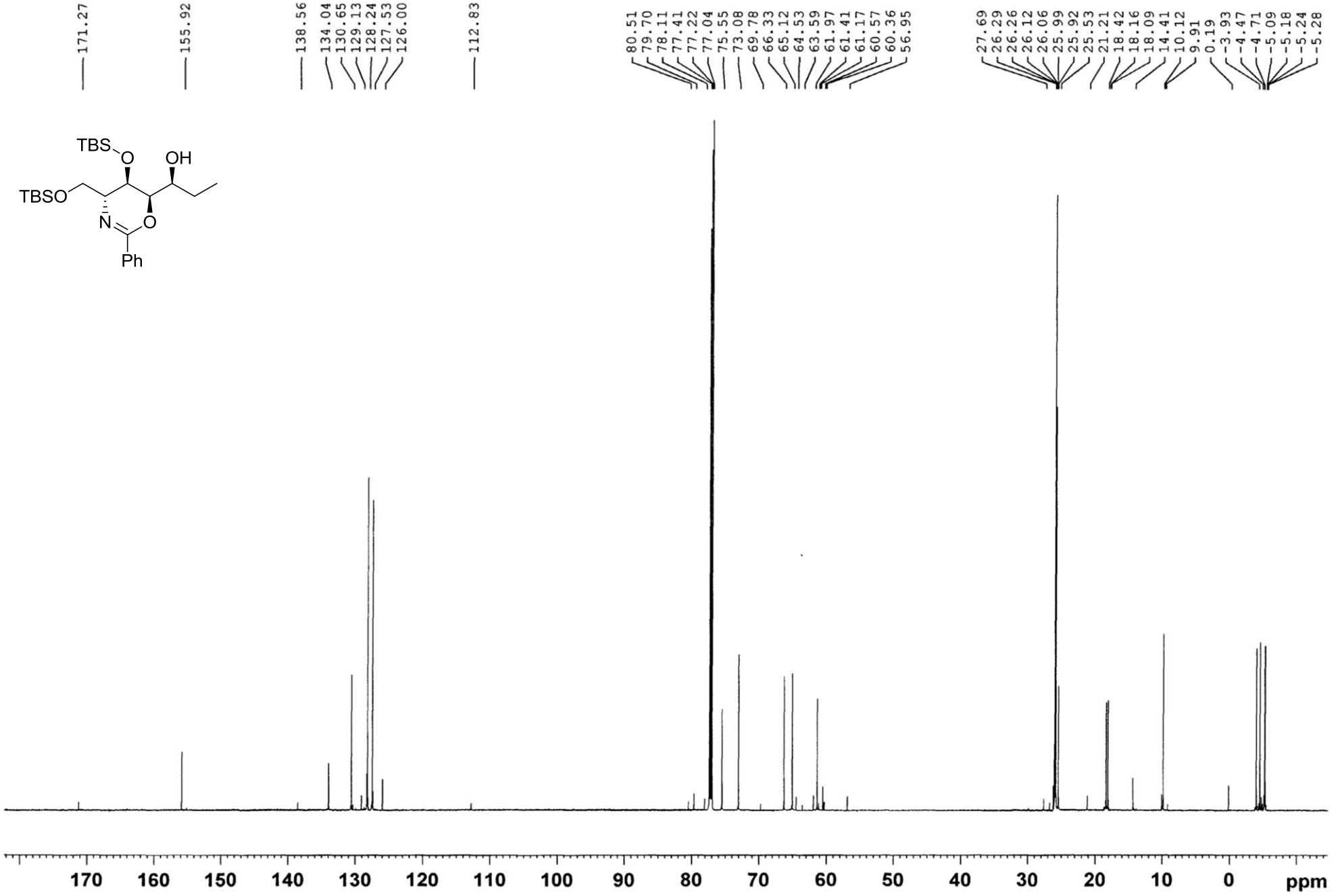

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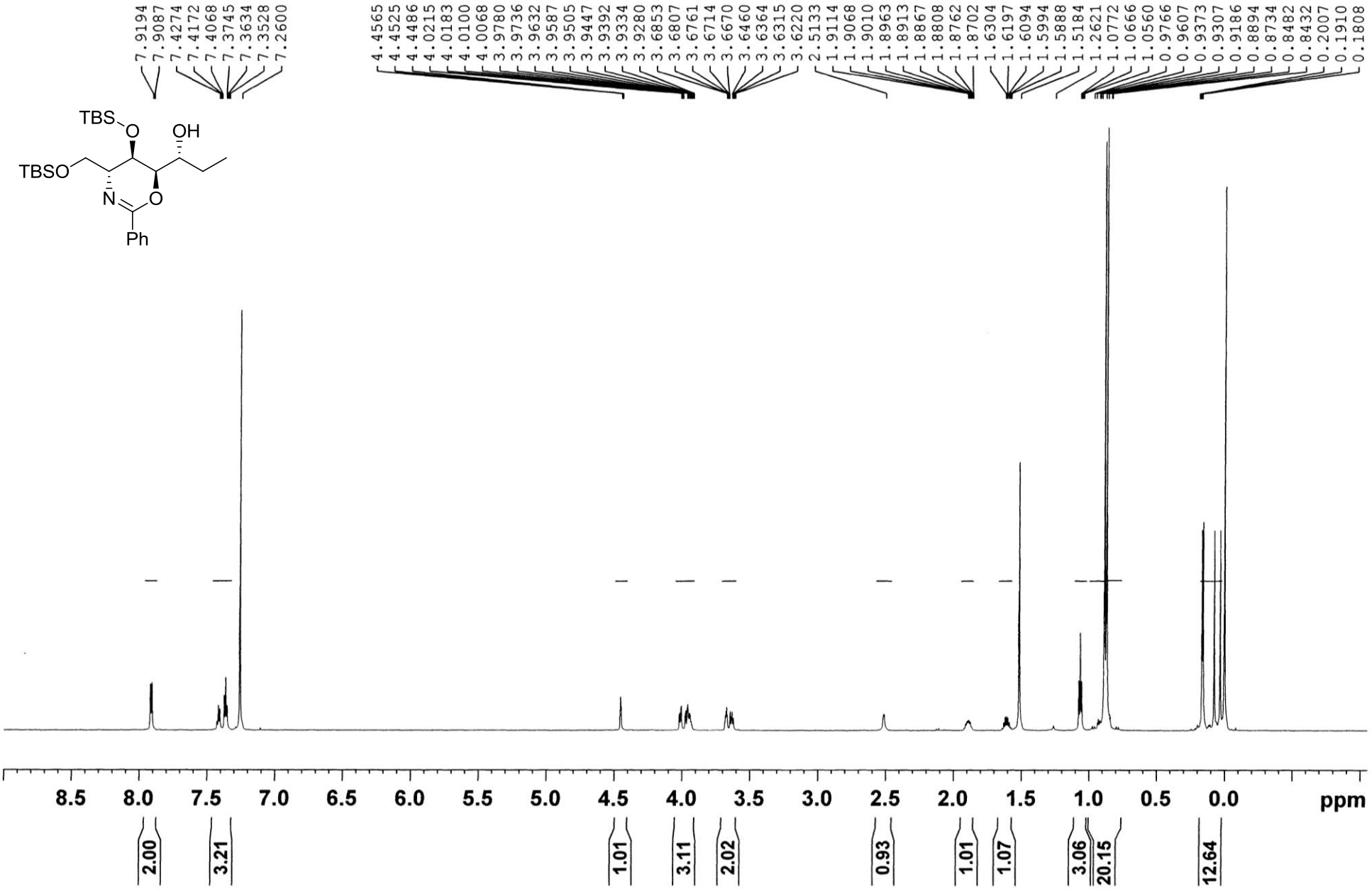

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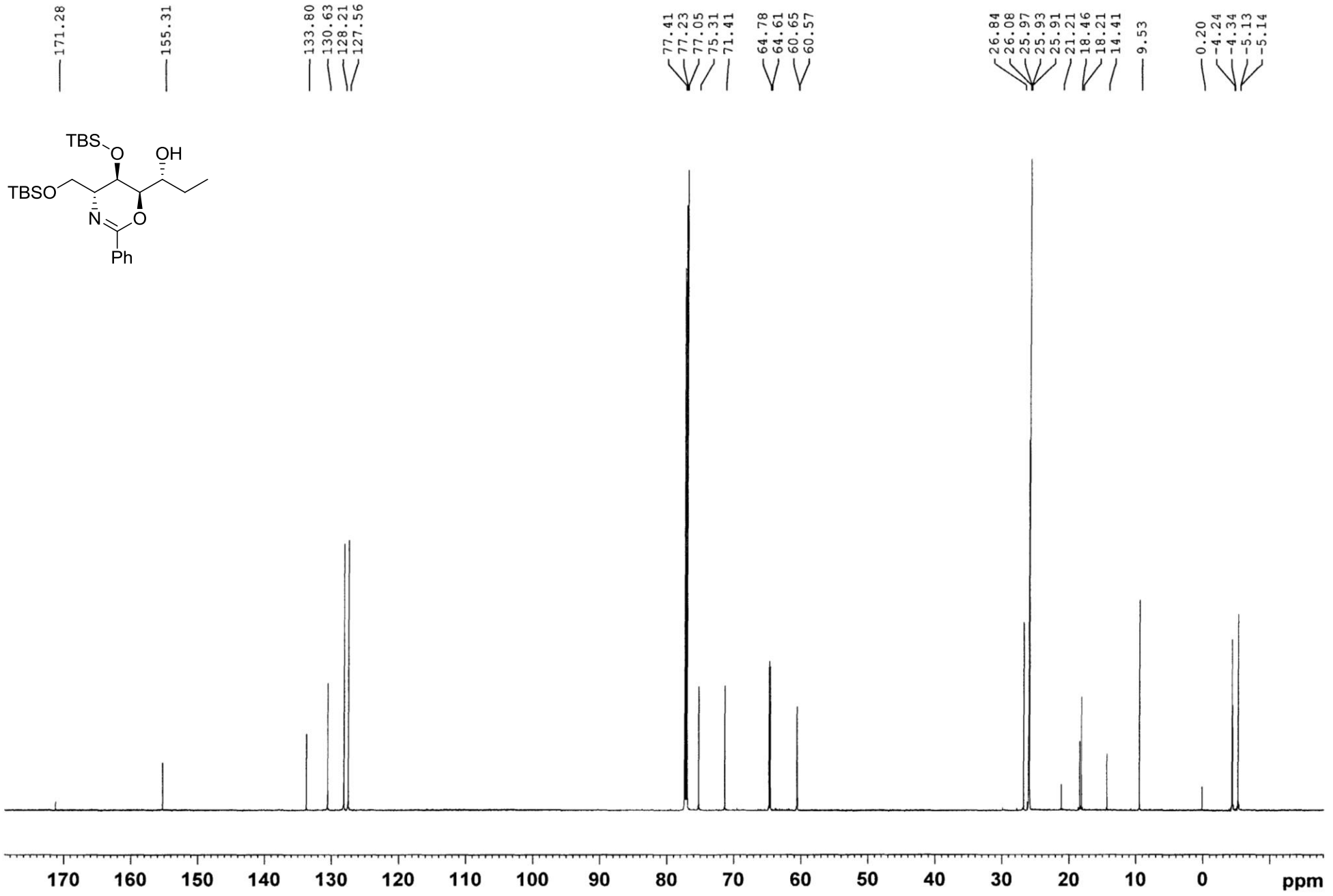

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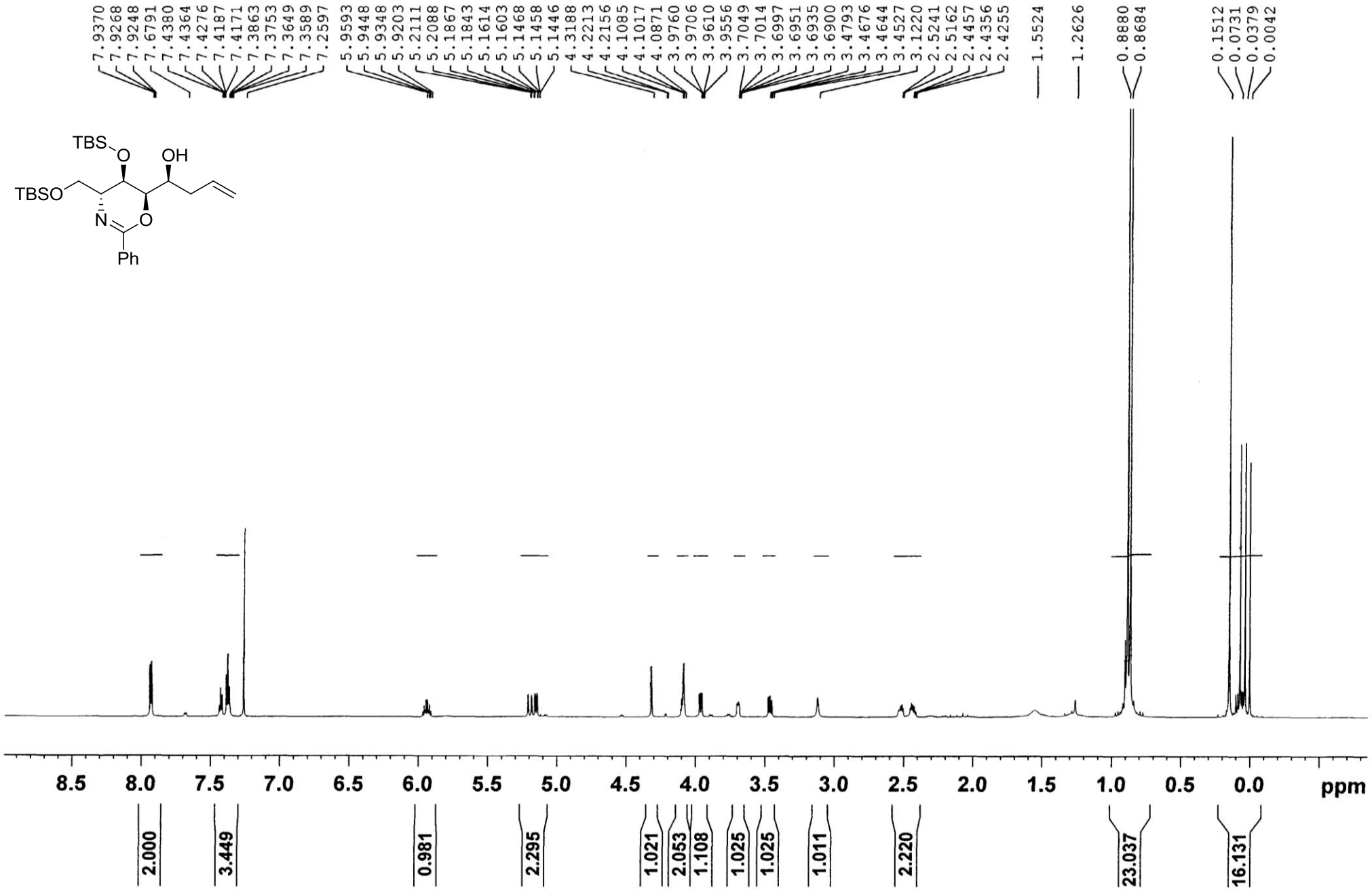

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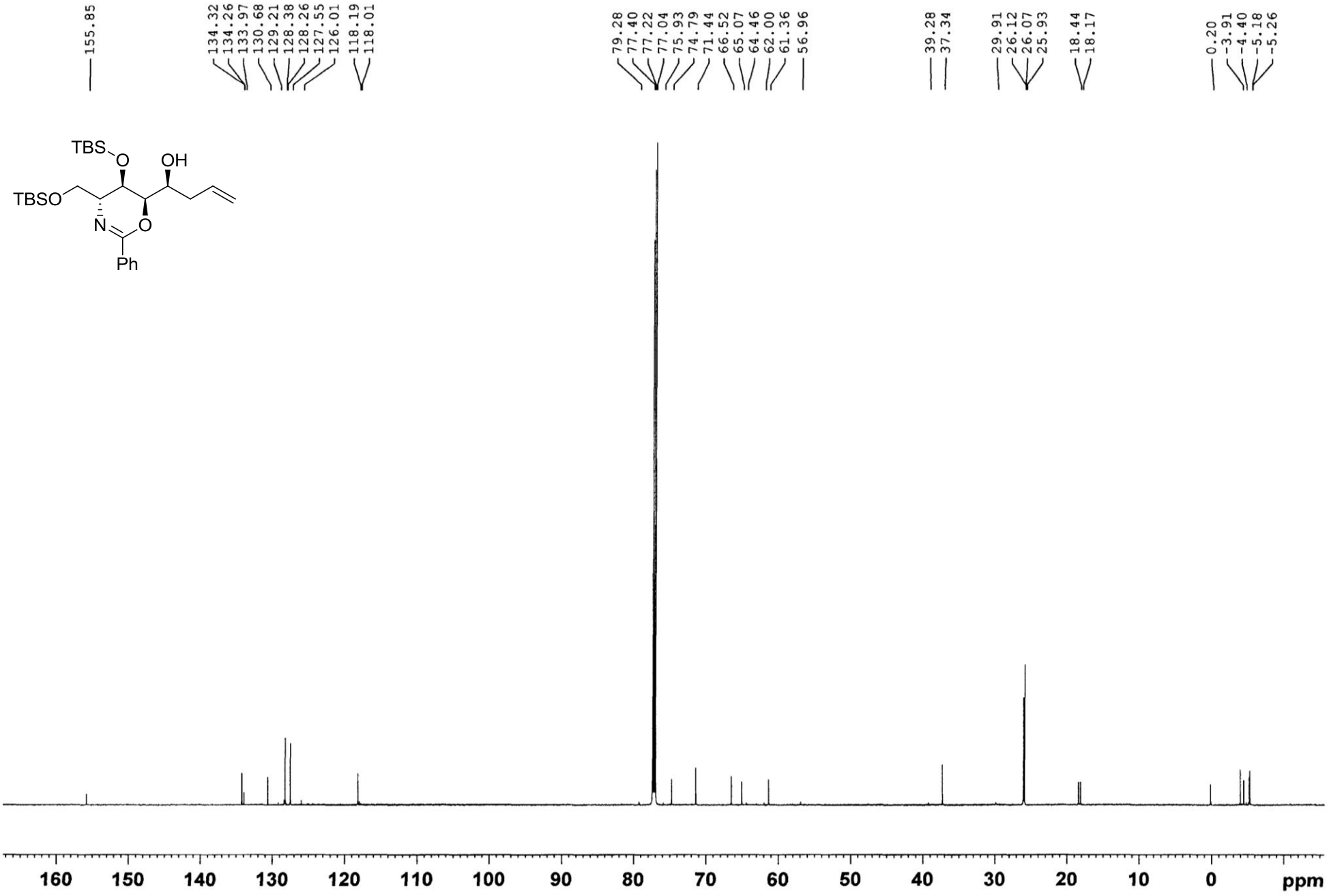

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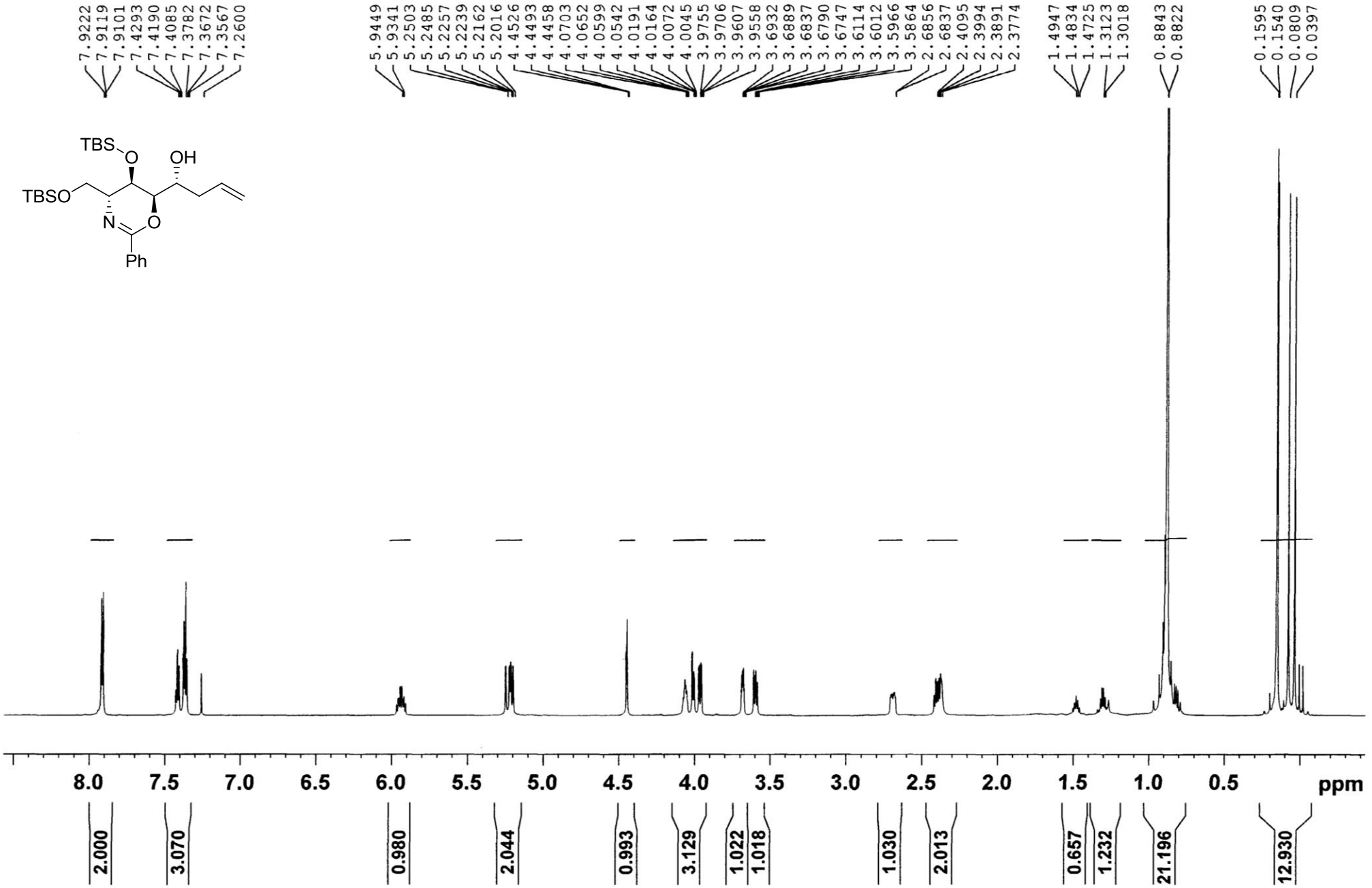

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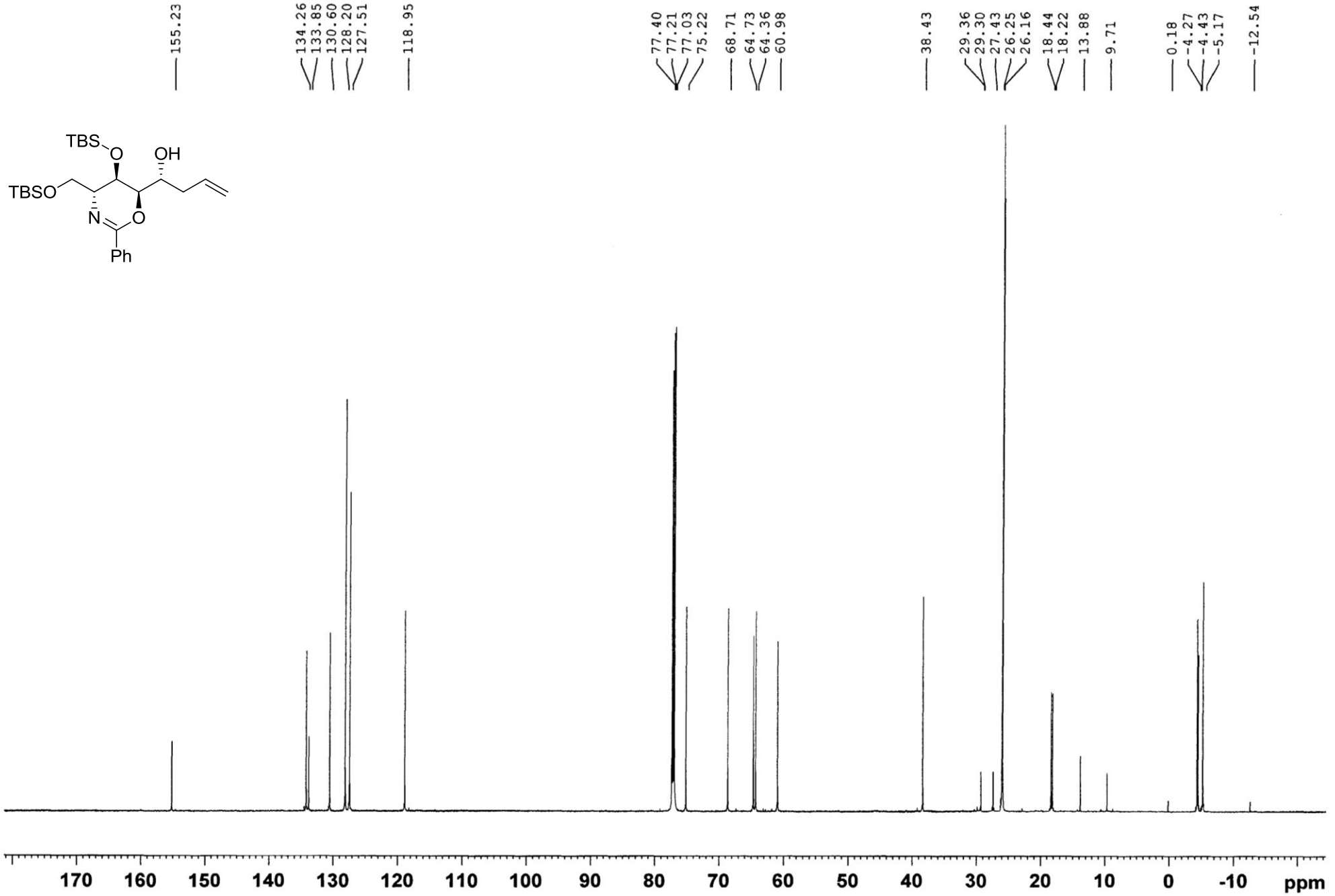
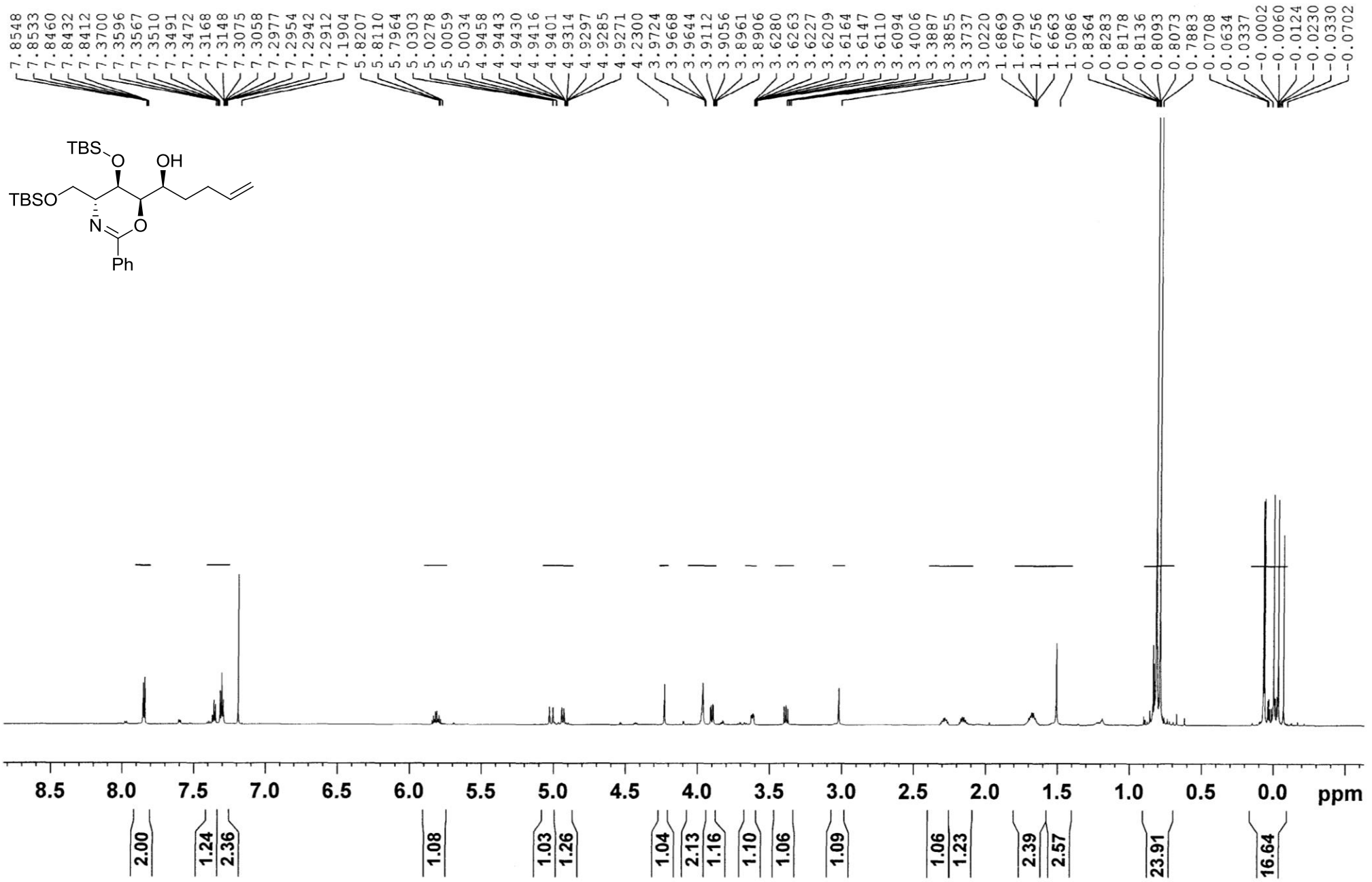


syn-**5e** (700 MHz, $CDCl_3$)



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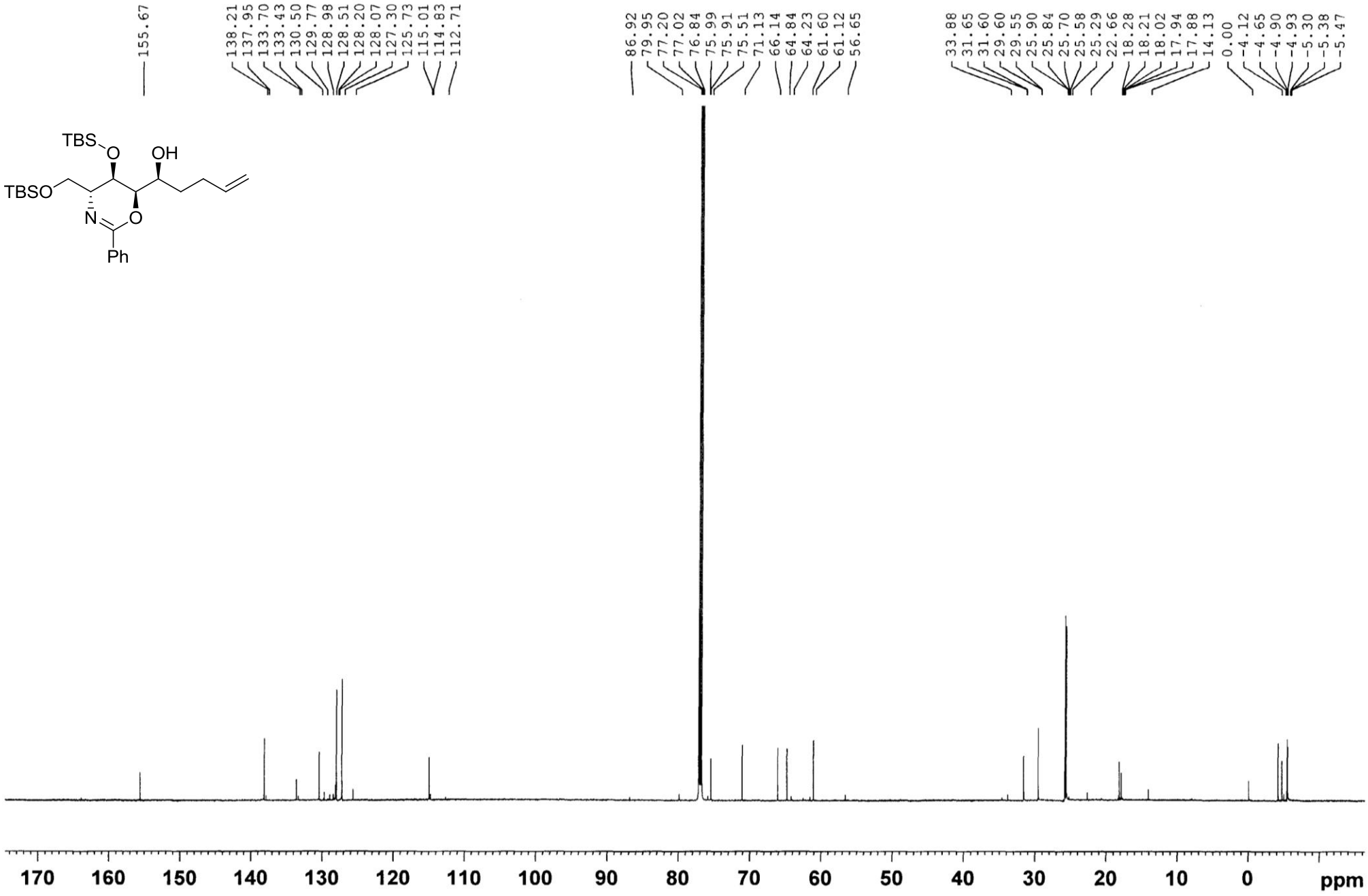
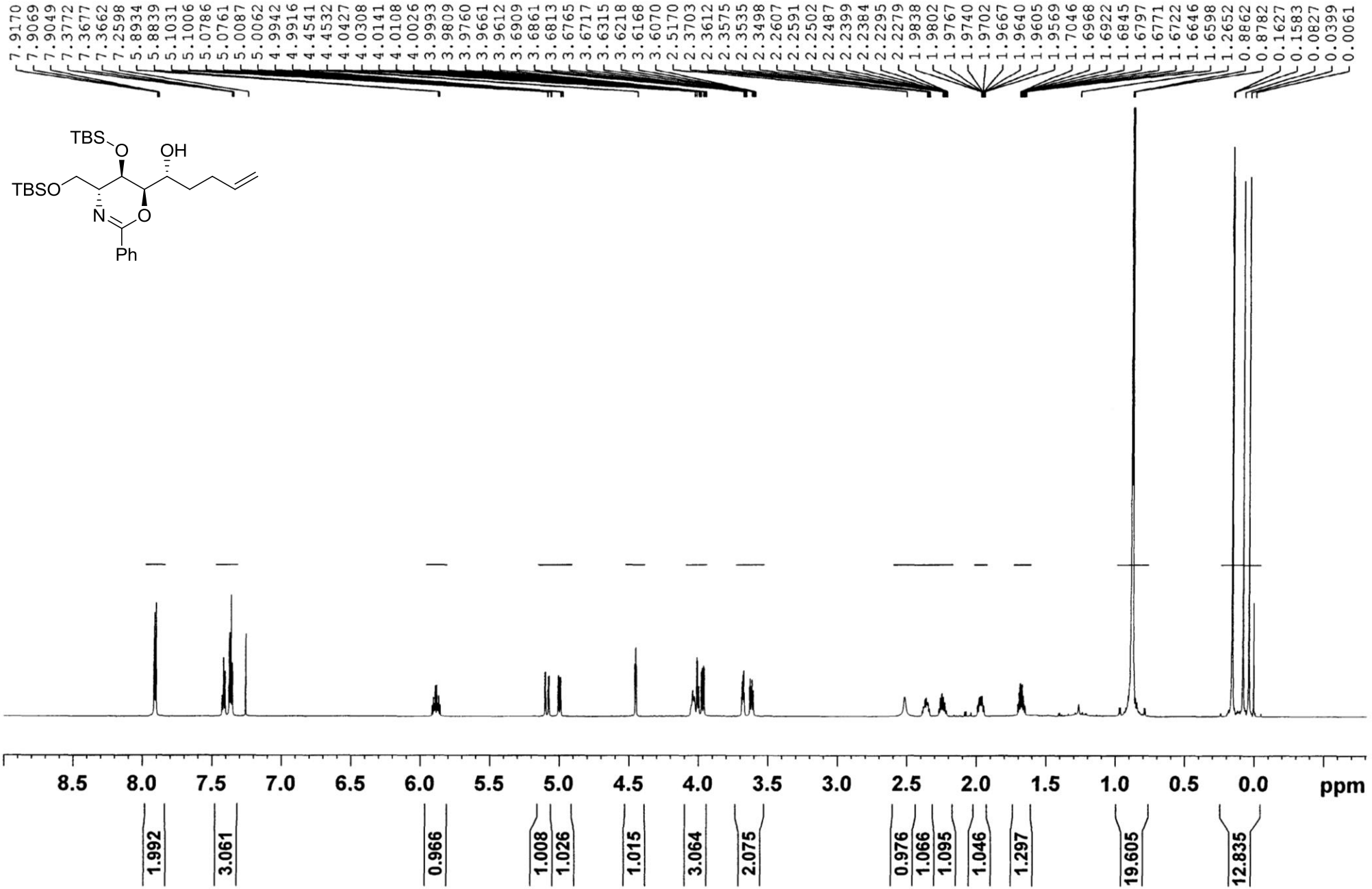


anti-**5e** (700 MHz, $CDCl_3$)



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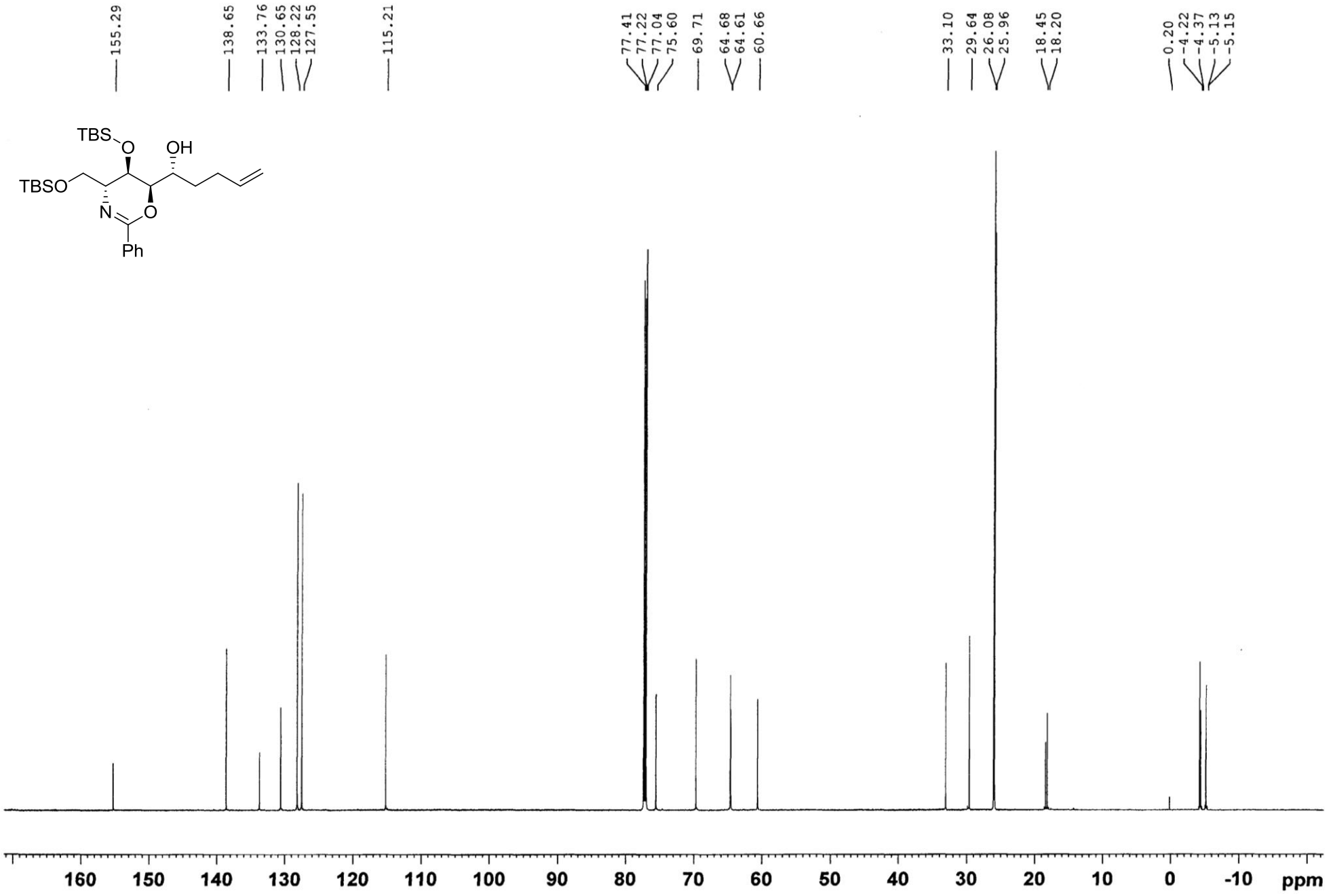

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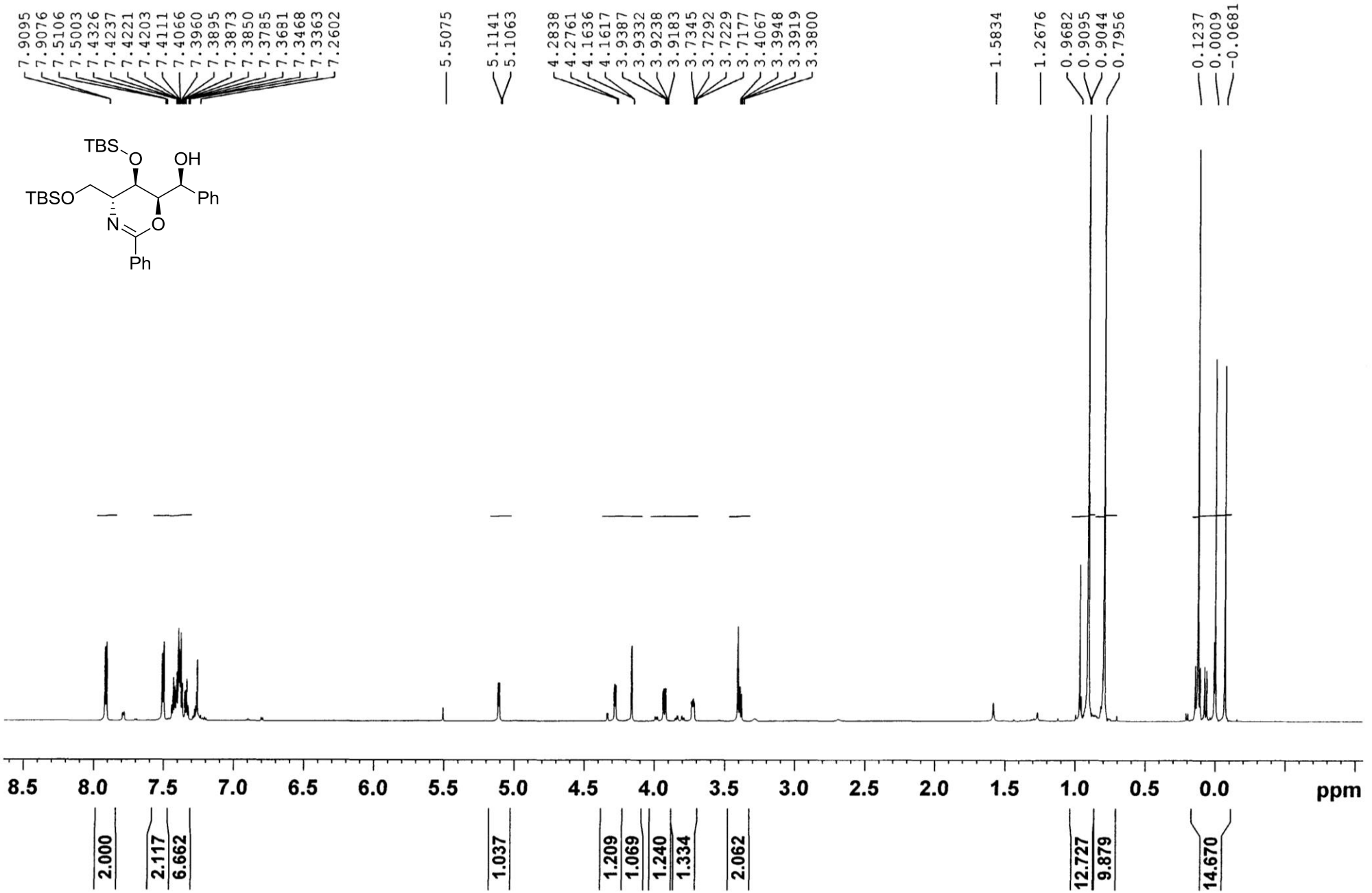

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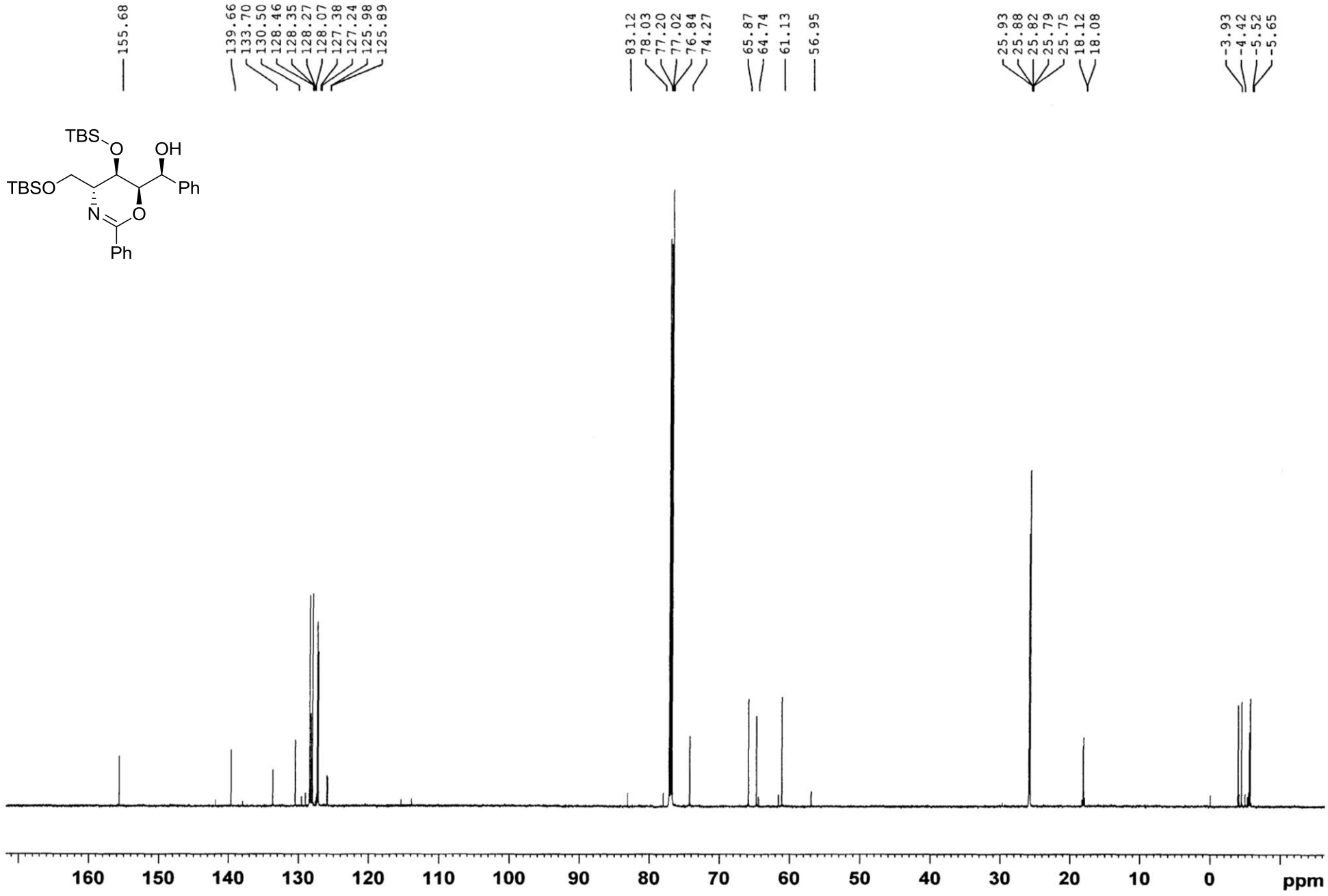

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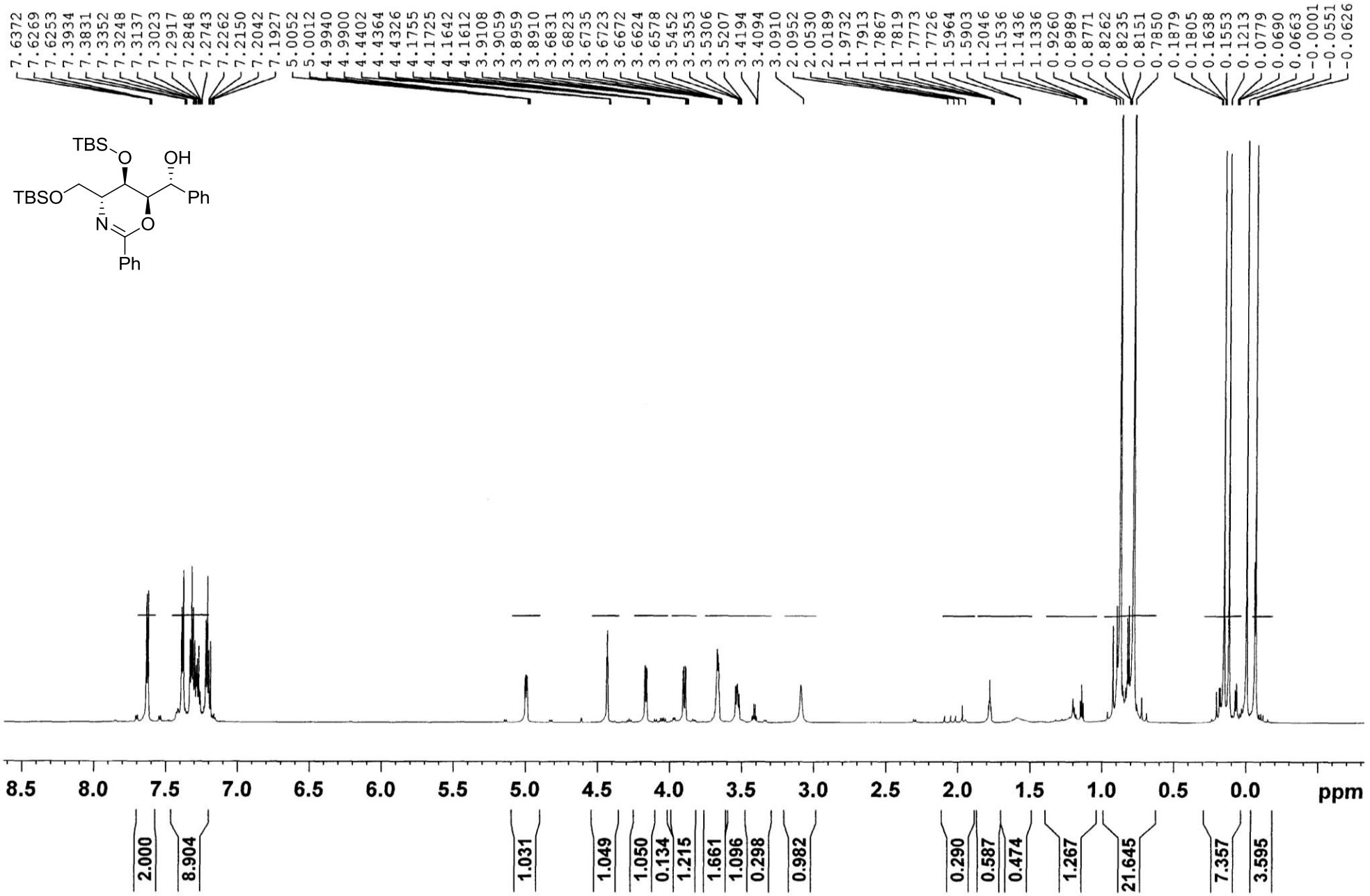

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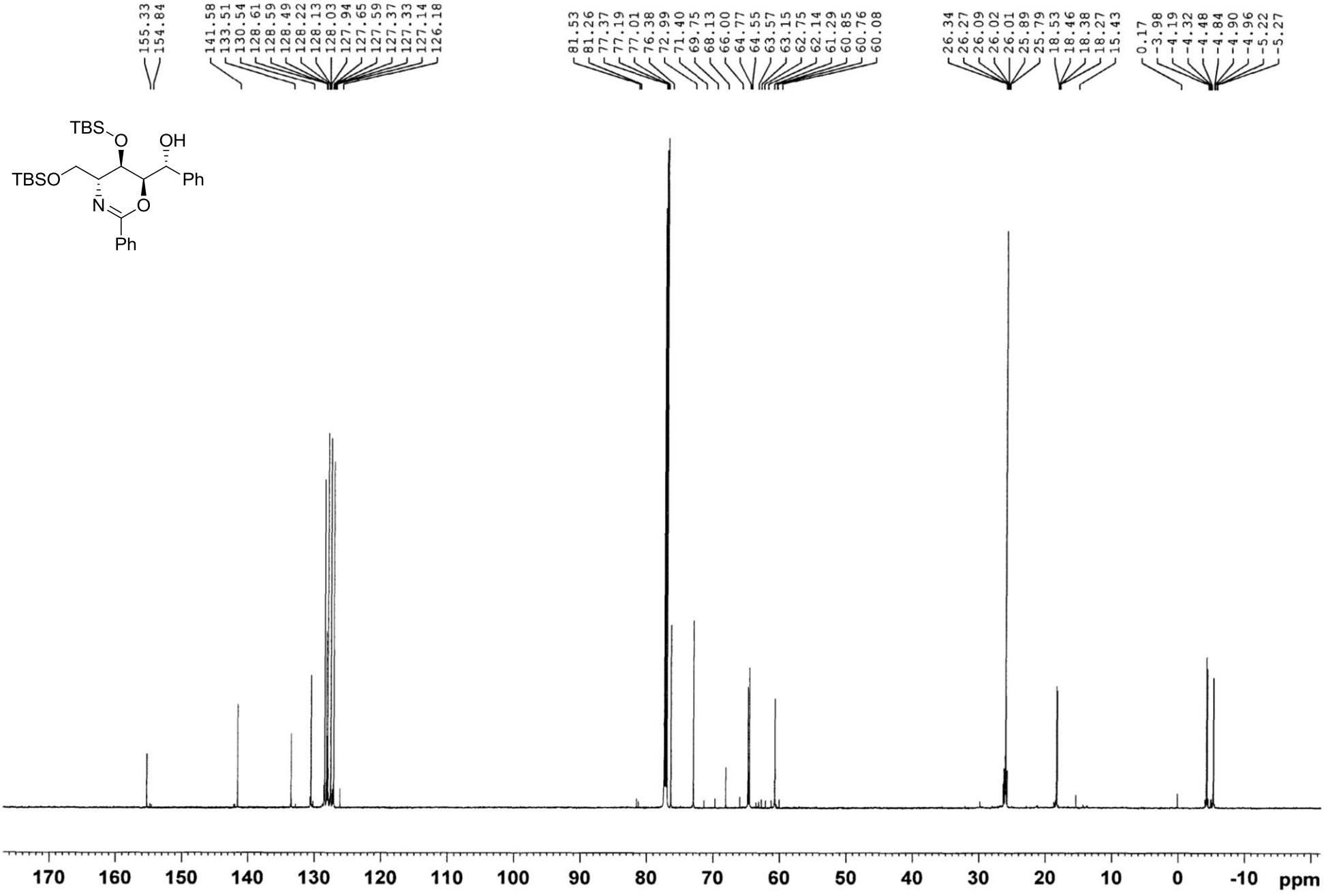
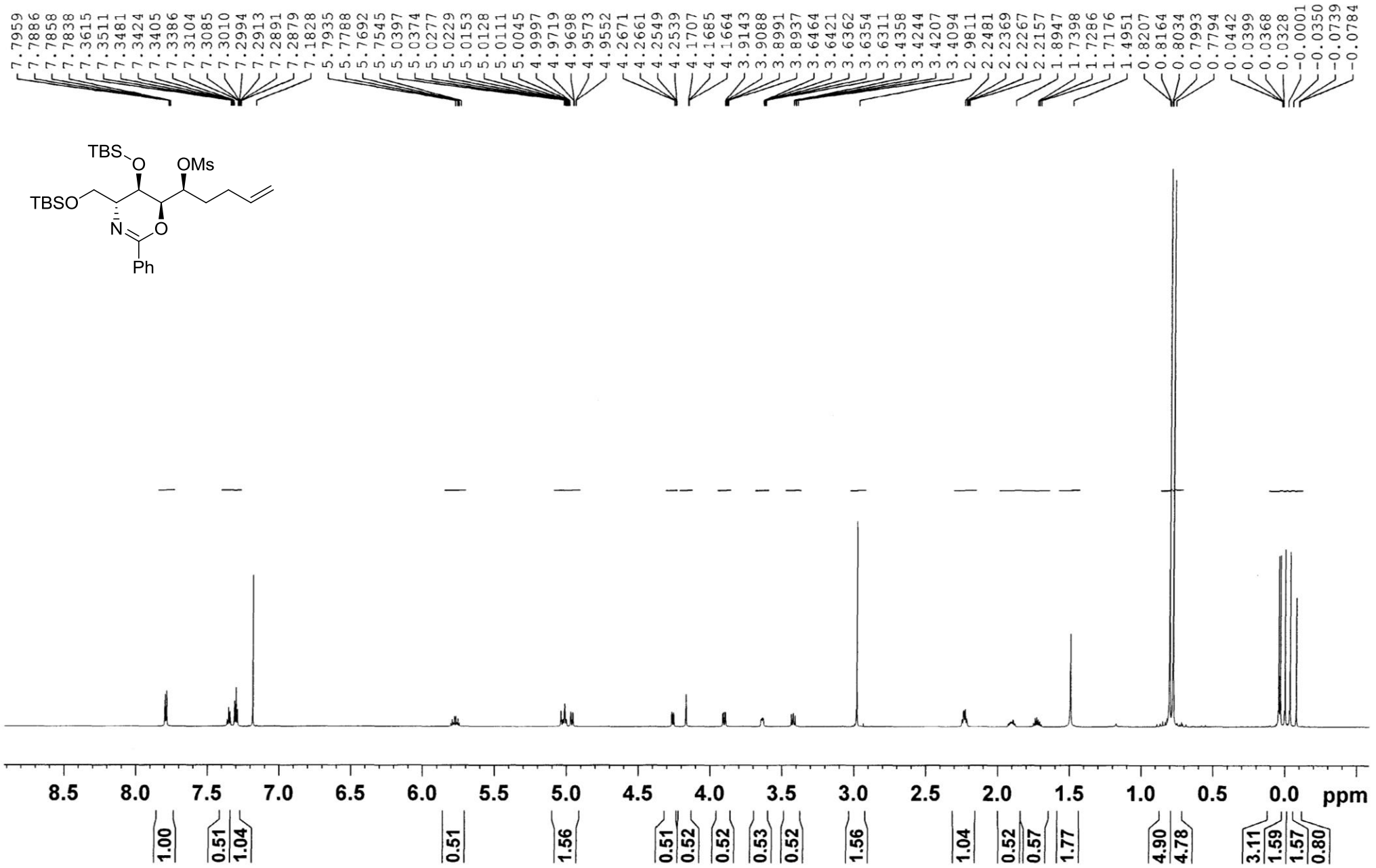
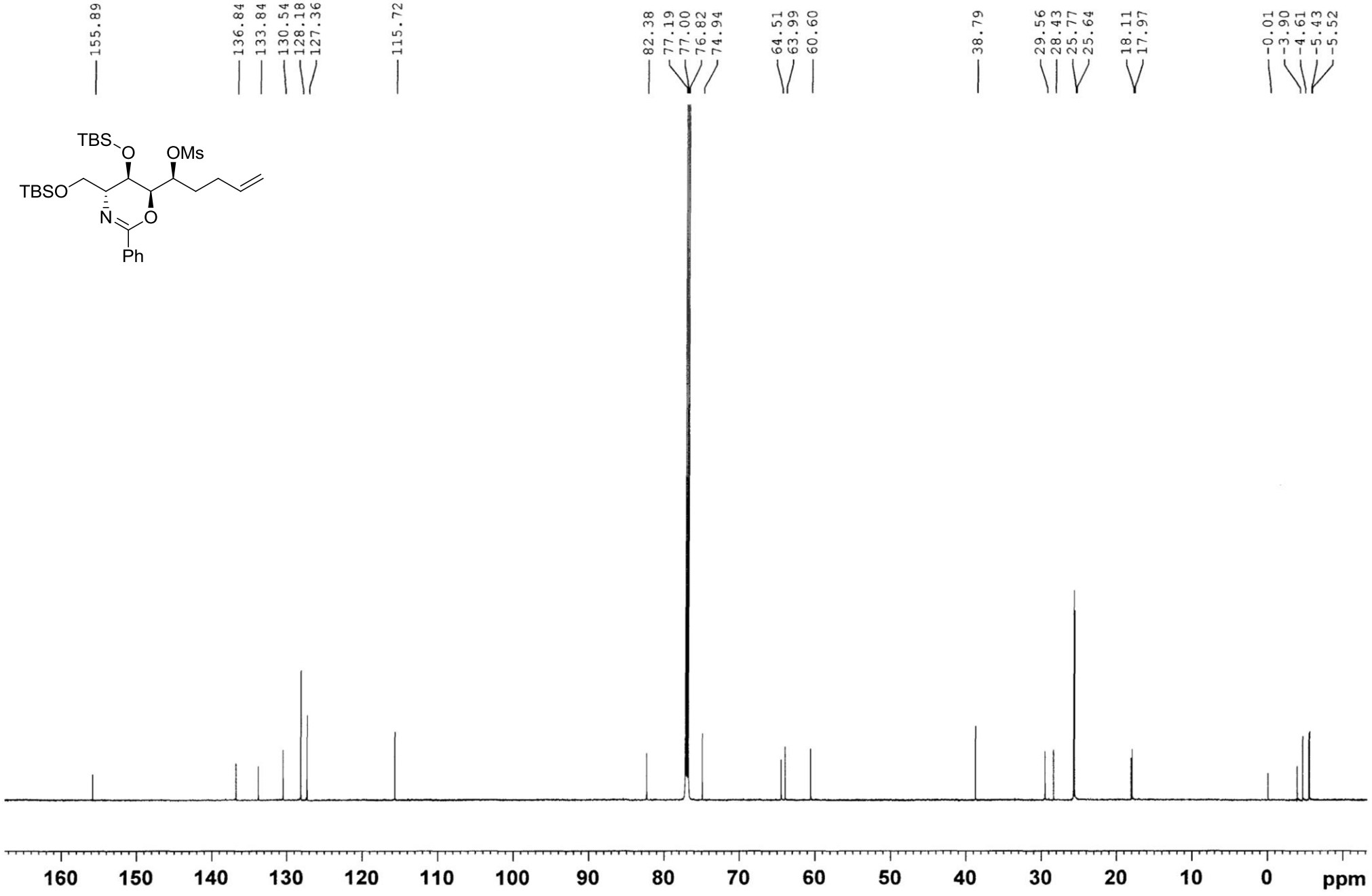


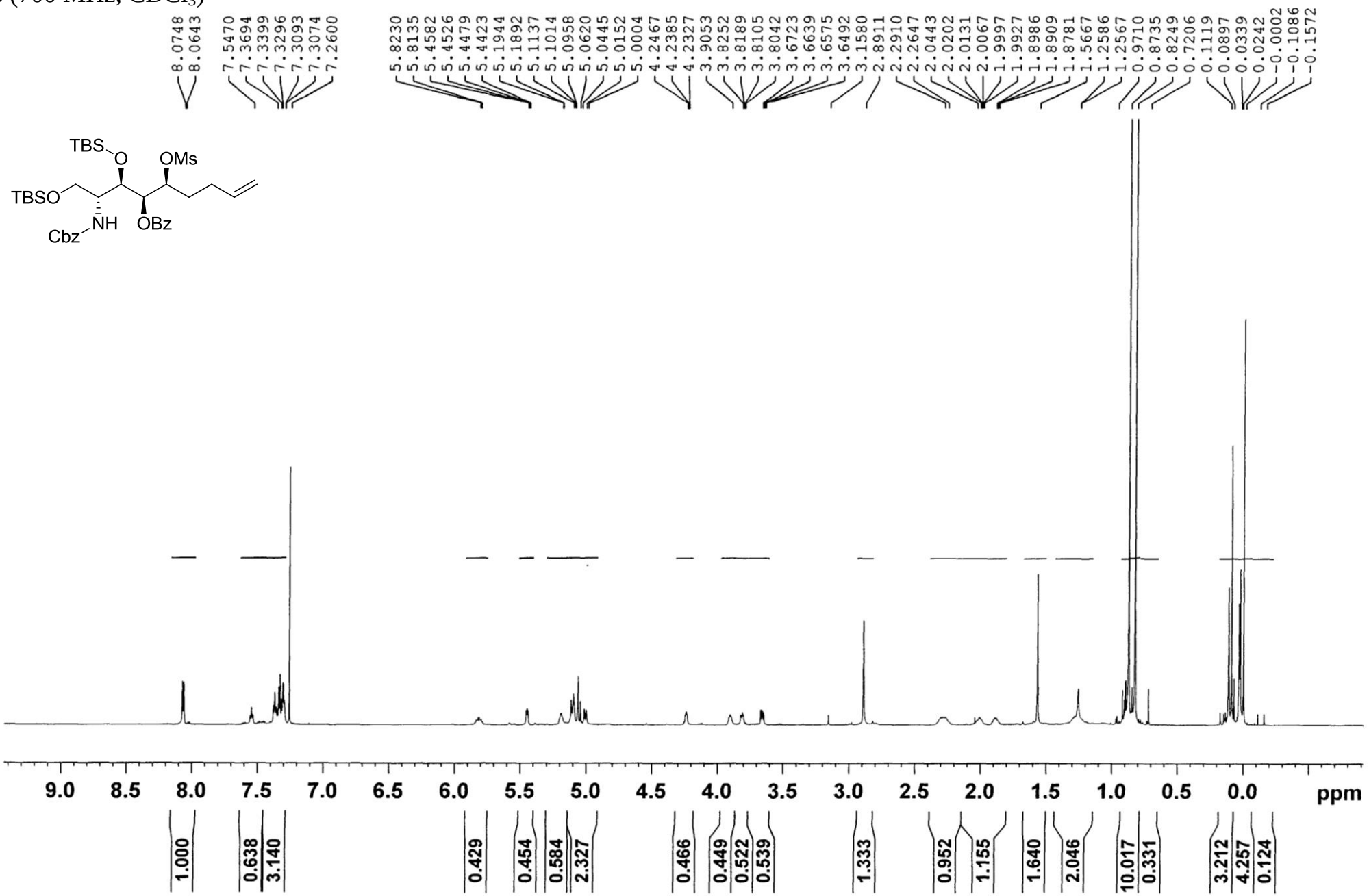
Precursor of **8** (700 MHz, $CDCl_3$)



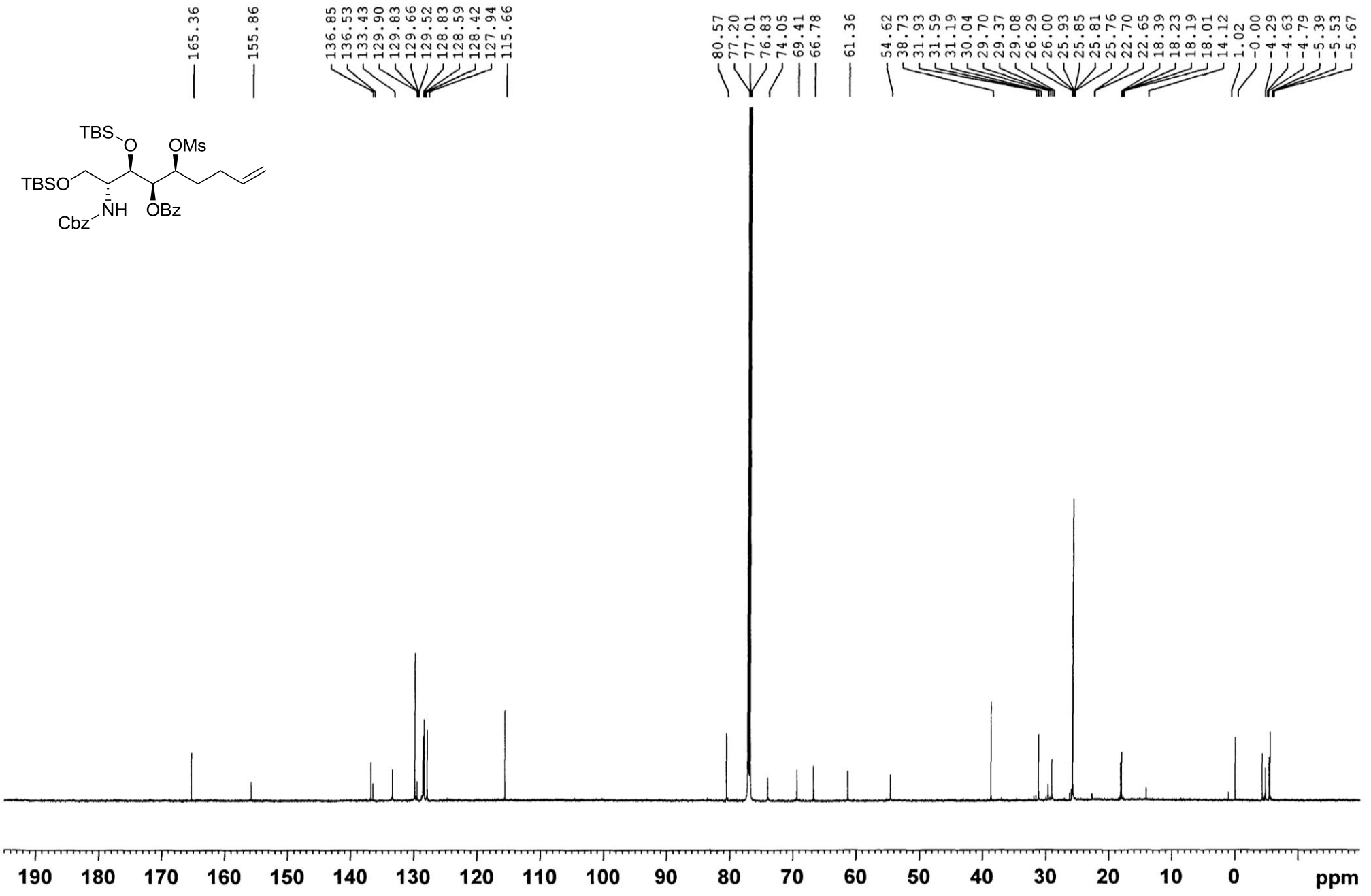
Precursor of **8** (175 MHz, $CDCl_3$)



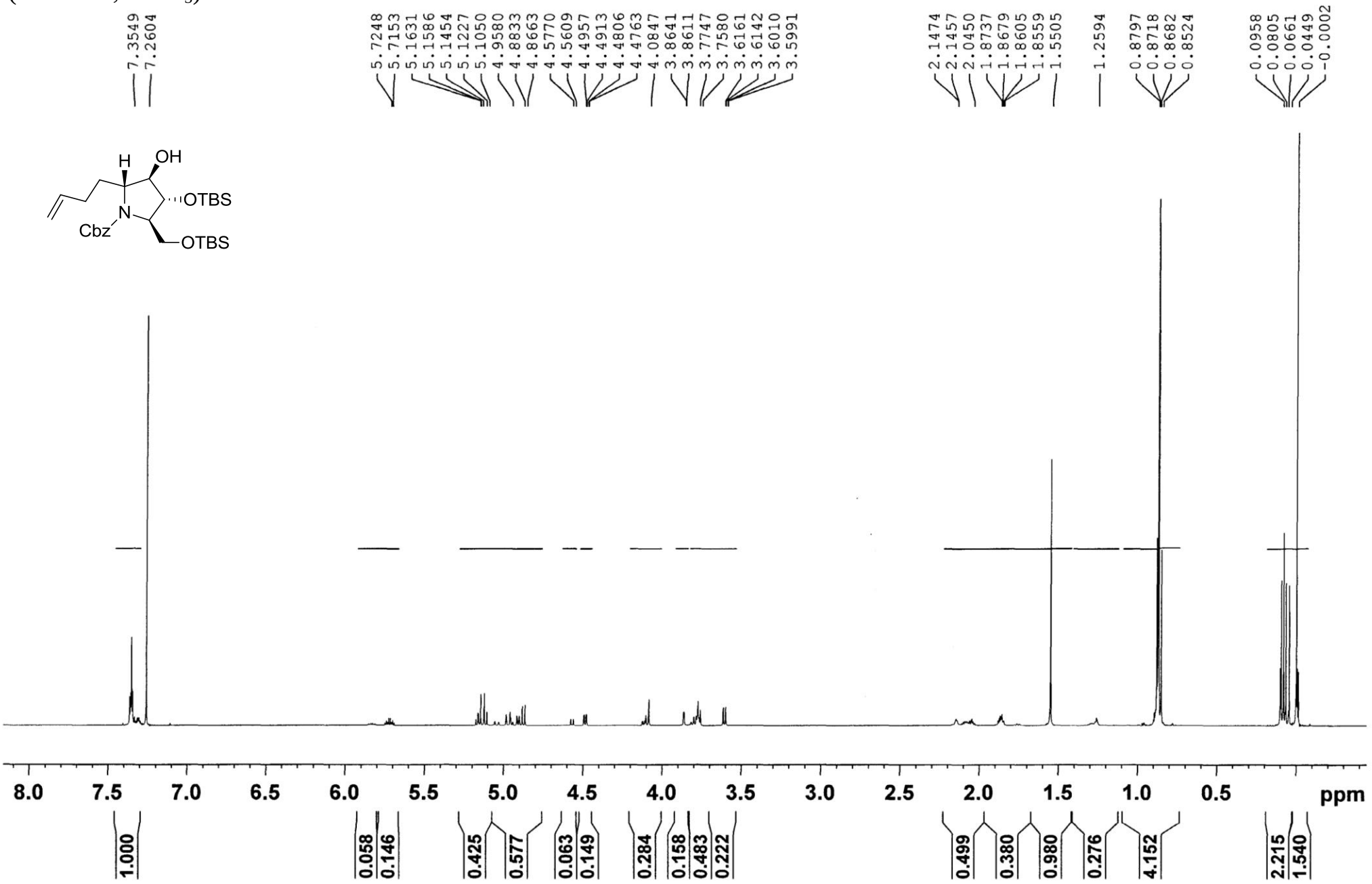
8 (700 MHz, $CDCl_3$)



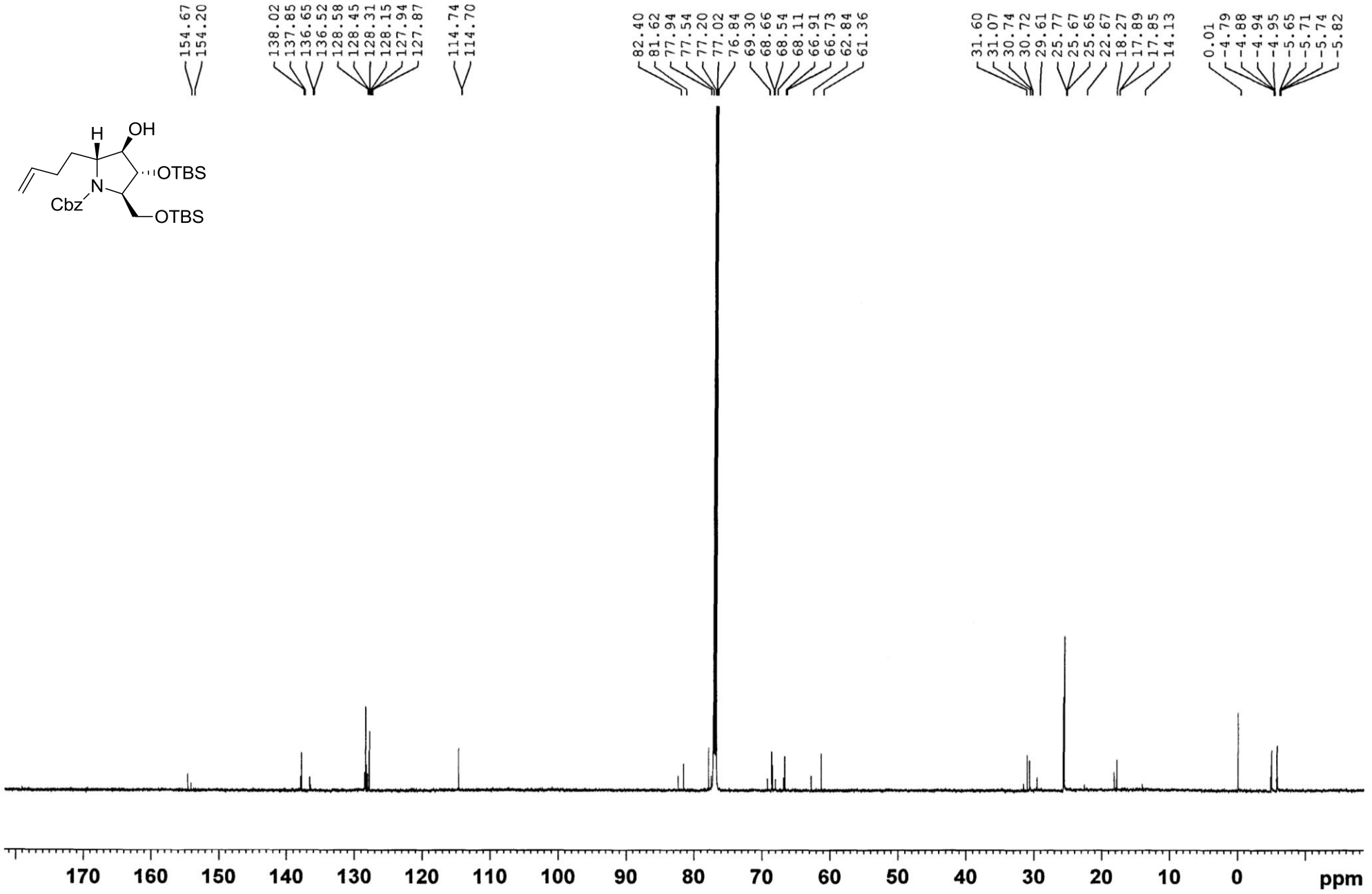
8 (175 MHz, $CDCl_3$)



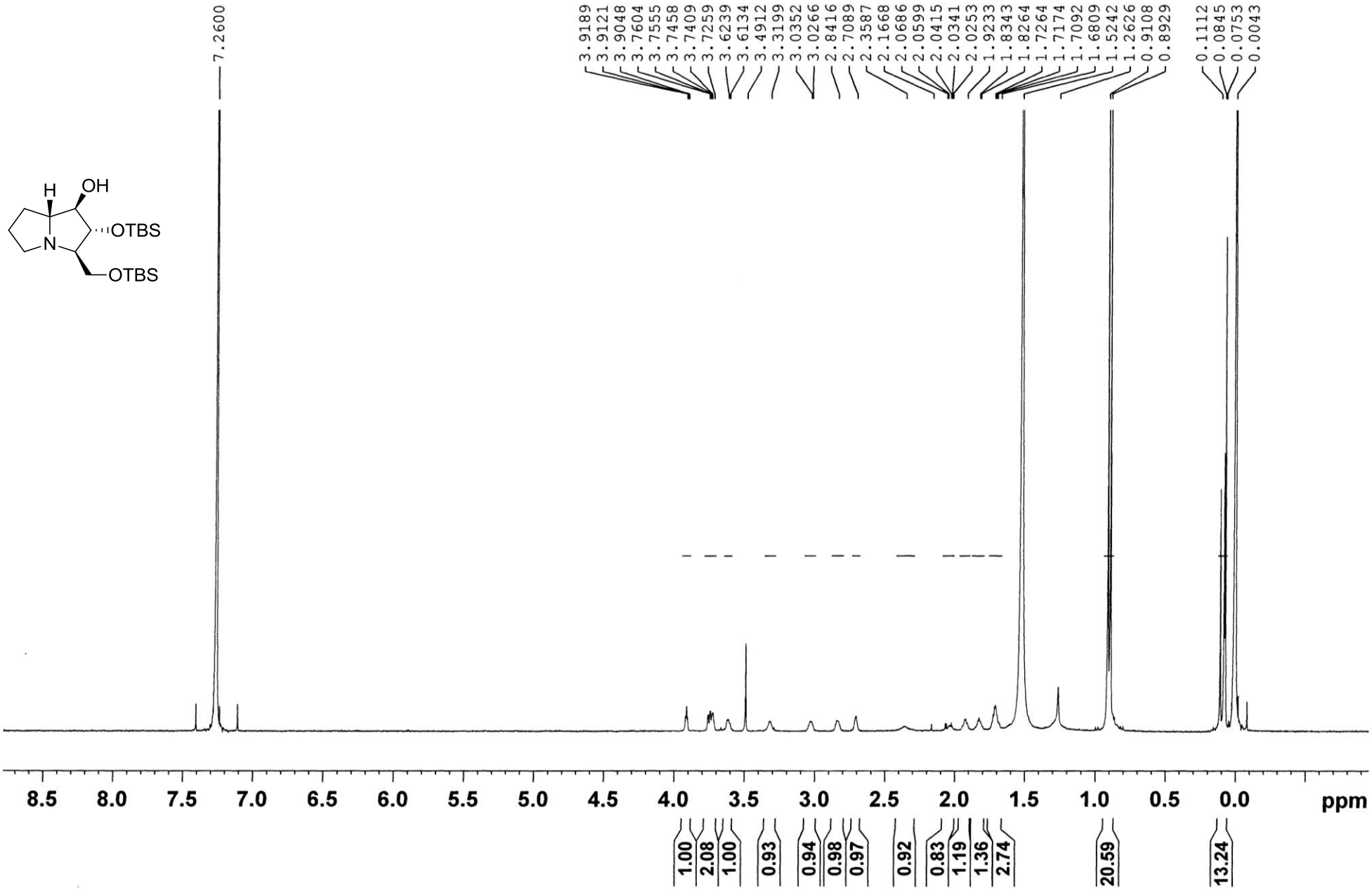
7 (700 MHz, $CDCl_3$)



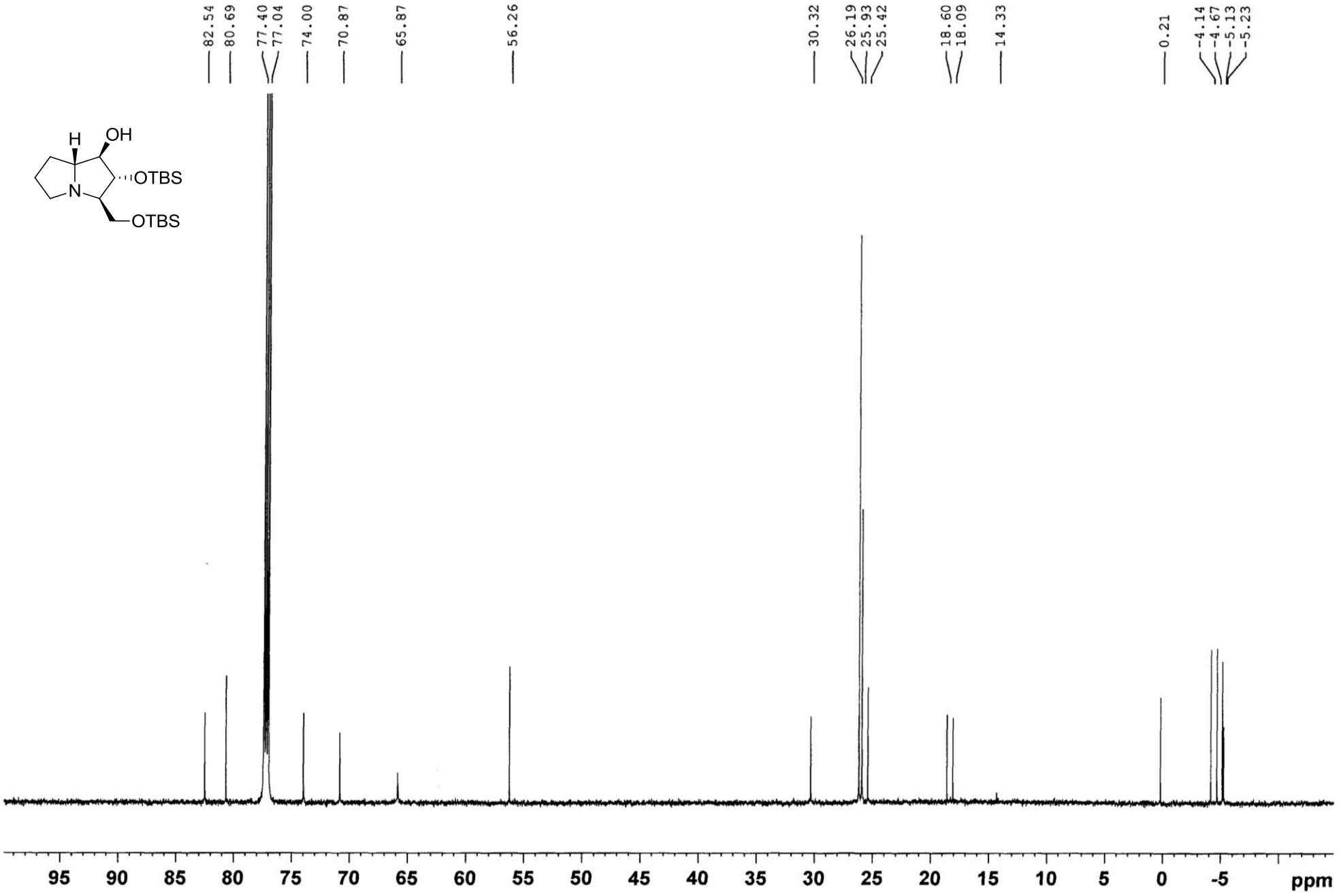
7 (175 MHz, $CDCl_3$)



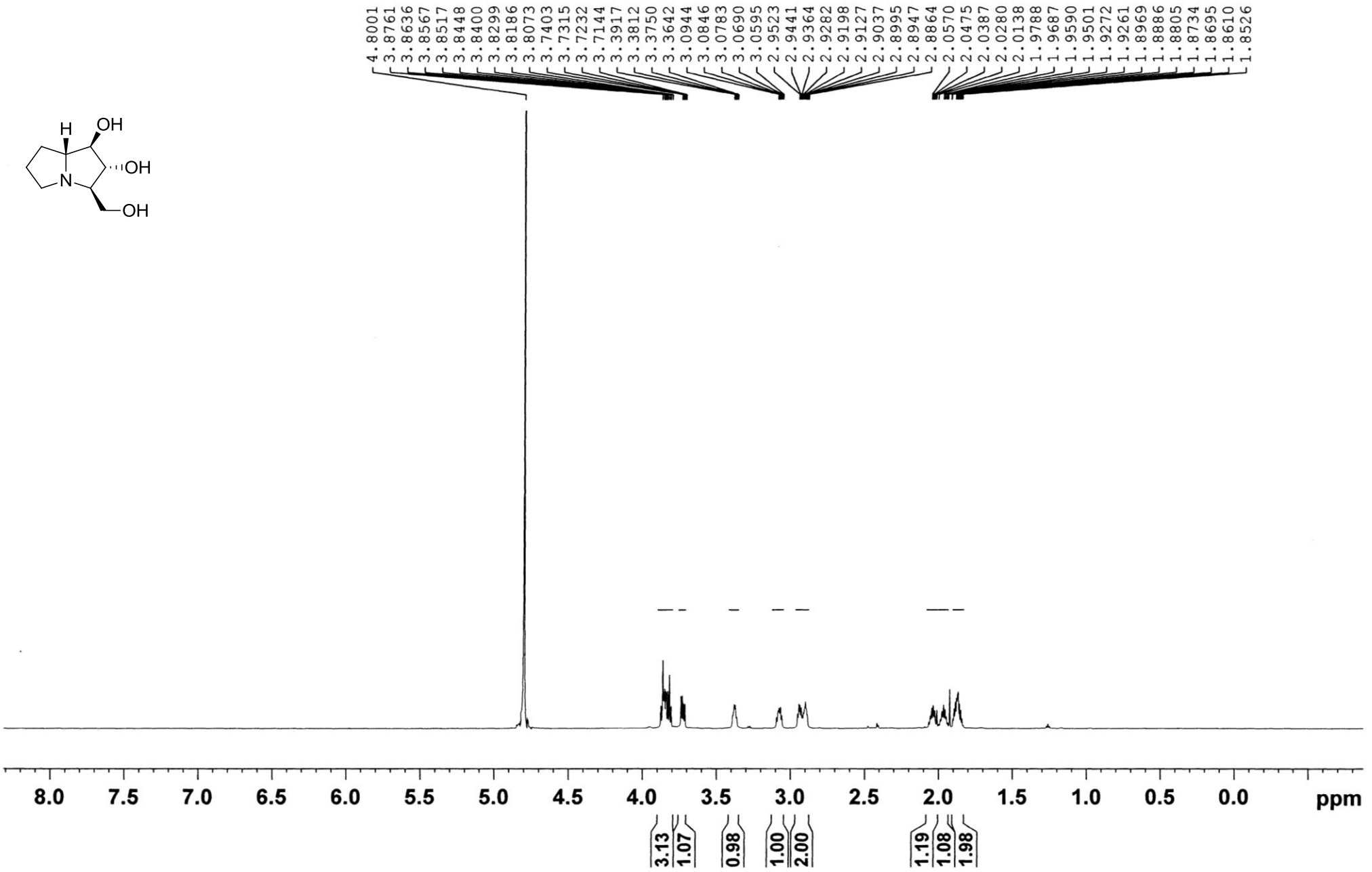
9 (700 MHz, $CDCl_3$)



9 (175 MHz, $CDCl_3$)



1 (700 MHz, D_2O)


4.8001
3.8761
3.8636
3.8567
3.8517
3.8448
3.8400
3.8299
3.8186
3.8073
3.7403
3.7315
3.7232
3.7144
3.3917
3.3812
3.3750
3.3642
3.0944
3.0846
3.0783
3.0690
3.0595
3.0523
2.9441
2.9364
2.9282
2.9198
2.9127
2.9037
2.8995
2.8947
2.8864
2.0570
2.0475
2.0387
2.0280
2.0138
1.9788
1.9687
1.9590
1.9501
1.9272
1.9261
1.8969
1.8886
1.8805
1.8734
1.8695
1.8610
1.8526
H
OH
OH
N
OH
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
ppm
3.13
1.07
0.98
1.00
2.00
1.19
1.08
1.98

1 (175 MHz, D_2O)

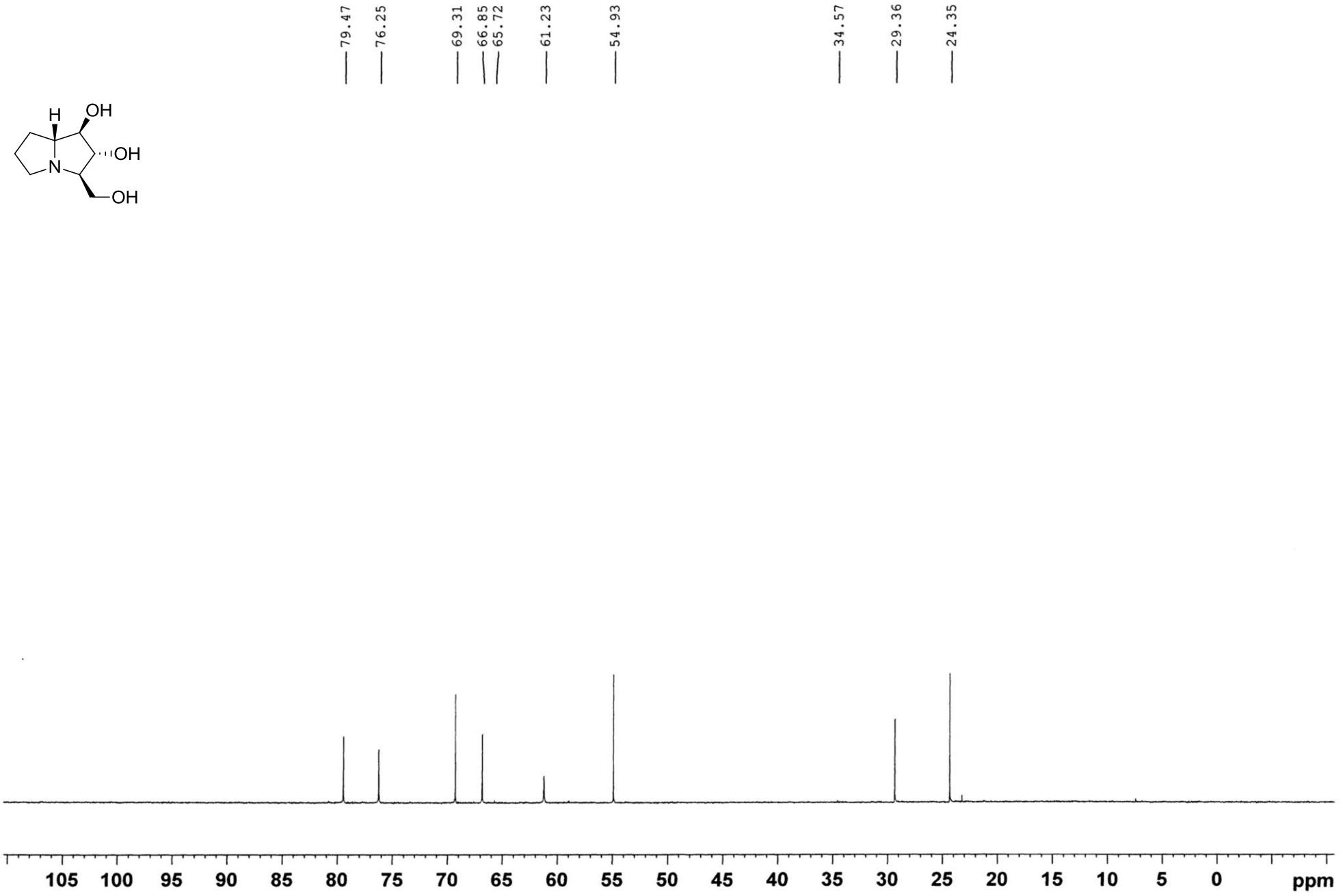

79.47
76.25
69.31
66.85
65.72
61.23
54.93
34.57
29.36
24.35
H
OH
OH
N
OH
105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 ppm

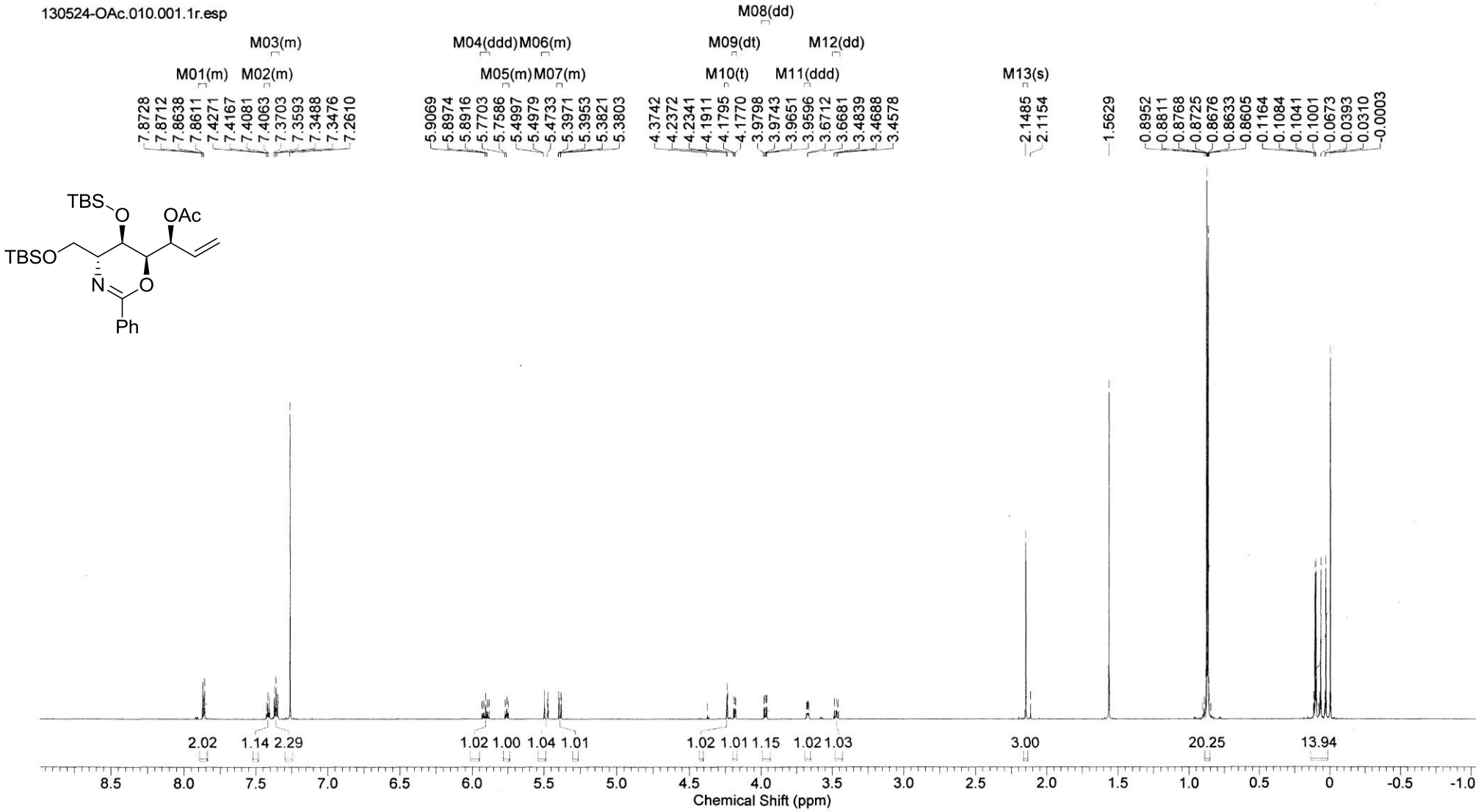
Table 1. Comparison of reported ^{1}H NMR data with those of **1**.

	Asano *et al.*[4] (natural product)	Fox *et al.*[5a] (pH 7.6)	Fox *et al.*[5a] (pH 9.0)	Izquierdo *et al.*[5i]	This work
Solvent	D_2O	D_2O	D_2O	D_2O	D_2O
H-2	3.81 (t, *J* = 8.8 Hz, 1H)	4.08−3.97 (m, 3H)	3.87−3.76 (m, 3H)	3.79−3.71 (m, 3H)	3.88−3.80 (m, 3H)
H-8’	3.80 (dd, *J* = 11.8, 3.9 Hz, 1H)	-	-	-	-
H-1	3.76 (dd, *J* = 8.8, 7.1 Hz, 1H)	-	-	-	-
H-8	3.67 (dd, *J* = 11.87, 6.5 Hz, 1H)	3.95−3.87 (m, 2H)	3.70 (dd, *J* = 12.0, 6.3 Hz, 1H)	3.63 (dd, *J* = 12.1, 6.0 Hz, 1H)	3.75−3.71 (m, 1H)
H-7a	3.32 (m, 1H)	-	3.37−3.30 (m, 1H)	3.37 (m, 1H)	3.40−3.36 (m, 1H)
H-5	2.96 (ddd, *J* = 11.0, 7.3, 5.9 Hz, 1H)	3.54−3.45 (m, 1H)	3.08−2.99 (m, 1H)	3.04 (broad dt, *J* = 11.7, 6.5 Hz, 1H)	3.10−3.05 (m, 1H)
H-5	2.81 (dt, *J* = 11.0, 5.6 Hz)	3.42−3.32 (m, 2H)	2.95−2.82 (m, 2H)	2.93−2.85 (m, 2H)	2.96−2.88 (m, 2H)
H-3	2.77 (ddd, *J* = 8.8, 6.5, 3.9 Hz, 1H)	-	-	-	-
H-7	1.97 (m, 1H)	2.30−2.07 (m, 4H)	2.07−1.91 (m, 2H)	1.96−1.72 (m, 4H)	2.06−2.00 (m, 1H)
H-6	1.90 (m, 1H)	-	-	-	2.00−1.95 (m, 1H)
H-6	1.82 (m, 1H)	-	1.91−1.77 (m, 2H)	-	1.93−1.85 (m, 2H)
H-7	1.77 (m, 1H)	-	-	-	-

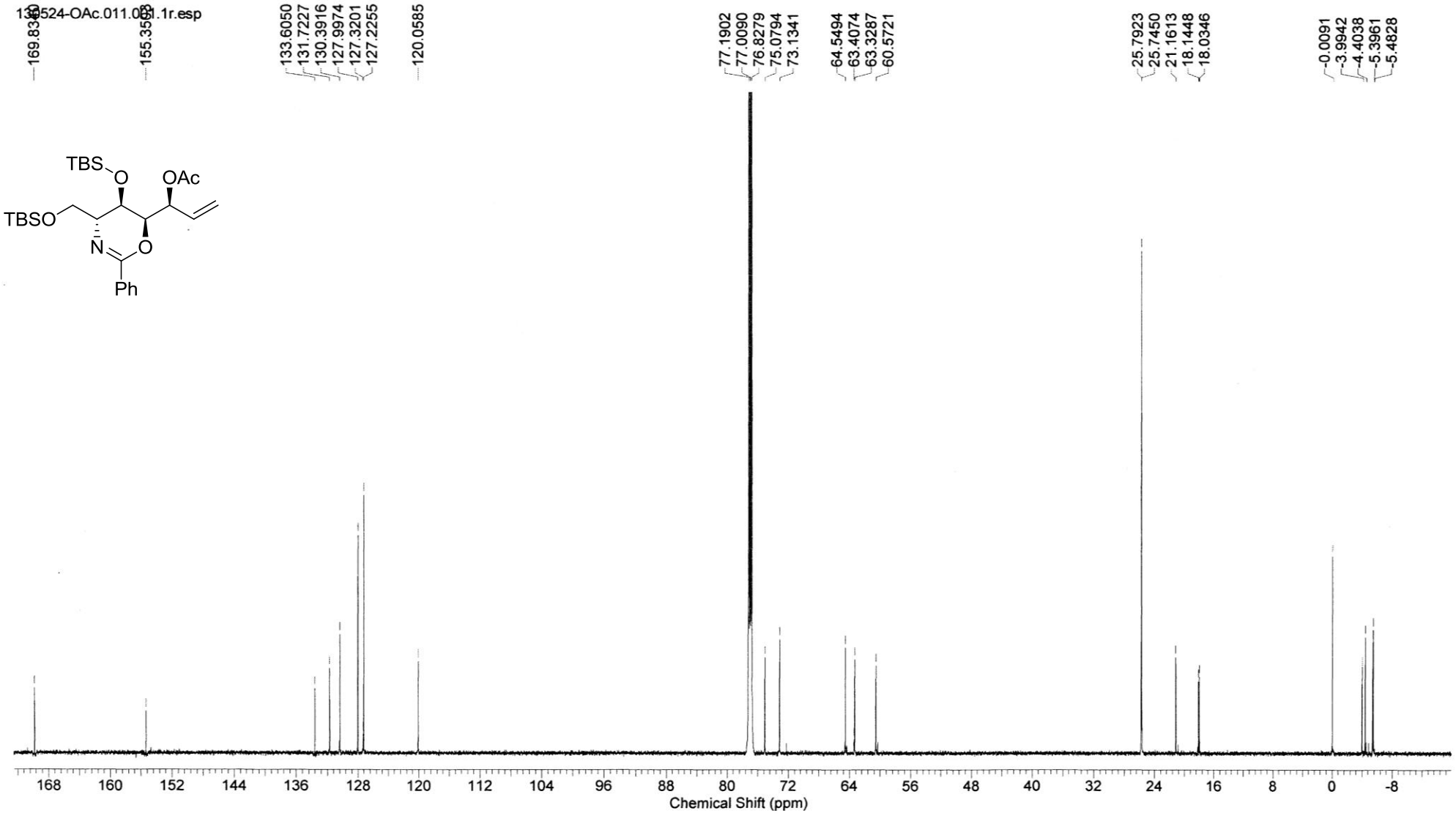
Table 2. Comparison of reported ^{13}C NMR data with those of **1**.

	Asano *et al.*[4] (natural product)	Fox *et al.*[5a] (pH 7.6)	Fox *et al.*[5a] (pH 9.0)	Izquierdo *et al.*[5i]	This work
Solvent	D_2O	D_2O	D_2O	D_2O	D_2O
C-1	82.9	81.0	82.5	81.09	79.4
C-2	79.8	77.2	79.3	77.72	76.3
C-3	72.1	73.0	72.2	71.47	69.3
C-7a	69.2	72.3	69.7	69.42	66.9
C-8	65.3	60.3	64.4	62.24	61.2
C-5	57.7	58.5	57.8	57.05	55.0
C-7	32.5	31.7	32.4	31.19	29.4
C-6	27.3	27.3	27.3	26.32	24.4

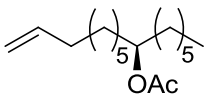
13 (700 MHz, $CDCl_3$)



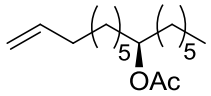
13 (175 MHz, $CDCl_3$)

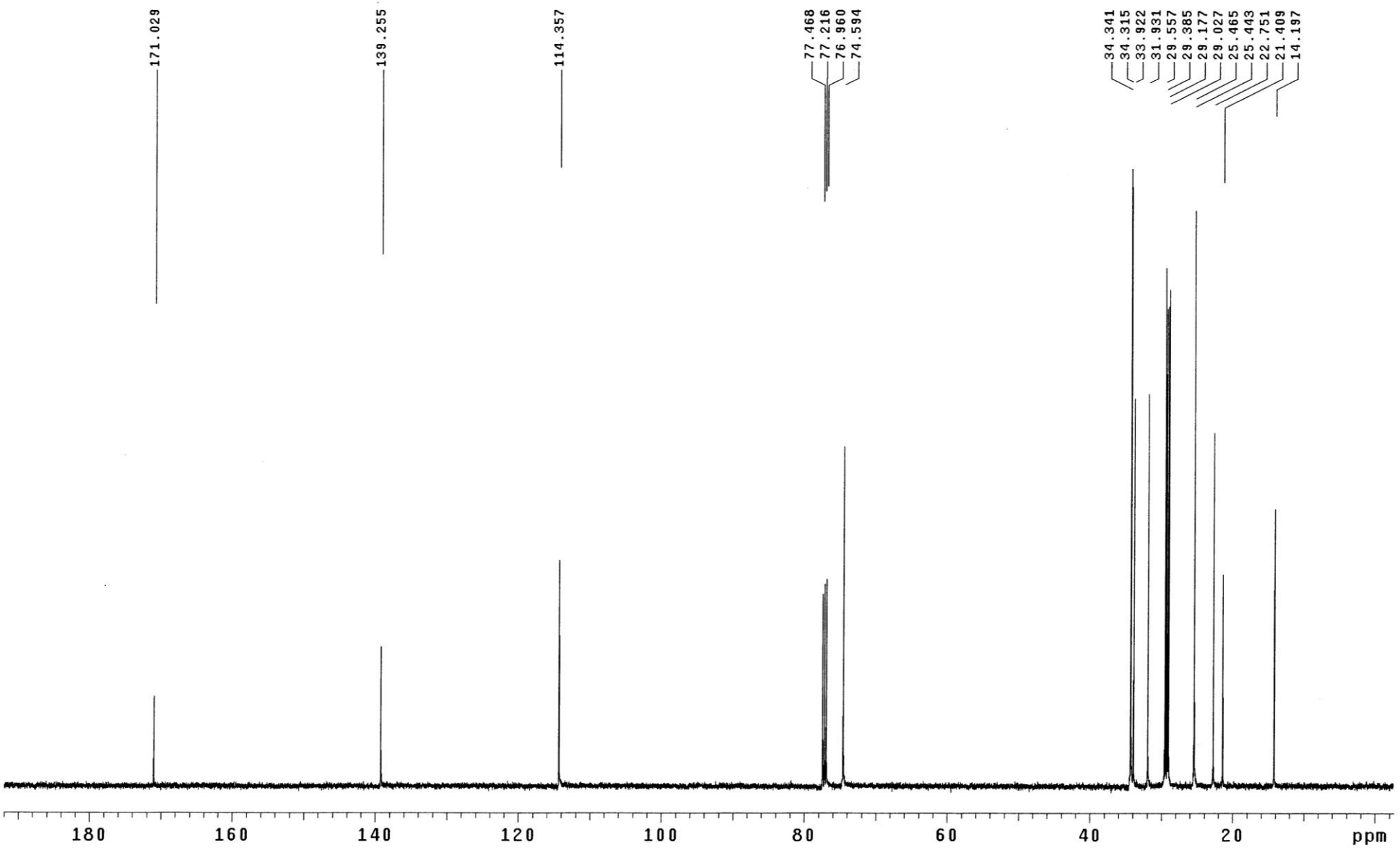


14 (500 MHz, $CDCl_3$)

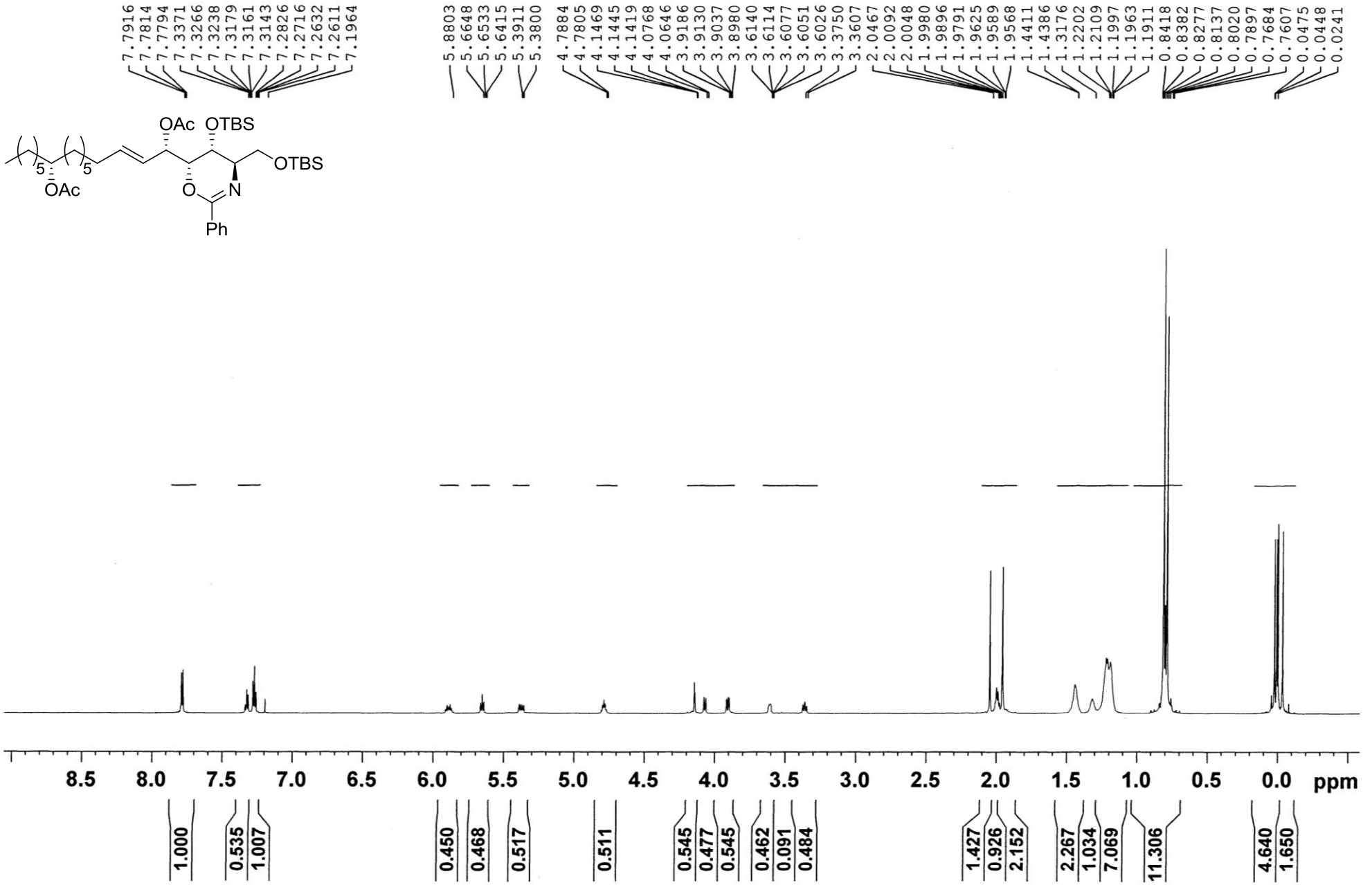


14 (125 MHz, $CDCl_3$)

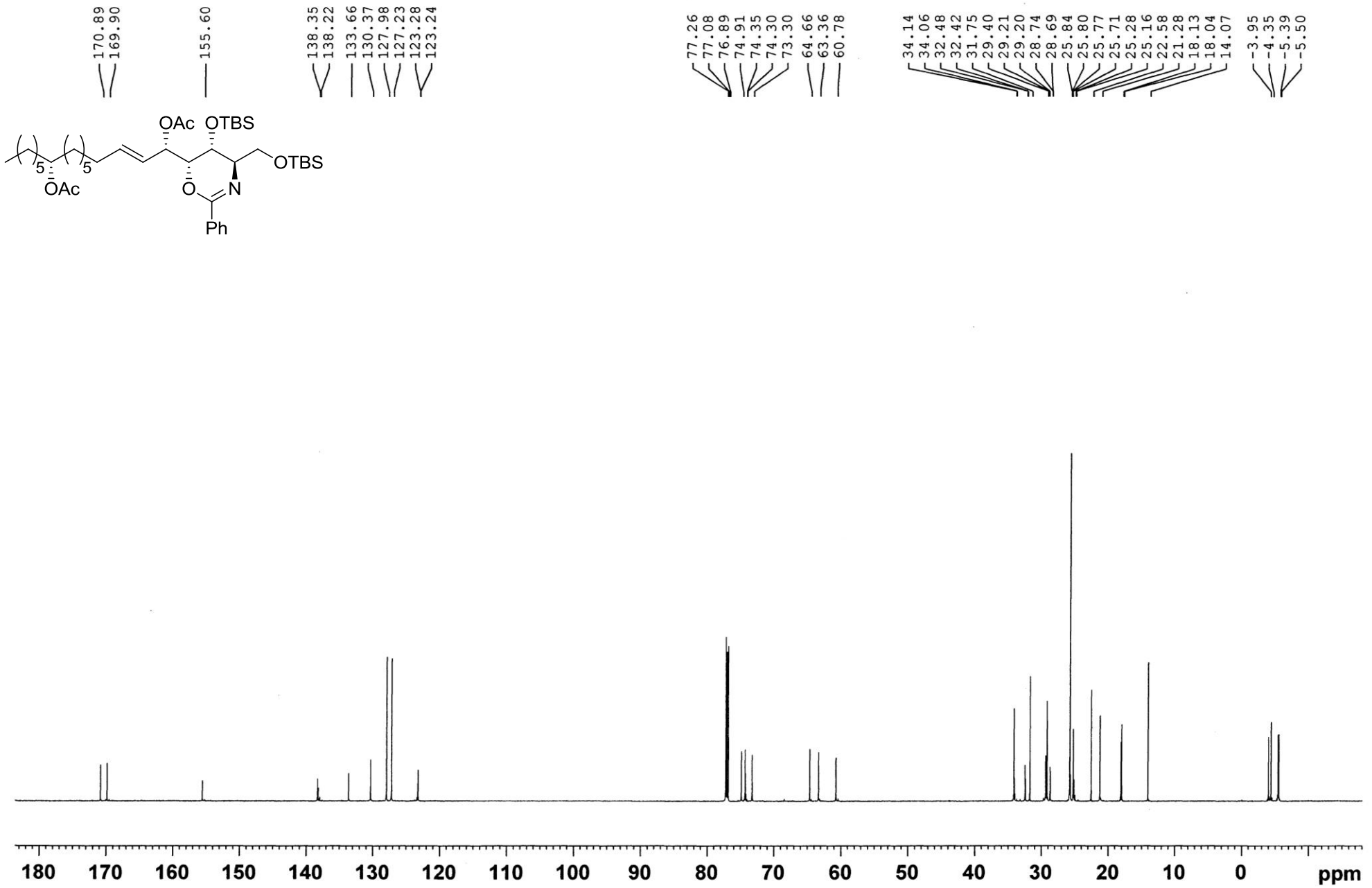




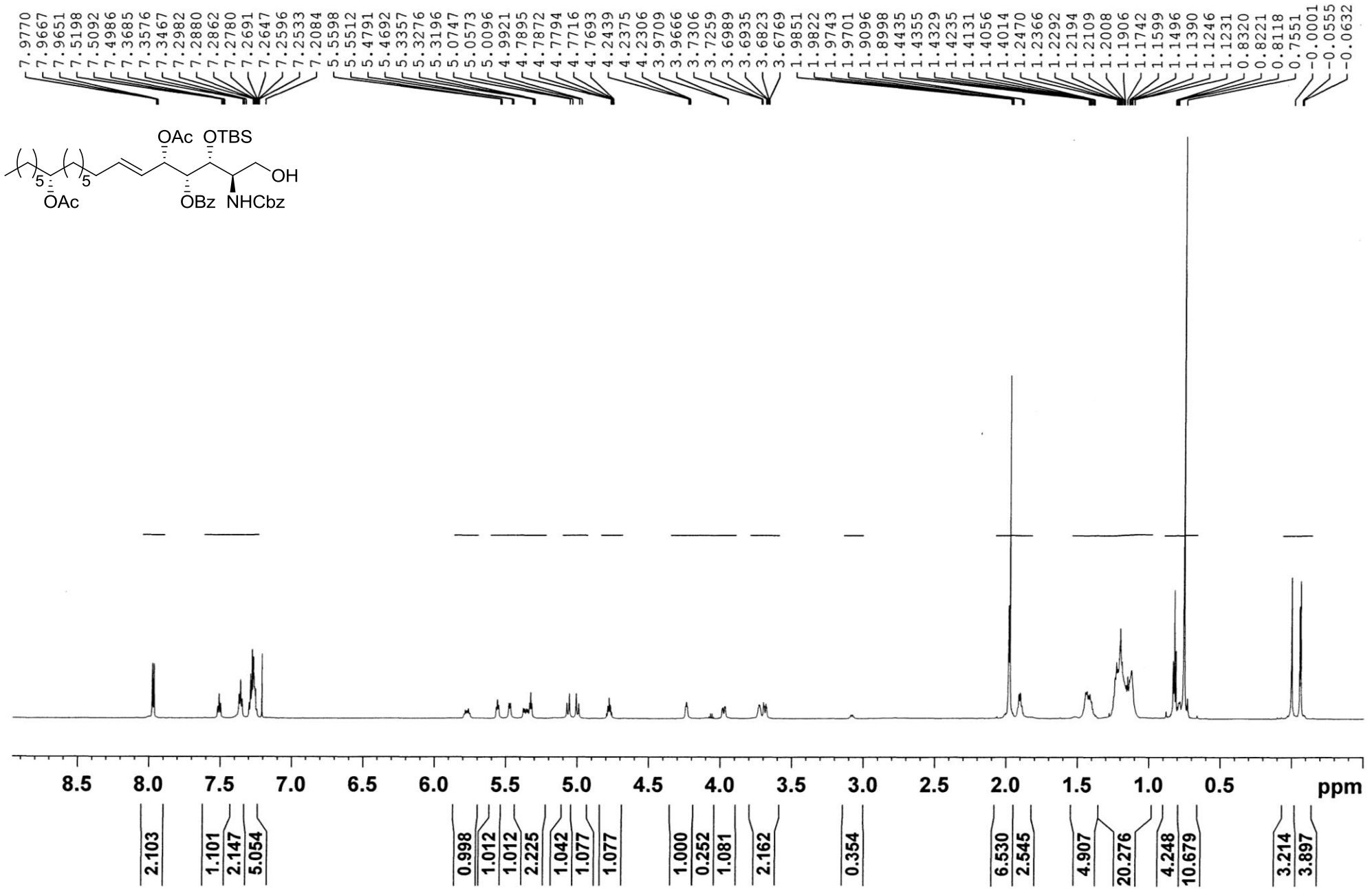
15 (700 MHz, $CDCl_3$)



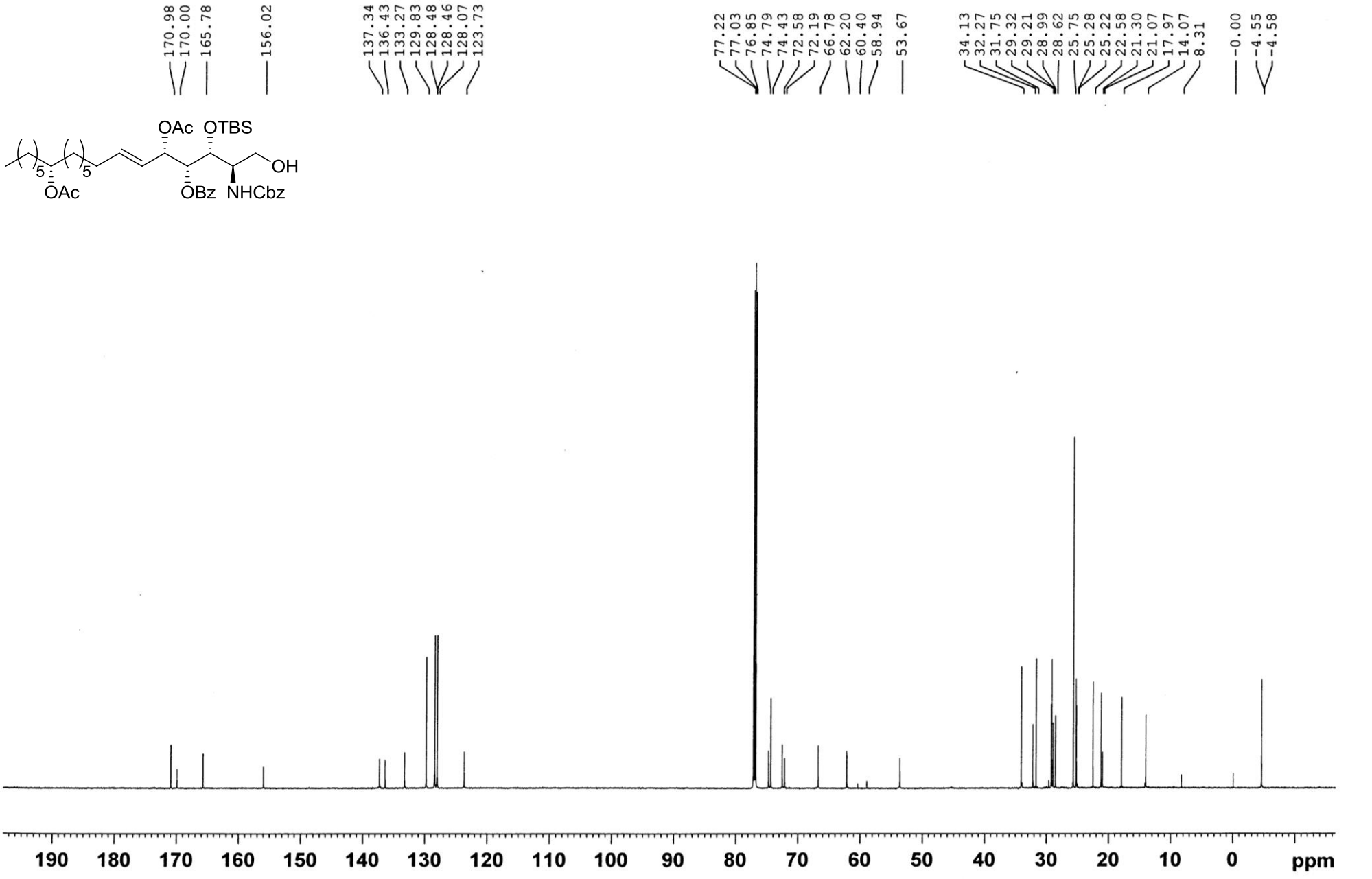
15 (175 MHz, $CDCl_3$)



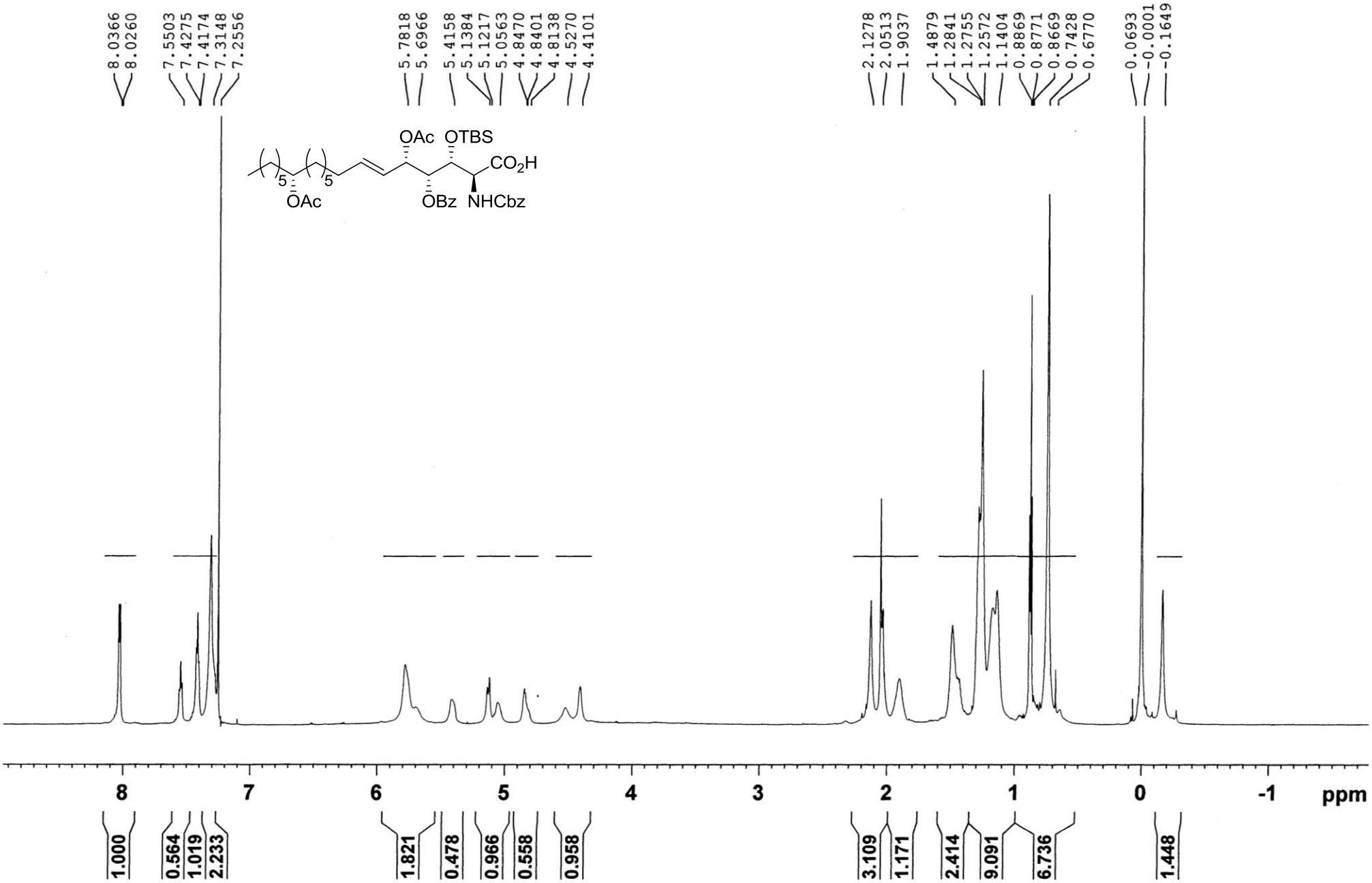
16 (700 MHz, $CDCl_3$)



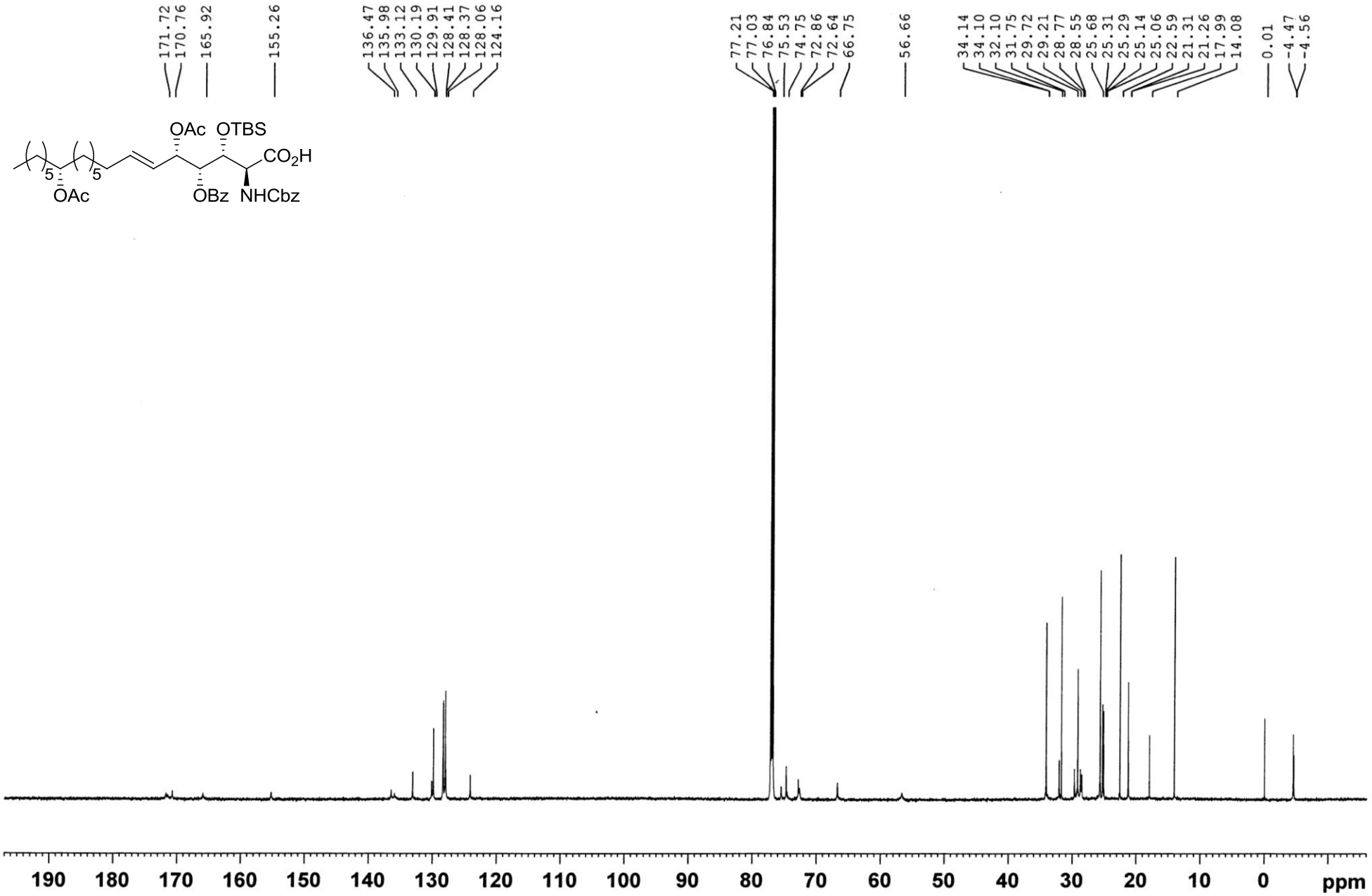
16 (175 MHz, $CDCl_3$)



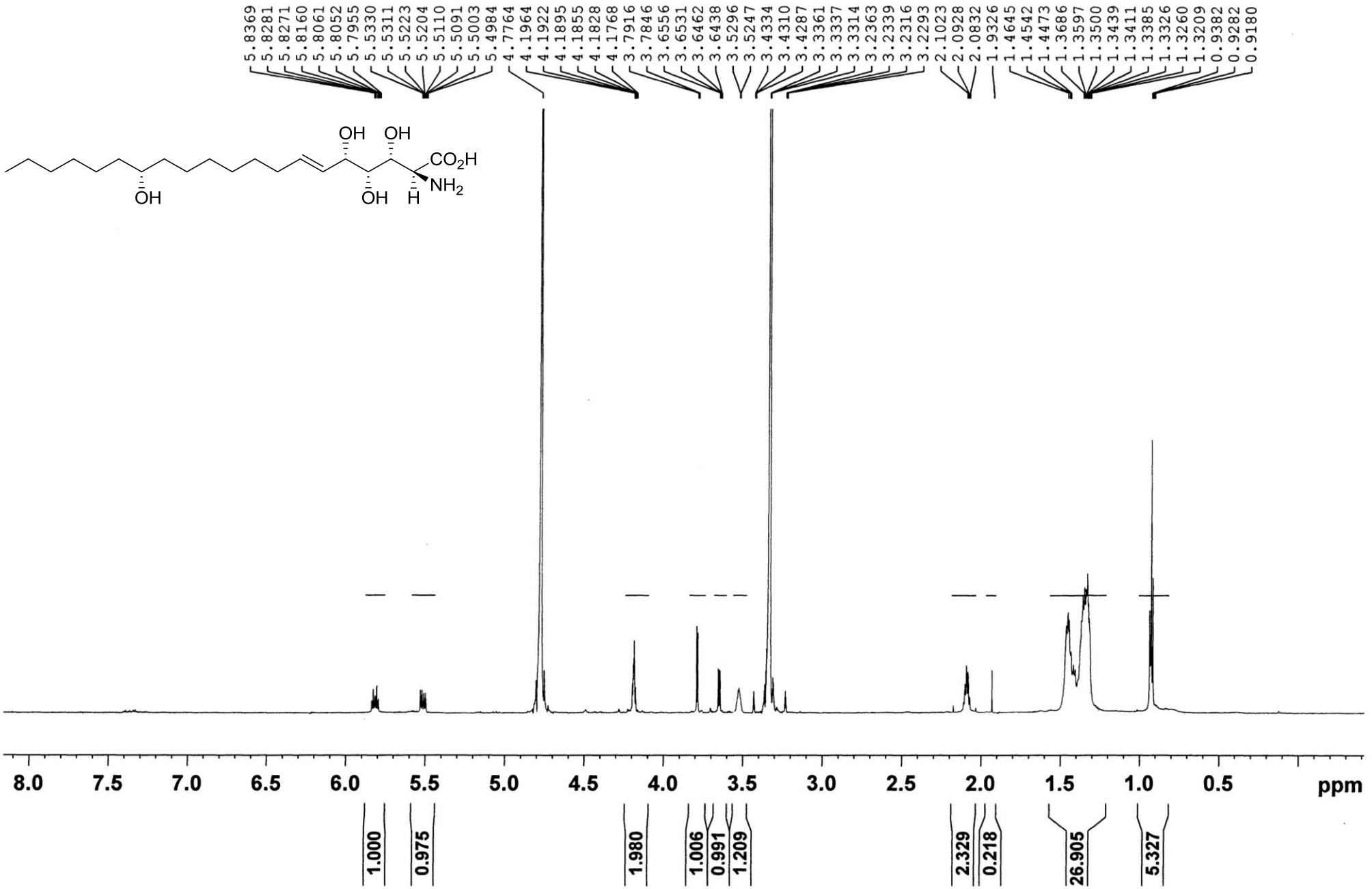
17 (700 MHz, $CDCl_3$)



17 (175 MHz, $CDCl_3$)



2 (700 MHz, CD_3OD)



2 (175 MHz, CD_3OD)

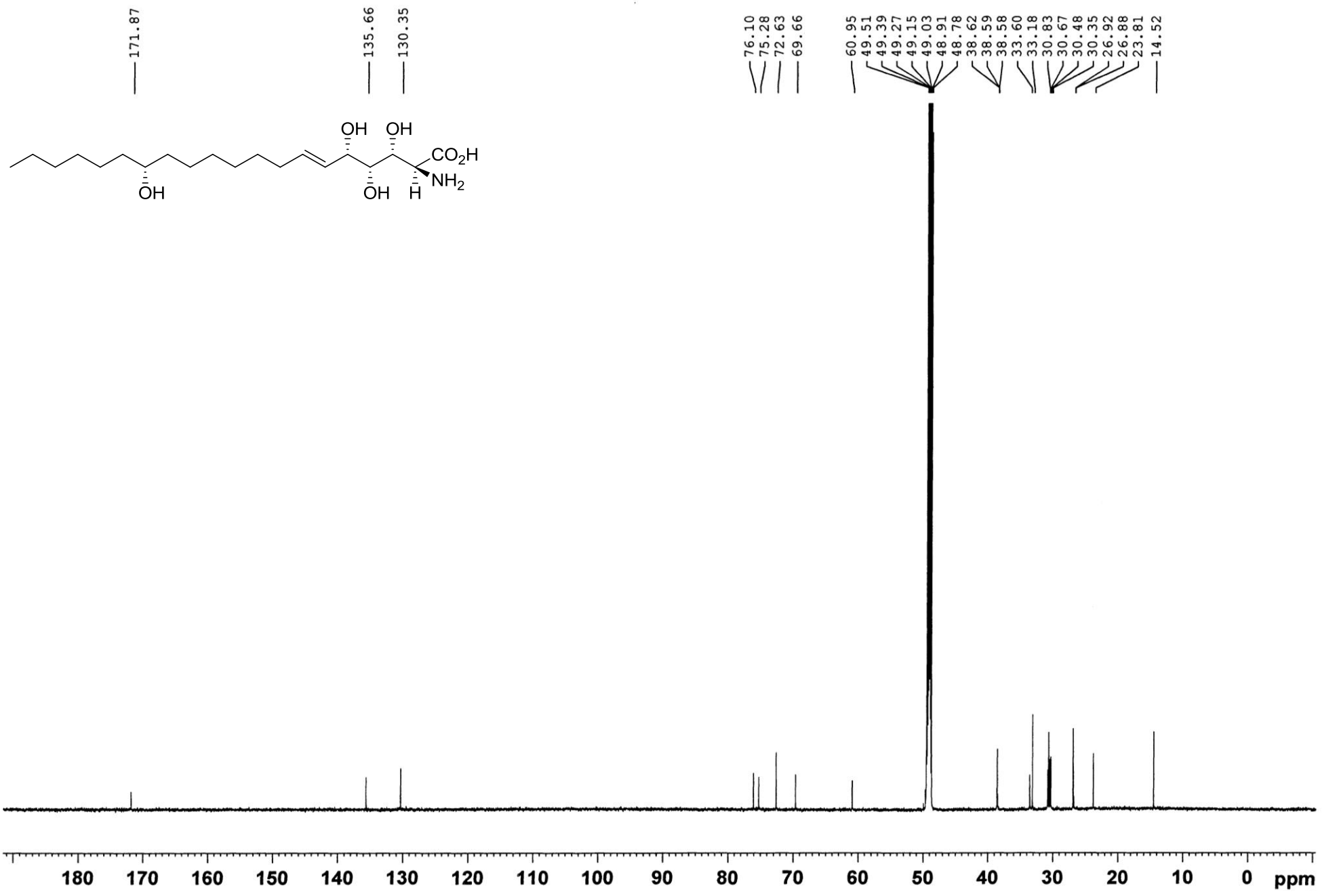


Table 3. Comparison of reported ^{1}H NMR data with those of **2**.

	Kobayashi *et al.*[9]	This work
Solvent	CD_3OD	CD_3OD
	0.89 (t, *J* = 6.4 Hz, 3H)	0.91 (t, *J* = 7.0 Hz, 3H)
	1.18−1.60 (m, 20H)	1.32−1.46 (m, 20H)
	1.98−2.06 (m, 2H)	2.08−2.10 (m, 2H)
	3.49 (brs, 1H)	3.52 (brs, 1H)
	3.60 (d, *J* = 6.9 Hz, 1H)	3.64 (dd, *J* = 6.5, 1.7 Hz, 1H)
	3.77 (d, *J* = 3.6Hz, 1H)	3.78 (d, *J* = 4.9 Hz, 1H)
	4.06−4.10 (m, 2H)	4.17−4.19 (m, 2H)
	5.47 (dd, *J* = 15.2, 7.3 Hz, 1H)	5.51 (dd, *J* = 15.4, 7.4 Hz, 1H)
	5.77 (dt, *J* = 15.2, 6.6 Hz, 1H)	5.80 (dt, *J* = 14.6, 6.4 Hz, 1H)

Table 4. Comparison of reported ^{13}C NMR data with those of **2**.

	Kobayashi *et al.*[9]	This work
Solvent	CD_3OD	CD_3OD
	14.4	14.5
	23.7	23.8
	26.79	26.9
	26.82	-
	30.2	30.4
	30.4	30.5
	30.6	30.7
	30.7	30.8
	33.1	33.2
	33.5	33.6
	38.5	38.6
	60.8	61.0
	69.4	69.7
	72.5	72.6
	75.2	75.3
	76.0	76.1
	130.2	130.4
	135.5	135.7
	172.4	171.9