Supporting Information

Synthesis and characterization of a new organocatalytic biosourced surfactant.

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General Information

Physical data and spectroscopic measurement

^{1}H NMR spectra were acquired with FOURIER300 (300 MHz) spectrometer from Brüker Coporation (Karlsruhe, Germzany). The chemical shifts δ are expressed in parts per million (ppm) and referenced to tetramethylsilane at 0 ppm. Coupling constants *J* are expressed in Hertz (Hz). Data are reported as follows: δ, multiplicity (br: broad, s: singlet, d: doublet, dd: doublet of doublet, t: triplet, q, quadruplet and m: multiplet), *J*, integration, assignment. All samples were diluted in deuterochloroform.

^{13}C NMR spectra were recorded on the same instrument at 75 MHz. Chemical shifts are referenced to the central peak of residual $CDCl_3$ (77.2 ppm).

Infrared (IR) spectra were recorded on a Spectrum 65 FT-IT spectrometer form Perkin-Elmer in ATR mode. Wavenumbers are expressed in cm^{-1}.

High Resolution Mass Spectra (HRMS) were obtained on a GCT Premier (Waters) mass spectrometer via direct introduction. Analysis were performed at the Institut Chimique de Toulouse, Université Paul Sabatier, 31062 Toulouse.

Chromatography

All reactions were monitored by thin-layer chromatography (TLC) on Merck pre-coated aluminium plates (silica gel 60 F_{254}) and spots were revealed by dipping into Ceric Ammonium Molybdate (CAM) solution. The CAM solution was prepared with $Ce(SO_4)_2$ (5 g), $(NH_4)6Mo_7O_{24}.4H_2O$ (25 g) and concentrated H_2SO_4 (50 mL) diluted in water (450 mL).

Flash chromatographies were performed using silica gel 60 (particle size 0.040-0.063 mm) on 15, 35, 125, 300, 430, 720 or 1000 mL columns from Sodipro.

Usual procedures

All reagents and solvents were obtained from commercial suppliers (SigmaAldrich, VWR and CarloErba) and used as received without further purification.

All air/moisture sensitive reactions were carried out in nitrogen atmosphere using dry glassware and commercial anhydrous solvents.

All heated reactions were carried out using Findenser condenser from Radley, which requires no running water to operate. Oil bath was used to eat the reaction medium.

Tensiometry

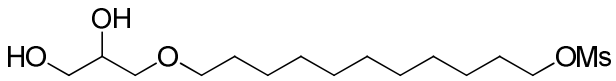
Surface tension analyses were recorded on a 3S blade tensiometer from GBX. All analyses were performed at 23°C. Each solution was measured three times until the surface tension was stabilized.

Dynamic Light Scattering

DLS analysis were performed on Zetasizer NanoZS from Malvern using semi-micro plastic dispensers of dimensions 12.5 x 12.5 x 45 mm from Brand. Each sample was run three times at 25°C.

Experimental Procedures and Spectroscopic Data

11-(2,3-dihydroxypropoxy)undecyl methanesulfonate (7)



To a solution of 5.00 g (13.1 mmol, 1.00 equiv) of acetonide **6** in 75.0 mL of MeOH was added a catalytic amount of *p*TSA. The resulting mixture was then stirred overnight at room temperature. Solvent was removed *in vacuo* and DCM was added to the resulting mixture. The organic layer was then washed twice with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified on silica pad (EtOAc/Pet 1:1 then 100% EtOH) to give 3.94 g (88%) of a white solid.

R$_f$ 0 (Pet/EtOAc 1:1)

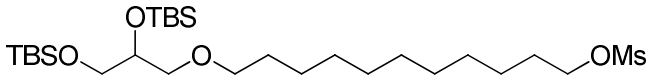
^{1}H NMR (300 MHz, $CDCl_3$) δ 4.21 (t, *J* = 6.6 Hz, 2H), 3.93 – 3.84 (m, 1H), 3.73 (dd, *J* = 11.3, 3.8 Hz, 1H), 3.64 (dd, *J* = 11.3, 5.5 Hz, 1H), 3.53 – 3.42 (m, 4H), 2.99 (s, 3H), 2.59 (br s, 2H), 1.80 – 1.67 (m, 2H), 1.63 – 1.49 (m, 2H), 1.45 – 1.22 (m, 14H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 72.4, 72.0, 70.6, 70.3, 64.2, 37.5, 29.7, 29.6, 29.5, 29.2, 29.1, 26.2, 25.5.

IR (ATR): 3330, 2917, 2849, 1461, 1335, 1169, 1117, 1054, 979, 948, 854 cm^{-1}

HRMS (DCI-CH_4) Cald for $C_{15}H_{33}O_6S$ 341.1998 $[M+H]^+$, Found 341.1994

11-(2,3-bis((*tert*-butyldimethylsilyl)oxy)propoxy)undecyl methanesulfonate (8)



To a solution of 13.0 g (38.5 mmol, 1.00 equiv) of diol **7** in 34.0 mL of THF was added 15.7 g (231 mmol, 6.00 equiv) of imidazole under nitrogen atmosphere. After total dissolution was added 14.5 g (96.2 mmol, 2.50 equiv) of TBSCl. The resulting mixture was then stirred overnight at room temperature. It was then quenched with addition of water and diluted with Et_2O. The organic layer was washed twice with water and once with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a yellow oil. The product was used without purification for the next step.

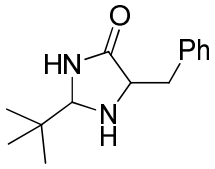
^{1}H NMR (300 MHz, CDCl3) δ 4.22 (t, *J* = 6.6 Hz, 2H), 3.84 – 3.75 (m, 1H), 3.61 – 3.48 (m, 2H), 3.48 – 3.37 (m, 4H), 2.99 (s, 3H), 1.80 – 1.69 (m, 2H), 1.61 – 1.49 (m, 2H), 1.45 – 1.22 (m, 14H), 0.89 (s, 9H), 0.88 (s, 9H), 0.07 (s, 6H), 0.04 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 72.9 (2C), 71.7, 70.3, 65.4, 37.5, 29.9, 29.7, 29.6 (2C), 29.6, 29.3, 29.2, 26.3, 26.1 (3C), 26.0 (3C), 25.6, 18.5, 18.4, -4.5 (2C), -5.3 (2C).

IR (ATR): 2926, 2845, 1469, 1359, 1251, 1175, 1102, 938, 830, 774 cm^{-1}

HRMS (DCI-CH_4) Cald for $C_{27}H_{61}O_6SSi_2$ 569.3727 $[M+H]^+$, Found 569.3723

5-benzyl-2-(*tert*-butyl)imidazolidin-4-one (9)



To a solution of 2.50 g (15.2 mmol, 1.00 equiv) of phenylalaninamide in 76.0 mL of THF was added, after total dissolution, 3.31 mL (30.4 mmol, 2.00 equiv) of pivaldehyde. Then, was added 0.247 g (1.52 mmol, 0.10 equiv) of $FeCl_3$. The resulting mixture was heated at 65°C for 18h. It was then filtered on celite and concentrated *in vacuo*. The crude product was purified on silica gel column (Pet/EtOAc 1:1) to give 3.03 g (86%) of product with a *ratio syn*:*anti* of 1:1.

9 *anti*

R_f 0.28 (Pet/EtOAc 1:1)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.20 (m, 5H), 4.02 (s, 1H), 3.82 – 3.77 (m, 1H), 3.09 (dd, *J* = 14.1, 4.4 Hz, 1H), 2.93 (dd, *J* = 14.1, 7.2 Hz, 1H), 2.00 (br s, 2H), 0.85 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 177.8, 137.3, 129.6 (2C), 128.8 (2C), 126.9, 77.8, 60.1, 38.2, 36.2, 24.4 (3C).

9 *syn*

R_f 0.15 (Pet/EtOAc 1:1)

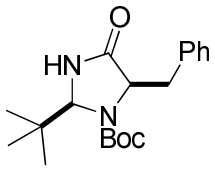
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.17 (m, 5H), 4.24 (s, 1H), 3.83 – 3.76 (m, 1H), 3.12 (dd, *J* = 13.7, 4.0 Hz, 1H), 2.90 (dd, *J* = 13.7, 7.7 Hz, 1H), 1.82 (s, 1H), 0.84 (s, 1H), 0.78 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 177.5, 138.0, 129.7 (2C), 128.7 (2C), 126.8, 77.3, 60.4, 37.9, 34.1, 24.4 (3C).

IR (ATR): 3193, 2962, 2857, 1697, 1436, 1368, 772, 745 cm^{-1}

HRMS (DCI-CH_4) Cald for $C_{14}H_{21}N_2O$ 233.1654 $[M+H]^+$, Found 233.1644

***tert*-butyl 5-benzyl-2-(*tert*-butyl)-4-oxoimidazolidine-1-carboxylate (10)**



To a solution of 0.500 g (2.15 mmol, 1.00 equiv) of imidazolidinone **9** *syn* in 4.00 mL of DCM was added 0.470 g (2.15 mmol, 1.00 equiv) of Boc_2O under nitrogen atmosphere. The resulting mixture was then stirred overnight at room temperature. Solvent was removed *in vacuo* and the crude product was purified on silica gel column (Pet/EtOAc 6:4) to give 0.650 g (91%) of a white solid.

R_f 0.36 (Pet/EtOAc 6:4)

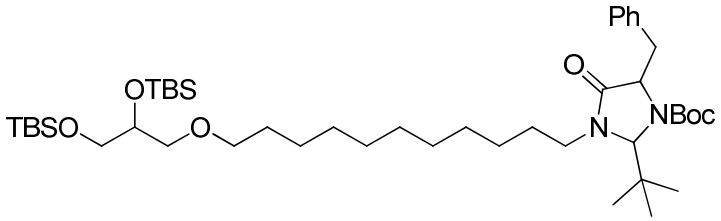
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.37 – 7.18 (m, 5H), 5.02 (s, 1H), 4.34 (t, J = 6.7 Hz, 1H), 3.17 (dd, J = 13.8, 6.7 Hz, 1H), 3.03 (dd, J = 13.8, 6.7 Hz, 1H), 1.28 (s, 9H), 0.98 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 173.9, 156.1, 138.2, 129.8 (2C), 128.4 (2C), 126.6, 81.3, 77.6, 61.7, 39.6, 36.7, 28.1 (3C), 25.8 (3C).

IR (ATR): 3181, 3065, 2966, 2924, 1701, 1366, 1354, 1299, 1172, 1163, 1077, 749 cm^{-1}

HRMS (DCI-CH_4) Cald for $C_{19}H_{29}N_2O_3$ 333.2178 $[M+H]^+$, Found 333.2182

***tert*-butyl 5-benzyl-3-(11-(2,3-bis((*tert*-butyldimethylsilyl)oxy)propoxy)undecyl)-2-(*tert*-butyl)-4-oxoimidazolidine-1-carboxylate (11)**



To a solution of 2.39 g (7.18 mmol, 1.00 equiv) of amide **10** in 14.0 mL of anhydrous DMF was added 0.287 g (7.18 mmol, 1.00 equiv) of NaH (60% dispersed in oil) under nitrogen atmosphere. After total solubilisation was added 4.50 g (7.90 mmol, 1.10 equiv) of mesylated alcohol **6**. The resulting mixture was heated at 60°C for 8h. It was then quenched with addition of water and diluted with EtOAc. The organic layer was washed three times with water and once with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified on silica gel column (Pet/EtOAc 9:1) to give 1.23 g (22%) of pure product.

R_f 0.11 (Pet/EtOAc 9:1)

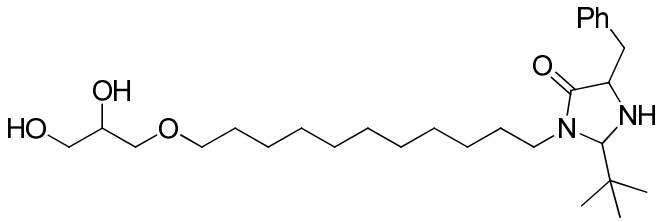
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.18 (m, 5H), 5.12 (s, 1H), 4.37 – 4.28 (m, 1H), 3.98 – 3.84 (m, 1H), 3.85 – 3.76 (m, 1H), 3.58 (dd, *J* = 10.2, 5.6 Hz, 1H), 3.52 (dd, *J* = 10.2, 5.6 Hz, 1H), 3.48 – 3.29 (m, 4H), 3.20 (dd, *J* = 13.8, 6.1 Hz, 1H), 3.09 – 2.93 (m, 2H), 1.61 – 1.48 (m, 4H), 1.38 – 1.17 (m, 23H), 1.06 (s, 9H), 0.89 (s, 9H), 0.88 (s, 9H), 0.07 (s, 6H), 0.04 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.6, 156.2, 138.5, 129.8 (2C), 128.5 (2C), 126.6, 81.2, 79.3, 72.9 (2C), 71.7, 65.4, 62.0, 42.9, 39.9, 37.6, 29.9, 29.7 (2C), 29.6 (2C), 29.3, 28.1 (3C), 27.1 (3C), 26.9, 26.7, 26.3, 26.1 (3C), 26.0 (3C), 18.5, 18.4, -4.5 (2C), -5.2 (2C).

IR (ATR): 3030, 2926, 2854, 1704, 1364, 1250, 1161, 1105, 832, 811, 775 cm^{-1}

HRMS (DCI-CH_4) Cald for $C_{45}H_{85}N_2O_6Si_2$ 805.5946 $[M+H]^+$, Found 805.5959

5-benzyl-2-(*tert*-butyl)-3-(11-(2,3-dihydroxypropoxy)undecyl)imidazolidin-4-one (1)



To a solution of 0.117 g (0.145 mmol, 1.00 equiv) of **11** in 0.420 mL of DCM was added 0.142 mL (1.88 mmol, 13.0 equiv) of TFA. The resulting mixture was then stirred overnight at room temperature. Solvent was removed *in vacuo*. This crude product was diluted with 2.00 mL of THF and 0.288 g (0.580 mmol, 4.00 equiv) of TBAF was added. The resulting mixture

was then stirred for 5h at room temperature. It was filtered on silica pad and evaporated *in vacuo*. The crude was purified on silica gel column (Pet/EtOAc 7:3 then 100% EtOAc) to give 0.008 g (8%) of a yellow oil.

R_f 0 (Pet/EtOAc 7:3)

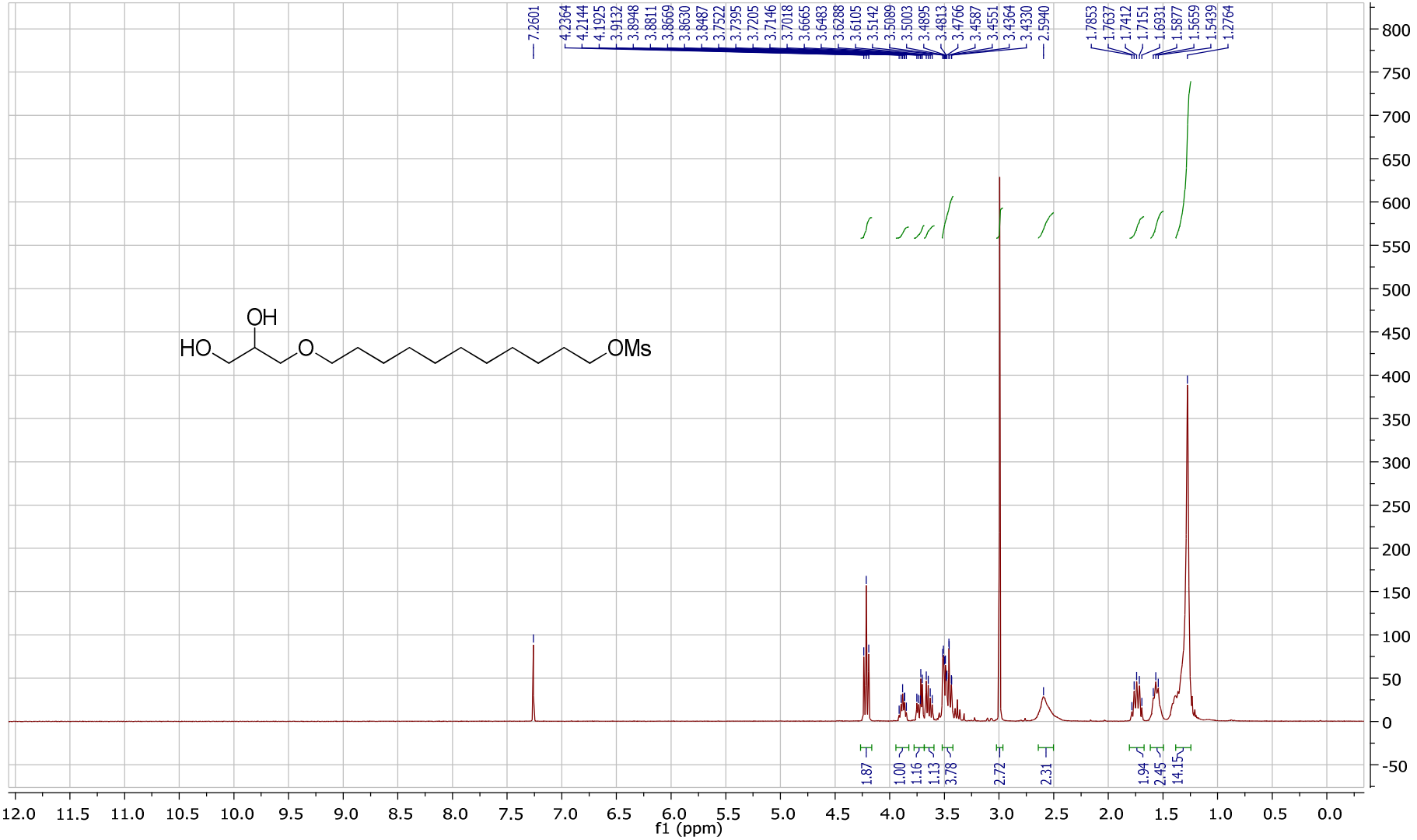
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 – 7.10 (m, 5H), 4.18 (s, 1H), 3.84 – 3.76 (m, 1H), 3.75 – 3.62 (m, 3H), 3.58 (dd, *J* = 11.4, 5.3 Hz, 1H), 3.50 – 3.35 (m, 4H), 3.08 (dd, *J* = 13.8, 4.0 Hz, 1H), 3.02 – 2.97 (m, 1H), 2.87 (dd, *J* = 13.8, 7.5 Hz, 1H), 2.54 (br s , 2H), 1.60 – 1.46 (m, 4H), 1.41 (br s, 1H), 1.25 – 1.14 (m, 14H), 0.77 (s, 9H).

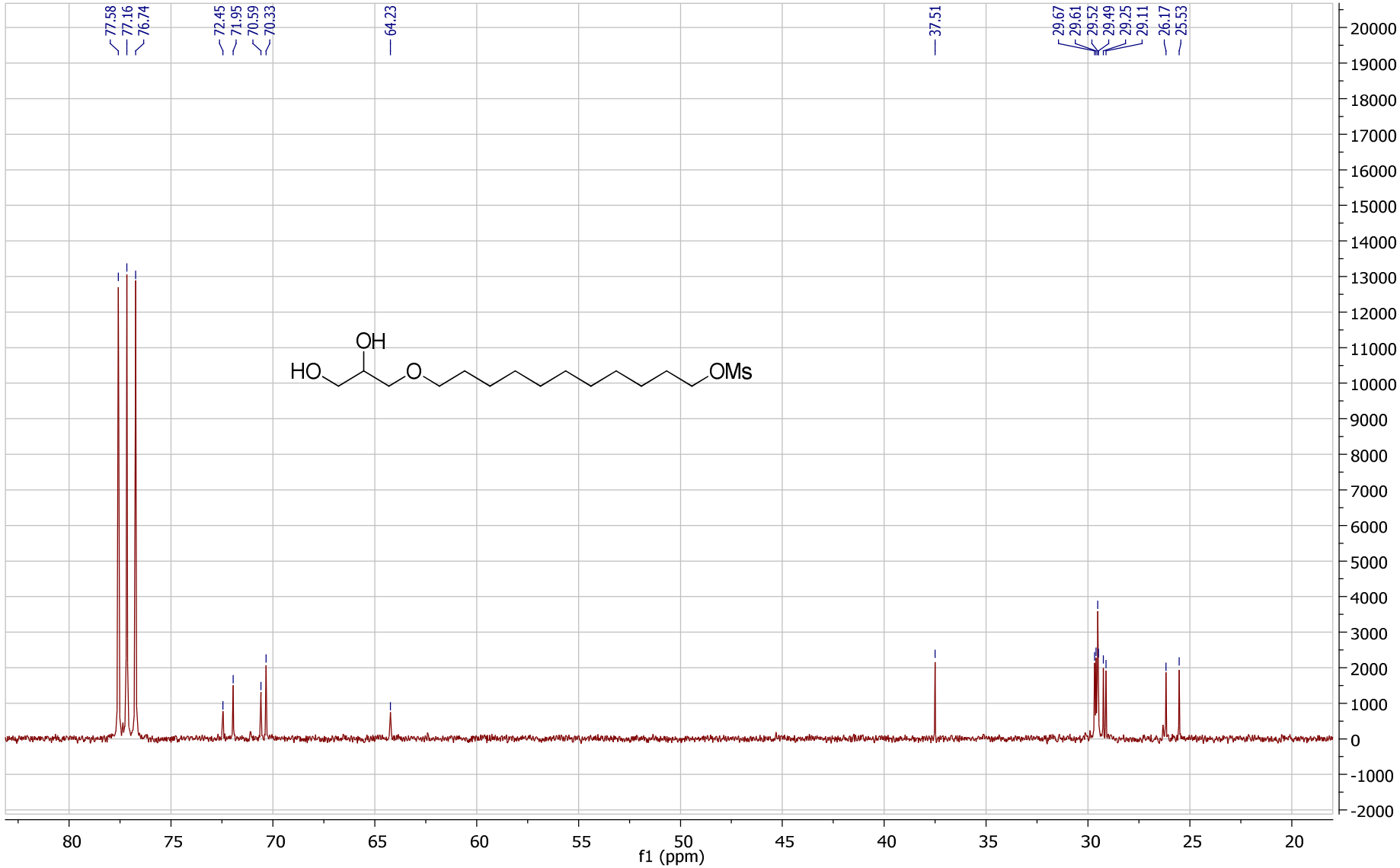
^{13}C NMR (75 MHz, $CDCl_3$) δ 175.4, 137.2, 129.8 (2C), 128.8 (2C), 126.8, 79.7, 72.7, 71.9, 70.6, 64.5, 59.3, 42.7, 38.3, 35.5, 29.7, 29.6 (2C), 29.5 (2C), 29.4, 27.1, 27.0, 26.2, 25.6 (3C).

IR (ATR): 3361, 3010, 2923, 2852, 1670, 1454, 1398, 1109, 1040, 720 cm^{-1}

HRMS (DCI-CH_4) Cald for $C_{28}H_{49}N_2O_4$ 477.3692 $[M+H]^+$, Found 477.3686

^{1}H and ^{13}C NMR spectra

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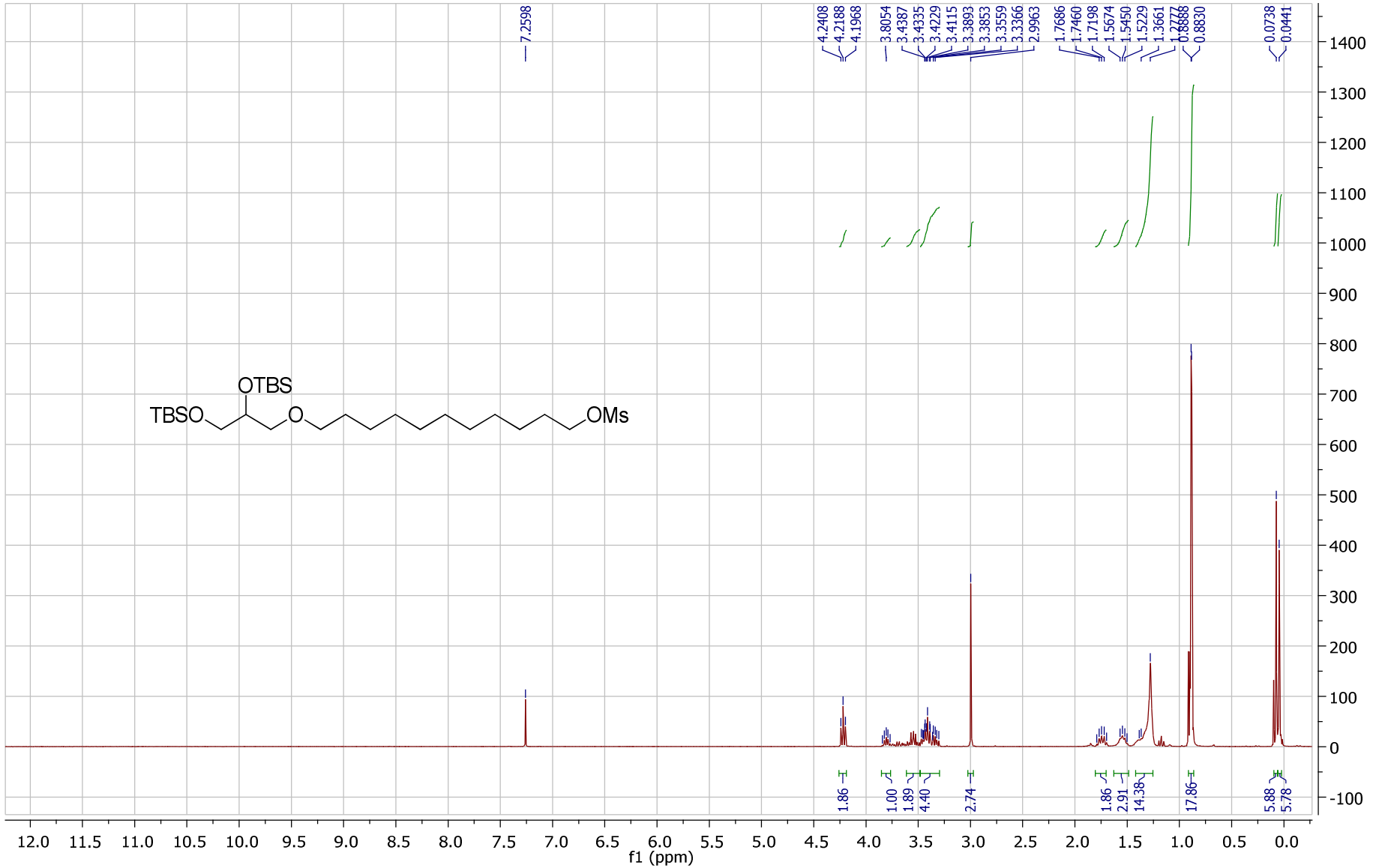
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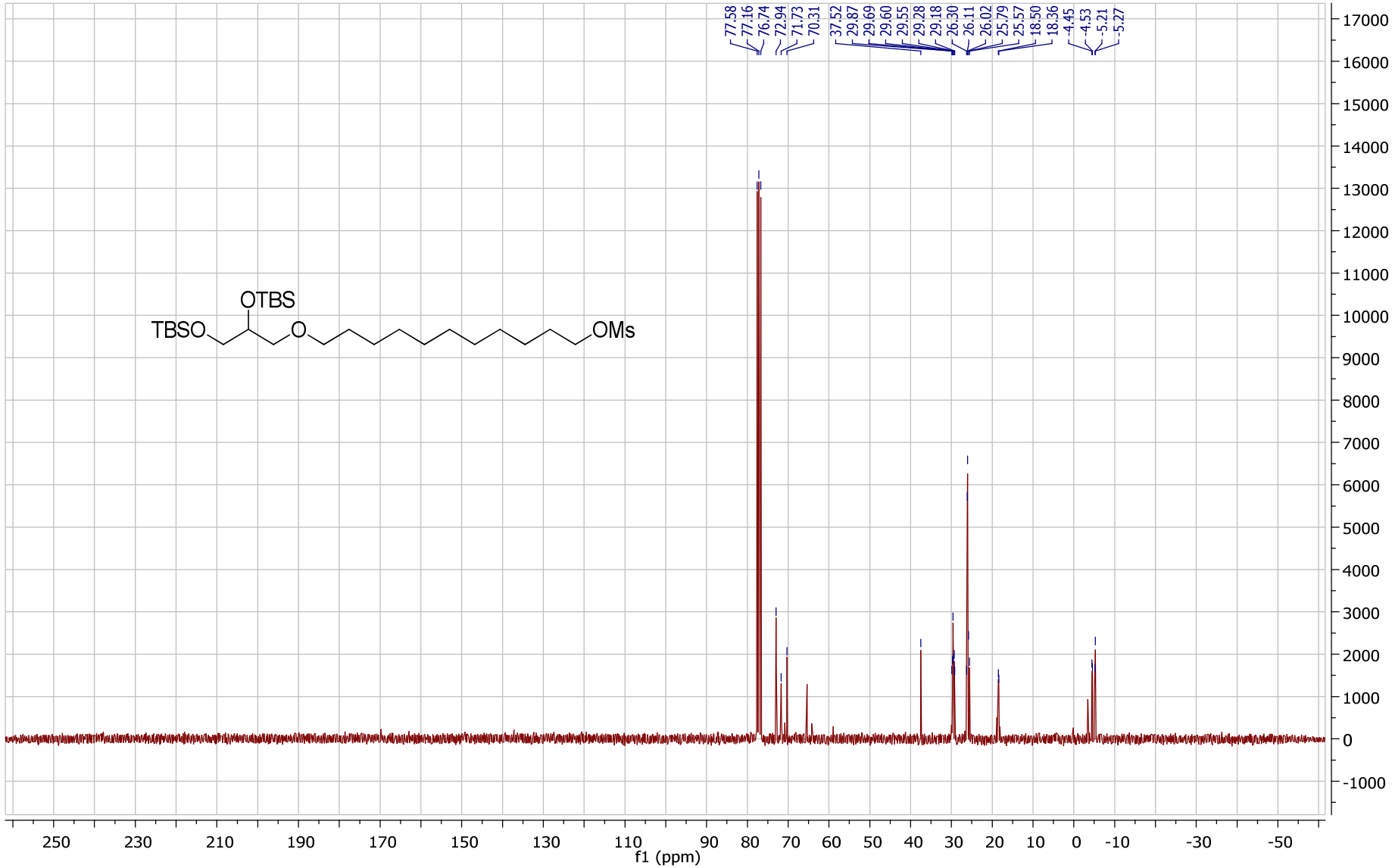
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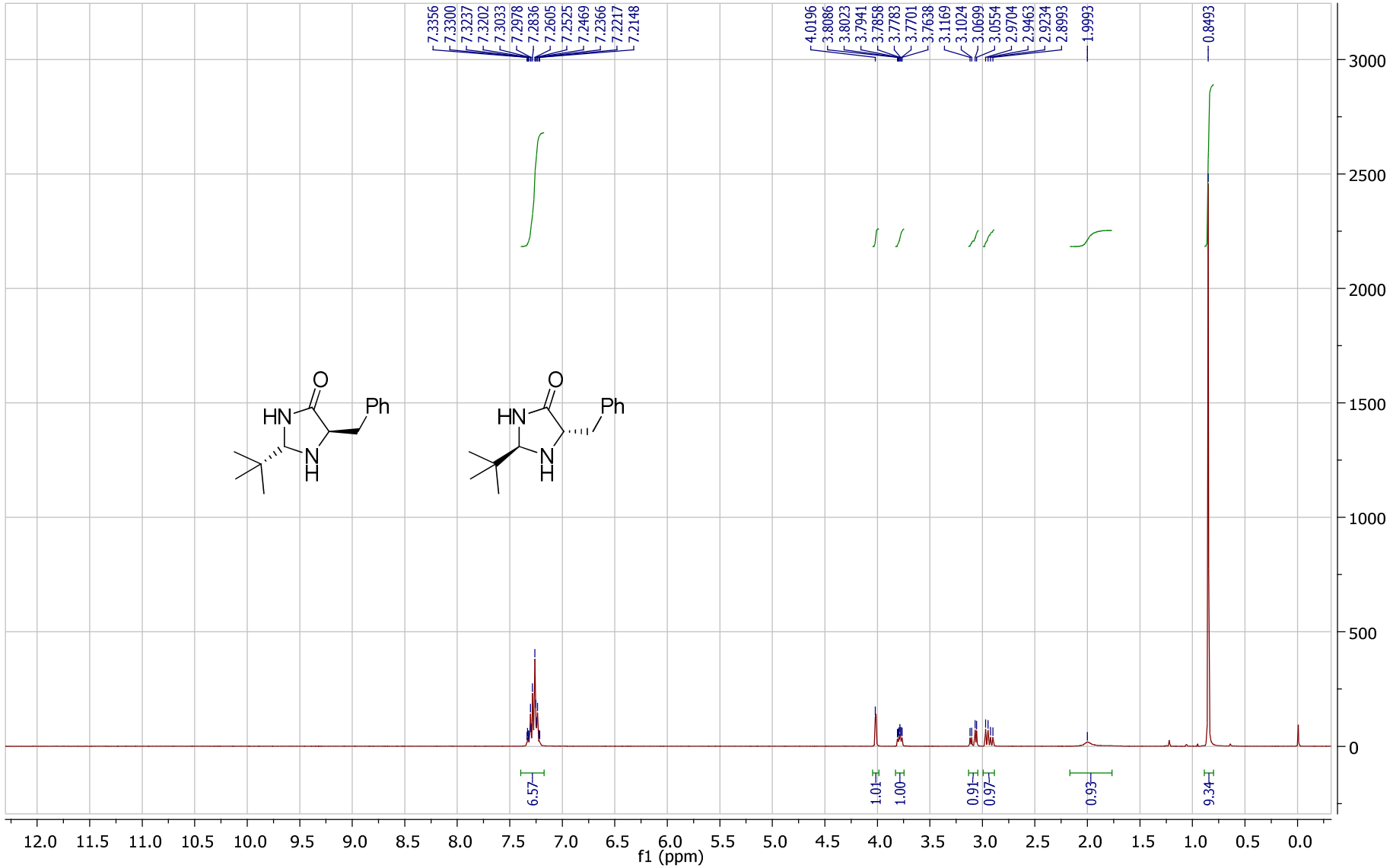
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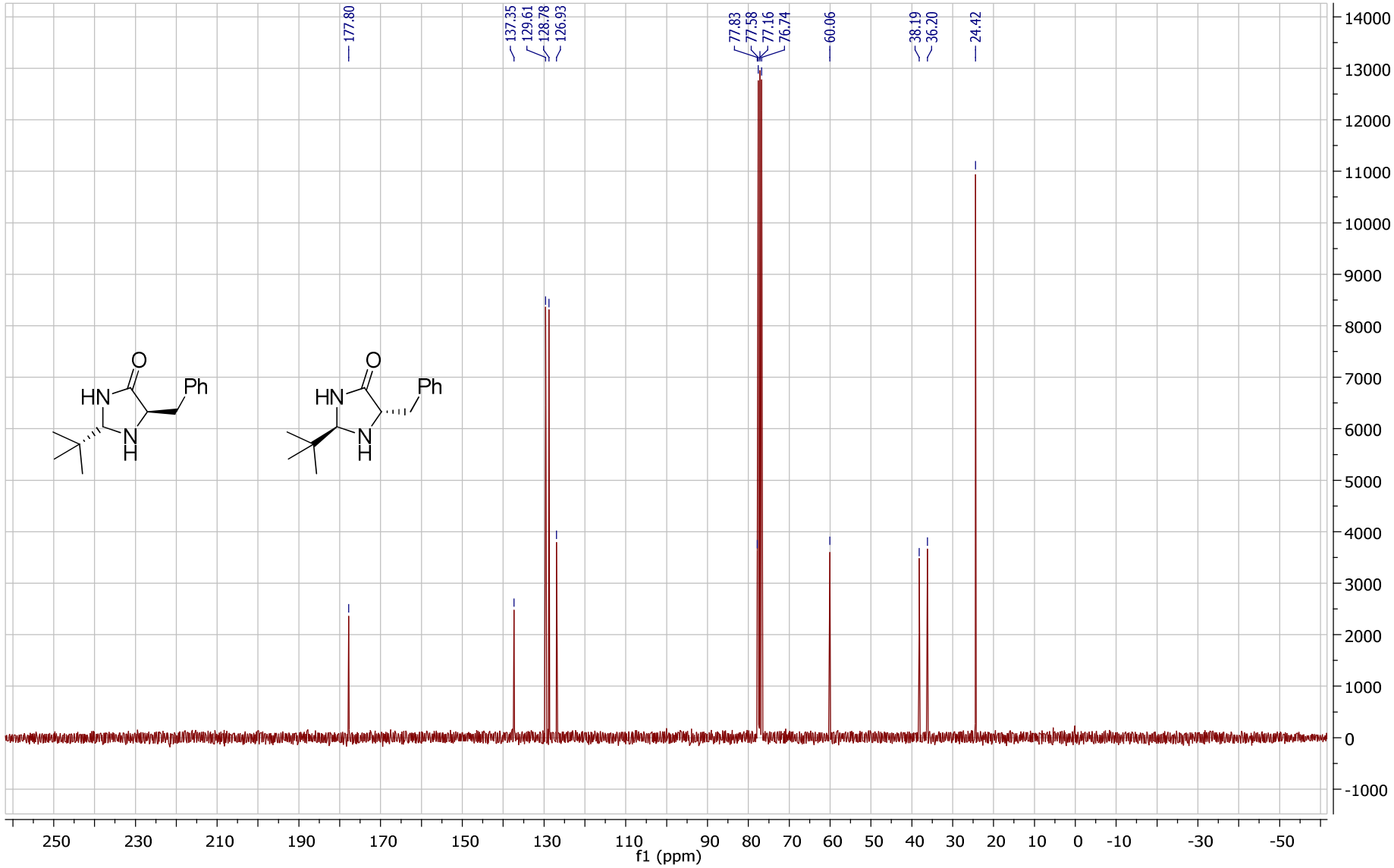
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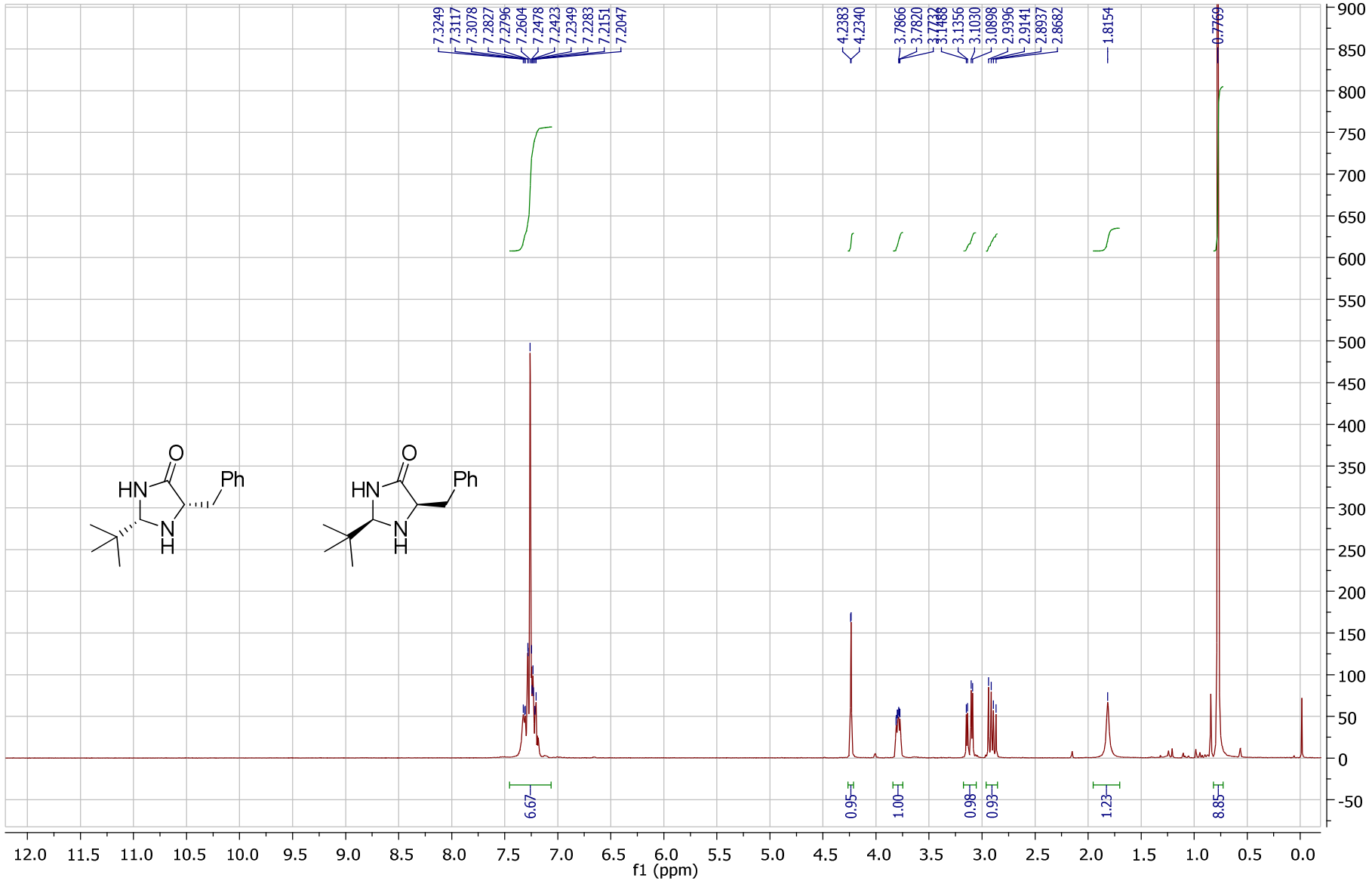
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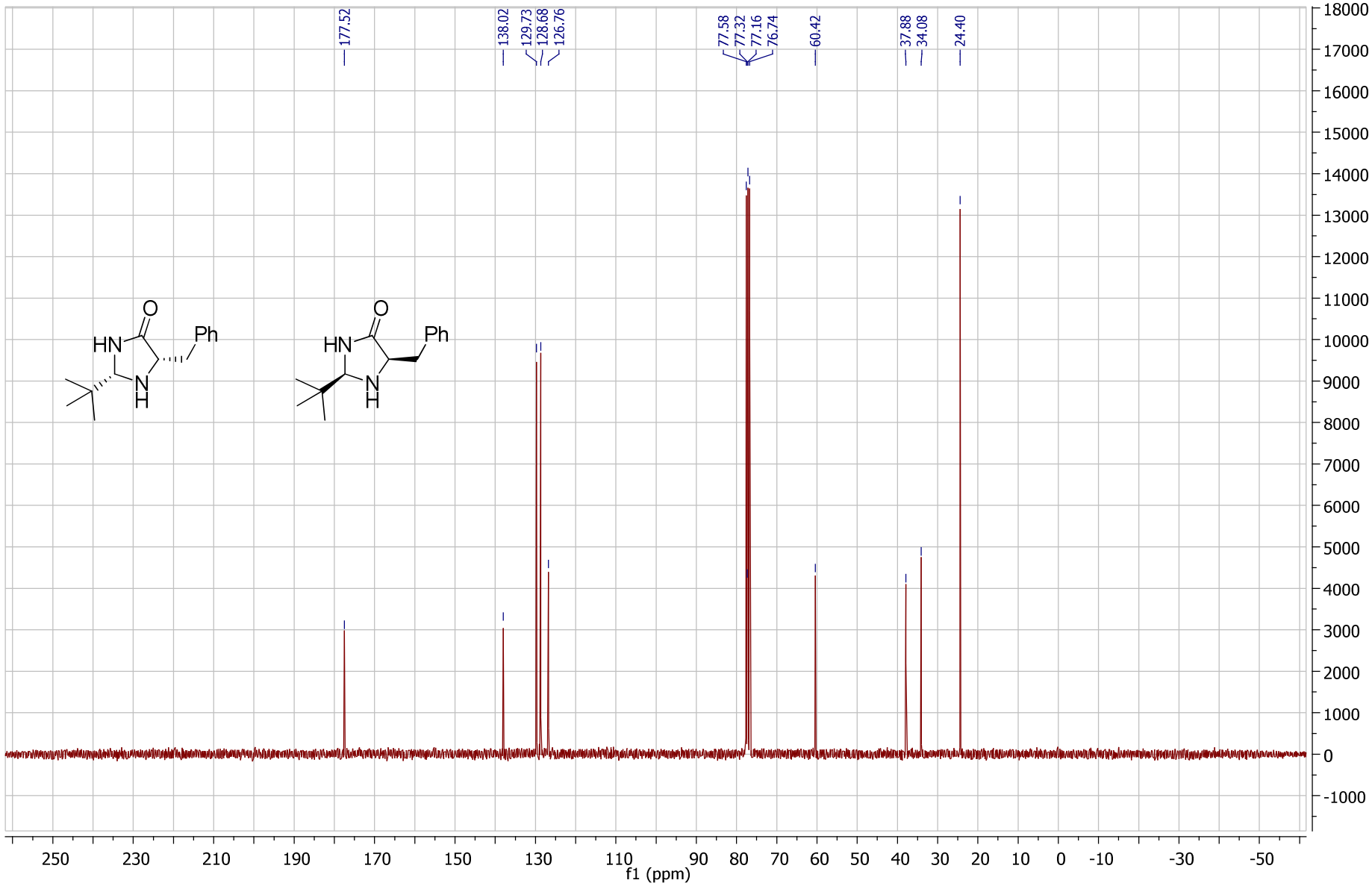
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7000
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3000
2000
1000
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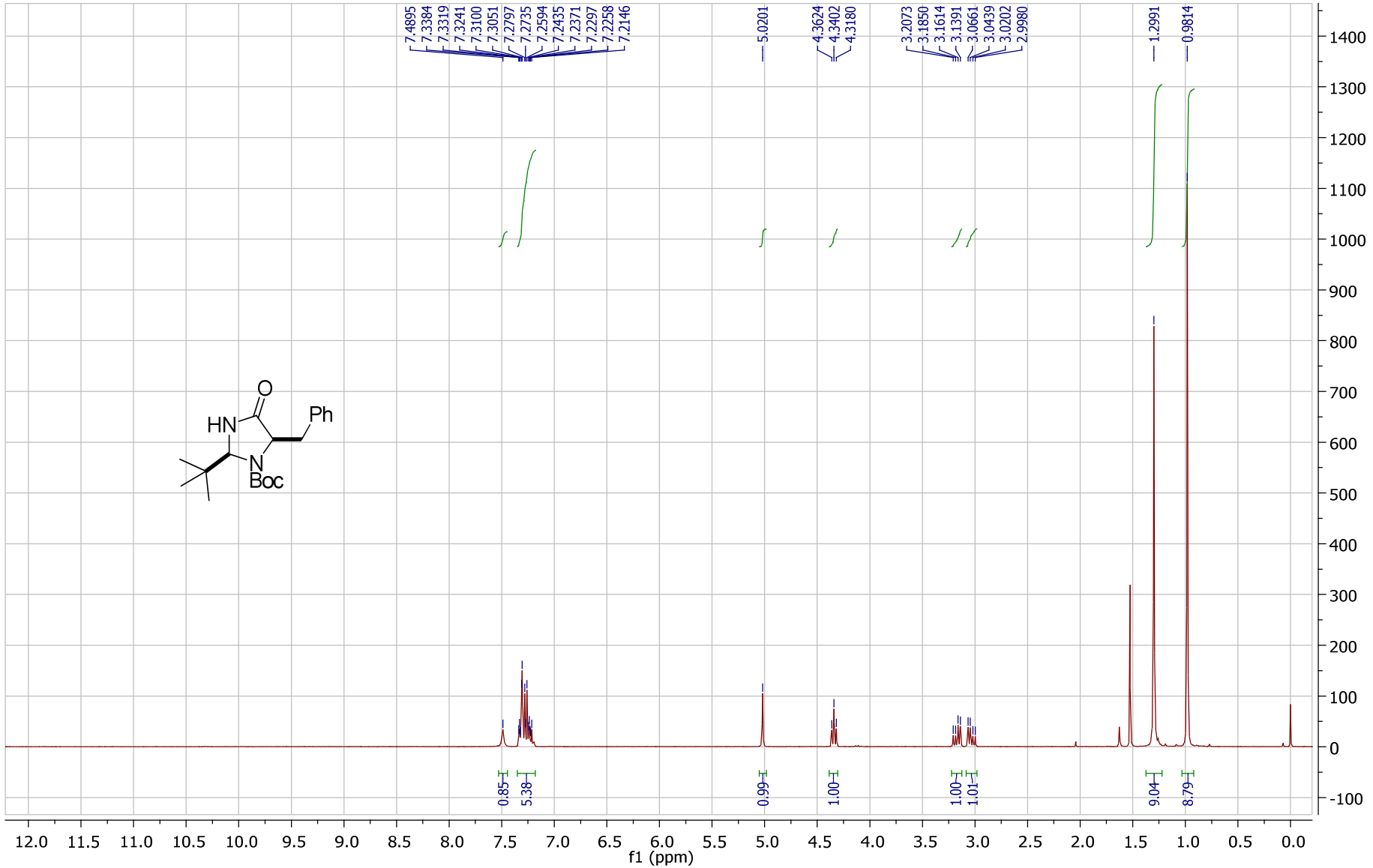
-50
f1 (ppm)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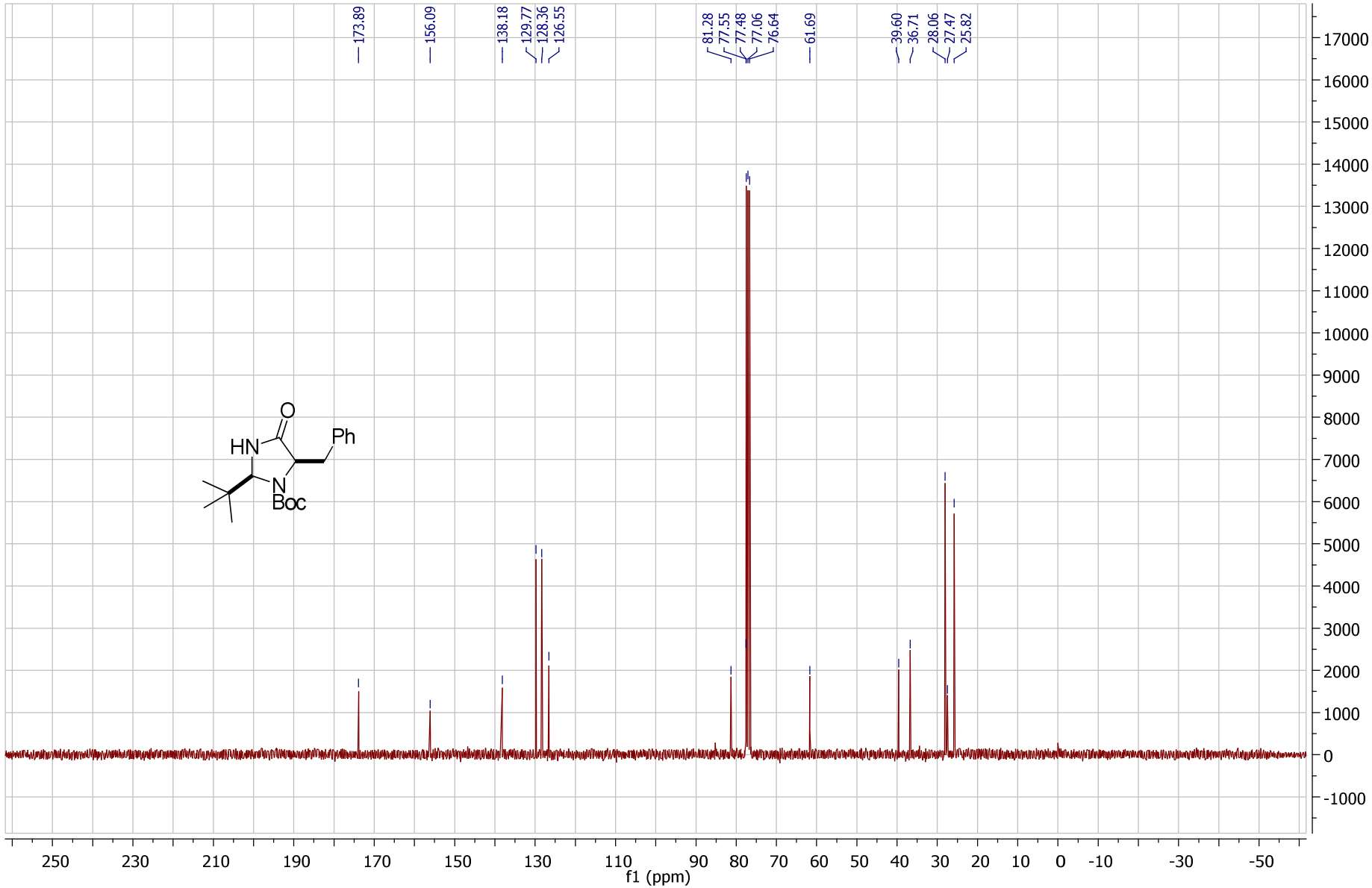
7.2797
7.2735
7.2594
7.2435
7.2371
7.2297
7.2258
7.2146
5.0201
4.3624
4.3402
4.3180
3.2073
3.1850
3.1614
3.1391
3.0661
3.0439
3.0202
2.9980
1.2991
0.9814
O
HN
Ph
N
Boc
0.85
5.38
0.99
1.00
1.00
1.01
9.04
8.79
f1 (ppm)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138.18
129.77
128.36
126.55
81.28
77.55
77.48
77.06
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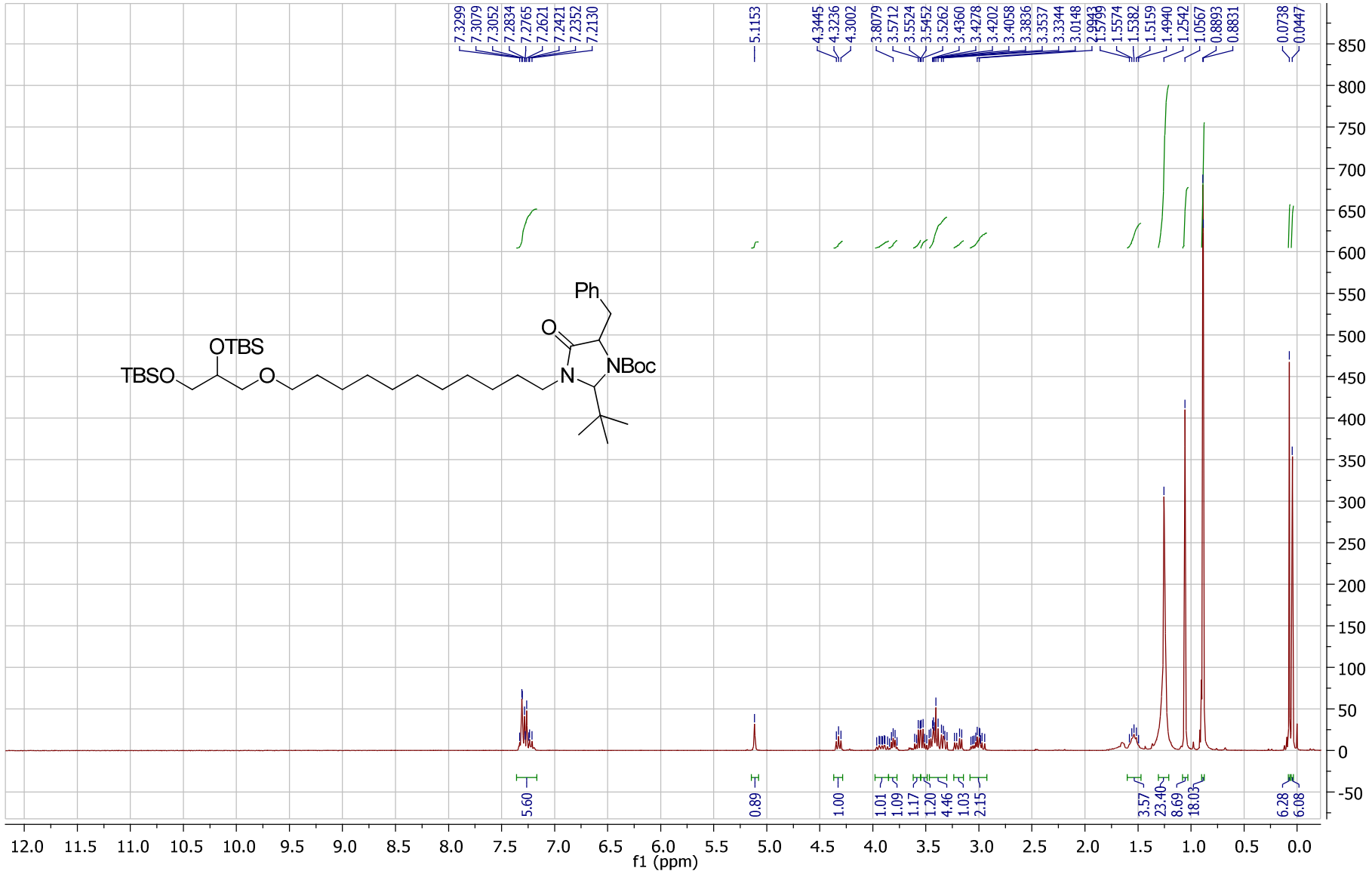
39.60
36.71
28.06
27.47
25.82
O
HN
Ph
N
Boc
f1 (ppm)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7.2765
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7.2130
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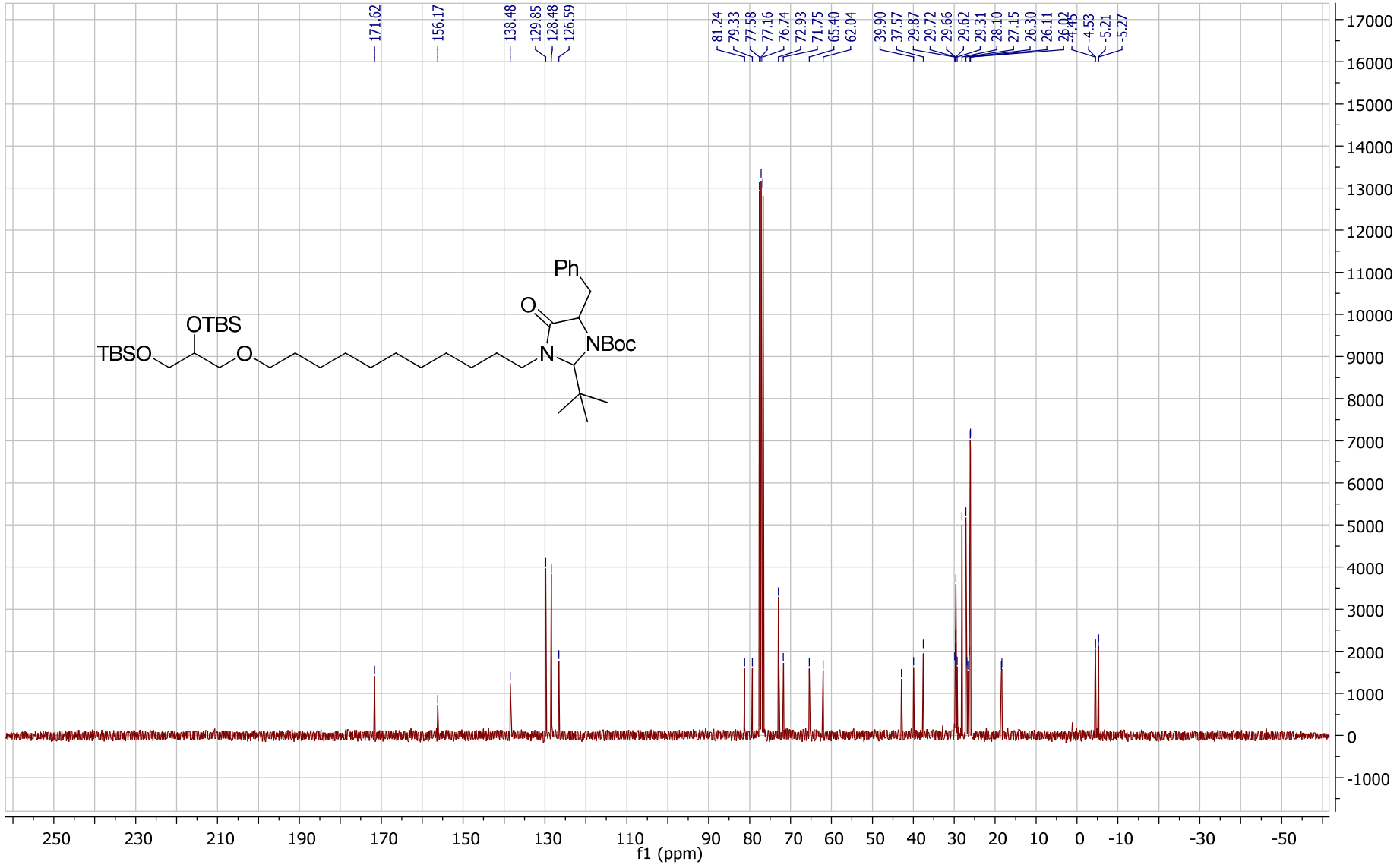
4.3445
4.3236
4.3002
3.8079
3.5712
3.5524
3.5452
3.5262
3.4360
3.4278
3.4202
3.4058
3.3836
3.3537
3.3344
3.0148
2.9943
1.5799
1.5574
1.5382
1.5159
1.4940
1.2542
1.0567
0.8893
0.8831
0.0738
0.0447
Ph
O
OTBS
TBSO
O
N
NBoc
5.60
0.89
1.00
1.01
1.09
1.17
1.20
4.46
1.03
2.15
3.57
23.40
8.69
18.03
6.28
6.08
f1 (ppm)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156.17
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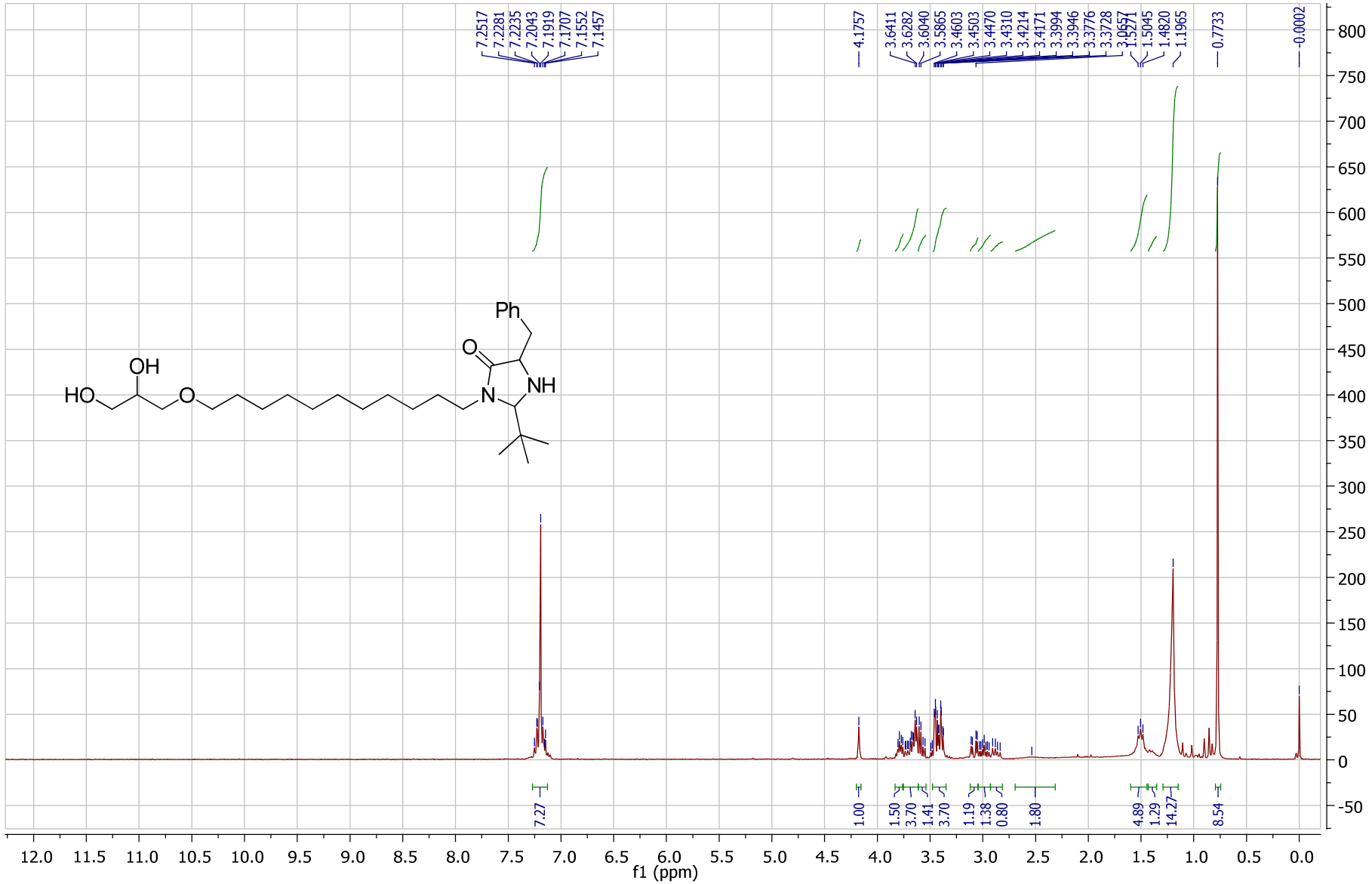
129.85
128.48
126.59
81.24
79.33
77.58
77.16
76.74
72.93
71.75
65.40
62.04
39.90
37.57
29.87
29.72
29.66
29.62
29.31
28.10
27.15
26.30
26.11
-4.53
-5.21
-5.27
Ph
O
OTBS
TBSO
O
N
NBoc
f1 (ppm)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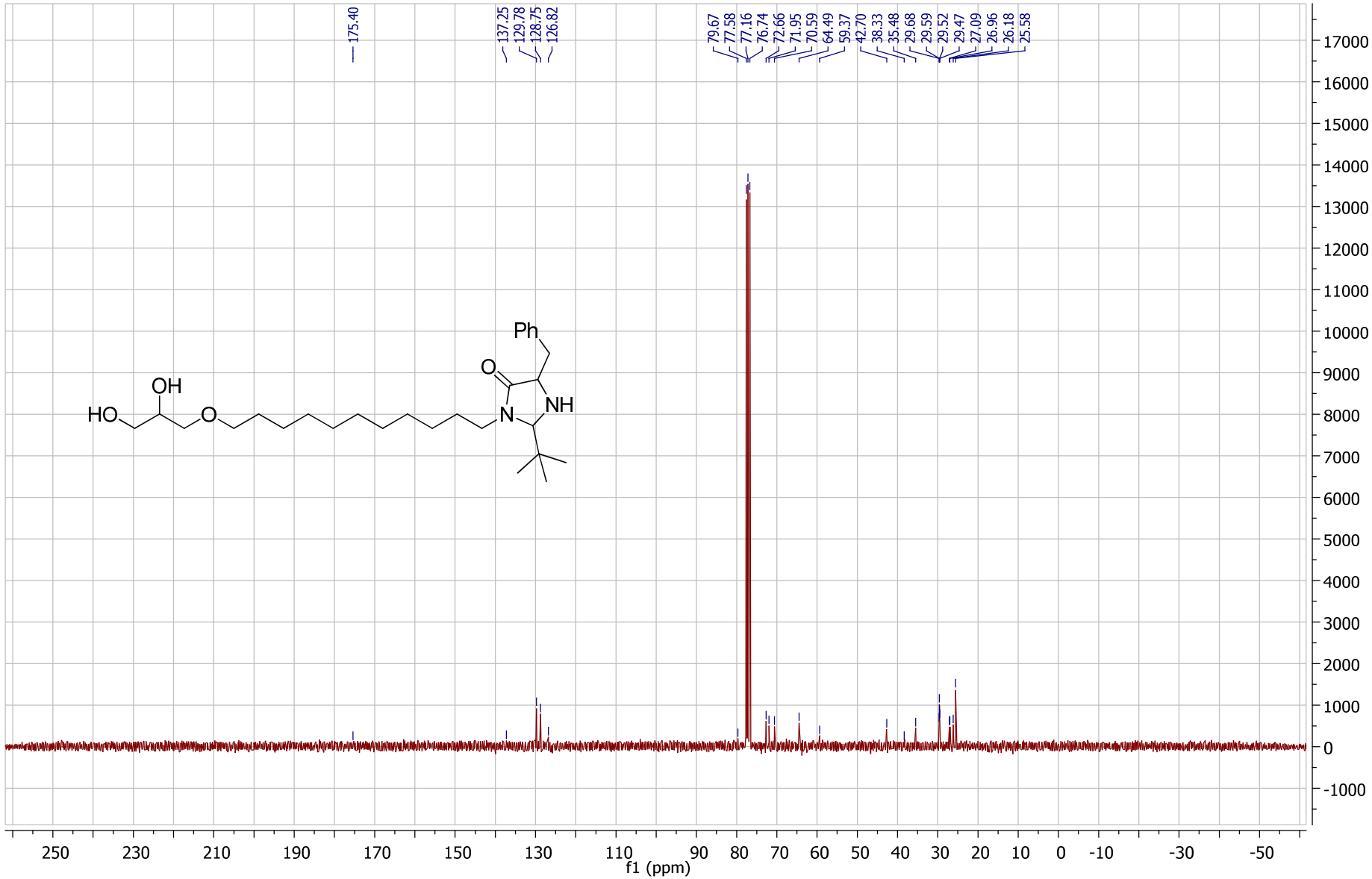
7.1457
4.1757
3.6411
3.6282
3.6040
3.5865
3.4603
3.4503
3.4470
3.4310
3.4214
3.4171
3.3994
3.3946
3.3776
3.3728
3.0657
1.5271
1.5045
1.4820
1.1965
0.7733
-0.0002
Ph
O
OH
HO
O
N
NH
7.27
1.00
1.50
3.70
1.41
3.70
1.19
1.38
0.80
1.80
4.89
1.29
14.27
8.54
f1 (ppm)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137.25
129.78
128.75
126.82
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77.58
77.16
76.74
72.66
71.95
70.59
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59.37
42.70
38.33
35.48
29.68
29.59
29.52
29.47
27.09
26.96
26.18
25.58
Ph
O
OH
HO
O
N
NH
f1 (ppm)