Supporting Information

Regioselective Base-Free Intermolecular Aminohydroxylations of Hindered and Functionalized Alkenes

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Structure Proofs of 33a and 33b. NMR data for **33a** and **33b**, including nOe correlations and coupling constants, were consistent with the proposed structures (Figure S1). The structure proposed for carbamate **33a** was proven by its conversion into known amino diol **S1** (Scheme S1). Spectral data for **S1** were in accordance with previously reported data.[1]

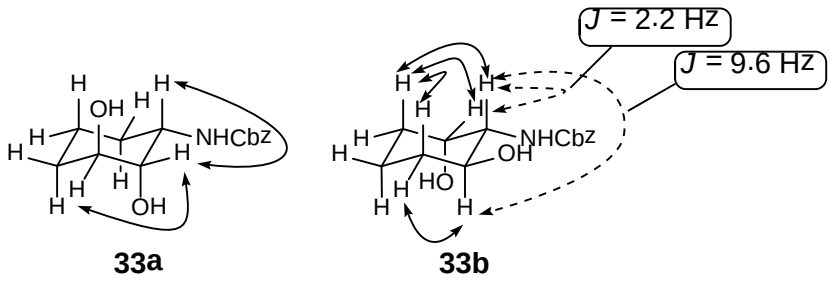
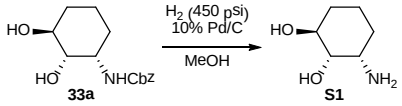


Figure S1. Diagnostic nOe Correlations and Coupling Constants of **33a** and **33b**.

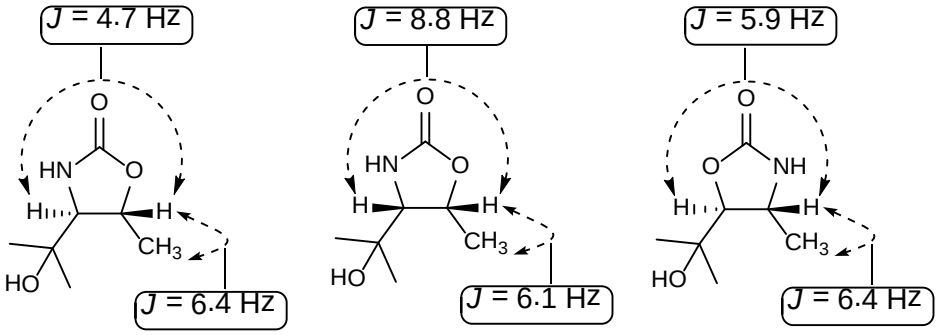


Scheme S1. Hydrogenation of **33a**.

Determination of Stereochemistry of 35a–c. Treatment of each carbamate **35a**, **35b**, and **35c** with base (7.5 N aq KOH, THF–MeOH, 16 h) afforded the corresponding oxazolidinones **S2**, **S3**, and **S4**. Assignment of the *trans* stereochemistry to **S2** and **S4** and the *cis* stereochemistry to **S3** is based on prior reports that the coupling constants of *trans* oxazolidinones are smaller than those of *cis* oxazolidinones[2] (Figure S2). The resulting structural assignments of **35a**, **35b**, and **35c** are consistent with the *syn* addition that is

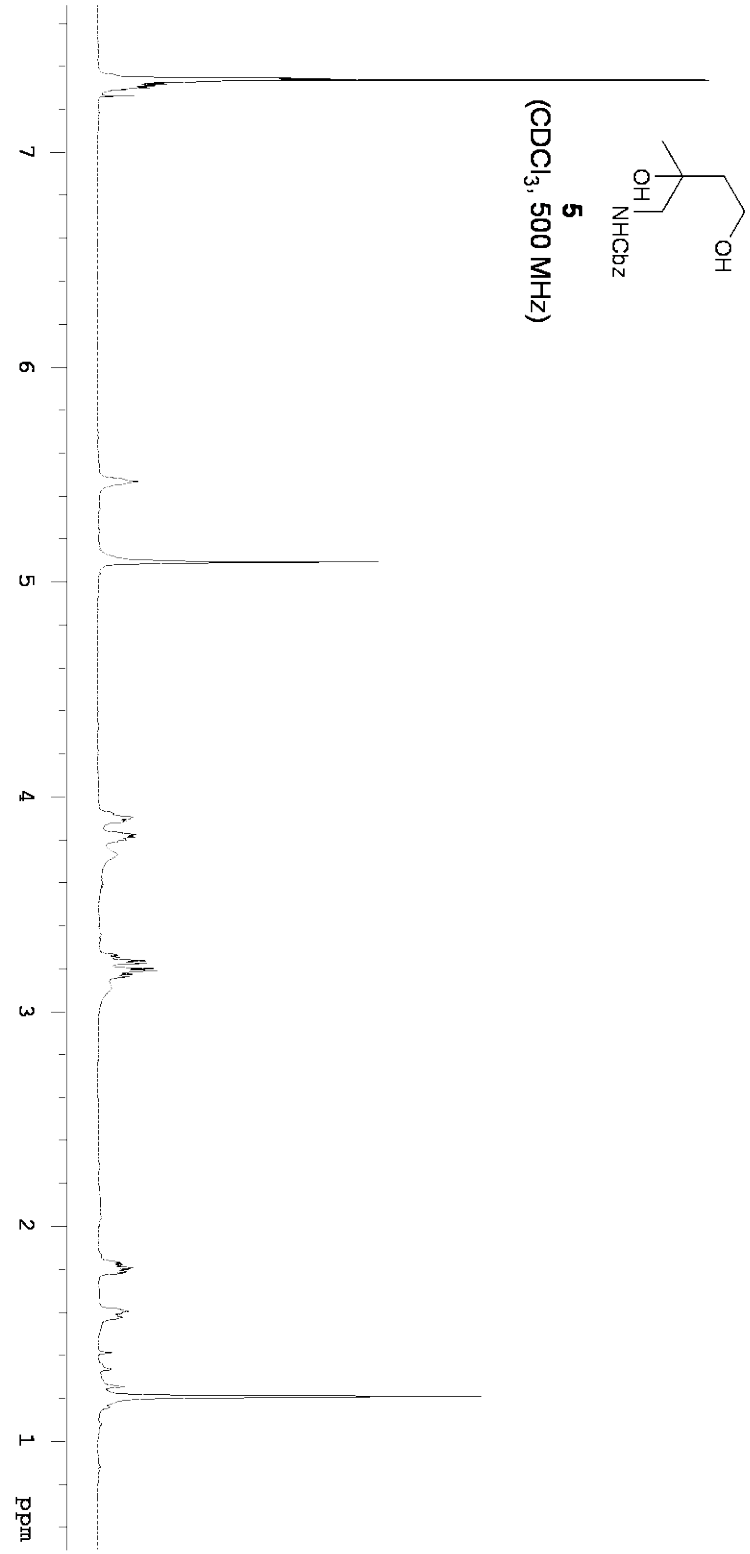
[1] Aciro, C.; Davies, S. G.; Roberts, P. M.; Russell, A. J.; Smith, A. D.; Thomson, J. E. *Org. Biomol. Chem.* **2008**, *6*, 3762.
[2] (a) Kobayashi, S.; Isobe, T.; Ohno, M. *Tetrahedron Lett.* **1984**, *25*, 5079. (b) Kano, S.; Yokomatsu, T.; Iwasawa, H.; Shibuya, S. *Chem. Lett.* **1987**, 1531.

characteristic of the aminohydroxylation reaction (i.e., **35a** and **35c** were formed in the aminohydroxylation of **36**, but **35b** was not).



S2 (from **35a**) **S3** (from **35b**) **S4** (from **35c**)

Figure S2. Diagnostic Coupling Constants of Oxazolidinones Derived from **35a–c**.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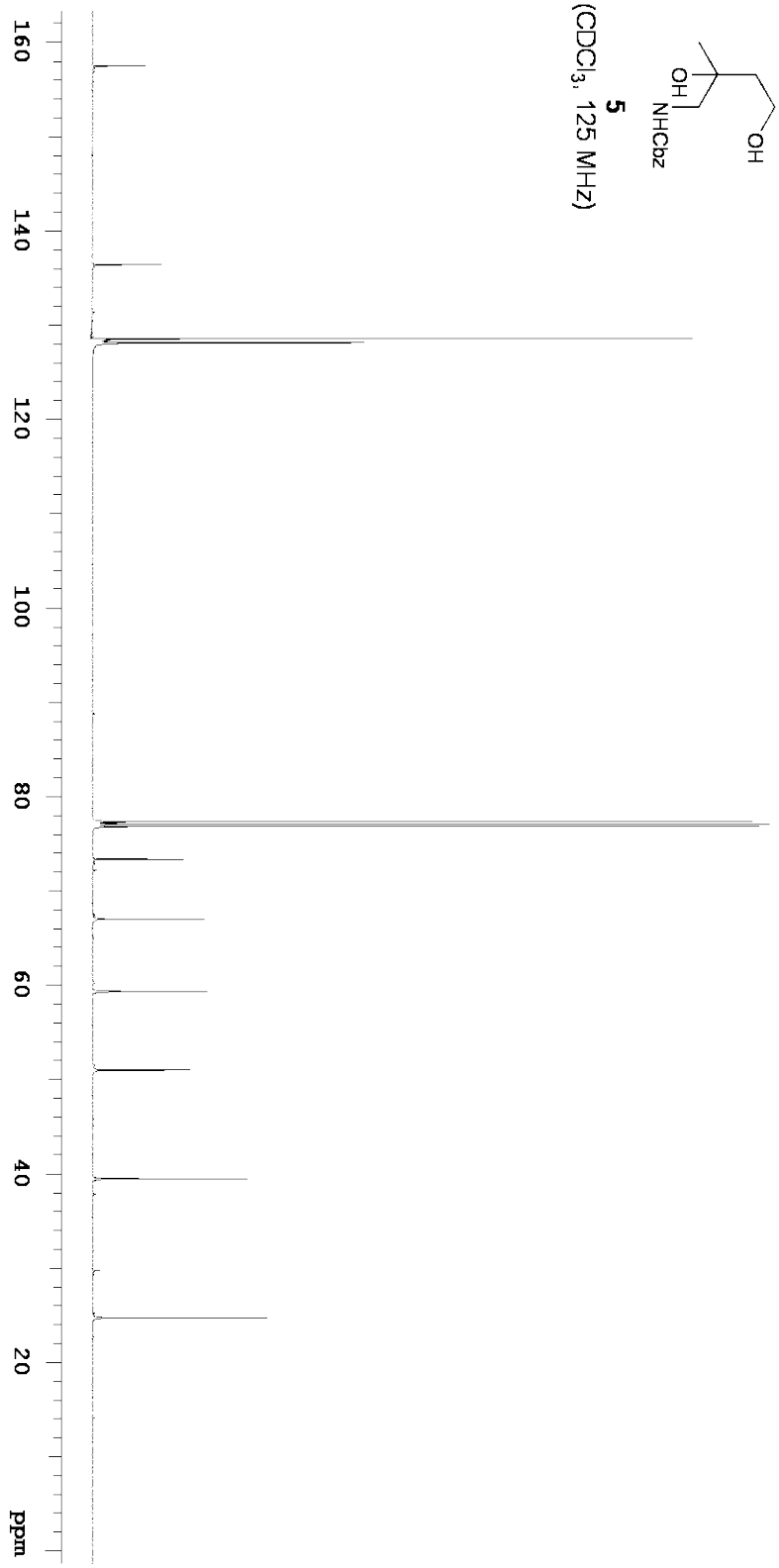
4
3
2
1
ppm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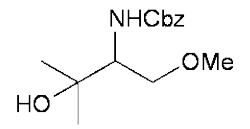

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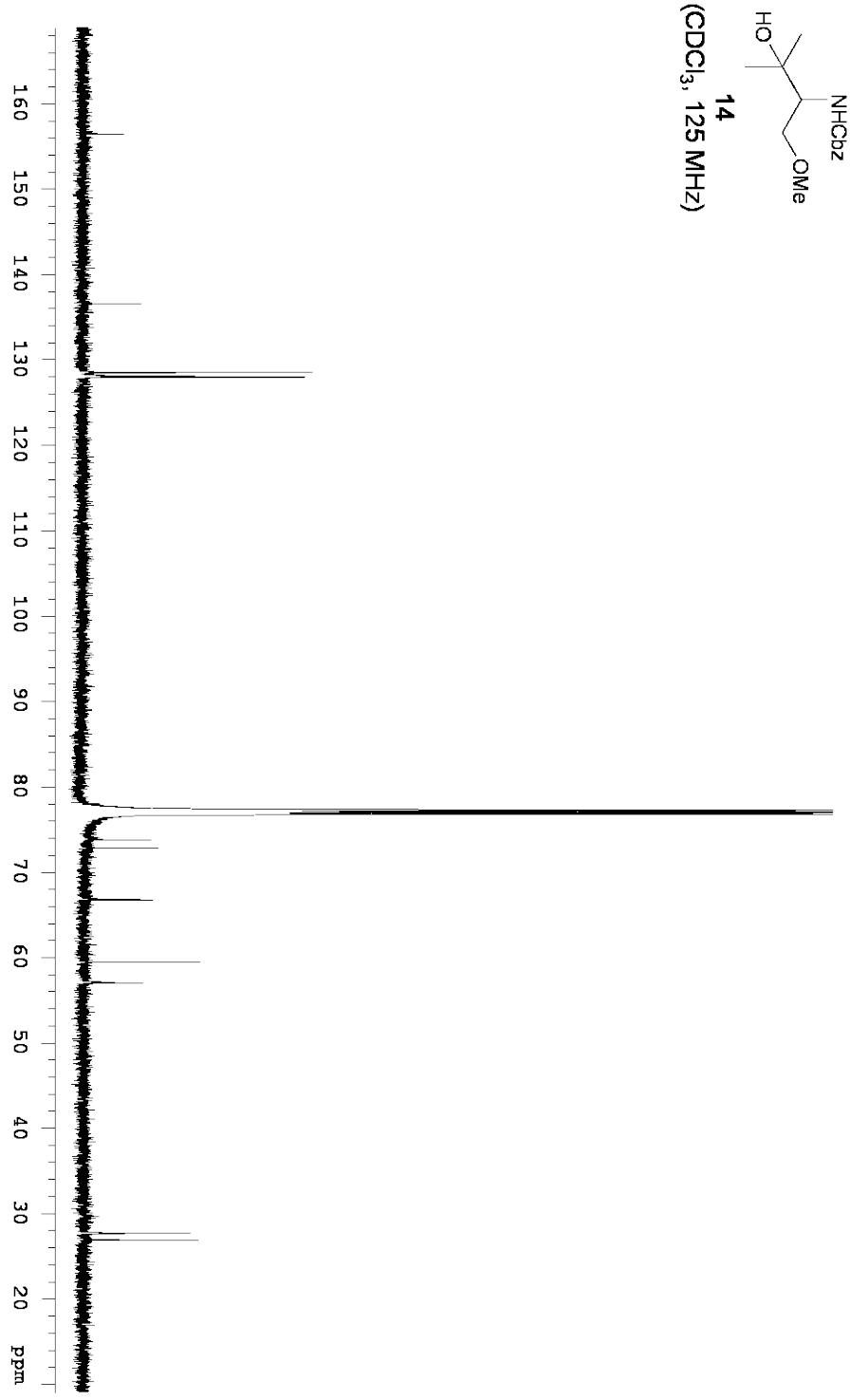
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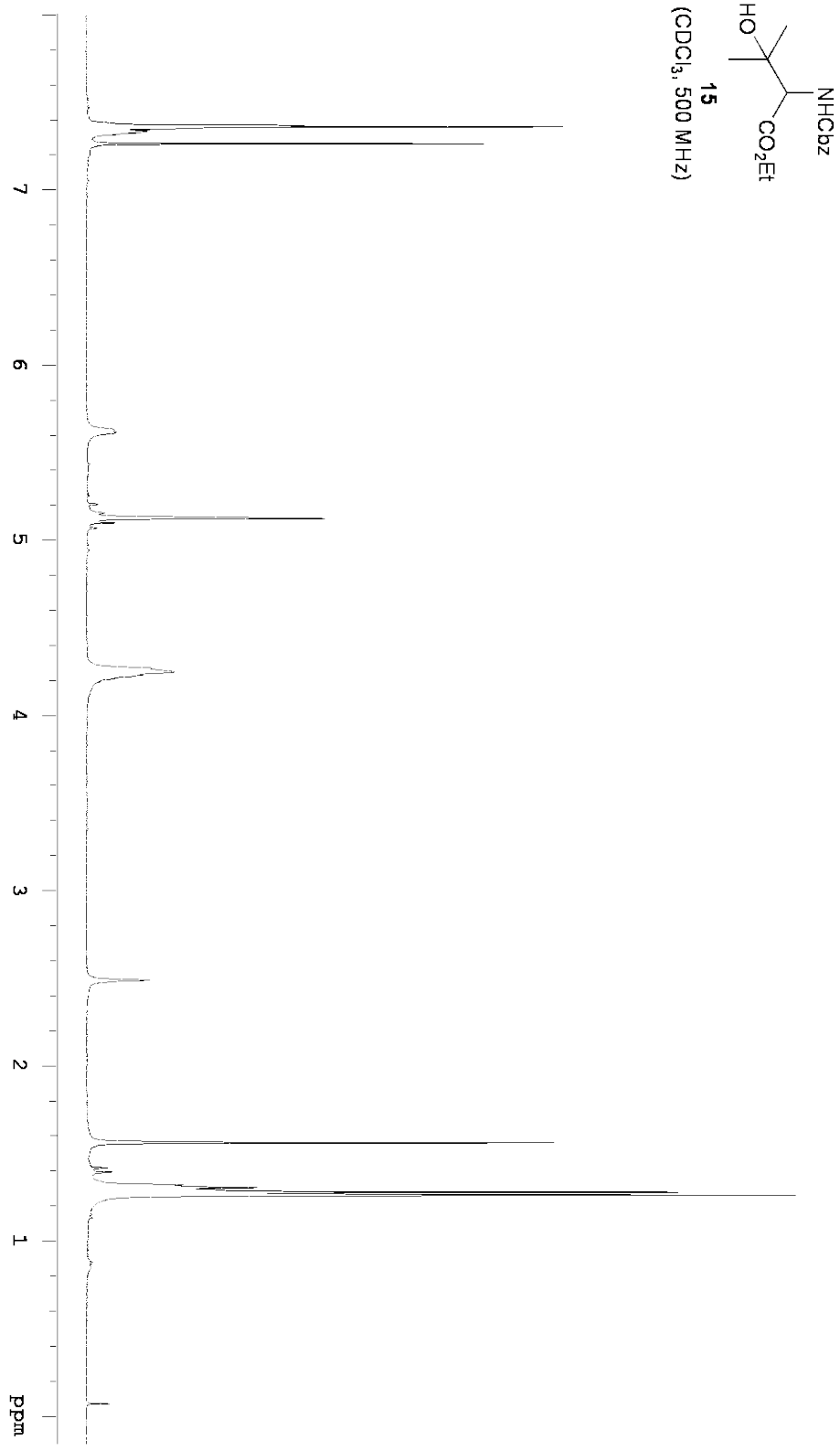
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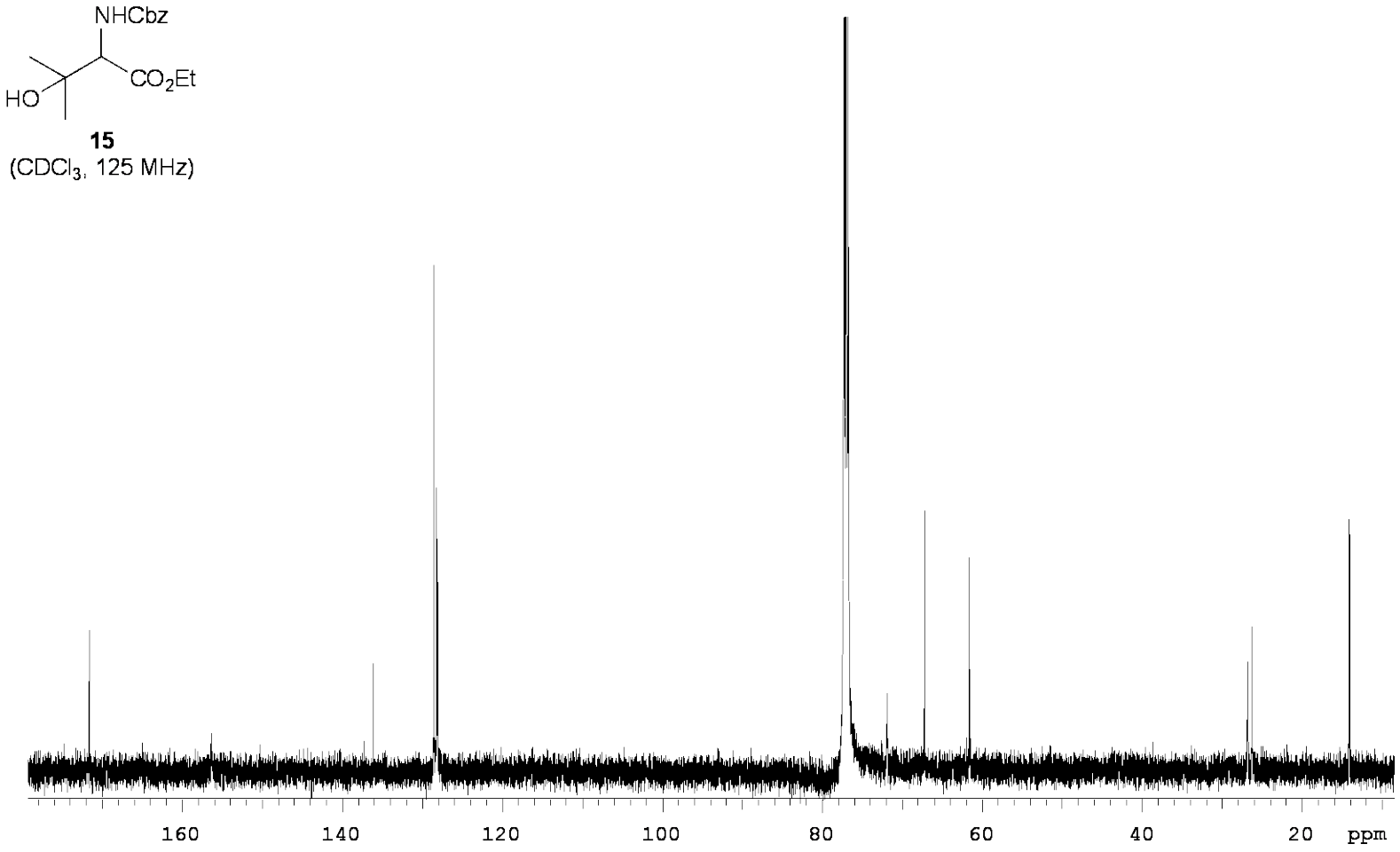
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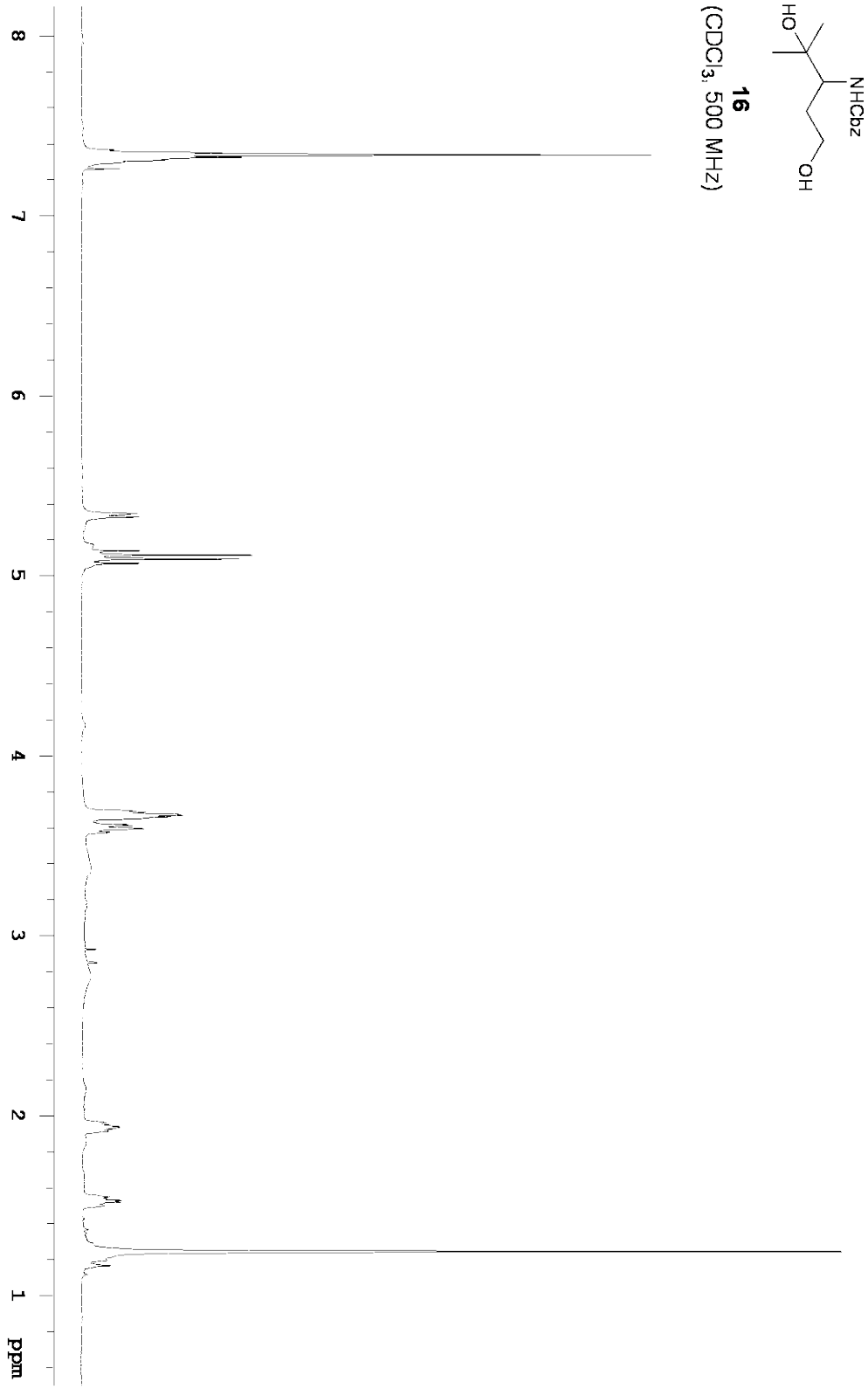
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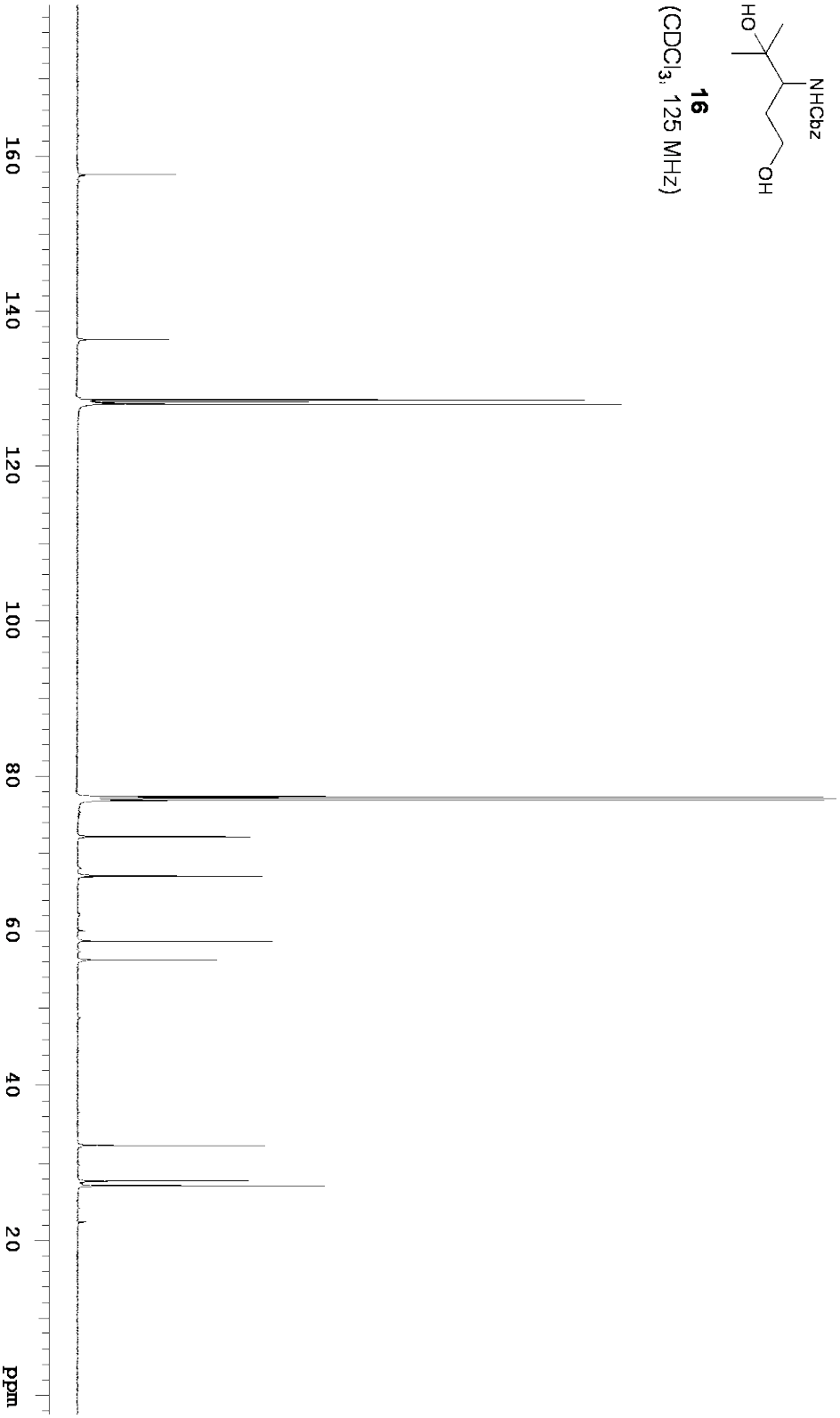
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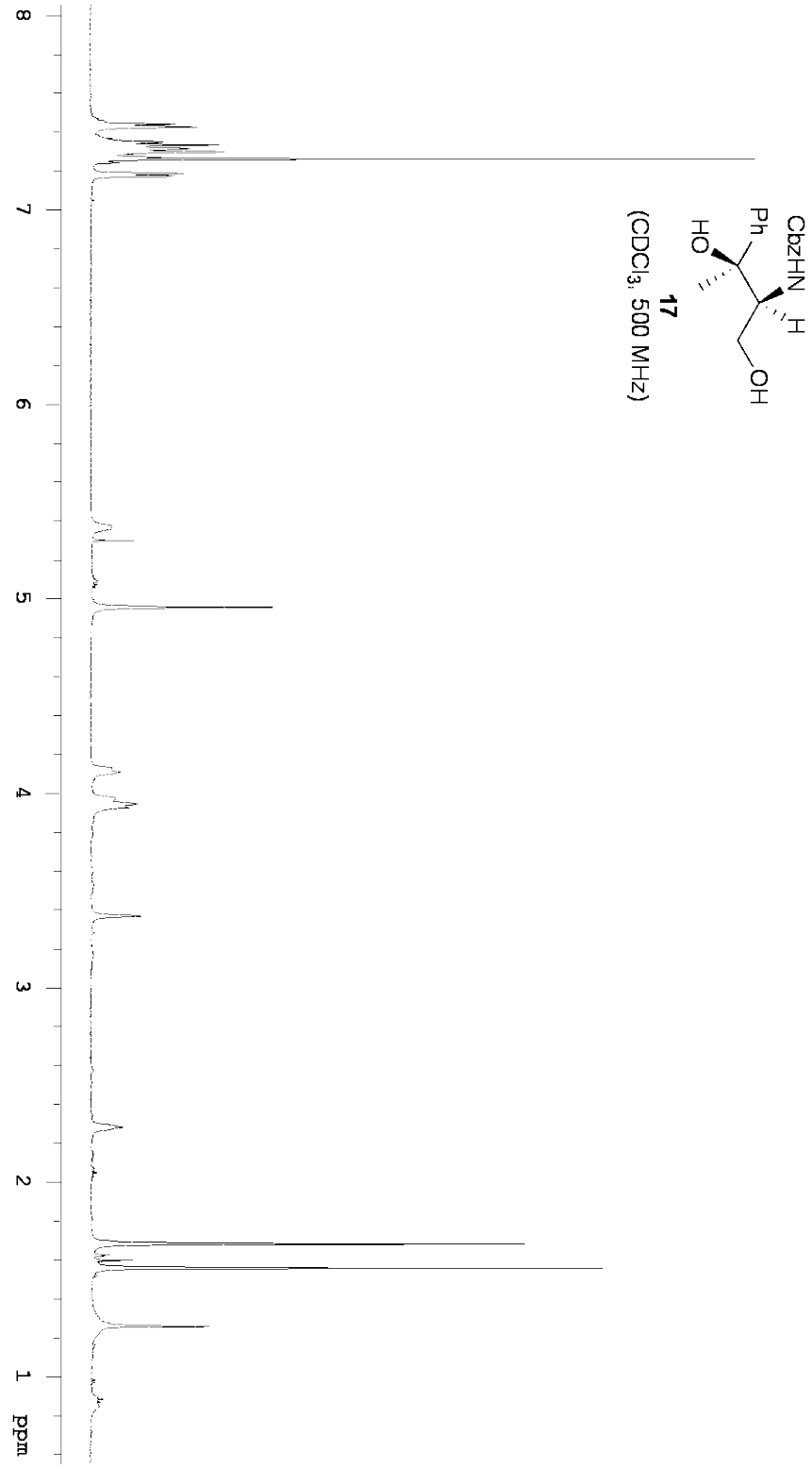
ppm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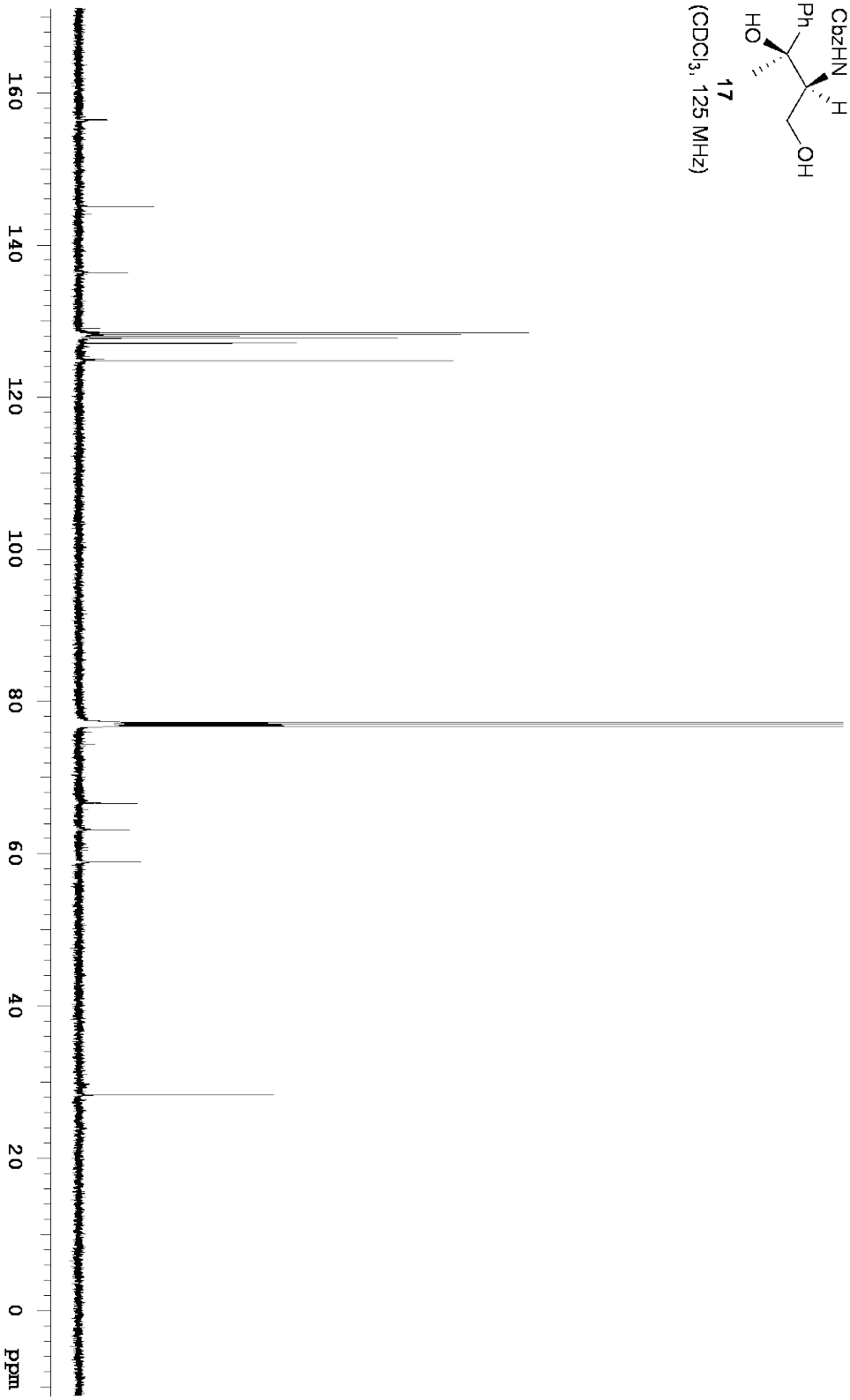
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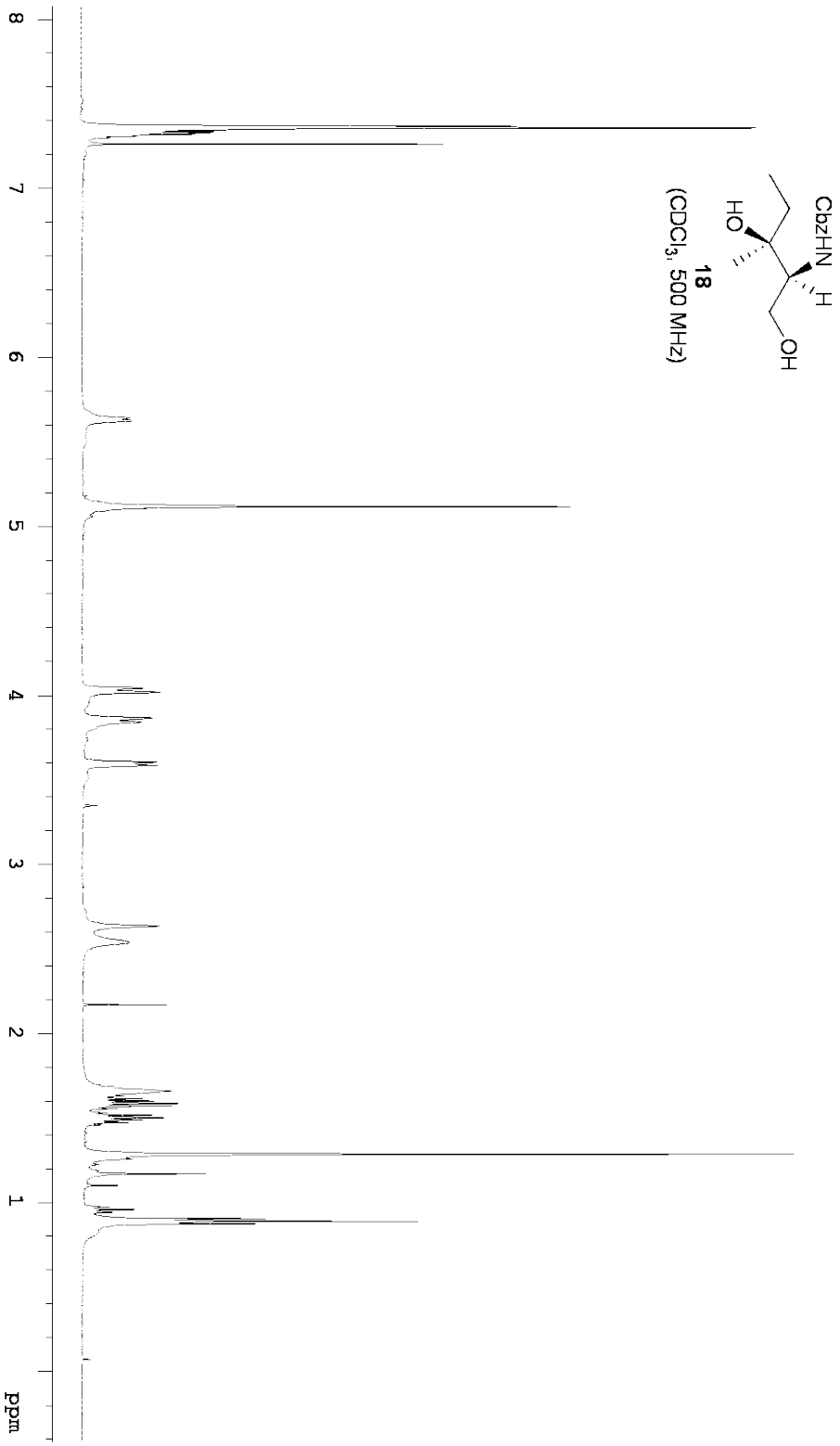
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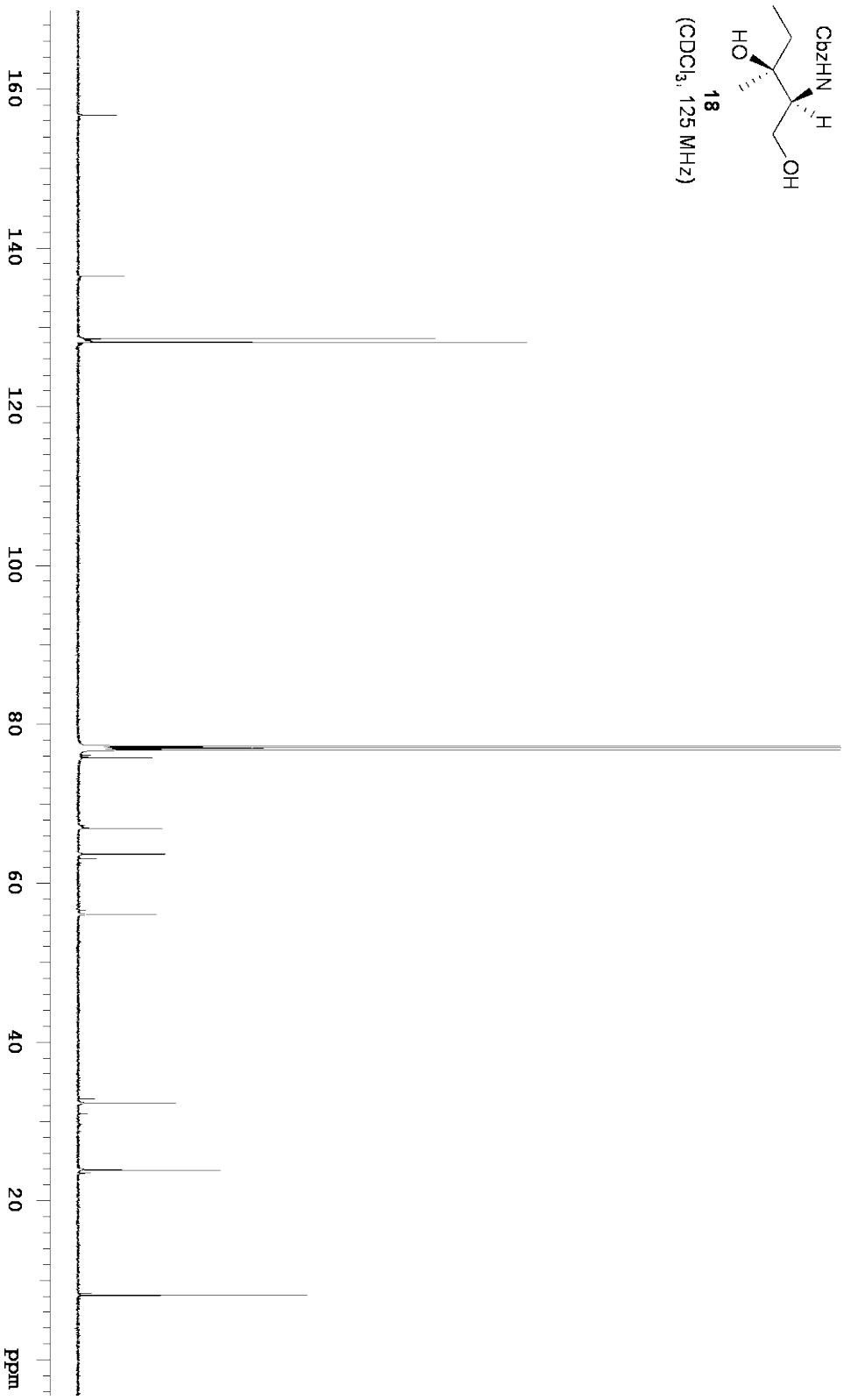
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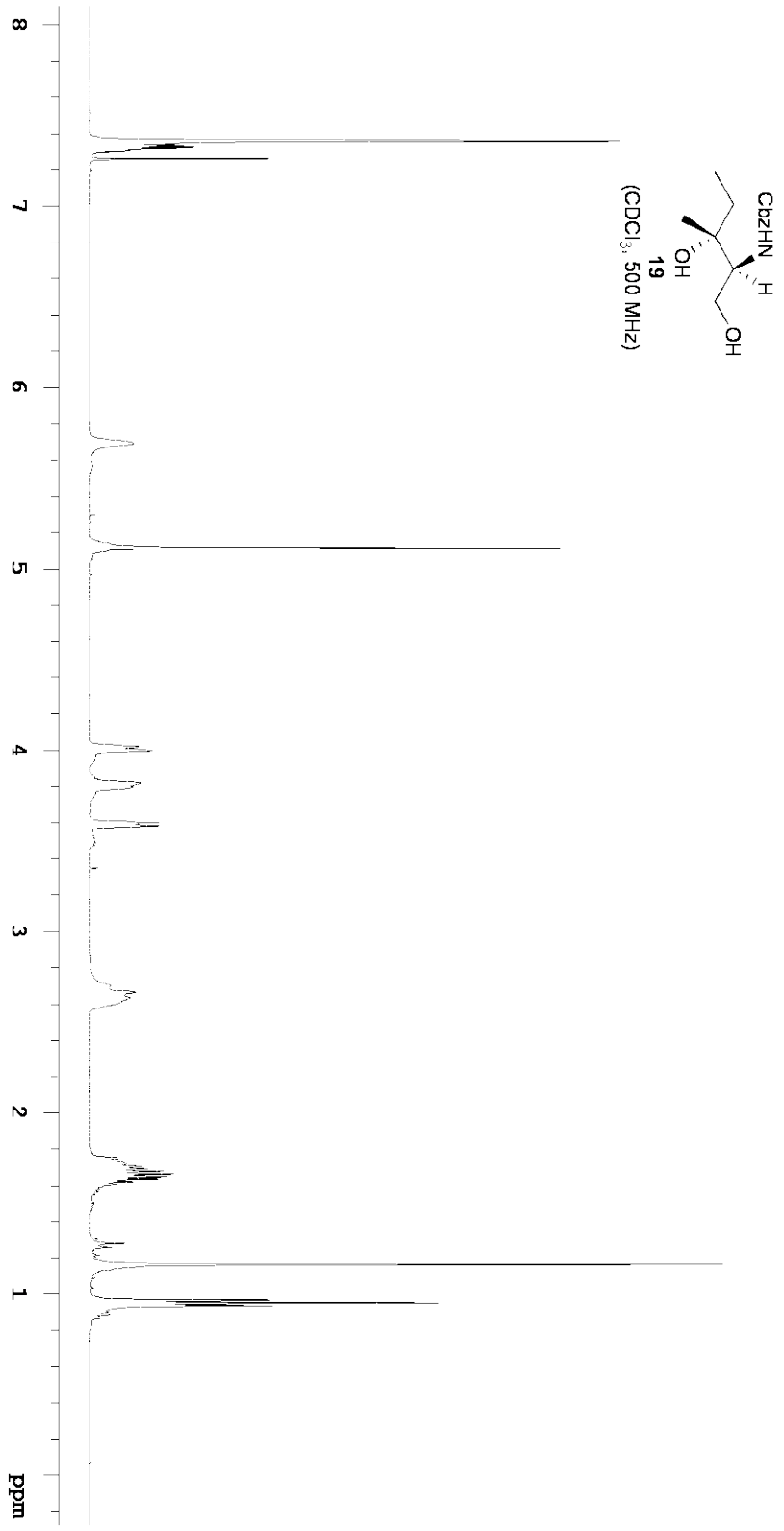
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ppm
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H
OH
OH
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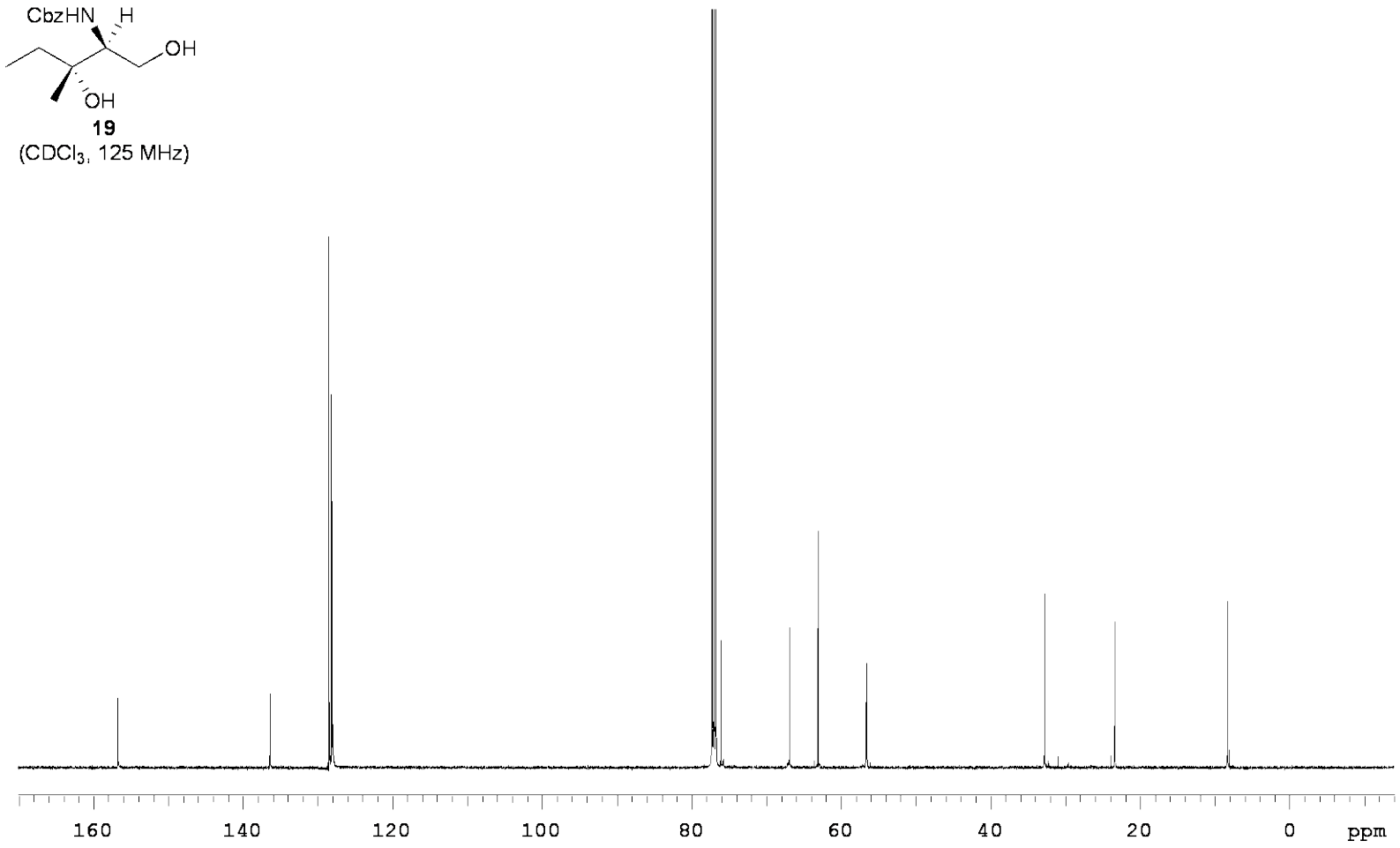
(CDCl3, 500 MHz)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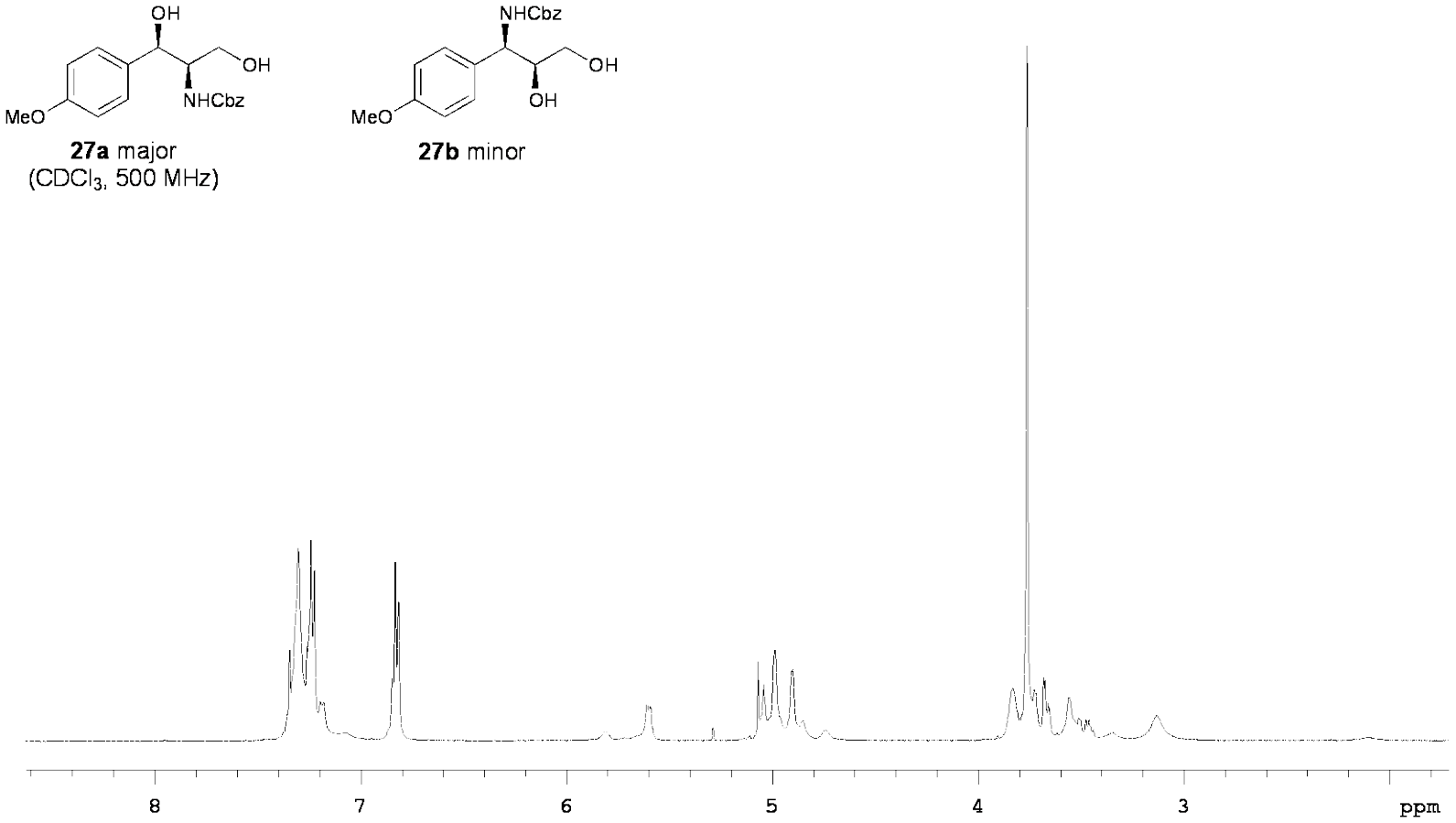
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OH
MeO
27b minor
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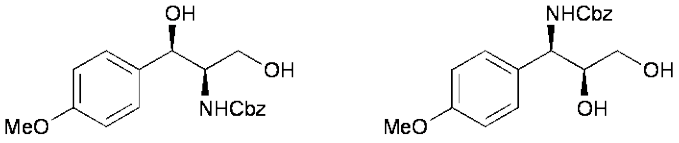
6
5
4
3
ppm



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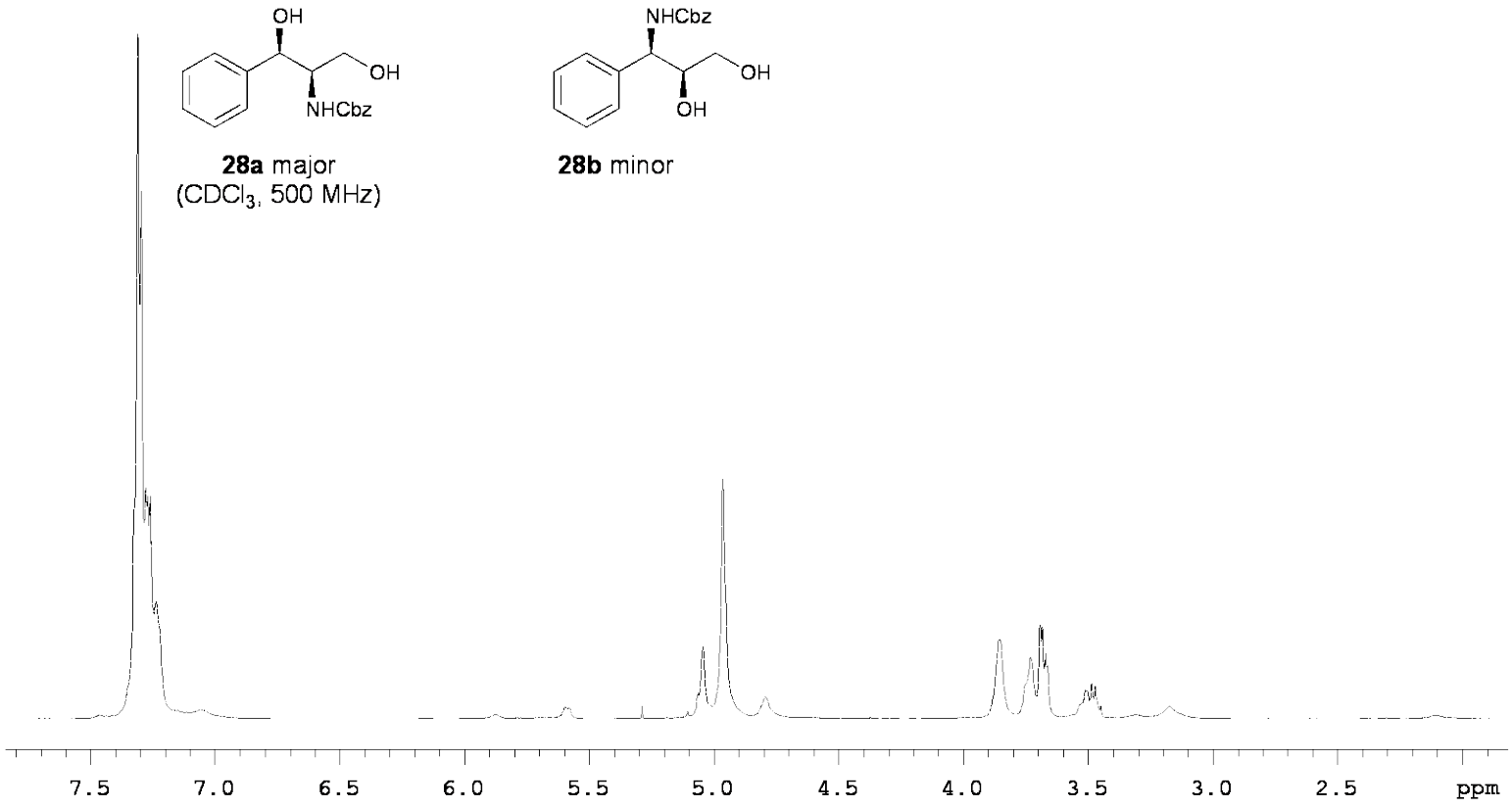
27b minor



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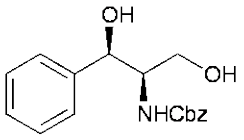
28b minor



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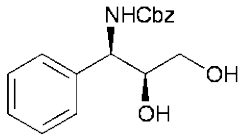

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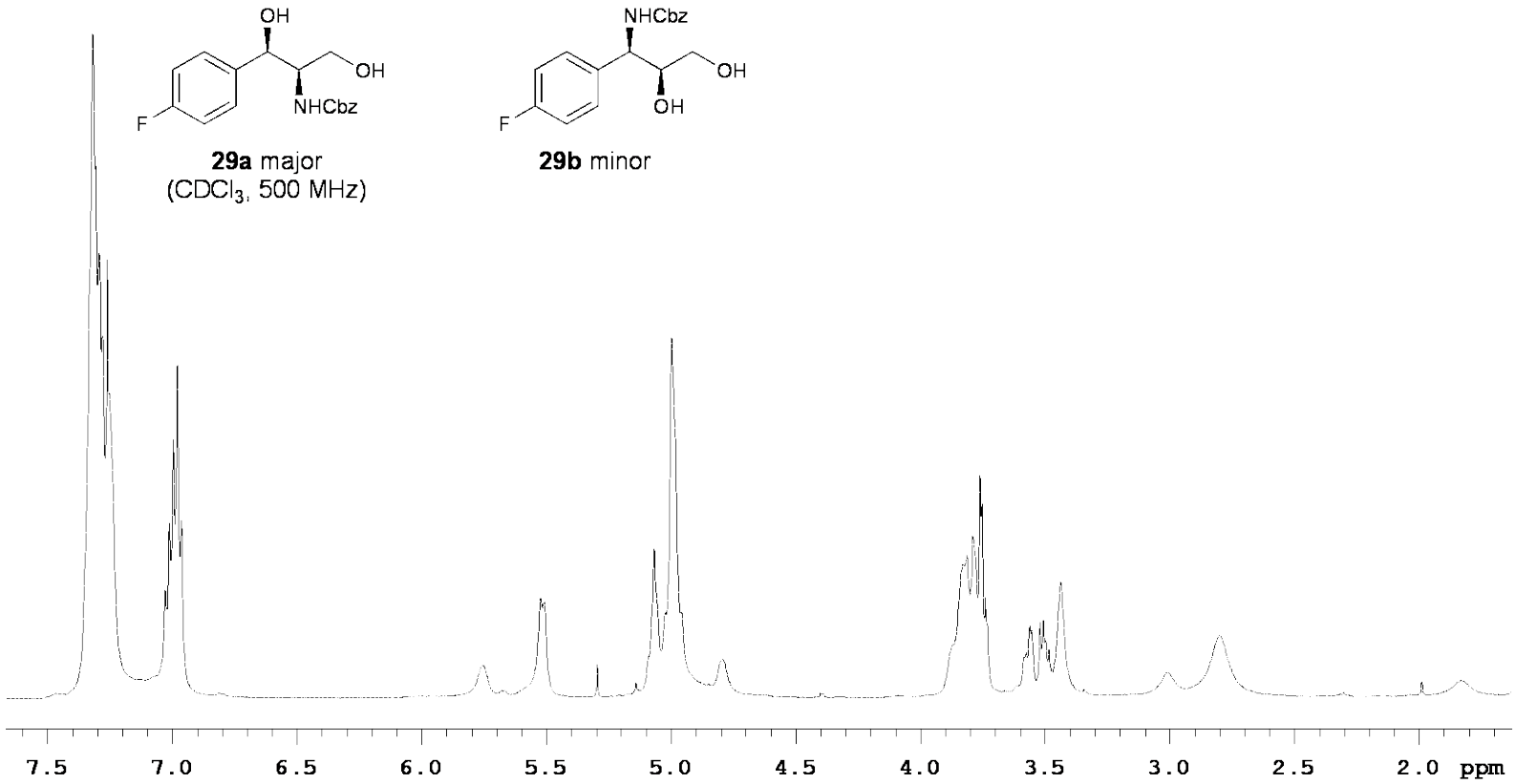

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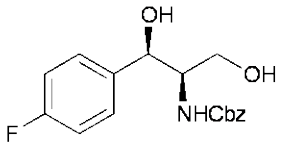
($CDCl_3$, 500 MHz)

29b minor



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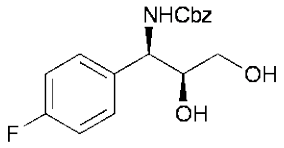
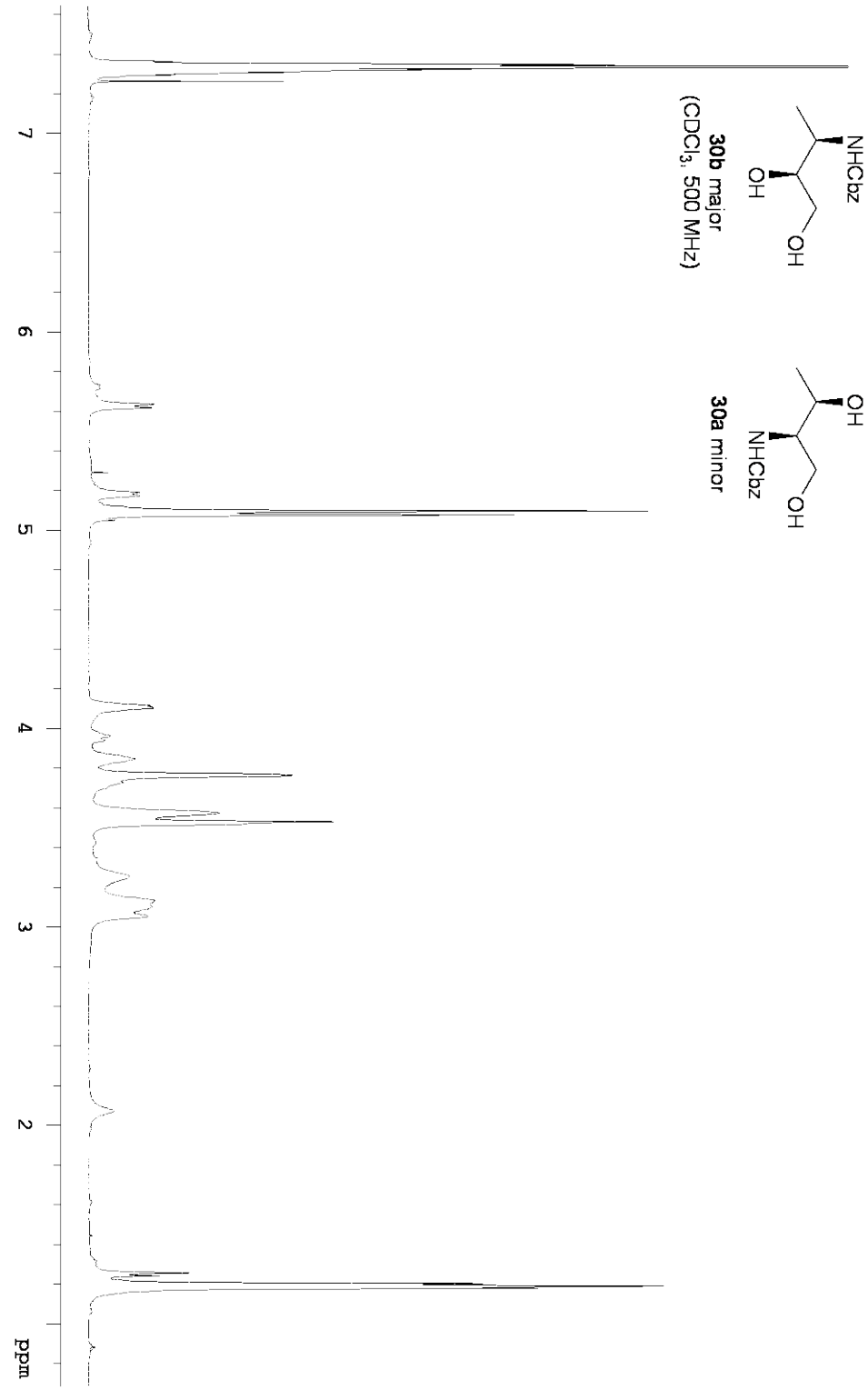


29b minor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OH
OH
30b major
(CDCl3, 500 MHz)
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NHCbz
OH
30a minor
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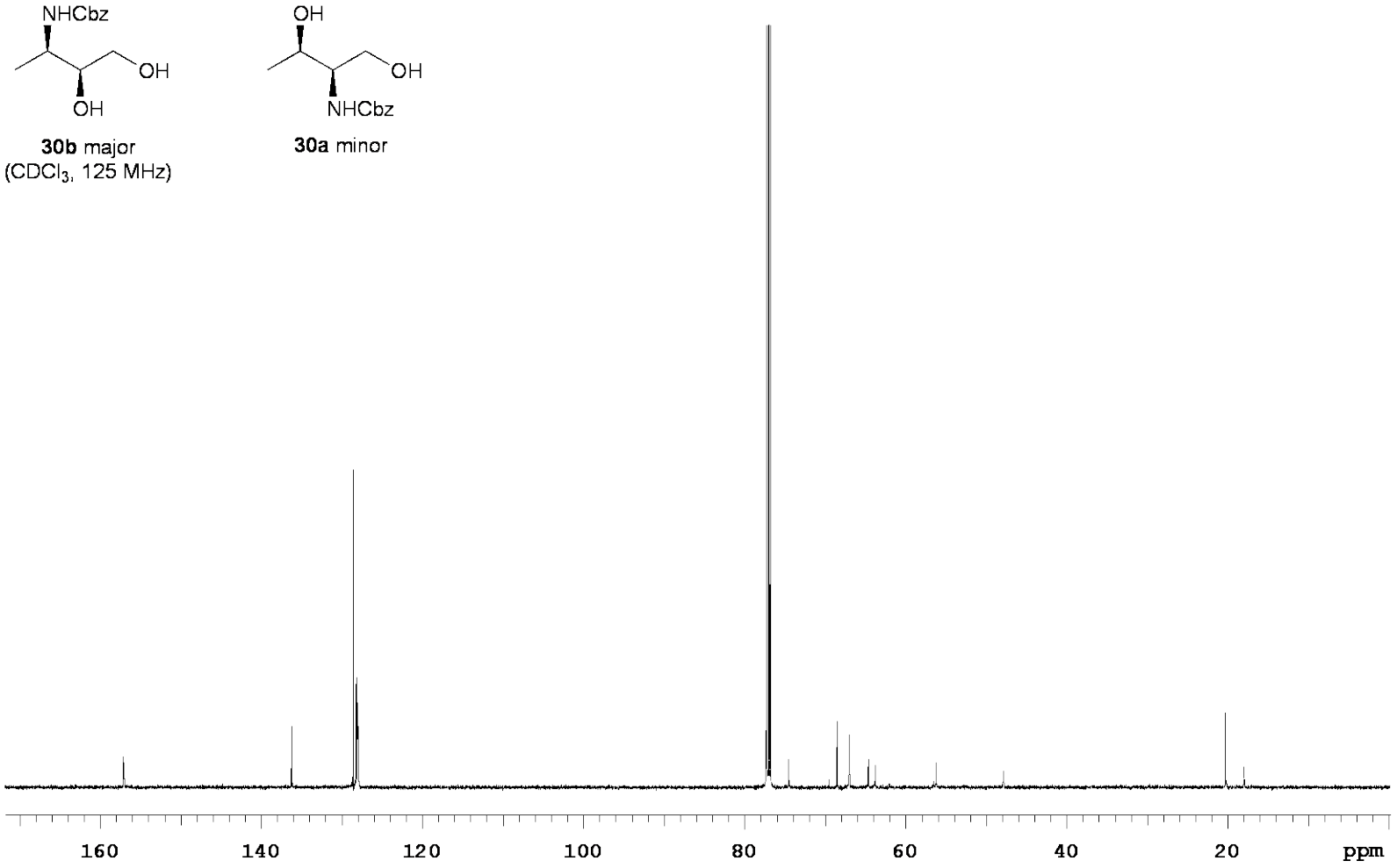
ppm



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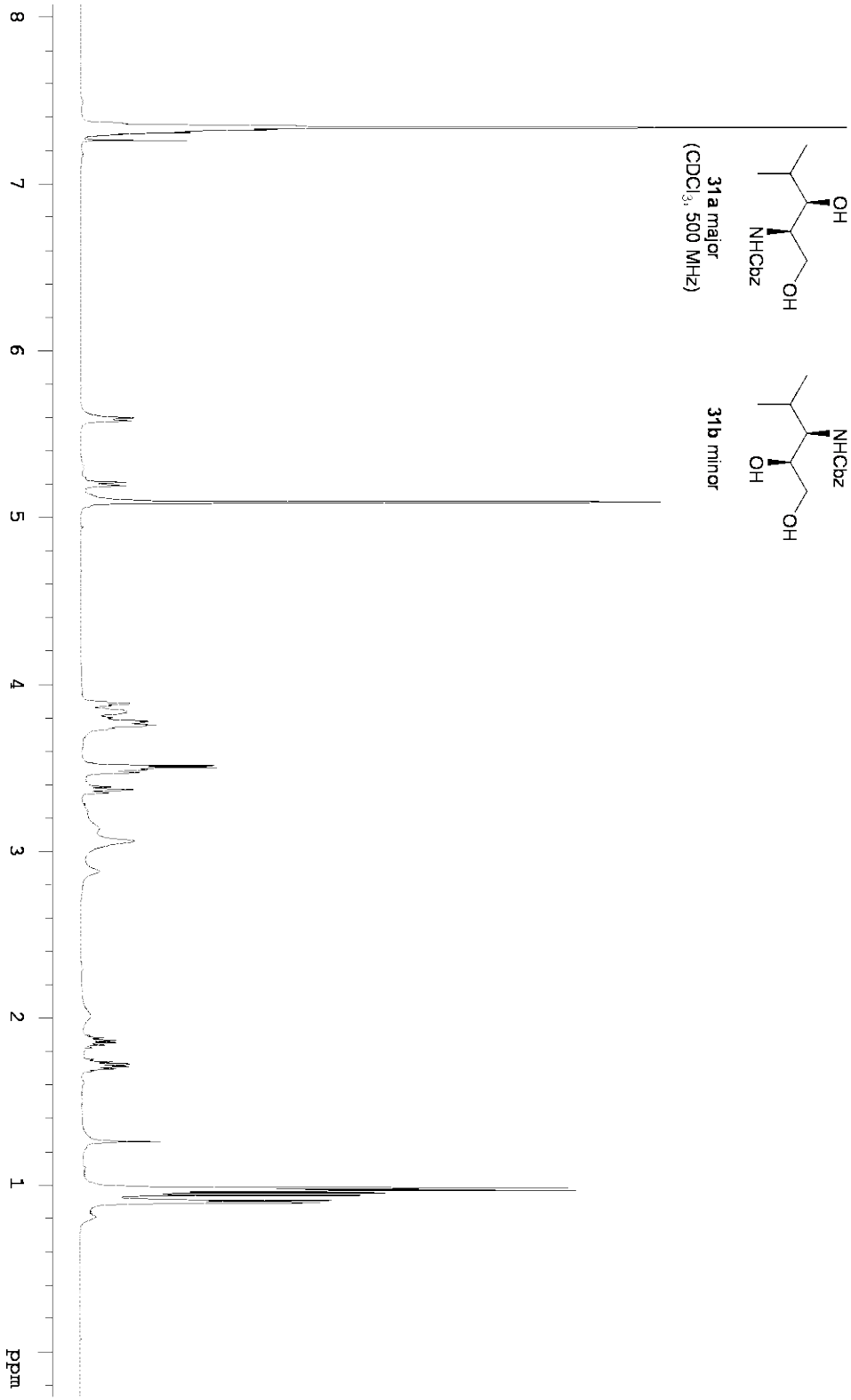
30a minor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7
6
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2
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ppm
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(CDCl3, 500 MHz)
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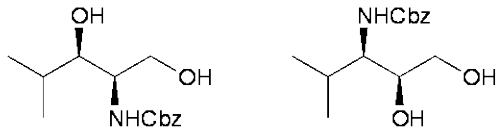
NHCbz
OH
31b minor
NHCbz
OH
OH



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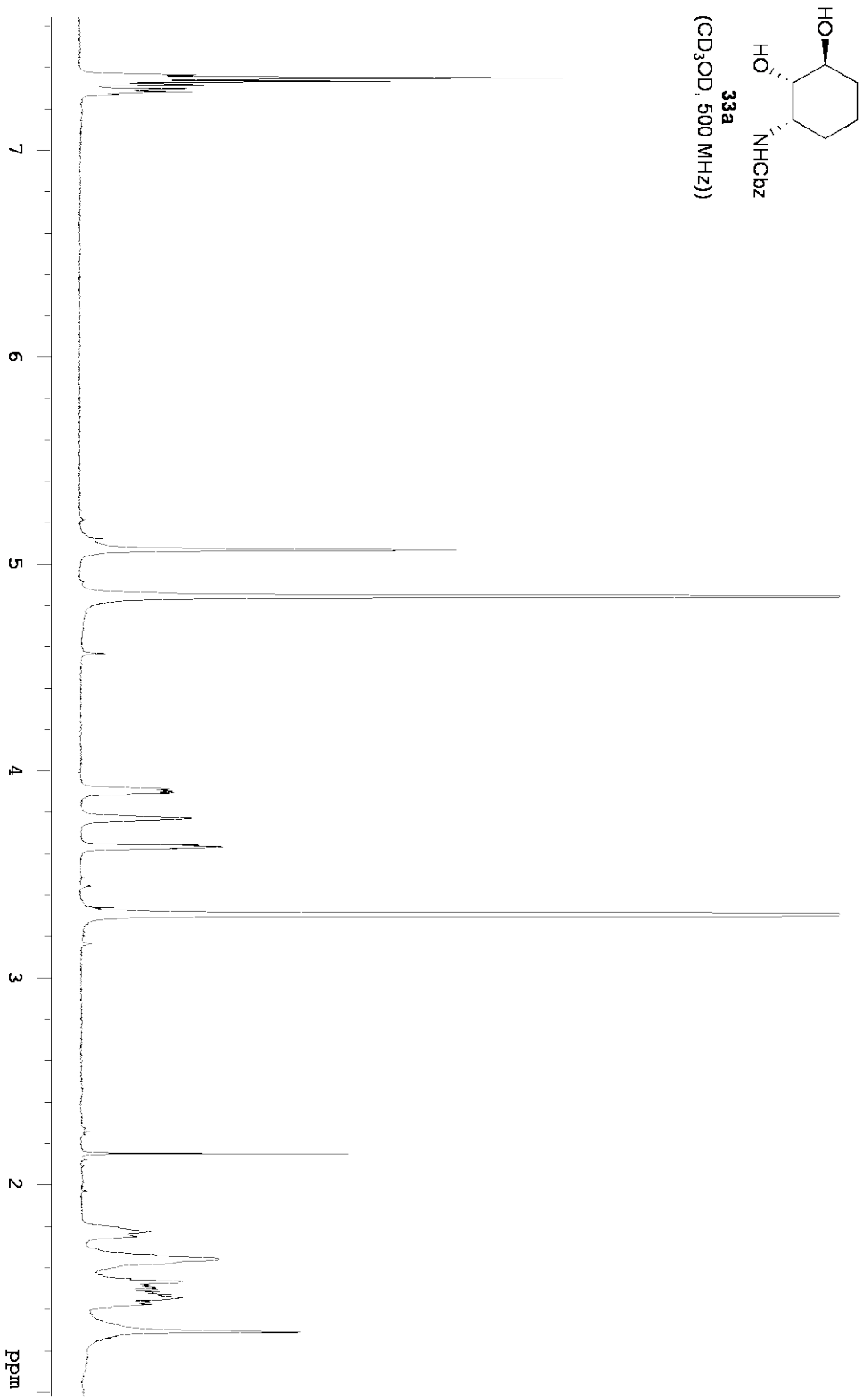
31b minor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NHCbz
33a
(CD3OD, 500 MHz))
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6
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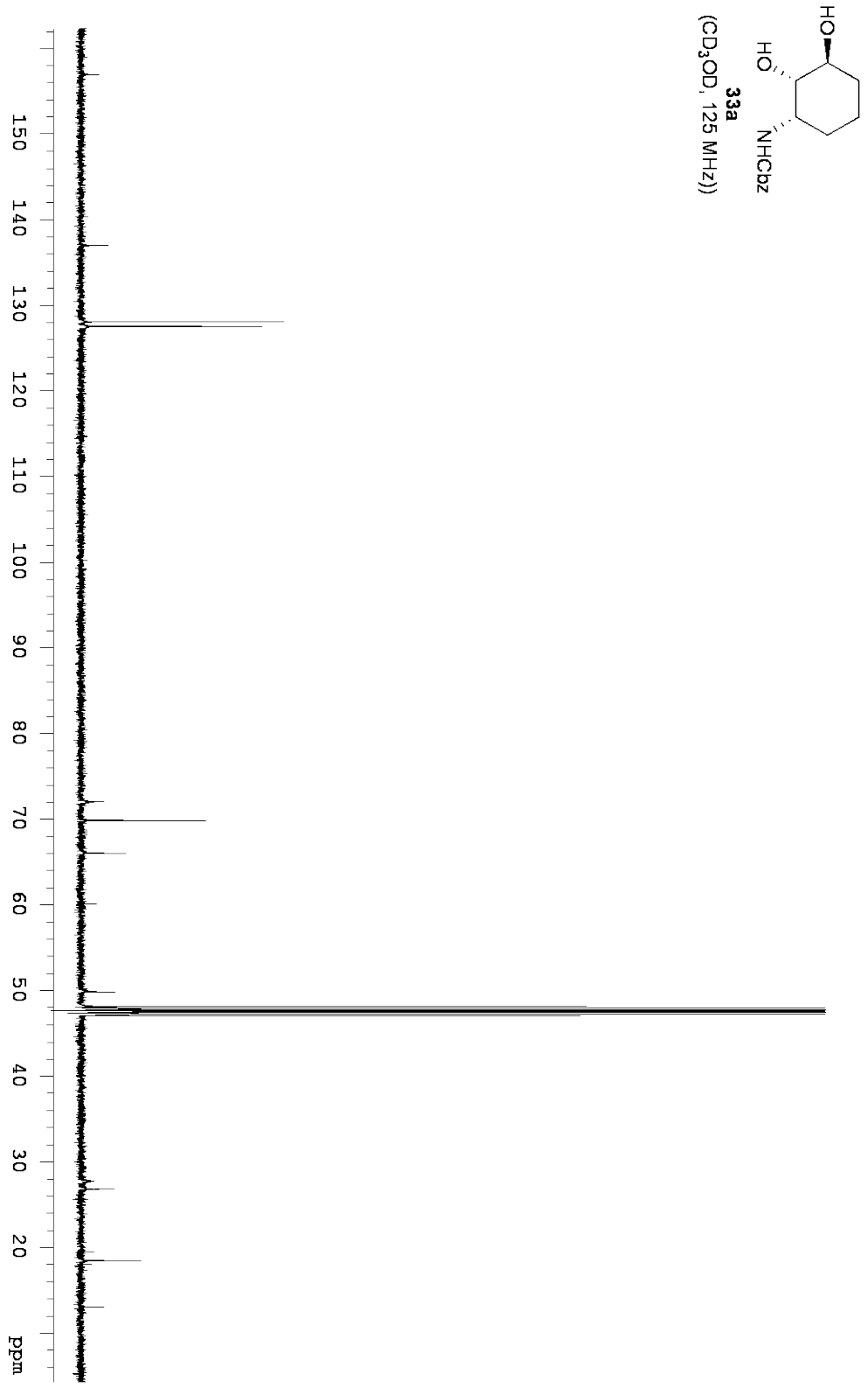
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HO
NHCbz
33a
(CD3OD, 125 MHz))
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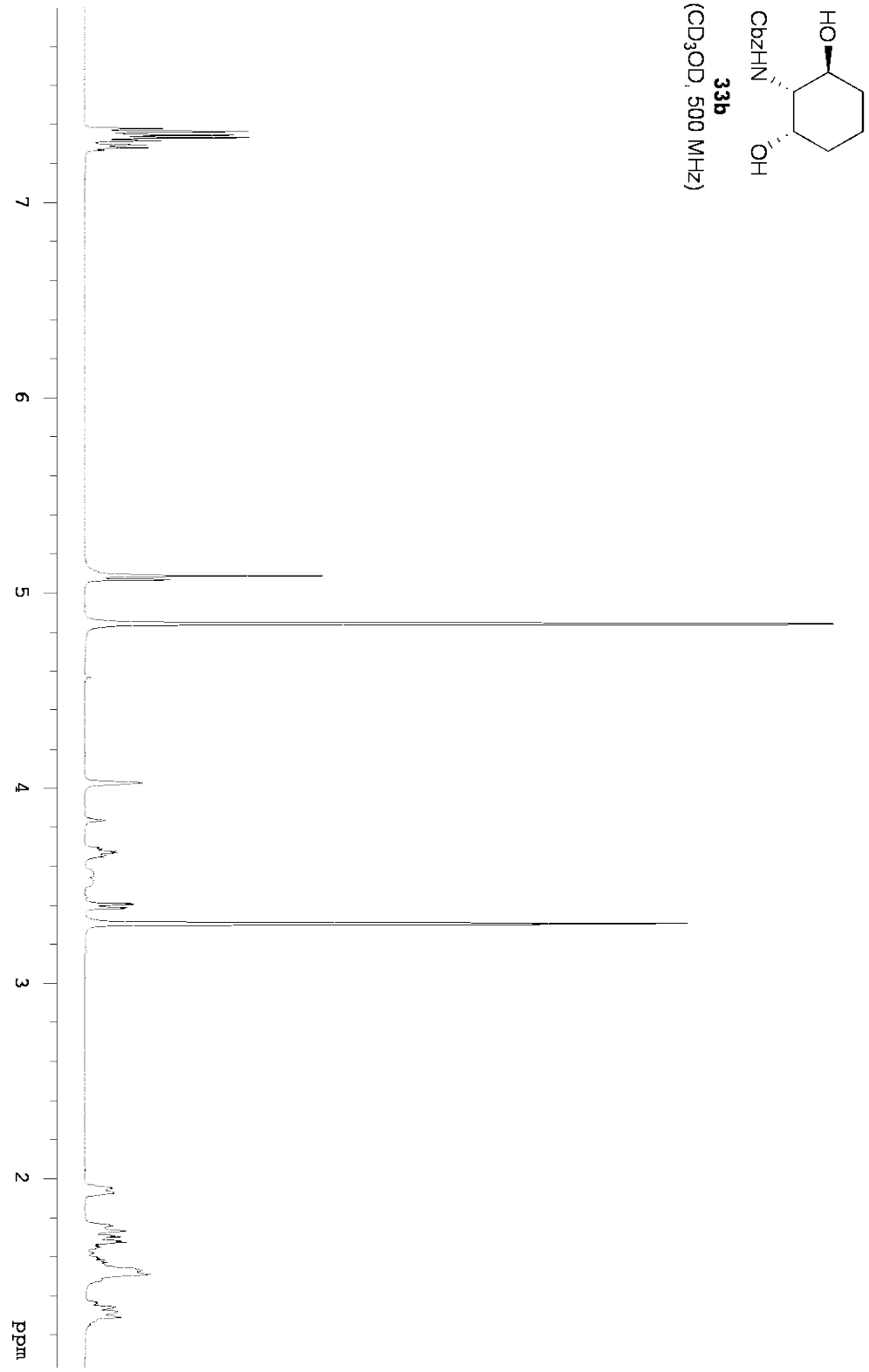
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3
2
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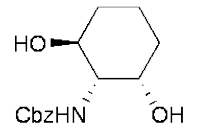

33b
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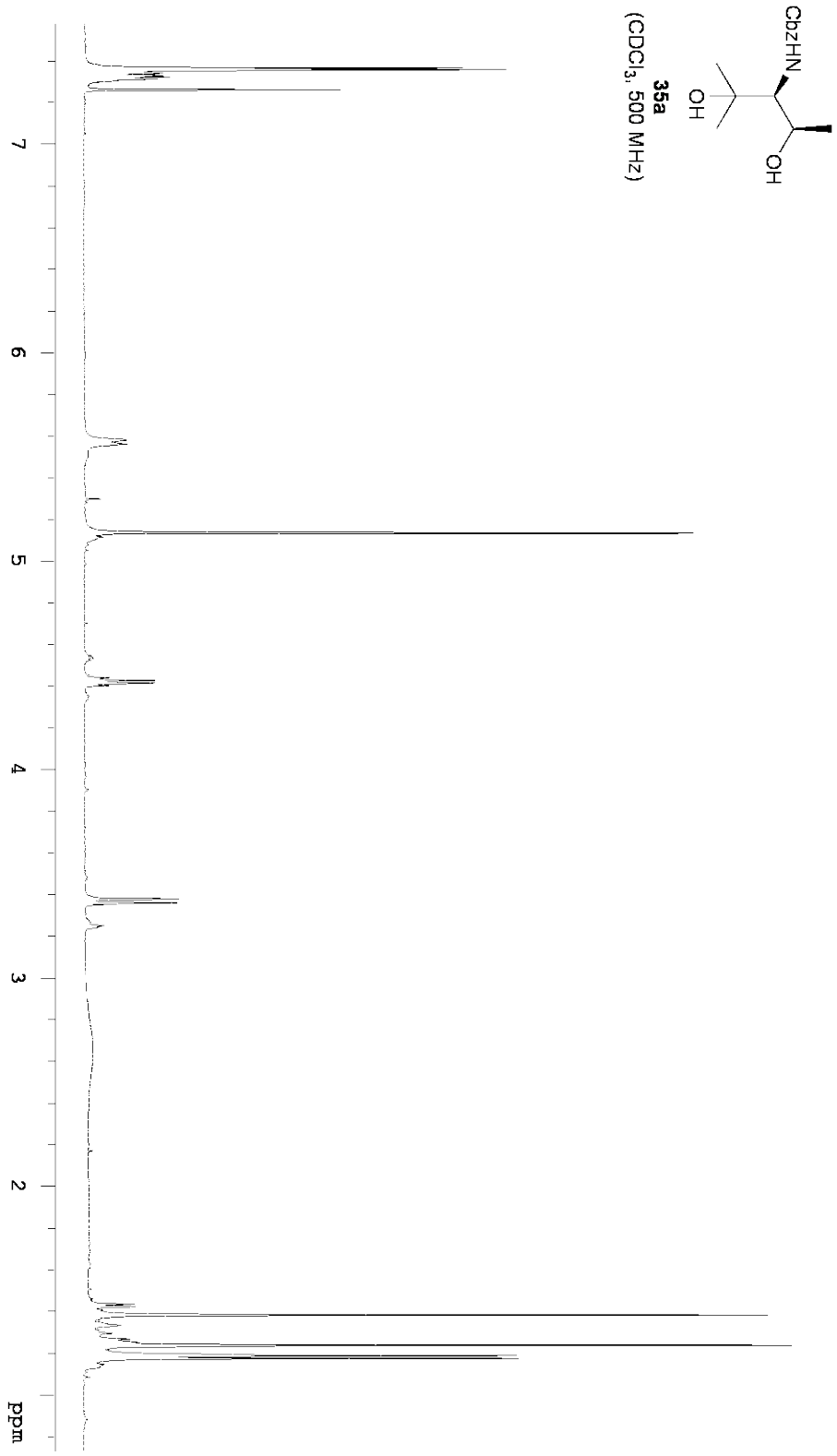
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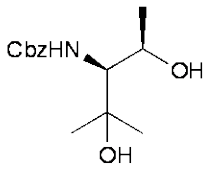

35a
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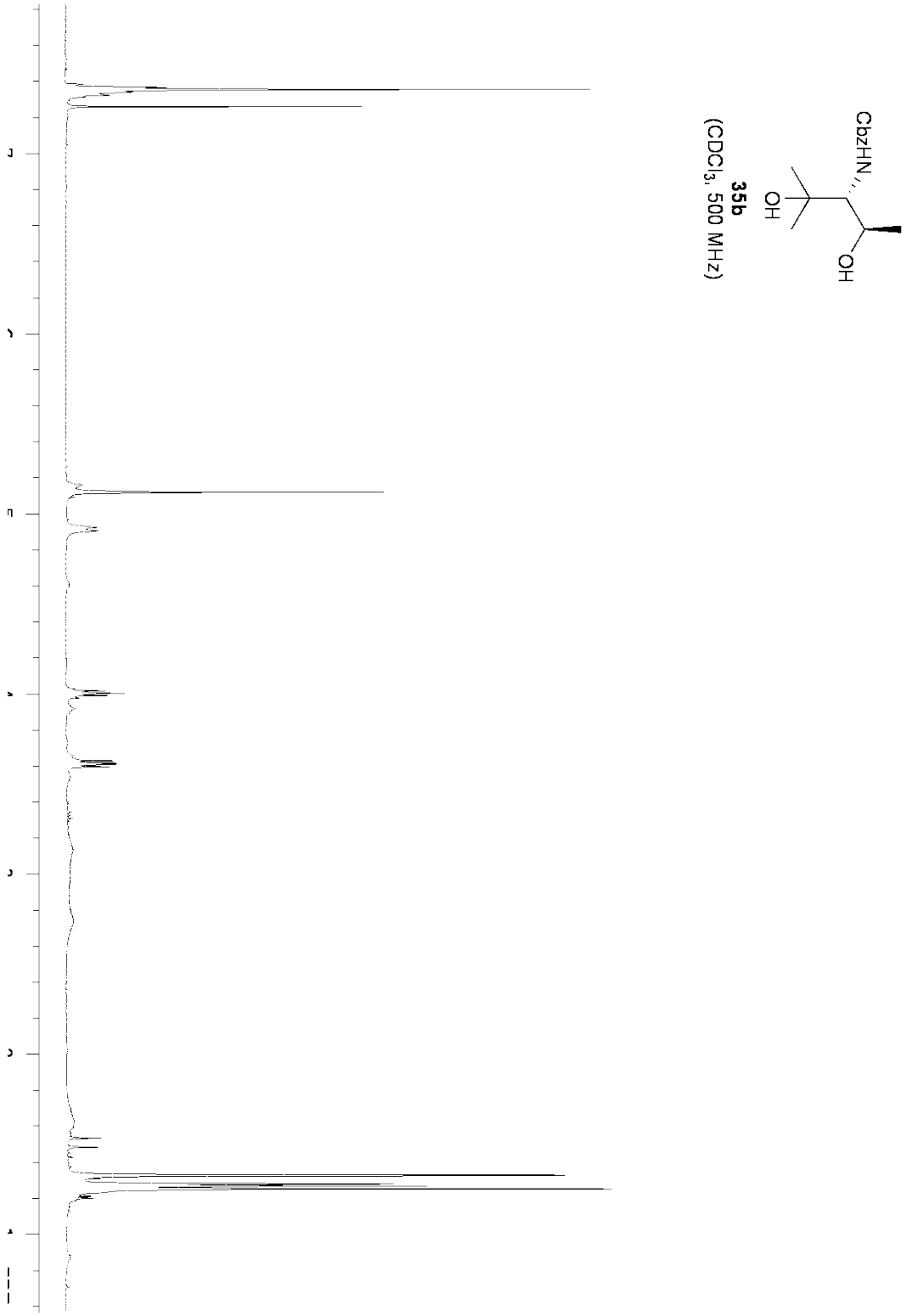
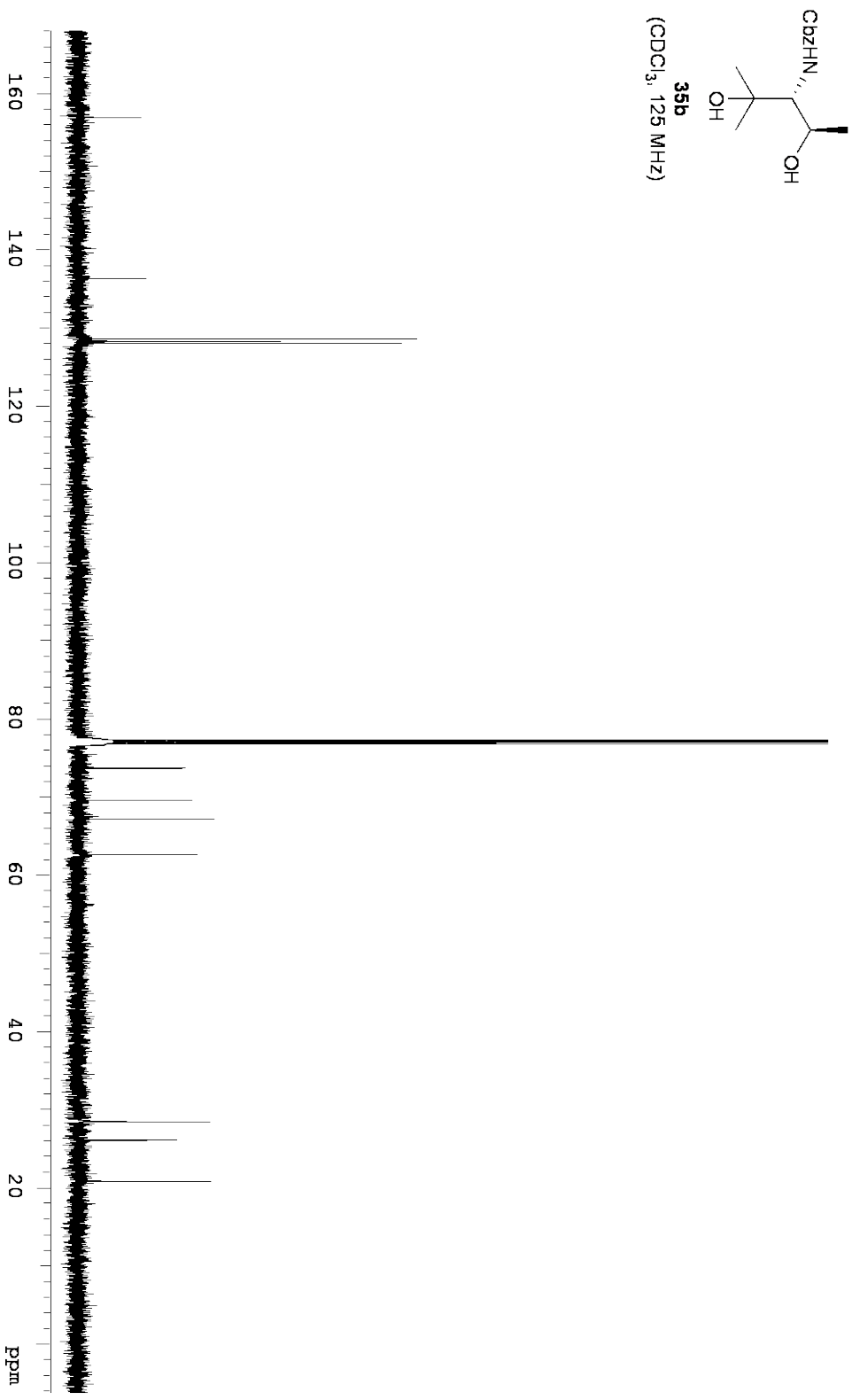


35b
($CDCl_3$, 500 MHz)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35b
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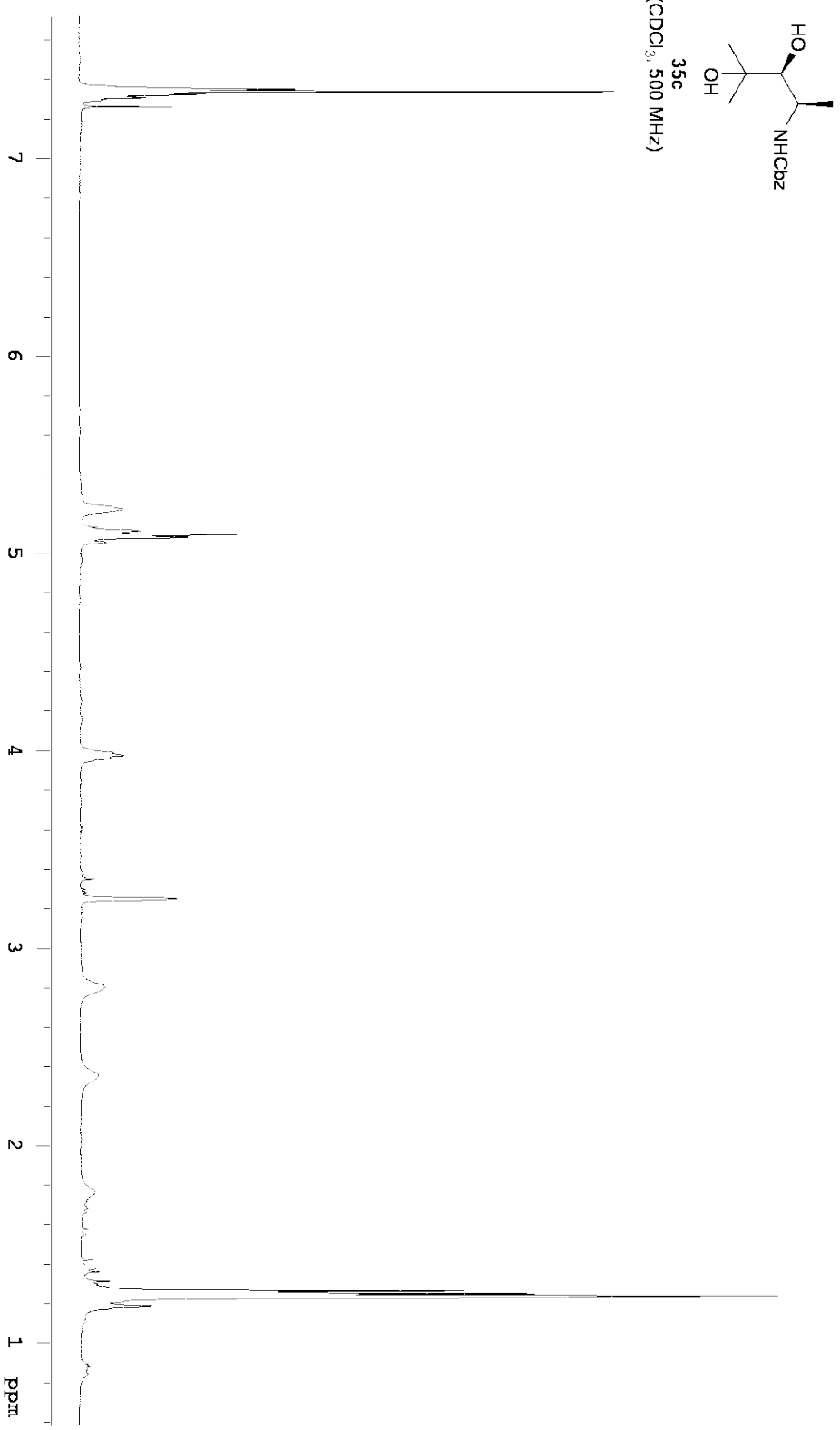
160
140
120
100
80
60
40
20
ppm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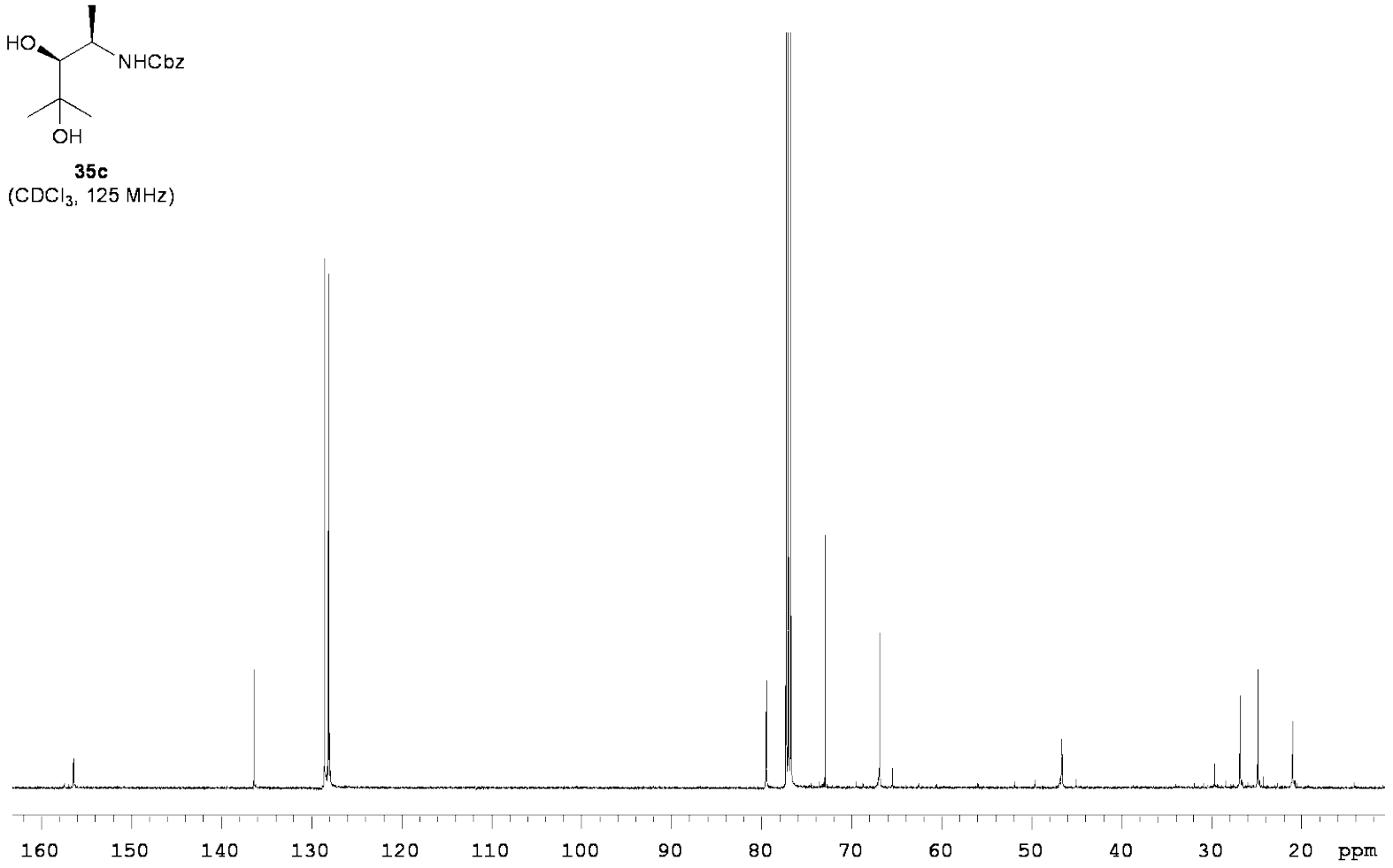
1
ppm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NHCbz
OH
35c
(CDCl3, 125 MHz)
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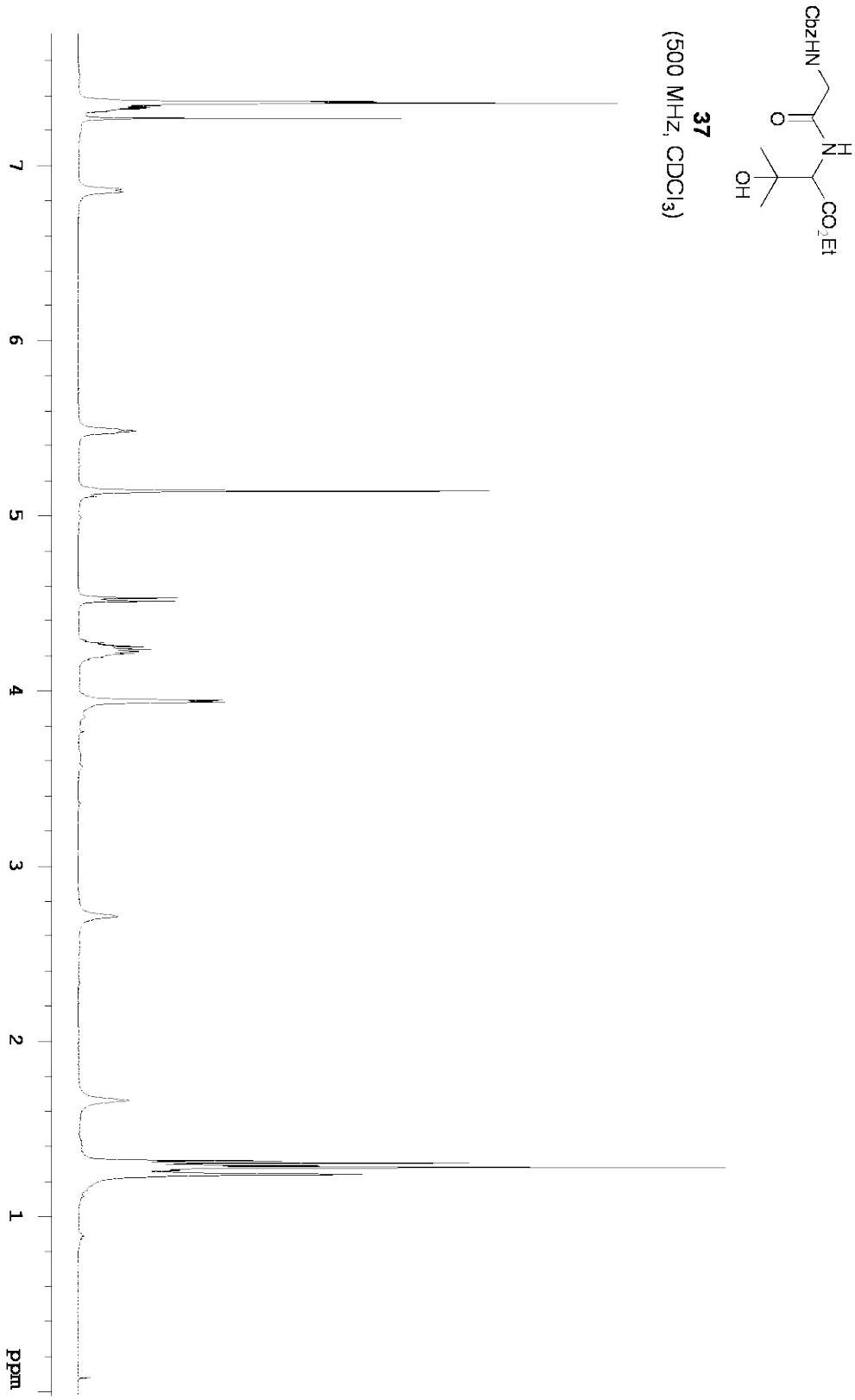
40
30
20
ppm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37
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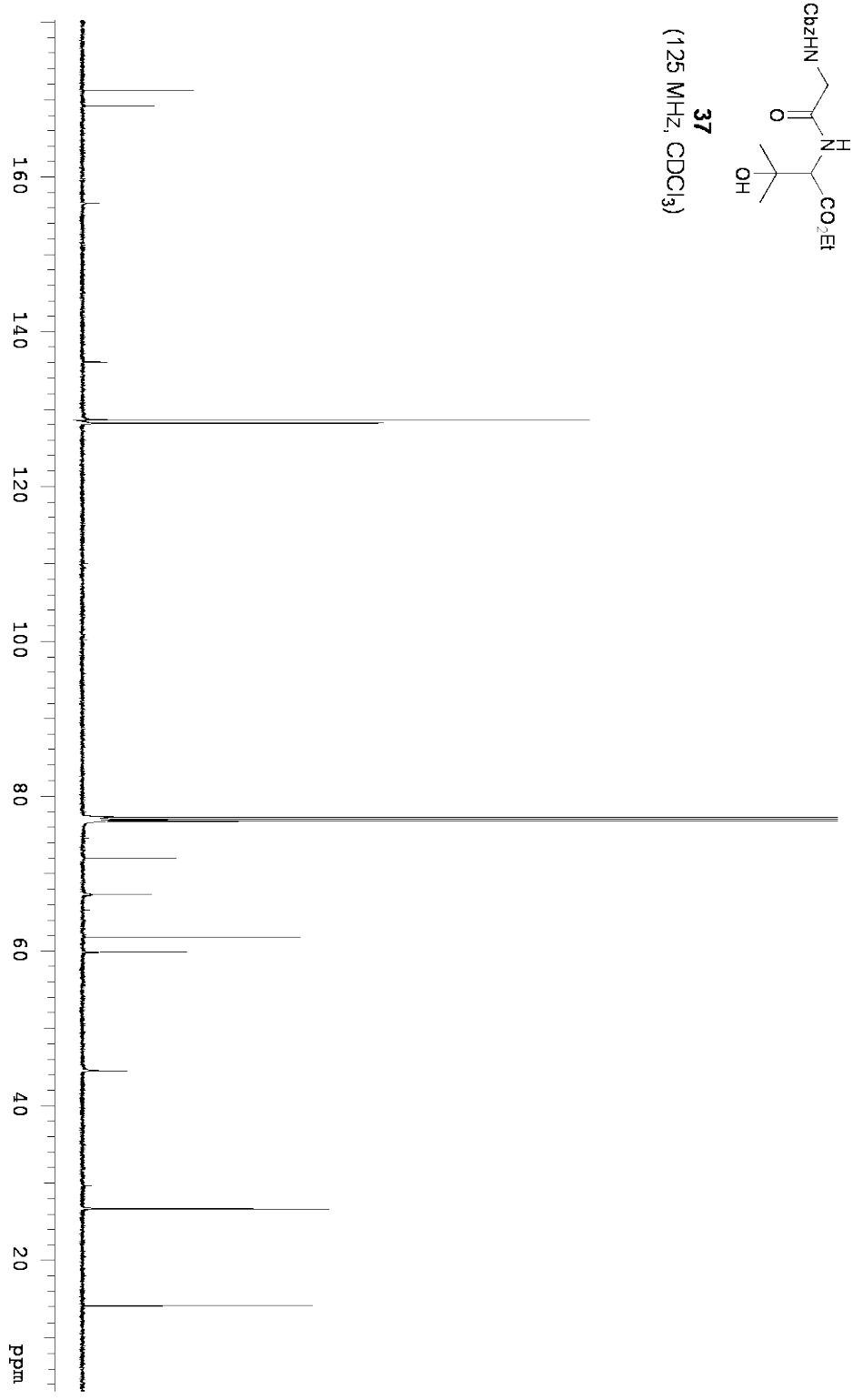
4
3
2
1
ppm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H
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CO2Et
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(125 MHz, CDCl3)
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140
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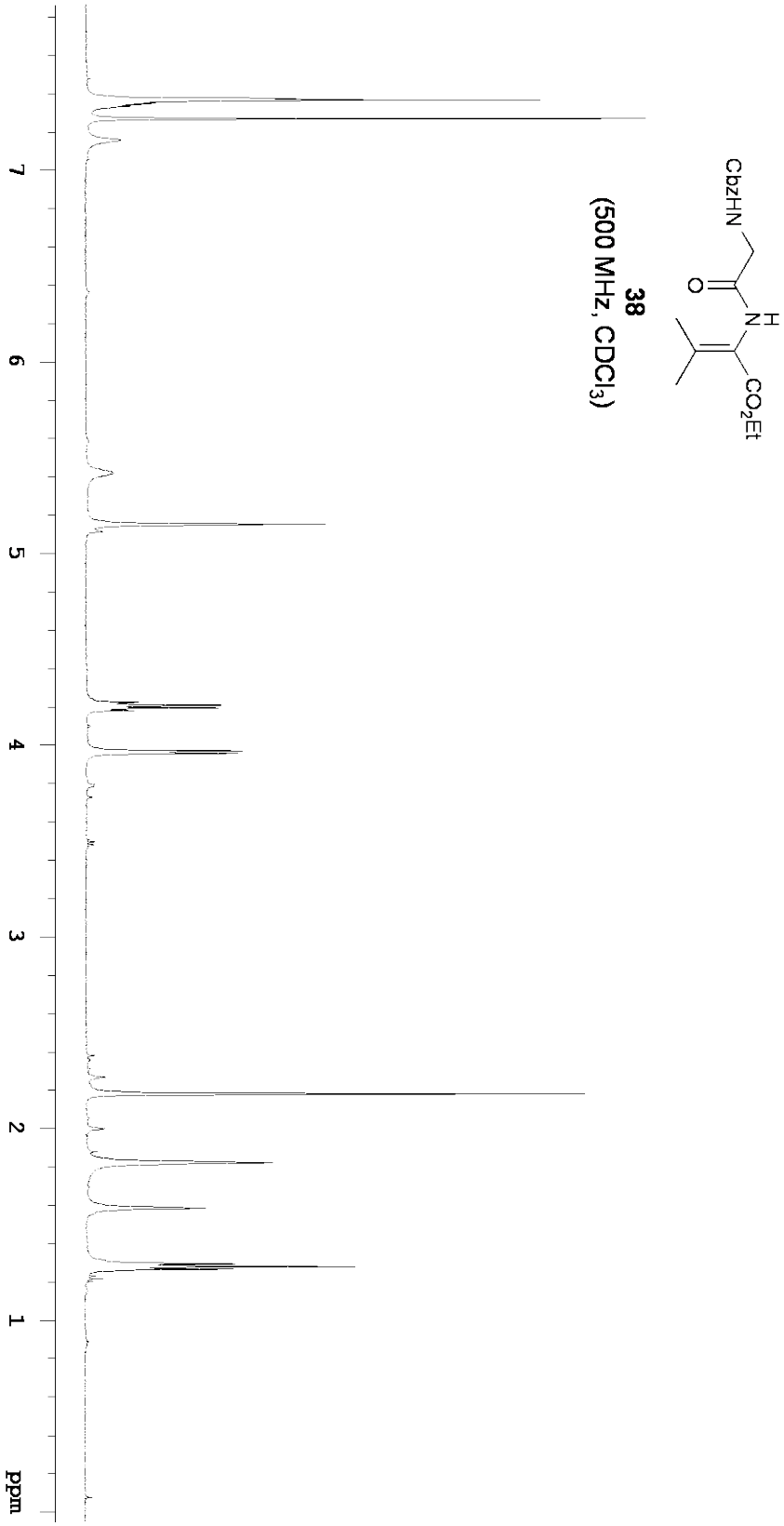
100
80
60
40
20
ppm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H
N
CO2Et
38
(500 MHz, CDCl3)
7
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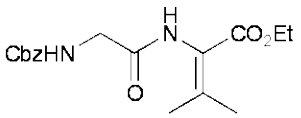
4
3
2
1
ppm



38
(125 MHz, $CDCl_3$)