

## Supporting Information

### Synthesis and Toll-Like Receptor 4 (TLR4) Activity of Phosphatidylinositol Dimannoside Analogues

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Compound <b>11</b> 300 MHz $^1\text{H}$ NMR $\text{CDCl}_3$ .....	5
Compound <b>11</b> MHz $^{13}\text{C}$ NMR $\text{CDCl}_3$ .....	6
Compound <b>11</b> 75 MHz $^{13}\text{C}$ NMR $\text{CDCl}_3$ .....	7
Compound <b>12</b> 300 MHz $^1\text{H}$ NMR $\text{CDCl}_3$ .....	8
Compound <b>12</b> 75 MHz $^{13}\text{C}$ NMR $\text{CDCl}_3$ .....	9
Compound <b>12</b> 75 MHz $^{13}\text{C}$ NMR $\text{CDCl}_3$ .....	10
Compound <b>13</b> 300 MHz $^1\text{H}$ NMR $\text{CDCl}_3$ .....	11
Compound <b>14</b> 300 MHz $^1\text{H}$ NMR $\text{CDCl}_3$ .....	12
Compound <b>14</b> 75 MHz $^{13}\text{C}$ NMR $\text{CDCl}_3$ .....	13
Compound <b>15</b> 500 MHz $^1\text{H}$ NMR $\text{CDCl}_3$ .....	14
Compound <b>15</b> 125 MHz $^{13}\text{C}$ NMR $\text{CDCl}_3$ .....	15
Compound <b>15</b> 125 MHz $^{13}\text{C}$ NMR $\text{CDCl}_3$ .....	16
Compound <b>20</b> 300 MHz $^1\text{H}$ NMR $\text{CDCl}_3$ .....	17
Compound <b>20</b> 75 MHz $^{13}\text{C}$ NMR $\text{CDCl}_3$ .....	18
Compound <b>21</b> 300 MHz $^1\text{H}$ NMR $\text{CDCl}_3$ .....	18
Compound <b>21</b> 300 MHz $^1\text{H}$ NMR $\text{CDCl}_3$ .....	19
Compound <b>21</b> 75 MHz $^{13}\text{C}$ NMR $\text{CDCl}_3$ .....	19
Compound <b>21</b> 75 MHz $^{13}\text{C}$ NMR $\text{CDCl}_3$ .....	20
Compound <b>17</b> 300 MHz $^1\text{H}$ NMR $\text{CDCl}_3$ .....	20
Compound <b>17</b> 300 MHz $^1\text{H}$ NMR $\text{CDCl}_3$ .....	21
Compound <b>17</b> 75 MHz $^{13}\text{C}$ NMR $\text{CDCl}_3$ .....	21
Compound <b>17</b> 75 MHz $^{13}\text{C}$ NMR $\text{CDCl}_3$ .....	22
Compound <b>17</b> 121 MHz $^{31}\text{P}$ NMR $\text{CDCl}_3$ .....	23
Compound <b>23</b> 300 MHz $^1\text{H}$ NMR $\text{CDCl}_3$ .....	24
Compound <b>23</b> 75 MHz $^{13}\text{C}$ NMR $\text{CDCl}_3$ .....	24
Compound <b>23</b> 75 MHz $^{13}\text{C}$ NMR $\text{CDCl}_3$ .....	25
Compound <b>24</b> 300 MHz $^1\text{H}$ NMR $\text{CDCl}_3$ .....	25
Compound <b>24</b> 300 MHz $^1\text{H}$ NMR $\text{CDCl}_3$ .....	26
Compound <b>18</b> 300 MHz $^1\text{H}$ NMR $\text{CDCl}_3$ .....	28

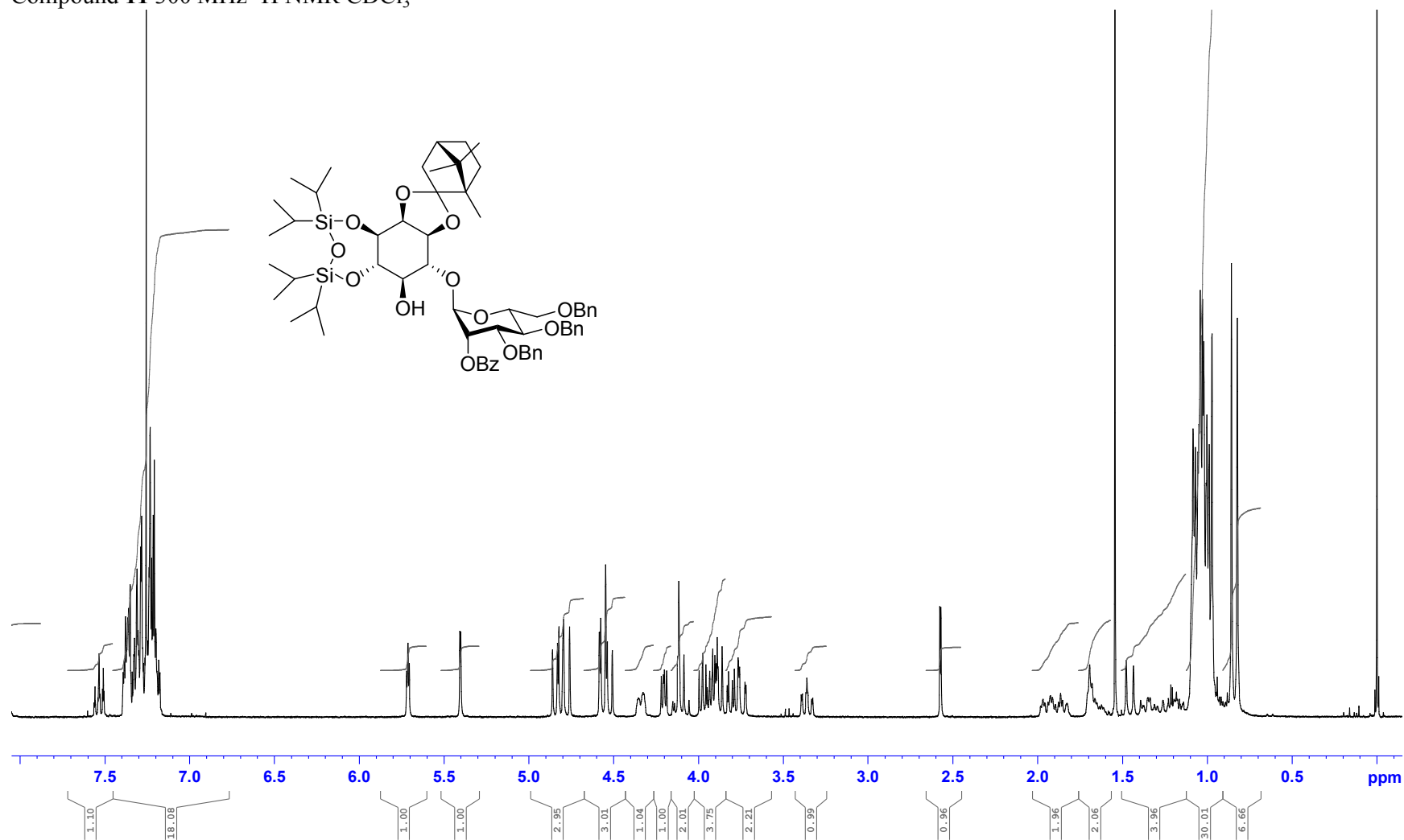
Compound <b>18</b> 121 MHz <sup>31</sup> P NMR CDCl <sub>3</sub> .....	29
Compound <b>25</b> 300 MHz <sup>1</sup> H NMR CDCl <sub>3</sub> .....	30
Compound <b>25</b> 75 MHz <sup>13</sup> C NMR CDCl <sub>3</sub> .....	31
Compound <b>26</b> 500 MHz <sup>1</sup> H NMR CDCl <sub>3</sub> .....	32
Compound <b>26</b> 125 MHz <sup>13</sup> C NMR CDCl <sub>3</sub> .....	33
Compound <b>26</b> 125 MHz <sup>13</sup> C NMR CDCl <sub>3</sub> .....	34
Compound <b>29</b> 300 MHz <sup>1</sup> H NMR CDCl <sub>3</sub> .....	35
Compound <b>29</b> 75 MHz <sup>13</sup> C NMR CDCl <sub>3</sub> .....	36
Compound <b>29</b> 125 MHz <sup>31</sup> P NMR CDCl <sub>3</sub> .....	37
Compound <b>4</b> 500 MHz <sup>1</sup> H NMR CDCl <sub>3</sub> /CD <sub>3</sub> OD/D <sub>2</sub> O 70:40:6.....	38
Compound <b>4</b> 500 MHz <sup>1</sup> H NMR CDCl <sub>3</sub> /CD <sub>3</sub> OD/D <sub>2</sub> O 70:40:6.....	38
Compound <b>4</b> 500 MHz <sup>1</sup> H NMR CDCl <sub>3</sub> /CD <sub>3</sub> OD/D <sub>2</sub> O 70:40:6.....	39
Compound <b>4</b> 126 MHz <sup>13</sup> C NMR CDCl <sub>3</sub> /CD <sub>3</sub> OD/D <sub>2</sub> O 70:40:6.....	40
Compound <b>4</b> 126 MHz <sup>13</sup> C NMR CDCl <sub>3</sub> /CD <sub>3</sub> OD/D <sub>2</sub> O 70:40:6.....	41
Compound <b>4</b> 121 MHz <sup>31</sup> P NMR CDCl <sub>3</sub> /CD <sub>3</sub> OD/D <sub>2</sub> O 70:40:6.....	42
Compound <b>30</b> 500 MHz <sup>1</sup> H NMR CDCl <sub>3</sub> .....	43
Compound <b>30</b> 126 MHz <sup>13</sup> C NMR CDCl <sub>3</sub> .....	44
Compound <b>30</b> 121 MHz <sup>31</sup> P NMR CDCl <sub>3</sub> .....	45
Compound <b>3</b> 500 MHz <sup>1</sup> H NMR CDCl <sub>3</sub> /CD <sub>3</sub> OD/D <sub>2</sub> O 40:40:10.....	46
Compound <b>3</b> 500 MHz <sup>1</sup> H NMR CDCl <sub>3</sub> /CD <sub>3</sub> OD/D <sub>2</sub> O 40:40:10.....	47
Compound <b>3</b> 126 MHz <sup>13</sup> C NMR CDCl <sub>3</sub> /CD <sub>3</sub> OD/D <sub>2</sub> O 40:40:10.....	48
Compound <b>3</b> 126 MHz <sup>13</sup> C NMR CDCl <sub>3</sub> /CD <sub>3</sub> OD/D <sub>2</sub> O 40:40:10.....	49
Compound <b>3</b> 121 MHz <sup>31</sup> P NMR CDCl <sub>3</sub> /CD <sub>3</sub> OD/D <sub>2</sub> O 40:40:10.....	50
Compound <b>33</b> 300 MHz <sup>1</sup> H NMR CDCl <sub>3</sub> .....	51
Compound <b>33</b> 75 MHz <sup>13</sup> C NMR CDCl <sub>3</sub> .....	52
Compound <b>31</b> 300 MHz <sup>1</sup> H NMR CDCl <sub>3</sub> .....	53
Compound <b>31 cmh653.1</b> 75 MHz <sup>13</sup> C NMR CDCl <sub>3</sub> .....	53
Compound <b>31 cmh653.1</b> 75 MHz <sup>13</sup> C NMR CDCl <sub>3</sub> .....	54
Compound <b>34</b> 300 MHz <sup>1</sup> H NMR CDCl <sub>3</sub> .....	55
Compound <b>34</b> 300 MHz <sup>1</sup> H NMR CDCl <sub>3</sub> .....	56
Compound <b>34</b> 75 MHz <sup>13</sup> C NMR CDCl <sub>3</sub> .....	57
Compound <b>34</b> 75 MHz <sup>13</sup> C NMR CDCl <sub>3</sub> .....	58
Compound <b>34</b> 300 MHz HSQC NMR without <sup>13</sup> C decoupling during acquisition.....	59
Compound <b>35</b> 300 MHz <sup>1</sup> H NMR CDCl <sub>3</sub> .....	60
Compound <b>35</b> 300 MHz <sup>1</sup> H NMR CDCl <sub>3</sub> .....	61
Compound <b>35</b> 75 MHz <sup>13</sup> C NMR CDCl <sub>3</sub> .....	62

Compound <b>35</b> 5 MHz <sup>13</sup> C NMR CDCl <sub>3</sub> .....	63
Compound <b>37</b> 300 MHz <sup>1</sup> H NMR CDCl <sub>3</sub> .....	64
Compound <b>37</b> 300 MHz <sup>1</sup> H NMR CDCl <sub>3</sub> .....	64
Compound <b>37</b> 300 MHz <sup>1</sup> H NMR CDCl <sub>3</sub> .....	65
Compound <b>37</b> 75 MHz <sup>13</sup> C NMR CDCl <sub>3</sub> .....	66
Compound <b>37</b> 121 MHz <sup>31</sup> P NMR CDCl <sub>3</sub> .....	67
Compound <b>38</b> 300 MHz <sup>1</sup> H NMR CDCl <sub>3</sub> .....	68
Compound <b>38</b> 300 MHz <sup>1</sup> H NMR CDCl <sub>3</sub> .....	69
Compound <b>38</b> 75 MHz <sup>13</sup> C NMR CDCl <sub>3</sub> .....	70
Compound <b>38</b> 121 MHz <sup>31</sup> P NMR CDCl <sub>3</sub> .....	71
Compound <b>5</b> 500 MHz <sup>1</sup> H NMR CDCl <sub>3</sub> /CD <sub>3</sub> OD/D <sub>2</sub> O 70:40:6 .....	72
Compound <b>5</b> 500 MHz <sup>1</sup> H NMR CDCl <sub>3</sub> /CD <sub>3</sub> OD/D <sub>2</sub> O 70:40:6 .....	73
Compound <b>5</b> 126 MHz <sup>13</sup> C NMR CDCl <sub>3</sub> /CD <sub>3</sub> OD/D <sub>2</sub> O 70:40:6 .....	74
Compound <b>5</b> 126 MHz <sup>13</sup> C NMR CDCl <sub>3</sub> /CD <sub>3</sub> OD/D <sub>2</sub> O 70:40:6 .....	74
Compound <b>5</b> 126 MHz <sup>13</sup> C NMR CDCl <sub>3</sub> /CD <sub>3</sub> OD/D <sub>2</sub> O 70:40:6 .....	75
Compound <b>5</b> 202 MHz <sup>31</sup> P NMR CDCl <sub>3</sub> /CD <sub>3</sub> OD/D <sub>2</sub> O 70:40:6 .....	76
Compound <b>40</b> 500 MHz <sup>1</sup> H NMR CDCl <sub>3</sub> .....	77
Compound <b>40</b> 125 MHz <sup>13</sup> C NMR CDCl <sub>3</sub> .....	78
Compound <b>41</b> 500 MHz <sup>1</sup> H NMR CDCl <sub>3</sub> .....	79
Compound <b>41</b> 125 MHz <sup>13</sup> C NMR CDCl <sub>3</sub> .....	80
Compound <b>41</b> 202 MHz <sup>31</sup> P NMR CDCl <sub>3</sub> .....	81
Compound <b>42</b> 500 MHz <sup>1</sup> H NMR 2:1 CDCl <sub>3</sub> /CD <sub>3</sub> OD .....	82
Compound <b>42</b> 125 MHz <sup>13</sup> C NMR 2:1 CDCl <sub>3</sub> /CD <sub>3</sub> OD .....	83
Compound <b>42</b> 202 MHz <sup>31</sup> P NMR 2:1 CDCl <sub>3</sub> /CD <sub>3</sub> OD .....	84
Compound <b>6</b> 500 MHz <sup>1</sup> H NMR CDCl <sub>3</sub> /CD <sub>3</sub> OD/D <sub>2</sub> O 70:35:6 .....	85
Compound <b>6</b> 500 MHz <sup>1</sup> H NMR CDCl <sub>3</sub> /CD <sub>3</sub> OD/D <sub>2</sub> O 70:35:6 .....	86
Compound <b>6</b> 126 MHz <sup>13</sup> C NMR CDCl <sub>3</sub> /CD <sub>3</sub> OD/D <sub>2</sub> O 70:35:6 .....	87
Compound <b>6</b> 126 MHz <sup>13</sup> C NMR CDCl <sub>3</sub> /CD <sub>3</sub> OD/D <sub>2</sub> O 70:35:6 .....	88
Compound <b>6</b> 202 MHz <sup>31</sup> P NMR CDCl <sub>3</sub> /CD <sub>3</sub> OD/D <sub>2</sub> O 70:35:6 .....	89
<b>HPLC Conditions</b> .....	90
<b>HPLC Data</b> .....	90
HPLC Compound <b>1</b> .....	90
HPLC Compound <b>2</b> .....	91
HPLC Compound <b>3</b> .....	91
HPLC Compound <b>4</b> .....	92
HPLC Compound <b>5</b> .....	92

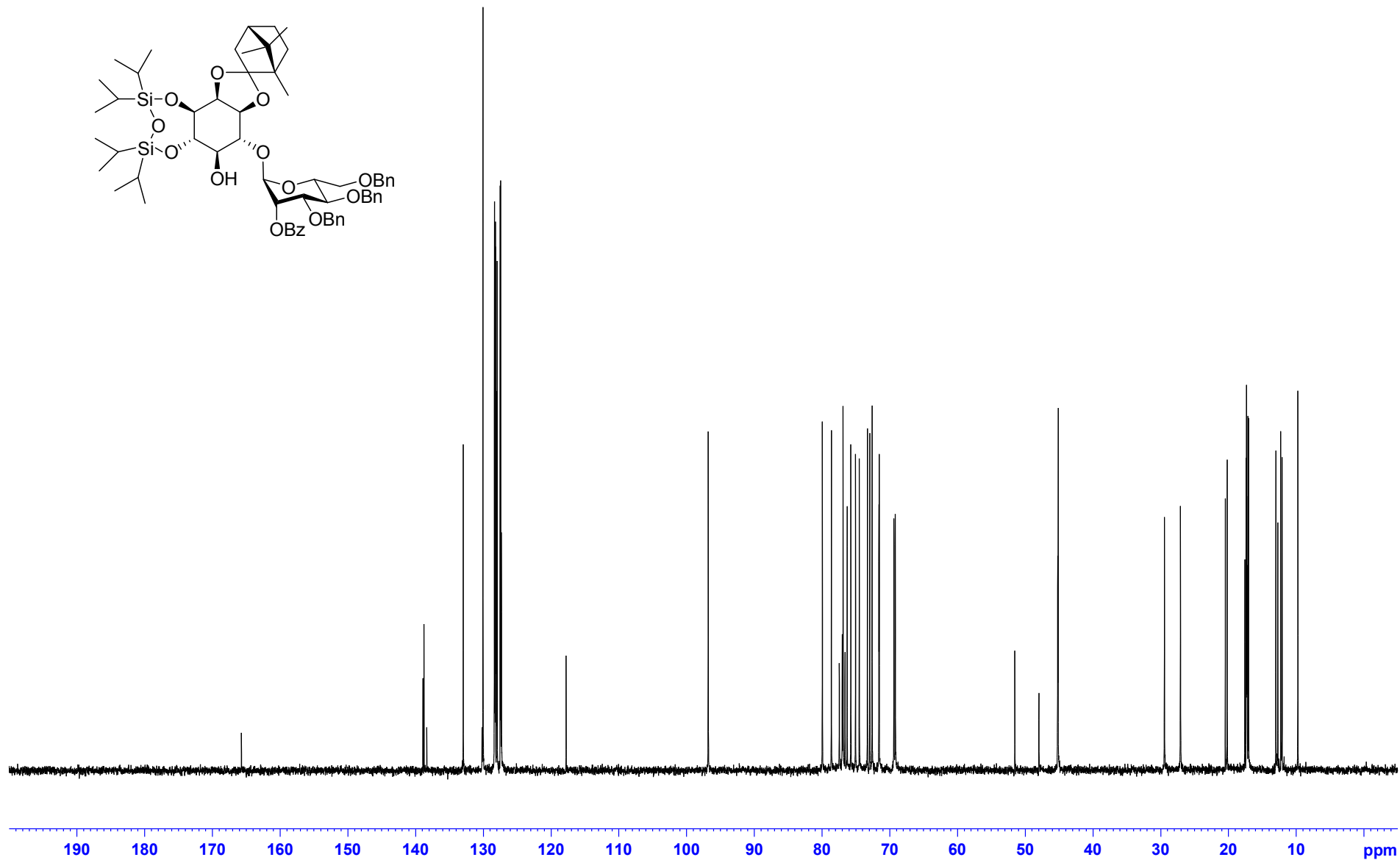
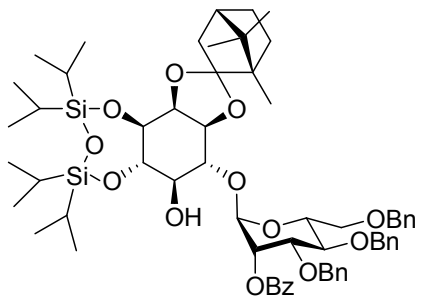
HPLC Compound <b>6</b> .....	93
HPLC Compound <b>7</b> .....	93
HPLC Compound <b>8</b> .....	94
Cell, thioglycollate-induced peritoneal macrophages, viability data, compounds <b>1 - 8</b> .....	95

# NMR Data

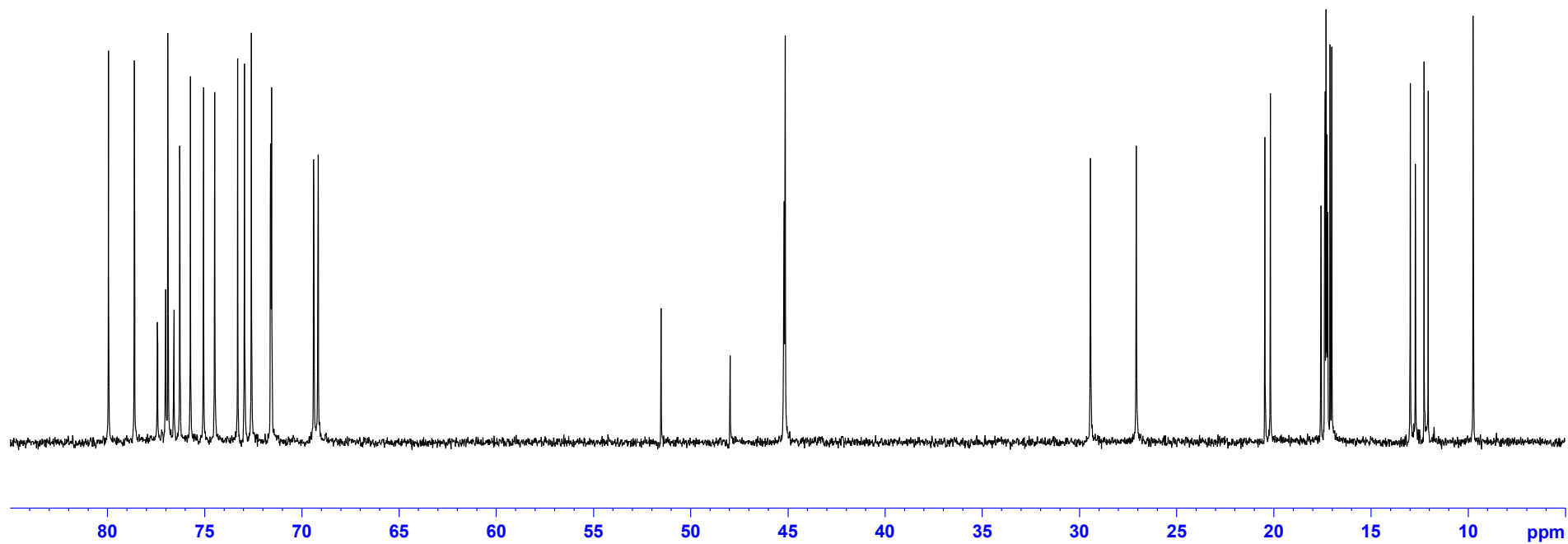
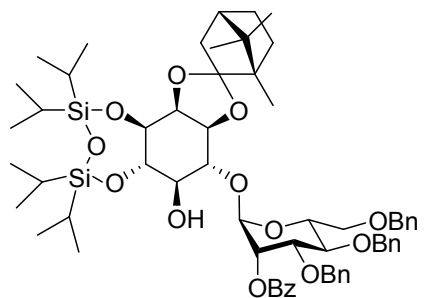
Compound **11** 300 MHz  $^1\text{H}$  NMR  $\text{CDCl}_3$



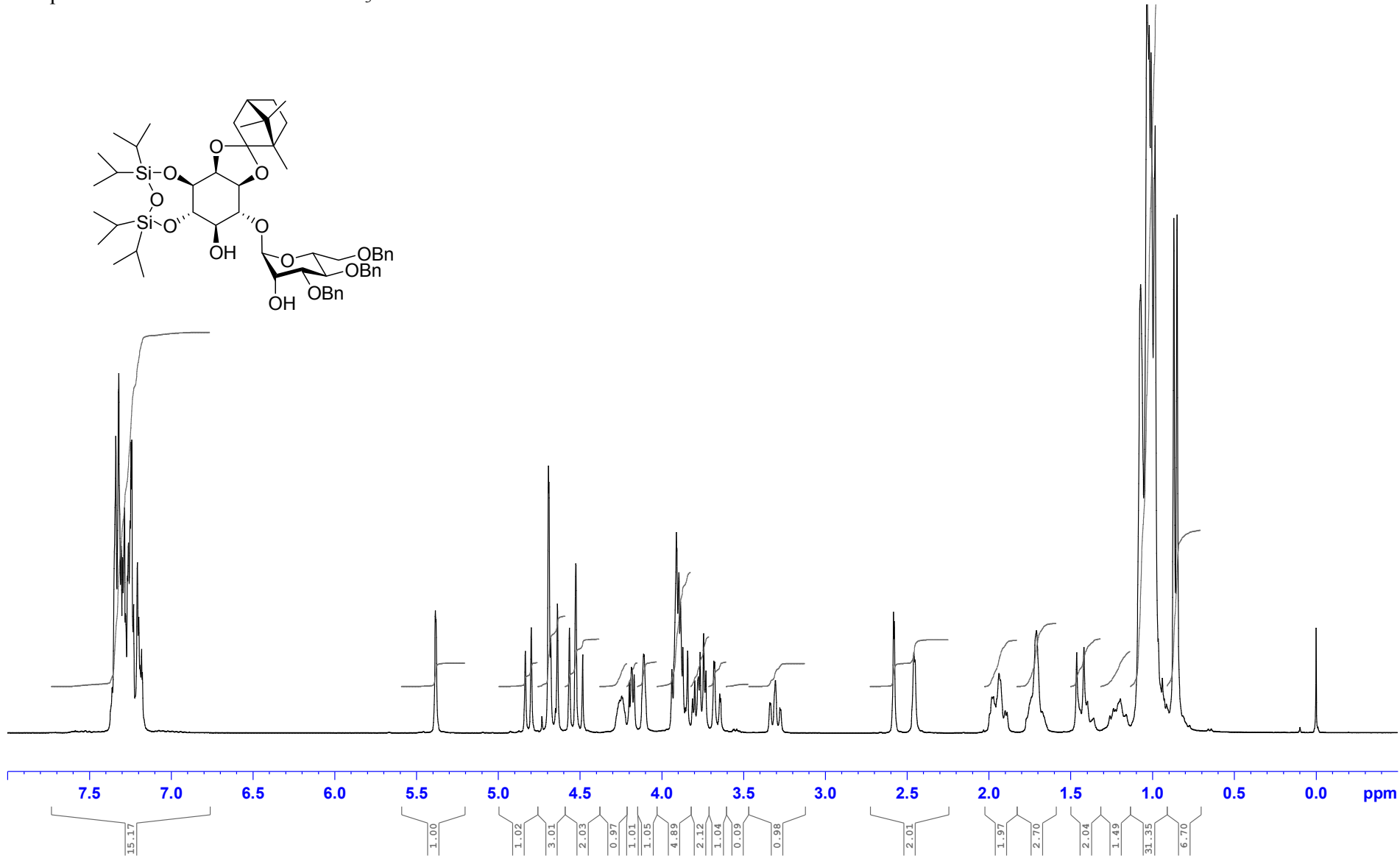
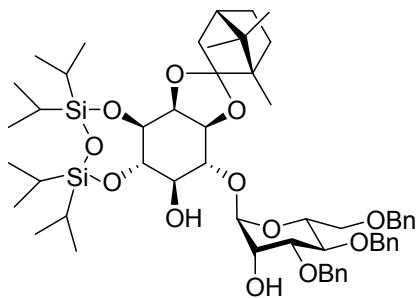
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Compound **11** 75 MHz  $^{13}\text{C}$  NMR  $\text{CDCl}_3$

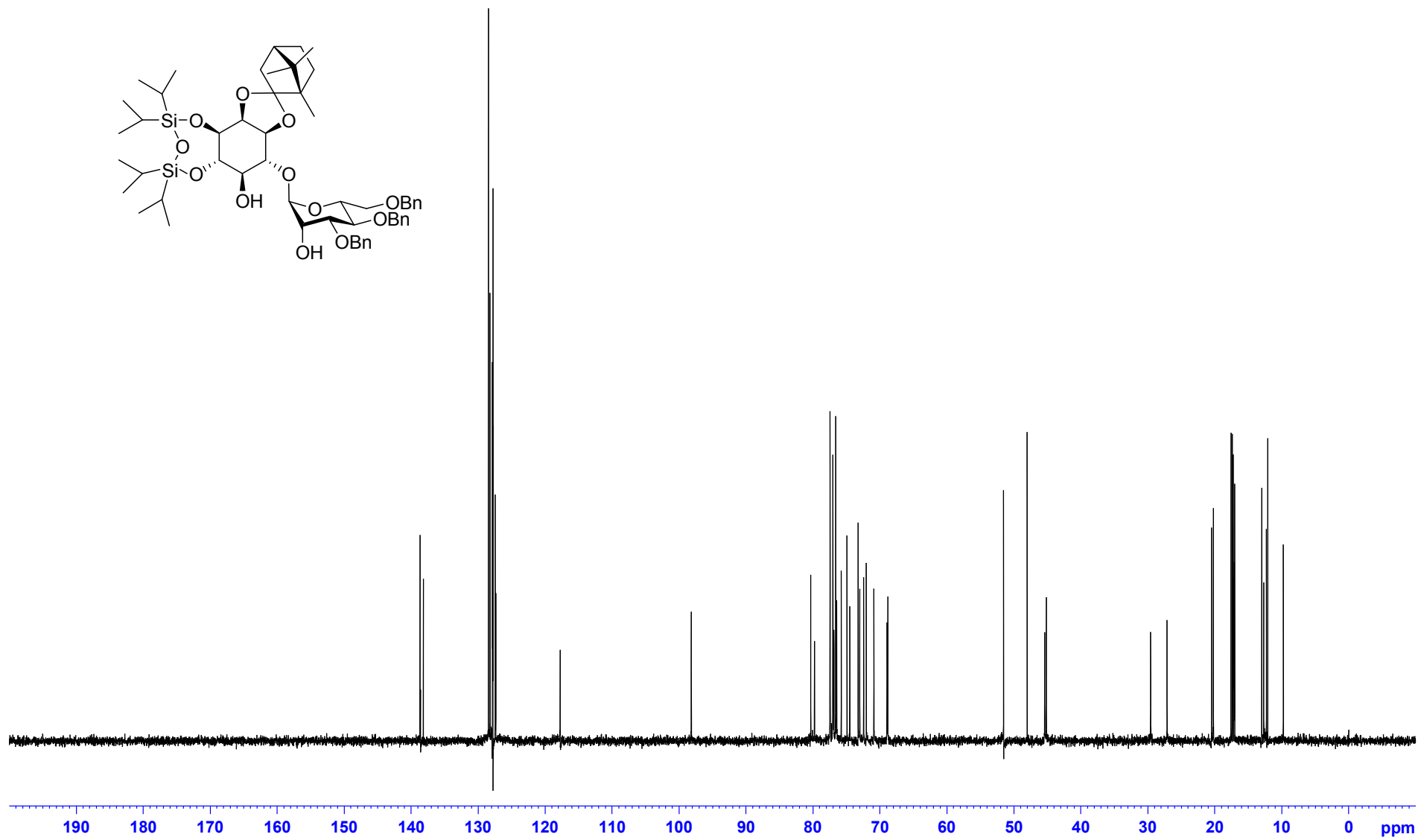
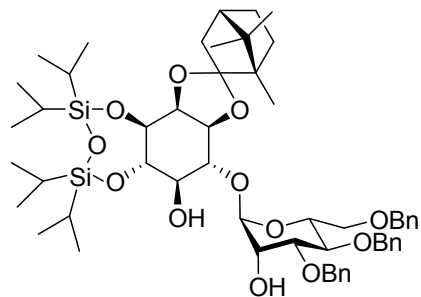


Compound **12** 300 MHz  $^1\text{H}$  NMR  $\text{CDCl}_3$

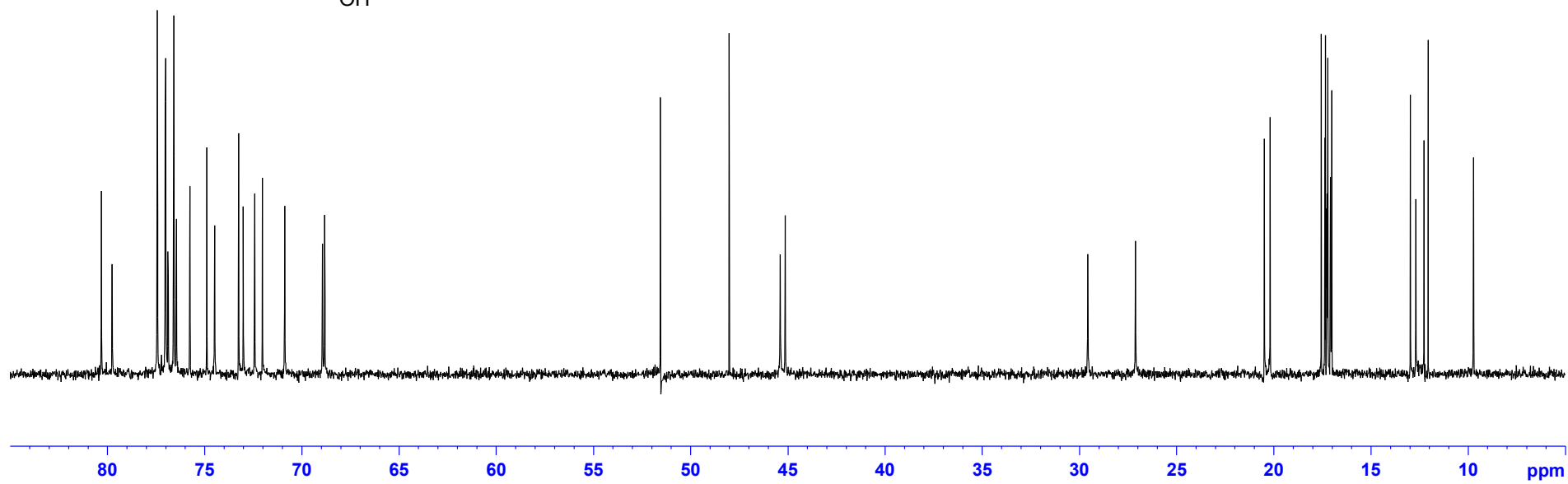
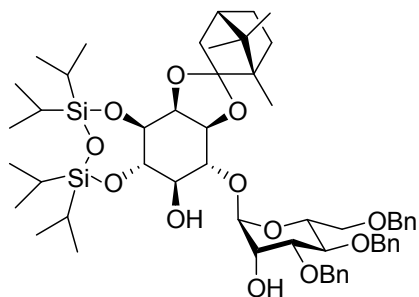




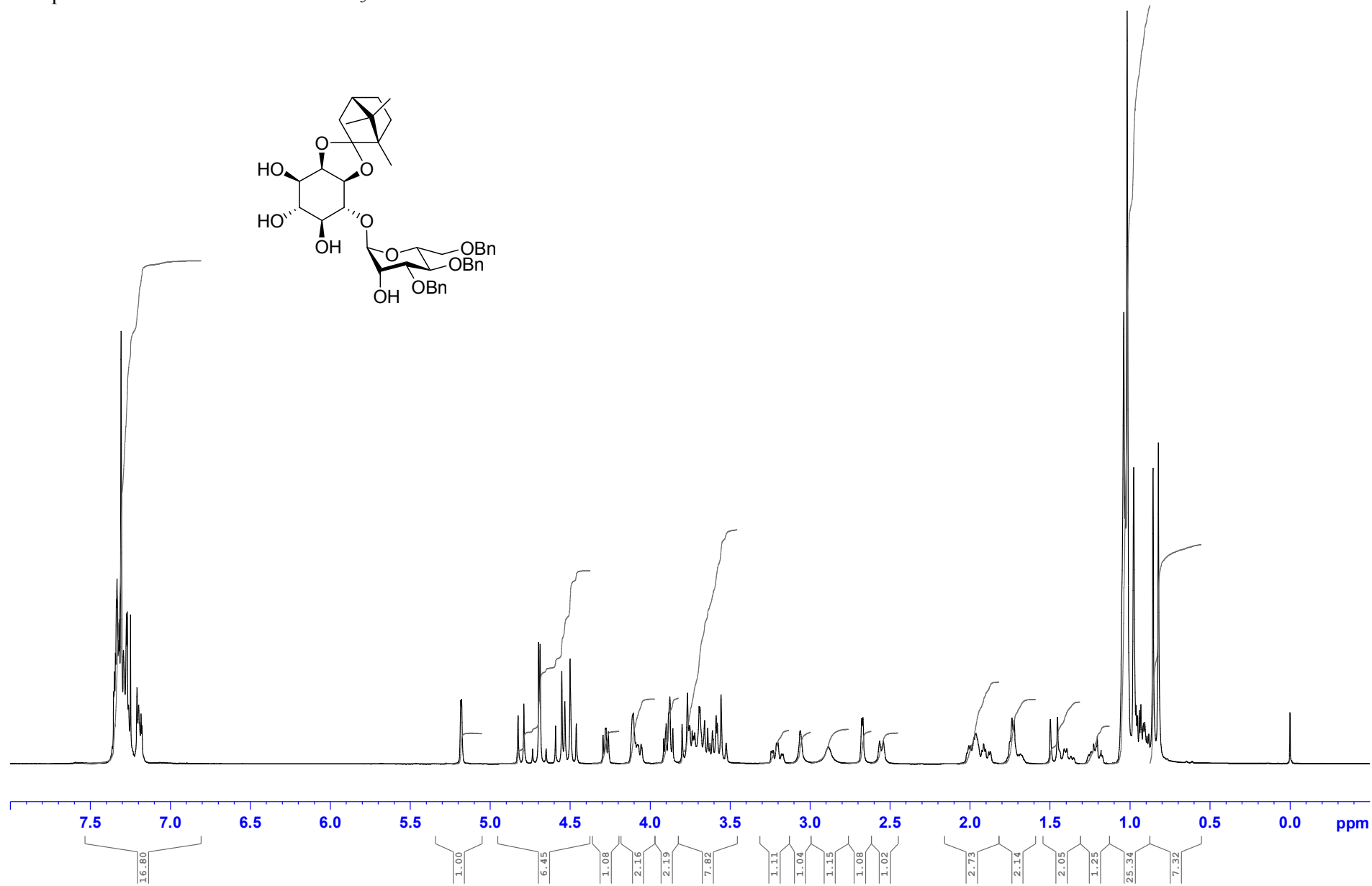
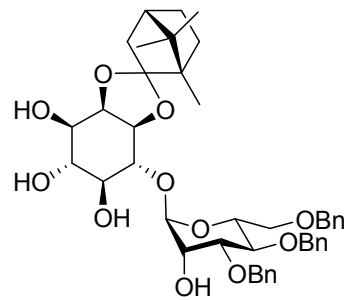
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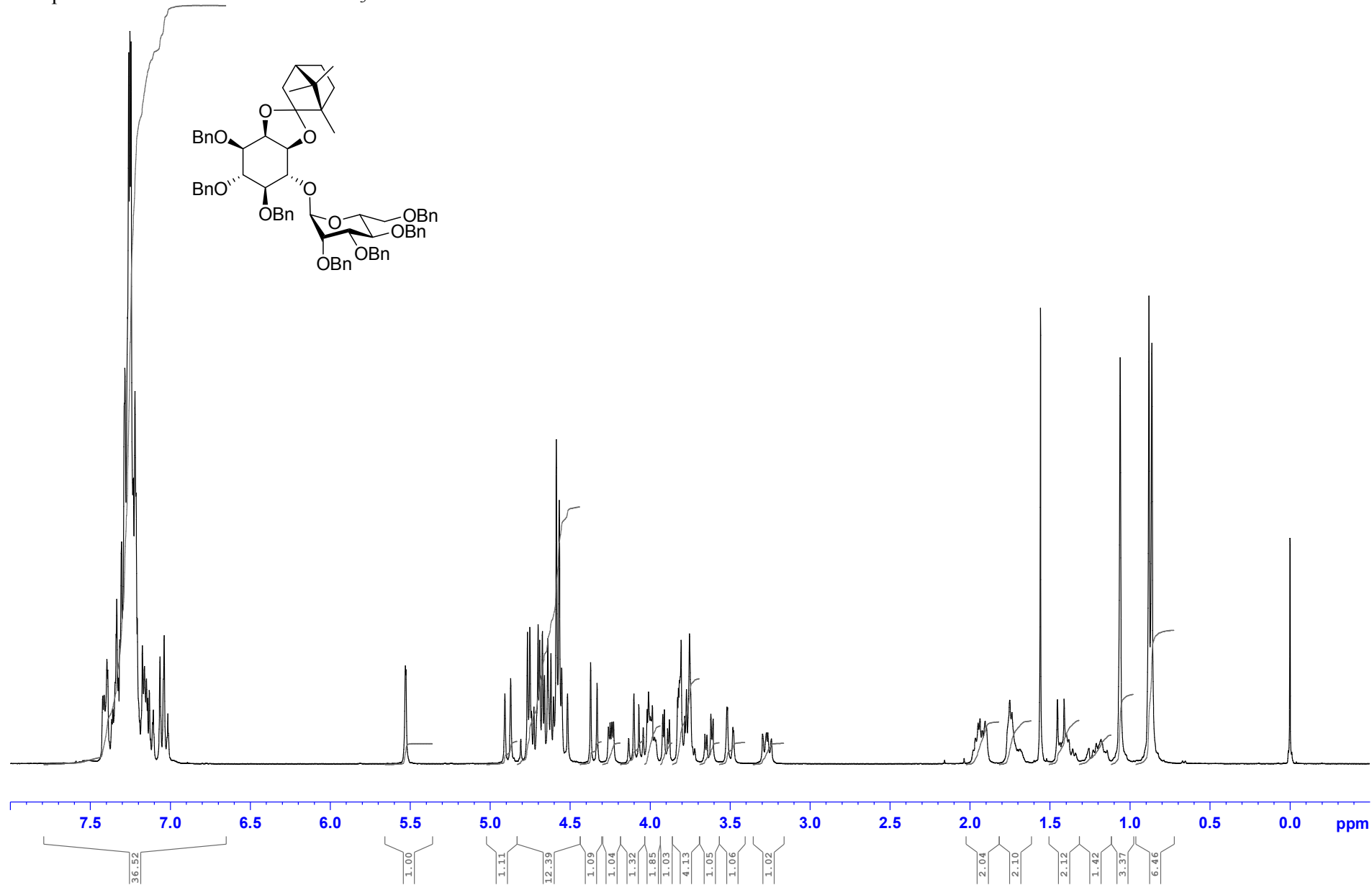
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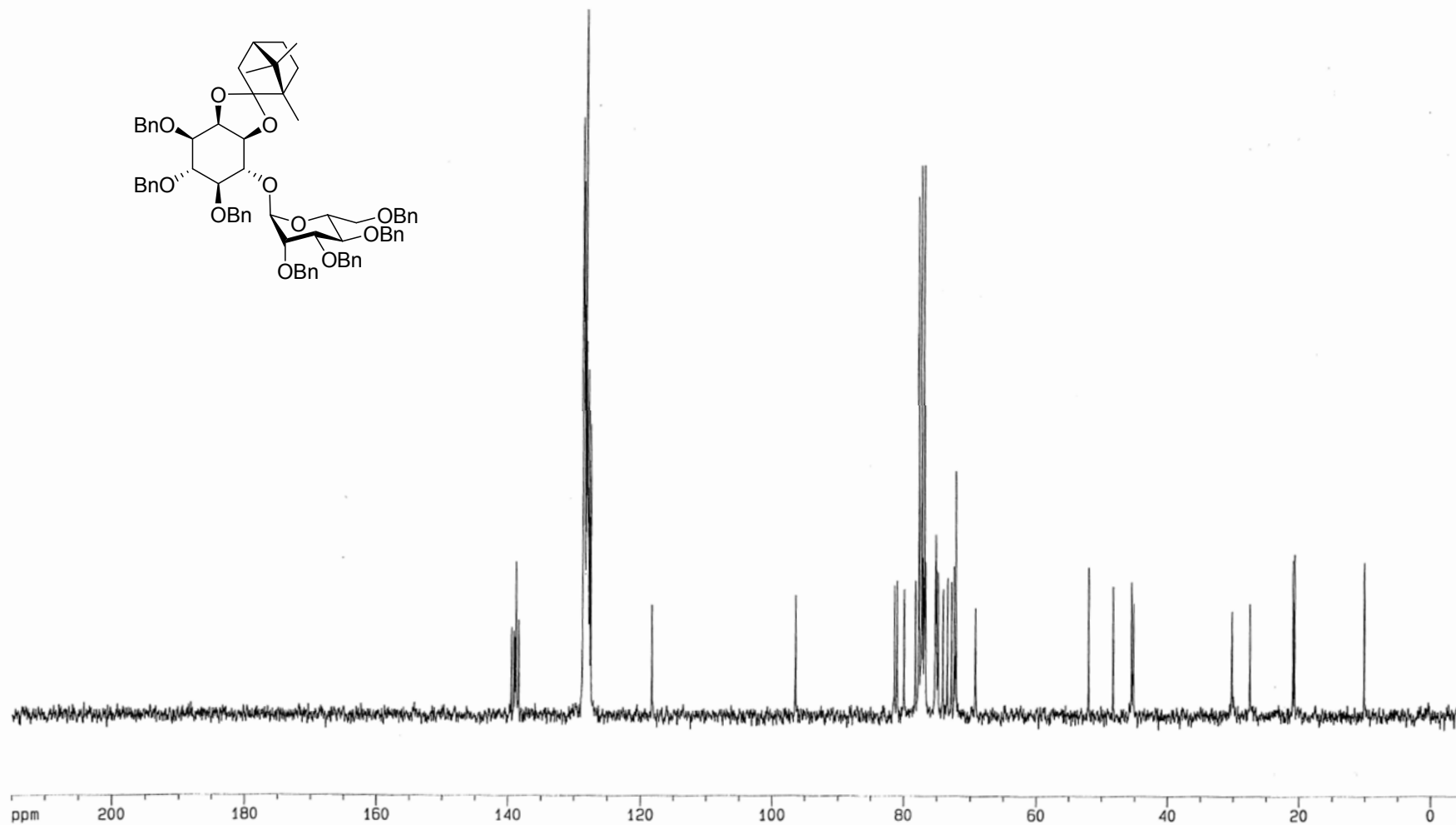
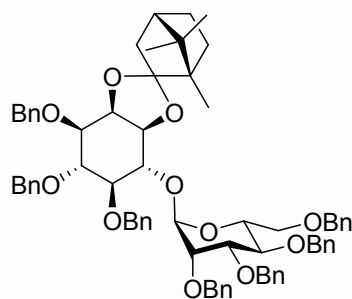
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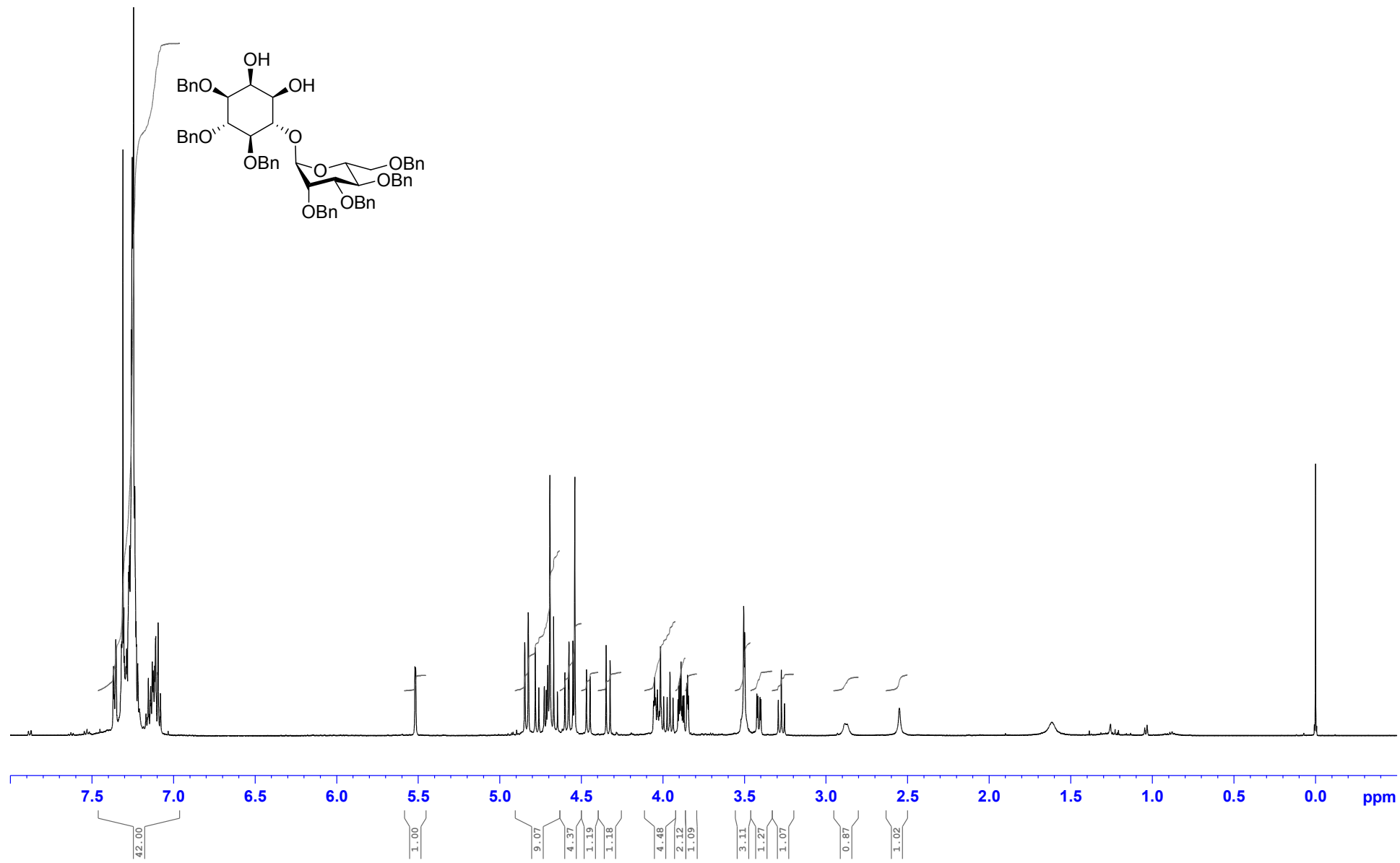
Compound **14** 300 MHz  $^1\text{H}$  NMR  $\text{CDCl}_3$



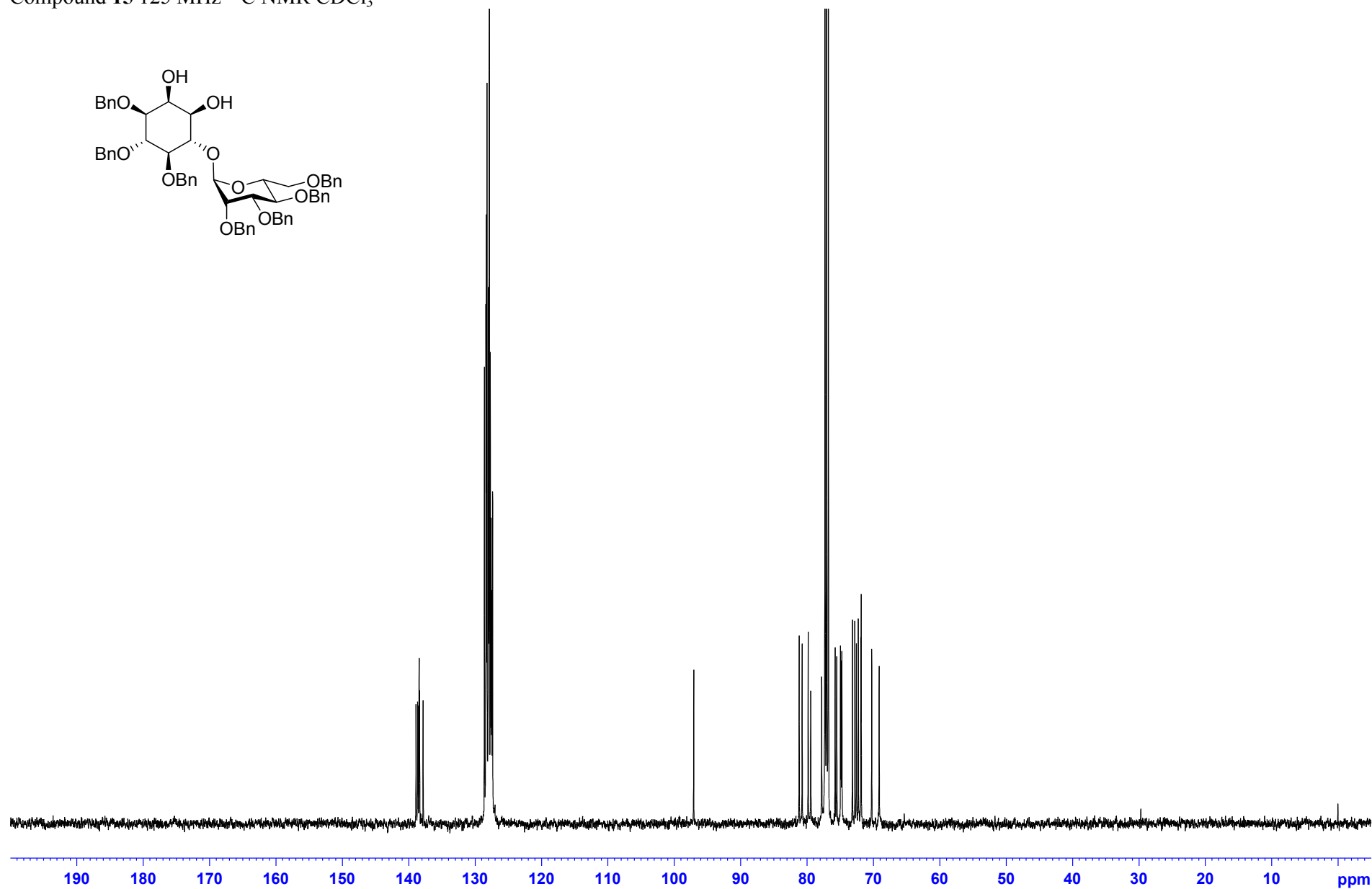
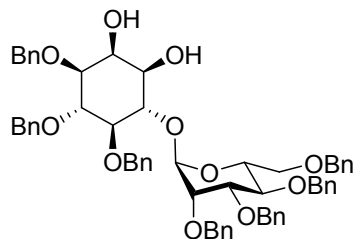
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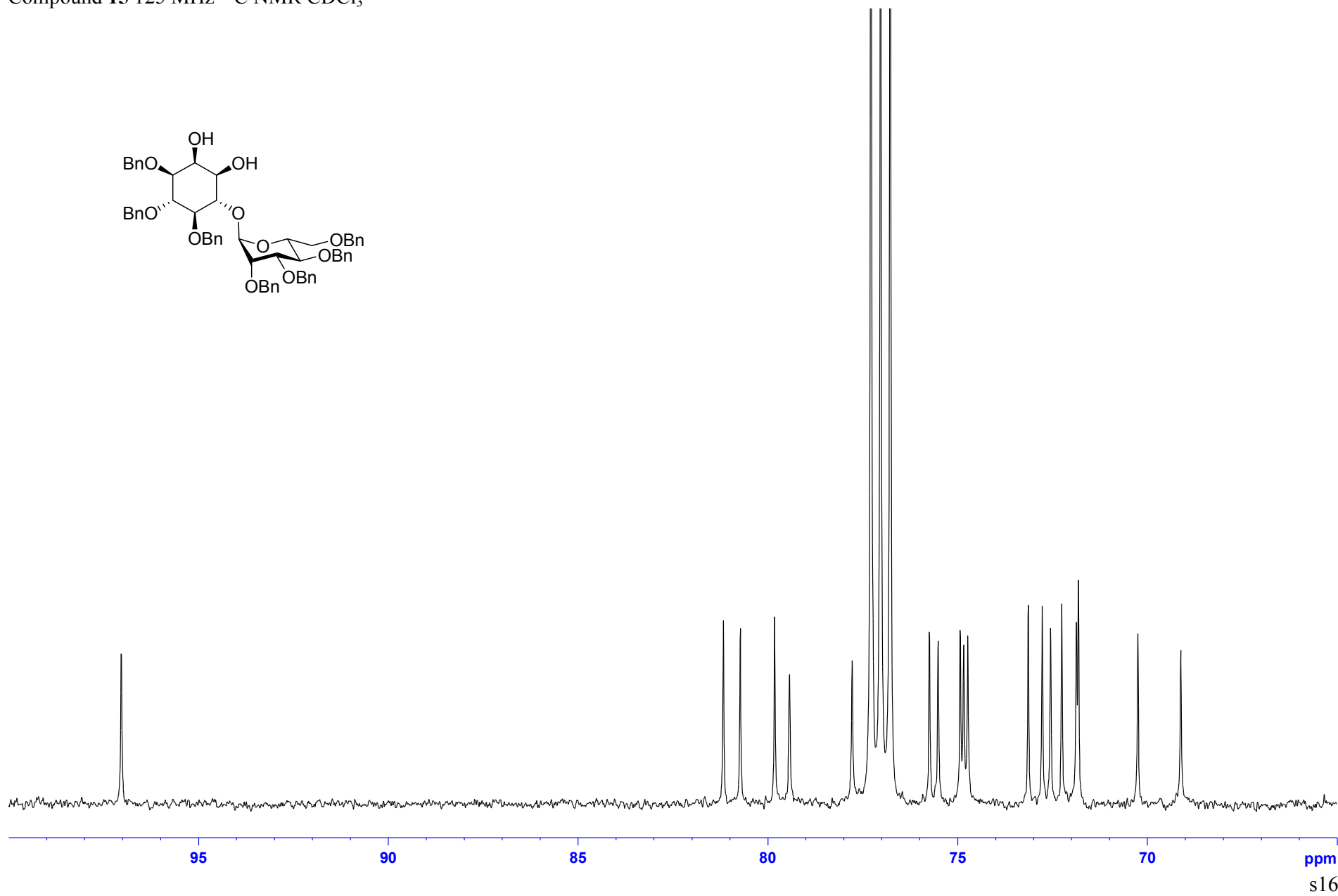
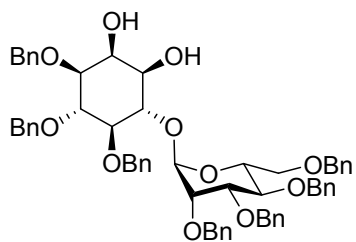
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Compound **15** 125 MHz  $^{13}\text{C}$  NMR  $\text{CDCl}_3$

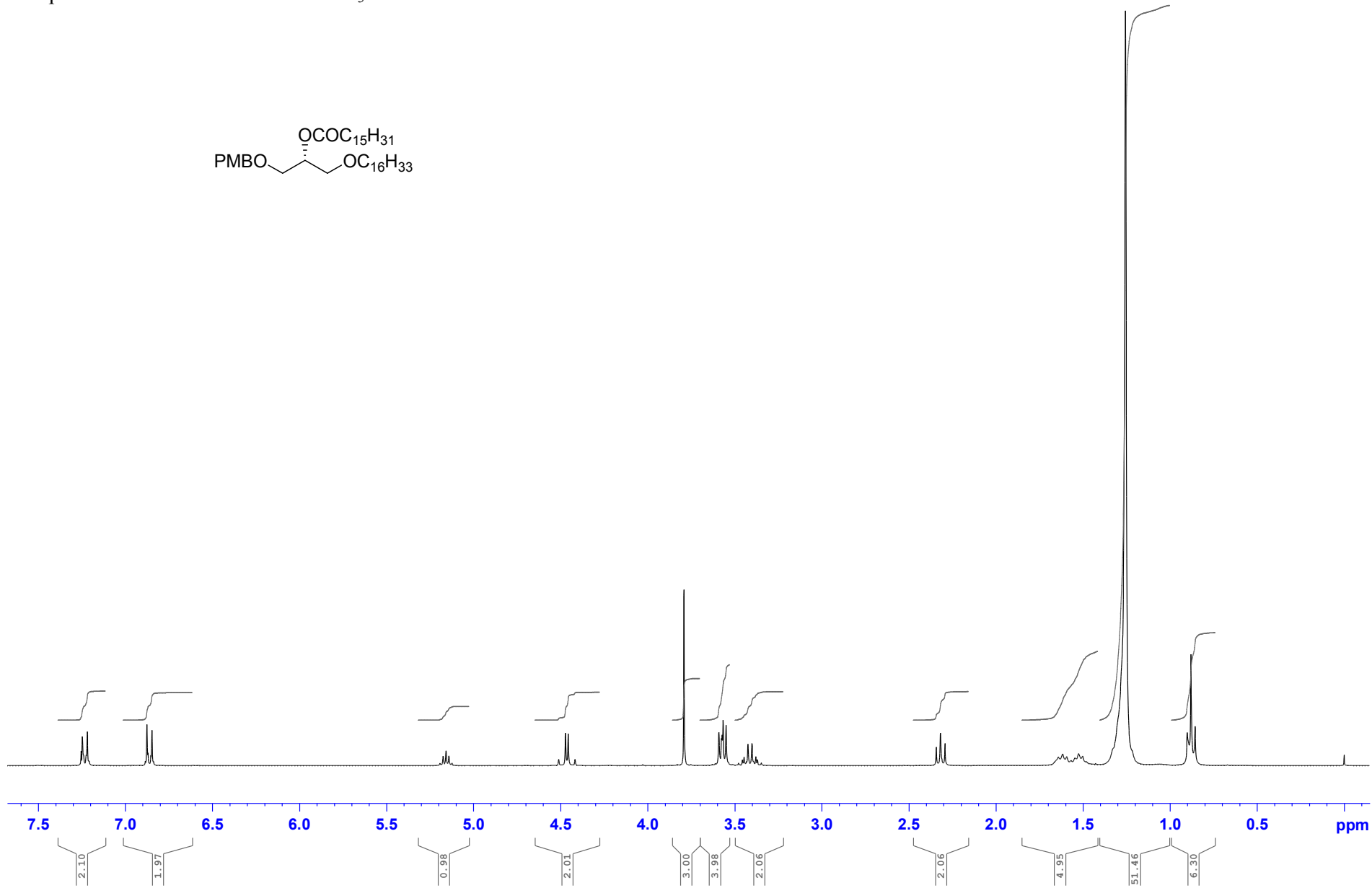
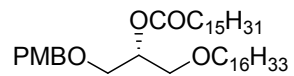


Compound **15** 125 MHz  $^{13}\text{C}$  NMR  $\text{CDCl}_3$

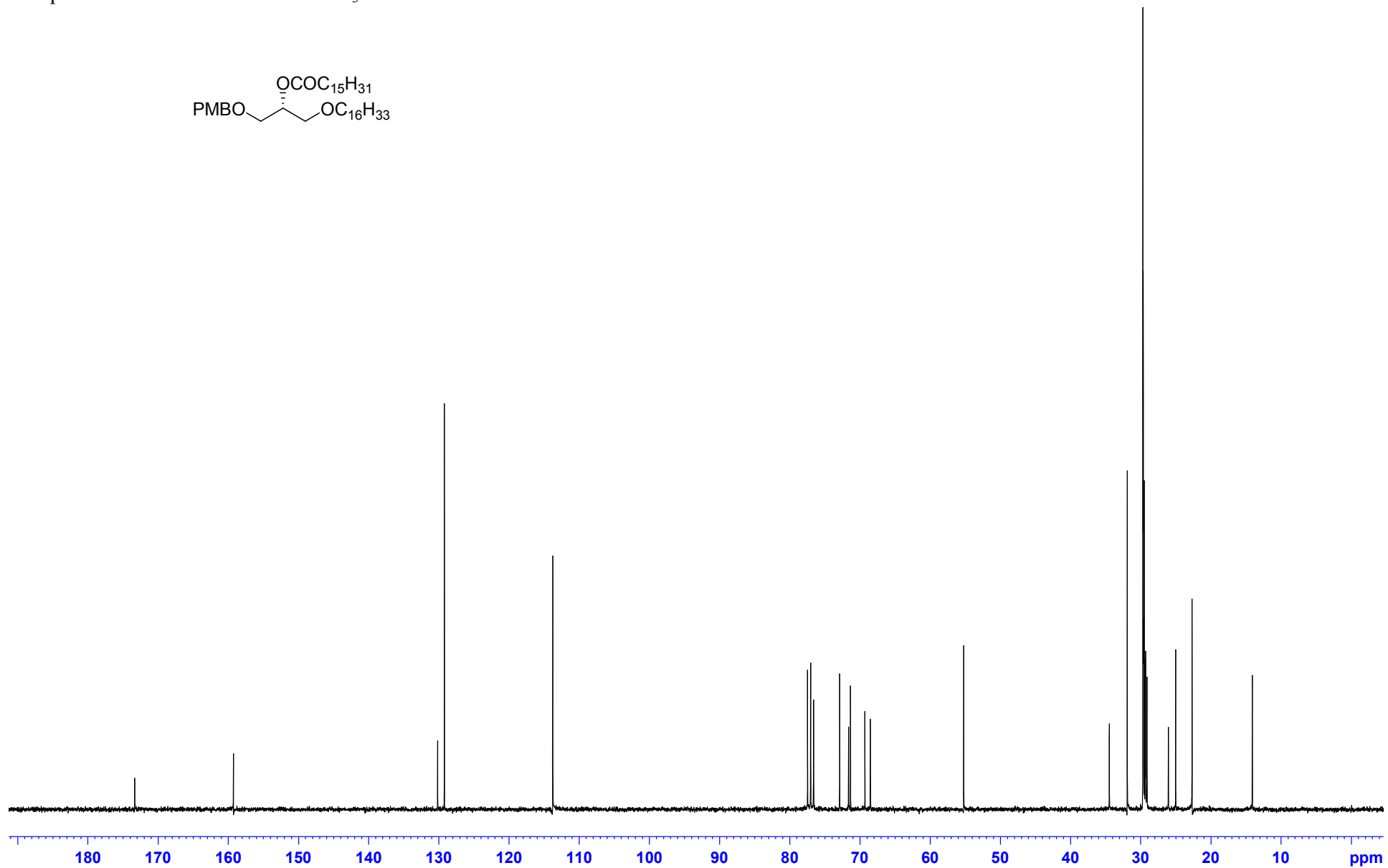
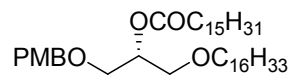




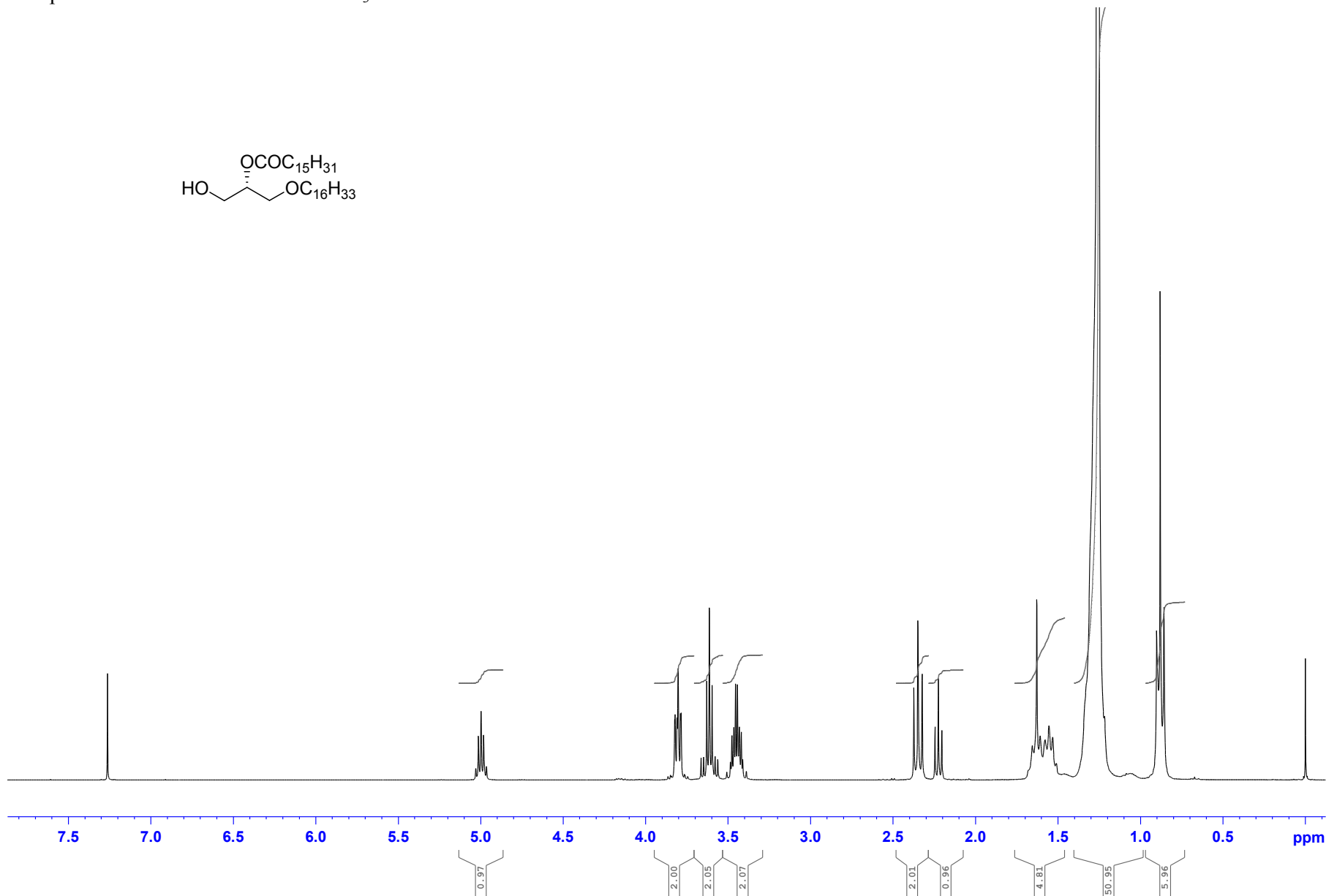
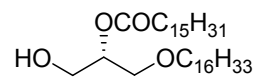
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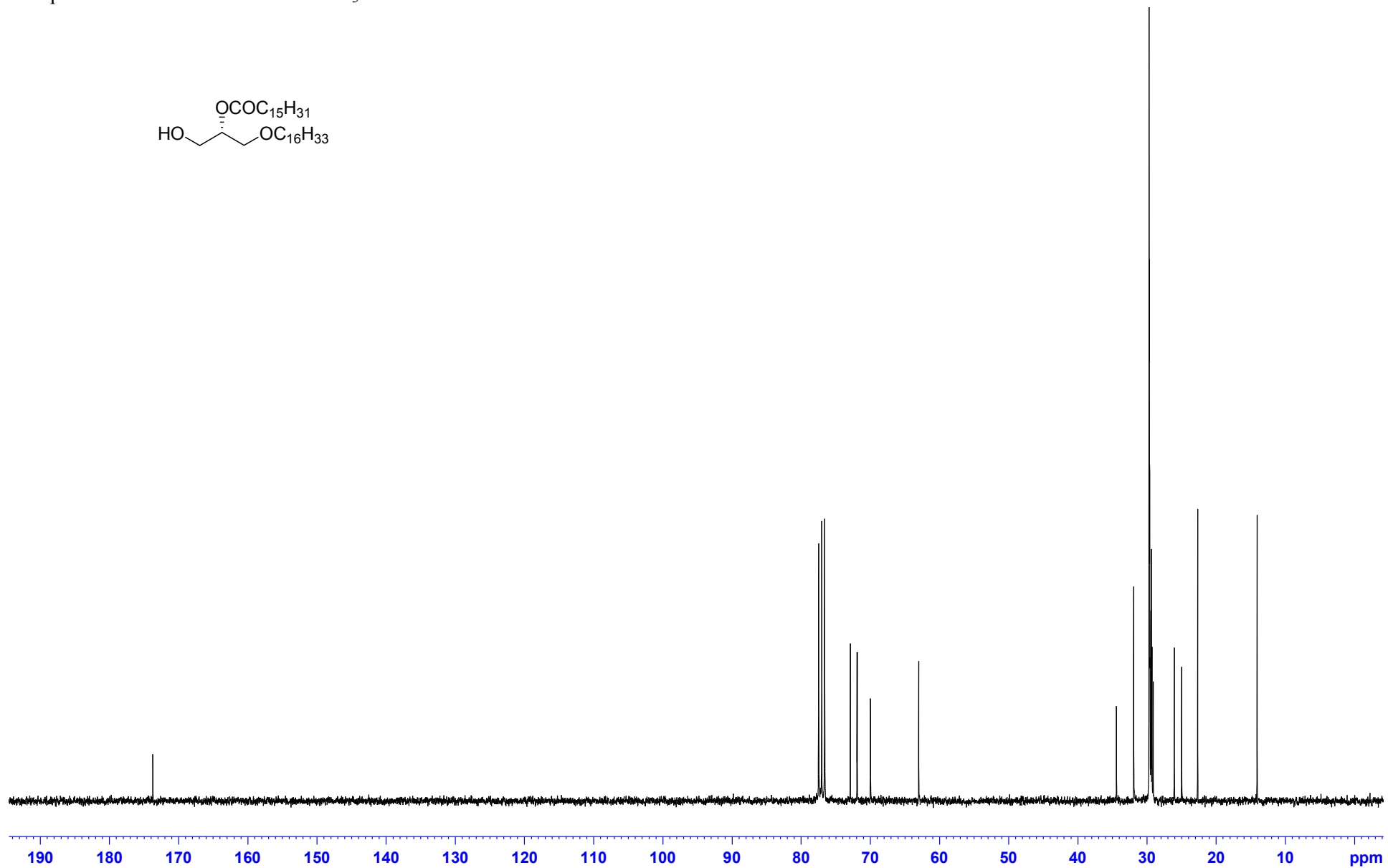
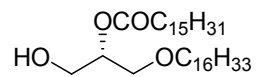
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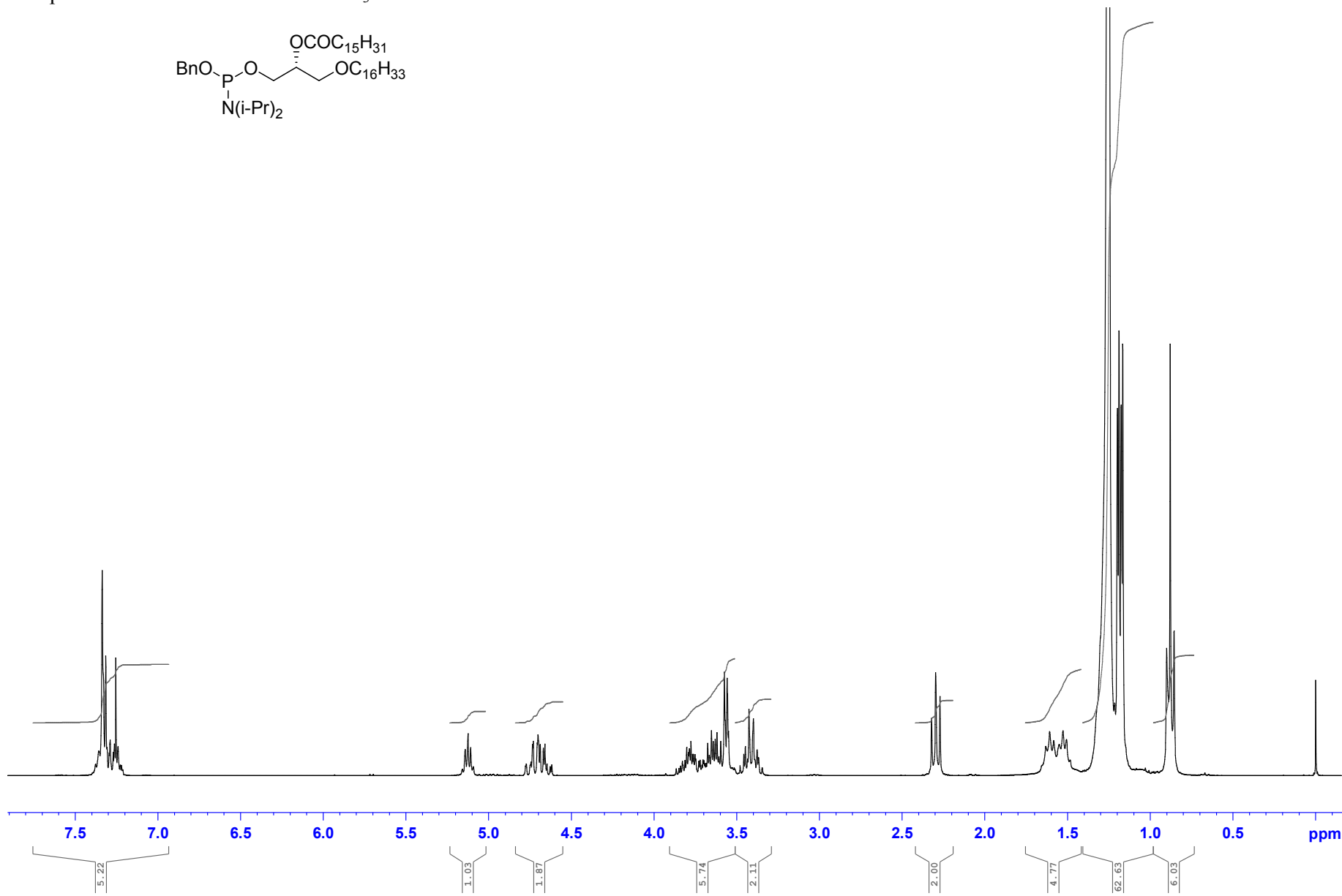
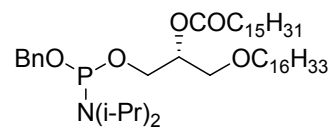
Compound **21** 300 MHz  $^1\text{H}$  NMR  $\text{CDCl}_3$



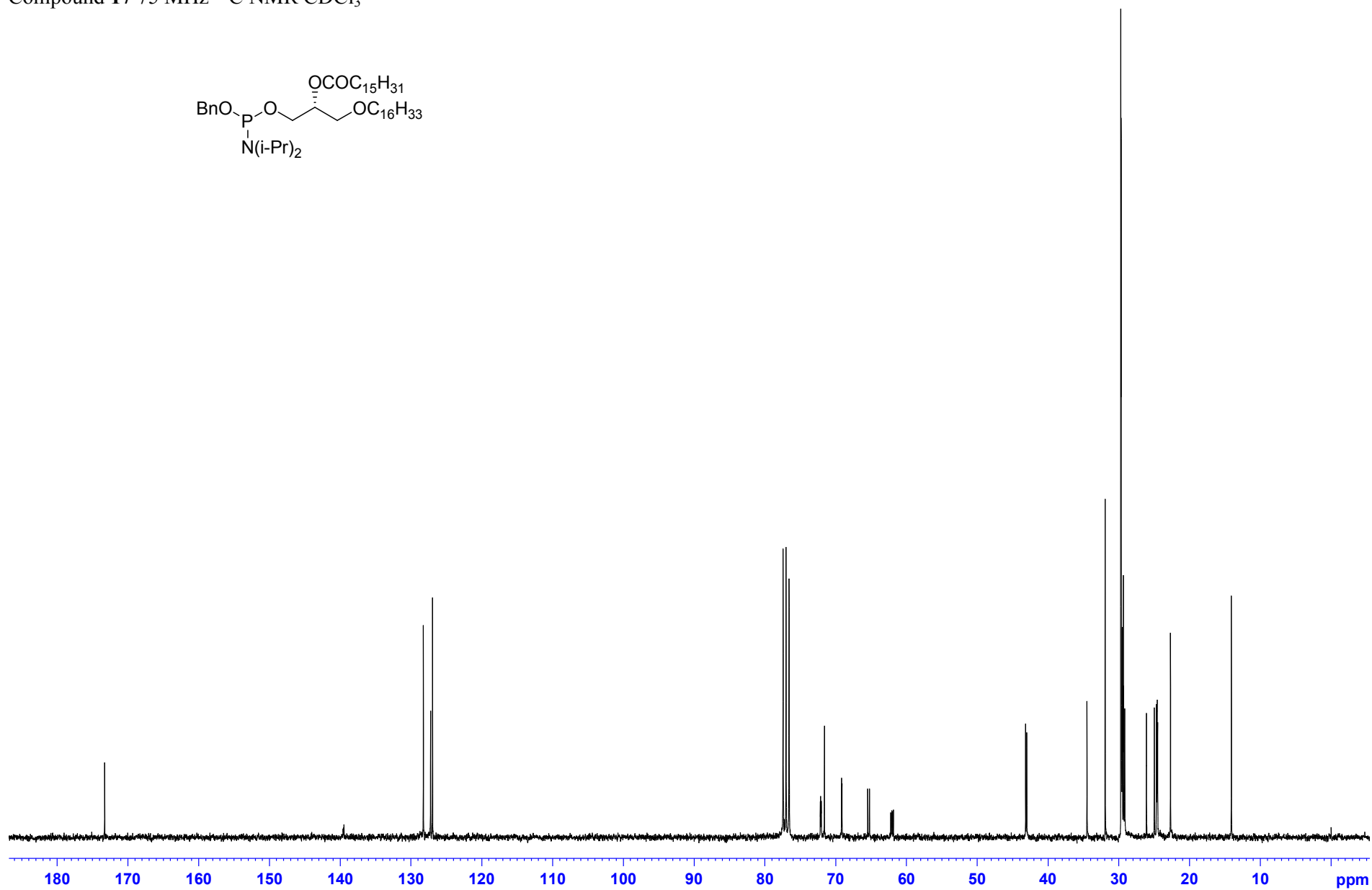
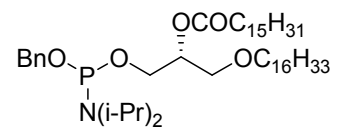
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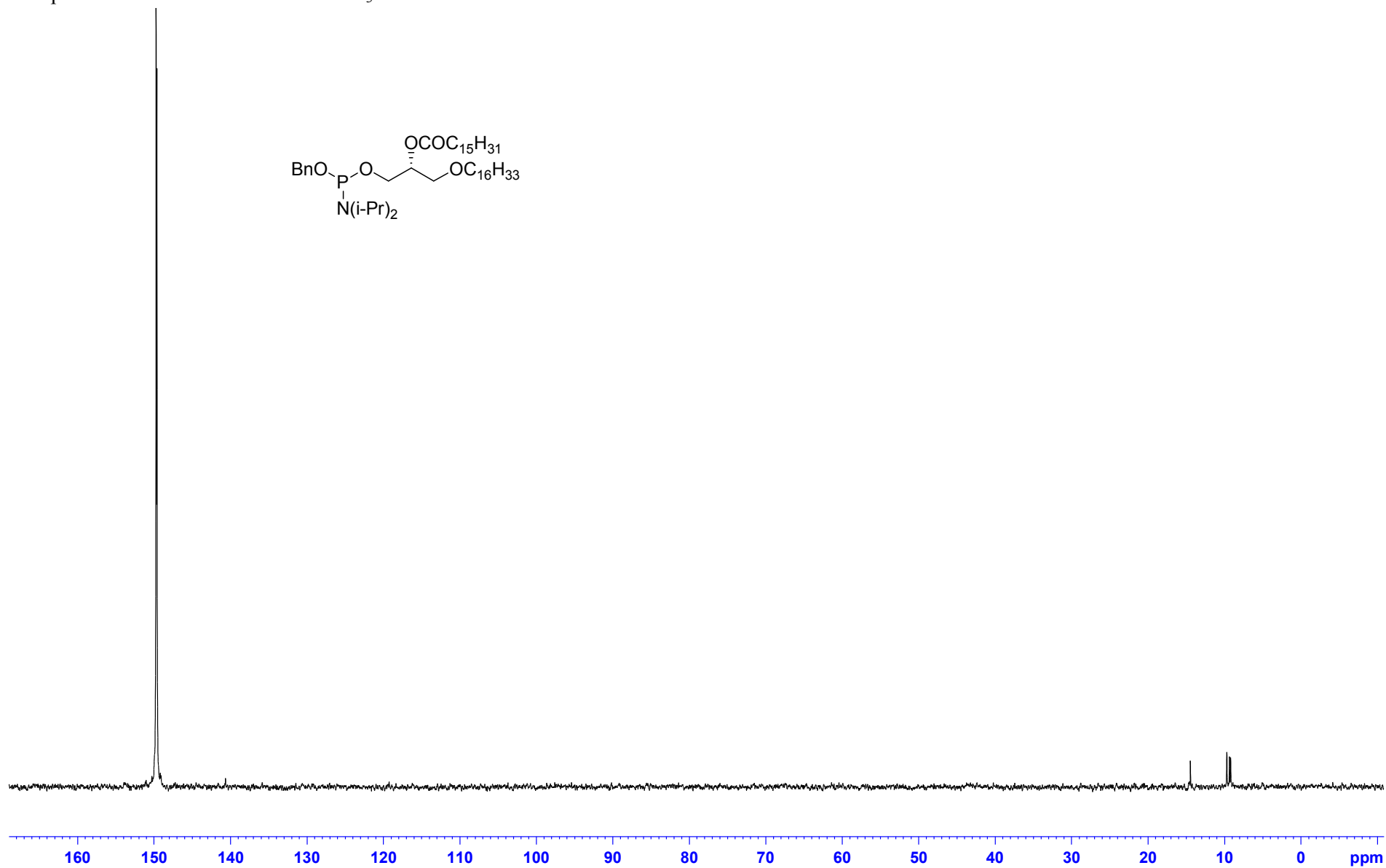
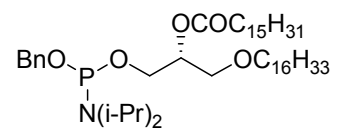
Compound **17** 300 MHz  $^1\text{H}$  NMR  $\text{CDCl}_3$



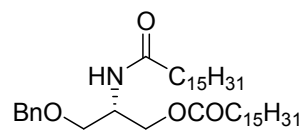
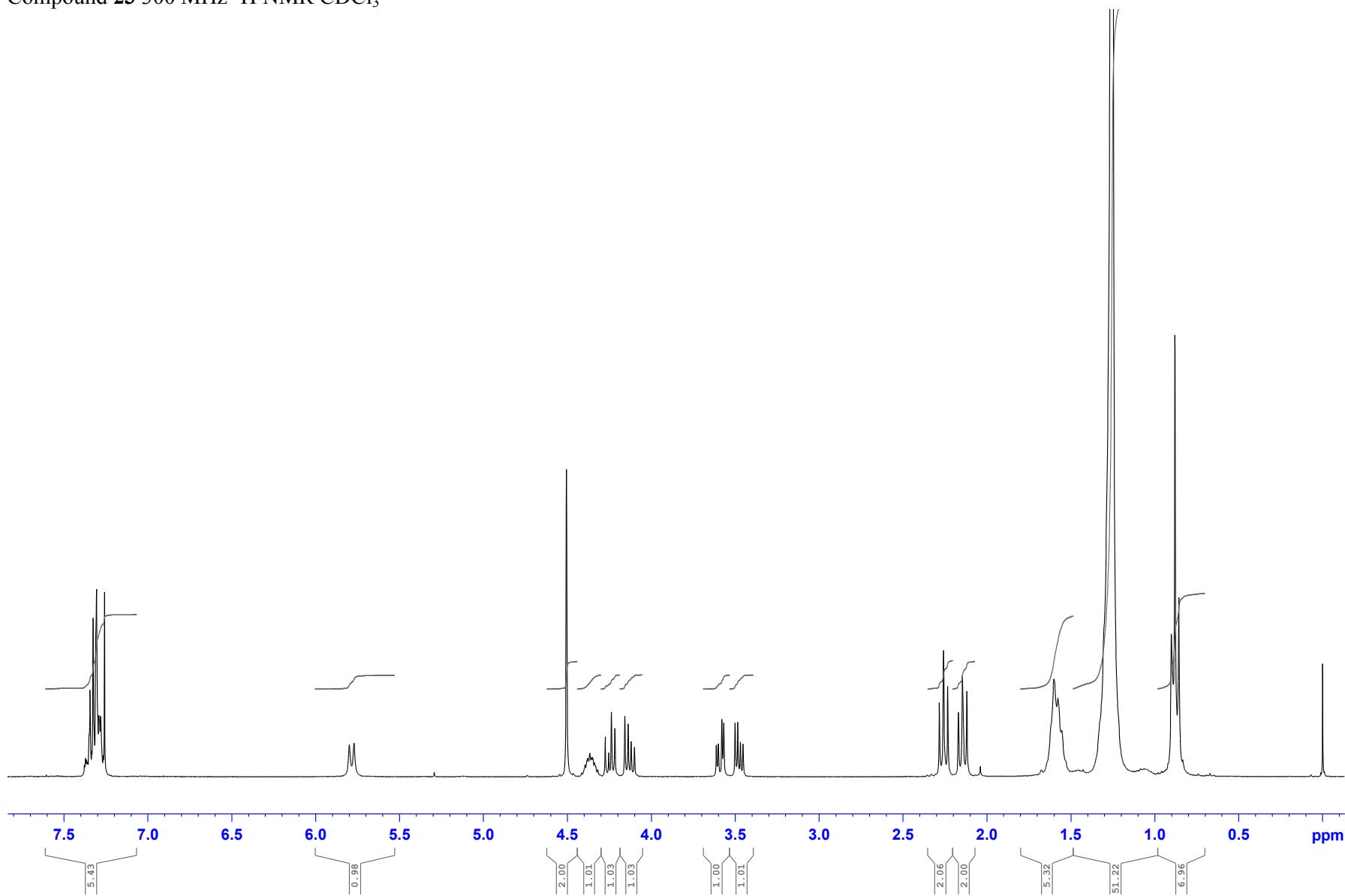
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Compound **17** 121 MHz  $^{31}\text{P}$  NMR  $\text{CDCl}_3$

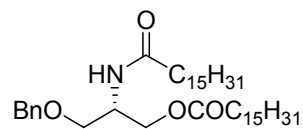
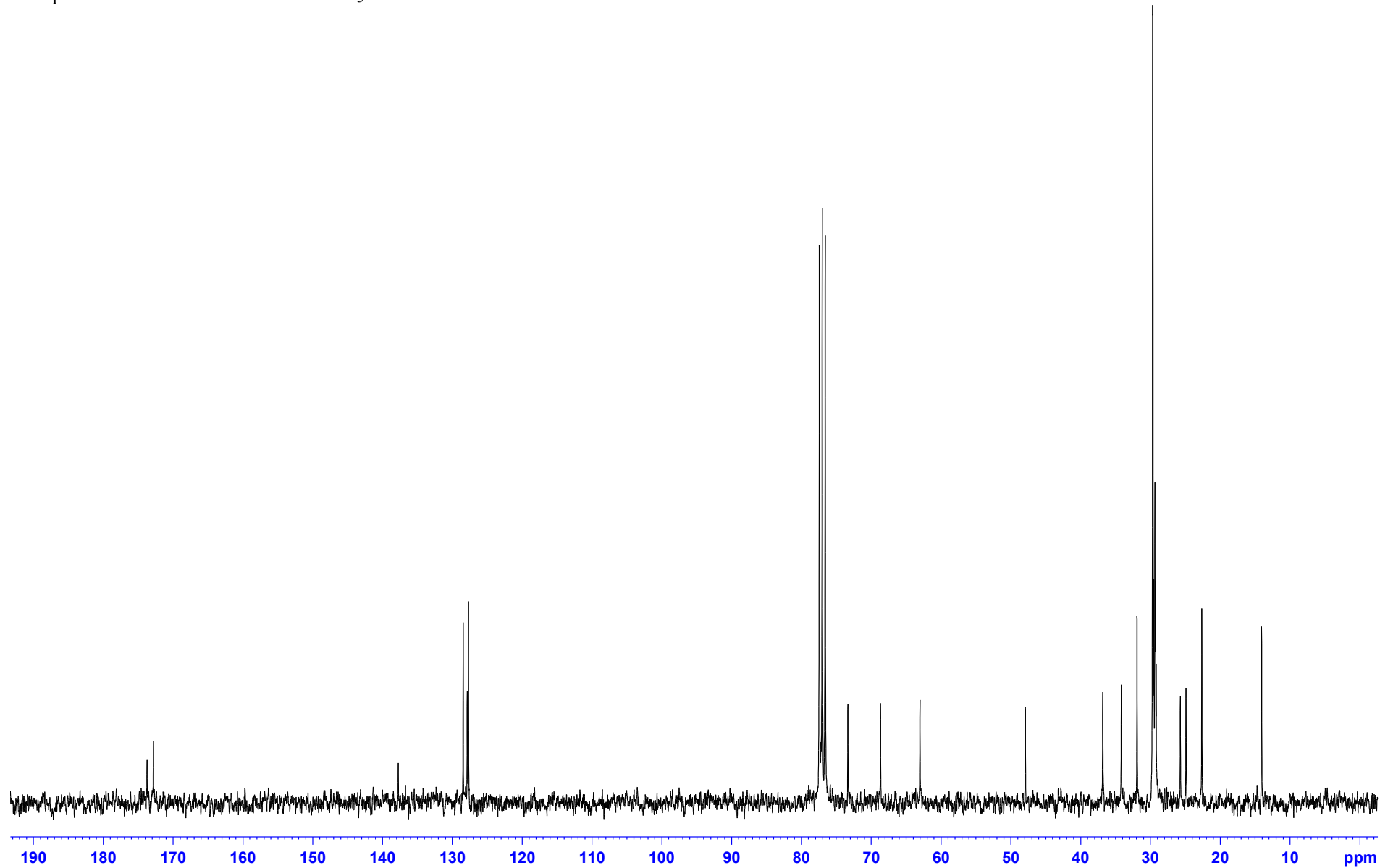


Compound **23** 300 MHz  $^1\text{H}$  NMR  $\text{CDCl}_3$

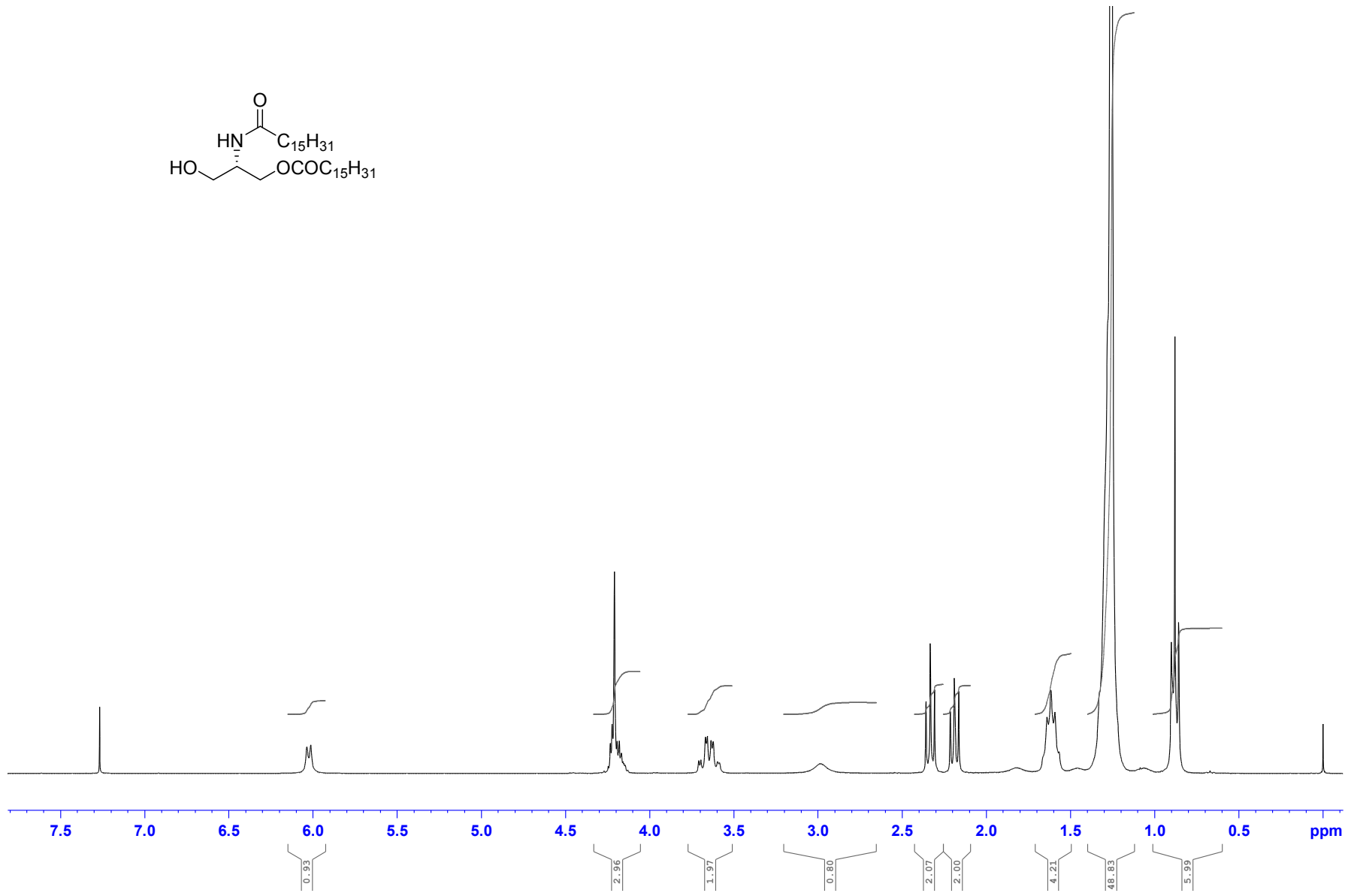
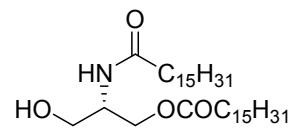




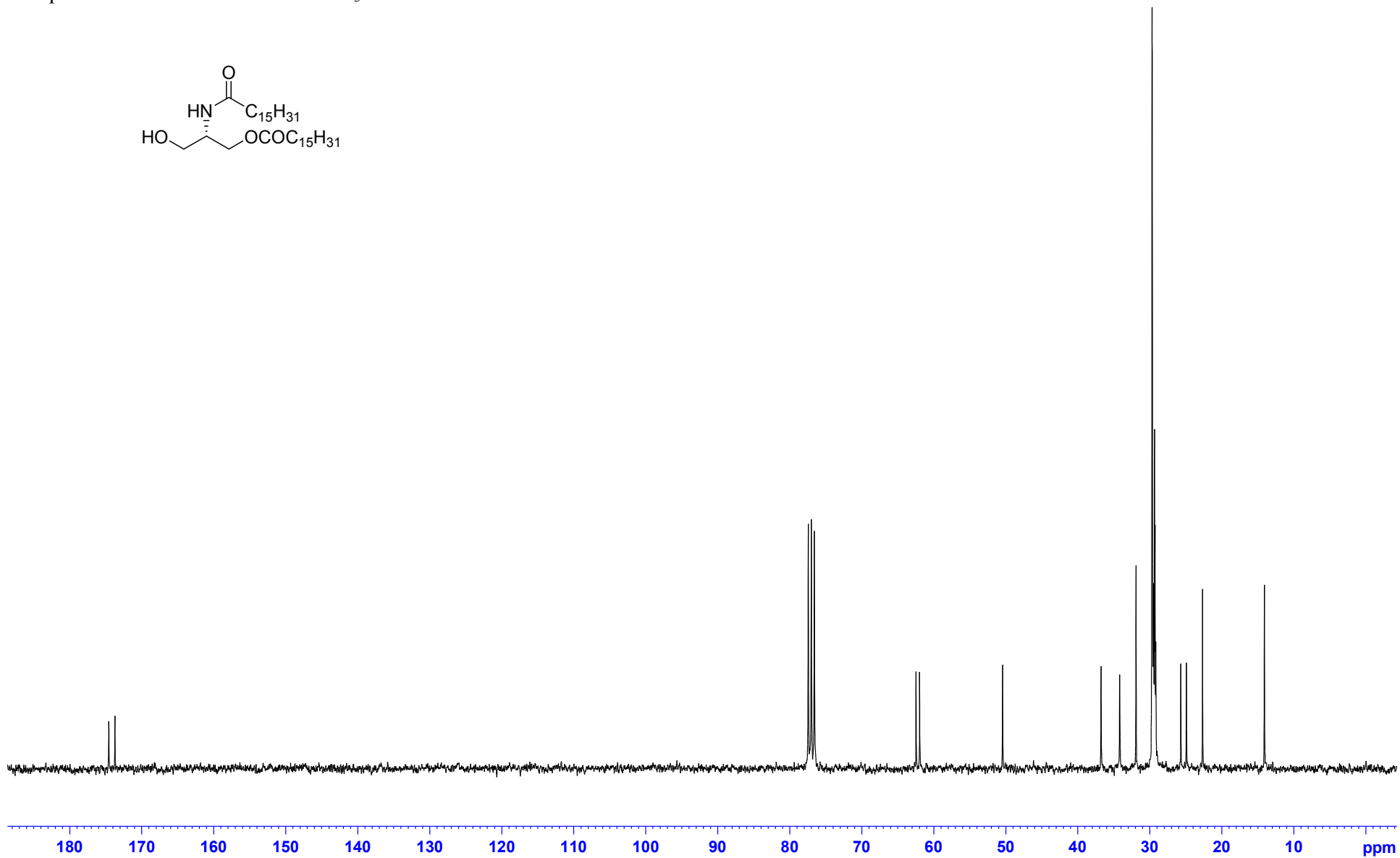
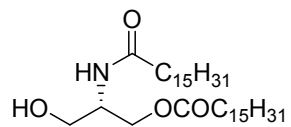
Compound **23** 75 MHz  $^{13}\text{C}$  NMR  $\text{CDCl}_3$



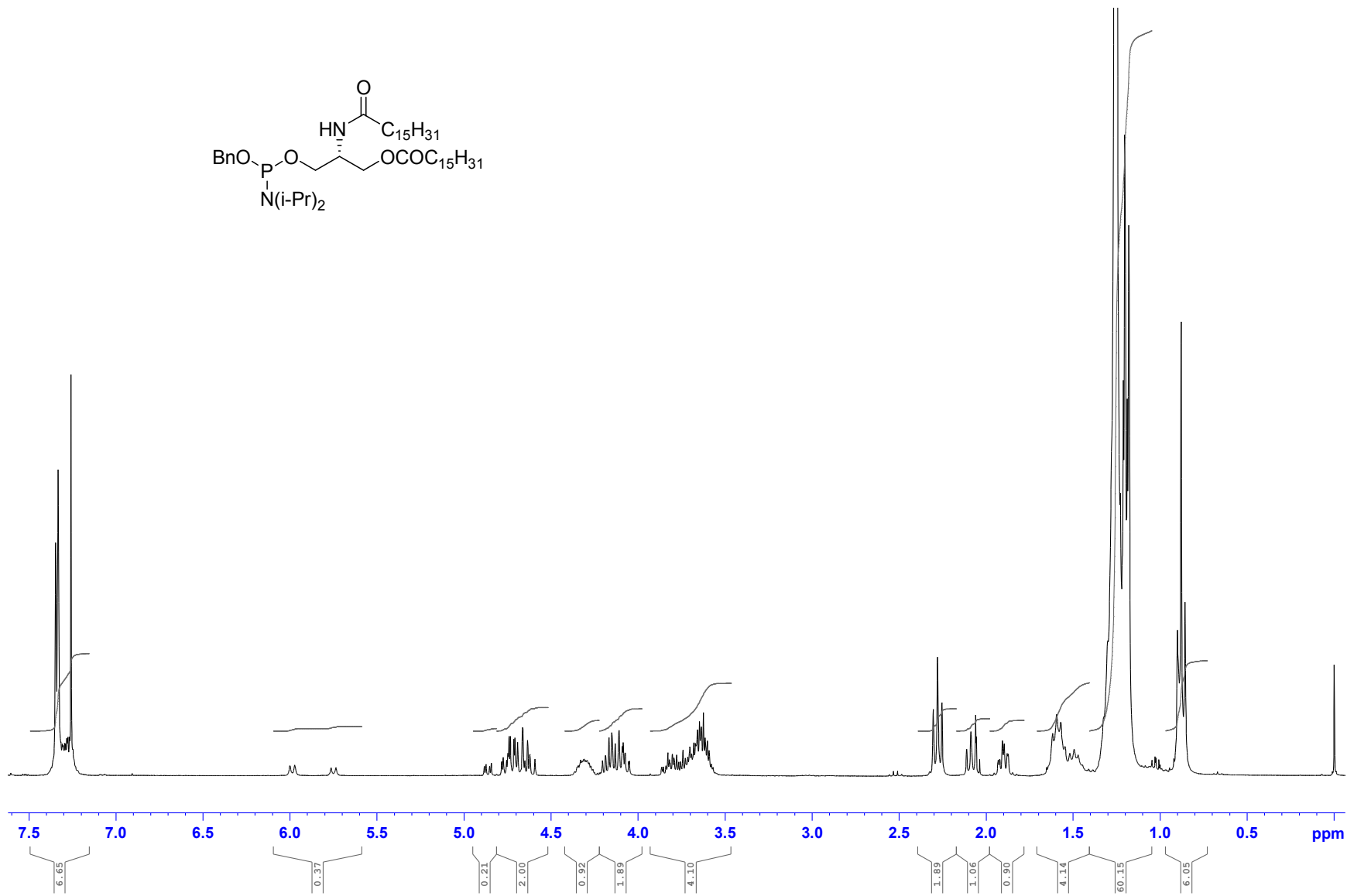
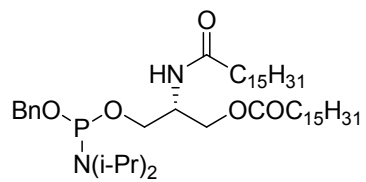
Compound **24** 300 MHz  $^1\text{H}$  NMR  $\text{CDCl}_3$



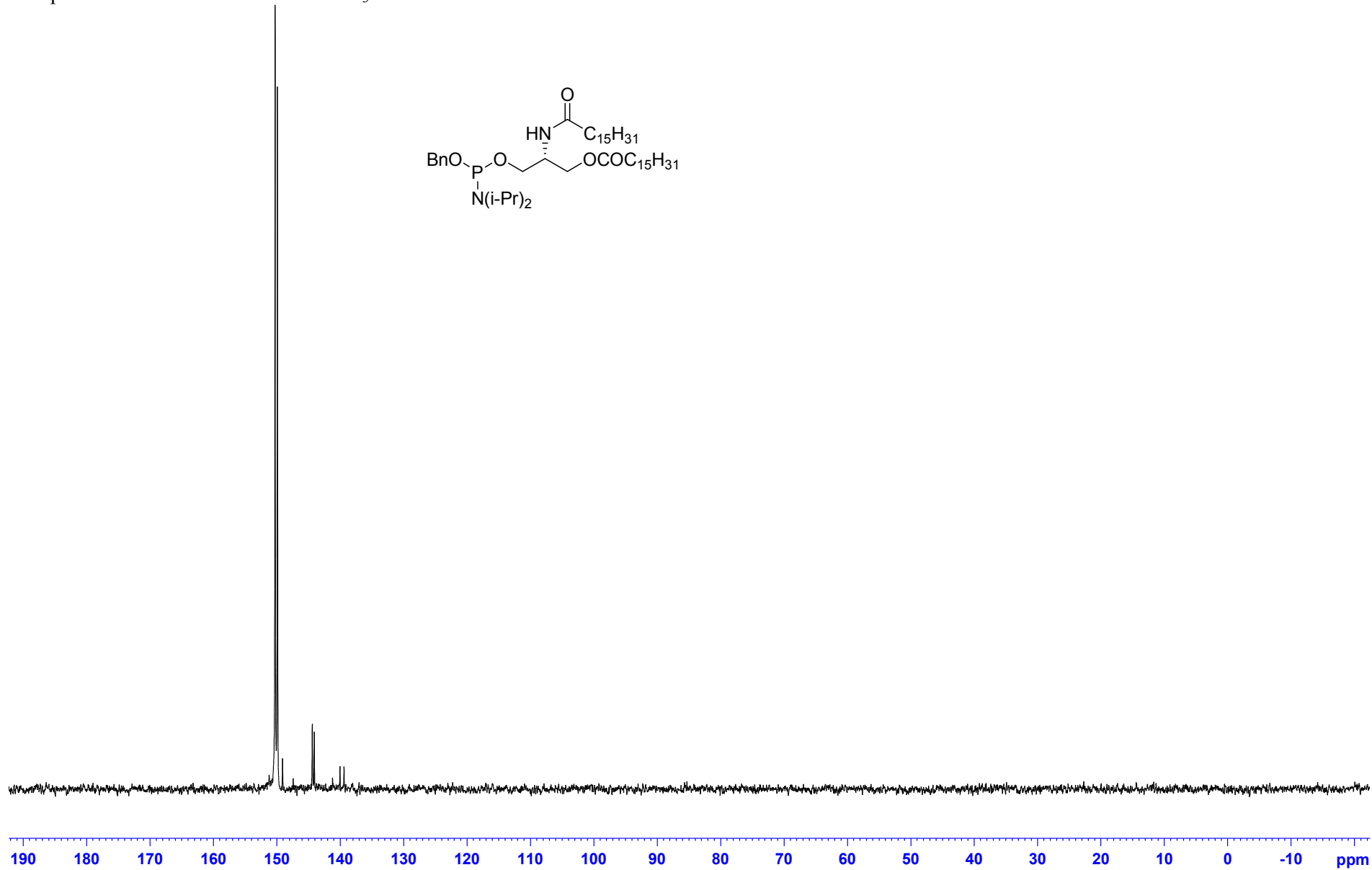
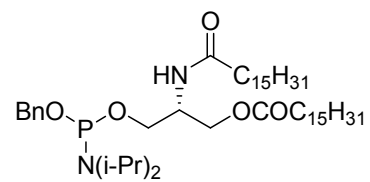
Compound **24** 75 MHz  $^{13}\text{C}$  NMR  $\text{CDCl}_3$



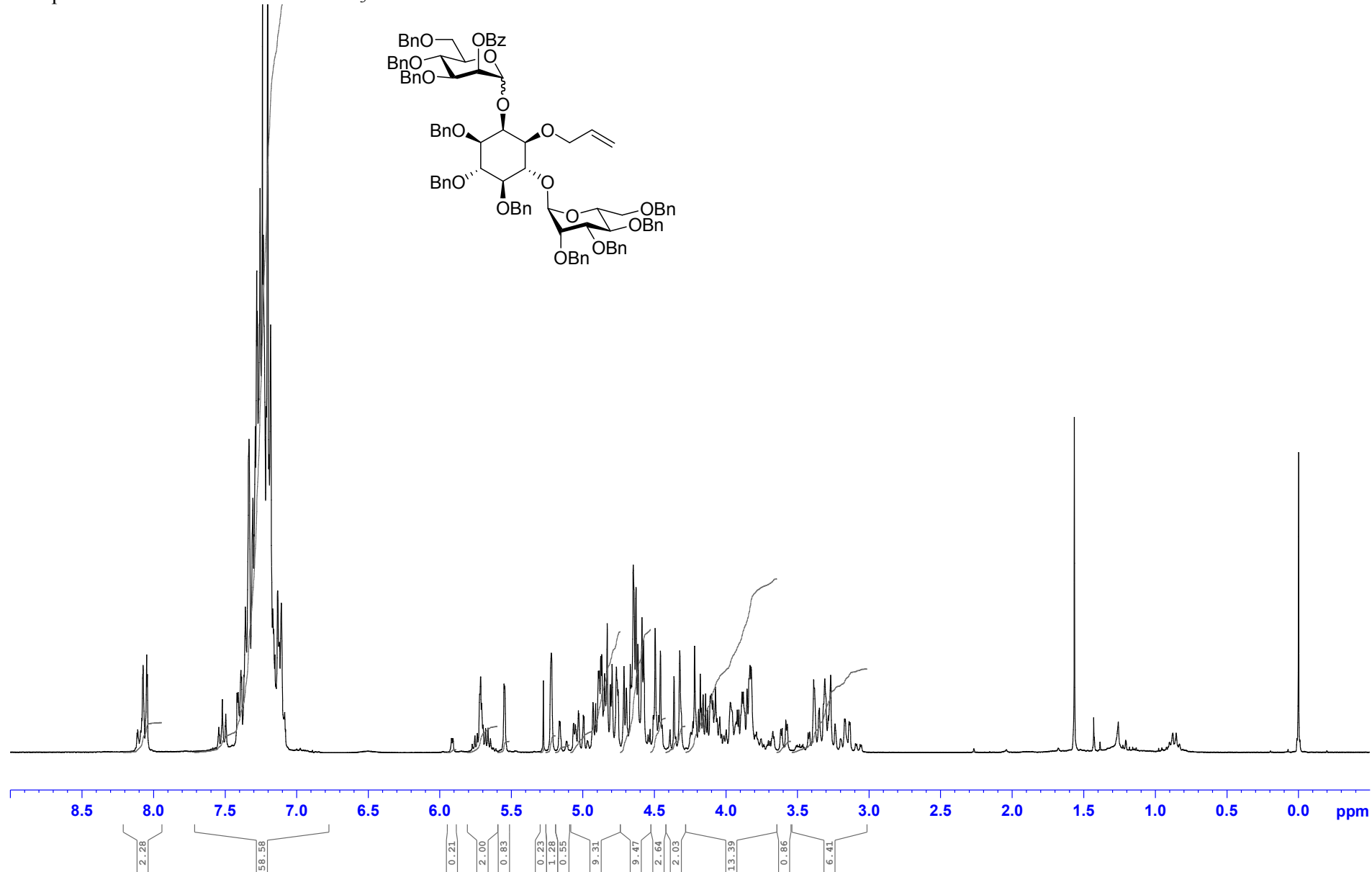
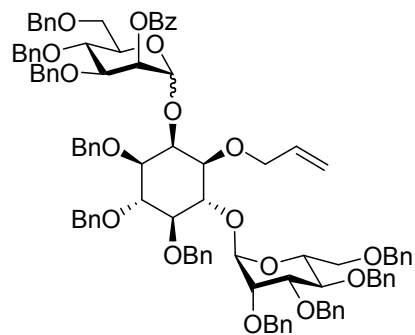
Compound **18** 300 MHz  $^1\text{H}$  NMR  $\text{CDCl}_3$



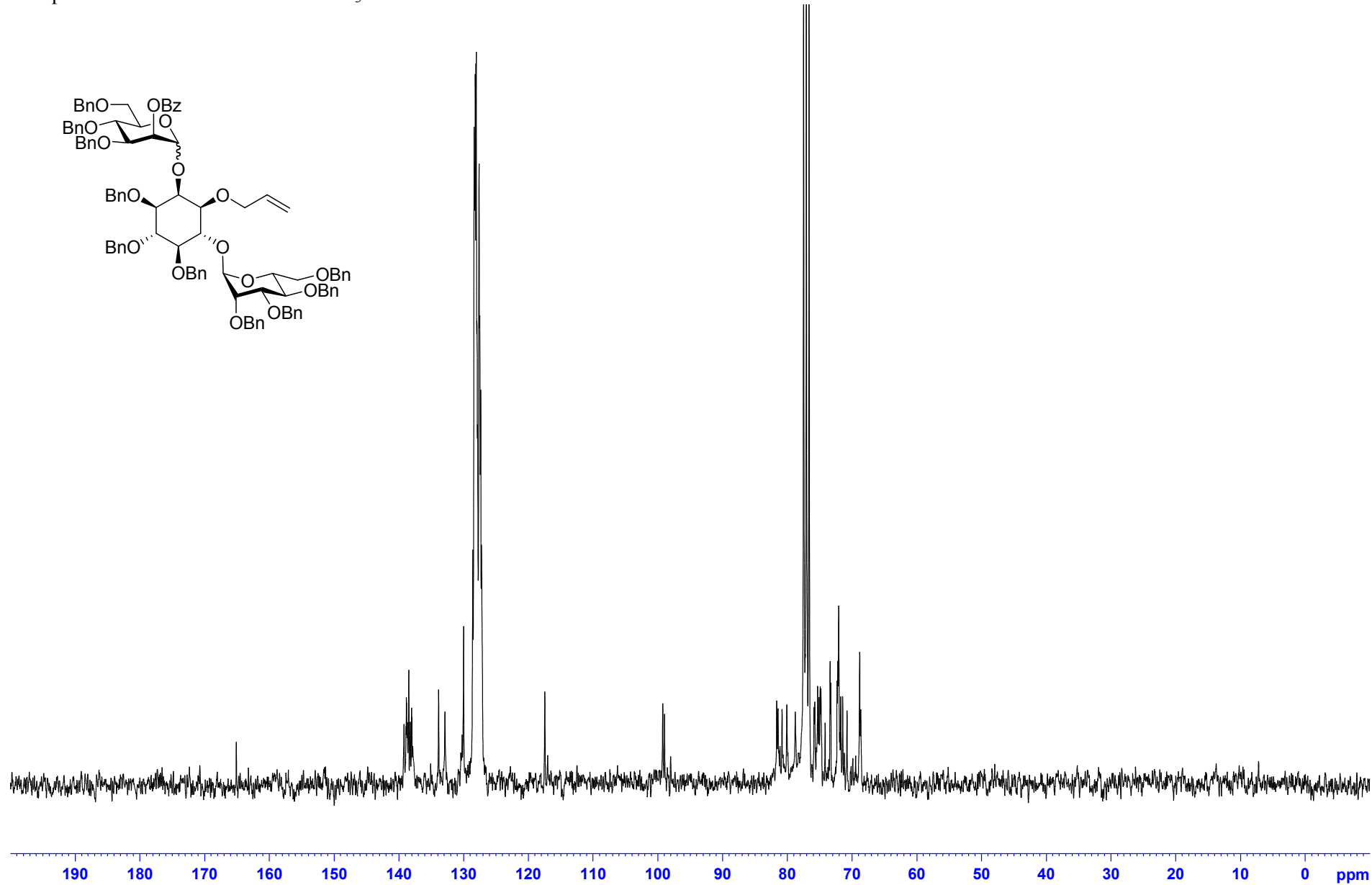
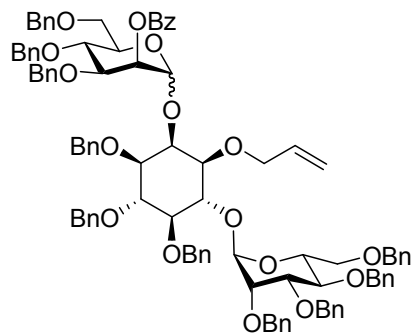
Compound **18** 121 MHz  $^{31}\text{P}$  NMR  $\text{CDCl}_3$



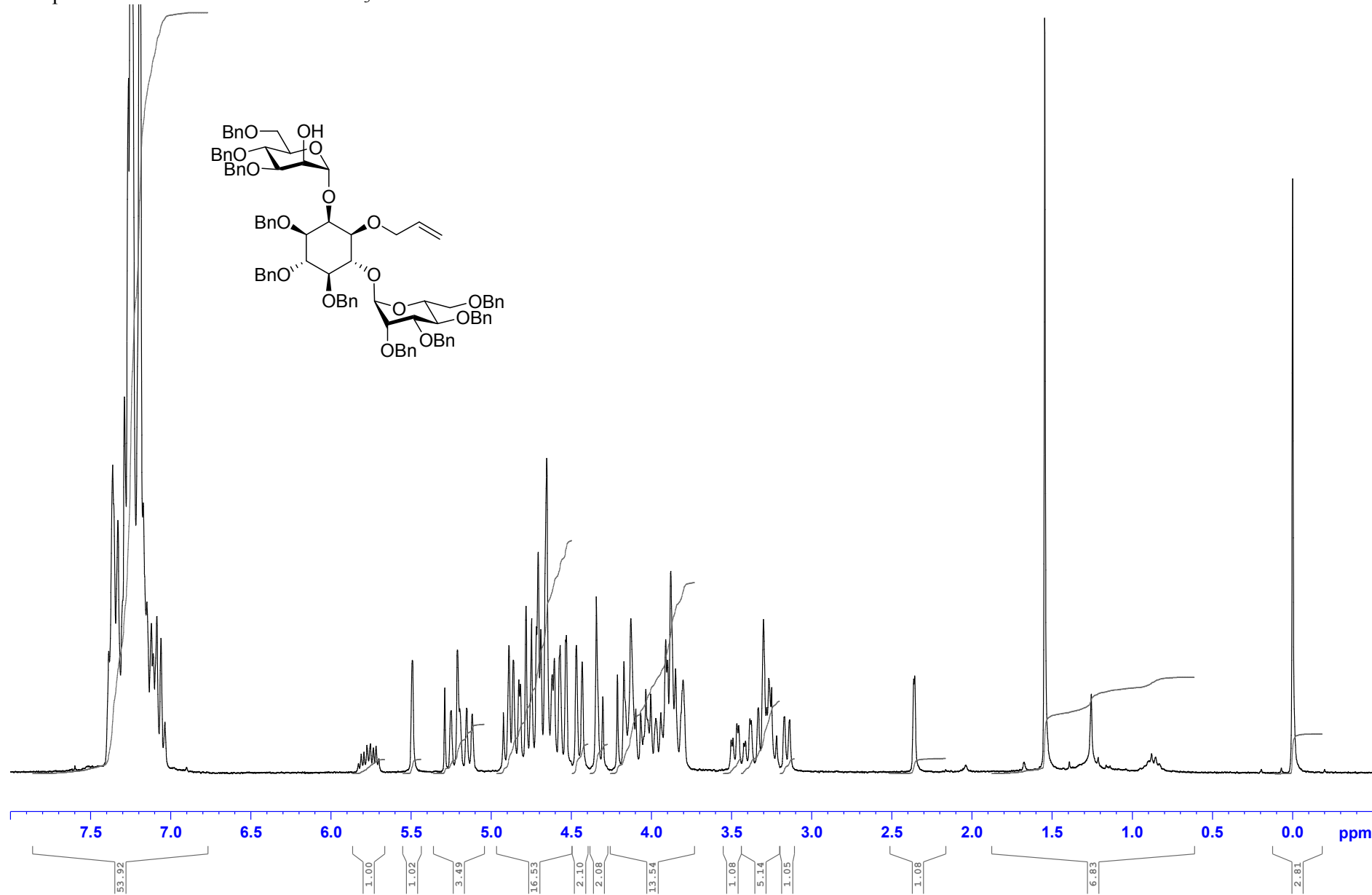
Compound **25** 300 MHz  $^1\text{H}$  NMR  $\text{CDCl}_3$



Compound **25** 75 MHz  $^{13}\text{C}$  NMR  $\text{CDCl}_3$

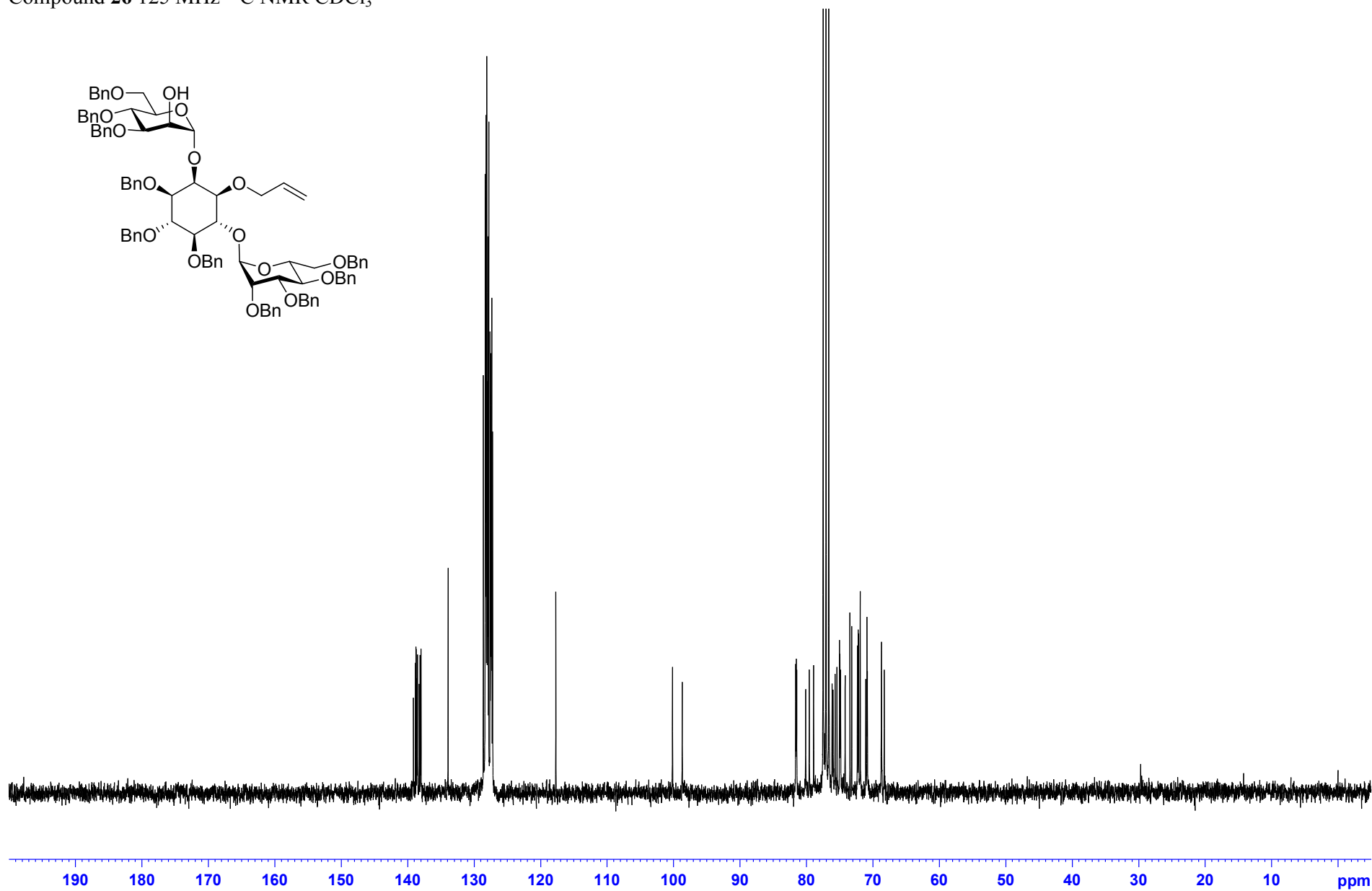
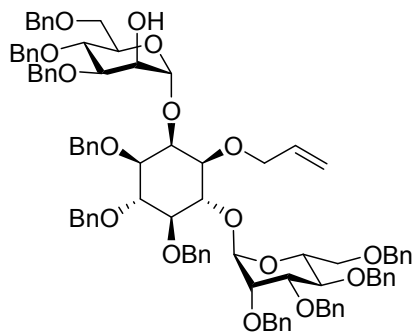


Compound **26** 500 MHz  $^1\text{H}$  NMR  $\text{CDCl}_3$

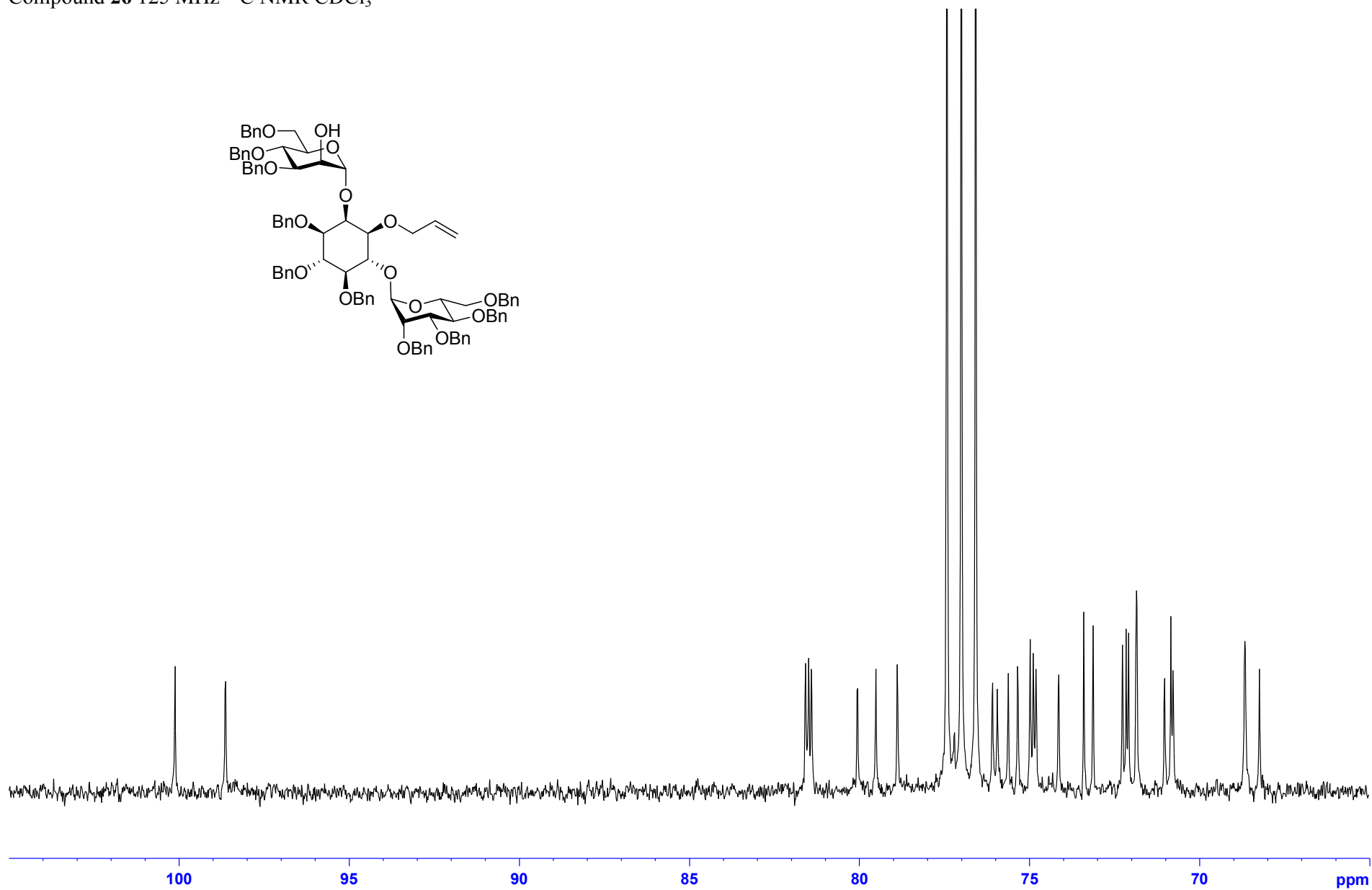
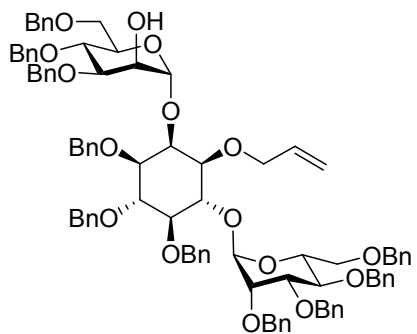




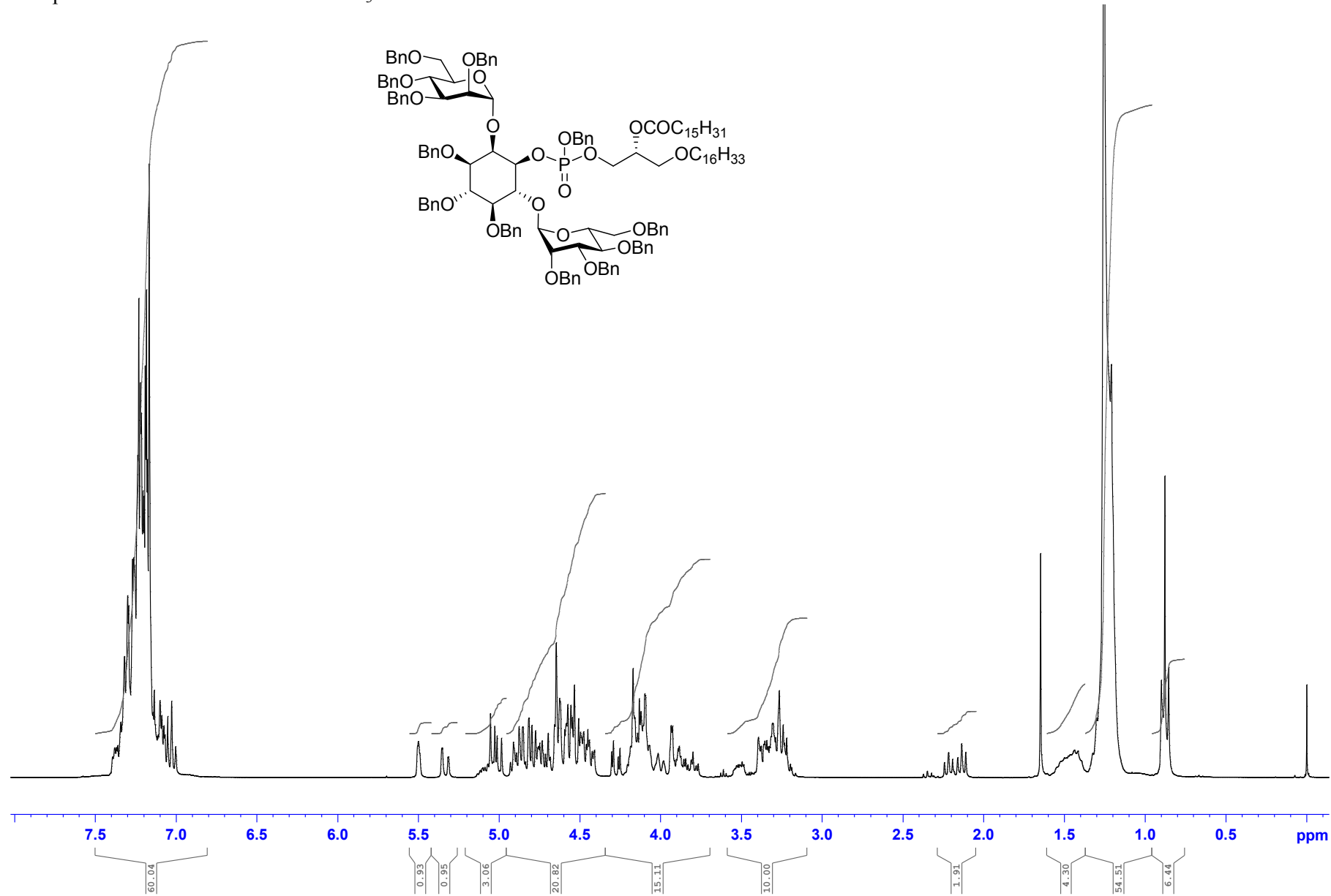
Compound **26** 125 MHz  $^{13}\text{C}$  NMR  $\text{CDCl}_3$



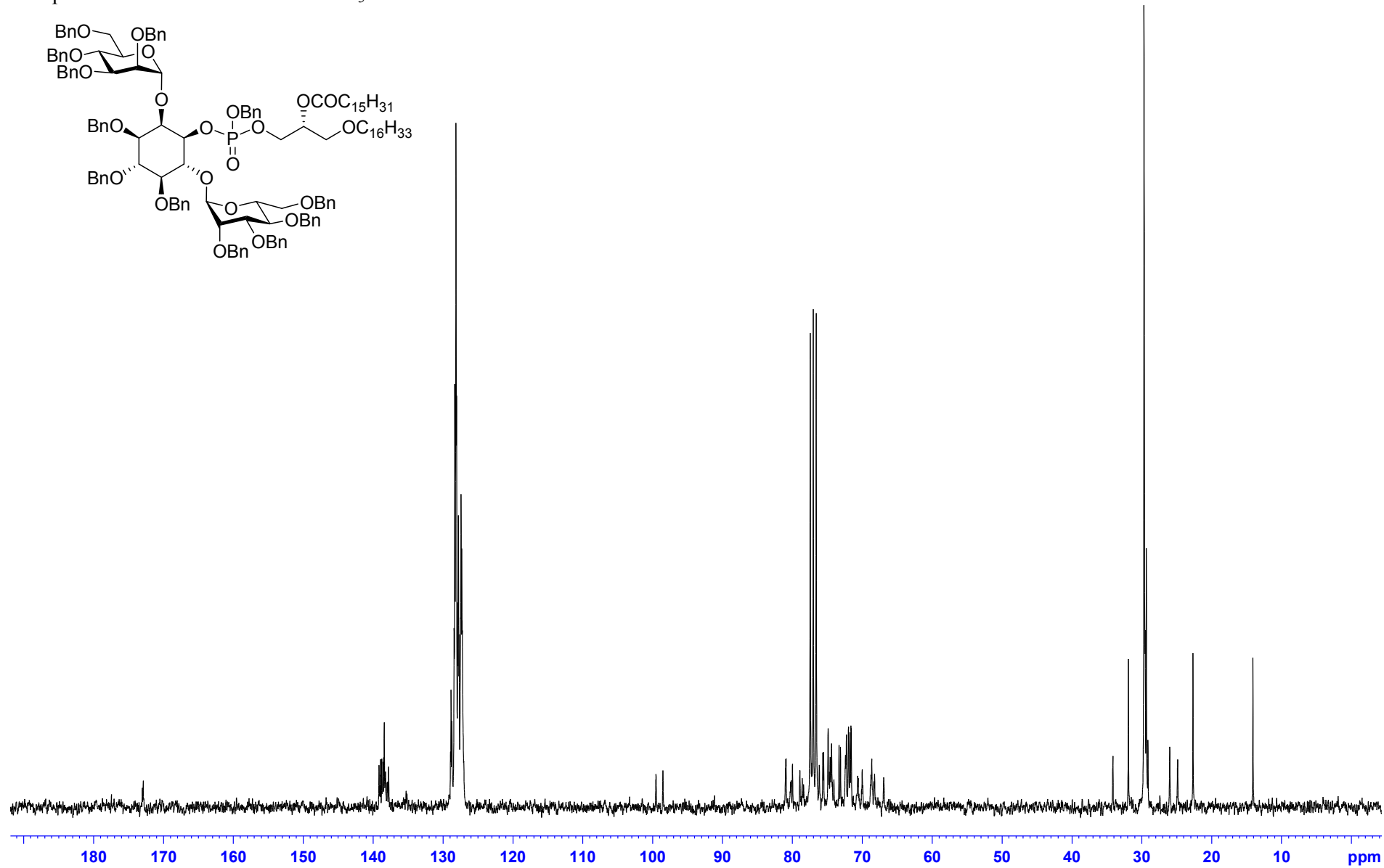
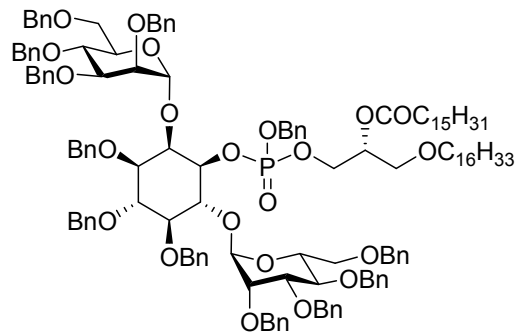
Compound **26** 125 MHz  $^{13}\text{C}$  NMR  $\text{CDCl}_3$



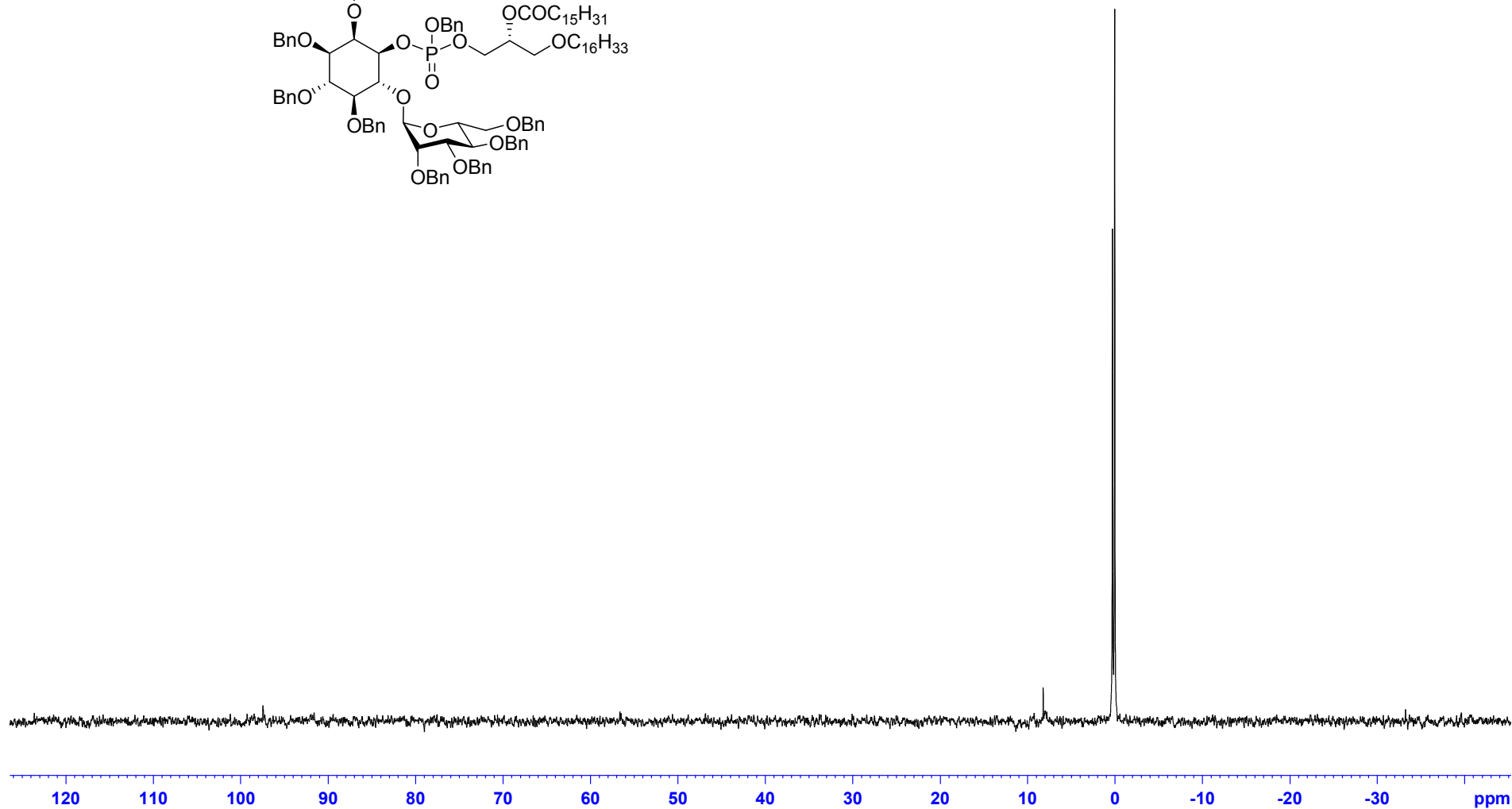
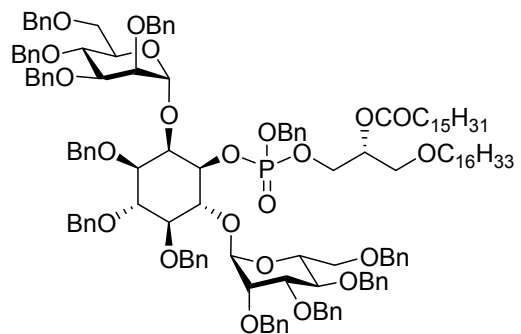
Compound **29** 300 MHz  $^1\text{H}$  NMR  $\text{CDCl}_3$



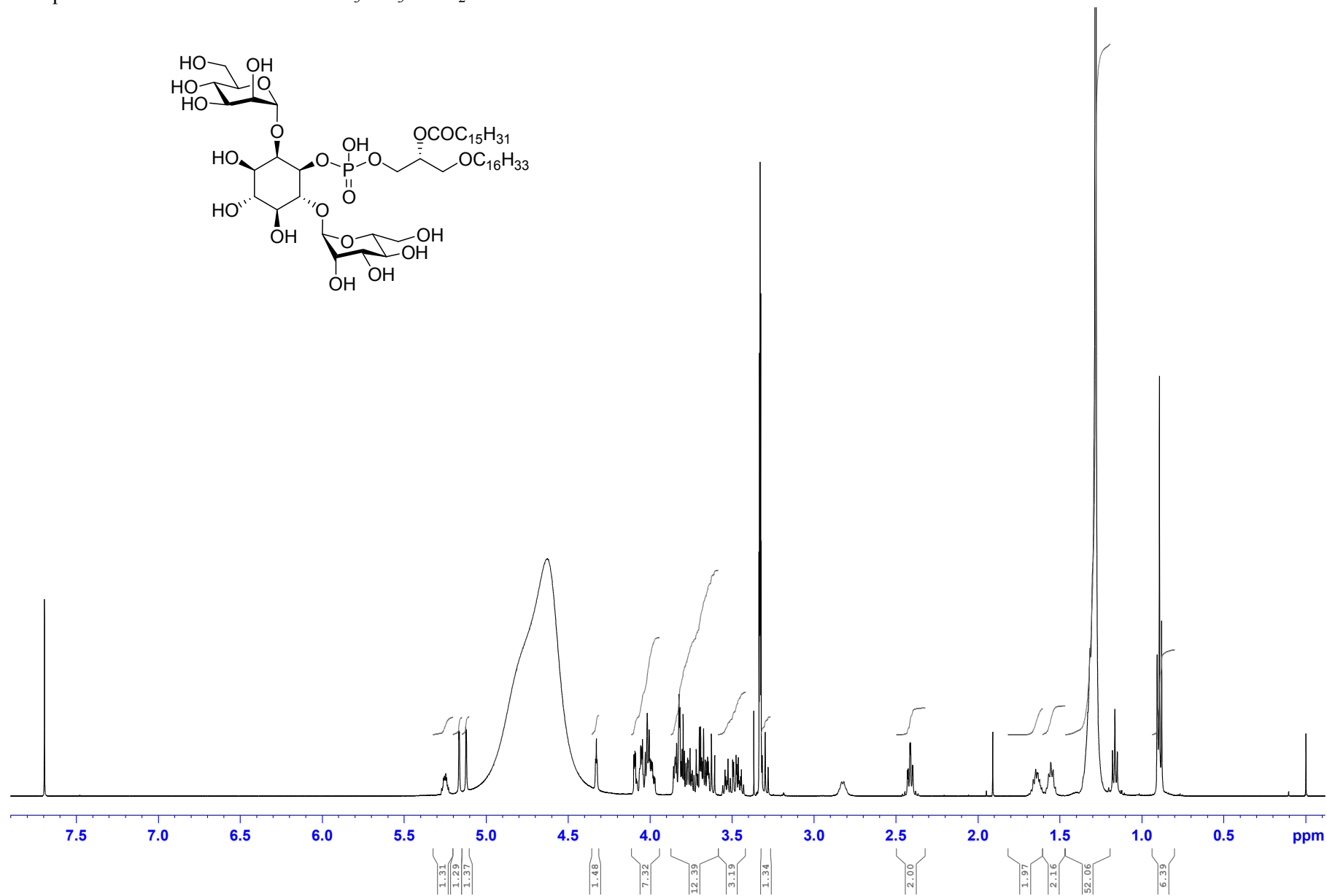
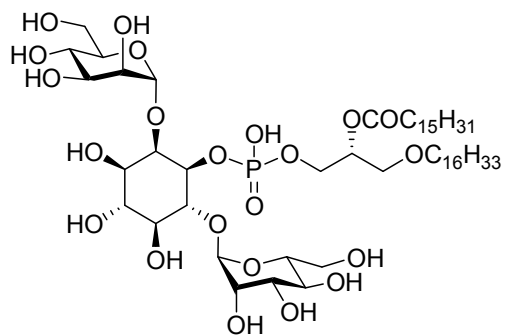
Compound **29** 75 MHz  $^{13}\text{C}$  NMR  $\text{CDCl}_3$



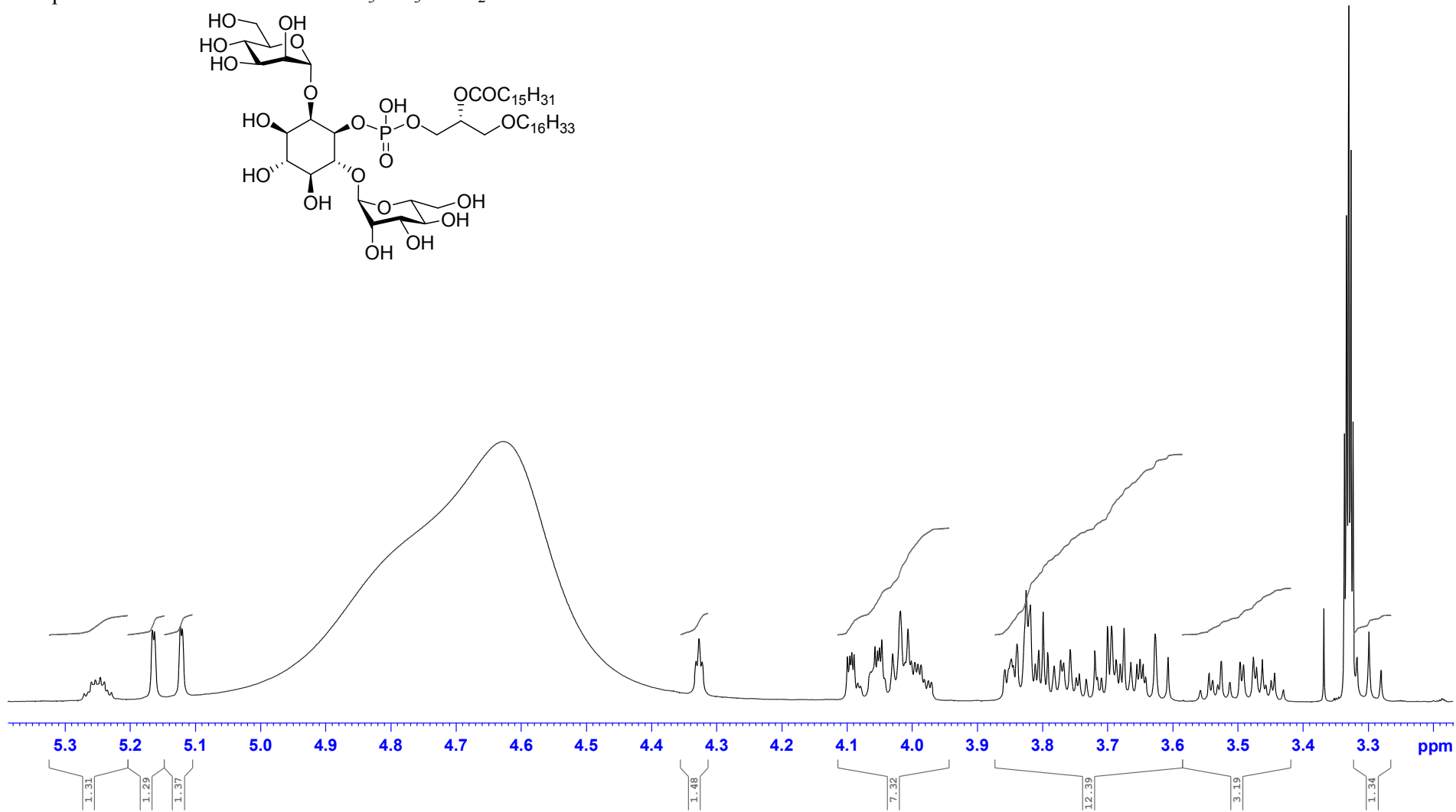
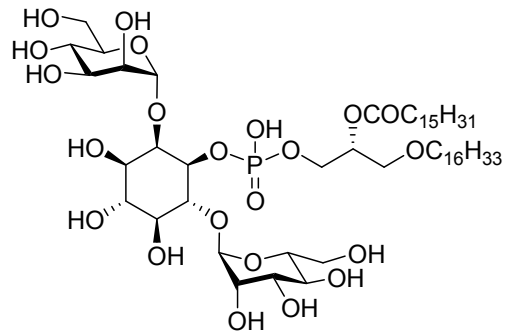
Compound **29** 125 MHz  $^{31}\text{P}$  NMR  $\text{CDCl}_3$



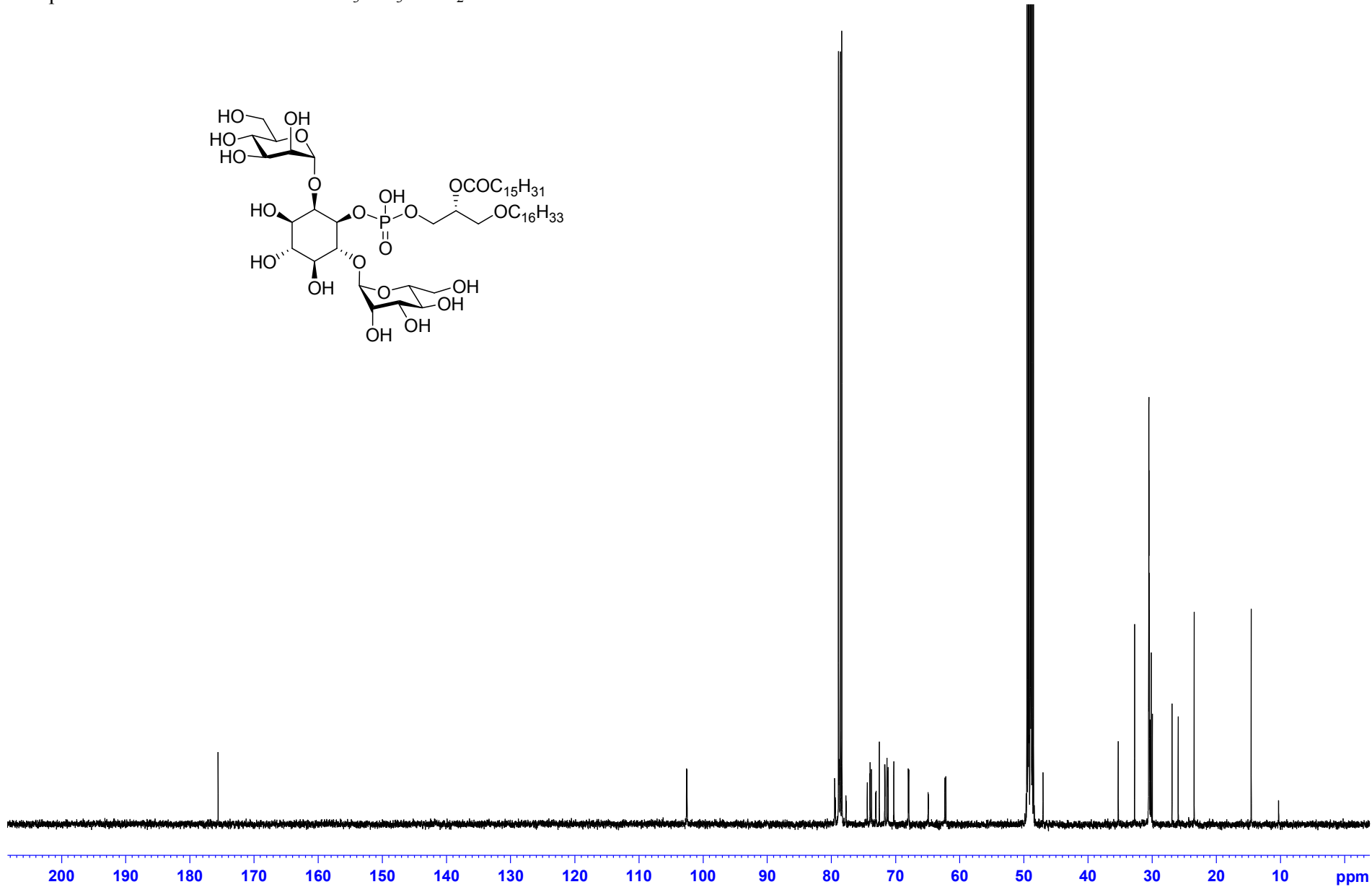
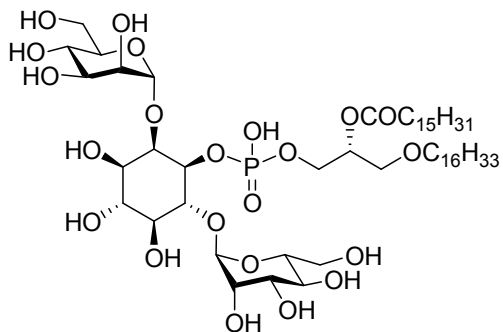
Compound 4 500 MHz  $^1\text{H}$  NMR  $\text{CDCl}_3/\text{CD}_3\text{OD}/\text{D}_2\text{O}$  70:40:6



Compound 4 500 MHz  $^1\text{H}$  NMR  $\text{CDCl}_3/\text{CD}_3\text{OD}/\text{D}_2\text{O}$  70:40:6

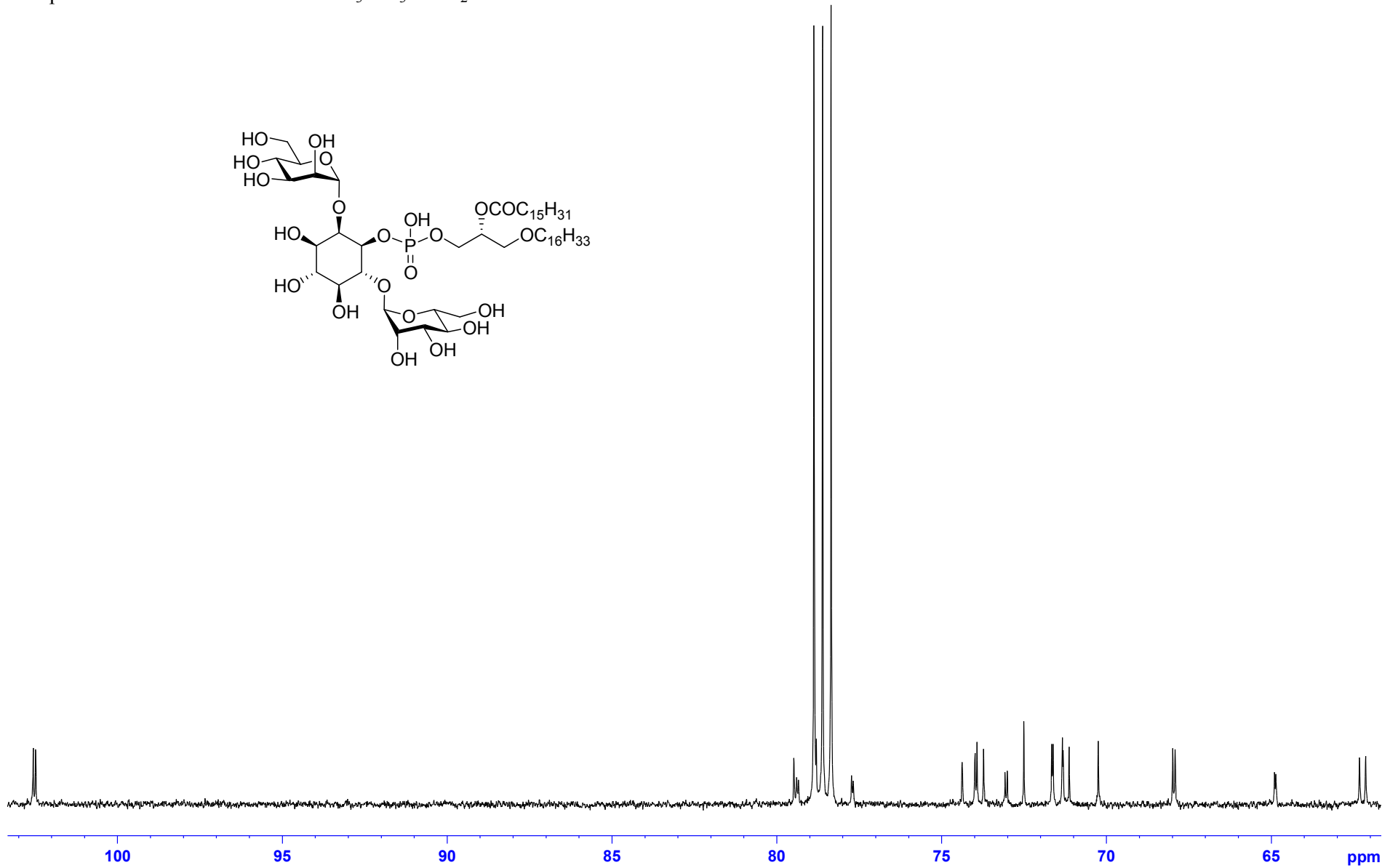
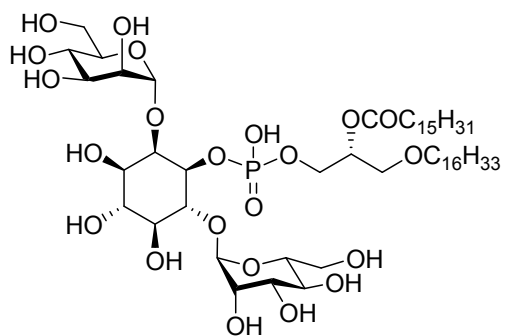


Compound 4 126 MHz  $^{13}\text{C}$  NMR  $\text{CDCl}_3/\text{CD}_3\text{OD}/\text{D}_2\text{O}$  70:40:6

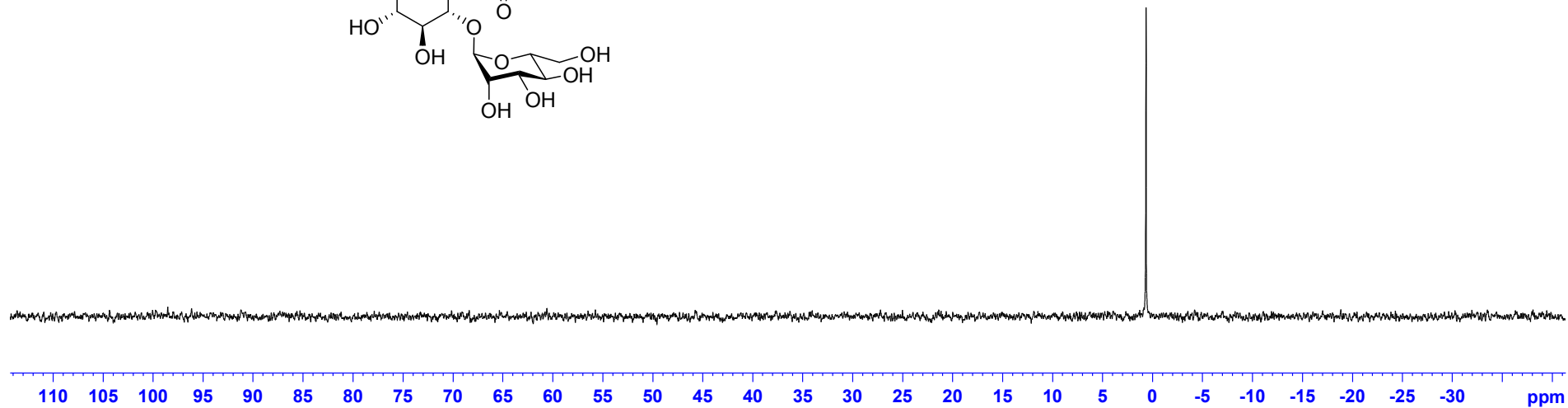
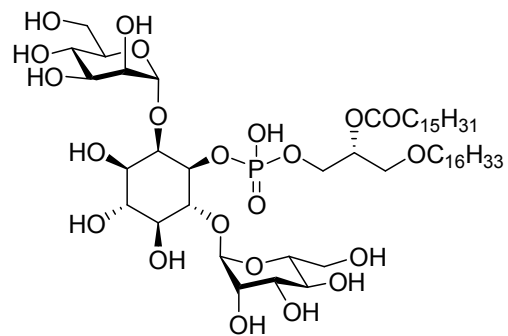




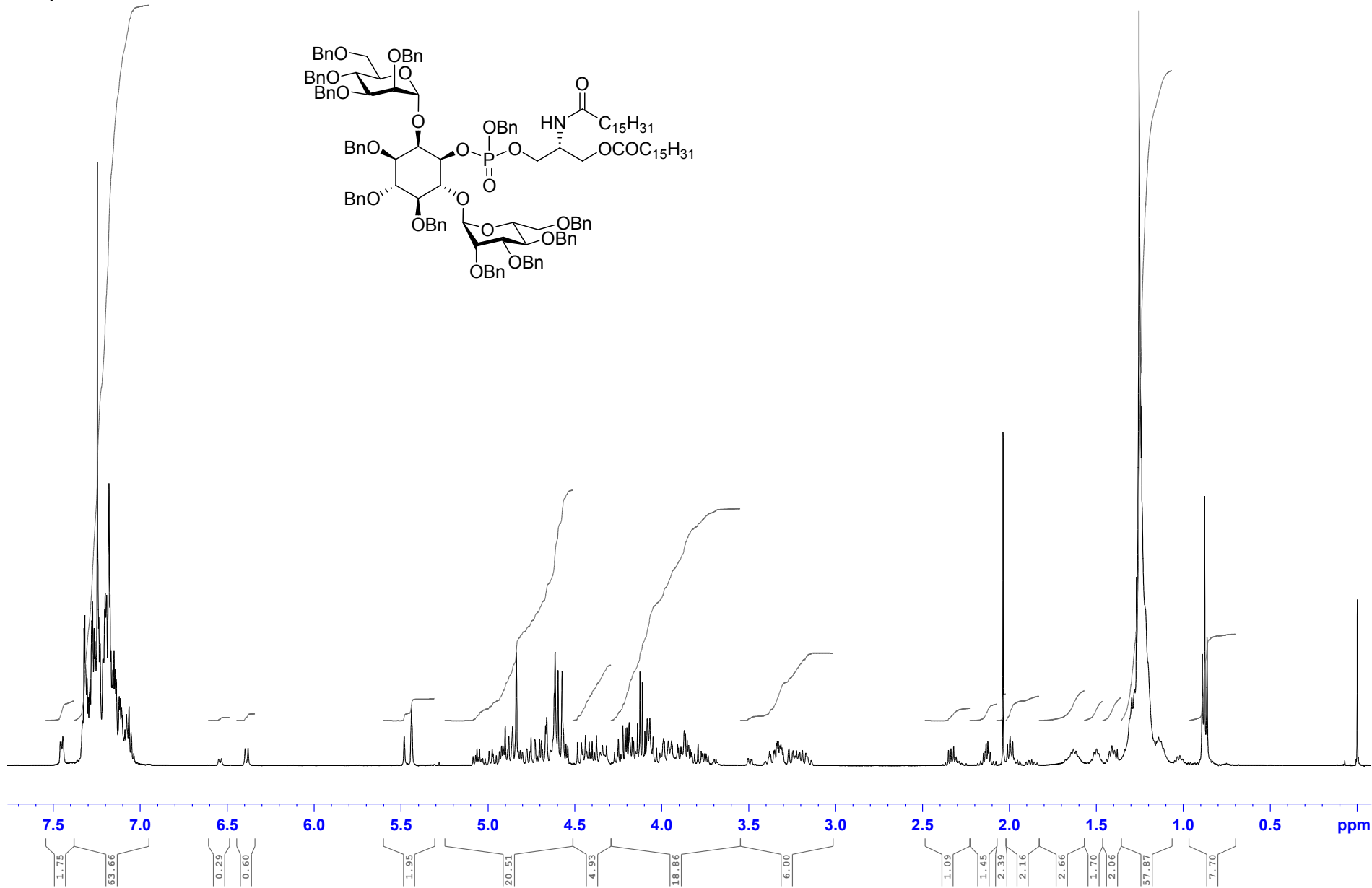
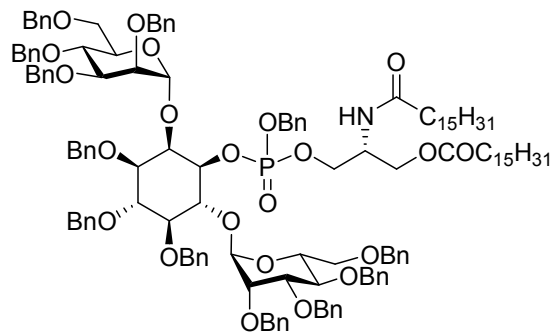
Compound 4 126 MHz  $^{13}\text{C}$  NMR  $\text{CDCl}_3/\text{CD}_3\text{OD}/\text{D}_2\text{O}$  70:40:6



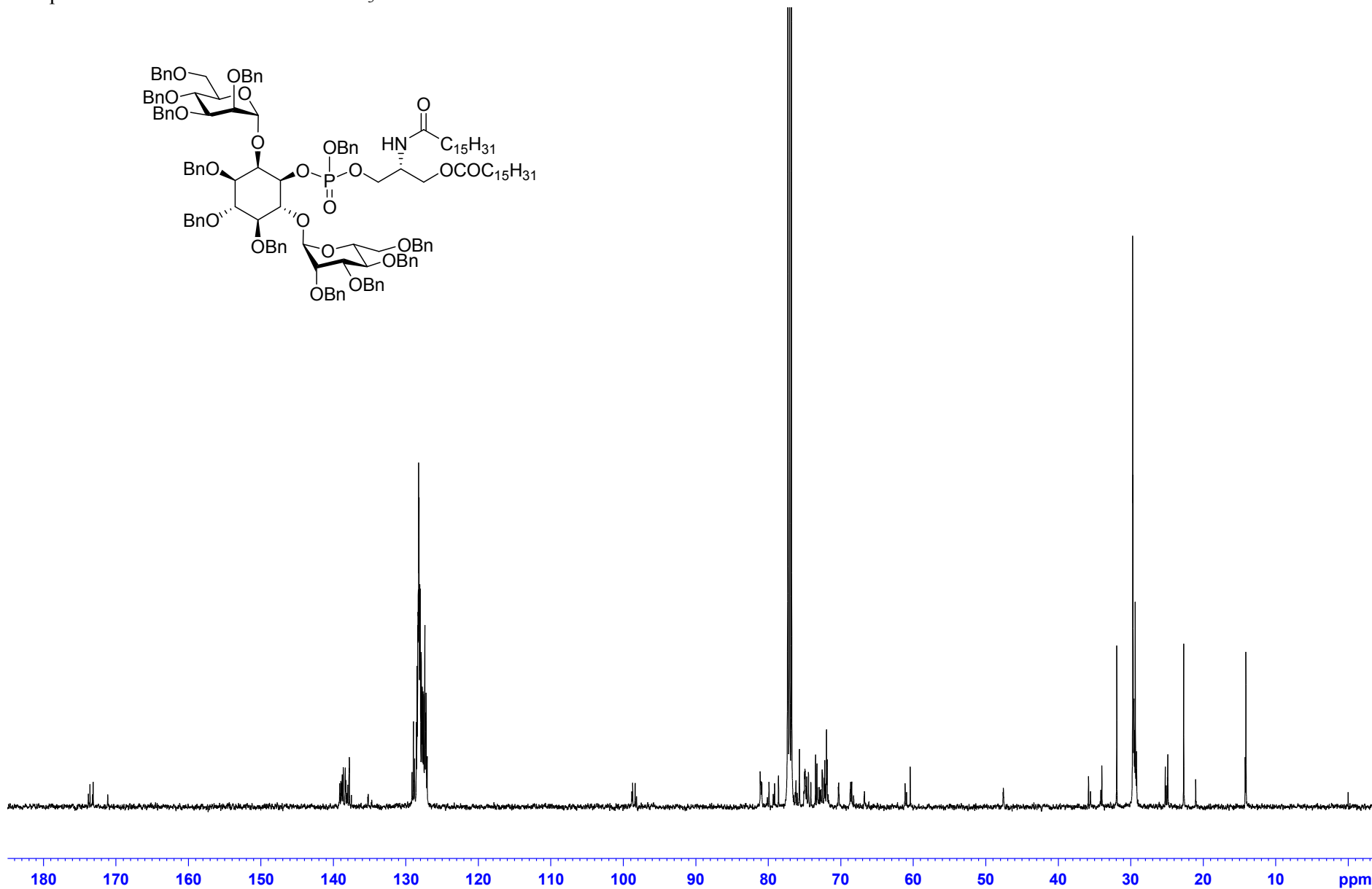
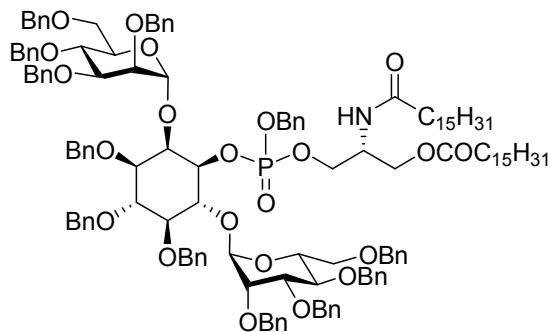
Compound 4 121 MHz  $^{31}\text{P}$  NMR  $\text{CDCl}_3/\text{CD}_3\text{OD}/\text{D}_2\text{O}$  70:40:6



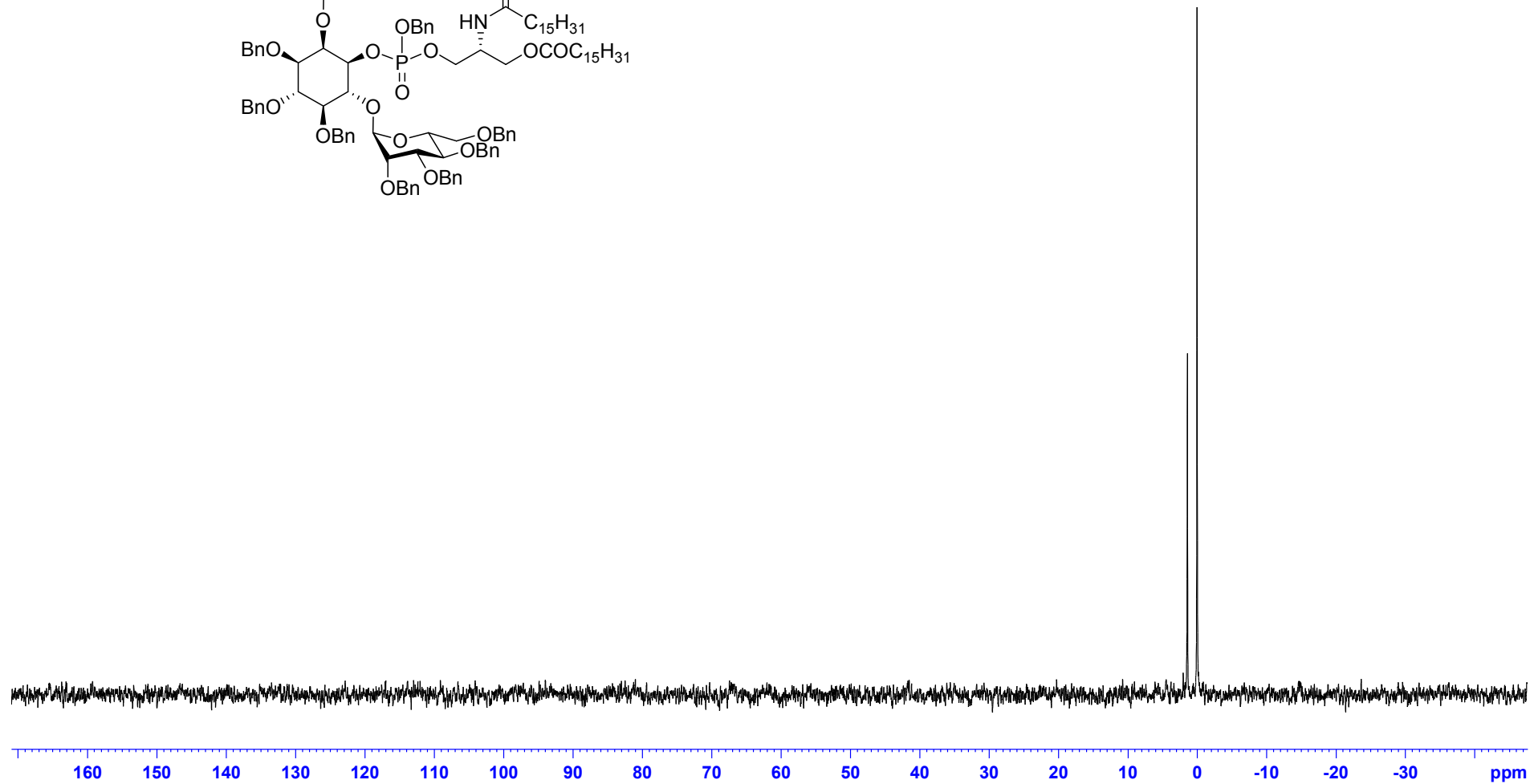
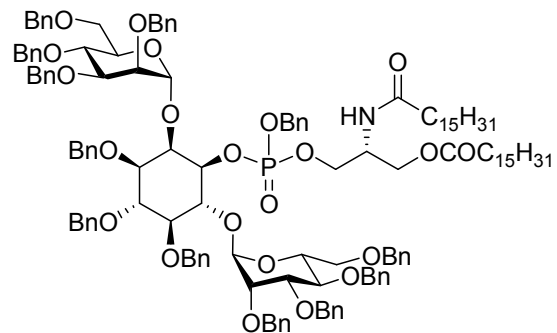
Compound **30** 500 MHz  $^1\text{H}$  NMR  $\text{CDCl}_3$



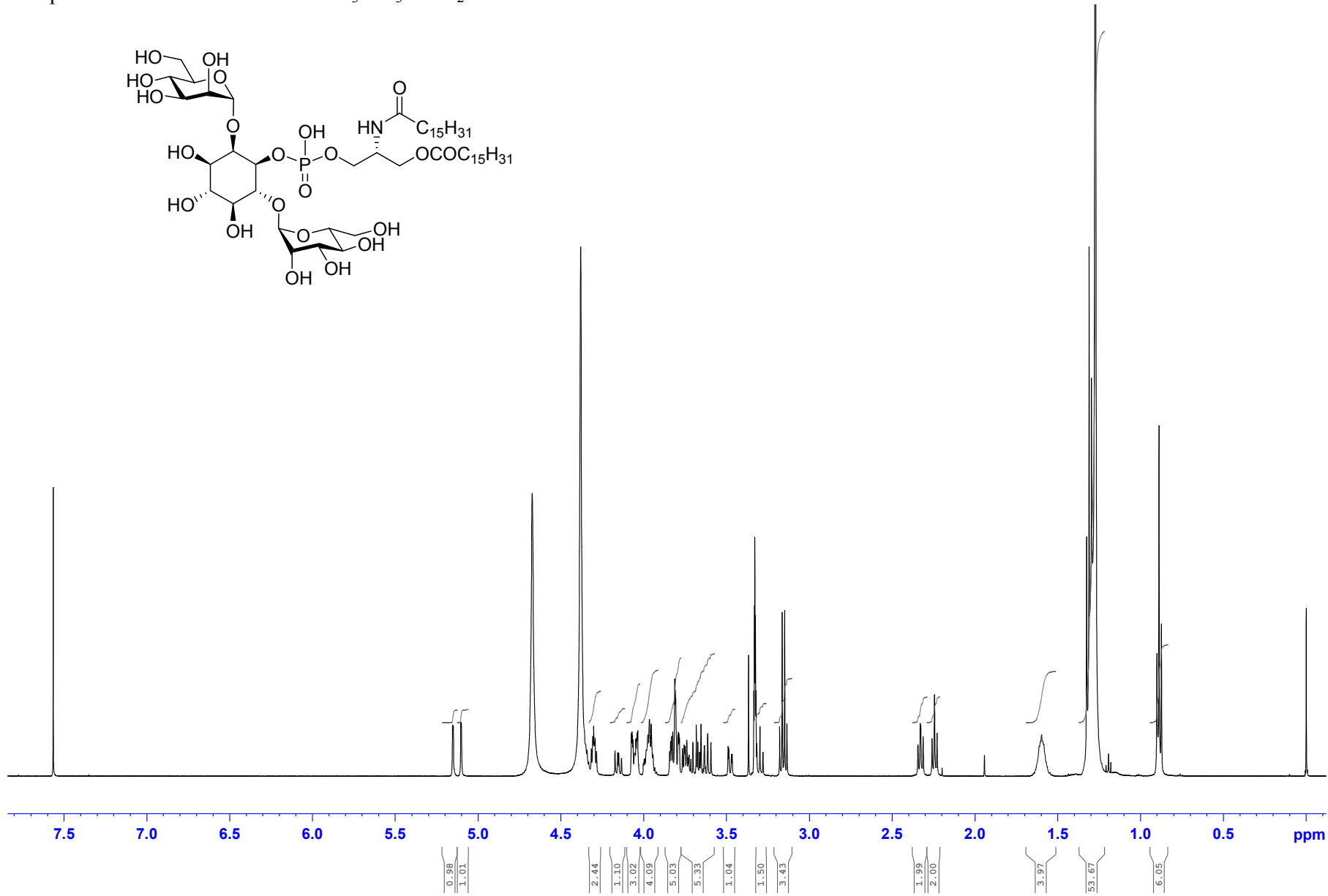
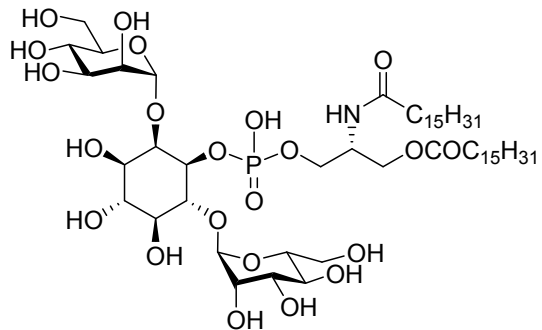
Compound **30** 126 MHz  $^{13}\text{C}$  NMR  $\text{CDCl}_3$



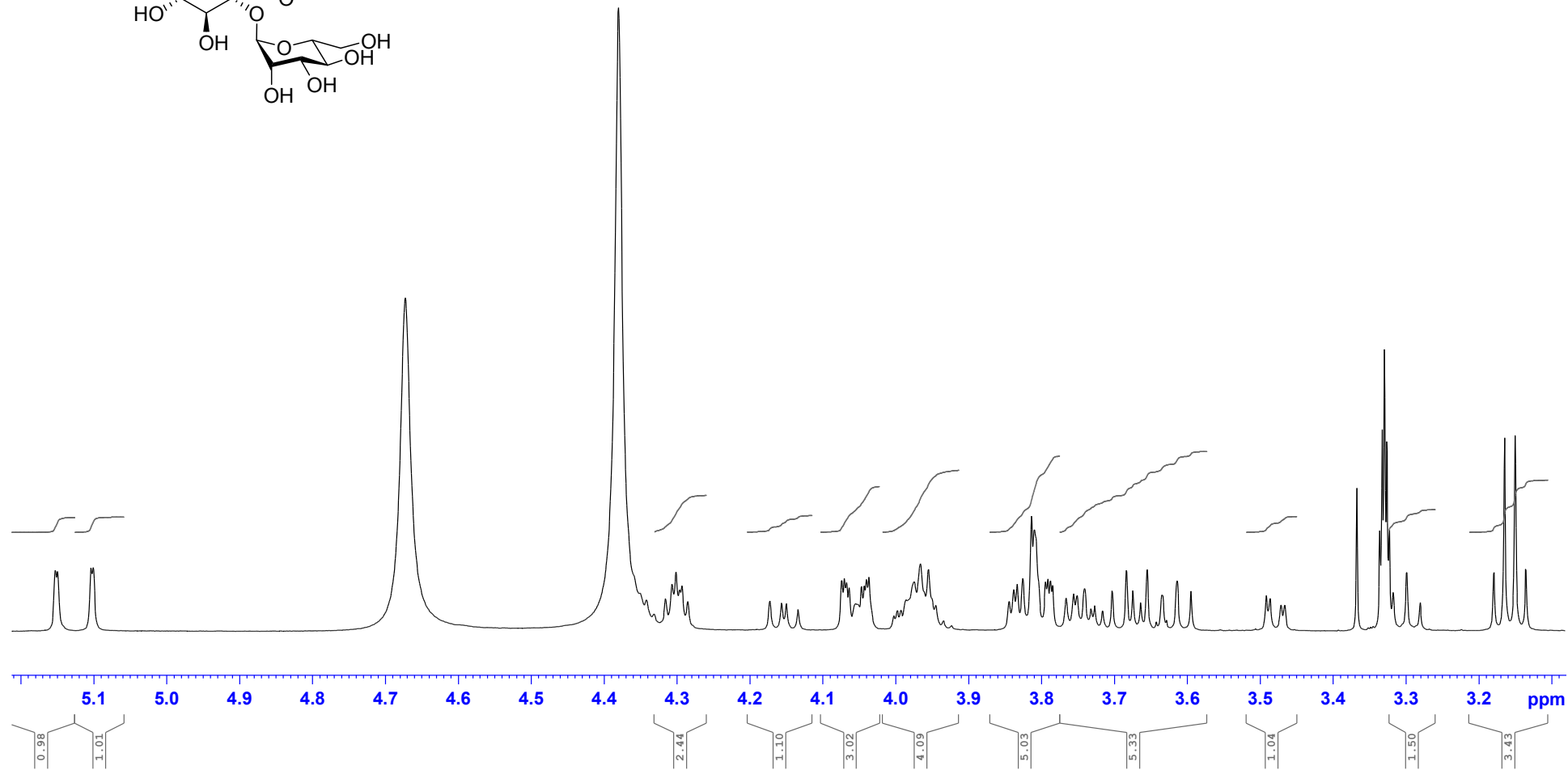
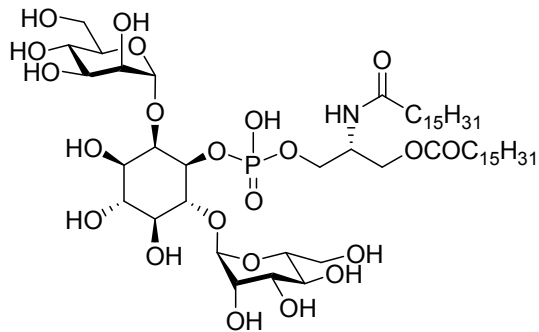
Compound **30** 121 MHz  $^{31}\text{P}$  NMR  $\text{CDCl}_3$



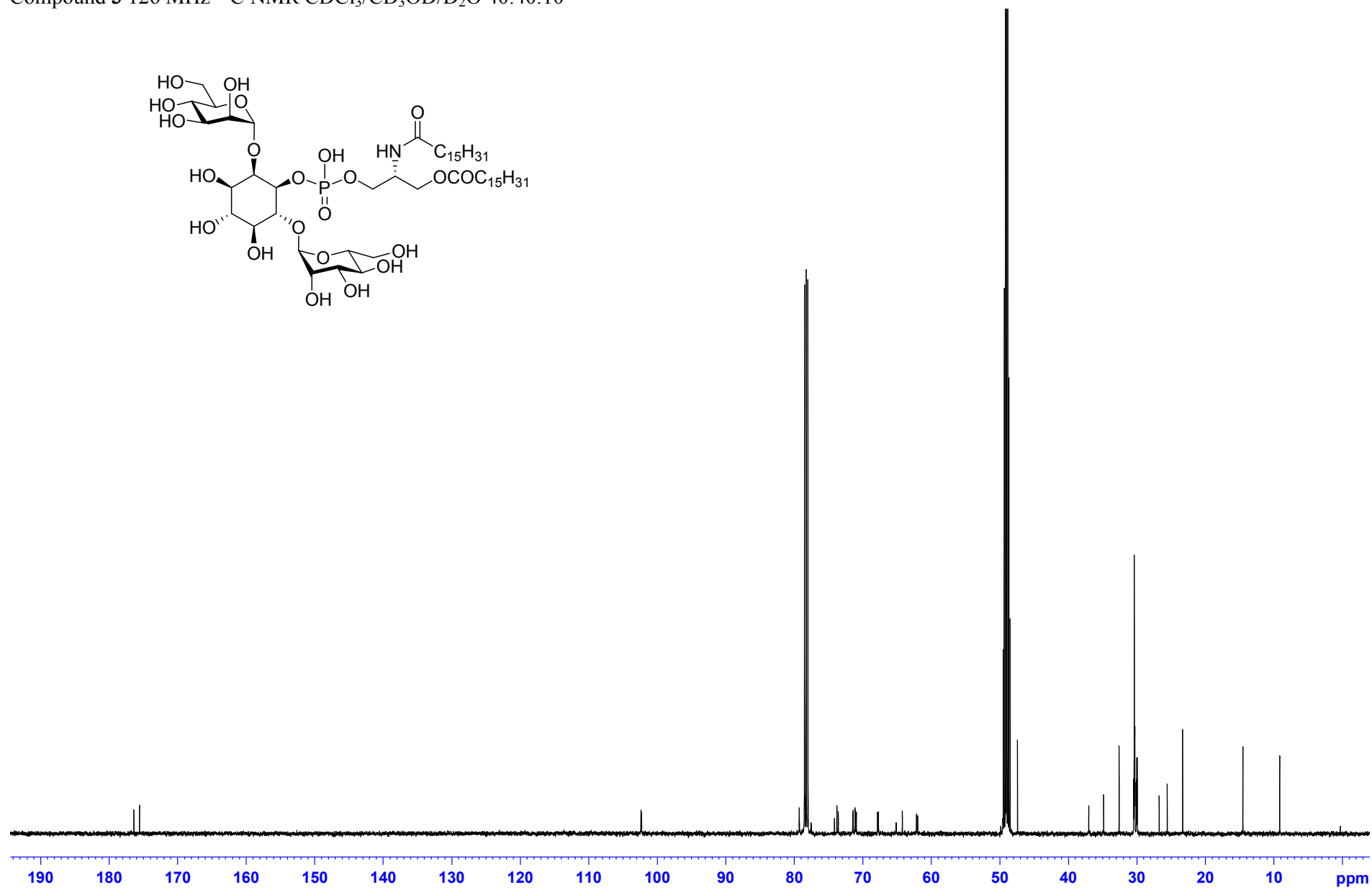
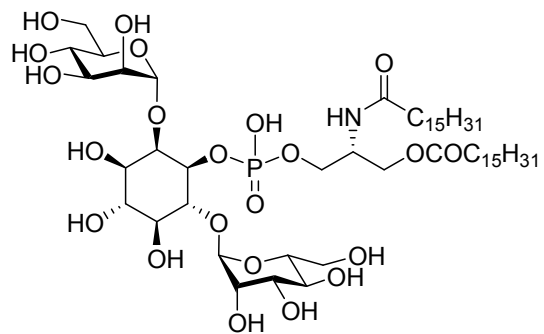
Compound 3 500 MHz  $^1\text{H}$  NMR  $\text{CDCl}_3/\text{CD}_3\text{OD}/\text{D}_2\text{O}$  40:40:10



Compound 3 500 MHz  $^1\text{H}$  NMR  $\text{CDCl}_3/\text{CD}_3\text{OD}/\text{D}_2\text{O}$  40:40:10

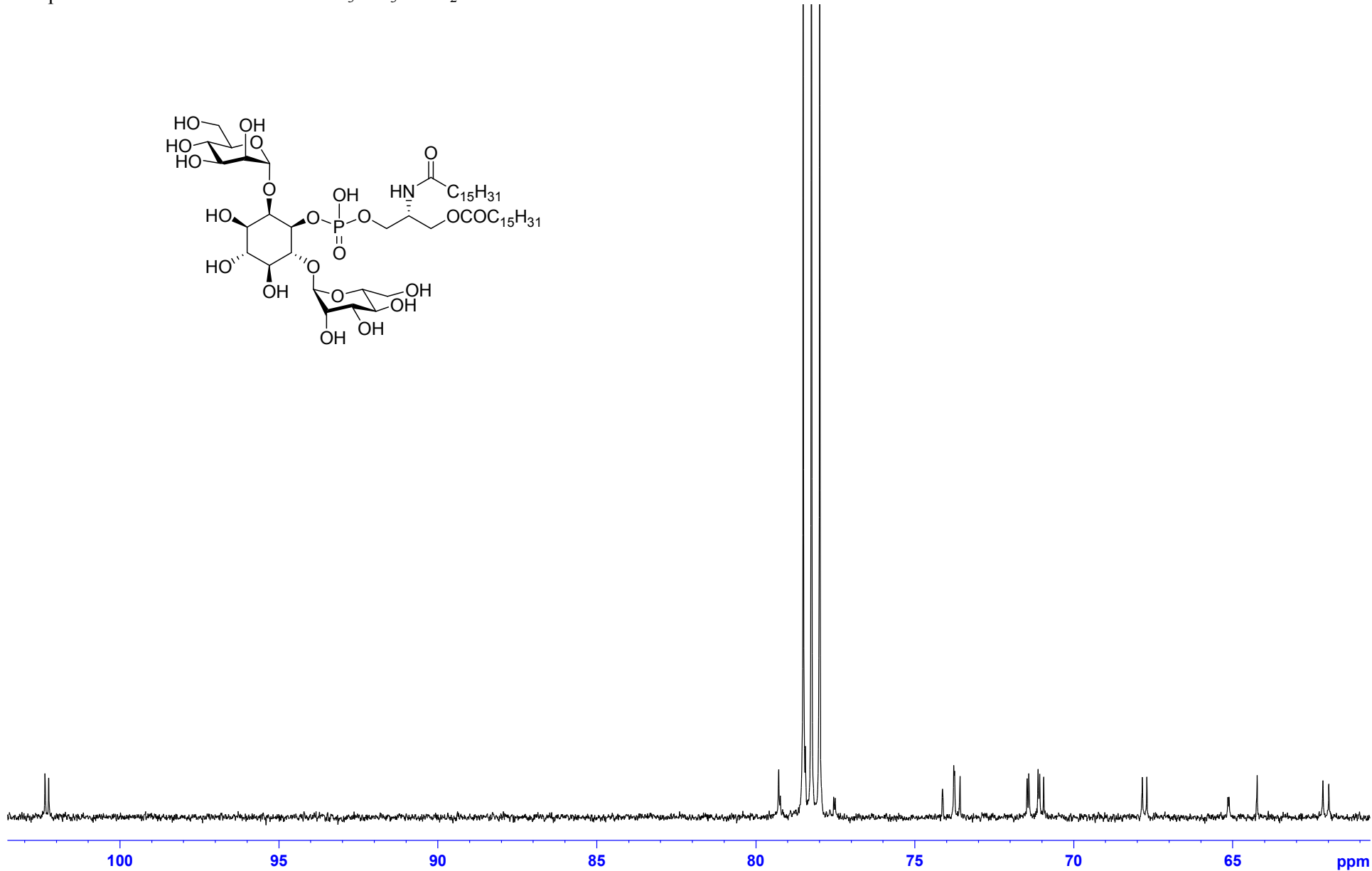
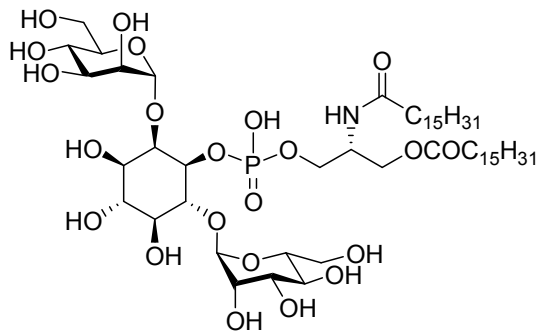


Compound **3** 126 MHz  $^{13}\text{C}$  NMR  $\text{CDCl}_3/\text{CD}_3\text{OD}/\text{D}_2\text{O}$  40:40:10

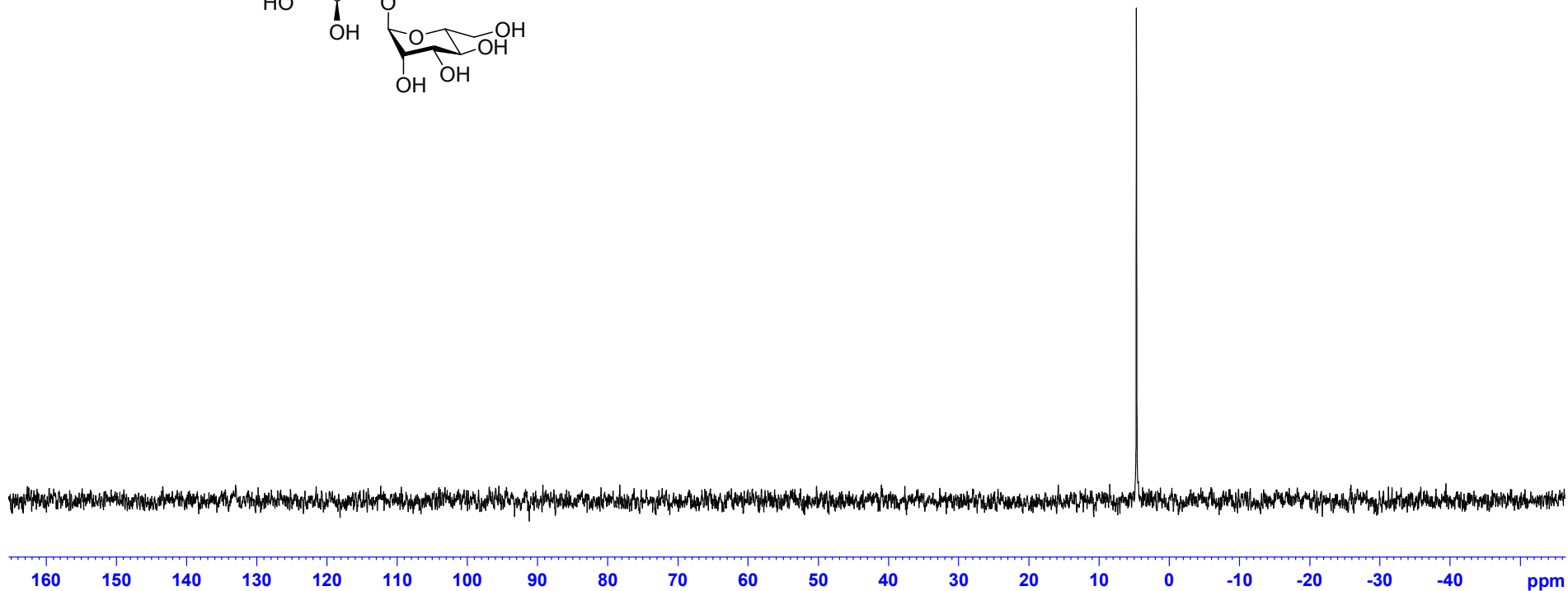
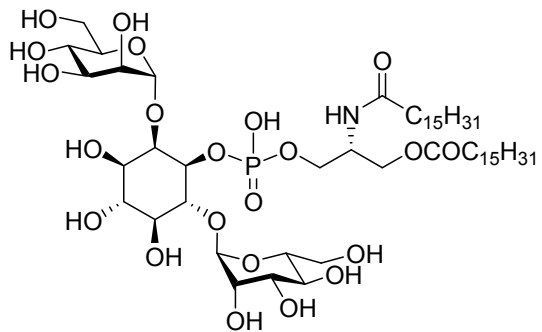




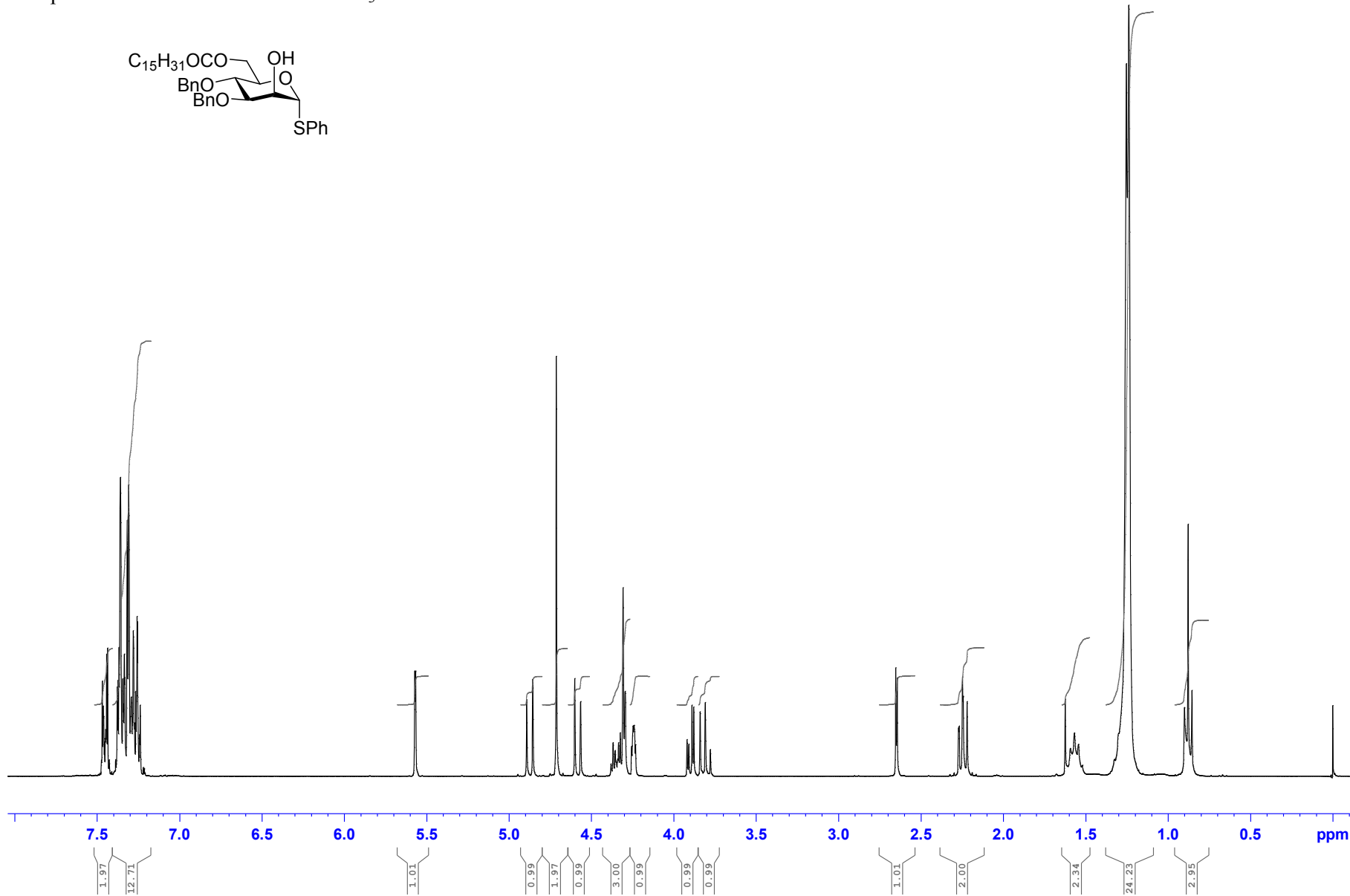
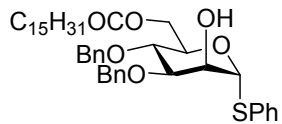
Compound **3** 126 MHz  $^{13}\text{C}$  NMR  $\text{CDCl}_3/\text{CD}_3\text{OD}/\text{D}_2\text{O}$  40:40:10



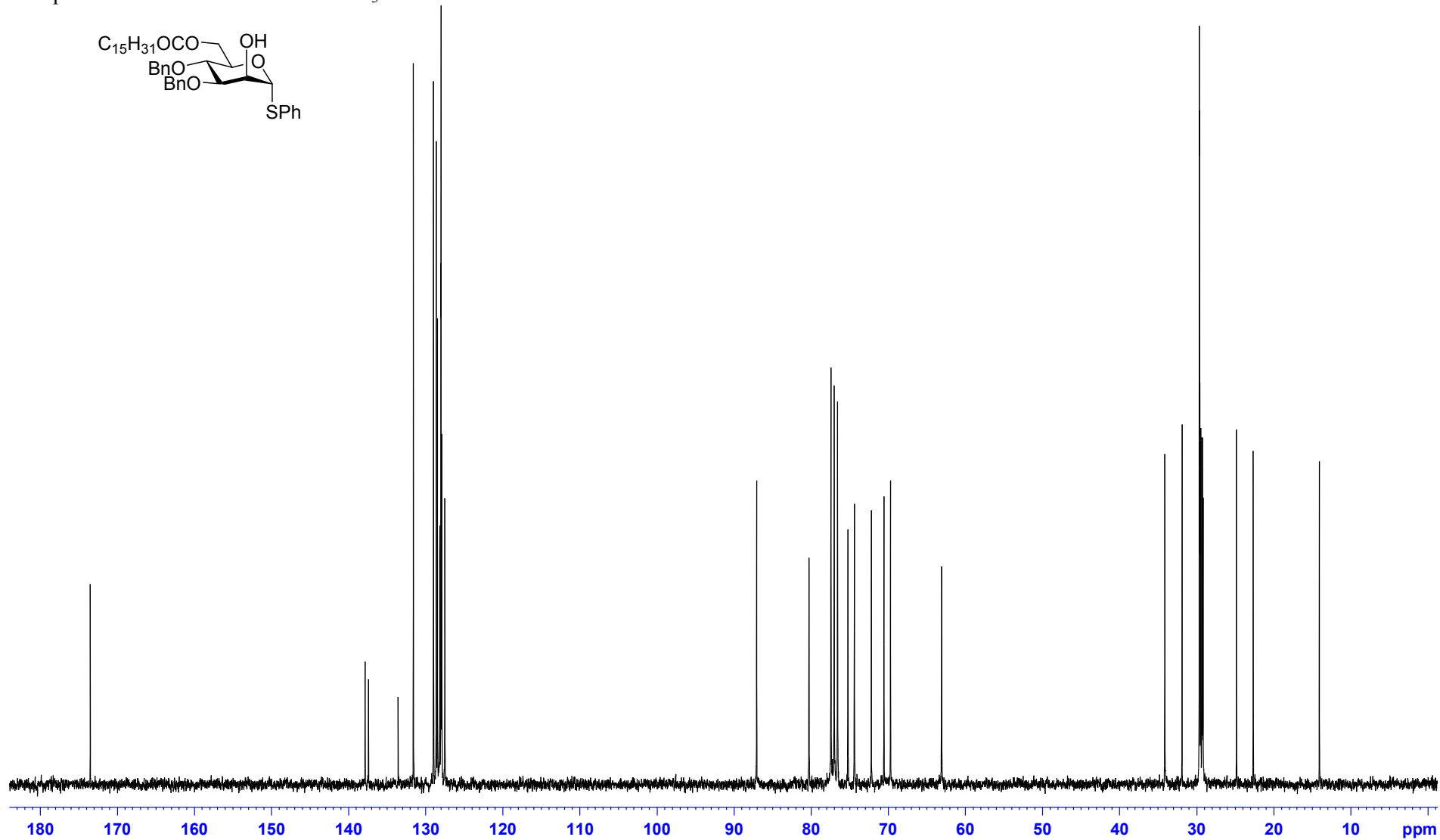
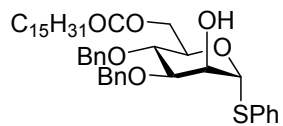
Compound **3** 121 MHz  $^{31}\text{P}$  NMR  $\text{CDCl}_3/\text{CD}_3\text{OD}/\text{D}_2\text{O}$  40:40:10



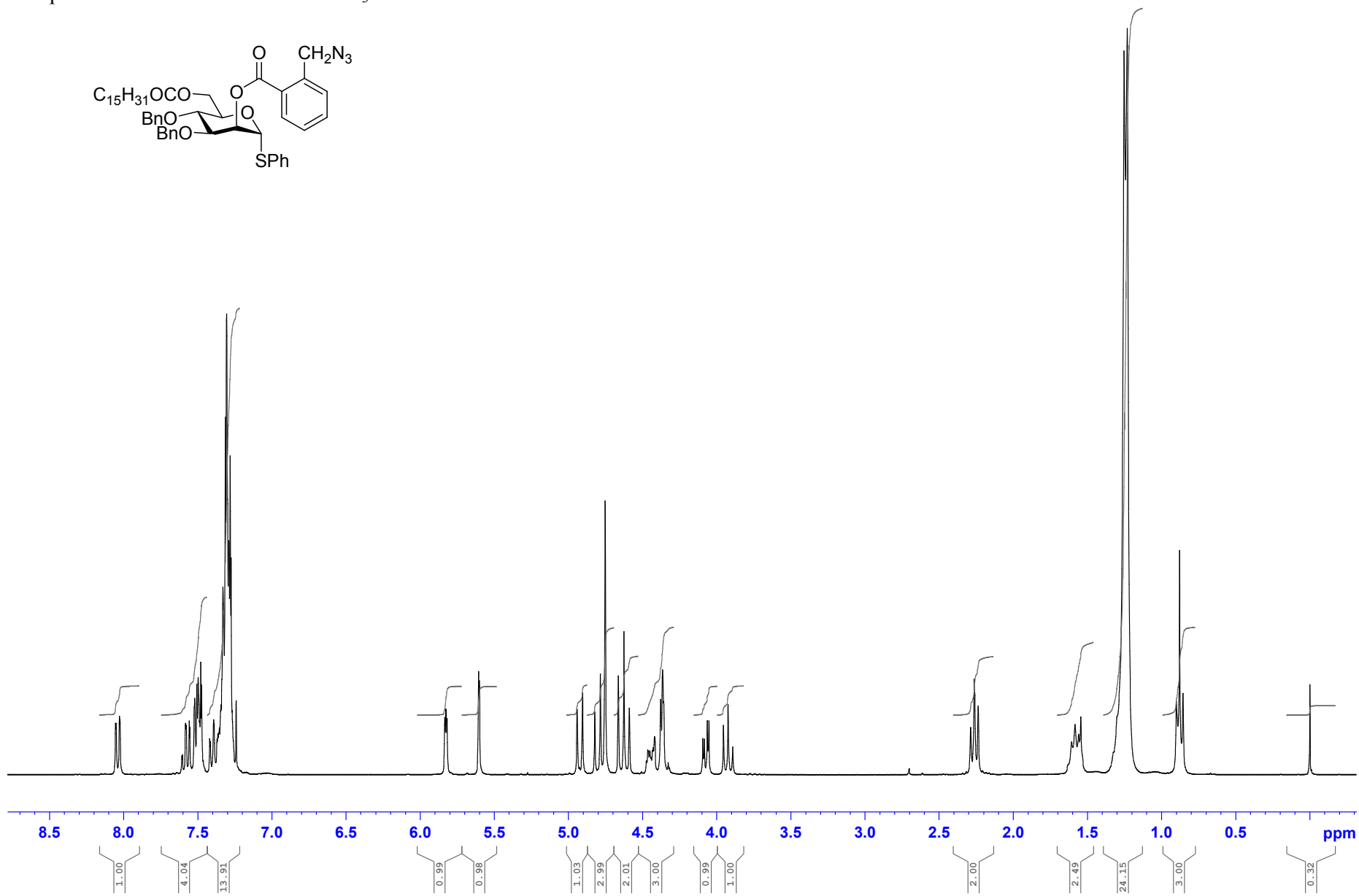
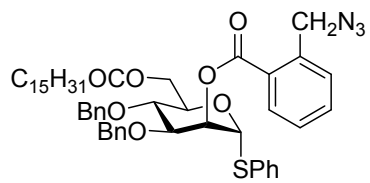
Compound **33** 300 MHz  $^1\text{H}$  NMR  $\text{CDCl}_3$



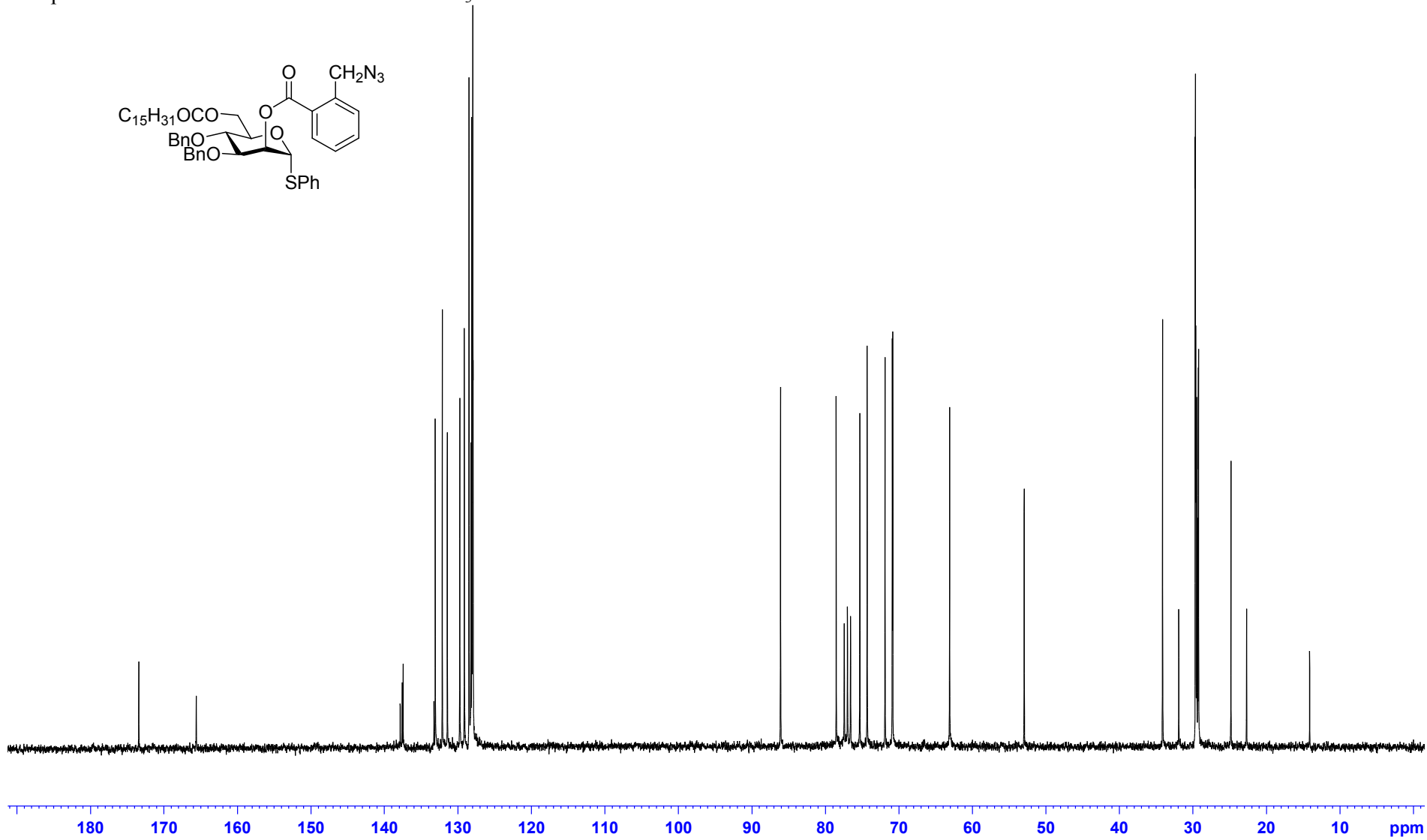
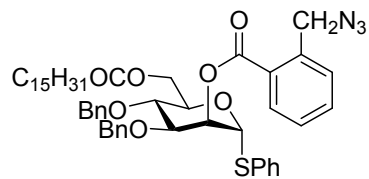
Compound **33** 75 MHz  $^{13}\text{C}$  NMR  $\text{CDCl}_3$



Compound **31** 300 MHz  $^1\text{H}$  NMR  $\text{CDCl}_3$



Compound **31** cmh653.1 75 MHz  $^{13}\text{C}$  NMR  $\text{CDCl}_3$

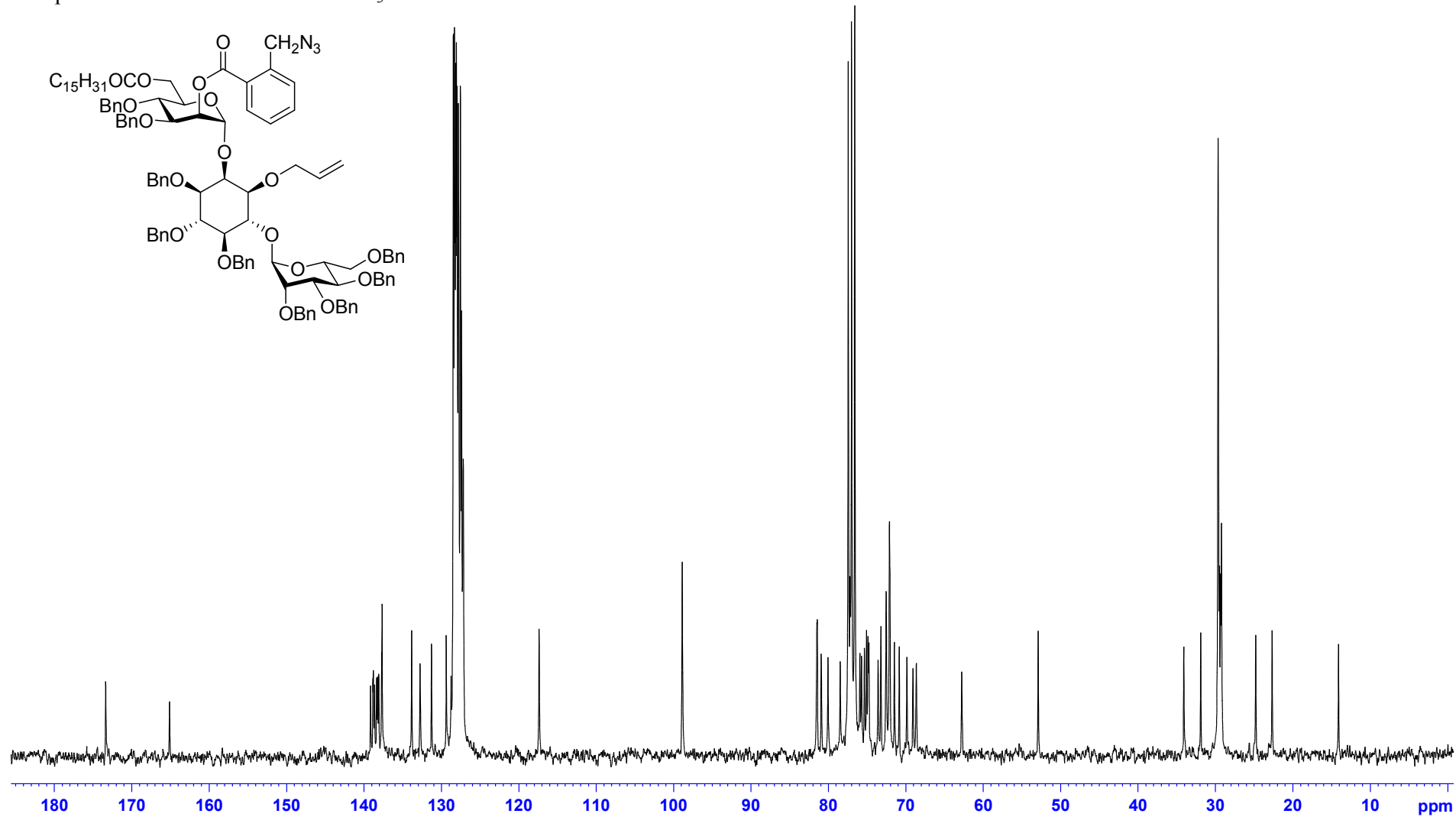
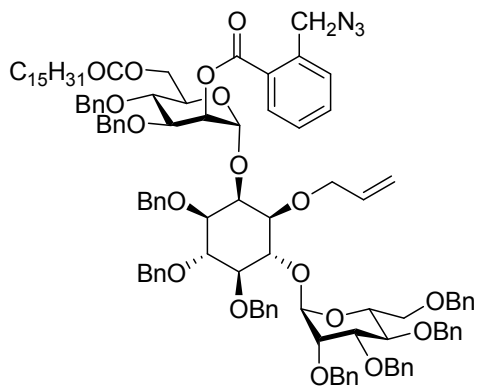




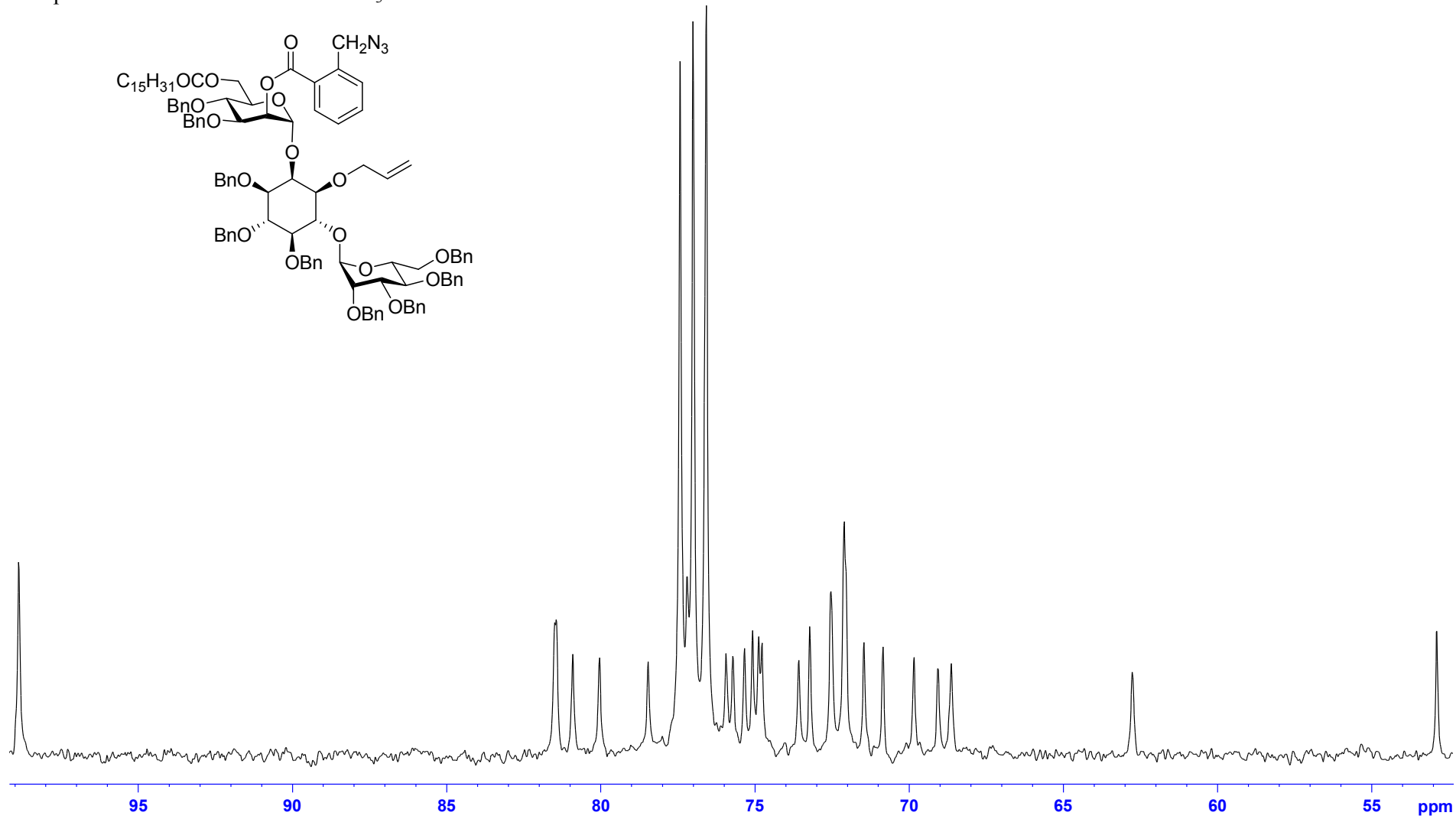
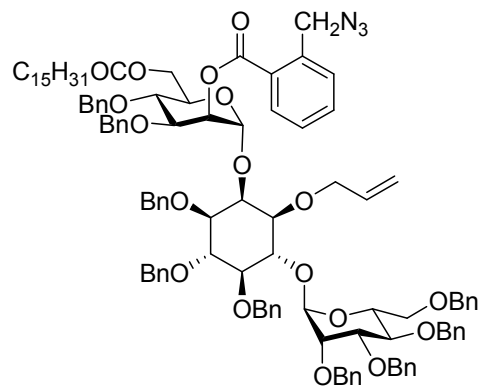




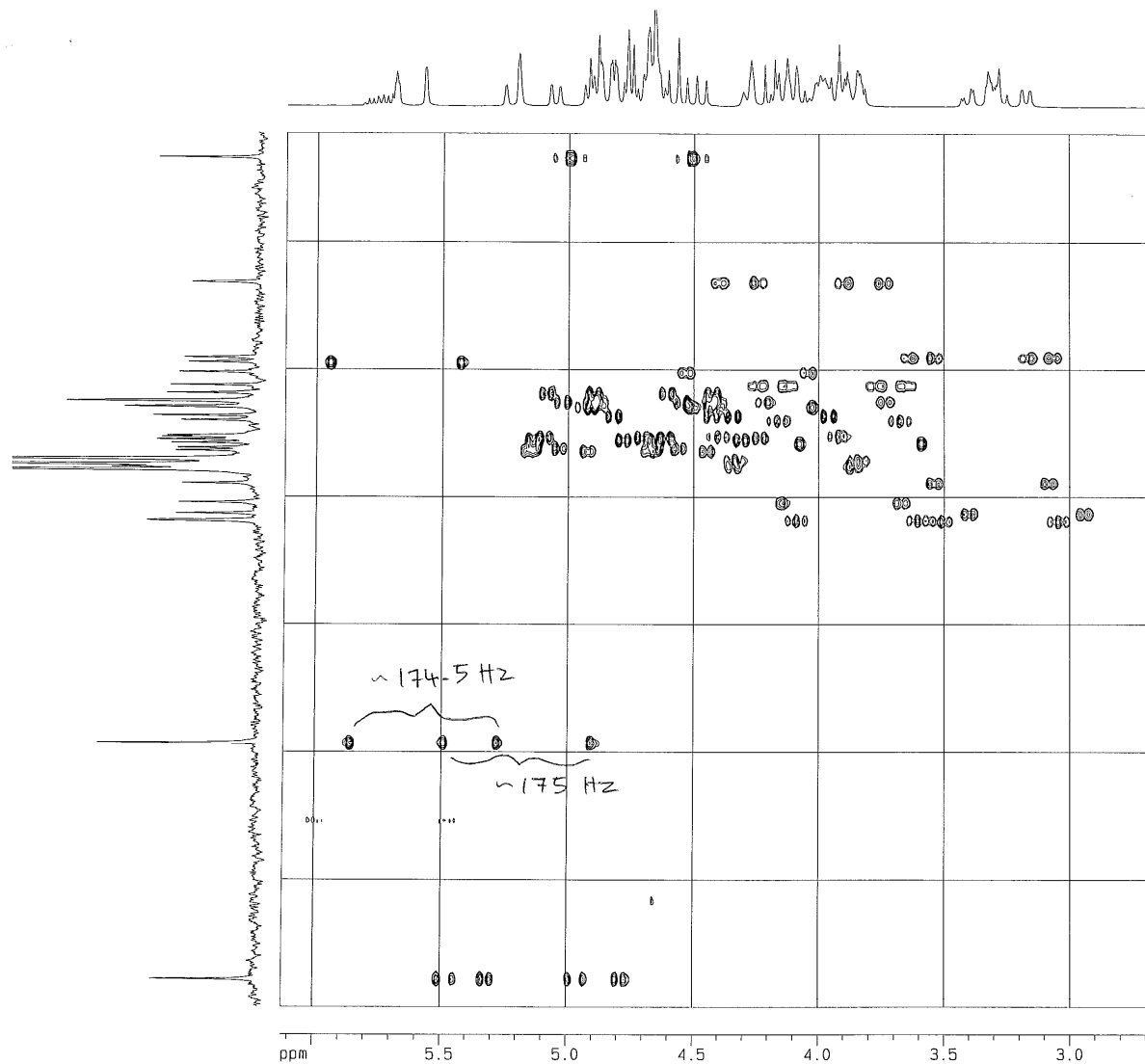
Compound **34** 75 MHz  $^{13}\text{C}$  NMR  $\text{CDCl}_3$



Compound **34** 75 MHz  $^{13}\text{C}$  NMR  $\text{CDCl}_3$



Compound **34** 300 MHz HSQC NMR without  $^{13}\text{C}$  decoupling during acquisition



Owner cmh  
 Sample cmh671b.1  
 Platform 355  
 Job No 35568911

*1H coupled HSQC*

```

Current Data Parameters
NAME          cmh671b1
EXPNO         11
PROCNO        1

F2 - Acquisition Parameters
Date_         20061216
Time          10.10
PROBHD        5 mm QNP 1H
PULPROG       invg1stg
TD            2048
SOLVENT       CDCl3
NS            40
DS            8
SWH           2540.650 Hz
AQ            0.4030964 sec
RG            18390.4
D0            0.0000300 sec
D1            0.85213429 sec
D4            0.00172500 sec
D11           0.03000000 sec
D13           0.00003000 sec
D15           0.00010000 sec
d20           0.00100000 sec
d21           0.00061800 sec
IND           0.00094733 sec

----- CHANNEL f1 -----
NUC1           1H
P1             11.50 usec
P2             23.00 usec
PL1            -3.00 dB
SF01          300.1313288 MHz

----- CHANNEL f2 -----
CPDPRG2       garrp
NUC2           13C
P3             9.00 usec
P4            18.00 usec
PCPD2         70.00 usec
PL2           -1.00 dB
PL12          120.00 dB
SF02          75.4741338 MHz

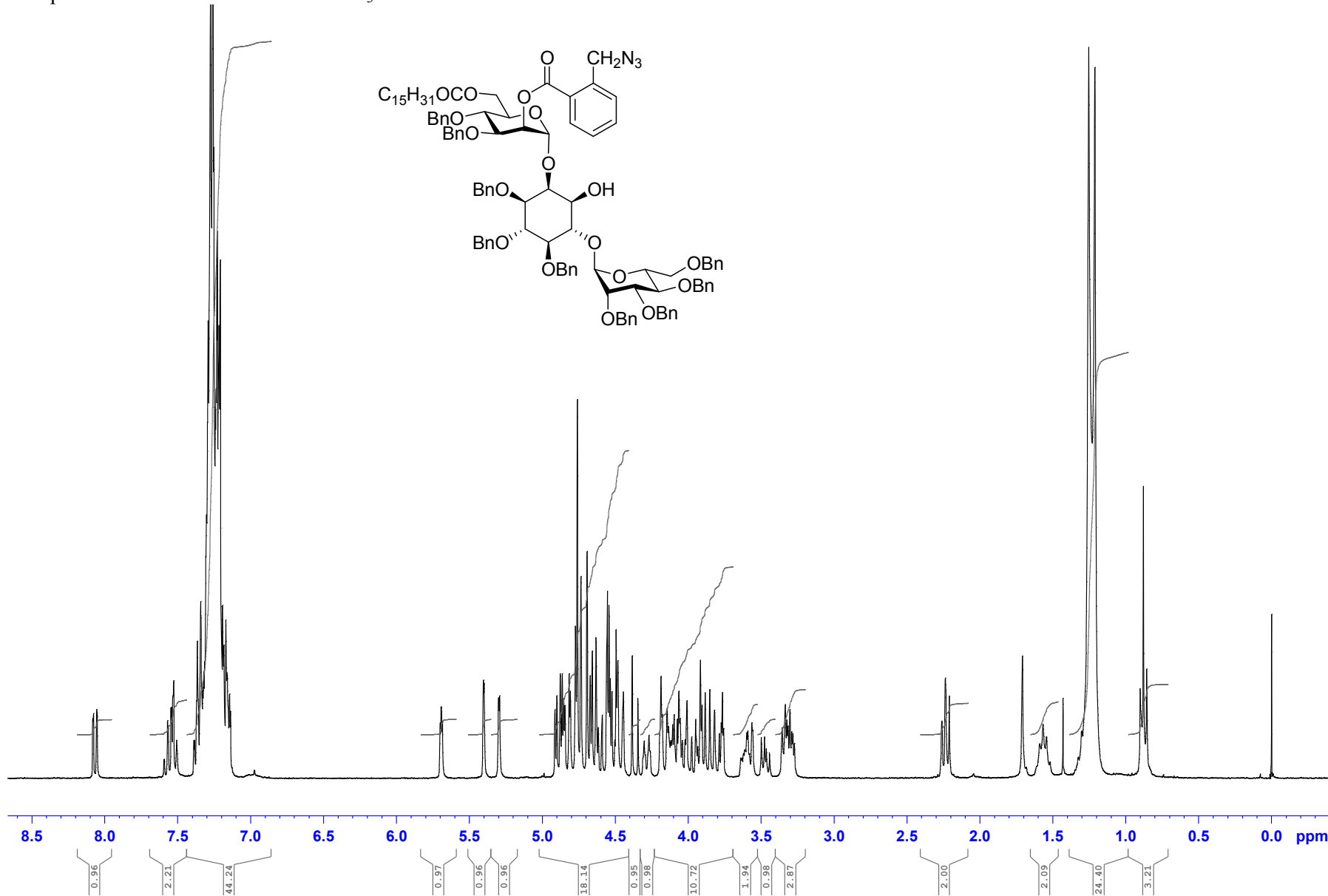
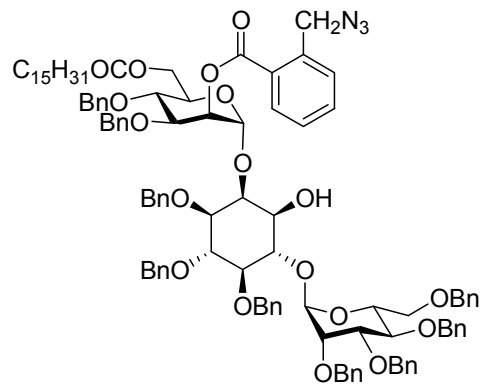
----- GRADIENT CHANNEL -----
P16           1000.00 usec

F1 - Acquisition parameters
ND0            4
TD             200
SF01          75.474133 MHz
FIDRES        25.413101 Hz
SH            69.892 ppm

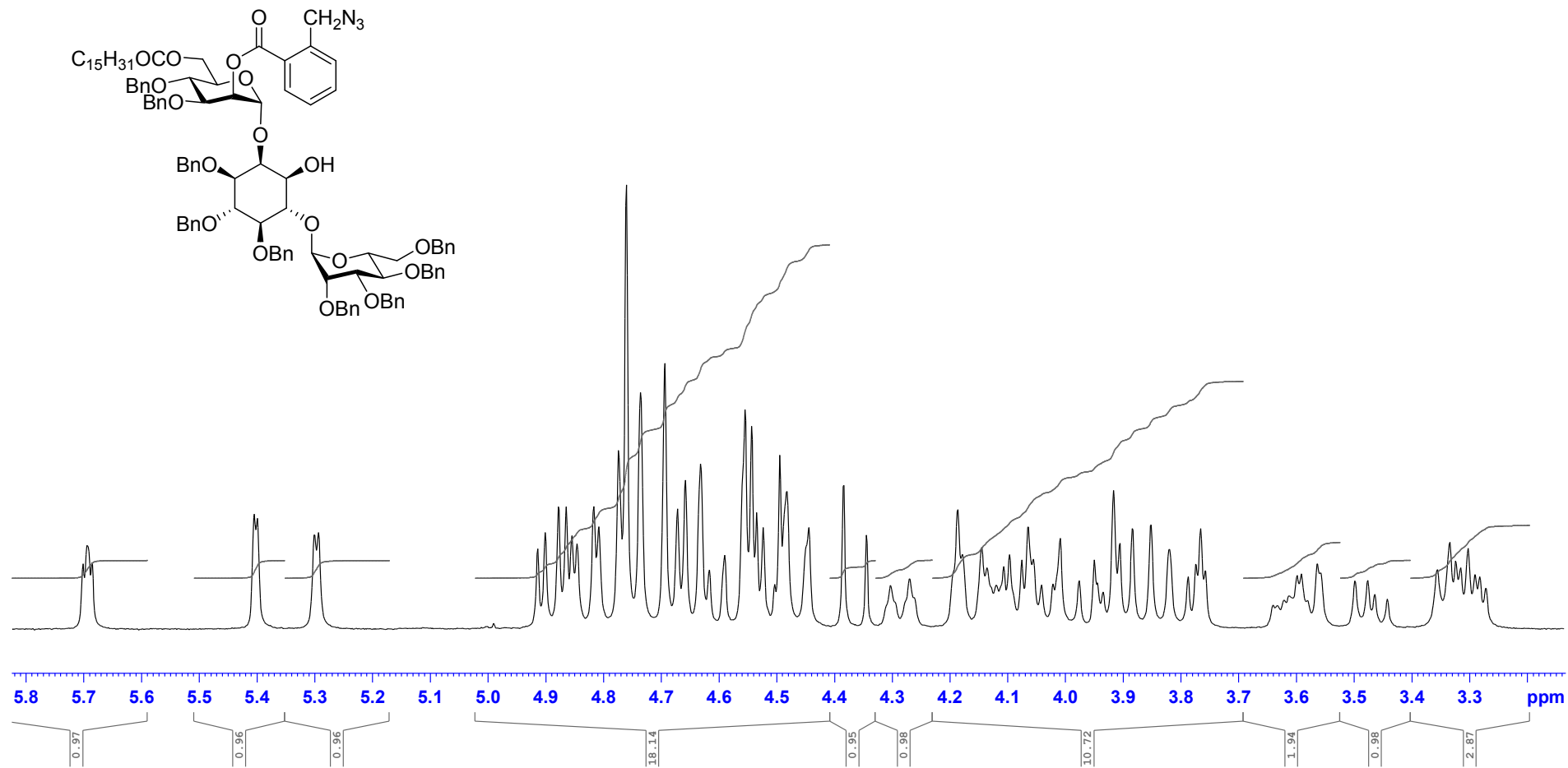
F2 - Processing parameters
SI            1024
SF            300.1300165 MHz
WDW           OSINE
SSB           2
LB            0.00 Hz
GB            0
PC            1.40

F1 - Processing parameters
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MC2           TPPI
SF            75.4677190 MHz
WDW           OSINE
SSB           2
LB            0.00 Hz
GB            0
    
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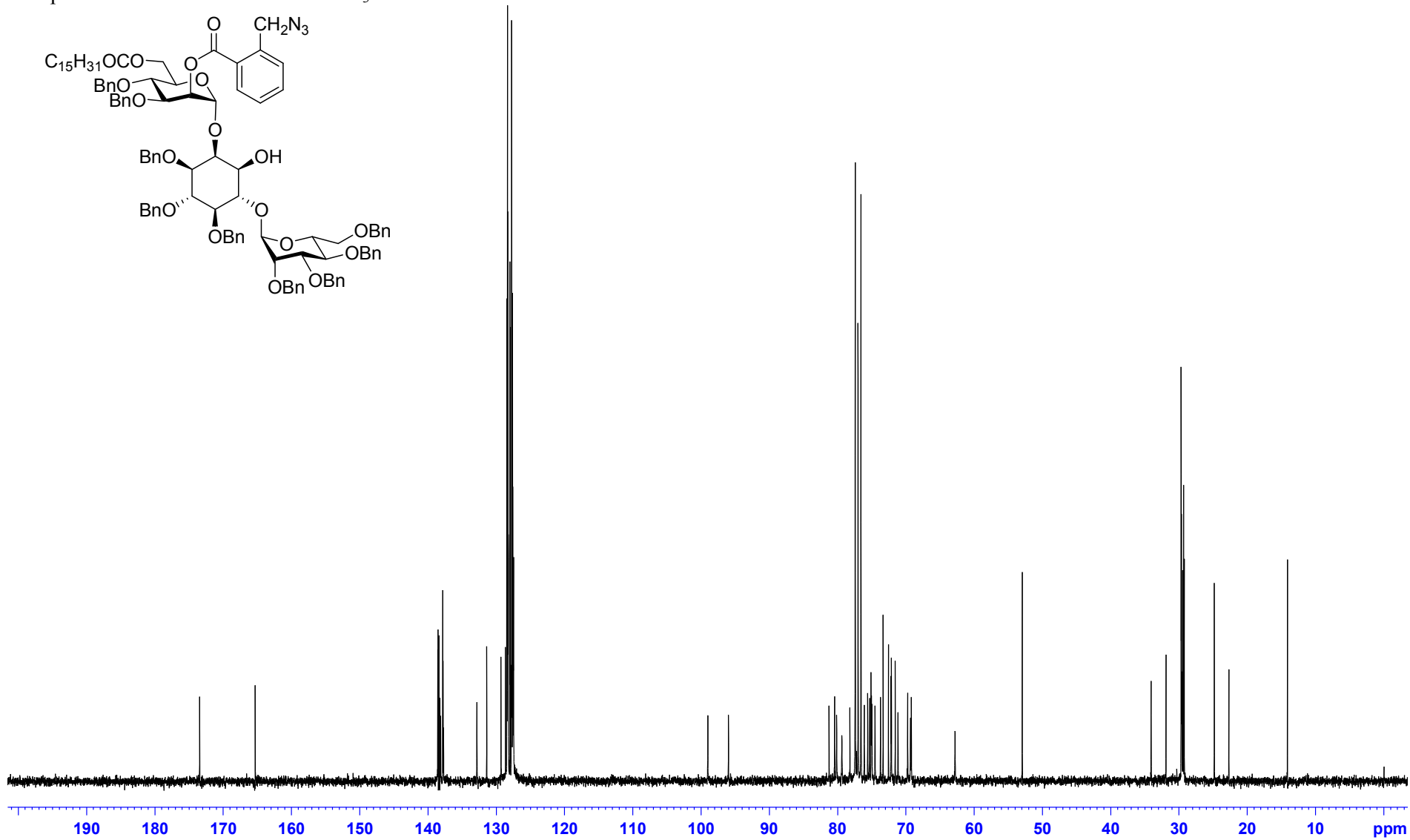
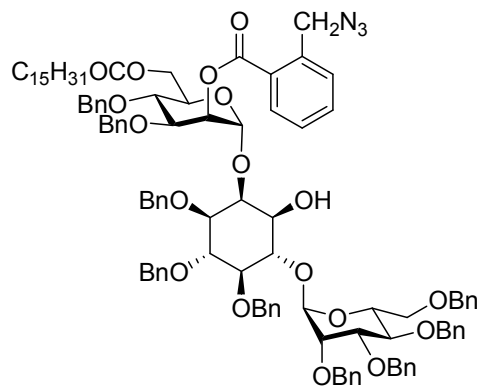
Compound **35** 300 MHz  $^1\text{H}$  NMR  $\text{CDCl}_3$



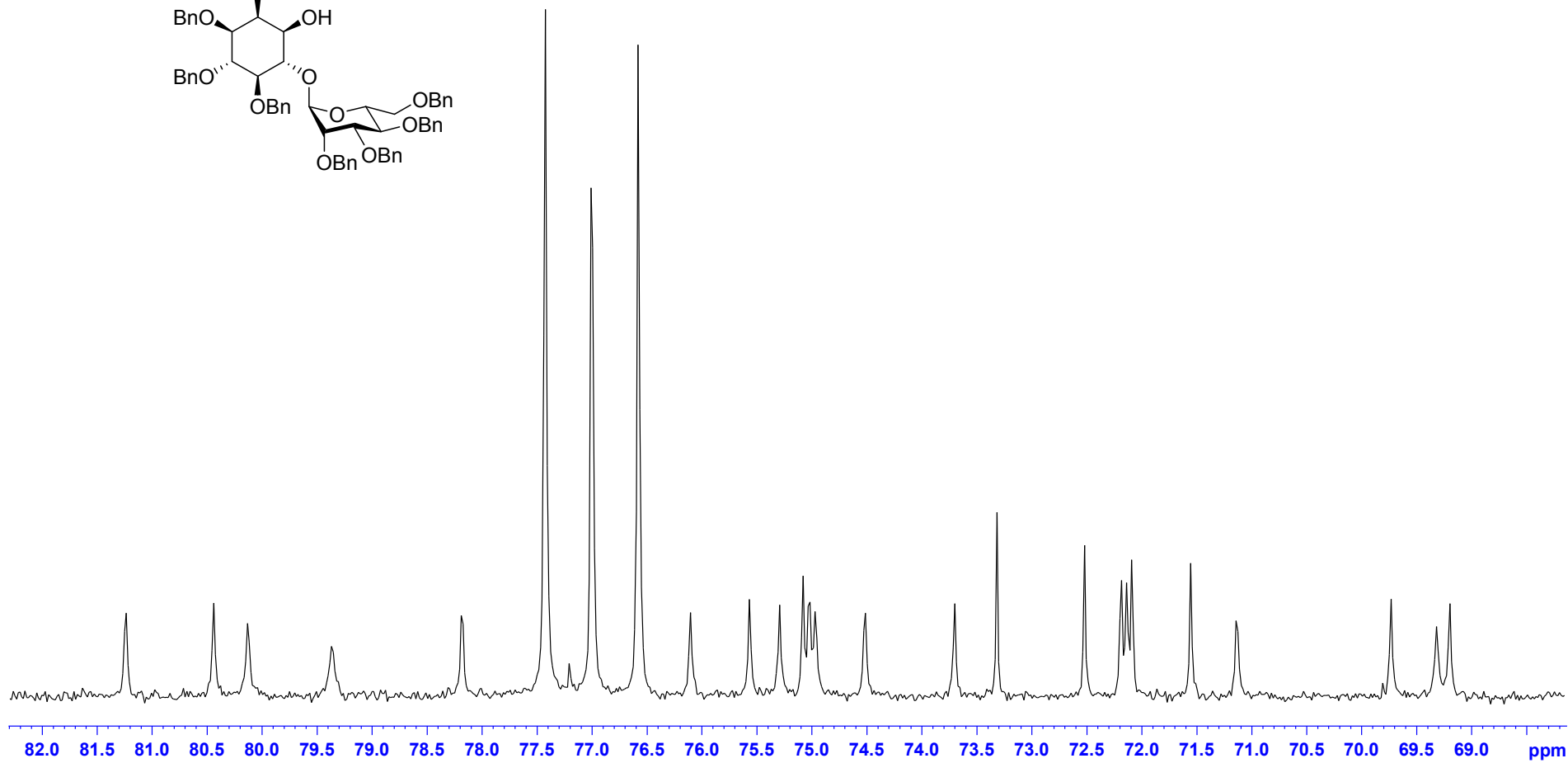
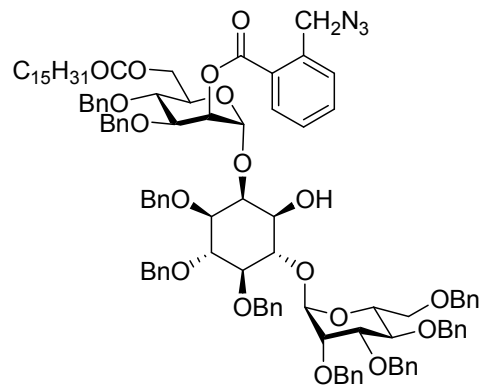
Compound **35** 300 MHz  $^1\text{H}$  NMR  $\text{CDCl}_3$



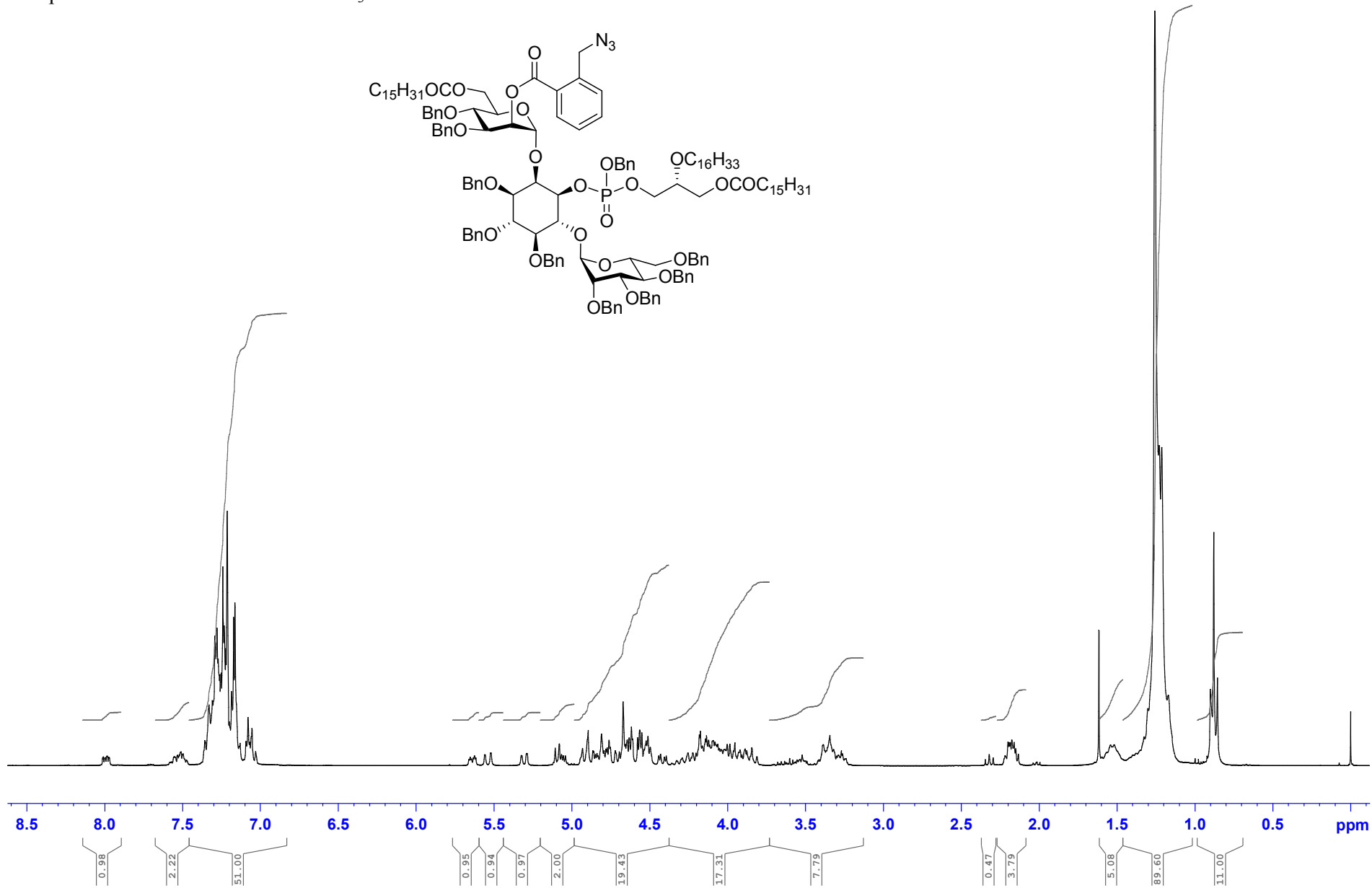
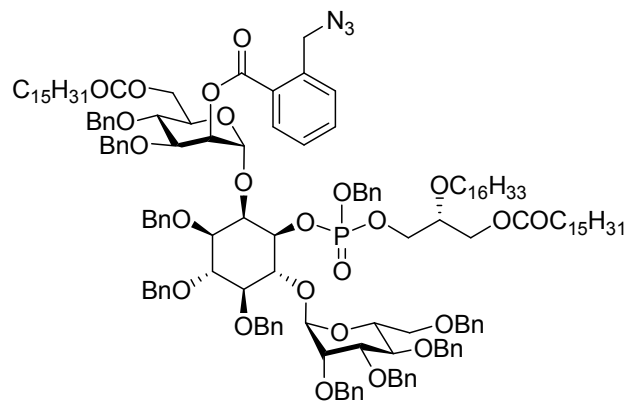
Compound **35** 75 MHz  $^{13}\text{C}$  NMR  $\text{CDCl}_3$



Compound **35** 5 MHz  $^{13}\text{C}$  NMR  $\text{CDCl}_3$

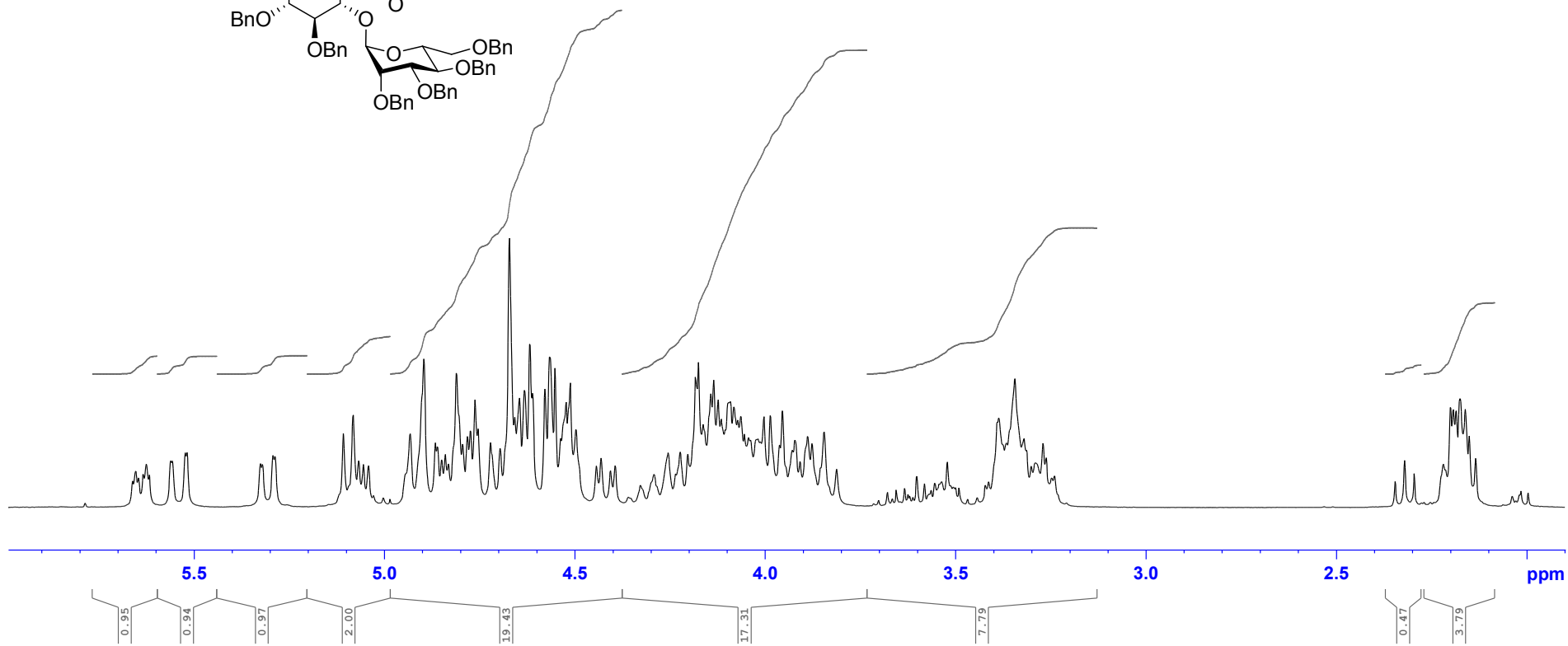
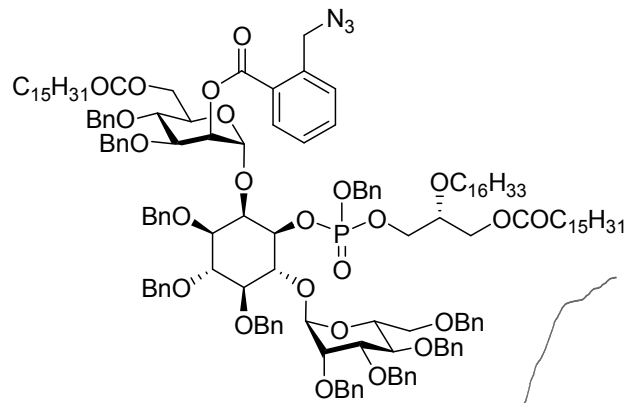


Compound **37** 300 MHz  $^1\text{H}$  NMR  $\text{CDCl}_3$



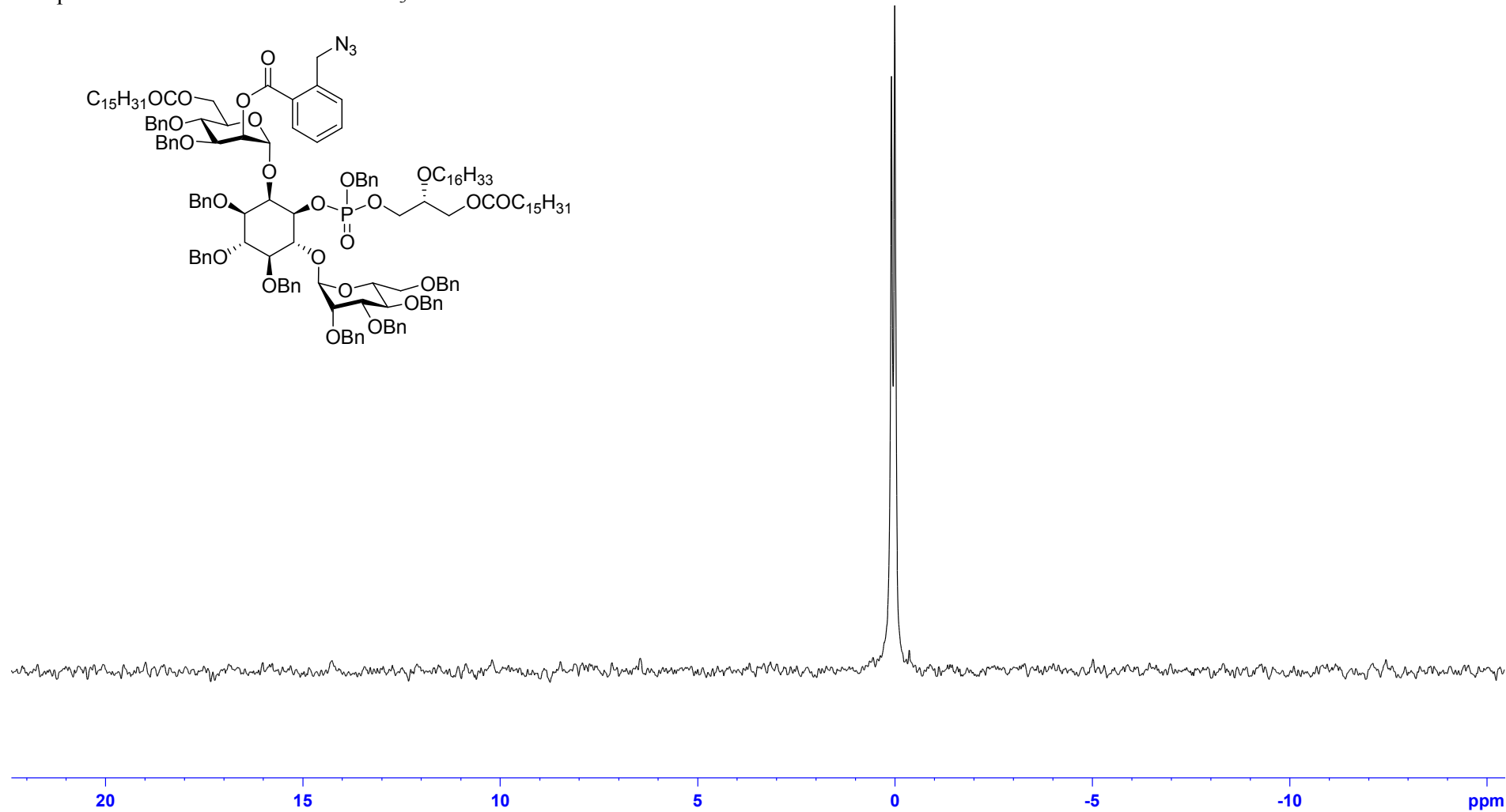
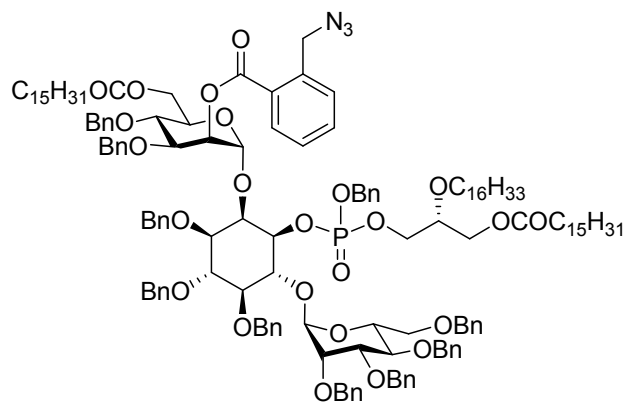


Compound **37** 300 MHz  $^1\text{H}$  NMR  $\text{CDCl}_3$

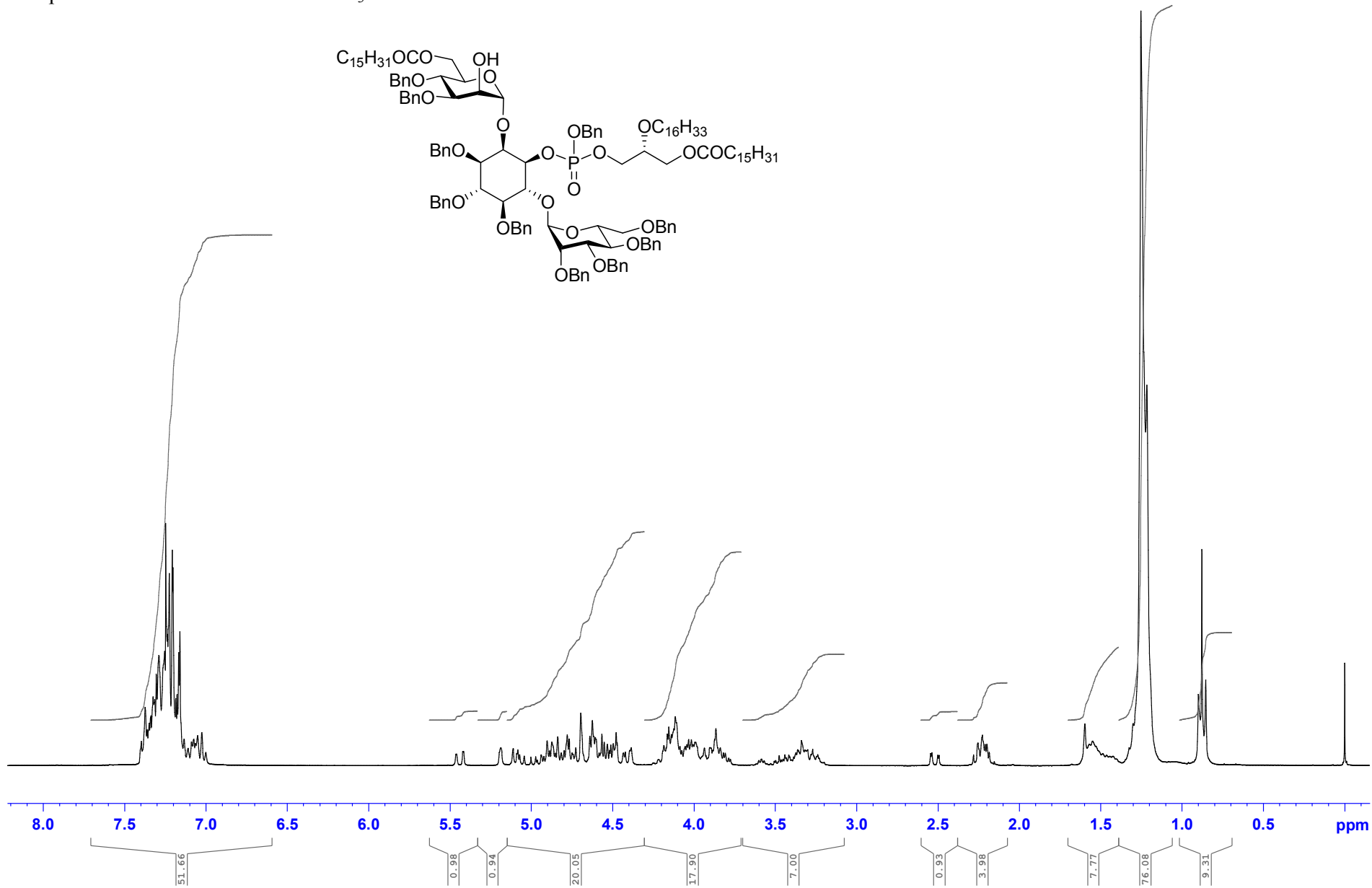
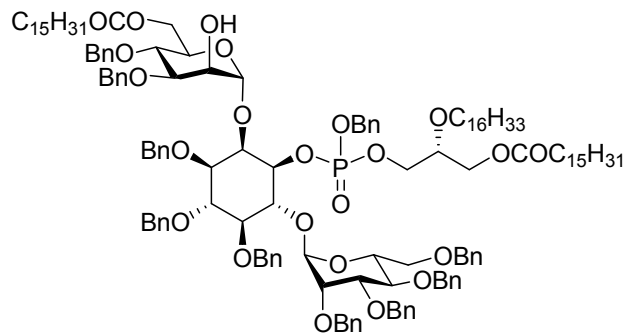




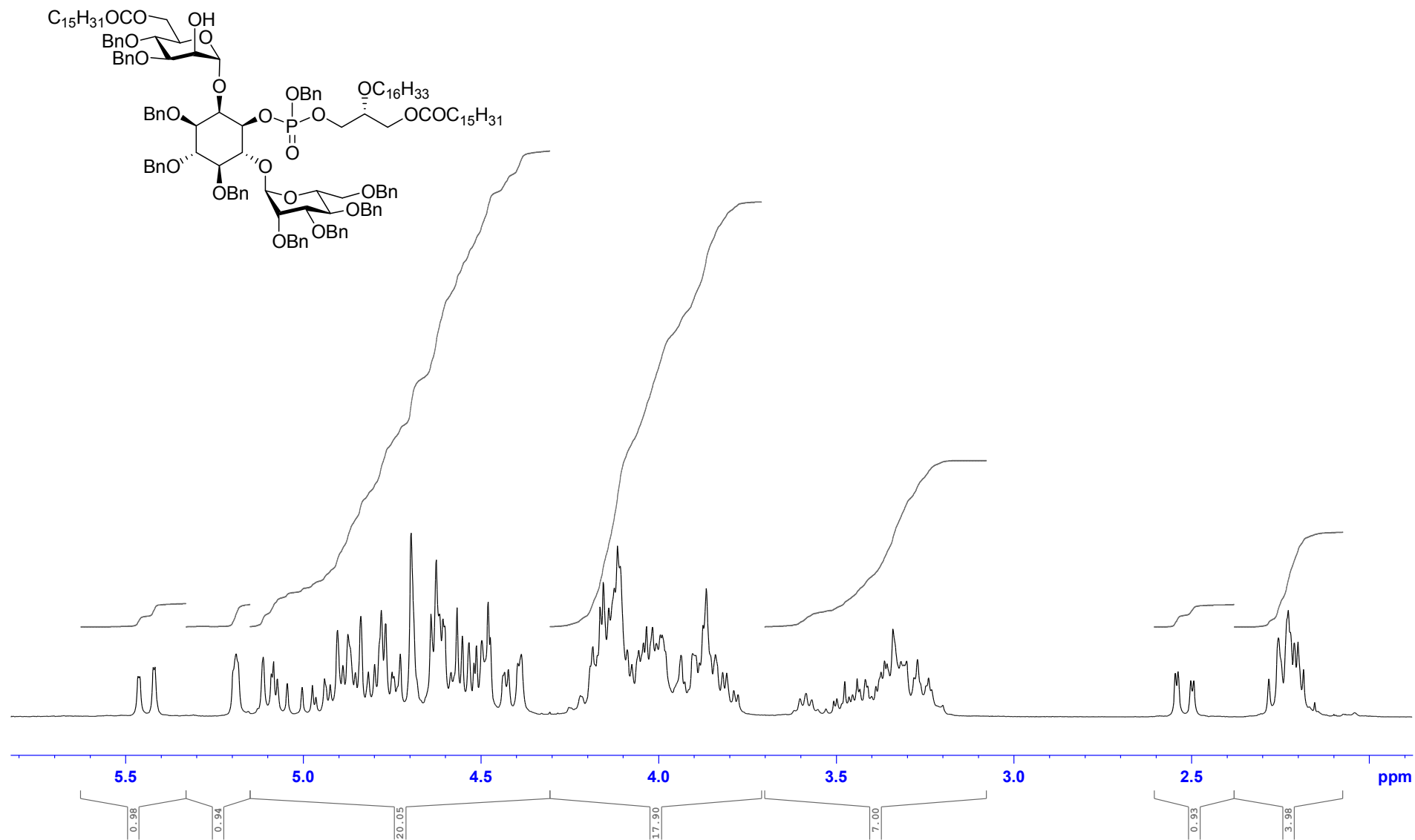
Compound **37** 121 MHz  $^{31}\text{P}$  NMR  $\text{CDCl}_3$



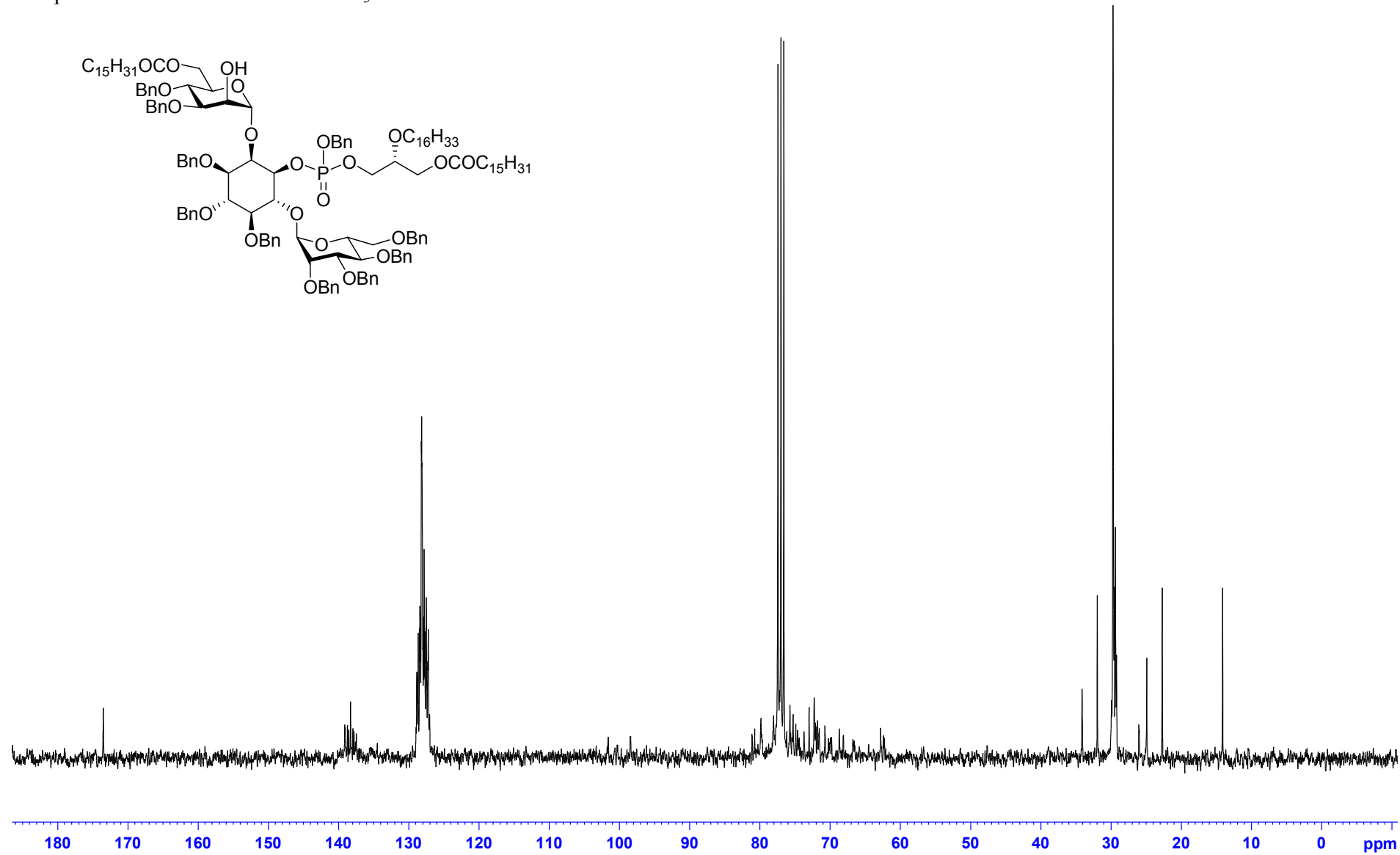
Compound **38** 300 MHz  $^1\text{H}$  NMR  $\text{CDCl}_3$



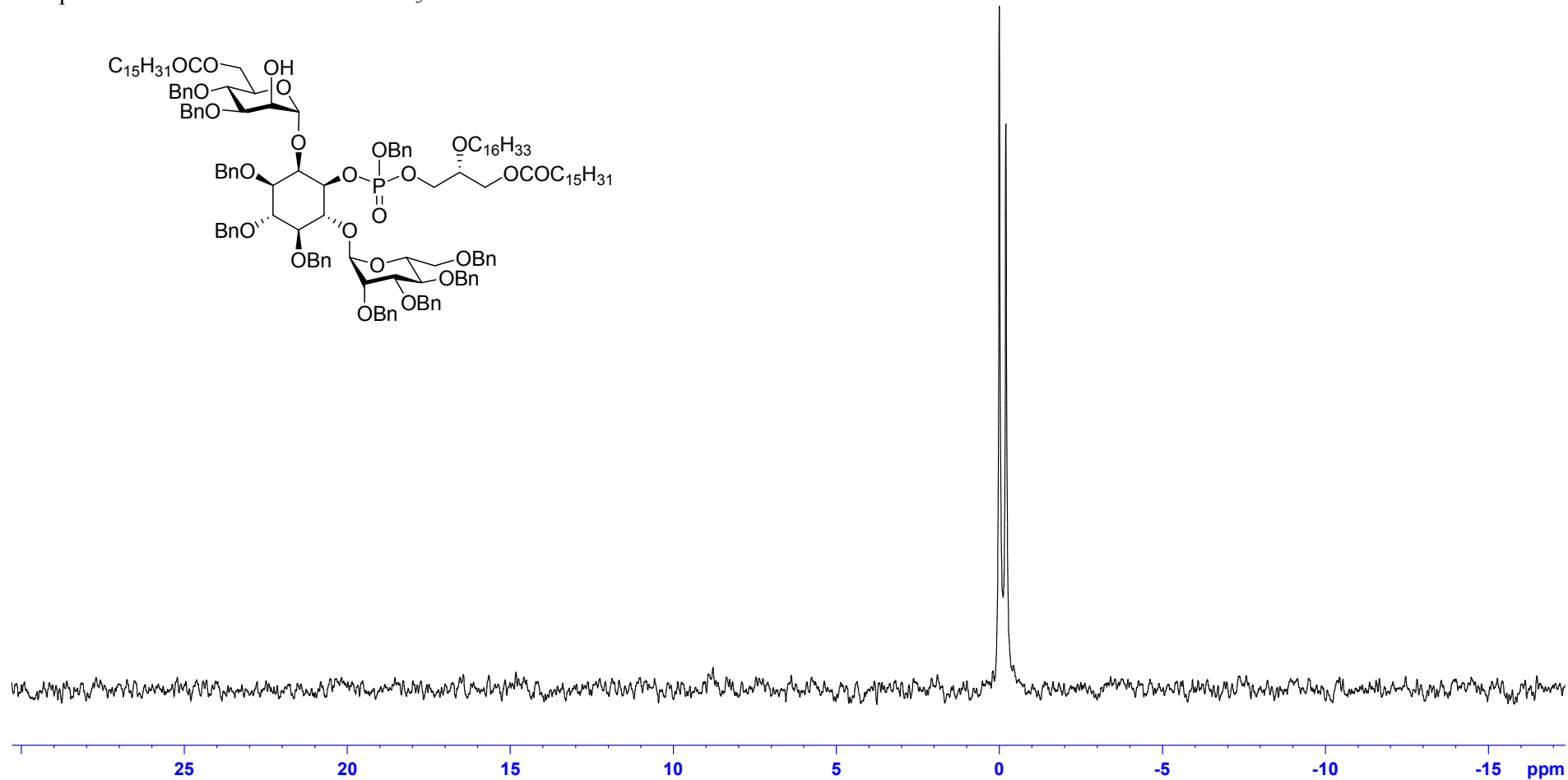
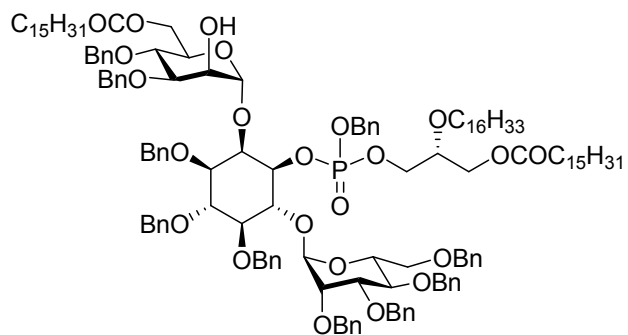
Compound **38** 300 MHz  $^1\text{H}$  NMR  $\text{CDCl}_3$



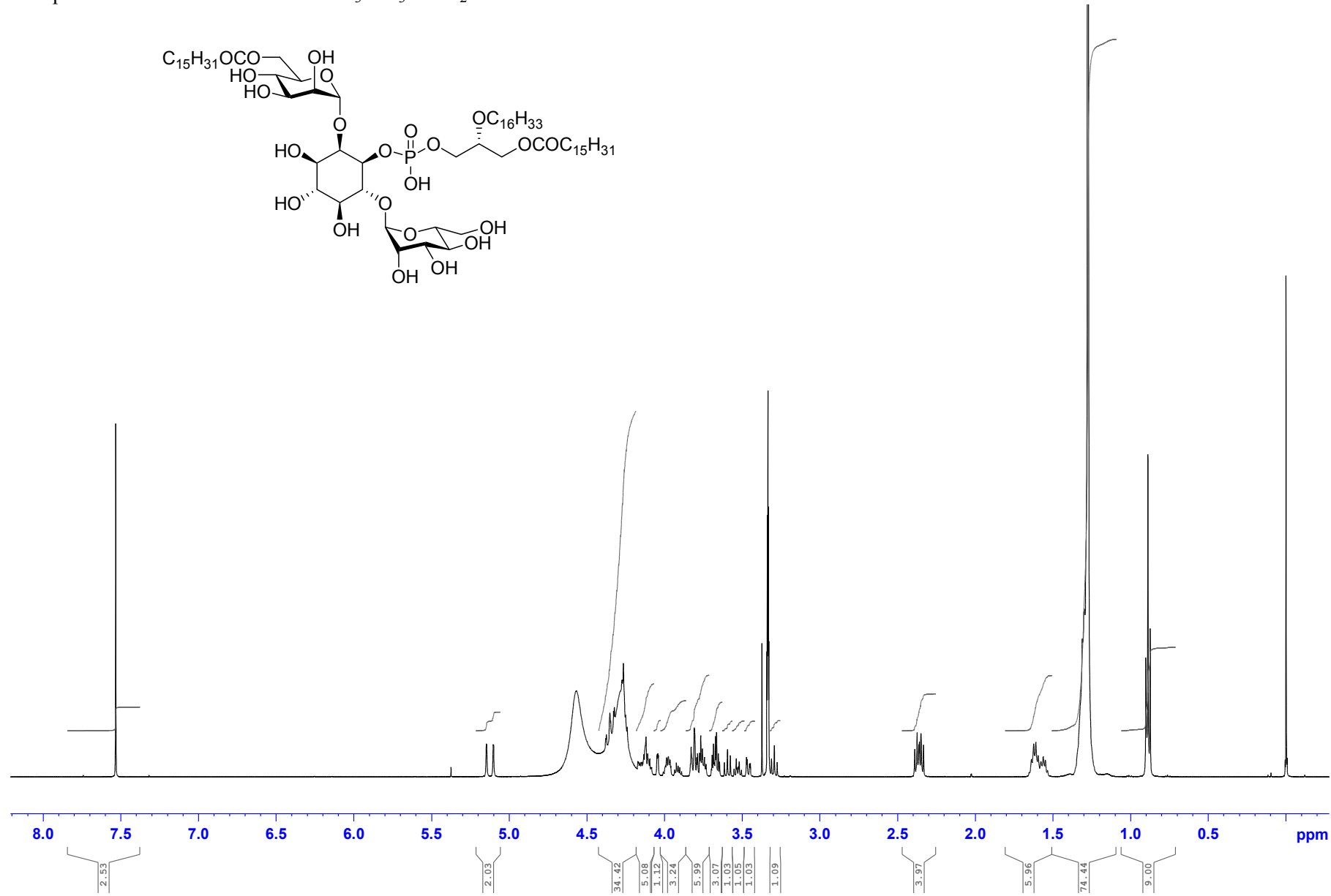
Compound **38** 75 MHz  $^{13}\text{C}$  NMR  $\text{CDCl}_3$



Compound **38** 121 MHz  $^{31}\text{P}$  NMR  $\text{CDCl}_3$

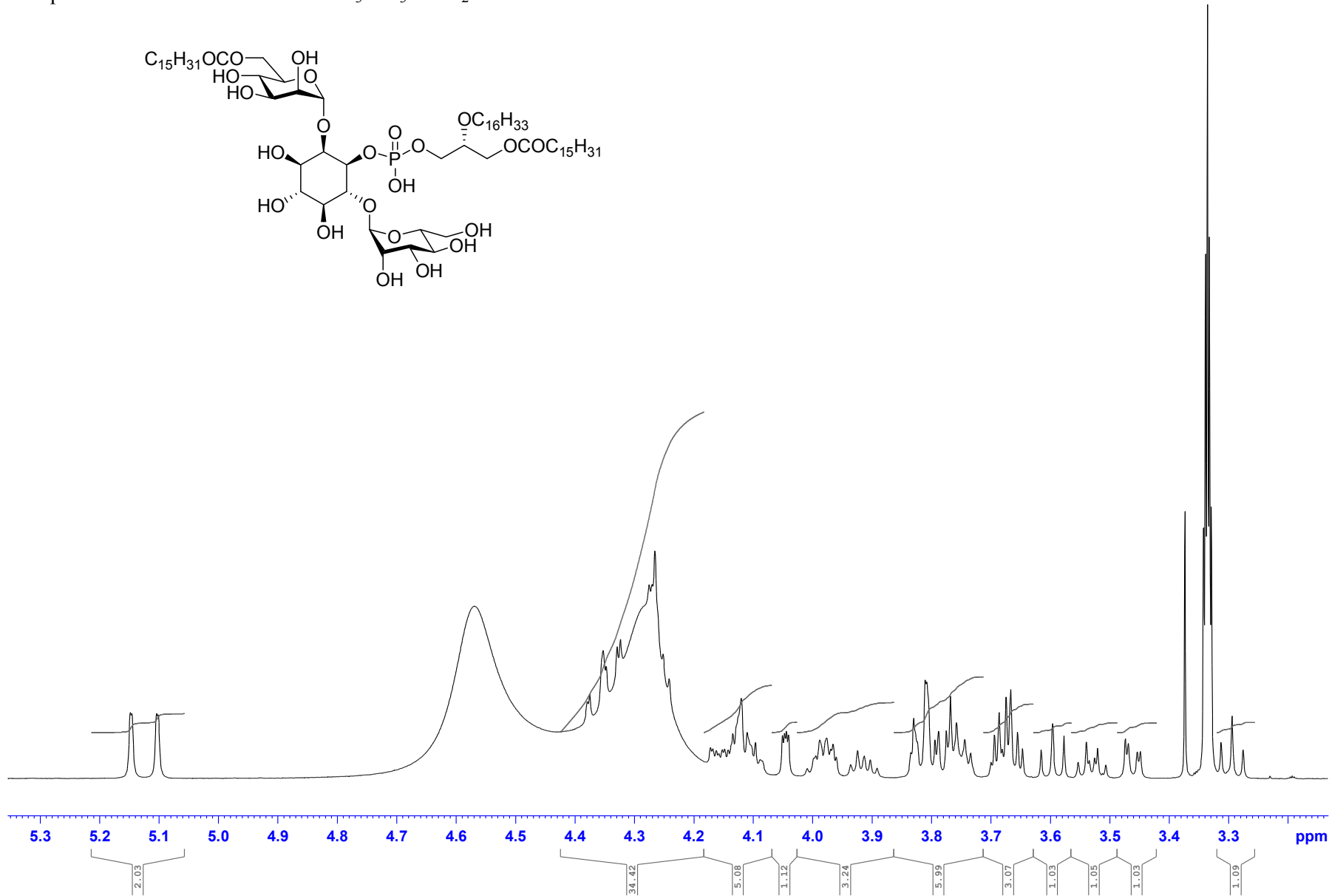
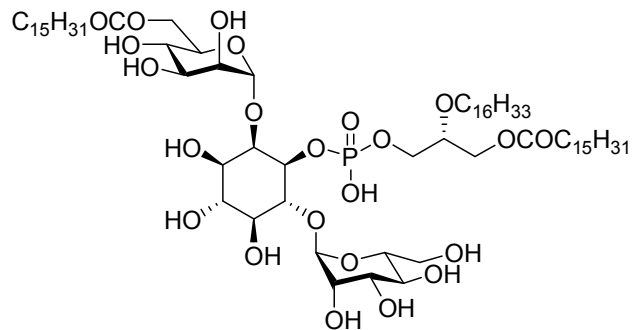


Compound **5** 500 MHz  $^1\text{H}$  NMR  $\text{CDCl}_3/\text{CD}_3\text{OD}/\text{D}_2\text{O}$  70:40:6

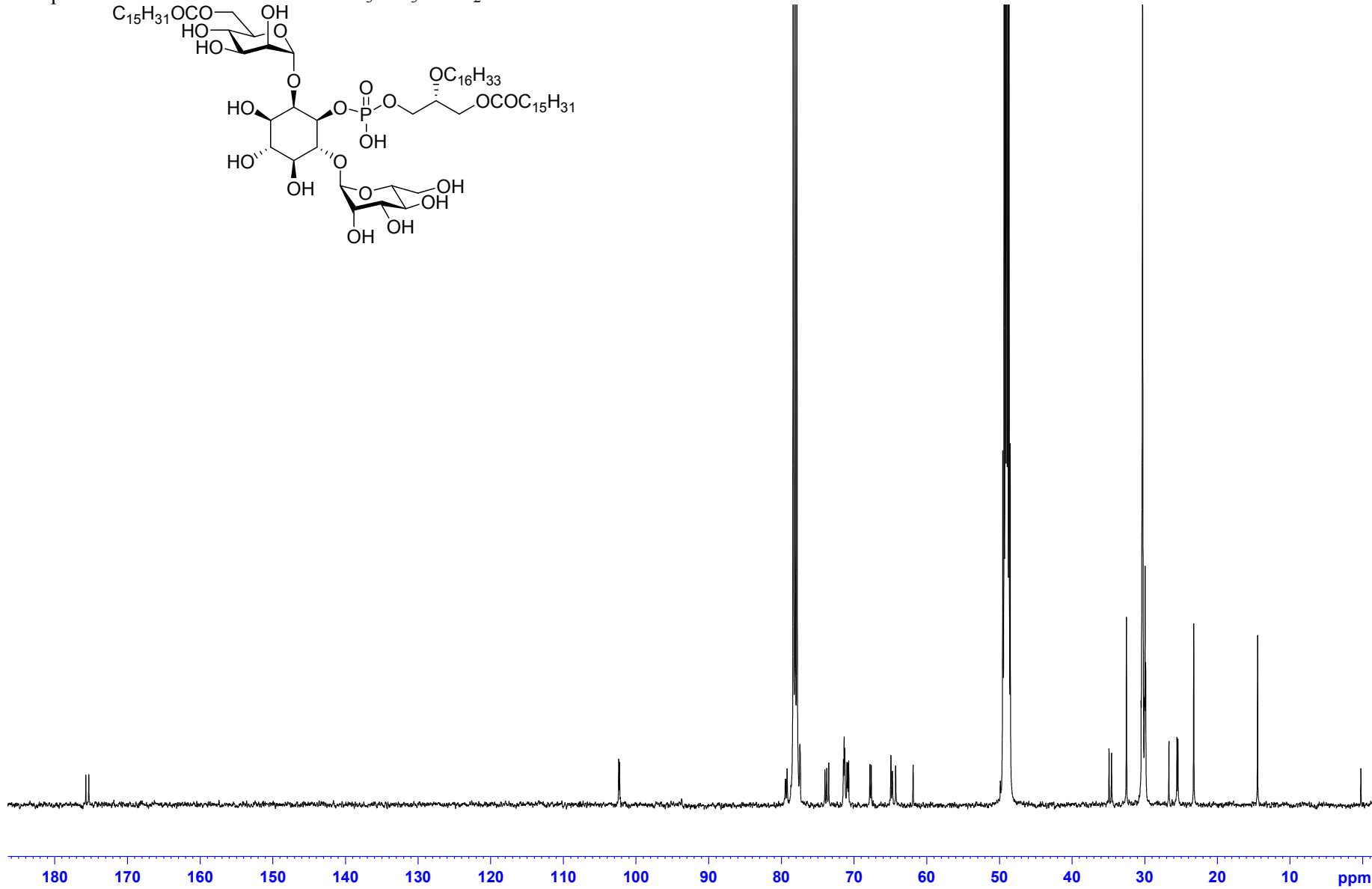
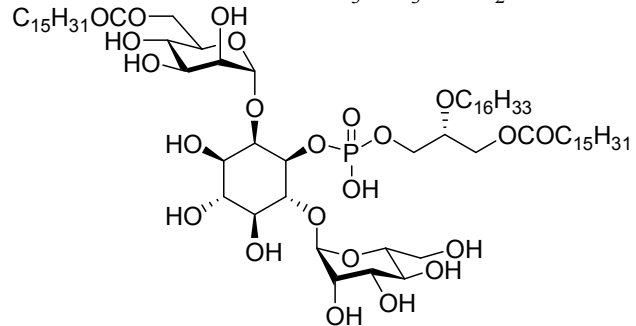




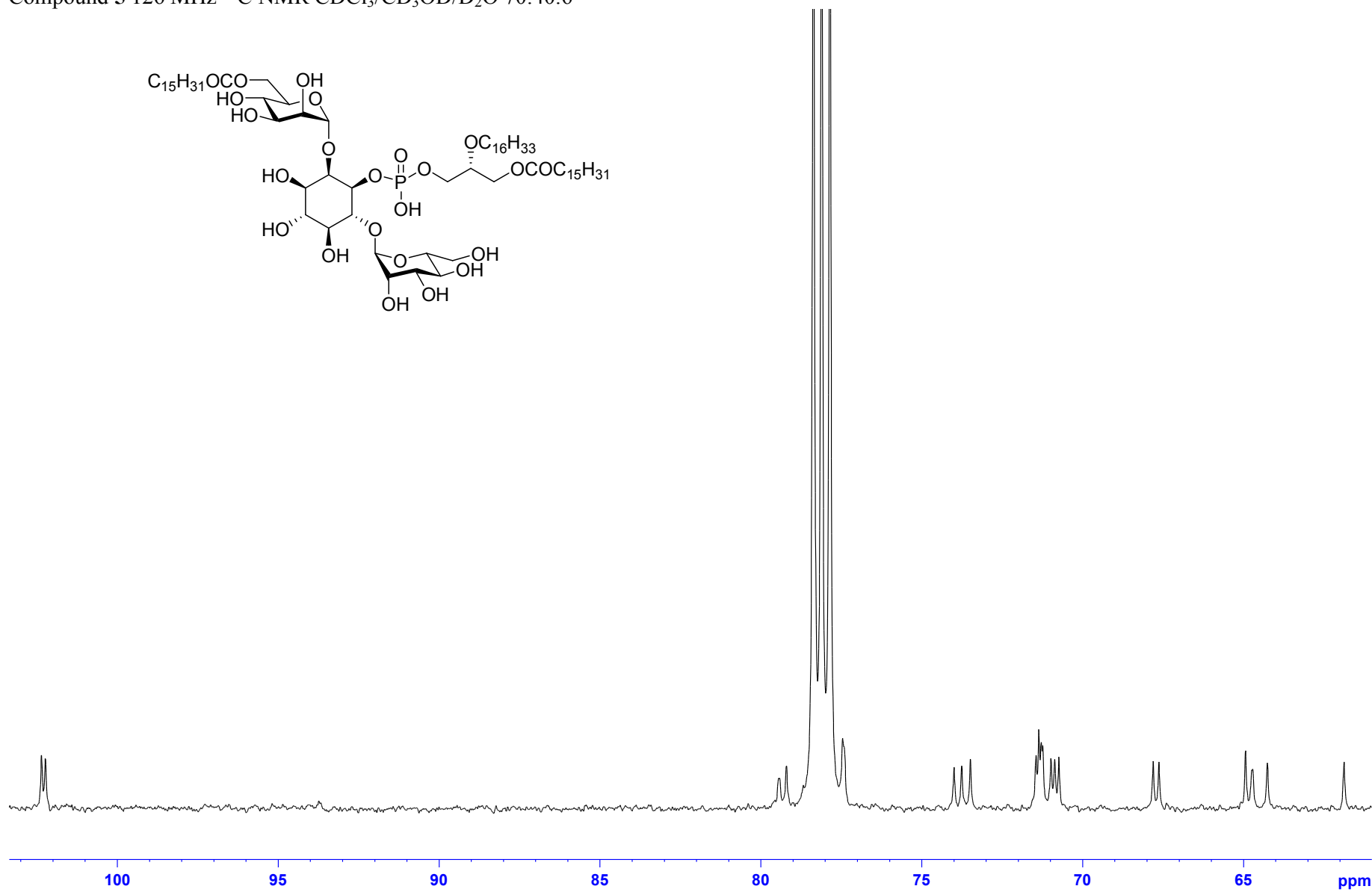
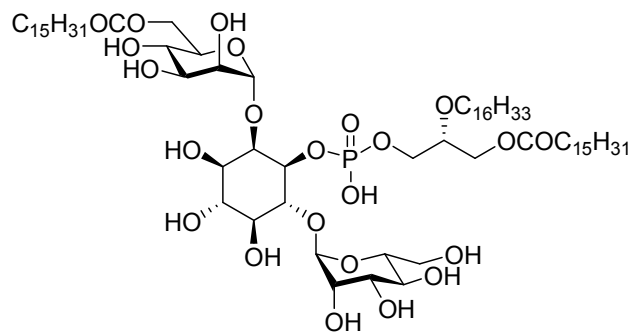
Compound **5** 500 MHz  $^1\text{H}$  NMR  $\text{CDCl}_3/\text{CD}_3\text{OD}/\text{D}_2\text{O}$  70:40:6



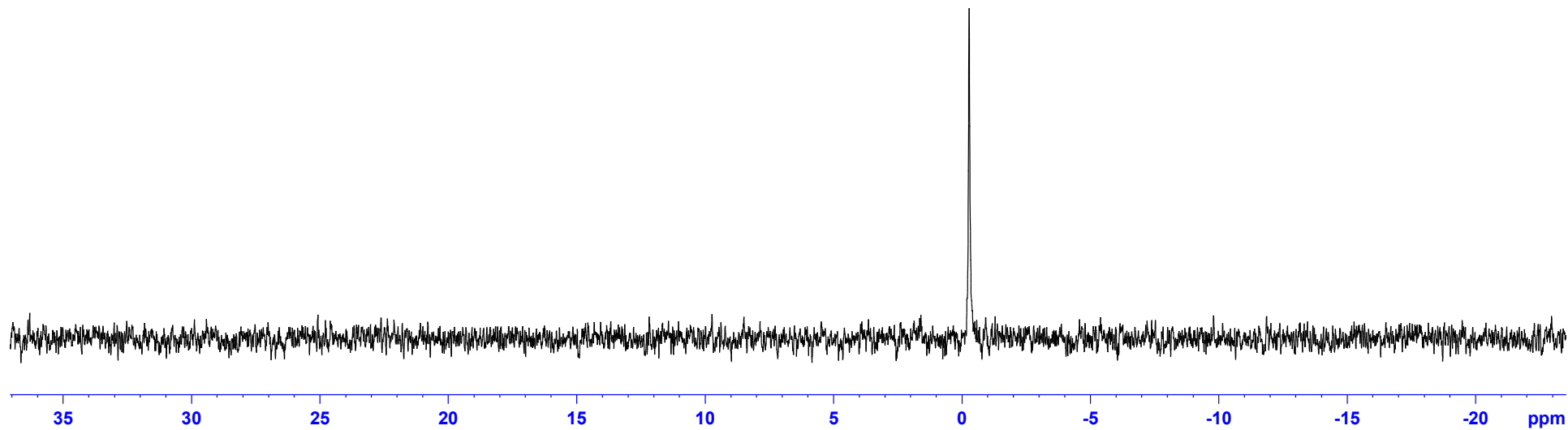
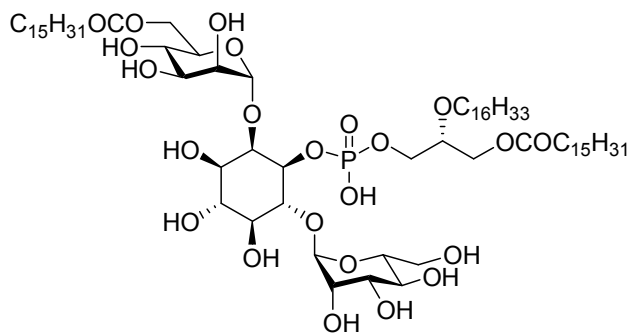
Compound **5** 126 MHz  $^{13}\text{C}$  NMR  $\text{CDCl}_3/\text{CD}_3\text{OD}/\text{D}_2\text{O}$  70:40:6



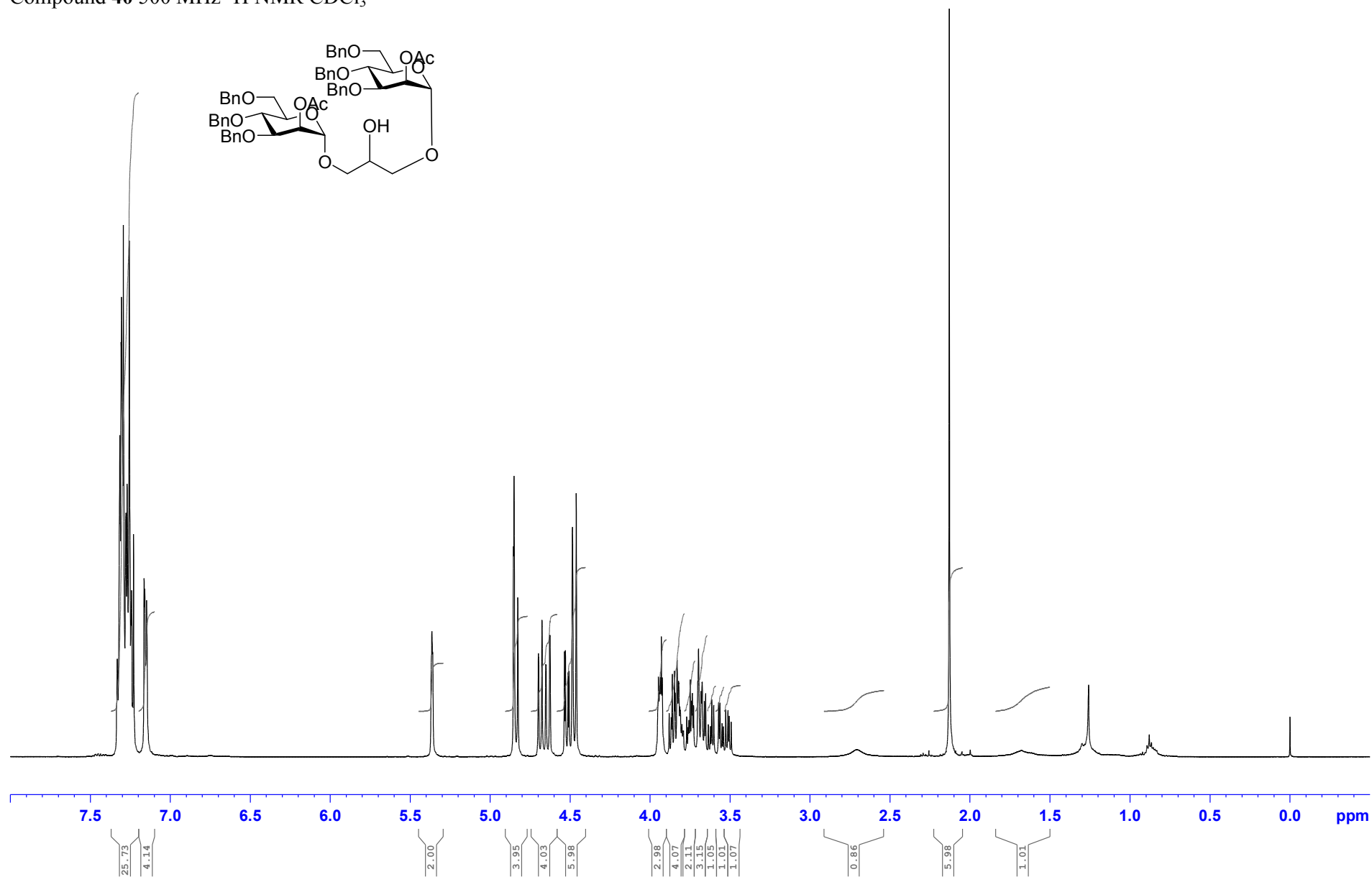
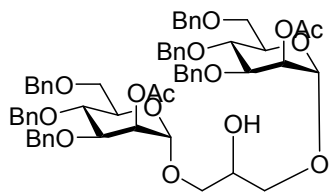
Compound **5** 126 MHz  $^{13}\text{C}$  NMR  $\text{CDCl}_3/\text{CD}_3\text{OD}/\text{D}_2\text{O}$  70:40:6



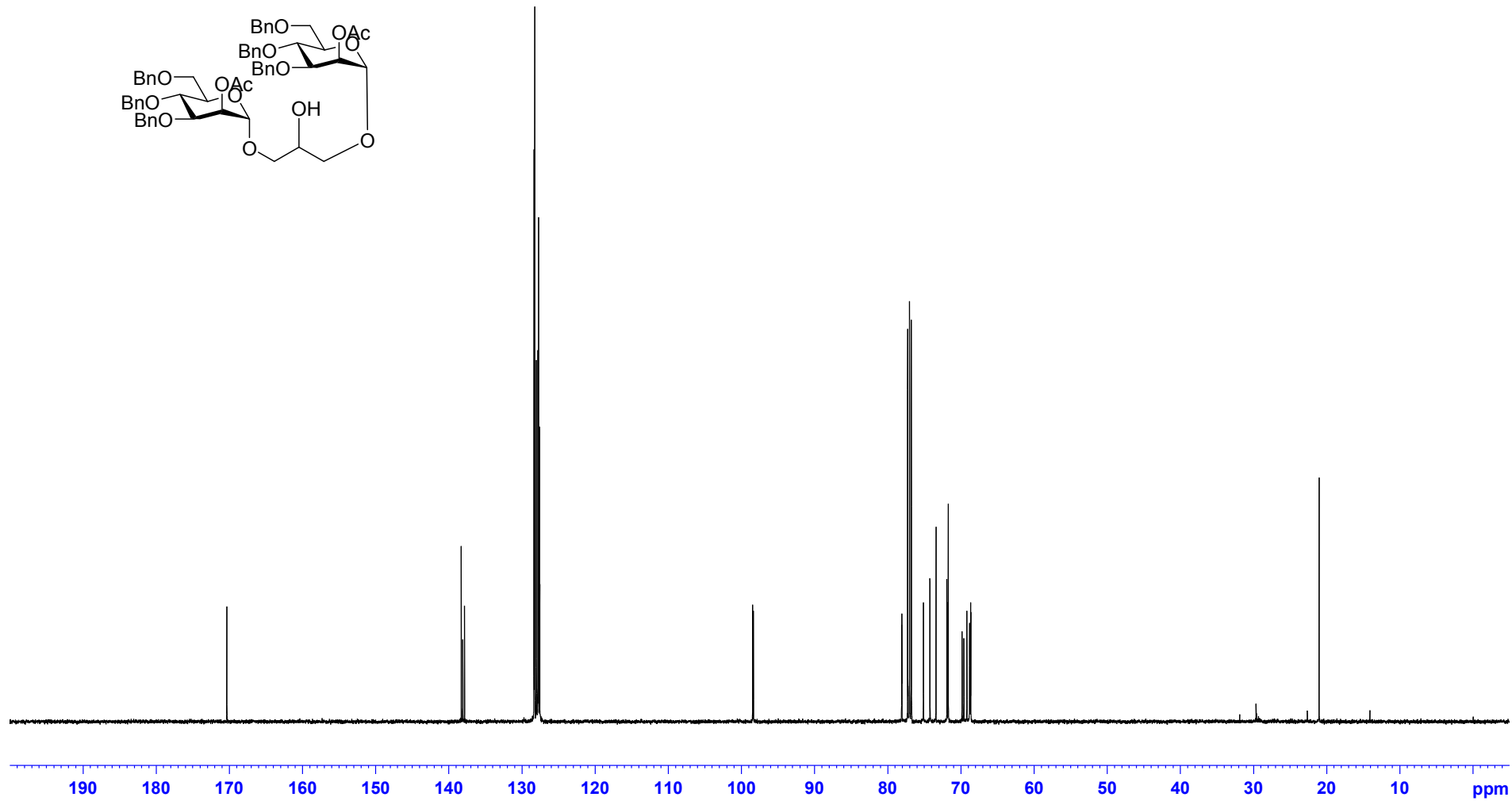
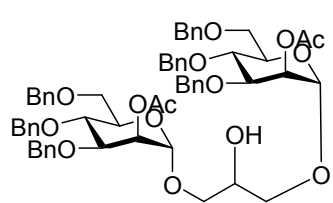
Compound **5** 202 MHz  $^{31}\text{P}$  NMR  $\text{CDCl}_3/\text{CD}_3\text{OD}/\text{D}_2\text{O}$  70:40:6



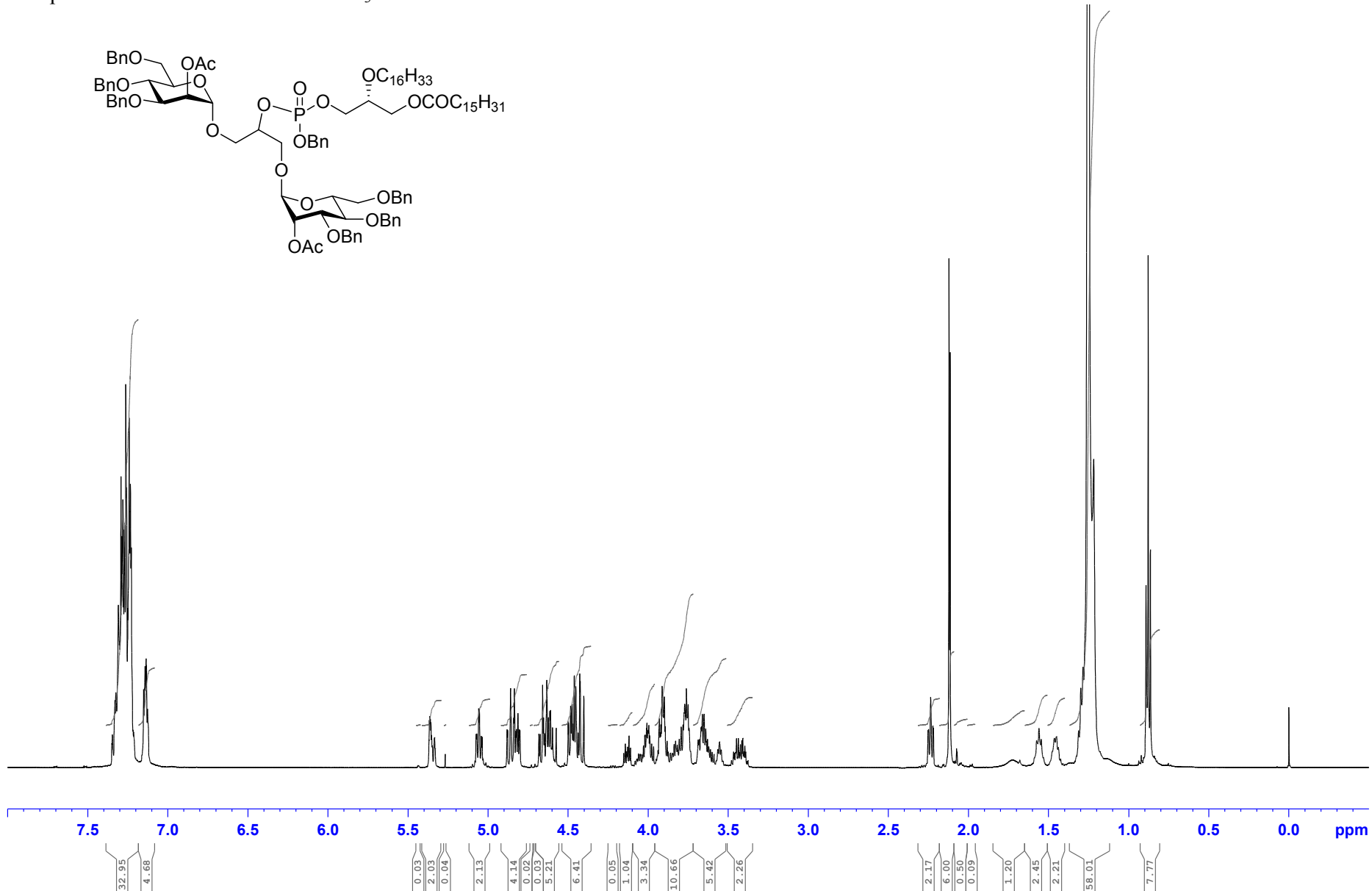
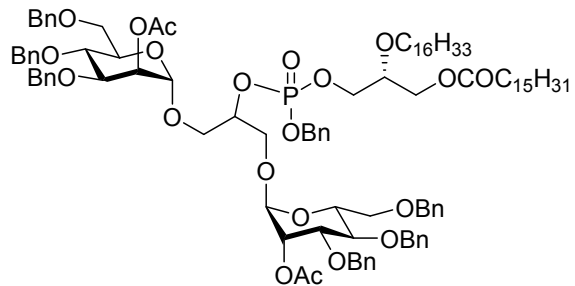
Compound **40** 500 MHz  $^1\text{H}$  NMR  $\text{CDCl}_3$



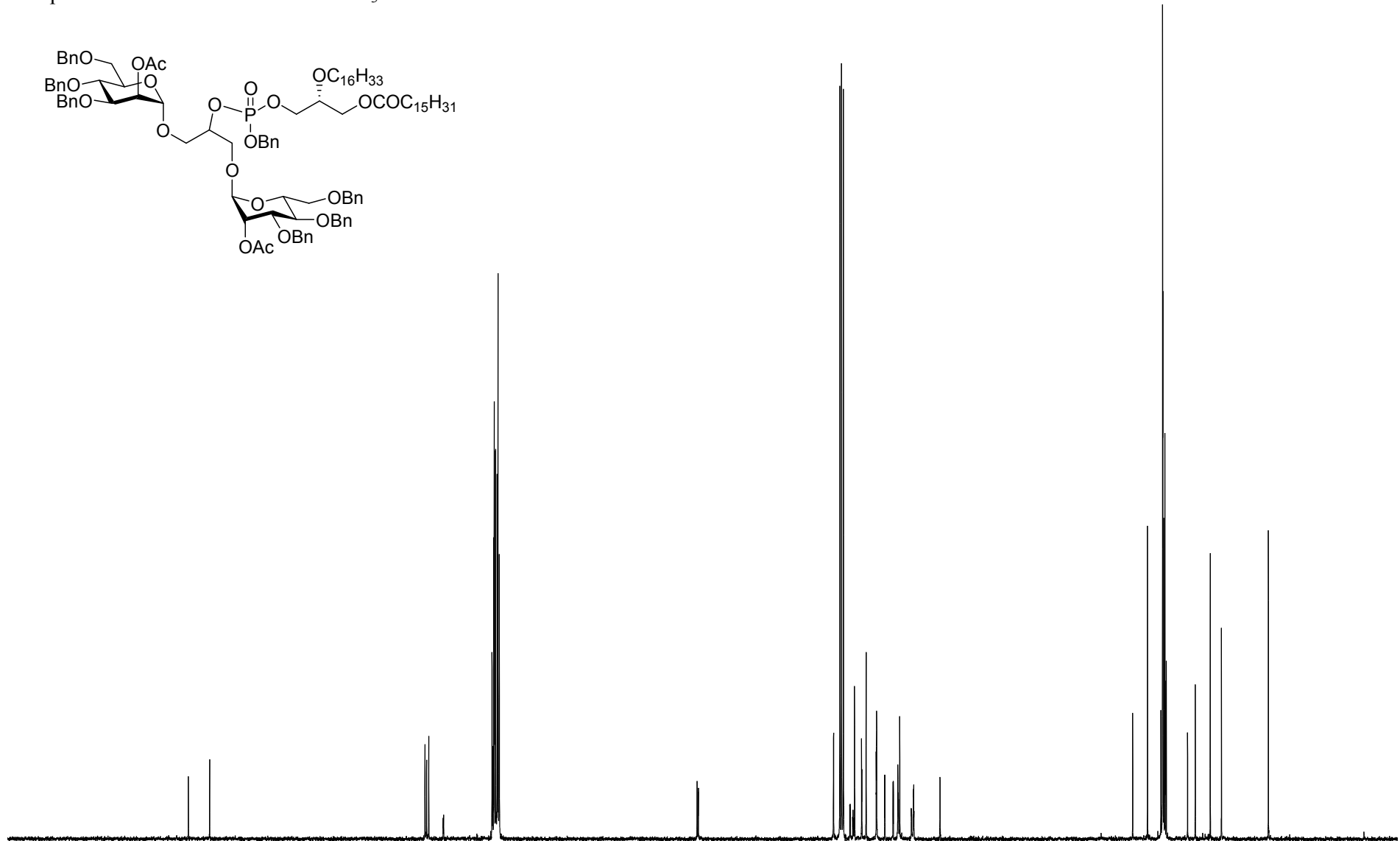
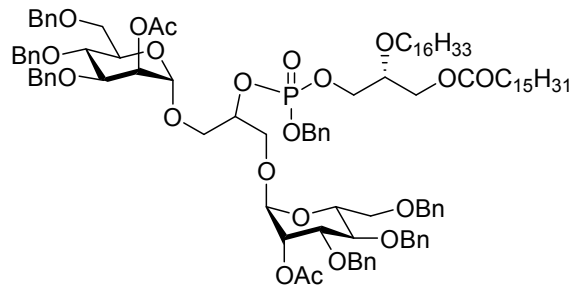
Compound **40** 125 MHz  $^{13}\text{C}$  NMR  $\text{CDCl}_3$



Compound **41** 500 MHz  $^1\text{H}$  NMR  $\text{CDCl}_3$



Compound **41** 125 MHz  $^{13}\text{C}$  NMR  $\text{CDCl}_3$

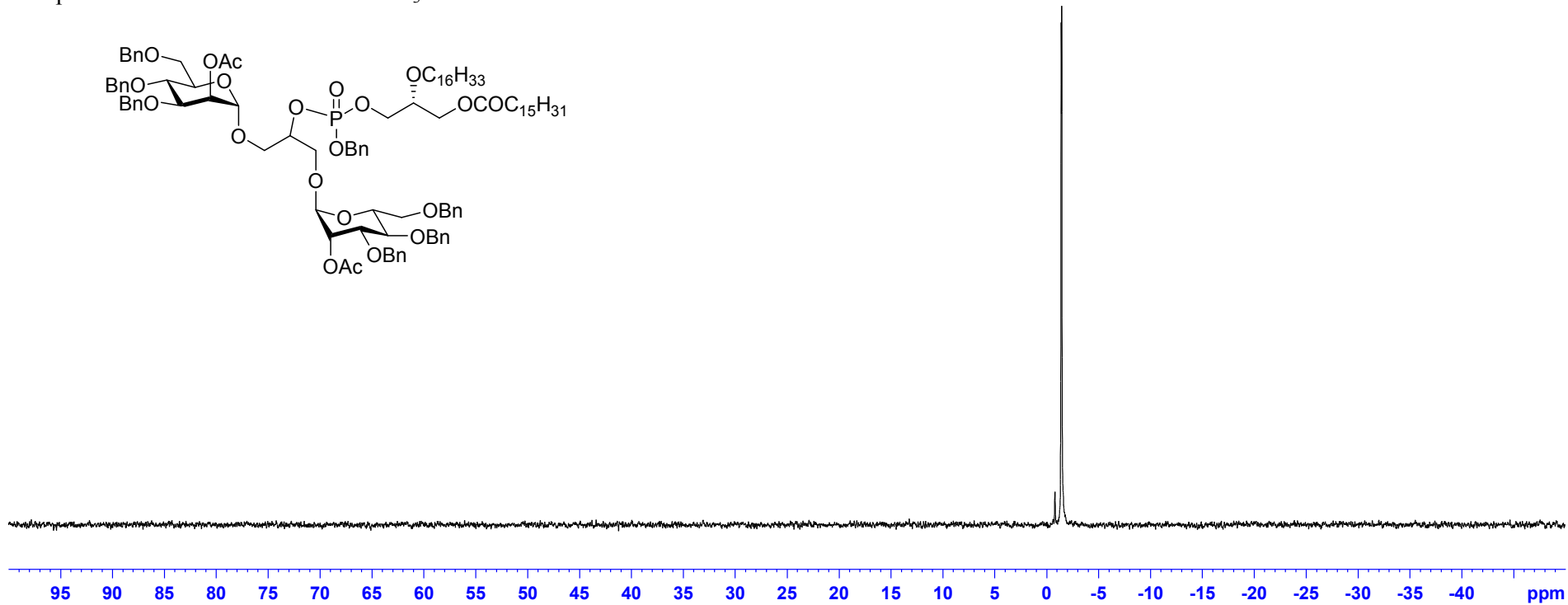
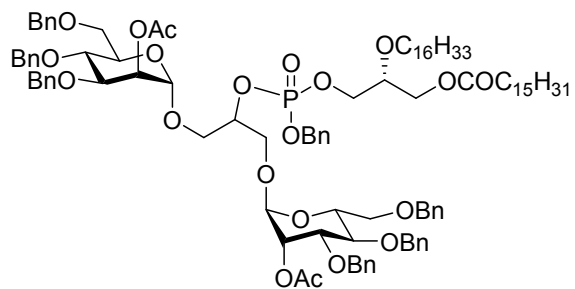


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

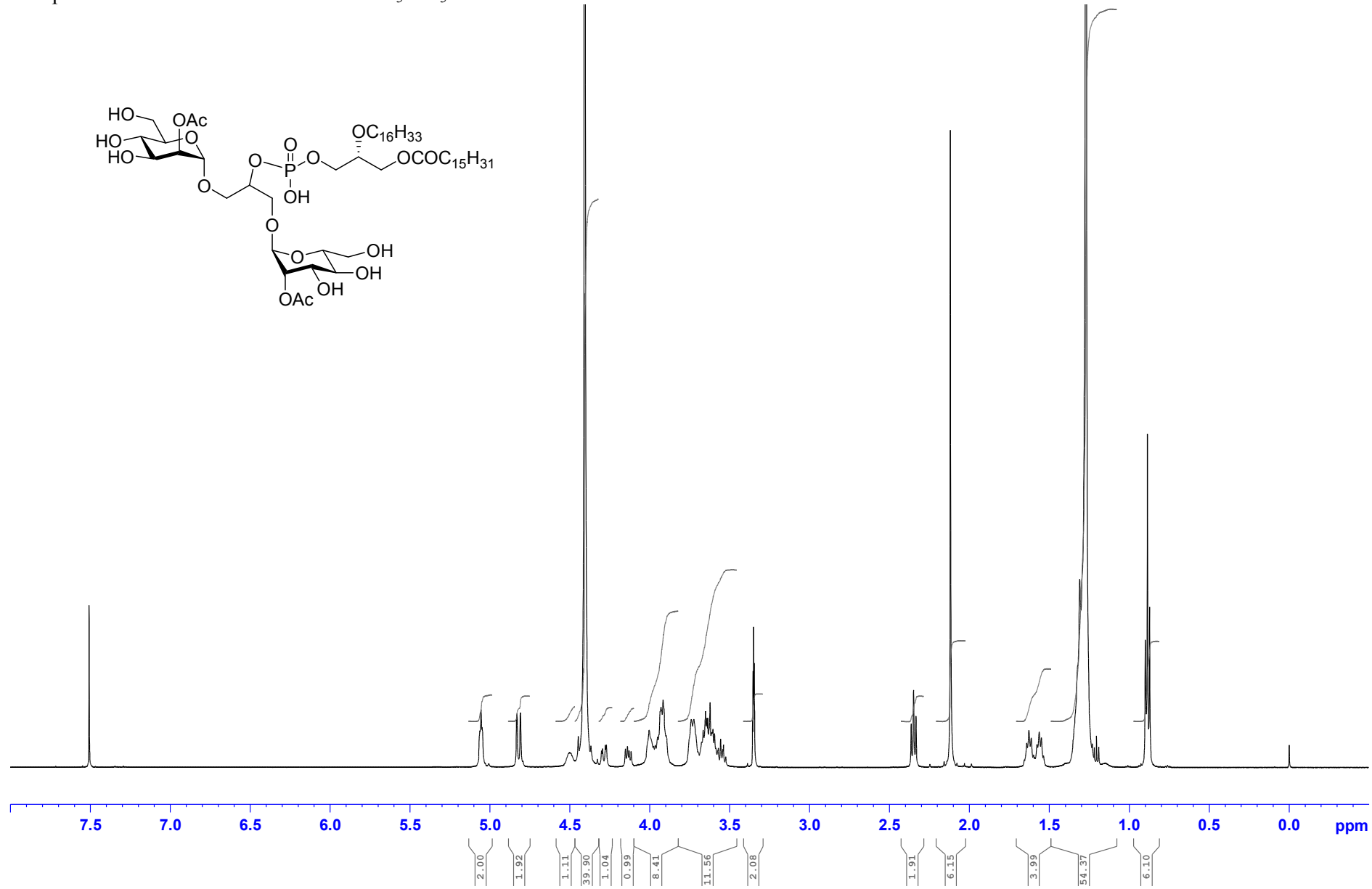
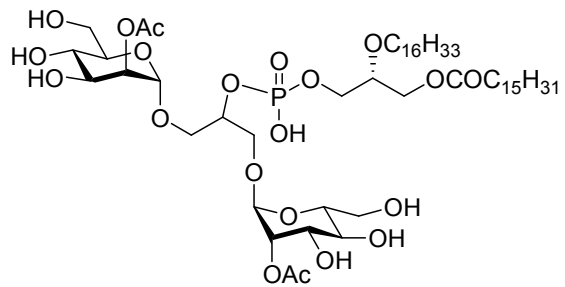
s80



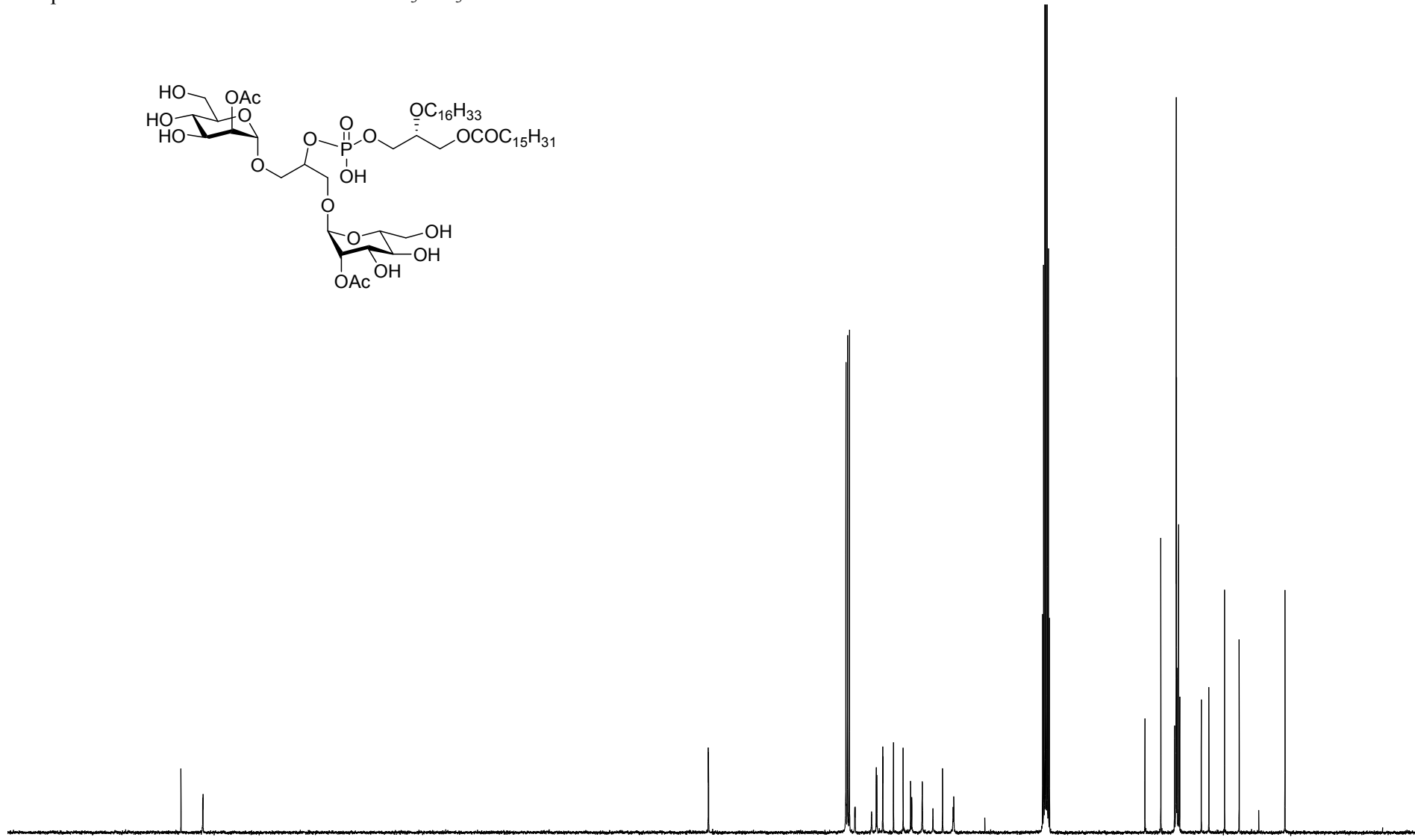
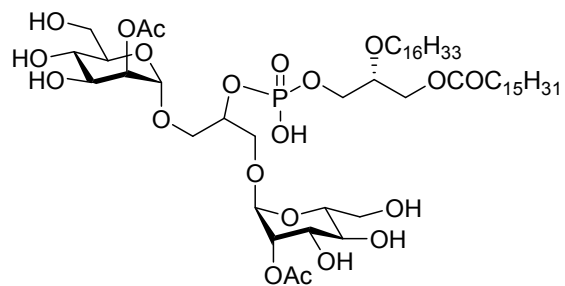
Compound **41** 202 MHz  $^{31}\text{P}$  NMR  $\text{CDCl}_3$



Compound **42** 500 MHz  $^1\text{H}$  NMR 2:1  $\text{CDCl}_3/\text{CD}_3\text{OD}$

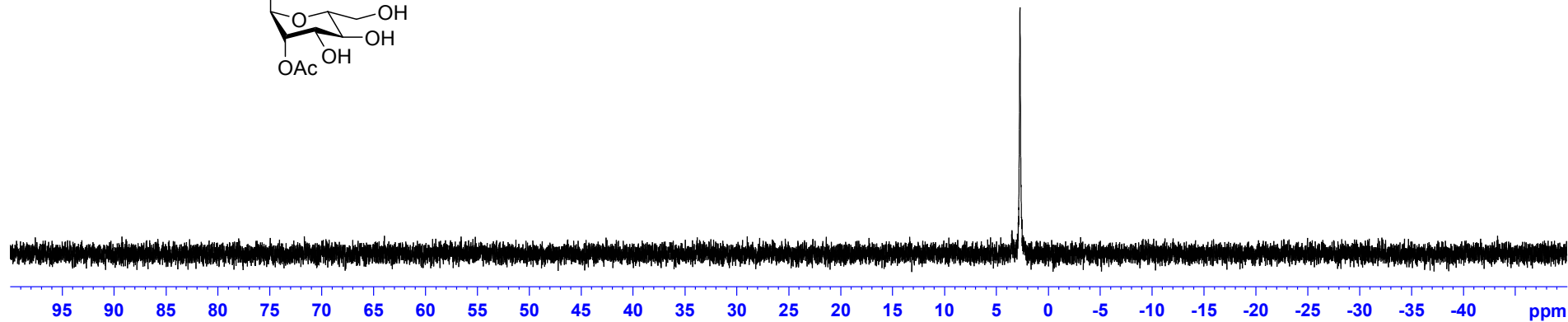
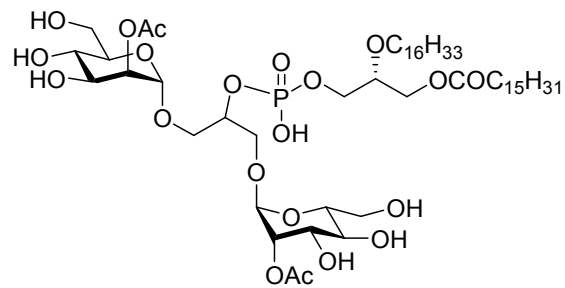


Compound **42** 125 MHz  $^{13}\text{C}$  NMR 2:1  $\text{CDCl}_3/\text{CD}_3\text{OD}$

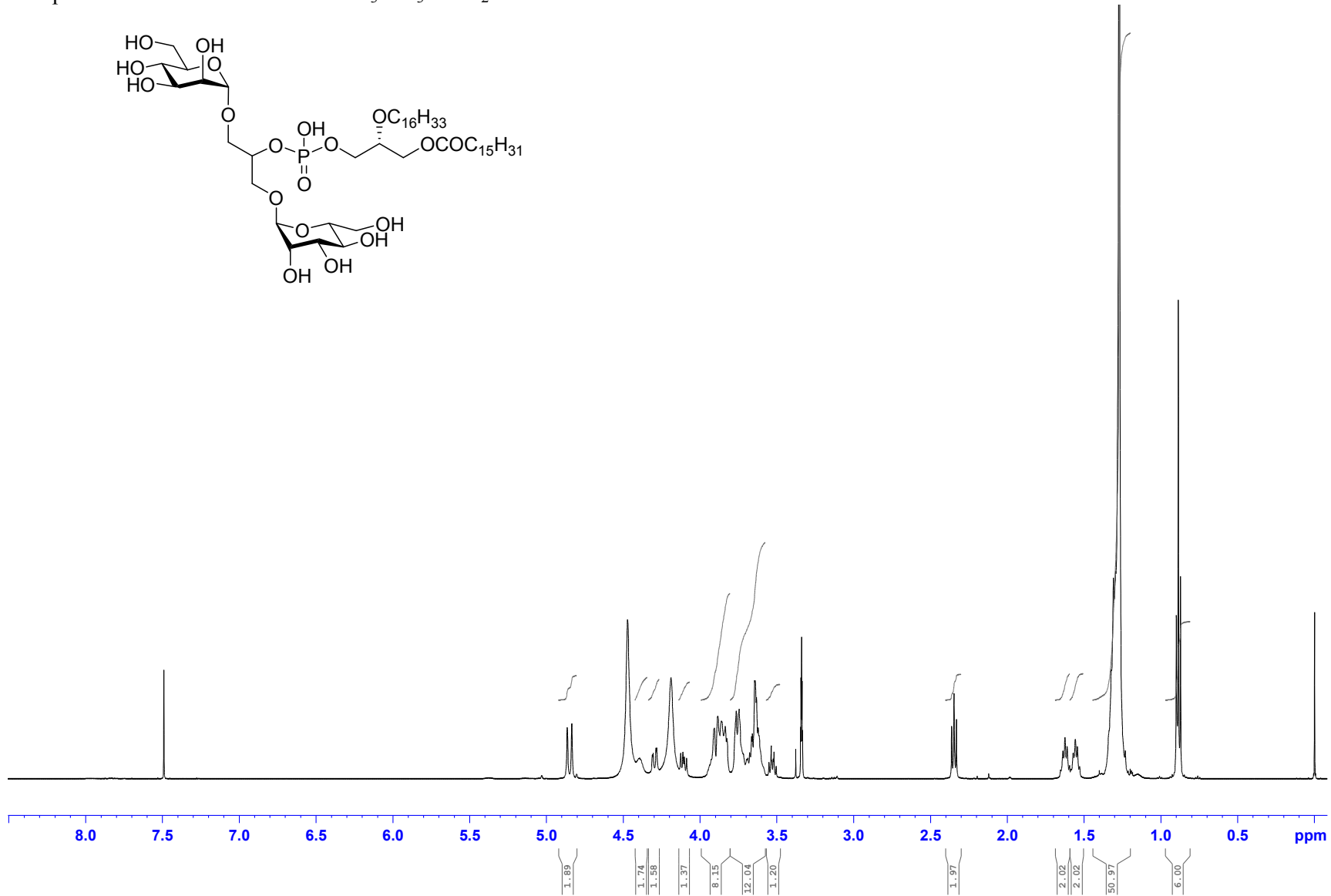
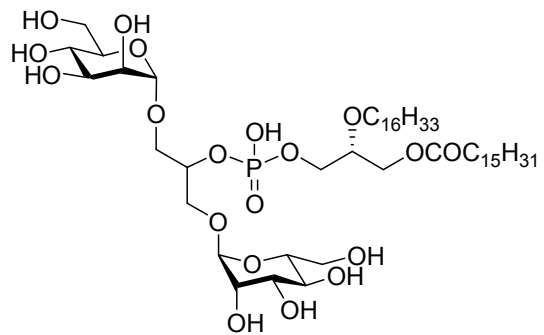


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

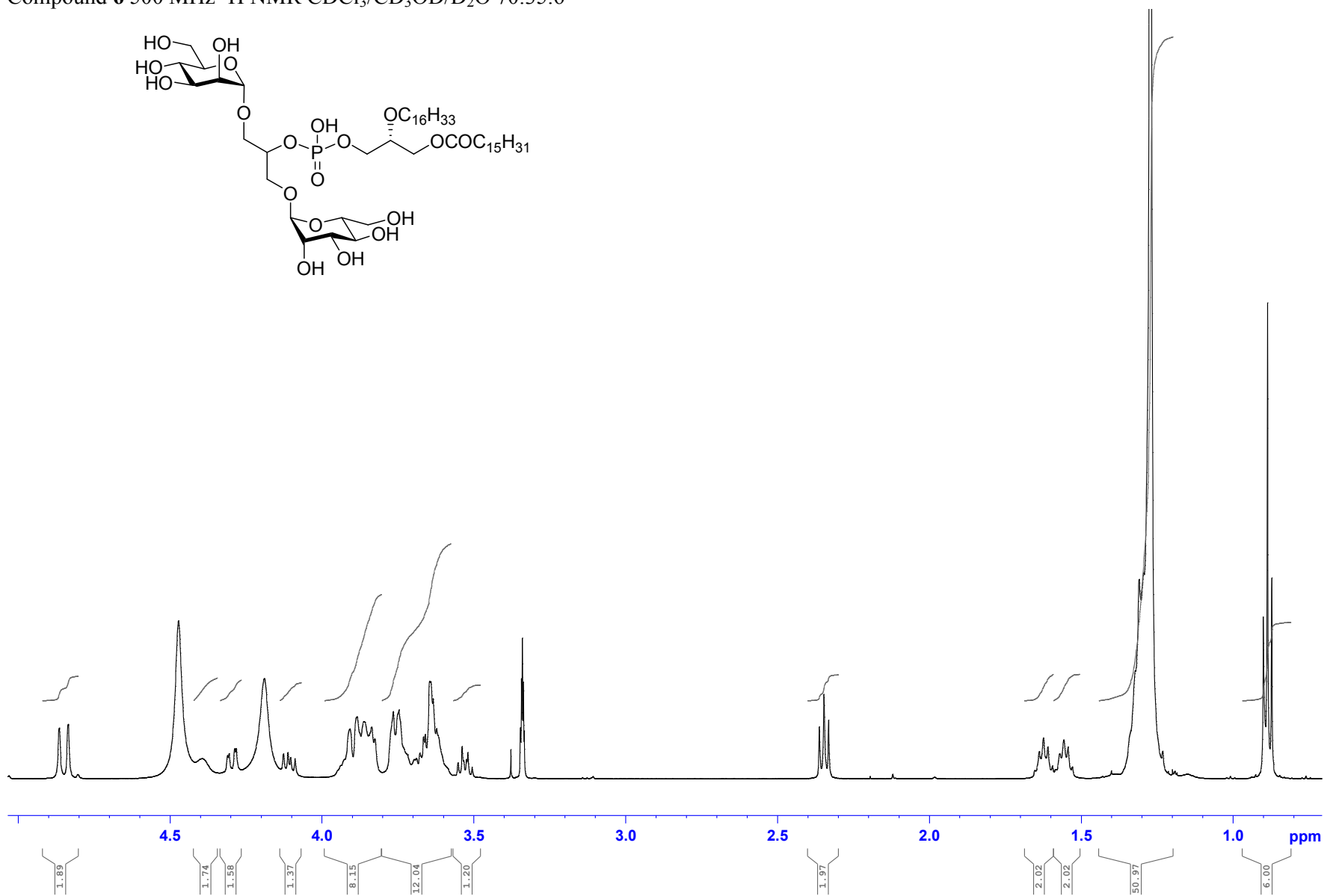
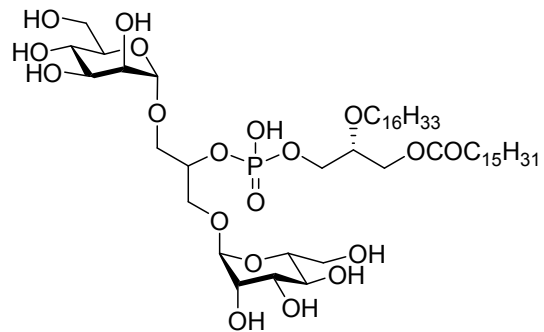
Compound **42** 202 MHz  $^{31}\text{P}$  NMR 2:1  $\text{CDCl}_3/\text{CD}_3\text{OD}$



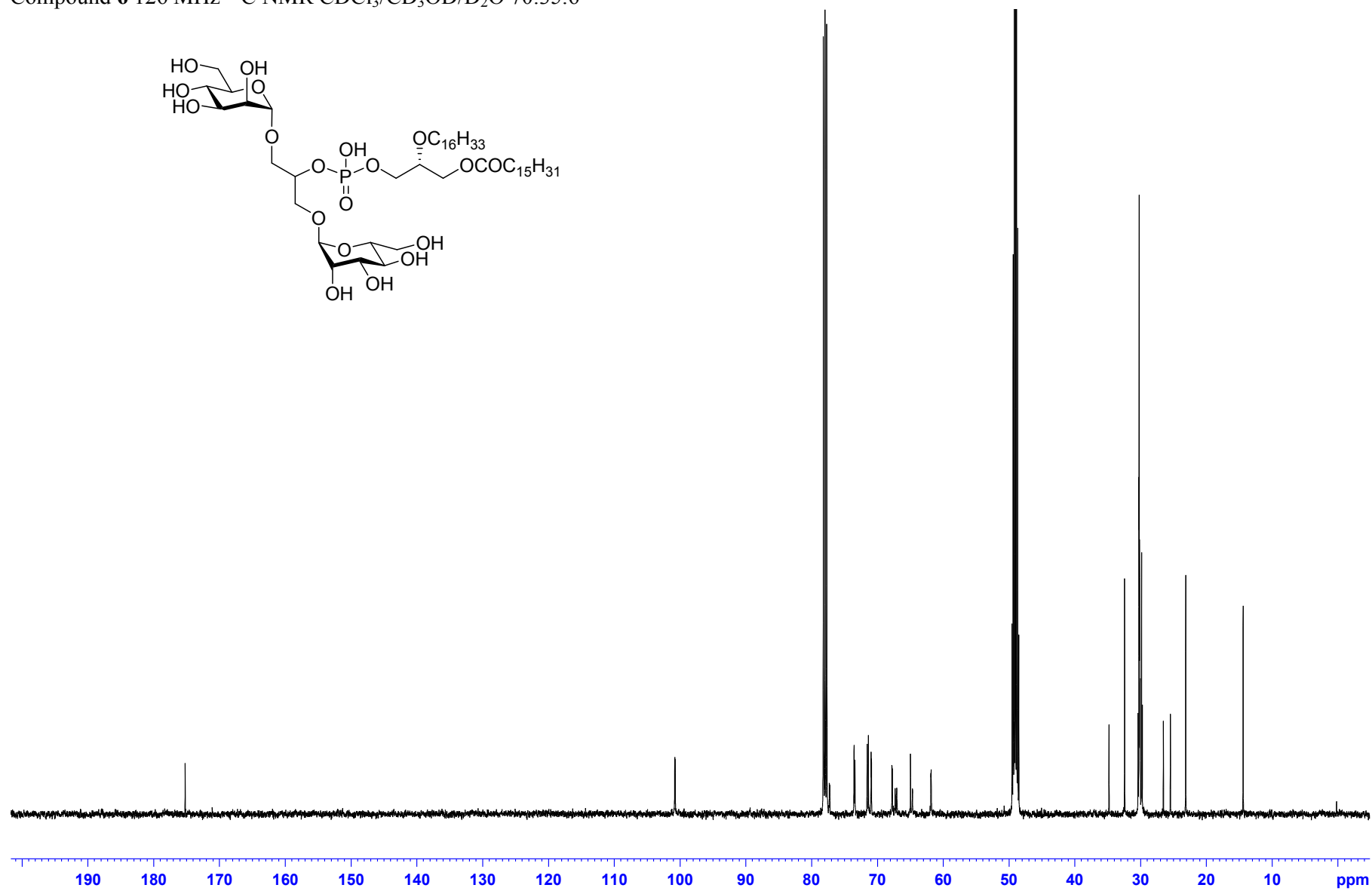
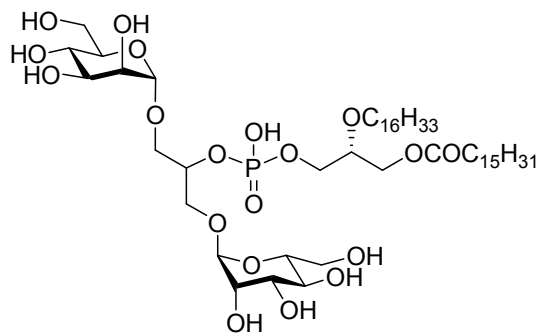
Compound **6** 500 MHz  $^1\text{H}$  NMR  $\text{CDCl}_3/\text{CD}_3\text{OD}/\text{D}_2\text{O}$  70:35:6



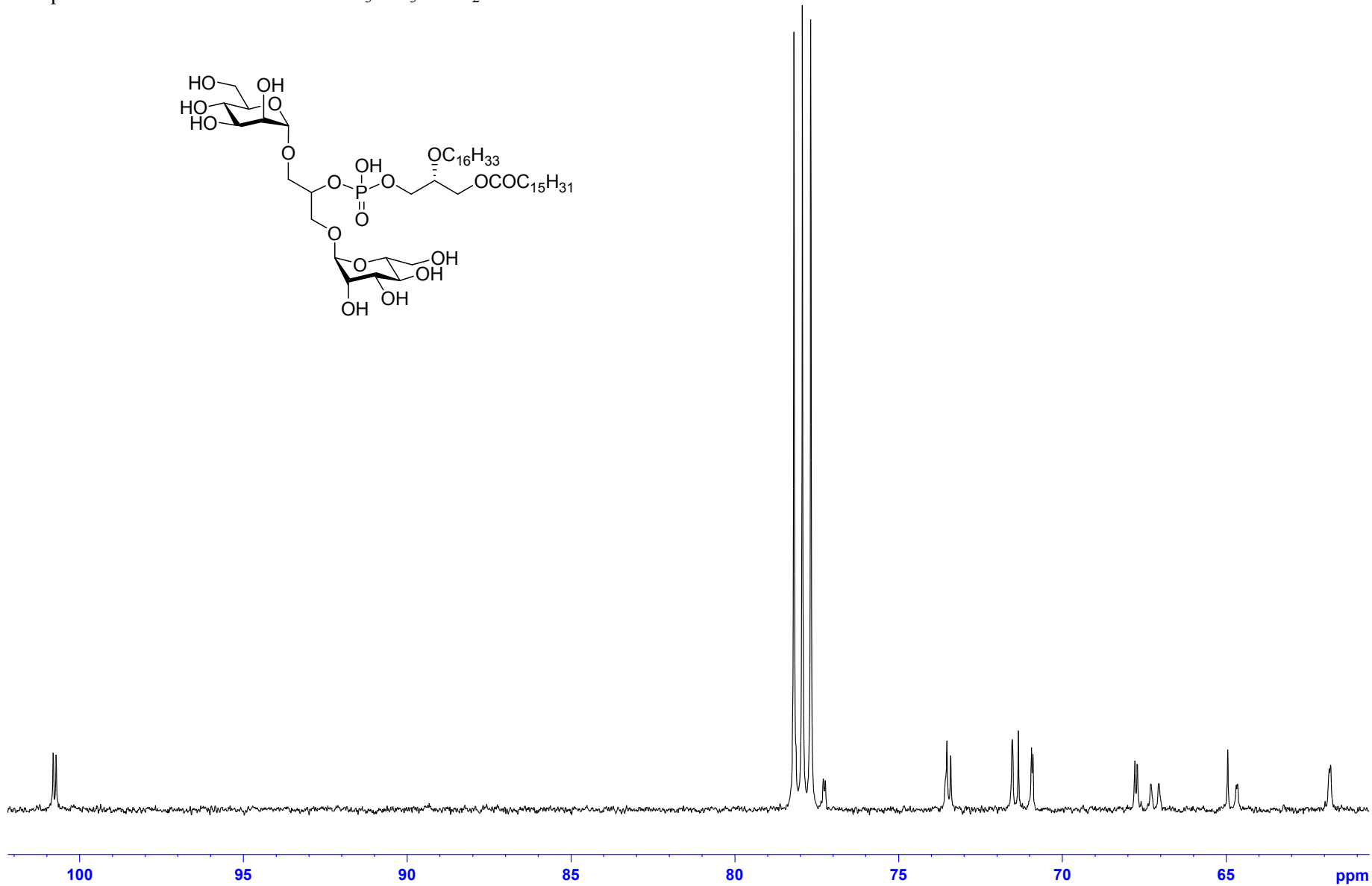
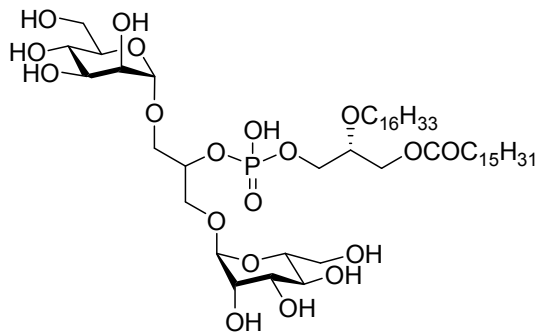
Compound 6 500 MHz  $^1\text{H}$  NMR  $\text{CDCl}_3/\text{CD}_3\text{OD}/\text{D}_2\text{O}$  70:35:6



Compound **6** 126 MHz  $^{13}\text{C}$  NMR  $\text{CDCl}_3/\text{CD}_3\text{OD}/\text{D}_2\text{O}$  70:35:6

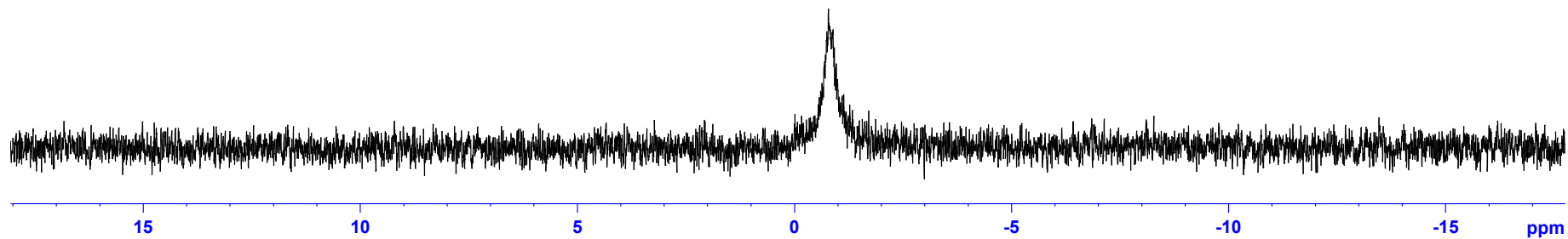
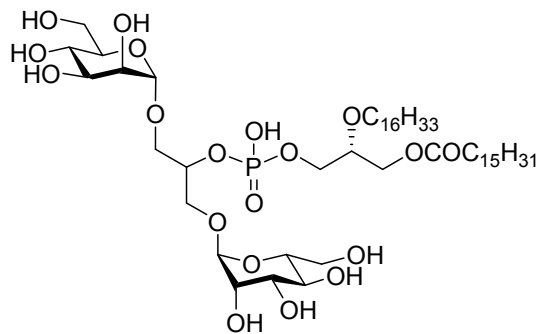


Compound **6** 126 MHz  $^{13}\text{C}$  NMR  $\text{CDCl}_3/\text{CD}_3\text{OD}/\text{D}_2\text{O}$  70:35:6





Compound 6 202 MHz  $^{31}\text{P}$  NMR  $\text{CDCl}_3/\text{CD}_3\text{OD}/\text{D}_2\text{O}$  70:35:6



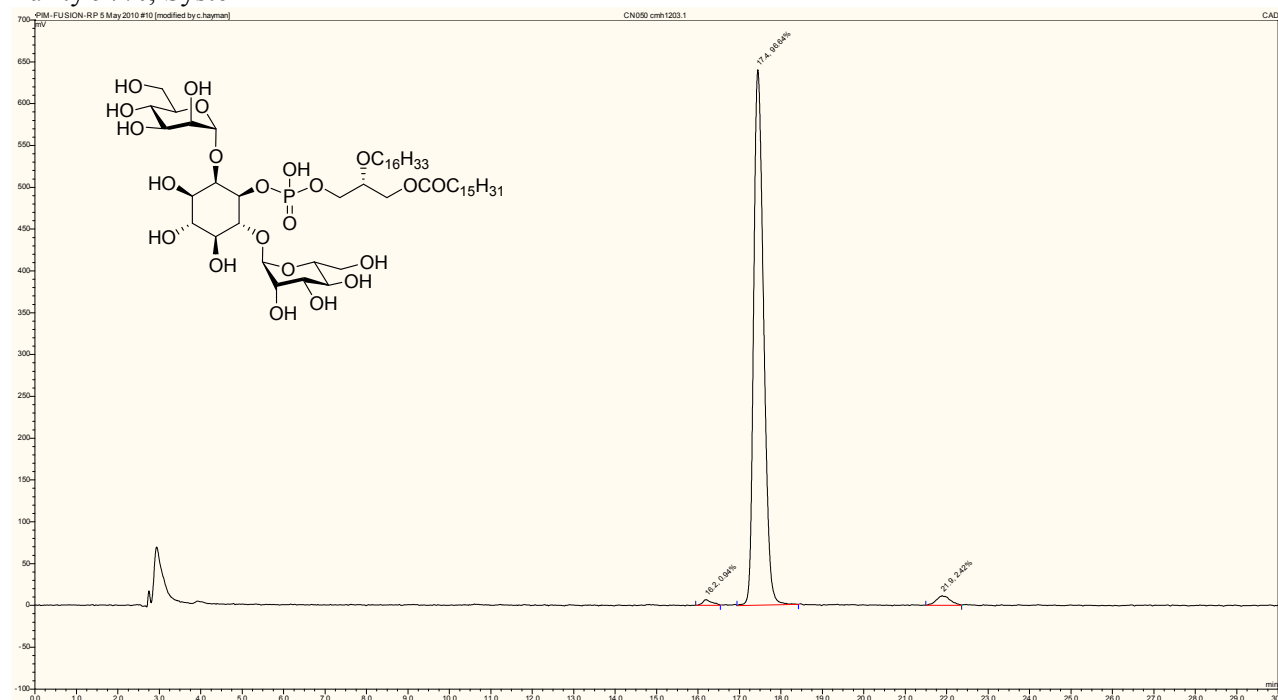
## HPLC Conditions

The HPLC analyses of **1-4** and **6-8** used System 1; HPLC: Column: Phenomenex Synergi 4  $\mu\text{m}$  Fusion-RP (80  $\text{\AA}$ , 3.0  $\times$  250 mm). Detection: ESA Corona charged aerosol detector (Filter = none). Flow rate; 1 mL/min. Column temperature; 40  $^{\circ}\text{C}$ . Solvents; A  $\text{H}_2\text{O}$ ; B Water containing 50 mM  $\text{NH}_4\text{OAc}$  adjusted to pH 5.0; C Methanol. Gradient Program; 0–10 min 10–0% A, 10% B, 80–90% C, 10–28 min hold (0% A, 10% B, 90% C), 28–30 min return to starting conditions then equilibrate for 10 min prior to next injection. The HPLC analysis of **5** used System 2; Column, detector and column temperature were as for System 1. Flow rate 0.8 ml/Min. Solvents; A 1:1 water/MeOH + 50 mM  $\text{NH}_4\text{OAc}$  adjusted to pH 5.0 prior to dilution; B MeOH; C Isopropanol. Gradient Program; 0 min 10% A, 90% C; 15min 10%A, 65% B, 25% C; 15–35 min hold 10%A, 65% B, 25% C; 35–40 min return to starting conditions then equilibrate for 10 min prior to next injection. All chromatograms were corrected by subtraction of a blank injection prior to integrating signals after a four min cut-off. Integration values are not corrected for detector non-linearity

## HPLC Data

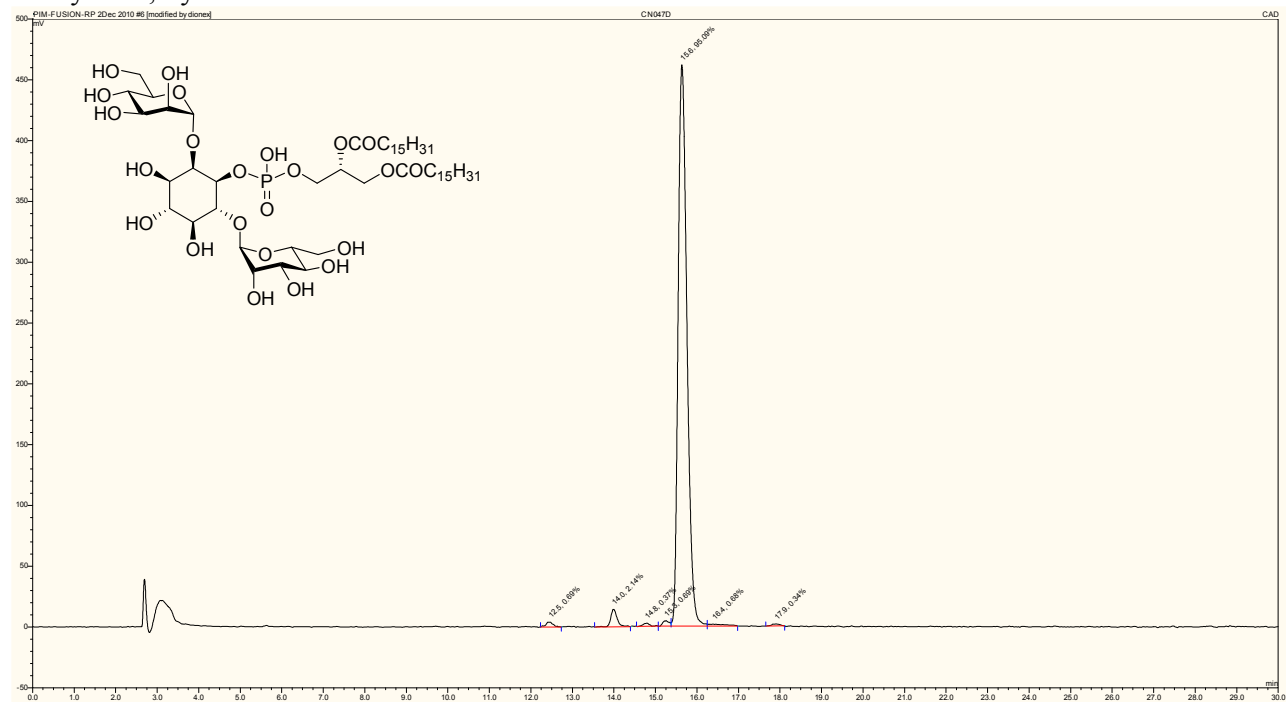
HPLC Compound 1

Purity 97%; System 1



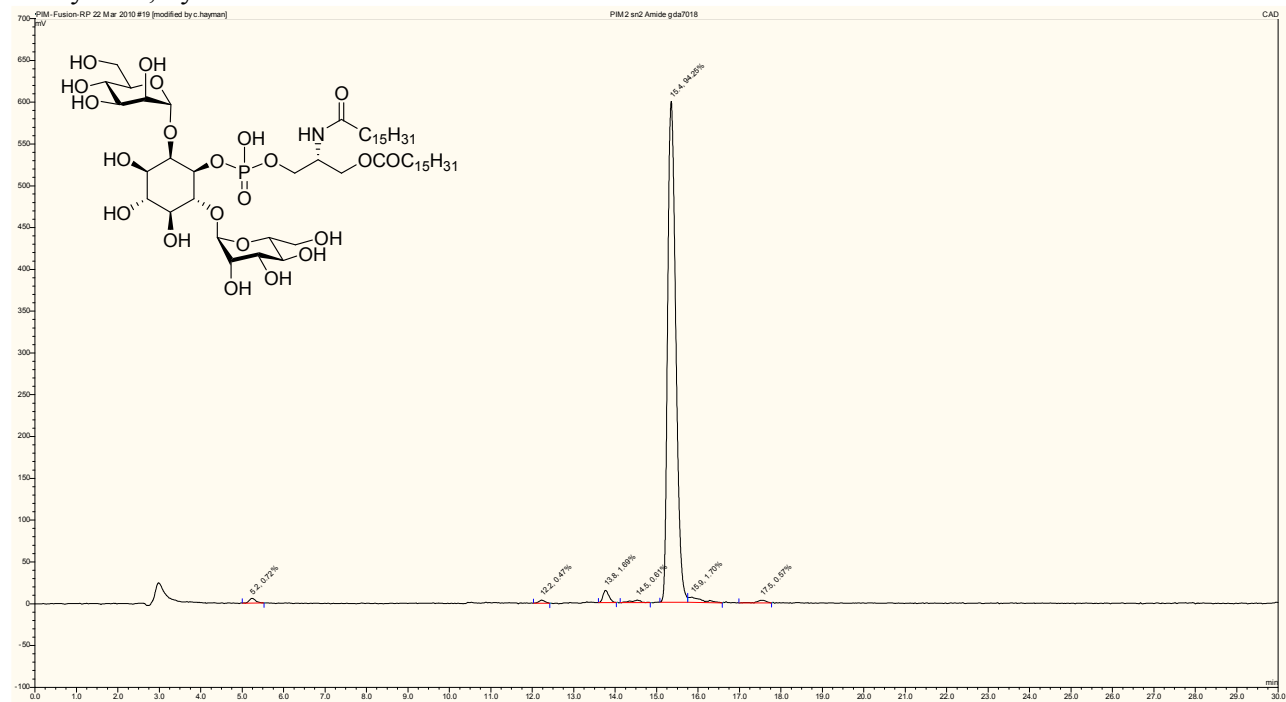
## HPLC Compound 2

Purity 95%; System 1



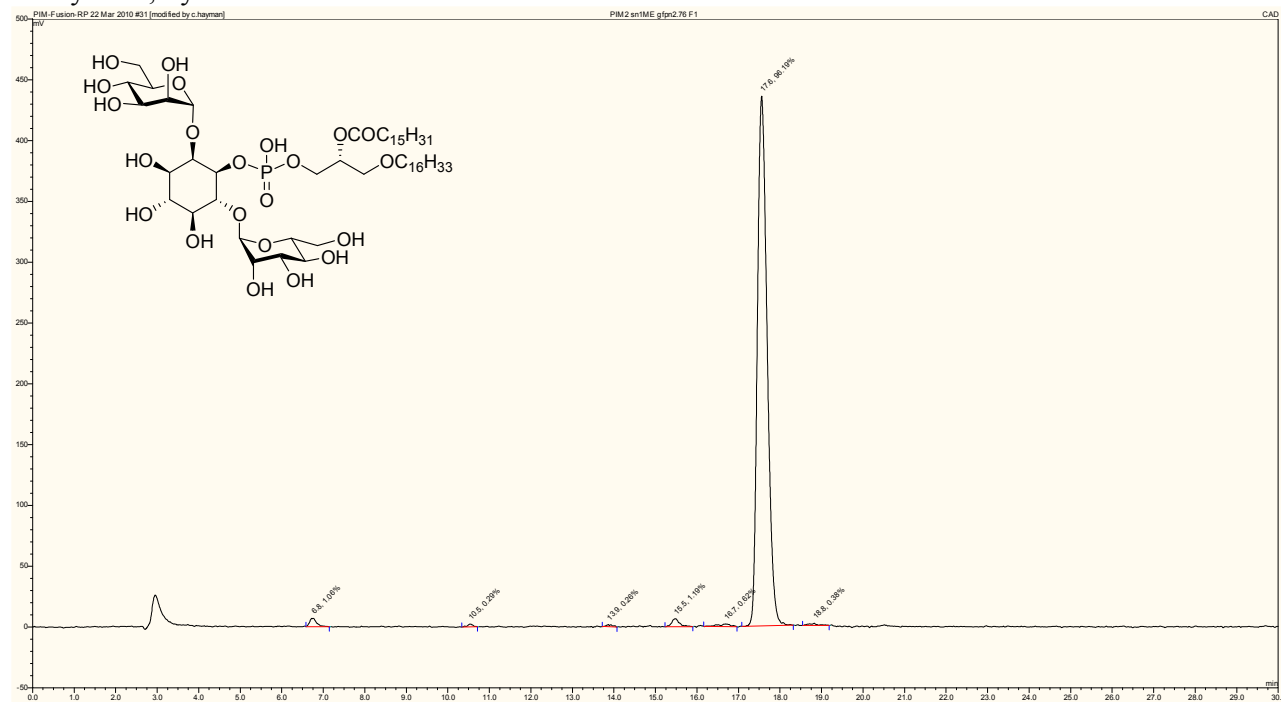
## HPLC Compound 3

Purity 94%; System 1



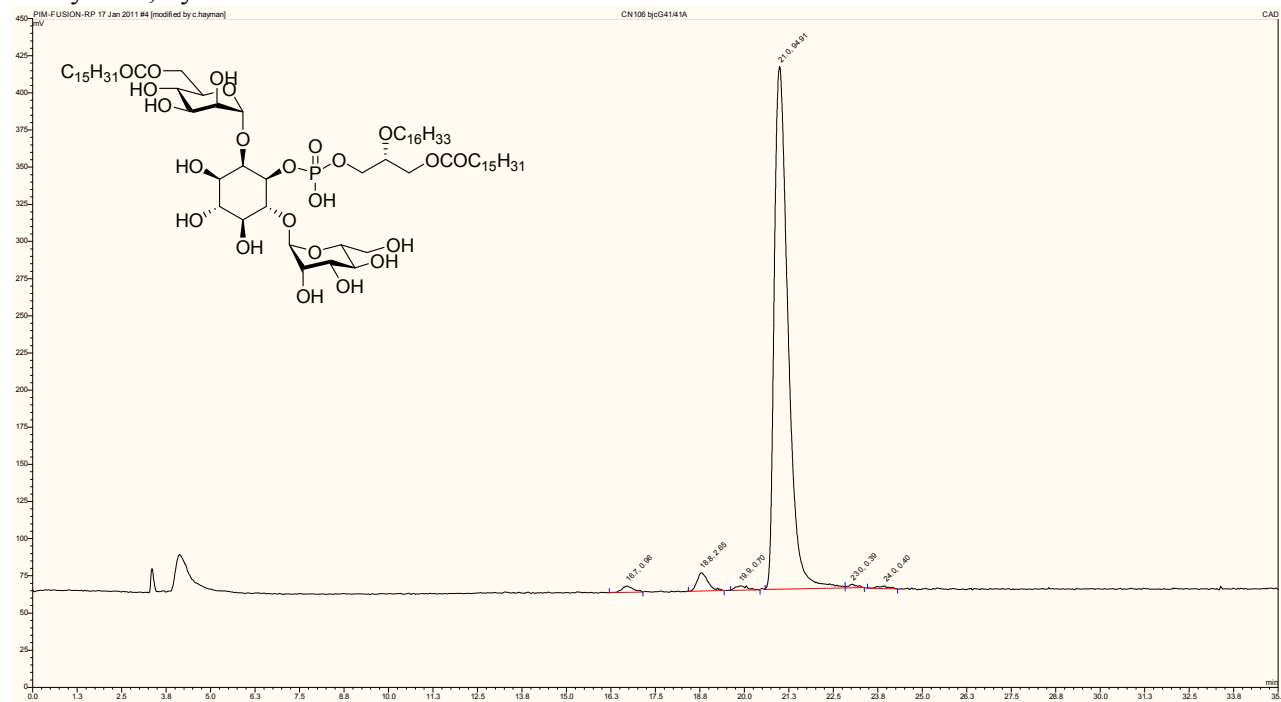
# HPLC Compound 4

Purity 96%; System 1

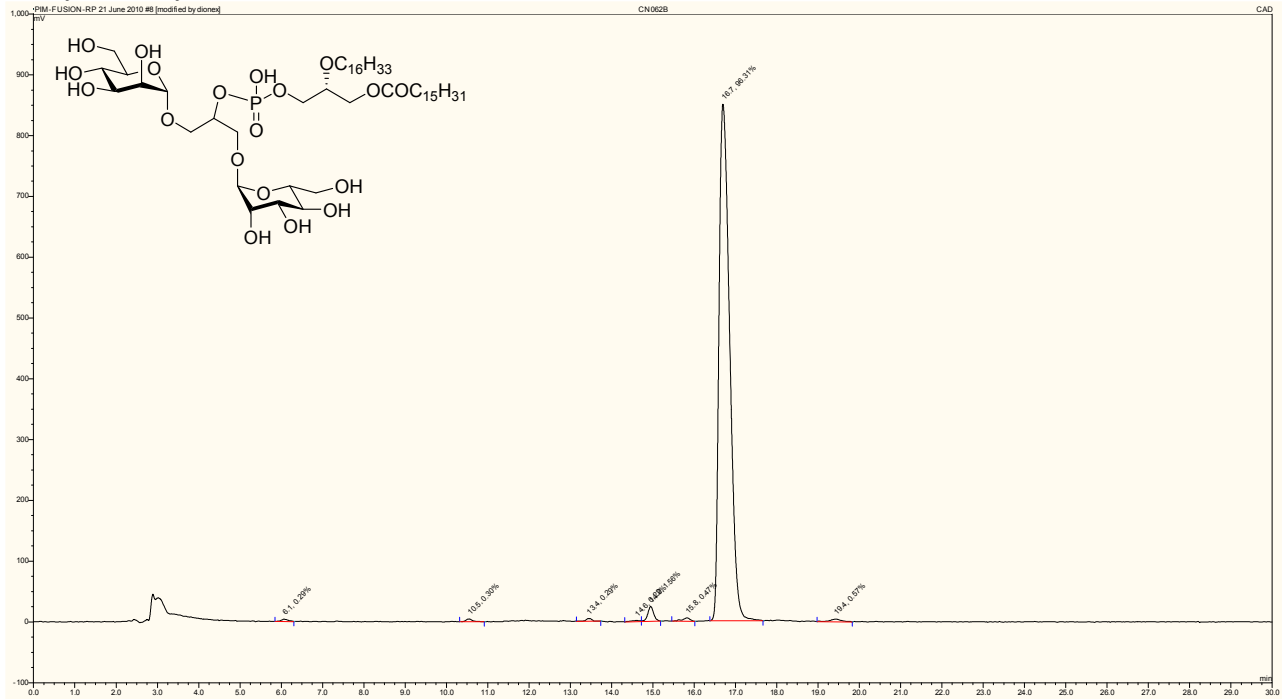


# HPLC Compound 5

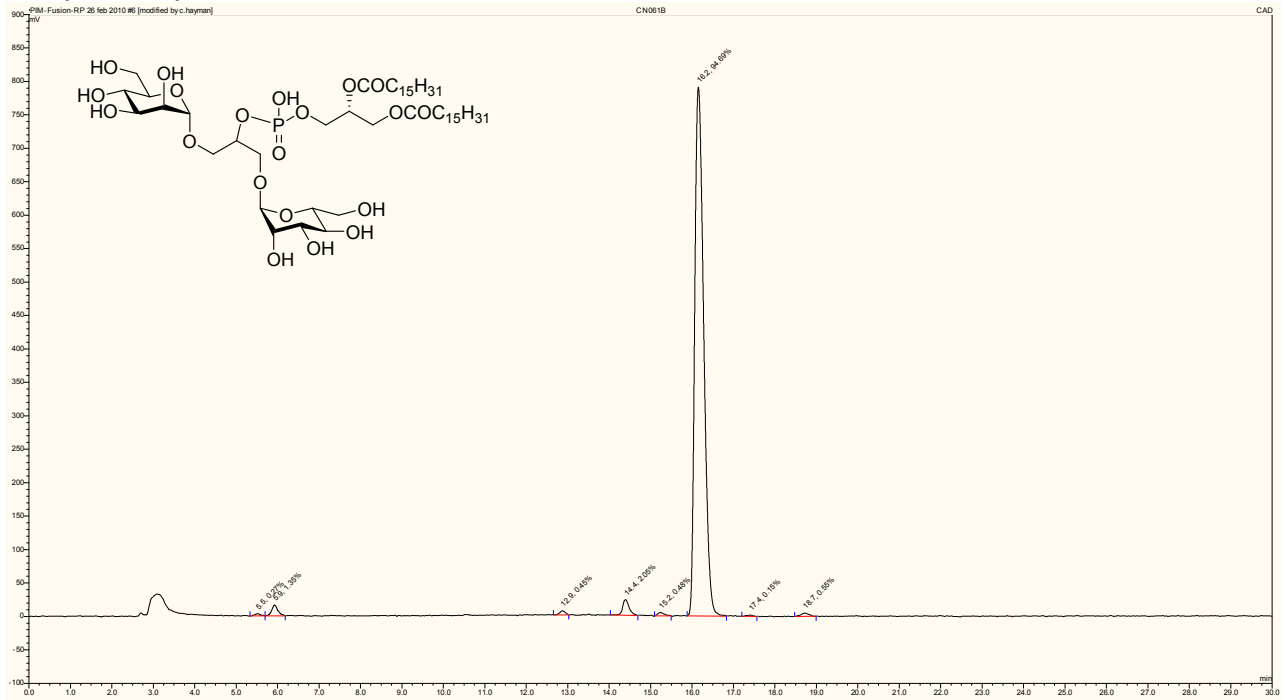
Purity 95%; System 2



HPLC Compound 6  
Purity 96%; System 1

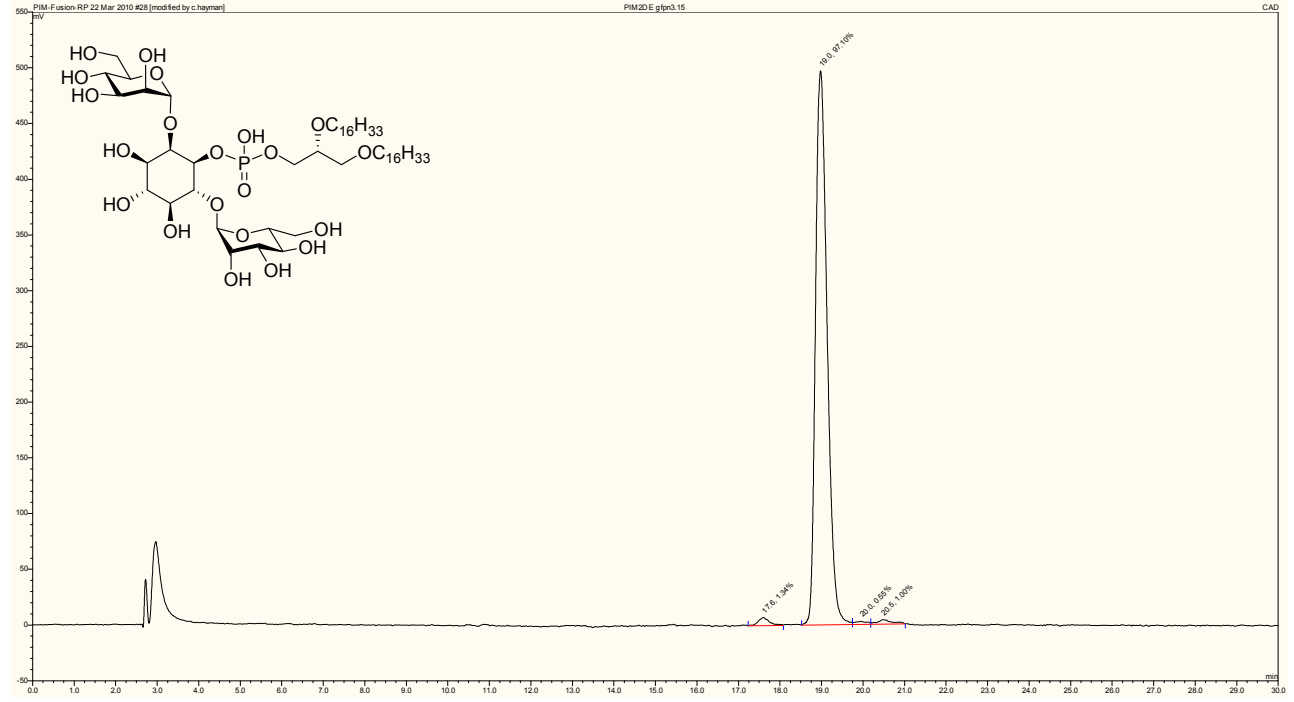


HPLC Compound 7  
Purity 95%; System 1



# HPLC Compound 8

Purity 97%; System 1



Cell, thioglycollate-induced peritoneal macrophages, viability data, compounds 1 - 8

