Electronic Supplementary Information (ESI)

The *α*-hydroxyphosphonate-phosphate rearrangement of a noncyclic substrate – Some new observations

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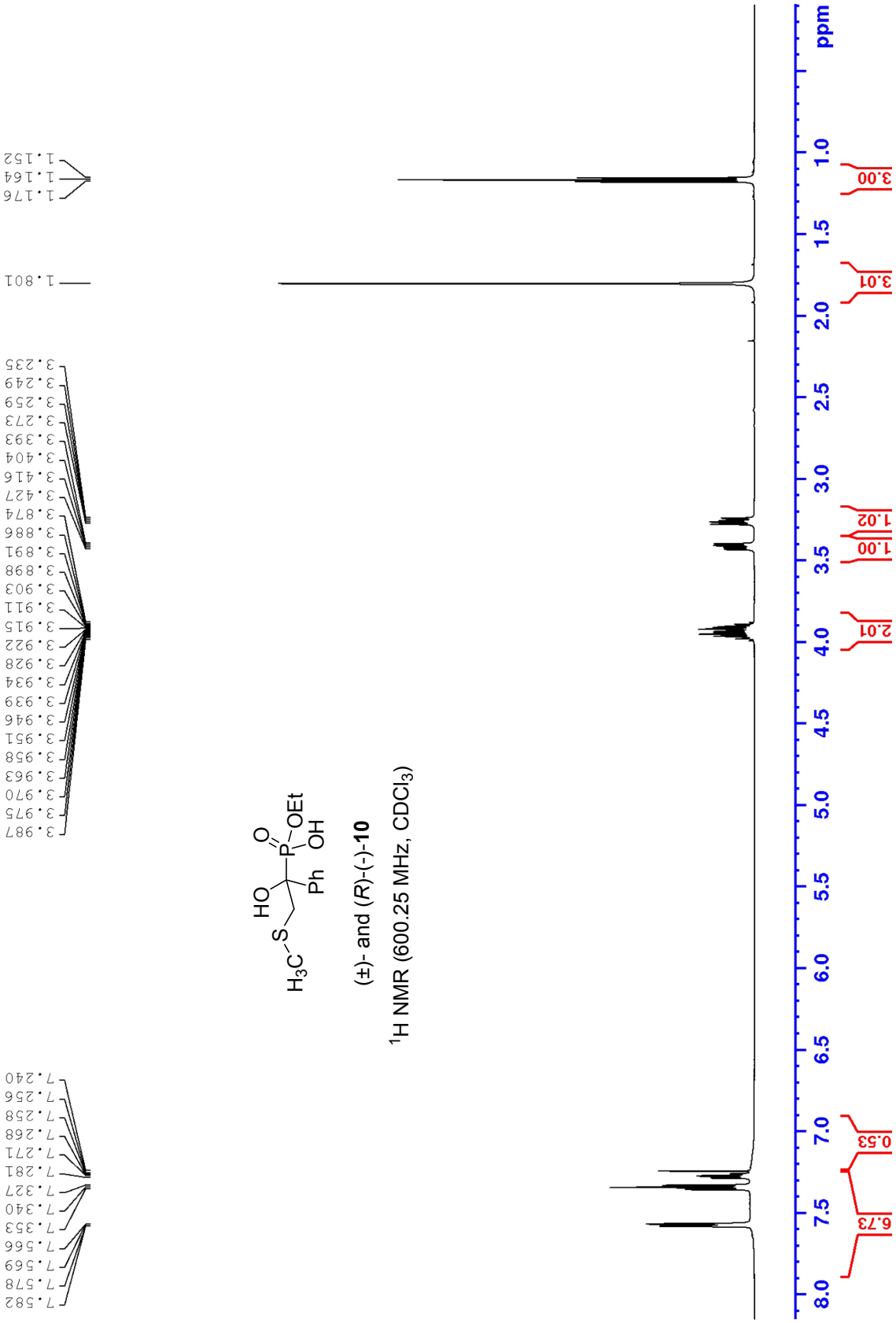
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3.915
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3.928
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3.939
3.946
3.951
3.958
3.963
3.970
3.975
3.987
7.240
7.256
7.258
7.268
7.271
7.281
7.327
7.340
7.353
7.566
7.569
7.578
7.582
HO
O
P
OEt
OH
Ph
S
H3C
(±)- and (R)-(-)-10
1H NMR (600.25 MHz, CDCl3)
ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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1.0
6.73
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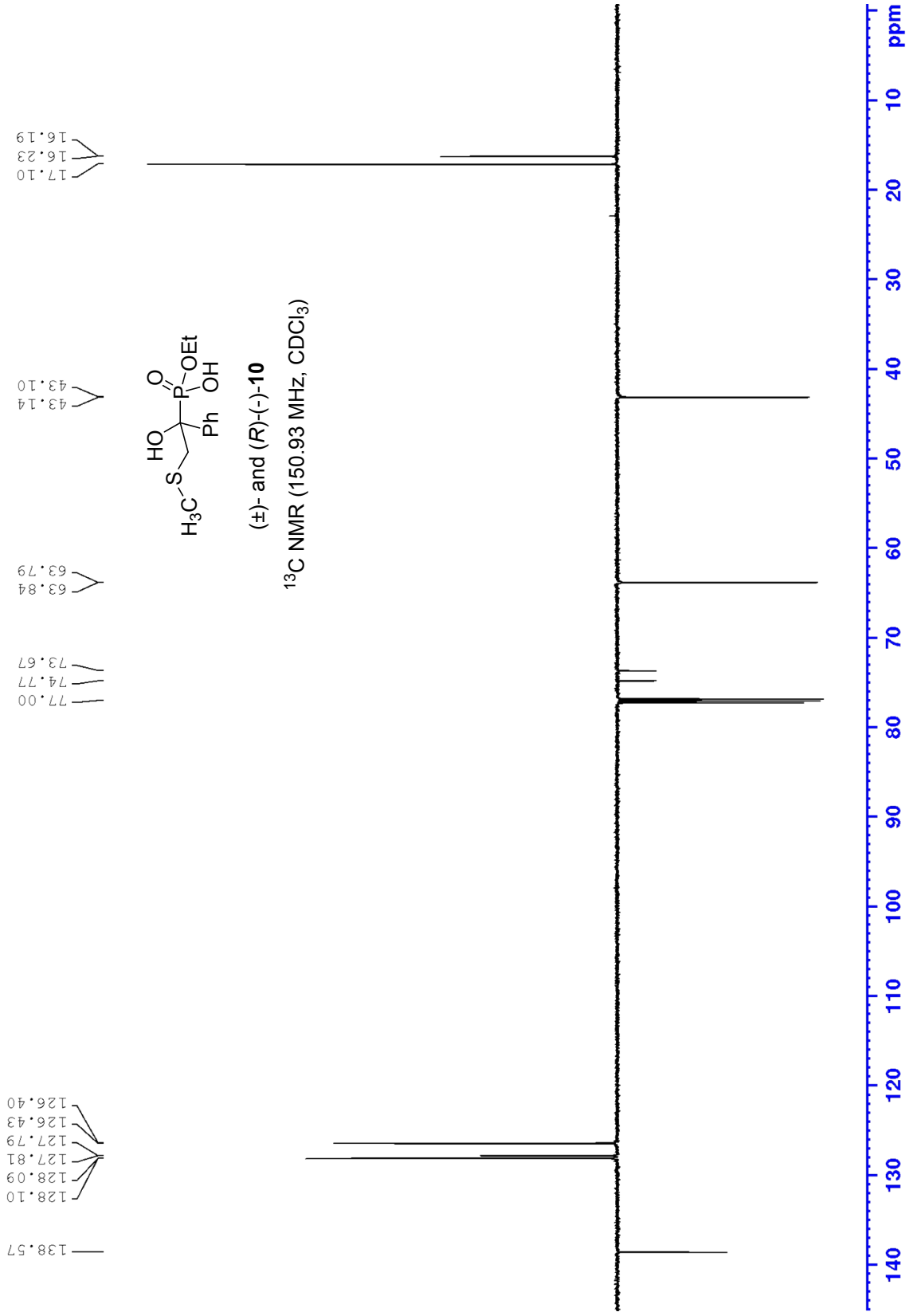
2.01
1.00
1.02
3.01
3.00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127.79
127.81
128.09
128.10
138.57
HO
O
P
OEt
Ph
OH
S
H3C
(±)- and (R)-(-)-10
13C NMR (150.93 MHz, CDCl3)
ppm
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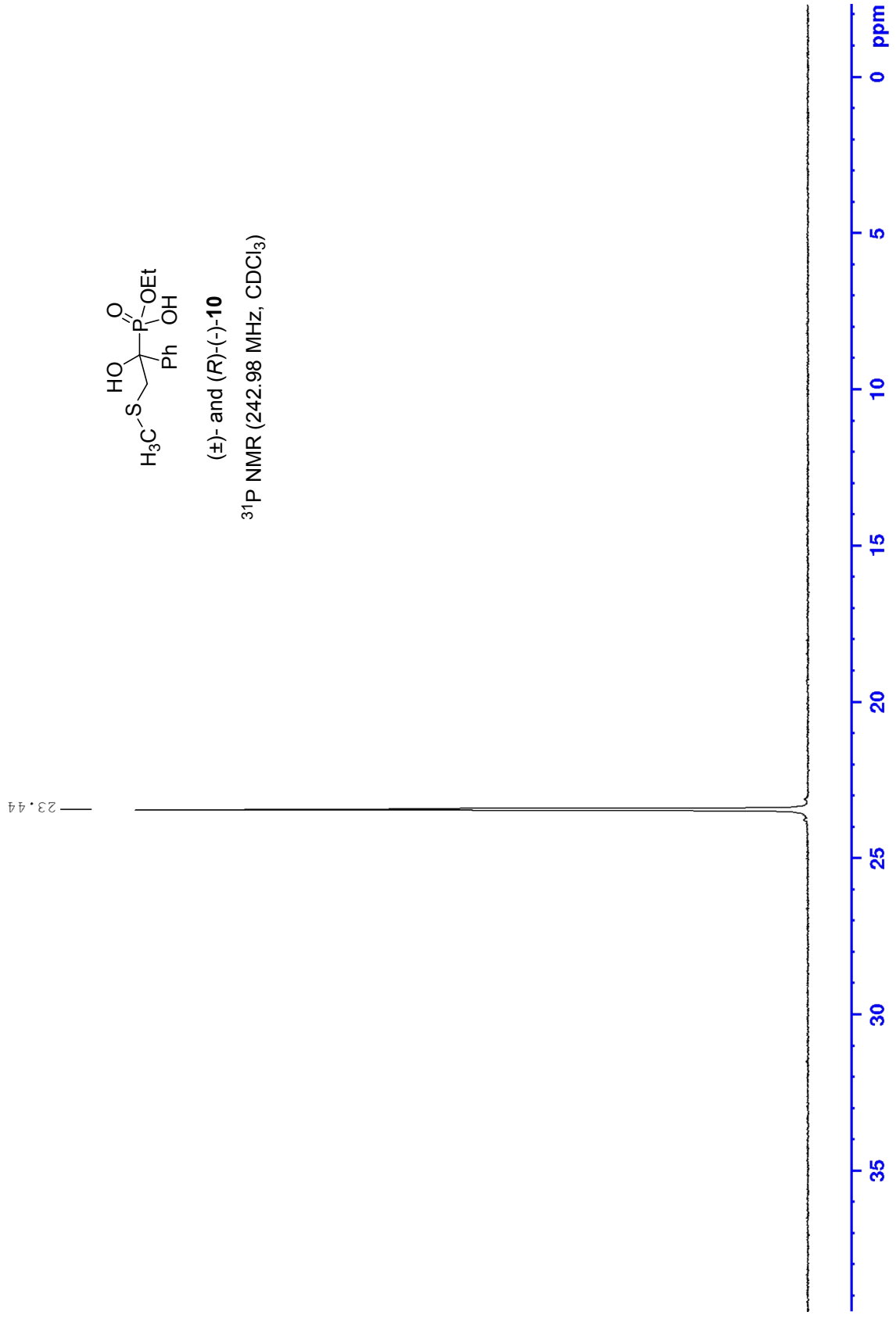
20
30
40
50
60
70
80
90
100
110
120
130
140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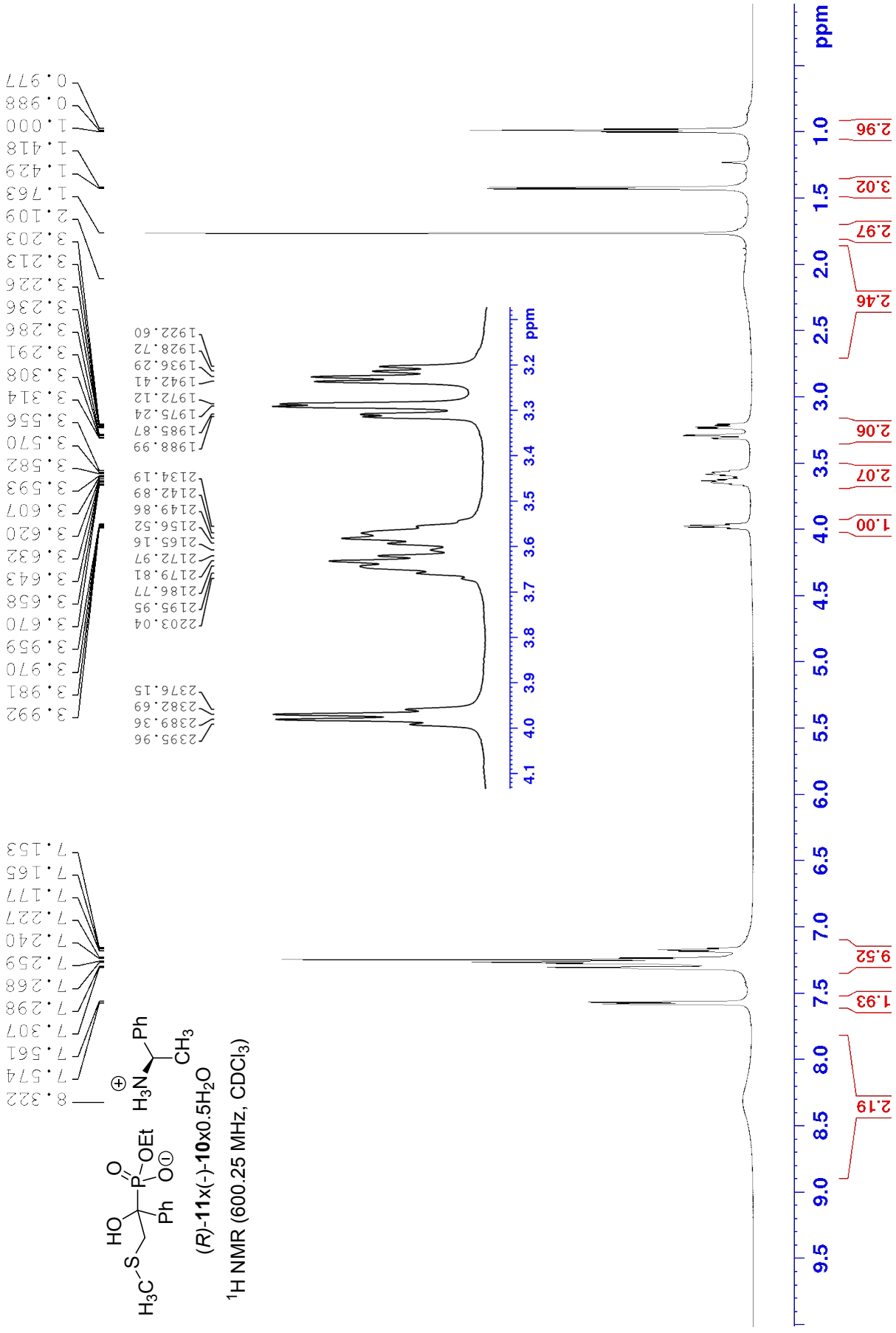
20
25
30
35
HO
O
P
OEt
OH
Ph
S
H3C
(±)- and (R)-(-)-10
31P NMR (242.98 MHz, CDCl3)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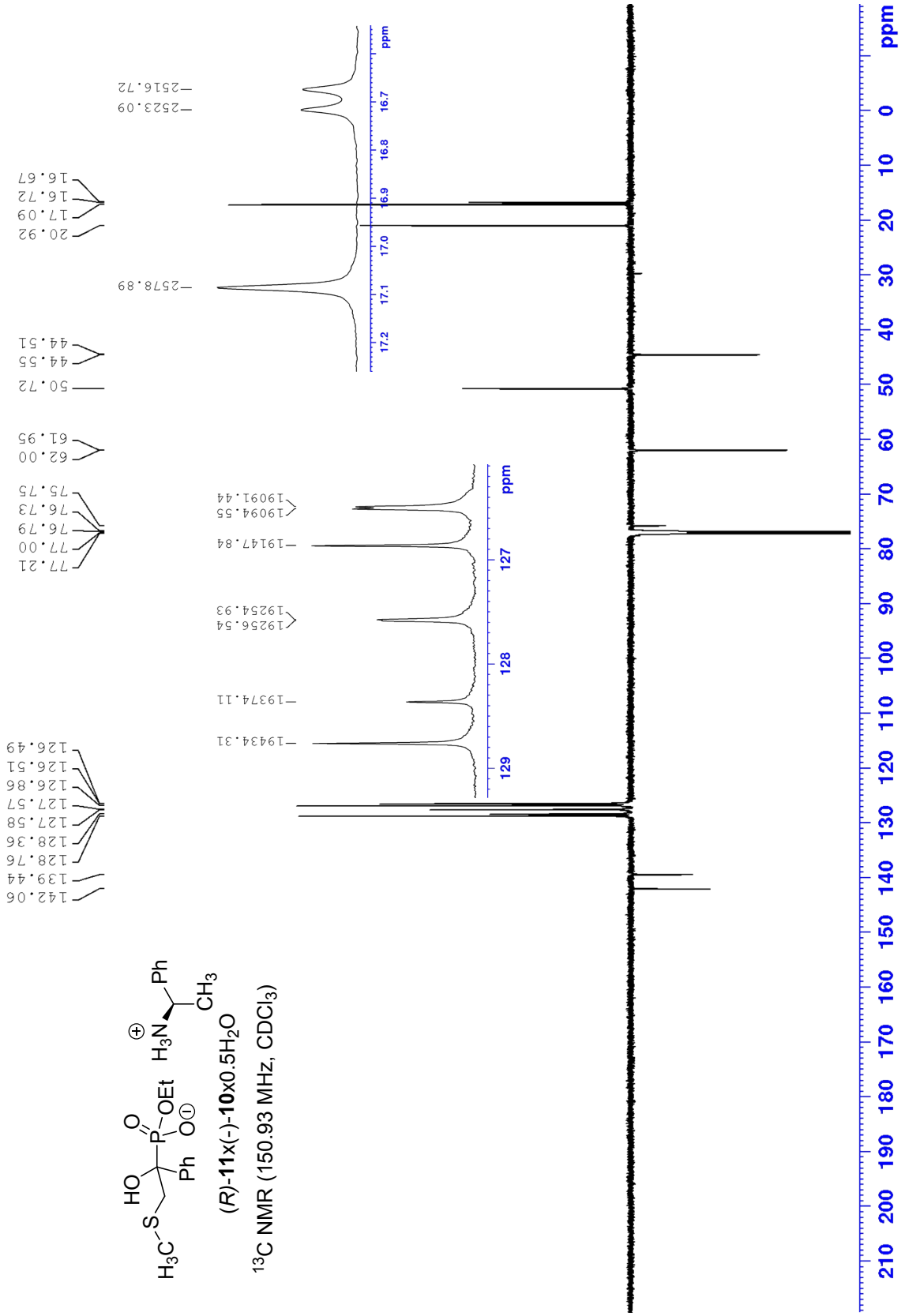
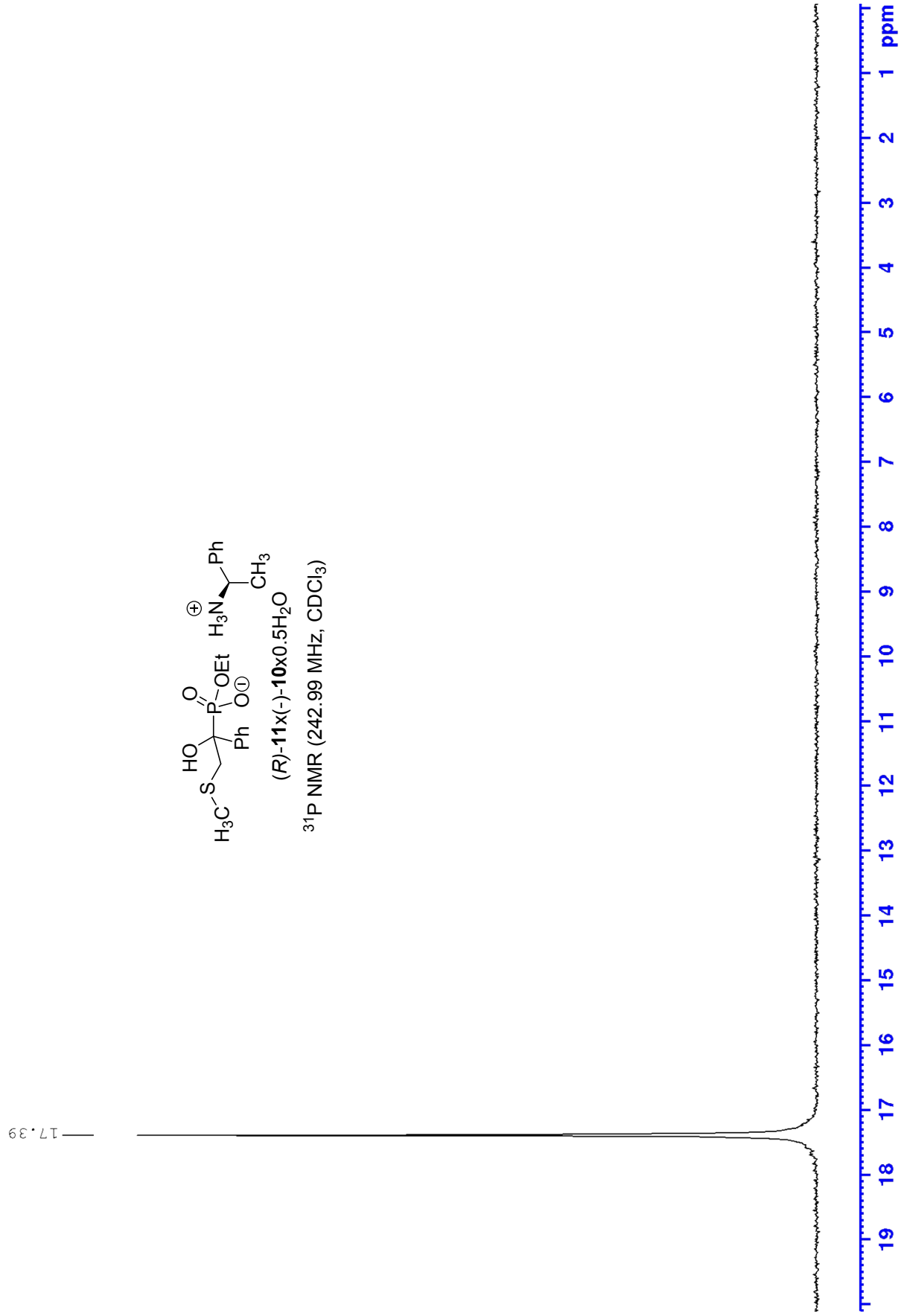
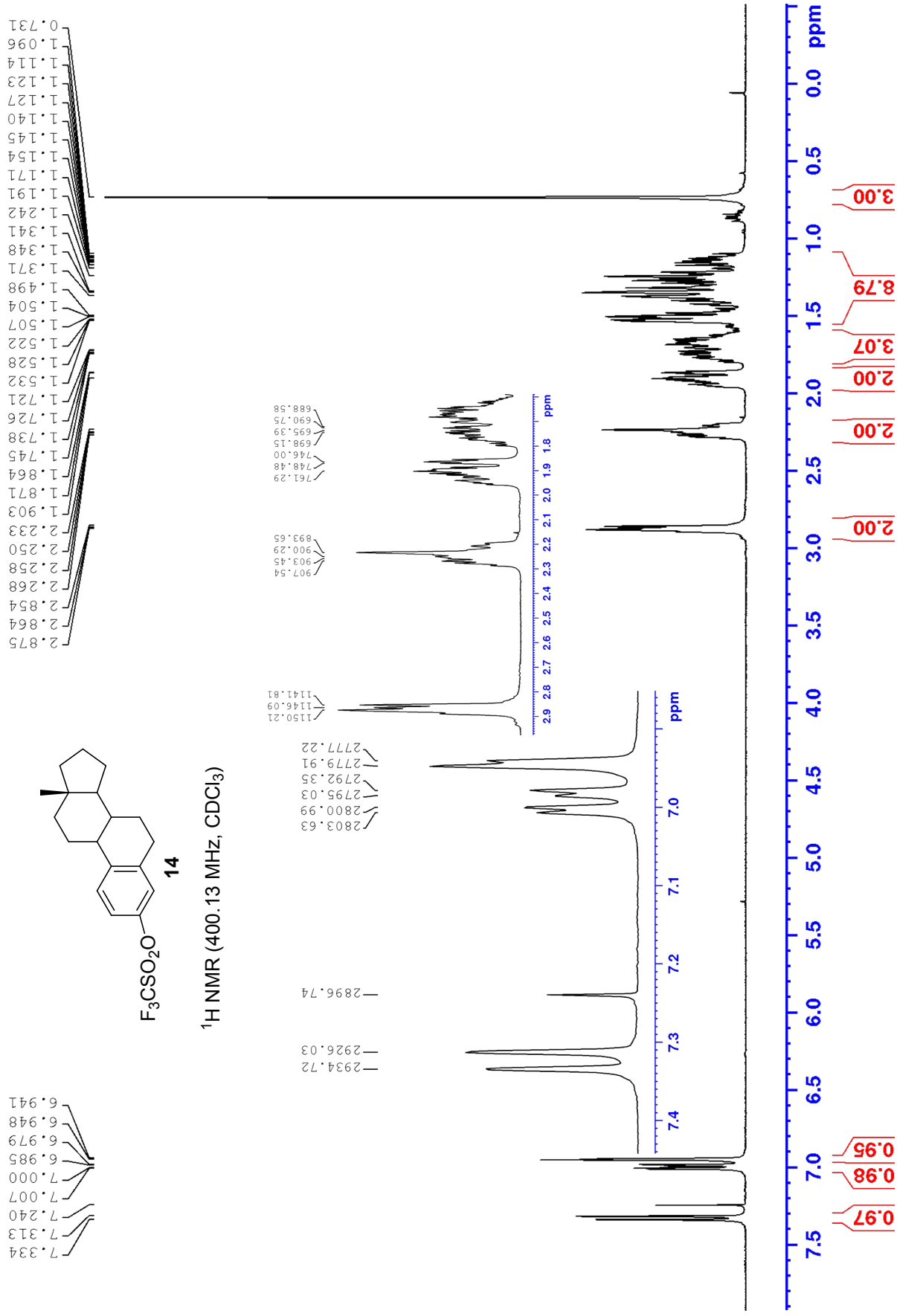
1H NMR (600.25 MHz, CDCl3)
ppm

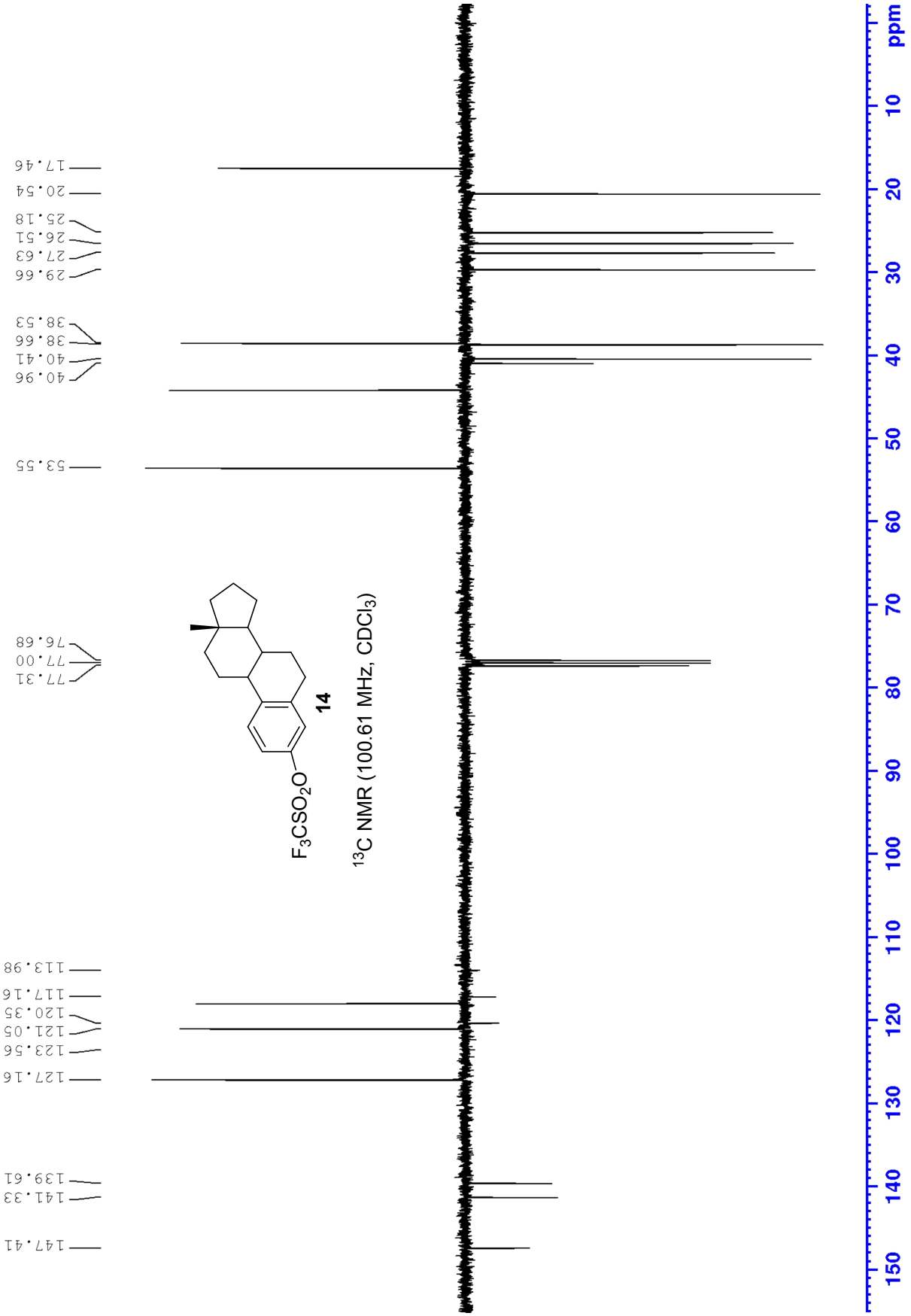

(R)-11x(-)-10x0.5H2O
13C NMR (150.93 MHz, CDCl3)
ppm



(*R*)-**11**x(-)-**10**x0.5H_2O

^{31}P NMR (242.99 MHz, $CDCl_3$)


F_3CSO_2O
14
^{1}H NMR (400.13 MHz, $CDCl_3$)
ppm
3.00
8.79
3.07
2.00
2.00
2.00
0.95
0.98
0.97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38.66
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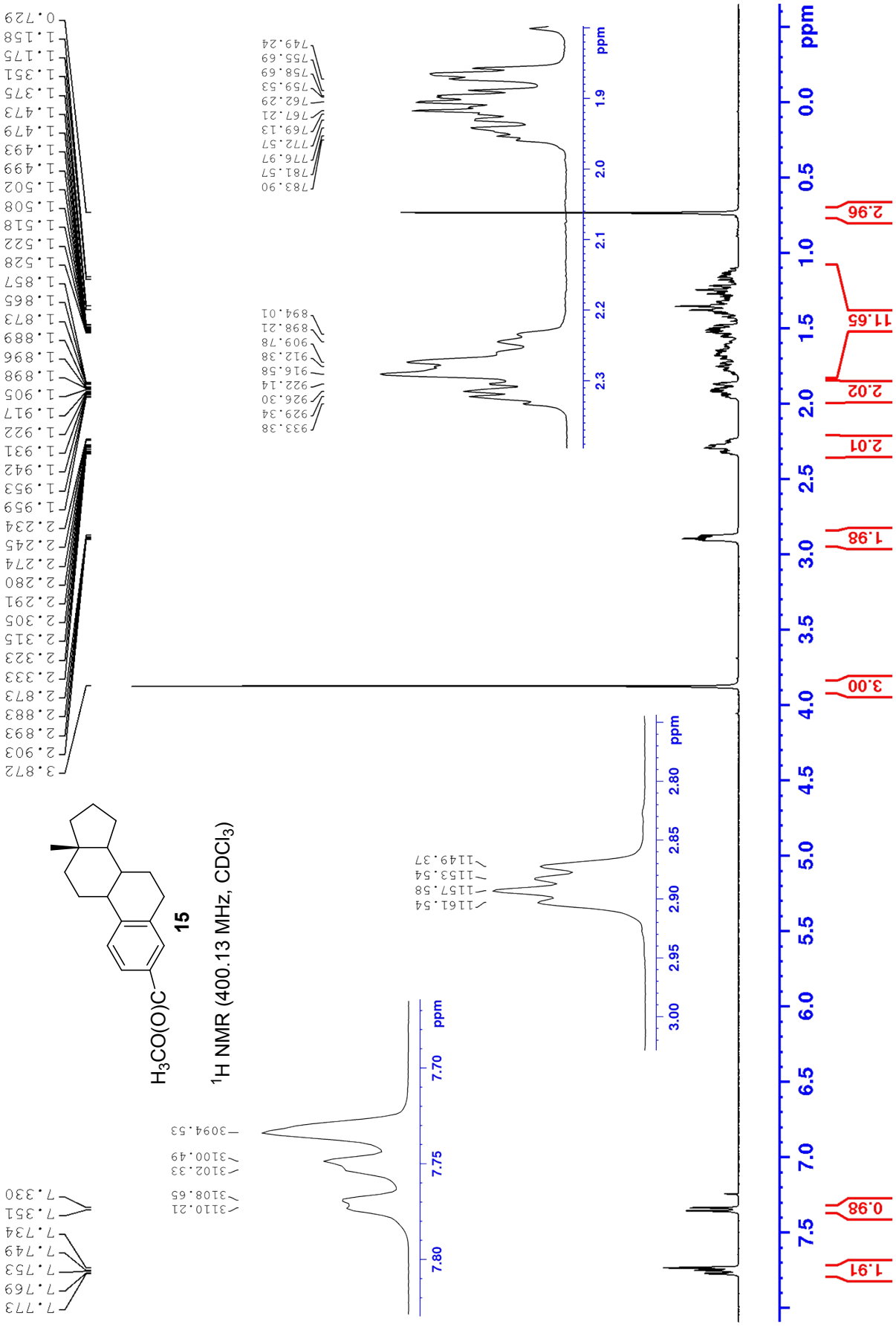
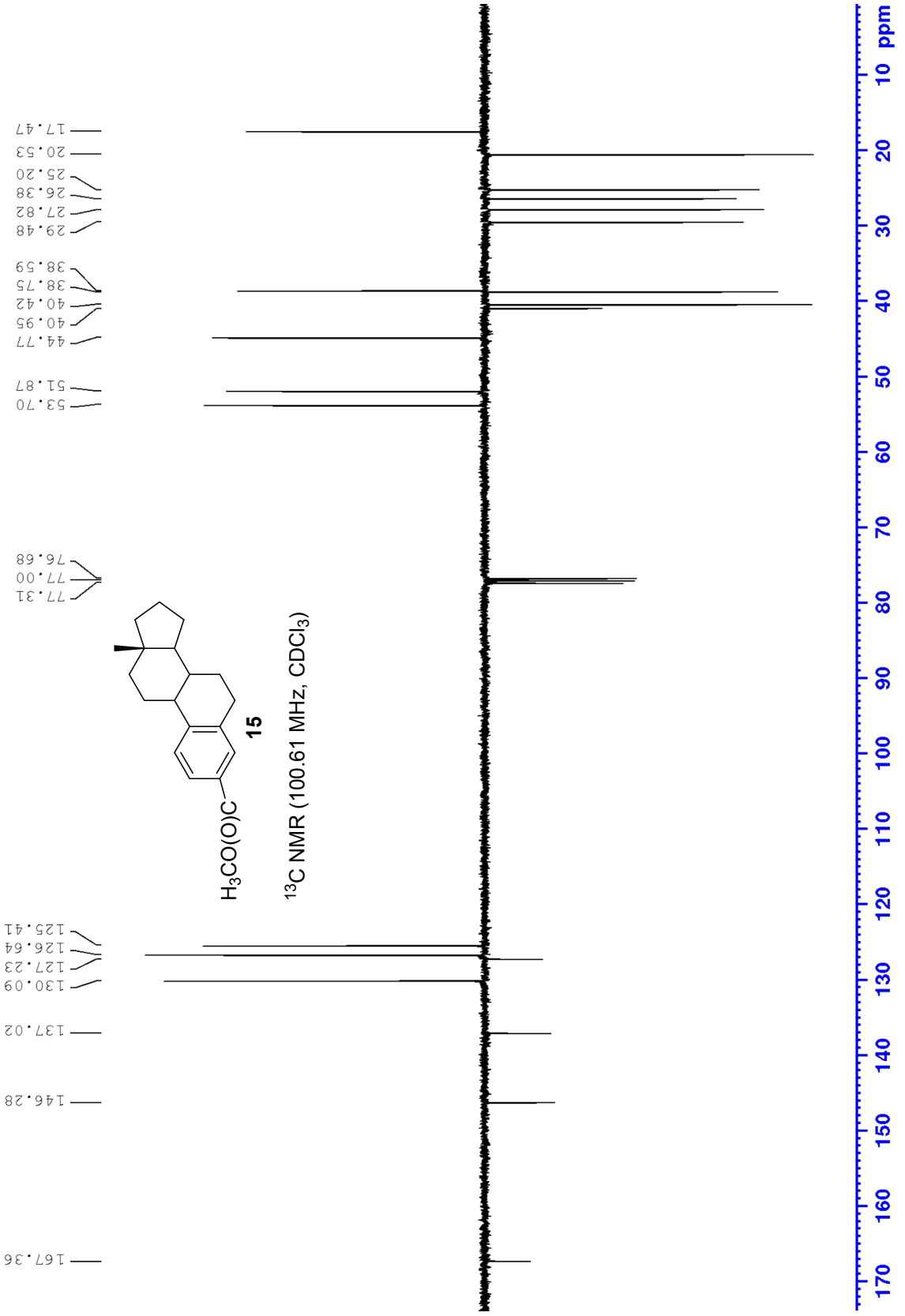
53.55
76.68
77.00
77.31
113.98
117.16
120.35
121.05
123.56
127.16
139.61
141.33
147.41
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
F3CSO2O
14
13C NMR (100.61 MHz, CDCl3)


^{1}H NMR (400.13 MHz, $CDCl_3$)
$H_3CO(O)C$
15
ppm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38.59
38.75
40.42
40.95
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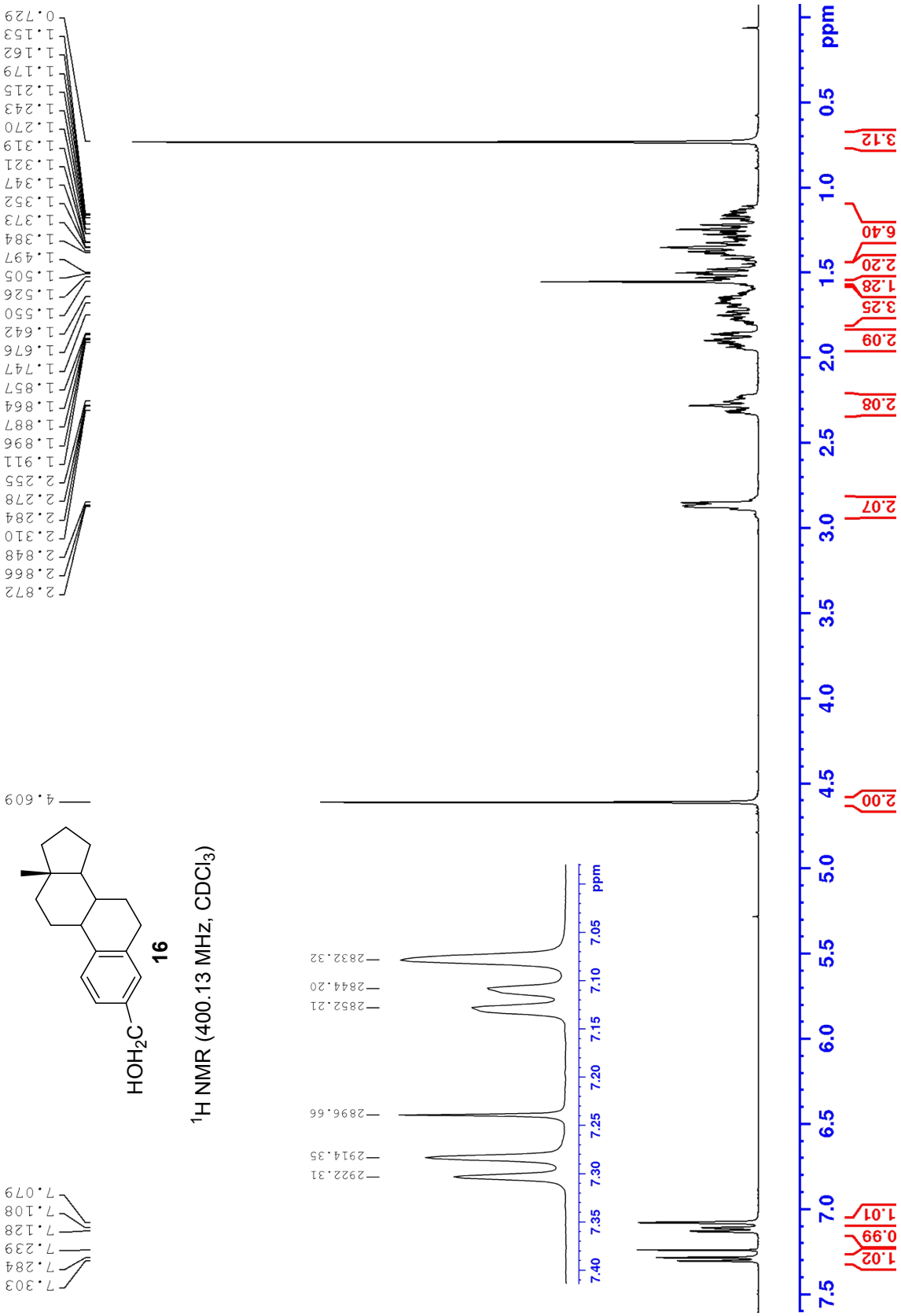
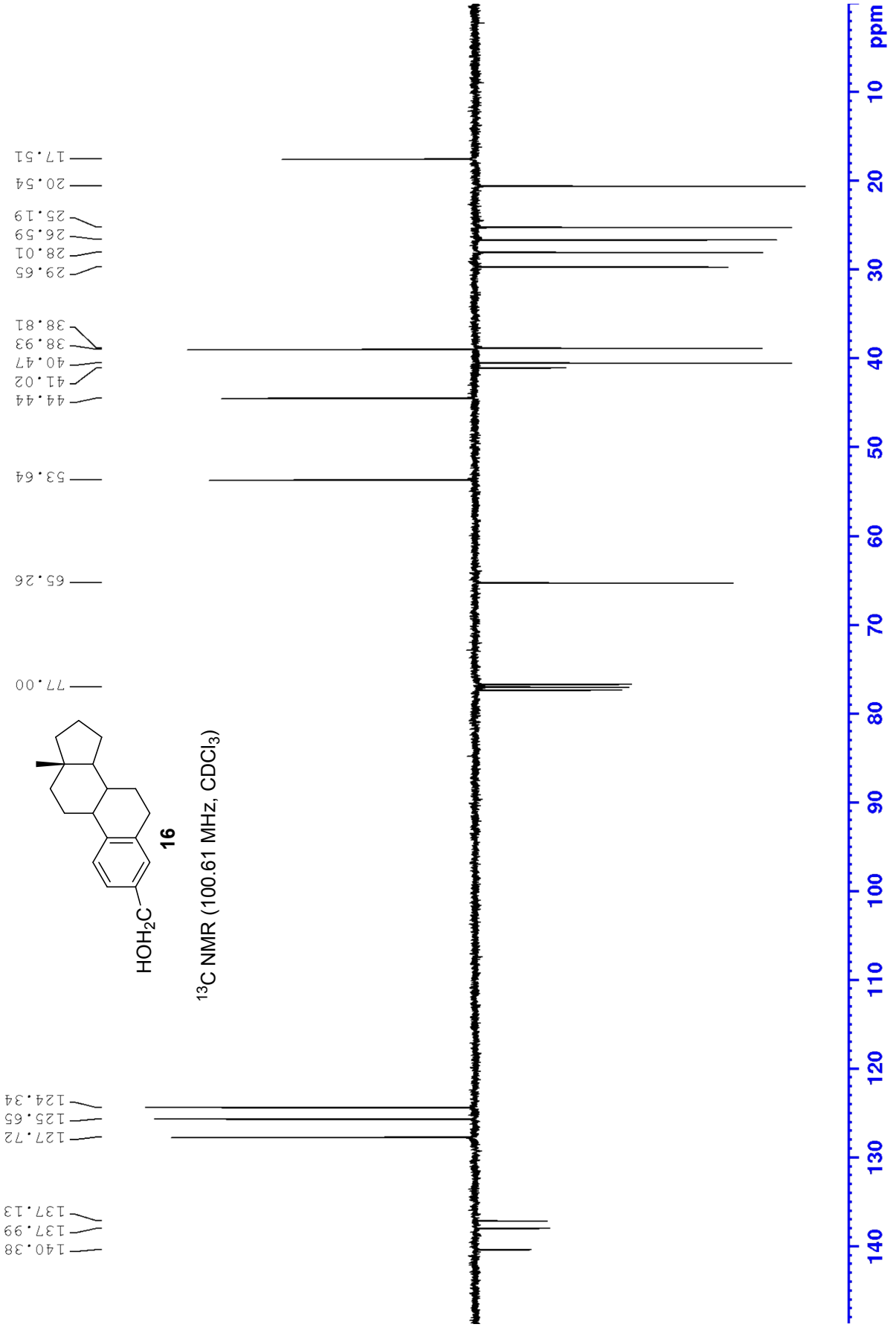
51.87
53.70
76.68
77.00
77.31
125.41
126.64
127.23
130.09
137.02
146.28
167.36
H3CO(O)C
15
13C NMR (100.61 MHz, CDCl3)
10 ppm
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170


^{1}H NMR (400.13 MHz, $CDCl_3$)
HOH_2C
16
ppm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38.93
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41.02
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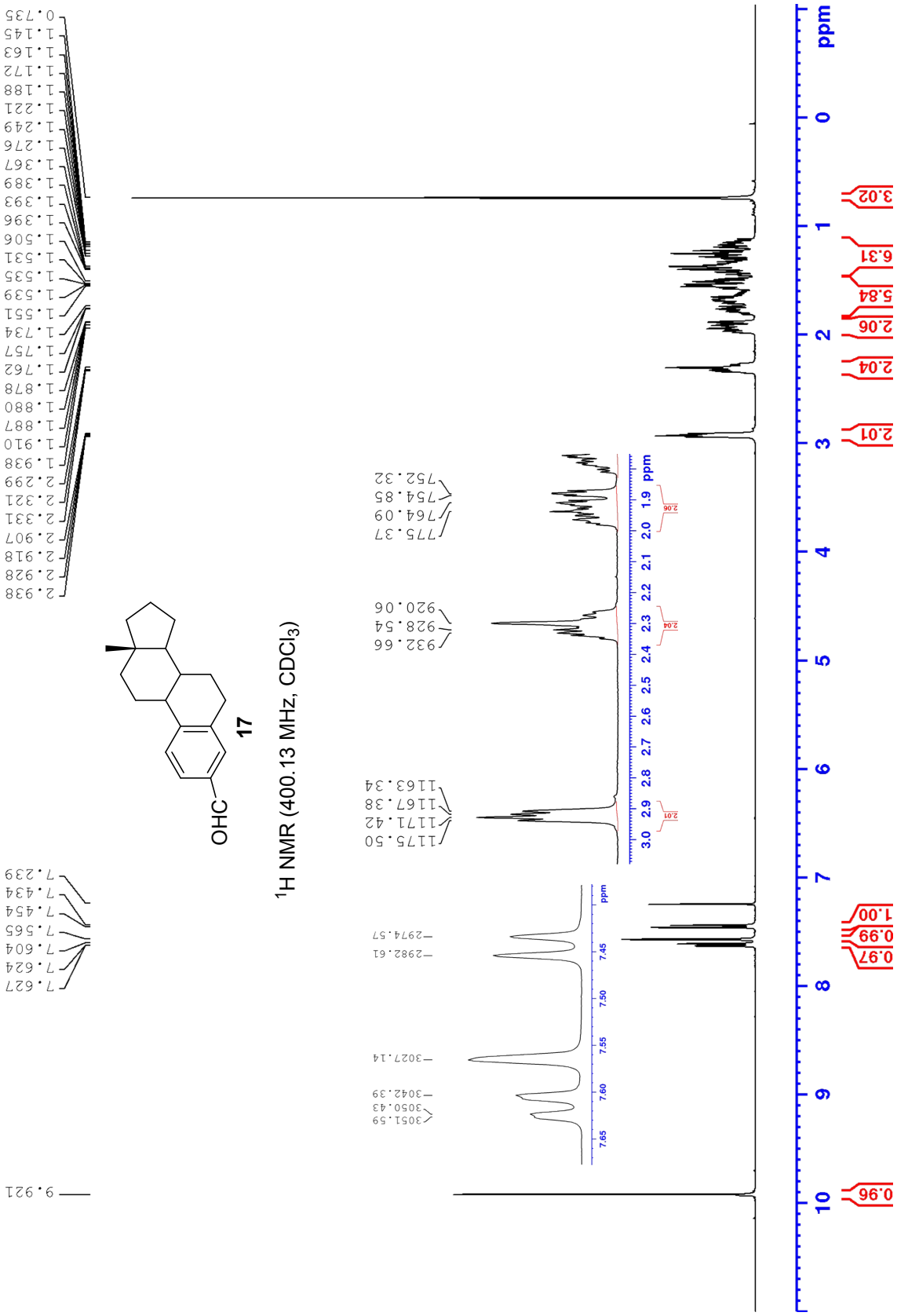
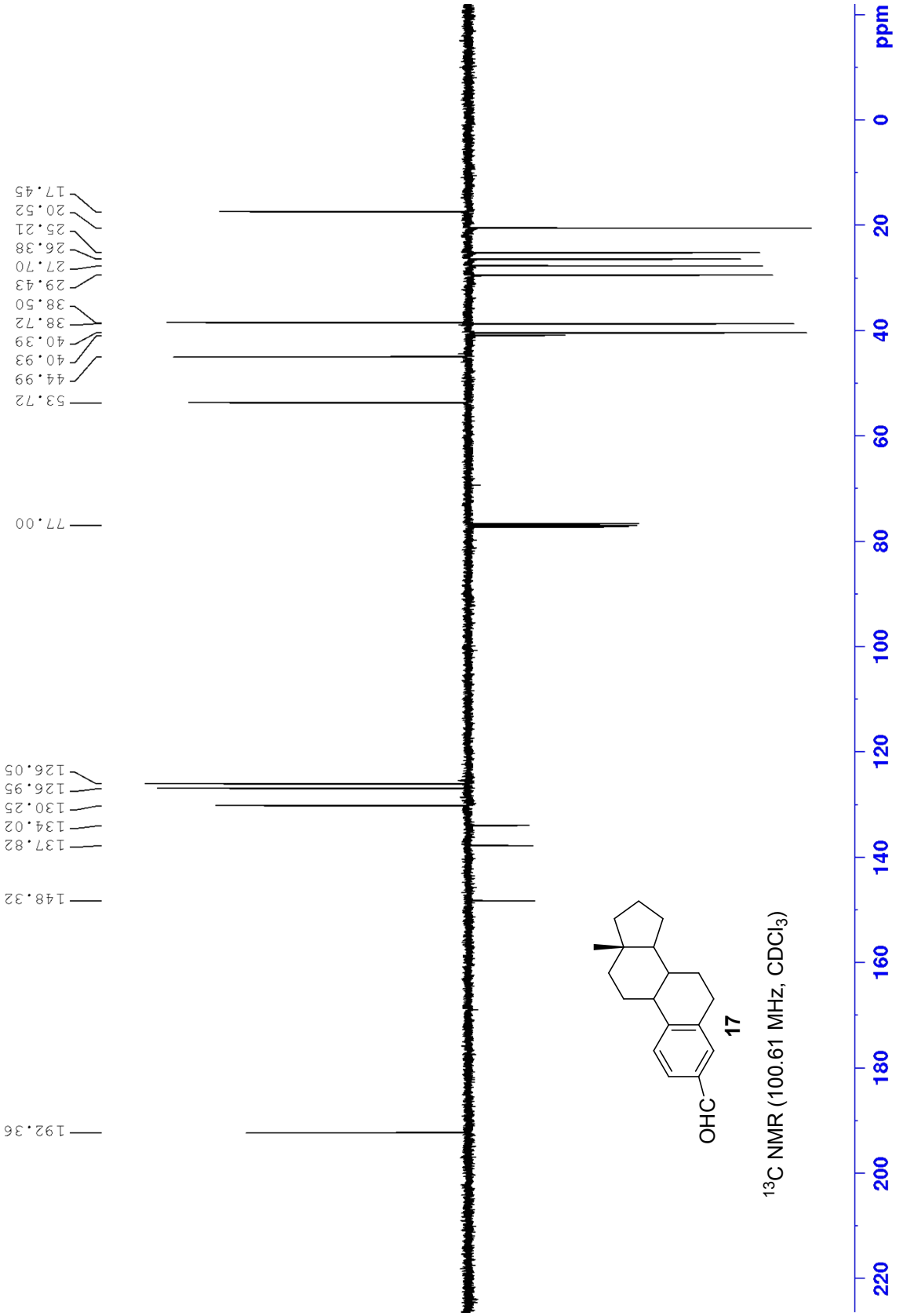
65.26
77.00
124.34
125.65
127.72
137.13
137.99
140.38
HOH2C
16
13C NMR (100.61 MHz, CDCl3)
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140


OHC
17
^{1}H NMR (400.13 MHz, CDCl$_3$)
ppm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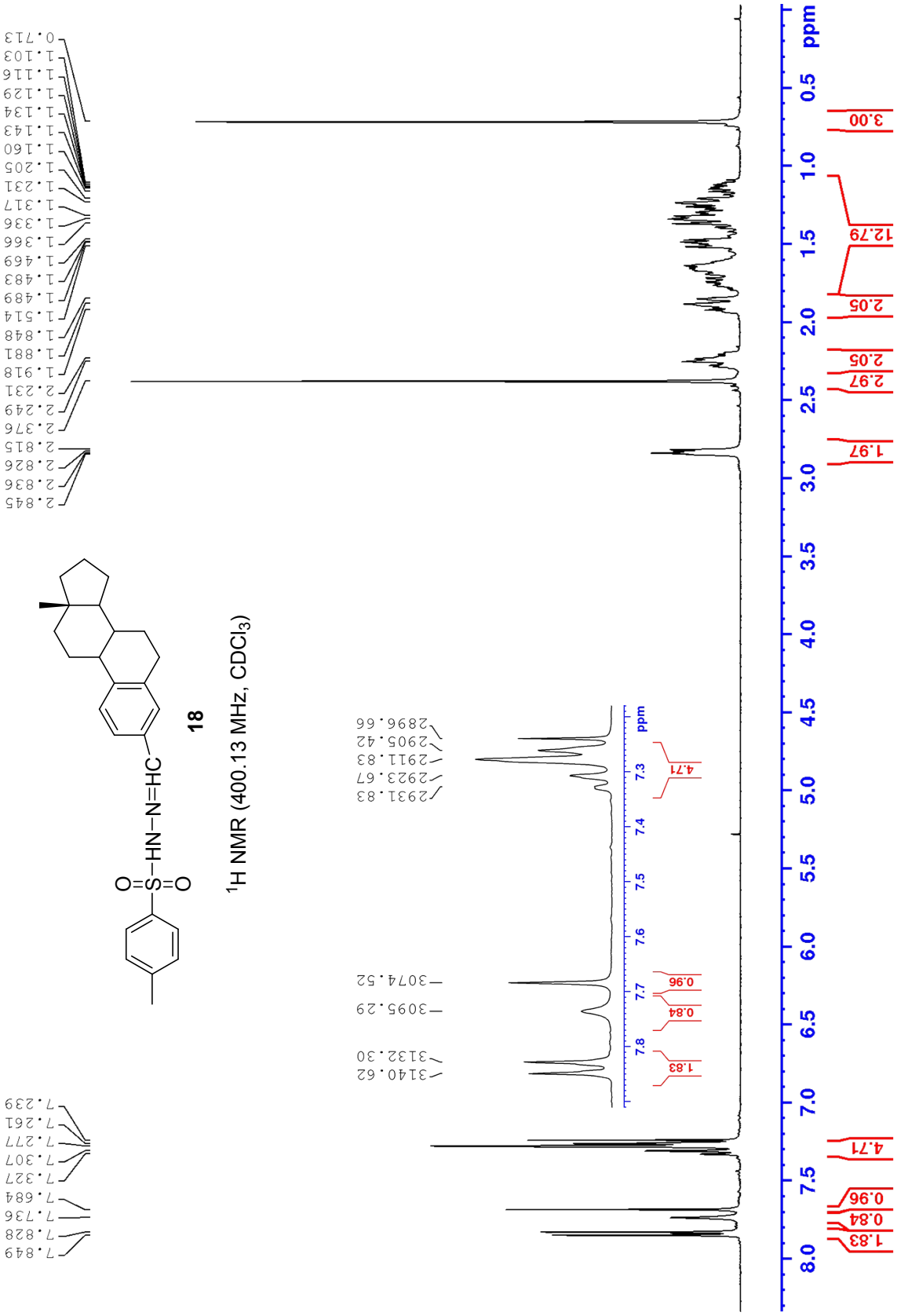
26.38
27.70
29.43
38.50
38.72
40.39
40.93
44.99
53.72
77.00
126.05
126.95
130.25
134.02
137.82
148.32
192.36
ppm
0
20
40
60
80
100
120
140
160
180
200
220
OHC
17
^{13}C NMR (100.61 MHz, CDCl$_3$)


18
^{1}H NMR (400.13 MHz, CDCl$_3$)
O=S=O
HN−N=HC
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
7.3
7.4
7.5
7.6
7.7
7.8
3.00
12.79
2.05
2.05
2.97
1.97
4.71
0.96
0.84
1.83
4.71
1.83
0.84
0.96
2931.83
2923.67
2911.83
2905.42
2896.66
3074.52
3095.29
3140.62
3132.30
0.713
1.103
1.116
1.129
1.134
1.143
1.160
1.205
1.231
1.317
1.336
1.366
1.469
1.483
1.489
1.514
1.848
1.881
1.918
2.231
2.249
2.376
2.815
2.826
2.836
2.845
7.239
7.261
7.277
7.307
7.327
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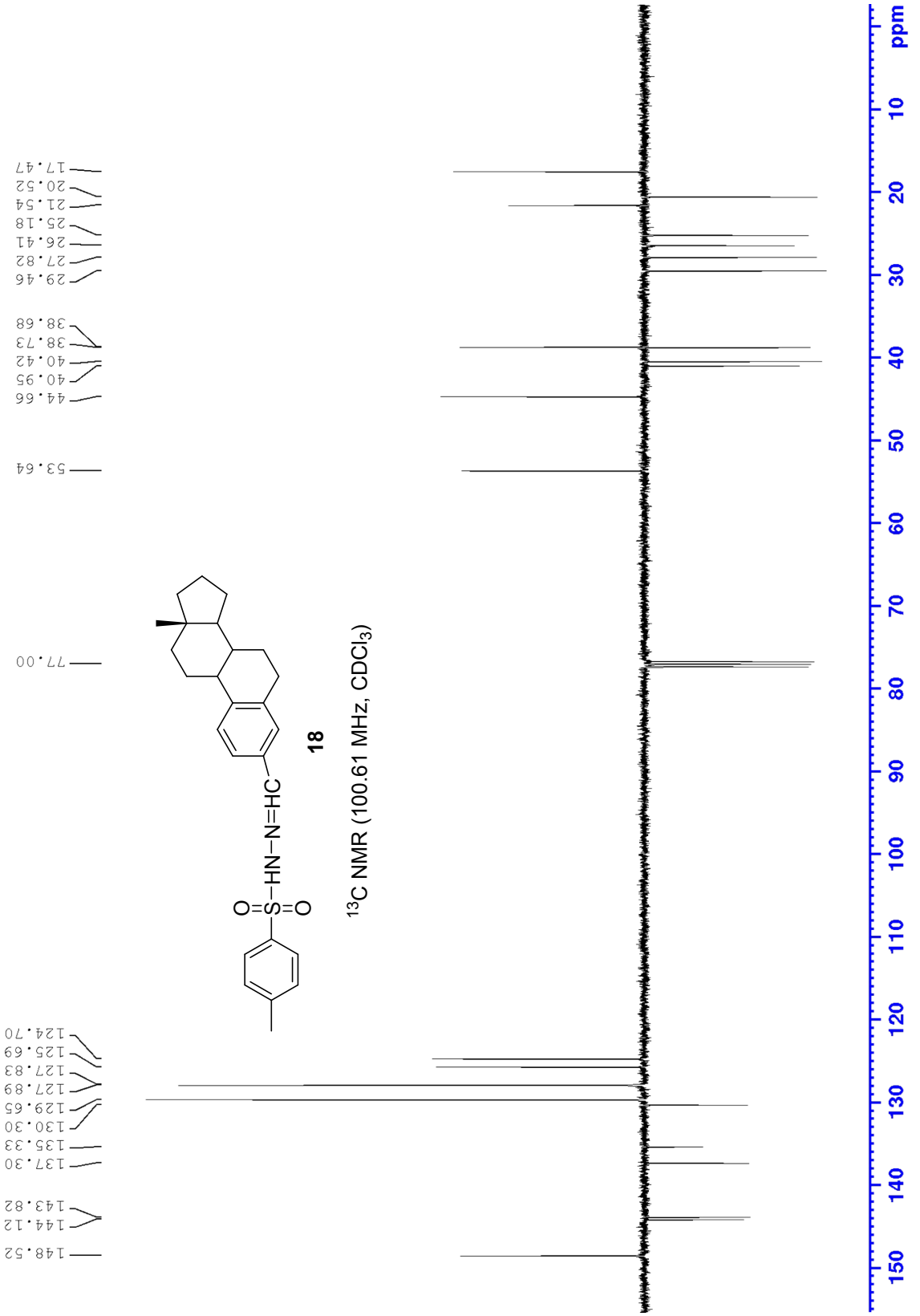
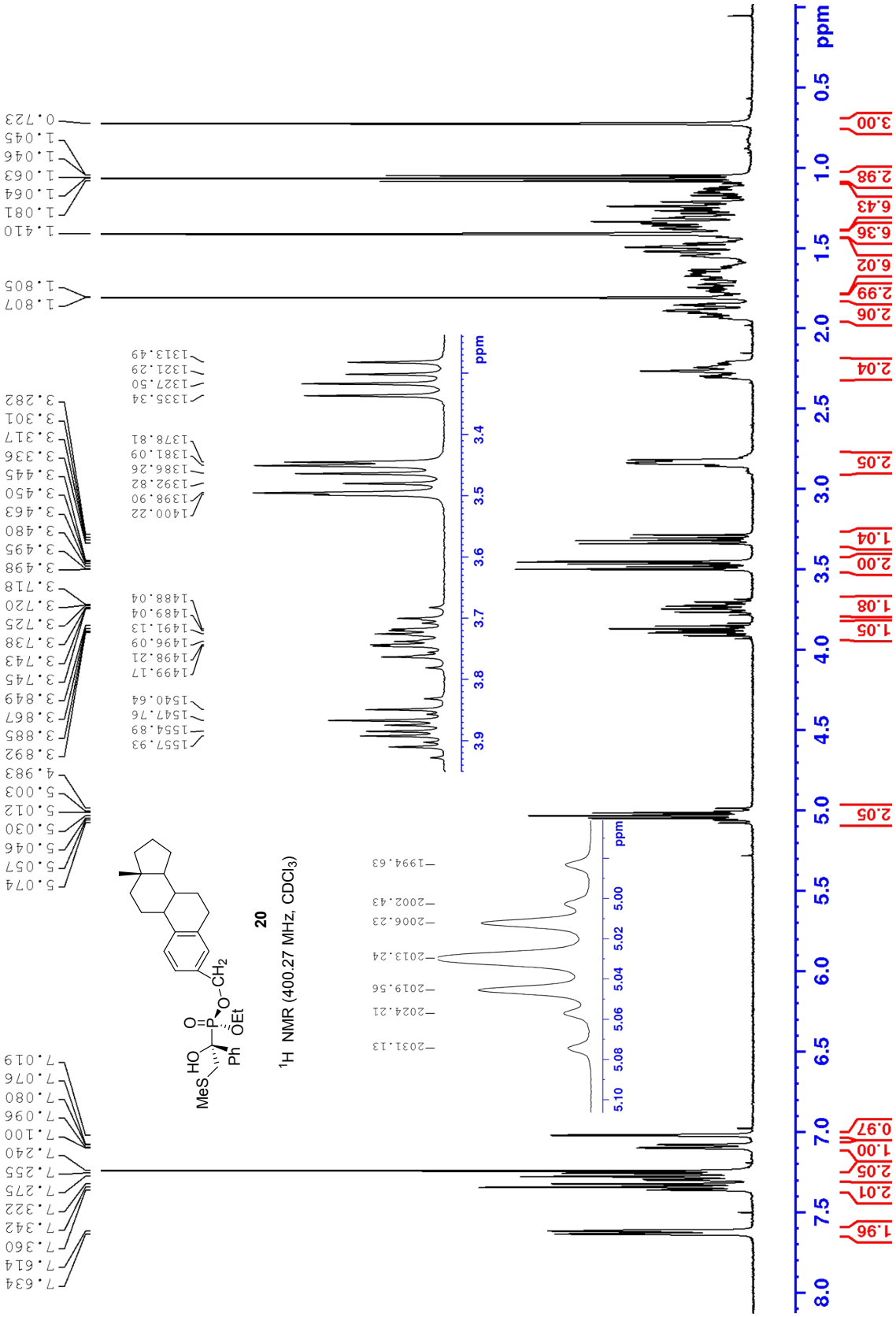
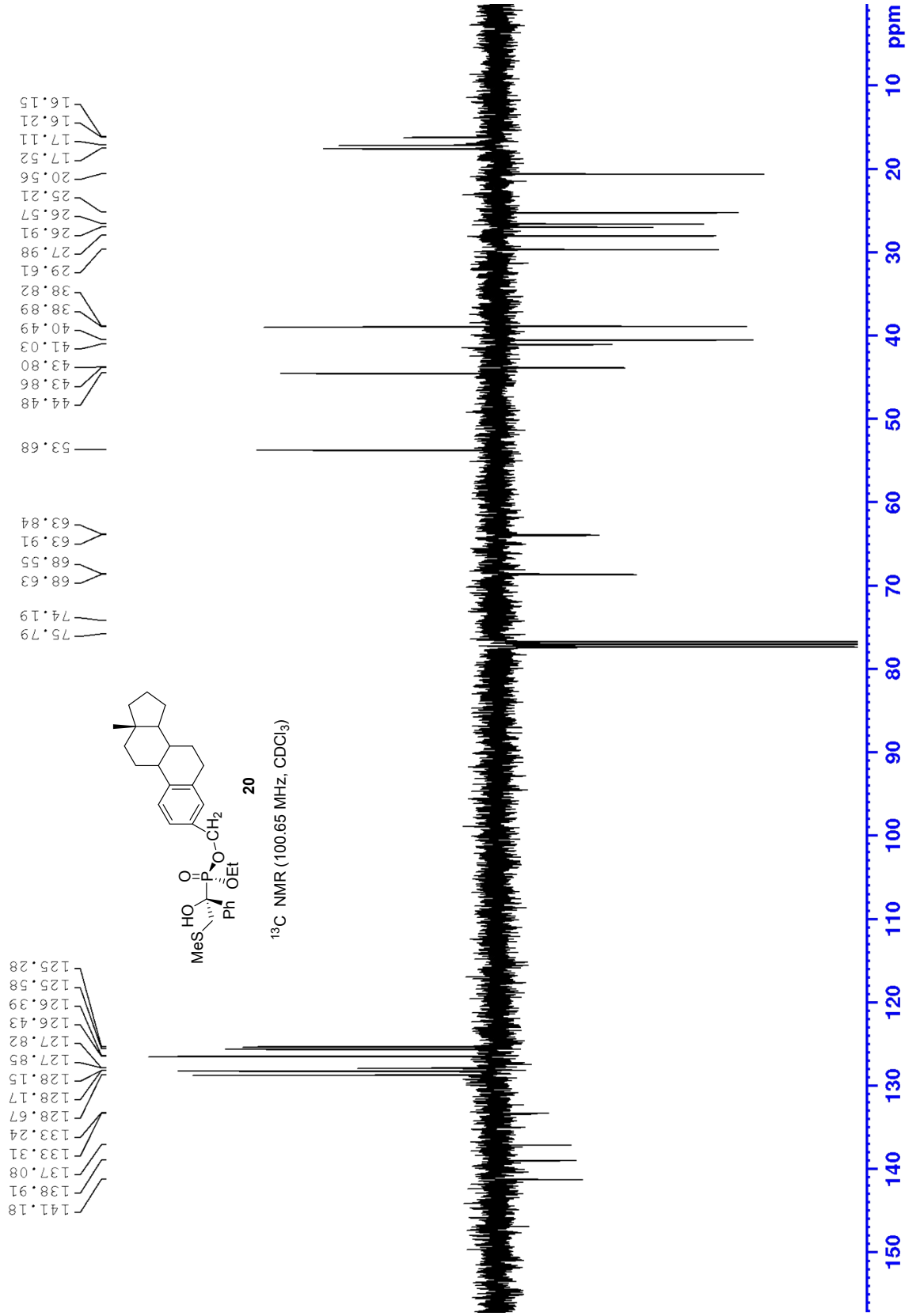
7.849


18
^{13}C NMR (100.61 MHz, CDCl$_3$)
O=S=O
HN–N=HC
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
17.47
20.52
21.54
25.18
26.41
27.82
29.46
38.68
38.73
40.42
40.95
44.66
53.64
77.00
124.70
125.69
127.83
127.89
129.65
130.30
135.33
137.30
143.82
144.12
148.52


20
^{1}H NMR (400.27 MHz, CDCl$_3$)
MeS
HO
Ph
OEt
O=P
O
CH$_2$
ppm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16.21
17.11
17.52
20.56
25.21
26.57
26.91
27.98
29.61
38.82
38.89
40.49
41.03
43.80
43.86
44.48
53.68
63.84
63.91
68.55
68.63
74.19
75.79
125.28
125.58
126.39
126.43
127.82
127.85
128.15
128.17
128.67
133.24
133.31
137.08
138.91
141.18
MeS
HO
O
P
O
CH2
Ph
OEt
20
13C NMR (100.65 MHz, CDCl3)
ppm
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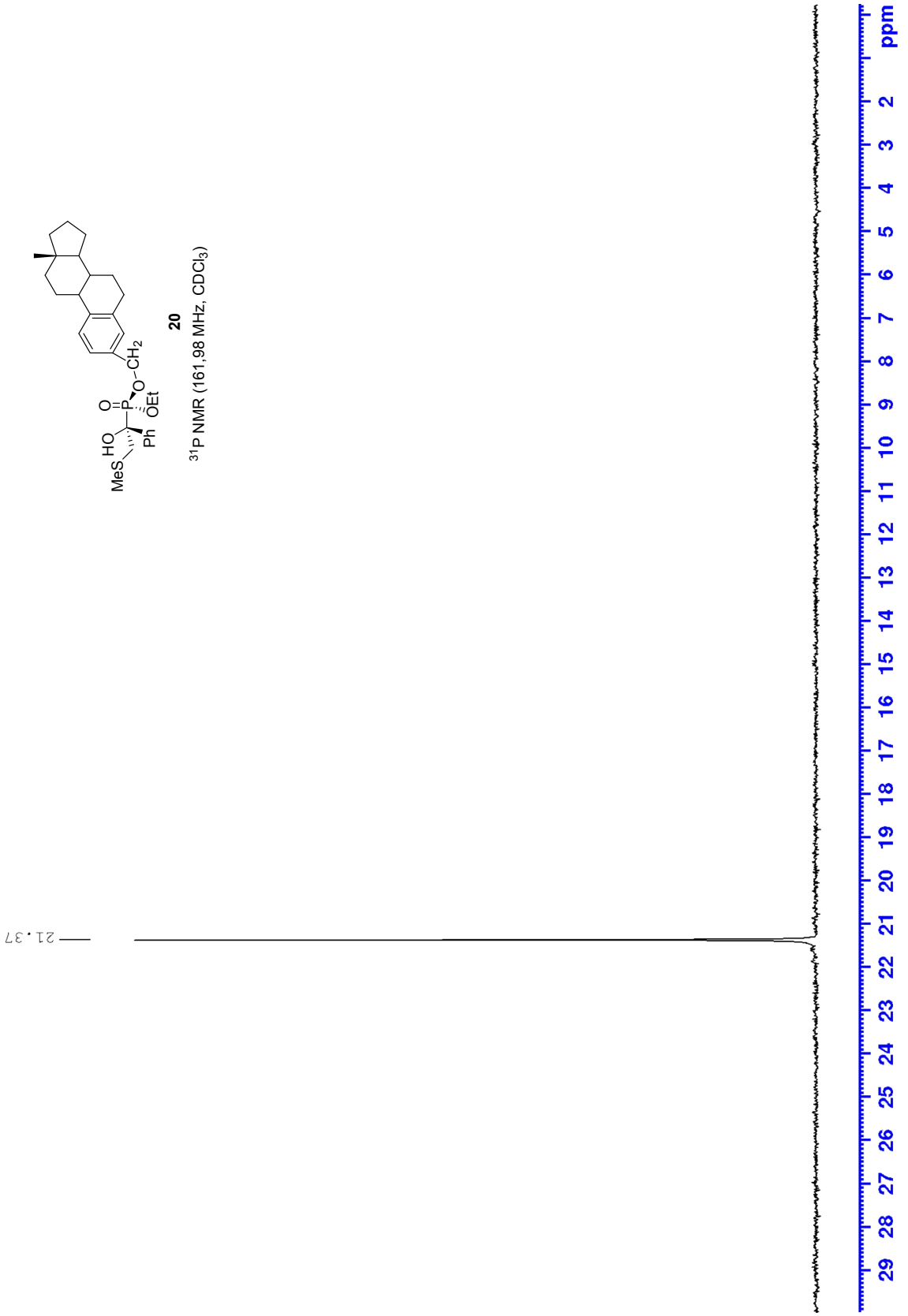
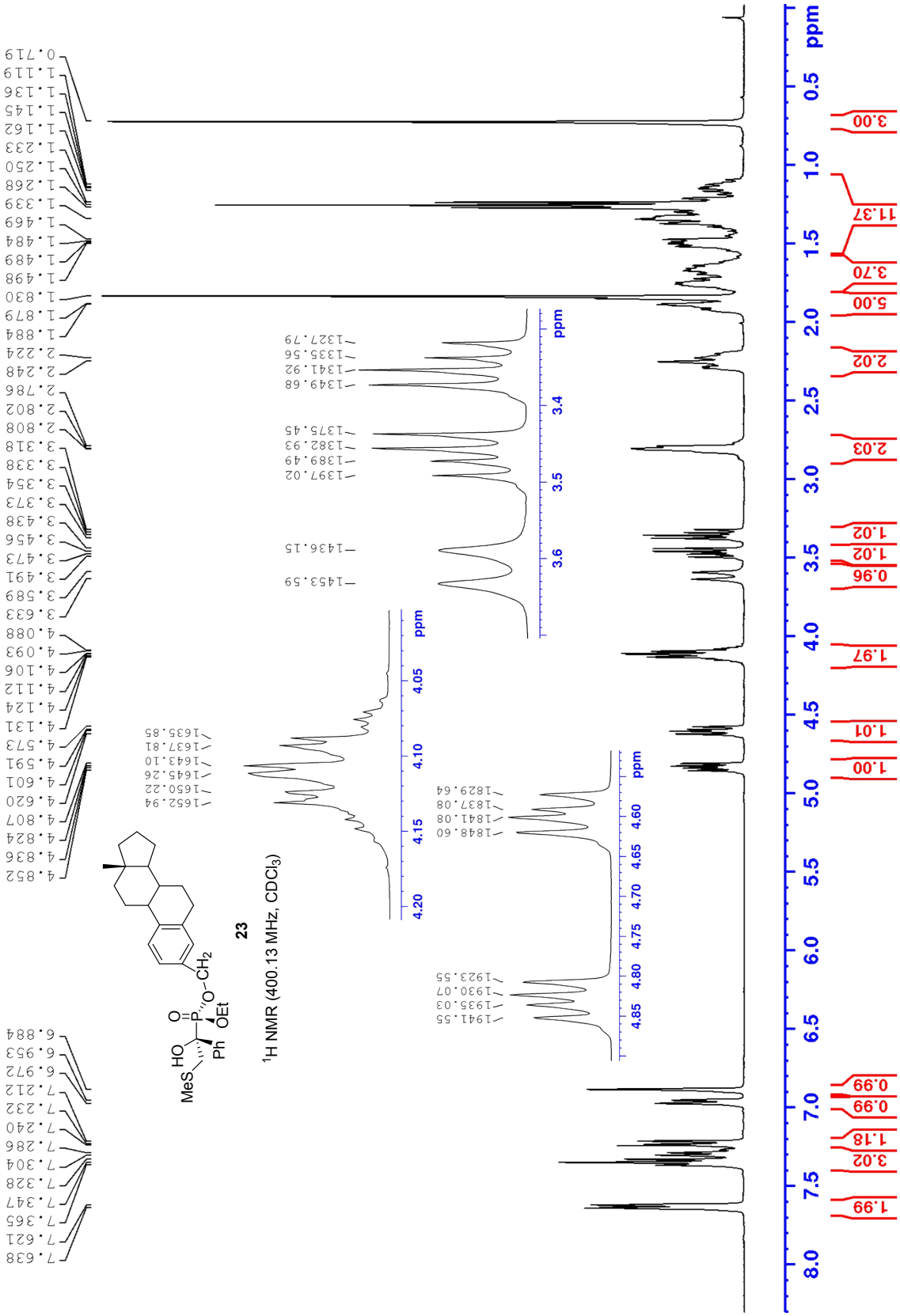
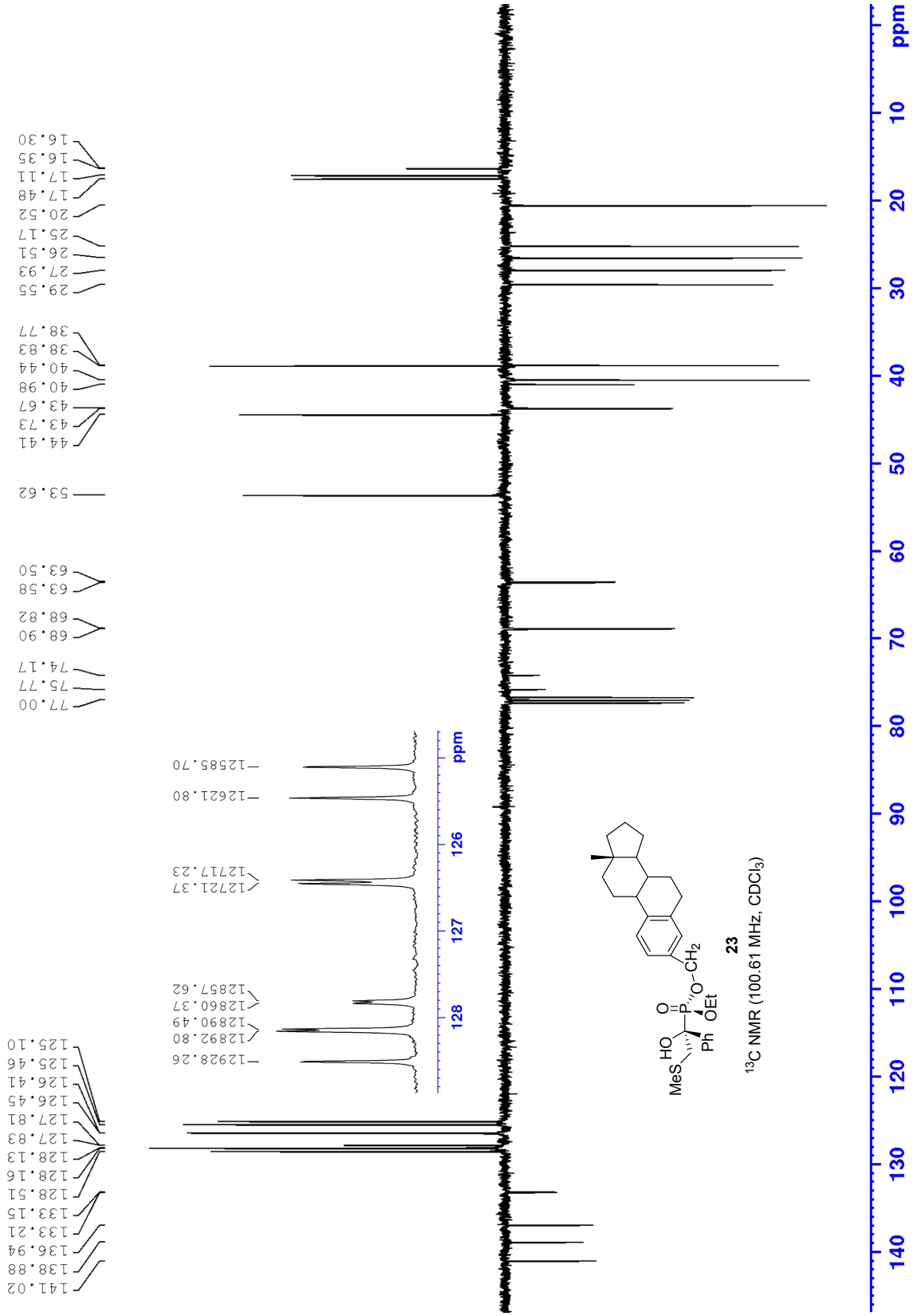
20
30
40
50
60
70
80
90
100
110
120
130
140
150



20

^{31}P NMR (161.98 MHz, $CDCl_3$)


23
^{1}H NMR (400.13 MHz, CDCl$_3$)
MeS
HO
Ph
OEt
ppm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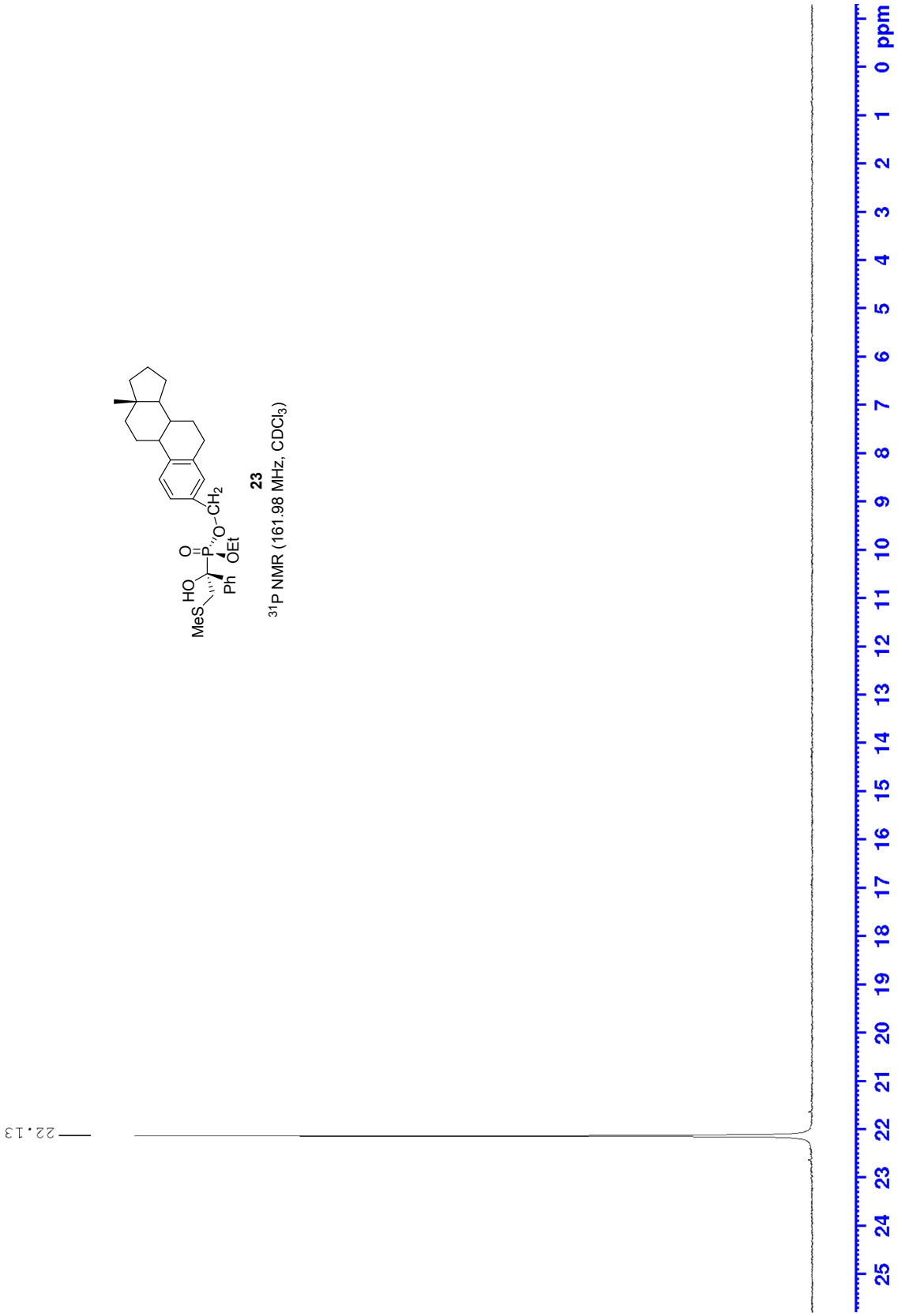
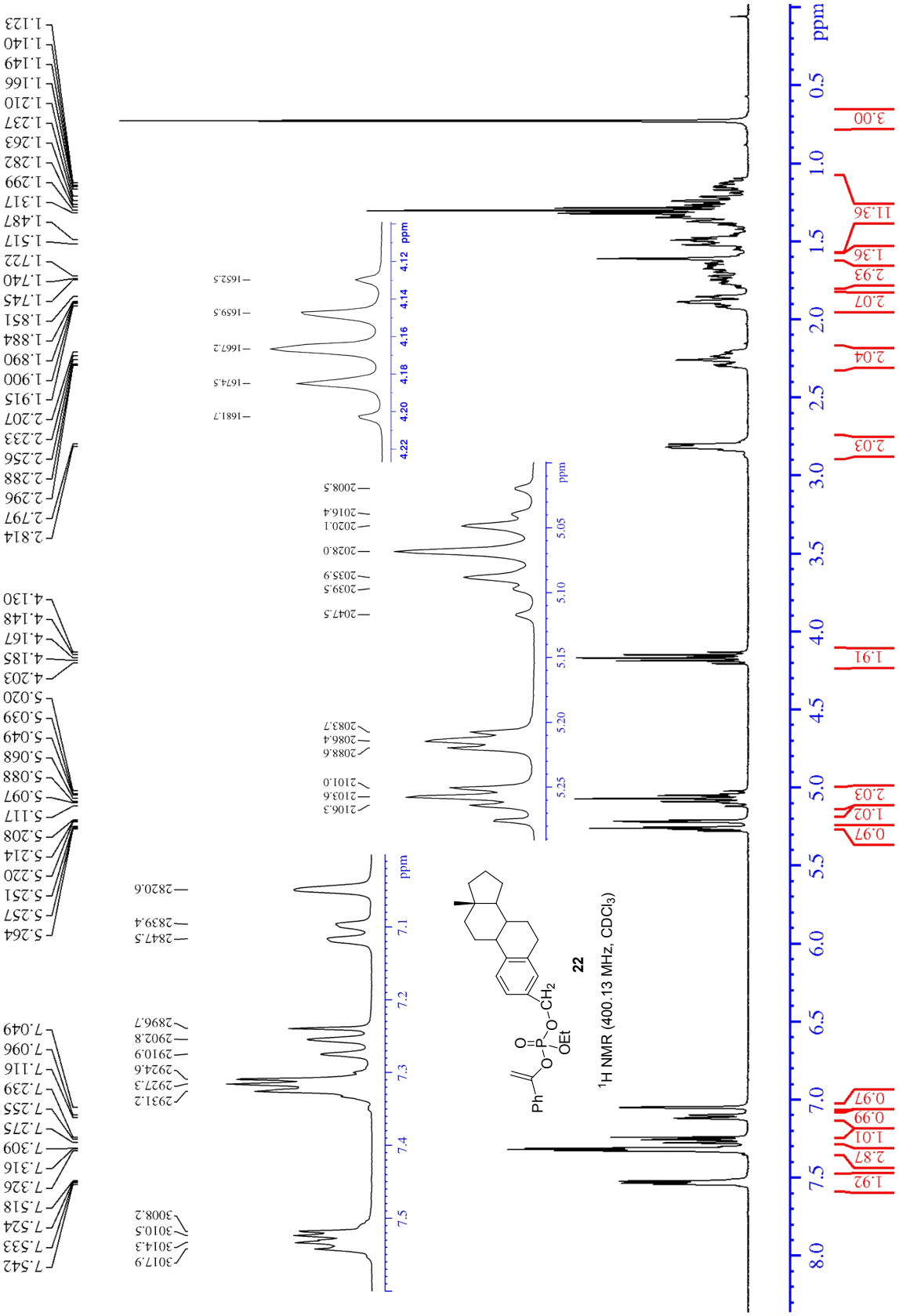
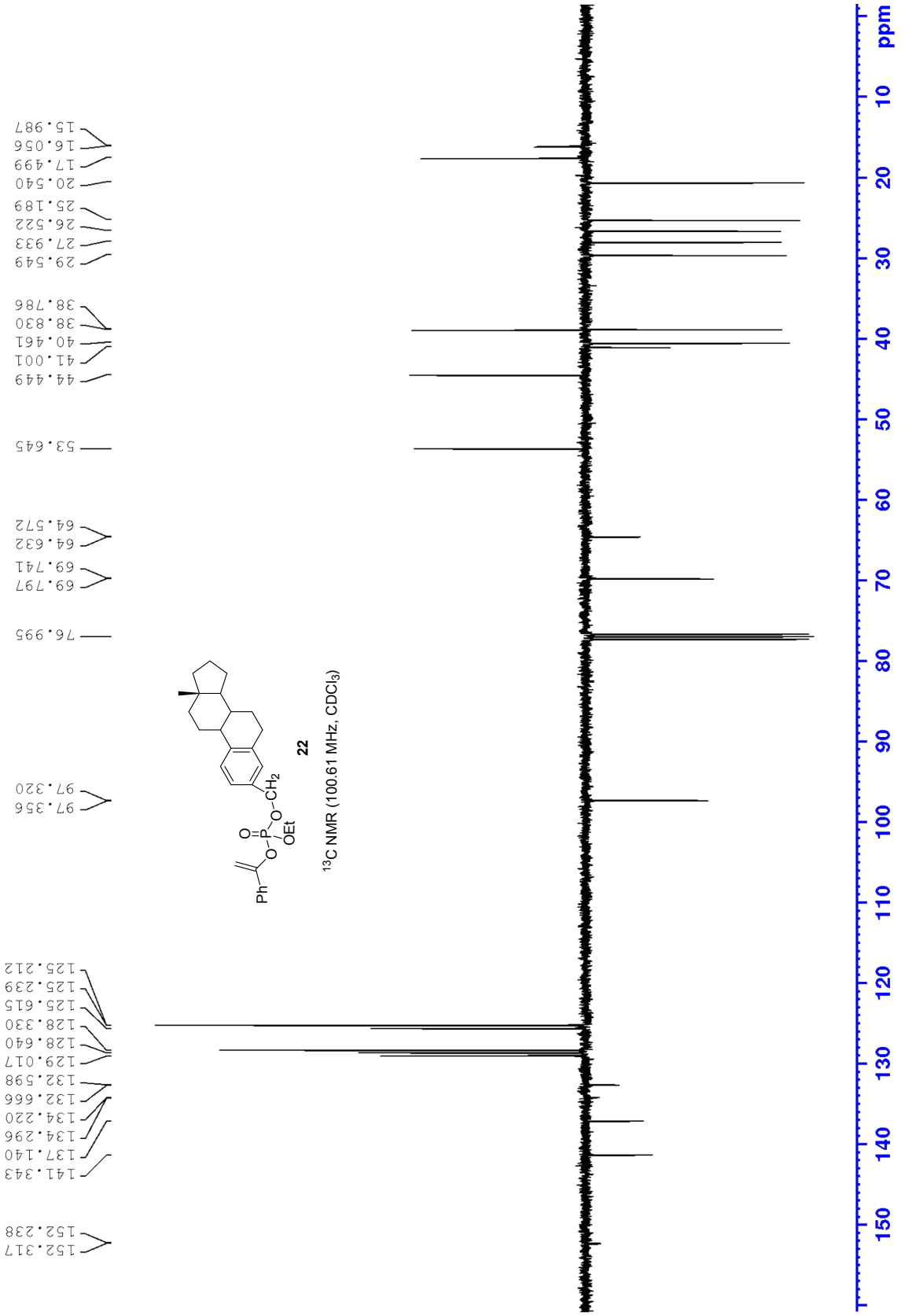
136.94
133.21
133.15
128.51
128.16
128.13
127.83
127.81
126.45
126.41
125.46
125.10
77.00
75.77
74.17
68.90
68.82
63.58
63.50
53.62
44.41
43.73
43.67
40.98
40.44
38.83
38.77
29.55
27.93
26.51
25.17
20.52
17.48
17.11
16.35
16.30
12928.26
12892.80
12890.49
12860.37
12857.62
12721.37
12717.23
12621.80
12585.70
ppm
128
127
126
MeS
HO
O
P
Ph
OEt
O
CH2
23
13C NMR (100.61 MHz, CDCl3)
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140

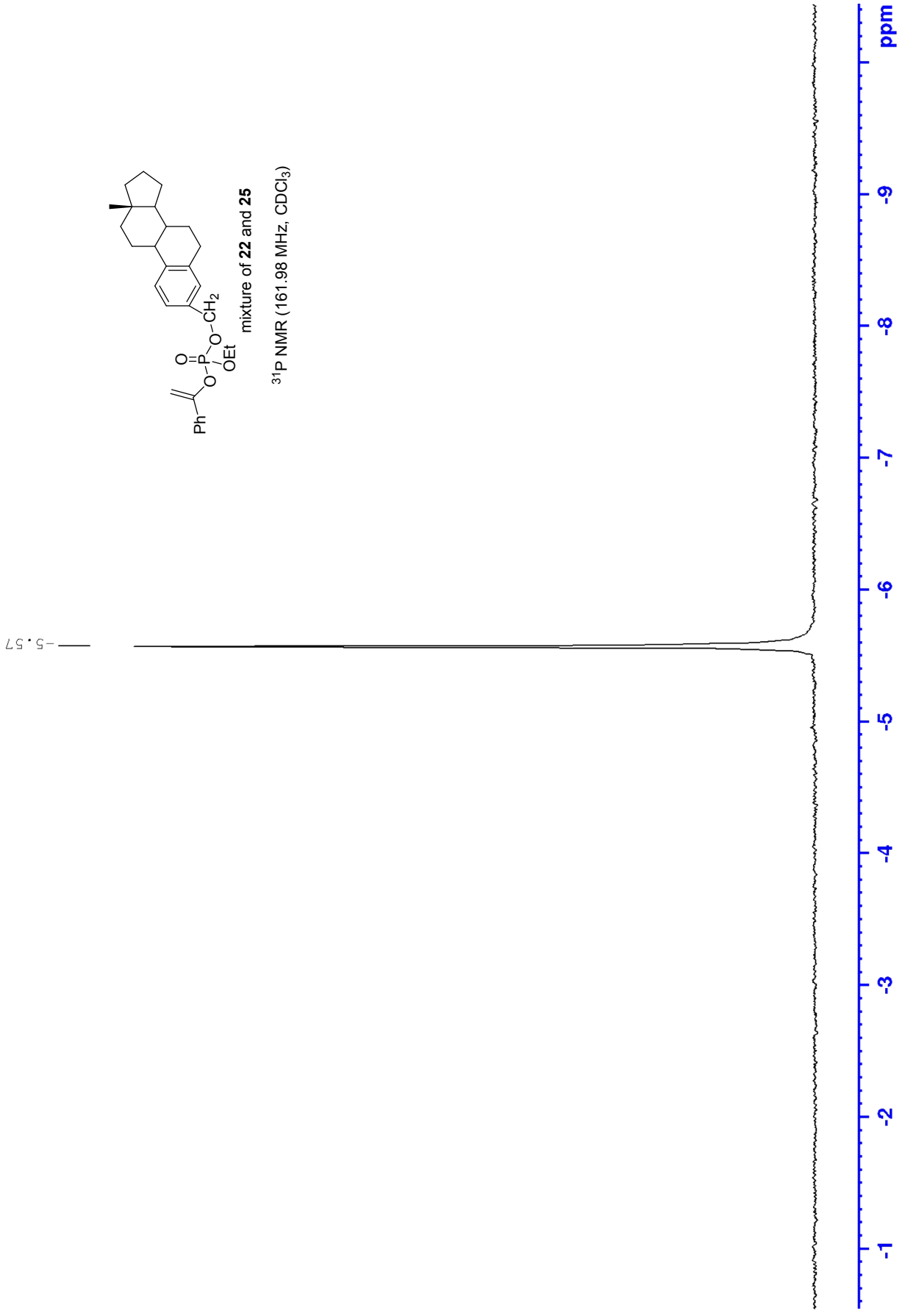


23

^{31}P NMR (161.98 MHz, $CDCl_3$)


22
^{1}H NMR (400.13 MHz, $CDCl_3$)
Ph
O
P
O
OEt
CH_2
ppm


15.987
16.056
17.499
20.540
25.189
26.522
27.933
29.549
38.786
38.830
40.461
41.001
44.449
53.645
64.572
64.632
69.741
69.797
76.995
97.320
97.356
125.212
125.239
125.615
128.330
128.640
129.017
132.598
132.666
134.220
134.296
137.140
141.343
152.238
152.317
Ph
O
O
P
O
OEt
O
CH2
22
13C NMR (100.61 MHz, CDCl3)
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150


mixture of 22 and 25
31P NMR (161.98 MHz, CDCl3)
-5.57
ppm
-1
-2
-3
-4
-5
-6
-7
-8
-9

Single crystal X-ray structure analysis of 23

Crystals of **23** were obtained by recrystallisation from hexanes/*i*-PrOH. Crystal data and experimental details are given in Table S1. X-ray diffraction data were collected on a *PHILIPS PW1100* four-circle diffractometer using graphite monochromated Mo-*K*α radiation (λ = 0.71073 Å) from a sealed tube and a szintillation detector. θ-2θ-scans with a scan range of 1.2°, a scan speed of 0.5°/min, and stationary background measurements at both sides of each scan were applied. The raw data were corrected for Lp, system stability, but not for absorption. The structure was solved with direct methods using program *SHELXS97*[1] and structure refinement on F^2 was carried out with program *SHELXL97*[1]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in idealized positions and were refined as riding on the atoms to which they are bonded. The absolute structure was assigned *via* the known handedness of the 1,3,5(10)-estratriene-3-yl moiety of **20**. For geometric analysis of the structure program *PLATON*[2] was used and selected bond distances and angles are reported in Table S2. Structure graphics (Fig. S1 and S2) was generated with program *MERCURY*[3]. The structure contains an intermolecular hydrogen bond between the C-bonded OH group of O1 as the donor and the phosphonate oxygen O2 as the acceptor (O1−H1 = 0.88 Å, H1···O2(-*x*,*y*,-*z*) = 1.86 Å, O1···O2(-*x*,*y*,-*z*) = 2.727(4) Å, O1−H1···O2(-*x*,*y*,-*z*) = 169°). Each two of these hydrogen bonds link two molecules cyclically into a pair (Fig. S2). The largest void in the structure, centered at *x*,*y*,*z* = 0.5, 0.255, 0.5 according to program *MERCURY*, has only a void volume of 18 Å^3, which is too small to accomodate any solvent molecule, in agreement with a maximum residual electron density of 0.16 e/Å^3. Atomic coordinates, thermal parameters, and bond distances and angles were deposited in CIF format with the journal. These data can also be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. CCDC number 1818362,

References

1. G. M. Sheldrick, *Acta Cryst.*, 2015,**C71**, 3.
2. *A. L.* Spek, *Acta Cryst*., 2009, **D65**, 148.
3. C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Cryst.*, 2006, **39**, 453.

Table S1. Crystal data and details of the structure determination for compound **23.**

Crystal Data			
Formula			C30 H41 O4 P S
Formula Weight			528.66
Crystal System			monoclinic
Space group		C2	(No. 5)
a, b, c [Angstrom]	21.157(6)	6.917(2)	20.174(6)
alpha, beta, gamma [deg]	90	98.00(3)	90
V [Ang^3]			2923.6(15)
Z			4
D(calc) [g/cm^3]			1.201
Mu(MoKα) [mm^{-1}]			0.197
F(000)			1136
Crystal Size [mm]		0.07 x 0.22 x	0.85

Data Collection			
Temperature (K)			293
Radiation [Angstrom]		MoKa	0.71073
Theta Min-Max [Deg]		2.5,	24.0
Dataset h,k,l min.:max.		-24: 23 ; 0: 7 ;	0: 23
Total Data, Unique Data, R(int)		2575, 2499,	0.028
Observed data [I > 2.0 sigma(I)]			2202

Refinement		
Nref, Npar		2496, 334
R, wR2, S	0.0441,	0.1197, 1.07
Max. and Av. Shift/Error		0.00, 0.00
Min. and Max. Resd. Dens. [e/Ang^3]		-0.23, 0.16

Table S2. Selected bond distances and angles (Å, deg.) for compound **23**.

S1	-C2	1.806(5)
S1	-C3	1.775(6)
P1	-O2	1.466(3)
P1	-O3	1.564(3)
P1	-O4	1.563(4)
P1	-C1	1.840(5)
O1	-C1	1.421(5)
O3	-C10	1.443(5)
O4	-C29	1.463(8)
O1	-H1	0.880
C1	-C4	1.513(6)
C1	-C2	1.530(7)
C4	-C9	1.374(8)
C4	-C5	1.387(7)
C5	-C6	1.398(8)
C6	-C7	1.359(15)
C7	-C8	1.362(11)
C8	-C9	1.383(8)
C10	-C13	1.478(8)
C11	-C20	1.396(7)
C11	-C12	1.373(7)
C12	-C13	1.380(6)
C13	-C14	1.385(8)
C14	-C15	1.366(7)
C15	-C16	1.523(7)
C15	-C20	1.395(6)
C16	-C17	1.487(8)
C17	-C18	1.509(6)
C18	-C24	1.503(7)
C18	-C19	1.539(6)
C19	-C20	1.512(6)
C19	-C21	1.524(6)
C21	-C22	1.535(8)
C22	-C23	1.514(7)
C23	-C27	1.534(9)
C23	-C28	1.531(8)
C23	-C24	1.528(6)
C24	-C25	1.529(8)
C25	-C26	1.526(9)
C26	-C27	1.526(9)
C29	-C30	1.432(11)

C2	-S1	-C3	104.2(2)
O2	-P1	-O3	114.7(2)
O2	-P1	-O4	114.0(2)
O2	-P1	-C1	112.6(2)
O3	-P1	-O4	103.3(2)
O3	-P1	-C1	103.7(2)
O4	-P1	-C1	107.6(2)
P1	-O3	-C10	122.7(3)
P1	-O4	-C29	123.3(4)
C1	-O1	-H1	108.0
P1	-C1	-O1	103.2(3)
P1	-C1	-C2	109.6(3)
O1	-C1	-C2	110.9(3)
O1	-C1	-C4	108.5(4)
P1	-C1	-C4	110.6(3)
S1	-C2	-C1	116.0(3)

Fig. S1. The molecular structure of **23** in solid state showing displacement ellipsoids at 20% probability.

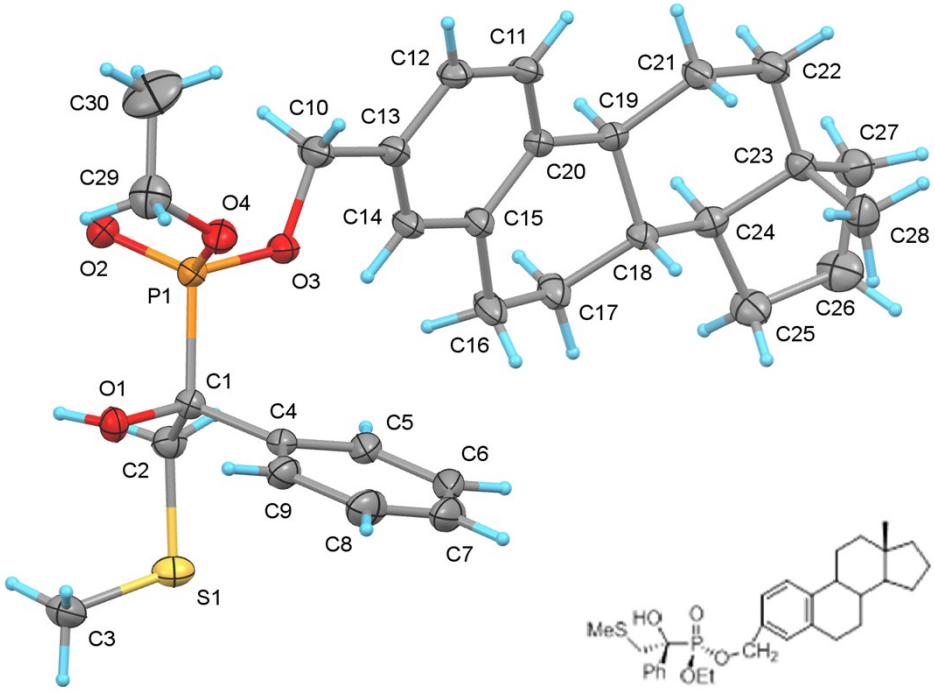


Fig. S2. Projection of the crystal structure of **23** along the *b*-axis (*b* = 6.917 Å). H-atoms omitted for clarity. The light blue dotted lines represent the hydrogen bonds O1−H1···O2.