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

Supporting Information

Solid-Phase Synthesis of Oligodeoxynucleotides Using Nucleobase *N*-Unprotected the Oxazaphospholidine Derivatives a Bearing Long Alkyl Chain

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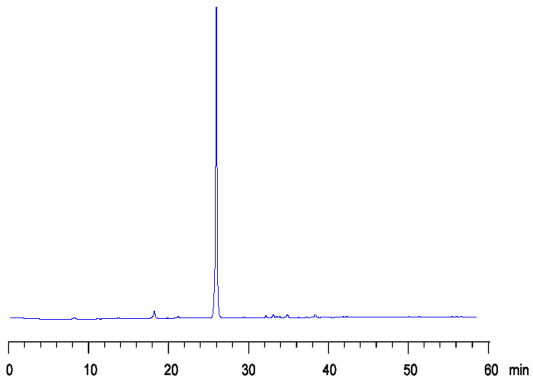
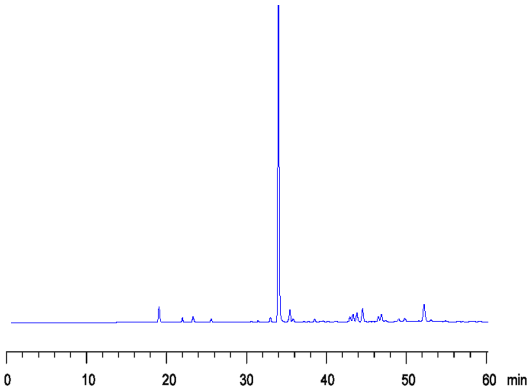
1. RP-HPLC profiles of dinucleotide phosphates (Table 1)

entry 1 (crude **10c (dC$_{PO}$T), R = Me**)



entry 2 (crude **10a (dA$_{PO}$T), R = Me**)



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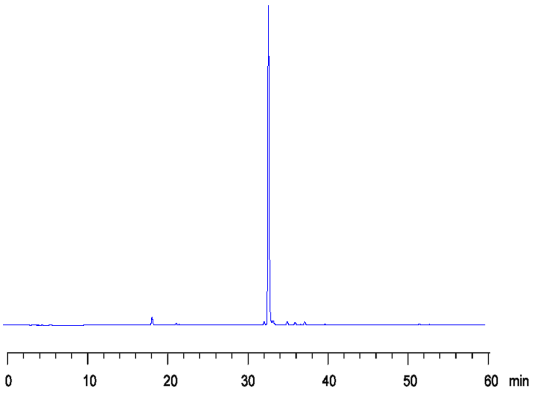

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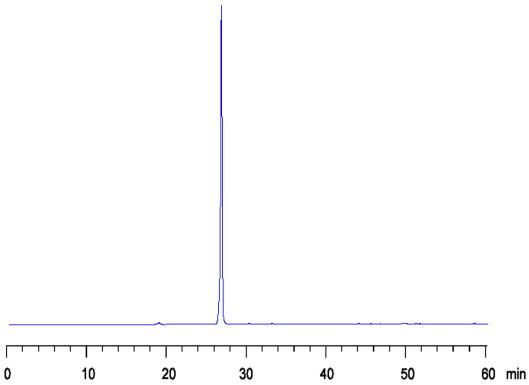

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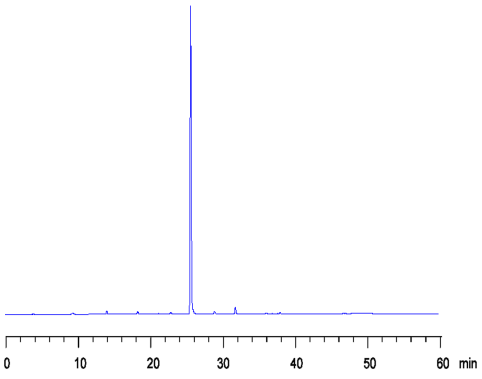

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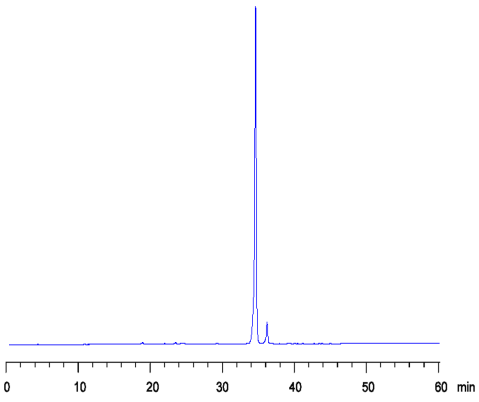
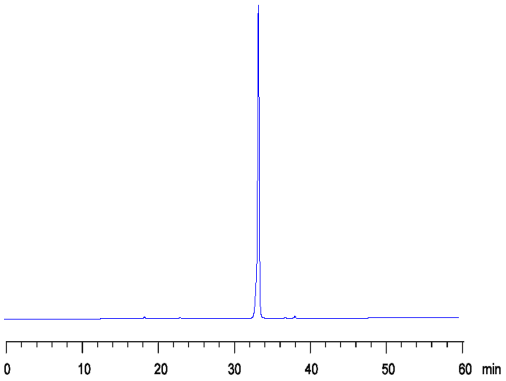


entry 7 (crude **10t** ($\mathbf{T_{PO}T}$)**, R = Thg**)



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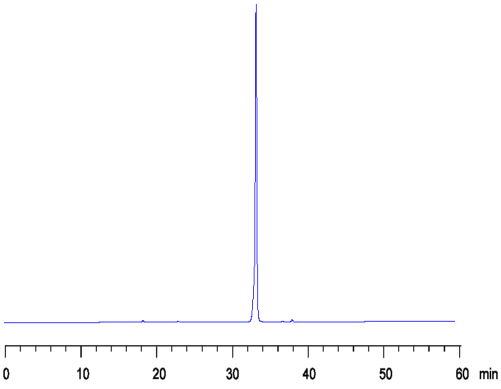


entry 9 (crude **10l** ($\mathbf{^{L}T_{PO}T}$), **R = Thg**)

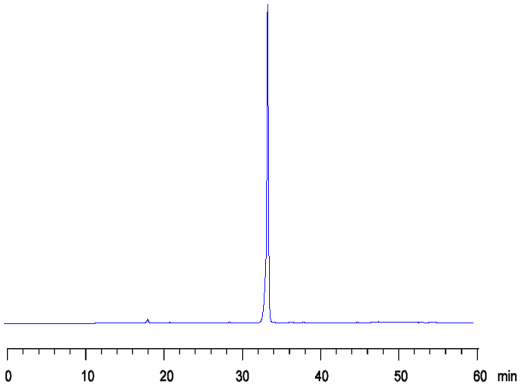


Figure S1 RP-HPLC profiles of the crude **10a-l** with detection at 260 nm. RP-HPLC was performed with a linear gradient of 0–20% CH_3CN for 60 min in 0.1 M TEAA buffer (pH 7.0) at 30 °C with a flow rate of 0.5 mL/min using a C18 column.

2. RP-HPLC profile of oligonucleotide phosphates (Table 1)

entry10 d($C_{PO}A_{PO}G_{PO}T_{PO}C_{PO}A_{PO}G_{PO}T_{PO}C_{PO}A_{PO}G_{PO}T$)

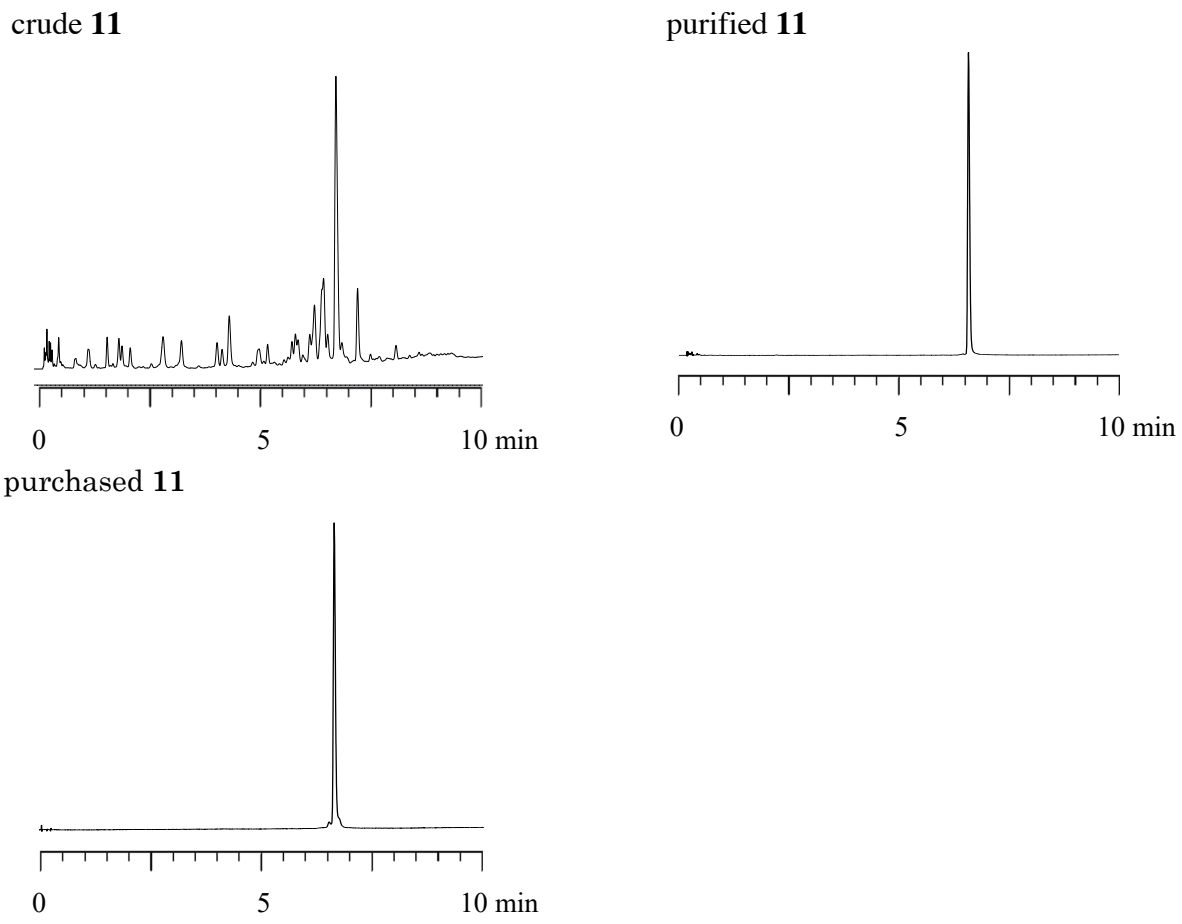


Figure S2 RP-HPLC profiles of the crude, the purified and the purchased **11** with detection at 260 nm. RP-UPLC was performed with a linear gradient of 5–25% MeOH for 10 min in a 0.4 M 1,1,1,3,3,3-hexafluoro-2-propanol, and 16 mM triethylamine at 50 °C with a flow rate of 0.5 mL/min using a C18 column. The product was eluted at 6.7 min.

3. Investigation of condensation efficiency after boronation (SI)

We investigated the condensation efficiency after a boronation because there is a possibility that the boronation reagent and/or its residue(s) inhibit the subsequent condensation reaction.

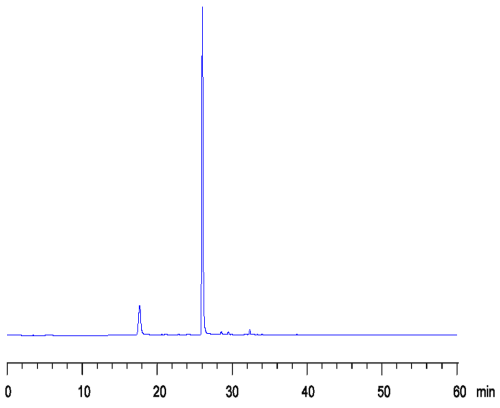
The HCP-loaded 5′-*O*-DMTr-Th (29.6 μmol/g, 0.50 μmol), via a succinyl linker, was boronated using the boronation conditions of following Table S1. Afterward, the HCP was washed with dry THF (3 × 1 mL) and dry EtOH (3 × 1 mL) dry CH_2Cl_2 (3 × 1 mL) and treated in a reaction vessel with 3% DCA in dry CH_2Cl_2 (5 × 12 s, 1 mL each) and washed with dry CH_2Cl_2 (3 × 1 mL) and CH_3CN (3 × 1 mL). Thereafter, it was dried in vacuo for 5 min. Then, the oxazaphospholidine monomer (**6c**, 30 μmol), which was dried in vacuo overnight, was added to the reaction vessel and dried in vacuo for 5 min. A 1.0 M solution of PhIMT (44.1 mg, 150 μmol) in dry CH_3CN–*i*PrCN (7:3, v/v, 150 μL), which was dried over MS 3Å overnight, was added under Ar atmosphere to the reaction vessel. After 10 min, the HCP was washed with dry CH_3CN (3 × 1 mL) and dry CH_2Cl_2 (3 × 1 mL) and dried in vacuo for 5 min. The resultant phosphite was oxidated upon treatment with a 1.0 M solution of TBHP (500 μL, 500 μmol) in dry toluene and the reaction vessel was shaken for 5 min. Then, the HCP was washed with dry CH_2Cl_2 (6 × 1 mL) and the detritylation reaction was carried out using 3% DCA in dry CH_2Cl_2 (5 × 12 s, 1 mL each). Then, the HCP was washed with dry CH_2Cl_2 (3 × 1 mL) and dry CH_3CN (3 × 1 mL). The HCP was then treated with a 25% NH_3 aqueous solution–EtOH (3:1, v/v, 5 mL) at rt for 3 h, filtered, and washed with CH_3CN. The filtrate and the washings were combined, concentrated under reduced pressure, and the obtained residue was analyzed by RP-HPLC, which was performed with a linear gradient of 0–20% CH_3CN for 60 min in a 0.1 M TEAA buffer (pH 7.0).

Table S1. Solid-Phase Synthesis of $dC_{PO}T$ Dimers after botonated treatment in advance.

entry	boronation condition	T:10c[a]
1	1 M BH_3・SMe_2/toluene for15 min	14.4:85.6
2	1 M BH_3・THF/THF for 15 min	6.7:93.3
3	0.05 M BH_3・THF/THF for 15 min	2.5:97.5
4	0.05 M BH_3・THF/THF for 2 min	1.6:98.4

[a] Determined by RP-HPLC.

entry 1



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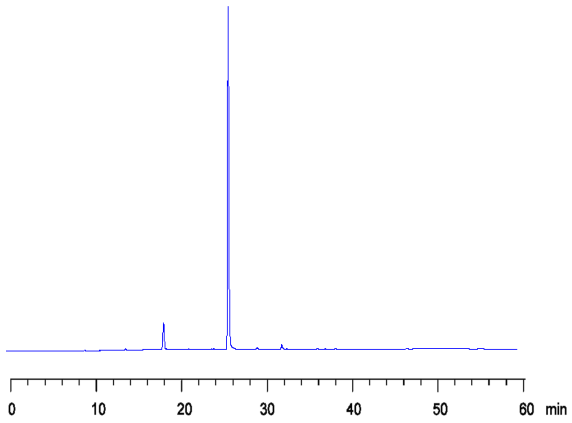

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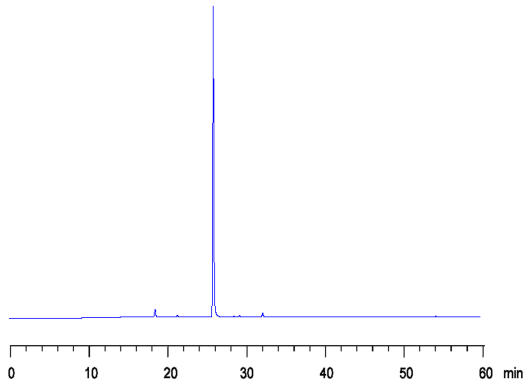

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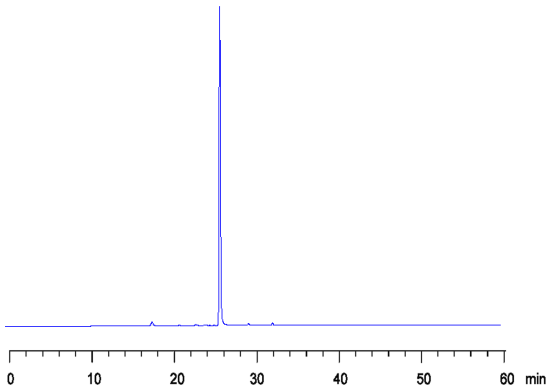
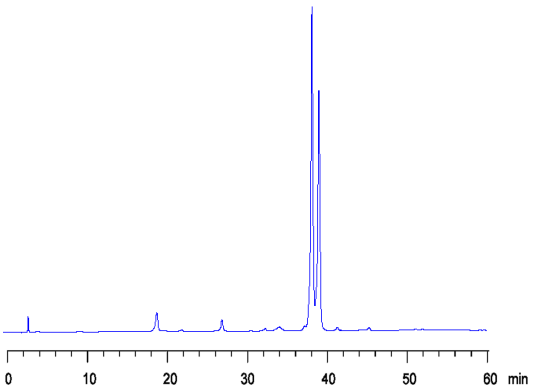


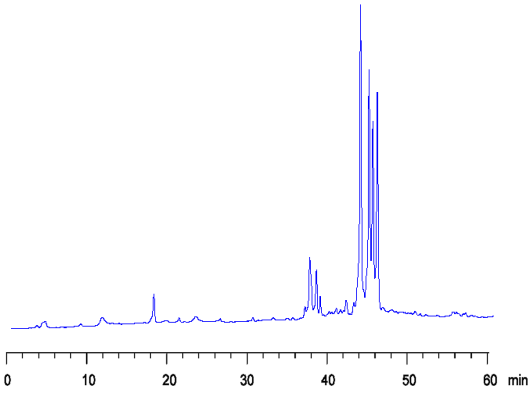
Figure S3 RP-HPLC profiles of crude **10c** with detection at 260 nm. RP-HPLC was performed with a linear gradient of 0–20% CH_3CN for 60 min in 0.1 M TEAA buffer (pH 7.0) at 30 °C with a flow rate of 0.5 mL/min using a C18 column.

4. RP-HPLC profiles of dinucleotide or trinucleotide boranophosphates (Table2)

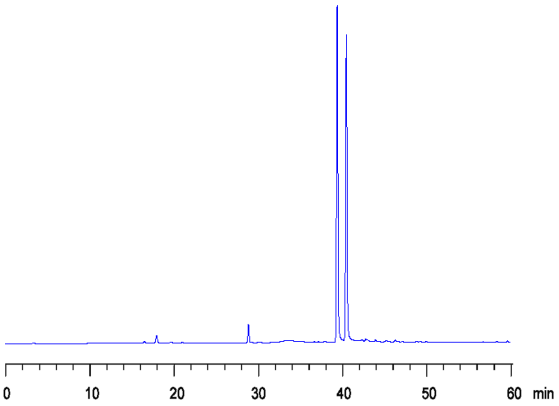
entry 1 (crude **14c** (**dC$_{PB}$T**))



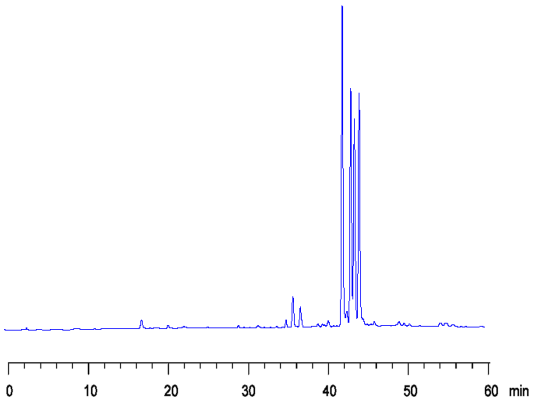
entry 2 (crude **15** (**d(C$_{PB}$C$_{PB}$T)**))



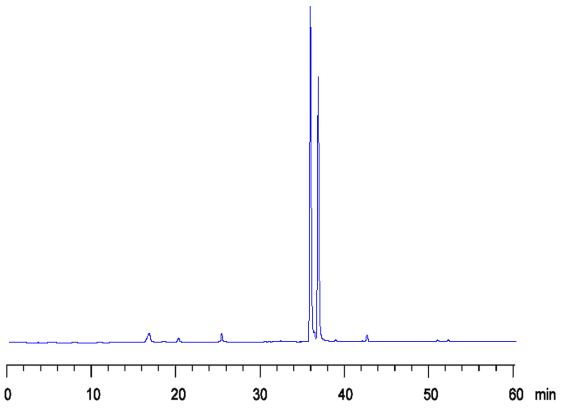
entry 3 (crude **14c** (**dC$_{PB}$T**))



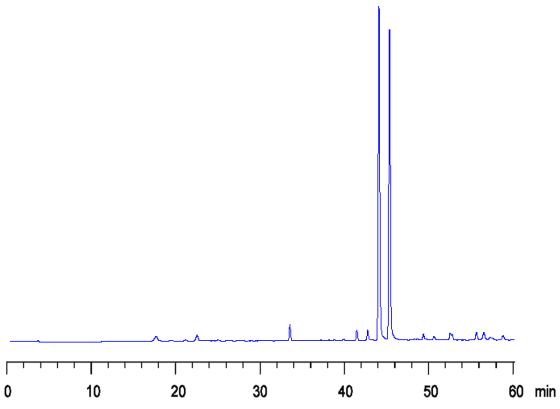
entry 4 (crude **15** (**d(C$_{PB}$C$_{PB}$T)**))



entry 5 (crude **14c** (**dA$_{PB}$T**))



entry 6 (crude **14g** (**dG$_{PB}$T**))



entry 7 (crude **14t** (**$T_{PB}T$**))

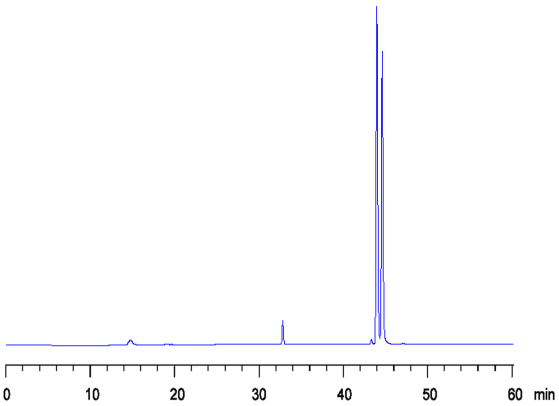
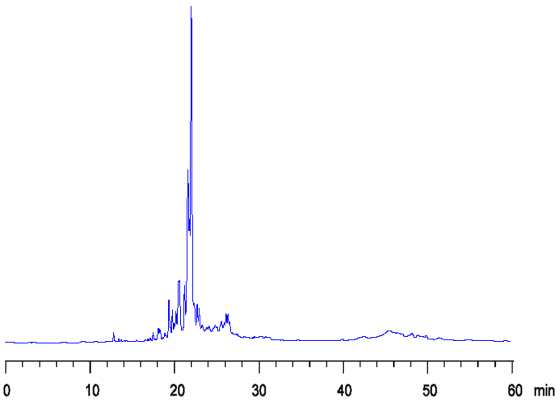


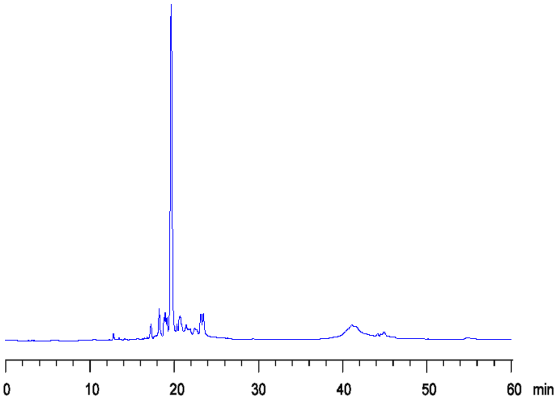
Figure S4 RP-HPLC profiles of crude **14a-t and 15** with detection at 260 nm. RP-HPLC was performed with a linear gradient of 0–20% CH_3CN for 60 in 0.1 M TEAA buffer (pH 7.0) at 30 °C min with a flow rate of 0.5 mL/min using a C18 column.

5. RP-HPLC profiles of tetranucleotide bearing boranophosphate linkages (Table3)

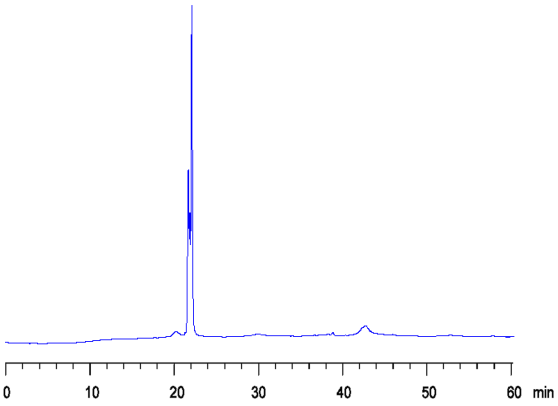
entry 1(crude **16** (**d**($C_{PB}A_{PB}G_{PB}T$)))



entry 2 (crude **17** (**d**($C_{PB}A_{PO}G_{PB}T$)))



purified **16**



purified **17**

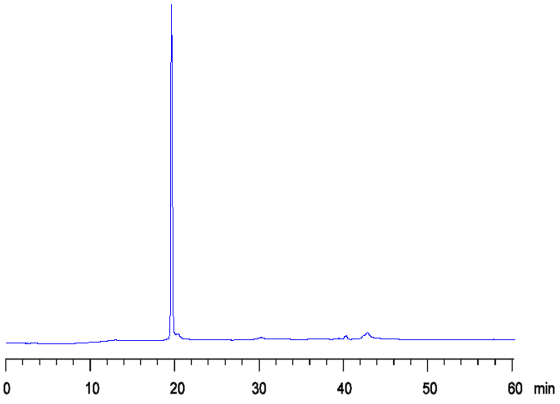
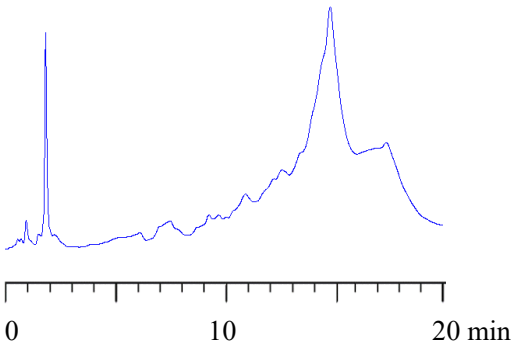


Figure S5 RP-HPLC profiles of the crude **16, 17 and** purified **16, 17** with detection at 260 nm. RP-HPLC was performed with a linear gradient of 0–60% CH_3CN for 60 min in 0.1 M TEAA buffer (pH 7.0) at 30 °C with a flow rate of 0.5 mL/min using a C18 column.

6. RP-HPLC profiles of dodecamer bearing boranophosphate linkages (Scheme 4)

d($C_{PB}A_{PO}G_{PB}C_{PO}T_{PB}A_{PO}G_{PB}T_{PO}C_{PB}A_{PO}G_{PB}T$)

crude **18**



purified **18**

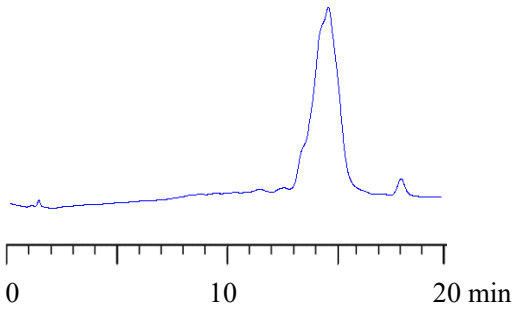
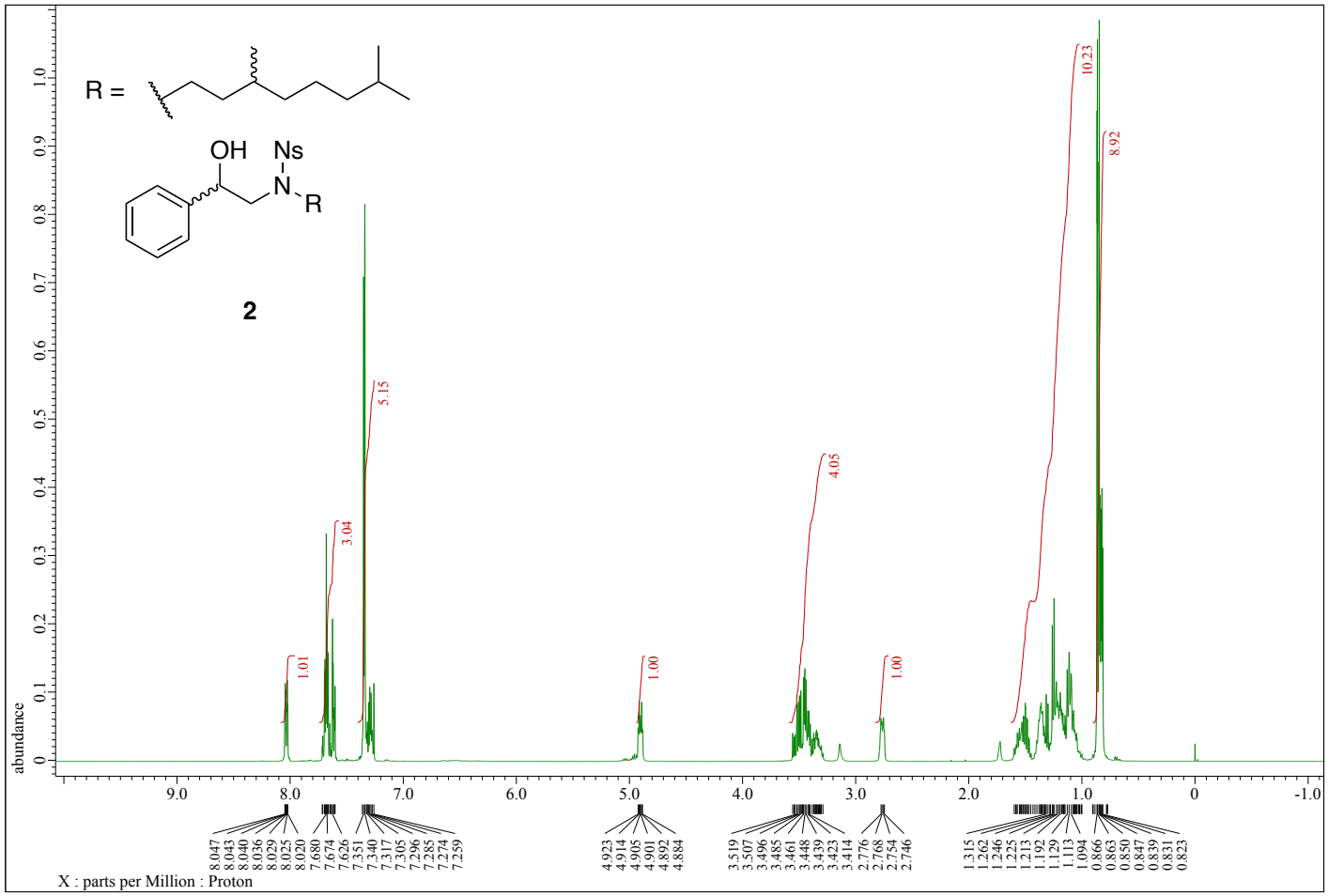


Figure S6 RP-HPLC profiles of crude **18** and purified **18** with detection at 260 nm. RP-HPLC was performed with a linear gradient of 5–40% MeOH for 20 min in 0.4 M 1,1,1,3,3,3-hexafluoro-2-propanol and 8 mM triethylamine at 60 °C with a flow rate of 0.5 mL/min using a C18 column.

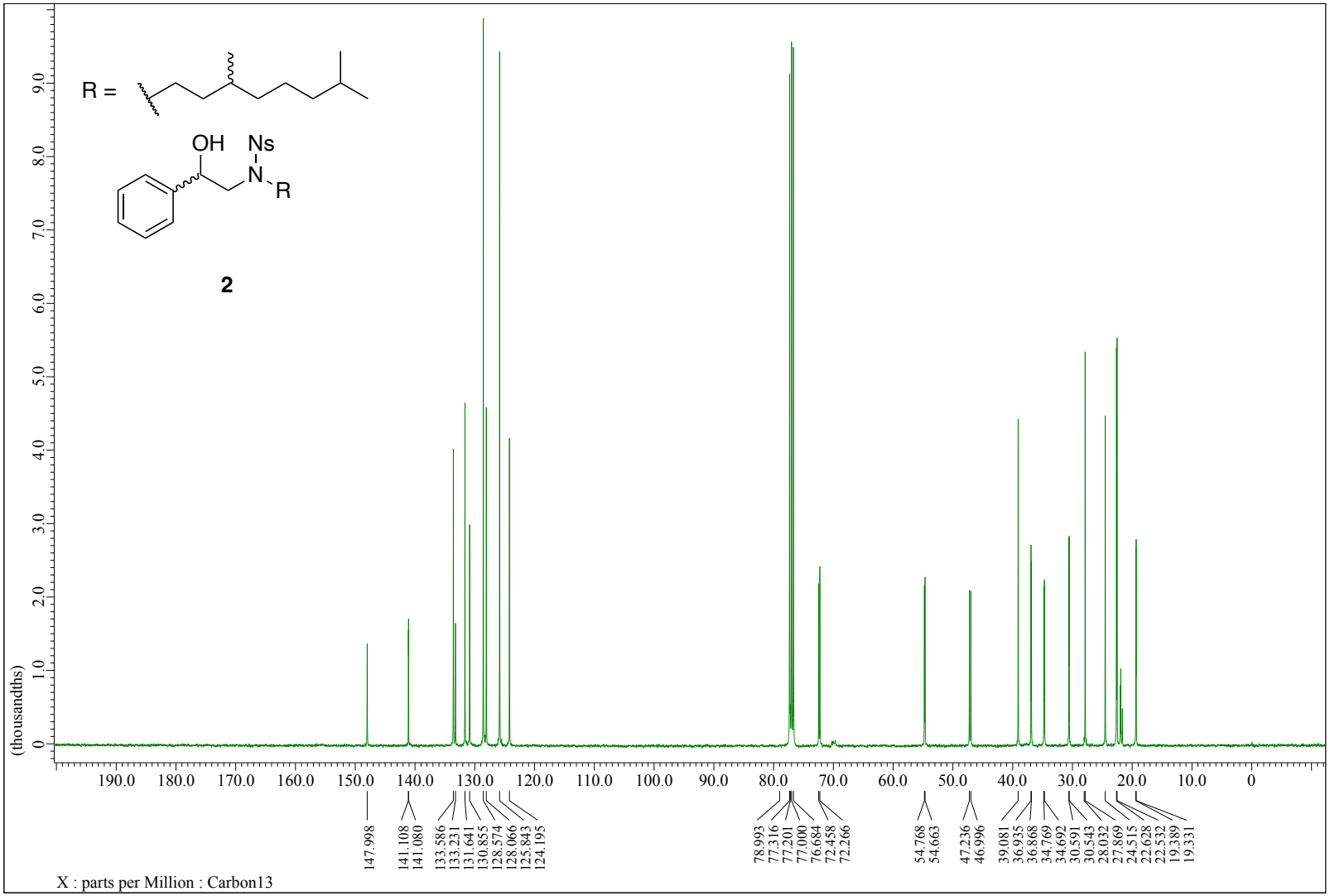
7. ^{1}H, ^{13}C, ^{31}P, COSY, HMQC, HMBC NMR spectra

***N*-(3,7-Dimethyloctyl)-*N*-(2-hydroxy-2-phenylethyl)-2-nitrobenzenesulfonamide (2)**

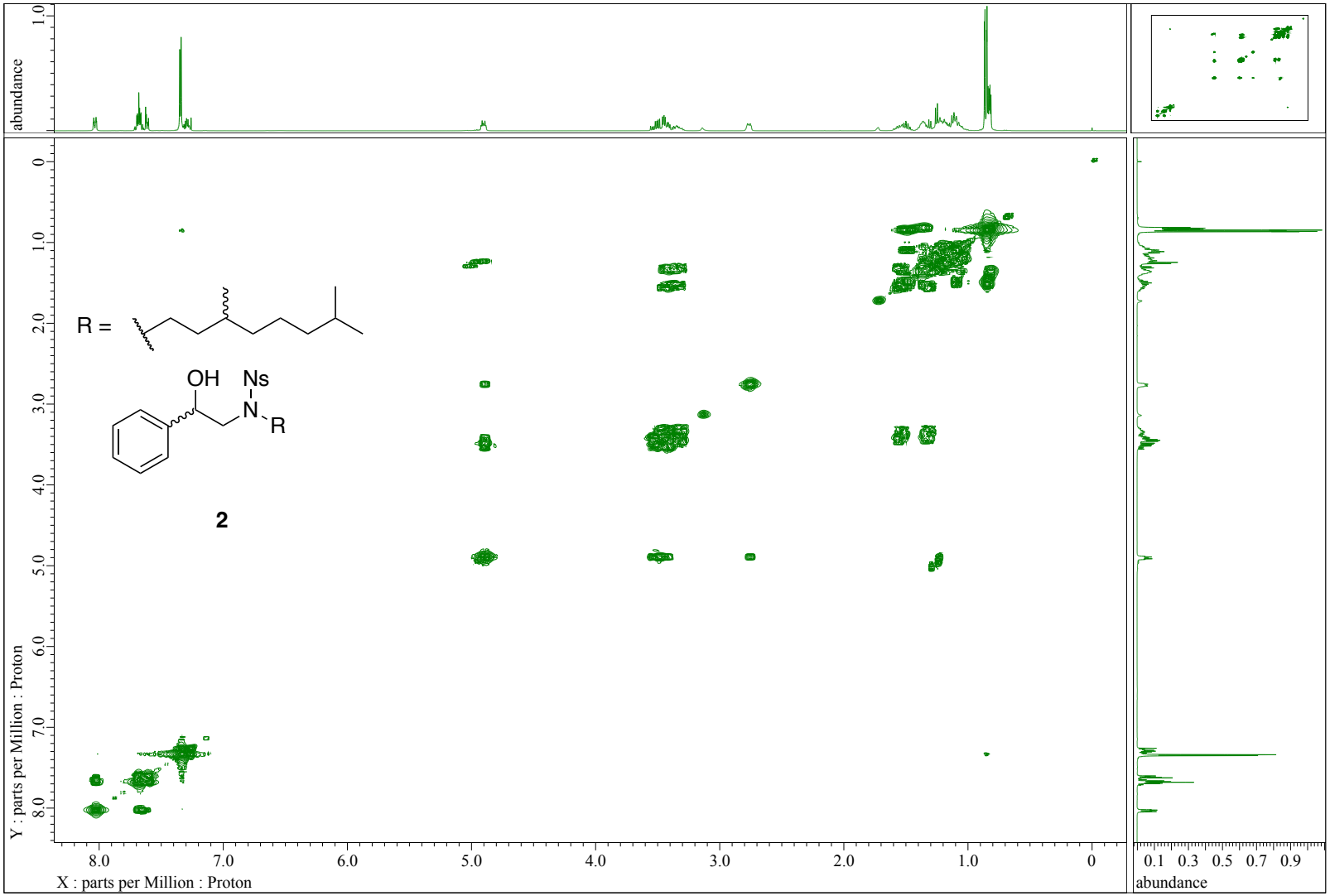
^{1}H NMR (400 MHz, $CDCl_3$)



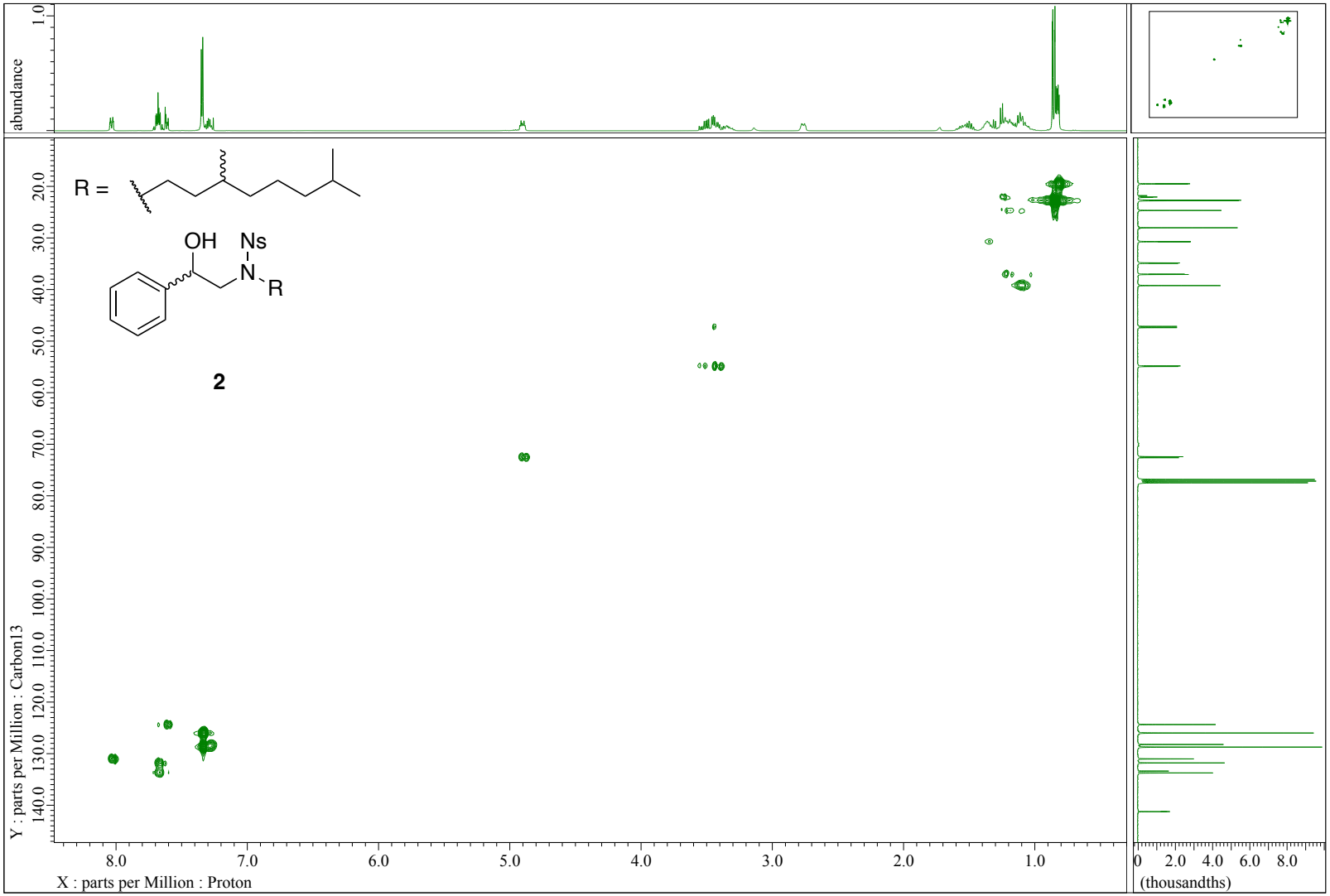
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)



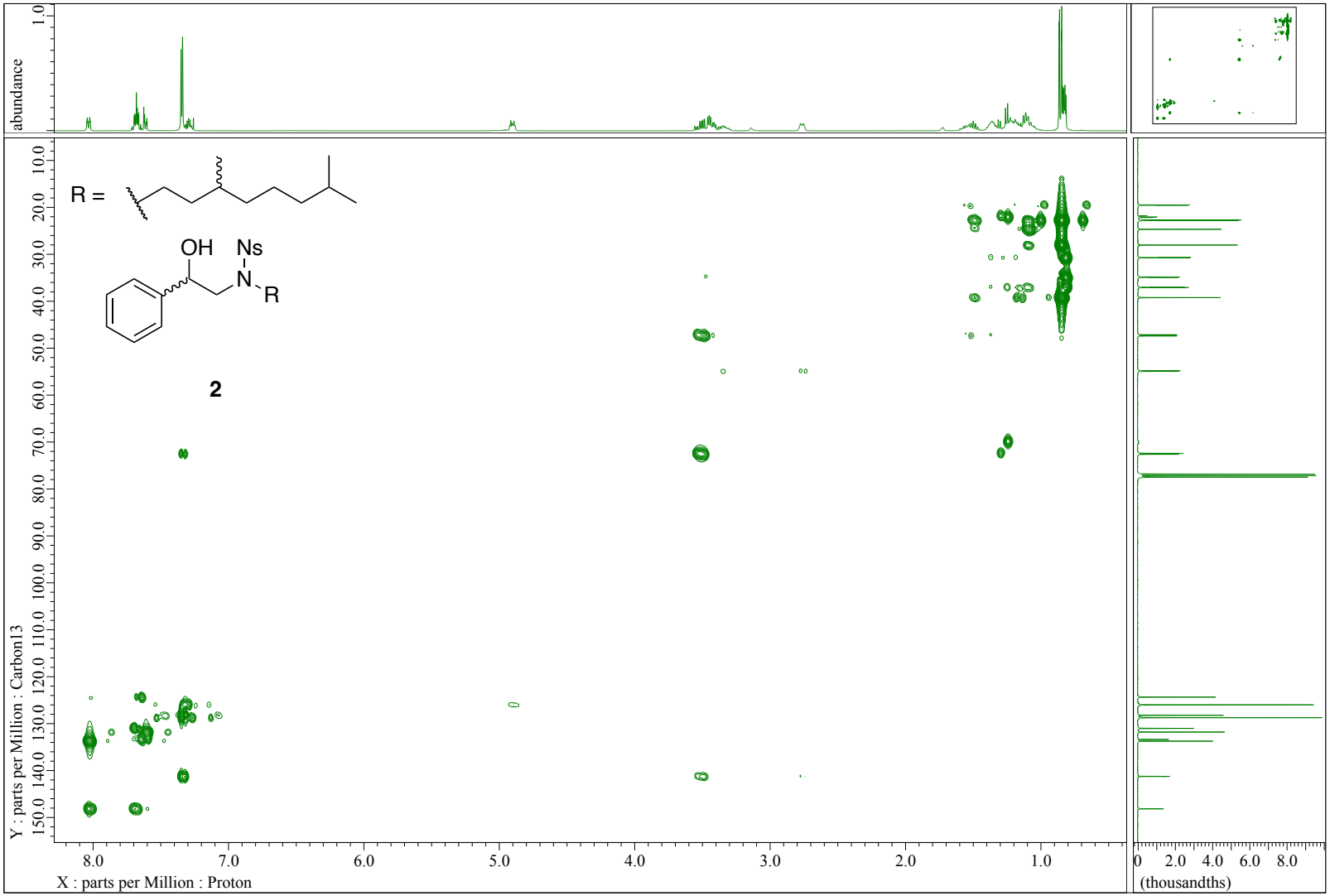
COSY ($CDCl_3$)


abundance
1.0
R =
OH
Ns
N
R
2
Y : parts per Million : Proton
X : parts per Million : Proton
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
0.1
0.3
0.5
0.7
0.9
abundance

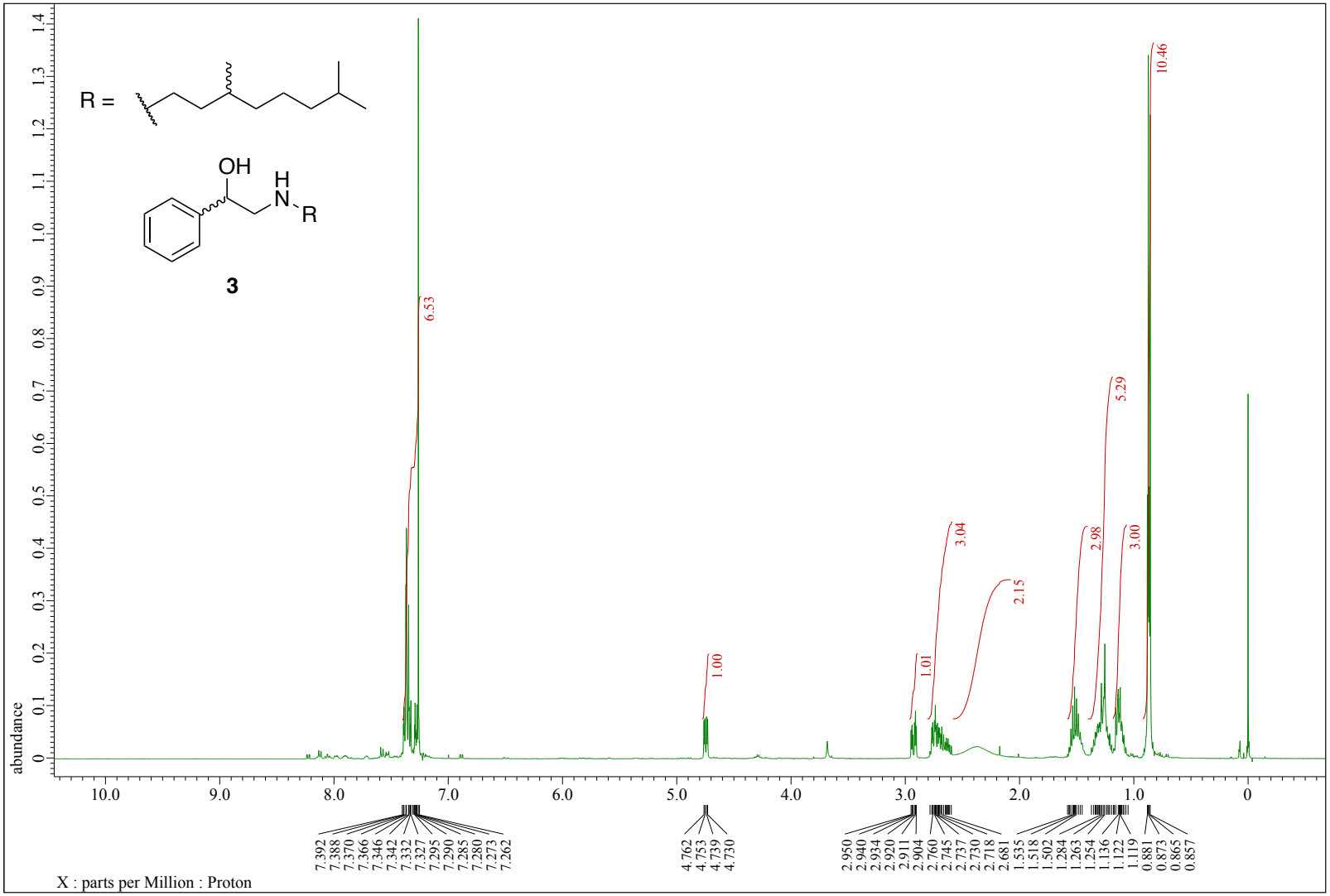
HMQC ($CDCl_3$)


abundance
1.0
R =
OH
Ns
N
R
2
Y : parts per Million : Carbon13
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
X : parts per Million : Proton
0
2.0
4.0
6.0
8.0
(thousandths)

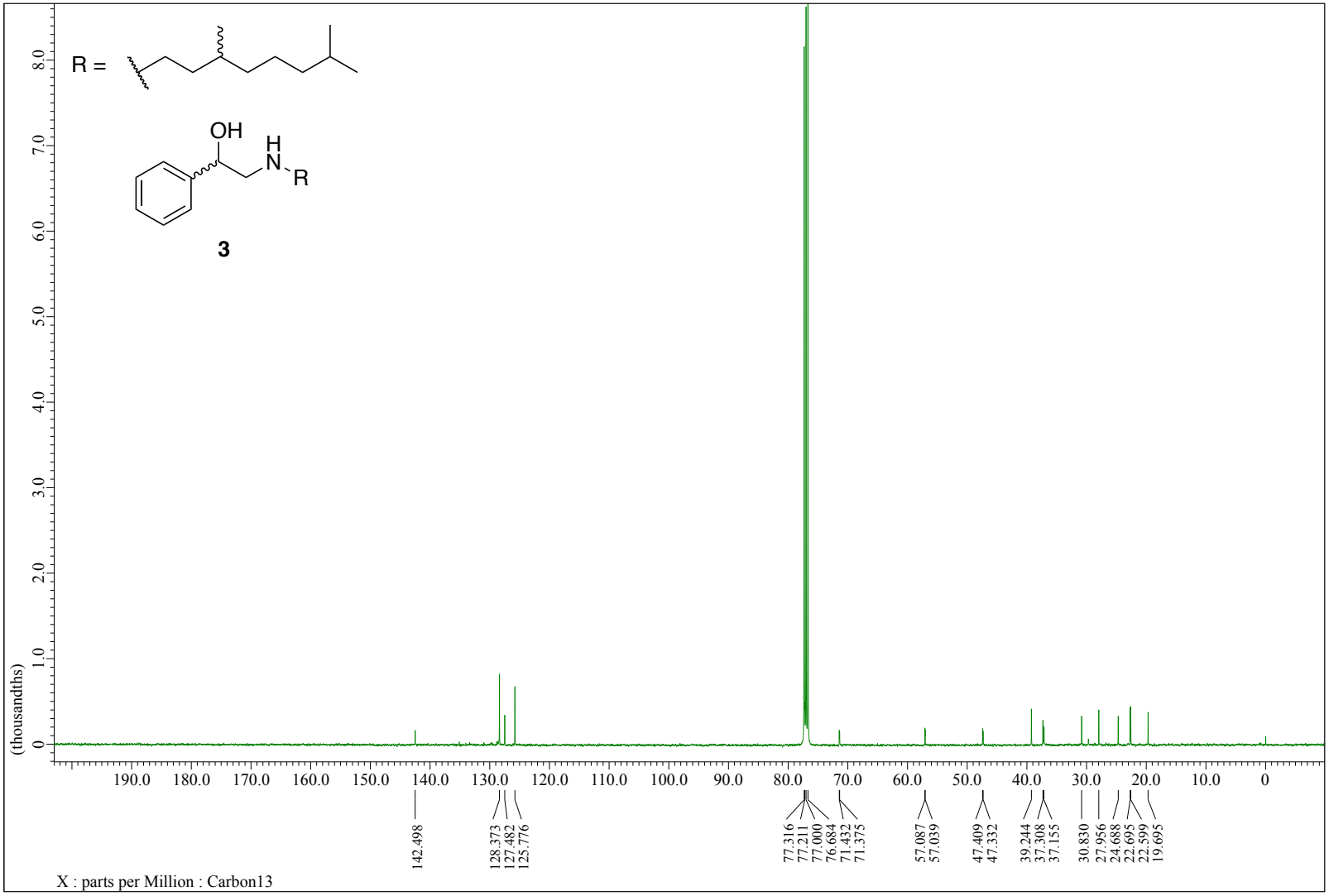
HMBC ($CDCl_3$)


abundance
1.0
R =
OH
Ns
N
R
2
Y : parts per Million : Carbon13
X : parts per Million : Proton
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
(thousandths)

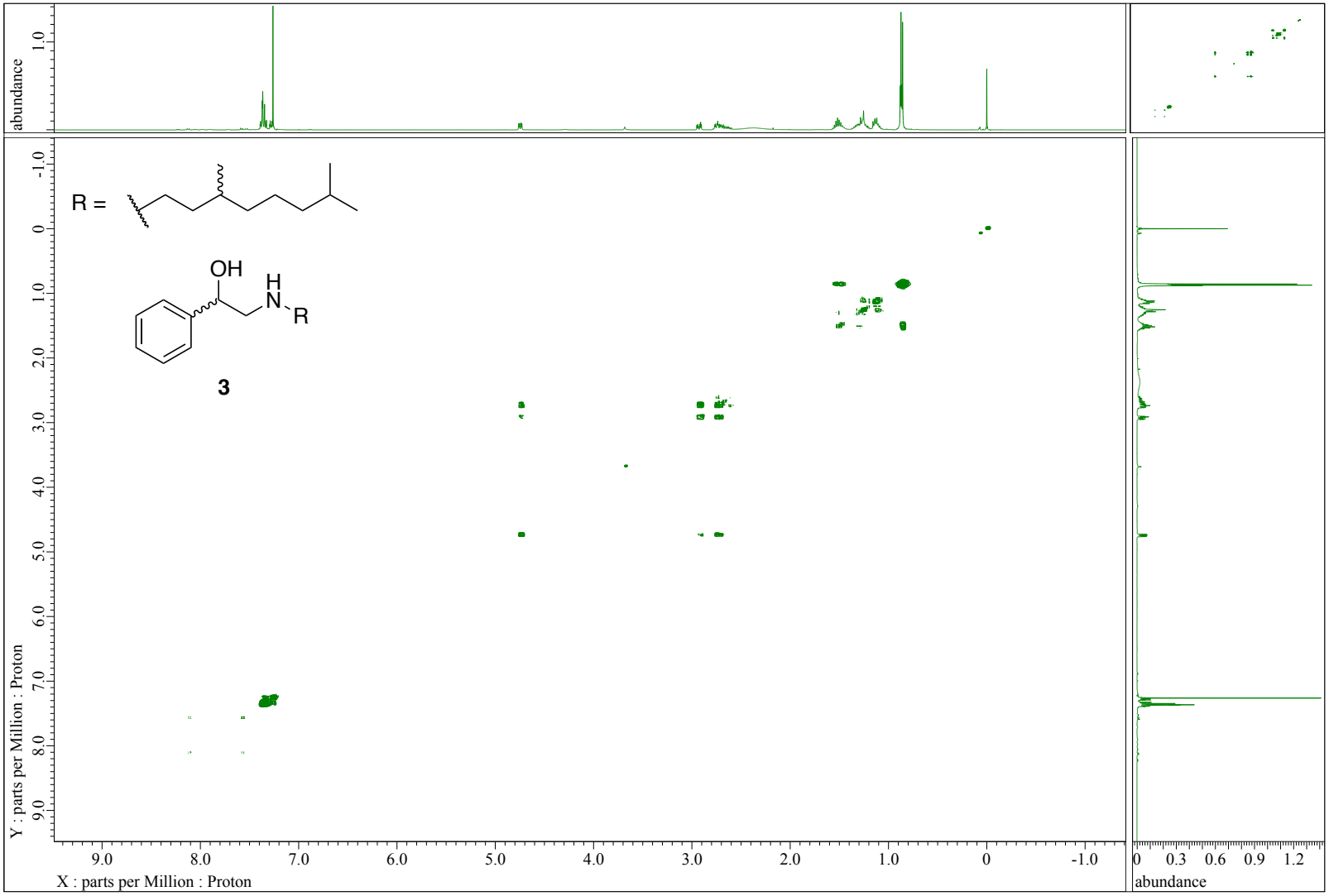
2-((3,7-Dimethyloctyl)amino)-1-phenylethan-1-ol (3)
^{1}H NMR (400 MHz, $CDCl_3$)



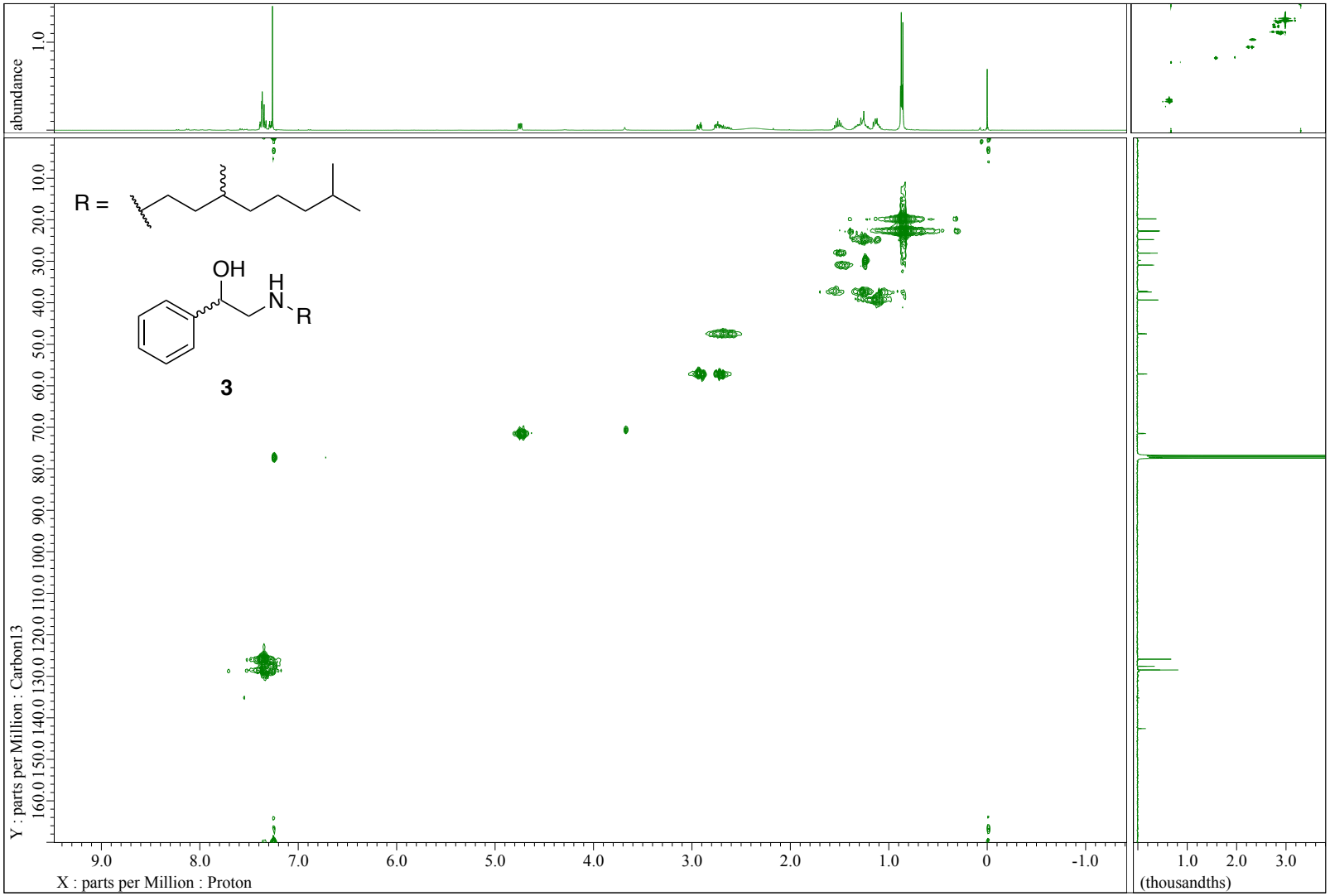
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)



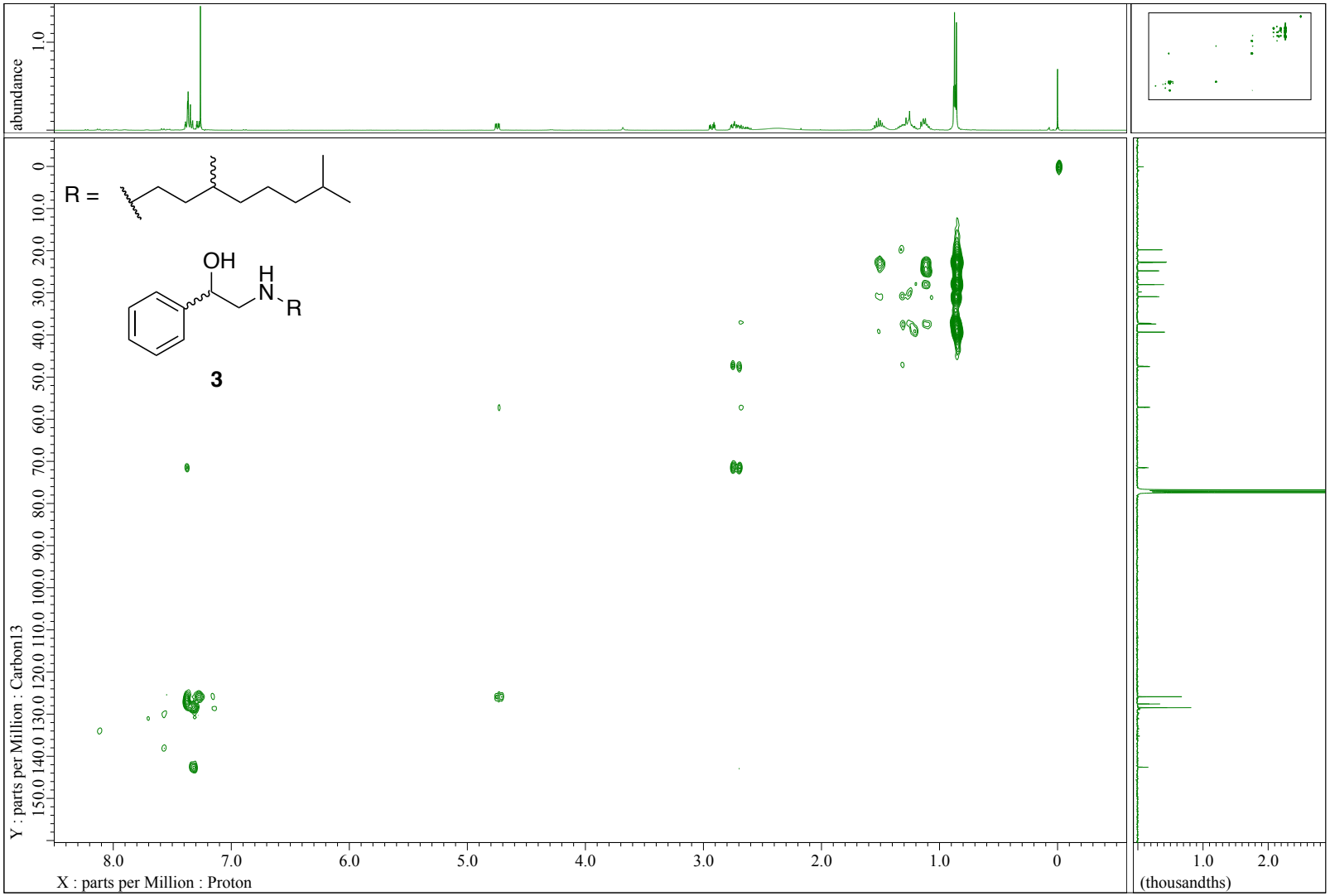
COSY ($CDCl_3$)


abundance
1.0
R =
OH
H
N
R
3
-1.0
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
Y : parts per Million : Proton
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
X : parts per Million : Proton
0
0.3
0.6
0.9
1.2
abundance

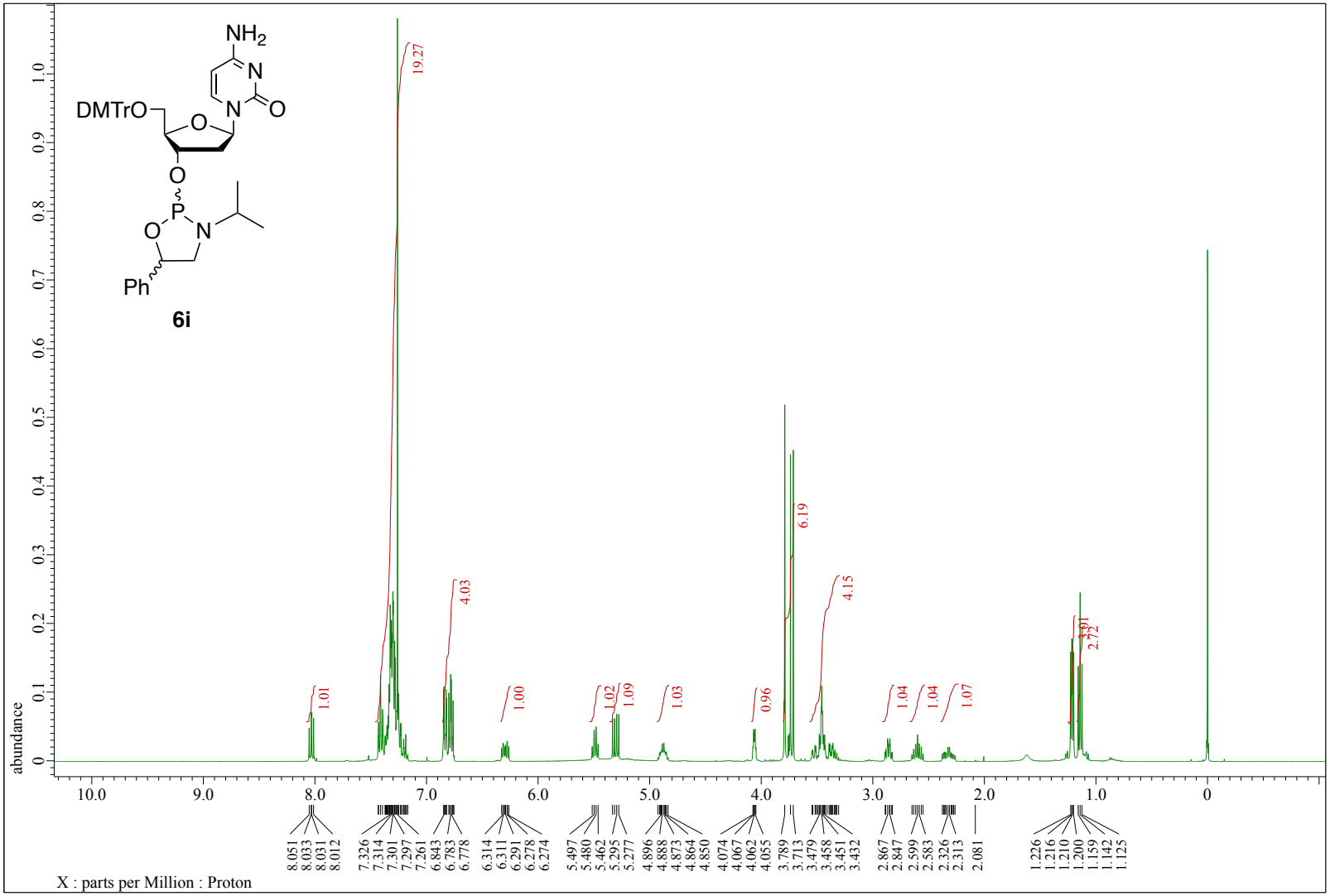
HMQC ($CDCl_3$)


abundance
1.0
R =
OH
H
N
R
3
Y : parts per Million : Carbon13
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
X : parts per Million : Proton
1.0
2.0
3.0
(thousandths)

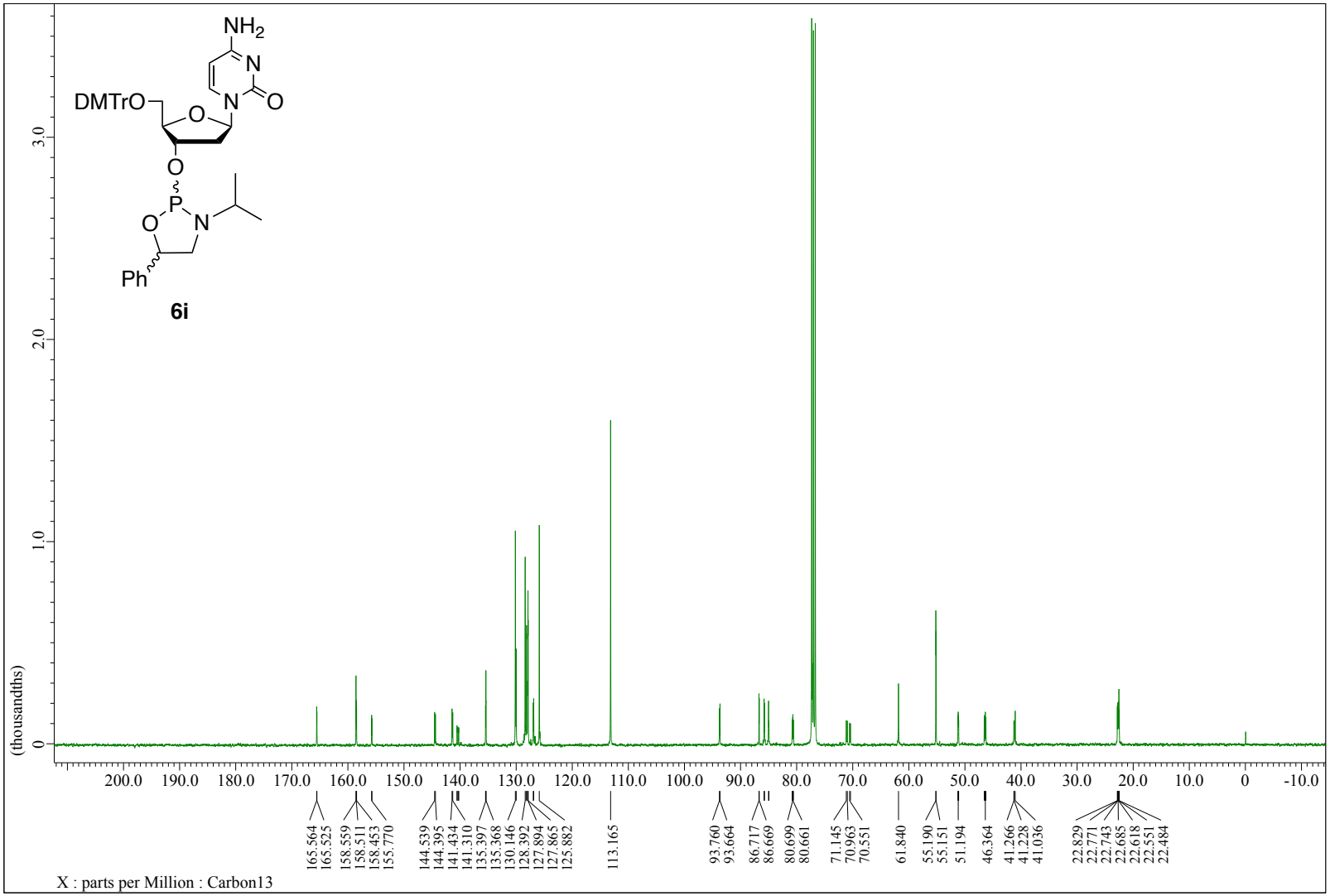
HMBC ($CDCl_3$)


abundance
R =
OH
H
N
R
3
Y : parts per Million : Carbon13
X : parts per Million : Proton
(thousandths)

dCy oxazaphospholidine *N-i*Pr monomer (6i)
^{1}H NMR (400 MHz, $CDCl_3$)

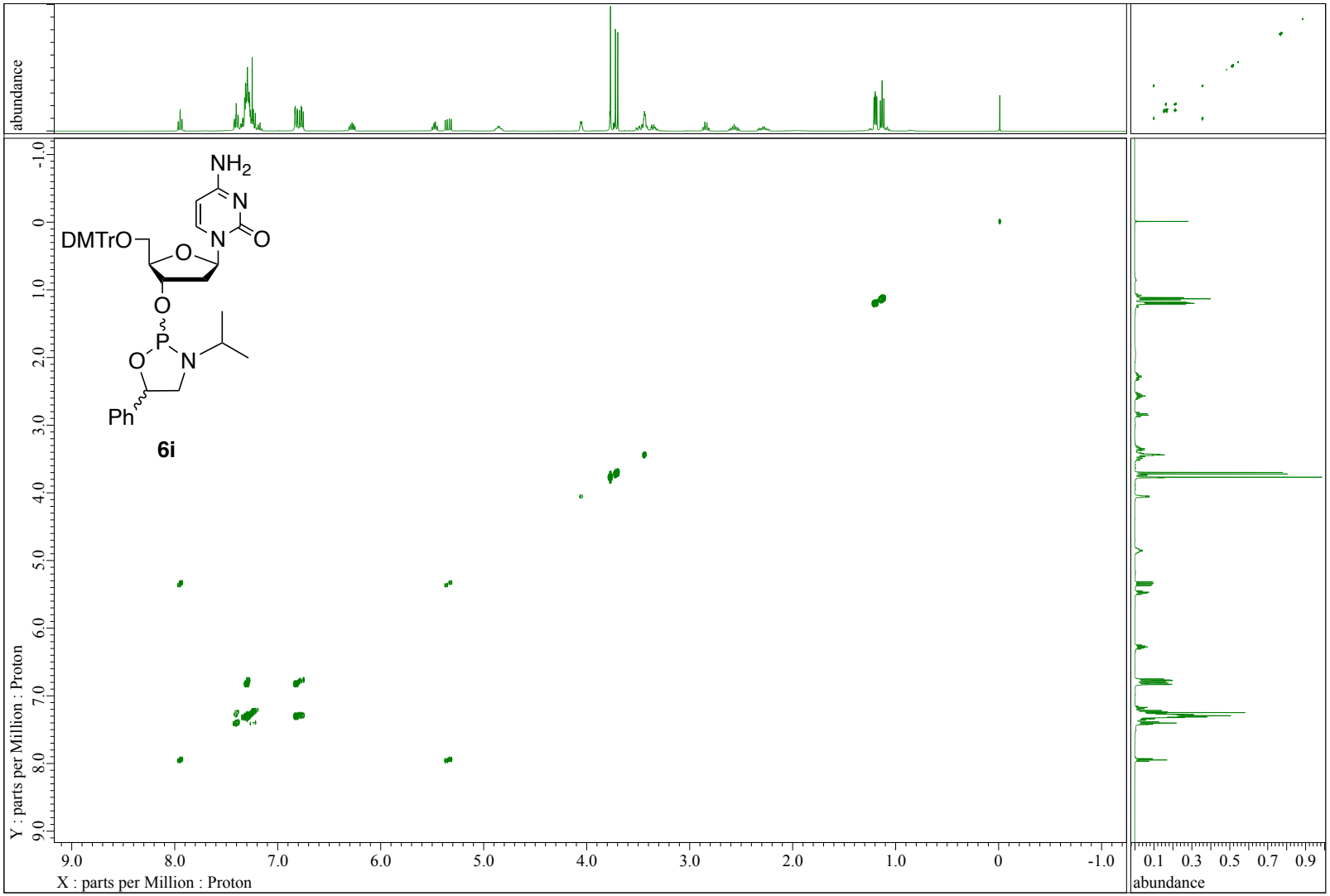


^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)

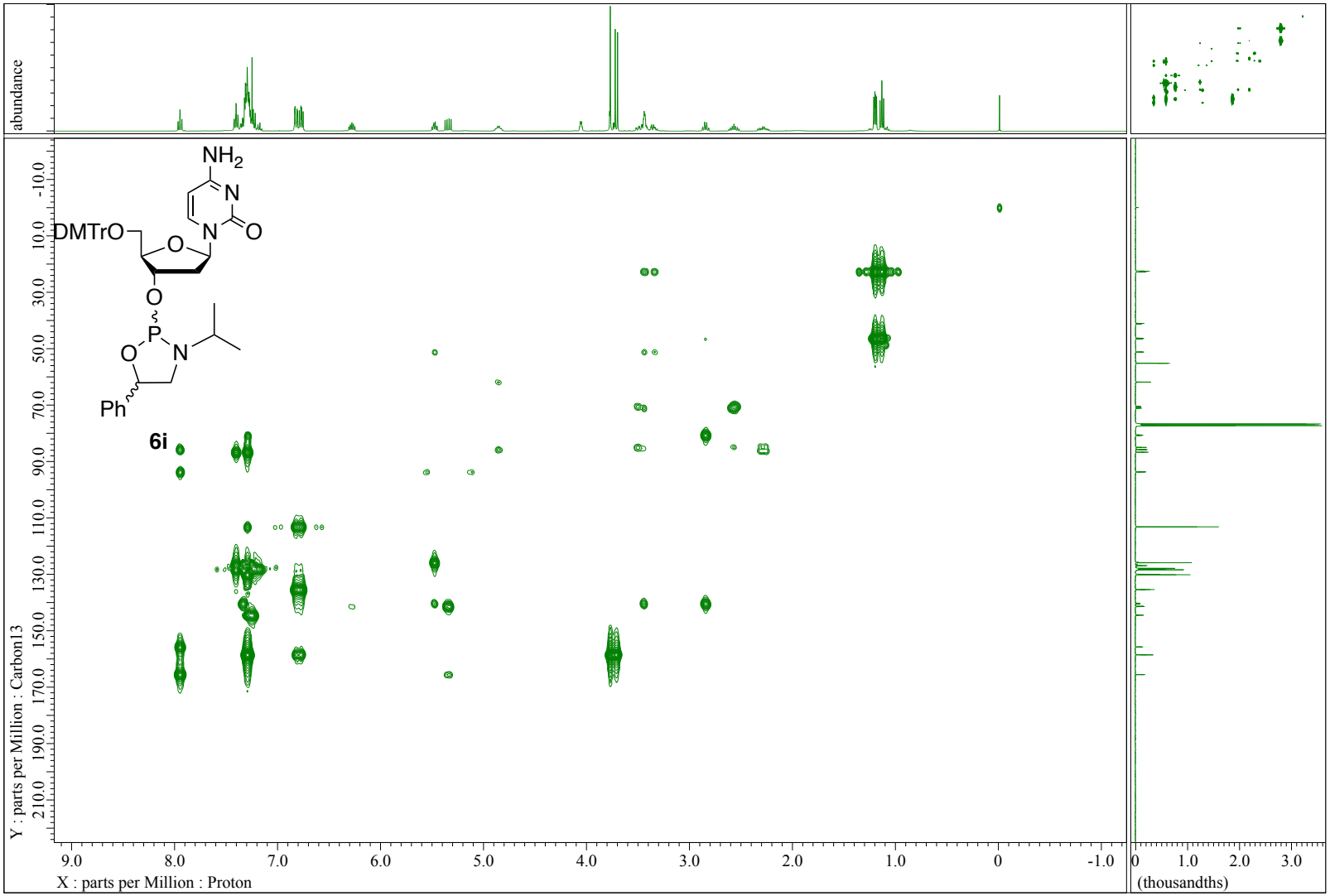


^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$)

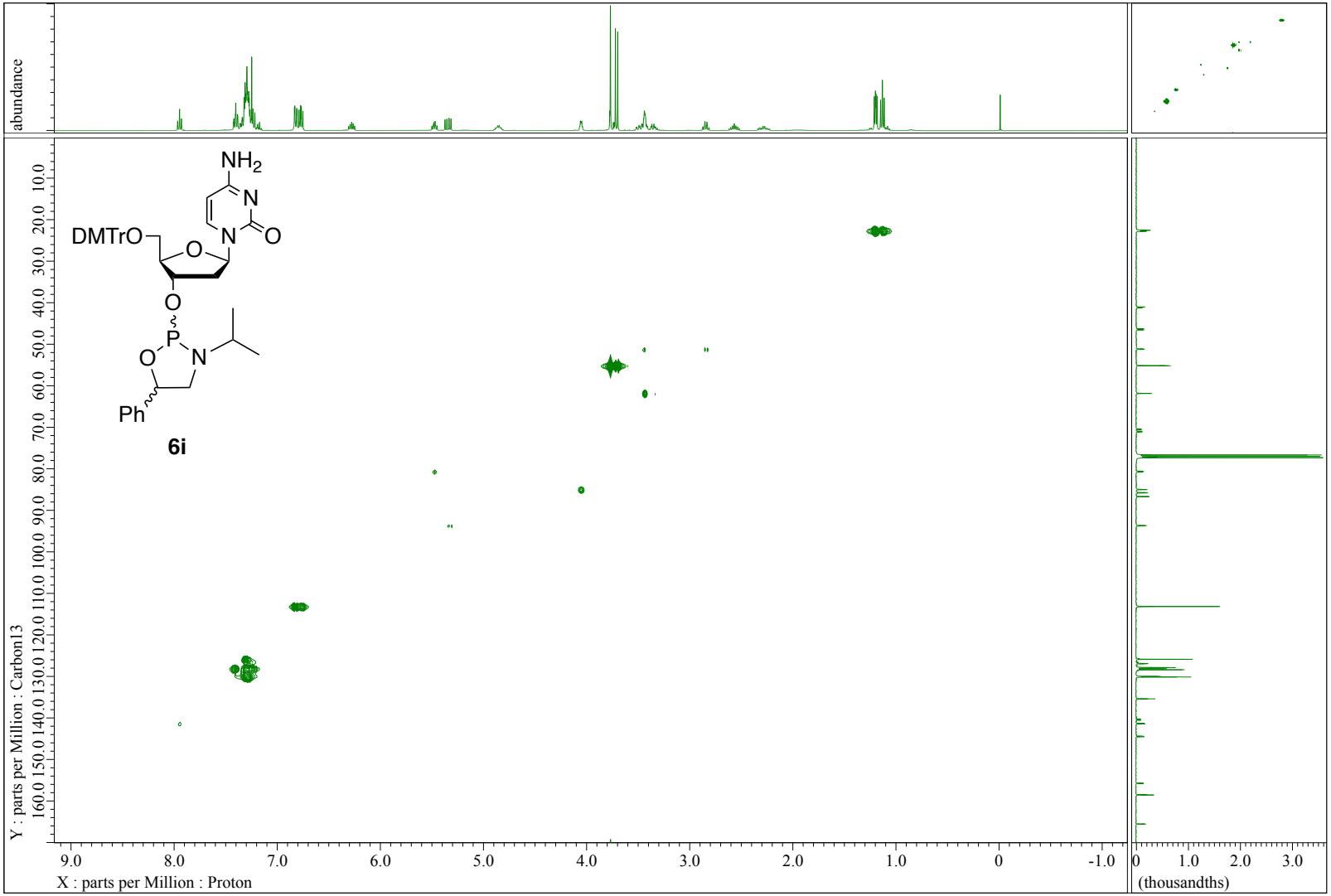
COSY ($CDCl_3$)


abundance
NH2
N
DMTrO
O
N
O
O
P
O
N
Ph
6i
Y : parts per Million : Proton
X : parts per Million : Proton
abundance

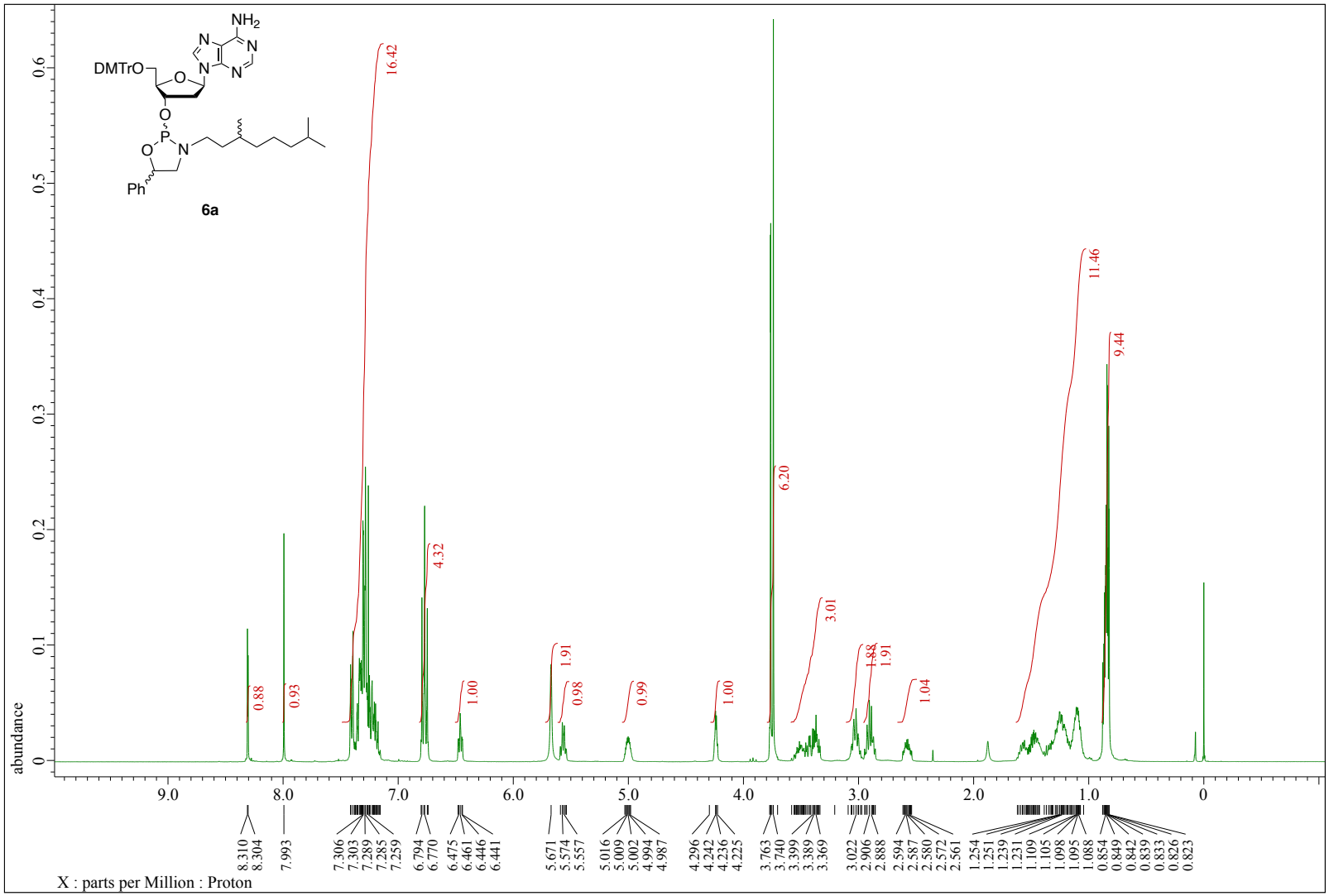
HMQC ($CDCl_3$)


abundance
NH2
N
DMTrO
O
N
O
O
P
O
N
Ph
6i
-10.0
10.0
30.0
50.0
70.0
90.0
110.0
130.0
150.0
170.0
190.0
210.0
Y : parts per Million : Carbon13
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
X : parts per Million : Proton
0
1.0
2.0
3.0
(thousandths)

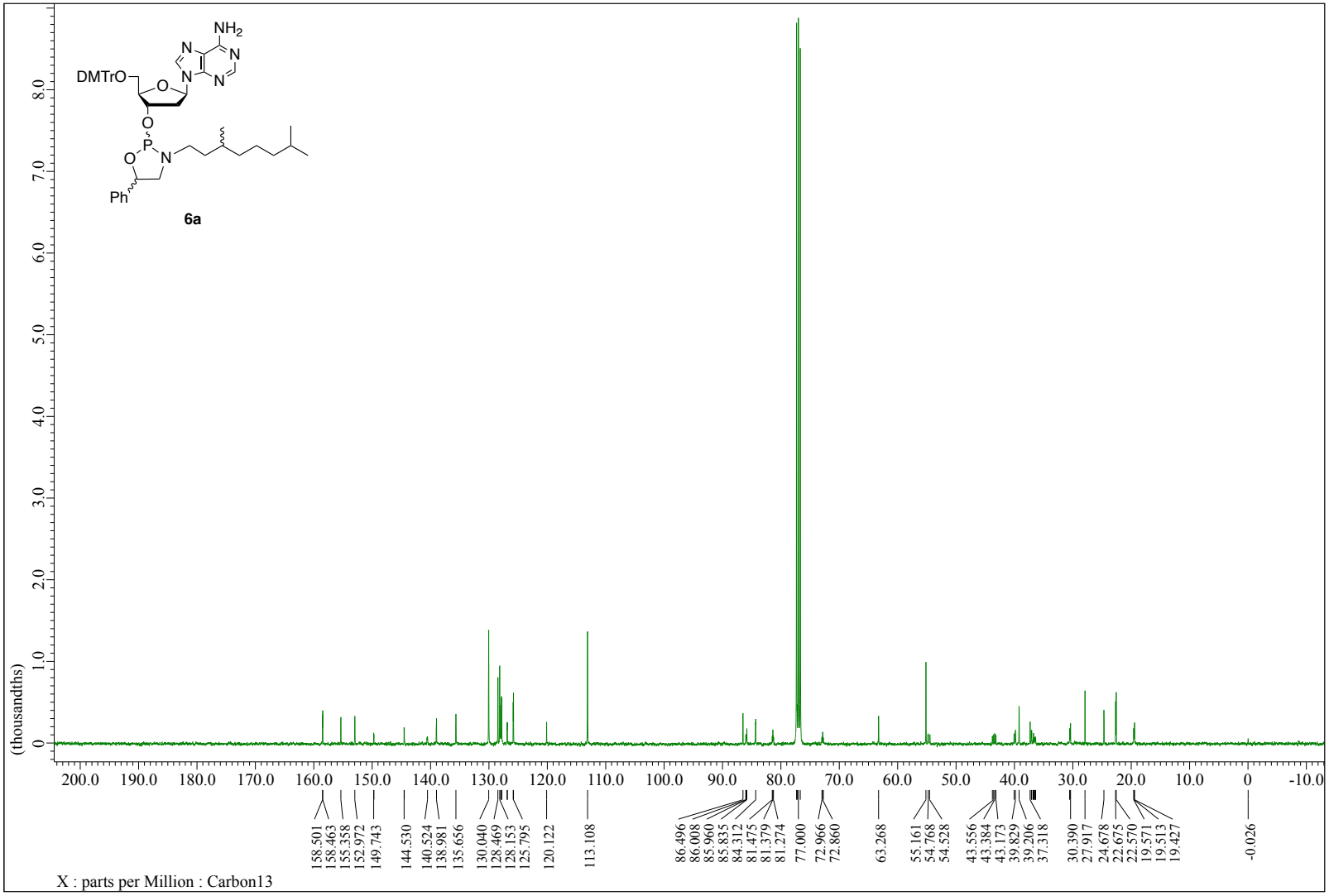
HMBC ($CDCl_3$)


abundance
NH2
N
DMTrO
O
N
O
O
P
O
N
Ph
6i
Y : parts per Million : Carbon13
X : parts per Million : Proton
(thousandths)

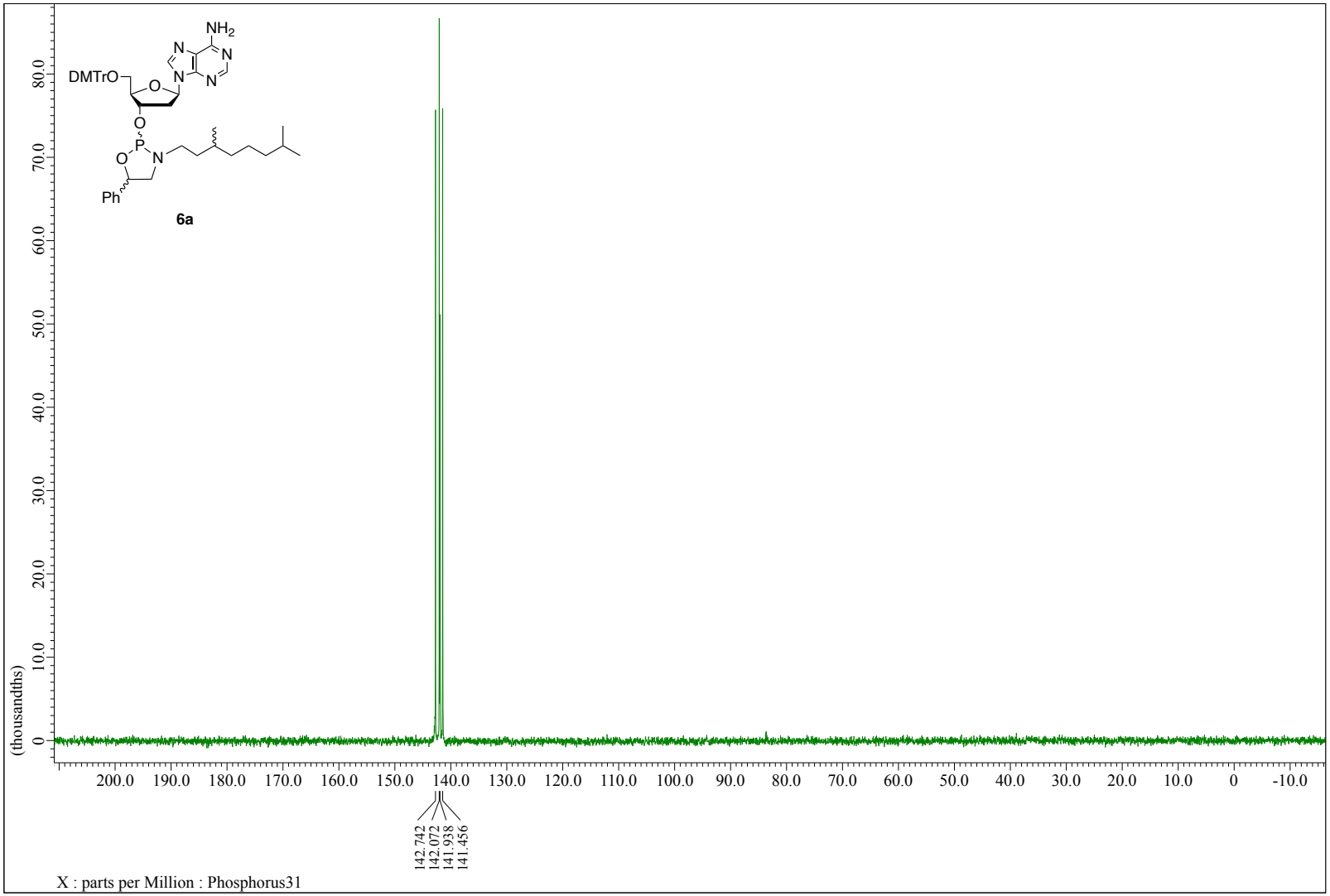
dAd oxazaphospholidine *N*-Thg monomer (6a)
^{1}H NMR (400 MHz, $CDCl_3$)



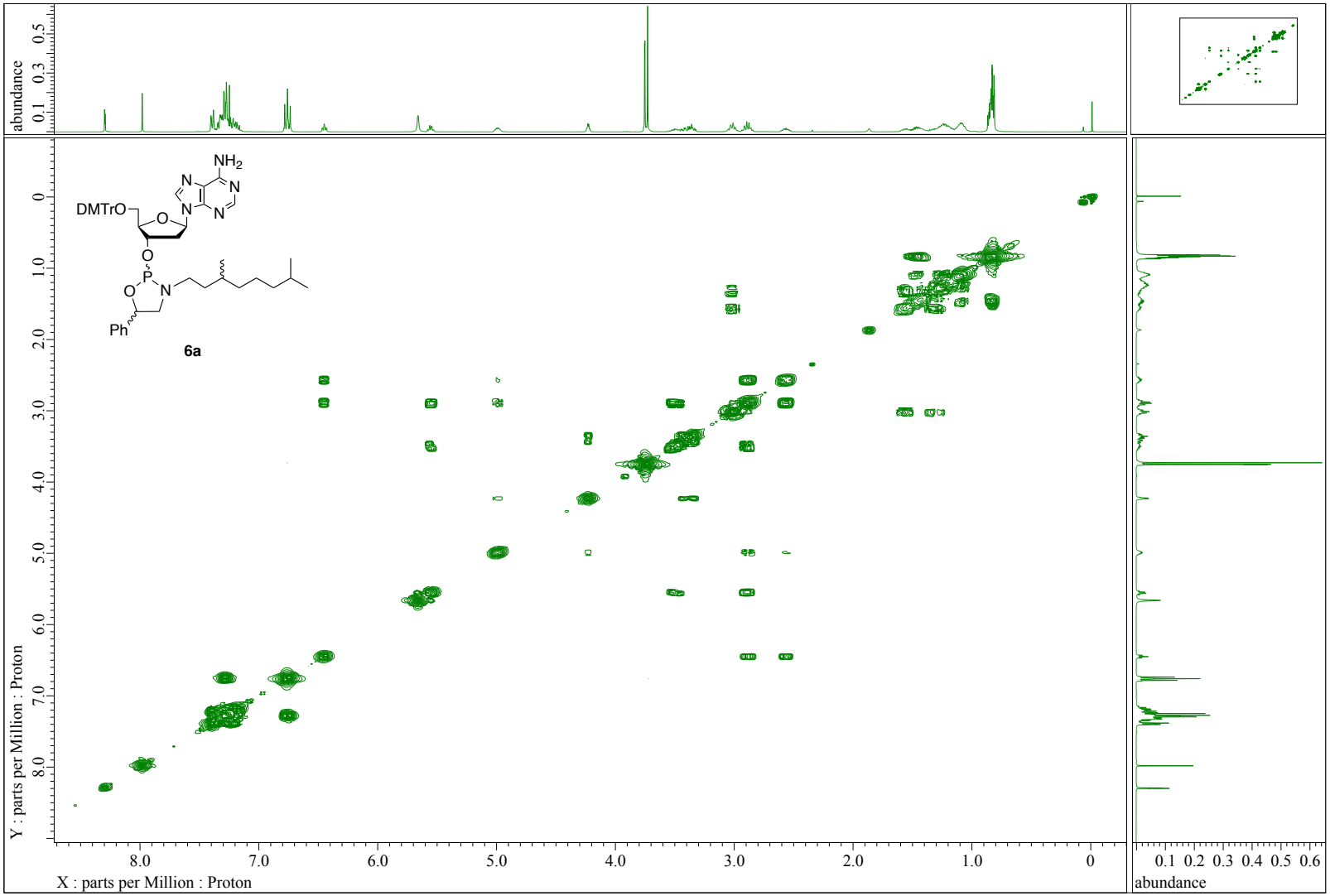
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)



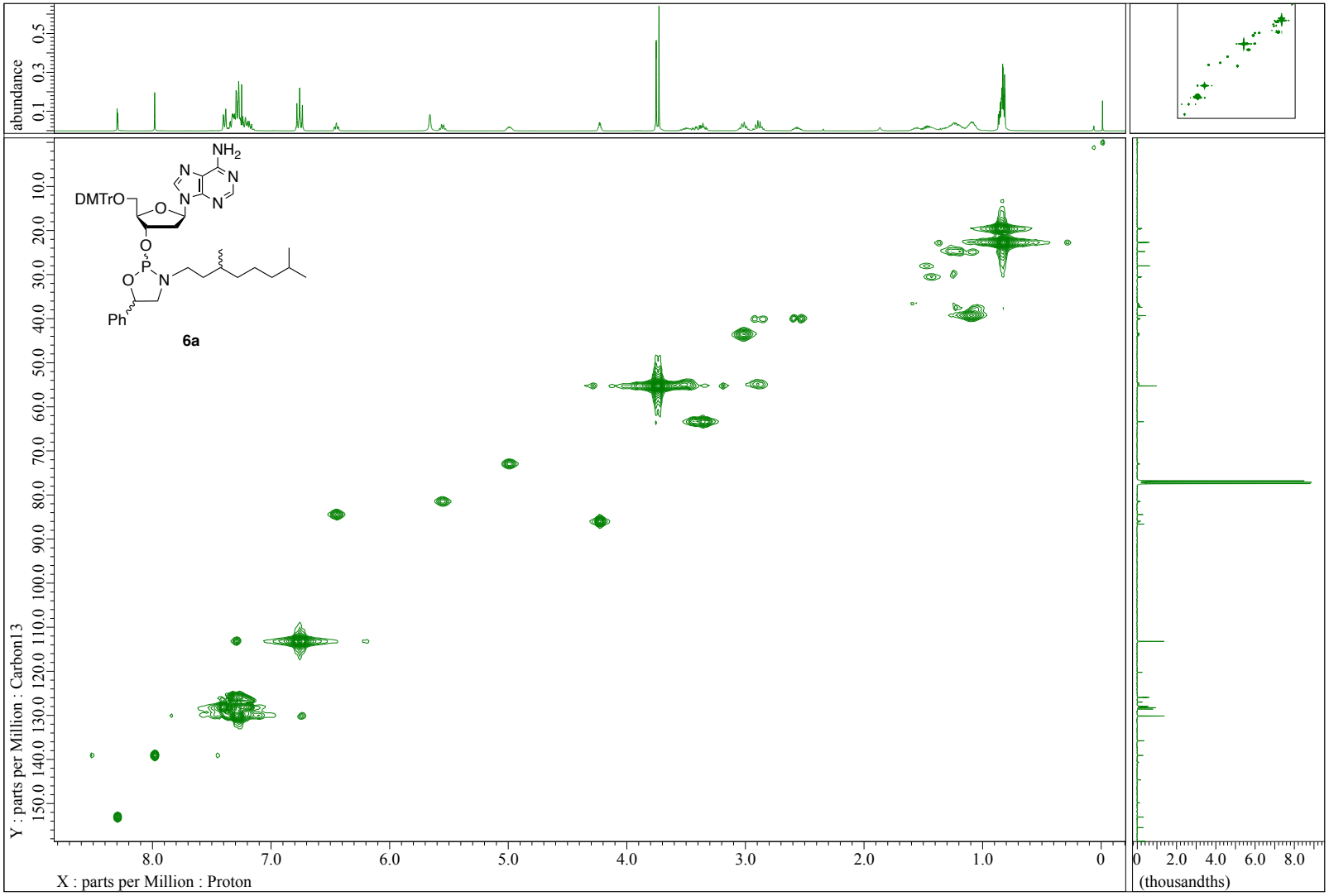
^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$)



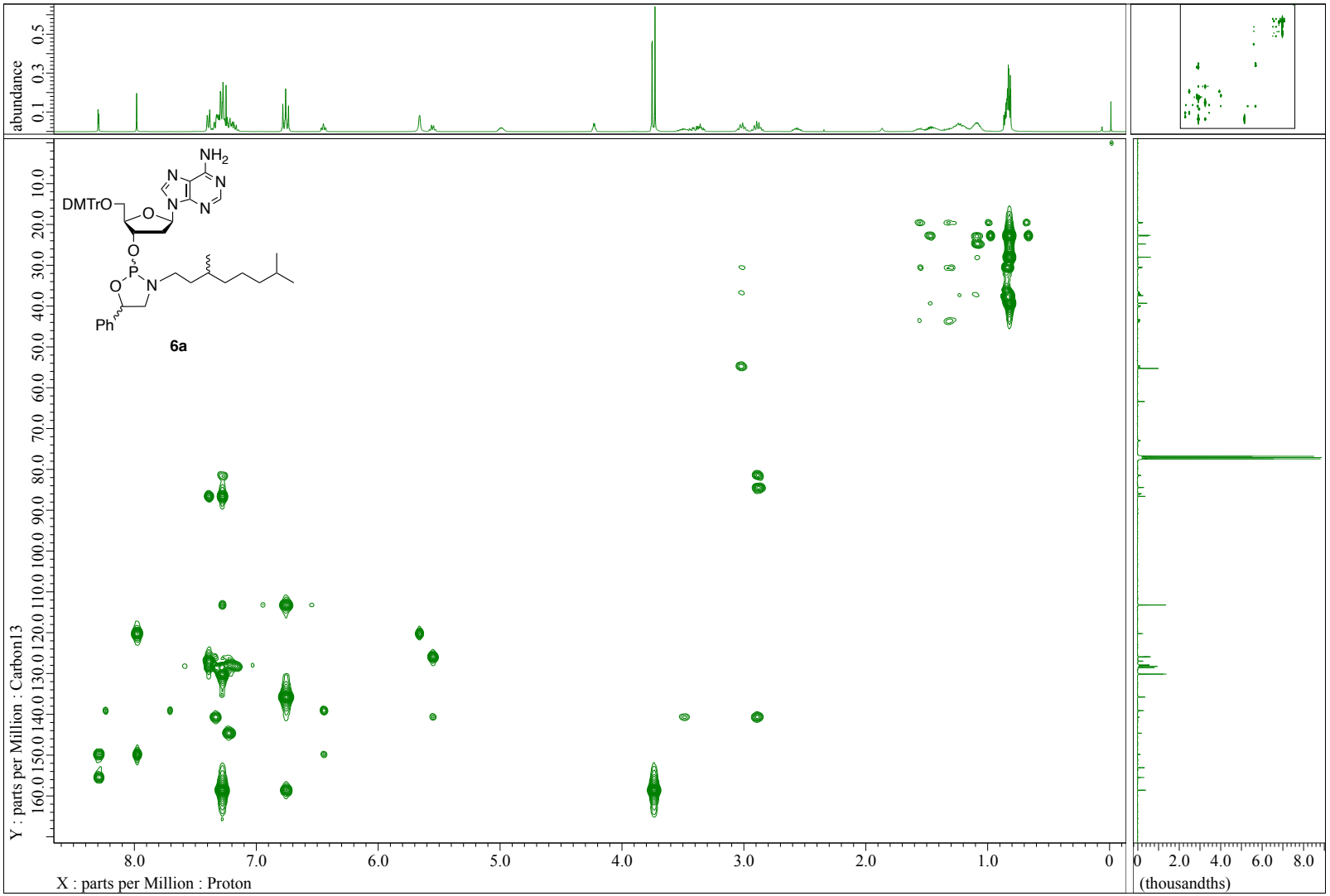
COSY ($CDCl_3$)


abundance
0.1
0.3
0.5
NH2
N
N
N
N
DMTrO
O
O
O
P
N
Ph
6a
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
Y : parts per Million : Proton
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton
0.1 0.2 0.3 0.4 0.5 0.6
abundance

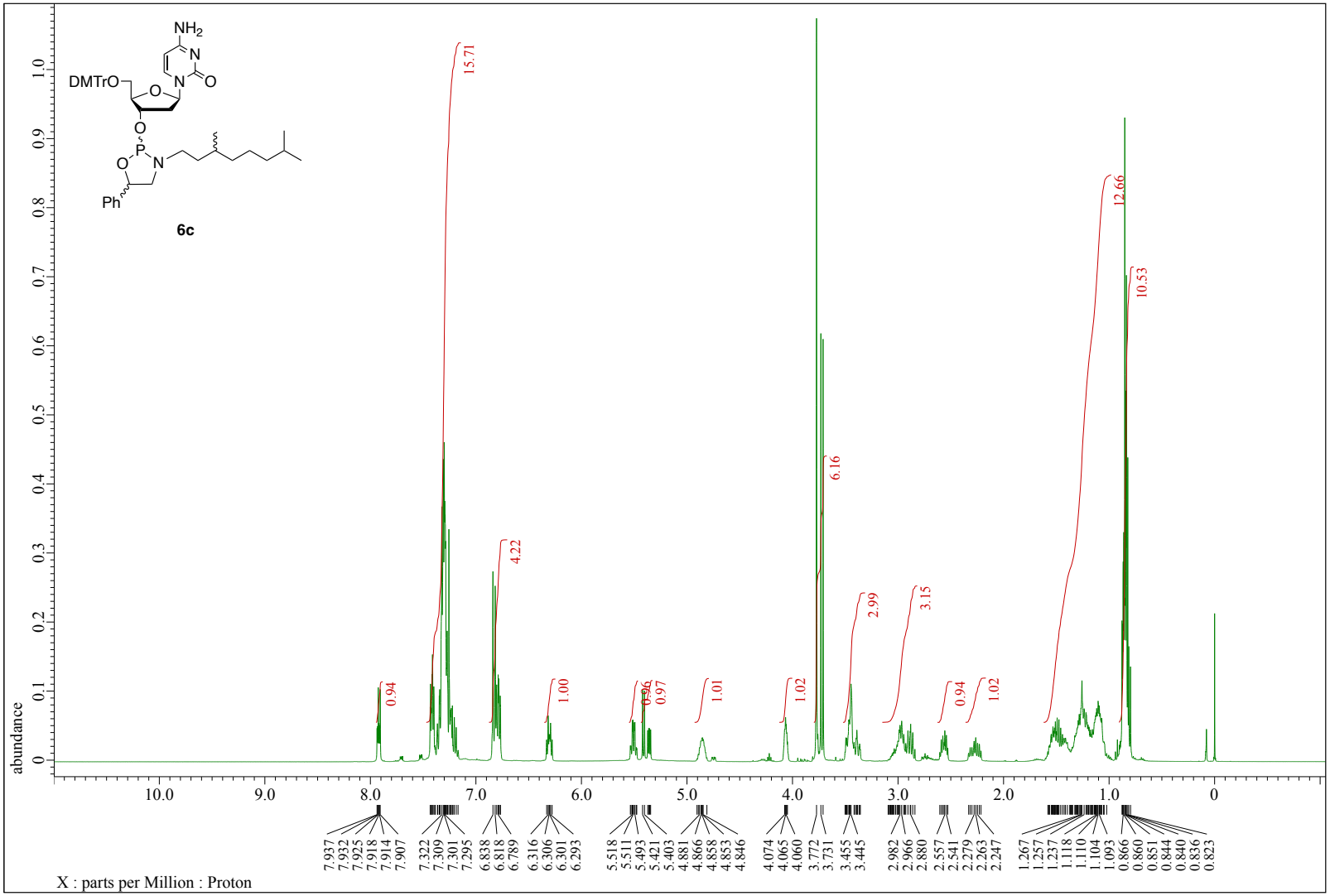
HMQC ($CDCl_3$)


abundance
0.1
0.3
0.5
NH2
N
N
N
N
DMTrO
O
O
P
O
N
Ph
6a
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
Y : parts per Million : Carbon13
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton
0
2.0
4.0
6.0
8.0
(thousandths)

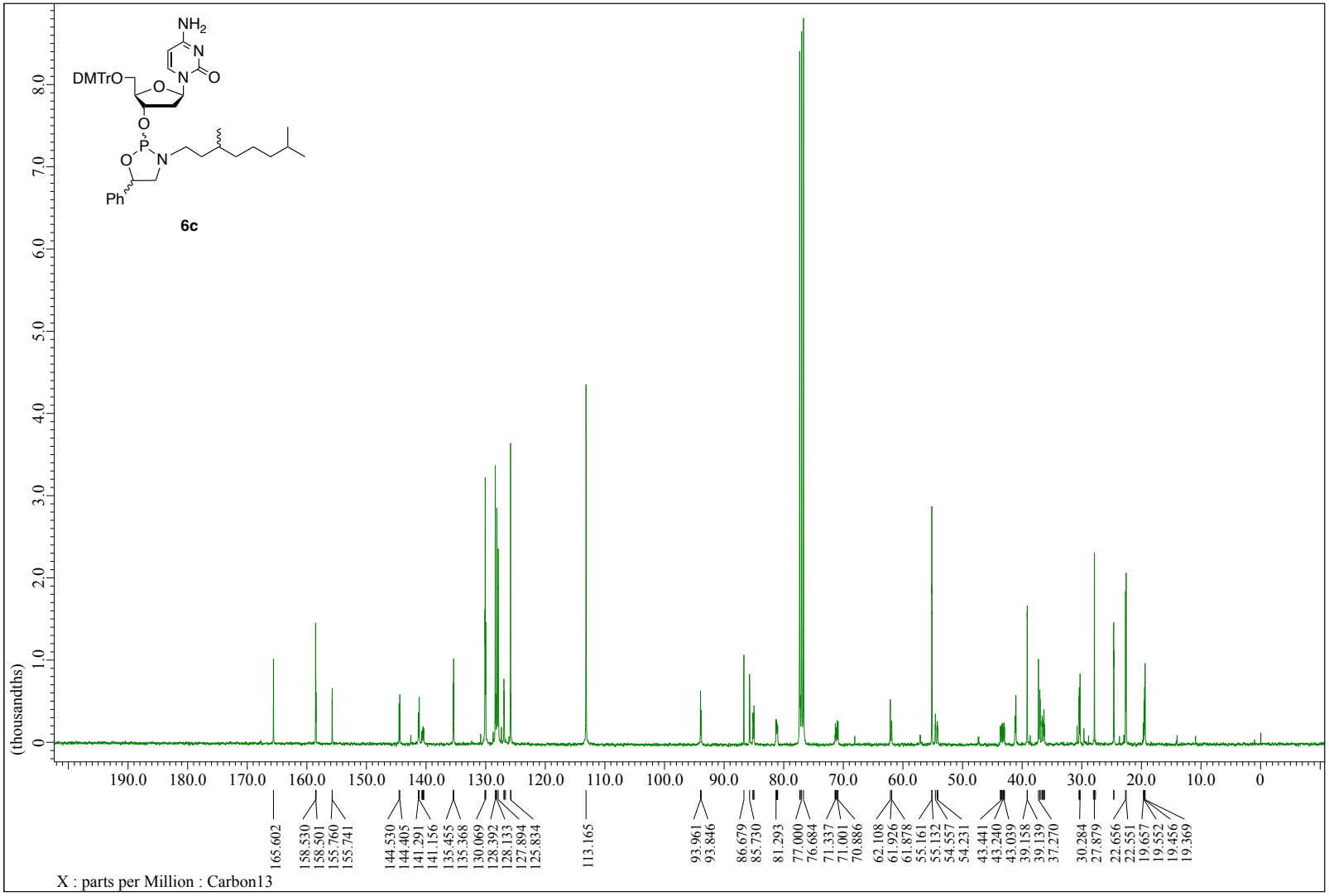
HMBC ($CDCl_3$)


abundance
0.1
0.3
0.5
NH2
N
N
N
N
DMTrO
O
O
P
O
N
Ph
6a
Y : parts per Million : Carbon13
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton
0
2.0
4.0
6.0
8.0
(thousandths)

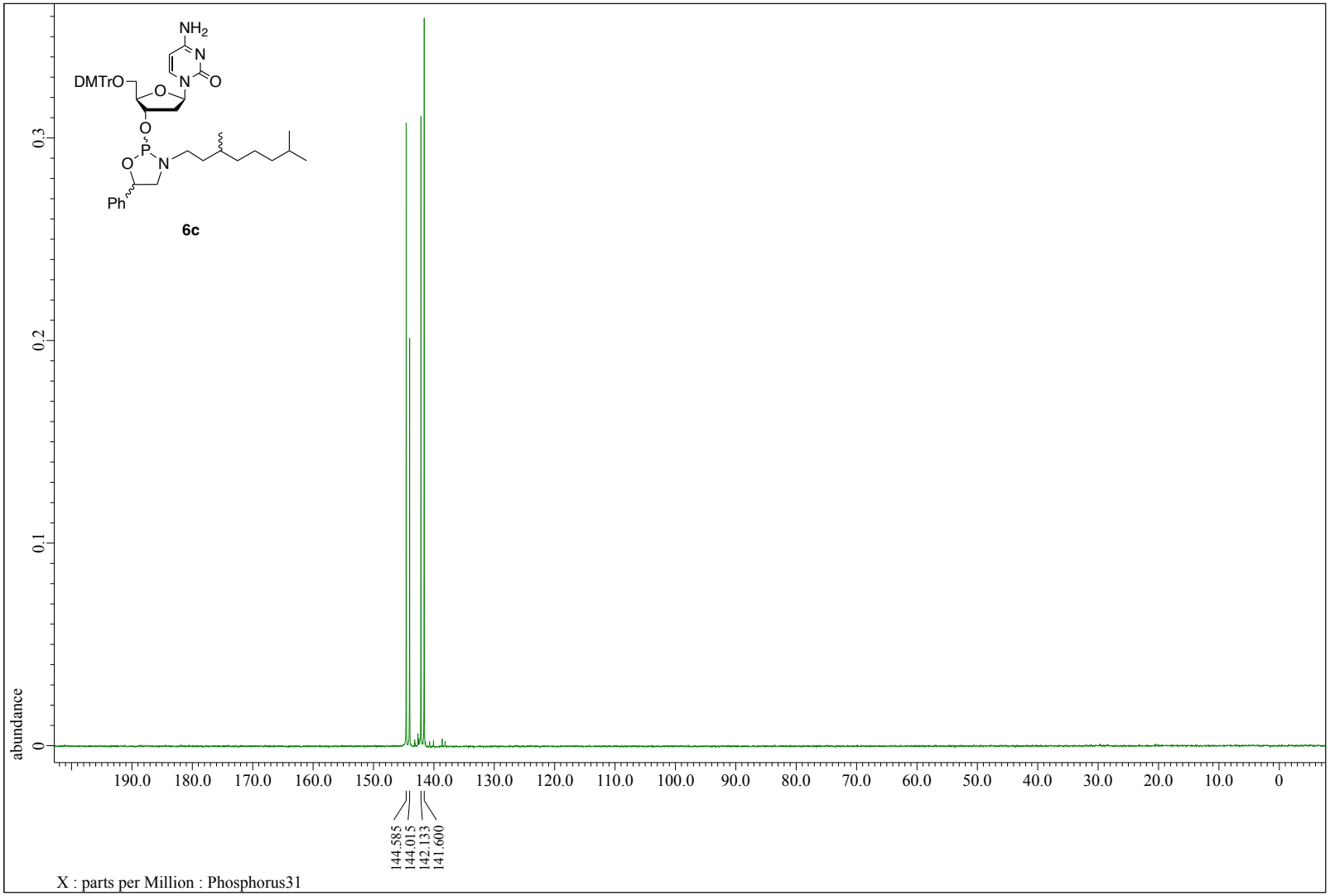
dCy oxazaphospholidine *N*-Thg monomer (6c)
^{1}H NMR (400 MHz, $CDCl_3$)



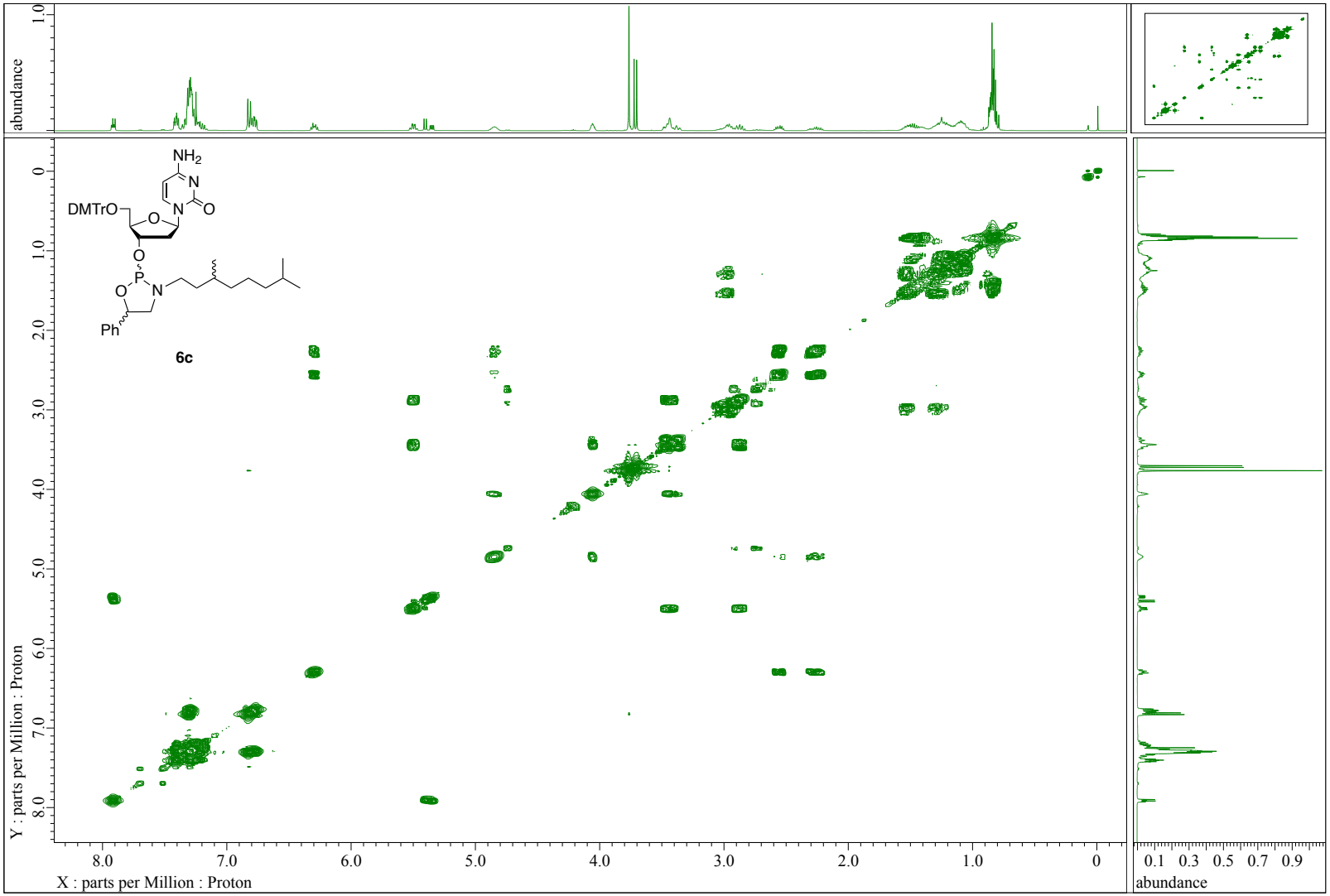
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)



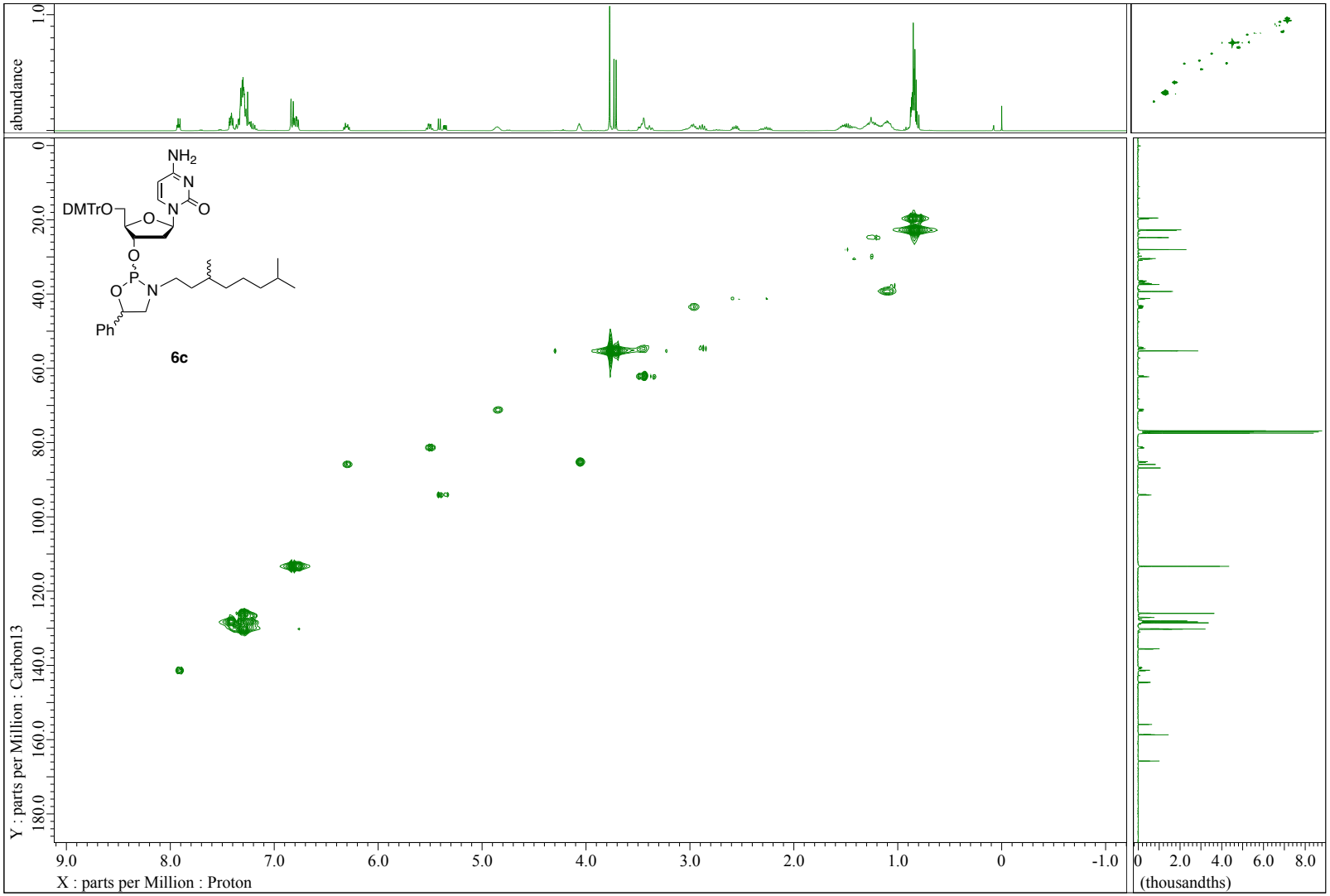
^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$)



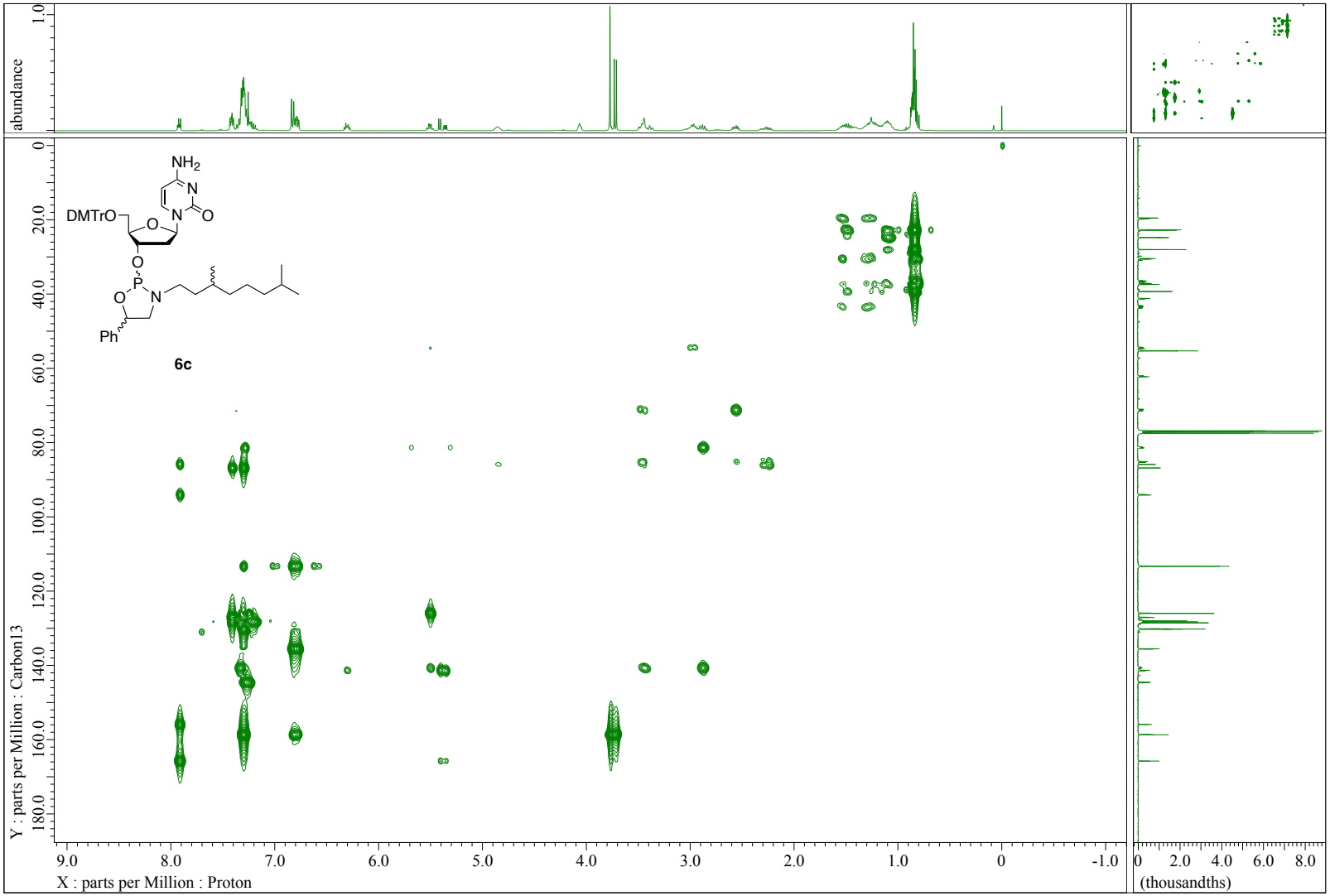
COSY ($CDCl_3$)


abundance
1.0
NH2
N
DMTrO
O
N
O
O
O
P
O
N
Ph
6c
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
Y : parts per Million : Proton
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton
0.1 0.3 0.5 0.7 0.9
abundance

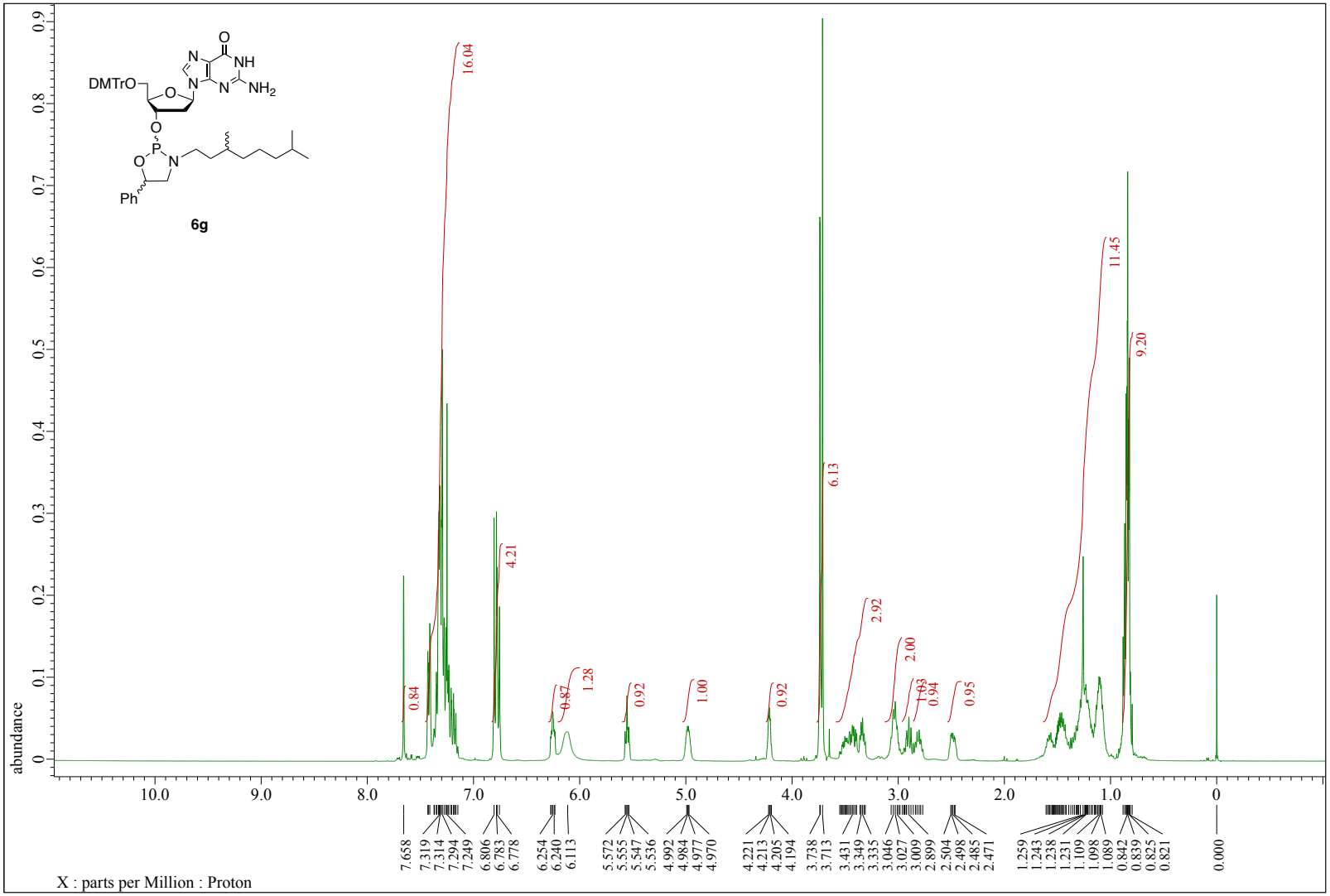
HMQC ($CDCl_3$)


abundance
1.0
NH2
N
N
O
DMTrO
O
O
P
N
Ph
6c
0
20.0
40.0
60.0
80.0
100.0
120.0
140.0
160.0
180.0
Y : parts per Million : Carbon13
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
X : parts per Million : Proton
0
2.0
4.0
6.0
8.0
(thousandths)

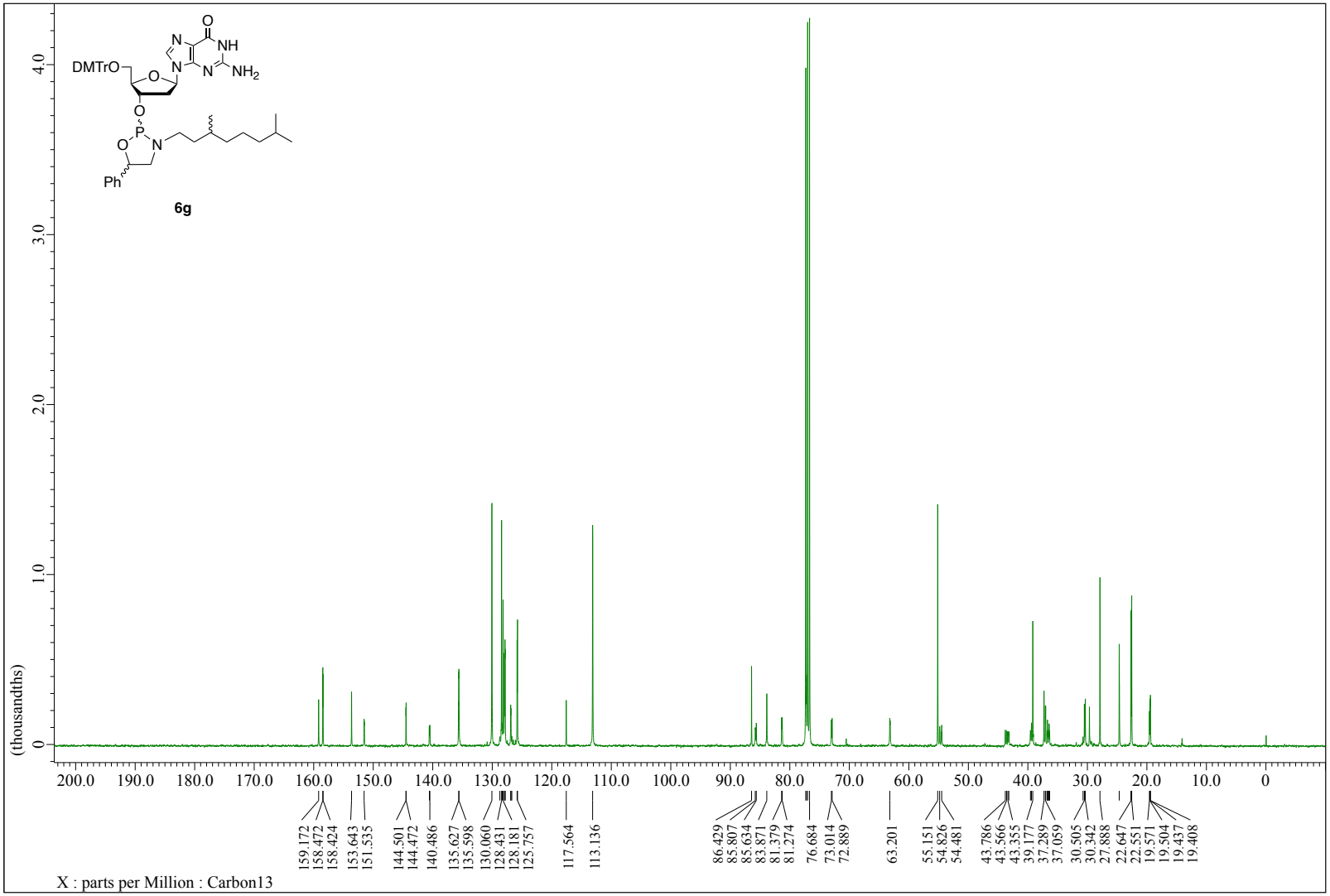
HMBC ($CDCl_3$)


abundance
1.0
NH2
N
N
O
DMTrO
O
O
P
O
N
Ph
6c
0
20.0
40.0
60.0
80.0
100.0
120.0
140.0
160.0
180.0
Y : parts per Million : Carbon13
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
X : parts per Million : Proton
0
2.0
4.0
6.0
8.0
(thousandths)

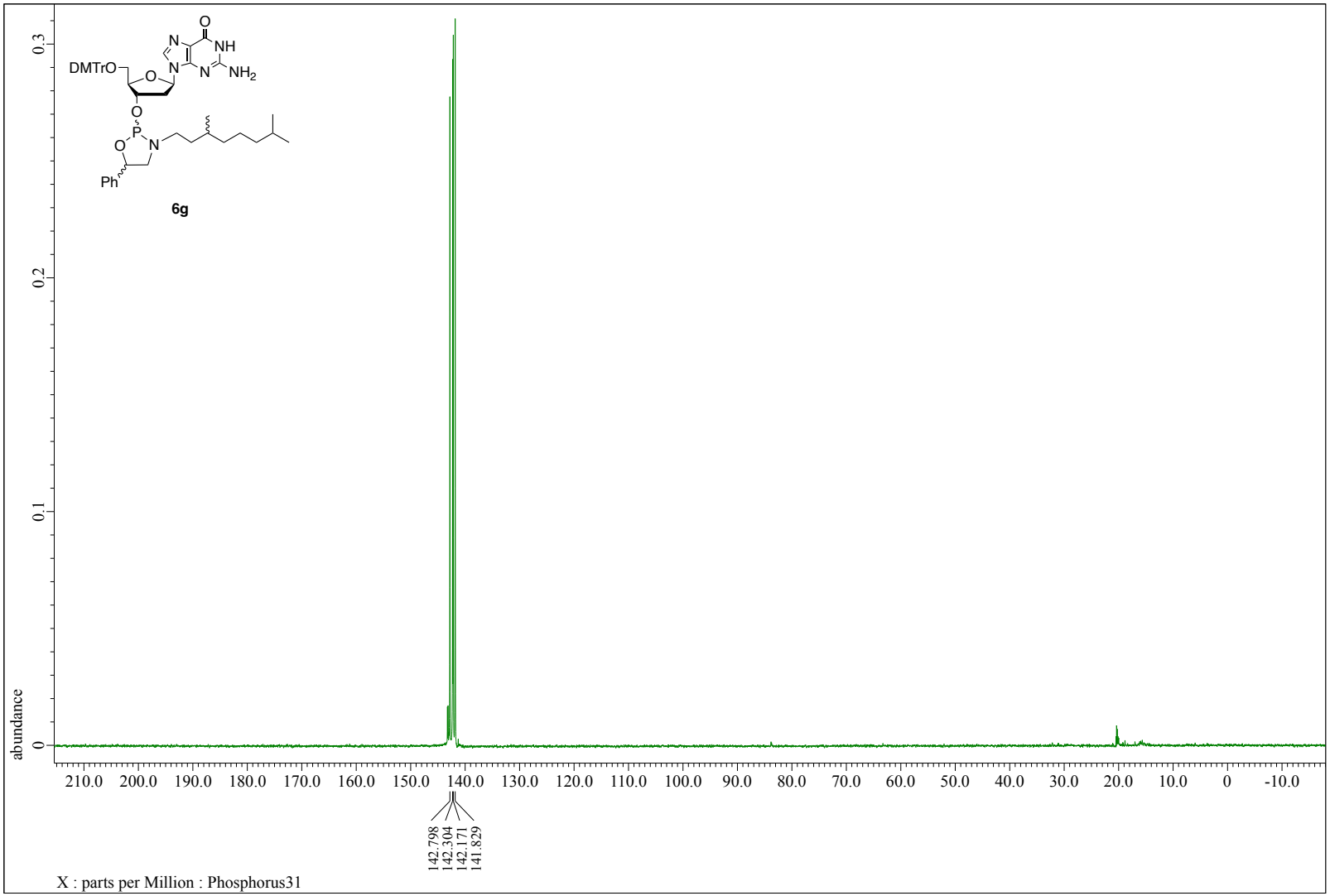
dGu oxazaphospholidine *N*-Thg monomer (6g)
^{1}H NMR (400 MHz, $CDCl_3$)



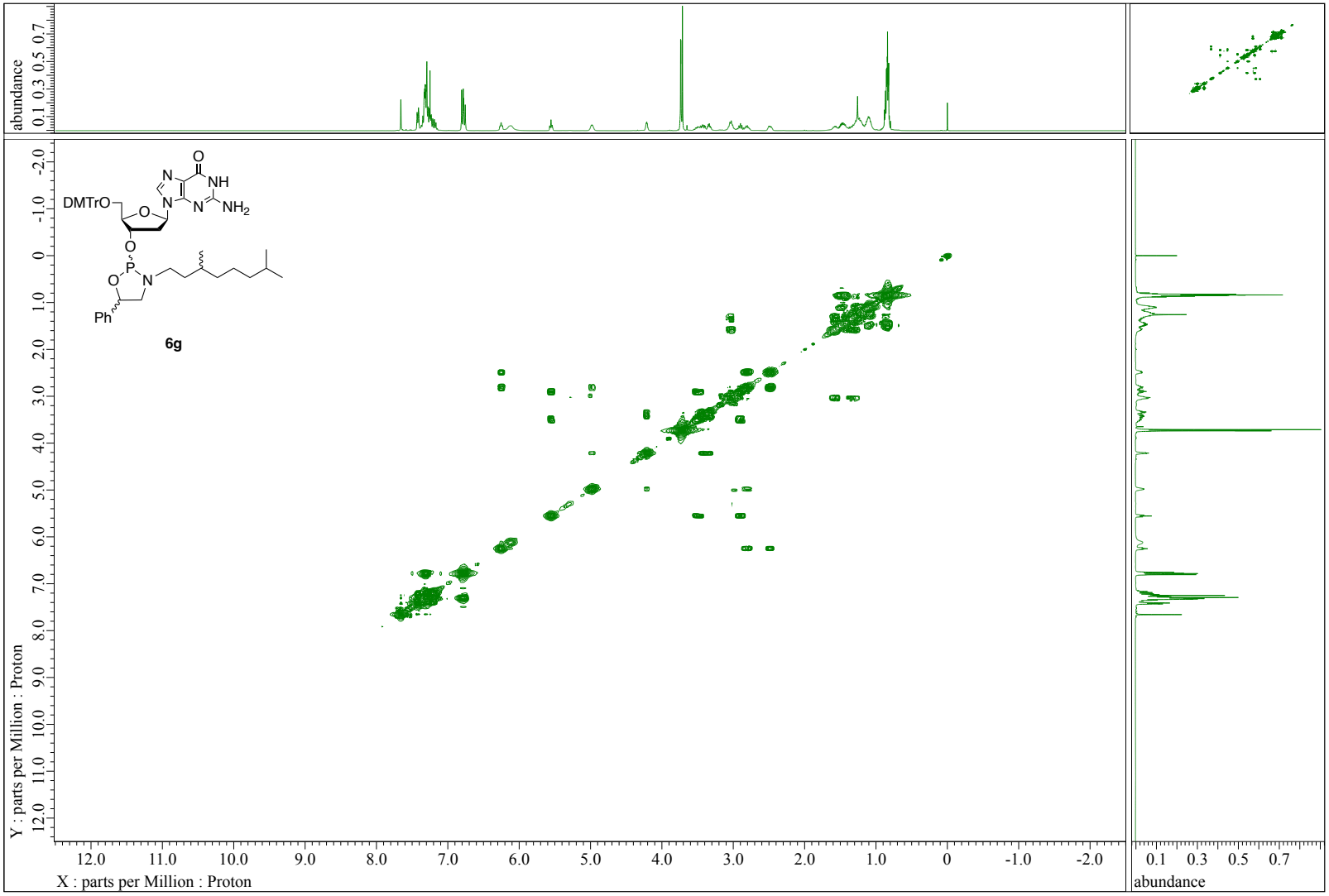
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)



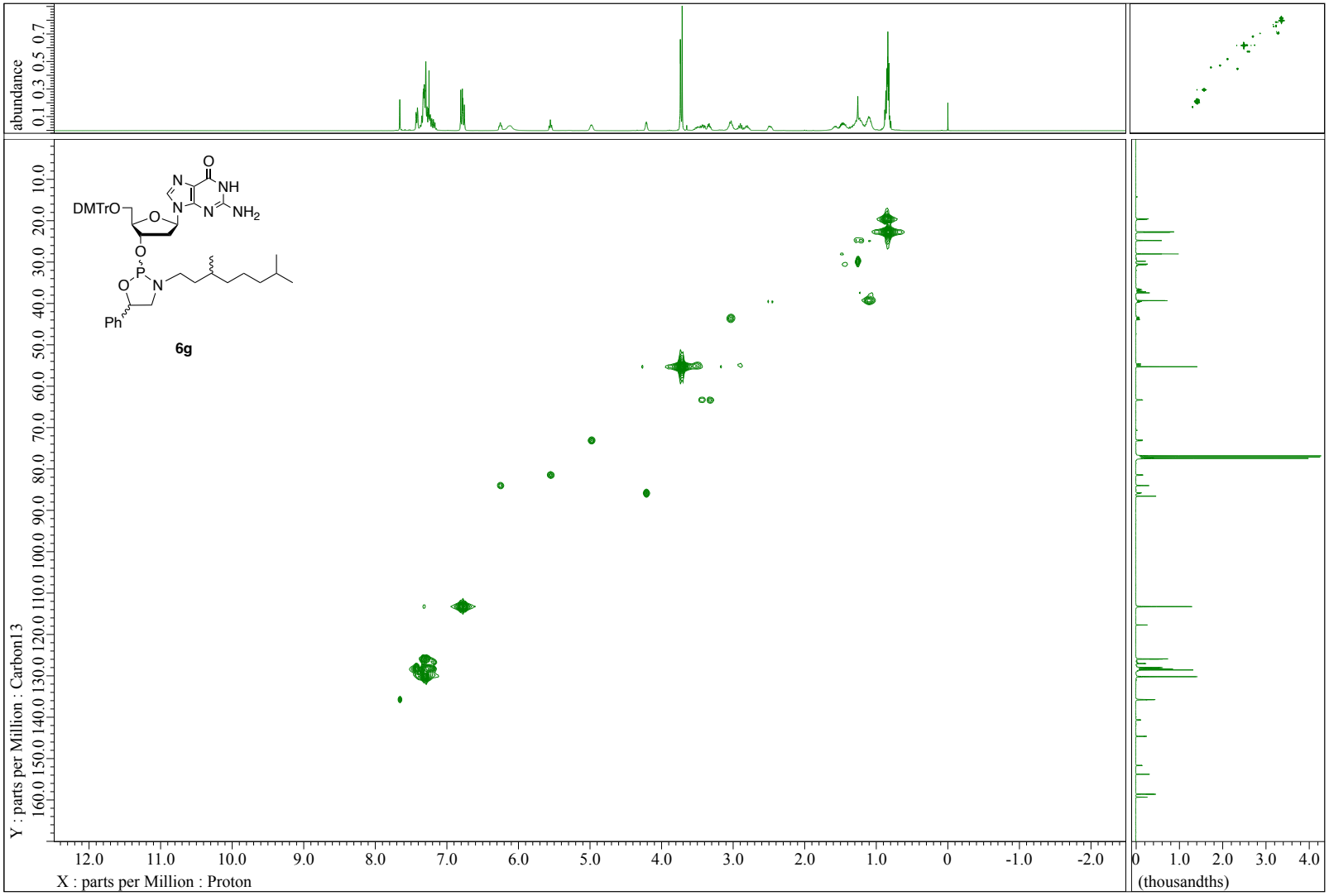
^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$)



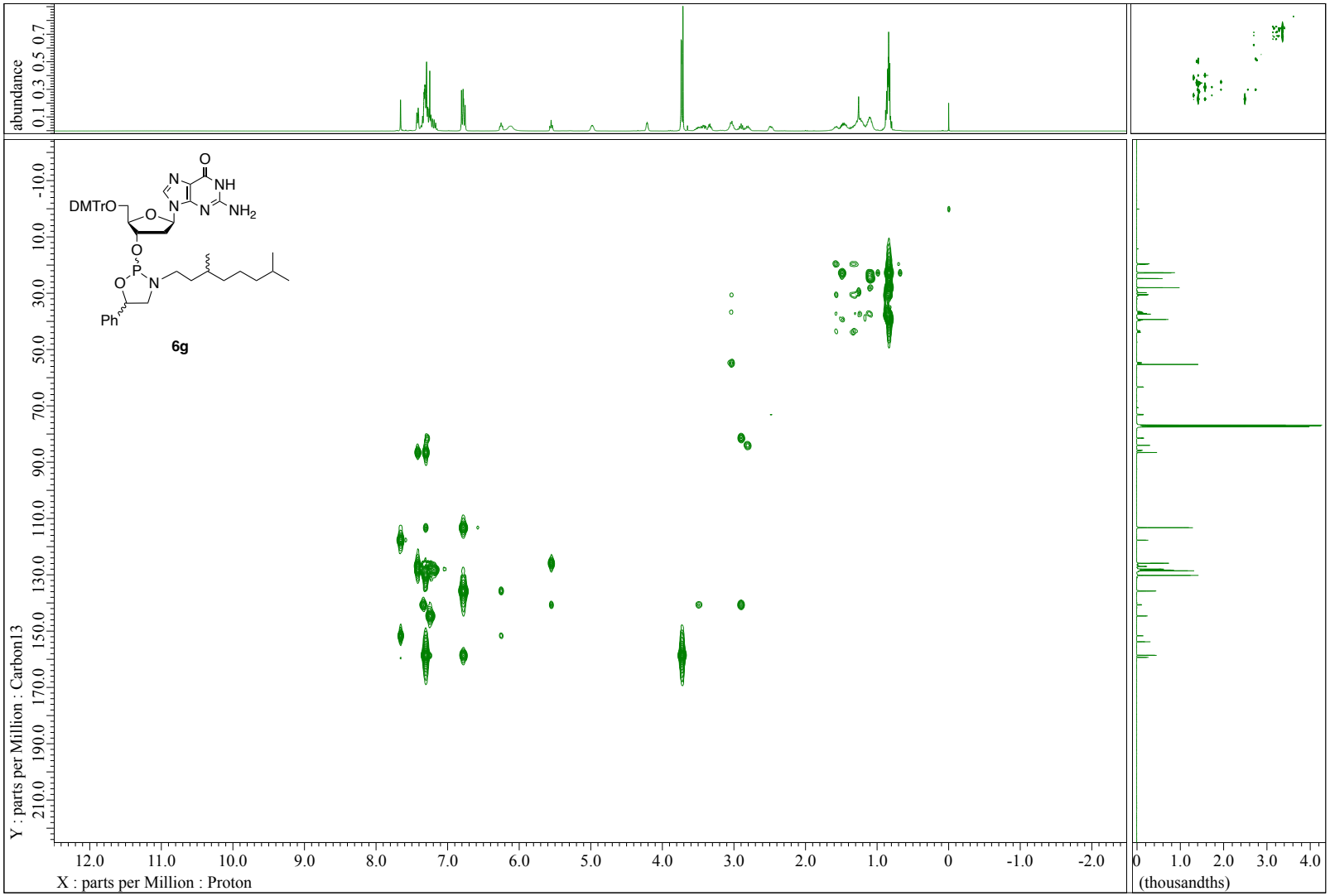
COSY ($CDCl_3$)


abundance
0.1 0.3 0.5 0.7
DMTrO
O
NH
N
NH2
O
P
O
N
Ph
6g
Y : parts per Million : Proton
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
X : parts per Million : Proton
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
0.1 0.3 0.5 0.7
abundance

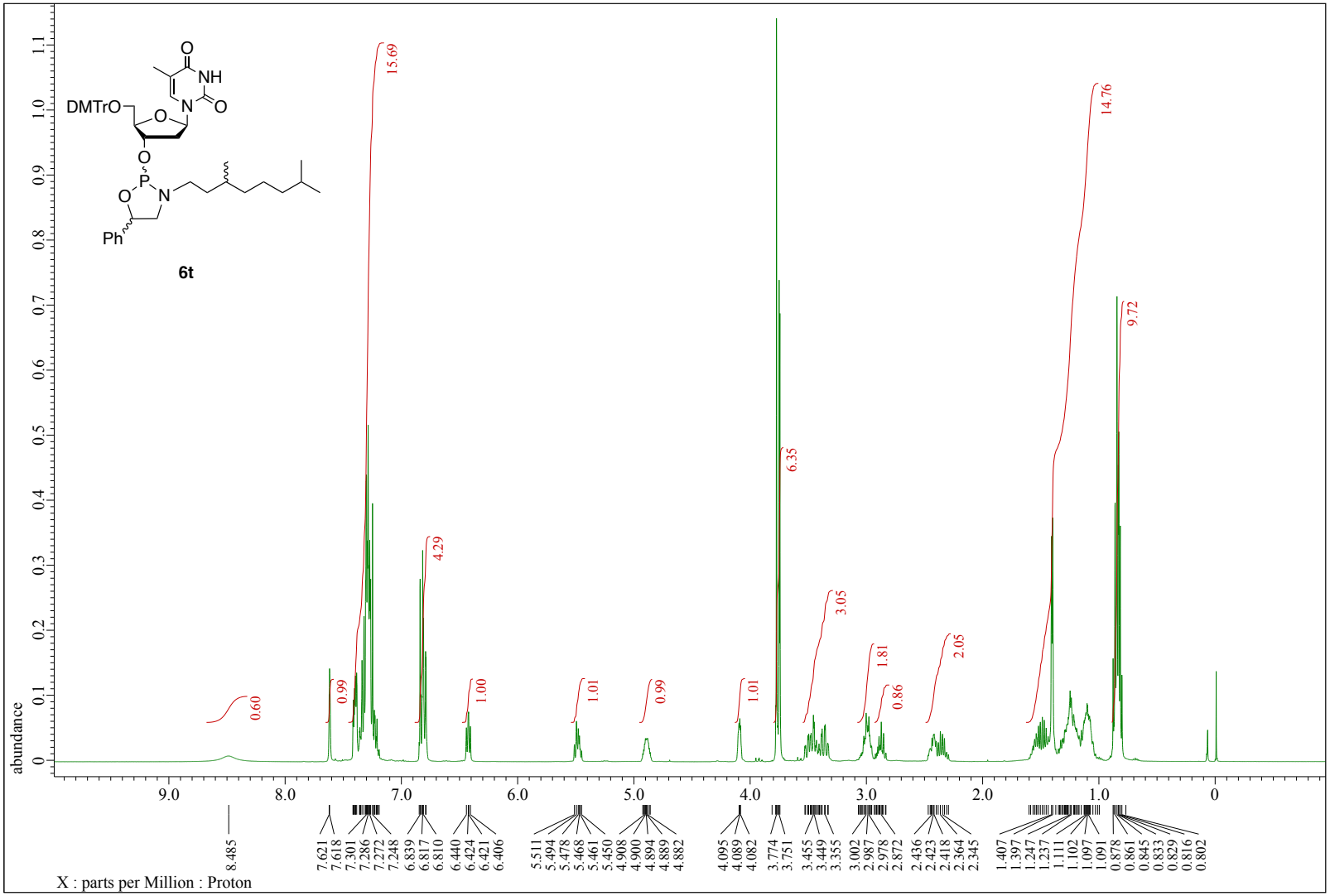
HMQC ($CDCl_3$)


abundance
0.1 0.3 0.5 0.7
DMTrO
O
NH
N
NH2
Ph
6g
Y : parts per Million : Carbon13
10.0 20.0 30.0 40.0 50.0 60.0 70.0 80.0 90.0 100.0 110.0 120.0 130.0 140.0 150.0 160.0
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
X : parts per Million : Proton
0 1.0 2.0 3.0 4.0
(thousandths)

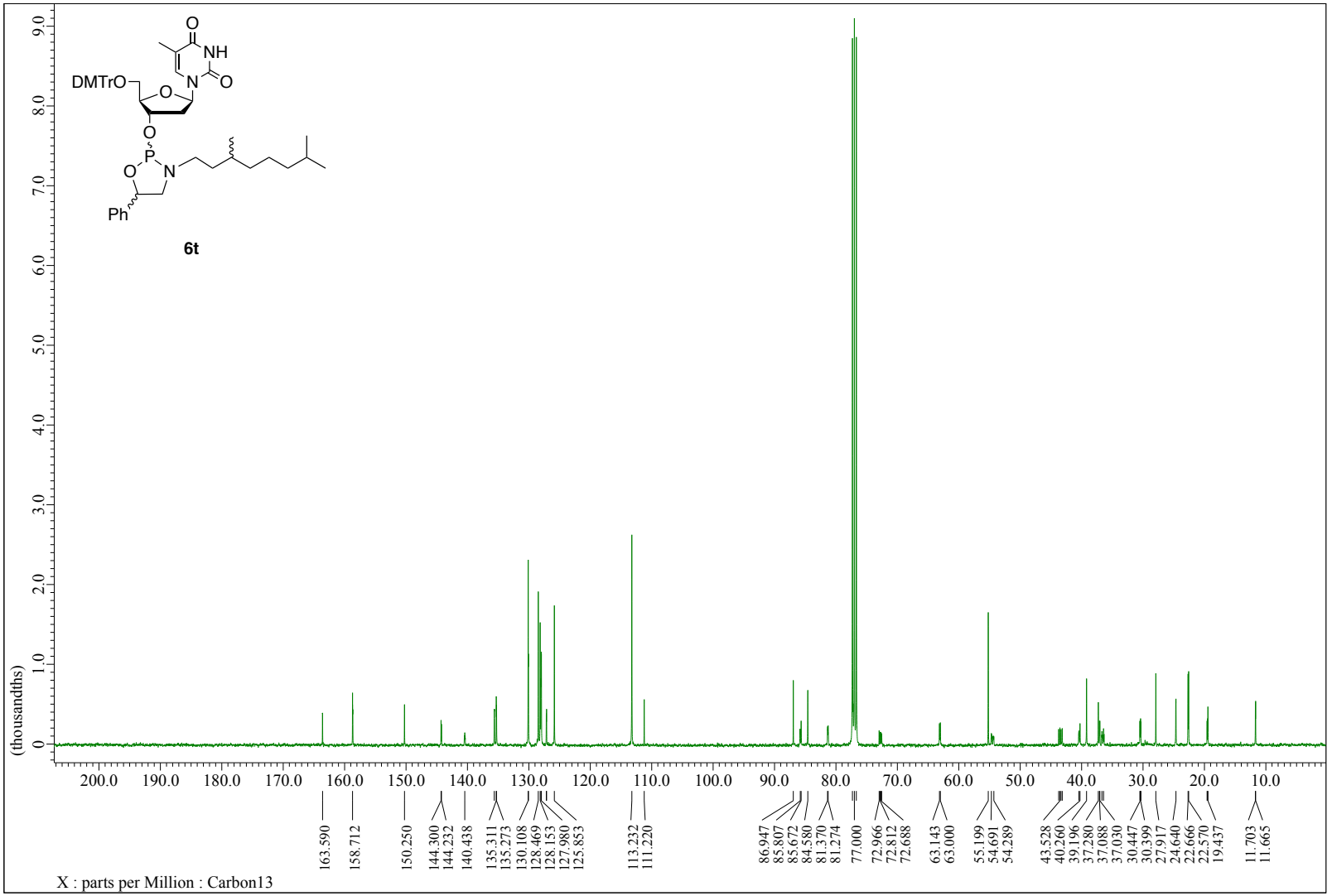
HMBC ($CDCl_3$)


abundance
0.1 0.3 0.5 0.7
DMTrO
O
N
NH
NH2
P
Ph
6g
-10.0 10.0 30.0 50.0 70.0 90.0 110.0 130.0 150.0 170.0 190.0 210.0
Y : parts per Million : Carbon13
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
X : parts per Million : Proton
0 1.0 2.0 3.0 4.0
(thousandths)

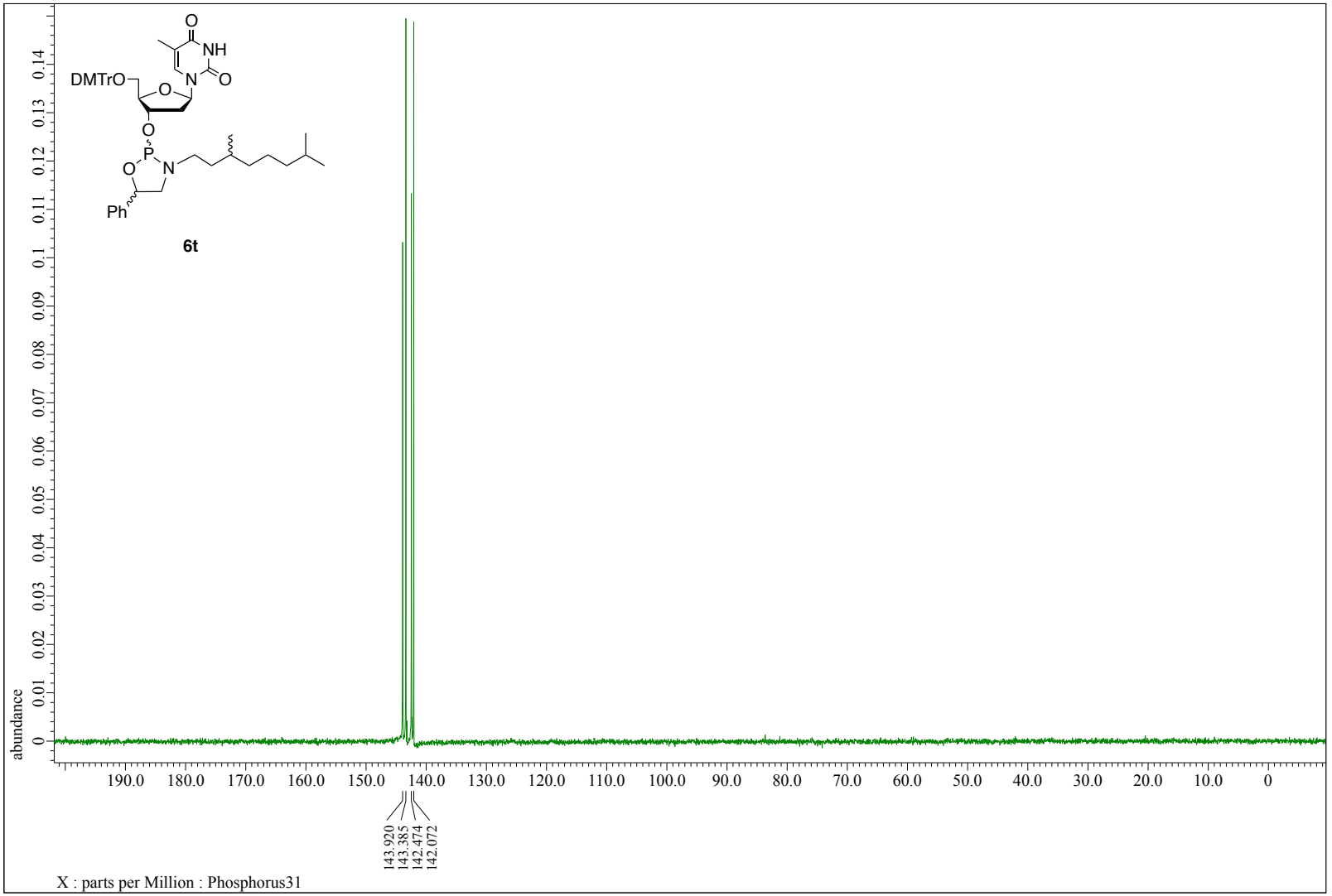
Th oxazaphospholidine *N*-Thg monomer (6t)
^{1}H NMR (400 MHz, $CDCl_3$)



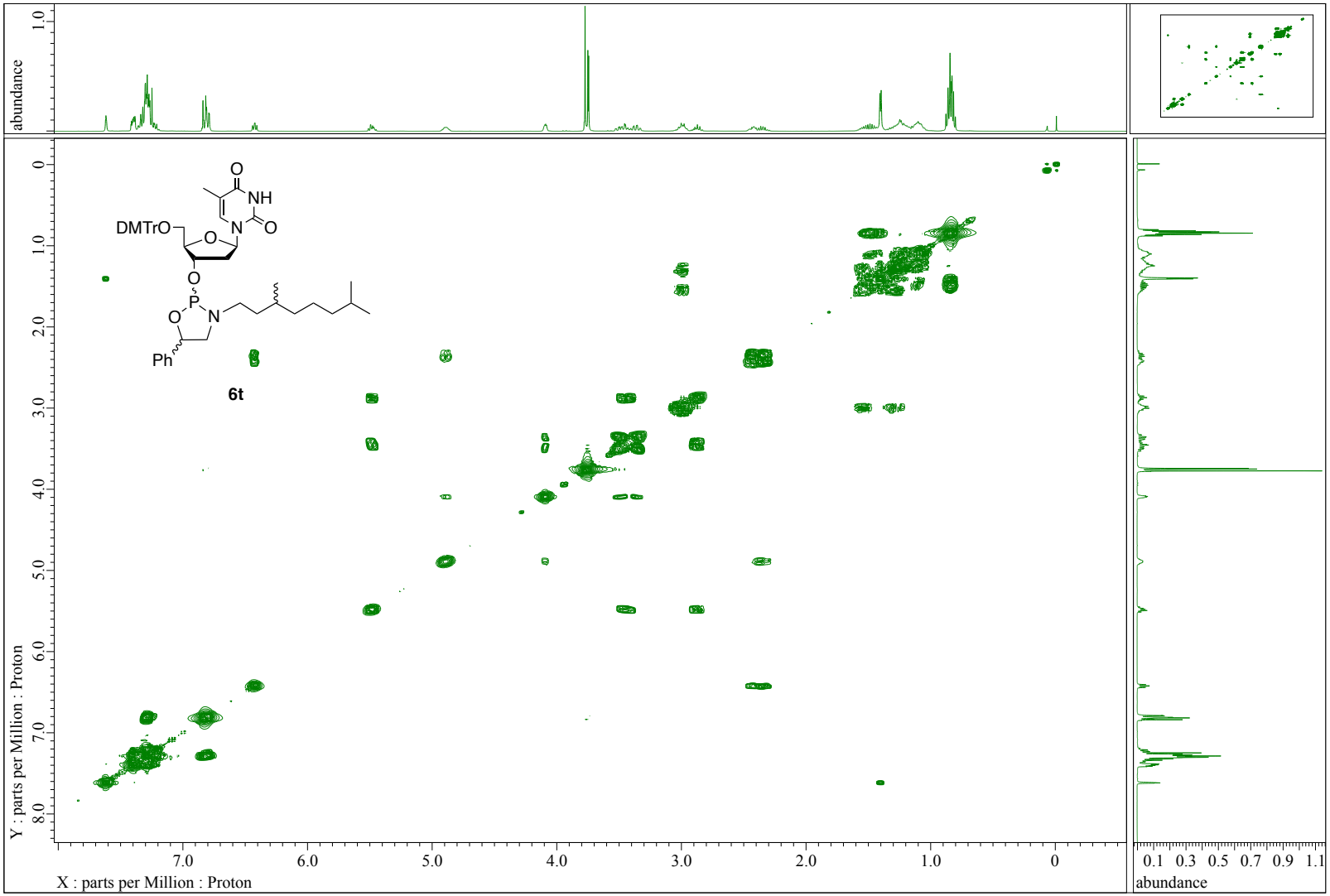
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)



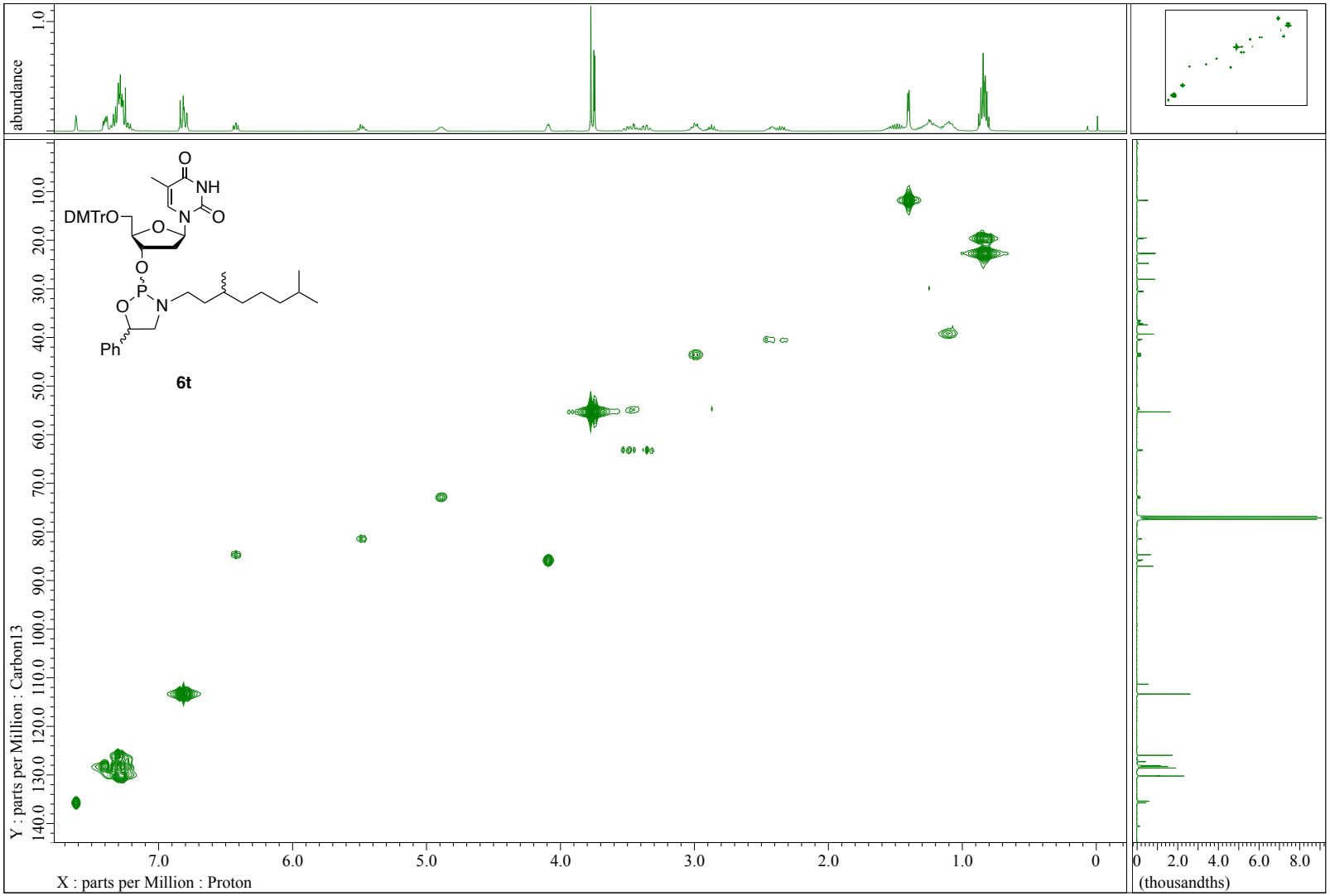
^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$)



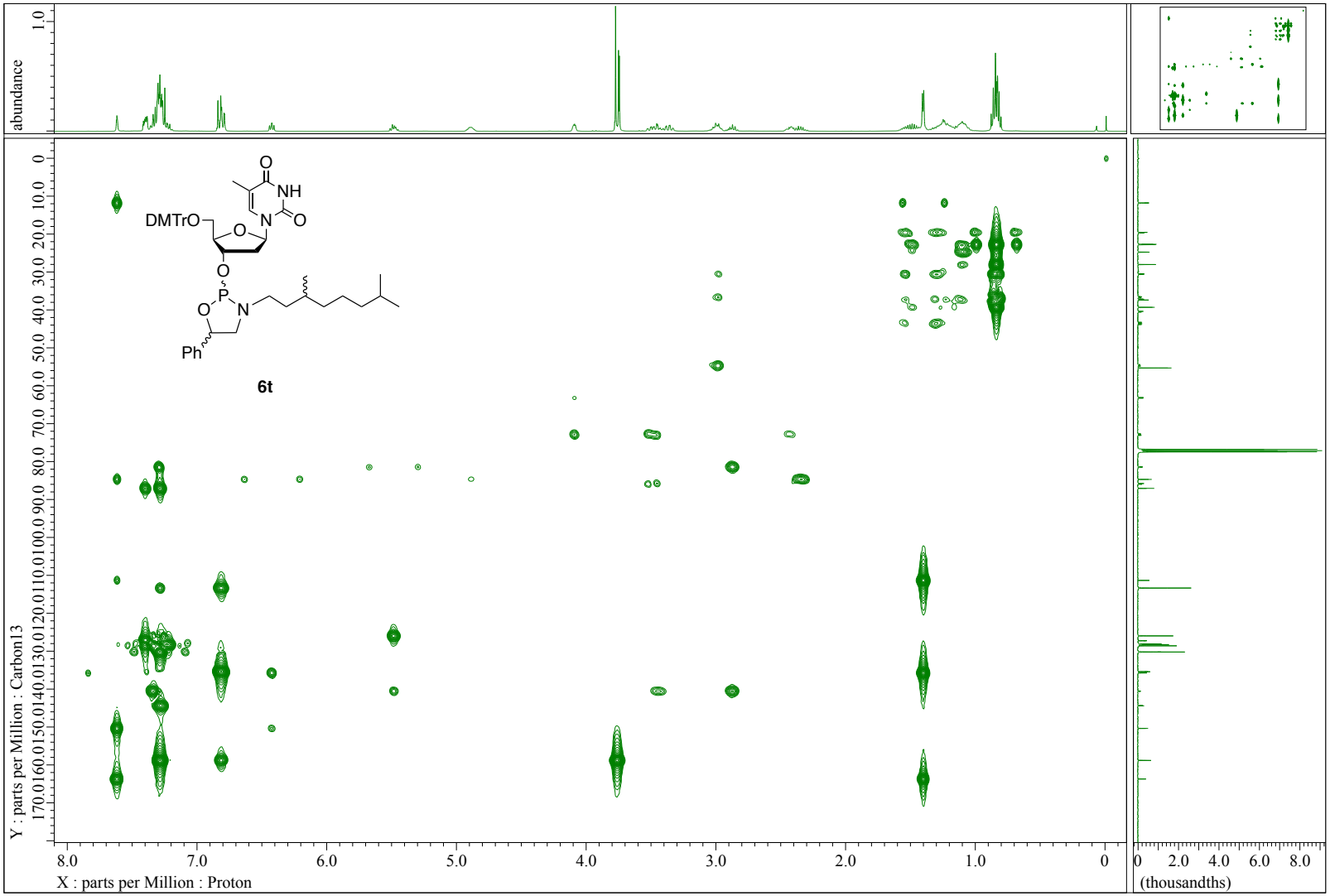
COSY ($CDCl_3$)


abundance
1.0
DMTrO
O
NH
N
O
O
O
P
N
O
Ph
6t
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
Y : parts per Million : Proton
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton
0.1 0.3 0.5 0.7 0.9 1.1
abundance

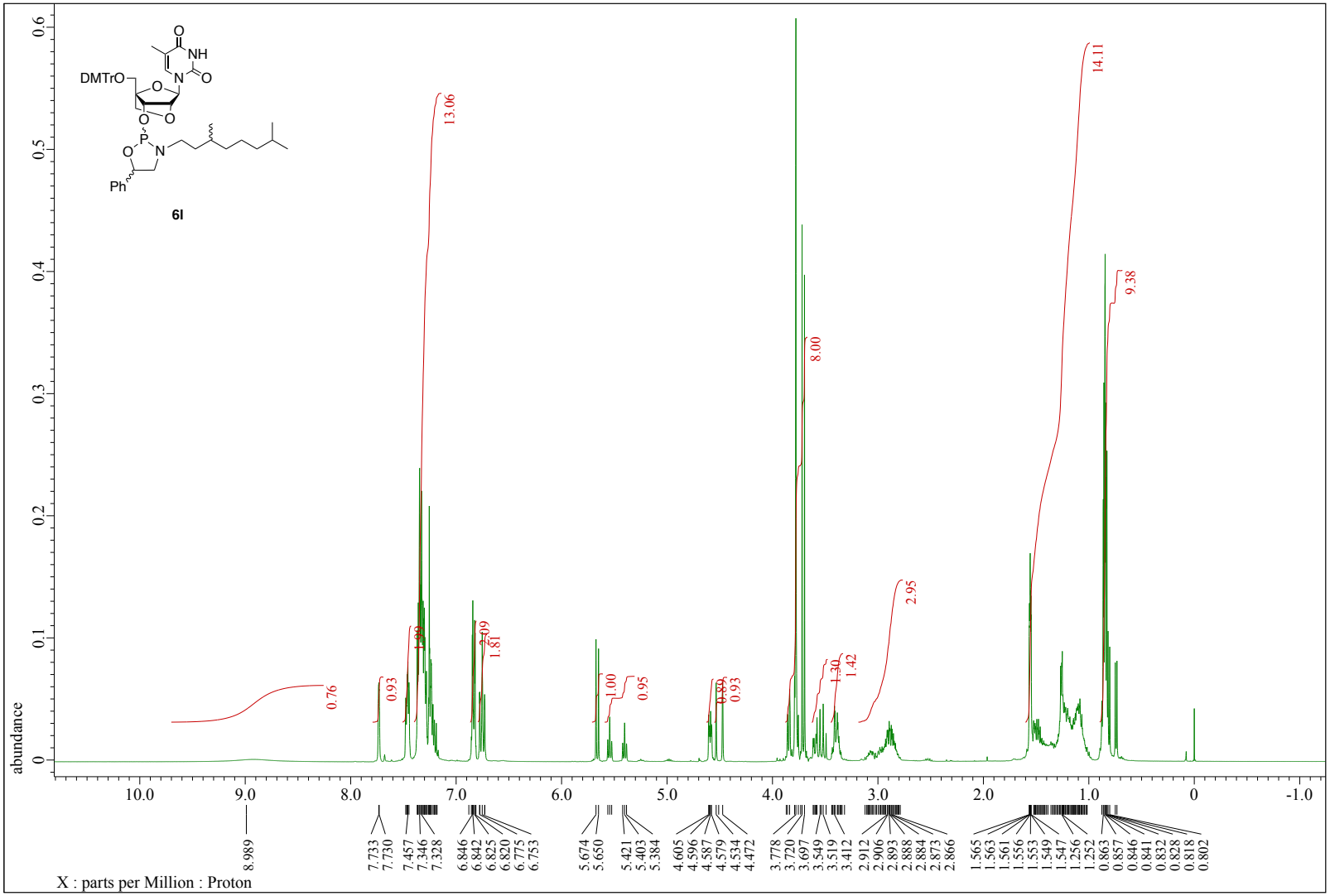
HMQC ($CDCl_3$)


abundance
1.0
DMTrO
O
NH
N
O
O
O
P
O
N
Ph
6t
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
Y : parts per Million : Carbon13
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton
0
2.0
4.0
6.0
8.0
(thousandths)

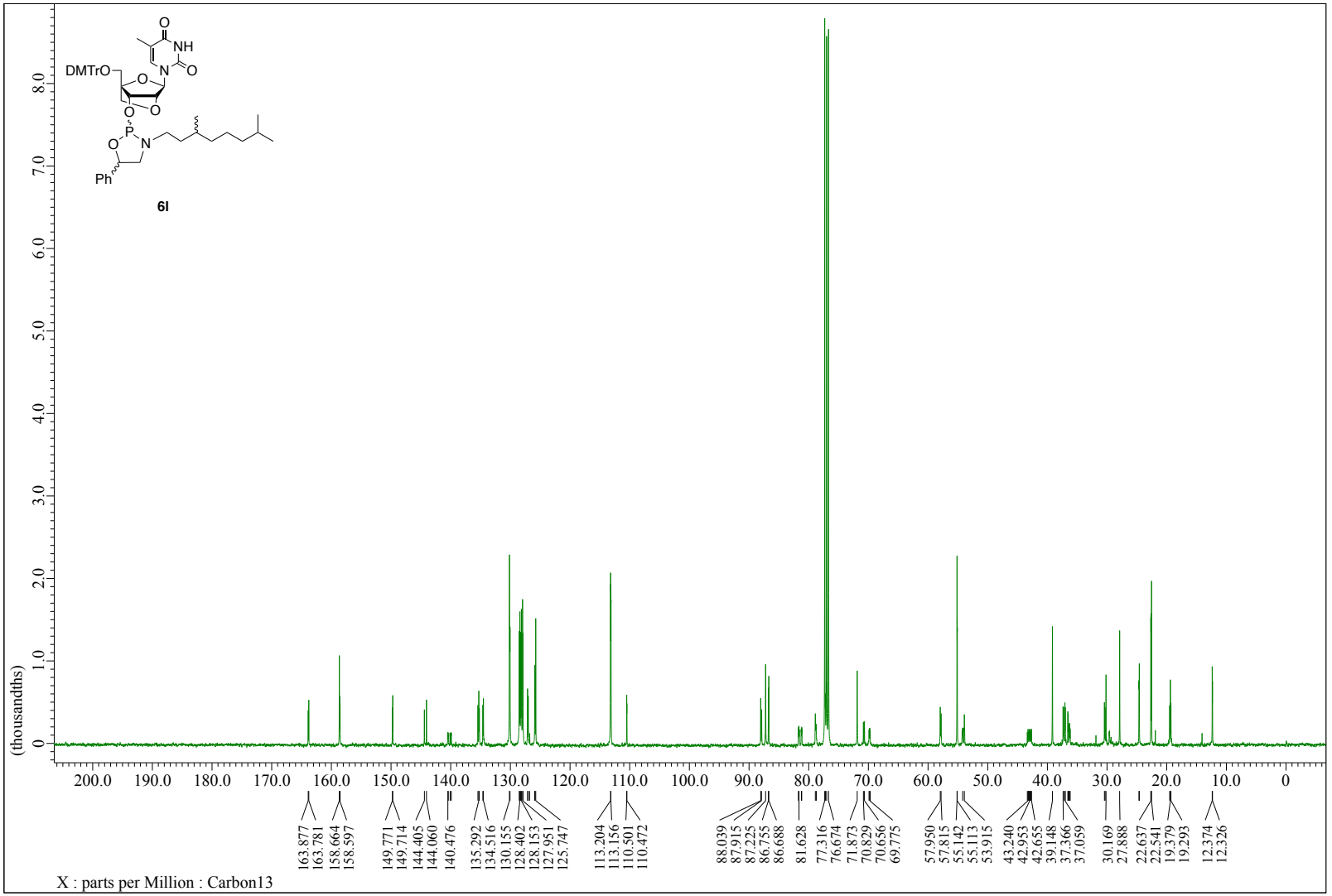
HMBC ($CDCl_3$)


abundance
1.0
DMTrO
O
NH
N
O
O
O
P
O
N
Ph
6t
Y : parts per Million : Carbon13
0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
170.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton
0
2.0
4.0
6.0
8.0
(thousandths)

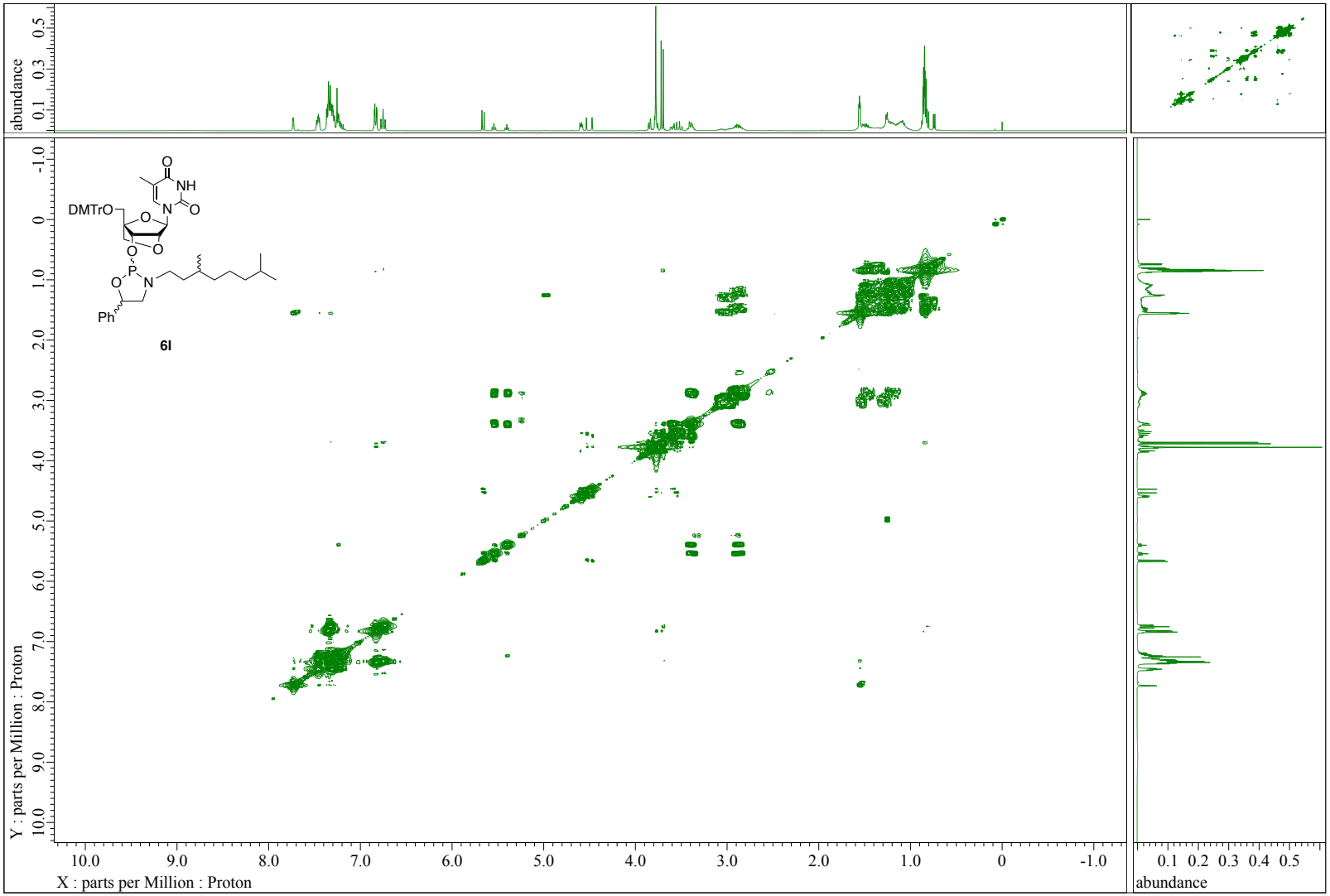
LNATh oxazaphospholidine *N*-Thg monomer (6l)
^{1}H NMR (400 MHz, $CDCl_3$)



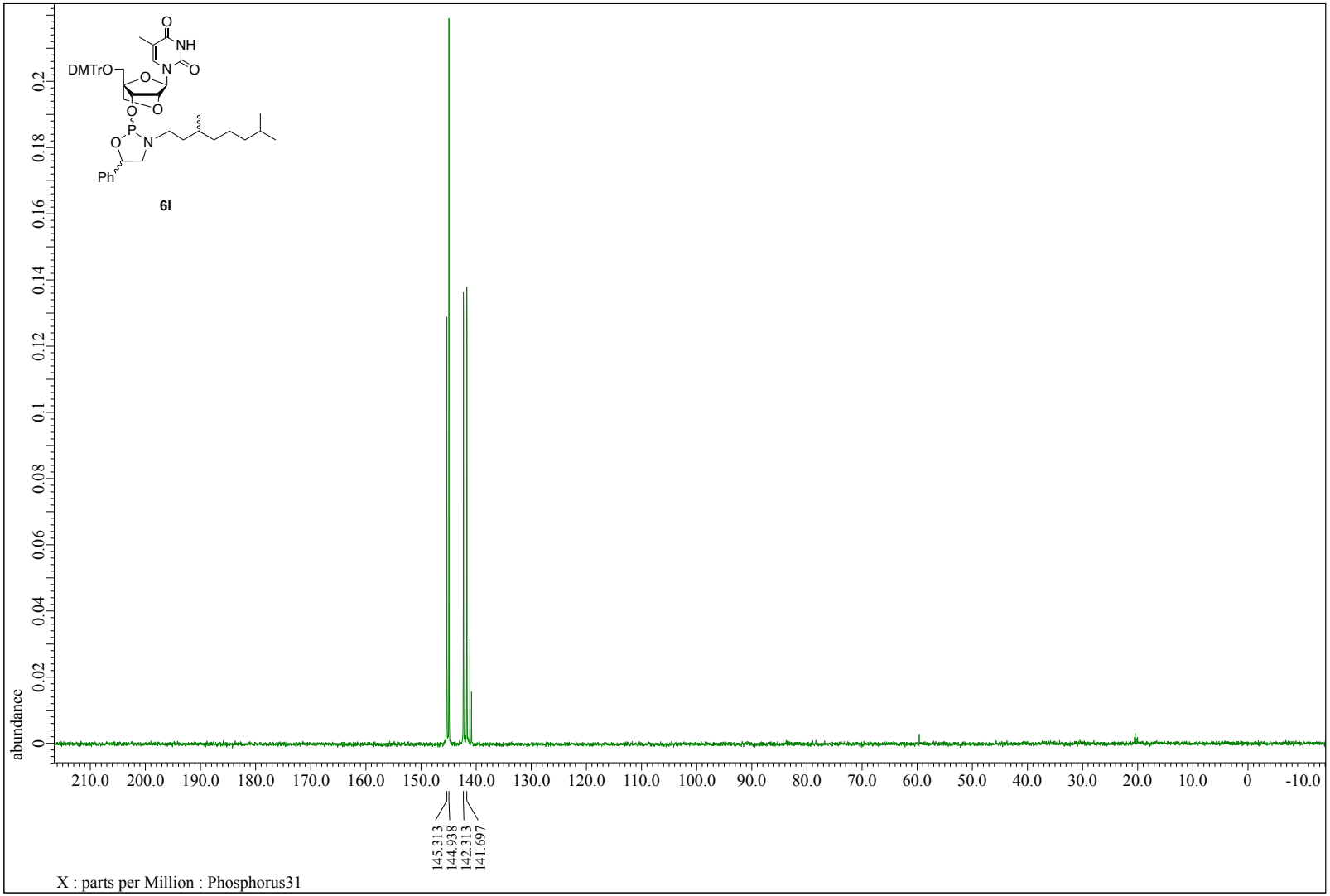
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)



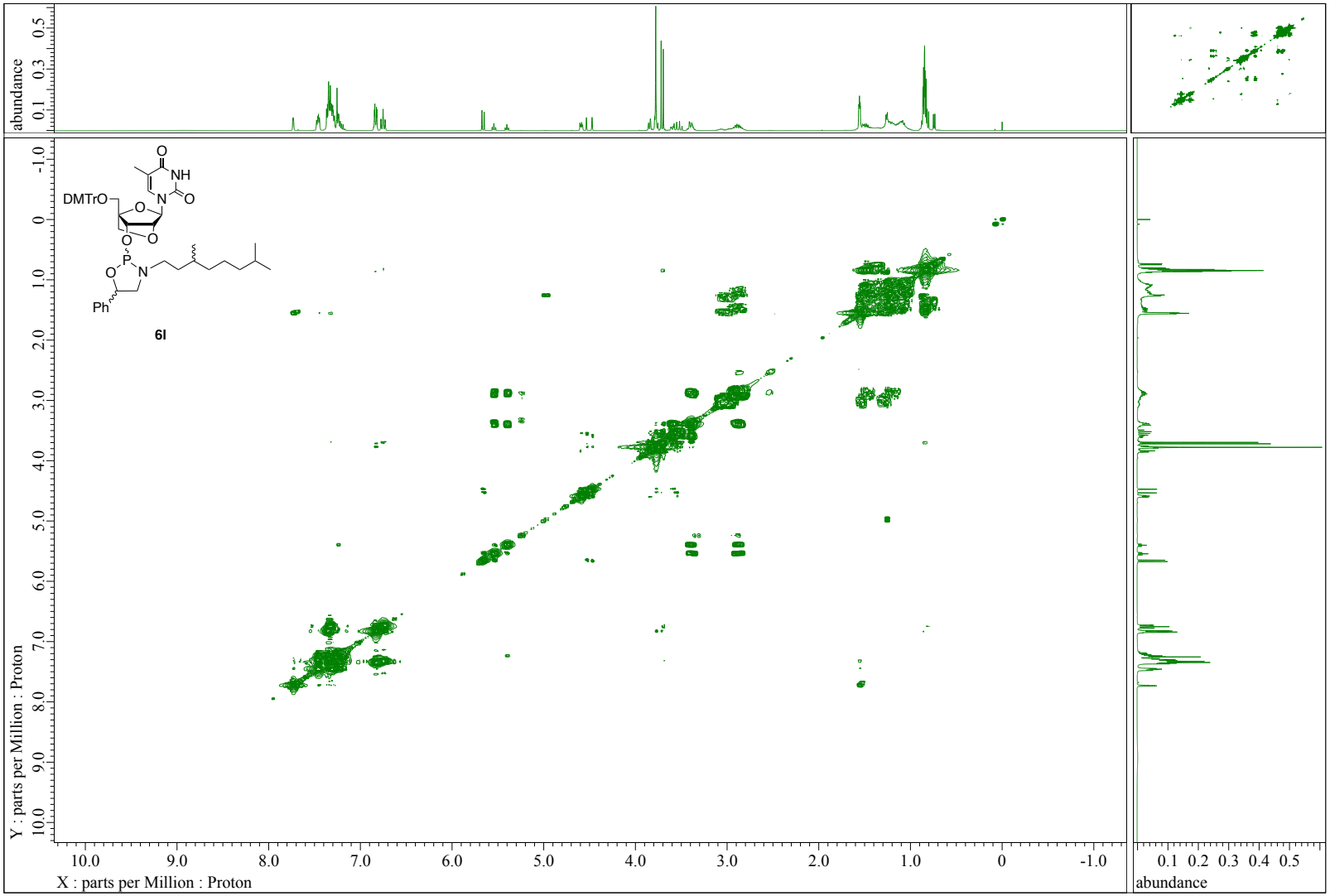
COSY ($CDCl_3$)


abundance
0.1 0.3 0.5
DMTrO
O
NH
N
O
O
O
O
P
O
N
Ph
6l
Y : parts per Million : Proton
-1.0 0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0
X : parts per Million : Proton
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0
0.1 0.2 0.3 0.4 0.5
abundance

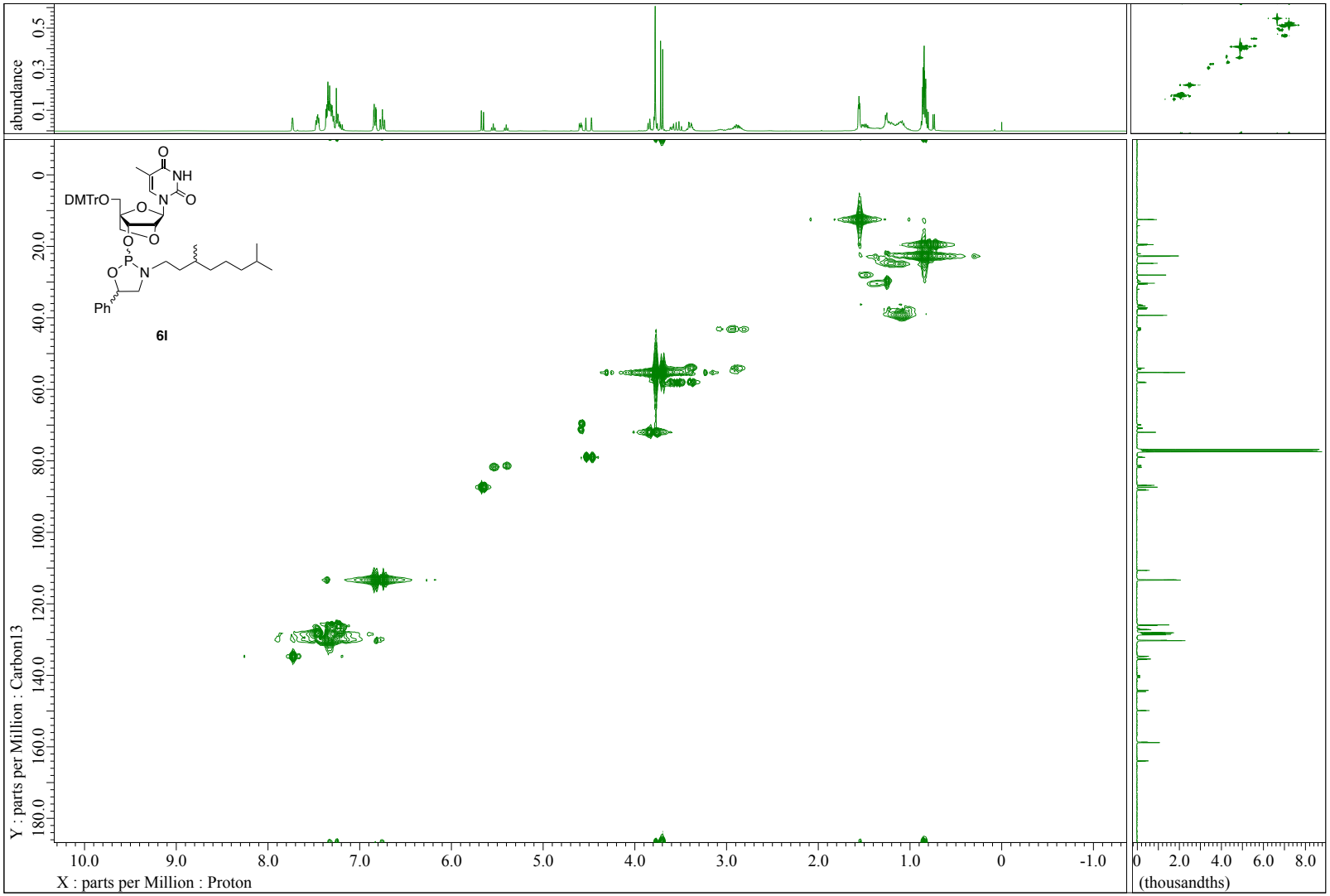
^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$)



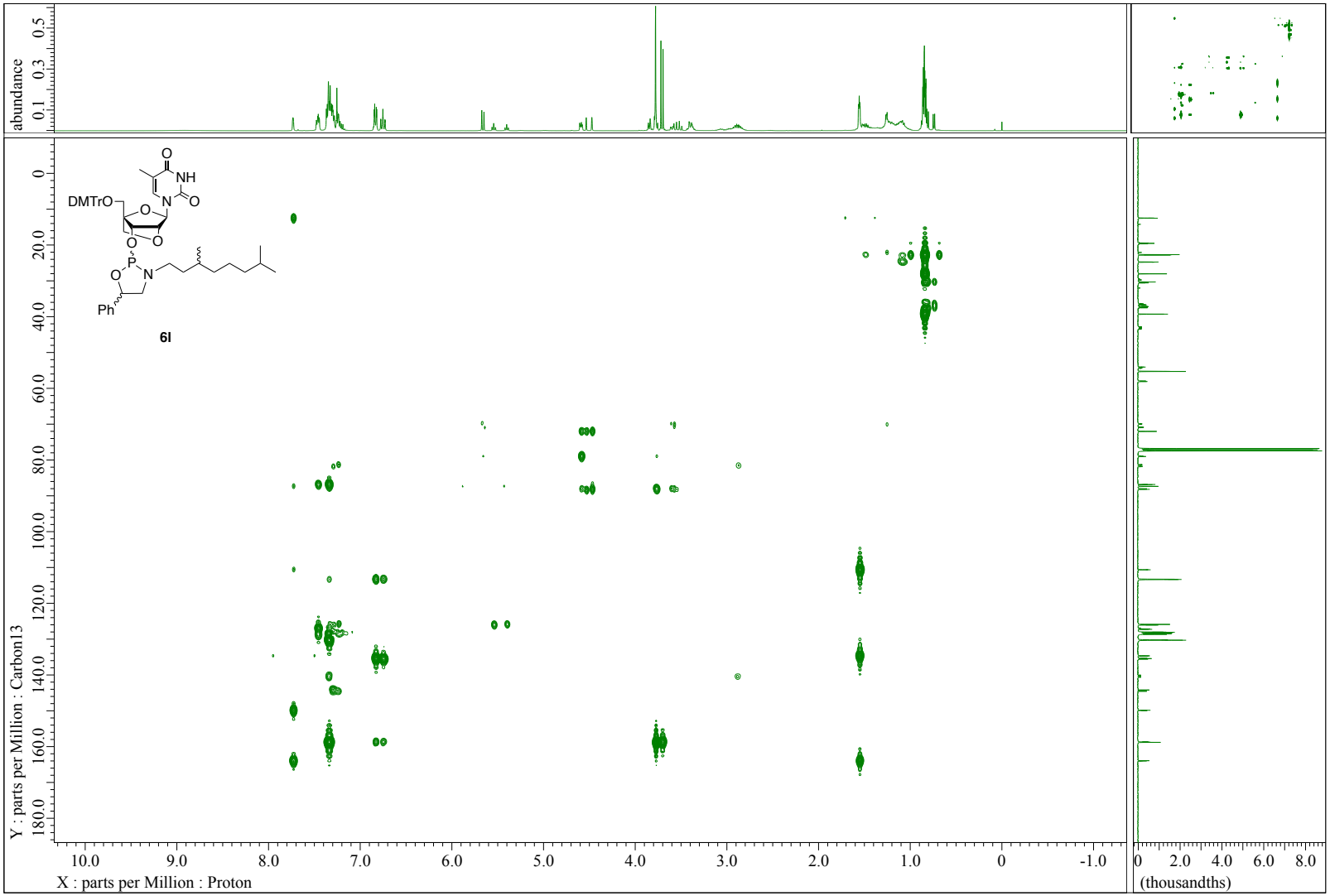
COSY ($CDCl_3$)


abundance
0.1 0.3 0.5
DMTrO
NH
O
N
O
O
O
O
P
O
N
Ph
6l
-1.0 0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0
Y : parts per Million : Proton
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0
X : parts per Million : Proton
0.1 0.2 0.3 0.4 0.5
abundance

HMQC ($CDCl_3$)


abundance
0.1
0.3
0.5
DMTrO
NH
O
N
O
O
O
O
P
O
N
Ph
6l
0
20.0
40.0
60.0
80.0
100.0
120.0
140.0
160.0
180.0
Y : parts per Million : Carbon13
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
X : parts per Million : Proton
0
2.0
4.0
6.0
8.0
(thousandths)

HMBC ($CDCl_3$)


abundance
0.1
0.3
0.5
DMTrO
NH
O
N
O
O
O
O
P
N
Ph
6l
Y : parts per Million : Carbon13
0
20.0
40.0
60.0
80.0
100.0
120.0
140.0
160.0
180.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
X : parts per Million : Proton
0
2.0
4.0
6.0
8.0
(thousandths)

PO-DNA dodecamer d(C$_{PO}$A$_{PO}$G$_{PO}$T$_{PO}$C$_{PO}$A$_{PO}$G$_{PO}$T$_{PO}$C$_{PO}$A$_{PO}$)T 11
^{1}H NMR (500 MHz, D$_2$O)

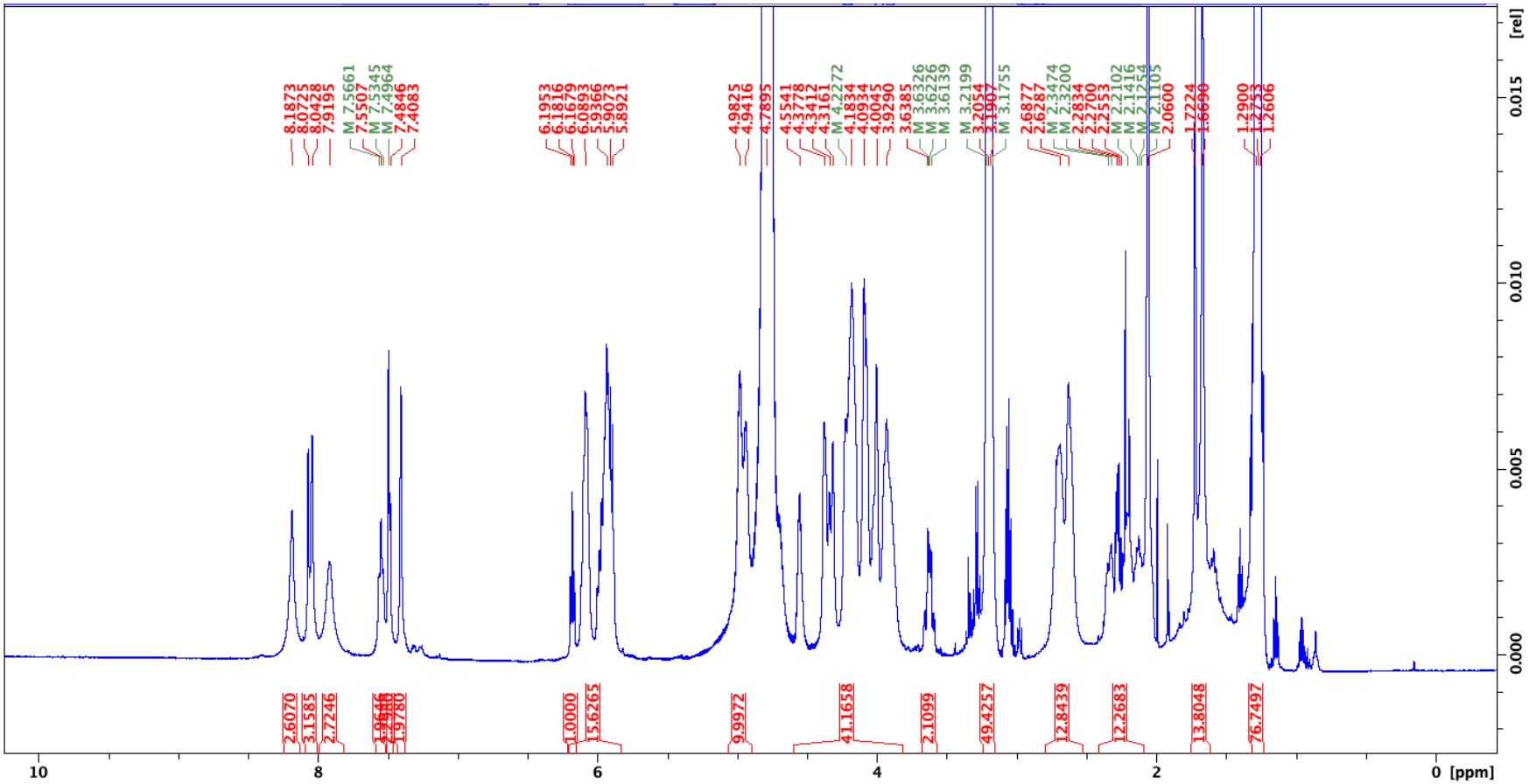


Figure S7 ^{1}H NMR spectra of PO-DNA dodecamer d(C$_{PO}$A$_{PO}$G$_{PO}$T$_{PO}$C$_{PO}$A$_{PO}$G$_{PO}$T$_{PO}$C$_{PO}$A$_{PO}$)T **11** (500 MHz, D$_2$O).

^{31}P {^{1}H} NMR (500 MHz, D_2O)

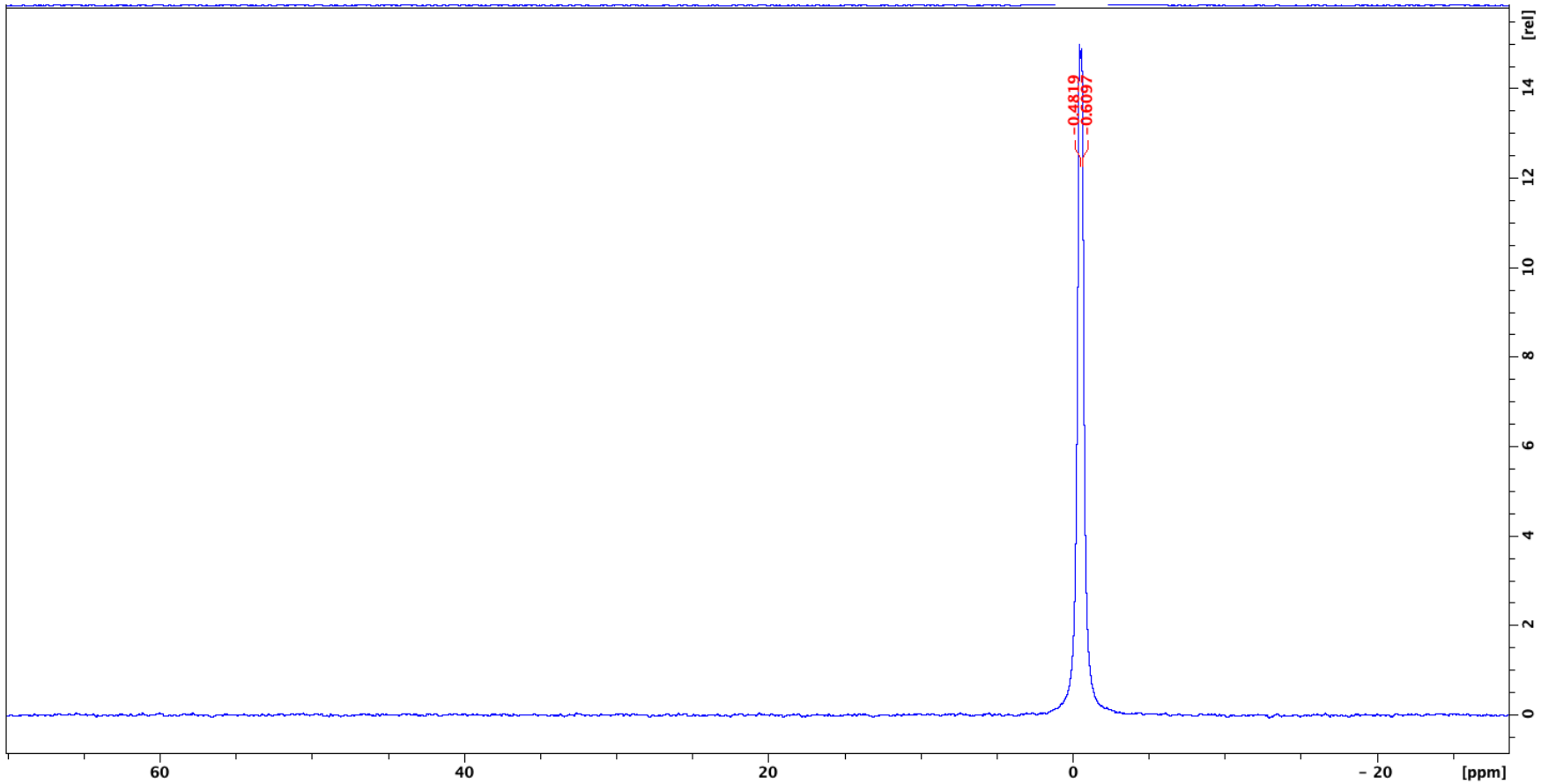
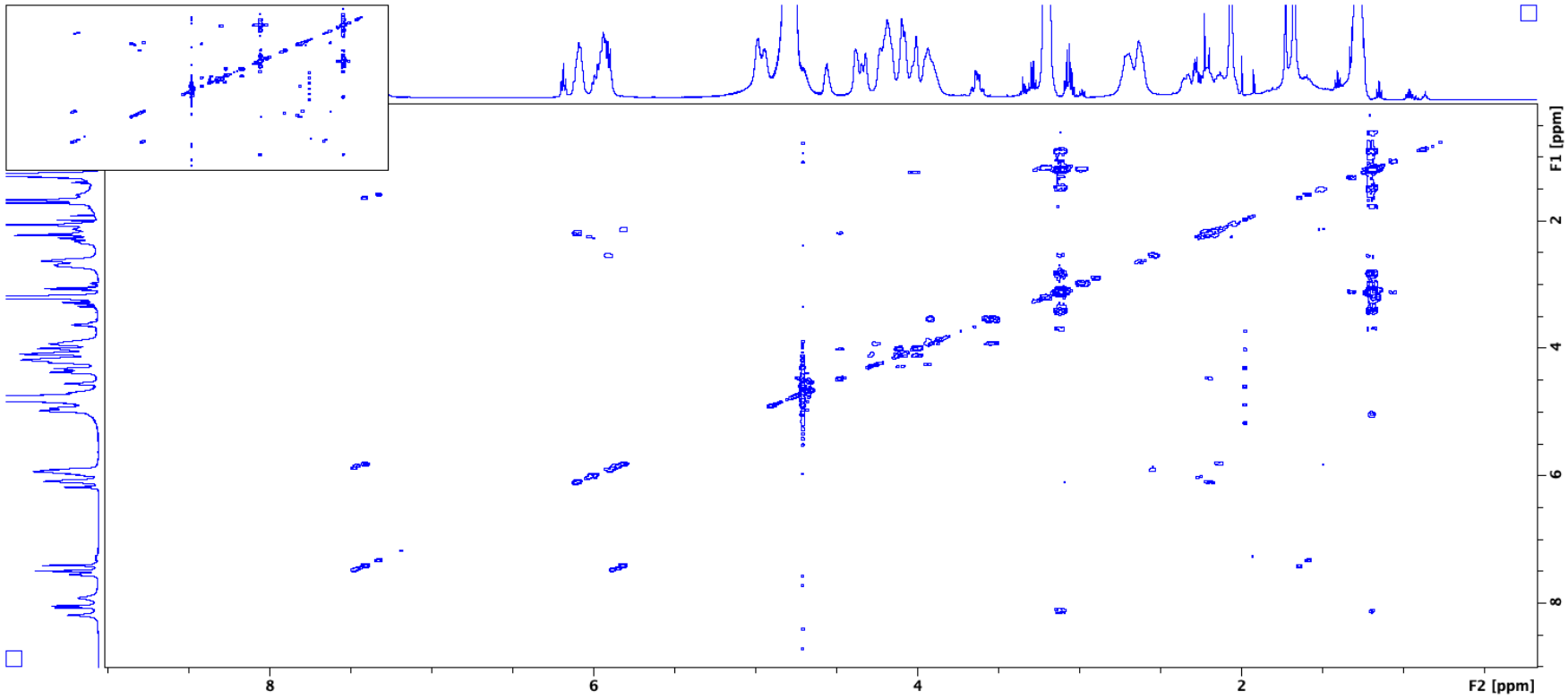


Figure S8 ^{31}P NMR spectra of PO-DNA dodecamer d($C_{PO}A_{PO}G_{PO}T_{PO}C_{PO}A_{PO}G_{PO}T_{PO}C_{PO}A_{PO}$)T **11** (500 MHz, D_2O).



COSY spectra of PO-DNA dodecamer d(C$_{PO}$A$_{PO}$G$_{PO}$T$_{PO}$C$_{PO}$A$_{PO}$G$_{PO}$T$_{PO}$C$_{PO}$A$_{PO}$)T **11** (500 MHz, D_2O).

PB-DNA tetramer d($C_{PB}A_{PB}G_{PB}T$) 16
^{1}H NMR (600 MHz, D_2O)

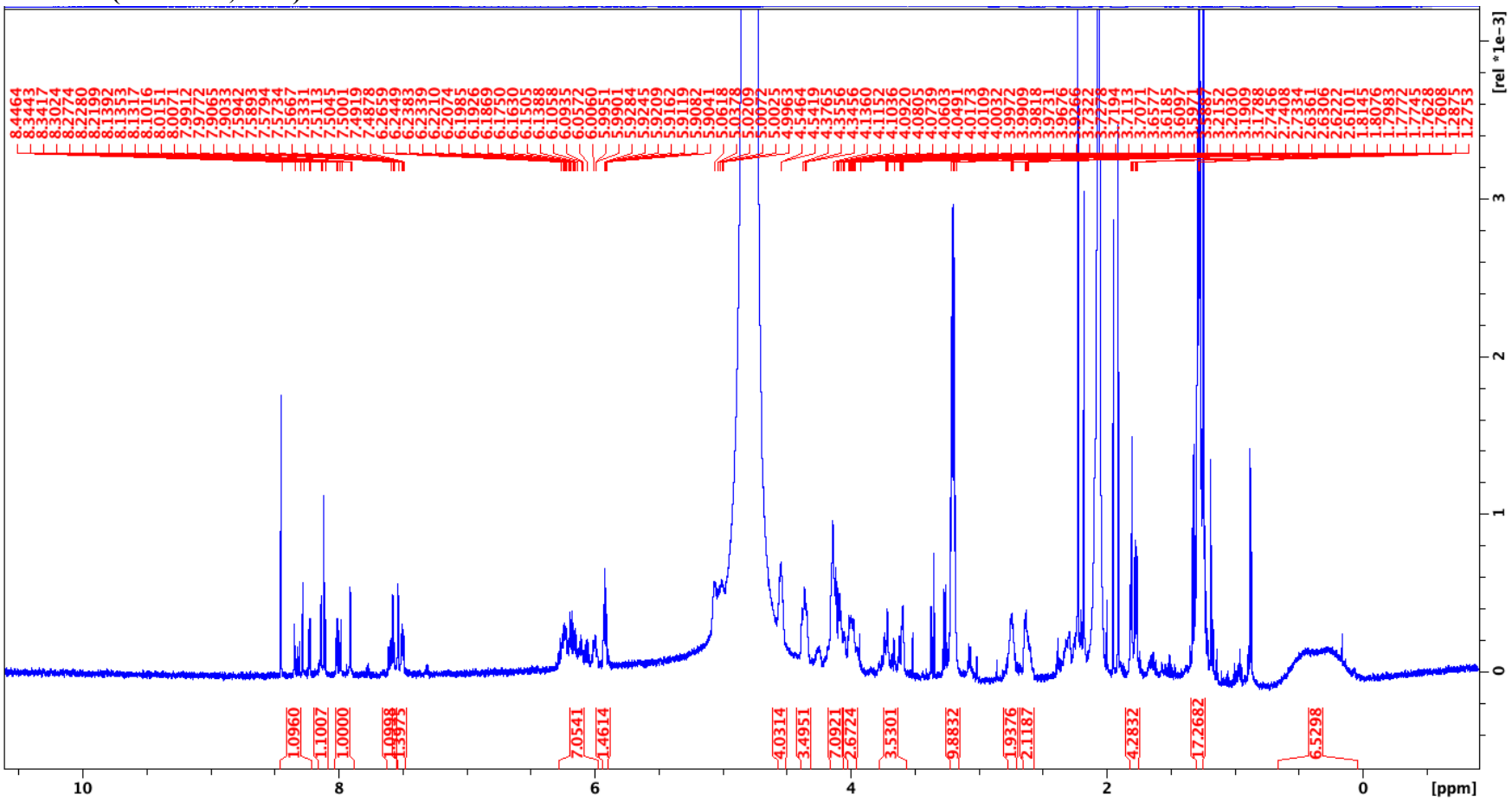


Figure S9 ^{1}H NMR spectra of PB-DNA tetramer d($C_{PB}A_{PB}G_{PB}T$) **16**(600 MHz, D_2O).

PB/POchimeric tetramer d($C_{PB}A_{PO}G_{PB}T$) 17
^{1}H NMR (600 MHz, D_2O)

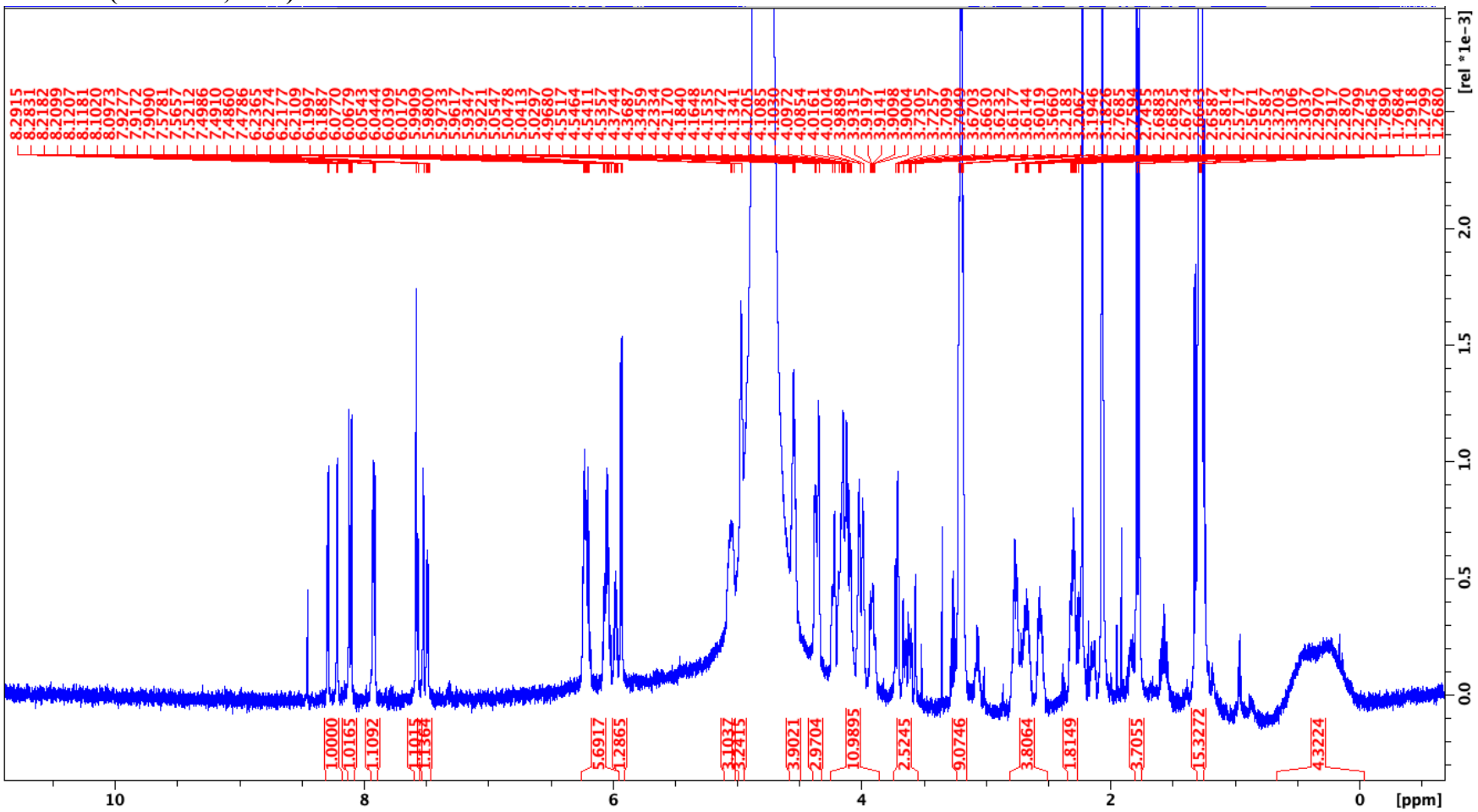


Figure S10 ^{1}H NMR spectra of PB/POchimeric tetramer d($C_{PB}A_{PO}G_{PB}T$) **17** (600 MHz, D_2O).