Electronic Supplementary Information

Synthesis and f-element ligation properties of CMPO-decorated pyridine N-oxide platforms.

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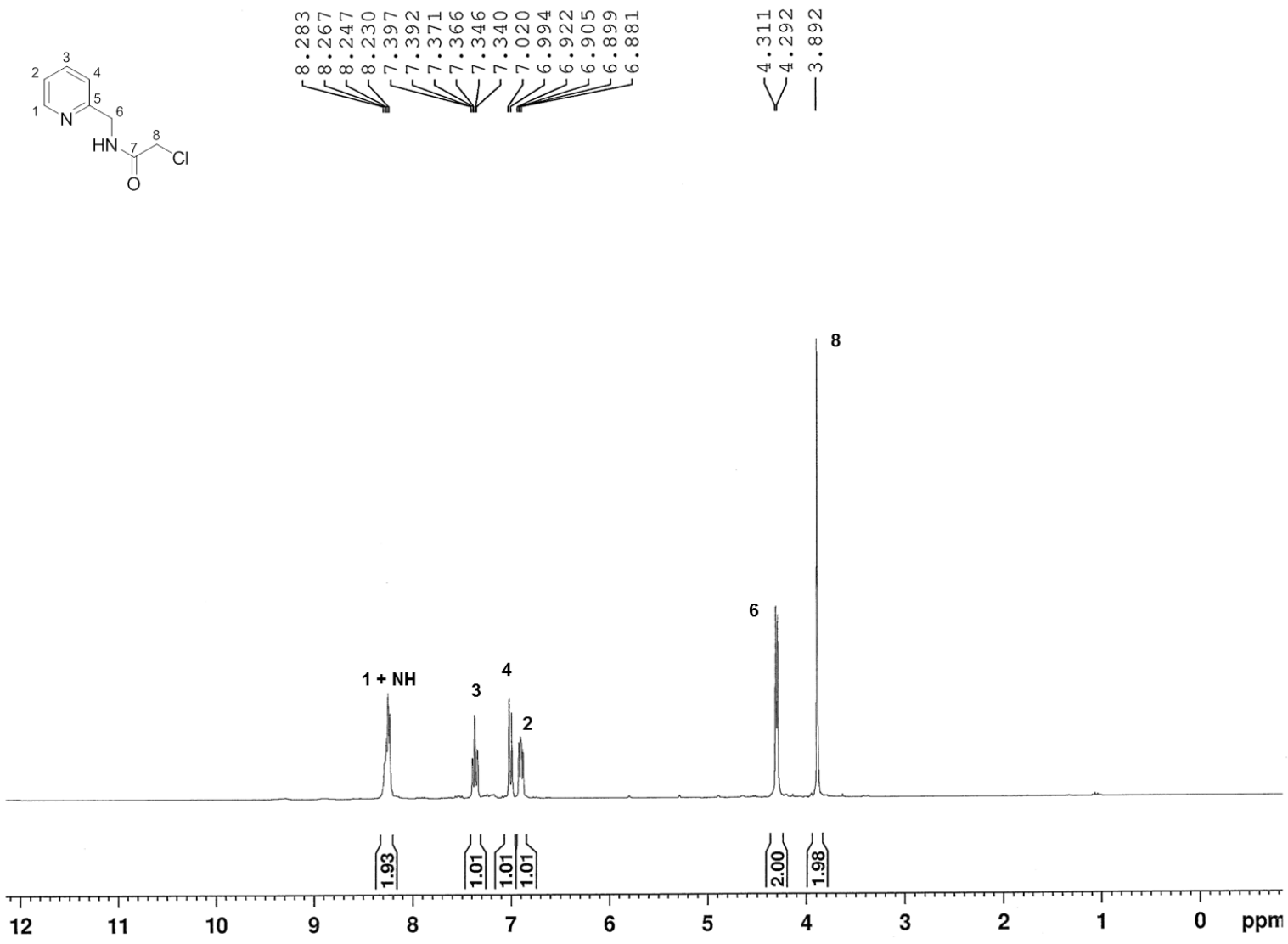
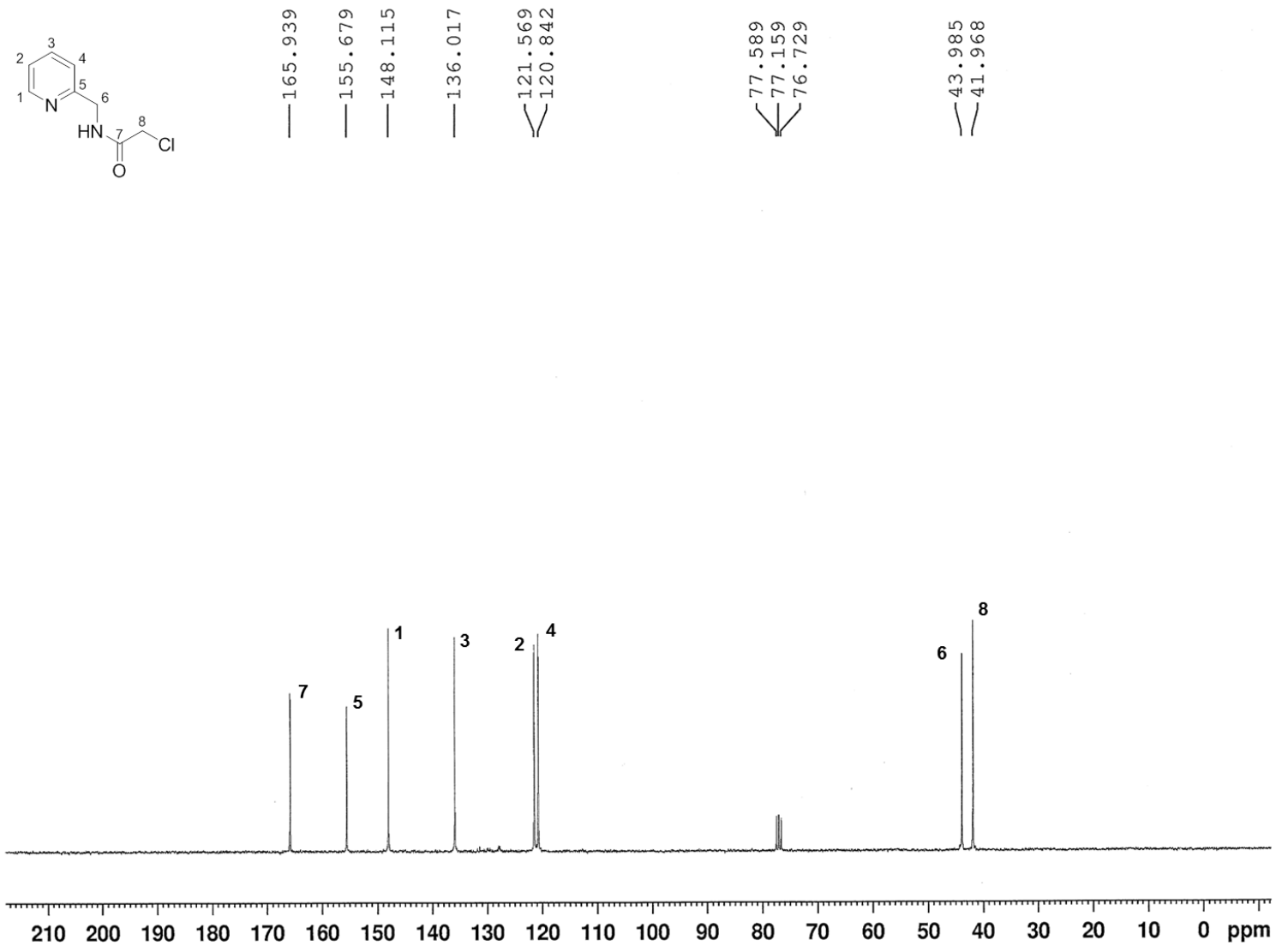


S.1 ^{1}H NMR spectrum for 9, in $CDCl_3$



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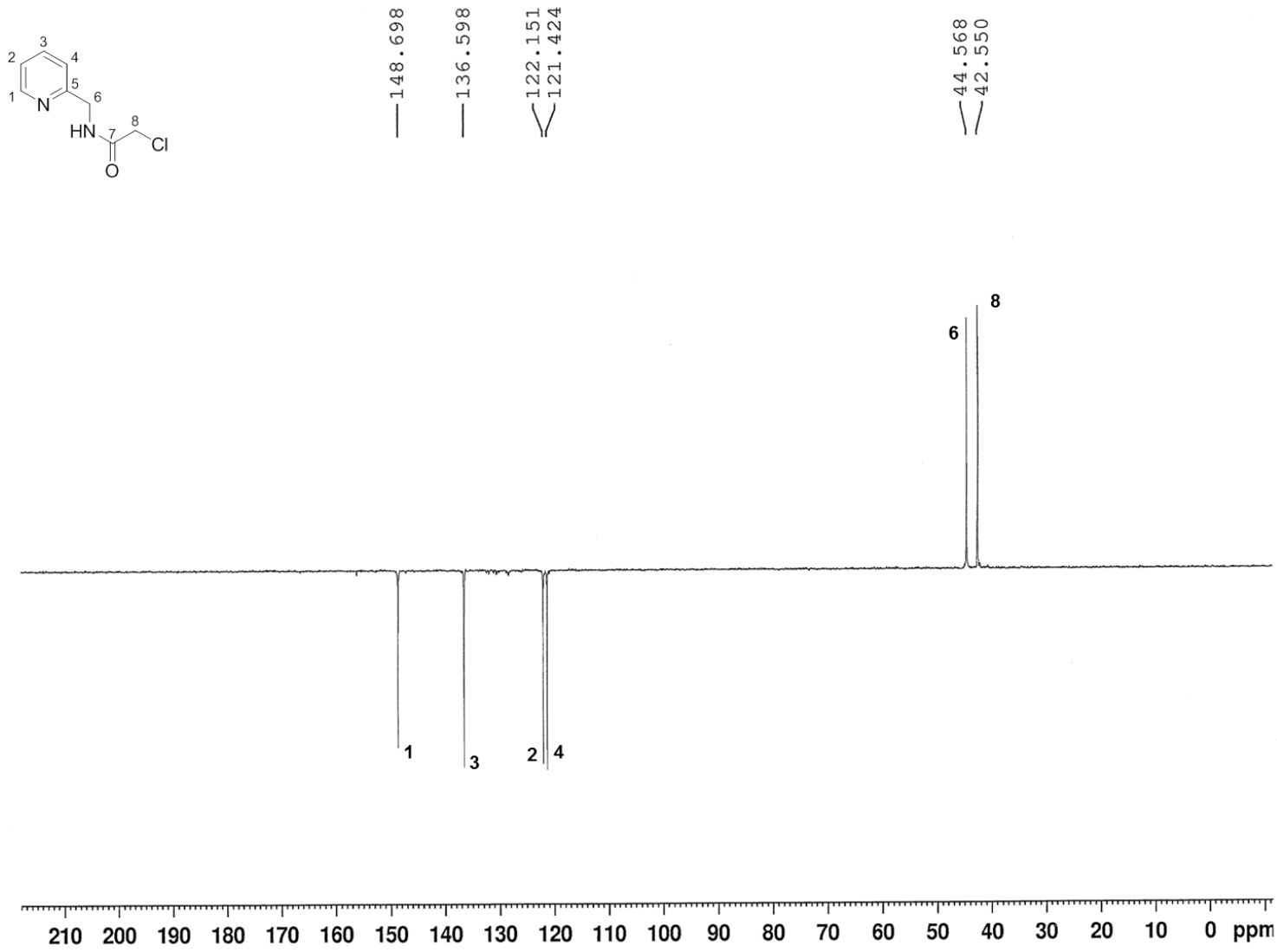

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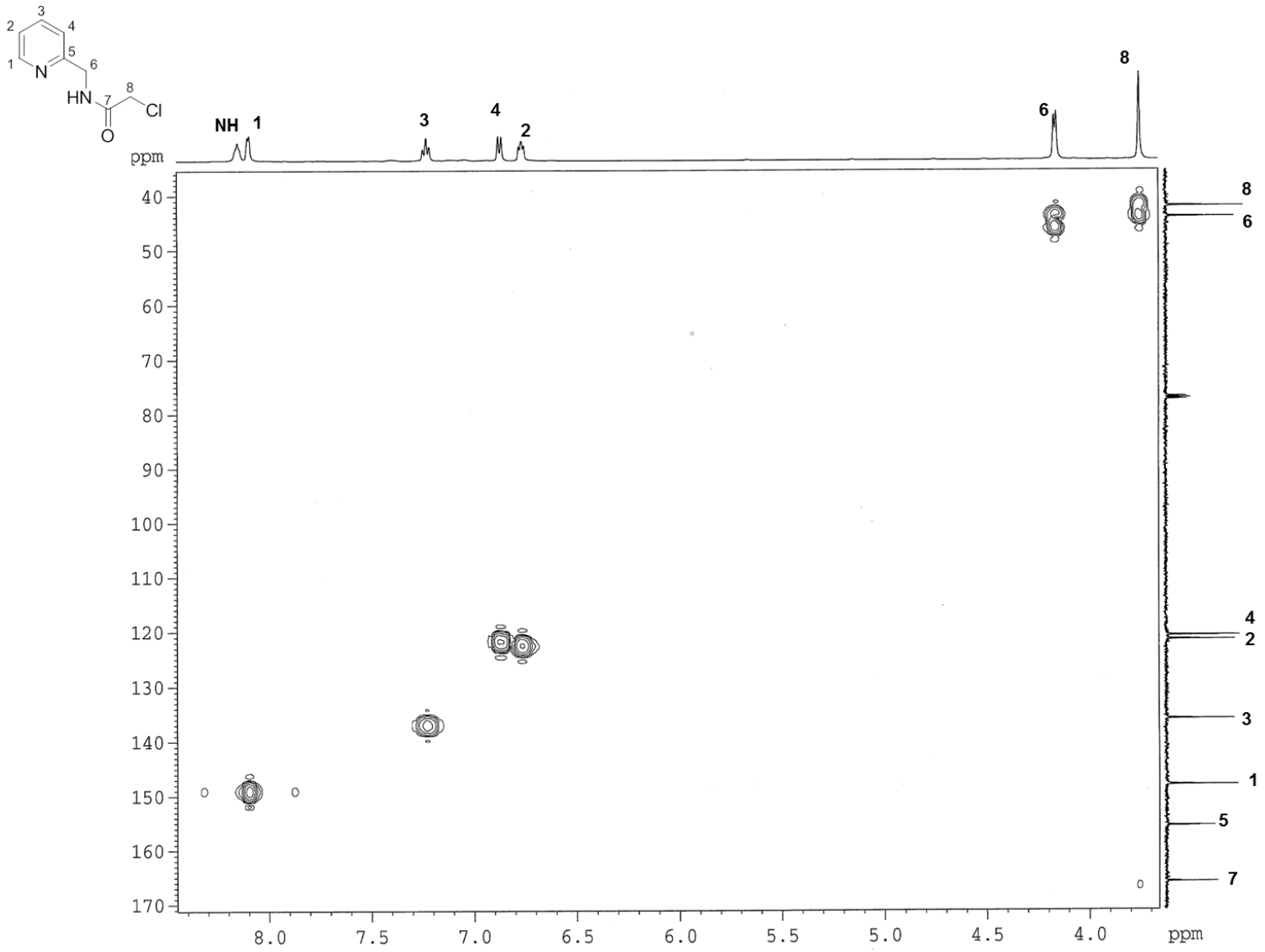

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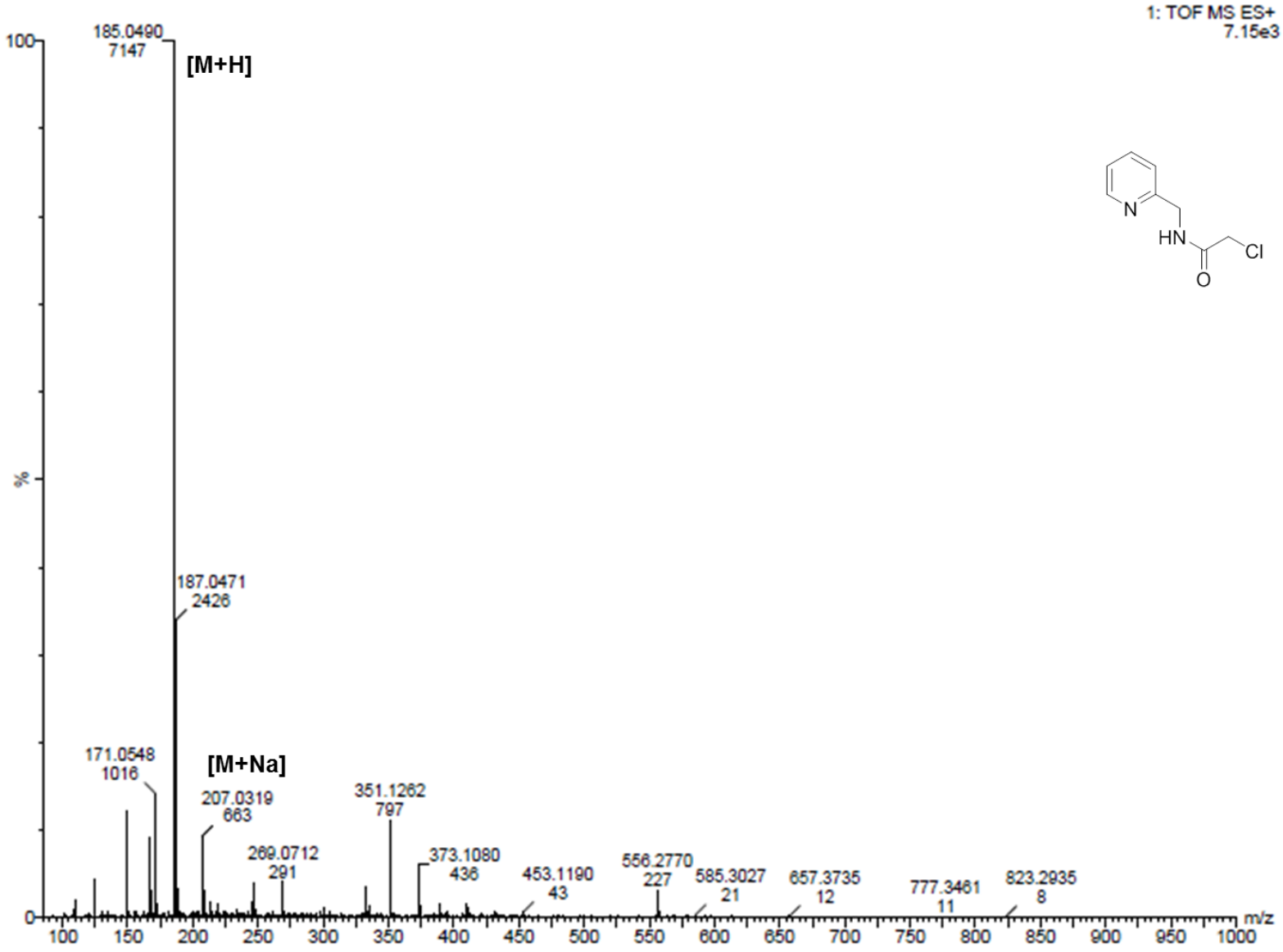

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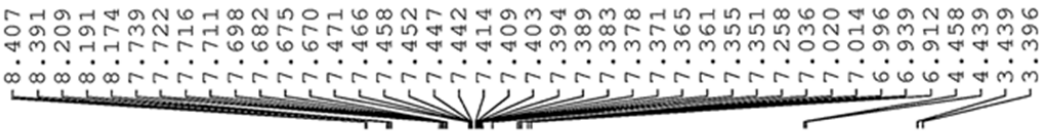

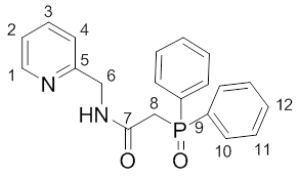

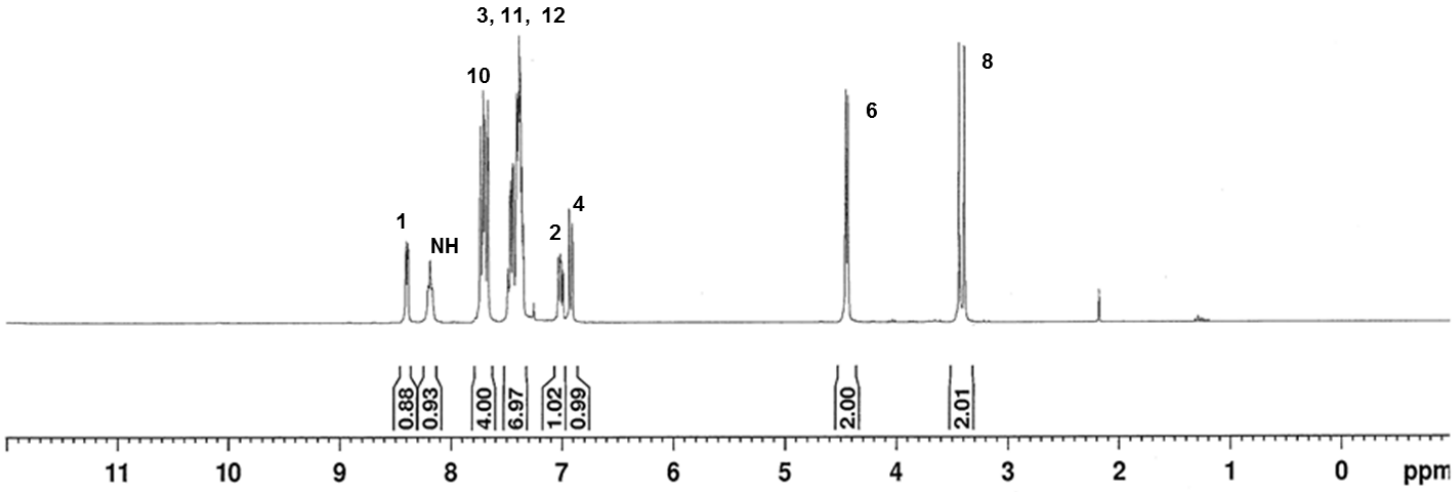

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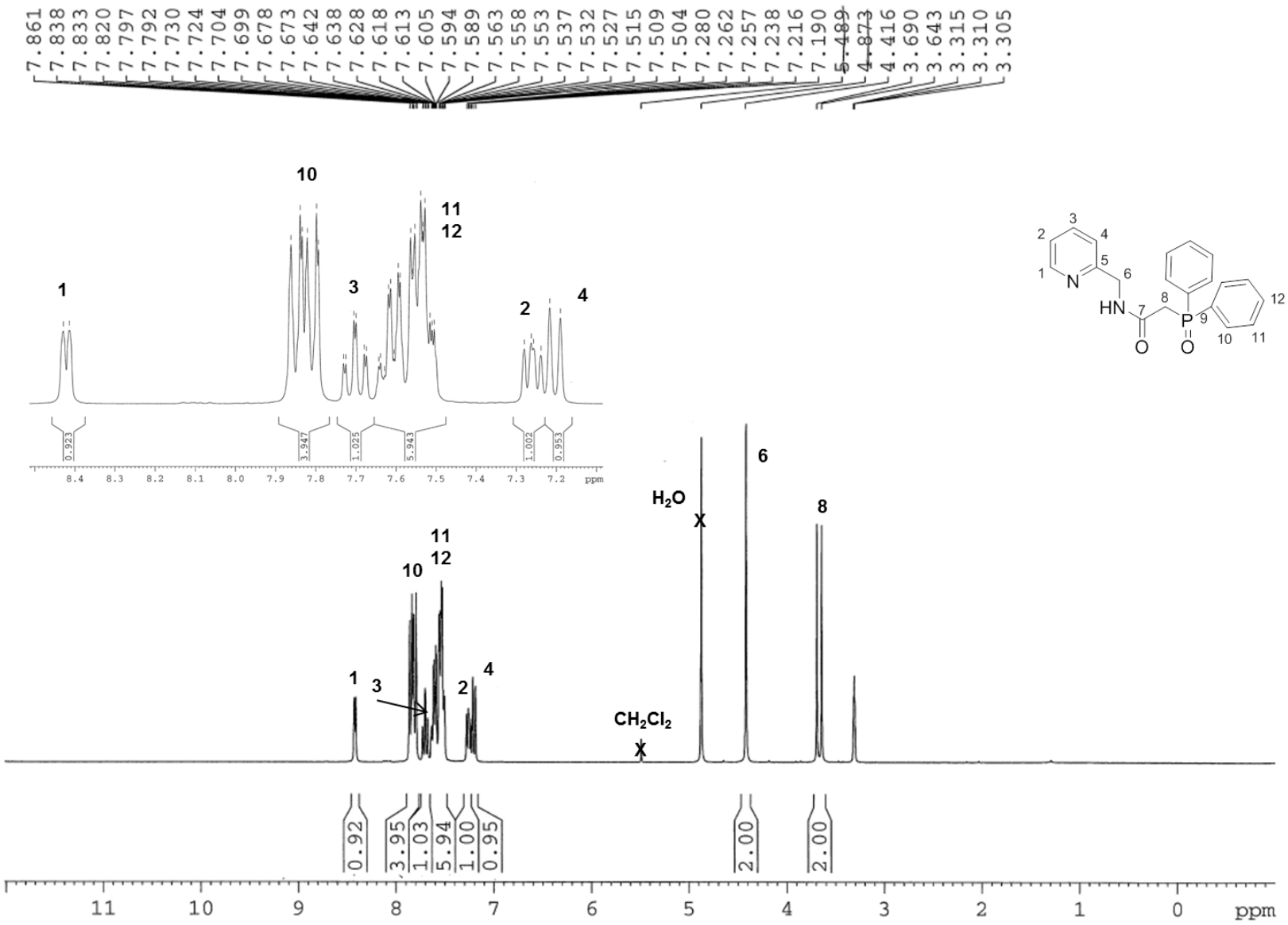
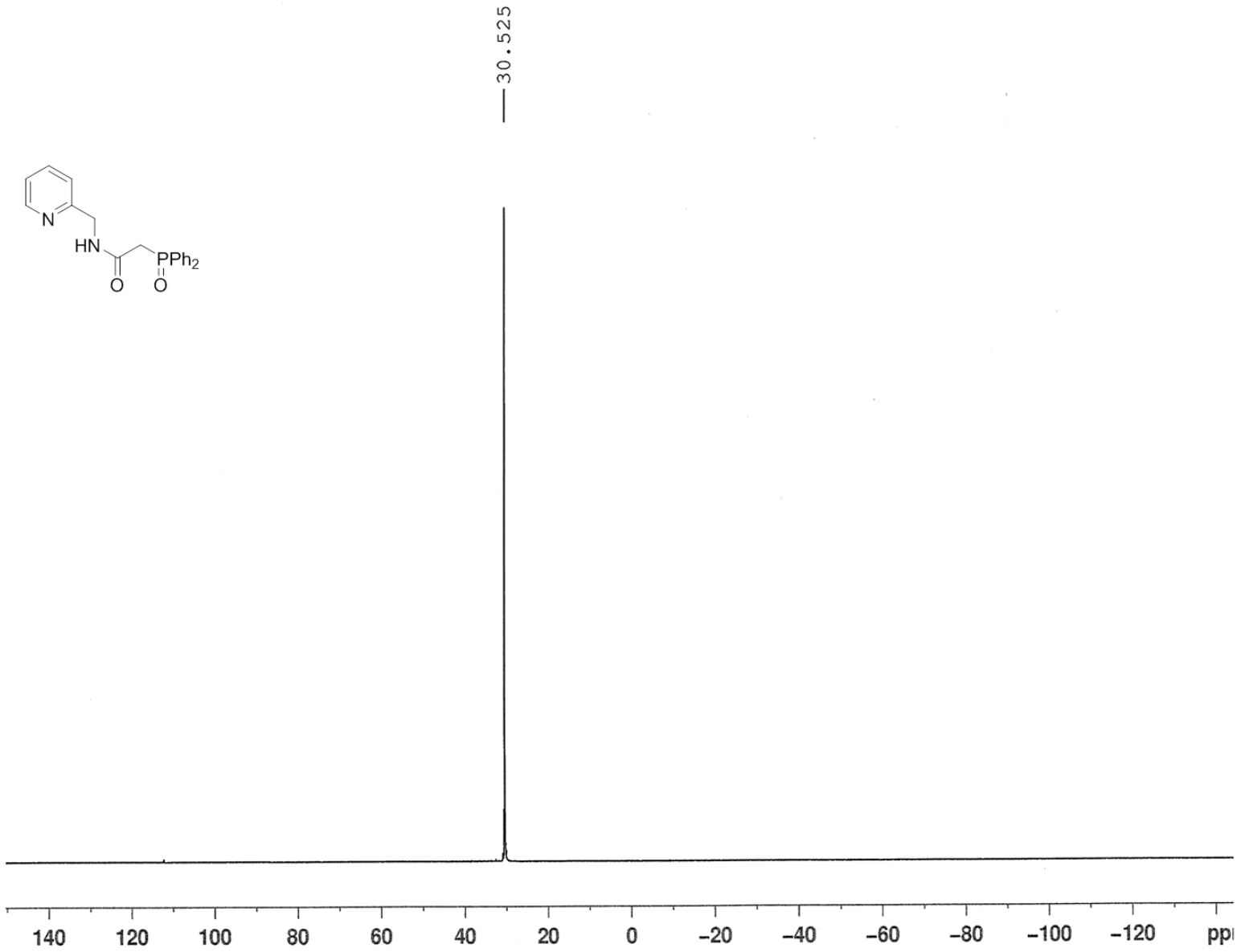


S.7 ^{1}H NMR spectrum for 10, in d_4-MeOH



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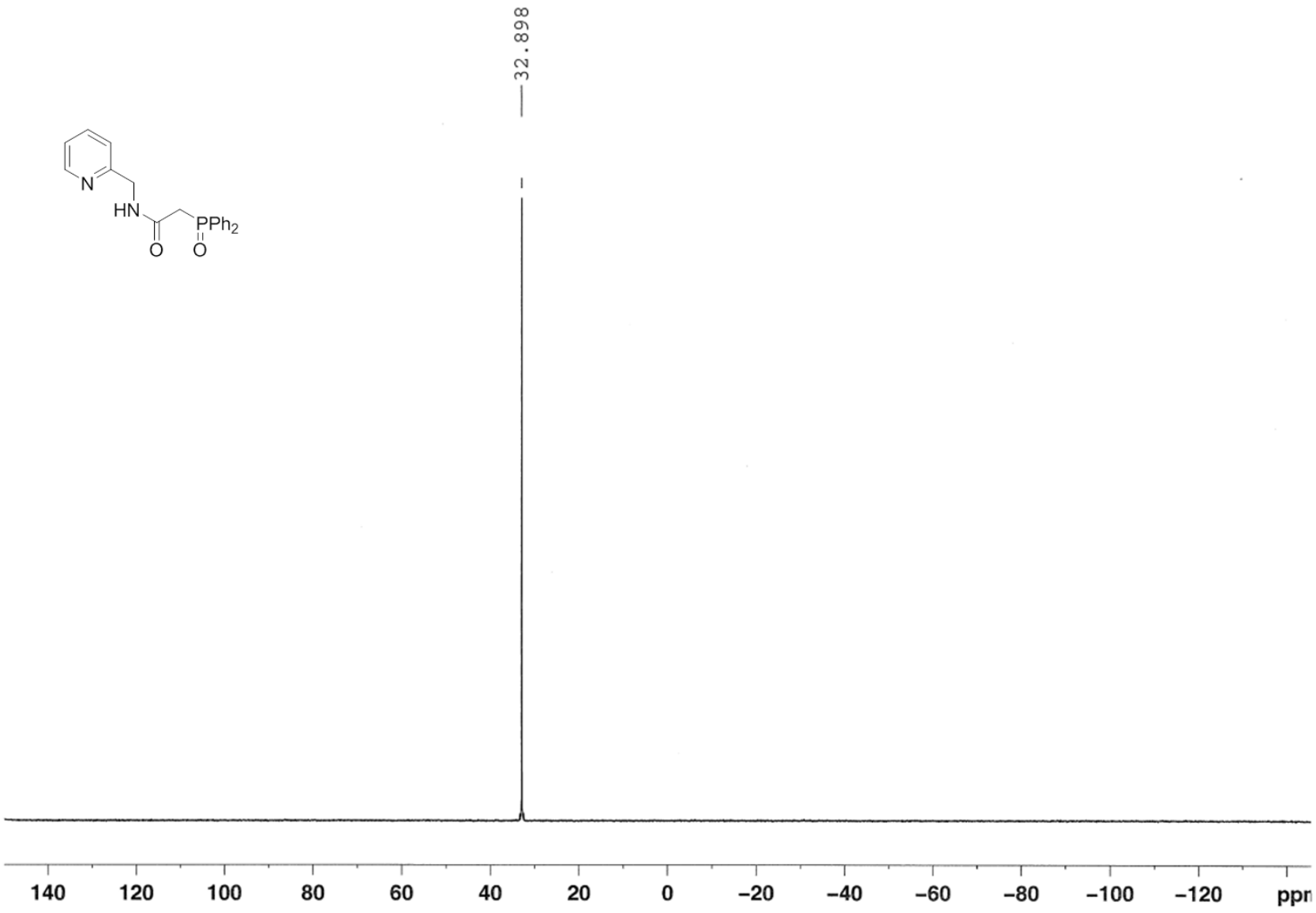

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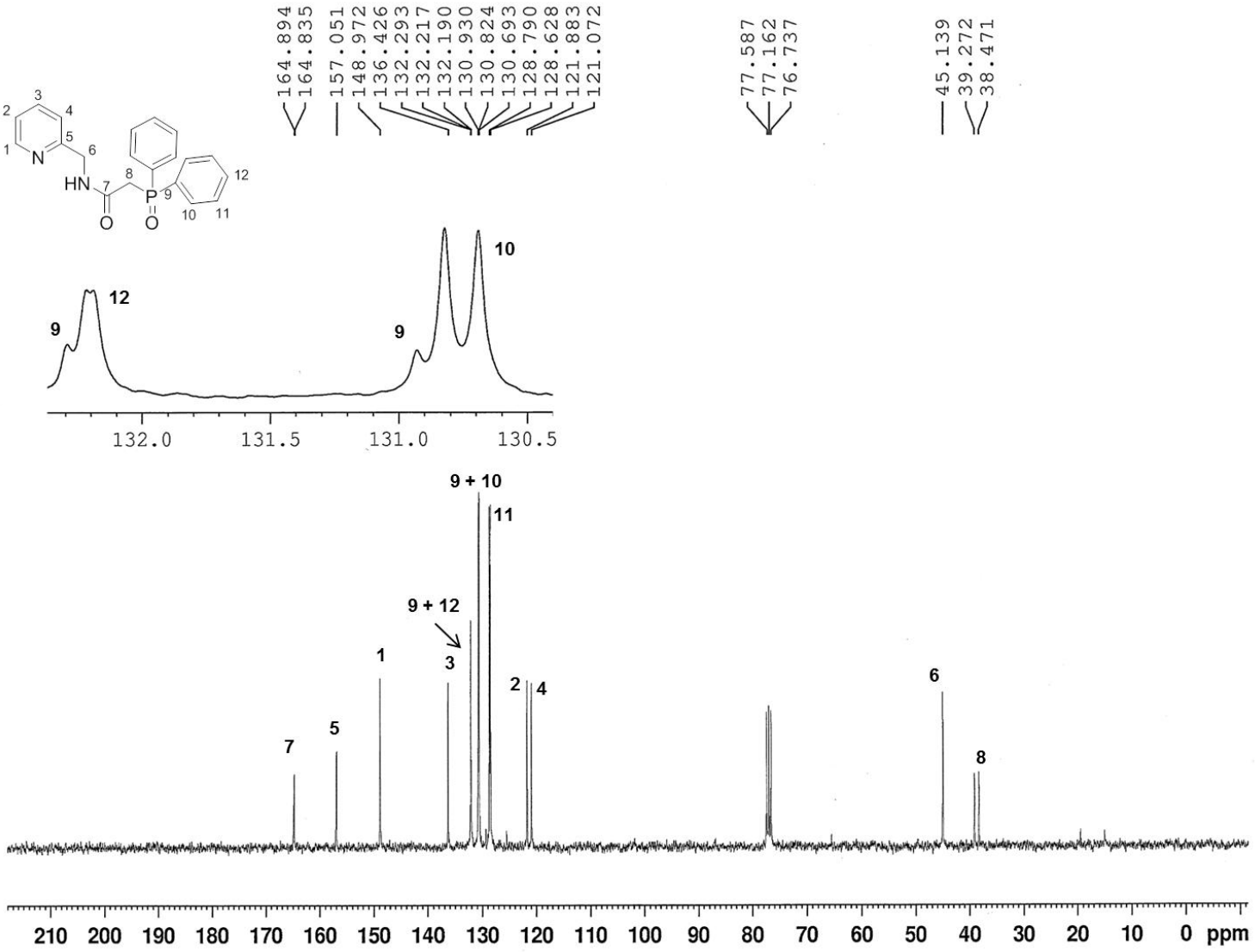

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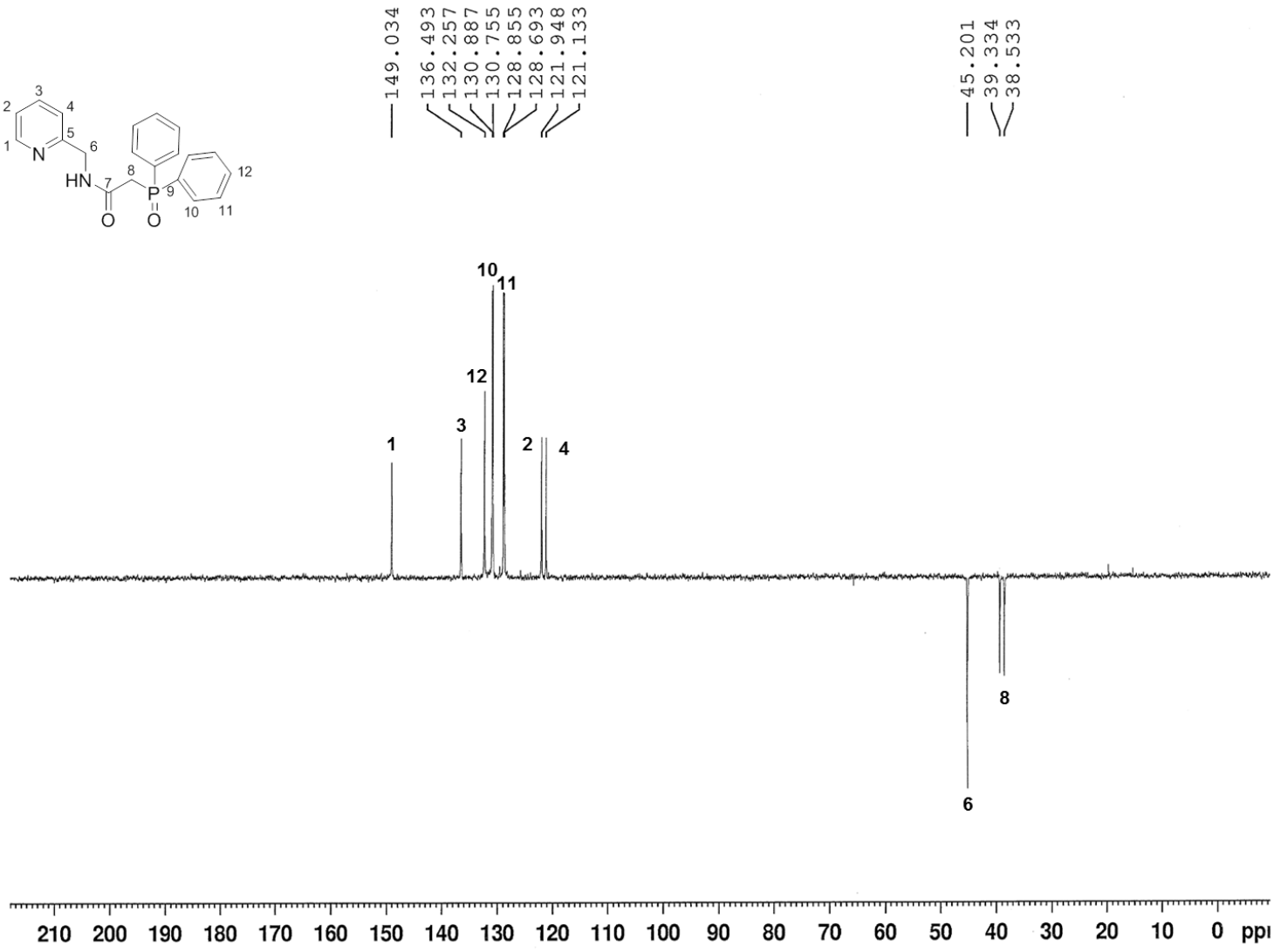

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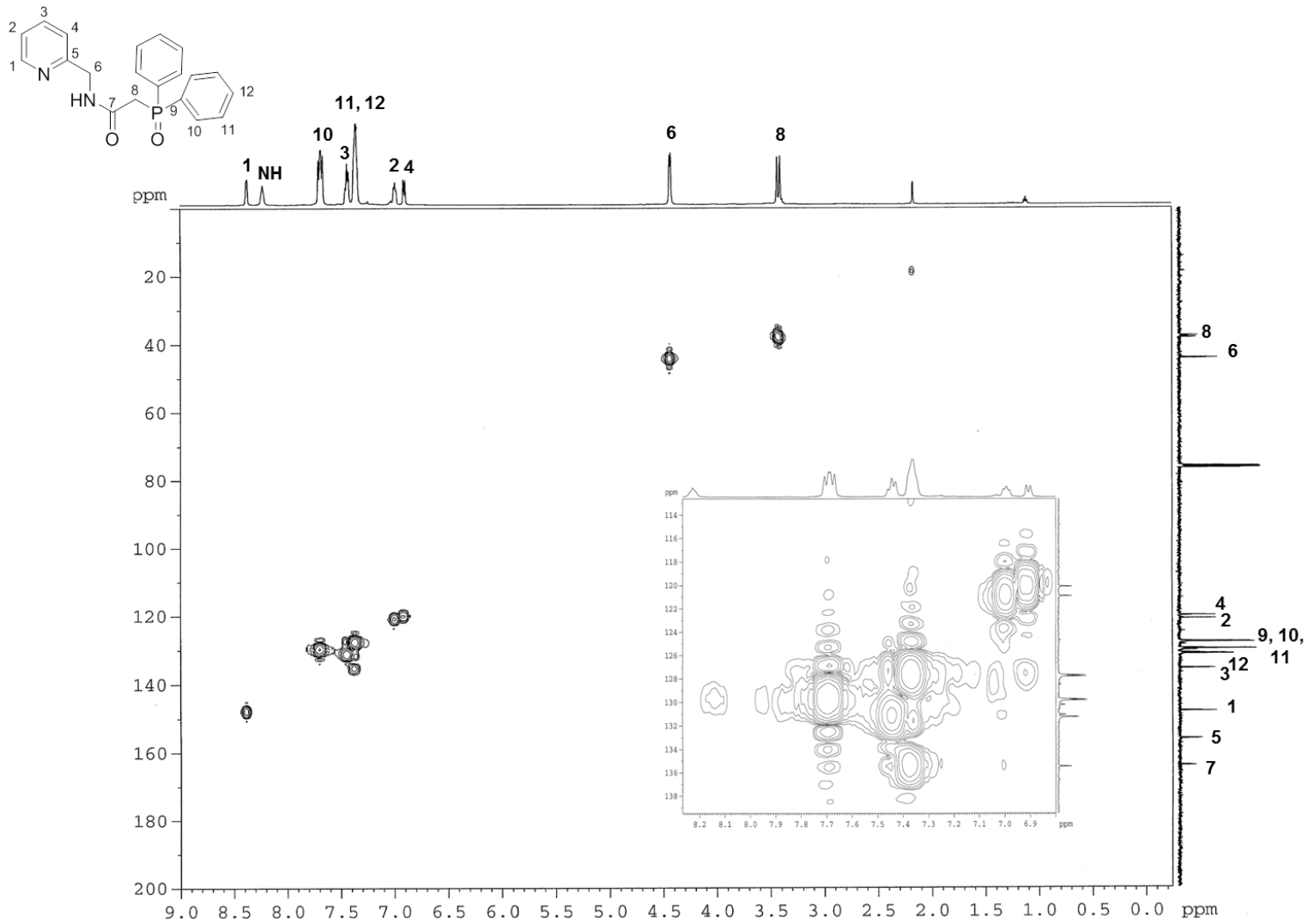

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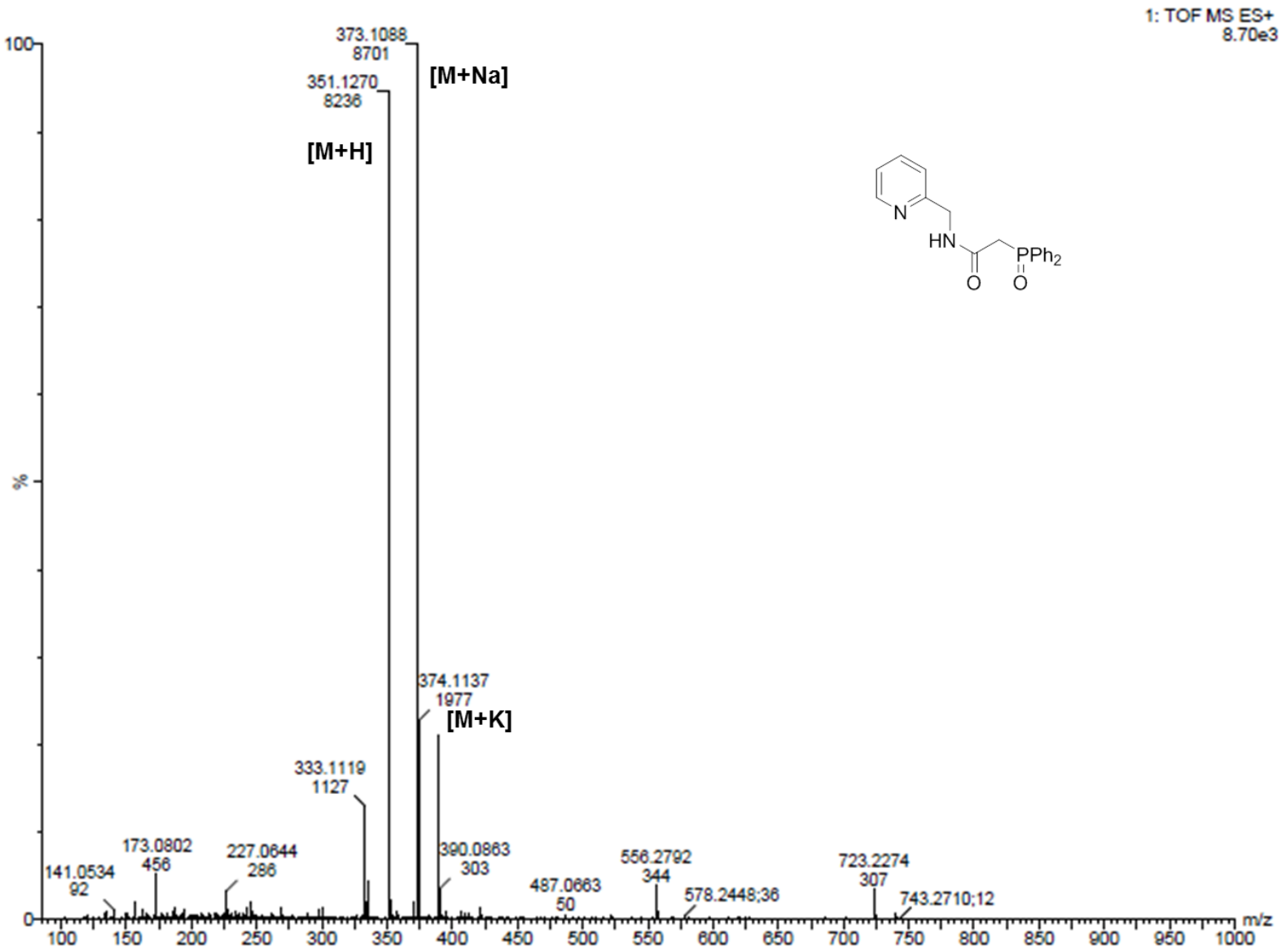

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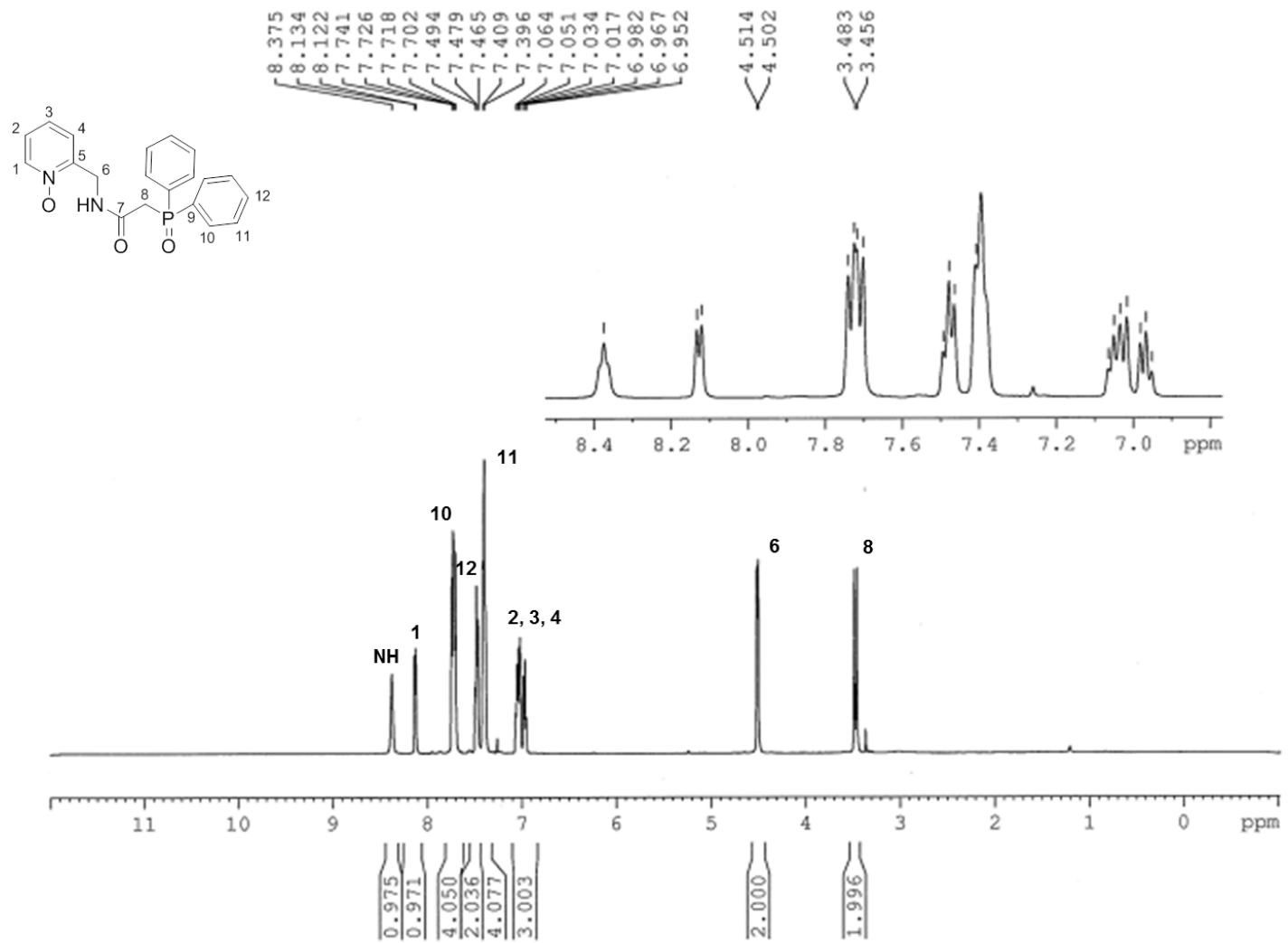

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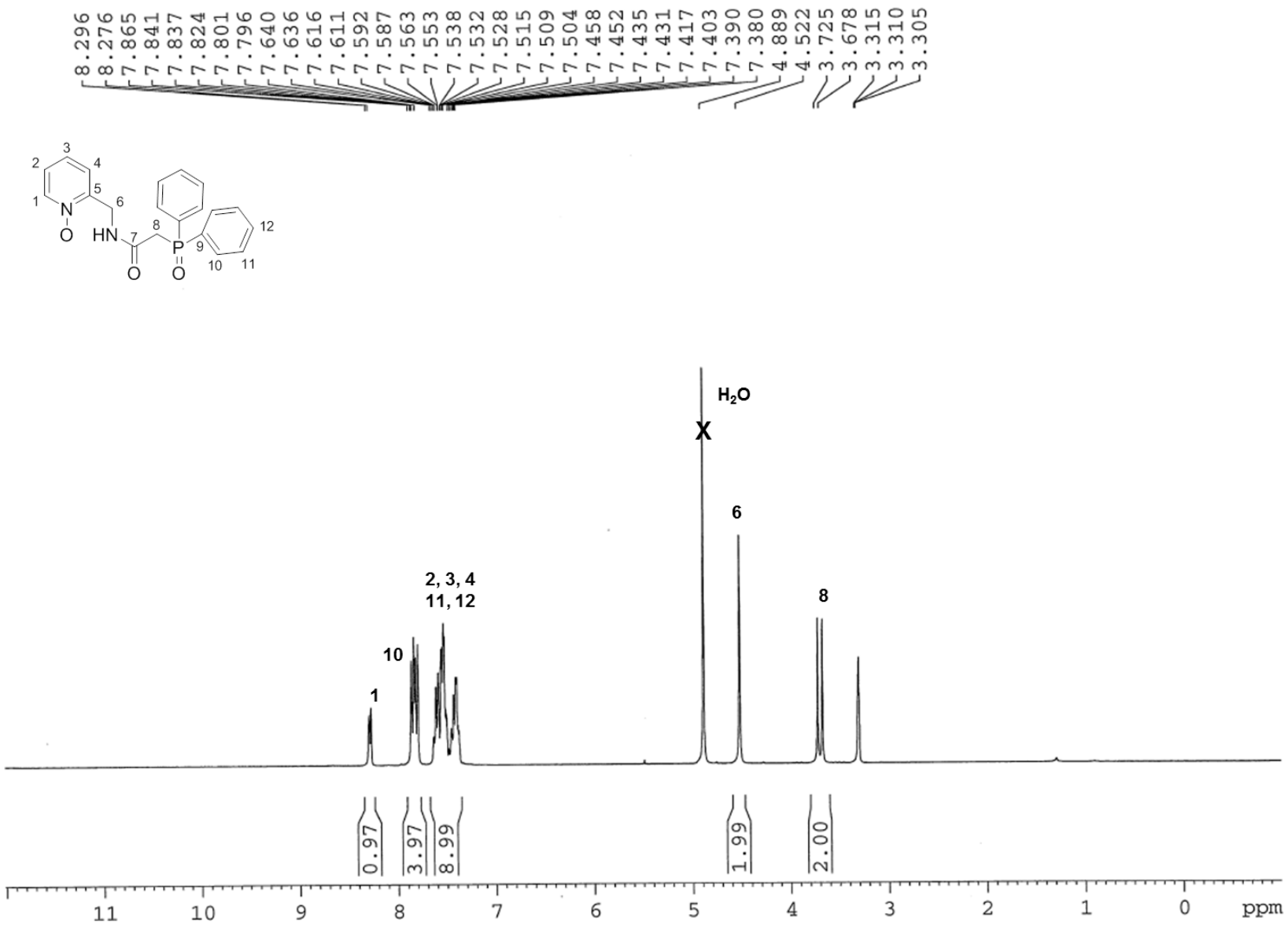

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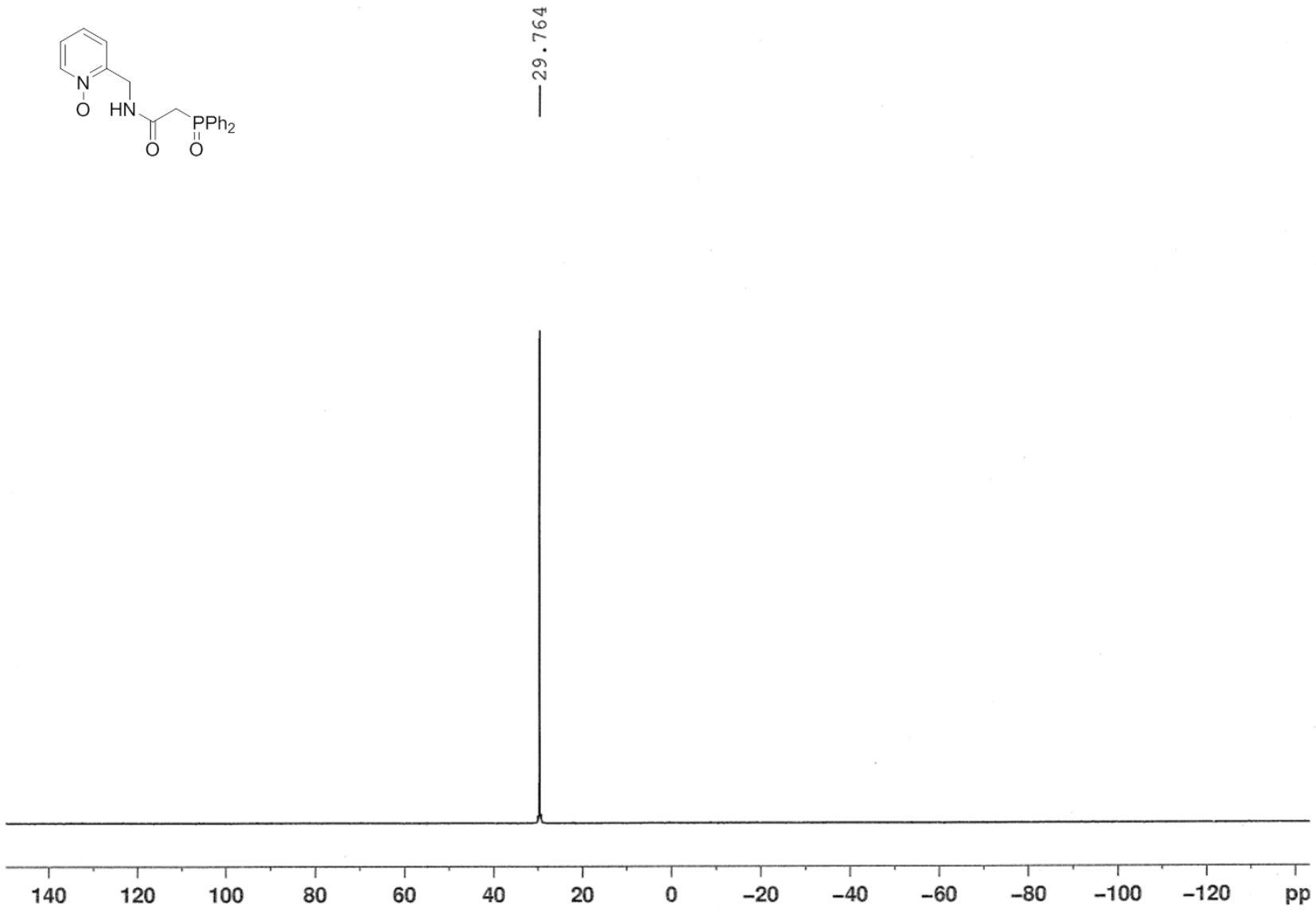

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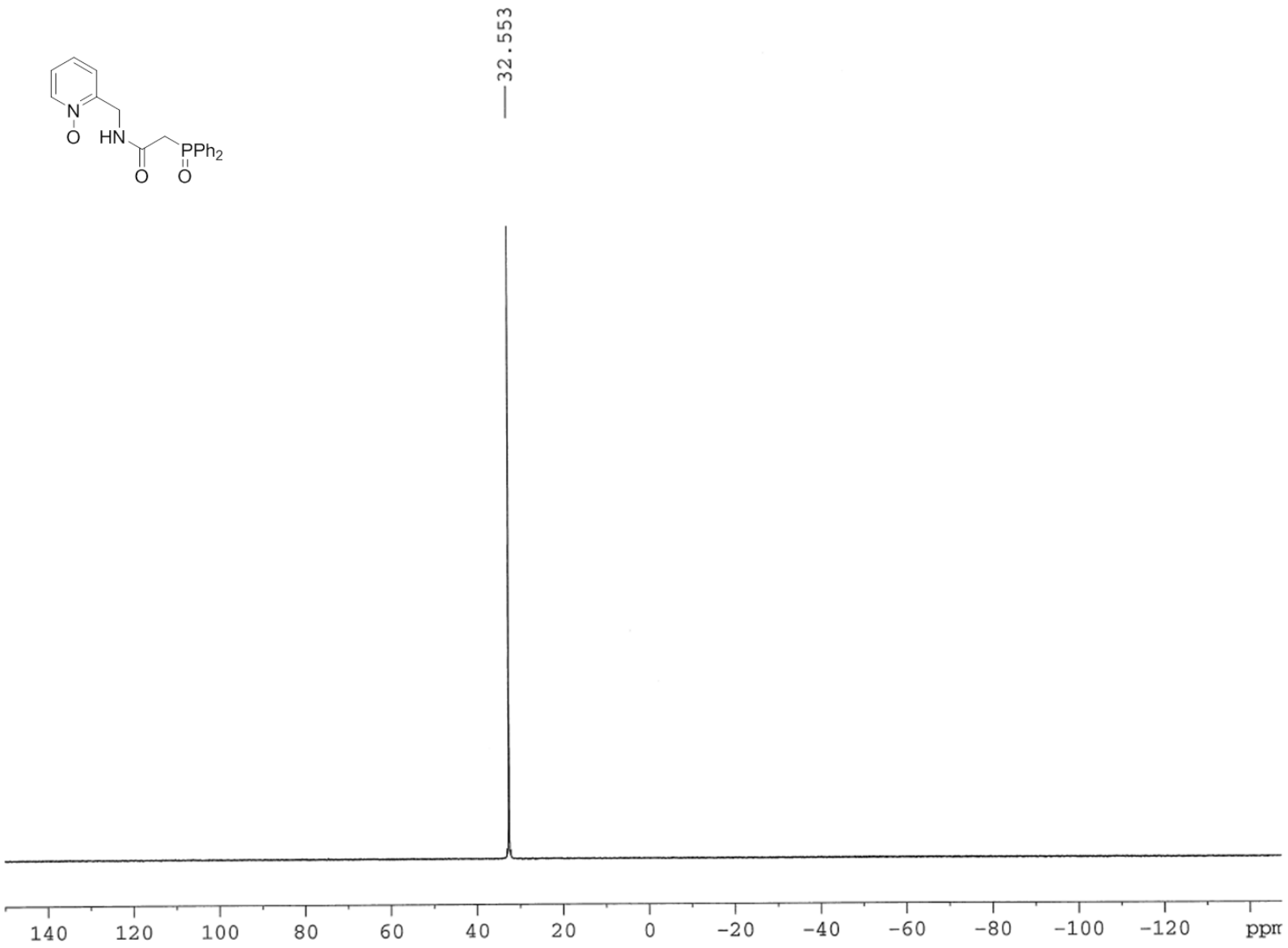

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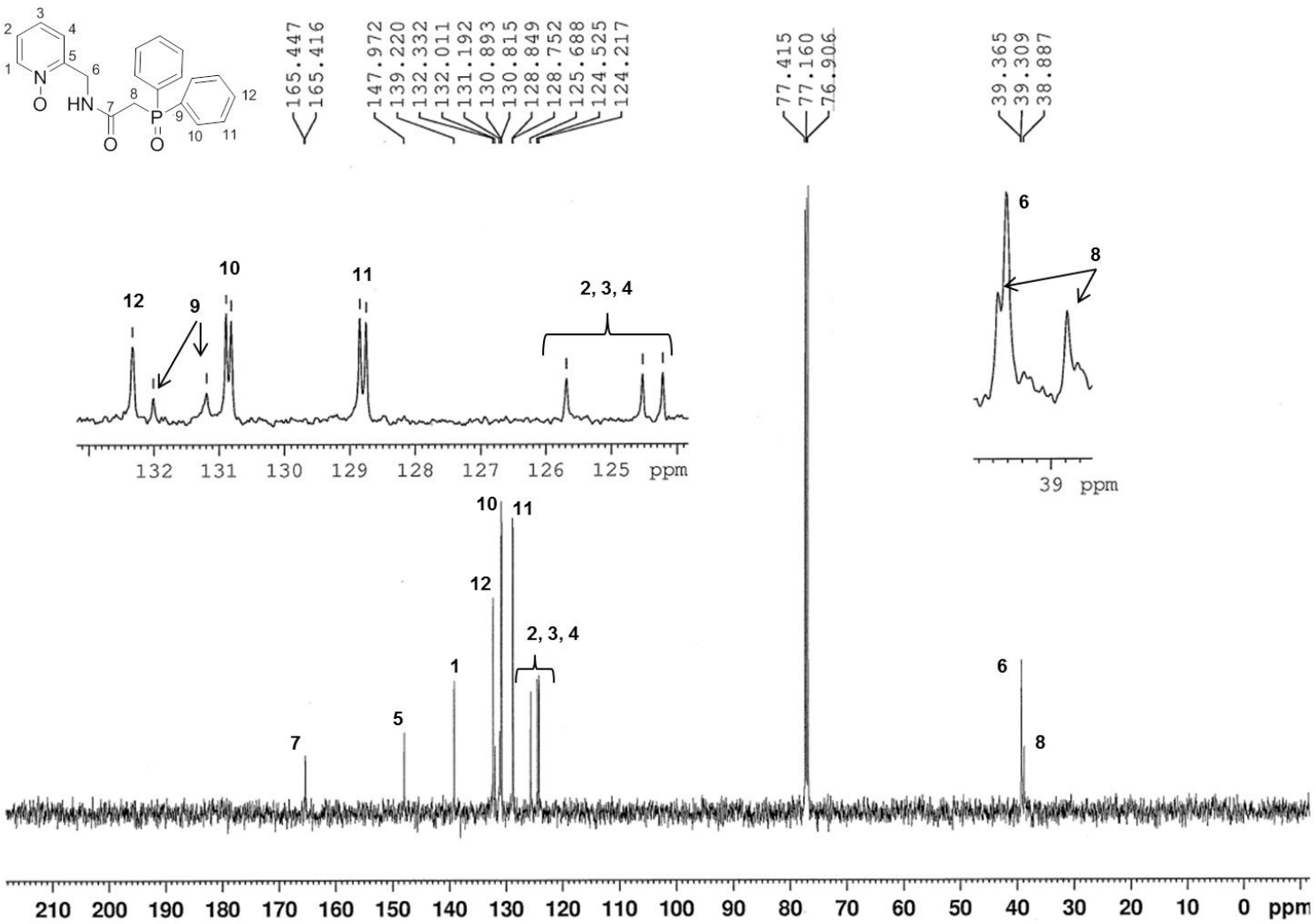

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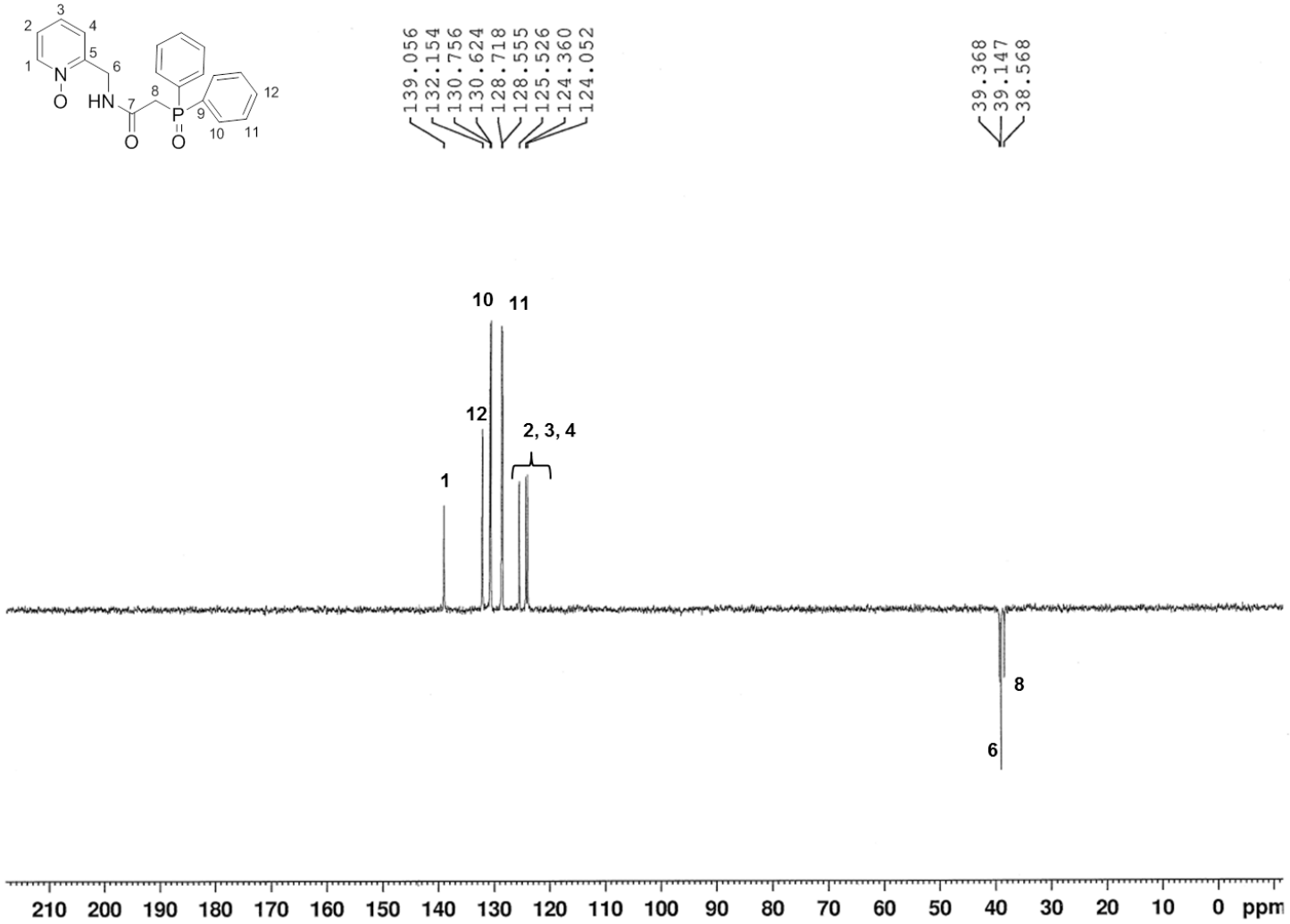

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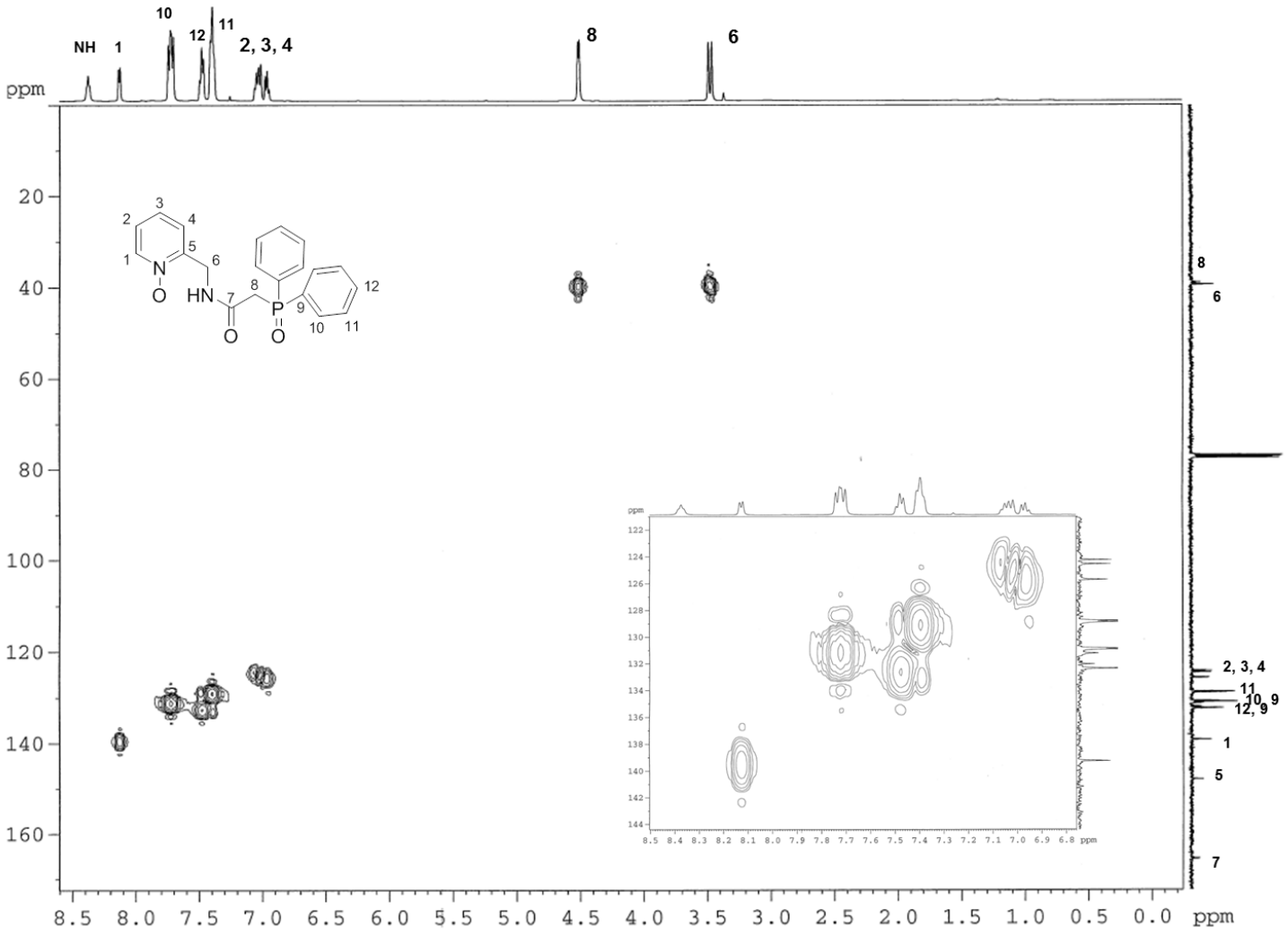

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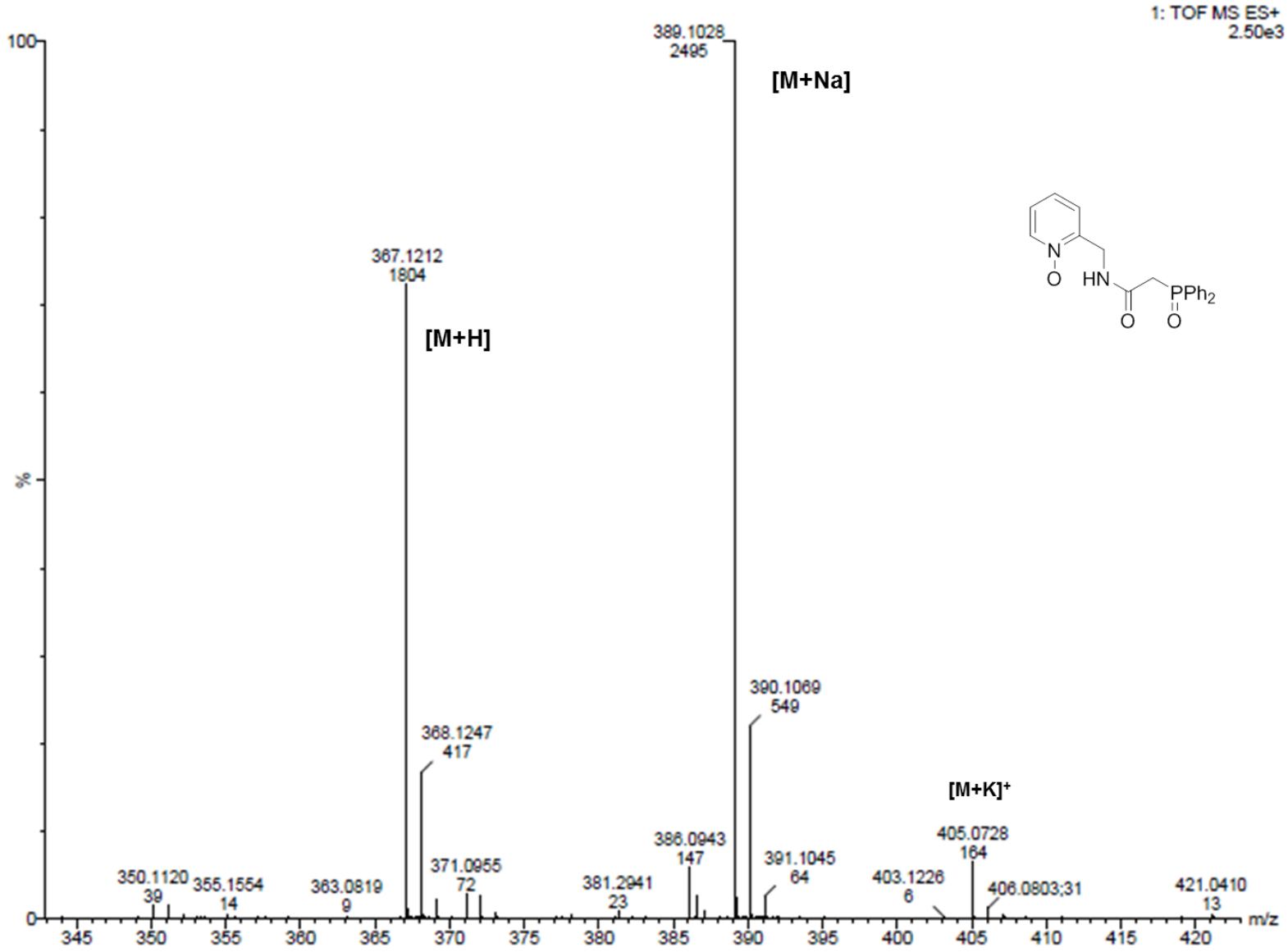

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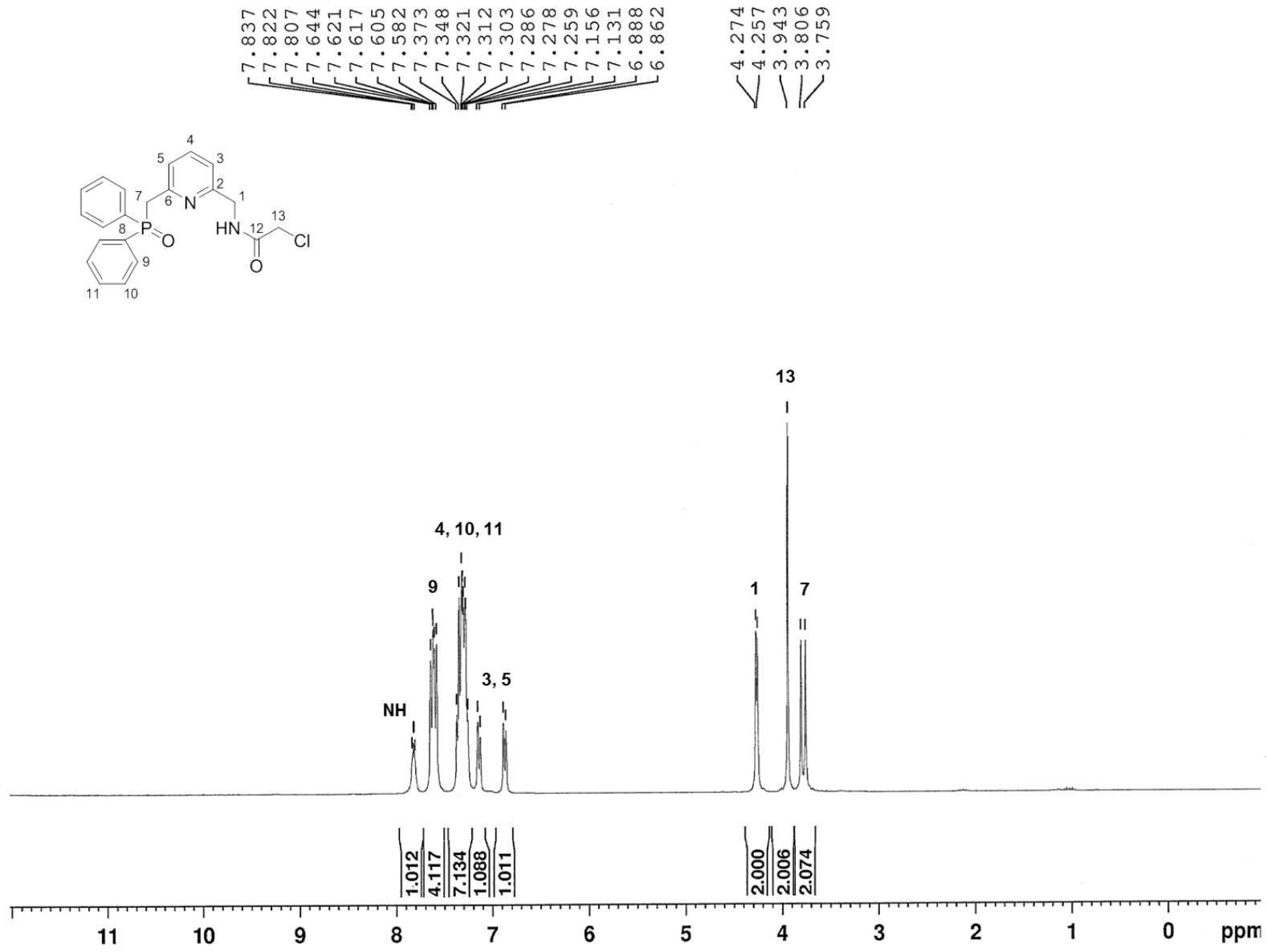

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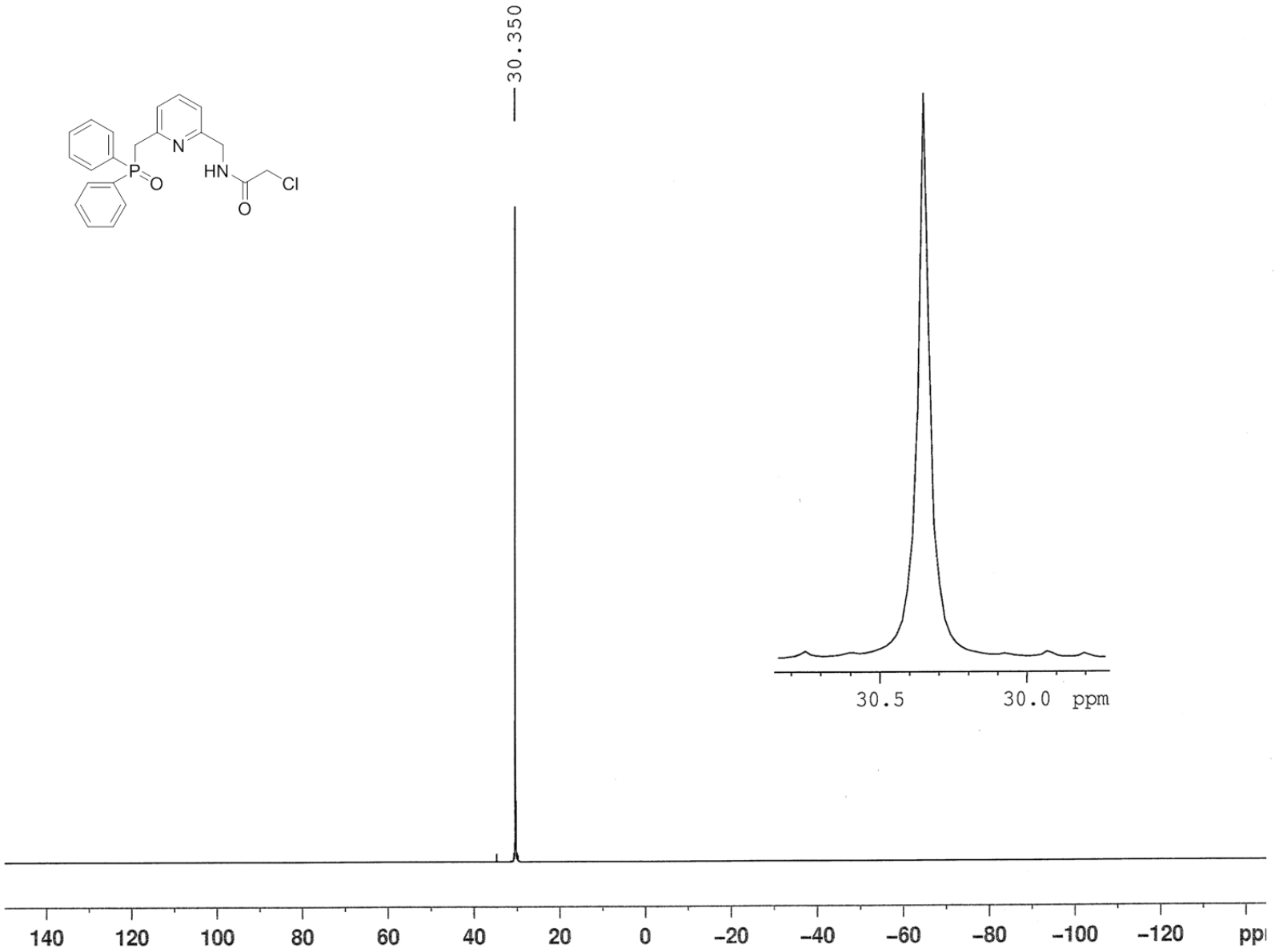

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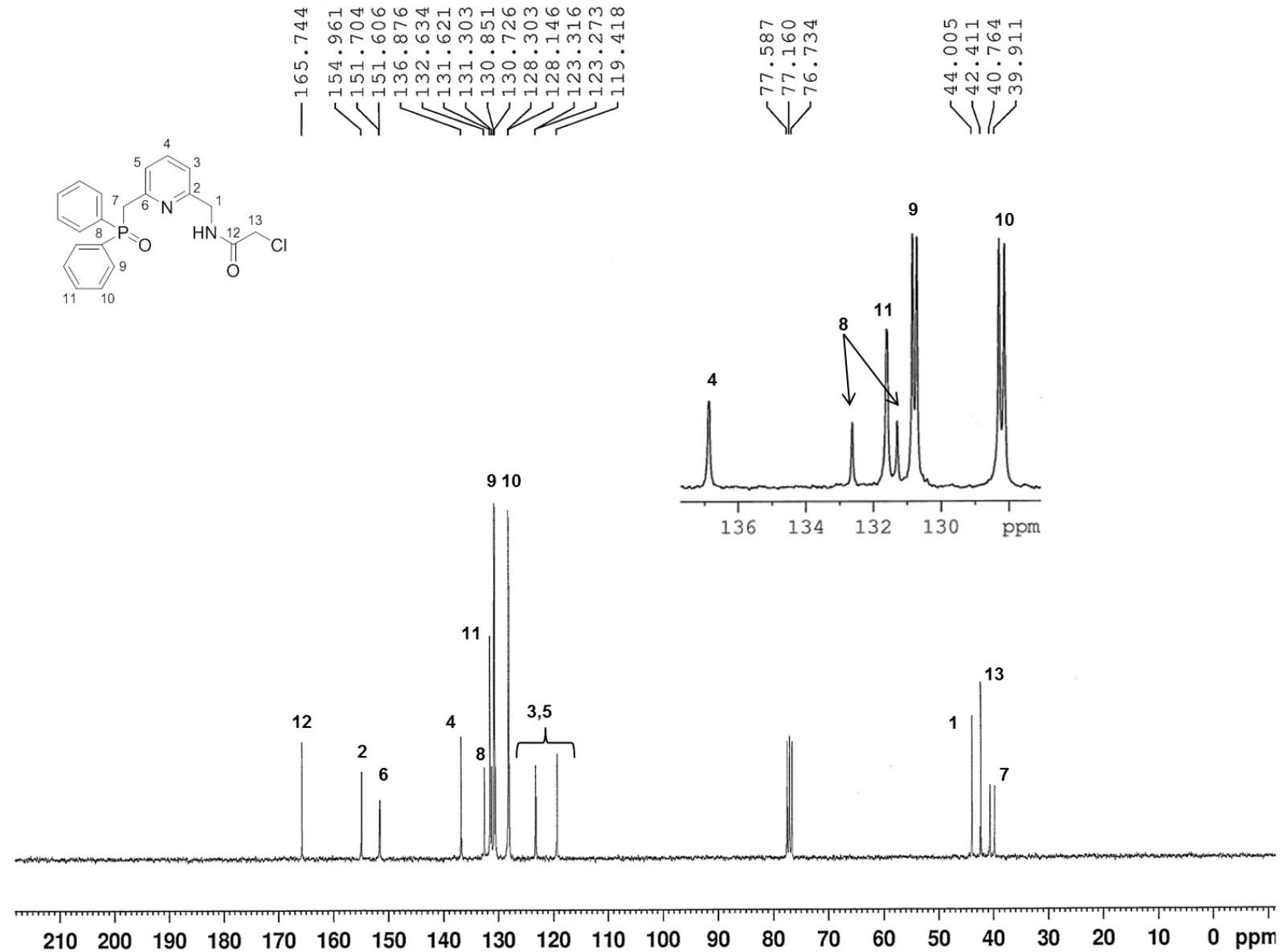

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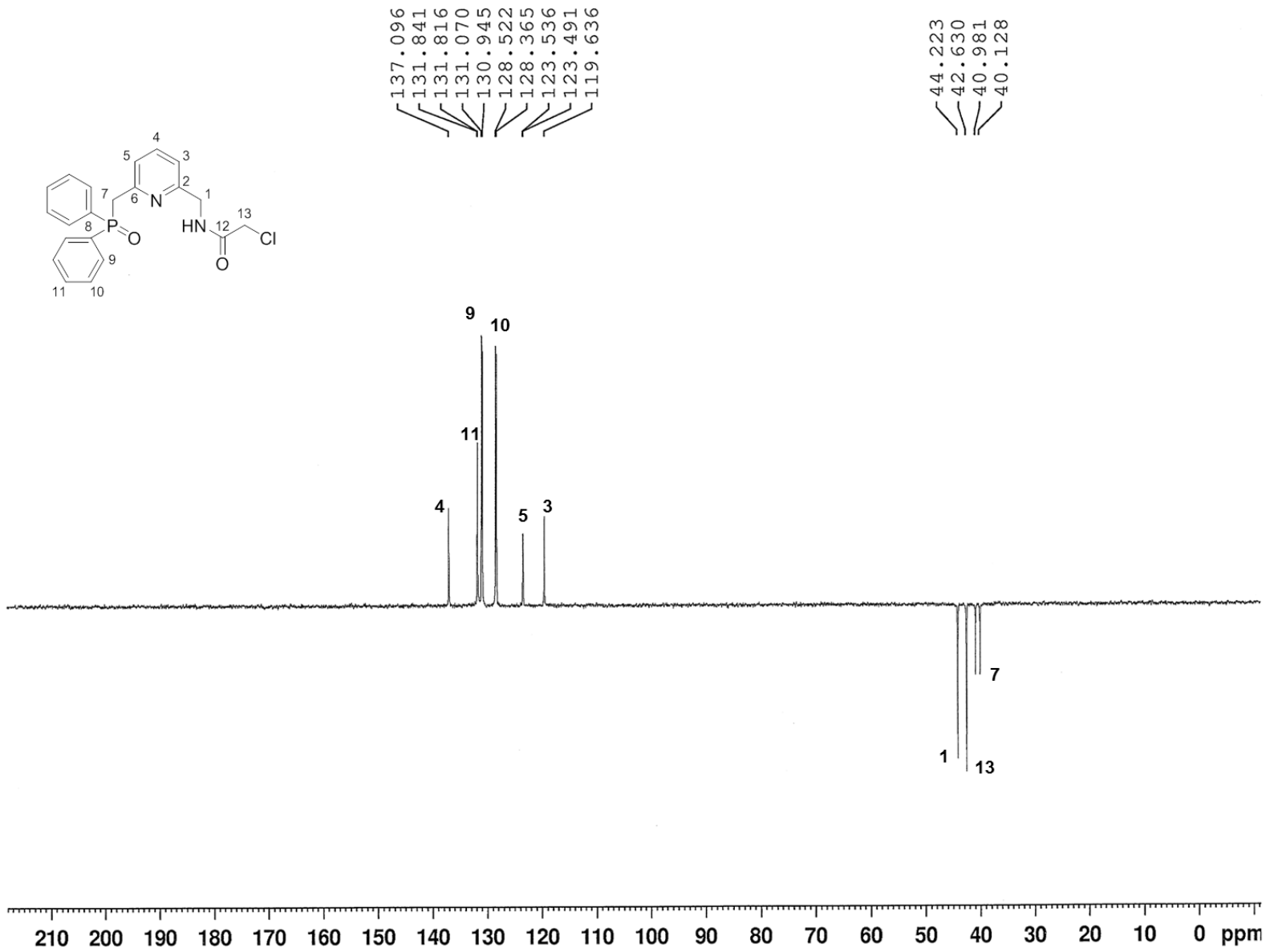

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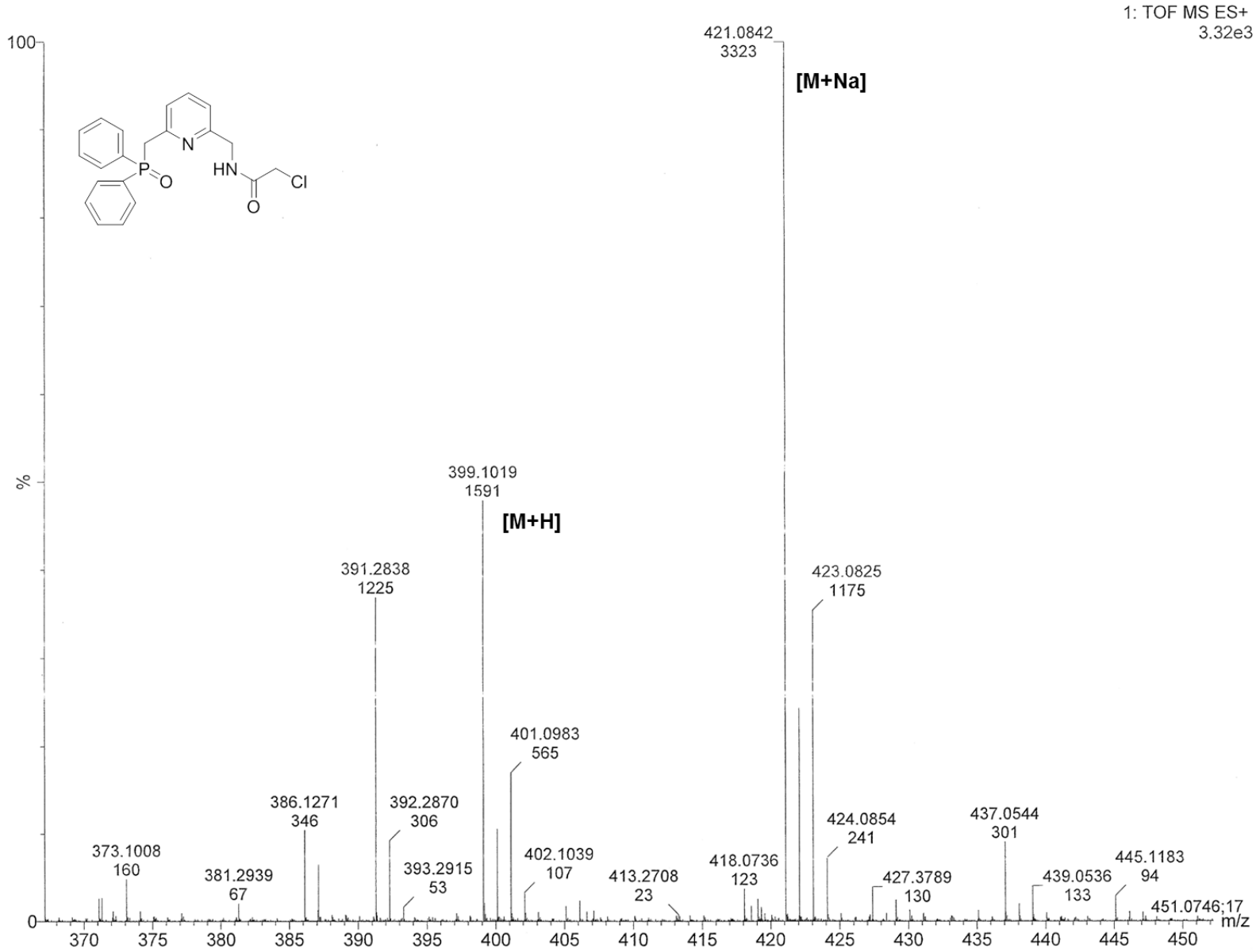
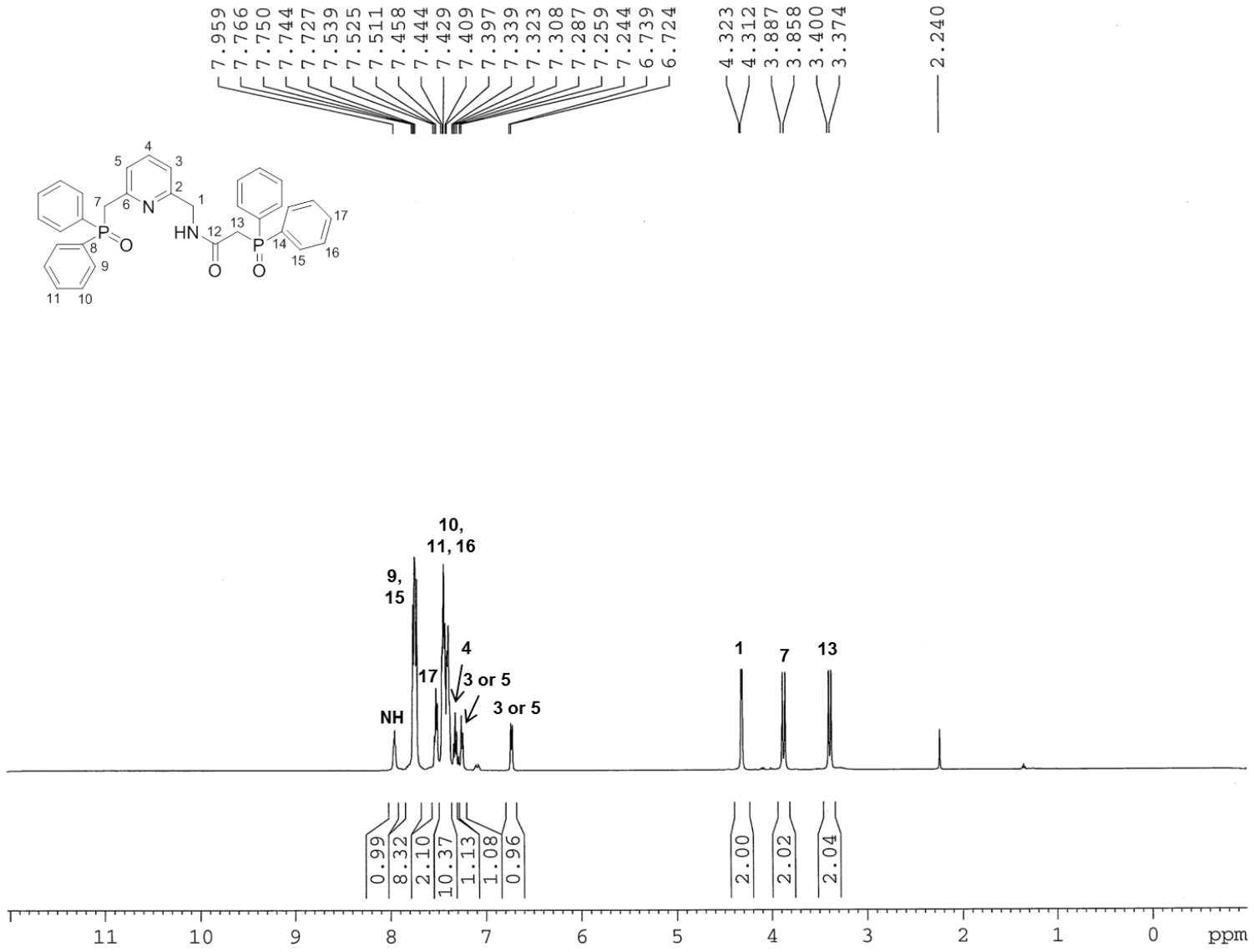
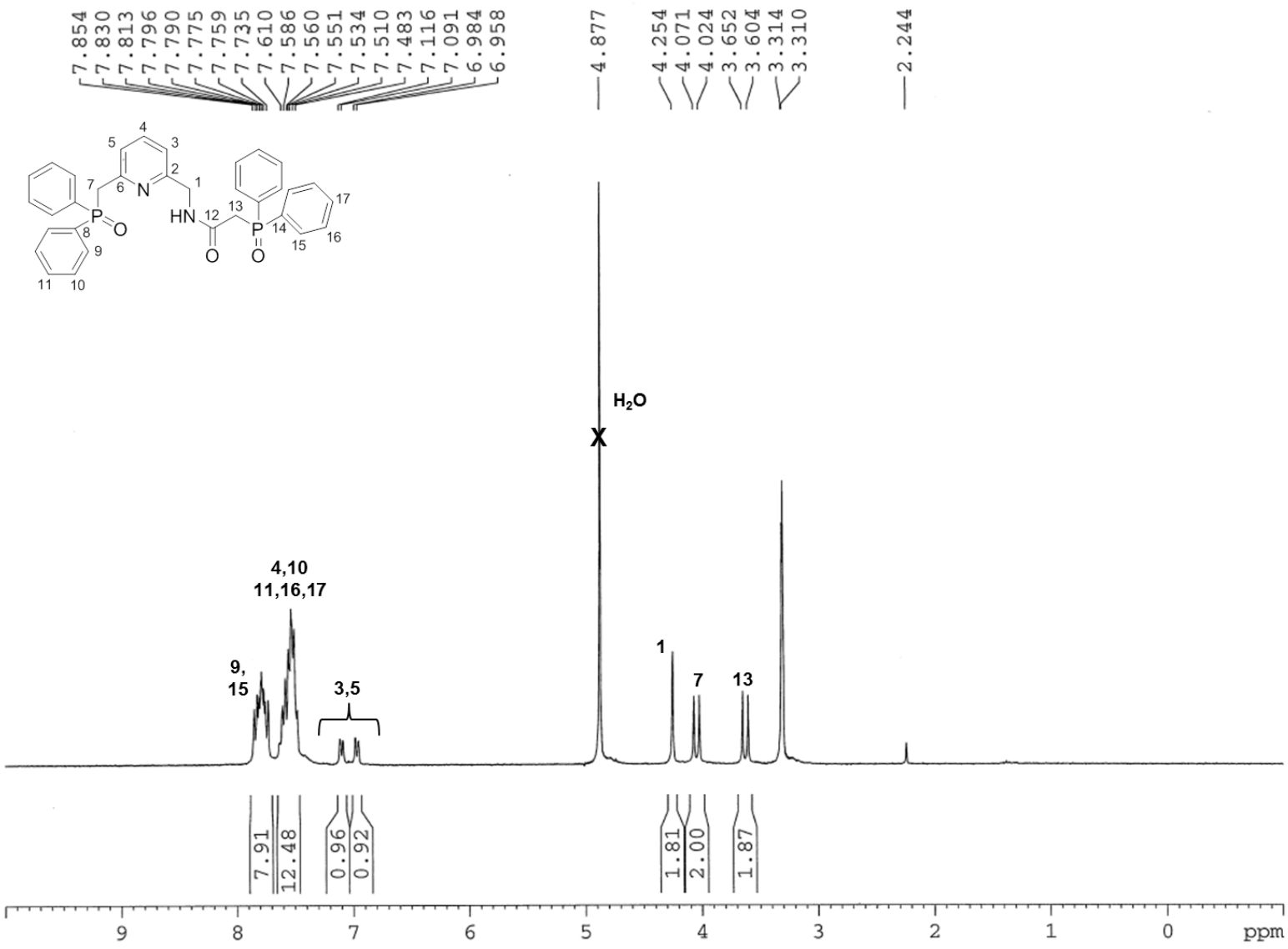


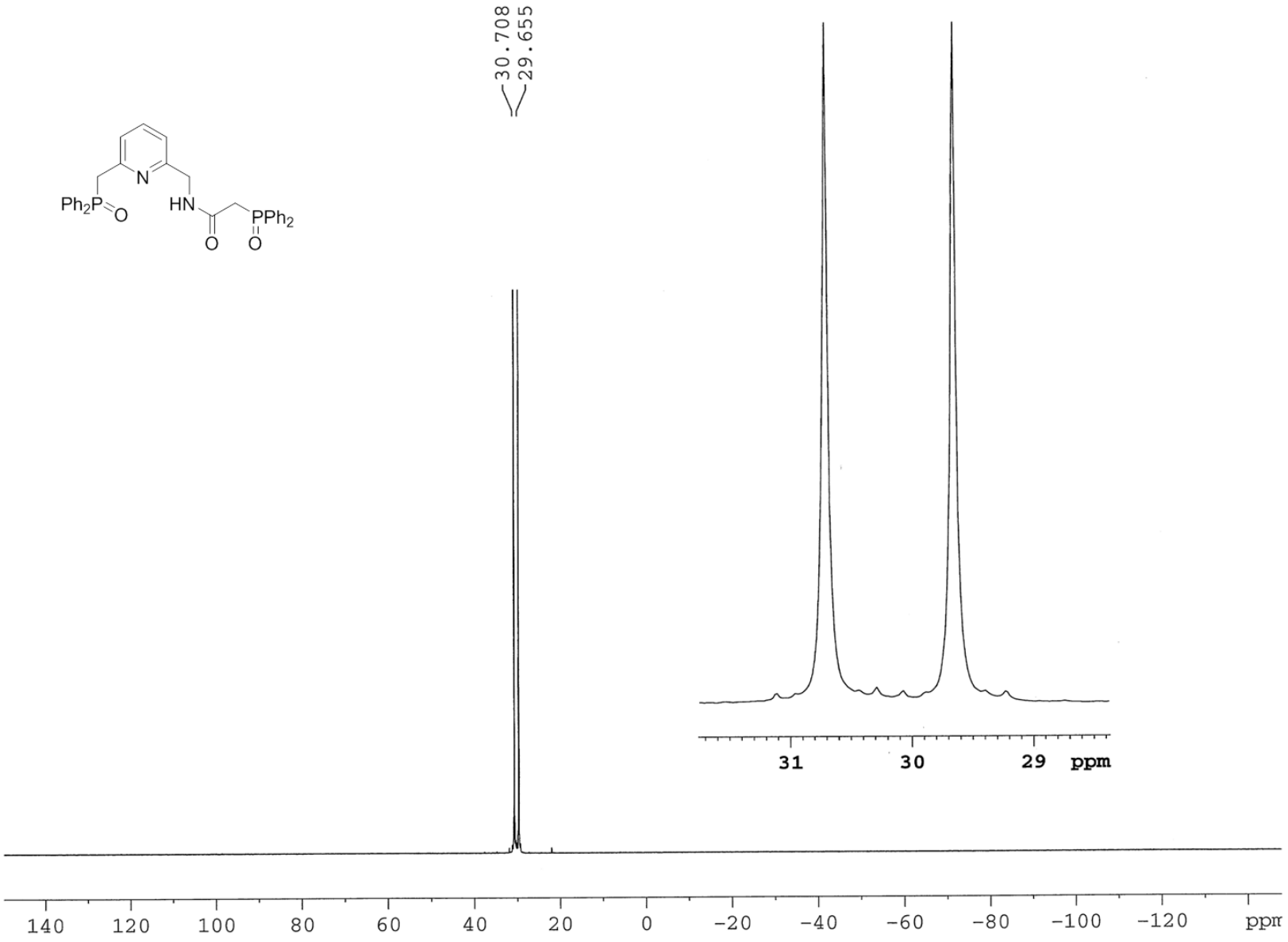
S.26 HRMS spectrum for 12



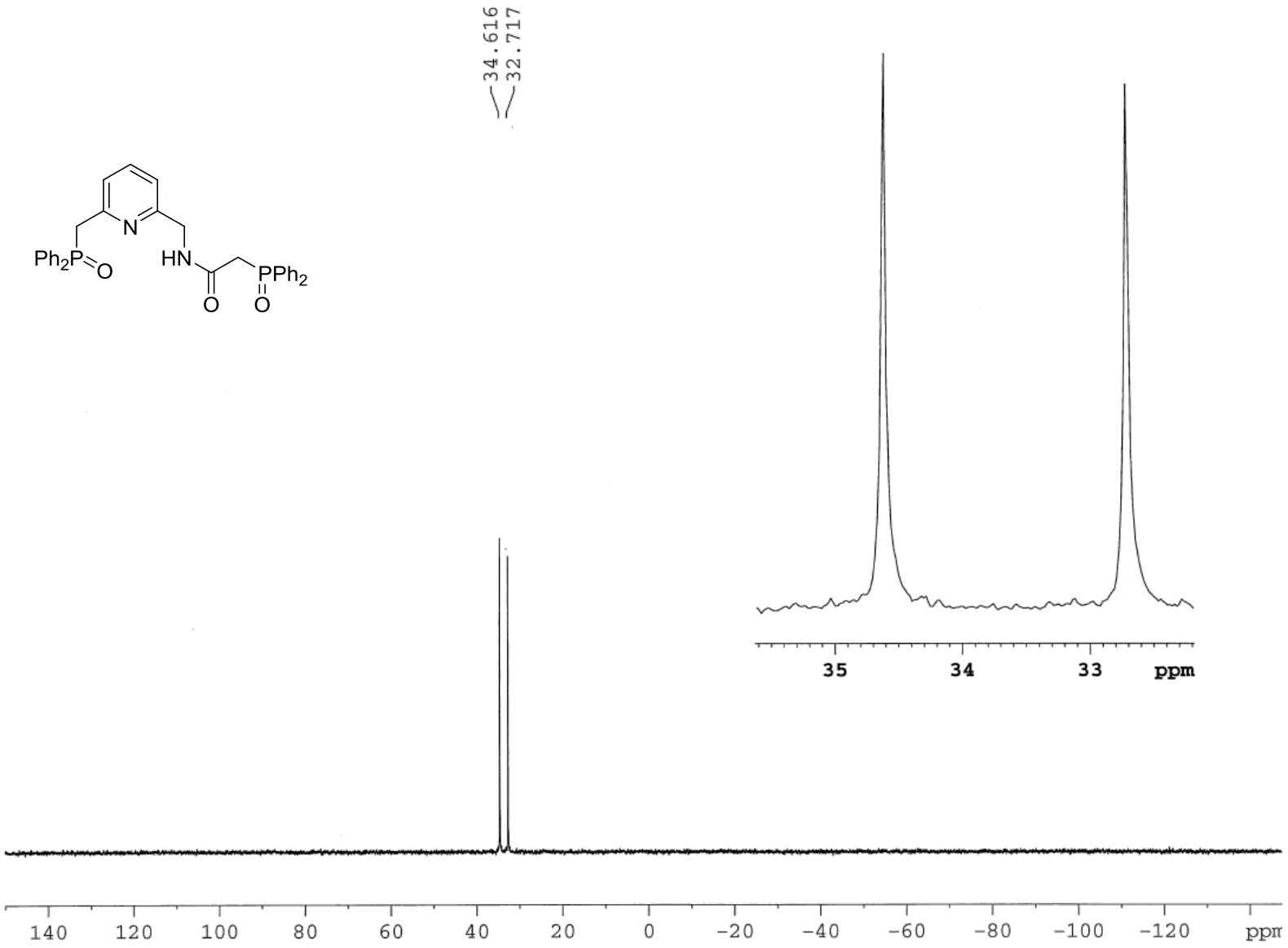
S.27 ^{1}H NMR spectrum for 13, in $CDCl_3$



S.28 ^{1}H NMR spectrum for 13, in d_4-MeOH



S.29 ^{31}P NMR spectrum for 13, in $CDCl_3$



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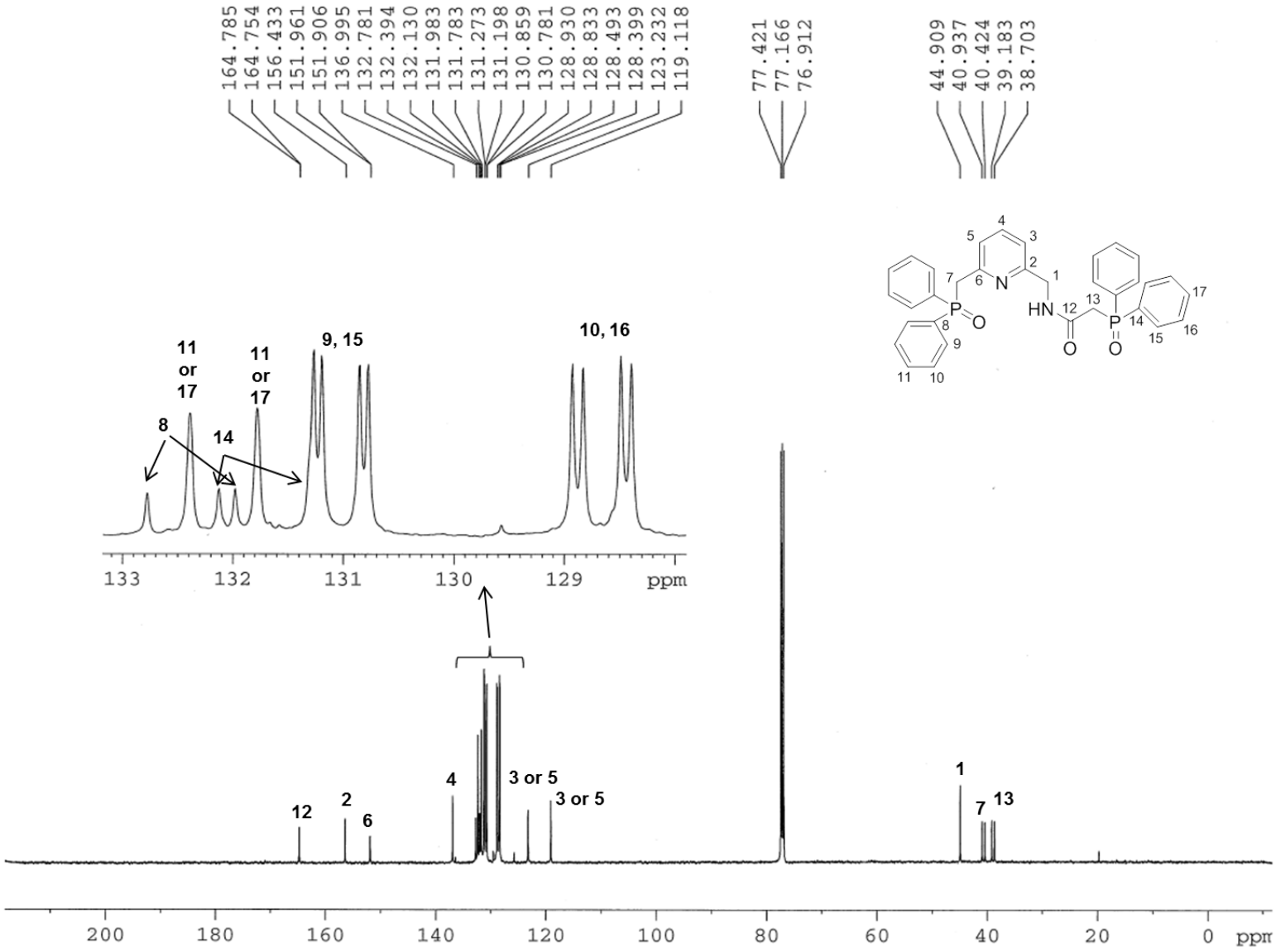

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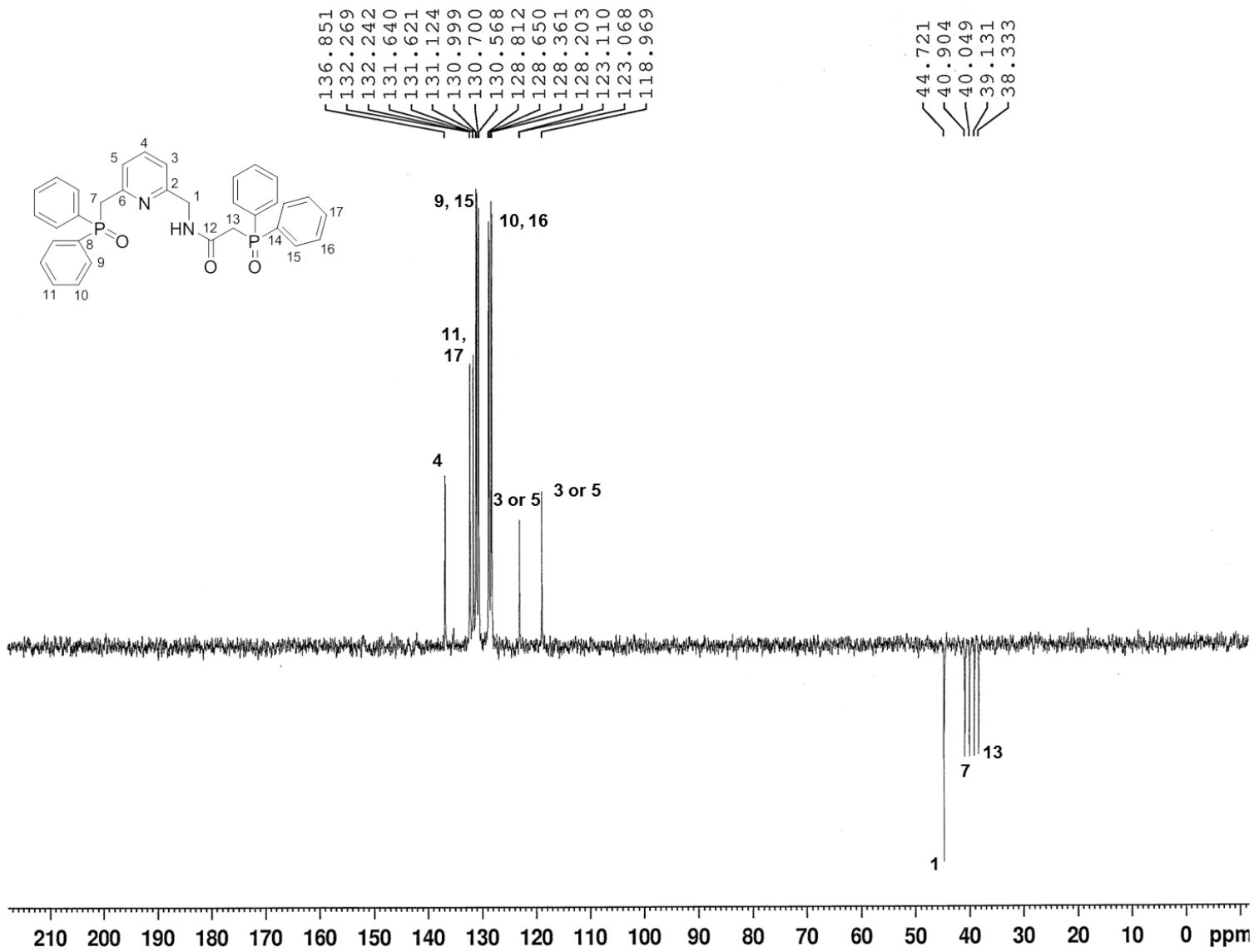

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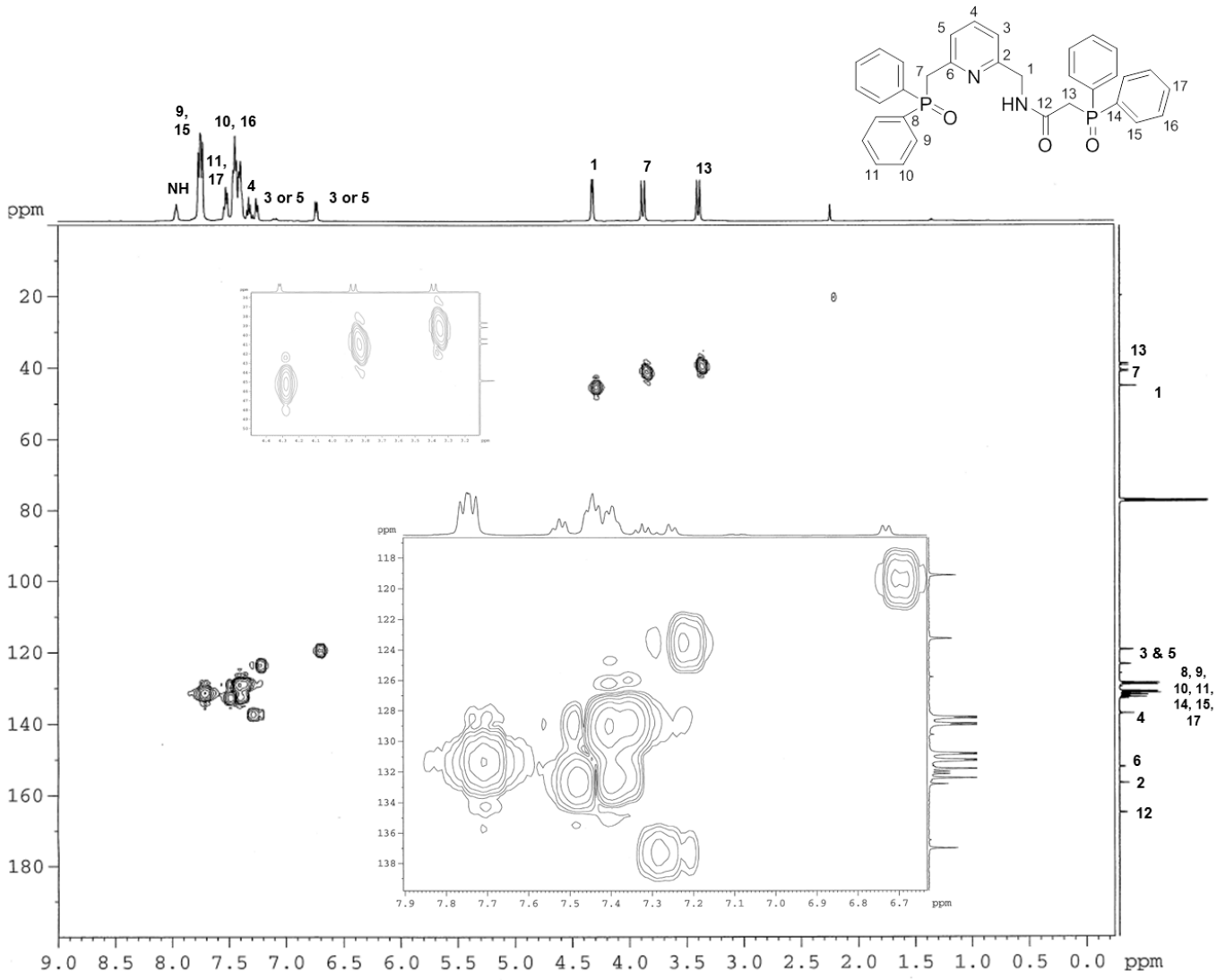

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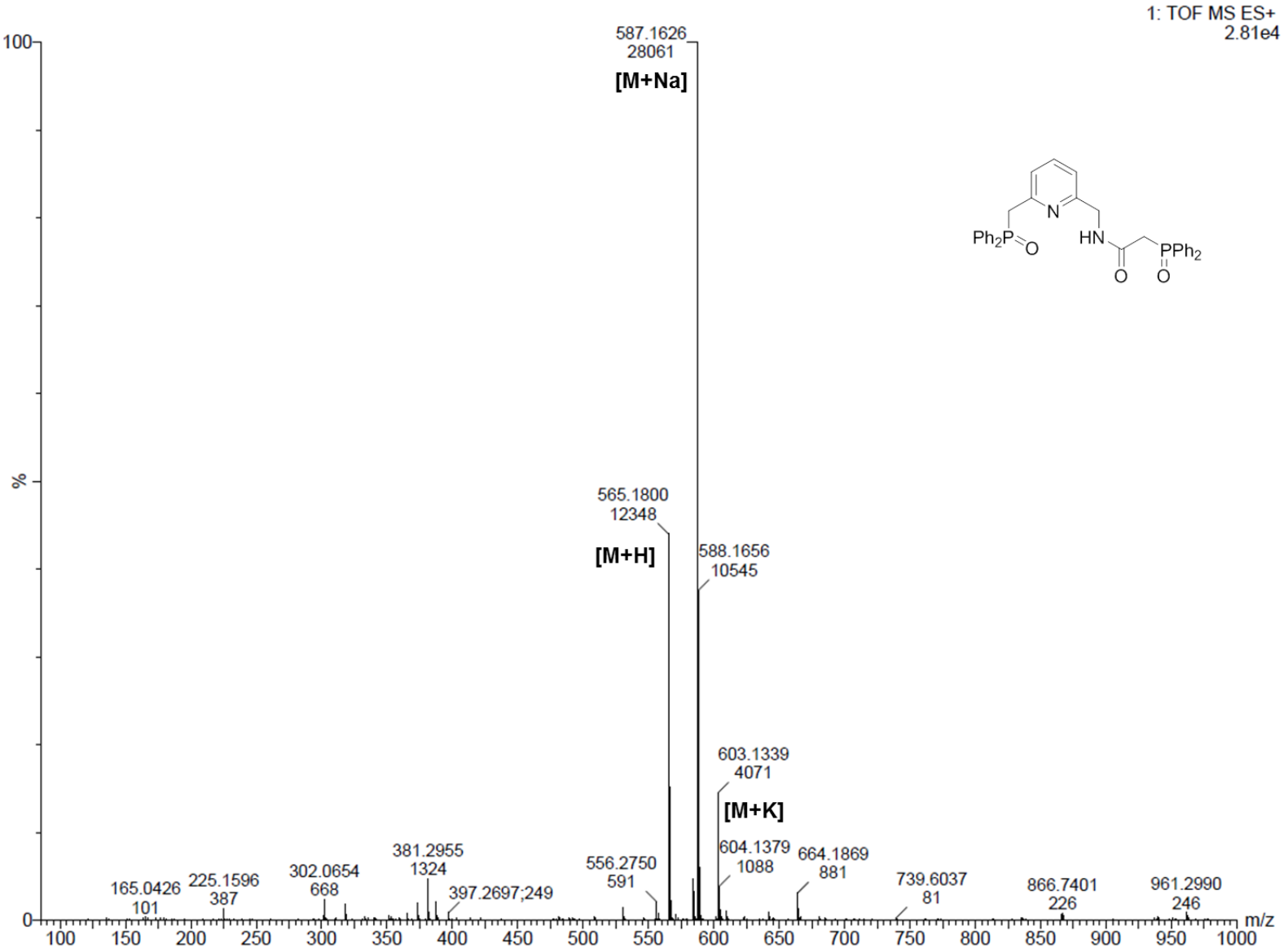

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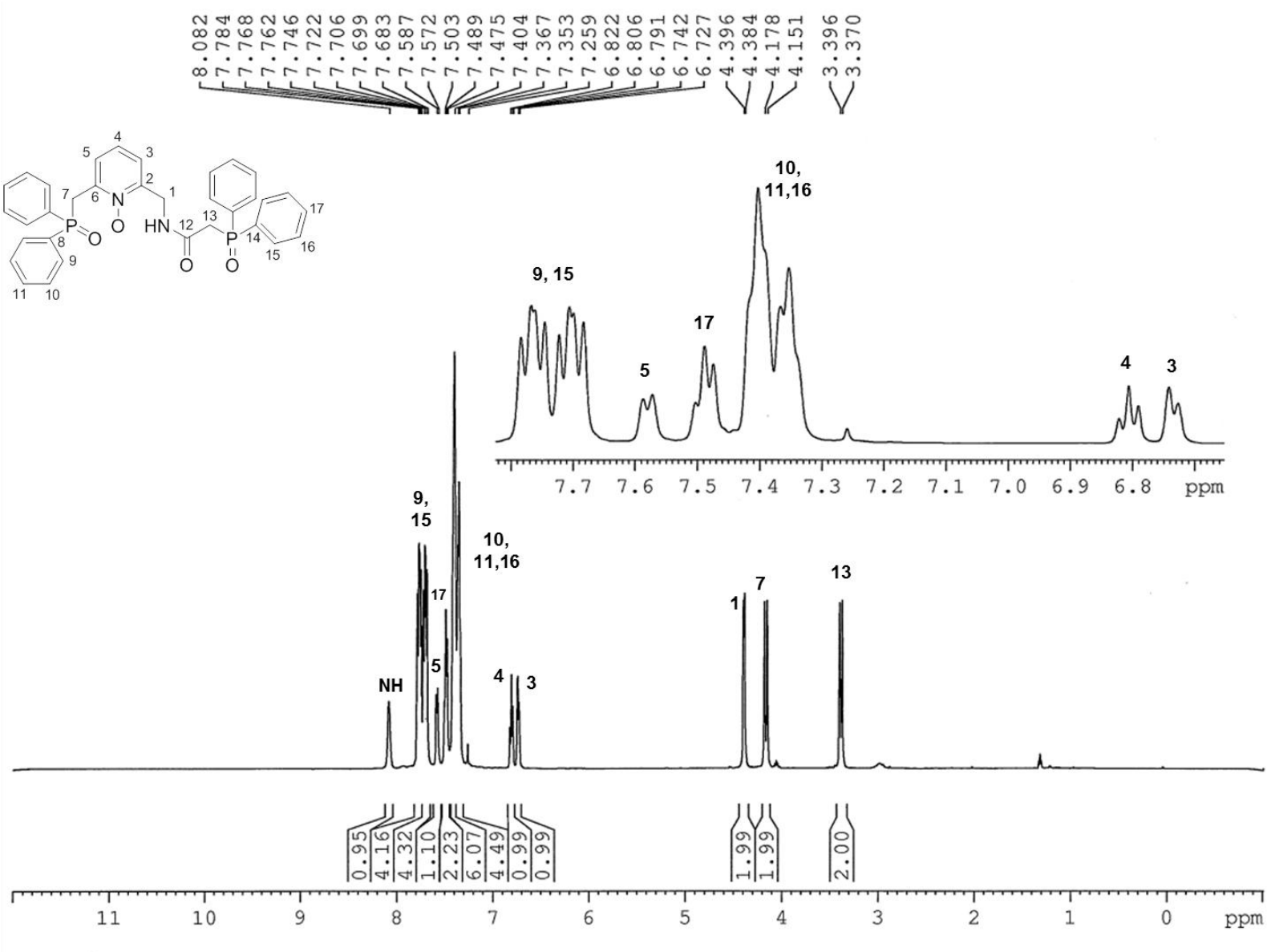
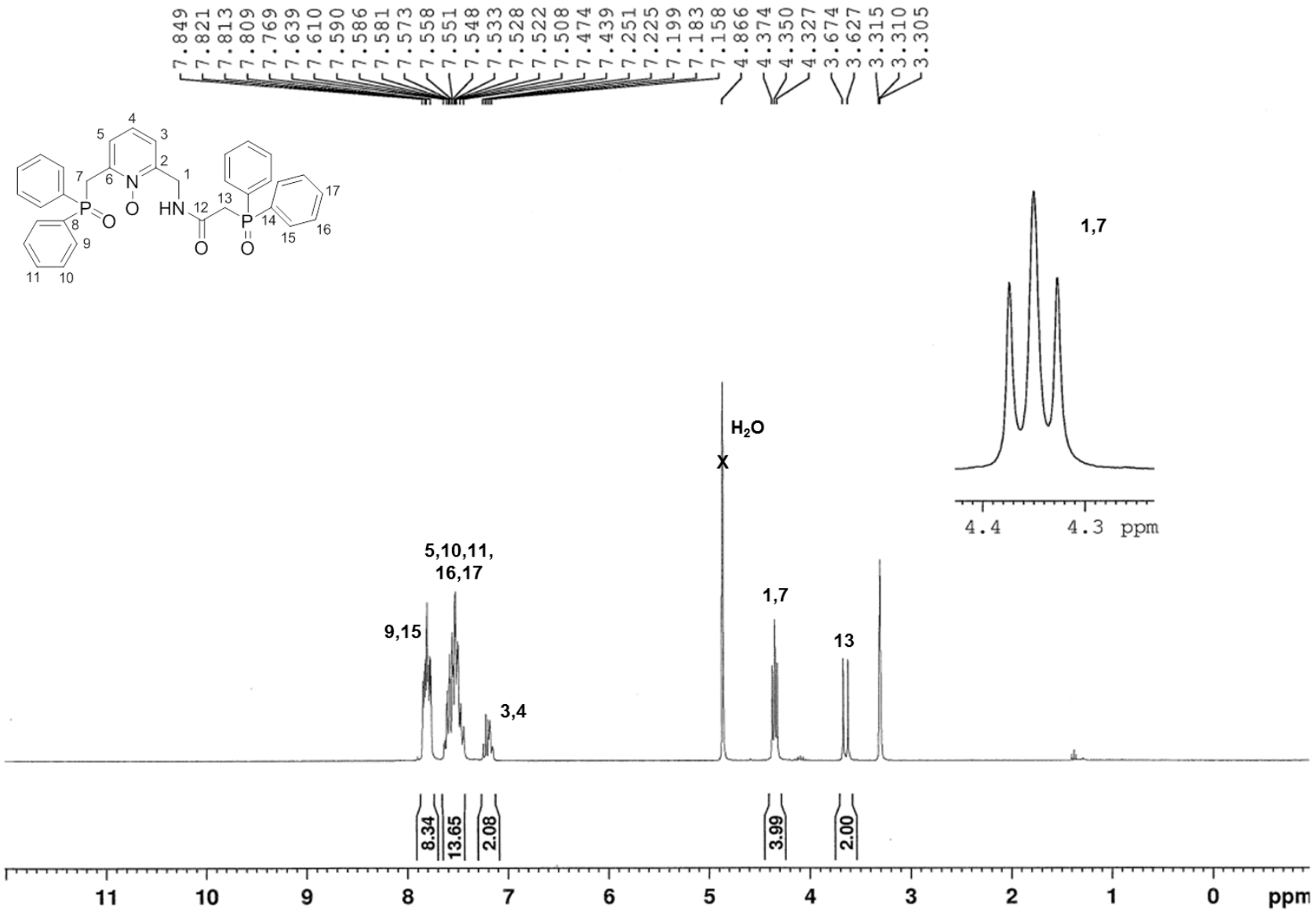
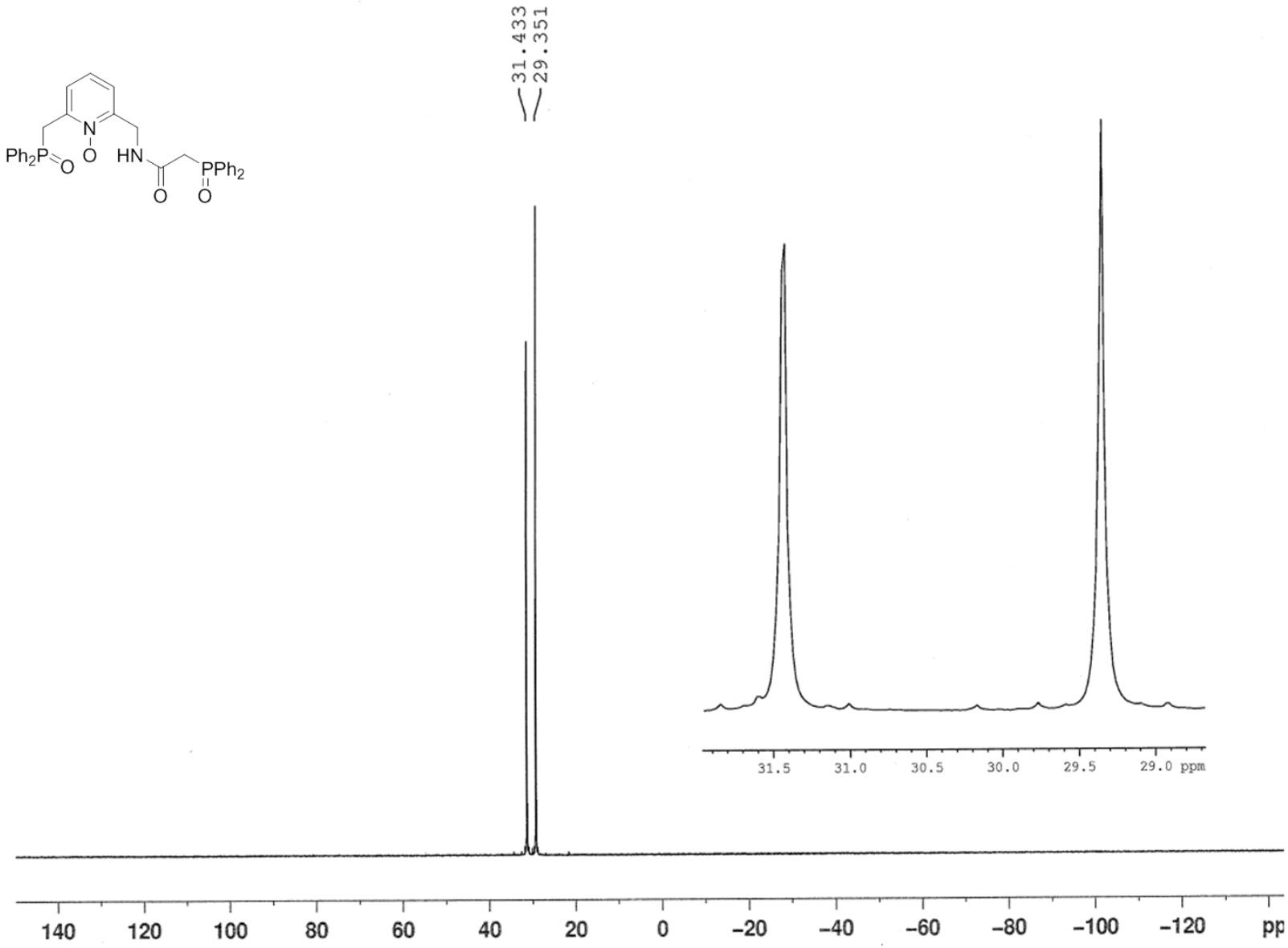


S.35 ^{1}H NMR spectrum for 7, in $CDCl_3$



S.36 ^{1}H NMR spectrum for 7, in d_4-MeOH



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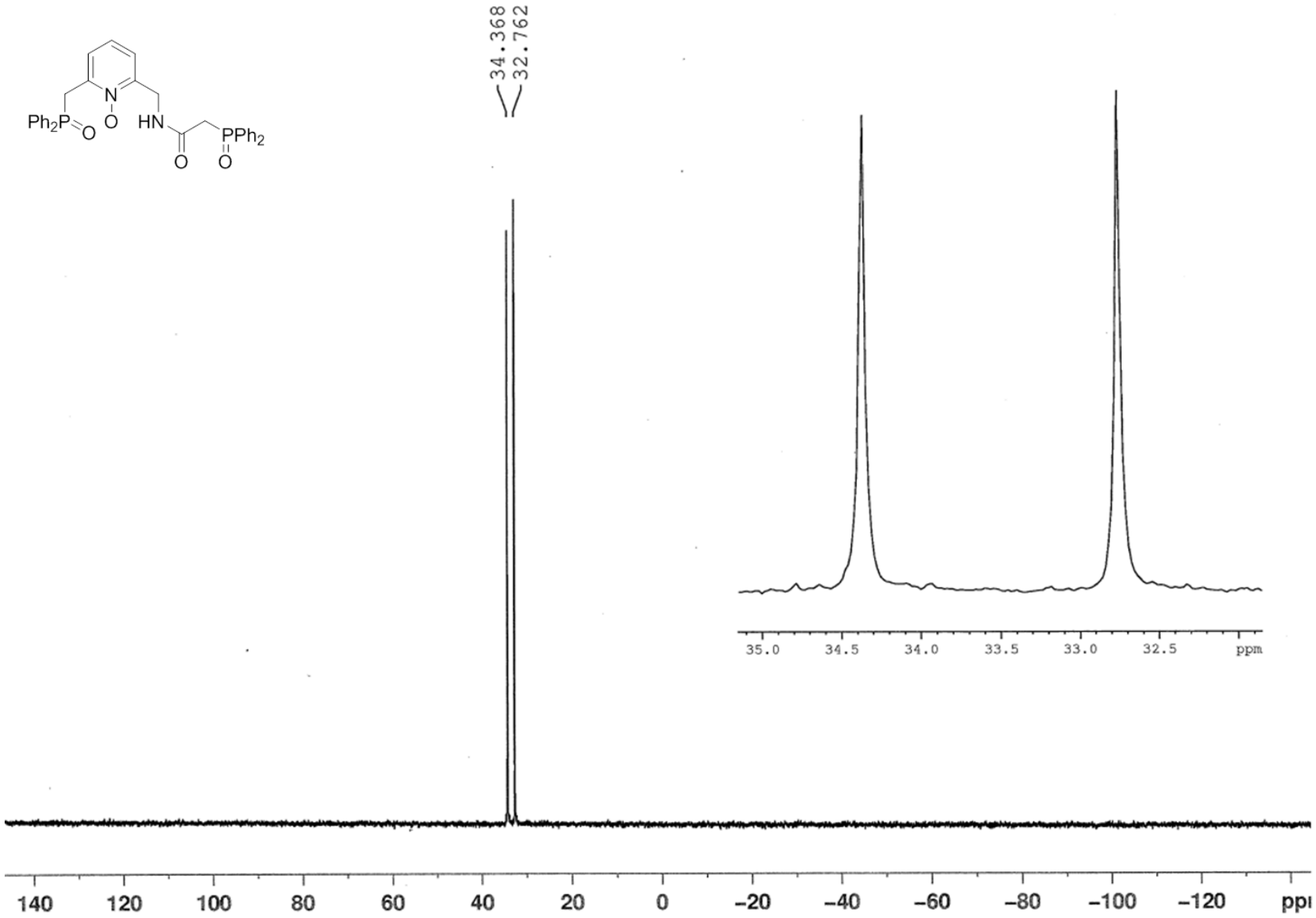

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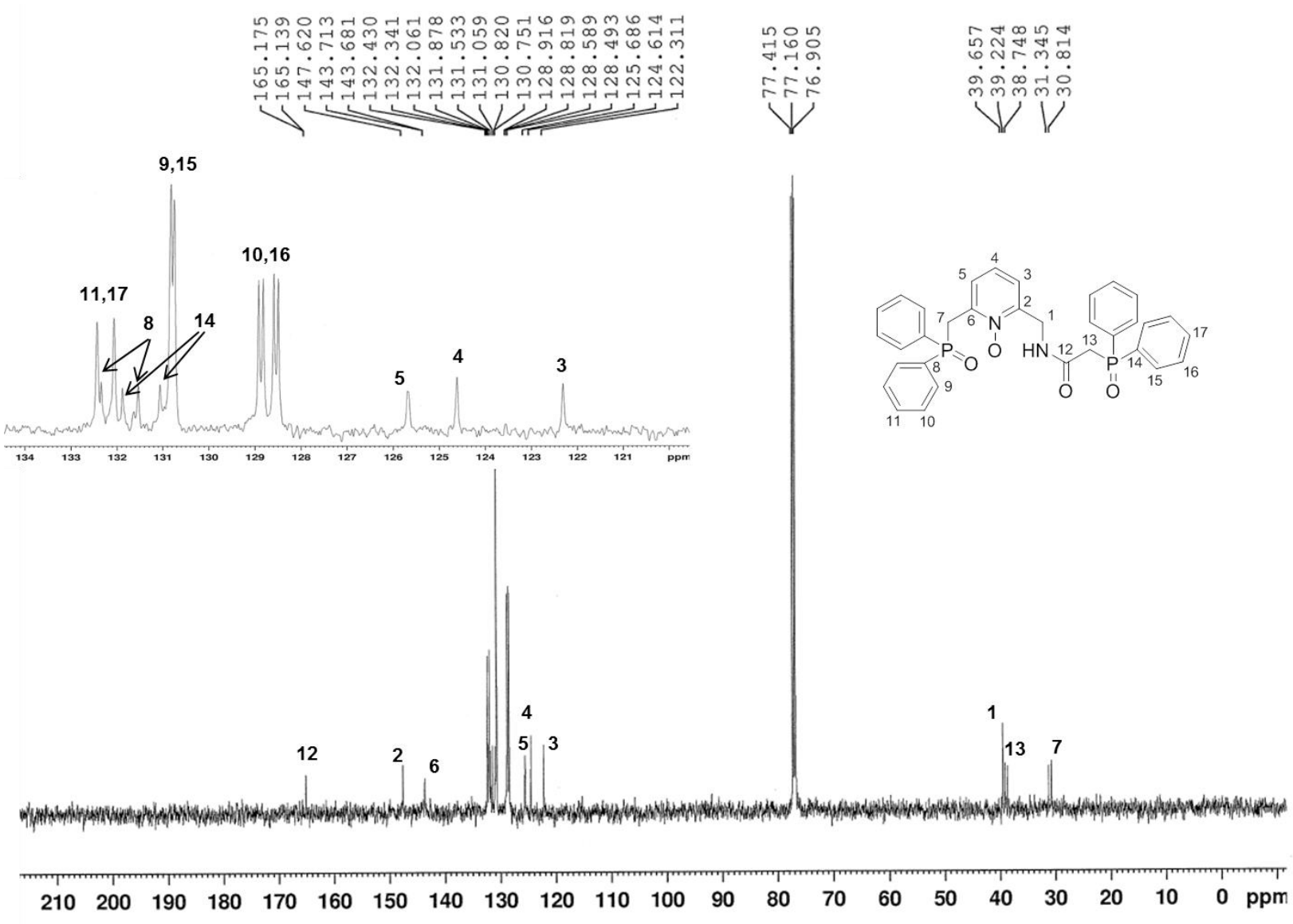

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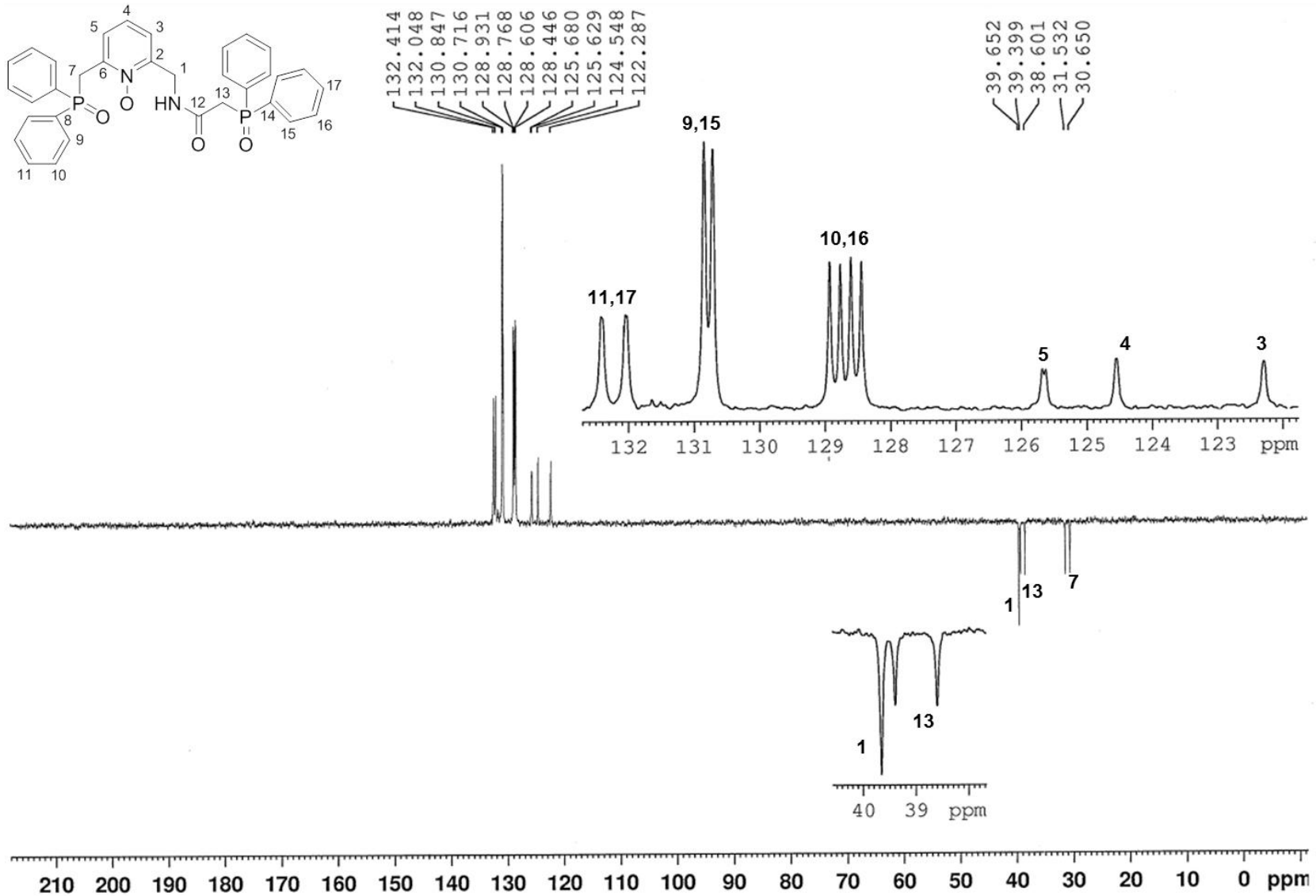

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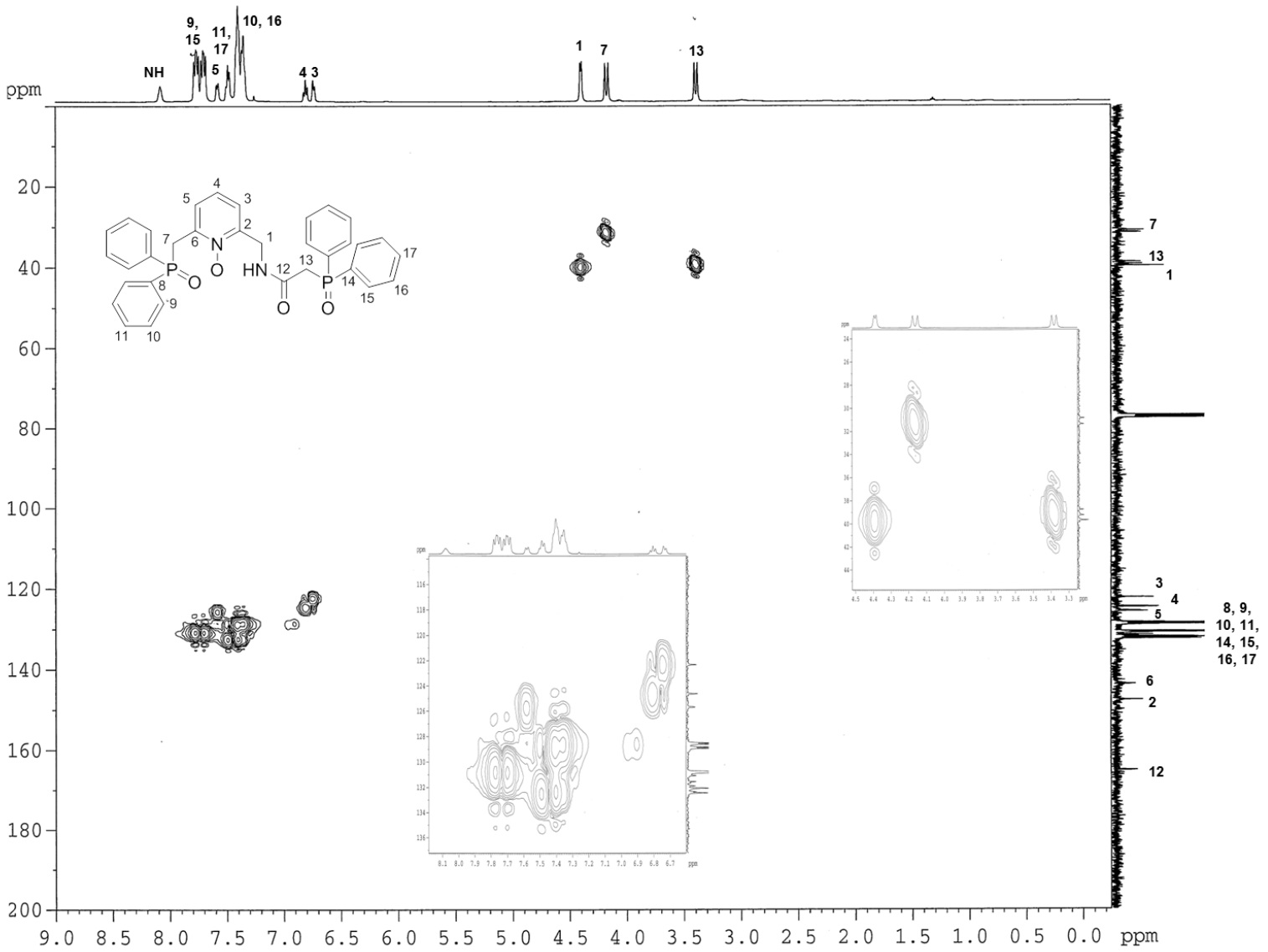

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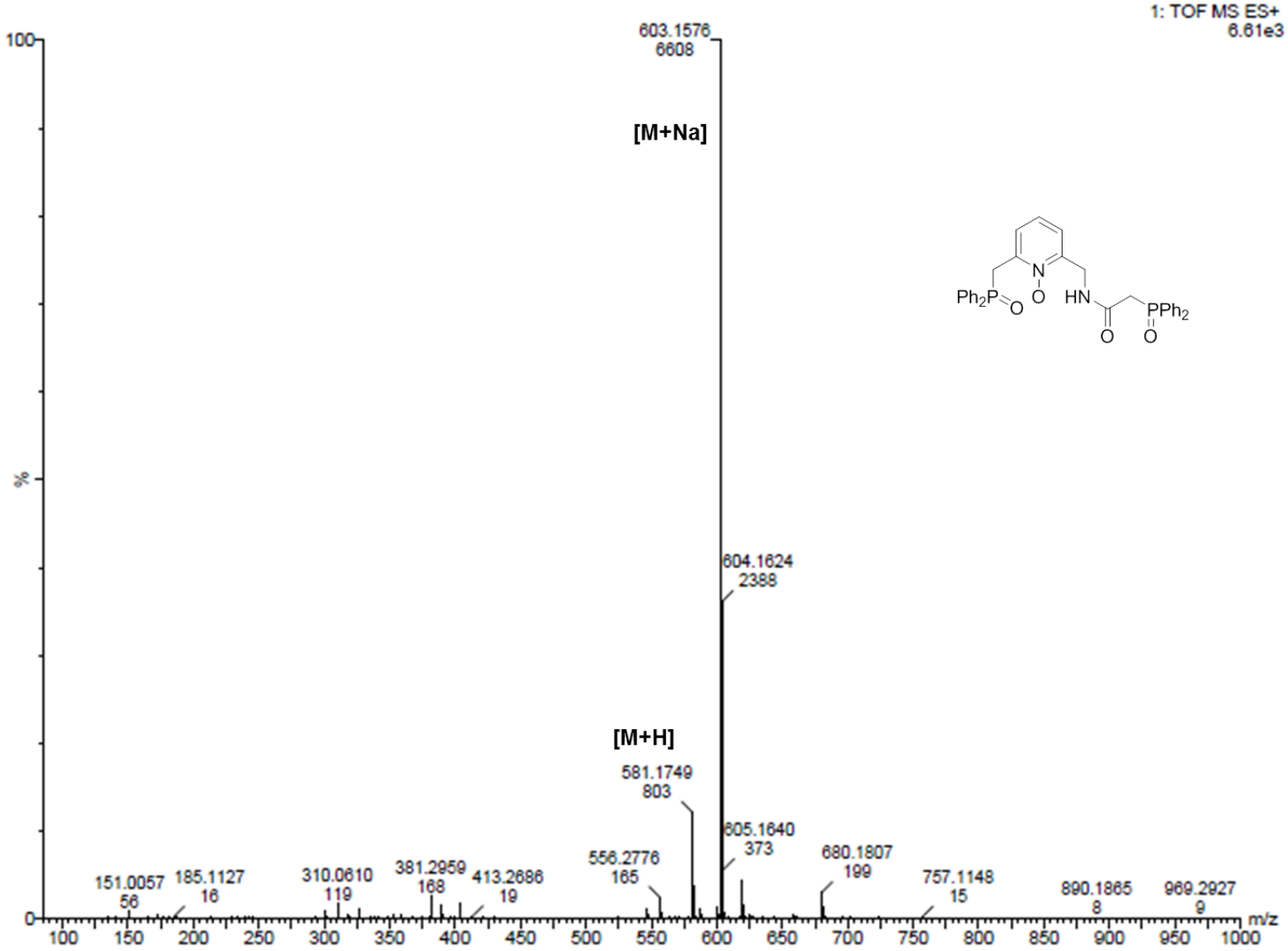
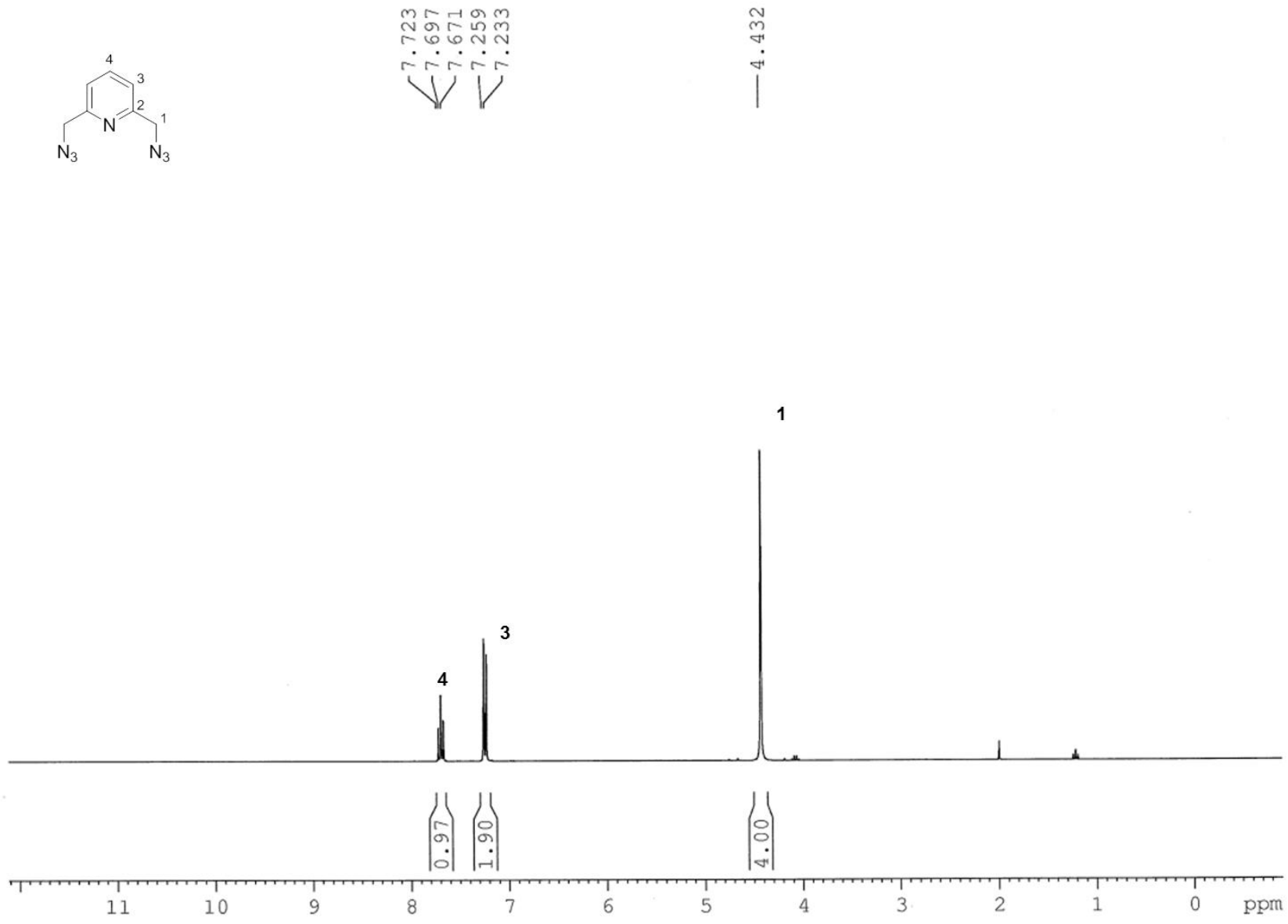


S.42 HRMS spectrum for 7



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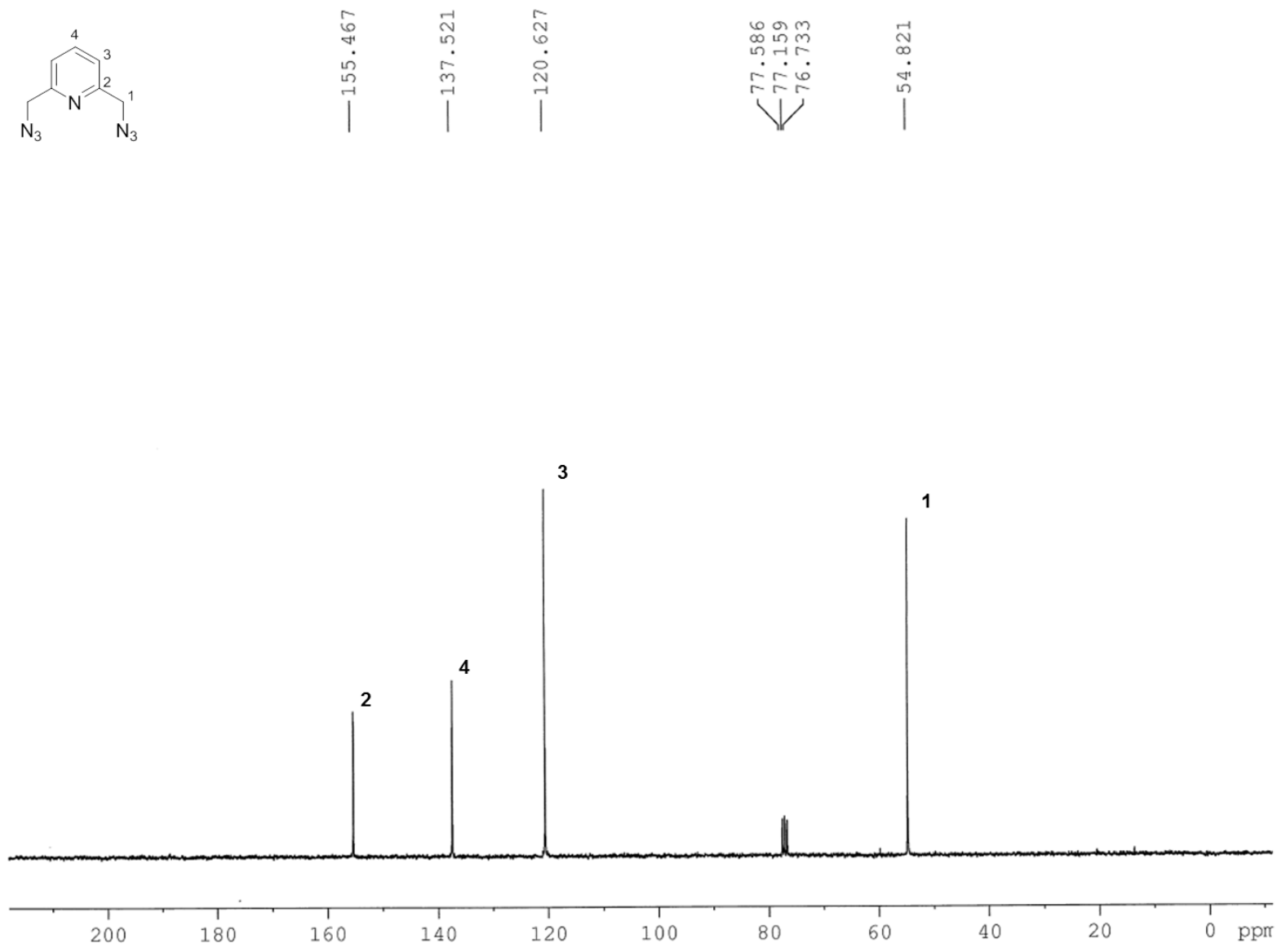
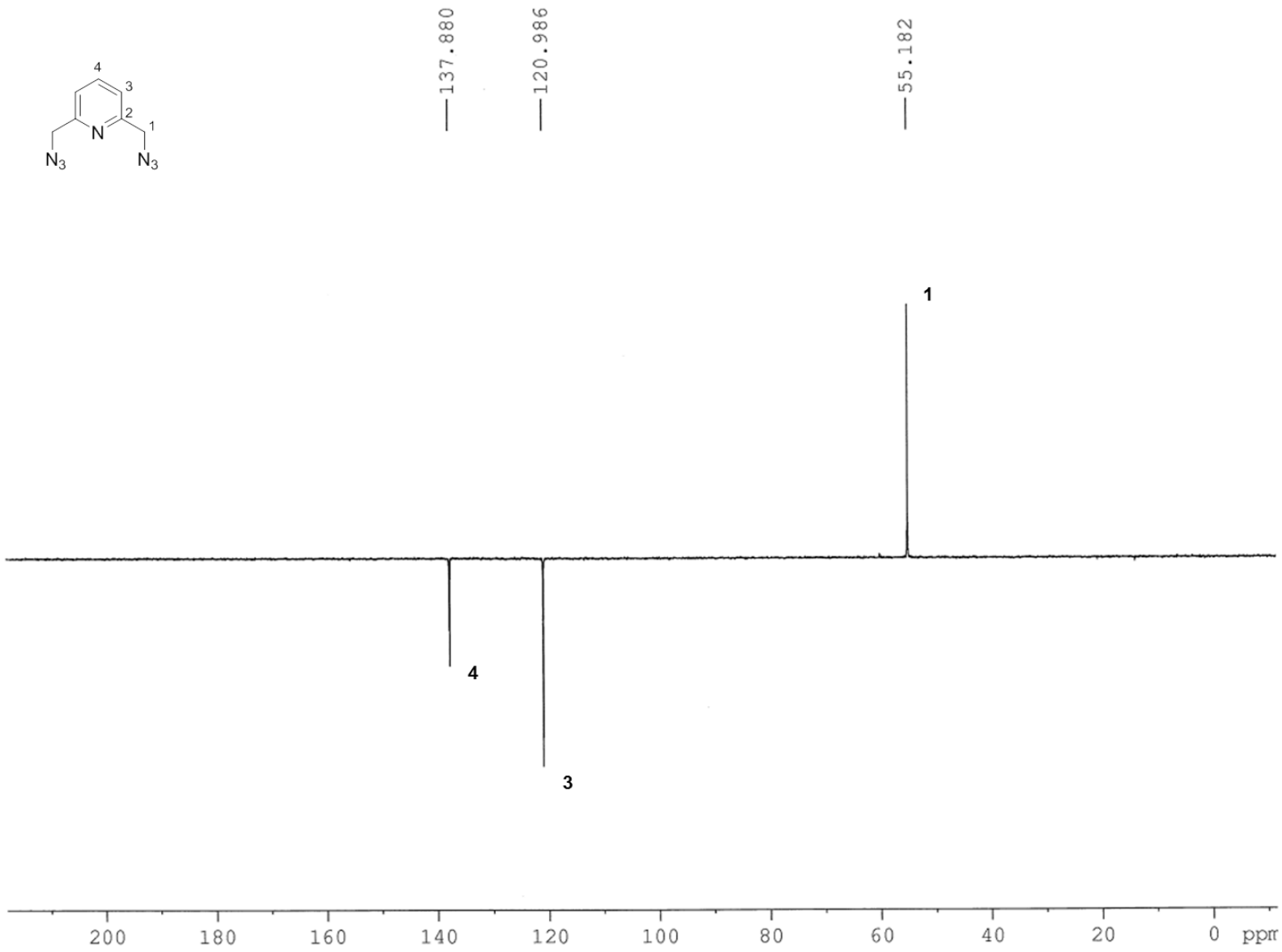


S.44 ^{13}C NMR spectrum for 15, in $CDCl_3$



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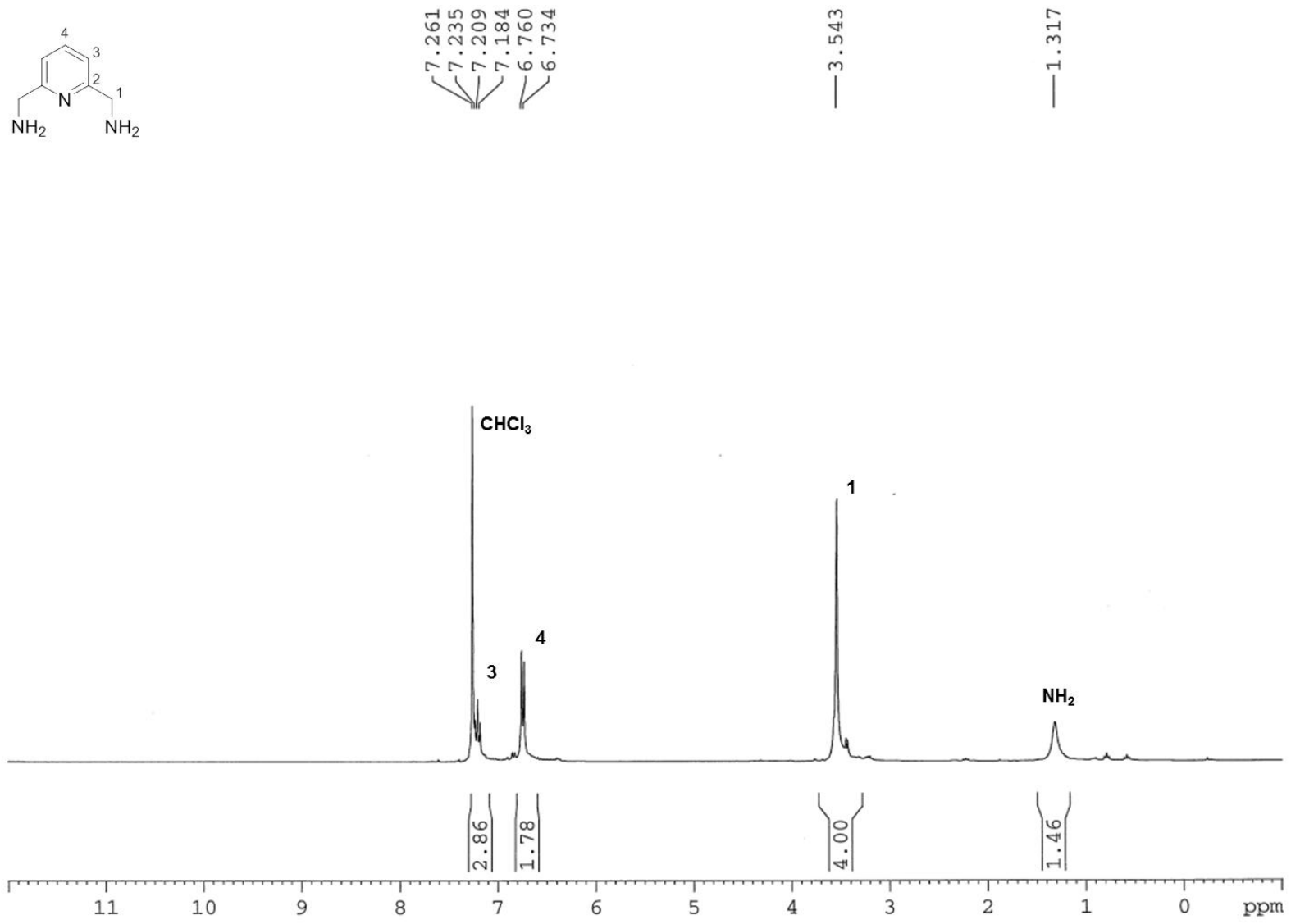
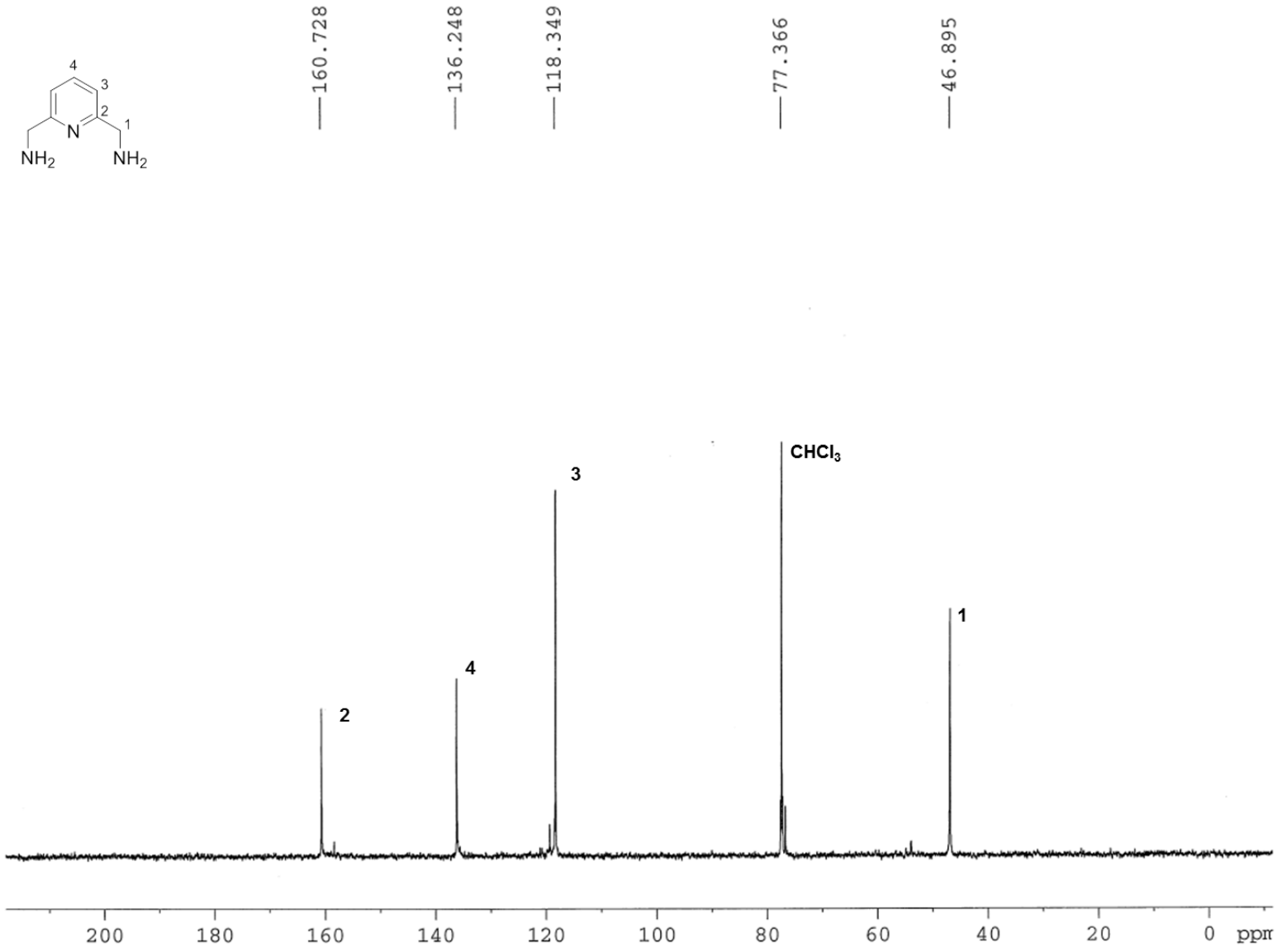


S.46 ^{1}H NMR spectrum for 16, in $CDCl_3$



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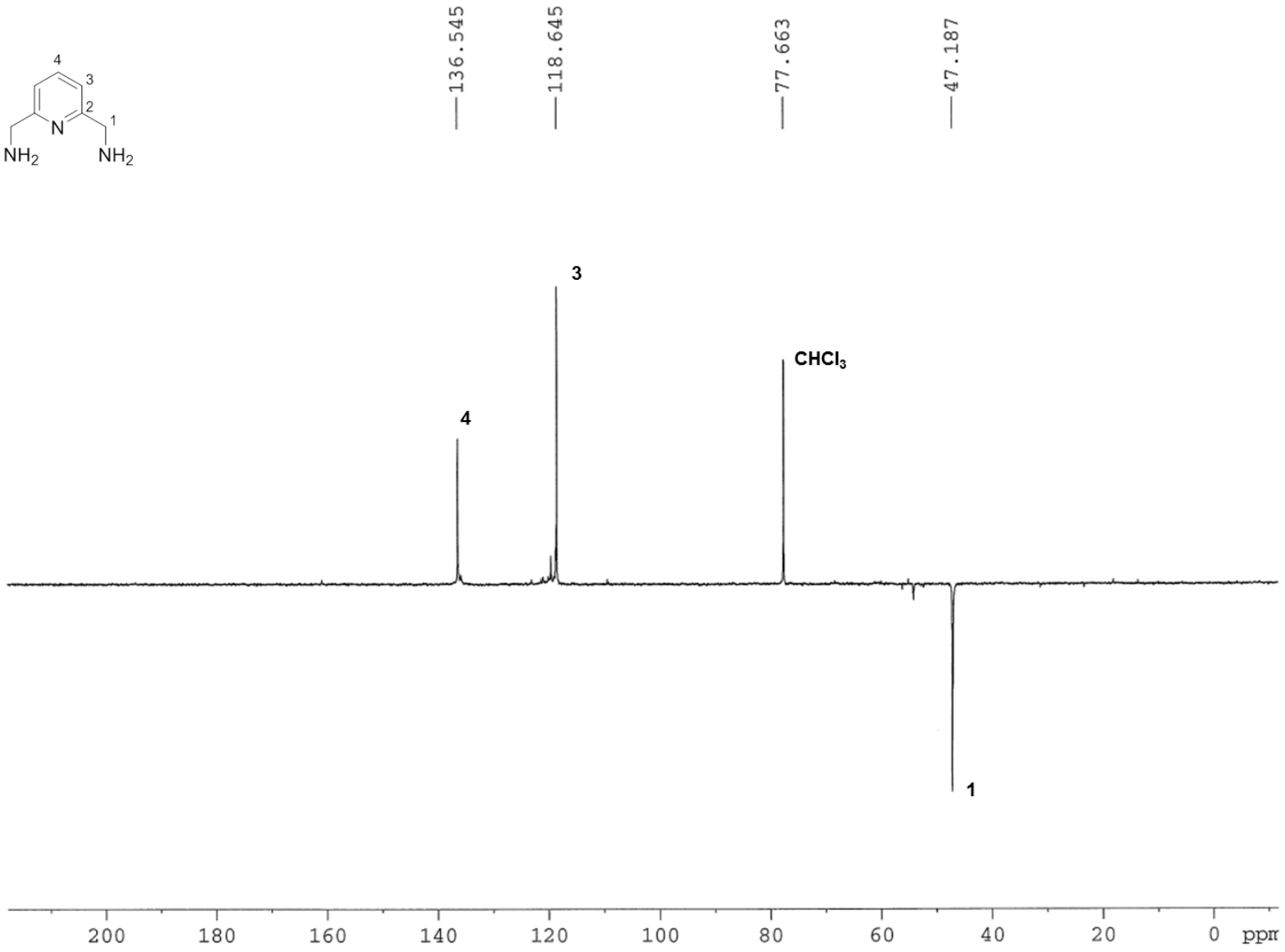

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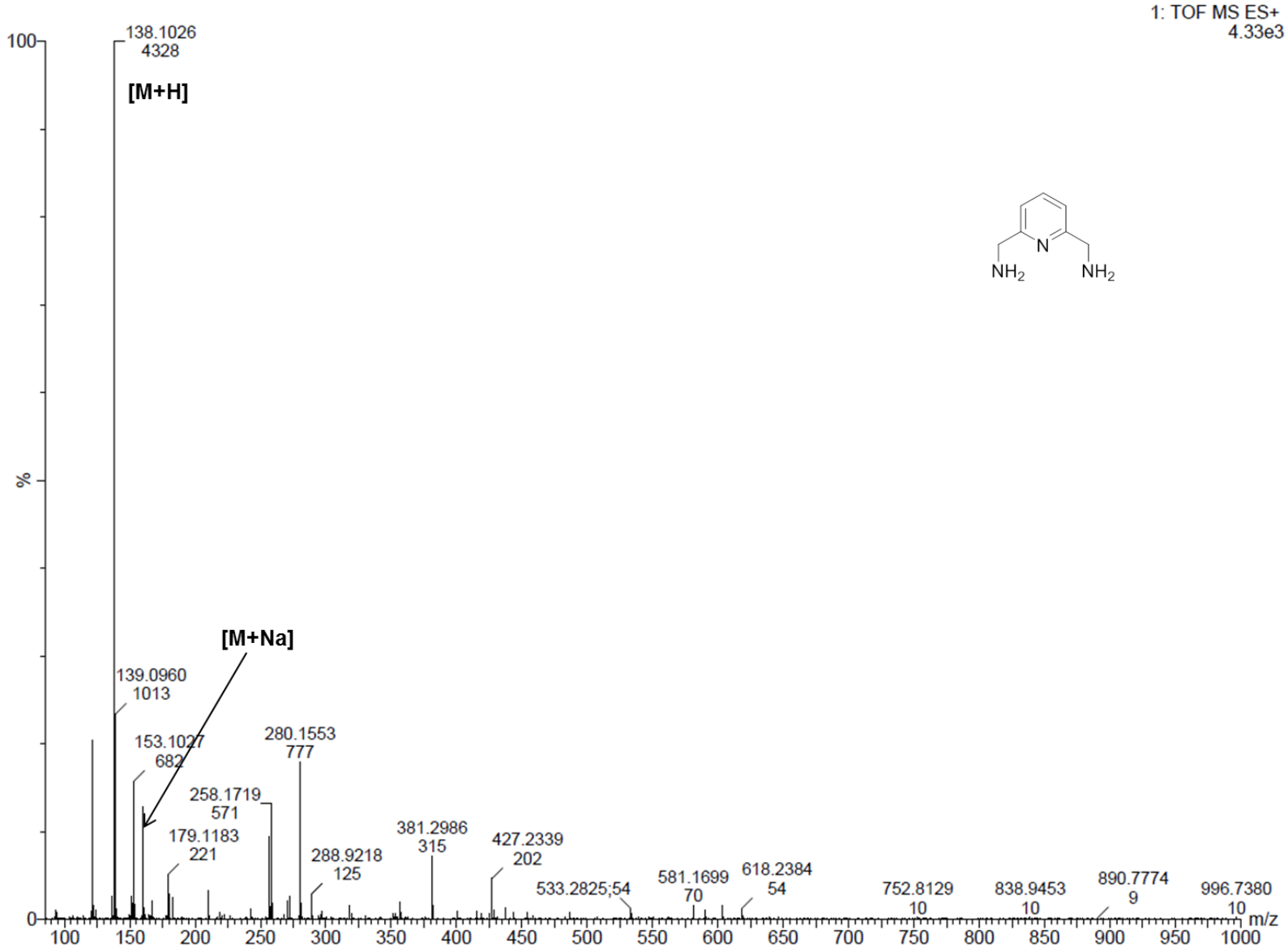
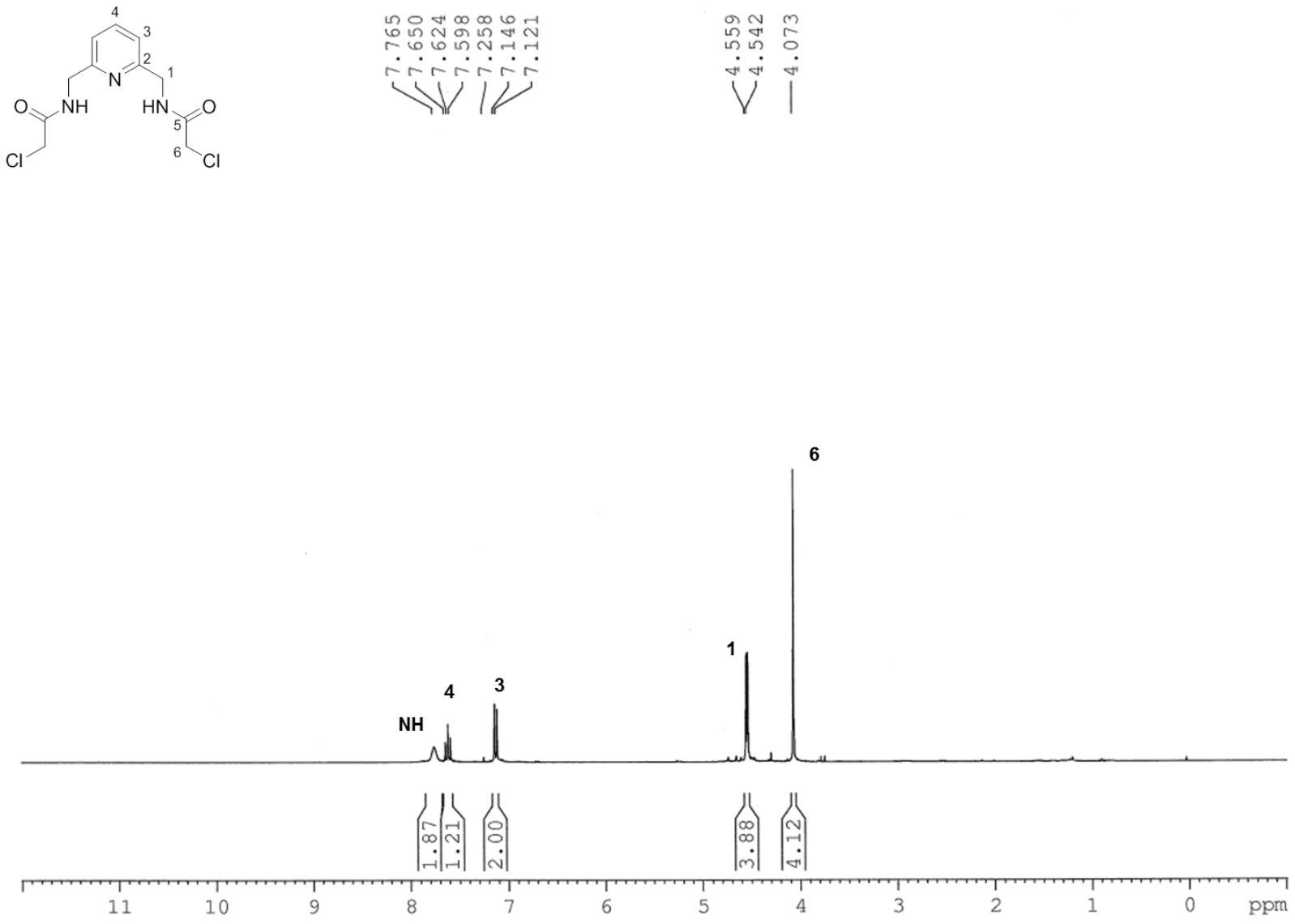
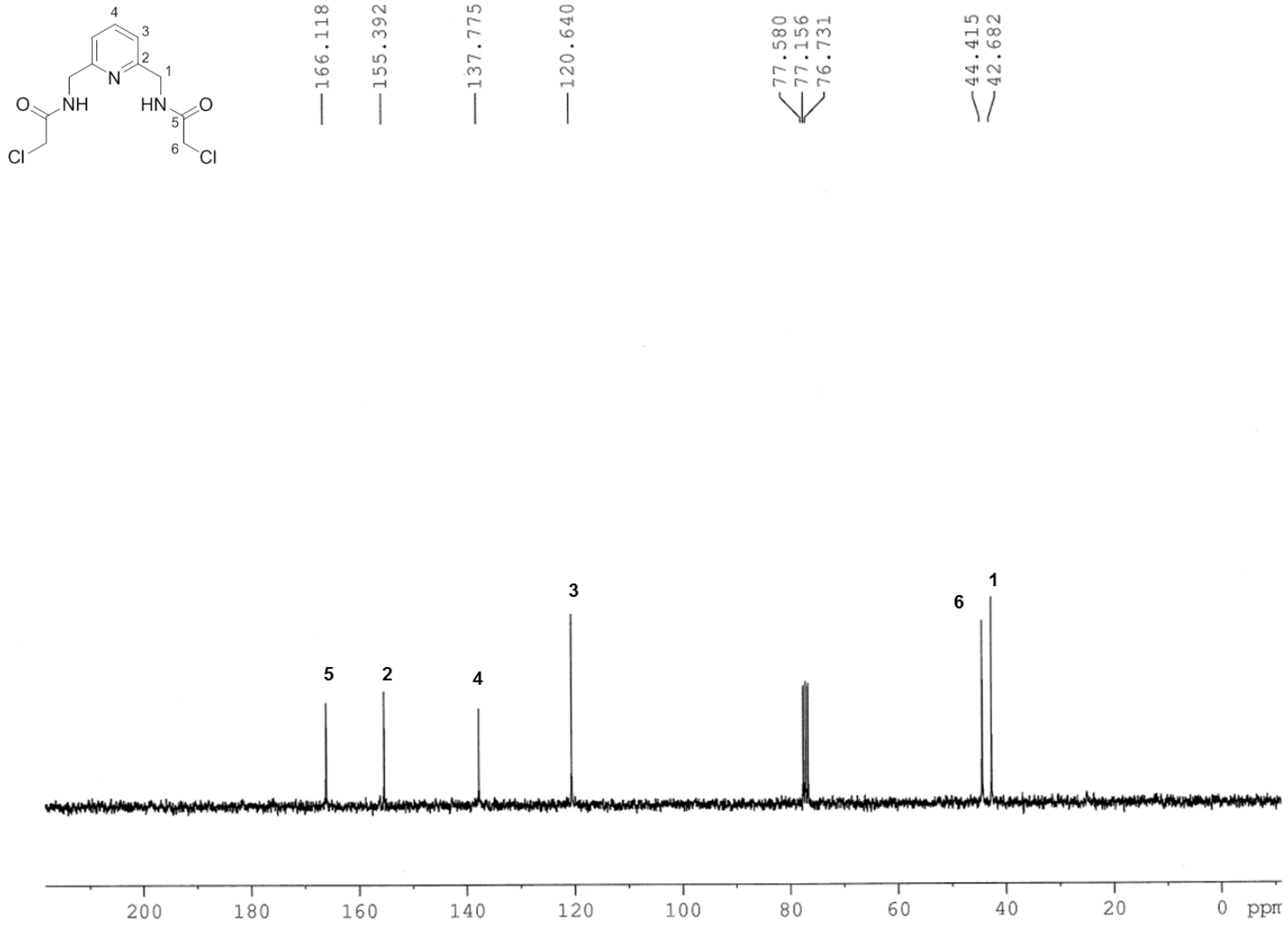


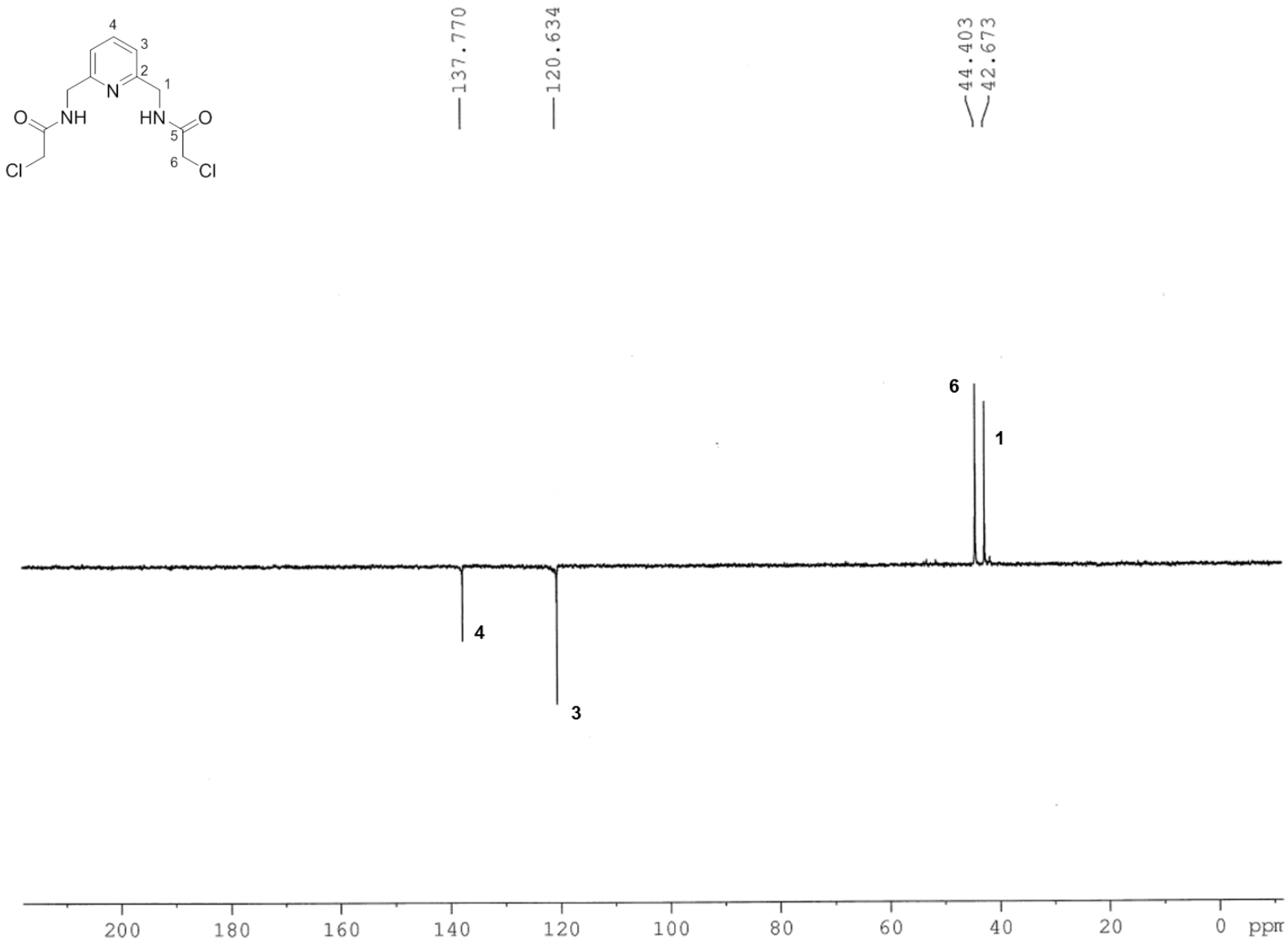
S.49 HRMS spectrum for 16



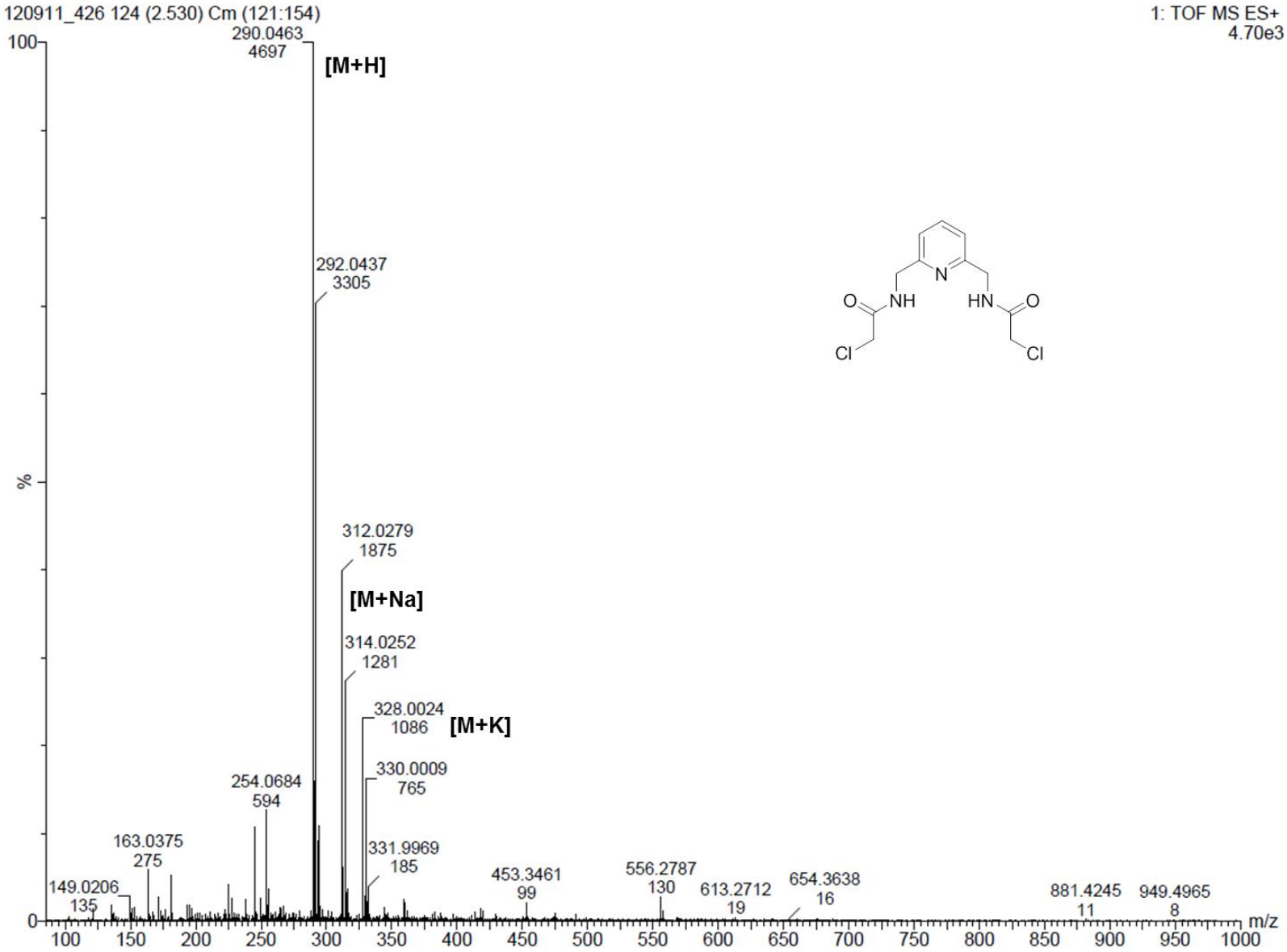
S.50 $^{+}$H NMR spectrum for 17, in $CDCl_3$



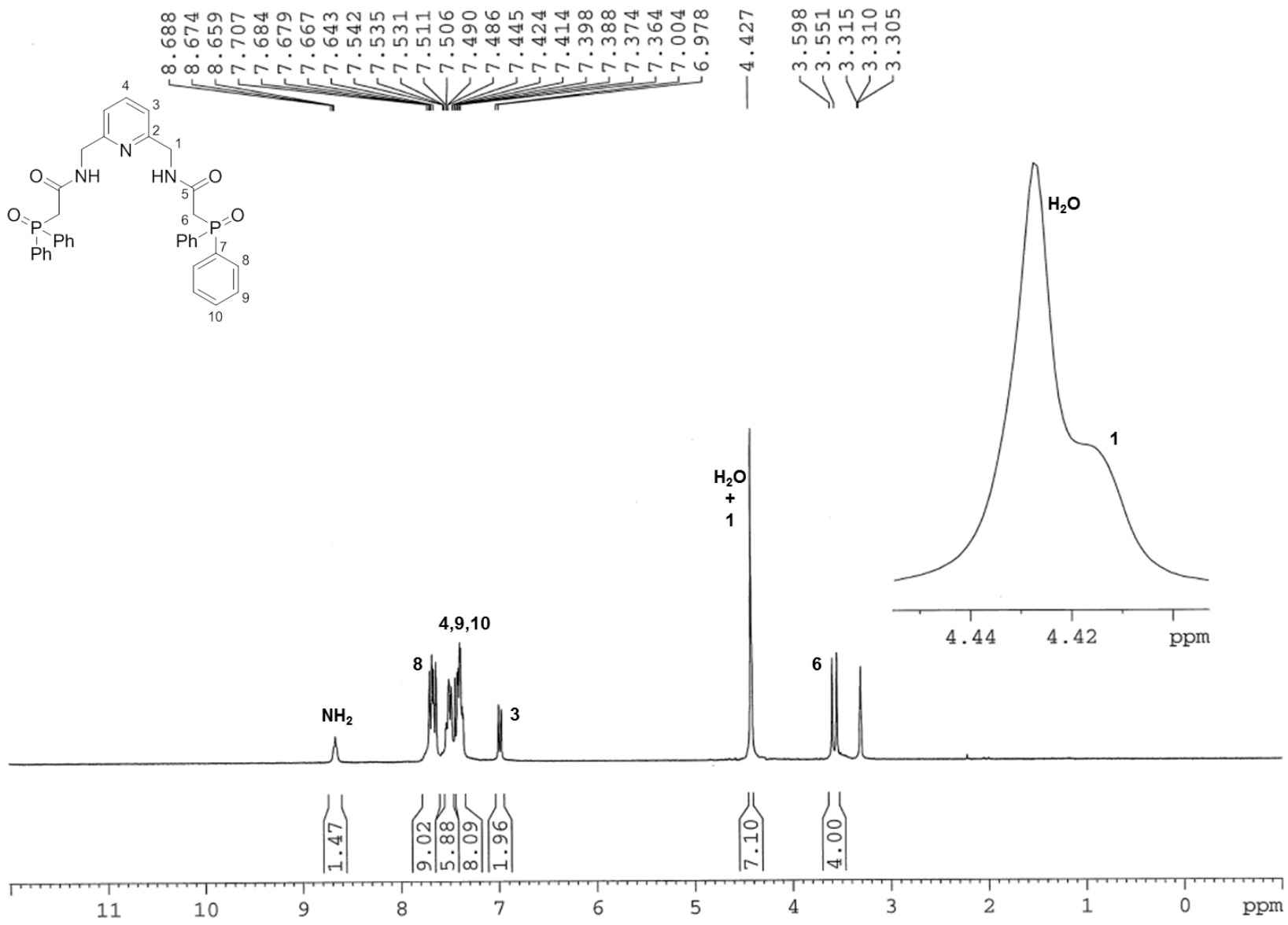
S.51 ^{13}C NMR spectrum for 17, in $CDCl_3$



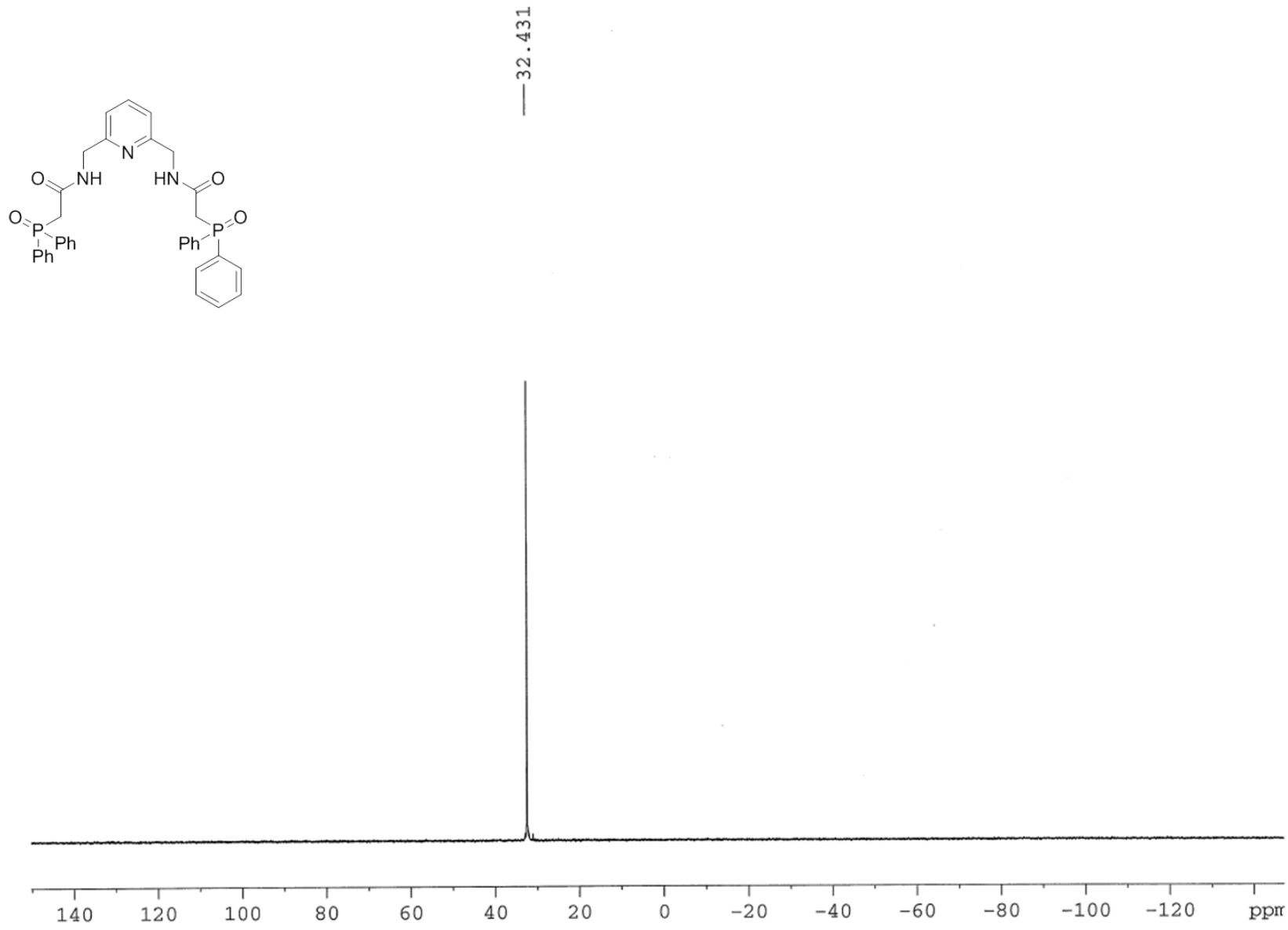
S.52 DEPT 135 NMR spectrum for 17, in $CDCl_3$



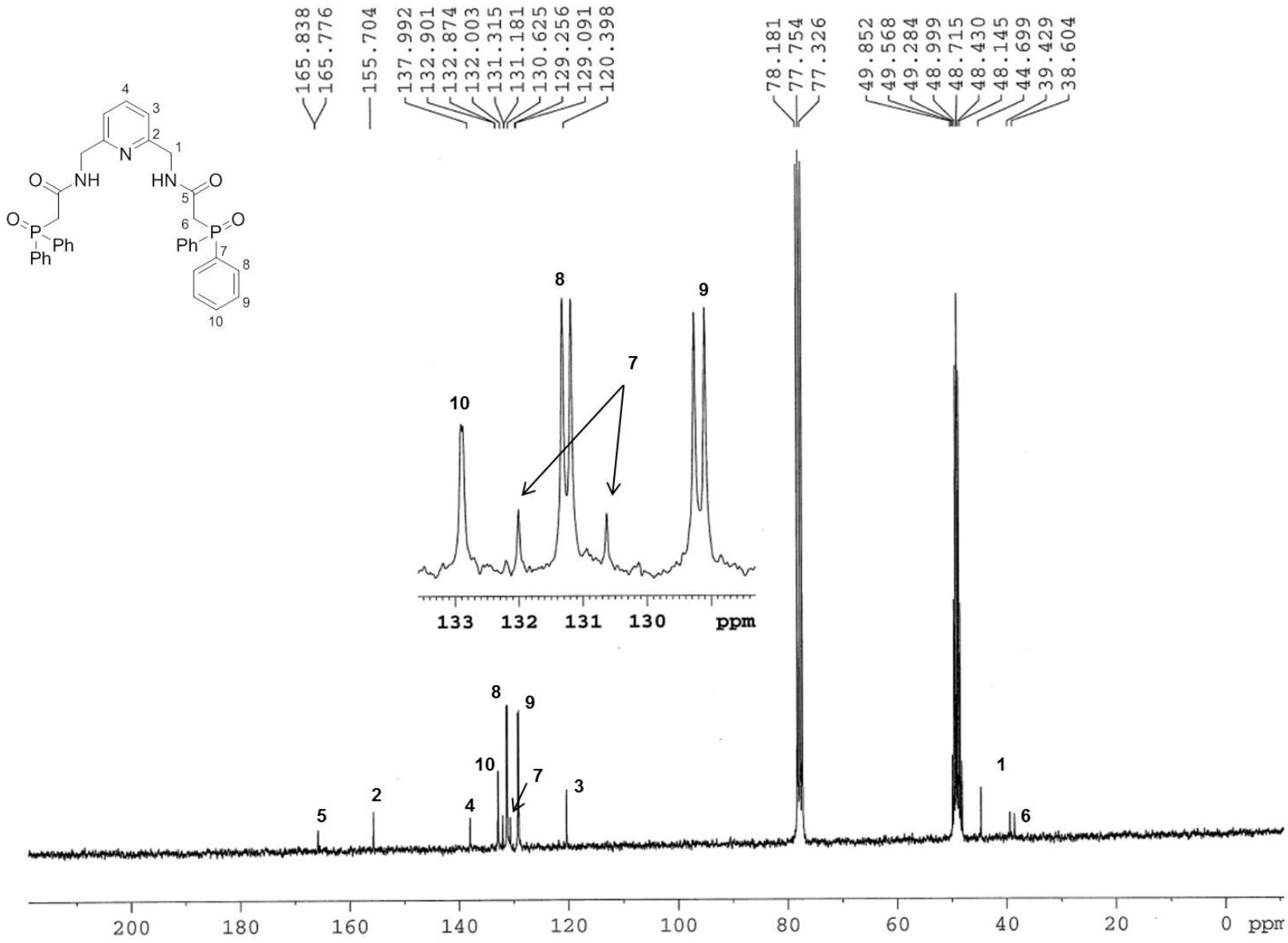
S.53 HRMS spectrum for 17



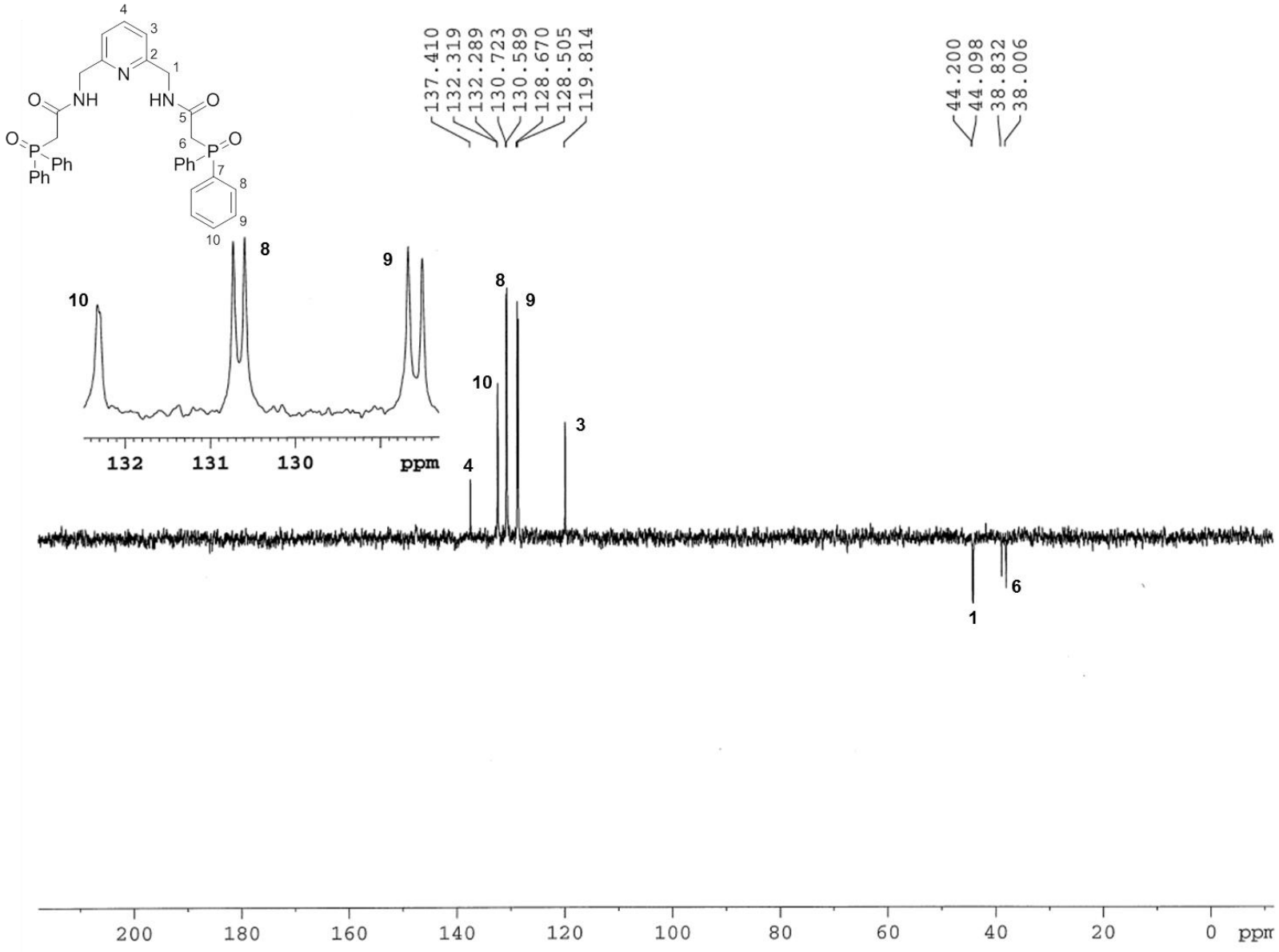
S.54 ^{1}H NMR spectrum for 18, in $CDCl_3$ / d_4-MeOH



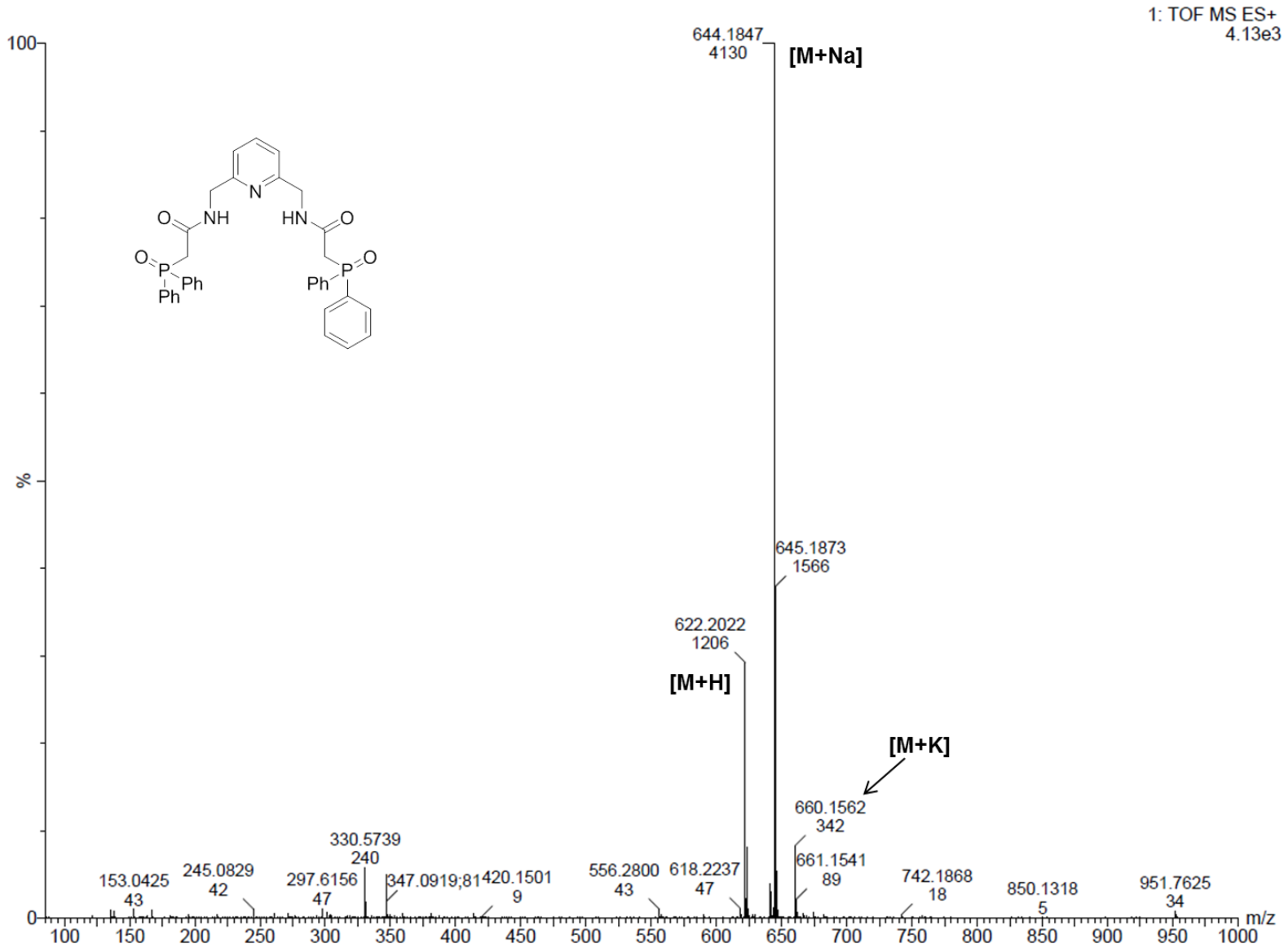
S.55 ^{31}P NMR spectrum for 18, in $CDCl_3$ / d_4-MeOH



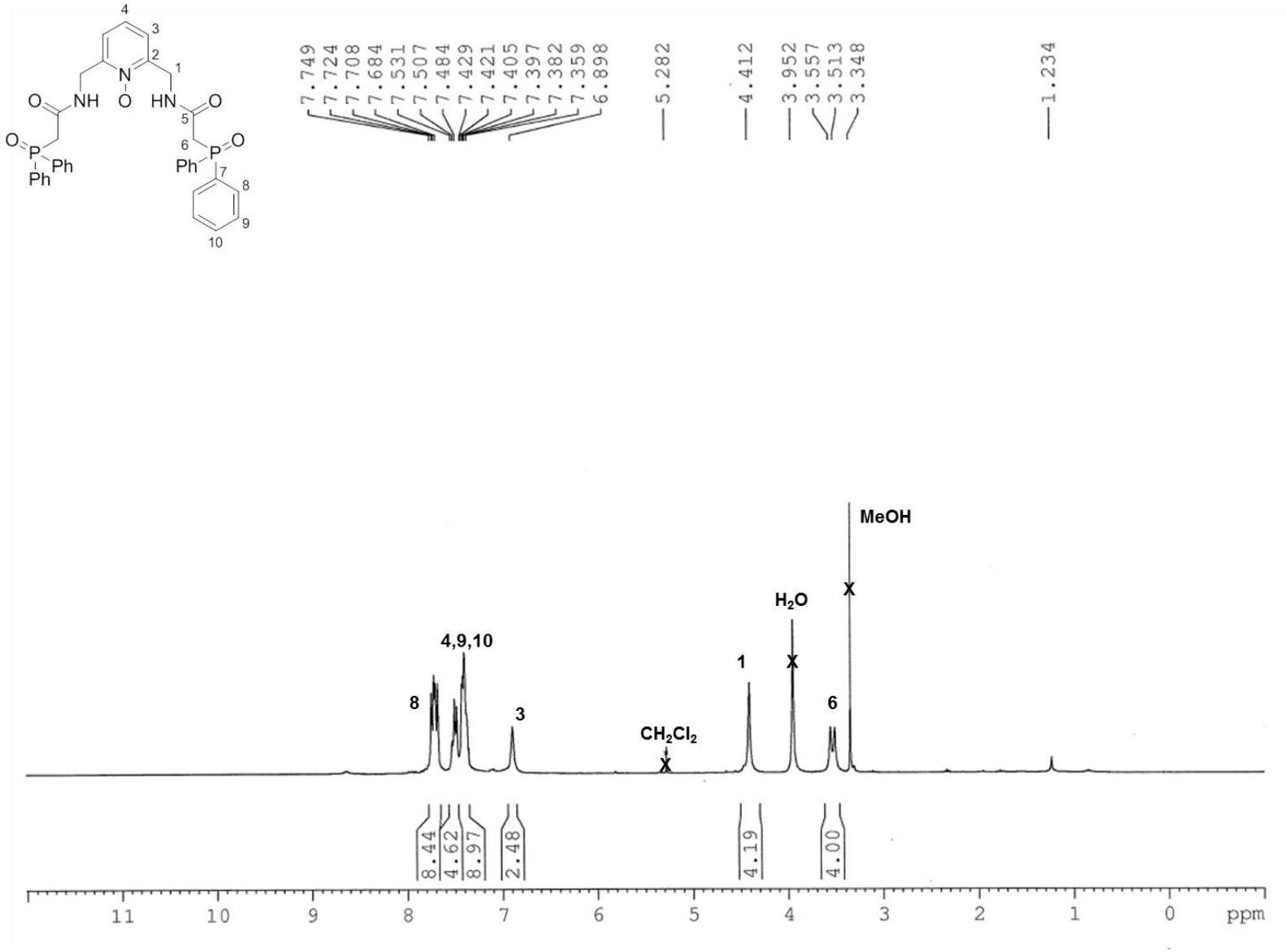
S.56 ^{13}C NMR spectrum for 18, in $CDCl_3$ / d_4-MeOH



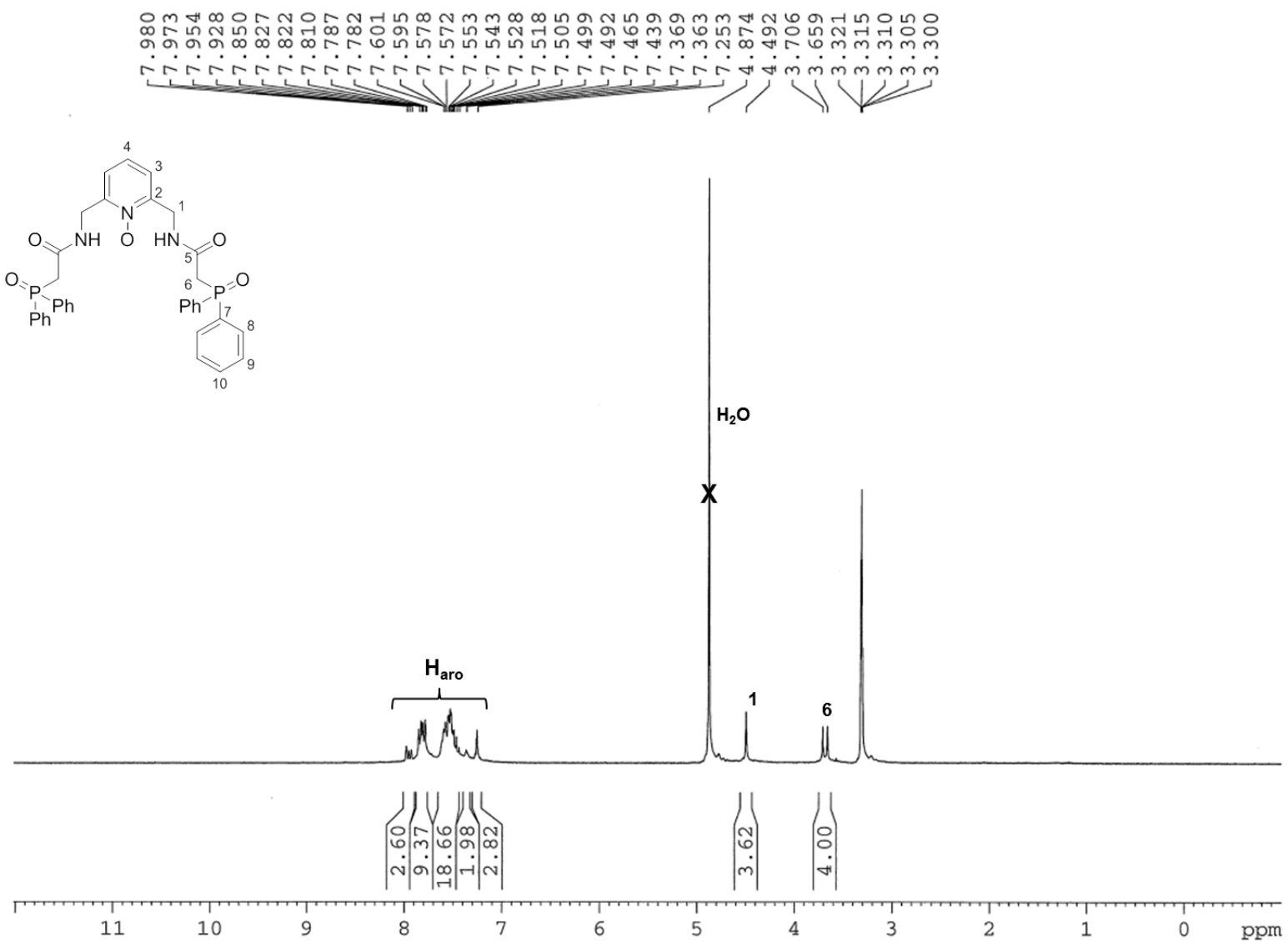
S.57 DEPT 135 NMR spectrum for 18, in $CDCl_3$ / d_4-MeOH



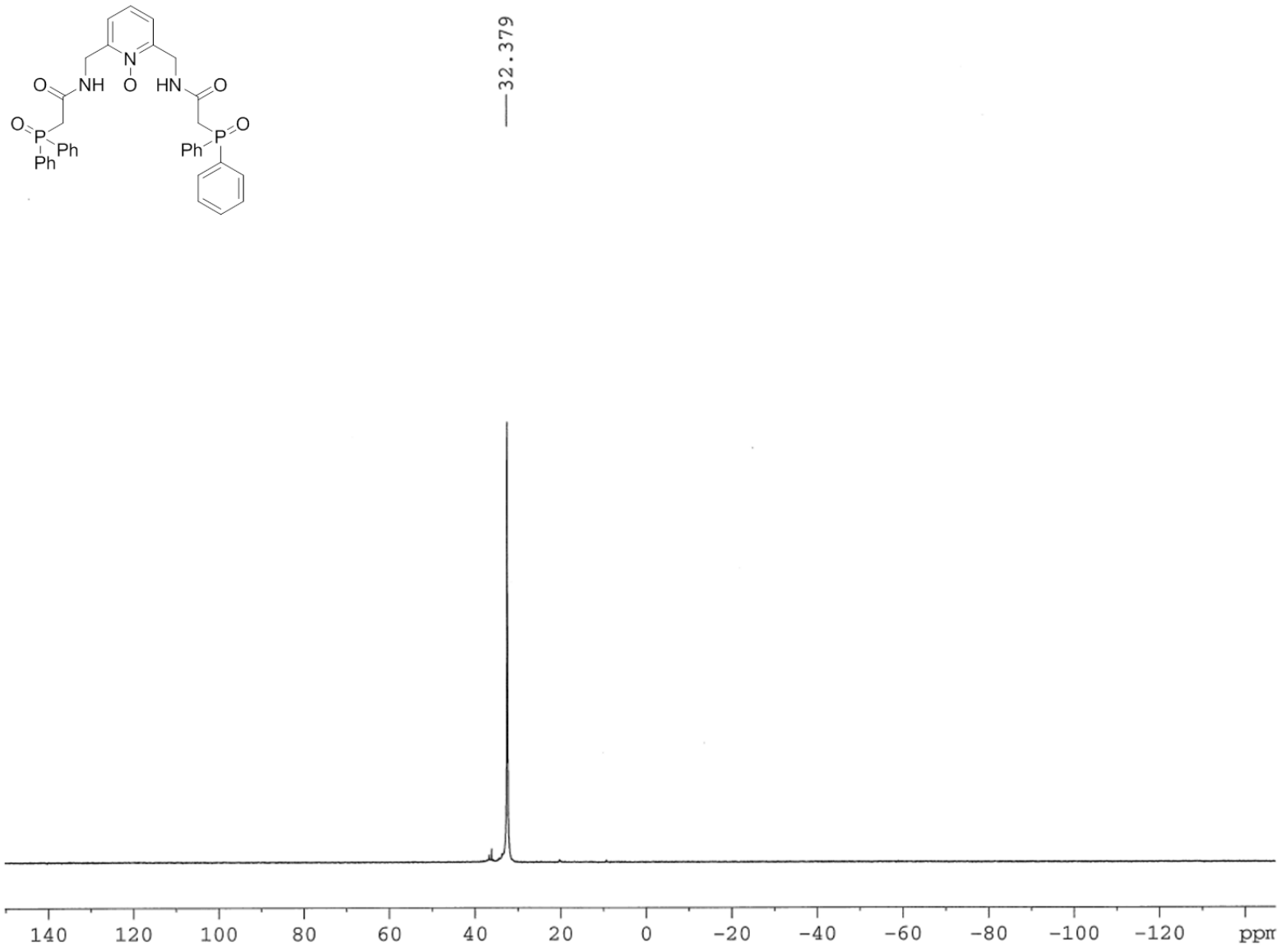
S.58 HRMS spectrum for 18



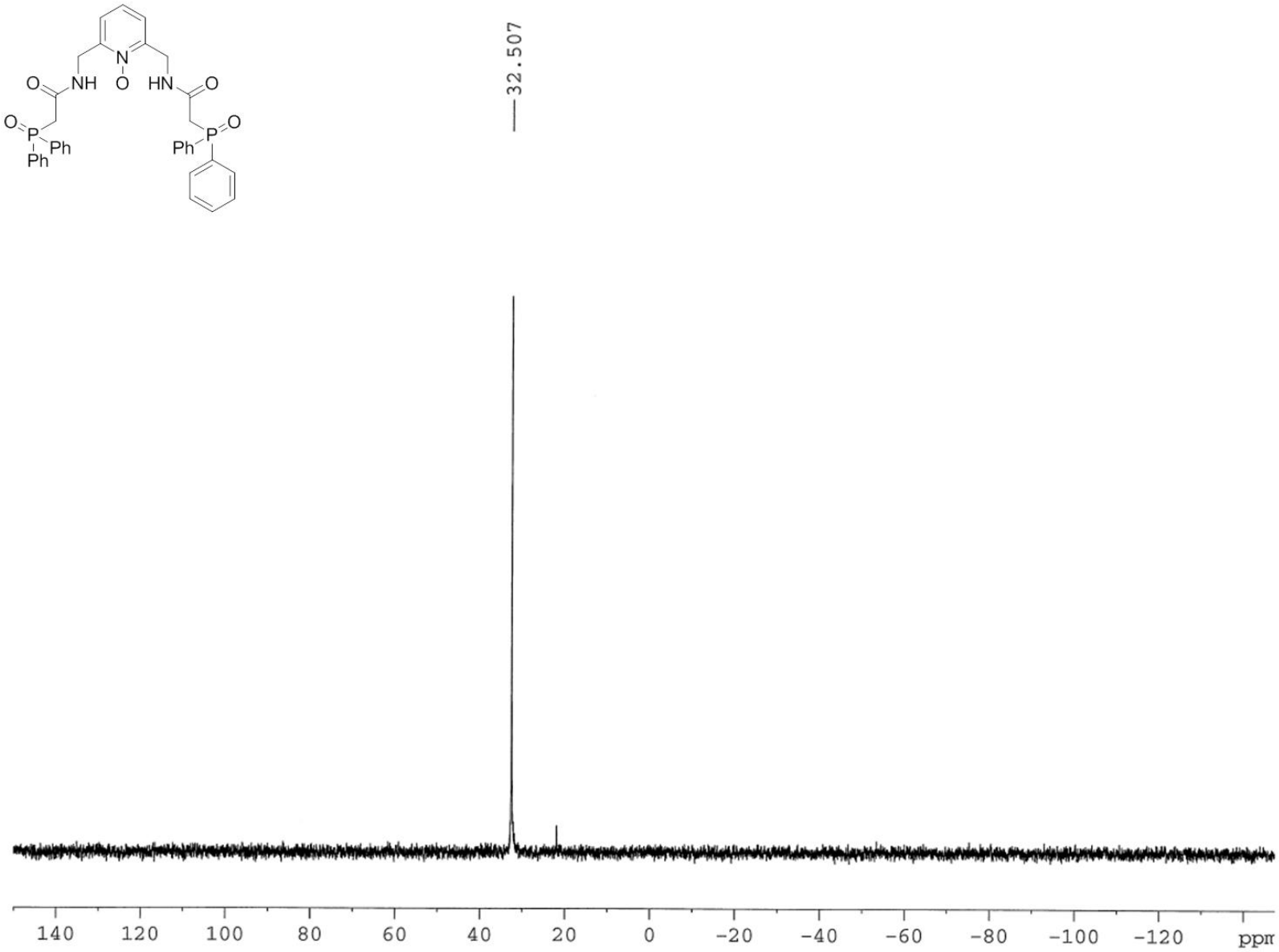
S.59 ^{1}H NMR spectrum for 8, in $CDCl_3$ / d_4-MeOH



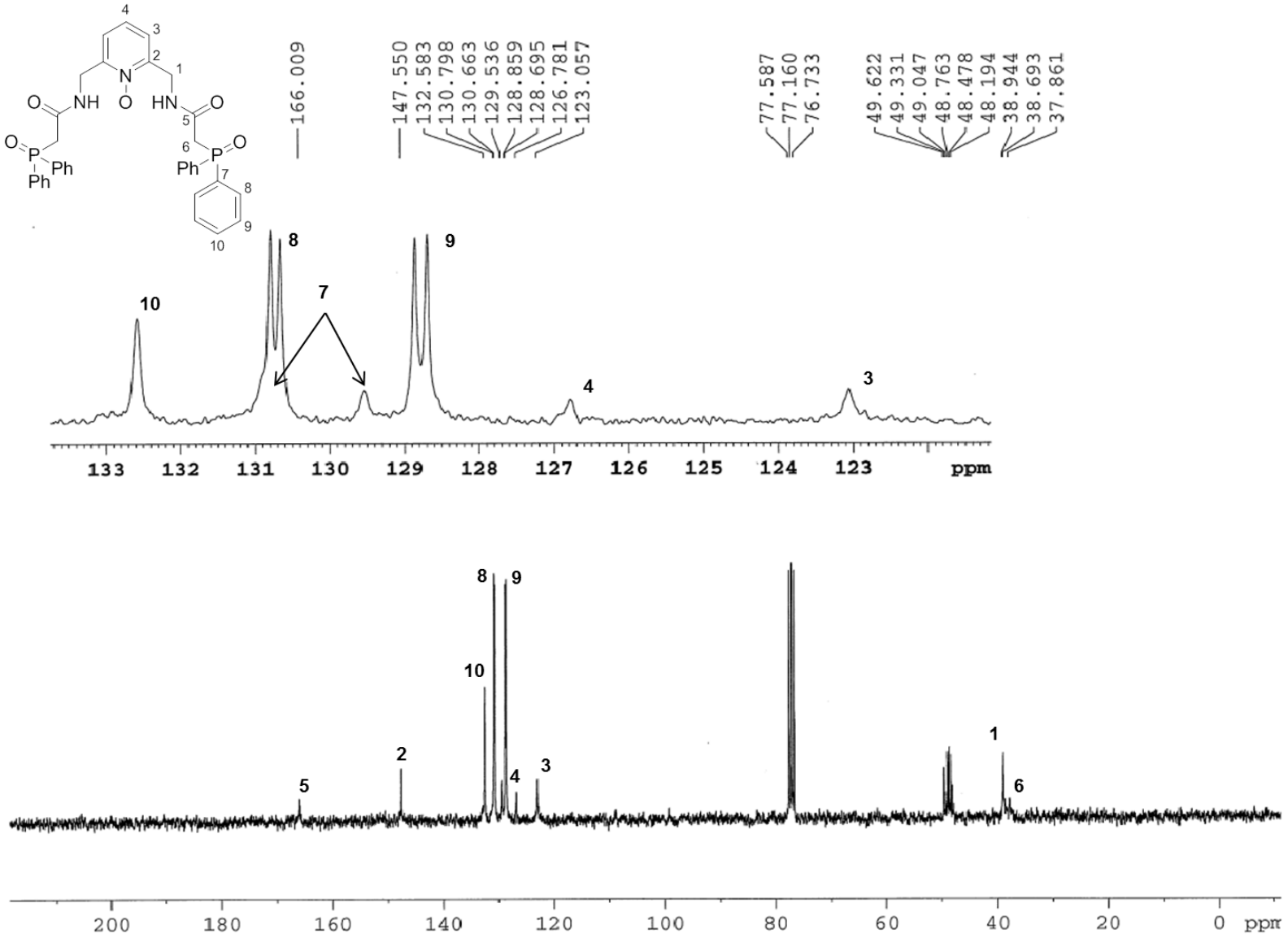
S.60 ^{1}H NMR spectrum for 8, in d_4-MeOH



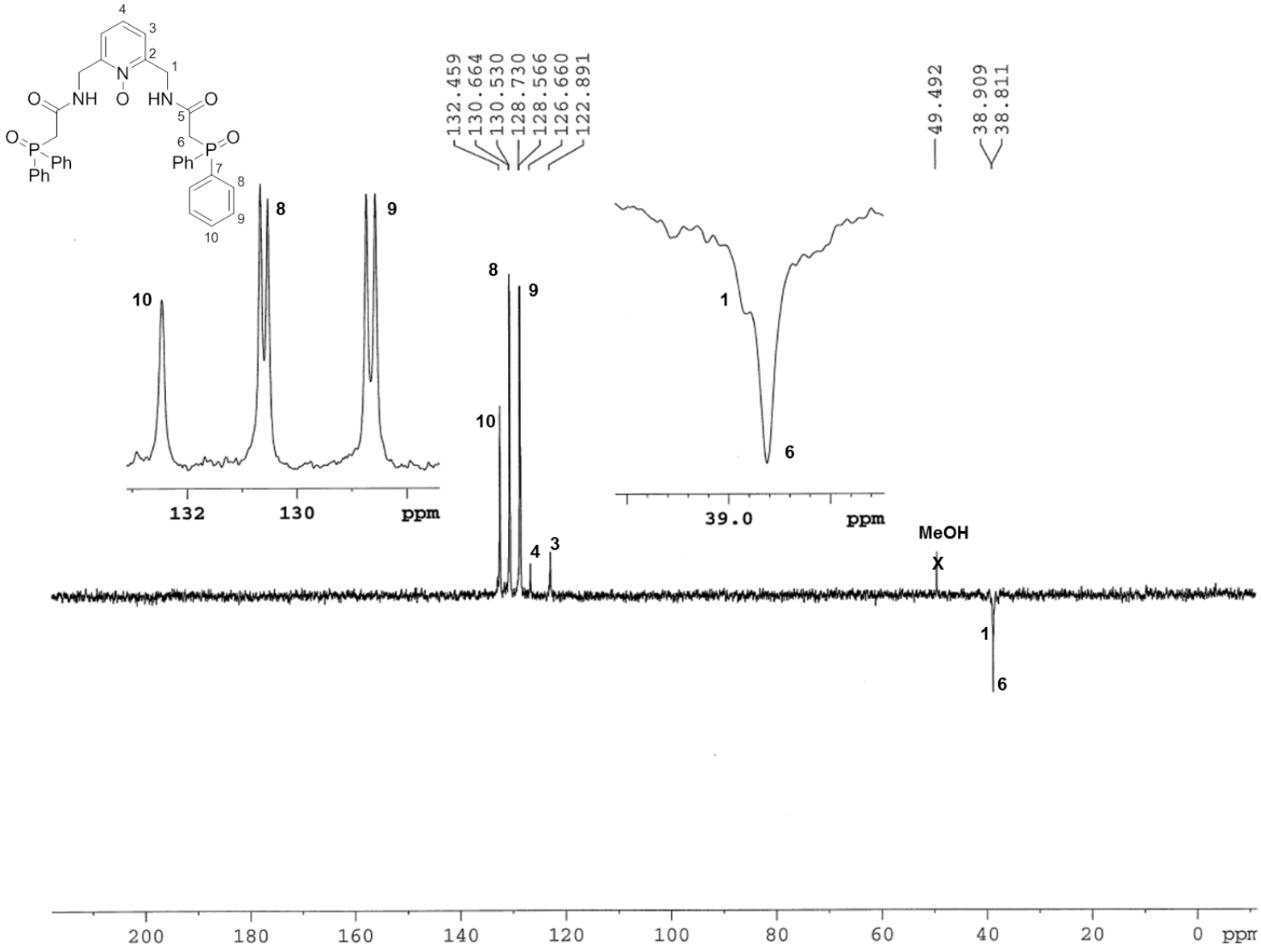
S.61 ^{31}P NMR spectrum for 8, in $CDCl_3$ / d_4-MeOH



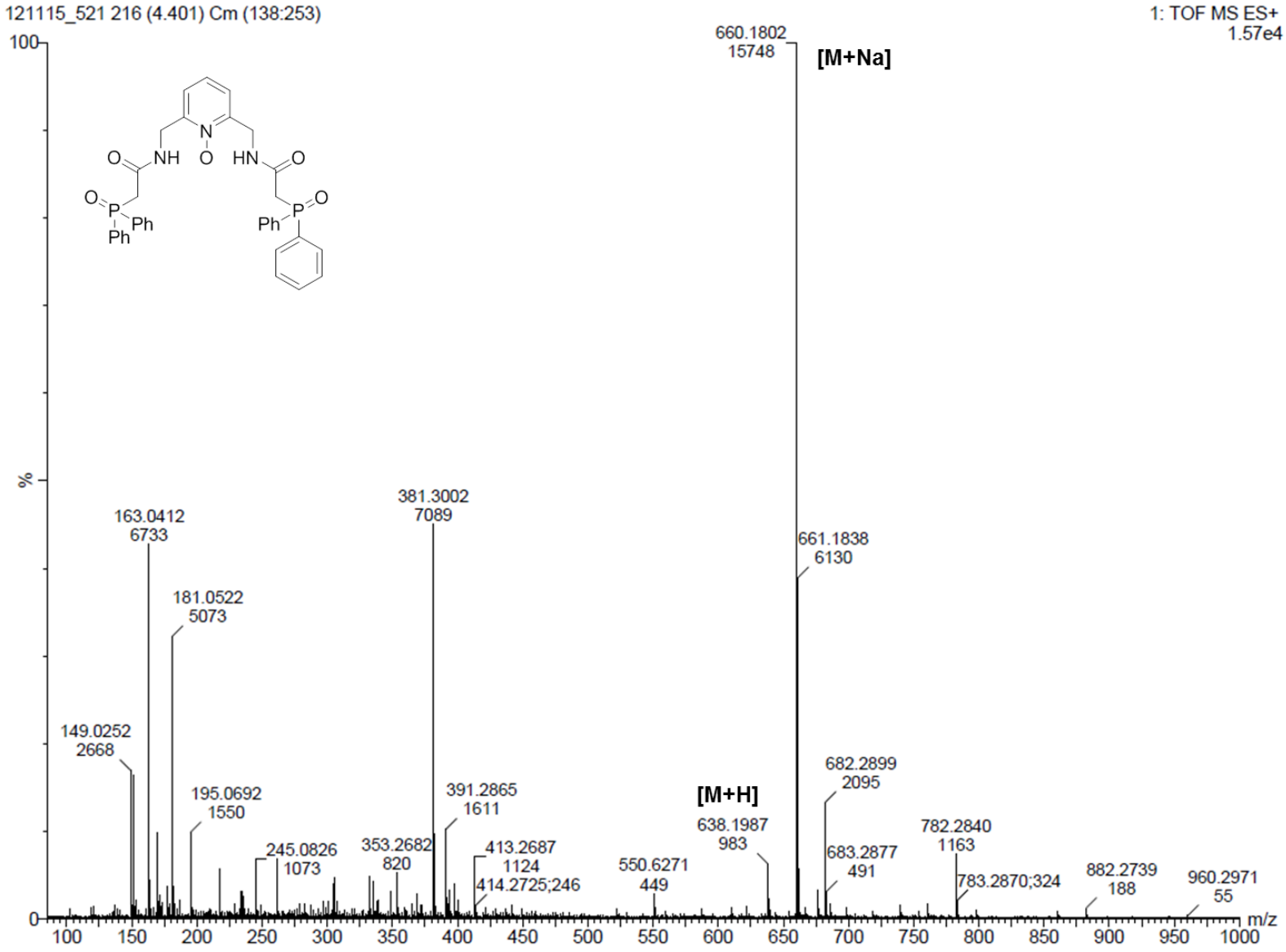
S.62 ^{31}P NMR spectrum for 8, in d_4-MeOH



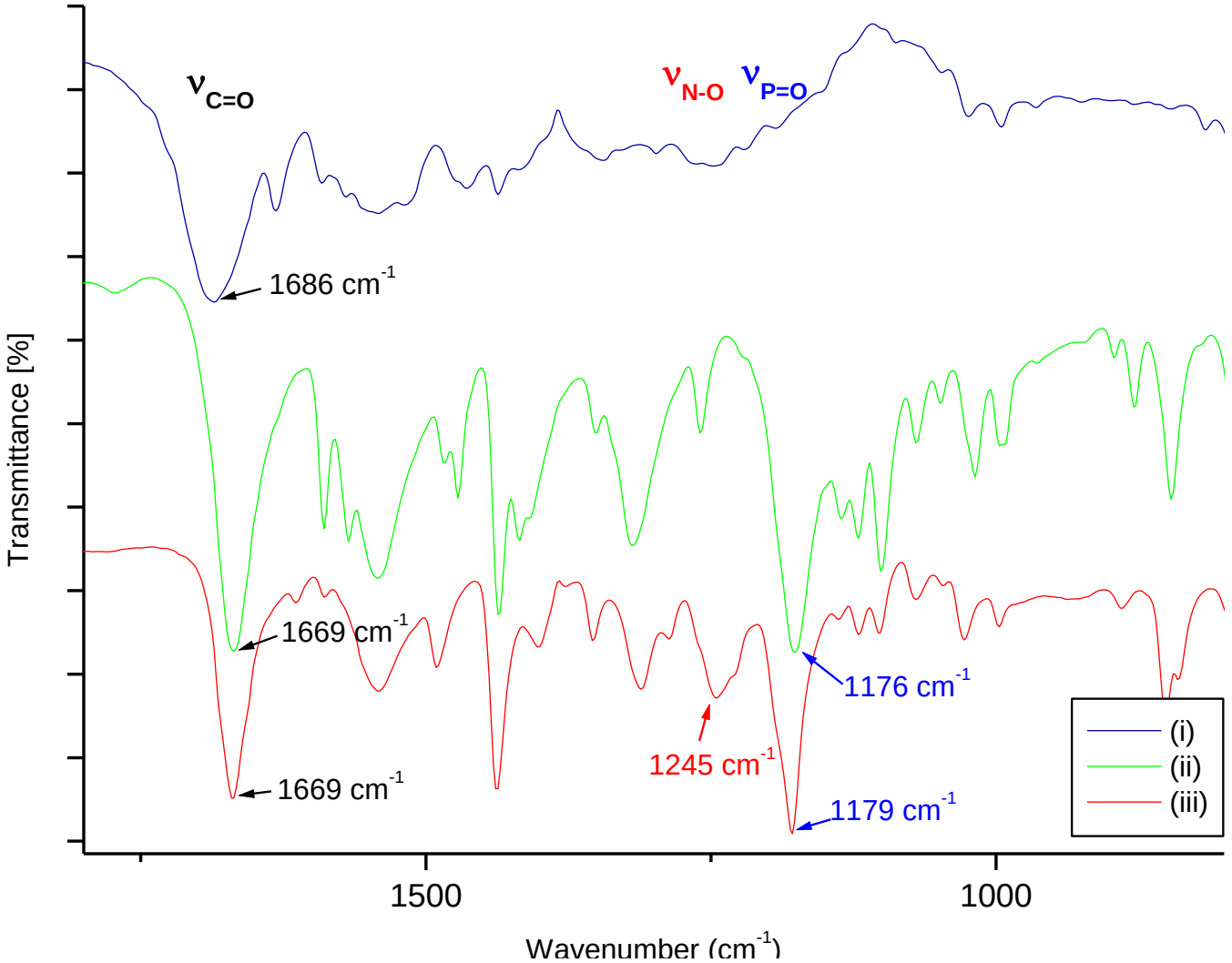
S.63 ^{13}C NMR spectrum for 8, in $CDCl_3$ / d_4-MeOH



S.64 DEPT 135 NMR spectrum for 8, in $CDCl_3$ / d_4-MeOH

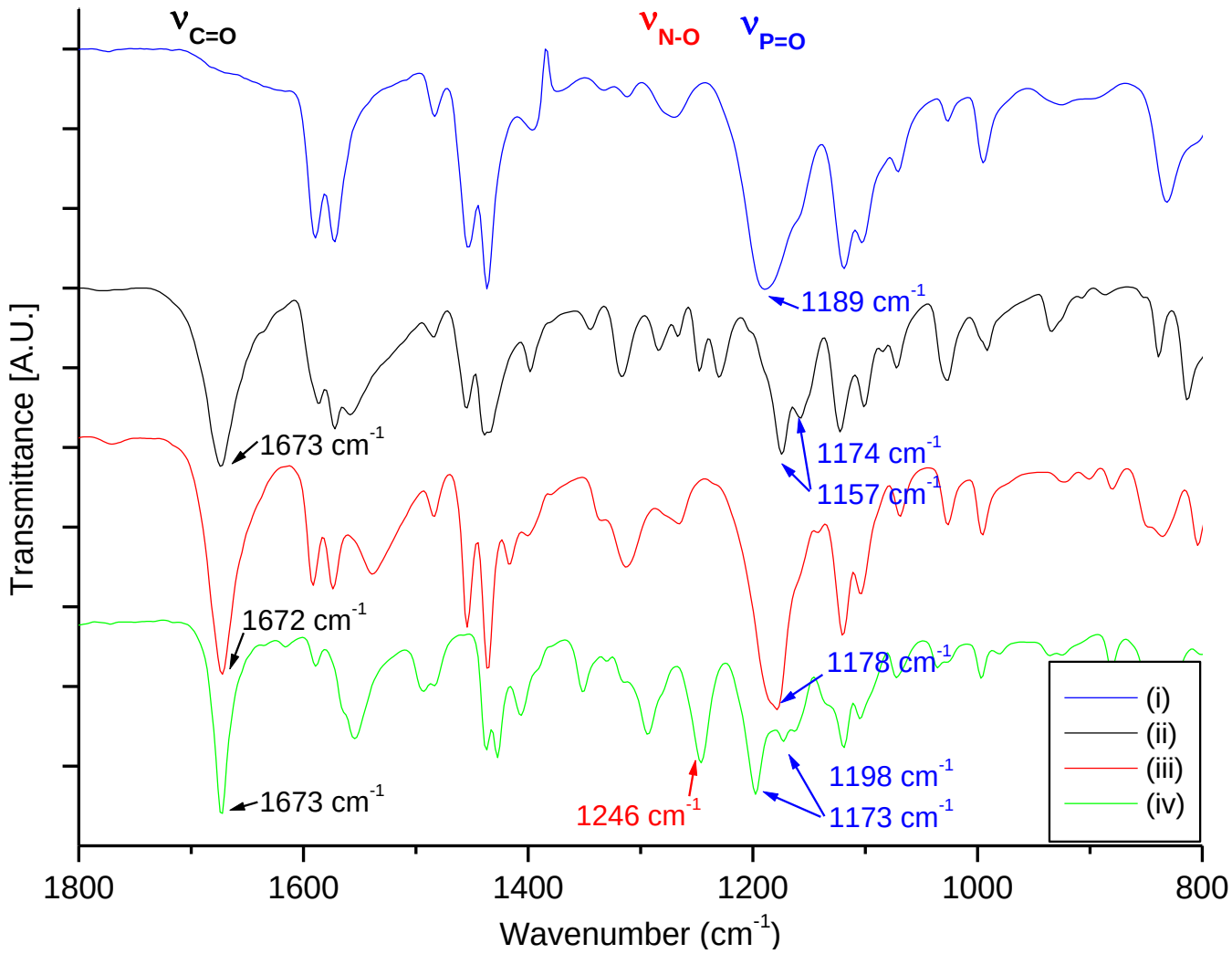


S.65 HRMS spectrum for 8



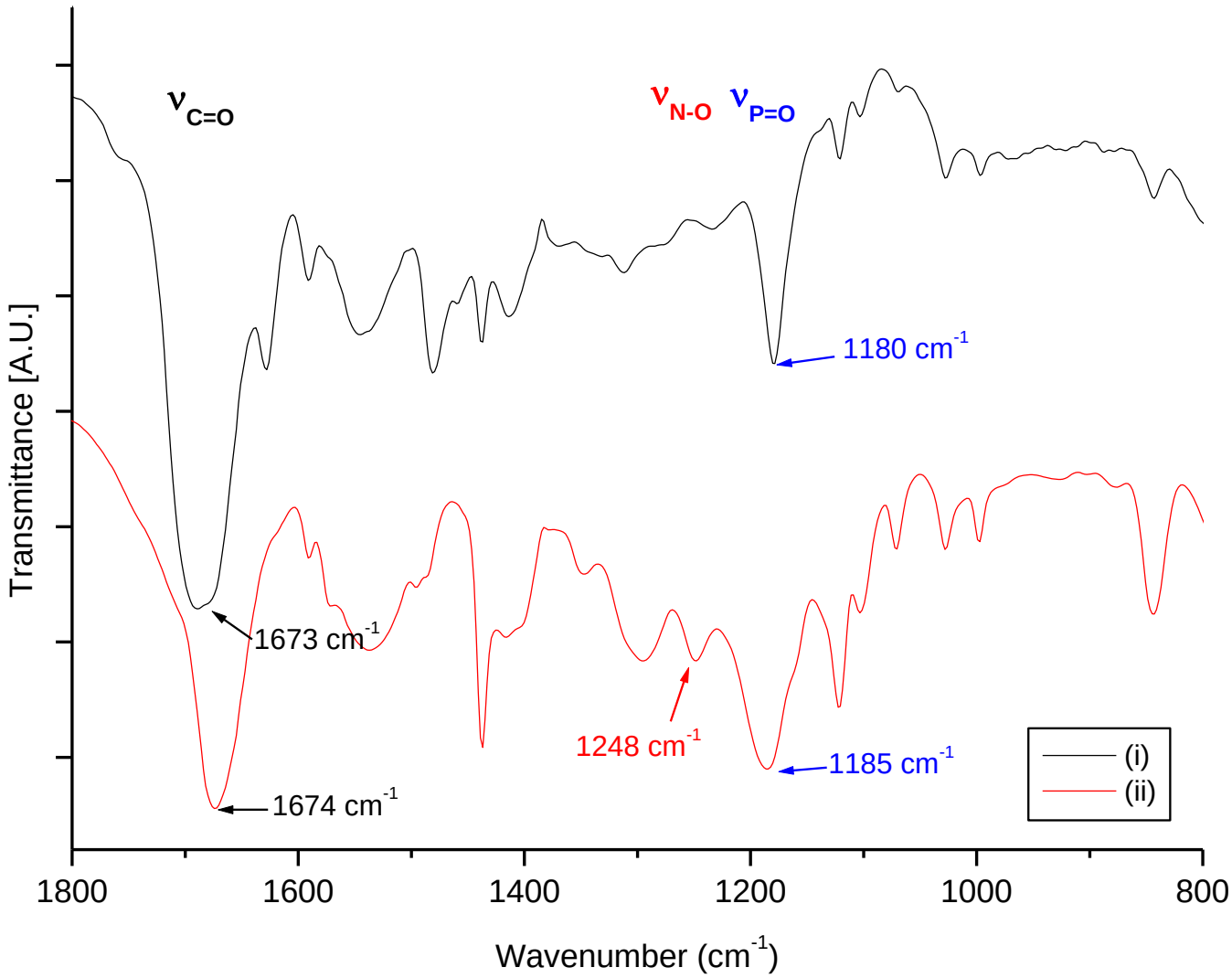
(i) **9**, (ii) **10**, (iii) **6**

S.66 FTIR spectra of 9, 10 and 6



(i) **11**, (ii) **12**, (iii) **13**, (iv) **7**

S.67 FTIR spectra 11, 12, 13 and 7



(i) **18**, (ii) **8**

S.68 FTIR spectra of 18, 8

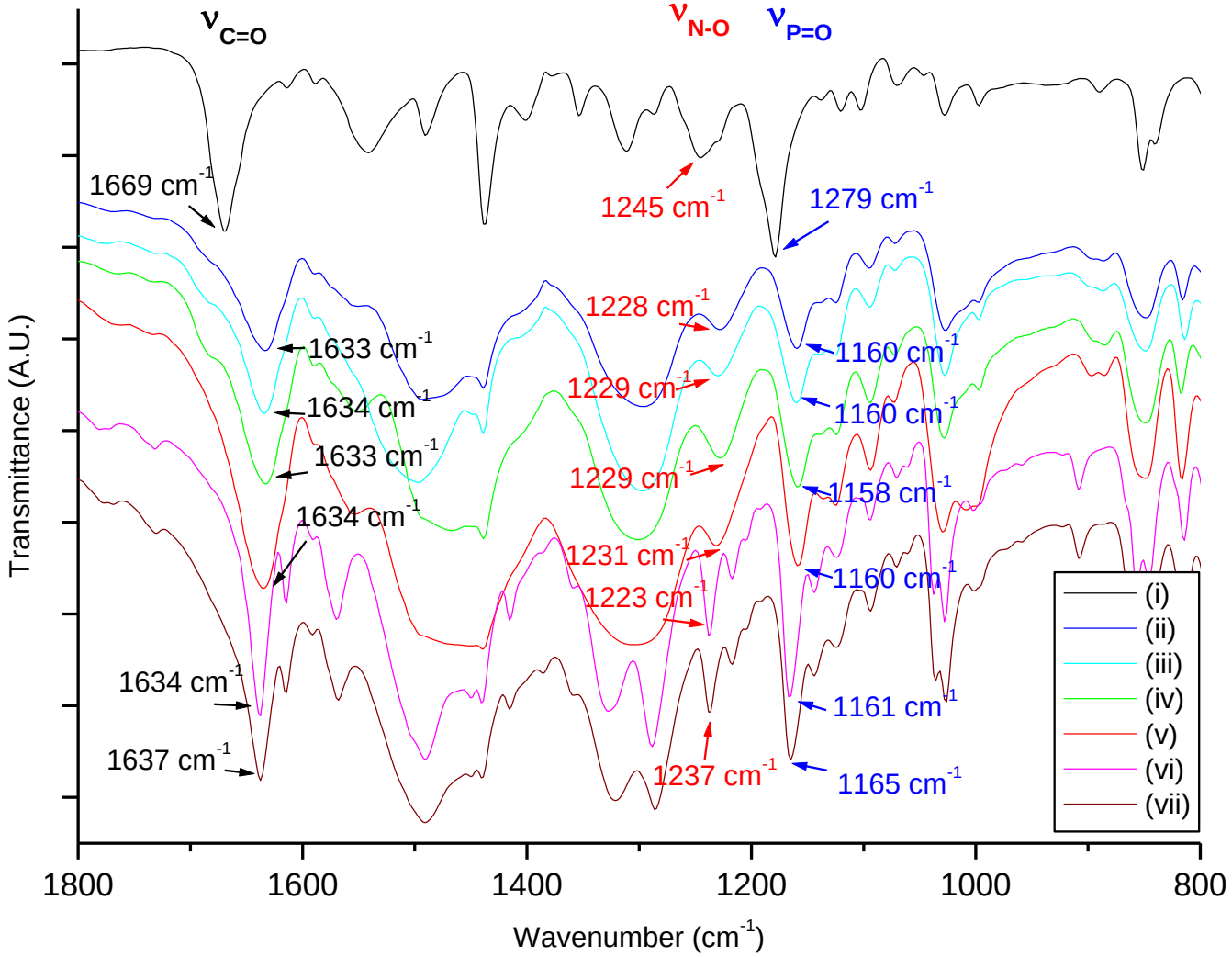
Data		9	10	6	11	12	13	7	DPhCMPO	Ph_2NOPO	Ph_2NPO
IR, ν (cm^{-1})	ν_{NH}	3201	3266	3254	-	3243	3282	3250	-	-	-
	ν_{CO}	1686	1669	1669	-	1673	1672	1673	1630	-	-
	ν_{NO}	-	-	1245	-	-	-	1246	-	-	-
	ν_{PO}	-	1177	1179	1189	1151 1174	1178	1173 1198	1205	1186	1184
^{31}P NMR, δ (ppm)		-	30.5	29.8	30.7	30.4	29.7 30.7	29.4 31.4	27.9	31.7	30.2
^{1}H NMR δ (ppm), (J, Hz)	ClCH_2C(O)	3.89	-	-	-	3.94	-	-	-	-	-
	P(O)CH_2C(O)	-	3.42 (12.9 Hz)	3.47 (13.5 Hz)	-	-	3.39 (13.0 Hz)	3.38 (13.0 Hz)	3.30 (15.7 Hz)	4.22 (14.0 Hz)	3.88 (14.2 Hz)
	PyrCH_2N(H)	4.30 (5.7 Hz)	4.44 (5.7 Hz)	4.51 (6.0 Hz)	3.70	4.26 (5.1 Hz)	4.32 (5.5 Hz)	4.39 (6.0 Hz)	-	-	-
	PyrCH_2P(O)	-	-	-	3.89 (14.1 Hz)	3.78 (14.1 Hz)	3.87 (14.5 Hz)	4.16 (13.5 Hz)	-	-	-
^{13}C NMR δ (ppm), (J, Hz)	ClCH$_2$C(O)	42.0	-	-	-	42.4	-	-	-	-	-
	ClCH$_2$$C$(O)	165.9	-	-	-	165.7	-	-	-	-	-
	P(O)CH$_2$C(O)	-	38.9 (60.0 Hz)	39.1 (59.1 Hz)	-	-	38.9 (60.0 Hz)	39.0 (59.5 Hz)	39.4 (60.9 Hz)	30.7 (66.0 Hz)	40.7 (64.0 Hz)
	P(O)CH$_2$$C$(O)	-	164.8 (4.4 Hz)	165.4	-	-	164.7 (3.9 Hz)	165.2	165.5 (5.0 Hz)	-	-
	Pyr$C$H$_2$N(H)	44.0	45.1	39.3	47.2	44.0	44.9	39.7	-	-	-
	Pyr$C$H$_2$P(O)	-	-	-	40.5 (64.3 Hz)	39.5 (64.0 Hz)	40.7 (64.1 Hz)	31.1 (66.4 Hz)	-	-	-

S.69 Spectroscopic Data Summary for 6-13, DPhCMPO, Ph_2NOPO, Ph_2NPO

S.70 Summary of analysis characterization for complexes

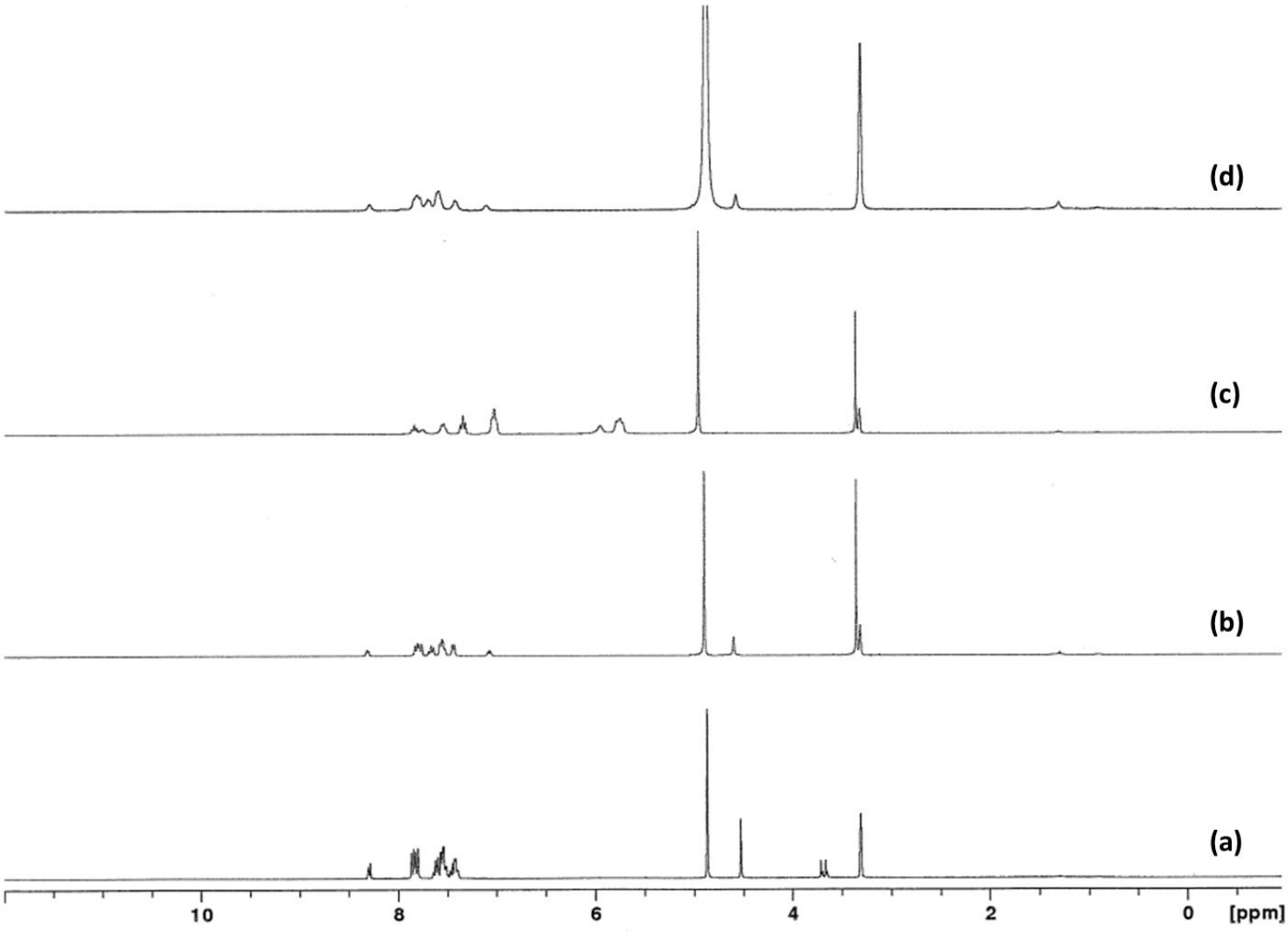
The 1:1 complexes were obtained from the addition of equimolar amounts (1 mmol) of metal nitrate (Pr, Eu, La, Yb) in MeOH (10 mL) to the ligand in MeOH (10 mL). The mixture was stirred for 2 h and evaporated to dryness. The resulting solid was vacuum-dried. Elemental analyses (CHN) and infrared spectra for representative samples were obtained, and selected samples were crystallized in order to obtain single crystals for X-ray diffraction analyses. [Eu(**6**)$(NO_3)_3$] $^{31}P\{^1H\}$ (121.49 MHz, d_4-MeOH) δ –19.04. ^1H NMR (300 MHz, d_4-MeOH) δ 5.71-5.77 (m, 4H, H_{10}), 5.94 (s, 2H, H_6), 7.01-7.03 (m, 4H, H_{aro}), 7.33 (t, J_{HH} = 7.4 Hz, 2H, H_{aro}), 7.52-7.54 (m, 2H, H_{aro}), 7.41-7.80 (m, 1H, H_{aro}), 7.83 (t, J_{HH} = 7.7 Hz, 1H, H_{aro}). Anal. Calcd for $C_{20}H_{19}EuN_5O_{12}P\cdot 2H_2O$: C 32.45, H 3.13, N 9.46. Found: C 32.11, H 3.10, N 9.37. FTIR (KBr, cm^{-1}) 1633 ($\nu_{C=O}$), 1228 (ν_{N-O}), 1160 ($\nu_{P=O}$). [La(**6**)$(NO_3)_3$] $^{31}P\{^1H\}$ (121.49 MHz, d_4-MeOH) δ 35.85. ^1H NMR (300 MHz, d_4-MeOH) δ 4.59 (s, 2H, H_6), 7.07 (pseudo t, J_{HH} = 5.0 Hz, 1H, H_4), 7.44 (pseudo t, J_{HH} = 3.8 Hz, 2H, H_{12}), 7.51-7.57 (m, 4H, H_{11}), 7.64-7.69 (m, 2H, $H_{2,3}$), 7.79 (dd, J_{HH} = 7.4, 12.8 Hz, 4H, H_{10}), 8.31 (pseudo t, J_{HH} = 3.4 Hz, 1H, H_1). FTIR (KBr, cm^{-1}) 1634 ($\nu_{C=O}$), 1231 (ν_{N-O}), 1160 ($\nu_{P=O}$). [Pr(**6**)$(NO_3)_3$] FTIR (KBr, cm^{-1}) 1633 ($\nu_{C=O}$), 1229 (ν_{N-O}), 1158 ($\nu_{P=O}$). [Er(**6**)$(NO_3)_3$] FTIR (KBr, cm^{-1}) 1637 ($\nu_{C=O}$), 1237 (ν_{N-O}), 1165 ($\nu_{P=O}$). [Er(**6**)$(NO_3)_3$] $^{31}P\{^1H\}$ (121.49 MHz, d_4-MeOH) δ -81.30. Crystals $\{[Yb(\mathbf{6})(NO_3)_3]\cdot(MeOH)\}_n$ grown by slow evaporation of MeOH at room temperature were suitable for crystallographic analysis. Anal. Calcd for $C_{20}H_{19}N_5O_{12}P_1Yb_1$: C 33.11, H 2.64, N 9.65. Found: C 33.08, H 2.91, N 9.44. FTIR (KBr, cm^{-1}) 1634 ($\nu_{C=O}$), 1229 (ν_{N-O}), 1160 ($\nu_{P=O}$). [Lu(**6**)$(NO_3)_3$] $^{31}P\{^1H\}$ (121.49 MHz, d_4-MeOH) δ 37.73. ^1H NMR (300 MHz, d_4-MeOH) δ 4.56 (s, 2H, H_6), 7.05-7.13 (m, 1H, H_4), 7.37-7.44 (m, 2H, H_{12}), 7.54-7.62 (m, 4H, H_{11}), 7.65-7.71 (m, 2H, $H_{2,3}$), 7.76-7.85 (m, 4H, H_{10}). $\{[Lu(\mathbf{6})(NO_3)_3]\cdot(MeOH)\}_n$ grown by slow evaporation of MeOH/CH_3CN 1:1 at room

temperature were suitable for crystallographic analysis. Anal. Calcd for $C_{20}H_{19}Lu_1N_5O_{12}P_1$: C 33.03, H 2.63, N 9.63. Found: C 32.88, H 2.46, N 9.48. FTIR (KBr, cm^{-1}) 1634 ($\nu_{C=O}$), 1223 (ν_{N-O}), 1161 ($\nu_{P=O}$). [Eu(**13**)$(NO_3)_3$], colorless powder: $^{31}P\{^1H\}$ (121.5 MHz, d_4-MeOH): δ –15.04. ^1H NMR (300 MHz, d_4-MeOH): δ 1.72-1.94 (br s, 2H, H_1 or H_{13}), 2.44-2.68 (br s, 2H, H_1 or H_{13}), 6.05-6.15 (m, 4H, CH_{Ph}), 6.77-6.86 (m, 4H, CH_{Ph}), 6.95-7.02 (m, 4H, CH_{Ph}), 7.22-7.24 (m, 5H, H_4 and CH_{Ph}), 7.32 (t, J_{HH} = 7.2 Hz, 2H, H_{11} or H_{17}), 7.44 (t, J_{HH} = 7.1 Hz, 2H, H_{11} or H_{17}), 7.87 (t, J_{HH} = 7.2 Hz, 1H, H_4), 8.05 (d, J_{HH} = 6.3 Hz, 1H, H_3 or H_5); FTIR (KBr, cm^{-1}): 1630 ($\nu_{C=O}$), 1154 ($\nu_{P=O}$). [La(**7**)$(NO_3)_3$] $^{31}P\{^1H\}$ (121.49 MHz, d_4-MeOH) δ 33.78, 36.35. FTIR (KBr, cm^{-1}) 1636 ($\nu_{C=O}$), 1215 (ν_{N-O}), 1160 ($\nu_{P=O}$). [Ce(**7**)Cl_3] $^{31}P\{^1H\}$ (121.49 MHz, d_4-MeOH) δ 51.64, 59.70. FTIR (KBr, cm^{-1}) 1631 ($\nu_{C=O}$), 1215 (ν_{N-O}), 1159 ($\nu_{P=O}$). [Pr(**7**)$(NO_3)_3$] FTIR (KBr, cm^{-1}) 1635 ($\nu_{C=O}$), 1215 (ν_{N-O}), 1158 ($\nu_{P=O}$). [Eu(**7**)$(NO_3)_3$], white powder: $^{31}P\{^1H\}$ (121.49 MHz, d_4-MeOH) δ –18.06, –35.47. HRMS (ESI) *m*/*z* (rel. inten. %): 437.7473 [Eu(**7**)$_2^+$] (100). $C_{66}H_{60}EuN_4O_8P_4$ requires 437.7525. Anal. Calcd for $C_{33}H_{30}EuN_5O_{13}P_2$•$2Et_2O$: C 46.16, H 4.72, N 6.56. Found: C 45.66, H 3.92, N 6.68. FTIR (KBr, cm^{-1}): 1635 ($\nu_{C=O}$), 1211 (ν_{N-O}), 1159 ($\nu_{P=O}$). [Yb(**7**)$(NO_3)_3$] FTIR (KBr, cm^{-1}) 1635 ($\nu_{C=O}$), 1211 (ν_{N-O}), 1160 ($\nu_{P=O}$). [Ce(**7**)Cl_3] FTIR (KBr, cm^{-1}) 1631 ($\nu_{C=O}$), 1233 (ν_{N-O}), 1159 ($\nu_{P=O}$). [Dy(**7**)$(NO_3)_3$] FTIR (KBr, cm^{-1}) 1642 ($\nu_{C=O}$), 1231, 1215 (ν_{N-O}), 1160 ($\nu_{P=O}$). [Eu(**8**)$(NO_3)_3$] FTIR (KBr, cm^{-1}) 1631 ($\nu_{C=O}$), 1231 (ν_{N-O}), 1159, 1138 ($\nu_{P=O}$). [La(**8**)$(NO_3)_3$] $^{31}P\{^1H\}$ (121.49 MHz, d_4-MeOH) δ 37.40. ^1H NMR (300 MHz, d_4-MeOH) δ 3.91 (d, 4H, J_{HP} = 12.6 Hz, H_6), 4.54 (s, 4H, H_4), 6.88-7.98 (m, CH_{aro}). FTIR (KBr, cm^{-1}) 1633 ($\nu_{C=O}$), 1249 (ν_{N-O}), 1162, 1124 ($\nu_{P=O}$). [Pr(**8**)$(NO_3)_3$] FTIR (KBr, cm^{-1}) 1631 ($\nu_{C=O}$), 1230 (ν_{N-O}), 1159, 1138 ($\nu_{P=O}$). [Yb(**8**)$(NO_3)_3$] FTIR (KBr, cm^{-1}) 1632 ($\nu_{C=O}$), 1221 (ν_{N-O}), 1161, 1136, 1126 ($\nu_{P=O}$).

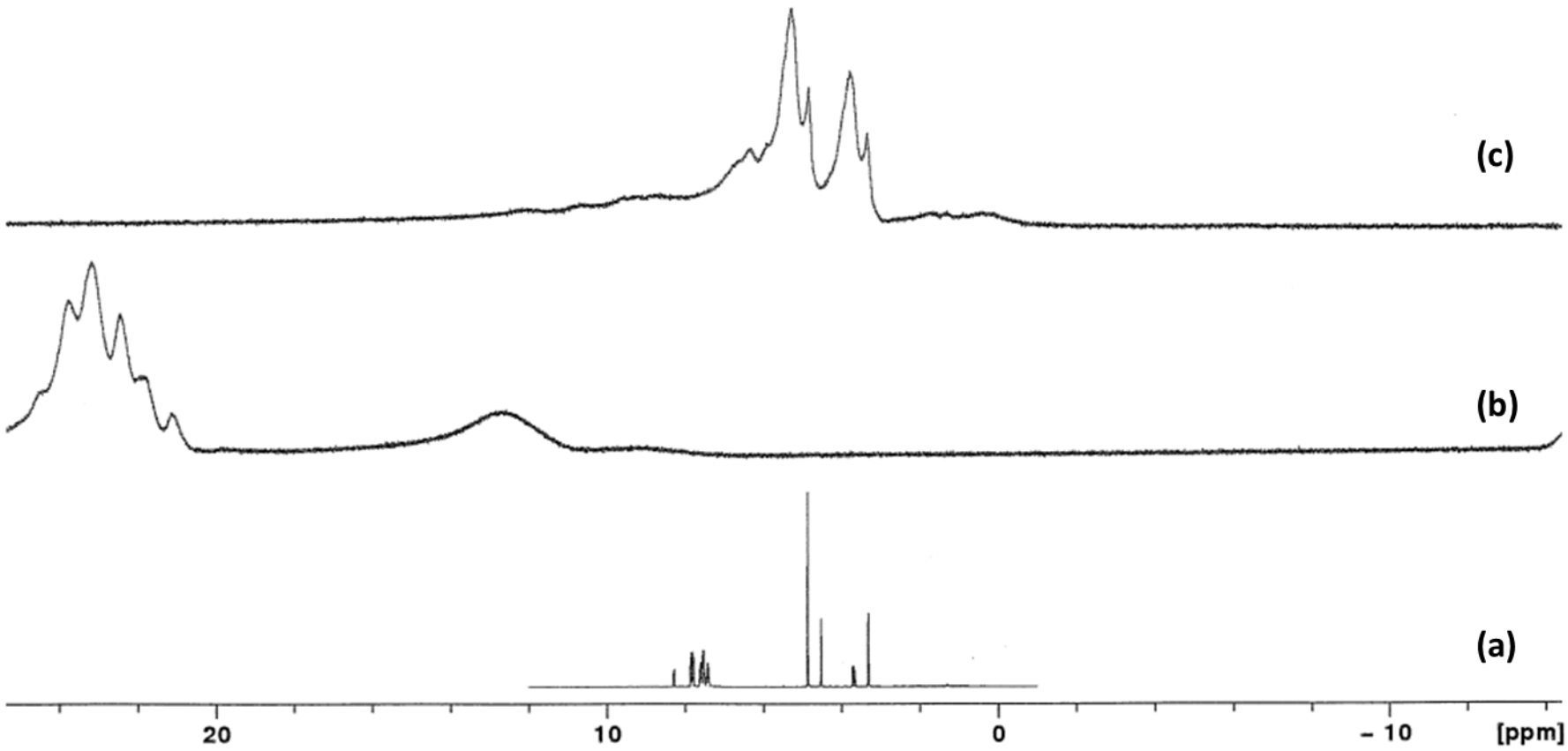


(i) **6**, (ii) 1:1 Eu-complex, (iii) $\{[Yb(\mathbf{6})(NO_3)_3]\cdot(MeOH)\}_n$, (iv) 1:1 Pr-complex, (v) 1:1 La-complex, (vi) $\{[Lu(\mathbf{6})(NO_3)_3]\cdot(MeOH)\}_n$, (vii) $\{[Er(\mathbf{6})_2(H_2O)_2]\cdot(NO_3)_3\cdot(H_2O)_4\}_n$

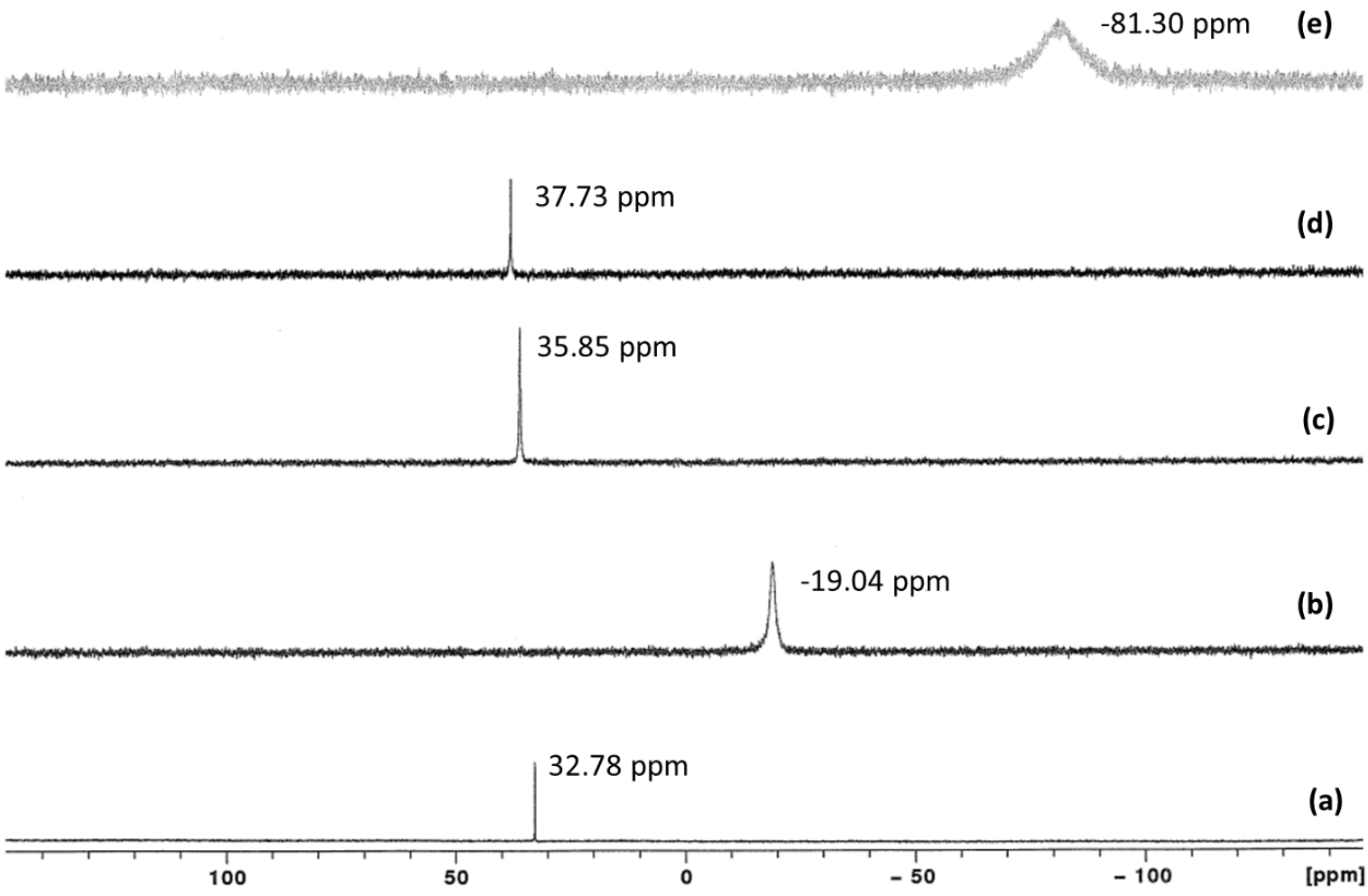
S.71 FTIR spectra of 6, 1:1 and 2:1 of 6 /Ln(III) complexes



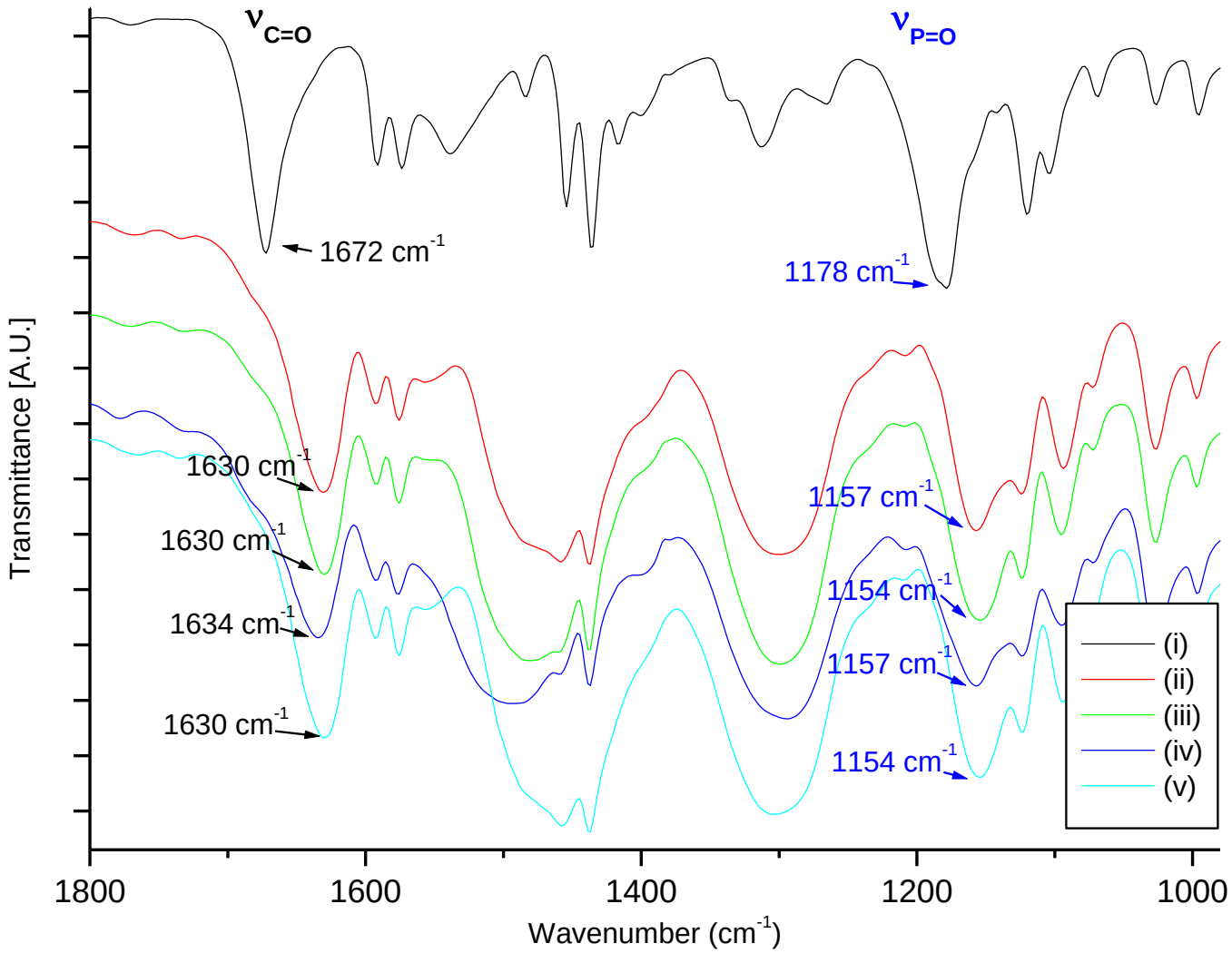
S.72 ^{1}H NMR spectrum for 6 (a), 1:1 La(III) (b), 1:1 Eu(III) (c) and 1:1 Lu(III) (d) Complexes in d_4-MeOH



S.73 ^{1}H NMR spectrum for 6 (a), 1:1 Er(III) complex (b) and 1:1 Yb(III) complex (c), in d_4-MeOH

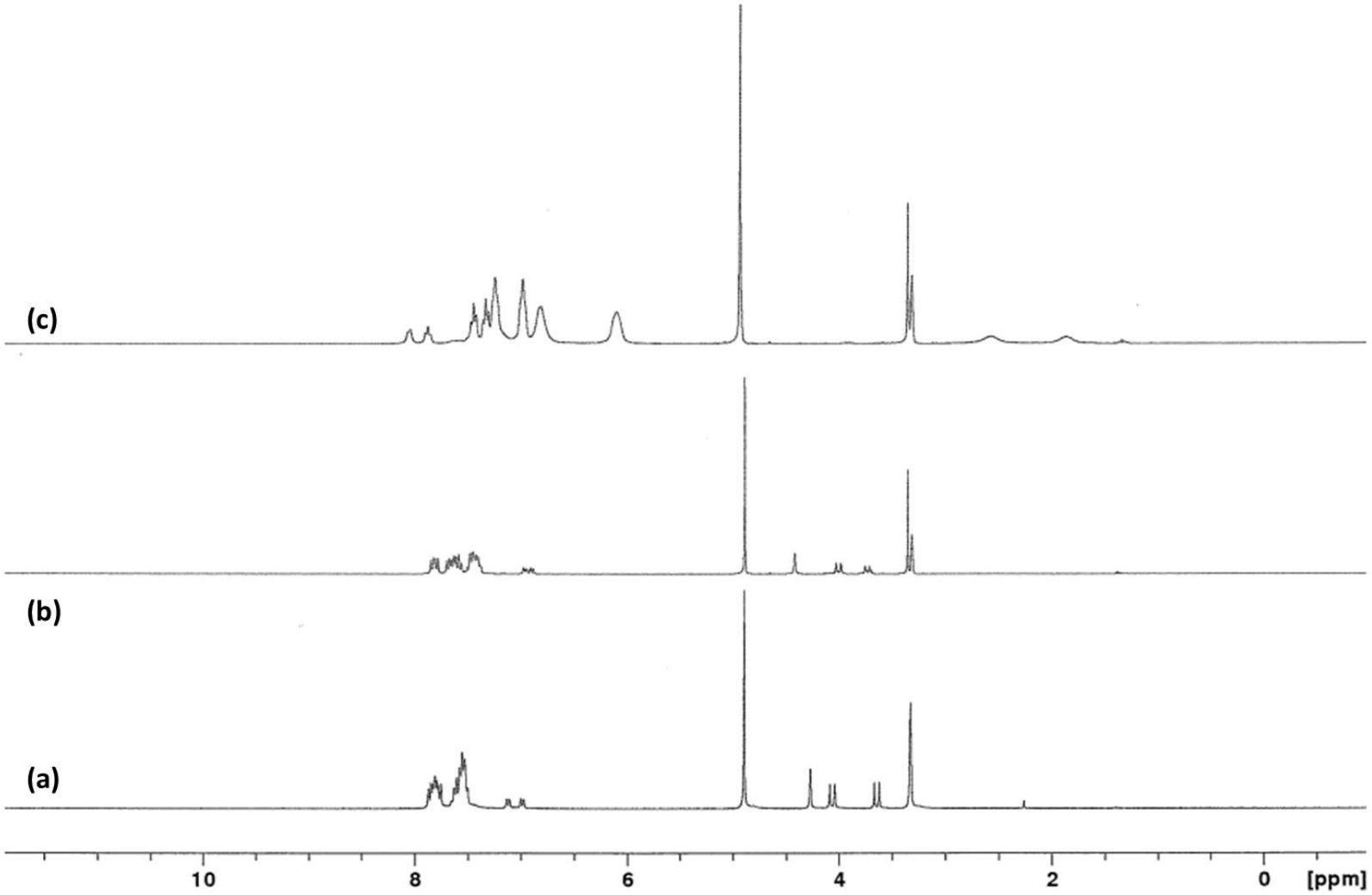


S.74 ^{31}P NMR spectrum for 6 (a), 1:1 Eu(III) (b), 1:1 La (III), (c), 1:1 Lu(III) (d), 1:1 Er(III) (e) Complexes, in d_4-MeOH

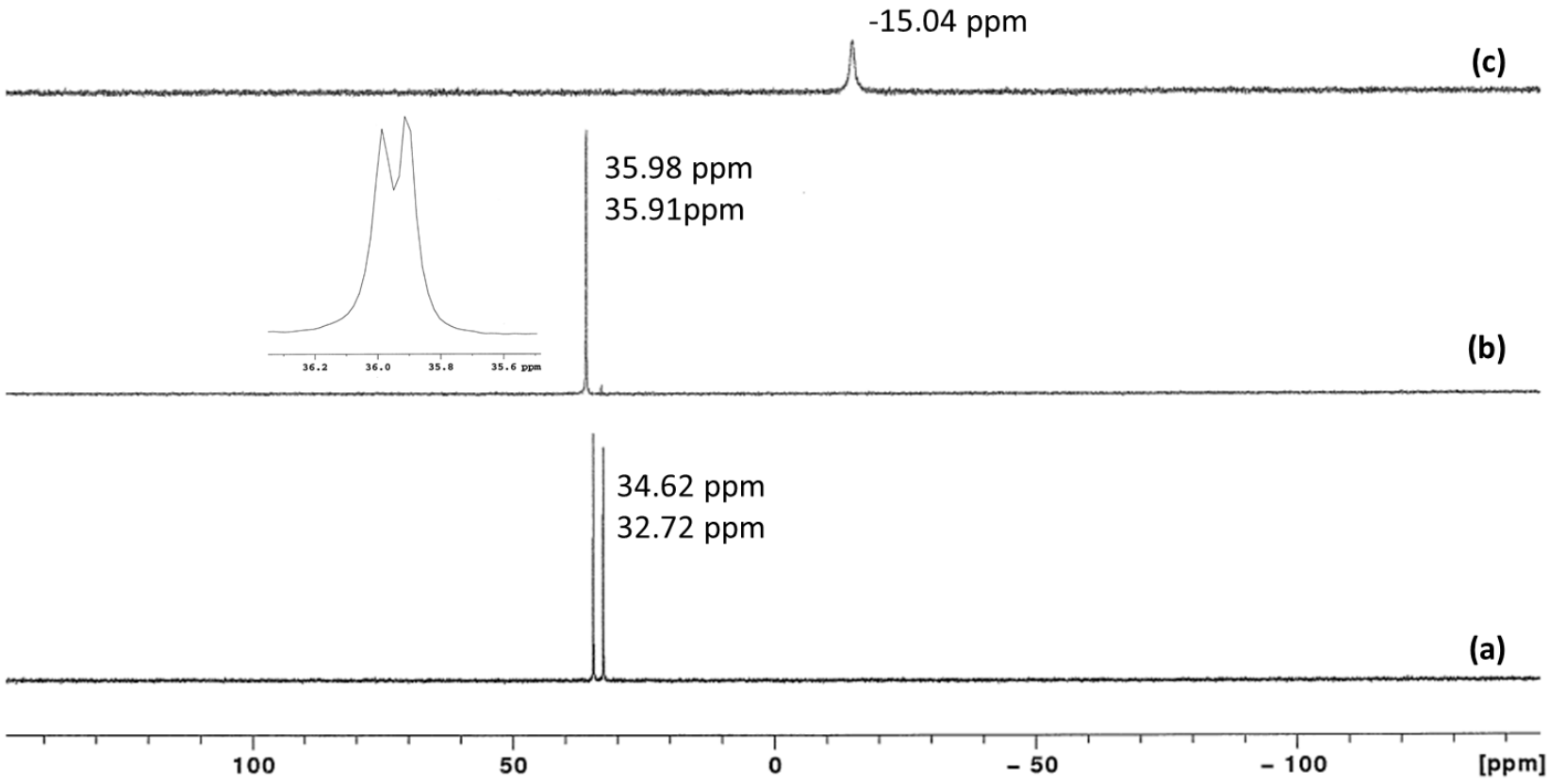


(i) **13**, (ii) 1:1 Pr-complex, (iii) 1:1 Eu-complex, (iv) 1:1 Yb-complex, (v) 1:1 La-complex

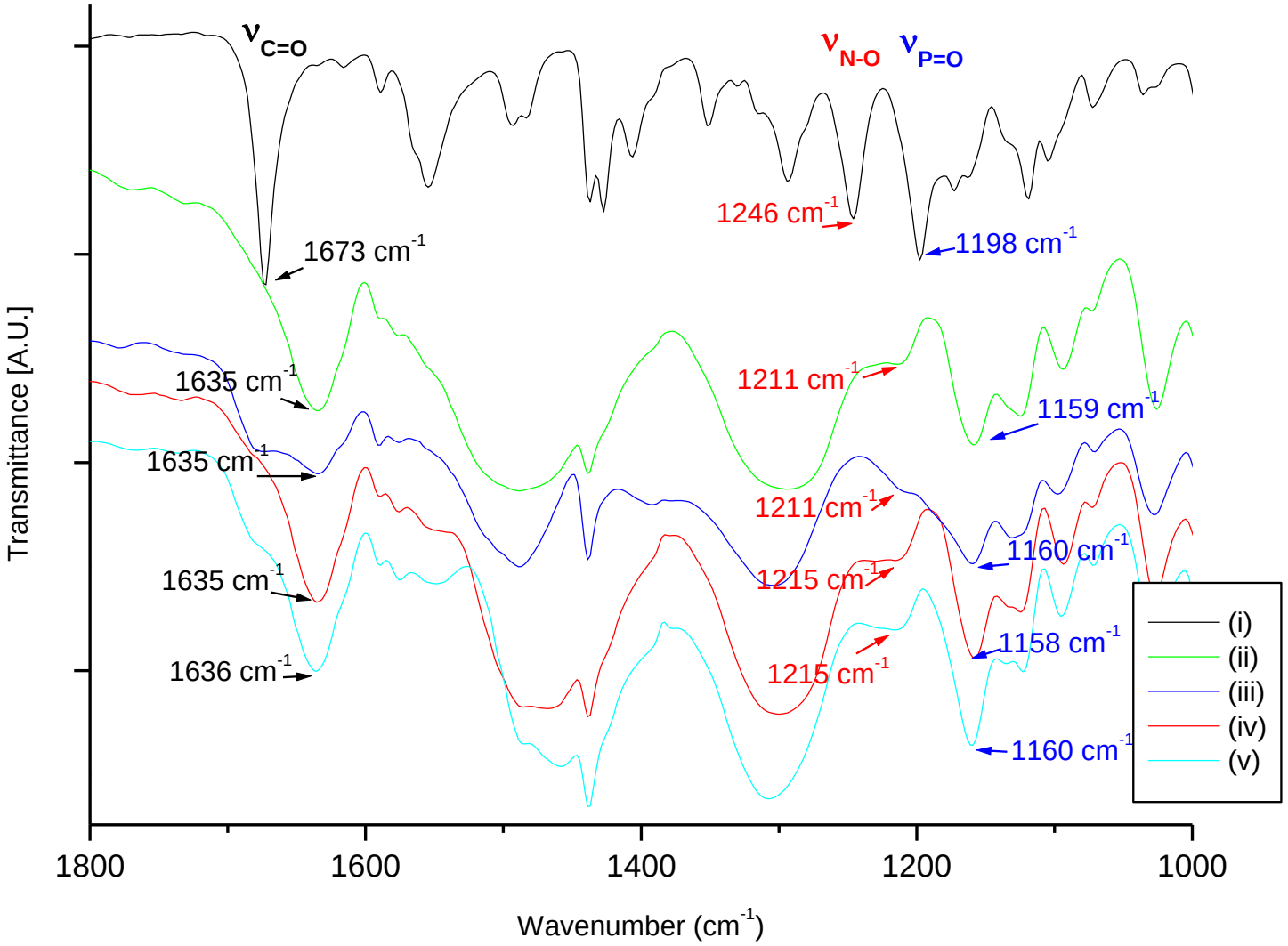
S.75 FTIR spectra of 13, 1:1 La(III) complex and 1:1 Ln(III) complex



S.76 ^{1}H NMR spectrum for 13 (a), 1:1 La(III) complex (b) and 1:1 Eu(III) complex (c), in d_4-MeOH

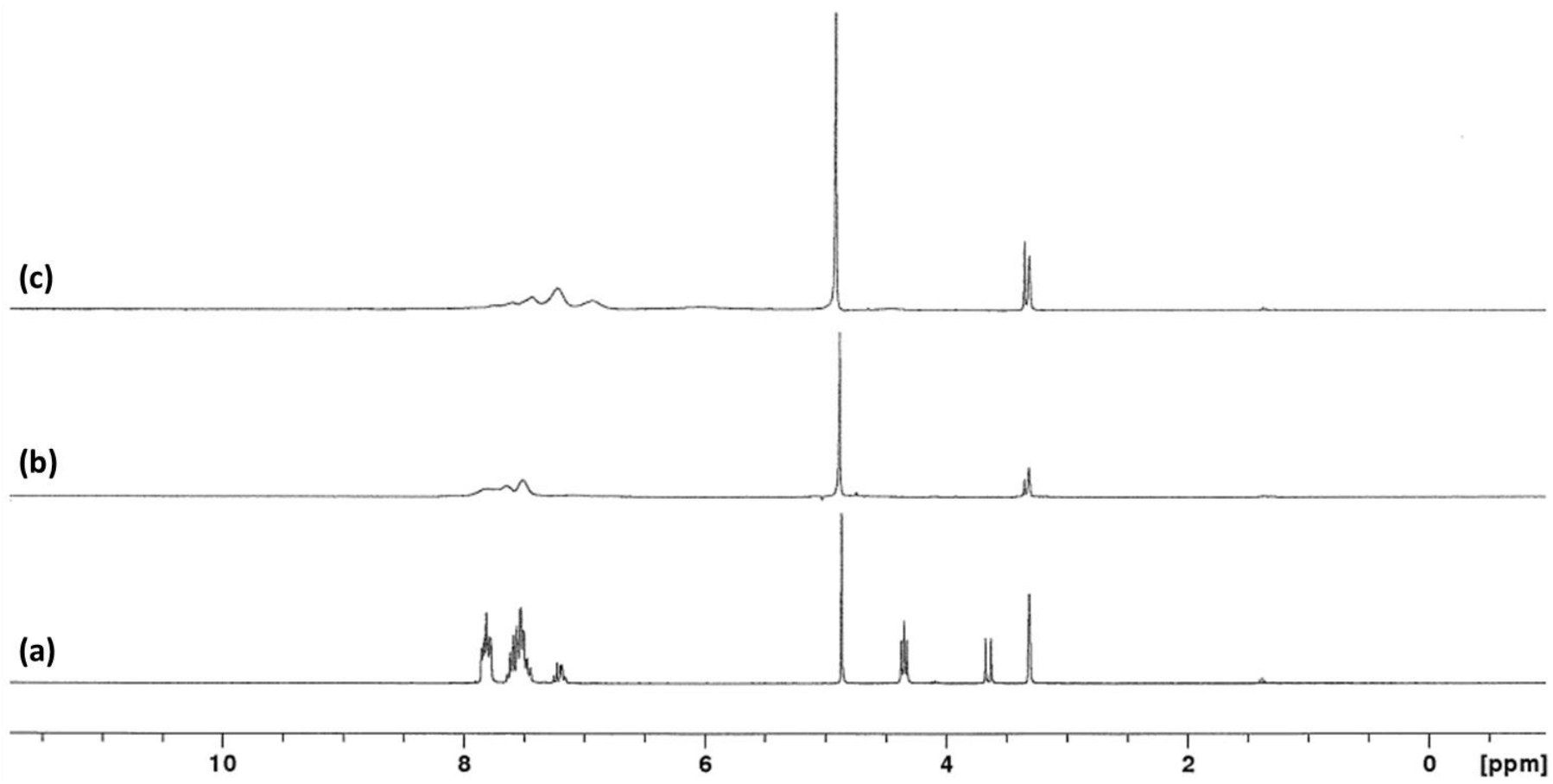


S.77 ^{31}P NMR spectrum for 13 (a), and 1:1 La(III) complex (b) and 1:1 Eu(III) complex (c), in d_4-MeOH

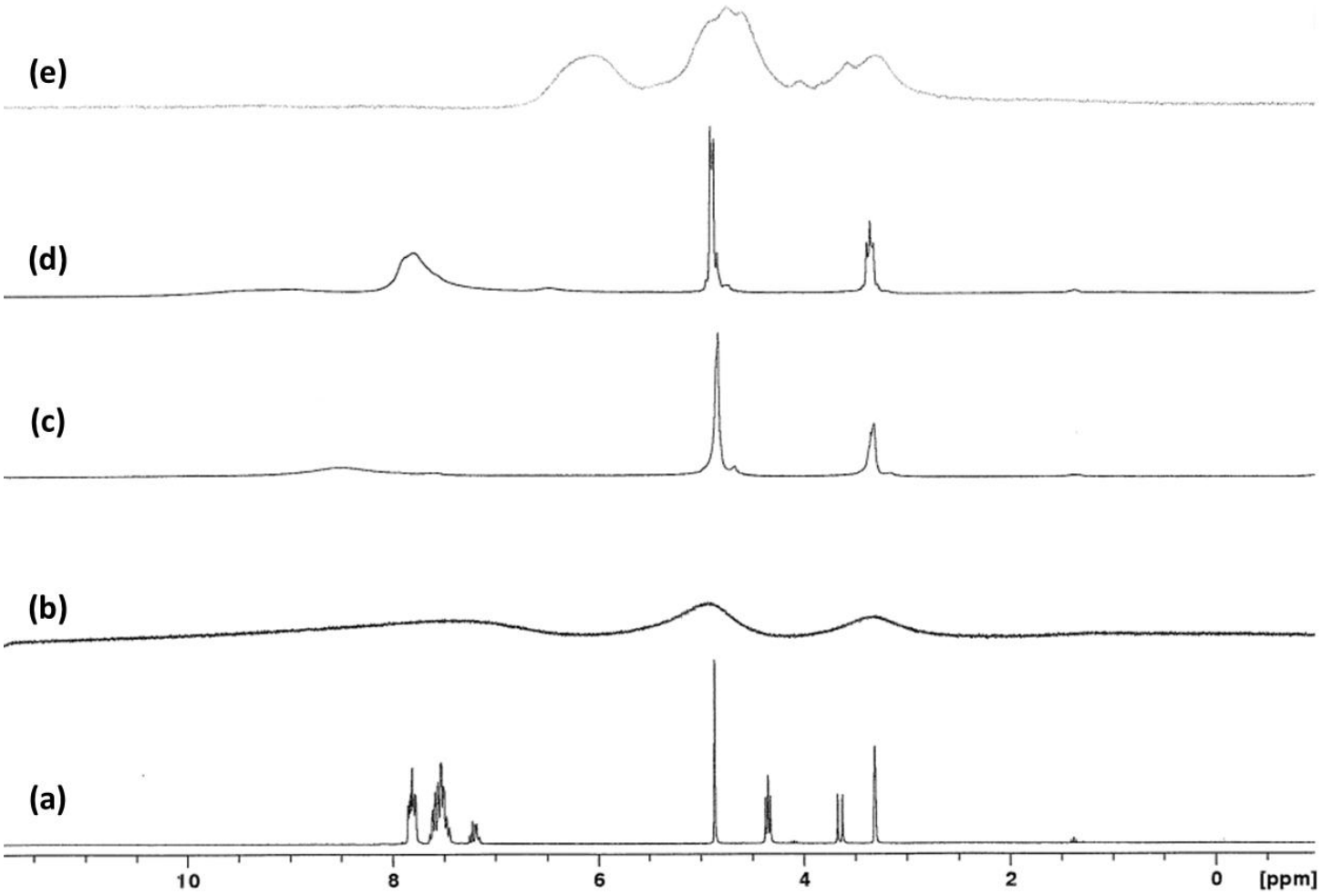


(i) **7**, (ii) 1:1 Eu-complex, (iii) 1:1 Yb-complex, (iv) 1:1 Pr-complex, (v) 1:1 La-complex

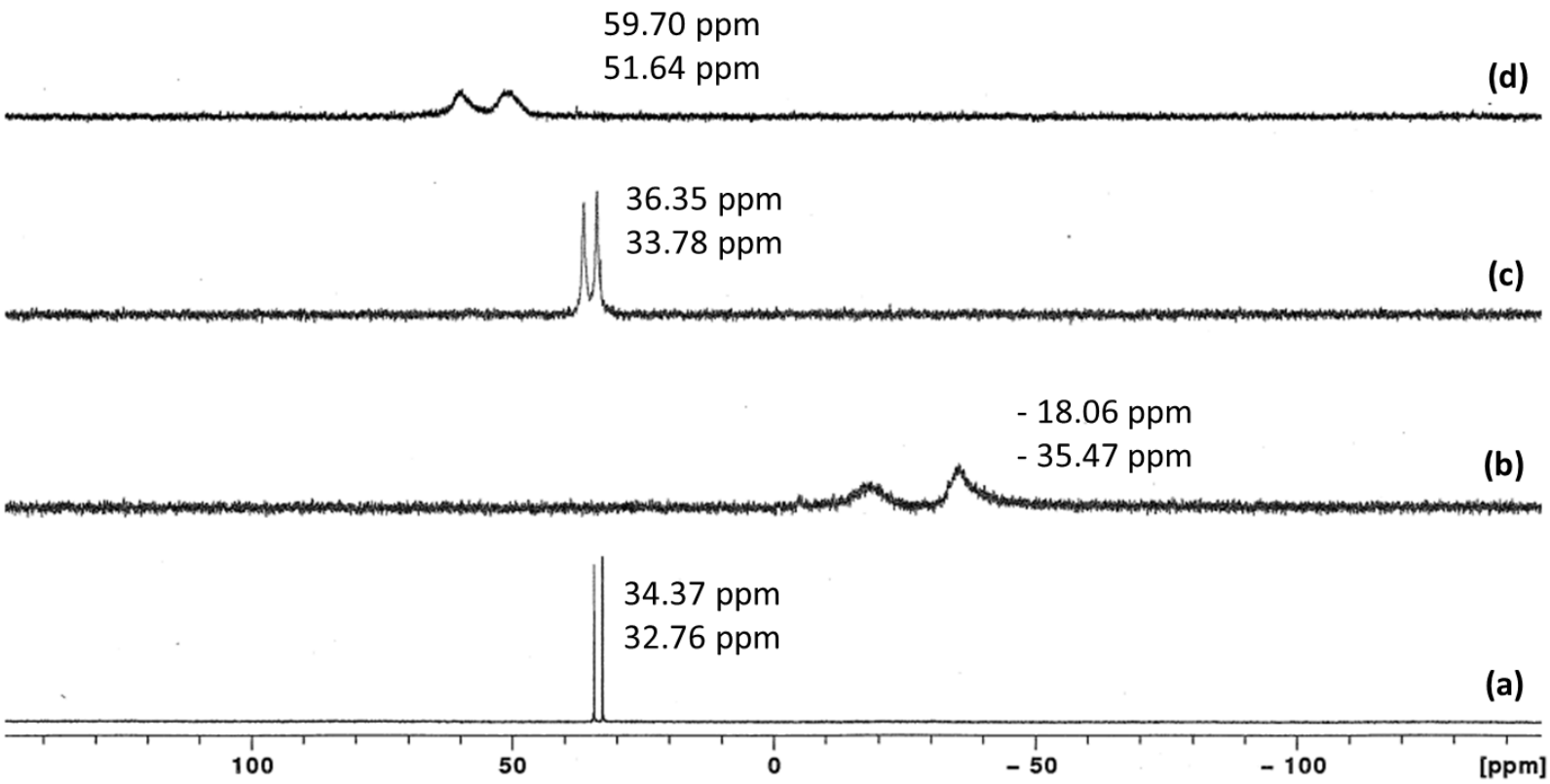
S.78 FTIR spectra of 7, 1:1 La(III) complex and 1:1 Ln(III) complex



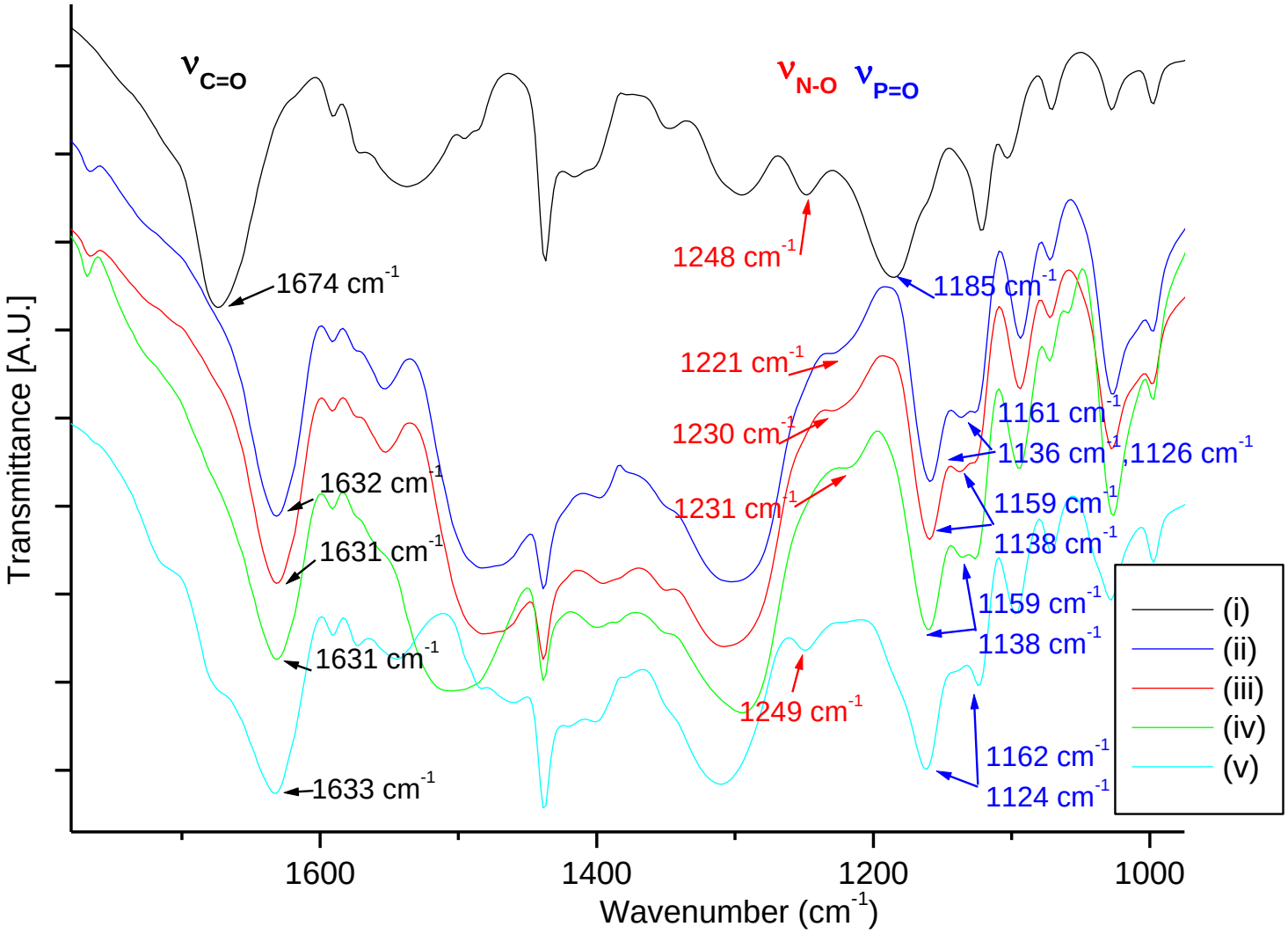
S.79 ^{1}H NMR spectrum for 7 (a), 1:1 La(III) complex (b) and 1:1 Eu(III) complex (c), in d_4-MeOH



S.80 ^{1}H NMR spectrum for 7 (a), 1:1 Yb(III) (b), 1:1 Pr(III) (c), 1:1 $CeCl_3$ (d), 1:1 Dy(III) (e) Complexes in d_4-MeOH

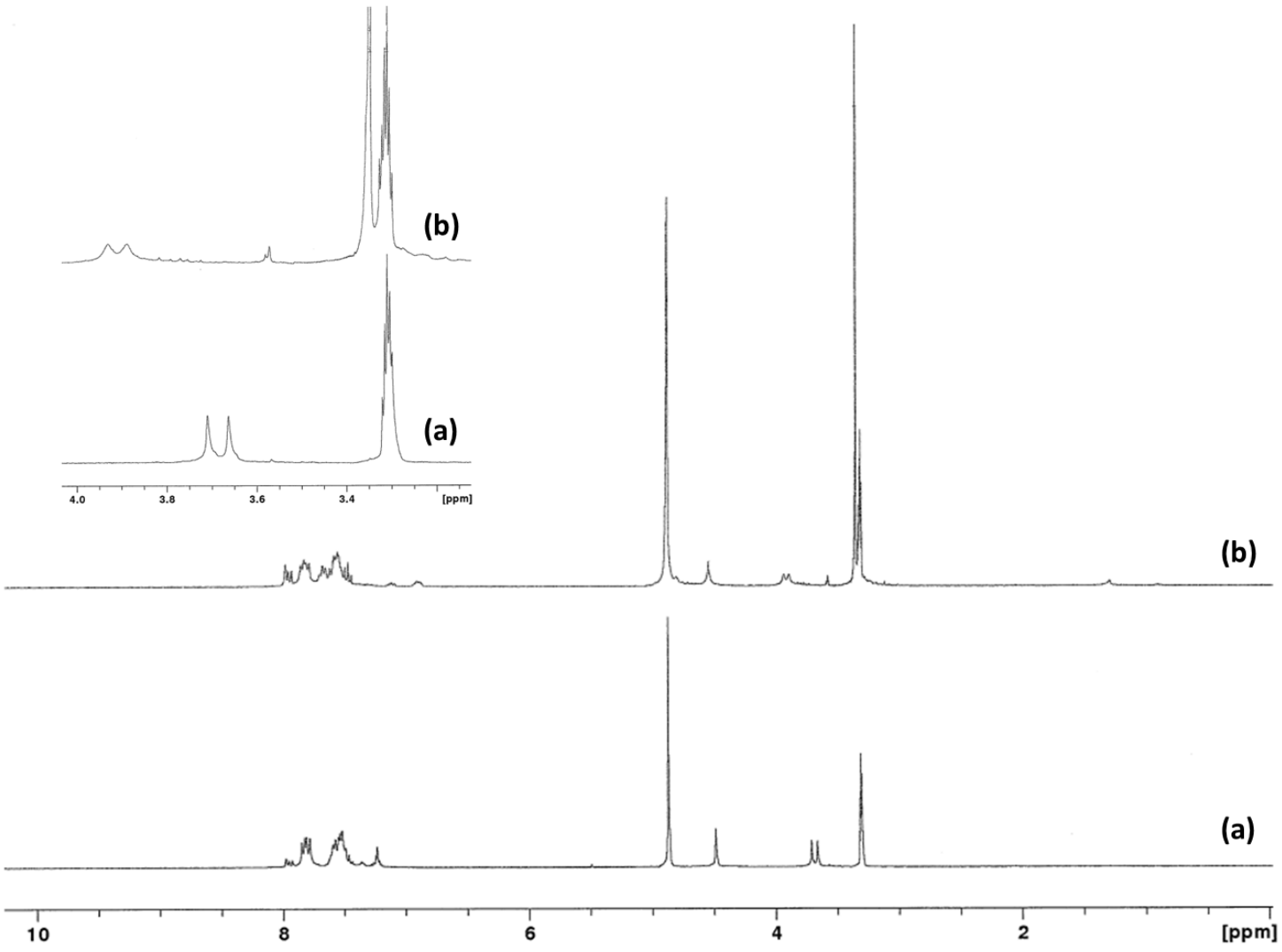


S.81 ^{31}P NMR spectrum for 7 (a), 1:1 Eu(III) (b), 1:1 La(III) (c), 1:1 $CeCl_3$(III) (d) Complexes in d_4-MeOH

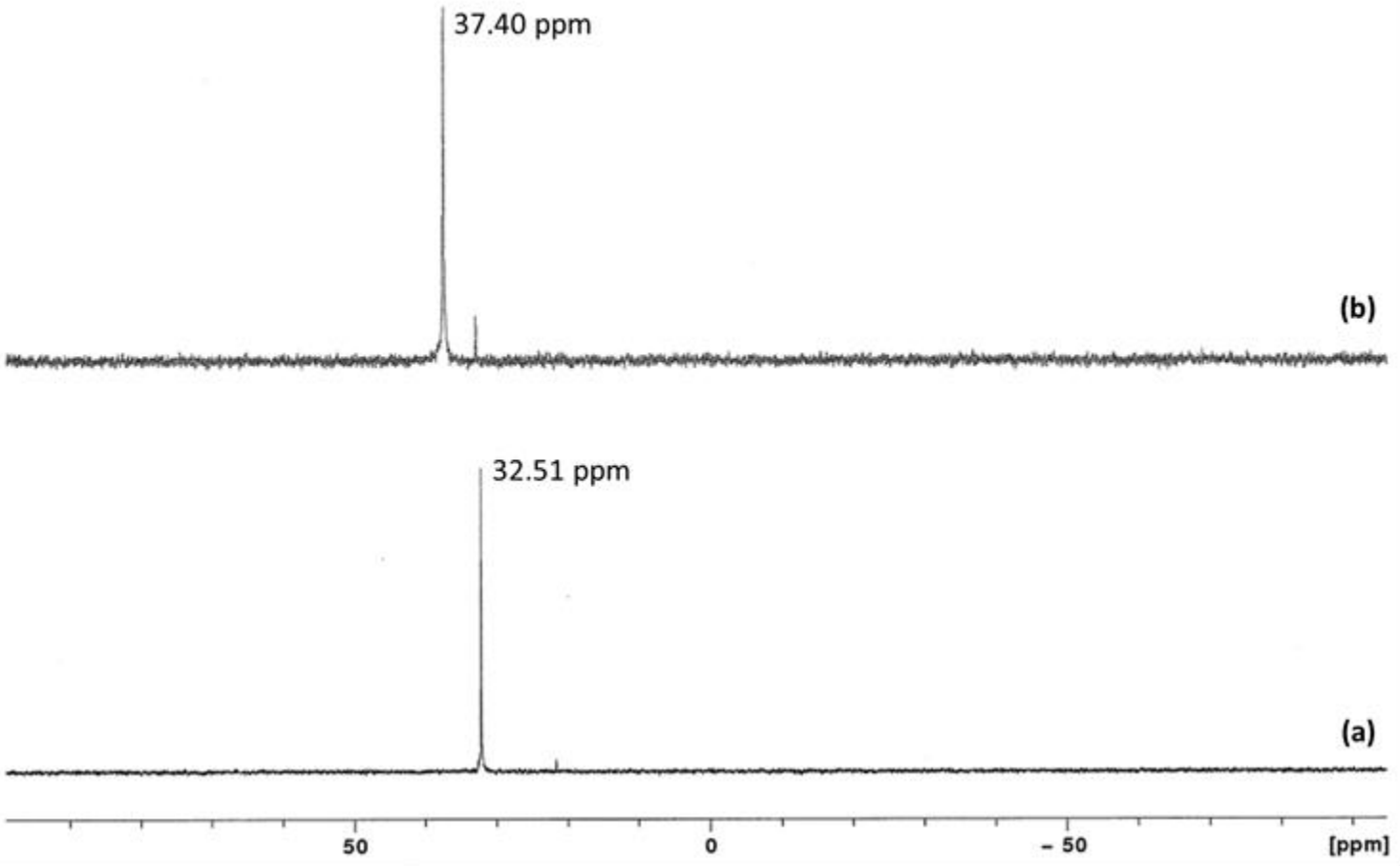


(i) **8**, (ii) 1:1 Yb-complex, (iii) 1:1 Pr-complex, (iv) 1:1 Eu-complex, (v) 1:1 La-complex

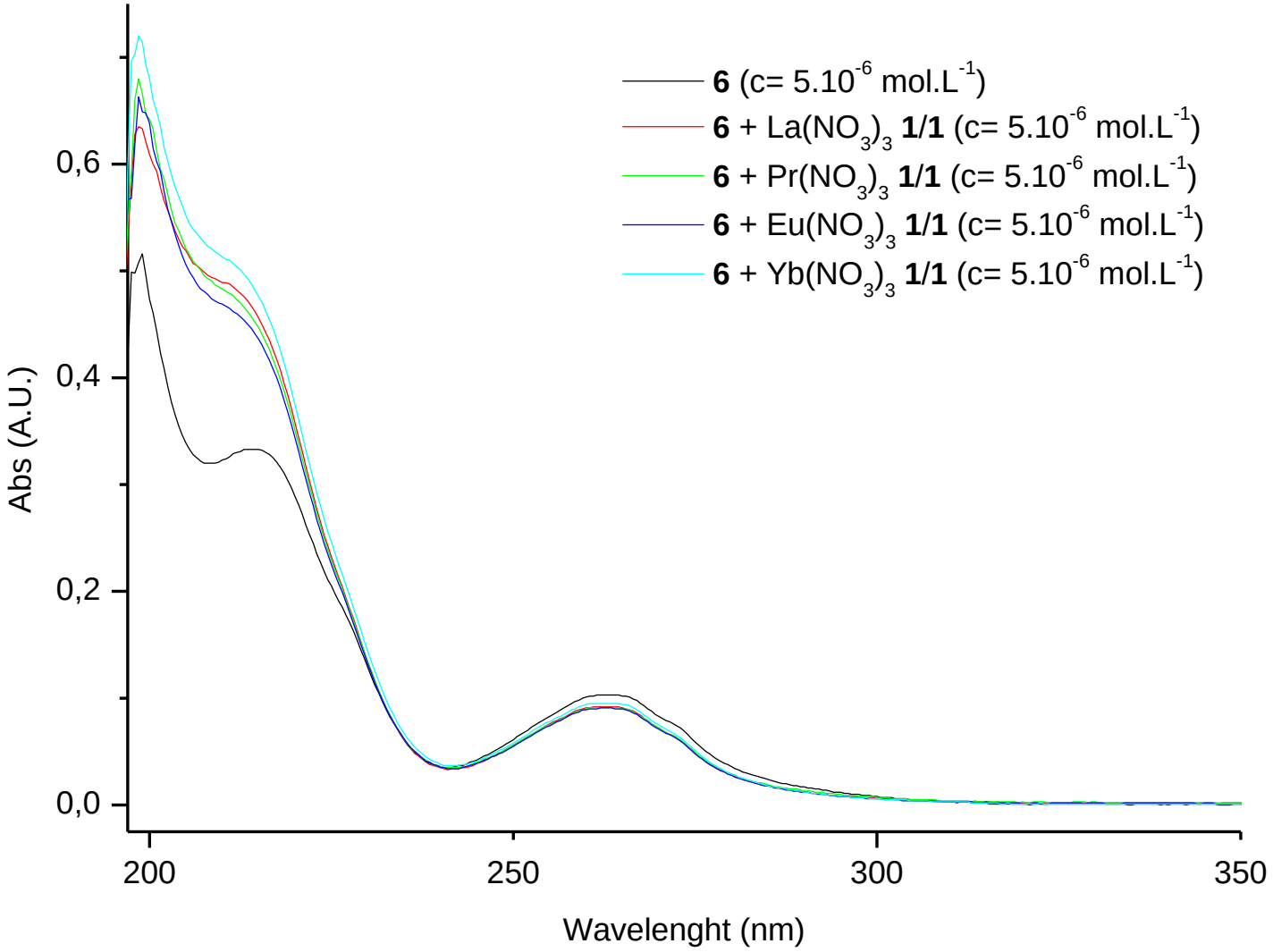
S.82 FTIR spectra of 8, 1:1 La(III) complex and 1:1 Ln(III) complex



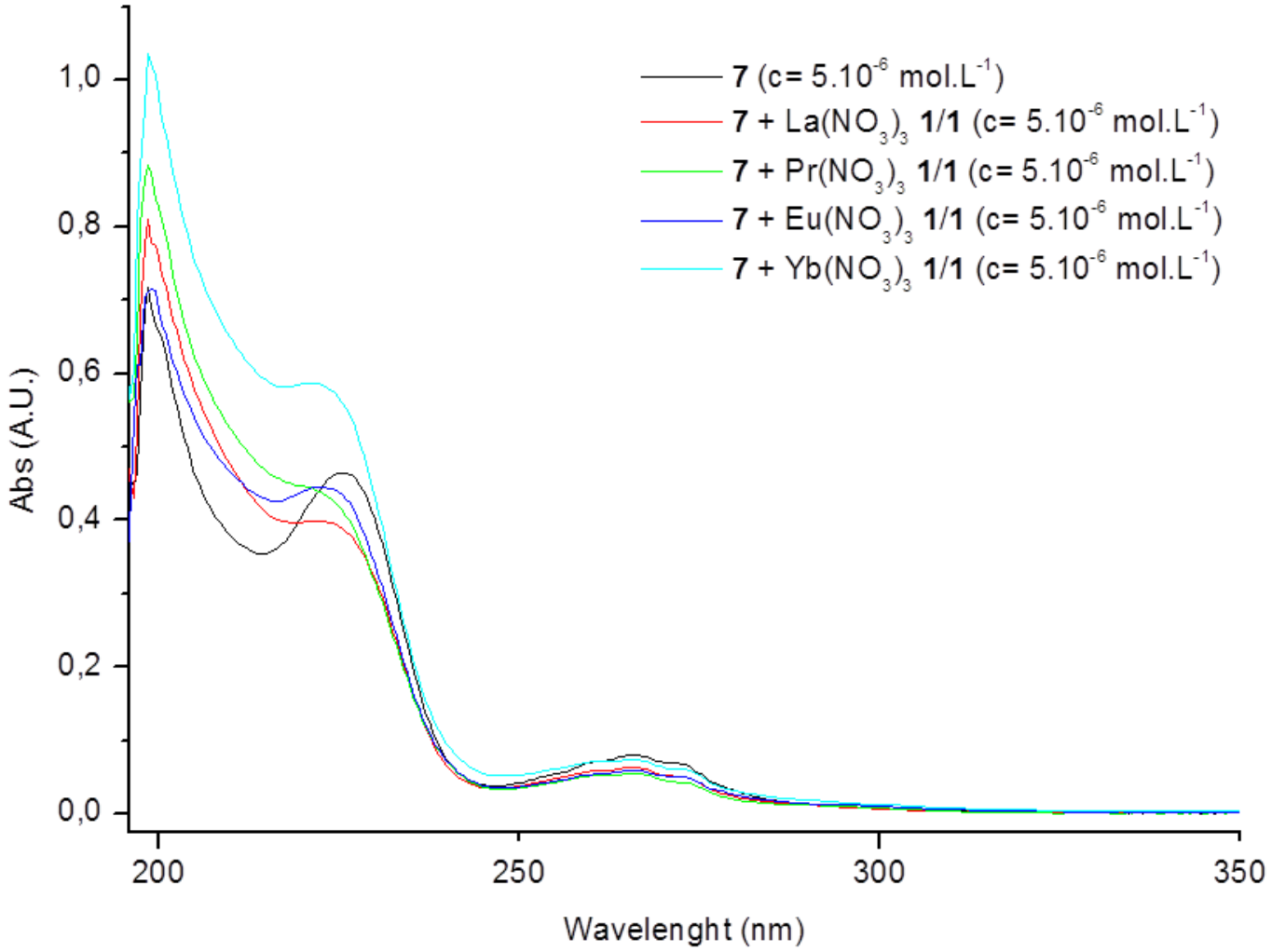
S.83 ^{1}H NMR spectrum for 8 (a) and 1:1 La(III) complex (b), in d_4-MeOH



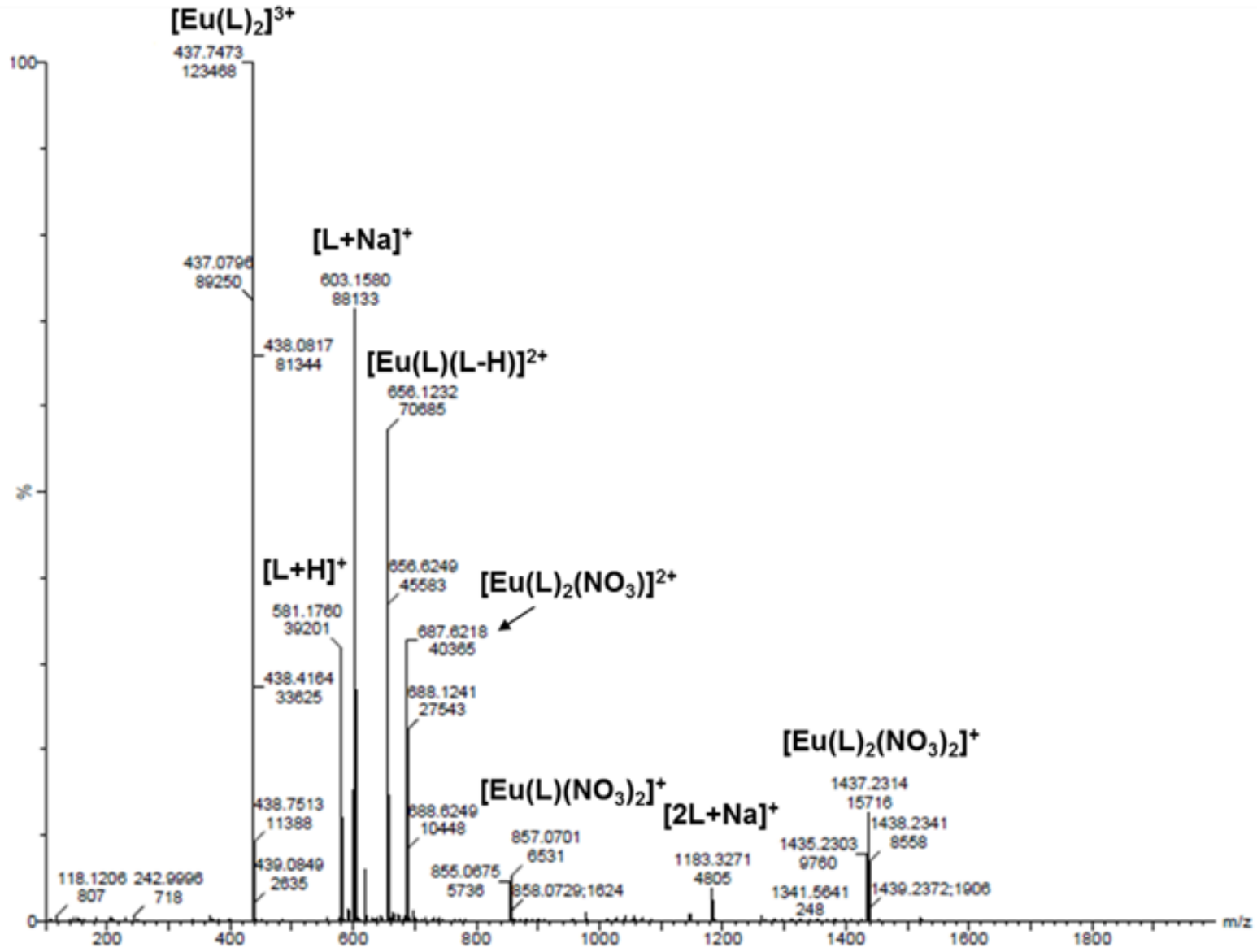
S.84 ^{31}P NMR spectrum for 8 (a) and 1:1 La(III) complex (b), in d_4-MeOH



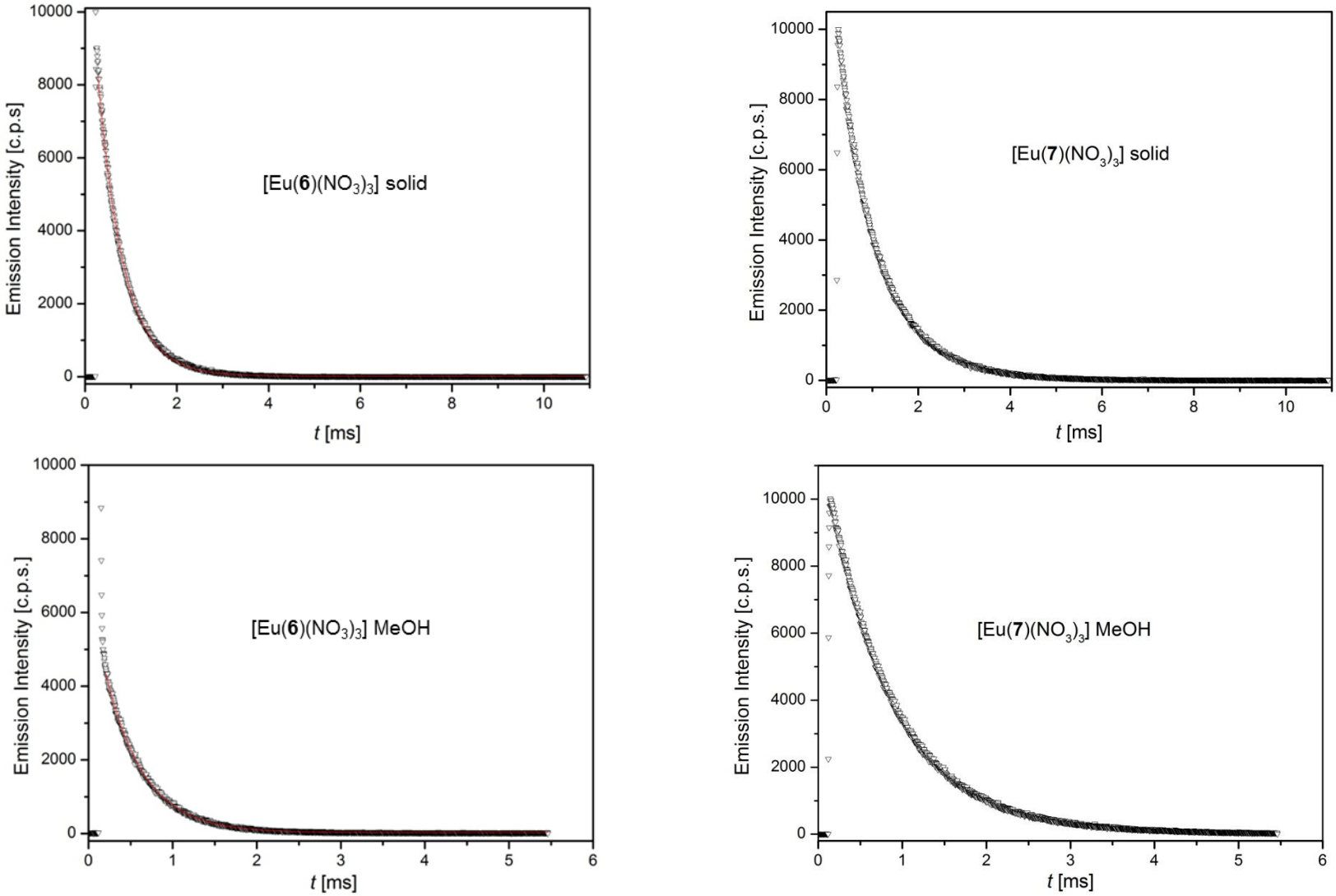
S.85 Vis-UV spectra of 6, 6/La(III) and 6/Ln(III), 1:1 complexes in MeOH



S.86 Vis-UV spectra of 7, 7/La(III) and 7/Ln(III), 1:1 complexes in MeOH

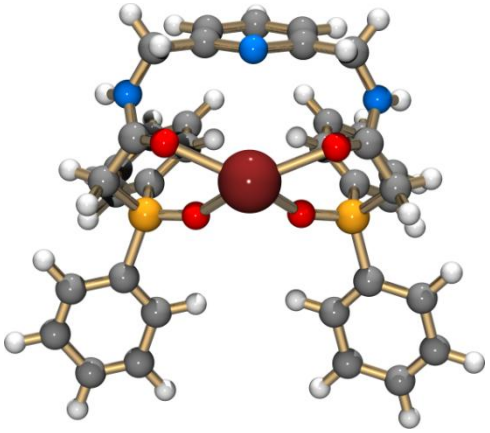


S.87 HRMS spectrum for $\{[Eu(7)(NO_3)_2(EtOAc)_{0.5}(H_2O)_{0.5}]\cdot(NO_3)\}_2\cdot(MeOH)$

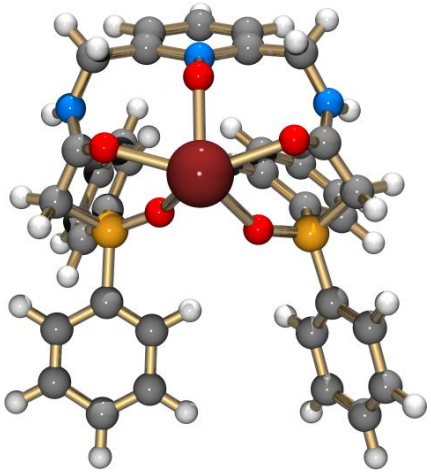


S.88 Emission intensity decay profiles for Eu(III) complexes with ligands 6 and 7 in the solid state and methanol solution at 25°C.

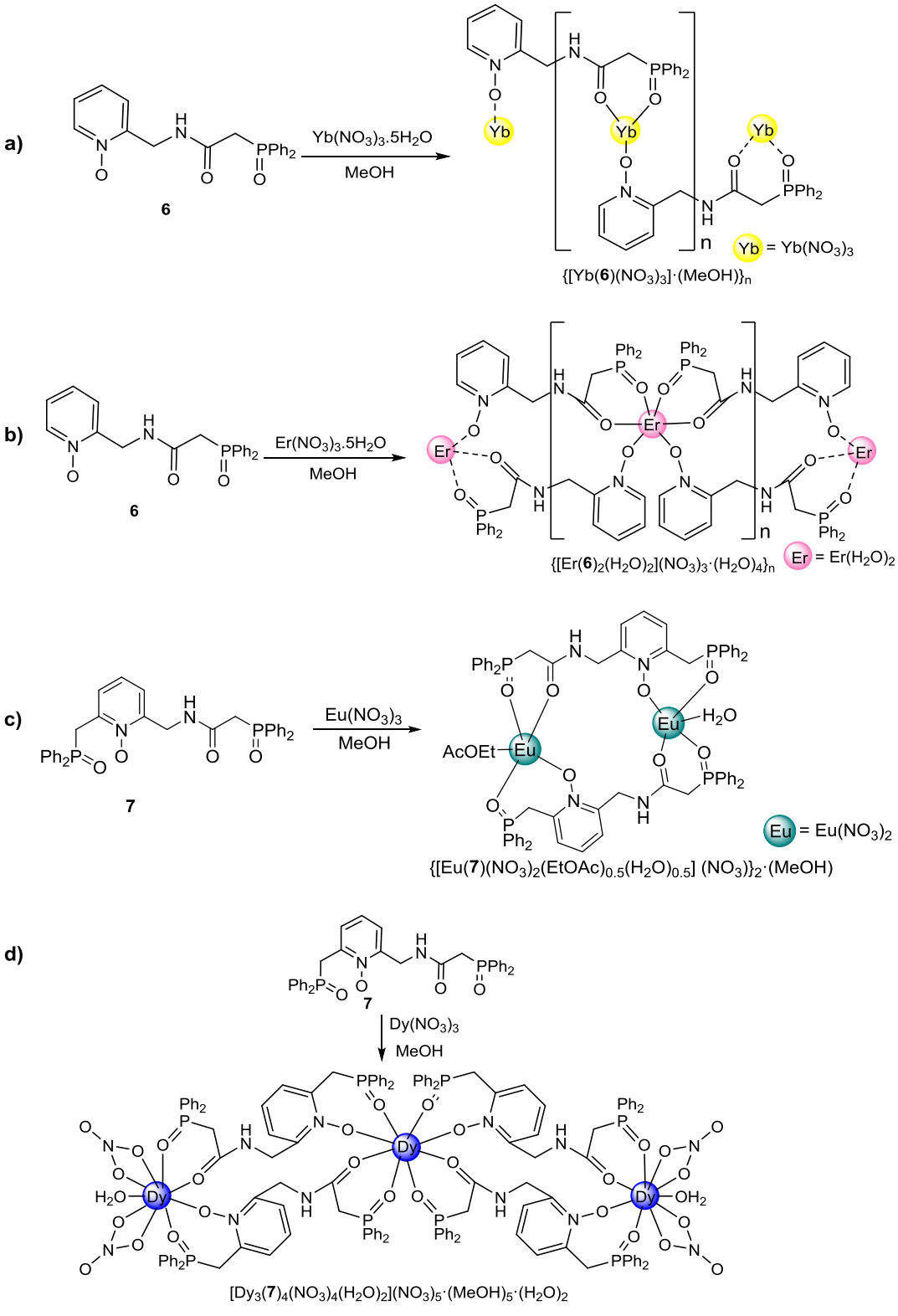
a)



b)



S.89 Computed lowest energy gas phase structure for a) 1:1 tetradentate $(OPOC)_2$ binding of 18 on Eu(III), b) 1:1 pentadentate $(OPOC)_2ON$ binding of 8 on Eu(III) .



S.90 Schematic views of coordination complexes of a) $\{[Yb(6)(NO_3)_3]\cdot(MeOH)\}_n$, b) $\{[Er(6)_2(H_2O)_2](NO_3)_3\cdot(H_2O)_4\}_n$ c) $\{[Eu(7)(NO_3)_2(EtOAc)_{0.5}(H_2O)_{0.5}]\ (NO_3)\}_2\cdot(MeOH)$, d) $[Dy_3(7)_4(NO_3)_4(H_2O)_2](NO_3)_5\cdot(MeOH)_5\cdot(H_2O)_2$

S.91 Parameter files for MM3 computations

Molecular mechanics strain energy calculations were performed with an extended MM3 model as implemented in PCModel. The added parameter file used to treat these ligands and metal complexes is given below:

```
#torsions
torsion          5    1    2   37       0.000 +1   0.000 -2  -0.090 +3
torsion        153    1    2    2      -0.700 +1  -0.200 -2  -0.550 +3
torsion        153    1    2   37      -0.700 +1  -0.200 -2  -0.550 +3
torsion          5    1    3    9       0.000 +1   0.000 -2  -0.254 +3
torsion          1    1    3    9      -0.457 +1   0.097 -2  -0.630 +3
torsion        153    1    3    7       0.000 +1   0.000 -2  -0.350 +3
torsion        153    1    3    9       0.185 +1  -2.296 -2  -0.923 +3
torsion          5    1    9    1       0.000 +1   0.000 -2   0.936 +3
torsion          2    1  153    2       1.100 +1   0.000 -2   1.500 +3
torsion          2    1  153   49       0.000 +1   0.000 -2   0.270 +3
torsion          2    2    2  153       0.000 +1   7.000 -2   0.000 +3
torsion          2    2  153   49      -0.150 +1   0.000 -2   0.200 +3
torsion          1    2   37    2      -0.610 +1   7.000 -2   0.000 +3
torsion          1    2   37  201      -0.610 +1   7.000 -2   0.000 +3
torsion          2    2   37  201       0.000 +1  12.000 -2   0.000 +3
torsion          5    2   37  201       0.000 +1  12.000 -2   0.000 +3
torsion          1    3    9    1       1.100 +1   6.270 -2   0.000 +3
torsion          7    3    9    1      -0.600 +1   6.930 -2   0.000 +3
torsion          9    3    7  345       0.000 +1   0.200 -2   0.000 +3
torsion          1    3    7  345       0.000 +1   0.200 -2   0.000 +3
torsion        345   49  153    1       0.000 +1   0.000 -2   0.000 +3
torsion        345   49  153    2       0.000 +1   0.000 -2   0.000 +3
torsion        345   49  153    3       0.000 +1   0.000 -2   0.000 +3
torsion          2   37  201  345       0.000 +1  -0.300 -2   0.000 +3

#vdw
vdw            345       1.60      0.09
vdwpr        5    7      2.580     0.400
vdwpr        5   49      2.580     0.400

#bonds
bond         3    7    10.1000    1.2230
bond         3    9     6.7000    1.3310
bond        49  153     8.7000    1.5000
bond        37  201     9.0000    1.3400
bond         7  345     1.0000    2.3900
bond        49  345     1.0000    2.3500
bond       201  345     1.0000    2.4000

#bond angles
angle          2    1  153     0.5000   109.5000
angle          1    2   37     0.4700   122.3000
angle          2    2  153     1.0000   120.0000
angle          3    7  345     0.0600   142.3000
angle          2   37  201     1.7300   121.7000
angle        153   49  345     0.1000   165.0000
angle          1  153    1     0.5000   108.5000
angle          1  153    2     0.5000   108.5000
angle          2  153    2     0.5000   108.5000
```

```
angle          1  153   49     0.5000   111.5000
angle          2  153   49     0.5000   111.5000
angle         37  201  345     0.1000   132.0000

# Atom typing
#aliphatic C   1
#benzene C     2
#carbonyl C    3
#CH hydrogen   5
#amide O       7
#amide N       9
#pyridine N   37
#P=O oxygen   49
#phosphorus  153
#N-O oxygen  201
#Ln metal    345

# NOTES ON M-O LENGTHS
#Early LN (La, Pr, Nd)  P=O 2.41; N-O 2.47; C=O 2.47
#Mid LN (Sm, Eu, Gd)    P=O 2.35; N-O 2.39; C=O 2.40
#Late LN (Tm, Yb, Lu)   P=O 2.24; N-O 2.30; C=O 2.29
```

Atomic coordinates and MM3 steric energies for species shown in Figures 5 and 6

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45
Fig5a, global minimum for 6, E = 5.467 kcal/mol
P     -1.577      1.186     -0.001
O      2.687     -1.155      3.759
O      1.495      2.877      0.197
O     -2.963      1.540     -0.460
N      2.826     -1.205      2.425
N      0.957      1.626      1.985
C      3.102     -2.375      1.797
C      3.237     -2.498      0.419
C      3.091     -1.373     -0.386
C      2.818     -0.158      0.241
C      2.685     -0.099      1.649
C      2.333      1.250      2.271
C      0.645      2.371      0.919
C     -0.795      2.601      0.680
C     -1.691     -0.052      1.365
C     -0.717     -1.047      1.508
C     -0.721     -1.884      2.625
C     -1.696     -1.734      3.611
C     -2.678     -0.738      3.477
C     -2.668      0.106      2.352
C     -0.660      0.456     -1.428
C     -0.932     -0.858     -1.827
C     -0.265     -1.420     -2.918
C      0.669     -0.669     -3.632
C      0.929      0.661     -3.256
C      0.254      1.222     -2.157
```

```
H      0.200      1.169      2.518
H      3.218     -3.279      2.420
H      3.454     -3.480     -0.035
H      3.182     -1.438     -1.483
H      2.685      0.752     -0.367
H      2.500      1.220      3.371
H      3.047      2.015      1.888
H     -0.949      3.480      0.025
H     -1.309      2.934      1.601
H      0.068     -1.177      0.746
H      0.054     -2.662      2.729
H     -1.697     -2.396      4.494
H     -3.454     -0.618      4.251
H     -3.446      0.881      2.245
H     -1.678     -1.461     -1.283
H     -0.480     -2.460     -3.218
H      1.196     -1.112     -4.494
H      1.661      1.263     -3.820
H      0.469      2.265     -1.871

45
Fig5(b), X-ray conformation of 6, E = 12.013 kcal/mol
P     -0.592      0.192      0.550
N      3.710      2.822      0.078
N      1.701      2.058      2.058
H      1.342      2.756      1.387
O      2.834      3.829      0.229
O      1.335      0.179      3.241
O      0.695      0.188     -0.225
C      4.382      2.689     -1.040
C      5.321      1.641     -1.262
C      5.513      0.727     -0.223
C      4.779      0.925      0.917
C      3.915      1.956      1.022
C      3.131      2.104      2.317
C      0.927      1.059      2.494
C     -0.481      1.108      2.043
C     -1.926      0.984     -0.448
C     -3.252      0.938     -0.005
C     -4.262      1.562     -0.742
C     -3.952      2.240     -1.922
C     -2.619      2.296     -2.369
C     -1.606      1.667     -1.625
C     -1.097     -1.550      0.895
C     -0.625     -2.209      2.035
C     -0.978     -3.538      2.281
C     -1.798     -4.224      1.383
C     -2.262     -3.576      0.225
C     -1.903     -2.238     -0.019
H      4.209      3.423     -1.846
H      5.871      1.552     -2.214
H      6.219     -0.116     -0.319
H      4.901      0.217      1.753
H      3.408      3.072      2.793
```

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H      3.432      1.318      3.047
H     -1.182      0.733      2.812
H     -0.843      2.145      1.911
H     -3.510      0.404      0.925
H     -5.306      1.518     -0.390
H     -4.750      2.732     -2.503
H     -2.370      2.831     -3.301
H     -0.561      1.708     -1.978
H      0.033     -1.686      2.749
H     -0.604     -4.047      3.185
H     -2.075     -5.274      1.578
H     -2.902     -4.116     -0.493
H     -2.262     -1.741     -0.936

46
Fig5(c), global minimum Eu-6 complex, E = 11.818 kcal/mol
Eu    -1.387     -4.116     -0.379
P      0.322     -0.916      0.229
O     -3.663     -3.359     -0.181
O     -1.346     -3.071      1.792
O     -0.117     -2.141     -0.519
N     -4.280     -2.175     -0.319
N     -2.299     -1.056      2.116
C     -4.893     -1.841     -1.481
C     -5.548     -0.633     -1.688
C     -5.587      0.308     -0.664
C     -4.956     -0.011      0.539
C     -4.312     -1.263      0.690
C     -3.658     -1.570      2.032
C     -1.242     -1.860      1.951
C      0.086     -1.199      1.948
C      2.094     -0.541     -0.112
C      3.090     -1.393      0.375
C      4.437     -1.127      0.116
C      4.798     -0.010     -0.640
C      3.802      0.842     -1.147
C      2.447      0.570     -0.884
C     -0.721      0.535     -0.225
C     -1.684      0.415     -1.230
C     -2.493      1.503     -1.564
C     -2.355      2.714     -0.885
C     -1.392      2.841      0.131
C     -0.572      1.747      0.457
H     -2.145     -0.037      2.132
H     -4.868     -2.576     -2.304
H     -6.032     -0.420     -2.656
H     -6.096      1.277     -0.801
H     -4.964      0.718      1.366
H     -4.281     -1.126      2.841
H     -3.688     -2.667      2.218
H      0.872     -1.833      2.399
H      0.151     -0.284      2.565
H      2.820     -2.288      0.960
H      5.216     -1.804      0.504
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H      5.862      0.198     -0.847
H      4.081      1.719     -1.755
H      1.674      1.237     -1.301
H     -1.814     -0.545     -1.758
H     -3.248      1.400     -2.362
H     -2.998      3.572     -1.149
H     -1.272      3.801      0.662
H      0.198      1.860      1.239

71
Fig6(a), global minimum form of 7, E = 7.643 kcal/mol
P     -5.379      0.421      0.827
O     -0.333      2.864      0.643
N     -0.494      2.877     -0.689
C     -1.603      3.439     -1.259
O     -6.843      0.724      0.687
C     -1.783      3.503     -2.642
P      1.627     -0.116     -0.914
C     -0.822      2.973     -3.494
C      0.300      2.376     -2.922
C      0.440      2.334     -1.516
C     -5.181     -1.265      1.555
O      1.314     -0.646     -2.285
N     -3.102      2.900      0.574
C     -5.259     -1.444      2.940
C     -5.136     -2.720      3.495
C     -4.946     -3.830      2.670
C     -4.887     -3.661      1.275
C     -5.010     -2.375      0.721
C     -4.560      0.433     -0.828
C     -3.225      0.037     -0.953
C     -2.600      0.042     -2.202
C     -3.306      0.445     -3.336
C     -4.645      0.857     -3.217
O     -5.228      3.606      0.800
C     -5.269      0.851     -1.957
C      1.706      1.702     -0.950
C      0.366     -0.715      0.293
C     -0.343     -1.891      0.023
C     -1.260     -2.393      0.949
C     -1.476     -1.724      2.155
C     -0.756     -0.551      2.442
C      0.177     -0.058      1.512
C      3.288     -0.721     -0.383
C      4.388     -0.543     -1.229
C      5.659     -0.970     -0.836
C      5.840     -1.579      0.407
C     -4.350      2.784      1.035
C     -2.700      3.952     -0.342
C      4.740     -1.763      1.262
C      3.462     -1.332      0.863
C     -4.599      1.591      1.876
H     -2.696      3.952     -3.067
H     -0.951      3.010     -4.589
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H      1.076      1.937     -3.571
H     -2.376      2.196      0.795
H     -5.419     -0.581      3.607
H     -5.195     -2.852      4.589
H     -4.853     -4.837      3.109
H     -4.748     -4.535      0.617
H     -4.972     -2.253     -0.375
H     -2.655     -0.271     -0.063
H     -1.543     -0.262     -2.290
H     -2.810      0.453     -4.321
H     -5.204      1.188     -4.109
H     -6.317      1.183     -1.862
H      1.920      2.084      0.068
H      2.572      2.012     -1.571
H     -0.188     -2.424     -0.930
H     -1.822     -3.315      0.725
H     -2.205     -2.118      2.883
H     -0.912     -0.028      3.400
H      0.763      0.840      1.763
H      4.257     -0.069     -2.216
H      6.520     -0.827     -1.510
H      6.844     -1.917      0.716
H     -3.566      4.307     -0.946
H     -2.319      4.838      0.216
H      4.877     -2.248      2.244
H      2.607     -1.489      1.541
H     -5.208      1.829      2.768
H     -3.679      1.184      2.339

71
Fig6(b), X-ray conformation of 7, E = 14.810 kcal/mol
P     -4.046     -0.415     -0.481
P      2.709      0.251     -0.385
N      0.894     -2.592      0.485
H     -1.615     -1.326      1.669
N     -2.071     -2.235      1.484
O      1.212     -2.247      1.743
O     -3.934     -3.352      0.904
O     -2.643     -0.082     -0.901
O      2.248      0.622     -1.765
C      1.705     -2.303     -0.519
C      1.387     -2.670     -1.865
C      0.173     -3.322     -2.098
C     -0.621     -3.552     -1.007
C     -0.228     -3.181      0.225
C     -1.208     -3.402      1.371
C     -3.367     -2.296      1.162
C     -4.102     -1.011      1.169
C     -5.089      1.102     -0.625
C     -5.761      1.376     -1.821
C     -6.514      2.545     -1.958
C     -6.591      3.457     -0.904
C     -5.905      3.197      0.296
C     -5.150      2.019      0.430
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C     -4.747     -1.691     -1.614
C     -3.945     -2.253     -2.613
C     -4.469     -3.213     -3.481
C     -5.800     -3.618     -3.356
C     -6.611     -3.058     -2.354
C     -6.079     -2.092     -1.481
C      2.996     -1.543     -0.268
C      4.254      1.174      0.021
C      5.509      0.592     -0.196
C      6.675      1.308      0.080
C      6.600      2.615      0.565
C      5.344      3.212      0.771
C      4.171      2.488      0.492
C      1.431      0.691      0.872
C      0.114      0.939      0.472
C     -0.871      1.217      1.421
C     -0.555      1.224      2.781
C      0.765      0.969      3.191
C      1.759      0.706      2.231
H      2.065     -2.428     -2.701
H     -0.140     -3.615     -3.114
H     -1.604     -4.031     -1.152
H     -1.793     -4.333      1.190
H     -0.666     -3.582      2.327
H     -3.695     -0.287      1.899
H     -5.141     -1.130      1.531
H     -5.706      0.671     -2.667
H     -7.046      2.749     -2.903
H     -7.185      4.380     -1.013
H     -5.959      3.918      1.129
H     -4.614      1.829      1.374
H     -2.892     -1.942     -2.716
H     -3.830     -3.655     -4.264
H     -6.213     -4.380     -4.040
H     -7.661     -3.380     -2.248
H     -6.716     -1.662     -0.690
H      3.417     -1.792      0.728
H      3.759     -1.849     -1.013
H      5.592     -0.437     -0.583
H      7.661      0.841     -0.088
H      7.522      3.180      0.782
H      5.278      4.247      1.148
H      3.189      2.965      0.649
H     -0.152      0.922     -0.599
H     -1.901      1.436      1.093
H     -1.335      1.439      3.530
H      1.022      0.976      4.264
H      2.793      0.505      2.559

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Fig6(c), global minimum Eu-7 complex, E = 14.799 kcal/mol
Eu     1.999     -1.047      2.763
P      3.979     -0.911     -0.342
O      1.797      1.313      3.223
```

N	1.822	2.389	2.420
C	3.004	2.981	2.074
O	2.786	-1.113	0.546
C	3.059	4.108	1.249
P	-0.990	0.746	1.346
C	1.891	4.664	0.745
C	0.682	4.052	1.074
C	0.671	2.911	1.906
C	4.188	-2.370	-1.450
O	0.031	-0.280	1.742
N	4.931	1.499	1.617
C	3.637	-2.355	-2.736
C	3.756	-3.469	-3.570
C	4.415	-4.614	-3.120
C	4.951	-4.646	-1.821
C	4.829	-3.522	-0.985
C	3.801	0.597	-1.386
C	2.754	1.489	-1.153
C	2.596	2.620	-1.957
C	3.506	2.884	-2.981
C	4.582	2.005	-3.204
O	4.305	-0.353	2.733
C	4.726	0.859	-2.403
C	-0.670	2.293	2.251
C	-0.922	1.049	-0.469
C	-0.266	0.133	-1.299
C	-0.205	0.346	-2.677
C	-0.809	1.472	-3.239
C	-1.487	2.388	-2.414
C	-1.546	2.169	-1.026
C	-2.674	0.157	1.813
C	-3.658	-0.038	0.837
C	-4.933	-0.477	1.200
C	-5.235	-0.729	2.540
C	4.837	0.173	1.762
C	4.324	2.410	2.578
C	-4.249	-0.544	3.525
C	-2.966	-0.102	3.156
C	5.399	-0.648	0.661
H	4.030	4.561	0.985
H	1.919	5.555	0.095
H	-0.260	4.466	0.679
H	5.294	1.873	0.728
H	3.099	-1.465	-3.103
H	3.322	-3.446	-4.584
H	4.505	-5.496	-3.777
H	5.459	-5.555	-1.455
H	5.236	-3.566	0.039
H	2.044	1.301	-0.331
H	1.747	3.302	-1.782
H	3.380	3.778	-3.615
H	5.304	2.209	-4.012
H	5.564	0.167	-2.589
H	-0.712	2.094	3.342

H	-1.492	3.010	2.046
H	0.226	-0.754	-0.863
H	0.331	-0.372	-3.321
H	-0.756	1.642	-4.327
H	-1.975	3.273	-2.855
H	-2.092	2.882	-0.387
H	-3.437	0.143	-0.227
H	-5.703	-0.630	0.425
H	-6.242	-1.078	2.825
H	4.166	1.912	3.562
H	5.019	3.253	2.794
H	-4.479	-0.749	4.584
H	-2.192	0.030	3.930
H	5.858	-1.583	1.032
H	6.242	-0.182	0.117