

Targeted library of phosphonic-type inhibitors of human neutrophil elastase

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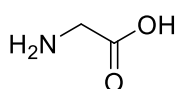
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Amino Acid Structures	5
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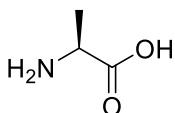
(38) Boc-L-Val-L-Phe- Val ^P (OPh-4-SCH ₃) ₂	82
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(63) Boc-D-Abu-L-Pro-Val ^P (OPh-4-SCH ₃) ₂	132
(64) Boc-AC4C-L-Pro-Val ^P (OPh-4-SCH ₃) ₂	134
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(69) Boc-D-Tle-L-Pro- Val ^P (OPh-4-SCH ₃) ₂	144
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(73) Boc-D-Leu-L-Pro-Val ^P (OPh-4-SCH ₃) ₂	152
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(80) Boc-D-Gln-L-Pro- Val ^P (OPh-4-SCH ₃) ₂	166
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(83) Boc-D-Pip-L-Pro- Val ^P (OPh-4-SCH ₃) ₂	172
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(88) Boc-L-Cpg-L-Pro-Val ^P (OPh-4-SCH ₃) ₂	182
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(95) Boc-L-Cha-L-Pro-Val ^P (OPh-4-SCH ₃) ₂	196
(96) Boc-L-HPhe-L-Pro-Val ^P (OPh-4-SCH ₃) ₂	198
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(98) Boc-L-Igl-L-Pro-Val ^P (OPh-4-SCH ₃) ₂	202
(99) Boc-D-Igl-L-Pro-Val ^P (OPh-4-SCH ₃) ₂	204
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(101) Boc-L-Cys(Bzl)-L-Pro- Val ^P (OPh-4-SCH ₃) ₂	208
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(104) Boc-D-Asp(Bzl)-L-Pro- Val ^P (OPh-4-SCH ₃) ₂	214
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(108) Boc-D-Orn(Z)-L-Pro-Val ^P (OPh-4-SCH ₃) ₂	222
(109) Boc-L-Lys(Z)-L-Pro-Val ^P (OPh-4-SCH ₃) ₂	224
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(113) Hm-L-Met(O ₂)-L-Pro-L-Val ^P (OPh-4-SCH ₃) ₂	232

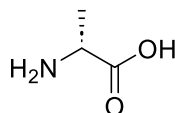
Amino Acid Structures



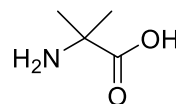
Gly
glycine



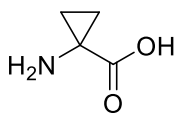
L-Ala
L-Alanine



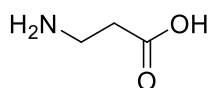
D-Ala
D-Alanine



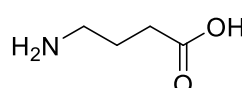
Aib
2-Aminoisobutyric acid



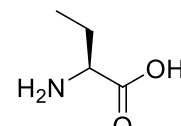
AC3C
1-Amino-1-cyclopropanecarboxylic acid



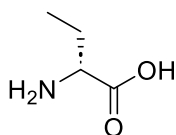
beta-Ala
beta Alanine



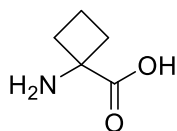
GABA
gamma-aminobutyric acid



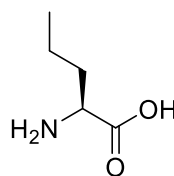
L-Abu
L-Aminobutyric acid



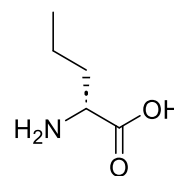
D-Abu
D-Aminobutyric acid



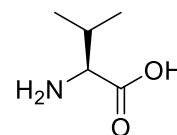
AC4C
1-cyclobutyl-1-carboxylic acid



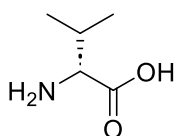
L-Nva
L-Norvaline



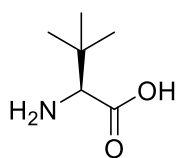
D-Nva
D-Norvaline



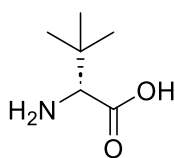
L-Val
L-Valine



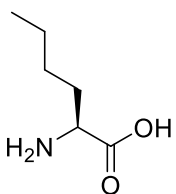
D-Val
D-Valine



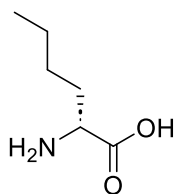
L-Tle
L-tert-Leucine



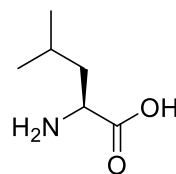
D-Tle
D-tert-Leucine



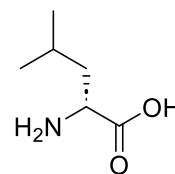
L-Nle
L-Norleucine



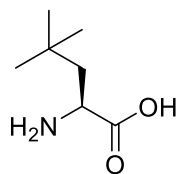
D-Nle
D-Norleucine



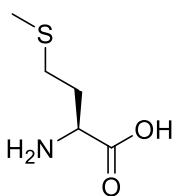
L-Leu
L-Leucine



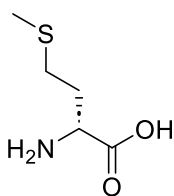
D-Leu
D-Leucine



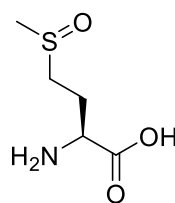
L-NptGly
L-Neopentylglycine



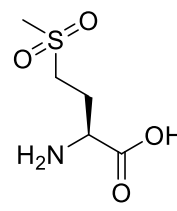
L-Met
L-Methionine



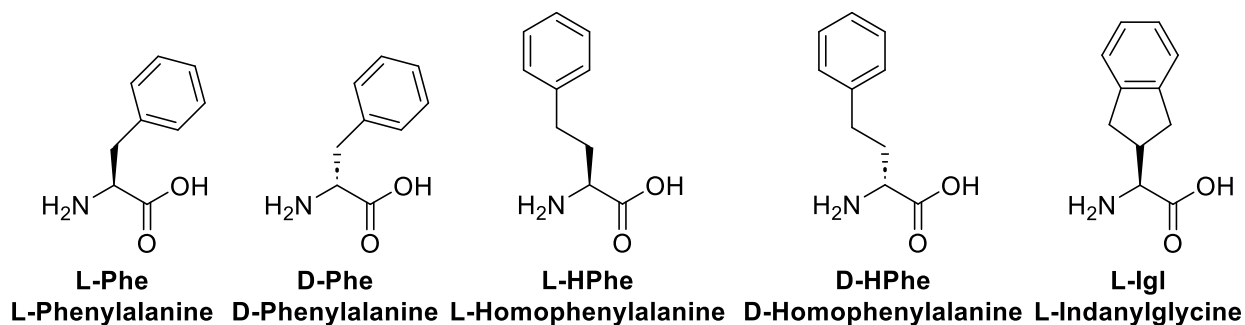
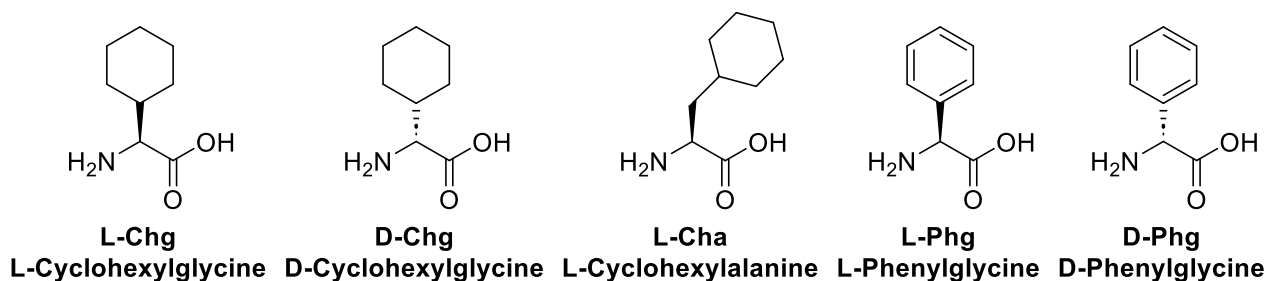
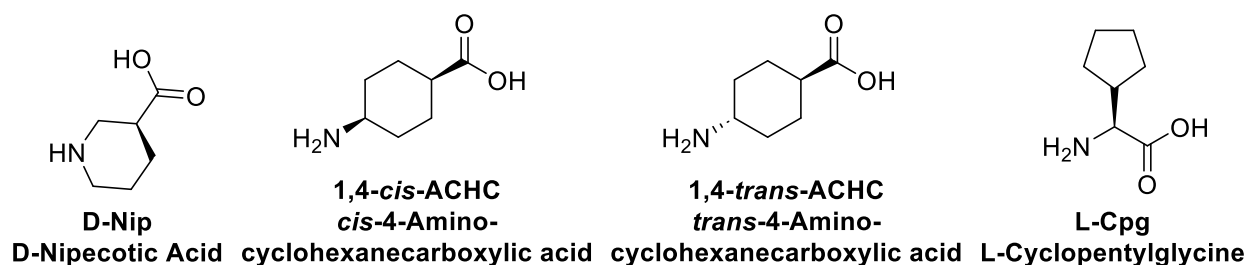
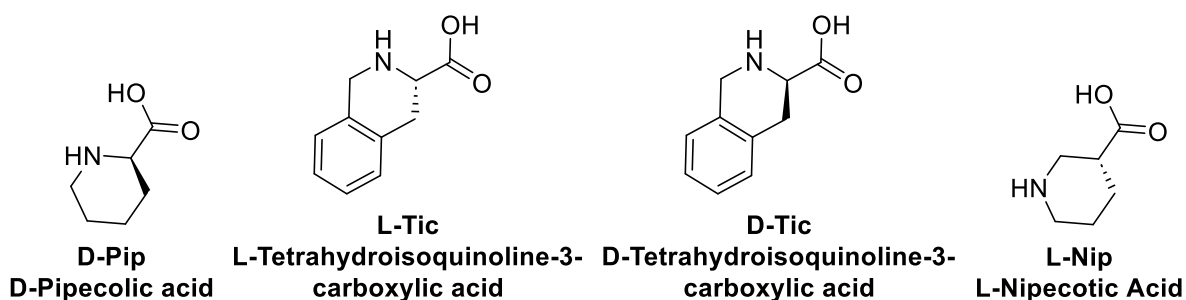
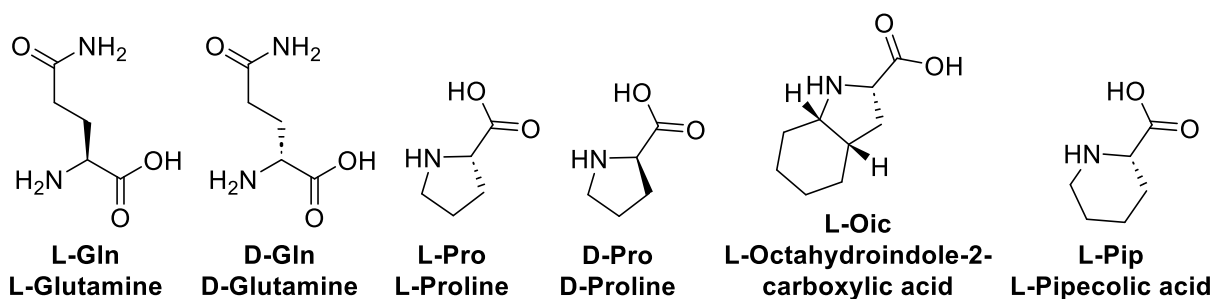
D-Met
D-Methionine

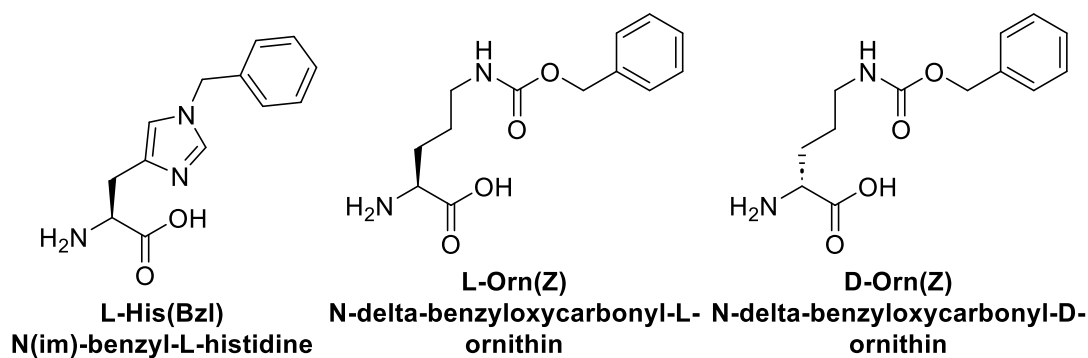
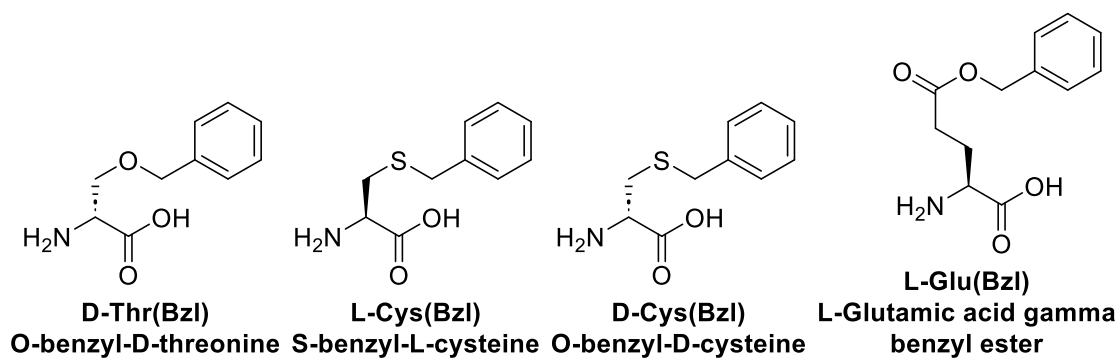
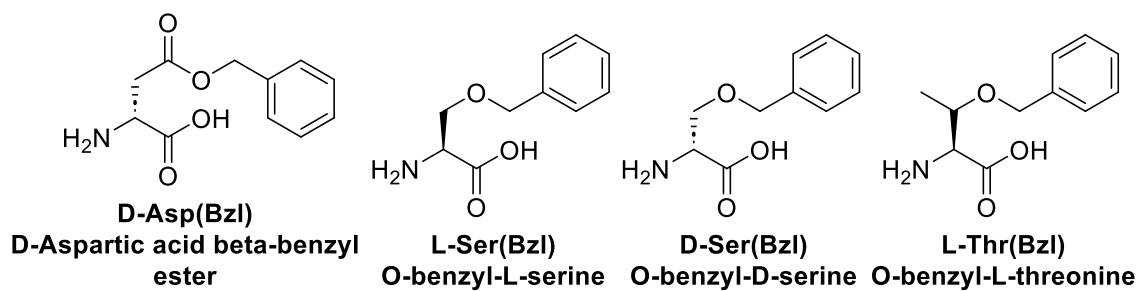
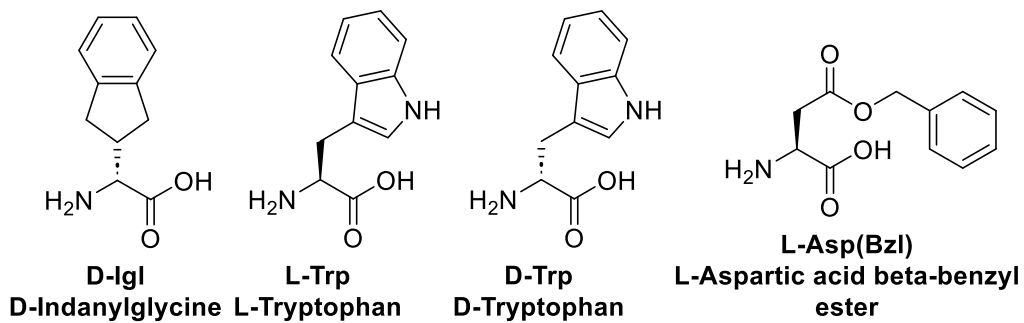


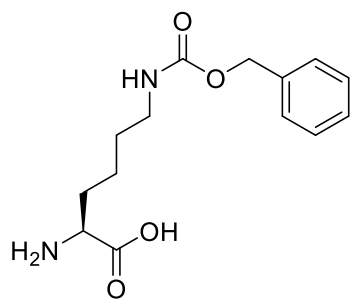
L-Met(O)
L-Methionine sulfoxide



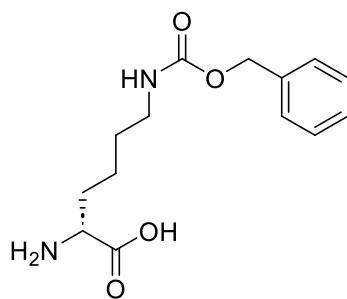
L-Met(O)₂
L-Methionine sulfone



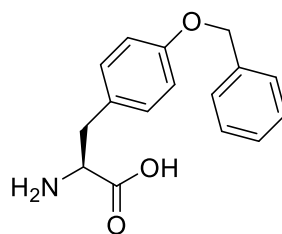




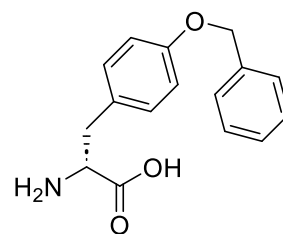
L-Lys(Z)
N-epsilon-
benzyloxycarbonyl-L-lysine



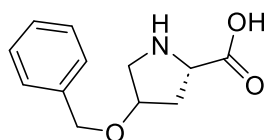
D-Lys(Z)
N-epsilon-
benzyloxycarbonyl-D-lysine



L-Tyr(Bzl)
O-benzyl-L-tyrosine

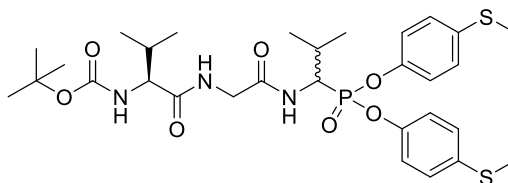


D-Tyr(Bzl)
O-benzyl-D-tyrosine



L-Hyp(Bzl)
O-benzyl-L-hydroxyproline

(1) Boc-L-Val-Gly-Val^P(OPh-4-SCH₃)₂



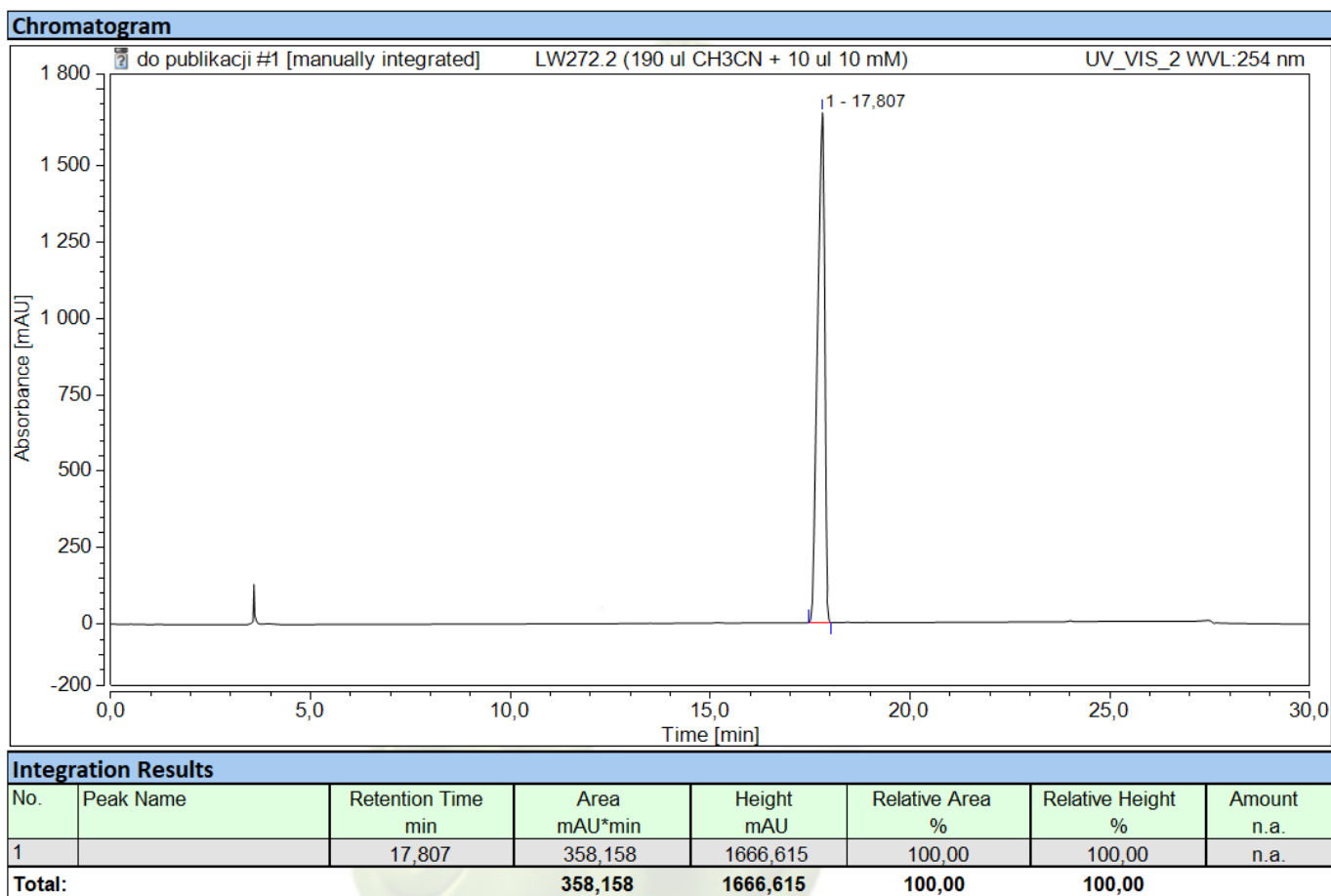
Name: *tert*-butyl ((2*S*)-1-((2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-2-oxoethyl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

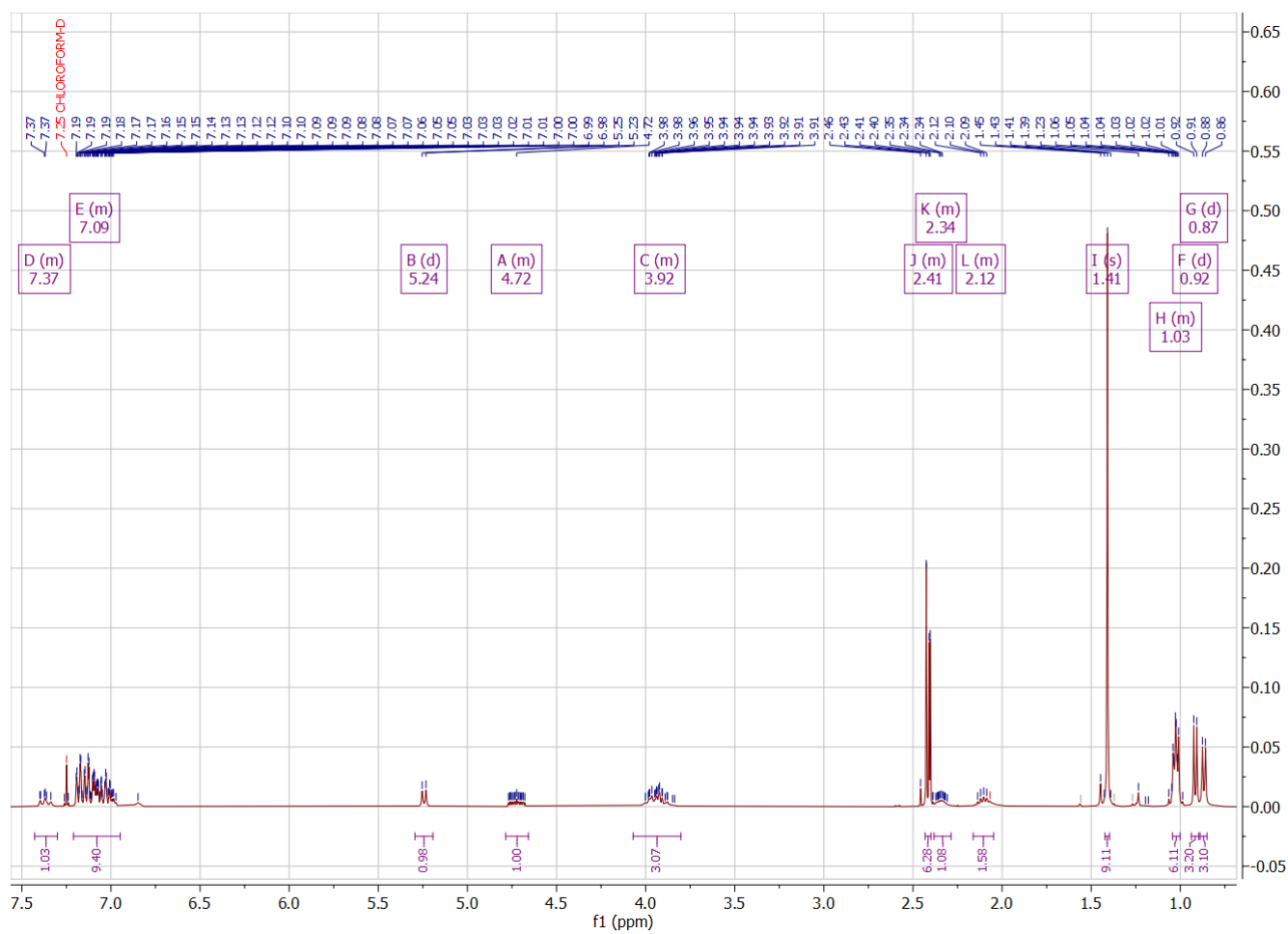
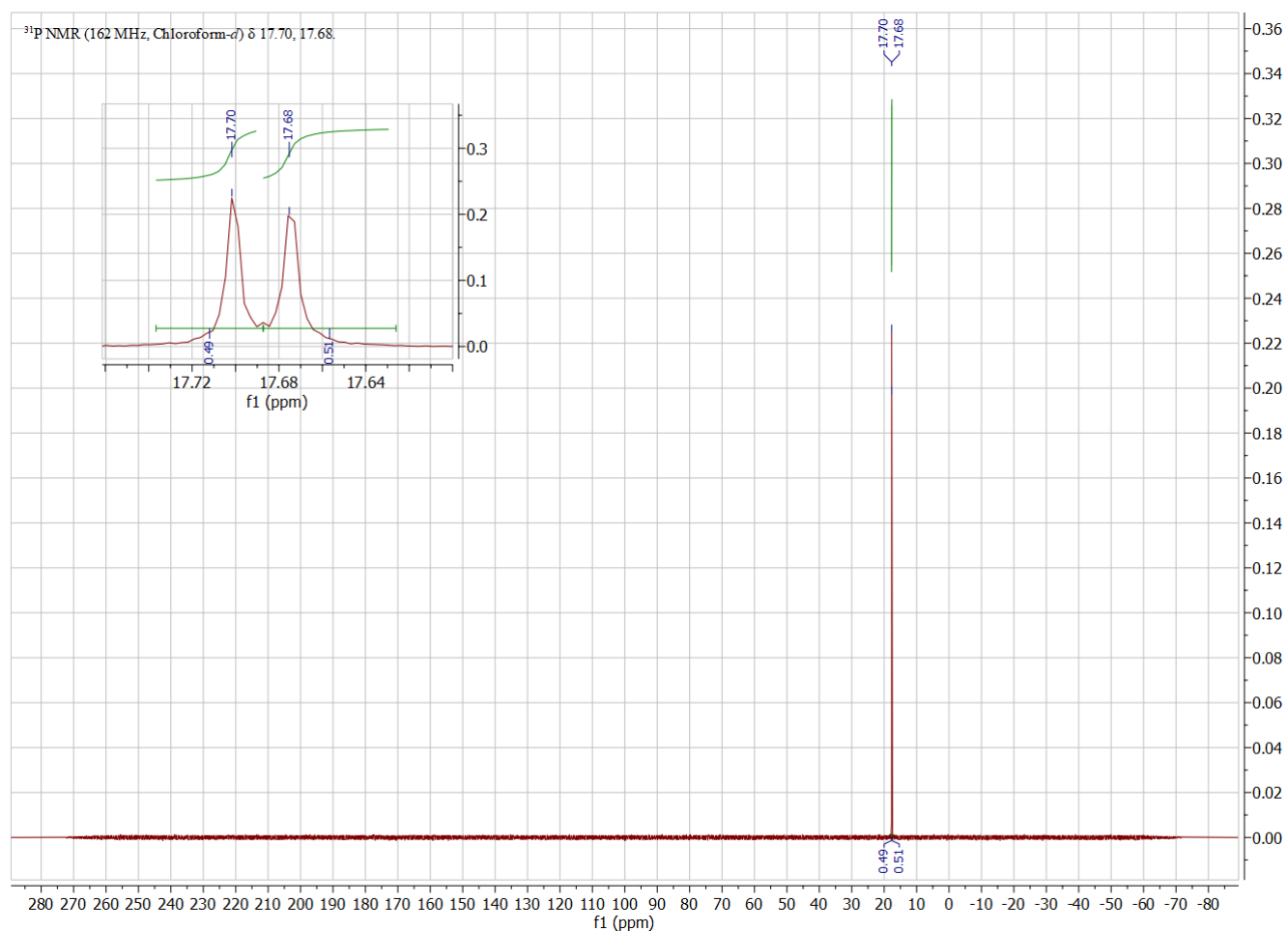
³¹P NMR (162 MHz, Chloroform-*d*) δ 17.70 (s, 49%), 17.68 (s, 51%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.30 (m, 1H, NH), 7.21 – 6.95 (m, 9H, 8xArH, NH), 5.24 (d, *J* = 8.6 Hz, 1H, NH), 4.79 – 4.66 (m, 1H, CHP), 4.07 – 3.80 (m, 3H, CH, CH₂), 2.43 – 2.40 (m, 6H, 2xSCH₃), 2.38 – 2.29 (m, 1H, CH), 2.16 – 2.05 (m, 1H, CH), 1.41 (s, 9H, Boc), 1.04 – 1.00 (m, 6H, 2xCH₃), 0.92 (d, *J* = 6.8 Hz, 3H, CH₃), 0.87 (d, *J* = 6.8 Hz, 3H, CH₃).

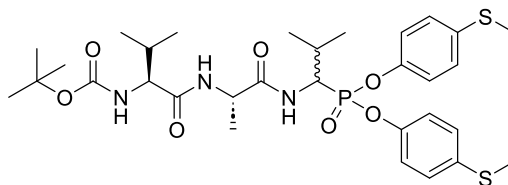
HRMS: C₃₀H₄₄N₃O₇PS₂ [M+Na]⁺ calc. 676.2256 found 676.2239

HPLC: purity >99%; retention time 17.807 min





(2) Boc-L-Val-L-Ala-Val^P(OPh-4-SCH₃)₂



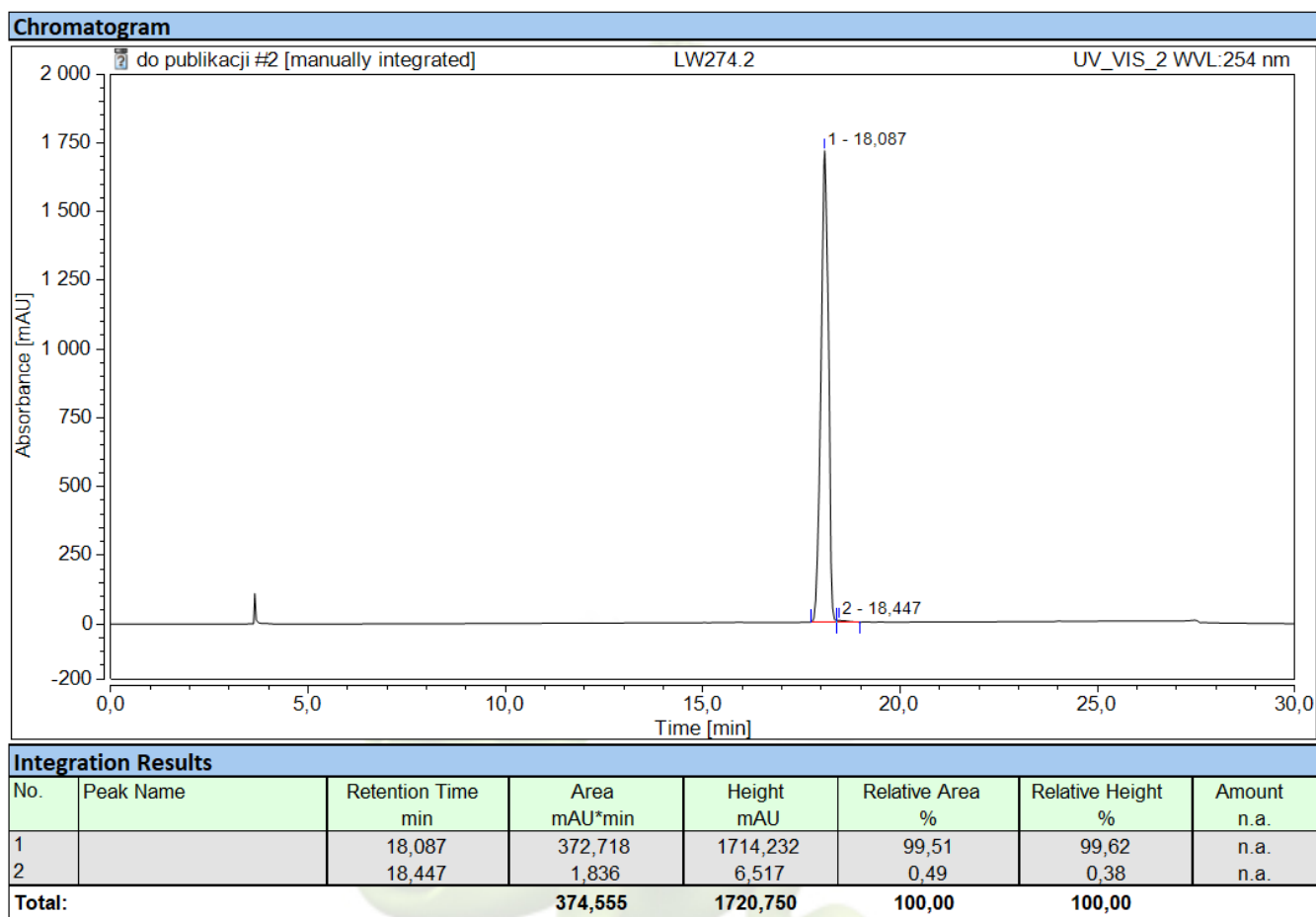
Name: *tert*-butyl ((2*S*)-1-(((2*S*)-1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-1-oxopropan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

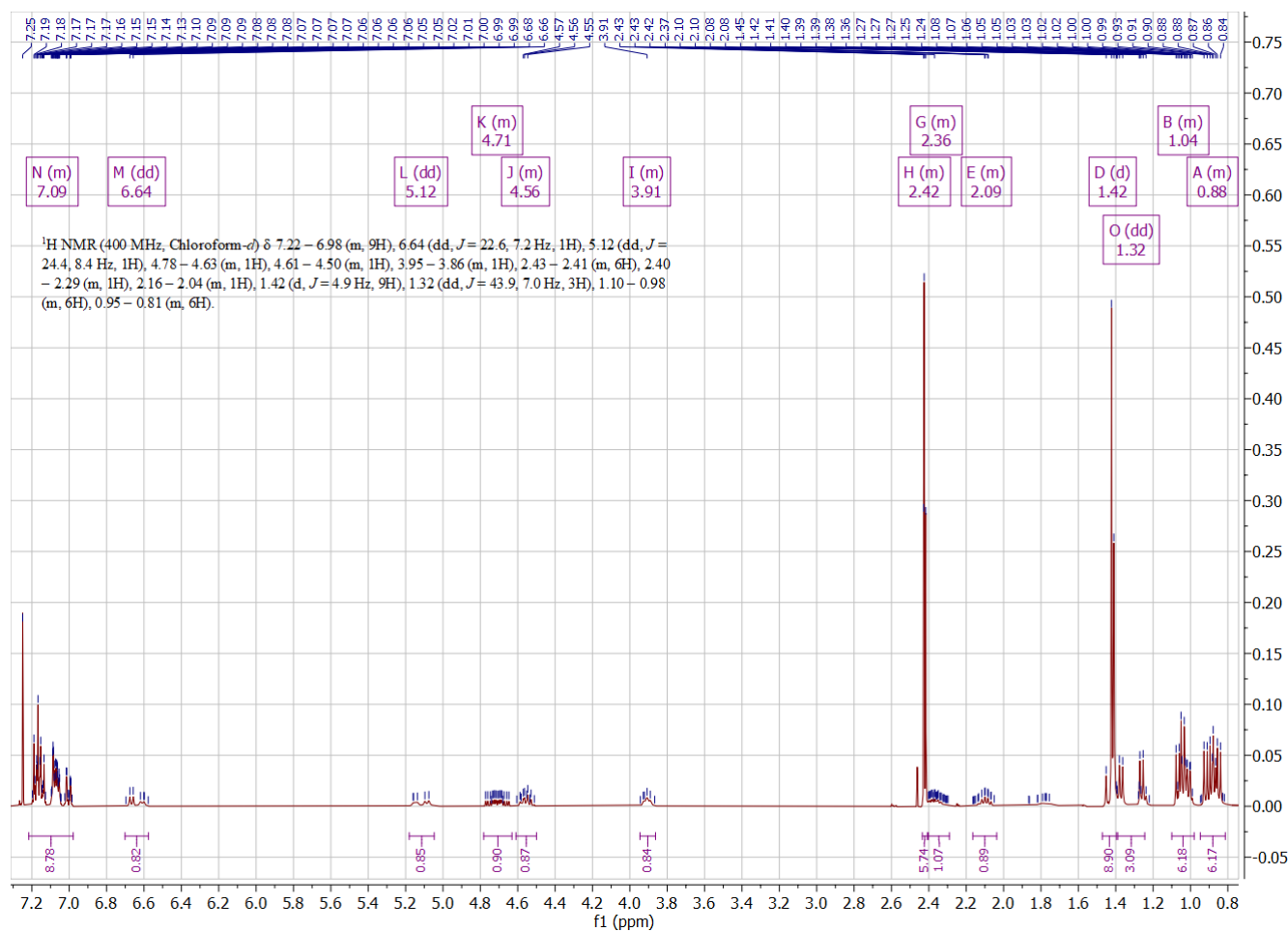
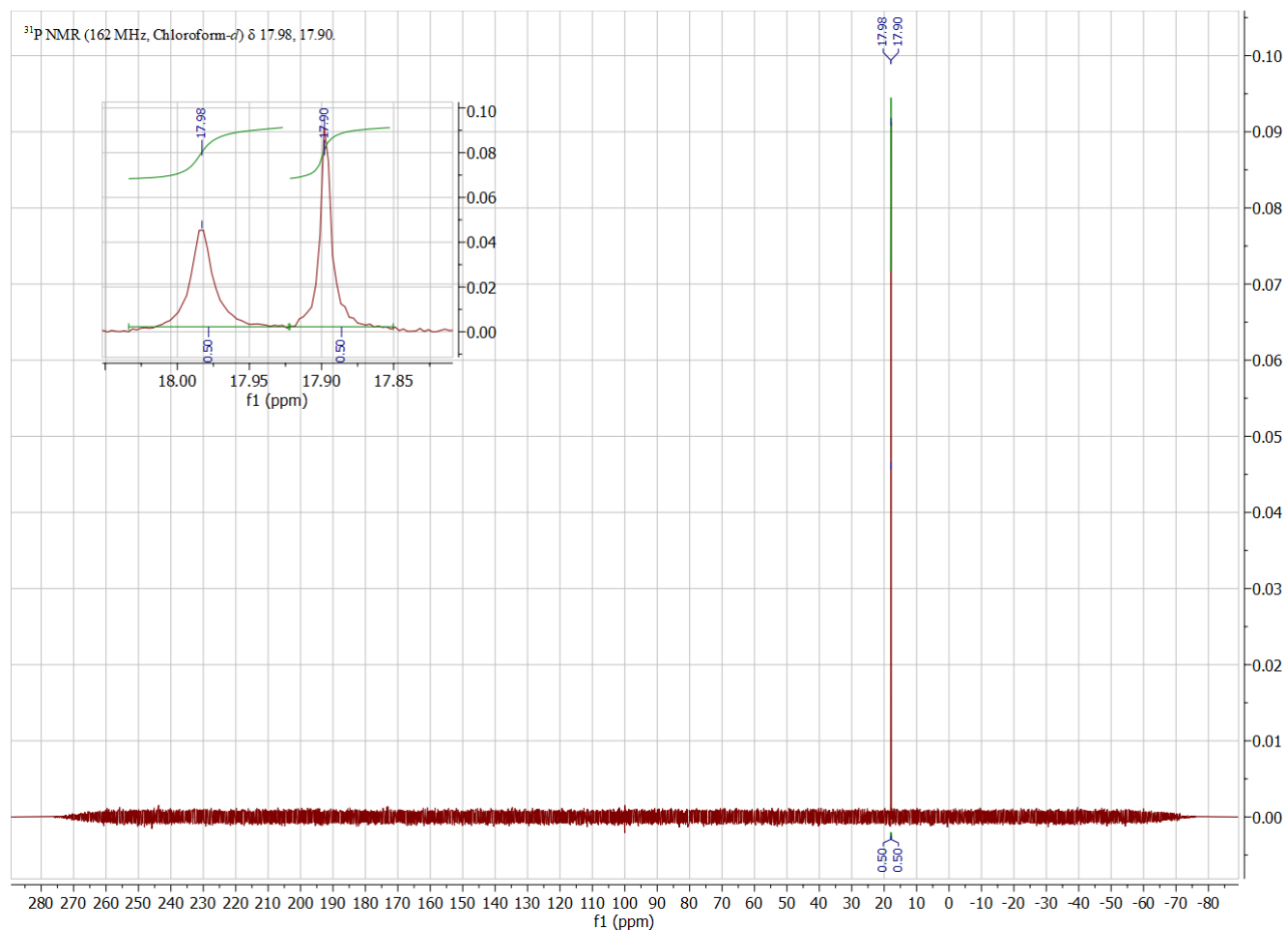
³¹P NMR (162 MHz, Chloroform-*d*) δ 17.98 (s, 50%), 17.90 (s, 50%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 6.98 (m, 9H, 8xArH, NH), 6.64 (dd, *J* = 22.6, 7.2 Hz, 1H, NH), 5.12 (dd, *J* = 24.4, 8.4 Hz, 1H, NH), 4.78 – 4.63 (m, 1H, CHP), 4.61 – 4.50 (m, 1H, CH), 3.95 – 3.86 (m, 1H, CH), 2.43 – 2.41 (m, 6H, 2xSCH₃), 2.40 – 2.29 (m, 1H, CH), 2.16 – 2.04 (m, 1H, CH), 1.42 (d, *J* = 4.9 Hz, 9H, Boc), 1.32 (dd, *J* = 43.9, 7.0 Hz, 3H, CH₃), 1.10 – 0.98 (m, 6H, 2xCH₃), 0.95 – 0.81 (m, 6H, 2xCH₃).

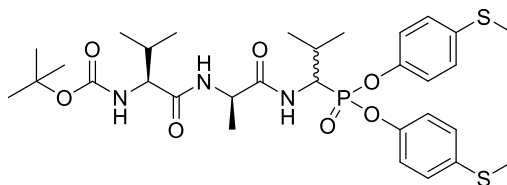
HRMS: C₃₁H₄₆N₃O₇PS₂ [M+Na]⁺ calc. 690.2412 found 690.2400

HPLC: purity >99%; retention time 18.087 min





(3) Boc-L-Val-D-Ala-Val^P(OPh-4-SCH₃)₂



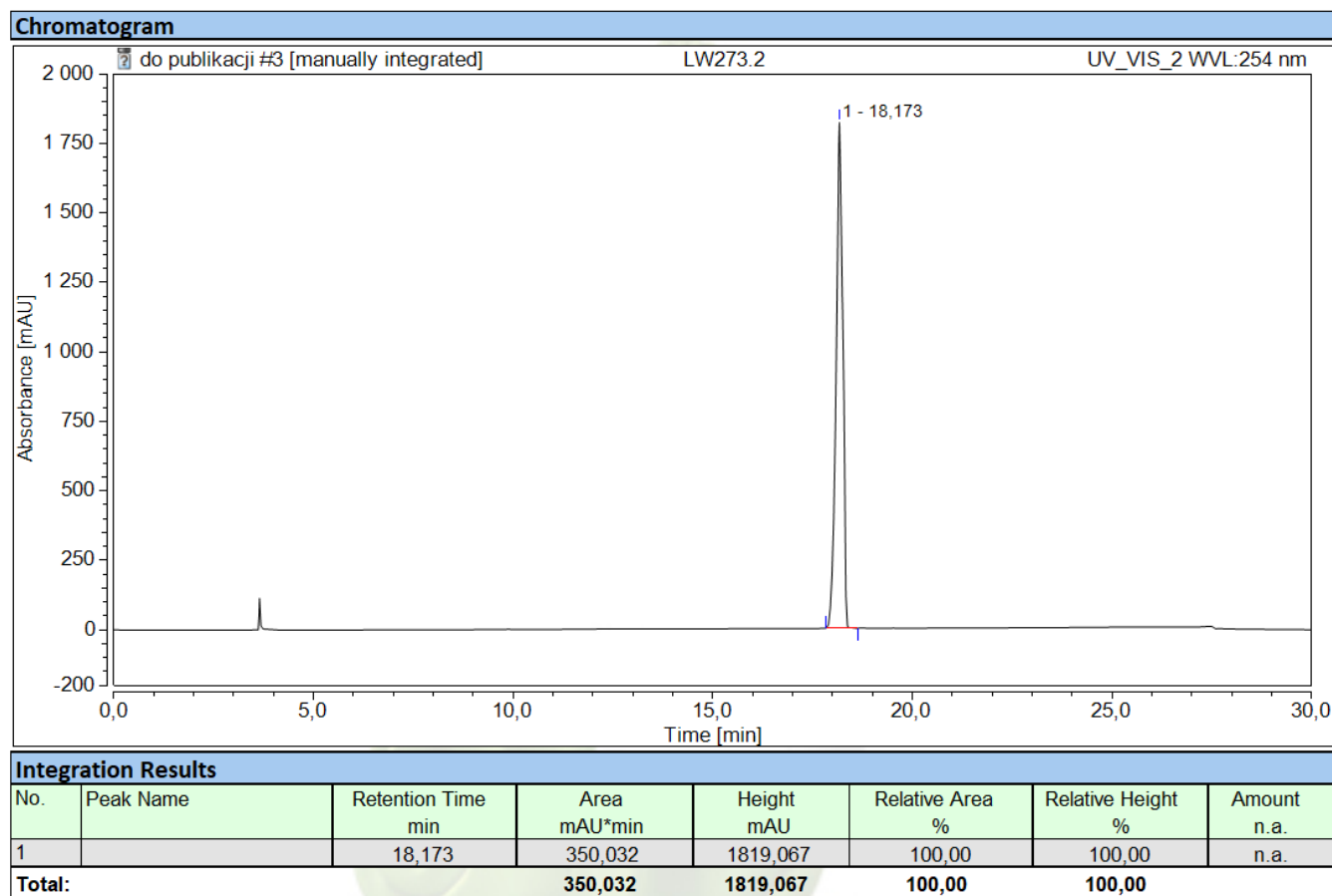
Name: *tert*-butyl ((2S)-1-(((2R)-1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-1-oxopropan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

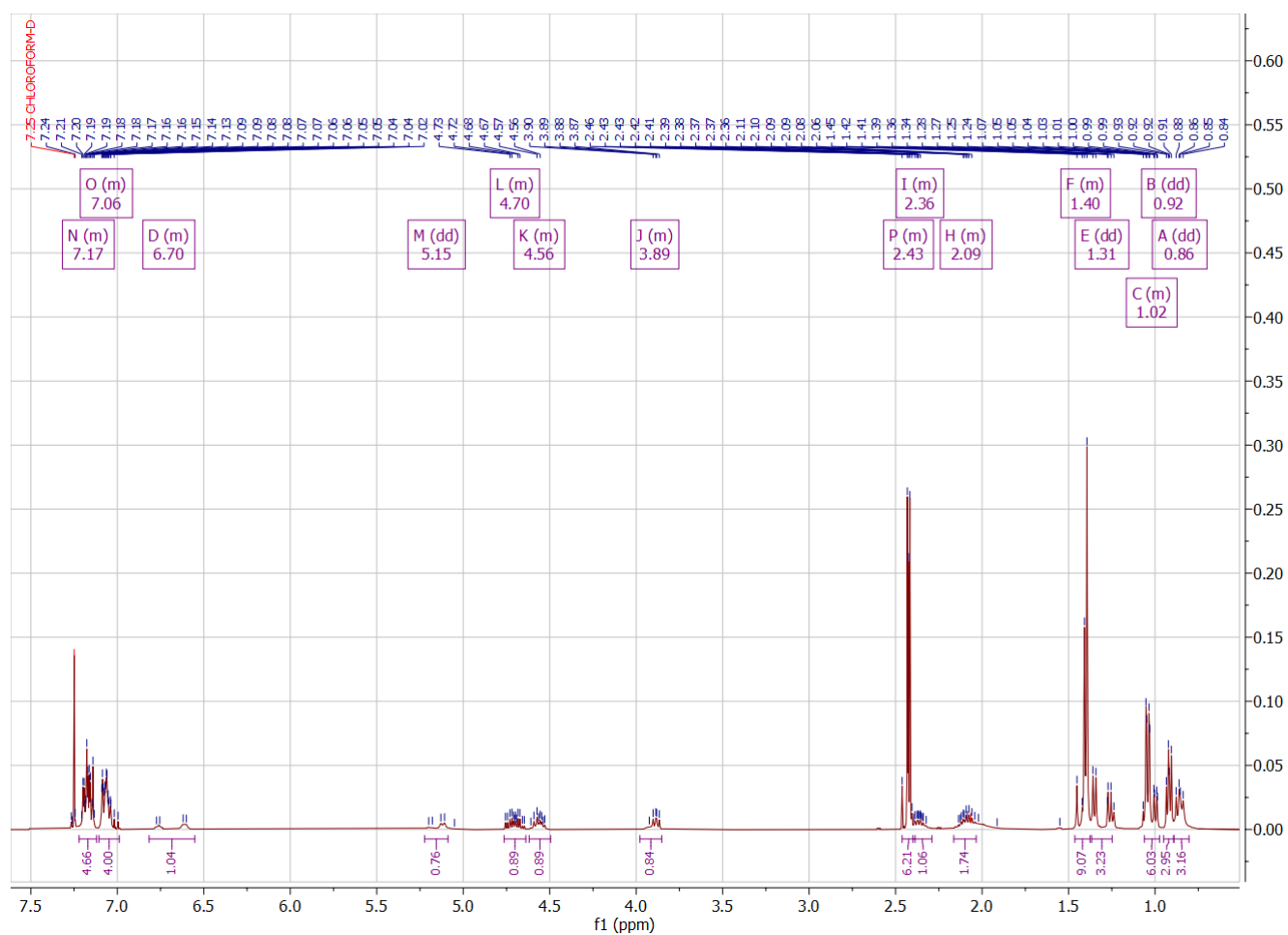
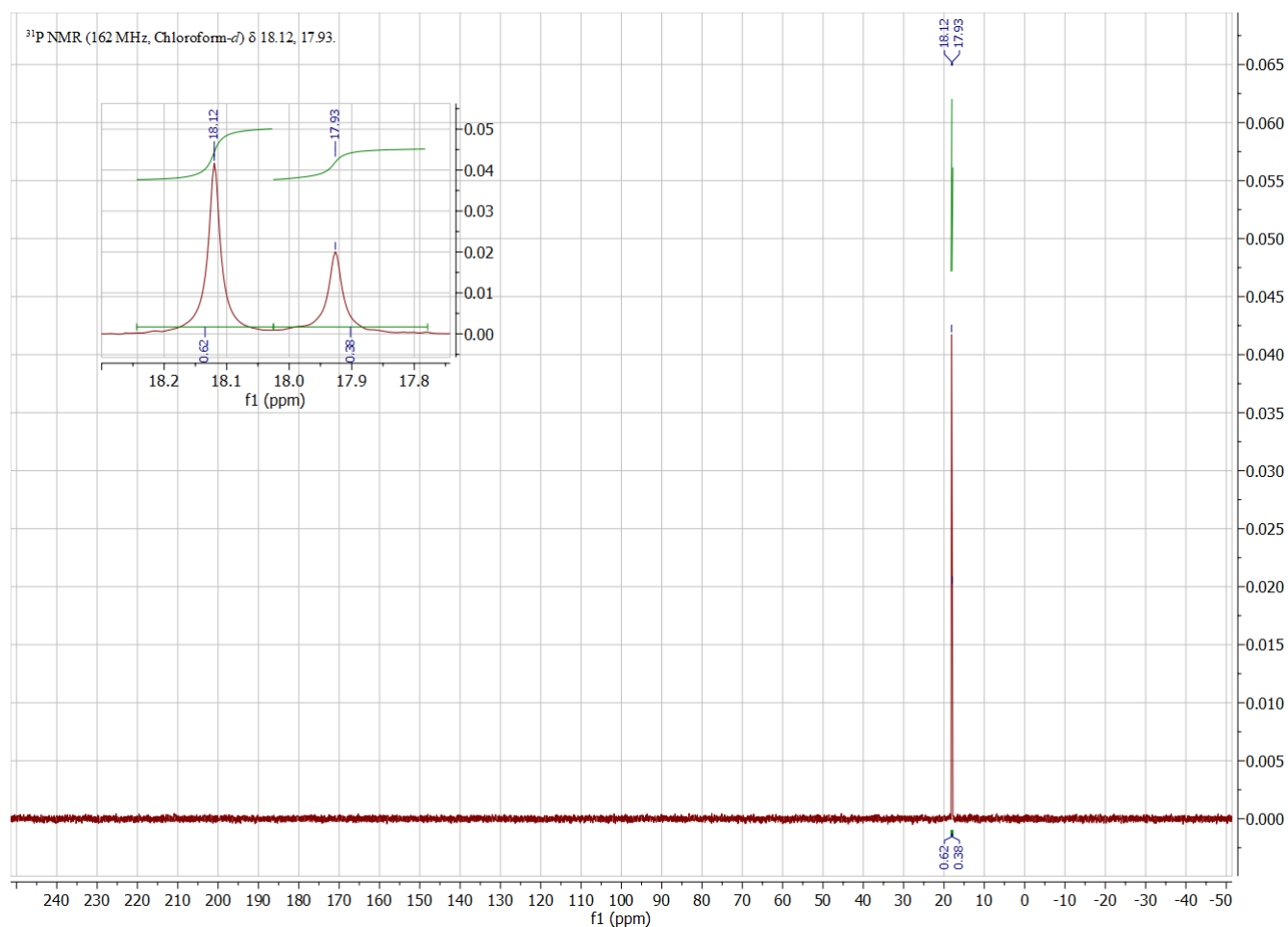
³¹P NMR (162 MHz, Chloroform-d) δ 18.12 (s, 62%), 17.93 (s, 38%).

¹H NMR (400 MHz, Chloroform-d) δ 7.22 – 7.12 (m, 5H, 4xArH, NH), 7.11 – 6.99 (m, 4H, 4xArH), 6.82 – 6.55 (m, 1H, NH), 5.15 (dd, J = 28.0, 8.4 Hz, 1H, NH), 4.76 – 4.64 (m, 1H, CHP), 4.62 – 4.49 (m, 1H, CH), 3.98 – 3.85 (m, 1H, CH), 2.46 – 2.39 (m, 6H, 2xSCH₃), 2.40 – 2.29 (m, 1H, CH), 2.16 – 2.03 (m, 1H, CH), 1.46 – 1.38 (m, 9H, Boc), 1.31 (dd, J = 35.0, 7.0 Hz, 3H, CH₃), 1.06 – 0.97 (m, 6H, 2xCH₃), 0.92 (dd, J = 6.8, 4.7 Hz, 3H, CH₃), 0.86 (dd, J = 9.5, 6.7 Hz, 3H, CH₃).

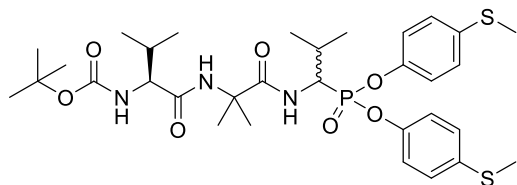
HRMS: C₃₁H₄₆N₃O₇PS₂ [M+Na]⁺ calc. 690.2412 found 690.2406

HPLC: purity >99%; retention time 18.173 min





(4) Boc-L-Val-Aib-Val^P(OPh-4-SCH₃)₂



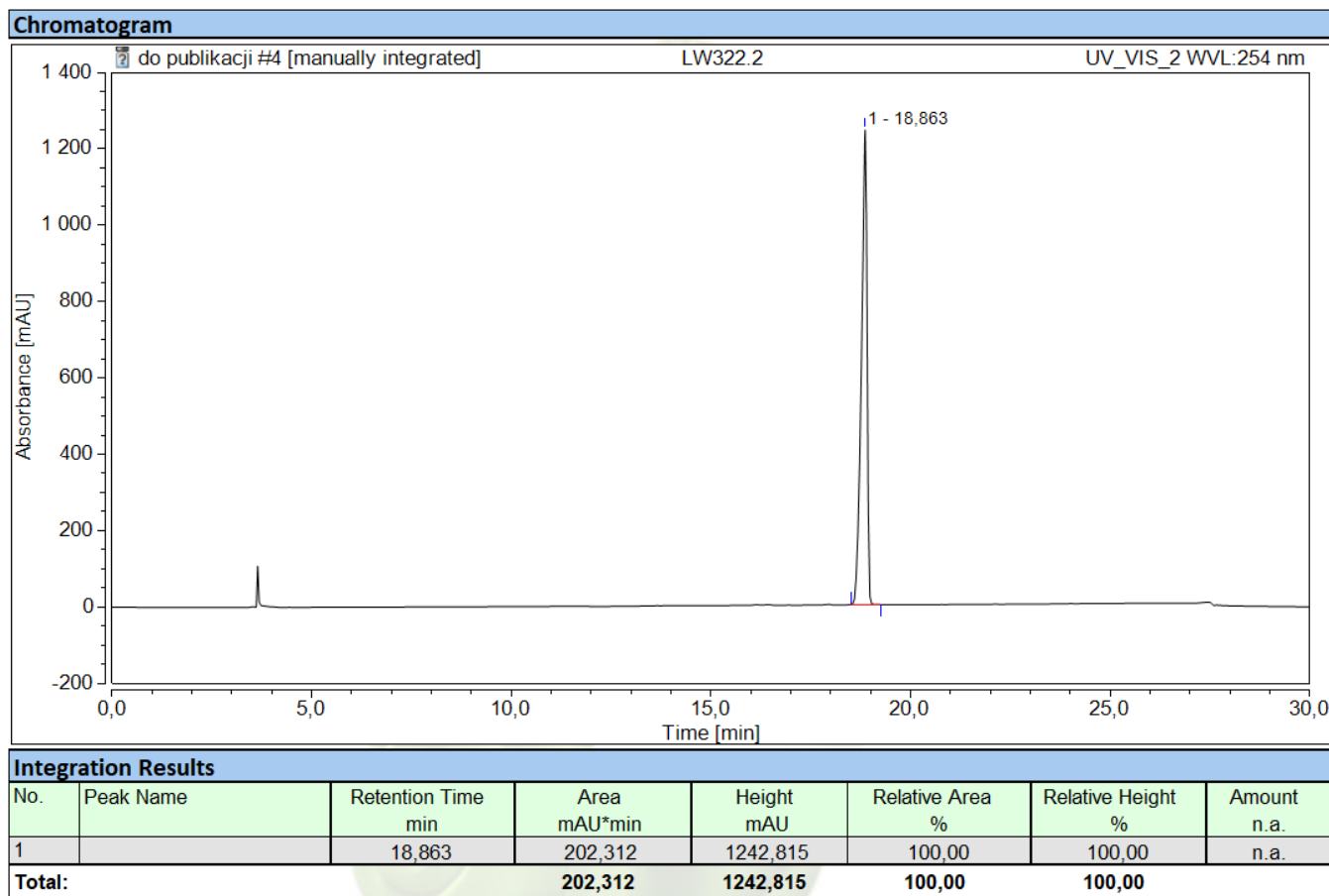
Name: *tert*-butyl ((2*S*)-1-((1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-2-methyl-1-oxopropan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

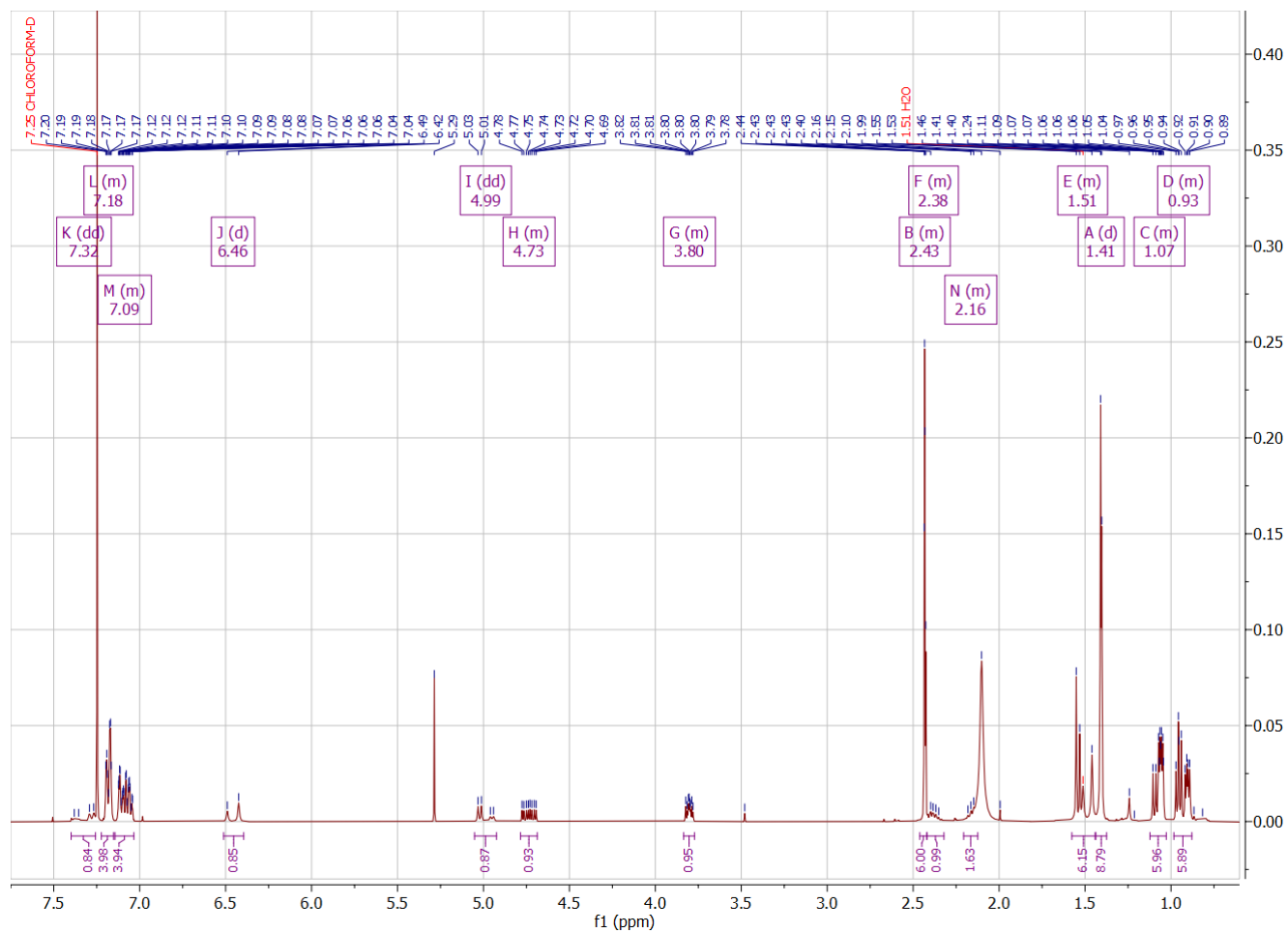
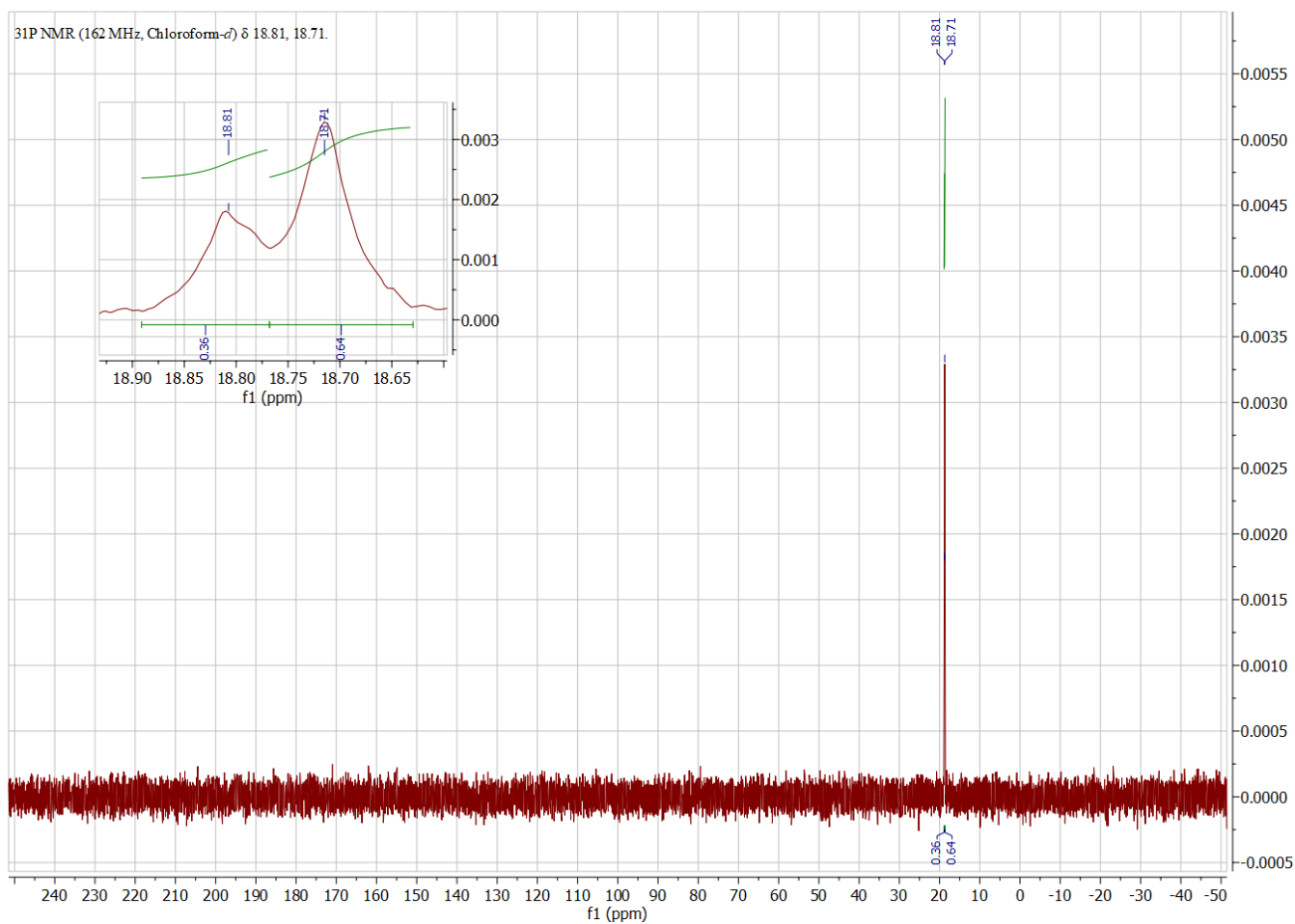
³¹P NMR (162 MHz, Chloroform-*d*) δ 18.81 (s, 36%), 18.71 (s, 64%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.32 (dd, *J* = 35.1, 10.0 Hz, 1H, NH), 7.22 – 7.15 (m, 4H, 4xArH), 7.14 – 7.03 (m, 4H, 4xArH), 6.46 (d, *J* = 26.2 Hz, 1H, NH), 4.99 (dd, *J* = 28.6, 7.7 Hz, 1H, NH), 4.78 – 4.69 (m, 1H, CHP), 3.84 – 3.77 (m, 1H, CH), 2.46 – 2.42 (m, 6H, 2xSCH₃), 2.42 – 2.32 (m, 1H, CH), 2.21 – 2.12 (m, 1H, CH), 1.58 – 1.44 (m, 6H, 2xCH₃), 1.41 (d, *J* = 2.7 Hz, 9H, Boc), 1.12 – 1.03 (m, 6H, 2xCH₃), 0.98 – 0.88 (m, 6H, 2xCH₃).

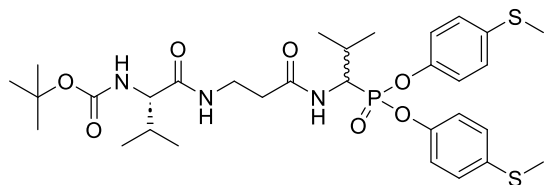
HRMS: C₃₂H₄₈N₃O₇PS₂ [M+Na]⁺ calc. 704.2569 found 704.2555

HPLC: purity >99%; retention time 18.863 min





(5) Boc-L-Val-beta-Ala-Val^P(OPh-4-SCH₃)₂



Name: *tert*-butyl ((2*S*)-1-((3-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-3-oxopropyl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

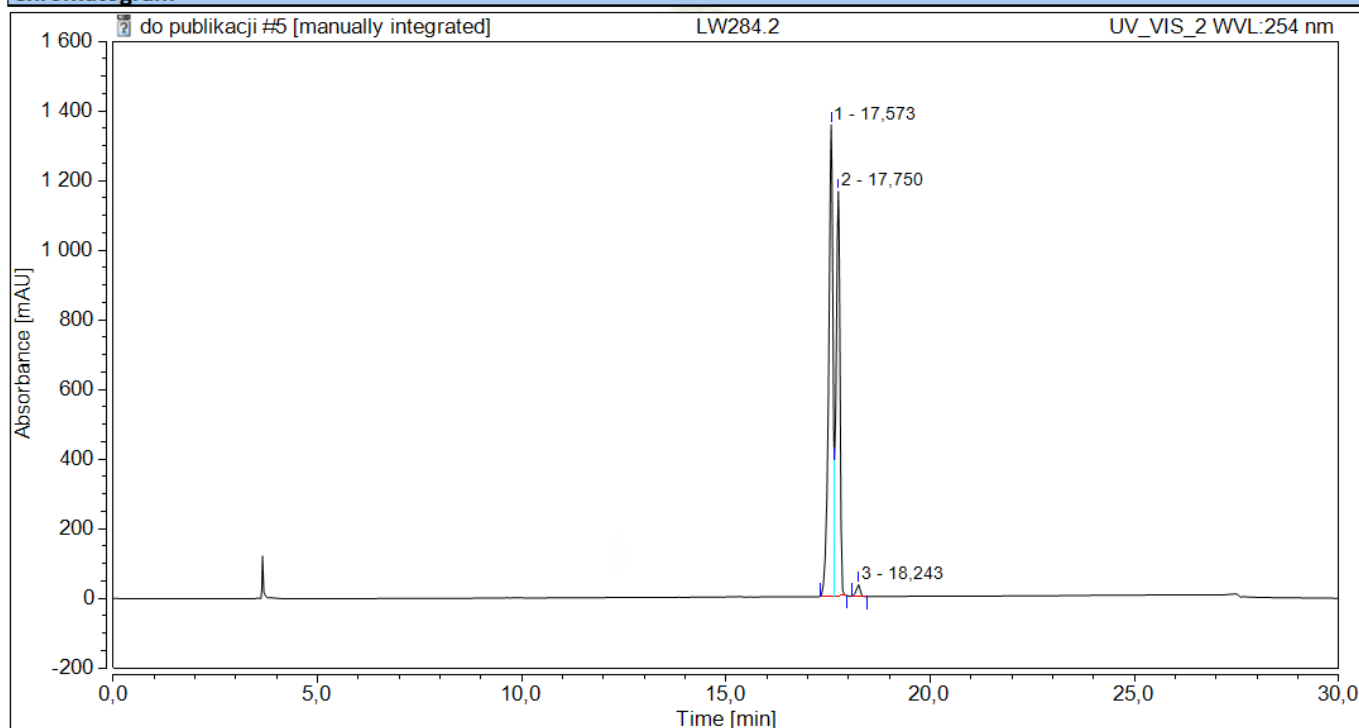
³¹P NMR (162 MHz, Chloroform-*d*) δ 20.82 (s, 50%), 18.45 (s, 50%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 9.3 Hz, 1H, NH), 7.23 – 6.97 (m, 8H, 8xArH), 6.93 – 6.70 (m, 1H, NH), 5.20 – 5.06 (m, 1H, NH), 4.77 – 4.59 (m, 1H, CHP), 3.87 – 3.72 (m, 1H, CH), 3.60 – 3.04 (m, 2H, CH₂), 2.53 – 2.40 (m, 7H, 2xSCH₃, CH), 2.39 – 2.22 (m, 2H, CH₂), 2.14 – 1.75 (m, 1H, CH), 1.41 (d, *J* = 6.3 Hz, 9H, Boc), 1.18 – 0.94 (m, 6H, 2xCH₃), 0.90 – 0.72 (m, 6H, 2xCH₃).

HRMS: C₃₁H₄₆N₃O₇PS₂ [M+Na]⁺ calc. 690.2412 found 690.2378

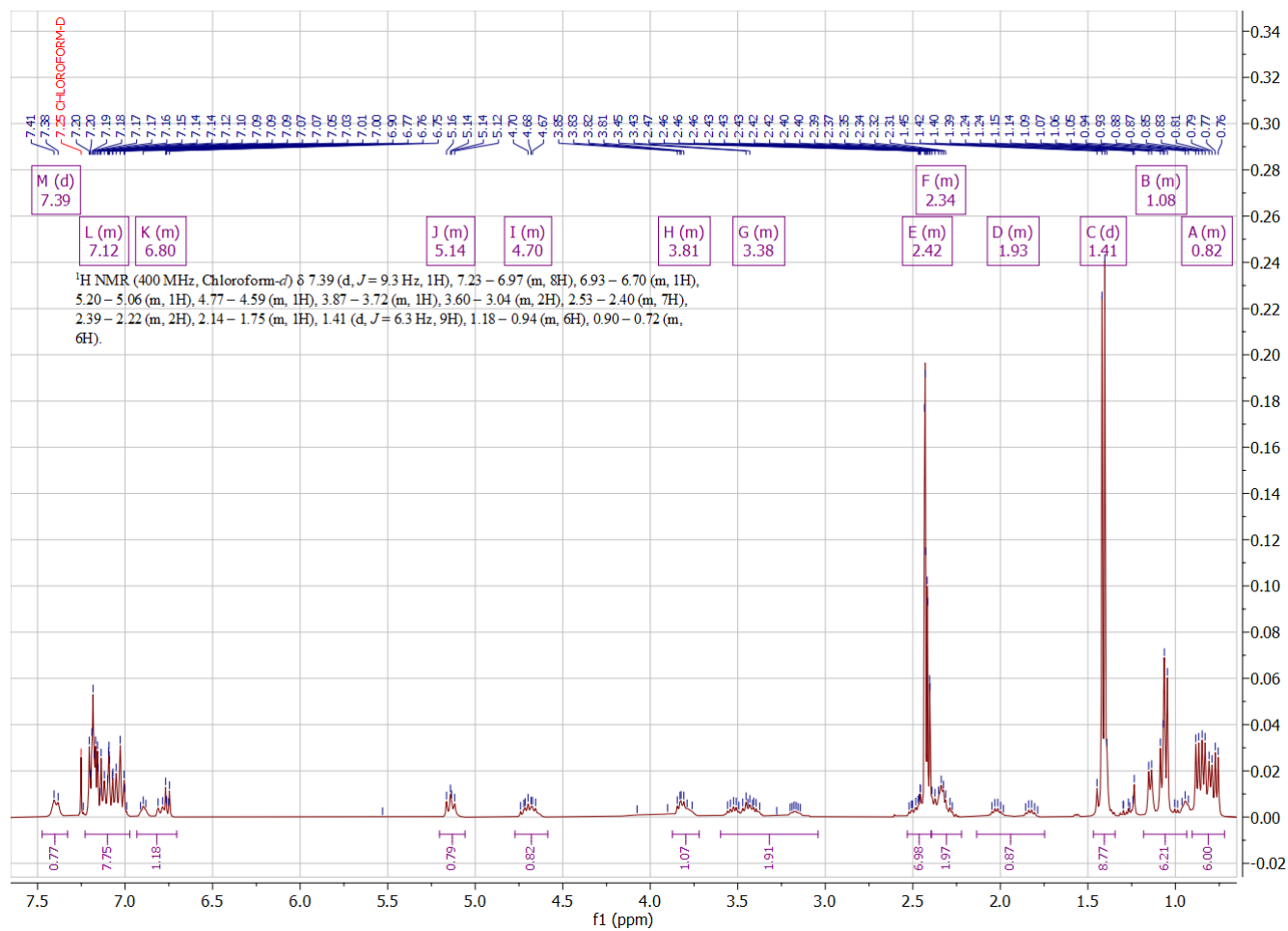
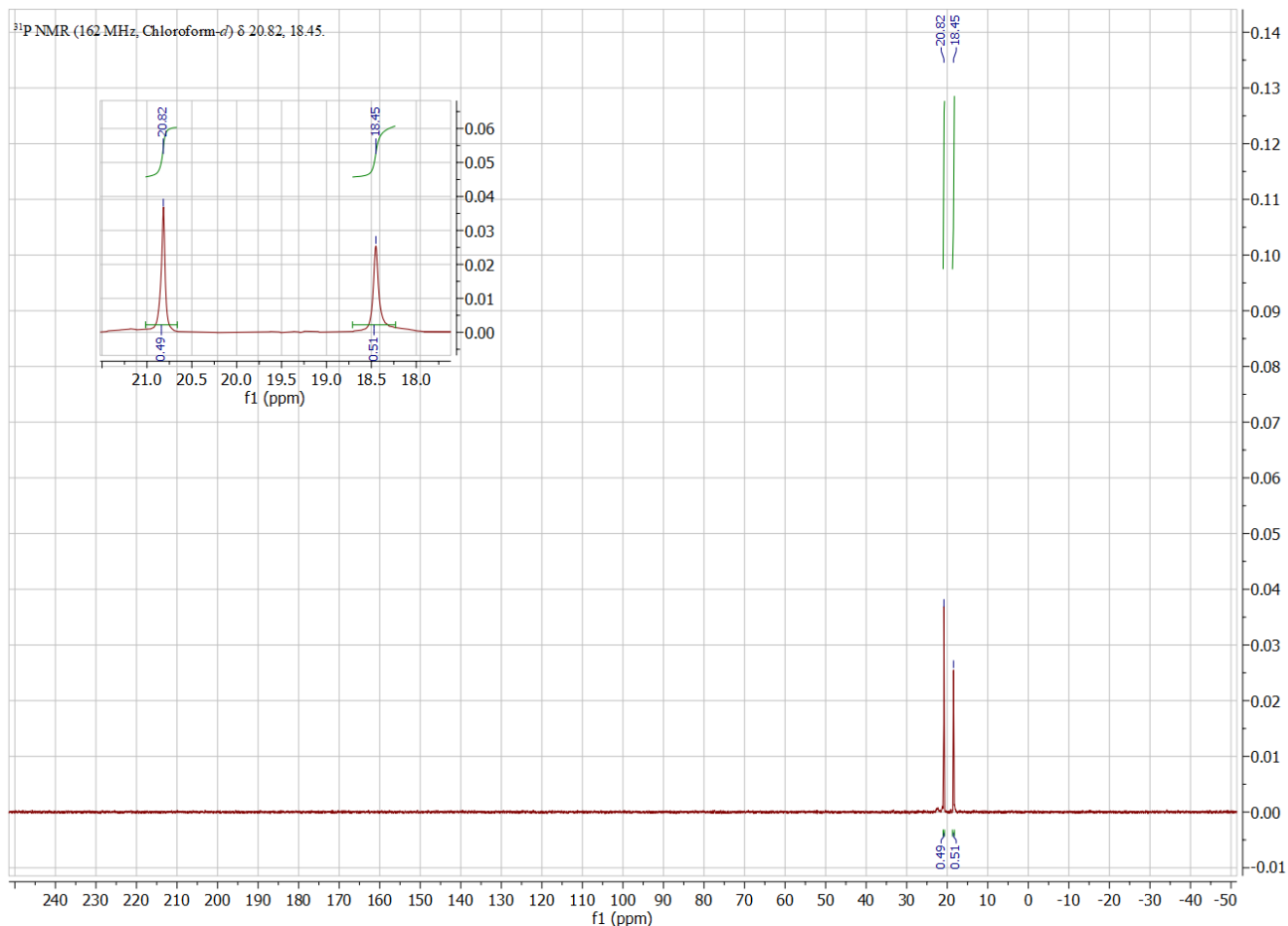
HPLC: purity >98%; retention time 17.573 and 17.750 min

Chromatogram

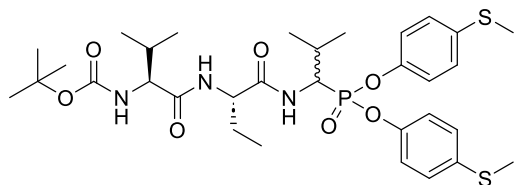


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17,573	164,434	1352,920	56,16	53,11	n.a.
2		17,750	124,739	1161,031	42,61	45,58	n.a.
3		18,243	3,601	33,565	1,23	1,32	n.a.
Total:			292,774	2547,516	100,00	100,00	



(6) Boc-L-Val-L-Abu-Val^P(OPh-4-SCH₃)₂



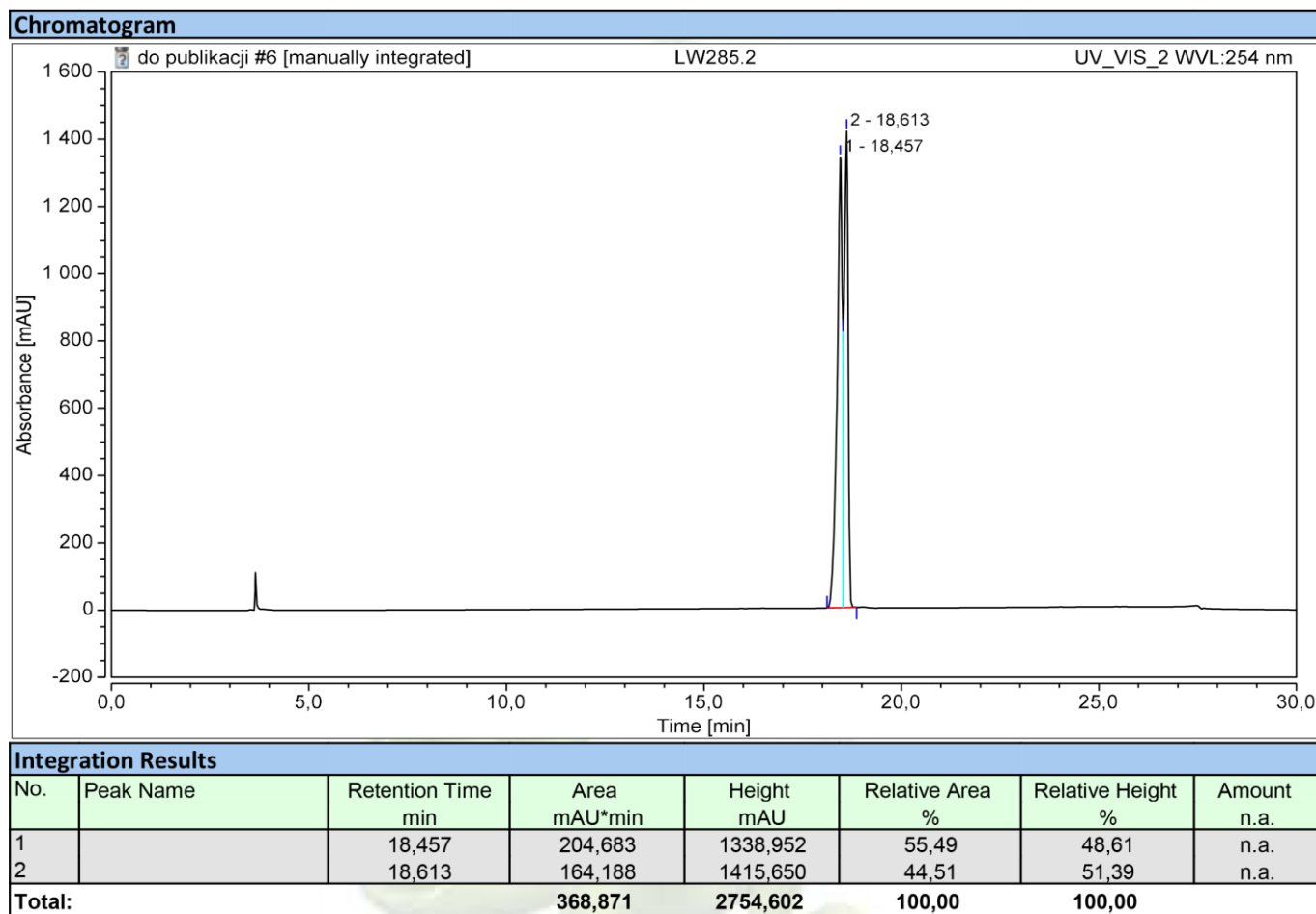
Name: *tert*-butyl ((2*S*)-1-(((2*S*)-1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-1-oxobutan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

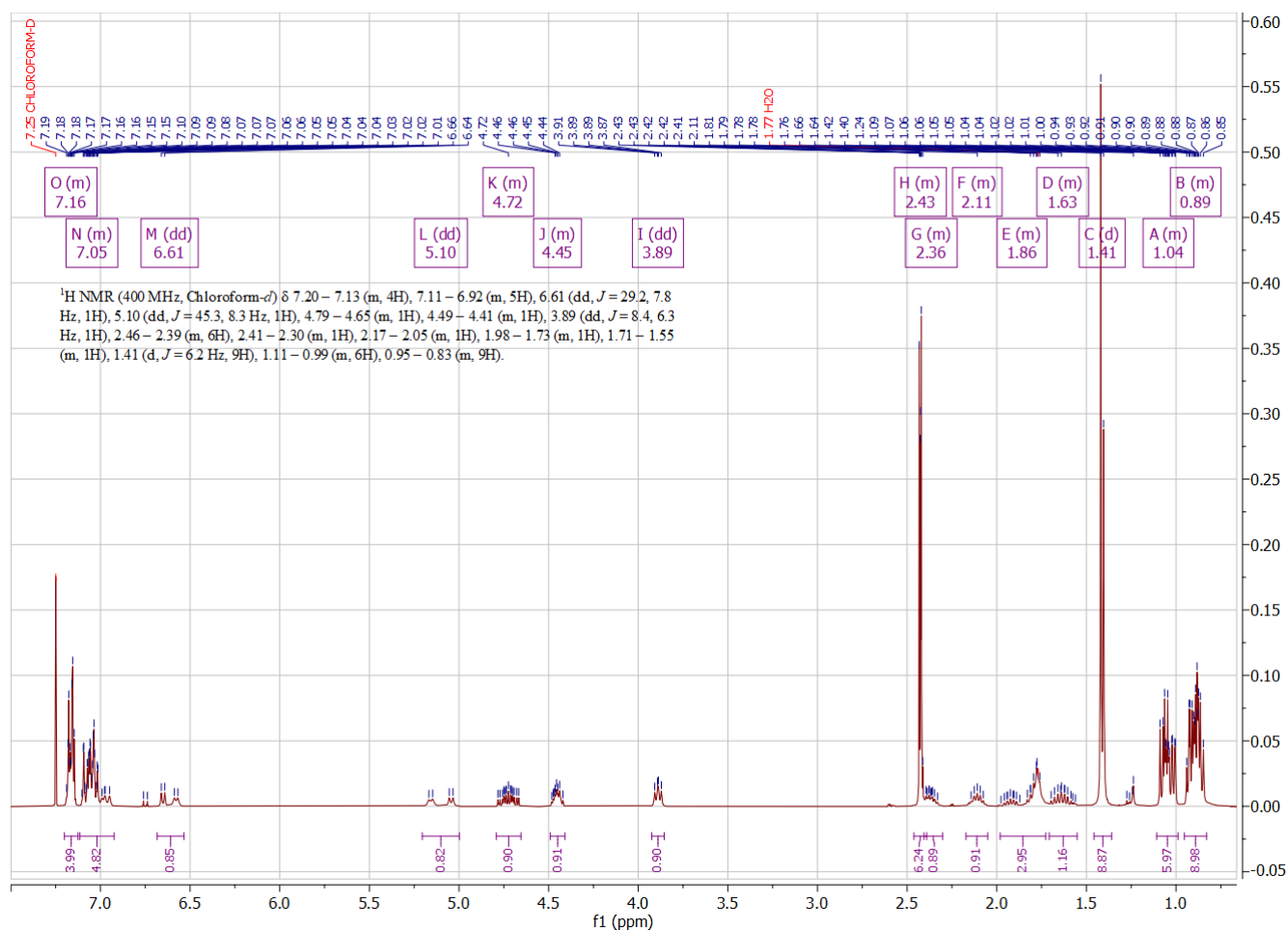
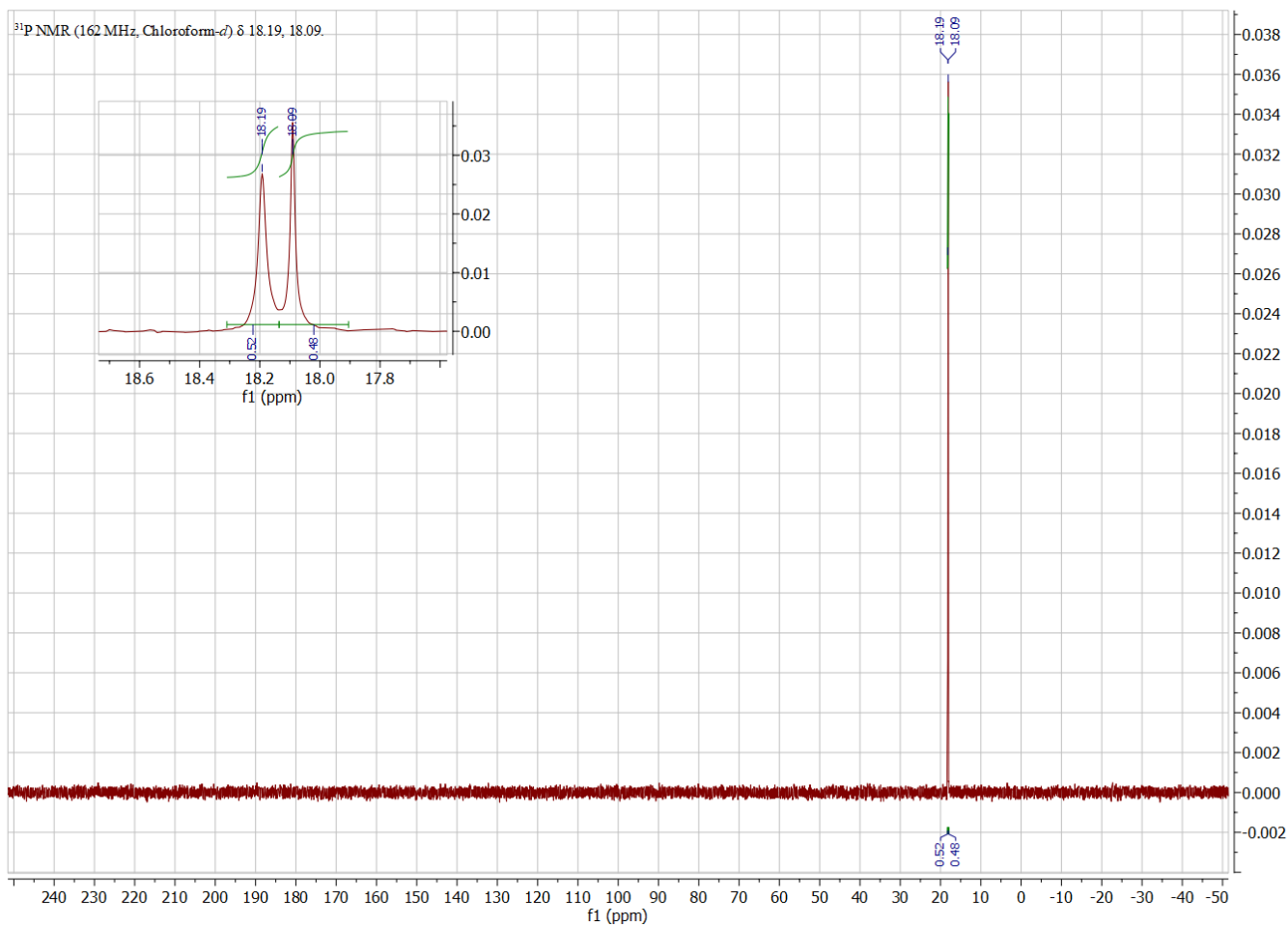
³¹P NMR (162 MHz, Chloroform-*d*) δ 18.19 (s, 53%), 18.09 (s, 47%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.20 – 7.13 (m, 4H, 4xArH), 7.11 – 6.92 (m, 5H, 4xArH, NH), 6.61 (dd, *J* = 29.2, 7.8 Hz, 1H, NH), 5.10 (dd, *J* = 45.3, 8.3 Hz, 1H, NH), 4.79 – 4.65 (m, 1H, CHP), 4.49 – 4.41 (m, 1H, CH), 3.89 (dd, *J* = 8.4, 6.3 Hz, 1H, CH), 2.46 – 2.39 (m, 6H, 2xSCH₃), 2.41 – 2.30 (m, 1H, CH), 2.17 – 2.05 (m, 1H, CH), 1.98 – 1.73 (m, 1H, CH₂), 1.71 – 1.55 (m, 1H, CH₂), 1.41 (d, *J* = 6.2 Hz, 9H, Boc), 1.11 – 0.99 (m, 6H, 2xCH₃), 0.95 – 0.83 (m, 9H, 3xCH₃).

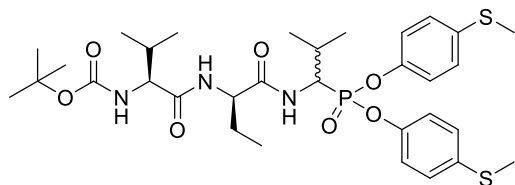
HRMS: C₃₂H₄₈N₃O₇PS₂ [M+Na]⁺ calc. 704.2569 found 704.2588

HPLC: purity >99%; retention time 18.457 and 18.613 min





(7) Boc-L-Val-D-Abu- Val^P(OPh-4-SCH₃)₂



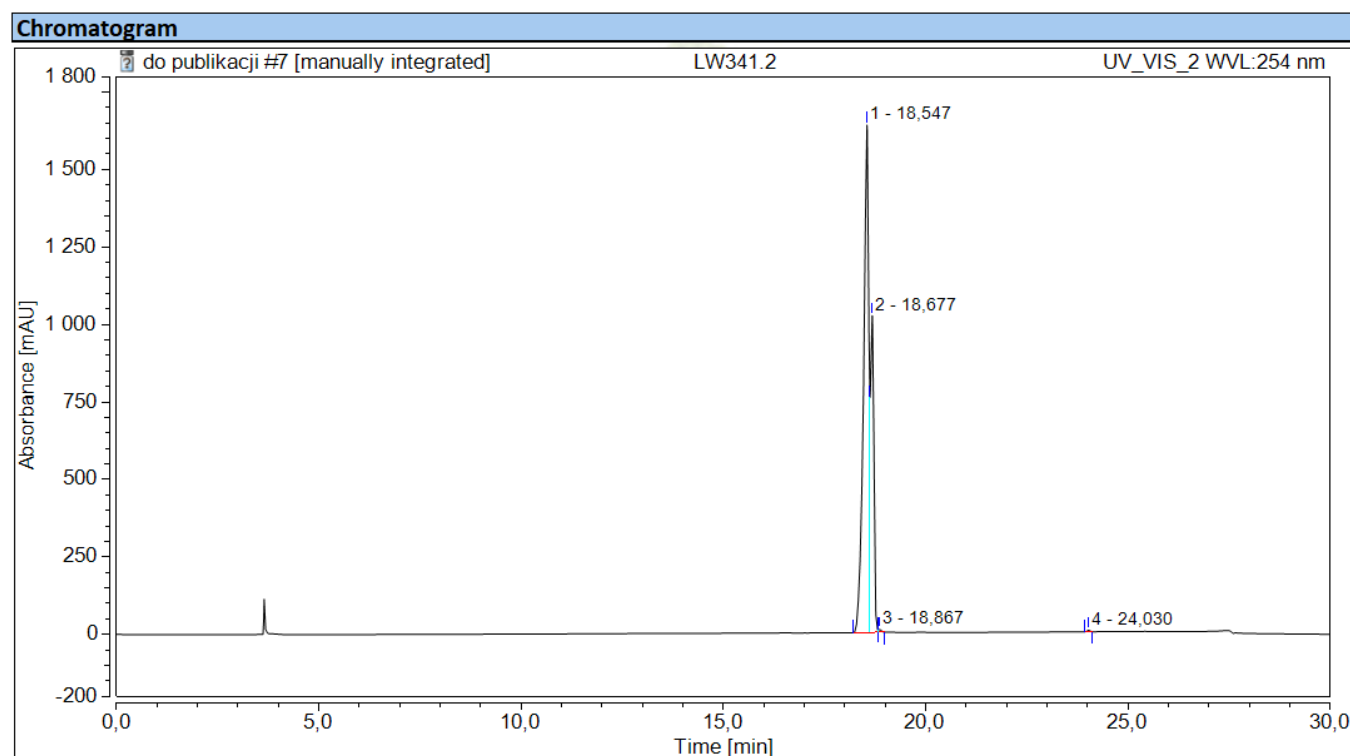
Name: *tert*-butyl ((2*S*)-1-(((2*R*)-1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-1-oxobutan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.19 (s, 43%), 18.06 (s, 57%).

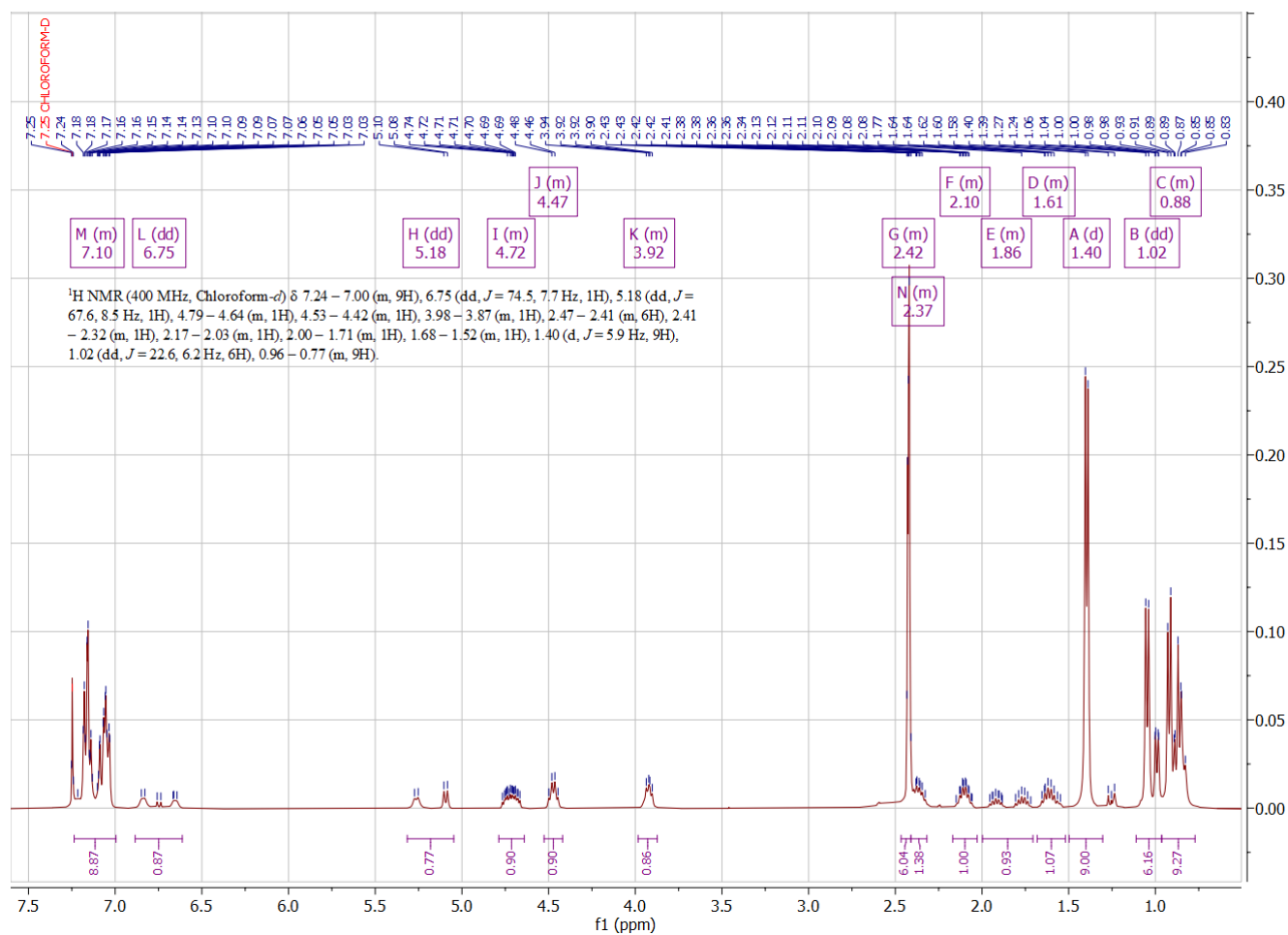
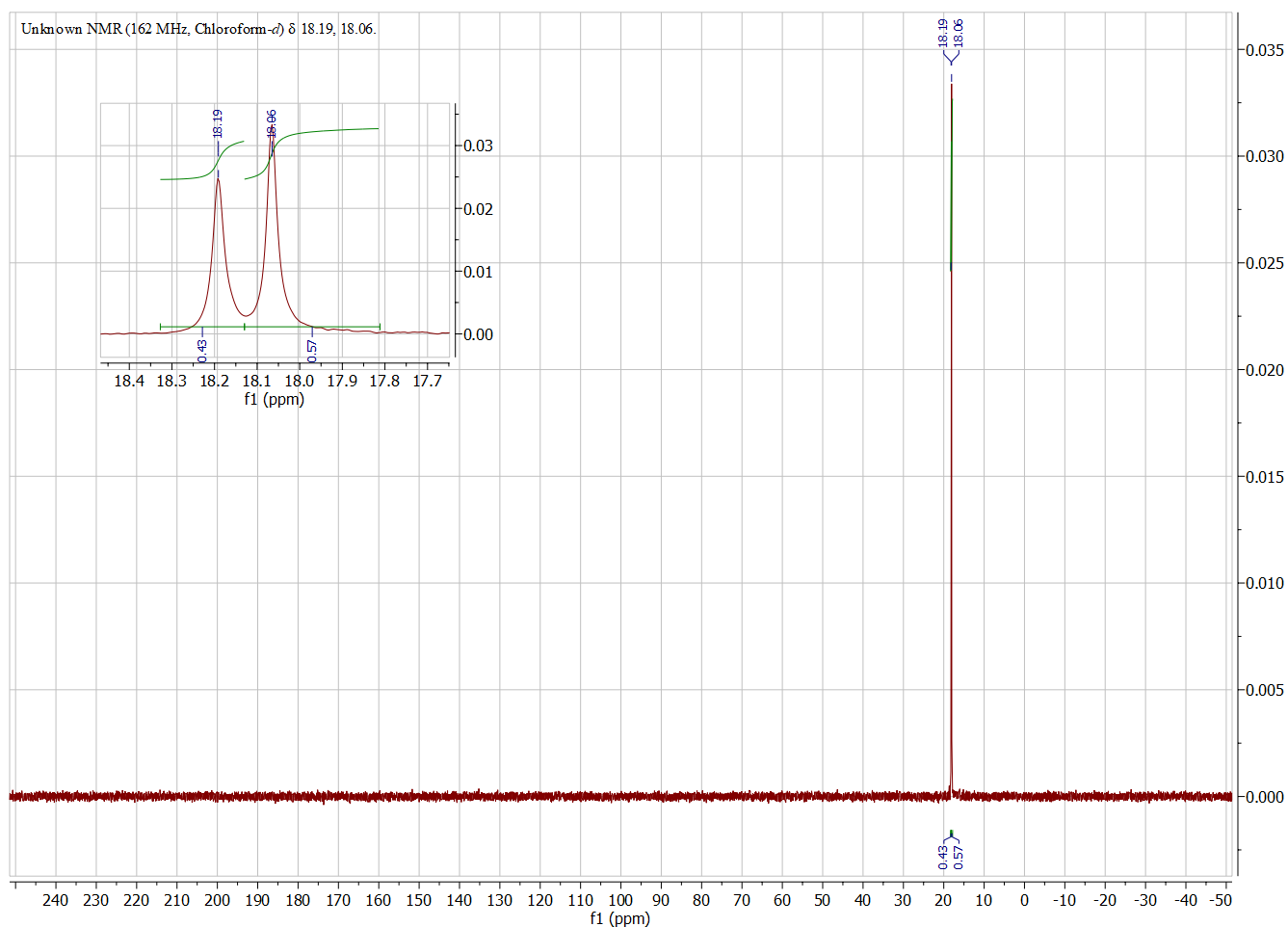
¹H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.00 (m, 9H, 8xArH, NH), 6.75 (dd, *J* = 74.5, 7.7 Hz, 1H, NH), 5.18 (dd, *J* = 67.6, 8.5 Hz, 1H, NH), 4.79 – 4.64 (m, 1H, CHP), 4.53 – 4.42 (m, 1H, CH), 3.98 – 3.87 (m, 1H, CH), 2.47 – 2.41 (m, 6H, 2xSCH₃), 2.41 – 2.32 (m, 1H, CH), 2.17 – 2.03 (m, 1H, CH), 2.00 – 1.71 (m, 1H, CH₂), 1.68 – 1.52 (m, 1H, CH₂), 1.40 (d, *J* = 5.9 Hz, 9H, Boc), 1.02 (dd, *J* = 22.6, 6.2 Hz, 6H, 2xCH₃), 0.96 – 0.77 (m, 9H, 3xCH₃).

HRMS: C₃₂H₄₈N₃O₇PS₂ [M+Na]⁺ calc. 704.2569 found 704.2545

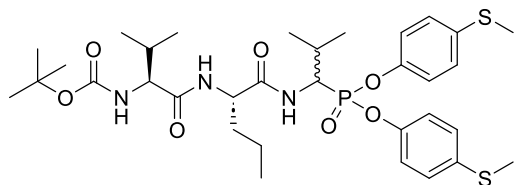
HPLC: purity >99%; retention time 18.547 and 18.677 min



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		18,547	247,363	1637,453	70,98	61,23	n.a.
2		18,677	99,783	1021,828	28,63	38,21	n.a.
3		18,867	0,923	9,002	0,26	0,34	n.a.
4		24,030	0,442	5,874	0,13	0,22	n.a.
Total:			348,511	2674,157	100,00	100,00	



(8) Boc-L-Val-L-Nva- Val^P(OPh-4-SCH₃)₂



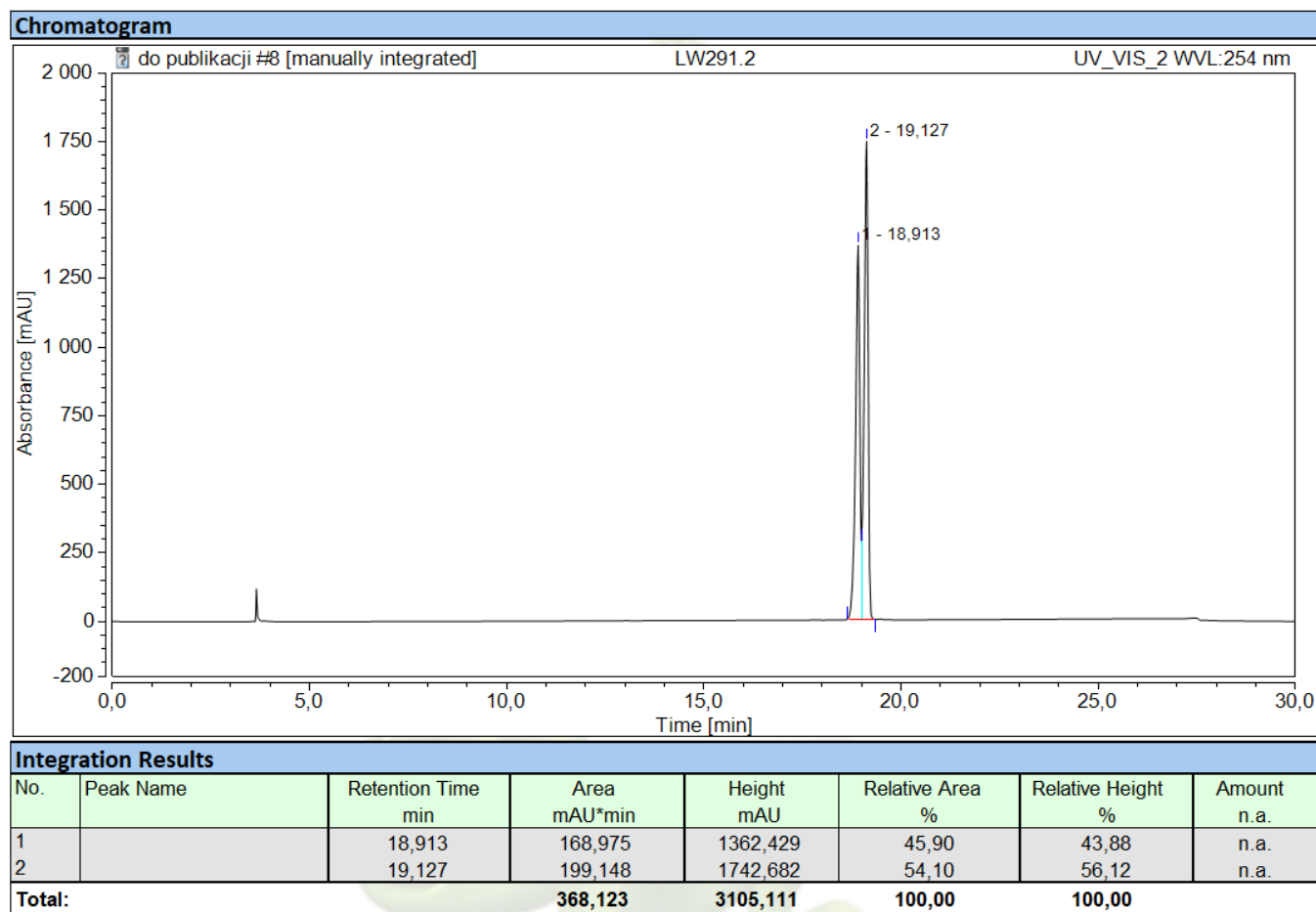
Name: *tert*-butyl ((2S)-1-(((2S)-1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-1-oxopentan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

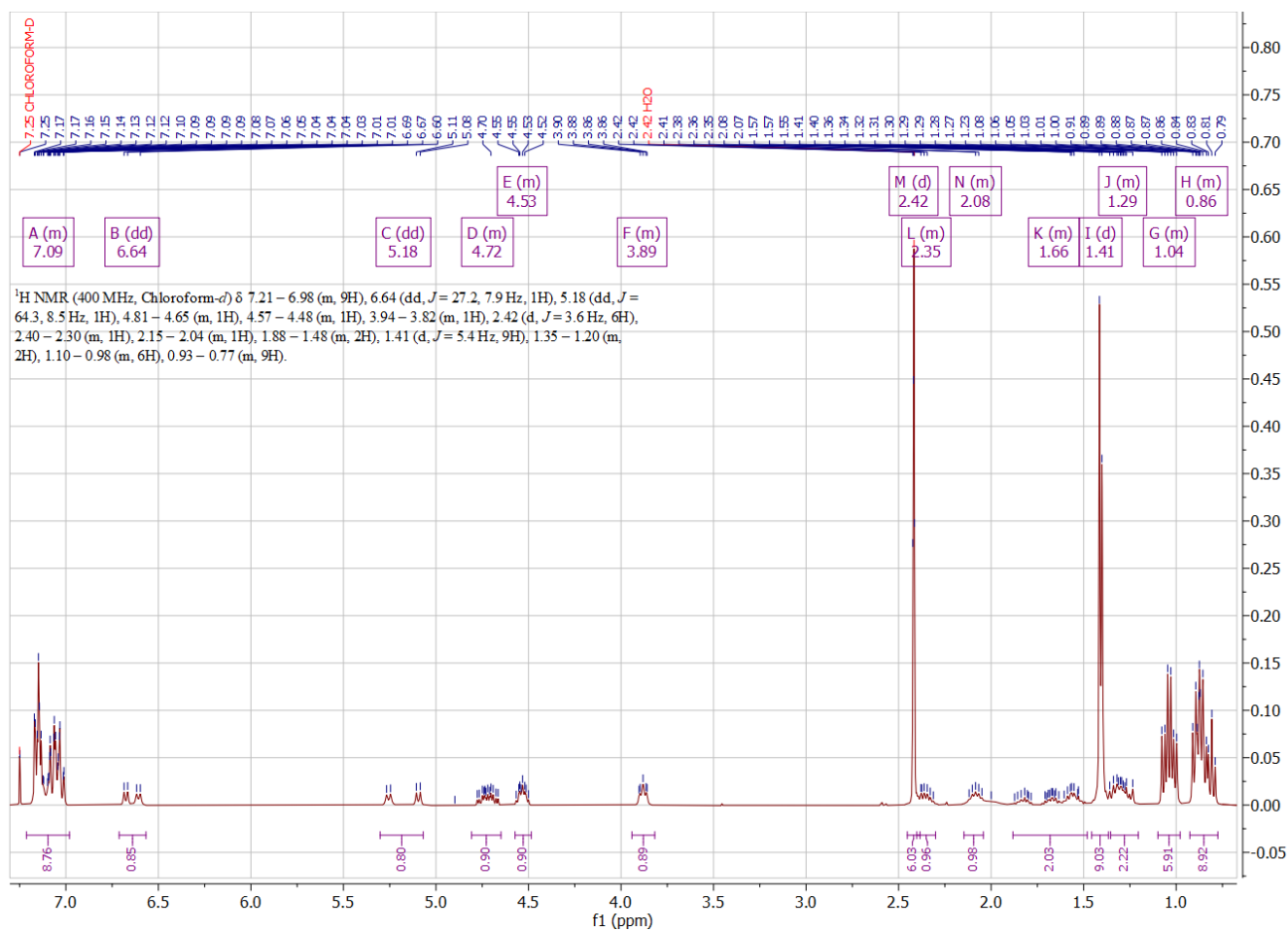
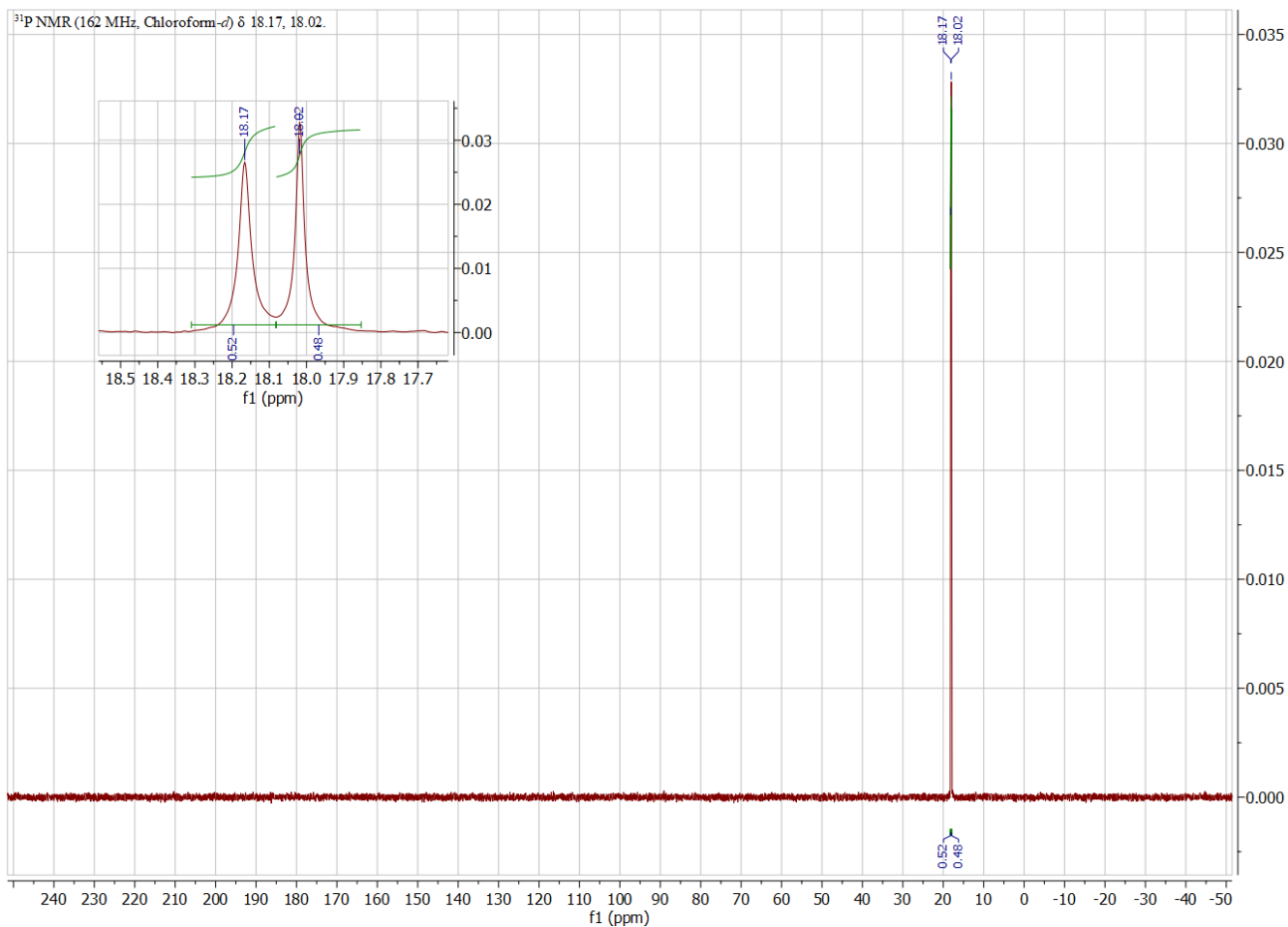
³¹P NMR (162 MHz, Chloroform-d) δ 18.17 (s, 51%), 18.02 (s, 49%).

¹H NMR (400 MHz, Chloroform-d) δ 7.21 – 6.98 (m, 9H, 8xArH, NH), 6.64 (dd, J = 27.2, 7.9 Hz, 1H, NH), 5.18 (dd, J = 64.3, 8.5 Hz, 1H, NH), 4.81 – 4.65 (m, 1H, CHP), 4.57 – 4.48 (m, 1H, CH), 3.94 – 3.82 (m, 1H, CH), 2.42 (d, J = 3.6 Hz, 6H, 2xSCH₃), 2.40 – 2.30 (m, 1H, CH), 2.15 – 2.04 (m, 1H, CH), 1.88 – 1.48 (m, 2H, CH₂), 1.41 (d, J = 5.4 Hz, 9H, Boc), 1.35 – 1.20 (m, 2H, CH₂), 1.10 – 0.98 (m, 6H, 2xCH₃), 0.93 – 0.77 (m, 9H, 3xCH₃).

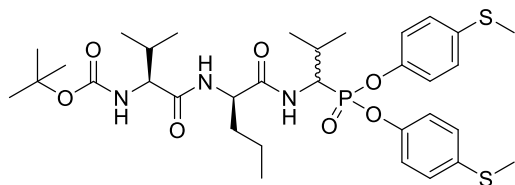
HRMS: C₃₃H₅₀N₃O₇PS₂ [M+Na]⁺ calc. 718.2725 found 718.2728

HPLC: purity >99%; retention time 18.913 and 19.127 min





(9) Boc-L-Val-D-Nva- Val^P(OPh-4-SCH₃)₂



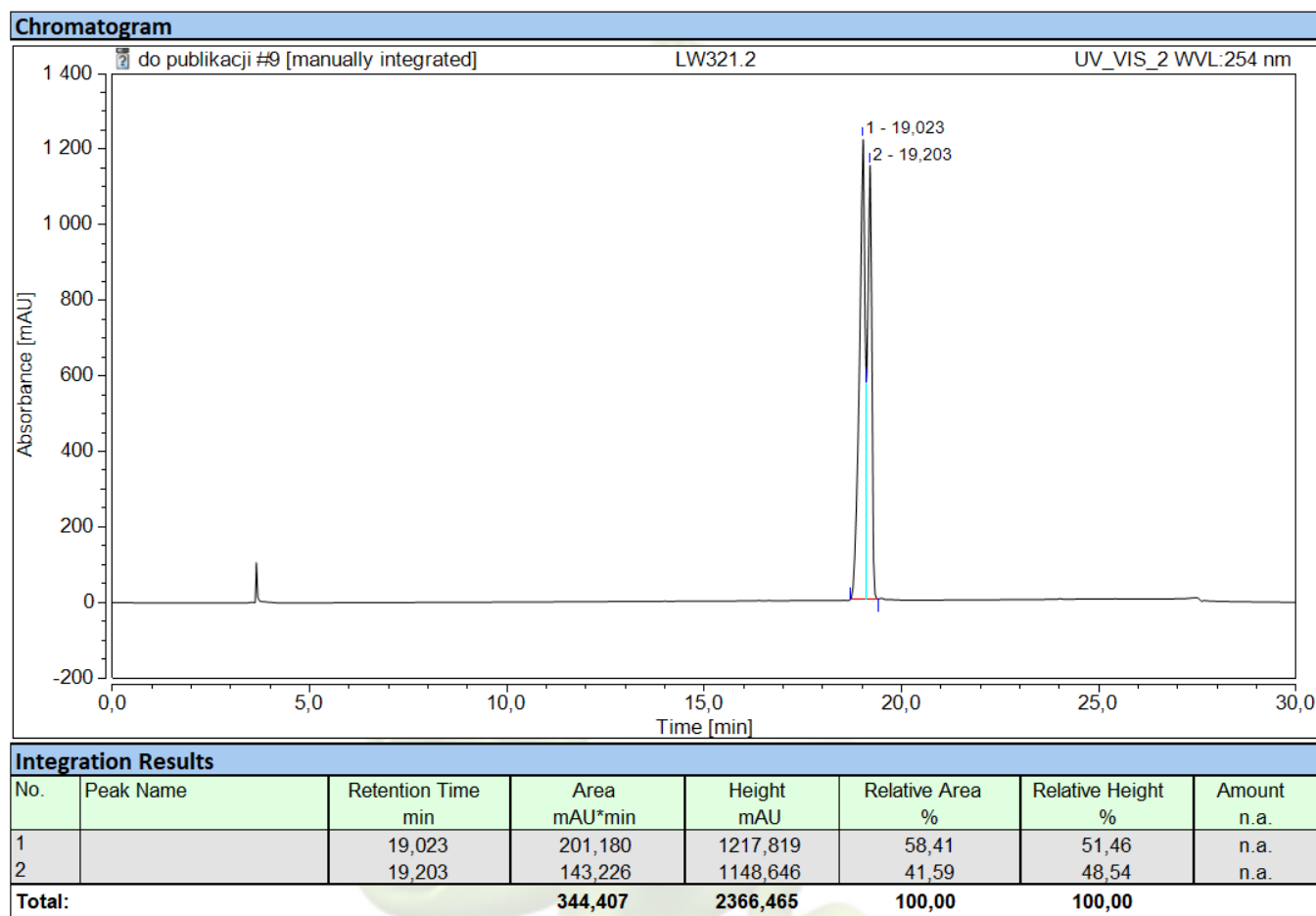
Name: *tert*-butyl ((2*S*)-1-(((2*R*)-1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-1-oxopentan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

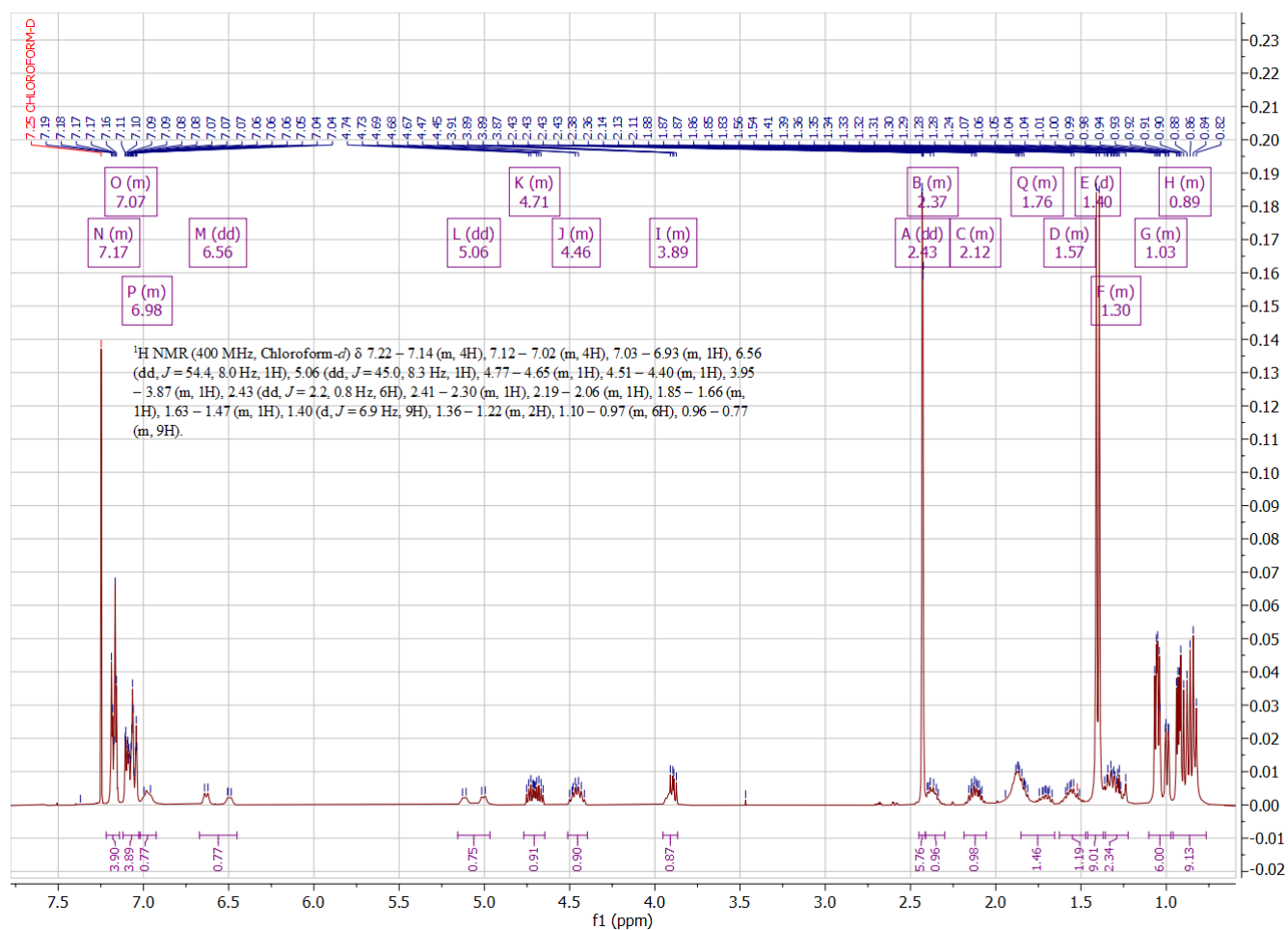
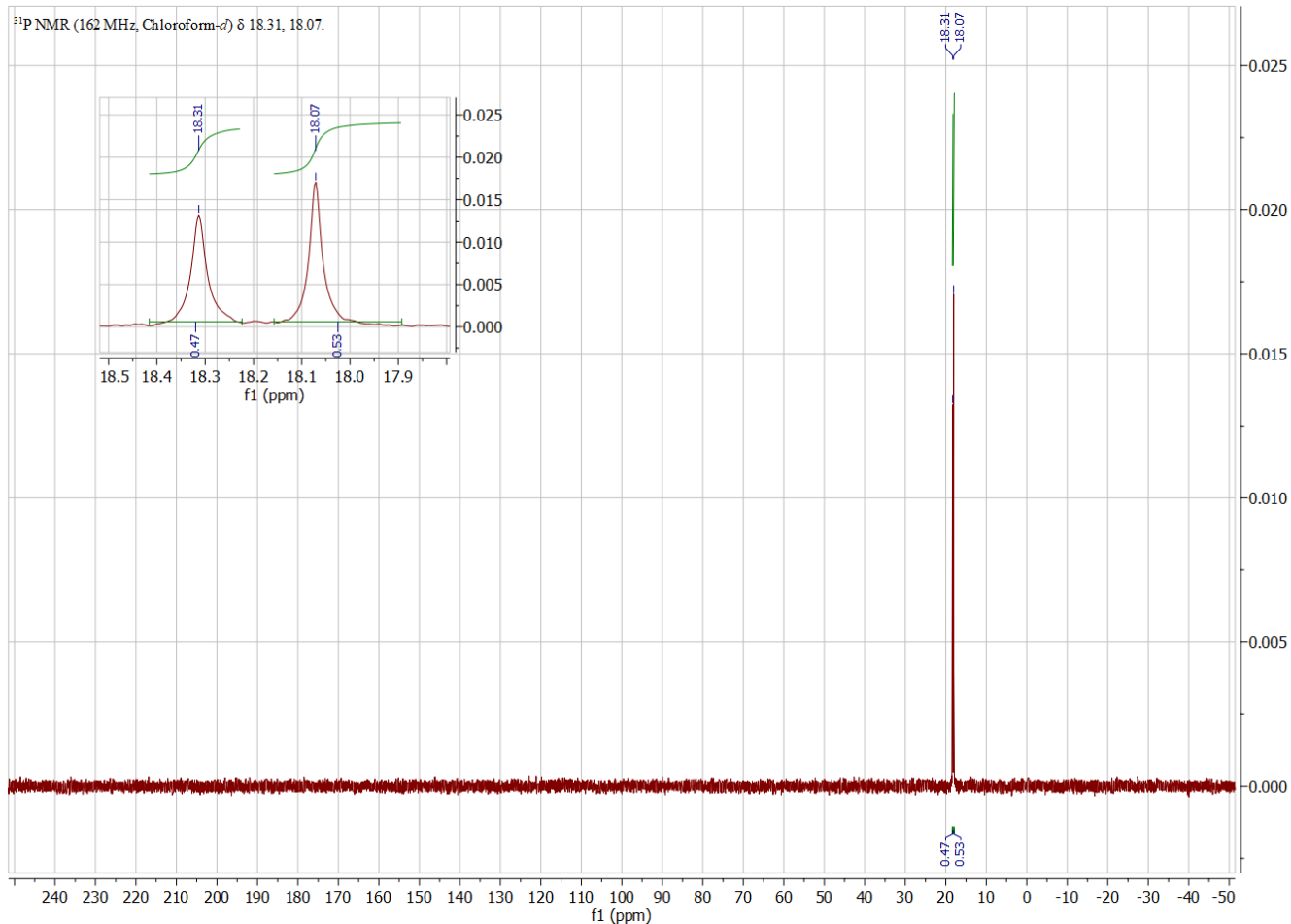
³¹P NMR (162 MHz, Chloroform-*d*) δ 18.31 (s, 47%), 18.07 (s, 53%).

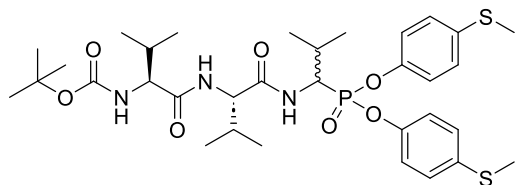
¹H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 7.14 (m, 4H, 4xArH), 7.12 – 7.02 (m, 4H, 4xArH), 7.03 – 6.93 (m, 1H, NH), 6.56 (dd, *J* = 54.4, 8.0 Hz, 1H, NH), 5.06 (dd, *J* = 45.0, 8.3 Hz, 1H, NH), 4.77 – 4.65 (m, 1H, CHP), 4.51 – 4.40 (m, 1H, CH), 3.95 – 3.87 (m, 1H, CH), 2.43 (dd, *J* = 2.2, 0.8 Hz, 6H, 3xSCH₃), 2.41 – 2.30 (m, 1H, CH), 2.19 – 2.06 (m, 1H, CH), 1.85 – 1.66 (m, 1H, CH₂), 1.63 – 1.47 (m, 1H, CH₂), 1.40 (d, *J* = 6.9 Hz, 9H, Boc), 1.36 – 1.22 (m, 2H, CH₂), 1.10 – 0.97 (m, 6H, 2xCH₃), 0.96 – 0.77 (m, 9H, 3xCH₃).

HRMS: C₃₃H₅₀N₃O₇PS₂ [M+Na]⁺ calc. 718.2725 found 718.2706

HPLC: purity >99%; retention time 19.023 and 19.203 min





(10) Boc-L-Val-L-Val-Val^P(OPh-4-SCH₃)₂

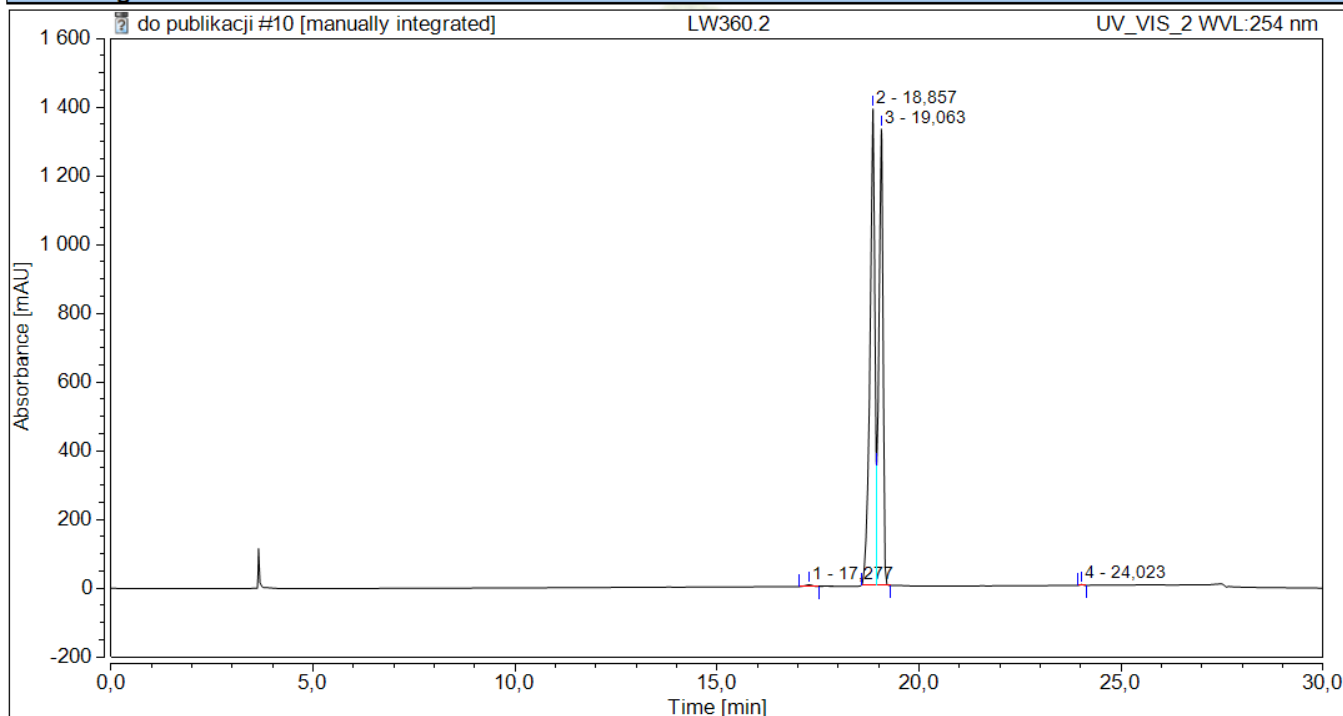
Name: *tert*-butyl ((2*S*)-1-(((2*S*)-1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-3-methyl-1-oxobutan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.36 (s).

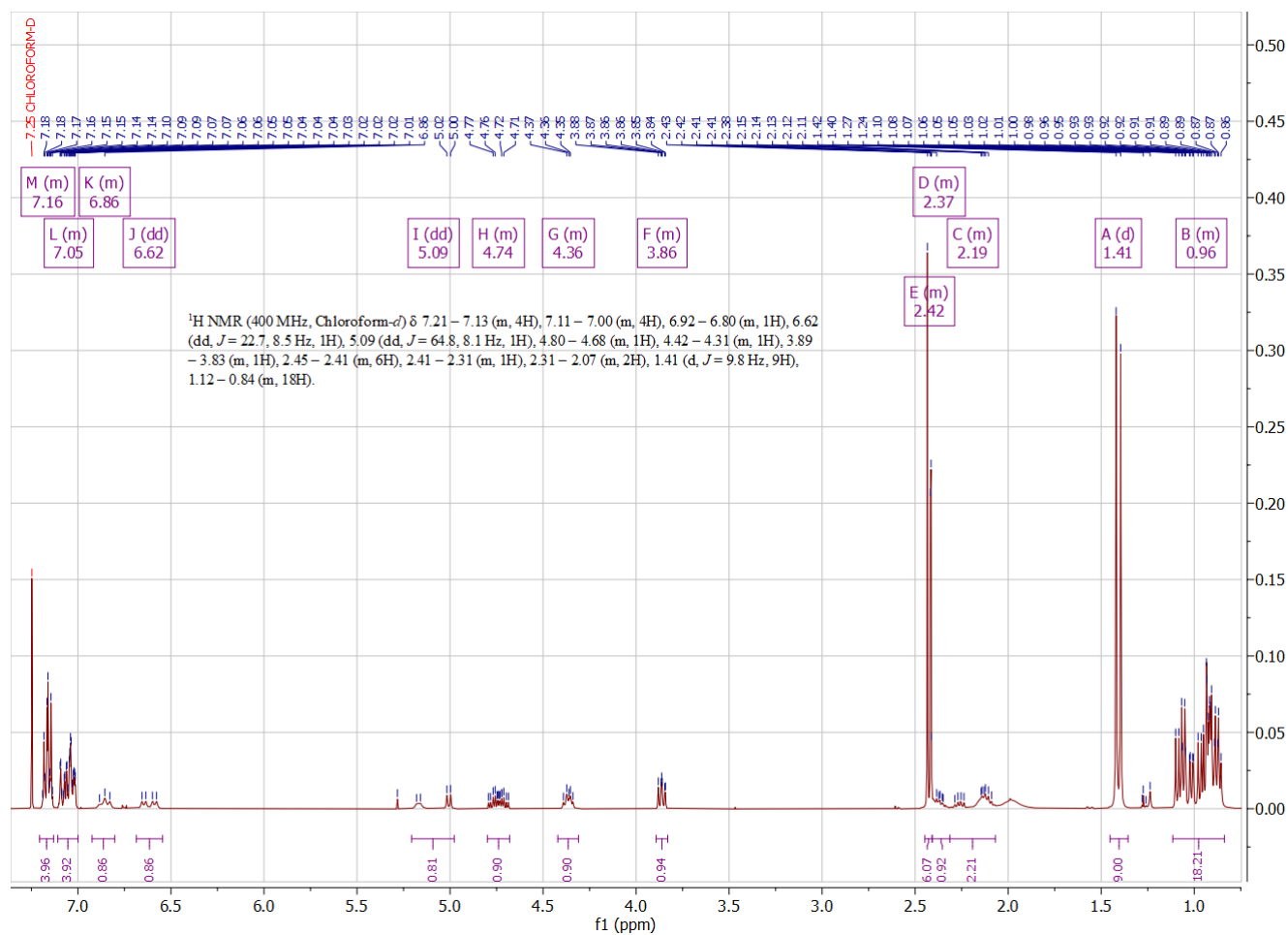
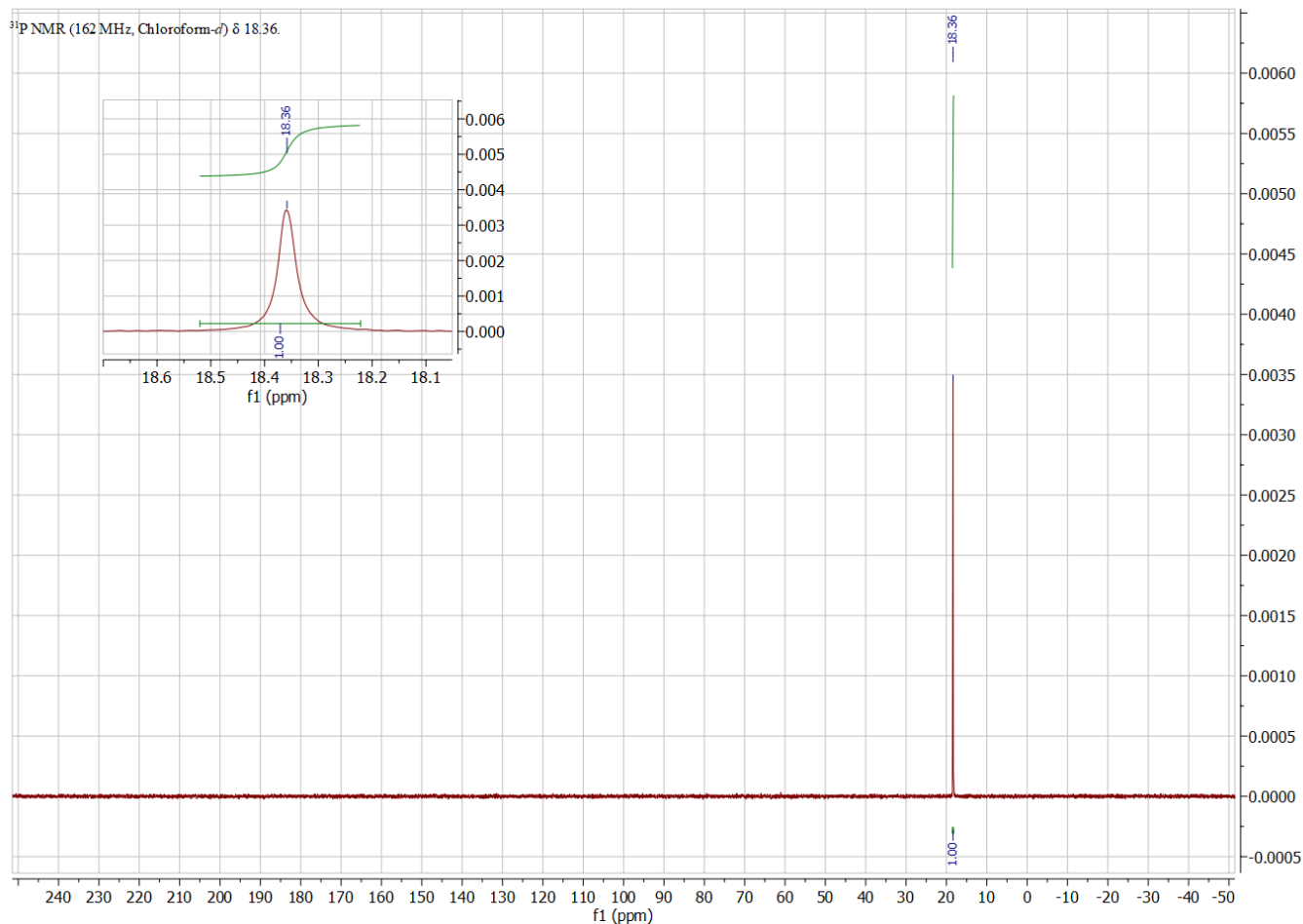
¹H NMR (400 MHz, Chloroform-*d*) δ 7.21 – 7.13 (m, 4H, 4xArH), 7.11 – 7.00 (m, 4H, 4xArH), 6.92 – 6.80 (m, 1H, NH), 6.62 (dd, *J* = 22.7, 8.5 Hz, 1H, NH), 5.09 (dd, *J* = 64.8, 8.1 Hz, 1H, NH), 4.80 – 4.68 (m, 1H, CHP), 4.42 – 4.31 (m, 1H, CH), 3.89 – 3.83 (m, 1H, CH), 2.45 – 2.41 (m, 6H, 2xSCH₃), 2.41 – 2.31 (m, 1H, CH), 2.31 – 2.07 (m, 2H, 2xCH), 1.41 (d, *J* = 9.8 Hz, 9H, Boc), 1.12 – 0.84 (m, 18H, 6xCH₃).

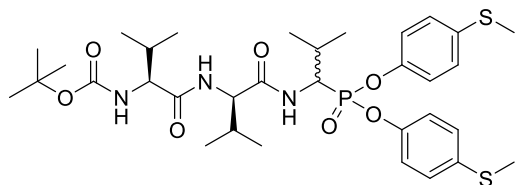
HRMS: C₃₃H₅₀N₃O₇PS₂ [M+Na]⁺ calc. 718.2725 found 718.2733

HPLC: purity >99%; retention time 18.857 and 19.063 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17,277	1,007	5,017	0,28	0,18	n.a.
2		18,857	195,298	1386,650	55,09	50,93	n.a.
3		19,063	158,019	1328,209	44,57	48,78	n.a.
4		24,023	0,213	2,824	0,06	0,10	n.a.
Total:			354,538	2722,699	100,00	100,00	



(11) Boc-L-Val-D-Val- Val^P(OPh-4-SCH₃)₂

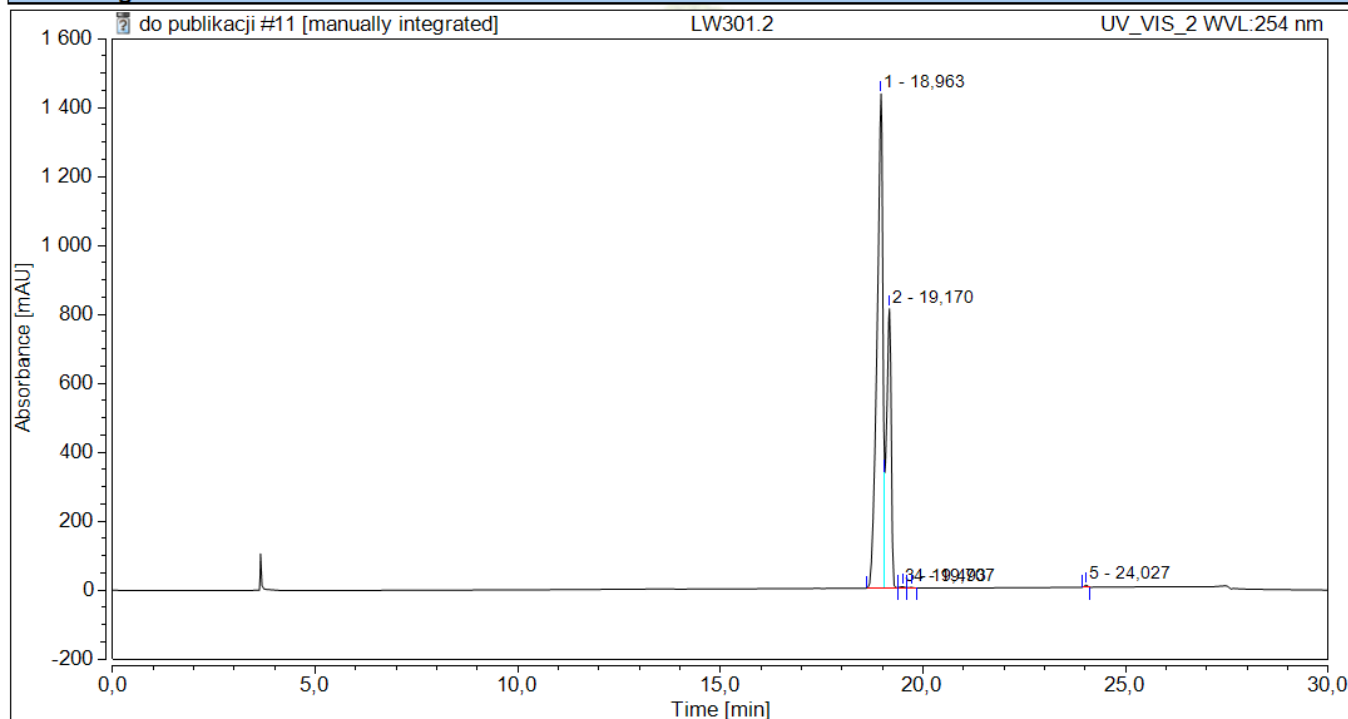
Name: *tert*-butyl ((2S)-1-(((2R)-1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-3-methyl-1-oxobutan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-d) δ 18.32 (s, 44%), 18.30 (s, 56%).

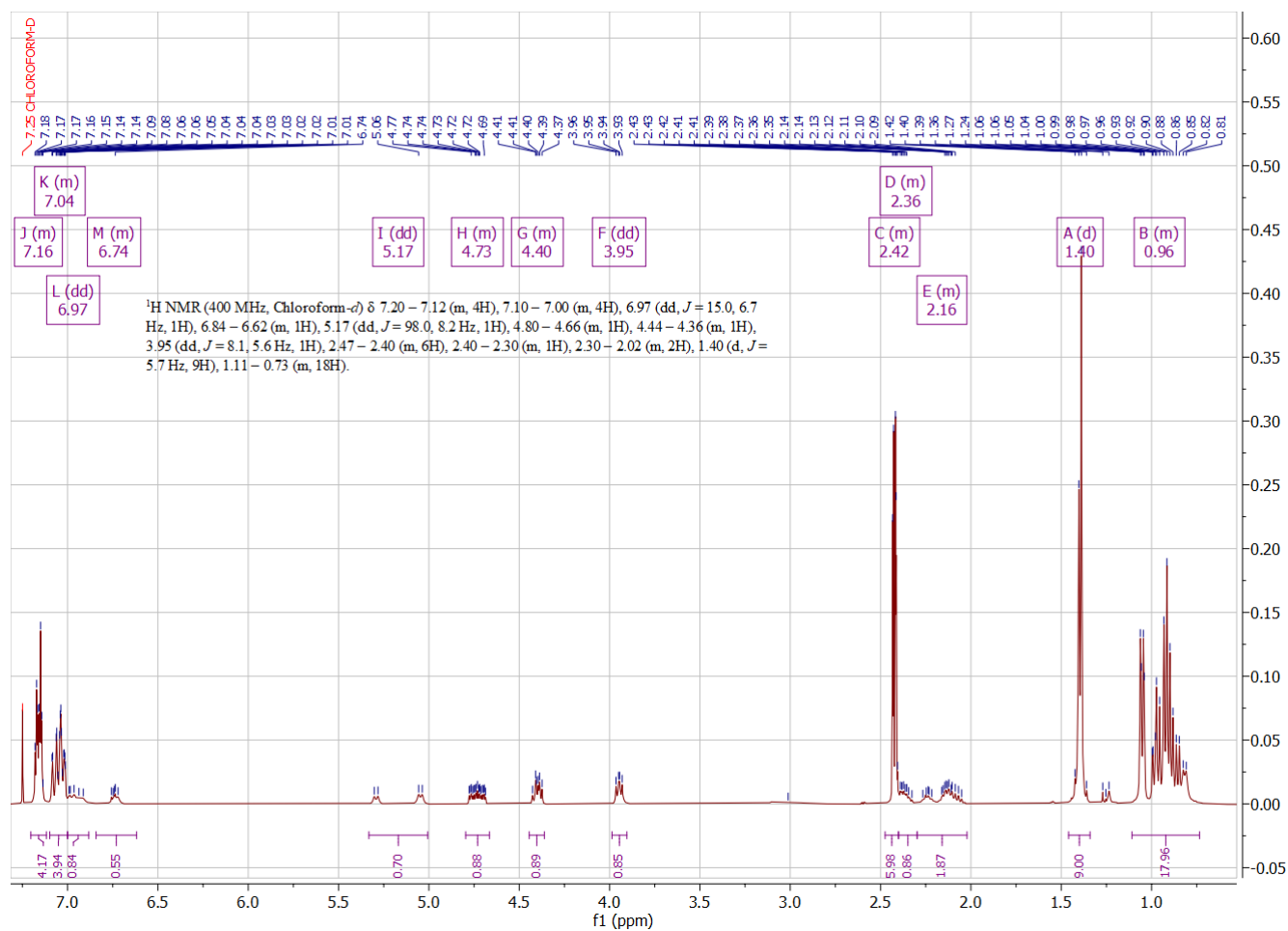
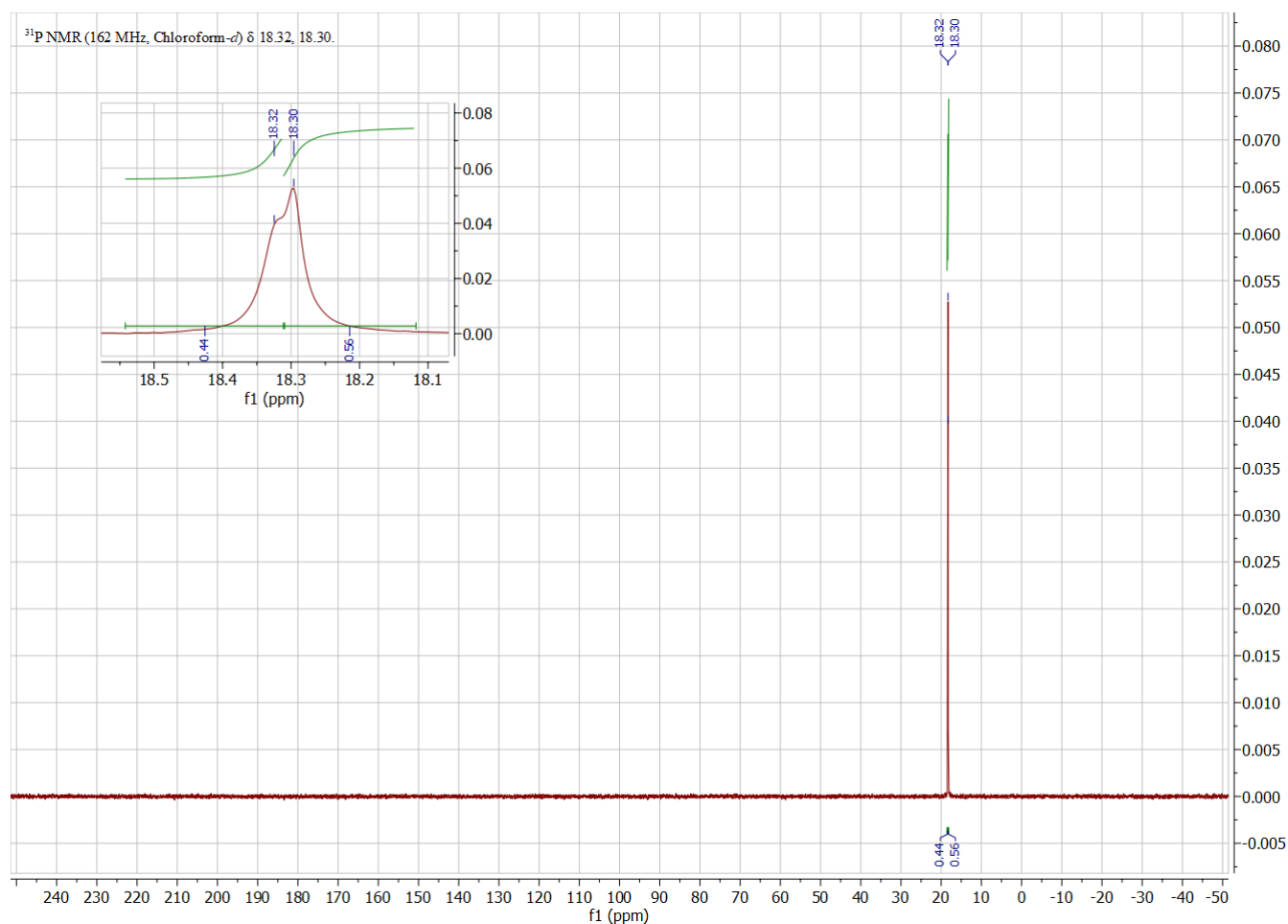
¹H NMR (400 MHz, Chloroform-d) δ 7.20 – 7.12 (m, 4H, 4xArH), 7.10 – 7.00 (m, 4H, 4xArH), 6.97 (dd, J = 15.0, 6.7 Hz, 1H, NH), 6.84 – 6.62 (m, 1H, NH), 5.17 (dd, J = 98.0, 8.2 Hz, 1H, NH), 4.80 – 4.66 (m, 1H, CHP), 4.44 – 4.36 (m, 1H, CH), 3.95 (dd, J = 8.1, 5.6 Hz, 1H, CH), 2.47 – 2.40 (m, 6H, 2xSCH₃), 2.40 – 2.30 (m, 1H, CH), 2.30 – 2.02 (m, 2H, 2xCH), 1.40 (d, J = 5.7 Hz, 9H, Boc), 1.11 – 0.73 (m, 18H, 6xCH₃).

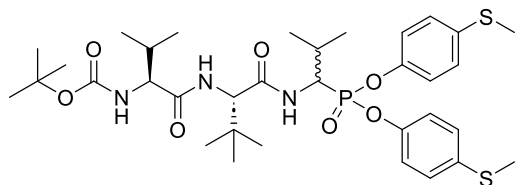
HRMS: C₃₃H₅₀N₃O₇PS₂ [M+Na]⁺ calc. 718.2725 found 718.2703

HPLC: purity >99%; retention time 18.963 and 19.170 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18,963	238,203	1432,966	69,31	63,57	n.a.
2		19,170	104,330	809,486	30,36	35,91	n.a.
3		19,493	0,367	3,179	0,11	0,14	n.a.
4		19,707	0,174	1,542	0,05	0,07	n.a.
5		24,027	0,585	7,043	0,17	0,31	n.a.
Total:			343,659	2254,215	100,00	100,00	



(12) Boc-L-Val-L-Tle- Val^P(OPh-4-SCH₃)₂

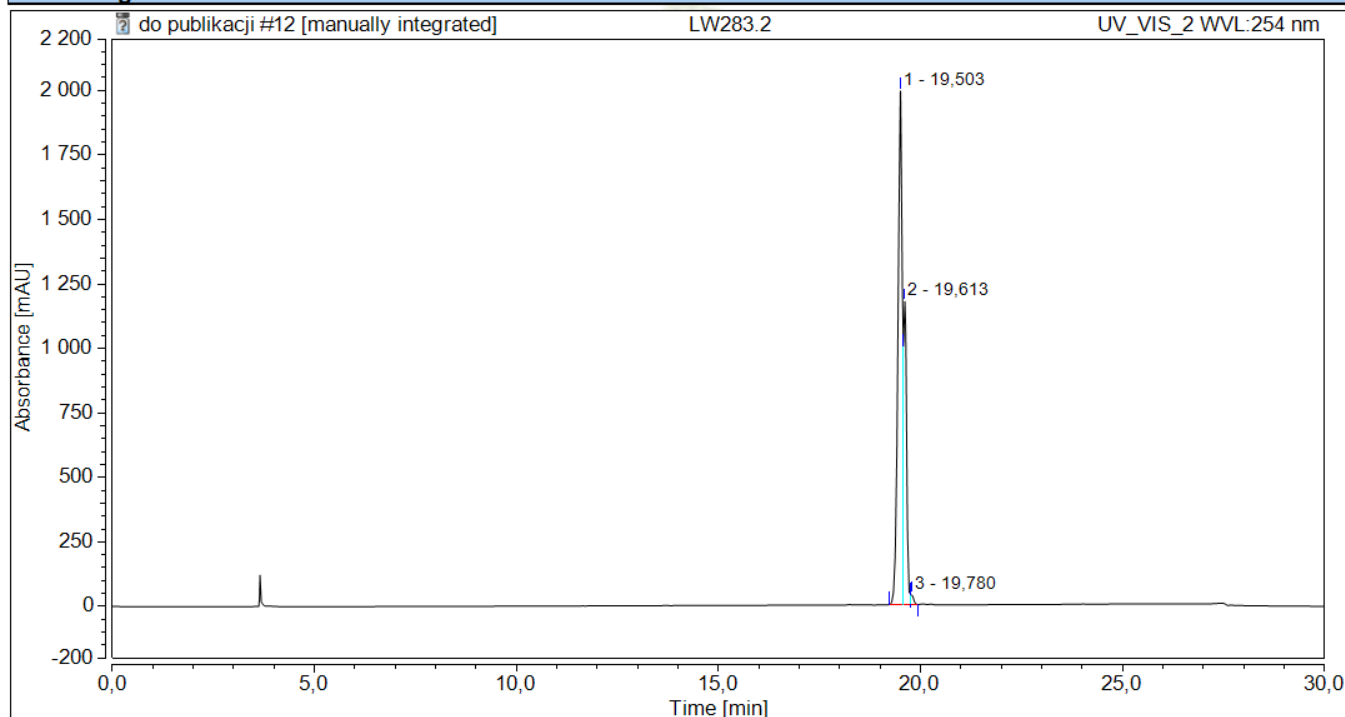
Name: *tert*-butyl ((2*S*)-1-(((2*S*)-1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-3,3-dimethyl-1-oxobutan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.54 (s, 61%), 18.51 (s, 39%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 6.90 (m, 9H, 8xArH, NH), 6.62 (d, *J* = 9.3 Hz, 1H, NH), 5.19 (dd, *J* = 133.0, 8.3 Hz, 1H, NH), 4.84 – 4.68 (m, 1H, CHP), 4.43 (dd, *J* = 69.9, 9.0 Hz, 1H, CH), 3.89 – 3.79 (m, 1H, CH), 2.45 – 2.40 (m, 6H, 2xSCH₃), 2.40 – 2.29 (m, 1H, CH), 2.16 – 2.00 (m, 1H, CH), 1.40 (d, *J* = 7.1 Hz, 9H, Boc), 1.13 – 0.97 (m, 15H, 5xCH₃), 0.92 – 0.78 (m, 6H, 2xCH₃).

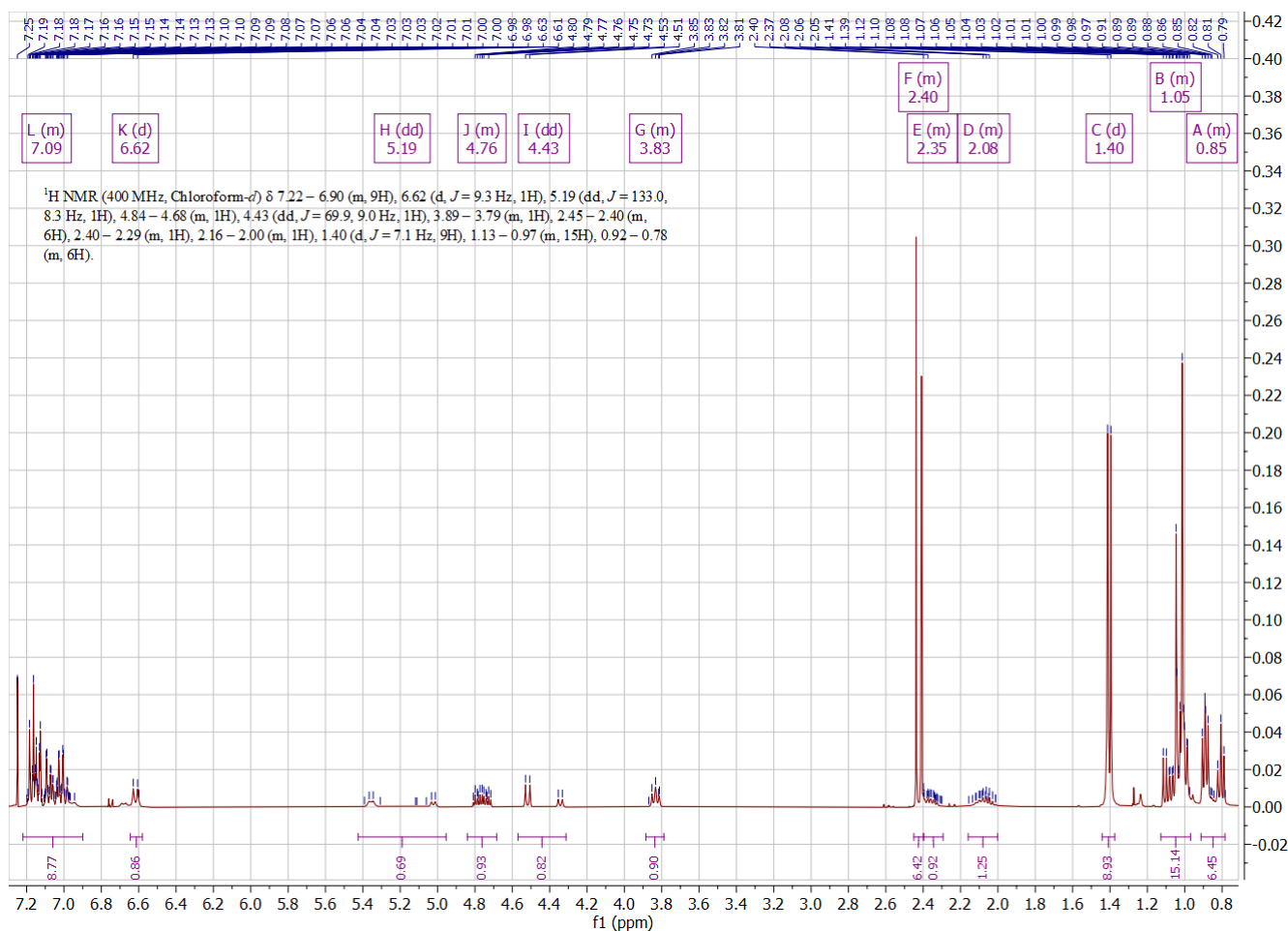
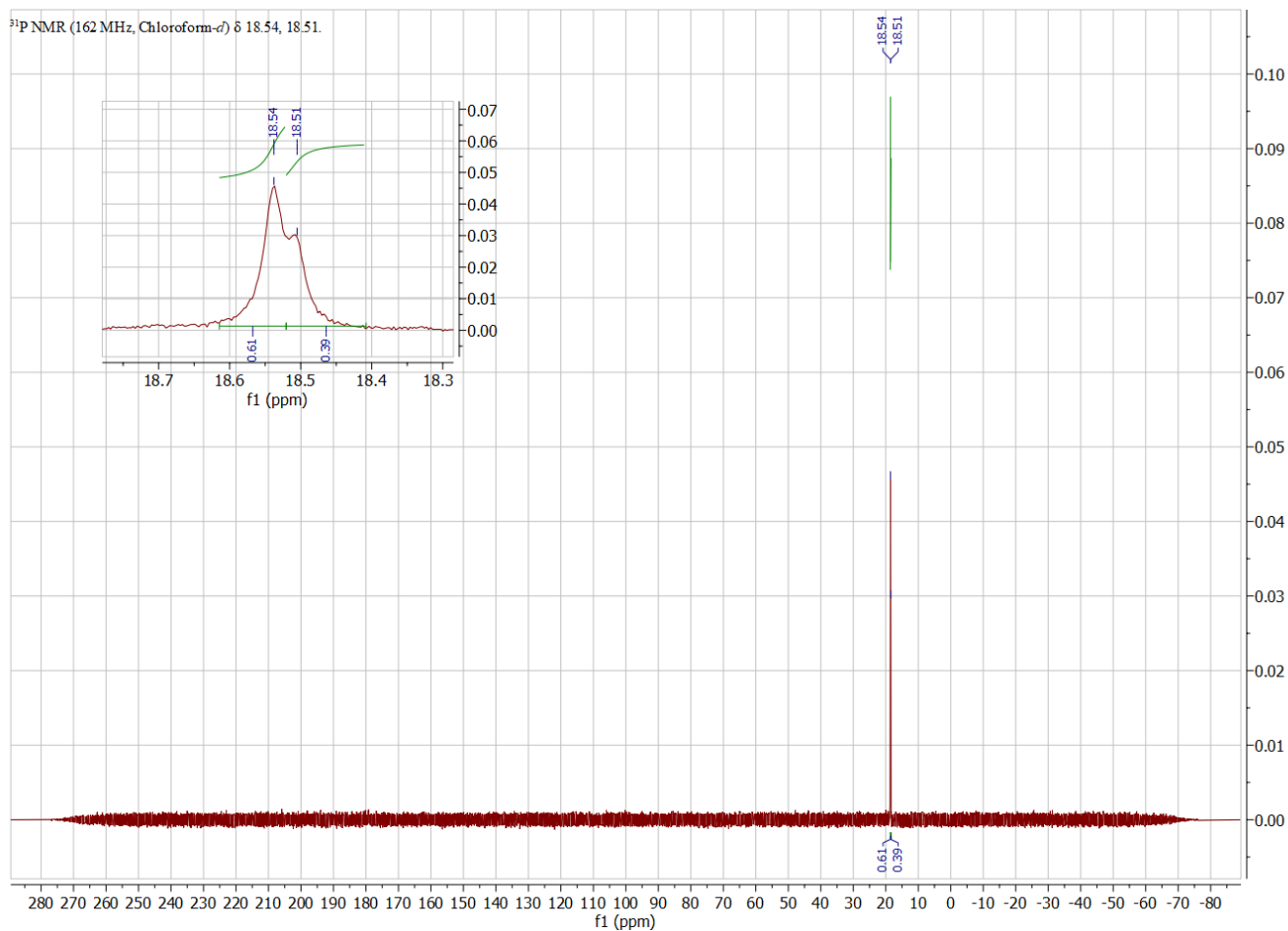
HRMS: C₃₄H₅₂N₃O₇PS₂ [M+Na]⁺ calc. 732.2882 found 732.2848

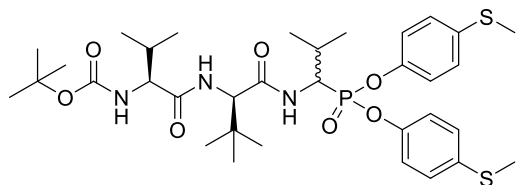
HPLC: purity >98%; retention time 19.503 and 19.613 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19,503	247,188	1990,786	70,12	62,14	n.a.
2		19,613	101,740	1174,462	28,86	36,66	n.a.
3		19,780	3,586	38,431	1,02	1,20	n.a.
Total:			352,515	3203,679	100,00	100,00	

^{31}P NMR (162 MHz, Chloroform- d) δ 18.54, 18.51.



(13) Boc-L-Val-D-Tle- Val^P(OPh-4-SCH₃)₂

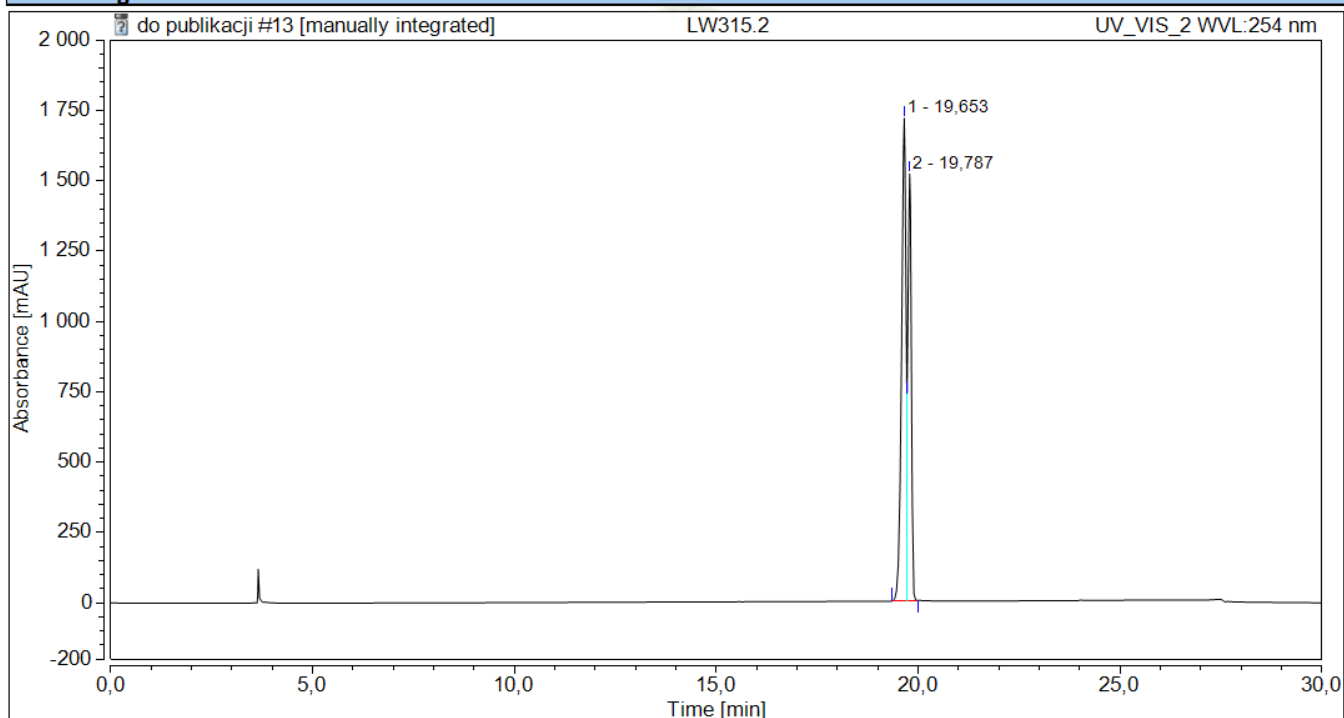
Name: *tert*-butyl ((2*S*)-1-(((2*R*)-1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-3,3-dimethyl-1-oxobutan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.52 (s, 33%), 18.47 (s, 67%).

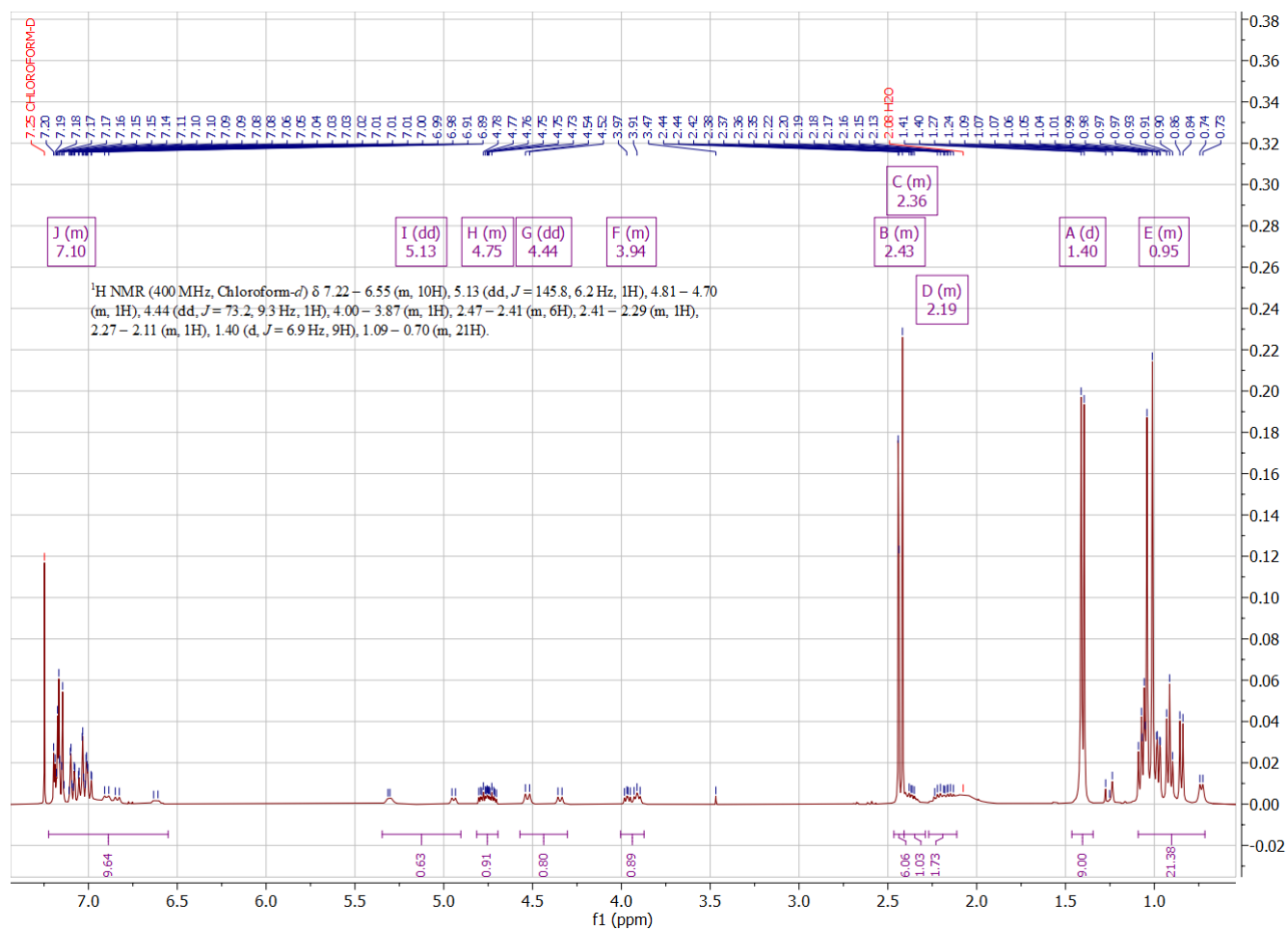
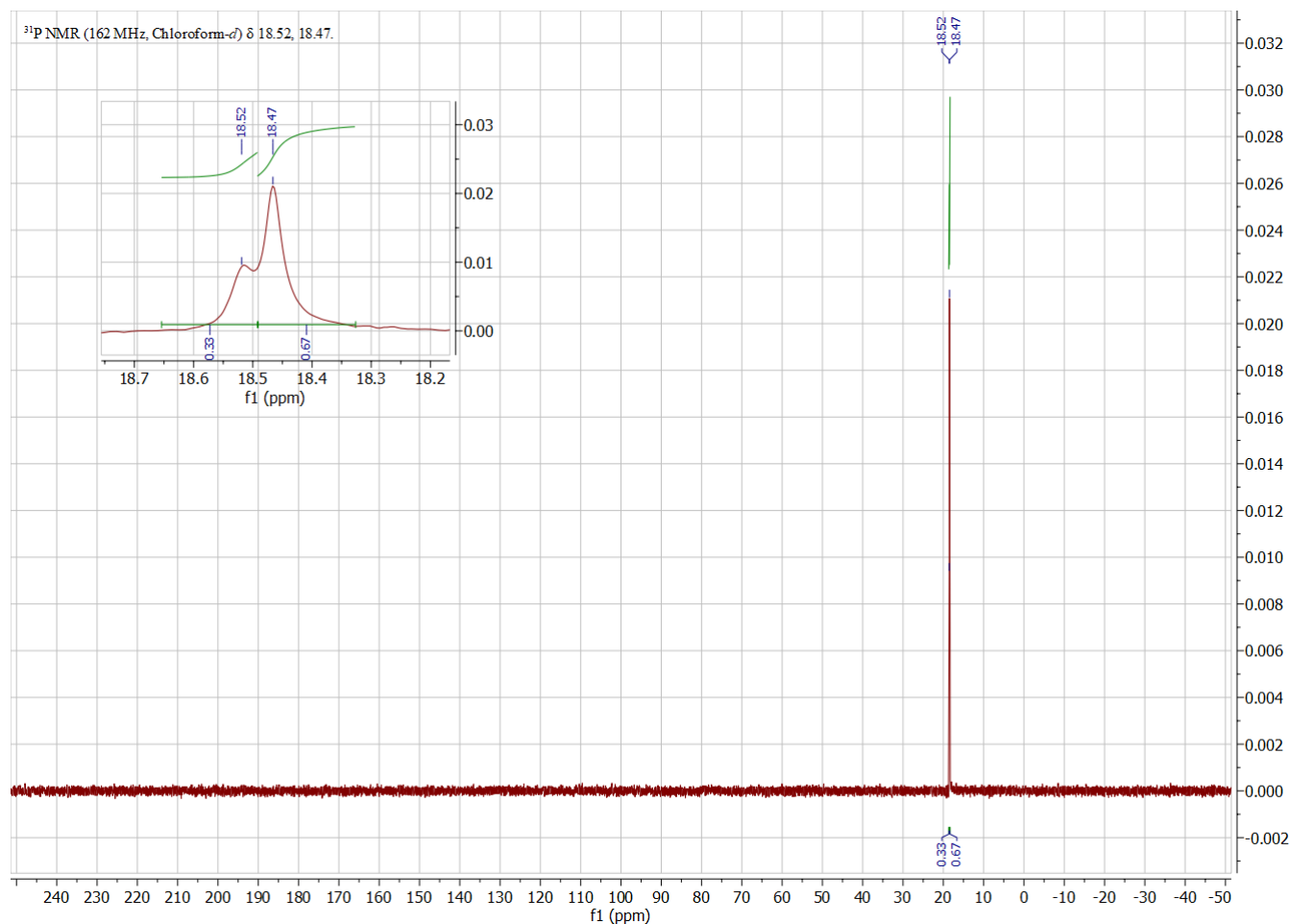
¹H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 6.55 (m, 10H, 8xArH, 2xNH), 5.13 (dd, *J* = 145.8, 6.2 Hz, 1H, NH), 4.81 – 4.70 (m, 1H, CHP), 4.44 (dd, *J* = 73.2, 9.3 Hz, 1H, CH), 4.00 – 3.87 (m, 1H, CH), 2.47 – 2.41 (m, 6H, 2xSCH₃), 2.41 – 2.29 (m, 1H, CH), 2.27 – 2.11 (m, 1H, CH), 1.40 (d, *J* = 6.9 Hz, 9H, Boc), 1.09 – 0.70 (m, 21H, 7xCH₃).

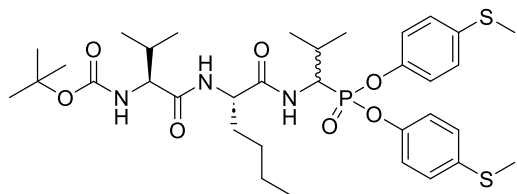
HRMS: C₃₄H₅₂N₃O₇PS₂ [M+Na]⁺ calc. 732.2882 found 732.2878

HPLC: purity >99%; retention time 19.653 and 19.787 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19,653	214,250	1713,689	59,04	53,06	n.a.
2		19,787	148,669	1516,088	40,96	46,94	n.a.
Total:			362,919	3229,777	100,00	100,00	



(14) Boc-L-Val-L-Nle- Val^P(OPh-4-SCH₃)₂

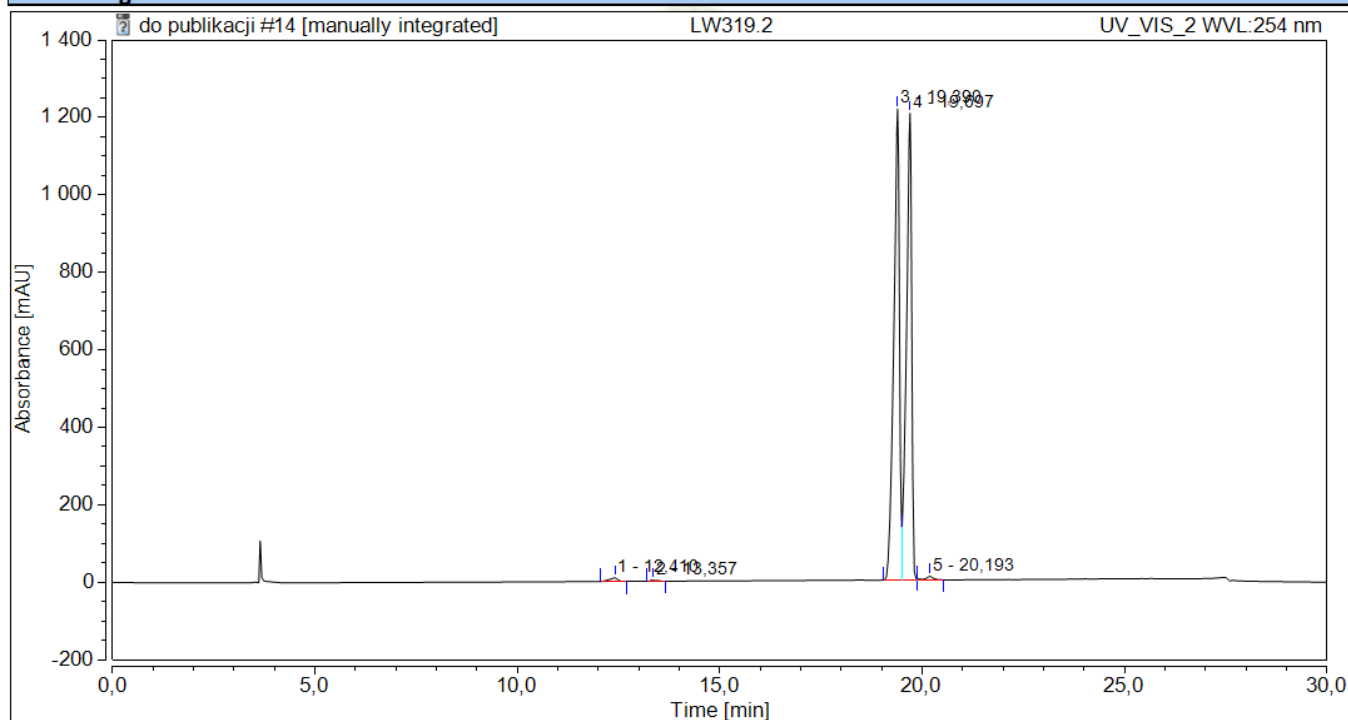
Name: *tert*-butyl ((2*S*)-1-(((2*S*)-1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-1-oxohexan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.17 (s, 43%), 18.15 (s, 57%).

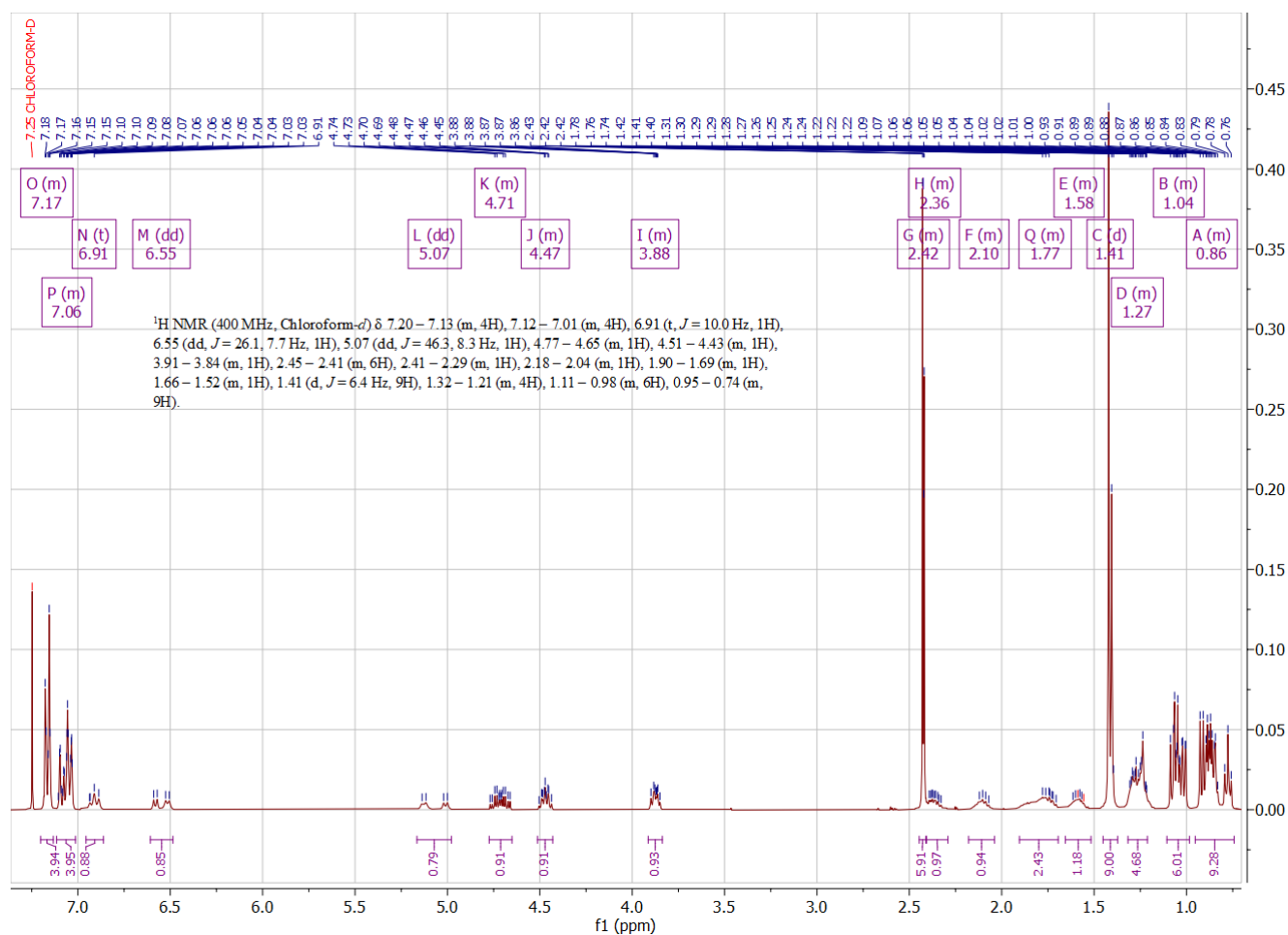
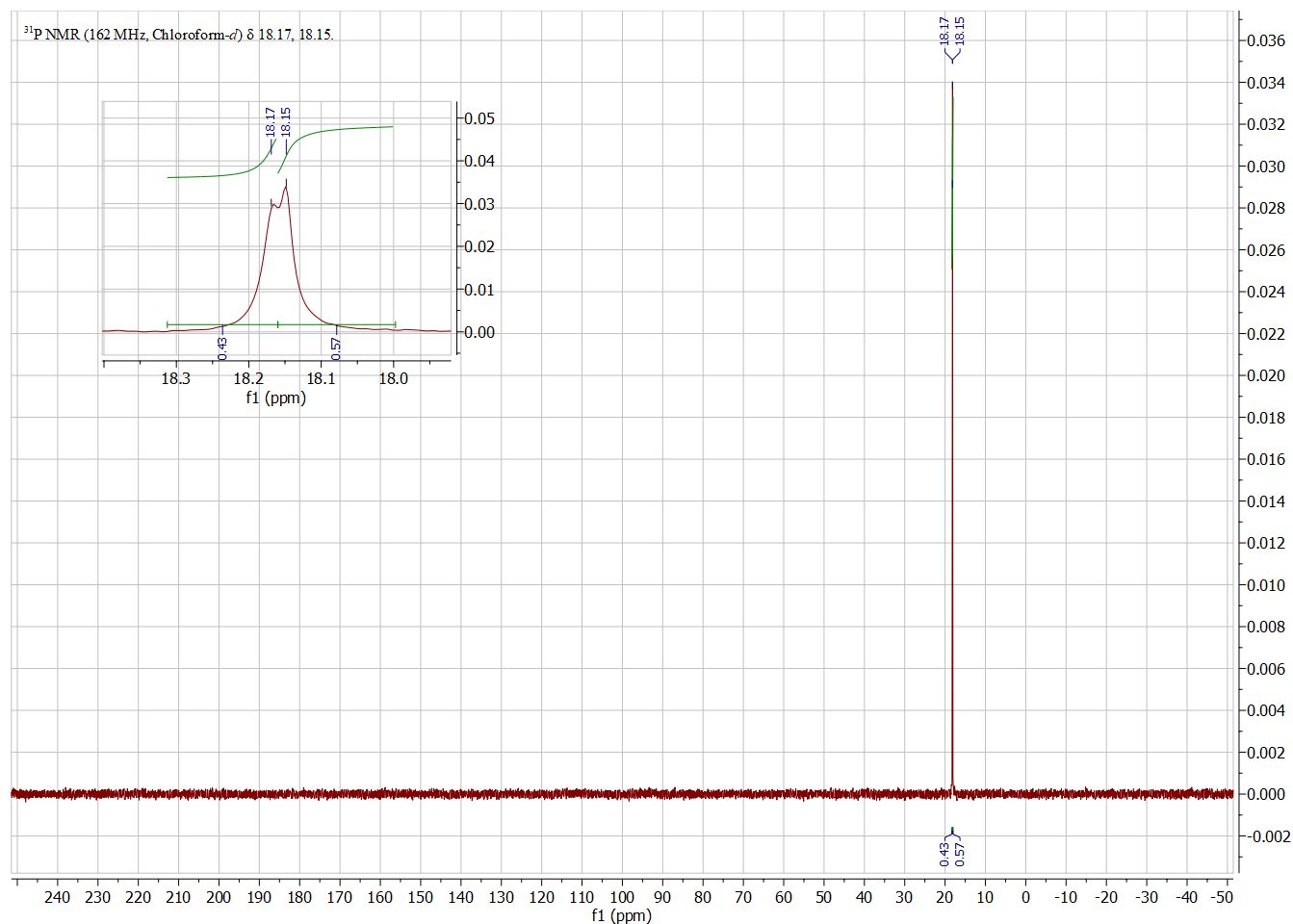
¹H NMR (400 MHz, Chloroform-*d*) δ 7.20 – 7.13 (m, 4H, 4xArH), 7.12 – 7.01 (m, 4H, 4xArH), 6.91 (t, *J* = 10.0 Hz, 1H, NH), 6.55 (dd, *J* = 26.1, 7.7 Hz, 1H, NH), 5.07 (dd, *J* = 46.3, 8.3 Hz, 1H, NH), 4.77 – 4.65 (m, 1H, CHP), 4.51 – 4.43 (m, 1H, CH), 3.91 – 3.84 (m, 1H, CH), 2.45 – 2.41 (m, 6H, 2xSCH₃), 2.41 – 2.29 (m, 1H, CH), 2.18 – 2.04 (m, 1H, CH), 1.90 – 1.69 (m, 1H, CH₂), 1.66 – 1.52 (m, 1H, CH₂), 1.41 (d, *J* = 6.4 Hz, 9H, Boc), 1.32 – 1.21 (m, 4H, 2xCH₂), 1.11 – 0.98 (m, 6H, 2xCH₃), 0.95 – 0.74 (m, 9H, 3xCH₃).

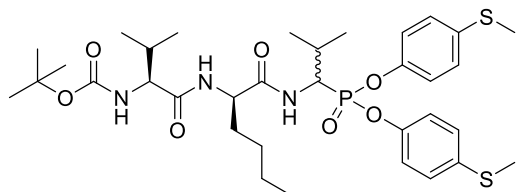
HRMS: C₃₄H₅₂N₃O₇PS₂ [M+Na]⁺ calc. 732.2882 found 732.2873

HPLC: purity >98%; retention time 19.390 and 19.697 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12,410	2,217	9,704	0,58	0,40	n.a.
2		13,357	0,464	2,402	0,12	0,10	n.a.
3		19,390	195,761	1216,305	51,45	49,80	n.a.
4		19,697	179,901	1204,540	47,28	49,32	n.a.
5		20,193	2,173	9,497	0,57	0,39	n.a.
Total:			380,517	2442,450	100,00	100,00	



(15) Boc-L-Val-D-Nle- Val^P(OPh-4-SCH₃)₂

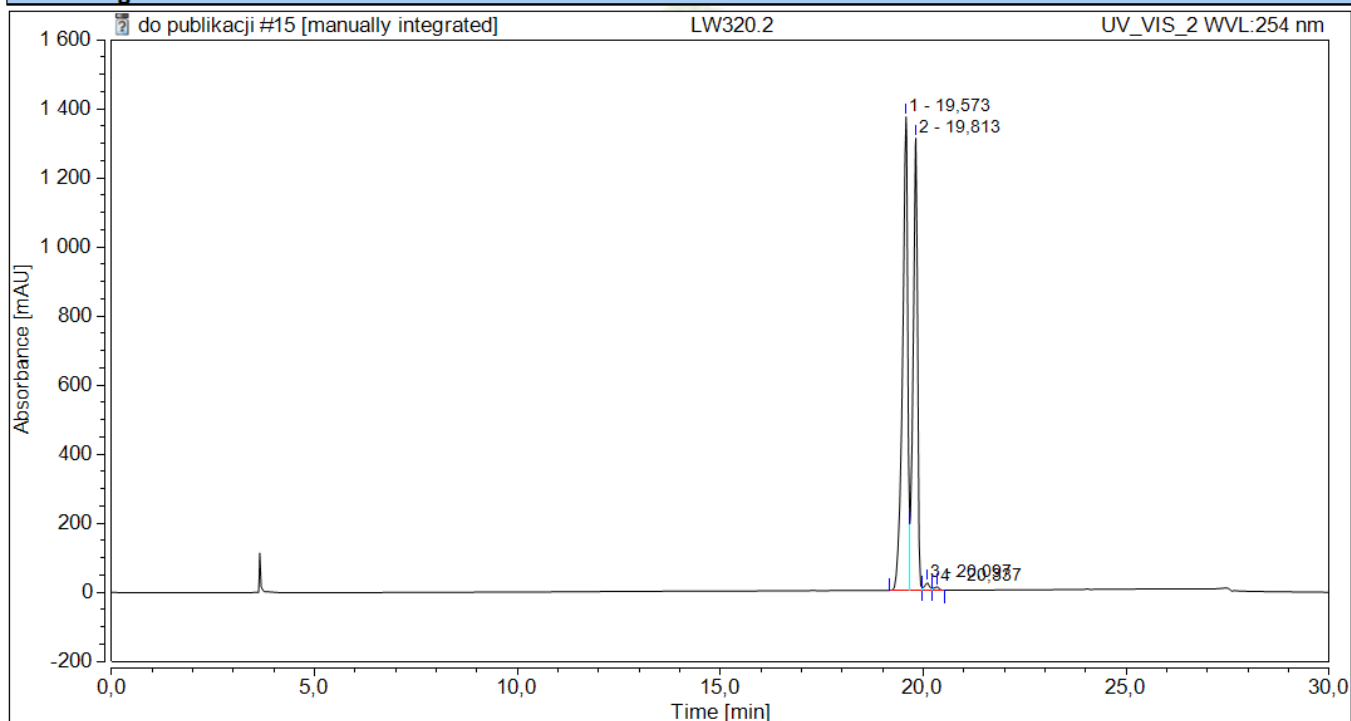
Name: *tert*-butyl ((2*S*)-1-(((2*R*)-1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-1-oxohexan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.31 (s, 55%), 18.08 (s, 45%).

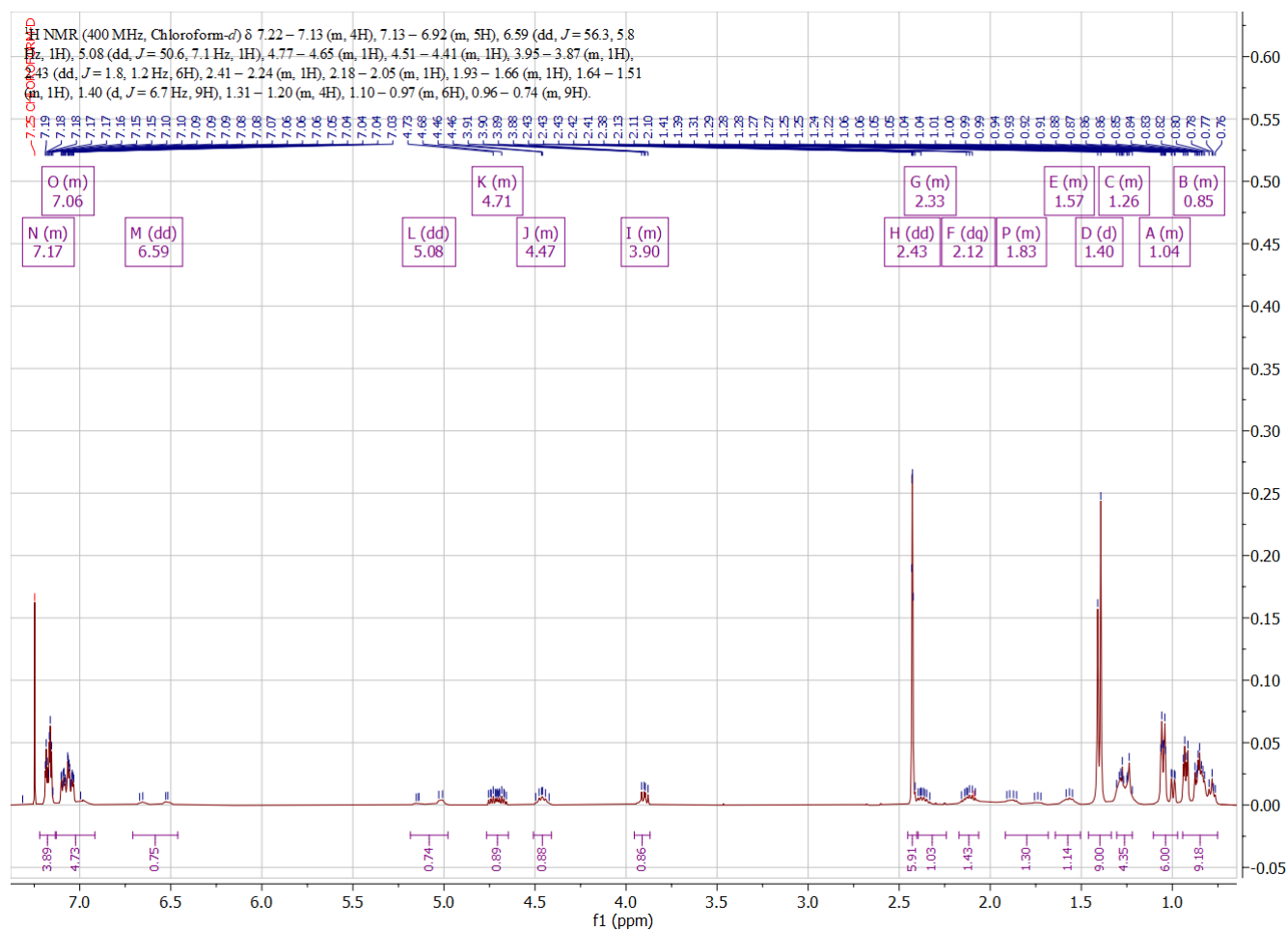
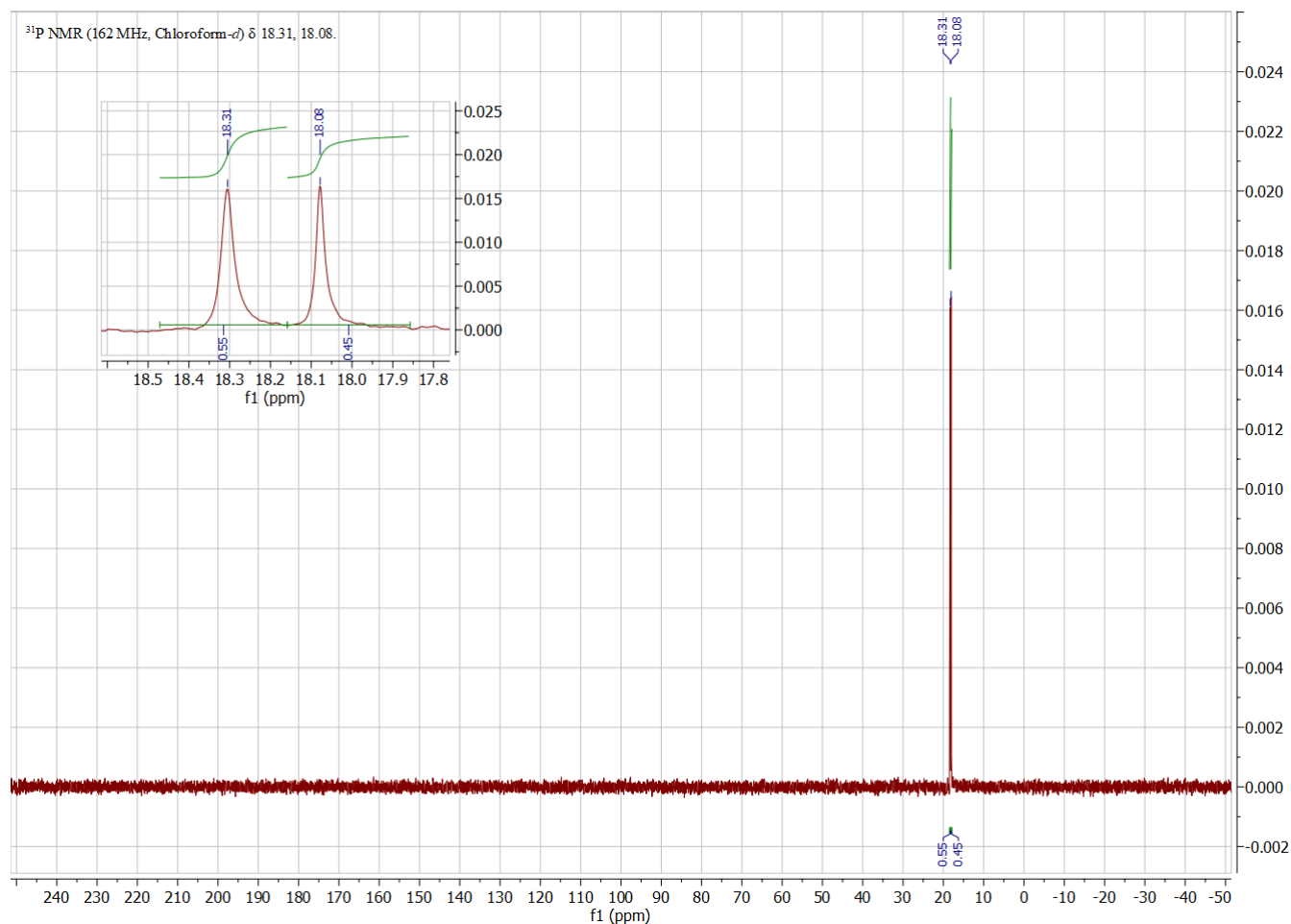
¹H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 7.13 (m, 4H), 7.13 – 6.92 (m, 5H), 6.59 (dd, *J* = 56.3, 5.8 Hz, 1H), 5.08 (dd, *J* = 50.6, 7.1 Hz, 1H), 4.77 – 4.65 (m, 1H), 4.51 – 4.41 (m, 1H), 3.95 – 3.87 (m, 1H), 2.43 (dd, *J* = 1.8, 1.2 Hz, 6H), 2.41 – 2.24 (m, 1H), 2.18 – 2.05 (m, 1H), 1.93 – 1.66 (m, 1H), 1.64 – 1.51 (m, 1H), 1.40 (d, *J* = 6.7 Hz, 9H), 1.31 – 1.20 (m, 4H), 1.10 – 0.97 (m, 6H), 0.96 – 0.74 (m, 9H).

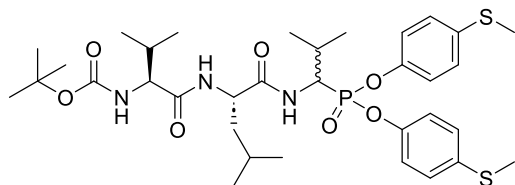
HRMS: C₃₄H₅₂N₃O₇PS₂ [M+Na]⁺ calc. 732.2882 found 732.2864

HPLC: purity >98%; retention time 19.573 and 19.813 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19,573	201,084	1370,770	54,50	50,55	n.a.
2		19,813	163,435	1308,748	44,29	48,26	n.a.
3		20,097	3,071	22,062	0,83	0,81	n.a.
4		20,337	1,392	10,322	0,38	0,38	n.a.
Total:			368,981	2711,902	100,00	100,00	



(16) Boc-L-Val-L-Leu-Val^P(OPh-4-SCH₃)₂

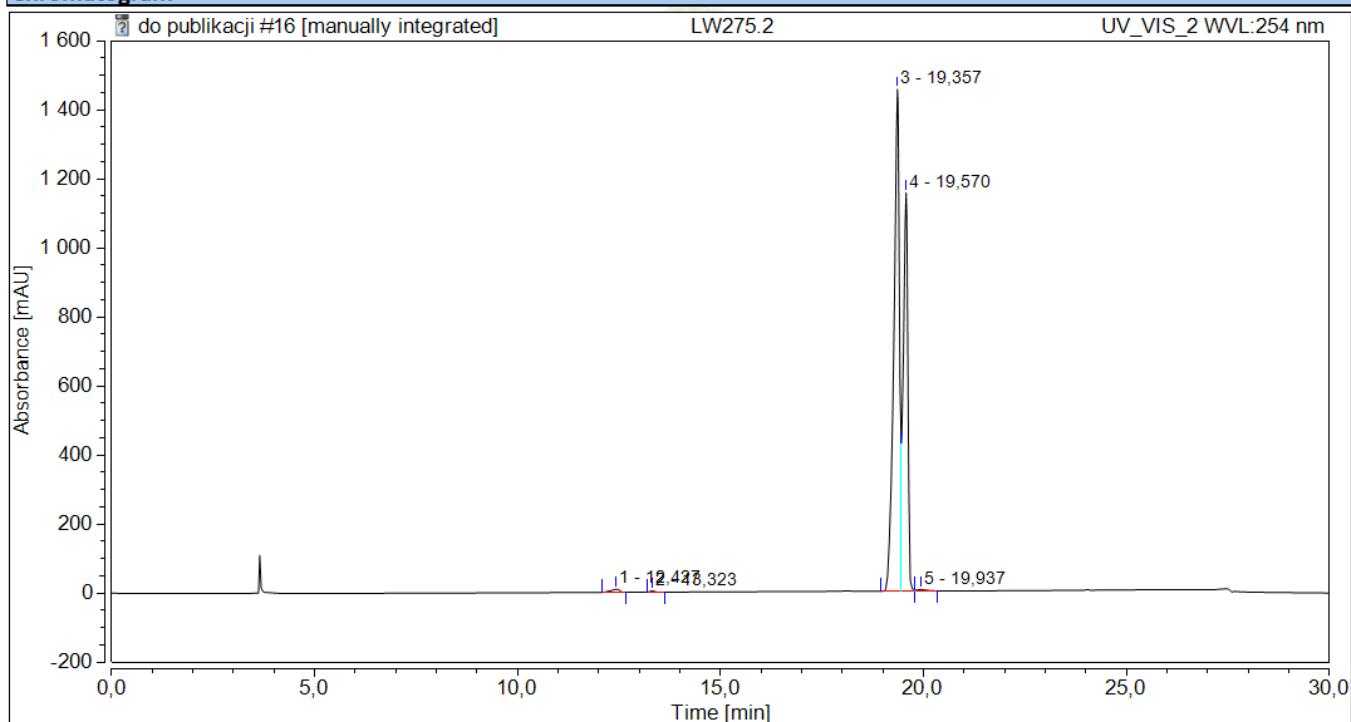
Name: *tert*-butyl ((2*S*)-1-(((2*S*)-1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-4-methyl-1-oxopentan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.37(s, 59%), 18.14 (s, 41%).

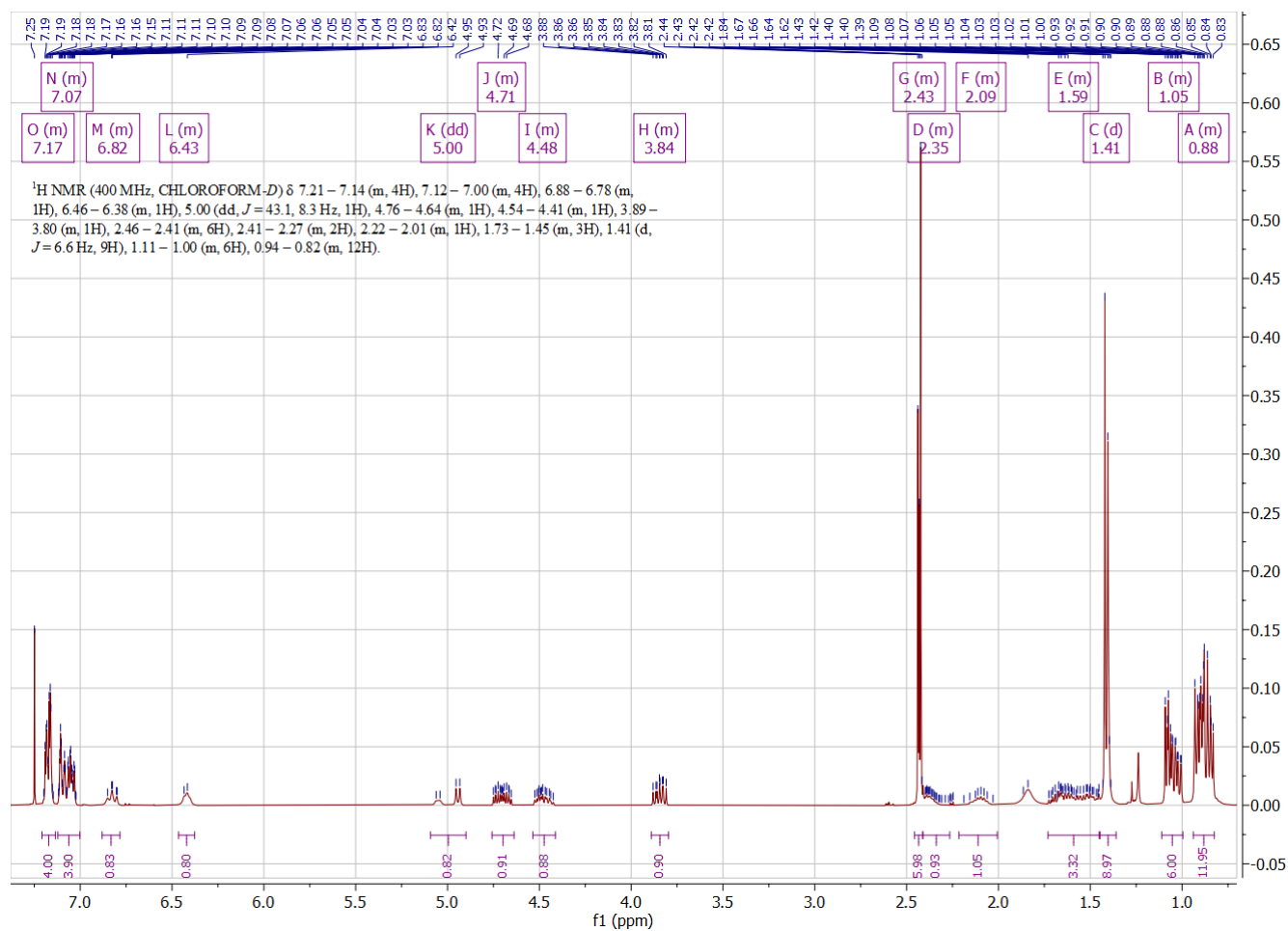
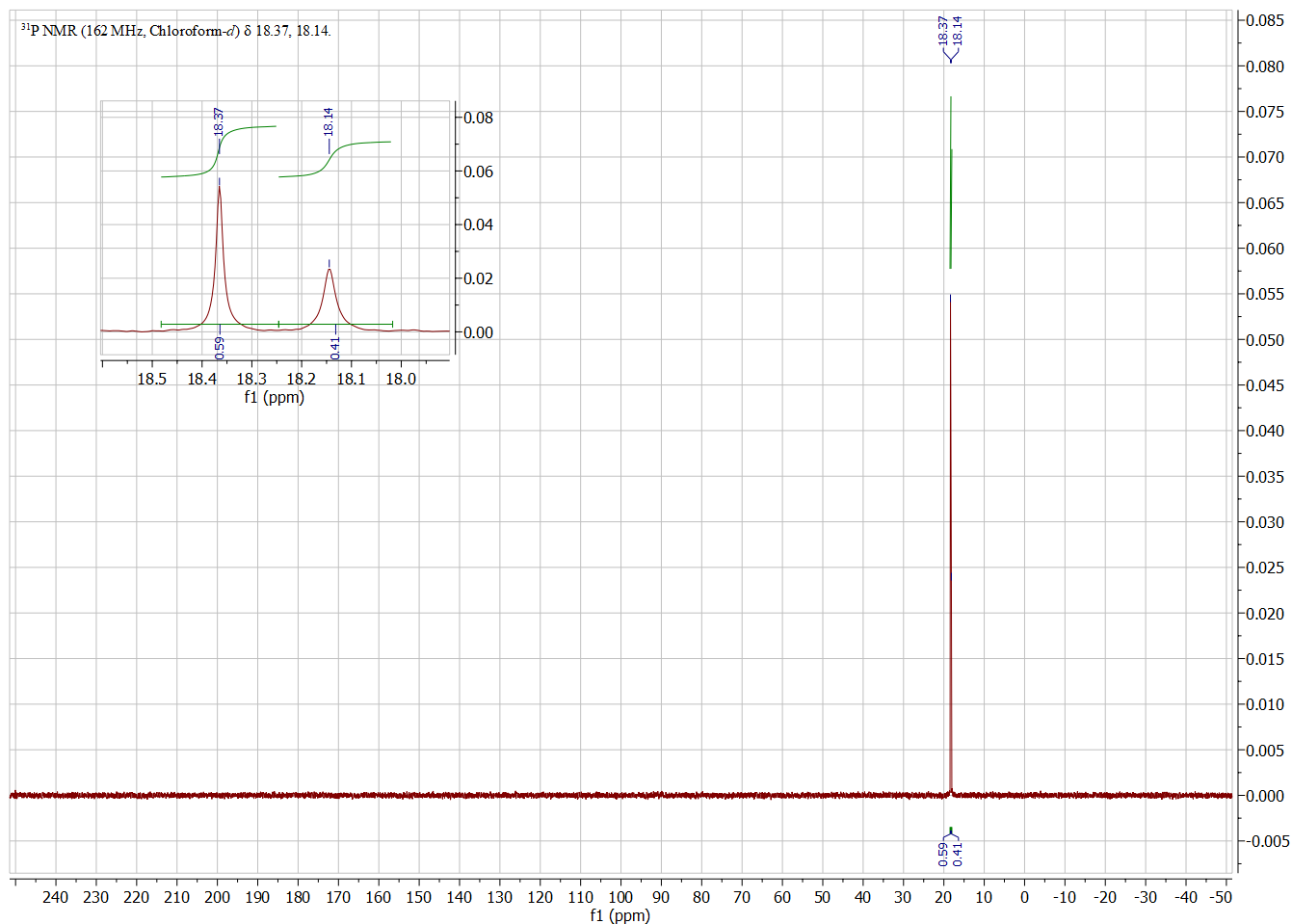
¹H NMR (400 MHz, Chloroform-*d*) δ ¹H NMR (400 MHz, CHLOROFORM-*D*) δ 7.21 – 7.14 (m, 4H, 4xArH), 7.12 – 7.00 (m, 4H, 4xArH), 6.88 – 6.78 (m, 1H, NH), 6.46 – 6.38 (m, 1H, NH), 5.00 (dd, *J* = 43.1, 8.3 Hz, 1H, NH), 4.76 – 4.64 (m, 1H, CHP), 4.54 – 4.41 (m, 1H, CH), 3.89 – 3.80 (m, 1H, CH), 2.46 – 2.41 (m, 6H, 2xSCH₃), 2.41 – 2.27 (m, 1H, CH), 2.22 – 2.01 (m, 1H, CH), 1.73 – 1.45 (m, 3H, CH₂, CH), 1.41 (d, *J* = 6.6 Hz, 9H, Boc), 1.11 – 1.00 (m, 6H, 2xCH₃), 0.94 – 0.82 (m, 12H, 4xCH₃).

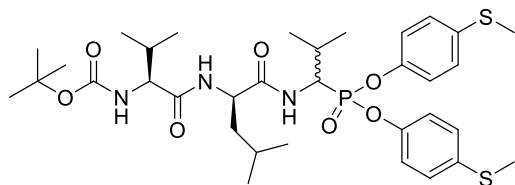
HRMS: C₃₄H₅₂N₃O₇PS₂ [M+Na]⁺ calc. 732.2882 found 732.2874

HPLC: purity >98%; retention time 19.357 and 19.570 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12,427	2,256	9,302	0,58	0,35	n.a.
2		13,323	0,405	3,354	0,10	0,13	n.a.
3		19,357	231,119	1453,677	59,79	55,38	n.a.
4		19,570	151,576	1153,570	39,21	43,95	n.a.
5		19,937	1,205	4,930	0,31	0,19	n.a.
Total:			386,562	2624,833	100,00	100,00	



(17) Boc-L-Val-D-Leu-Val^P(OPh-4-SCH₃)₂

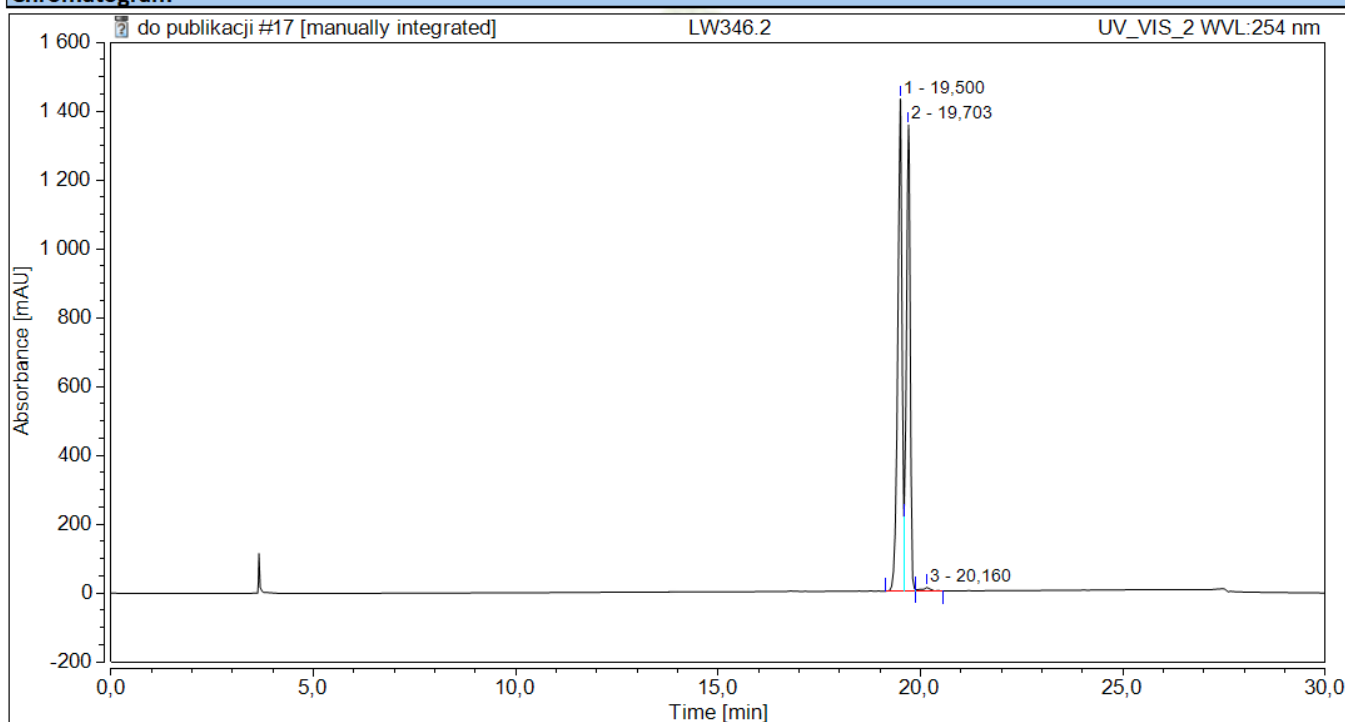
Name: *tert*-butyl ((2S)-1-(((2R)-1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-4-methyl-1-oxopentan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-d) δ 18.43 (s, 45%), 18.02 (s, 55%).

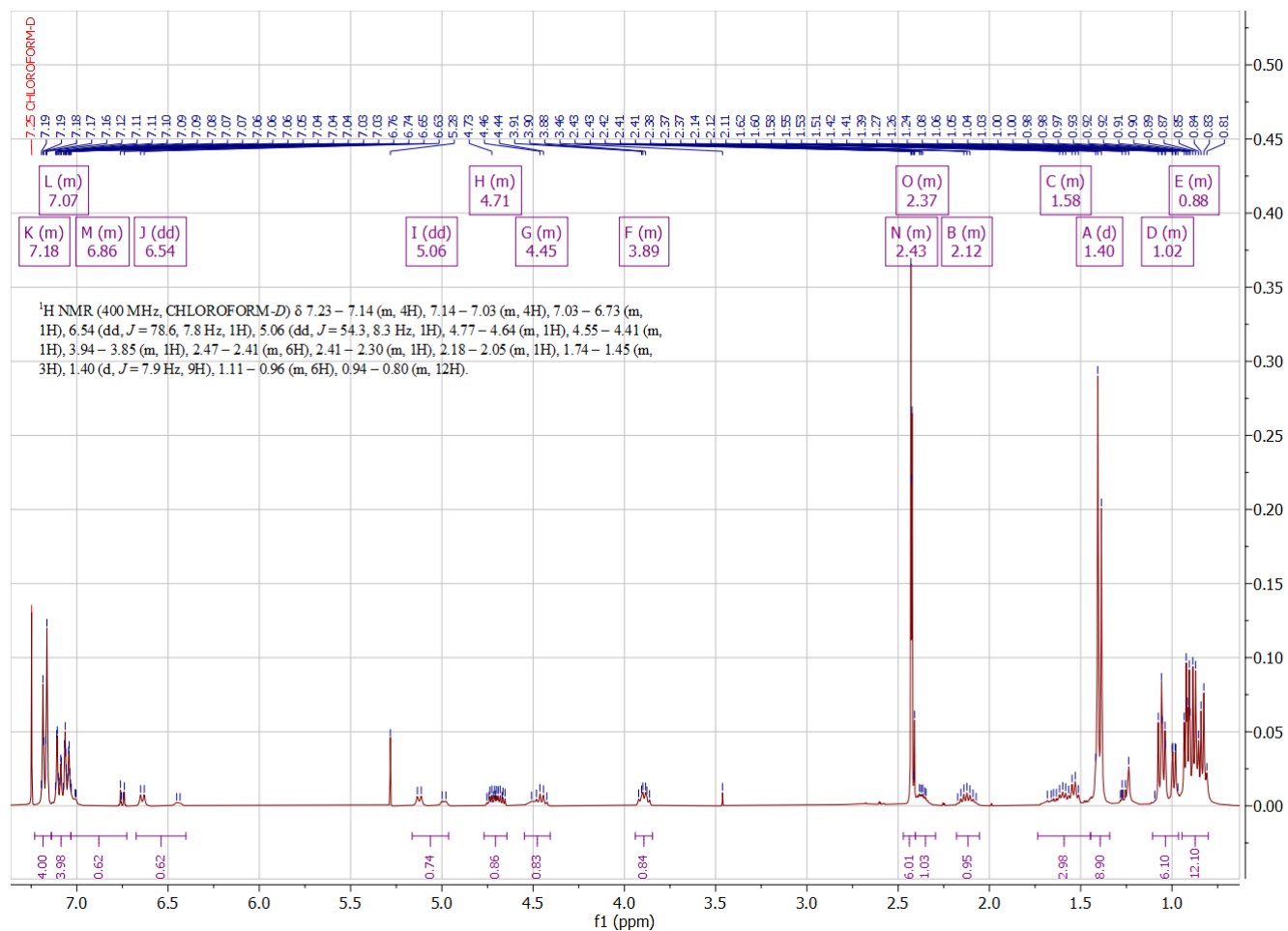
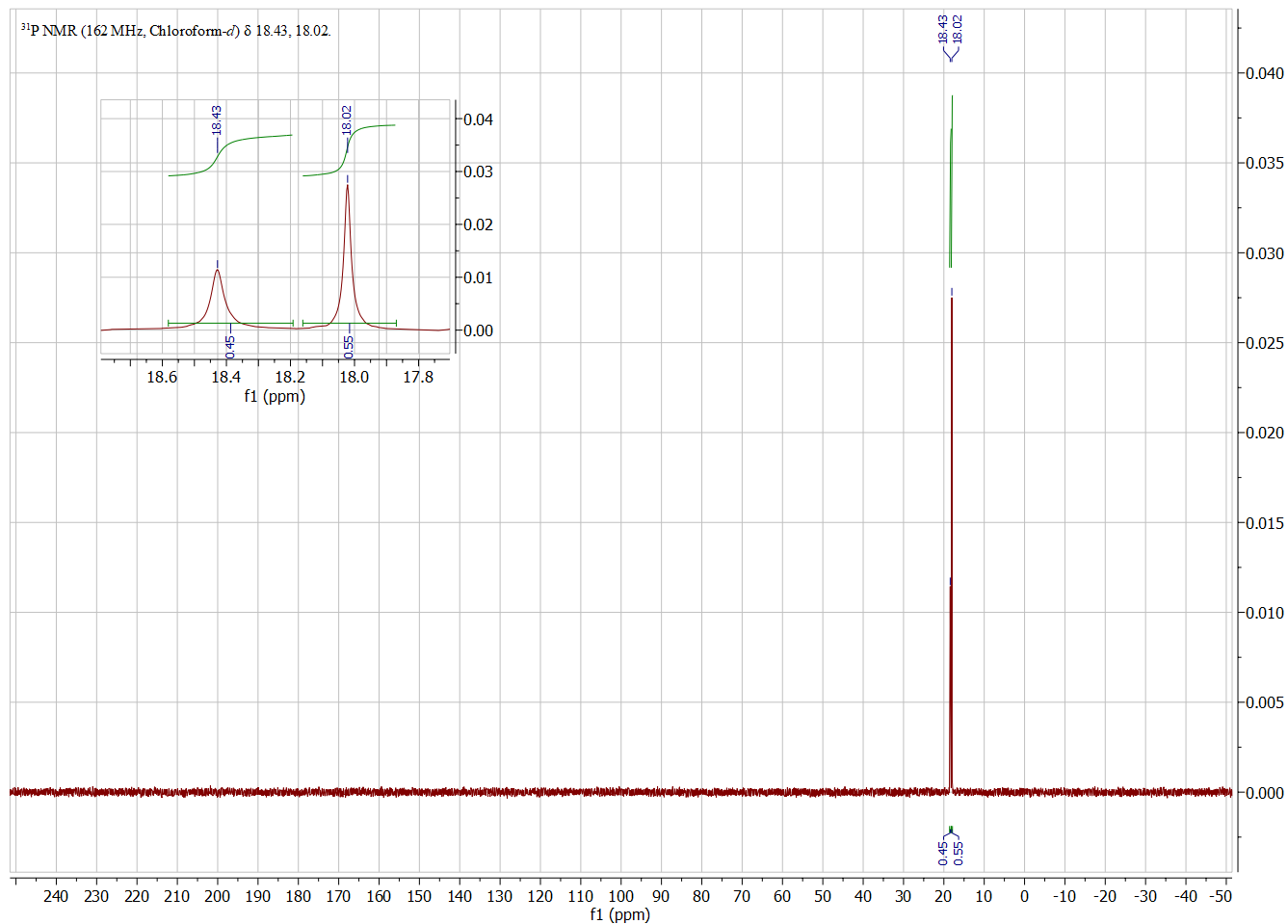
¹H NMR (400 MHz, Chloroform-d) δ 7.23 – 7.14 (m, 4H, 4xArH), 7.14 – 7.03 (m, 4H, 4xArH), 7.03 – 6.73 (m, 1H, NH), 6.54 (dd, *J* = 78.6, 7.8 Hz, 1H, NH), 5.06 (dd, *J* = 54.3, 8.3 Hz, 1H, NH), 4.77 – 4.64 (m, 1H, CHP), 4.55 – 4.41 (m, 1H, CH), 3.94 – 3.85 (m, 1H, CH), 2.47 – 2.41 (m, 6H, , 2xSCH₃), 2.41 – 2.30 (m, 1H, CH), 2.18 – 2.05 (m, 1H, CH), 1.74 – 1.45 (m, 3H, CH₂, CH), 1.40 (d, *J* = 7.9 Hz, 9H, Boc), 1.11 – 0.96 (m, 6H, 2xCH₃), 0.94 – 0.80 (m, 12H, 4xCH₃).

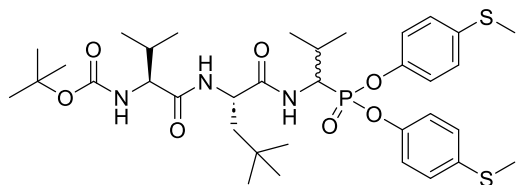
HRMS: C₃₄H₅₂N₃O₇PS₂ [M+Na]⁺ calc. 732.2882 found 732.2891

HPLC: purity >99%; retention time 19.500 and 19.703 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19,500	172,959	1429,321	53,22	51,16	n.a.
2		19,703	149,534	1354,174	46,02	48,47	n.a.
3		20,160	2,469	10,525	0,76	0,38	n.a.
Total:			324,962	2794,020	100,00	100,00	



(18) Boc-L-Val-L-NptGly-ValP(OPh-4-SCH3)2

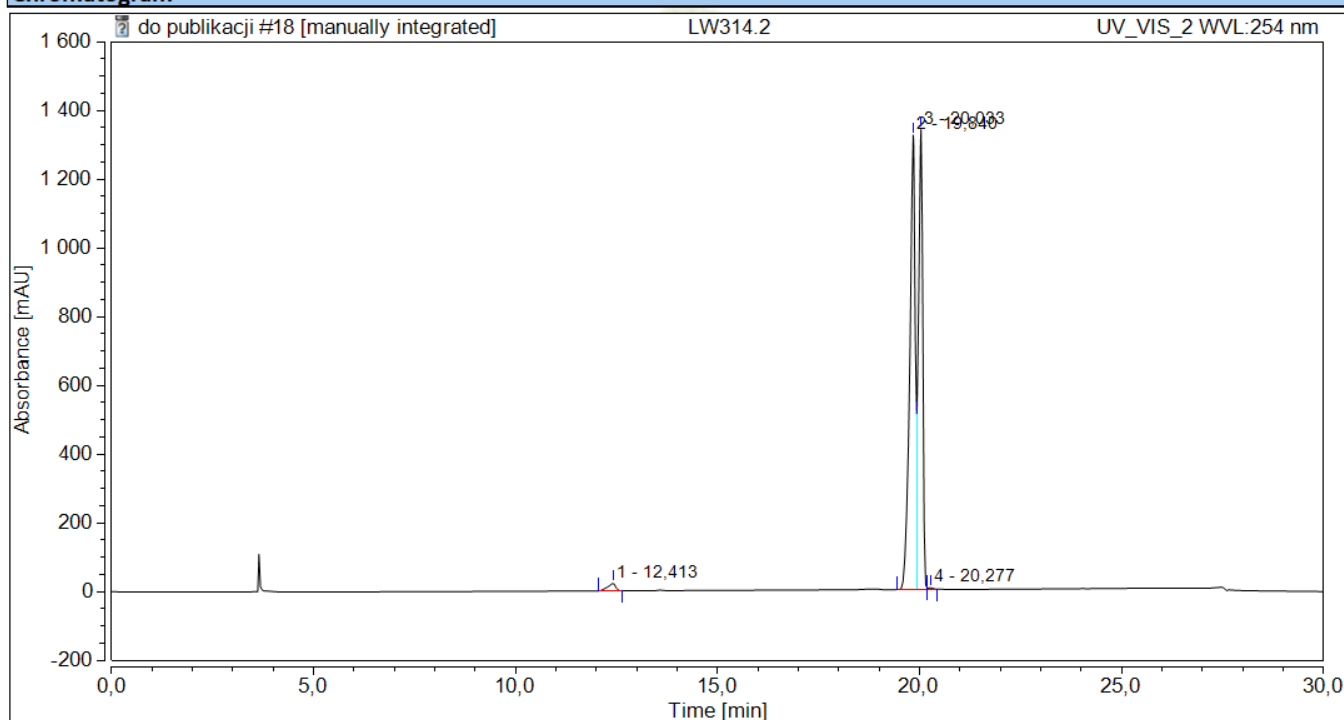
Name: *tert*-butyl ((2*S*)-1-(((2*S*)-1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-4,4-dimethyl-1-oxopentan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.53 (s, 50%), 18.32 (s, 50%).

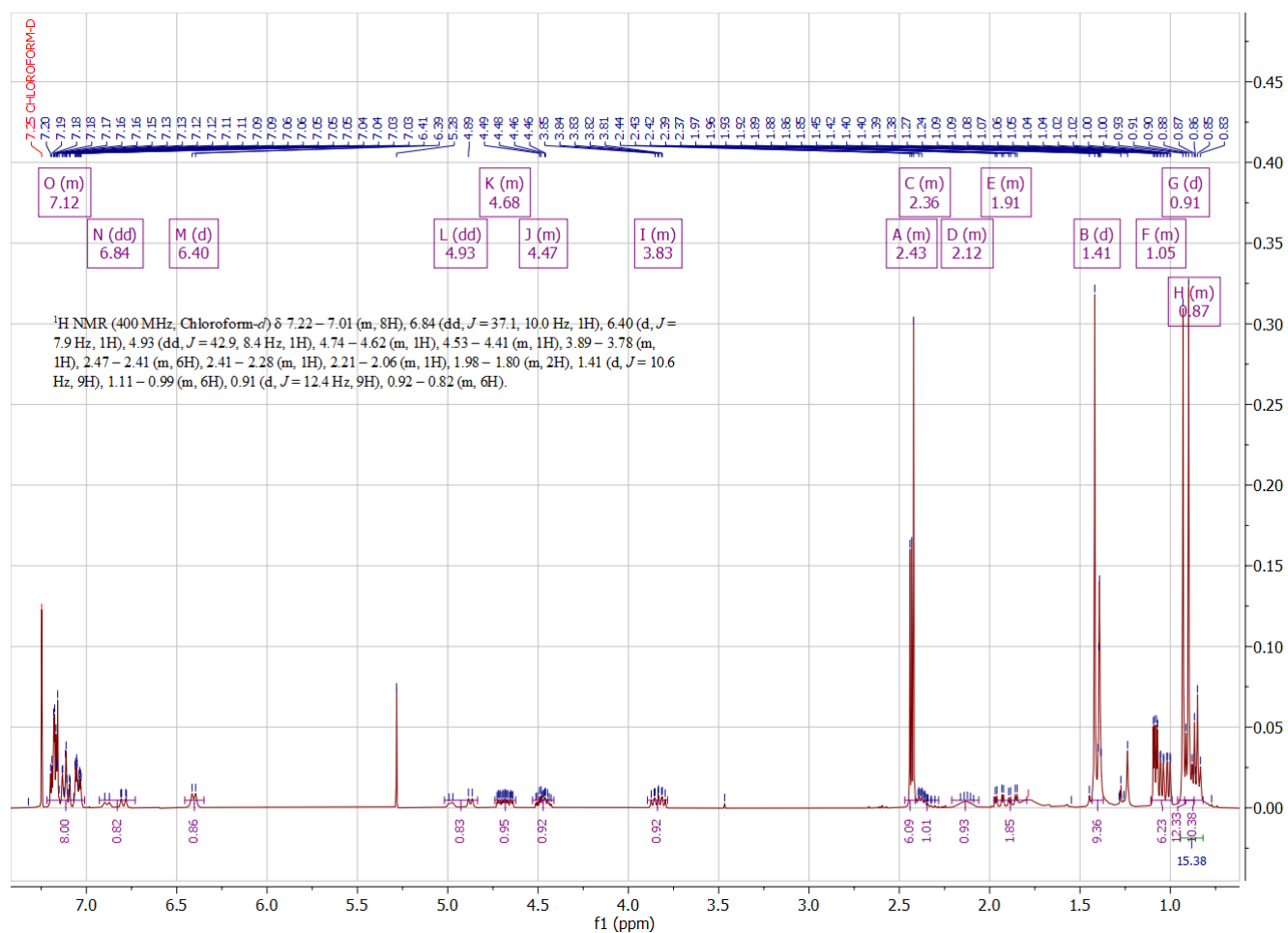
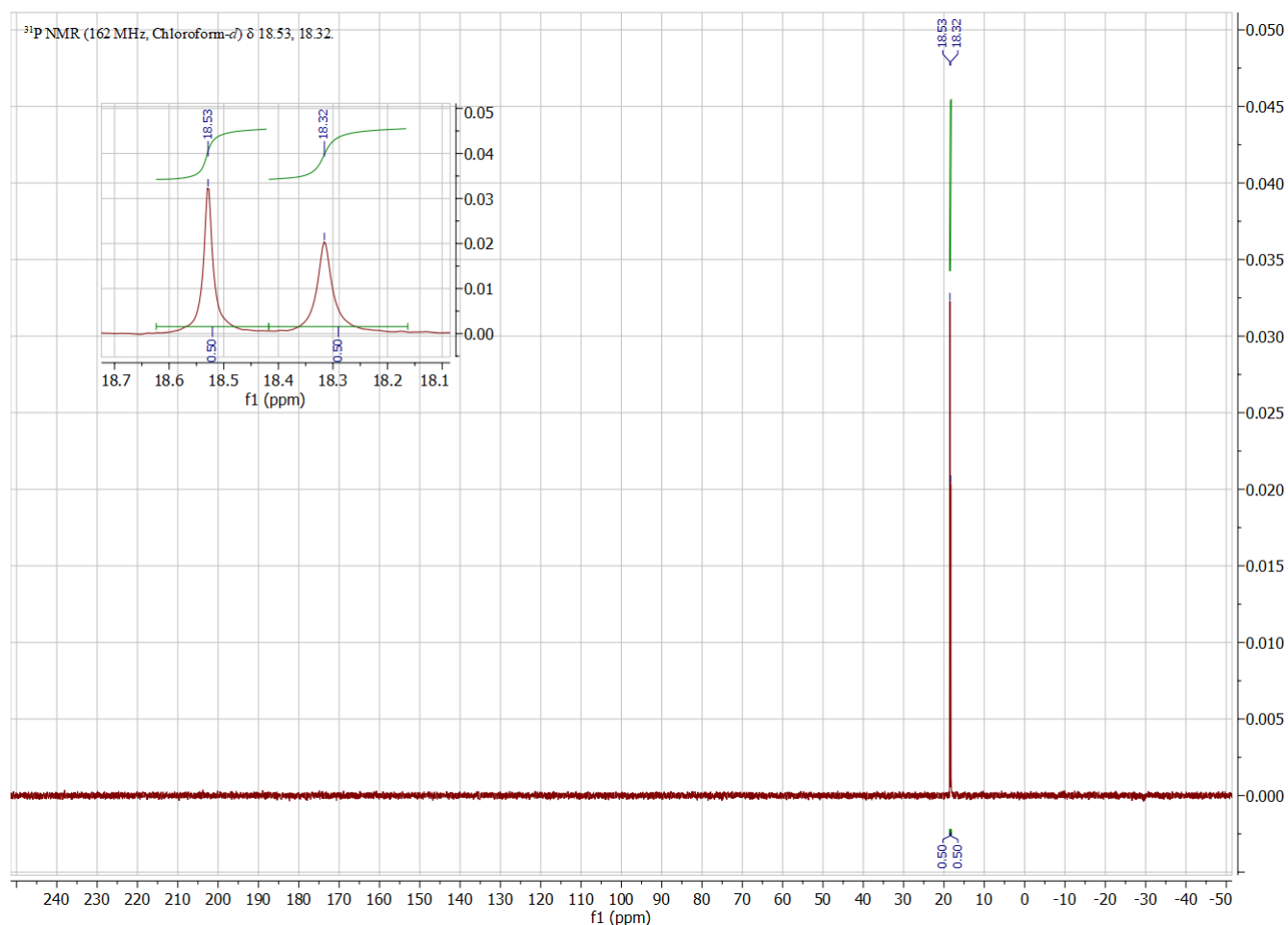
¹H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 7.01 (m, 8H, 8XArH), 6.84 (dd, *J* = 37.1, 10.0 Hz, 1H, NH), 6.40 (d, *J* = 7.9 Hz, 1H, NH), 4.93 (dd, *J* = 42.9, 8.4 Hz, 1H, NH), 4.74 – 4.62 (m, 1H, CHP), 4.53 – 4.41 (m, 1H, CH), 3.89 – 3.78 (m, 1H, CH), 2.47 – 2.41 (m, 6H, 2xSCH₃), 2.41 – 2.28 (m, 1H, CH), 2.21 – 2.06 (m, 1H, CH), 1.98 – 1.80 (m, 2H, CH₂), 1.41 (d, *J* = 10.6 Hz, 9H, Boc), 1.11 – 0.99 (m, 6H, 2xCH₃), 0.91 (d, *J* = 12.4 Hz, 9H, 3xCH₃), 0.92 – 0.82 (m, 6H, 2xCH₃).

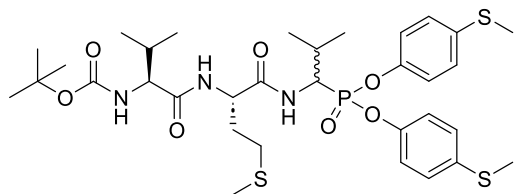
HRMS: C₃₅H₅₄N₃O₇PS₂ [M+Na]⁺ calc. 746.3038 found 746.3046

HPLC: purity >98%; retention time 19.840 and 20.033 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		12,413	4,915	22,539	1,31	0,84	n.a.
2		19,840	205,463	1321,675	54,68	49,21	n.a.
3		20,033	164,804	1337,354	43,86	49,79	n.a.
4		20,277	0,567	4,424	0,15	0,16	n.a.
Total:			375,749	2685,992	100,00	100,00	



(19) Boc-L-Val-L-Met-Val^P(OPh-4-SCH₃)₂

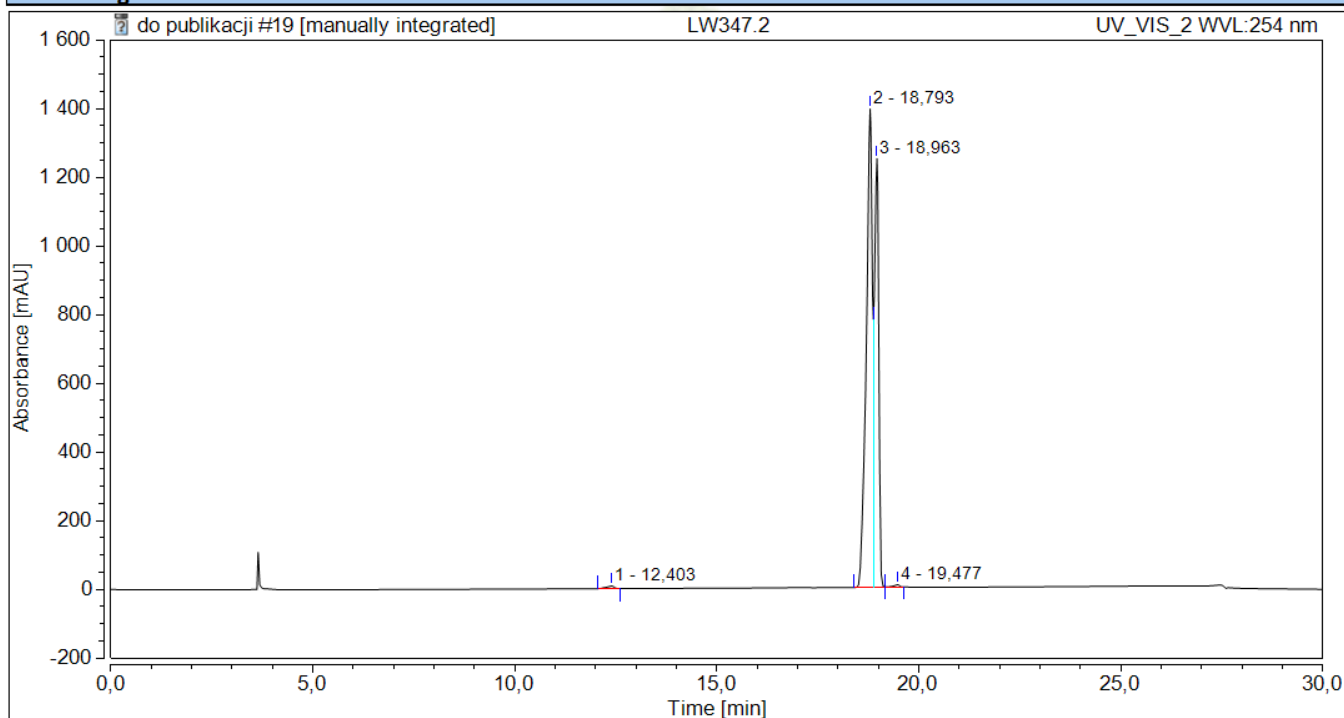
Name: *tert*-butyl ((2*S*)-1-(((2*S*)-1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-4-(methylthio)-1-oxobutan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.08 (s).

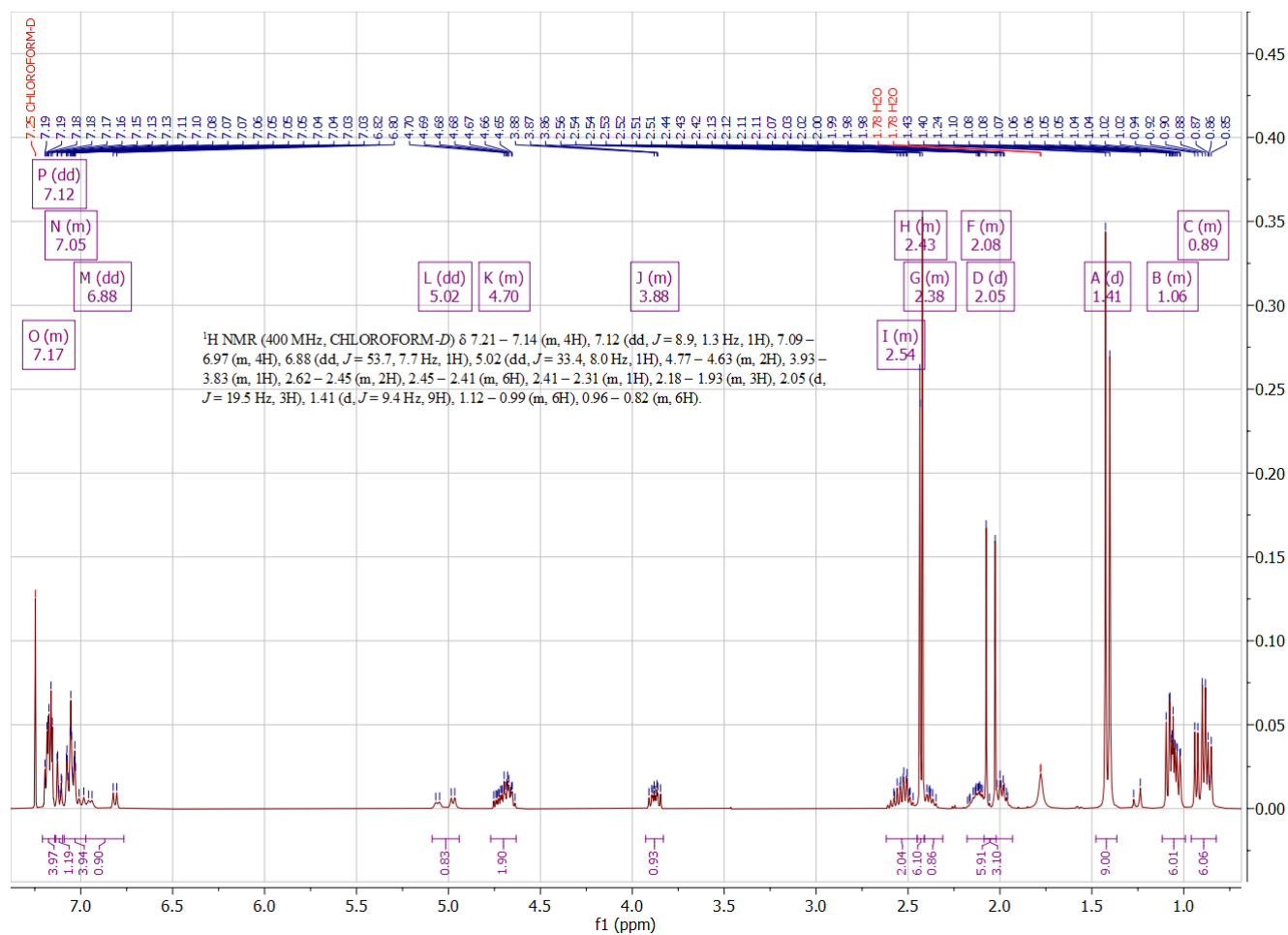
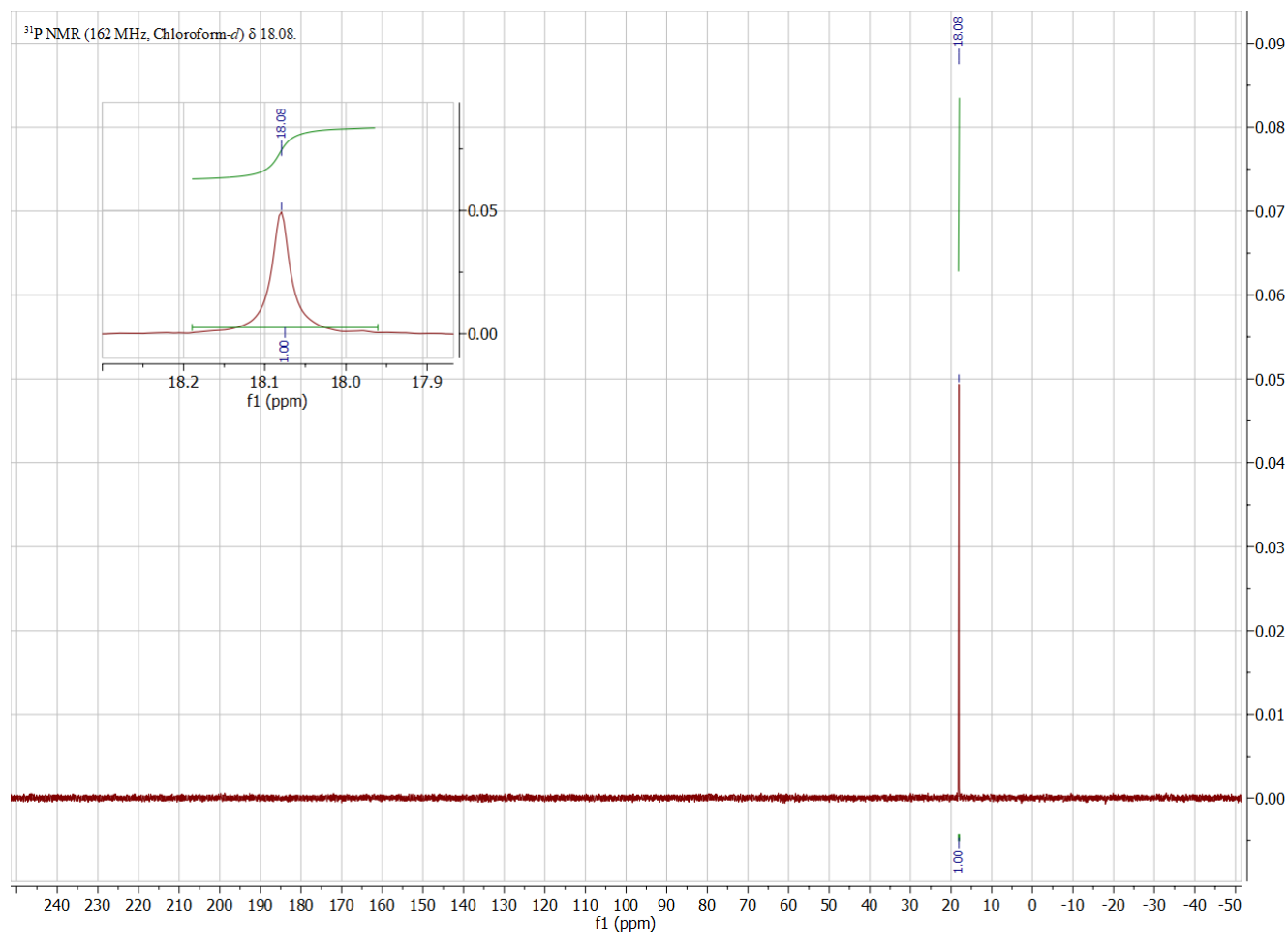
¹H NMR (400 MHz, Chloroform-*d*) δ 7.21 – 7.14 (m, 4H, 4xArH), 7.12 (dd, *J* = 8.9, 1.3 Hz, 1H, NH), 7.09 – 6.97 (m, 4H, 4xArH), 6.88 (dd, *J* = 53.7, 7.7 Hz, 1H, NH), 5.02 (dd, *J* = 33.4, 8.0 Hz, 1H, NH), 4.77 – 4.63 (m, 2H, CHP, CH), 3.93 – 3.83 (m, 1H, CH), 2.62 – 2.45 (m, 2H, CH₂), 2.45 – 2.41 (m, 6H, 2xSCH₃), 2.41 – 2.31 (m, 1H, CH), 2.18 – 1.93 (m, 3H, CH₂, CH), 2.05 (d, *J* = 19.5 Hz, 3H, CH₃), 1.41 (d, *J* = 9.4 Hz, 9H, Boc), 1.12 – 0.99 (m, 6H, 2xCH₃), 0.96 – 0.82 (m, 6H, 2xCH₃).

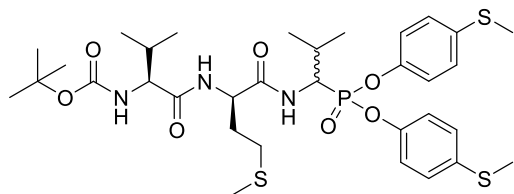
HRMS: C₃₃H₅₀N₃O₇PS₃ [M+Na]⁺ calc. 750.2446 found 750.2450

HPLC: purity >99%; retention time 18.793 and 18.963 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12,403	1,749	7,865	0,44	0,30	n.a.
2		18,793	237,376	1392,708	59,64	52,44	n.a.
3		18,963	157,496	1248,058	39,57	46,99	n.a.
4		19,477	1,362	7,378	0,34	0,28	n.a.
Total:			397,984	2656,009	100,00	100,00	



(20) Boc-L-Val-D-Met-Val^P(OPh-4-SCH₃)₂

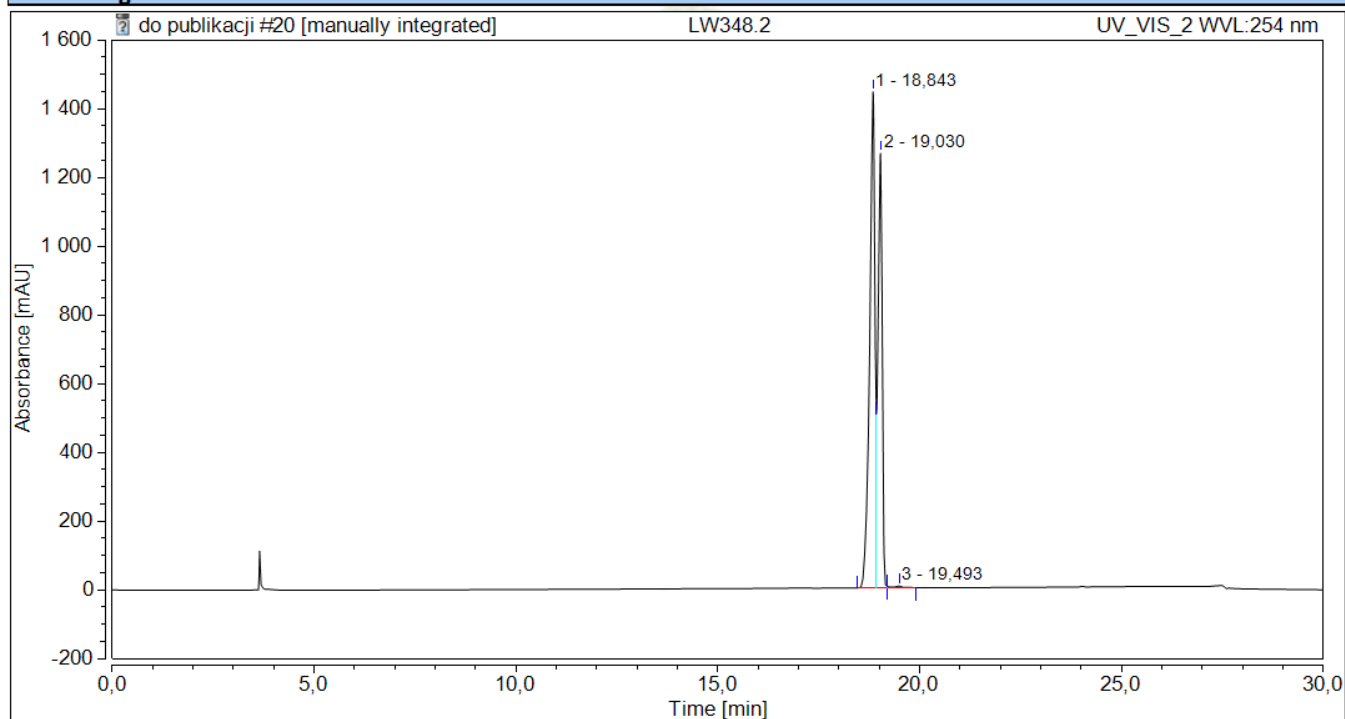
Name: *tert*-butyl ((2*S*)-1-(((2*R*)-1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-4-(methylthio)-1-oxobutan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.15 (s, 46%), 18.00 (s, 54%).

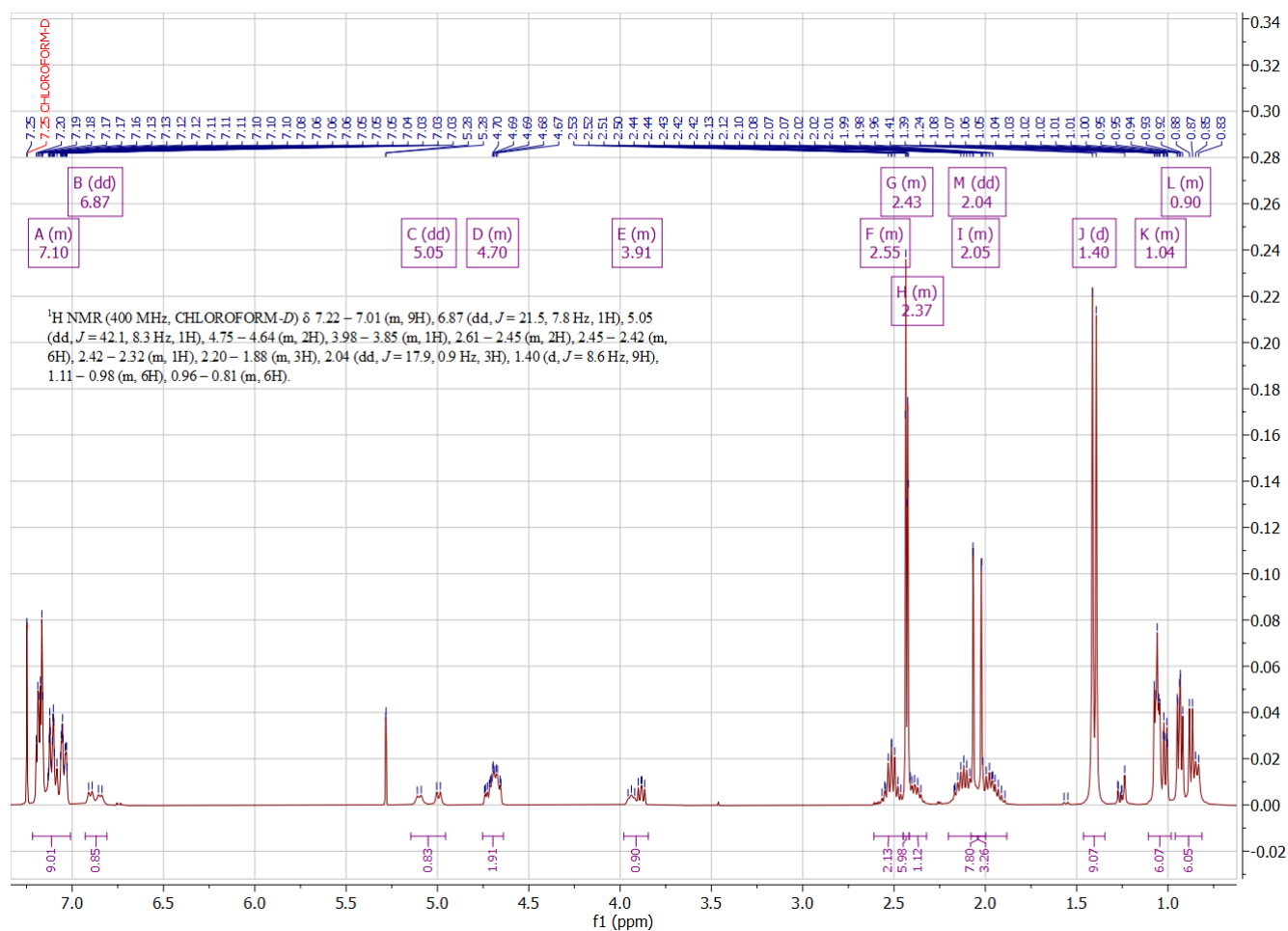
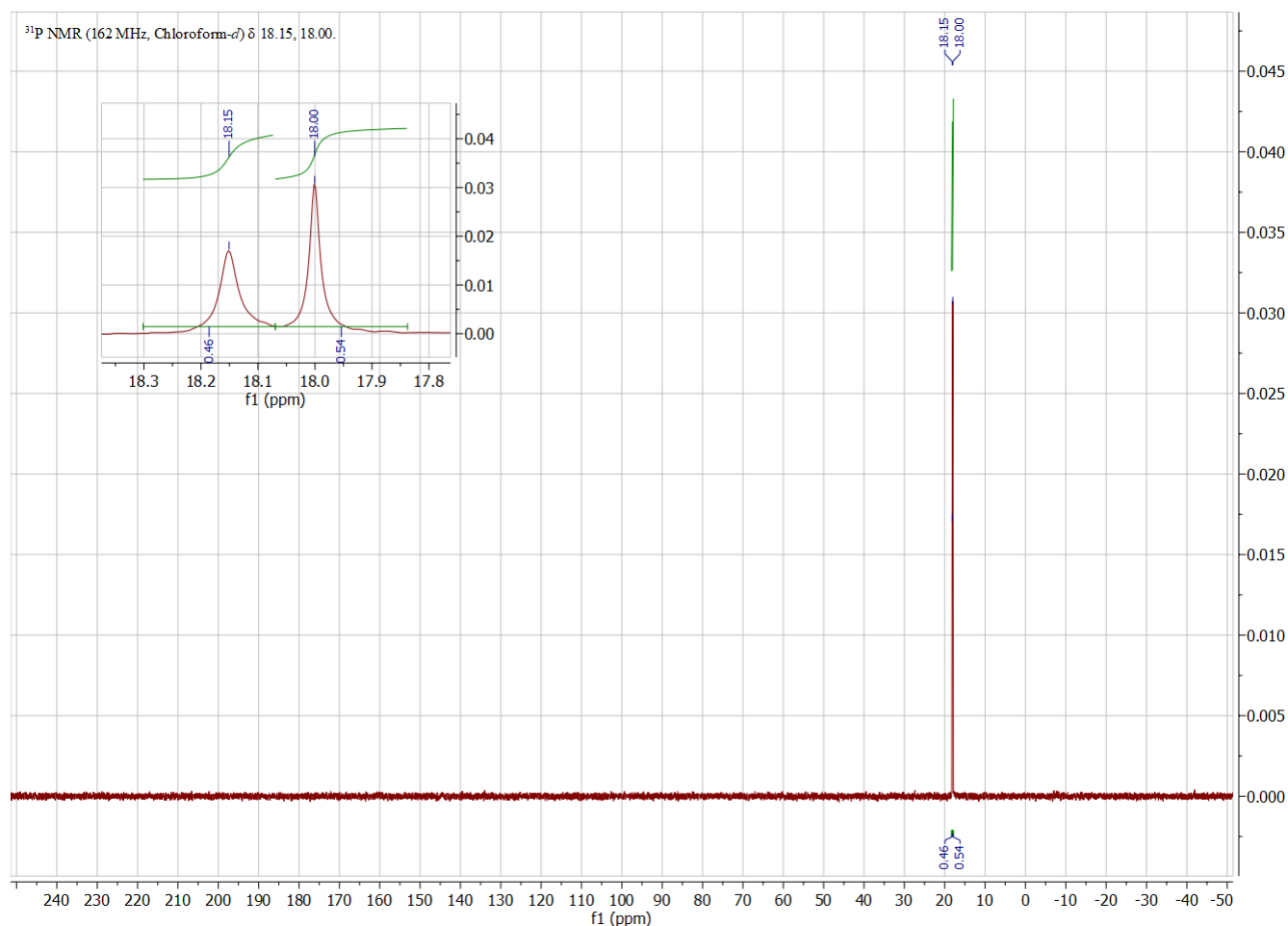
¹H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 7.01 (m, 9H, 8xArH, NH), 6.87 (dd, *J* = 21.5, 7.8 Hz, 1H, NH), 5.05 (dd, *J* = 42.1, 8.3 Hz, 1H, NH), 4.75 – 4.64 (m, 2H, CHP, CH), 3.98 – 3.85 (m, 1H, CH), 2.61 – 2.45 (m, 2H, CH₂), 2.45 – 2.42 (m, 6H, , 2xSCH₃), 2.42 – 2.32 (m, 1H, CH), 2.20 – 1.88 (m, 3H, CH₂, CH), 2.04 (dd, *J* = 17.9, 0.9 Hz, 3H, CH₃), 1.40 (d, *J* = 8.6 Hz, 9H, Boc), 1.11 – 0.98 (m, 6H, 2xCH₃), 0.96 – 0.81 (m, 6H, 2xCH₃).

HRMS: C₃₃H₅₀N₃O₇PS₃ [M+Na]⁺ calc. 750.2446 found 750.2456

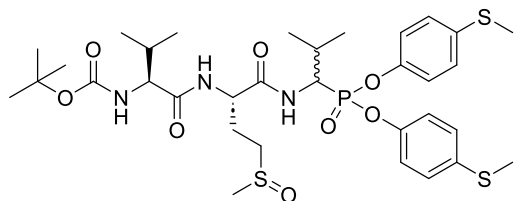
HPLC: purity >99%; retention time 18.843 and 19.030 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		18,843	217,010	1443,215	58,32	53,20	n.a.
2		19,030	153,499	1264,124	41,25	46,60	n.a.
3		19,493	1,607	5,578	0,43	0,21	n.a.
Total:			372,116	2712,917	100,00	100,00	



(21) Boc-L-Val-L-Met(O)- Val^P(OPh-4-SCH₃)₂



Name: *tert*-butyl ((2*S*)-1-(((2*S*)-1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-4-(methylsulfinyl)-1-oxobutan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

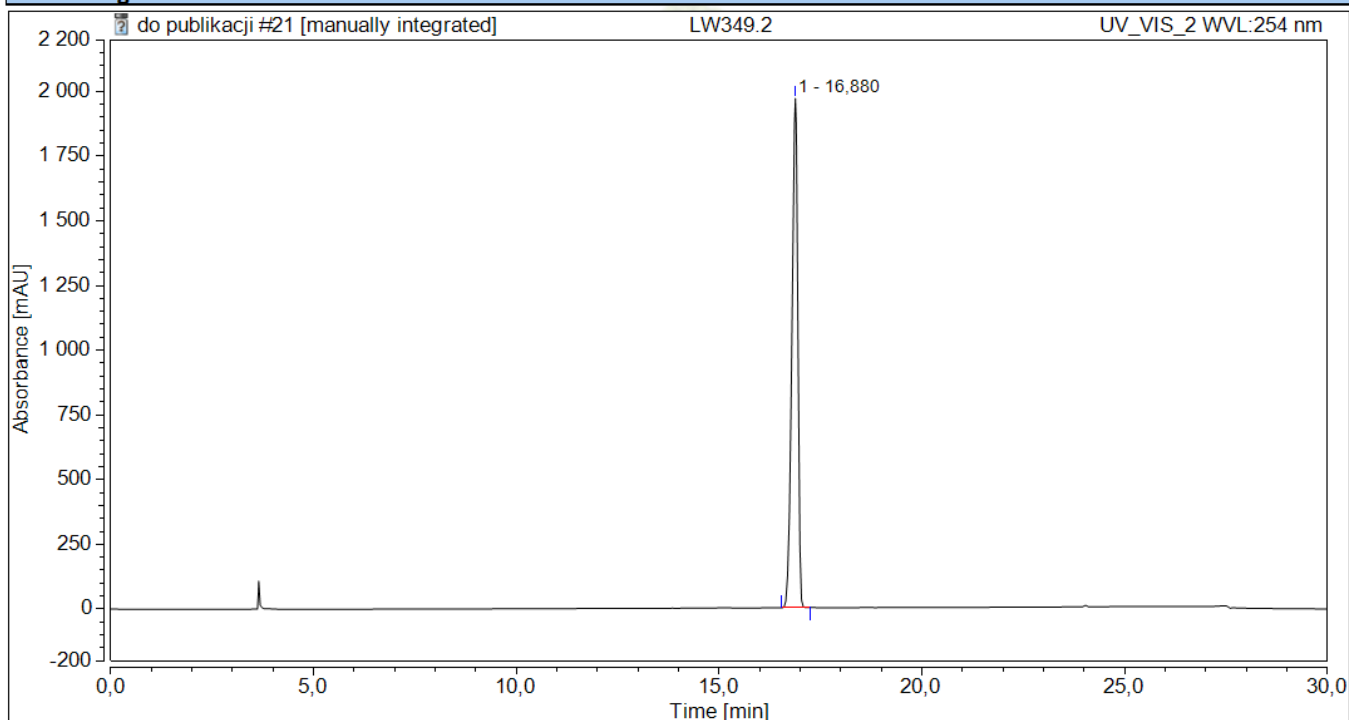
³¹P NMR (162 MHz, Chloroform-*d*) δ 18.50 (s, 26%), 18.48 (s, 25%), 18.28 (s, 18%), 18.16 (s, 31%).

¹H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 7.41 (m, 1H, NH), 7.29 – 6.97 (m, 9H, 8xArH, NH), 5.23 – 5.09 (m, 1H, NH), 4.92 – 4.63 (m, 2H, CHP, CH), 3.99 – 3.85 (m, 1H, CH), 3.11 – 2.60 (m, 2H, CH₂), 2.60 – 2.45 (m, 3H, CH₃), 2.43 (dd, *J* = 3.8, 2.3 Hz, 6H, 2xSCH₃), 2.42 – 1.98 (m, 4H, CH₂, 2xCH), 1.41 (d, *J* = 9.9 Hz, 9H, Boc), 1.11 – 1.01 (m, 6H, 2xCH₃), 0.95 – 0.85 (m, 6H, 2xCH₃).

HRMS: C₃₃H₅₀N₃O₈PS₃ [M+Na]⁺ calc. 766.2395 found 766.2402

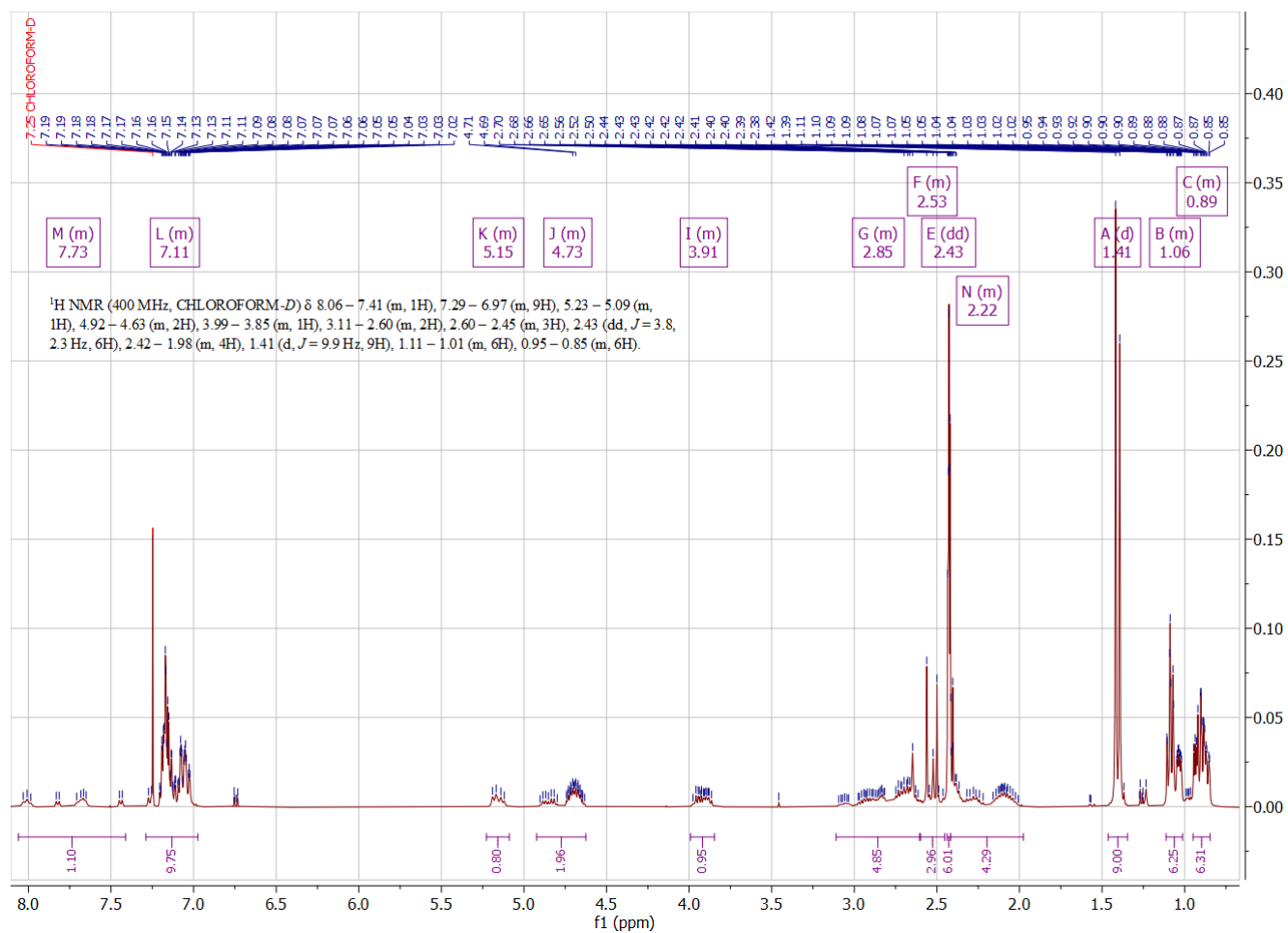
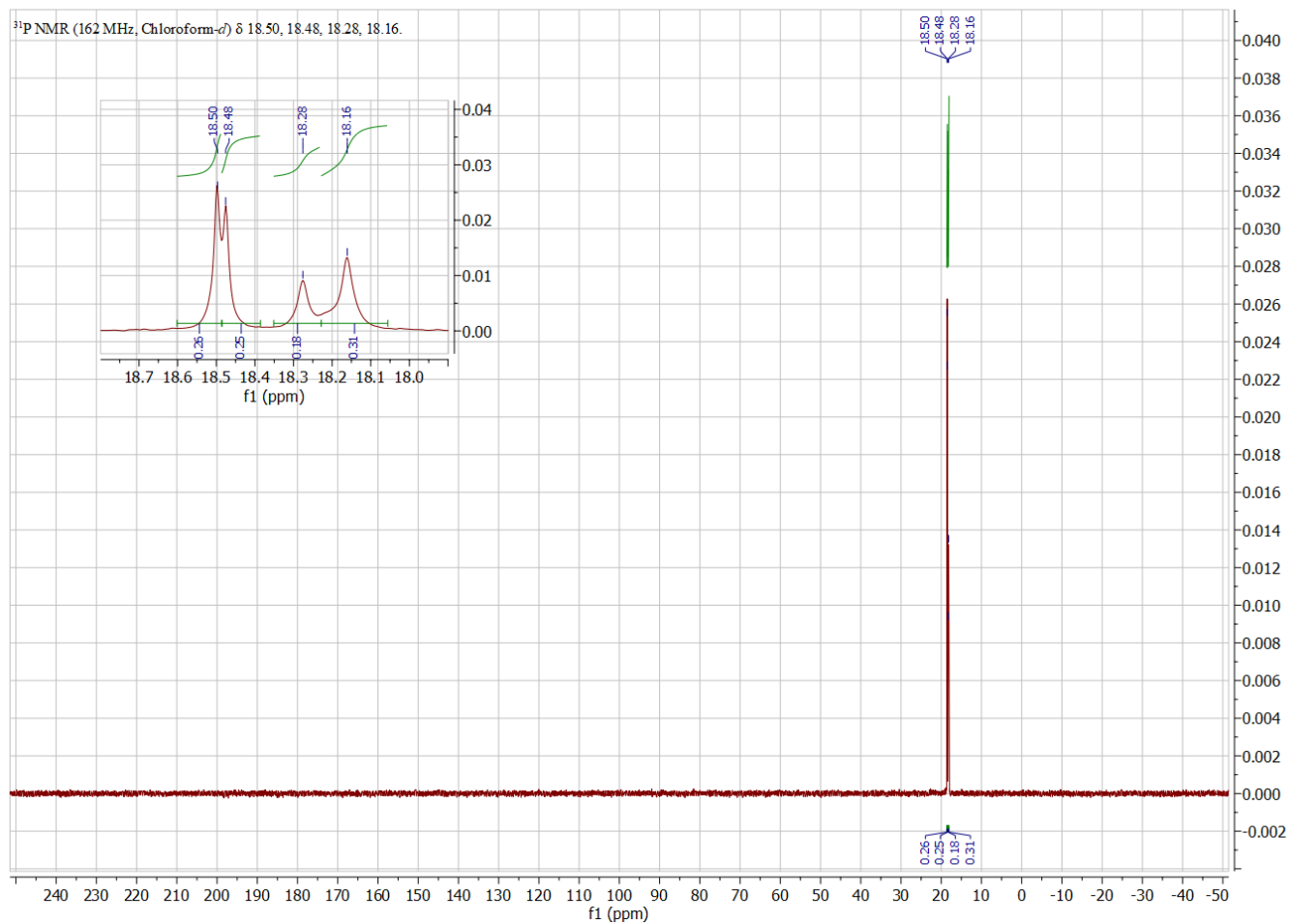
HPLC: purity >99%; retention time 16.880 min

Chromatogram

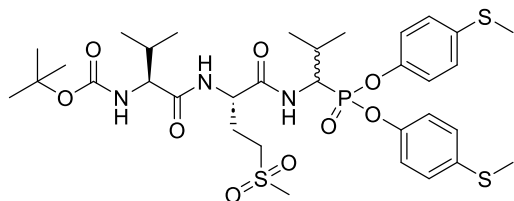


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16,880	331,419	1967,646	100,00	100,00	n.a.
Total:			331,419	1967,646	100,00	100,00	



(22) Boc-L-Val-L-Met(O₂)- Val^P(OPh-4-SCH₃)₂



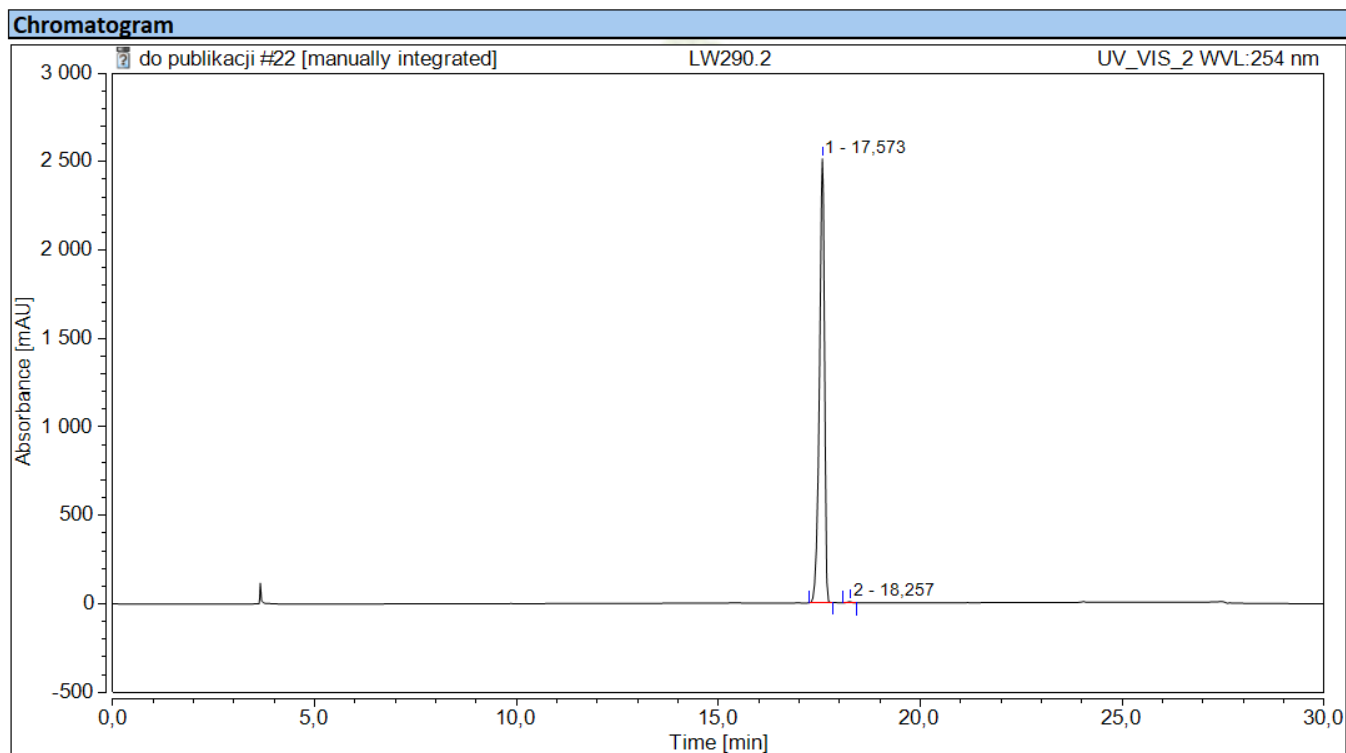
Name: *tert*-butyl ((2*S*)-1-(((2*S*)-1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-4-(methylsulfonyl)-1-oxobutan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.06 (s, 52%), 17.73 (s, 48%).

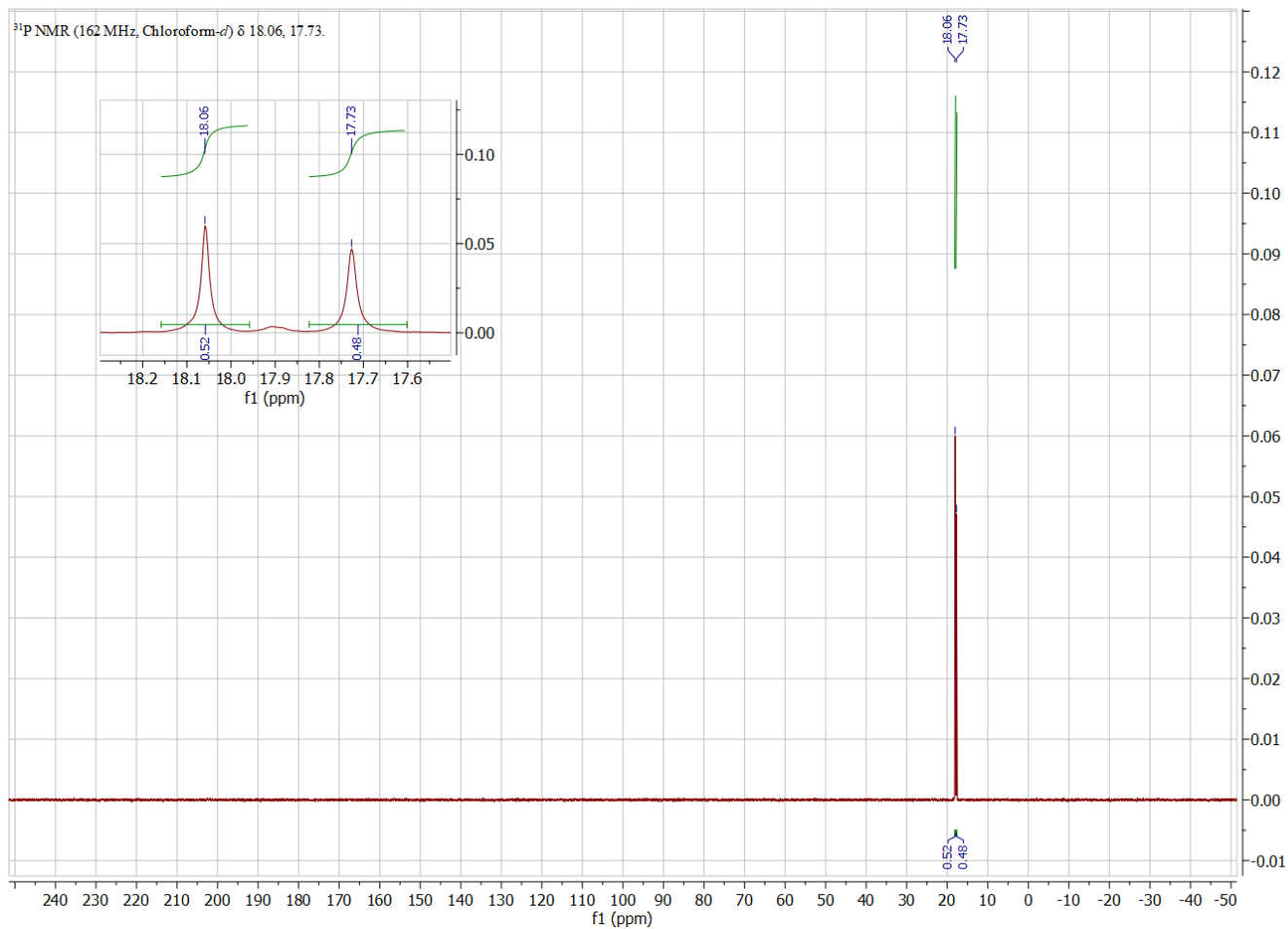
¹H NMR (400 MHz, Chloroform-*d*) δ 7.56 (dd, *J* = 50.6, 10.2 Hz, 1H, NH), 7.23 – 6.95 (m, 9H, 8xArH, NH), 5.19 (dd, *J* = 49.4, 7.6 Hz, 1H, NH), 4.87 – 4.62 (m, 2H, CHP, CH), 3.93 – 3.80 (m, 1H, CH), 3.29 – 3.03 (m, 2H, CH₂), 2.85 (d, *J* = 27.7 Hz, 3H, CH₃), 2.42 (d, *J* = 2.8 Hz, 6H, 2xSCH₃), 2.39 – 2.31 (m, 1H, CH), 2.30 – 2.13 (m, 2H, CH₂), 2.13 – 2.00 (m, 1H, CH), 1.41 (d, *J* = 8.4 Hz, 9H, Boc), 1.14 – 0.99 (m, 6H, 2xCH₃), 0.96 – 0.77 (m, 6H, 2xCH₃).

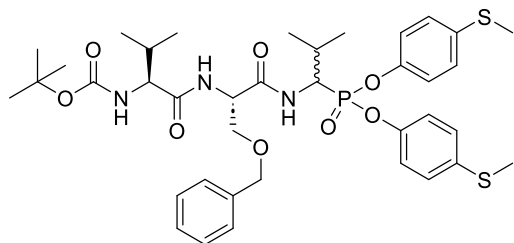
HRMS: C₃₃H₅₀N₃O₉PS₃ [M+Na]⁺ calc. 782.2344 found 782.2357

HPLC: purity >99%; retention time 17.573 min



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17,573	362,729	2509,071	99,78	99,71	n.a.
2		18,257	0,808	7,248	0,22	0,29	n.a.
Total:			363,536	2516,319	100,00	100,00	



(23) Boc-L-Val-L-Ser(Bzl)-Val^P(OPh-4-SCH₃)₂

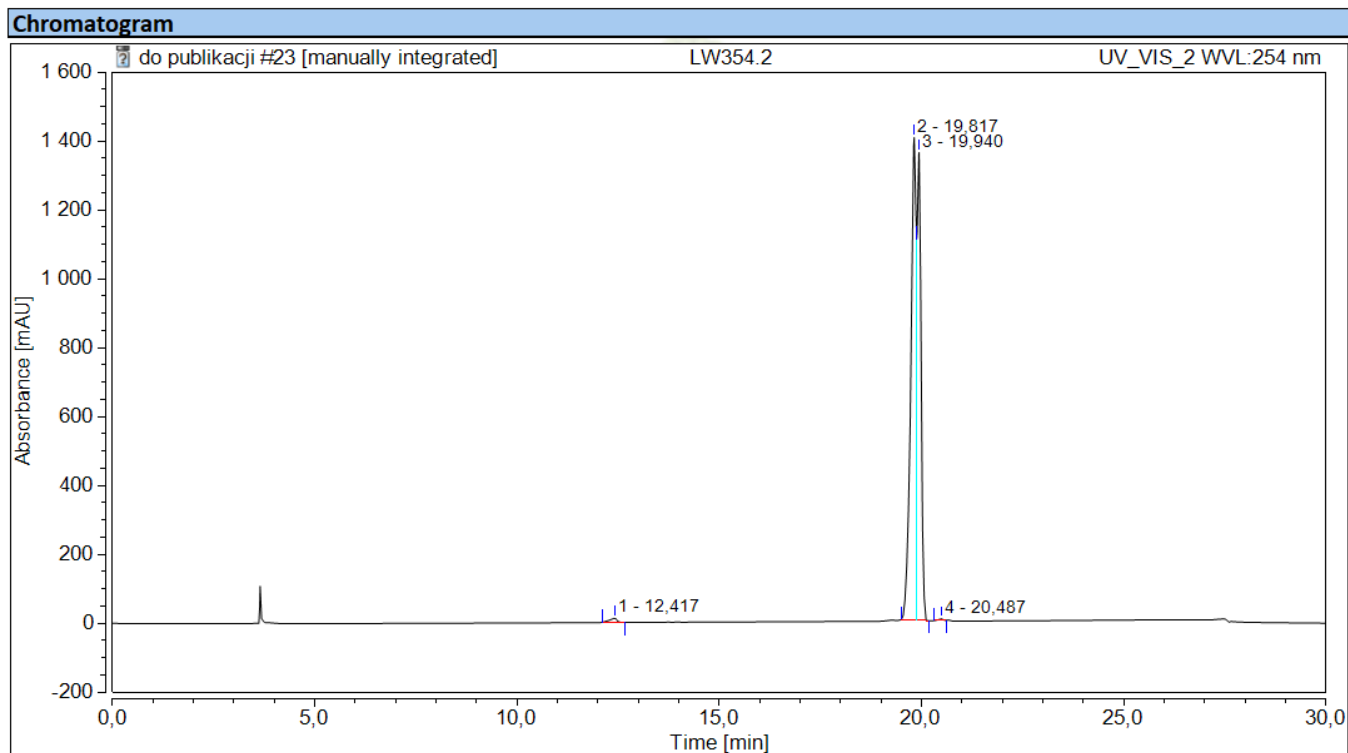
Name: *tert*-butyl ((2*S*)-1-(((2*S*)-3-(benzyloxy)-1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-1-oxopropan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.15 (s, 36%), 18.04 (s, 14%), 17.93 (s, 50%).

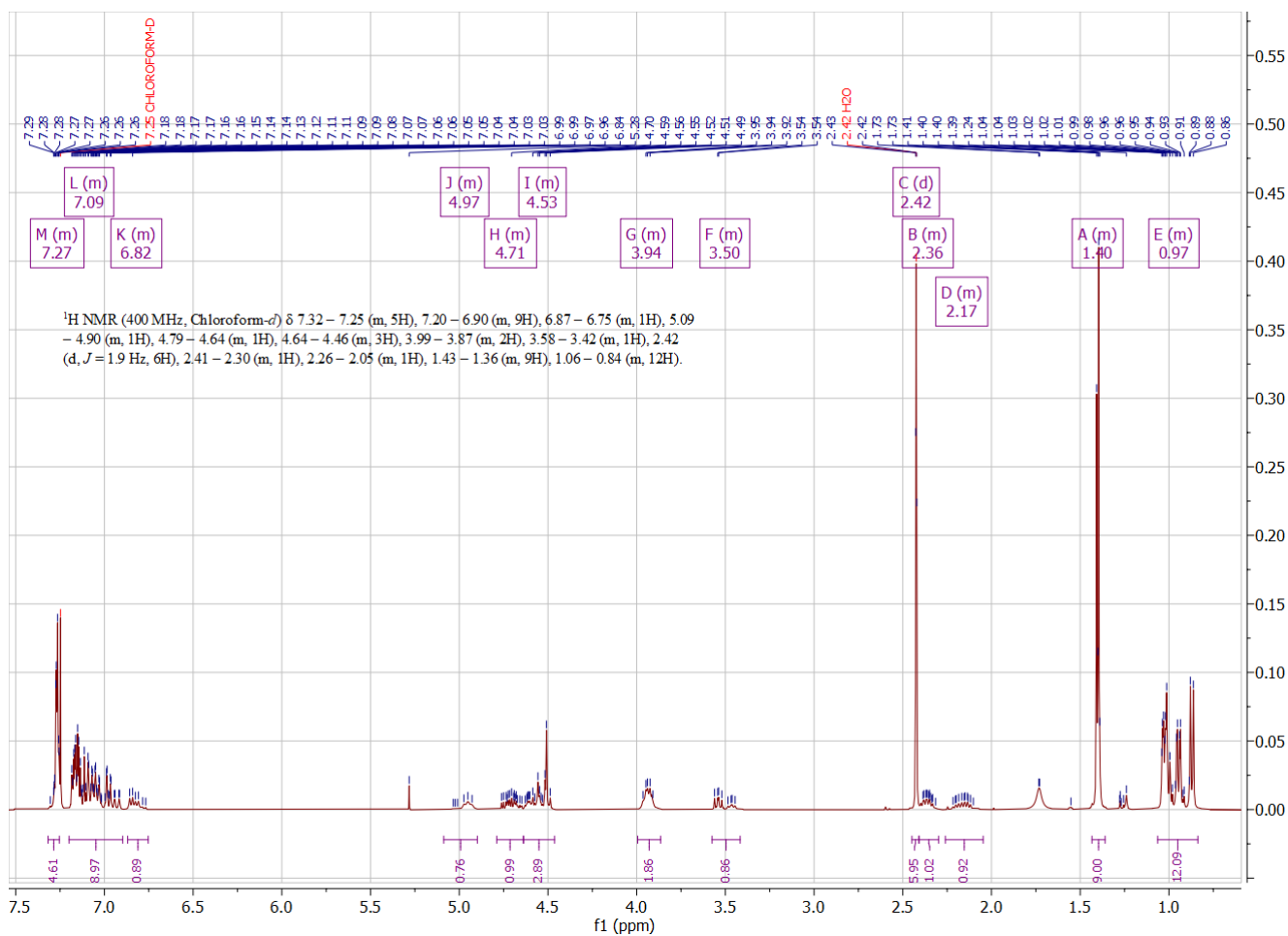
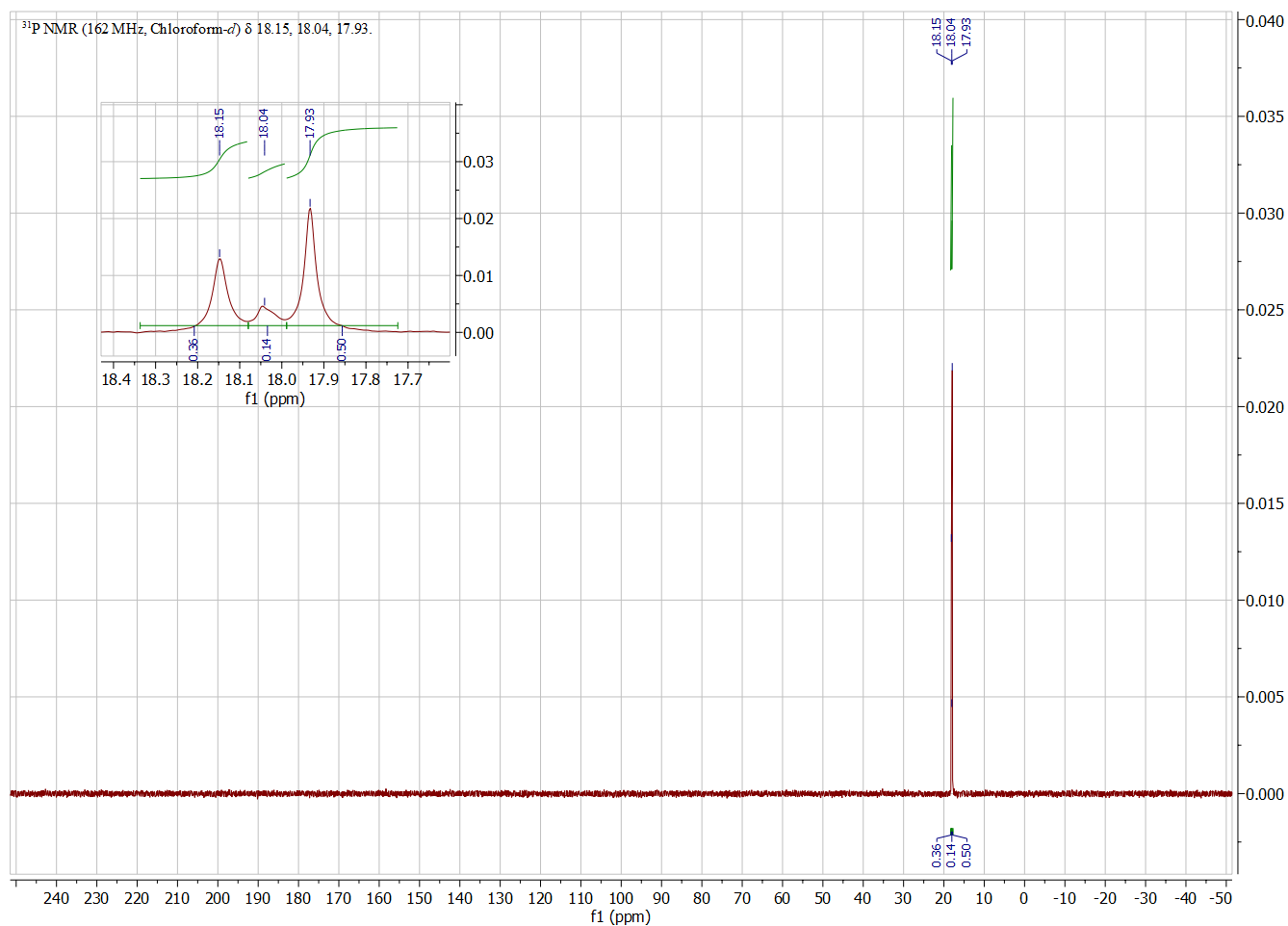
¹H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.25 (m, 5H, 5xArH), 7.20 – 6.90 (m, 9H, 8xArH, NH), 6.87 – 6.75 (m, 1H, NH), 5.09 – 4.90 (m, 1H, NH), 4.79 – 4.64 (m, 1H, CHP), 4.64 – 4.46 (m, 3H, CH₂, CH), 3.99 – 3.87 (m, 2H, CH₂), 3.58 – 3.42 (m, 1H, CH), 2.42 (d, *J* = 1.9 Hz, 6H, 2xSCH₃), 2.41 – 2.30 (m, 1H, CH), 2.26 – 2.05 (m, 1H, CH), 1.43 – 1.36 (m, 9H, Boc), 1.06 – 0.84 (m, 12H, 4xCH₃).

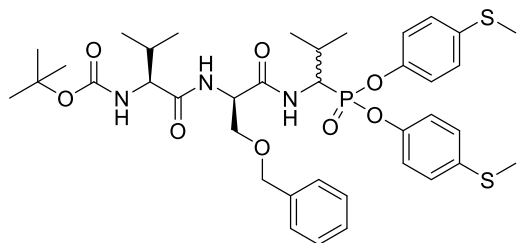
HRMS: C₃₈H₅₂N₃O₈PS₂ [M+Na]⁺ calc. 796.2831 found 796.2838

HPLC: purity >99%; retention time 19.817 and 19.940 min



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12,417	2,569	12,368	0,69	0,45	n.a.
2		19,817	214,920	1400,877	57,64	50,47	n.a.
3		19,940	154,836	1358,220	41,52	48,93	n.a.
4		20,487	0,559	4,434	0,15	0,16	n.a.
Total:			372,883	2775,899	100,00	100,00	



(24) Boc-L-Val-D-Ser(Bzl)-Val^P(OPh-4-SCH₃)₂

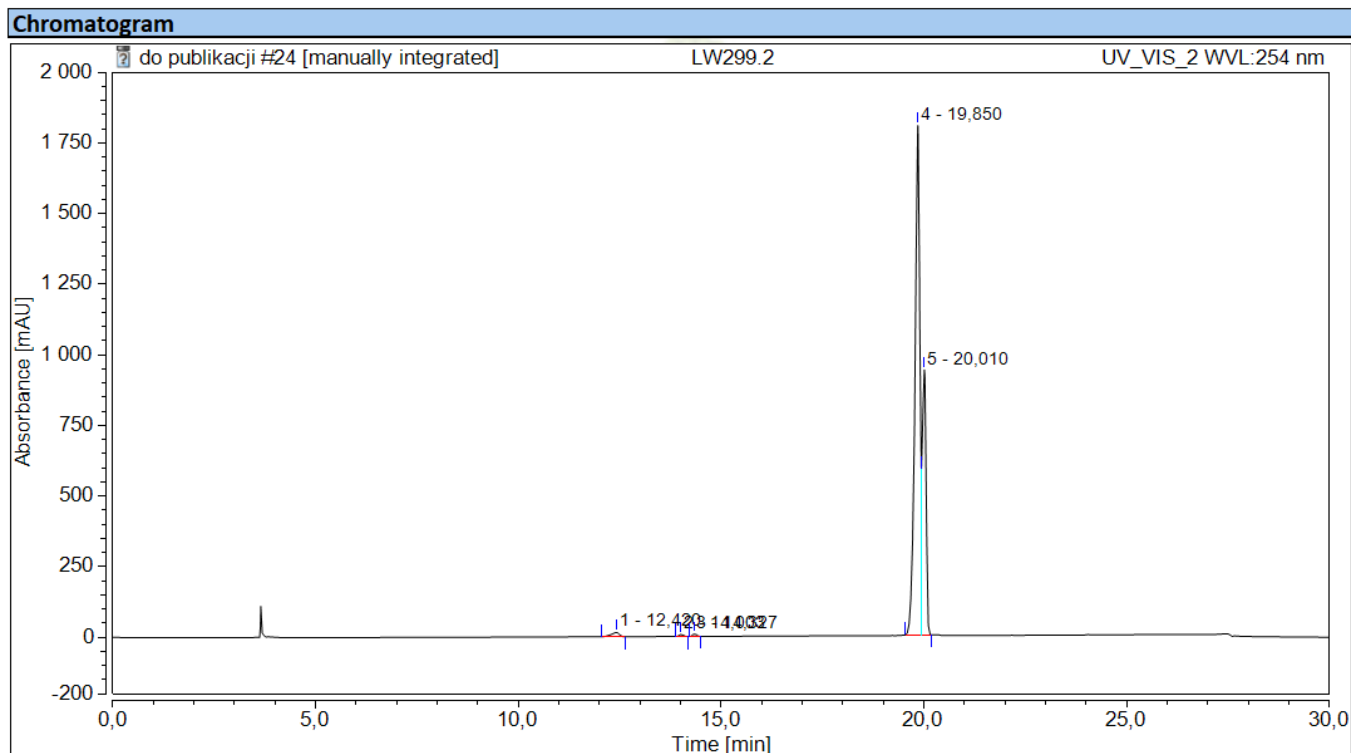
Name: *tert*-butyl ((2*S*)-1-(((2*R*)-3-(benzyloxy)-1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-1-oxopropan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.04 (s, 51%), 18.00 (s, 49%).

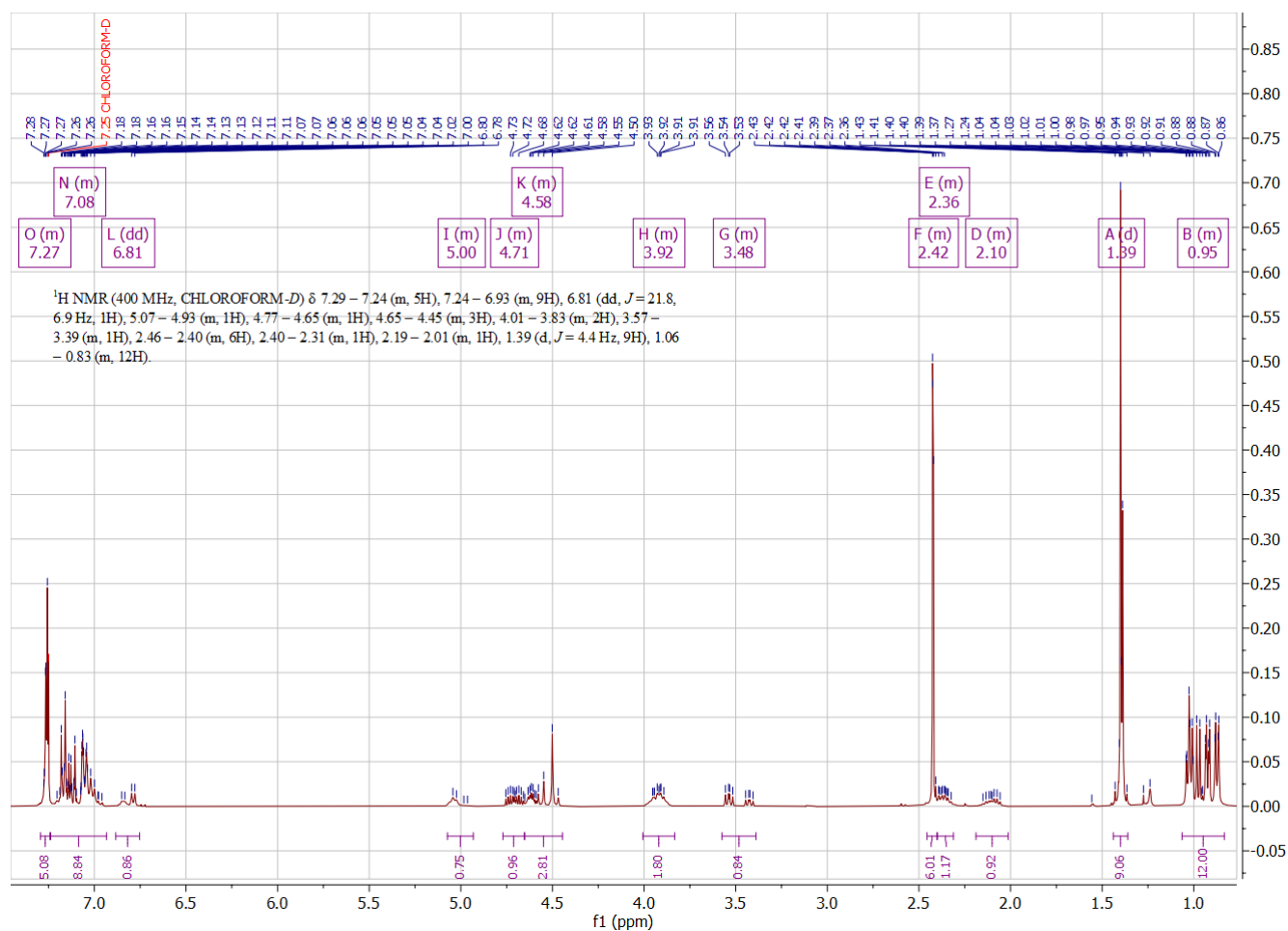
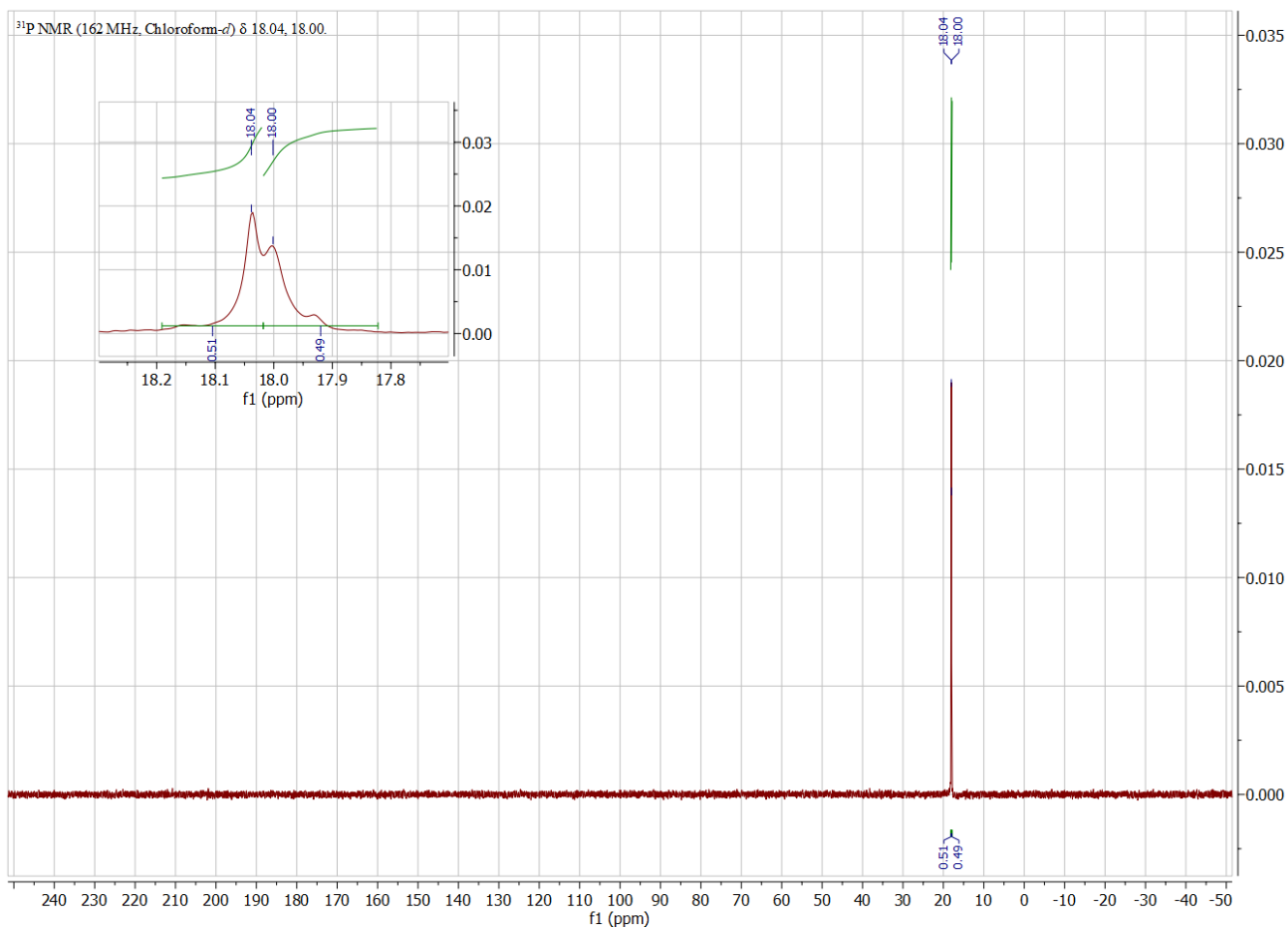
¹H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.24 (m, 5H, 5×ArH), 7.24 – 6.93 (m, 9H, 8×ArH, NH), 6.81 (dd, *J* = 21.8, 6.9 Hz, 1H, NH), 5.07 – 4.93 (m, 1H, NH), 4.77 – 4.65 (m, 1H, CHP), 4.65 – 4.45 (m, 3H, CH₂, CH), 4.01 – 3.83 (m, 2H, CH₂), 3.57 – 3.39 (m, 1H, CH), 2.46 – 2.40 (m, 6H, 2×SCH₃), 2.40 – 2.31 (m, 1H, CH), 2.19 – 2.01 (m, 1H, CH), 1.39 (d, *J* = 4.4 Hz, 9H, Boc), 1.06 – 0.83 (m, 12H, 4×CH₃).

HRMS: C₃₈H₅₂N₃O₈PS₂ [M+Na]⁺ calc. 796.2831 found 796.2821

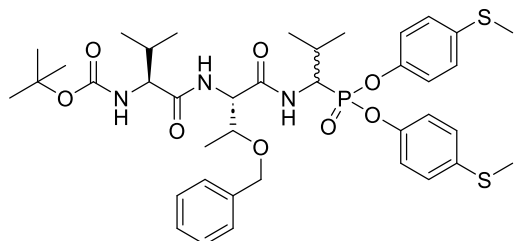
HPLC: purity >98%; retention time 19.850 and 20.010 min



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12,420	3,485	15,880	0,96	0,57	n.a.
2		14,003	0,816	6,782	0,23	0,24	n.a.
3		14,327	1,032	8,124	0,29	0,29	n.a.
4		19,850	251,688	1802,596	69,69	65,05	n.a.
5		20,010	104,145	937,750	28,84	33,84	n.a.
Total:			361,166	2771,133	100,00	100,00	



(25) Boc-L-Val-L-Thr(Bzl)-Val^P(OPh-4-SCH₃)₂



Name: *tert*-butyl ((2S)-1-(((2S,3S)-3-(benzyloxy)-1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-1-oxobutan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

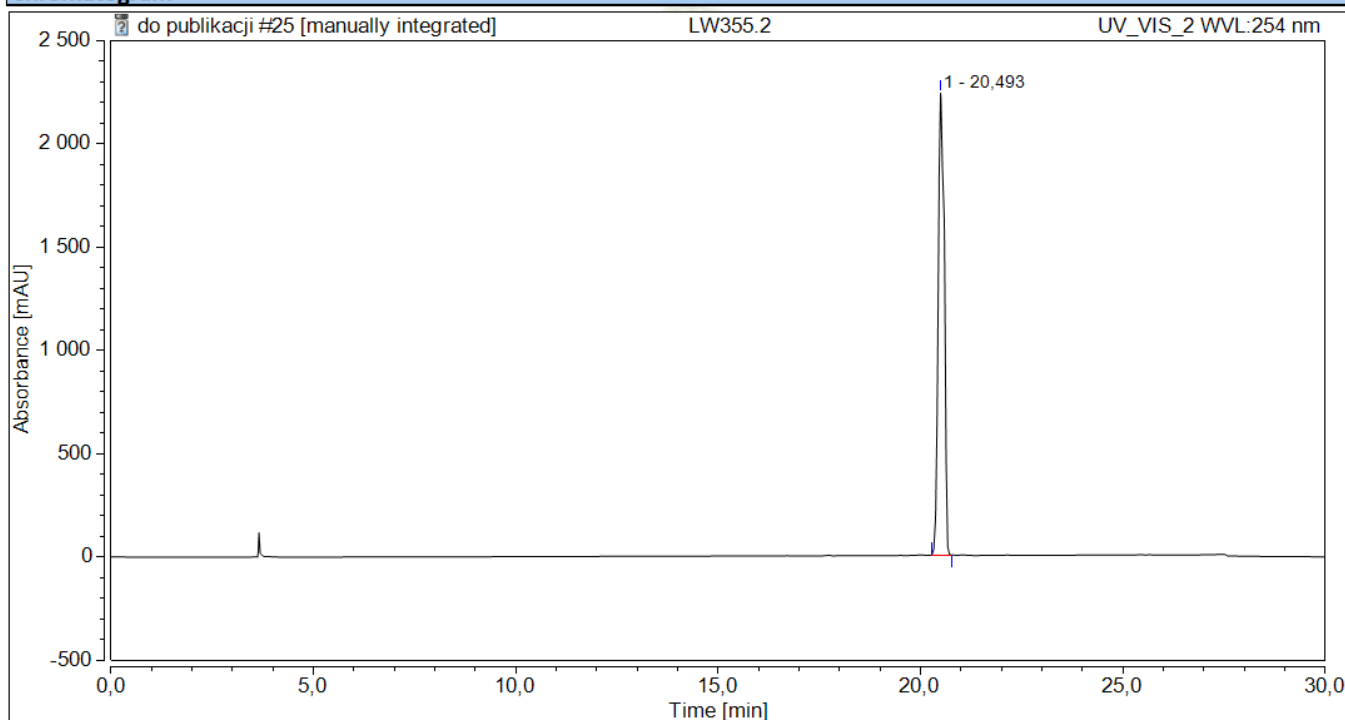
³¹P NMR (162 MHz, Chloroform-d) δ 18.45 (s, 46%), 17.94 (s, 54%).

¹H NMR (400 MHz, Chloroform-d) δ 7.33 – 6.91 (m, 15H, 13xArH, 2xNH), 4.97 (d, *J* = 5.5 Hz, 1H, NH), 4.78 – 4.48 (m, 4H, CH₂, CHP, CH), 4.31 – 4.18 (m, 1H, CH), 4.01 – 3.92 (m, 1H, CH), 2.47 – 2.41 (m, 6H, 2xSCH₃), 2.41 – 2.30 (m, 1H, CH), 2.26 – 2.11 (m, 1H, CH), 1.40 (d, *J* = 3.8 Hz, 9H, Boc), 1.19 (dd, *J* = 10.4, 6.5 Hz, CH₃), 1.07 – 0.88 (m, 12H, 4xCH₃).

HRMS: C₃₉H₅₄N₃O₈PS₂ [M+Na]⁺ calc. 810.2988 found 810.3001

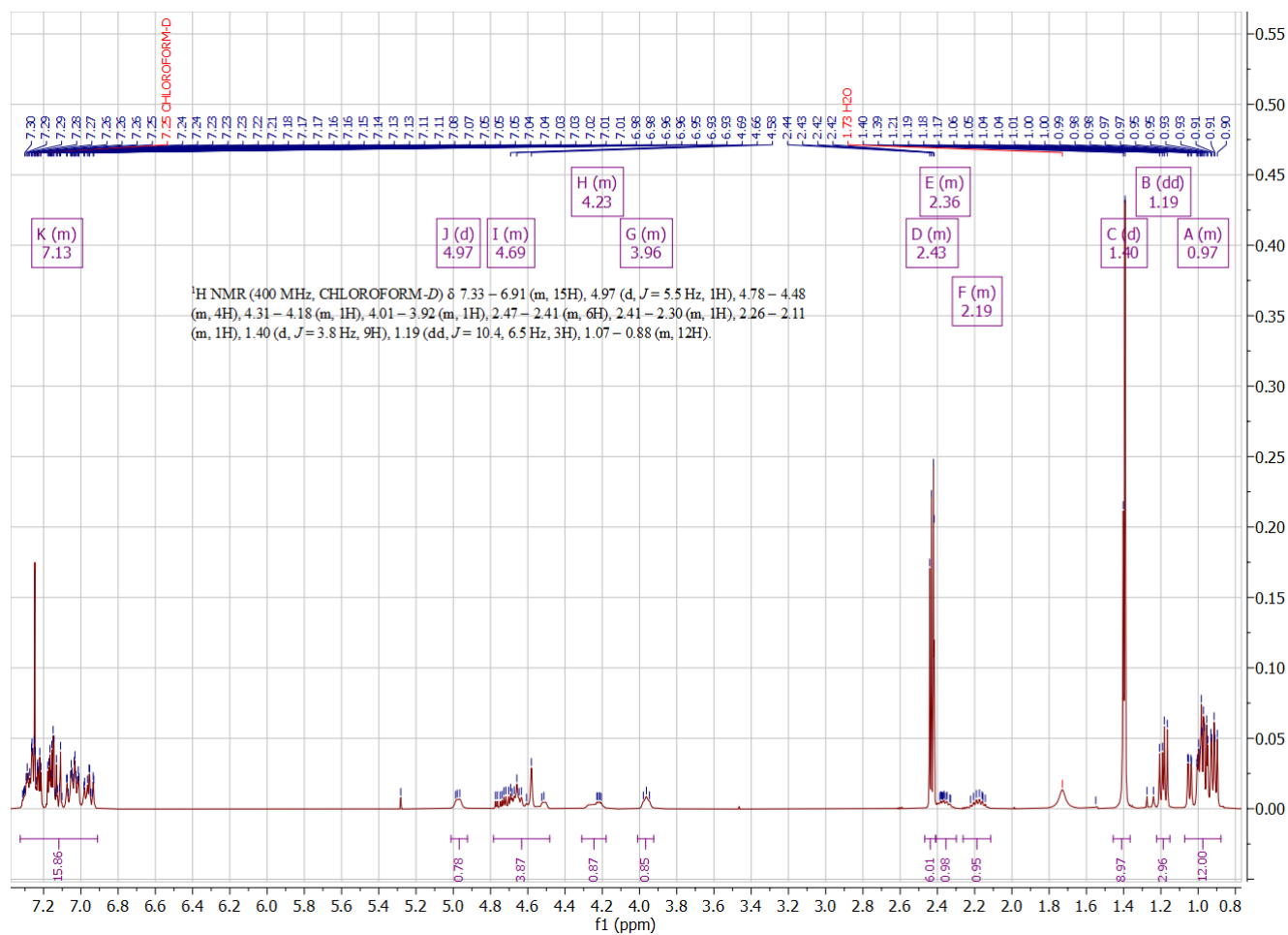
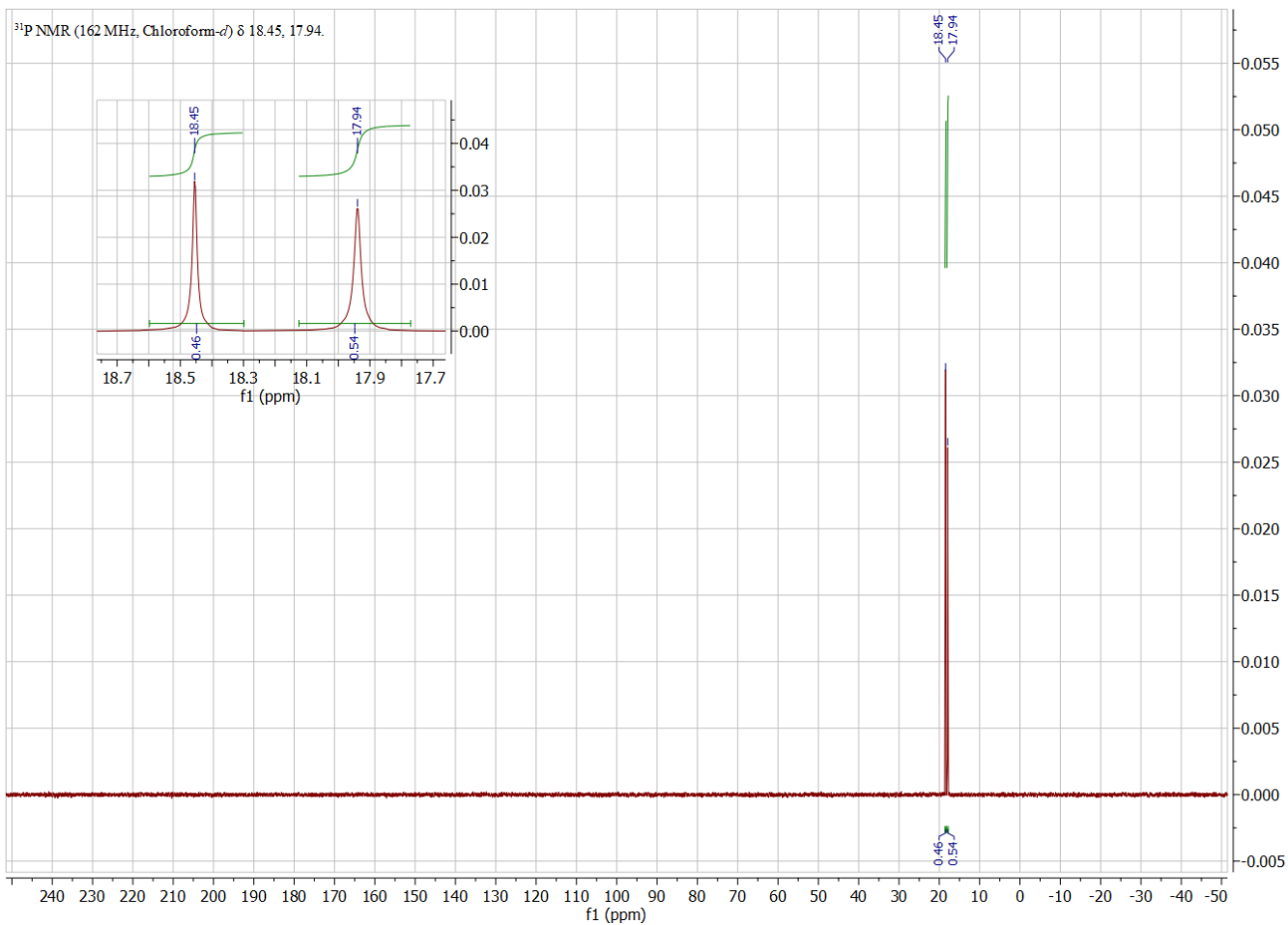
HPLC: purity >99%; retention time 20.493 min

Chromatogram

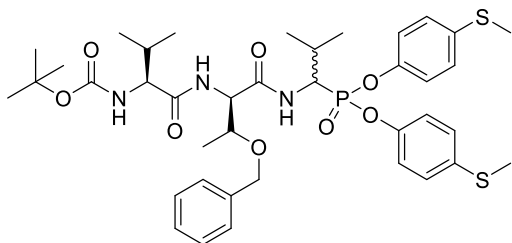


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20,493	388,048	2235,403	100,00	100,00	n.a.
Total:			388,048	2235,403	100,00	100,00	



(26) Boc-L-Val-D-Thr(Bzl)- Val^P(OPh-4-SCH₃)₂



Name: *tert*-butyl ((2*S*)-1-(((2*R*,3*R*)-3-(benzyloxy)-1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-1-oxobutan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

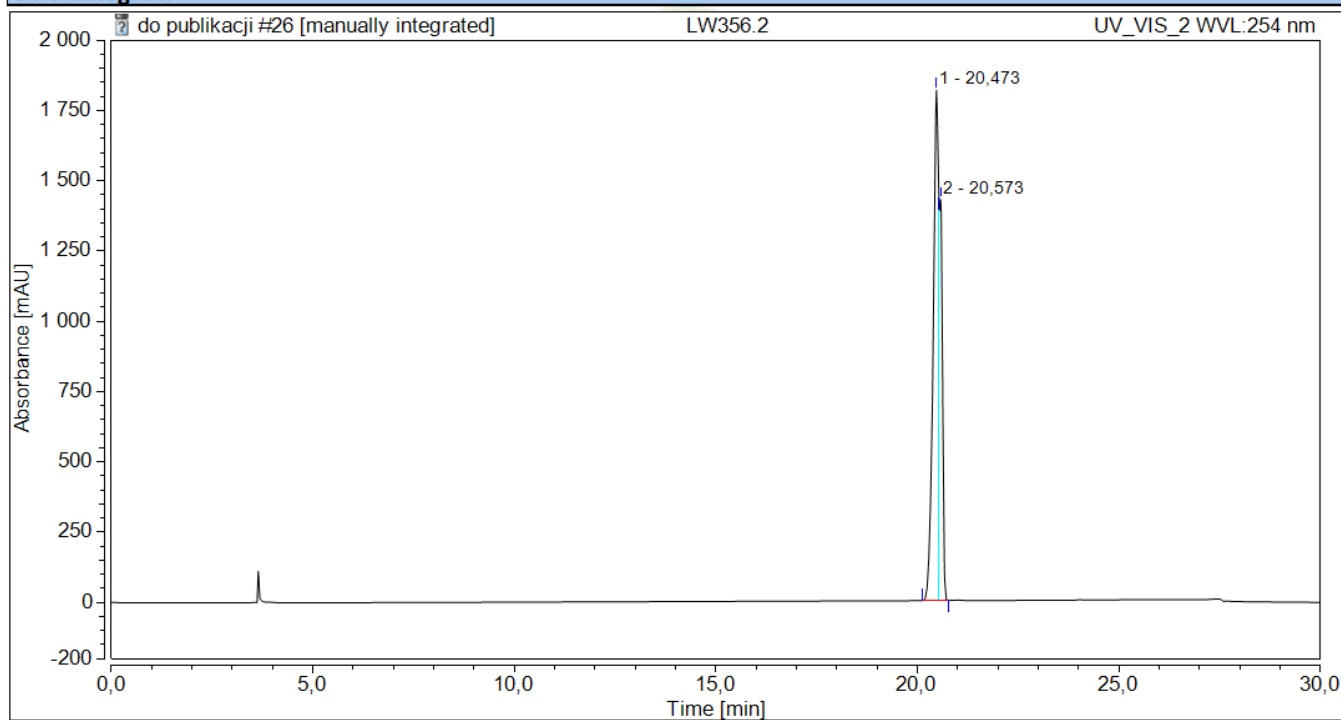
³¹P NMR (162 MHz, Chloroform-*d*) δ 18.43 (s, 69%), 18.00 (s, 31%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.25 (m, 4H, 3xArH, NH), 7.24 – 6.85 (m, 11H, 10xArH, NH), 5.02 (d, *J* = 8.0 Hz, 1H, NH), 4.78 – 4.48 (m, 4H, CH₂, CHP, CH), 4.28 – 4.16 (m, 1H, CH), 4.05 – 3.92 (m, 1H, CH), 2.45 – 2.40 (m, 6H, 2xSCH₃), 2.40 – 2.30 (m, 1H, CH), 2.22 – 2.07 (m, 1H, CH), 1.40 (d, *J* = 1.9 Hz, 9H, Boc), 1.18 (dd, *J* = 7.3, 6.5 Hz, 3H, CH₃), 1.03 – 0.85 (m, 12H, 4xCH₃).

HRMS: C₃₉H₅₄N₃O₈PS₂ [M+Na]⁺ calc. 810.2988 found 810.3005

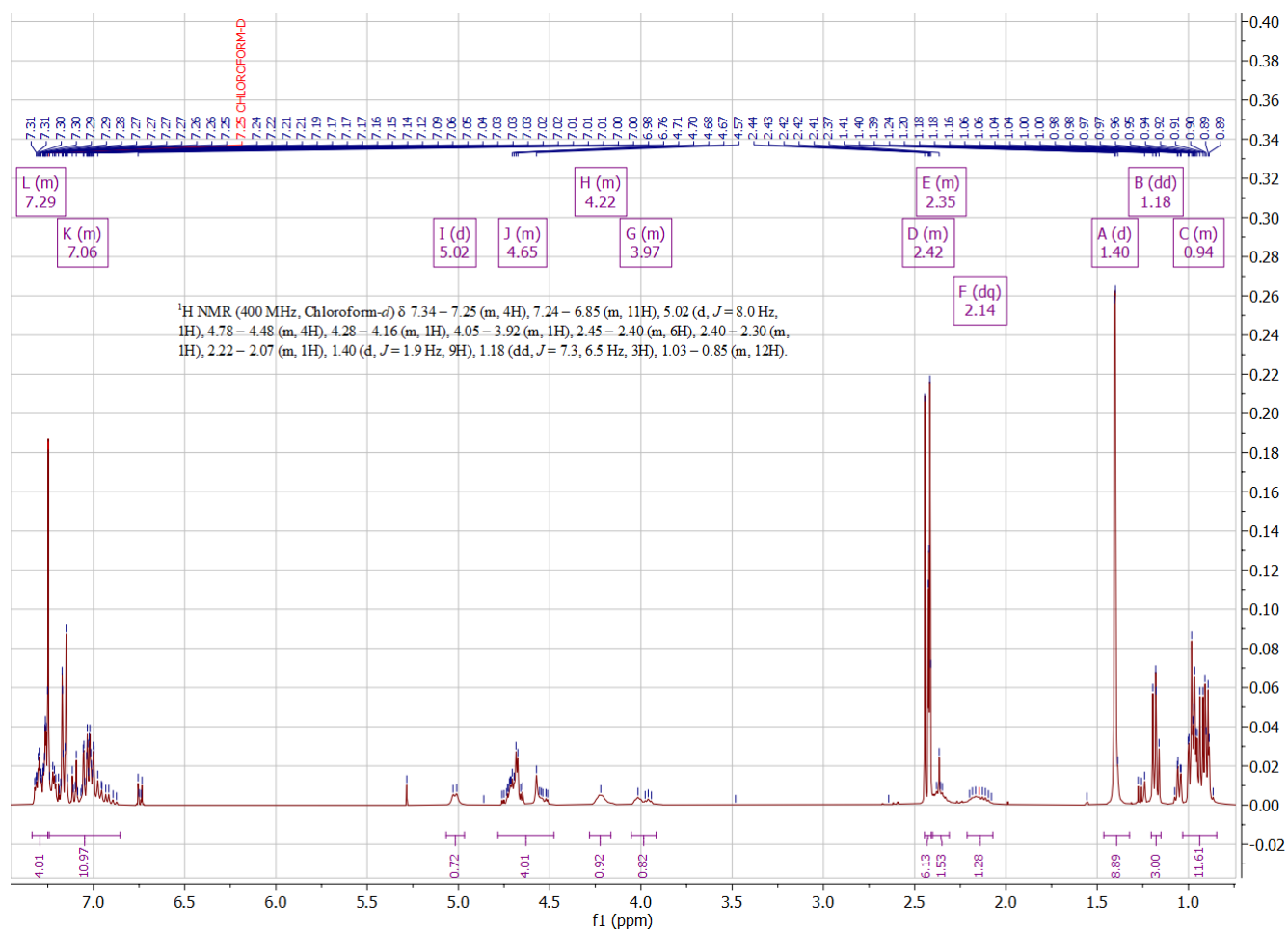
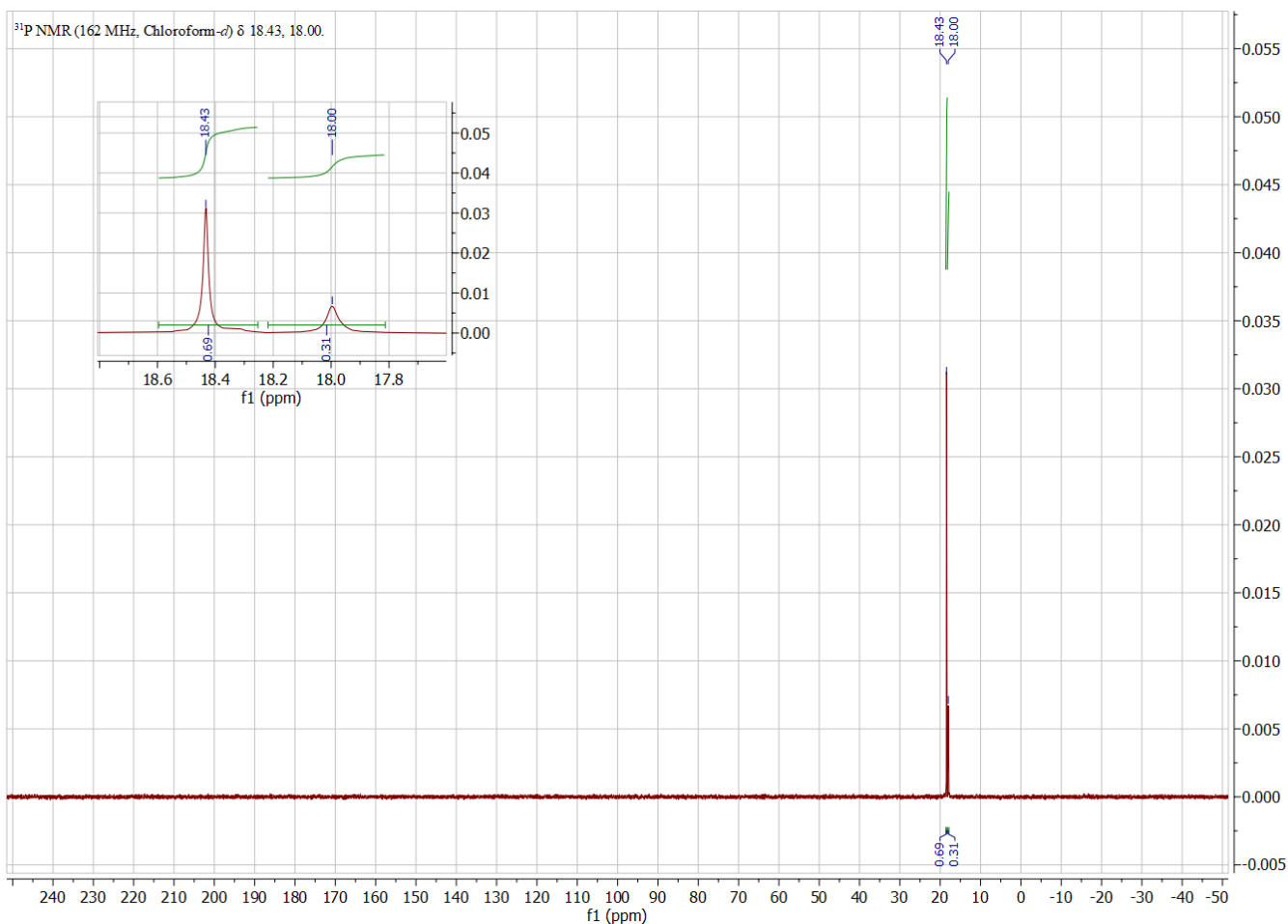
HPLC: purity >99%; retention time 20.473 and 20.573 min

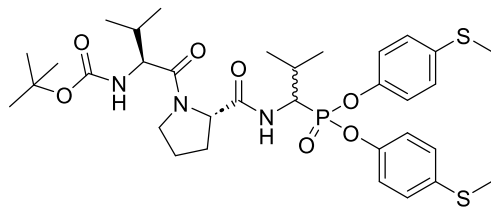
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20,473	280,574	1814,893	68,58	56,01	n.a.
2		20,573	128,523	1425,596	31,42	43,99	n.a.
Total:			409,097	3240,489	100,00	100,00	



(27) Boc-L-Val-L-Pro-Val^P(OPh-4-SCH₃)₂

Reference compound, analytical data from our previous publication: Winiarski, Ł.; Oleksyszyn, J.; Sieńczyk, M. Human neutrophil elastase phosphonic inhibitors with improved potency of action. *J. Med. Chem.* **2012**, *55*, 6541–6553.

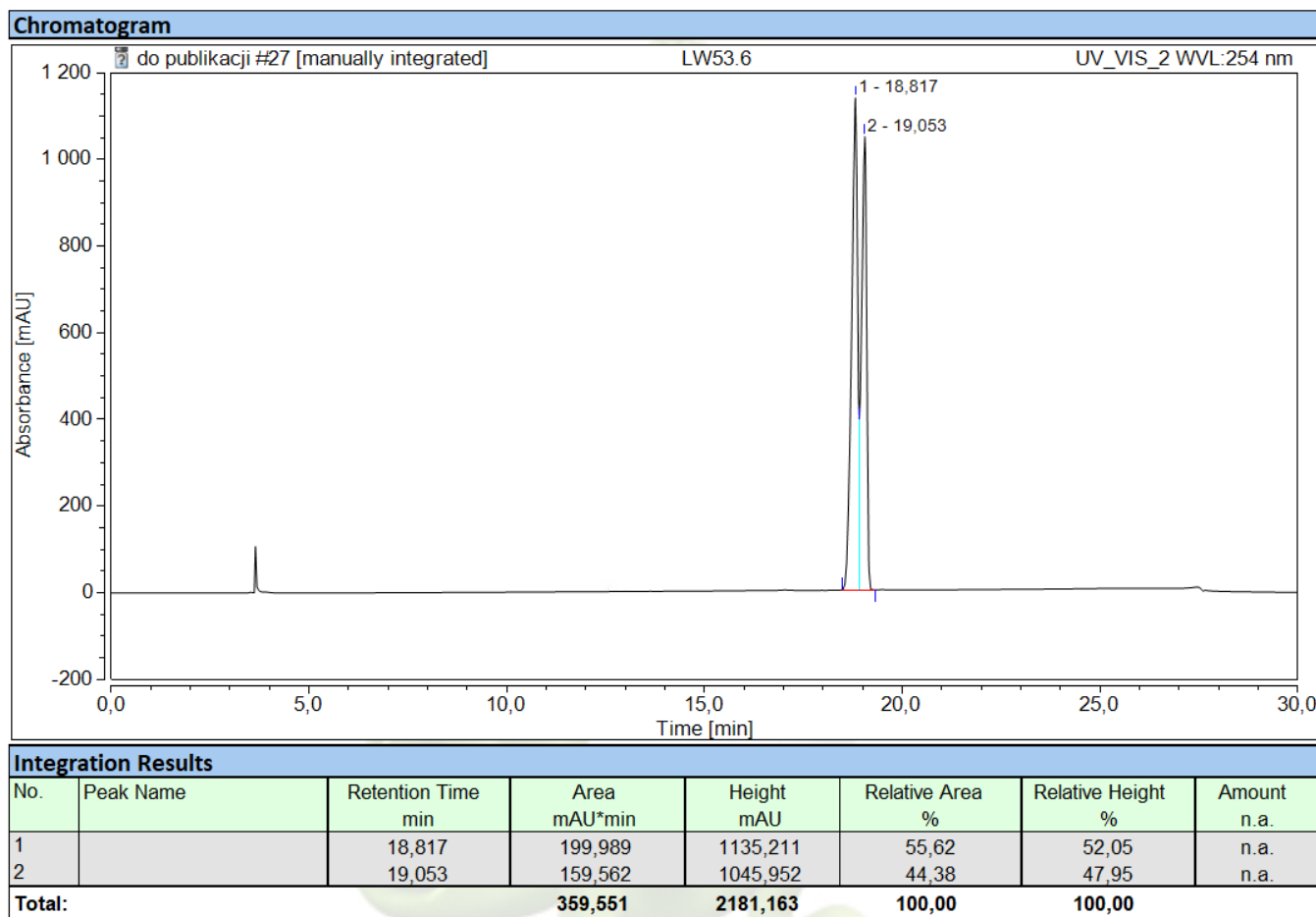
Name: *tert*-butyl ((2*S*)-1-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-3-methyl-1-oxobutan-2-yl)carbamate

³¹P NMR (121 MHz, CDCl₃) δ 18.15 (s, 52%), 18.48 (s, 48%).

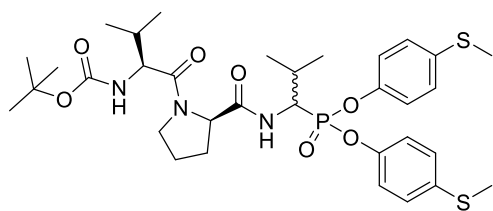
¹H NMR (300 MHz, CDCl₃) δ 7.03–7.23 (m, 8H), 5.30 (dd, *J* = 61.7, 9.3 Hz, 1H), 4.49–4.78 (m, 2H), 4.20–4.34 (m, 1H), 3.43–3.80 (m, 2H), 2.44 (d, *J* = 2.7 Hz, 6H), 2.04–2.41 (m, 2H), 1.74–2.03 (m, 4H), 1.42 (d, *J* = 2.0 Hz, 9H), 0.81–1.14 (m, 12H).

HRMS: C₃₃H₄₈N₃O₇PS₂ [M+H]⁺ calc. 694.2750 found 694.2738

HPLC: purity >99%; retention time 18.817 and 19.053 min



(28) Boc-L-Val-D-Pro-Val^P(OPh-4-SCH₃)₂



Name: *tert*-butyl ((2S)-1-((2R)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-3-methyl-1-oxobutan-2-yl)carbamate

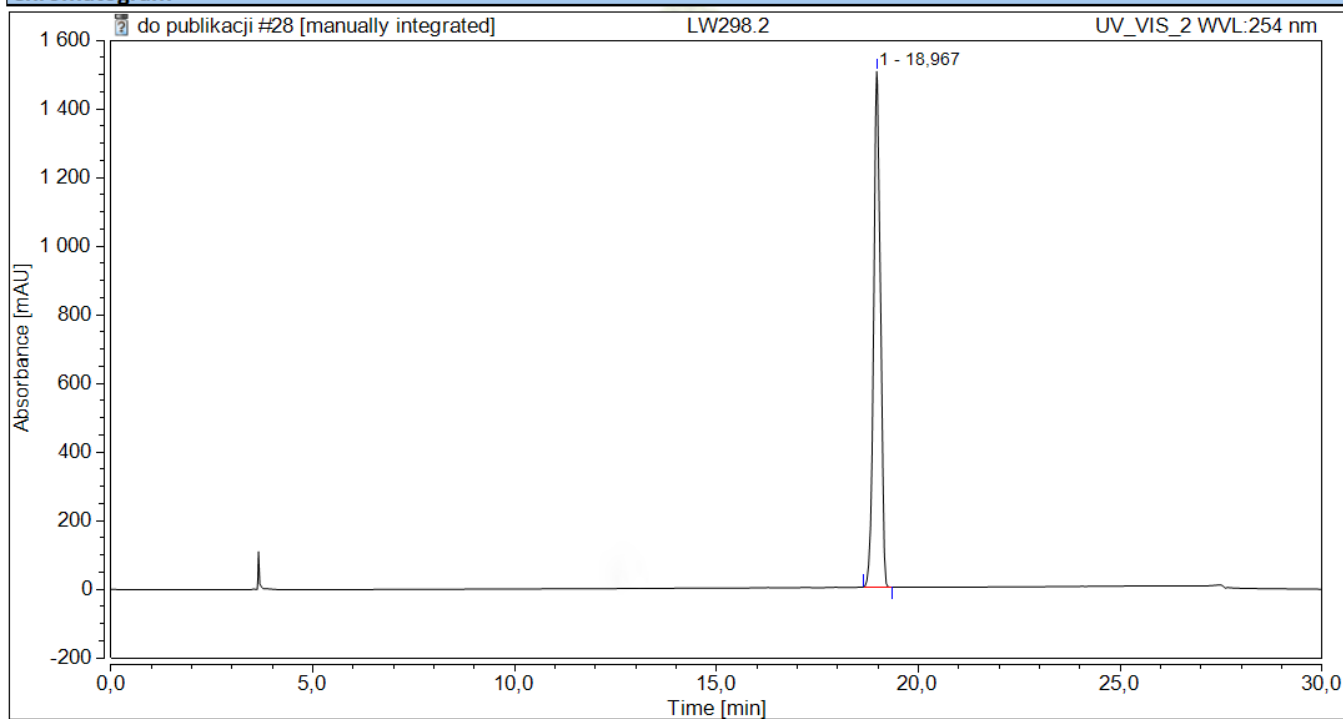
³¹P NMR (162 MHz, Chloroform-d) δ 18.42 (s, 58%), 18.19 (s, 42%).

¹H NMR (400 MHz, Chloroform-d) δ 7.57 (dd, *J* = 122.0, 9.7 Hz, 1H, NH), 7.22 – 7.00 (m, 8H, 8xArH), 5.23 (t, *J* = 8.0 Hz, 1H, NH), 4.74 – 4.53 (m, 2H, CHP, CH), 4.31 – 4.19 (m, 1H, CH), 3.90 – 3.76 (m, 1H, CH₂), 3.58 – 3.44 (m, 1H, CH₂), 2.43 (d, *J* = 4.6 Hz, 6H, 3xSCH₃), 2.42 – 1.73 (m, 6H, 2xCH₂, 2xCH), 1.45 – 1.30 (m, 9H, Boc), 1.20 – 0.83 (m, 12H, 4xCH₃).

HRMS: C₃₃H₄₈N₃O₇PS₂ [M+Na]⁺ calc. 716.2569 found 716.2552

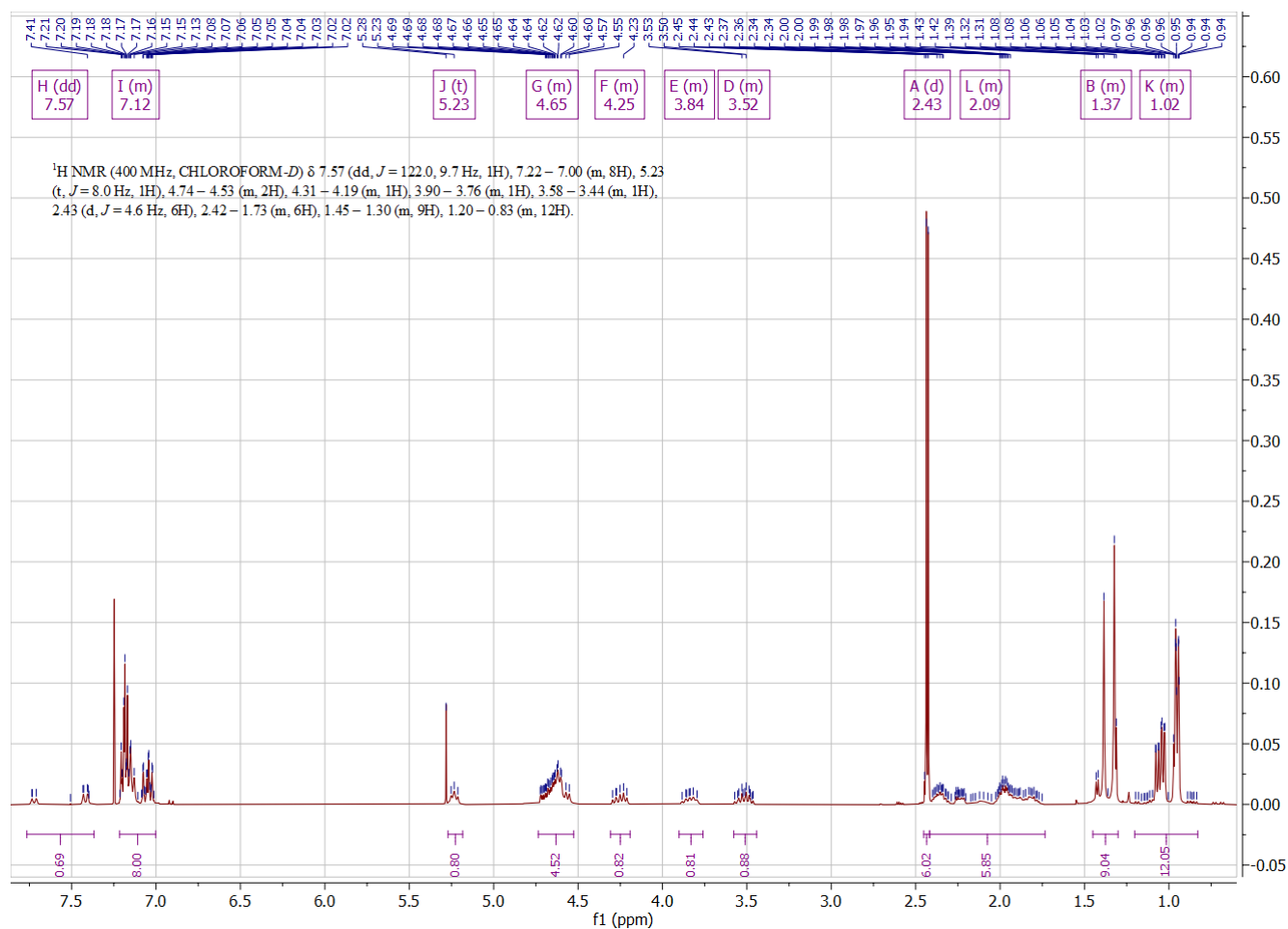
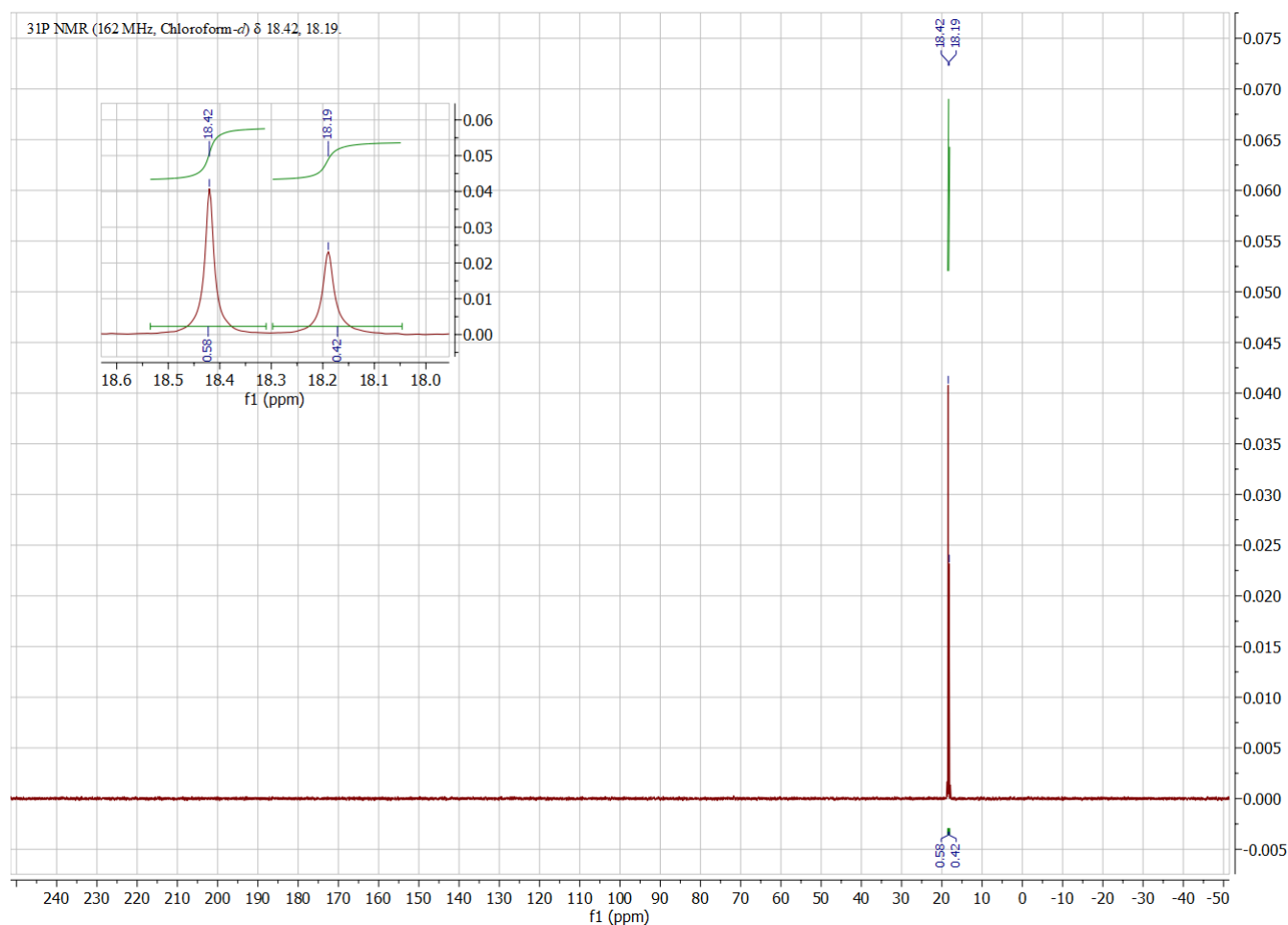
HPLC: purity >99%; retention time 18.967 min

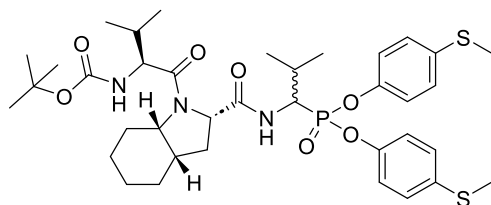
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18,967	292,341	1502,416	100,00	100,00	n.a.
Total:			292,341	1502,416	100,00	100,00	



(29) Boc-L-Val-L-Oic-Val^P(OPh-4-SCH₃)₂

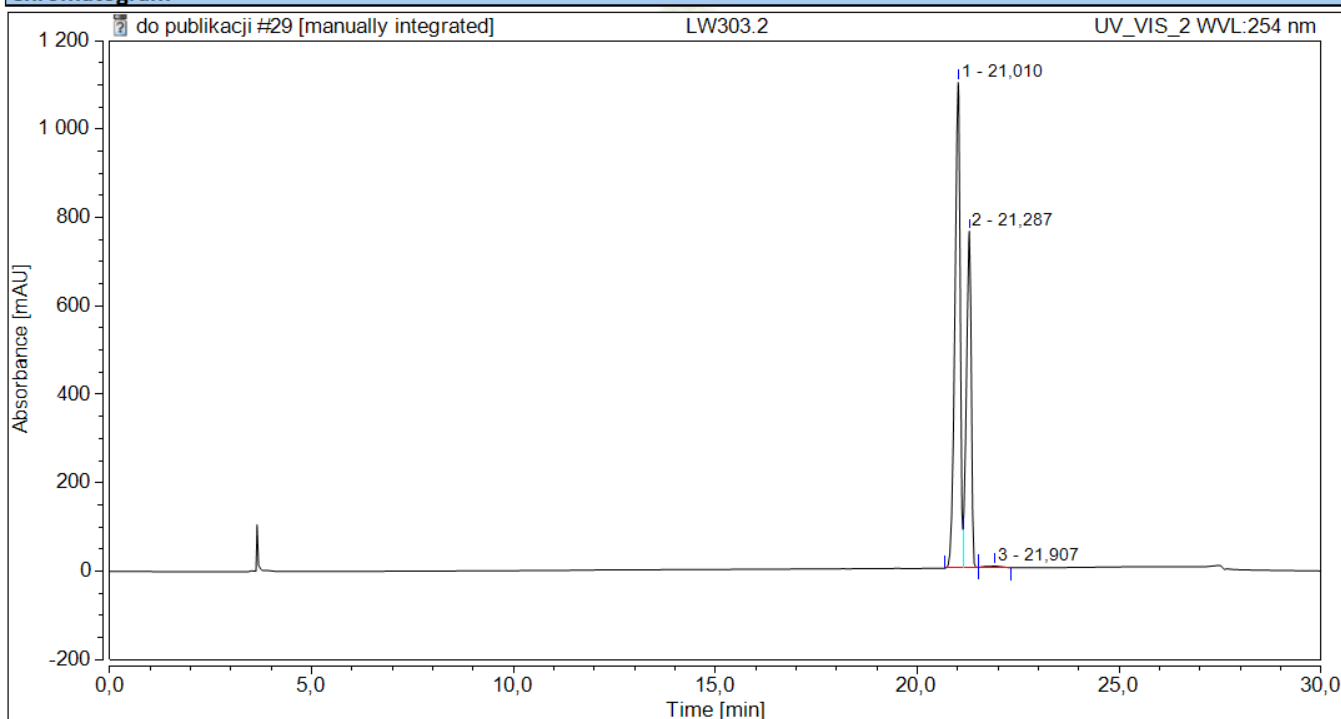
Name: *tert*-butyl ((2*S*)-1-((2*S*,3*aS*,7*aS*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)octahydro-1*H*-indol-1-yl)-3-methyl-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.96(s, 44%), 18.27 (s, 56%). ¹H NMR

¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 (dd, *J* = 66.0, 10.1 Hz, 1H, NH), 7.27 – 6.99 (m, 8H, 8*x*ArH), 5.16 (dd, *J* = 37.5, 9.9 Hz, 1H, NH), 4.79 – 4.59 (m, 1H, CHP), 4.51 – 4.10 (m, 2H, 2*x*CH), 2.48 – 2.40 (m, 6H, 2*x*SCH₃), 2.40 – 2.18 (m, 3H, CH₂, CH), 2.09 – 1.84 (m, 2H, 2*x*CH), 1.84 – 1.55 (m, 5H, 2*x*CH₂, CH), 1.55 – 1.44 (m, 2H, CH₂), 1.42 (d, *J* = 5.6 Hz, 9H, Boc), 1.30 – 1.13 (m, 2H, CH₂), 1.13 – 0.97 (m, 6H, 2*x*CH₃), 0.97 – 0.78 (m, 6H, 2*x*CH₃).

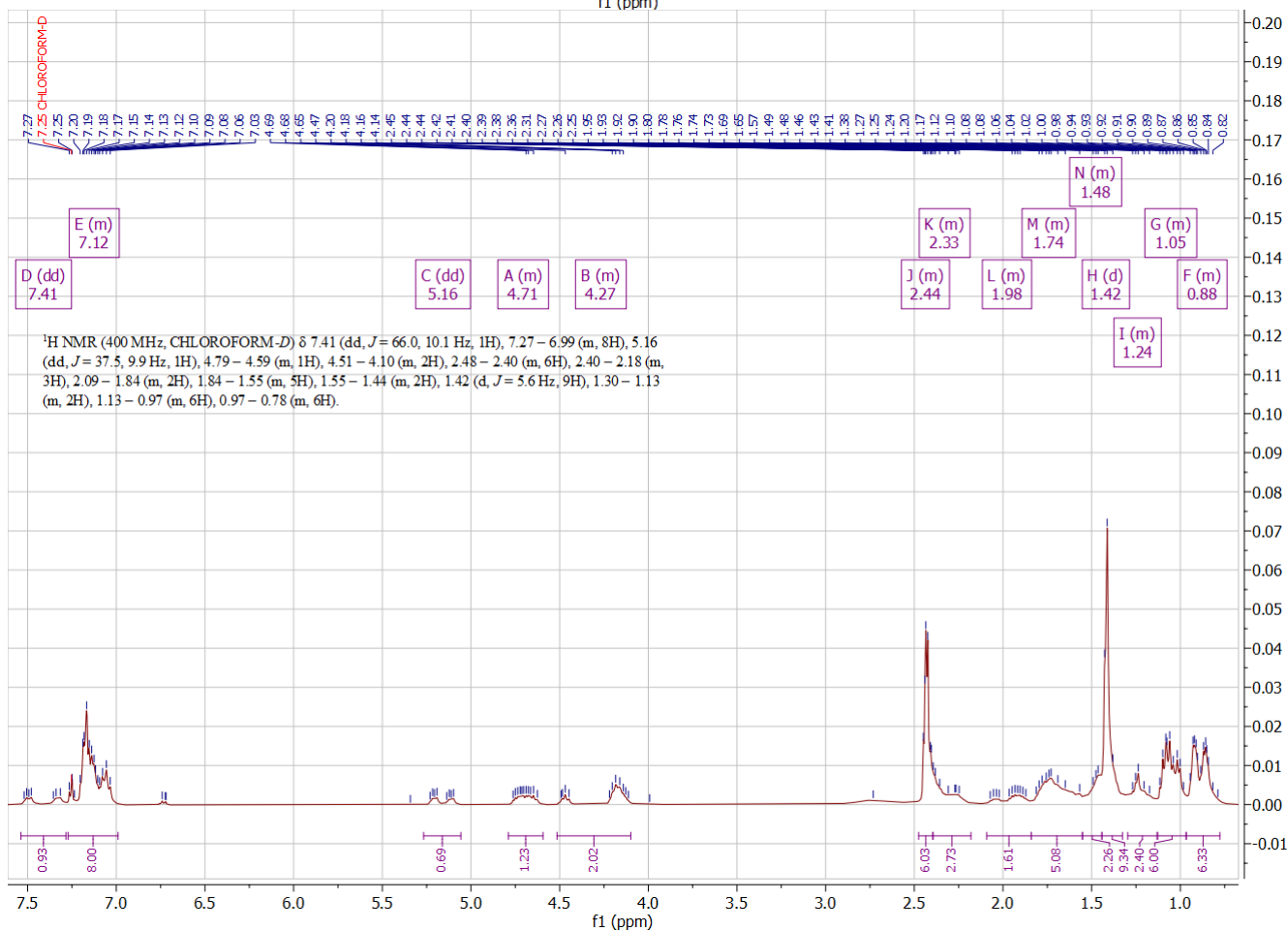
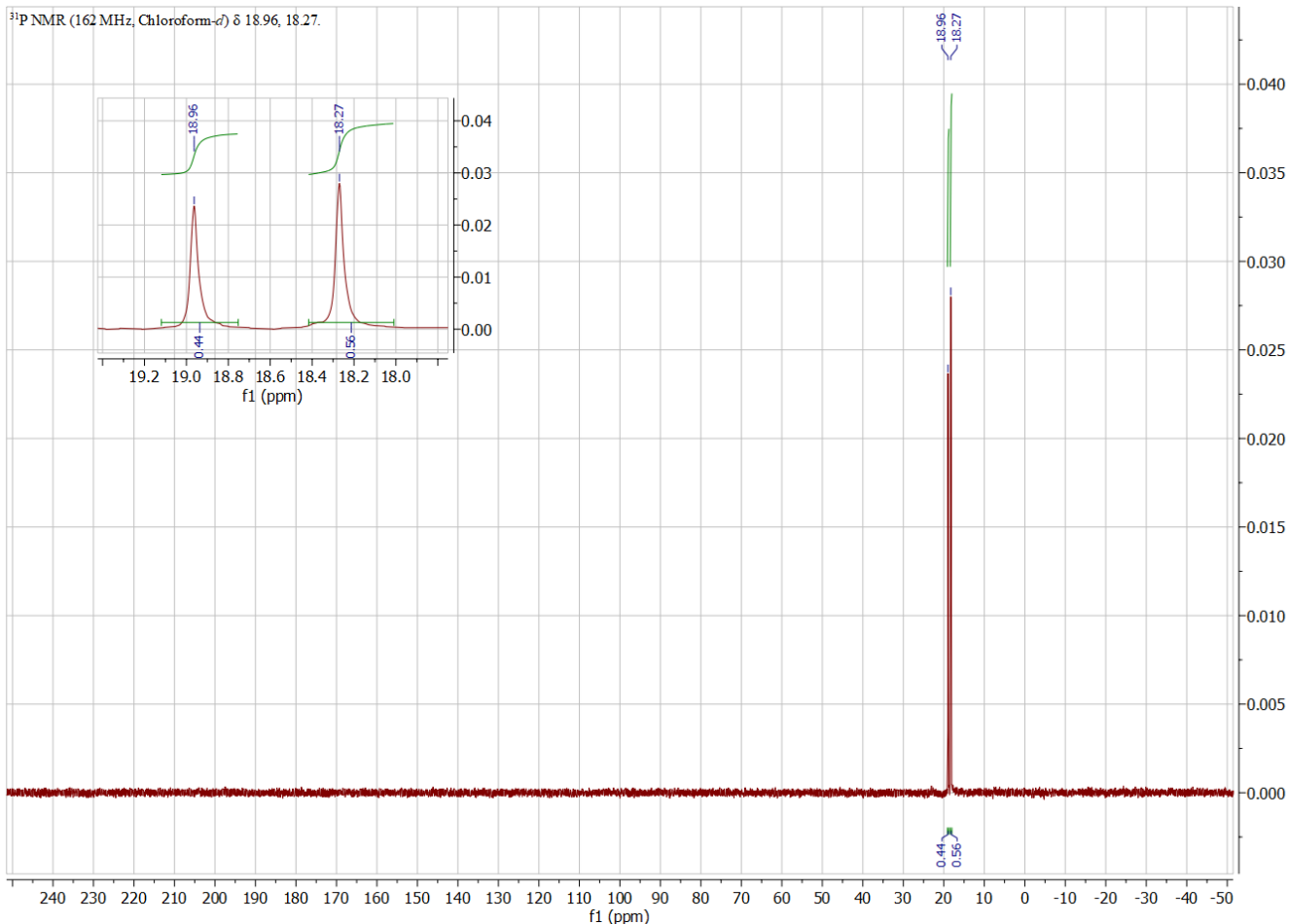
HRMS: C₃₇H₅₄N₃O₇PS₂ [M+Na]⁺ calc. 770.3038 found 770.3038

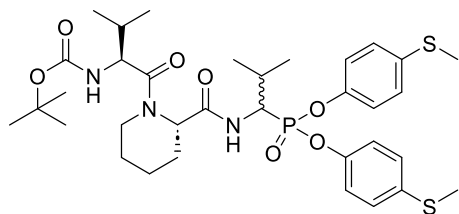
HPLC: purity >99%; retention time 21.010 and 21.287 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		21,010	166,256	1098,398	60,69	58,93	n.a.
2		21,287	105,767	761,811	38,61	40,87	n.a.
3		21,907	1,931	3,737	0,70	0,20	n.a.
Total:			273,954	1863,946	100,00	100,00	

^{31}P NMR (162 MHz, Chloroform- d) δ 18.96, 18.27.



(30) Boc-L-Val-L-Pip-Val^P(OPh-4-SCH₃)₂

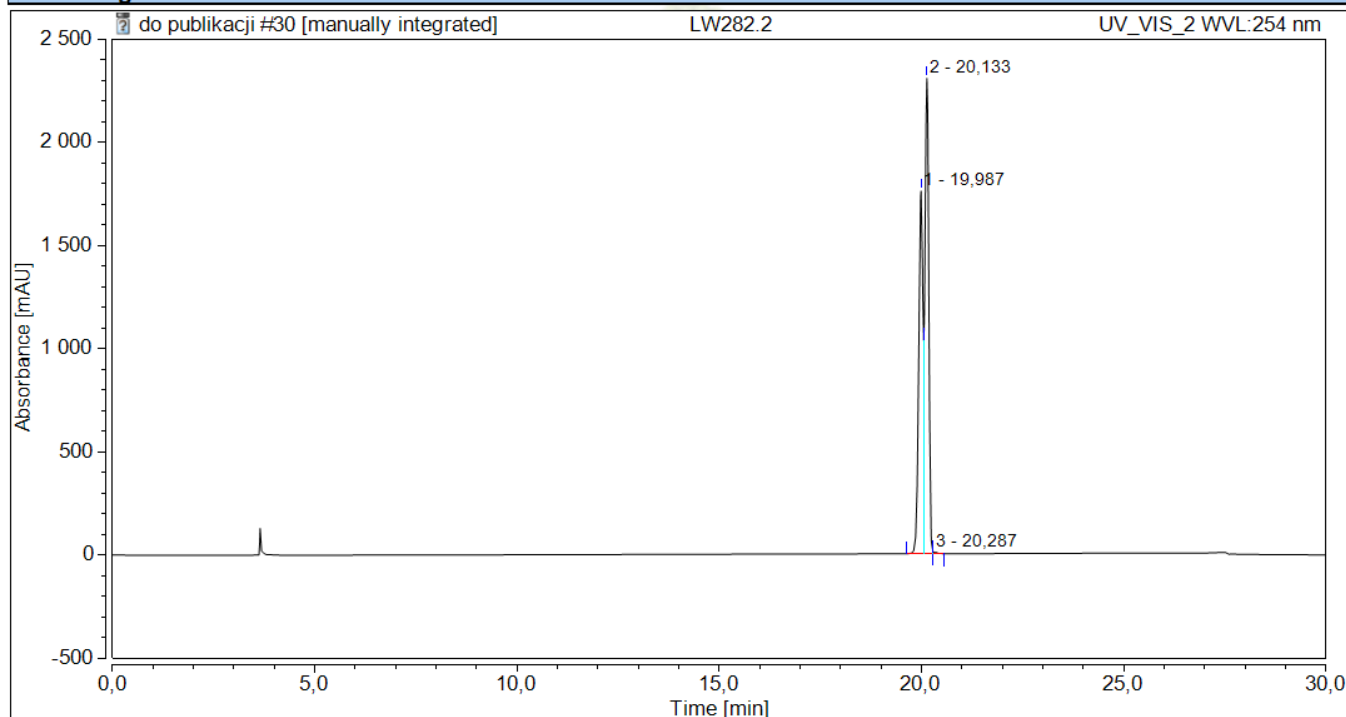
Name: *tert*-butyl ((2*S*)-1-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)piperidin-1-yl)-3-methyl-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.97 (s, 19%), 18.69 (s, 39%), 18.11 (s, 42%).

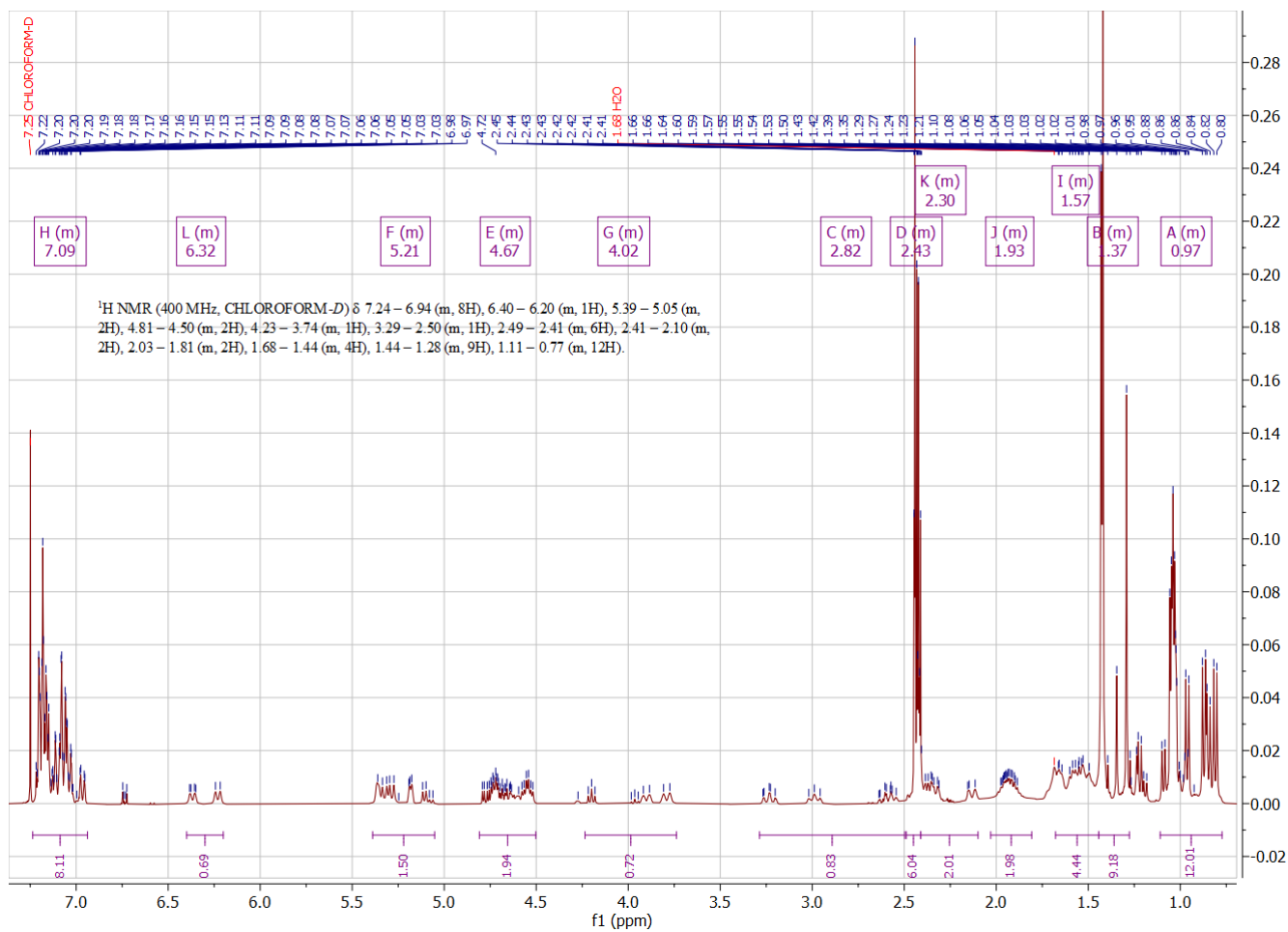
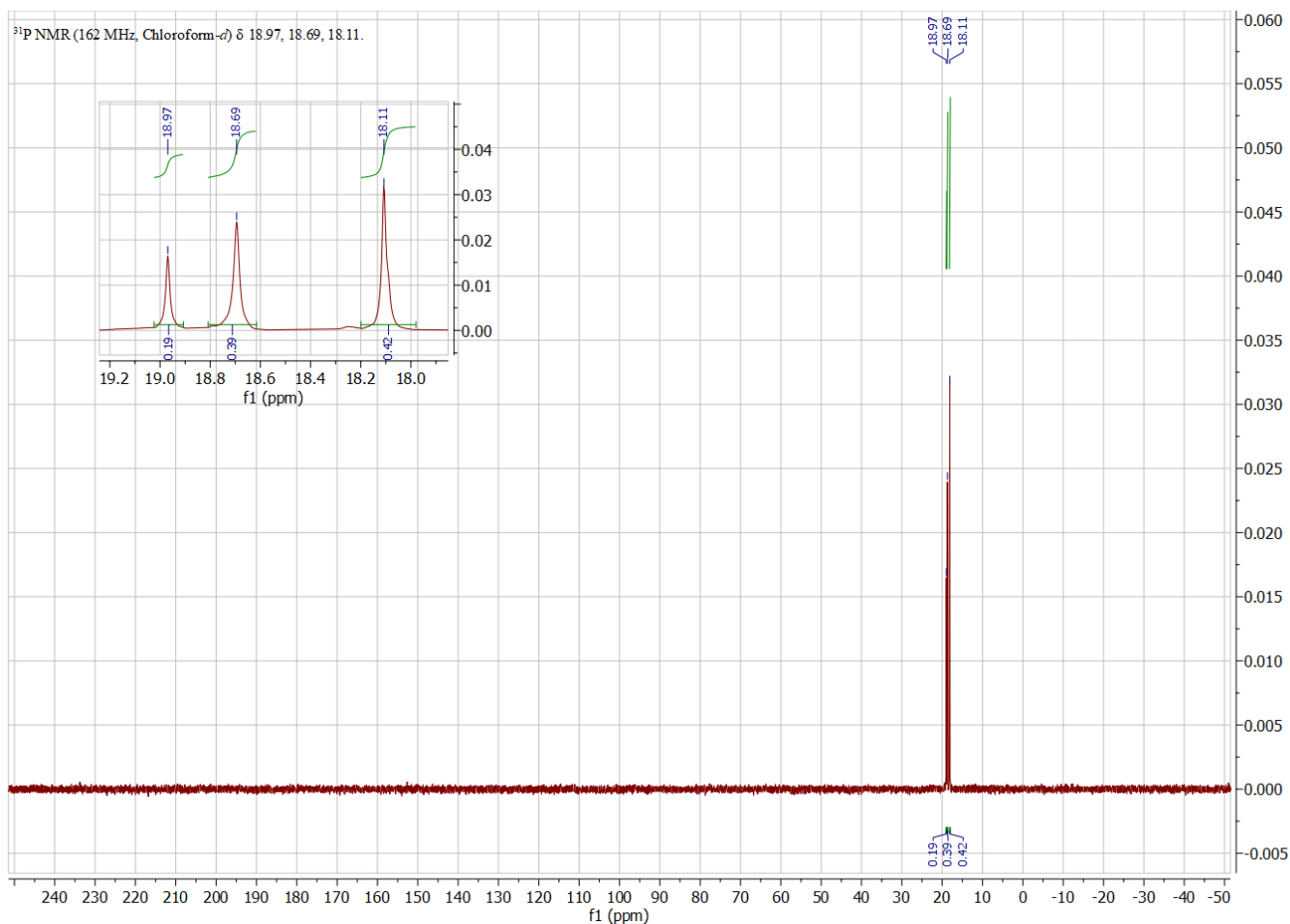
¹H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 6.94 (m, 8H, 8xArH), 6.40 – 6.20 (m, 1H, NH), 5.39 – 5.05 (m, 2H, NH, CH), 4.81 – 4.50 (m, 2H, CH₂), 4.23 – 3.74 (m, 1H, CHP), 3.29 – 2.50 (m, 1H, CH), 2.49 – 2.41 (m, 6H, 2xSCH₃), 2.41 – 2.10 (m, 2H, 2xCH), 2.03 – 1.81 (m, 2H, CH₂), 1.68 – 1.44 (m, 4H, 2xCH₂), 1.44 – 1.28 (m, 9H, Boc), 1.11 – 0.77 (m, 12H, 4xCH₃).

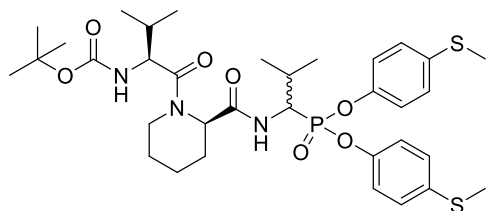
HRMS: C₃₄H₅₀N₃O₇PS₂ [M+Na]⁺ calc. 730.2725 found 730.2708

HPLC: purity >99%; retention time 19.987 and 20.133 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19,987	208,225	1756,423	44,81	43,20	n.a.
2		20,133	255,759	2302,715	55,04	56,64	n.a.
3		20,287	0,720	6,307	0,15	0,16	n.a.
Total:			464,704	4065,445	100,00	100,00	



(31) Boc-L-Val-D-Pip-Val^P(OPh-4-SCH₃)₂

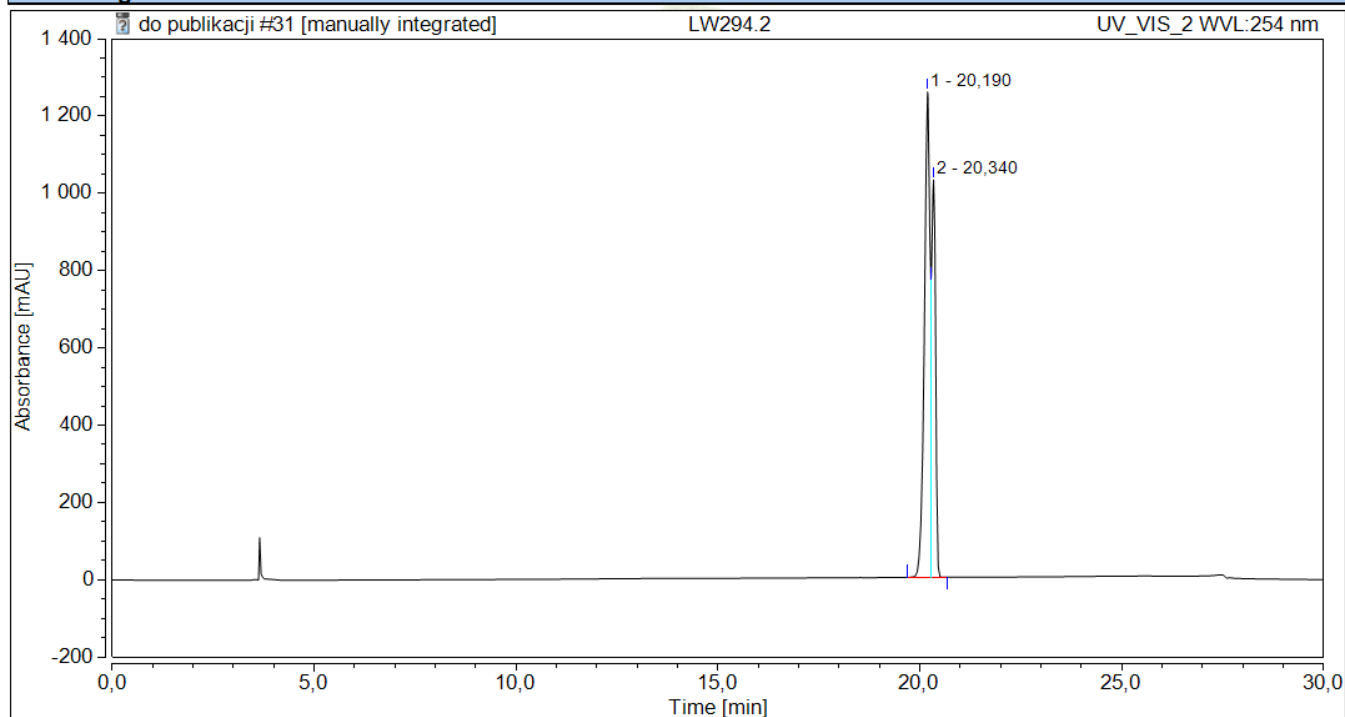
Name: *tert*-butyl ((2*S*)-1-((2*R*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)piperidin-1-yl)-3-methyl-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.66 (s, 53%), 18.10 (s, 47%).

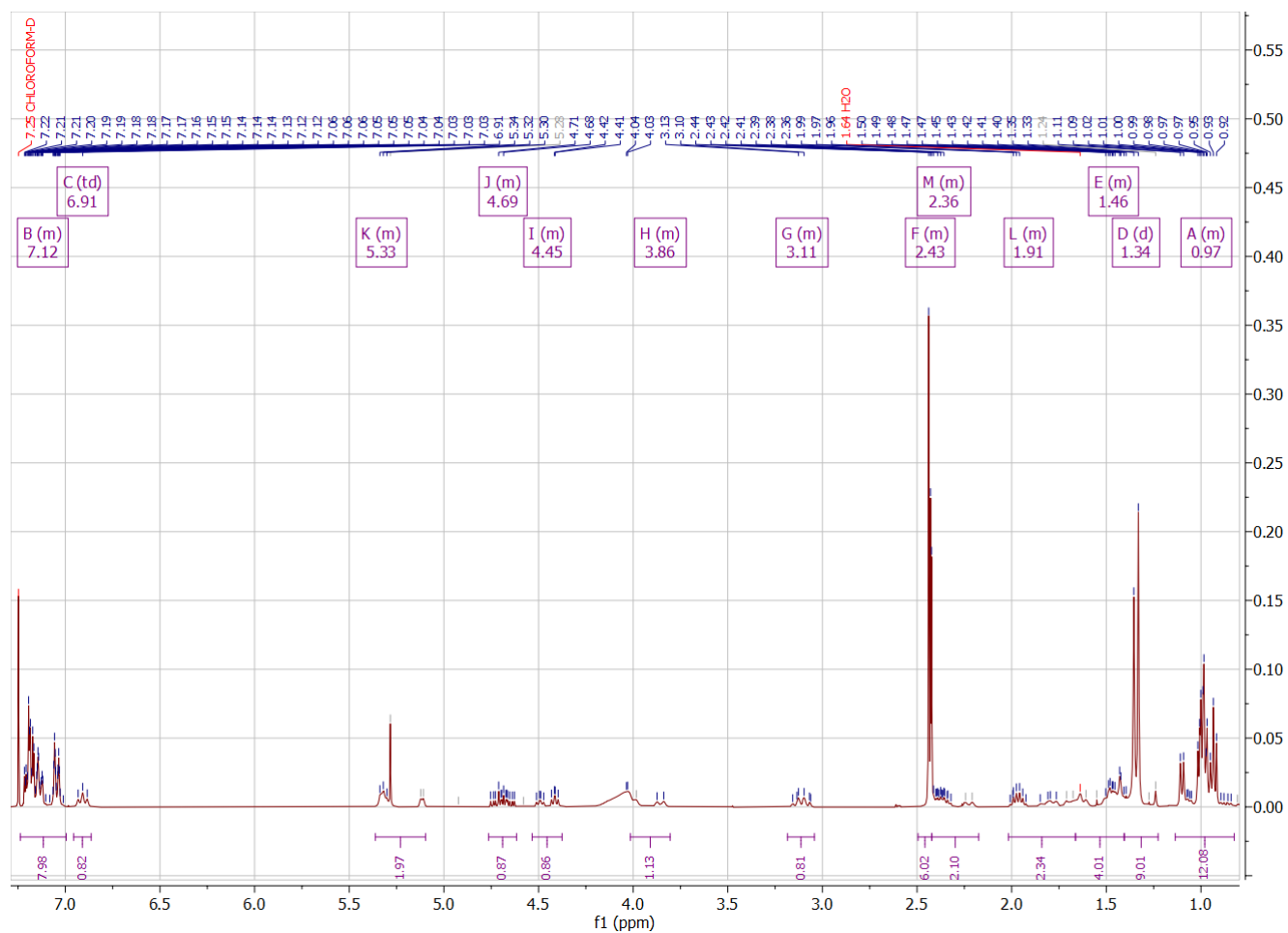
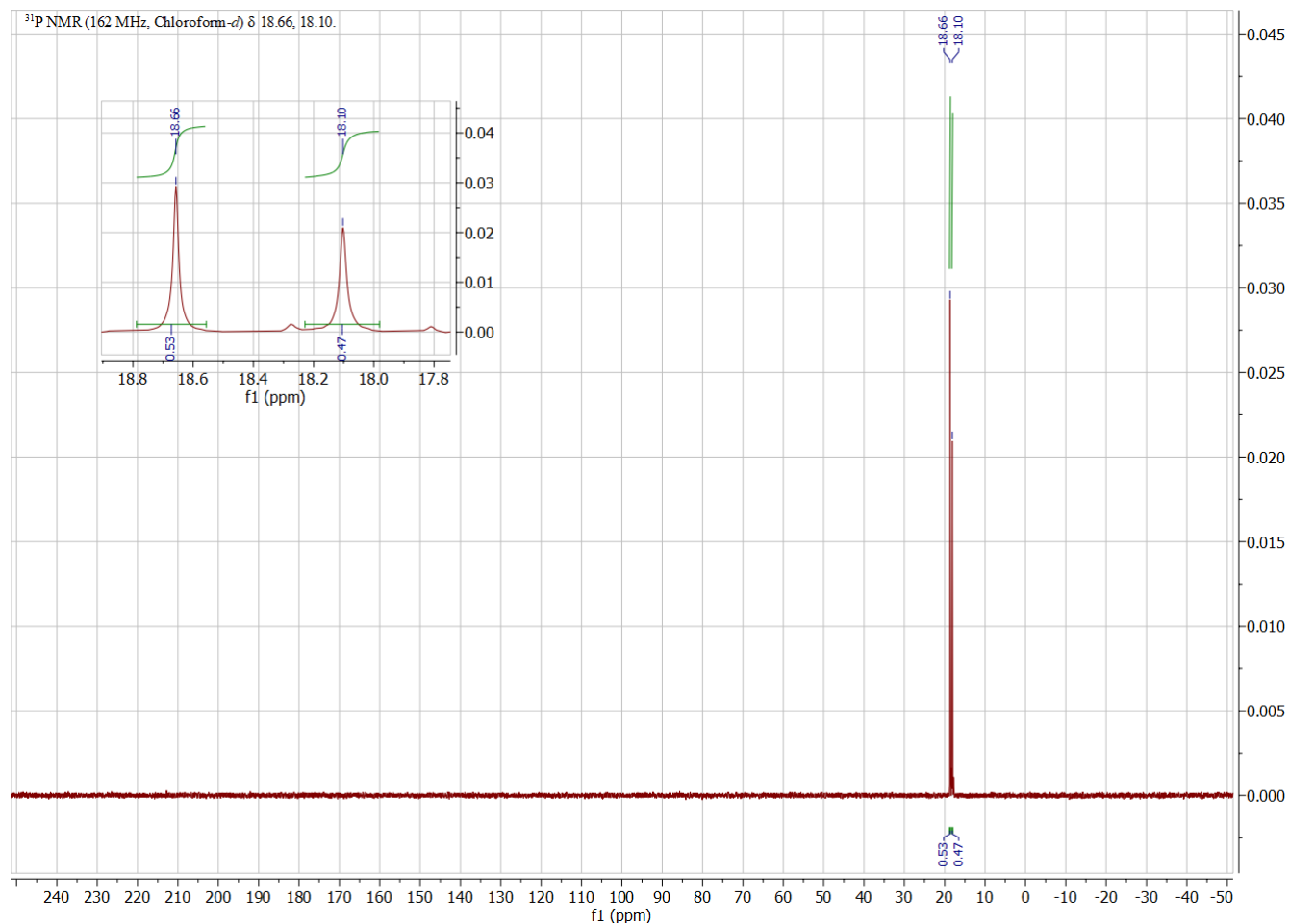
¹H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.00 (m, 8H, 8xArH), 6.91 (td, *J* = 9.6, 9.6 Hz, 1H, NH), 5.36 – 5.10 (m, 2H, NH, CH), 4.76 – 4.62 (m, 1H, CHP), 4.53 – 4.38 (m, 1H, CH), 4.01 – 3.80 (m, 1H, CH₂), 3.18 – 3.04 (m, 1H, CH₂), 2.49 – 2.42 (m, 6H, 2xSCH₃), 2.42 – 2.17 (m, 2H, 2xCH), 2.02 – 1.66 (m, 2H, CH₂), 1.66 – 1.41 (m, 4H, 2xCH₂), 1.34 (d, *J* = 9.6 Hz, 9H, Boc), 1.14 – 0.82 (m, 12H, 4xCH₃).

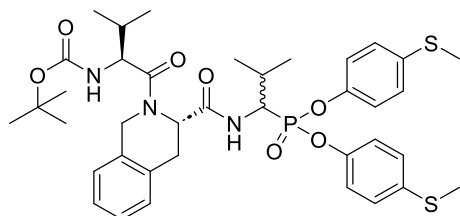
HRMS: C₃₄H₅₀N₃O₇PS₂ [M+Na]⁺ calc. 730.2725 found 730.2713

HPLC: purity >99%; retention time 20.190 and 20.340 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20,190	199,441	1256,077	62,39	54,98	n.a.
2		20,340	120,237	1028,374	37,61	45,02	n.a.
Total:			319,679	2284,451	100,00	100,00	



(32) Boc-L-Val-L-Tic-Val^P(OPh-4-SCH₃)₂

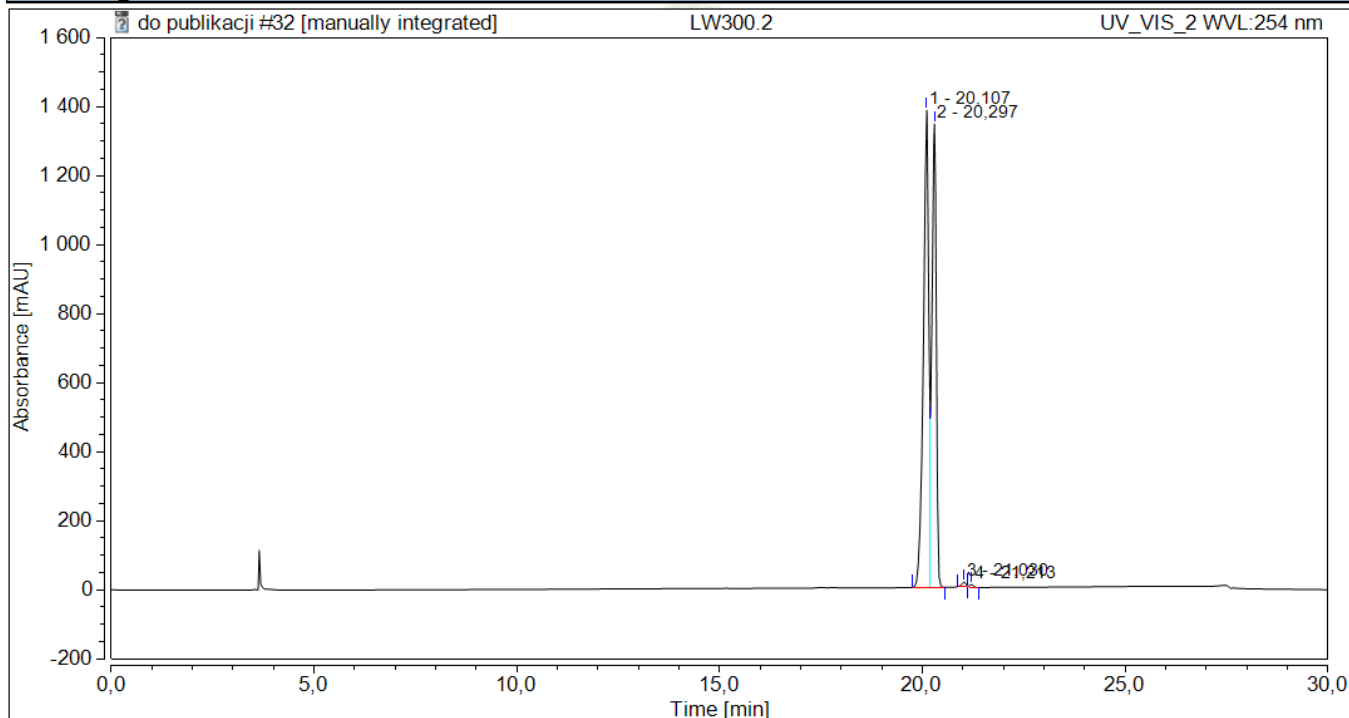
Name: *tert*-butyl ((2*S*)-1-((3*S*)-3-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)-3,4-dihydroisoquinolin-2(1*H*)-yl)-3-methyl-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 19.08 (s, 21%), 18.64 (s, 25%), 18.21 (s, 47%), 17.96 (s, 7%).

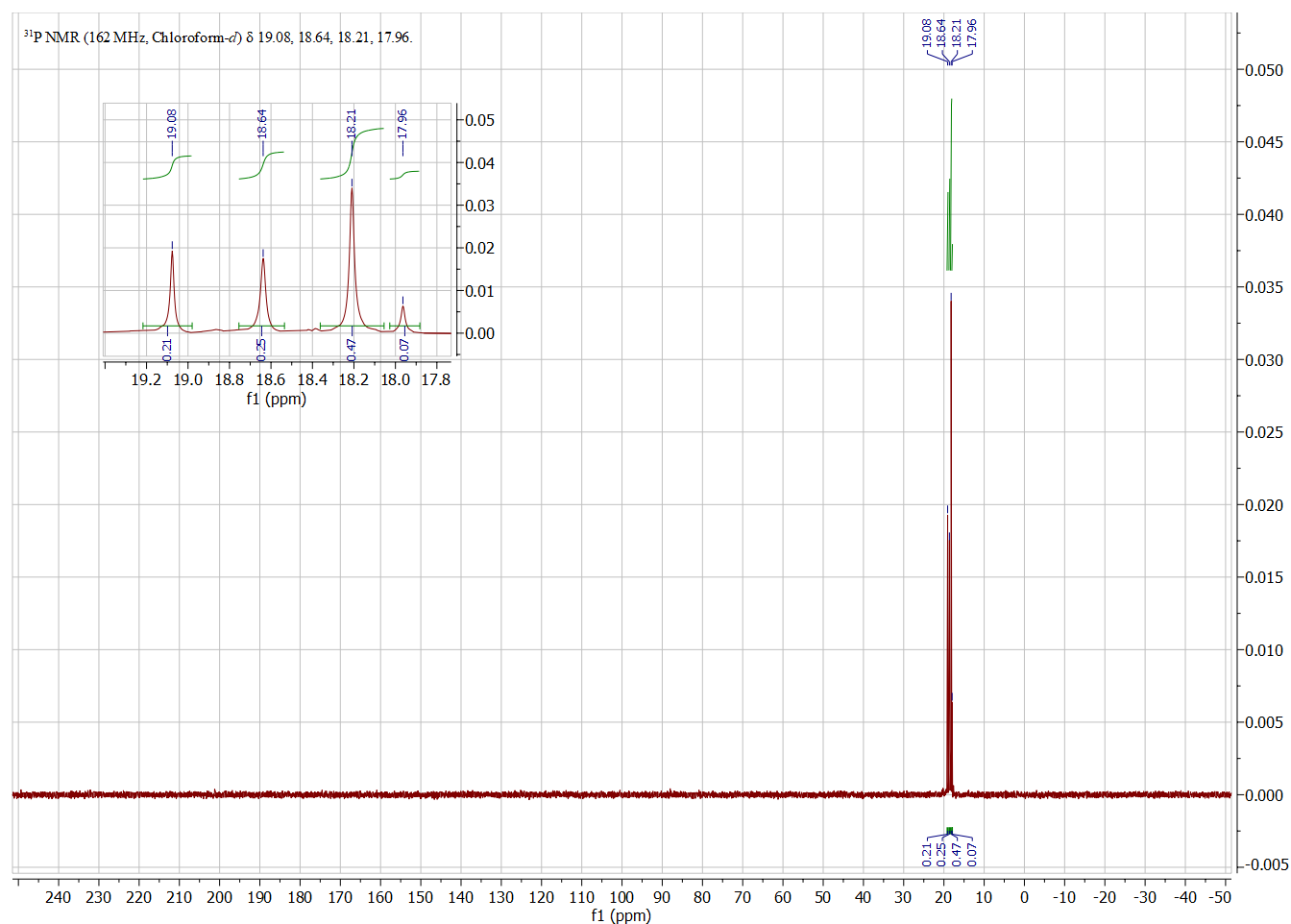
¹H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 6.80 (m, 12H, 12xArH), 6.77 – 6.41 (m, 1H, NH), 5.47 – 5.14 (m, 1H, NH), 4.99 – 4.87 (m, 1H, CH), 4.74 – 4.11 (m, 3H, CH₂, CHP), 3.71 – 2.56 (m, 3H, CH₂, CH), 2.49 – 2.37 (m, 6H, 2xSCH₃), 2.36 – 2.17 (m, 1H, CH), 2.12 – 1.88 (m, 1H, CH), 1.44 – 1.30 (m, 9H, Boc), 1.15 – 0.81 (m, 12H, 4xCH₃).

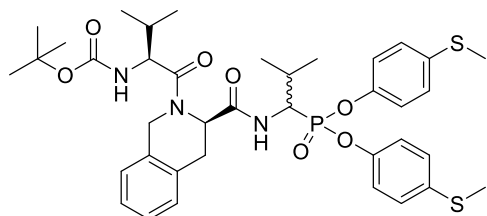
HRMS: C₃₈H₅₀N₃O₇PS₂ [M+Na]⁺ calc. 778.2725 found 778.2715

HPLC: purity >99%; retention time 20.107 and 20.297 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		20,107	208,628	1381,674	54,93	50,32	n.a.
2		20,297	168,529	1341,930	44,37	48,87	n.a.
3		21,030	1,793	14,491	0,47	0,53	n.a.
4		21,213	0,843	7,849	0,22	0,29	n.a.
Total:			379,794	2745,945	100,00	100,00	



(33) Boc-L-Val-D-Tic- Val^P(OPh-4-SCH₃)₂

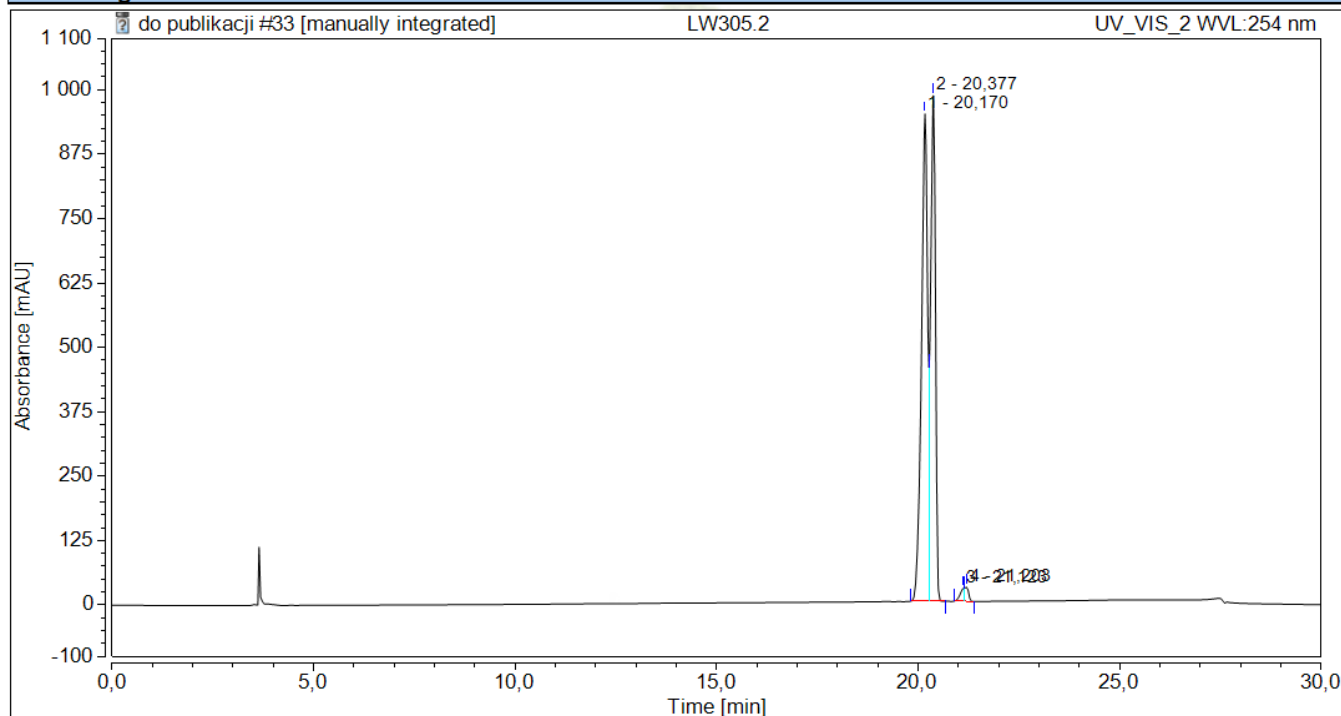
Name: *tert*-butyl ((2*S*)-1-((3*R*)-3-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)-3,4-dihydroisoquinolin-2(1*H*)-yl)-3-methyl-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.79 (s, 46%), 18.32 (s, 54%).

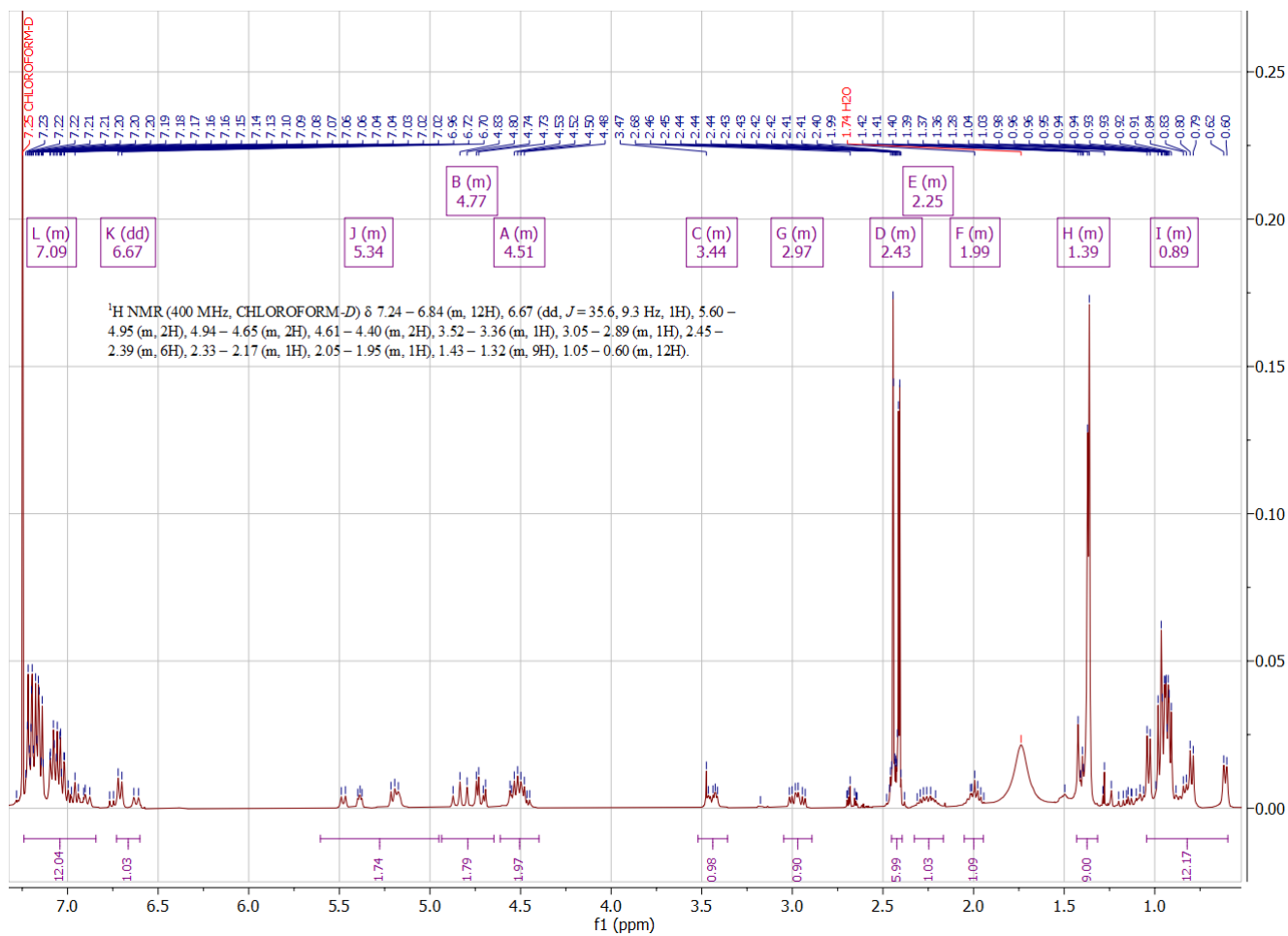
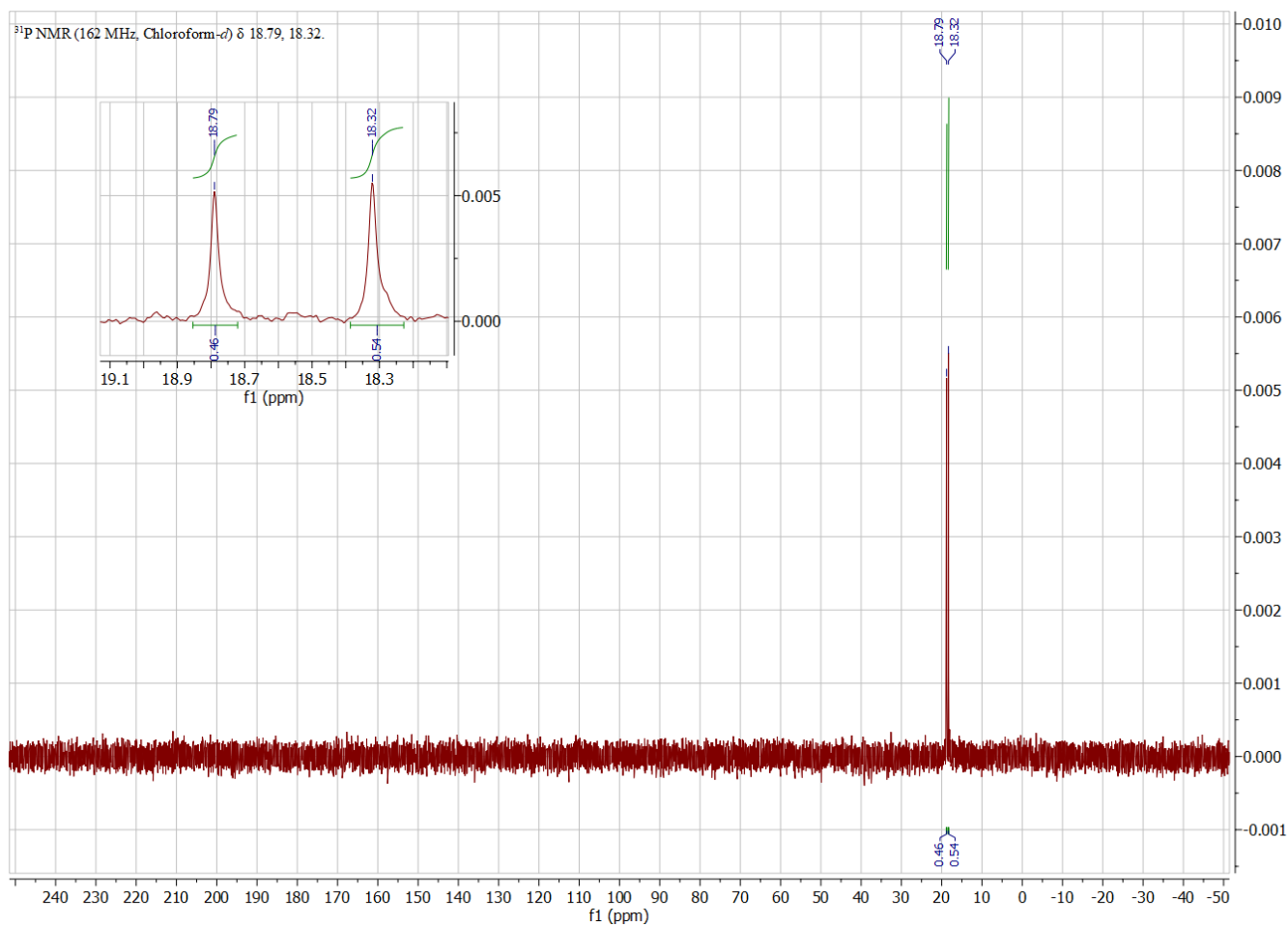
¹H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 6.84 (m, 12H, 12xArH), 6.67 (dd, *J* = 35.6, 9.3 Hz, 1H, NH), 5.60 – 4.95 (m, 2H, NH, CH), 4.94 – 4.65 (m, 2H, CH₂), 4.61 – 4.40 (m, 2H, CH₂), 3.52 – 3.36 (m, 1H, CHP), 3.05 – 2.89 (m, 1H, CH), 2.45 – 2.39 (m, 6H, 2xSCH₃), 2.33 – 2.17 (m, 1H, CH), 2.05 – 1.95 (m, 1H, CH), 1.43 – 1.32 (m, 9H, Boc), 1.05 – 0.60 (m, 12H, 4xCH₃).

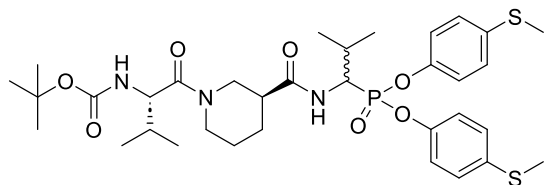
HRMS: C₃₈H₅₀N₃O₇PS₂ [M+Na]⁺ calc. 778.2725 found 778.2731

HPLC: purity >98%; retention time 20.377 and 20.170 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20,170	165,523	945,909	53,52	47,76	n.a.
2		20,377	137,718	981,307	44,53	49,55	n.a.
3		21,123	3,150	25,049	1,02	1,26	n.a.
4		21,203	2,907	28,320	0,94	1,43	n.a.
Total:			309,298	1980,585	100,00	100,00	



(34) Boc-L-Val-L-Nip-Val^P(OPh-4-SCH₃)₂

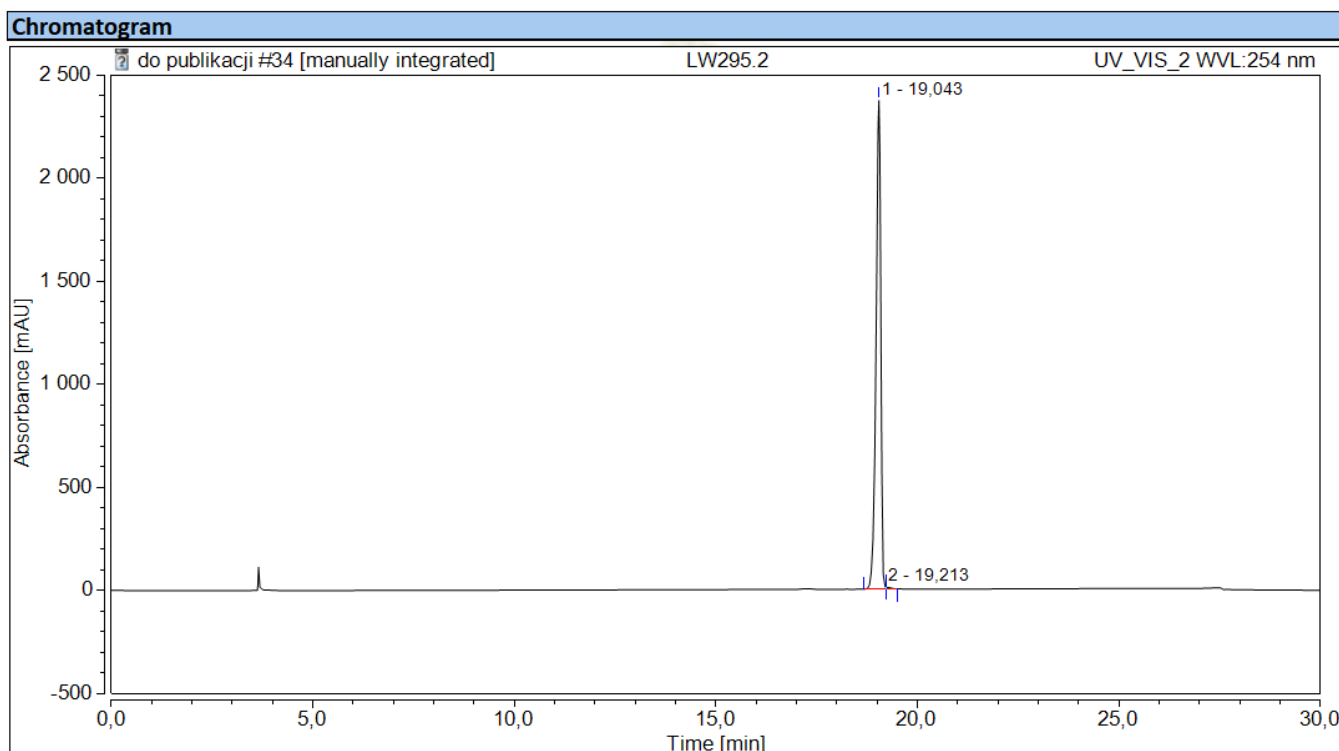
Name: *tert*-butyl ((2*S*)-1-((3*S*)-3-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)piperidin-1-yl)-3-methyl-1-oxobutan-2-yl)carbamate

³¹P NMR (243 MHz, CDCl₃) δ 18.42 (s, 32%), 17.78 (s, 30%), 17.57 (s, 13%), 17.44 (s, 25%).

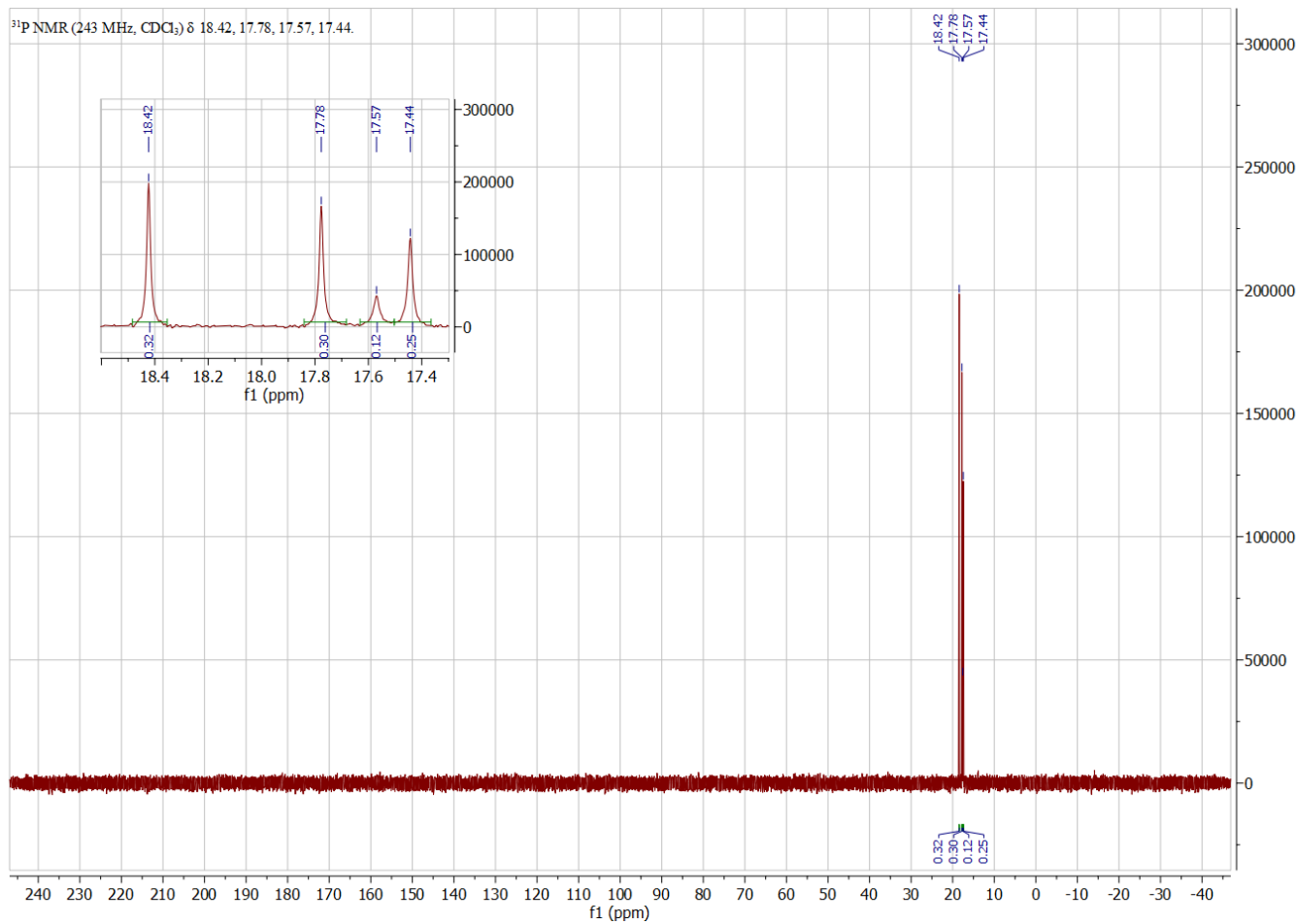
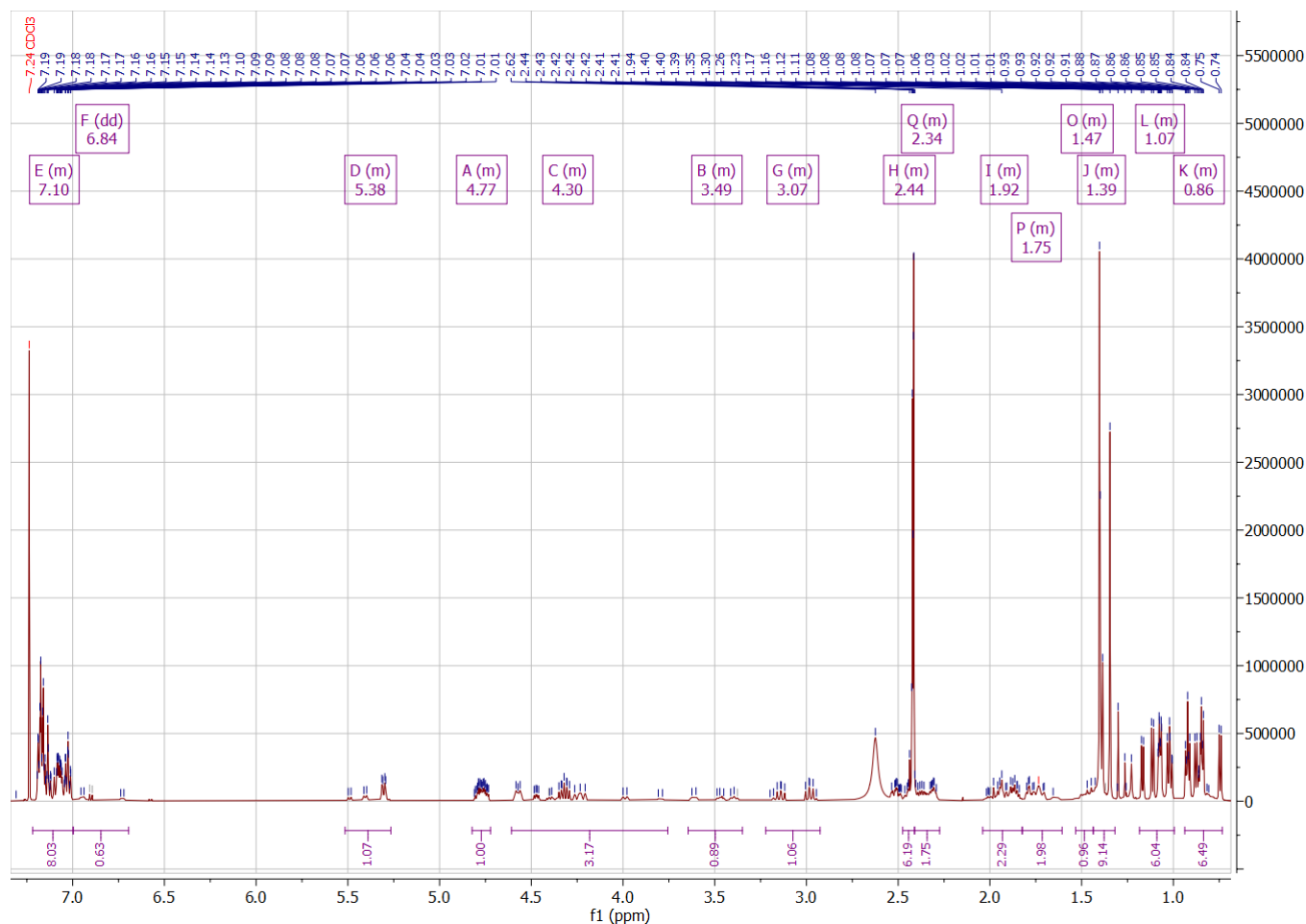
¹H NMR (601 MHz, CDCl₃) δ 7.22 – 7.00 (m, 8H, 8xArH), 6.84 (dd, *J* = 130.5, 10.2 Hz, 1H, NH), 5.52 – 5.27 (m, 1H, NH), 4.82 – 4.72 (m, 1H, CHP), 4.61 – 3.76 (m, 3H, CH₂, CH), 3.64 – 3.35 (m, 1H, CH₂), 3.22 – 2.93 (m, 1H, CH₂), 2.48 – 2.41 (m, 6H, 2xSCH₃), 2.41 – 2.27 (m, 2H, 2xCH), 2.04 – 1.82 (m, 2H, CH₂), 1.82 – 1.61 (m, 2H, CH₂), 1.53 – 1.44 (m, 1H, CH), 1.44 – 1.32 (m, 9H, Boc), 1.18 – 1.00 (m, 6H, 2xCH₃), 0.94 – 0.73 (m, 6H, 2xCH₃).

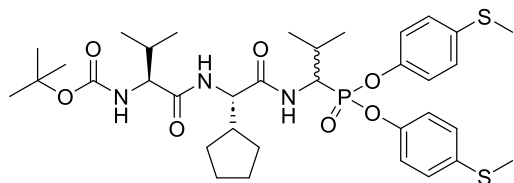
HRMS: C₃₄H₅₀N₃O₇PS₂ [M+Na]⁺ calc. 730.2725 found 730.2718

HPLC: purity >99%; retention time 19.043 min



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19,043	322,319	2369,236	99,63	99,61	n.a.
2		19,213	1,206	9,201	0,37	0,39	n.a.
Total:			323,524	2378,436	100,00	100,00	



(35) Boc-L-Val-L-Cpg-Val^P(OPh-4-SCH₃)₂

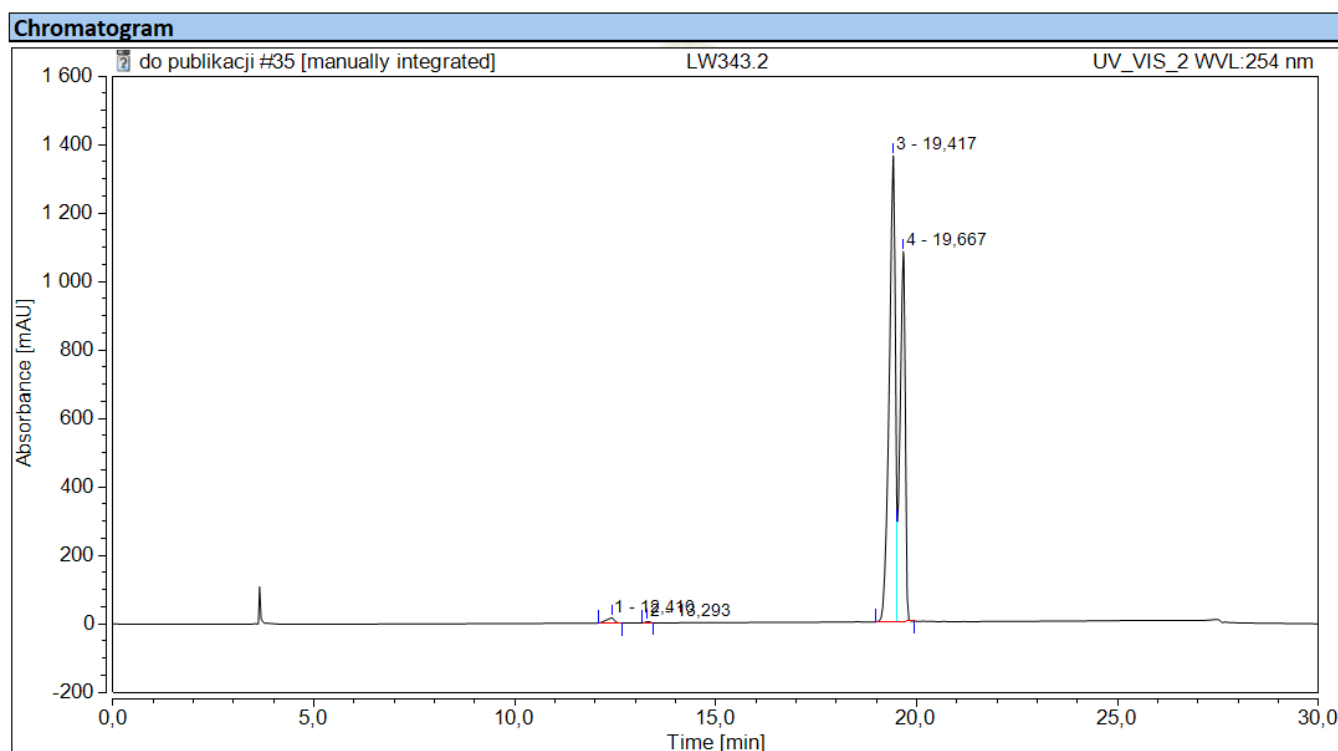
Name: *tert*-butyl ((2*S*)-1-(((1*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-1-cyclopentyl-2-oxoethyl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.43 (s, 45%), 18.40 (s, 55%).

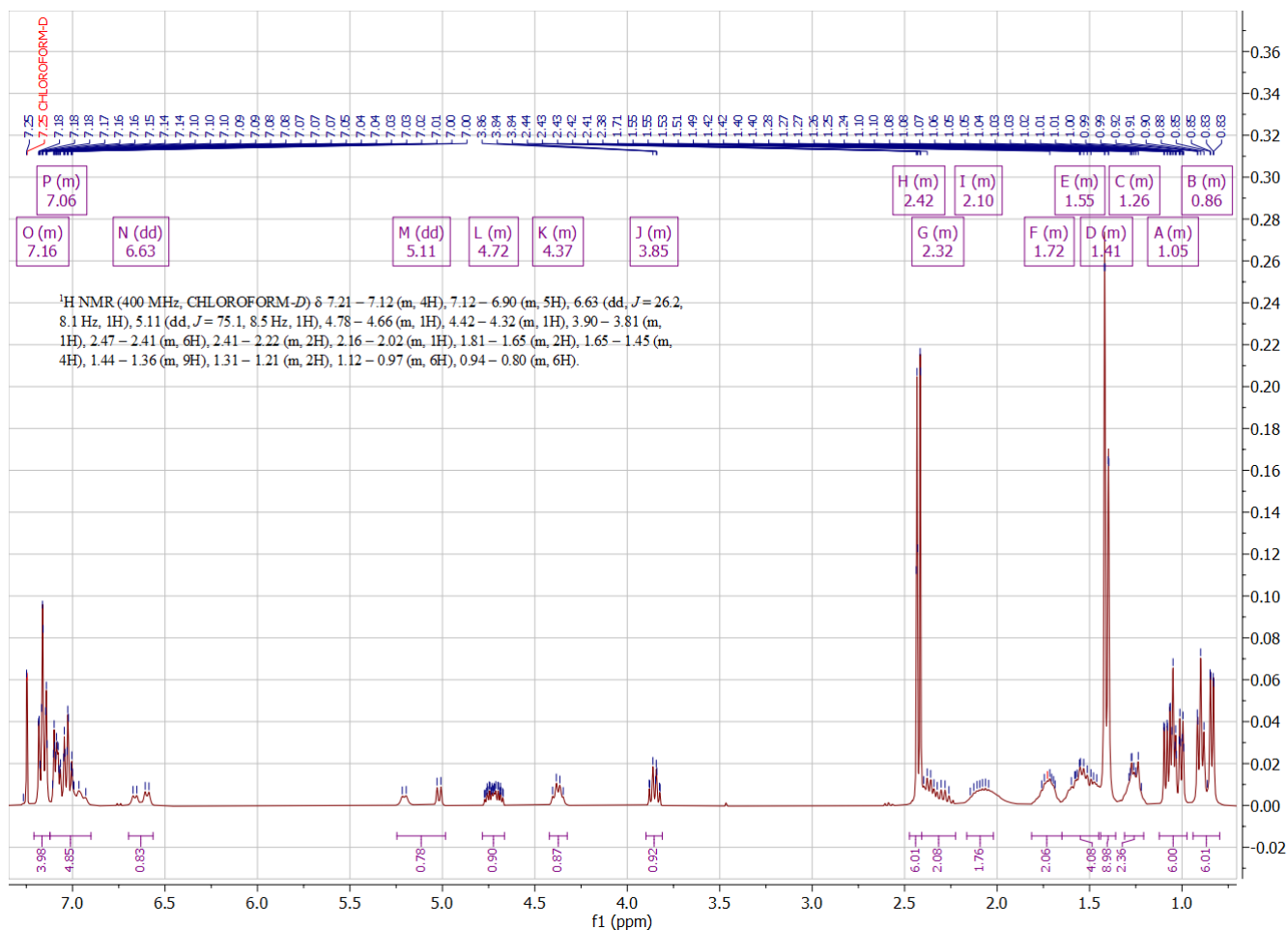
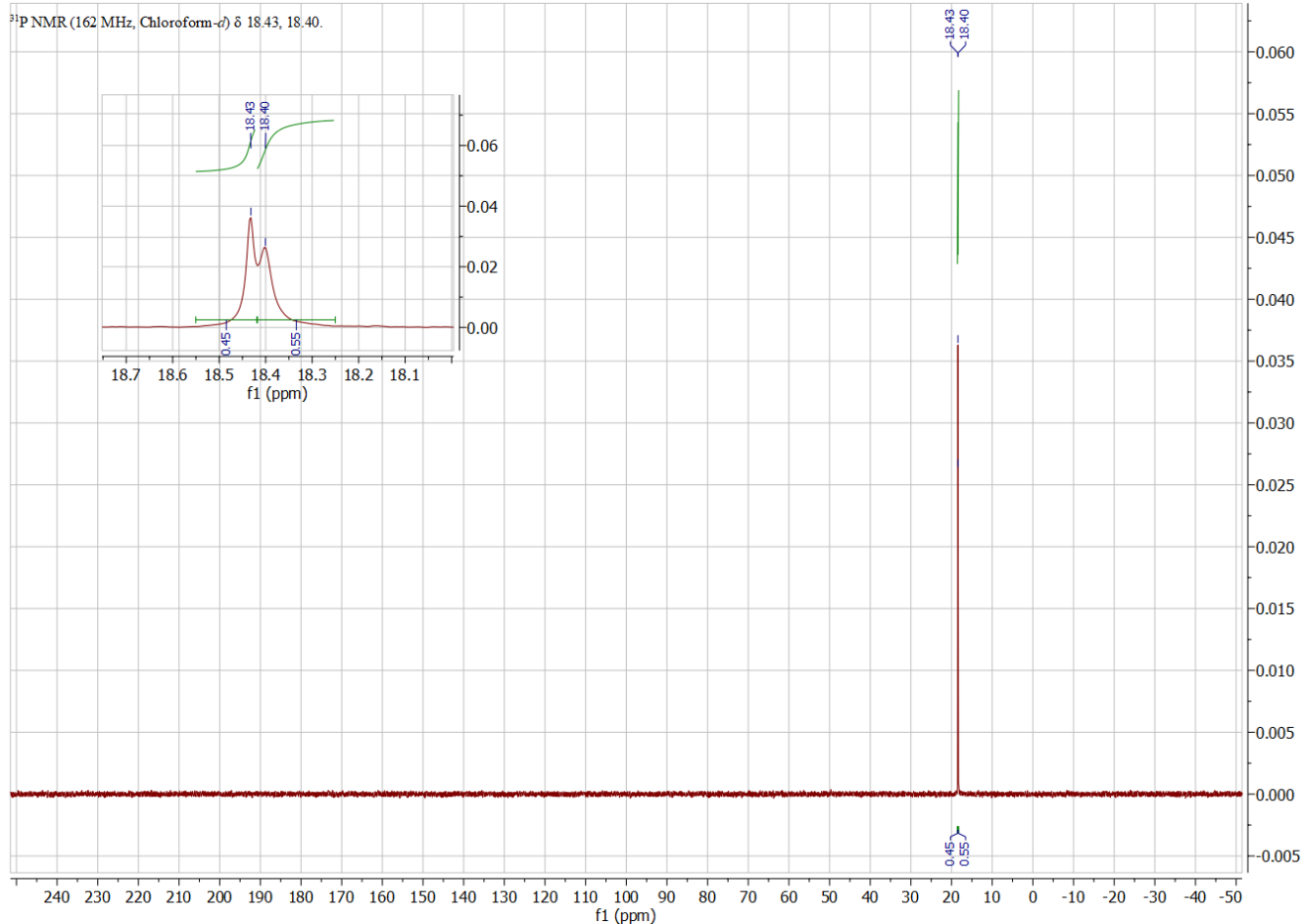
¹H NMR (400 MHz, Chloroform-*d*) δ 7.21 – 7.12 (m, 4H, 4xArH), 7.12 – 6.90 (m, 5H, 4xArH, NH), 6.63 (dd, *J* = 26.2, 8.1 Hz, 1H, NH), 5.11 (dd, *J* = 75.1, 8.5 Hz, 1H, NH), 4.78 – 4.66 (m, 1H, CHP), 4.42 – 4.32 (m, 1H, CH), 3.90 – 3.81 (m, 1H, CH), 2.47 – 2.41 (m, 6H, 2xSCH₃), 2.41 – 2.22 (m, 2H, 2xCH), 2.16 – 2.02 (m, 1H, CH), 1.81 – 1.65 (m, 2H, CH₂), 1.65 – 1.45 (m, 4H, 2xCH₂), 1.44 – 1.36 (m, 9H, Boc), 1.31 – 1.21 (m, 2H, CH₂), 1.12 – 0.97 (m, 6H, 2xCH₃), 0.94 – 0.80 (m, 6H, 2xCH₃).

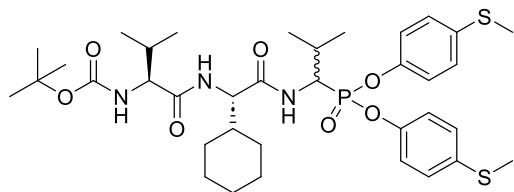
HRMS: C₃₅H₅₂N₃O₇PS₂ [M+Na]⁺ calc. 744.2882 found 744.2879

HPLC: purity >99%; retention time 19.417 and 19.667 min



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		12,410	3,516	15,279	0,87	0,62	n.a.
2		13,293	0,464	3,574	0,11	0,15	n.a.
3		19,417	240,607	1360,620	59,44	55,31	n.a.
4		19,667	160,180	1080,339	39,57	43,92	n.a.
Total:			404,768	2459,812	100,00	100,00	



(36) 344.2 Boc-L-Val-L-Chg-Val^P(OPh-4-SCH₃)₂

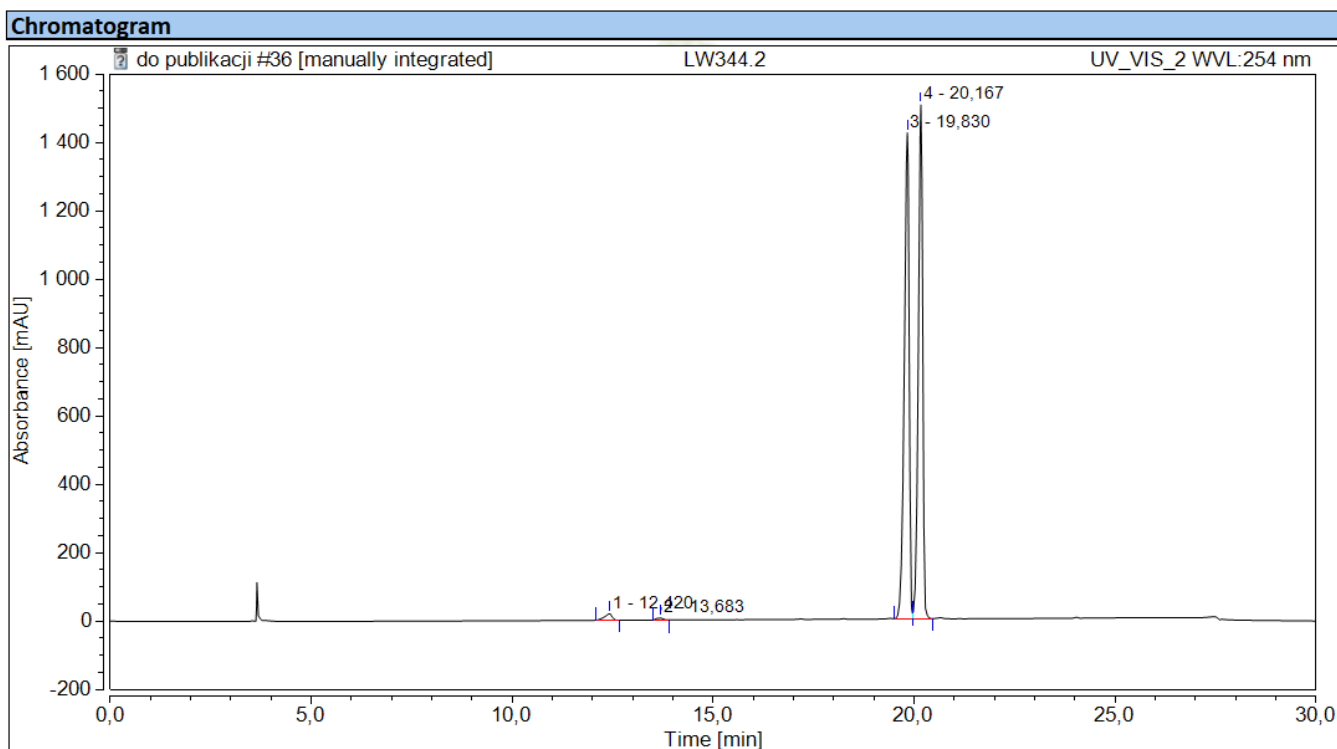
Name: *tert*-butyl ((2*S*)-1-(((1*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-1-cyclohexyl-2-oxoethyl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.34 (s).

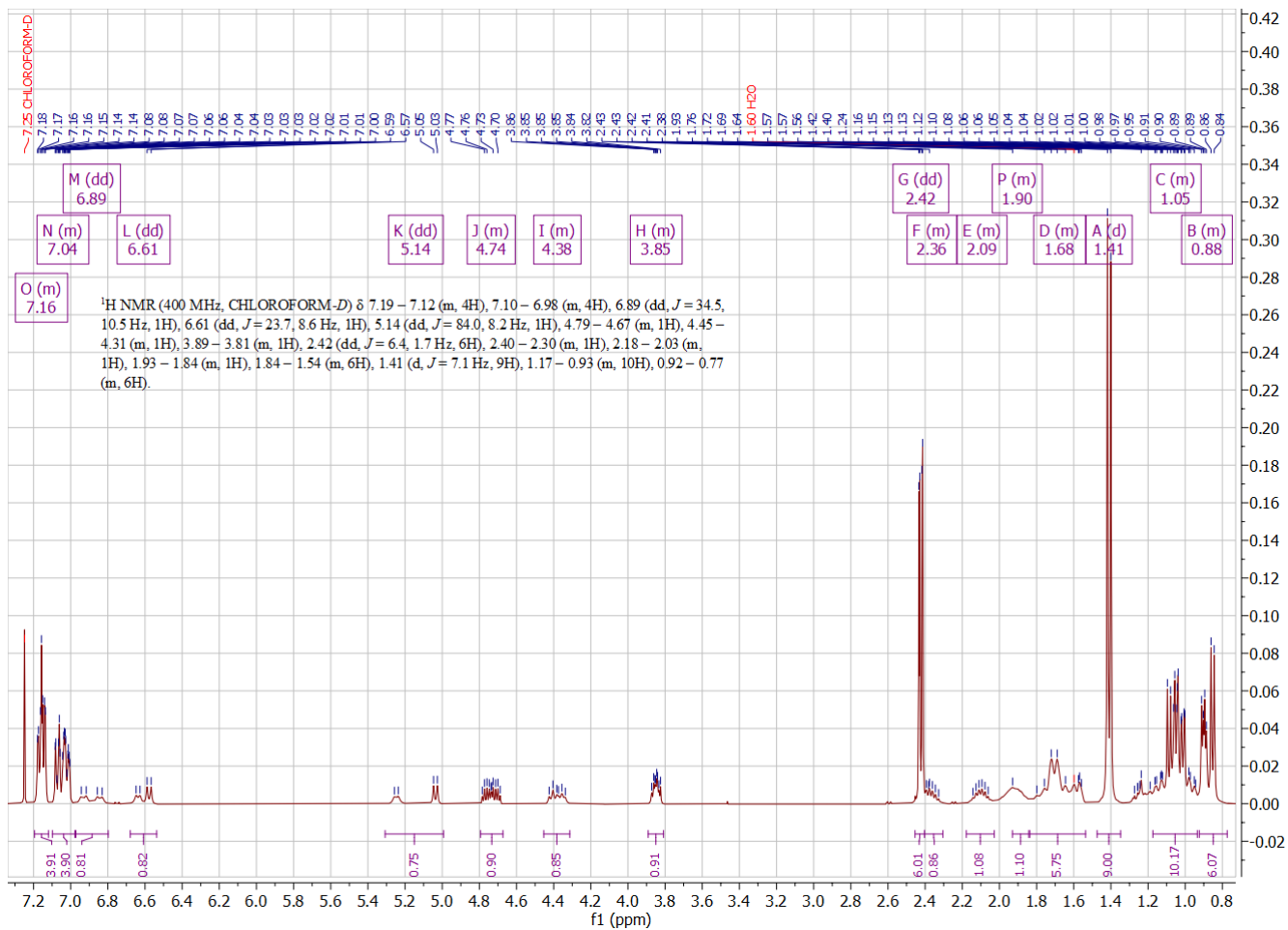
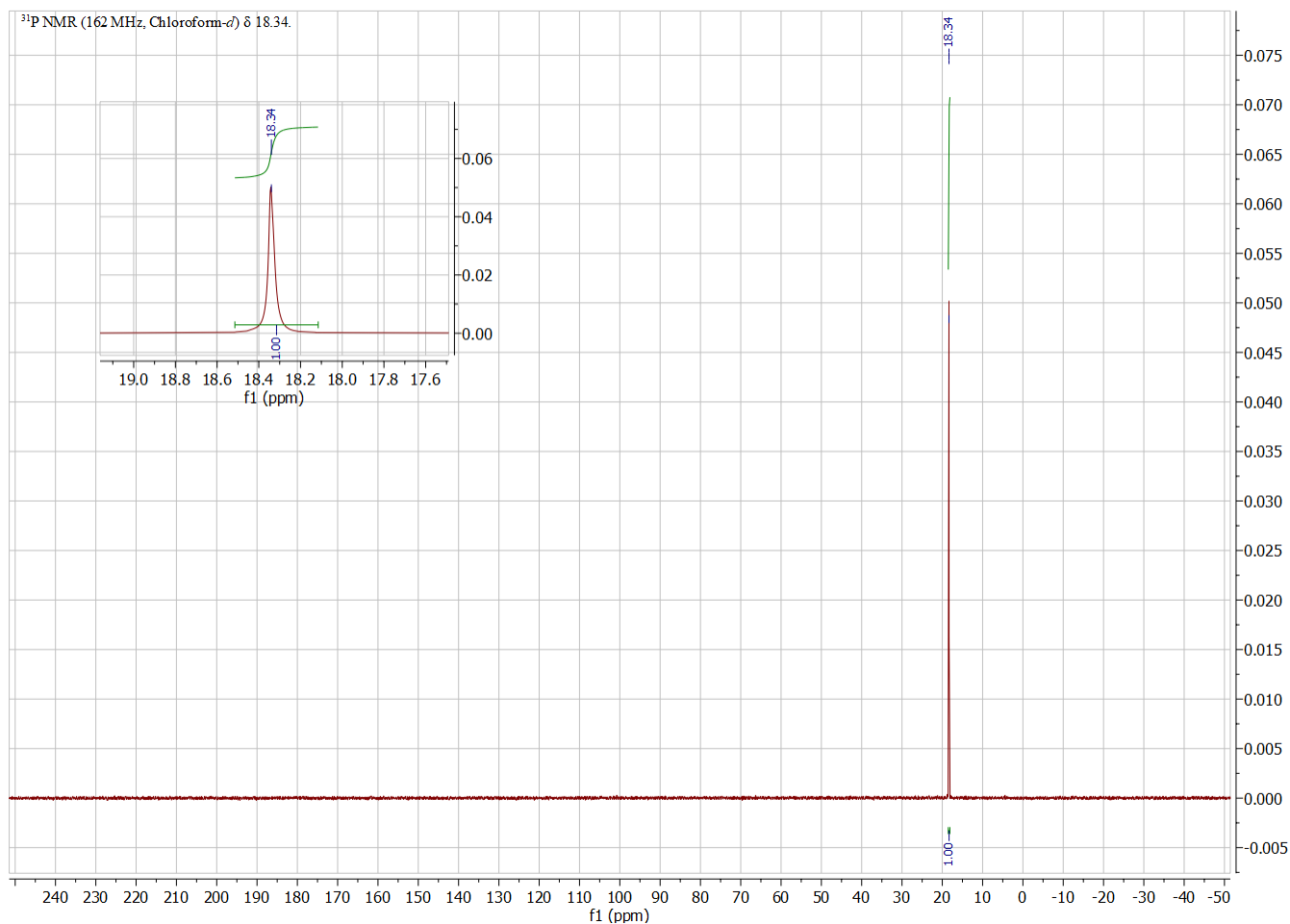
¹H NMR (400 MHz, Chloroform-*d*) δ 7.19 – 7.12 (m, 4H, 4xArH), 7.10 – 6.98 (m, 4H, 4xArH), 6.89 (dd, *J* = 34.5, 10.5 Hz, 1H, NH), 6.61 (dd, *J* = 23.7, 8.6 Hz, 1H, NH), 5.14 (dd, *J* = 84.0, 8.2 Hz, 1H, NH), 4.79 – 4.67 (m, 1H, CHP), 4.45 – 4.31 (m, 1H, CH), 3.89 – 3.81 (m, 1H, CH), 2.42 (dd, *J* = 6.4, 1.7 Hz, 6H, 2xSCH₃), 2.40 – 2.30 (m, 1H, CH), 2.18 – 2.03 (m, 1H, CH), 1.93 – 1.84 (m, 1H, CH), 1.84 – 1.54 (m, 6H, 3xCH₂), 1.41 (d, *J* = 7.1 Hz, 9H, Boc), 1.17 – 0.93 (m, 10H, 2xCH₃, 2xCH₂), 0.92 – 0.77 (m, 6H, 2xCH₃).

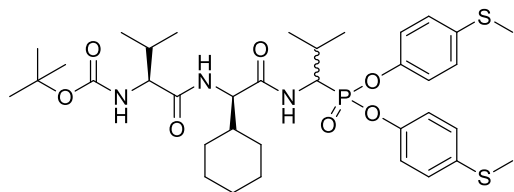
HRMS: C₃₆H₅₄N₃O₇PS₂ [M+Na]⁺ calc. 758.3038 found 758.3048

HPLC: purity >98%; retention time 19.830 and 20.167 min



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12,420	4,171	19,482	1,07	0,66	n.a.
2		13,683	1,126	6,356	0,29	0,22	n.a.
3		19,830	197,108	1420,715	50,46	48,18	n.a.
4		20,167	188,222	1502,174	48,18	50,94	n.a.
Total:			390,626	2948,726	100,00	100,00	



(37) Boc-L-Val-D-Chg-Val^P(OPh-4-SCH₃)₂

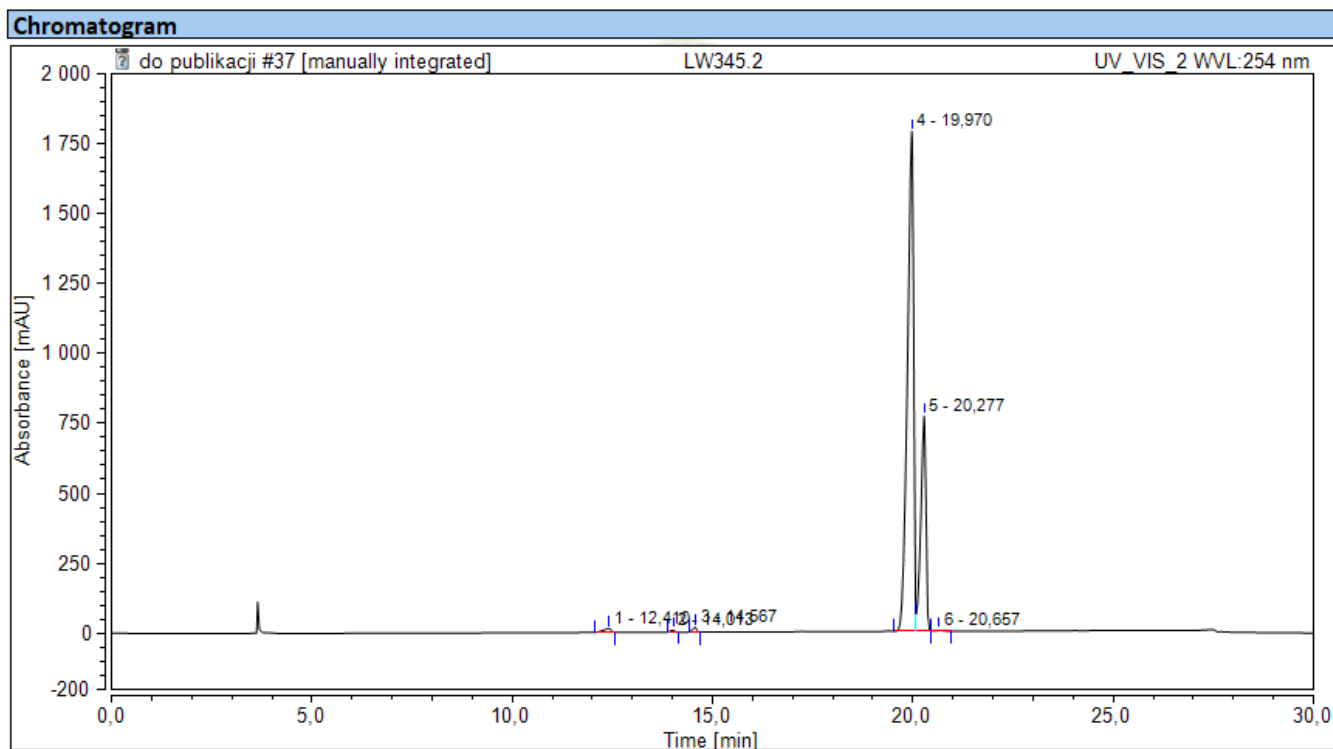
Name: *tert*-butyl ((2*S*)-1-(((1*R*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-1-cyclohexyl-2-oxoethyl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.39 (s, 47%), 18.21 (s, 53%).

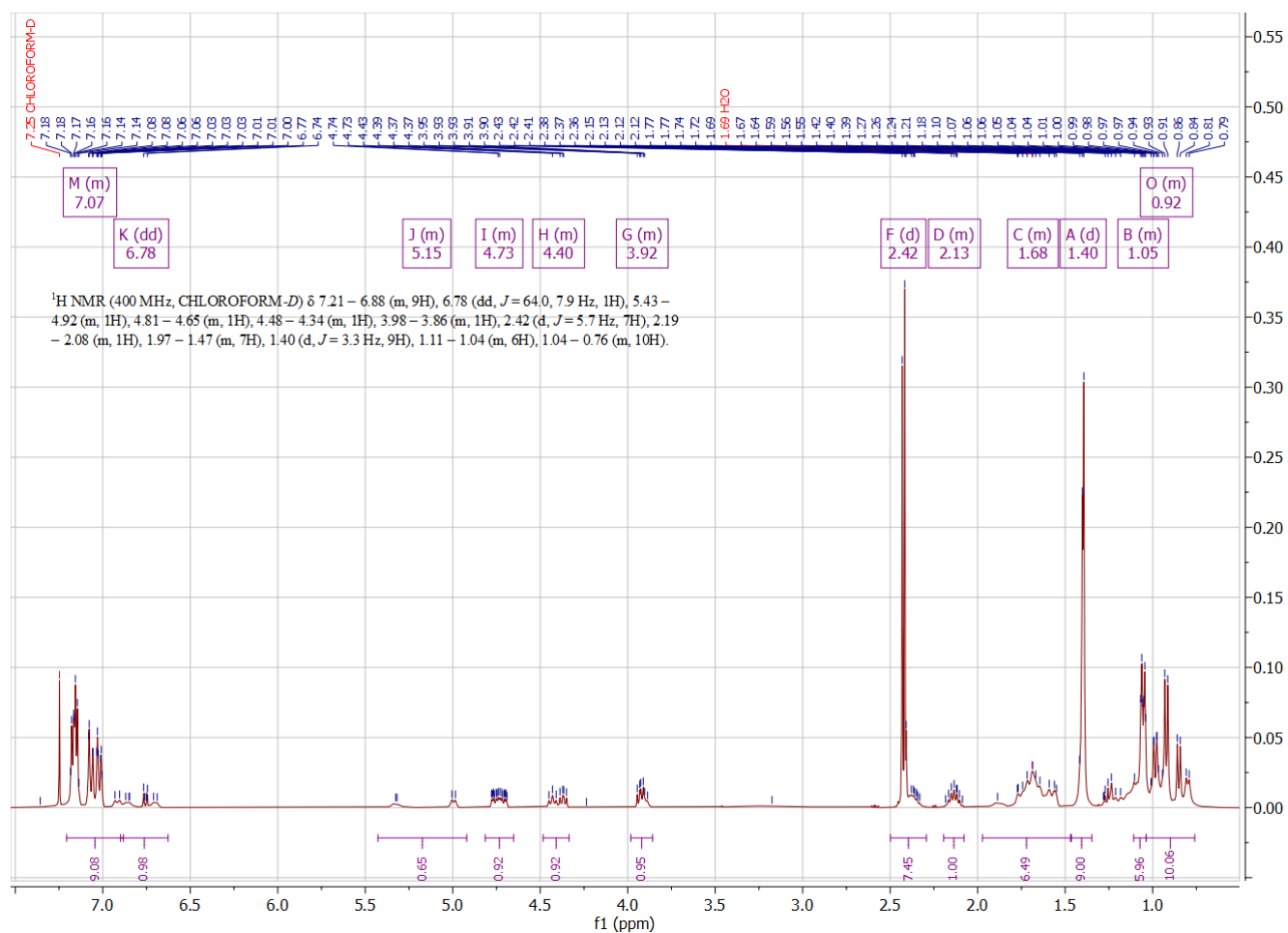
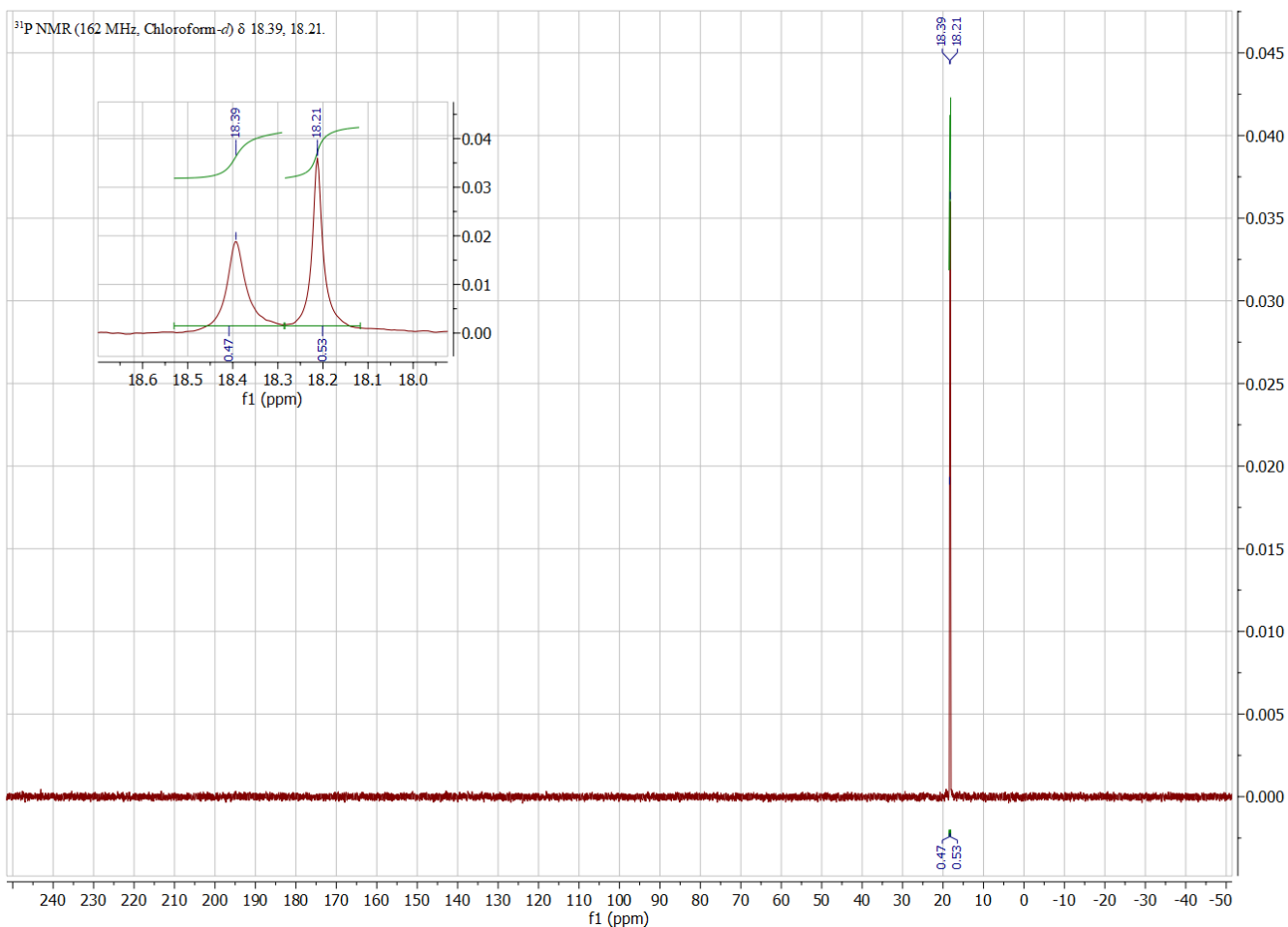
¹H NMR (400 MHz, Chloroform-*d*) δ 7.21 – 6.88 (m, 9H, 8xArH, NH), 6.78 (dd, *J* = 64.0, 7.9 Hz, 1H, NH), 5.43 – 4.92 (m, 1H, NH), 4.81 – 4.65 (m, 1H, CHP), 4.48 – 4.34 (m, 1H, CH), 3.98 – 3.86 (m, 1H, CH), 2.42 (d, *J* = 5.7 Hz, 7H, 2xSCH₃, CH), 2.19 – 2.08 (m, 1H, CH), 1.97 – 1.47 (m, 7H, 3xCH₂, CH), 1.40 (d, *J* = 3.3 Hz, 9H, Boc), 1.11 – 1.04 (m, 6H, 2xCH₃), 1.04 – 0.76 (m, 10H, 2xCH₃, 2xCH₂).

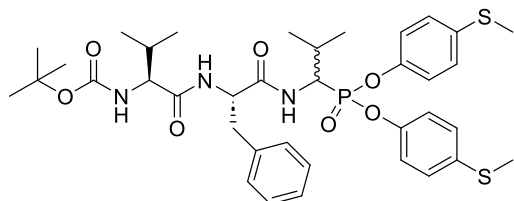
HRMS: C₃₆H₅₄N₃O₇PS₂ [M+Na]⁺ calc. 758.3038 found 758.3044

HPLC: purity >98%; retention time 19.970 and 20.277 min



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		12.410	3.235	14.505	0.74	0.56	n.a.
2		14.013	0.850	7.091	0.19	0.27	n.a.
3		14.567	2.034	17.931	0.46	0.69	n.a.
4		19.970	317.954	1788.303	72.27	68.77	n.a.
5		20.277	114.974	769.457	26.13	29.59	n.a.
6		20.657	0.912	3.168	0.21	0.12	n.a.
Total:			439,958	2600,456	100,00	100,00	



(38) Boc-L-Val-L-Phe- Val^P(OPh-4-SCH₃)₂

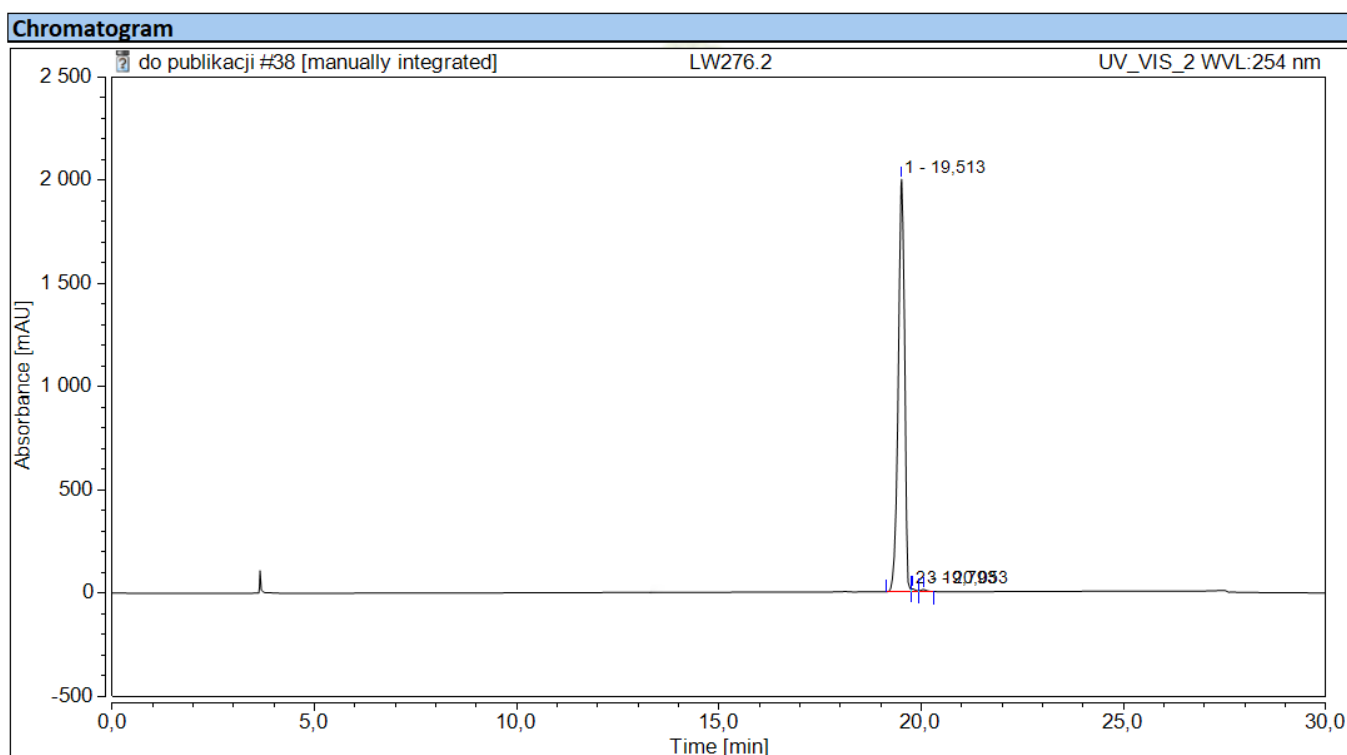
Name: *tert*-butyl ((2*S*)-1-(((2*S*)-1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-1-oxo-3-phenylpropan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.13 (s, 48%), 18.01 (s, 52%).

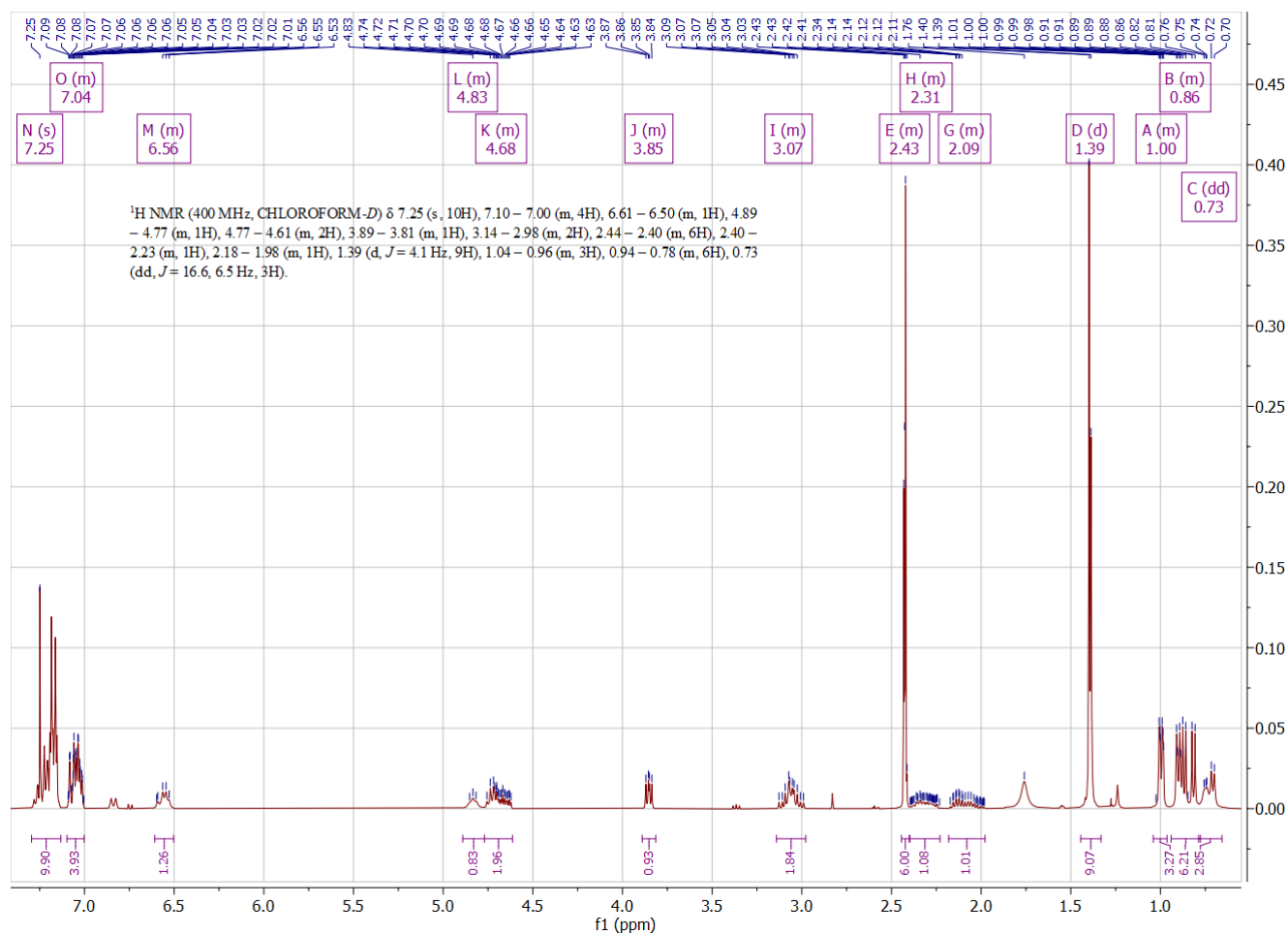
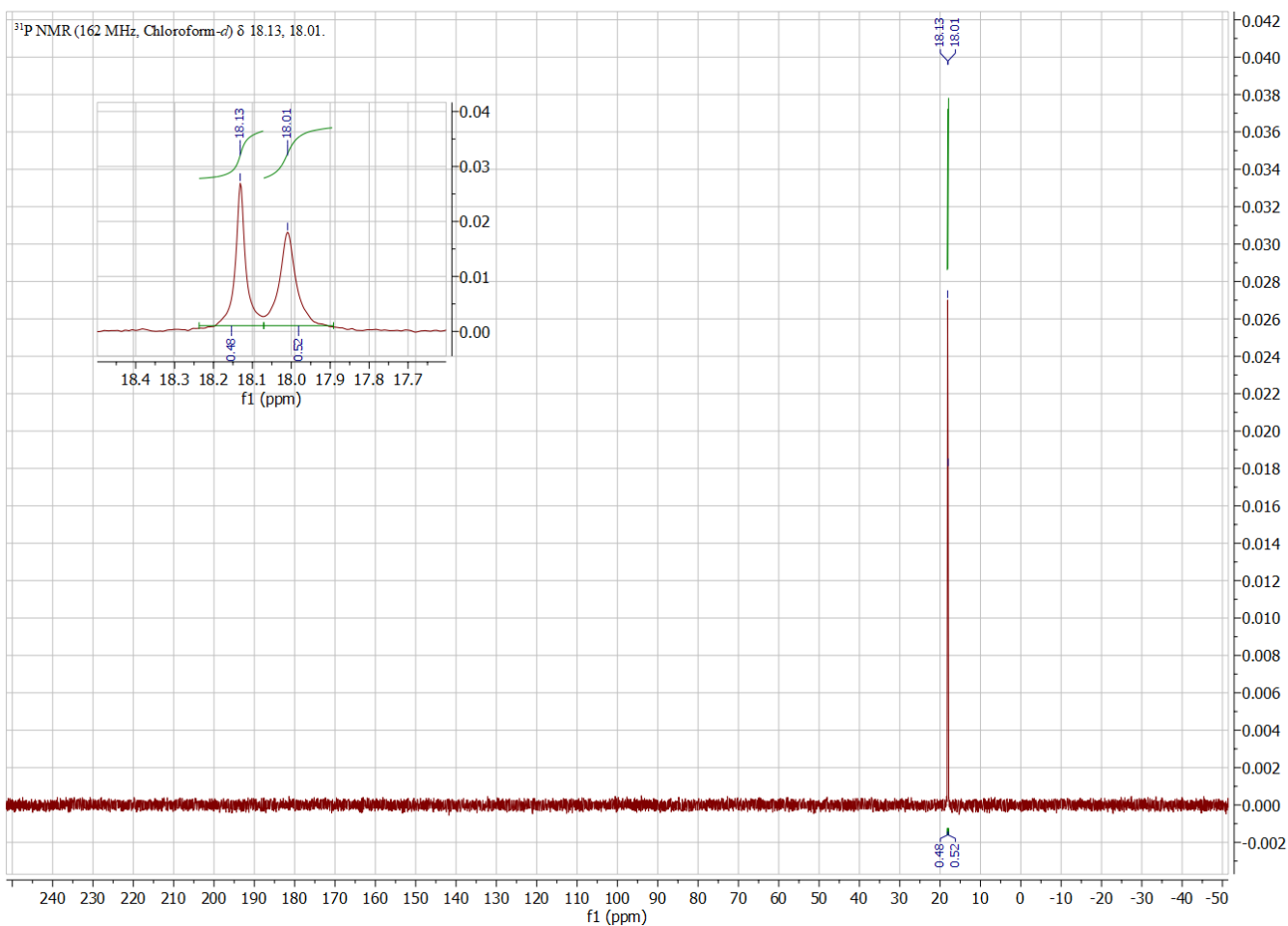
¹H NMR (400 MHz, Chloroform-*d*) δ 7.25 (s, 10H, 9xArH, NH), 7.10 – 7.00 (m, 4H, 4xArH), 6.61 – 6.50 (m, 1H, NH), 4.89 – 4.77 (m, 1H, NH), 4.77 – 4.61 (m, 2H, CHP, CH), 3.89 – 3.81 (m, 1H, CH), 3.14 – 2.98 (m, 2H, CH₂), 2.44 – 2.40 (m, 6H, 2xSCH₃), 2.40 – 2.23 (m, 1H, CH), 2.18 – 1.98 (m, 1H, CH), 1.39 (d, *J* = 4.1 Hz, 9H, Boc), 1.04 – 0.96 (m, 3H, CH₃), 0.94 – 0.78 (m, 6H, 2xCH₃), 0.73 (dd, *J* = 16.6, 6.5 Hz, 3H, CH₃).

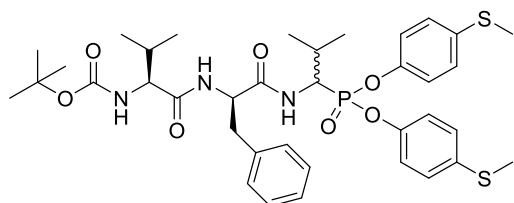
HRMS: C₃₇H₅₀N₃O₇PS₂ [M+Na]⁺ calc. 766.2725 found 766.2703

HPLC: purity >99%; retention time 19.513 min



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19,513	361,273	1997,430	99,09	98,82	n.a.
2		19,793	1,592	13,202	0,44	0,65	n.a.
3		20,053	1,730	10,573	0,47	0,52	n.a.
Total:			364,596	2021,205	100,00	100,00	



(39) Boc-L-Val-D-Phe-Val^P(OPh-4-SCH₃)₂

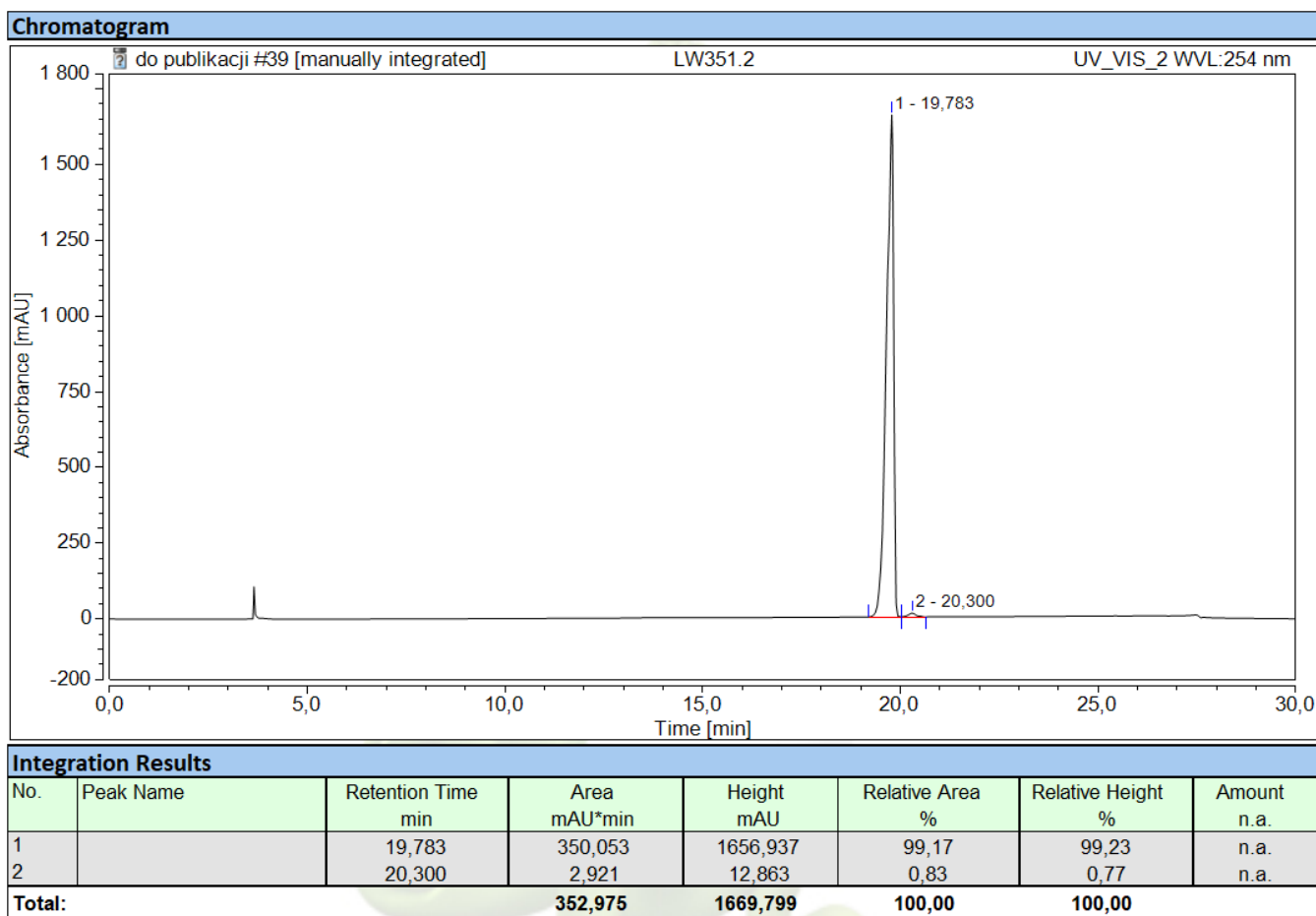
Name: *tert*-butyl ((2*S*)-1-(((2*R*)-1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-1-oxo-3-phenylpropan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

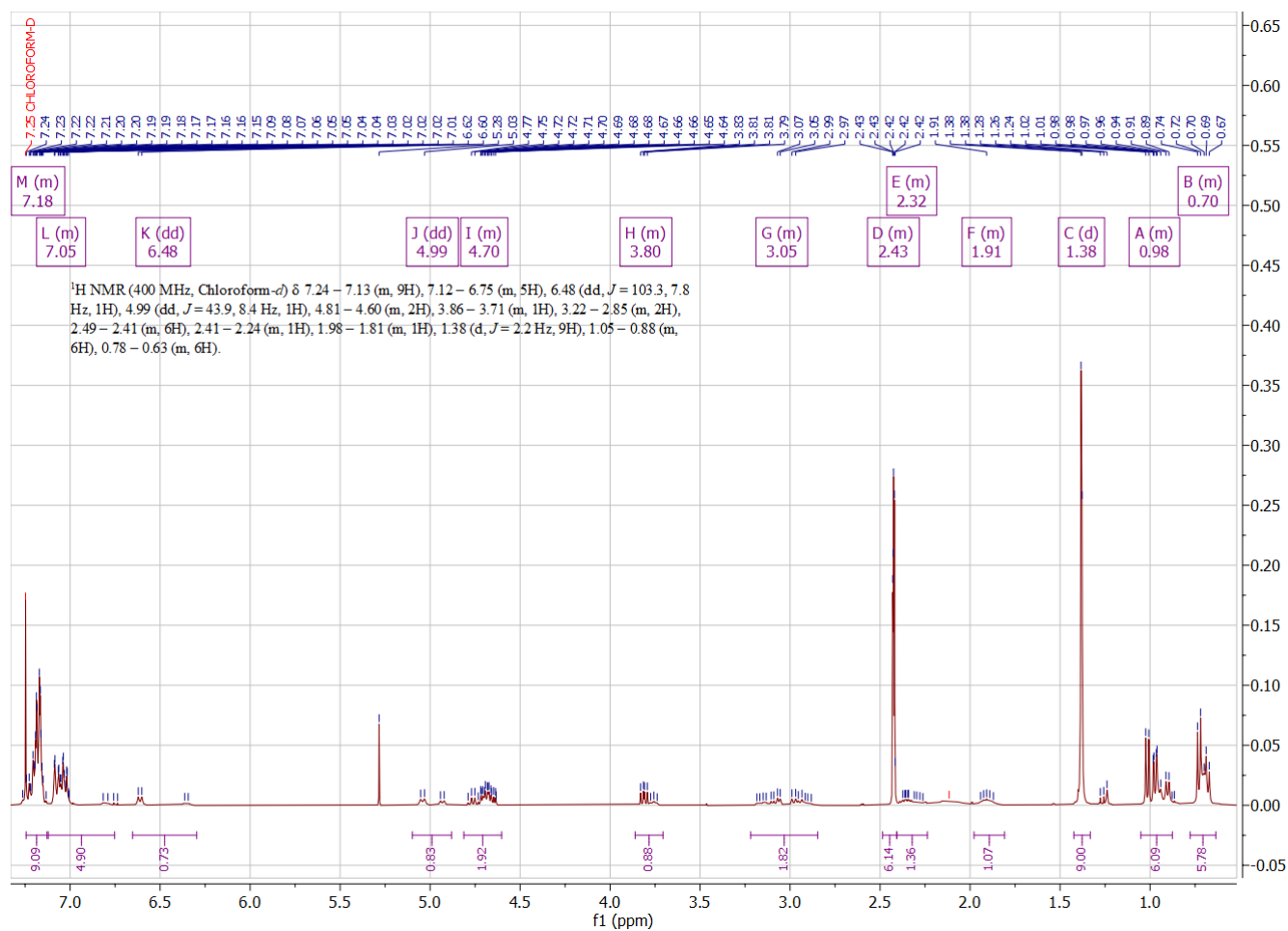
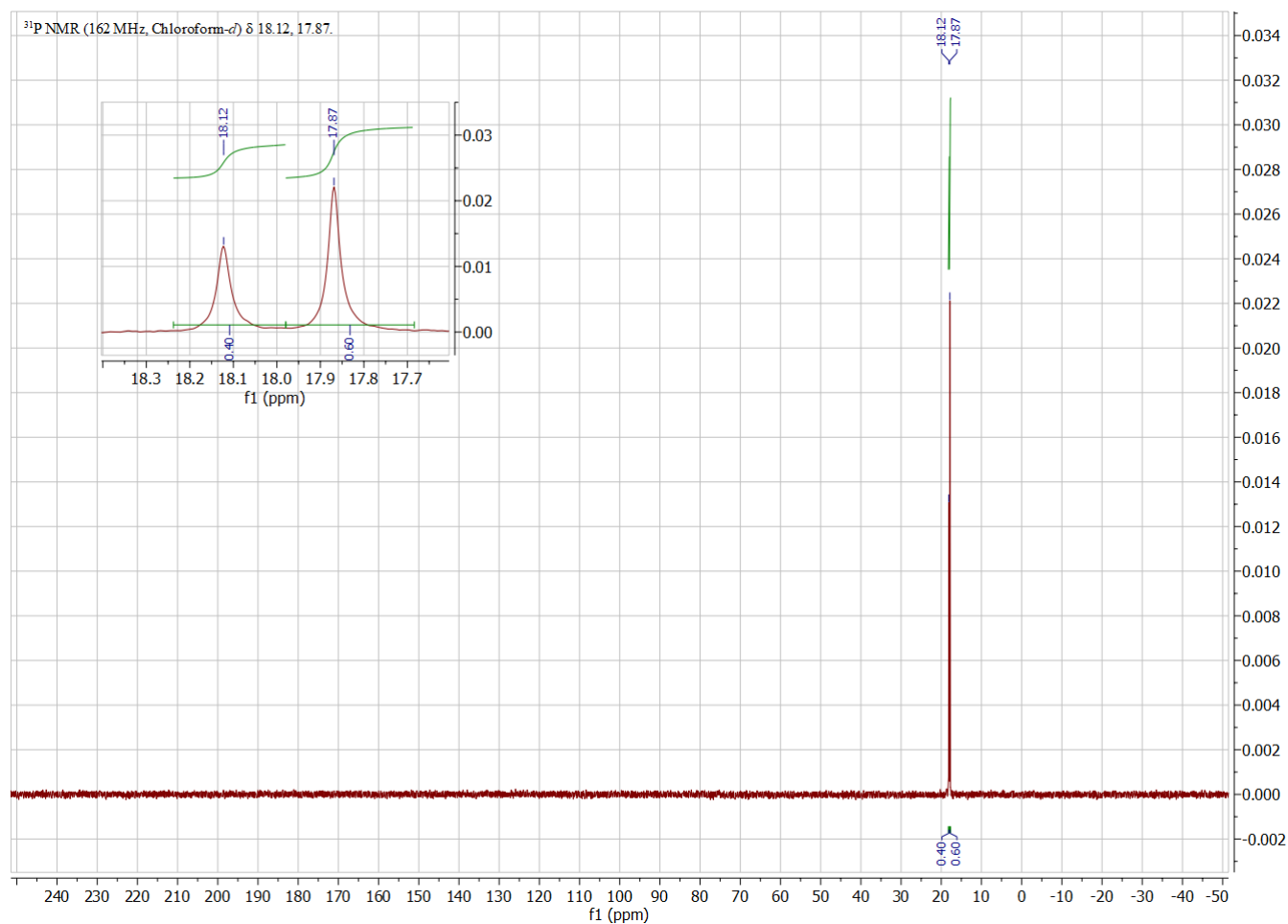
³¹P NMR (162 MHz, Chloroform-*d*) δ 18.12 (s, 40%), 17.87 (s, 60%).

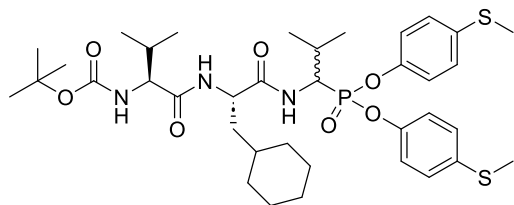
¹H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.13 (m, 9H, 9xArH), 7.12 – 6.75 (m, 5H, 4xArH, NH), 6.48 (dd, *J* = 103.3, 7.8 Hz, 1H, NH), 4.99 (dd, *J* = 43.9, 8.4 Hz, 1H, NH), 4.81 – 4.60 (m, 2H, CHP, CH), 3.86 – 3.71 (m, 1H, CH), 3.22 – 2.85 (m, 2H, CH₂), 2.49 – 2.41 (m, 6H, 2xSCH₃), 2.41 – 2.24 (m, 1H, CH), 1.98 – 1.81 (m, 1H, CH), 1.38 (d, *J* = 2.2 Hz, 9H, Boc), 1.05 – 0.88 (m, 6H, 2xCH₃), 0.78 – 0.63 (m, 6H, 2xCH₃).

HRMS: C₃₇H₅₀N₃O₇PS₂ [M+Na]⁺ calc. 766.2725 found 766.2735

HPLC: purity >99%; retention time 19.783 min





(40) Boc-L-Val-L-Cha- Val^P(OPh-4-SCH₃)₂

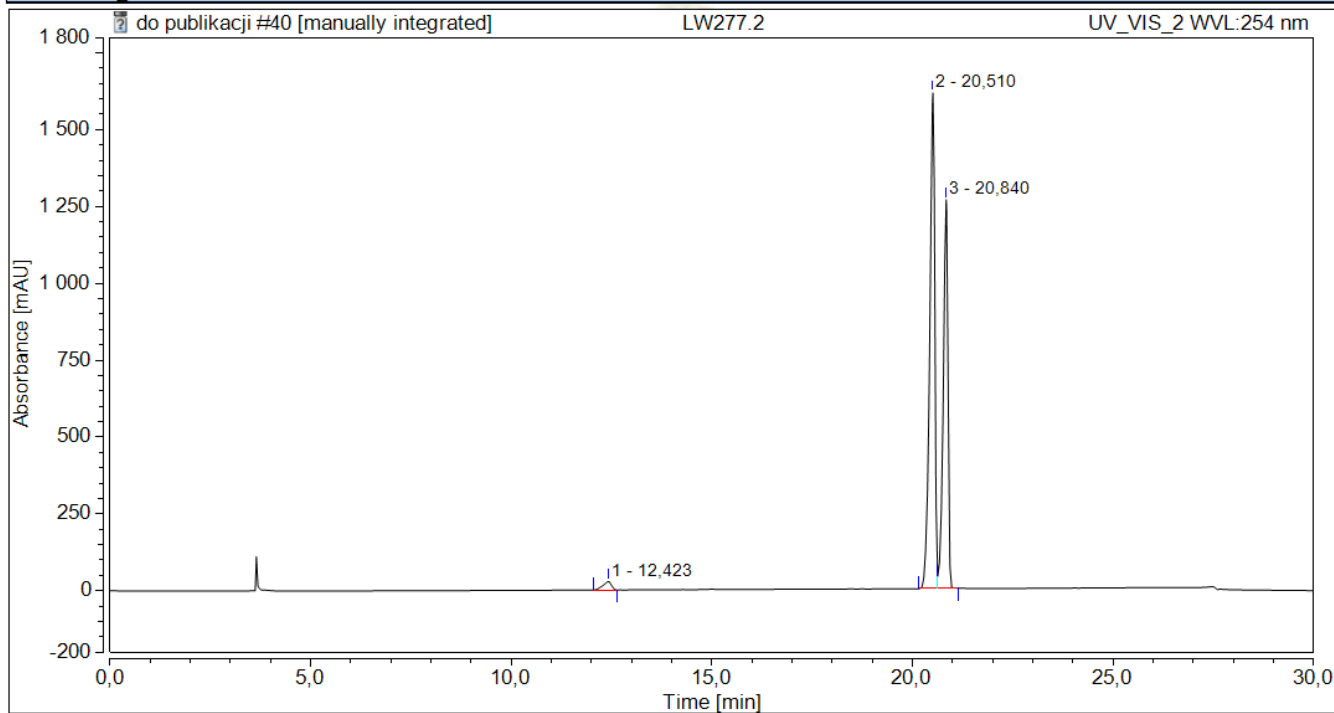
Name: *tert*-butyl ((2*S*)-1-(((2*S*)-1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-3-cyclohexyl-1-oxopropan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.36 (s, 56%), 18.17 (s, 44%).

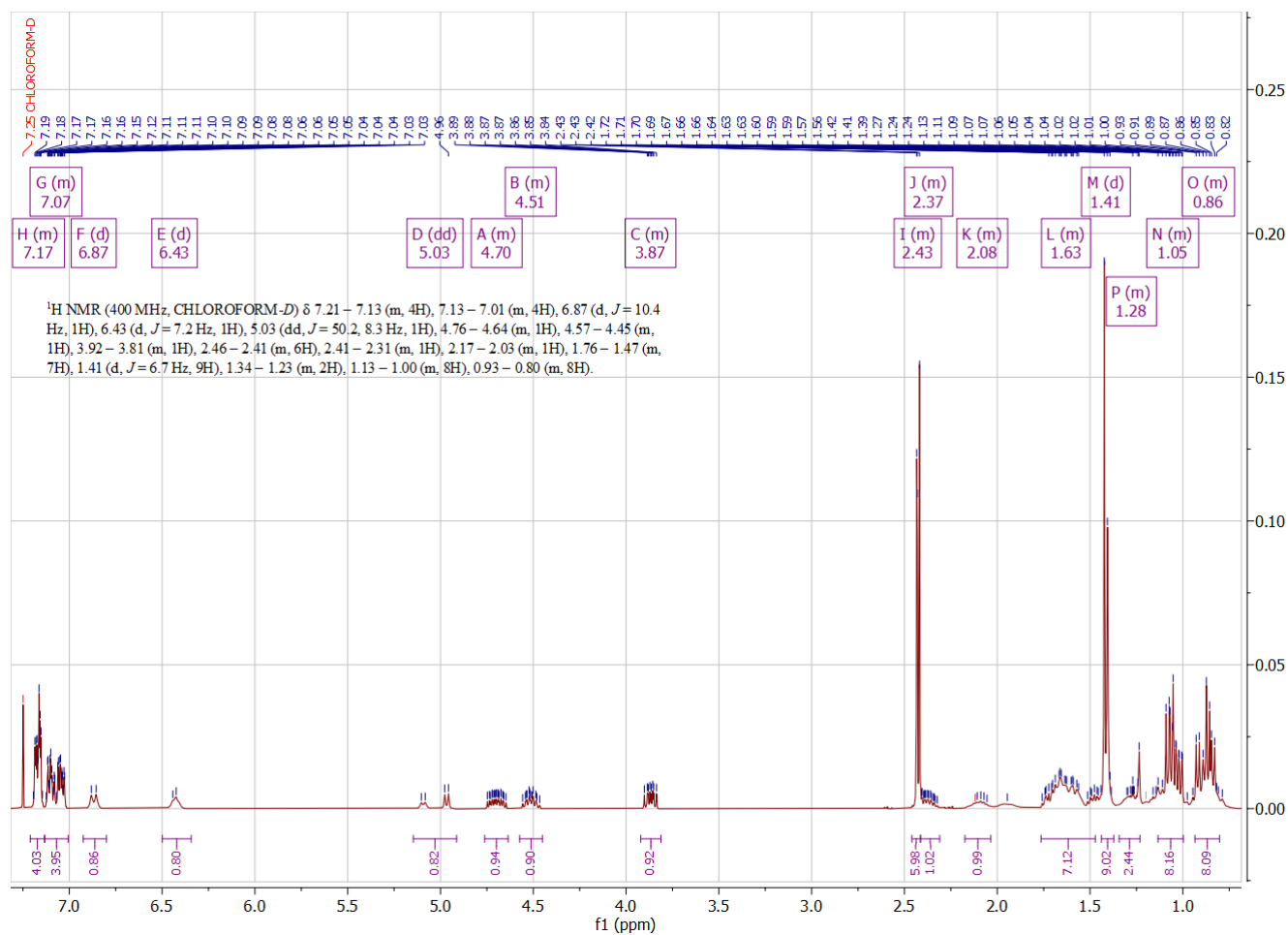
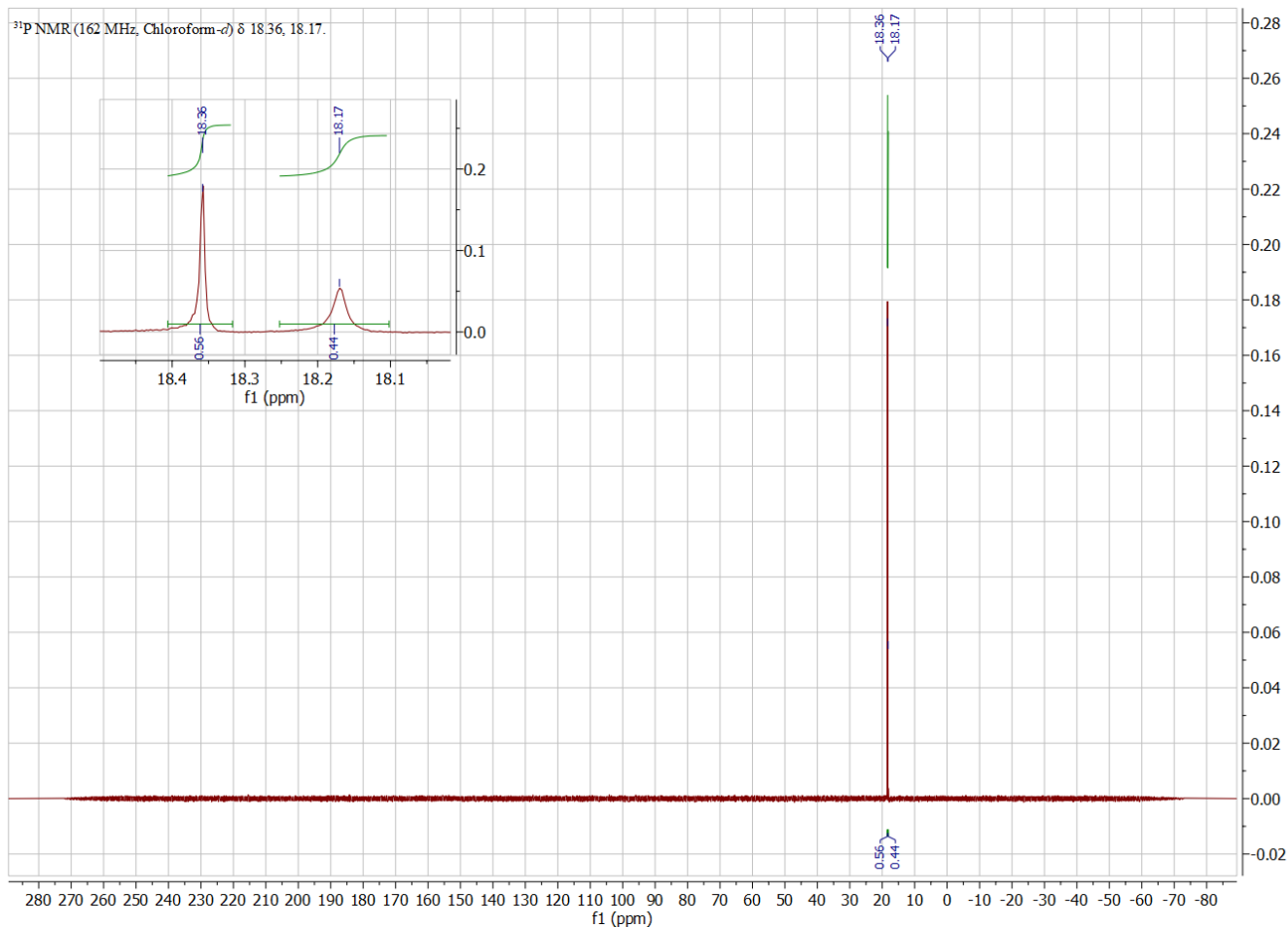
¹H NMR (400 MHz, Chloroform-*d*) δ 7.21 – 7.13 (m, 4H, 4xArH), 7.13 – 7.01 (m, 4H, 4xArH), 6.87 (d, *J* = 10.4 Hz, 1H, NH), 6.43 (d, *J* = 7.2 Hz, 1H, NH), 5.03 (dd, *J* = 50.2, 8.3 Hz, 1H, NH), 4.76 – 4.64 (m, 1H, CHP), 4.57 – 4.45 (m, 1H, CH), 3.92 – 3.81 (m, 1H, CH), 2.46 – 2.41 (m, 6H, 2xSCH₃), 2.41 – 2.31 (m, 1H, CH), 2.17 – 2.03 (m, 1H, CH), 1.76 – 1.47 (m, 7H, 3xCH₂, CH), 1.41 (d, *J* = 6.7 Hz, 9H, Boc), 1.34 – 1.23 (m, 2H, CH₂), 1.13 – 1.00 (m, 8H, 2xCH₃, CH₂), 0.93 – 0.80 (m, 8H, 2xCH₃, CH₂).

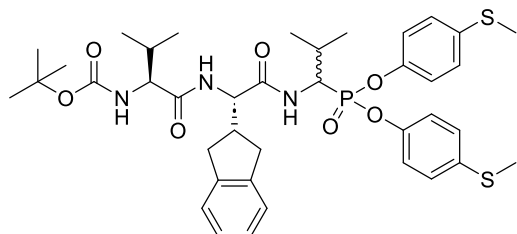
HRMS: C₃₇H₅₆N₃O₇PS₂ [M+Na]⁺ calc. 772.3195 found 772.3164

HPLC: purity >98%; retention time 20.510 and 20.840 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12,423	6,650	28,147	1,62	0,97	n.a.
2		20,510	235,122	1612,276	57,11	55,50	n.a.
3		20,840	169,933	1264,335	41,28	43,53	n.a.
Total:			411,706	2904,757	100,00	100,00	



(41) Boc-L-Val-D-Igl-Val^P(OPh-4-SCH₃)₂

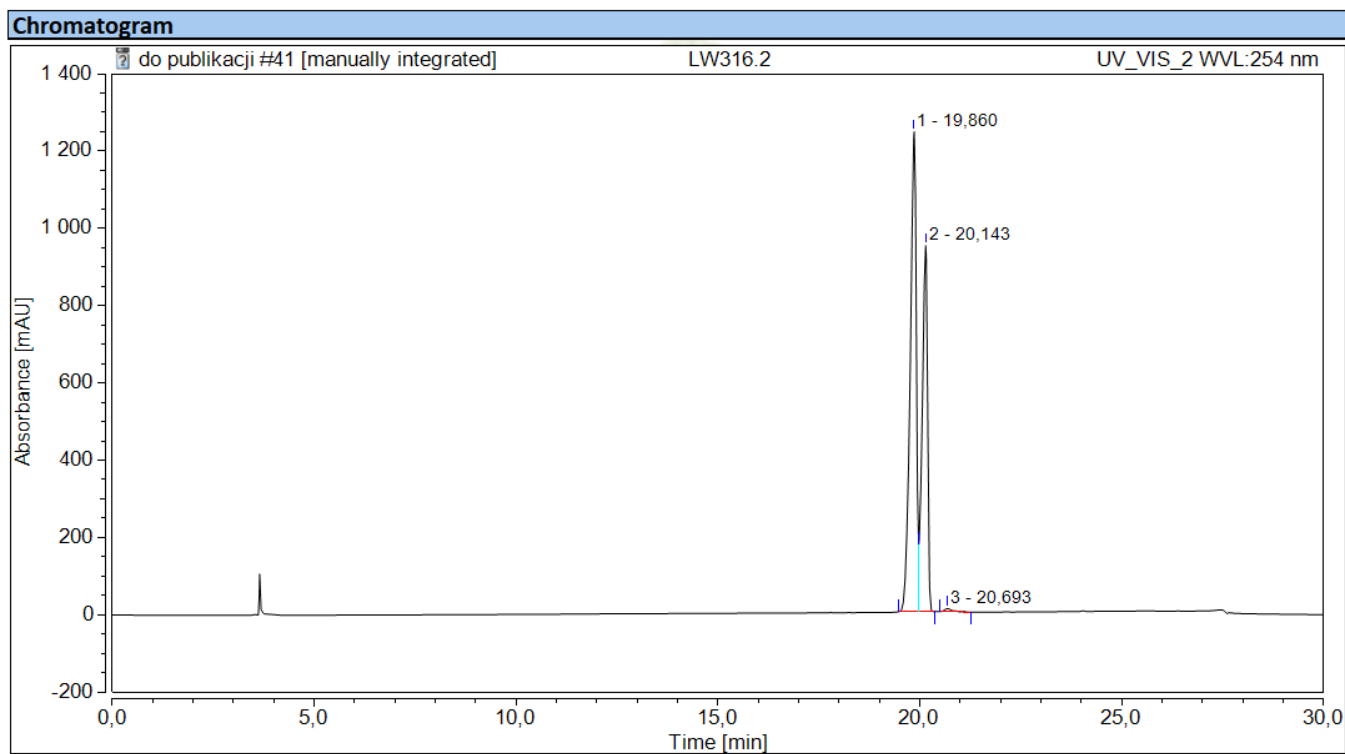
Name: *tert*-butyl ((2*S*)-1-(((1*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-1-(2,3-dihydro-1*H*-inden-2-yl)-2-oxoethyl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.32 (s, 42%), 18.27 (s, 58%).

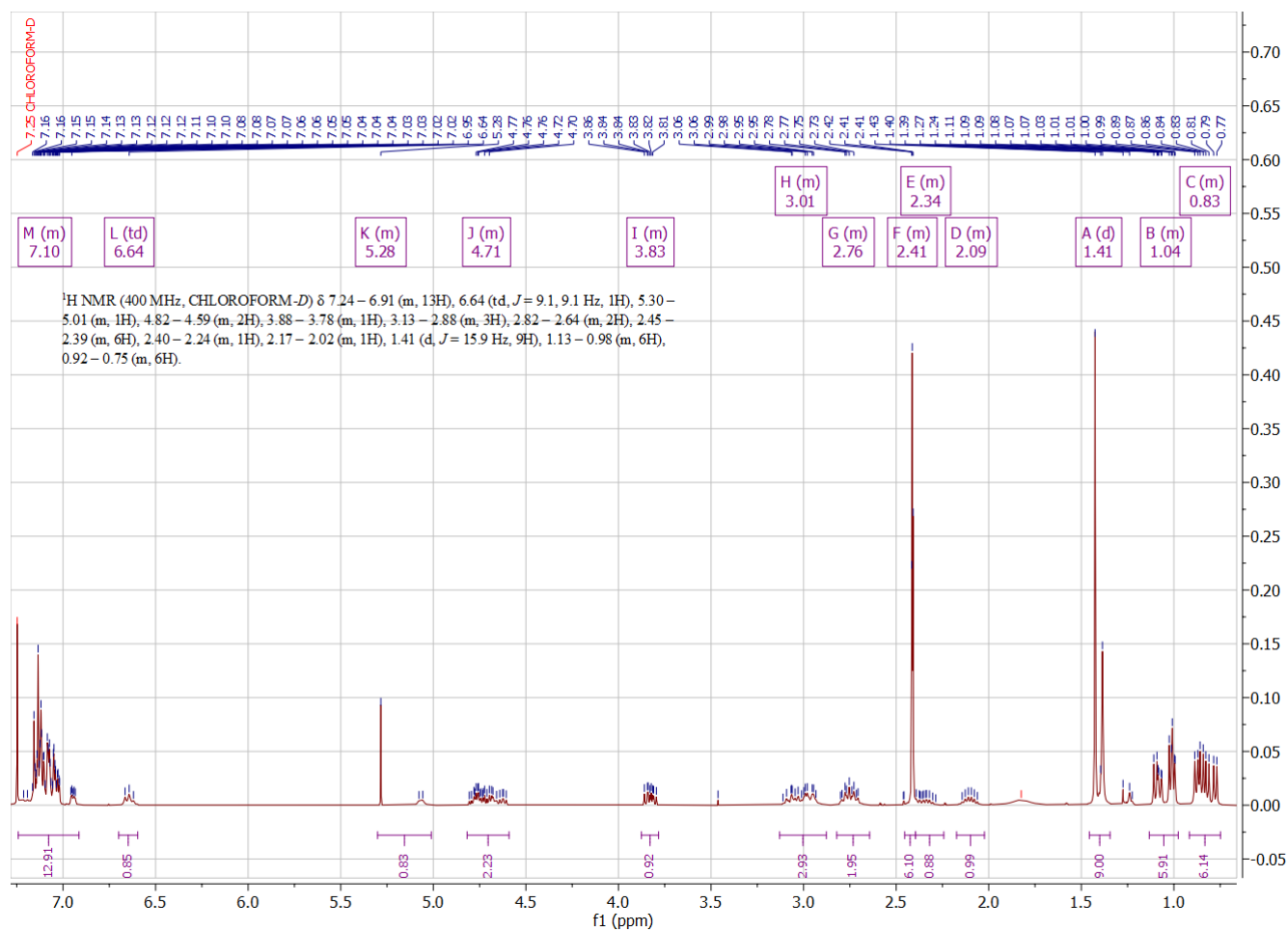
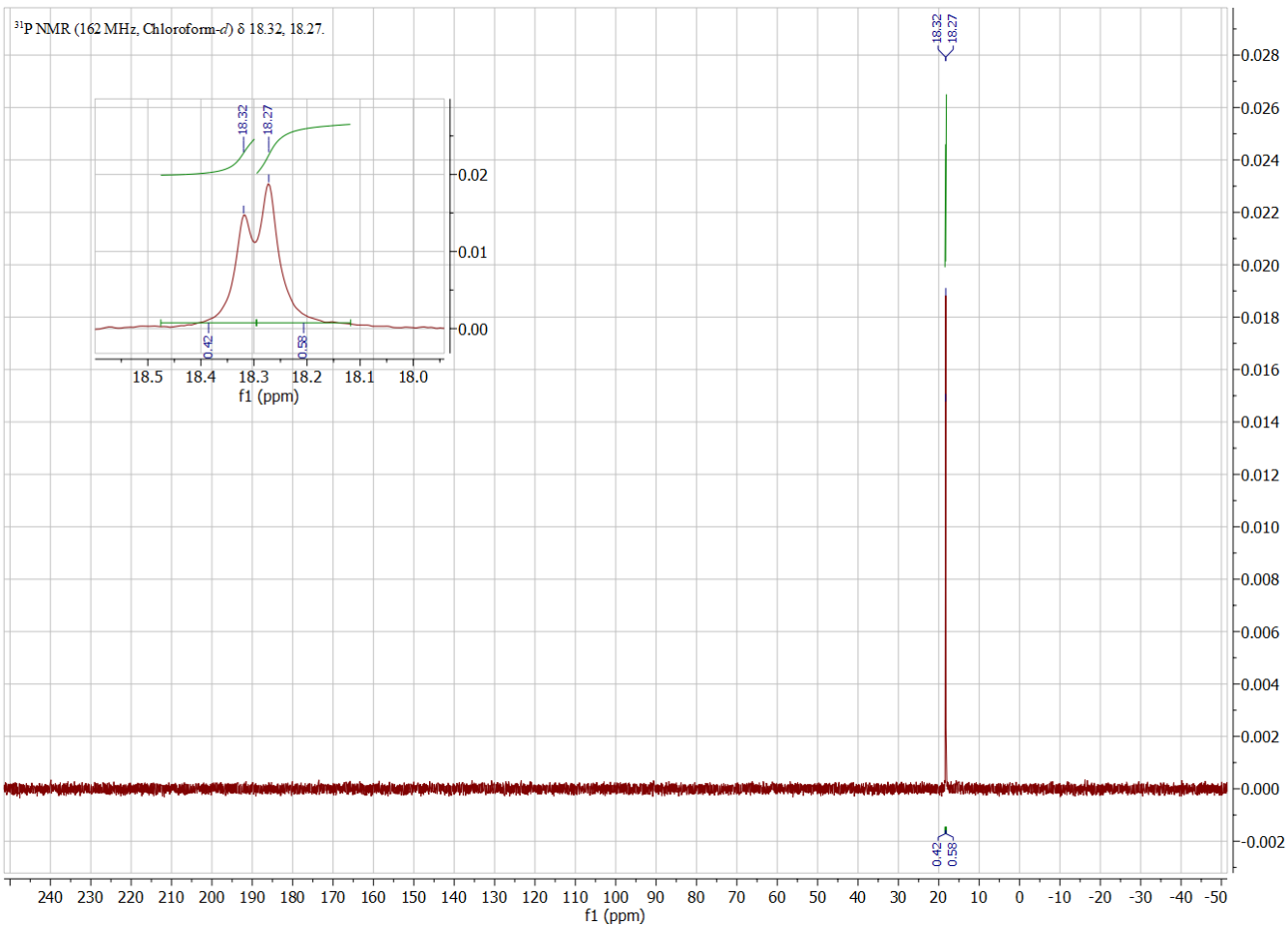
¹H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 6.91 (m, 13H, 12xArH, NH), 6.64 (td, *J* = 9.1, 9.1 Hz, 1H, NH), 5.30 – 5.01 (m, 1H, NH), 4.82 – 4.59 (m, 2H, CHP, CH), 3.88 – 3.78 (m, 1H, CH), 3.13 – 2.88 (m, 3H, CH₂, CH), 2.82 – 2.64 (m, 2H, CH₂), 2.45 – 2.39 (m, 6H, 2xSCH₃), 2.40 – 2.24 (m, 1H, CH), 2.17 – 2.02 (m, 1H, CH), 1.41 (d, *J* = 15.9 Hz, 9H, Boc), 1.13 – 0.98 (m, 6H, 2xCH₃), 0.92 – 0.75 (m, 6H, 2xCH₃)

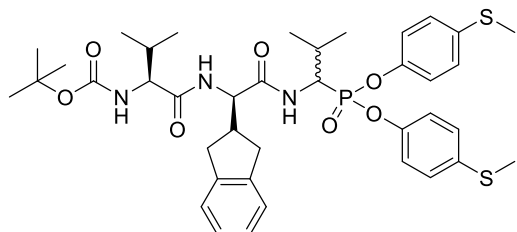
HRMS: C₃₉H₅₂N₃O₇PS₂ [M+Na]⁺ calc. 792.2882 found 792.2878

HPLC: purity >98%; retention time 19.860 and 20.143 min



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19,860	216,488	1241,757	59,59	56,51	n.a.
2		20,143	144,883	947,324	39,88	43,11	n.a.
3		20,693	1,897	8,412	0,52	0,38	n.a.
Total:			363,267	2197,493	100,00	100,00	



(42) Boc-L-Val-D-Igl-Val^P(OPh-4-SCH₃)₂

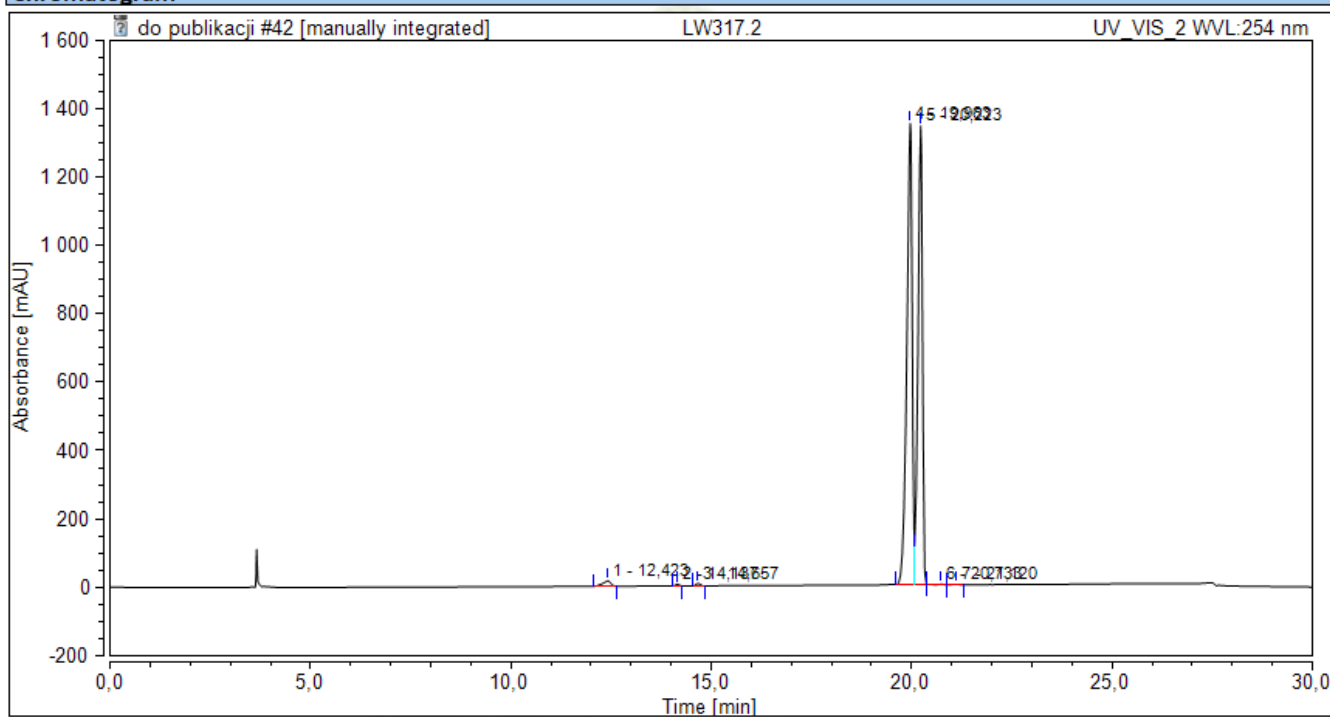
Name: *tert*-butyl ((2*S*)-1-(((1*R*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-1-(2,3-dihydro-1*H*-inden-2-yl)-2-oxoethyl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

³¹P NMR 162 MHz, Chloroform-*d*) δ 18.41 (s, 60%), 18.14 (s, 40%).

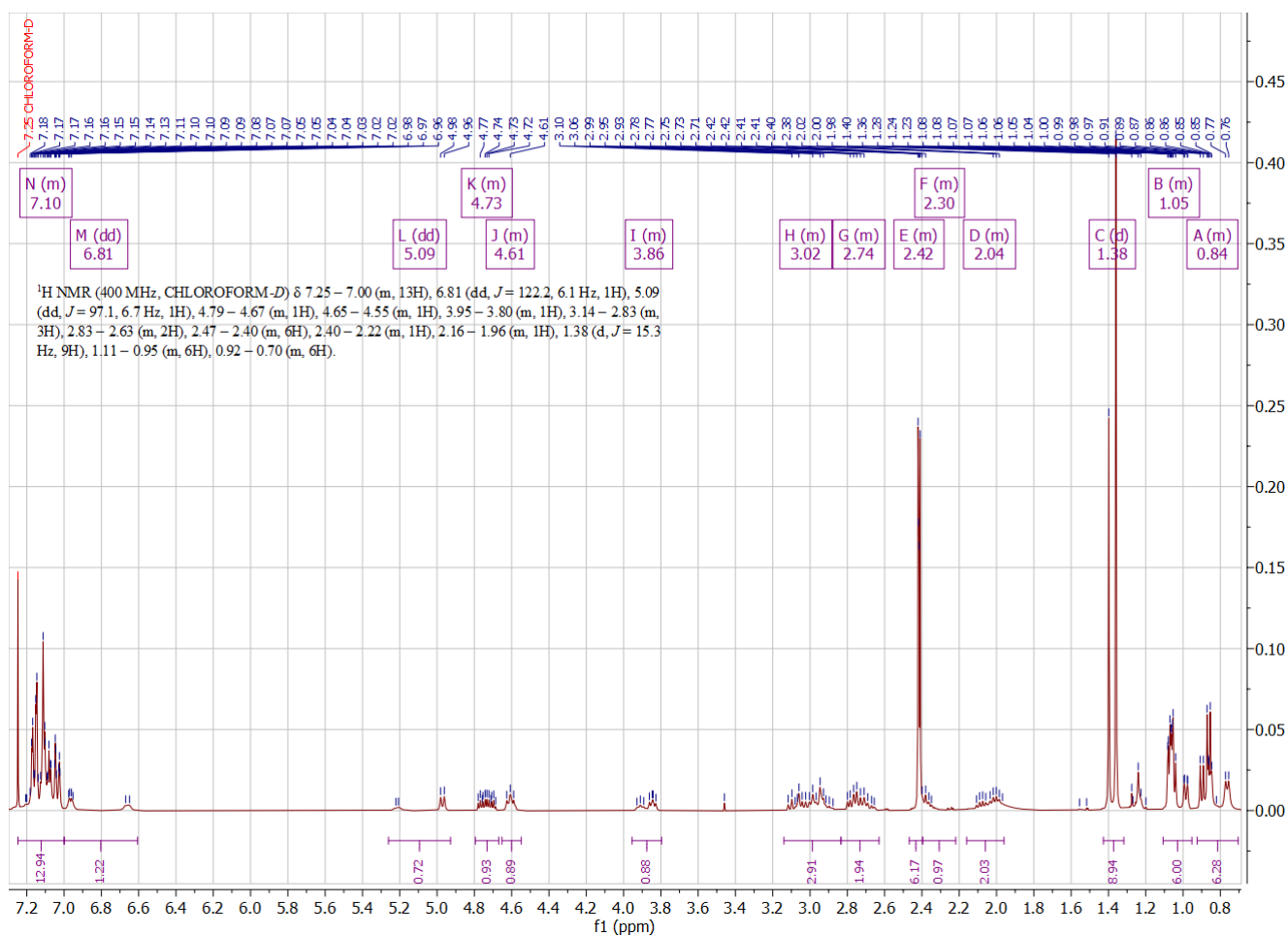
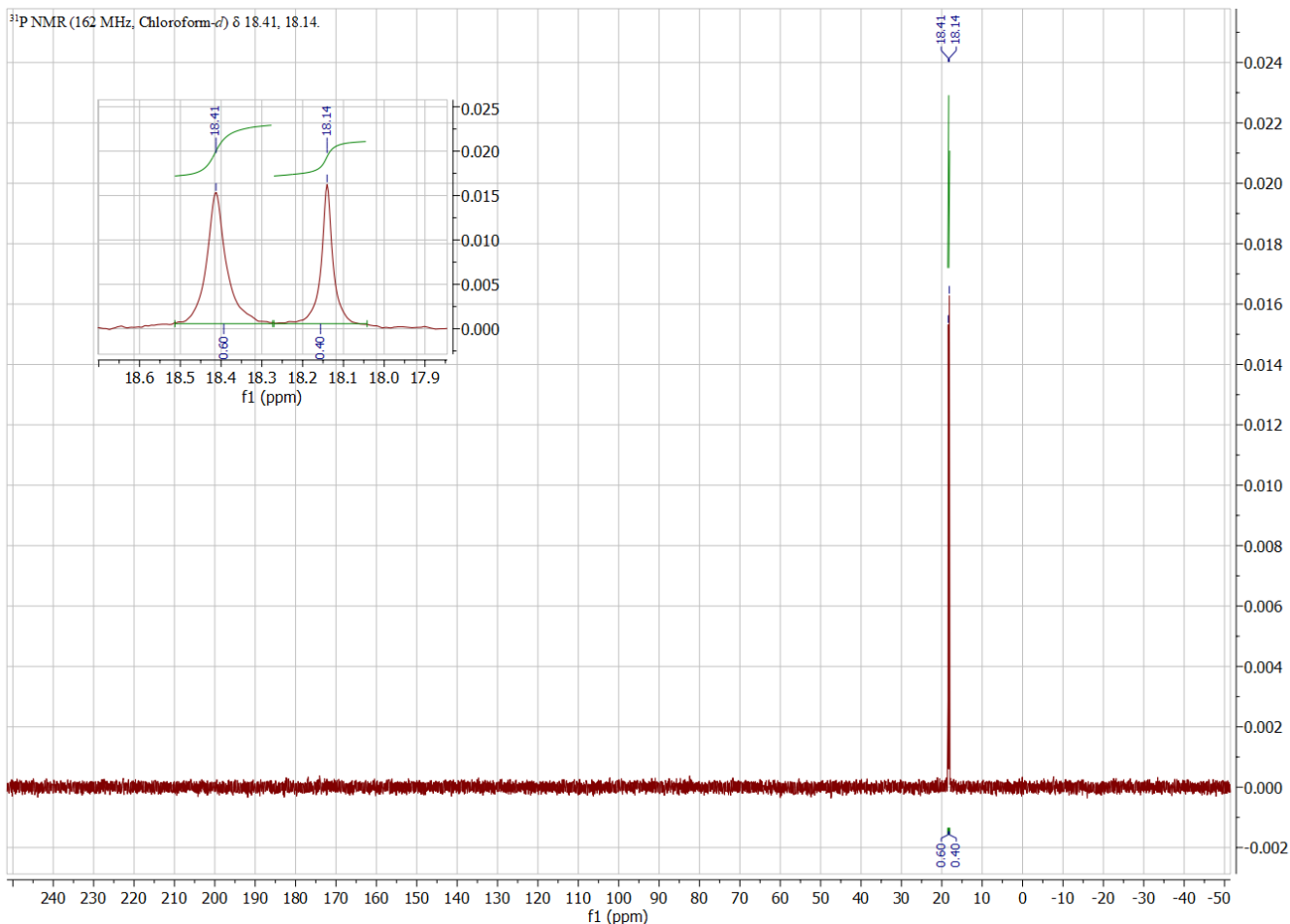
¹H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.00 (m, 13H, 12xArH, NH), 6.81 (dd, *J* = 122.2, 6.1 Hz, 1H, NH), 5.09 (dd, *J* = 97.1, 6.7 Hz, 1H, NH), 4.79 – 4.67 (m, 1H, CHP), 4.65 – 4.55 (m, 1H, CH), 3.95 – 3.80 (m, 1H, CH), 3.14 – 2.83 (m, 3H, CH₂, CH), 2.83 – 2.63 (m, 2H, CH₂), 2.47 – 2.40 (m, 6H, 2xSCH₃), 2.40 – 2.22 (m, 1H, CH), 2.16 – 1.96 (m, 1H, CH), 1.38 (d, *J* = 15.3 Hz, 9H, Boc), 1.11 – 0.95 (m, 6H, 2xCH₃), 0.92 – 0.70 (m, 6H, 2xCH₃).

HRMS: C₃₉H₅₂N₃O₇PS₂ [M+Na]⁺ calc. 792.2882 found 792.2873

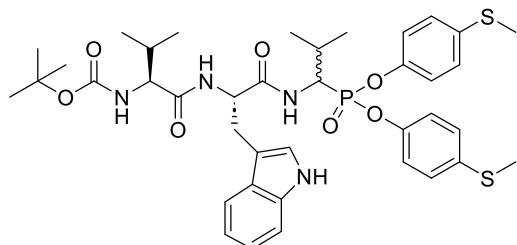
HPLC: purity >98%; retention time 19.963 and 20.223 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.423	3.662	16.318	0.95	0.60	n.a.
2		14.137	0.520	4.604	0.14	0.17	n.a.
3		14.657	0.907	6.915	0.24	0.25	n.a.
4		19.963	206.125	1350.546	53.74	49.58	n.a.
5		20.223	171.893	1343.027	44.82	49.30	n.a.
6		20.733	0.273	1.536	0.07	0.06	n.a.
7		21.120	0.182	1.140	0.05	0.04	n.a.
Total:			383,560	2724,086	100,00	100,00	



(43) Boc-L-Val-L-Trp- Val^P(OPh-4-SCH₃)₂



Name: *tert*-butyl ((2S)-1-(((2S)-1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-3-(1H-indol-3-yl)-1-oxopropan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

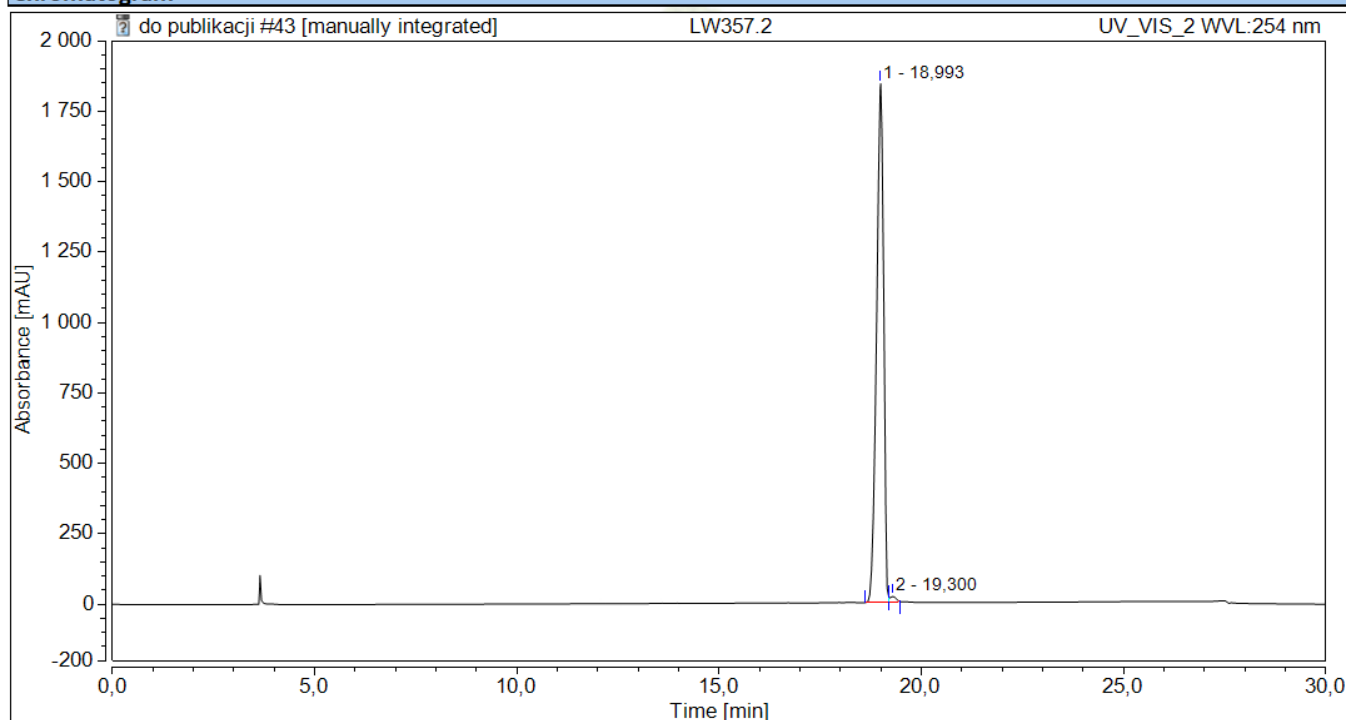
³¹P NMR (162 MHz, Chloroform-d) δ 17.96 (s, 48%), 17.74 (s, 52%).

¹H NMR (400 MHz, Chloroform-d) δ 8.07 (d, J = 33.2 Hz, 1H, NH), 7.71 – 7.59 (m, 1H, NH), 7.35 – 7.26 (m, 1H, NH), 7.23 – 7.09 (m, 6H, 6xArH), 7.09 – 6.68 (m, 7H, 6xArH, CH), 4.95 – 4.77 (m, 2H, CHP, NH), 4.75 – 4.63 (m, 1H, CH), 3.94 – 3.81 (m, 1H, CH), 3.34 – 3.07 (m, 2H, CH₂), 2.48 – 2.35 (m, 6H, 2xSCH₃), 2.36 – 2.19 (m, 1H, CH), 2.18 – 1.99 (m, 1H, CH), 1.35 (d, J = 5.8 Hz, 9H, Boc), 0.99 – 0.61 (m, 12H, 4xCH₃).

HRMS: C₃₉H₅₁N₄O₇PS₂ [M+Na]⁺ calc. 805.2834 found 805.2843

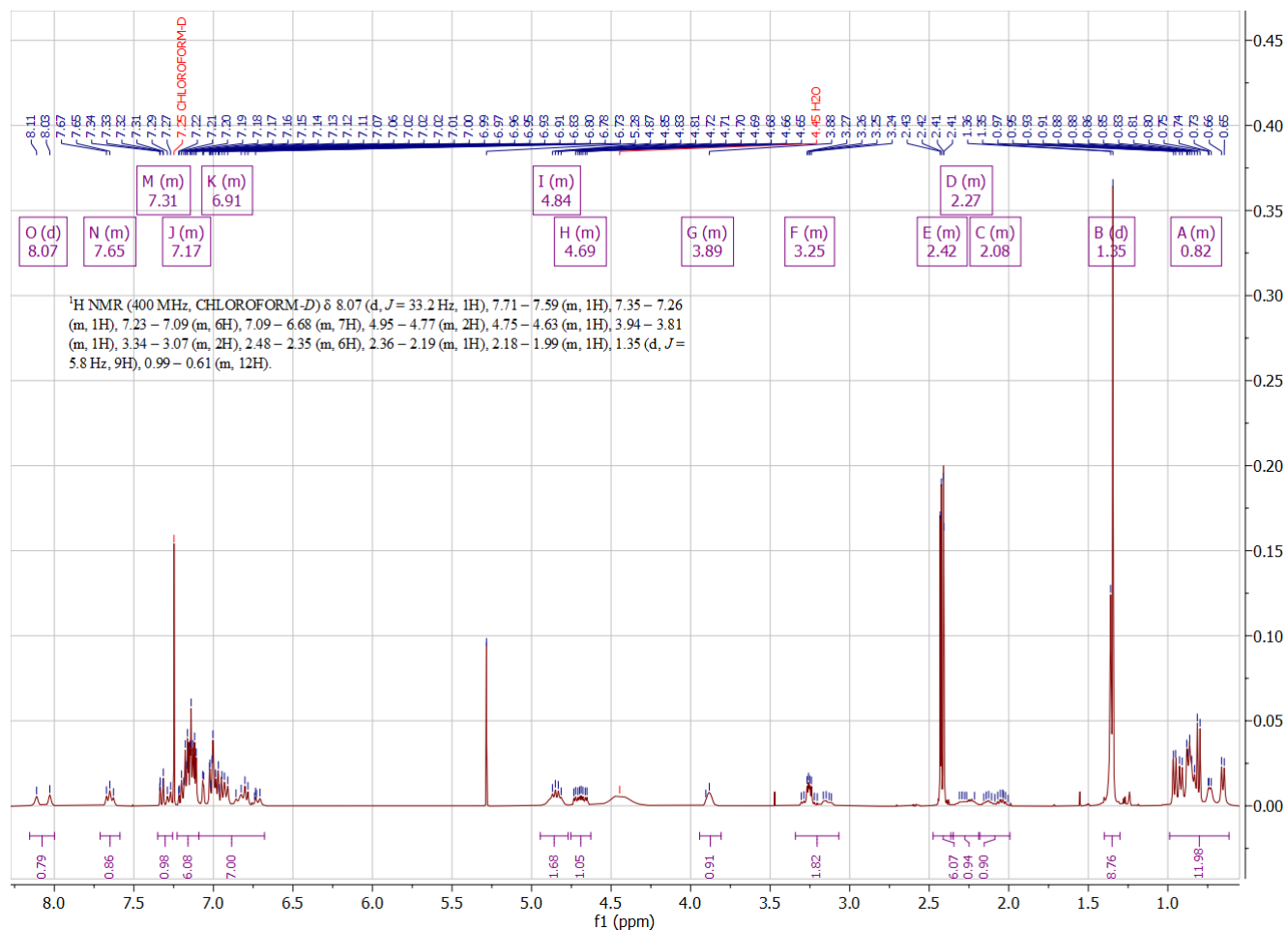
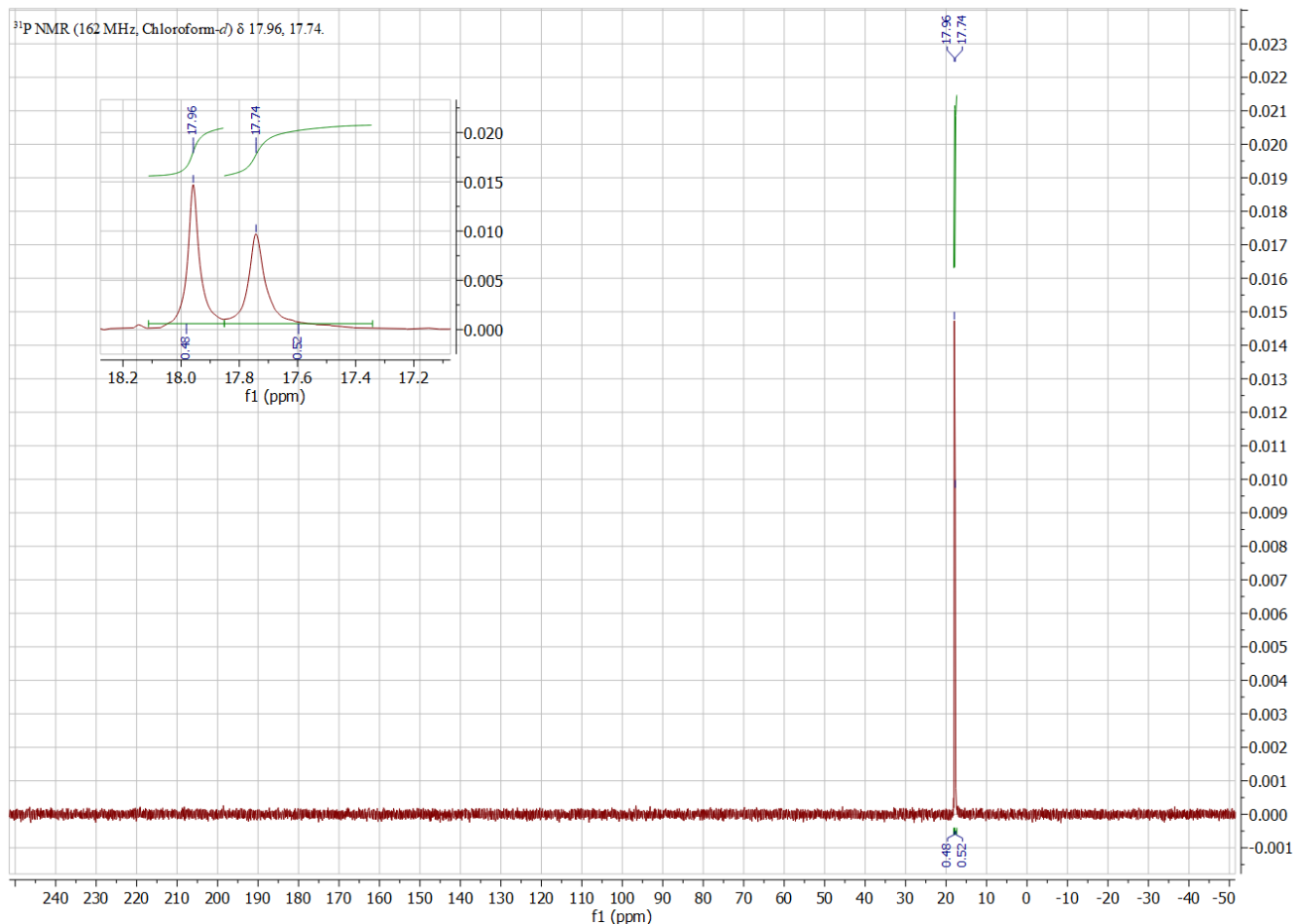
HPLC: purity >99%; retention time 18.993 min

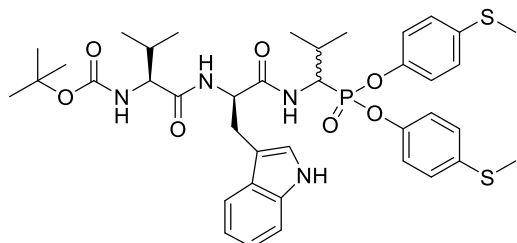
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		18,993	372,330	1839,923	99,15	98,97	n.a.
2		19,300	3,177	19,106	0,85	1,03	n.a.
Total:			375,508	1859,029	100,00	100,00	



(44) Boc-L-Val-D-Trp-Val^P(OPh-4-SCH₃)₂

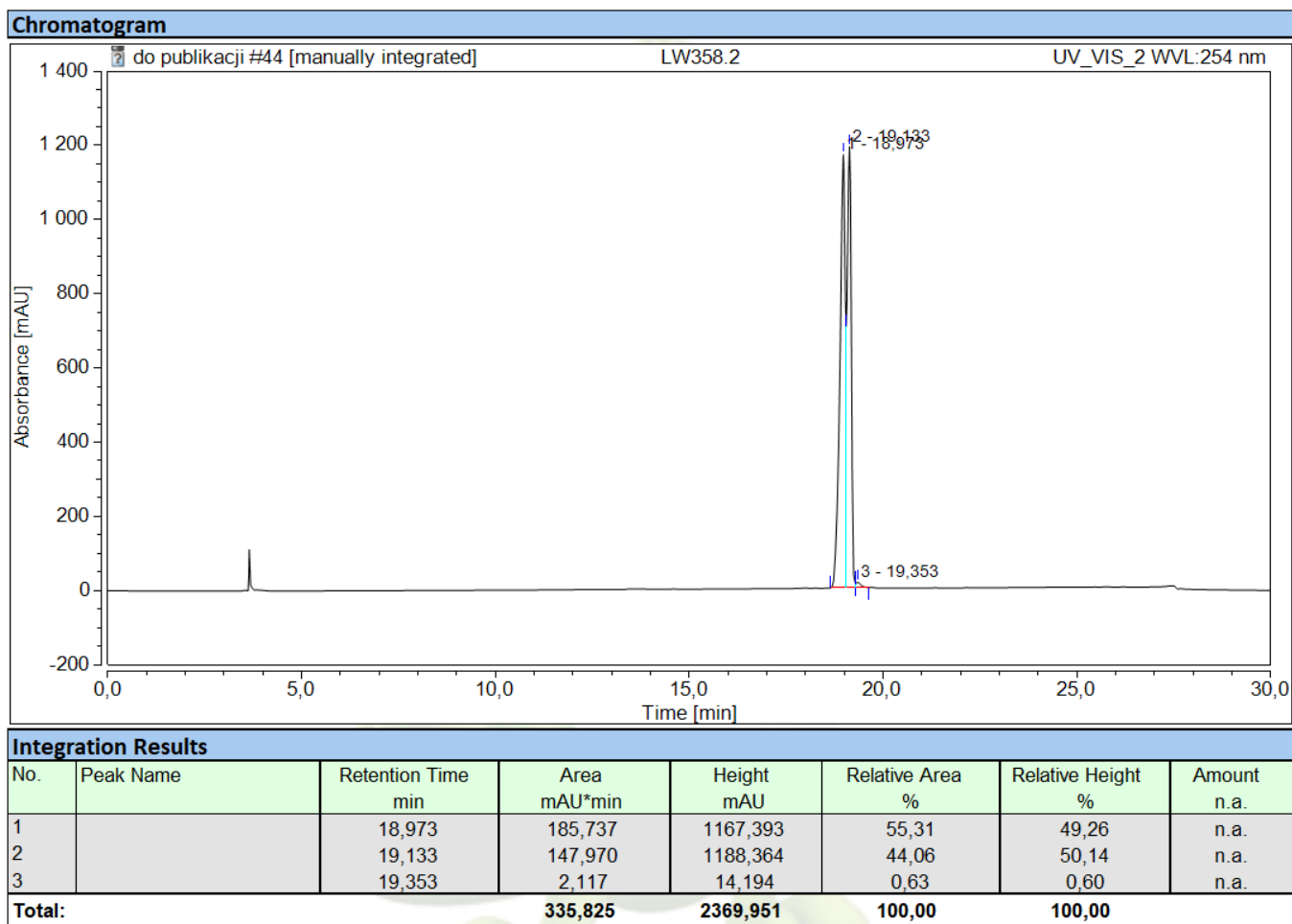
Name: *tert*-butyl ((2*S*)-1-(((2*R*)-1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-3-(1*H*-indol-3-yl)-1-oxopropan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

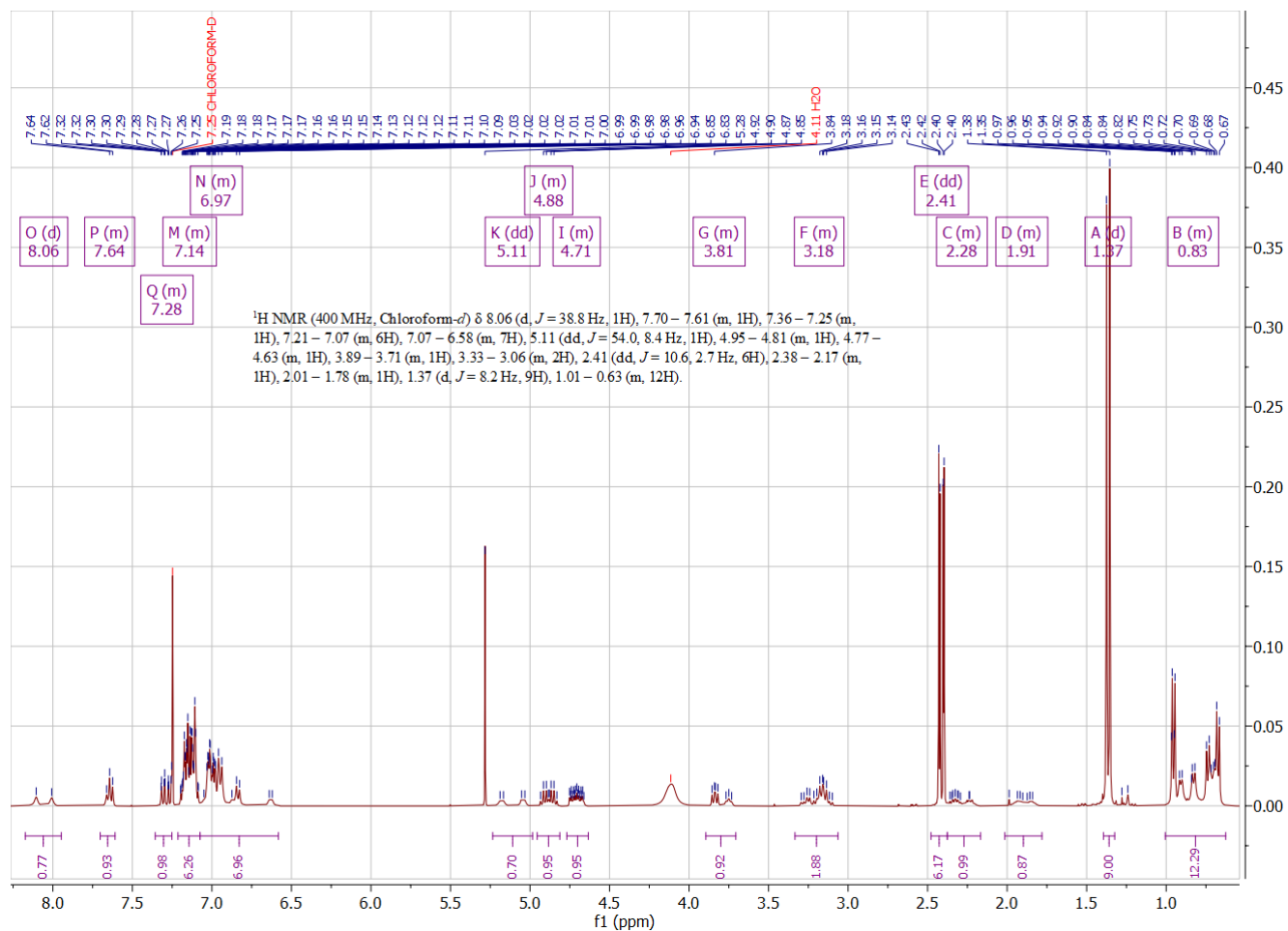
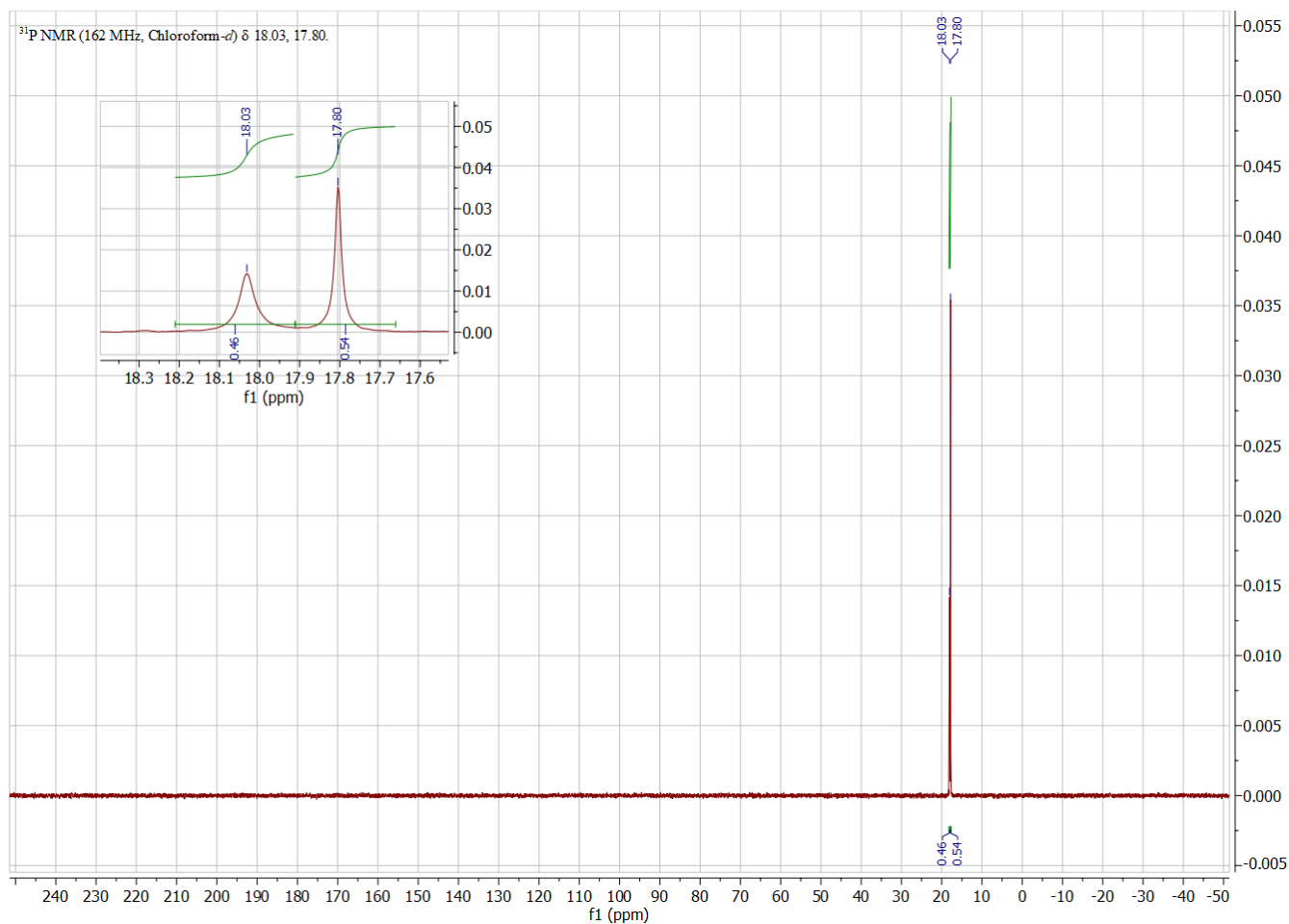
³¹P NMR (162 MHz, Chloroform-*d*) δ 18.03 (s, 46%), 17.80 (s, 54%).

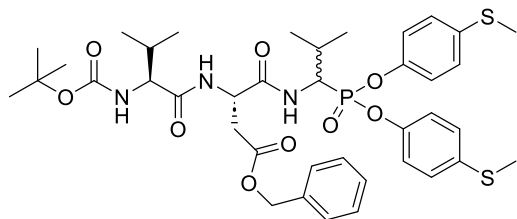
¹H NMR (400 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 38.8 Hz, 1H), 7.70 – 7.61 (m, 1H, NH), 7.36 – 7.25 (m, 1H, NH), 7.21 – 7.07 (m, 6H, 6xArH), 7.07 – 6.58 (m, 7H, 6xArH, CH), 5.11 (dd, *J* = 54.0, 8.4 Hz, 1H, NH), 4.95 – 4.81 (m, 1H, CH), 4.77 – 4.63 (m, 1H, CHP), 3.89 – 3.71 (m, 1H, CH), 3.33 – 3.06 (m, 2H, CH₂), 2.41 (dd, *J* = 10.6, 2.7 Hz, 6H, 2xSCH₃), 2.38 – 2.17 (m, 1H, CH), 2.01 – 1.78 (m, 1H, CH), 1.37 (d, *J* = 8.2 Hz, 9H, Boc), 1.01 – 0.63 (m, 12H, 4xCH₃).

HRMS: C₃₉H₅₁N₄O₇PS₂ [M+Na]⁺ calc. 805.2834 found 805.2846

HPLC: purity >99%; retention time 18.973 and 19.133 min





(45) Boc-L-Val-L-Asp(Bzl)-Val^P(OPh-4-SCH₃)₂

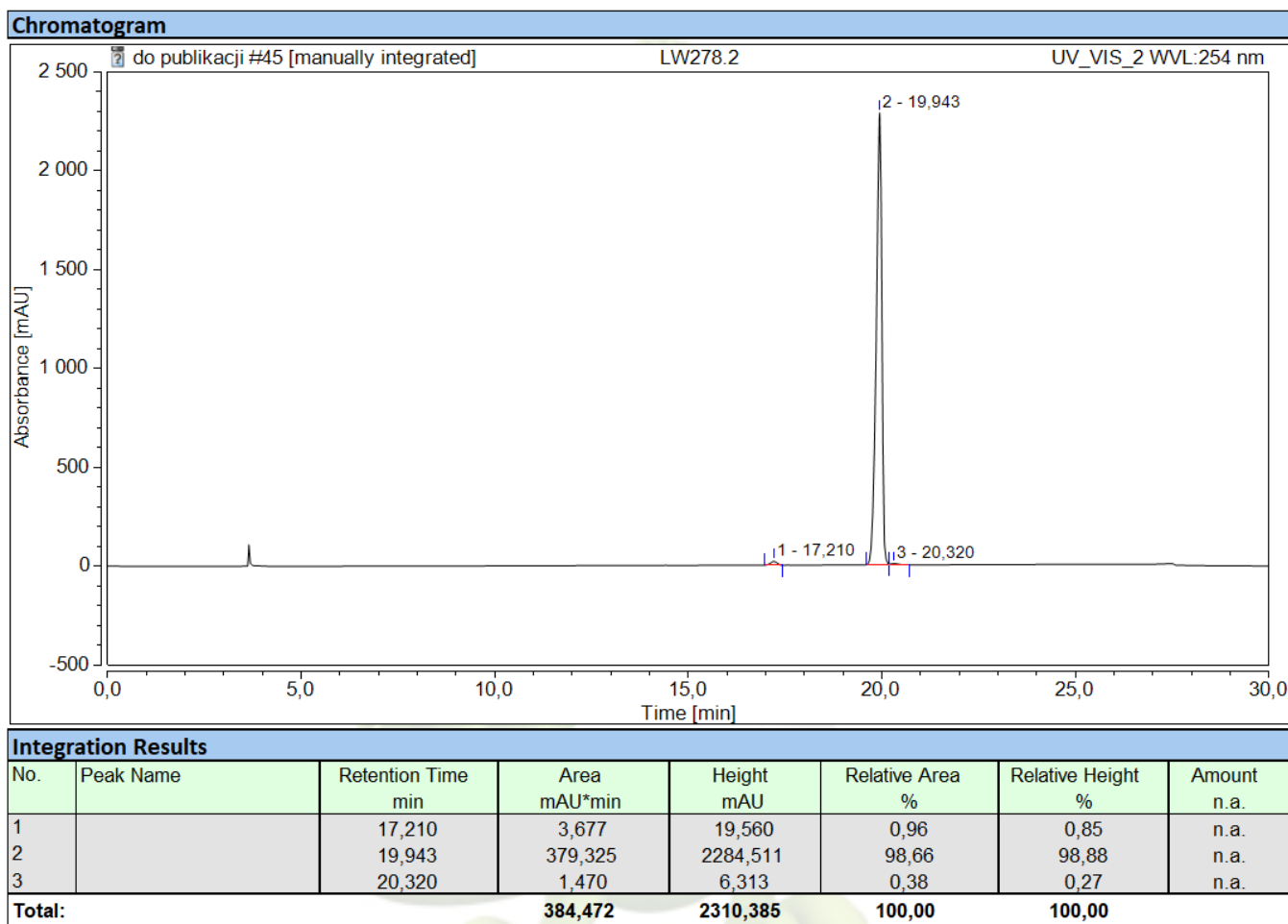
Name: benzyl (3S)-4-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-3-((S)-2-((tert-butoxycarbonyl)amino)-3-methylbutanamido)-4-oxobutanoate

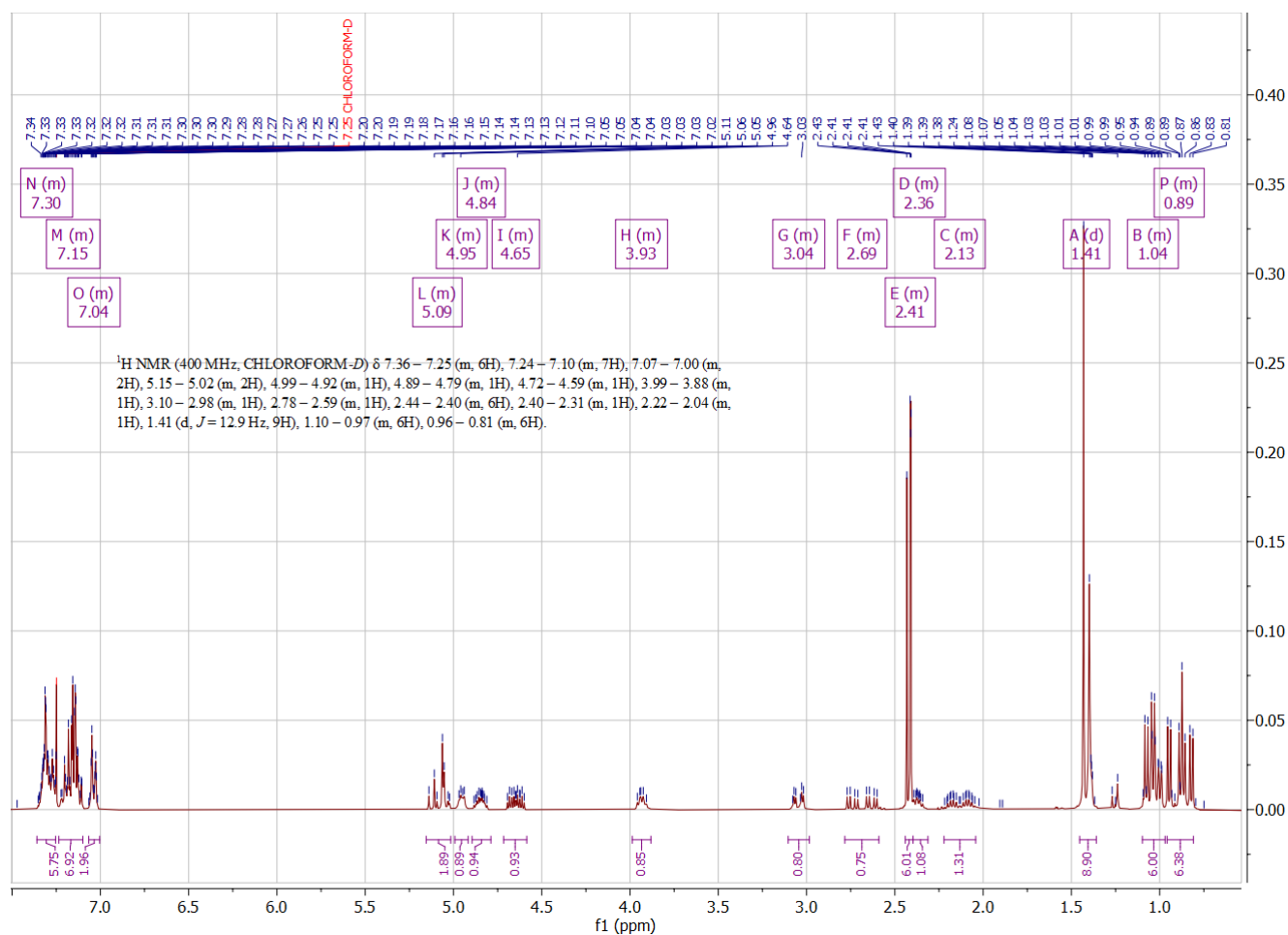
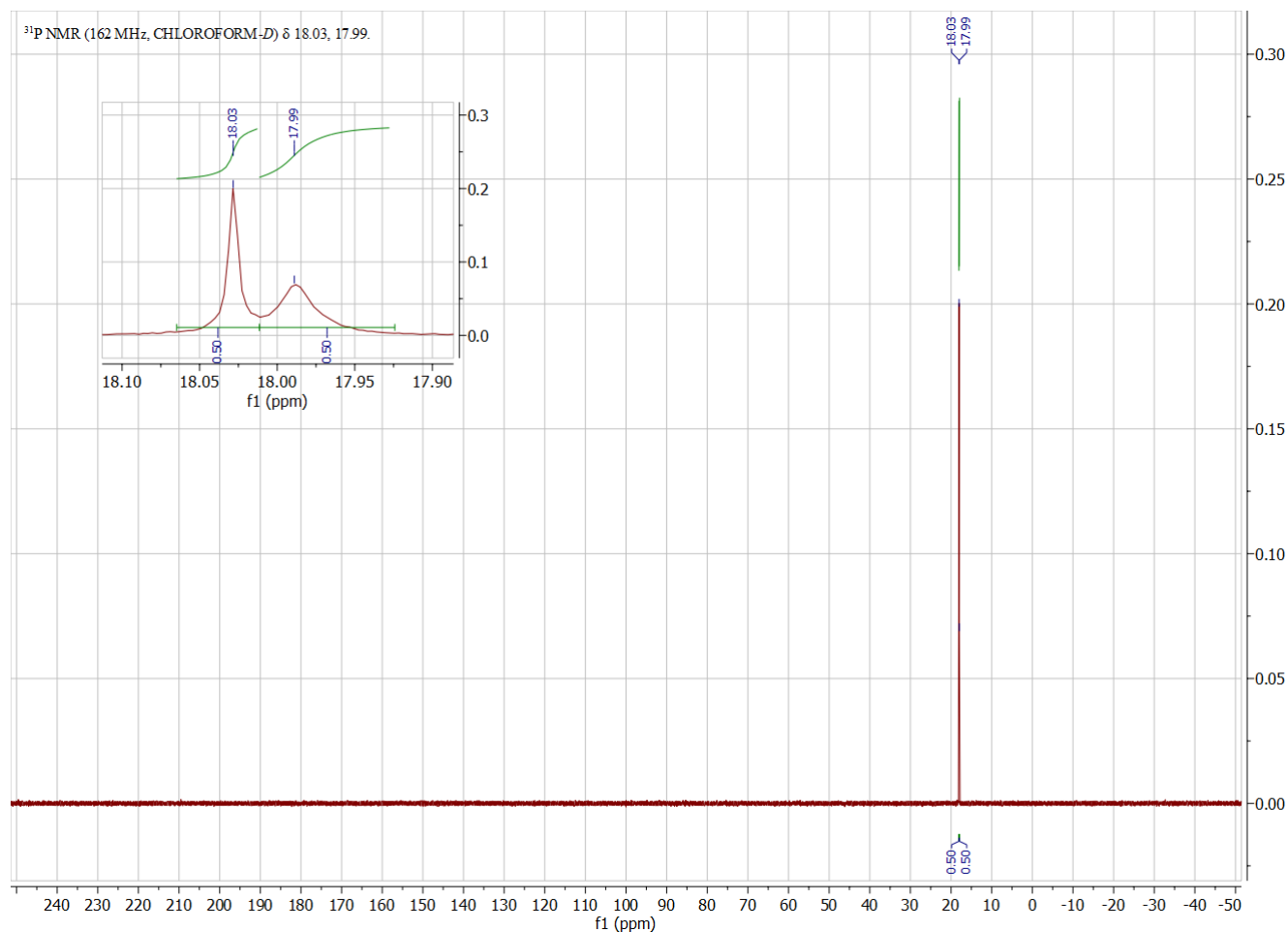
³¹P NMR (162 MHz, Chloroform-d) δ 18.03 (s, 50%), 17.99 (s, 50%).

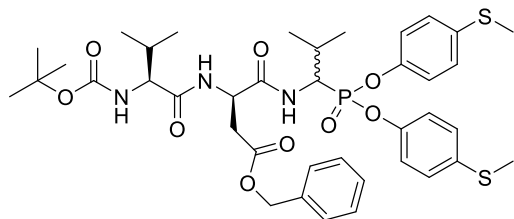
¹H NMR (400 MHz, Chloroform-d) δ 7.36 – 7.25 (m, 6H, 5xArH, NH), 7.24 – 7.10 (m, 7H, 6xArH, NH), 7.07 – 7.00 (m, 2H, 2xArH), 5.15 – 5.02 (m, 2H, CH₂), 4.99 – 4.92 (m, 1H, NH), 4.89 – 4.79 (m, 1H, CH), 4.72 – 4.59 (m, 1H, CHP), 3.99 – 3.88 (m, 1H, CH), 3.10 – 2.98 (m, 1H, 0.5xCH₂), 2.78 – 2.59 (m, 1H, 0.5xCH₂), 2.44 – 2.40 (m, 6H, 2xSCH₃), 2.40 – 2.31 (m, 1H, CH), 2.22 – 2.04 (m, 1H, CH), 1.41 (d, J = 12.9 Hz, 9H, Boc), 1.10 – 0.97 (m, 6H, 2xCH₃), 0.96 – 0.81 (m, 6H, 2xCH₃).

HRMS: C₃₉H₅₂N₃O₉PS₂ [M+Na]⁺ calc. 824.2780 found 824.2771

HPLC: purity >98%; retention time 19.943 min





(46) Boc-L-Val-D-Asp(Bzl)-Val^P(OPh-4-SCH₃)₂

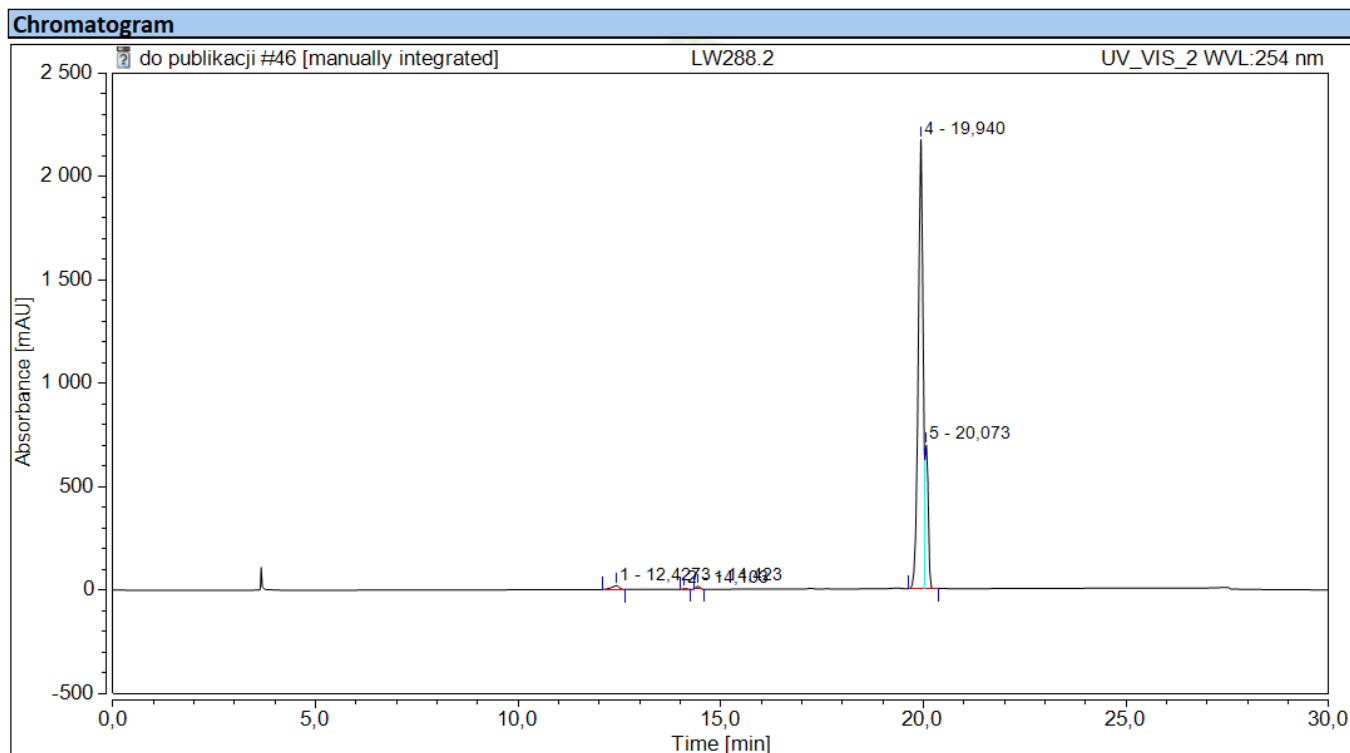
Name: benzyl (3R)-4-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-3-((S)-2-((tert-butoxycarbonyl)amino)-3-methylbutanamido)-4-oxobutanoate

³¹P NMR (162 MHz, Chloroform-d) δ 18.14 (s, 54%), 17.96 (s, 46%).

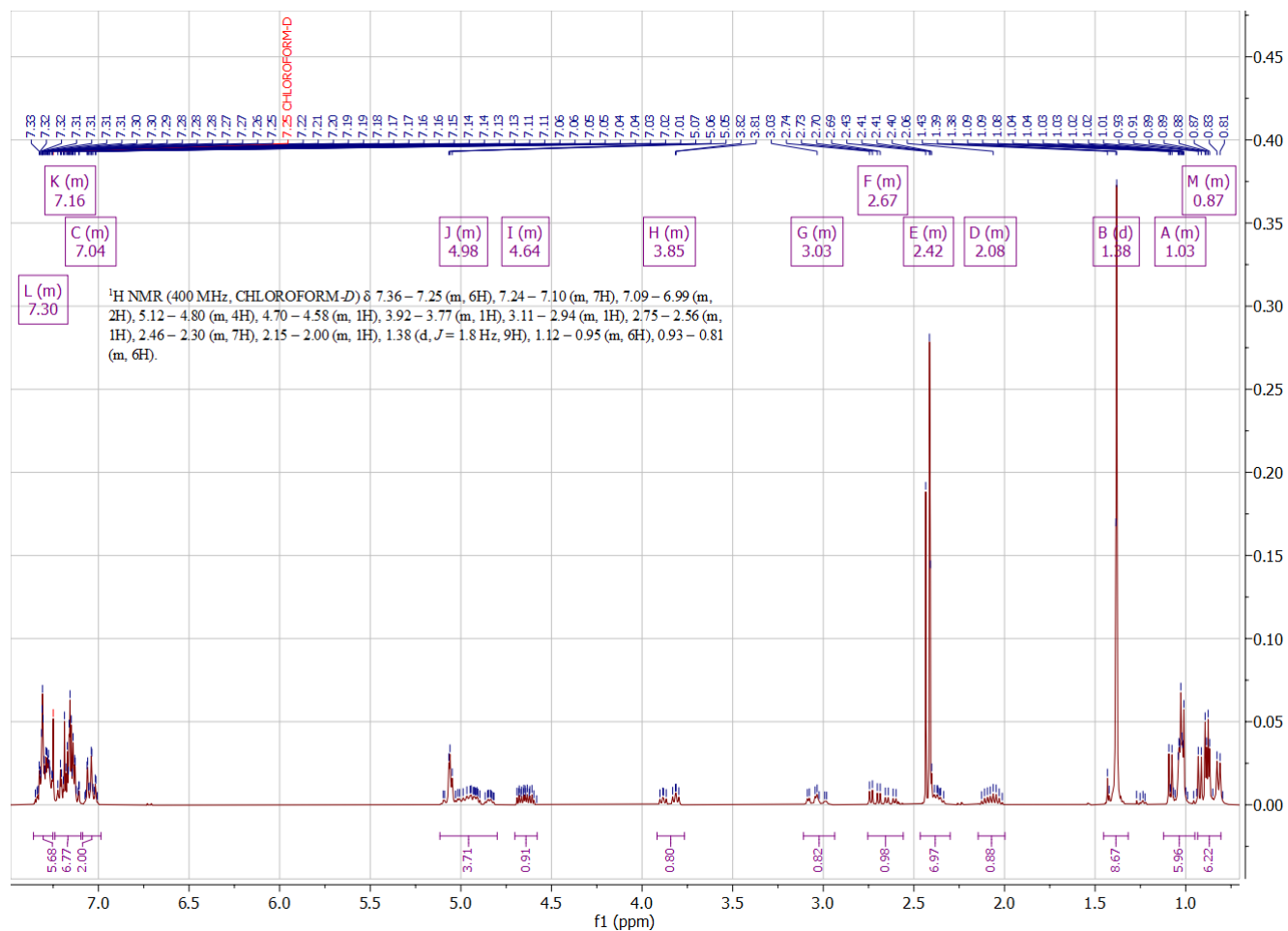
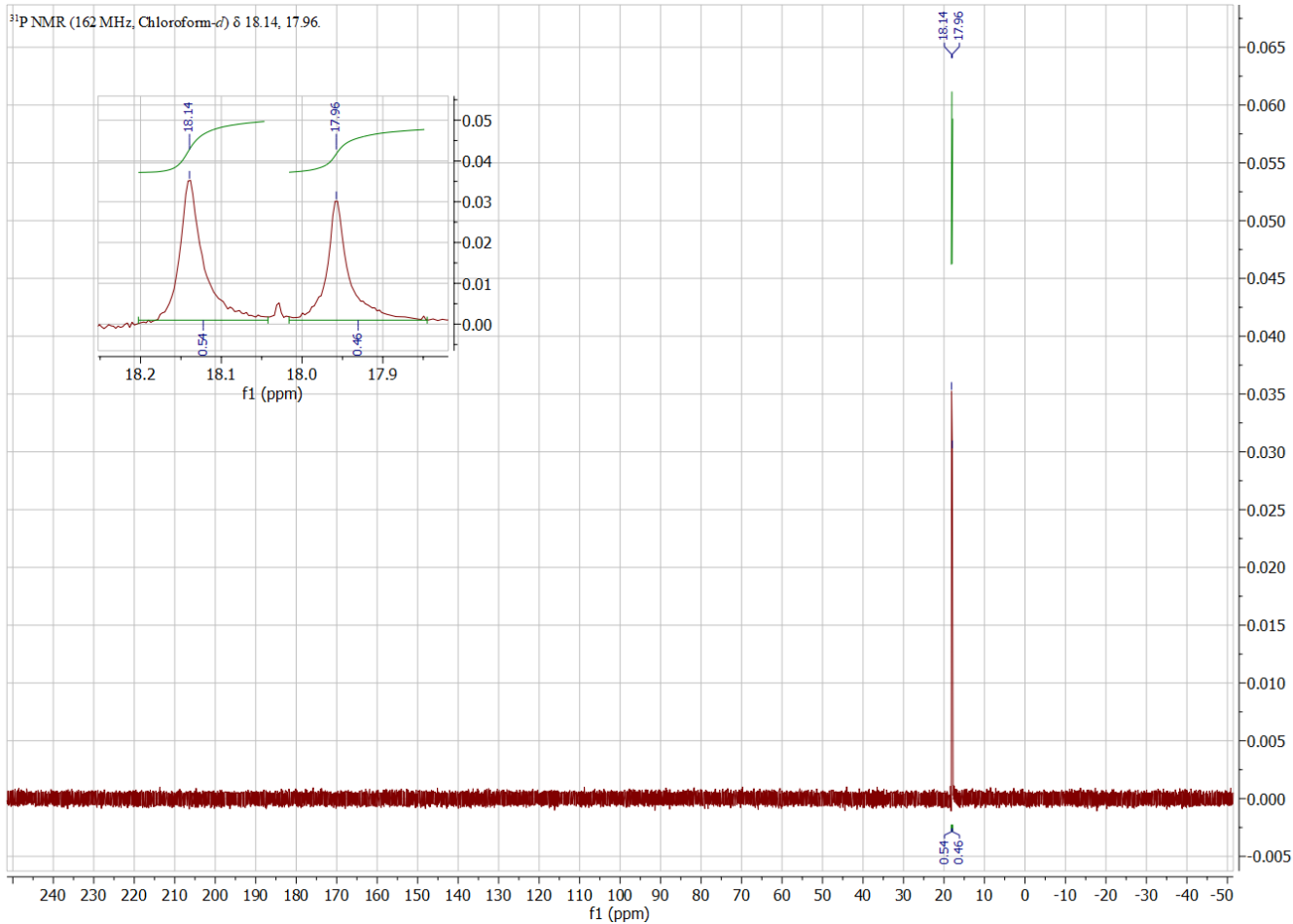
¹H NMR (400 MHz, Chloroform-d) δ 7.36 – 7.25 (m, 6H, 5xArH, NH), 7.24 – 7.10 (m, 7H, 6xArH, NH), 7.09 – 6.99 (m, 2H, 2xArH), 5.12 – 4.80 (m, 4H, CH₂, NH, CH), 4.70 – 4.58 (m, 1H, CHP), 3.92 – 3.77 (m, 1H, CH), 3.11 – 2.94 (m, 1H, 0.5xCH₂), 2.75 – 2.56 (m, 1H, 0.5xCH₂), 2.46 – 2.30 (m, 7H, 2xSCH₃, CH), 2.15 – 2.00 (m, 1H, CH), 1.38 (d, J = 1.8 Hz, 9H, Boc), 1.12 – 0.95 (m, 6H, 2xCH₃), 0.93 – 0.81 (m, 6H, 2xCH₃).

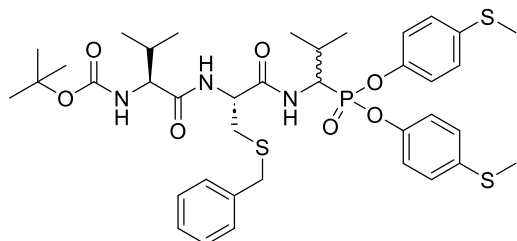
HRMS: C₃₉H₅₂N₃O₉PS₂ [M+Na]⁺ calc. 824.2780 found 824.2800

HPLC: purity >98%; retention time 19.940 and 20.073 min



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12,427	4,162	19,201	1,14	0,66	n.a.
2		14,103	0,379	3,490	0,10	0,12	n.a.
3		14,423	1,608	14,055	0,44	0,48	n.a.
4		19,940	298,778	2170,841	81,85	74,83	n.a.
5		20,073	60,102	693,562	16,47	23,91	n.a.
Total:			365,030	2901,149	100,00	100,00	



(47) Boc-L-Val-L-Cys(Bzl)-Val^P(OPh-4-SCH₃)₂

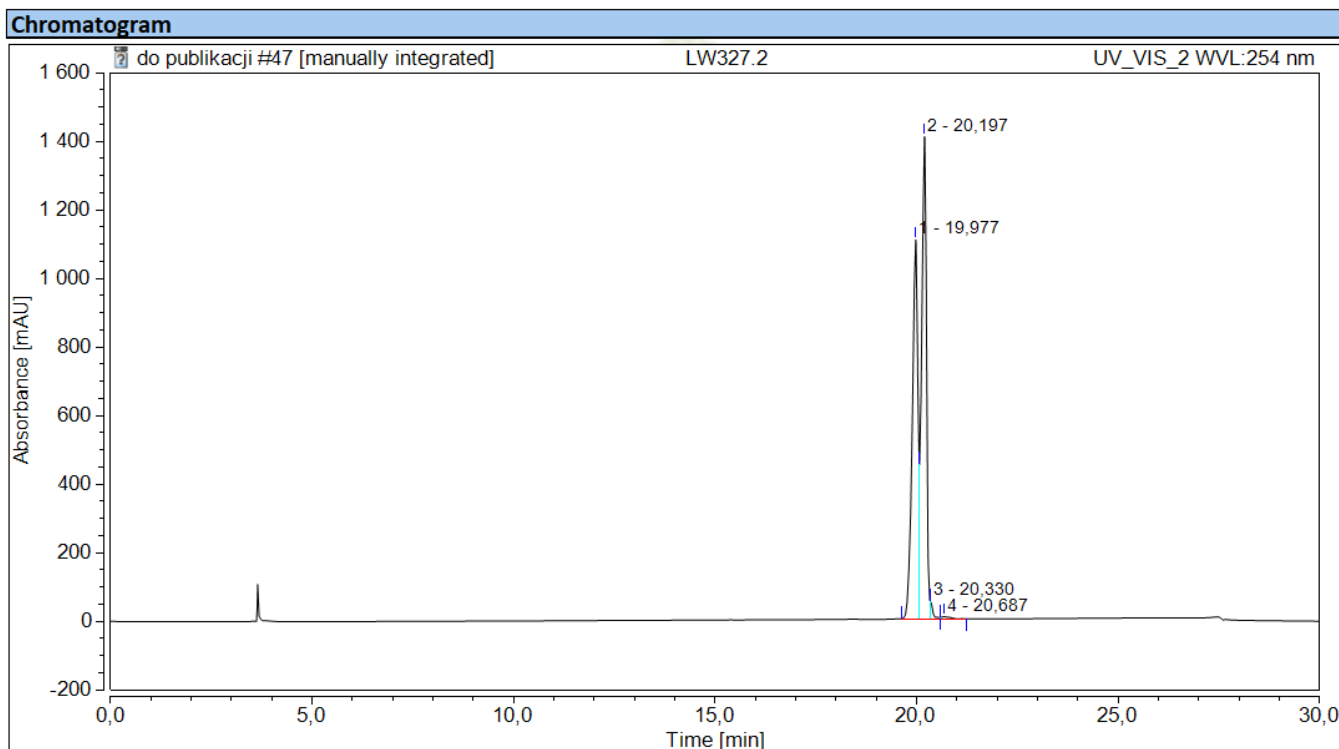
Name: *tert*-butyl ((2*S*)-1-(((2*R*)-3-(benzylthio)-1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-1-oxopropan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 17.89 (s).

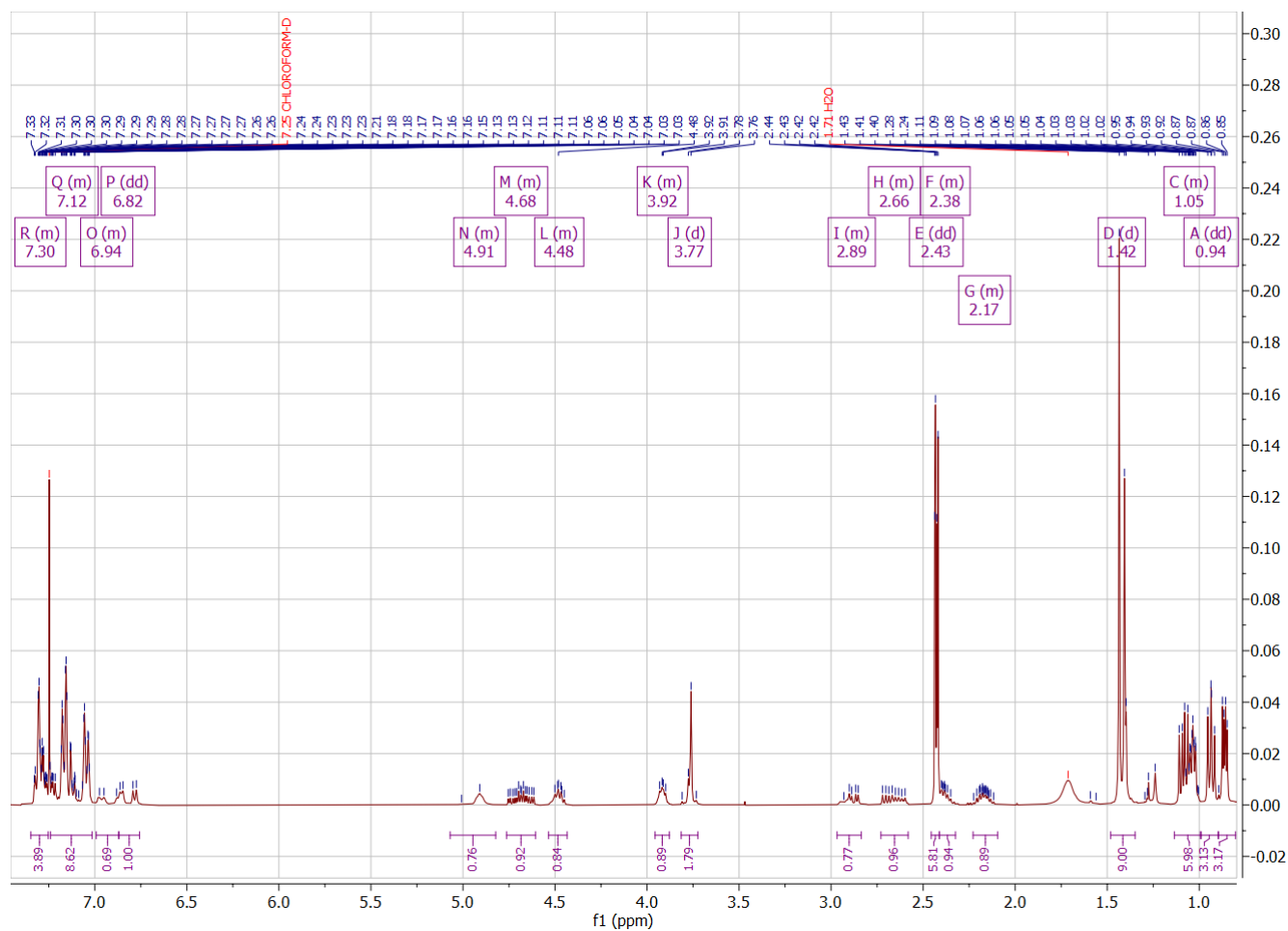
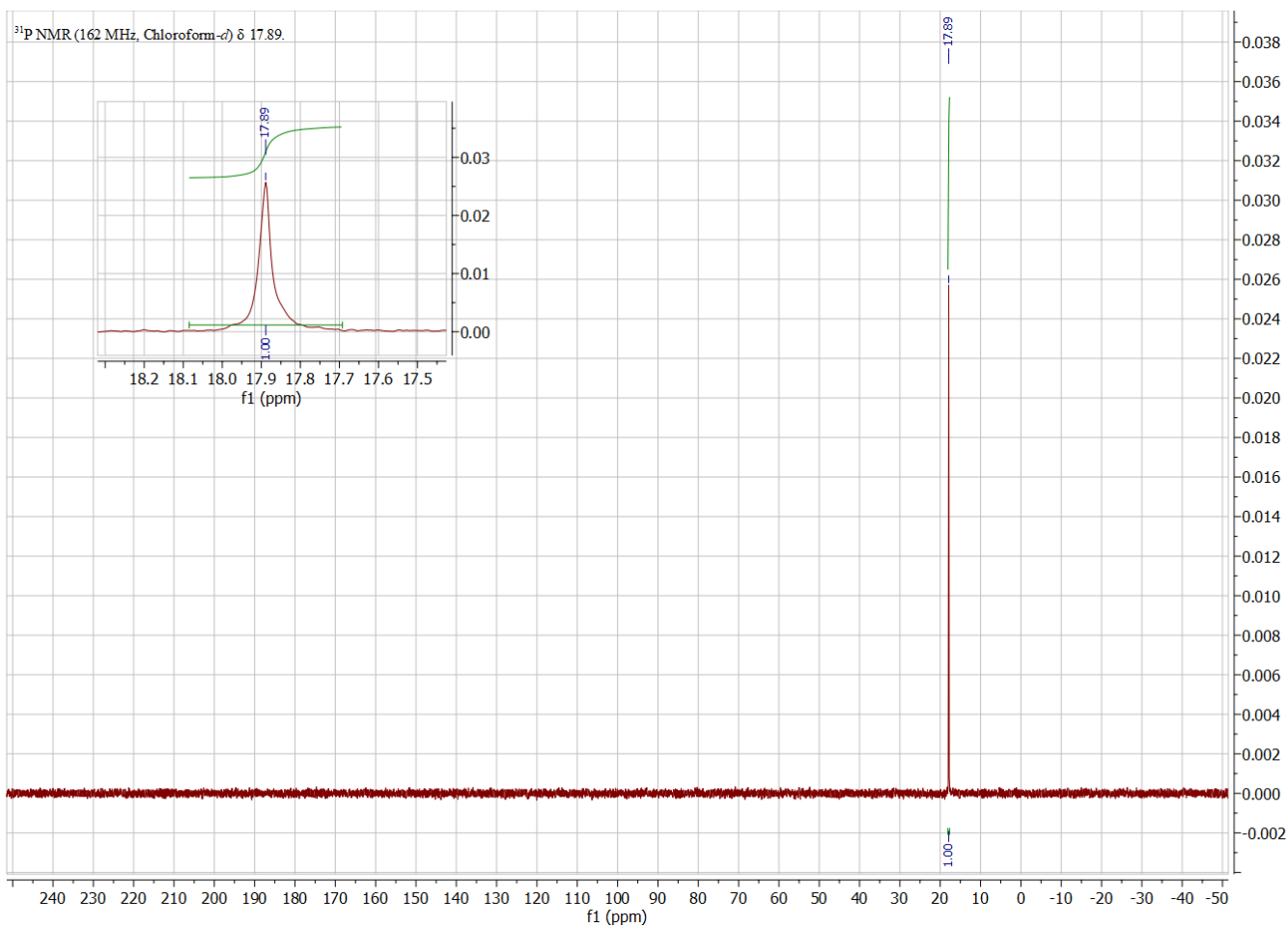
¹H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.25 (m, 4H, 4xArH), 7.24 – 7.01 (m, 9H, 9xArH), 6.99 – 6.87 (m, 1H, NH), 6.82 (dd, *J* = 28.6, 6.9 Hz, 1H, NH), 5.07 – 4.82 (m, 1H, NH), 4.76 – 4.61 (m, 1H, CHP), 4.54 – 4.43 (m, 1H, CH), 3.96 – 3.88 (m, 1H, CH), 3.77 (d, *J* = 5.9 Hz, 2H, CH₂), 2.97 – 2.84 (m, 1H, 0.5xCH₂), 2.73 – 2.58 (m, 1H, 0.5xCH₂), 2.43 (dd, *J* = 5.3, 2.1 Hz, 6H, 2xSCH₃), 2.41 – 2.32 (m, 1H, CH), 2.23 – 2.09 (m, 1H, CH), 1.42 (d, *J* = 11.5 Hz, 9H, Boc), 1.14 – 0.99 (m, 6H, 2xCH₃), 0.94 (dd, *J* = 7.9, 6.8 Hz, 3H, CH₃), 0.86 (dd, *J* = 6.9, 3.5 Hz, 3H, CH₃).

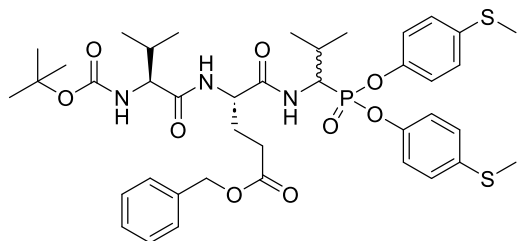
HRMS: C₃₈H₅₂N₃O₇PS₃ [M+Na]⁺ calc. 812.2603 found 812.2574

HPLC: purity >98%; retention time 19.977 and 20.197 min



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19,977	178,894	1105,174	46,95	42,99	n.a.
2		20,197	196,546	1406,187	51,58	54,70	n.a.
3		20,330	4,038	52,855	1,06	2,06	n.a.
4		20,687	1,570	6,283	0,41	0,24	n.a.
Total:			381,048	2570,498	100,00	100,00	



(48) Boc-L-Val-L-Glu(Bzl)- Val^P(OPh-4-SCH₃)₂

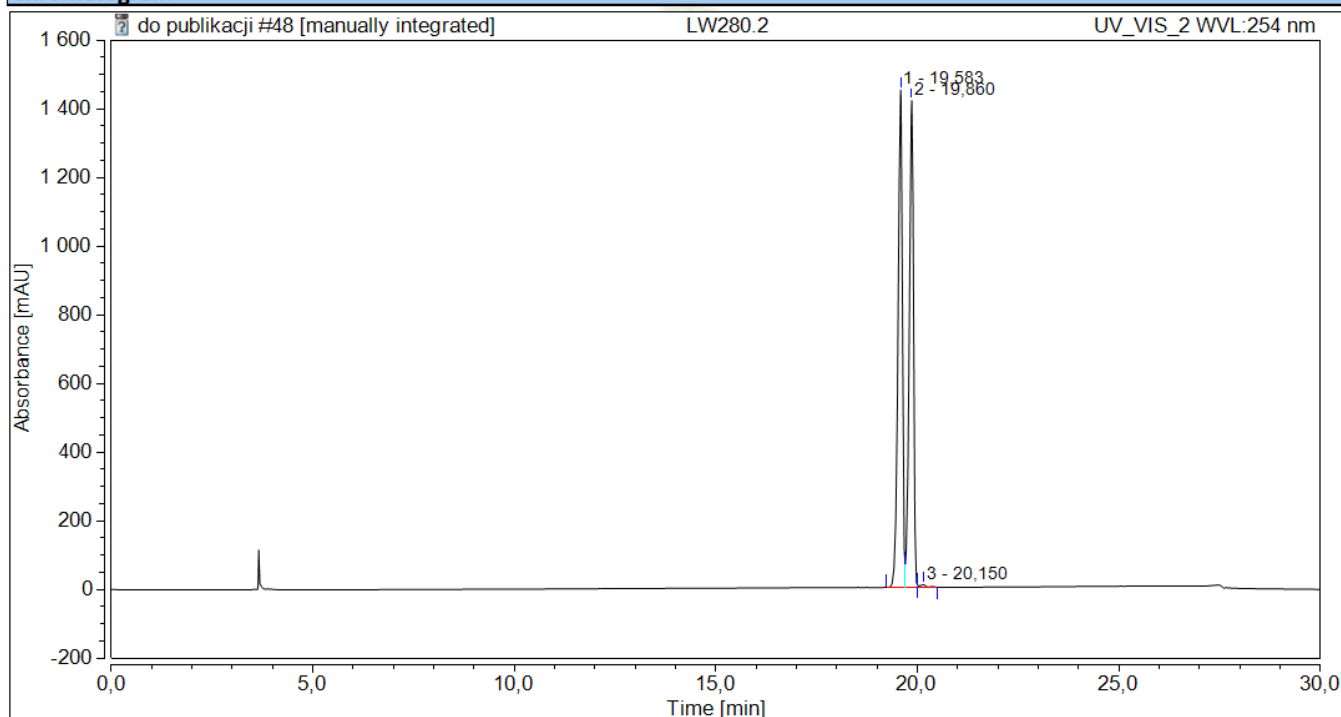
Name: benzyl (4S)-5-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-4-((S)-2-((tert-butoxycarbonyl)amino)-3-methylbutanamido)-5-oxopentanoate

³¹P NMR (162 MHz, Chloroform-d) δ 18.23 (s, 43%), 18.17 (s, 57%).

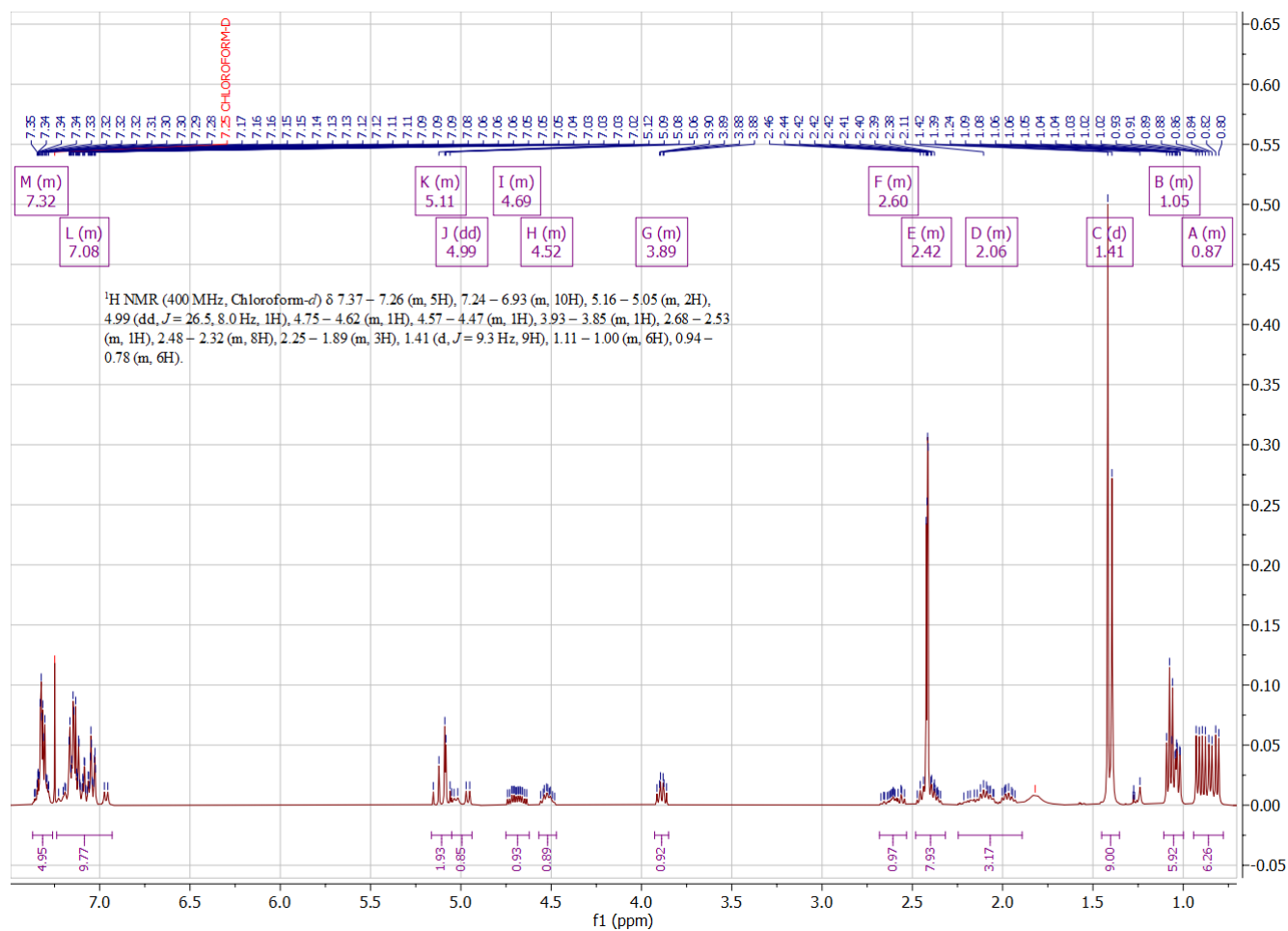
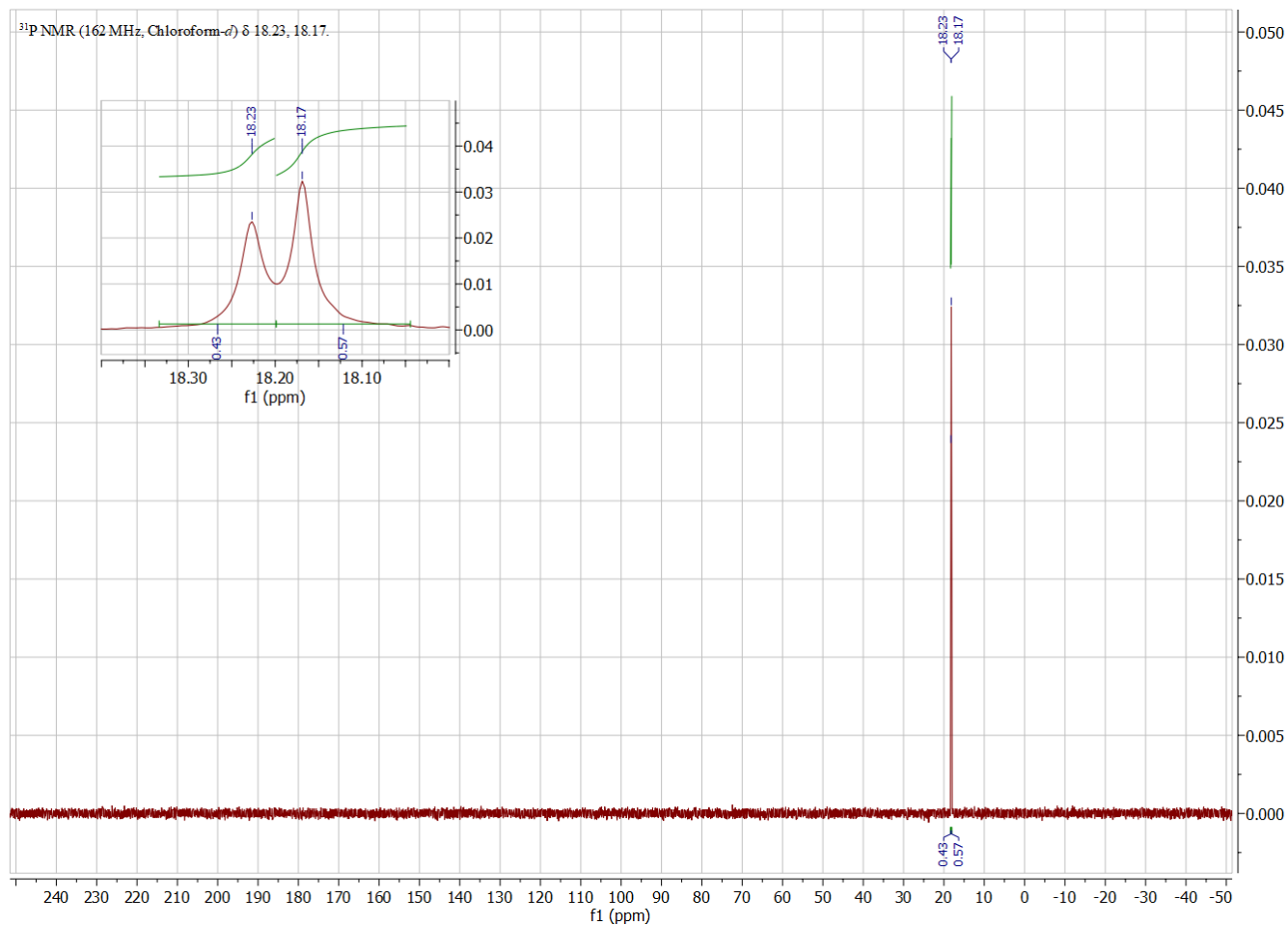
¹H NMR (400 MHz, Chloroform-d) δ 7.37 – 7.26 (m, 5H, 5xArH), 7.24 – 6.93 (m, 10H, 8xArH, 2xNH), 5.16 – 5.05 (m, 2H, CH₂), 4.99 (dd, J = 26.5, 8.0 Hz, 1H, NH), 4.75 – 4.62 (m, 1H, CHP), 4.57 – 4.47 (m, 1H, CH), 3.93 – 3.85 (m, 1H, CH), 2.68 – 2.53 (m, 1H, 0.5xCH₂), 2.48 – 2.32 (m, 8H, 2xSCH₃, 0.5xCH₂, CH), 2.25 – 1.89 (m, 3H, CH₂, CH), 1.41 (d, J = 9.3 Hz, 9H, Boc), 1.11 – 1.00 (m, 6H, 2xCH₃), 0.94 – 0.78 (m, 6H, 2xCH₃).

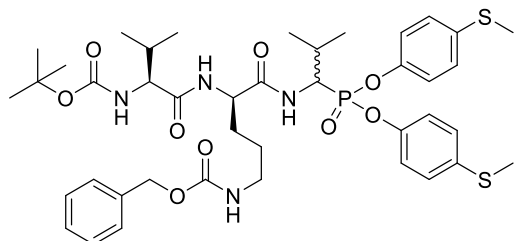
HRMS: C₄₀H₅₄N₃O₉PS₂ [M+Na]⁺ calc. 838.2937 found 838.2911

HPLC: purity >99%; retention time 19.583 and 19.860 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19,583	182,891	1448,310	51,26	50,41	n.a.
2		19,860	172,513	1417,250	48,35	49,33	n.a.
3		20,150	1,401	7,558	0,39	0,26	n.a.
Total:			356,805	2873,118	100,00	100,00	



(49) Boc-L-Val-D-Orn(Z)-Val^P(OPh-4-SCH₃)₂

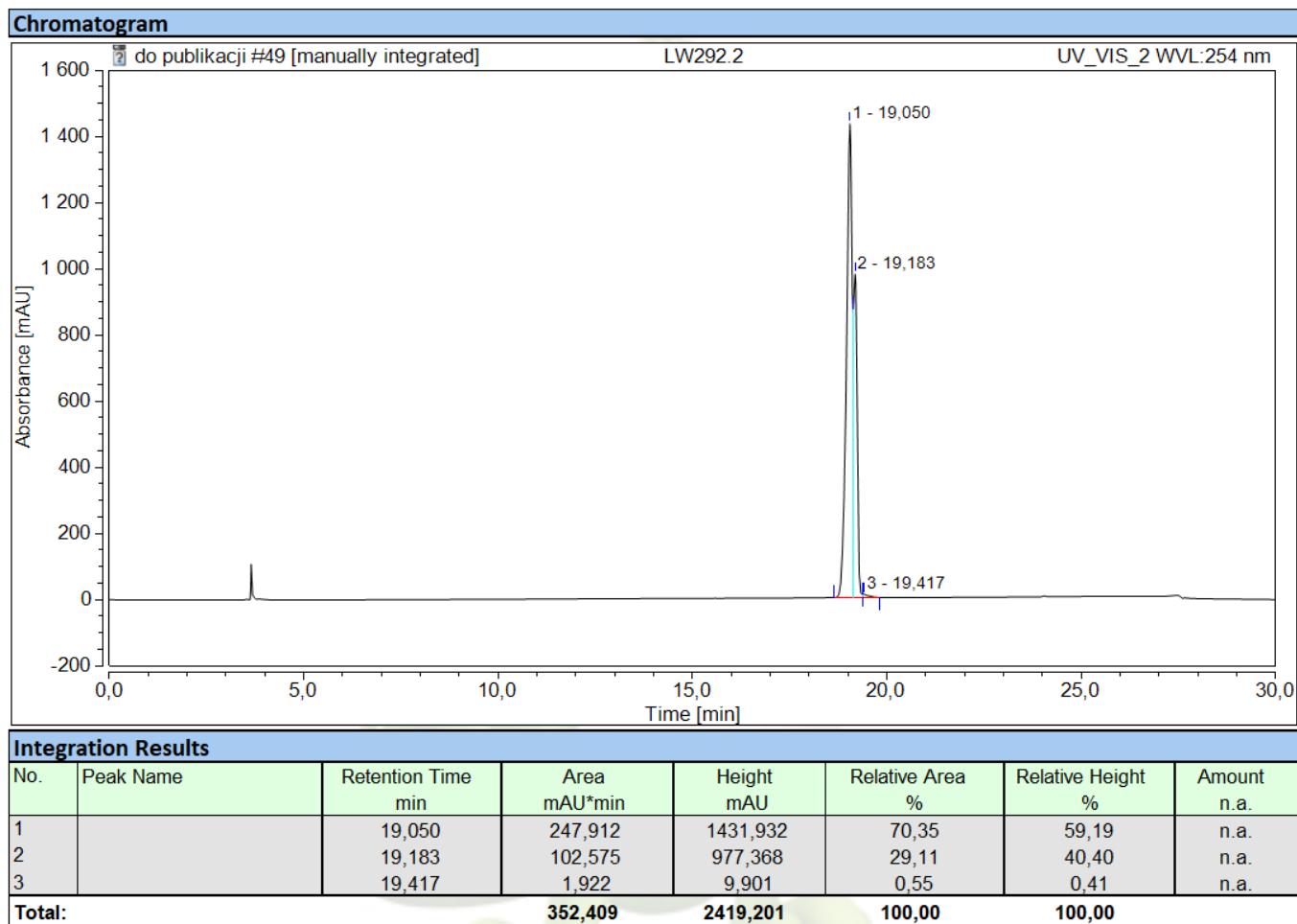
Name: *tert*-butyl ((2S)-1-(((2R)-5-(((benzyloxy)carbonyl)amino)-1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-1-oxopentan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

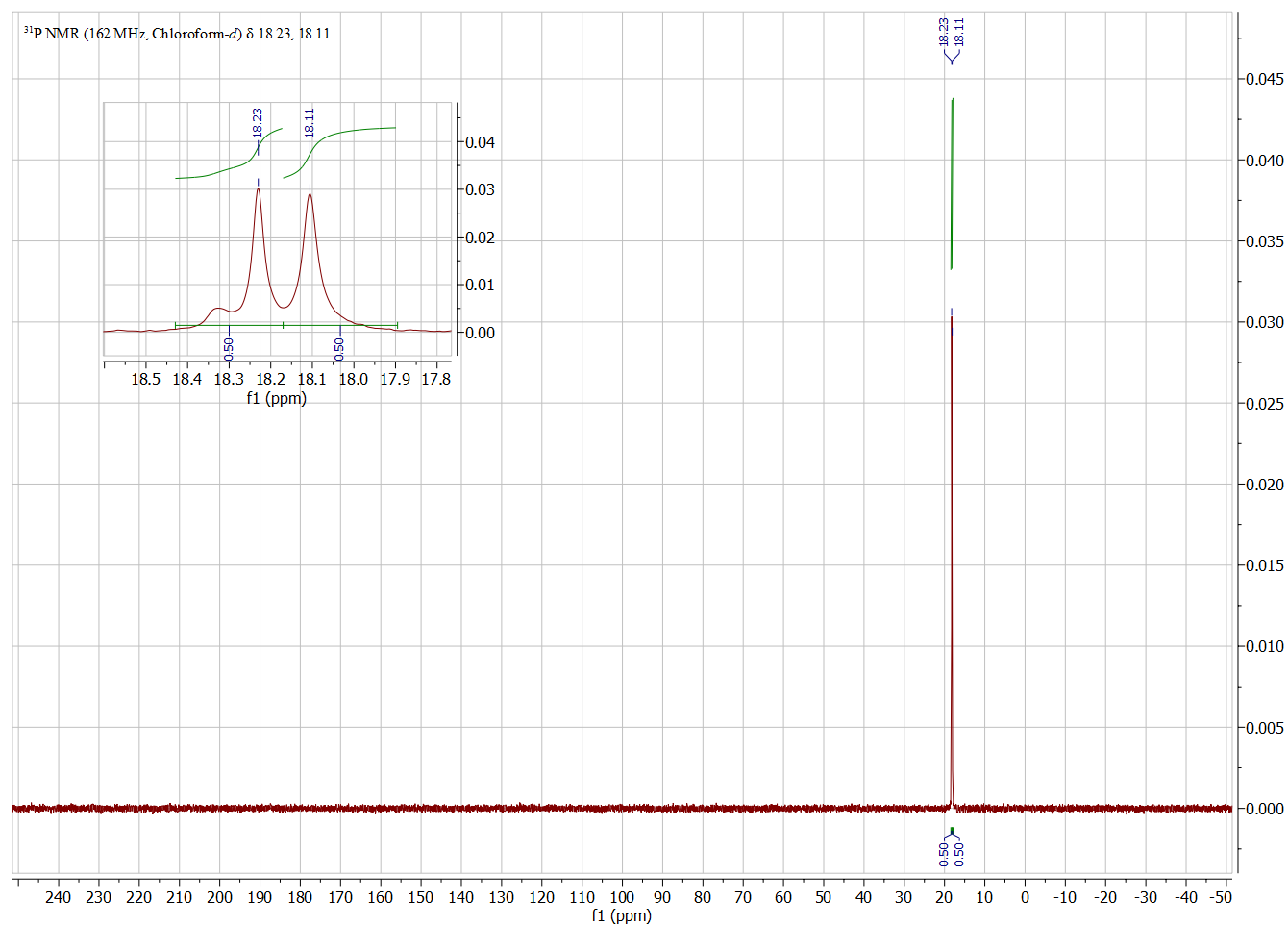
³¹P NMR (162 MHz, Chloroform-d) δ 18.23 (s, 50%), 18.11 (s, 50%).

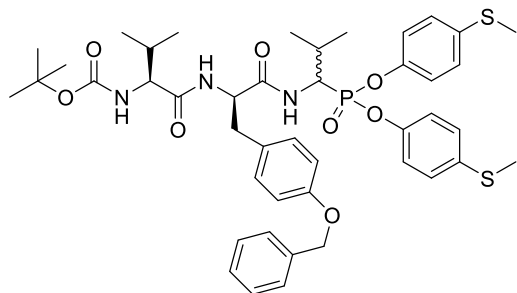
¹H NMR (400 MHz, Chloroform-d) δ 7.51 (dd, J = 32.6, 10.3 Hz, 1H, NH), 7.34 – 7.22 (m, 5H, 5xArH), 7.19 – 7.01 (m, 8H, 8xArH), 7.00 – 6.90 (m, 1H, NH), 5.32 – 5.14 (m, 2H, 2xNH), 5.15 – 4.91 (m, 2H, CH₂), 4.81 – 4.55 (m, 2H, CHP, CH), 4.02 – 3.88 (m, 1H, CH), 3.47 – 3.30 (m, 1H, 0.5xCH₂), 3.17 – 2.94 (m, 1H, 0.5xCH₂), 2.45 – 2.38 (m, 6H, 2xSCH₃), 2.38 – 2.29 (m, 1H, CH), 2.16 – 2.03 (m, 1H, CH), 1.95 – 1.65 (m, 1H, 0.5x CH₂), 1.65 – 1.42 (m, 3H, 1.5 CH₂), 1.39 (d, J = 7.4 Hz, 9H, Boc), 1.16 – 0.97 (m, 6H, 2xCH₃), 0.93 – 0.80 (m, 6H, 2xCH₃).

HRMS: C₄₁H₅₇N₄O₉PS₂ [M+Na]⁺ calc. 867.3202 found 867.3196

HPLC: purity >99%; retention time 19.050 and 19.183 min





(50) Boc-L-Val-D-Tyr(Bzl)- Val^P(OPh-4-SCH₃)₂

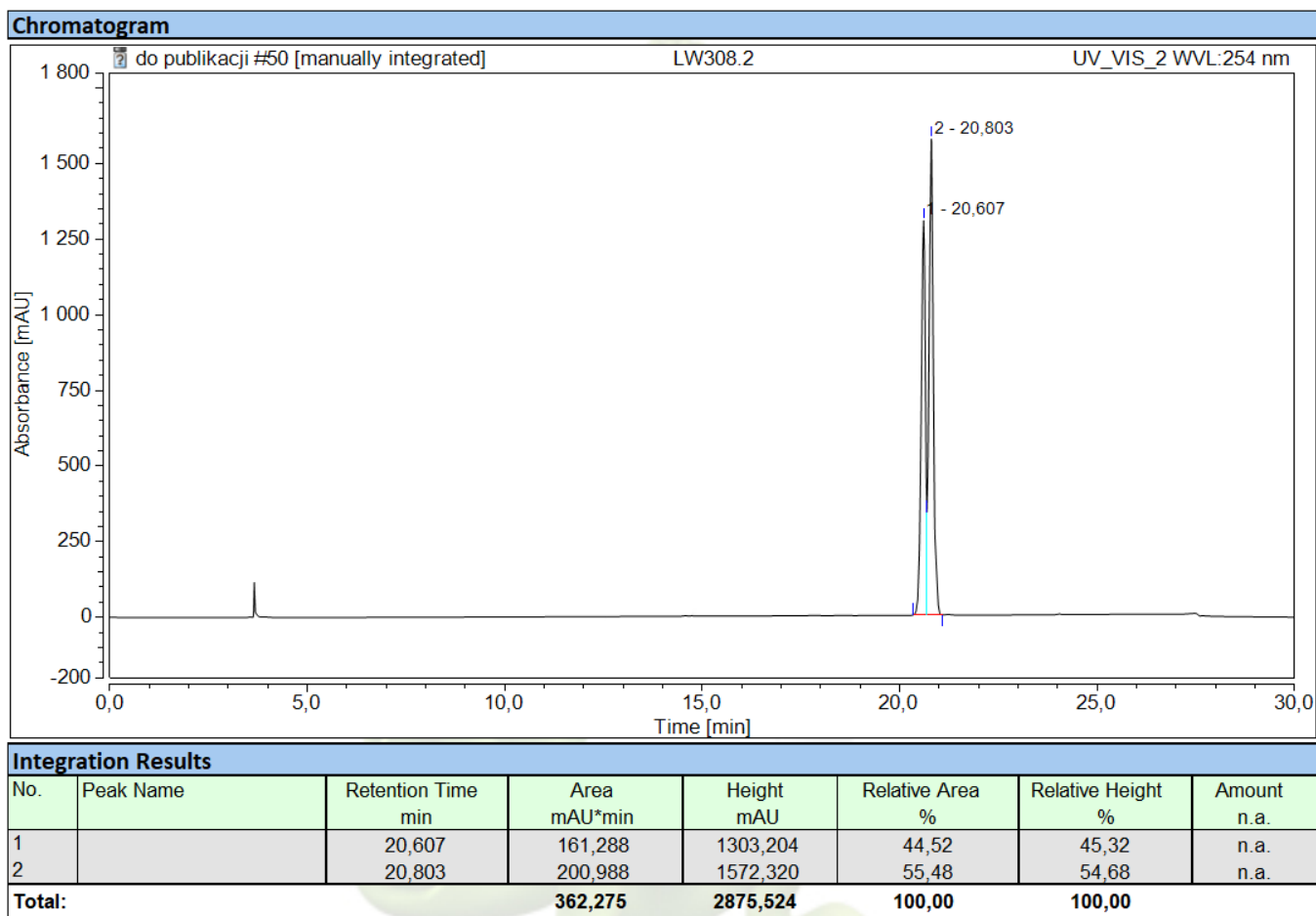
Name: *tert*-butyl ((2*S*)-1-(((2*R*)-3-(4-(benzyloxy)phenyl)-1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-1-oxopropan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

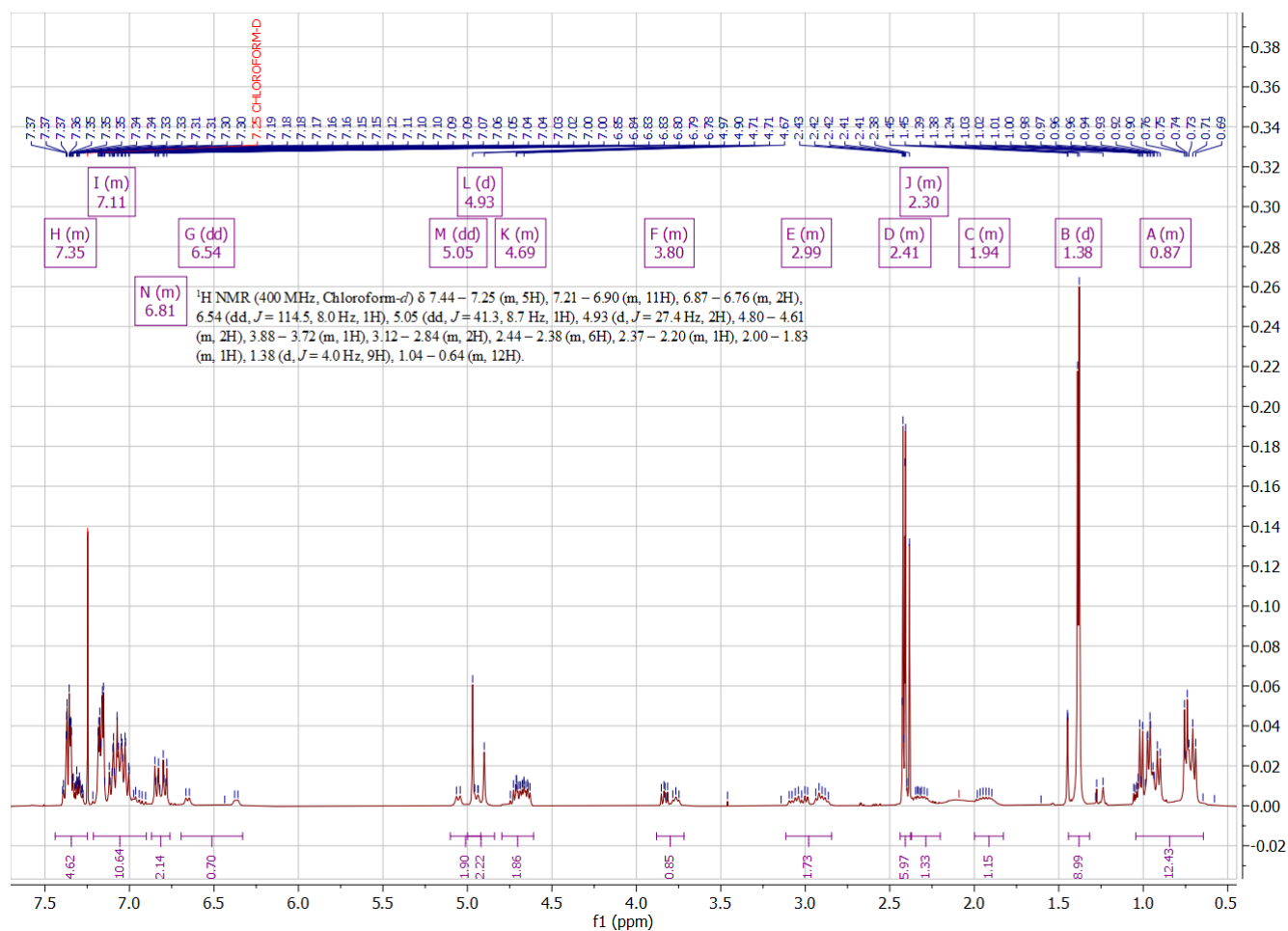
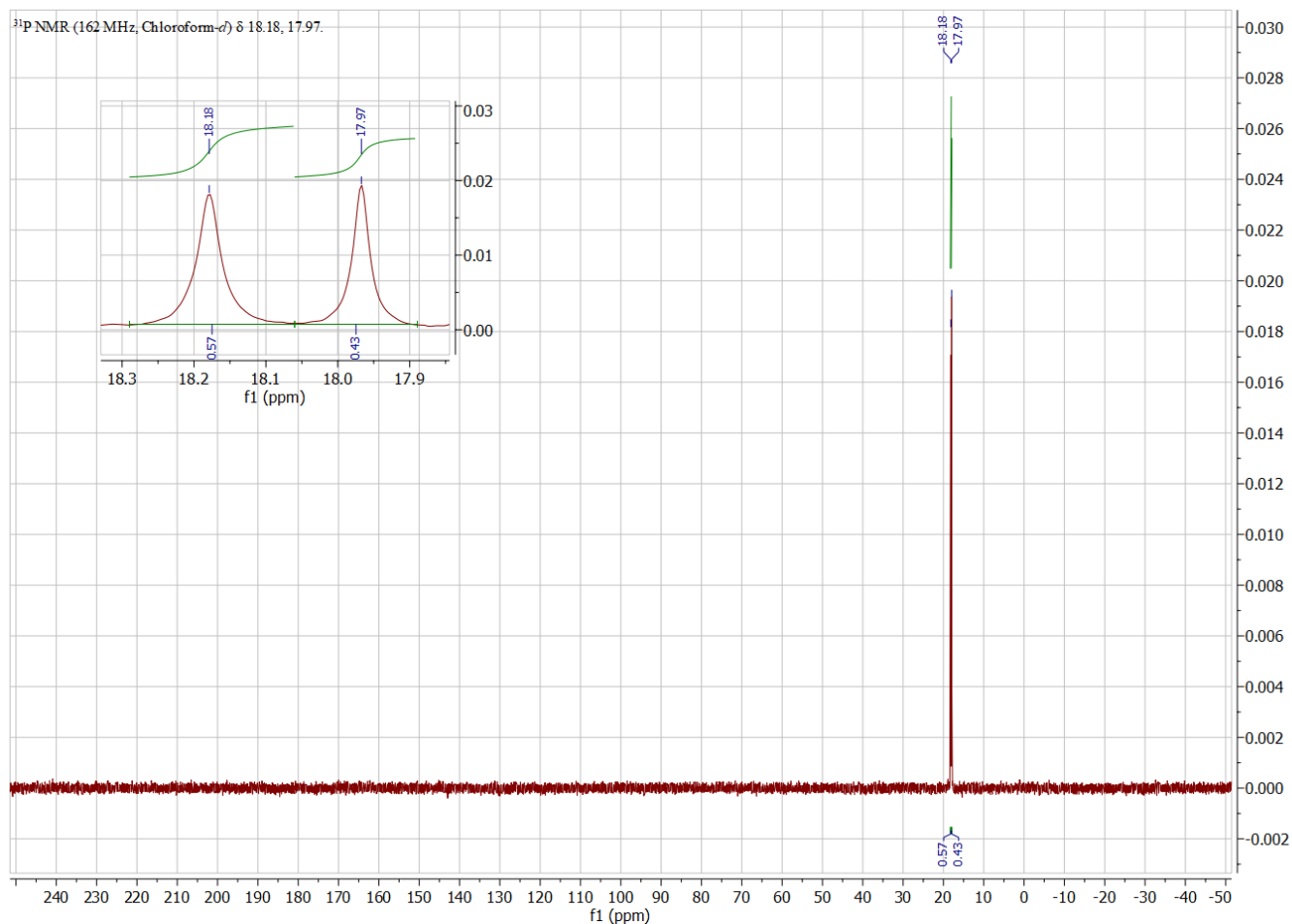
³¹P NMR (162 MHz, Chloroform-*d*) δ 18.18 (s, 57%), 17.97 (s, 43%).

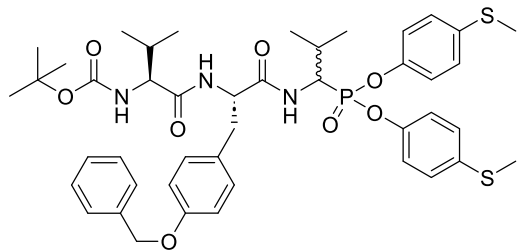
¹H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.25 (m, 5H, 5xArH), 7.21 – 6.90 (m, 11H, 10xArH, NH), 6.87 – 6.76 (m, 2H, 2xArH), 6.54 (dd, *J* = 114.5, 8.0 Hz, 1H, NH), 5.05 (dd, *J* = 41.3, 8.7 Hz, 1H, NH), 4.93 (d, *J* = 27.4 Hz, 2H, CH₂), 4.80 – 4.61 (m, 2H, CHP, CH), 3.88 – 3.72 (m, 1H, CH), 3.12 – 2.84 (m, 2H, CH₂), 2.44 – 2.38 (m, 6H, 2xSCH₃), 2.37 – 2.20 (m, 1H, CH), 2.00 – 1.83 (m, 1H, CH), 1.38 (d, *J* = 4.0 Hz, 9H, Boc), 1.04 – 0.64 (m, 12H, 4xCH₃).

HRMS: C₄₄H₅₆N₃O₈PS₂ [M+Na]⁺ calc. 872.3144 found 872.3152

HPLC: purity >99%; retention time 20.607 and 20.803 min





(51) Boc-L-Val-L-Tyr(Bzl)-Val^P(OPh-4-SCH₃)₂

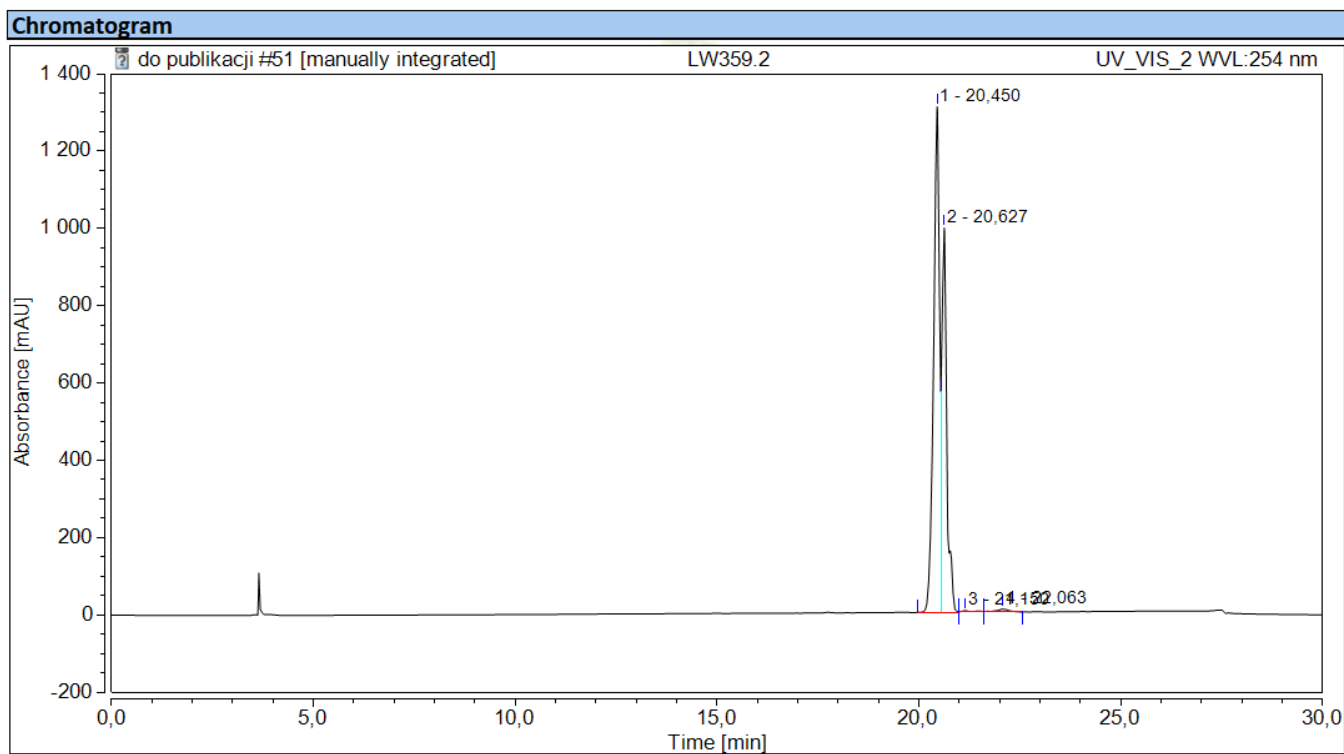
Name: *tert*-butyl ((2*S*)-1-(((2*S*)-3-(4-(benzyloxy)phenyl)-1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-1-oxopropan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.13 (s, 42%), 18.06 (s, 58%).

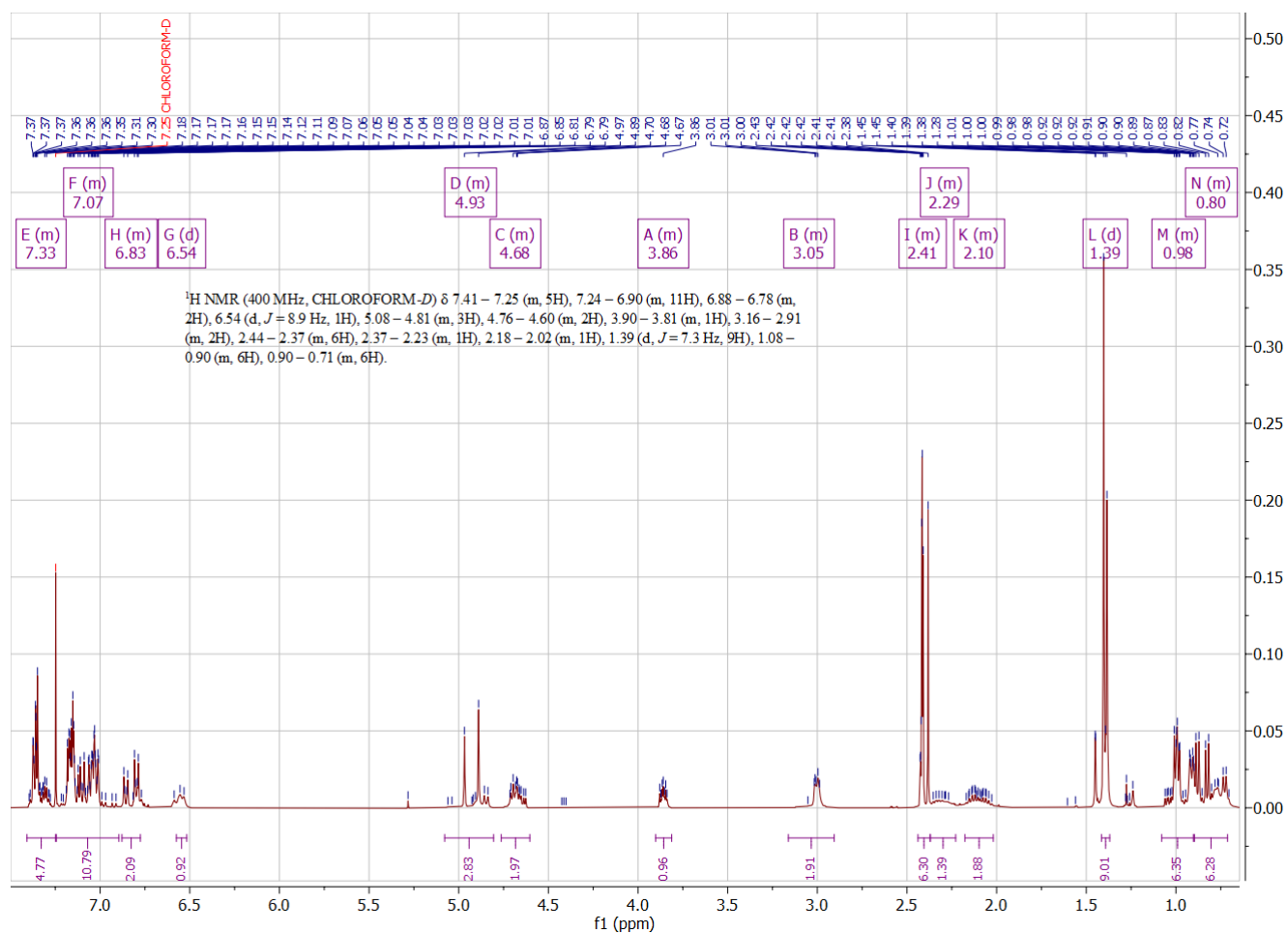
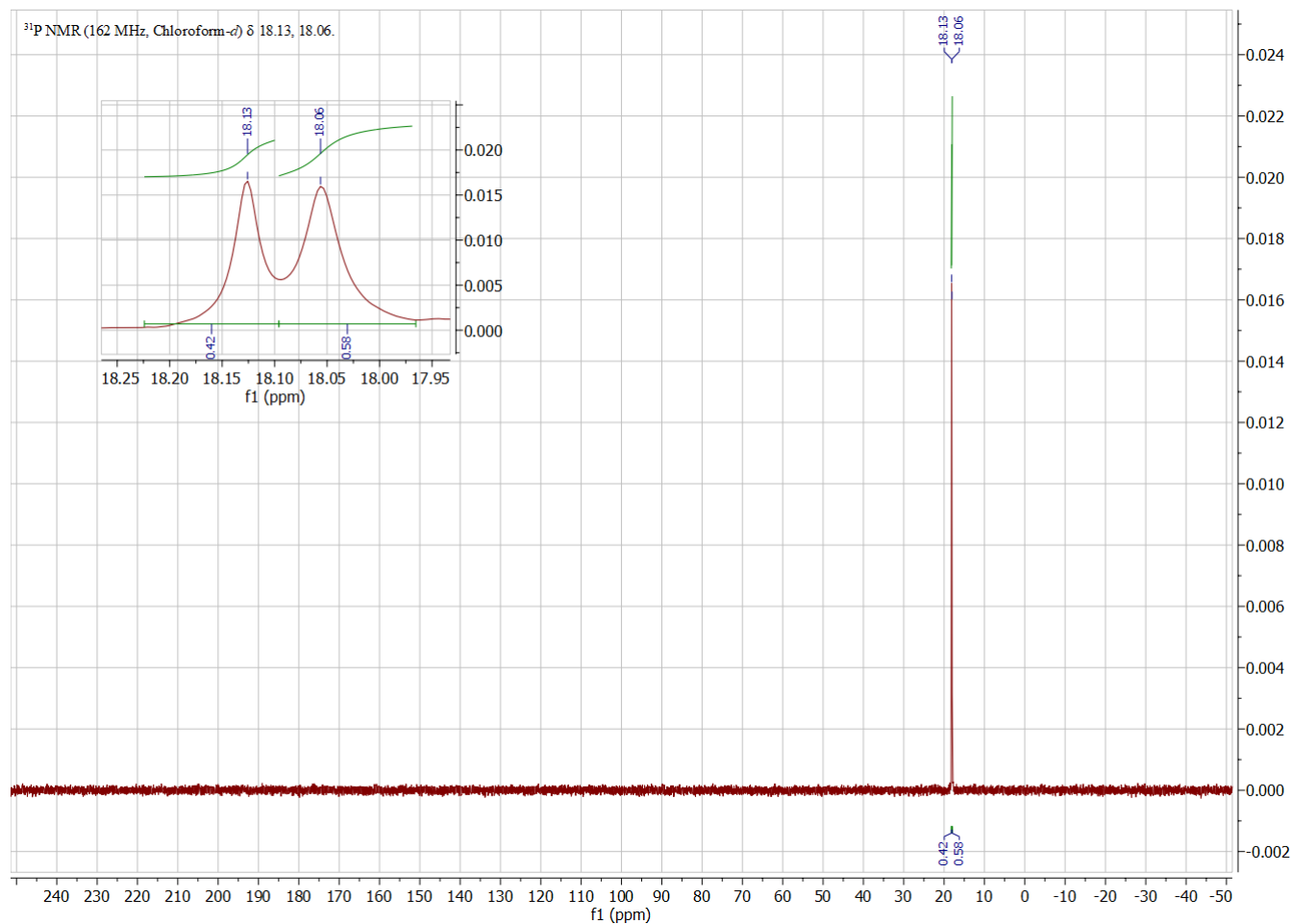
¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.25 (m, 5H, 5xArH), 7.24 – 6.90 (m, 11H, 10xArH, NH), 6.88 – 6.78 (m, 2H, 2xArH), 6.54 (d, *J* = 8.9 Hz, 1H, NH), 5.08 – 4.81 (m, 3H, CH₂, NH), 4.76 – 4.60 (m, 2H, CHP, CH), 3.90 – 3.81 (m, 1H, CH), 3.16 – 2.91 (m, 2H, CH₂), 2.44 – 2.37 (m, 6H, 2xSCH₃), 2.37 – 2.23 (m, 1H, CH), 2.18 – 2.02 (m, 1H, CH), 1.39 (d, *J* = 7.3 Hz, 9H, Boc), 1.08 – 0.90 (m, 6H, 2xCH₃), 0.90 – 0.71 (m, 6H, 2xCH₃).

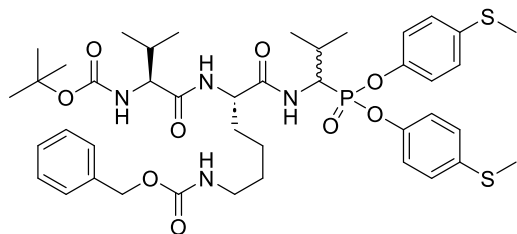
HRMS: C₄₄H₅₆N₃O₈PS₂ [M+Na]⁺ calc. 872.3144 found 872.3138

HPLC: purity >98%; retention time 20.450 and 20.627 min



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20,450	217,666	1308,190	59,62	56,54	n.a.
2		20,627	143,035	994,418	39,18	42,98	n.a.
3		21,150	1,514	3,923	0,41	0,17	n.a.
4		22,063	2,867	7,411	0,79	0,32	n.a.
Total:			365,082	2313,942	100,00	100,00	



(52) Boc-L-Val-L-Lys(Z)-Val^P(OPh-4-SCH₃)₂

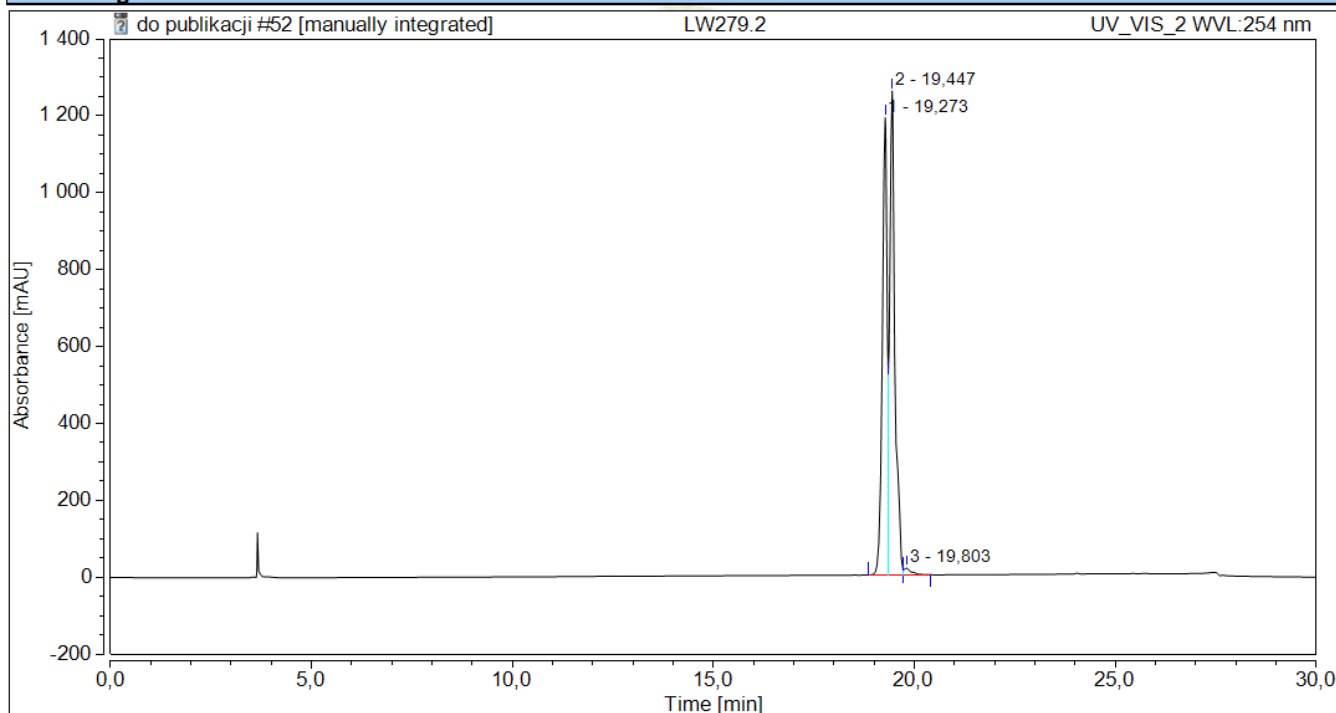
Name: *tert*-butyl ((2*S*)-1-(((2*S*)-6-(((benzyloxy)carbonyl)amino)-1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-1-oxohexan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.21 (s, 49%), 18.12 (s, 51%).

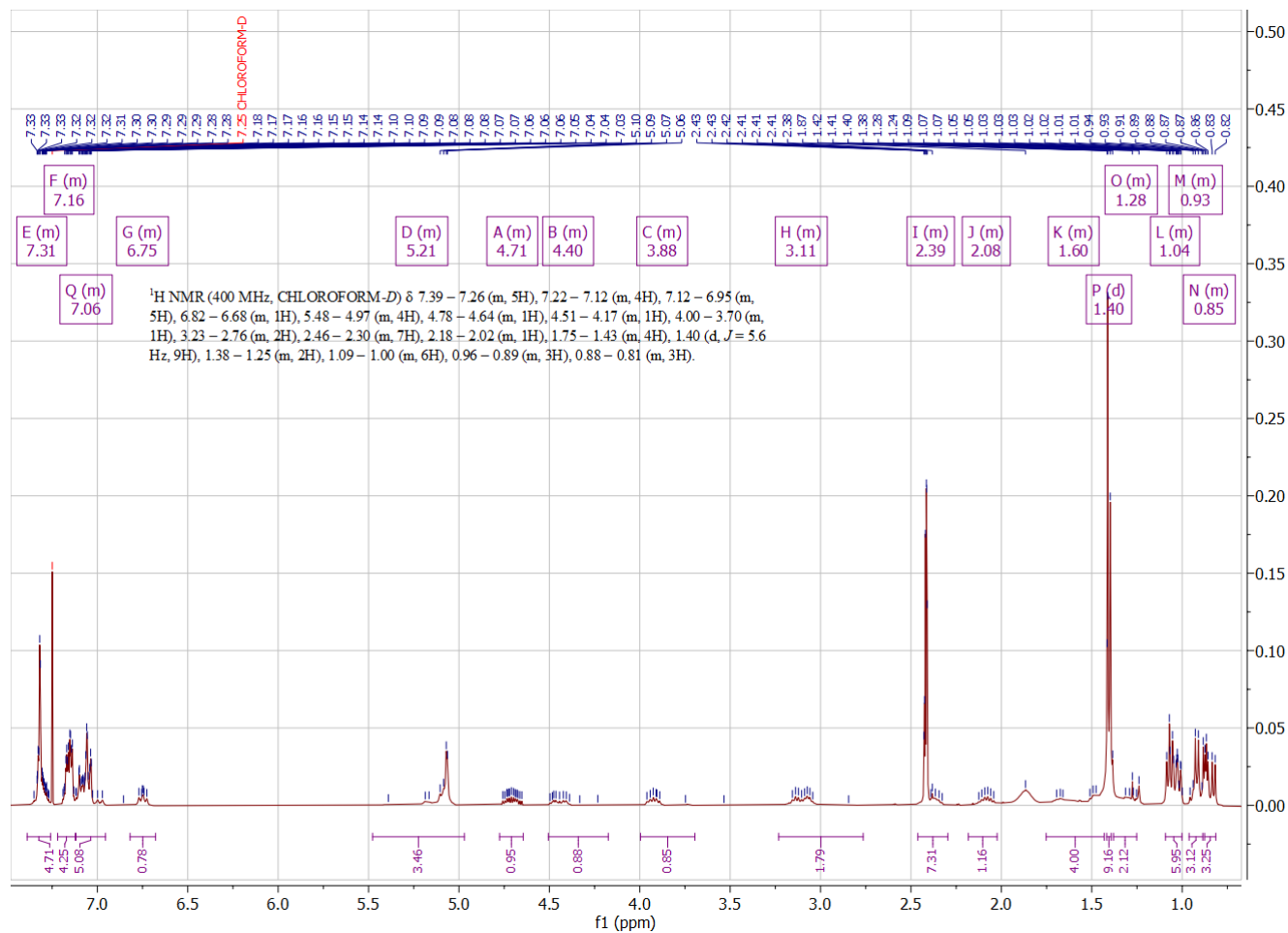
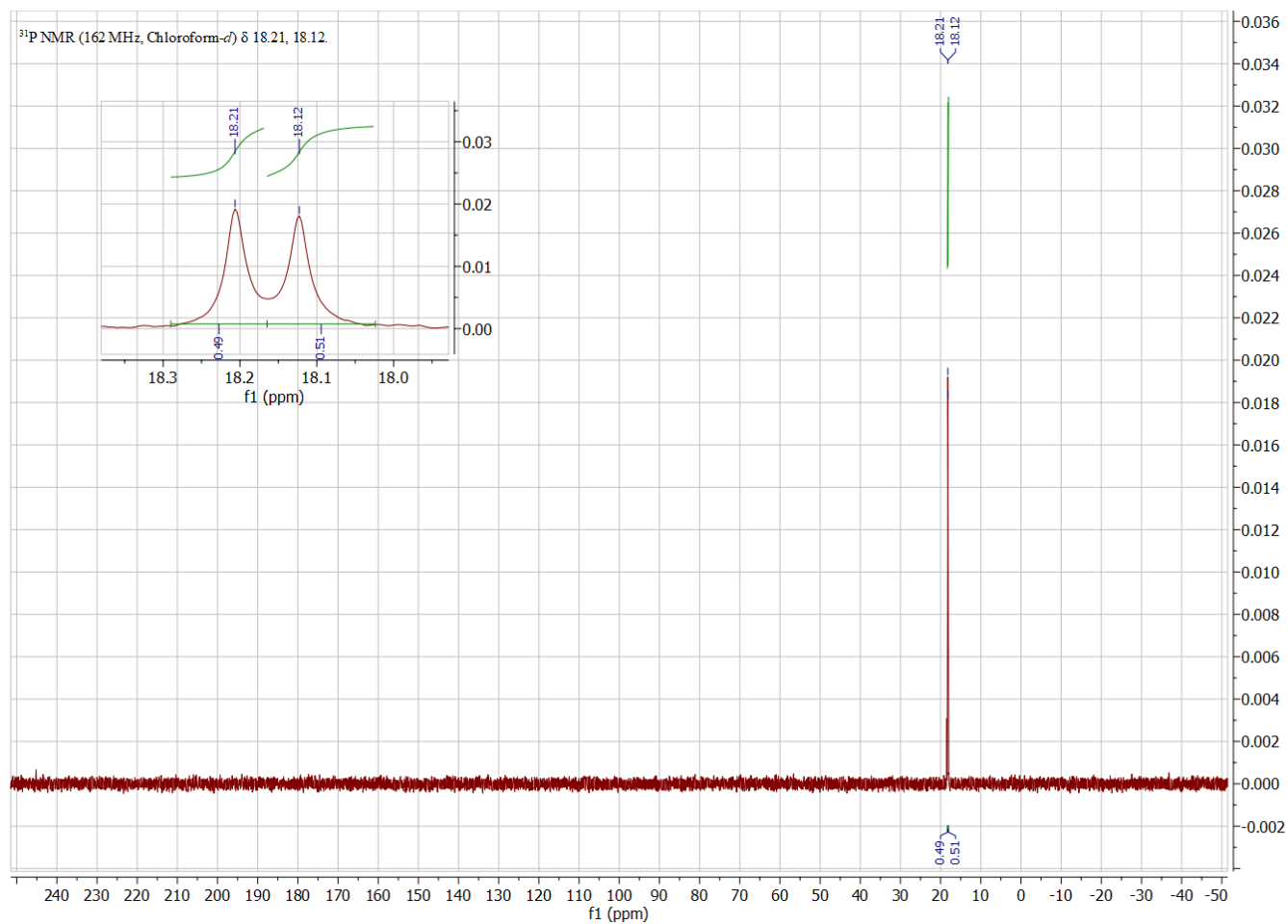
¹H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.26 (m, 5H, 5xArH), 7.22 – 7.12 (m, 4H, 4xArH), 7.12 – 6.95 (m, 5H, 4xArH, NH), 6.82 – 6.68 (m, 1H, NH), 5.48 – 4.97 (m, 4H, CH₂, 2xNH), 4.78 – 4.64 (m, 1H, CHP), 4.51 – 4.17 (m, 1H, CH), 4.00 – 3.70 (m, 1H, CH), 3.23 – 2.76 (m, 2H, CH₂), 2.46 – 2.30 (m, 7H, 2xSCH₃, CH), 2.18 – 2.02 (m, 1H, CH), 1.75 – 1.43 (m, 4H, 2xCH₂), 1.40 (d, *J* = 5.6 Hz, 9H, Boc), 1.38 – 1.25 (m, 2H, CH₂), 1.09 – 1.00 (m, 6H, 2xCH₃), 0.96 – 0.89 (m, 3H, CH₃), 0.88 – 0.81 (m, 3H, CH₃).

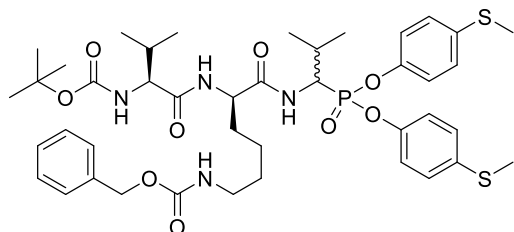
HRMS: C₄₂H₅₉N₄O₉PS₂ [M+Na]⁺ calc. 881.3359 found 881.3330

HPLC: purity >98%; retention time 19.273 and 19.447 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19,273	164,458	1189,753	46,12	48,24	n.a.
2		19,447	188,357	1258,740	52,82	51,03	n.a.
3		19,803	3,809	17,933	1,07	0,73	n.a.
Total:			356,624	2466,426	100,00	100,00	



(53) Boc-L-Val-D-Lys(Z)-Val^P(OPh-4-SCH₃)₂

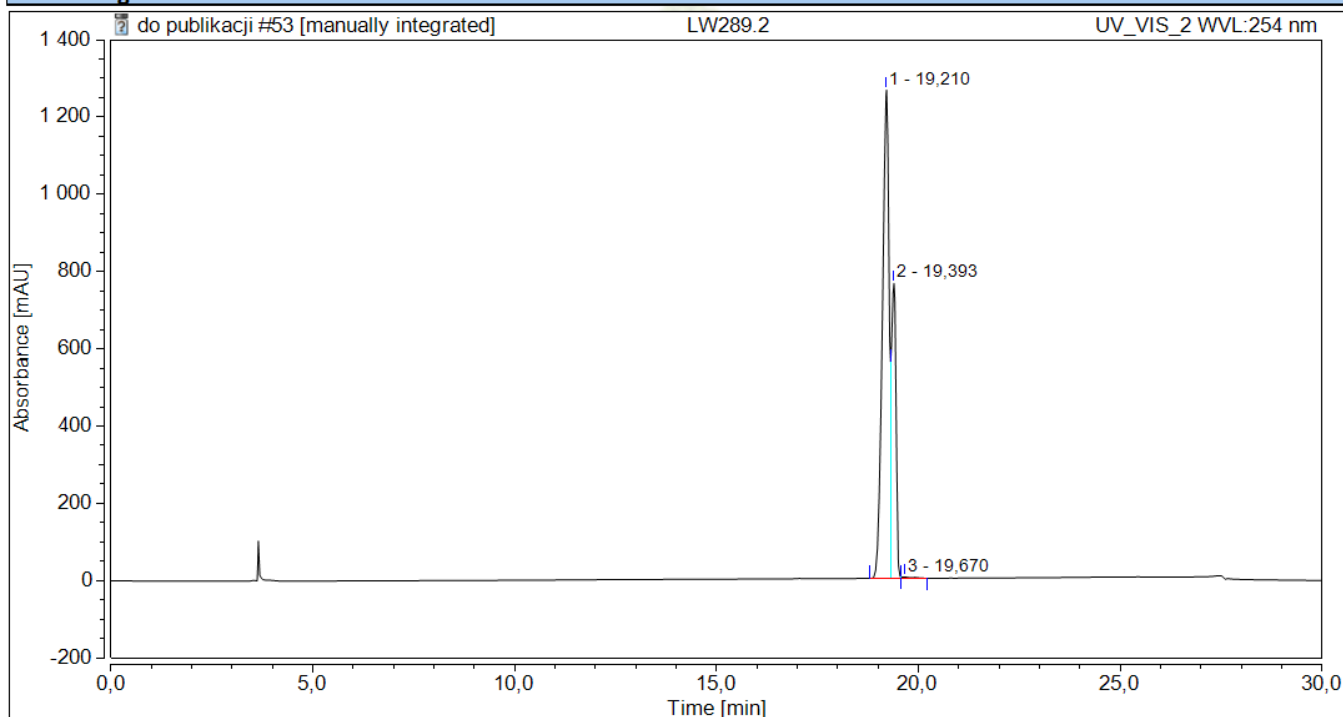
Name: *tert*-butyl ((2*S*)-1-(((2*R*)-6-(((benzyloxy)carbonyl)amino)-1-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)amino)-1-oxohexan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.14 (s, 56%), 18.00 (s, 44%).

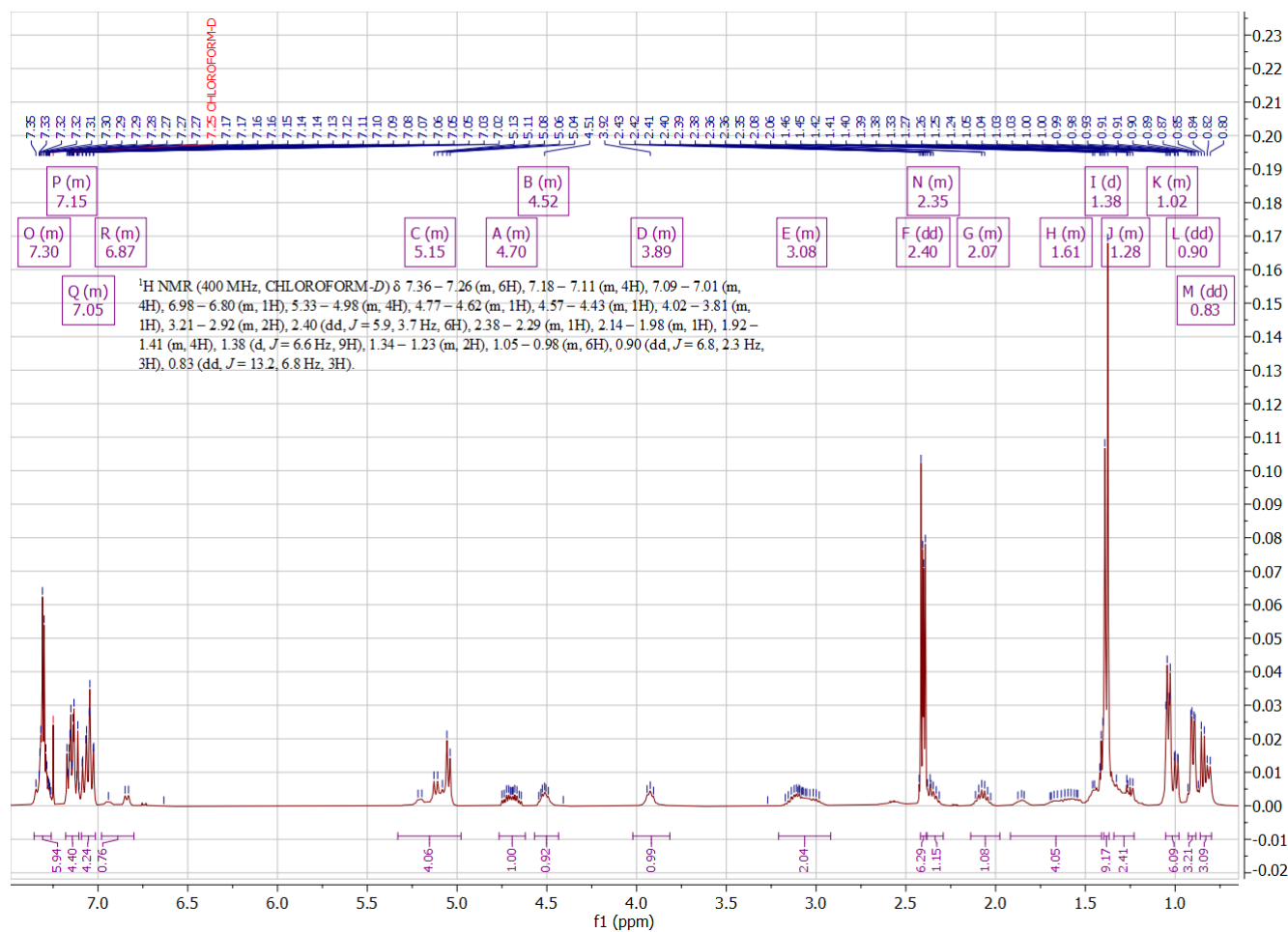
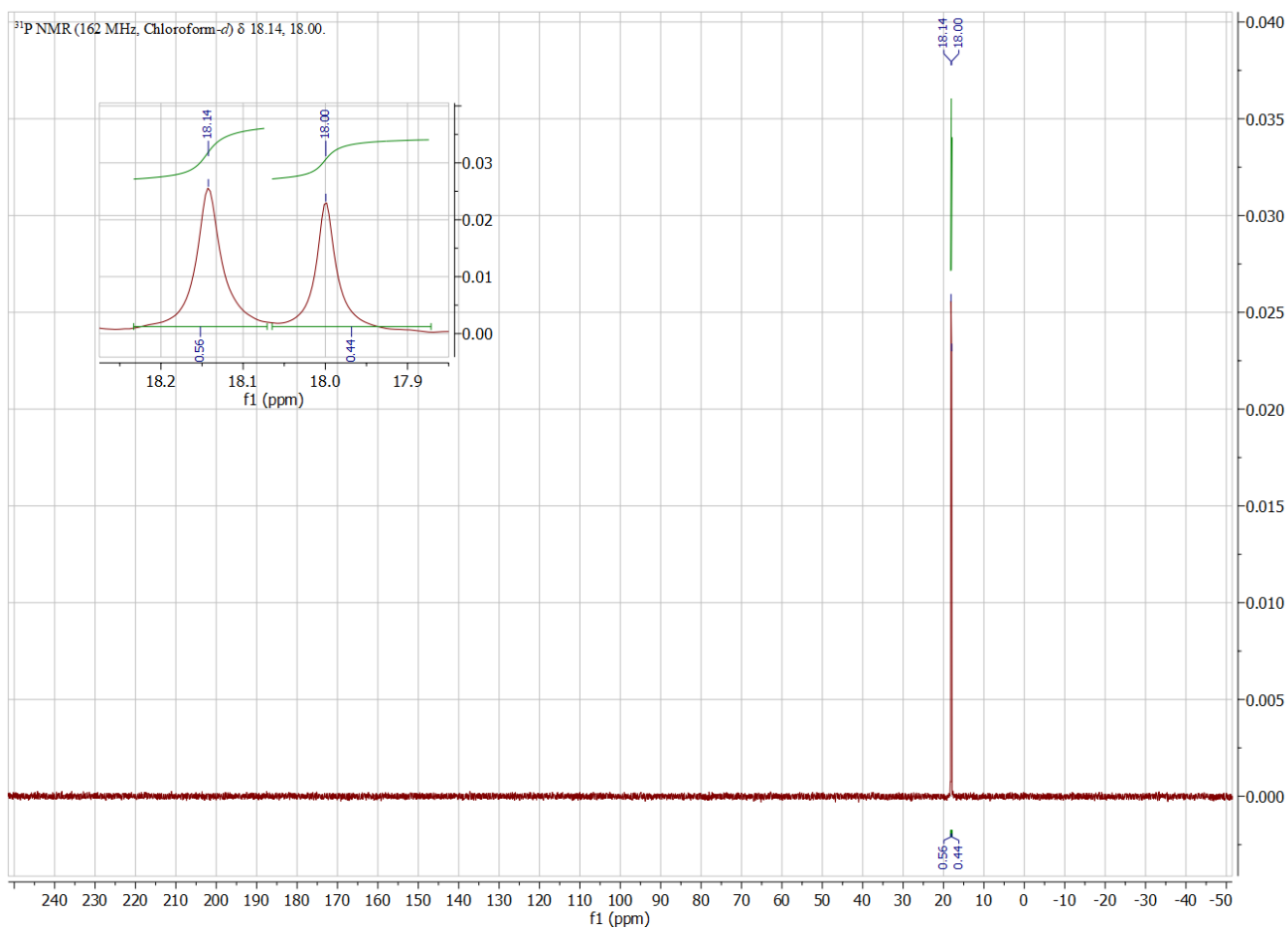
¹H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.26 (m, 6H, 5xArH, NH), 7.18 – 7.11 (m, 4H, 4xArH), 7.09 – 7.01 (m, 4H, 4xArH), 6.98 – 6.80 (m, 1H, NH), 5.33 – 4.98 (m, 4H, CH₂, 2xNH), 4.77 – 4.62 (m, 1H, CHP), 4.57 – 4.43 (m, 1H, CH), 4.02 – 3.81 (m, 1H, CH), 3.21 – 2.92 (m, 2H, CH₂), 2.40 (dd, *J* = 5.9, 3.7 Hz, 6H, 2xSCH₃), 2.38 – 2.29 (m, 1H, CH), 2.14 – 1.98 (m, 1H, CH), 1.92 – 1.41 (m, 4H, 2xCH₂), 1.38 (d, *J* = 6.6 Hz, 9H, Boc), 1.34 – 1.23 (m, 2H, CH₂), 1.05 – 0.98 (m, 6H, 2xCH₃), 0.90 (dd, *J* = 6.8, 2.3 Hz, 3H, CH₃), 0.83 (dd, *J* = 13.2, 6.8 Hz, 3H, CH₃).

HRMS: C₄₂H₅₉N₄O₉PS₂ [M+Na]⁺ calc. 881.3359 found 881.3366

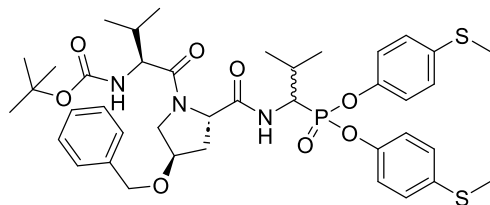
HPLC: purity >99%; retention time 19.210 and 19.393 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19,210	237,330	1263,966	69,01	62,23	n.a.
2		19,393	105,510	763,671	30,68	37,60	n.a.
3		19,670	1,076	3,348	0,31	0,16	n.a.
Total:			343,916	2030,985	100,00	100,00	



(54) 353.2 Boc-L-Val-L-Hyp(Bzl)-Val^P(OPh-4-SCH₃)₂



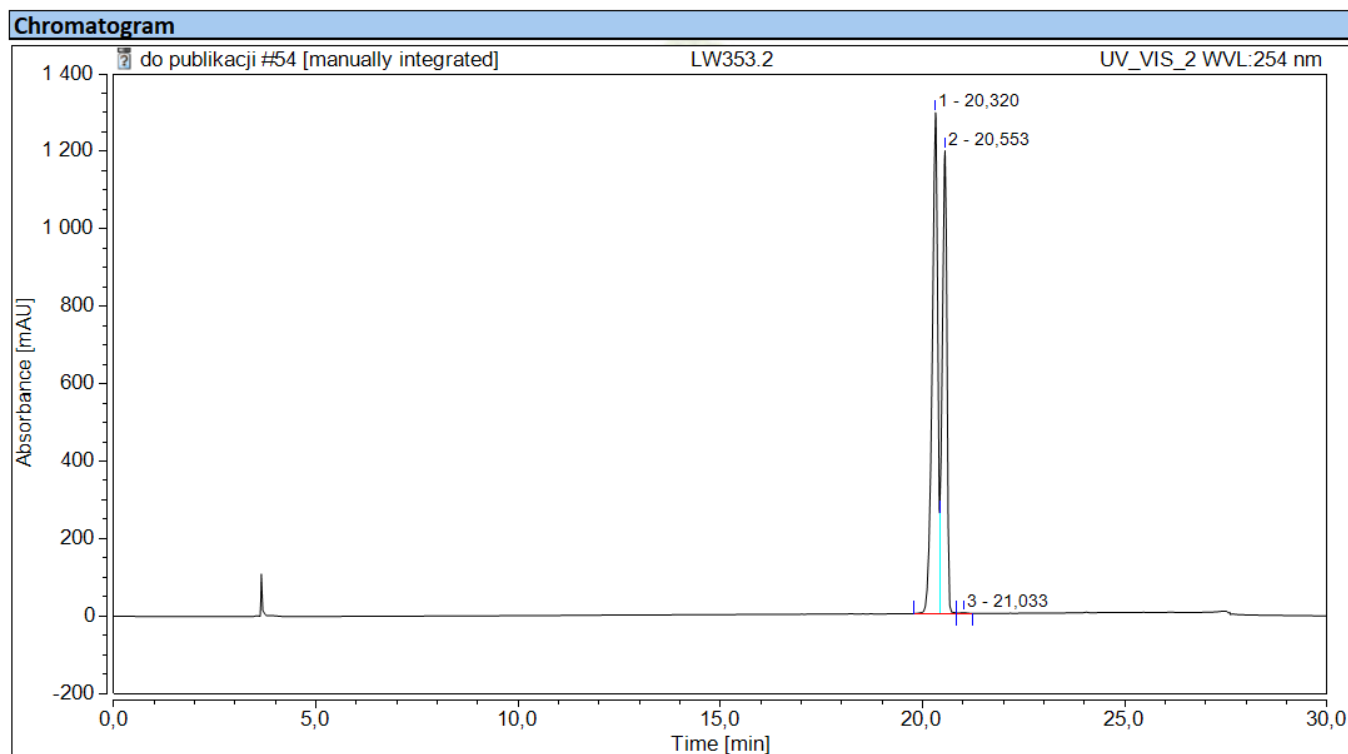
Name: *tert*-butyl ((2*S*)-1-((2*S*,4*R*)-4-(benzyloxy)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-3-methyl-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.31 (s, 30%), 17.83 (s, 70%).

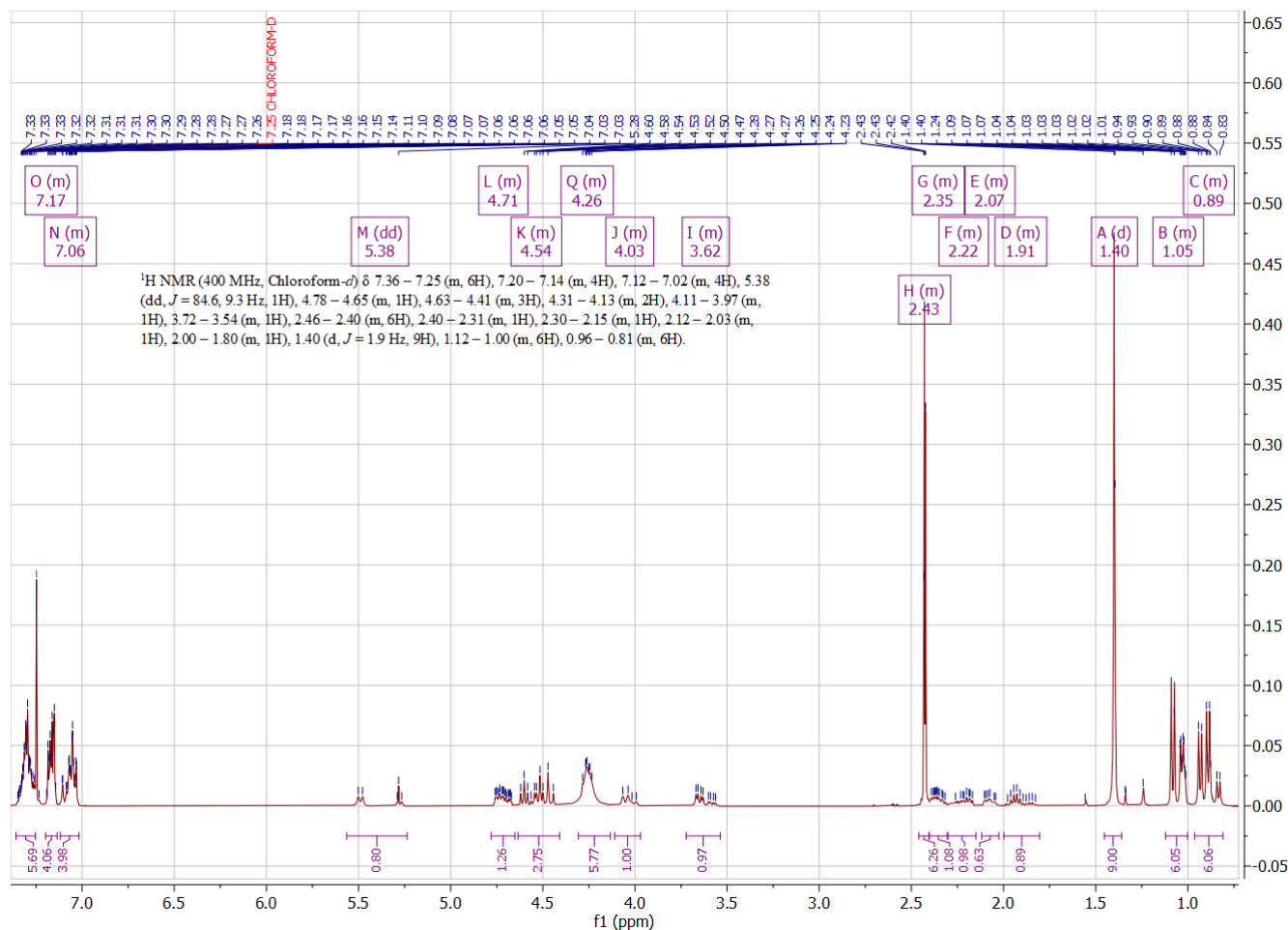
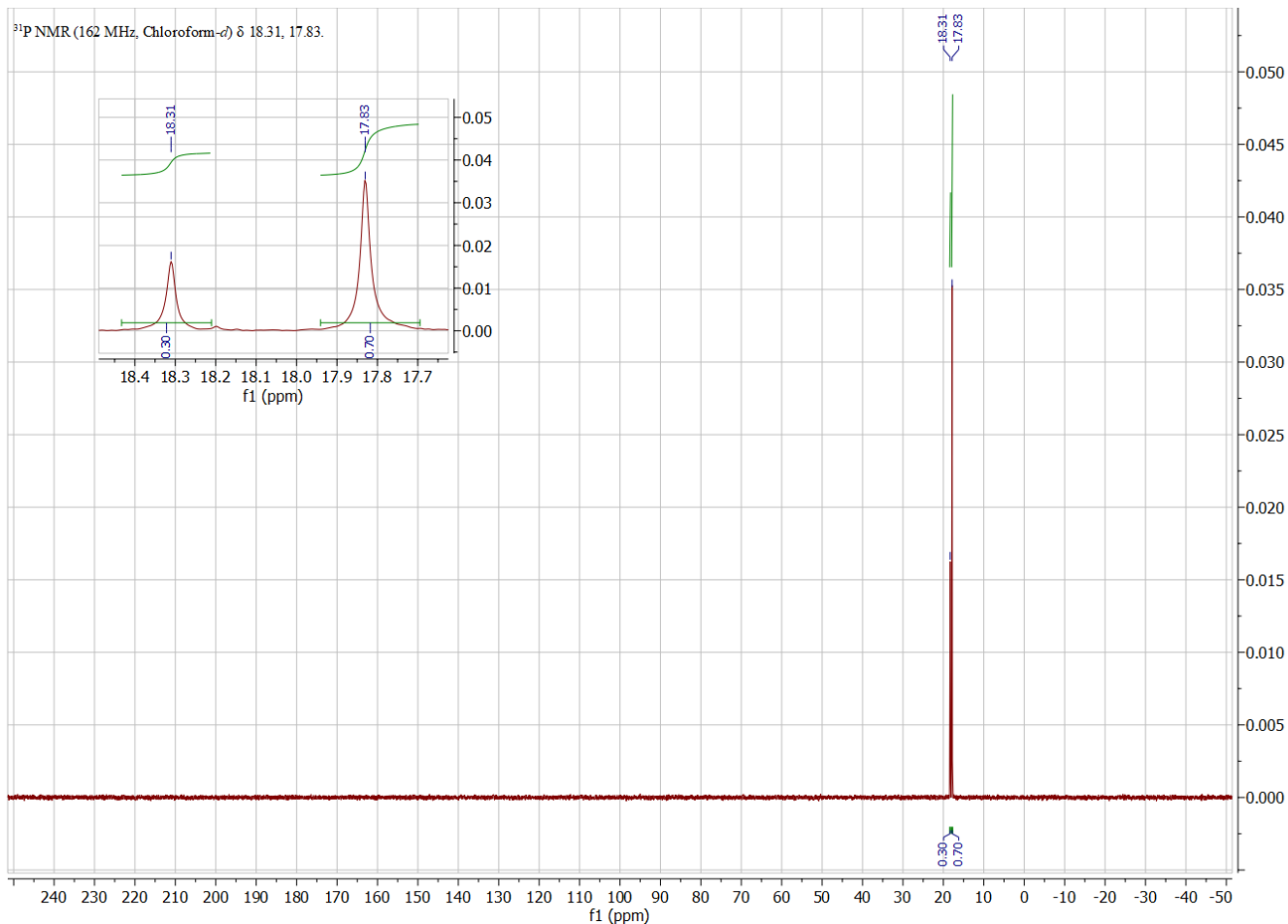
¹H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.25 (m, 6H, 5xArH, NH), 7.20 – 7.14 (m, 4H, 4xArH), 7.12 – 7.02 (m, 4H, 4xArH), 5.38 (dd, *J* = 84.6, 9.3 Hz, 1H, NH), 4.78 – 4.65 (m, 1H, CHP), 4.63 – 4.41 (m, 3H, CH₂, CH), 4.31 – 4.13 (m, 2H, CH₂), 4.11 – 3.97 (m, 1H, CH), 3.72 – 3.54 (m, 1H, CH), 2.46 – 2.40 (m, 6H, 2xSCH₃), 2.40 – 2.31 (m, 1H, CH), 2.30 – 2.15 (m, 1H, CH), 2.12 – 2.03 (m, 1H, 0.5xCH₂), 2.00 – 1.80 (m, 1H, 0.5xCH₂), 1.40 (d, *J* = 1.9 Hz, 9H, Boc), 1.12 – 1.00 (m, 6H, 2xCH₃), 0.96 – 0.81 (m, 6H, 2xCH₃).

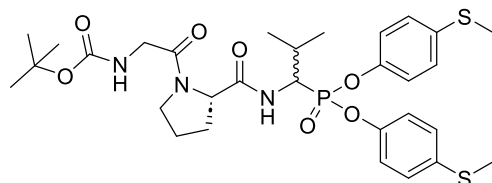
HRMS: C₄₀H₅₄N₃O₈PS₂ [M+Na]⁺ calc. 822.2988 found 822.2994

HPLC: purity >99%; retention time 20.320 and 20.553 min



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20,320	203,490	1293,574	55,66	51,93	n.a.
2		20,553	161,688	1195,335	44,23	47,99	n.a.
3		21,033	0,421	1,901	0,12	0,08	n.a.
Total:			365,599	2490,810	100,00	100,00	



(55) Boc-Gly-L-Pro-Val^P(OPh-4-SCH₃)₂

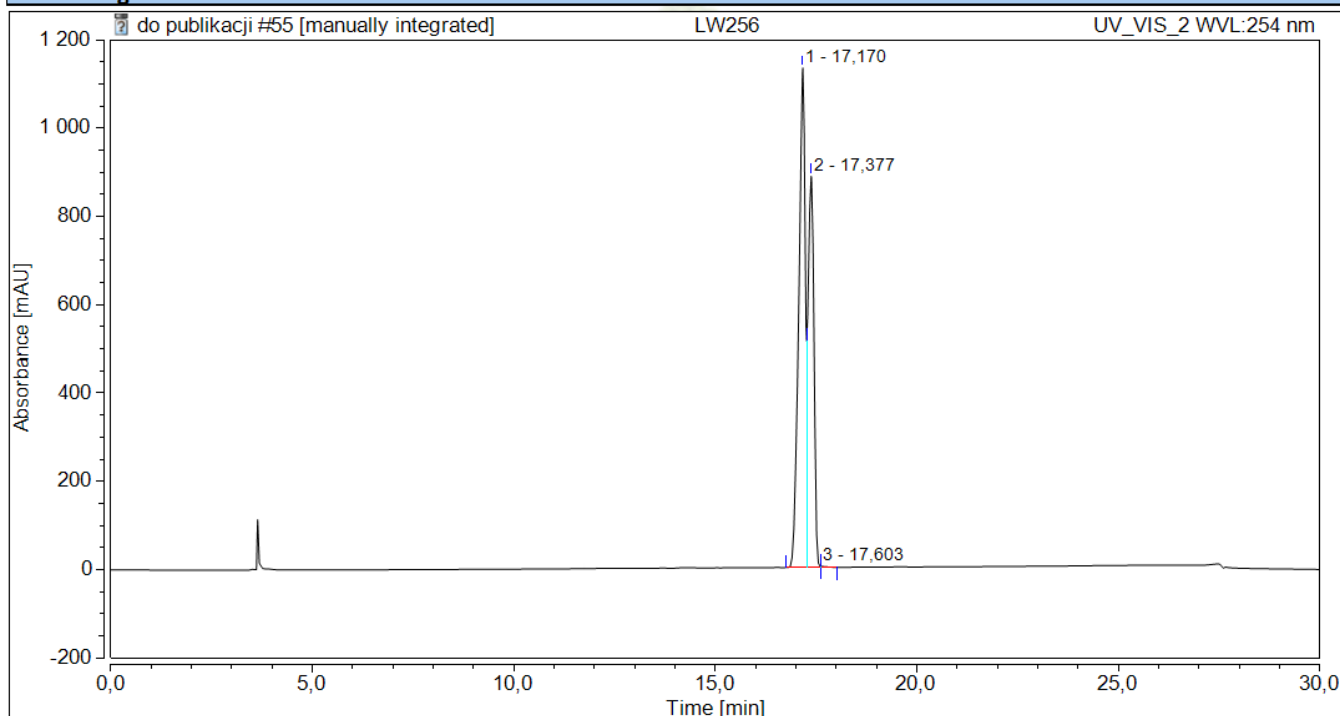
Name: *tert*-butyl (2-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-2-oxoethyl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.38 (s, 63%), 18.11 (s, 37%).

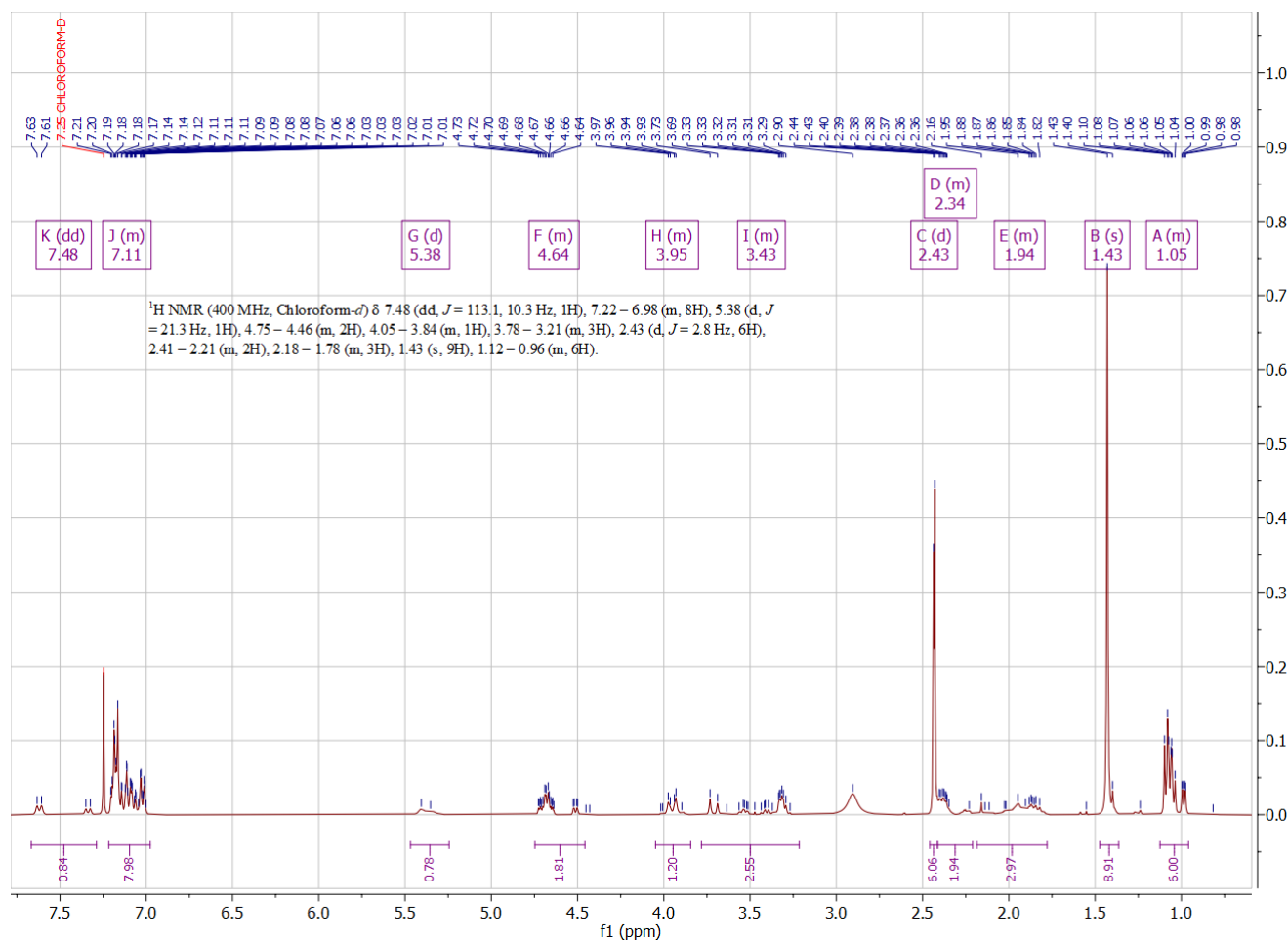
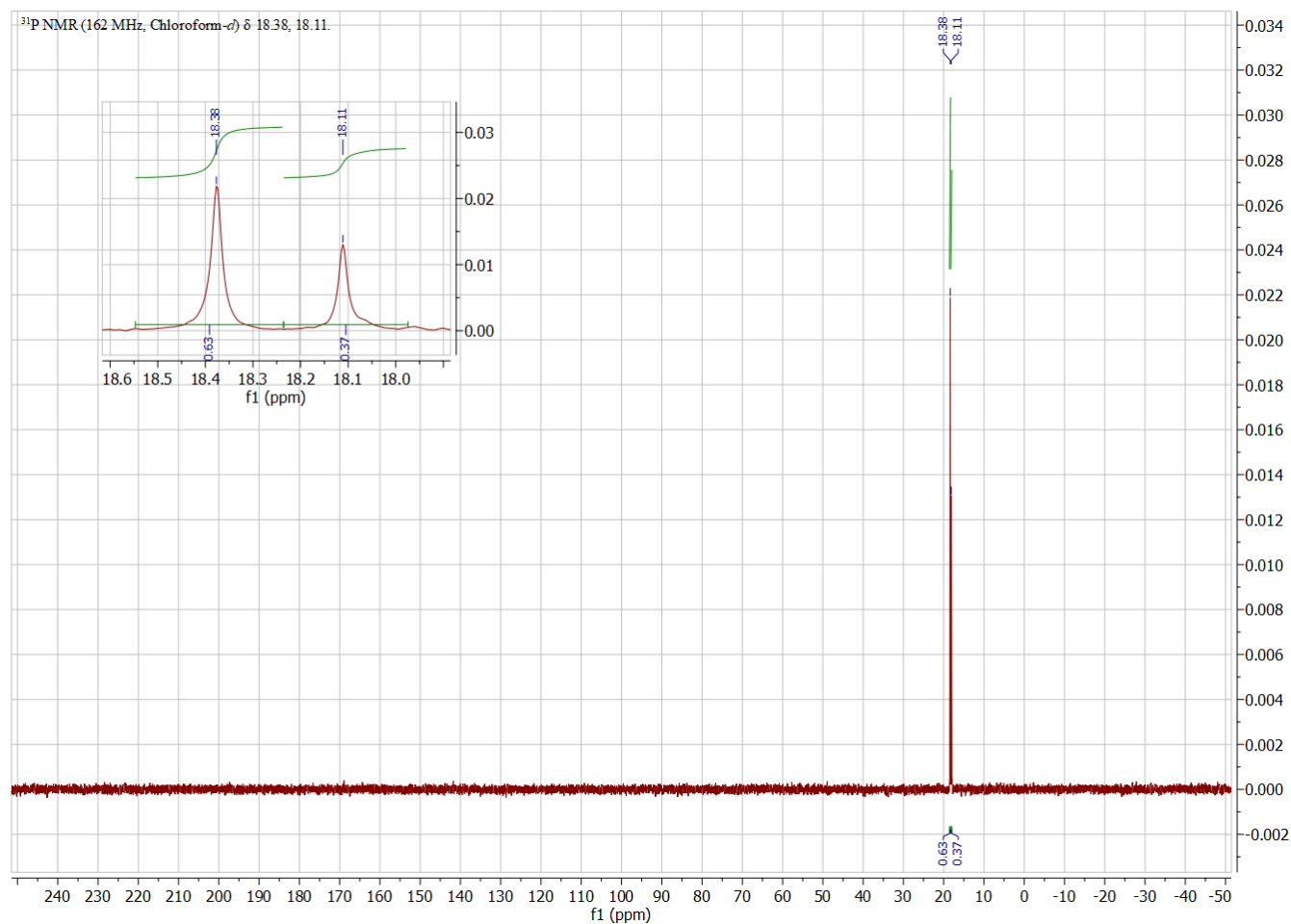
¹H NMR (400 MHz, Chloroform-*d*) δ 7.48 (dd, *J* = 113.1, 10.3 Hz, 1H, NH), 7.22 – 6.98 (m, 8H, 8xArH), 5.38 (d, *J* = 21.3 Hz, 1H, NH), 4.75 – 4.46 (m, 2H, CH₂), 4.05 – 3.84 (m, 1H, CHP), 3.78 – 3.21 (m, 3H, CH₂, CH), 2.43 (d, *J* = 2.8 Hz, 6H, 2xSCH₃), 2.41 – 2.21 (m, 2H, CH₂), 2.18 – 1.78 (m, 3H, CH₂, CH), 1.43 (s, 9H, Boc), 1.12 – 0.96 (m, 6H, 2xCH₃).

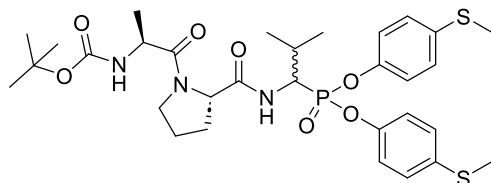
HRMS: C₃₀H₄₂N₃O₇PS₂ [M+Na]⁺ calc. 674.2099 found 674.2091

HPLC: purity >99%; retention time 17.170 and 17.377 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17,170	209,025	1131,362	57,83	56,02	n.a.
2		17,377	152,080	886,066	42,07	43,87	n.a.
3		17,603	0,349	2,116	0,10	0,10	n.a.
Total:			361,453	2019,545	100,00	100,00	



(56) Boc-L-Ala-L-Pro-Val^P(OPh-4-SCH₃)₂

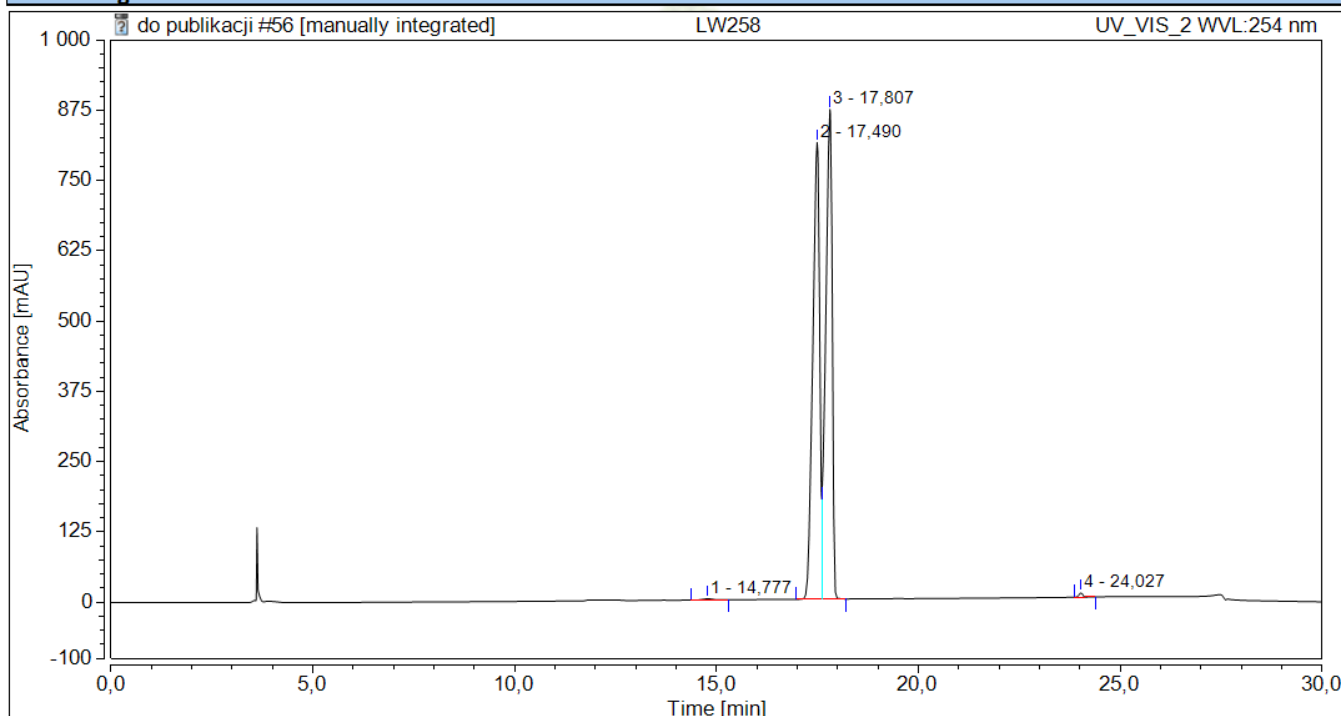
Name: *tert*-butyl ((2*S*)-1-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-1-oxopropan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.31 (s, 54%), 17.97 (s, 46%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.43 (t, *J* = 11.4 Hz, 1H, NH), 7.23 – 7.14 (m, 4H, 4xArH), 7.14 – 7.00 (m, 4H, 4xArH), 5.40 (dd, *J* = 37.1, 8.1 Hz, 1H, NH), 4.77 – 4.53 (m, 2H, CHP, CH), 4.53 – 4.35 (m, 1H, CH), 3.73 – 3.59 (m, 1H, 0.5xCH₂), 3.59 – 3.39 (m, 1H, 0.5xCH₂), 2.47 – 2.42 (m, 6H, 2xSCH₃), 2.42 – 2.16 (m, 2H, CH₂), 2.17 – 1.77 (m, 3H, CH₂, CH), 1.41 (d, *J* = 3.0 Hz, 9H, Boc), 1.23 (dd, *J* = 66.2, 6.9 Hz, 3H, CH₃), 1.10 – 0.93 (m, 6H, 3xCH₃).

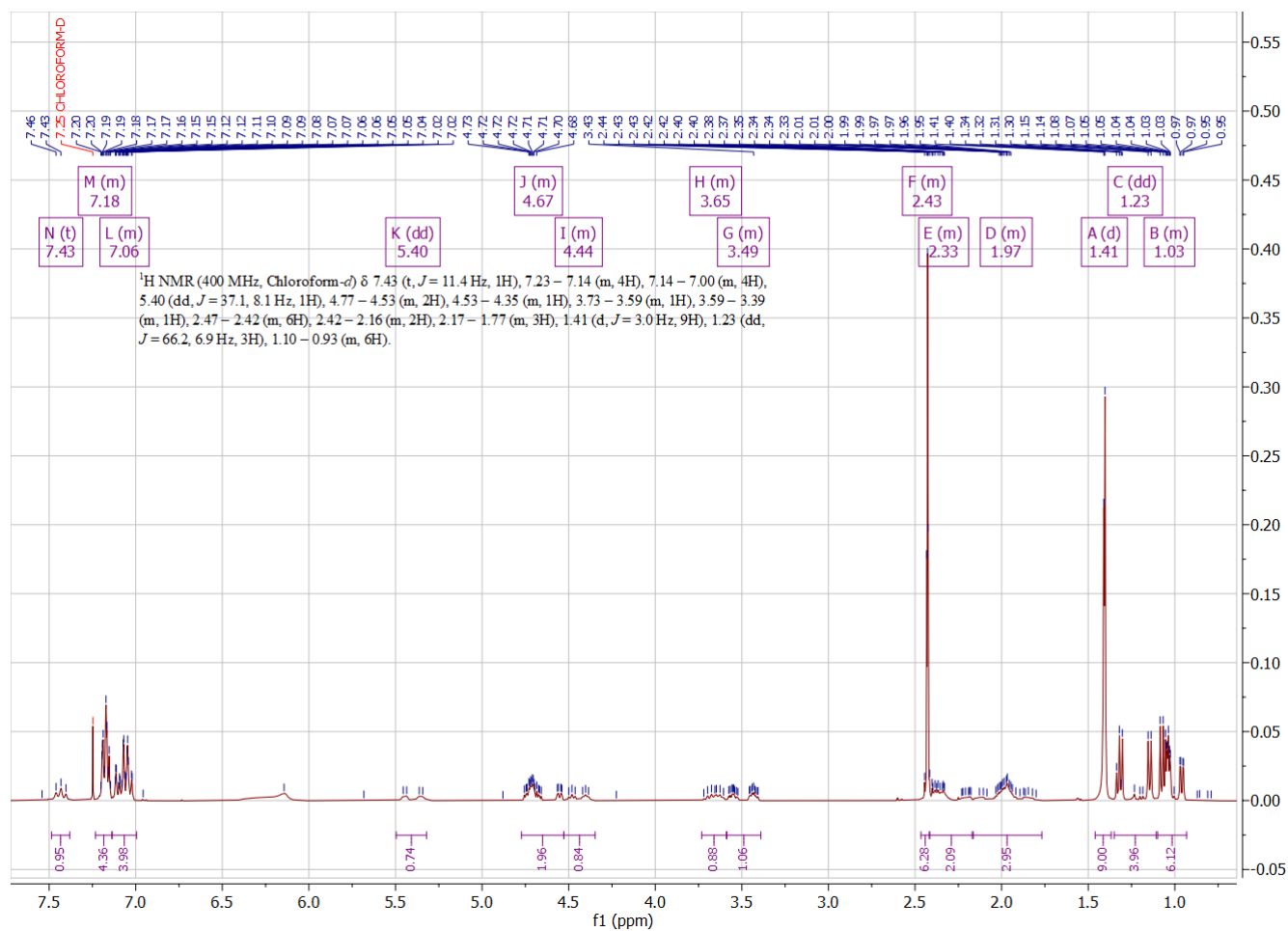
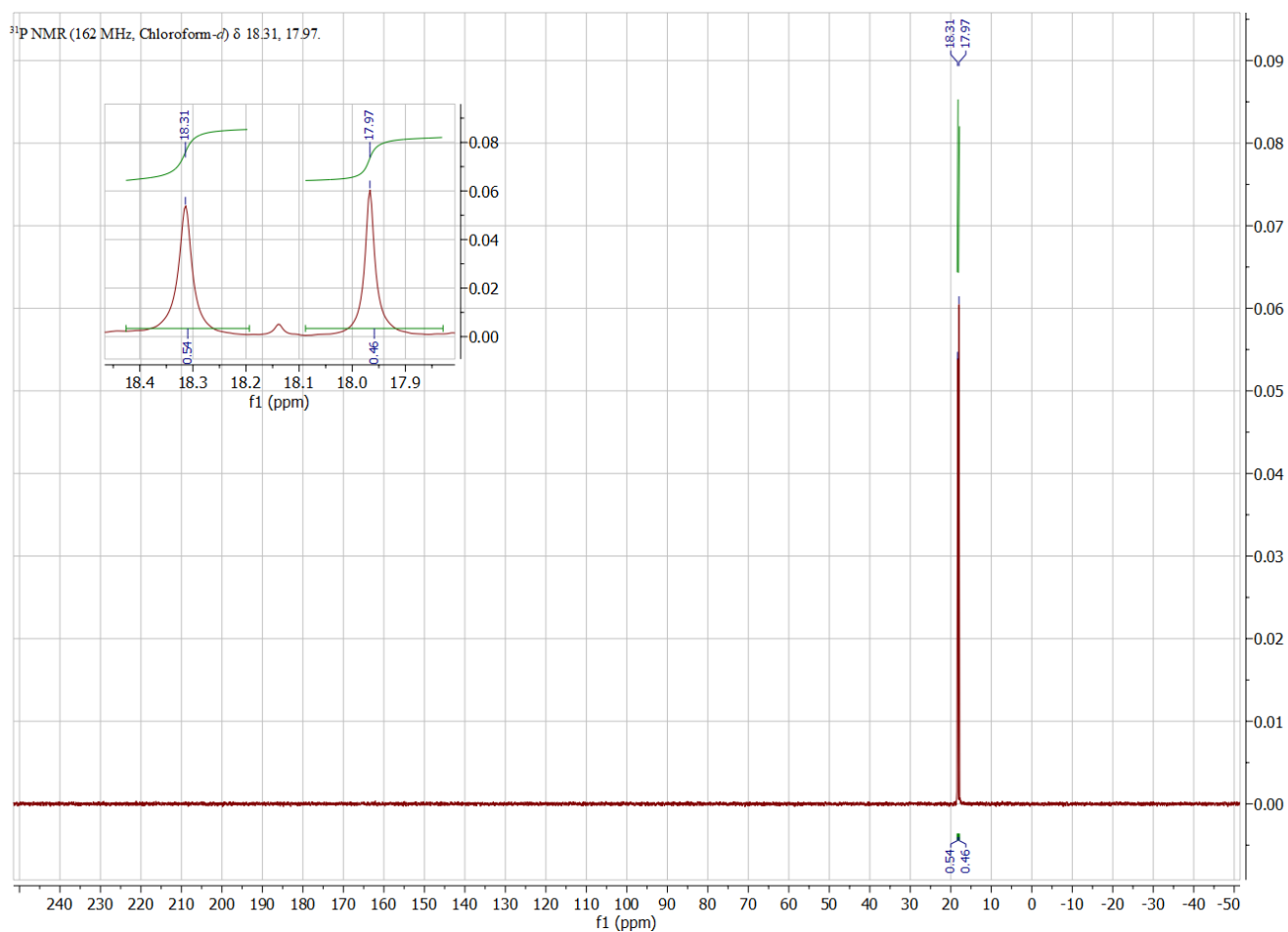
HRMS: C₃₁H₄₄N₃O₇PS₂ [M+Na]⁺ calc. 688.2256 found 688.2241

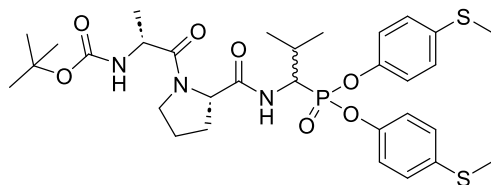
HPLC: purity >99%; retention time 17.490 and 17.807 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14,777	0,630	2,121	0,19	0,13	n.a.
2		17,490	159,743	812,195	49,26	47,97	n.a.
3		17,807	163,058	870,795	50,28	51,43	n.a.
4		24,027	0,861	7,912	0,27	0,47	n.a.
Total:			324,292	1693,023	100,00	100,00	

^{31}P NMR (162 MHz, Chloroform- d) δ 18.31, 17.97.



(57) Boc-D-Ala-L-Pro-Val^P(OPh-4-SCH₃)₂

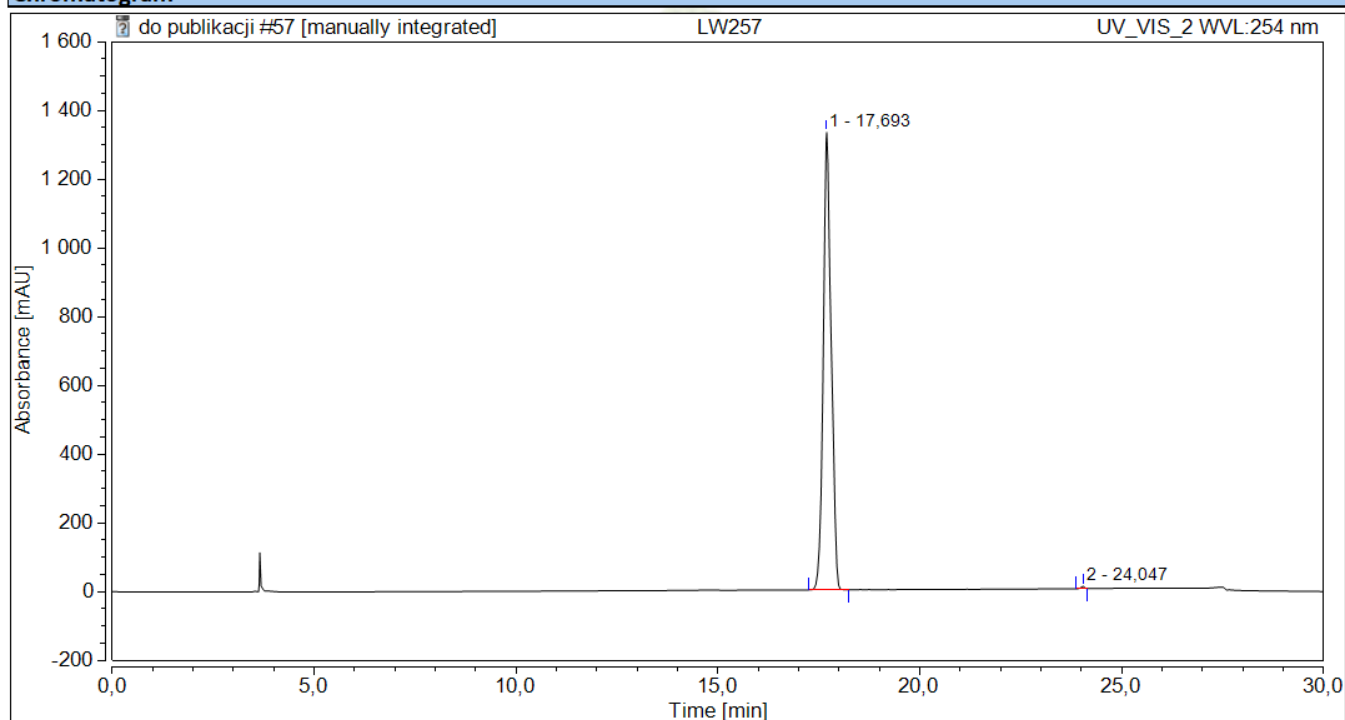
Name: *tert*-butyl ((2*R*)-1-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-1-oxopropan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.57 (s, 67%), 18.25 (s, 33%).

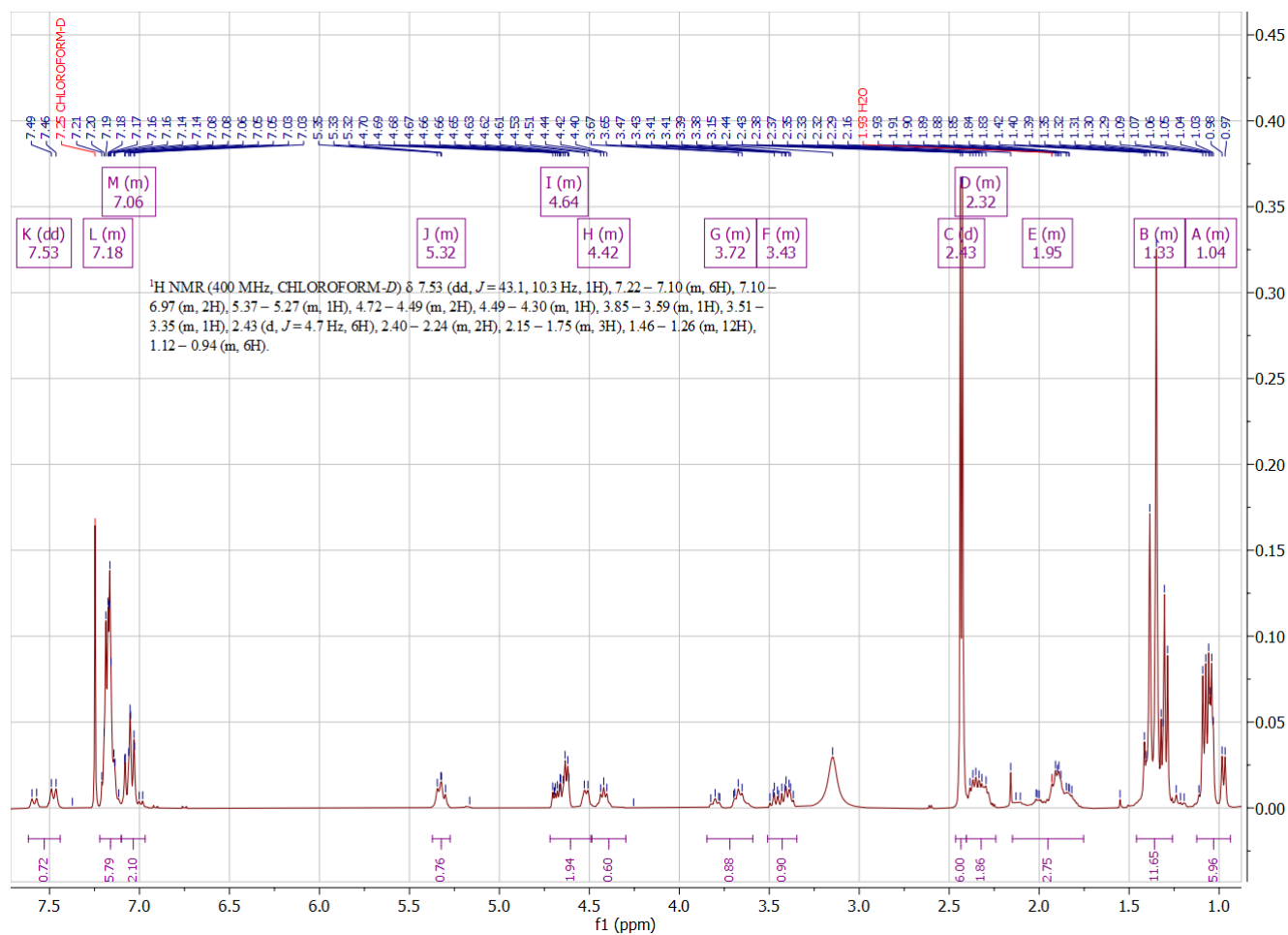
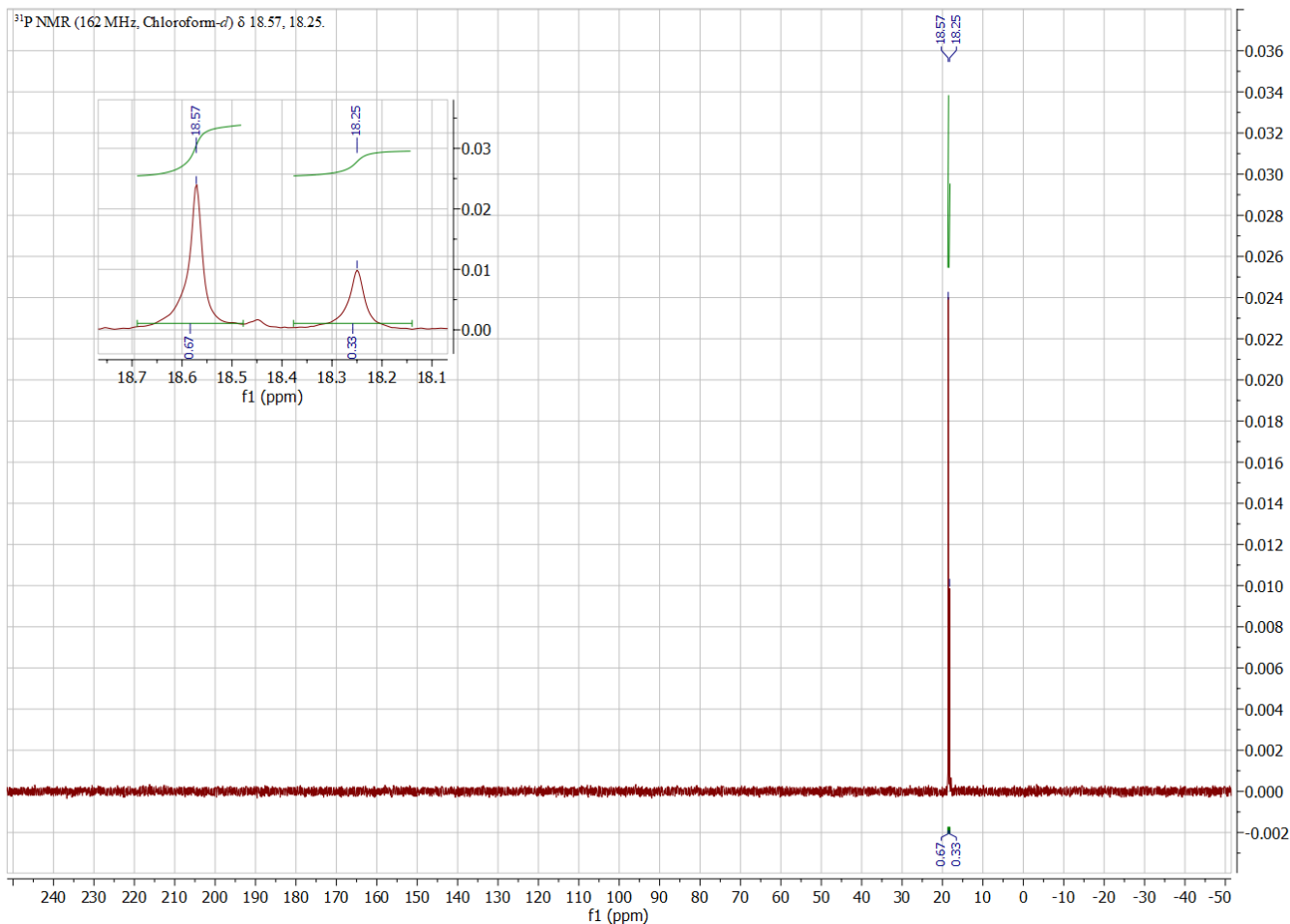
¹H NMR (400 MHz, Chloroform-*d*) δ 7.53 (dd, *J* = 43.1, 10.3 Hz, 1H, NH), 7.22 – 7.10 (m, 6H, 6xArH), 7.10 – 6.97 (m, 2H, 2xArH), 5.37 – 5.27 (m, 1H, NH), 4.72 – 4.49 (m, 2H, CHP, CH), 4.49 – 4.30 (m, 1H, CH), 3.85 – 3.59 (m, 1H, 0.5xCH₂), 3.51 – 3.35 (m, 1H, 0.5xCH₂), 2.43 (d, *J* = 4.7 Hz, 6H, 2xSCH₃), 2.40 – 2.24 (m, 2H, CH₂), 2.15 – 1.75 (m, 3H, CH₂, CH), 1.46 – 1.26 (m, 12H, Boc, CH₃), 1.12 – 0.94 (m, 6H, 2xCH₃).

HRMS: C₃₁H₄₄N₃O₇PS₂ [M+Na]⁺ calc. 688.2256 found 688.2244

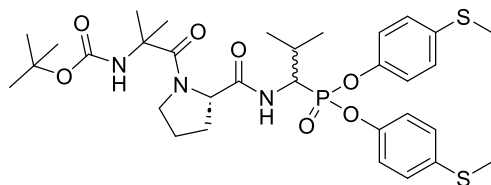
HPLC: purity >99%; retention time 17.693 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		17,693	300,297	1330,908	99,76	99,45	n.a.
2		24,047	0,710	7,375	0,24	0,55	n.a.
Total:			301,007	1338,283	100,00	100,00	



(58) Boc-Aib-L-Pro- Val^P(OPh-4-SCH₃)₂



Name: tert-butyl (1-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-2-methyl-1-oxopropan-2-yl)carbamate

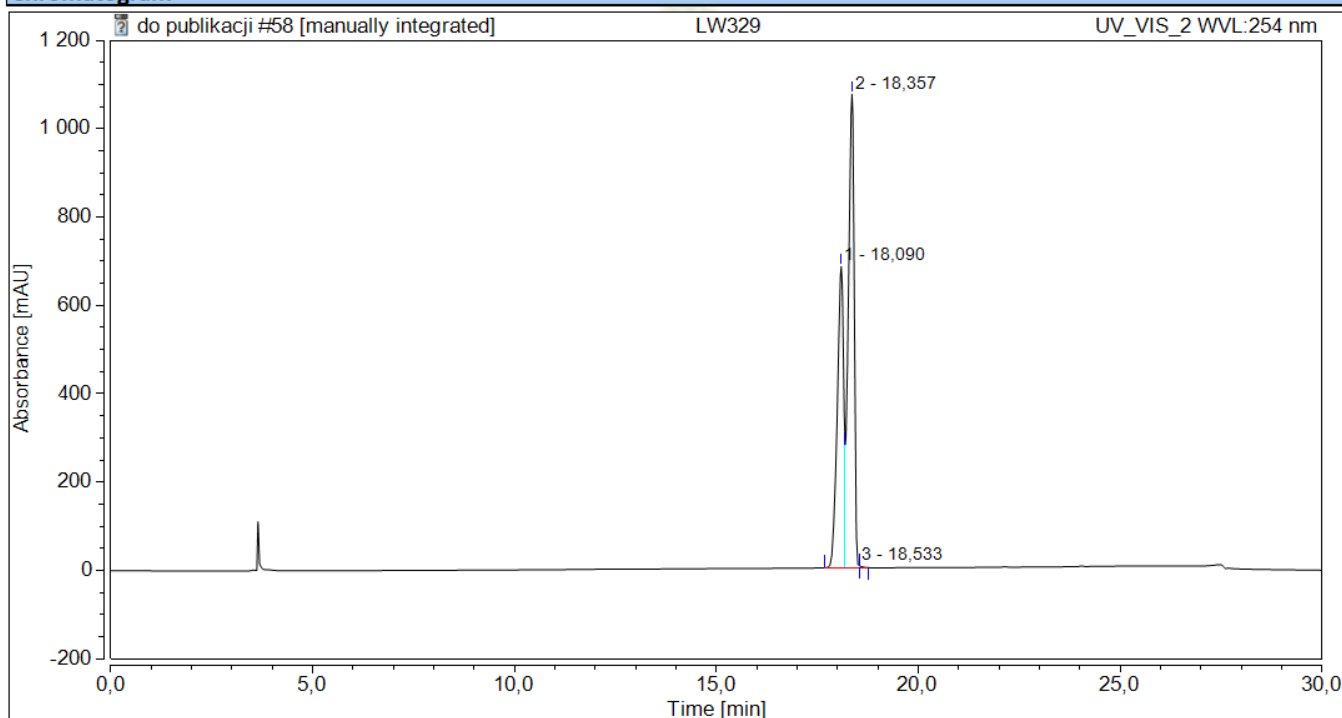
³¹P NMR (162 MHz, Chloroform-*d*) δ 19.13 (s). **¹H NMR**

(400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 9.6 Hz, 1H, NH), 7.21 – 7.12 (m, 4H, 4xArH), 7.10 – 6.99 (m, 4H, 4xArH), 4.79 (s, 1H, NH), 4.74 – 4.56 (m, 2H, CHP, CH), 3.84 – 3.73 (m, 1H, 0.5xCH₂), 3.52 – 3.41 (m, 1H, 0.5xCH₂), 2.48 – 2.37 (m, 7H, 2xSCH₃, CH), 2.26 – 2.14 (m, 1H, 0.5xCH₂), 1.92 – 1.65 (m, 3H, 1.5xCH₂), 1.50 (s, 3H, CH₃), 1.38 (s, 3H, CH₃), 1.35 (s, 9H, Boc), 1.16 (dd, *J* = 10.5, 6.8 Hz, 6H, 2xCH₃).

HRMS: C₃₂H₄₆N₃O₇PS₂ [M+Na]⁺ calc. 702.2412 found 702.2403

HPLC: purity >99%; retention time 18.090 and 18.357 min

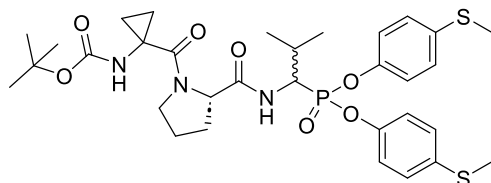
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18,090	125,510	682,107	41,05	38,81	n.a.
2		18,357	179,879	1071,643	58,84	60,97	n.a.
3		18,533	0,343	3,934	0,11	0,22	n.a.
Total:			305,732	1757,685	100,00	100,00	

(59) Boc-AC3C-L-Pro- Val^P(OPh-4-SCH₃)₂



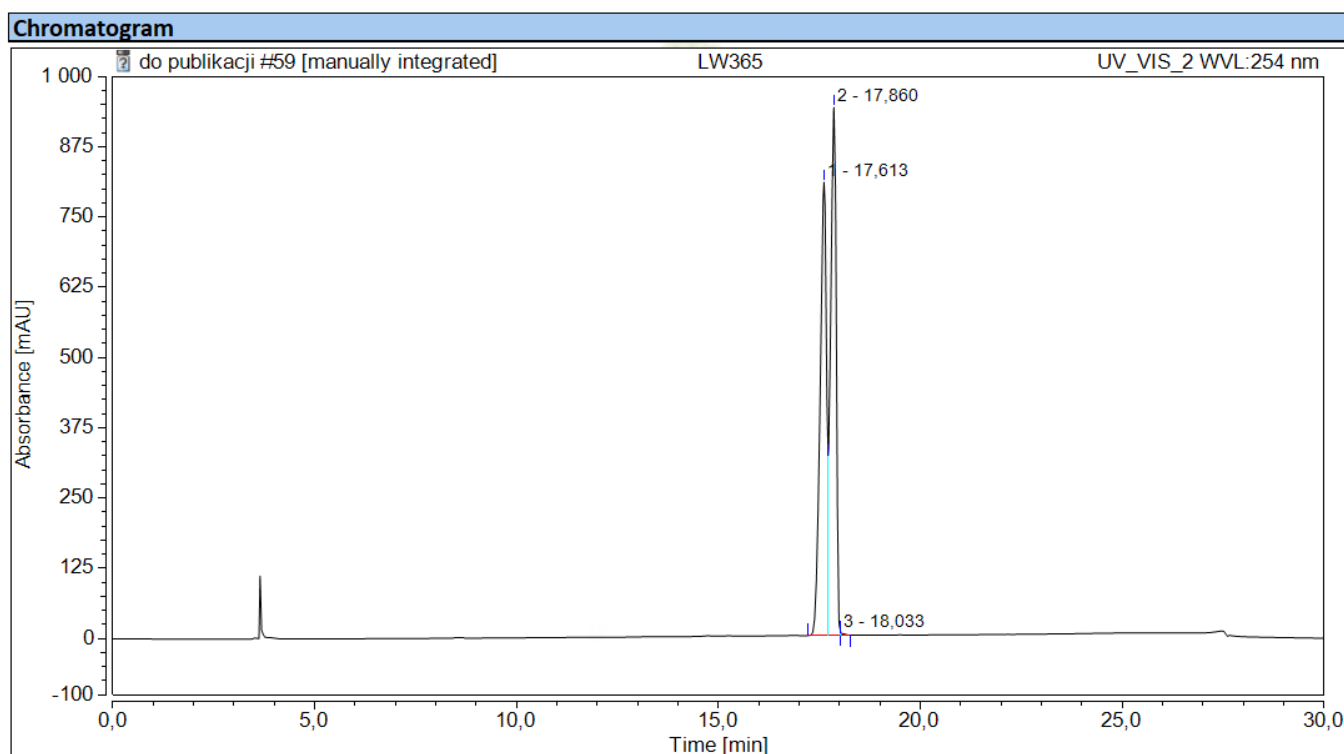
Name: *tert*-butyl (1-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidine-1-carbonyl)cyclopropyl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.71 (s, 75%), 18.27 (s, 25%).

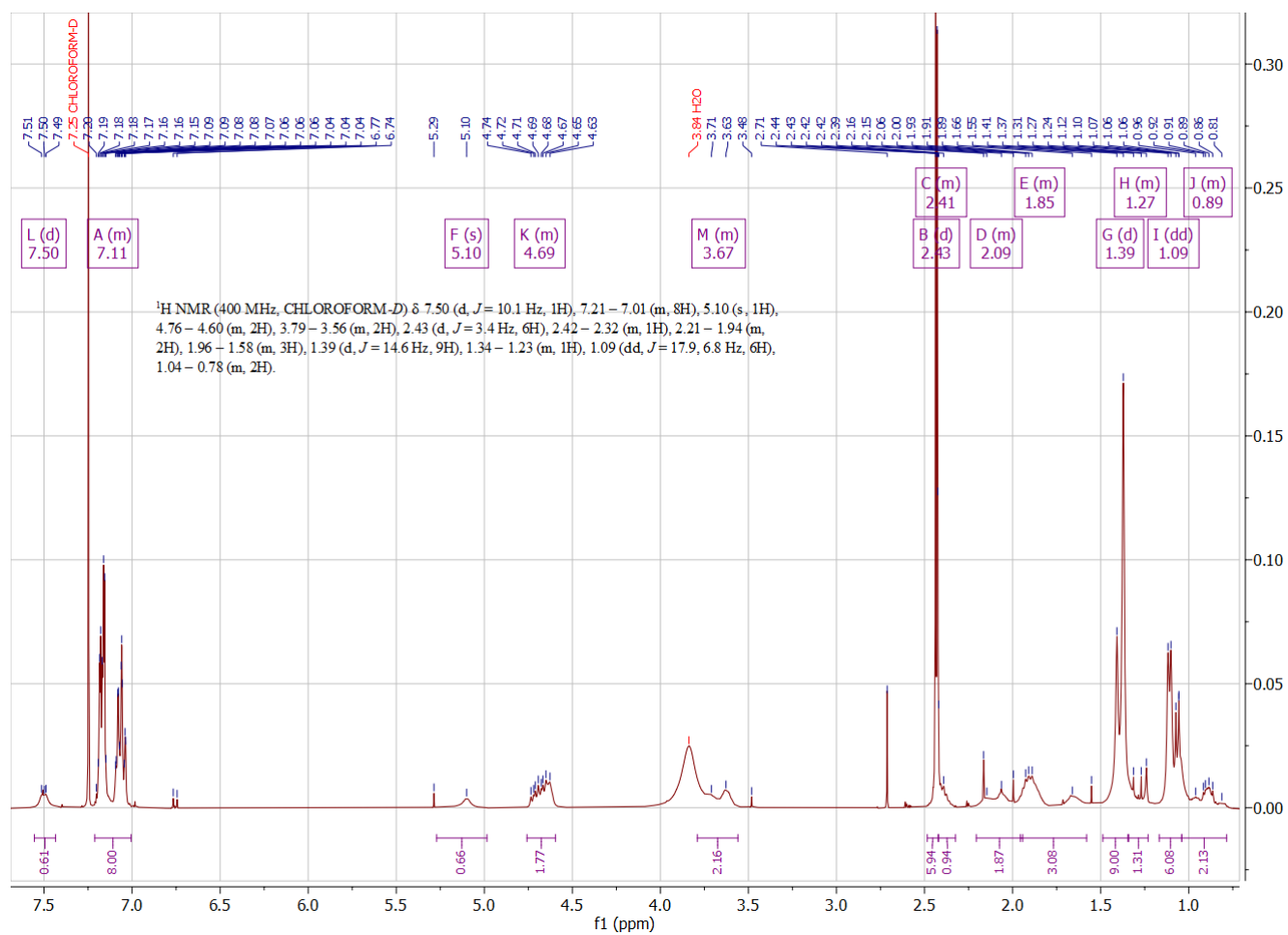
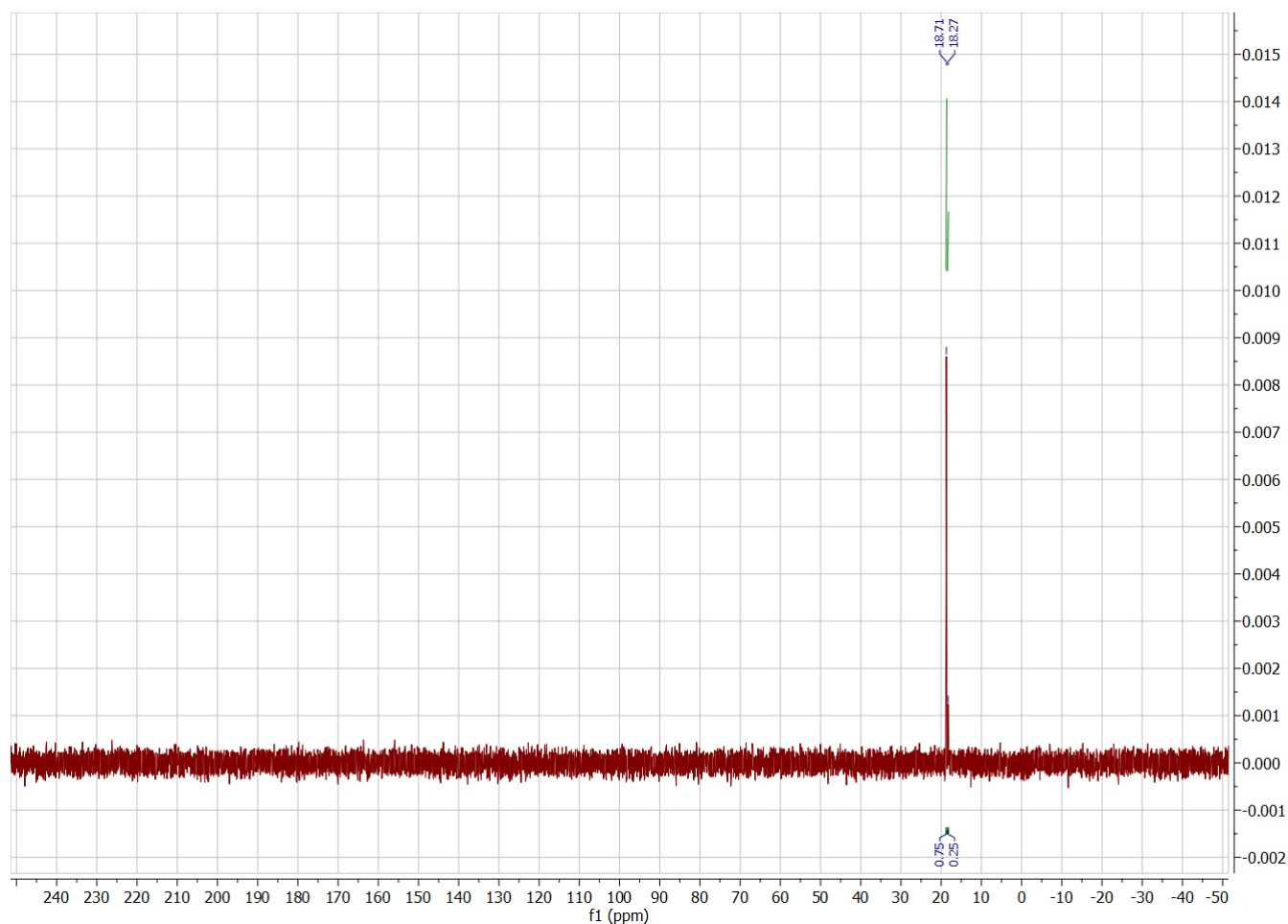
¹H NMR (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 10.1 Hz, 1, NH), 7.21 – 7.01 (m, 8H, 8xArH), 5.10 (s, 1H, NH), 4.76 – 4.60 (m, 2H, CHP, CH), 3.79 – 3.56 (m, 2H, CH₂), 2.43 (d, *J* = 3.4 Hz, 6H, 2xSCH₃), 2.42 – 2.32 (m, 1H, CH), 2.21 – 1.94 (m, 2H, CH₂), 1.96 – 1.58 (m, 3H, 1.5xCH₂), 1.39 (d, *J* = 14.6 Hz, 9H, Boc), 1.34 – 1.23 (m, 1H, 0.5xCH₂), 1.09 (dd, *J* = 17.9, 6.8 Hz, 6H, 3xCH₃), 1.04 – 0.78 (m, 2H, CH₂).

HRMS: C₃₂H₄₄N₃O₇PS₂ [M+Na]⁺ calc. 700.2256 found 700.2229

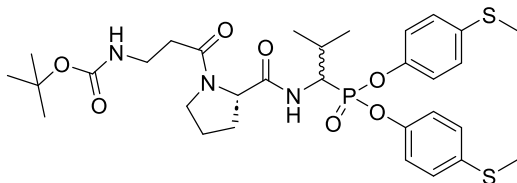
HPLC: purity >99%; retention time 17.613 and 17.860 min



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17,613	147,528	806,259	49,03	46,09	n.a.
2		17,860	152,991	939,103	50,85	53,68	n.a.
3		18,033	0,365	4,110	0,12	0,23	n.a.
Total:			300,885	1749,472	100,00	100,00	



(60) Boc-beta-Ala-L-Pro- Val^P(OPh-4-SCH₃)₂



Name: *tert*-butyl (3-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-3-oxopropyl)carbamate

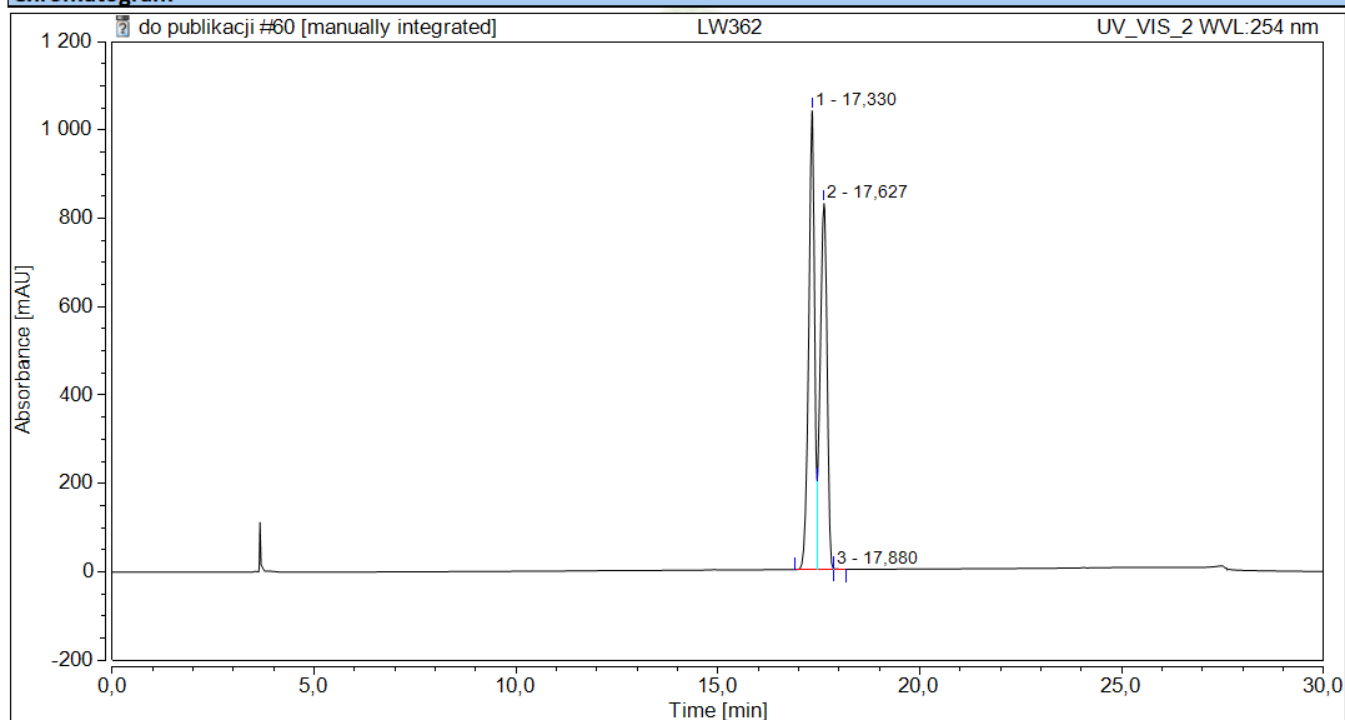
³¹P NMR (162 MHz, Chloroform-*d*) δ 18.18 (s, 51%), 18.04 (s, 49%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.66 (dd, *J* = 101.1, 10.1 Hz, 1H, NH), 7.23 – 6.98 (m, 8H, 8xArH), 5.66 – 5.26 (m, 1H, NH), 4.78 – 4.66 (m, 1H, CHP), 4.66 – 4.50 (m, 1H, CH), 3.65 – 3.26 (m, 4H, 2xCH₂), 2.62 – 2.46 (m, 1H, CH), 2.46 – 2.42 (m, 6H, 2xSCH₃), 2.42 – 1.95 (m, 4H, 2xCH₂), 1.95 – 1.78 (m, 2H, CH₂), 1.39 (d, *J* = 10.6 Hz, 9H, Boc), 1.14 – 0.91 (m, 6H, 2xCH₃).

HRMS: C₃₁H₄₄N₃O₇PS₂ [M+Na]⁺ calc. 688.2256 found 688.2258

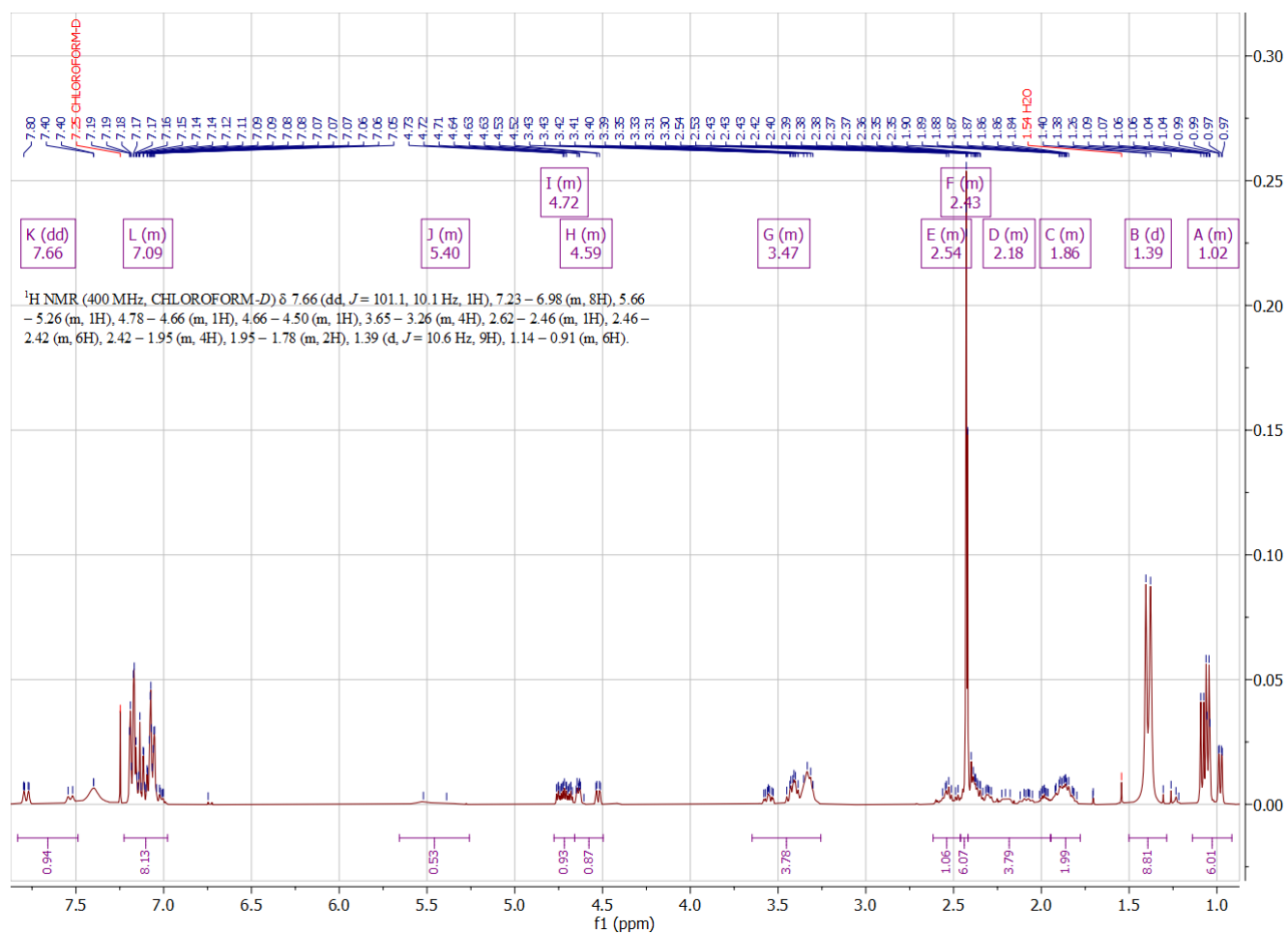
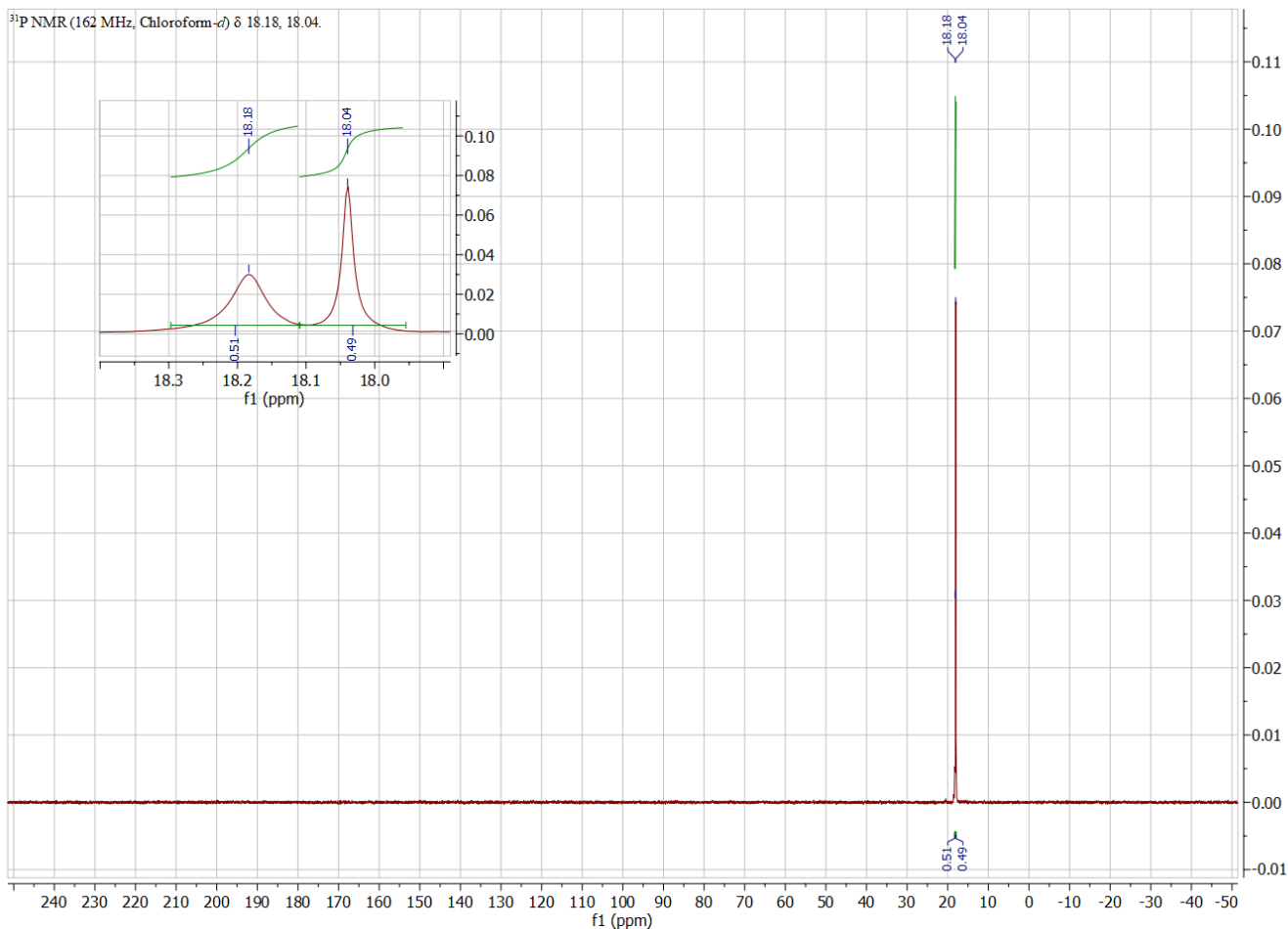
HPLC: purity >99%; retention time 17.330 and 17.627 min

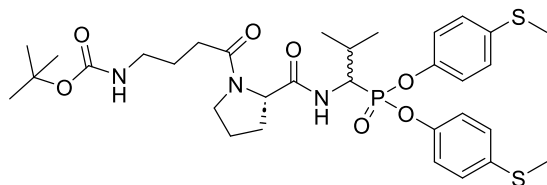
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		17,330	173,059	1038,616	51,36	55,59	n.a.
2		17,627	163,741	828,615	48,60	44,35	n.a.
3		17,880	0,128	1,199	0,04	0,06	n.a.
Total:			336,928	1868,431	100,00	100,00	



(61) Boc-GABA-L-Pro-Val^P(OPh-4-SCH₃)₂

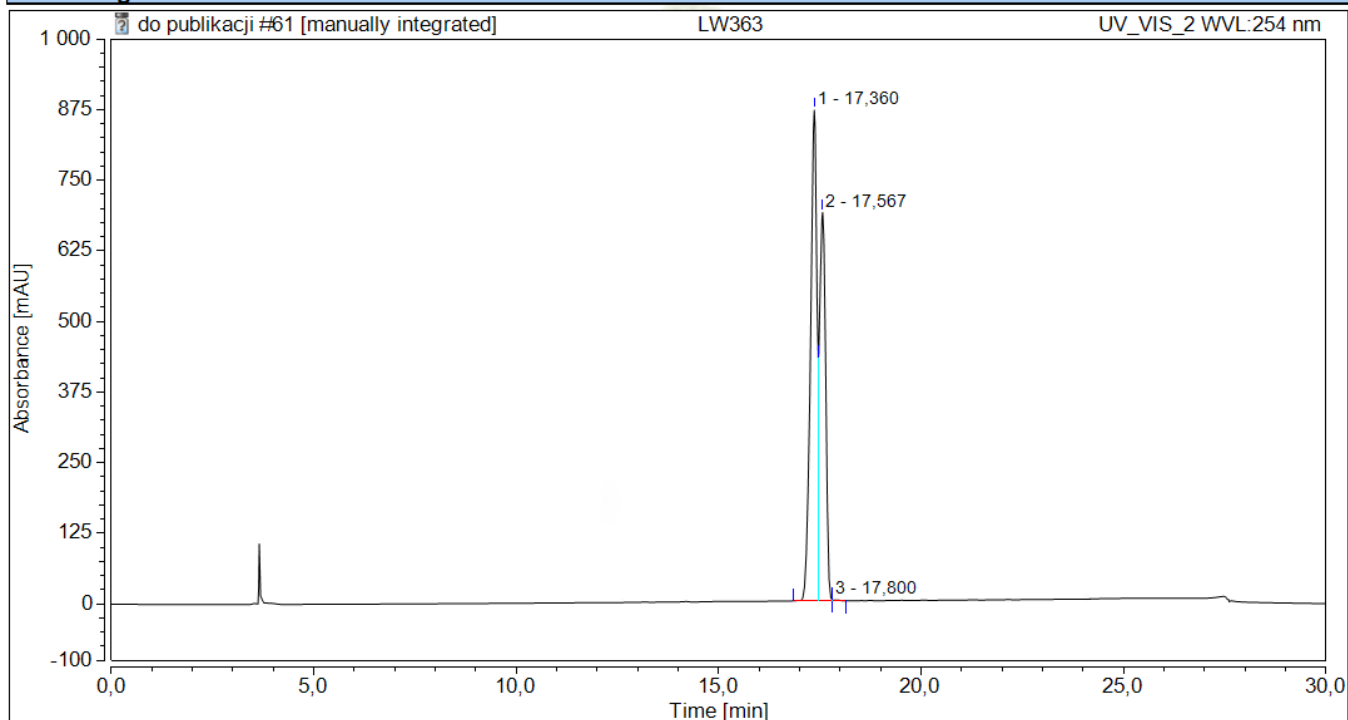
Name: *tert*-butyl (4-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-4-oxobutyl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.44 (s, 73%), 18.25 (s, 27%).

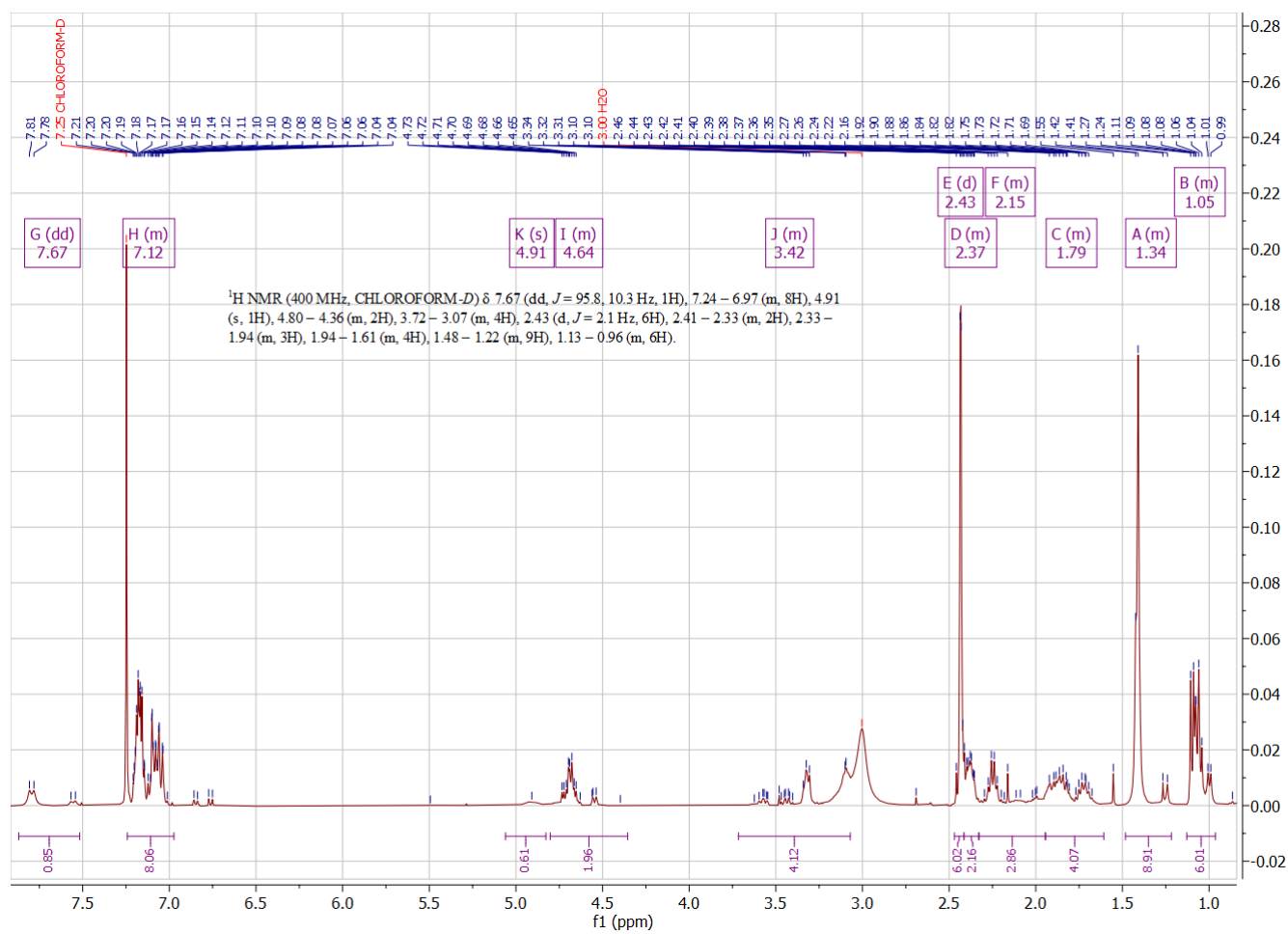
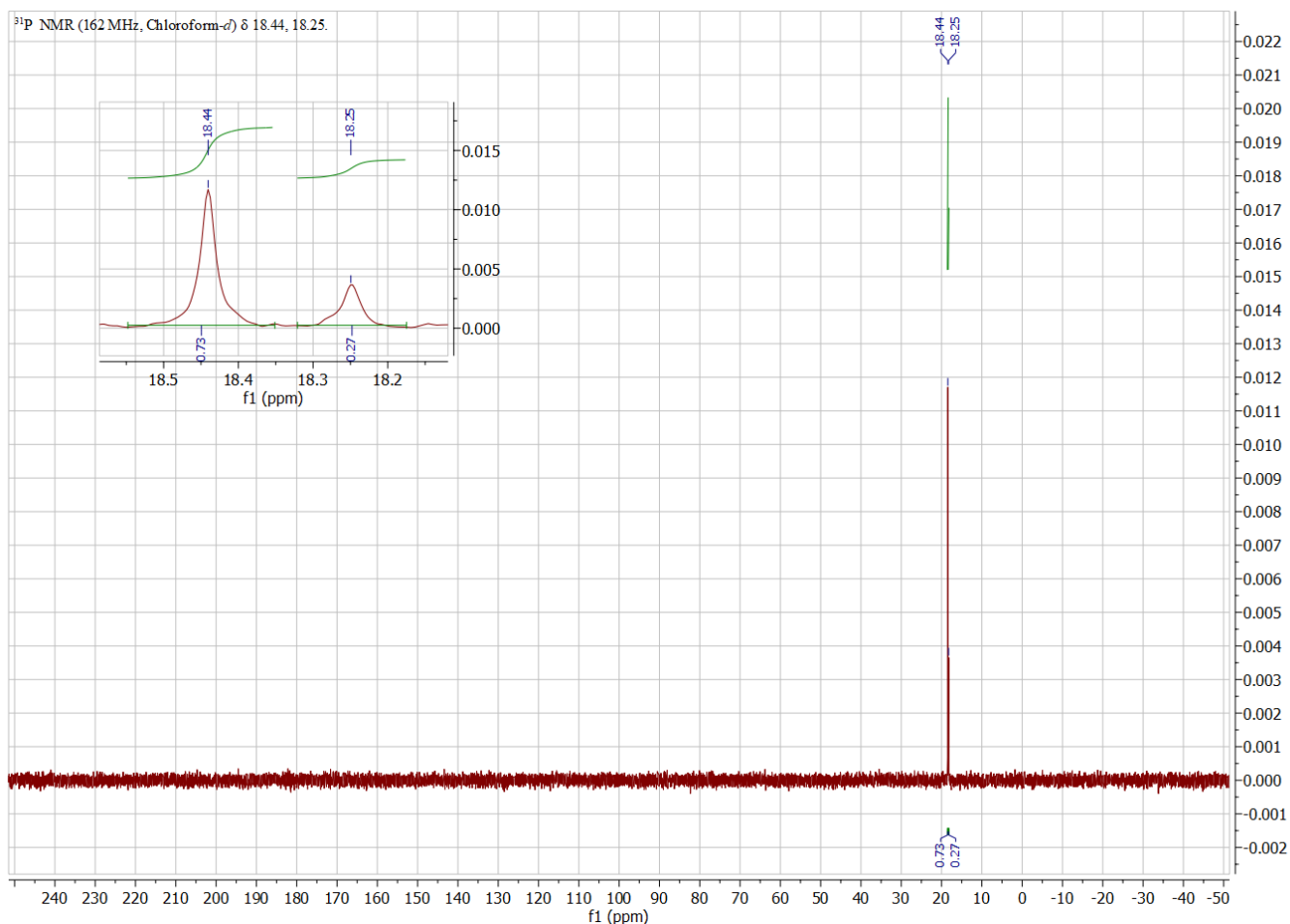
¹H NMR (400 MHz, Chloroform-*d*) δ 7.67 (dd, *J* = 95.8, 10.3 Hz, 1H, NH), 7.24 – 6.97 (m, 8H, 8xArH), 4.91 (s, 1H, NH), 4.80 – 4.36 (m, 2H, CHP, CH), 3.72 – 3.07 (m, 4H, 2xCH₂), 2.43 (d, *J* = 2.1 Hz, 6H, 2xSCH₃), 2.41 – 2.33 (m, 2H, CH₂), 2.33 – 1.94 (m, 3H, 2xCH₂, CH), 1.94 – 1.61 (m, 4H, 2xCH₂), 1.48 – 1.22 (m, 9H, Boc), 1.13 – 0.96 (m, 6H, 2xCH₃).

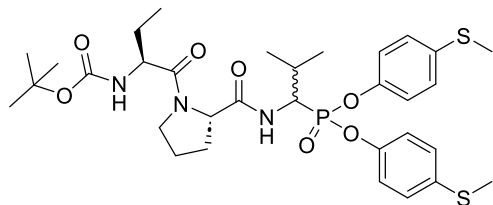
HRMS: C₃₂H₄₆N₃O₇PS₂ [M+Na]⁺ calc. 702.2412 found 702.2399

HPLC: purity >99%; retention time 17.360 and 17.567 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17,360	157,500	868,493	56,40	55,75	n.a.
2		17,567	121,485	687,522	43,50	44,13	n.a.
3		17,800	0,268	1,886	0,10	0,12	n.a.
Total:			279,252	1557,901	100,00	100,00	



(62) Boc-L-Abu-L-Pro-Val^P(OPh-4-SCH₃)₂

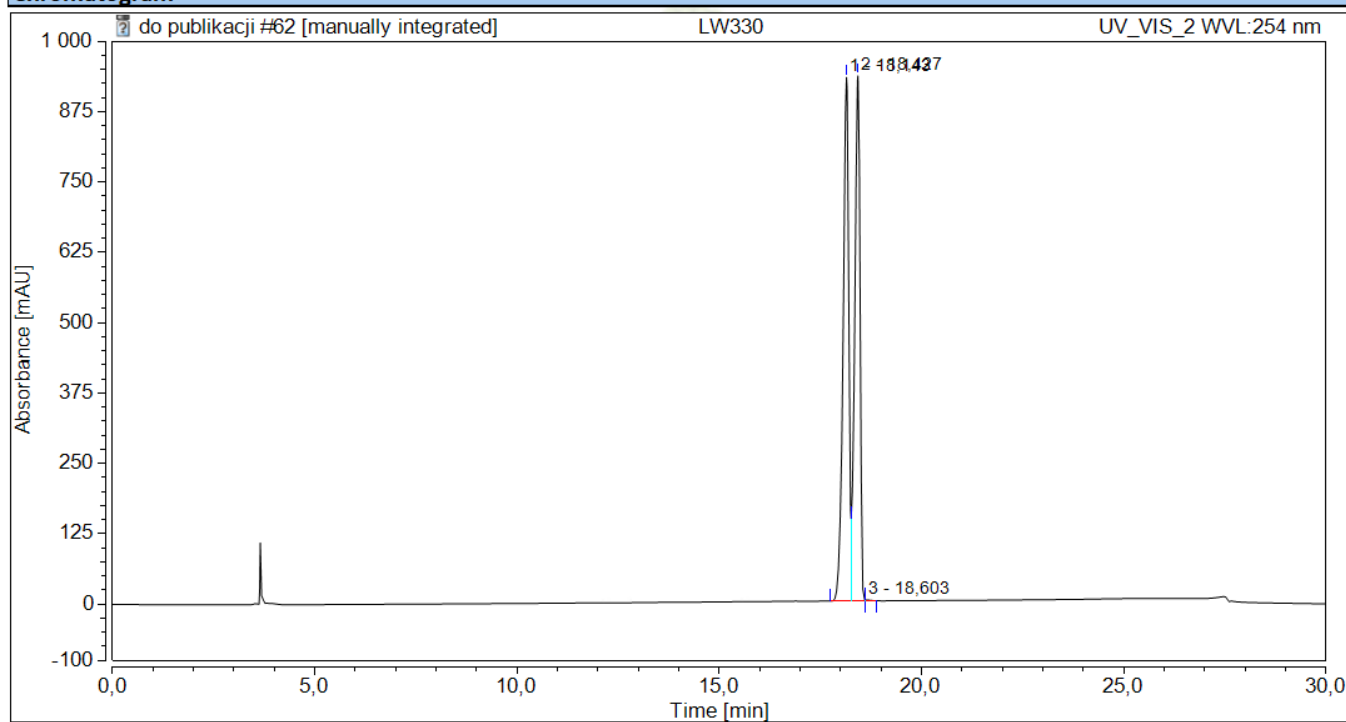
Name: *tert*-butyl ((2*S*)-1-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.49 (s, 59%), 18.14 (s, 41%).

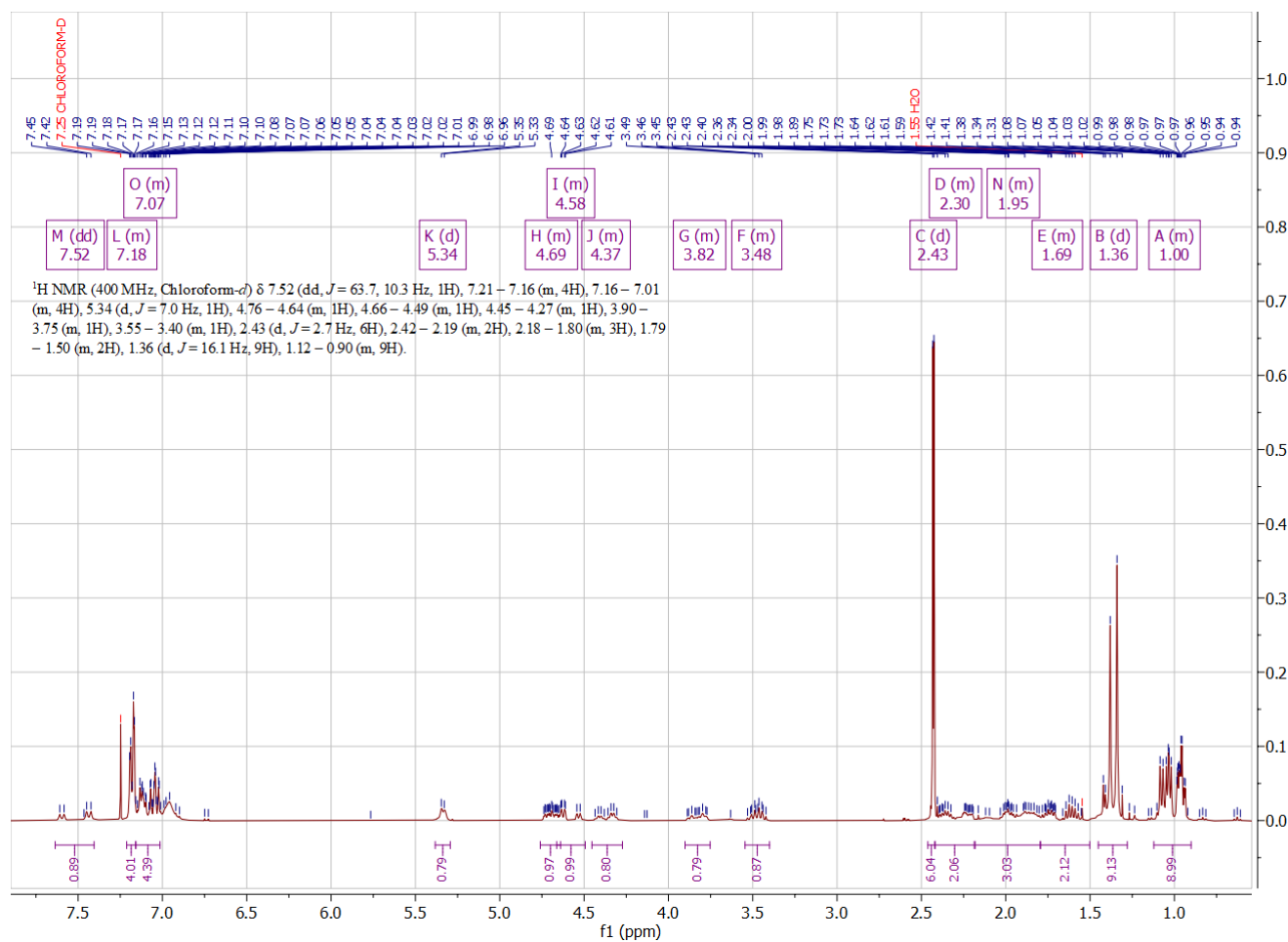
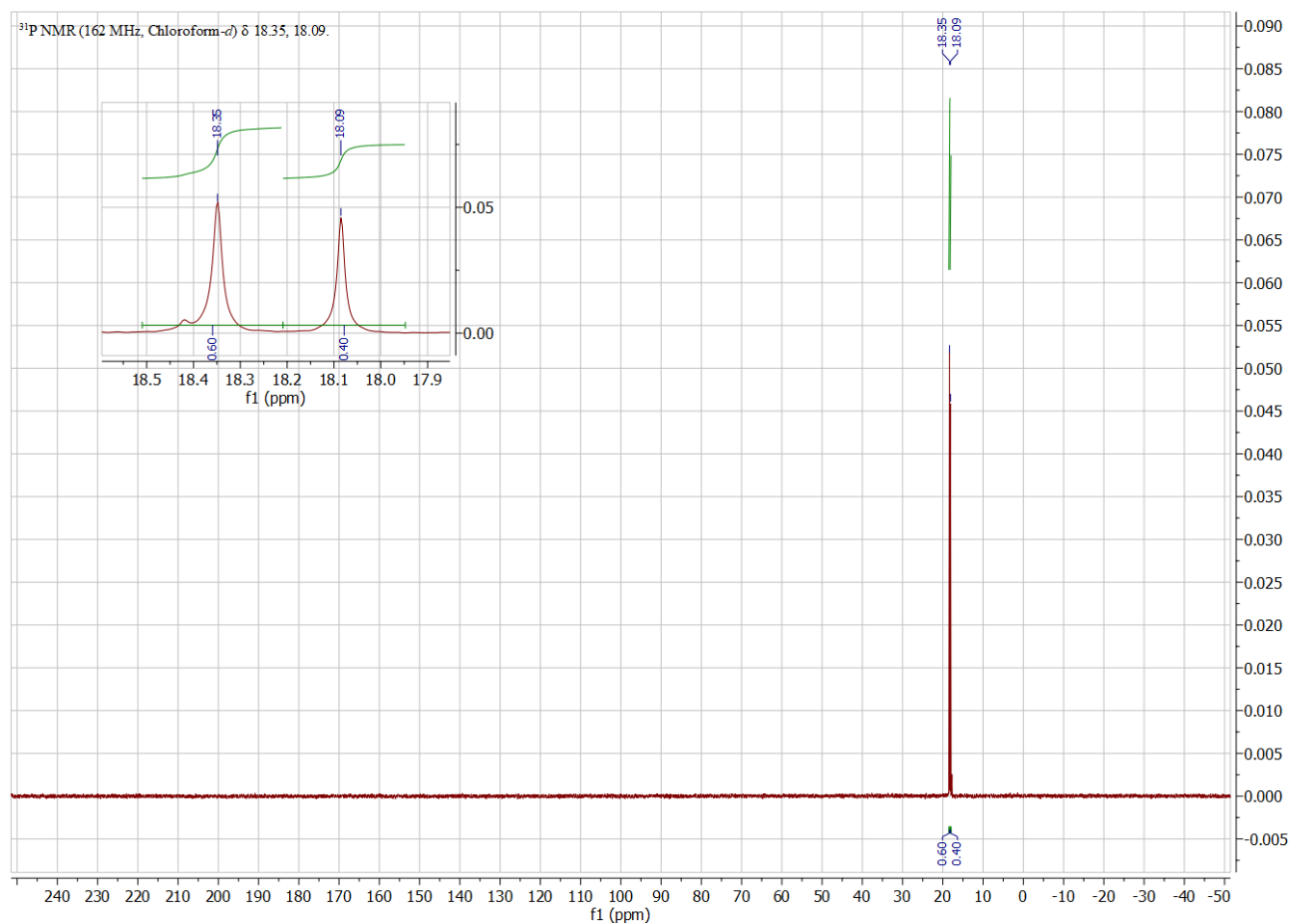
¹H NMR (400 MHz, Chloroform-*d*) δ 1H NMR (400 MHz, CHLOROFORM-*D*) δ 7.41 (dd, *J* = 28.0, 10.5 Hz, 1H, NH), 7.21 – 6.70 (m, 8H, 8xArH), 5.22 (dd, *J* = 40.6, 8.8 Hz, 1H, NH), 4.77 – 3.96 (m, 3H, CHP, 2xCH), 3.85 – 3.32 (m, 2H, CH₂), 2.47 – 2.39 (m, 6H, 2xSCH₃), 2.39 – 2.27 (m, 1H, CH), 2.27 – 2.13 (m, 1H, 0.5xCH₂), 2.13 – 1.85 (m, 3H, 1.5xCH₂), 1.85 – 1.46 (m, 2H, CH₂), 1.46 – 1.22 (m, 9H, Boc), 1.11 – 0.80 (m, 9H, 3xCH₃).

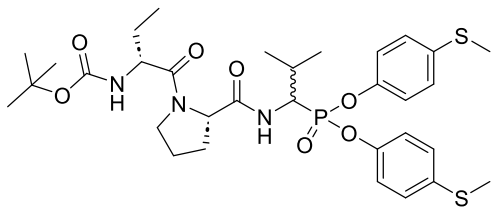
HRMS: C₃₂H₄₆N₃O₇PS₂ [M+Na]⁺ calc. 702.2412 found 702.2396

HPLC: purity >99%; retention time 18.143 and 18.427 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18,143	150,403	930,113	51,36	49,89	n.a.
2		18,427	142,241	932,688	48,57	50,02	n.a.
3		18,603	0,192	1,695	0,07	0,09	n.a.
Total:			292,836	1864,496	100,00	100,00	



(63) Boc-D-Abu-L-Pro-Val^P(OPh-4-SCH₃)₂

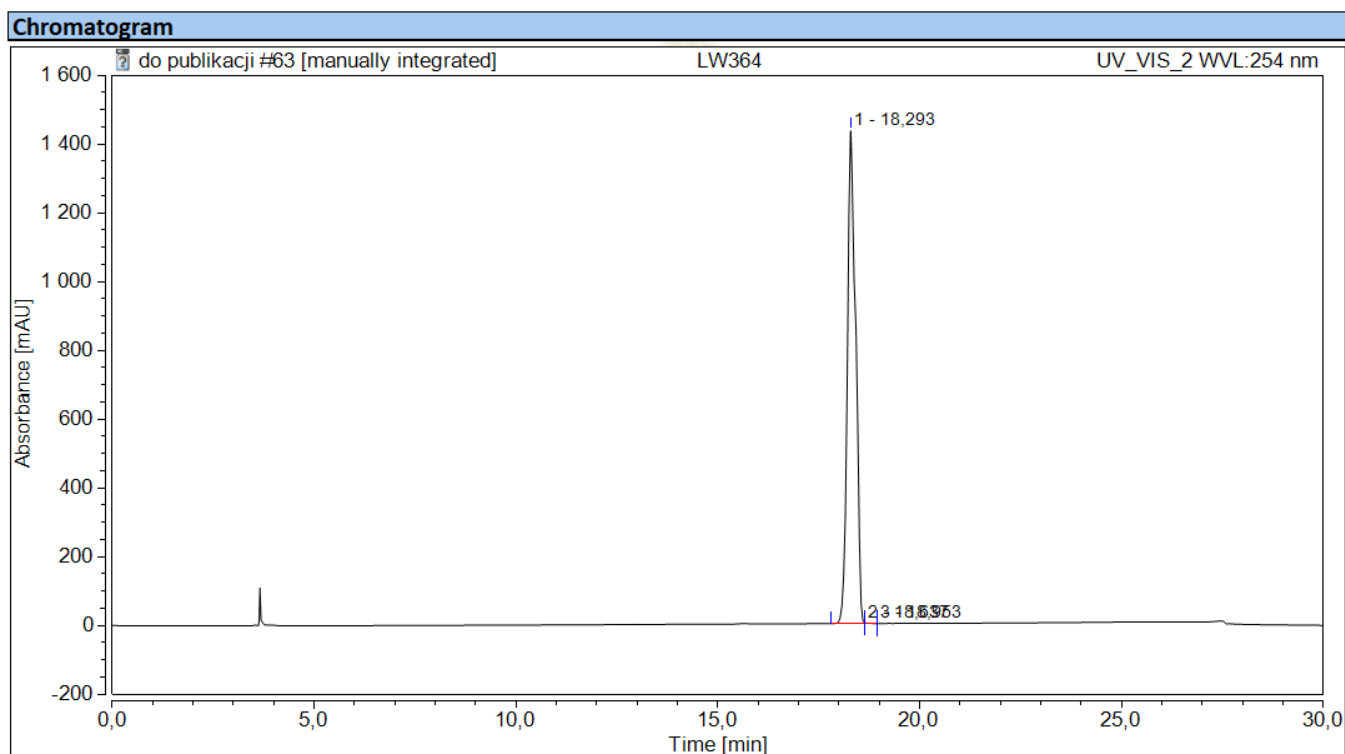
Name: *tert*-butyl ((2*R*)-1-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.35 (s, 60%), 18.09 (s, 40%).

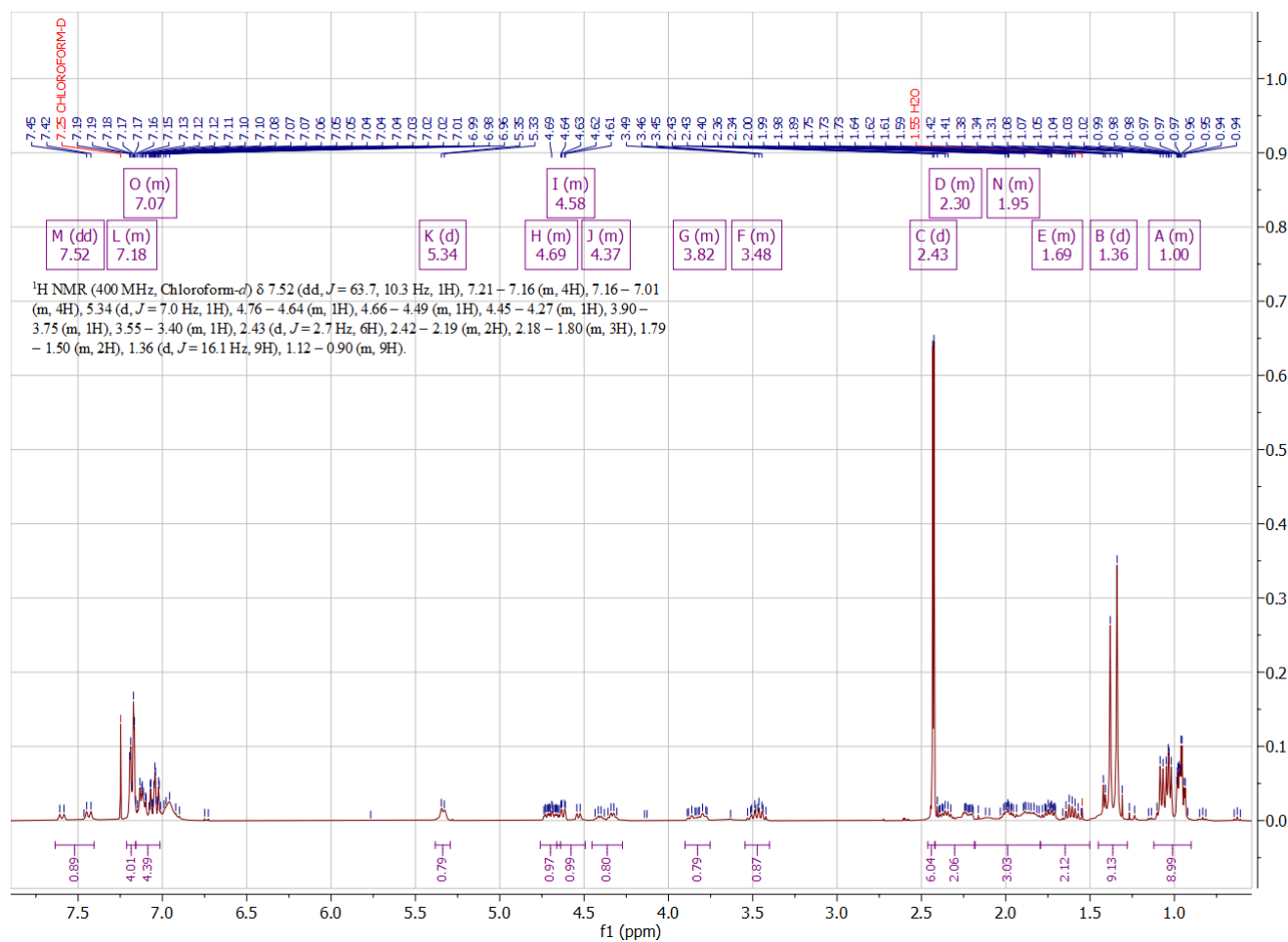
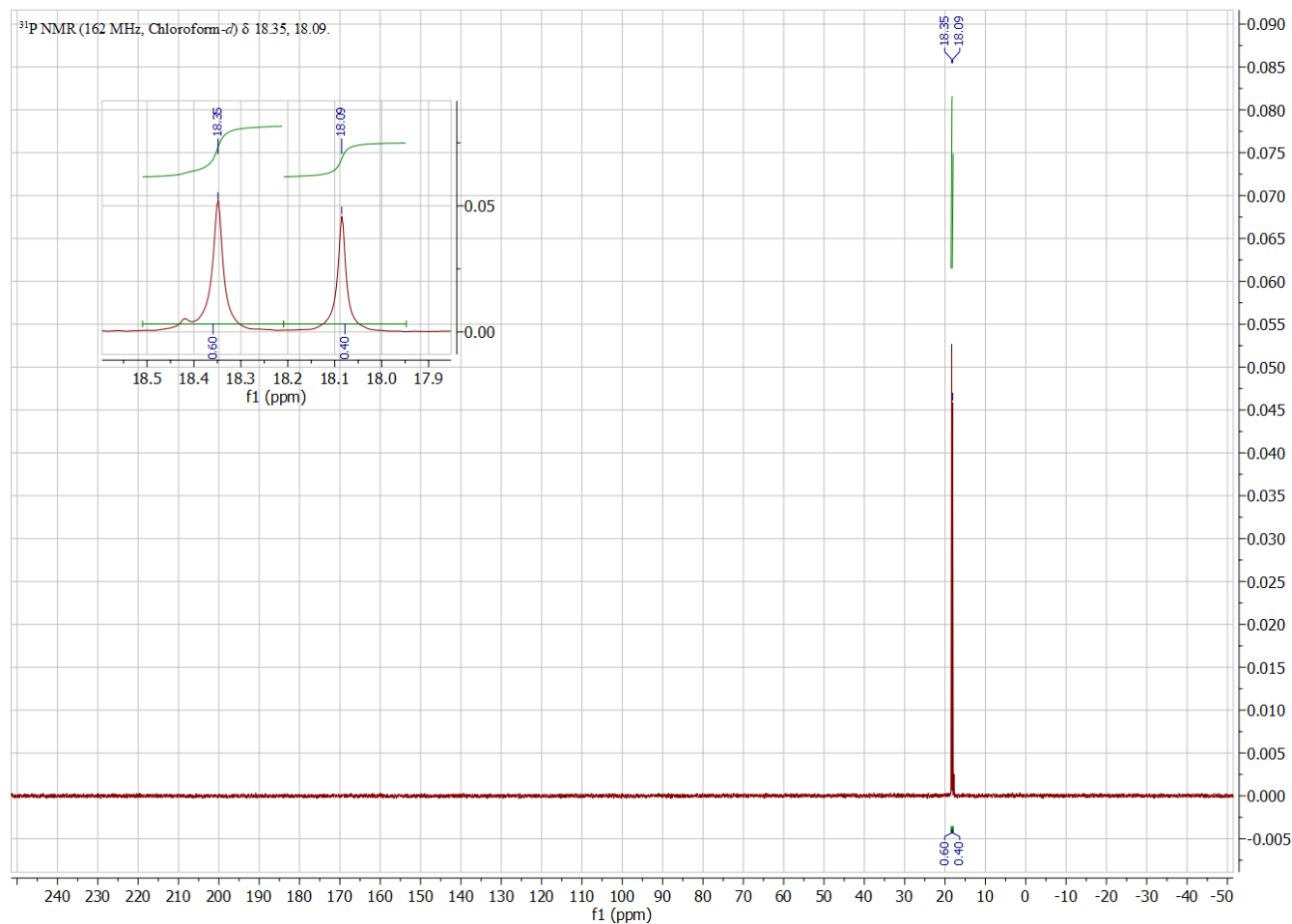
¹H NMR (400 MHz, Chloroform-*d*) δ 7.52 (dd, *J* = 63.7, 10.3 Hz, 1H, NH), 7.21 – 7.16 (m, 4H, 4xArH), 7.16 – 7.01 (m, 4H, 4xArH), 5.34 (d, *J* = 7.0 Hz, 1H, NH), 4.76 – 4.64 (m, 1H, CHP), 4.66 – 4.49 (m, 1H, CH), 4.45 – 4.27 (m, 1H, CH), 3.90 – 3.75 (m, 1H, 0.5xCH₂), 3.55 – 3.40 (m, 1H, 0.5xCH₂), 2.43 (d, *J* = 2.7 Hz, 6H, 2xSCH₃), 2.42 – 2.19 (m, 2H, 0.5xCH₂, CH), 2.18 – 1.80 (m, 3H, 1.5xCH₂), 1.79 – 1.50 (m, 2H, CH₂), 1.36 (d, *J* = 16.1 Hz, 9H, Boc), 1.12 – 0.90 (m, 9H, 3xCH₃).

HRMS: C₃₂H₄₆N₃O₇PS₂ [M+Na]⁺ calc. 702.2412 found 702.2405

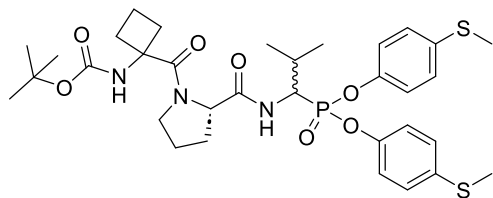
HPLC: purity >99%; retention time 18.293 min



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		18,293	340,133	1432,720	99,95	99,88	n.a.
2		18,637	0,167	1,753	0,05	0,12	n.a.
3		18,953	0,000	0,000	0,00	0,00	n.a.
Total:			340,300	1434,472	100,00	100,00	



(64) Boc-AC4C-L-Pro-Val^P(OPh-4-SCH₃)₂



Name: *tert*-butyl (1-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidine-1-carbonyl)cyclobutyl)carbamate

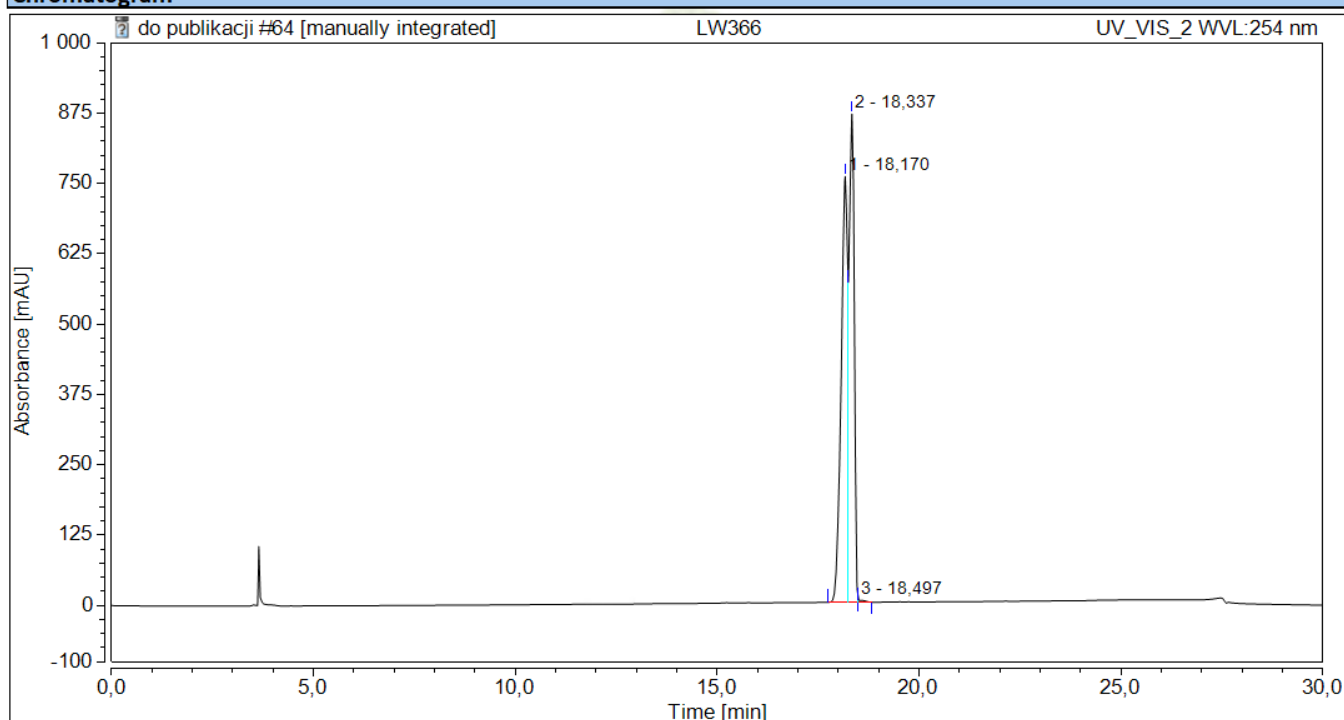
³¹P NMR (162 MHz, Chloroform-*d*) δ 18.78 (s, 75%), 18.06 (s, 25%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 7.8 Hz, 1H, NH), 7.21 – 6.98 (m, 8H, 8xArH), 5.27 – 5.15 (m, 1H, NH), 4.81 – 4.58 (m, 2H, CHP, CH), 3.62 – 3.31 (m, 2H, CH₂), 3.08 – 2.88 (m, 1H, 0.5xCH₂), 2.54 – 2.34 (m, 8H, 2xSCH₃, 0.5xCH₂, CH), 2.29 – 1.93 (m, 4H, 2xCH₂), 1.93 – 1.73 (m, 4H, 2xCH₂), 1.37 (d, *J* = 7.9 Hz, 9H, Boc), 1.22 – 0.99 (m, 6H, 2xCH₃).

HRMS: C₃₃H₄₆N₃O₇PS₂ [M+Na]⁺ calc. 714,2412 found 714.2411

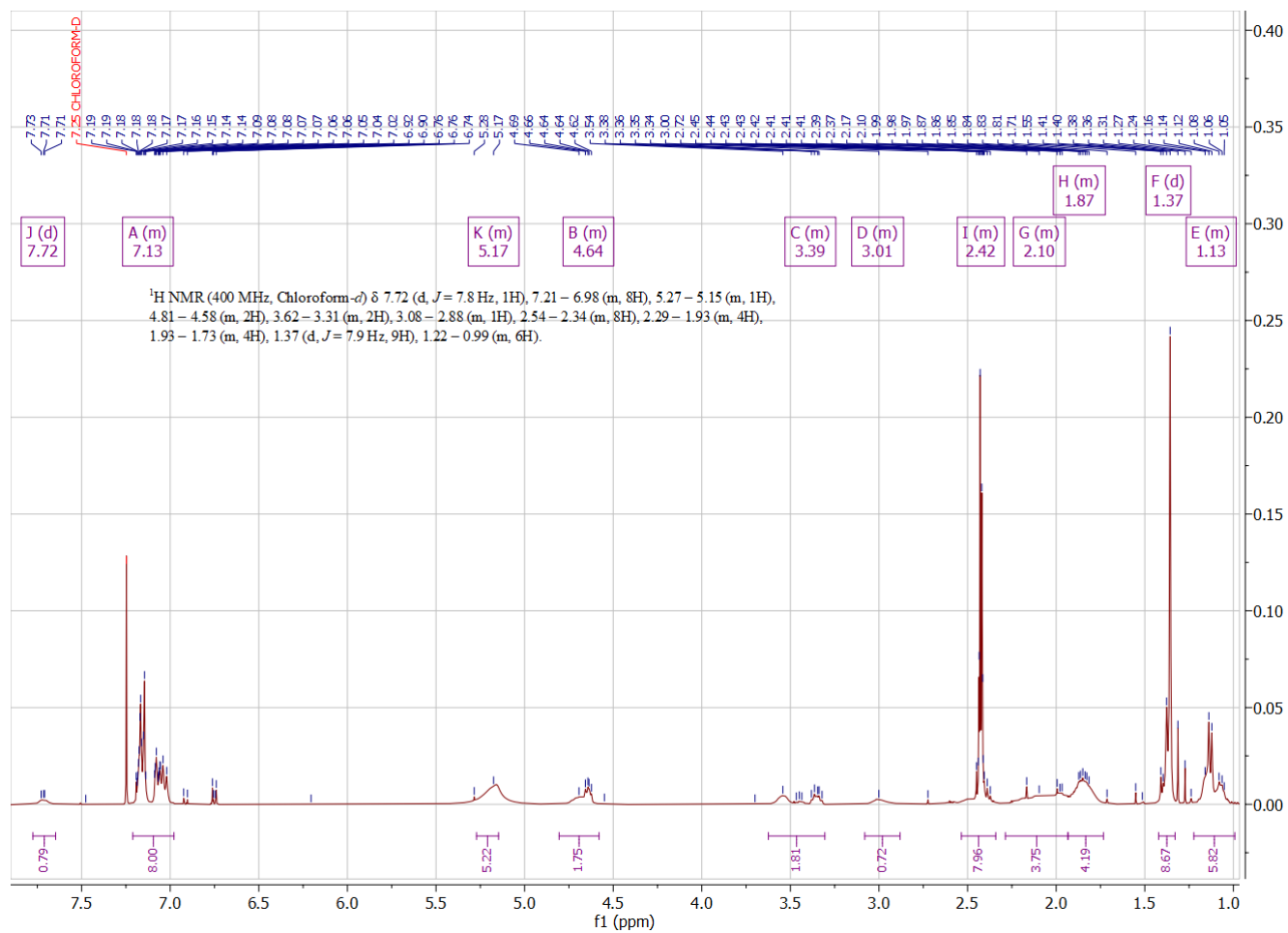
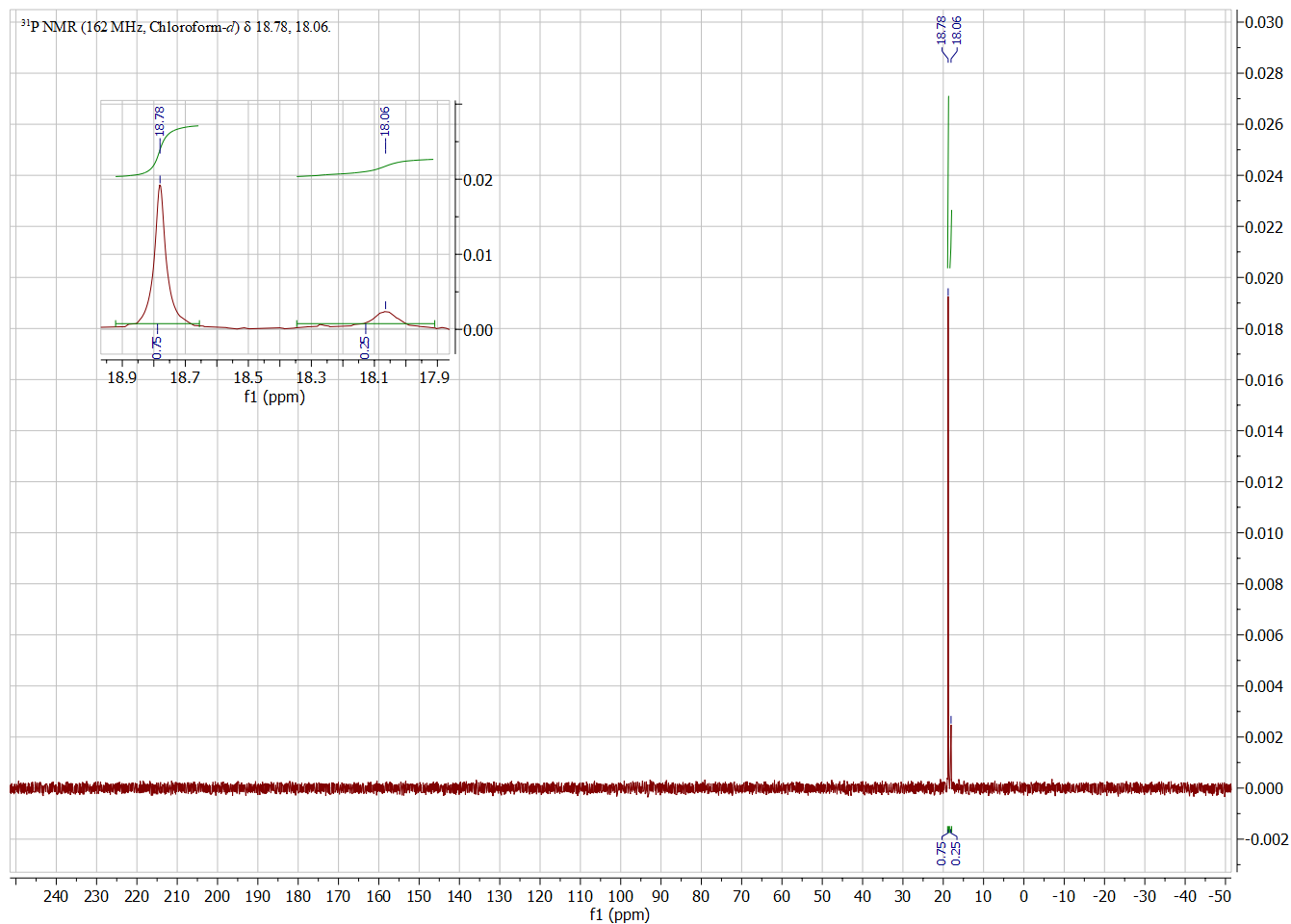
HPLC: purity >99%; retention time 18.170 and 18.337 min

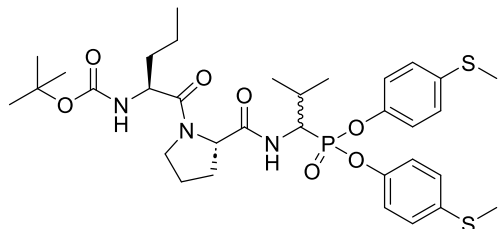
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18,170	136,879	756,613	51,63	46,46	n.a.
2		18,337	127,577	867,601	48,12	53,27	n.a.
3		18,497	0,657	4,437	0,25	0,27	n.a.
Total:			265,113	1628,651	100,00	100,00	



(65) Boc-L-Nva-L-Pro- Val^P(OPh-4-SCH₃)₂

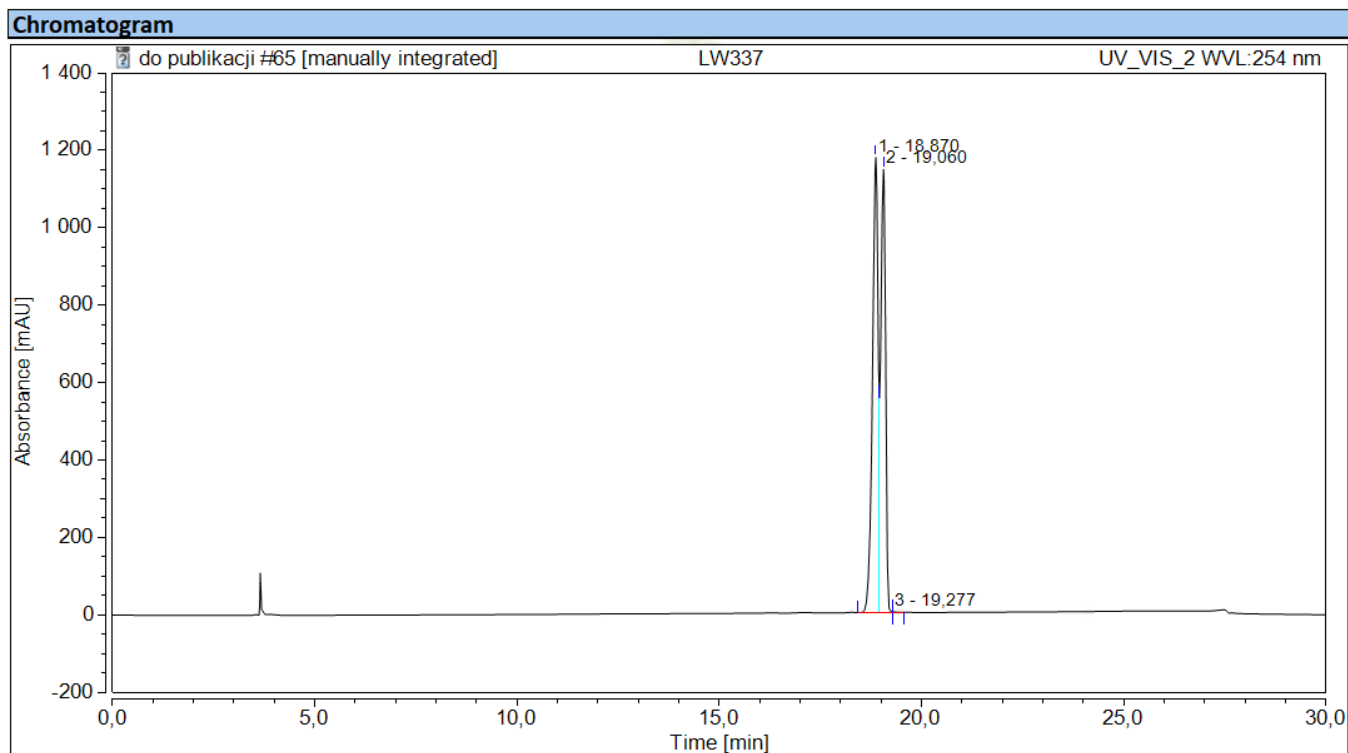
Name: *tert*-butyl ((2*S*)-1-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-1-oxopentan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.37 (s, 53%), 17.97 (s, 47%).

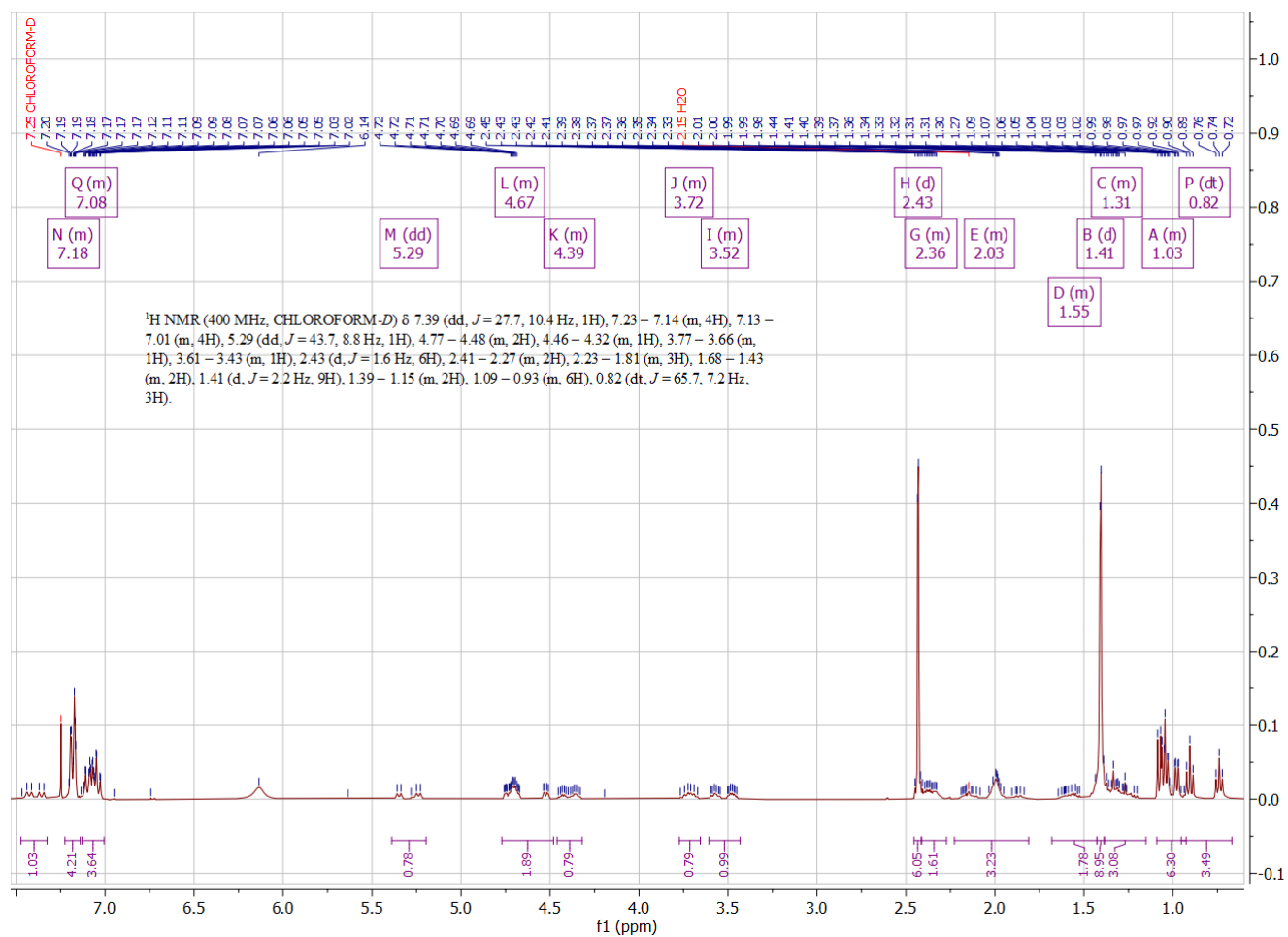
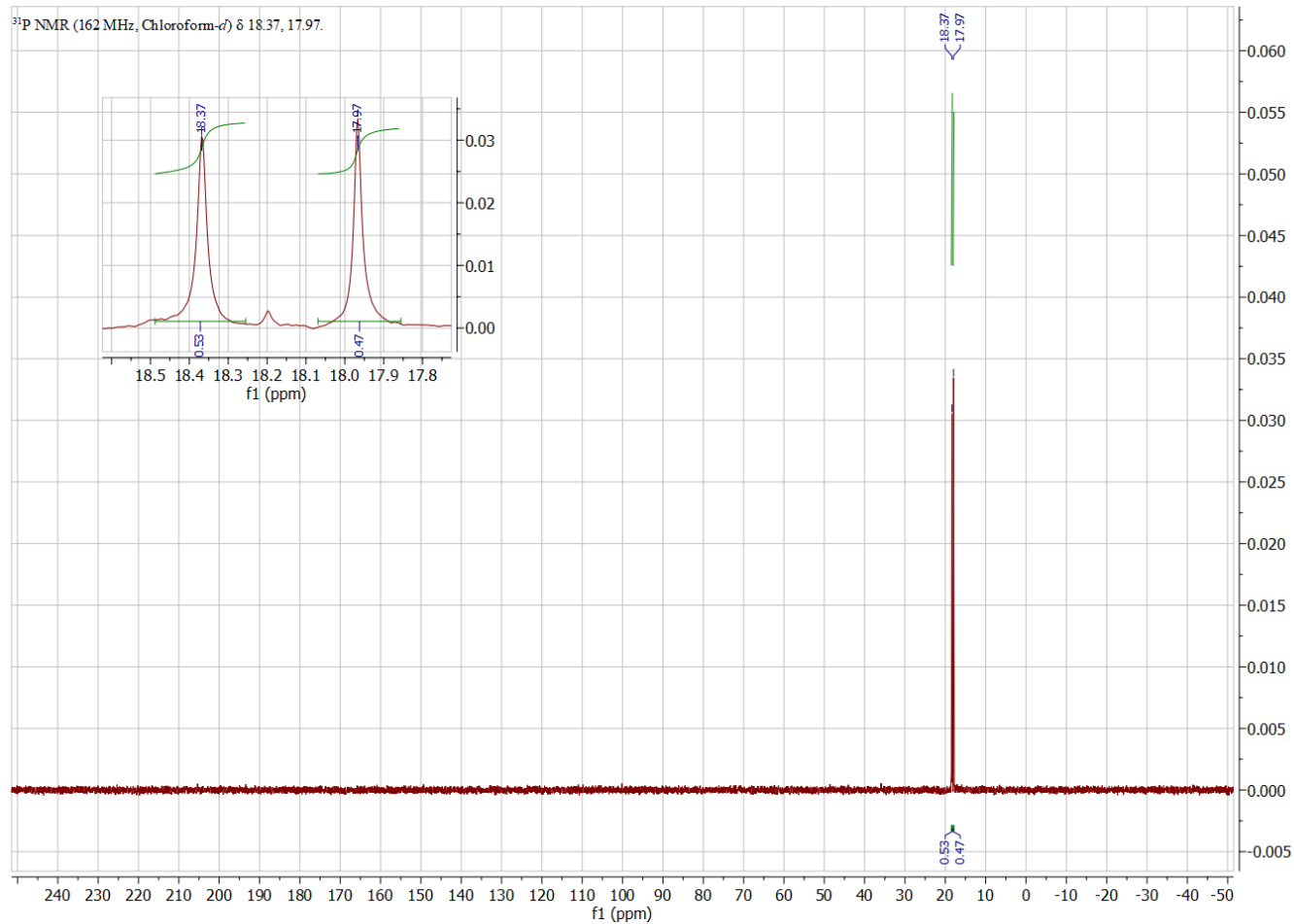
¹H NMR (400 MHz, Chloroform-*d*) δ 7.39 (dd, *J* = 27.7, 10.4 Hz, 1H, NH), 7.23 – 7.14 (m, 4H, 4xArH), 7.13 – 7.01 (m, 4H, 4xArH), 5.29 (dd, *J* = 43.7, 8.8 Hz, 1H, NH), 4.77 – 4.48 (m, 2H, CHP, CH), 4.46 – 4.32 (m, 1H, CH), 3.77 – 3.66 (m, 1H, 0.5xCH₂), 3.61 – 3.43 (m, 1H, 0.5xCH₂), 2.43 (d, *J* = 1.6 Hz, 6H, 2xSCH₃), 2.41 – 2.27 (m, 2H, CH₂), 2.23 – 1.81 (m, 3H, CH₂, CH), 1.68 – 1.43 (m, 2H, CH₂), 1.41 (d, *J* = 2.2 Hz, 9H, Boc), 1.39 – 1.15 (m, 2H, CH₂), 1.09 – 0.93 (m, 6H, 2xCH₃), 0.82 (dt, *J* = 65.7, 7.2 Hz, 3H, CH₃).

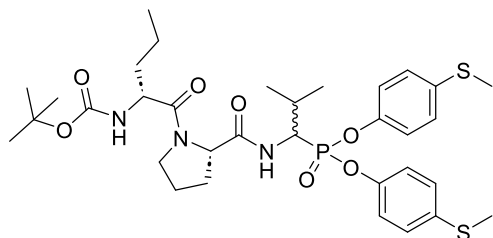
HRMS: C₃₃H₄₈N₃O₇PS₂ [M+Na]⁺ calc. 716.2569 found 716.2538

HPLC: purity >99%; retention time 18.870 and 19.060 min



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18,870	190,967	1175,642	54,73	50,62	n.a.
2		19,060	157,749	1144,759	45,21	49,29	n.a.
3		19,277	0,233	1,940	0,07	0,08	n.a.
Total:			348,948	2322,342	100,00	100,00	



(66) Boc-D-Nva-L-Pro-Val^P(OPh-4-SCH₃)₂

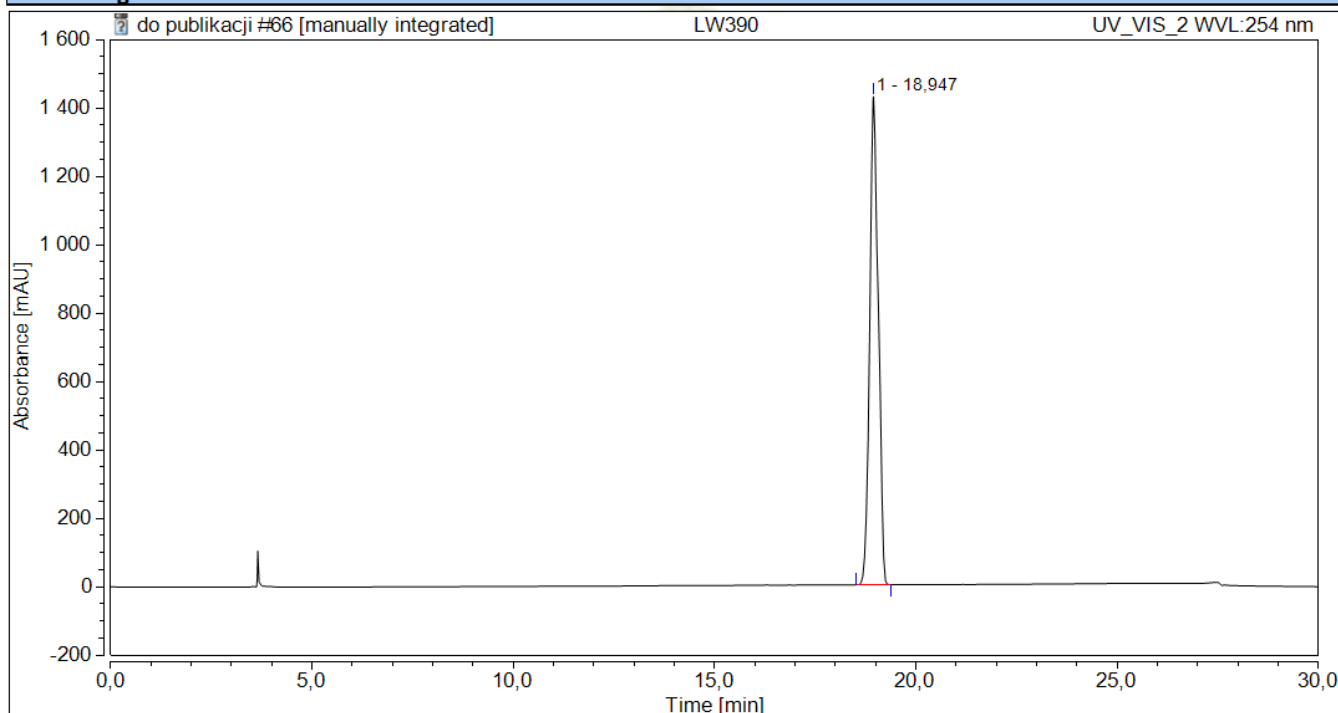
Name: *tert*-butyl ((2*R*)-1-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-1-oxopentan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.46 (s, 50%), 18.17 (s, 50%).

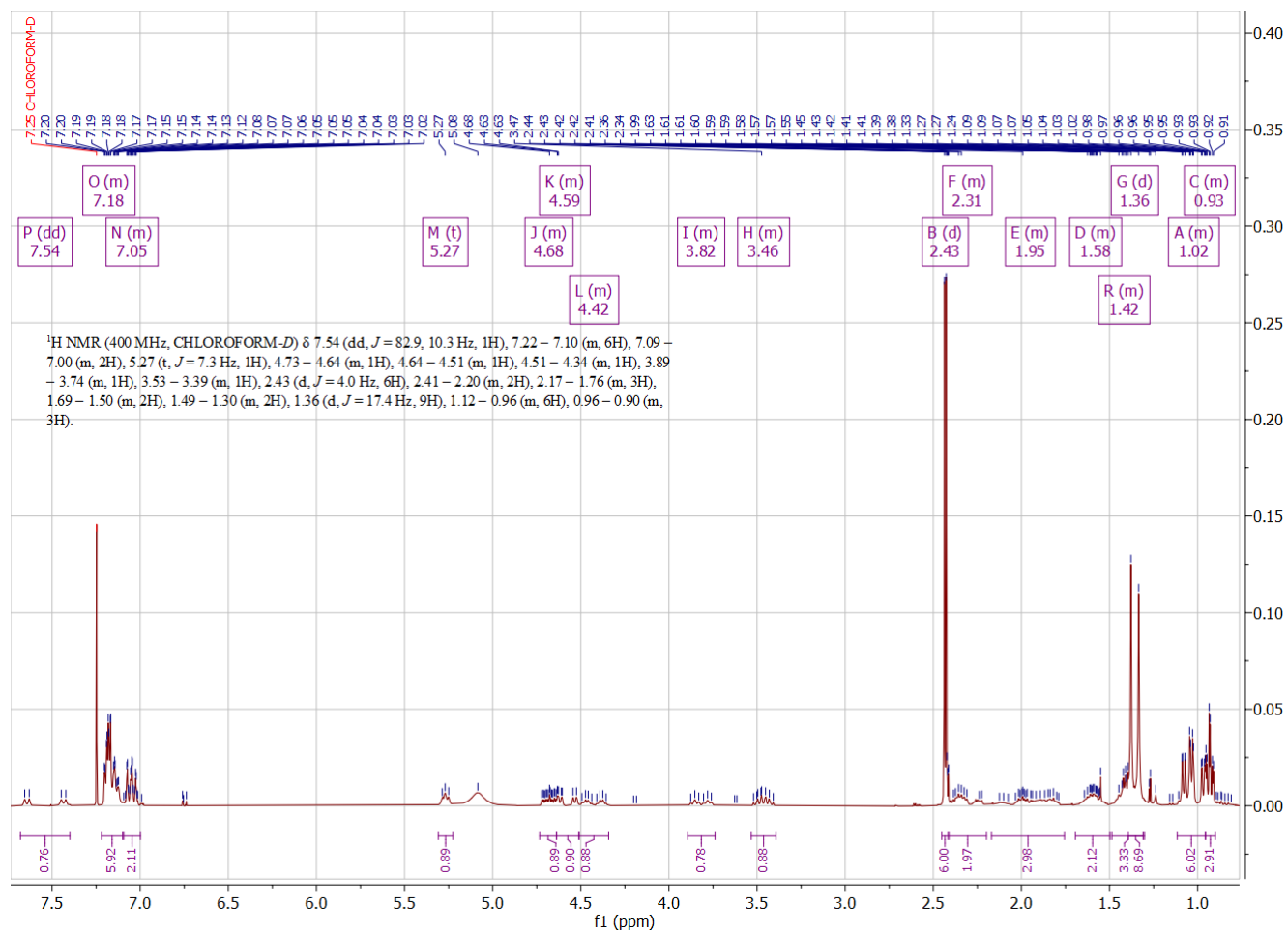
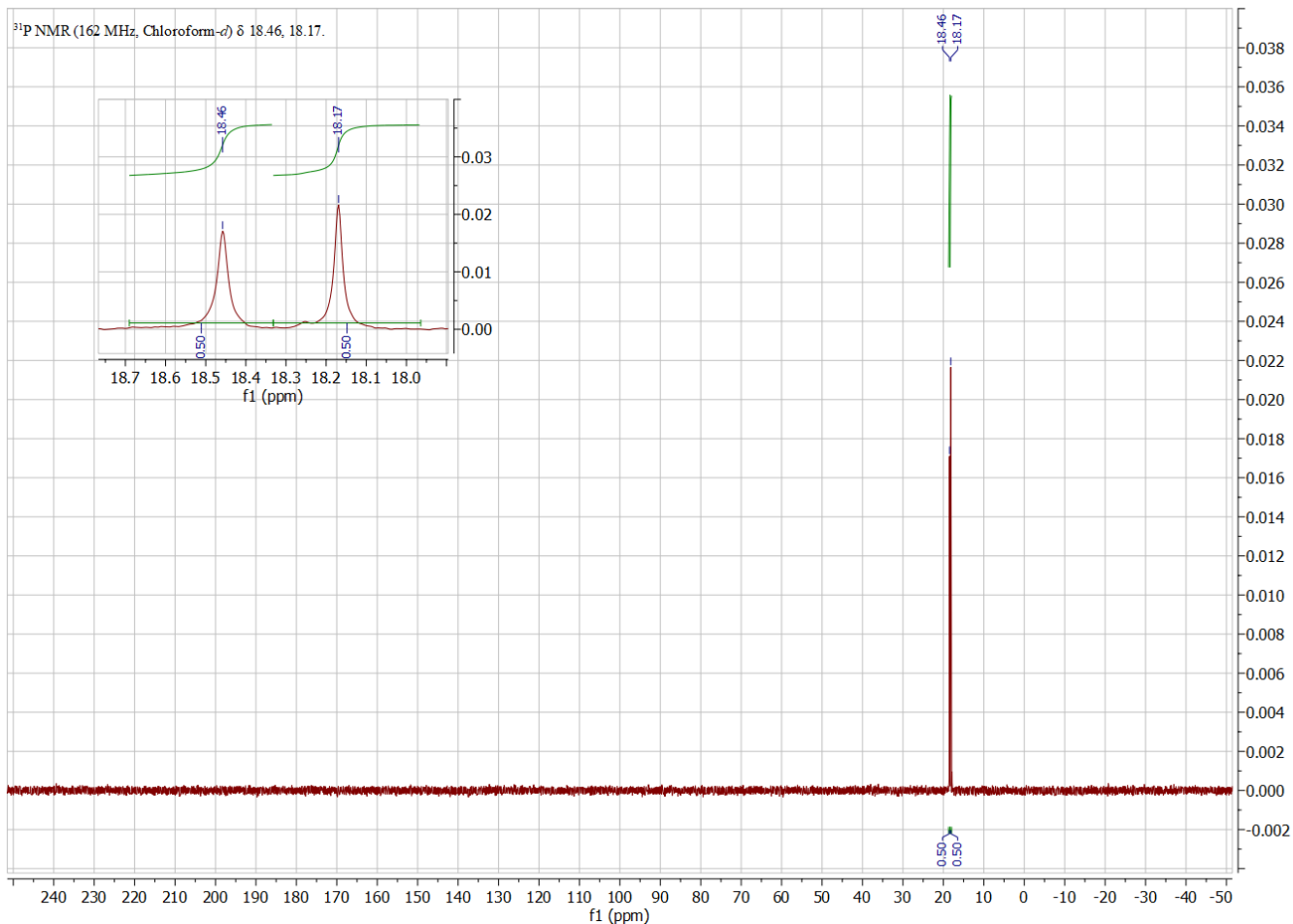
¹H NMR (400 MHz, Chloroform-*d*) δ 7.54 (dd, *J* = 82.9, 10.3 Hz, 1H, NH), 7.22 – 7.10 (m, 6H, 6xArH), 7.09 – 7.00 (m, 2H, 2xArH), 5.27 (t, *J* = 7.3 Hz, 1H, NH), 4.73 – 4.64 (m, 1H, CHP), 4.64 – 4.51 (m, 1H, CH), 4.51 – 4.34 (m, 1H, CH), 3.89 – 3.74 (m, 1H, 0.5xCH₂), 3.53 – 3.39 (m, 1H, 0.5xCH₂), 2.43 (d, *J* = 4.0 Hz, 6H, 2xSCH₃), 2.41 – 2.20 (m, 2H, CH₂), 2.17 – 1.76 (m, 3H, CH₂, CH), 1.69 – 1.50 (m, 2H, CH₂), 1.49 – 1.30 (m, 2H, CH₂), 1.36 (d, *J* = 17.4 Hz, 9H, Boc), 1.12 – 0.96 (m, 6H, 2xCH₃), 0.96 – 0.90 (m, 3H, CH₃).

HRMS: C₃₃H₄₈N₃O₇PS [M+Na]⁺ calc. 716.2569 found 716.2576

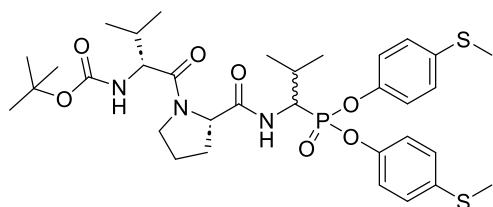
HPLC: purity >99%; retention time 18.947 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18,947	350,989	1427,156	100,00	100,00	n.a.
Total:			350,989	1427,156	100,00	100,00	



(67) Boc-D-Val-L-Pro-Val^P(OPh-4-SCH₃)₂



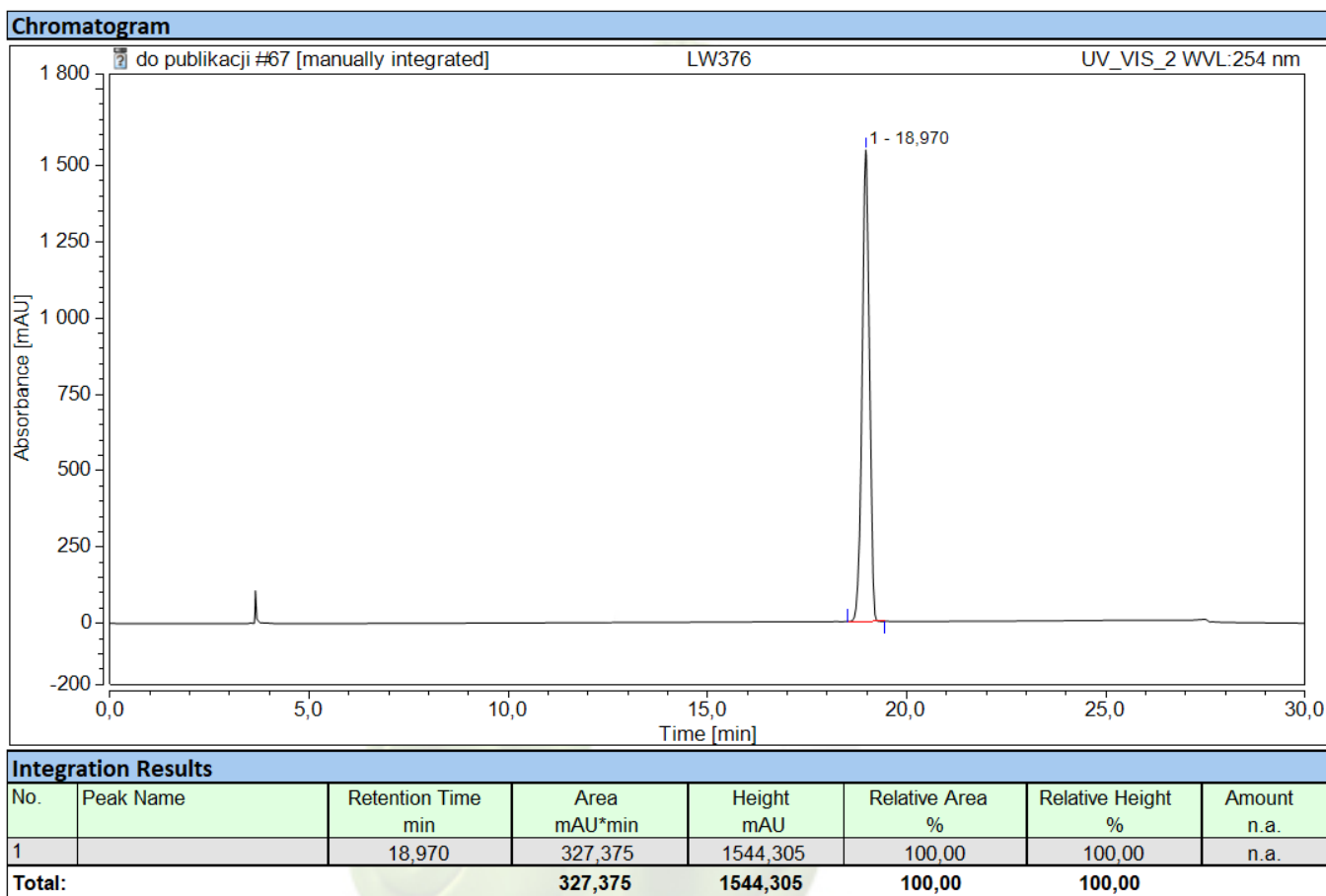
Name: *tert*-butyl ((2*R*)-1-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-3-methyl-1-oxobutan-2-yl)carbamate

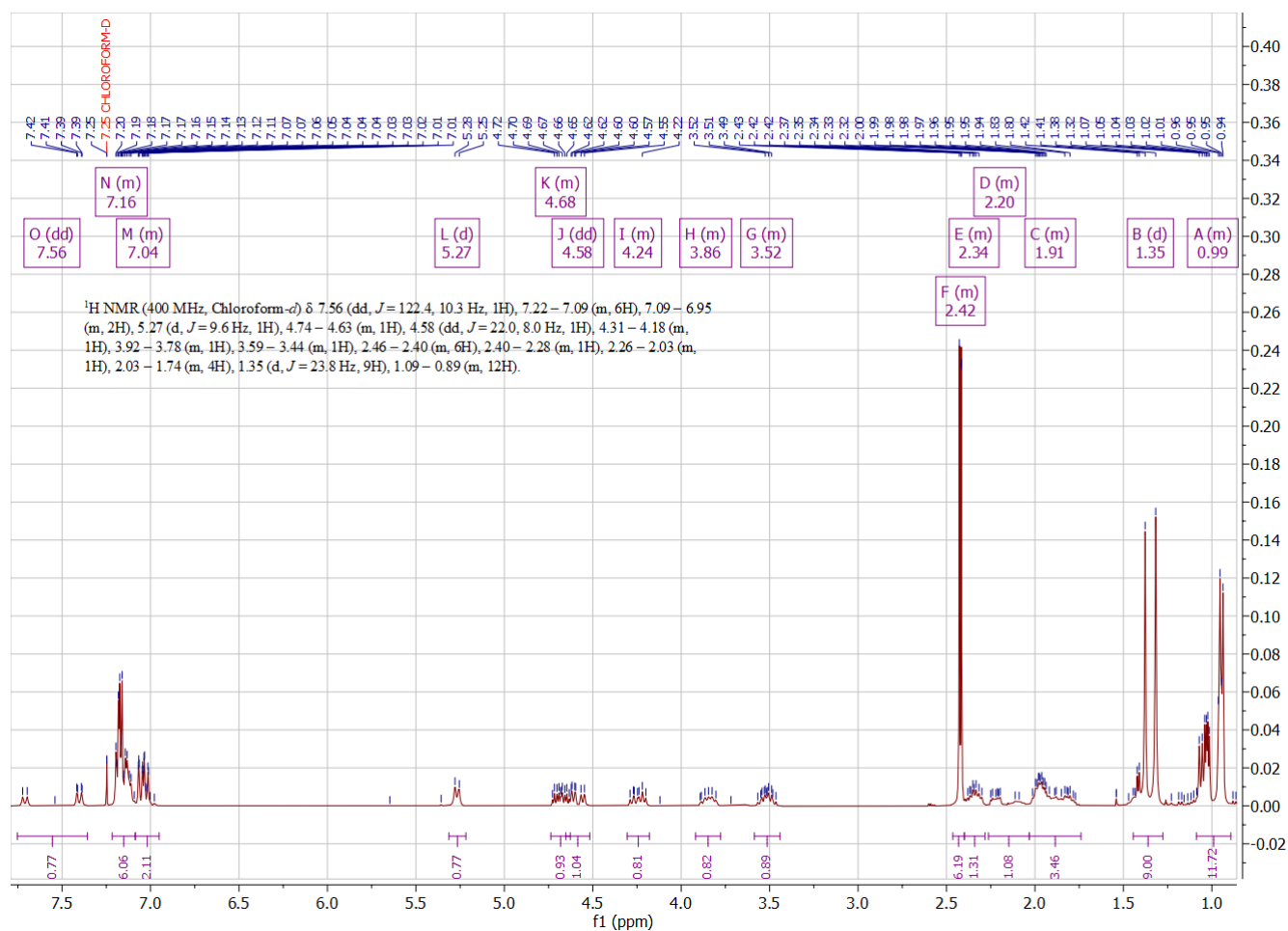
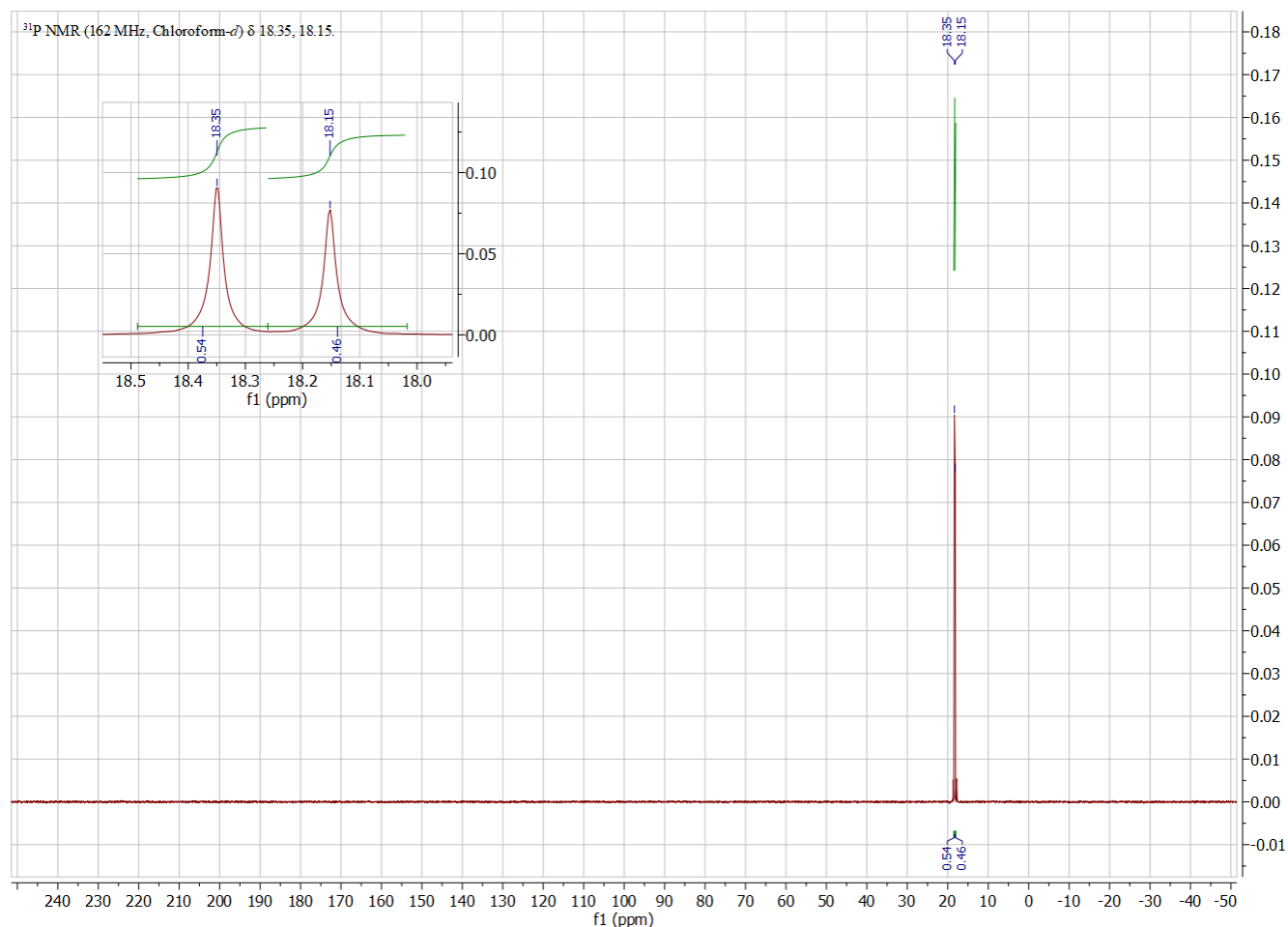
³¹P NMR (162 MHz, Chloroform-*d*) δ 18.35 (s, 54%), 18.15 (s, 46%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.56 (dd, *J* = 122.4, 10.3 Hz, 1H, NH), 7.22 – 7.09 (m, 6H, 6xArH), 7.09 – 6.95 (m, 2H, 2xArH), 5.27 (d, *J* = 9.6 Hz, 1H, NH), 4.74 – 4.63 (m, 1H, CHP), 4.58 (dd, *J* = 22.0, 8.0 Hz, 1H, CH), 4.31 – 4.18 (m, 1H, CH), 3.92 – 3.78 (m, 1H, 0.5xCH₂), 3.59 – 3.44 (m, 1H, 0.5xCH₂), 2.46 – 2.40 (m, 6H, 2xSCH₃), 2.40 – 2.28 (m, 1H, CH), 2.26 – 2.03 (m, 1H, CH), 2.03 – 1.74 (m, 4H, 2xCH₂), 1.35 (d, *J* = 23.8 Hz, 9H, Boc), 1.09 – 0.89 (m, 12H, 4xCH₃).

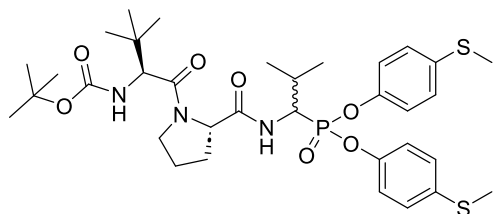
HRMS: C₃₃H₄₈N₃O₇PS₂ [M+Na]⁺ calc. 716.2569 found 716.2557

HPLC: purity >99%; retention time 18.970 min





(68) Boc-L-Tle-L-Pro-Val^P(OPh-4-SCH₃)₂



Name: *tert*-butyl ((2*S*)-1-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-3,3-dimethyl-1-oxobutan-2-yl)carbamate

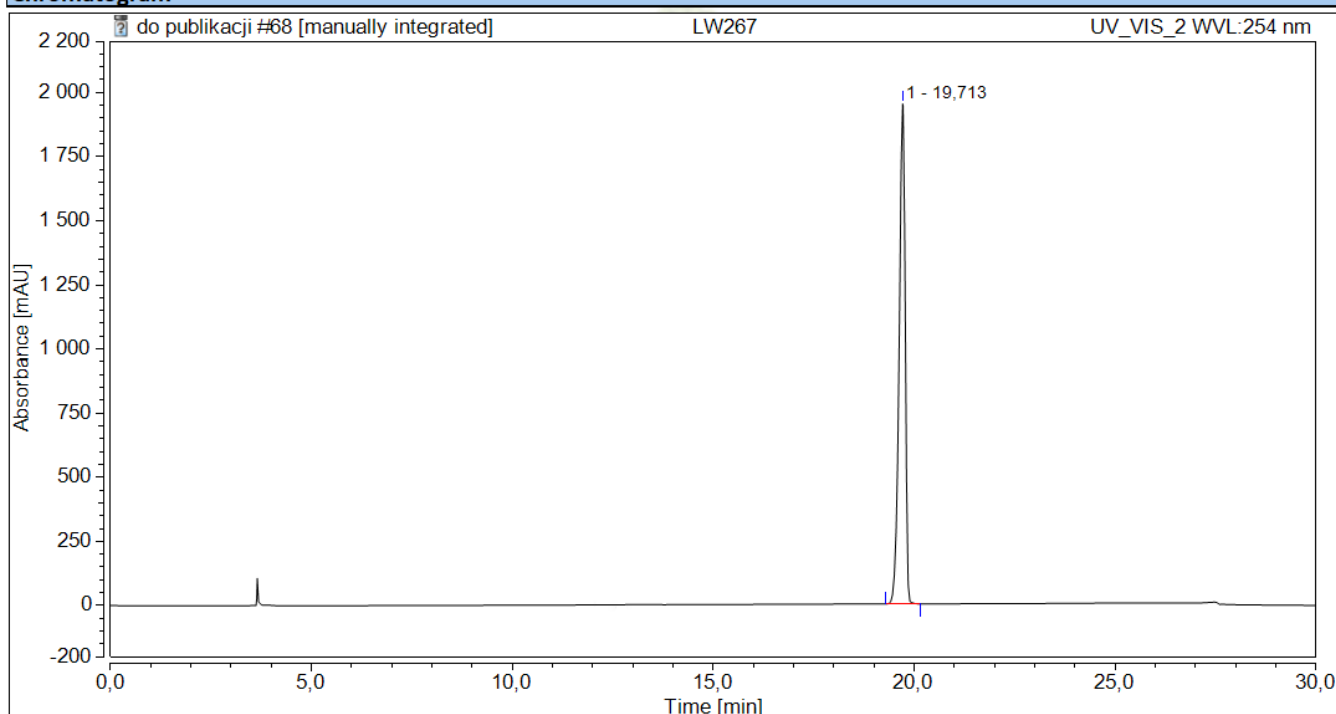
³¹P NMR (162 MHz, Chloroform-*d*) δ 18.70 (s, 35%), 18.16 (s, 65%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.28 (dd, *J* = 28.3, 9.8 Hz, 1H, NH), 7.20 – 7.13 (m, 4H, 4xArH), 7.13 – 7.02 (m, 4H, 4xArH), 5.30 (dd, *J* = 41.6, 9.9 Hz, 1H, NH), 4.76 – 4.65 (m, 1H, CHP), 4.47 (dd, *J* = 8.1, 3.4 Hz, 1H, CH), 4.35 – 4.25 (m, 1H, CH), 3.90 – 3.54 (m, 2H, CH₂), 2.46 – 2.41 (m, 6H, 2xSCH₃), 2.40 – 2.29 (m, 1H, CH), 2.22 – 1.77 (m, 4H, 2xCH₂), 1.41 (d, *J* = 2.6 Hz, 9H, Boc), 1.13 – 0.91 (m, 15H, 5xCH₃).

HRMS: C₃₄H₅₀N₃O₇PS₂ [M+Na]⁺ calc. 730.2725 found 730.2714

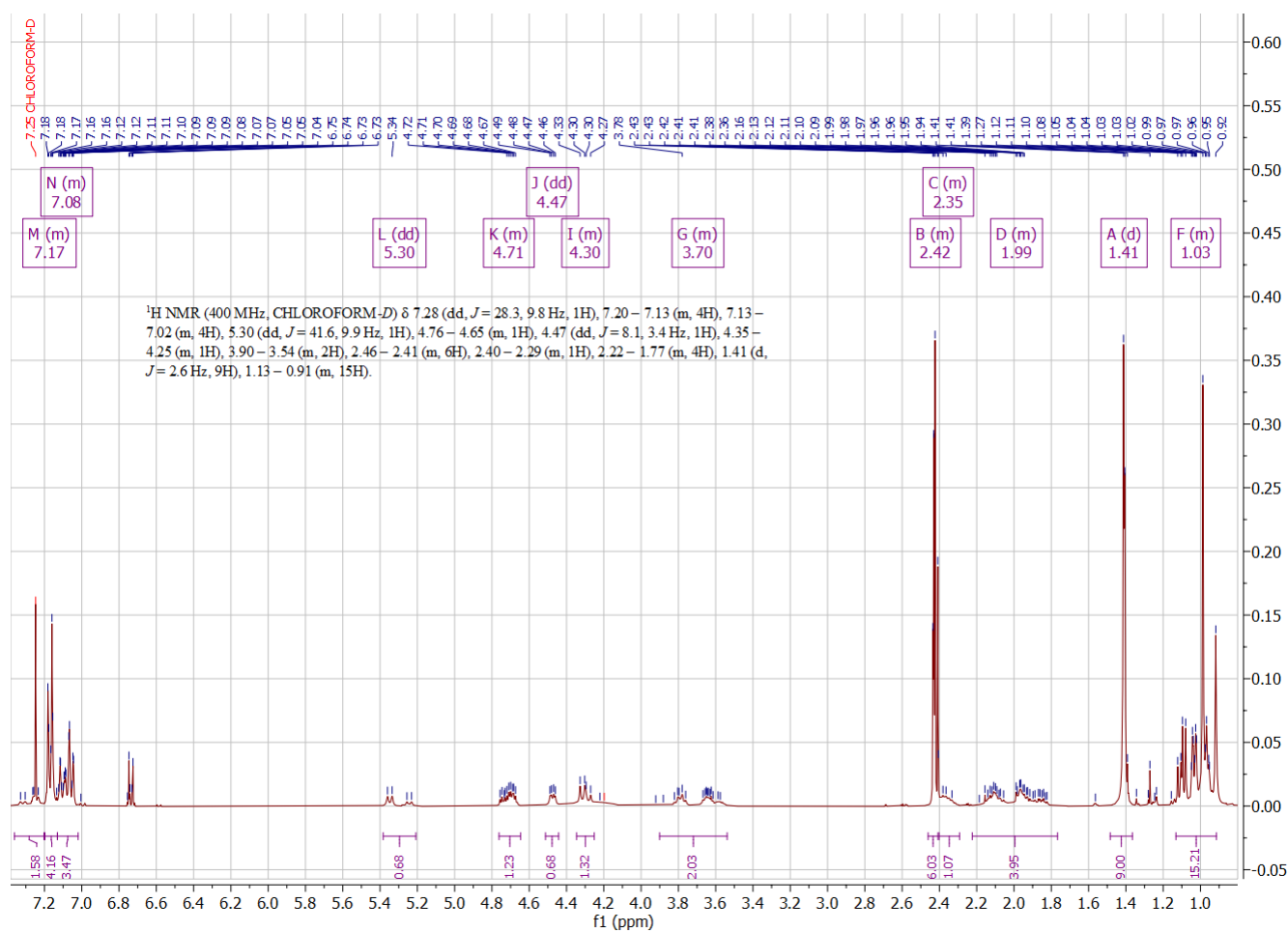
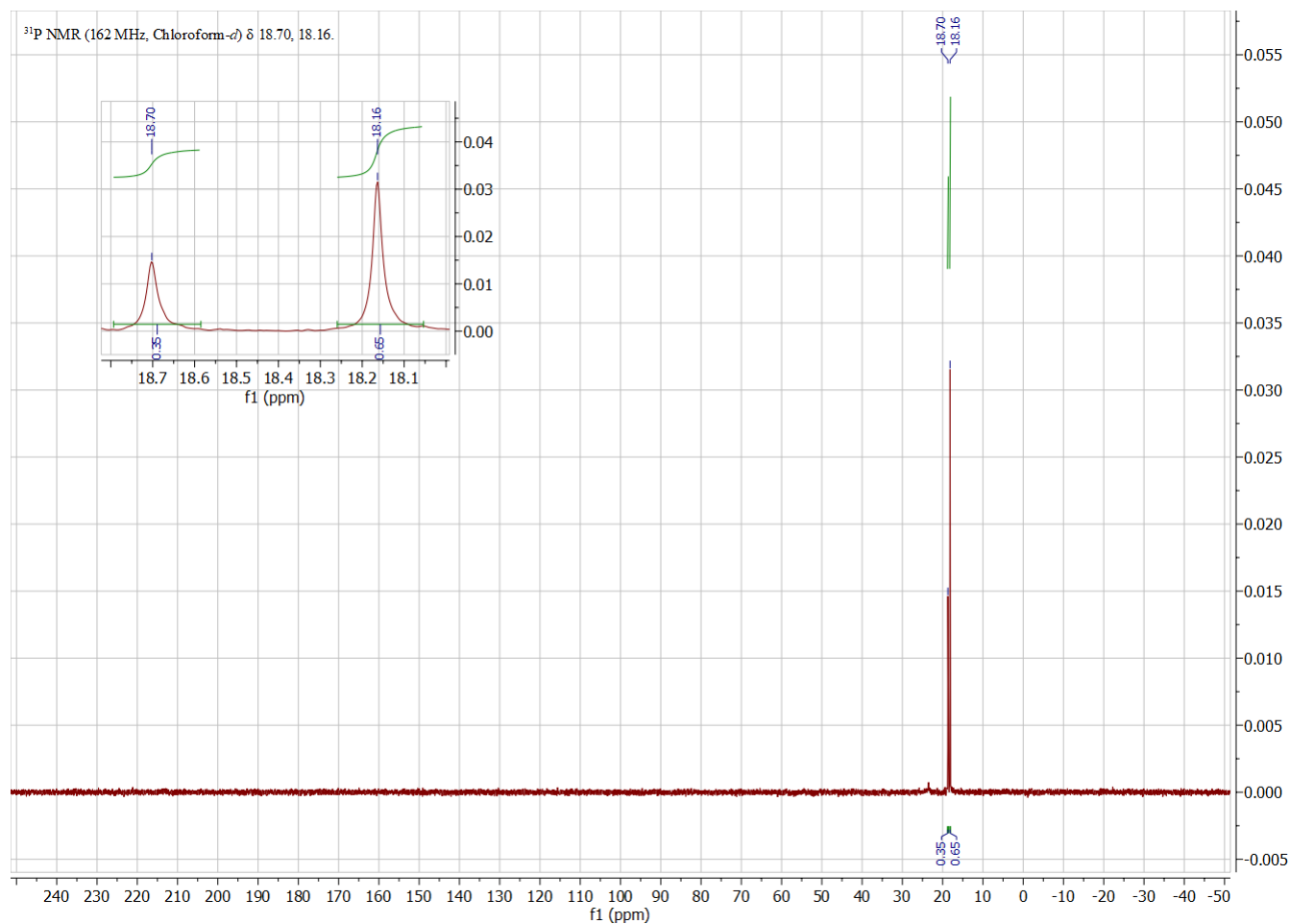
HPLC: purity >99%; retention time 19.713 min

Chromatogram

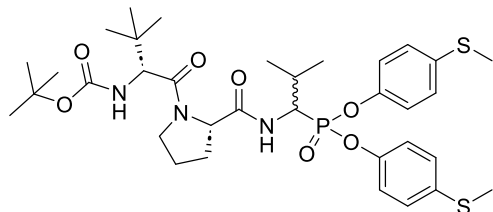


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19,713	339,869	1949,761	100,00	100,00	n.a.
Total:			339,869	1949,761	100,00	100,00	



(69) Boc-D-Tle-L-Pro- Val^P(OPh-4-SCH₃)₂



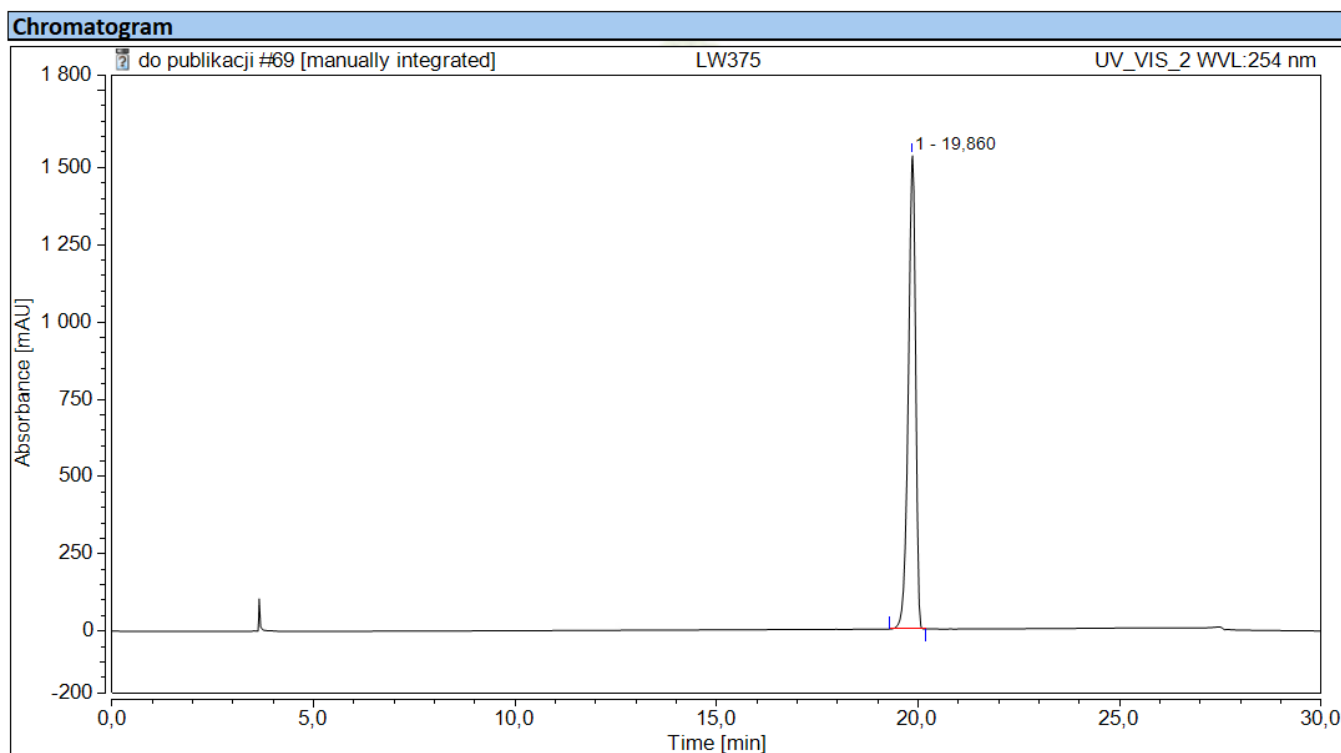
Name: *tert*-butyl ((2*R*)-1-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-3,3-dimethyl-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.27 (s, 54%), 18.12 (s, 46%).

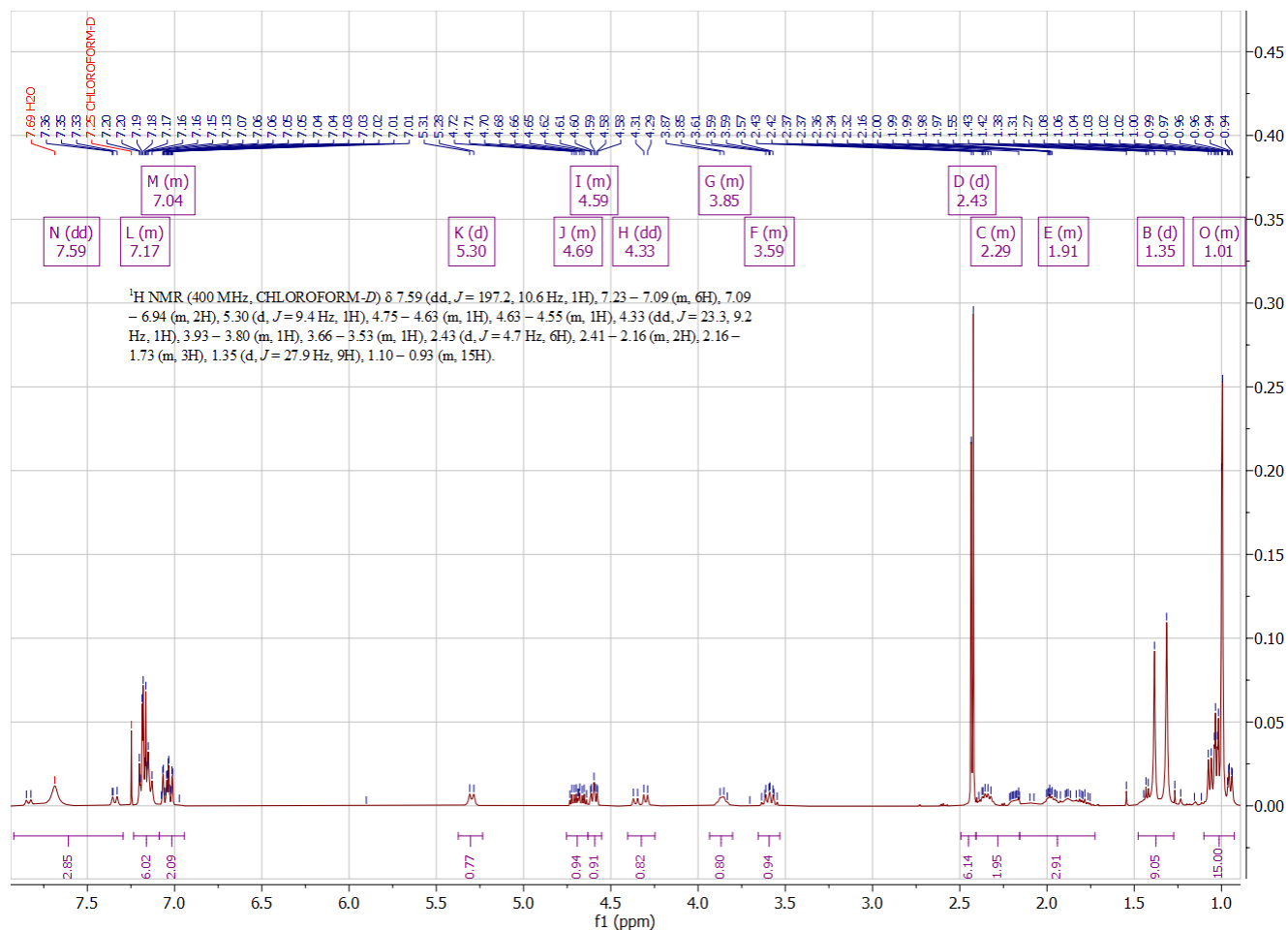
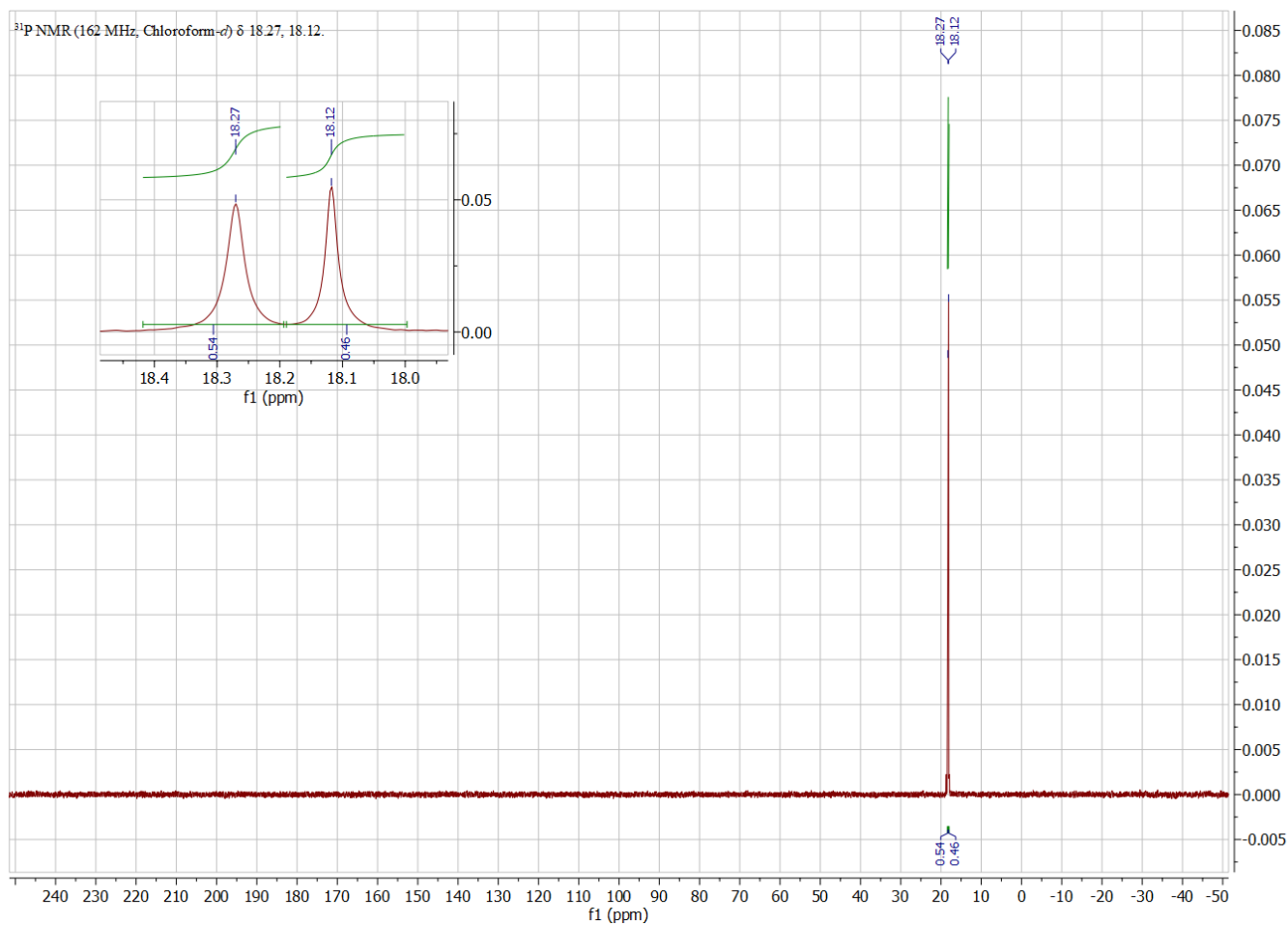
¹H NMR (400 MHz, Chloroform-*d*) δ 7.59 (dd, *J* = 197.2, 10.6 Hz, 1H, NH), 7.23 – 7.09 (m, 6H, 6xArH), 7.09 – 6.94 (m, 2H, 2xArH), 5.30 (d, *J* = 9.4 Hz, 1H, NH), 4.75 – 4.63 (m, 1H, CHP), 4.63 – 4.55 (m, 1H, CH), 4.33 (dd, *J* = 23.3, 9.2 Hz, 1H, CH), 3.93 – 3.80 (m, 1H, 0.5xCH₂), 3.66 – 3.53 (m, 1H, 0.5xCH₂), 2.43 (d, *J* = 4.7 Hz, 6H, 2xSCH₃), 2.41 – 2.16 (m, 2H, 0.5xCH₂, CH), 2.16 – 1.73 (m, 3H, 1.5xCH₂), 1.35 (d, *J* = 27.9 Hz, 9H, Boc), 1.10 – 0.93 (m, 15H, 5xCH₃).

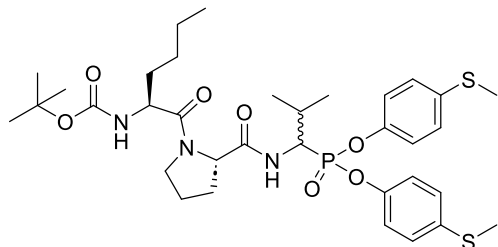
HRMS: C₃₄H₅₀N₃O₇PS₂ [M+Na]⁺ calc. 730.2725 found 730.2716

HPLC: purity >99%; retention time 19.860 min



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19,860	320,962	1531,024	100,00	100,00	n.a.
Total:			320,962	1531,024	100,00	100,00	



(70) Boc-L-Nle-L-Pro-Val^P(OPh-4-SCH₃)₂

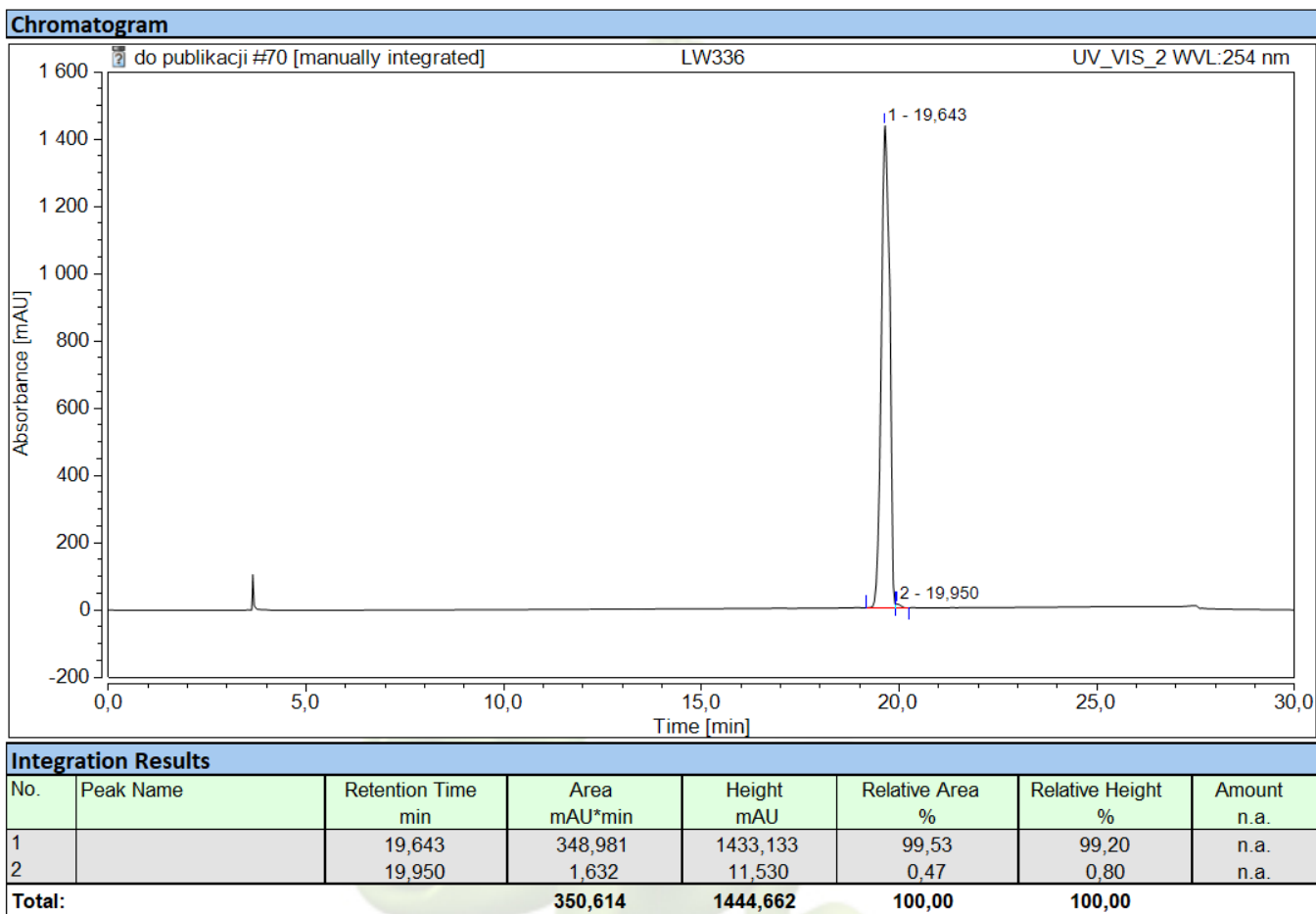
Name: *tert*-butyl ((2*S*)-1-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-1-oxohexan-2-yl)carbamate

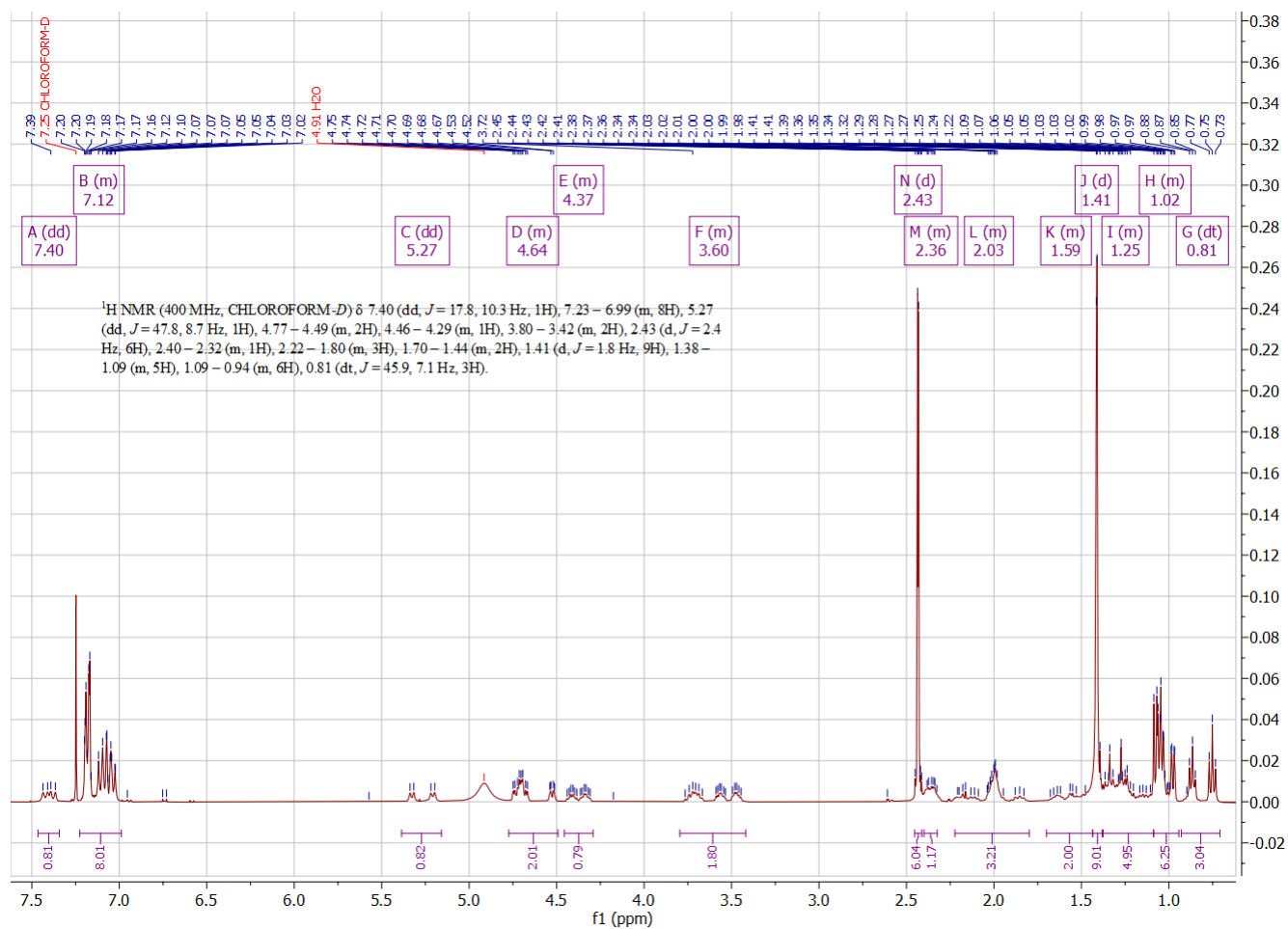
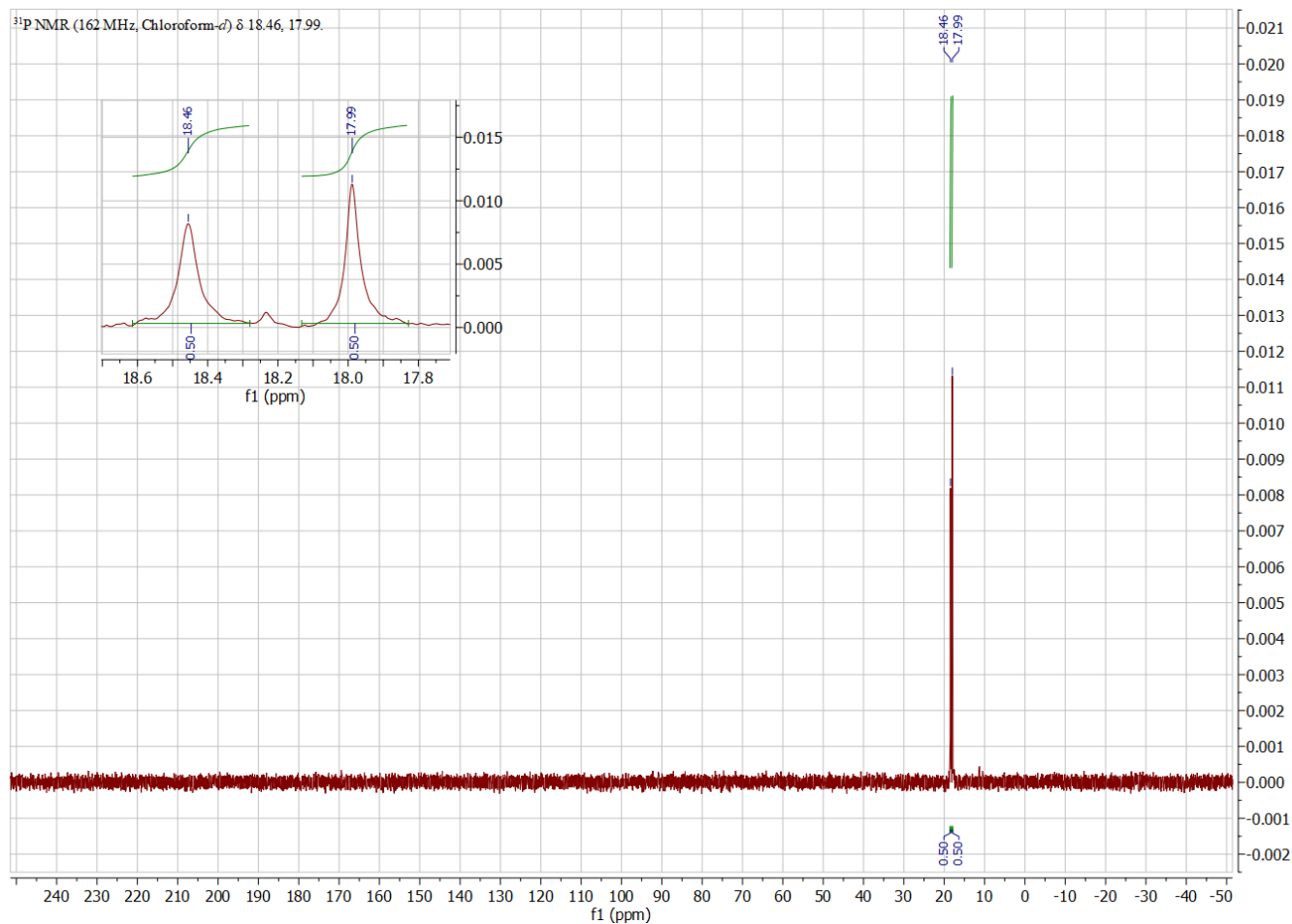
³¹P NMR (162 MHz, Chloroform-*d*) δ 18.46 (s, 50%), 17.99 (s, 50%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.40 (dd, *J* = 17.8, 10.3 Hz, 1H, NH), 7.23 – 6.99 (m, 8H, 8xArH), 5.27 (dd, *J* = 47.8, 8.7 Hz, 1H, NH), 4.77 – 4.49 (m, 2H, CHP, CH), 4.46 – 4.29 (m, 1H, CH), 3.80 – 3.42 (m, 2H, CH₂), 2.43 (d, *J* = 2.4 Hz, 6H, 2xSCH₃), 2.40 – 2.32 (m, 1H, CH), 2.22 – 1.80 (m, 3H, 1.5xCH₂), 1.70 – 1.44 (m, 2H, CH₂), 1.41 (d, *J* = 1.8 Hz, 9H, Boc), 1.38 – 1.09 (m, 5H, 2.5xCH₂), 1.09 – 0.94 (m, 6H, 2xCH₃), 0.81 (dt, *J* = 45.9, 7.1 Hz, 3H, CH₃).

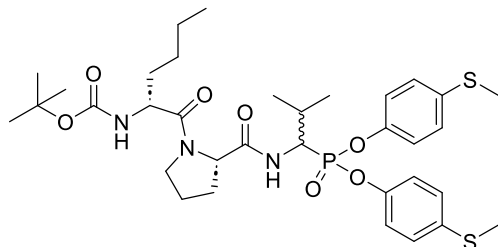
HRMS: C₃₄H₅₀N₃O₇PS₂ [M+Na]⁺ calc. 730.2725 found 730.2683

HPLC: purity >99%; retention time 19.643 min





(71) Boc-D-Nle-L-Pro-Val^P(OPh-4-SCH₃)₂



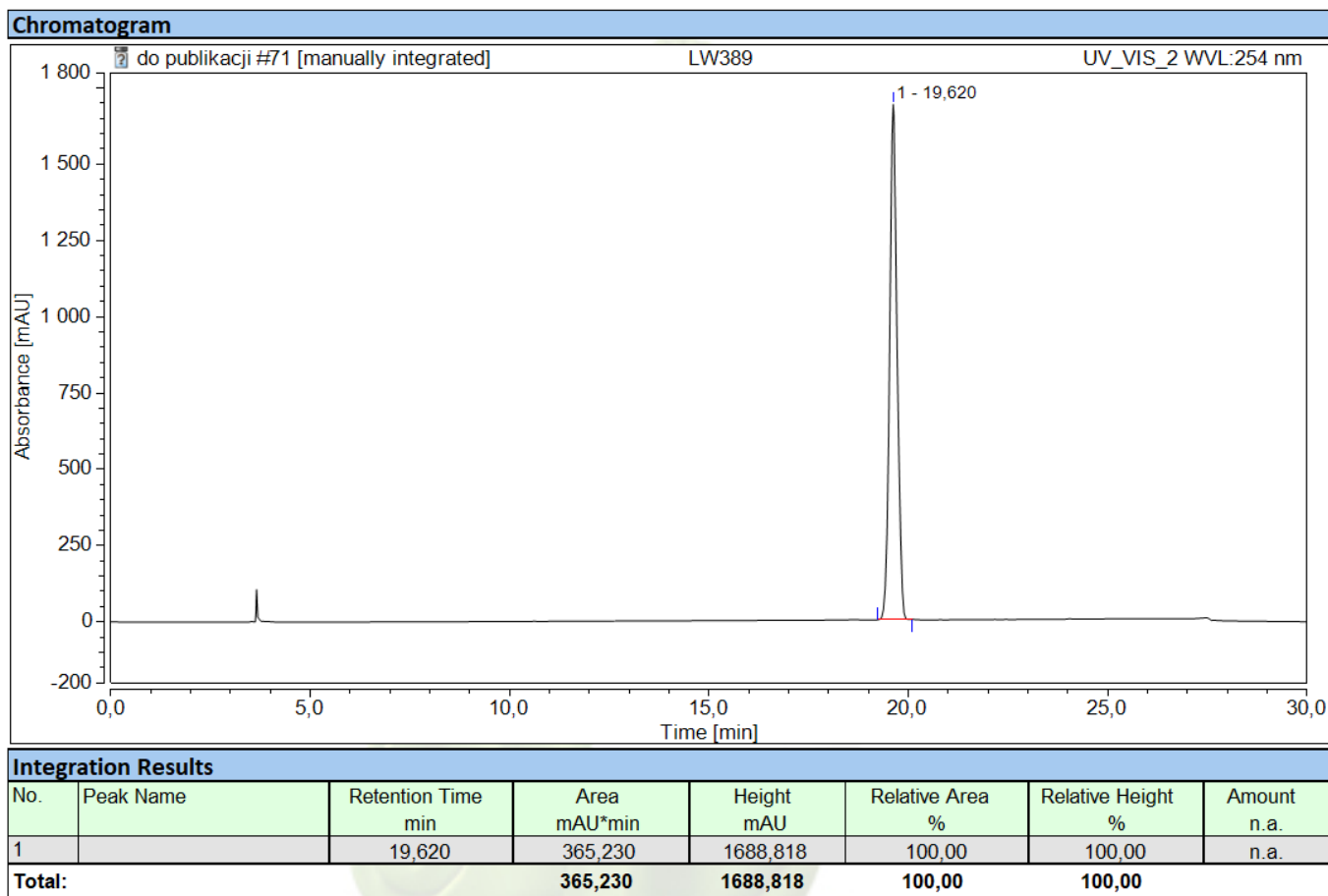
Name: *tert*-butyl ((2R)-1-((2S)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-1-oxohexan-2-yl)carbamate

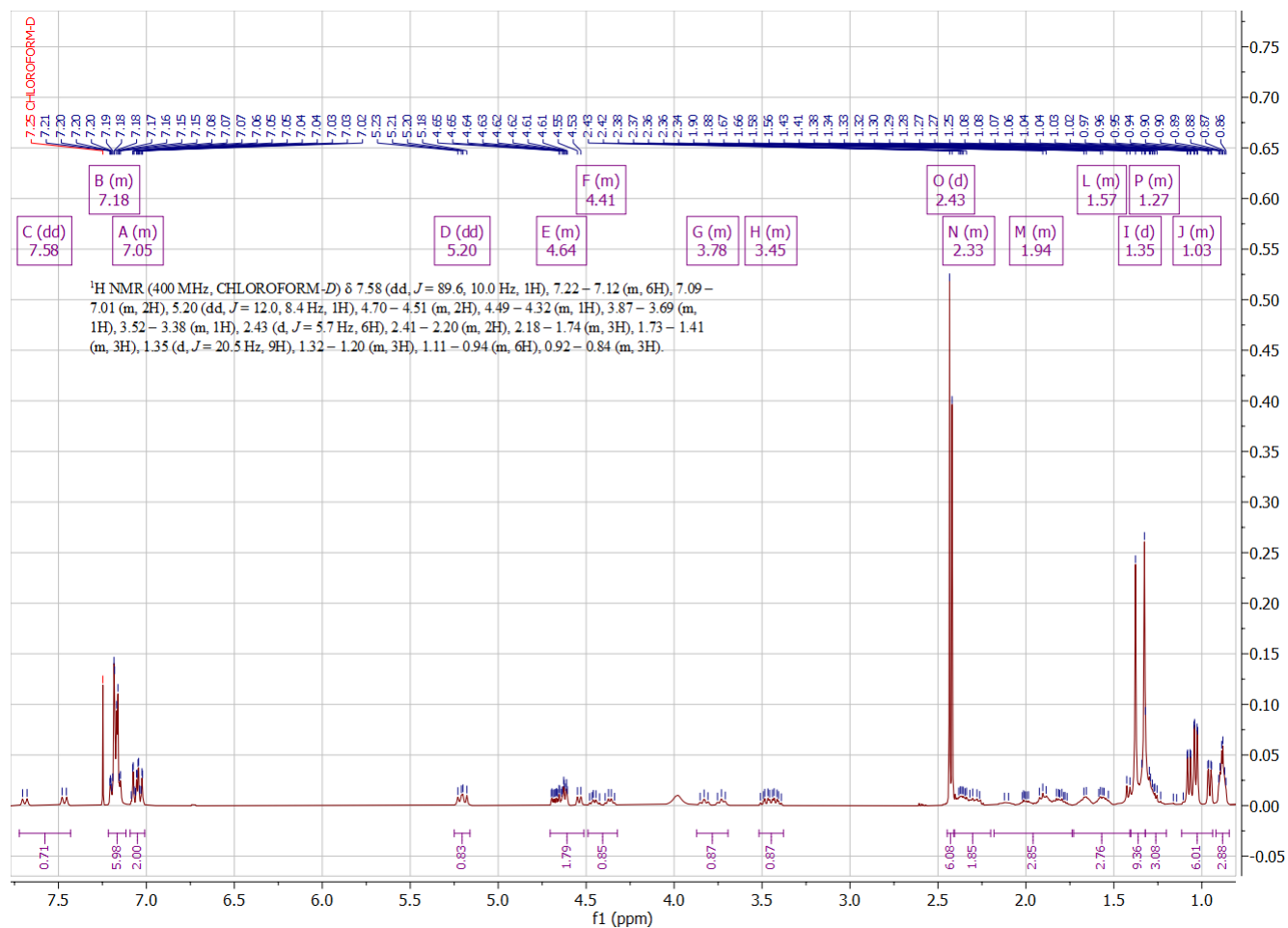
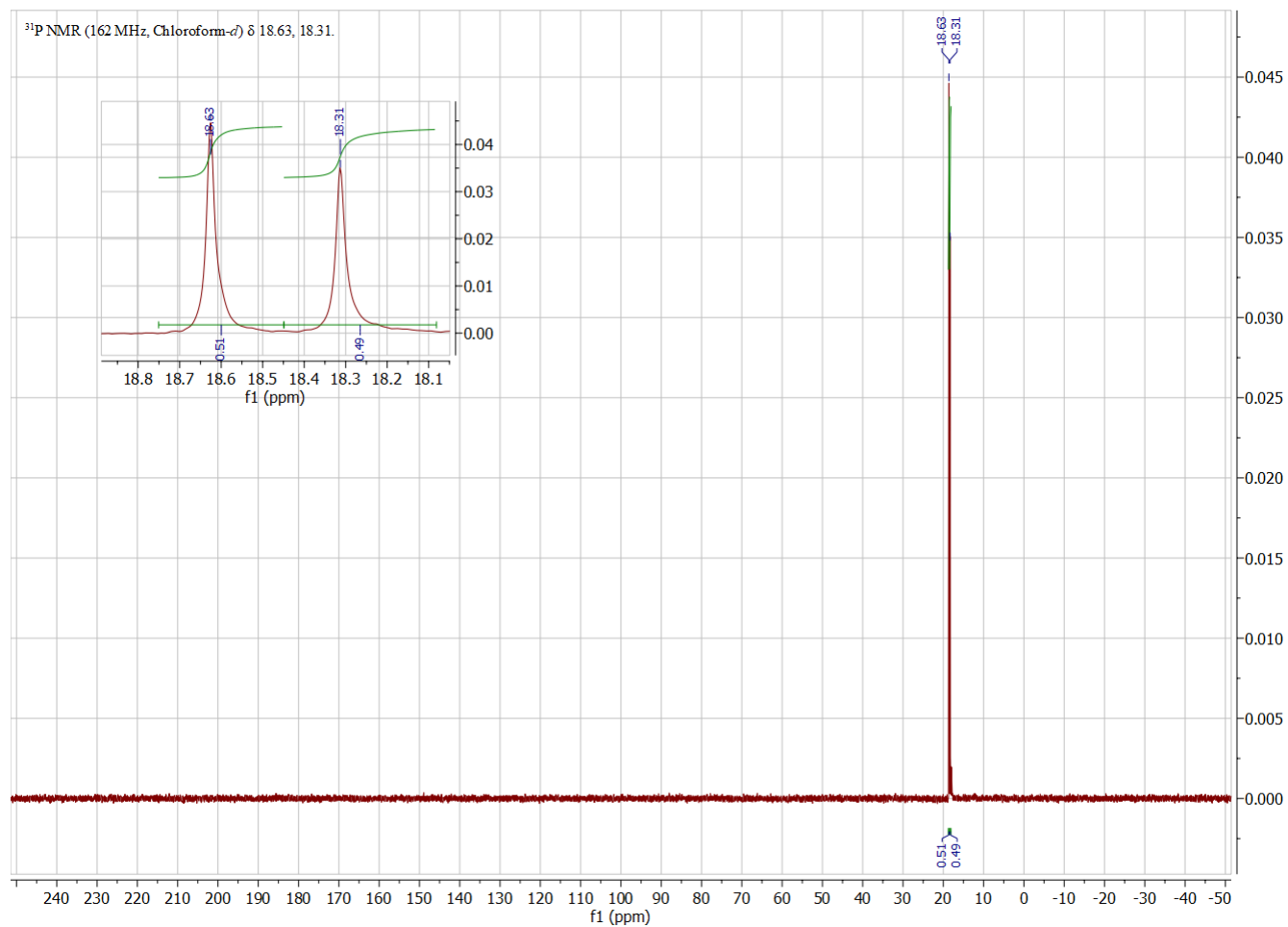
³¹P NMR (162 MHz, Chloroform-d) δ 18.63 (s, 51%), 18.31 (s, 49%).

¹H NMR (400 MHz, Chloroform-d) δ 7.58 (dd, J = 89.6, 10.0 Hz, 1H, NH), 7.22 – 7.12 (m, 6H, 6xArH), 7.09 – 7.01 (m, 2H, 2xArH), 5.20 (dd, J = 12.0, 8.4 Hz, 1H, NH), 4.70 – 4.51 (m, 2H, CHP, CH), 4.49 – 4.32 (m, 1H, CH), 3.87 – 3.69 (m, 1H, 0.5xCH₂), 3.52 – 3.38 (m, 1H, 0.5xCH₂), 2.43 (d, J = 5.7 Hz, 6H, 2xSCH₃), 2.41 – 2.20 (m, 2H, 0.5xCH₂, CH), 2.18 – 1.74 (m, 3H, 1.5xCH₂), 1.73 – 1.41 (m, 3H, 1.5xCH₂), 1.35 (d, J = 20.5 Hz, 9H, Boc), 1.32 – 1.20 (m, 3H, 1.5xCH₂), 1.11 – 0.94 (m, 6H, 2xCH₃), 0.92 – 0.84 (m, 3H, CH₃).

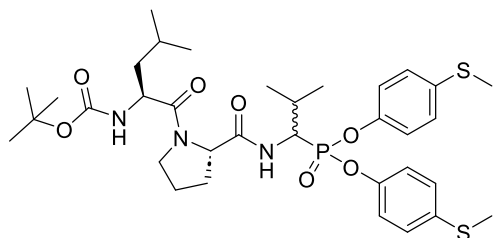
HRMS: C₃₄H₅₀N₃O₇PS₂ [M+Na]⁺ calc. 730.2725 found 730.2729

HPLC: purity >99%; retention time 19.620 min





(72) Boc-L-Leu-L-Pro- Val^P(OPh-4-SCH₃)₂



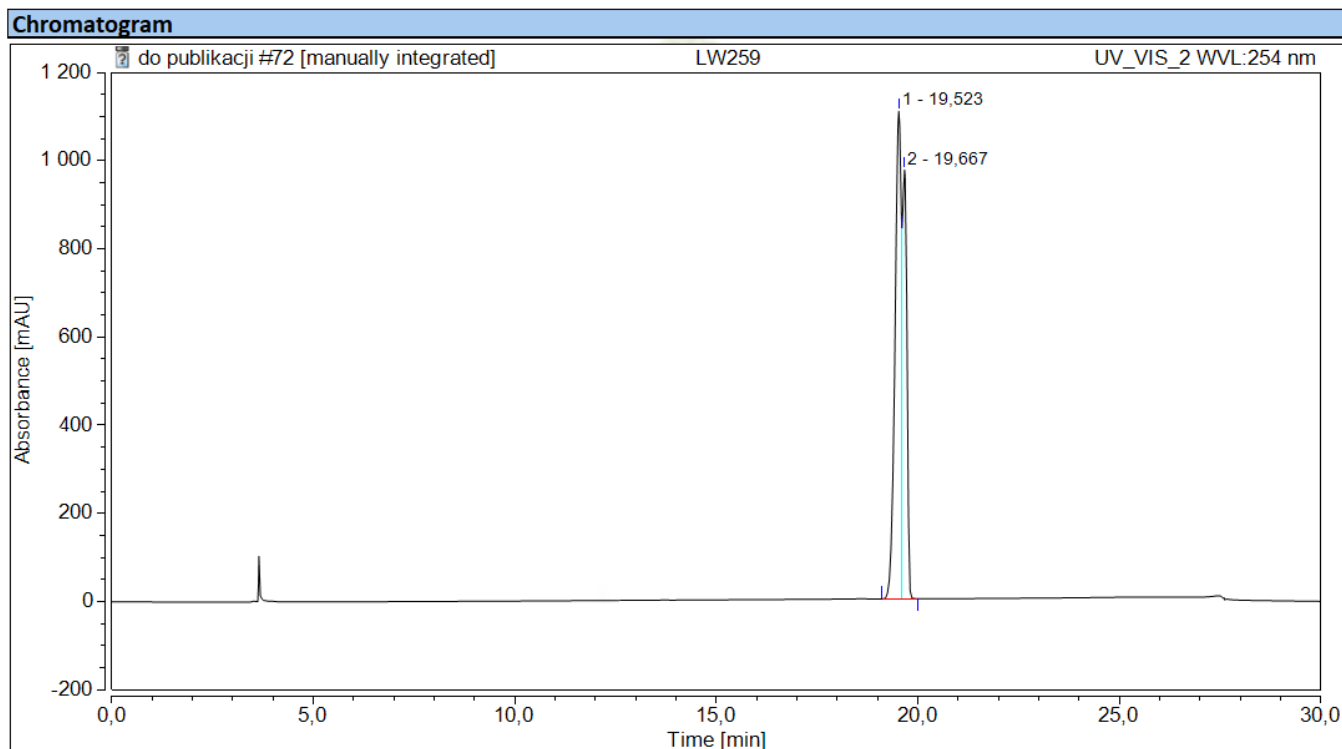
Name: *tert*-butyl ((2*S*)-1-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-4-methyl-1-oxopentan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.51 (s, 55%), 18.04 (s, 45%).

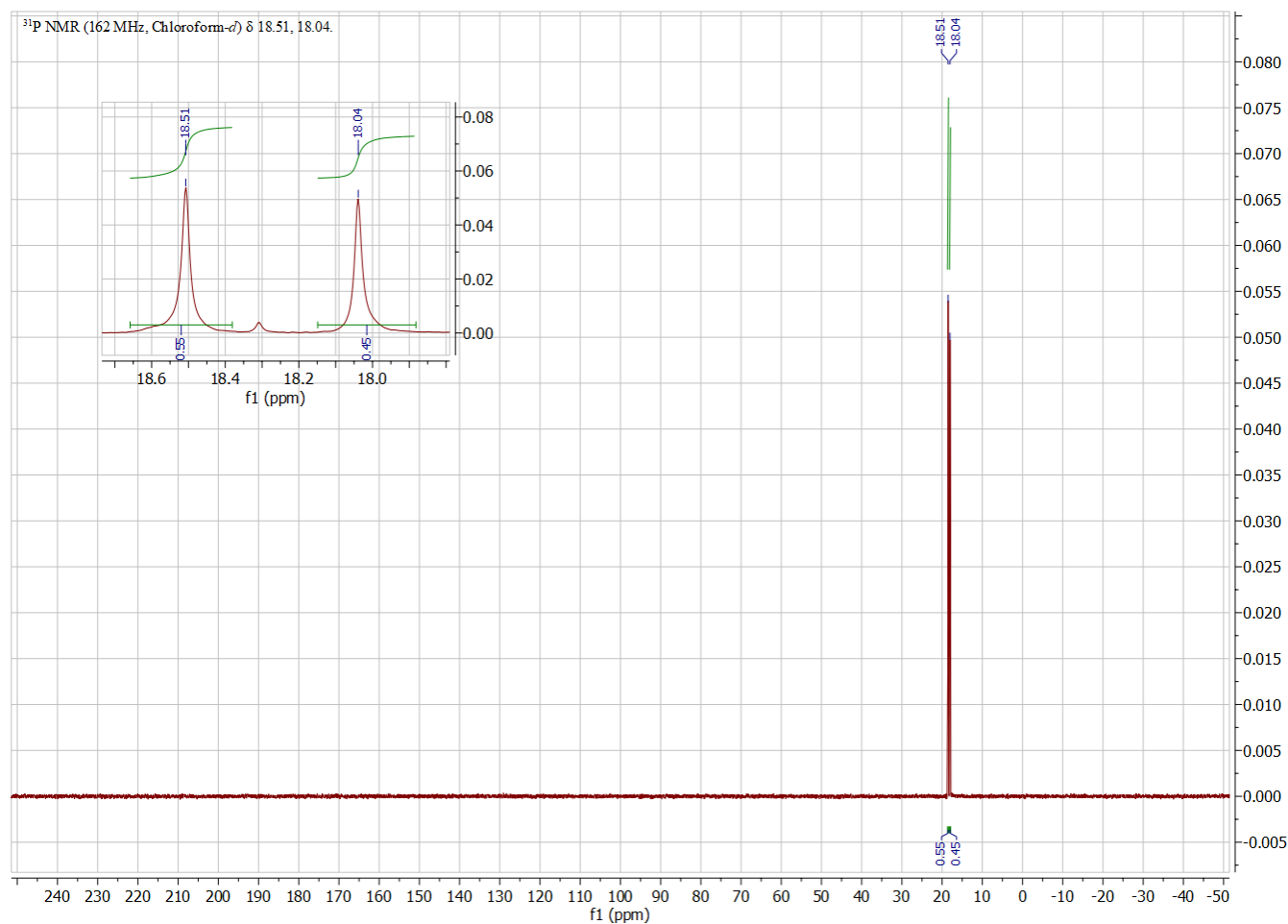
¹H NMR (400 MHz, Chloroform-*d*) δ 7.43 (dd, *J* = 36.3, 9.9 Hz, 1H, NH), 7.24 – 7.15 (m, 4H, 4xArH), 7.15 – 7.00 (m, 4H, 4xArH), 5.18 (dd, *J* = 49.4, 8.9 Hz, 1H, NH), 4.76 – 4.69 (m, 1H, CHP), 4.69 – 4.51 (m, 1H, CH), 4.51 – 4.36 (m, 1H, CH), 3.78 – 3.64 (m, 1H, 0.5xCH₂), 3.58 – 3.39 (m, 1H, 0.5xCH₂), 2.43 (d, *J* = 3.2 Hz, 6H, 2xSCH₃), 2.39 – 2.31 (m, 1H, CH), 2.26 – 2.04 (m, 1H, CH), 2.04 – 1.85 (m, 2H, CH₂), 1.85 – 1.45 (m, 2H, CH₂), 1.41 (d, *J* = 1.4 Hz, 9H, Boc), 1.36 – 1.11 (m, 2H, CH₂), 1.06 – 0.93 (m, 6H, 2xCH₃), 0.99 (dd, *J* = 68.2, 6.8 Hz, 3H, CH₃), 0.76 (dd, *J* = 58.0, 6.6 Hz, 3H, CH₃).

HRMS: C₃₄H₅₀N₃O₇PS₂ [M+Na]⁺ calc. 730.2725 found 730.2708

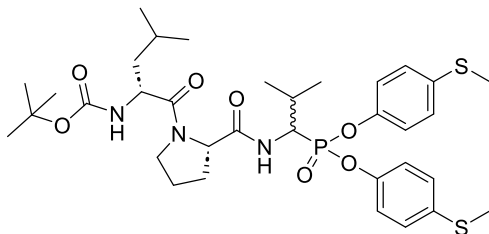
HPLC: purity >99%; retention time 19.523 and 19.667 min



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19,523	199,505	1106,050	61,21	53,20	n.a.
2		19,667	126,434	972,904	38,79	46,80	n.a.
Total:			325,939	2078,953	100,00	100,00	



(73) Boc-D-Leu-L-Pro-Val^F(OPh-4-SCH₃)₂



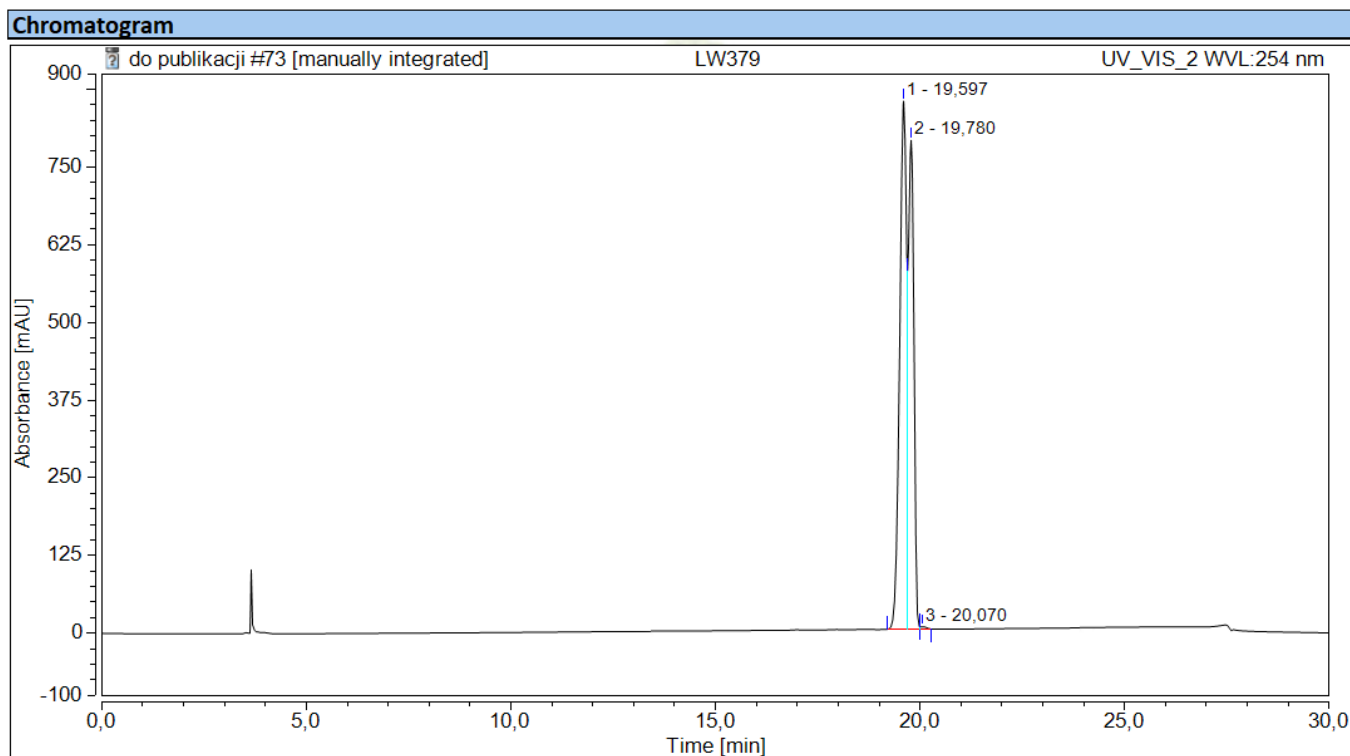
Name: *tert*-butyl ((2*R*)-1-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-4-methyl-1-oxopentan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.54 (s, 64%), 18.23 (s, 36%).

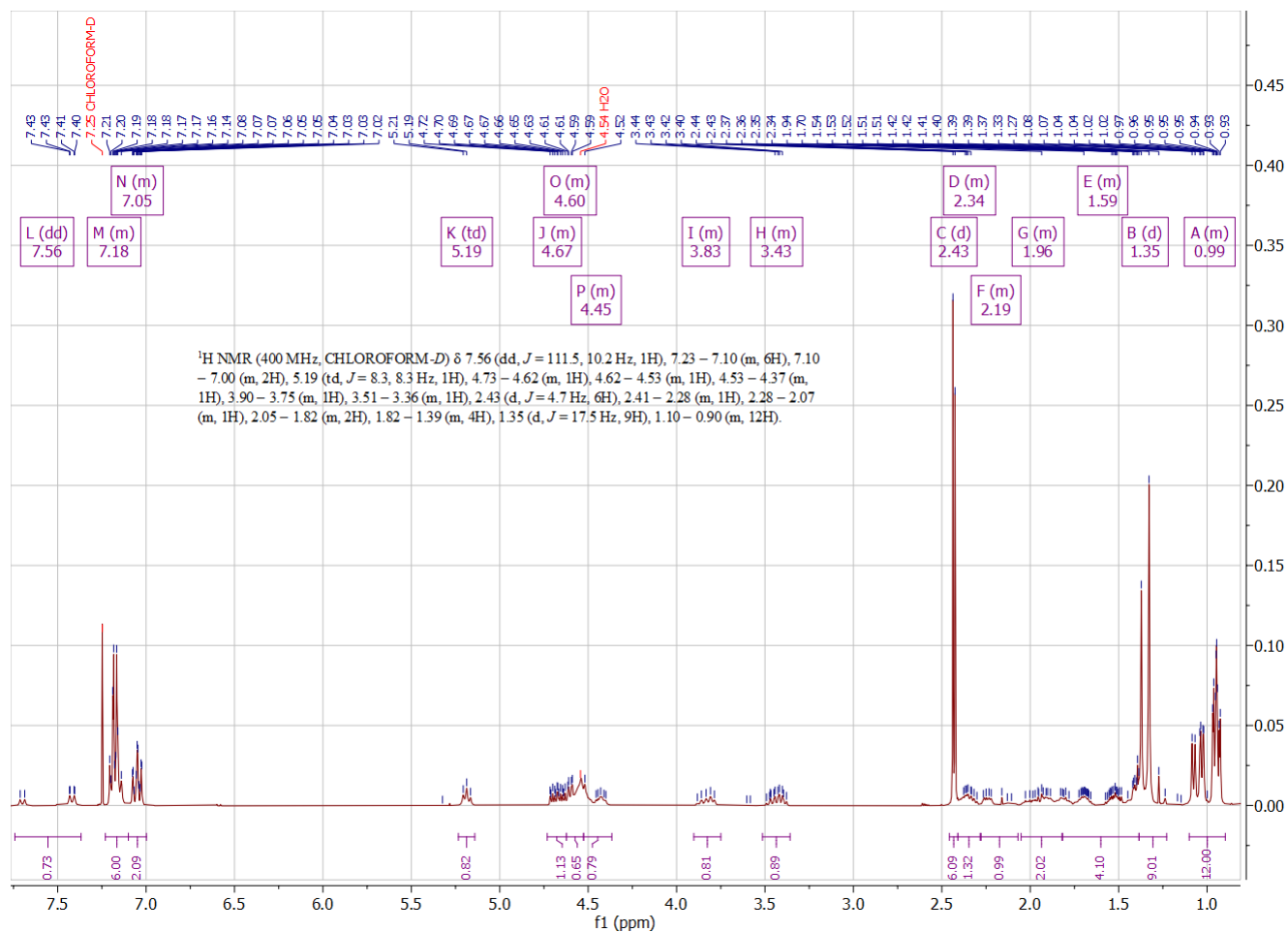
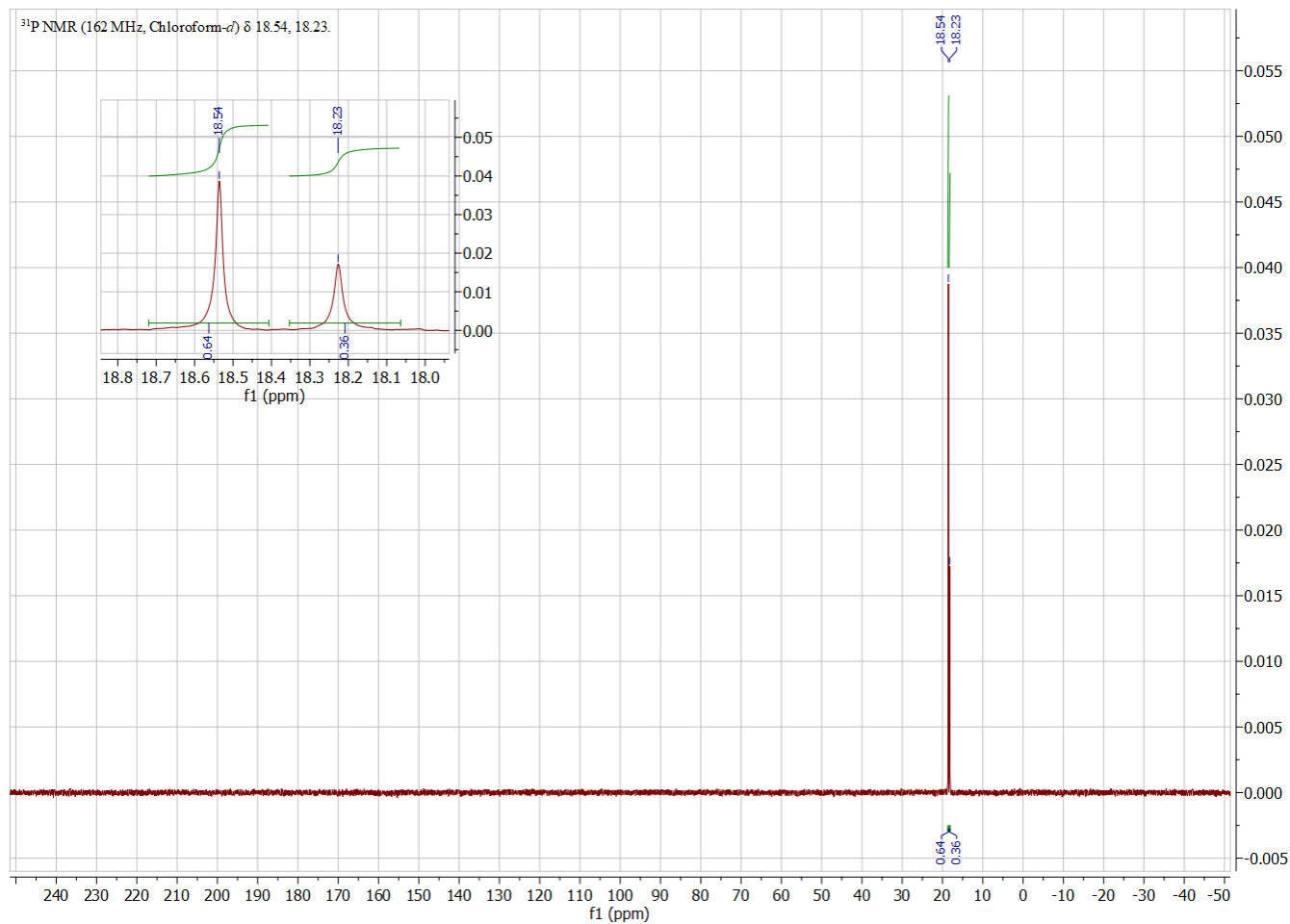
¹H NMR (400 MHz, Chloroform-*d*) δ 7.56 (dd, *J* = 111.5, 10.2 Hz, 1H, NH), 7.23 – 7.10 (m, 6H, 6xArH), 7.10 – 7.00 (m, 2H, 2xArH), 5.19 (td, *J* = 8.3, 8.3 Hz, 1H, NH), 4.73 – 4.62 (m, 1H, CHP), 4.62 – 4.53 (m, 1H, CH), 4.53 – 4.37 (m, 1H, CH), 3.90 – 3.75 (m, 1H, 0.5xCH₂), 3.51 – 3.36 (m, 1H, 0.5xCH₂), 2.43 (d, *J* = 4.7 Hz, 6H, 2xSCH₃), 2.41 – 2.28 (m, 1H, CH), 2.28 – 2.07 (m, 1H, CH), 2.05 – 1.82 (m, 2H, 2xCH₂), 1.82 – 1.39 (m, 4H, 2xCH₂), 1.35 (d, *J* = 17.5 Hz, 9H, Boc), 1.10 – 0.90 (m, 12H, 4xCH₃).

HRMS: C₃₄H₅₀N₃O₇PS₂ [M+Na]⁺ calc. 730.2725 found 730.2708

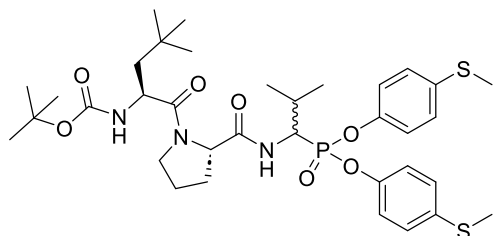
HPLC: purity >99%; retention time 19.597 and 19.780 min



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19,597	164,217	849,469	56,93	51,81	n.a.
2		19,780	123,581	786,363	42,84	47,96	n.a.
3		20,070	0,679	3,862	0,24	0,24	n.a.
Total:			288,476	1639,694	100,00	100,00	



(74) Boc-L-NptGly-L-Pro-Val^P(OPh-4-SCH₃)₂



Name: *tert*-butyl ((2*S*)-1-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-4,4-dimethyl-1-oxopentan-2-yl)carbamate

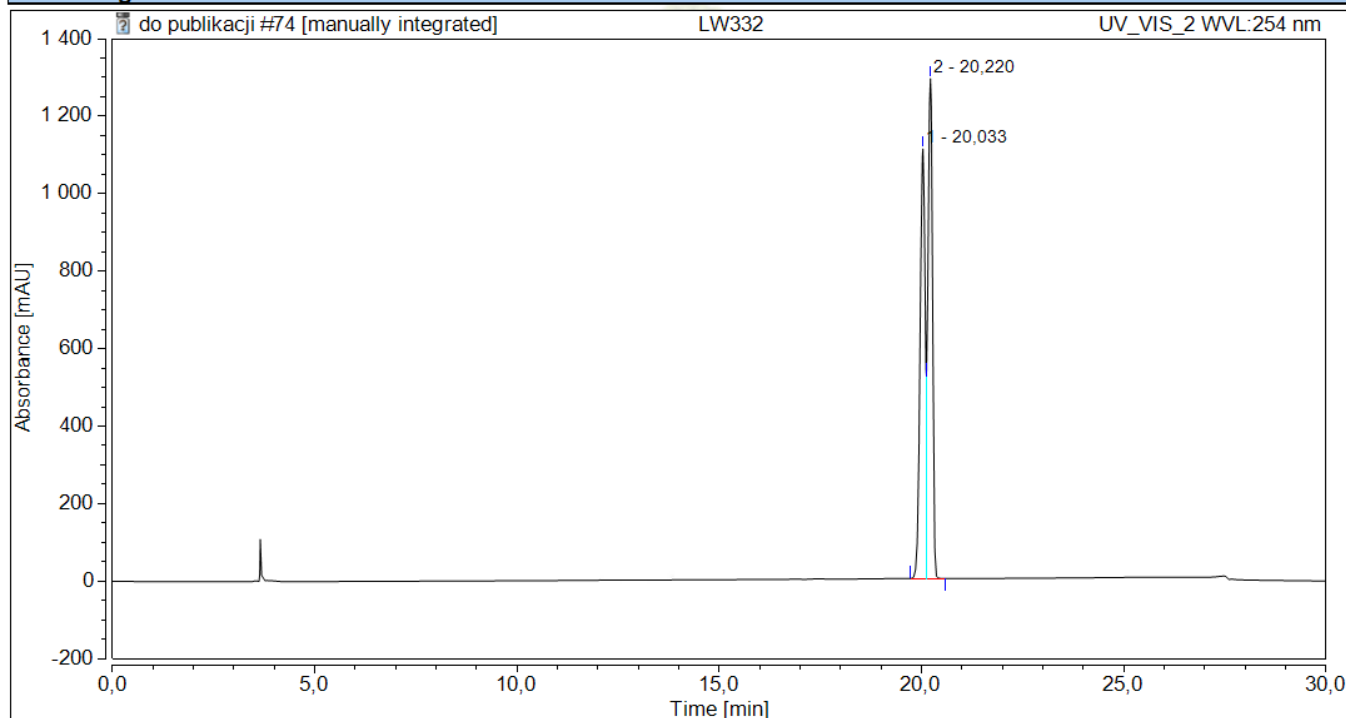
³¹P NMR (162 MHz, Chloroform-*d*) δ 18.56 (s, 55%), 18.00 (s, 45%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 (dd, *J* = 60.7, 10.2 Hz, 1H, NH), 7.23 – 7.15 (m, 4H, 4xArH), 7.15 – 7.09 (m, 2H, 2xArH), 7.09 – 6.99 (m, 2H, 2xArH), 5.18 (dd, *J* = 52.7, 9.1 Hz, 1H, NH), 4.76 – 4.62 (m, 2H, CHP, CH), 4.58 – 4.41 (m, 1H, CH), 3.78 – 3.67 (m, 1H, 0.5xCH₂), 3.58 – 3.42 (m, 1H, 0.5xCH₂), 2.43 (d, *J* = 3.7 Hz, 6H, 2xSCH₃), 2.42 – 2.30 (m, 2H, 0.5xCH₂, CH), 2.21 – 1.80 (m, 3H, 1.5xCH₂), 1.40 (s, 9H, Boc), 1.35 – 1.22 (m, 2H, CH₂), 1.11 – 0.98 (m, 6H, 2xCH₃), 0.89 (d, *J* = 65.0 Hz, 9H, 3xCH₃)

HRMS: C₃₅H₅₂N₃O₇PS₂ [M+Na]⁺ calc. 744.2882 found 744.2855

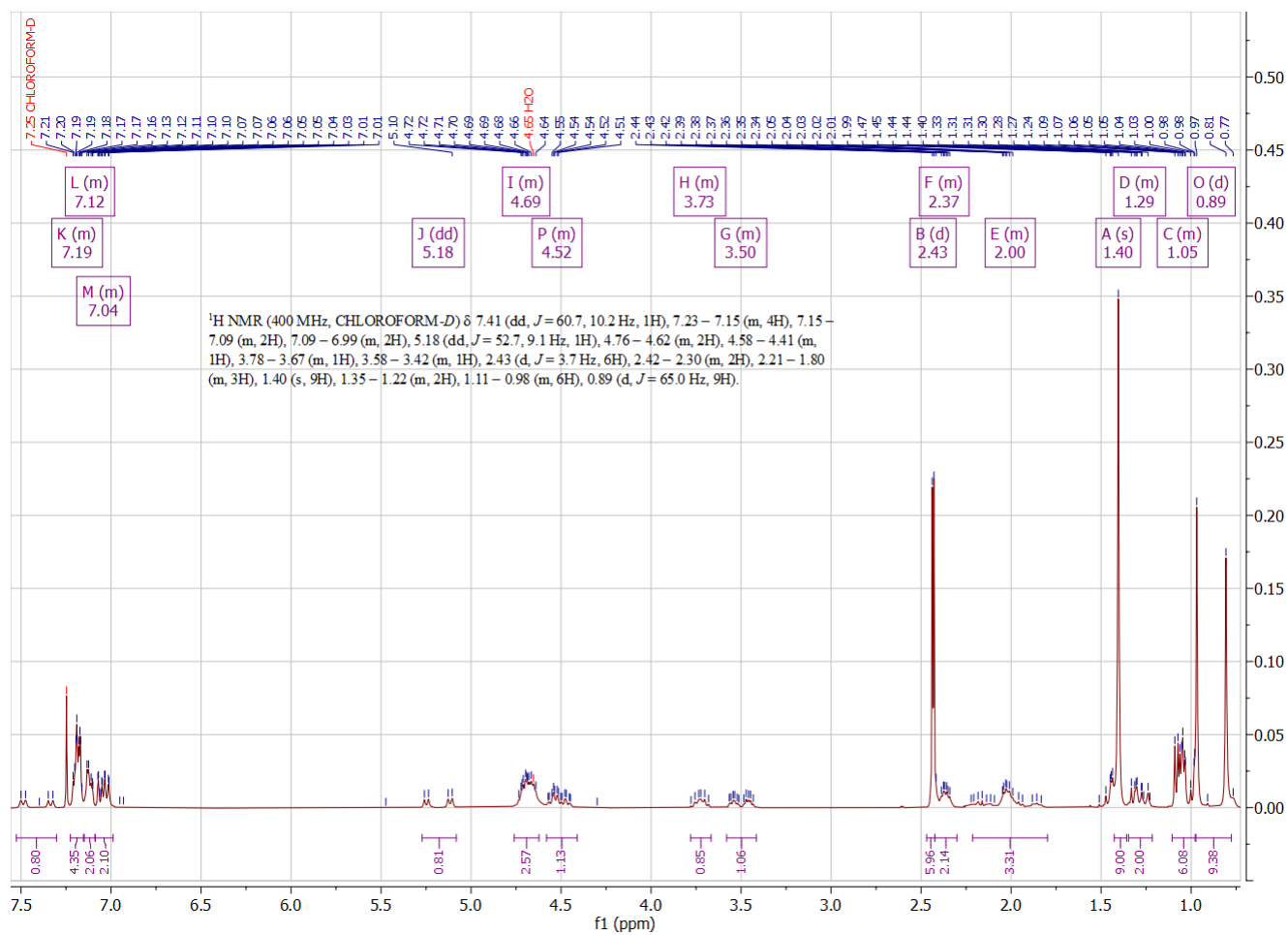
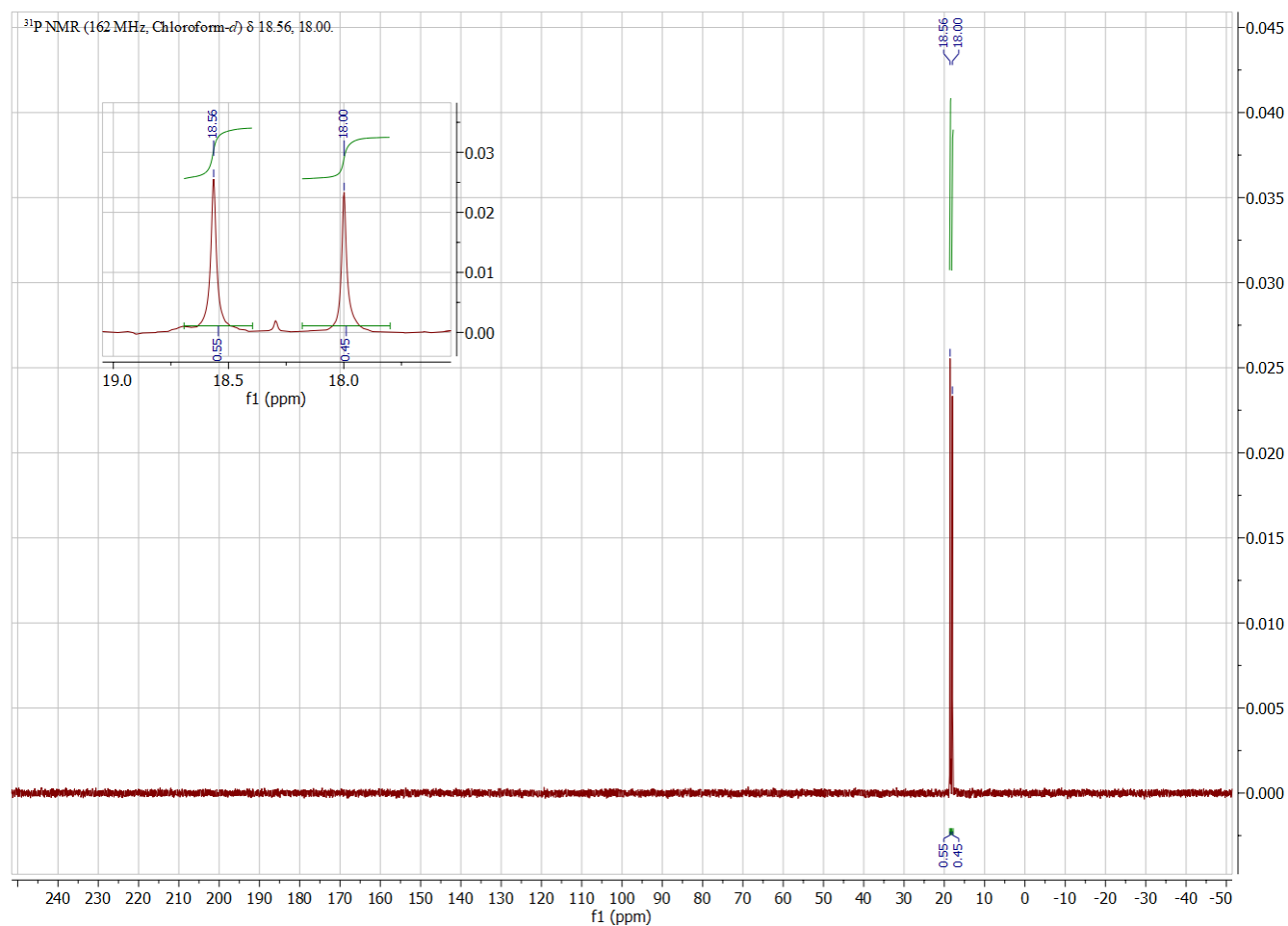
HPLC: purity >99%; retention time 20.033 and 20.220 min

Chromatogram

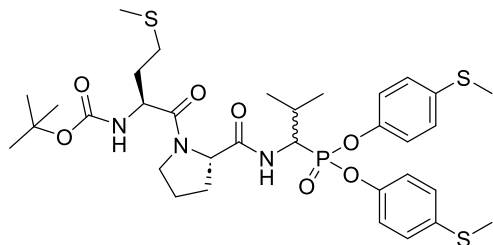


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20,033	160,914	1108,590	48,31	46,22	n.a.
2		20,220	172,163	1290,159	51,69	53,78	n.a.
Total:			333,077	2398,750	100,00	100,00	



(75) Boc-L-Met-L-Pro- Val^P(OPh-4-SCH₃)₂



Name: *tert*-butyl ((2*S*)-1-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-4-(methylthio)-1-oxobutan-2-yl)carbamate

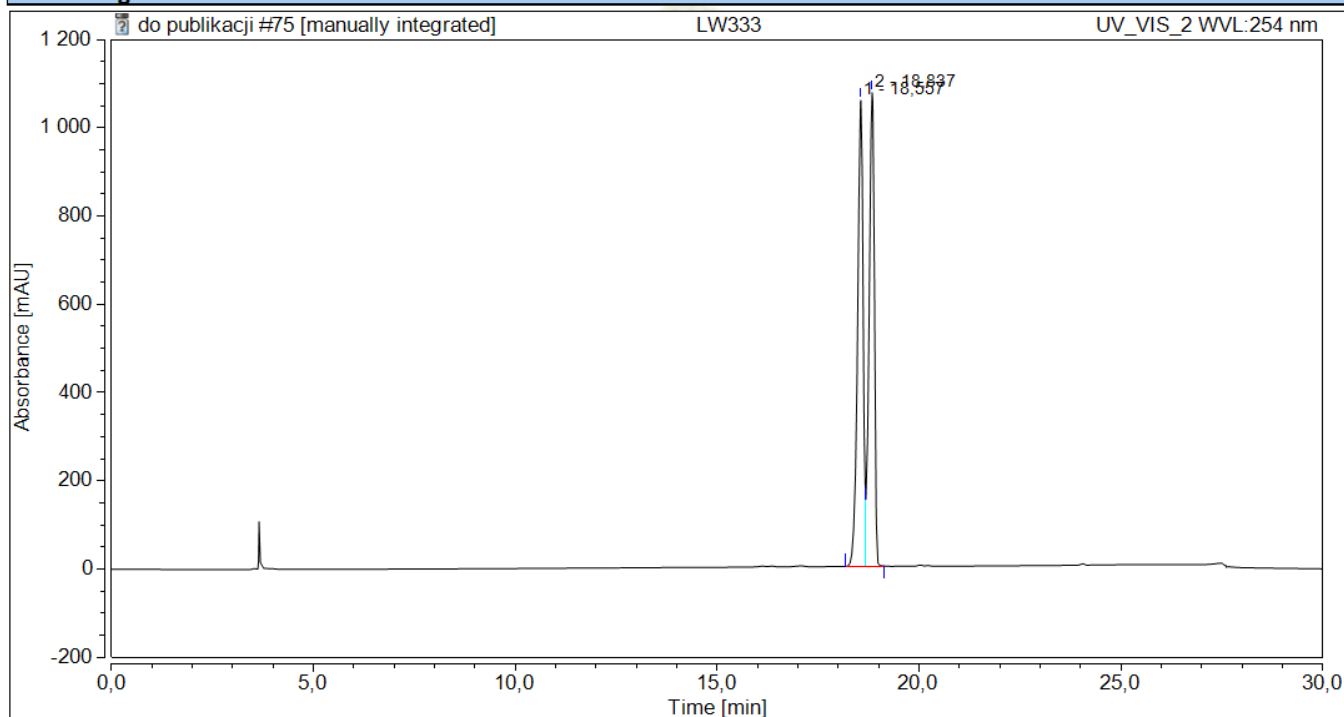
³¹P NMR (162 MHz, Chloroform-*d*) δ 18.46 (s, 53%), 17.96 (s, 47%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.33 (dd, *J* = 90.0, 10.0 Hz, 1H, NH), 7.21 – 7.00 (m, 8H, 8xArH), 5.33 (dd, *J* = 45.1, 8.8 Hz, 1H, NH), 4.77 – 4.45 (m, 3H, CHP, 2xCH), 3.81 – 3.51 (m, 2H, CH₂), 2.62 – 2.49 (m, 1H, CH), 2.46 – 2.43 (m, 6H, 2xSCH₃), 2.43 – 2.29 (m, 2H, CH₂), 2.19 – 1.62 (m, 8H, CH₃, 2.5xCH₂), 1.50 – 1.31 (m, 9H, Boc), 1.31 – 1.22 (m, 1H, 0.5xCH₂), 1.11 – 0.96 (m, 6H, 2xCH₃).

HRMS: C₃₃H₄₈N₃O₇PS₃ [M+Na]⁺ calc. 748.2290 found 748.2264

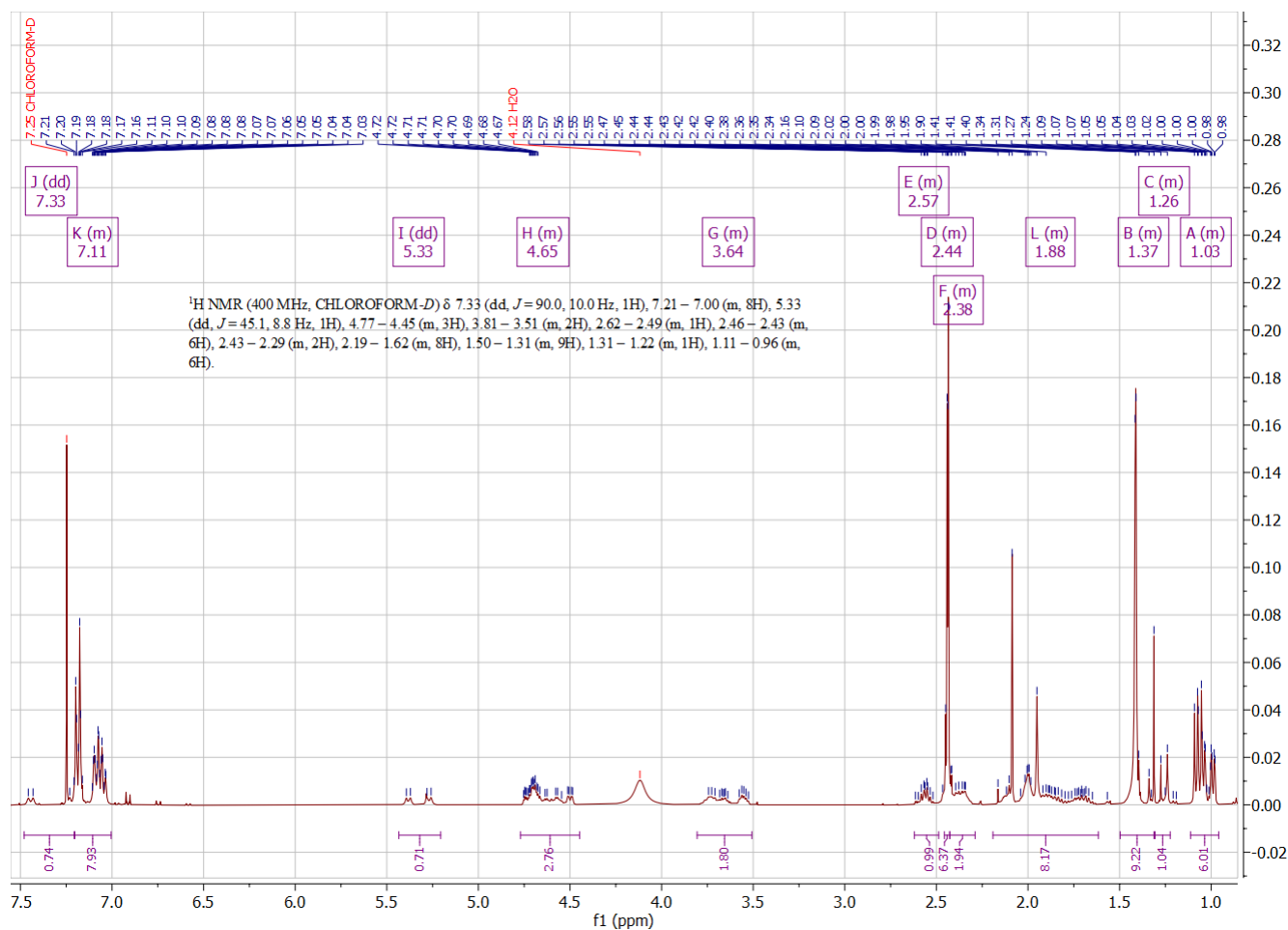
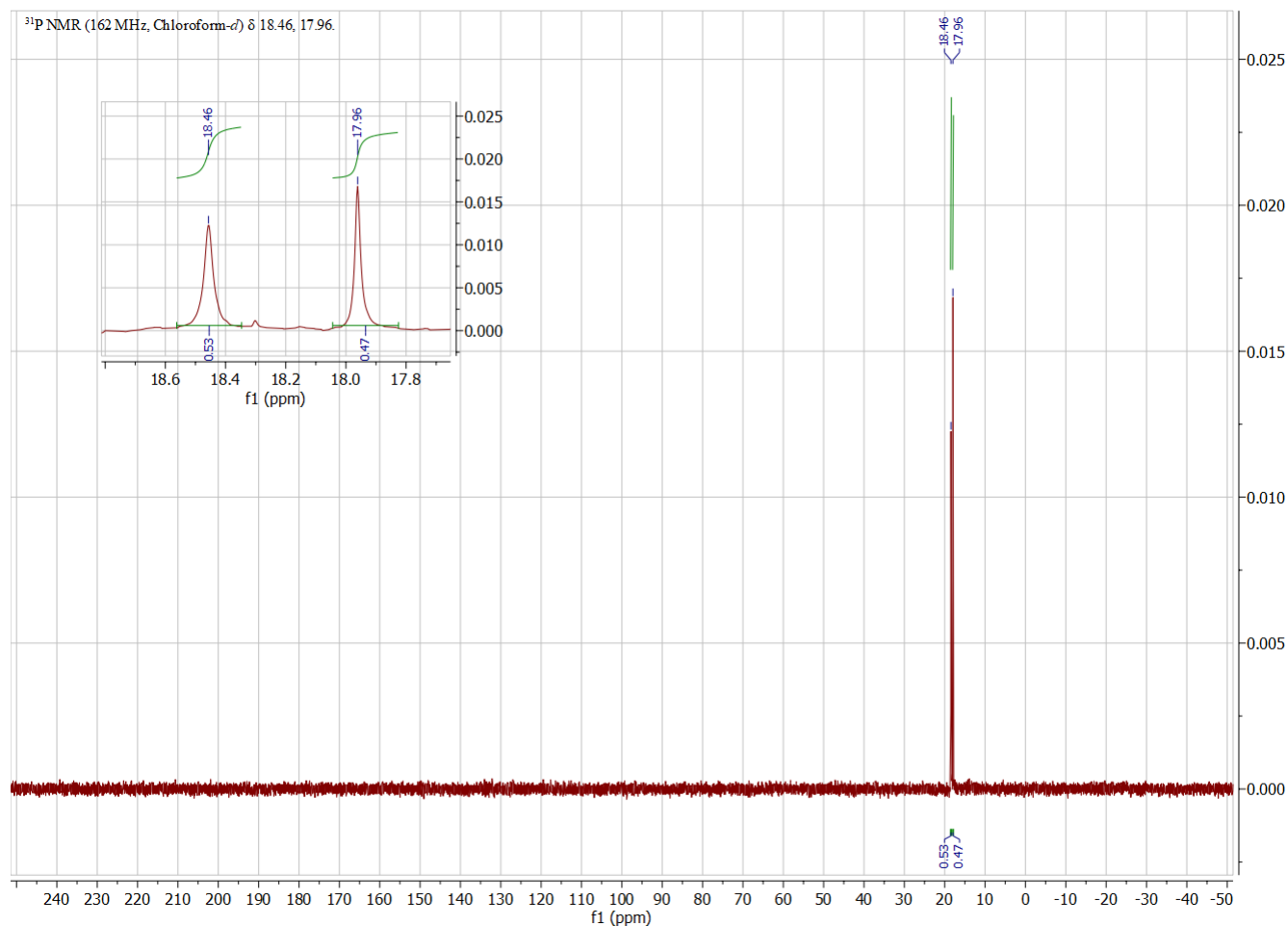
HPLC: purity >99%; retention time 18.557 and 18.837 min

Chromatogram

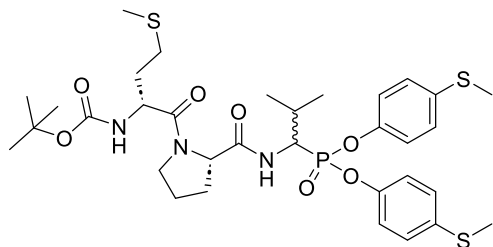


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18,557	167,954	1055,893	50,88	49,59	n.a.
2		18,837	162,154	1073,161	49,12	50,41	n.a.
Total:			330,108	2129,054	100,00	100,00	



(76) Boc-D-Met-L-Pro-Val^P(OPh-4-SCH₃)₂



Name: *tert*-butyl ((2*R*)-1-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-4-(methylthio)-1-oxobutan-2-yl)carbamate

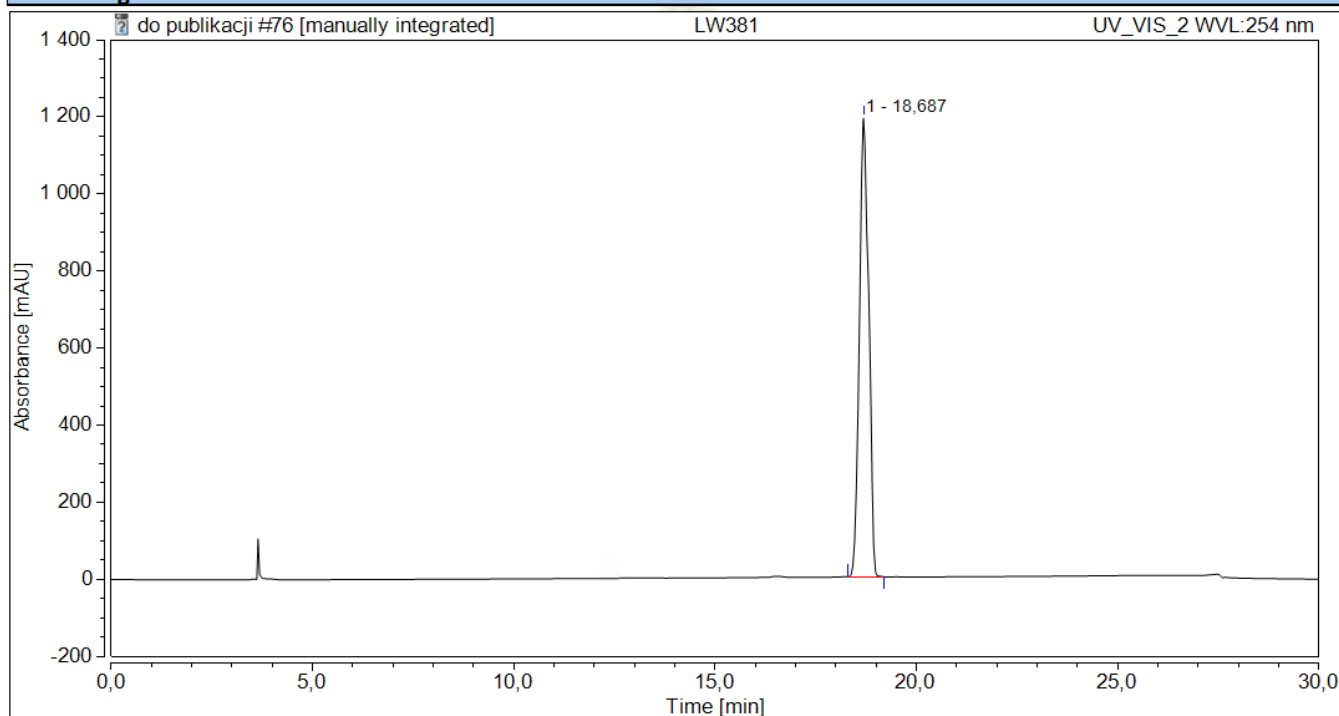
³¹P NMR (162 MHz, Chloroform-*d*) δ 18.46 (s, 59%), 18.15 (s, 41%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.53 (dd, *J* = 39.7, 10.0 Hz, 1H, NH), 7.22 – 7.10 (m, 6H, 6xArH), 7.10 – 7.00 (m, 2H, 2xArH), 5.35 (dd, *J* = 30.3, 8.5 Hz, 1H, NH), 4.73 – 4.59 (m, 2H, CHP, CH), 4.59 – 4.49 (m, 1H, CH), 3.89 – 3.68 (m, 1H, 0.5xCH₂), 3.66 – 3.46 (m, 1H, 0.5xCH₂), 2.59 – 2.50 (m, 2H, CH₂), 2.43 (d, *J* = 3.7 Hz, 6H, 2xSCH₃), 2.41 – 2.21 (m, 2H, 0.5xCH₂, CH), 2.09 (d, *J* = 3.1 Hz, 3H, CH₃), 2.04 – 1.77 (m, 5H, 2.5xCH₂), 1.36 (d, *J* = 19.1 Hz, 9H, Boc), 1.10 – 0.94 (m, 6H, 2xCH₃).

HRMS: C₃₃H₄₈N₃O₇PS₃ [M+Na]⁺ calc. 748.2290 found 748.2278

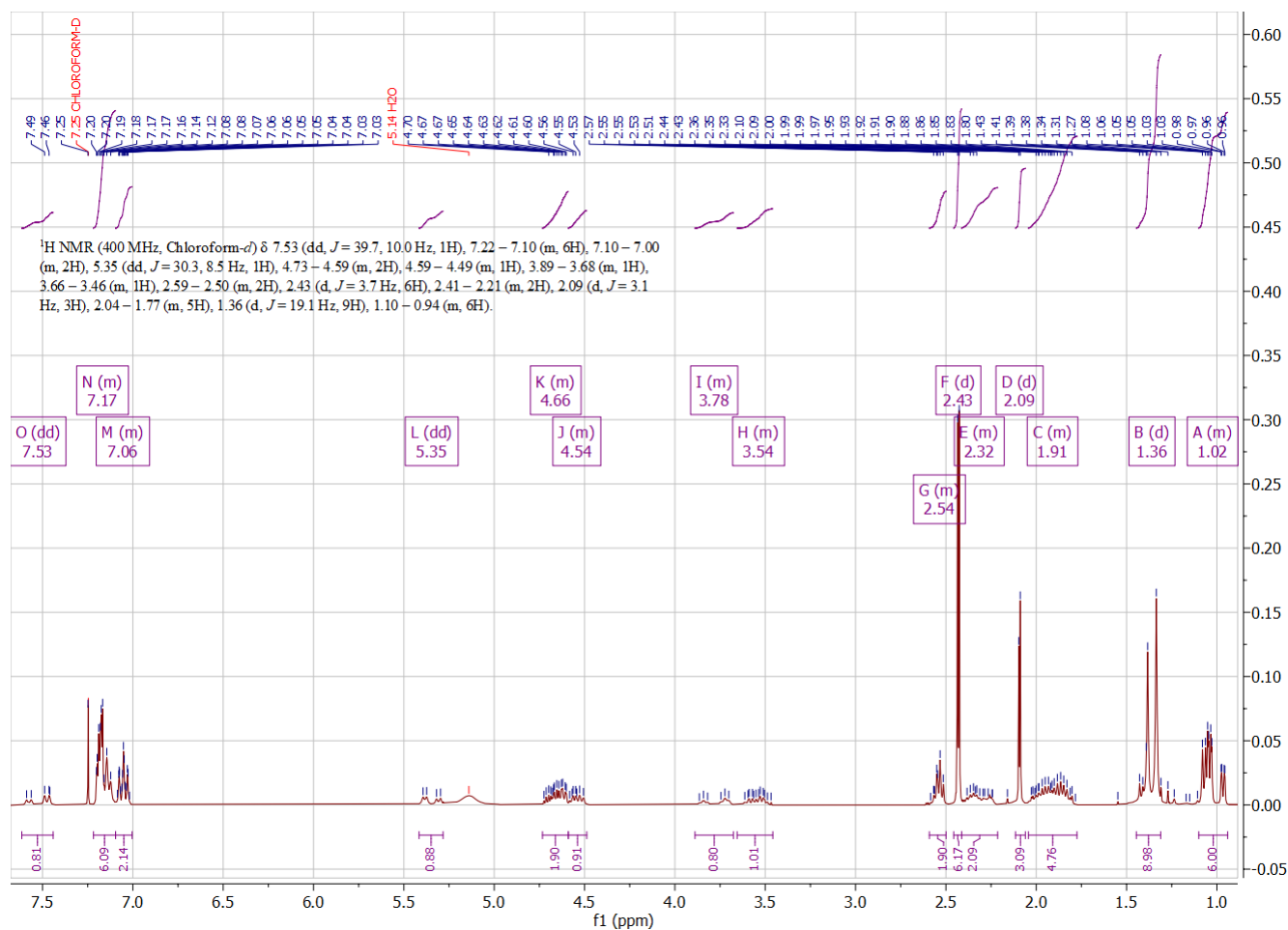
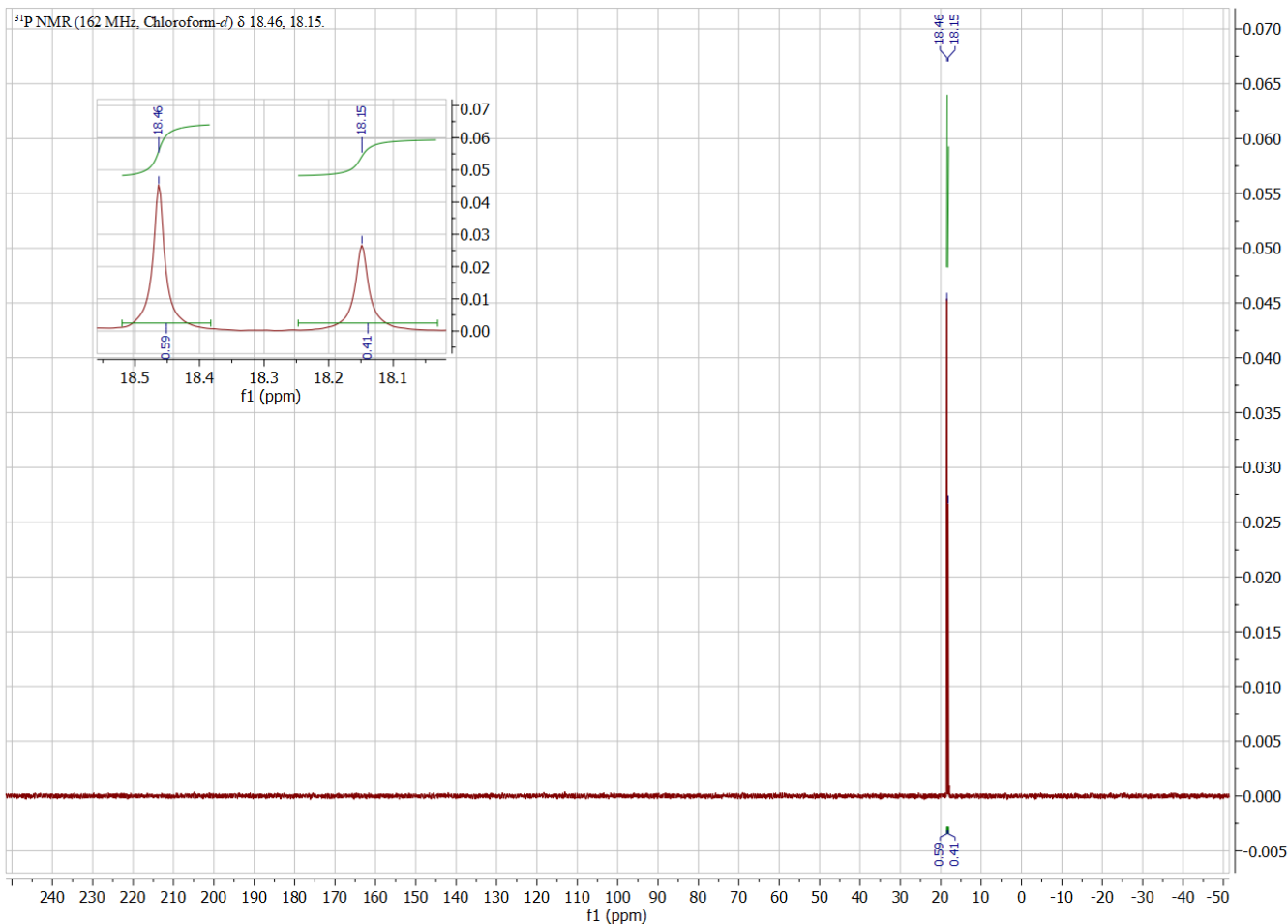
HPLC: purity >99%; retention time 18.687 min

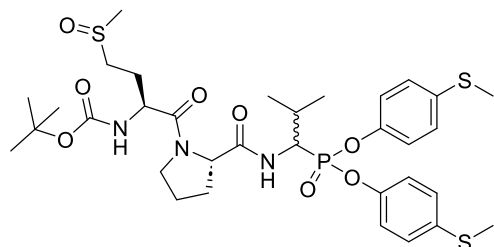
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18,687	319,783	1190,076	100,00	100,00	n.a.
Total:			319,783	1190,076	100,00	100,00	



(77) Boc-L-Met(O)-L-Pro-Val^P(OPh-4-SCH₃)₂

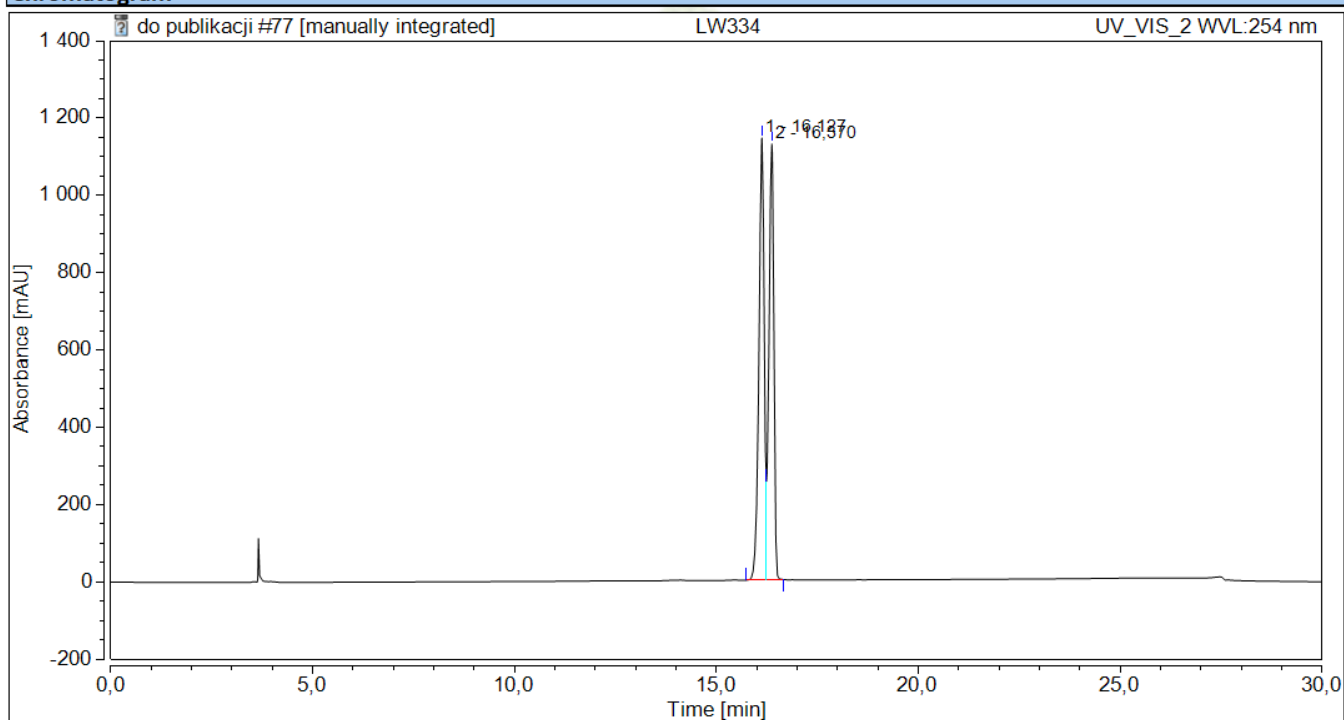
Name: *tert*-butyl ((2*S*)-1-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-4-(methylsulfinyl)-1-oxobutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.37 (s, 27%), 18.16 (s, 19%), 17.94 (d, *J* = 2.2 Hz, 52%).

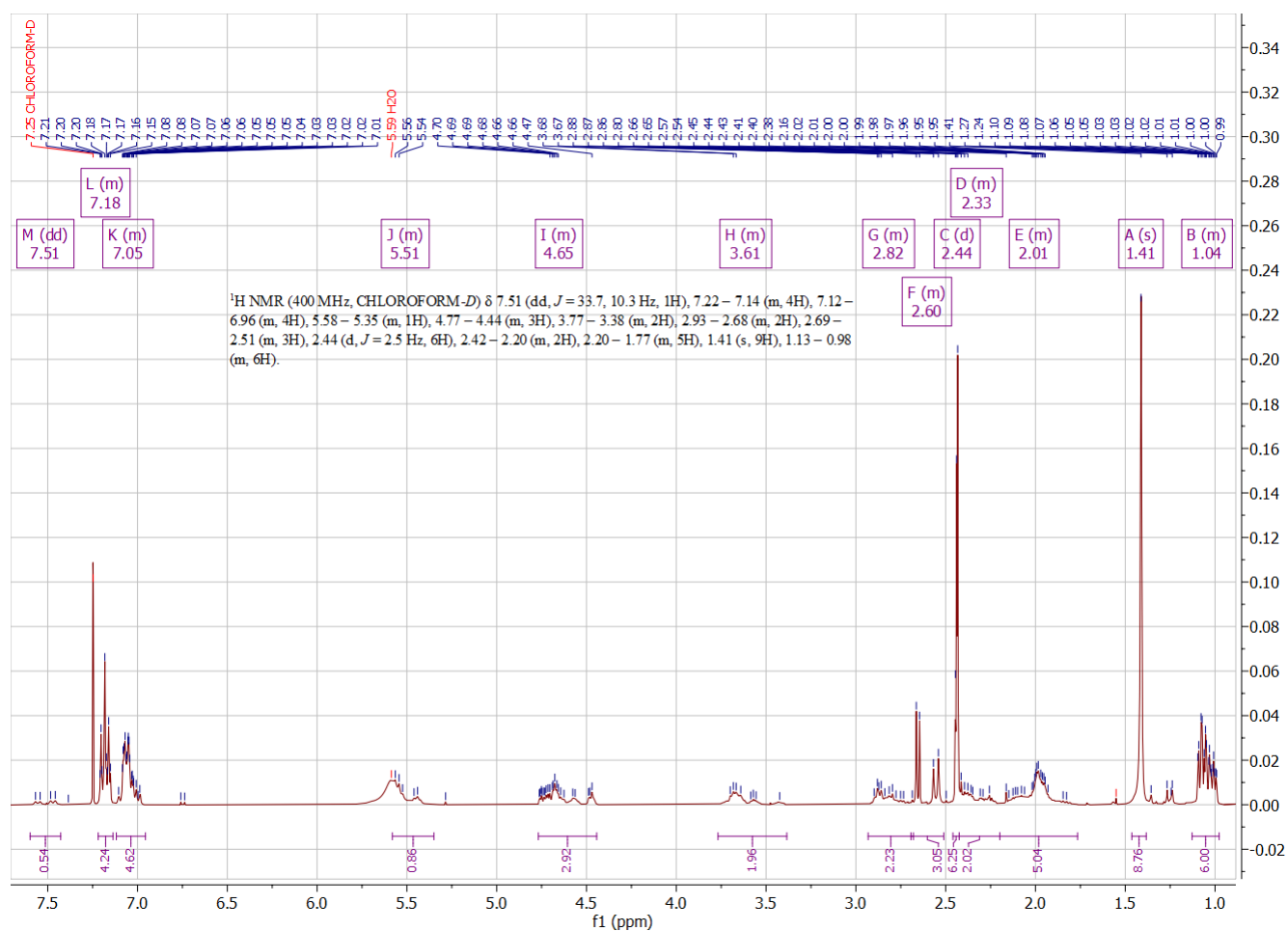
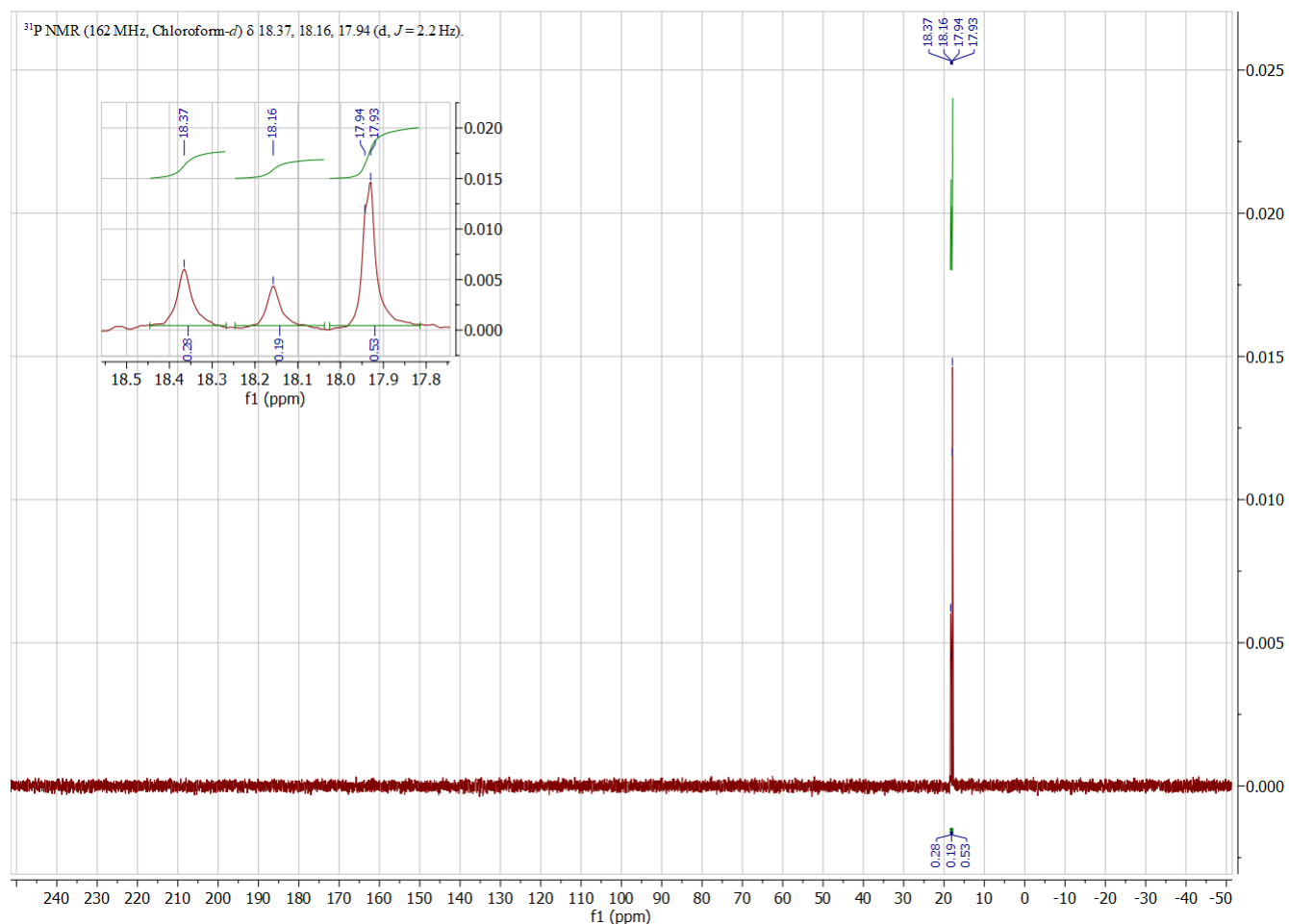
¹H NMR (400 MHz, Chloroform-*d*) δ 7.51 (dd, *J* = 33.7, 10.3 Hz, 1H, NH), 7.22 – 7.14 (m, 4H, 4xArH), 7.12 – 6.96 (m, 4H, 4xArH), 5.58 – 5.35 (m, 1H, NH), 4.77 – 4.44 (m, 3H, CHP, 2xCH), 3.77 – 3.38 (m, 2H, CH₂), 2.93 – 2.68 (m, 2H, CH₂), 2.69 – 2.51 (m, 3H, CH₃), 2.44 (d, *J* = 2.5 Hz, 6H, 2xSCH₃), 2.42 – 2.20 (m, 2H, 0.5xCH₂, CH), 2.20 – 1.77 (m, 5H, 2.5xCH₂), 1.41 (s, 9H, Boc), 1.13 – 0.98 (m, 6H, 2xCH₃).

HRMS: C₃₃H₄₈N₃O₈PS₃ [M+Na]⁺ calc. 764.2239 found 764.2211

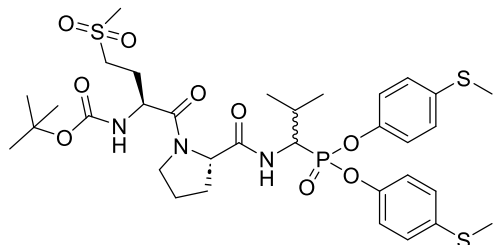
HPLC: purity >99%; retention time 16.127 and 16.370 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16,127	173,711	1143,549	52,21	50,35	n.a.
2		16,370	158,999	1127,545	47,79	49,65	n.a.
Total:			332,711	2271,093	100,00	100,00	



(78) Boc-L-Met(O)₂-L-Pro- Val^P(OPh-4-SCH₃)₂



Name: *tert*-butyl ((2*S*)-1-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-4-(methylsulfonyl)-1-oxobutan-2-yl)carbamate

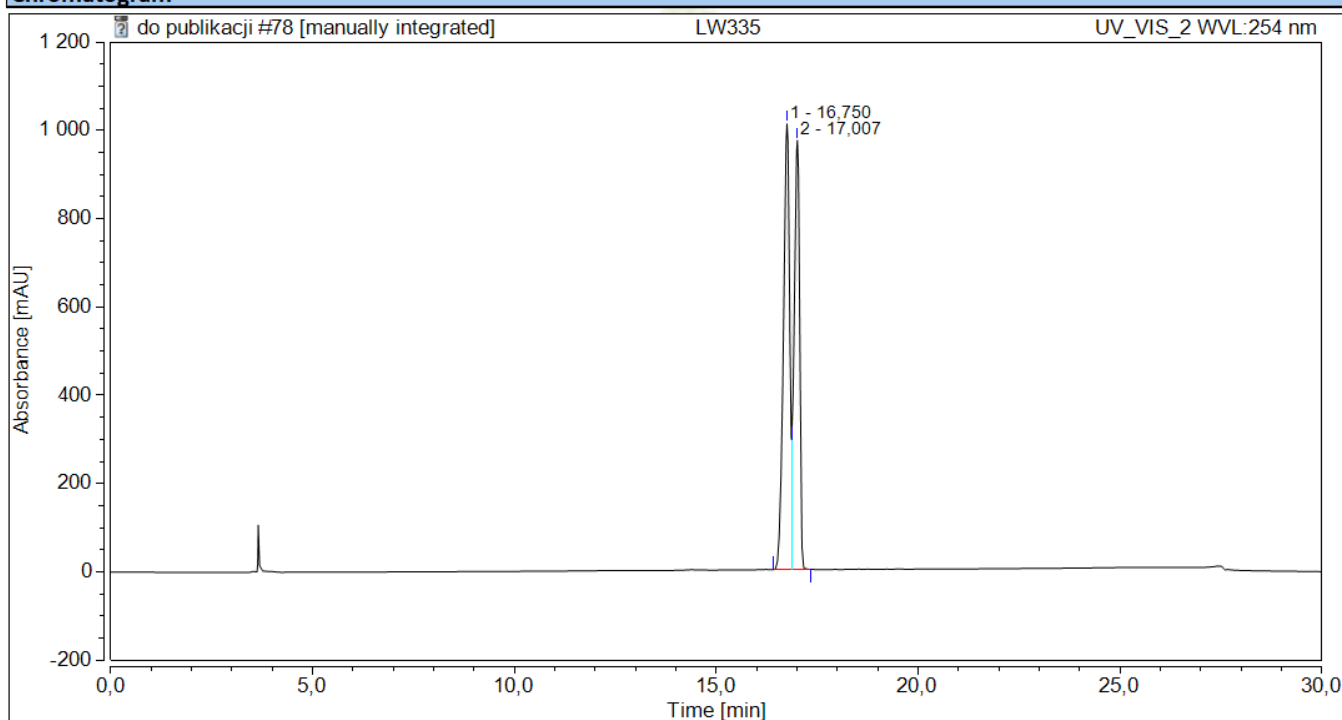
³¹P NMR (162 MHz, Chloroform-*d*) δ 18.19 (s, 42%), 17.79 (s, 58%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.29 (dd, *J* = 142.1, 10.3 Hz, 1H, NH), 7.23 – 7.14 (m, 4H, 4xArH), 7.09 – 6.95 (m, 4H, 4xArH), 5.51 (dd, *J* = 25.8, 8.4 Hz, 1H, NH), 4.85 – 4.44 (m, 3H, CHP, 2xCH), 3.77 – 3.51 (m, 2H, CH₂), 3.19 – 2.99 (m, 2H, CH₂), 2.87 (d, *J* = 46.8 Hz, 3H, CH₃), 2.47 – 2.42 (m, 6H, 2xSCH₃), 2.43 – 2.11 (m, 3H, CH₂, CH), 2.11 – 1.79 (m, 4H, 2xCH₂), 1.41 (s, 9H, Boc), 1.11 – 0.98 (m, 6H, 2xCH₃).

HRMS: C₃₃H₄₈N₃O₉PS₃ [M+H]⁺ 758.2369 found 758.2386.

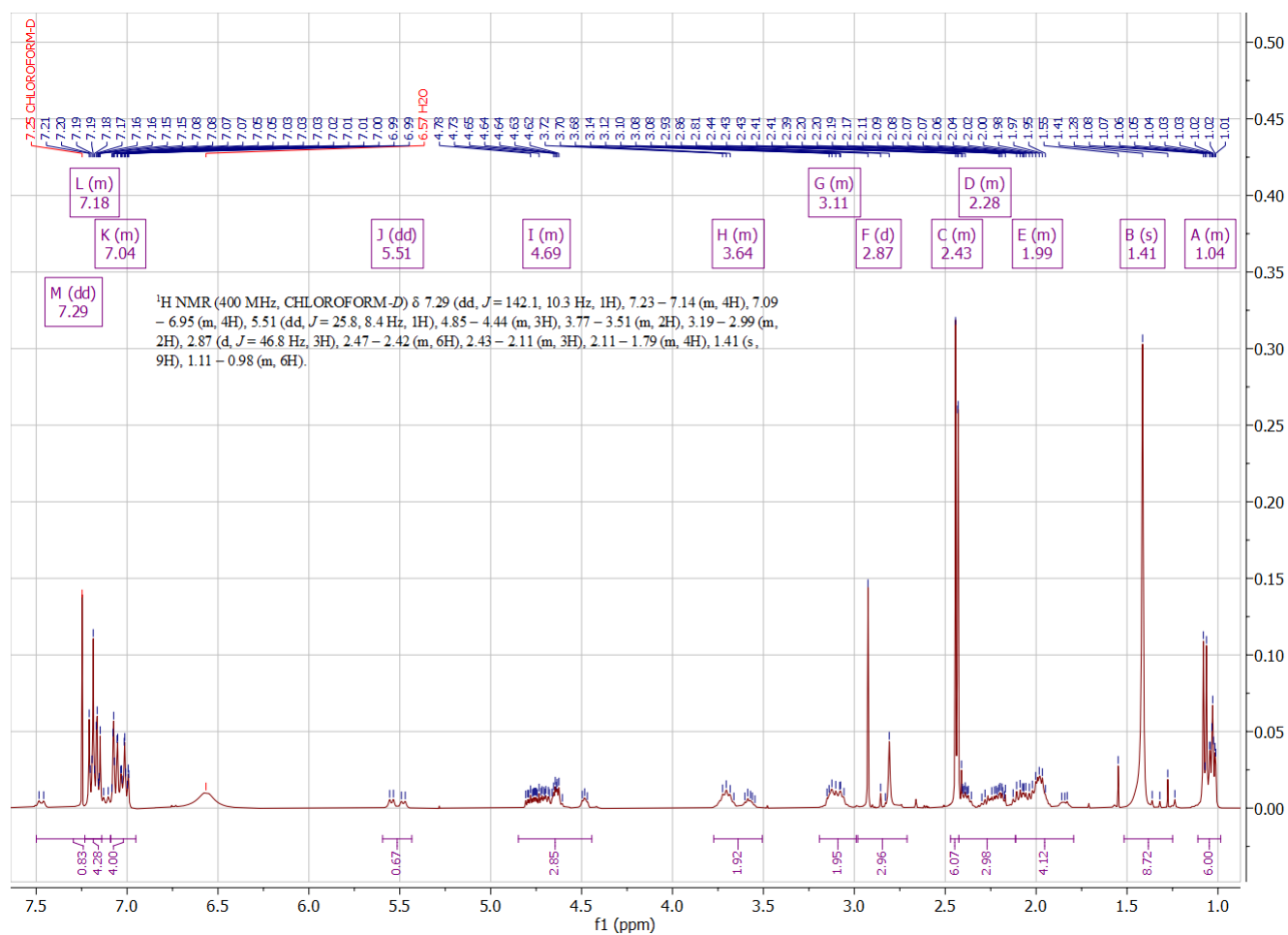
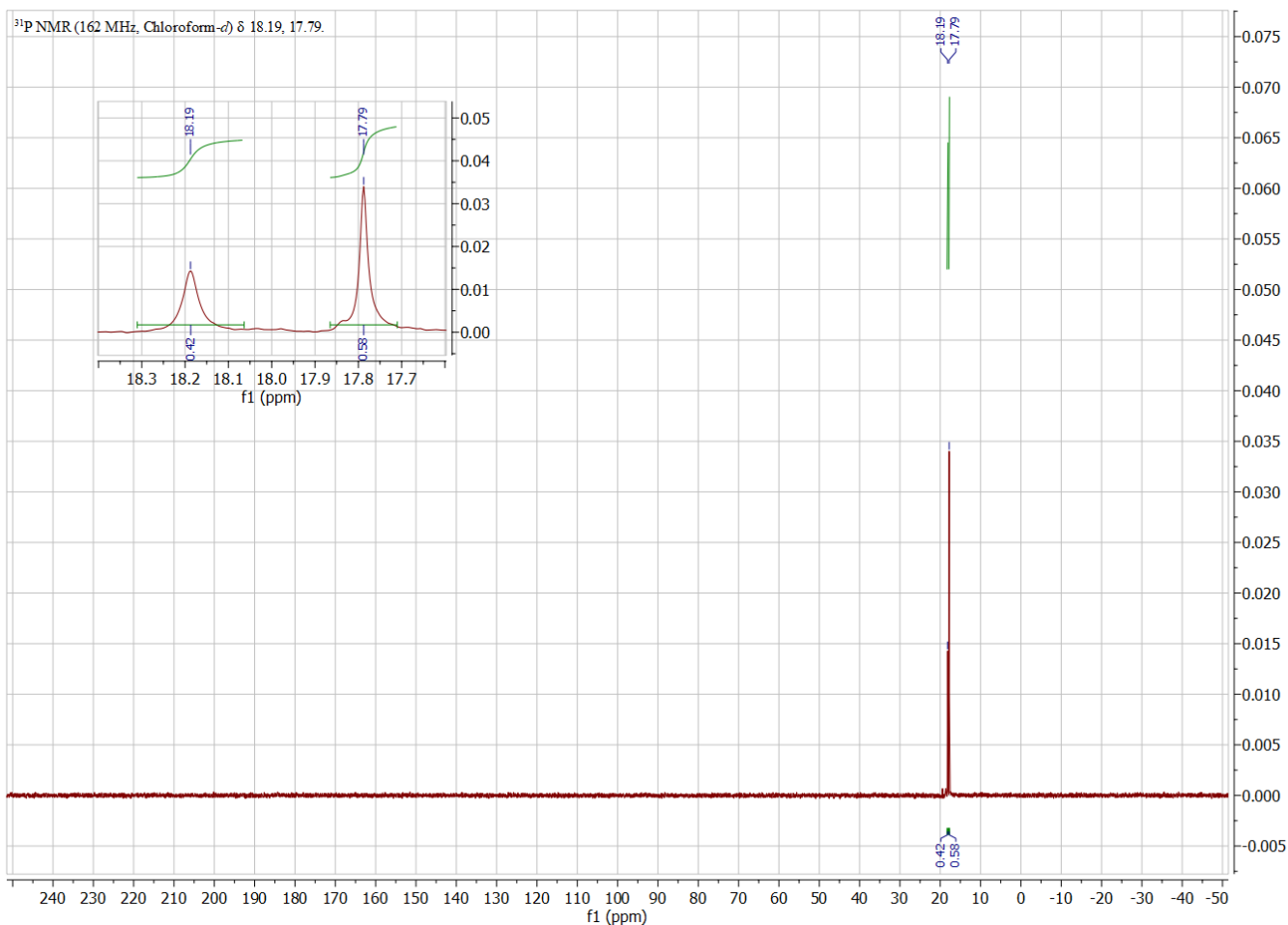
HPLC: purity >99%; retention time 16.750 and 17.007 min

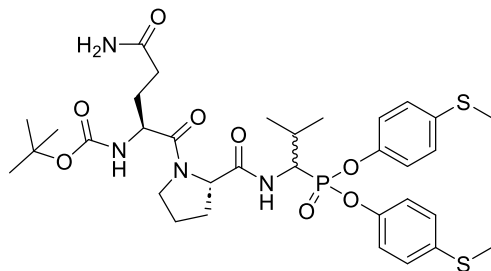
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		16,750	177,842	1009,523	53,38	50,95	n.a.
2		17,007	155,310	971,858	46,62	49,05	n.a.
Total:			333,152	1981,381	100,00	100,00	



(79) Boc-L-Gln-L-Pro-Val^P(OPh-4-SCH₃)₂

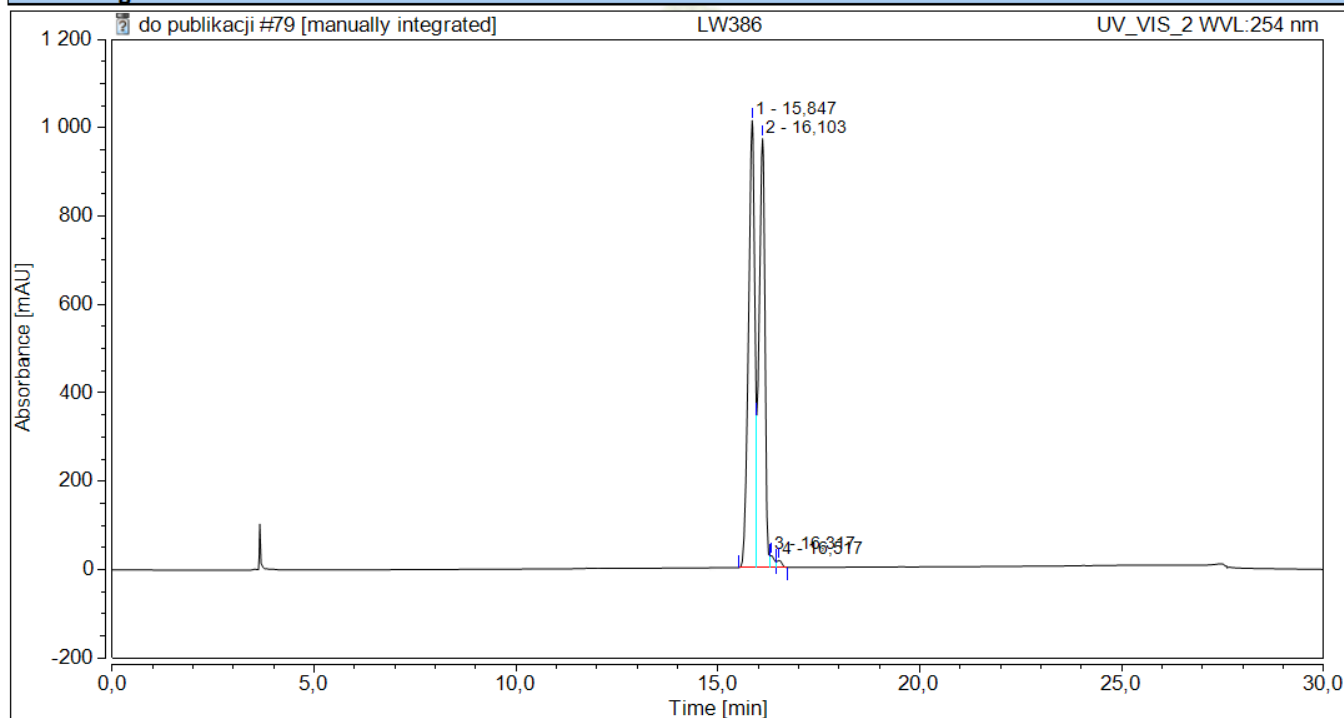
Name: *tert*-butyl ((2*S*)-5-amino-1-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-1,5-dioxopentan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.15 (s, 56%), 18.00 (s, 44%).

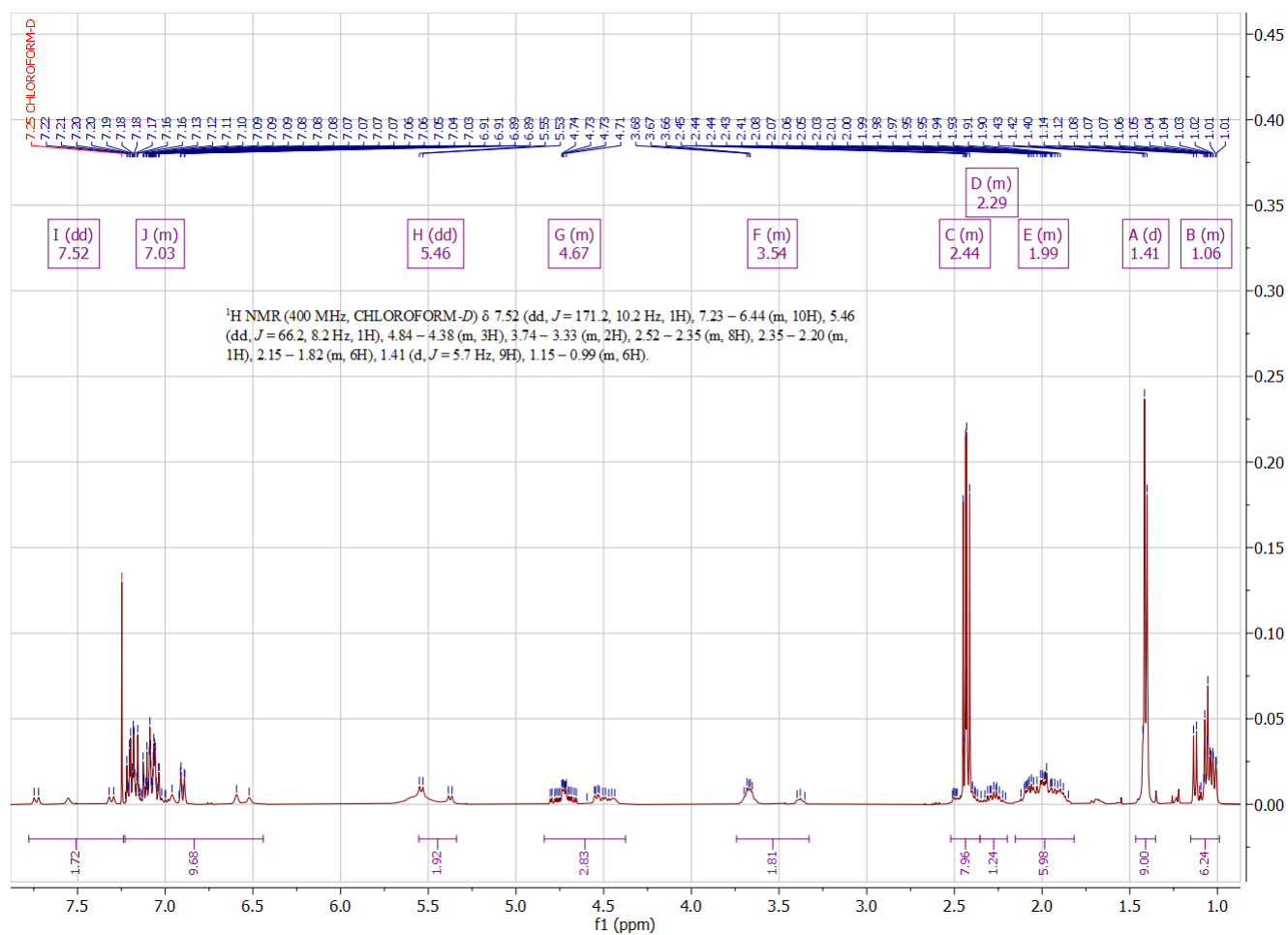
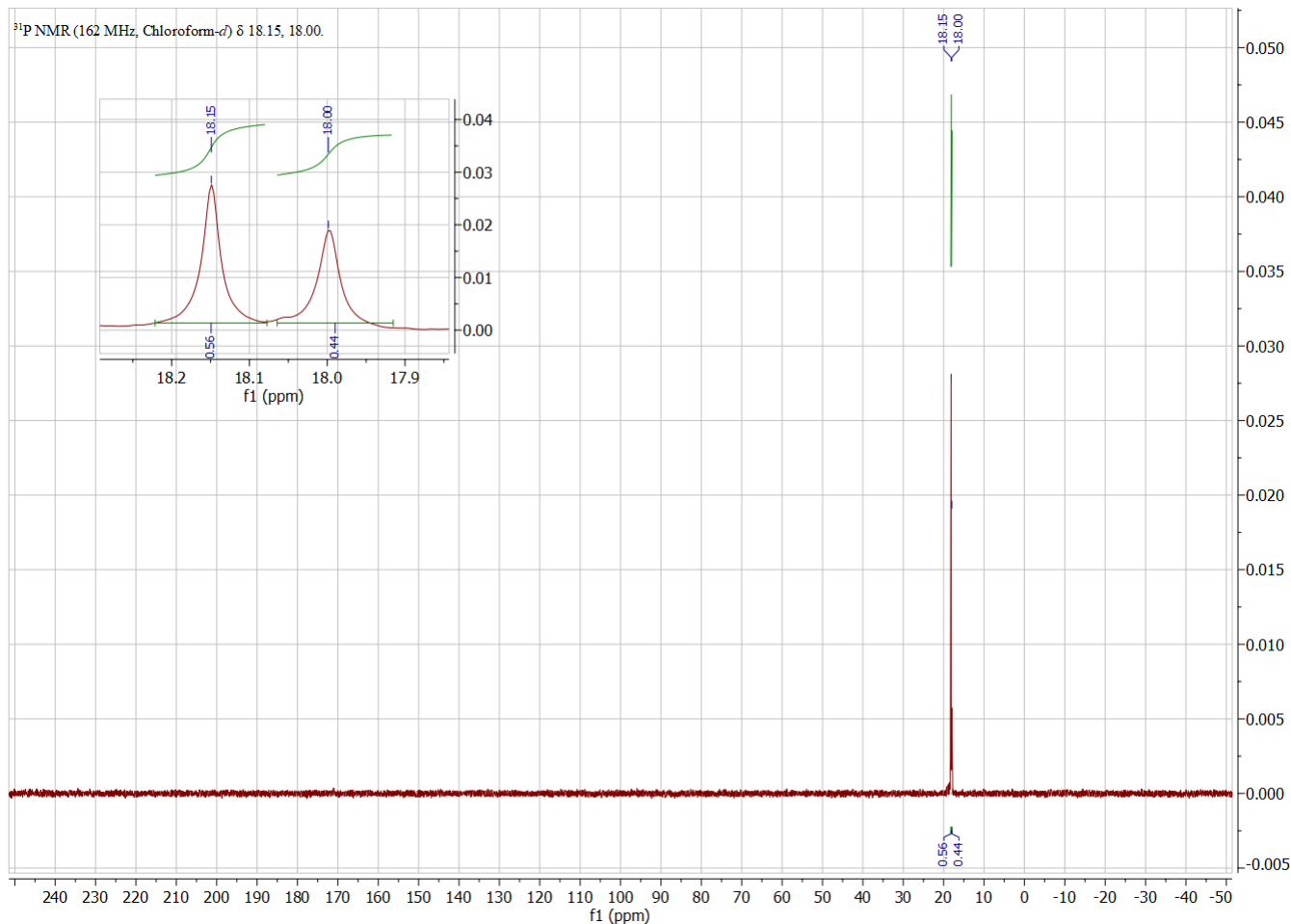
¹H NMR (400 MHz, Chloroform-*d*) δ 7.52 (dd, *J* = 171.2, 10.2 Hz, 1H, NH), 7.23 – 6.44 (m, 10H, 8xArH, NH₂), 5.46 (dd, *J* = 66.2, 8.2 Hz, 1H, NH), 4.84 – 4.38 (m, 3H, CHP, 2xCH), 3.74 – 3.33 (m, 2H, CH₂), 2.52 – 2.35 (m, 8H, 2xSCH₃, CH₂), 2.35 – 2.20 (m, 1H, CH), 2.15 – 1.82 (m, 6H, 3xCH₂), 1.41 (d, *J* = 5.7 Hz, 9H, Boc), 1.15 – 0.99 (m, 6H, 2xCH₃).

HRMS: C₃₃H₄₇N₄O₈PS₂ [M+Na]⁺ calc. 745.2471 found 745.2467

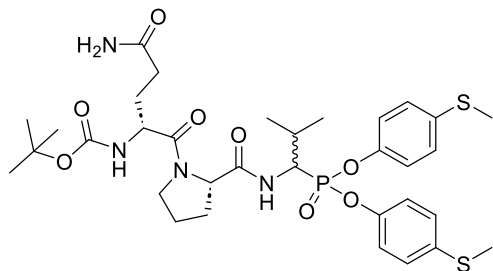
HPLC: purity >98%; retention time 15.847 and 16.103 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15,847	182,632	1011,941	52,23	49,95	n.a.
2		16,103	161,153	970,643	46,09	47,91	n.a.
3		16,317	3,500	27,406	1,00	1,35	n.a.
4		16,517	2,360	16,113	0,67	0,80	n.a.
Total:			349,645	2026,103	100,00	100,00	



(80) Boc-D-Gln-L-Pro- Val^P(OPh-4-SCH₃)₂



Name: *tert*-butyl ((2*R*)-5-amino-1-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-1,5-dioxopentan-2-yl)carbamate

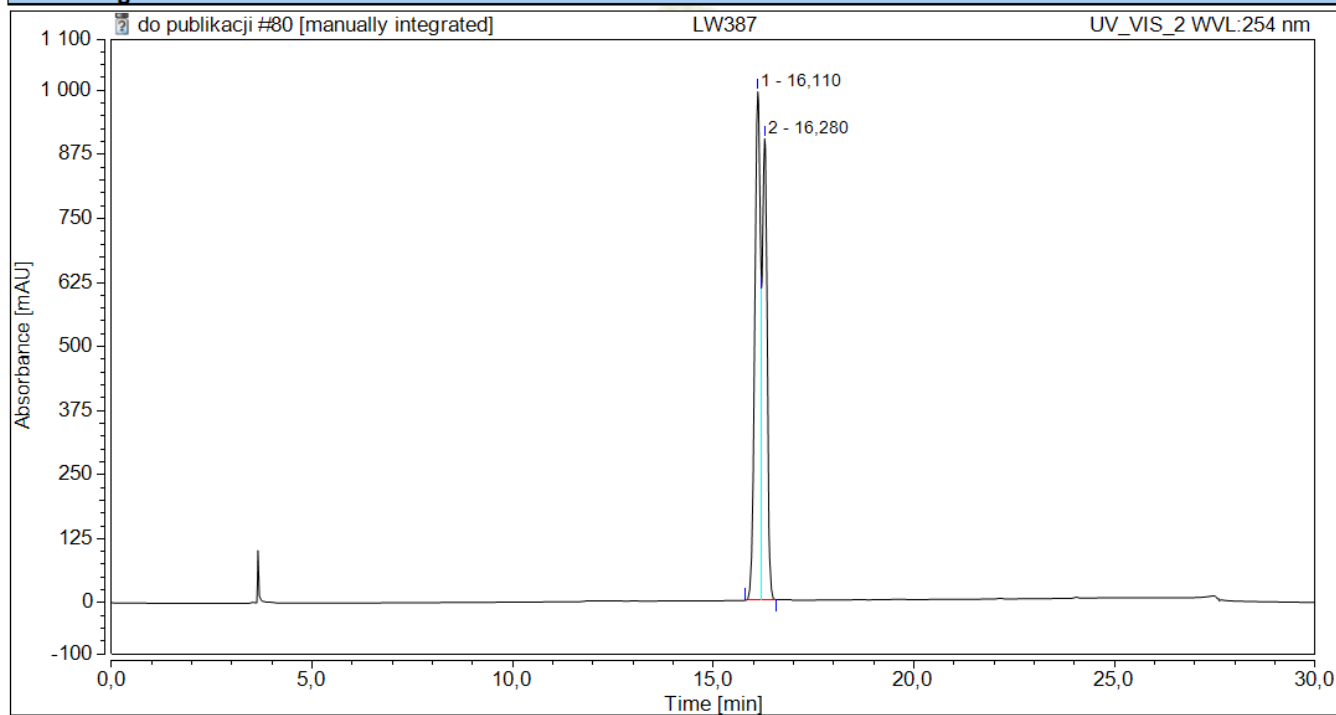
³¹P NMR (162 MHz, Chloroform-*d*) δ 18.38 (s, 53%), 18.18 (s, 47%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.46 (dd, *J* = 44.0, 10.3 Hz, 1H, NH), 7.22 – 7.04 (m, 9H, 8xArH, 0.5xNH₂), 6.92 – 6.05 (m, 1H, 0.5xNH₂), 5.64 (dd, *J* = 44.7, 8.2 Hz, 1H, NH), 4.73 – 4.35 (m, 3H, CHP, 2xCH), 3.74 – 3.38 (m, 2H, CH₂), 2.44 – 2.43 (m, 6H, 2xSCH₃), 2.41 – 2.29 (m, 3H, CH₂, CH), 2.27 – 1.73 (m, 6H, 3xCH₂), 1.38 (d, *J* = 15.4 Hz, 9H, Boc), 1.09 – 0.94 (m, 6H, 2xCH₃).

HRMS: C₃₃H₄₇N₄O₈PS₂ [M+Na]⁺ calc. 745.2471 found 745.2472

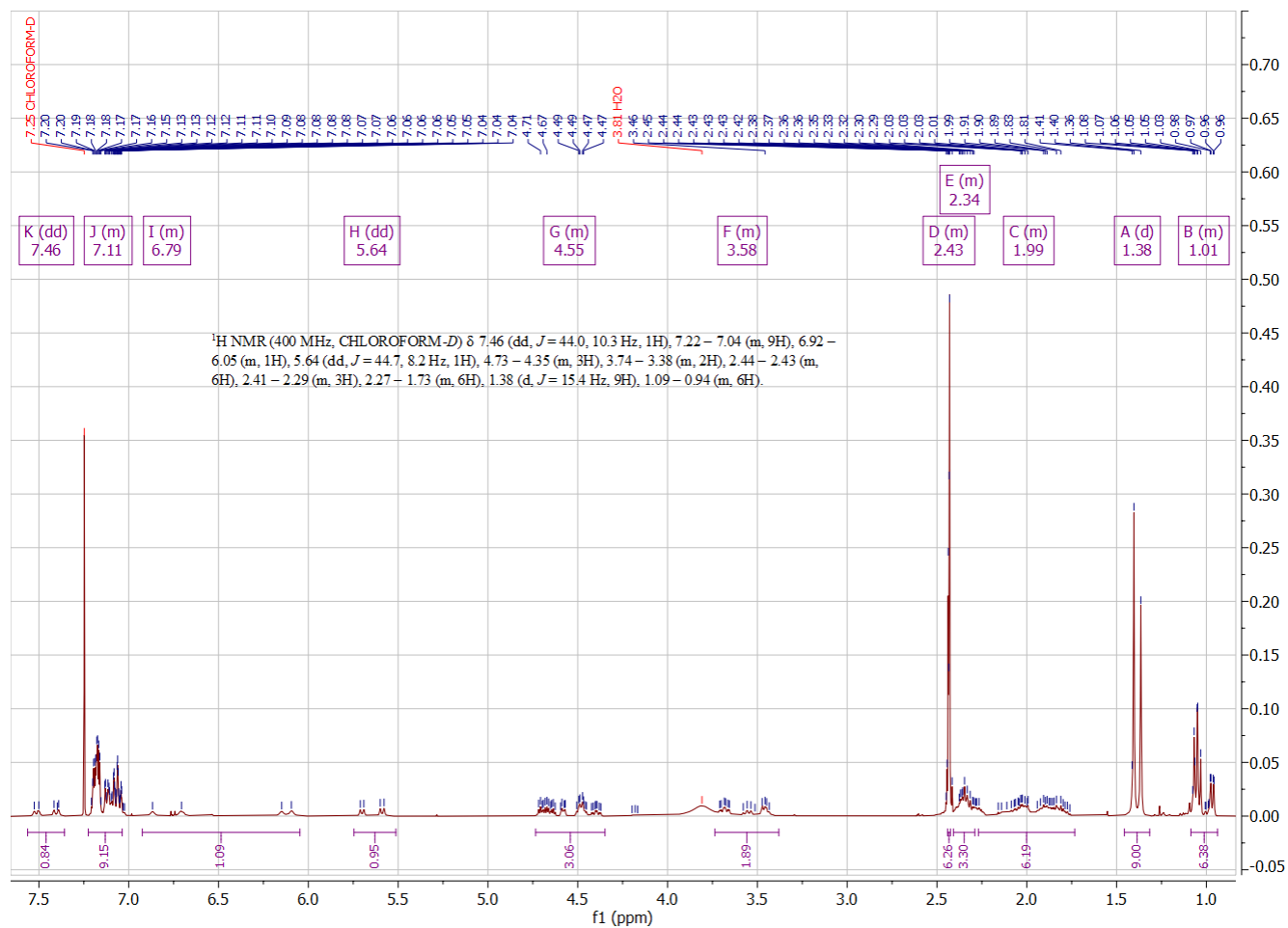
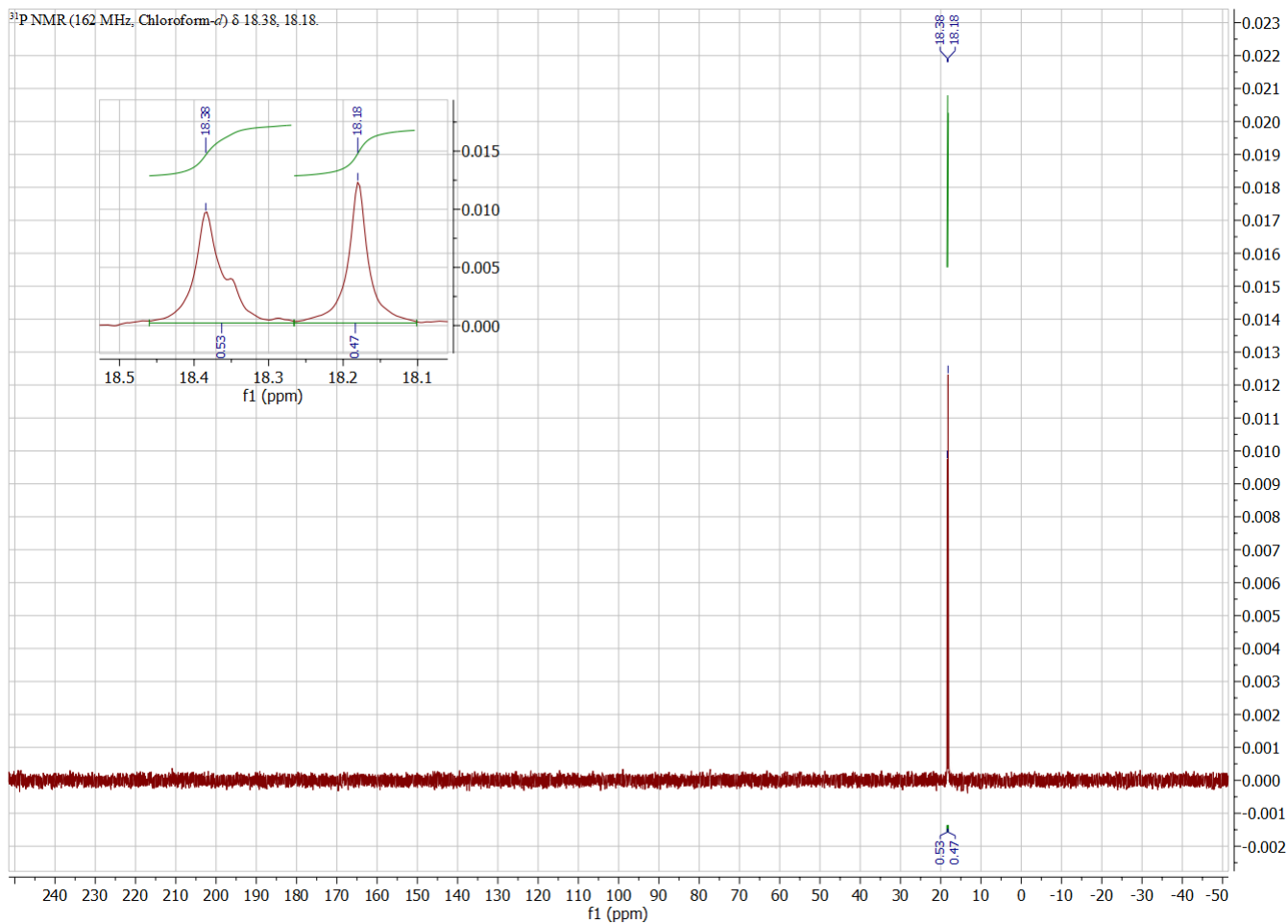
HPLC: purity >99%; retention time 16.110 and 16.280 min

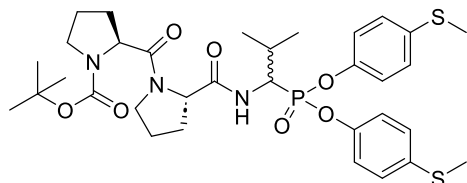
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16,110	161,880	992,559	56,17	52,42	n.a.
2		16,280	126,328	900,913	43,83	47,58	n.a.
Total:			288,209	1893,473	100,00	100,00	



(81) Boc-L-Pro-L-Pro-Val^P(OPh-4-SCH₃)₂

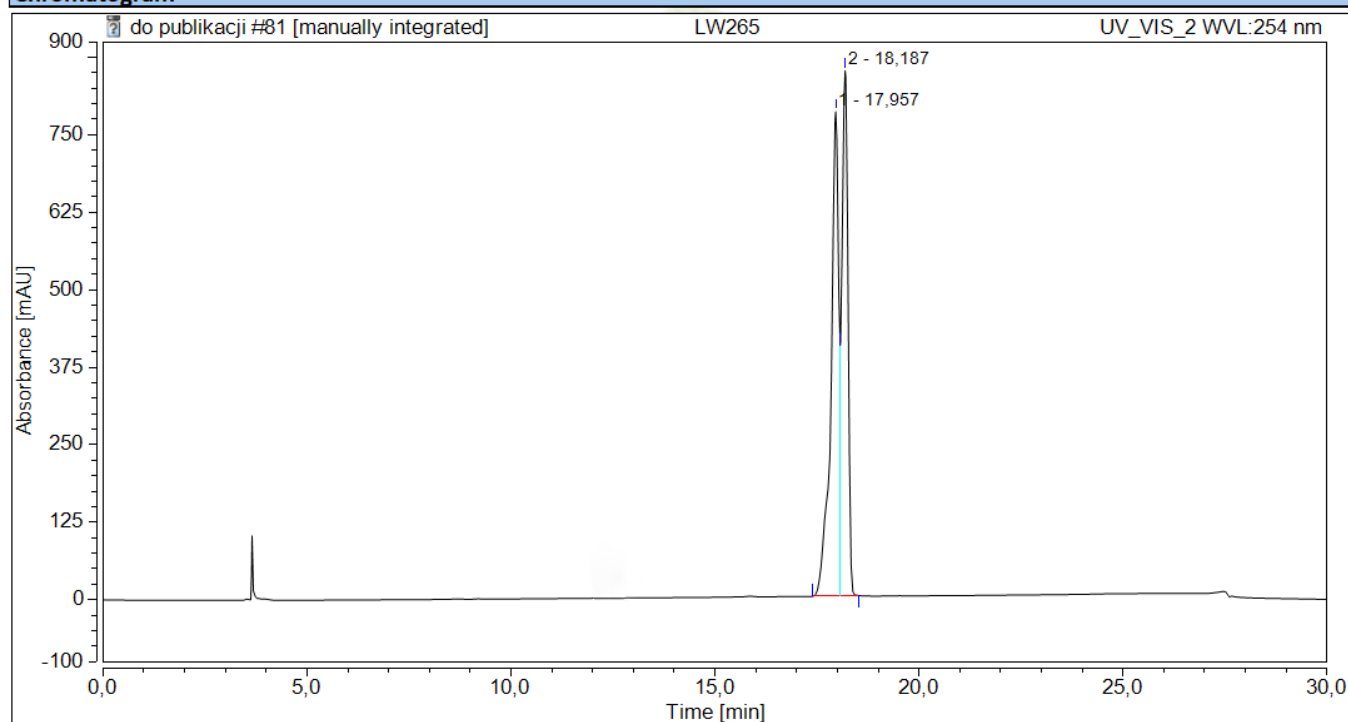
Name: *tert*-butyl (2*S*)-2-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidine-1-carbonyl)pyrrolidine-1-carboxylate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.78 (s, 62%), 18.17 (s, 26%), 18.06 (s, 12%).

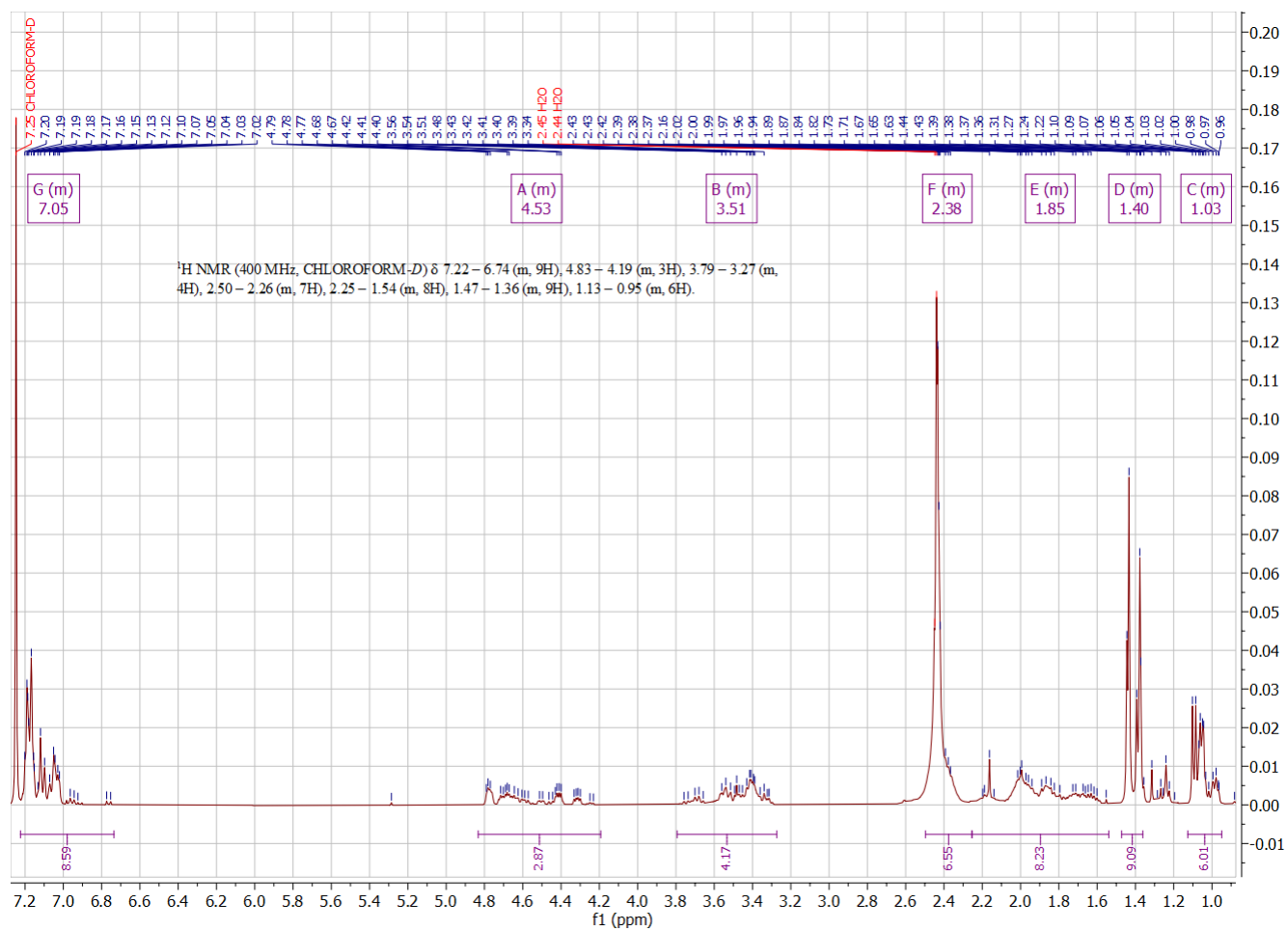
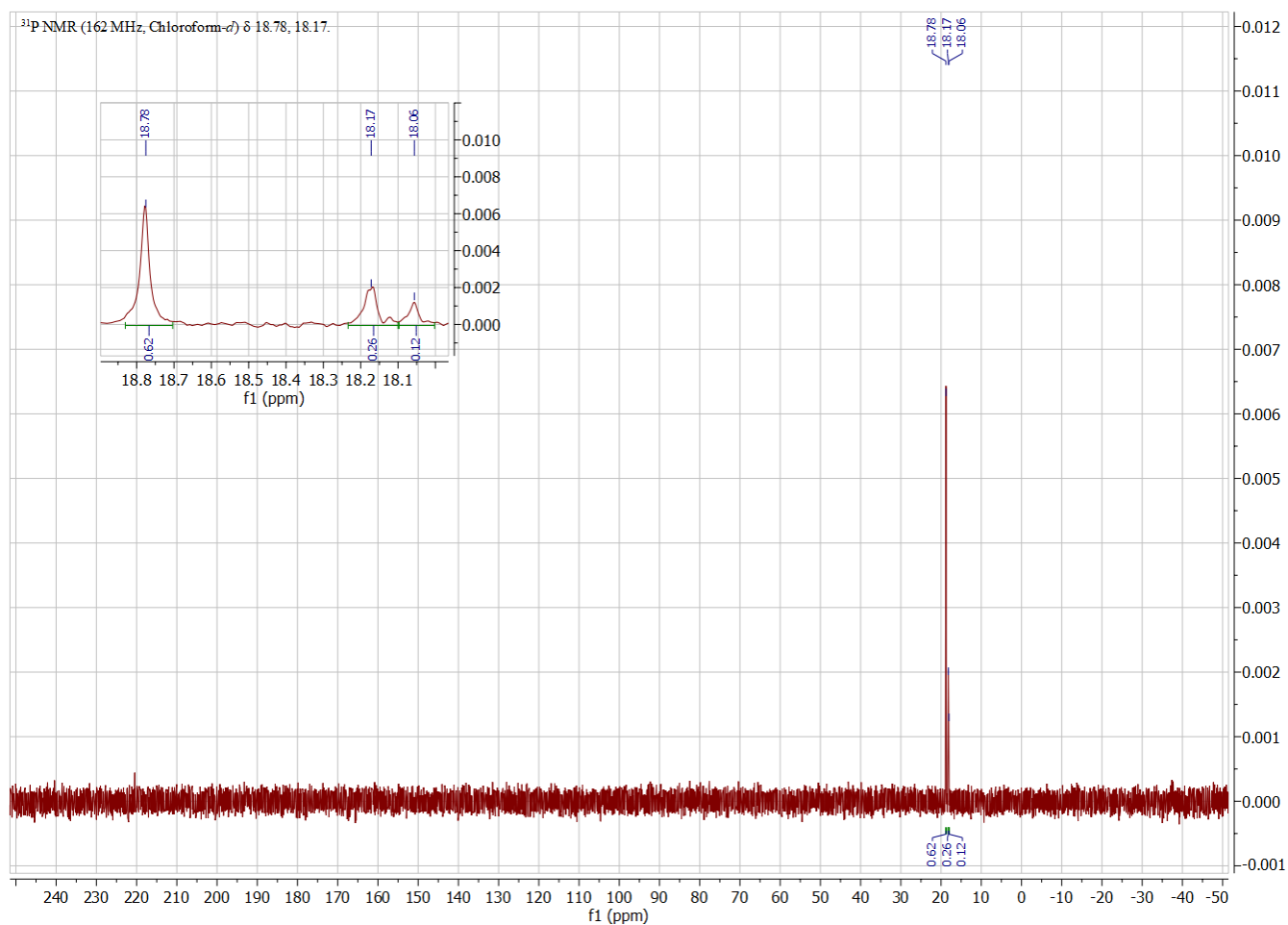
¹H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 6.74 (m, 9H, 8xArH, NH), 4.83 – 4.19 (m, 3H, CHP, 2xCH), 3.79 – 3.27 (m, 4H, 2xCH₂), 2.50 – 2.26 (m, 7H, 2xSCH₃, CH), 2.25 – 1.54 (m, 8H, 4xCH₂), 1.47 – 1.36 (m, 9H, Boc), 1.13 – 0.95 (m, 6H, 2xCH₃).

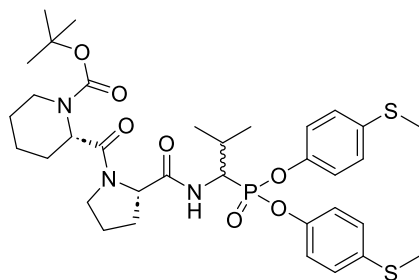
HRMS: C₃₃H₄₆N₃O₇PS₂ [M+Na]⁺ calc. 714.2412 found 714.2397

HPLC: purity >99%; retention time 17.957 and 18.187 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17,957	171,868	781,102	54,03	47,97	n.a.
2		18,187	146,213	847,087	45,97	52,03	n.a.
Total:			318,082	1628,189	100,00	100,00	



(82) Boc-L-Pip-L-Pro-Val^P(OPh-4-SCH₃)₂

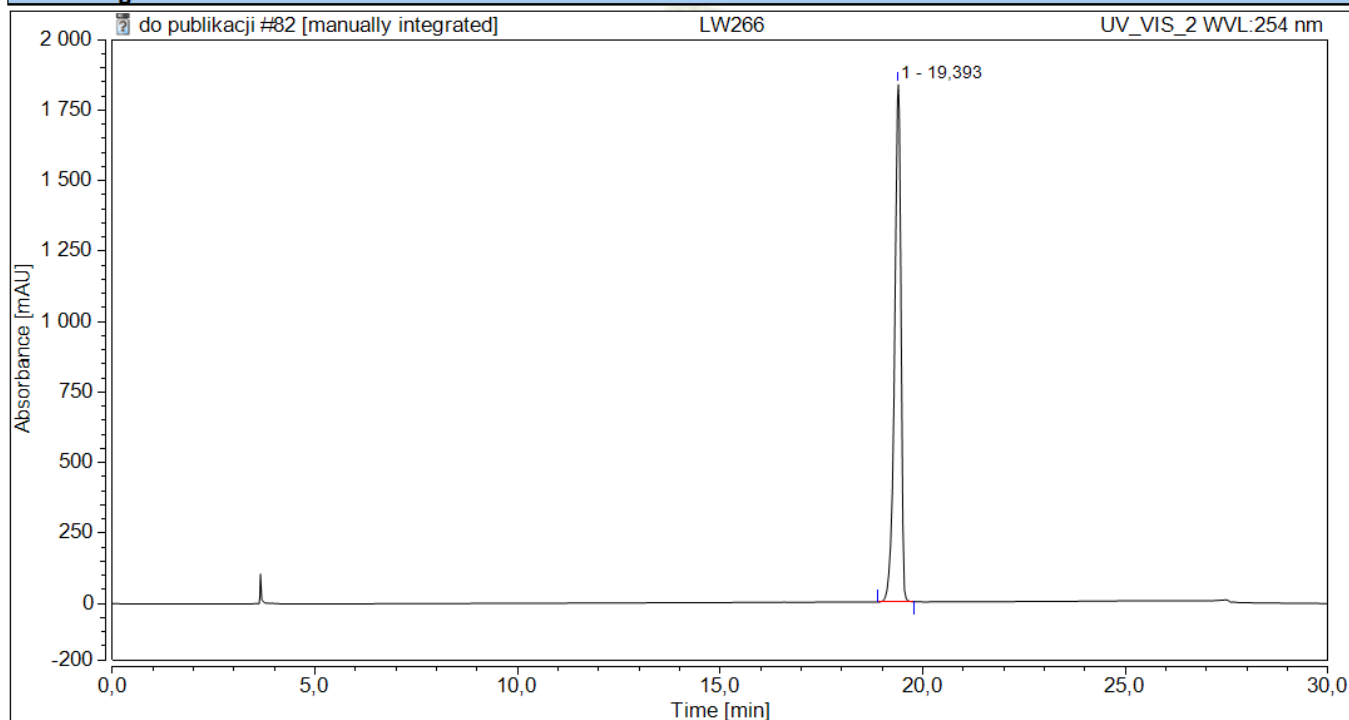
Name: *tert*-butyl (2*S*)-2-(((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidine-1-carbonyl)piperidine-1-carboxylate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.58 (s, 62%), 18.15 (s, 38%).

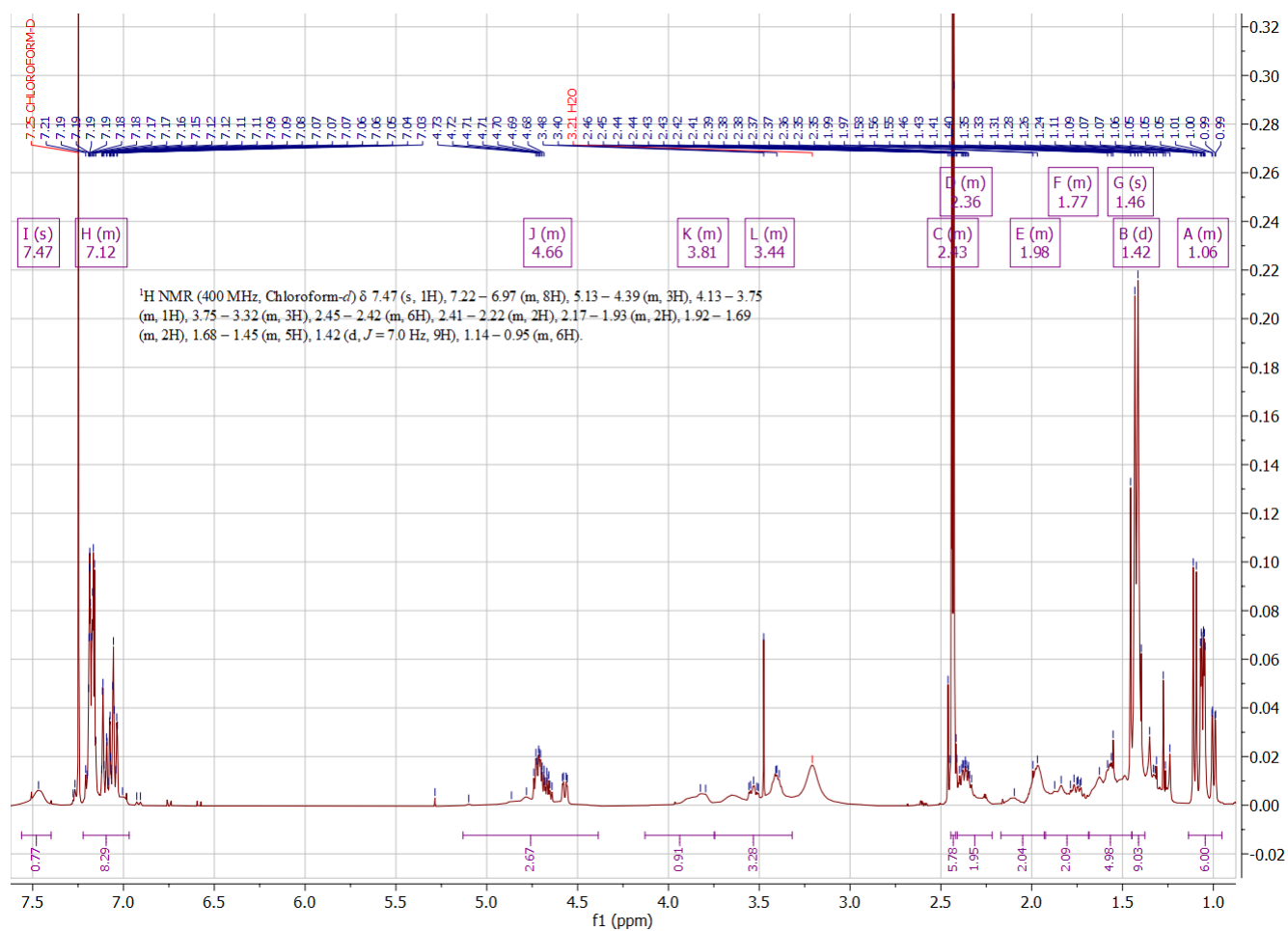
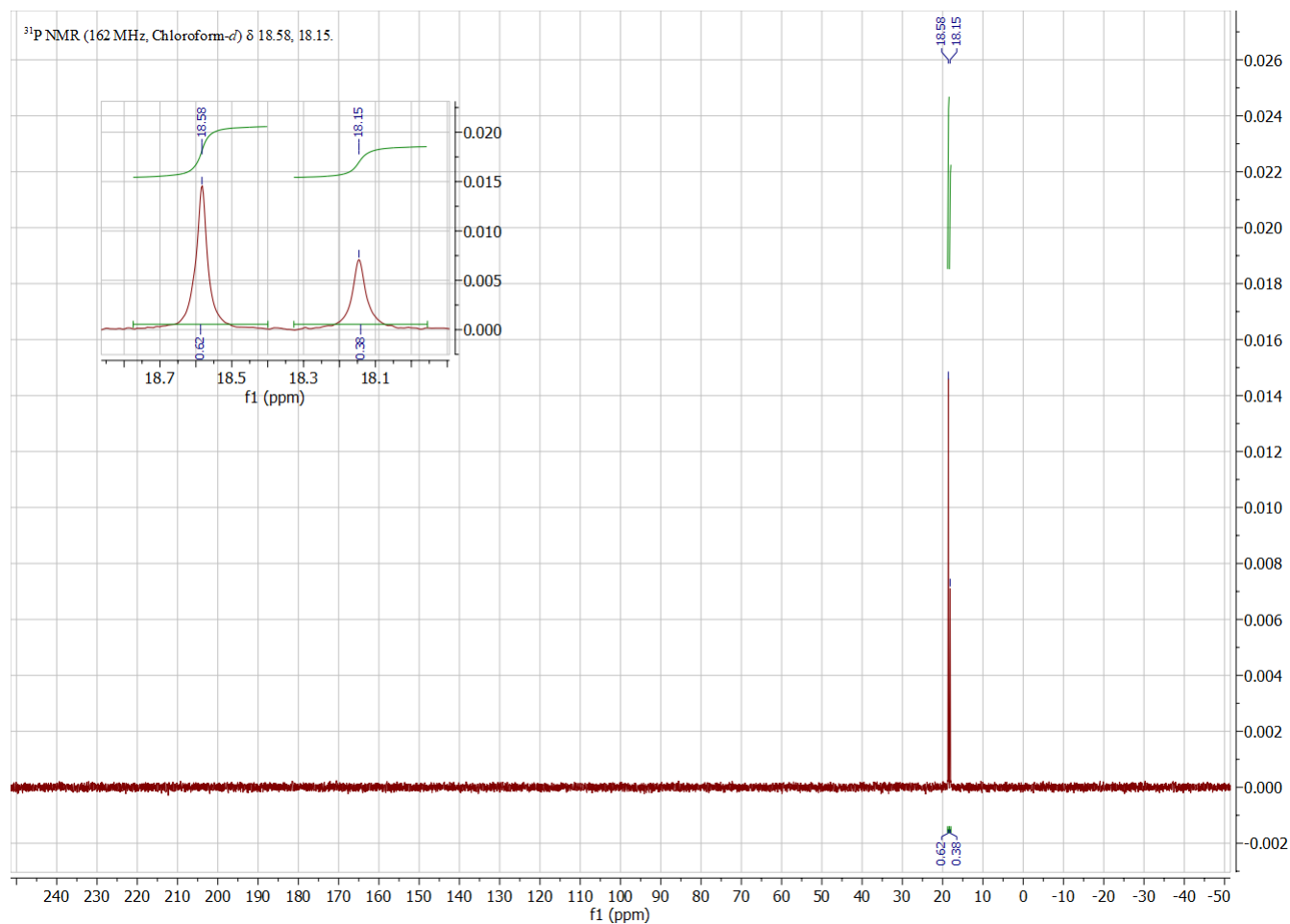
¹H NMR (400 MHz, Chloroform-*d*) δ 7.47 (s, 1H, NH), 7.22 – 6.97 (m, 8H, 8xArH), 5.13 – 4.39 (m, 3H, CHP, 2xCH), 4.13 – 3.75 (m, 1H, 0.5xCH₂), 3.75 – 3.32 (m, 3H, 1.5xCH₂), 2.45 – 2.42 (m, 6H, 2xSCH₃), 2.41 – 2.22 (m, 2H, 0.5xCH₂, CH), 2.17 – 1.93 (m, 2H, CH₂), 1.92 – 1.69 (m, 2H, CH₂), 1.68 – 1.45 (m, 5H, 2.5xCH₂), 1.42 (d, *J* = 7.0 Hz, 9H, Boc), 1.14 – 0.95 (m, 6H, 2xCH₃).

HRMS: C₃₄H₄₈N₃O₇PS₂ [M+Na]⁺ calc. 728.2569 found 728.2562

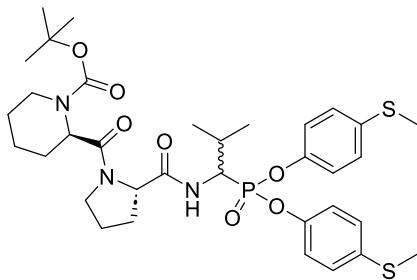
HPLC: purity >99%; retention time 19.393 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19,393	332,232	1834,347	100,00	100,00	n.a.
Total:			332,232	1834,347	100,00	100,00	



(83) Boc-D-Pip-L-Pro- Val^P(OPh-4-SCH₃)₂



Name: *tert*-butyl (2R)-2-((2S)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidine-1-carbonyl)piperidine-1-carboxylate

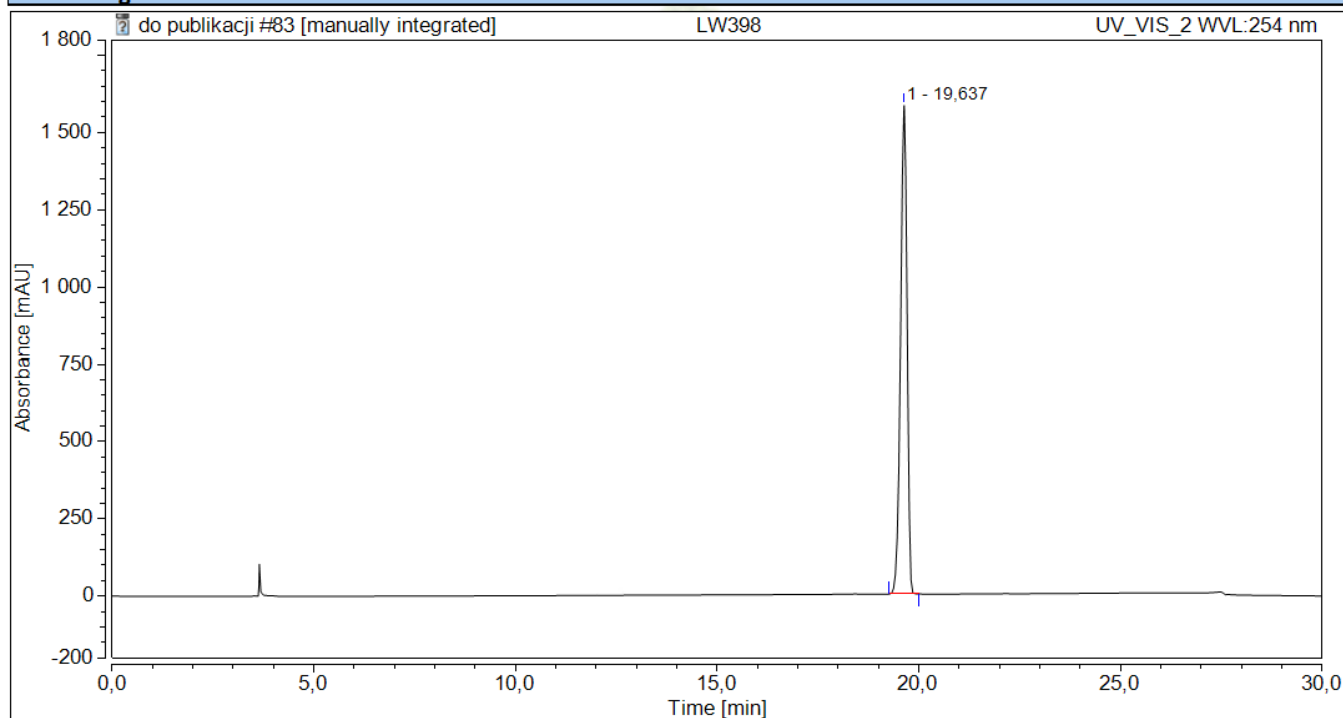
³¹P NMR (162 MHz, Chloroform-d) δ 18.78 (s, 61%), 18.24 (s, 39%).

¹H NMR (400 MHz, Chloroform-d) δ 7.69 – 7.25 (m, 1H, NH), 7.23 – 6.96 (m, 8H, 8xArH), 4.93 – 4.41 (m, 3H, CHP, 2xCH), 4.07 – 2.93 (m, 4H, 2xCH₂), 2.49 – 2.41 (m, 6H, 2xSCH₃), 2.41 – 2.11 (m, 2H, 0.5xCH₂, CH), 2.10 – 1.80 (m, 4H, 2xCH₂), 1.80 – 1.43 (m, 5H, 2.5xCH₂), 1.39 (d, J = 5.4 Hz, 9H, Boc), 1.16 – 0.97 (m, 6H, 2xCH₃).

HRMS: C₃₄H₄₈N₃O₇PS₂ [M+Na]⁺ calc. 728.2569 found 728.2559

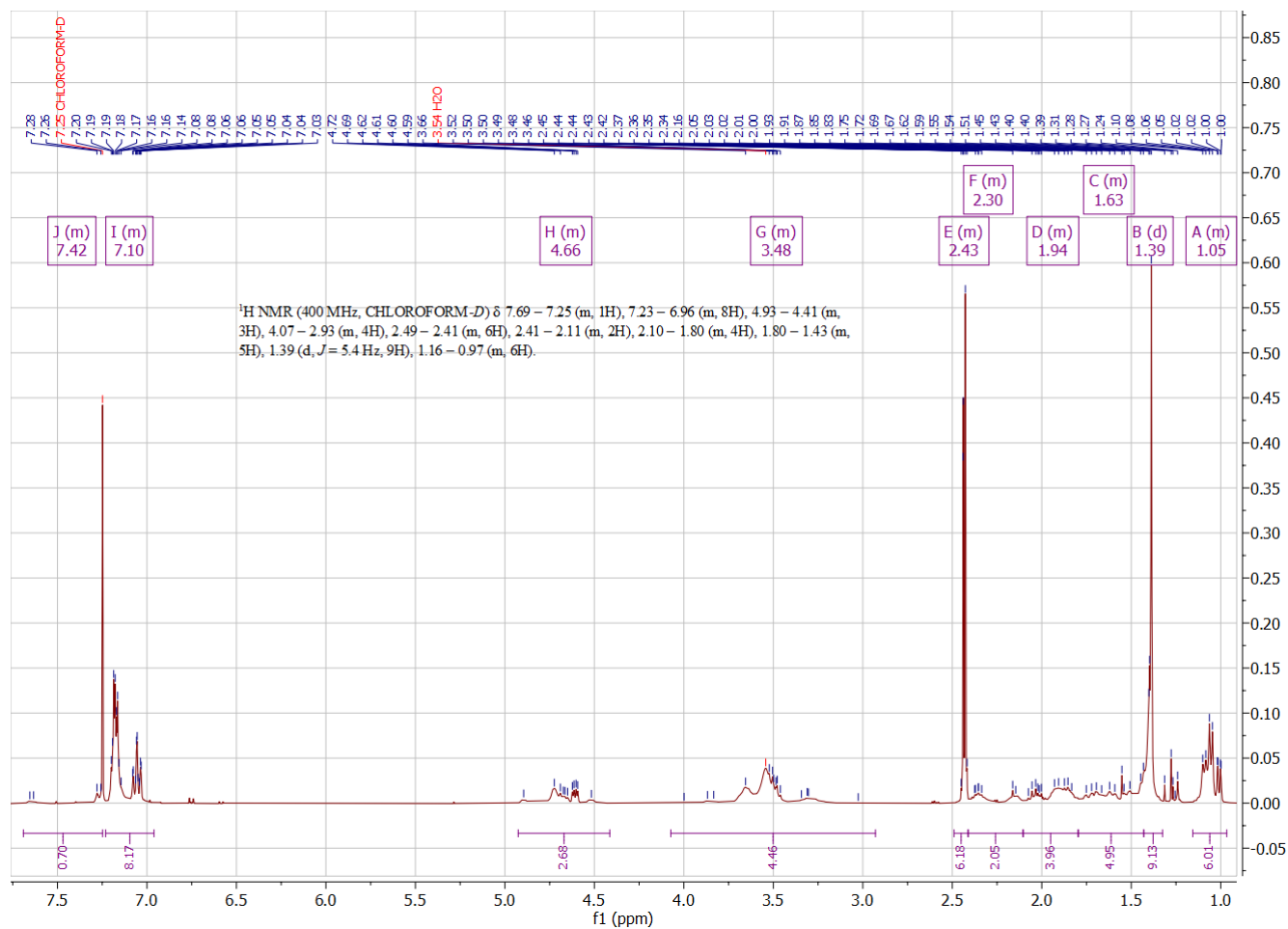
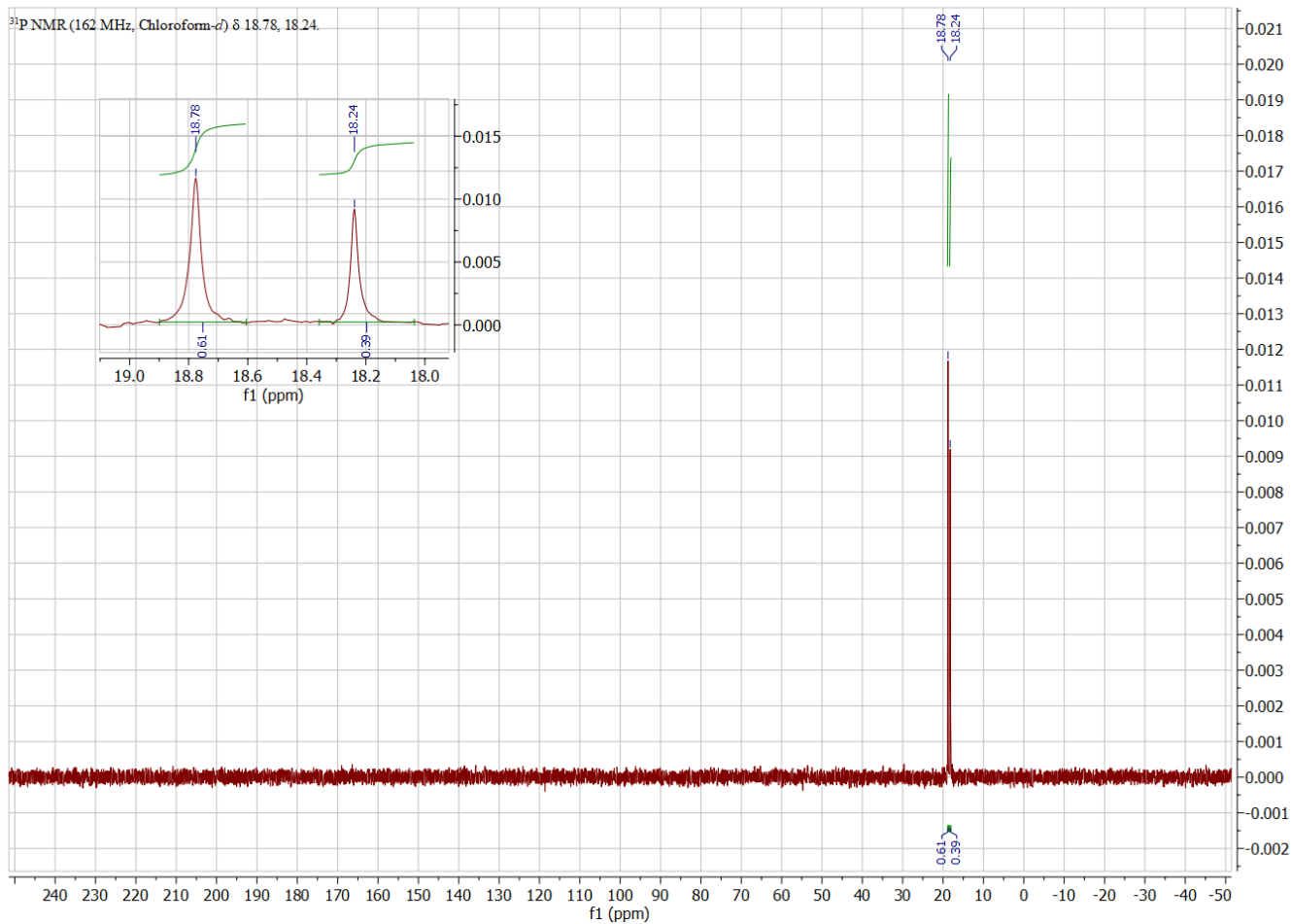
HPLC: purity >99%; retention time 19.637 min

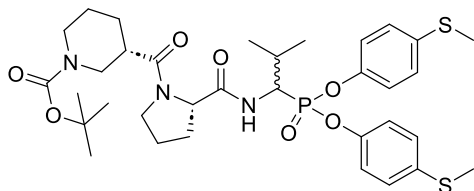
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19,637	295,547	1580,758	100,00	100,00	n.a.
Total:			295,547	1580,758	100,00	100,00	



(84) Boc-L-Nip-L-Pro- Val^P(OPh-4-SCH₃)₂

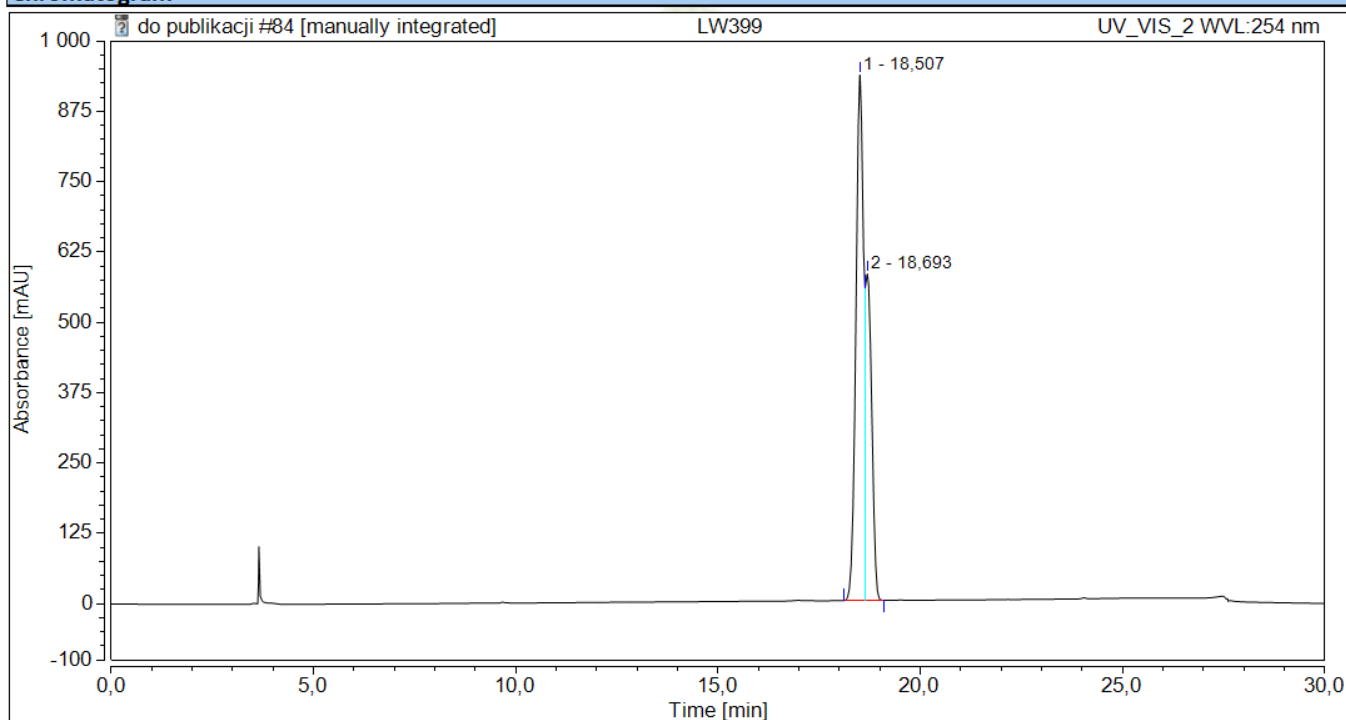
Name: *tert*-butyl (3*S*)-3-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidine-1-carbonyl)piperidine-1-carboxylate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.61 (s, 63%), 18.20 (s, 37%).

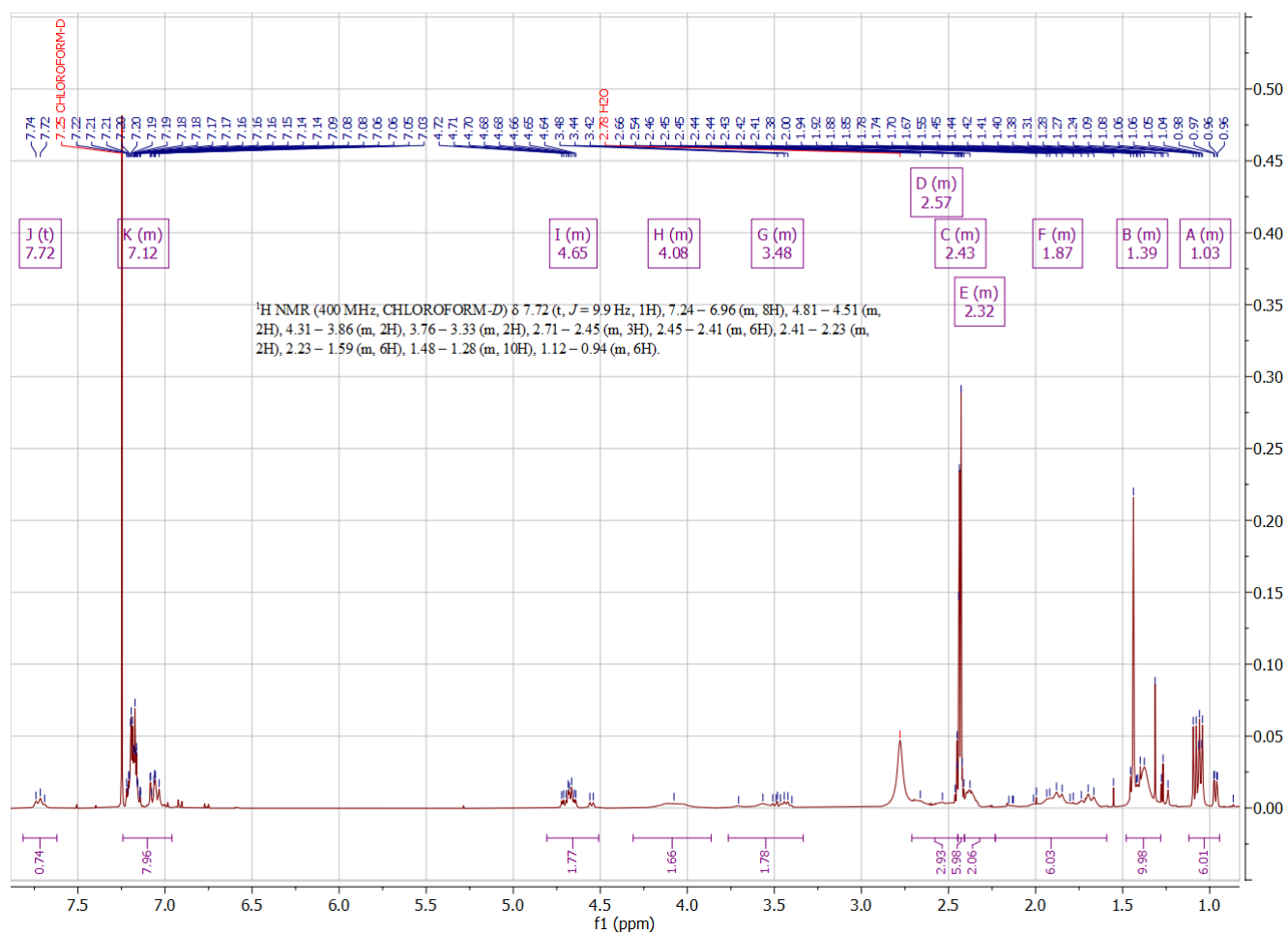
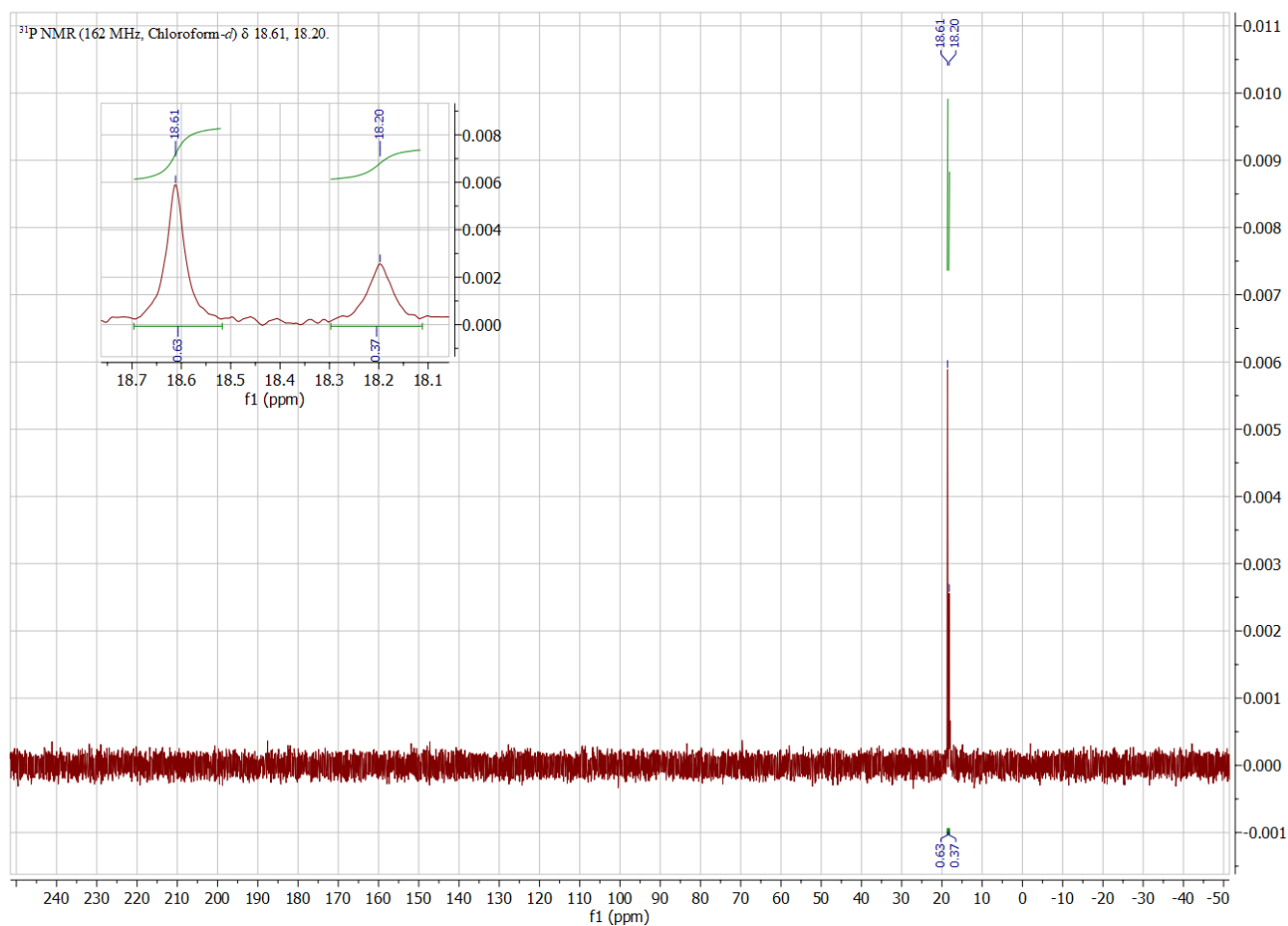
¹H NMR (400 MHz, Chloroform-*d*) δ 7.72 (t, *J* = 9.9 Hz, 1H, NH), 7.24 – 6.96 (m, 8H, 8xArH), 4.81 – 4.51 (m, 2H, CHP, CH), 4.31 – 3.86 (m, 2H, CH, 0.5xCH₂), 3.76 – 3.33 (m, 2H, CH₂), 2.71 – 2.45 (m, 3H, CH₂, CH), 2.45 – 2.41 (m, 6H, 2xSCH₃), 2.41 – 2.23 (m, 2H, CH₂), 2.23 – 1.59 (m, 6H, 3xCH₂), 1.48 – 1.28 (m, 10H, Boc, 0.5xCH₂), 1.12 – 0.94 (m, 6H, 2xCH₃).

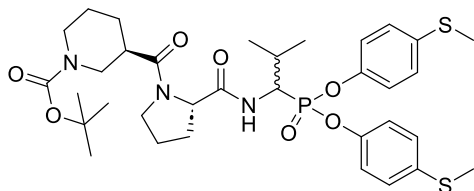
HRMS: C₃₄H₄₈N₃O₇PS₂ [M+Na]⁺ calc. 728.2569 found 728.2551

HPLC: purity >99%; retention time 18.507 and 18.693 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18,507	201,725	933,655	65,80	61,67	n.a.
2		18,693	104,834	580,257	34,20	38,33	n.a.
Total:			306,558	1513,912	100,00	100,00	



(85) Boc-D-Nip-L-Pro- Val^P(OPh-4-SCH₃)₂

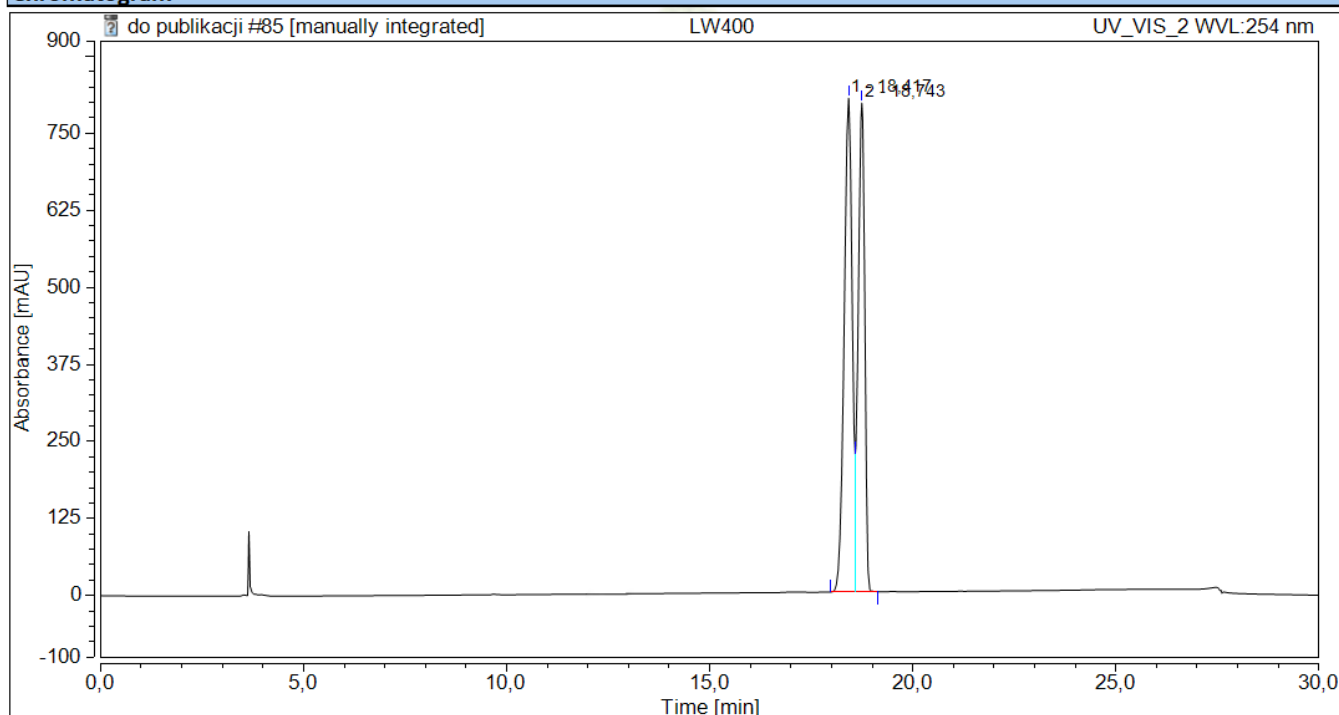
Name: *tert*-butyl (3R)-3-((2S)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidine-1-carboxylate

³¹P NMR (162 MHz, Chloroform-d) δ 18.42 (s, 64%), 18.16 (s, 36%).

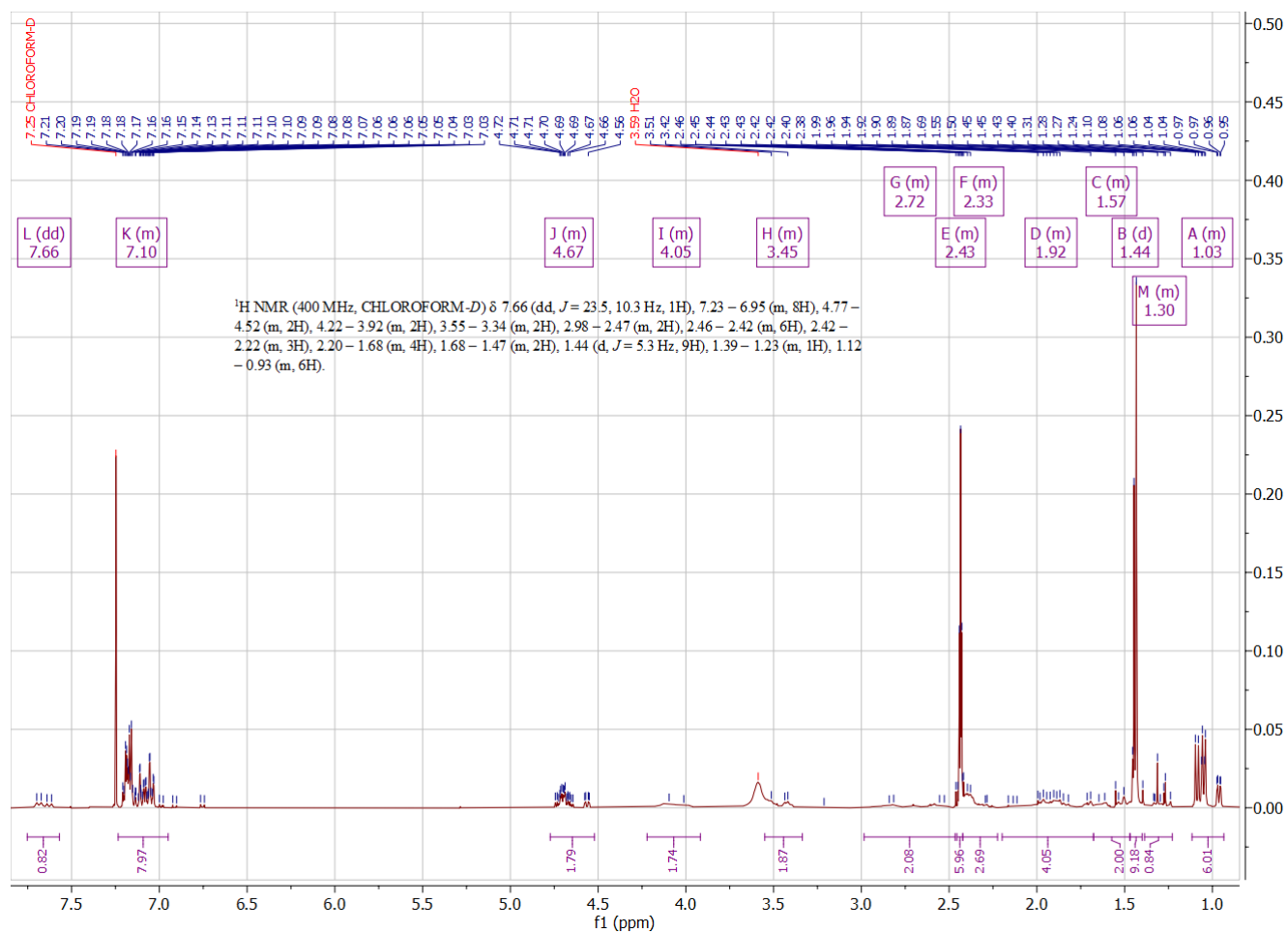
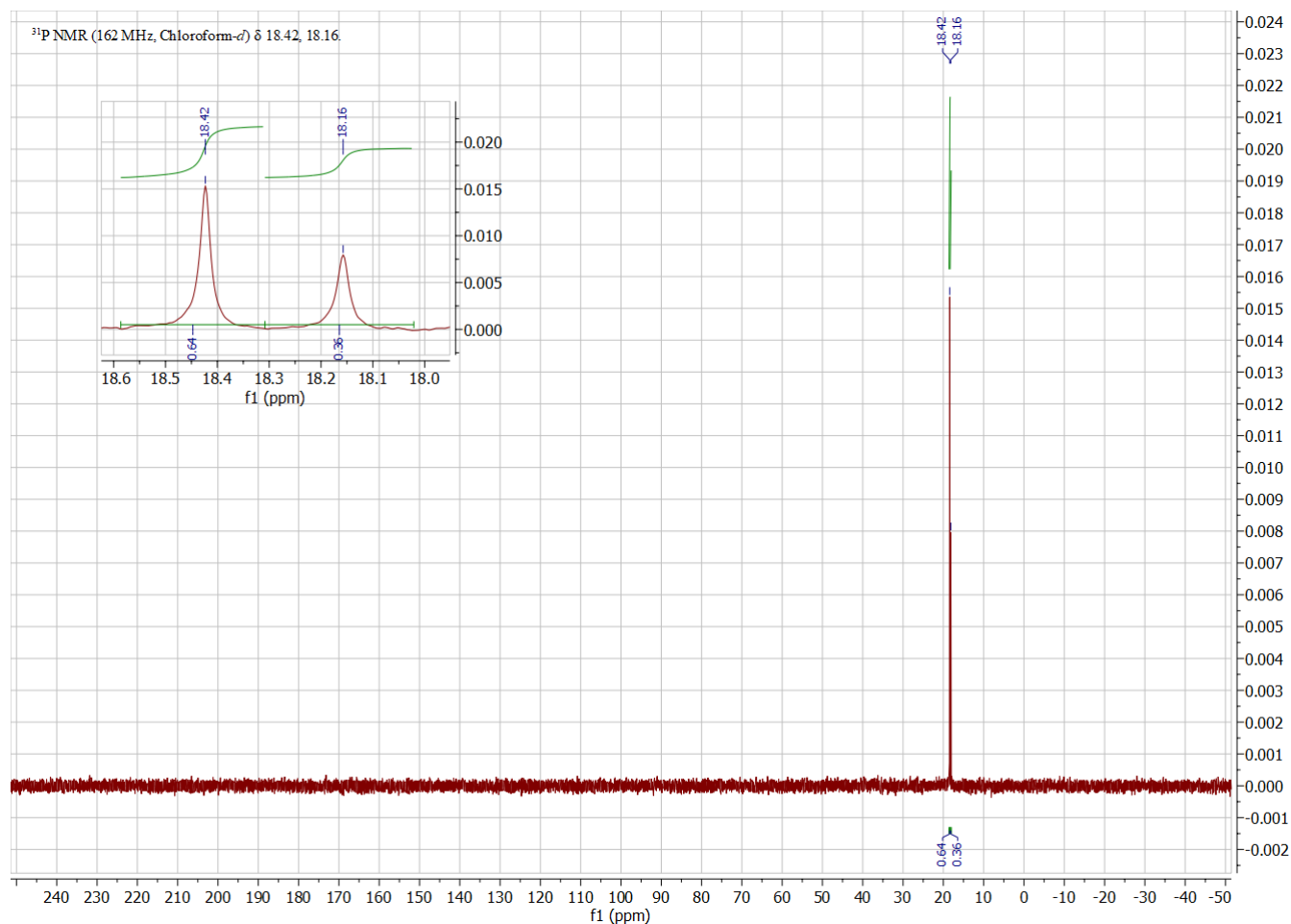
¹H NMR (400 MHz, Chloroform-d) δ 7.66 (dd, J = 23.5, 10.3 Hz, 1H, NH), 7.23 – 6.95 (m, 8H, 8xArH), 4.77 – 4.52 (m, 2H, CHP, CH), 4.22 – 3.92 (m, 2H, 0.5xCH₂, CH), 3.55 – 3.34 (m, 2H, CH₂), 2.98 – 2.47 (m, 2H, CH₂), 2.46 – 2.42 (m, 6H, 2xSCH₃), 2.42 – 2.22 (m, 3H, CH₂, CH), 2.20 – 1.68 (m, 4H, 2xCH₂), 1.68 – 1.47 (m, 2H, CH₂), 1.44 (d, J = 5.3 Hz, 9H, Boc), 1.39 – 1.23 (m, 1H, 0.5xCH₂), 1.12 – 0.93 (m, 6H, 2xCH₃).

HRMS: C₃₄H₄₈N₃O₇PS₂ [M+Na]⁺ calc. 728.2569 found 728.2559

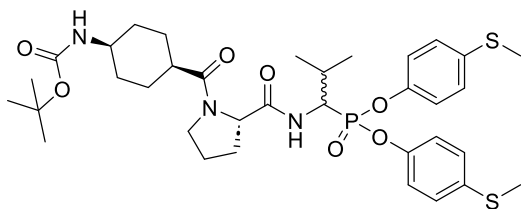
HPLC: purity >99%; retention time 18.417 and 18.743 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		18,417	183,706	801,197	55,23	50,25	n.a.
2		18,743	148,924	793,146	44,77	49,75	n.a.
Total:			332,631	1594,343	100,00	100,00	



(86) Boc-1,4-cis-ACHC-L-Pro-Val^P(OPh-4-SCH₃)₂



Name: *tert*-butyl ((1*R*,4*s*)-4-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidine-1-carbonyl)cyclohexyl)carbamate

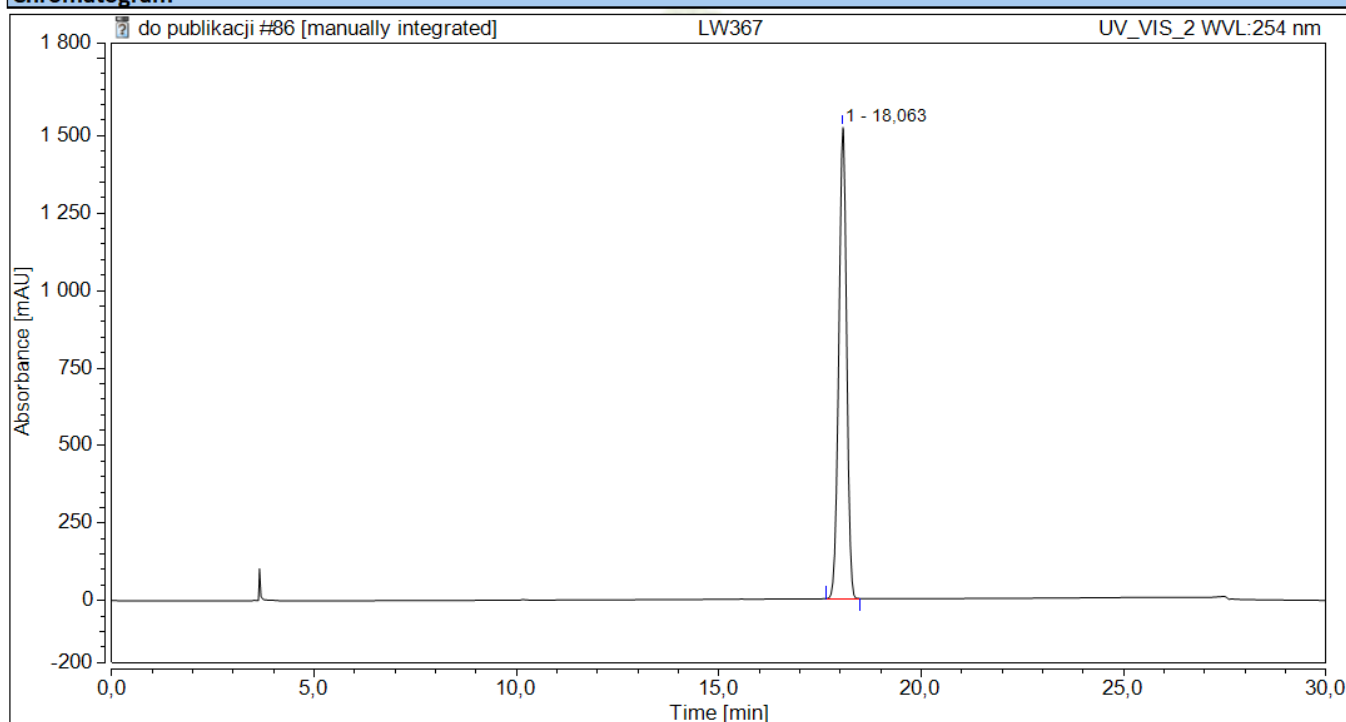
³¹P NMR (162 MHz, Chloroform-*d*) δ 18.01 (s, 48%), 17.96 (s, 52%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.53 (dd, *J* = 30.1, 10.4 Hz, 1H, NH), 7.22 – 6.89 (m, 8H, 8xArH), 4.84 – 4.47 (m, 2H, NH, CHP), 3.88 – 3.39 (m, 3H, CH, CH₂), 2.45 – 2.42 (m, 6H, 2xSCH₃), 2.42 – 1.46 (m, 15H, 6xCH₂, 3xCH), 1.43 (s, 9H, Boc), 1.16 – 0.95 (m, 6H, 2xCH₃).

HRMS: C₃₅H₅₀N₃O₇PS₂ [M+Na]⁺ calc. 742.2725 found 742.2712

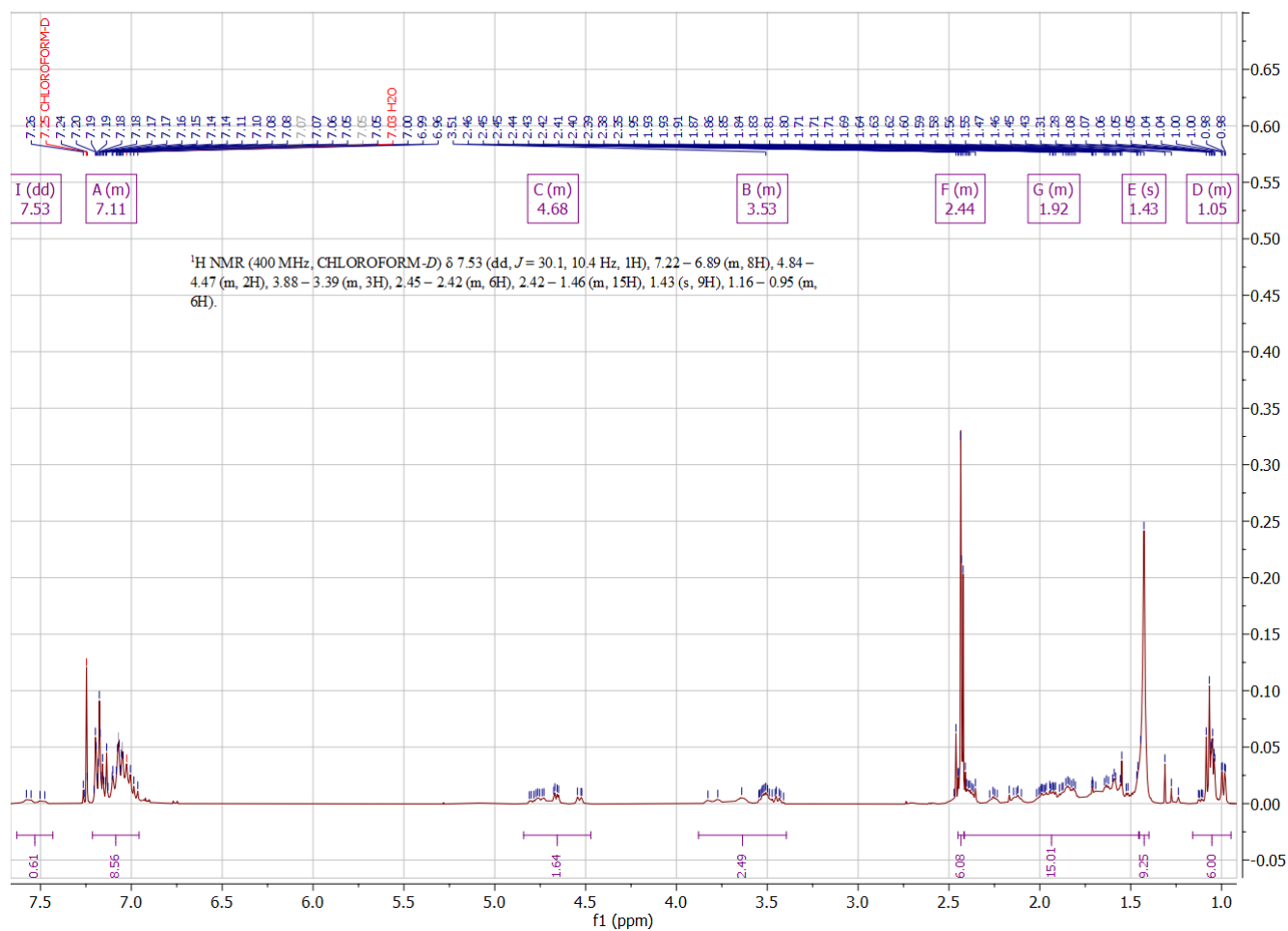
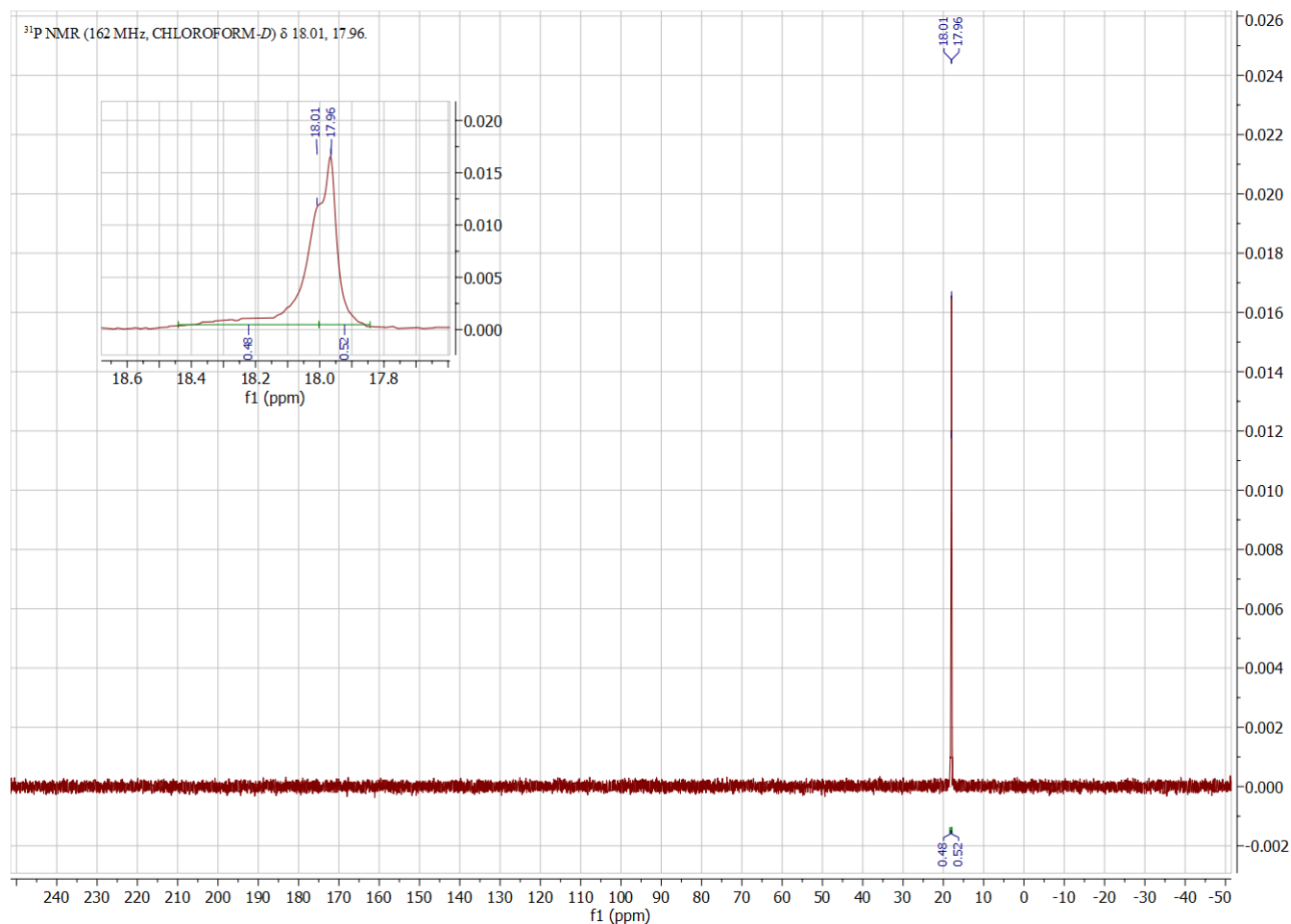
HPLC: purity >99%; retention time 18.063 min

Chromatogram

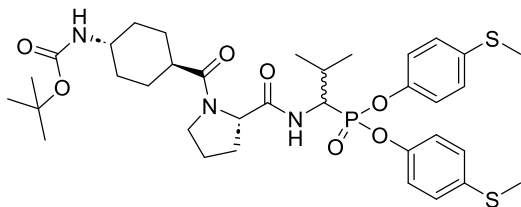


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18,063	341,633	1520,614	100,00	100,00	n.a.
Total:			341,633	1520,614	100,00	100,00	



(87) Boc-1,4-trans-ACHC-L-Pro-Val^P(OPh-4-SCH₃)₂



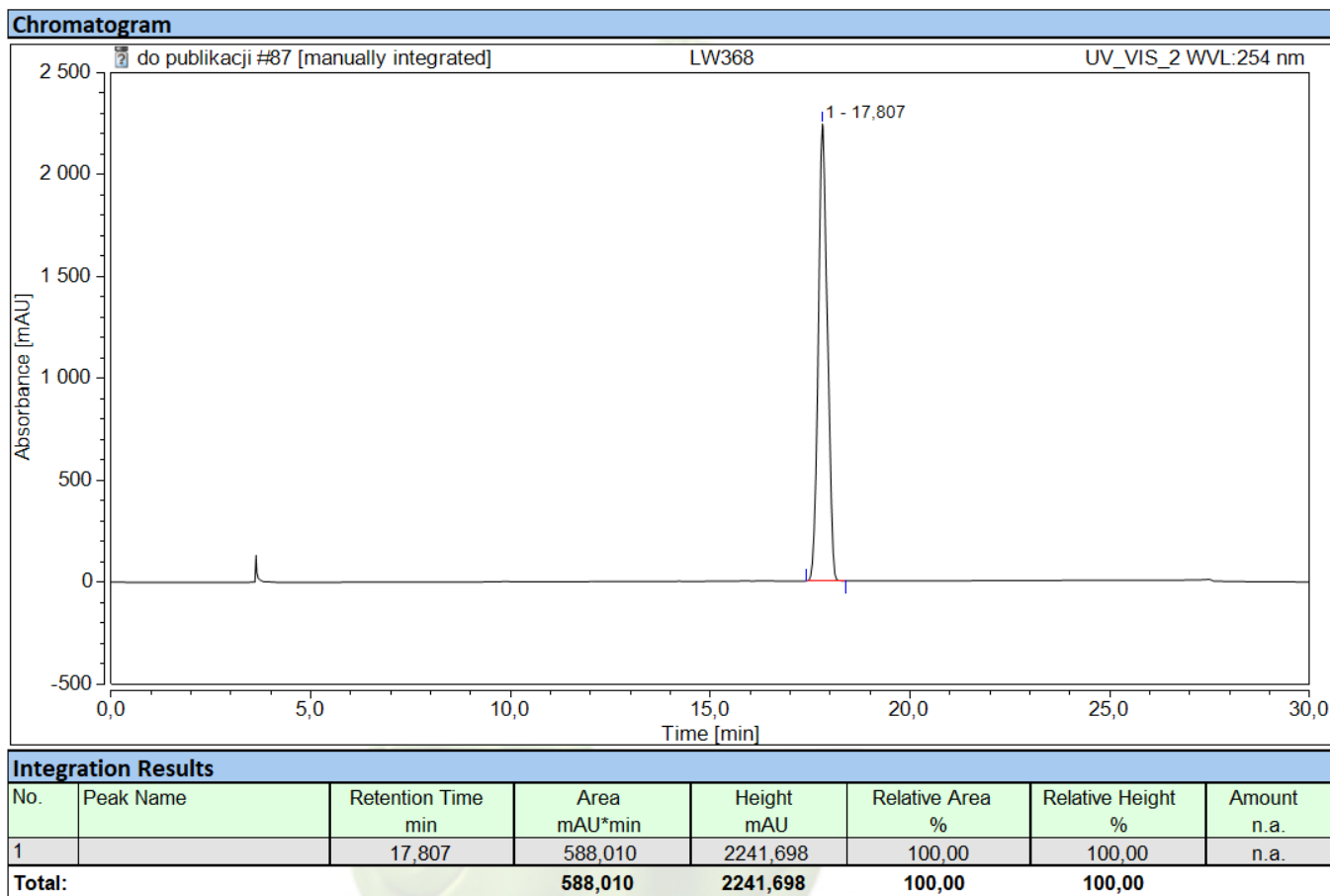
Name: *tert*-butyl ((1*S*,4*r*)-4-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidine-1-carbonyl)cyclohexyl)carbamate

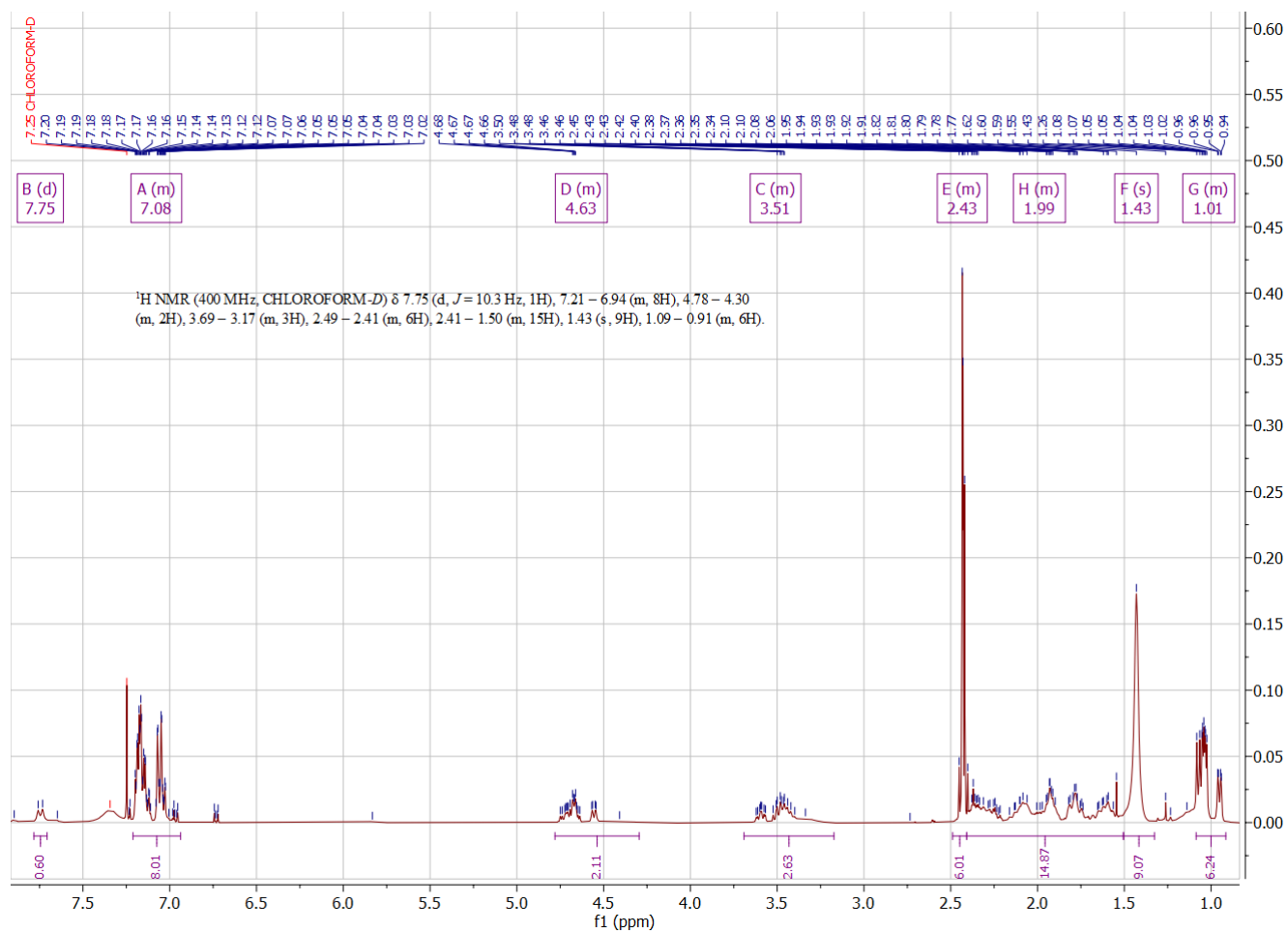
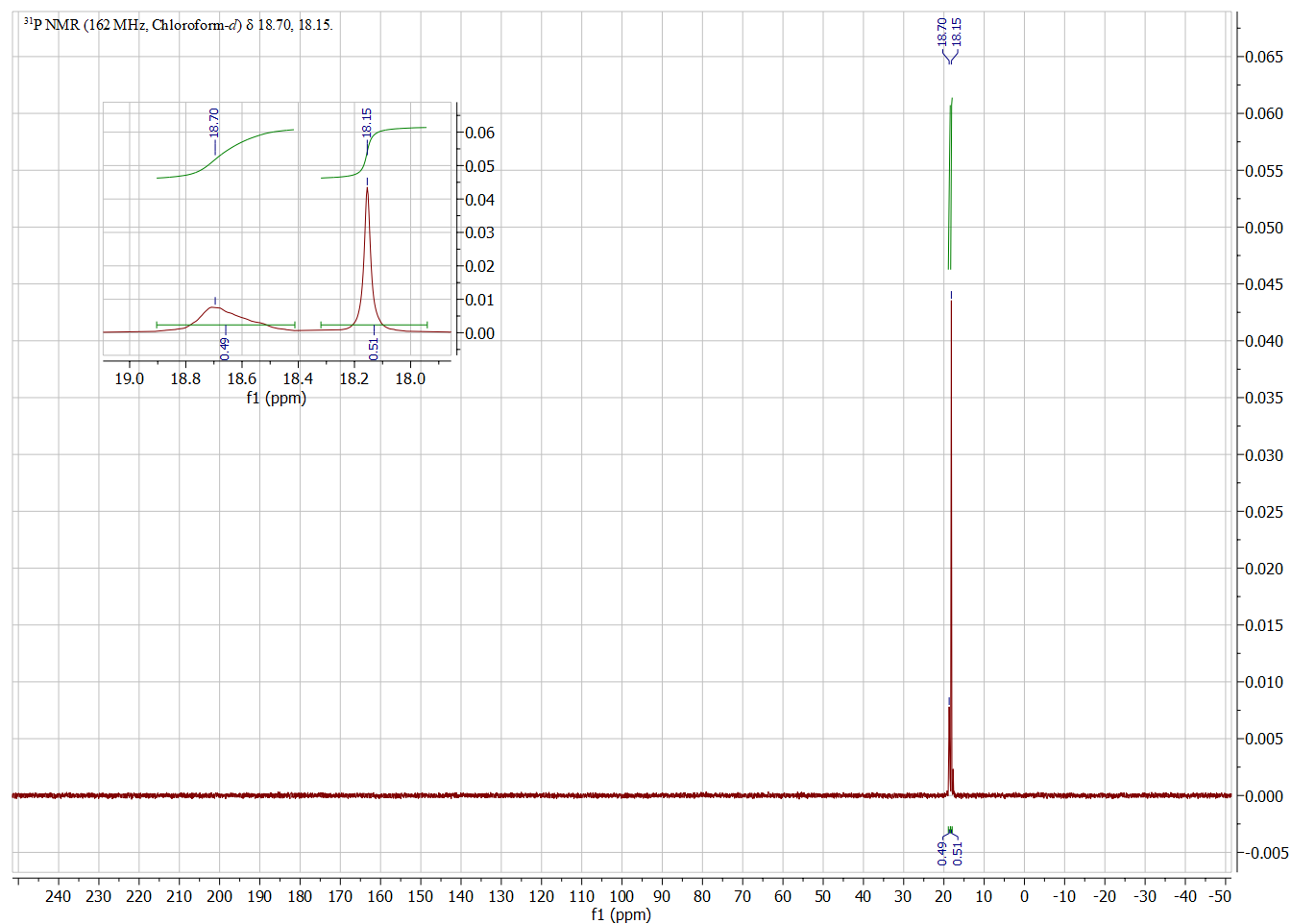
³¹P NMR (162 MHz, Chloroform-*d*) δ 18.70 (s, 49%), 18.15 (s, 51%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 10.3 Hz, 1H, NH), 7.21 – 6.94 (m, 8H, 8xArH), 4.78 – 4.30 (m, 2H, NH, CHP), 3.69 – 3.17 (m, 3H, CH₂, CH), 2.49 – 2.41 (m, 6H), 2.41 – 1.50 (m, 15H, 6xCH₂, 3xCH), 1.43 (s, 9H, Boc), 1.09 – 0.91 (m, 6H, 2xCH₃).

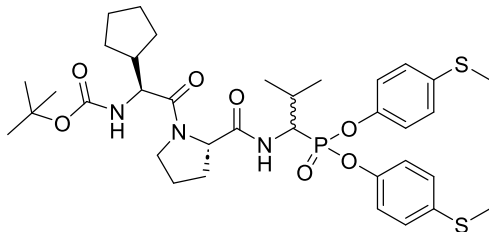
HRMS: C₃₅H₅₀N₃O₇PS₂ [M+Na]⁺ calc. 742.2725 found 742.2707

HPLC: purity >99%; retention time 17.807 min





(88) Boc-L-Cpg-L-Pro-Val^P(OPh-4-SCH₃)₂



Name: *tert*-butyl ((1*S*)-2-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-1-cyclopentyl-2-oxoethyl)carbamate

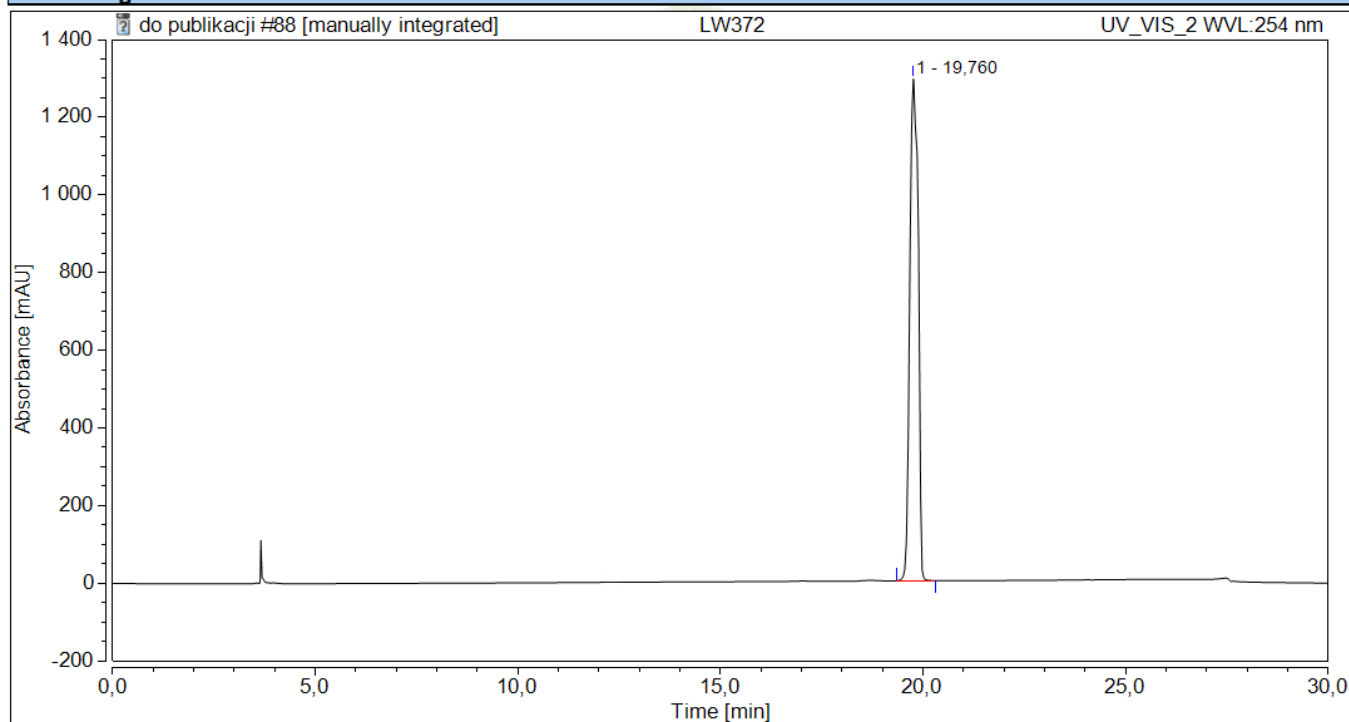
³¹P NMR (162 MHz, Chloroform-*d*) δ 18.36 (s, 48%), 17.98 (s, 52%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.25 (m, 1H, NH), 7.23 – 7.13 (m, 4H, 4xArH), 7.13 – 7.02 (m, 4H, 4xArH), 5.35 (dd, *J* = 30.9, 8.9 Hz, 1H, NH), 4.79 – 4.69 (m, 1H, CHP), 4.69 – 4.46 (m, 1H, CH), 4.40 – 4.27 (m, 1H, CH), 3.88 – 3.77 (m, 1H, 0.5xCH₂), 3.69 – 3.53 (m, 1H, 0.5xCH₂), 2.43 (d, *J* = 1.2 Hz, 6H, 2xSCH₃), 2.42 – 2.16 (m, 2H, 2xCH), 2.16 – 1.82 (m, 4H, 2xCH₂), 1.74 – 1.58 (m, 3H, 1.5xCH₂), 1.57 – 1.45 (m, 2H, CH₂), 1.40 (d, *J* = 2.3 Hz, 9H, Boc), 1.38 – 1.22 (m, 3H, 1.5xCH₂), 1.11 – 0.99 (m, 6H, 2xCH₃).

HRMS: C₃₅H₅₀N₃O₇PS₂ [M+Na]⁺ calc. 742.2725 found 742.2720

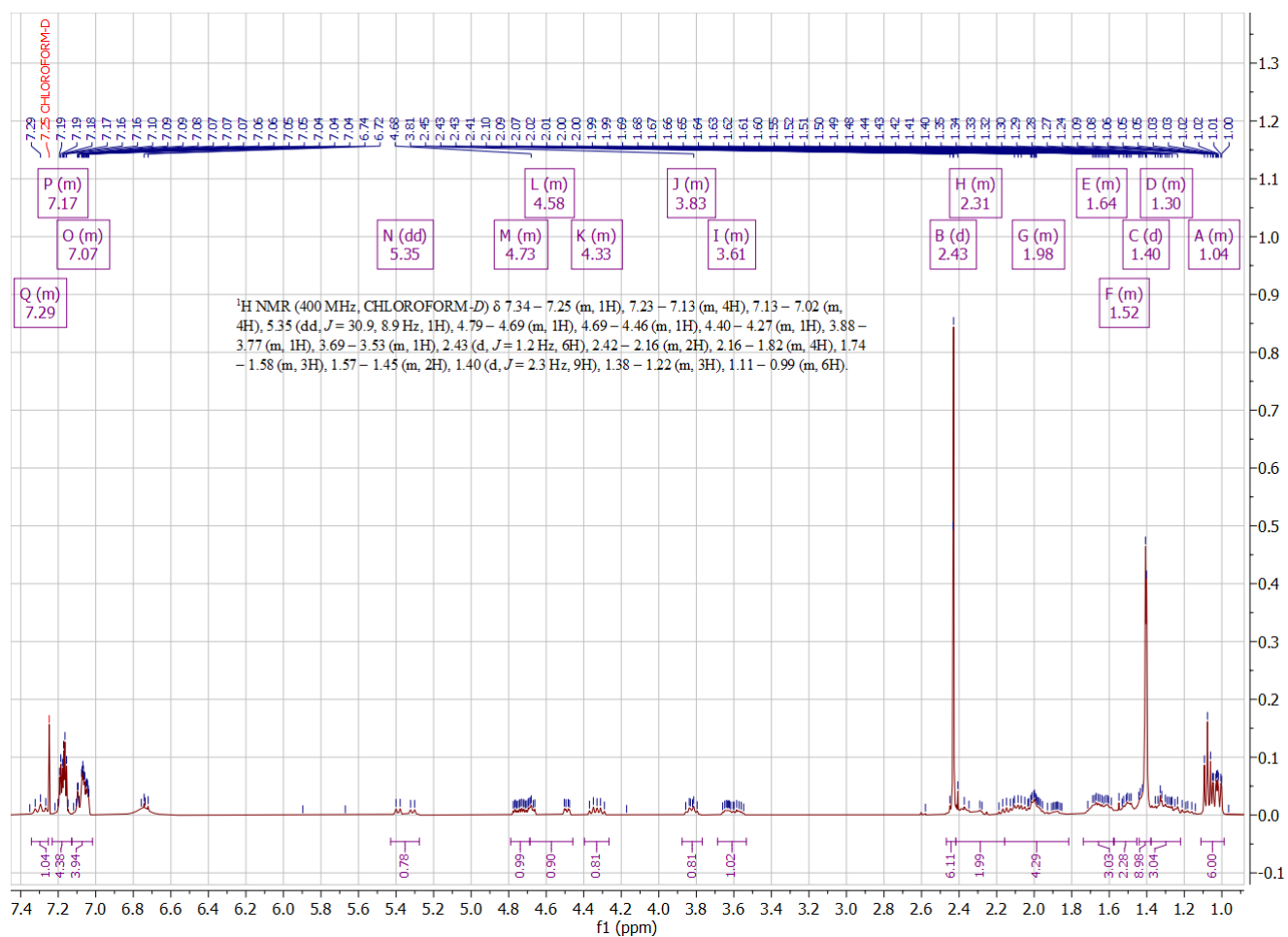
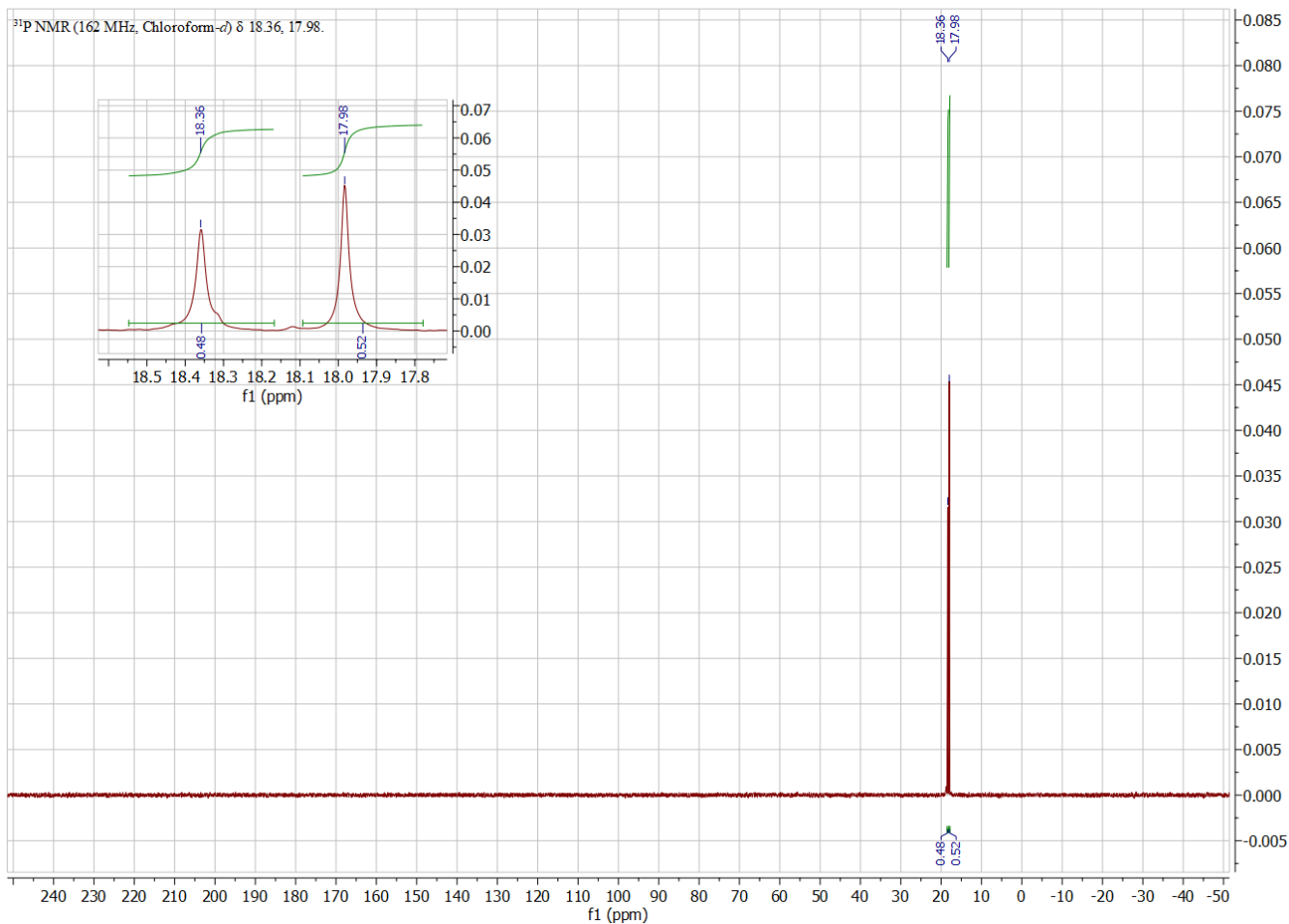
HPLC: purity >99%; retention time 19.760 min

Chromatogram

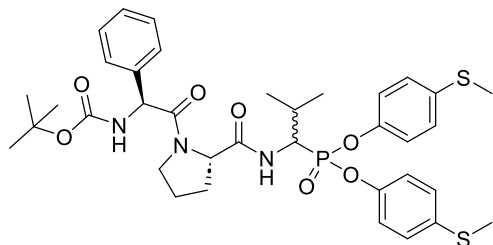


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19,760	312,769	1292,252	100,00	100,00	n.a.
Total:			312,769	1292,252	100,00	100,00	



(89) Boc-L-Phg-L-Pro-Val^P(OPh-4-SCH₃)₂



Name: *tert*-butyl ((1*S*)-2-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-2-oxo-1-phenylethyl)carbamate

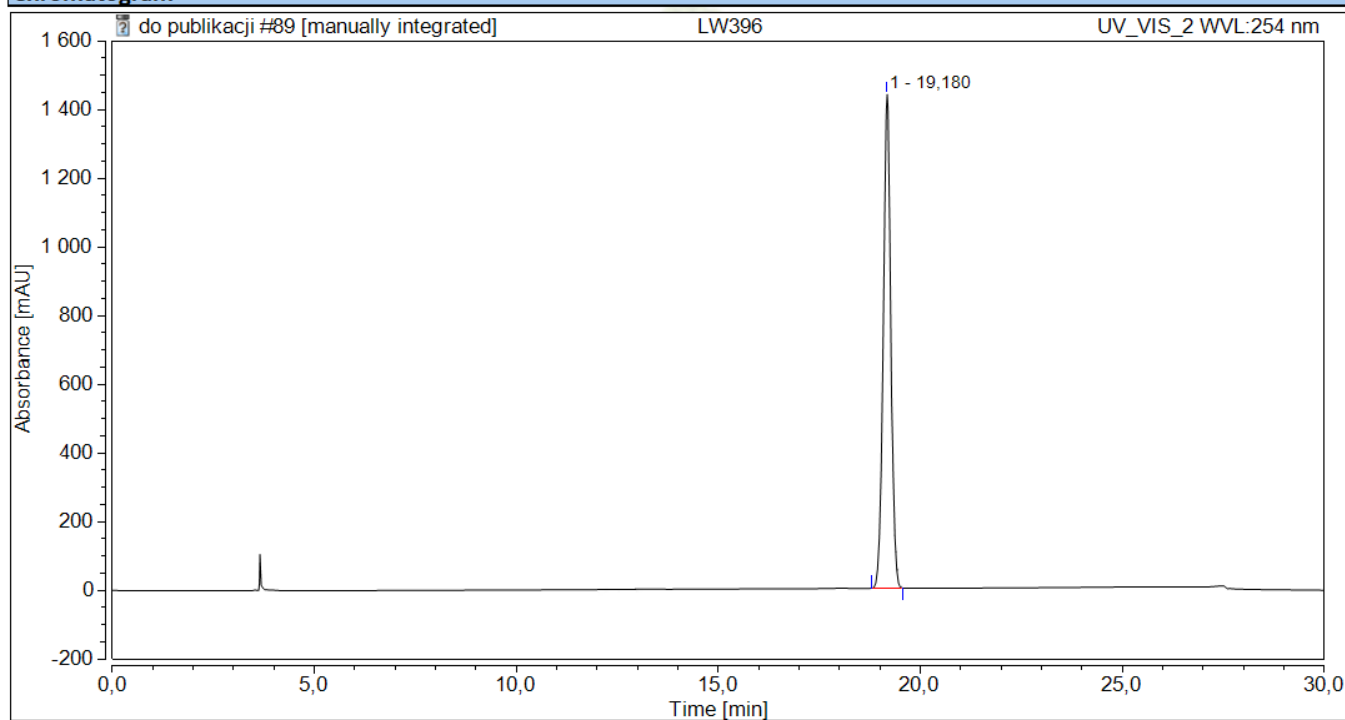
³¹P NMR (162 MHz, Chloroform-*d*) δ 18.39 (d, *J* = 4.2 Hz, 45%), 18.21 (s, 19%), 17.98 (s, 36%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.25 (m, 5H, 4xArH, NH), 7.22 – 7.11 (m, 6H, 6xArH), 7.11 – 6.96 (m, 3H, 3xArH), 5.92 – 5.72 (m, 1H, NH), 5.40 (dd, *J* = 31.5, 7.2 Hz, 1H, CH), 4.78 – 4.51 (m, 2H, CHP, CH), 3.76 – 3.53 (m, 1H, 0.5xCH₂), 3.34 – 3.01 (m, 1H, 0.5xCH₂), 2.46 – 2.40 (m, 6H, 2xSCH₃), 2.40 – 2.13 (m, 2H, 0.5xCH₂ CH), 2.03 – 1.62 (m, 3H, 1.5xCH₂), 1.45 – 1.31 (m, 9H, Boc), 1.13 – 0.85 (m, 6H, 2xCH₃).

HRMS: C₃₆H₄₆N₃O₇PS₂ [M+Na]⁺ calc. 750.2412 found 750.2407

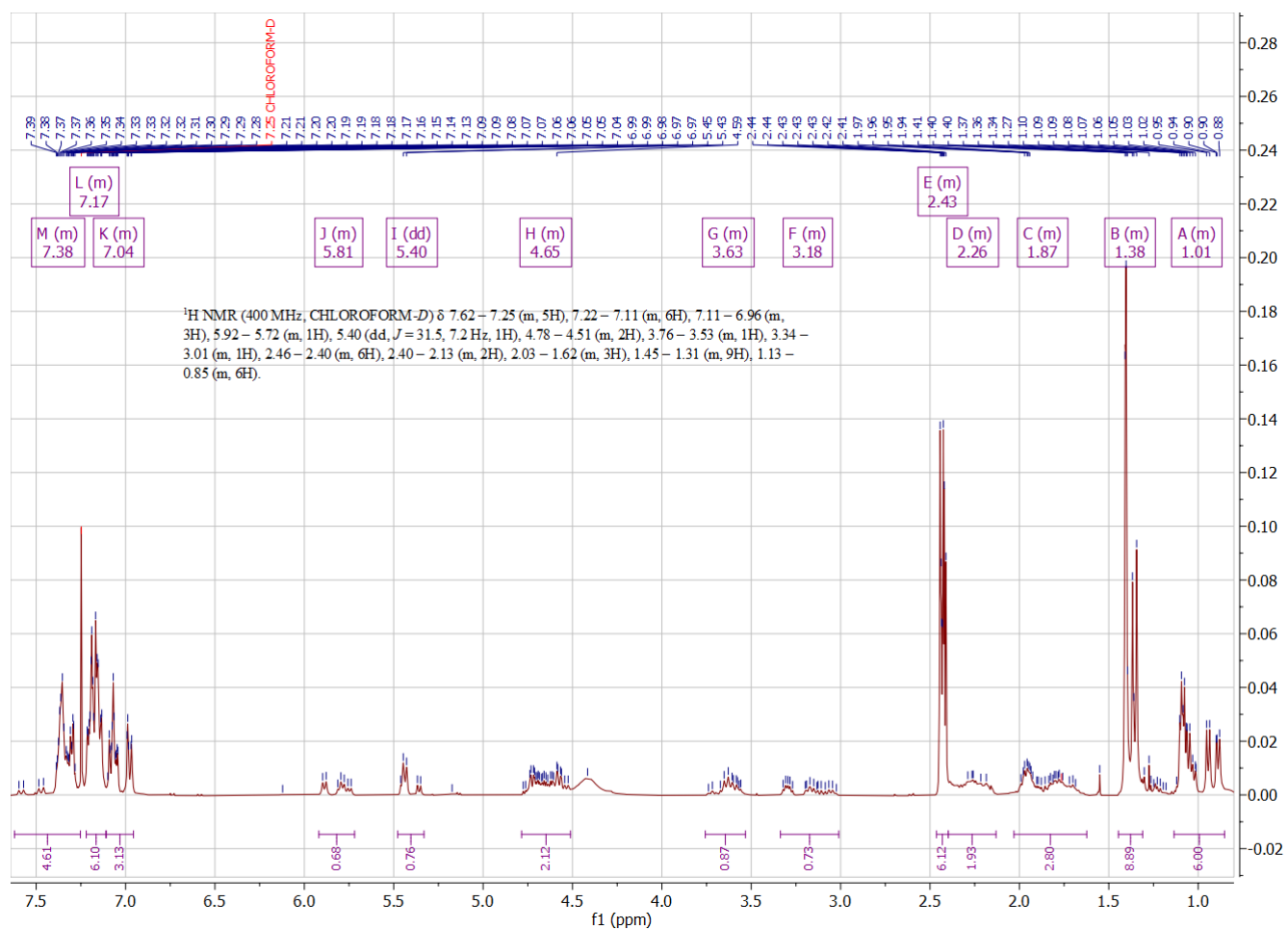
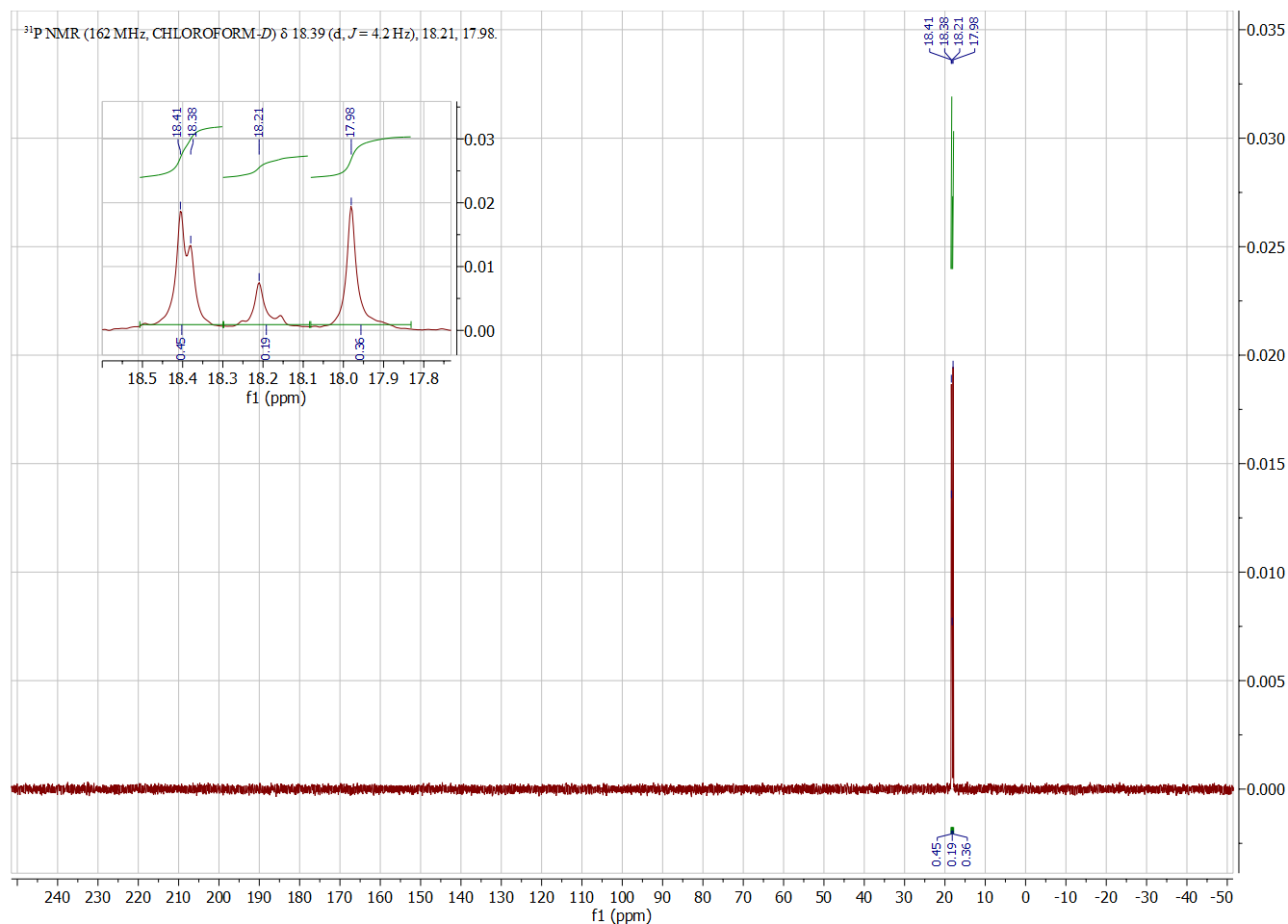
HPLC: purity >99%; retention time 19.180 min

Chromatogram

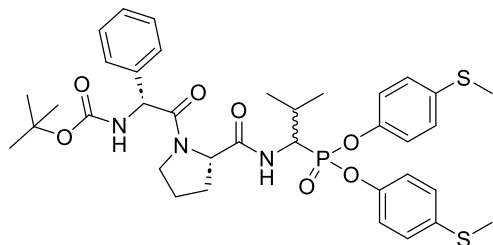


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19,180	334,417	1437,657	100,00	100,00	n.a.
Total:			334,417	1437,657	100,00	100,00	



(90) Boc-D-Phg-L-Pro- Val^P(OPh-4-SCH₃)₂



Name: *tert*-butyl ((1*R*)-2-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-2-oxo-1-phenylethyl)carbamate

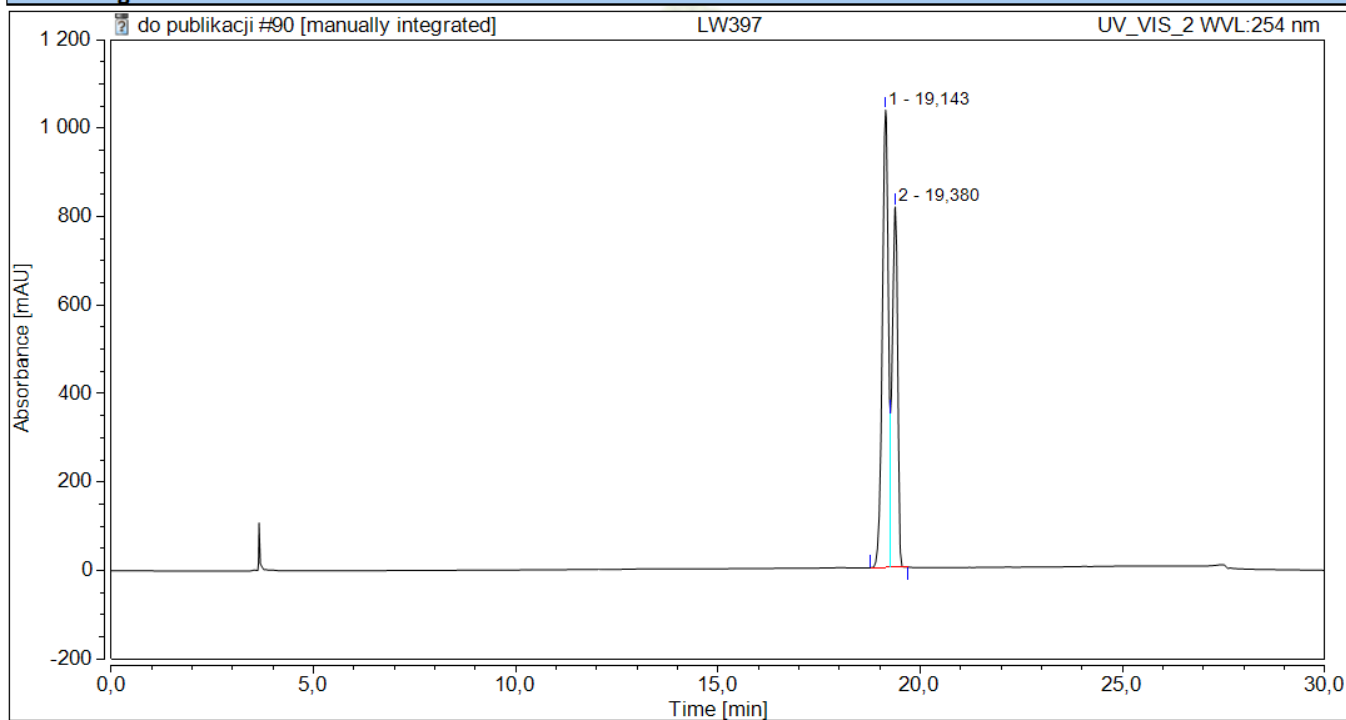
³¹P NMR (162 MHz, Chloroform-*d*) δ 18.46(s, 61%), 18.28 (s, 39%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.42 (m, 1H, NH), 7.42 – 7.27 (m, 5H, 5xArH), 7.22 – 7.14 (m, 6H, 6xArH), 7.13 – 7.03 (m, 2H, 2xArH), 5.77 (dd, *J* = 18.9, 7.6 Hz, 1H, NH), 5.40 (dd, *J* = 37.6, 7.5 Hz, 1H, CH), 4.79 – 4.64 (m, 1H, CHP), 4.64 – 4.50 (m, 1H, CH), 3.77 – 3.53 (m, 1H, 0.5xCH₂), 3.23 – 2.95 (m, 1H, 0.5xCH₂), 2.49 – 2.42 (m, 6H, 2xSCH₃), 2.42 – 1.86 (m, 3H, CH₂, CH), 1.86 – 1.59 (m, 2H, CH₂), 1.41 – 1.30 (m, 9H, Boc), 1.13 – 0.91 (m, 6H, 2xCH₃).

HRMS: C₃₆H₄₆N₃O₇PS₂ [M+Na]⁺ calc. 750.2412 found 750.2410

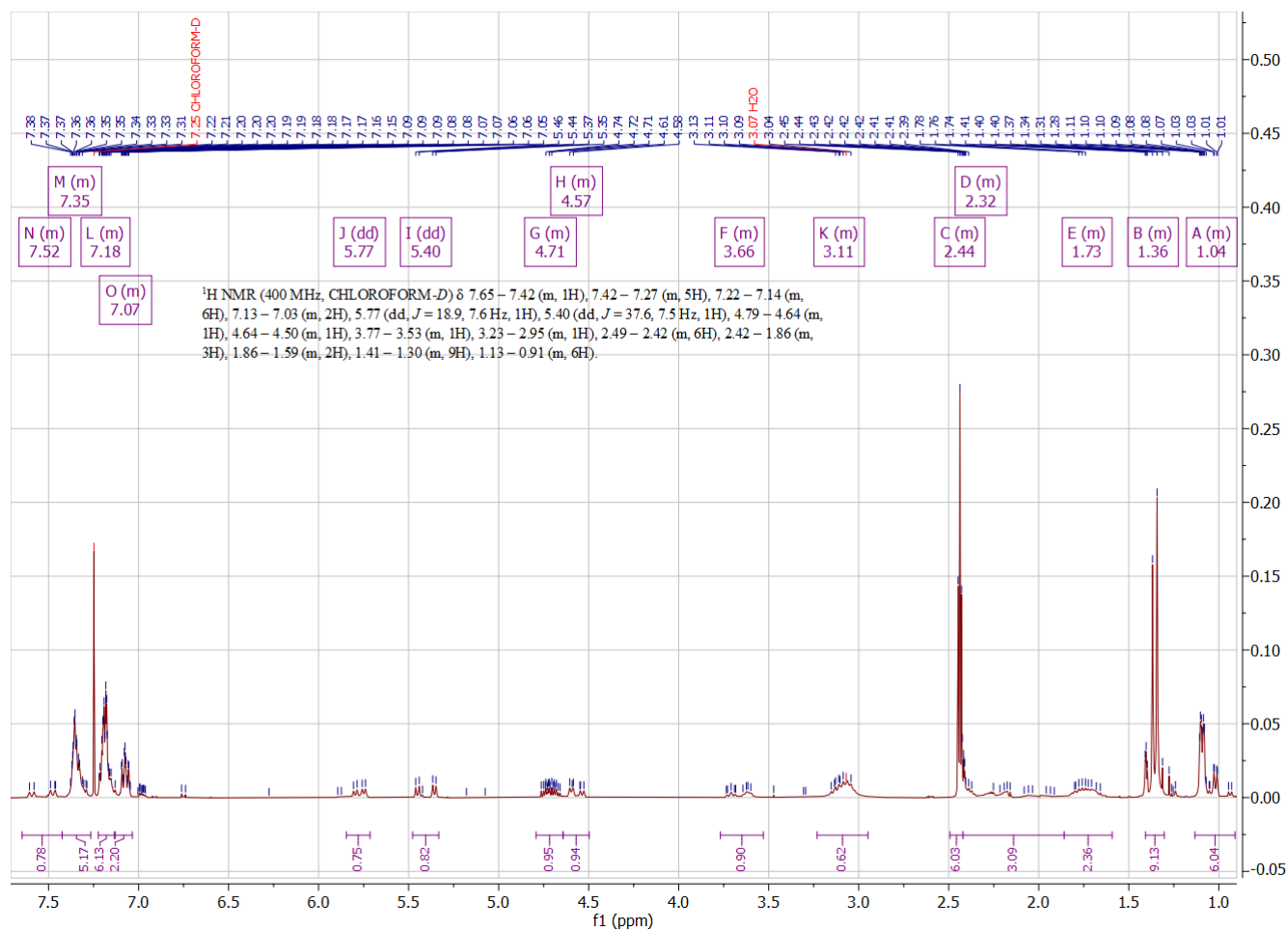
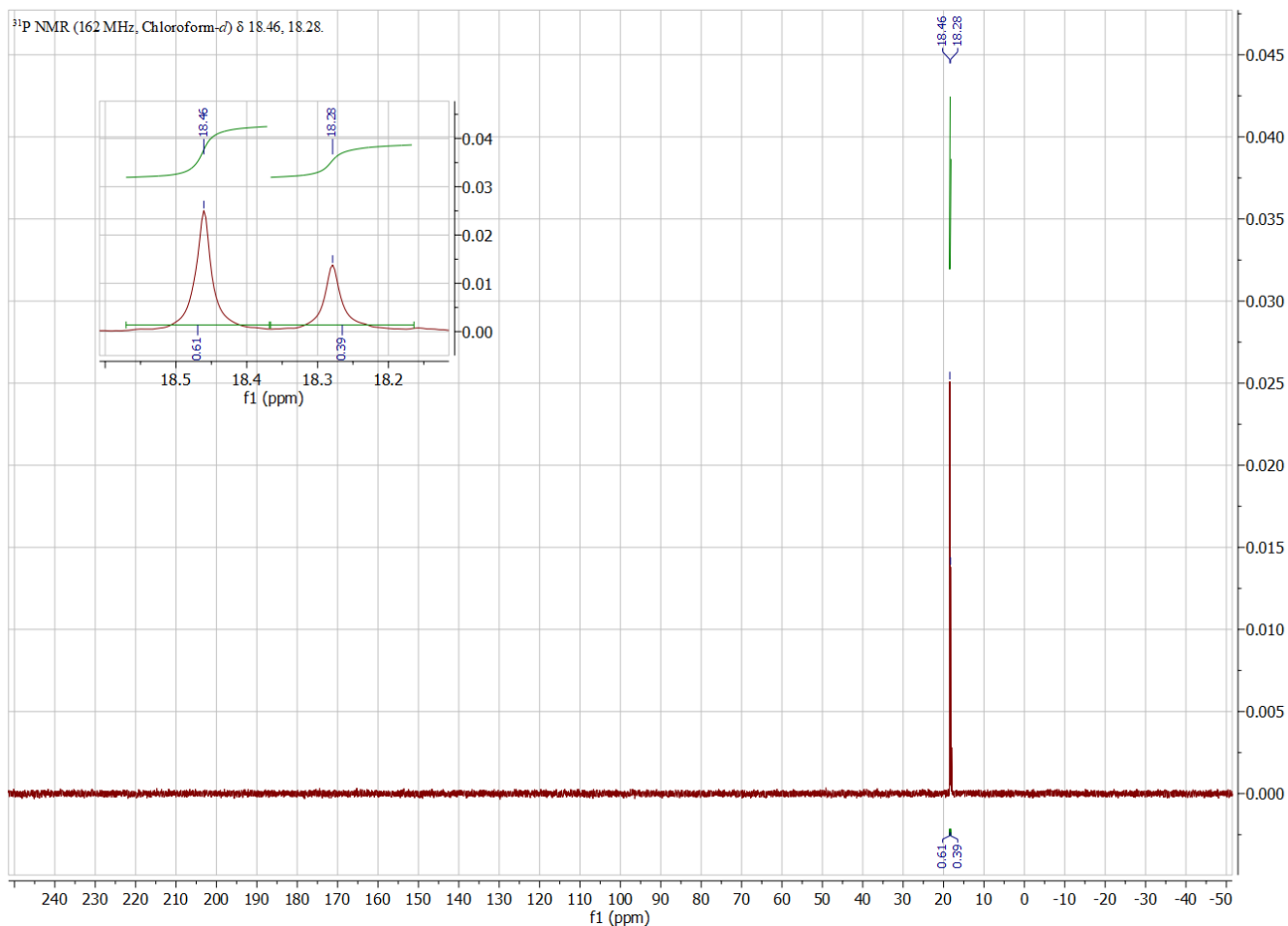
HPLC: purity >99%; retention time 19.143 and 19.380 min

Chromatogram

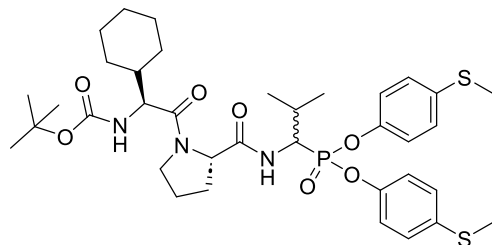


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		19,143	177,972	1034,360	58,38	55,93	n.a.
2		19,380	126,870	814,931	41,62	44,07	n.a.
Total:			304,843	1849,291	100,00	100,00	



(91) Boc-L-Chg-L-Pro-Val^P(OPh-4-SCH₃)₂



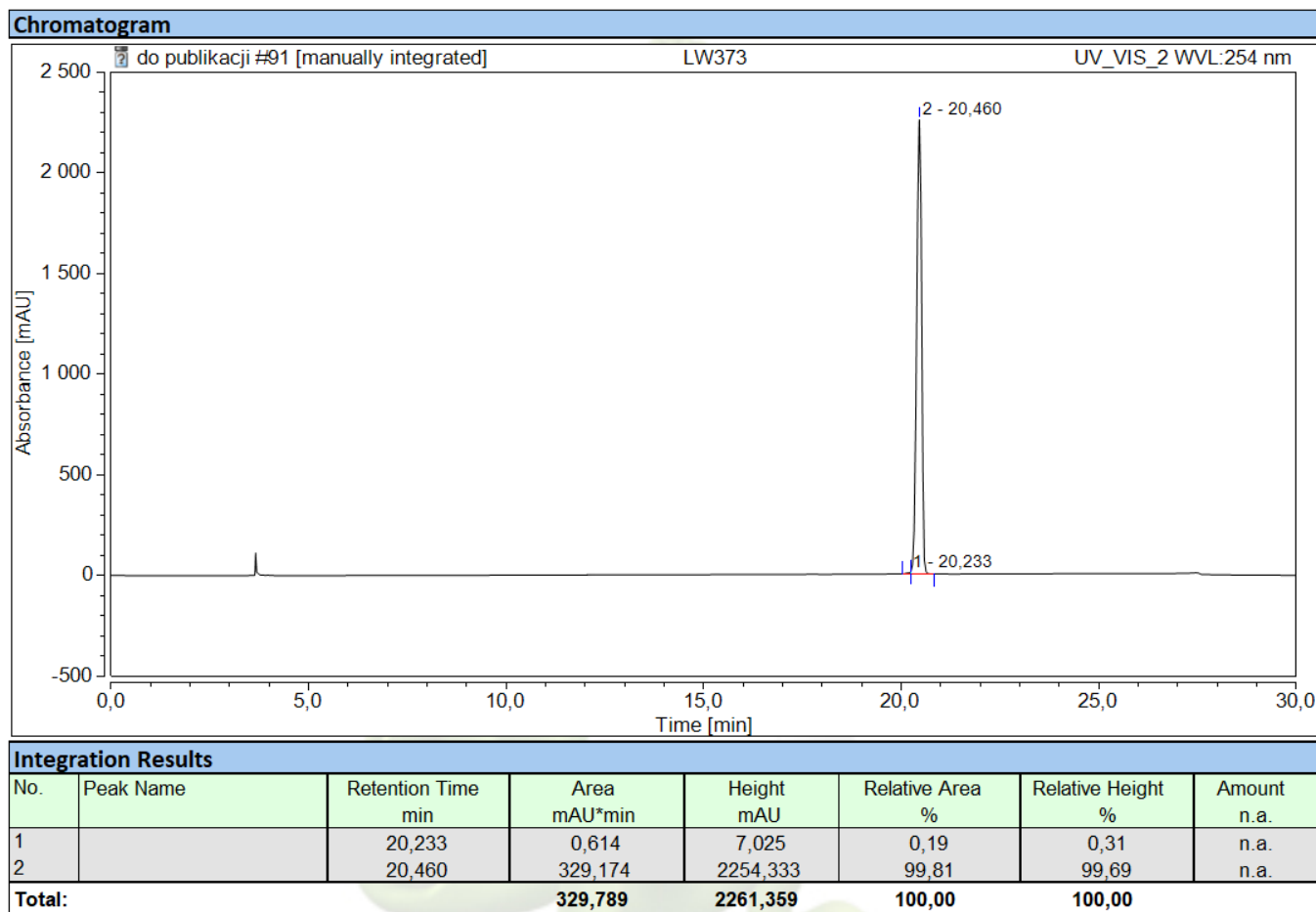
Name: *tert*-butyl ((1*S*)-2-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-1-cyclohexyl-2-oxoethyl)carbamate

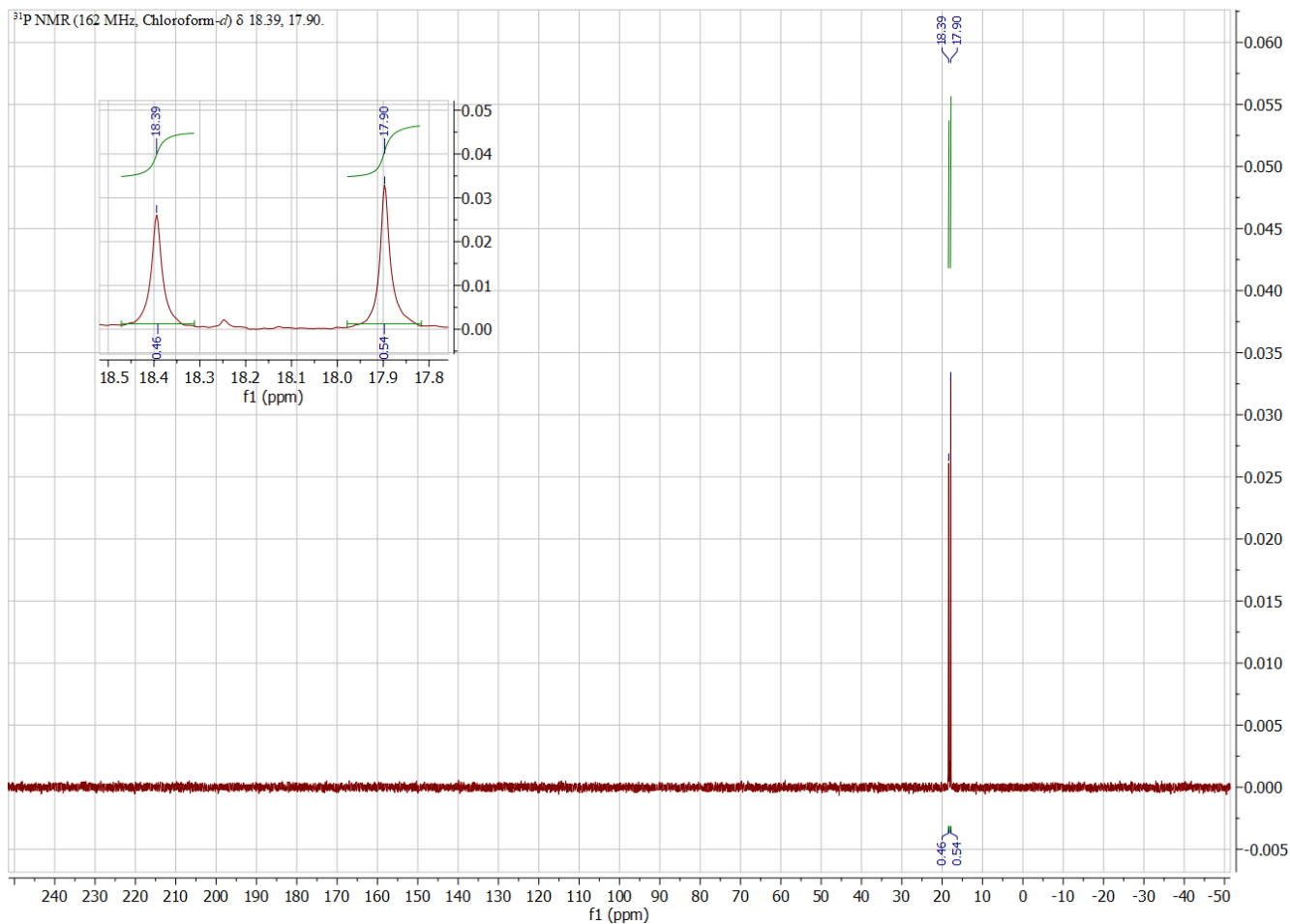
³¹P NMR (162 MHz, Chloroform-*d*) δ 18.39 (s, 46%), 17.90 (s, 54%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.35 (dd, *J* = 35.8, 10.1 Hz, 1H, NH), 7.23 – 7.02 (m, 8H, 8xArH), 5.35 (dd, *J* = 19.6, 9.2 Hz, 1H, NH), 4.79 – 4.68 (m, 1H, CHP), 4.68 – 4.47 (m, 1H, CH), 4.30 – 4.21 (m, 1H, CH), 3.86 – 3.74 (m, 1H, 0.5xCH₂), 3.67 – 3.55 (m, 1H, 0.5xCH₂), 2.47 – 2.42 (m, 6H, 2xSCH₃), 2.42 – 2.30 (m, 1H, CH), 2.30 – 1.98 (m, 3H, CH₂, CH), 1.98 – 1.47 (m, 7H, 3.5xCH₂), 1.41 (s, 9H, Boc), 1.26 – 0.86 (m, 11H, 2xCH₃, 2.5xCH₂).

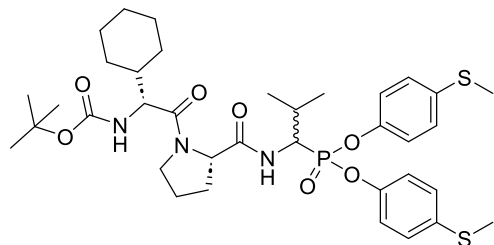
HRMS: C₃₆H₅₂N₃O₇PS₂ [M+Na]⁺ calc. 756.2882 found 756.2870

HPLC: purity >99%; retention time 20.460 min





(92) Boc-D-Chg-L-Pro-Val^P(OPh-4-SCH₃)₂



Name: *tert*-butyl ((1*R*)-2-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-1-cyclohexyl-2-oxoethyl)carbamate

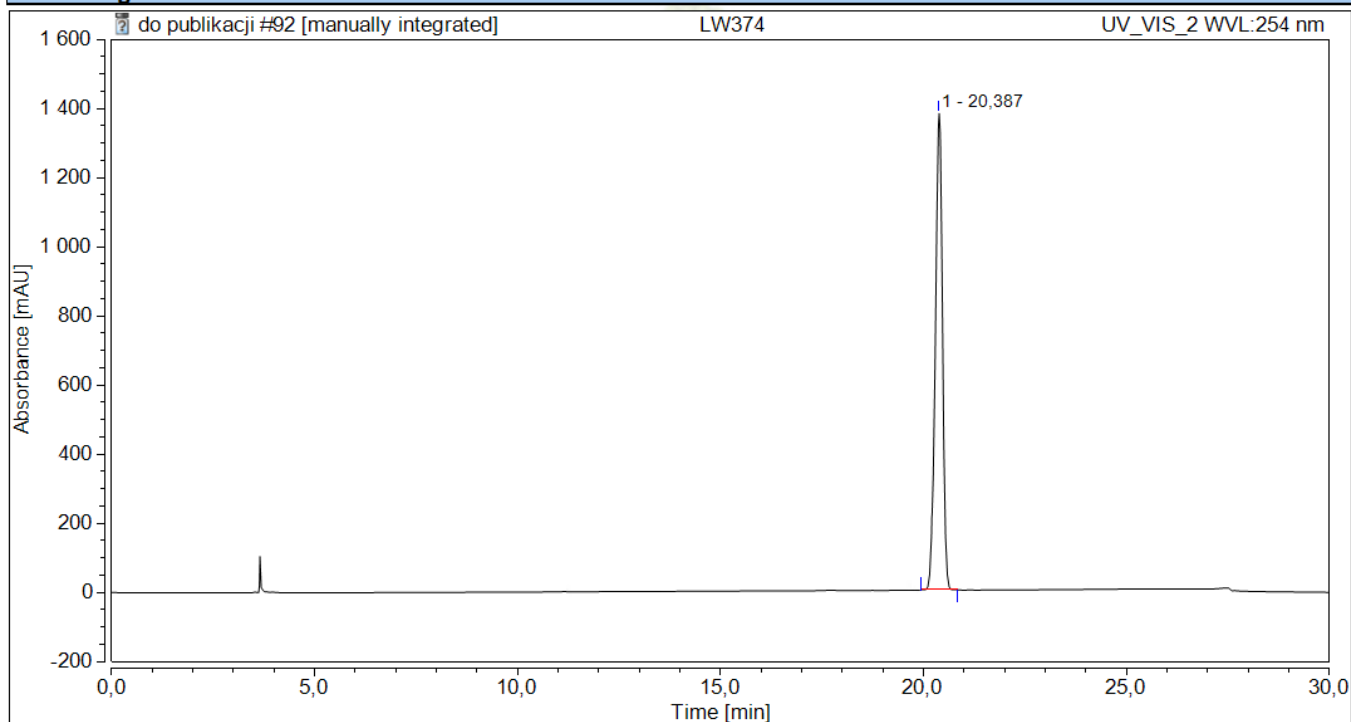
³¹P NMR (162 MHz, Chloroform-*d*) δ 18.19 (s, 55%), 18.04 (s, 45%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.54 (dd, *J* = 112.7, 10.2 Hz, 1H, NH), 7.23 – 7.15 (m, 4H, 4xArH), 7.14 – 6.96 (m, 4H, 4xArH), 5.37 – 5.25 (m, 1H, NH), 4.77 – 4.64 (m, 1H, CHP), 4.59 (dd, *J* = 26.1, 8.1 Hz, 1H, CH), 4.34 – 4.17 (m, 1H, CH), 3.95 – 3.82 (m, 1H, 0.5xCH₂), 3.62 – 3.46 (m, 1H, 0.5xCH₂), 2.43 (d, *J* = 3.1 Hz, 6H, 2xSCH₃), 2.40 – 2.24 (m, 1H, CH), 2.24 – 1.94 (m, 2H, 0.5xCH₂, CH), 1.94 – 1.52 (m, 8H, 4xCH₂), 1.46 – 1.30 (m, 9H, Boc), 1.29 – 0.93 (m, 11H, 2xCH₃, 2.5xCH₂).

HRMS: C₃₆H₅₂N₃O₇PS₂ [M+Na]⁺ calc. 756.2882 found 756.2872

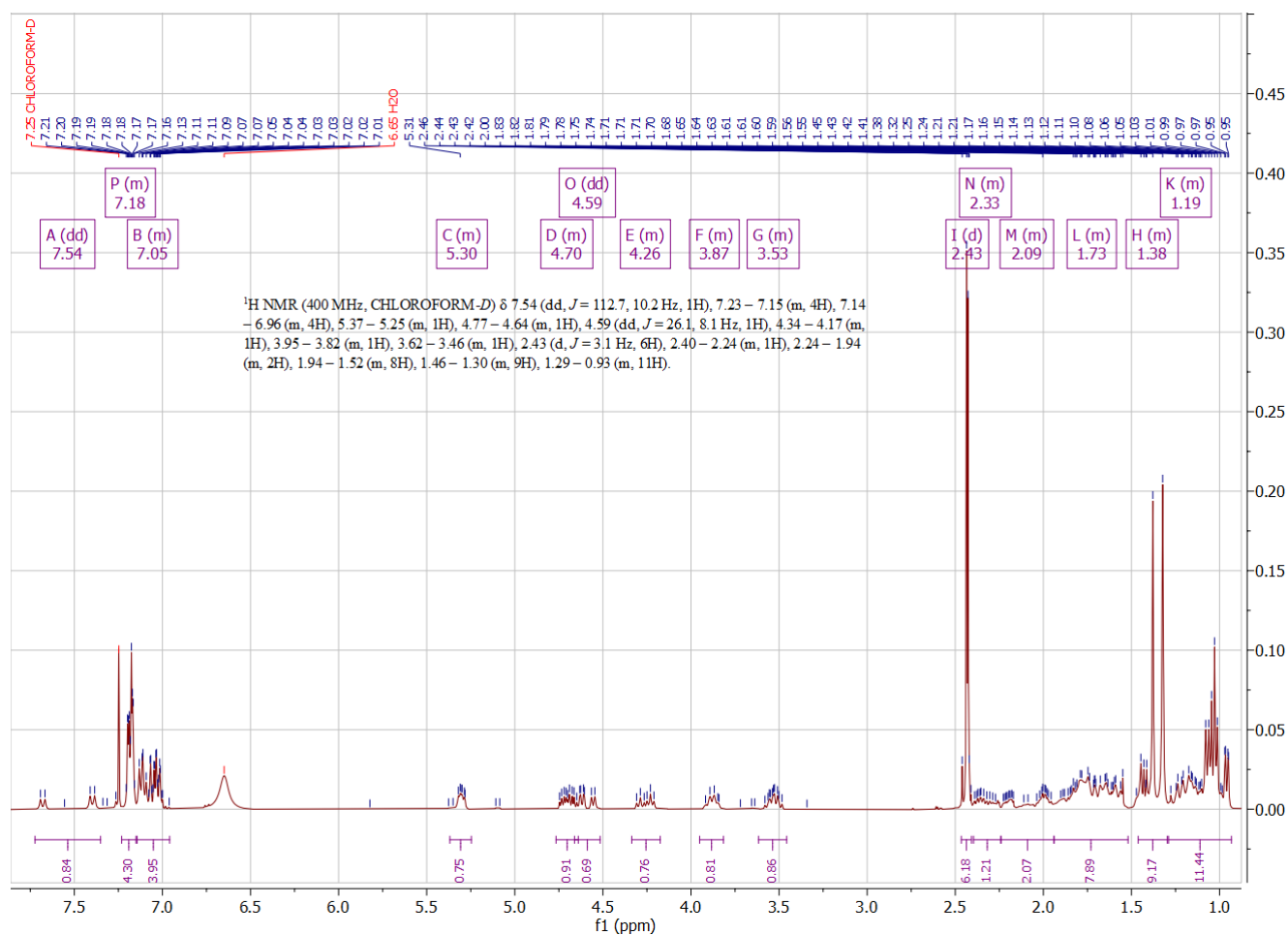
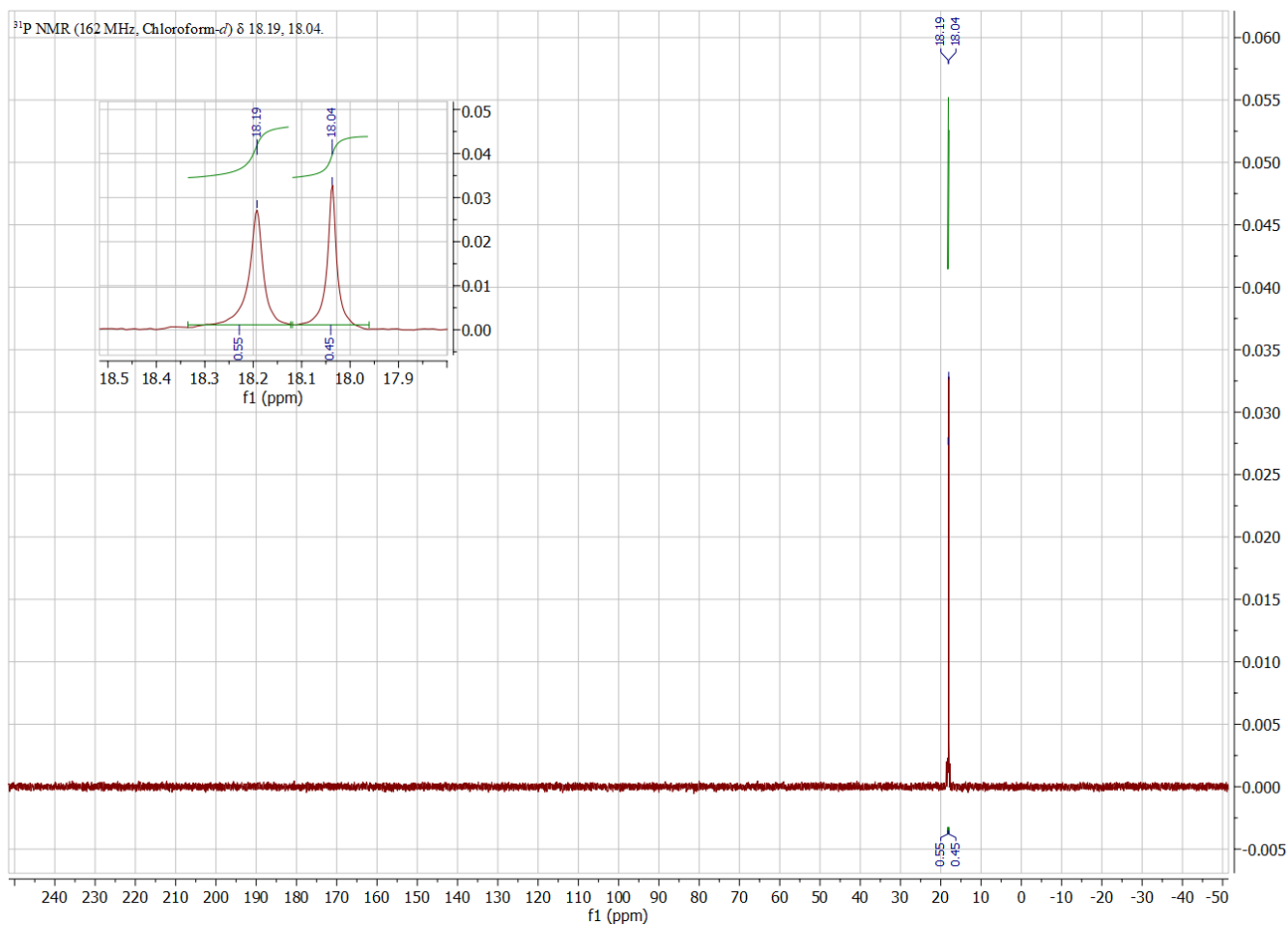
HPLC: purity >99%; retention time 20.387 min

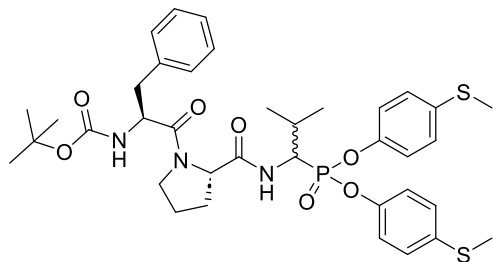
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20,387	280,330	1377,415	100,00	100,00	n.a.
Total:			280,330	1377,415	100,00	100,00	



(93) Boc-L-Phe-L-Pro-Val^P(OPh-4-SCH₃)₂

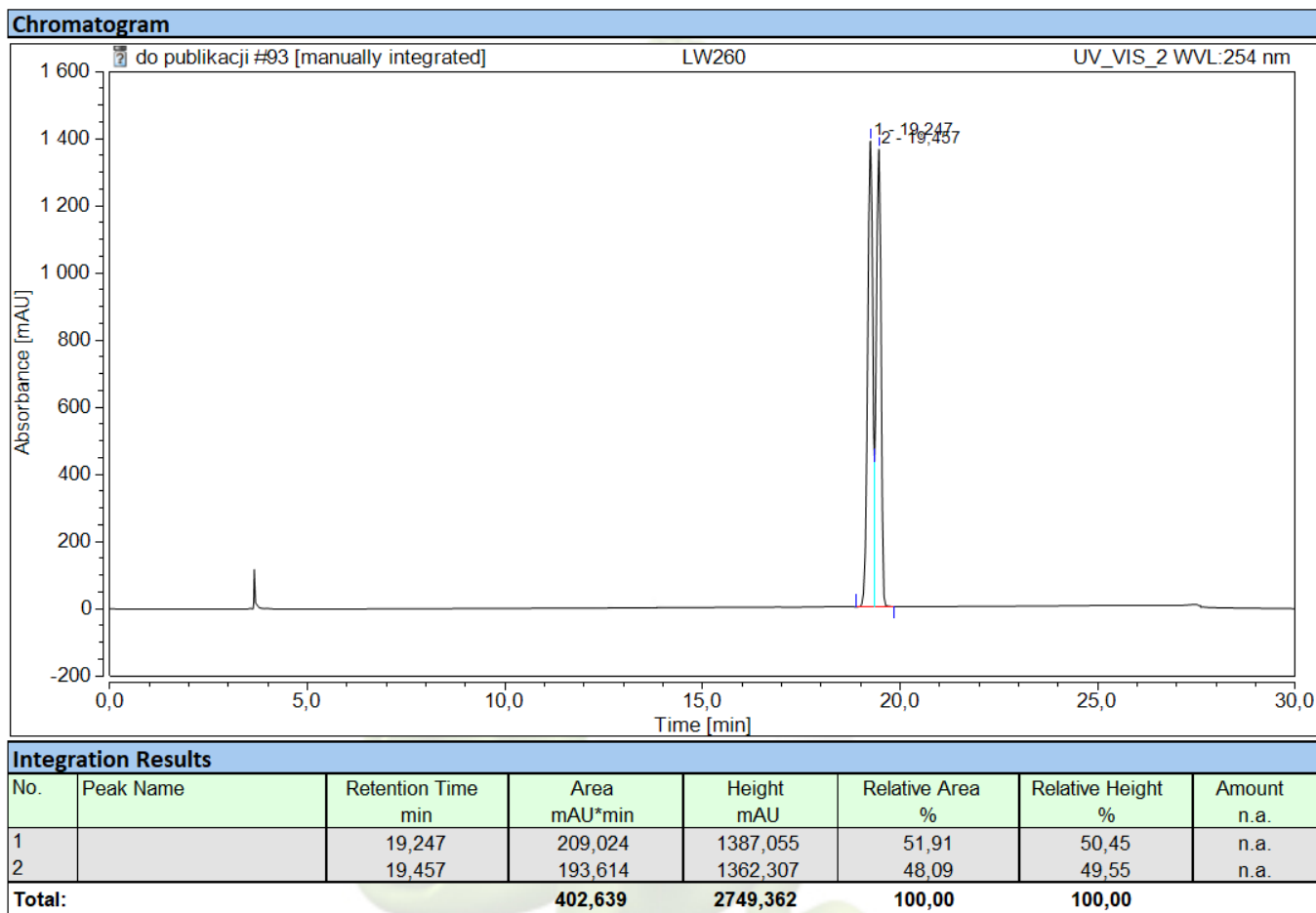
Name: *tert*-butyl ((2*S*)-1-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-1-oxo-3-phenylpropan-2-yl)carbamate

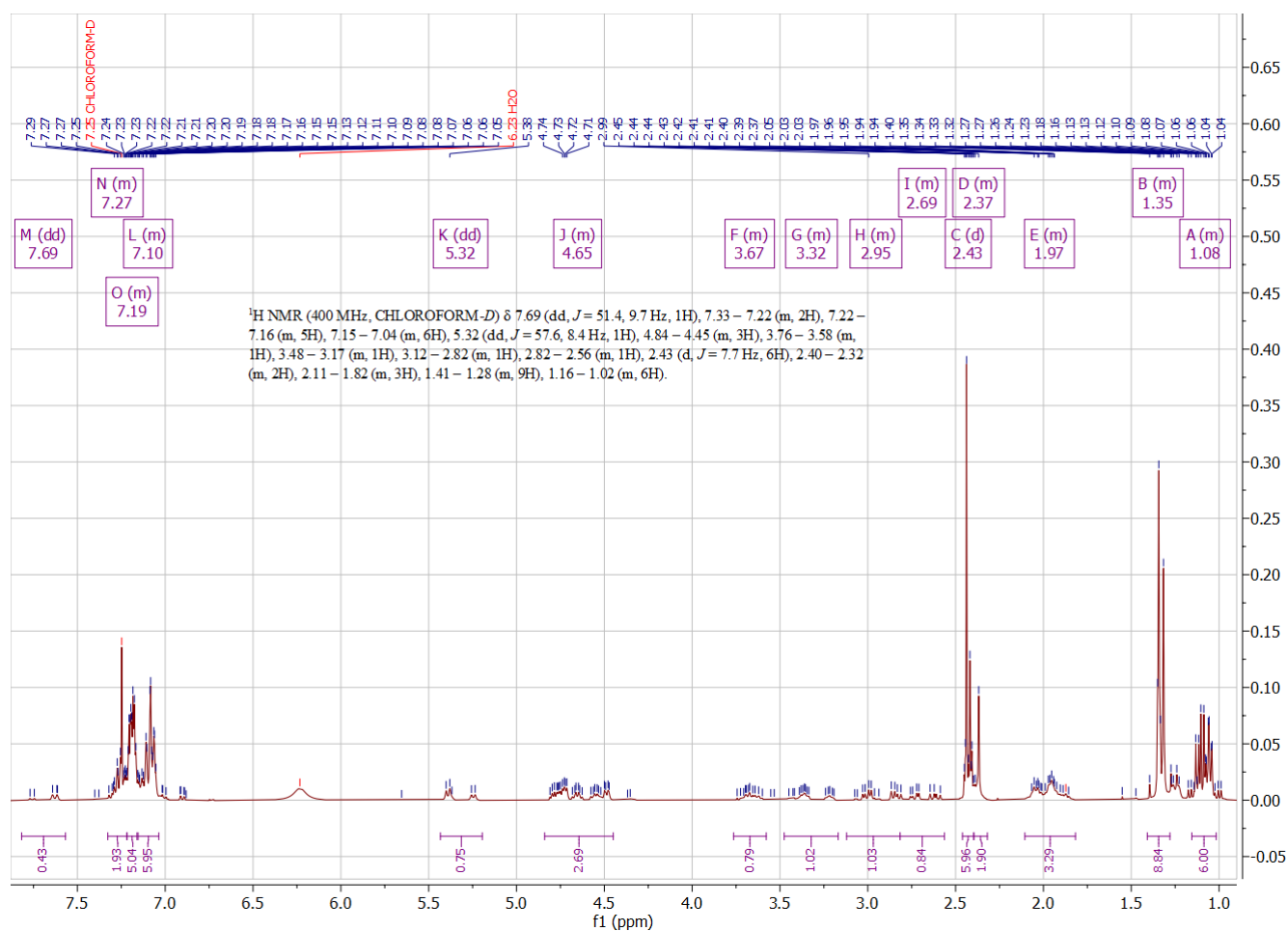
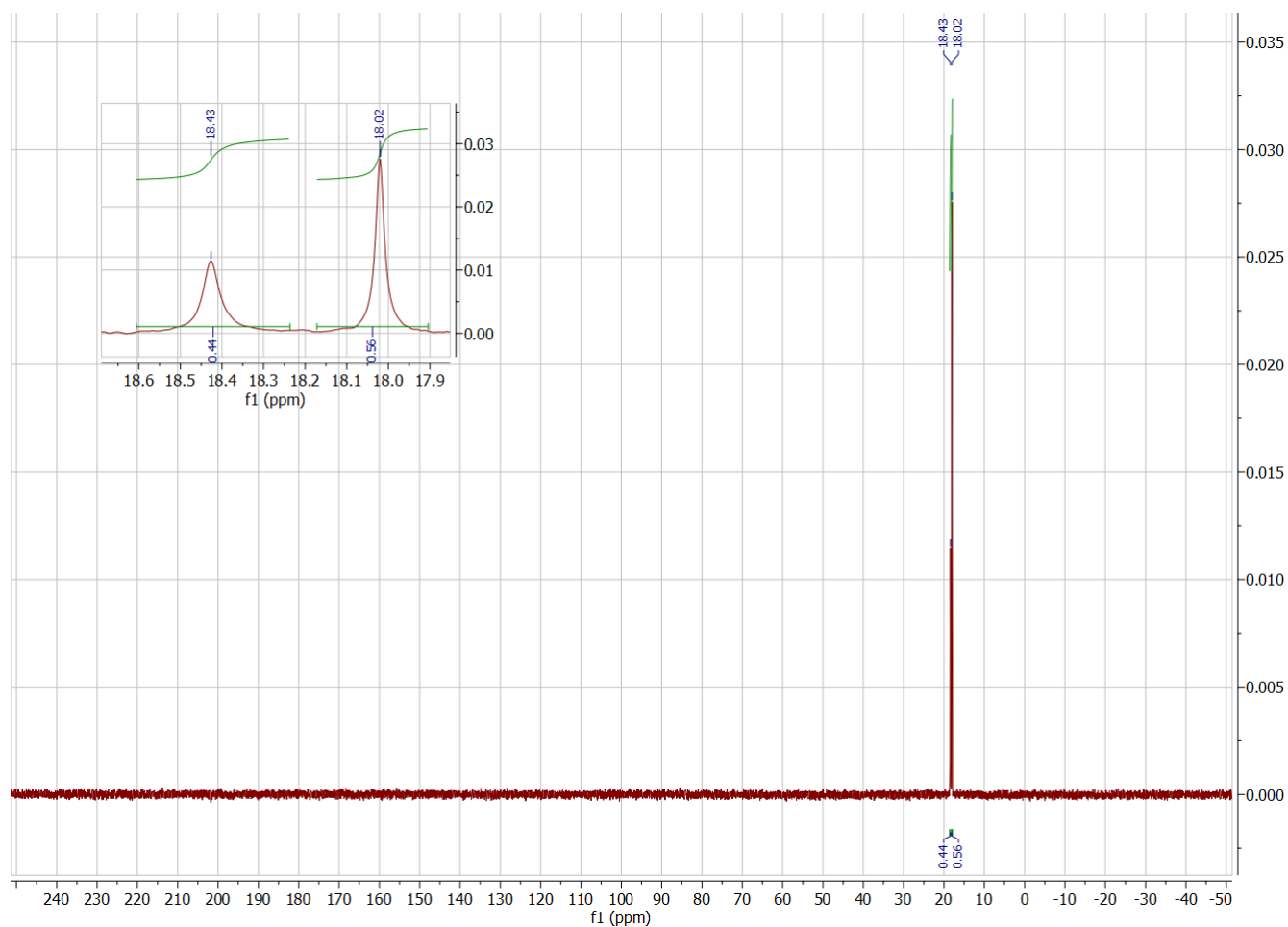
³¹P NMR (162 MHz, Chloroform-*d*) δ 18.43 (s, 44%), 18.02 (s, 56%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.69 (dd, *J* = 51.4, 9.7 Hz, 1H, NH), 7.33 – 7.22 (m, 2H, 2xArH), 7.22 – 7.16 (m, 5H, 5xArH), 7.15 – 7.04 (m, 6H, 6xArH), 5.32 (dd, *J* = 57.6, 8.4 Hz, 1H, NH), 4.84 – 4.45 (m, 3H, CHP, 2xCH), 3.76 – 3.58 (m, 1H, 0.5xCH₂), 3.48 – 3.17 (m, 1H, 0.5xCH₂), 3.12 – 2.82 (m, 1H, 0.5xCH₂), 2.82 – 2.56 (m, 1H, 0.5xCH₂), 2.43 (d, *J* = 7.7 Hz, 6H, 2xSCH₃), 2.40 – 2.32 (m, 2H, 0.5xCH₂, CH), 2.11 – 1.82 (m, 3H, 1.5xCH₂), 1.41 – 1.28 (m, 9H, Boc), 1.16 – 1.02 (m, 6H, 2xCH₃).

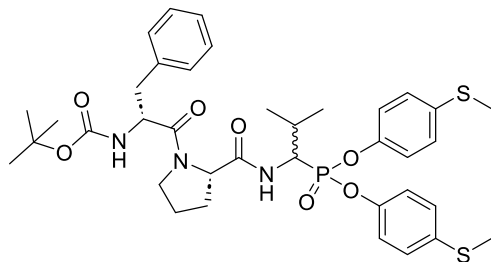
HRMS: C₃₇H₄₈N₃O₇PS₂ [M+Na]⁺ calc. 764.2569 found 764.2561

HPLC: purity >99%; retention time 19.247 and 19.457 min





(94) Boc-D-Phe-L-Pro- Val^P(OPh-4-SCH₃)₂



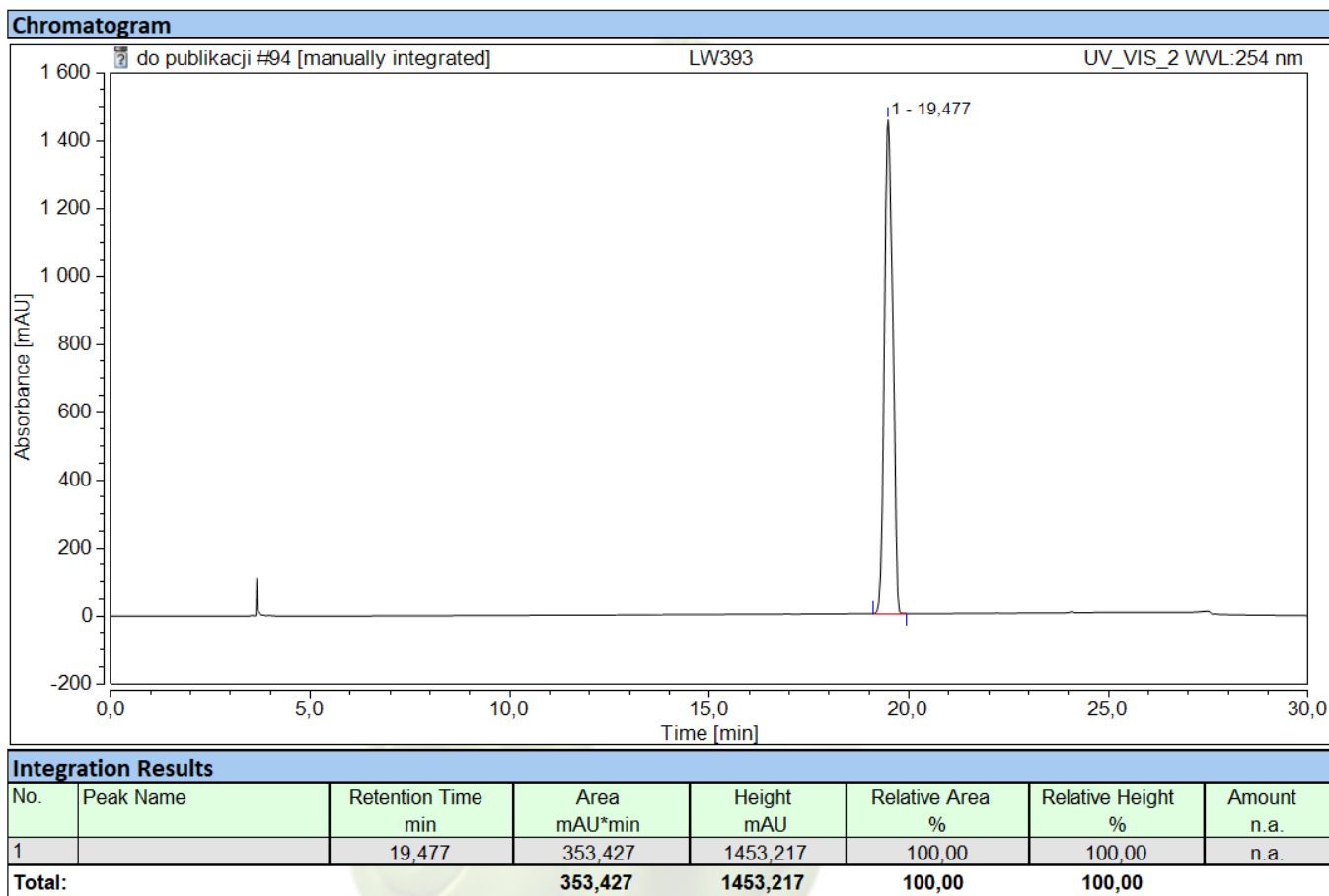
Name: *tert*-butyl ((2*R*)-1-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-1-oxo-3-phenylpropan-2-yl)carbamate

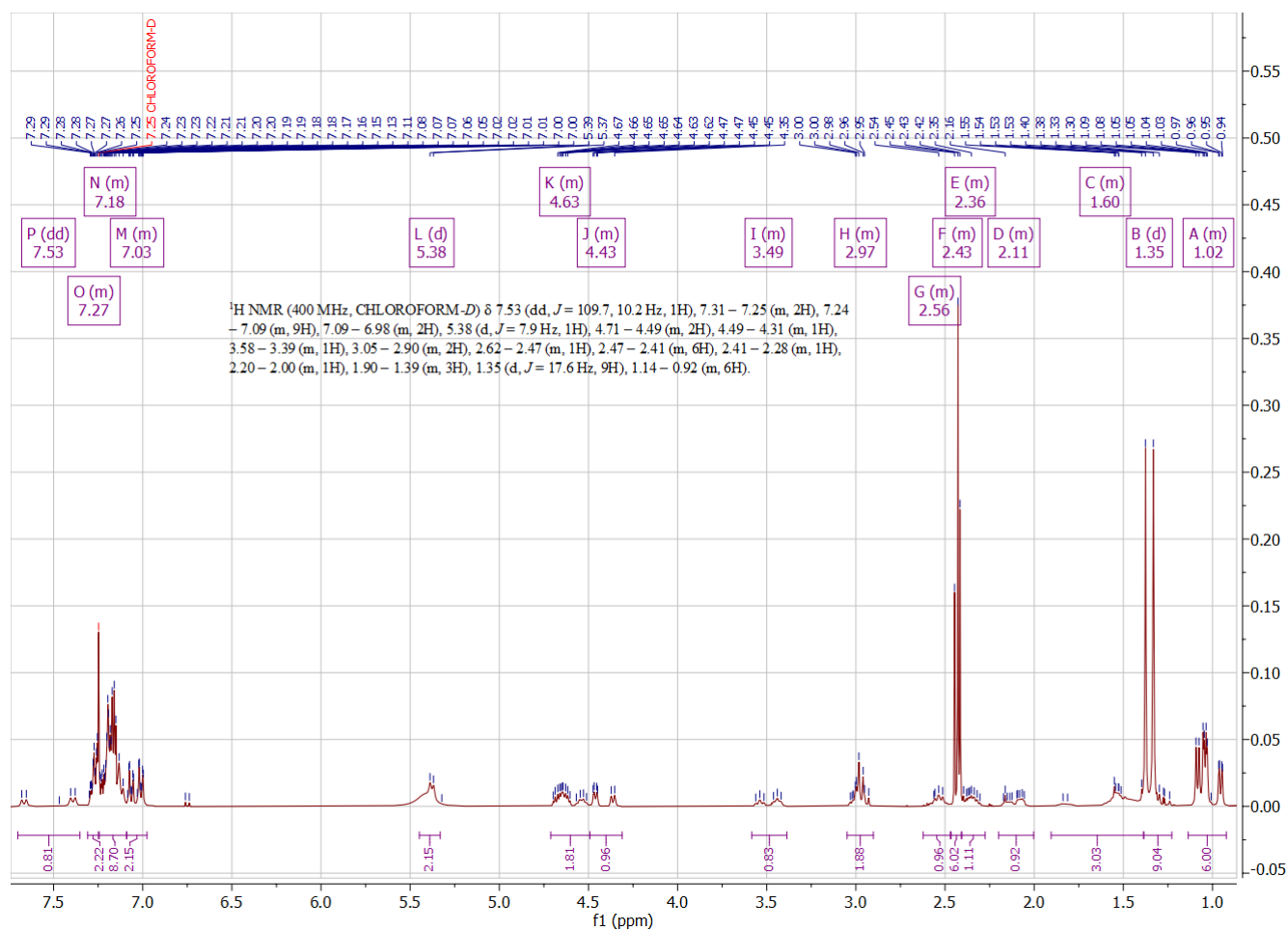
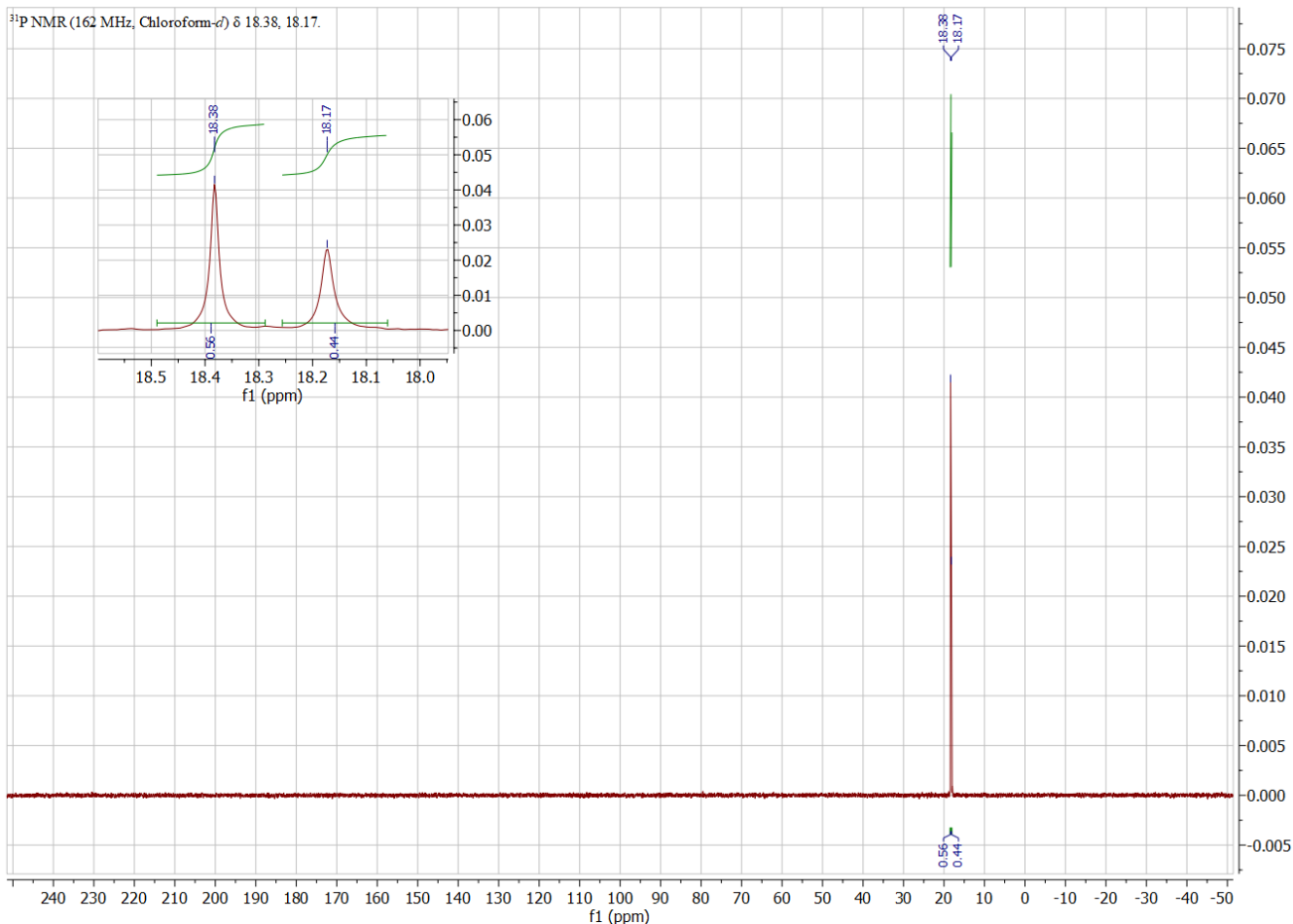
³¹P NMR (162 MHz, Chloroform-*d*) δ 18.38 (s, 56%), 18.17 (s, 44%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.53 (dd, *J* = 109.7, 10.2 Hz, 1H, NH), 7.31 – 7.25 (m, 2H, 2xArH), 7.24 – 7.09 (m, 9H, 9xArH), 7.09 – 6.98 (m, 2H, 2xArH), 5.38 (d, *J* = 7.9 Hz, 1H, NH), 4.71 – 4.49 (m, 2H, CHP, CH), 4.49 – 4.31 (m, 1H, CH), 3.58 – 3.39 (m, 1H, 0.5xCH₂), 3.05 – 2.90 (m, 2H, CH₂), 2.62 – 2.47 (m, 1H, 0.5xCH₂), 2.47 – 2.41 (m, 6H, 2xSCH₃), 2.41 – 2.28 (m, 1H, CH), 2.20 – 2.00 (m, 1H, 0.5xCH₂), 1.90 – 1.39 (m, 3H, 1.5xCH₂), 1.35 (d, *J* = 17.6 Hz, 9H, Boc), 1.14 – 0.92 (m, 6H, 2xCH₃).

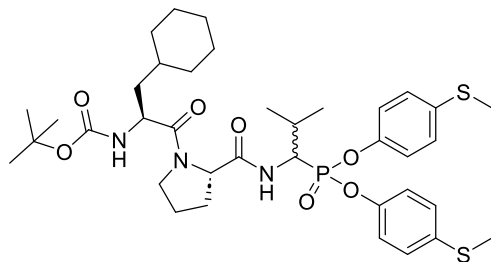
HRMS: C₃₇H₄₈N₃O₇PS₂ [M+Na]⁺ calc. 764.2569 found 764.2543

HPLC: purity >99%; retention time 19.477 min





(95) Boc-L-Cha-L-Pro-Val^P(OPh-4-SCH₃)₂



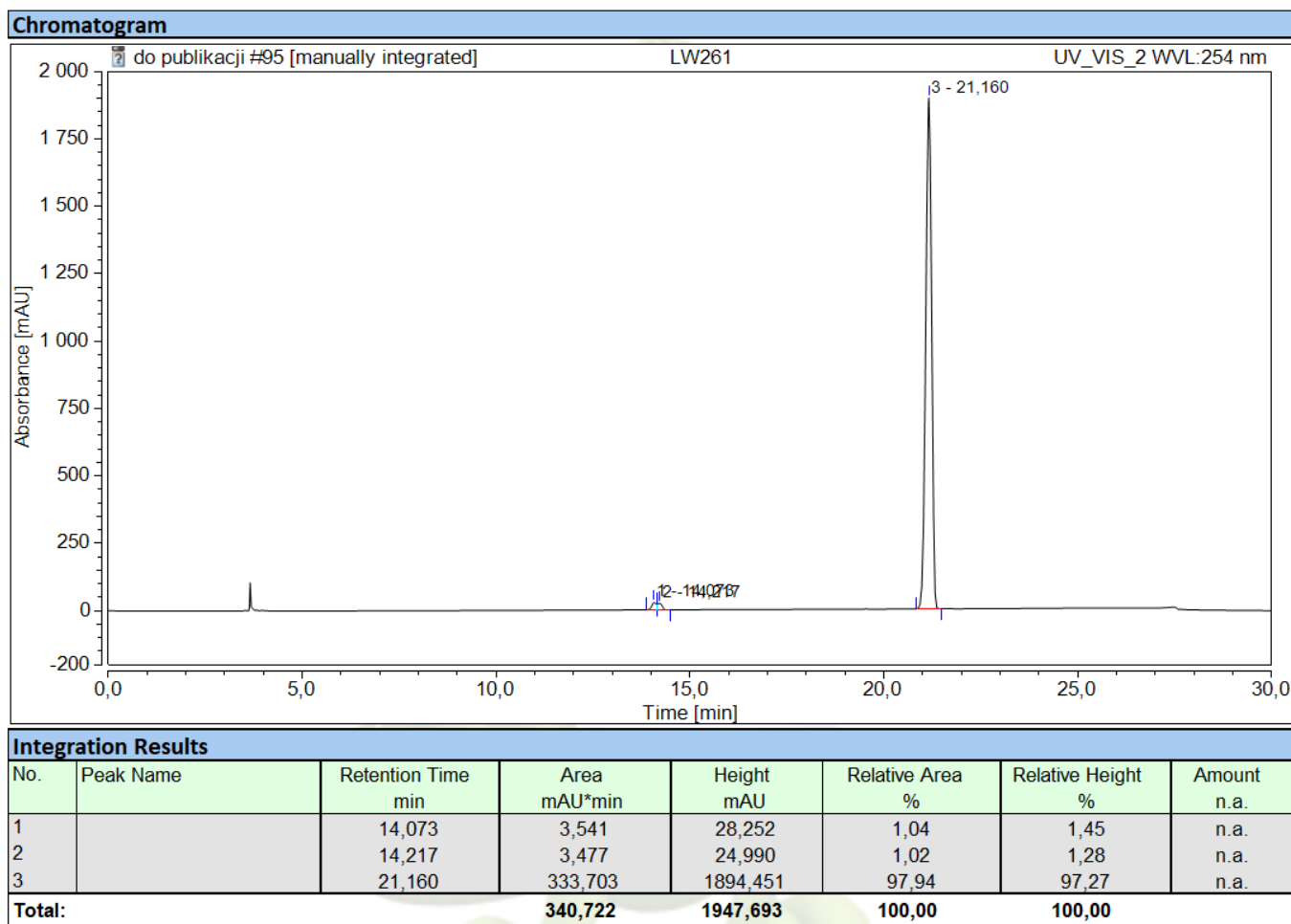
Name: *tert*-butyl ((2*S*)-1-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-3-cyclohexyl-1-oxopropan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.34 (s, 49%), 17.96 (s, 51%).

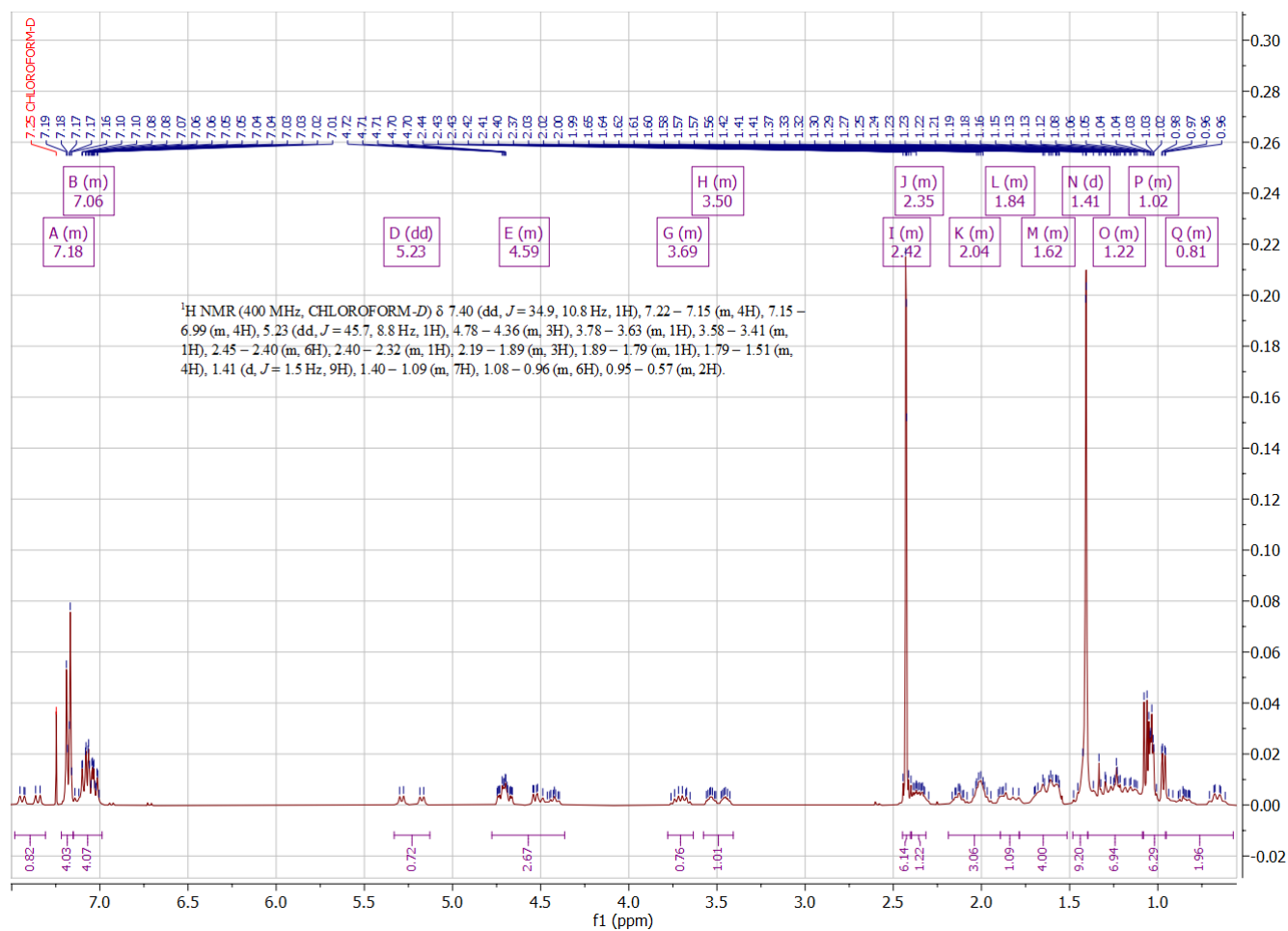
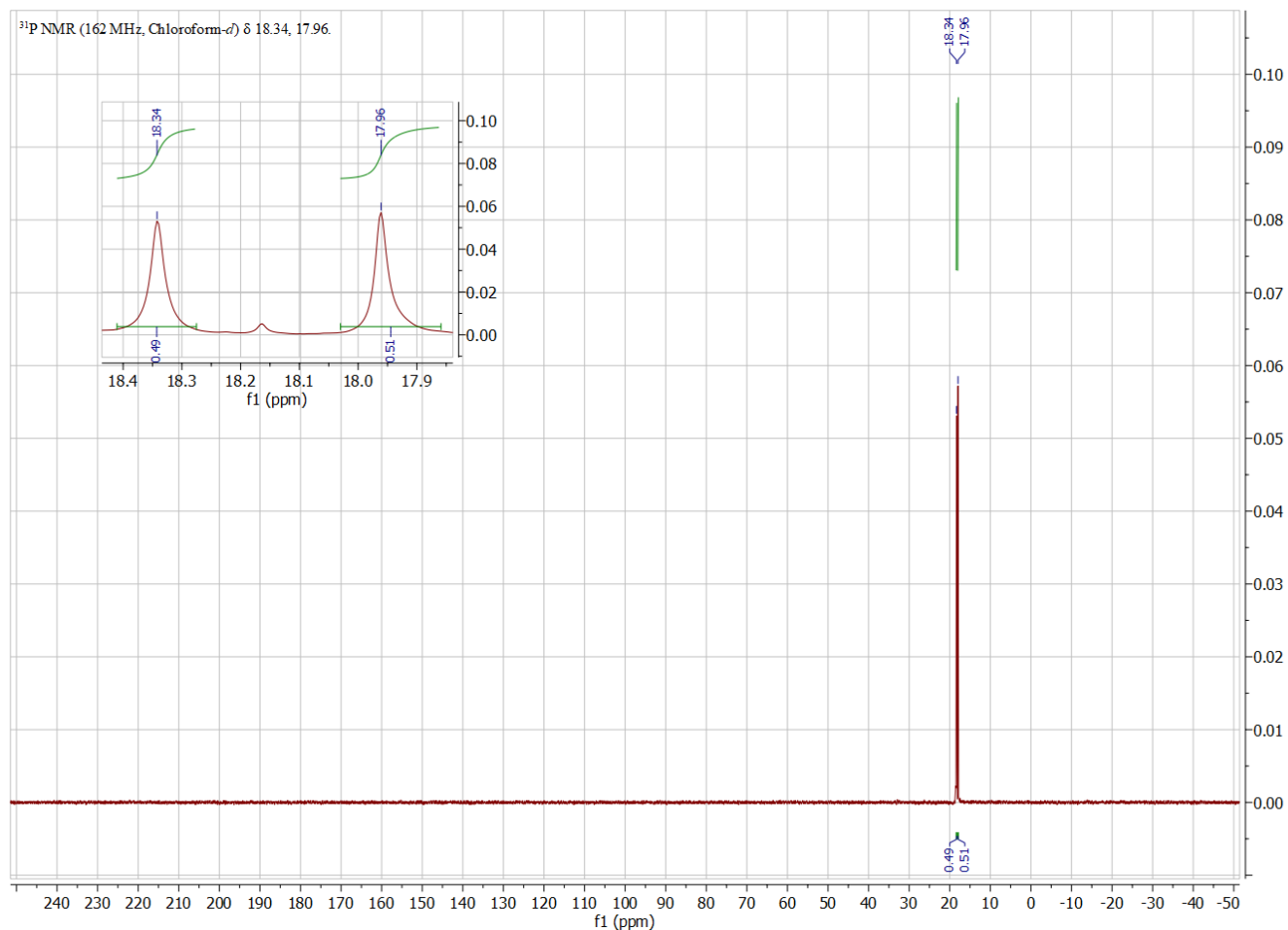
¹H NMR (400 MHz, Chloroform-*d*) δ 7.40 (dd, *J* = 34.9, 10.8 Hz, 1H, NH), 7.22 – 7.15 (m, 4H, 4xArH), 7.15 – 6.99 (m, 4H, 4xArH), 5.23 (dd, *J* = 45.7, 8.8 Hz, 1H, NH), 4.78 – 4.36 (m, 3H, CHP, 2xCH), 3.78 – 3.63 (m, 1H, 0.5xCH₂), 3.58 – 3.41 (m, 1H, 0.5xCH₂), 2.45 – 2.40 (m, 6H, 2xSCH₃), 2.40 – 2.32 (m, 1H, CH), 2.19 – 1.89 (m, 3H, 1.5xCH₂), 1.89 – 1.79 (m, 1H, CH), 1.79 – 1.51 (m, 4H, 2xCH₂), 1.41 (d, *J* = 1.5 Hz, 9H, Boc), 1.40 – 1.09 (m, 7H, 3.5xCH₂), 1.08 – 0.96 (m, 6H, 2xCH₃), 0.95 – 0.57 (m, 2H, CH₂).

HRMS: C₃₇H₅₄N₃O₇PS₂ [M+Na]⁺ calc. 770.3038 found 770.3029

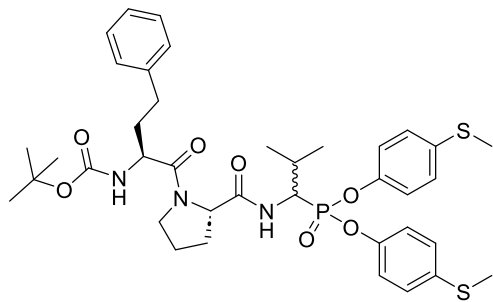
HPLC: purity >97%; retention time 21.160 min



^{31}P NMR (162 MHz, Chloroform-*d*) δ 18.34, 17.96.



(96) Boc-L-HPhe-L-Pro-Val^P(OPh-4-SCH₃)₂



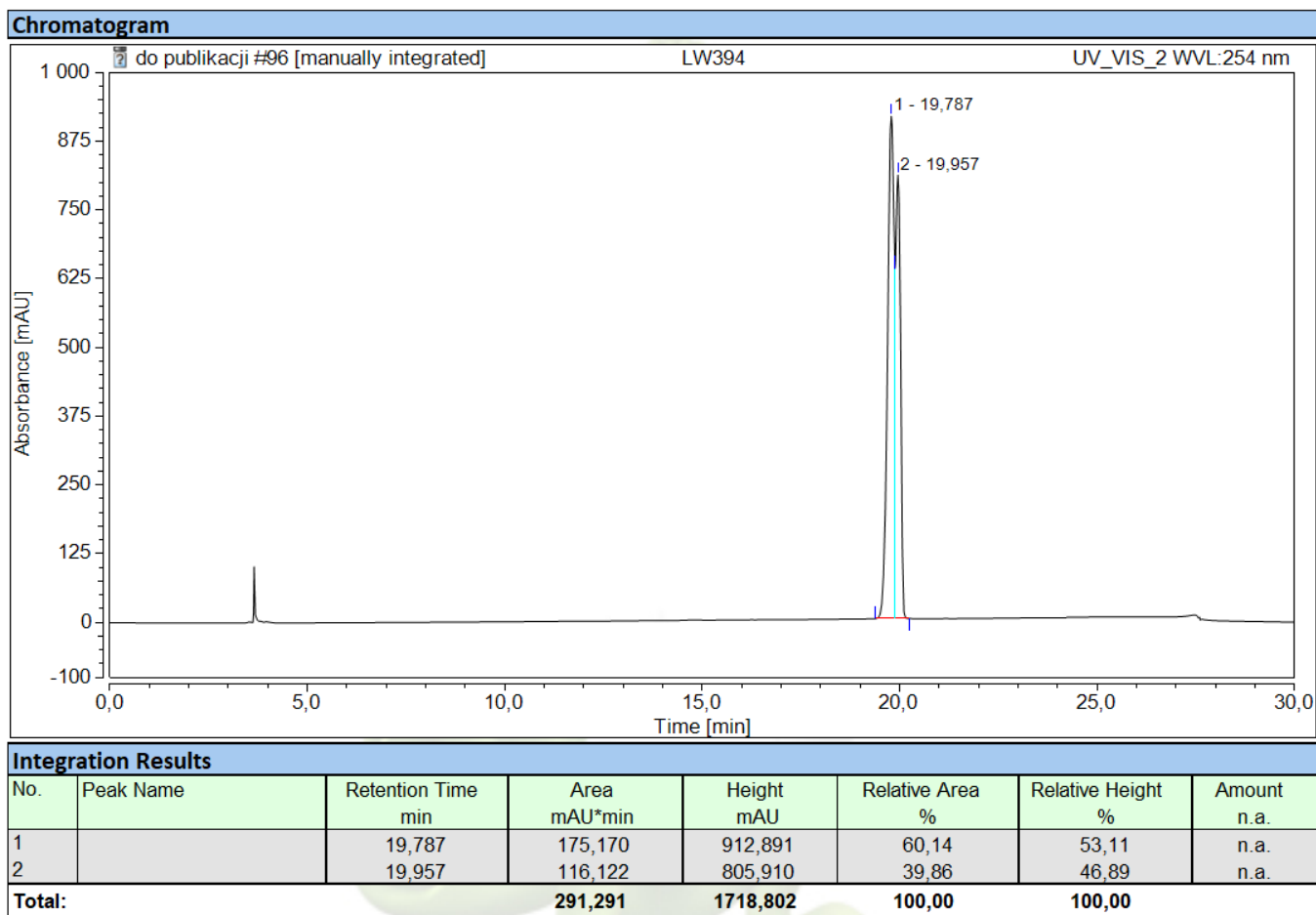
Name: *tert*-butyl ((2*S*)-1-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-1-oxo-4-phenylbutan-2-yl)carbamate

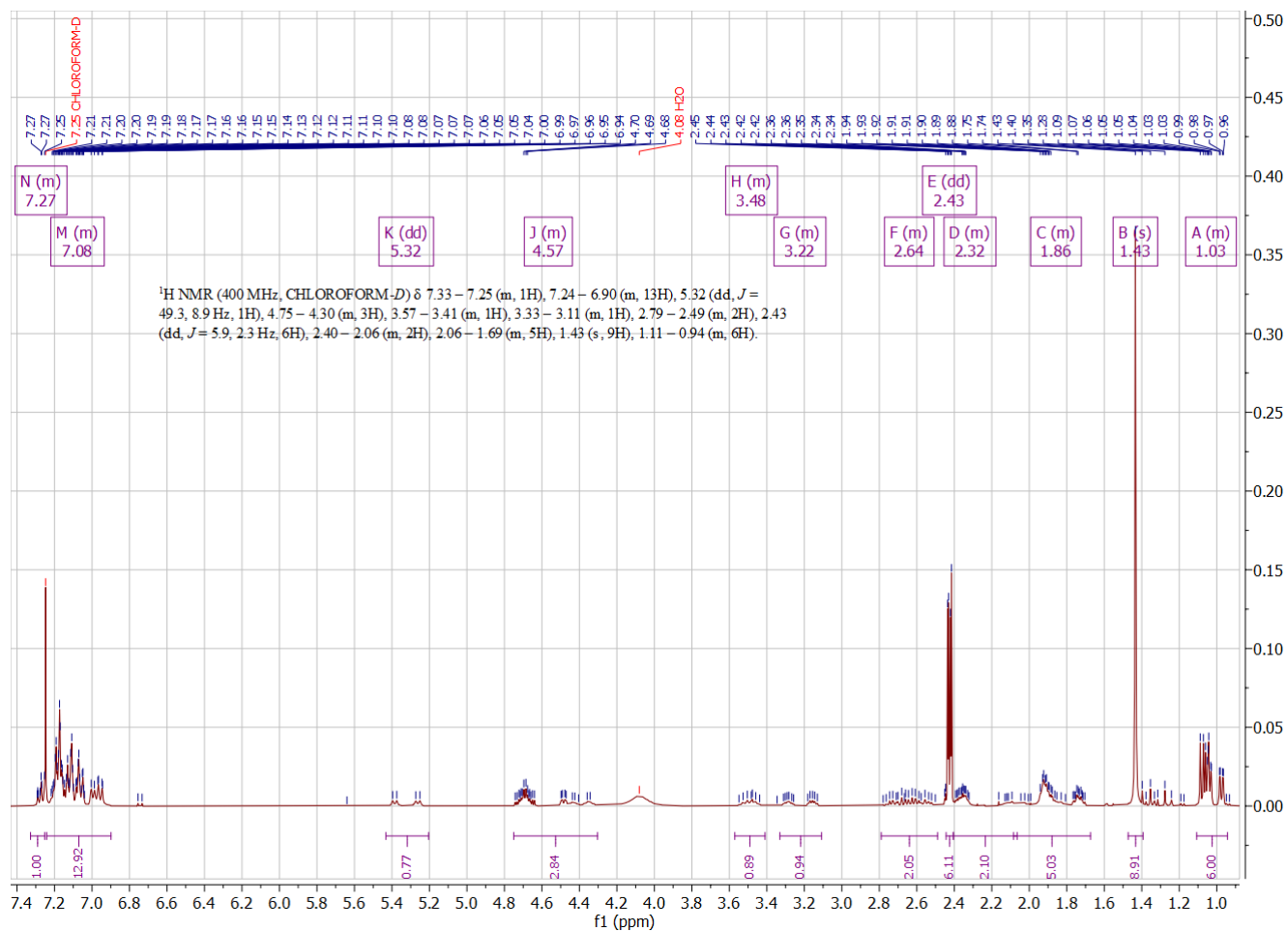
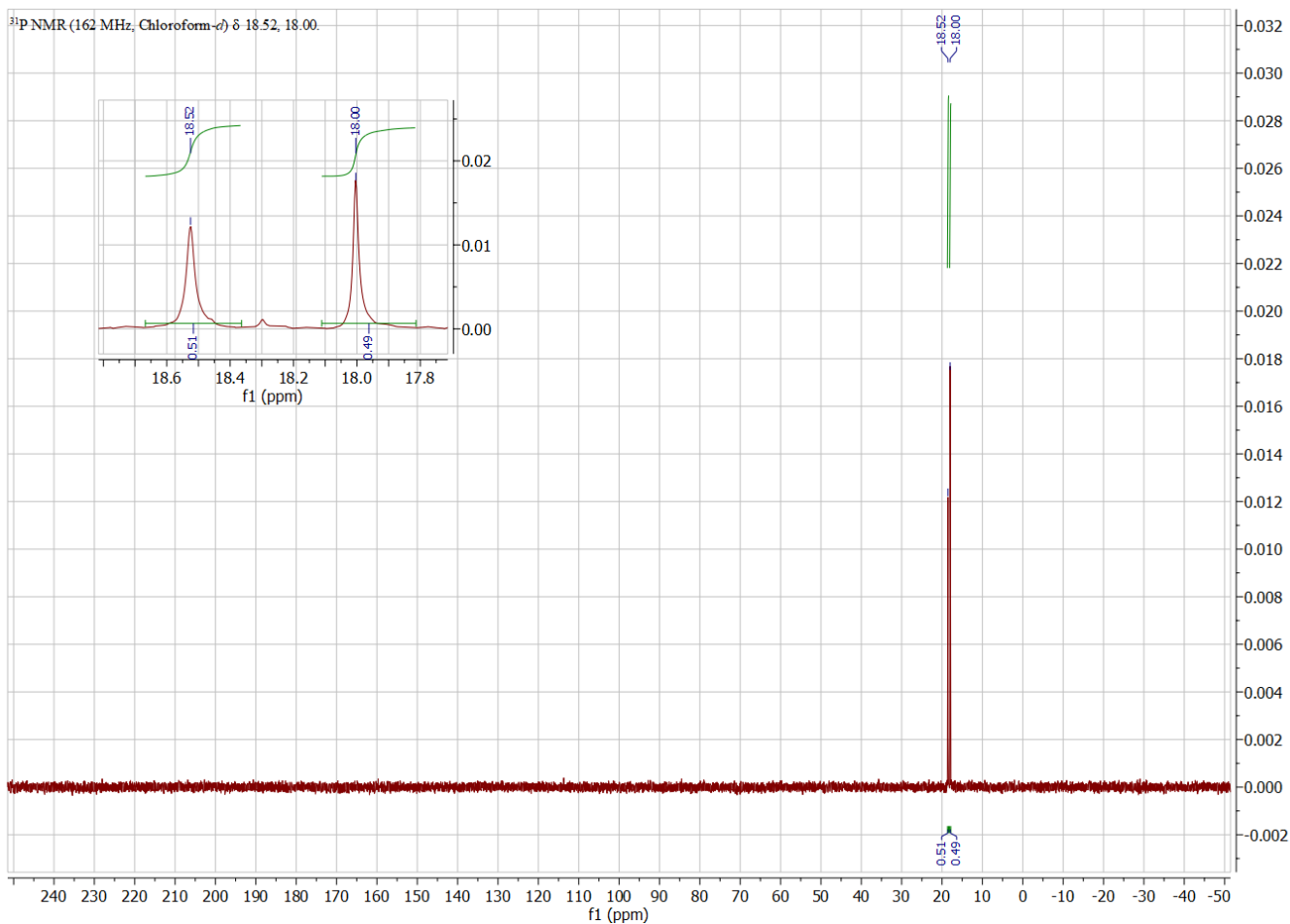
³¹P NMR (162 MHz, Chloroform-*d*) δ 18.52 (s, 51%), 18.00 (s, 49%).

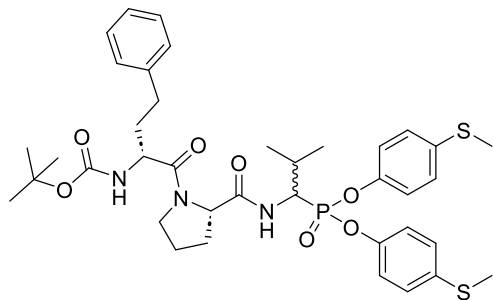
¹H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.25 (m, 1H, NH), 7.24 – 6.90 (m, 13H, 13xArH), 5.32 (dd, *J* = 49.3, 8.9 Hz, 1H, NH), 4.75 – 4.30 (m, 3H, CHP, 2xCH), 3.57 – 3.41 (m, 1H, 0.5xCH₂), 3.33 – 3.11 (m, 1H, 0.5xCH₂), 2.79 – 2.49 (m, 2H, CH₂), 2.43 (dd, *J* = 5.9, 2.3 Hz, 6H, 2xSCH₃), 2.40 – 2.06 (m, 2H, 0.5xCH₂, CH), 2.06 – 1.69 (m, 5H, 2.5xCH₂), 1.43 (s, 9H, Boc), 1.11 – 0.94 (m, 6H, 2xCH₃).

HRMS: C₃₈H₅₀N₃O₇PS₂ [M+Na]⁺ calc. 778.2725 found 778.2719

HPLC: purity >99%; retention time 19.787 and 19.957 min





(97) Boc-D-HPhe-L-Pro-Val^P(OPh-4-SCH₃)₂

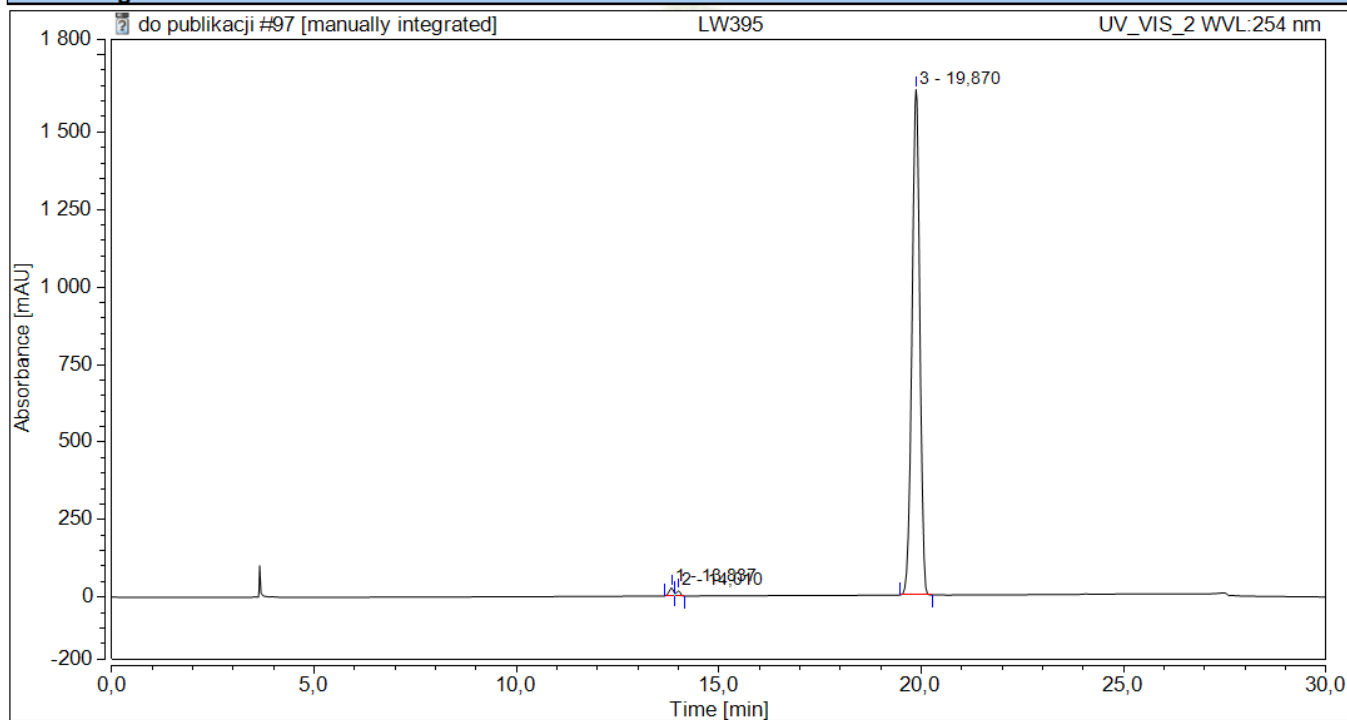
Name: *tert*-butyl ((2*R*)-1-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-1-oxo-4-phenylbutan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.48 (s, 57%), 18.18 (s, 43%).

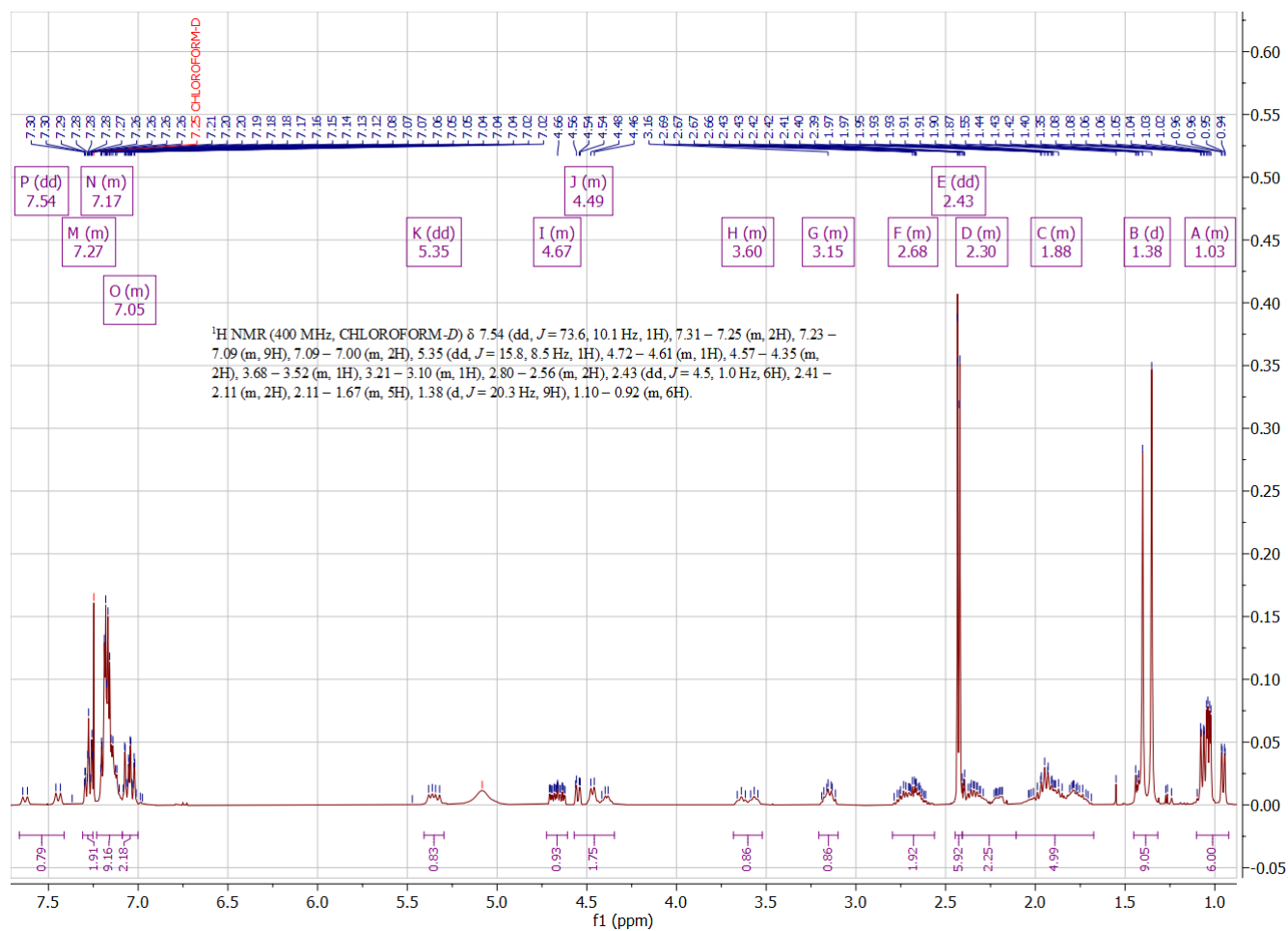
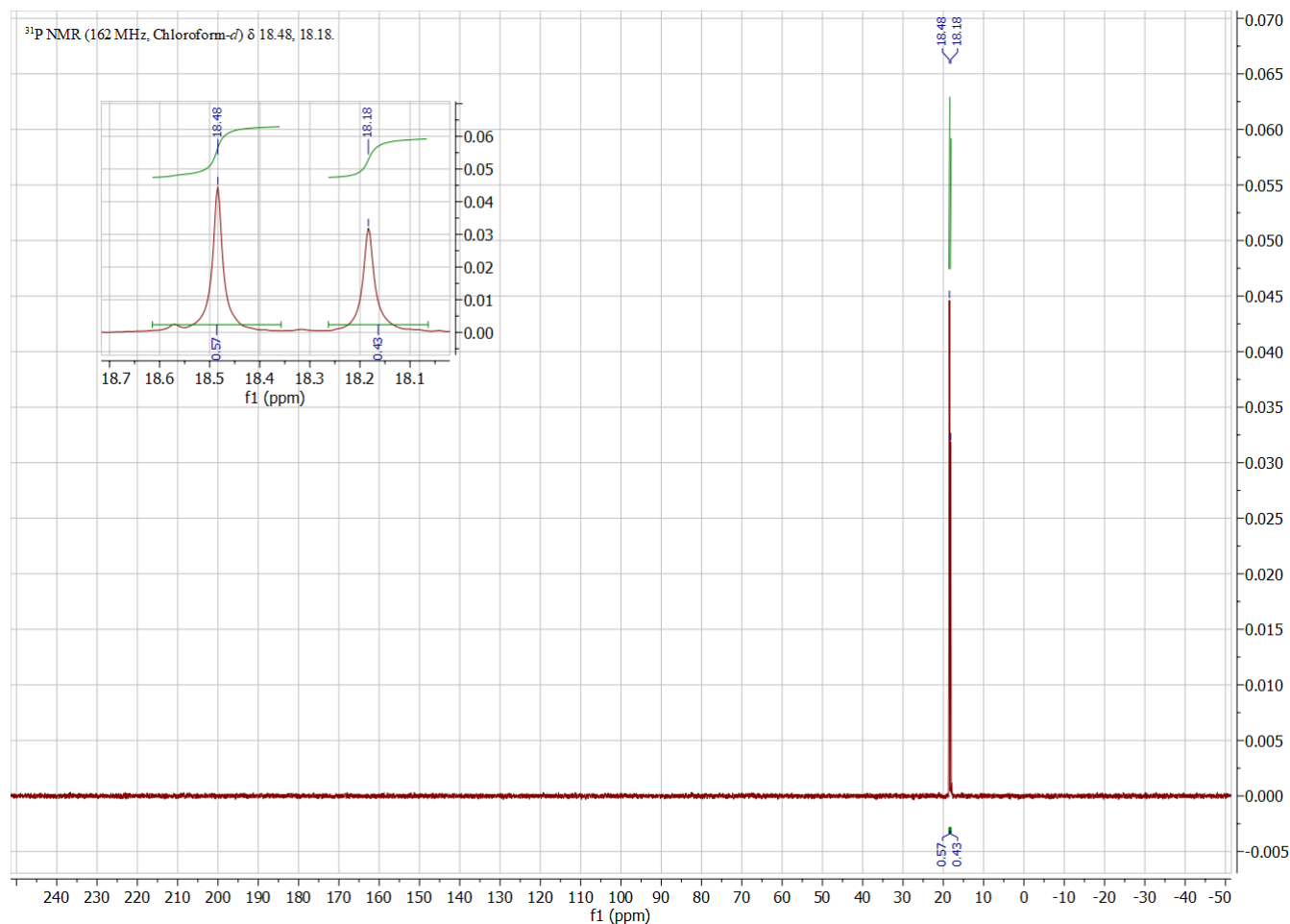
¹H NMR (400 MHz, Chloroform-*d*) δ 7.54 (dd, *J* = 73.6, 10.1 Hz, 1H, NH), 7.31 – 7.25 (m, 2H, 2xArH), 7.23 – 7.09 (m, 9H, 9xArH), 7.09 – 7.00 (m, 2H, 2xArH), 5.35 (dd, *J* = 15.8, 8.5 Hz, 1H, NH), 4.72 – 4.61 (m, 1H, CHP), 4.57 – 4.35 (m, 2H, 2xCH), 3.68 – 3.52 (m, 1H, 0.5xCH₂), 3.21 – 3.10 (m, 1H, 0.5xCH₂), 2.80 – 2.56 (m, 2H, CH₂), 2.43 (dd, *J* = 4.5, 1.0 Hz, 6H, 2xSCH₃), 2.41 – 2.11 (m, 2H, 0.5xCH₂, CH), 2.11 – 1.67 (m, 5H, 2.5xCH₂), 1.38 (d, *J* = 20.3 Hz, 9H, Boc), 1.10 – 0.92 (m, 6H, 3xCH₃).

HRMS: C₃₈H₅₀N₃O₇PS₂ [M+Na]⁺ calc. 778.2725 found 778.2717

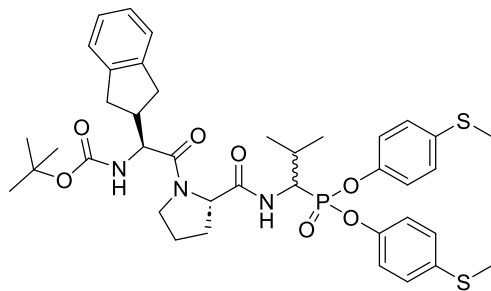
HPLC: purity >98%; retention time 19.870 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13,837	3,329	27,341	0,91	1,63	n.a.
2		14,010	1,939	17,184	0,53	1,03	n.a.
3		19,870	361,799	1630,562	98,56	97,34	n.a.
Total:			367,067	1675,087	100,00	100,00	



(98) Boc-L-Igl-L-Pro-Val^P(OPh-4-SCH₃)₂



Name: tert-butyl ((1S)-2-((2S)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-1-(2,3-dihydro-1H-inden-2-yl)-2-oxoethyl)carbamate

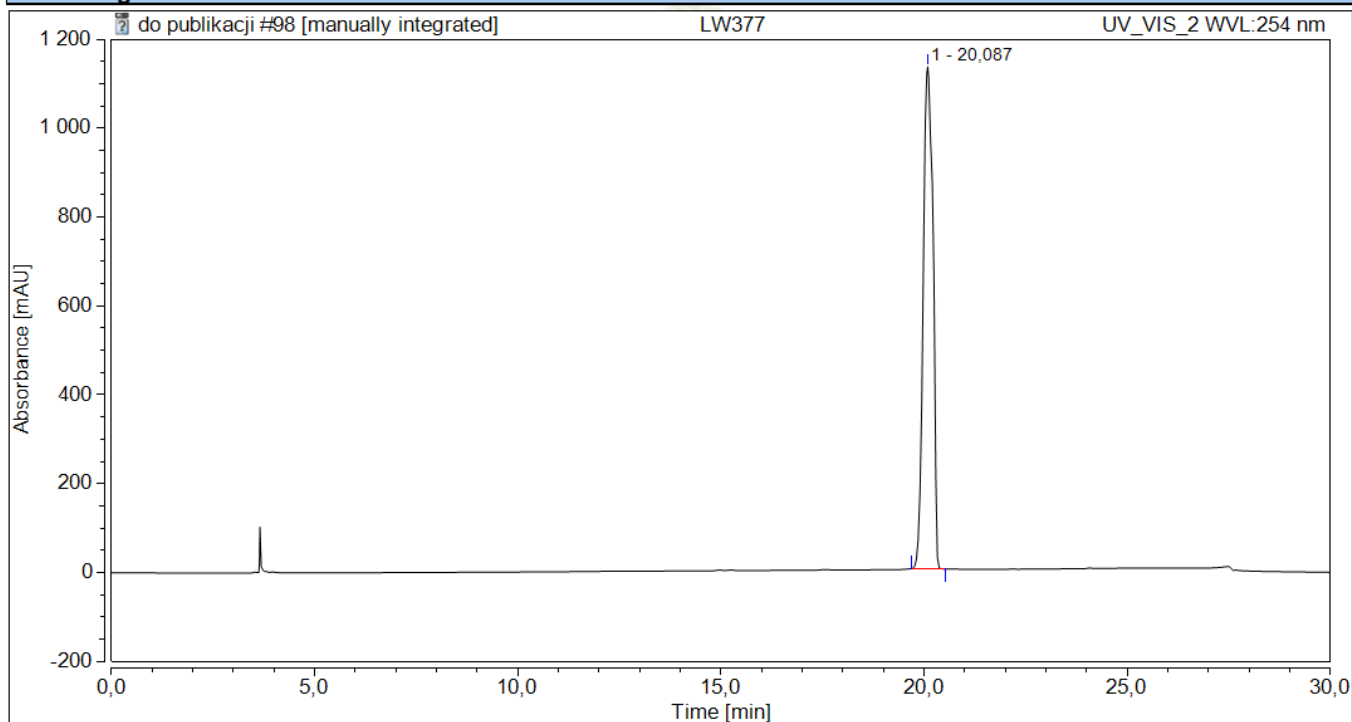
³¹P NMR (162 MHz, Chloroform-d) δ 18.20 (s, 46%), 17.92 (s, 54%).

¹H NMR (400 MHz, Chloroform-d) δ 7.34 (dd, J = 80.7, 10.3 Hz, 1H, NH), 7.22 – 6.97 (m, 12H, 12xArH), 5.48 (dd, J = 37.9, 8.9 Hz, 1H, NH), 4.84 – 4.74 (m, 1H, CHP), 4.71 – 4.52 (m, 1H, CH), 4.52 – 4.46 (m, 1H, CH), 3.84 – 3.73 (m, 1H, 0.5xCH₂), 3.63 – 3.47 (m, 1H, 0.5xCH₂), 3.05 – 2.53 (m, 5H, 2xCH₂, CH), 2.47 – 2.34 (m, 7H, 2xSCH₃, CH), 2.34 – 1.86 (m, 4H, 2xCH₂), 1.40 (d, J = 2.6 Hz, 9H, Boc), 1.14 – 1.02 (m, 6H, 2xCH₃).

HRMS: C₃₉H₅₀N₃O₇PS₂ [M+Na]⁺ calc. 790.2725 found 790.2709

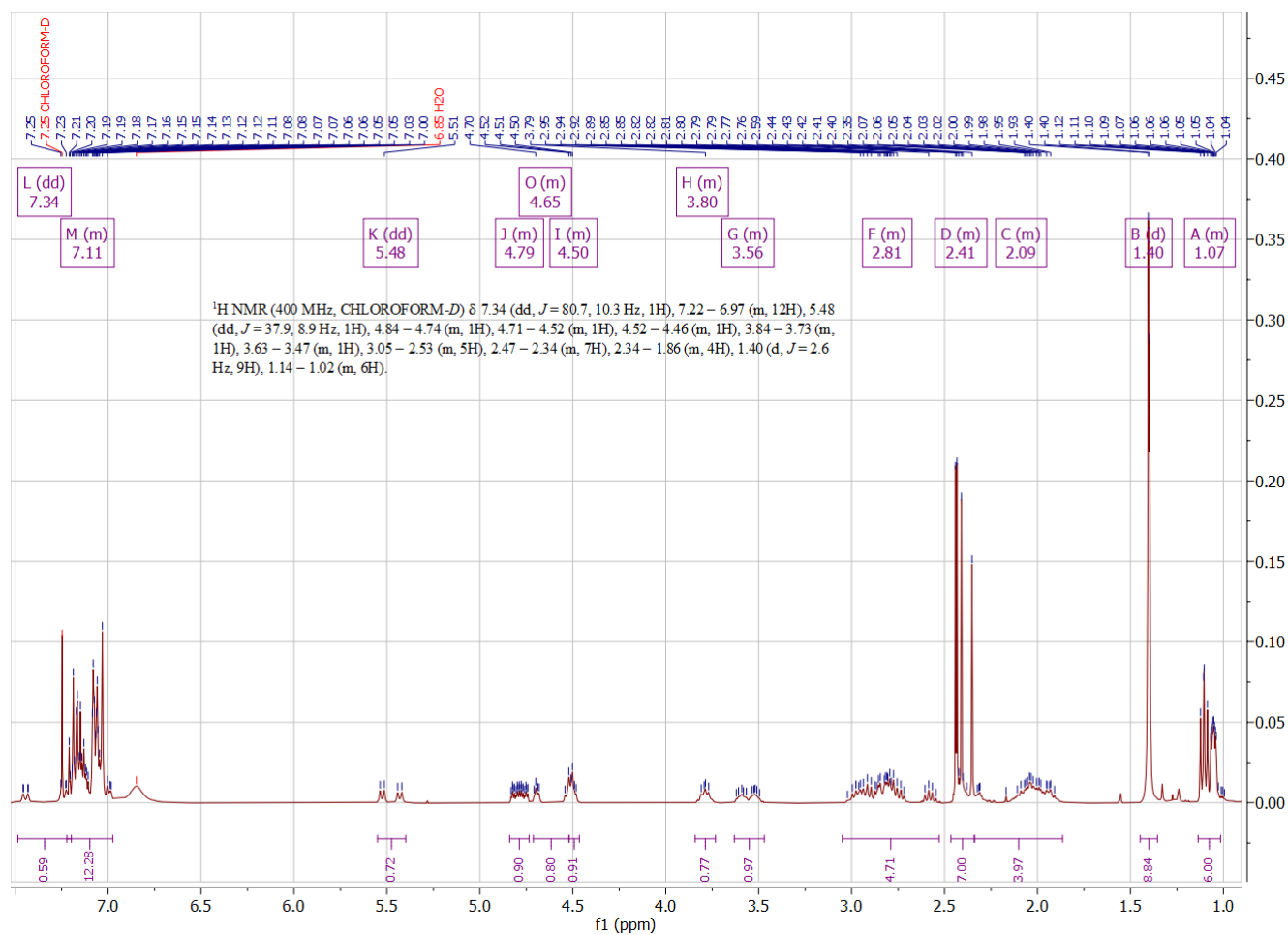
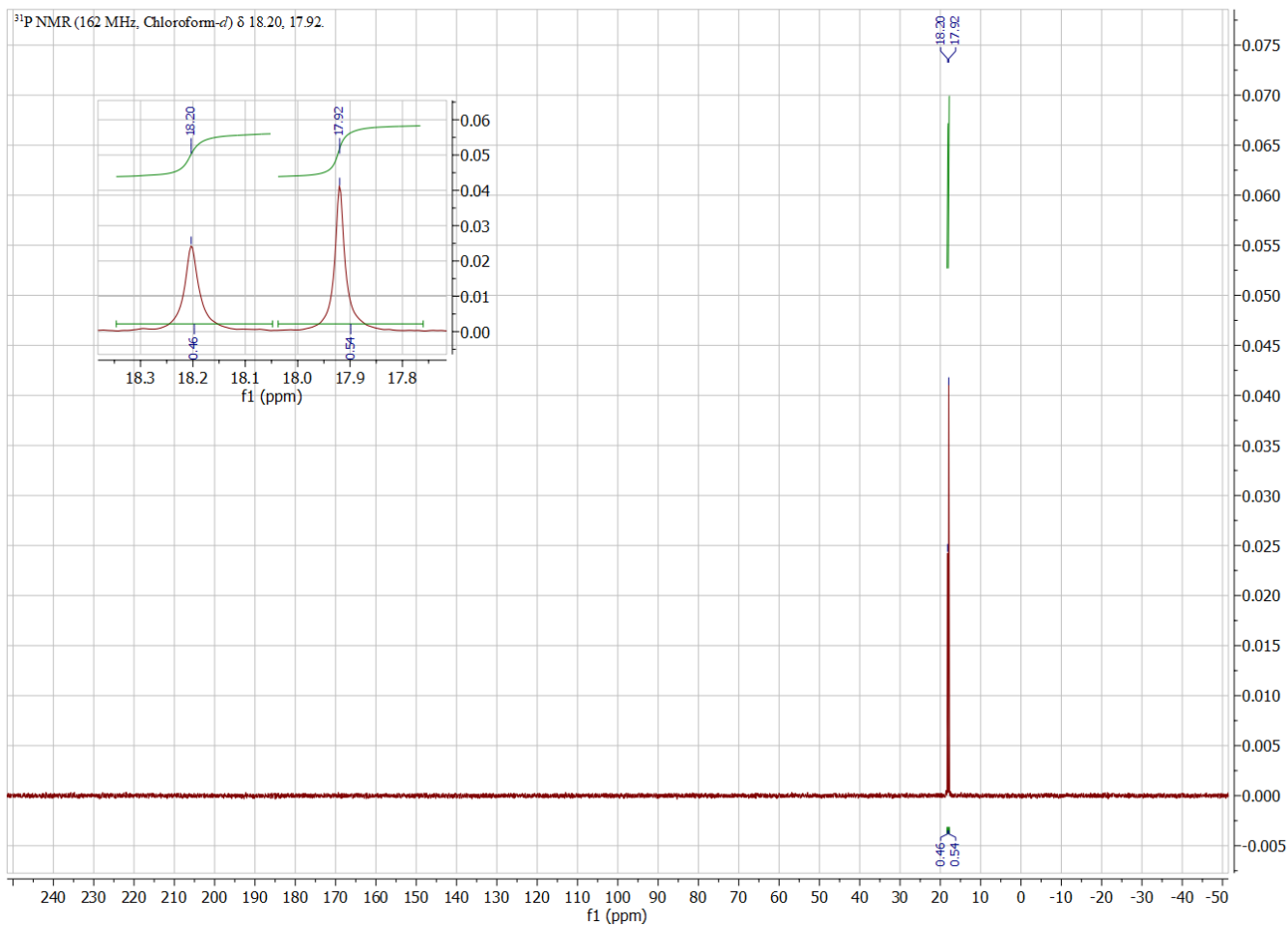
HPLC: purity >99%; retention time 20.087 min

Chromatogram

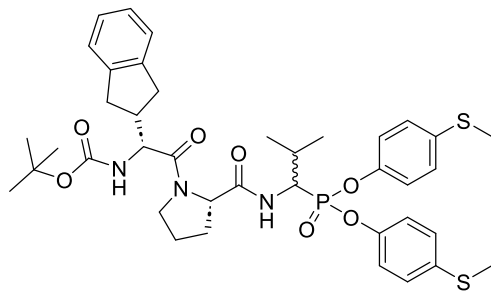


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20,087	314,259	1129,711	100,00	100,00	n.a.
Total:			314,259	1129,711	100,00	100,00	



(99) Boc-D-Igl-L-Pro-Val^P(OPh-4-SCH₃)₂



Name: tert-butyl ((1R)-2-((2S)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-1-(2,3-dihydro-1H-inden-2-yl)-2-oxoethyl)carbamate

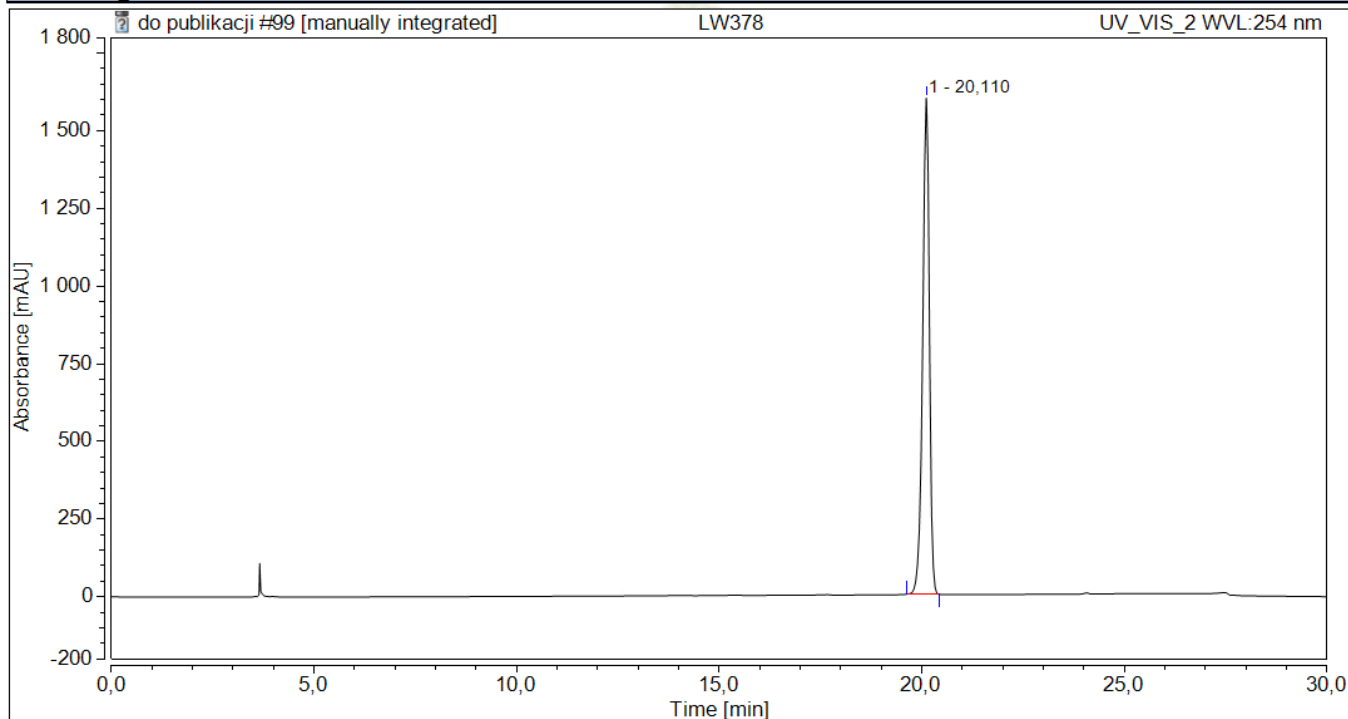
³¹P NMR (162 MHz, Chloroform-d) δ 18.33 (s, 50%), 18.07 (s, 50%).

¹H NMR (400 MHz, Chloroform-d) δ 7.52 (dd, J = 80.8, 10.4 Hz, 1H, NH), 7.22 – 7.11 (m, 9H, 9xArH), 7.11 – 7.01 (m, 3H, 3xArH), 5.40 (t, J = 8.8 Hz, 1H, NH), 4.77 – 4.67 (m, 1H, CHP), 4.67 – 4.58 (m, 1H, CH), 4.58 – 4.47 (m, 1H, CH), 3.90 – 3.77 (m, 1H, 0.5xCH₂), 3.54 – 3.41 (m, 1H, 0.5xCH₂), 3.05 – 2.91 (m, 2H, CH₂), 2.91 – 2.76 (m, 2H, CH₂), 2.74 – 2.63 (m, 1H, CH), 2.43 (dd, J = 3.1, 2.1 Hz, 6H, 2xSCH₃), 2.42 – 2.20 (m, 2H, 0.5xCH₂, CH), 2.17 – 1.81 (m, 3H, 1.5xCH₂), 1.36 (d, J = 23.4 Hz, 9H, Boc), 1.12 – 0.94 (m, 6H, 2xCH₃).

HRMS: C₃₉H₅₀N₃O₇PS₂ [M+Na]⁺ calc. 790.2725 found 790.2712

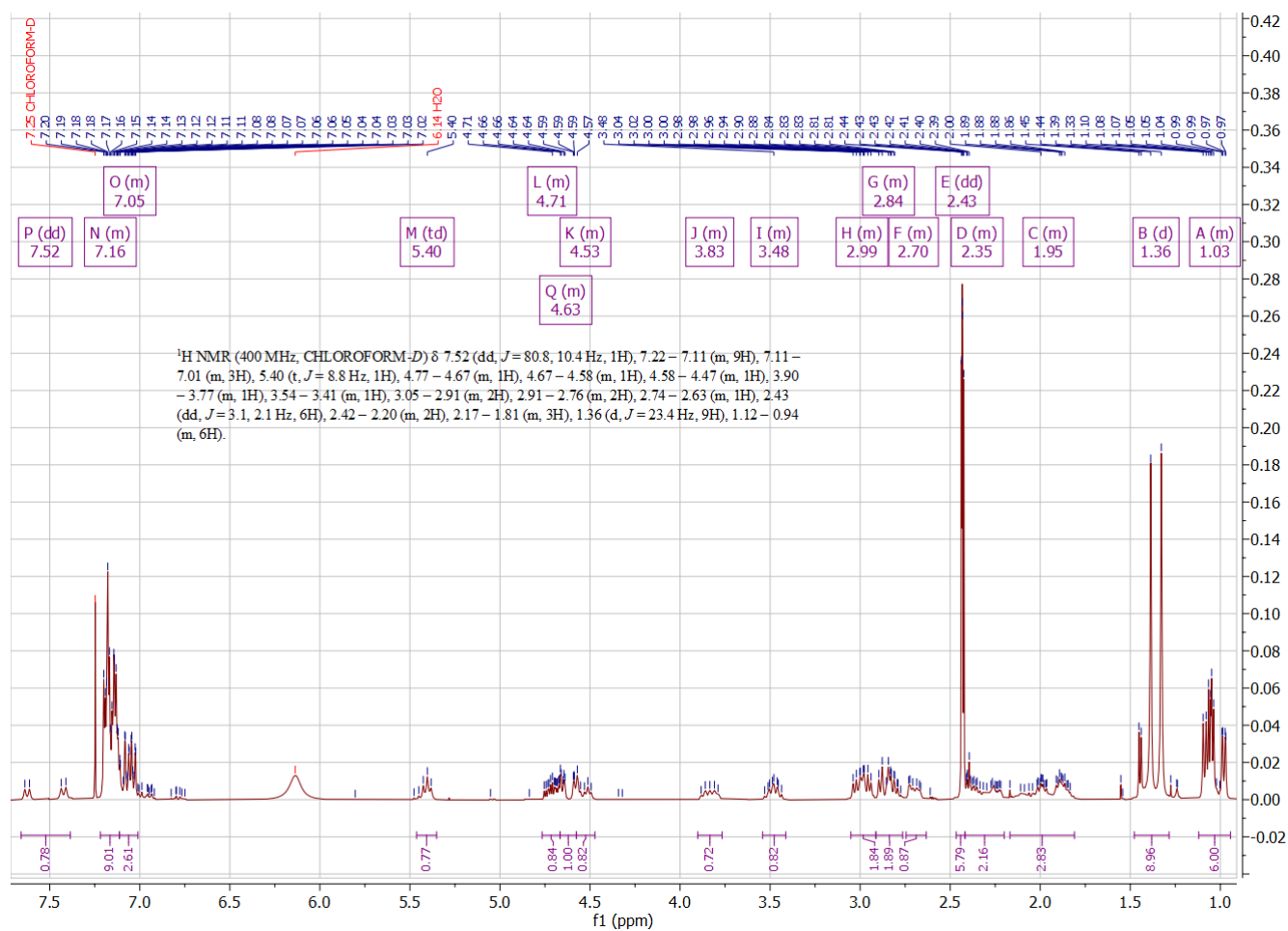
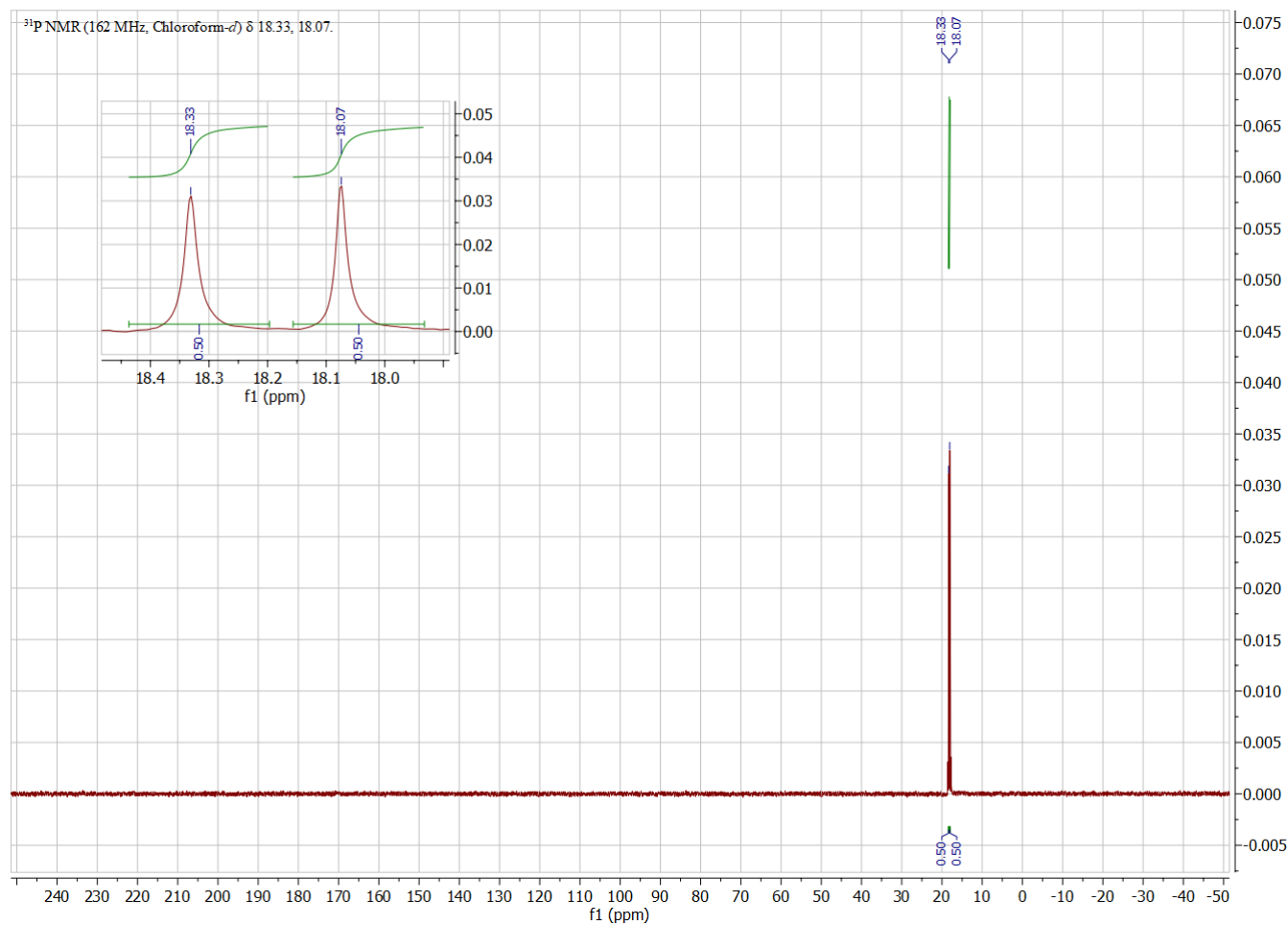
HPLC: purity >99%; retention time 20.110 min

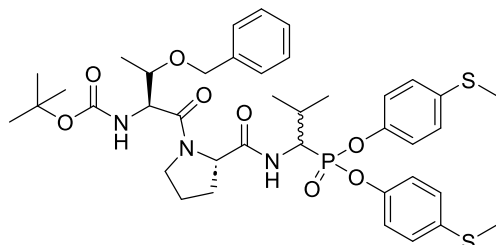
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20,110	307,149	1596,423	100,00	100,00	n.a.
Total:			307,149	1596,423	100,00	100,00	



(100) Boc-L-Thr(Bzl)-L-Pro- Val^P(OPh-4-SCH₃)₂

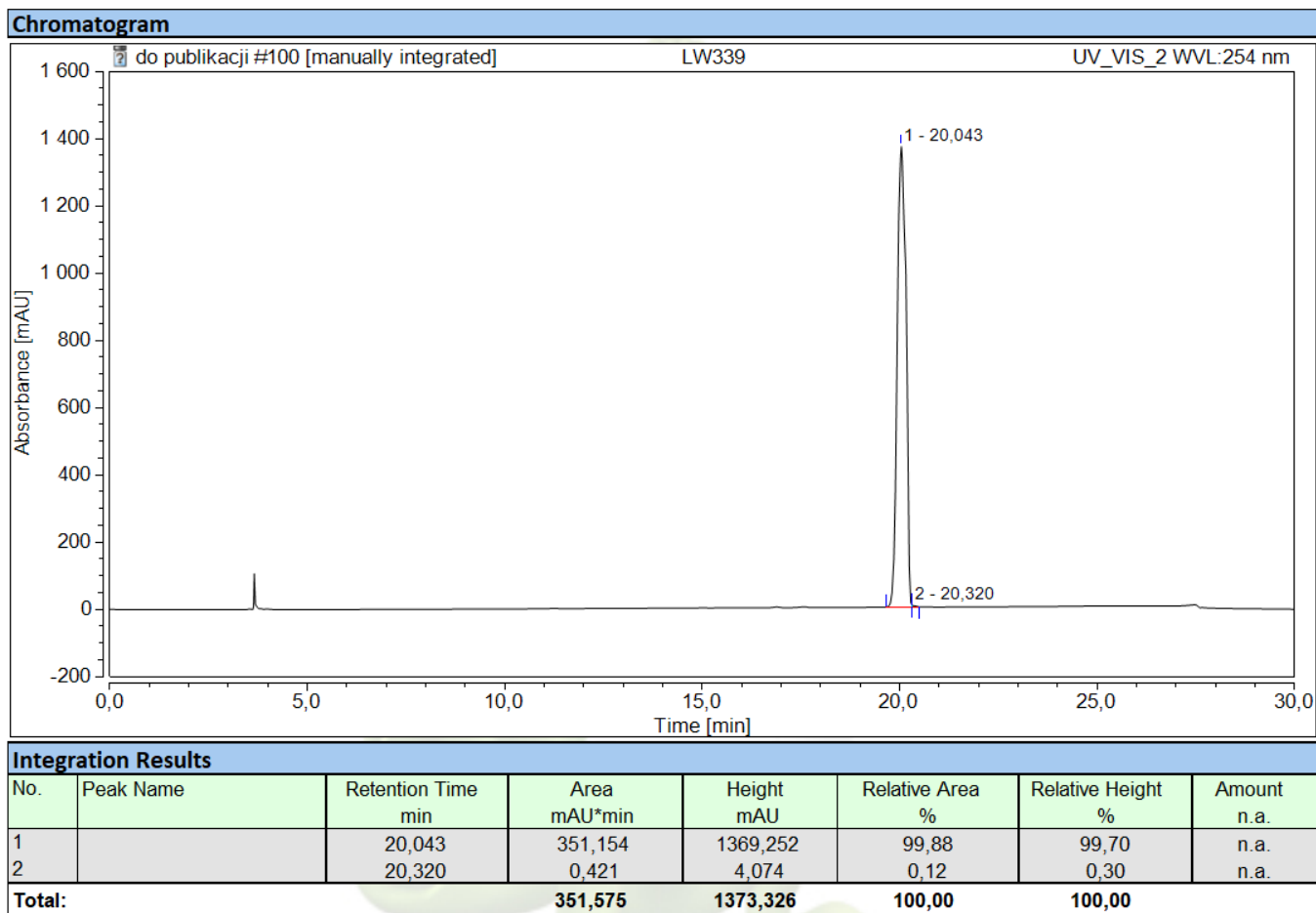
Name: *tert*-butyl ((2*S*,3*S*)-3-(benzyloxy)-1-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-1-oxobutan-2-yl)carbamate

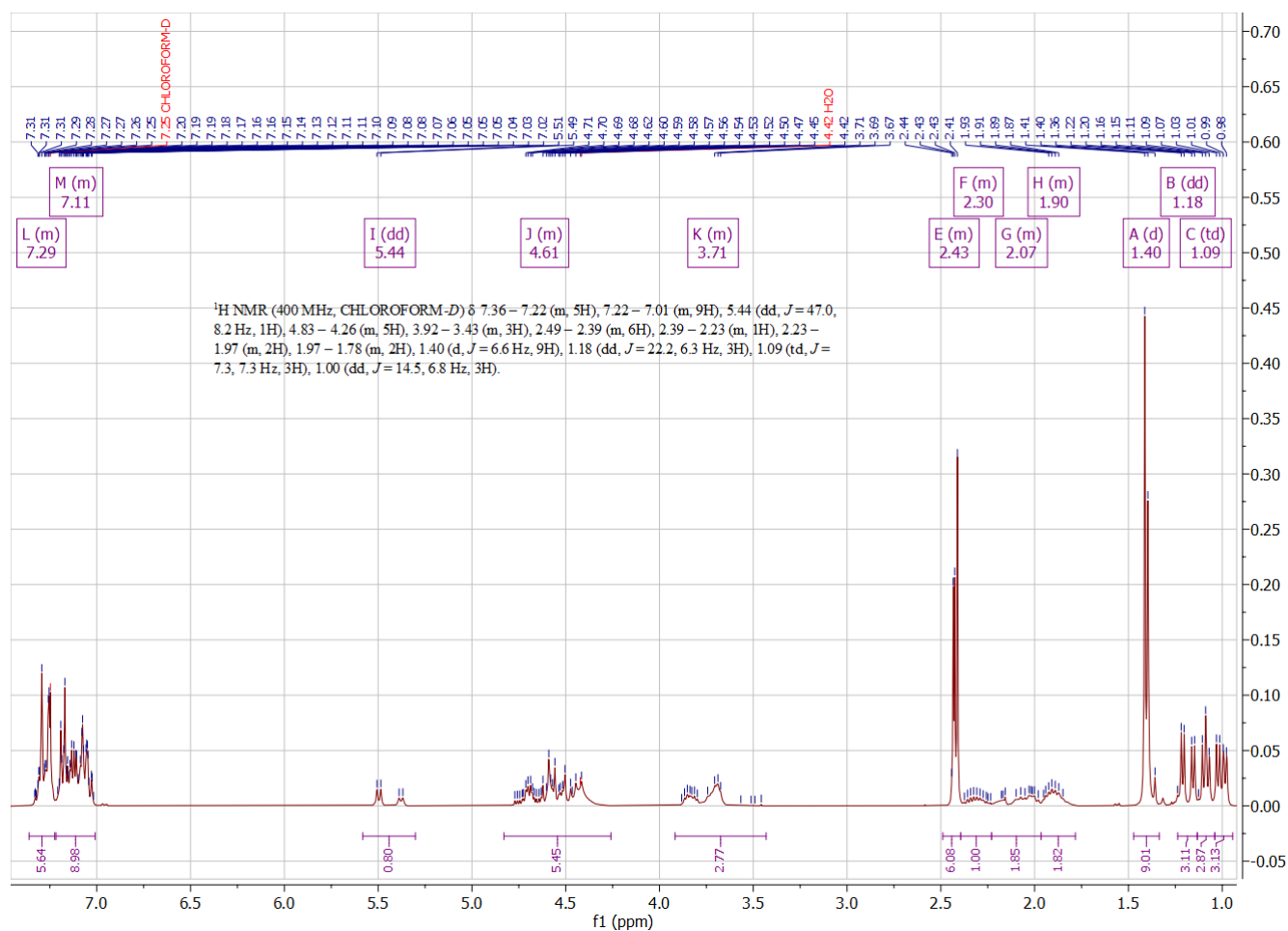
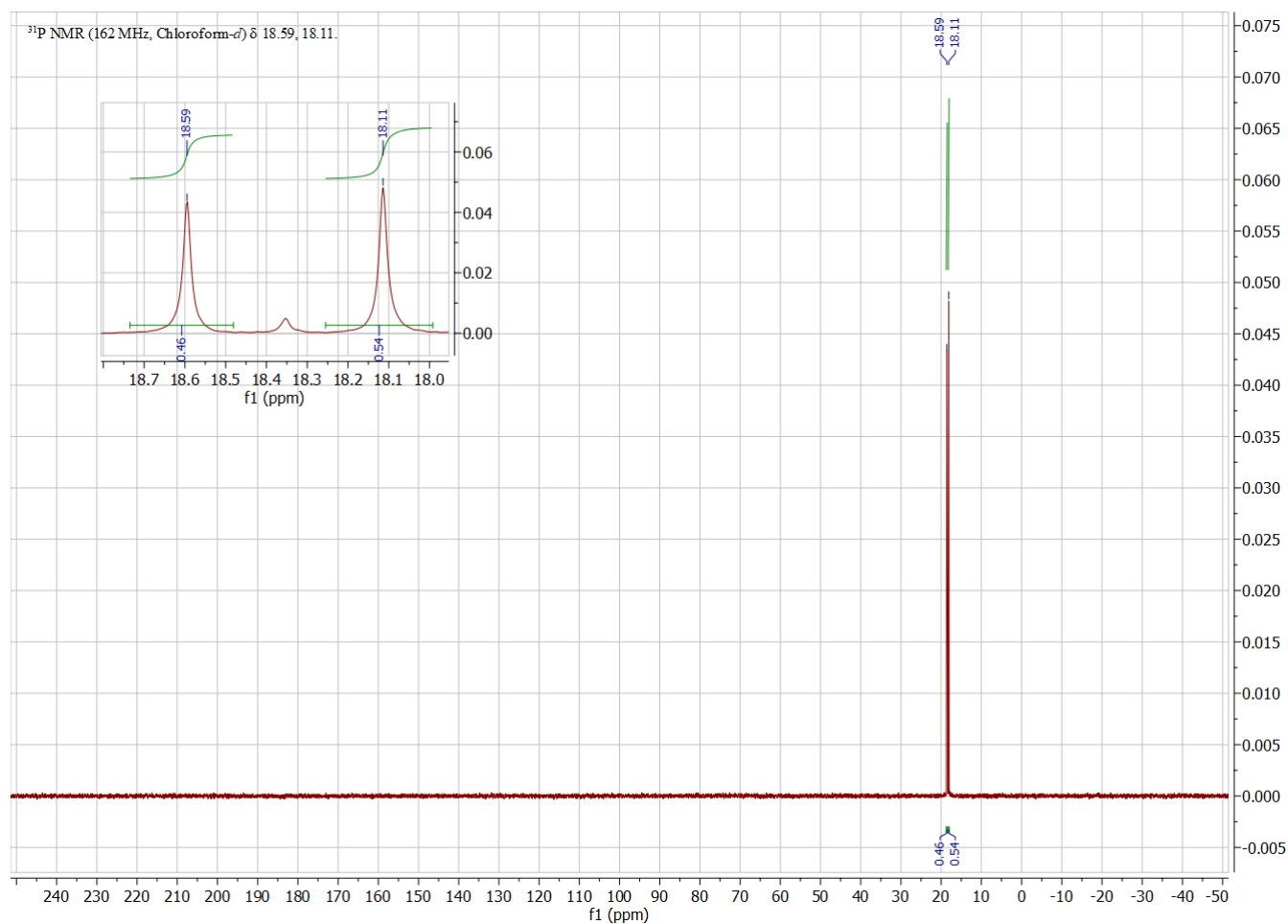
³¹P NMR (162 MHz, Chloroform-*d*) δ 18.59 (s, 46%), 18.11 (s, 54%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.22 (m, 5H, 4xArH, NH), 7.22 – 7.01 (m, 9H, 9xArH), 5.44 (dd, *J* = 47.0, 8.2 Hz, 1H, NH), 4.83 – 4.26 (m, 5H, CH₂, CHP, 2xCH), 3.92 – 3.43 (m, 3H, CH₂, CH), 2.49 – 2.39 (m, 6H, 2xSCH₃), 2.39 – 2.23 (m, 1H, CH), 2.23 – 1.97 (m, 2H, CH₂), 1.97 – 1.78 (m, 2H, CH₂), 1.40 (d, *J* = 6.6 Hz, 9H, Boc), 1.18 (dd, *J* = 22.2, 6.3 Hz, 3H, CH₃), 1.09 (td, *J* = 7.3, 7.3 Hz, 3H, CH₃), 1.00 (dd, *J* = 14.5, 6.8 Hz, 3H, CH₃).

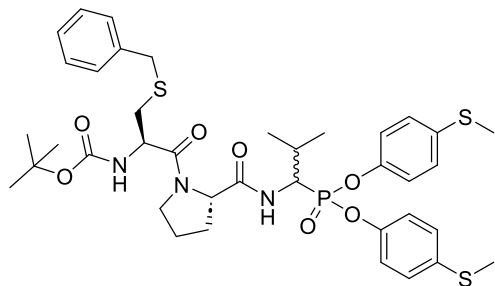
HRMS: C₃₉H₅₂N₃O₈PS₂ [M+Na]⁺ calc. 808.2831 found 808.2800

HPLC: purity >99%; retention time 20.043 min





(101) Boc-L-Cys(Bzl)-L-Pro- Val^P(OPh-4-SCH₃)₂



Name: *tert*-butyl ((2R)-3-(benzylthio)-1-((2S)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-1-oxopropan-2-yl)carbamate

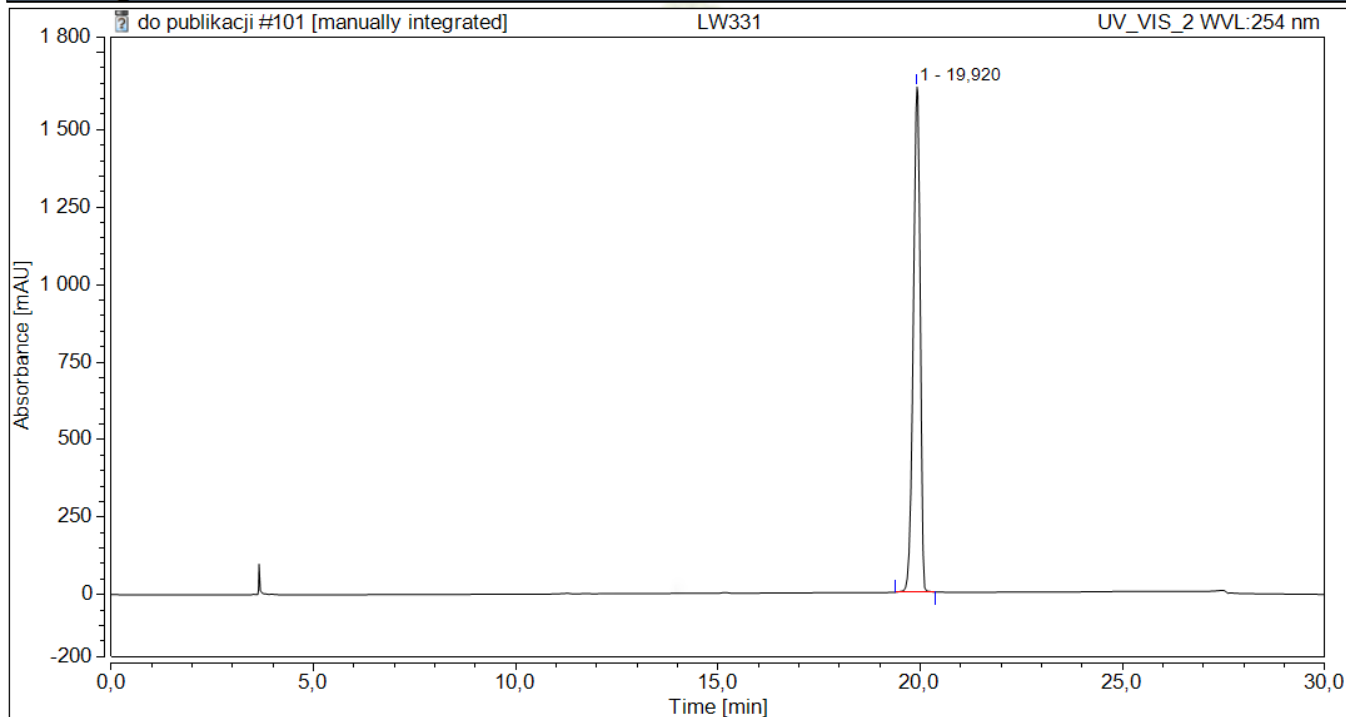
³¹P NMR (162 MHz, Chloroform-d) δ 18.44 (s, 54%), 17.92 (s, 46%).

¹H NMR (400 MHz, Chloroform-d) δ 7.35 – 7.25 (m, 3H, 2xArH, NH), 7.25 – 7.14 (m, 7H, 7xArH), 7.14 – 6.98 (m, 4H, 4xArH), 5.34 (dd, J = 22.6, 8.7 Hz, 1H, NH), 4.76 – 4.49 (m, 3H, CHP, 2xCH), 3.75 – 3.55 (m, 3H, 1.5xCH₂), 3.50 – 3.34 (m, 1H, 0.5xCH₂), 2.75 – 2.50 (m, 2H, CH₂), 2.46 – 2.41 (m, 6H, 2xSCH₃), 2.41 – 2.28 (m, 1H, CH), 2.28 – 2.15 (m, 1H, 0.5xCH₂), 2.11 – 1.78 (m, 3H, 1.5xCH₂), 1.42 (d, J = 4.5 Hz, 9H, Boc), 1.11 – 0.95 (m, 6H, 2xCH₃).

HRMS: C₃₈H₅₀N₃O₇PS₃ [M+Na]⁺ calc. 810.2446 found 810.2424

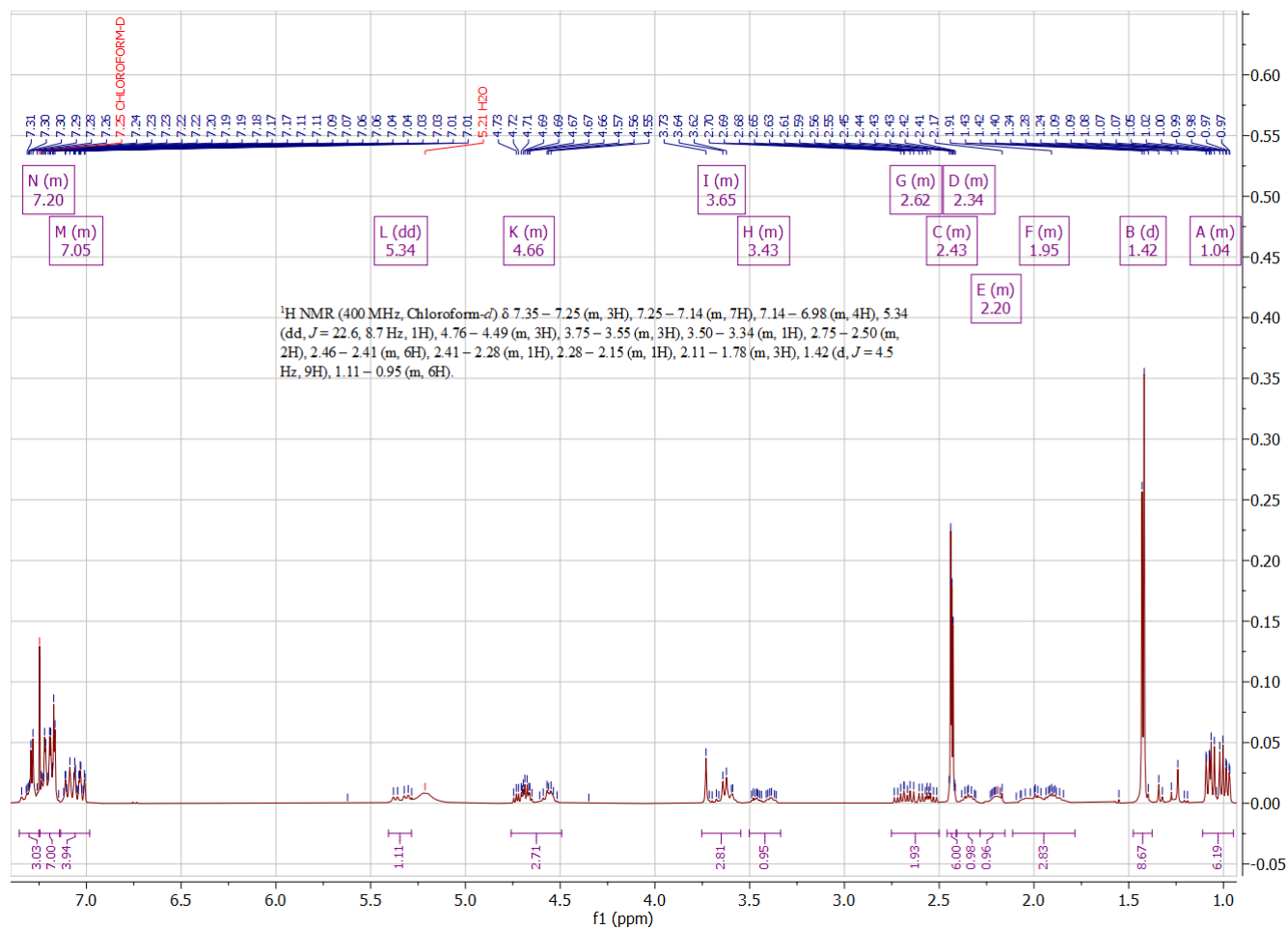
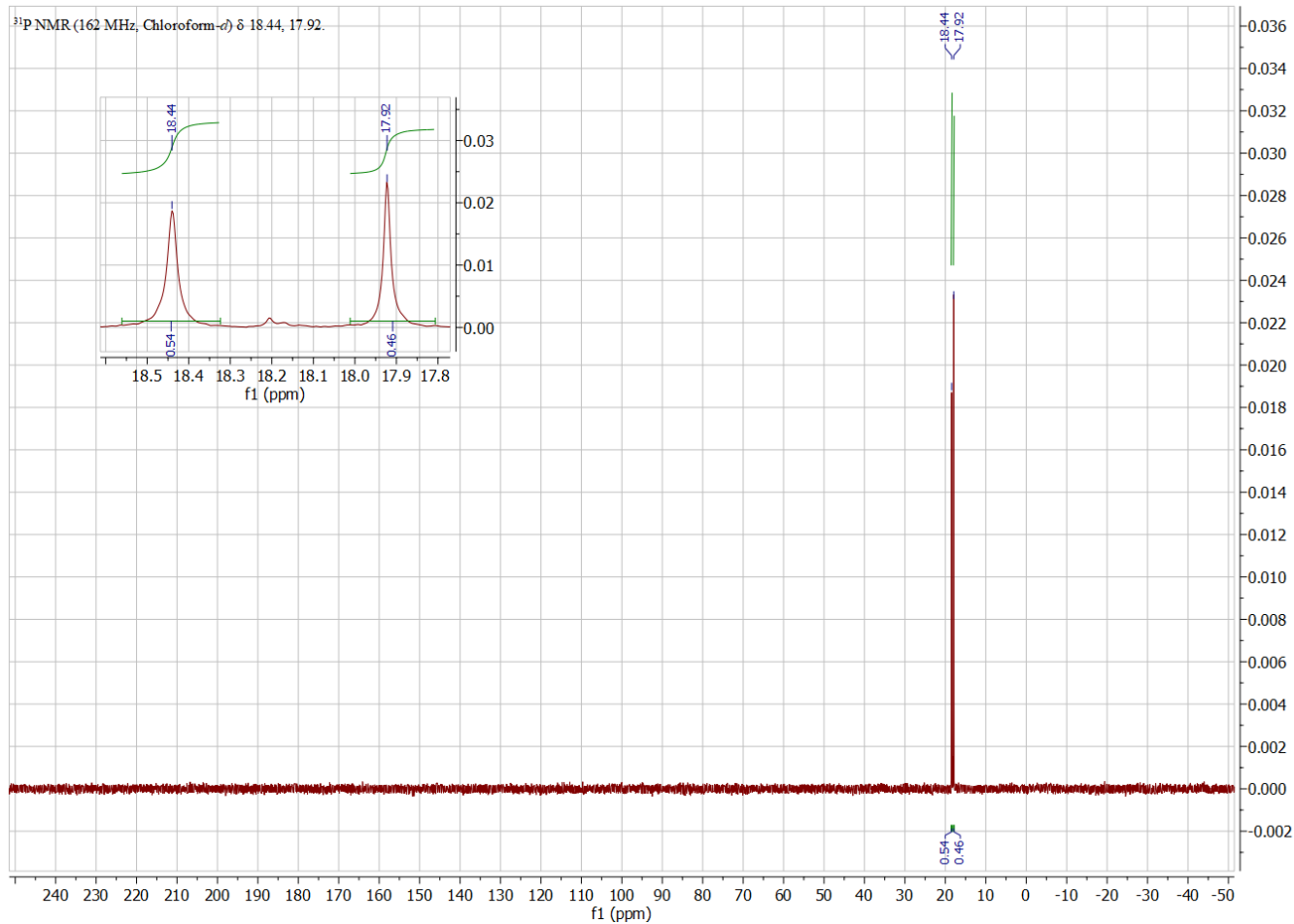
HPLC: purity >99%; retention time 19.920 min

Chromatogram

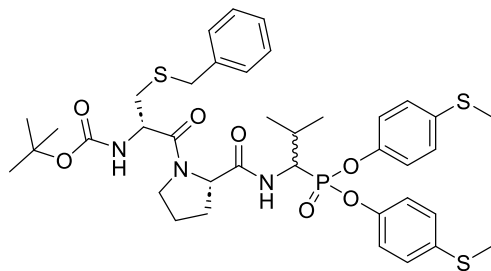


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19,920	320,986	1630,093	100,00	100,00	n.a.
Total:			320,986	1630,093	100,00	100,00	



(102) Boc-D-Cys(Bzl)-L-Pro-Val^P(OPh-4-SCH₃)₂



Name: *tert*-butyl ((2*S*)-3-(benzylthio)-1-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-1-oxopropan-2-yl)carbamate

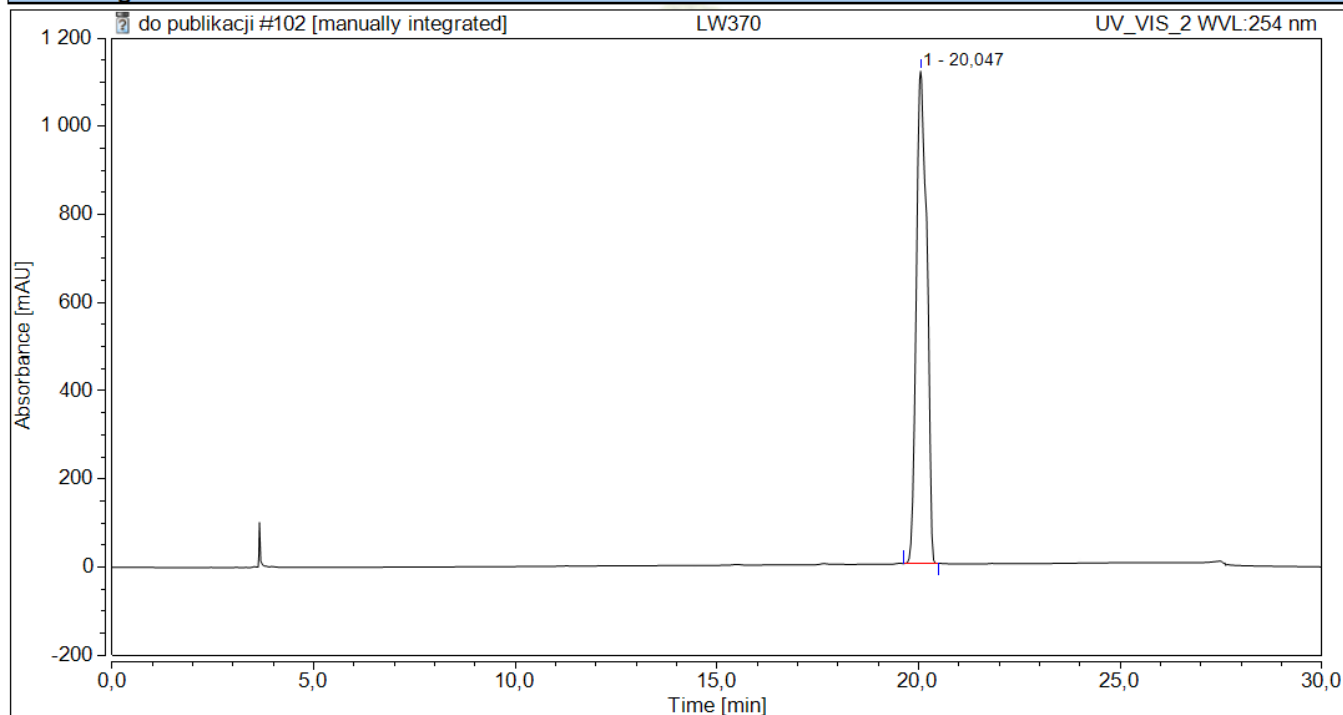
³¹P NMR (162 MHz, Chloroform-*d*) δ 18.72 (s, 52%), 18.28 (s, 48%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.51 (m, 1H, NH), 7.35 – 7.25 (m, 4H, 4xArH), 7.24 – 7.09 (m, 7H, 7xArH), 7.09 – 6.99 (m, 2H, 2xArH), 5.36 (dd, *J* = 87.1, 8.5 Hz, 1H, NH), 4.75 – 4.35 (m, 3H, CHP, 2xCH), 3.76 – 3.66 (m, 2H, CH₂), 3.58 – 3.24 (m, 2H, CH₂), 2.81 – 2.58 (m, 2H, CH₂), 2.45 – 2.39 (m, 6H, 2xSCH₃), 2.38 – 2.30 (m, 2H, 0.5xCH₂, CH), 2.09 – 1.96 (m, 1H, 0.5xCH₂), 1.95 – 1.73 (m, 2H, CH₂), 1.37 (d, *J* = 22.5 Hz, 9H, Boc), 1.09 – 0.93 (m, 6H, 2xCH₃).

HRMS: C₃₈H₅₀N₃O₇PS₃ [M+Na]⁺ calc. 810.2446 found 810.2432

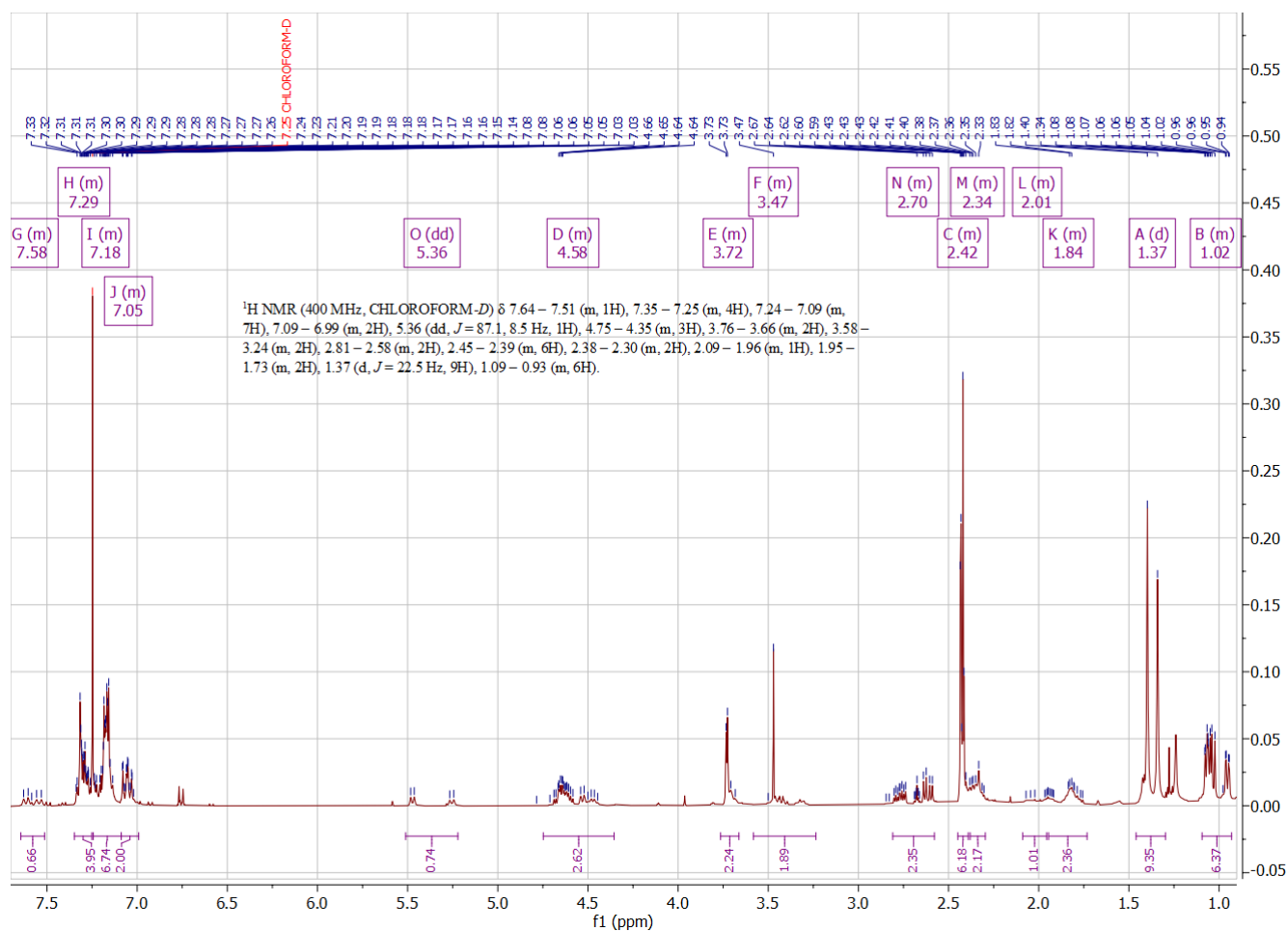
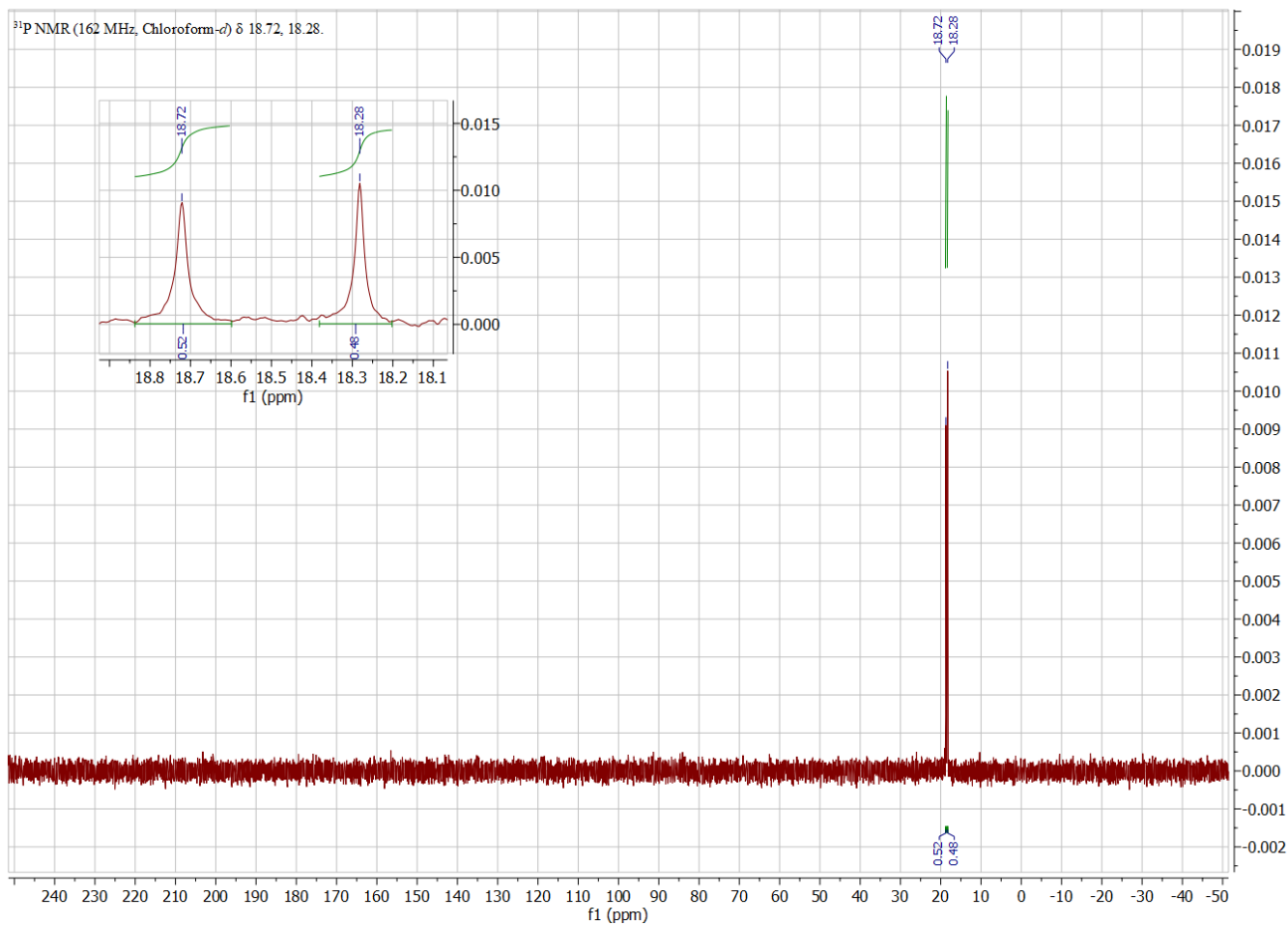
HPLC: purity >99%; retention time 20.047 min

Chromatogram

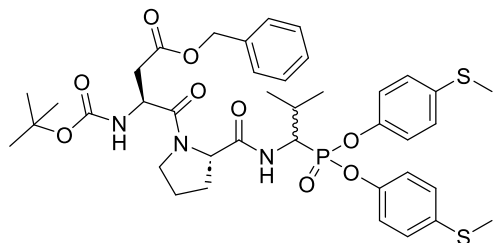


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20,047	336,444	1116,895	100,00	100,00	n.a.
Total:			336,444	1116,895	100,00	100,00	



(103) Boc-L-Asp(Bzl)-L-Pro- Val^P(OPh-4-SCH₃)₂



Name: benzyl (3S)-4-((2S)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-3-((*tert*-butoxycarbonyl)amino)-4-oxobutanoate

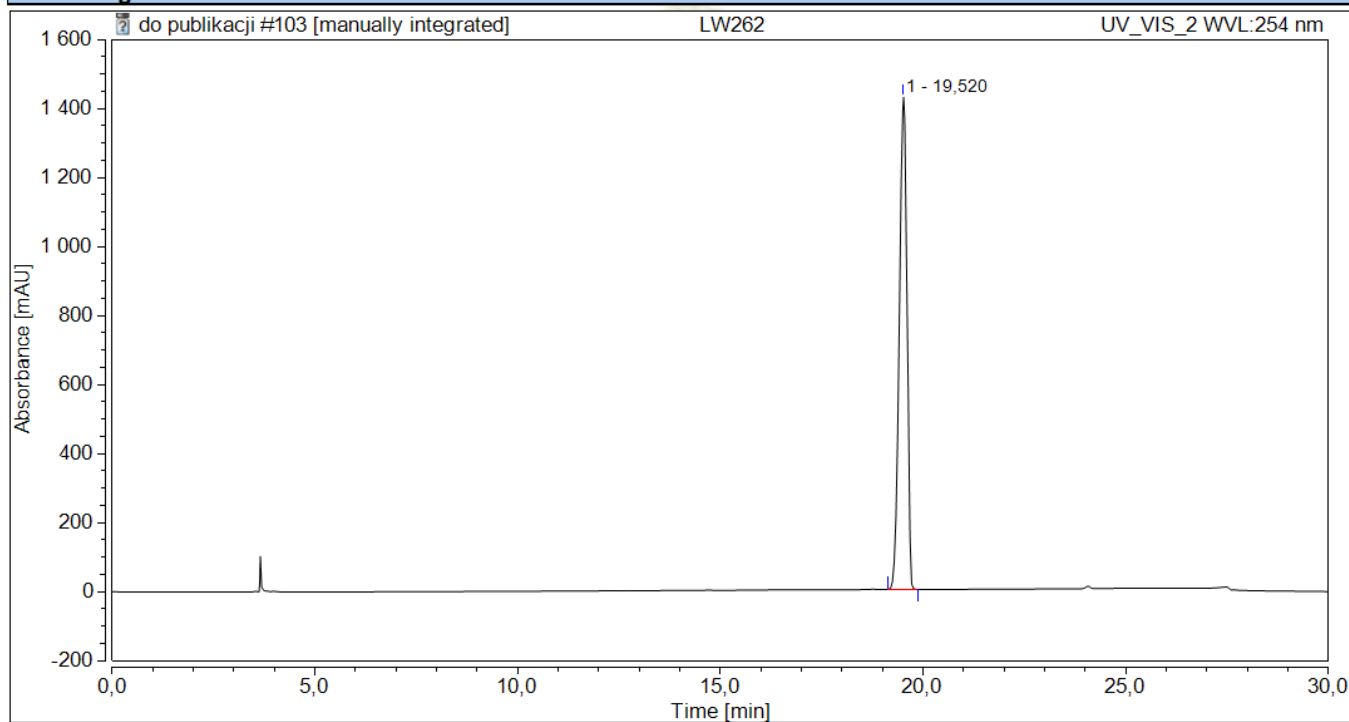
³¹P NMR (162 MHz, Chloroform-*d*) δ 18.58 (s, 48%), 18.19 (s, 52%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.32 (m, 1H, NH), 7.32 – 7.27 (m, 3H, 3xArH), 7.22 – 7.10 (m, 8H, 8xArH), 7.06 – 6.97 (m, 2H, 2xArH), 5.26 (dd, *J* = 21.4, 9.3 Hz, 1H, NH), 5.12 – 4.85 (m, 2H, CH₂), 4.85 – 4.77 (m, 1H, CHP), 4.75 – 4.62 (m, 2H, 2xCH), 3.86 – 3.69 (m, 2H, CH₂), 2.97 – 2.86 (m, 1H, 0.5xCH₂), 2.72 – 2.62 (m, 1H, 0.5xCH₂), 2.43 – 2.38 (m, 6H, 2xSCH₃), 2.40 – 2.17 (m, 2H, 0.5xCH₂, CH), 2.12 – 1.81 (m, 3H, 1.5xCH₂), 1.41 (d, *J* = 1.4 Hz, 9H, Boc), 1.13 – 0.93 (m, 6H, 2xCH₃).

HRMS: C₃₉H₅₀N₃O₉PS₂ [M+Na]⁺ calc. 822.2624 found 822.2603

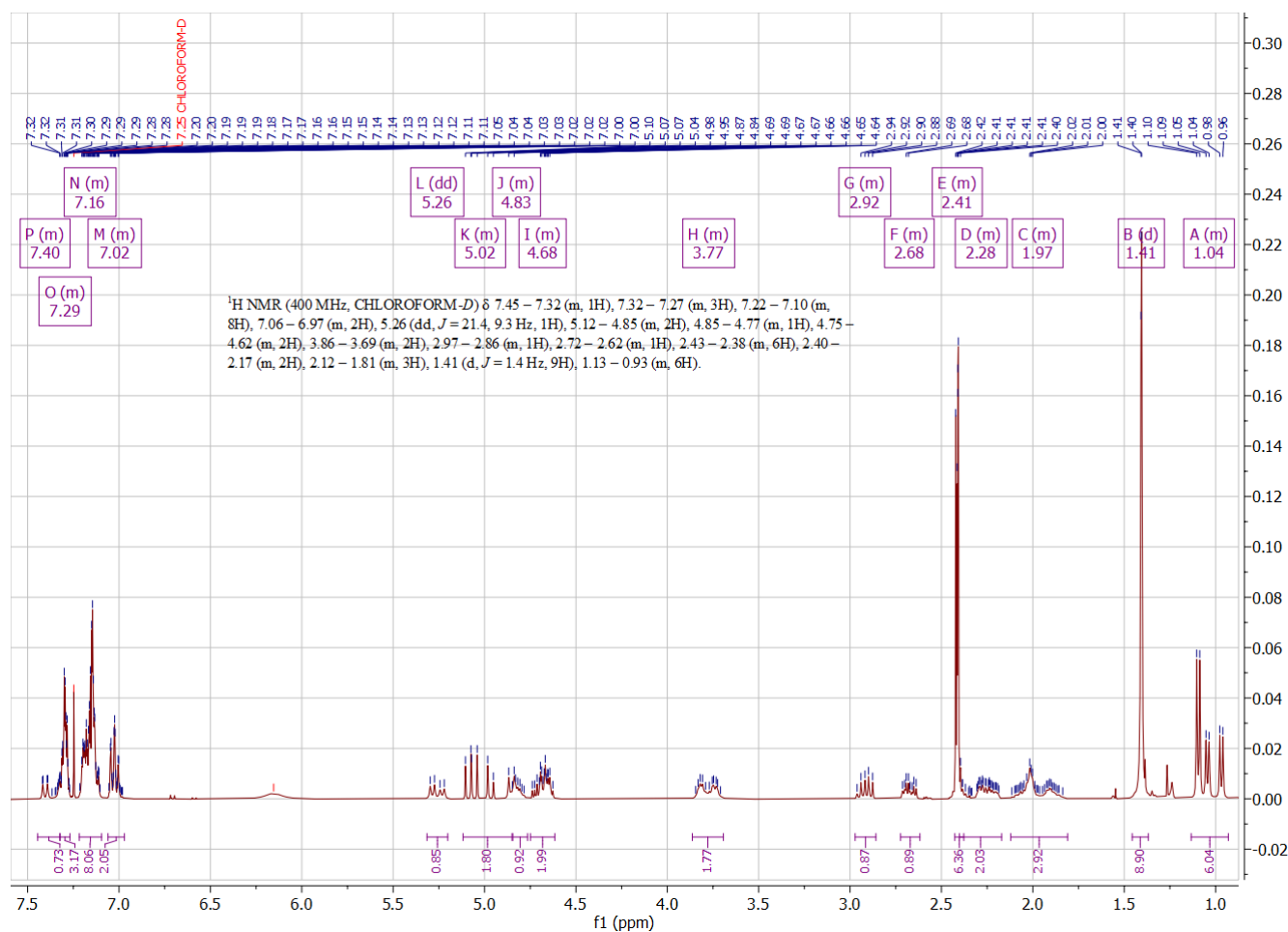
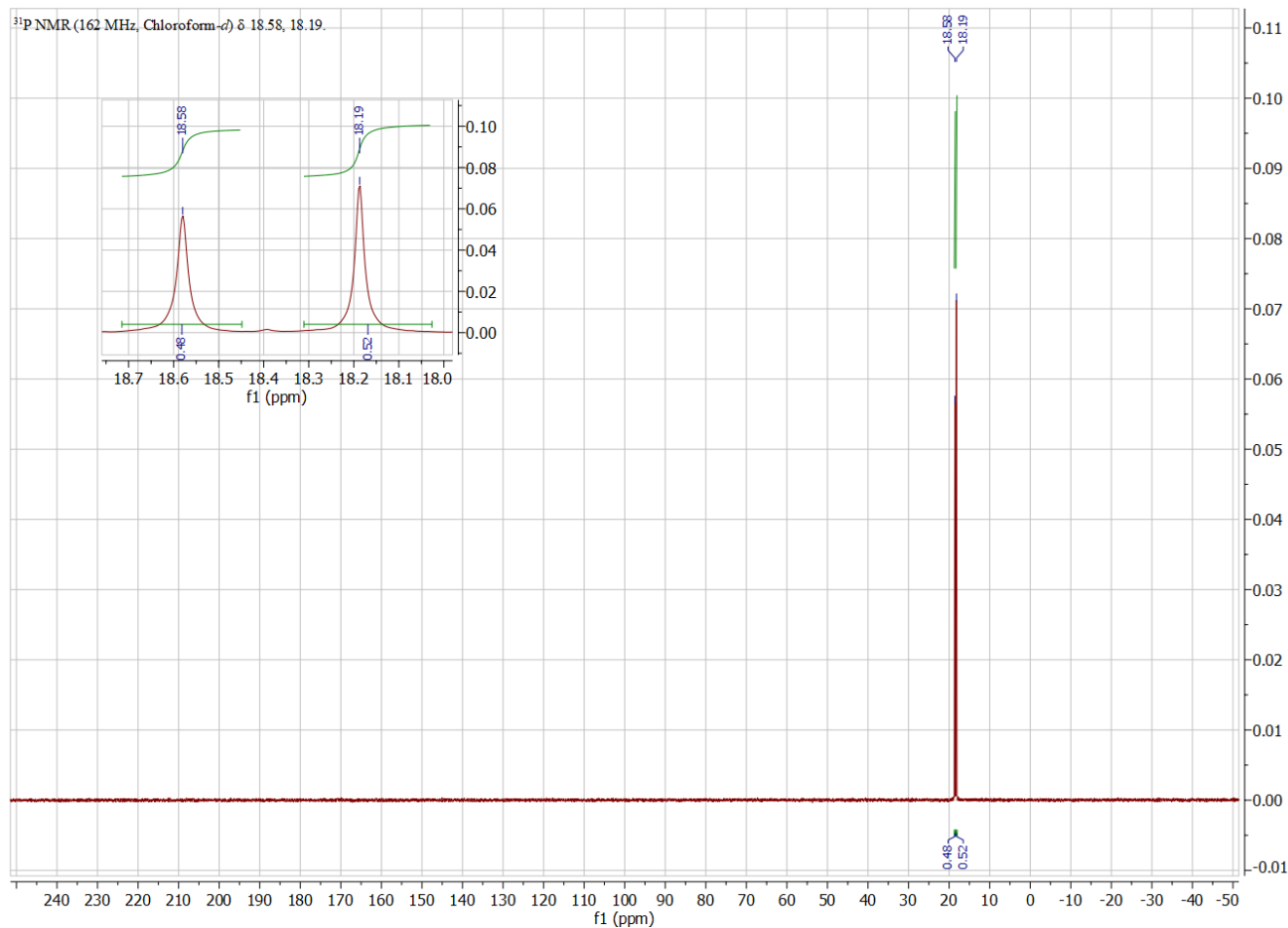
HPLC: purity >99%; retention time 19.520 min

Chromatogram

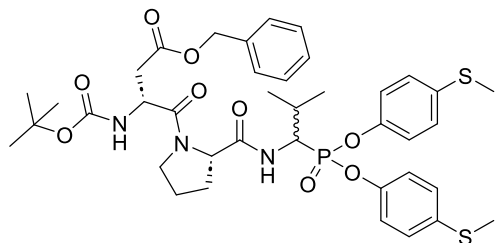


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		19,520	312,780	1425,797	100,00	100,00	n.a.
Total:			312,780	1425,797	100,00	100,00	



(104) Boc-D-Asp(Bzl)-L-Pro- Val^P(OPh-4-SCH₃)₂



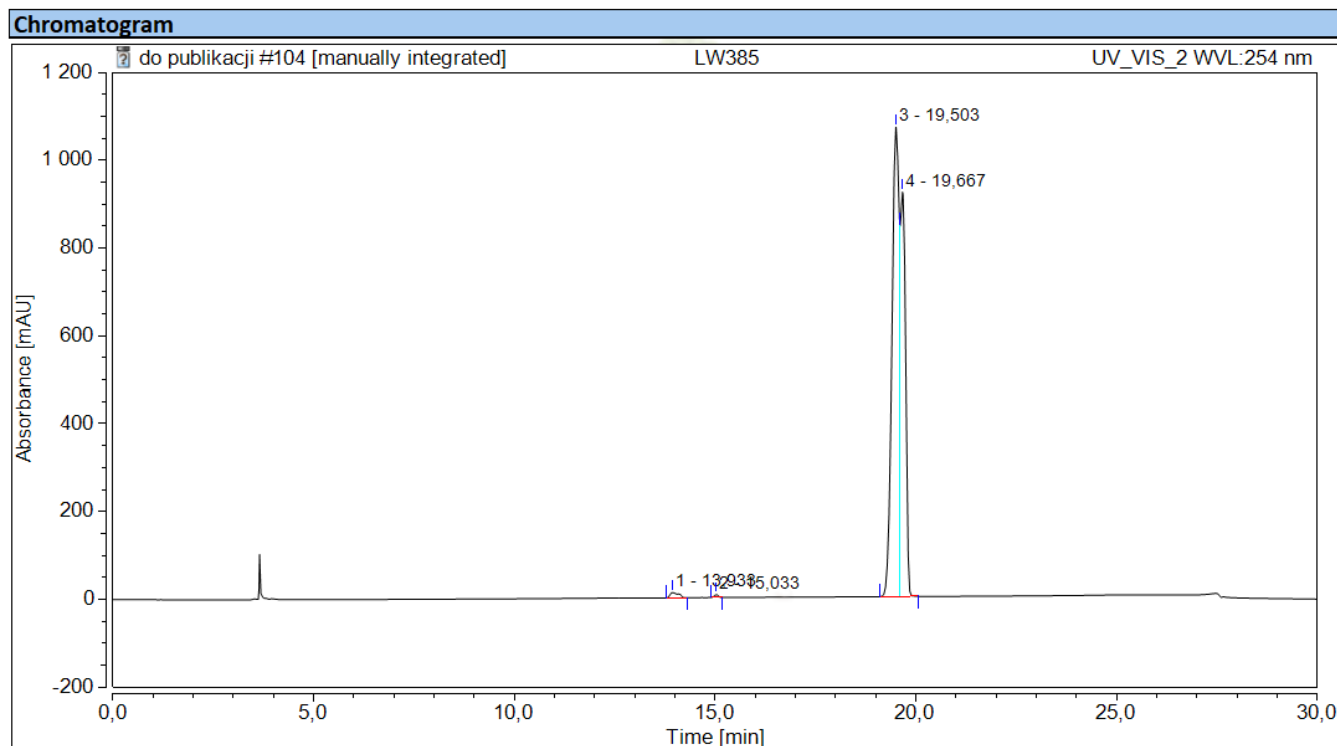
Name: benzyl (3R)-4-((2S)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-3-((*tert*-butoxycarbonyl)amino)-4-oxobutanoate

³¹P NMR (162 MHz, Chloroform-d) δ 18.78 (s, 47%) 18.24 (s, 53%).

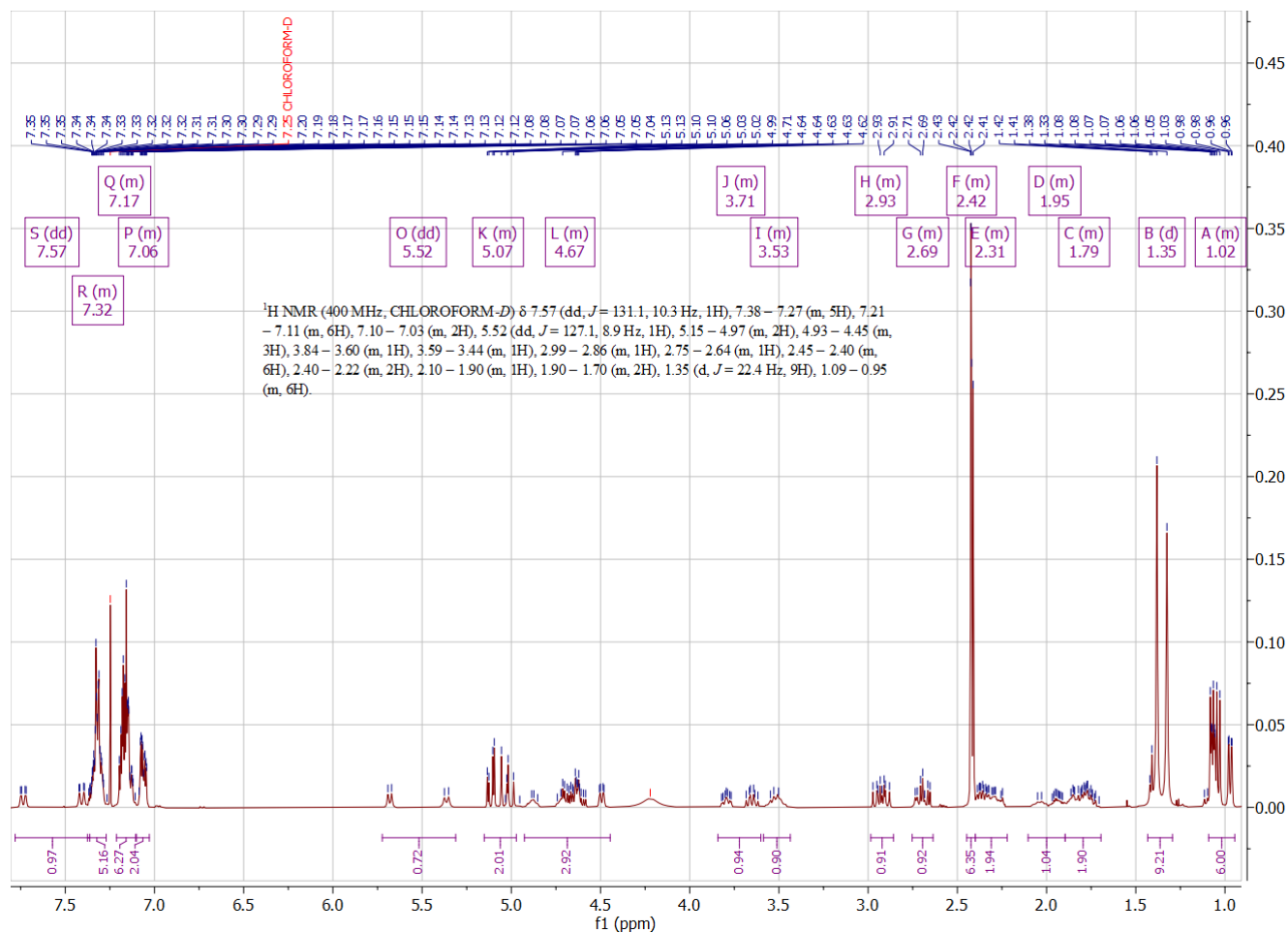
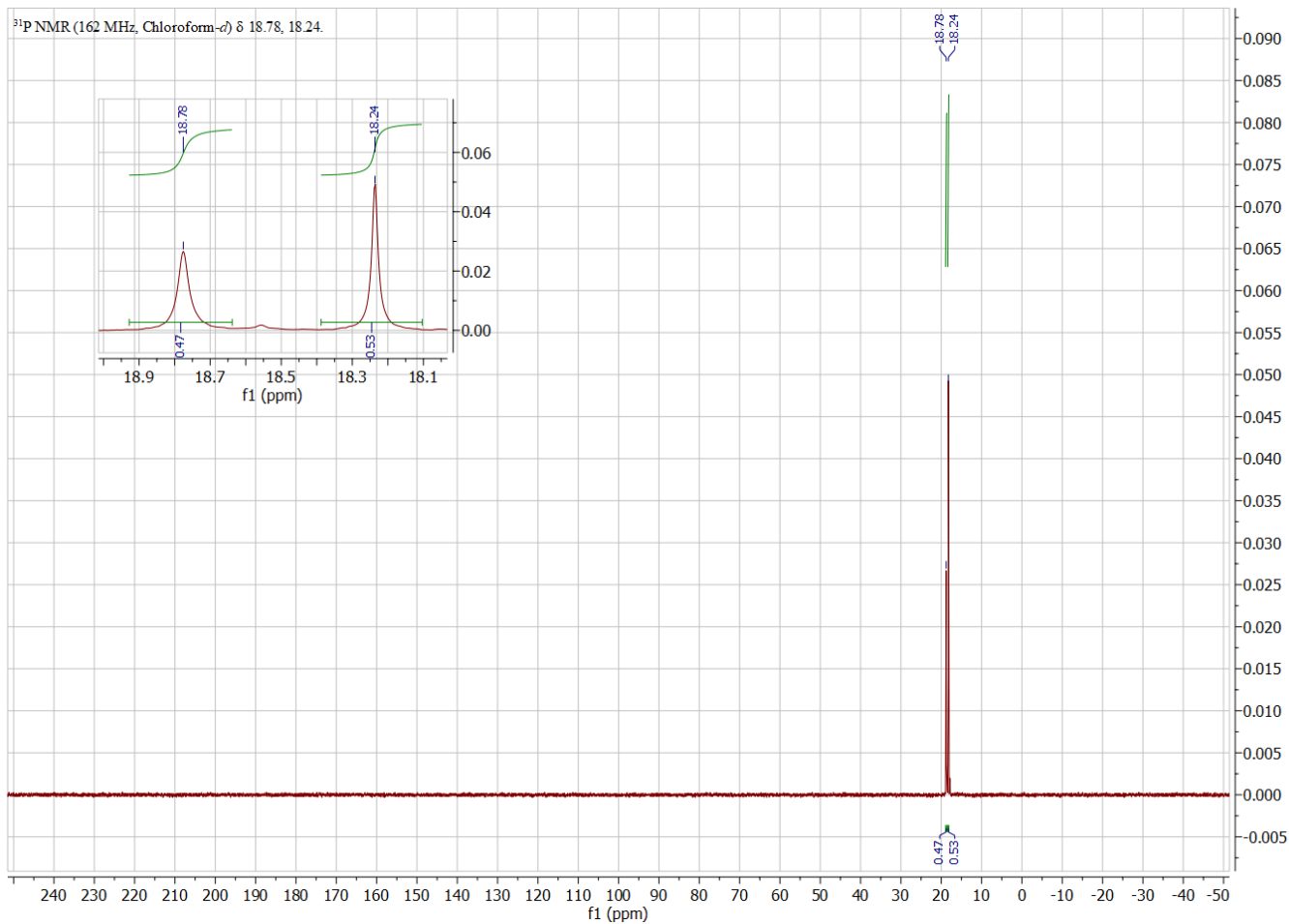
¹H NMR (400 MHz, Chloroform-d) δ 7.57 (dd, J = 131.1, 10.3 Hz, 1H, NH), 7.38 – 7.27 (m, 5H, 5xArH), 7.21 – 7.11 (m, 6H, 6xArH), 7.10 – 7.03 (m, 2H, 2xArH), 5.52 (dd, J = 127.1, 8.9 Hz, 1H, NH), 5.15 – 4.97 (m, 2H, CH₂), 4.93 – 4.45 (m, 3H, CHP, 2xCH), 3.84 – 3.60 (m, 1H, 0.5xCH₂), 3.59 – 3.44 (m, 1H, 0.5xCH₂), 2.99 – 2.86 (m, 1H, 0.5xCH₂), 2.75 – 2.64 (m, 1H, 0.5xCH₂), 2.45 – 2.40 (m, 6H, 2xSCH₃), 2.40 – 2.22 (m, 2H, 0.5xCH₂, CH), 2.10 – 1.90 (m, 1H, 0.5xCH₂), 1.90 – 1.70 (m, 2H, CH₂), 1.35 (d, J = 22.4 Hz, 9H, Boc), 1.09 – 0.95 (m, 6H, 2xCH₃).

HRMS: C₃₉H₅₀N₃O₉PS₂ [M+Na]⁺ calc. 822.2624 found 822.2617

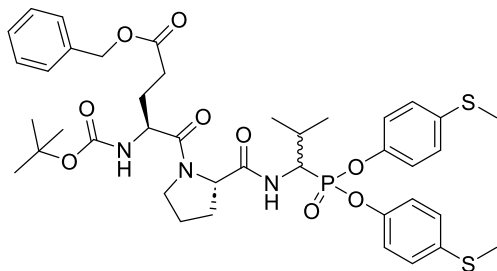
HPLC: purity >98%; retention time 19.503 and 19.667 min



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13,933	3,023	12,309	0,83	0,61	n.a.
2		15,033	0,779	6,792	0,21	0,34	n.a.
3		19,503	217,680	1069,098	59,74	53,21	n.a.
4		19,667	142,872	921,015	39,21	45,84	n.a.
Total:			364,354	2009,214	100,00	100,00	



(105) Boc-L-Glu(Bzl)-L-Pro- Val^P(OPh-4-SCH₃)₂



Name: benzyl (4S)-5-((2S)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-4-((*tert*-butoxycarbonyl)amino)-5-oxopentanoate

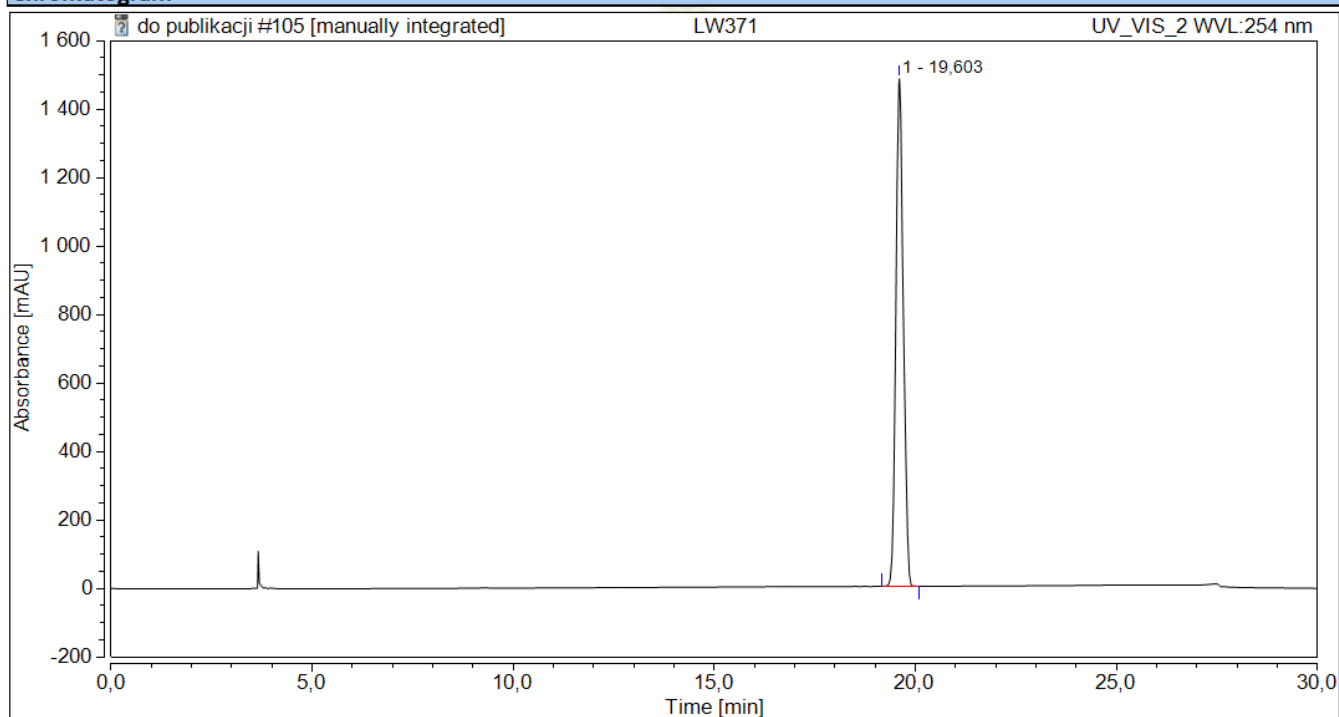
³¹P NMR (162 MHz, Chloroform-d) δ 18.26 (s, 50%), 18.06 (s, 50%).

¹H NMR (400 MHz, Chloroform-d) δ 7.47 (dd, J = 36.8, 10.6 Hz, 1H, NH), 7.36 – 7.28 (m, 5H, 5xArH), 7.21 – 7.14 (m, 4H, 4xArH), 7.14 – 7.01 (m, 4H, 4xArH), 5.41 (dd, J = 20.2, 7.7 Hz, 1H, NH), 5.11 (s, 2H, CH₂), 4.76 – 4.64 (m, 1H, CHP), 4.60 – 4.39 (m, 2H, 2xCH), 3.79 – 3.45 (m, 2H, CH₂), 2.59 – 2.44 (m, 2H, CH₂), 2.44 – 2.40 (m, 6H, 2xSCH₃), 2.40 – 2.30 (m, 1H, CH), 2.27 – 2.15 (m, 1H, 0.5xCH₂), 2.15 – 1.88 (m, 3H, 1.5xCH₂), 1.88 – 1.75 (m, 2H, CH₂), 1.36 (d, J = 16.4 Hz, 9H, Boc), 1.12 – 0.93 (m, 6H, 2xCH₃).

HRMS: C₄₀H₅₂N₃O₉PS₂ [M+Na]⁺ calc. 836.2780 found 836.2769

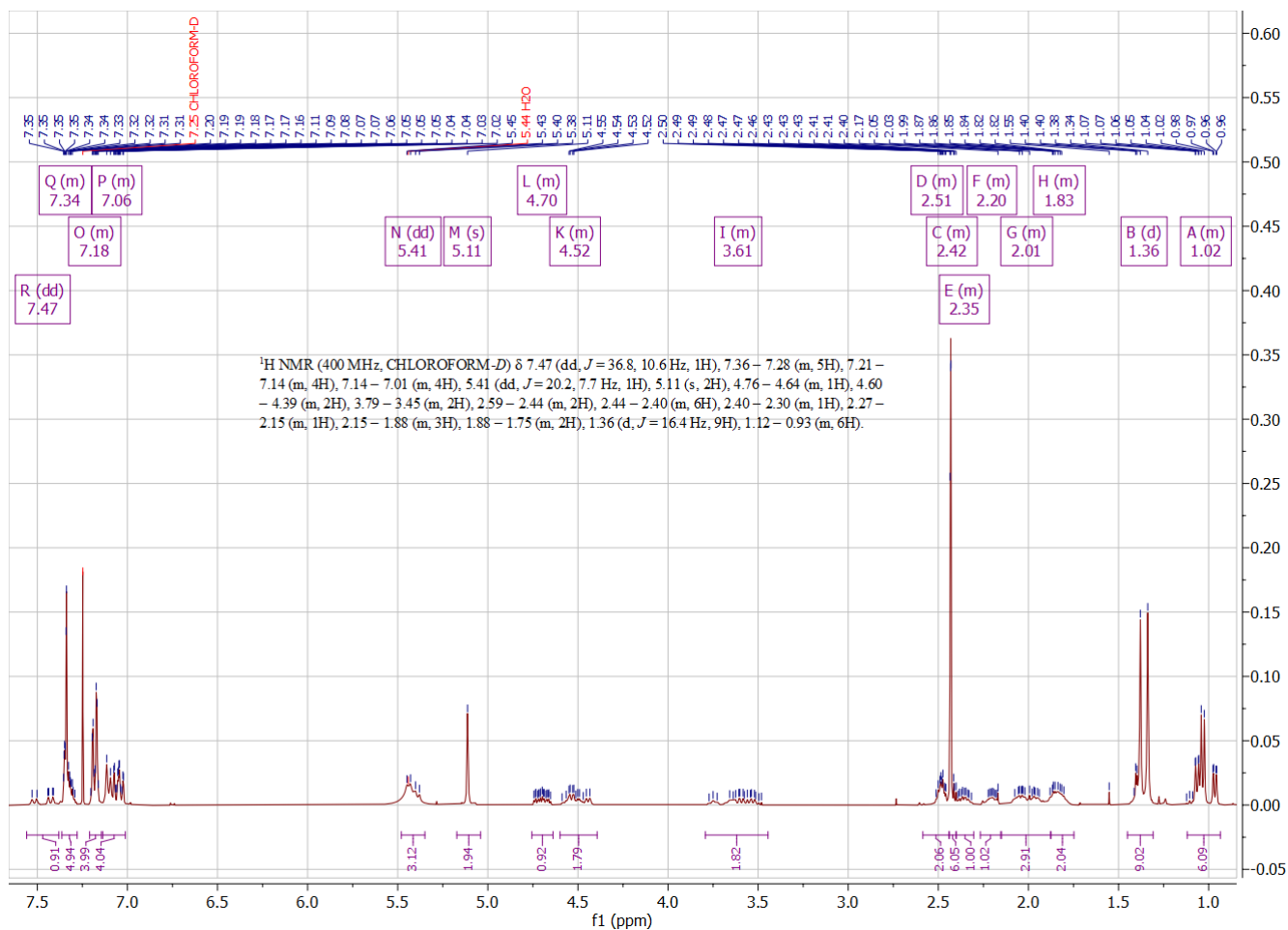
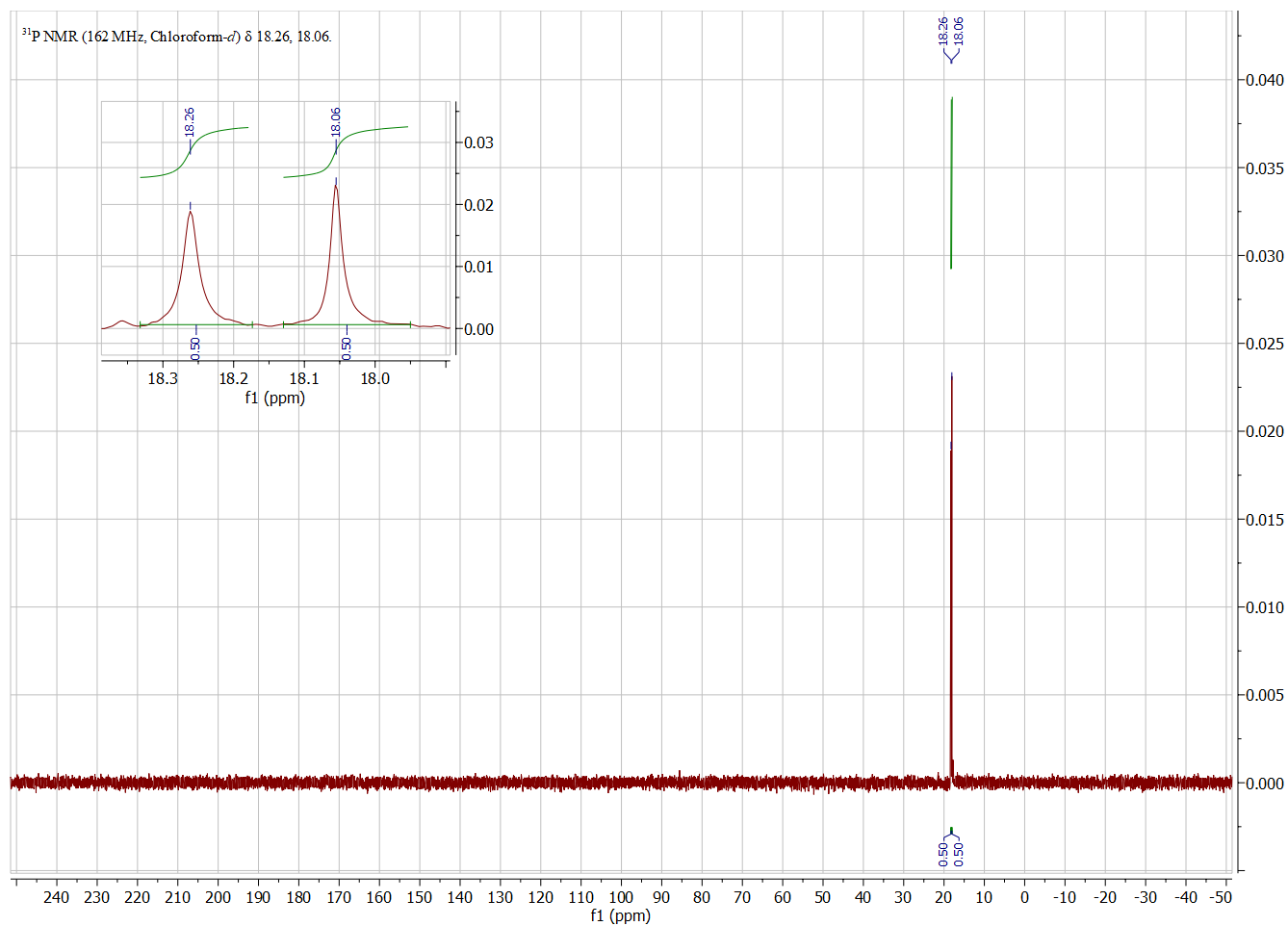
HPLC: purity >99%; retention time 19.603 min

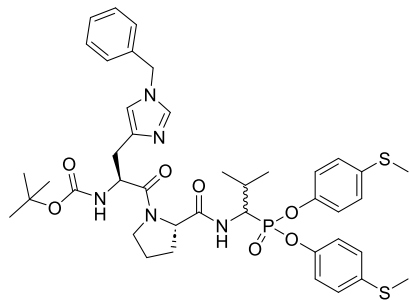
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19,603	316,657	1482,385	100,00	100,00	n.a.
Total:			316,657	1482,385	100,00	100,00	



(106) Boc-L-His(Bzl)-L-Pro-Val^P(OPh-4-SCH₃)₂

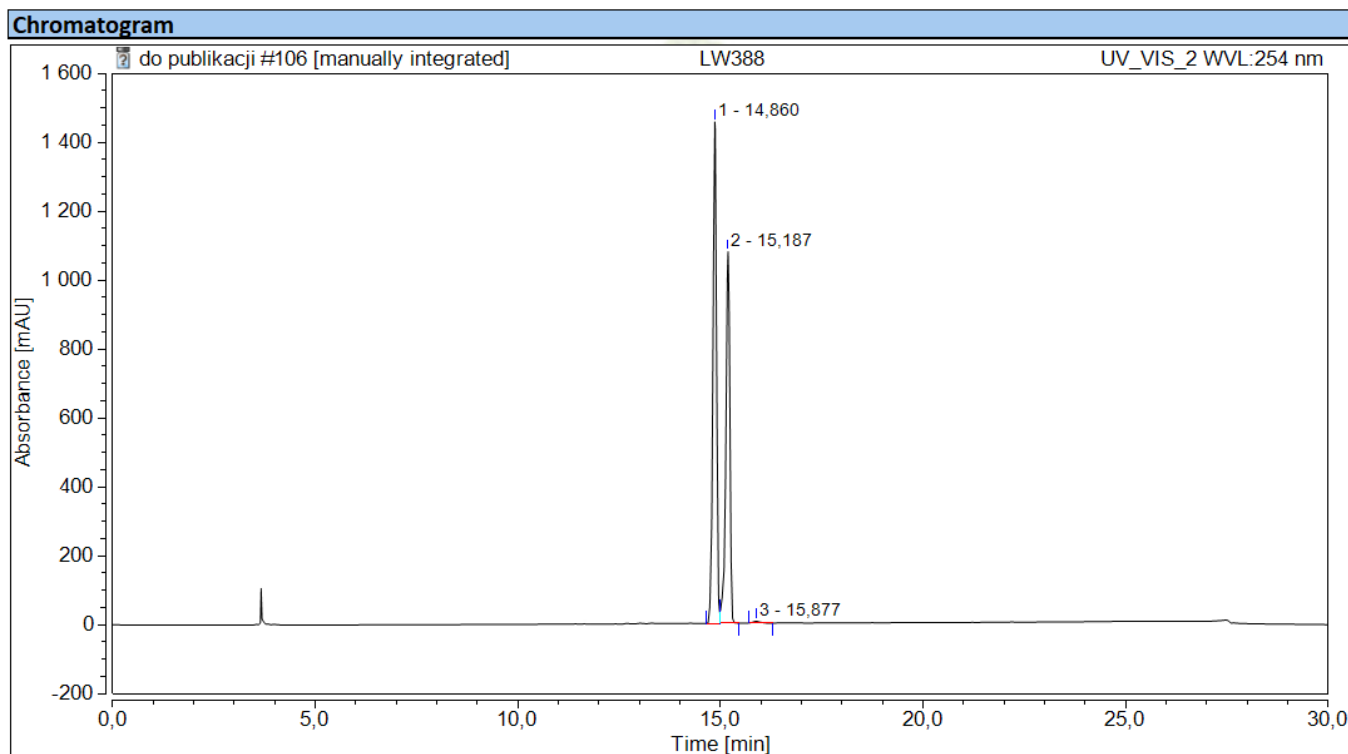
Name: *tert*-butyl ((2*S*)-3-(1-benzyl-1*H*-imidazol-4-yl)-1-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-1-oxopropan-2-yl)carbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.55 (s, 68%), 18.05 (s, 32%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.27 (m, 4H, 3xArH, NH), 7.23 – 6.90 (m, 12H, 10xArH, 2xCH), 5.72 (dd, *J* = 16.9, 8.2 Hz, 1H, NH), 5.11 (d, *J* = 35.9 Hz, 2H, CH₂), 4.78 – 4.40 (m, 3H, CHP, 2xCH), 3.68 – 3.42 (m, 2H, CH₂), 3.18 – 2.68 (m, 2H, CH₂), 2.47 – 2.37 (m, 8H, 2xSCH₃, CH₂), 2.25 – 2.15 (m, 1H, CH), 2.03 – 1.83 (m, 3H, 1.5xCH₂), 1.32 (d, *J* = 6.5 Hz, 9H, Boc), 1.12 – 1.00 (m, 6H, 2xCH₃).

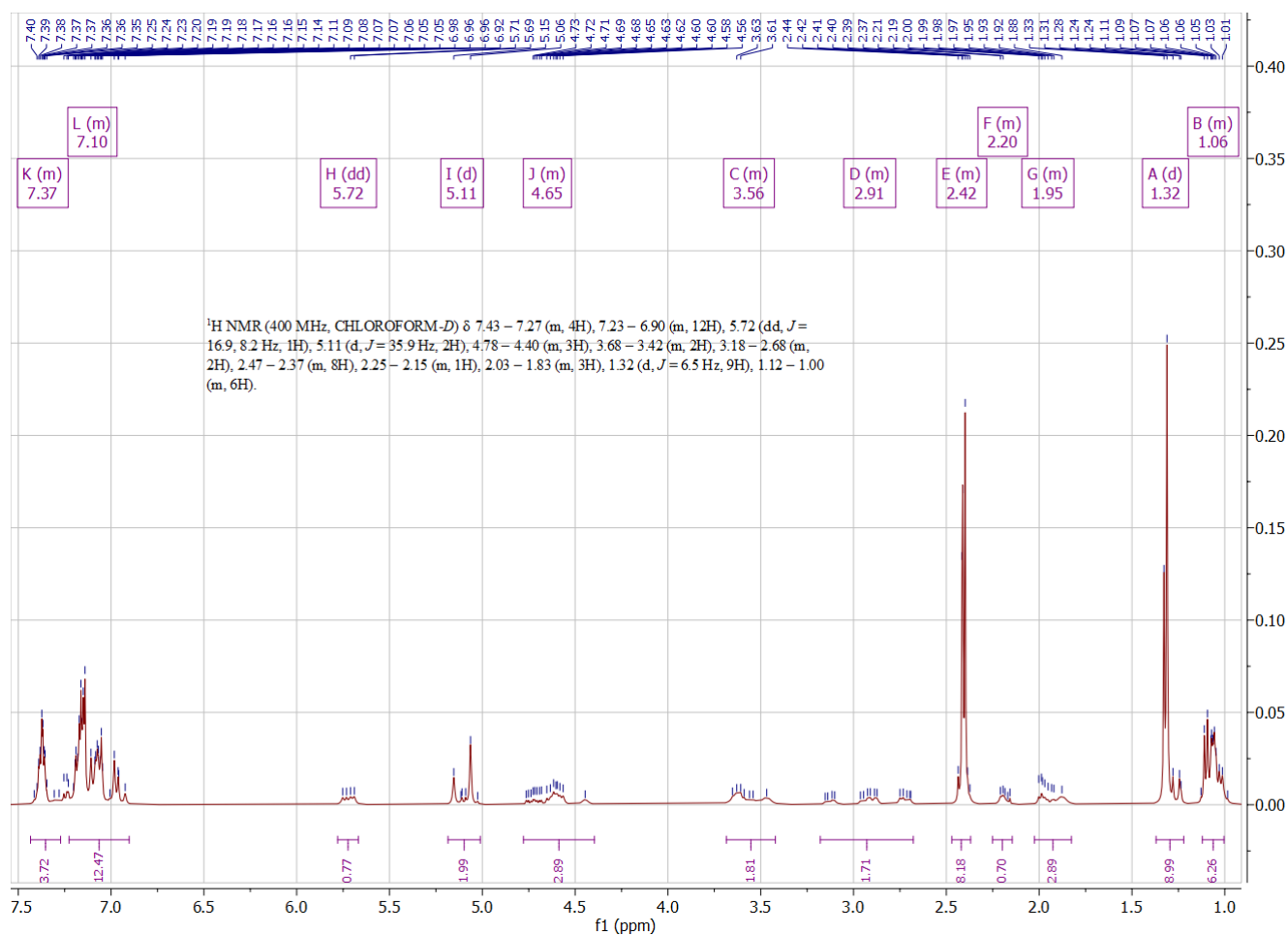
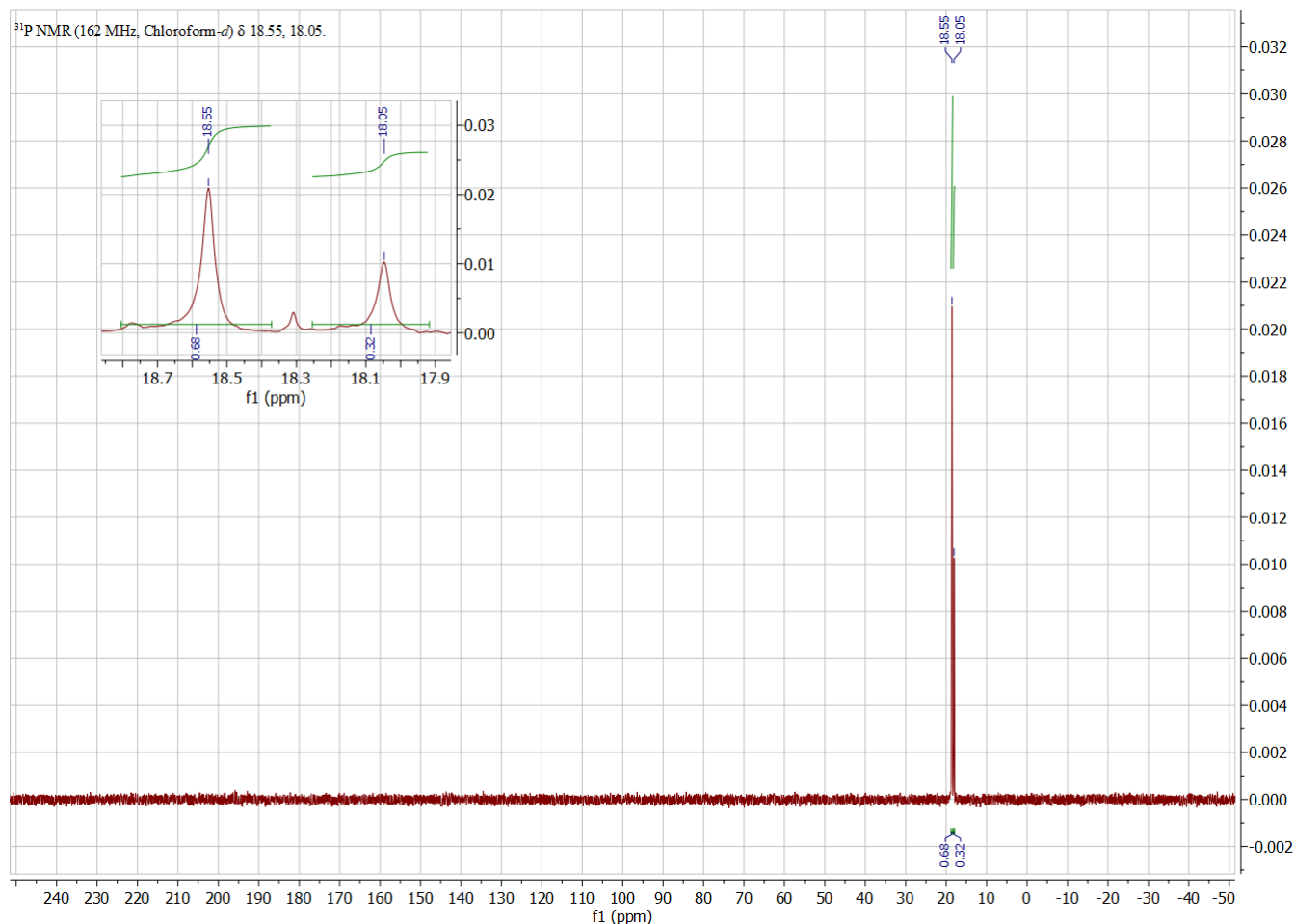
HRMS: C₄₁H₅₂N₅O₇PS₂ [M+Na]⁺ calc. 844.2943 found 844.2914

HPLC: purity >99%; retention time 14.860 and 15.187 min

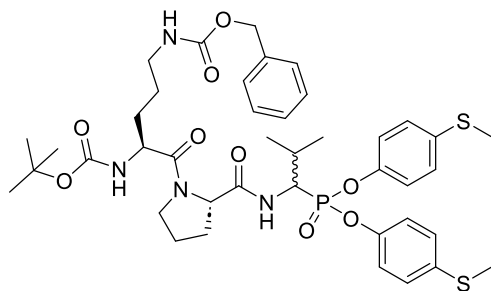


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14,860	151,070	1455,037	54,65	57,33	n.a.
2		15,187	124,343	1077,908	44,98	42,47	n.a.
3		15,877	1,032	5,198	0,37	0,20	n.a.
Total:			276,446	2538,143	100,00	100,00	

^{31}P NMR (162 MHz, Chloroform- d) δ 18.55, 18.05.



(107) Boc-L-Orn(Z)-L-Pro-Val^P(OPh-4-SCH₃)₂



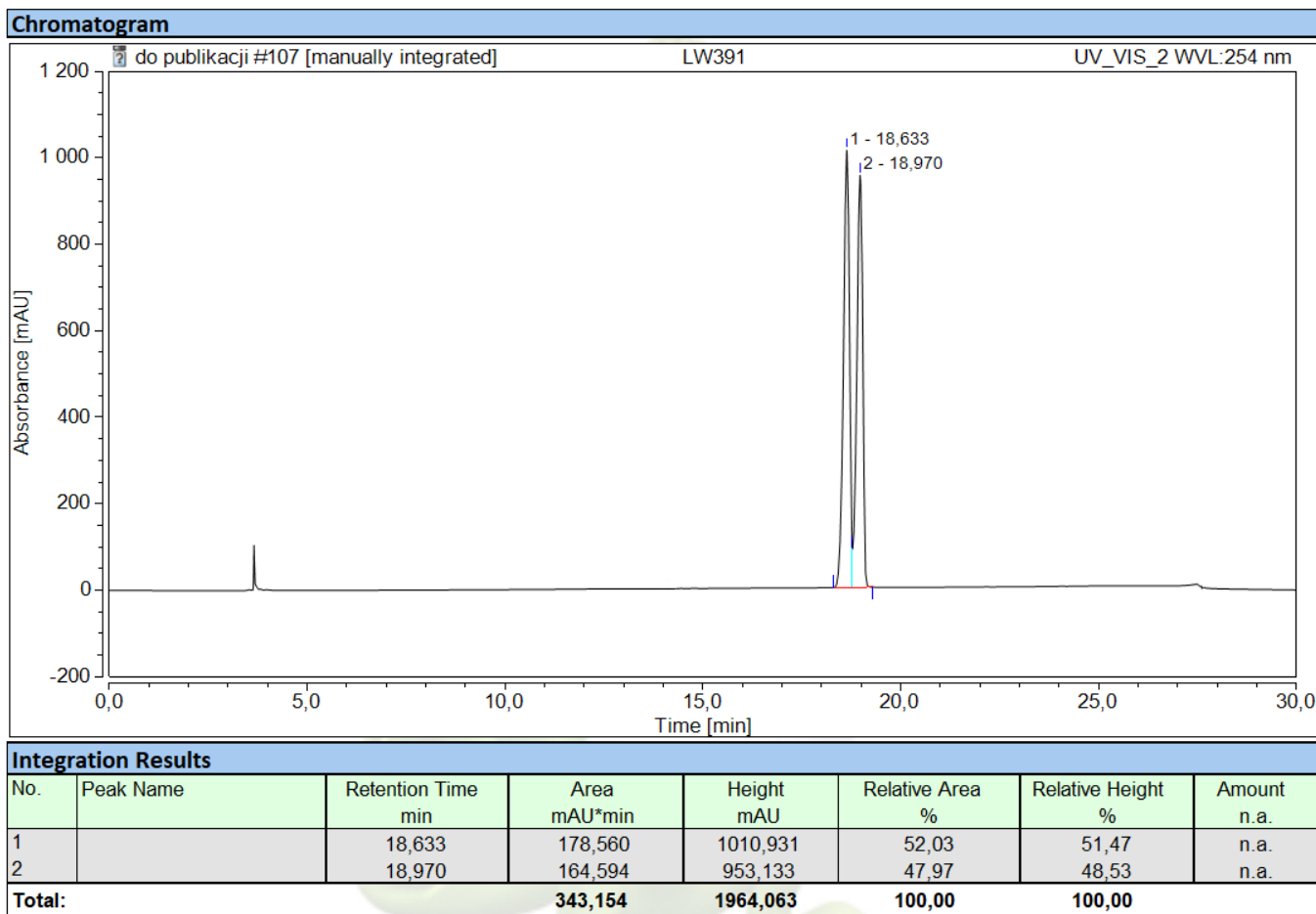
Name: benzyl *tert*-butyl ((4*S*)-5-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-5-oxopentane-1,4-diyl)dicarbamate

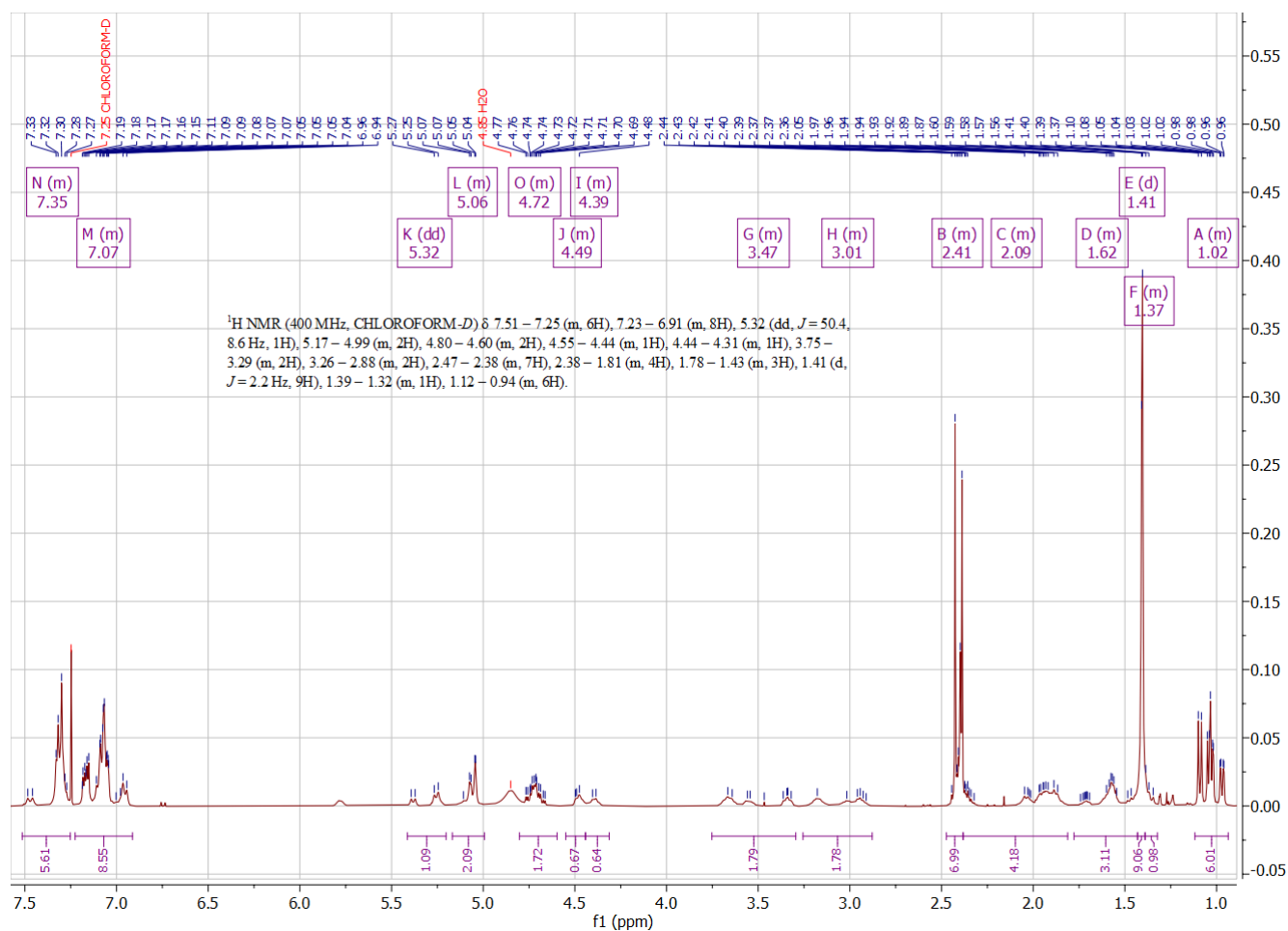
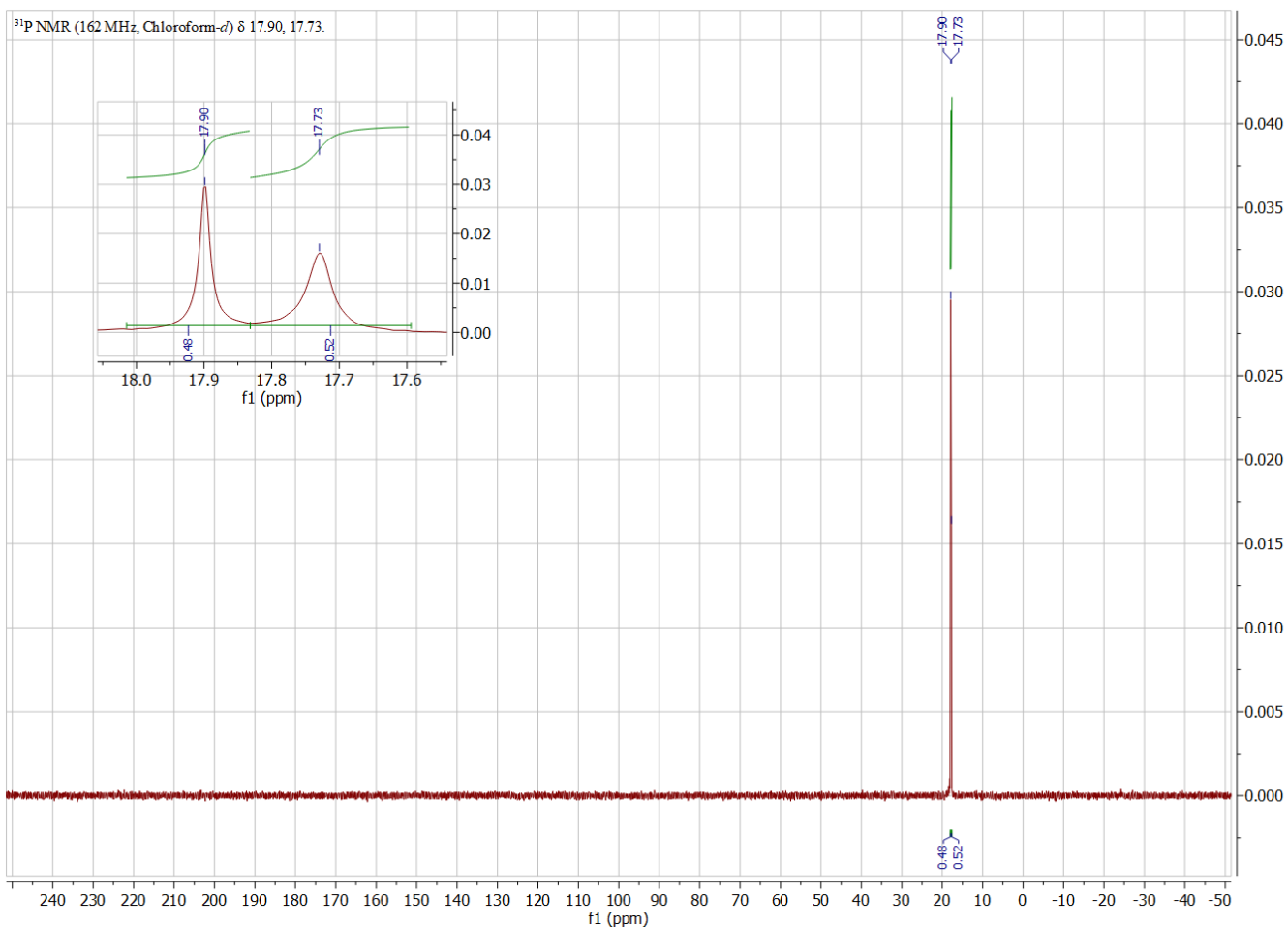
³¹P NMR (162 MHz, Chloroform-*d*) δ 17.90 (s, 48%), 17.73 (s, 52%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.25 (m, 6H, 5xArH, NH), 7.23 – 6.91 (m, 8H, 8xArH), 5.32 (dd, *J* = 50.4, 8.6 Hz, 1H, NH), 5.17 – 4.99 (m, 2H, CH₂), 4.80 – 4.60 (m, 2H, CHP, NH), 4.55 – 4.44 (m, 1H, CH), 4.44 – 4.31 (m, 1H, CH), 3.75 – 3.29 (m, 2H, CH₂), 3.26 – 2.88 (m, 2H, CH₂), 2.47 – 2.38 (m, 7H, 2xSCH₃, CH), 2.38 – 1.81 (m, 4H, 2xCH₂), 1.78 – 1.43 (m, 3H, 1.5xCH₂), 1.41 (d, *J* = 2.2 Hz, 9H, Boc), 1.39 – 1.32 (m, 1H, 0.5xCH₂), 1.12 – 0.94 (m, 6H, 2xCH₃).

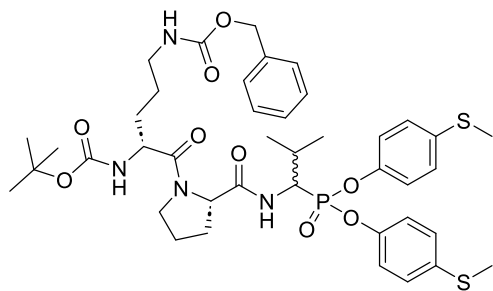
HRMS: C₄₁H₅₅N₄O₉PS₂ [M+Na]⁺ calc. 865.3046 found 865.3028

HPLC: purity >99%; retention time 18.633 and 18.970 min





(108) Boc-D-Orn(Z)-L-Pro-Val^P(OPh-4-SCH₃)₂



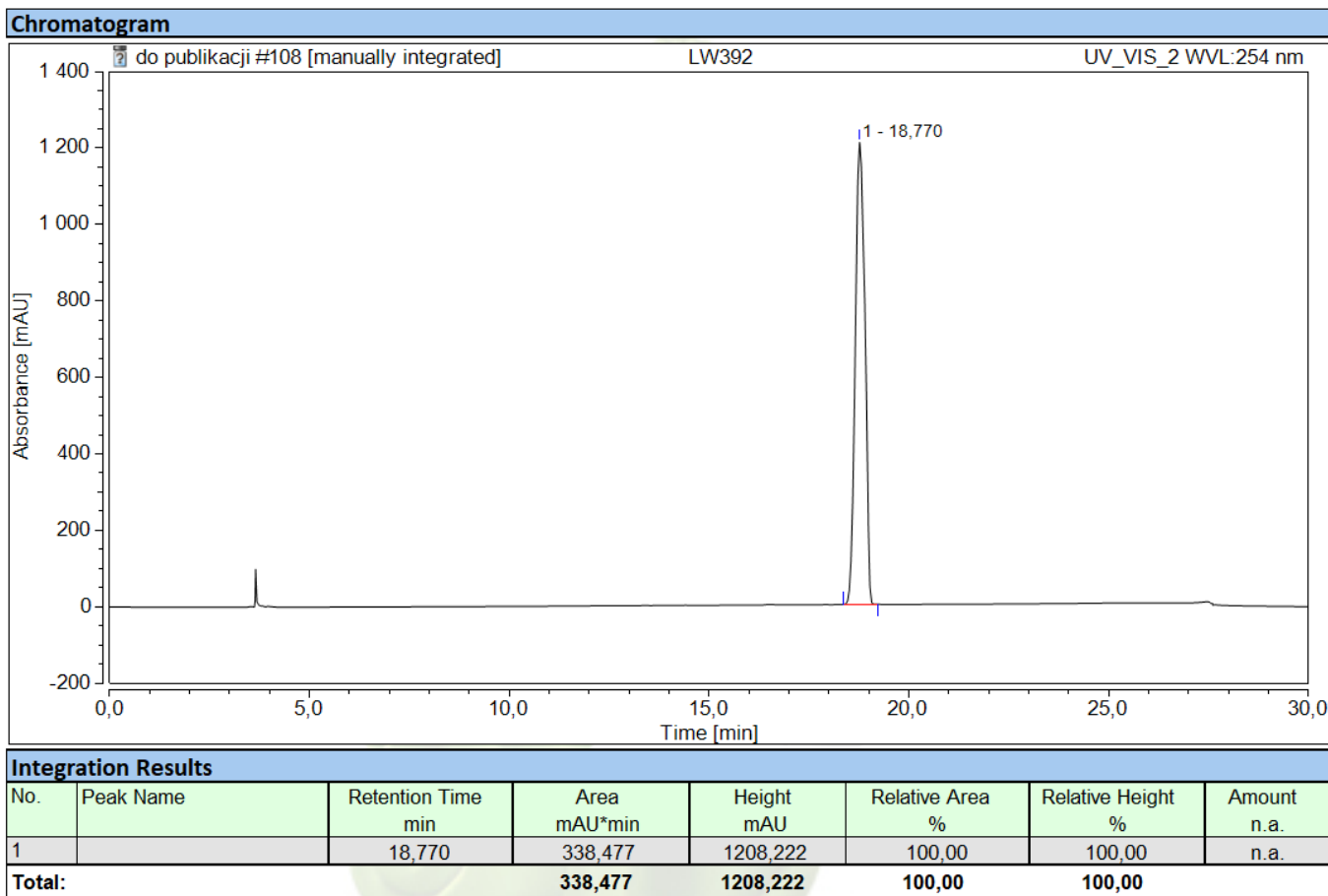
Name: benzyl *tert*-butyl ((4*R*)-5-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-5-oxopentane-1,4-diyl)dicarbamate

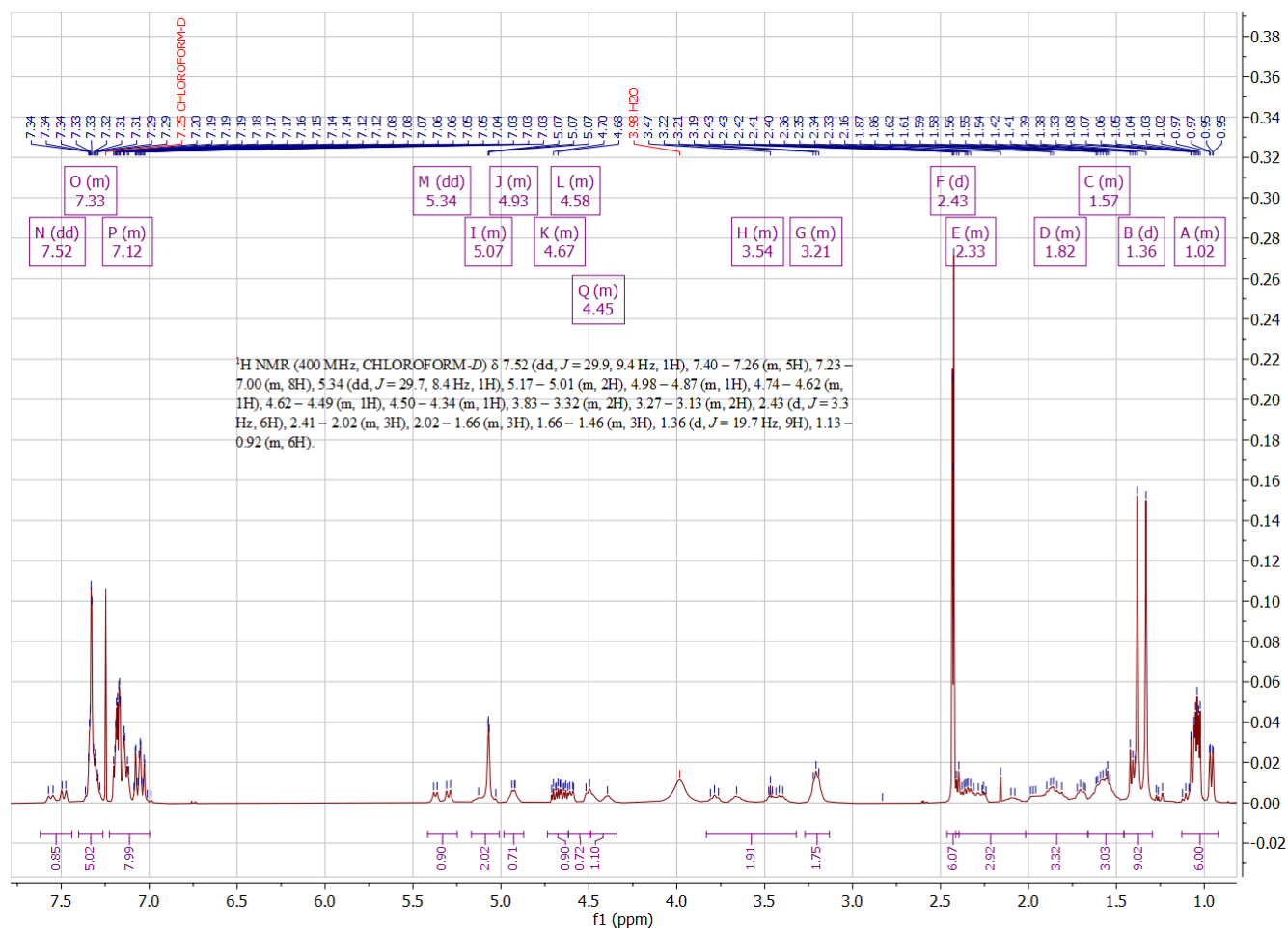
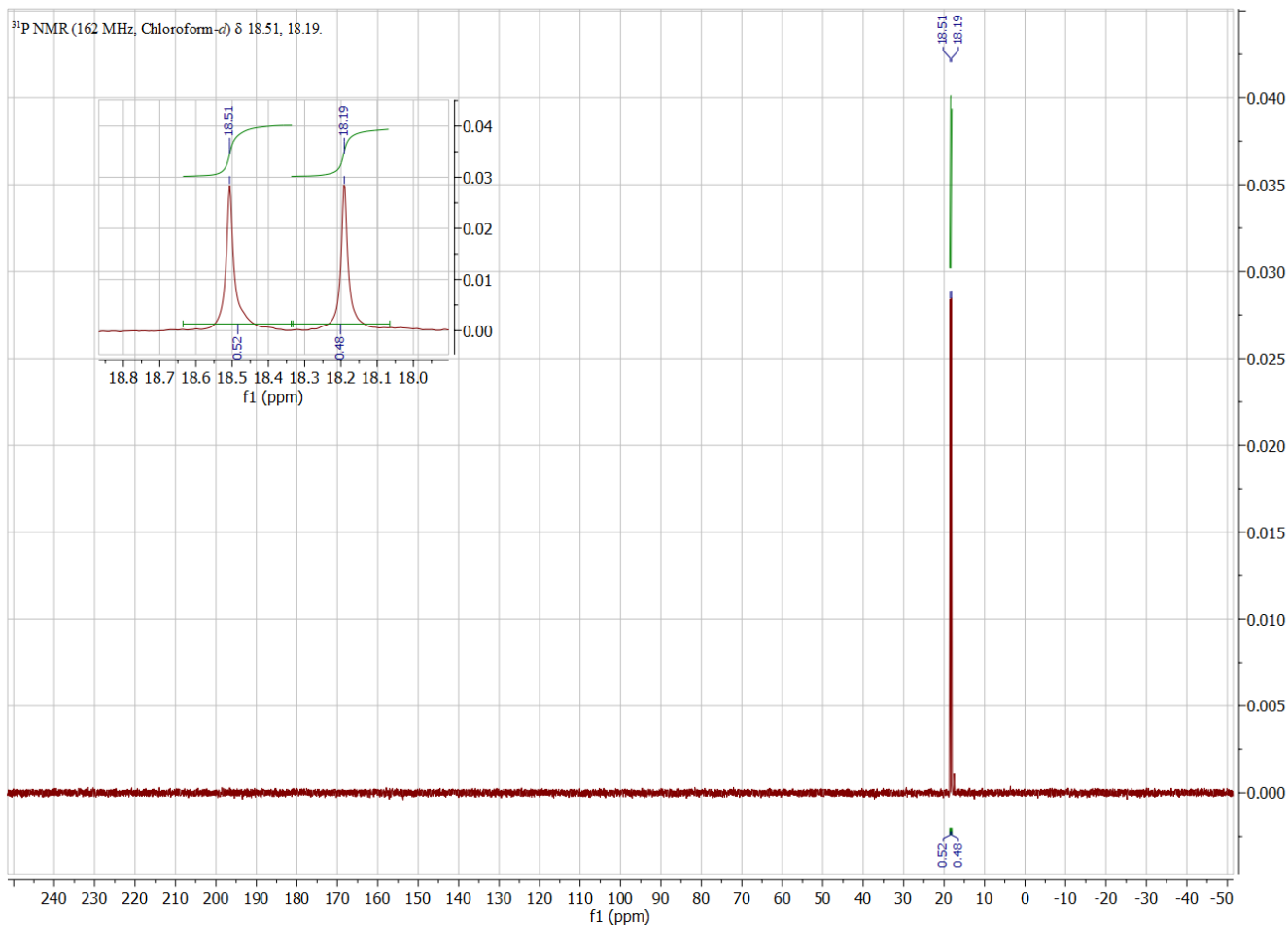
³¹P NMR (162 MHz, Chloroform-*d*) δ 18.51 (s, 52%), 18.19 (s, 48%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.52 (dd, *J* = 29.9, 9.4 Hz, 1H, NH), 7.40 – 7.26 (m, 5H, 5xArH), 7.23 – 7.00 (m, 8H, 8xArH), 5.34 (dd, *J* = 29.7, 8.4 Hz, 1H, NH), 5.17 – 5.01 (m, 2H, CH₂), 4.98 – 4.87 (m, 1H, NH), 4.74 – 4.62 (m, 1H, CHP), 4.62 – 4.49 (m, 1H, CH), 4.50 – 4.34 (m, 1H, CH), 3.83 – 3.32 (m, 2H, CH₂), 3.27 – 3.13 (m, 2H, CH₂), 2.43 (d, *J* = 3.3 Hz, 6H, 2xSCH₃), 2.41 – 2.02 (m, 3H, CH₂, CH), 2.02 – 1.66 (m, 3H, 1.5xCH₂), 1.66 – 1.46 (m, 3H, 1.5xCH₂), 1.36 (d, *J* = 19.7 Hz, 9H, Boc), 1.13 – 0.92 (m, 6H, 2xCH₃).

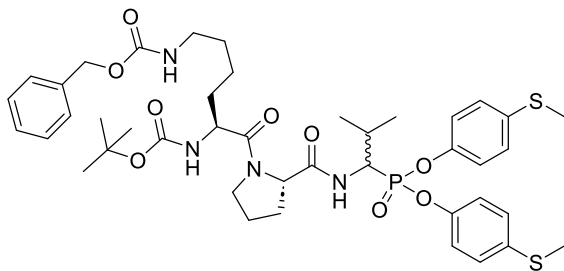
HRMS: C₄₁H₅₅N₄O₉PS₂ [M+Na]⁺ calc. 865.3046 found 865.3023

HPLC: purity >99%; retention time 18.770 min





(109) Boc-L-Lys(Z)-L-Pro-Val^P(OPh-4-SCH₃)₂



Name: benzyl *tert*-butyl ((5*S*)-6-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-6-oxohexane-1,5-diyl)dicarbamate

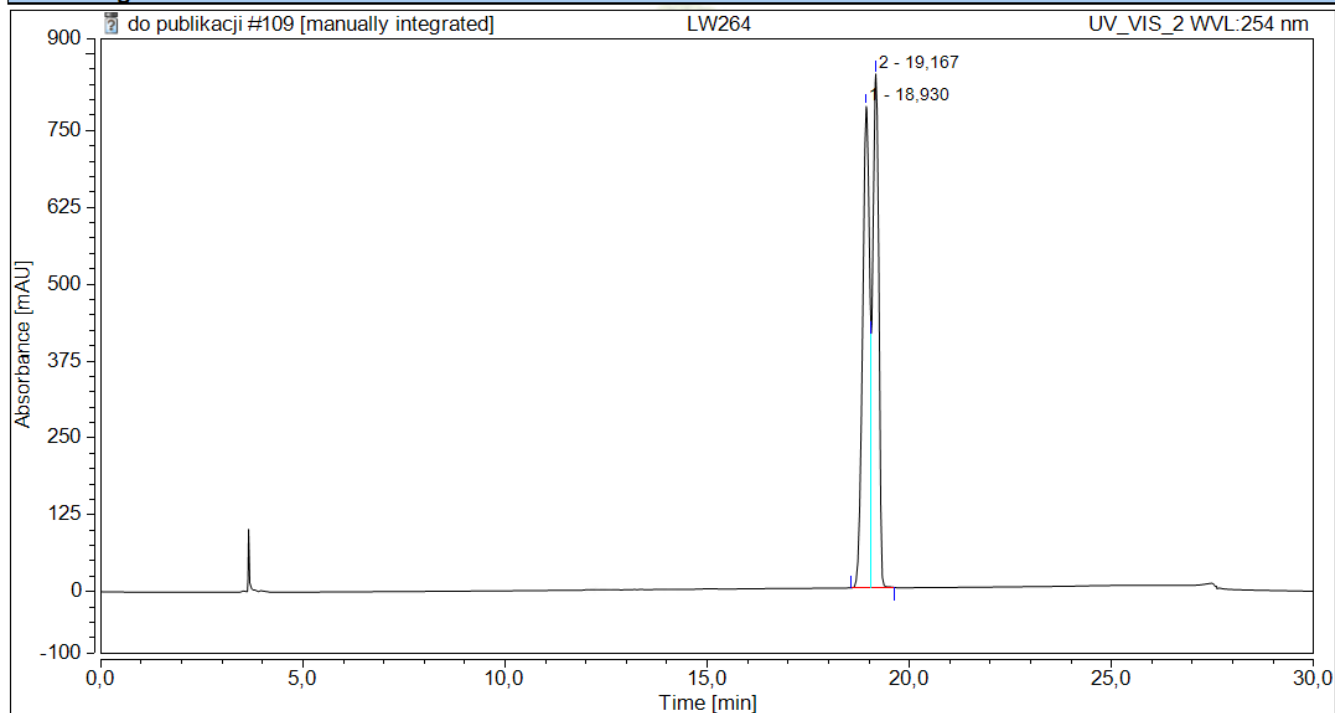
³¹P NMR (162 MHz, Chloroform-*d*) δ 18.25 (s, 54%), 18.10 (s, 46%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.25 (m, 6H, 5×ArH, NH), 7.20 – 6.94 (m, 8H, 8×ArH), 5.45 – 5.20 (m, 1H, NH), 5.12 – 5.03 (m, 2H, CH₂), 4.95 – 4.64 (m, 2H, CHP, NH), 4.58 – 3.95 (m, 2H, 2×CH), 3.73 – 3.34 (m, 2H, CH₂), 3.24 – 2.89 (m, 2H, CH₂), 2.46 – 2.40 (m, 6H, 2×SCH₃), 2.40 – 2.19 (m, 2H, 0.5×CH₂, CH), 2.20 – 2.09 (m, 1H, 0.5×CH₂), 2.09 – 1.70 (m, 4H, 2×CH₂), 1.70 – 1.47 (m, 2H, CH₂), 1.39 (d, *J* = 7.0 Hz, 9H, Boc), 1.32 – 1.24 (m, 2H, CH₂), 1.10 – 0.87 (m, 6H, 2×CH₃).

HRMS: C₄₂H₅₇N₄O₉PS₂ [M+Na]⁺ calc. 879.3202 found 879.3179

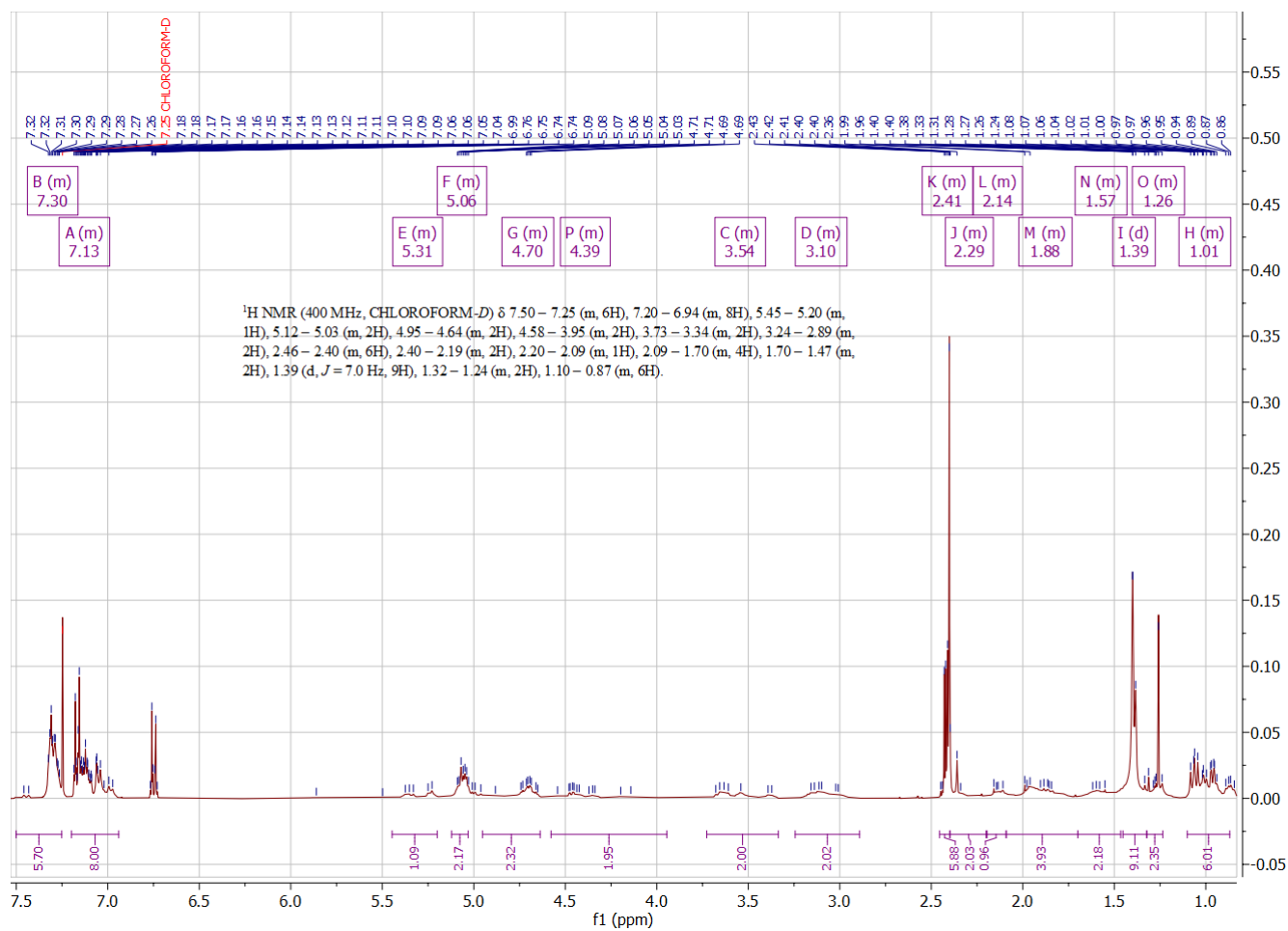
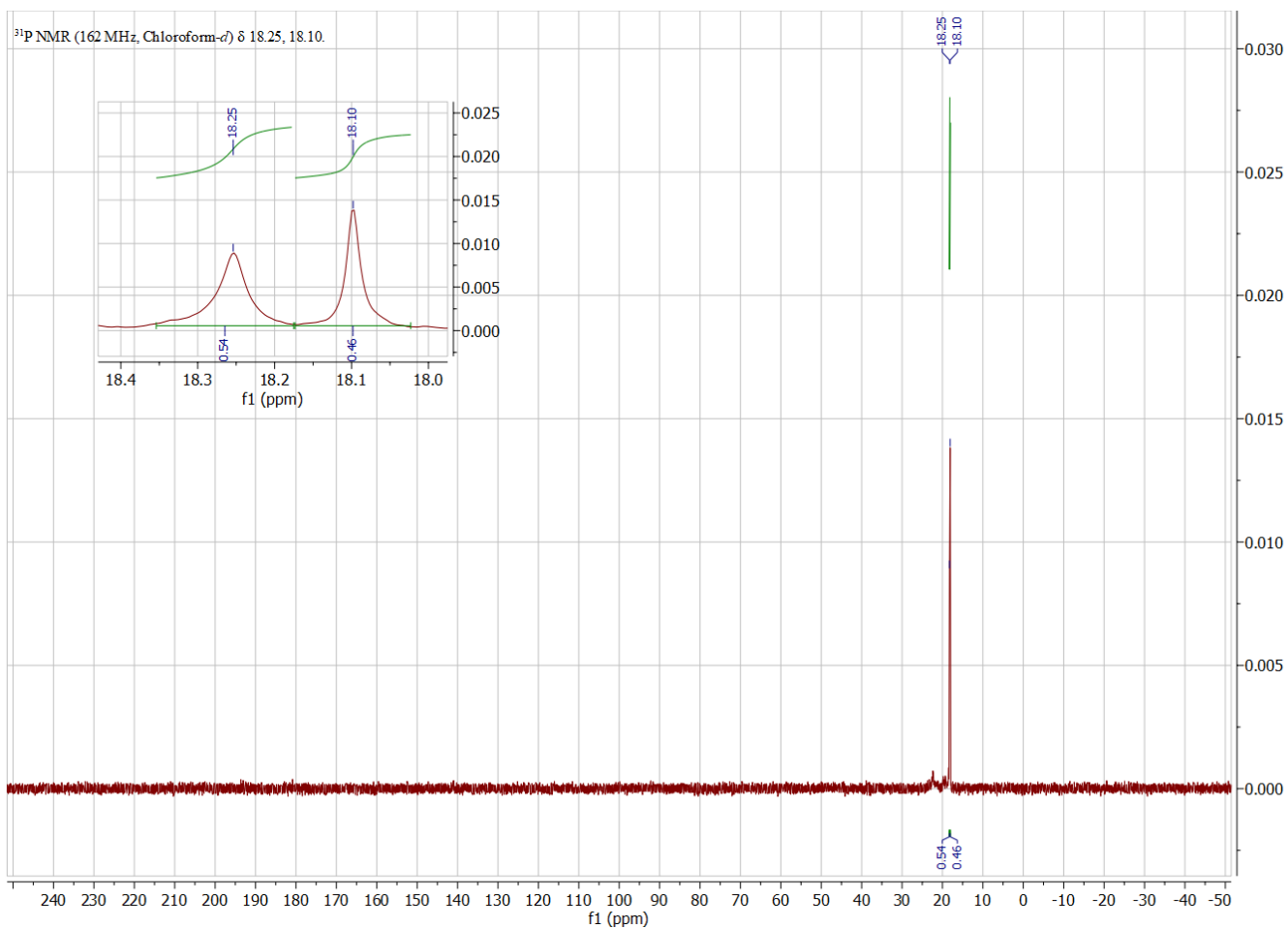
HPLC: purity >99%; retention time 18.930 and 19.167 min

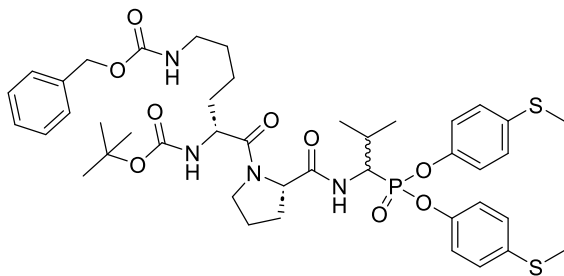
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18,930	157,219	783,143	52,23	48,37	n.a.
2		19,167	143,785	835,823	47,77	51,63	n.a.
Total:			301,004	1618,966	100,00	100,00	



(110) Boc-D-Lys(Z)-L-Pro-Val^P(OPh-4-SCH₃)₂

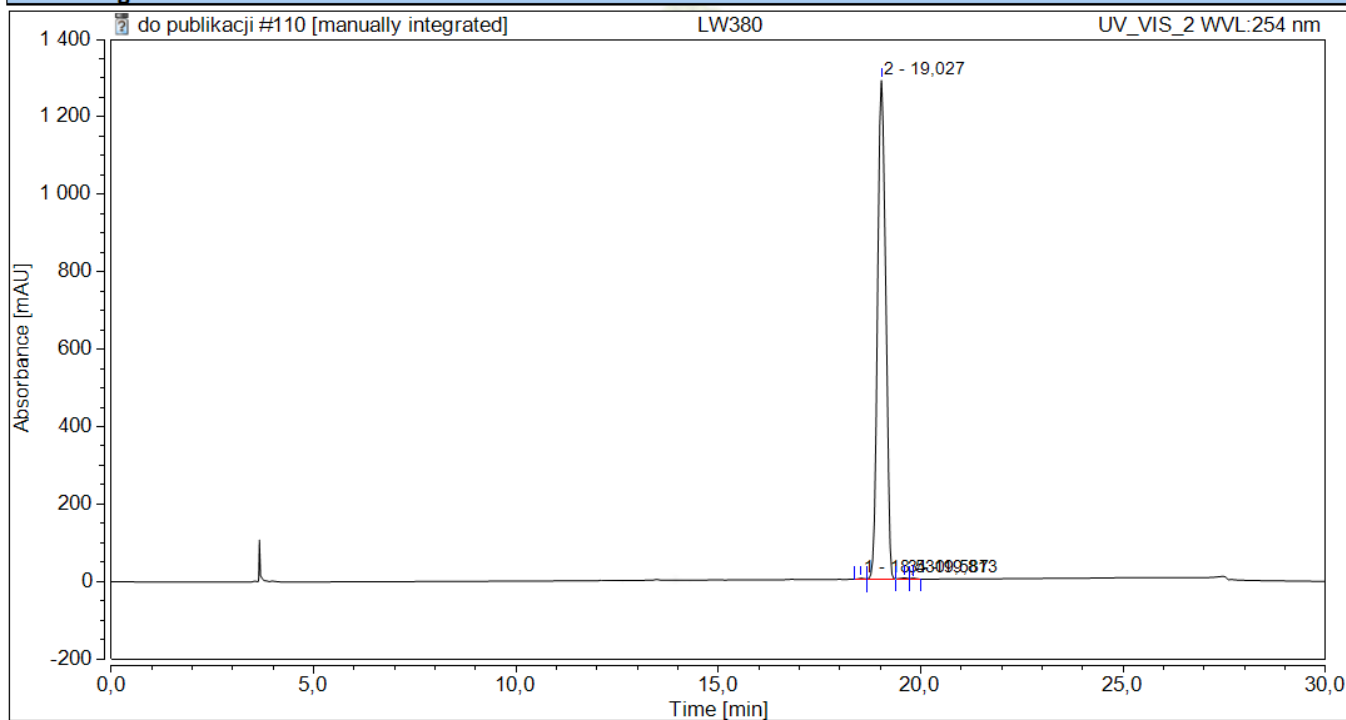
Name: benzyl *tert*-butyl ((5*R*)-6-((2*S*)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-6-oxohexane-1,5-diyl)dicarbamate

³¹P NMR (162 MHz, Chloroform-*d*) δ 18.48 (s, 66%), 18.20 (s, 34%).

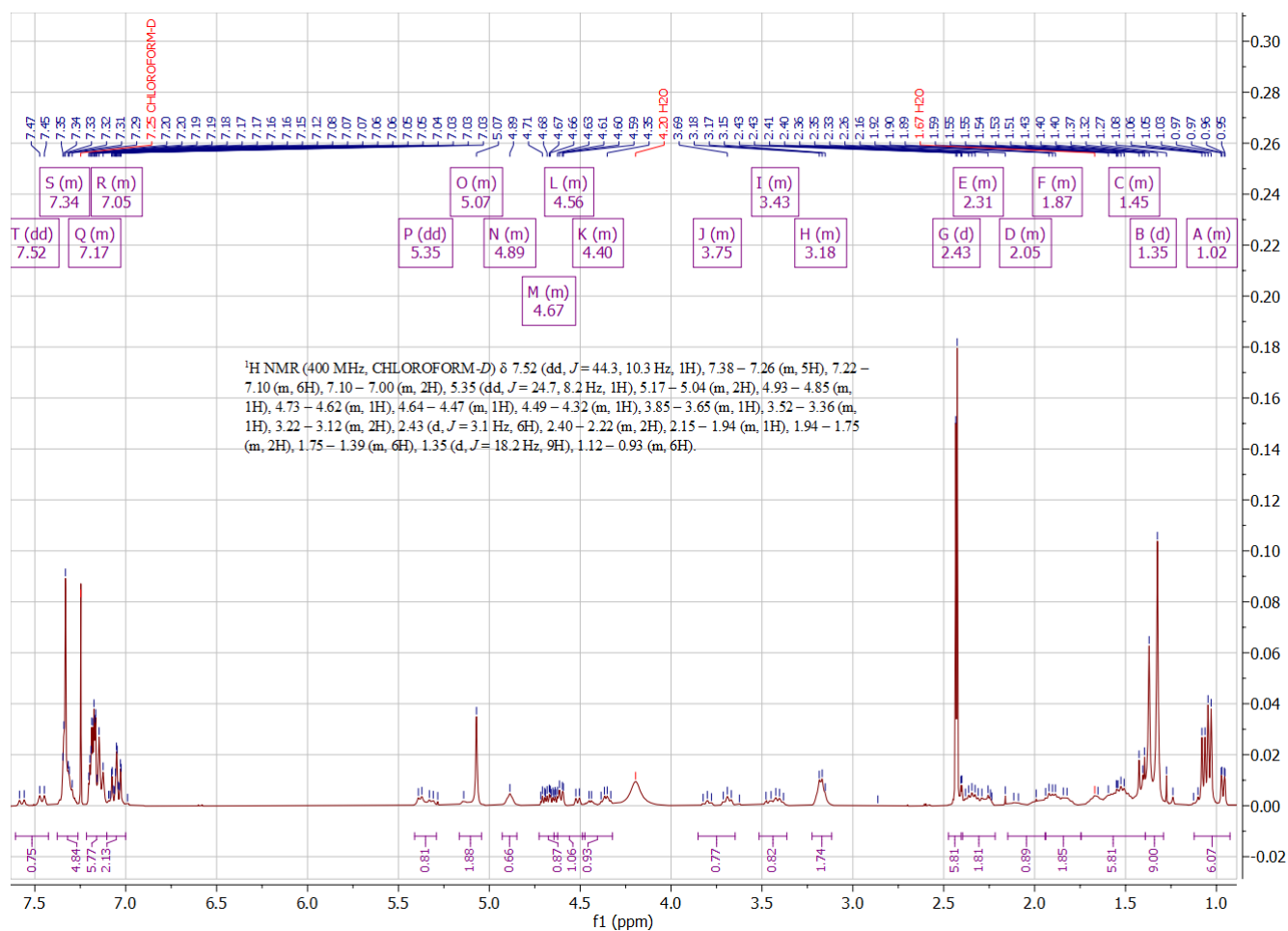
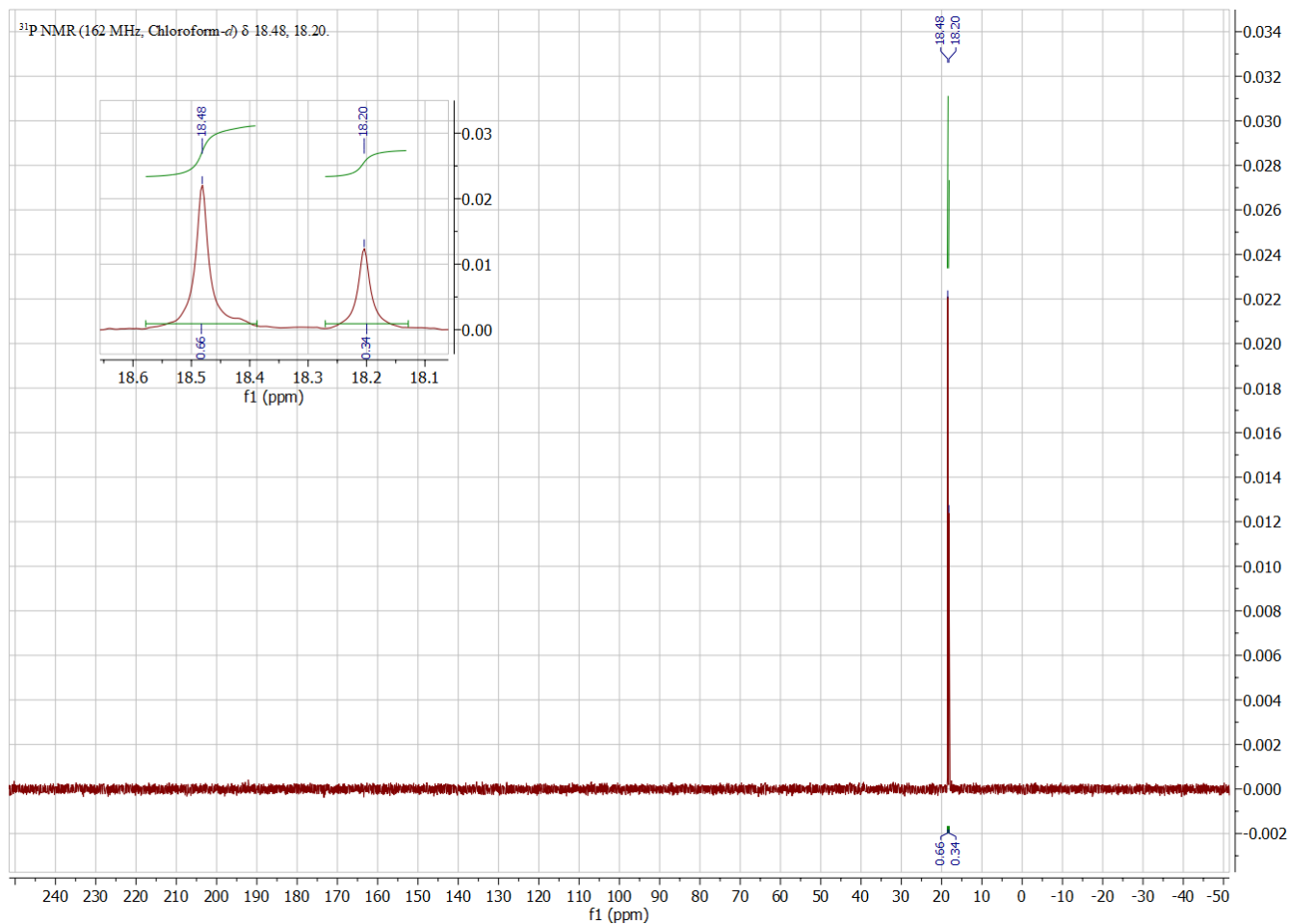
¹H NMR (400 MHz, Chloroform-*d*) δ 7.52 (dd, *J* = 44.3, 10.3 Hz, 1H, NH), 7.38 – 7.26 (m, 5H, 5xArH), 7.22 – 7.10 (m, 6H, 6xArH), 7.10 – 7.00 (m, 2H, 2xArH), 5.35 (dd, *J* = 24.7, 8.2 Hz, 1H, NH), 5.17 – 5.04 (m, 2H, CH₂), 4.93 – 4.85 (m, 1H, NH), 4.73 – 4.62 (m, 1H, CHP), 4.64 – 4.47 (m, 1H, CH), 4.49 – 4.32 (m, 1H, CH), 3.85 – 3.65 (m, 1H, 0.5xCH₂), 3.52 – 3.36 (m, 1H, 0.5xCH₂), 3.22 – 3.12 (m, 2H, CH₂), 2.43 (d, *J* = 3.1 Hz, 6H, 2xSCH₃), 2.40 – 2.22 (m, 2H, 0.5xCH₂, CH), 2.15 – 1.94 (m, 1H, 0.5xCH₂), 1.94 – 1.75 (m, 2H, CH₂), 1.75 – 1.39 (m, 6H, 3xCH₂), 1.35 (d, *J* = 18.2 Hz, 9H, Boc), 1.12 – 0.93 (m, 6H, 2xCH₃).

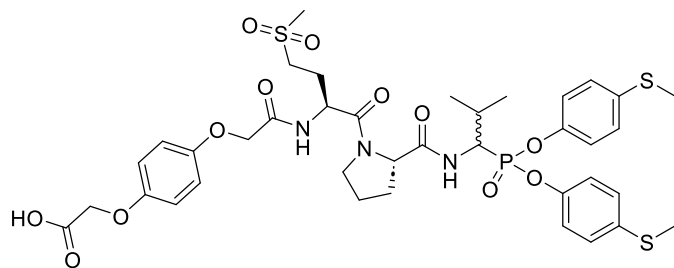
HRMS: C₄₂H₅₇N₄O₉PS₂ [M+Na]⁺ calc. 879.3202 found 879.3180

HPLC: purity >99%; retention time 19.027 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18,530	0,394	2,408	0,13	0,19	n.a.
2		19,027	300,981	1288,143	99,53	99,41	n.a.
3		19,587	0,636	2,927	0,21	0,23	n.a.
4		19,813	0,382	2,265	0,13	0,17	n.a.
Total:			302,392	1295,743	100,00	100,00	



(111) Hm-L-Met(O₂)-L-Pro- Val^P(OPh-4-SCH₃)₂

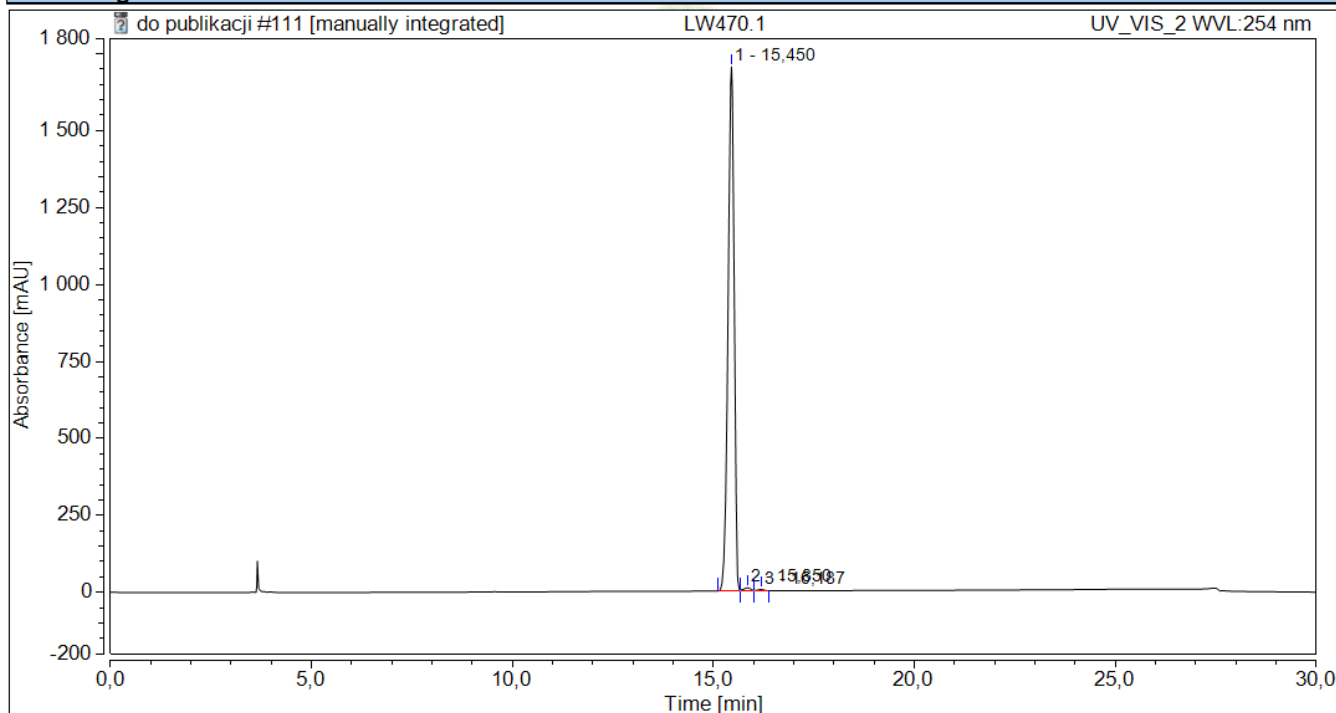
Name: 2-(4-(2-(((2S)-1-((2S)-2-((1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-4-(methylsulfonyl)-1-oxobutan-2-yl)amino)-2-oxoethoxy)phenoxy)acetic acid

³¹P NMR (243 MHz, Methanol-*d*₄) δ 18.45 (s, 47%), 18.20 (s, 53%).

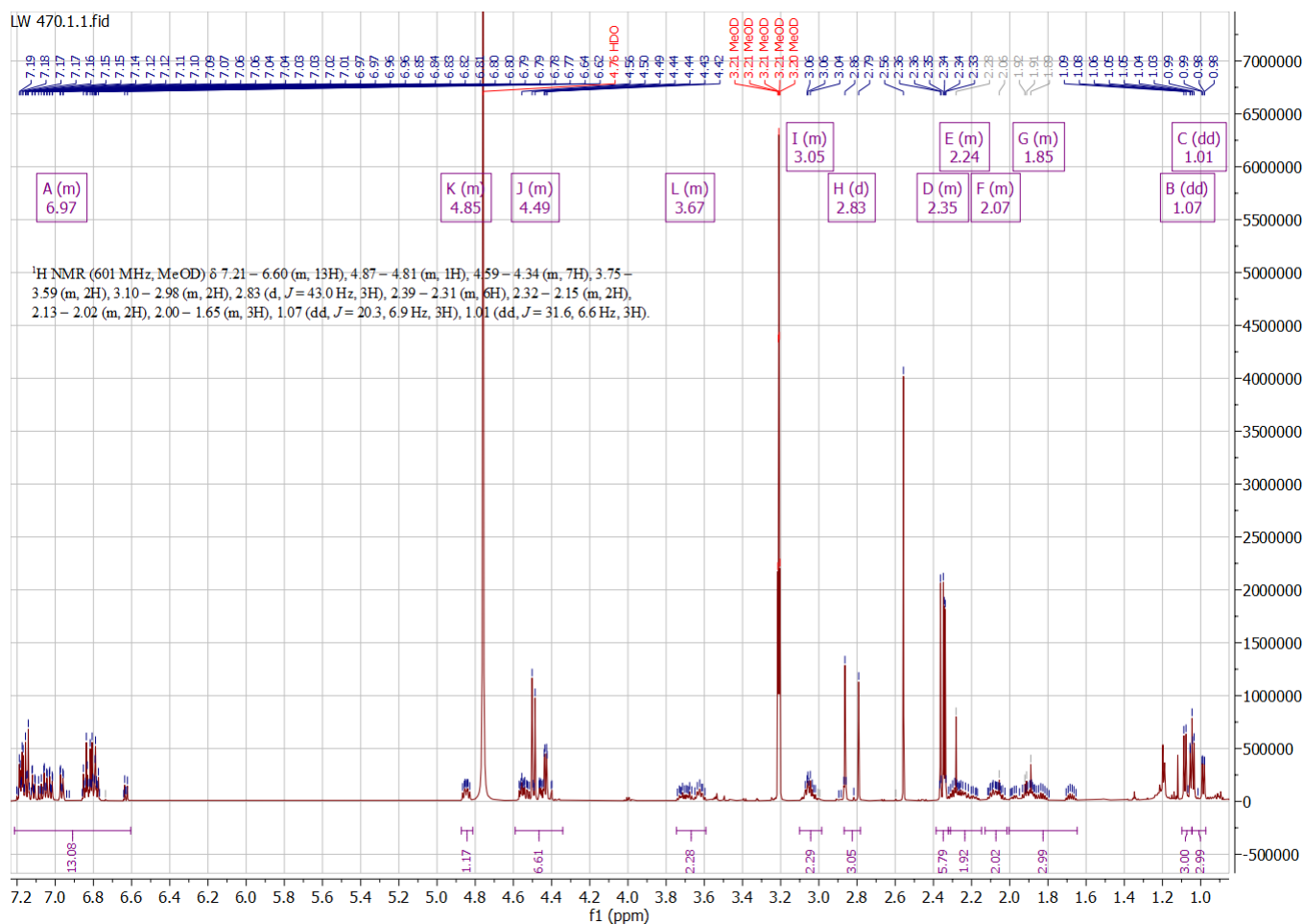
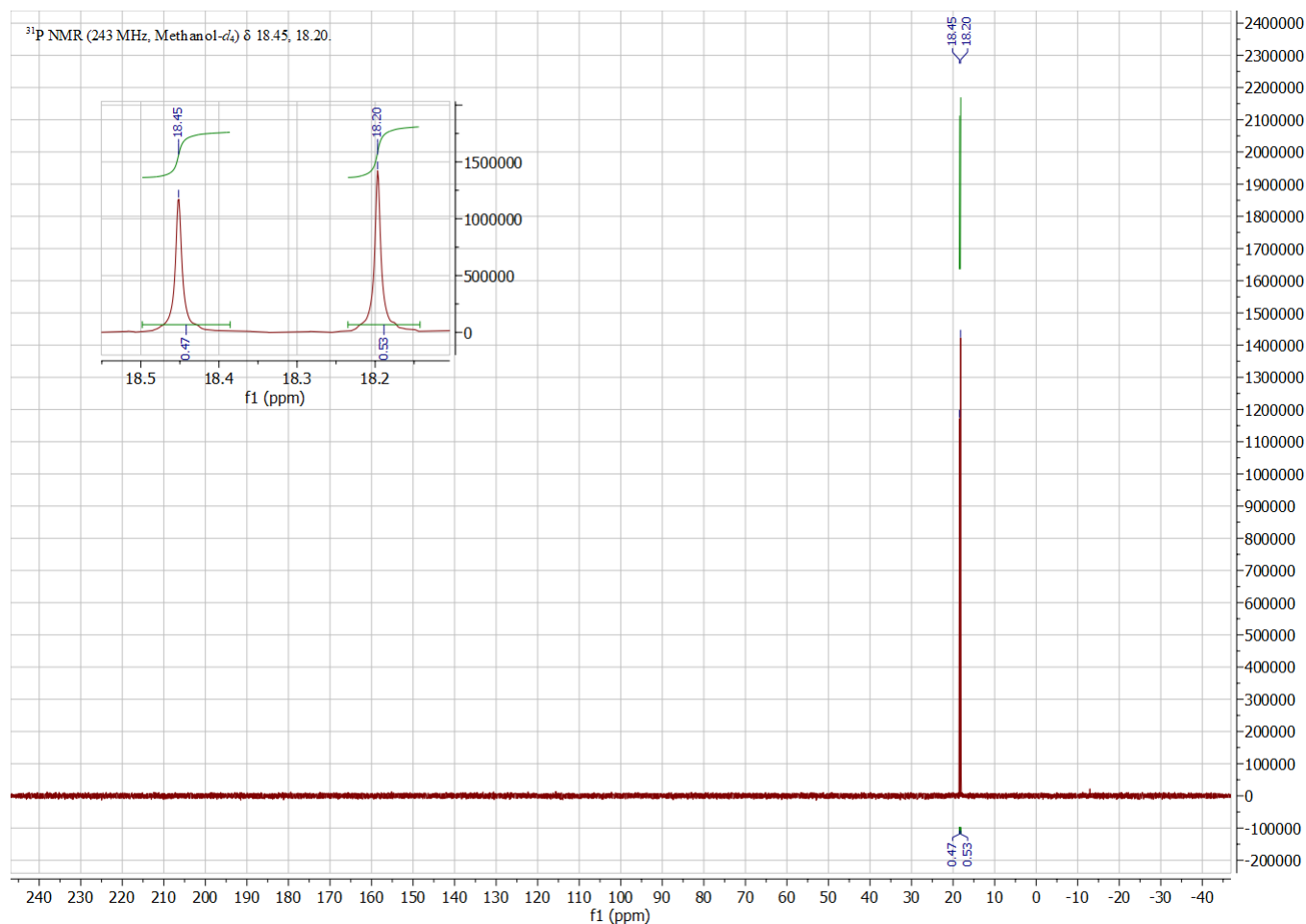
¹H NMR (601 MHz, MeOD) δ 7.21 – 6.60 (m, 13H, 12xArH, NH), 4.87 – 4.81 (m, 1H, NH), 4.59 – 4.34 (m, 7H, 2xCH₂, CHP, 2xCH), 3.75 – 3.59 (m, 2H, CH₂), 3.10 – 2.98 (m, 2H, CH₂), 2.83 (d, J = 43.0 Hz, 3H, CH₃), 2.39 – 2.31 (m, 6H, 2xSCH₃), 2.32 – 2.15 (m, 2H, 0.5xCH₂, CH), 2.13 – 2.02 (m, 2H, CH₂), 2.00 – 1.65 (m, 3H, 1.5xCH₂), 1.07 (dd, J = 20.3, 6.9 Hz, 3H, CH₃), 1.01 (dd, J = 31.6, 6.6 Hz, 3H, CH₃).

HRMS: C₃₈H₄₈N₃O₁₂PS₃ [M+H]⁺ calc. 866.2216 found 866.2238

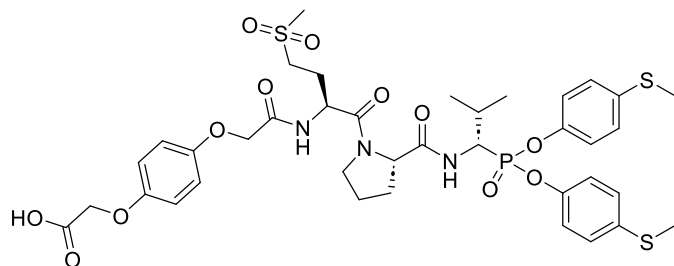
HPLC: purity >99%; retention time 15.450 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15,450	299,634	1703,150	99,08	99,17	n.a.
2		15,850	2,051	10,168	0,68	0,59	n.a.
3		16,187	0,738	4,025	0,24	0,23	n.a.
Total:			302,423	1717,343	100,00	100,00	



(112) Hm-L-Met(O₂)-L-Pro-D-Val^P(OPh-4-SCH₃)₂



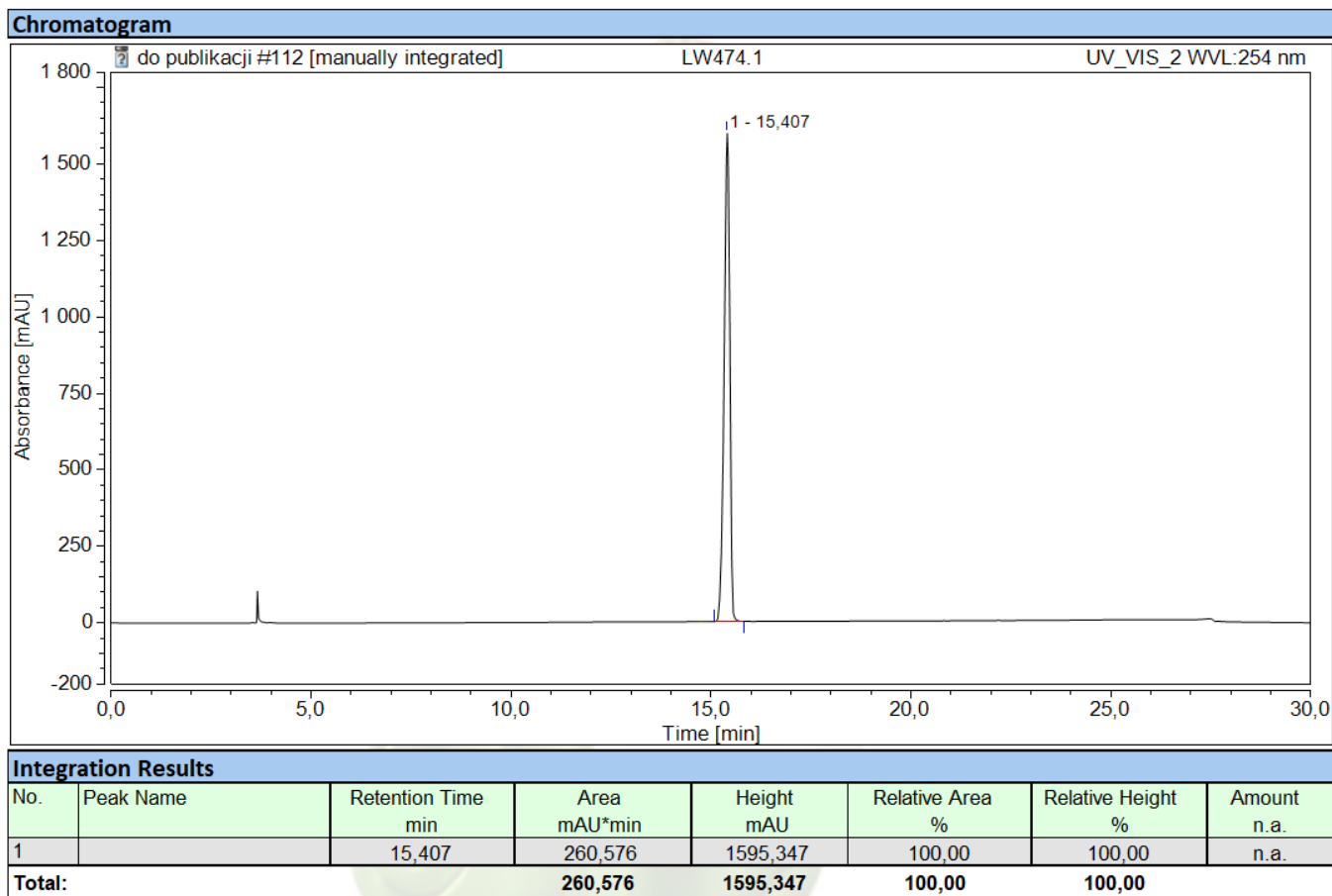
Name: 2-(4-(2-(((S)-1-((S)-2-(((S)-1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-4-(methylsulfonyl)-1-oxobutan-2-yl)amino)-2-oxoethoxy)phenoxy)acetic acid

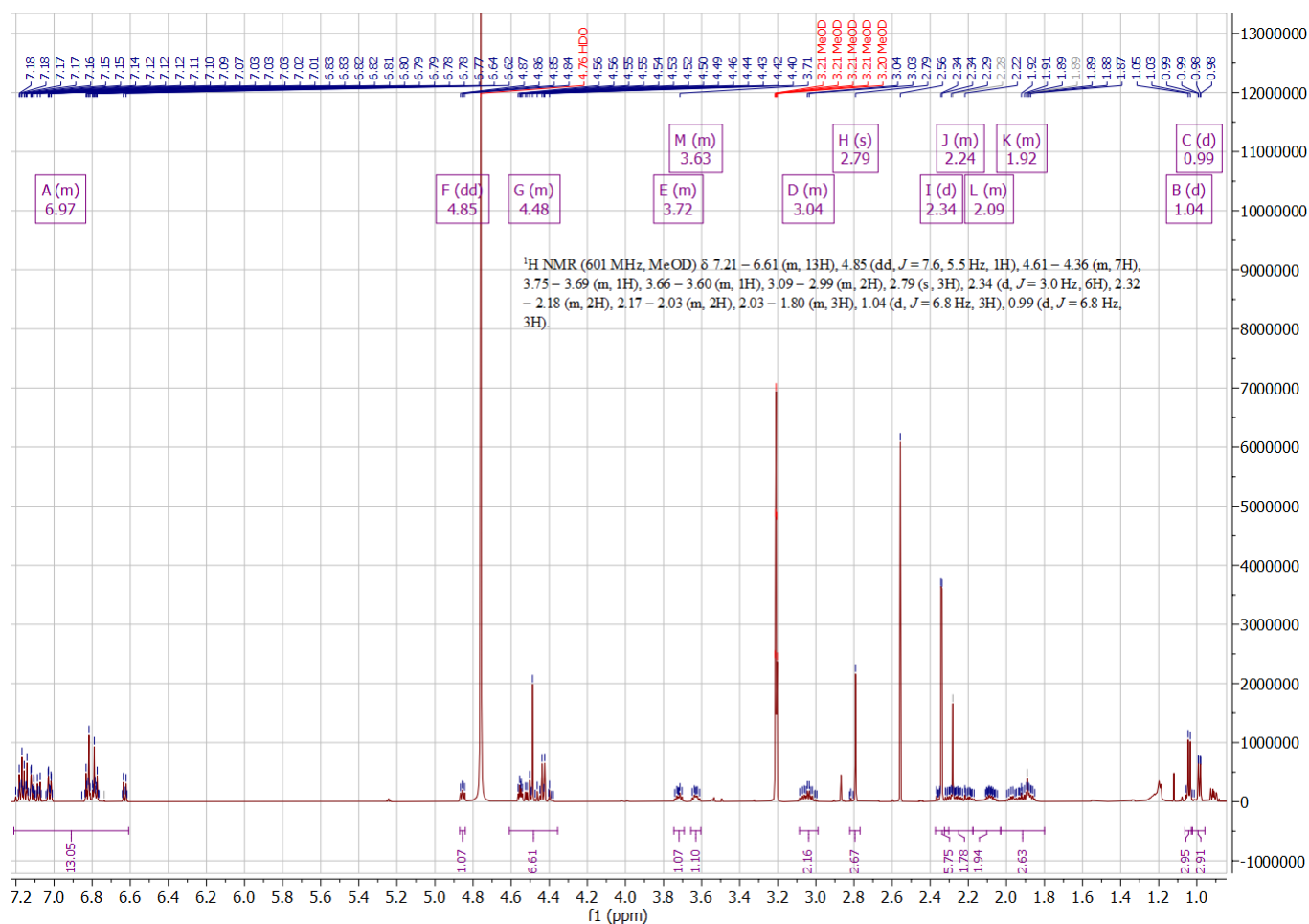
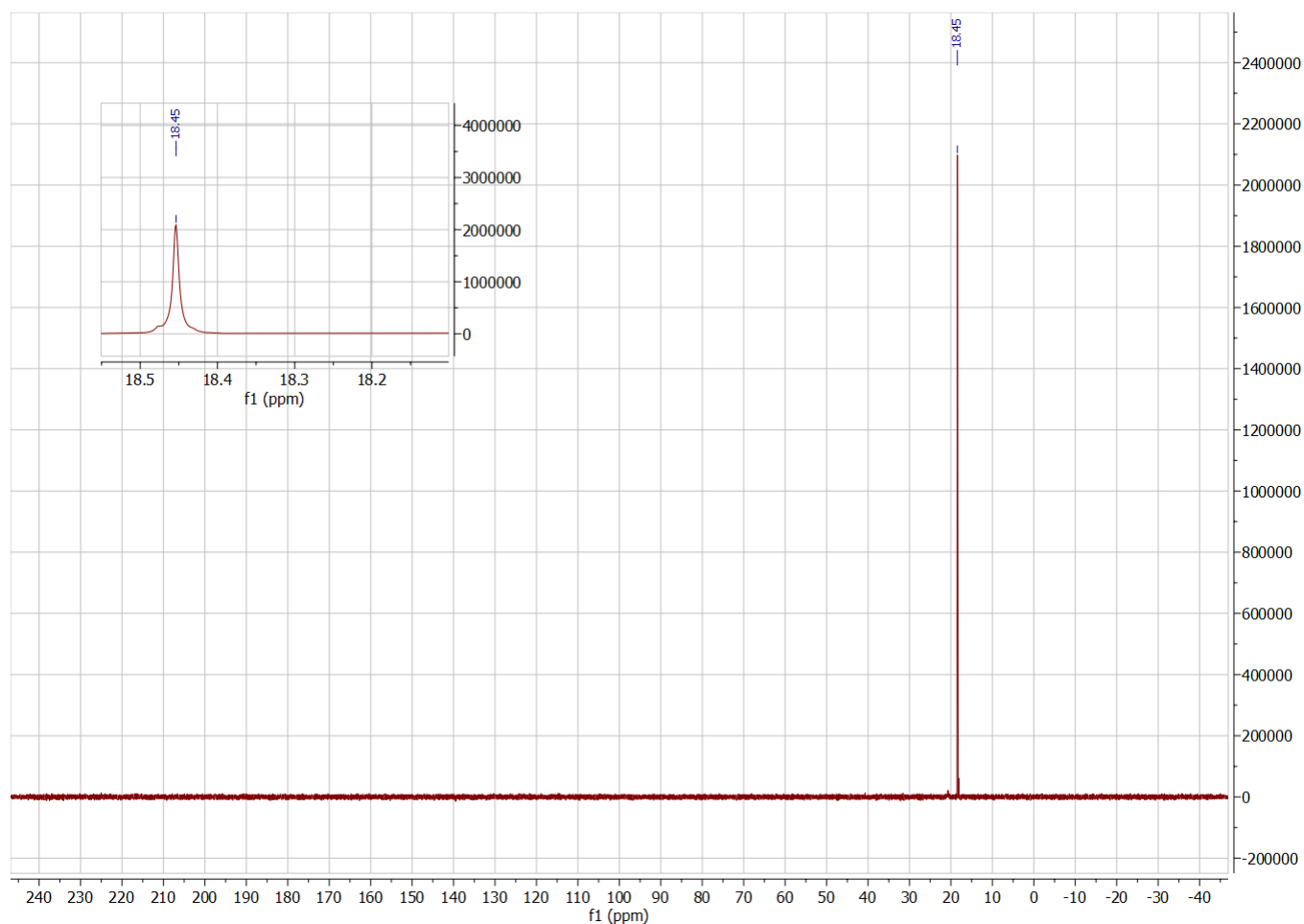
³¹P NMR (243 MHz, MeOD) δ 18.45 (s).

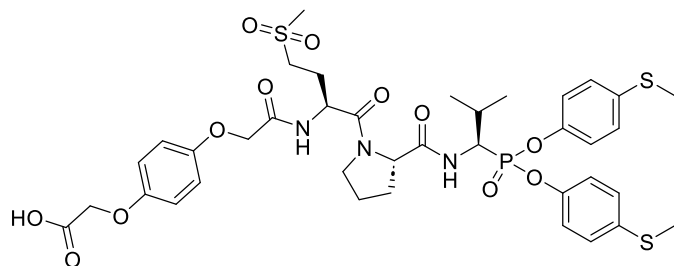
¹H NMR (601 MHz, MeOD) δ 7.21 – 6.61 (m, 13H, 12xArH, NH), 4.85 (dd, J = 7.6, 5.5 Hz, 1H, NH), 4.61 – 4.36 (m, 7H, 2xCH₂, CHP, 2xCH), 3.75 – 3.69 (m, 1H, 0.5xCH₂), 3.66 – 3.60 (m, 1H, 0.5xCH₂), 3.09 – 2.99 (m, 2H, CH₂), 2.79 (s, 3H, CH₃), 2.34 (d, J = 3.0 Hz, 6H, 2xSCH₃), 2.32 – 2.18 (m, 2H, 0.5xCH₂, CH), 2.17 – 2.03 (m, 2H, CH₂), 2.03 – 1.80 (m, 3H, 1.5xCH₂), 1.04 (d, J = 6.8 Hz, 3H, CH₃), 0.99 (d, J = 6.8 Hz, 3H, CH₃).

HRMS: C₃₈H₄₈N₃O₁₂PS₃ [M+H]⁺ calc. 866.2216 found 866.2233

HPLC: purity >99%; retention time 15.407 min





(113) Hm-L-Met(O₂)-L-Pro-L-Val^P(OPh-4-SCH₃)₂

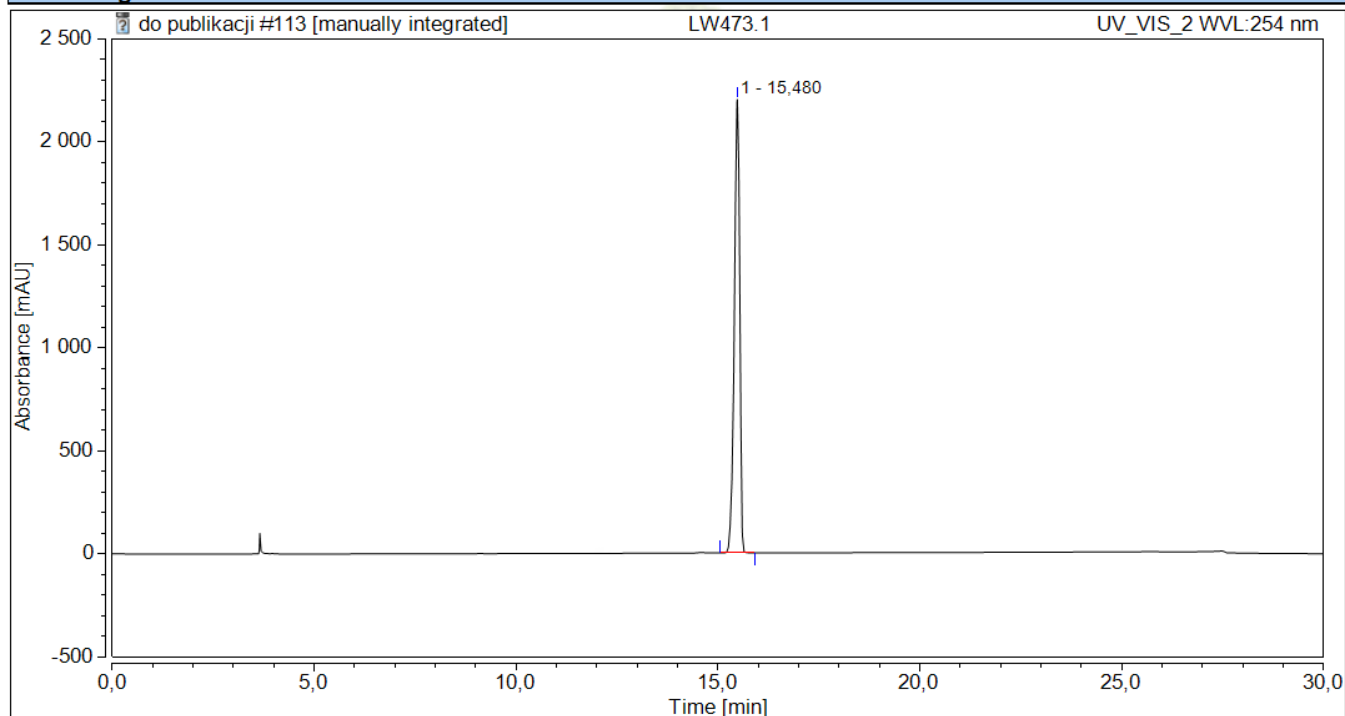
Name: 2-(4-(2-(((S)-1-((S)-2-(((R)-1-(bis(4-(methylthio)phenoxy)phosphoryl)-2-methylpropyl)carbamoyl)pyrrolidin-1-yl)-4-(methylsulfonyl)-1-oxobutan-2-yl)amino)-2-oxoethoxy)phenoxy)acetic acid

³¹P NMR (243 MHz, MeOD) δ 18.20 (s).

¹H NMR (601 MHz, MeOD) δ 7.24 – 6.73 (m, 13H, 12xArH, NH), 4.85 – 4.82 (m, 1H, NH), 4.60 – 4.35 (m, 7H, 2xCH₂, CHP, 2xCH), 3.71 – 3.59 (m, 2H, CH₂), 3.06 (t, J = 8.0 Hz, 2H, CH₂), 2.86 (s, 3H, CH₃), 2.36 (d, J = 9.1 Hz, 6H, 2xSCH₃), 2.31 – 2.22 (m, 2H, 0.5xCH₂, CH), 2.12 – 2.02 (m, 2H, CH₂), 1.94 – 1.80 (m, 2H, CH₂), 1.72 – 1.64 (m, 1H, 0.5xCH₂), 1.08 (d, J = 6.8 Hz, 3H, CH₃), 1.05 (d, J = 6.8 Hz, 3H, CH₃).

HRMS: C₃₈H₄₈N₃O₁₂PS₃ [M+H]⁺ calc. 866.2216 found 866.2238

HPLC: purity >99%; retention time 15.480 min

Chromatogram**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15,480	341,486	2200,731	100,00	100,00	n.a.
Total:			341,486	2200,731	100,00	100,00	

