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1. Crystallographic Data Collection, Structure Determination and Refinement.

The single crystal X-ray diffraction experiments were carried out using a RIGAKU XtaLabPro diffractometer equipped with a Mo microfocus sealed tube generator coupled to a double-bounce confocal Max-Flux® multilayer optic, and a HPAD PILATUS3 R 200K detector and controlled by CrysalisPro[1] software, that also ensured the data processing.

For crystal of compound (*R*)-**4k**, data collection was performed on a small colourless block grown in dichloromethane, and of dimensions 0.12 × 0.10 × 0.06 mm^3, at low temperature 153K, and at ambient temperature for (*S*)-**1a** that crystallized as red platelets with dimensions of 0.18 × 0.15 × 0.04 mm^3. Both structures were solved by *Intrinsic Phasing* methods (SHELXT program),[2] in non-centrosymmetric Sohncke space groups, $P2_1$ and $P2_12_12_1$, for (*R*)-**4k** and (*S*)-**1a** respectively. Structure refinements were performed by full-matrix least-squares methods (SHELXL-2018/3 program).[3] All non-hydrogen atoms were improved by anisotropic refinement. While H atoms were mostly identified in difference maps, they were all idealized and included as rigid groups, allowed to rotate but not tip in the case of methyl groups, and refined with U_{iso} set to xU_{eq}(C) of the parent carbon atom (x =1.5 for methyl groups, 1.2 for the others). Only the position of the amine H atom was permitted to refine.

In (*R*)-**4k**, one ethyl chain appeared disordered over two sites whose occupancy factors were refined to values of 0.86(1):0.14(1). That slight disorder required the application of soft restraints on anisotropic displacement parameters (*DELU* and *SIMU instructions*[3]) and distances (*SADI*). The crystal structure of compound (*S*)-**1a** contains a channel propagating along the *b* direction in zig-zag around the two-fold screwed axis located at the unit cell origin. Examination of the refined structure using the SQUEEZE procedure as implemented within

(1) O. D. Rigaku, *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, Oxfordshire, England, 2015.
(2) G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3.
(3) G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3.

PLATON,[4] showed the presence of 88 electrons per unit cell. But there were no significant peaks in the difference maps, thus no plausible solvent model -possibly one disordered or mobile hexane molecule (50 electrons) per complex- could be developed. Nevertheless, the SQUEEZE procedure by omitting the solvent contribution to the diffraction did not improve at all the model refinement, so it was abandoned for the present crystal structure.

The presence of strong resonant atoms allowed us establish the correct absolute configuration for each compound based on the Flack *x* parameters: for ((*S*)-**1a**) $x = 0.001(5)$ calculated using 2076 quotients,[5] and for ((*R*)-**4k**) $x = –0.02$ (3) calculated using 1262 quotients.

Crystal structure determination of (*R*)-**4k**:

Crystal Data for *(R)-2-((tert-butoxycarbonyl)amino)-3-(diethoxyphosphoryl)propanoic acid*: $C_{12}H_{24}NO_7P$ (M = 325.29 g/mol): orthorhombic, space group $P2_12_12_1$(no. 19), a = 9.4385(3) Å, b = 10.4341(2) Å, c = 16.9555(4) Å, V = 1669.82(7) Å^3, Z = 4, T = 153 (2) K, μ(MoKα) =0.194 mm^{-1}, Dcalc = 1.294 g/cm^3, 20342 reflections measured (3.906° ≤ θ ≤ 26.372°), 3414 unique (Rint = 0.043) which were used in all calculations. The final R1 was 0.0379 (for 3154 $I > 2\sigma(I)$) and wR2 was 0.0945 (all data). The final difference Fourier map showed minimum and maximum values of 0.282 and –0.265 e Å^{-3}, respectively.

Crystal structure determination of (*S*)-**1a**:

Crystal Data for $C_{28}H_{22}Cl_3N_3NiO_3$ (M = 613.54 g/mol): Monoclinic, space group $P2_1$(no. 5), a = 9.80049(17) Å, b = 11.6264(2) Å, c = 13.6934(3) Å, β = 108.1849(17)°, ,V = 1482.36(5) Å^3, Z = 2, T = 293 (2) K, μ(MoKα) =0.957 mm^{-1}, Dcalc = 1.375 g/cm^3, 27122 reflections measured (3.062° ≤ θ ≤ 25.349°), 5410 unique (Rint = 0.043) which were used in all calculations. The

(4) A. L. Spek, *Acta Cryst.*, 2020, **E76**, 1.
(5) (a) H. D. Flack, *Acta Cryst.*, 1983, **A39**, 876; (b) S. Parsons, H. D. Flack and T. Wagner, *Acta Cryst.*, 2013, **B69**, 249.

final R1 was 0.0376 (for 4849 $I > 2\sigma(I)$) and wR2 was 0.0974 (all data). The final difference Fourier map showed minimum and maximum values of 0.652 and –0.309 e Å^{-3}, respectively.

CCDC 2036929 (compound (*S*)-**1a**) and 2036930 (compound (*R*)-**4k**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

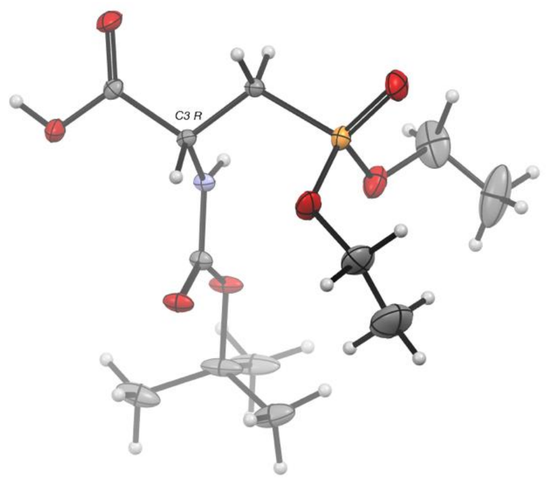


Figure 1. Ortep view of compound (*R*)-**4k**. The minor disordered ethyl group is not shown for clarity. Ellipsoids are drawn at 30% of probability.

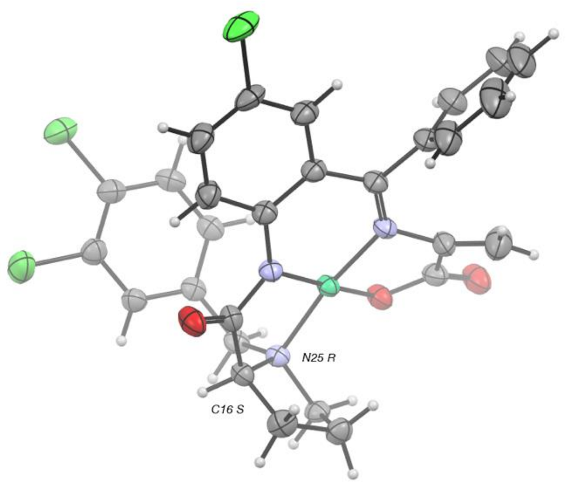


Figure 2. Ortep view of compound (*S*)-**1a**. Ellipsoids are drawn at 30% of probability.

2. Crystallographic Analysis of DehydroAla Schiff Base Complex (*S*)-1a and Rationale for the Scalemic Formation of β-Phosphorus Adducts.

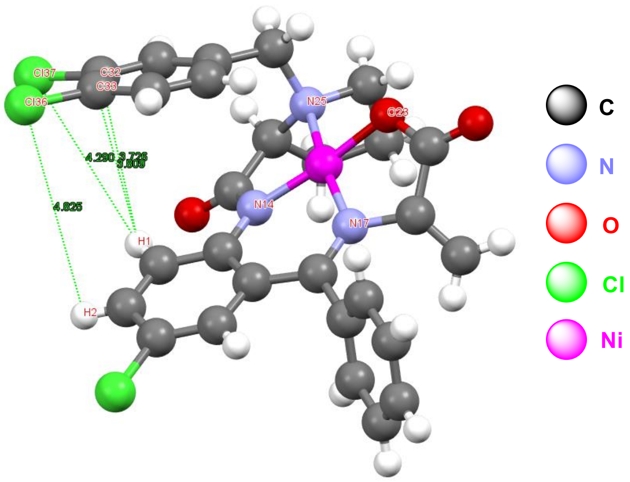


Figure 3. Ball and stick crystallographic structure of dehydroAla Schiff base complex (*S*)-**1a**.

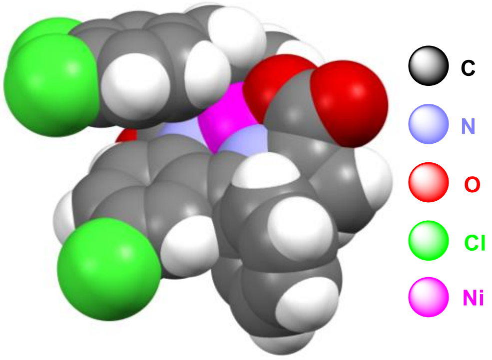


Figure 4. Spacefill crystallographic structure of dehydroAla Schiff base complex (*S*)-**1a**.

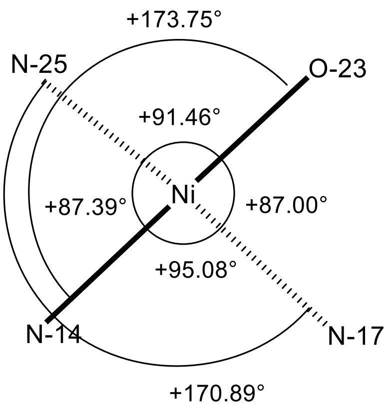


Figure 5. Deviation from the planarity of the Ni(II) coordination sphere of dehydroAla Schiff base complex (*S*)-**1a**.

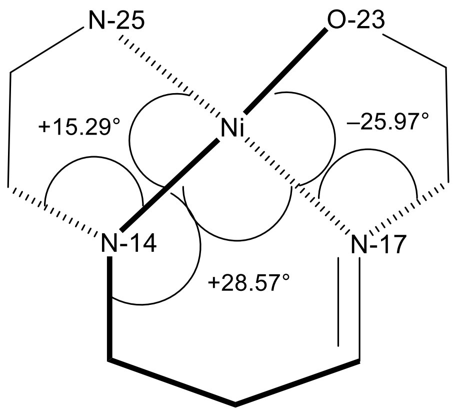
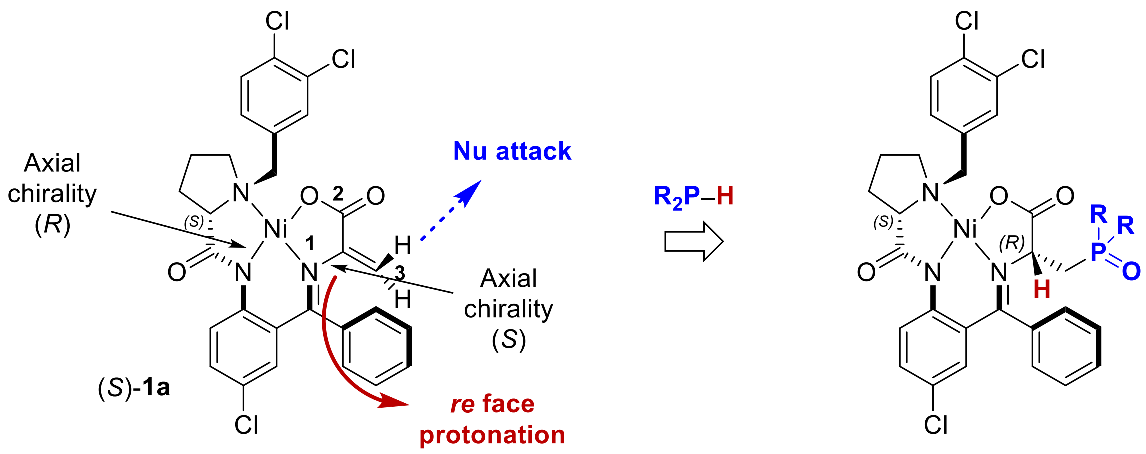


Figure 6. Dihedral angles of the chelate rings around the Ni(II)of dehydroAla Schiff base complex (*S*)-**1a**.



Scheme 1. Axial chirality of the chelate rings and rationale for the scalemic formation of β-phosphorus adducts.

3. General Remarks.

Unless otherwise stated, all reagents and starting materials were purchased from commercial sources and used as received. All solvents were reagent grade. NMR spectra were recorded at 298 K with a Bruker Avance III HD nanobay 400 MHz spectrometer equipped with a BBO probe. The structures of the new compounds were assigned with the aid of 1 D [^{1}H NMR, ^{13}C NMR, Distortionless Enhancement by Polarization Transfer (DEPT)] and 2 D Correlation Spectroscopy [(^{1}H–^{1}H COSY and ^{1}H–^{13}C Heteronuclear Single Quantum Coherence (HSQC)]. When appropriate or in the event of ambiguous proton and carbon, assignments were established using ^{19}F NMR, ^{31}P NMR and ^{1}H–^{13}C Heteronuclear Multiple-bond Correlation (HMBC) experiments. ^{13}C and ^{19}F spectra were acquired on a broad band decoupled mode. ^{1}H NMR (400 MHz) chemical shift values are listed in parts per million (ppm). Tetramethylsilane (TMS) was used as an internal standard, or alternatively, spectra were calibrated using the signals of the corresponding non-deuterated solvent. Data are reported as follows: chemical shift (ppm on the δ scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and po = partially overlapped), coupling constant *J* (Hz), and integration. ^{13}C NMR (101 MHz) chemical shifts are given in ppm. Spectra were calibrated using the corresponding non-deuterated solvent. ^{19}F (376 MHz) and ^{31}P (162 MHz) NMR chemical shifts are given in ppm. Primary NMR data files were processed by MestReNova. High-resolution mass spectra were recorded with a Bruker maXis ESI qTOF ultrahigh-resolution mass spectrometer coupled to a Dionex Ultimate 3000 RSLC system (FR2708, Orléans). MS data were acquired in positive mode and were processed using Data Analysis 4.4 software (Bruker). Infrared spectra were recorded with a Thermo Scientific Nicolet IS10 FTIR spectrometer using diamond ATR golden gate sampling and are reported in wave numbers (cm^{-1}). Specific optical rotations were measured with a JASCO P-2000 digital polarimeter, in a thermostated (20 °C) 1 dm long cell with high-pressure sodium lamp and are reported as follows: $[\alpha]_D^T$ [solvent, *c* (g/100 mL)].

Analytical thin-layer chromatography (TLC) was performed with Merck Silica Gel 60 F254 precoated plates. Visualization of the developed chromatogram was performed under ultraviolet light (254 nm) and on staining by immersion in aqueous, acidic ceric ammonium molybdate followed by charring at 150 °C. Flash chromatography was performed in air on Silica Gel 60 (230–400 mesh) with dichloromethane and acetone as eluents, unless otherwise stated. Organic solutions were concentrated under reduced pressure with a Buchi rotary evaporator. Supercritical fluid chromatography (SFC) was employed to determine enantiomeric excesses of compounds **4a** and **4k**. Samples were dissolved in methanol at 1 mg mL^{-1}. SFC analyses were carried out on an ACQUITY UPC^2 instrument from Waters. The stationary phase was a Chiralpak IC-U column from Chiral Technologies (100 × 3.0 mm, 1.6 µm). Oven temperature was set at 25 °C, backpressure at 15 MPa and flow rate at 1 mL min^{-1}. For the analysis of aminoacid **4a**, the mobile phase was CO_2/methanol 80:20 (v/v) and UV detection was set at 210 nm. For **4k** analysis, mobile phase was CO_2/methanol 75:15 (v/v) and samples were detected by mass spectrometry (ACQUITY QDa from Waters) with electrospray ionization in positive (ESI+) and negative (ESI–) modes, and ion acquisition from 100 to 800 m/z. Make-up solvent for MS detection was methanol/water (98/2) + 20 mM NH_4OH. Data are reported as follows: column type, eluent, flow rate, temperature, backpressure, wavelength and retention times (t_R).

4. Experimental procedures and characterization data.

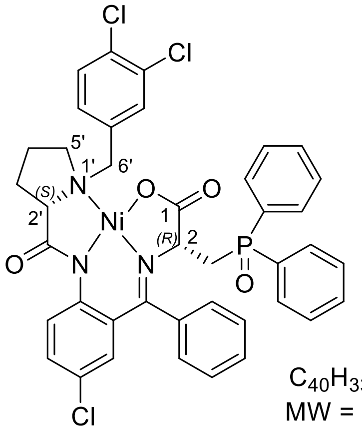
4.1. General Procedures.

4.1.1. General Procedure for the Michael Addition of Phosphine Nucleophiles to the Dehydroalanine Ni(II) Complex (*R*)-1 or (*S*)-1 (G.P.A).

To a stirred solution of the dehydroalanine Ni(II) complex (*R*)-**1** or (*S*)-**1** (1.0 equiv., 100 mg, 0.164 mmol) in MeCN (5 mL) was successively added the phosphine nucleophile (1.5 equiv., 0.246 mmol) and K_2CO_3 (for secondary phosphine oxides) or Cs_2CO_3 (for dialkyl phosphites) (0.25 equiv., 0.041 mmol) and the reaction mixture was stirred at 60 °C for 4h. Next, the reaction was quenched by addition of 5% aq. acetic acid and the aqueous phase was extracted twice with CH_2Cl_2. Combined organic layers were successively washed with H_2O and brine. The organic phase was dried over $MgSO_4$, filtered through a cotton plug and evaporated under reduced pressure. Then, the residue was purified by column chromatography over silicagel ($CHCl_3$/acetone 4:1 to 0:1, v/v) to give related compound as a red solid.

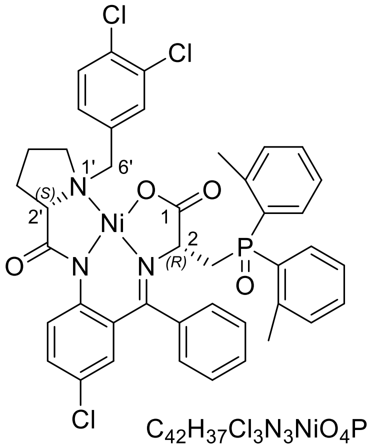
4.1.2. General Procedure for the Disassemblies of the 3-Phosphinyl Alanine Ni(II) Complexes (3) and Boc Protection to Afford Compounds of Type 4.

To a vigorously stirred solution of compound (*R*)-**3a**, (*S*)-**3a**, (*R*)-**3k** or (*S*)-**3k** (1.0 equiv., 200 mg) in THF (4 mL) was added an aqueous solution of HCl (4 N, 1 mL), and the reaction mixture was stirred for 10 min at room temperature (ca. 20 °C). Next, the mixture was diluted (H_2O) and the aqueous layer was washed twice with AcOEt. Saturated aq. $NaHCO_3$, ethylenediaminetetraacetic acid (EDTA, 1.0 equiv.), and a solution of di-*tert*-butyl dicarbonate (Boc_2O, 5.0 equiv.) in 1,4-dioxane (6 mL) were subsequently added to the aqueous phase and the reaction mixture was stirred for 12 h at 20 °C. Water was then added, and the aqueous layer was washed with Et_2O (2 ×). An aqueous solution of HCl (2 M) was added to the aqueous layer (until pH = 1.0) and the mixture was extracted three times with AcOEt. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered through a cotton plug and evaporated *in vacuo* to give the corresponding amino acid as a white solid.



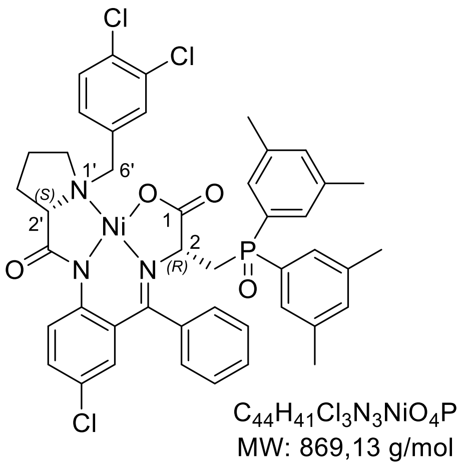
Ni(II)-(*S*)-*N*-(2-Benzoyl-4-chlorophenyl)-1-(3,4-dichlorobenzyl)-pyrrolidine-2-carboxamide/(*R*)-3-(diphenylphosphinyl)-alanine Schiff Base Complex (*S*,*R*)-3a.

Isolated yield: 89%. R_f 0.11 (SiO_2, CH_2Cl_2/acetone 4:1, v/v). Mp. 140 °C. $[\alpha]_D^{20}$ + 219.4 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ 9.10 (d, *J* = 2.0 Hz, 1H, H_{Ar}), 8.30 (d, *J* = 9.4 Hz, 1H, H_{Ar}), 7.82 – 7.63 (po, 5H, H_{Ar}), 7.57 – 7.39 (po, 5H, H_{Ar}), 7.36 – 7.18 (po, 6H, H_{Ar}), 7.08 (dd, *J* = 9.4, 2.6 Hz, 1H, H_{Ar}), 6.36 (d, *J* = 2.6 Hz, 1H, H_{Ar}), 6.01 (br d, *J* = 8.2 Hz, 1H, H_{Ar}), 4.38 (ddd, *J* = 24.0, 8.0, 4.0 Hz, 1H, H-2), 4.32 (d, *J* = 12.4 Hz, 1H, H-6’), 3.99 – 3.88 (m, 1H, H-Pro), 3.76 – 3.60 (m, 1H, H-Pro), 3.41 (dd, *J* = 10.0, 7.1 Hz, 1H, H-2’), 3.23 (d, *J* = 12.4 Hz, 1H, H-6’), 3.12 – 2.99 (m, 1H, H-Pro), 2.92 (td, *J* = 16.0, 4.0 Hz, 1H, P(O)CH_2), 2.66 – 2.50 (m, 1H, H-Pro), 2.30 – 2.19 (po, 2H, P(O)CH_2, H-Pro), 2.10 – 1.97 (m, 1H, H-Pro) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 180.2 (C, *C*ON), 178.3(C, *C*OO), 171.6 (C, *C*N), 141.7 (C, C_{Ar}), 135.5 (C, C_{Ar}), 134.1 (CH, CH_{Ar}), 133.3 (C, C_{Ar}), 133.2 (C, C_{Ar}), 133.1 (C, C_{Ar}), 132.3 – 127.1 (CH, CH_{Ar}), 126.7 (C, C_{Ar}), 125.1 (C, C_{Ar}), 124.1 (CH, CH_{Ar}), 72.1 (CH, C-2’), 66.2 (d, *J* = 5.3 Hz, CH, C-2), 63.8 (CH_2, C-6’), 59.4 (CH_2, C-5’), 33.3 (d, *J* = 69.0 Hz, CH_2, P(O)*C*H_2), 31.2 (CH_2, *C*H_2 Pro), 23.6 (CH_2, *C*H_2 Pro) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ + 28.2 – 27.5 (m) ppm. IR (neat): ṽ = 1700, 1630, 1459, 1394, 1338, 1240, 1166, 1116, 1067, 1029, 843, 821, 695 cm^{-1}. HRMS (ESI): m/z calcd. for $C_{40}H_{33}Cl_3N_3NiO_4P$ $[M + H]^+$ 814.0706, found 814.0700.



Ni(II)-(*S*)-*N*-(2-Benzoyl-4-chlorophenyl)-1-(3,4-dichlorobenzyl)-pyrrolidine-2-carboxamide/(*R*)-3-[bis(2-methylphenyl)phosphinyl]-alanine Schiff Base Complex (*S*,*R*)-3b.

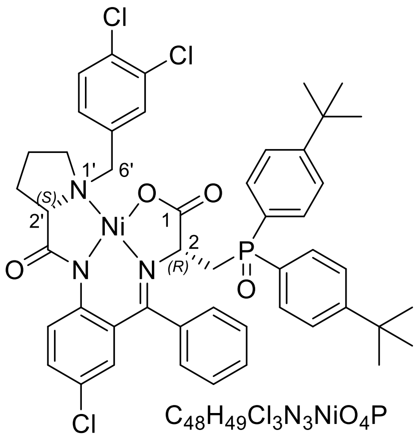
Isolated yield: 65%. R_f 0.13 (SiO_2, CH_2Cl_2/acetone 4:1, v/v). M.p. 150 °C. $[\alpha]_D^{20}$ + 219.9 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (d, *J* = 2.0 Hz, 1H, H_{Ar}), 8.34 (dd, *J* = 13.0, 7.6 Hz, 1H, H_{Ar}), 8.25 (d, *J* = 9.3 Hz, 1H, H_{Ar}), 7.71 (dd, *J* = 8.2, 2.1 Hz, 1H, H_{Ar}), 7.56 – 7.32 (po, 4H, H_{Ar}), 7.32 – 7.22 (po, 2H, H_{Ar}), 7.23 – 7.10 (po, 4H, H_{Ar}), 7.10 – 7.01 (po, 2H, H_{Ar}), 6.91 (br t, *J* = 7.7 Hz, 1H, H_{Ar}), 6.32 (d, *J* = 2.6 Hz, 1H, H_{Ar}), 5.74 (d, *J* = 7.7 Hz, 1H, H_{Ar}), 4.50 (ddd, *J* = 25.2, 7.3, 3.3 Hz, 1H, H-2), 4.31 (d, *J* = 12.4 Hz, 1H, H-6'), 4.01 – 3.90 (m, 1H, H-Pro), 3.70 – 3.53 (m, 1H, H-Pro), 3.41 (dd, *J* = 9.9, 7.3 Hz, 1H, H-2'), 3.25 (po, 2H, P(O)CH_2, H-6'), 3.11 – 2.98 (m, 1H, H-Pro), 2.61 – 2.47 (m, 1H, H-Pro), 2.41 (s, 3H, CH_3), 2.29 – 2.19 (m, 1H, H-Pro), 2.12 – 2.02 (m, 1H, P(O)CH_2), 2.00-1.94 (m, 1H, H-Pro), 1.91 (s, 3H, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 179.9 (C, *C*ON), 178.4 (d, *J* = 2.6 Hz, C, *C*OO), 171.2 (C, *C*N), 142.5 – 124.1 (C_{Ar} + CH_{Ar}), 72.2 (CH, C-2'), 66.4 (d, *J* = 5.1 Hz, CH, C-2), 63.8 (CH_2, C-6'), 58.3 (CH_2, C-5'), 31.0 (CH_2, *C*H_2 Pro), 30.4 (d, *J* = 69.7 Hz, CH_2, P(O)*C*H_2), 23.4 (CH_2, *C*H_2 Pro), 21.5 (d, *J* = 3.7 Hz, CH_3), 21.4 (d, *J* = 4.8 Hz, CH_3) ppm. ^{31}P NMR (162 MHz, decpld., $CDCl_3$): δ + 28.6 ppm. IR (neat): ṽ = 2972, 1642, 1460, 1340, 1251, 1164, 1081, 826, 854, 721 cm^{-1}. HRMS (ESI): m/z calcd. for $C_{42}H_{38}Cl_3N_3NiO_4P$ $[M + H]^+$ 842.1013, found 842.1003.



Ni(II)-(*S*)-*N*-(2-benzoyl-4-chlorophenyl)-1-(3,4-dichlorobenzyl)-pyrrolidine-2-carboxamide/(*R*)-3-[bis(3,5-dimethylphenyl)phosphinyl]-alanine Schiff Base Complex (*S*,*R*)-3c.

Isolated yield: 63%. R_f 0.12 (SiO_2, CH_2Cl_2/acetone 4:1, v/v). Mp. 115 °C. $[\alpha]_D^{20}$ + 210.2 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ 9.17 (d, *J* = 2.1 Hz, 1H, H_{Ar}), 8.33 (d, *J* = 9.4 Hz, 1H, H_{Ar}), 7.72 (dd, *J* = 8.2, 2.1 Hz, 1H, H_{Ar}), 7.54 – 7.39 (m, 2H, H_{Ar}), 7.35 – 7.27 (po, 5H, H_{Ar}), 7.24 (dt, *J* = 7.2, 1.7 Hz, 1H, H_{Ar}), 7.19 (td, *J* = 7.5, 1.5 Hz, 1H, H_{Ar}), 7.12 (br s, 1H, H_{Ar}), 7.06 (dd, *J* = 9.4, 2.6 Hz, 1H, H_{Ar}), 6.92 (br s, 1H, H_{Ar}), 6.34 (d, *J* = 2.6 Hz, 1H, H_{Ar}), 5.58 (dt, *J* = 8.0, 1.4 Hz, 1H, H_{Ar}), 4.42 (ddd, *J* = 26.0, 8.0, 2.6 Hz, 1H, H-2), 4.34 (d, *J* = 12.4 Hz, 1H, H-6’), 4.11 – 4.02 (m, 1H, H-Pro), 3.73 – 3.59 (m, 1H, H-Pro), 3.40 (dd, *J* = 9.6, 7.7 Hz, 1H, H-2’), 3.24 (d, *J* = 12.4 Hz, 1H, H-6’), 3.21 – 3.09 (m, 1H, H-Pro), 2.96 (td, *J* = 14.8, 2.6 Hz, 1H, P(O)CH_2), 2.65 – 2.50 (m, 1H, H-Pro), 2.35 – 2.27 (m, 1H, H-Pro), 2.31 (s, 6H, CH_3), 2.06 (s, 6H, CH_3), 2.10 – 1.95 (po, 2H, H-Pro, P(O)CH_2) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 180.2 (C, *C*ON), 178.6 (C, *C*OO), 171.5 (C, *C*N), 141.8 – 124.5 (C_{Ar} + CH_{Ar}), 72.2 (CH, C-2’), 66.3 (d, *J* = 5.3 Hz, CH, C-2), 63.9 (CH_2, C-6’), 59.5 (CH_2, C-5’), 32.7 (d, *J* = 69.0

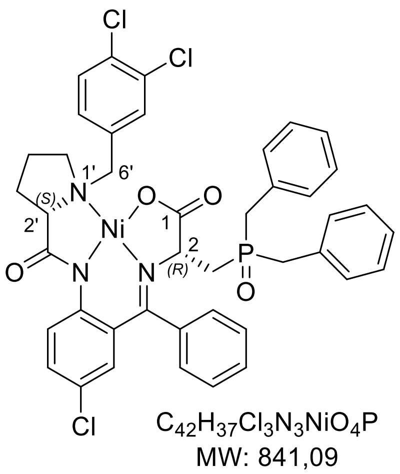
Hz, CH_2, P(O)CH_2), 31.2 (CH_2, CH_2 Pro), 23.5 (CH_2, CH_2 Pro), 21.4 (CH_3), 21.1 (CH_3) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ + 28.7 – 28.2 (m) ppm. IR (neat): ṽ = 3008, 2926, 1642, 1602, 1470, 1399, 1350, 1273, 1248, 1131, 854, 746, 687, 592 cm^{-1}. HRMS (ESI): m/z calcd. for $C_{44}H_{41}Cl_3N_3NiO_4P$ $[M + H]^+$ 870.1326, found 870.1317.



$C_{48}H_{49}Cl_3N_3NiO_4P$
MW: 925,19 g/mol

Ni(II)-(*S*)-*N*-(2-Benzoyl-4-chlorophenyl)-1-(3,4-dichlorobenzyl)-pyrrolidine-2-carboxamide/(*R*)-3-[bis(4-*tert*-butylphenyl)phosphinyl]-alanine Schiff Base Complex (*S*,*R*)-3d.

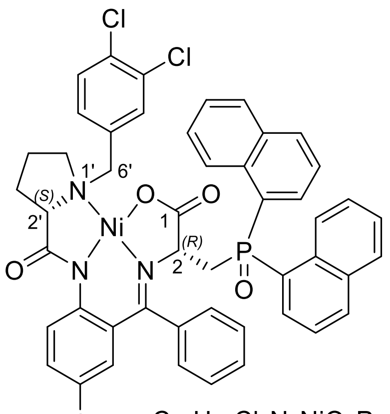
Isolated yield: 79%. R_f 0.12 (SiO_2, CH_2Cl_2/acetone 4:1, v/v). M.p. 90 °C. $[\alpha]_D^{20}$ + 103.0 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ 9.16 (d, *J* = 2.3 Hz, 1H, H_{Ar}), 8.40 (d, *J* = 9.4 Hz, 1H, H_{Ar}), 7.77 – 7.61 (po, 5H, H_{Ar}), 7.54 – 7.40 (po, 4H, H_{Ar}), 7.34 – 7.19 (po, 3H, H_{Ar}), 7.15 (dd, *J* = 8.4, 2.6 Hz, 2H, H_{Ar}), 7.06 (dd, *J* = 9.4, 2.6 Hz, 1H, H_{Ar}), 6.28 (d, *J* = 2.6 Hz, 1H, H_{Ar}), 5.69 (br d, *J* = 8.9 Hz, 1H, H_{Ar}), 4.48 – 4.25 (m, 2H, H-2, H-6'), 4.09 – 3.99 (m, 1H, H-Pro), 3.83 – 3.68 (m, 1H, H-Pro), 3.42 (dd, *J* = 9.9, 7.3 Hz, 1H, H-2'), 3.23 (d, *J* = 12.5 Hz, 1H, H-6'), 3.19 – 3.08 (m, 1H, H-Pro), 2.95 (td, 1H, *J* = 14.9, 2.7 Hz, P(O)CH_2), 2.64 – 2.51 (m, 1H, H-Pro), 2.33 – 2.21 (m, 1H, H-Pro), 2.08 – 1.94 (po, 2H, P(O)CH_2, H-Pro), 1.30 (s, 9H, CH_3), 1.08 (s, 9H, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 180.2 (C, *C*ON), 178.6 (d, *J* = 1.8 Hz, C, *C*OO), 171.7 (C, *C*N), 155.6 – 124.1 (C_{Ar} + CH_{Ar}), 72.3 (CH, C-2'), 66.4 (d, *J* = 5.5 Hz, CH, C-2), 63.9 (CH_2, C-6'), 59.6 (CH_2, C-5'), 35.1 (C, *C*$(CH_3)_3$), 34.9 (C, *C*$(CH_3)_3$), 33.1 (d, J = 69.7 Hz, CH_2, P(O)*C*H_2), 31.9 (CH_2, *C*H_2 Pro), 31.2 (C, C(*C*$H_3)_3$), 30.9 (C, C(*C*$H_3)_3$), 23.6 (CH_2, *C*H_2 Pro) ppm. ^{31}P NMR (162 MHz, decpld., $CDCl_3$): δ + 27.9 ppm. IR (neat): ṽ = 2960, 1660, 1636, 1467, 1392, 1365, 1334, 1254, 1091, 909, 817, 721 cm^{-1}. HRMS (ESI): m/z calcd. for $C_{48}H_{50}Cl_3N_3NiO_4P$ $[M + H]^+$ 926.1952, found 926.1945.



Ni(II)-(*S*)-*N*-(2-Benzoyl-4-chlorophenyl)-1-(3,4-dichlorobenzyl)-pyrrolidine-2-carboxamide/(*R*)-3-(Dibenzylphosphinyl)-alanine Schiff Base Complex (*S*,*R*)-3e.

Isolated yield: 63%. R_f 0.13 (SiO_2, CH_2Cl_2/acetone 4:1, v/v). M.p. 95 °C. $[\alpha]_D^{20}$ + 230.7 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.95 (d, J = 2.0 Hz, 1H, H_{Ar}), 8.11 (d, J = 9.3 Hz, 1H, H_{Ar}), 7.76 (dd, J = 8.2, 2.1 Hz, 1H, H_{Ar}), 7.61 – 7.46 (po, 2H, H_{Ar}), 7.42 – 7.33 (po, 2H, H_{Ar}), 7.33 – 7.20 (po, 9H, H_{Ar}), 7.20 – 7.14 (po, 2H, H_{Ar}), 7.11 (dd, J = 9.3, 2.6 Hz, 1H, H_{Ar}), 6.56 – 6.42 (po, 2H, H_{Ar}), 4.35 (d, J = 12.5 Hz, 1H, H-6'), 4.19 – 4.08 (m, 1H, H-2), 3.65 (dd, J = 10.8, 6.3 Hz, 1H), 3.37 – 2.99 (po, 7H), 2.77 – 2.65 (m, 1H, H-Pro), 2.63 – 2.46 (m, 2H, P(O)C*H_2*, H-Pro), 2.40 (t, J = 14.9 Hz, 1H, PC*H_2*Ph), 2.15 – 2.03 (m, 1H, H-Pro), 1.81 (td, J = 15.3, 3.3 Hz, 1H, P(O)C*H_2*) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 180.0 (C, *C*ON), 177.8 (br s, C, *C*OO), 170.6 (C, *C*N), 141.1 (C, C_{Ar}), 135.0 – 124.6 (C_{Ar} + CH_{Ar}), 71.4 (CH, C-2'), 65.6 (CH, C-2), 63.2 (CH_2, C-6'), 58.7 (CH_2, C-5'), 36.0 (d, J = 62.5 Hz, CH_2, P*C*H_2Ph), 35.9 (d, J

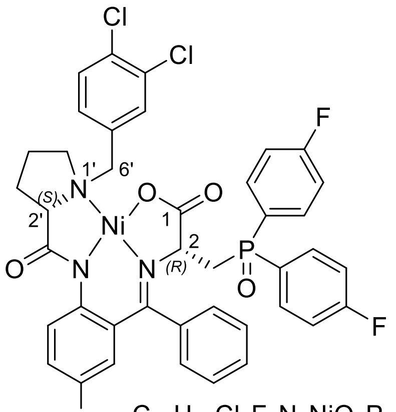
= 61.0 Hz, CH_2, P*C*H_2Ph), 32.3 (d, *J* = 58.0 Hz, CH_2, P(O)*C*H_2), 30.9 (CH_2, *C*H_2 Pro), 24.2 (CH_2, *C*H_2 Pro) ppm. ^{31}P NMR (162 MHz, decpld., $CDCl_3$): δ + 38.4 ppm. IR (neat): ṽ = 1670, 1632, 1460, 1334, 1254, 1174, 909, 733, 700 cm^{-1}. HRMS (ESI): m/z calcd. for $C_{42}H_{37}Cl_3N_3NiO_4P$ $[M + H]^+$ 842.1013, found 842.0998.



$C_{48}H_{37}Cl_3N_3NiO_4P$
MW: 913,09 g/mol

Ni(II)-(*S*)-*N*-(2-Benzoyl-4-chlorophenyl)-1-(3,4-dichlorobenzyl)-pyrrolidine-2-carboxamide/(*R*)-3-(di-1-naphtlenylphosphinyl)-alanine Schiff Base Complex (*S*,*R*)-3f.

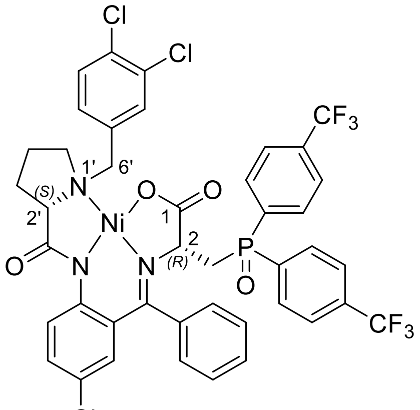
Isolated yield: 41%. R_f 0.14 (SiO_2, CH_2Cl_2/acetone 4:1, v/v). M.p. 175 °C. $[\alpha]_D^{20}$ + 216.2 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 9.17 (d, *J* = 2.0 Hz, 1H, H_{Ar}), 9.01 (d, *J* = 8.6 Hz, 1H, H_{Ar}), 8.75 (br dd, *J* = 14.6, 7.1 Hz, 1H, H_{Ar}), 8.33 (d, *J* = 9.4 Hz, 1H, H_{Ar}), 7.98 (d, *J* = 8.3 Hz, 1H, H_{Ar}), 7.92 – 7.84 (m, 2H, H_{Ar}), 7.80 (br d, *J* = 8.6 Hz, 1H, H_{Ar}), 7.73 – 7.60 (po, 4H, H_{Ar}), 7.57 – 7.46 (m, 2H, H_{Ar}), 7.40 – 7.12 (po, 7H, H_{Ar}), 7.06 (dd, *J* = 9.4, 2.6 Hz, 1H, H_{Ar}), 6.50 (td, *J* = 7.6, 1.3 Hz, 1H, H_{Ar}), 6.16 (d, *J* = 2.6 Hz, 1H, H_{Ar}), 4.78 (br d, *J* = 7.7 Hz, 1H), 4.49 (ddd, *J* = 27.2, 6.8, 3.4 Hz, 1H, H-2), 4.30 (d, *J* = 12.4 Hz, 1H, H-6’), 4.13 – 4.01 (m, 1H), 3.60 – 3.37 (po, 3H, P(O)C*H*$_2$, H-Pro), 3.26 (d, *J* = 12.4 Hz, 1H, H-6’), 3.19 – 3.03 (m, 1H H-Pro), 2.66 – 2.49 (m, 1H, H-Pro), 2.45 – 2.23 (po, 2H, P(O)C*H*$_2$, H-Pro), 1.96 – 1.76 (m, 1H, H-Pro) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 179.9 (C, *C*ON), 178.6 (d, *J* = 3.0 Hz, C, *C*OO), 171.6 (C, *C*N), 141.2 – 124.0 (C_{Ar} + CH_{Ar}), 72.3 (CH, C-2’), 66.7 (d, *J* = 5.8 Hz, CH, C-2), 64.0 (CH_2, C-6’), 59.5 (CH_2, C-5’), 31.7 (d, J = 69.9 Hz, CH_2, P(O)$\mathit{C}H_2$), 31.1 (CH_2, $\mathit{C}H_2$ Pro), 23.6 (CH_2, $\mathit{C}H_2$ Pro) ppm. ^{31}P NMR (162 MHz, decpld., $CDCl_3$): δ + 31.6 ppm. IR (neat): ṽ = 3000, 1660, 1636, 1460, 1399, 1340, 1244, 1174, 1081, 993, 934, 854, 807, 749, 663 cm^{-1}. HRMS (ESI): m/z calcd. for $C_{48}H_{37}Cl_3N_3NiO_4P$ $[M + H]^+$ 914.1013, found 914.1001.



Ni(II)-(*S*)-*N*-(2-Benzoyl-4-chlorophenyl)-1-(3,4-dichlorobenzyl)-pyrrolidine-2-carboxamide/(*R*)-3-[bis(4-fluorophenyl)phosphinyl]-alanine Schiff Base Complex (*S*,*R*)-3g.

Isolated yield: 71%. R_f 0.11 (SiO_2, CH_2Cl_2/acetone 4:1, v/v). M.p. 120 °C. $[\alpha]_D^{20}$ + 85.2 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ 9.02 (d, J = 2.0 Hz, 1H, H_{Ar}), 8.24 (d, J = 9.3 Hz, 1H, H_{Ar}), 7.83 – 7.60 (po, 5H, H_{Ar}), 7.53 – 7.43 (2H, H_{Ar}), 7.36 – 7.28 (2H, H_{Ar}), 7.26 – 7.21 (m, 1H, H_{Ar}), 7.18 – 7.06 (po, 3H, H_{Ar}), 6.98 (td, J = 8.6, 2.1 Hz, 2H, H_{Ar}), 6.41 (d, J = 2.6 Hz, 1H, H_{Ar}), 6.29 (br d, J = 7.6 Hz, 1H, H_{Ar}), 4.39 – 4.20 (po, 2H, H-2, H6’), 3.85 – 3.70 (m, 1H, H-Pro), 3.65 – 3.53 (m, 1H, H-Pro), 3.40 (dd, J = 10.2, 6.8 Hz, 1H, H-2’), 3.22 (d, J = 12.5 Hz, 1H, H-6’), 3.01 – 2.89 (m, 1H, H-Pro), 2.85 – 2.72 (m, 1H, P(O)CH_2), 2.62 – 2.51 (m, 1H, H-Pro), 2.44 (dt, J = 15.7, 8.0 Hz, 1H, H-Pro), 2.25 – 2.15 (m, 1H, P(O)CH_2), 2.13 – 2.03 (m, 1H, H-Pro) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 180.2 (C, *C*ON), 177.8 (d, J = 1.9 Hz, C, *C*OO), 171.5 (C, *C*N), 165.1 (dd, J = 254.5, 3.0 Hz, C, *C*F), 164.8 (dd, J = 255.5, 3.0 Hz, C, *C*F), 141.5

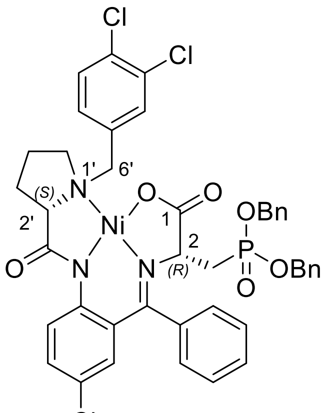
(C, C_{Ar}), 135.3 (C, C_{Ar}), 134.0 – 115.8 (C_{Ar} + CH_{Ar}), 71.9 (CH, C-2’), 65.9 (d, J = 4.0 Hz, CH, C-2), 63.7 (CH_2, C-6’), 59.2 (CH_2, C-5’), 34.0 (d, J = 69.6 Hz, CH_2, P(O)CH_2), 31.1 (CH_2, CH_2 Pro), 23.7 (CH_2, CH_2 Pro) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ – 105.9 (m), – 106.1 (m) ppm. ^{31}P NMR (162 MHz, decpld., $CDCl_3$): δ + 26.9 ppm. IR (neat): ṽ = 2972, 1667, 1636, 1584, 1506, 1460, 1398, 1238, 1164, 1116, 829, 746, 721, 663 cm^{-1}. IR (neat): ṽ = 2972, 1667, 1636, 1583, 1507, 1460, 1399, 1337, 1239, 1164, 1116, 829, 746, 721, 663 cm^{-1}. HRMS (ESI): m/z calcd. for $C_{40}H_{31}Cl_3F_2N_3NiO_4P$ $[M + H]^+$ 850.0512, found 850.0496.



$C_{42}H_{31}Cl_3F_6N_3NiO_4P$
MW: 949,04 g/mol

Ni(II)-(*S*)-*N*-(2-Benzoyl-4-chlorophenyl)-1-(3,4-dichlorobenzyl)-pyrrolidine-2-carboxamide/(*R*)-3-[bis(4-trifluoromethylphenyl)phosphinyl]-alanine Schiff Base Complex (*S*,*R*)-3h.

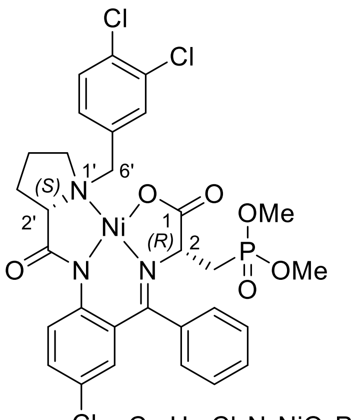
Isolated yield: 43%. R_f 0.11 (SiO_2, CH_2Cl_2/acetone 4:1, v/v). M.p. 150 °C. $[\alpha]_D^{20}$ + 210.6 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, J = 2.0 Hz, 1H, H_{Ar}), 8.24 (d, J = 9.3 Hz, 1H, H_{Ar}), 7.93 – 7.73 (po, 4H, H_{Ar}), 7.73 – 7.64 (po, 3H, H_{Ar}), 7.58 (dd, J = 8.3, 2.4 Hz, 2H, H_{Ar}), 7.52 – 7.42 (m, 2H, H_{Ar}), 7.39 – 7.26 (po, 2H, H_{Ar}), 7.26 – 7.19 (m, 1H, H_{Ar}), 7.10 (dd, J = 9.3, 2.6 Hz, 1H, H_{Ar}), 6.49 (br d, J = 8.3 Hz, 1H, H_{Ar}), 6.43 (d, J = 2.6 Hz, 1H, H_{Ar}), 4.34 – 4.20 (po, 2H, H-2, H-6’), 3.74 – 3.62 (m, 1H, H-Pro), 3.65 – 3.50 (m, 1H, H-Pro), 3.43 (dd, J = 10.5, 6.5 Hz, 1H, H-2’), 3.23 (d, J = 12.5 Hz, 1H, H-6’), 2.98 – 2.76 (po, 2H, H-Pro, P(O)C*H*2), 2.74 – 2.52 (m, 2H, H-Pro), 2.22 – 2.06 (m, 2H, P(O)C*H*2, H-Pro) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 180.2 (C, *C*ON), 177.5 (d, *J* = 1.9 Hz, C, *C*OO), 171.8 (C, *C*N), 141.3 – 121.9 (C_{Ar} + CH_{Ar}), 71.7 (CH, C-2'), 66.6 (d, *J* = 3.4 Hz, CH, C-2), 63.6 (CH_2, C-6'), 59.1 (CH_2, C-5'), 33.8 (d, *J* = 68.8 Hz, CH_2, P(O)*C*H2), 31.0 (CH_2, *C*H2 Pro), 23.8 (CH_2, *C*H2 Pro) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ – 63.3 (s), – 63.3 (s) ppm. ^{31}P NMR (162 MHz, decpld., $CDCl_3$): δ + 26.8 ppm. IR (neat): ṽ = 1675, 1632, 1470, 1402, 1325, 1171, 1211, 1060, 826, 715, 599 cm^{-1}. HRMS (ESI): m/z calcd. for $C_{42}H_{32}Cl_3F_6N_3NiO_4P$ $[M + H]^+$ 950.0448, found 950.0441.



Ni(II)-(*S*)-*N*-(2-Benzoyl-4-chlorophenyl)-1-(3,4-dichlorobenzyl)-pyrrolidine-2-carboxamide/(*R*)-3-(dibenzyloxyphosphinyl)-alanine Schiff Base Complex (*S*,*R*)-3i.

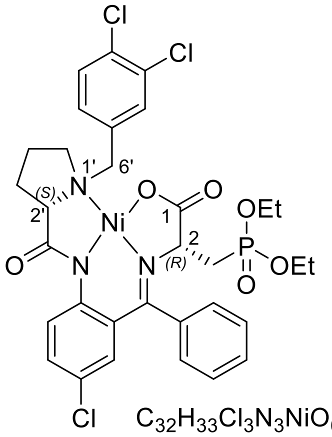
Isolated yield: 85%. R_f 0.11 (SiO_2, CH_2Cl_2/acetone 4:1, v/v). M.p. 177 °C. $[\alpha]_D^{20}$ + 192.8 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ 9.05 (d, *J* = 2.1 Hz, 1H, H_{Ar}), 8.26 (d, *J* = 9.3 Hz, 1H, H_{Ar}), 7.70 (dd, *J* = 8.1, 2.1 Hz, 1H, H_{Ar}), 7.56 – 7.42 (m, 2H, H_{Ar}), 7.40 – 7.26 (po, 3H, H_{Ar}), 7.23 – 7.07 (po, 5H, H_{Ar}), 6.44 (dt, *J* = 7.8, 1.2 Hz, 1H, H_{Ar}), 6.40 (d, *J* = 2.6 Hz, 1H, H_{Ar}), 5.18 – 5.07 (po, 2H, C*H*2Ph), 5.02 (dd, *J* = 11.5, 8.0 Hz, 1H, C*H*2Ph), 4.86 (dd, *J* = 11.1, 7.3 Hz, 1H, C*H*2Ph), 4.29 (d, *J* = 12.5 Hz, 1H, H-6'), 4.19 (ddd, *J* = 34.9, 8.1, 2.5 Hz, 1H, H-2), 3.75 – 3.65 (m, 1H, H-5'), 3.50 – 3.38 (m, 1H, H-Pro), 3.35 (dd, *J* = 10.1, 6.9 Hz, 1H, H-

2’), 3.20 (d, J = 12.5 Hz, 1H, H-6’), 2.85 – 2.71 (m, 1H, H-Pro), 2.46 (ddt, J = 13.1, 10.0, 8.2 Hz, 1H, H-Pro), 2.24 (ddd, J = 19.3, 15.8, 2.5 Hz, 1H, P(O)CH_2), 2.11 – 1.99 (po, 2H, H-Pro), 1.88 – 1.71 (m, 2H, P(O)CH_2, H-5’) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 180.4 (C, *C*ON), 178.4 (d, J = 1.9 Hz, C, *C*OO), 171.9 (C, *C*N), 141.4 (C, C_{Ar}), 135.8 (d, J = 6.0 Hz, C, P(O)OCH_2Ph), 135.6 (d, J = 7.3 Hz, C, P(O)OCH_2Ph), 135.3 (C, C_{Ar}), 134.0 (CH, CH_{Ar}), 133.4 (C, C_{Ar}), 133.3 (C, C_{Ar}), 133.2 (C, C_{Ar}), 132.5 (CH, CH_{Ar}), 132.3 (CH, CH_{Ar}), 131.0 (CH, CH_{Ar}), 130.3 (CH, CH_{Ar}), 130.0 (CH, CH_{Ar}), 129.4 (CH, CH_{Ar}), 129.3 (CH, CH_{Ar}), 128.7 – 128.4 (CH, CH_{Ar}), 127.7 (CH, CH_{Ar}), 127.0 (C, C_{Ar}), 126.7 (CH, CH_{Ar}), 125.4 (C, C_{Ar}), 124.3 (CH, CH_{Ar}), 72.0 (CH, C-2’), 68.0 (d, J = 6.1 Hz, CH_2, P(O)OCH_2Ph), 67.9 (d, J = 6.2 Hz, CH, P(O)O*C*H_2Ph), 65.2 (d, J = 5.9 Hz, CH, C-2), 63.7 (CH_2, C-6’), 59.1 (CH_2, C-5’), 31.2 (CH_2, *C*H_2 Pro), 29.0 (d, J = 140.1 Hz, CH_2, P(O)*C*H_2), 23.1 (CH_2, *C*H_2 Pro) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.0 – 26.4 ppm. IR (neat): ṽ = 1670, 1636, 1463, 1393, 1340, 1245, 1020, 983, 964, 878, 850, 817, 749, 721, 700 cm^{-1}. HRMS (ESI): m/z calcd. for $C_{42}H_{38}Cl_3N_3NiO_4P$ $[M + H]^+$ 874.0912, found 874.0902.



Ni(II)-(*S*)-*N*-(2-Benzoyl-4-chlorophenyl)-1-(3,4-dichlorobenzyl)-pyrrolidine-2-carboxamide/(*R*)-3-(Dimethoxyphosphinyl)-alanine Schiff Base Complex (*S*,*R*)-3j.

Isolated yield: 51%. R_f 0.1 (SiO_2, CH_2Cl_2/acetone 4:1, v/v). M.p. 190 °C (decomposed). $[\alpha]_D^{20}$ + 191.9 (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ ^1H NMR (400 MHz, $CDCl_3$/TMS) δ 9.07 (d, *J* = 2.1 Hz, 1H, H_{Ar}), 8.21 (d, *J* = 9.3 Hz, 1H, H_{Ar}), 7.69 (dd, *J* = 8.2, 2.1 Hz, 1H, H_{Ar}), 7.62 – 7.45 (po, 3H, H_{Ar}), 7.34 (d, *J* = 8.1 Hz, 1H, H_{Ar}), 7.31 – 7.26 (m, 2H, H_{Ar}), 7.11 (dd, *J* = 9.3, 2.6 Hz, 1H, H_{Ar}), 6.99 (br d, *J* = 7.6 Hz, 1H, H_{Ar}), 6.58 (d, *J* = 2.6 Hz, 1H, H_{Ar}), 4.30 (d, *J* = 12.5 Hz, 1H, H-6'), 4.19 (ddd, *J* = 33.4, 8.1, 2.6 Hz, 1H, H-2), 3.85 – 3.74 (m, 1H, H-Pro), 3.74 (d, *J* = 11.0 Hz, 3H, OMe), 3.69 (d, *J* = 11.0 Hz, 3H, OMe), 3.66 – 3.47 (m, 1H, H-Pro), 3.38 (dd, *J* = 10.2, 6.9 Hz, 1H, H-2'), 3.24 (d, *J* = 12.5 Hz, 1H, H-6'), 2.92 – 2.78 (m, 1H, H-Pro), 2.64 – 2.47 (m, 1H, H-Pro), 2.28 – 2.00 (m, 3H, H-Pro, P(O)CH_2), 1.84 (td, *J* = 16.2, 8.1 Hz, 1H, P(O)CH_2) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 180.3 (C, *C*ON), 178.3 (d, *J* = 1.8 Hz, C, *C*OO), 172.0 (C, *C*N), 141.3 (C, C_{Ar}), 135.3 (C, C_{Ar}), 134.0 (CH, CH_{Ar}), 133.4 (C, C_{Ar}), 133.4 (C, C_{Ar}), 133.3 (C, C_{Ar}), 132.8 (CH, CH_{Ar}), 132.4 (CH, CH_{Ar}), 131.0 (CH, CH_{Ar}), 130.5 (CH, CH_{Ar}), 129.9 (CH, CH_{Ar}), 129.6 (CH, CH_{Ar}), 129.5 (CH, CH_{Ar}), 127.8 (CH, CH_{Ar}), 127.0 (C, C_{Ar}), 126.9 (CH, CH_{Ar}), 125.6 (C, C_{Ar}), 124.1 (CH, CH_{Ar}), 72.0 (CH, C-2'), 65.2 (d, *J* = 5.6 Hz, CH, C-2), 63.9 (CH_2, C-6'), 59.0 (CH_2, C-5'), 52.9 (d, *J* = 6.3 Hz, CH_3, OMe), 52.7 (d, *J* = 6.3 Hz, CH_3, OMe), 31.2 (CH_2, *C*H_2 Pro), 27.8 (d, *J* = 141.3 Hz, CH_2, P(O)*C*H_2), 23.0 (CH_2, *C*H_2 Pro) ppm. ^{31}P NMR (162 MHz, decpld., $CDCl_3$): δ + 28.4 ppm. IR (neat): ṽ = 3051, 2960, 1734, 1672, 1638, 1467, 1399, 1359, 1331, 1248, 1168, 1057, 1026, 863, 811, 734, 703 cm^{-1}. HRMS (ESI): m/z calcd. for $C_{30}H_{29}Cl_3N_3NiO_6P$ $[M + H]^+$ 722.0286, found 722.0273.

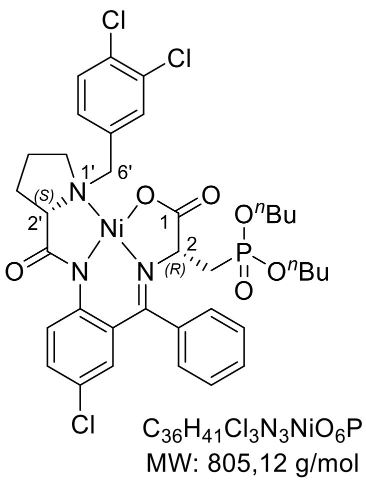


$C_{32}H_{33}Cl_3N_3NiO_6P$
MW: 749,05 g/mol

Ni(II)-(*S*)-*N*-(2-Benzoyl-4-chlorophenyl)-1-(3,4-dichlorobenzyl)-pyrrolidine-2-carboxamide/(*R*)-3-(diethoxyphosphinyl)-alanine Schiff Base Complex (*S*,*R*)-3k.

Isolated yield: 64%. R_f 0.12 (SiO_2, CH_2Cl_2/acetone 4:1, v/v). M.p. 110 °C. $[\alpha]_D^{20}$ + 211.5 (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$/TMS): δ 9.09 (d, *J* = 2.0 Hz, 1H, H_{Ar}), 8.22 (d, *J* = 9.3 Hz, 1H, H_{Ar}), 7.68 (dd, *J* = 8.2, 2.1 Hz, 1H, H_{Ar}), 7.63 – 7.44 (po, 3H, H_{Ar}), 7.34 (d, *J* = 8.1 Hz, 1H, H_{Ar}), 7.31 – 7.25 (m, 1H, H_{Ar}), 7.10 (dd, *J* = 9.3, 2.6 Hz, 1H, H_{Ar}), 7.00 (dt, *J* = 8.2, 1.5 Hz, 1H, H_{Ar}), 6.57 (d, *J* = 2.6 Hz, 1H, H_{Ar}), 4.31 (d, *J* = 12.5 Hz, 1H, H-6'), 4.25 – 3.97 (po, 5H, H-2, 2 × P(O)OCH_2CH$_3$), 3.79 (ddd, *J* = 10.2, 6.7, 3.0 Hz, 1H, H-5'), 3.71 – 3.53 (m, 1H, H-Pro), 3.37 (dd, *J* = 10.3, 6.8 Hz, 1H, H-2'), 3.23 (d, *J* = 12.5 Hz, 1H, H-6'), 2.87 – 2.72 (m, 1H, H-Pro), 2.60 – 2.47 (m, 1H, H-Pro), 2.25 – 2.09 (po, 2H, P(O)CH_2, H-Pro), 2.10 – 1.96 (m, 1H, H-Pro), 1.82 (td, *J* = 16.1, 8.2 Hz, 1H, P(O)CH_2), 1.23 (t, *J* = 7.1 Hz, 3H, P(O)OCH$_2$CH_3), 1.10 (t, *J* = 7.1 Hz, 3H, P(O)OCH$_2$CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 180.2 (C, *C*ON), 178.3 (d, *J* = 1.8 Hz, C, *C*OO), 171.8 (C, *C*N), 141.3 (C, C_{Ar}), 135.4 (C, C_{Ar}), 134.0 (CH, CH_{Ar}), 133.4 (C, C_{Ar}), 133.3 (C, C_{Ar}), 133.2 (C, C_{Ar}), 132.6 (CH, CH_{Ar}), 132.3 (CH, CH_{Ar}), 131.0 (CH, CH_{Ar}), 130.4 (CH, CH_{Ar}), 129.9 (CH, CH_{Ar}), 129.5 (CH, CH_{Ar}), 129.4 (CH, CH_{Ar}), 127.7 (CH, CH_{Ar}), 126.9 (C, C_{Ar}), 126.9 (CH, CH_{Ar}), 125.4 (C, C_{Ar}), 124.1 (CH, CH_{Ar}), 71.9 (CH, C-2'), 65.3 (d, *J* = 6.0 Hz, CH, C-2), 63.8 (CH_2, C-6'), 62.3 (d, *J* = 6.1 Hz, CH_2, P(O)O*C*H$_2$CH$_3$), 62.1 (d, *J* = 6.2 Hz, CH_2, P(O)O*C*H$_2$CH$_3$), 59.0 (CH_2, C-5'), 31.1 (CH_2, *C*H$_2$ Pro), 28.5 (d, *J* = 140.8

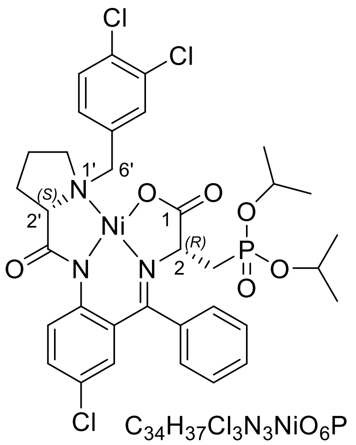
Hz, CH_2, P(O)CH_2), 23.2 (CH_2, CH_2 Pro), 16.3 (d, *J* = 6.4 Hz, CH_3, P(O)OCH_2CH_3), 16.2 (d, *J* = 6.4 Hz, CH_3, P(O)OCH_2CH_3) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.0 – 25.5 (m) ppm. IR (neat): ṽ = 2990, 2926, 1667, 1633, 1460, 1399, 1337, 1242, 1174, 1051, 1017, 961, 860, 746, 706, 672 cm^{-1}. HRMS (ESI): m/z calcd. for $C_{32}H_{34}Cl_3N_3NiO_6P$ $[M + H]^+$ 750.0599, found 750.0587.



Ni(II)-(*S*)-*N*-(2-Benzoyl-4-chlorophenyl)-1-(3,4-dichlorobenzyl)-pyrrolidine-2-carboxamide/(*R*)-3-(Dibutoxyphosphinyl)-alanine Schiff Base Complex (*S*,*R*)-3l.

Isolated yield: 48%. R_f 0.12 (SiO_2, CH_2Cl_2/acetone 4:1, v/v). M.p. 142 °C. $[\alpha]_D^{20}$ + 97.5 (*c* 1.00, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 9.08 (d, *J* = 2.0 Hz, 1H, H_{Ar}), 8.27 (d, *J* = 9.3 Hz, 1H, H_{Ar}), 7.67 (dd, *J* = 8.2, 2.1 Hz, 1H, H_{Ar}), 7.61 – 7.46 (po, 3H, H_{Ar}), 7.33 (d, *J* = 8.2 Hz, 1H, H_{Ar}), 7.32 – 7.24 (m, 1H, H_{Ar}), 7.10 (dd, *J* = 9.4, 2.6 Hz, 1H, H_{Ar}), 7.00 (dt, *J* = 8.0, 1.5 Hz, 1H, H_{Ar}), 6.57 (d, *J* = 2.6 Hz, 1H, H_{Ar}), 4.31 (d, *J* = 12.5 Hz, 1H, H-6’), 4.24 – 3.90 (po, 5H, H-2, 2 × P(O)$OCH_2CH_2CH_2CH_3$), 3.81 (ddd, *J* = 10.2, 6.7, 3.1 Hz, 1H, H-5’), 3.74 – 3.57 (m, 1H, H-Pro), 3.35 (dd, *J* = 10.2, 6.9 Hz, 1H, H-2’), 3.22 (d, *J* = 12.5 Hz, 1H, H-6’), 2.89 – 2.76 (m, 1H, H-Pro), 2.53 (ddt, *J* = 13.2, 10.2, 8.2 Hz, 1H, H-Pro), 2.25 – 1.97 (po, 4H, H-5’, H-Pro, P(O)CH_2), 1.84 (td, *J* = 16.1, 8.1 Hz, 1H, P(O)CH_2), 1.63 – 1.50 (m, 2H, P(O)$OCH_2CH_2CH_2CH_3$), 1.46 – 1.24 (po, 4H, P(O)$OCH_2CH_2CH_2CH_3$,

$P(O)OCH_2CH_2CH_2CH_3$), 1.17 (h, *J* = 7.4 Hz, 2H, $P(O)OCH_2CH_2C\mathit{H}_2CH_3$), 0.85 (t, *J* = 7.4 Hz, 3H, $P(O)OCH_2CH_2CH_2C\mathit{H}_3$), 0.75 (t, *J* = 7.4 Hz, 3H, $P(O)OCH_2CH_2CH_2C\mathit{H}_3$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 180.2 (C, *C*ON), 178.2 (d, *J* = 1.8 Hz, C, *C*OO), 171.8 (C, *C*N), 141.4 (C, C_{Ar}), 135.4 (C, C_{Ar}), 134.1 (CH, CH_{Ar}), 133.5 (C, C_{Ar}), 133.4 (C, C_{Ar}), 133.2 (C, C_{Ar}), 132.6 (CH, CH_{Ar}), 132.2 (CH, CH_{Ar}), 131.0 (CH, CH_{Ar}), 130.4 (CH, CH_{Ar}), 129.9 (CH, CH_{Ar}), 129.6 (CH, CH_{Ar}), 129.4 (CH, CH_{Ar}), 127.7 (CH, CH_{Ar}), 127.0 (CH, CH_{Ar}), 126.9 (C, C_{Ar}), 125.4 (C, C_{Ar}), 124.2 (CH, CH_{Ar}), 72.0 (CH, C-2'), 66.1 (d, *J* = 6.4 Hz, CH_2, $P(O)O\mathit{C}H_2CH_2CH_2CH_3$), 65.8 (d, *J* = 6.4 Hz, CH_2, $P(O)O\mathit{C}H_2CH_2CH_2CH_3$), 65.5 (d, *J* = 5.7 Hz, CH, C-2), 63.7 (CH_2, C-6'), 59.1 (CH_2, C-5'), 32.5 (d, *J* = 6.3 Hz, CH_2, $P(O)OCH_2\mathit{C}H_2CH_2CH_3$), 32.4 (d, *J* = 6.2 Hz, CH_2, $P(O)OCH_2\mathit{C}H_2CH_2CH_3$), 31.2 ($CH_2$, $\mathit{C}H_2$ Pro), 30.2 (d, *J* = 167.6 Hz, CH_2, $P(O)\mathit{C}H_2$), 23.2 (CH_2, $\mathit{C}H_2$ Pro), 18.8 (CH_2, $P(O)OCH_2CH_2\mathit{C}H_2CH_3$), 18.7 ($CH_2$, $P(O)OCH_2CH_2\mathit{C}H_2CH_3$), 13.6 ($CH_3$, $P(O)OCH_2CH_2CH_2\mathit{C}H_3$), 13.6 ($CH_3$, $P(O)OCH_2CH_2CH_2\mathit{C}H_3$) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.0 – 25.5 (m) ppm. IR (neat): ṽ = 2962, 2248, 1710, 1664, 1642, 1463, 1392, 1359, 1217, 1168, 1063, 986, 897, 730 cm^{-1}. HRMS (ESI): m/z calcd. for $C_{36}H_{41}Cl_3N_3NiO_6P$ $[M + H]^+$ 806.1225, found 806.1214.

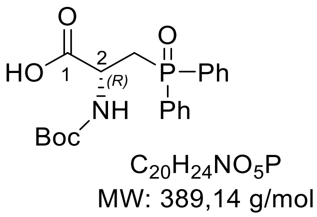


$C_{34}H_{37}Cl_3N_3NiO_6P$
MW: 777,08 g/mol

Ni(II)-(*S*)-*N*-(2-Benzoyl-4-chlorophenyl)-1-(3,4-dichlorobenzyl)-pyrrolidine-2-carboxamide/(*R*)-3-(diisopropyloxyphosphinyl)-alanine Schiff Base Complex (*S,R*)-3m.

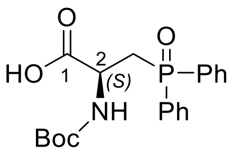
Isolated yield: 35%. R_f 0.12 (SiO_2, CH_2Cl_2/acetone 4:1, v/v). M.p. 95 °C. $[\alpha]_D^{20}$ + 222.1 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ 9.12 (d, *J* = 2.1 Hz, 1H, H_{Ar}), 8.24 (d, *J* = 9.4 Hz, 1H, H_{Ar}), 7.65 (dd, *J* = 8.2, 2.1 Hz, 1H, H_{Ar}), 7.61 – 7.45 (po, 3H, H_{Ar}), 7.33 (d, *J* = 8.1 Hz, 1H, H_{Ar}), 7.31 – 7.22 (m, 1H, H_{Ar}), 7.09 (dd, *J* = 9.3, 2.6 Hz, 1H, H_{Ar}), 7.04 (br d, *J* = 7.9 Hz, 1H, H_{Ar}), 6.57 (d, *J* = 2.6 Hz, 1H, H_{Ar}), 4.88 – 4.68 (m, 2H, 2 × P(O)OC*H*(CH_3)$_2$), 4.32 (d, *J* = 12.5 Hz, 1H, H-6'), 4.15 (ddd, *J* = 32.9, 8.3, 2.5 Hz, 1H, H-2), 3.90 – 3.70 (m, 1H, H-Pro), 3.79 – 3.62 (m, 1H, H-Pro), 3.36 (dd, *J* = 10.3, 6.7 Hz, 1H, H-Pro), 3.21 (d, *J* = 12.5 Hz, 1H, H-6'), 2.90 – 2.73 (m, 1H, H-Pro), 2.58 – 2.41 (m, 1H, H-Pro), 2.21 – 1.97 (po, 3H, P(O)CH_2, H-Pro), 1.84 (td, *J* = 16.3, 8.3 Hz, 1H, P(O)CH_2), 1.34 (d, *J* = 6.2 Hz, 3H, P(O)OCH(CH_3)$_2$), 1.24 (d, *J* = 6.2 Hz, 3H, P(O)OCH(CH_3)$_2$), 1.20 (d, *J* = 6.2 Hz, 3H, P(O)OCH(CH_3)$_2$), 1.02 (d, *J* = 6.2 Hz, 3H, P(O)OCH(CH_3)$_2$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 180.3 (C, *C*ON), 178.5 (d, *J* = 1.7 Hz, C, *C*OO), 171.8 (C, *C*N), 141.4 (C, C_{Ar}), 135.5 (C, C_{Ar}), 134.2 (CH, CH_{Ar}), 133.6 (C, C_{Ar}), 133.4 (C, C_{Ar}), 133.2 (C, C_{Ar}), 132.6 (CH, CH_{Ar}), 132.3 (CH, CH_{Ar}), 131.0 (CH, CH_{Ar}), 130.4 (CH, CH_{Ar}), 129.9 (CH, CH_{Ar}), 129.5 (CH, CH_{Ar}), 129.3 (CH, CH_{Ar}), 127.7 (CH, CH_{Ar}), 127.0 (C, C_{Ar}), 127.0 (CH, CH_{Ar}), 125.4 (C, C_{Ar}), 124.1 (CH, CH_{Ar}), 71.9 (CH, C-2'), 71.3 (d, *J* = 6.1 Hz, CH, P(O)O*C*H(CH_3)$_2$), 71.1 (d, *J* = 6.1 Hz, CH, P(O)O*C*H(CH_3)$_2$), 65.8 (d, *J* = 5.6

Hz, CH, C-2), 63.8 (CH_2, C-6'), 59.2 (CH_2, C-5'), 31.5 (d, J = 142.1 Hz, CH_2, P(O)CH_2), 31.1 (CH_2, CH_2 Pro), 24.3 (d, J = 4.4 Hz, CH, P(O)CH(CH_3)$_2$), 24.2 (d, J = 4.0 Hz, CH, P(O)OCH(CH_3)$_2$), 24.0 (d, J = 4.6 Hz, CH, P(O)OCH(CH_3)$_2$), 23.7 (d, J = 5.7 Hz, CH, P(O)CH(CH_3)$_2$), 23.3 (CH_2, CH_2 Pro) ppm. ^{31}P NMR (162 MHz, decpld., $CDCl_3$): δ + 23.8 ppm. IR (neat): ṽ = 2984, 2251, 1710, 1670, 1633, 1587, 1531, 1467, 1405, 1334, 1365, 1242, 1171, 999, 974, 903, 820, 728 cm^{-1}. HRMS (ESI): m/z calcd. for $C_{34}H_{37}Cl_3N_3NiO_6P$ [M + H]$^+$ 800.0731, found 800.0719.



(*R*)-Boc-3-(diphenylphosphinyl)-alanine [(+)-4a].

Isolated yield: 60%. Enantiomeric excess: 96%. R_f 0.09 (SiO_2, CH_2Cl_2/acetone 4:1, v/v). M.p. 79 °C. $[\alpha]_D^{20}$ + 105.9 (c 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ 7.82 (dd, J = 12.0, 7.5 Hz, 2H, H_{Ar}), 7.75 (dd, J = 12.2, 7.0 Hz, 2H, H_{Ar}), 7.59 – 7.42 (po, 6H, H_{Ar}), 5.75 (d, J = 5.8 Hz, 1H, NH), 4.68 – 4.48 (m, 1H, H-2), 3.27 – 3.11 (m, 1H, H-3), 3.03 (dt, J = 15.6, 7.9 Hz, 1H, H-3), 1.29 (s, 9H, C(CH_3)$_3$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.2 (C, C-1), 156.0 (C, NHCOO), 132.6 (CH, CH_{Ar}), 132.5 (CH, CH_{Ar}), 132.3 (CH, CH_{Ar}), 132.3 (CH, CH_{Ar}), 132.1 (C, C_{Ar}), 131.8 (C, C_{Ar}), 131.2 (CH, CH_{Ar}), 131.1 (CH, CH_{Ar}), 130.9 (CH, CH_{Ar}), 130.8 (CH, CH_{Ar}), 129.1 (CH, CH_{Ar}), 129.0 (CH, CH_{Ar}), 79.8 (C, C(CH_3)$_3$), 49.8 (CH, C-2), 31.6 (d, J = 69.0 Hz, CH_2, C-3), 28.4 (CH_3, C(CH_3)$_3$). ^{31}P NMR (162 MHz, decpld., $CDCl_3$): δ + 34.0 ppm. IR (neat): ṽ = 1704, 1510, 1442, 1171, 759, 693, 534 cm^{-1}. HRMS (ESI): m/z calcd. for $C_{20}H_{25}NO_5P$ [M + H]$^+$ 390.1465, found 390.1462.



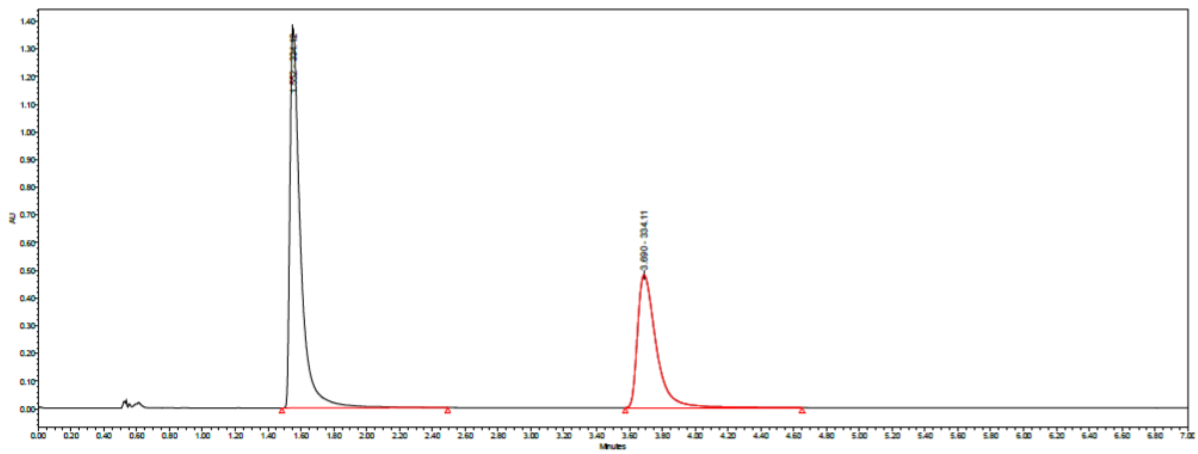
$C_{20}H_{24}NO_5P$
MW: 389,14 g/mol

(*S*)-Boc-3-(diphenylphosphinyl)-alanine [(–)-4a].

Isolated yield: 59%. Enantiomeric excess: 96%. $[\alpha]_D^{20}$ – 120.1 (*c* 1.0, $CHCl_3$).

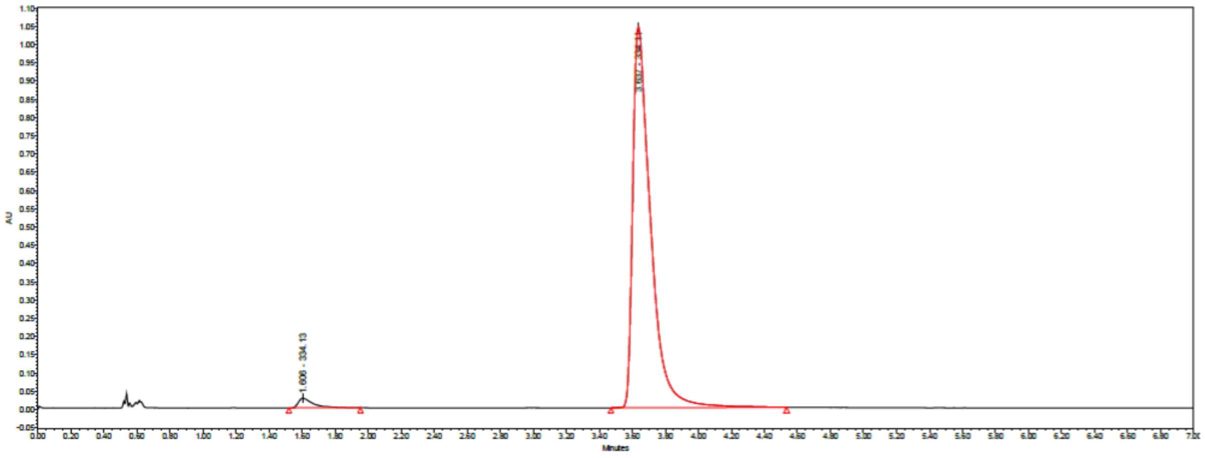
The enantiomeric excesses of compounds (+)-**4a** and (–)-**4a** were determined respectively by SFC analyses on Chiralpak IC-U stationary phase using 20% methanol in carbon dioxide. Mobile phase was set up at 1 mL.min^{-1}, temperature at 25 °C, pressure at 150 bar, and wavelength at 210 nm; t_R [(–)-**4a**, 1.6 min], t_R [(+)-**4a**, 3.7 min]. First, compounds were injected in mixture in order to optimize peak separation and then, they were injected alone to determine elution order and calculate the enantiomeric excess for each enantiomer.

UV chromatogram of compounds (-)-4a and (+)-4a in mixture:



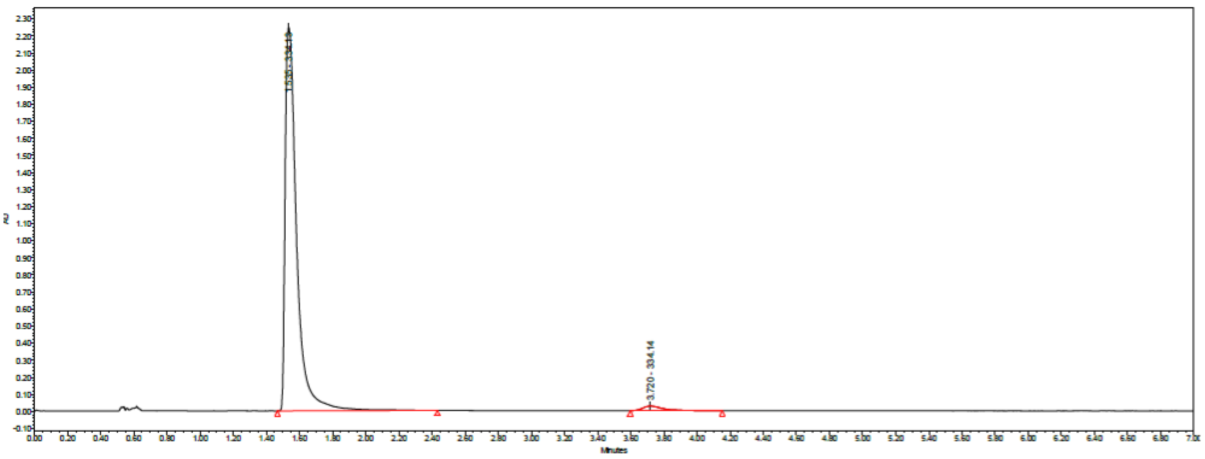
Peak	t_R (min)	% area	Masses in ESI (+)	Masses in ESI (-)
1	1.6	**62.03**	334.12 / 290.14 / 390.28	314.10 / 388.19 / 271.12
2	3.7	**37.97**	334.11 / 290.15 / 390.25	314.09 / 388.21 / 271.16

UV chromatogram of compound (+)-4a:



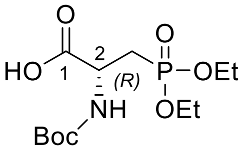
Peak	t_R (min)	% area	Masses in ESI (+)	Masses in ESI (-)
1	1.6	**2.10**	334.13 / 290.13 / 390.29	314.06 / 388.22 / 271.09
2	3.7	**97.90**	334.11 / 290.14 / 390.26	314.10 / 388.19 / 271.15

UV chromatogram of compound (–)-4a:



Peak	tR (min)	% area	Masses in ESI (+)	Masses in ESI (-)
1	1.6	**97.91**	334.13 / 290.15 / 390.26	314.09 / 388.19 / 271.13
2	3.7	**2.09**	334.14 / 290.15 / 390.28	314.10 / 388.21 / 271.22

In positive mode, $[M+H]^+$ ion was observed at 390.3 m/z and $[M–Boc+H]^+$ ion at 290.2 m/z respectively. In negative mode, $[M–H]^–$ ion was observed at 388.2 m/z.



$C_{12}H_{24}NO_7P$
MW: 325,2978 g/mol

(*R*)-Boc-3-(diethoxyphosphinyl)-alanine [(+)-4k].

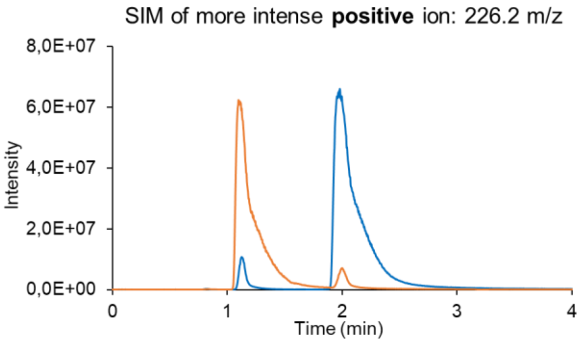
Isolated yield: 49%. Enantiomeric excess: 97%. R_f 0.08 (SiO_2, CH_2Cl_2/acetone 4:1, v/v). M.p. 166 °C. $[\alpha]_D^{20}$ + 23.9 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ 9.27 (br s, 1H, COO*H*), 5.76 (d, *J* = 7.1 Hz, 1H, N*H*), 4.65 – 4.40 (m, 1H, H-1), 4.25 – 3.99 (m, 4H, OCH_2CH_3), 2.65 – 2.28 (po, 2H, H-3), 1.44 (s, 9H, $C(CH_3)_3$), 1.33 (t, *J* = 7.1 Hz, 6H, OCH_2CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.4 (d, *J* = 7.4 Hz, C, *C*OOH), 155.3 (C, NH*C*O), 80.0 (C, $C(CH_3)_3$), 62.7 (d, *J* = 7.4 Hz, CH_2, OCH_2CH_3), 62.6 (d, *J* = 6.7 Hz, CH_2, OCH_2CH_3), 49.2 (d, *J* = 4.9 Hz, CH, C-2), 28.5 (d, *J* = 141.7 Hz, CH_2, C-3), 28.4 (CH_3, $C(CH_3)_3$), 16.4 (CH_3, OCH_2CH_3), 16.4 (CH_3, OCH_2CH_3) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.0 – 27.5 (m) ppm. IR (neat): ṽ = 3332, 1722, 1679, 1537, 1368, 1158, 1035, 952, 648 cm^{-1}. HRMS (ESI): m/z calcd. for $C_{12}H_{25}NO_7P$ $[M + H]^+$ 326.1363, found 326.1359.

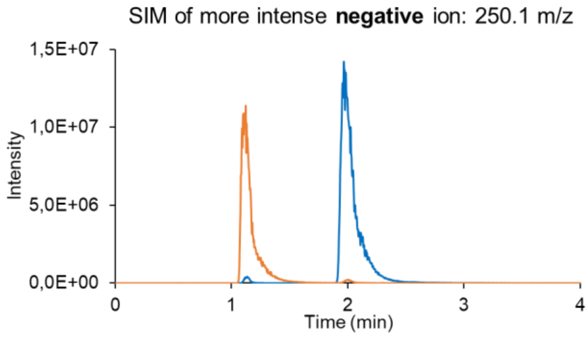
(*S*)-Boc-3-(diethoxyphosphinyl)-alanine [(–)-4k].

Isolated yield: 45%. Enantiomeric excess: 97%. $[\alpha]_D^{20}$ – 30.7 (*c* 1.0, $CHCl_3$).

The enantiomeric excesses of compounds (+)-**4k** and (–)-**4k** were respectively determined by SFC analyses on Chiralpak IC-U stationary phase using 20% methanol in carbon dioxide. Mobile phase was set up at 1 $mL.min^{-1}$, temperature at 25°C and pressure at 150 bar; t_R [(–)-**4k**, 1.1 min], t_R [(+)-**4k**, 2.0 min]. As this molecule does not have chromophores, mass spectrometry was used to identify enantiomers and to calculate enantiomeric excesses.

<u>Mass chromatogram (SIM) of compounds (-)-4k and (+)-4k:</u>



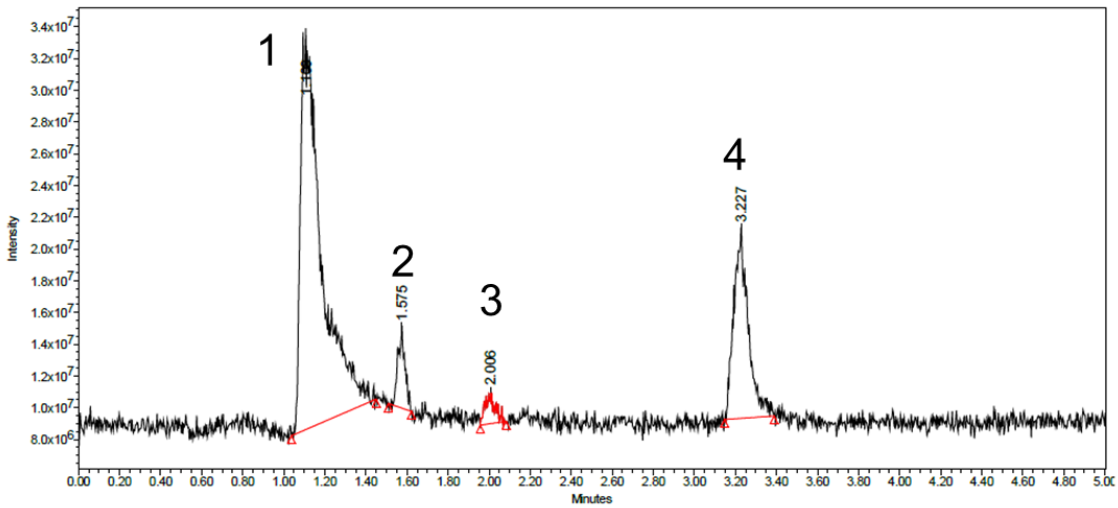


t_R (min)	1.1	2.0
% area	95.3	4.7
% area	4.5	95.5

t_R (min)	1.1	2.0
% area	98.8	1.2
% area	1.2	98.8

On these chromatograms, (–)-**4k** is in orange (t_R = 1.1 min) and (+)-**4k** is in blue (t_R = 2.0 min). The SIM signal at 226.2 m/z corresponds to the $[M\text{-}Boc+H]^+$ ion, the most intense positive ion. These results allowed to calculate enantiomeric purity *i.e.* enantiomeric excess. The chemical purity of compounds could be determined by looking at the amount of impurities in the sample. For this purpose, analyses were recorded in SCAN positive mode (from 100 to 800 m/z) to see the overall sample composition.

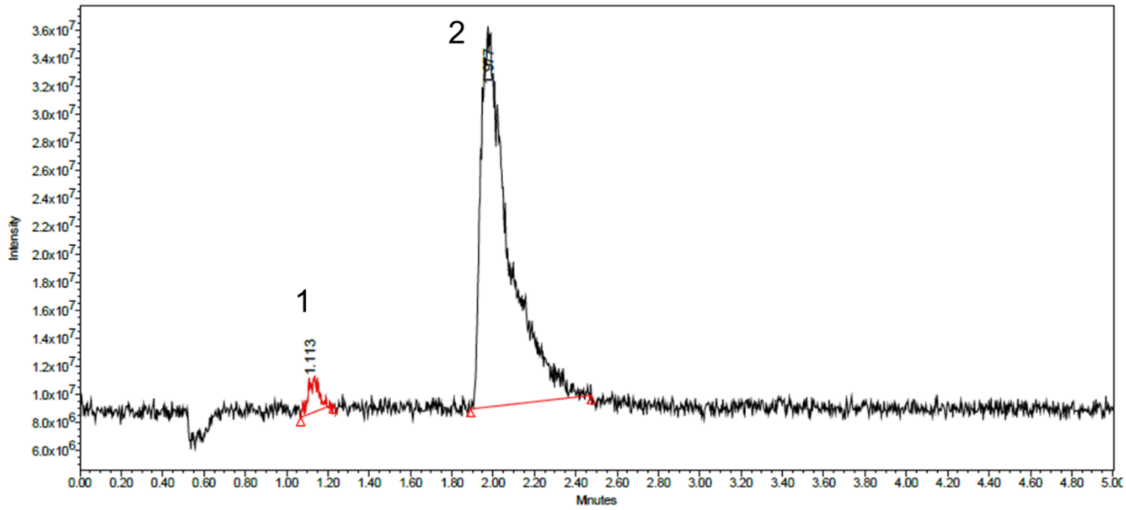
<u>Chemical purity of compounds (–)-4k: SCAN in positive mode</u>



Peak No.	1	2	3	4
t_R (min)	1.10	1.58	2.00	3.23
Compound	(-)-4k	Impurity 1	(+)-4k	Impurity 2

% area	69.6	4.8	2.5	23.1

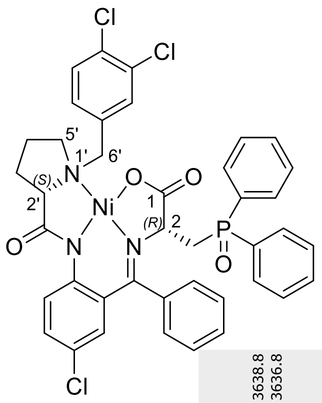
Chemical purity of compounds (+)-4k: SCAN in positive mode

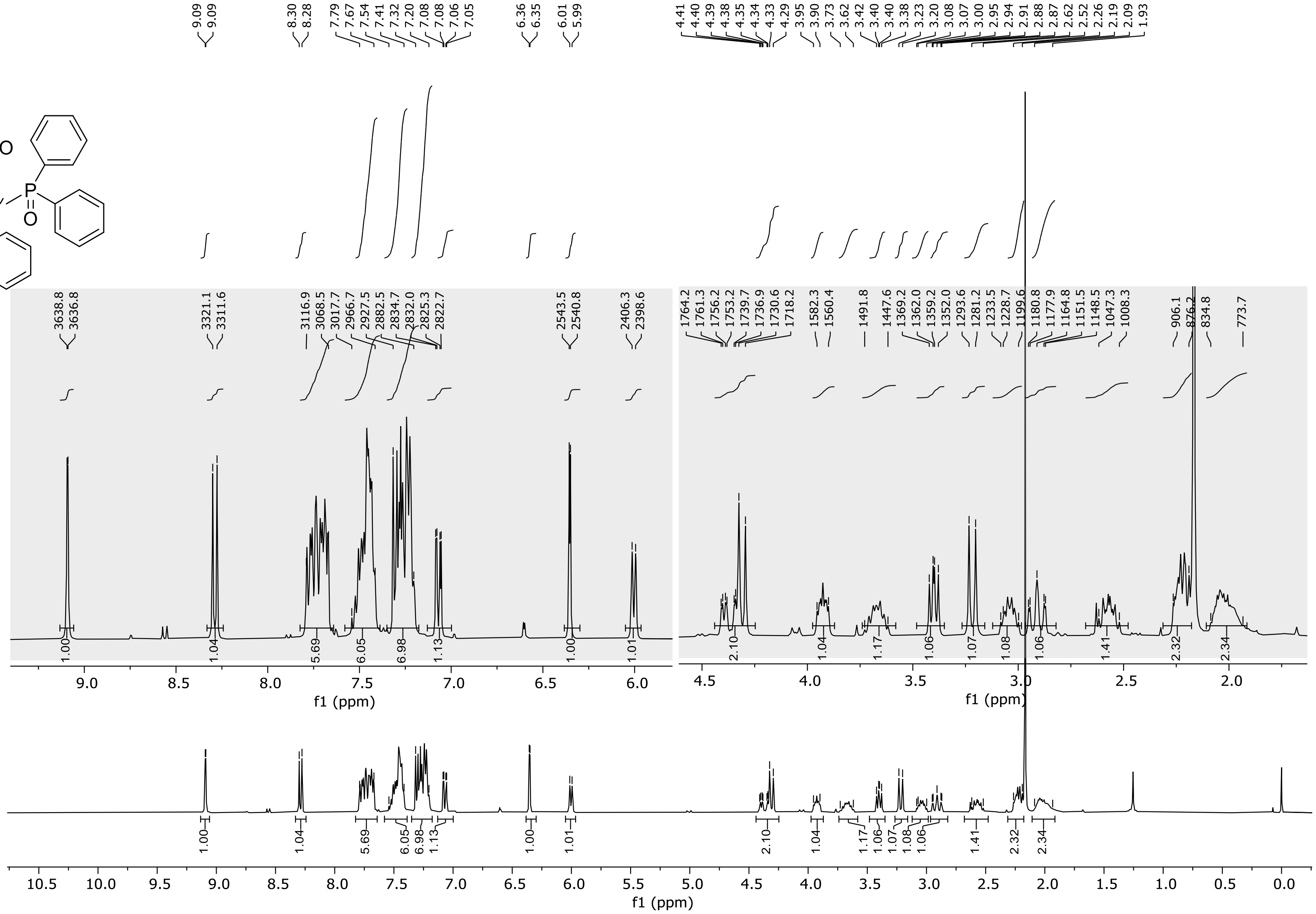


Peak No.	**1**	**2**
t_R (min)	1.10	2.00
Compound	(-)-4k	(+)-4k
% area	3.6	96.4

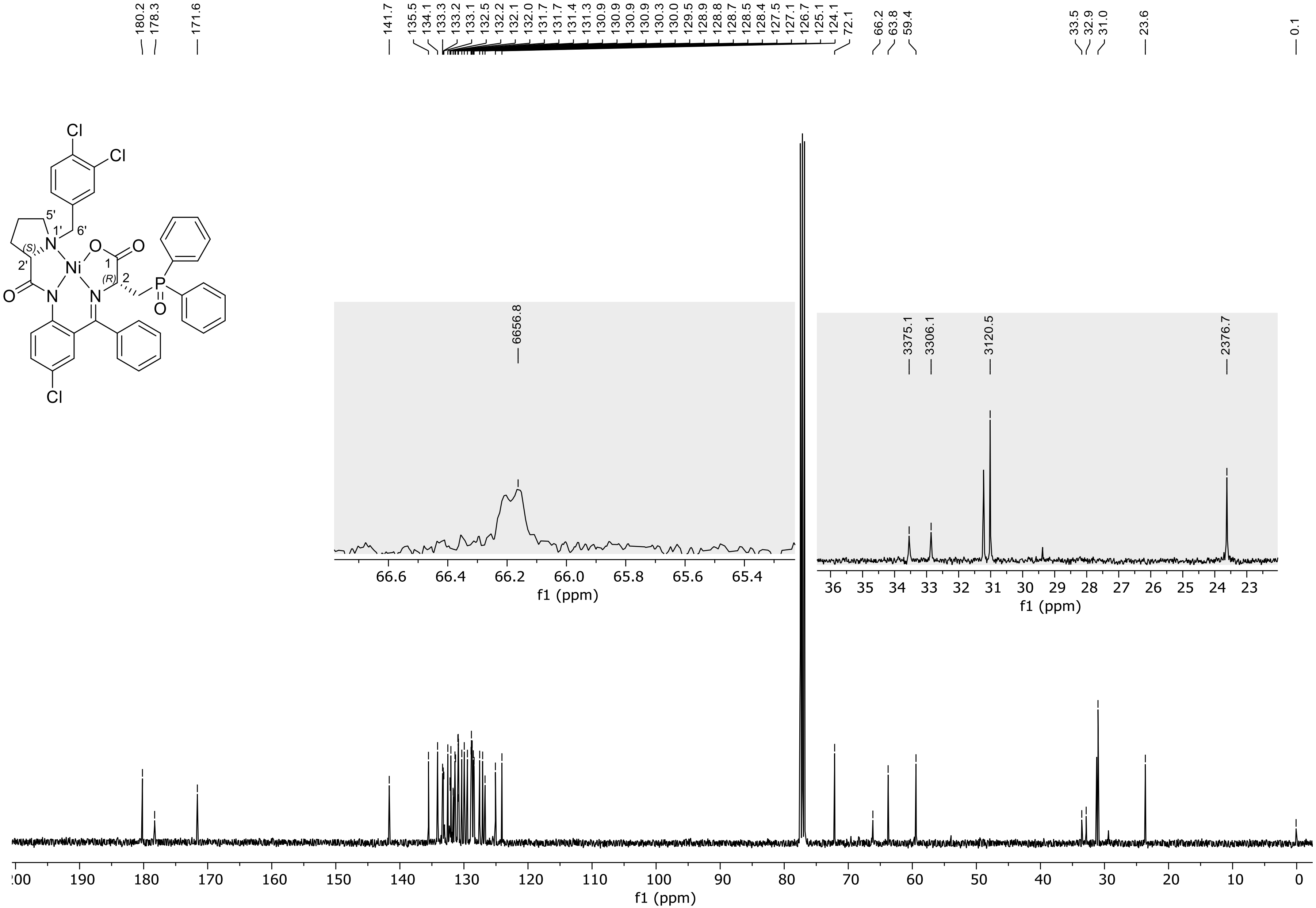
5. Copies of ^{1}H and ^{13}C NMR Spectra of New Compounds.

^{1}H NMR (400 MHz, $CDCl_3$/TMS) Analysis of Compound (*S*,*R*)-3a.



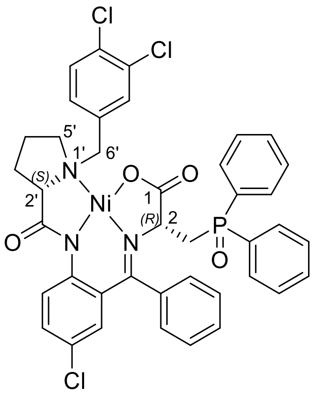


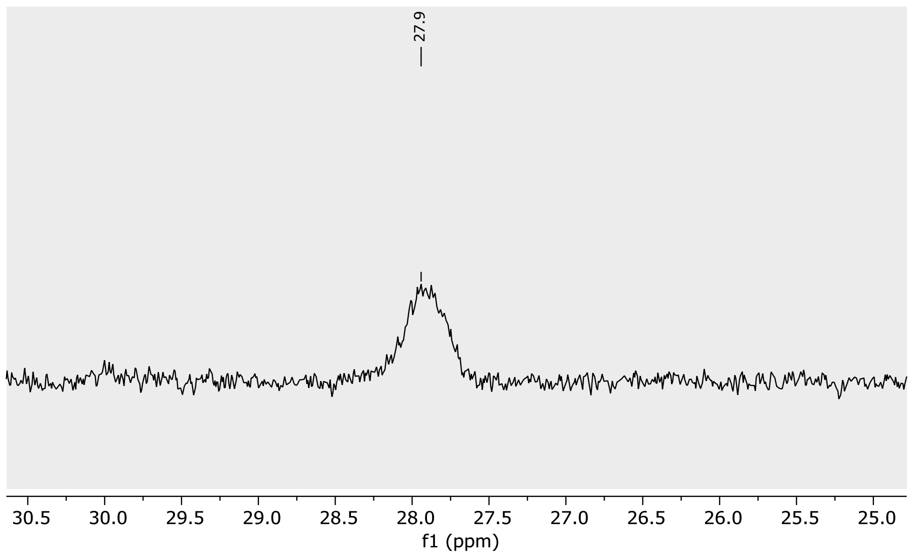
^{13}C NMR (101 MHz, $CDCl_3$) Analysis of Compound (*S*,*R*)-3a.

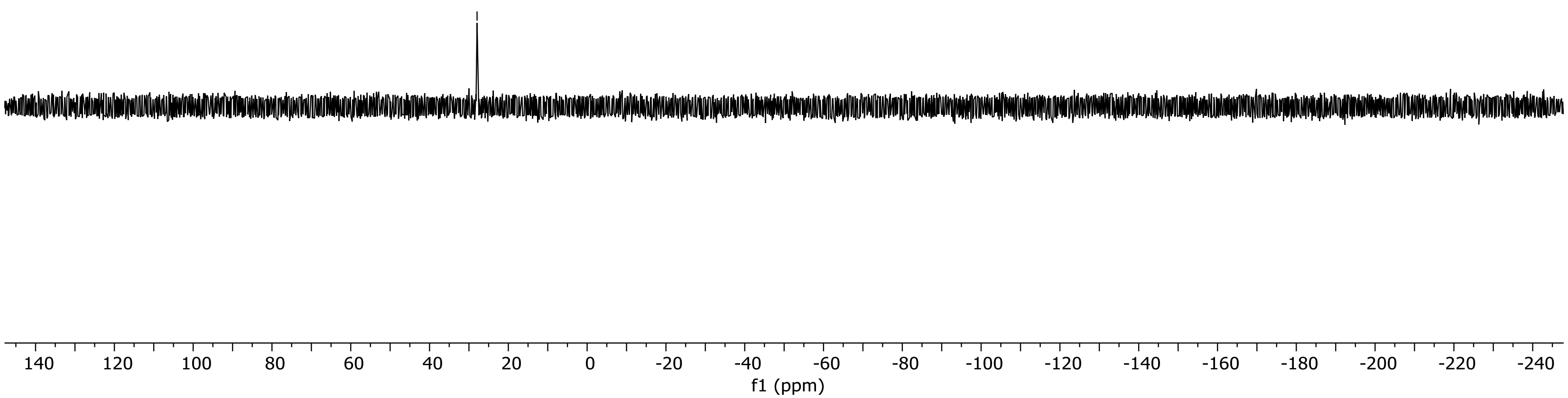


^{13}P NMR (162 MHz, $CDCl_3$) Analysis of Compound (*S*,*R*)-3a.

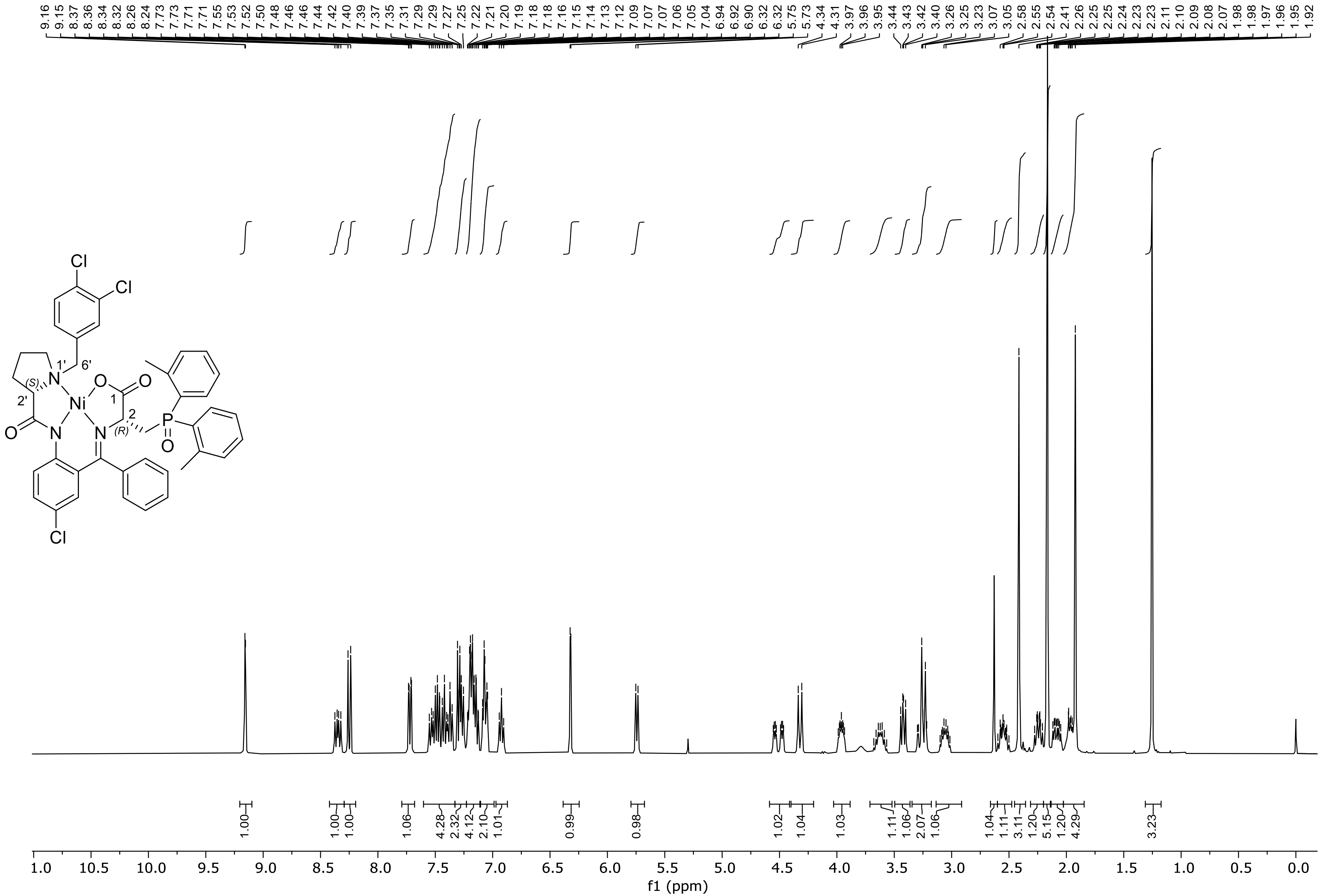
27.9



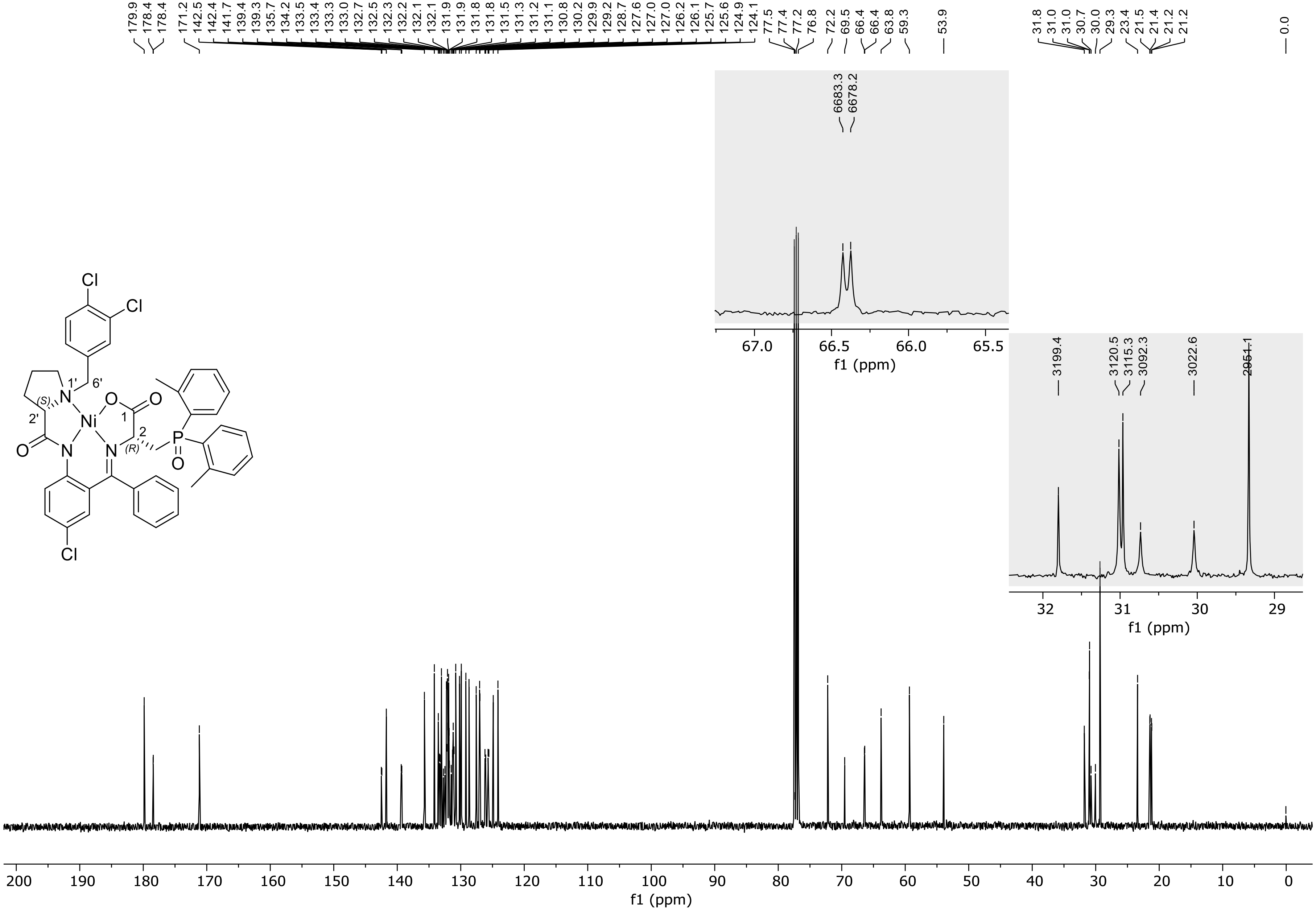




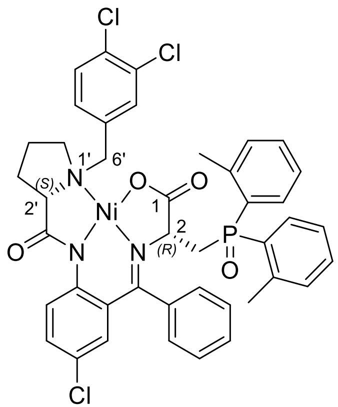
^{1}H NMR (400 MHz, CDCl$_3$/TMS) Analysis of Compound (*S*,*R*)-3b.

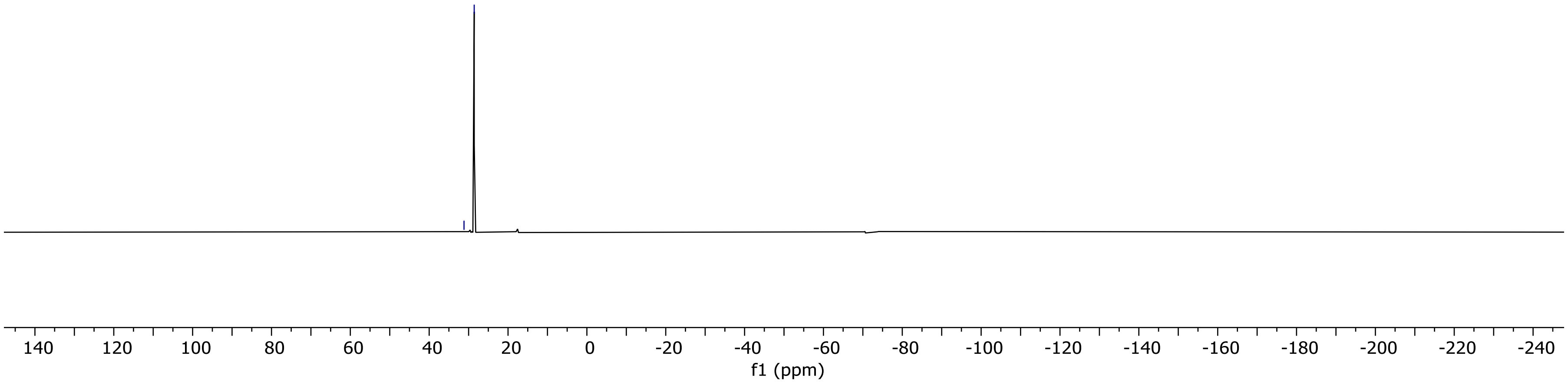


^{13}C NMR (101 MHz, $CDCl_3$) Analysis of Compound (*S*,*R*)-3b.

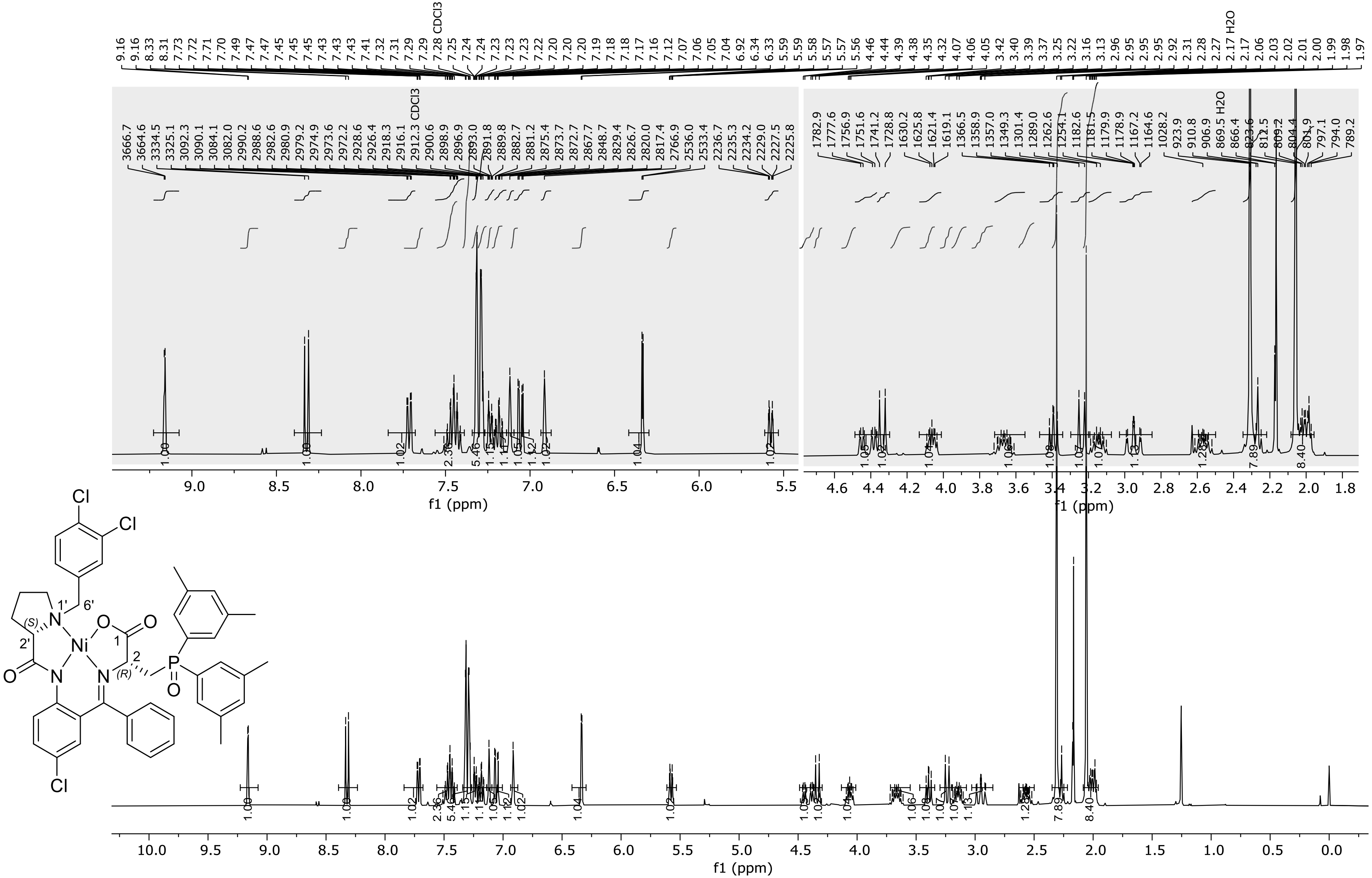


^{13}P NMR (162 MHz, $CDCl_3$) Analysis of Compound (*S*,*R*)-3b.

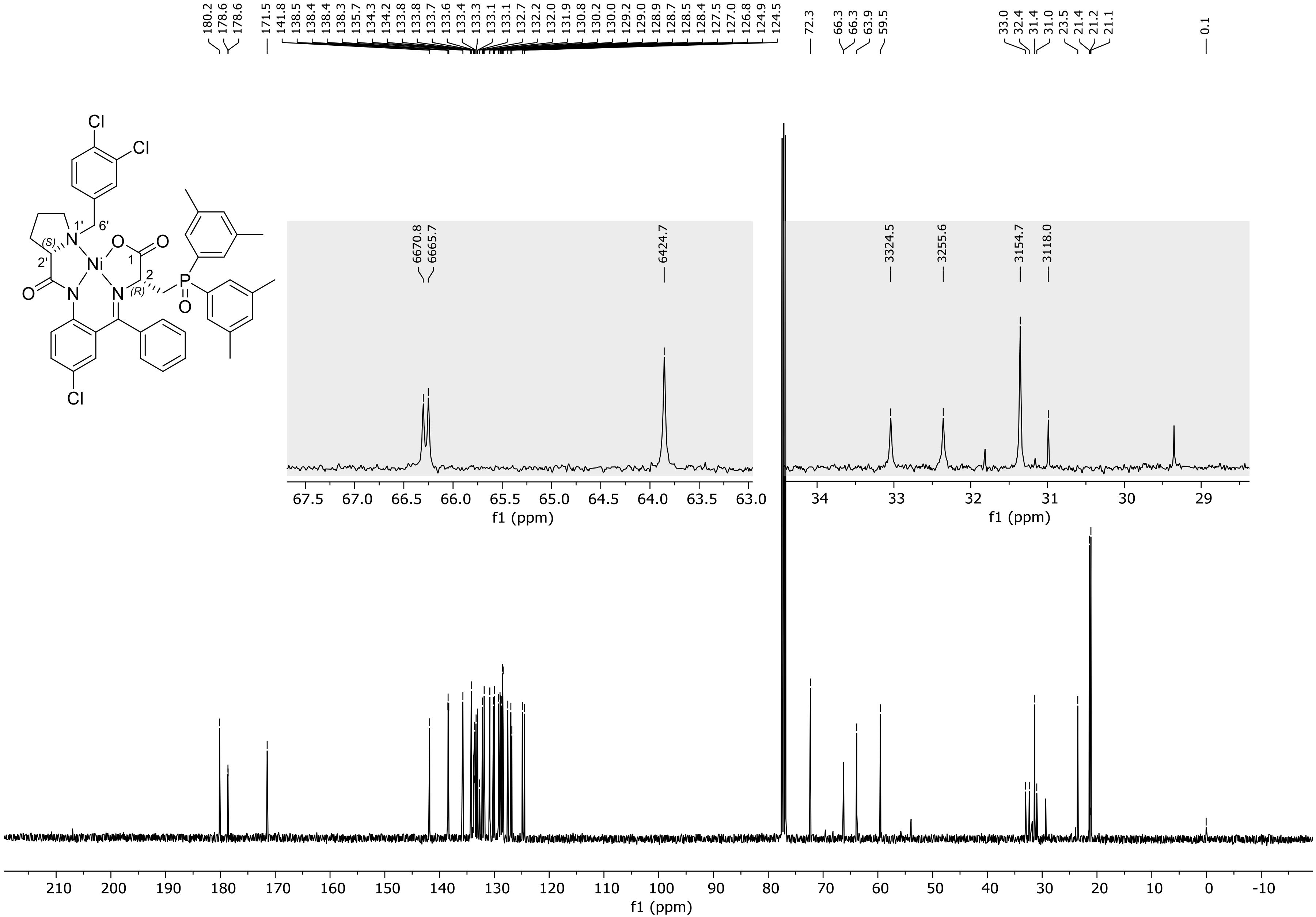




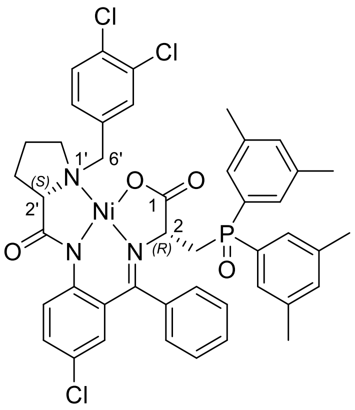
^{1}H NMR (400 MHz, $CDCl_3$/TMS) Analysis of Compound (*S*,*R*)-3c.

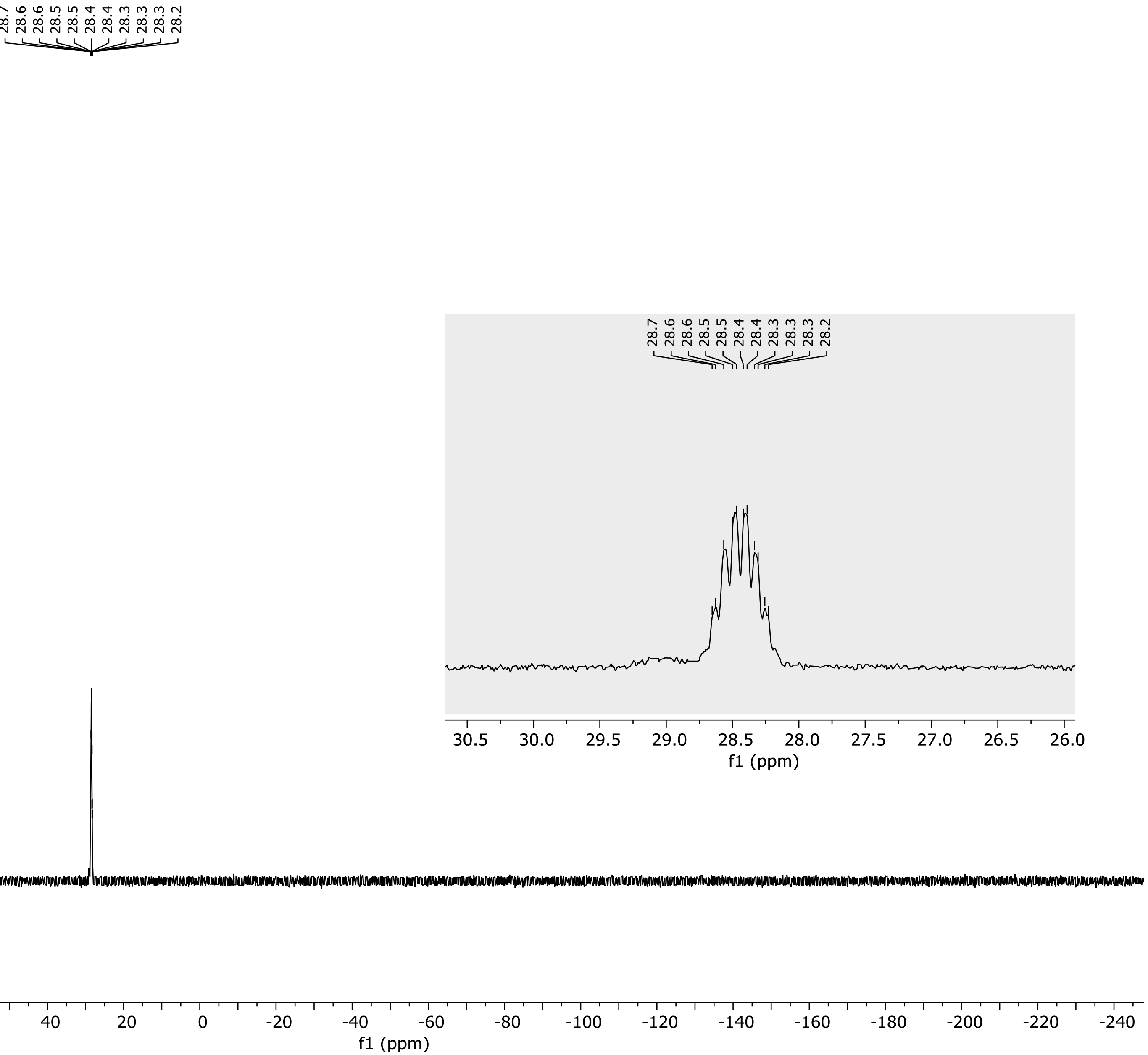


^{13}C NMR (101 MHz, CDCl$_3$) Analysis of Compound (*S*,*R*)-3c.

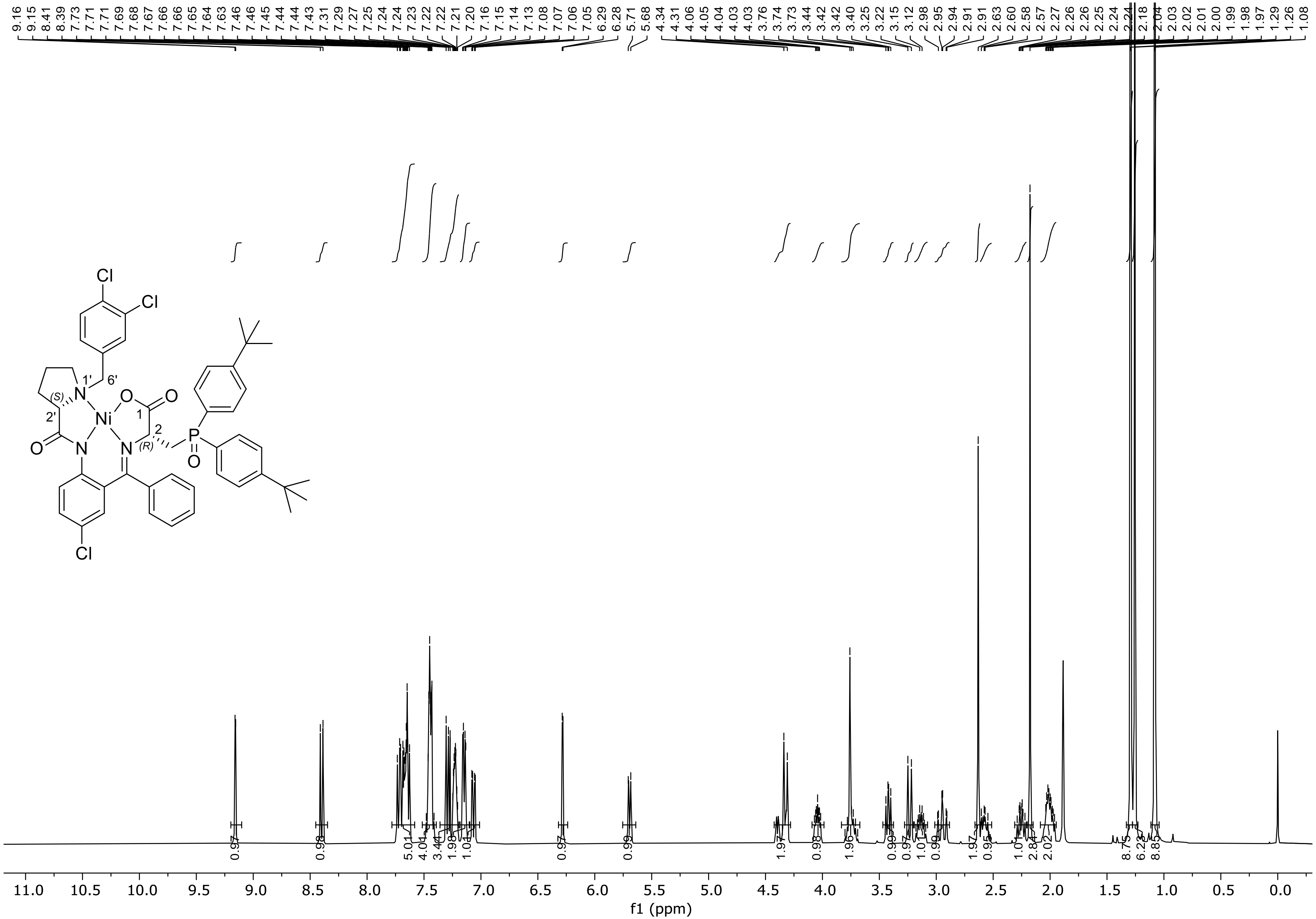


^{13}P NMR (162 MHz, $CDCl_3$) Analysis of Compound (*S*,*R*)-3c.

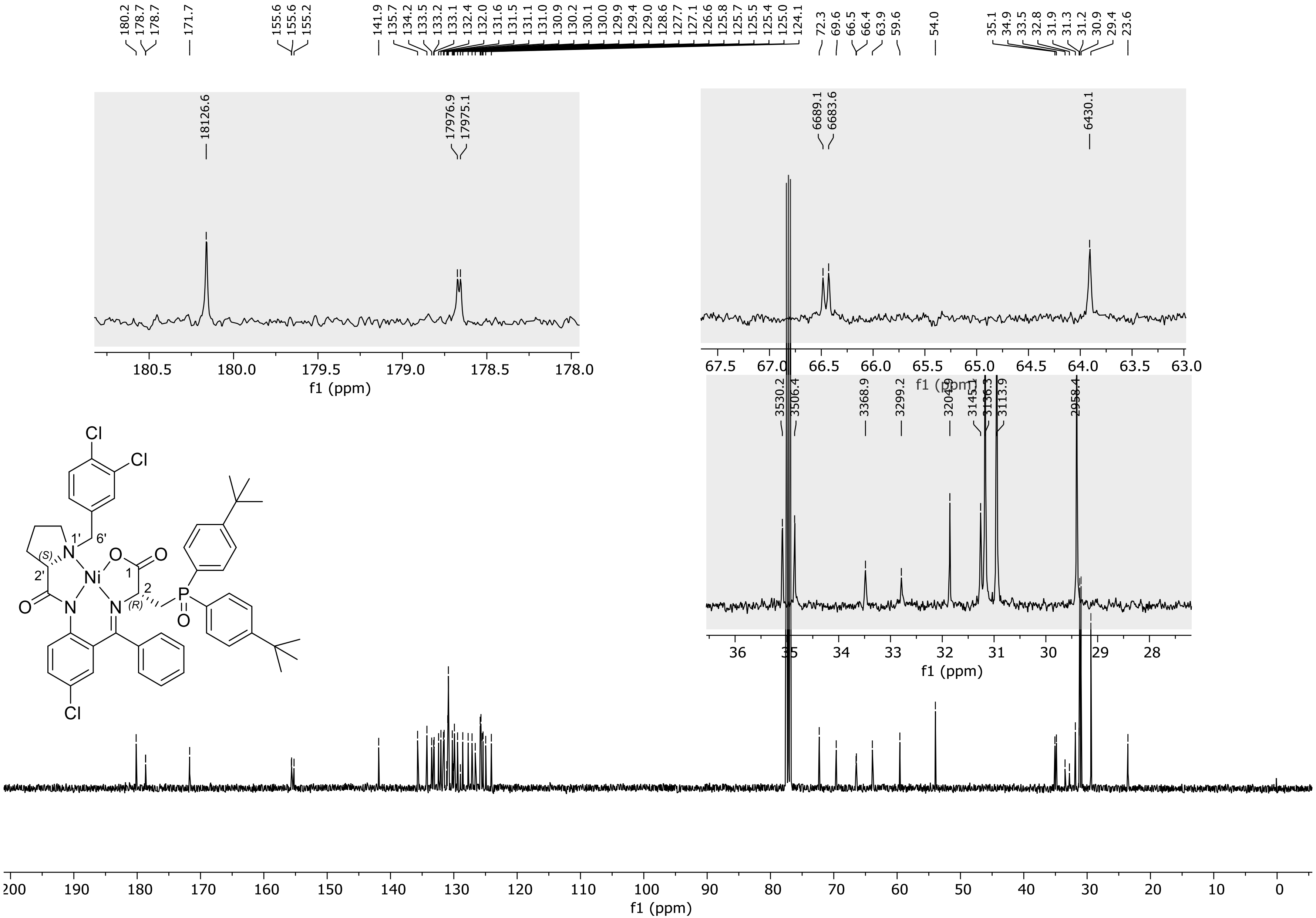




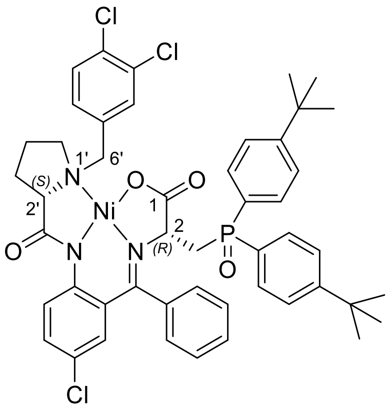
^{1}H NMR (400 MHz, $CDCl_3$/TMS) Analysis of Compound (*S*,*R*)-3d.

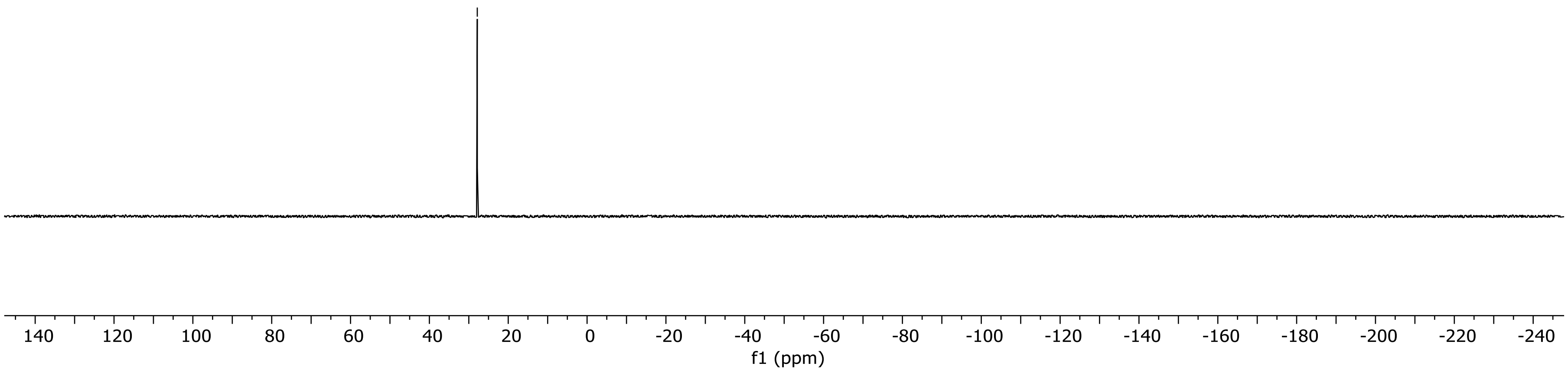


^{13}C NMR (101 MHz, $CDCl_3$) Analysis of Compound (*S*,*R*)-3d.

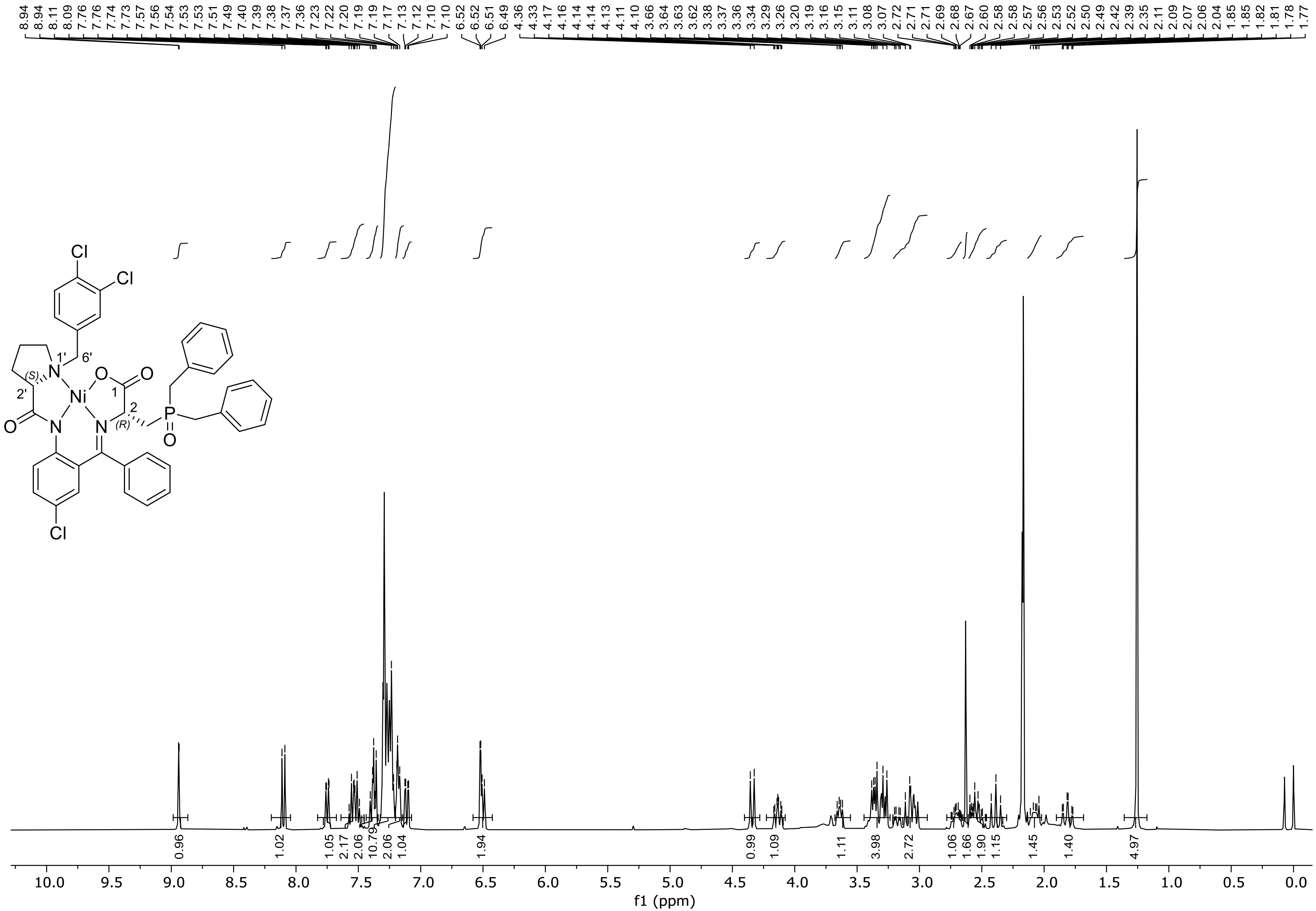


13P NMR (162 MHz, $CDCl_3$) Analysis of Compound (*S*,*R*)-3d.

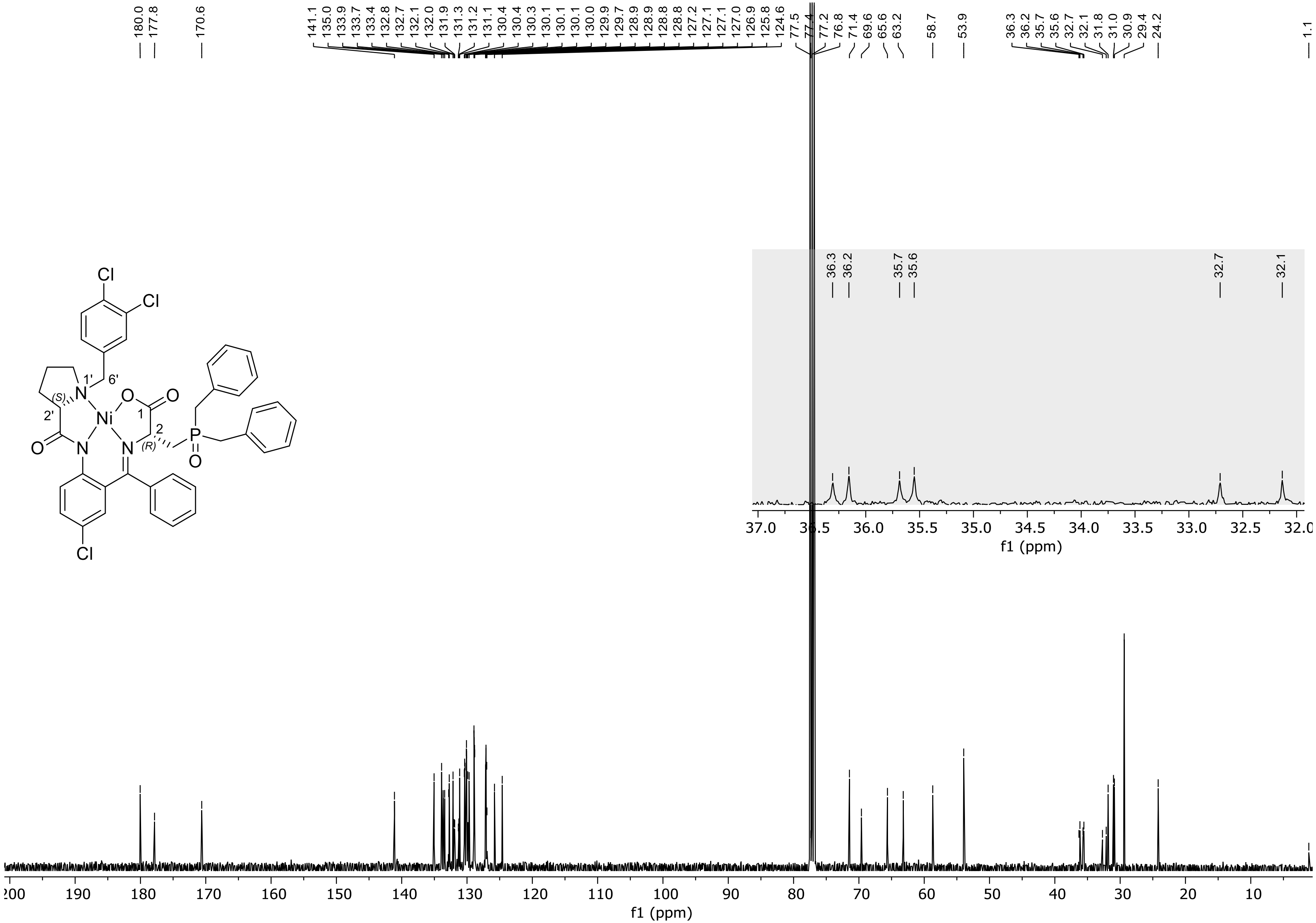




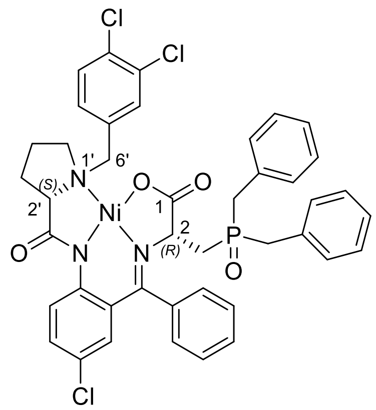
[1]H NMR (400 MHz, $CDCl_3$/TMS) Analysis of Compound (*S*,*R*)-3e.

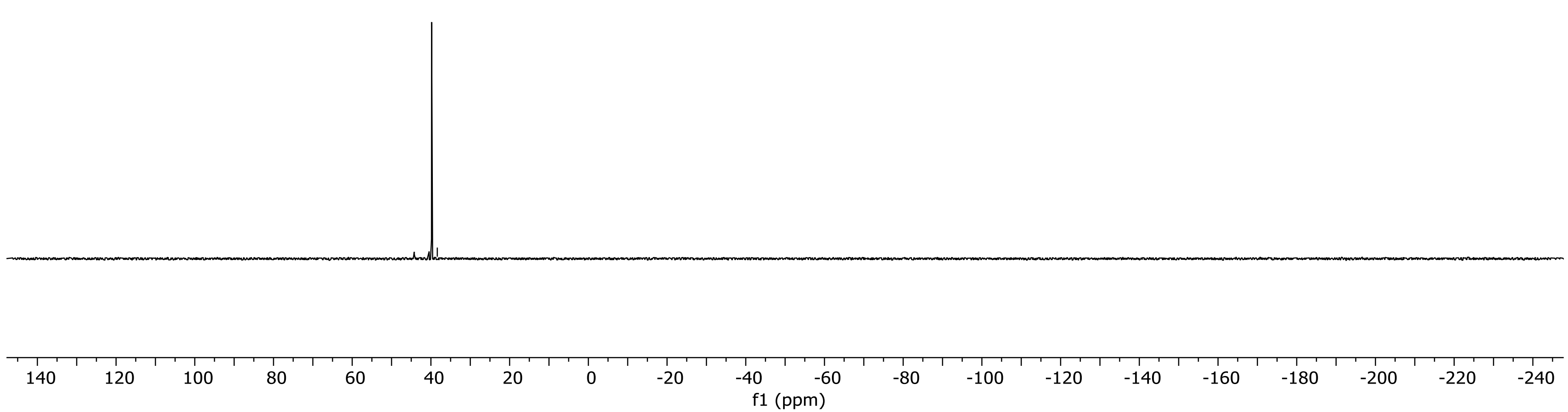


^{13}C NMR (101 MHz, CDCl$_3$) Analysis of Compound (*S*,*R*)-3e.

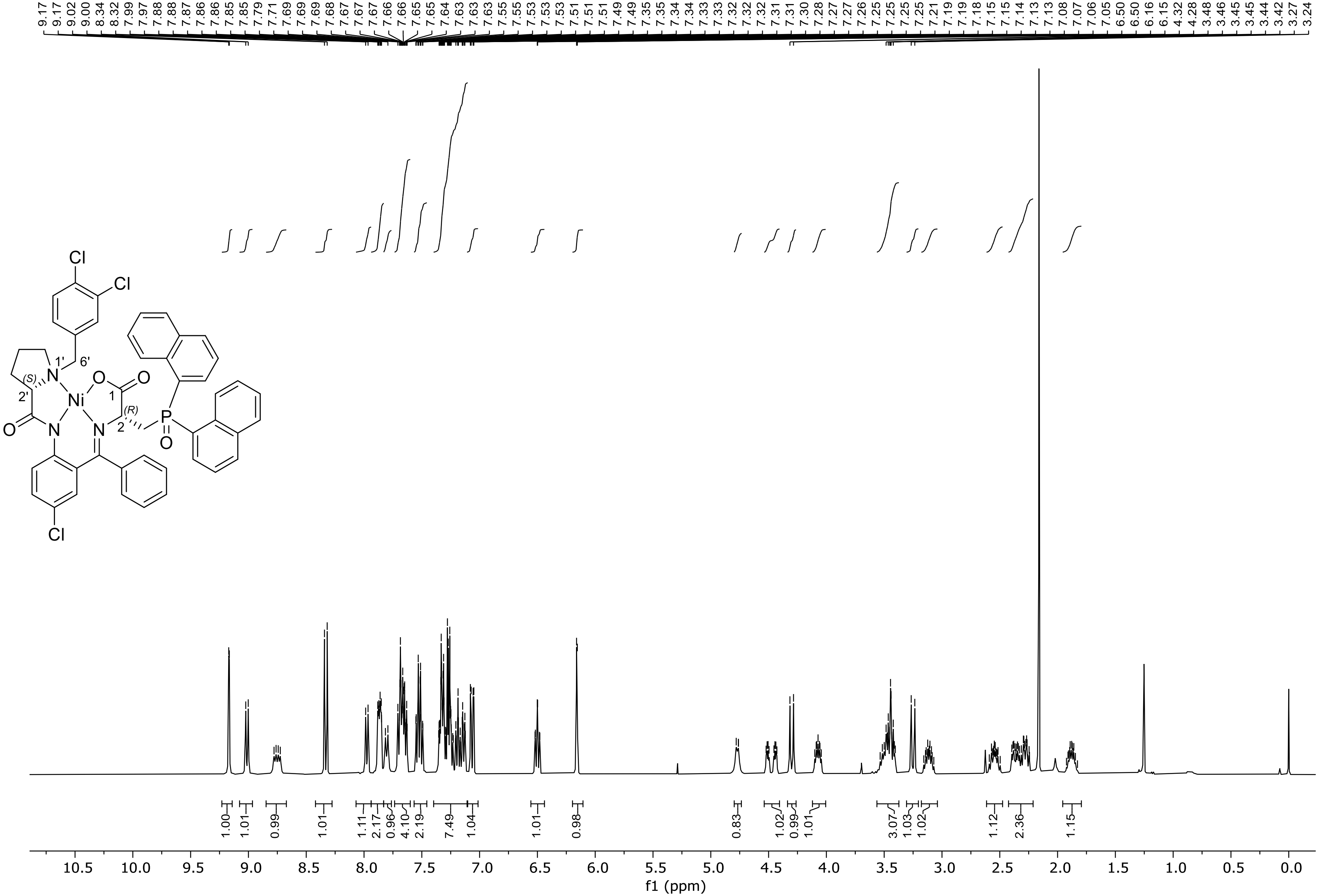


^{13}P NMR (162 MHz, CDCl$_3$) Analysis of Compound (*S*,*R*)-3e.

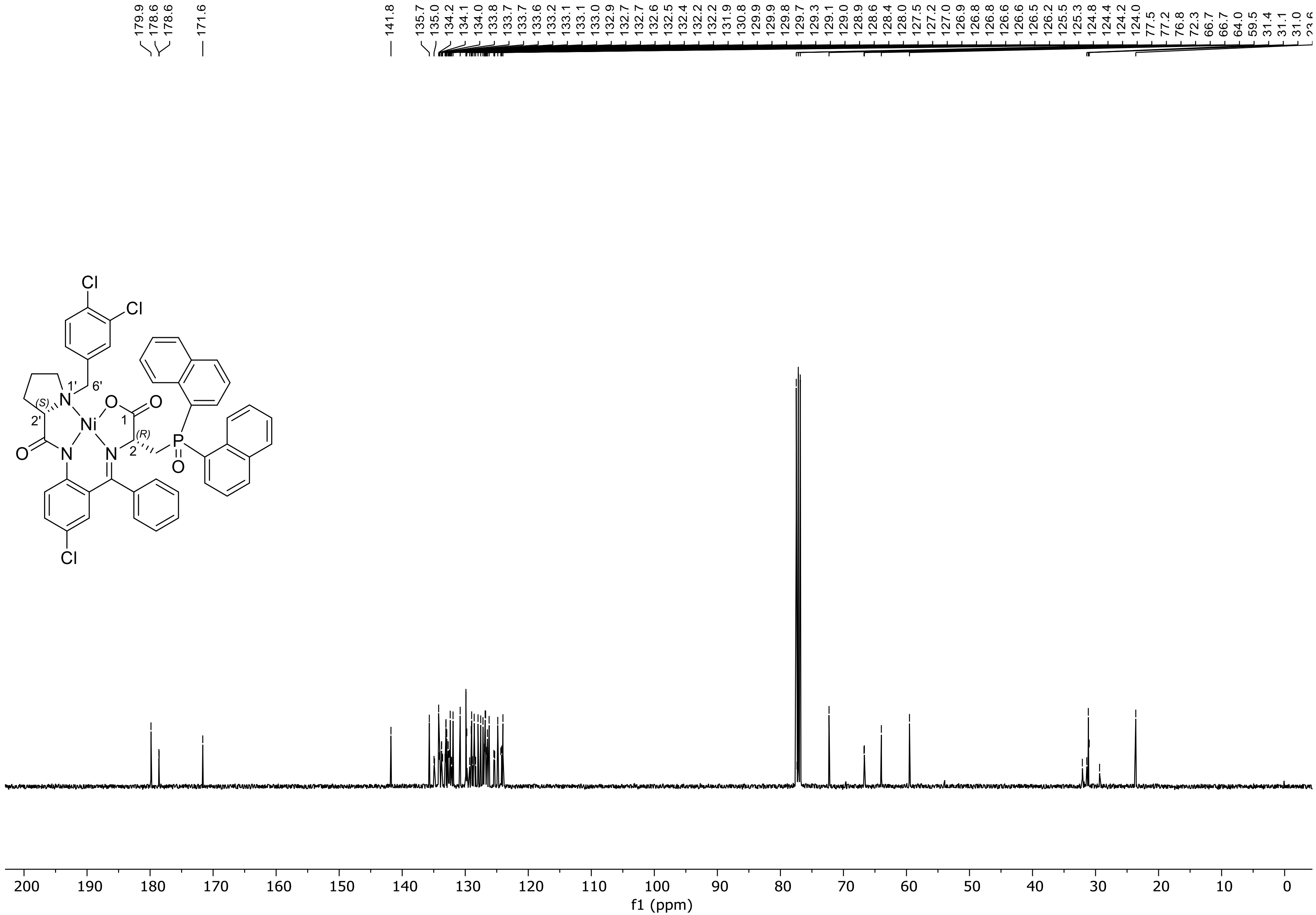




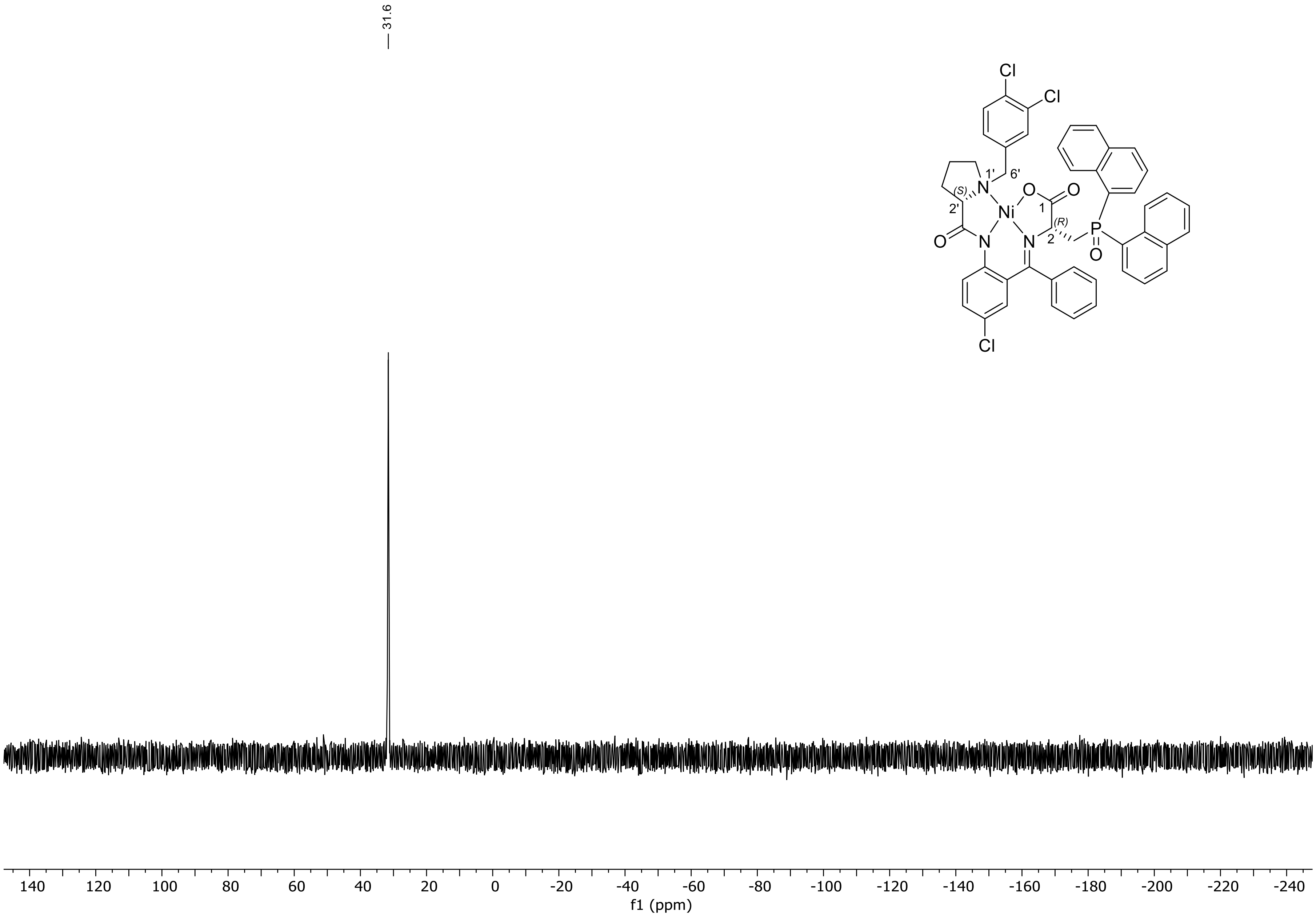
^{1}H NMR (400 MHz, $CDCl_3$/TMS) Analysis of Compound (*S*,*R*)-3f.



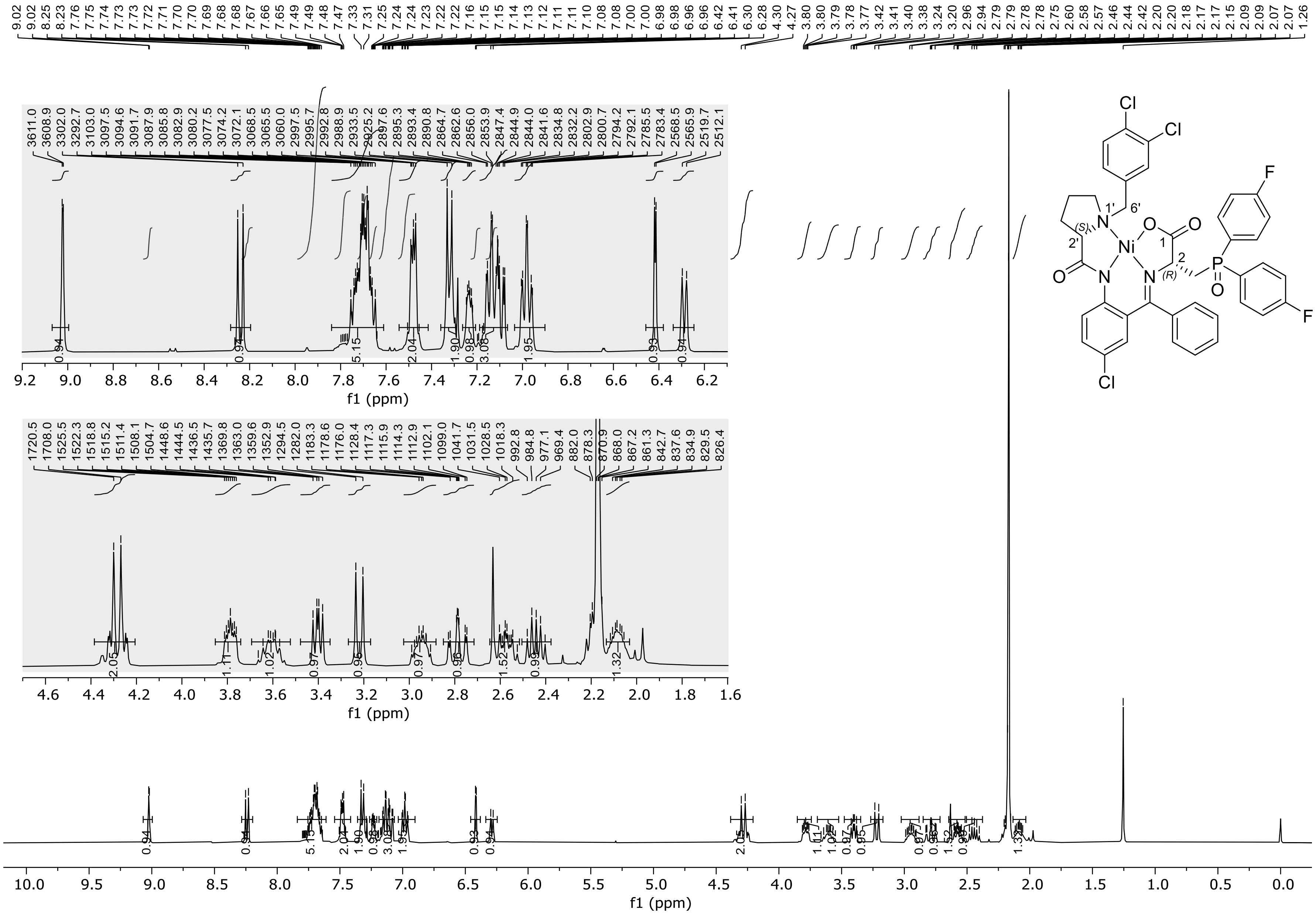
^{13}C NMR (101 MHz, CDCl$_3$) Analysis of Compound (*S*,*R*)-3f.



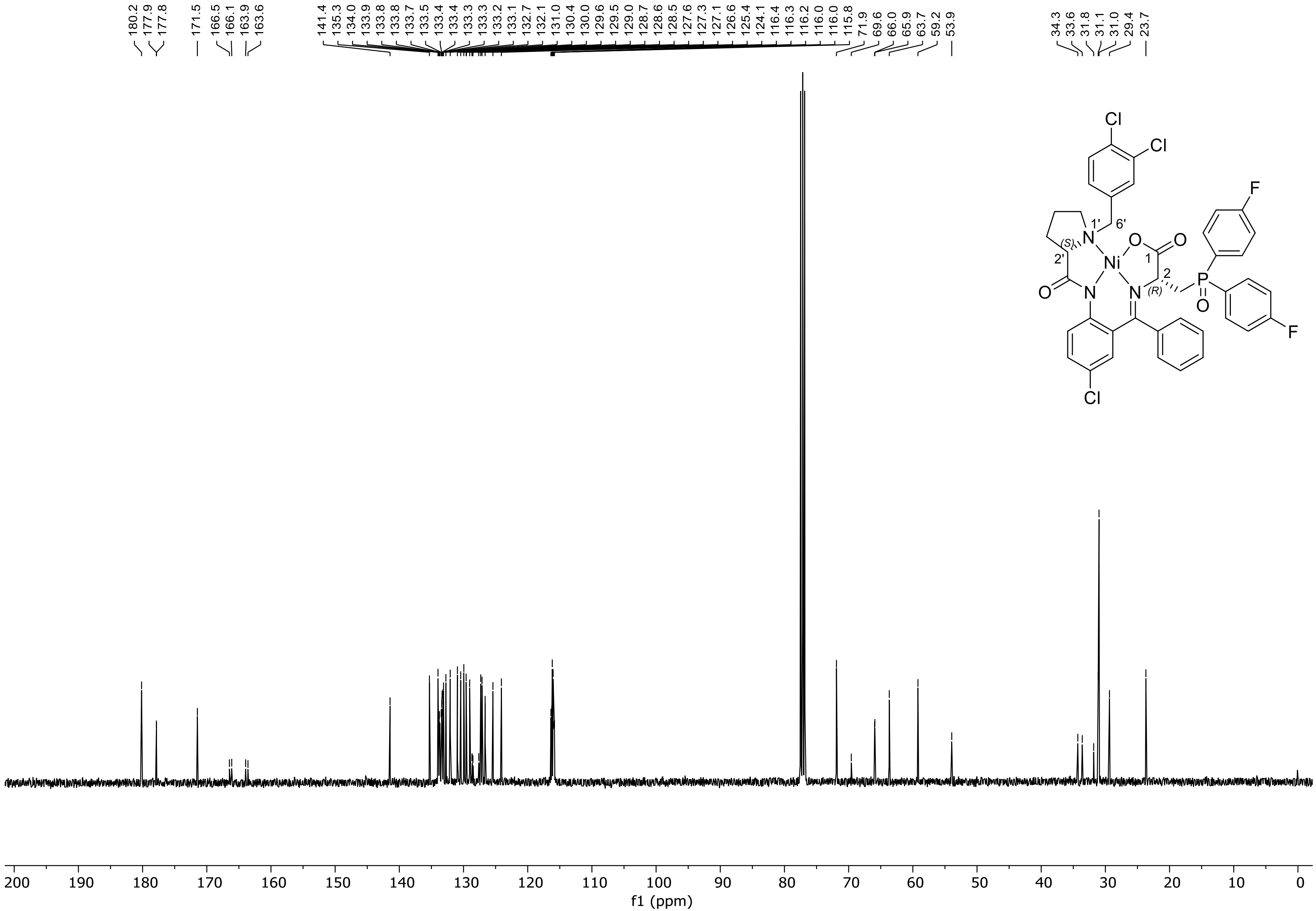
^{13}P NMR (162 MHz, $CDCl_3$) Analysis of Compound (*S*,*R*)-3f.



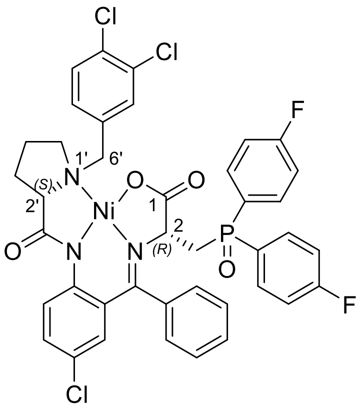
^{1}H NMR (400 MHz, $CDCl_3$/TMS) Analysis of Compound (*S*,*R*)-3g.

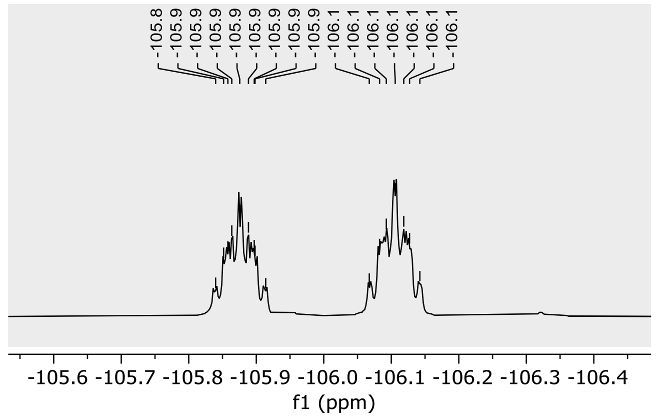


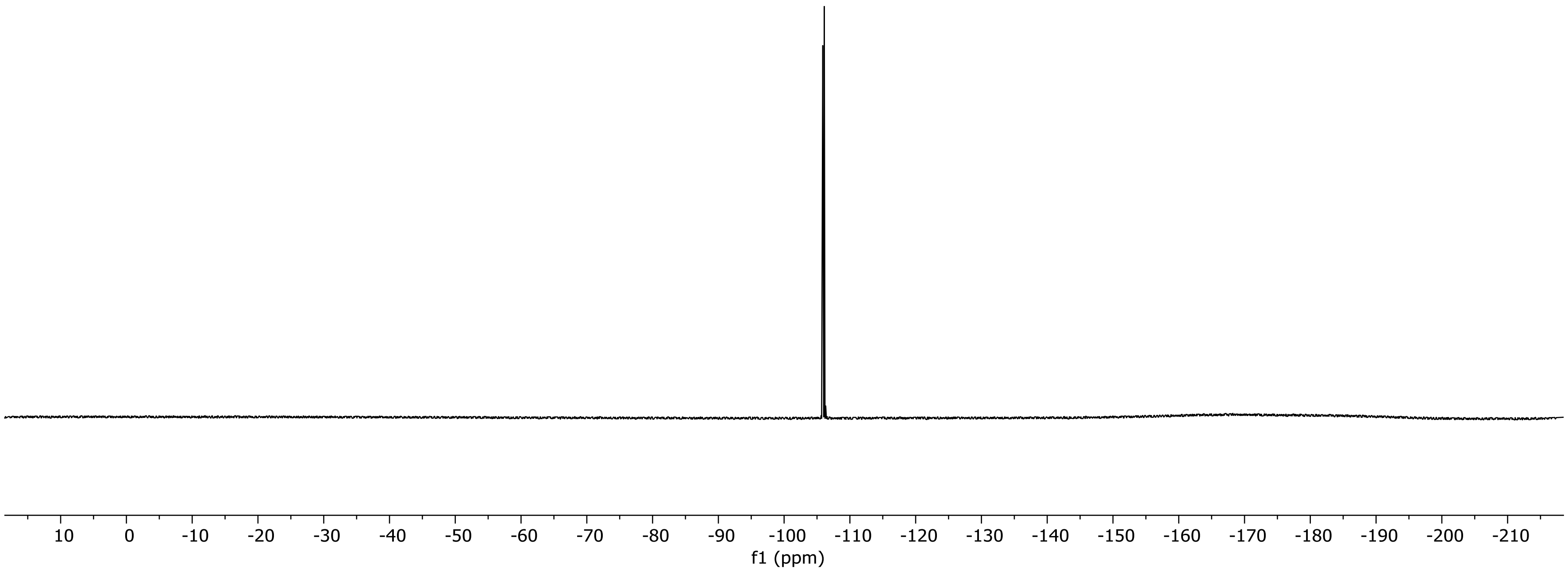
^{13}C NMR (101 MHz, CDCl$_3$) Analysis of Compound (*S*,*R*)-3g.



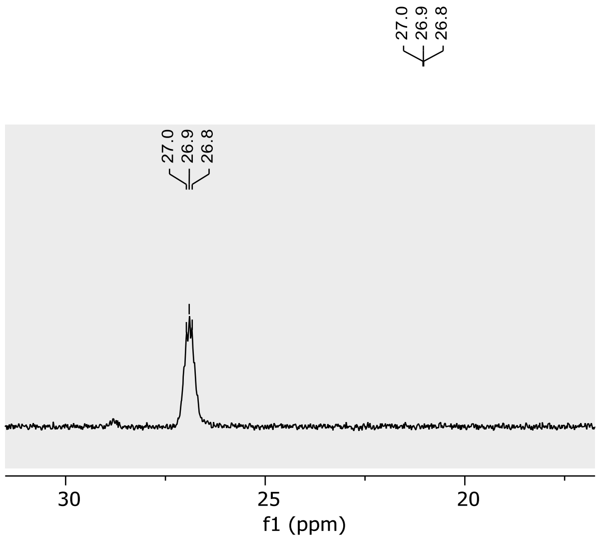
^{19}F NMR (376 MHz, $CDCl_3$) Analysis of Compound (*S*,*R*)-3g.

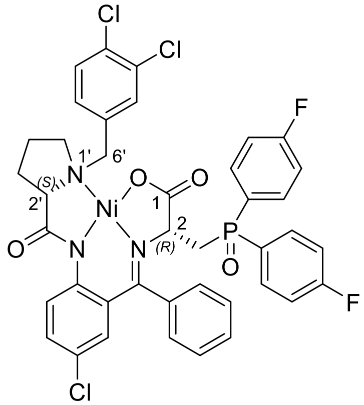


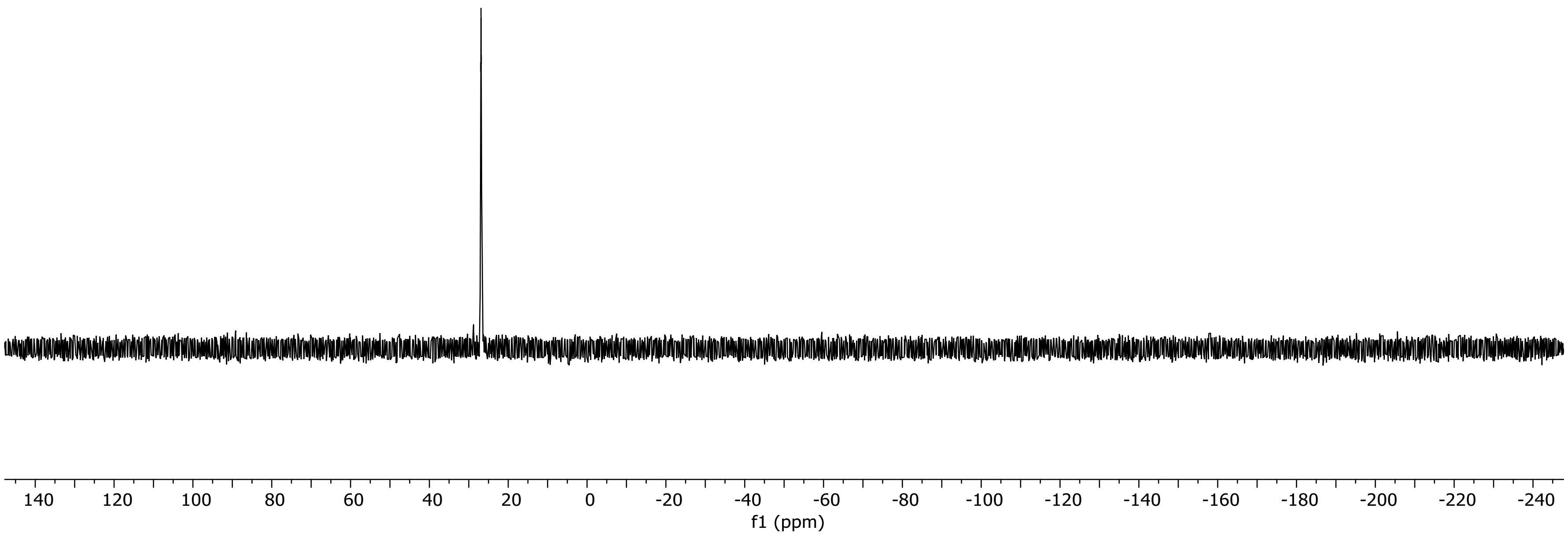




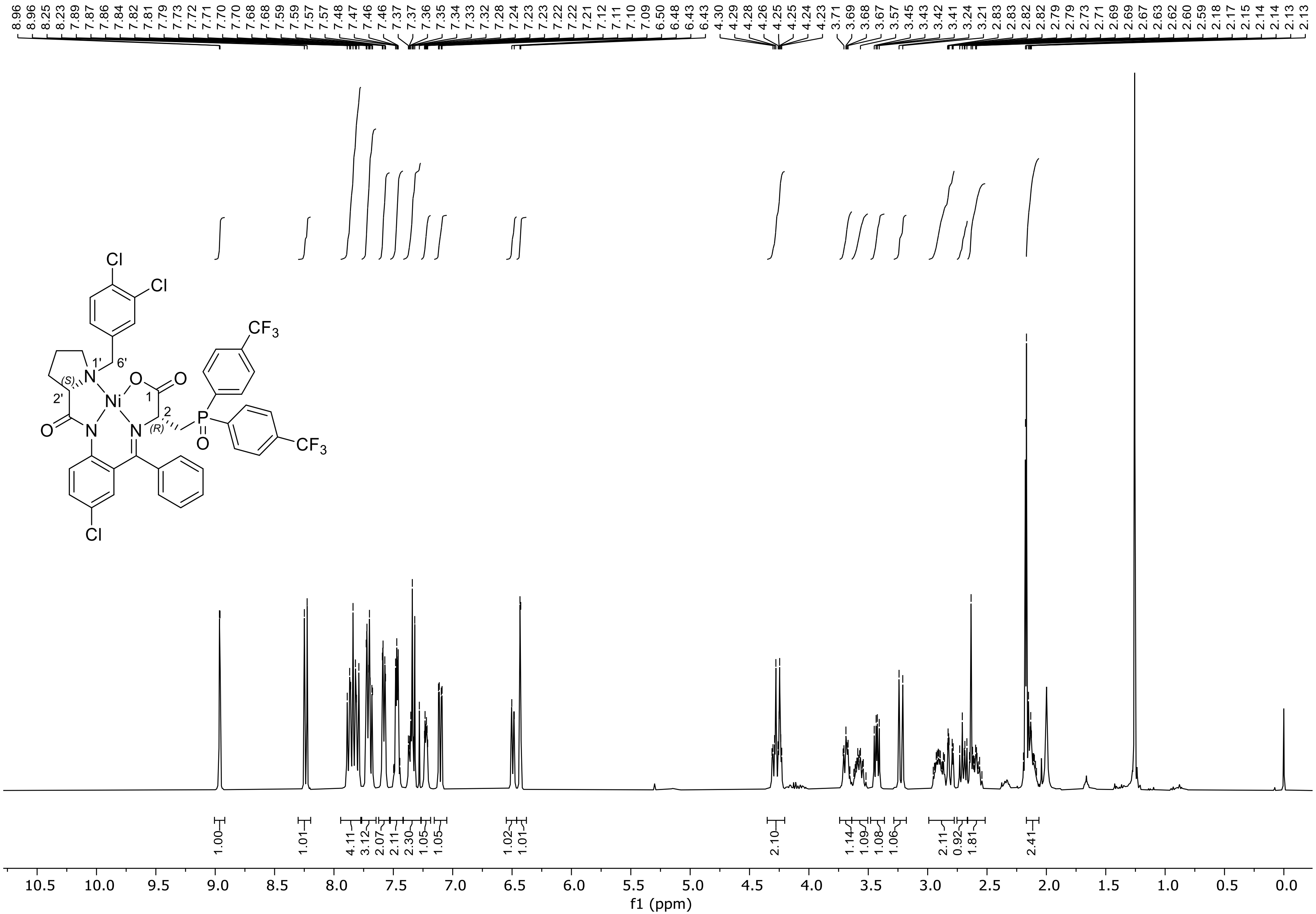
^{13}P NMR (162 MHz, $CDCl_3$) Analysis of Compound (*S*,*R*)-3g.



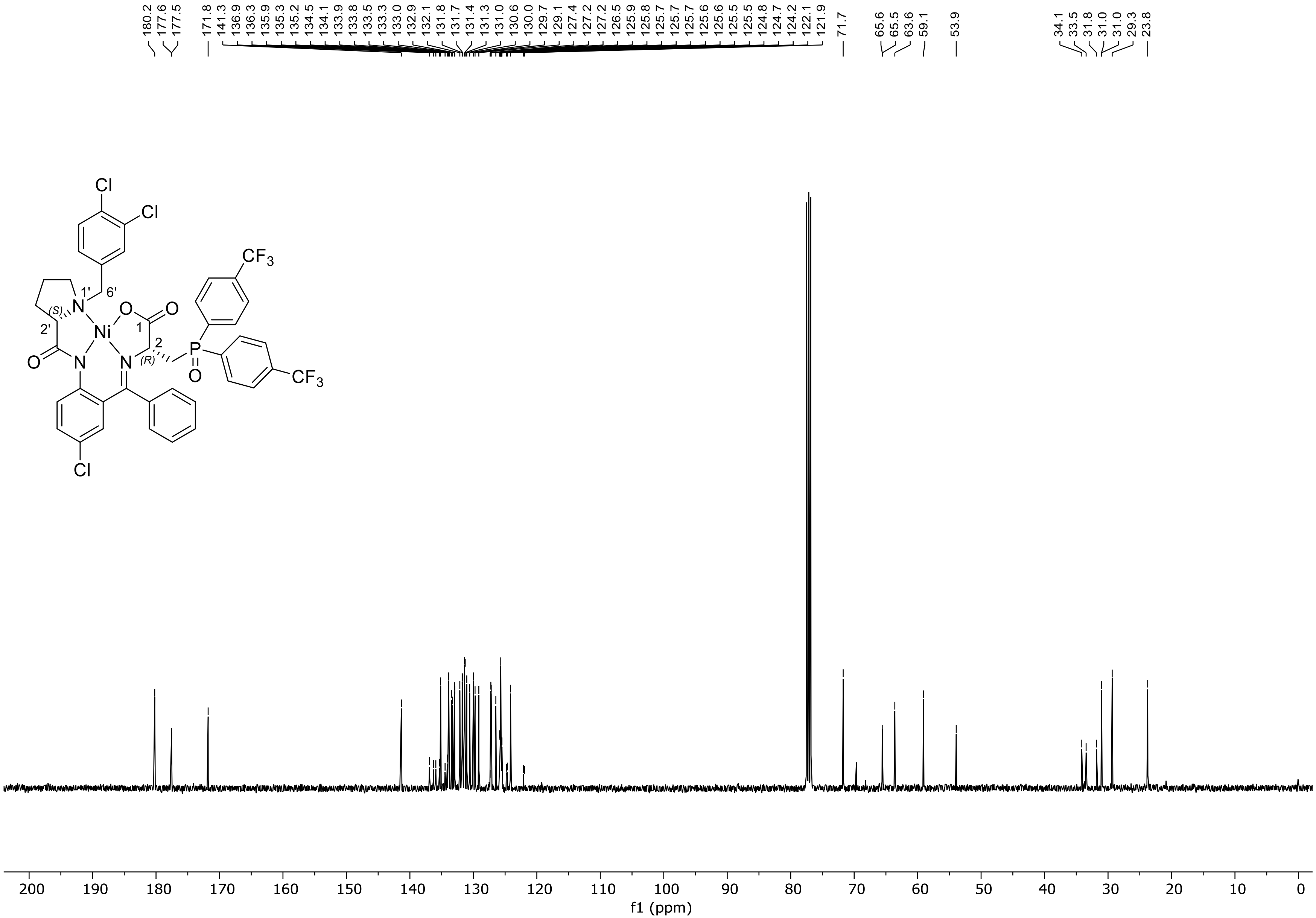




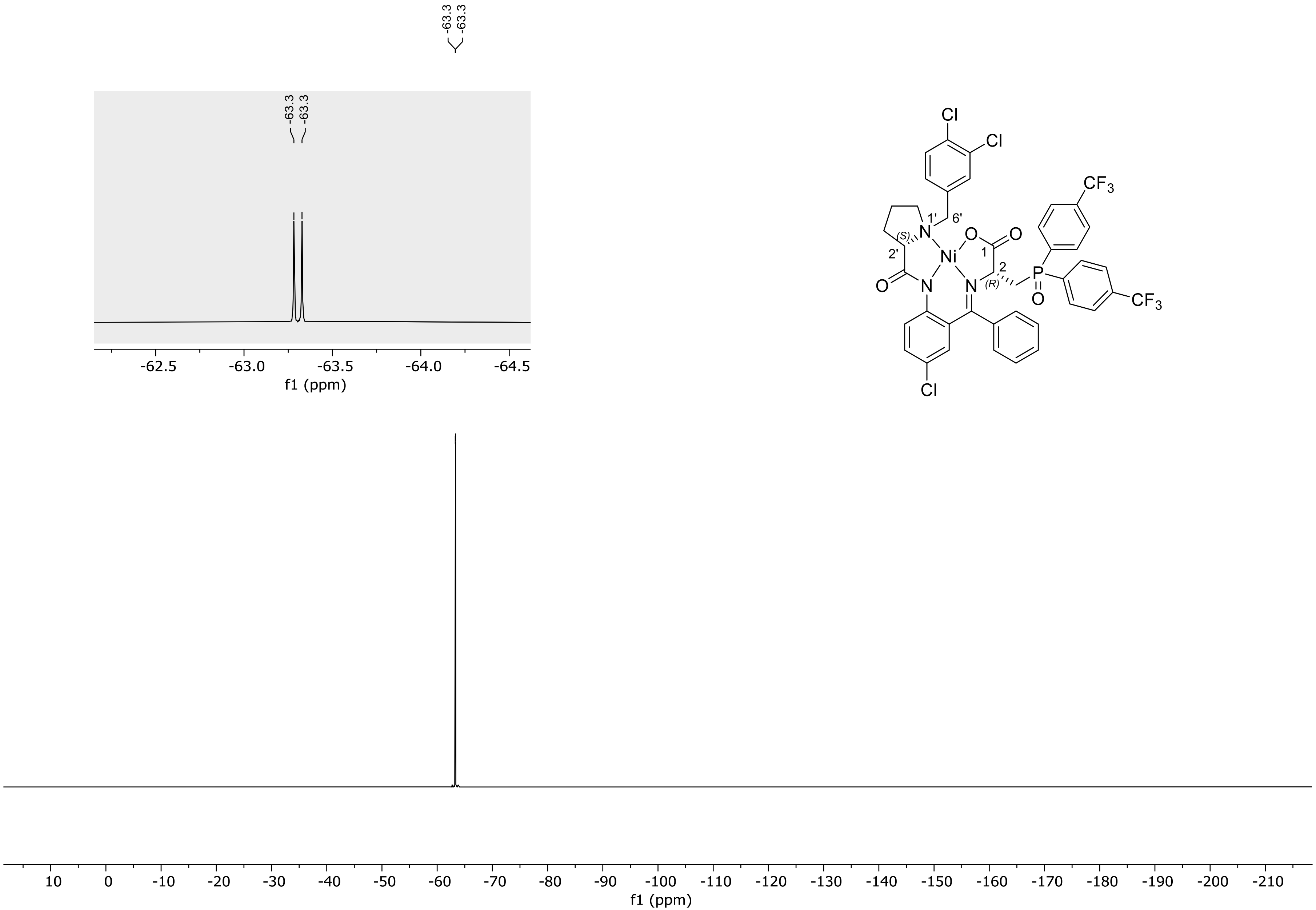
^{1}H NMR (400 MHz, $CDCl_3$/TMS) Analysis of Compound (*S*,*R*)-3h.



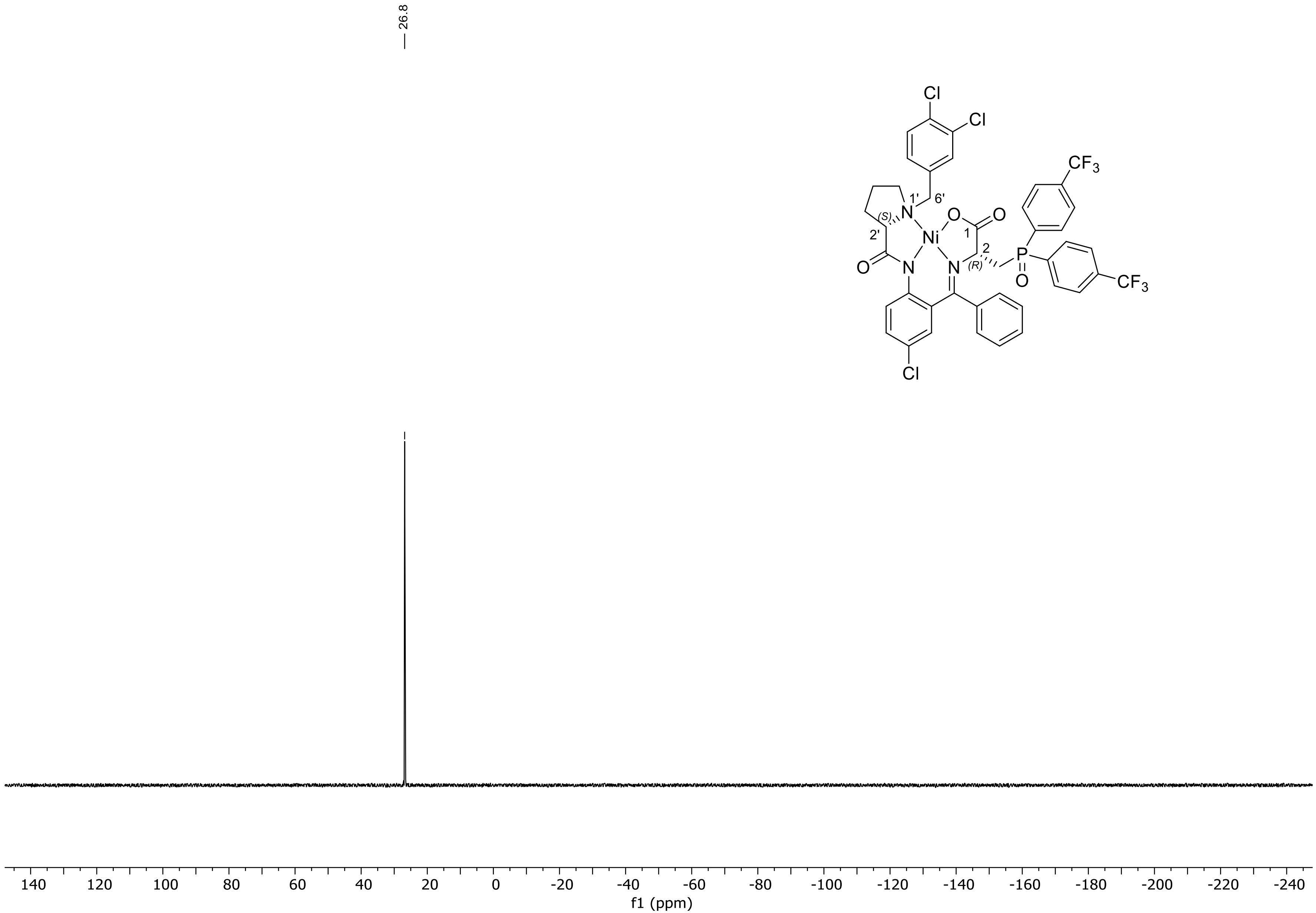
^{13}C NMR (101 MHz, $CDCl_3$) Analysis of Compound (*S*,*R*)-3h.



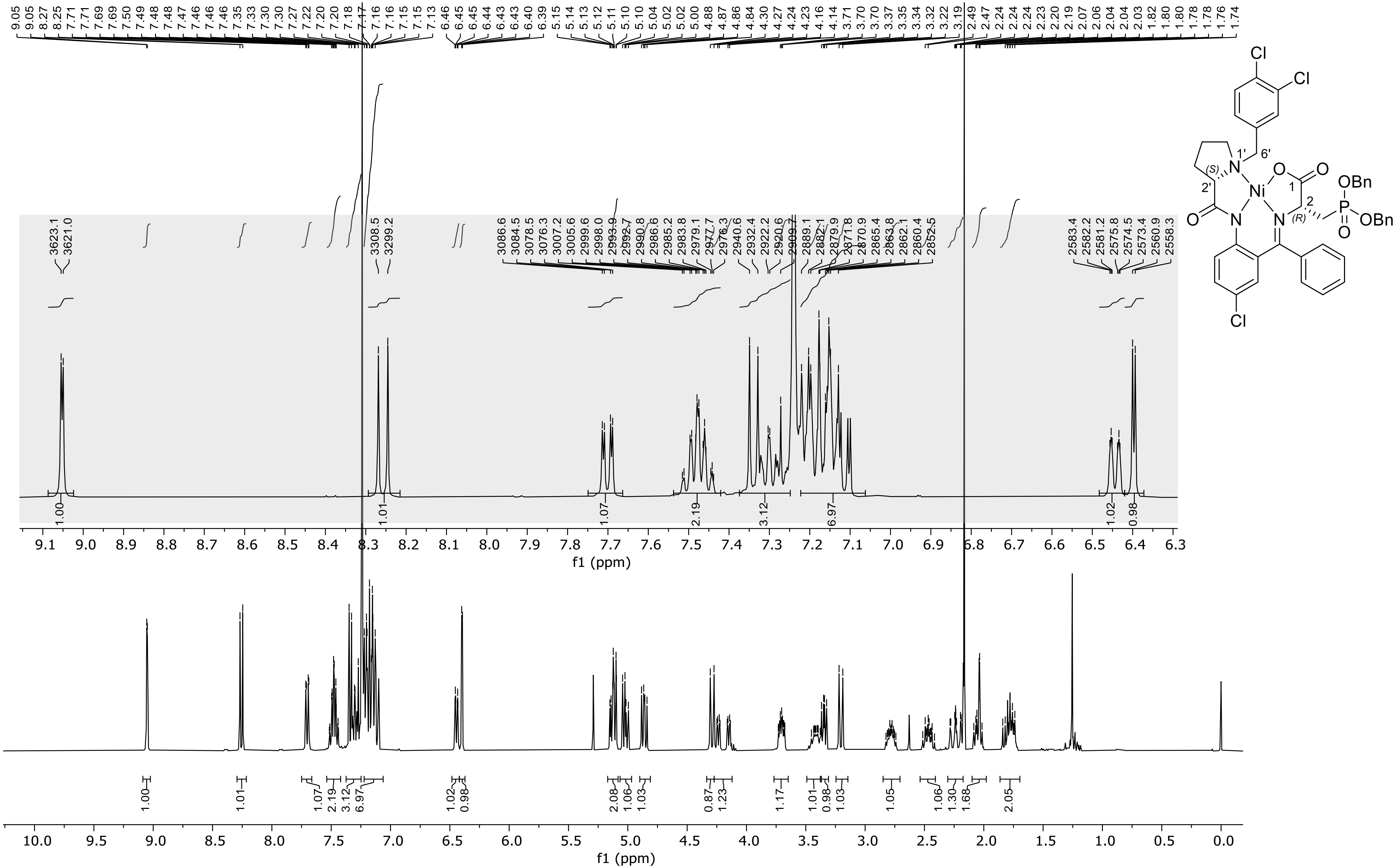
[19]F NMR (376 MHz, CDCl₃) Analysis of Compound (*S*,*R*)-3h.



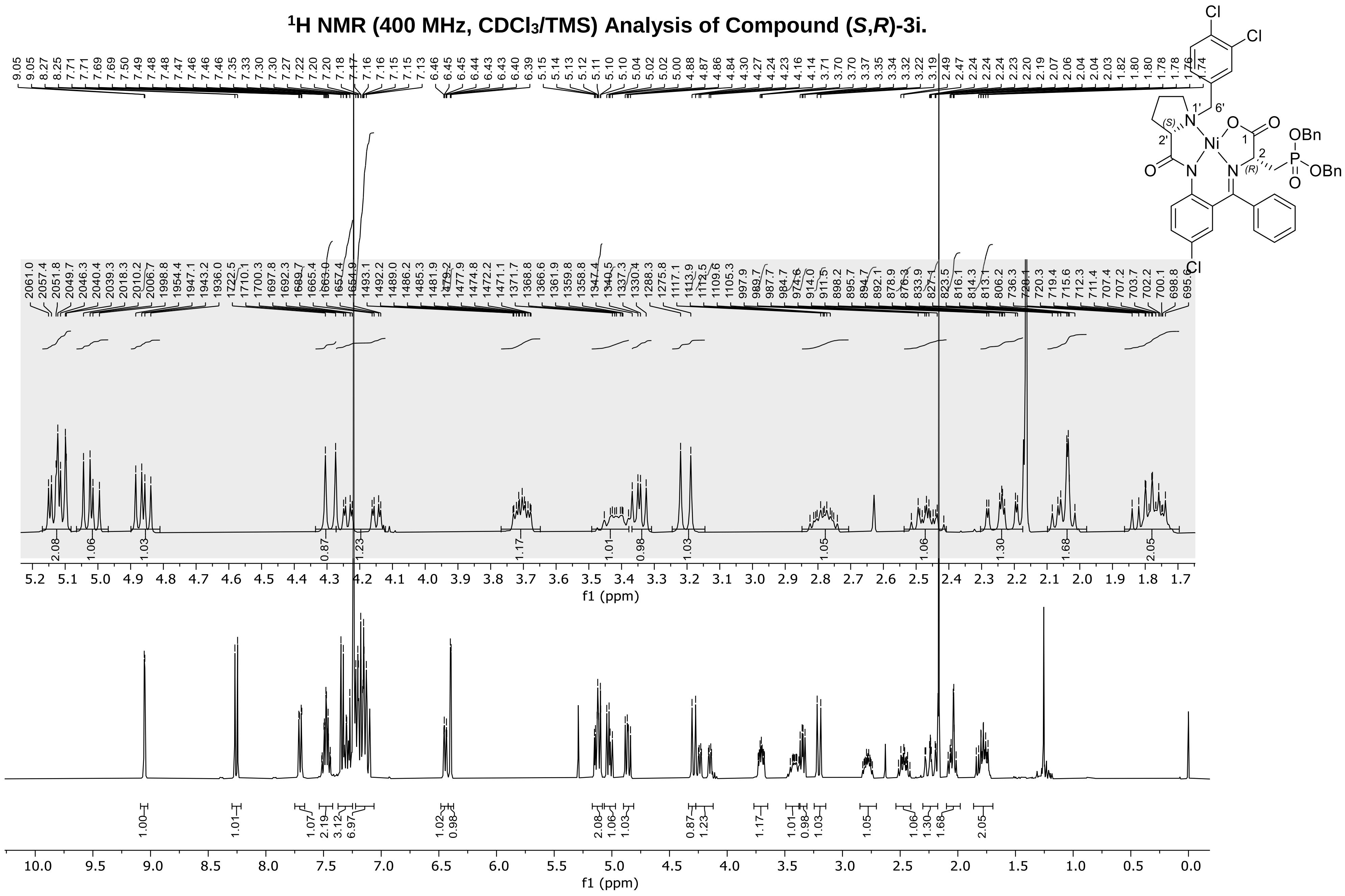
^{13}P NMR (162 MHz, $CDCl_3$) Analysis of Compound (*S*,*R*)-3h.



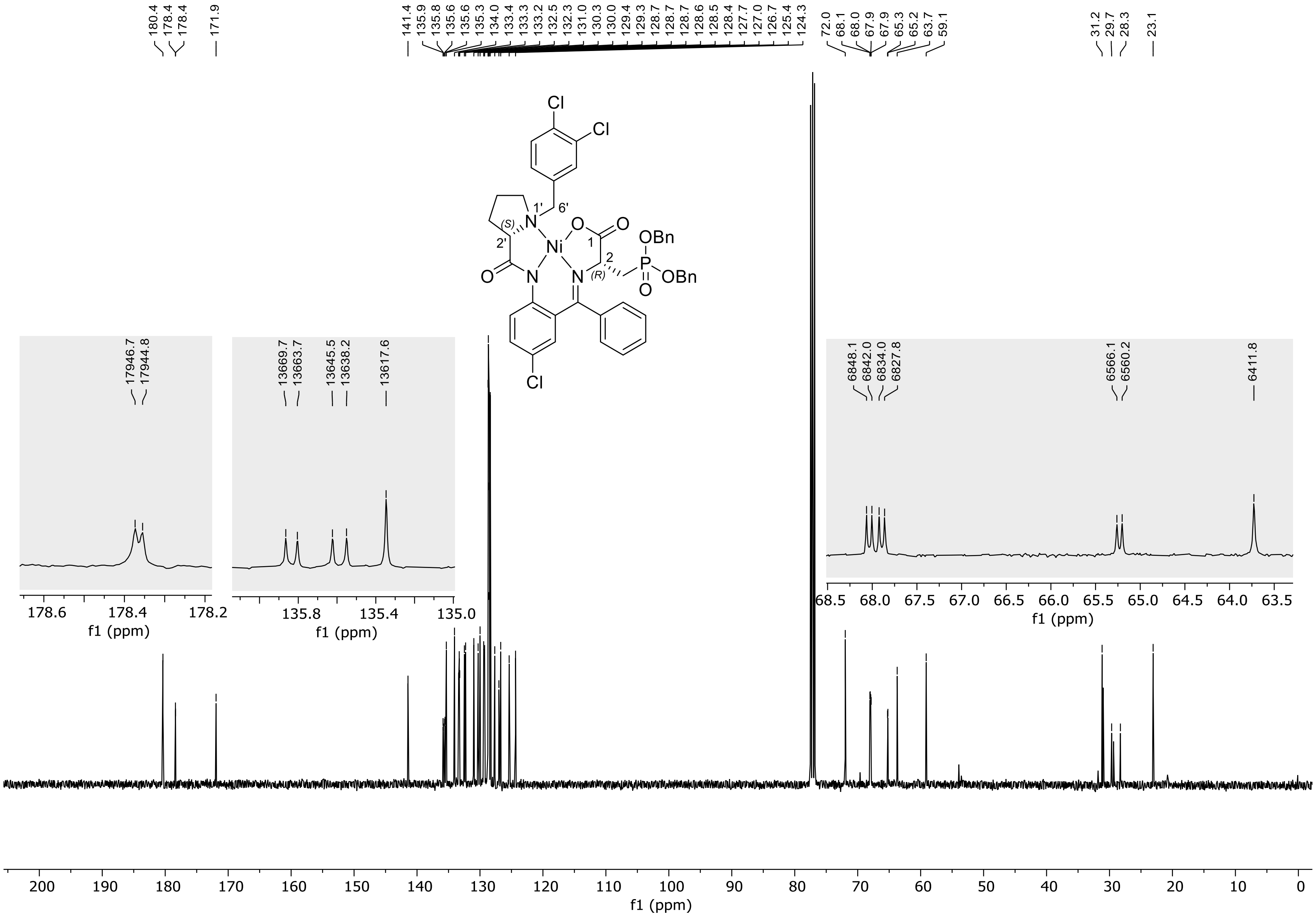
^{1}H NMR (400 MHz, $CDCl_3$/TMS) Analysis of Compound (*S*,*R*)-3i.



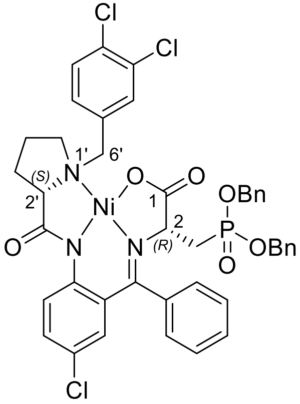
[1]H NMR (400 MHz, CDCl$_3$/TMS) Analysis of Compound (*S*,*R*)-3i.

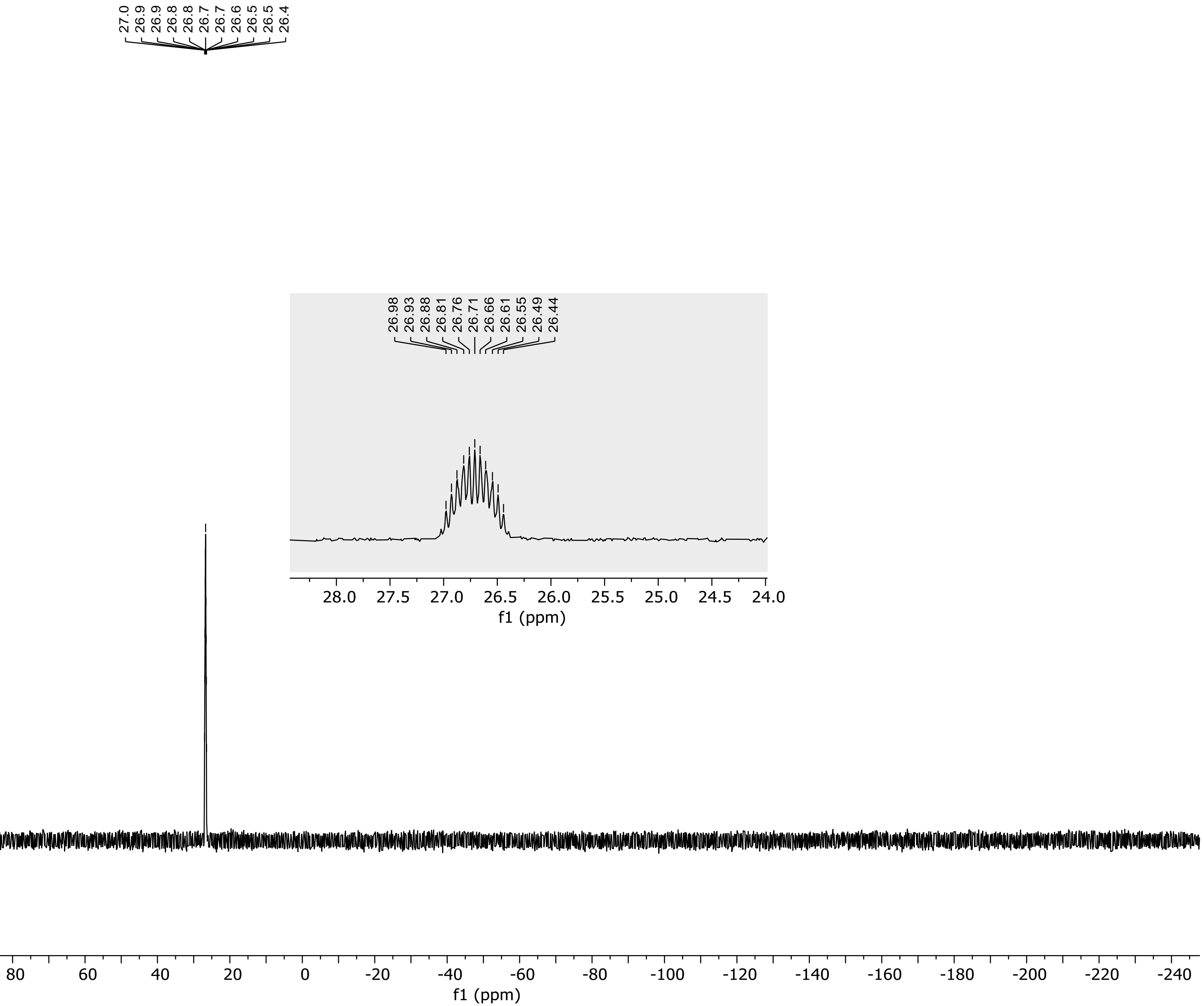


^{13}C NMR (101 MHz, $CDCl_3$) Analysis of Compound (*S*,*R*)-3i.

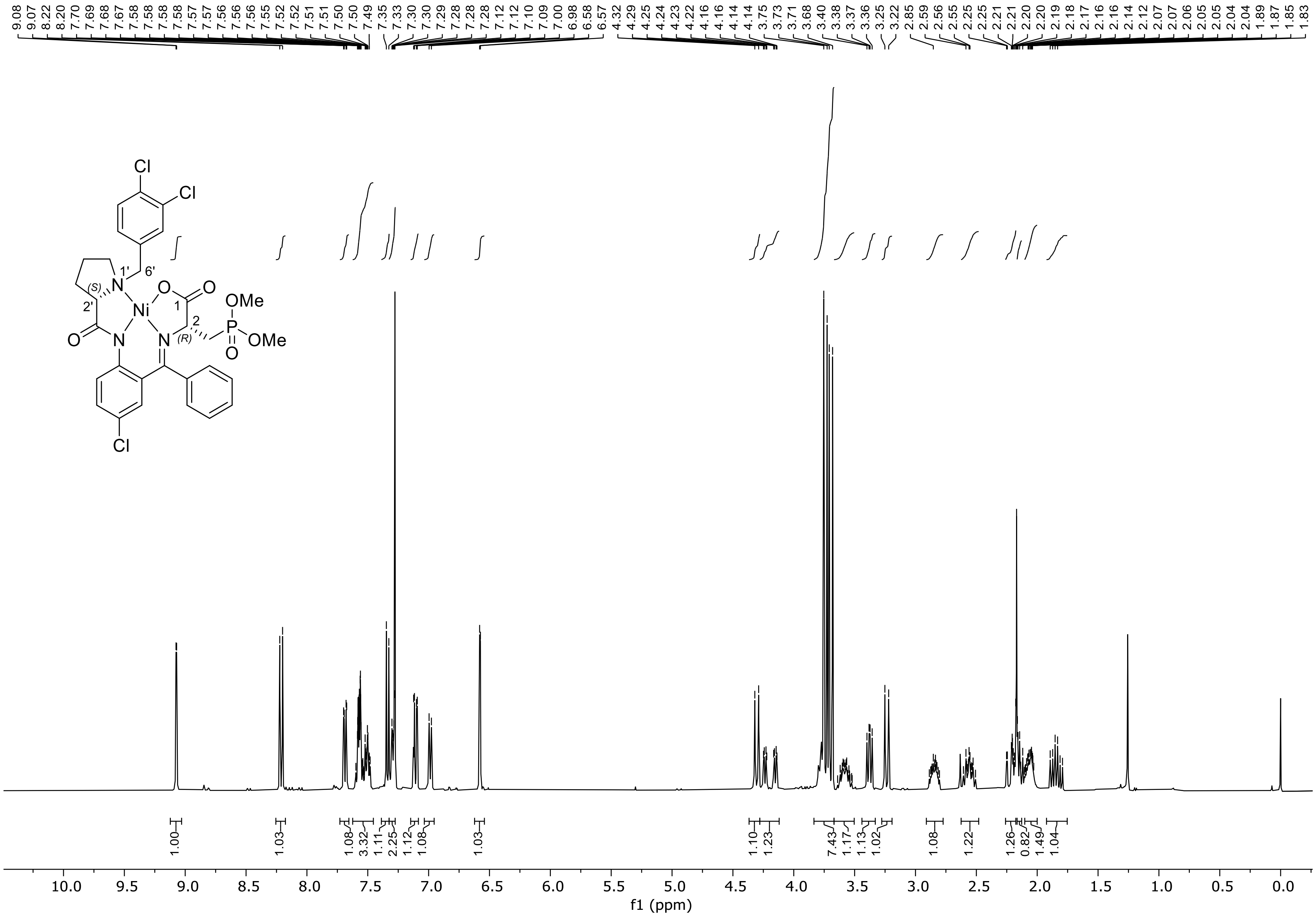


^{13}P NMR (162 MHz, $CDCl_3$) Analysis of Compound (*S*,*R*)-3i.

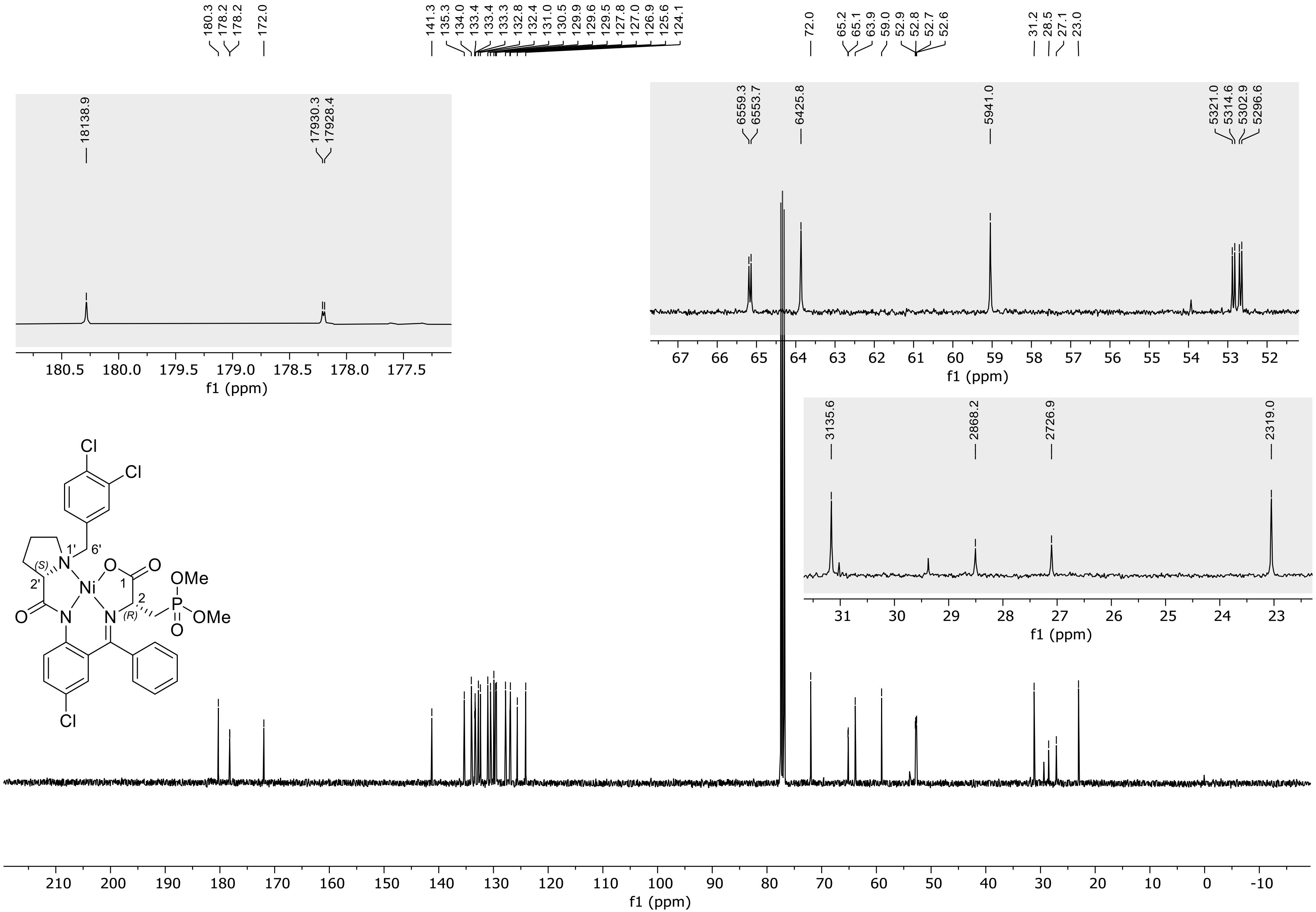




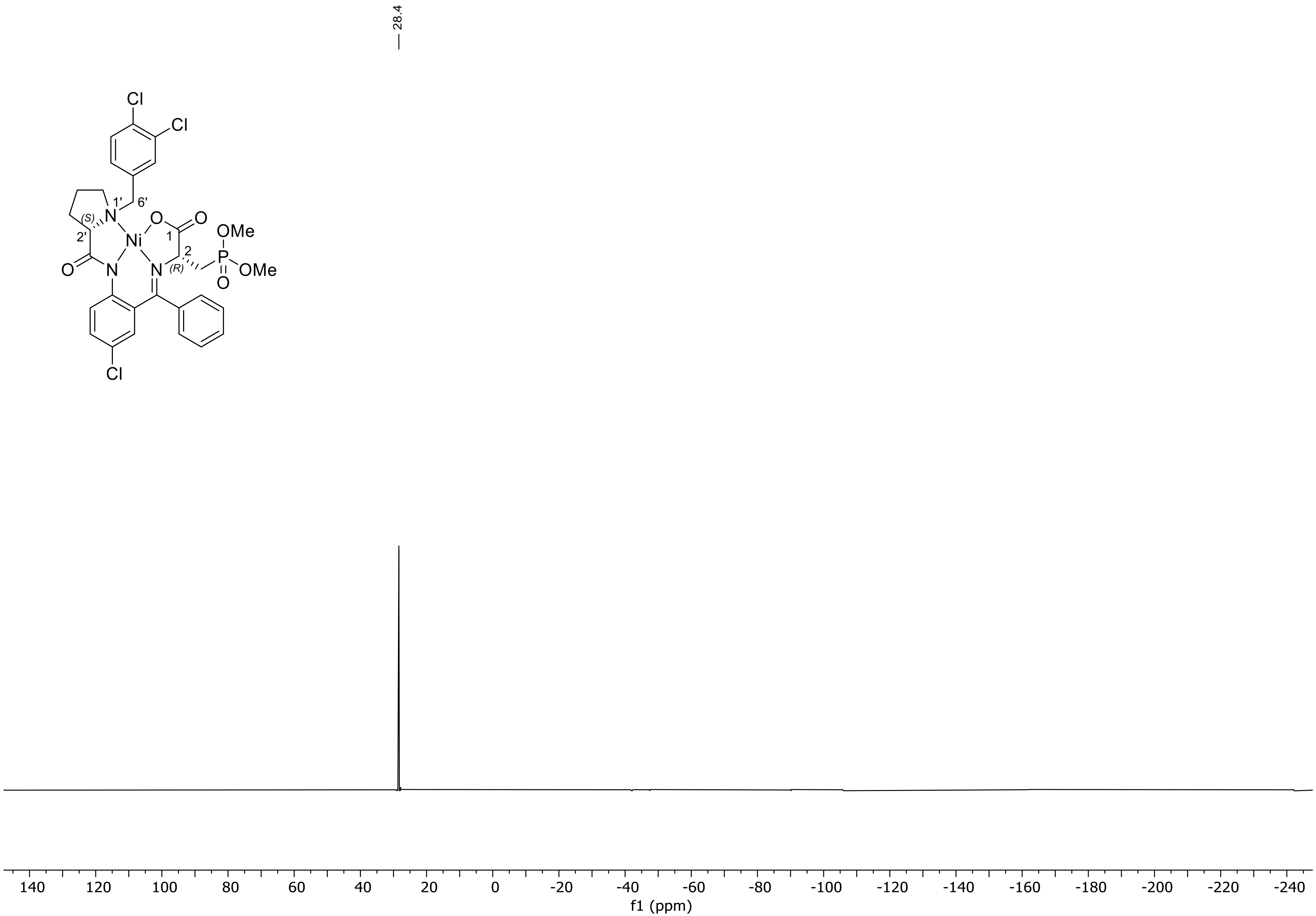
^{1}H NMR (400 MHz, $CDCl_3$/TMS) Analysis of Compound (*S*,*R*)-3j.



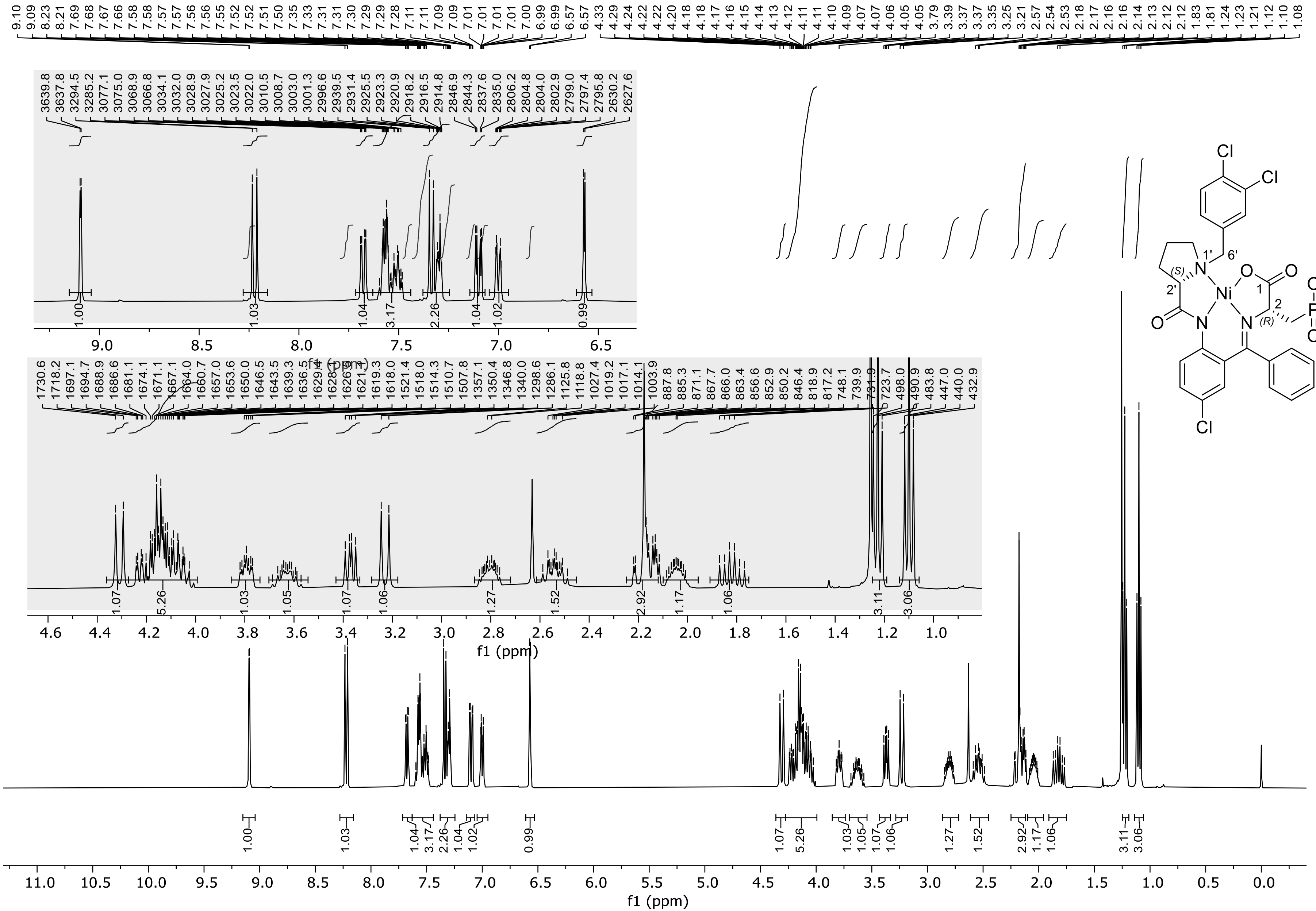
^{13}C NMR (101 MHz, CDCl$_3$) Analysis of Compound (*S*,*R*)-3j.



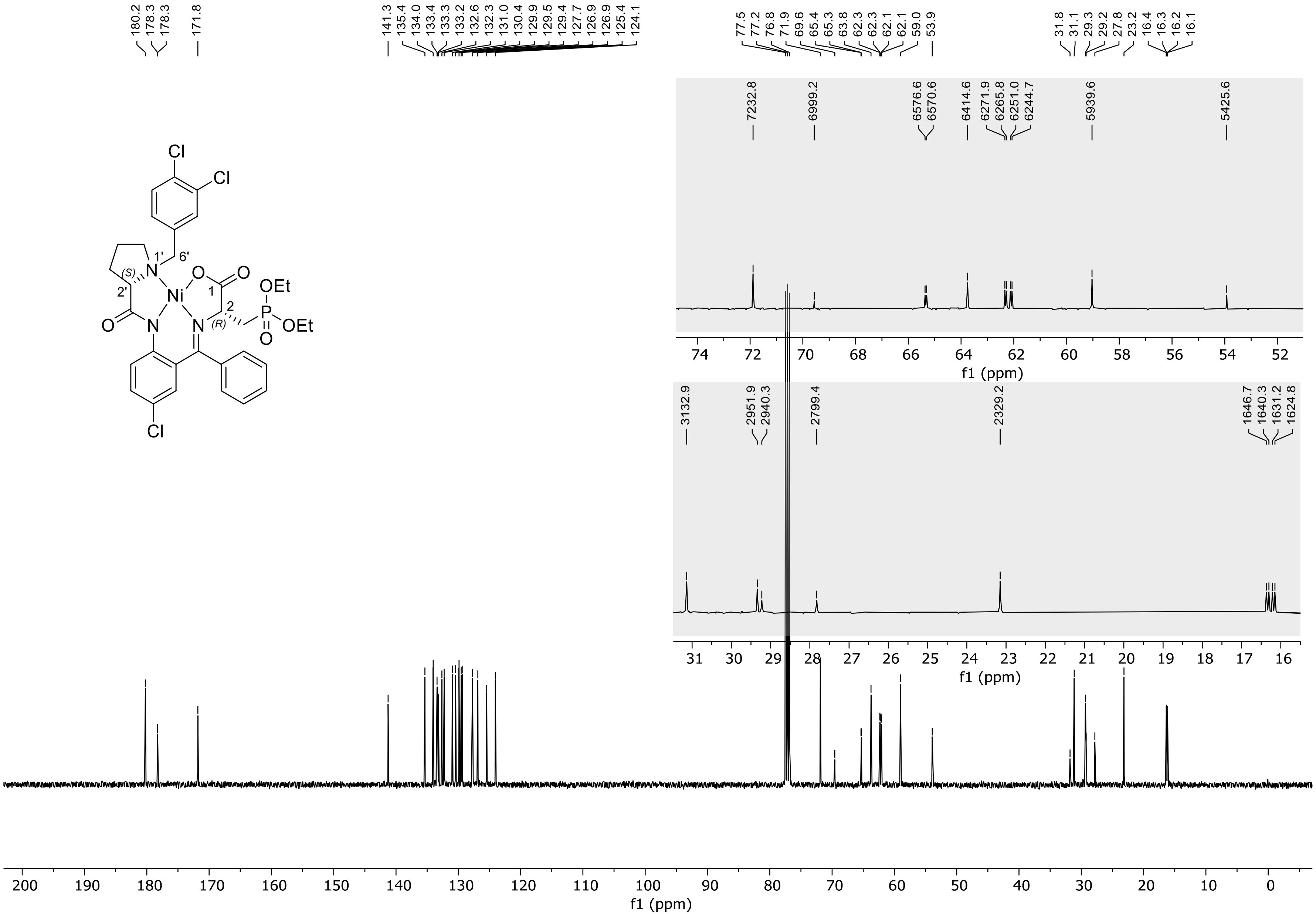
^{13}P NMR (162 MHz, $CDCl_3$) Analysis of Compound (*S*,*R*)-3j.



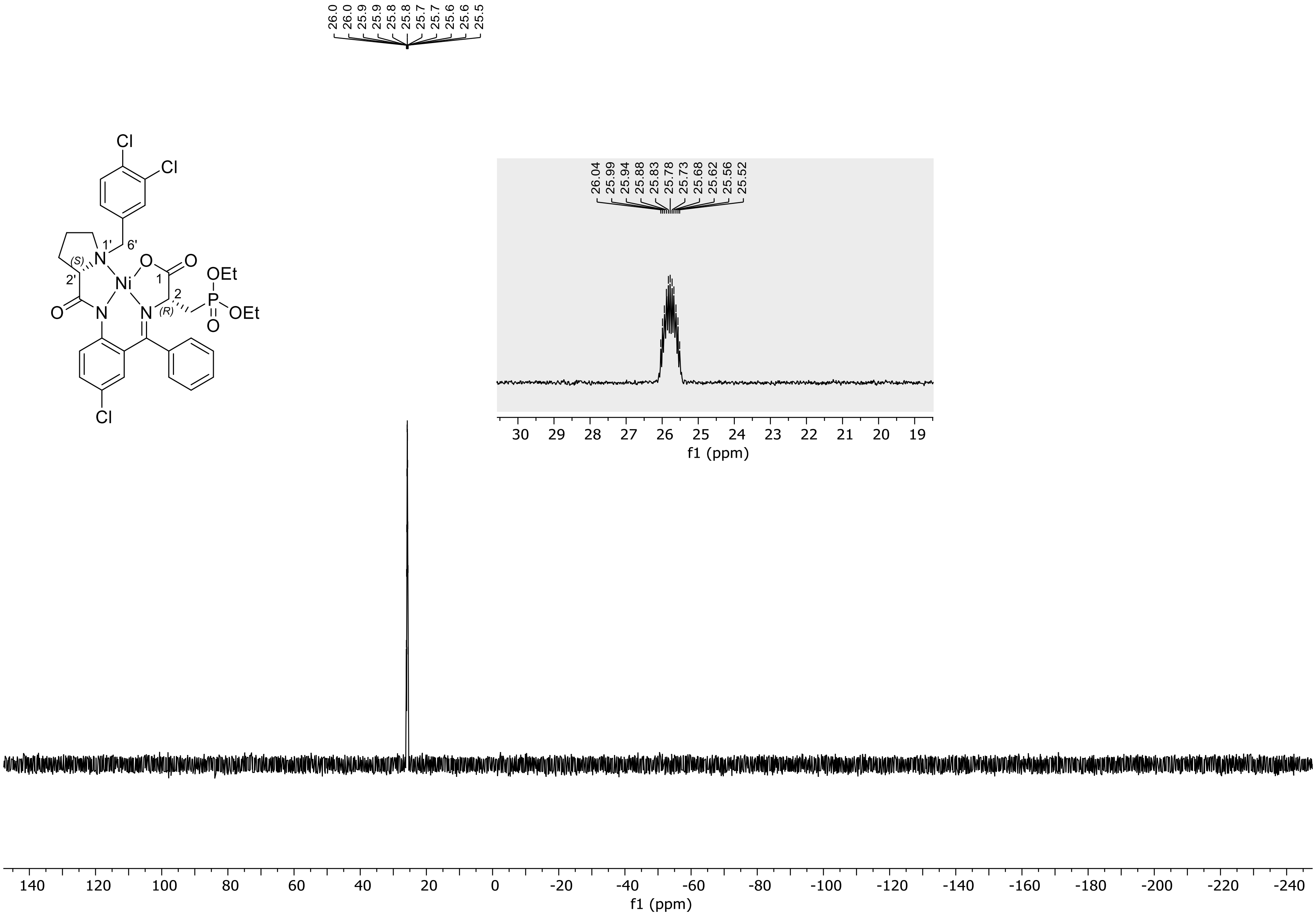
^{1}H NMR (400 MHz, $CDCl_3$/TMS) Analysis of Compound (*S*,*R*)-3k.



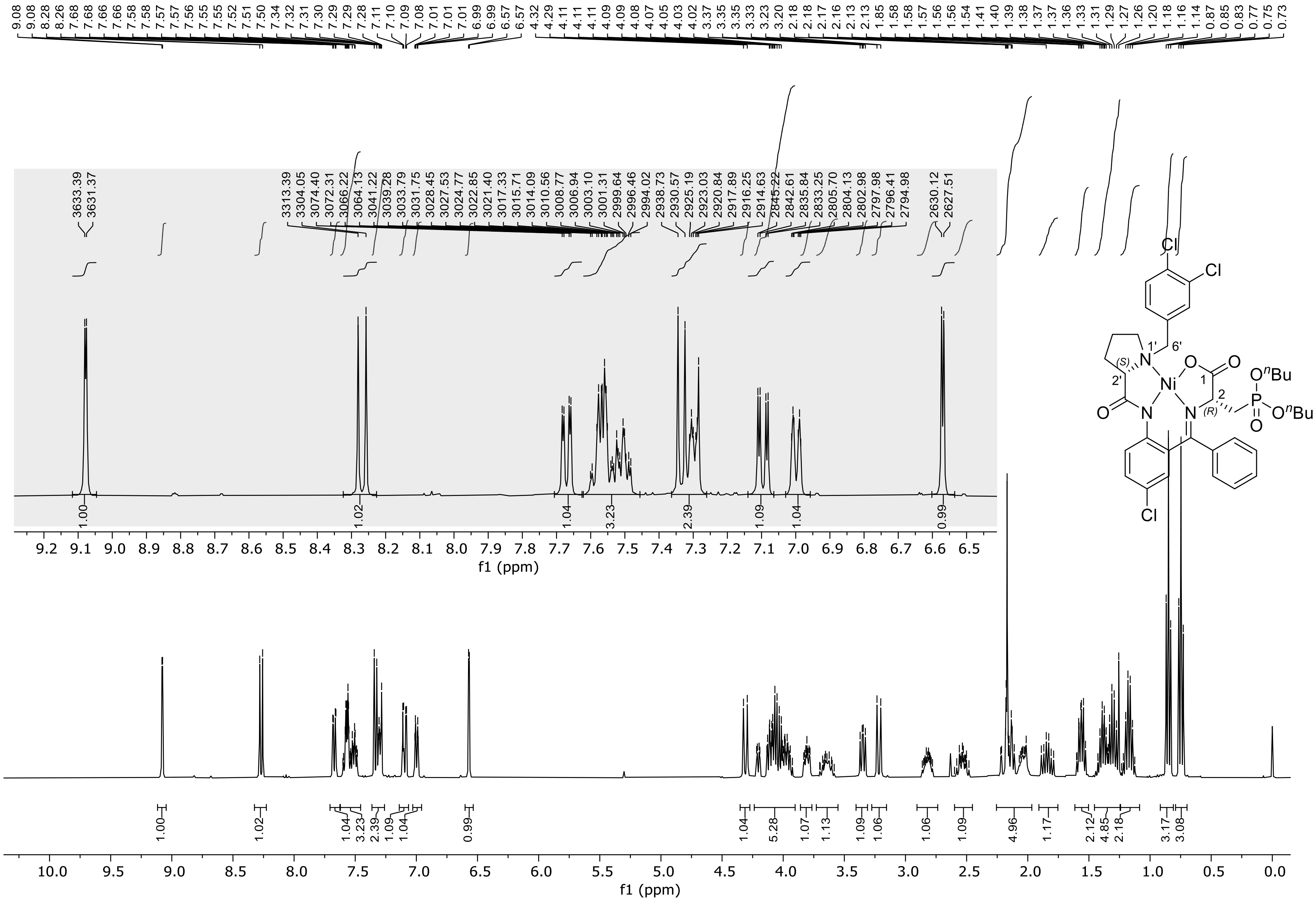
^{13}C NMR (101 MHz, $CDCl_3$) Analysis of Compound (*S*,*R*)-3k.



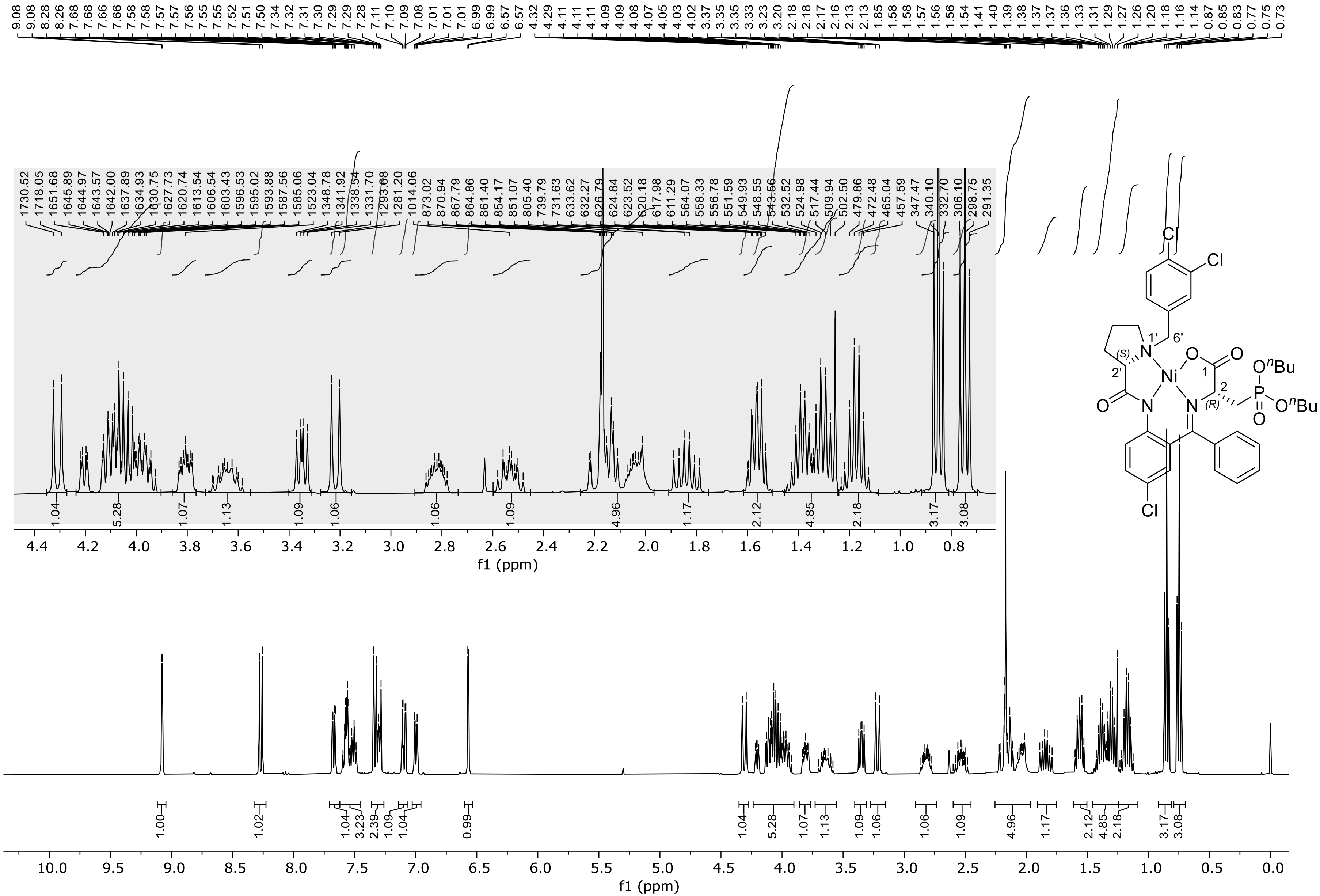
^{13}P NMR (162 MHz, $CDCl_3$) Analysis of Compound (*S*,*R*)-3k.



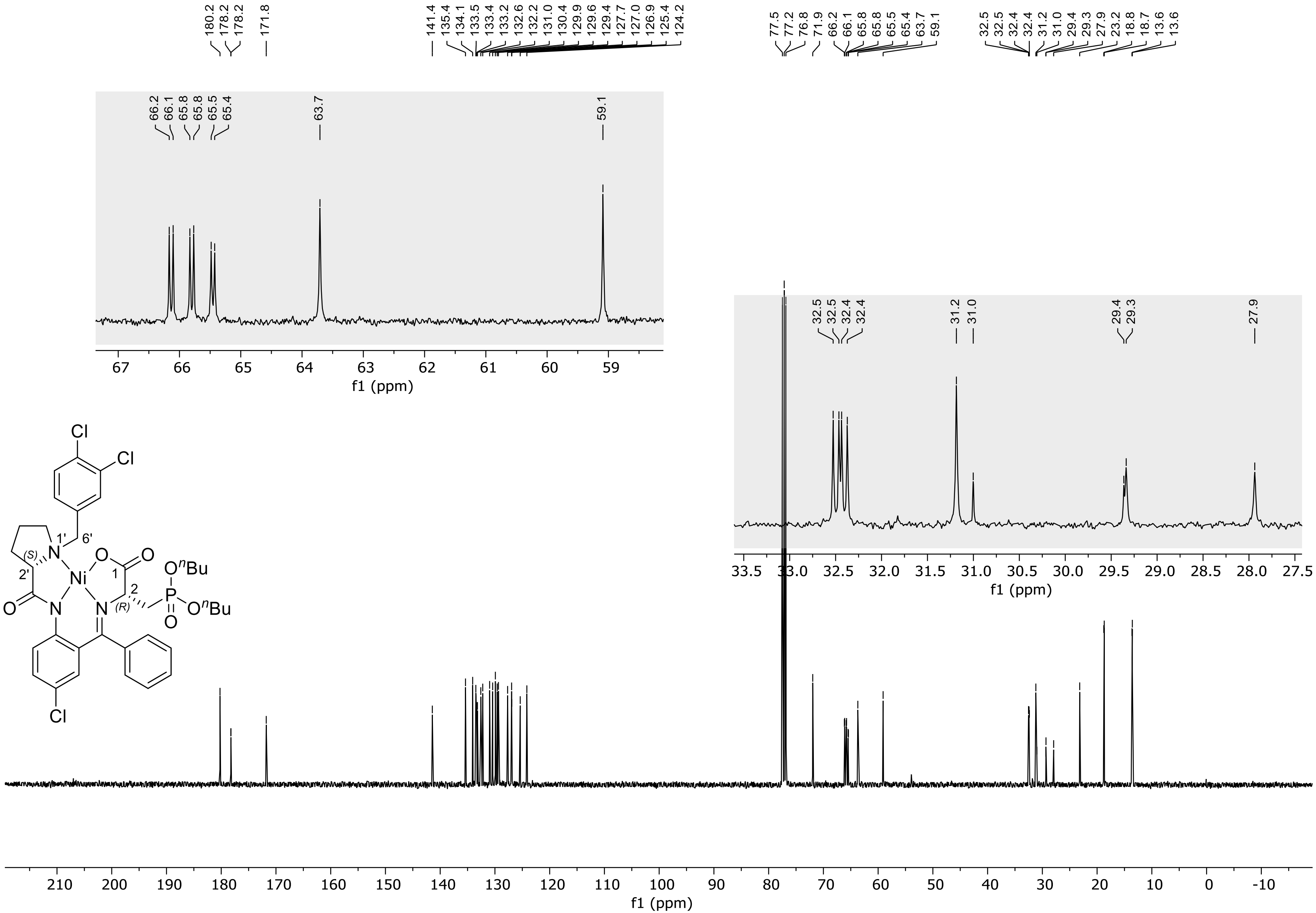
^{1}H NMR (400 MHz, $CDCl_3$/TMS) Analysis of Compound (*S*,*R*)-3l.



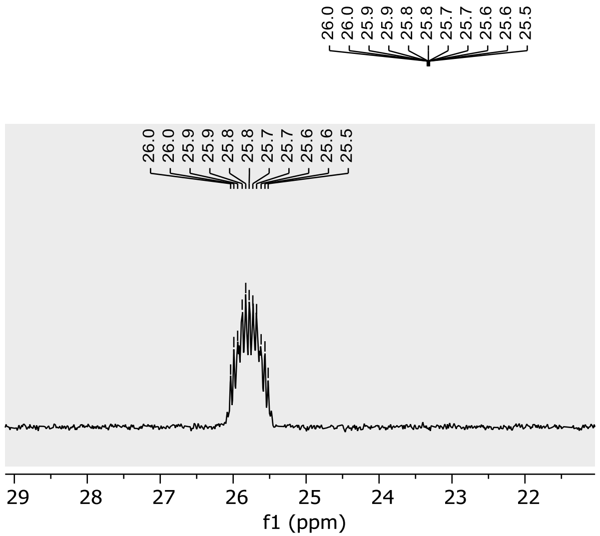
[1]H NMR (400 MHz, $CDCl_3$/TMS) Analysis of Compound (*S*,*R*)-3l.

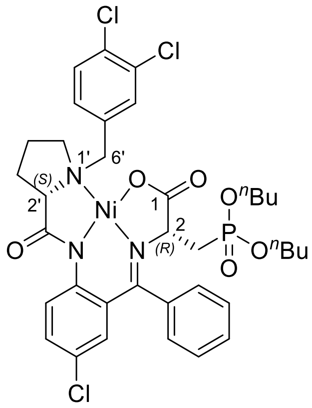


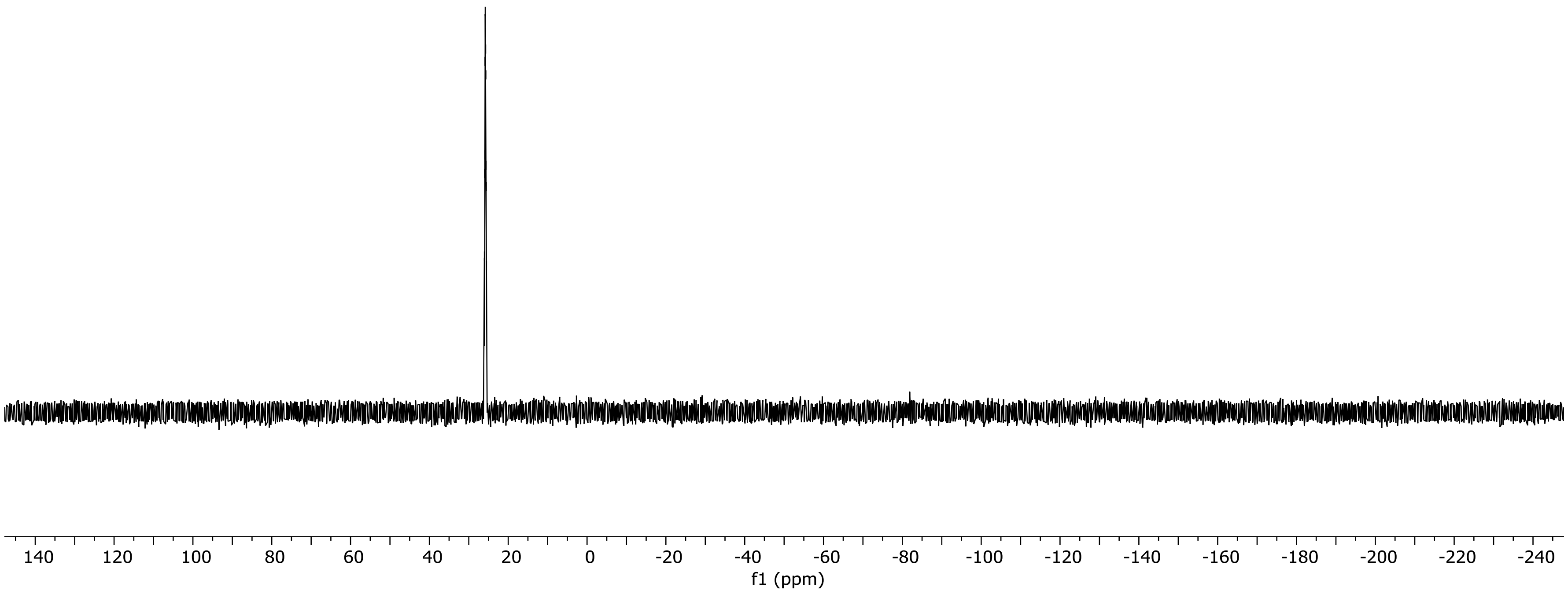
^{13}C NMR (101 MHz, CDCl$_3$) Analysis of Compound (*S*,*R*)-3l.



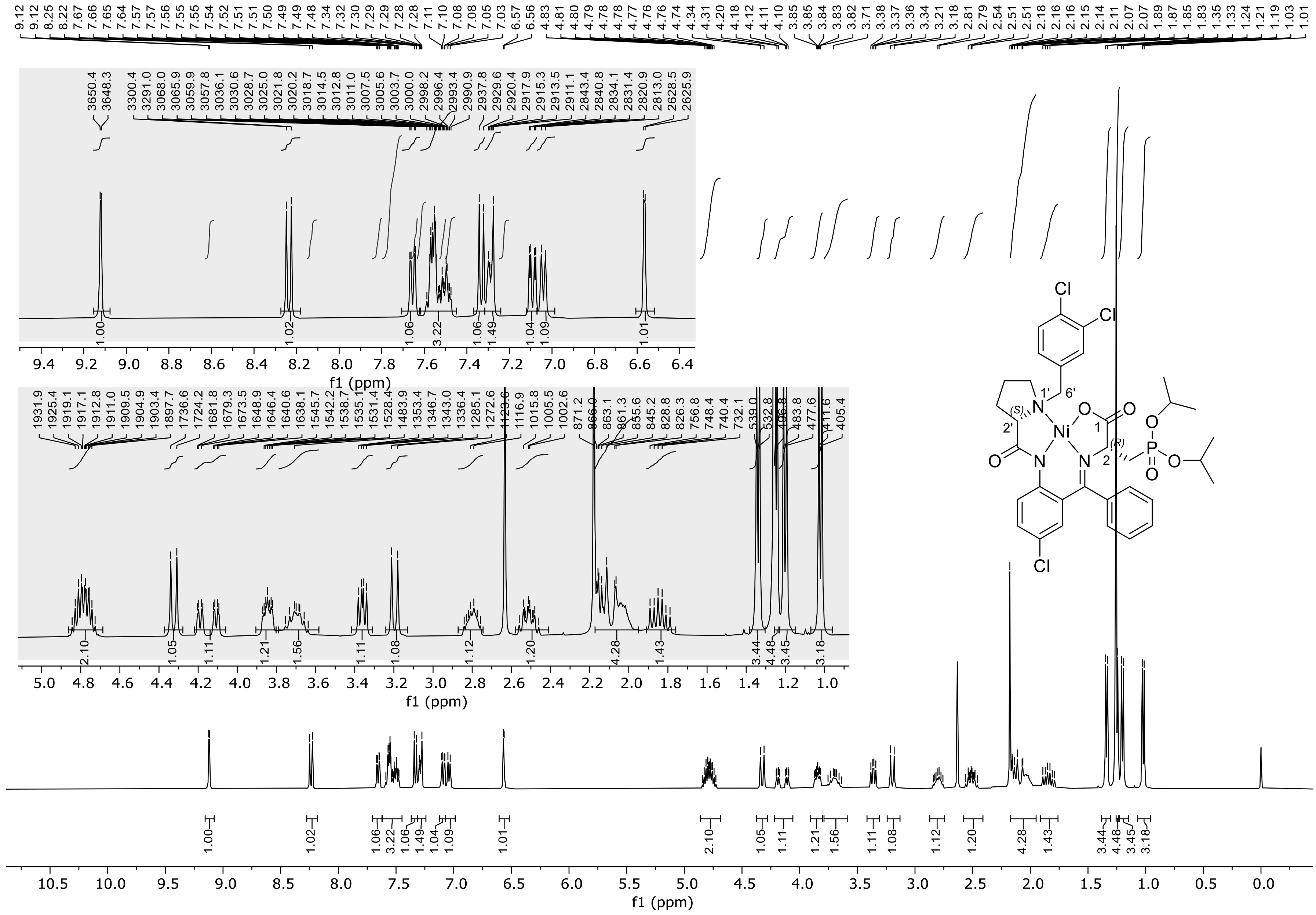
^{13}P NMR (162 MHz, $CDCl_3$) Analysis of Compound (*S*,*R*)-3l.



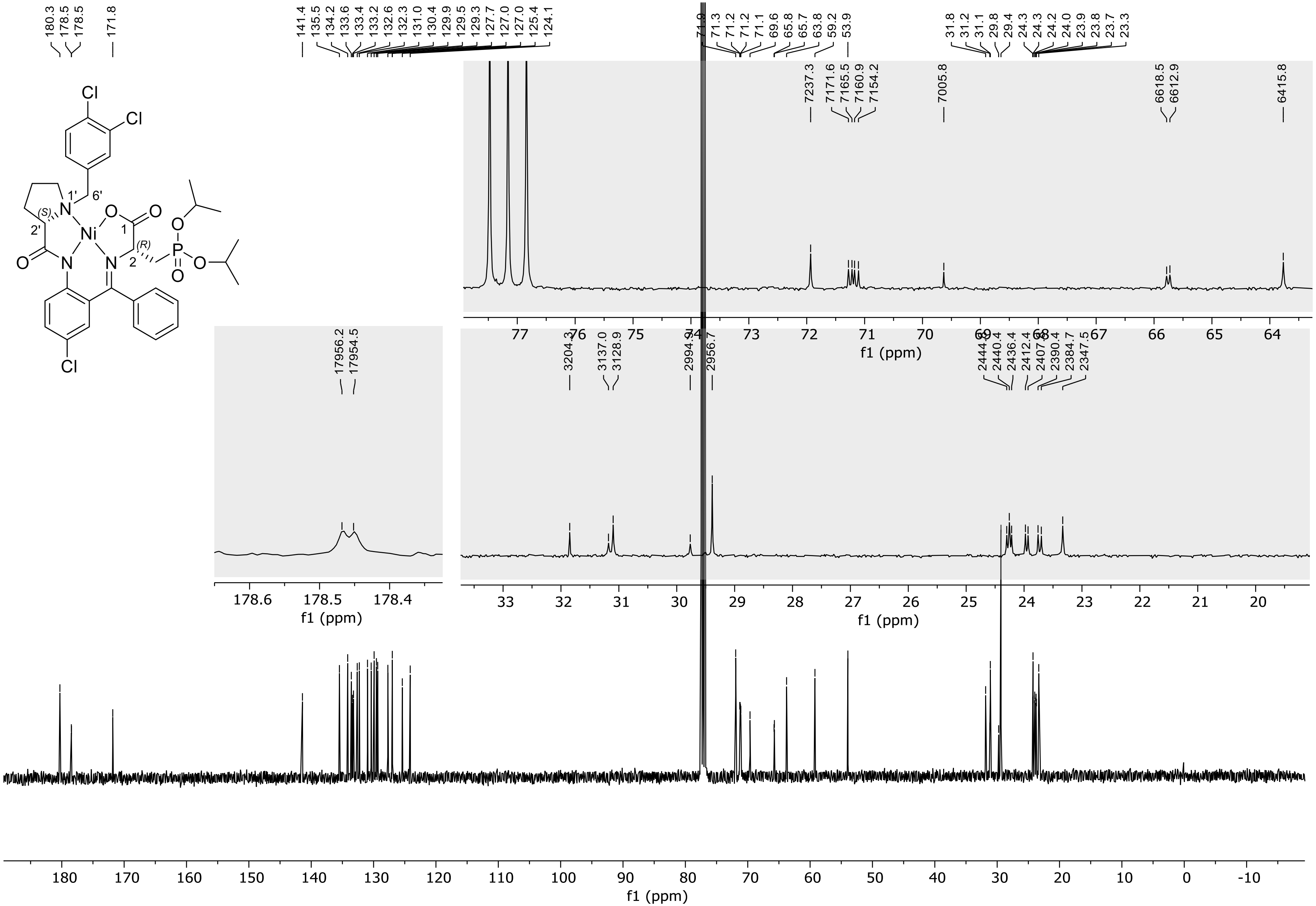




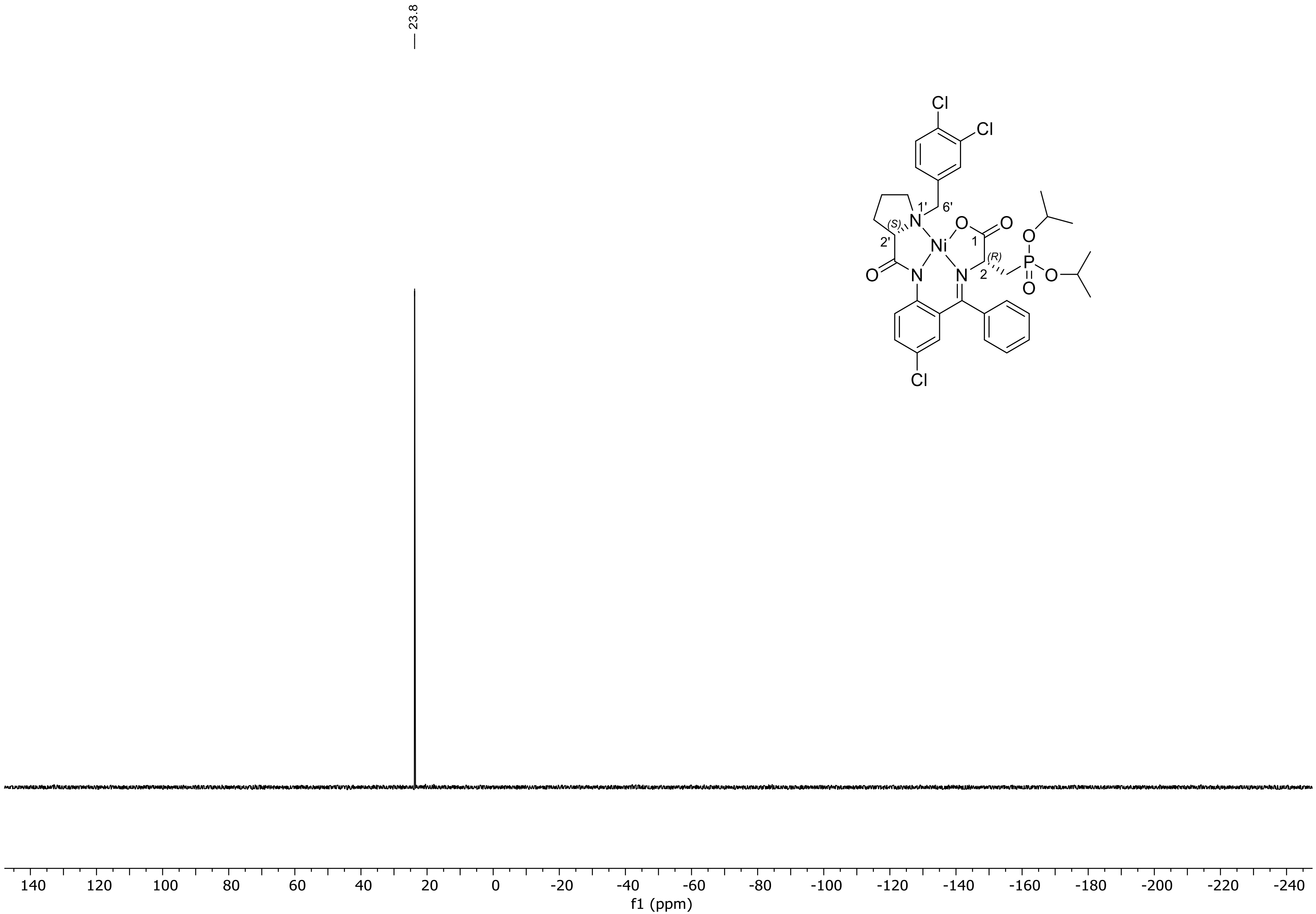
^{1}H NMR (400 MHz, $CDCl_3$/TMS) Analysis of Compound (*S*,*R*)-3m.



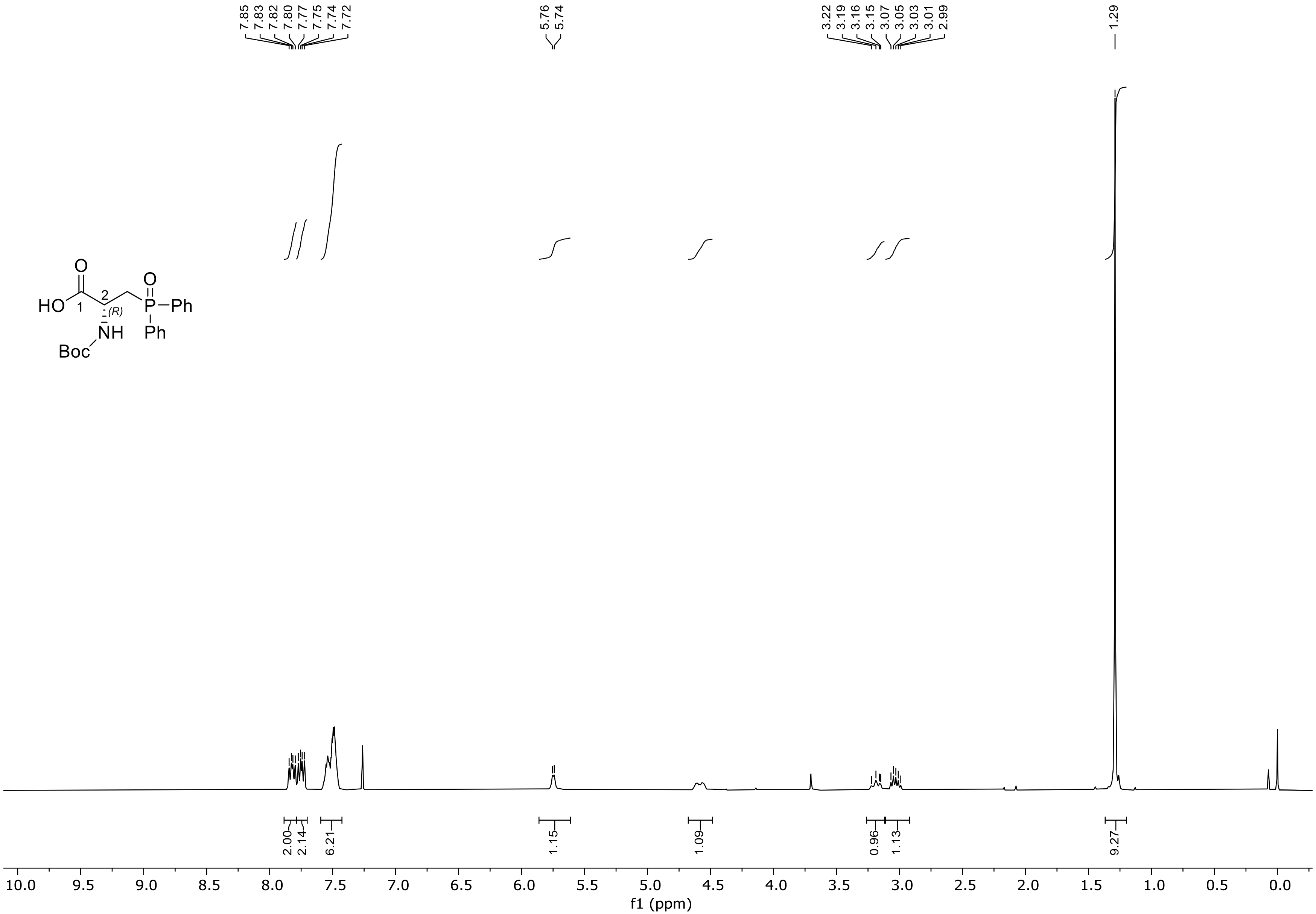
^{13}C NMR (101 MHz, $CDCl_3$) Analysis of Compound (*S*,*R*)-3m.



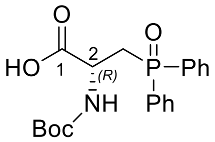
¹³P NMR (162 MHz, $CDCl_3$) Analysis of Compound (*S*,*R*)-3m.

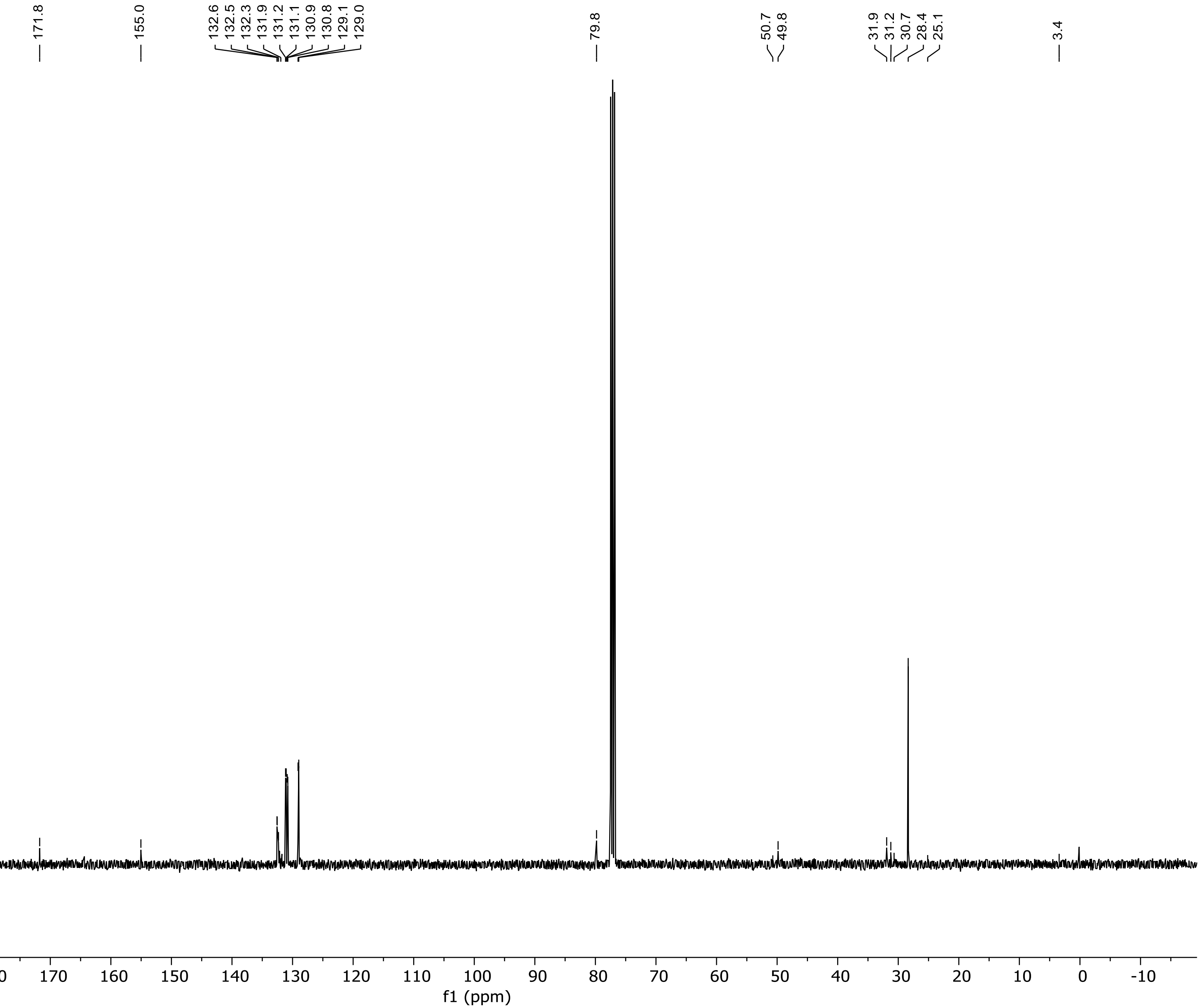


^{1}H NMR (400 MHz, $CDCl_3$/TMS) Analysis of Compound (+)-4a.

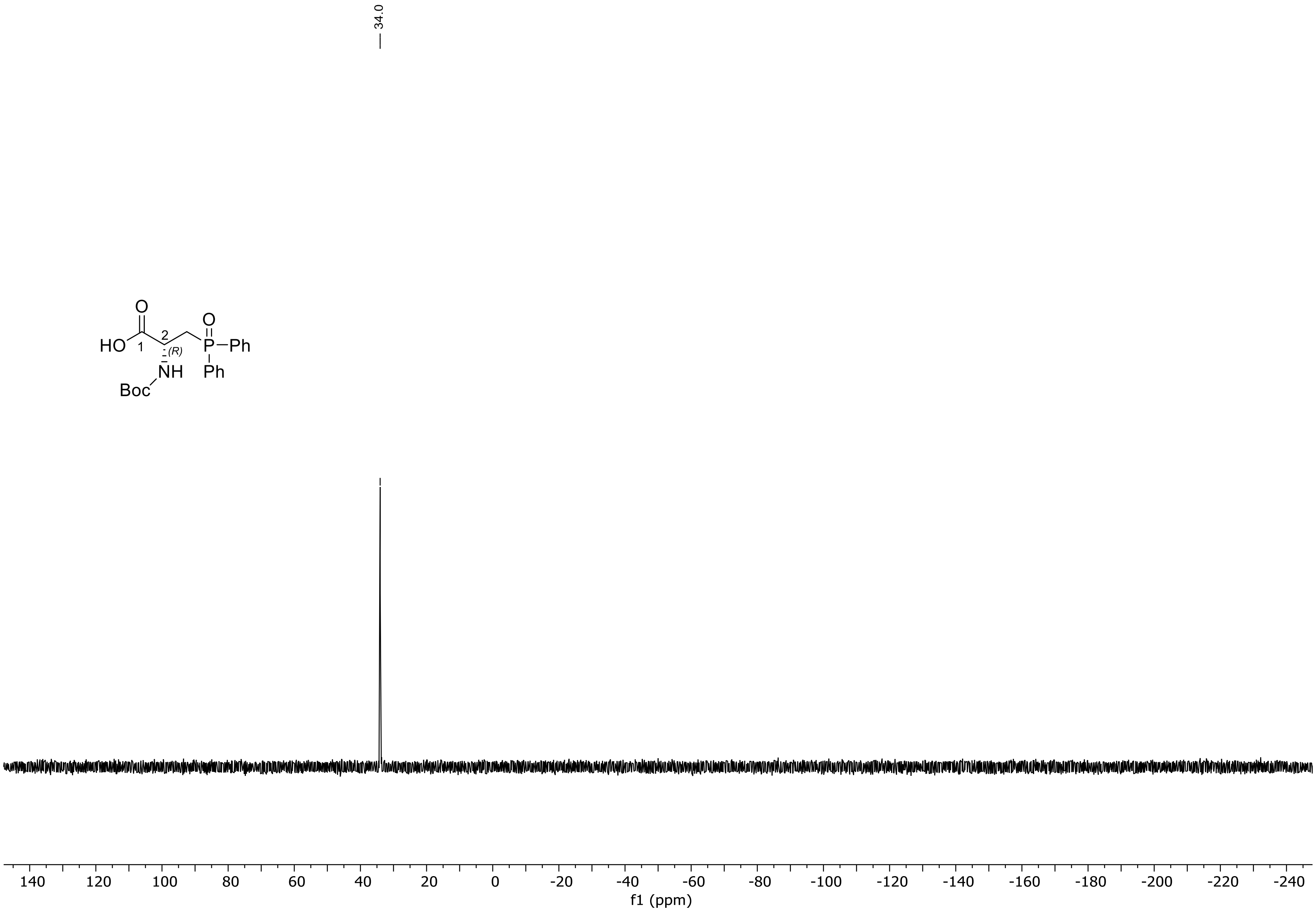


^{13}C NMR (101 MHz, $CDCl_3$) Analysis of Compound (+)-4a.

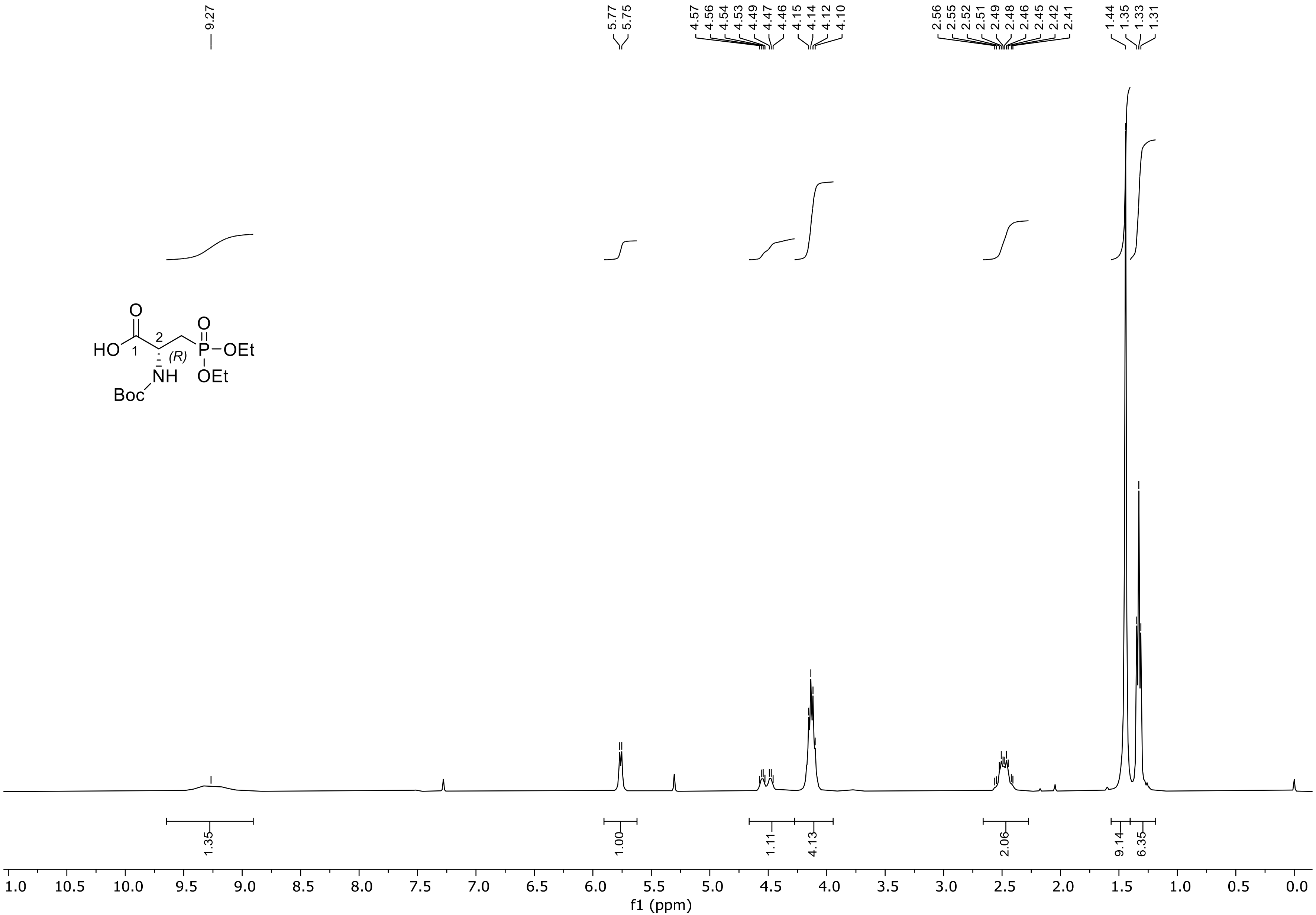




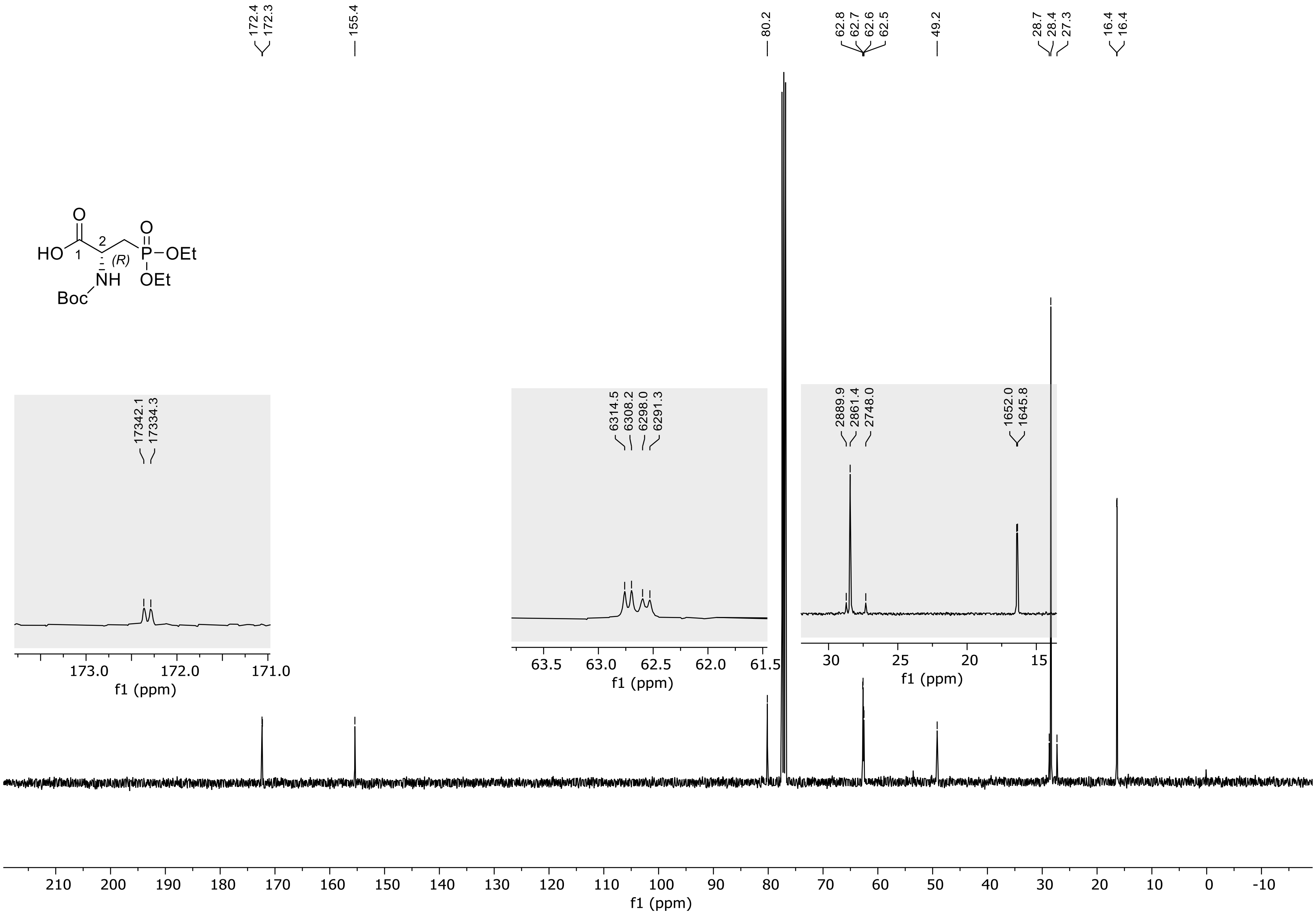
^{13}P NMR (162 MHz, $CDCl_3$) Analysis of Compound (+)-4a.



^{1}H NMR (400 MHz, $CDCl_3$/TMS) Analysis of Compound (+)-4k.



^{13}C NMR (101 MHz, $CDCl_3$) Analysis of Compound (+)-4k.



^{13}P NMR (162 MHz, $CDCl_3$) Analysis of Compound (+)-4k.