SUPPLEMENTARY INFORMATION

Application of mixed phosphorus/sulfur ligands based on terpenoids to Pd-catalyzed asymmetric allylic substitution and Rh-catalyzed hydrogenation

Konstantin N. Gavrilov, Ilya V. Chuchelkin, Vladislav K. Gavrilov, Ilya D. Firsin, Valeria M. Trunina, Alexey A. Shiryaev, Alena O. Shkirdova, Evgeniya V. Bermesheva, Victor A. Tafeenko, Vladimir V. Chernyshev, Vladislav S. Zimarev and Nataliya S. Goulioukina

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GENERAL

$^{31}P\{^{1}H\}$, $^{13}C\{^{1}H\}$ and ^{1}H NMR spectra were recorded with Bruker Avance 600 (242.9 MHz for $^{31}P\{^{1}H\}$, 150.9 MHz for $^{13}C\{^{1}H\}$ and 600.1 MHz for ^{1}H), Bruker Avance 400 (162.0 MHz for $^{31}P\{^{1}H\}$, 100.6 MHz for $^{13}C\{^{1}H\}$ and 400.1 MHz for ^{1}H) and Varian Inova 500 (202.3 MHz for ^{31}P, 125.7 MHz for $^{13}C\{^{1}H\}$ and 499.8 MHz for ^{1}H) instruments. ^{1}H and $^{13}C\{^{1}H\}$ NMR signals were attributed using APT, DEPT, $^{1}H,^{1}H$ – COSY, $^{1}H,^{1}H$ – NOESY and $^{13}C,^{1}H$ – HSQC techniques. The chemical shifts are referenced to residual $CHCl_3$ or $CHDCl_2$peaks (^{1}H, NMR); $CDCl_3$ or CD_2Cl_2 peaks ($^{13}C\{^{1}H\}$) and H_3PO_4 85% as external standard ($^{31}P\{^{1}H\}$ NMR). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), *J*, Hz. HPLC analyses were performed on a Stayer instrument using Kromasil 5-CelluCoat and Daicel Chiralcel OD-H columns. Optical rotations were measured on a Krüss P8000 polarimeter. Elemental analyses were performed on a CHN-microanalyzer Carlo Erba EA1108 CHNS-O. HRMS spectra were recorded on a AB Sciex TripleTOF 5600+ mass spectrometer with Turbo Ion Spray ionization (ESI). The sample (0.2 μL) was injected into the 0.3 mL/min methanol stream without chromatographic separation directly into the ion source. The spectra were recorded in the positive ion mode.

The molecular structure of **L1a** was confirmed by X-ray structure determination from powder data measured at room temperature on the laboratory diffractometer EMPYREAN (Ni-filtered Cu K_{α} radiation) equipped with linear detector X'celerator. All observed diffraction peaks were indexed in orthorhombic unit cell and space group $P2_12_12_1$. The crystal structure was solved with the use of simulated annealing technique[1] and refined with the program MRIA[2] following the known procedures described by us earlier.[3] The experimental and calculated diffraction profiles after the final bond-restrained Rietveld refinement are shown in Fig. S1. The crystal data, data collection and refinement parameters are given in Table S3. The molecular structure and portion of the crystal packing of **L1a** are shown on Figs. 1 and S2, respectively, prepared with *Mercury*.[4]

The data of **L1b** and [Pd(allyl)(**L2a**)]BF_4 were collected by using STOE diffractometer Pilatus100K detector, monocapillary (0.5 mm diameter) collimation, Mo Kα (0.71073Å) radiation and Cu Kα (1.54086Å) radiation was used for data collection of **L2b**, focusing mirror collimation - rotation method mode for all crystals. STOE X-AREA software was used for cells refinement and data reduction. Data collection and image processing was performed with X-Area 1.67 (STOE & Cie GmbH, Darmstadt, Germany, 2013). Intensity data were scaled with LANA (part of X-Area) in order to minimize differences of intensities of symmetry-equivalent reflections (multi-scan method). Selected crystal data of **L1b**, **L2b** and [Pd(allyl)(**L2a**)]BF_4 one can see in the Table S4. The structures were solved and refined with SHELX program.[5] The non-hydrogen atoms were refined by using the anisotropic full matrix least-square procedure. All hydrogen atoms were placed in the calculated positions and allowed to ride on their

parent atoms. Molecular geometry calculations were performed with the SHELX program, and the molecular graphics were prepared by using DIAMOND software.[6] Crystal data, molecular geometry and structure can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (CCDC numbers: **L1a** – 2235512; **L1b** – 2272241; **L2b** – 2272240; [Pd(allyl)(**L2a**)]BF_4 – 2272242).

All reactions were carried out under a dry argon atmosphere in flame-dried glassware and in freshly dried and distilled solvents. Triethylamine and pyrrolidine were distilled over KOH and then over a small amount of $LiAlH_4$ before use. PCl_3 was freshly distilled. Thin-layer chromatography was performed on E. Merck pre-coated silica gel 60 F254 and Macherey-Nagel Alugram Alox N/UV_{254} plates. Column chromatography was performed using silica gel MN Kieselgel 60 (230 – 400 mesh) and MN-Aluminum oxide, basic, Brockmann Activity 1. For the preparation of analytically pure samples, the obtained compounds were additionally dried in high vacuum (10^{-3} Torr) for 16 h.

The following compounds were synthesized according to literature procedures: ((1*S*,2*R*,3*S*,5*R*)-6,6-dimethyl-3-(phenylthio)bicyclo[3.1.1]heptan-2-yl)methanol,[7] (1*S*,2*R*,4*R*)-7,7-dimethyl-1((methylthio)methyl)bicyclo[2.2.1]heptan-2-ol,[8] (5*S*)-2-chloro-3-phenyl-1,3-diaza-2phosphabicyclo[3.3.0]octane and (5*R*)-2-chloro-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane ((S_C)-**1** and (R_C)-**1**),[9] (9a*S*,10a*S*)-5-Chloro-10,10-dimethyloctahydro-1*H*,5*H*-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaphosphinane (**2**),[10a] 2-chloro-1,3-diphenyl-1,3,2-diazaphospholidine (**3**),[10b] $[Pd(allyl)Cl]_2$ and (*E*)-1,3-diphenylallyl acetate (**4**),[11] ethyl 2-acetamido-3-oxobutanoate (**9**),[12] $[Rh(Cod)_2]BF_4$,[13] methyl (*Z*)-2-acetamido-3-phenylacrylate (**11b**)[14] and methyl (*Z*)-2-acetamido-3-(4-fluorophenyl)acrylate (**11c**).[15]

Pd-catalyzed allylic alkylation of (*E*)-1,3-diphenylallyl acetate (**4**) with dimethyl malonate, its amination with pyrrolidine, allylic alkylation of cinnamyl acetate (**6**) with ethyl 2-oxocyclohexane-1-carboxylate (**7**) or ethyl 2-acetamido-3-oxobutanoate (**9**) and Rh-catalyzed hydrogenation of **11a-c** were performed according to the appropriate procedures.[3,16]

3-(Methylthio)propan-1-ol, dimethyl malonate, BSA (*N*,*O*-bis(trimethylsilyl)acetamide), cinnamyl acetate (**6**), ethyl 2-oxocyclohexane-1-carboxylate (**7**) and dimethyl itaconate (**11a**) were purchased from Aldrich and Acros Organics.

EXPERIMENTAL SECTION

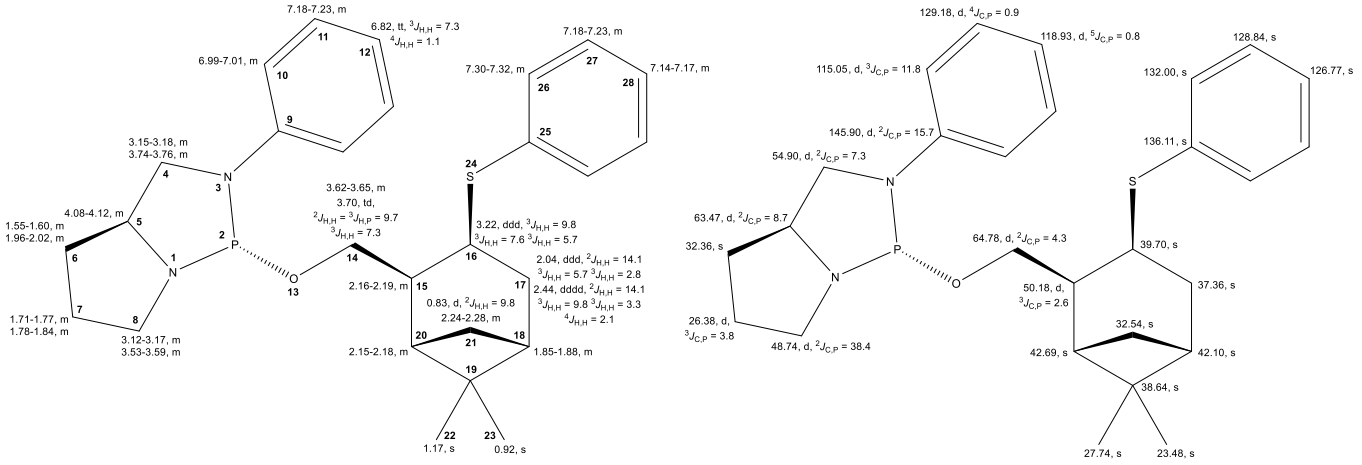
General Procedure for the Preparation of Ligands. The relevant 1,3-thioether alcohol (2 mmol) was added at −70 °C in one portion to a vigorously stirred solution of the appropriate phosphorylating reagent (S_C)-**1**, (R_C)-**1**, **2** or **3** (2 mmol) and Et_3N (0.56 mL, 4 mmol) in toluene (15 mL). The mixture that obtained was stirred for 16 h at −20 °C, then cooling was removed and the reaction mixture was stirred at 20 °C for 5 h. The resulting suspension was filtered through a short plug of SiO_2/Al_2O_3, the column was washed with toluene (2 x 20 mL), and the solvent was evaporated under reduced pressure (40 Torr). Products were additionally purified by flash chromatography on SiO_2 (toluene). The obtained ligands were dried in vacuum (10^{-3} Torr).

General procedure for the preparation of [Pd(allyl)(L)]BF_4 complexes. A solution of the appropriate ligand (0.2 mmol) in THF (3 mL) was added dropwise over 30 min to a stirred solution of $[Pd(allyl)Cl]_2$ (37 mg, 0.1 mmol) in THF (3 mL) at 20 °C. The reaction mixture was stirred for a further 1 h at 20 °C. $AgBF_4$ (39 mg, 0.2 mmol) was added to the resulting solution, and the reaction mixture was stirred for 1.5 h at 20 °C. The precipitate of AgCl formed was separated by centrifugation, solvent was removed in vacuum (40 Torr) and the crude product was dried in air and in vacuum (10^{-3} Torr). The product was dissolved in CH_2Cl_2 (0.3 mL) and reprecipitated from pentane (10 mL). The precipitate of the product was separated by centrifugation and dried in air and in vacuum (10^{-3} Torr).

***In situ* preparation of [Pd(allyl)(L1a)$_2$]BF_4. L1a** (23.3 mg, 0.05 mmol) was placed in the NMR tube with a solution of [Pd(allyl)(**L1a**)]BF_4 (35.0 mg, 0.05 mmol) in CD_2Cl_2 (0.7 mL). The reaction mixture was left overnight at 20 °C and an NMR experiment was carried out.

EXPERIMENTAL SECTION

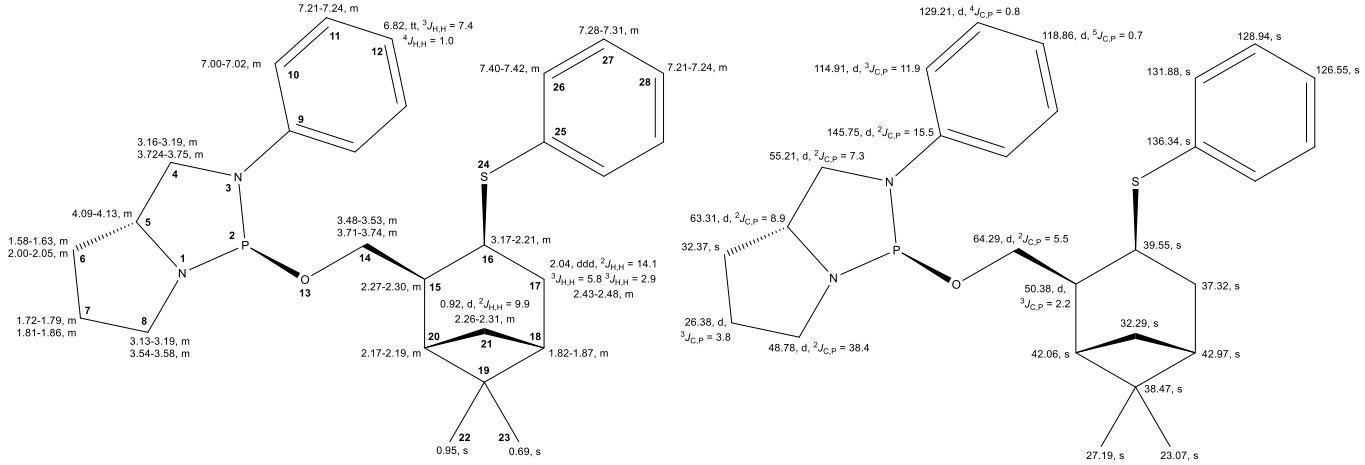
(1*R*,3a*S*)-1-(((1*S*,2*R*,3*S*,5*R*)-6,6-dimethyl-3-(phenylthio)bicyclo[3.1.1]heptan-2-yl)methoxy)-2-phenylhexahydro-1*H*-pyrrolo[1,2-*c*][1,3,2]diazaphospholidine (**L1a**): White crystals, yield 0.62 g (66 %). $[\alpha]_{\mathrm{D}}^{24}$ = +36.8 (*c* = 0.7, $CHCl_3$). ^{1}H NMR (600.1 MHz, $CDCl_3$, 25°C): 0.83 (d, ^2J(H,H) = 9.8, 1H; C(21)H_2), 0.92 (s, 3H; C(23)H_3), 1.17 (s, 3H; C(22)H_3), 1.55-1.60 (m, 1H; C(6)H_2), 1.71-1.77 (m, 1H; C(7)H_2), 1.78-1.84 (m, 1H; C(7)H_2), 1.85-1.88 (m, 1H; C(18)H), 1.96-2.02 (m, 1H; C(6)H_2), 2.04 (ddd, ^2J(H,H) = 14.1, ^3J(H,H) = 5.7, ^3J(H,H) = 2.8, 1H; C(17)H_2), 2.15-2.18 (m, 1H; C(20)H), 2.16-2.19 (m, 1H; C(15)H), 2.24-2.28 (m, 1H; C(21)H_2), 2.44 (dddd, ^2J(H,H) = 14.1, ^3J(H,H) = 9.8, ^3J(H,H) = 3.3, ^4J(H,H) = 2.1, 1H; C(17)H_2), 3.12-3.17 (m, 1H; C(8)H_2), 3.15-3.18 (m, 1H; C(4)H_2), 3.22 (ddd, ^3J(H,H) = 9.8, ^3J(H,H) = 7.6, ^3J(H,H) = 5.7, 1H; C(16)H), 3.53-3.59 (m, 1H; C(8)H_2), 3.62-3.65 (m, 1H; C(14)H_2), 3.70 (td, ^2J(H,H) = ^3J(H,P) = 9.7, ^3J(H,H) = 7.4, 1H; C(14)H_2), 3.74-3.76 (m, 1H; C(4)H_2), 4.08-4.12 (m, 1H; C(5)H), 6.82 (tt, ^3J(H,H) = 7.3, ^4J(H,H) = 1.1, 1H; C(12)H), 6.99-7.01 (m, 2H; C(10)H), 7.14-7.17 (m, 1H; C(28)H), 7.18-7.23 (m, 4H; C(11)H, C(27)H), 7.30-7.32 (m, 2H; C(26)H) ppm. ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$, 25°C): 23.48 (s; C(23)H_3), 26.38 (d, ^3J(C,P) = 3.8; C(7)H_2), 27.74 (s; C(22)H_3), 32.36 (s; C(6)H_2), 32.54 (s; C(21)H_2), 37.36 (s; C(17)H_2), 38.64 (s; C(19)), 39.70 (s; C(16)H), 42.10 (s; C(18)H), 42.69 (s; C(20)H), 48.74 (d, ^2J(C,P) = 38.4; C(8)H_2), 50.18 (d, ^3J(C,P) = 2.6; C(15)H), 54.90 (d, ^2J(C,P) = 7.3; C(4)H_2), 63.47 (d, ^2J(C,P) = 8.7; C(5)H), 64.78 (d, ^2J(C,P) = 4.3; C(14)H_2), 115.05 (d, ^3J(C,P) = 11.8; C(10)H), 118.93 (d, ^5J(C,P) = 0.8; C(12)H), 126.77 (s; C(28)H), 128.84 (s; C(27)H), 129.18 (d, ^4J(C,P) = 0.9; C(11)H), 132.00 (s; C(26)H), 136.11 (s; C(25)), 145.90 (d, ^2J(C,P) = 15.7; C(9)) ppm. ^{31}P{^{1}H} NMR (242.9 MHz, $CDCl_3$, 25°C): 122.15 (s) ppm. $C_{27}H_{35}N_2OPS$ (466.22): calcd. C, 69.50; H, 7.56; N, 6.00; found C, 69.71; H, 8.02; N, 5.88. Melting point 135-137 °C (with decomposition).



Atom numbering as well as ^{1}H (left) and ^{13}C{^{1}H} (right) NMR signal assignment for **L1a**.

EXPERIMENTAL SECTION

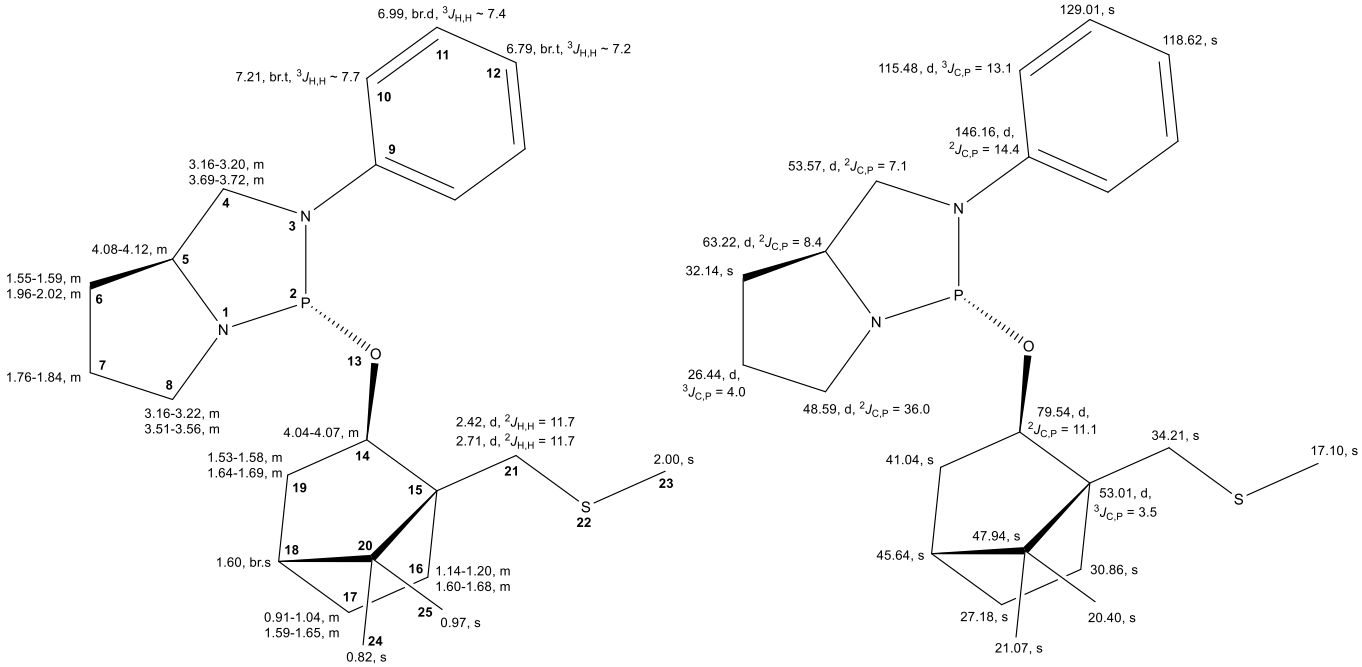
(1*S*,3a*R*)-1-(((1*S*,2*R*,3*S*,5*R*)-6,6-dimethyl-3-(phenylthio)bicyclo[3.1.1]heptan-2-yl)methoxy)-2-phenylhexahydro-1*H*-pyrrolo[1,2-*c*][1,3,2]diazaphospholidine (**L1b**): White crystals, yield 0,85 g (91 %). $[\alpha]_{\mathrm{D}}^{24}$ = +185.2 (*c* = 1.2, $CHCl_3$). ^{1}H NMR (600.1 MHz, $CDCl_3$, 25^{o}C): 0.69 (s, 3H; C(23)H_3), 0.92 (d, ^2J(H,H) = 9.9, 1H; C(21)H_2), 0.95 (s, 3H; C(22)H_3), 1.58-1.63 (m, 1H; C(6)H_2), 1.72-1.79 (m, 1H; C(7)H_2), 1.81-1.86 (m, 1H; C(7)H_2), 1.82-1.87 (m, 1H; C(18)H), 2.00-2.05 (m, 1H; C(6)H_2), 2.04 (ddd, ^2J(H,H) = 14.4, ^3J(H,H) = 5.8, ^3J(H,H) = 2.9, 1H; C(17)H_2), 2.17-2.19 (m, 1H; C(20)H), 2.26-2.31 (m, 1H; C(21)H_2), 2.27-2.30 (m, 1H; C(15)H), 2.43-2.48 (m, 1H; C(17)H_2), 3.13-3.19 (m, 1H; C(8)H_2), 3.16-3.19 (m, 1H; C(4)H_2), 3.17-3.21 (m, 1H; C(16)H), 3.48-3.53 (m, 1H; C(14)H_2), 3.54-3.58 (m, 1H; C(8)H_2), 3.71-3.74 (m, 1H; C(14)H_2), 3.72-3.75 (m, 1H; C(4)H_2), 4.09-4.13 (m, 1H; C(5)H), 6.82 (tt, ^3J(H,H) = 7.4, ^4J(H,H) = 1.0, 1H; C(12)H), 7.00-7.02 (m, 2H; C(10)H), 7.21-7.24 (m, 3H; C(11)H and C(28)H), 7.28-7.31 (m, 2H; C(27)H), 7.40-7.42 (m, 2H; C(26)H) ppm. ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$, 25^{o}C): 23.07 (s; CH_3), 26.38 (d, ^3J(C,P) = 3.8; C(7)H_2), 27.19 (s; CH_3), 32.29 (s; C(21)H_2), 32.37 (s; C(6)H_2), 37.32 (s; C(17)H_2), 38.47 (s; C(19)), 39.55 (s; C(16)H), 42.06 (s; C(20)H), 42.97 (s; C(18)H), 48.78 (d, ^2J(C,P) = 38.4; C(8)H_2), 50.38 (d, ^3J(C,P) = 2.2; C(15)H), 55.21 (d, ^2J(C,P) = 7.3; C(4)H_2), 63.31 (d, ^2J(C,P) = 8.9; C(5)H), 64.29 (d, ^2J(C,P) = 5.5; C(14)H_2), 114.91 (d, ^3J(C,P) = 11.9; C(10)H), 118.86 (d, ^5J(C,P) = 0.7; C(12)H), 126.55 (s; C(28)H), 128.94 (s; C(27)H), 129.21 (d, ^4J(C,P) = 0.8; C(11)H), 131.88 (s; C(26)H), 136.34 (s; C(25)), 145.75 (d, ^2J(C,P) = 15.5; C(9)) ppm. ^{31}P{^{1}H} NMR (242.9 MHz, $CDCl_3$, 25^{o}C): 120.48 (s) ppm. $C_{27}H_{35}N_2OPS$ (466.22): calcd. C, 69.50; H, 7.56; N, 6.00; found C, 69.68; H, 8.03; N, 6.09. Melting point 132-134 ^{o}C (with decomposition).



Atom numbering as well as ^{1}H (left) and ^{13}C{^{1}H} (right) NMR signal assignment for **L1b**.

EXPERIMENTAL SECTION

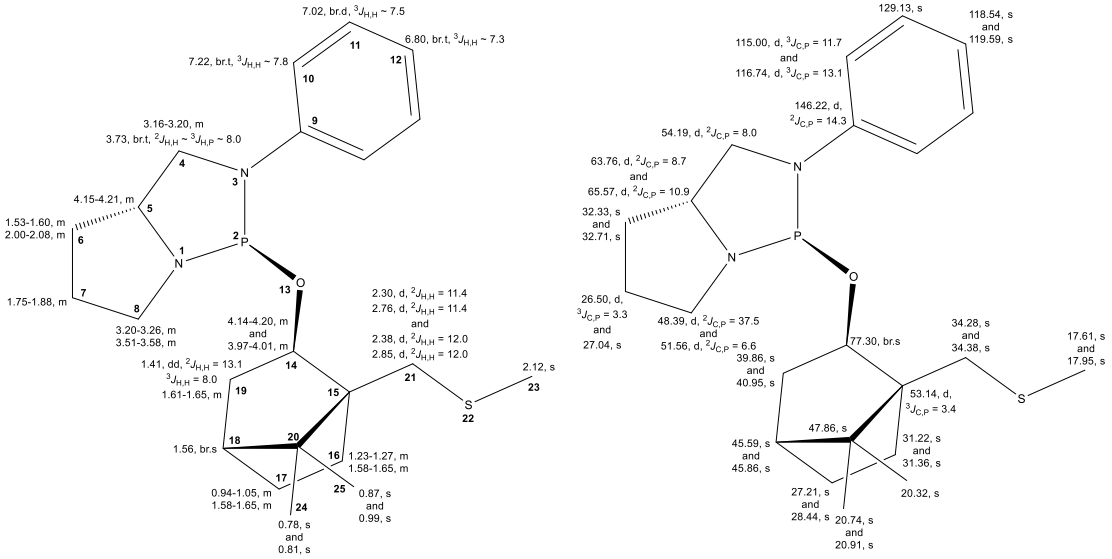
(1*R*,3a*S*)-1-(((1*S*,2*R*,4*R*)-7,7-dimethyl-1-((methylthio)methyl)bicyclo[2.2.1]heptan-2-yl)oxy)-2-phenylhexahydro-1*H*-pyrrolo[1,2-*c*][1,3,2]diazaphospholidine (**L2a**): Colorless oil, yield 0.33 g (41 %). $[\alpha]_D^{24}$ = -167.5 (*c* = 1.5, $CHCl_3$). ^{1}H NMR (600.1 MHz, $CDCl_3$, 25°C): 0.82 (s, 3H; C(24)H_3), 0.91-1.04 (m, 1H; C(17)H_2), 0.97 (s, 3H; C(25)H_3), 1.14-1.20 (m, 1H; C(16)H_2), 1.53-1.58 (m, 1H; C(19)H_2), 1.55-1.59 (m, 1H; C(6)H_2), 1.59-1.65 (m, 1H; C(17)H_2), 1.60 (br.s, 1H; C(18)H), 1.60-1.68 (m, 1H; C(16)H_2), 1.64-1.69 (m, 1H; C(19)H_2), 1.76-1.84 (m, 2H; C(7)H_2), 1.96-2.02 (m, 1H; C(6)H_2), 2.00 (s, 3H; C(23)H_3), 2.42 (d, ^2J(H,H) = 11.7, 1H; C(21)H_2), 2.71 (d, ^2J(H,H) = 11.7, 1H; C(21)H_2), 3.16-3.20 (m, 1H; C(4)H_2), 3.16-3.22 (m, 1H; C(8)H_2), 3.51-3.56 (m, 1H; C(8)H_2), 3.69-3.72 (m, 1H; C(4)H_2), 4.04-4.07 (m, 1H; C(14)H), 4.08-4.12 (m, 1H; C(5)H), 6.79 (br.t, ^3J(H,H) ~ 7.2, 1H; C(12)H), 6.99 (br.d, ^3J(H,H) ~ 7.4, 2H; C(11)H), 7.21 (br.t, ^3J(H,H) ~ 7.7, 2H; C(10)H), ppm. ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$, 25°C): 17.10 (s; C(23)H_3), 20.40 (s; C(25)H_3), 21.07 (s; C(24)H_3), 26.44 (d, ^3J(C,P) = 4.0; C(7)H_2), 27.18 (s; C(17)H_2), 30.86 (s; C(16)H_2), 32.14 (s; C(6)H_2), 34.21 (s; C(21)H_2), 41.04 (s; C(19)H_2), 45.64 (s; C(18)H), 47.94 (s; C(20)), 48.59 (d, ^2J(C,P) = 36.0; C(8)H_2), 53.01 (d, ^3J(C,P) = 3.5; C(15)), 53.57 (d, ^2J(C,P) = 7.1; C(4)H_2), 63.22 (d, ^2J(C,P) = 8.4; C(5)H), 79.54 (d, ^2J(C,P) = 11.1; C(14)H), 115.48 (d, ^3J(C,P) = 13.1; C(10)H), 118.62 (s; C(12)H), 129.01 (s; C(11)H), 146.16 (d, ^2J(C,P) = 14.4; C(9)) ppm. ^{31}P{^{1}H} NMR (242.9 MHz, $CDCl_3$, 25°C): 133.12 (s) ppm. $C_{22}H_{33}N_2OPS$ (404.21): calcd. C, 65.32; H, 8.22; N, 6.92; found C, 65.57; H, 8.32; N, 7.02.



Atom numbering as well as ^{1}H (left) and ^{13}C{^{1}H} (right) NMR signal assignment for **L2a**.

EXPERIMENTAL SECTION

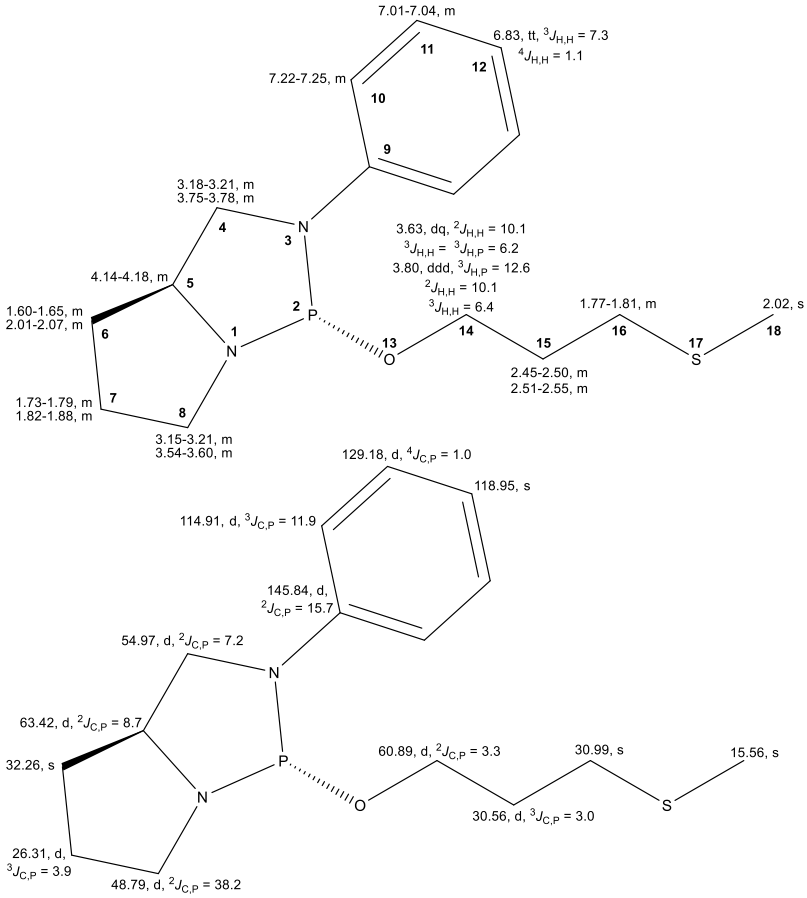
(1*S*,3a*R*)-1-(((1*S*,2*R*,4*R*)-7,7-dimethyl-1-((methylthio)methyl)bicyclo[2.2.1]heptan-2-yl)oxy)-2-phenylhexahydro-1*H*-pyrrolo[1,2-*c*][1,3,2]diazaphospholidine (**L2b**): White powder, yield 0.54 g (67 %). $[\alpha]_{\mathrm{D}}^{24}$ = +206.1 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (499.9 MHz, $CDCl_3$, r.t.): 0.78 (~ 10%) and 0.81 (~ 90%) (s, 3H; C(24)H_3), 0.87 (~ 10%) and 0.99 (~ 90%) (s, 3H; C(25)H_3), 0.94-1.05 (m, 1H; C(17)H_2), 1.23-1.27 (m, 1H; C(16)H_2), 1.41 (dd, ^2J(H,H) = 13.1, ^3J(H,H) = 8.0, 1H; C(19)H_2), 1.53-1.60 (m, 1H; C(6)H_2), 1.56 (br.s, 1H; C(18)H), 1.58-1.65 (m, 2H; C(16)H_2) and C(17)H_2), 1.61-1.65 (m, 1H; C(19)H_2), 1.75-1.88 (m, 2H; C(7)H_2), 2.00-2.08 (m, 1H; C(6)H_2), 2.12 (s, 3H; C(23)H_3), 2.30 (~ 10%) and 2.38 (~ 90%) (d, ^2J(H,H) = 11.4 and d, ^2J(H,H) = 12.0, 1H; C(21)H_2), 2.76 (~ 10%) and 2.85 (~ 90%) (d, ^2J(H,H) = 11.4 and d, ^2J(H,H) = 12.0, 1H; C(21)H_2), 3.16-3.20 (m, 1H; C(4)H_2), 3.20-3.26 (m, 1H; C(8)H_2), 3.51-3.58 (m, 1H; C(8)H_2), 3.73 (br.t, ^3J(H,H) ~ ^3J(H,P) ~ 8.0, 1H; C(4)H_2), 3.97-4.01 (~ 10%) and 4.14-4.20 (~ 90%) (m, 1H; C(14)H), 4.15-4.21 (m, 1H; C(5)H), 6.80 (br.t, ^3J(H,H) ~ 7.3, 1H; C(12)H), 7.02 (br.d, ^3J(H,H) ~ 7.5, 2H; C(11)H), 7.22 (br.t, ^3J(H,H) ~ 7.8, 2H; C(10)H), ppm. ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, r.t.): 17.95 (s; C(23)H_3), 20.32 (s; C(25)H_3), 20.91 (s; C(24)H_3), 26.50 (d, ^3J(C,P) = 3.3; C(7)H_2), 27.21 (s; C(17)H_2), 31.22 (s; C(16)H_2), 32.71 (s; C(6)H_2), 34.28 (s; C(21)H_2), 39.86 (s; C(19)H_2), 45.86 (s; C(18)H), 47.86 (s; C(20)), 48.39 (d, ^2J(C,P) = 37.5; C(8)H_2), 53.14 (d, ^3J(C,P) = 3.4; C(15)), 54.19 (d, ^2J(C,P) = 8.0; C(4)H_2), 63.76 (d, ^2J(C,P) = 8.7; C(5)H), 77.30 (br.s; C(14)H), 115.00 (d, ^3J(C,P) = 11.7; C(10)H), 118.54 (s; C(12)H), 129.13 (s; C(11)H), 146.22 (d, ^2J(C,P) = 14.3; C(9)) (93.0%) 17.61 (s; C(23)H_3), 20.32 (s; C(25)H_3), 20.74 (s; C(24)H_3), 27.04 (s; C(7)H_2), 28.44 (s; C(17)H_2), 31.36 (s; C(16)H_2), 32.33 (s; C(6)H_2), 34.38 (s; C(21)H_2), 40.95 (s; C(19)H_2), 45.59 (s; C(18)H), 47.86 (s; C(20)), 51.56 (d, ^2J(C,P) = 6.6; C(8)H_2), 53.14 (d, ^3J(C,P) = 3.4; C(15)), 54.19 (d, ^2J(C,P) = 8.0; C(4)H_2), 65.57 (d, ^2J(C,P) = 10.9; C(5)H), 77.30 (br.s; C(14)H), 116.74 (d, ^3J(C,P) = 13.1; C(10)H), 119.59 (s; C(12)H), 129.13 (s; C(11)H), 146.22 (d, ^2J(C,P) = 14.3; C(9)) (7.0%) ppm. ^{31}P{^{1}H} NMR (202.4 MHz, $CDCl_3$, r.t.): 117.43 (93%), 125.38 (7%) (s) ppm. $C_{22}H_{33}N_2OPS$ (404.21): calcd. C, 65.32; H, 8.22; N, 6.92; found C, 65.46; H, 8.27; N, 6.81. Melting point 88-90 ^{o}C (with decomposition).



Atom numbering as well as ^{1}H (left) and ^{13}C{^{1}H} (right) NMR signal assignment for **L2b**.

EXPERIMENTAL SECTION

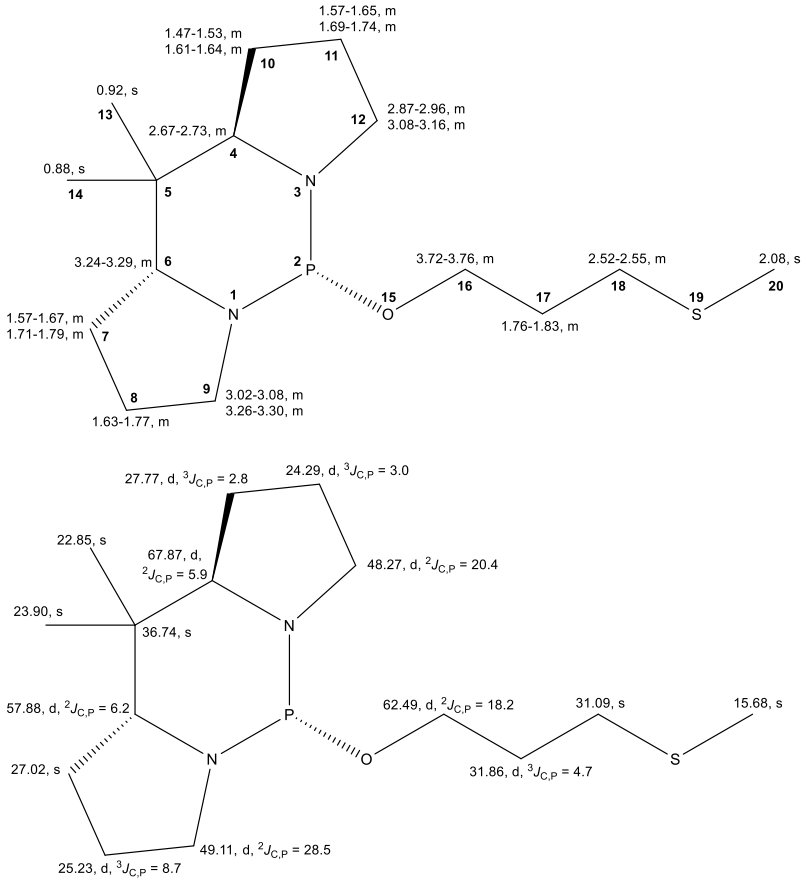
(1*R*,3a*S*)-1-(3-(methylthio)propoxy)-2-phenylhexahydro-1*H*-pyrrolo[1,2*c*][1,3,2]diazaphospholidine (**L3**): Colorless oil, yield 0.60 g (97 %). $[\alpha]_D^{24}$ = -218.3 (*c* = 2.8, $CHCl_3$). ^{1}H NMR (600.1 MHz, $CDCl_3$, 25^{o}C): 1.60-1.65 (m, 1H; C(6)H_2), 1.73-1.79 (m, 1H; C(7)H_2), 1.77-1.81 (m, 2H; C(16)H_2), 1.82-1.88 (m, 1H; C(7)H_2), 2.01-2.07 (m, 1H; C(6)H_2), 2.02 (s, 3H; C(18)H_3), 2.45-2.50 (m, 1H; C(15)H_2), 2.51-2.55 (m, 1H; C(15)H_2), 3.18-3.21 (m, 1H; C(4)H_2), 3.63 (dq, ^2J(H,H) = 10.1, ^3J(H,H) = ^3J(H,P) = 6.2, 1H; C(14)H_2), 3.75-3.78 (m, 1H; C(4)H_2), 3.80 (ddd, ^3J(H,P) = 12.6, ^2J(H,H) = 10.1, ^3J(H,H) = 6.4, 1H; C(14)H_2), 4.14-4.18 (m, 1H; C(5)H), 6.83 (tt, ^3J(H,H) = 7.3, ^4J(H,H) = 1.1, 1H; C(12)H), 7.01-7.04 (m, 2H; C(11)H), 7.22-7.25 (m, 2H; C(10)H), ppm. ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$, 25^{o}C): 15.56 (s; C(18)H_3), 26.31 (d, ^3J(C,P) = 3.9; C(7)H_2), 30.56 (d, ^3J(C,P) = 3.0; C(15)H_2), 30.99 (s; C(16)H_2), 32.26 (s; C(6)H_2), 48.79 (d, ^2J(C,P) = 38.2; C(8)H_2), 54.97 (d, ^2J(C,P) = 7.2; C(4)H_2), 60.89 (d, ^2J(C,P) = 3.3; C(14)H_2), 63.42 (d, ^2J(C,P) = 8.7; C(5)H), 114.91 (d, ^3J(C,P) = 11.9; C(10)H), 118.95 (s; C(12)H), 129.18 (d, ^4J(C,P) = 1.0; C(11)H), 145.84 (d, ^2J(C,P) = 15.7; C(9)) ppm. ^{31}P{^{1}H} NMR (242.9 MHz, $CDCl_3$, 25^{o}C): 122.40 (s) ppm. $C_{15}H_{23}N_2OPS$ (310.13): calcd. C, 58.04; H, 7.47; N, 9.03; found C, 58.21; H, 7.40; N, 9.09.



Atom numbering as well as ^{1}H (top) and ^{13}C{^{1}H} (bottom) NMR signal assignment for **L3**.

EXPERIMENTAL SECTION

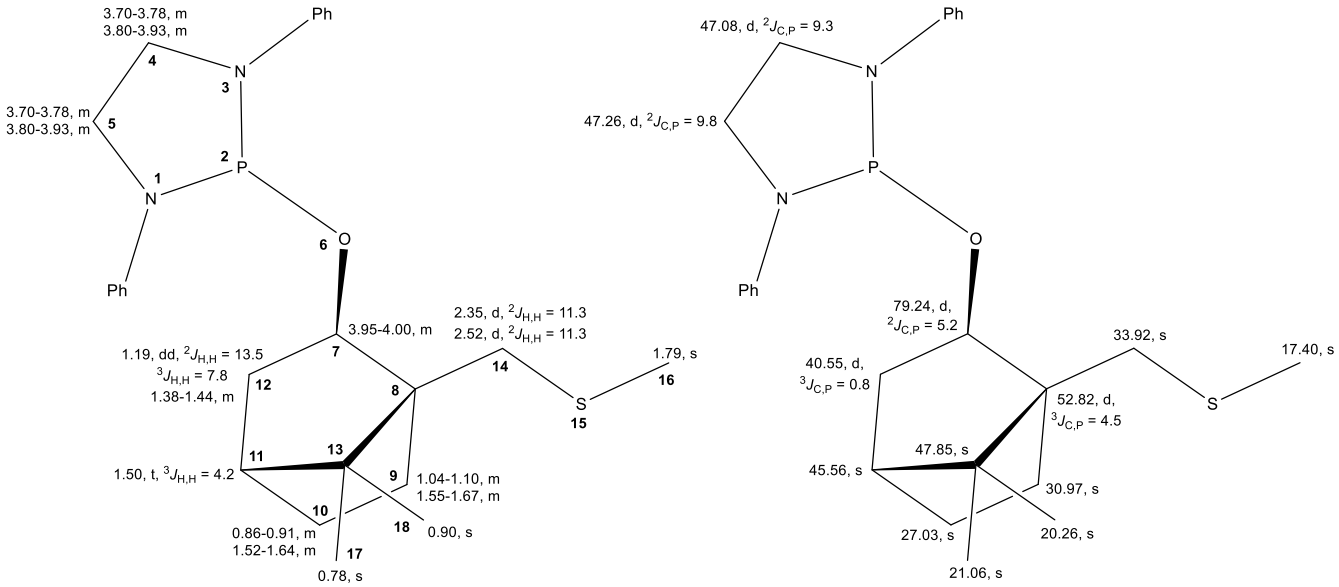
(9a*R*,10a*R*)-10,10-dimethyl-5-(3-(methylthio)propoxy)octahydro-1*H*,5*H*-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaphosphinane (**L4**): Colorless oil, yield 0.53g (84 %). $[\alpha]_D^{24}$ = +62.3 (*c* = 2.5, $CHCl_3$). ^{1}H NMR (499.9 MHz, $CDCl_3$, 25°C): 0.88 (s, 3H; C(14)H_3), 0.92 (s, 3H; C(13)H_3), 1.47-1.53 (m, 1H; C(10)H_2), 1.57-1.65 (m, 1H; C(11)H_2), 1.57-1.67 (m, 1H; C(7)H_2), 1.61-1.64 (m, 1H; C(10)H_2), 1.63-1.77 (m, 2H; C(8)H_2), 1.69-1.74 (m, 1H; C(11)H_2), 1.71-1.79 (m, 1H; C(7)H_2), 1.76-1.83 (m, 2H; C(17)H_2), 2.08 (s, 3H; C(20)H_3), 2.52-2.55 (m, 2H; C(18)H_2), 2.67-2.73 (m, 1H; C(4)H), 2.87-2.96 (m, 1H; C(12)H_2), 3.02-3.08 (m, 1H; C(9)H_2), 3.08-3.16 (m, 1H; C(12)H_2), 3.24-3.29 (m, 1H; C(6)H), 3.26-3.30 (m, 1H; C(9)H_2), 3.72-3.76 (m, 2H; C(16)H_2) ppm. ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 25°C): 15.68 (s; C(20)H_3), 22.85 (s; C(13)H_3), 23.90 (s; C(14)H_3), 24.29 (d, ^3J(C,P) = 3.0; C(11)H_2), 25.23 (d, ^3J(C,P) = 8.7; C(8)H_2), 27.02 (s; C(7)H_2), 27.77 (d, ^3J(C,P) = 2.8; C(10)H_2), 31.09 (s; C(18)H_2), 31.86 (d, ^3J(C,P) = 4.7; C(17)H_2), 36.74 (s; C(5)), 48.27 (d, ^2J(C,P) = 20.4; C(12)H_2), 49.11 (d, ^2J(C,P) = 28.5; C(9)H_2), 57.88 (d, ^2J(C,P) = 6.2; C(6)H), 62.49 (d, ^2J(C,P) = 18.2; C(16)H_2), 67.87 (d, ^2J(C,P) = 5.9; C(4)H) ppm. ^{31}P{^{1}H} NMR (202.3 MHz, $CDCl_3$, 25°C): 126.74 (s) ppm. $C_{15}H_{29}N_2OPS$ (316.17): calcd. C, 56.93; H, 9.24; N, 8.85; found C, 57.13; H, 9.19; N, 8.75.



Atom numbering as well as ^{1}H (top) and ^{13}C{^{1}H} (bottom) NMR signal assignment for **L4**.

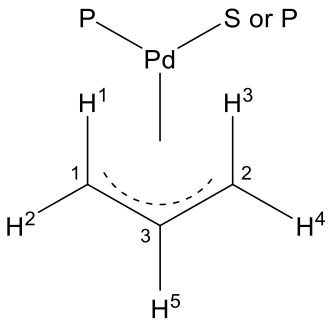
EXPERIMENTAL SECTION

2-(((1S,2R,4R)-7,7-dimethyl-1-((methylthio)methyl)bicyclo[2.2.1]heptan-2-yl)oxy)-1,3-diphenyl-1,3,2-diazaphospholidine (**L5**): White powder, yield 0.79 g (90 %). $[\alpha]_D^{24}$ = -32.3 (*c* = 2.5, $CHCl_3$). ^{1}H NMR (400.1 MHz, $CDCl_3$, 25^{o}C): 0.78 (s, 3H; C(17)H_3), 0.86-0.91 (m, 1H; C(10)H_2), 0.90 (s, 3H; C(18)H_3), 1.04-1.10 (m, 1H; C(9)H_2), 1.19 (dd, ^2J(H,H) = 13.5, ^3J(H,H) = 7.8, 1H; C(12)H_2), 1.38-1.44 (m, 1H; C(12)H_2), 1.50 (t, ^3J(H,H) = 4.2, 1H; C(11)H), 1.52-1.64 (m, 1H; C(10)H_2), 1.55-1.67 (m, 1H; C(9)H_2), 1.79 (s, 3H; C(16)H_3), 2.35 (d, ^2J(H,H) = 11.3, 1H; C(14)H_2), 2.52 (d, ^2J(H,H) = 11.7, 1H; C(14)H_2), 3.70-3.78 (m, 2H; C(4)H_2 and C(5)H_2), 3.80-3.93 (m, 2H; C(4)H_2 and C(5)H_2), 3.95-4.00 (m, 1H; C(7)H), 6.86-6.90 (m, 2H; CH), 7.15-7.19 (m, 4H; CH), 7.25-7.29 (m, 4H; CH) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 25^{o}C): 17.40 (s; C(16)H_3), 20.26 (s; C(18)H_3), 21.06 (s; C(17)H_3), 27.03 (s; C(10)H_2), 30.97 (s; C(9)H_2), 33.92 (s; C(14)H_2), 40.55 (d, ^3J(C,P) = 0.8; C(12)H_2), 45.56 (s; C(11)H), 47.08 (d, ^2J(C,P) = 9.3; C(4)H_2), 47.26 (d, ^2J(C,P) = 9.8; C(5)H_2), 47.85 (s; C(13)), 52.82 (d, ^3J(C,P) = 4.5; C(8)), 79.24 (d, ^2J(C,P) = 5.2; C(7)H), 115.31 (d, ^3J(C,P) = 14.8; CH), 115.93 (d, ^3J(C,P) = 14.6; CH), 119.62 (d, ^5J(C,P) = 1.6; CH), 119.91 (d, ^5J(C,P) = 2.0; CH), 129.23 (s; CH), 129.32 (d, ^4J(C,P) = 1.1; CH), 145.44 (d, ^2J(C,P) = 4.6; C), 145.62 (d, ^2J(C,P) = 5.8; C) ppm. ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$, 25^{o}C): 105.57 (s) ppm. $C_{25}H_{33}N_2OPS$ (440.21): calcd. C, 68.15; H, 7.55; N, 6.36; found C, 68.22; H, 7.49; N, 6.39. Melting point 144-146 ^{o}C (with decomposition).



Aliphatic atom numbering as well as aliphatic ^{1}H (left) and ^{13}C{^{1}H} (right) NMR signal assignment for **L5**.

EXPERIMENTAL SECTION



Proton and carbon numbering for the η^3-allyl ligand for NMR signals assignment of allylpalladium(II) complexes.

[Pd(allyl)(**L1a**)]BF_4: Yellowish powder, yield 0.112 g (80 %). ^{1}H NMR (600.1 MHz, $CDCl_3$, 25^{o}C): 0.94 and 0.97 (s and s, 3H; C(23)H_3), 1.24 (s, 3H; C(22)H_3), 1.33 and 1.39 (d, ^2J(H,H) = 10.3 and d, ^2J(H,H) = 10.4, 1H; C(21)H_2), 1.87-1.95 (m, 2H; C(6)H_2 and C(7)H_2), 2.02-2.06 (m, 2H; C(18)H and C(20)H), 2.06-2.11 (m, 1H; C(7)H_2), 2.19-2.25 (m, 1H; C(6)H_2), 2.21-2.26 (m, 1H; C(17)H_2), 2.26-2.36 (m, 1H; C(17)H_2), 2.48-2.54 (m, 1H; C(21)H_2), 2.53-2.56 and 2.71-2.73 (m and m, 1H; C(15)H), 3.24-3.30 and 3.36-3.41 (m and m, 1H; C(8)H_2), 3.42-3.47 (m, 1H; C(4)H_2), 3.42-3.47 and 3.70-3.76 (m and m, 1H; C(8)H_2), 3.80-3.84 (m, 1H; C(4)H_2), 4.08-4.30 (m, 3H; C(14)H_2 and C(16)H), 4.34-4.40 (m, 1H; C(5)H), 7.04 (t, ^3J(H,H) = 7.4, 1H; C(12)H), 7.08 and 7.18 (d, ^3J(H,H) = 8.1 and d, ^3J(H,H) = 8.1, 2H; C(10)H), 7.31-7.34 and 7.34-7.36 (m, 2H; C(11)H), 7.53-7.59 (m, 3H; C(27)H and C(28)H), 7.68-7.69 and 7.76-7.78 (m, 2H; C(26)H) (**L1a**), 2.28-2.30 (m, 1H; C(1)H_2(*anti*)), 2.60 (t, ^3J(H,H) = ^3J(H,P) = 13.8, 1H; C(3)H_2(*anti*)), 3.80-3.82 (m, 1H; C(1)H_2(*syn*)), 4.25-4.30 (m, 1H; C(3)H_2(*syn*)), 5.59-5.66 (m, 1H; C(2)H) (η^3-allyl ligand, 53%), 2.97 (d, ^3J(H,H) = 12.5, 1H; C(1)H_2(*anti*)), 3.51 (br.d, ^3J(H,H) ~ 6.7, 1H; C(1)H_2(*syn*)), 3.64 (t, ^3J(H,H) = ^3J(H,P) = 13.4, 1H; C(3)H_2(*anti*)), 3.68 (td, ^3J(H,H) = ^3J(H,P) = 7.6, ^4J(H,H) = 1.9, 1H; C(3)H_2(*syn*)), 4.92-4.99 (m, 1H; C(2)H) (η^3-allyl ligand, 47%) ppm. ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$, 25^{o}C): 23.68 and 23.70 (s and s; C(23)H_3), 26.57 and 26.59 (s and s; C(22)H_3), 26.75 (d, ^3J(C,P) = 4.2; C(7)H_2), 30.37 (s; C(21)H_2), 31.29 and 31.44 (s and s; C(6)H_2), 35.02 and 35.13 (s and s; C(17)H_2), 38.29 and 38.33 (s and s; C(19)), 41.62 (s; C(18)H), 42.23 and 42.53 (d, ^3J(C,P) = 1.9 and s; C(16)H), 43.08 and 43.14 (s and s; C(20)H), 46.33 and 46.51 (s and s; C(15)H), 50.03 and 50.20 (d, ^2J(C,P) = 20.5 and d, ^2J(C,P) = 20.7; C(8)H_2), 54.37 and 54.67 (d, ^2J(C,P) = 2.8 and d, ^2J(C,P) = 2.6; C(4)H_2), 62.86 and 62.89 (s and s; C(5)H), 68.72 and 68.86 (d, ^2J(C,P) = 5.3 and d, ^2J(C,P) = 5.6; C(14)H_2), 116.71 and 116.87 (d, ^3J(C,P) = 8.0 and d, ^3J(C,P) = 8.3; C(10)H), 122.35 and 122.38 (s and s; C(12)H), 129.83 and 129.88 (s and s; C(11)H), 130.52 and 130.55 (s and s; C(27)H), 131.33 and 131.42 (s and s; C(28)H), 131.84 and 133.41 (s and s; C(25)), 132.59 and 132.75 (s and s; C(26)H), 142.67 and 142.79 (d, ^2J(C,P) = 11.8 and d, ^2J(C,P) = 11.9; C(9)) (**L1a**), 62.56 (d, ^2J(C,P) = 4.2; C(1)H_2), 82.56 (d, ^2J(C,P) = 36.9; C(3)H_2), 123.72 (d, ^2J(C,P) = 8.2; C(2)H) (η^3-allyl ligand, 53.2%), 62.46 (d, ^2J(C,P) = 3.9; C(1)H_2), 84.04 (d, ^2J(C,P) = 35.7; C(3)H_2), 123.50 (d, ^2J(C,P) = 8.0; C(2)H) (η^3-allyl ligand, 46.8%) ppm. ^{31}P{^{1}H} NMR

(242.9 MHz, $CDCl_3$, 25°C): 128.28 (s) (53.2%), 128.45 (s) (46.8%) ppm. $C_{30}H_{40}BF_4N_2OPPdS$ (700.17): calcd. C 51.41, H 5.75, N 4.00; found C 51.69, H 5.84, N 4.15; M/z = 613.1656 (calcd 613.1628) Da for [Pd(allyl)(**L1a**)]$^+$.

Pd(allyl)(**L1b**)]BF_4: Yellowish powder, yield 0.108 g (77 %). $^{31}P\{^1H\}$ NMR (242.9 MHz, $CDCl_3$, 25°C): 117.55 (s) (12.2%), 118.08 (s) (2.0%), 127.21 (s) (26.1%), 127.54 (s) (37.5%), 133.22 (s) (3.6%), 133.49 (s) (6.7%), 140.65 (s) (4.5%), 140.89 (s) (7.3%) ppm. $C_{30}H_{40}BF_4N_2OPPdS$ (700.17): calcd. C 51.41, H 5.75, N 4.00; found C 51.62, H 5.80, N 3.87; M/z = 613.1652 (calcd 613.1628) Da for [Pd(allyl)(**L1b**)]$^+$.

[Pd(allyl)(**L2a**)]BF_4: White powder, yield 0.115 g (90 %). ^1H NMR (600.1 MHz, $CDCl_3$, 25°C): 0.91-1.06 (m, 6H; CH_3), 1.20-1.35 (m, 6H; CH_2 and CH_2(pentane)), 1.65-2.26 (m, 12H; CH_2, CH and CH_2(pentane)), 2.67-2.74 (m, 3H; CH_3), 2.80-2.94 (m, 1H; CH_2), 3.03-3.08 (m, 1H; CH_2), 3.23-3.44 (m, 4H; CH_2), 3.52-3.84 (m, 4H; CH_2), 4.24-4.31 (m, 1H; CH), 4.44-4.83 (m, 2H; CH_2 and CH), 5.55-5.62 (m, 1H; CH), 6.77-6.88 (m, 2H; CH (Ph)), 7.00-7.03 (m, 1H; CH(Ph)), 7.30-7.35 (m, 2H; CH(Ph)) ppm. $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$, 25°C): 19.98 (s; C(25)H_3), 20.49 (s; C(24)H_3), 23.31 (s; C(23)H_3), 26.82 (d, ^3J(C,P) = 5.5; C(7)H_2), 27.14 (s; C(17)H_2), 30.94 (d, ^3J(C,P) = 3.5; C(6)H_2), 31.03 (s; C(16)H_2), 38.84 (d, ^3J(C,P) = 7.8; C(21)H_2), 40.87 (d, ^3J(C,P) = 5.1; C(19)H_2), 45.61 (s; C(18)H), 49.17 (s; C(20)), 50.31 (d, ^2J(C,P) = 23.5; C(8)H_2), 52.83 (s; C(15)), 54.77 (d, ^2J(C,P) = 2.3; C(4)H_2), 61.84 (s; C(5)H), 82.13 (d, ^2J(C,P) = 13.5; C(14)H), 116.48 (d, ^3J(C,P) = 8.3; C(10)H), 121.68 (s; C(12)H), 129.90 (s; C(11)H), 142.94 (d, ^2J(C,P) = 11.1; C(9)) (**L2a**), 64.23 (d, ^2J(C,P) = 4.7; C(1)H_2), 79.96 (d, ^2J(C,P) = 35.3; C(3)H_2), 123.91 (d, ^2J(C,P) = 8.1; C(2)H) (η^3-allyl ligand) (44.8%), 19.99 (s; C(25)H_3), 20.51 (s; C(24)H_3), 24.25 (d, ^3J(C,P) = 0.9; C(23)H_3), 26.70 (d, ^3J(C,P) = 5.7; C(7)H_2), 27.23 (s; C(17)H_2), 31.13 (s; C(16)H_2), 31.28 (d, ^3J(C,P) = 3.2; C(6)H_2), 38.96 (d, ^3J(C,P) = 8.4; C(21)H_2), 40.52 (d, ^3J(C,P) = 4.6; C(19)H_2), 45.65 (s; C(18)H), 49.33 (s; C(20)), 49.99 (d, ^2J(C,P) = 22.3; C(8)H_2), 53.02 (s; C(15)), 55.26 (d, ^2J(C,P) = 3.1; C(4)H_2), 61.73 (s; C(5)H), 82.17 (d, ^2J(C,P) = 15.2; C(14)H), 116.91 (d, ^3J(C,P) = 7.9; C(10)H), 121.90 (s; C(12)H), 129.90 (s; C(11)H), 142.94 (d, ^2J(C,P) = 11.1; C(9)) (**L2a**), 63.97 (d, ^2J(C,P) = 4.8; C(1)H_2), 79.98 (d, ^2J(C,P) = 35.8; C(3)H_2), 123.01 (d, ^2J(C,P) = 8.3; C(2)H) (η^3-allyl ligand) (40.5%) ppm. $^{31}P\{^1H\}$ NMR (242.9 MHz, $CDCl_3$, 25°C): 119.43 (s) (4.9%), 119.92 (s) (5.7%), 124.60 (s) (1.3%), 125.51 (s) (1.7%), 128.61 (s) (45.3%), 130.47 (s) (41.0%) ppm. $C_{25}H_{38}BF_4N_2OPPdS$ (638.15): calcd. C 47.00, H 6.00, N 4.39; found C 46.71, H 6.11, N 4.59; M/z = 551.1492 (calcd 551.1472) Da for [Pd(allyl)(**L2a**)]$^+$.

[Pd(allyl)(**L2b**)]BF_4: White powder, yield 0.112 g (88 %).^1H NMR (600.1 MHz, $CDCl_3$, 25°C): 0.91 (s, 3H; CH_3), 0.91 (s, 3H; CH_3), 1.16-1.20 (m, 1H; CH_2), 1.45-1.50 (m, 1H; CH_2), 1.61-2.06 (m, 9H; CH_2 and CH), 2.14-2.20 (m, 1H; CH_2), 2.68-2.76 (br.m, 1H; CH_2), 2.72 (s, 3H; CH_3), 3.26-3.59 (m, 6H; CH_2), 3.78-3.82 (m, 1H; CH_2), 4.22-4.31 (m, 2H; CH), 4.66-4.69 (m, 1H; CH_2), 5.42-5.63 (br.m, 1H; CH), 7.01-7.05 (m,

3H; CH (Ph)), 7.32-7.35 (m, 2H; CH(Ph)) ppm. $^{13}C\{^{1}H\}$ NMR (150.9 MHz, $CDCl_3$, 25°C): 19.85 (s; C(25)H_3), 20.24 (s; C(24)H_3), 26.31 (br.s; C(23)H_3), 26.98 (d, ^{3}J(C,P) = 4.7; C(7)H_2), 27.14 (s; C(17)H_2), 31.12 (br.s; C(6)H_2), 31.19 (s; C(16)H_2), 39.44 (d, ^{3}J(C,P) = 2.3; C(21)H_2), 40.64 (br.s; C(19)H_2), 46.02 (s; C(18)H), 49.23 (s; C(15)), 49.45 (d, ^{2}J(C,P) = 18.9; C(8)H_2), 52.88 (s; C(20)), 54.93 (d, ^{2}J(C,P) = 2.2; C(4)H_2), 62.07 (s; C(5)H), 77.54 (s; C(14)H), 116.84 (d, ^{3}J(C,P) = 7.8; C(10)H), 122.43 (s; C(12)H), 130.02 (s; C(11)H), 142.88 (d, ^{2}J(C,P) = 11.1; C(9)) (**L2b**), 61.14 (br.s; C(1)H_2), 80.83-81.21 (br.m; C(3)H_2), 123.58 (br.s; C(2)H) (η^3-allyl ligand) ppm. $^{31}P\{^{1}H\}$ NMR (242.9 MHz, $CDCl_3$, 25°C): 125.03 (s) (93.6%), 129.71 (br.s) (6.4%) ppm. $C_{25}H_{38}BF_4N_2OPPdS$ (638.15): calcd. C 47.00, H 6.00, N 4.39; found C 47.21, H 6.07, N 4.30; M/z = 551.1488 (calcd 551.1472) Da for [Pd(allyl)(**L2b**)]$^+$.

[Pd(allyl)(**L4**)]BF_4: Gray powder, yield 0.103 g (94 %). ^{1}H NMR (600.1 MHz, $CDCl_3$, 25°C): 0.88 (s, 3H; CH_3), 0.92 (s, 3H; CH_3), 2.08 (s, 3H; CH_3), 1.47-1.53 (m, 1H; CH_2), 1.57-1.67 (m, 2H; CH_2), 1.61-1.64 (m, 1H; CH_2), 1.63-1.77 (m, 2H; CH_2), 1.69-1.74 (m, 1H; CH_2), 1.71-1.79 (m, 1H; CH_2), 1.76-1.83 (m, 2H; CH_2), 2.52-2.55 (m, 2H; CH_2), 2.67-2.73 (m, 1H; CH), 2.87-2.96 (m, 1H; CH_2), 3.02-3.08 (m, 1H; CH_2), 3.08-3.16 (m, 1H; CH_2), 3.24-3.29 (m, 1H; CH), 3.26-3.30 (m, 1H; CH_2), 3.72-3.76 (m, 2H; CH_2) (**L4**), 3.18-3.20 (m, 1H; C(1)H_2(*anti*)), 3.55 (t, ^{3}J(H,H) = ^{3}J(H,P) = 13.6, 1H; C(3)H_2(*anti*)), 4.05 (dt, ^{3}J(H,H) = 6.9, ^{4}J(H,H) = ^{3}J(H,P) = 2.1, 1H; C(1)H_2(*syn*)), 4.69 (td, ^{3}J(H,H) = ^{3}J(H,P) = 8.2, ^{4}J(H,H) = 2.1, 1H; C(3)H_2(*syn*)), 5.68-5.75 (m, 1H; C(2)H) (η^3-allyl ligand, 55.0%), 3.12-3.15 (m, 1H; C(1)H_2(*anti*)), 3.62 (t, ^{3}J(H,H) = ^{3}J(H,P) = 13.6, 1H; C(3)H_2(*anti*)), 4.07 (dt, ^{3}J(H,H) = 6.9, ^{4}J(H,H) = ^{3}J(H,P) = 2.0, 1H; C(1)H_2(*syn*)), 4.67 (td, ^{3}J(H,H) = ^{3}J(H,P) = 8.4, ^{4}J(H,H) = 2.0, 1H; C(3)H_2(*syn*)), 5.72-5.79 (m, 1H; C(2)H) (η^3-allyl ligand, 45.0%) ppm. $^{13}C\{^{1}H\}$ NMR (150.9 MHz, $CDCl_3$, 25°C): 22.55 (d, ^{3}J(C,P) = 1.9; CH_3), 22.89 (s; CH_3), 22.92 (s; CH_3), 22.94 (s; CH_3), 23.02 (s; CH_3), 25.36 (d, ^{3}J(C,P) = 10.6; CH_2), 25.37 (d, ^{3}J(C,P) = 6.8; CH_2), 25.50 (d, ^{3}J(C,P) = 6.9; CH_2), 25.61 (d, ^{3}J(C,P) = 10.0; CH_2), 27.21 (d, ^{3}J(C,P) = 4.2; CH_2), 27.27 (d, ^{3}J(C,P) = 4.3; CH_2), 27.92 (d, ^{3}J(C,P) = 4.4; CH_2), 28.00 (d, ^{3}J(C,P) = 4.5; CH_2), 26.94 (d, ^{3}J(C,P) = 2.6; CH_2), 26.96 (d, ^{3}J(C,P) = 2.6; CH_2), 34.65 (d, ^{3}J(C,P) = 1.6; CH_2), 34.73 (d, ^{3}J(C,P) = 1.4; CH_2), 38.61 (s; C), 38.71 (s; C), 47.41 (d, ^{3}J(C,P) = 12.4; CH_2), 47.56 (d, ^{3}J(C,P) = 12.4; CH_2), 49.66 (d, ^{3}J(C,P) = 18.1; CH_2), 49.81 (d, ^{3}J(C,P) = 18.0; CH_2), 60.10 (d, ^{2}J(C,P) = 5.4; CH_2), 60.40 (d, ^{2}J(C,P) = 5.4; CH_2), 64.46 (d, ^{2}J(C,P) = 5.7; CH_2), 64.48 (d, ^{2}J(C,P) = 5.8; CH_2), 67.04 (d, ^{2}J(C,P) = 2.5; CH_2), 67.15 d, ^{2}J(C,P) = 2.6; CH_2) (**L4**), 60.84 (d, ^{2}J(C,P) = 5.5; C(1)H_2), 79.50 (d, ^{2}J(C,P) = 38.2; C(3)H_2), 122.94 (d, ^{2}J(C,P) = 8.6; C(2)H) (η^3-allyl ligand, 55.0%), 60.22 (d, ^{2}J(C,P) = 5.6; C(1)H_2), 80.02 (d, ^{2}J(C,P) = 37.9; C(3)H_2), 123.30 (d, ^{2}J(C,P) = 8.4; C(2)H) (η^3-allyl ligand, 45.0%) ppm. $^{31}P\{^{1}H\}$ NMR (242.9 MHz, $CDCl_3$, 25°C): 118.40 (s) (55.0%), 118.42 (s) (45.0%) ppm. $C_{18}H_{34}BF_4N_2OPPdS$ (550.12): calcd. C 39.26, H 6.22, N 5.09; found C 39.48, H 6.29, N 4.98; M/z = 463.1177 (calcd 463.1159) Da for [Pd(allyl)(**L4**)]$^+$.

EXPERIMENTAL SECTION

[Pd(allyl)(**L1a**)$_2$]BF_4:^{1}H NMR (600.1 MHz, $CDCl_3$, 25^{o}C): 0.86-0.91 (m, 2H; CH_2), 0.94 (s, 6H; CH_3), 1.25 (s, 3H; CH_3), 1.26 (s, 3H; CH_3), 1.59-1.66 (m, 2H; CH_2), 1.88-1.99 (m, 4H; CH_2 and CH), 2.01-2.09 (m, 4H; CH_2), 2.12-2.19 (m, 4H; CH_2 and CH), 2.21-2.28 (m, 2H; CH), 2.31-2.37 (m, 2H; CH_2), 2.45-2.52 (br.m, 2H; CH_2), 2.95-3.02 (br.m, 2H; CH_2), 3.20-3.35 (m, 4H; CH_2 and CH), 3.41-3.46 (br.m, 1H; CH_2), 3.48-3.53 (br.m, 1H; CH_2), 3.77-3.90 (m, 6H; CH_2), 4.18-4.24 (br.m, 2H; CH), 6.83-6.86 (m, 4H; CH(Ph)), 6.98-7.02 (m, 2H; CH(Ph)), 7.18-7.29 (m, 14H; CH(Ph)) (2 **L1a**), 2.74-2.79 (br.m, 1H; CH_2(*anti*)), 2.89-2.94 (m, 1H; CH_2(*anti*)), 4.10-4.17 (br.m, 1H; CH_2(*syn*)), 4.26-4.34 (br.m, 1H; CH_2(*syn*)), 5.21-5.28 (m, 1H; CH) (η^3-allyl ligand) ppm. $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$, 25^{o}C): 23.56 (s; C(23)H_3), 27.55-27.58 and 27.67-27.70 (m and m; C(7)H_2), 27.74 and 27.76 (s an s; C(22)H_3), 31.69 and 31.77 (s and s; C(6)H_2), 32.33 and 32.40 (s and s; C(21)H_2), 37.33 (s; C(17)H_2), 38.74 and 38.75 (s and s; C(19)), 39.41 and 39.47 (s and s; C(16)H), 42.24 and 42.26 (s and s; C(18)H), 43.04 and 43.13 (s and s; C(20)H), 48.98-49.12 and 49.22-49.37 (m and m; C(8)H_2), 50.06 and 50.11 (s and s; C(15)H), 54.52 and 54.67 (s and s; C(4)H_2), 62.93 and 63.09 (s and s; C(5)H), 67.92-68.07 (m; C(14)H_2), 115.63-115.67 and 115.71-115.76 (m and m; C(10)H), 121.63 and 121.70 (s and s; C(12)H), 127.22 and 127.23 (s and s; C(28)H), 129.30 (s; C(27)H), 130.01 (s; C(26)H), 131.55 and 131.58 (s and s; C(11)H), 136.05 (s; C(25)), 143.01-143.13 (m; C(9)) (2 **L1a**), 71.52-71.95 (m, C(1)H_2 and C(3)H_2), 123.96 (t, ^2J(C,P) = 8.5; C(2)H) (η^3-allyl ligand) ppm. $^{31}P\{^1H\}$ NMR (242.9 MHz, $CDCl_3$, 25^{o}C): 115.53 (s) ppm.

Table S1 $^{31}P\{^{1}H\}$ NMR data for the ligands and their Pd(II)-complexes, δ [ppm] (%)[a].

L	Free **L**	Pd(allyl)(**L**)]BF_4	[Pd(allyl)(**L**)$_2$]BF_4
L1a	122.15	128.28 (53.2), 128.45 (46.8)	115.53
L1b	120.48	117.55 (12.2), 118.08 (2.0), 127.21 (26.1), 127.54 (37.5), 133.22 (3.6), 133.49 (6.7), 140.65 (4.5), 140.89 (7.3)	-
L2a	133.12	119.43 (4.9), 119.92 (5.7), 124.60 (1.3), 125.51 (1.7), 128.61 (45.3), 130.47 (41.0)	-
L2b	117.43 (93), 125.38 (7)	125.03 (93.6), 129.71 (6.4)	-
L3	122.40	Mixture of unidentifiable complexes	-
L4	126.74	118.40 (55.0), 118.42 (45.0)	-

[a] In accordance with the $^{31}P\{^{1}H\}$ integral.

Table S2 $^{13}C\{^{1}H\}$ NMR data for the η^3-allyl ligands of the Pd(II)-complexes, δ [ppm] (multiplicity, ^{2}J(C,P) [Hz]).

Complex	%[a]	$C(1)H_2$	$C(3)H_2$	$C(2)H_2$
[Pd(allyl)(**L1a**)]BF_4	53.2	62.56 (d, 4.2)	82.56 (d, 36.9)	123.72 (d, 8.2)
	46.8	62.46 (d, 3.9)	84.04 (d, 35.7)	123.50 (d, 8.0)
[Pd(allyl)(**L1b**)]BF_4[b]	43.9	65.08 (s)	82.78 (d, 36.0)	123.80 (d, 8.2)
	30.6	63.84 (s)	83.87 (d, 35.8)	123.16 (d, 8.0)
[Pd(allyl)(**L2a**)]BF_4[c]	44.8	64.23 (d, 4.7)	79.96 (d, 35.3)	123.91 (d, 8.1)
	40.5	63.97 (d, 4.8)	79.98 (d, 35.8)	123.01 (d, 8.3)
[Pd(allyl)(**L2b**)]BF_4[d]	93.6	61.14 (br.s)	80.83-81.21 (br.m)	123.58 (br.s)
[Pd(allyl)(**L4**)]BF_4	55.0	60.84 (d, 5.5)	79.50 (d, 38.2)	122.94 (d, 8.6)
	45.0	60.22 (d, 5.6)	80.02 (d, 37.9)	123.30 (d, 8.4)
[Pd(allyl)(**L1a**)$_2$]BF_4	96.5	71.52-71.95 (m)		123.96 (t, 8.5)

[a] In accordance with the $^{31}P\{^{1}H\}$ integral. [b] Signals of several minor chelates, amounting to a total of 25.5%, cannot be assigned due to small quantity of each form. [c] Signals of several minor chelates, amounting to a total of 14.7%, cannot be assigned due to small quantity of each form. [d] Signals of minor epimer stemming from the orientation of the η^3-allyl cannot be assigned due to broadening.

EXPERIMENTAL SECTION

Palladium-Catalyzed Asymmetric Allylic Alkylation of (*E*)-1,3-Diphenylallyl Acetate with Dimethyl Malonate: A solution of $[Pd(allyl)Cl]_2$ (0.001 g, 0.0025 mmol) and the appropriate ligand (0.005 mmol or 0.01 mmol) in the appropriate solvent (1.5 mL) was stirred for 40 min or the appropriate cationic complex (0.005 mmol) was dissolved in the appropriate solvent (1.5 mL). (*E*)-1,3-diphenylallyl acetate (**4**) (0.05 mL, 0.25 mmol) was added and the solution stirred for 15 min. Dimethyl malonate (0.05 ml, 0.44 mmol), BSA (0.11 mL, 0.44 mmol) and KOAc (0.002 g) were added. The reaction mixture was stirred for 24 h, diluted with CH_2Cl_2 (2 mL) and filtered through a thin layer of SiO_2. The filtrate was evaporated at reduced pressure (40 Torr) and dried in vacuum (10^{-3} Torr) affording a residue containing dimethyl (*E*)-2-(1,3-diphenylallyl)malonate (**5a**).[17] In order to evaluate *ee* and conversion, the obtained residue was dissolved in an appropriate eluent mixture (8 mL) and a sample was taken for HPLC analysis. The conversion of substrate **4** and enantiomeric excess of **5a** were determined using a Kromasil 5-CelluCoat column, C_6H_{14}/*i*PrOH = 99/1, 0.6 mL/min, 254 nm, t(*R*) = 21.2 min, t(*S*) = 22.8 min.

Palladium-Catalyzed Asymmetric Allylic Amination of (*E*)-1,3-Diphenylallyl Acetate with Pyrrolidine: A solution of $[Pd(allyl)Cl]_2$ (0.001 g, 0.0025 mmol) and the appropriate ligand (0.005 mmol or 0.01 mmol) in the appropriate solvent (1.5 mL) was stirred for 40 min or the appropriate cationic complex (0.005 mmol) was dissolved in the appropriate solvent (1.5 mL). (*E*)-1,3-diphenylallyl acetate (**4**) (0.05 mL, 0.25 mmol) was added and the solution stirred for 15 min, then freshly distilled pyrrolidine (0.06 mL, 0.75 mmol) was added. The reaction mixture was stirred for 24 h, diluted with CH_2Cl_2 (2 mL) and filtered through a thin layer of SiO_2. The filtrate was evaporated at reduced pressure (40 Torr) and dried in vacuum (10^{-3} Torr) affording a residue containing (*E*)-1-(1,3-diphenylallyl)pyrrolidine (**5b**).[18] In order to evaluate *ee* and conversion, the obtained residue was dissolved in an appropriate eluent mixture (8 mL) and a sample was taken for HPLC analysis. The conversion of substrate **4** and enantiomeric excess of **5b** were determined using a Daicel Chiralcel OD-H column, C_6H_{14}/*i*PrOH = 95/5, 0.4 mL/min, 254 nm, t(*R*) = 9.7 min, t(*S*) = 10.3 min.

Palladium-Catalyzed Asymmetric Allylic Alkylation of Cinnamyl Acetate with Ethyl 2-Oxocyclohexane-1-Carboxylate: A solution of $[Pd(allyl)Cl]_2$ (0.001 g, 0.0025 mmol) and the appropriate ligand (0.005 mmol or 0.01 mmol) in toluene (1.5 mL) was stirred for 40 min or the appropriate cationic complex (0.005 mmol) was dissolved in toluene (1.5 mL). Cinnamyl acetate (**6**) (0.04 mL, 0.25 mmol) was added and the solution stirred for 15 min. β-Ketoether **7** (0.06 mL, 0.375 mmol), BSA (0.125 mL, 0.5 mmol) and $Zn(OAc)_2$ (0.005 g) were added. The reaction mixture was stirred for 24 h, diluted with toluene (2 mL) and filtered through a thin layer of SiO_2. The filtrate was evaporated at reduced pressure (40 Torr) and dried in vacuum (10^{-3} Torr) affording a residue containing ethyl 1-cinnamyl-2-oxocyclohexane-1-carboxylate (**8**).[16] In order to evaluate *ee* and conversion, the obtained residue was

dissolved in an appropriate eluent mixture (8 mL) and a sample was taken for HPLC analysis. The conversion of substrate **6** and enantiomeric excess of **8** were determined using a Kromasil 5-CelluCoat column, C_6H_{14}/*i*PrOH = 95/5, 0.4 mL/min, 254 nm, t(*R*) = 14.0 min, t(*S*) = 16.2 min.

Palladium-Catalyzed Asymmetric Allylic Alkylation of Cinnamyl Acetate with Ethyl 2-Acetamido-3-Oxobutanoate: A solution of $[Pd(allyl)Cl]_2$ (0.001 g, 0.0025 mmol) and the appropriate ligand (0.005 mmol or 0.01 mmol) in toluene (1.5 mL) was stirred for 40 min or the appropriate cationic complex (0.005 mmol) was dissolved in toluene (1.5 mL). Cinnamyl acetate (**6**) (0.04 mL, 0.25 mmol) was added and the solution stirred for 15 min. α-Acetamido-β-Ketoether **9** (0.07 g, 0.375 mmol), BSA (0.125 mL, 0.5 mmol) and KOAc (0.003 g) were added. The reaction mixture was stirred for 24 h, diluted with toluene (2 mL) and filtered through a thin layer of SiO_2. The filtrate was evaporated at reduced pressure (40 Torr) and dried in vacuum (10^{-3} Torr) affording a residue containing ethyl (*E*)-2-acetamido-2-acetyl-5-phenylpent-4-enoate (**10**).[19] In order to evaluate *ee* and conversion, the obtained residue was dissolved in an appropriate eluent mixture (8 mL) and a sample was taken for HPLC analysis. The conversion of substrate **6** and enantiomeric excess of **10** were determined using a Daicel Chiralcel OD-H column, C_6H_{14}/*i*PrOH = 85/15, 0.8 mL/min, 254 nm, *t*(*S*) = 9.8 min, *t*(*R*) = 10.7 min.

Rhodium-Catalyzed Asymmetric Hydrogenation of Dimethyl Itaconate, Methyl (*Z*)-2-Acetamido-3-phenylacrylate or Methyl (*Z*)-2-Acetamido-3-(4-fluorophenyl)acrylate: A solution of $[Rh(Cod)_2]BF_4$ (1 mg, 0.0025 mmol) and the appropriate ligand (2.0 mg, 0.0025 mmol) in CH_2Cl_2 (2 ml) was stirred for 40 min. Then appropriate substrate (0.25 mmol) was added. Catalytic vessel containing the resulting solution was filled with hydrogen to a pressure of 6.0 atm and the reaction mixture was stirred for 24 h. The solvent was evaporated at reduced pressure (40 Torr), the residue was dissolved in diethyl ether (2 ml) and filtered through a thin layer of SiO_2. The filtrate was evaporated at reduced pressure (40 Torr) and dried in vacuum (10 Torr, 12 h) affording a residue containing dimethyl 2-methylsuccinate (**12a**), methyl 2-acetamido-3-phenylpropanoate (**12b**) or methyl 2-acetamido-3-(4-fluorophenyl)propanoate (**12c**).[20] In order to evaluate *ee* and conversion, the obtained residue was dissolved in an appropriate eluent mixture (8 mL) and a sample was taken for HPLC analysis. The conversion of substrates **11a-c** and enantiomeric excesses of **12a-c** were determined using a Daicel Chiralcel OD-H column, C_6H_{14}/*i*PrOH = 98/2, 0.8 mL/min, 215 nm, t(*R*) = 9.2 min, t(*S*) = 16.7 min (**12a**); C_6H_{14}/*i*PrOH = 4/1, 0.6 mL/min, 215 nm, t(*R*) = 9.8 min, t(*S*) = 11.8 min (**12b**); C_6H_{14}/*i*PrOH = 9/1, 1.0 mL/min, 219 nm, *t*(*R*) = 10.7 min, *t*(*S*) = 14.0 min (**12c**).

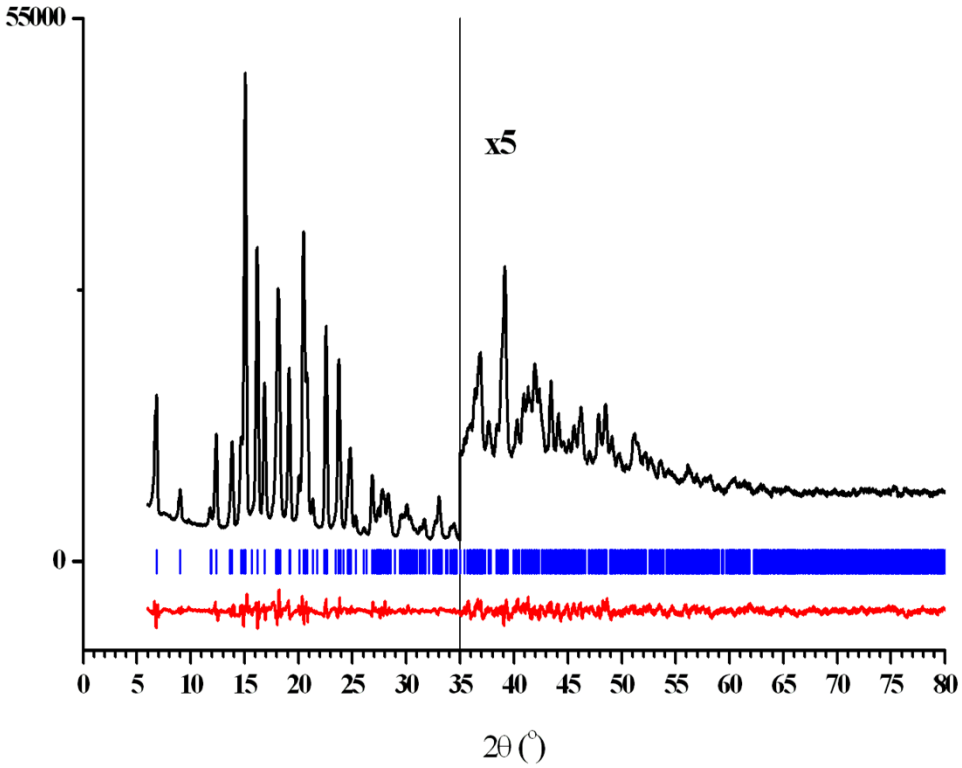


Figure S1 The final Rietveld plot for **L1a**. The experimental diffraction profile is indicated in black, and the difference profile is shown as the bottom red curve. The vertical blue bars correspond to the calculated positions of the Bragg peaks.

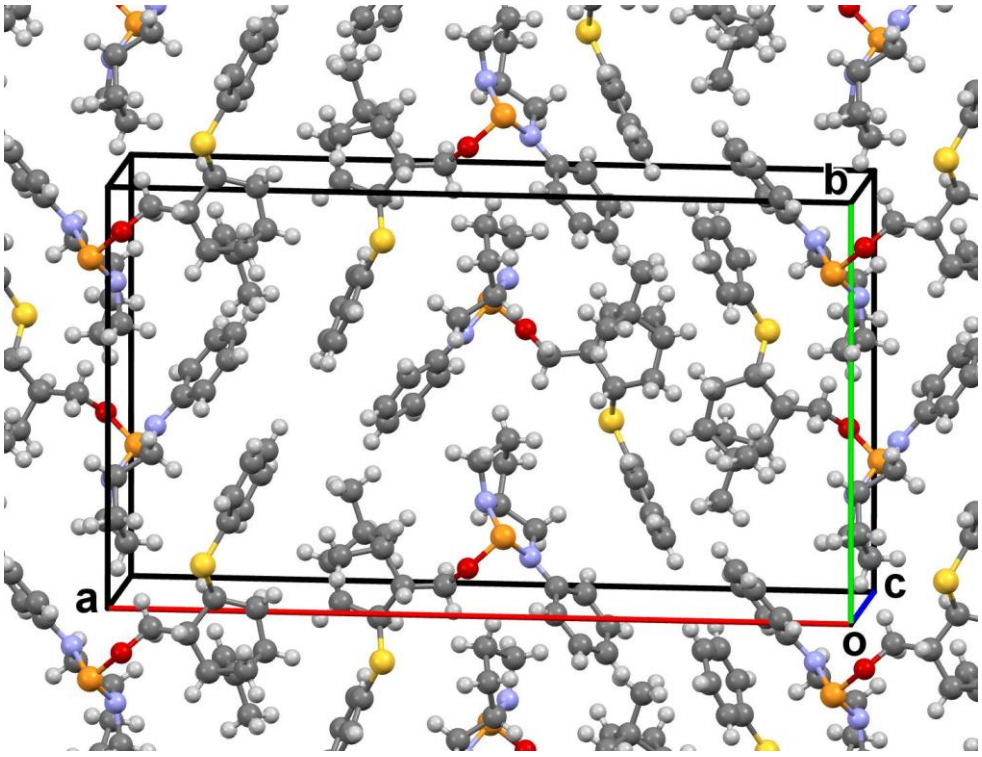


Figure S2 A portion of the crystal packing of **L1a** viewing approximately along the *c* axis.

CRYSTAL DATA FOR NEW COMPOUNDS

Table S3. Crystal data for **L1a**.

Identification code	**L1a**
CCDC number	2235512
empirical formula	$C_{27}H_{35}N_2OPS$
M_r	466.60
crystal system	Orthorhombic
space group	$P2_12_12_1$
diffractometer	EMPYREAN
wavelength, Å	1.5418
unit cell dimensions	
a, Å	26.0217(18)
b, Å	14.8896(12)
c, Å	6.6057(6)
volume, Å^3	2559.4(4)
Z	4
D_x (g cm^{-3})	1.211
μ, mm^{-1}	1.868
$2\theta_{min}$ - $2\theta_{max}$, $\Delta 2\theta$ (^{o})	5.996 – 79.997, 0.017
no. params/restraints	135/123
R_p, R_{wp}, R_{exp}	0.0298, 0.0386, 0.0160

CRYSTAL DATA FOR NEW COMPOUNDS

Table S4 Crystal data and structure refinement for [Pd(allyl)(**L2a**)]BF_4, **L1b** and **L2b**.

Identification code	[Pd(allyl)(**L2a**)]BF_4	**L1b**	**L2b**
CCDC number	2272242	2272241	2272240
Empirical formula	$C_{25}H_{38}BF_4N_2OPPdS$	$C_{27}H_{35}N_2OPS$	$C_{22}H_{33}N_2OPS$
Formula weight	638.81	466.60	404.53
Temperature	295(2)K	295(2) K	295(2) K
Wavelength	0.71073 Å	0.71073 Å	1.54186
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	P 21 21 21	P21	P21
Unit cell dimensions	a = 10.7033(7) Å b = 17.1681(8) Å c = 15.4840(8) Å	a = 5.9569(5) Å b = 18.7798(7) Å β = 100.637(6)° c = 11.6407(6) Å	a =6.8320(4) Å b = 19.1764(8) Å β = 90.016(5)° c = 9.1559(6) Å
Volume	2845.3(3) $Å^3$	1279.86(14) $Å^3$	1199.54(12) $Å^3$
Z	4	2	2
Density (calculated)	1.491 Mg/m^3	1.211 Mg/m^3	1.120 Mg/m^3
Absorption coefficient	0.829 mm^{-1}	0.210 mm^{-1}	1.917 mm^{-1}
F(000)	1312	500	436
Theta range for data collection	2.3 to 28.3°	2.8 to 28.7°	4.6 to 66.2°
Reflections collected	38833	28353	10845
Independent reflections	6891	5795	3738
Completeness to theta = 25.242°	99.9%	99.6%	98.2%
Refinement method	Full-matrix least-squares on F^2		
Data / restraints / par.	6891 / 10 / 329	5795 / 1 / 295	3738 / 1 / 247
Goodness-of-fit on F^2	0.769	0.775	0.943
Final R indices [I>2sigma(I)]	R1 = 0.0487	R1 = 0.0537	R1 = 0.0598
R indices (all data)	R1 = 0.1502	R1 = 0.2467	R1 = 0.0844
Absolute structure parameter	-0.04(3)	-0.05(15)	-0.09(4)
Largest diff. peak and hole e. $Å^{-3}$	0.560 and -0.412	0.178 and -0.175	0.227 and -0.270

REFERENCES

1. S. G. Zhukov, V. V. Chernyshev, E. V. Babaev, E. J. Sonneveld, H. *Z.* Schenk, *Kristallogr.*, 2001, **216**, 5–9.

2. V. B. Zlokazov and V. V. Chernyshev, *J. Appl. Crystallogr.*, 1992, **25**, 447–451.

3. a) K. N. Gavrilov, I. S. Mikhel, S. V. Zheglov, V. K. Gavrilov, I. V. Chuchelkin, I. D. Firsin, K. P. Birin, I. S. Pytskii, K. A. Paseshnichenko, V. A. Tafeenko, V. V. Chernyshev, A. A. Shiryaev, *Org. Chem. Front*., 2019, **6**, 1637–1648; b) K. N. Gavrilov, I. V. Chuchelkin, V. S. Zimarev, S. V. Zheglov, V. K. Gavrilov, I. D. Firsin, A. V. Maximychev, A. M. Perepukhov, V. V. Chernyshev, N. S. Goulioukina, *J. Organomet. Chem.* **2020**, 121199; c) I. V. Chuchelkin, K. N. Gavrilov, V. K. Gavrilov, S. V. Zheglov, I. D. Firsin, A. M. Perepukhov, A. V. Maximychev, N. E. Borisova, I. A. Zamilatskov, V. S. Tyurin, C. Dejoie, V. V. Chernyshev, V. S. Zimarev, N. S. Goulioukina, *Organometallics*, 2021, **40**, 3645–3658.

4. C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Cryst.*, 2006, **39**, 453–457.

5. G. M. Sheldrick, *Acta Crystallogr*., 2008, **A64**, 112–122.

6. K. Brandenburg, DIAMOND, Release 2.1d; Crystal Impact GbR: Bonn, Germany, 2000.

7. M. Zielinska-Blajet, P. Rewucki, S. Walenczak, *Tetrahedron*, 2016, **72**, 3851–3857.

8. a) N. Furukawa, Y. Sugihara, and H. Fujihara, *J. Org. Chem*., 1989, **54**, 4222–4224; b) Y. Arai, M. Matsui, T. Koizumi, *Synthesis*, 1990, **1990**, 320–323; c) V. K. Aggarwala, A. Thompson, R. V.H. Jones and M. Standen, *Tetrahedron: Asymmetry*, 1995, **6**, 2557–2564.

9. V. N. Tsarev, S. E. Lyubimov, A. A. Shiryaev, S. V. Zheglov, O. G. Bondarev, V. A. Davankov, A. A. Kabro, S. K. Moiseev, V. N. Kalinin, K. N. Gavrilov, *Eur. J. Org. Chem*., 2004, 2214–2222.

10. a) K. N. Gavrilov, I. V. Chuchelkin, V. K. Gavrilov, S. V. Zheglov, I. D. Firsin, V. M. Trunina, N. E. Borisova, Y. P. Bityak, O. A. Maloshitskaya, V. A. Tafeenko, V. S. Zimarev and N. S. Goulioukina, *Organometallics*, 2023, **42**, 1985-1996; b) M. R. Marre, M. Sanchez, J. F. Brazier, R. Wolf, J. Bellan, *Can. J. Chem*. 1982, **60**, 456.

11. P. R. Auburn, P. B. Mackenzie, B. Bosnich, *J. Am. Chem. Soc*., 1985, **107**, 2033–2046.

12. H. J. Seo, E.-J. Park, M. J. Kim, S. Y. Kang, S. H. Lee, H. J. Kim, K. N. Lee, M. E. Jung, M. W. Lee, M.-S. Kim, E.-J. Son, W.-K. Park, J. Kim, J. Lee, *J. Med. Chem*., 2011, **54**, 6305–6318.

13. T. V. RajanBabu, T. A. Ayers, G. A. Halliday, K. K. You, J. C. Calabrese, *J. Org. Chem*., 1997, **62**, 6012–6028.

14. S. Gladiali, L. Pinna, *Tetrahedron: Asymmetry*, 1991, **2**, 623–632.

15. G.-H. Ouyang, Y.-M. He, Y. Li, J.-F. Xiang, Q.-H. Fan, *Angew. Chem., Int. Ed*., 2015, **54**, 4334–4337.

16. a) T. Nemoto, T. Matsumoto, T. Masuda, T. Hitomi, K. Hatano, Y. Hamada, *J. Am. Chem. Soc*., 2004, **126**, 3690–3691; b) T. Nemoto, T. Masuda, T. Matsumoto, Y. Hamada, *J. Org. Chem*., 2005, **70**, 7172–7178.

REFERENCES

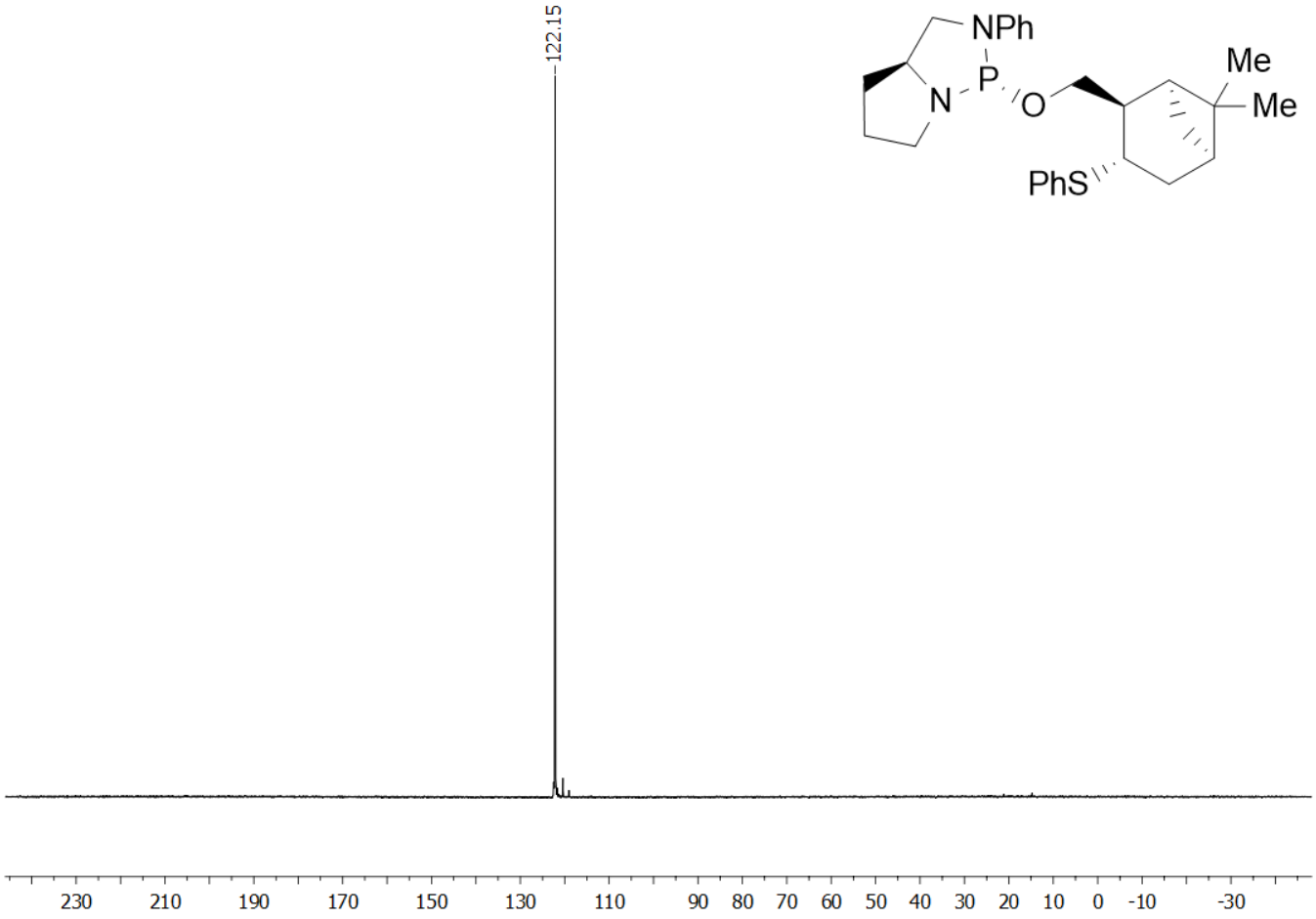
17. a) S. Breeden, M. Wills, *J. Org. Chem*., 1999, **64**, 9735−9738; b) L.-Y. Mei, Z.-L. Yuan, M. Shi, *Organometallics*, 2011, **30**, 6466−6475.

18. a) D. Smyth, H. Tye, C. Eldred, N. W. Alcock, M. Wills, *J. Chem. Soc., Perkin Trans. 1*, 2001, 2840−2849; b) J. Chen, F. Lang, D. Li, L. Cun, J. Zhu, J. Deng, J. Liao, *Tetrahedron: Asymmetry*, 2009, **20**, 1953−1956.

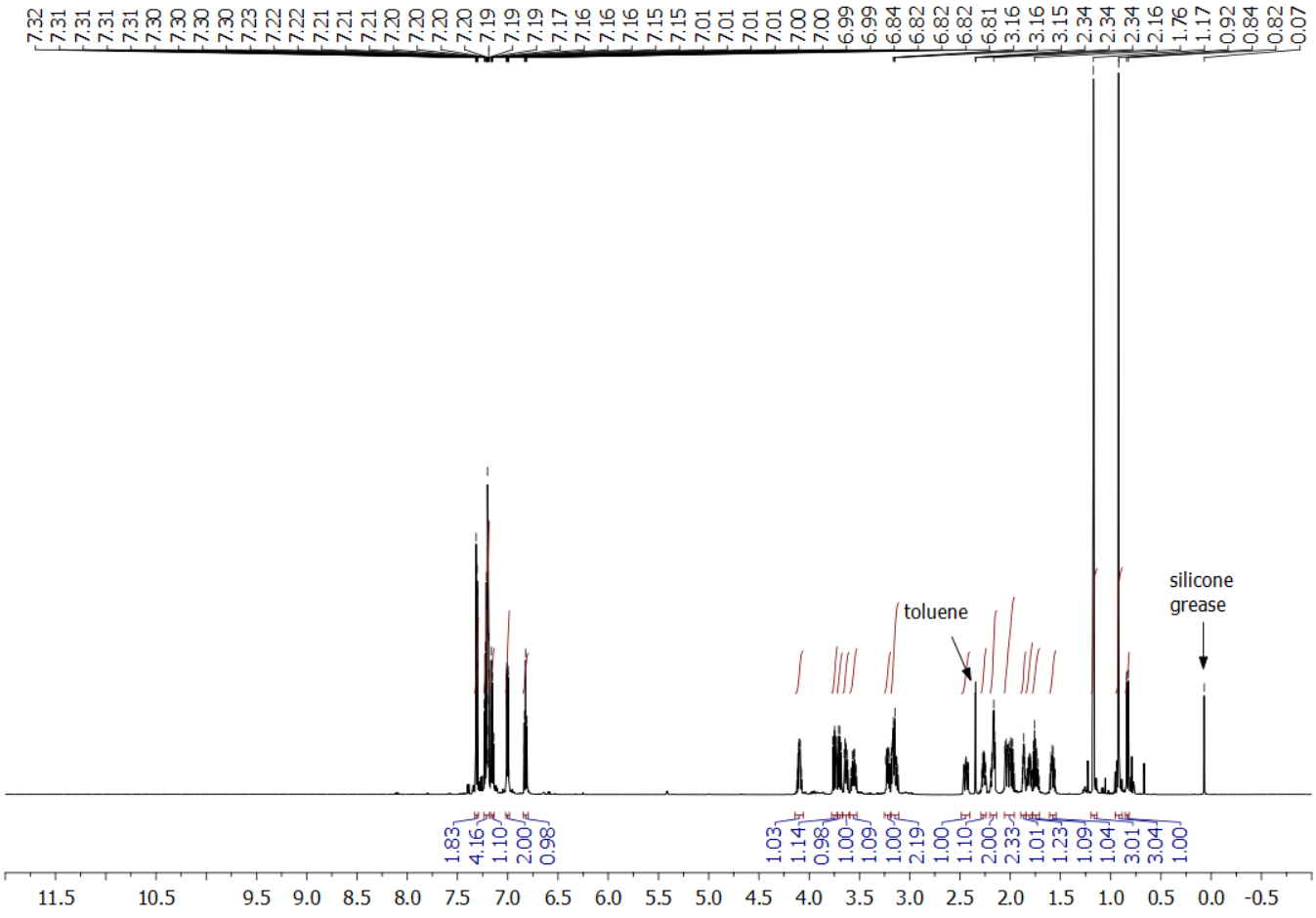
19. T. Nemoto, T. Harada, T. Matsumoto, Y. Hamada, *Tetrahedron Lett*., 2007, **48**, 6304–6307.

20. a) E. B. Benetskiy, C. Bolm, *Tetrahedron:Asymmetry*, 2011, **22**, 373–378; b) L. Navarre, R. Martinez, J.-P. Genet, S. Darses, *J. Am. Chem. Soc*., 2008, **130**, 6159–6169; c) B. Mohar, M. Stephan, *Adv. Synth. Catal*., 2013, **355**, 594–600; (*d*) X.-C. Zhang, Y.-H. Hu, C.-F. Chen, Q. Fang, L.-Y. Yang, Y.-B. Lu, L.-J. Xie, J. Wu, S. Li, W. Fang, *Chem. Sci*., 2016, **7**, 4594–4599.

NMR AND HRMS SPECTRA

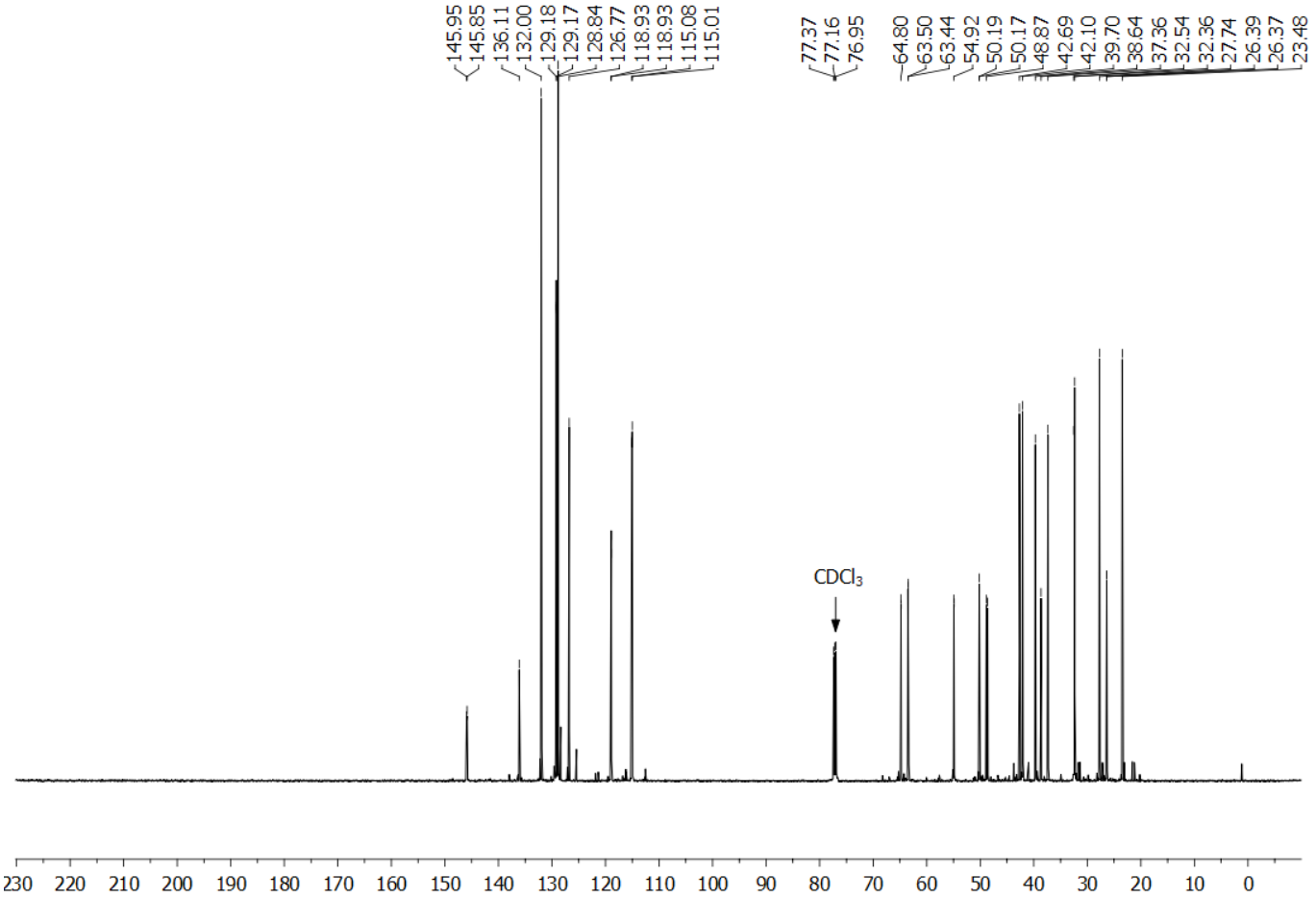


L1a, $^{31}P\{^{1}H\}$ spectrum.



L1a, ^{1}H spectrum.

NMR AND HRMS SPECTRA



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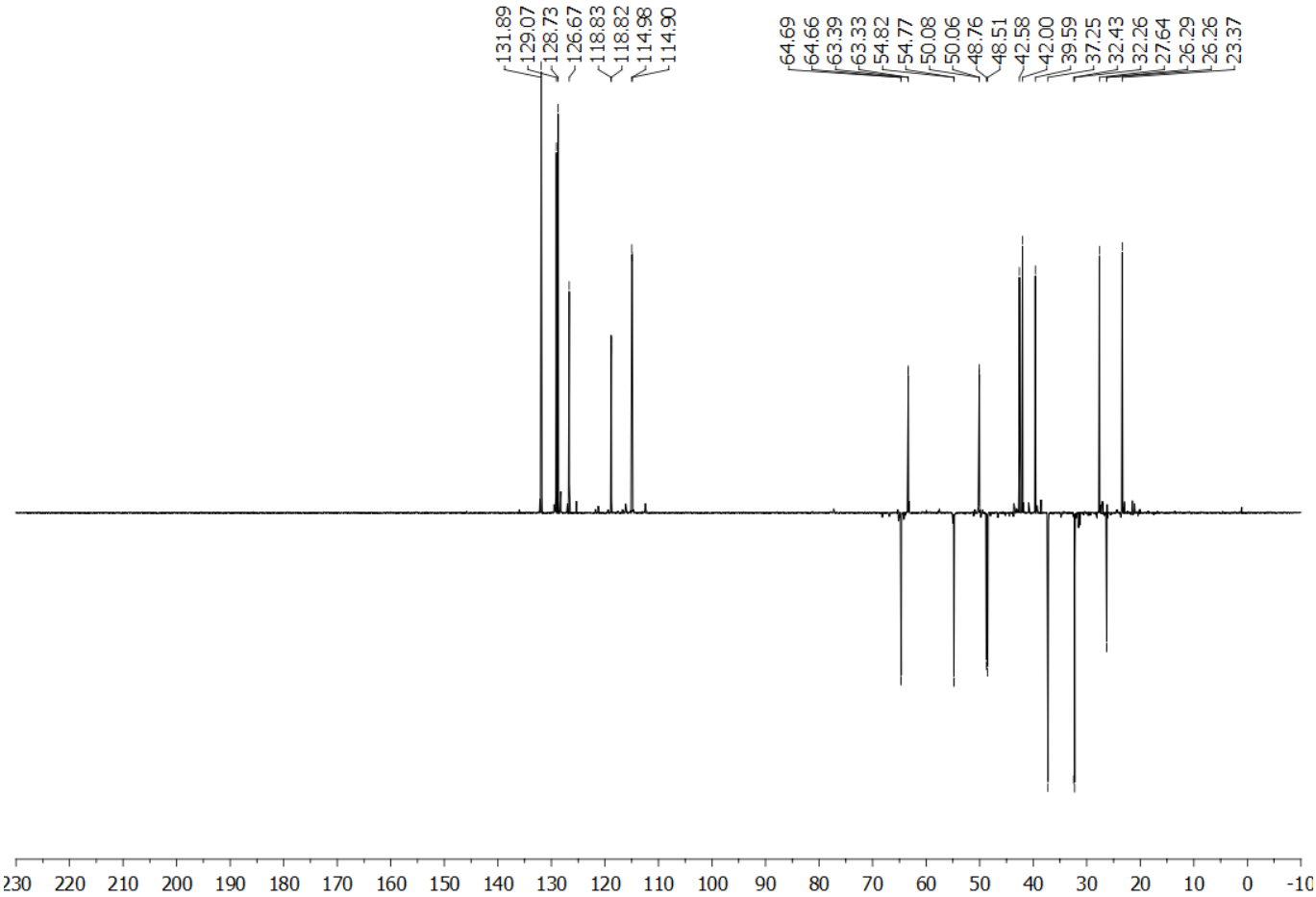
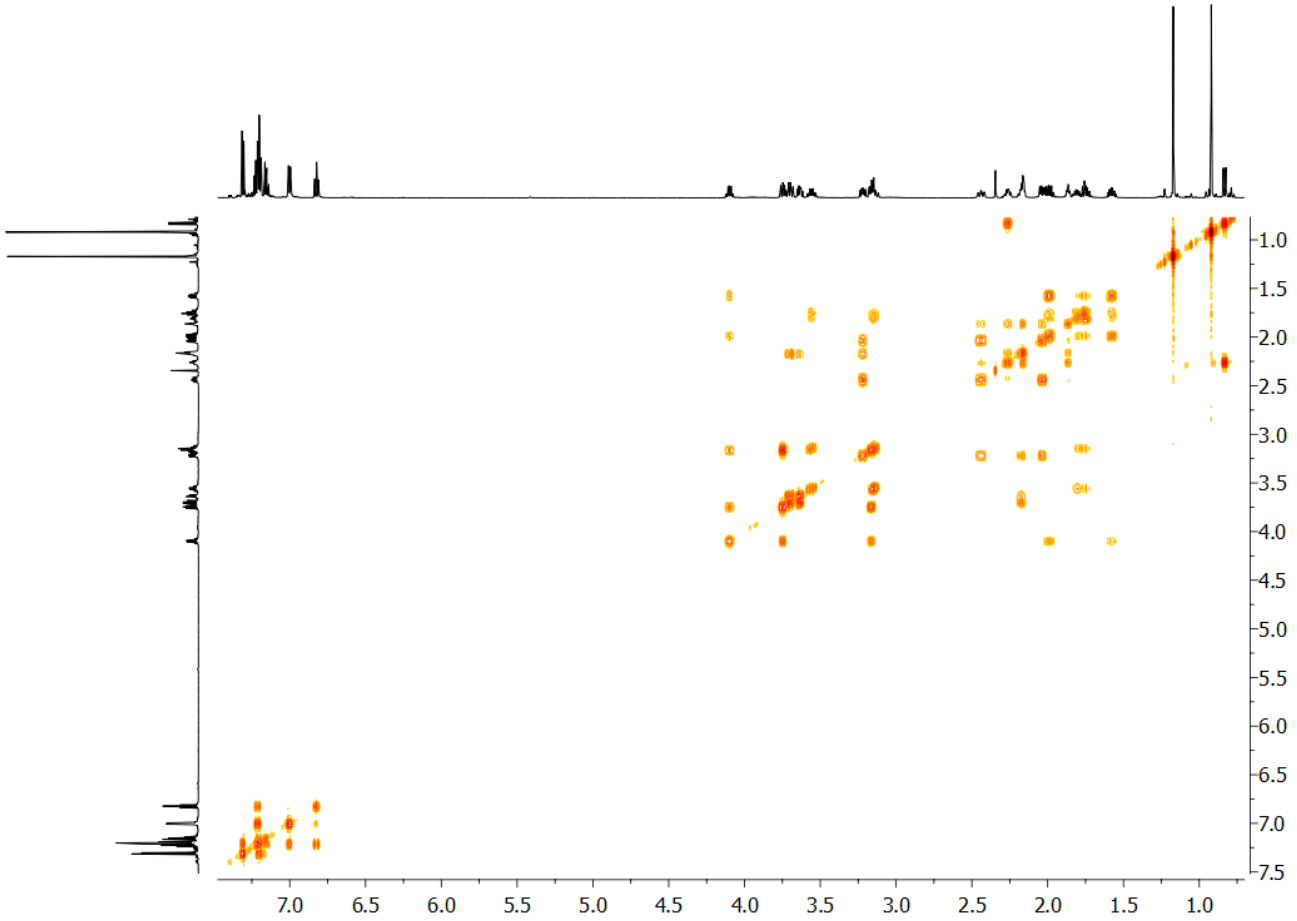


L1a, $^{13}C\{^{1}H\}$ DEPT spectrum.

NMR AND HRMS SPECTRA



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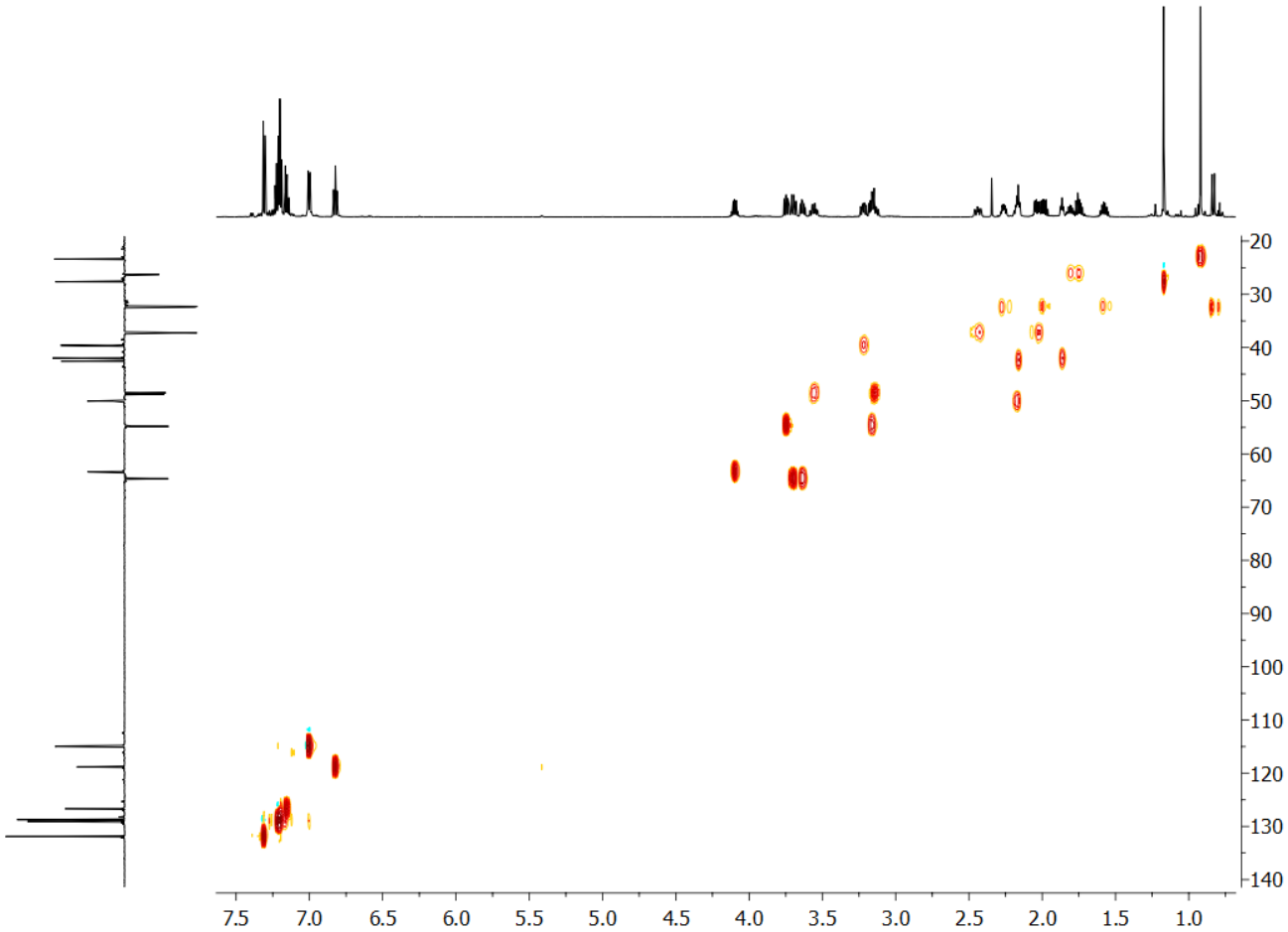
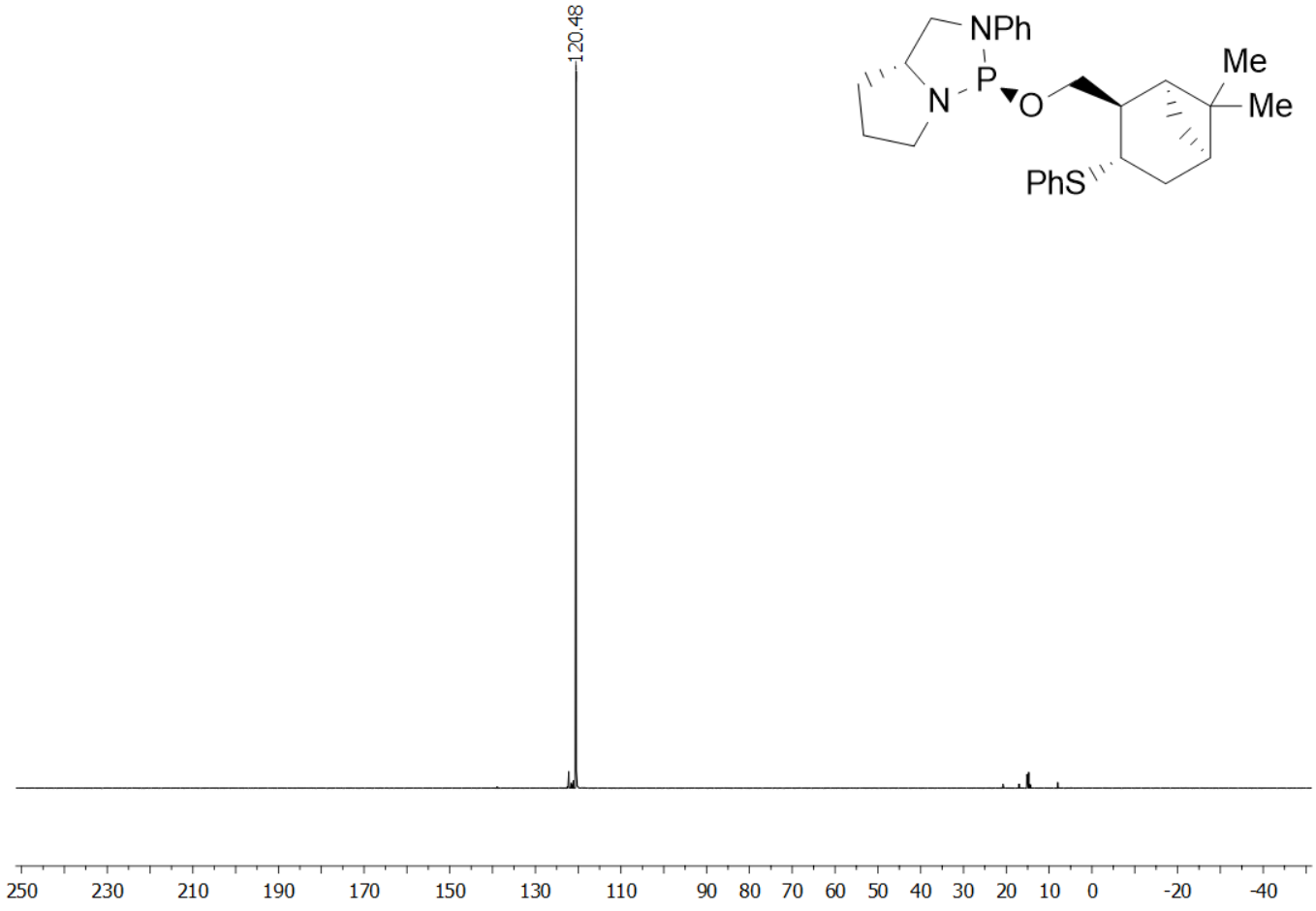
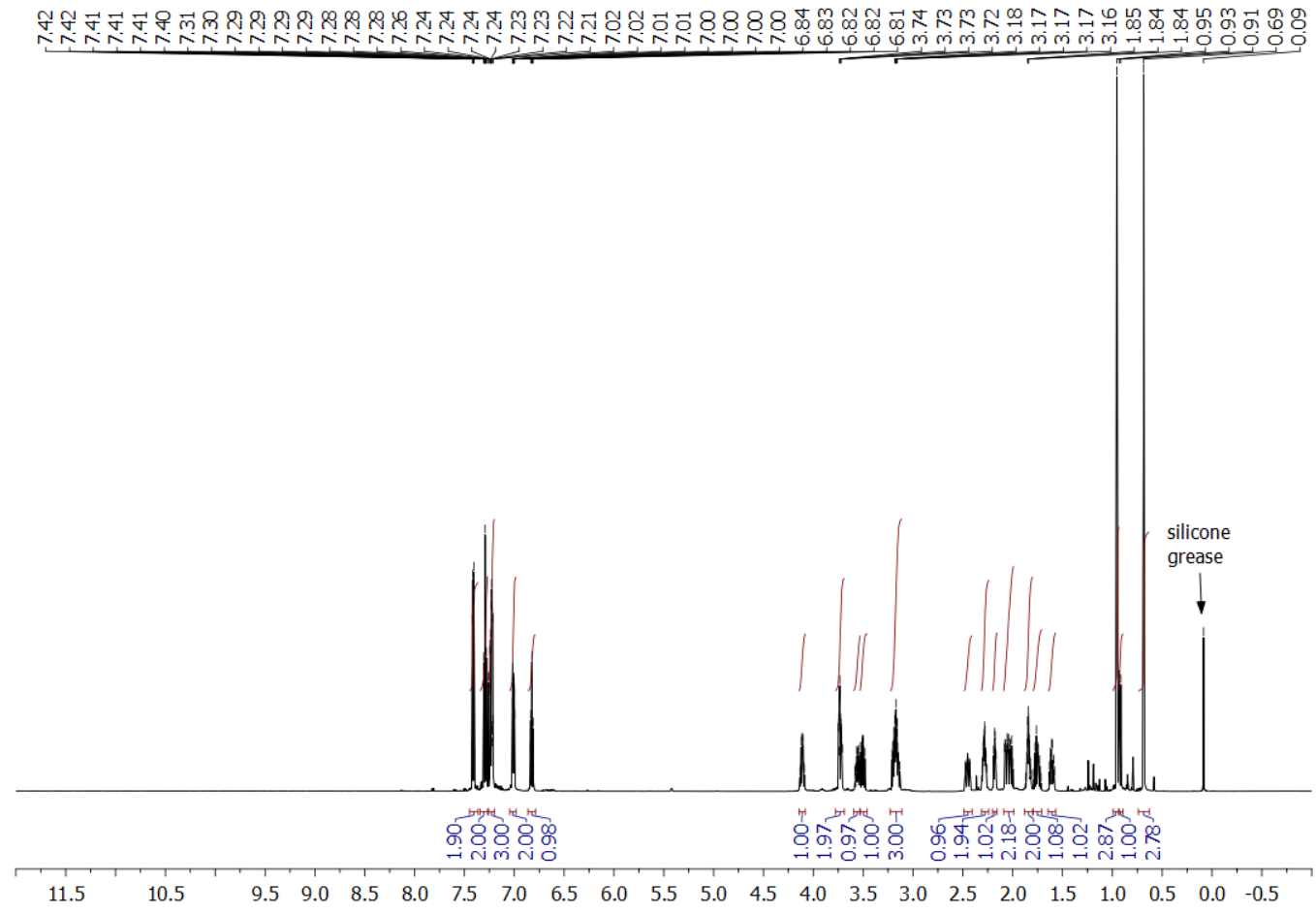


L1a, ^{1}H-^{13}C HSQC spectrum.

NMR AND HRMS SPECTRA

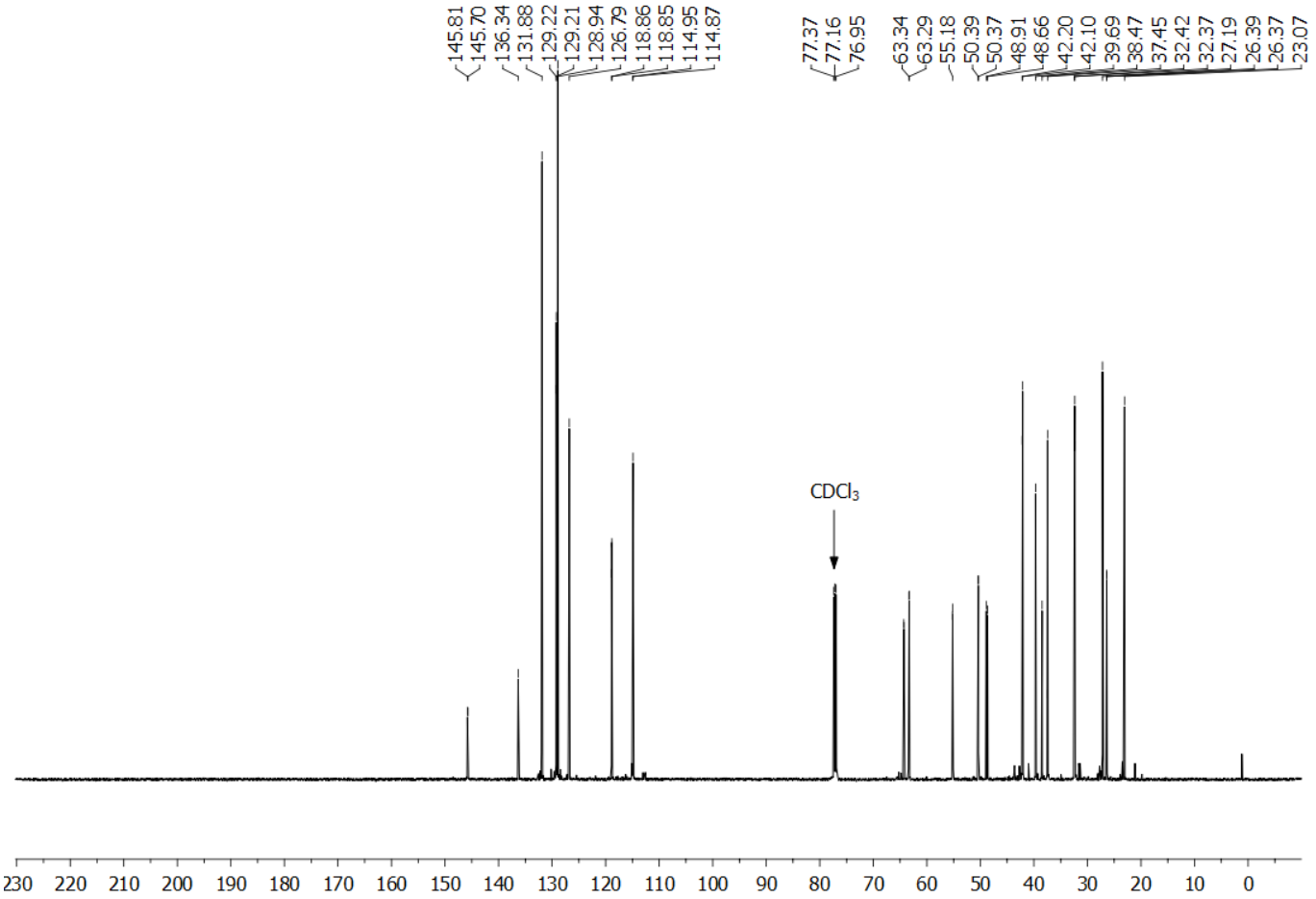


L1b, $^{31}P\{^{1}H\}$ spectrum.



L1b, ^{1}H spectrum.

NMR AND HRMS SPECTRA



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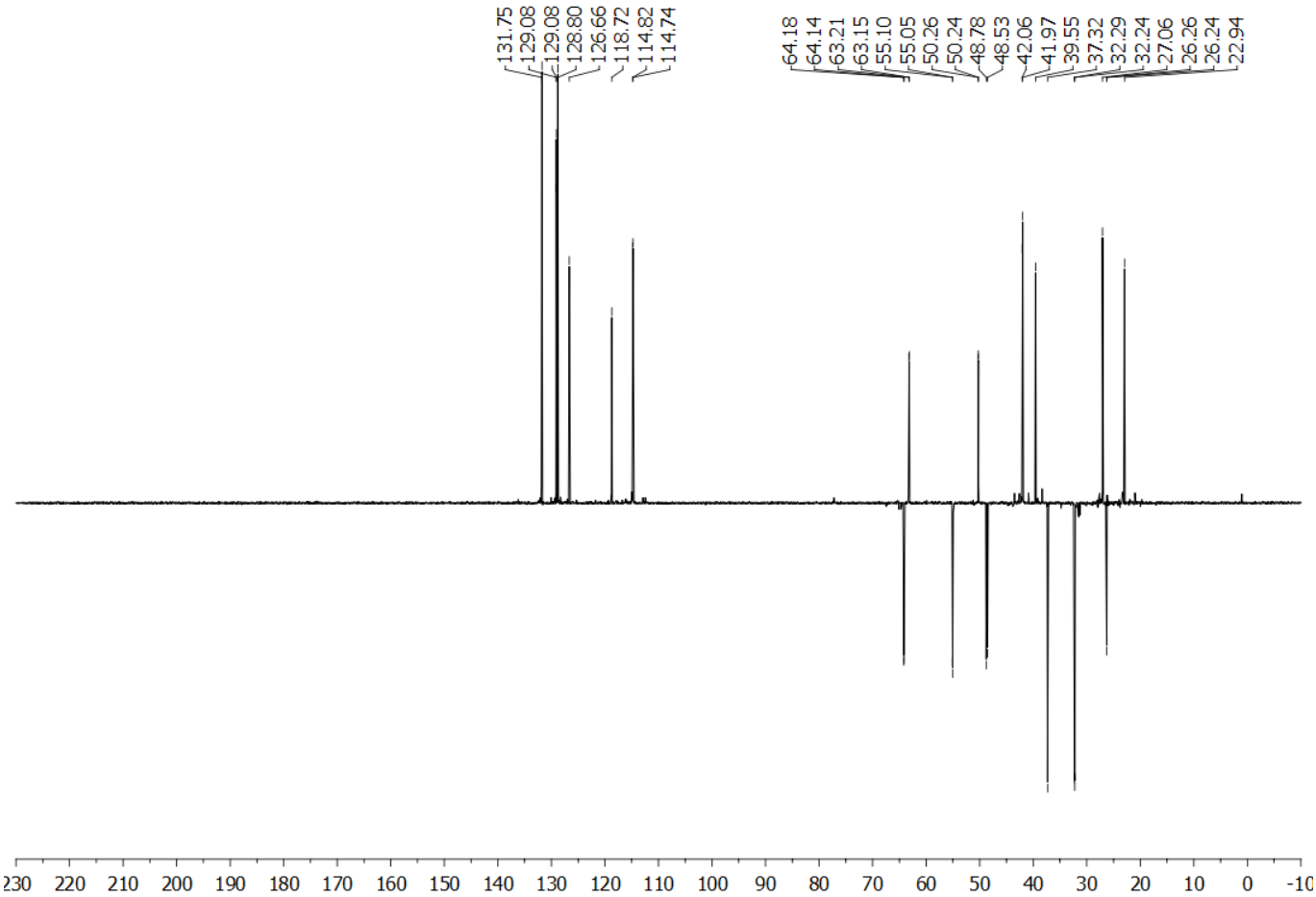

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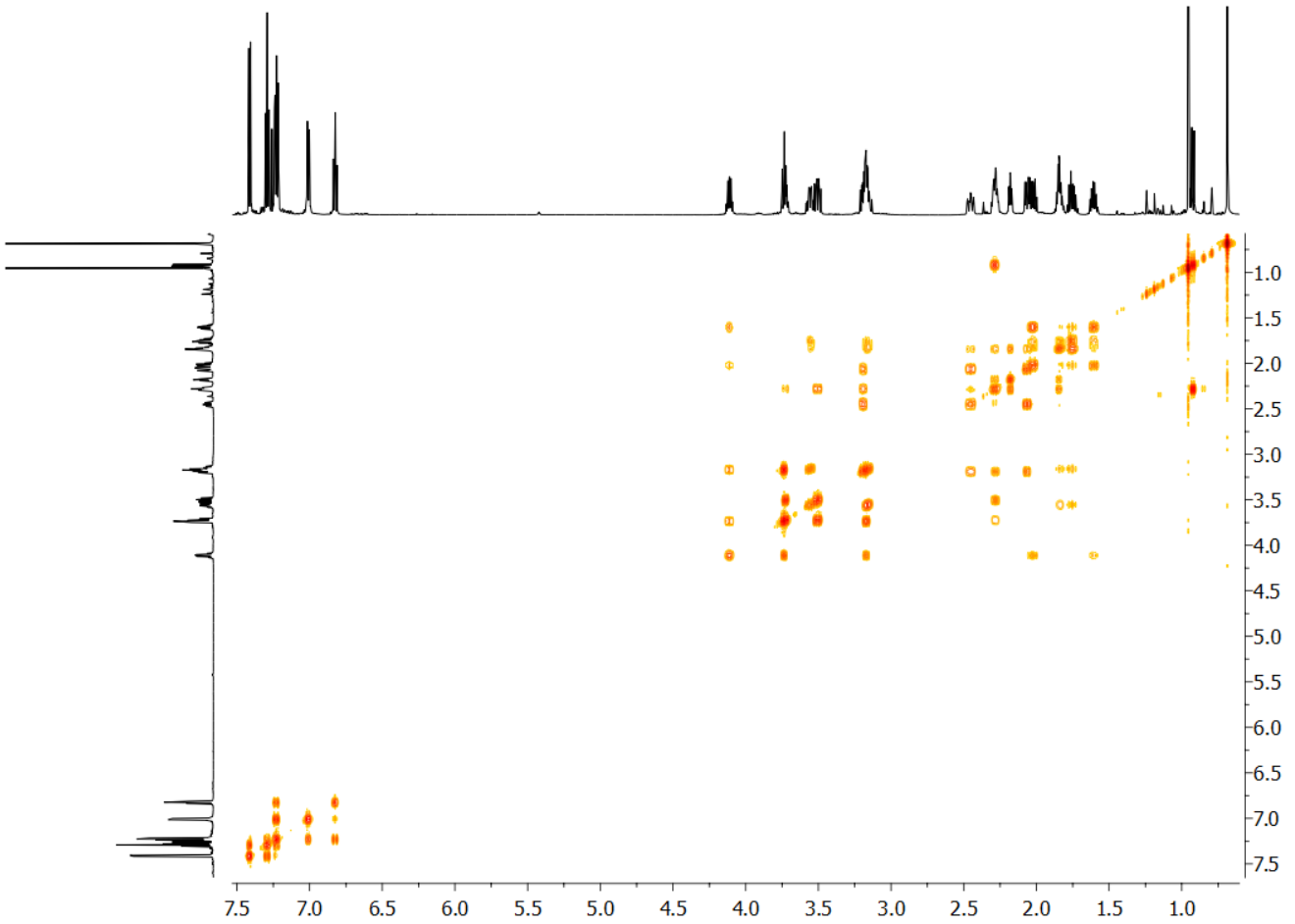
NMR AND HRMS SPECTRA



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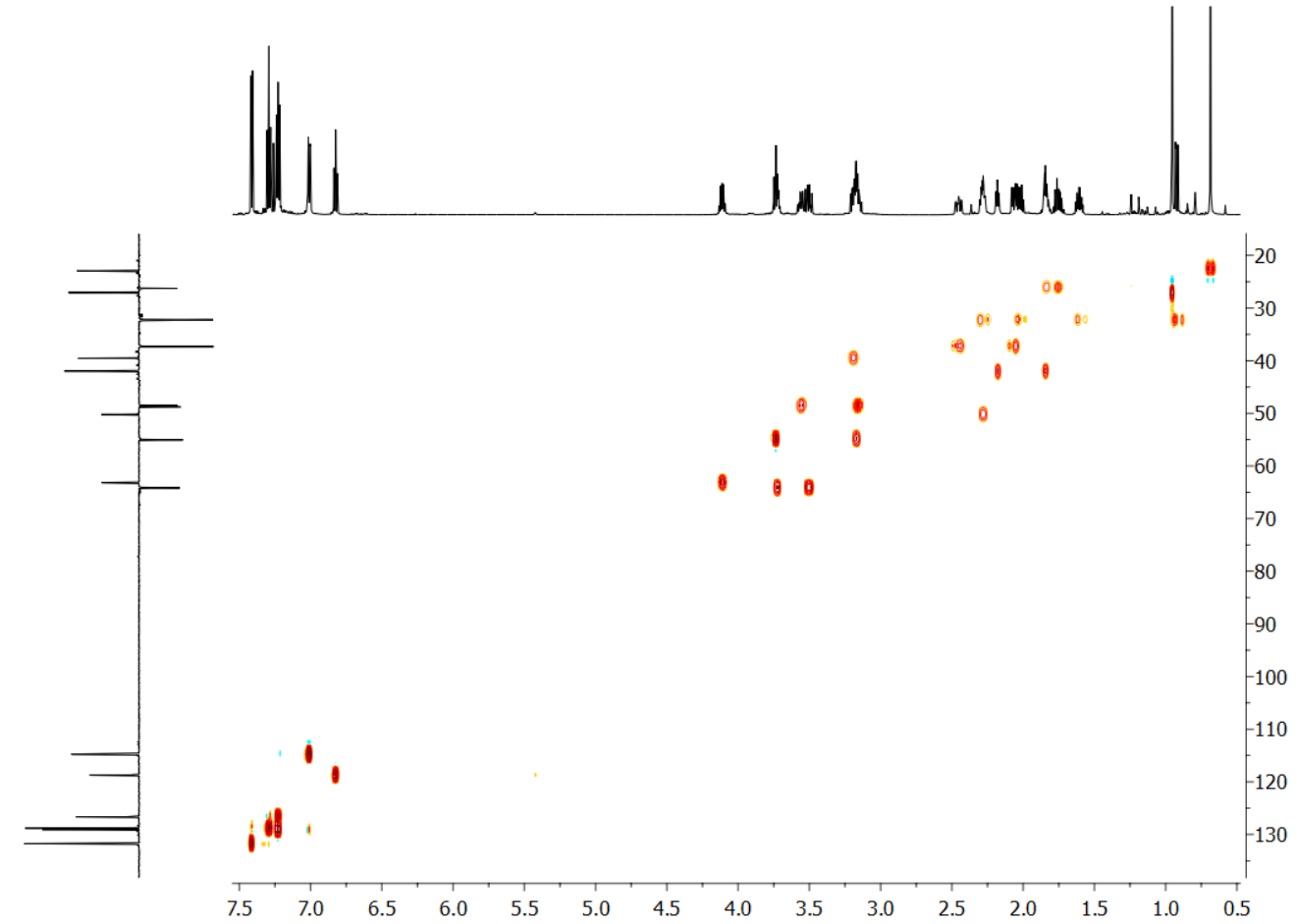

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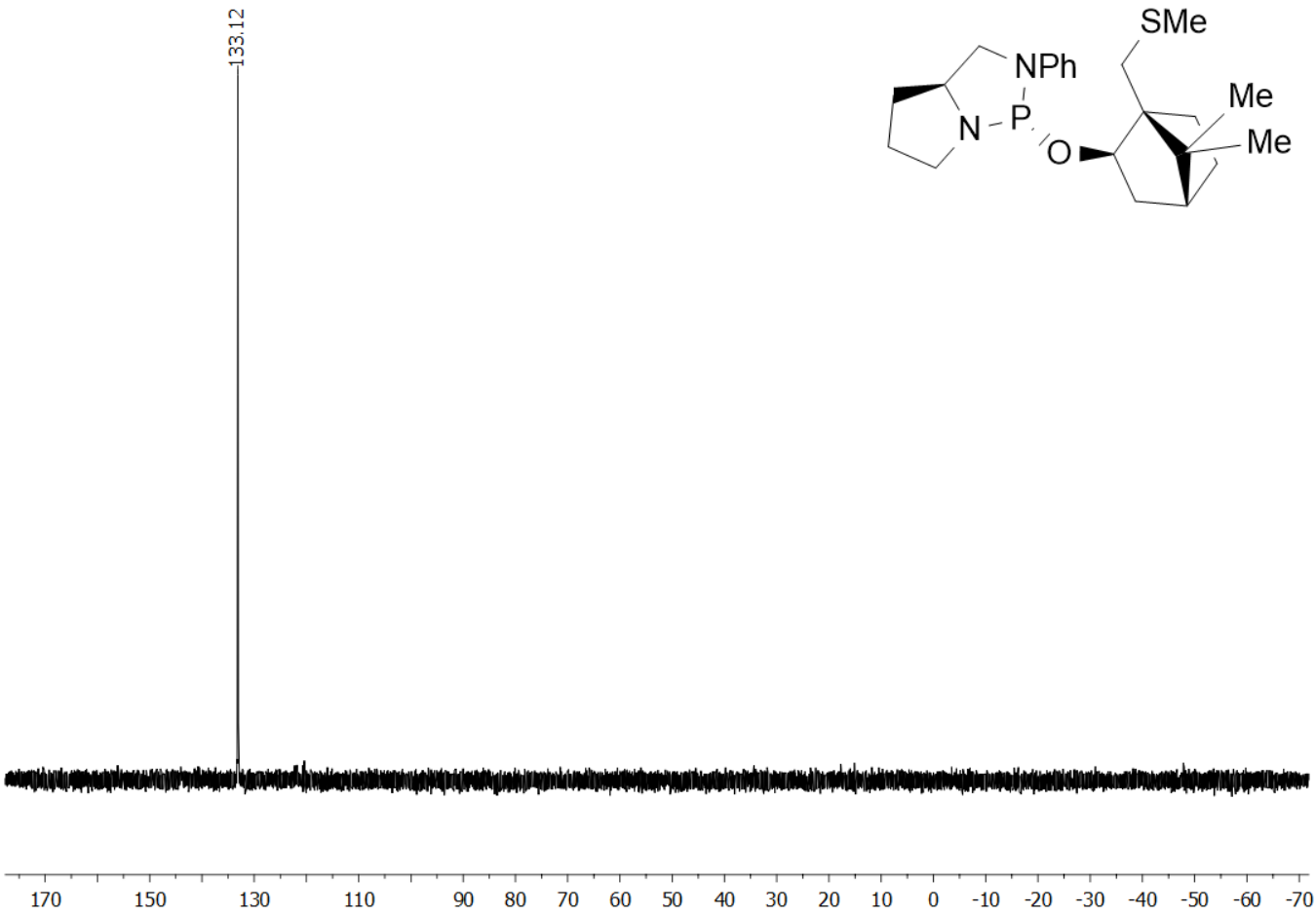
NMR AND HRMS SPECTRA



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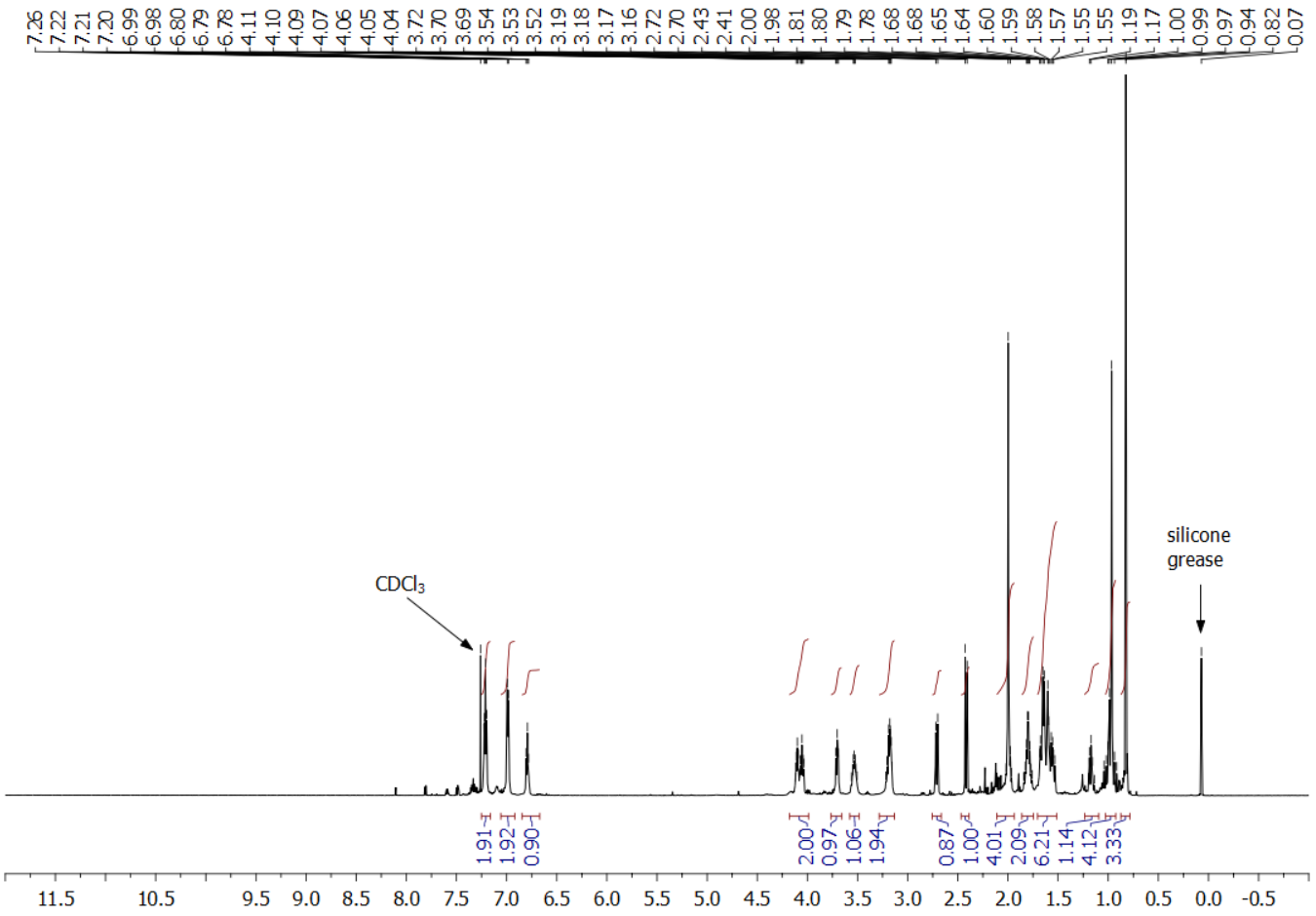
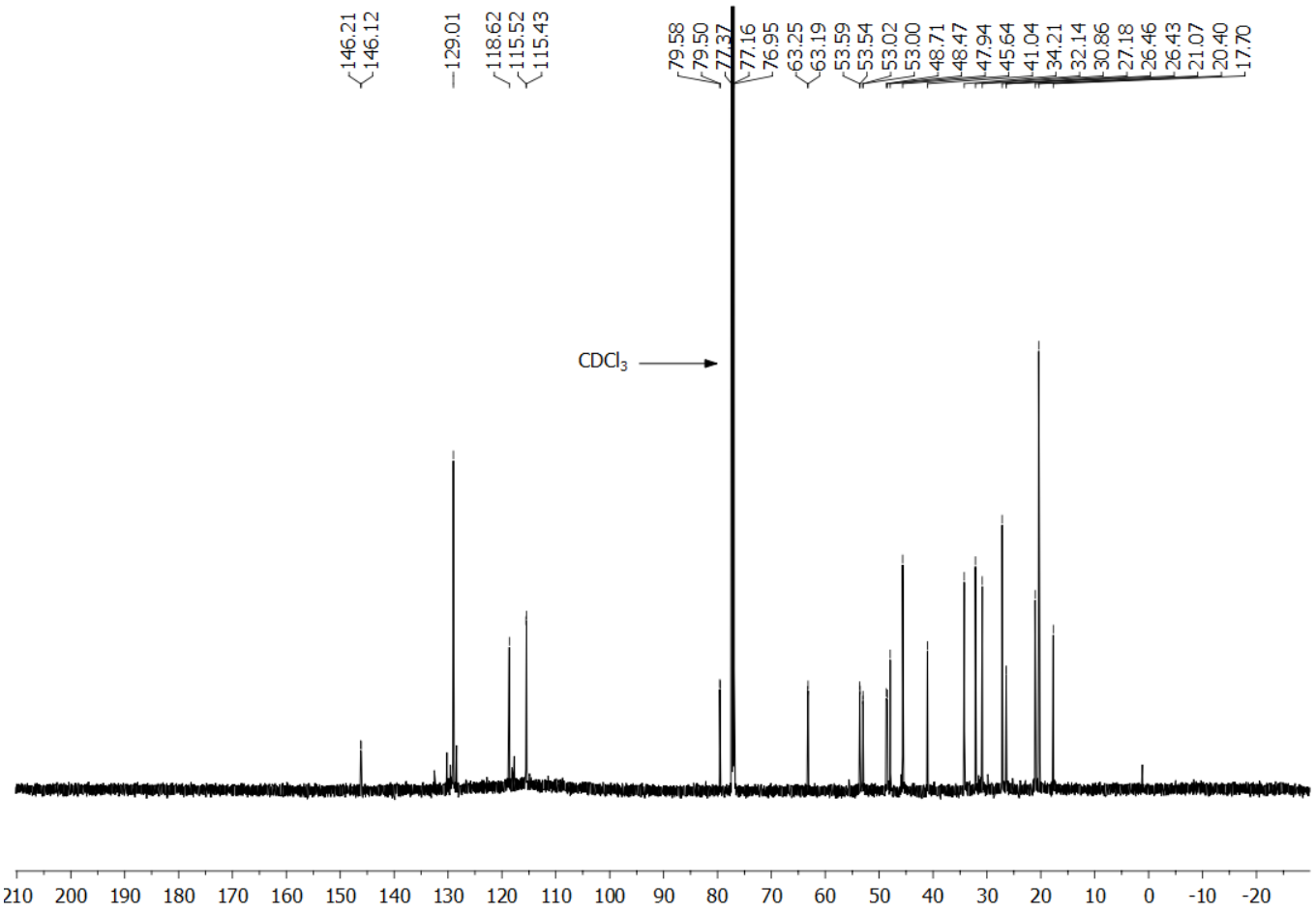
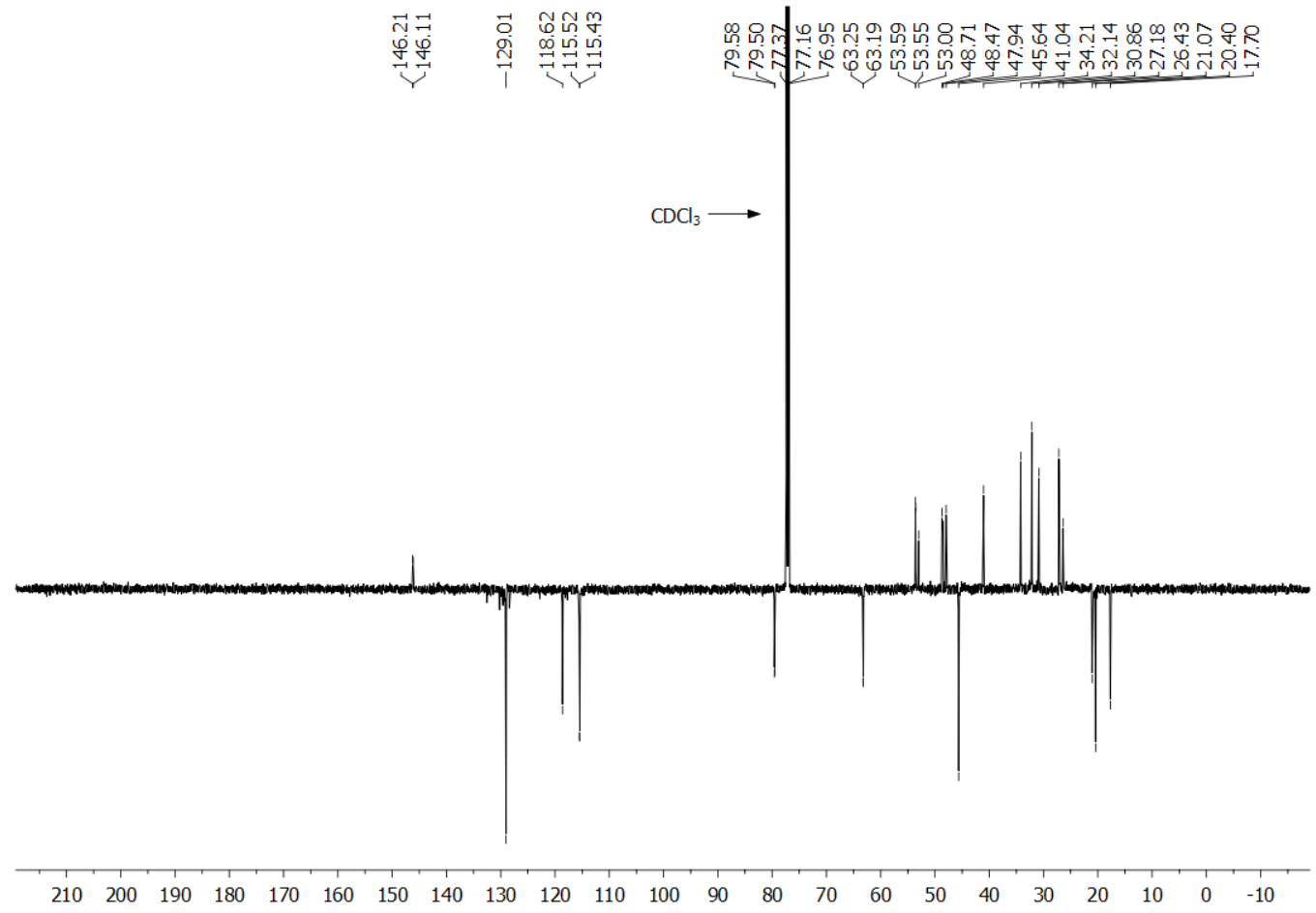


L2a, ^{1}H spectrum.

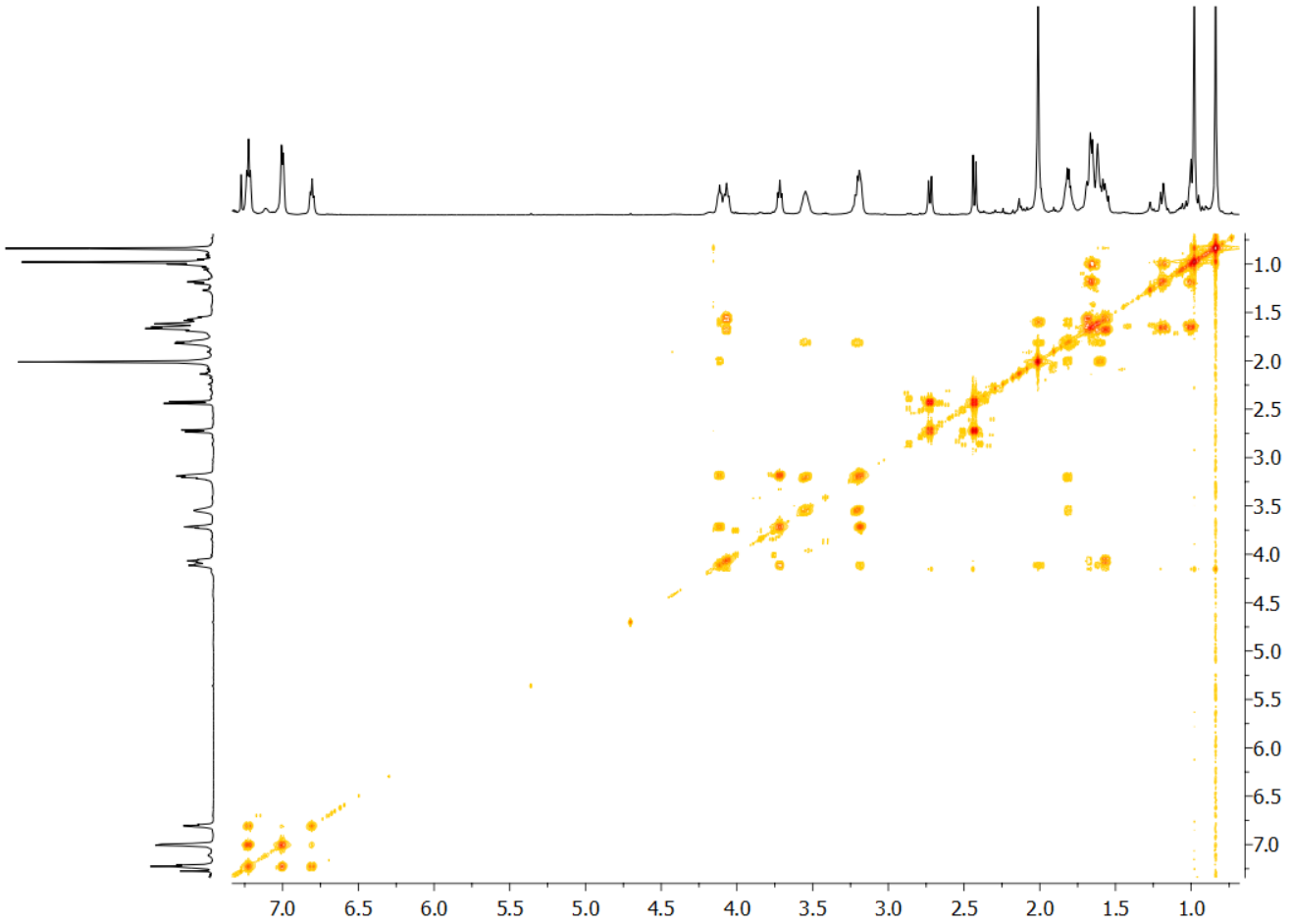
NMR AND HRMS SPECTRA



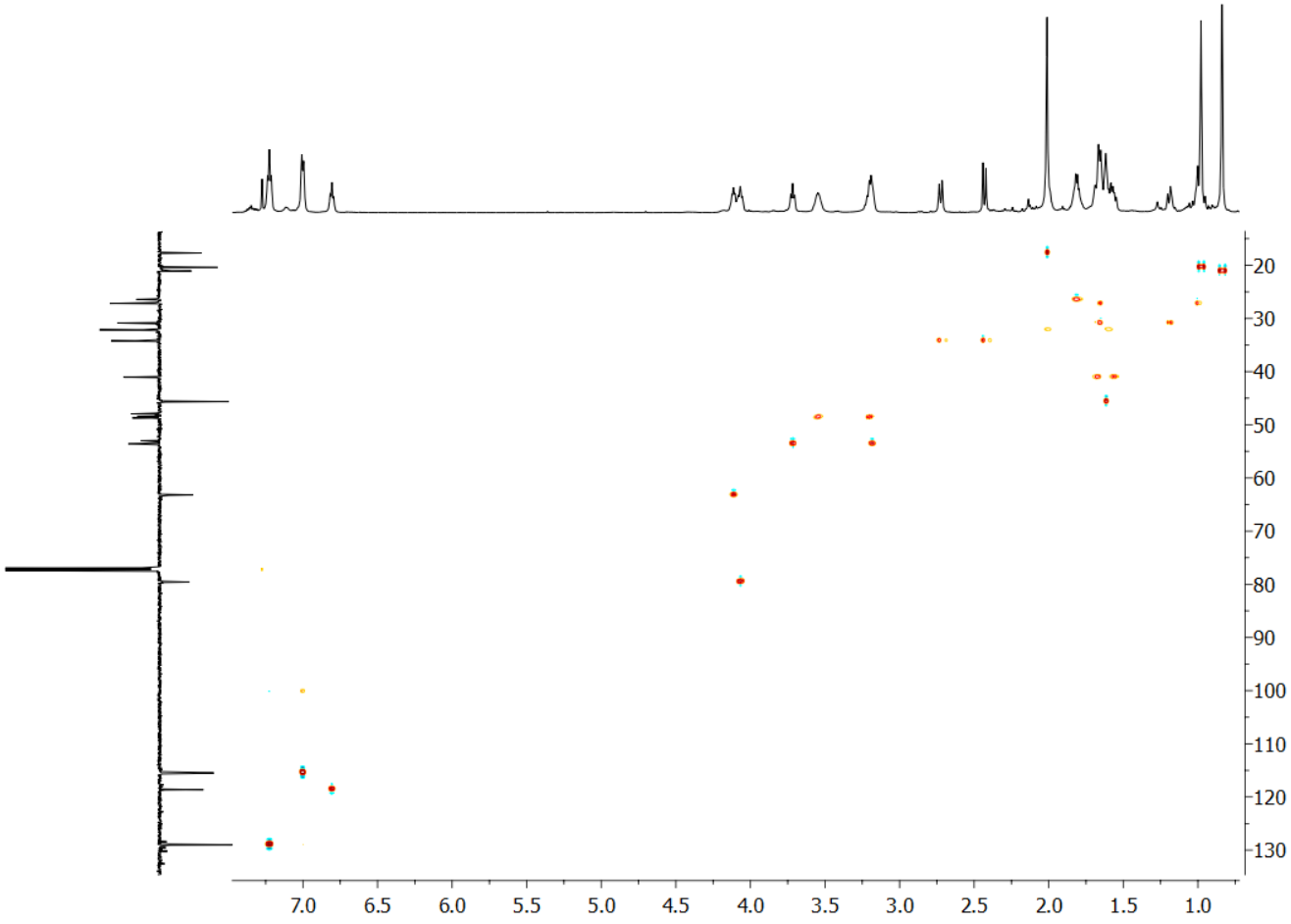
L2a, $^{13}C\{^{1}H\}$ spectrum.



L2a, $^{13}C\{^{1}H\}$ DEPT spectrum.

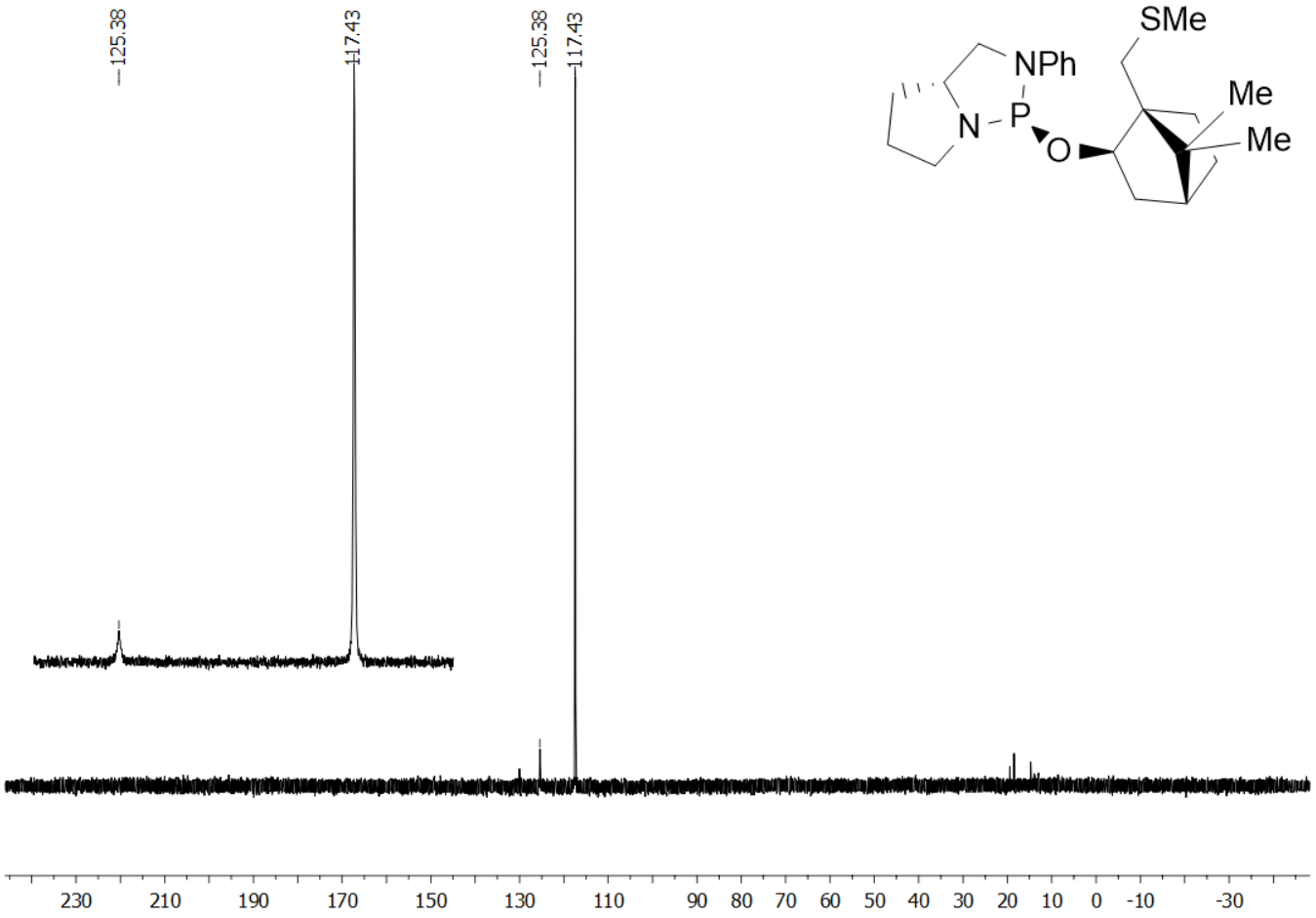


L2a, ^{1}H-^{1}H COSY spectrum.

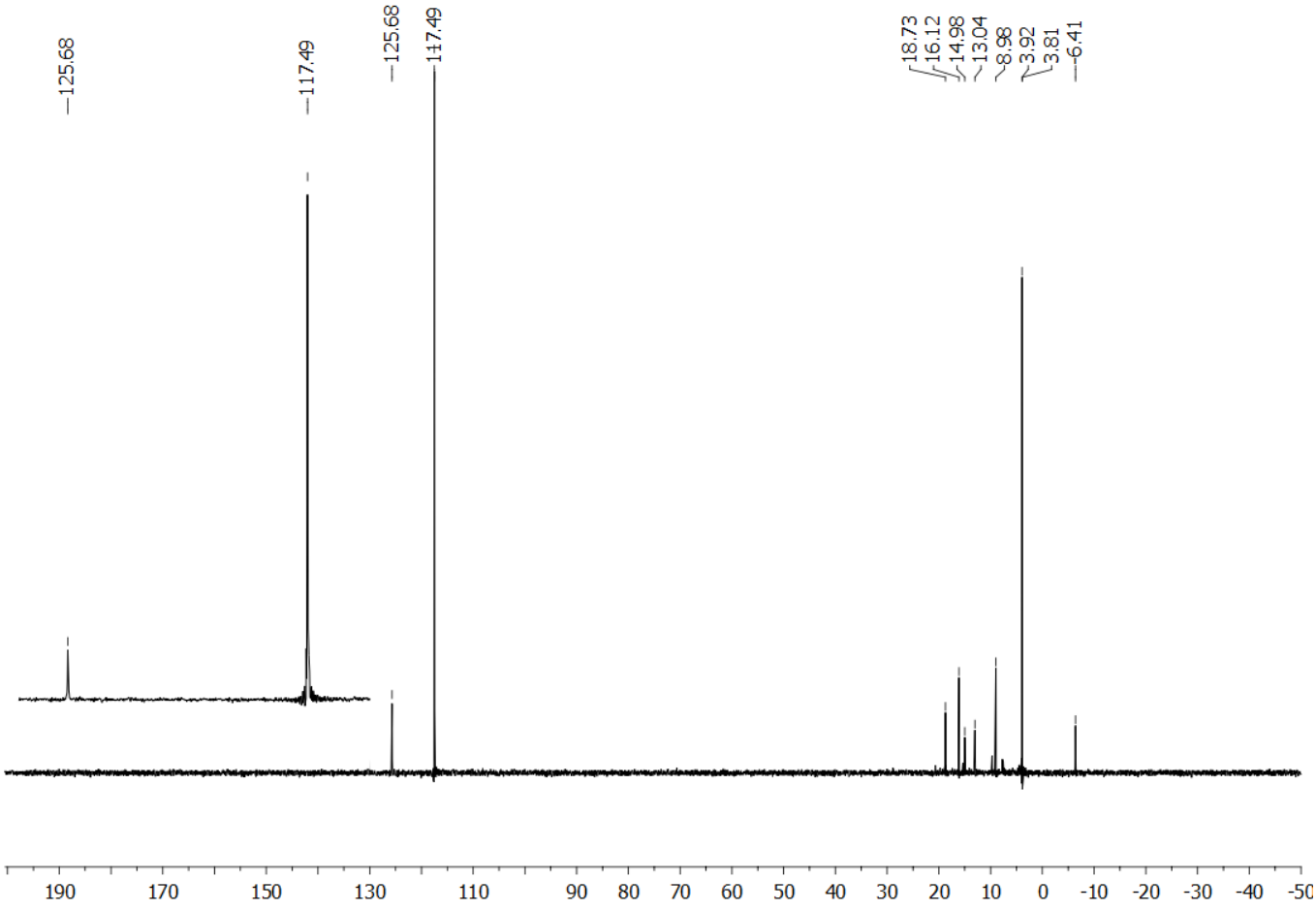


L2a, ^{1}H-^{13}C HSQC spectrum.

NMR AND HRMS SPECTRA

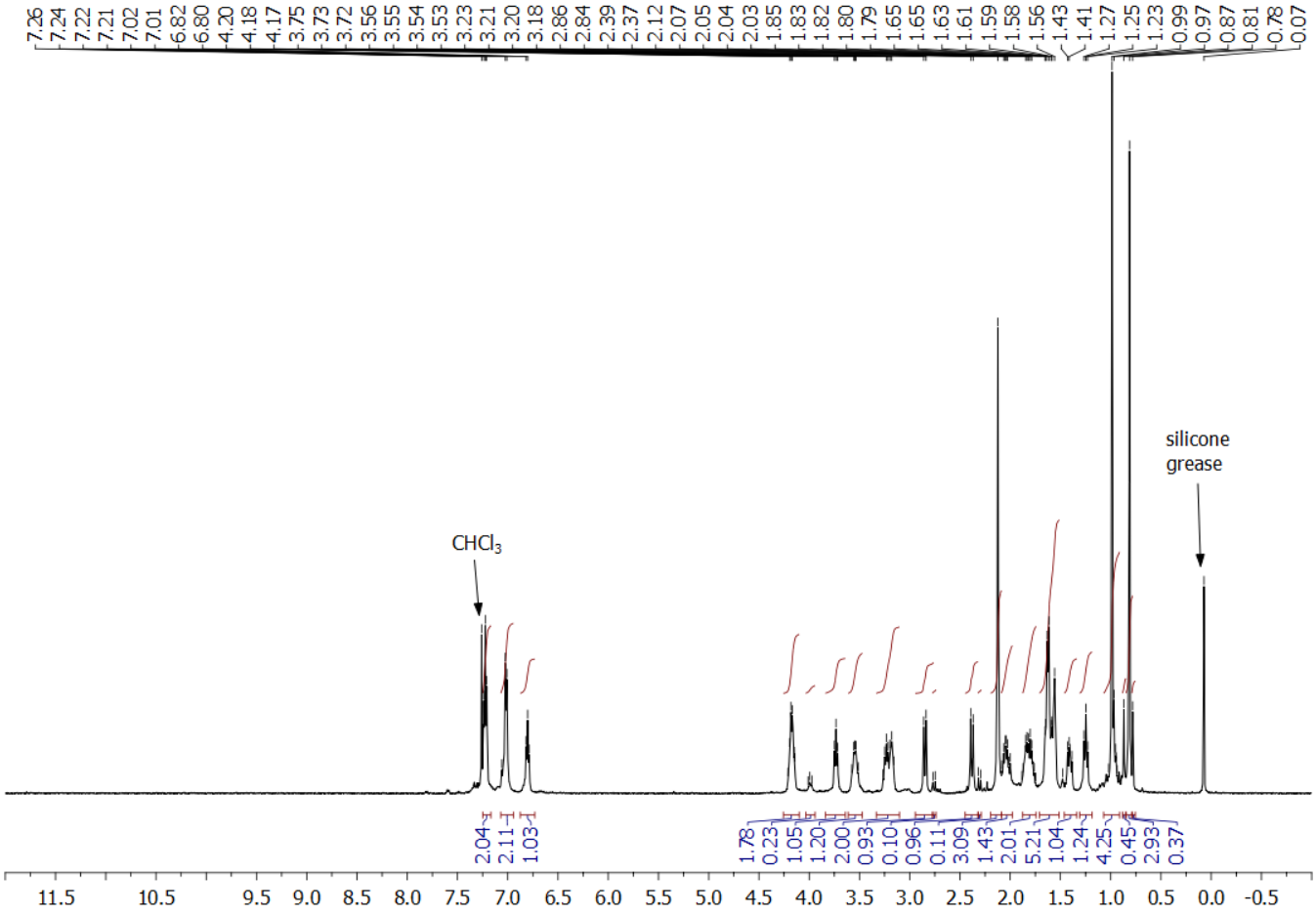


L2b, $^{31}P\{^{1}H\}$ spectrum.

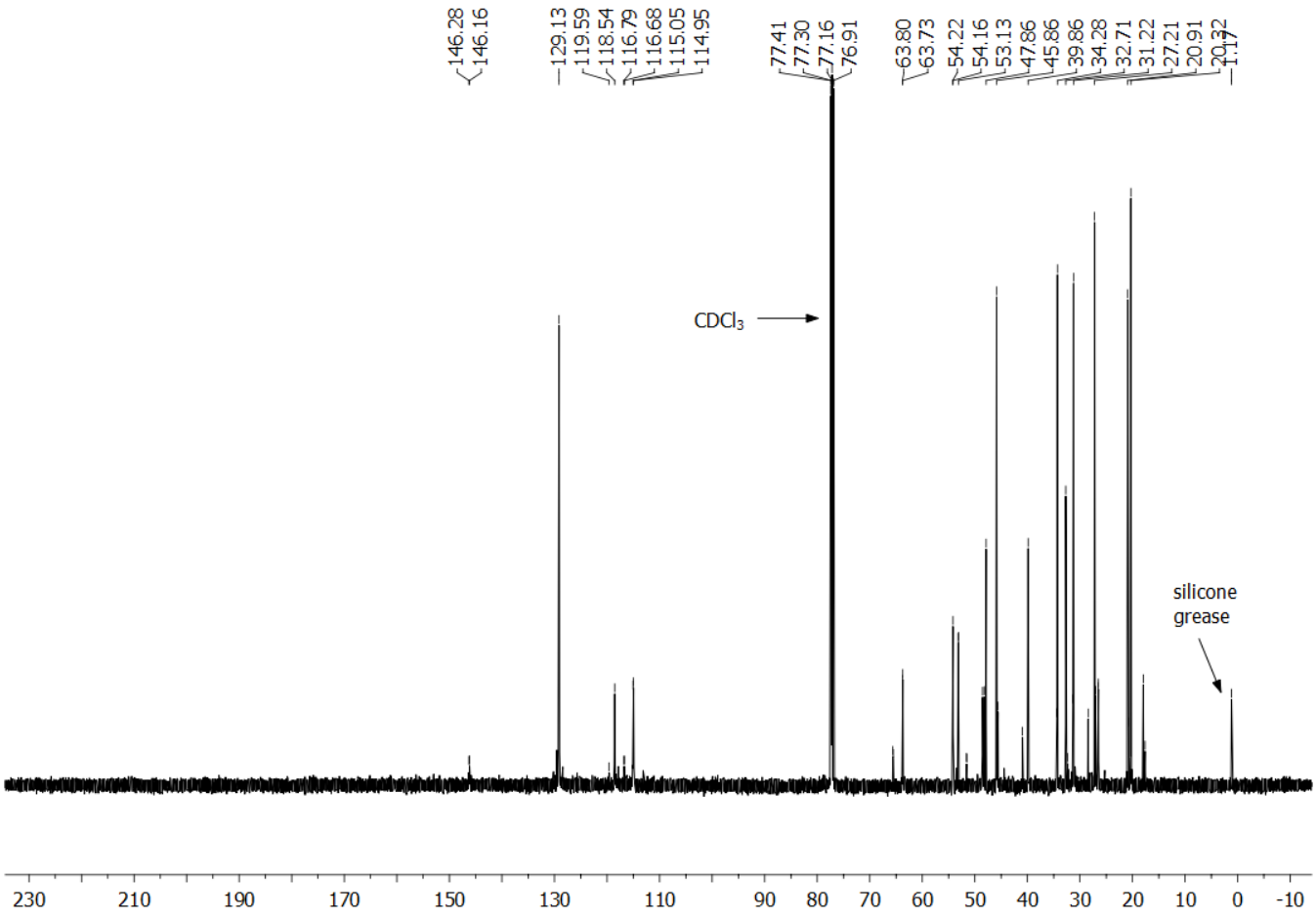


L2b after refluxing, $^{31}P\{^{1}H\}$ spectrum.

NMR AND HRMS SPECTRA

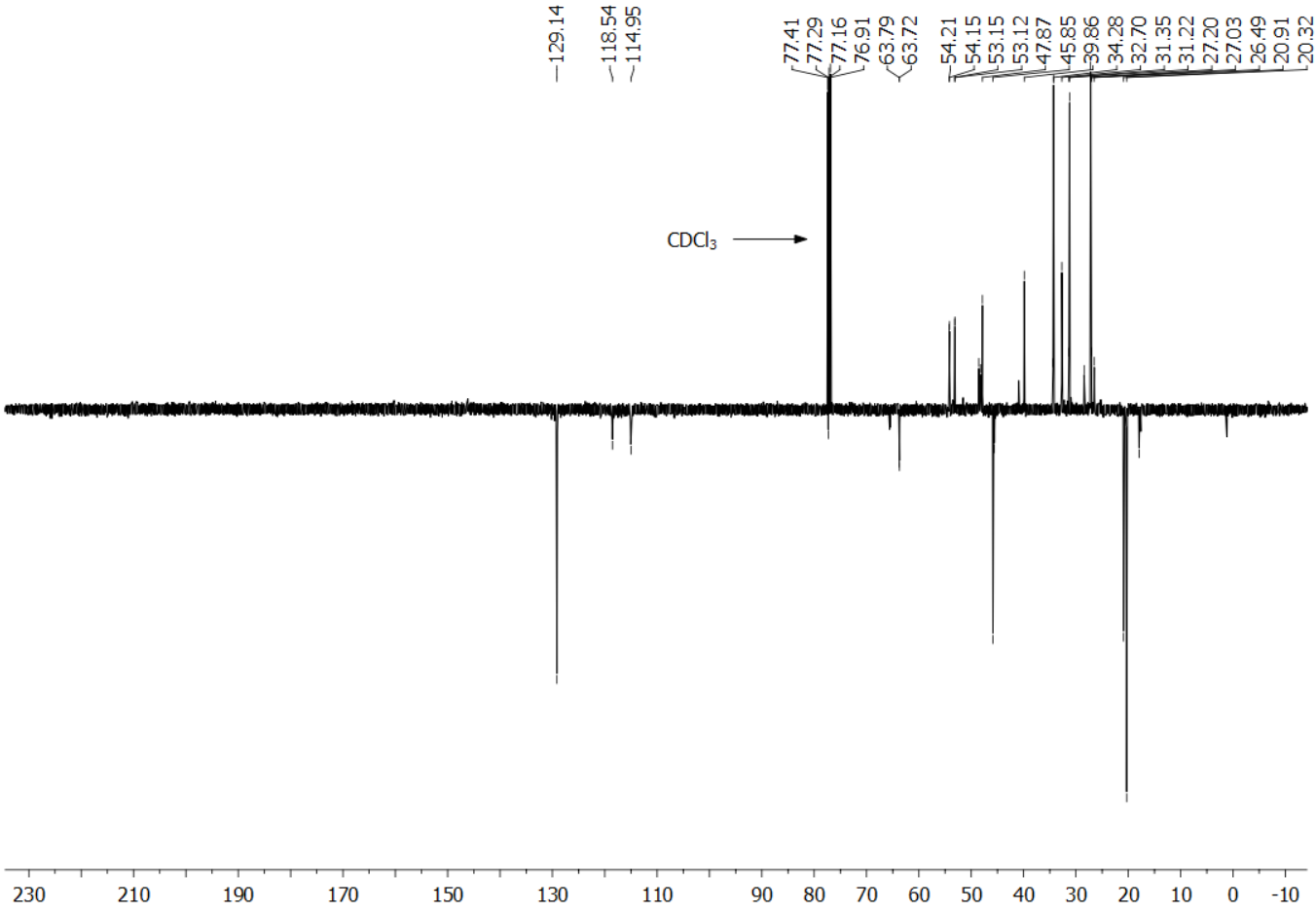


L2b, ^{1}H spectrum.

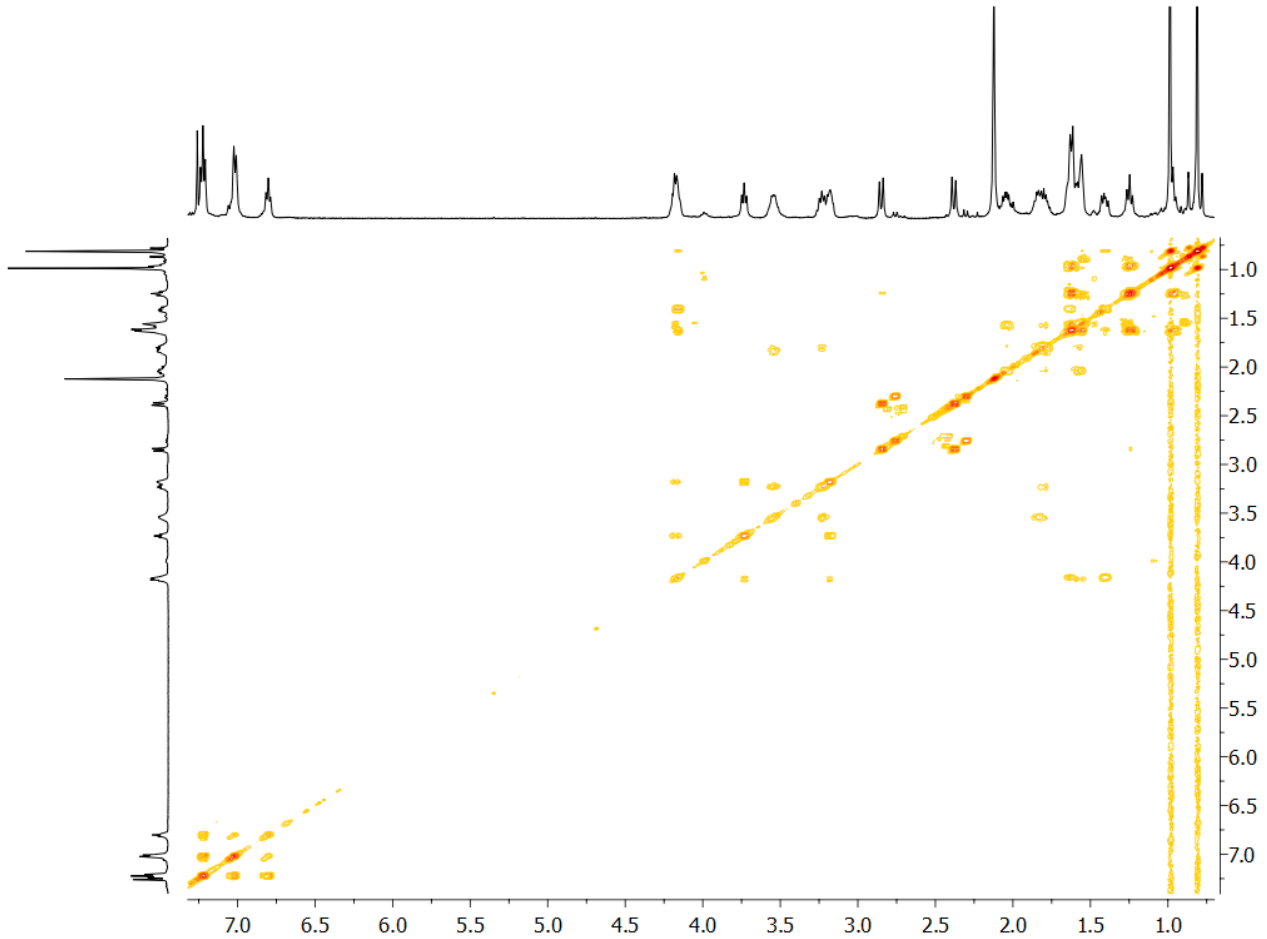


L2b, ^{13}C{^{1}H} spectrum.

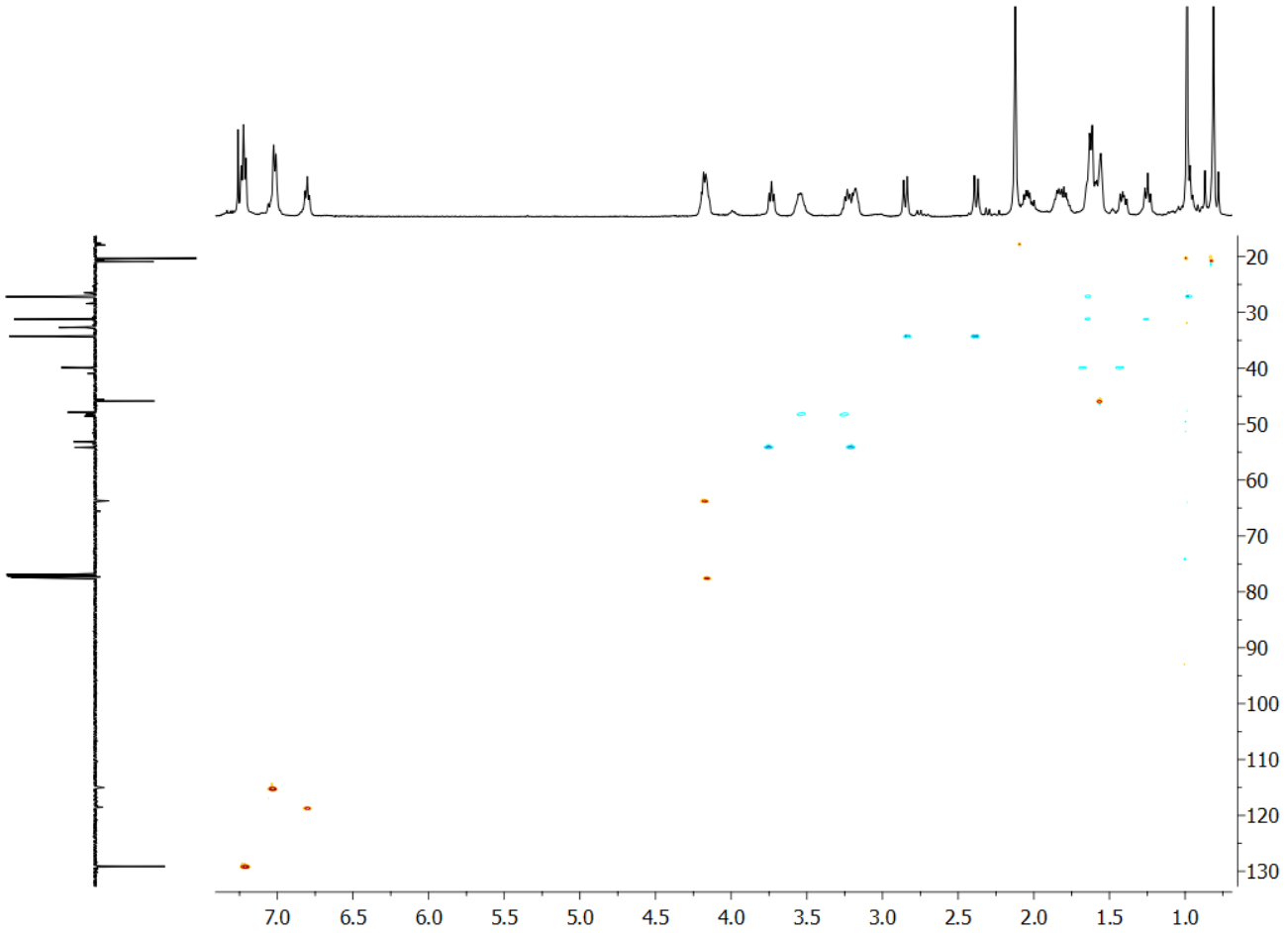
NMR AND HRMS SPECTRA



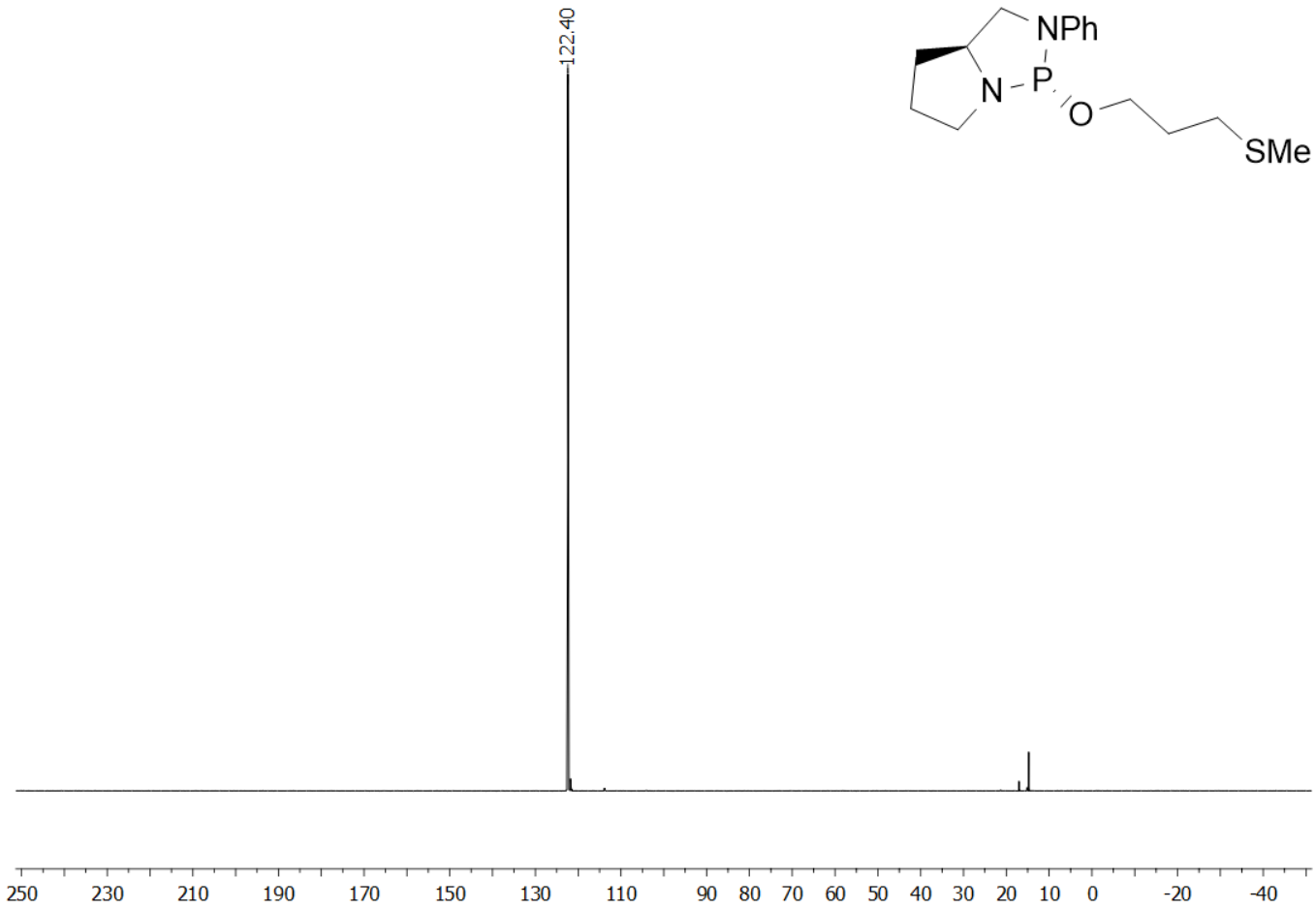
L2b, $^{13}C\{^{1}H\}$ APT spectrum.



L2b, ^{1}H-^{1}H COSY spectrum.

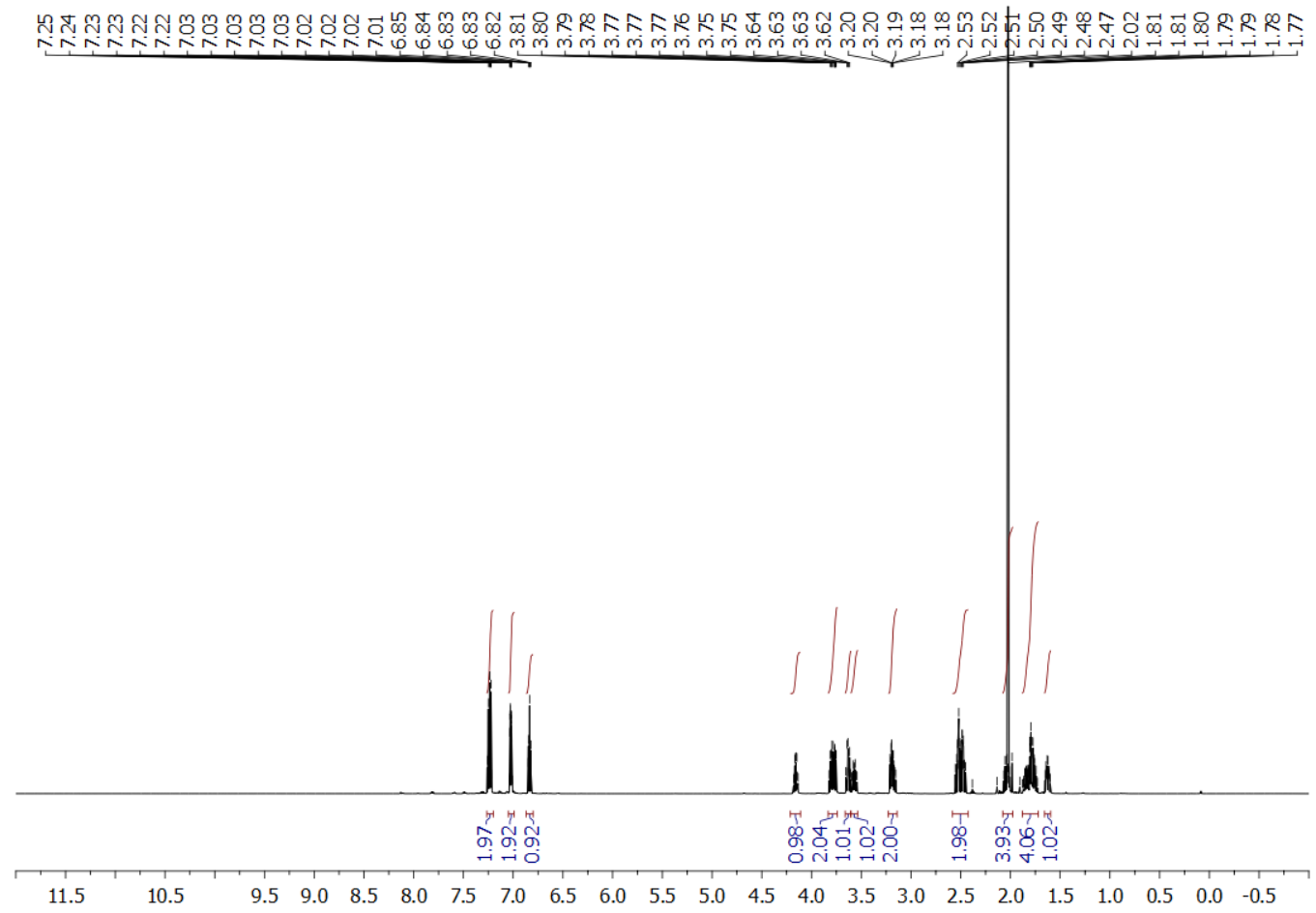


L2b, ^{1}H-^{13}C HSQC spectrum.

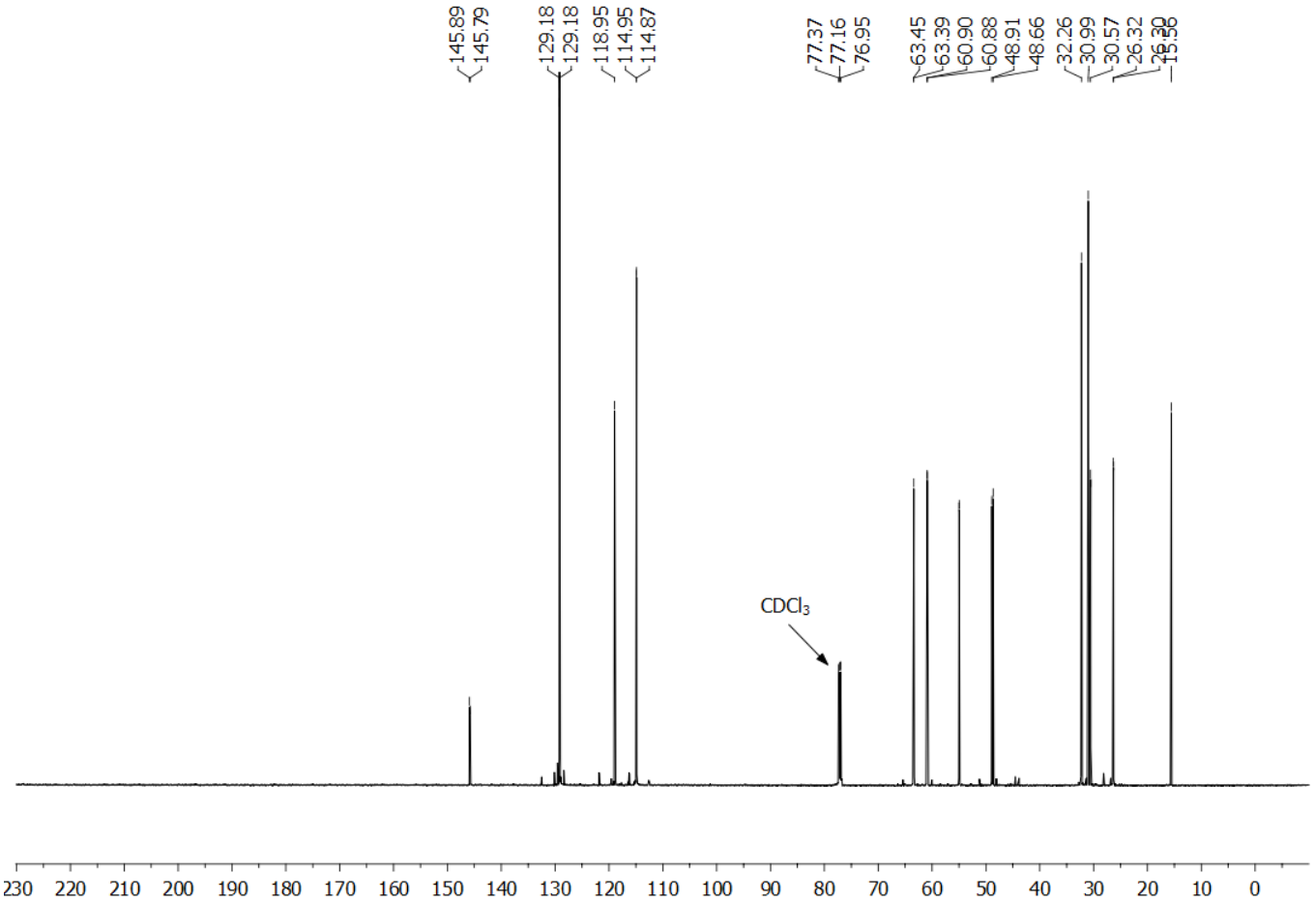


L3, $^{31}P\{^{1}H\}$ spectrum.

NMR AND HRMS SPECTRA

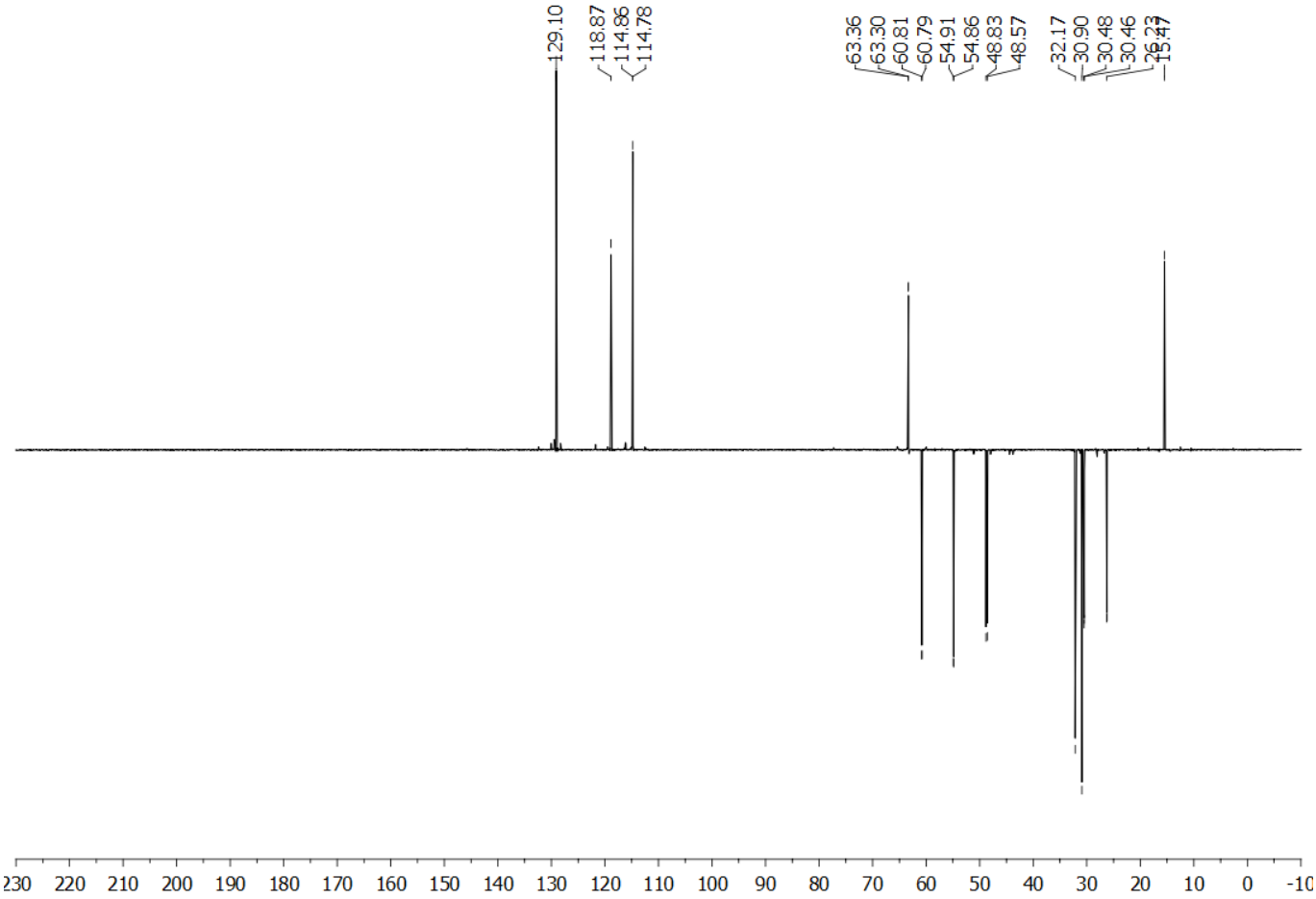


L3, ^{1}H spectrum.

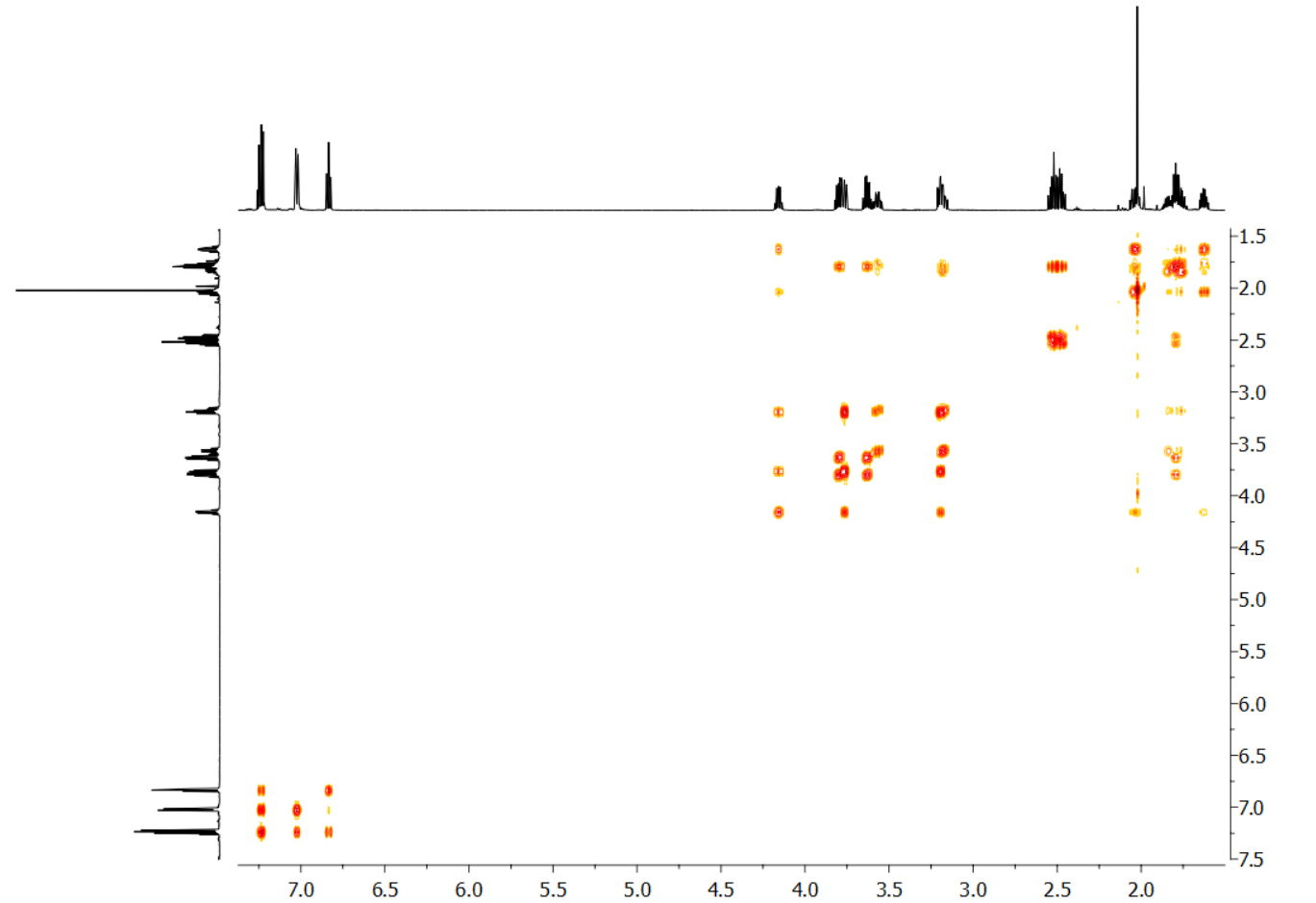


L3, $^{13}C\{^{1}H\}$ spectrum.

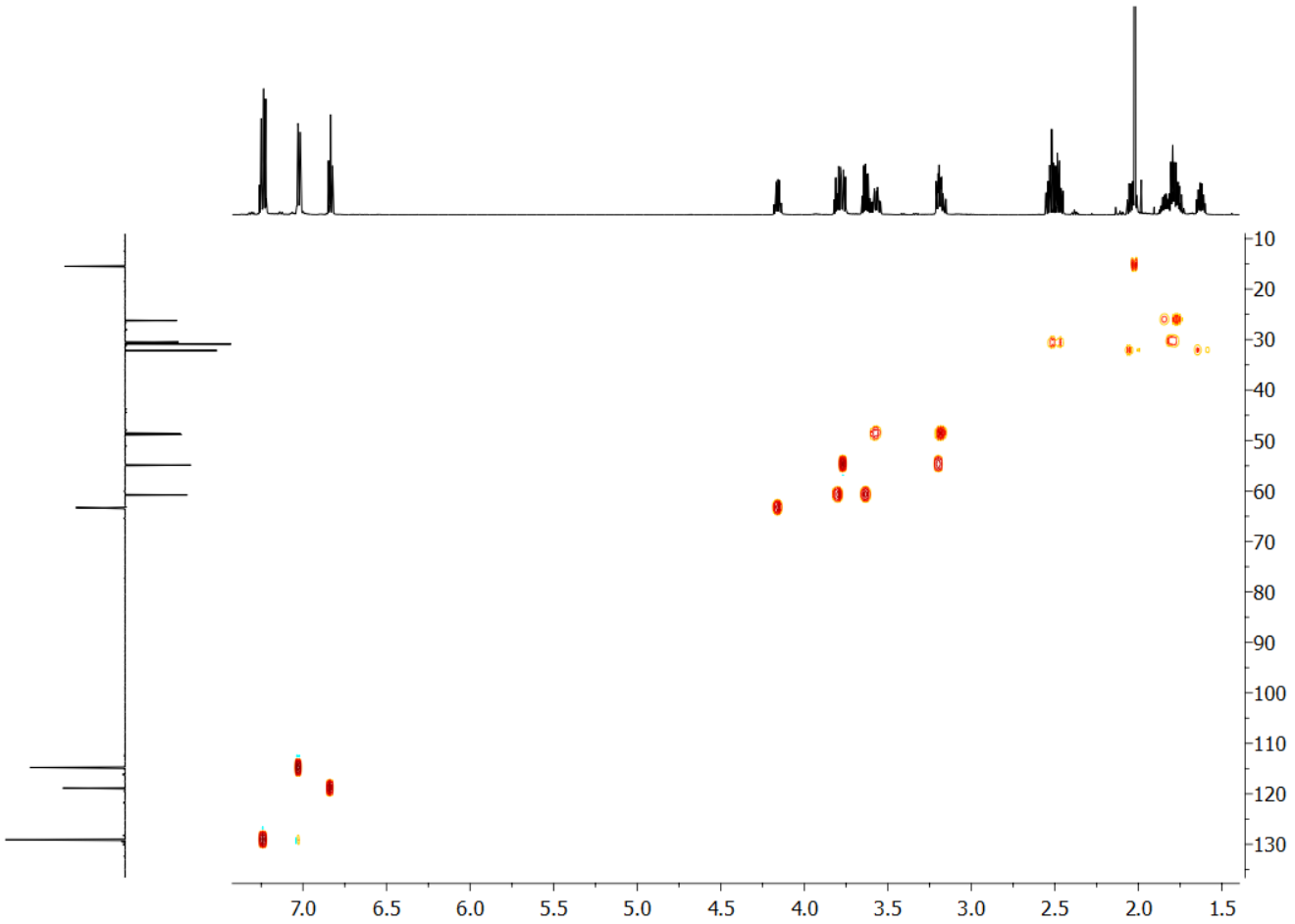
NMR AND HRMS SPECTRA



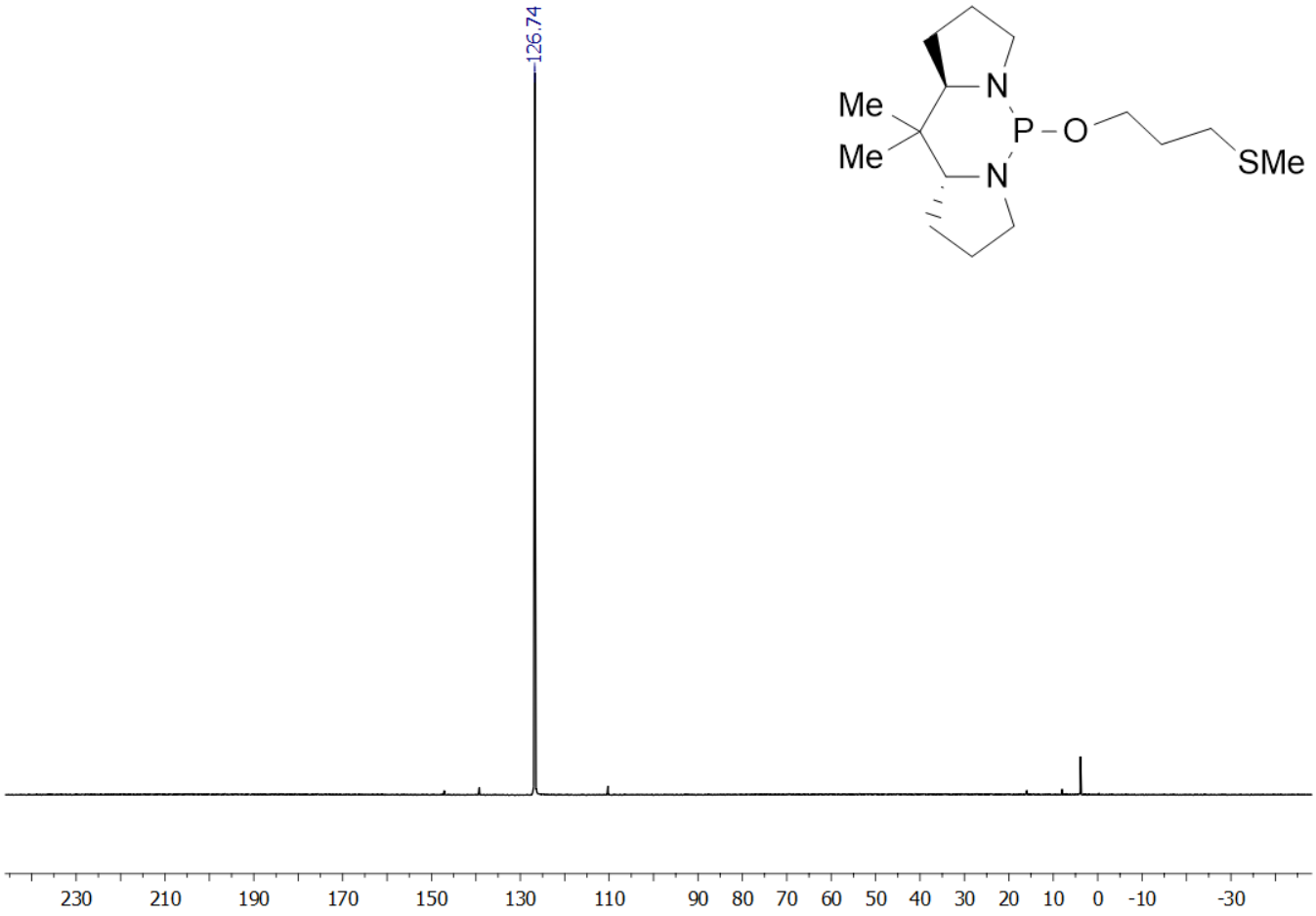
L3, $^{13}C\{^{1}H\}$ DEPT spectrum.



L3, ^{1}H-^{1}H COSY spectrum.

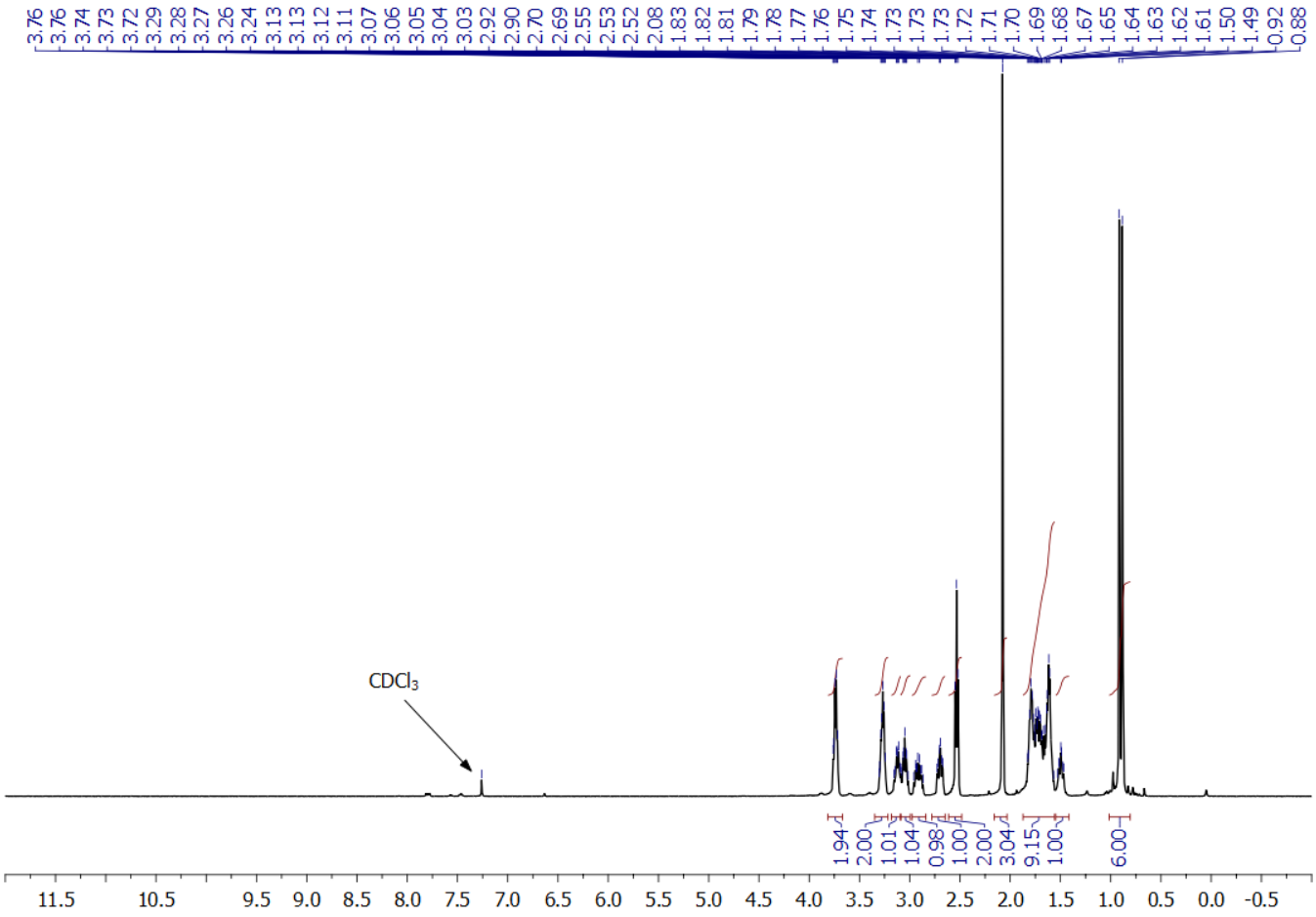


L3, ^{1}H-^{13}C HSQC spectrum.

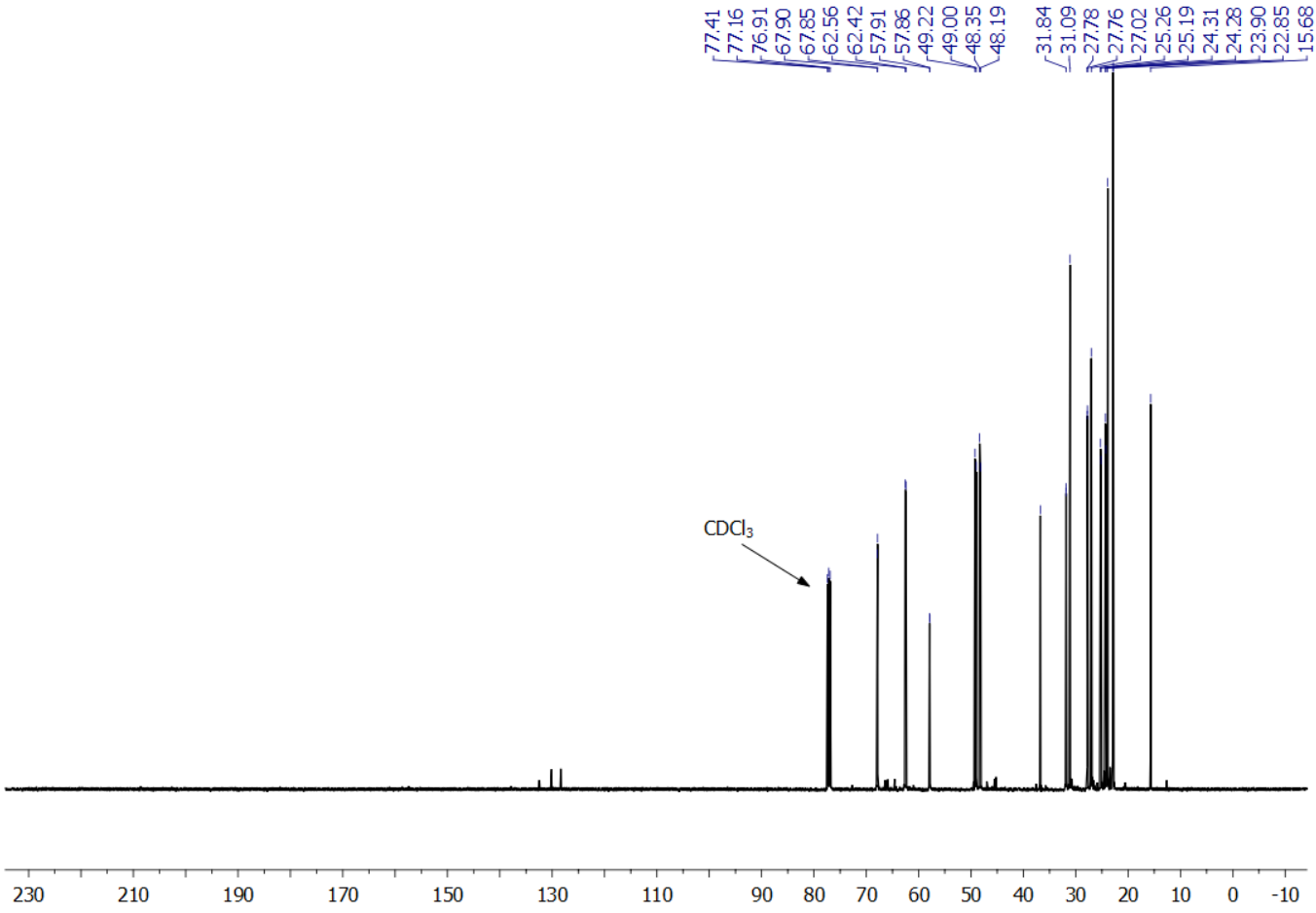


L4, $^{31}P\{^{1}H\}$ spectrum.

NMR AND HRMS SPECTRA

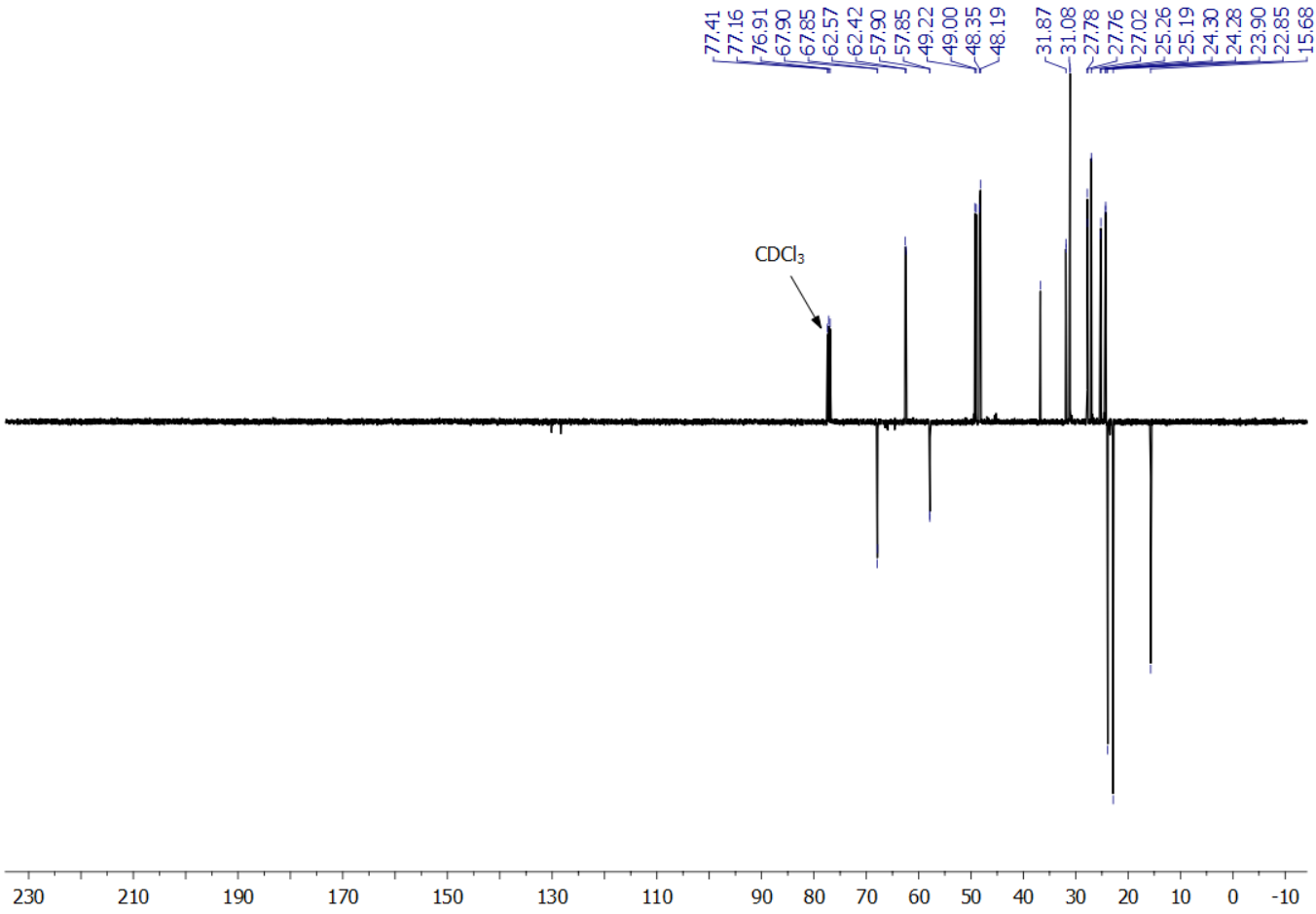


L4, ^{1}H spectrum.

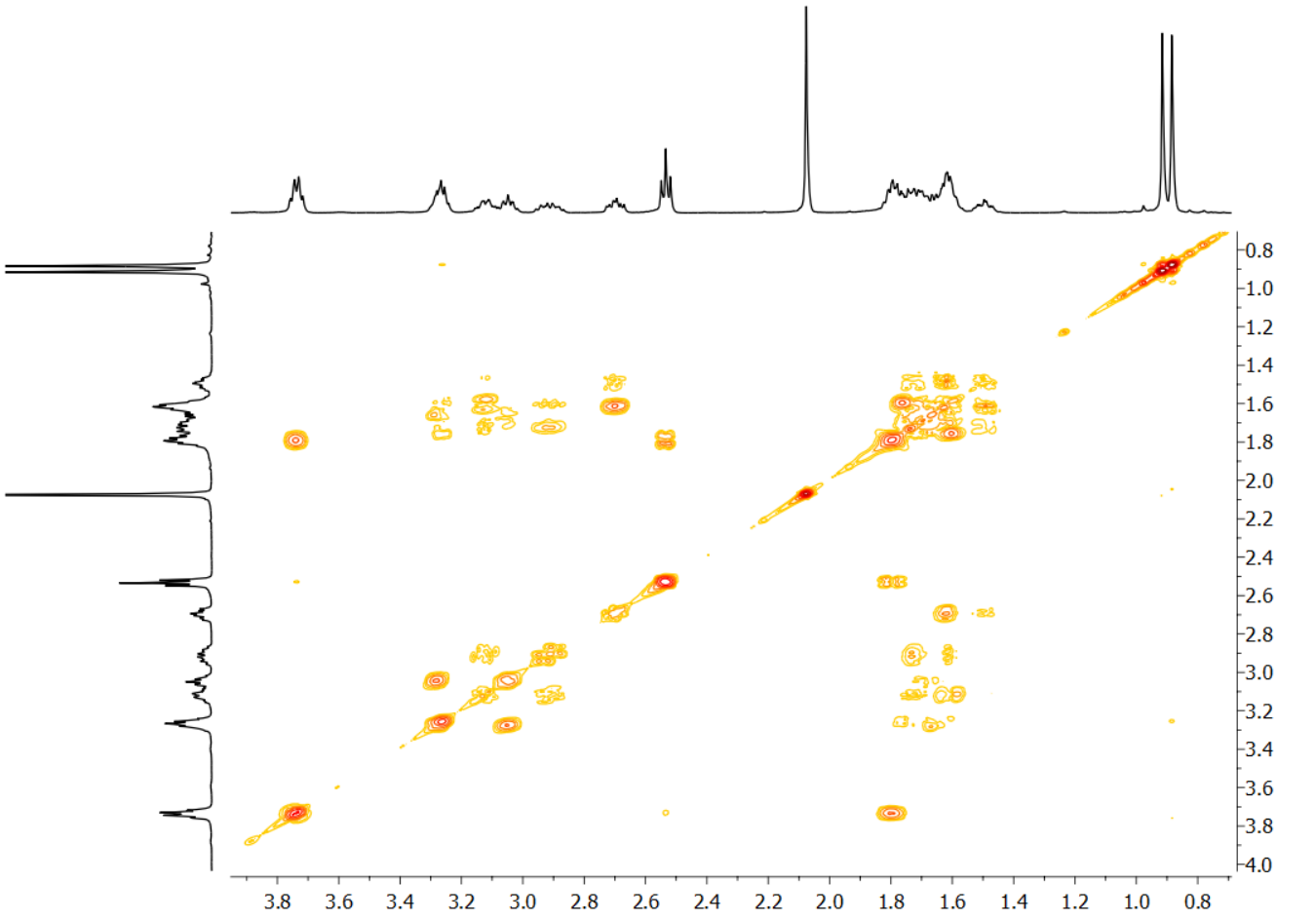


L4, ^{13}C{^{1}H} spectrum.

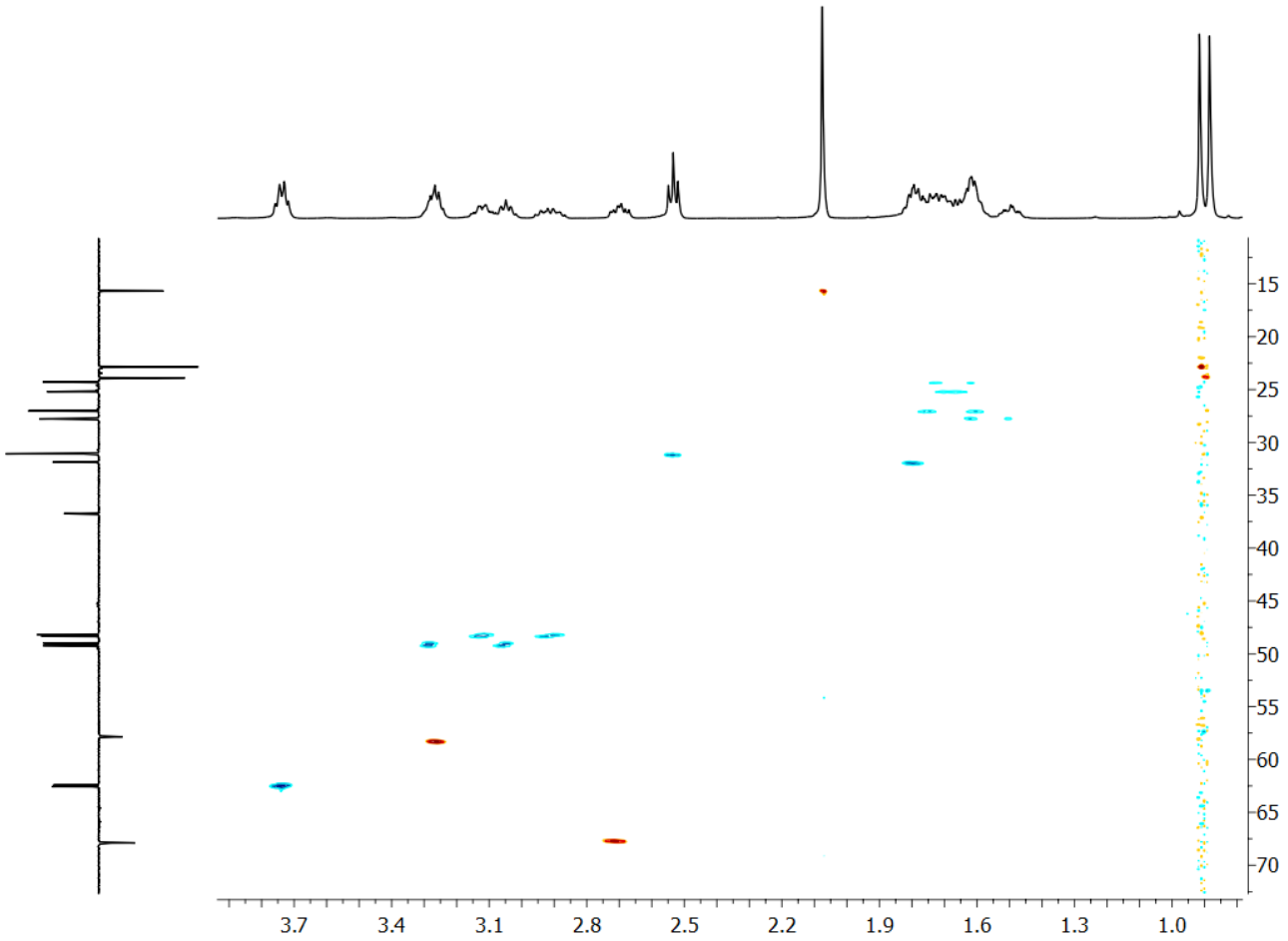
NMR AND HRMS SPECTRA



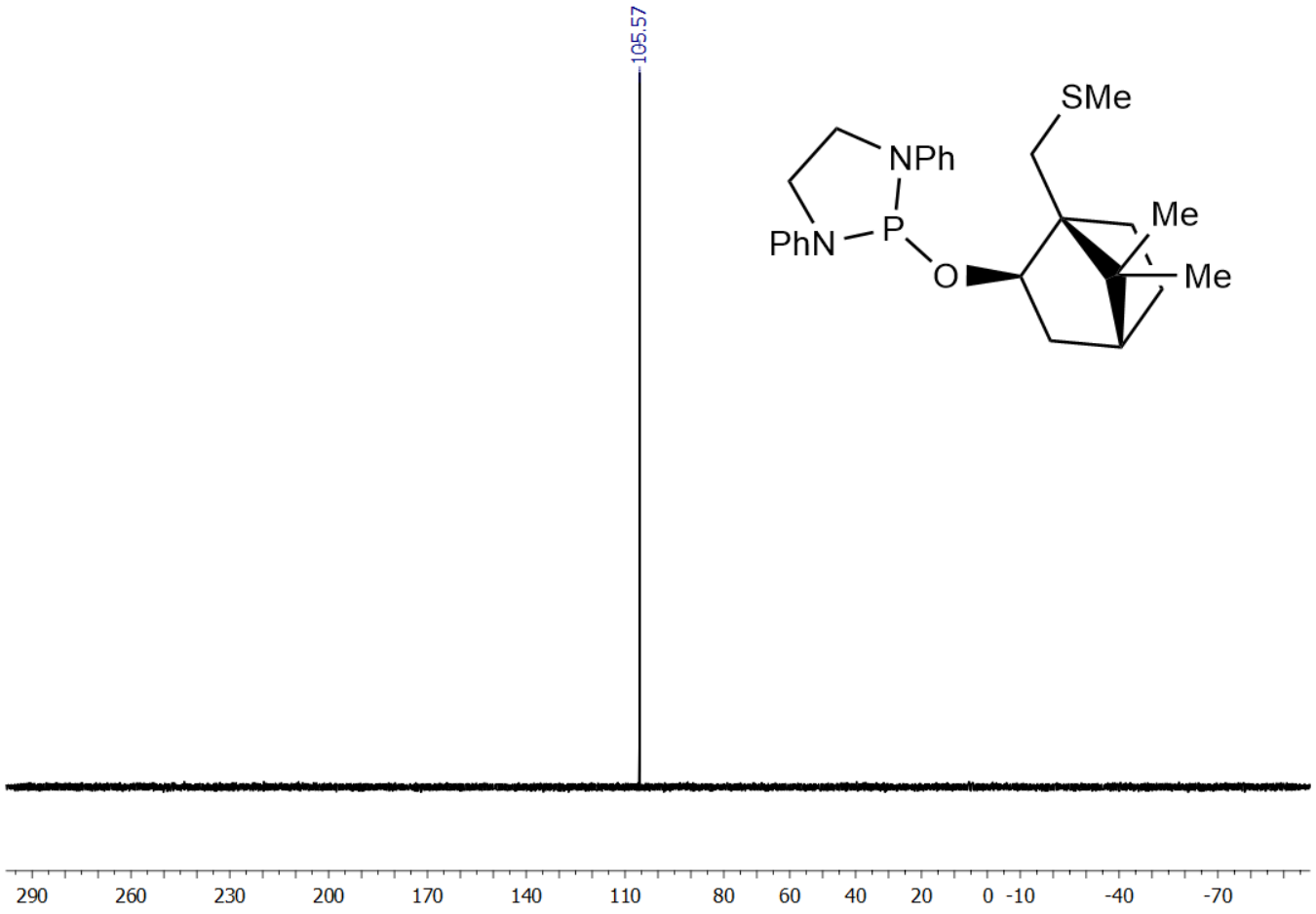
L4, $^{13}C\{^{1}H\}$ APT spectrum.



L4, ^{1}H-^{1}H COSY spectrum.

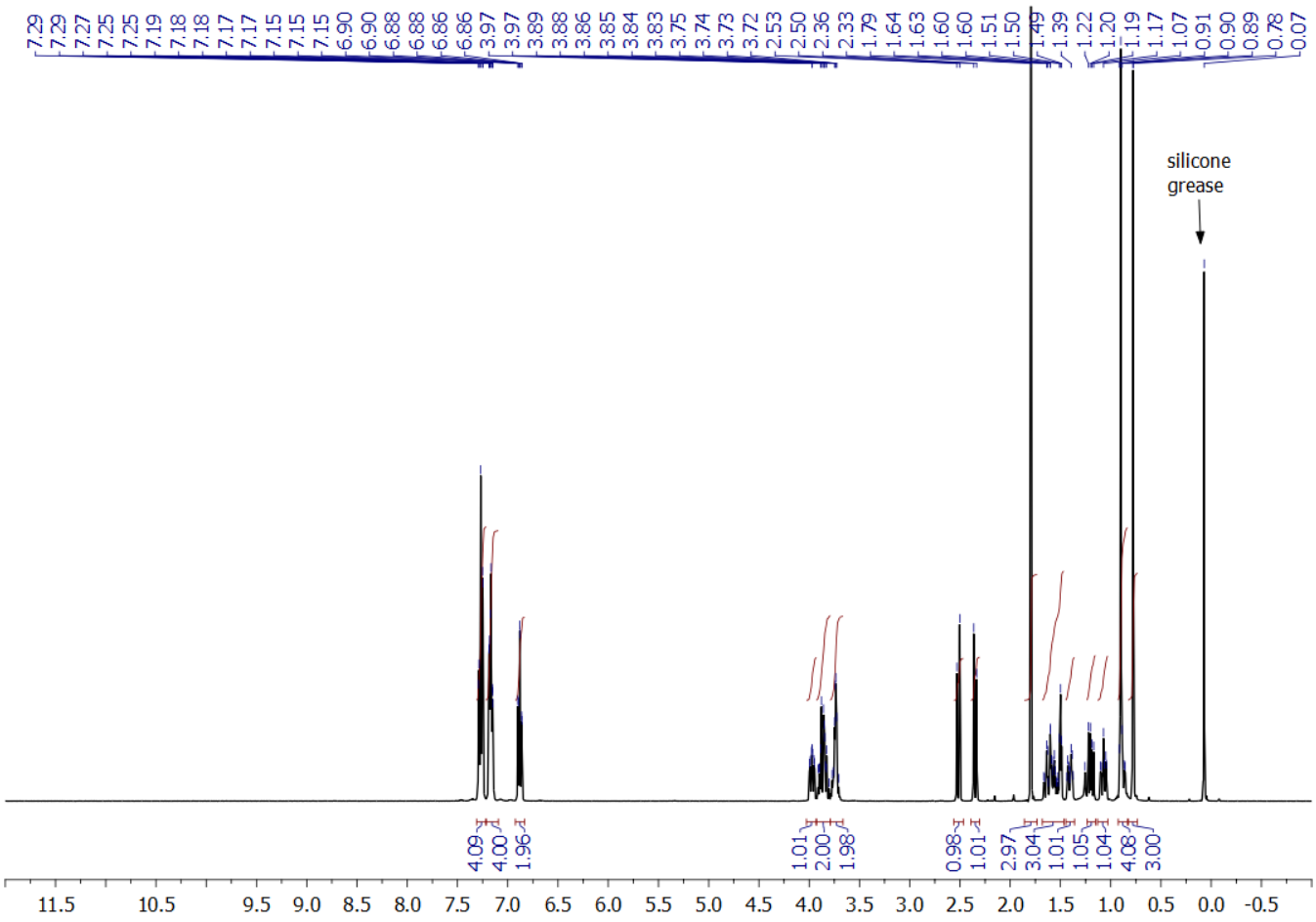


L4, ^{1}H-^{13}C HSQC spectrum.

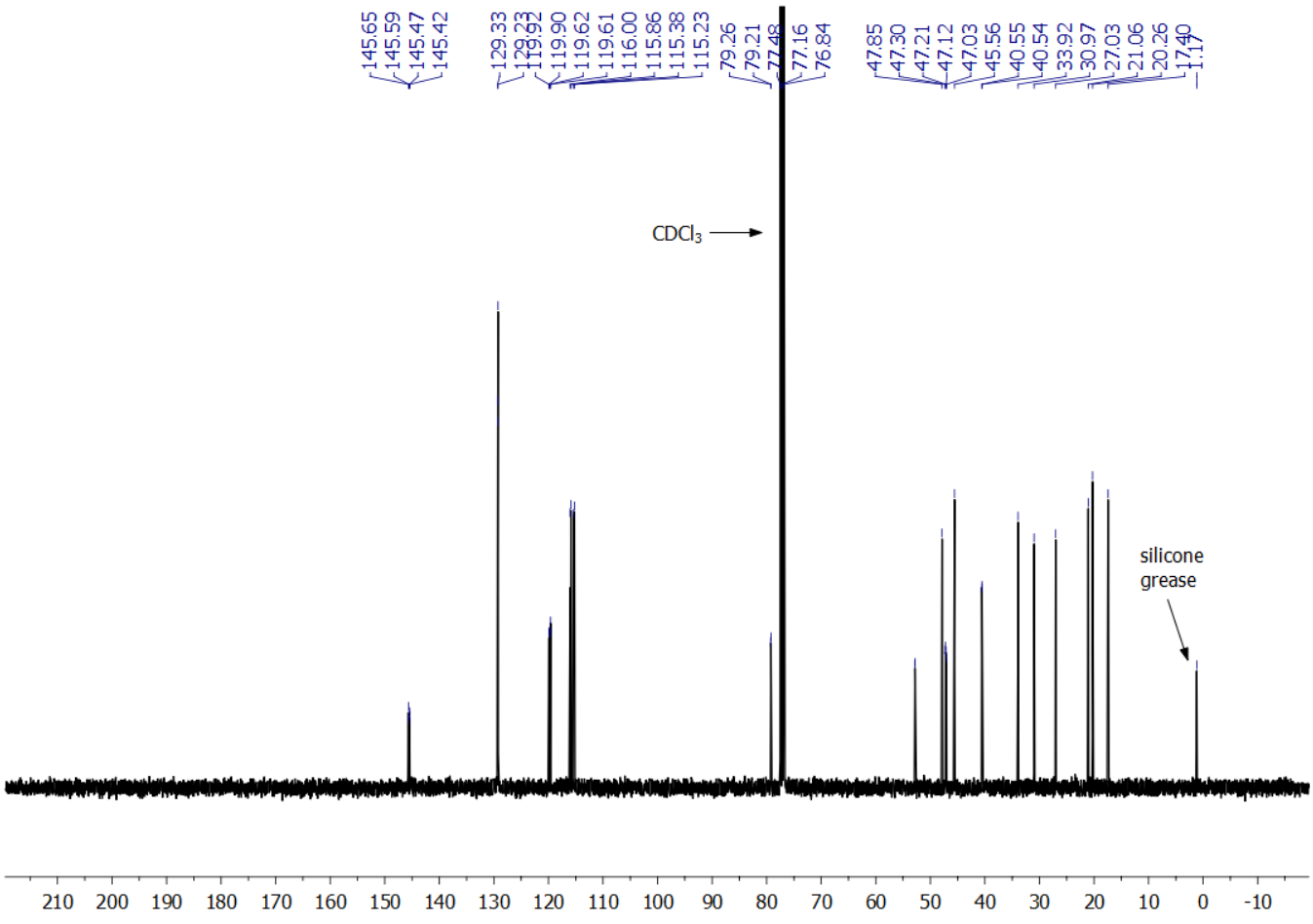


L5, $^{31}P\{^{1}H\}$ spectrum.

NMR AND HRMS SPECTRA

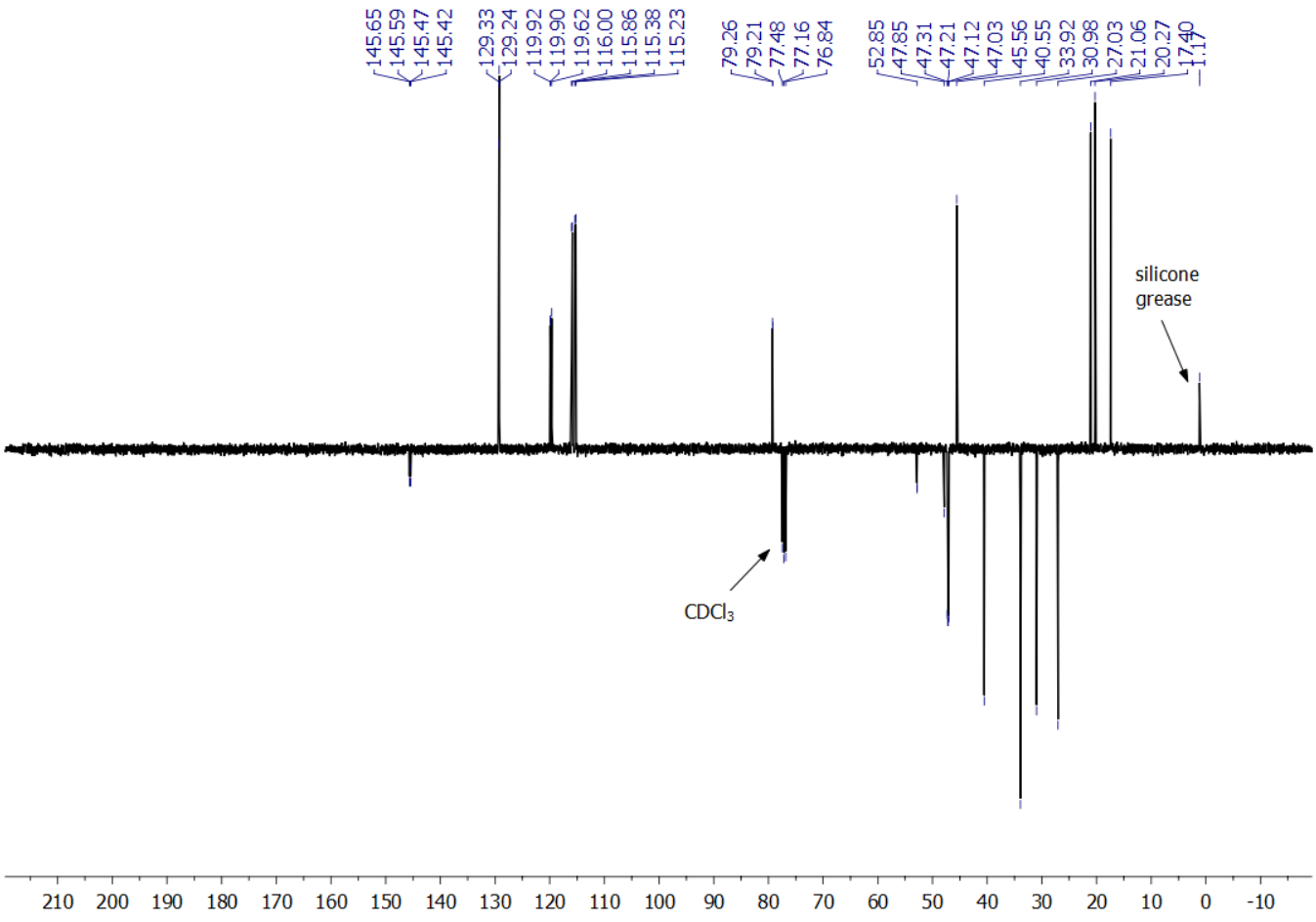


L5, ^{1}H spectrum.

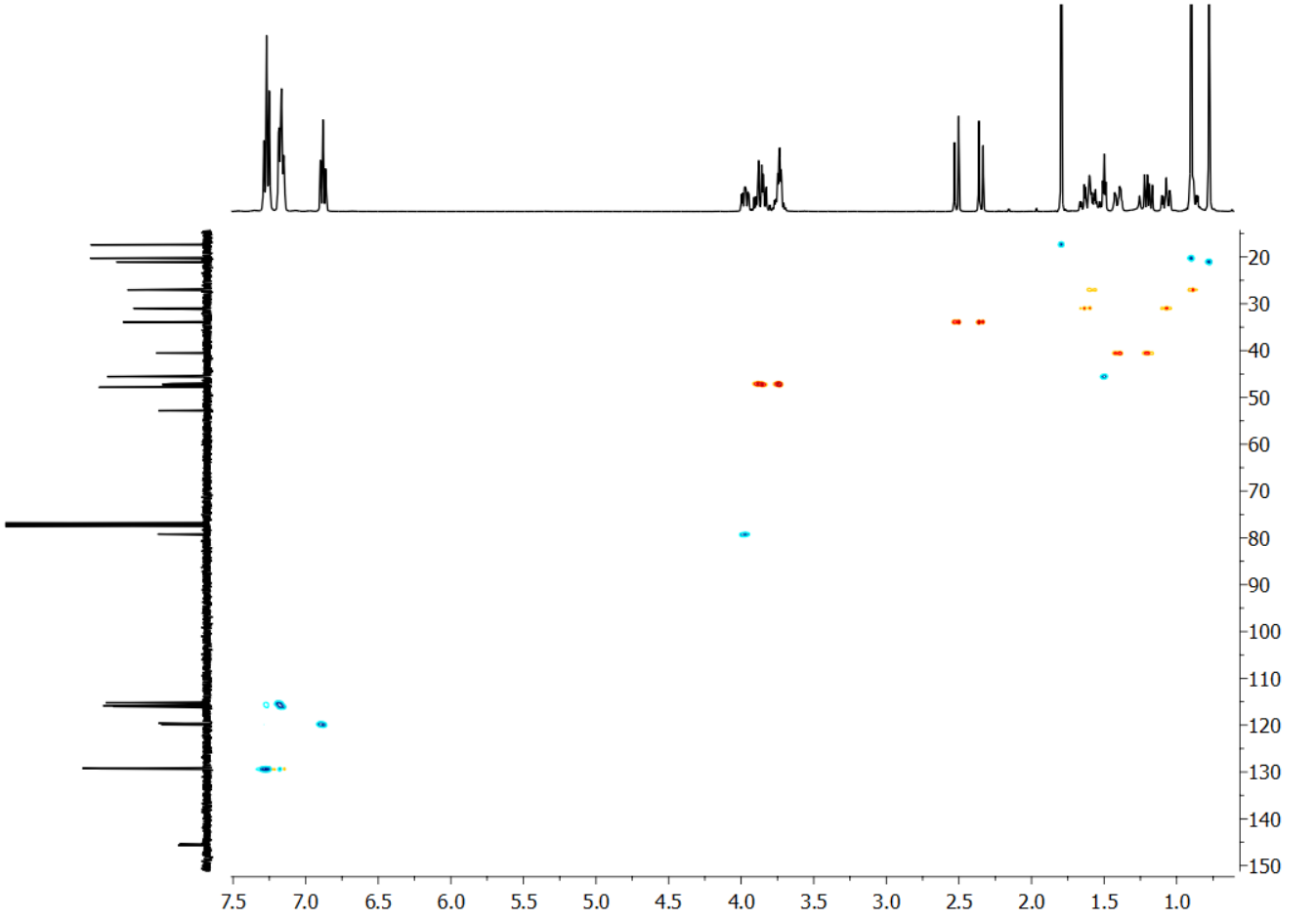


L5, $^{13}C\{^{1}H\}$ spectrum.

NMR AND HRMS SPECTRA

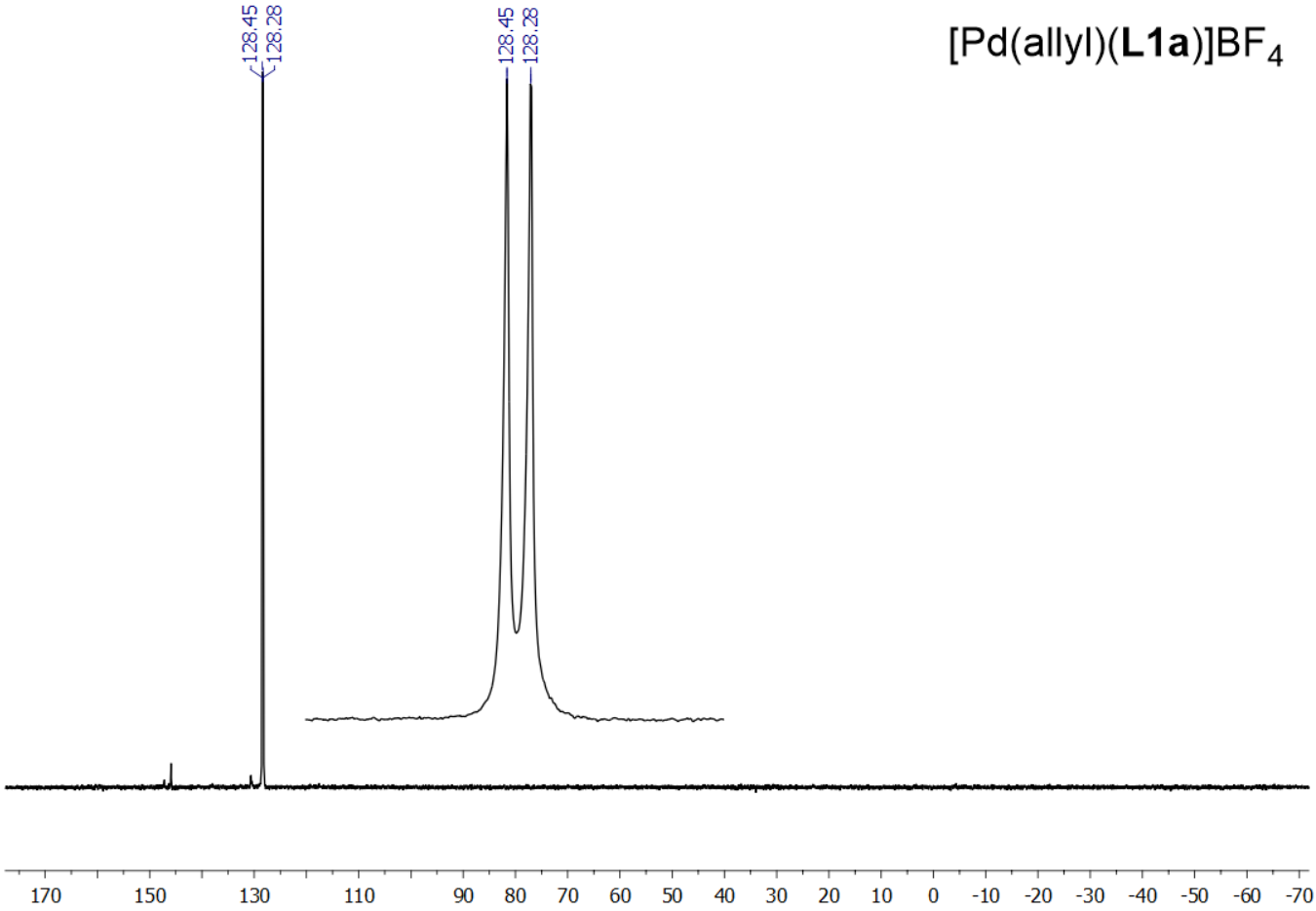


L5, $^{13}C\{^{1}H\}$ DEPT spectrum.

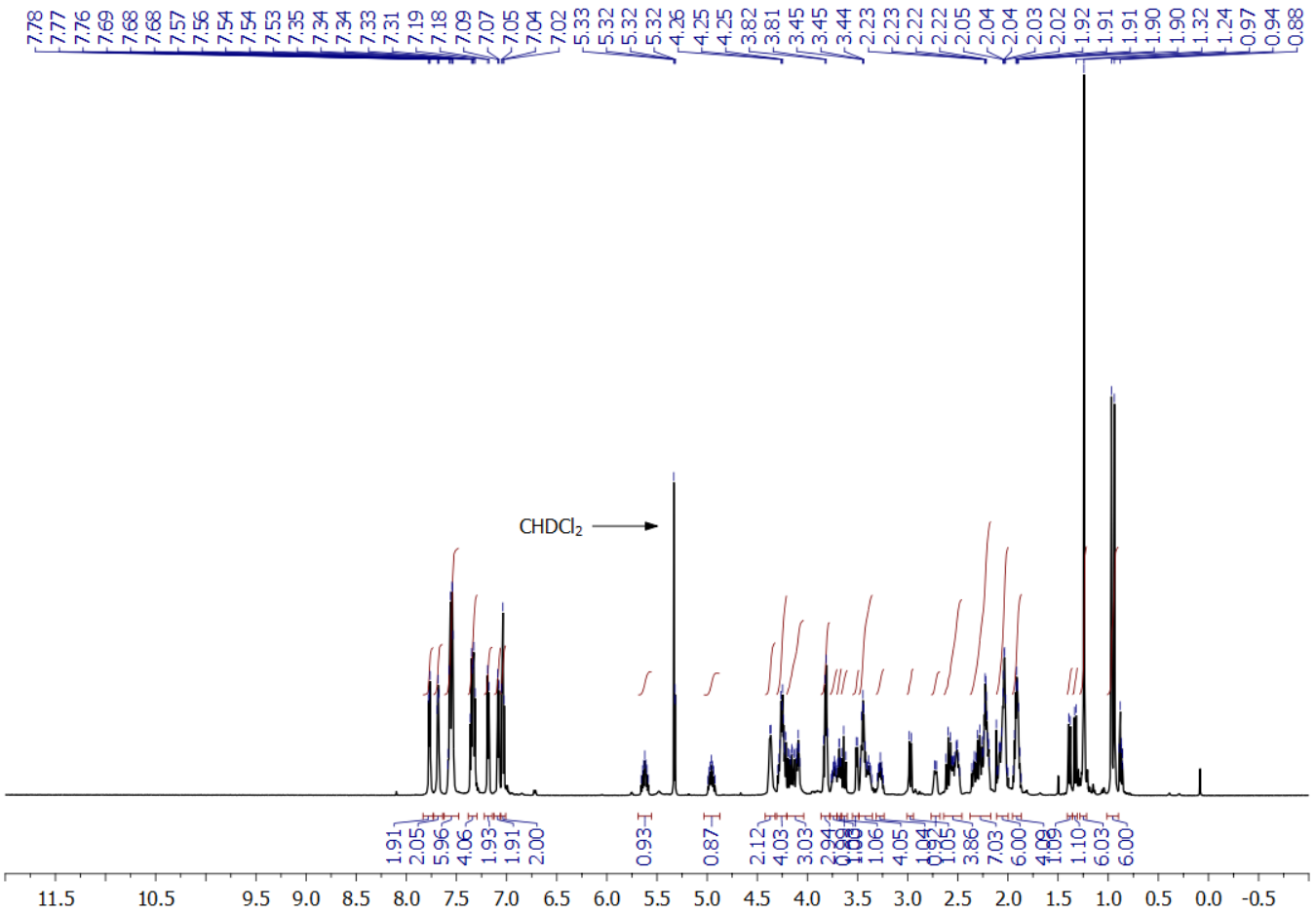


L5, ^{1}H-^{13}C HSQC spectrum.

NMR AND HRMS SPECTRA

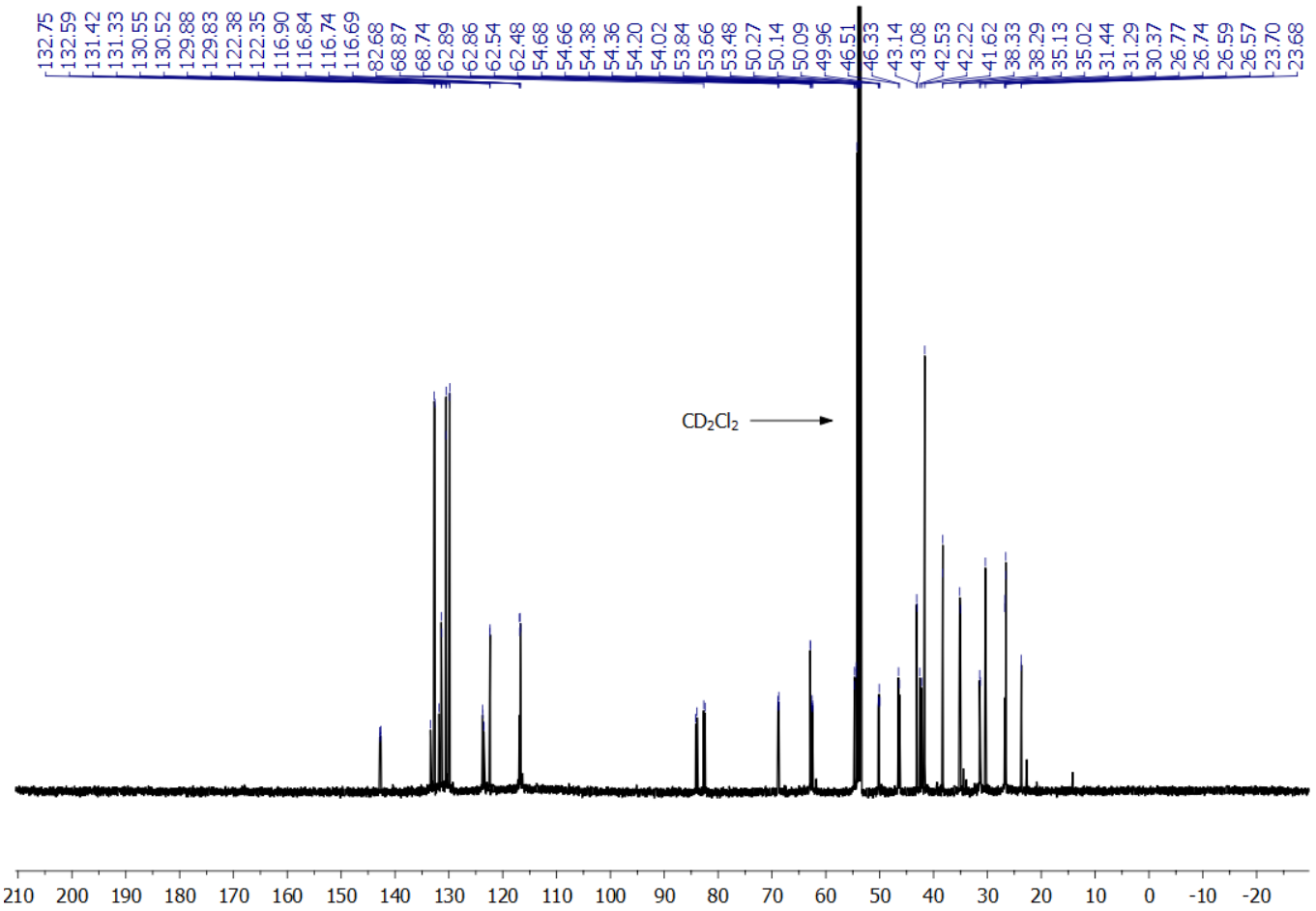


[Pd(allyl)(**L1a**)]BF_4, $^{31}P\{^1H\}$ spectrum.

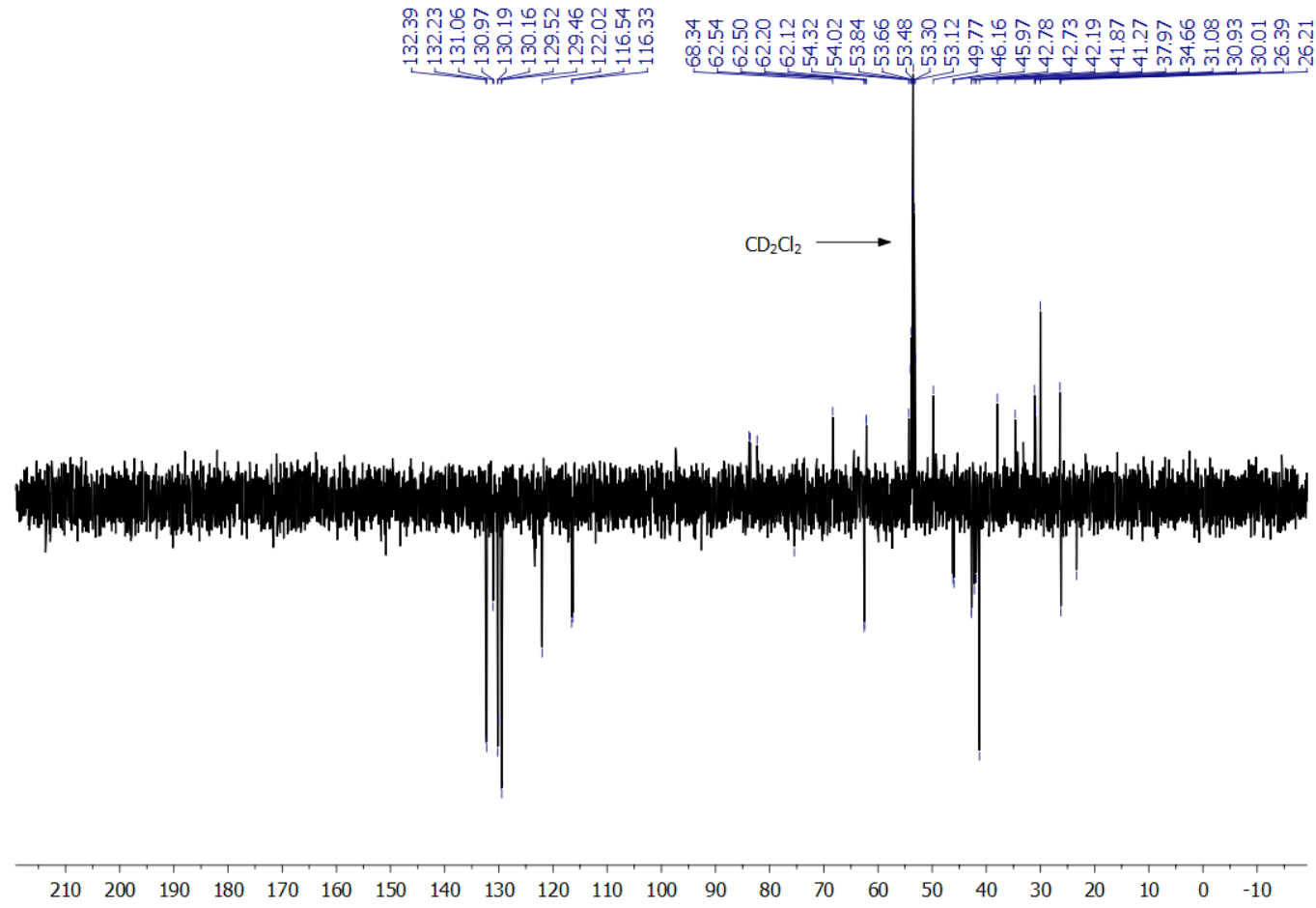


[Pd(allyl)(**L1a**)]BF_4, ^1H spectrum.

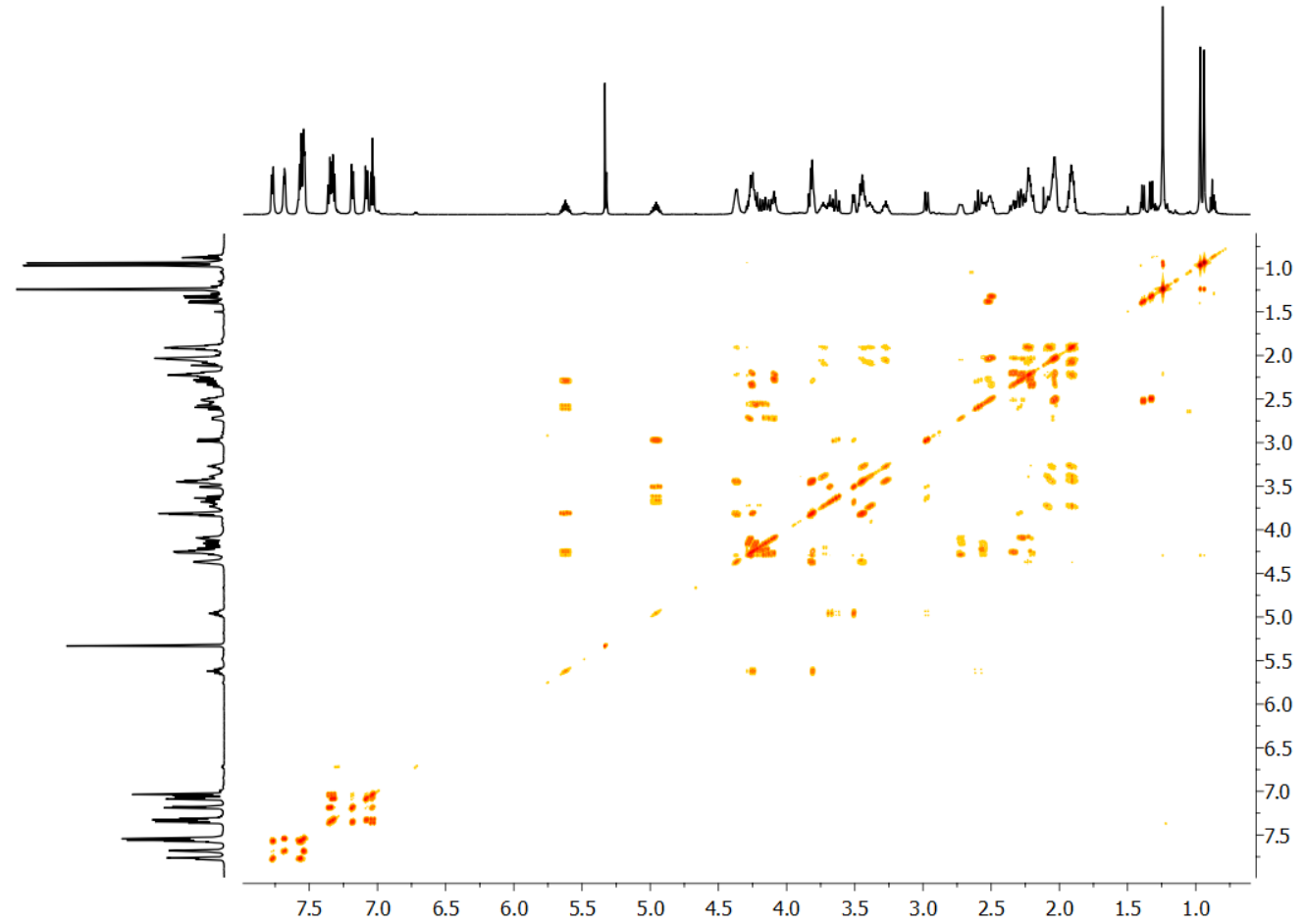
NMR AND HRMS SPECTRA



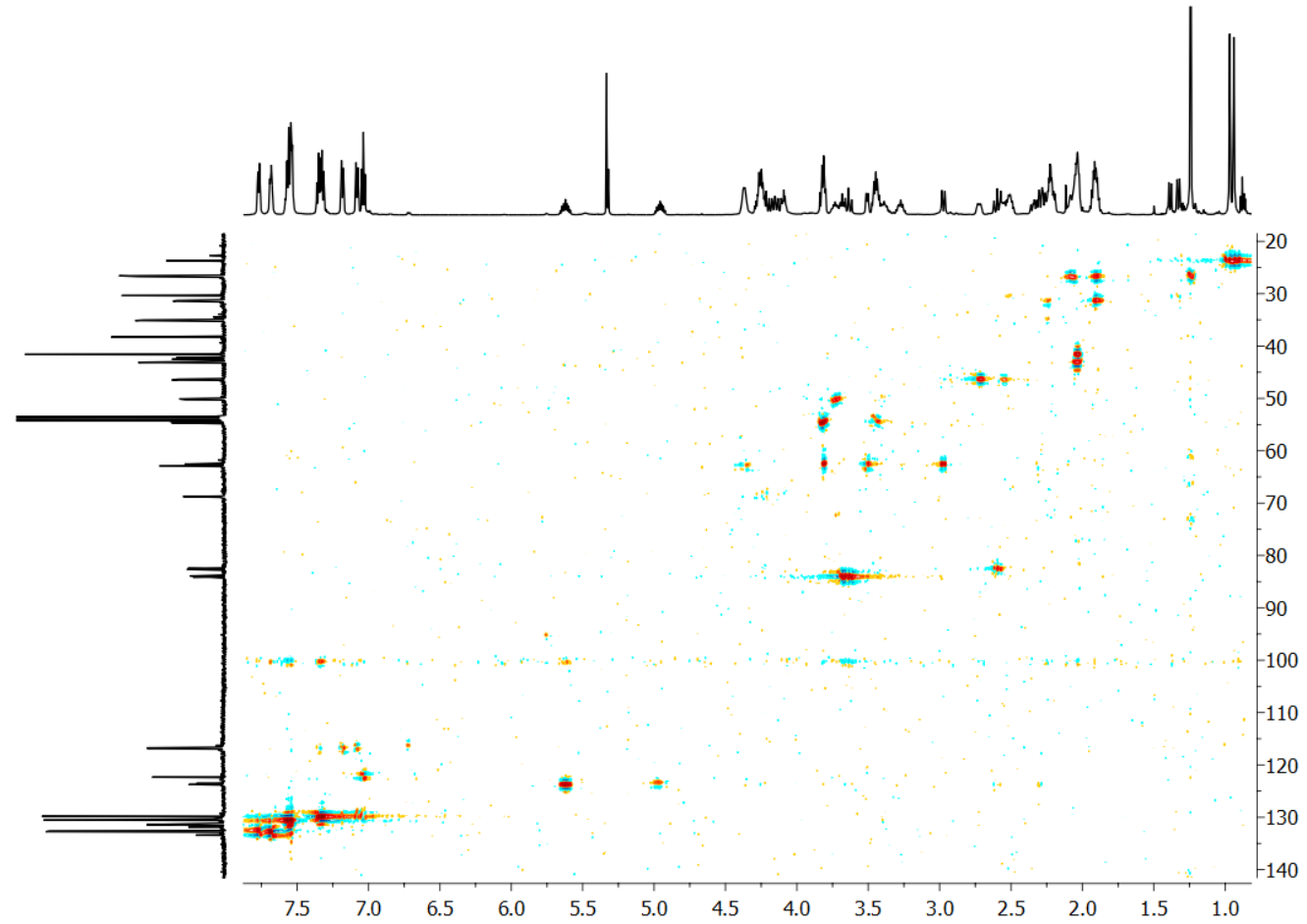
[Pd(allyl)(**L1a**)]BF_4, $^{13}C\{^1H\}$ spectrum.



[Pd(allyl)(**L1a**)]BF_4, $^{13}C\{^1H\}$ DEPT spectrum.

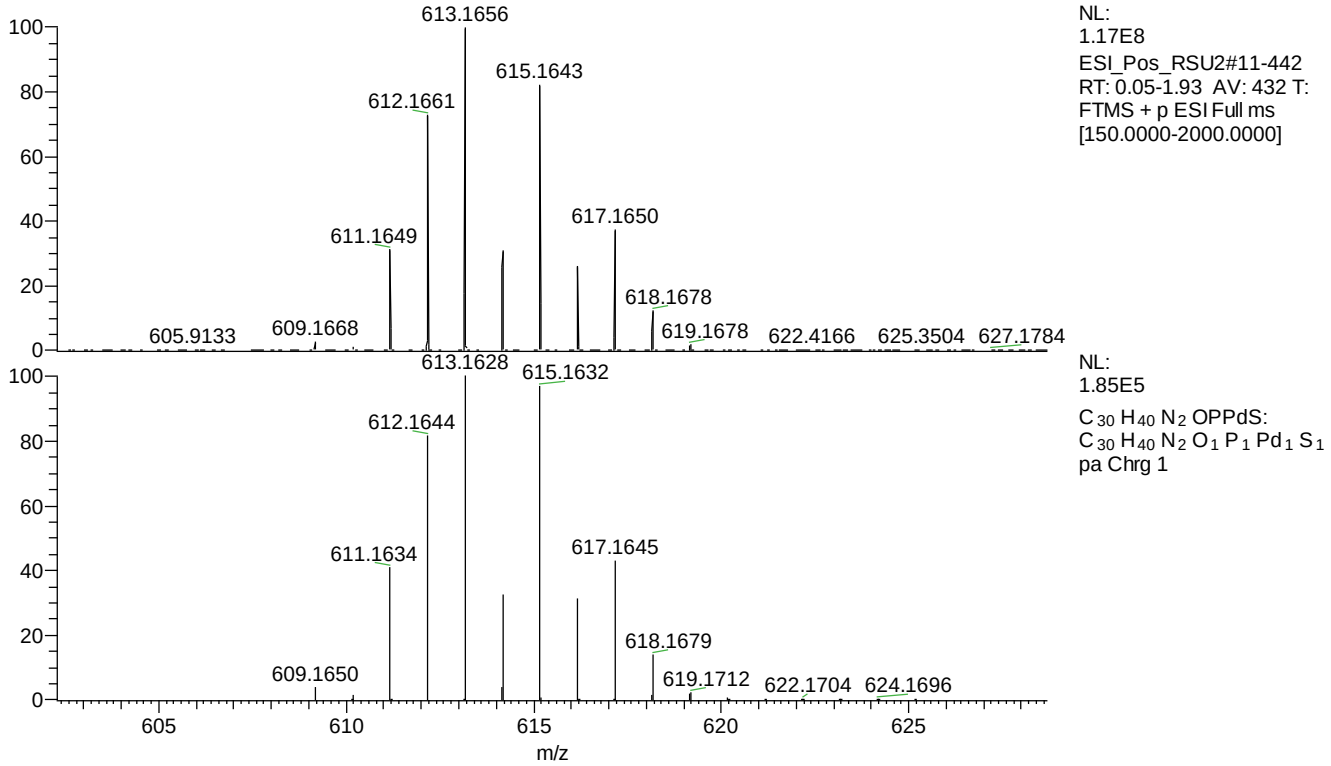


[Pd(allyl)(**L1a**)]BF_4, ^{1}H-^{1}H COSY spectrum.

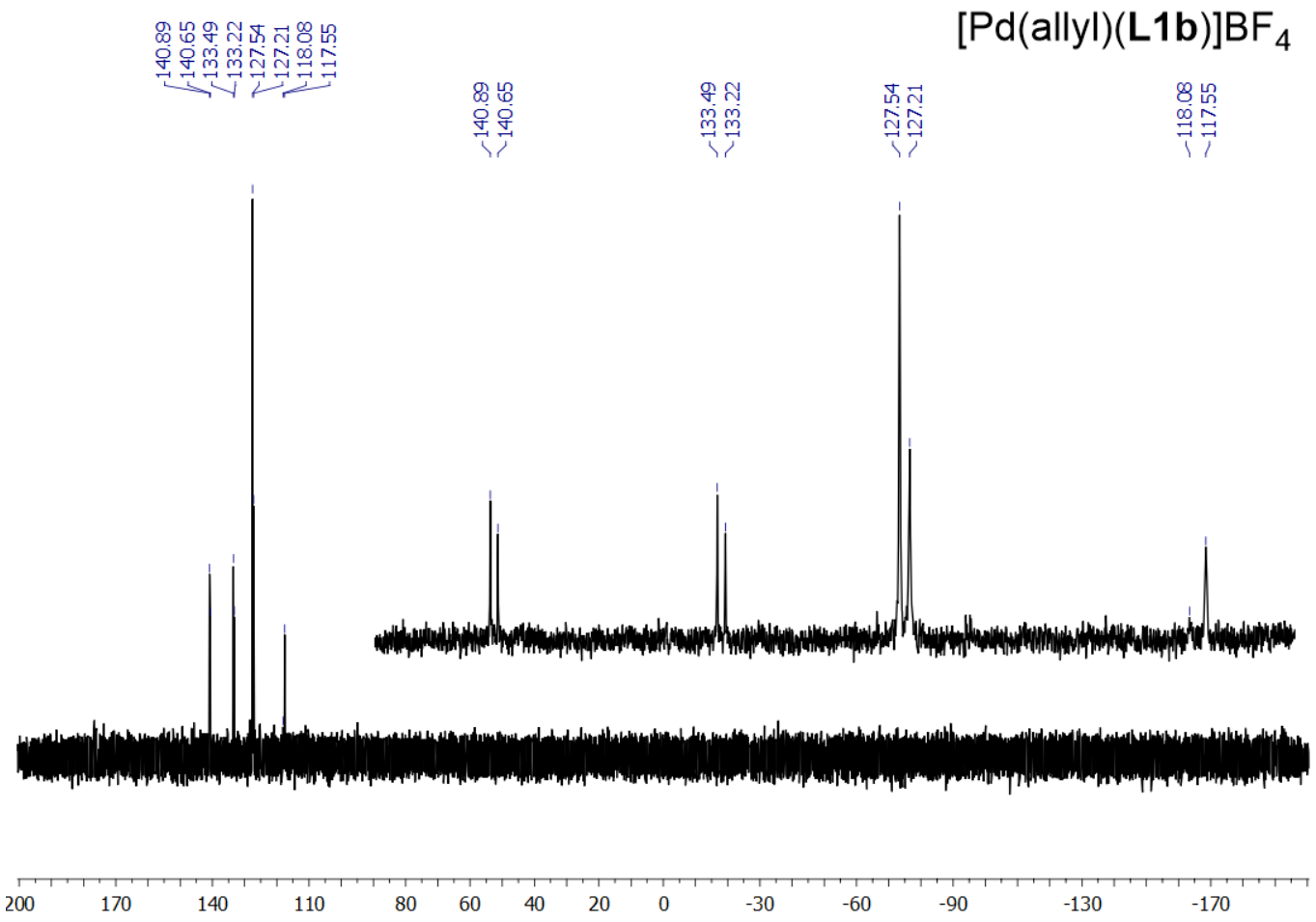


[Pd(allyl)(**L1a**)]BF_4, ^{1}H-^{13}C HSQC spectrum.

NMR AND HRMS SPECTRA

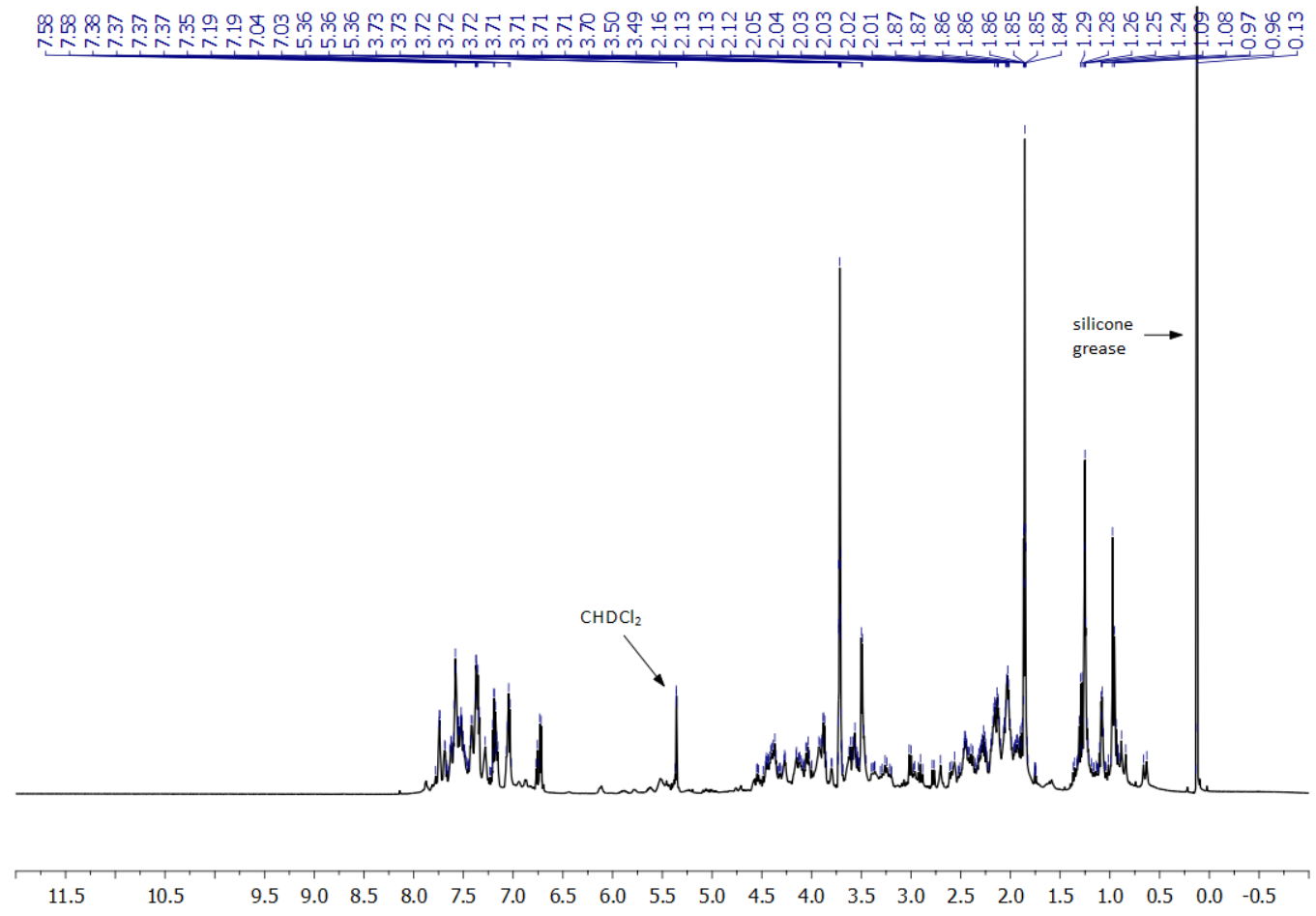


[Pd(allyl)(**L1a**)]BF_4, HRMS-spectrum. [Pd(allyl)(**L1a**)]$^+$, experimental (top) and calculated (bottom) peaks.

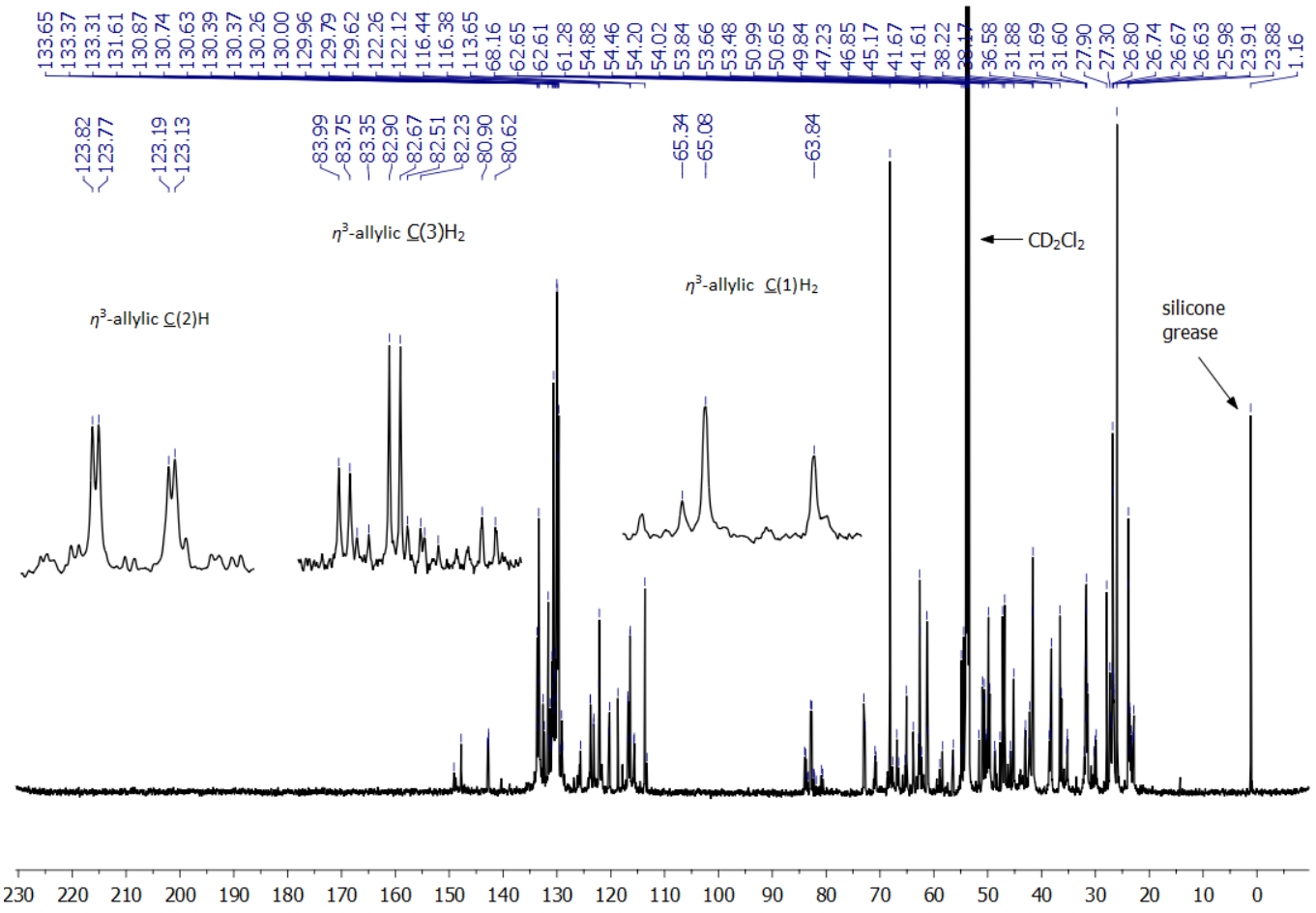


[Pd(allyl)(**L1b**)]BF_4, $^{31}P\{^1H\}$ spectrum.

NMR AND HRMS SPECTRA

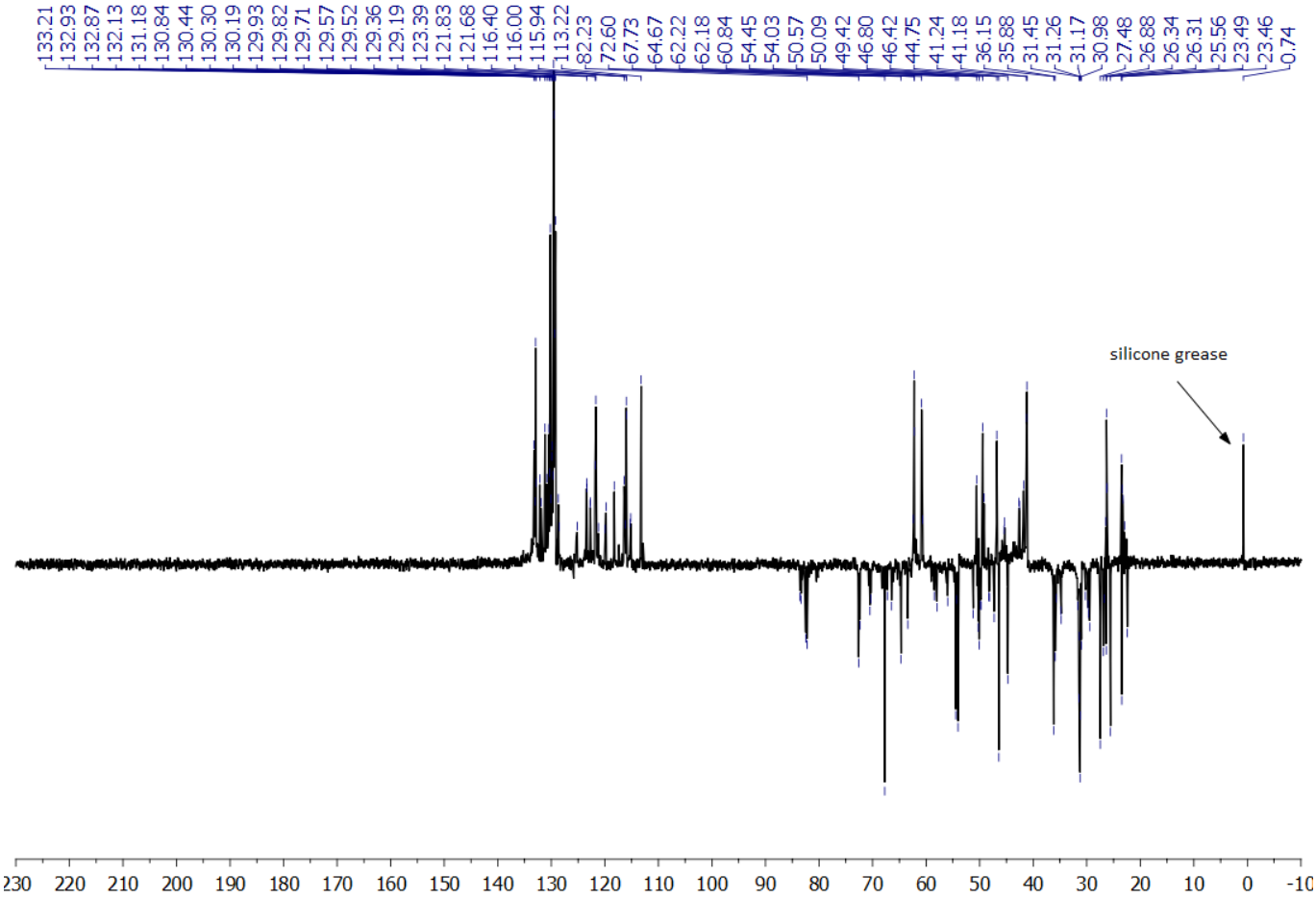


[Pd(allyl)(**L1b**)]BF_4, ^1H spectrum.

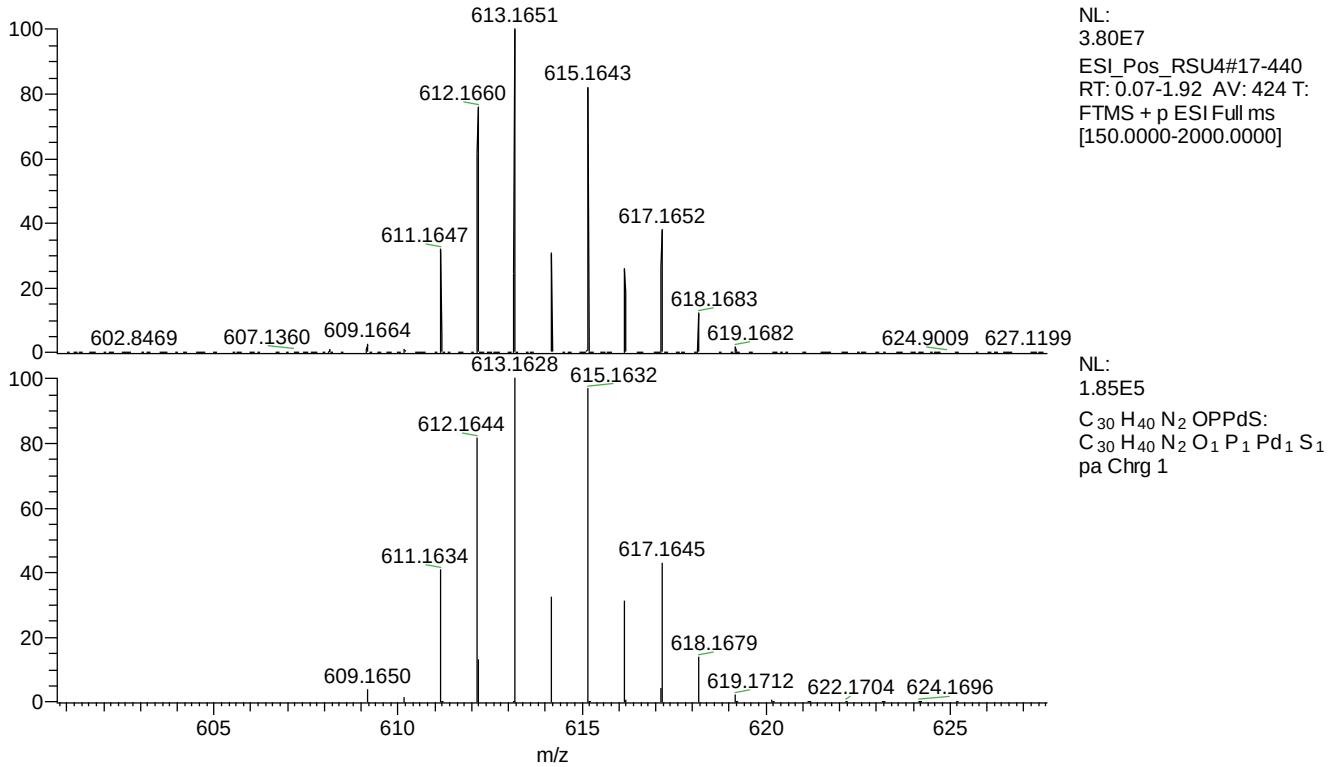


[Pd(allyl)(**L1b**)]BF_4, $^{13}C\{^1H\}$ spectrum.

NMR AND HRMS SPECTRA

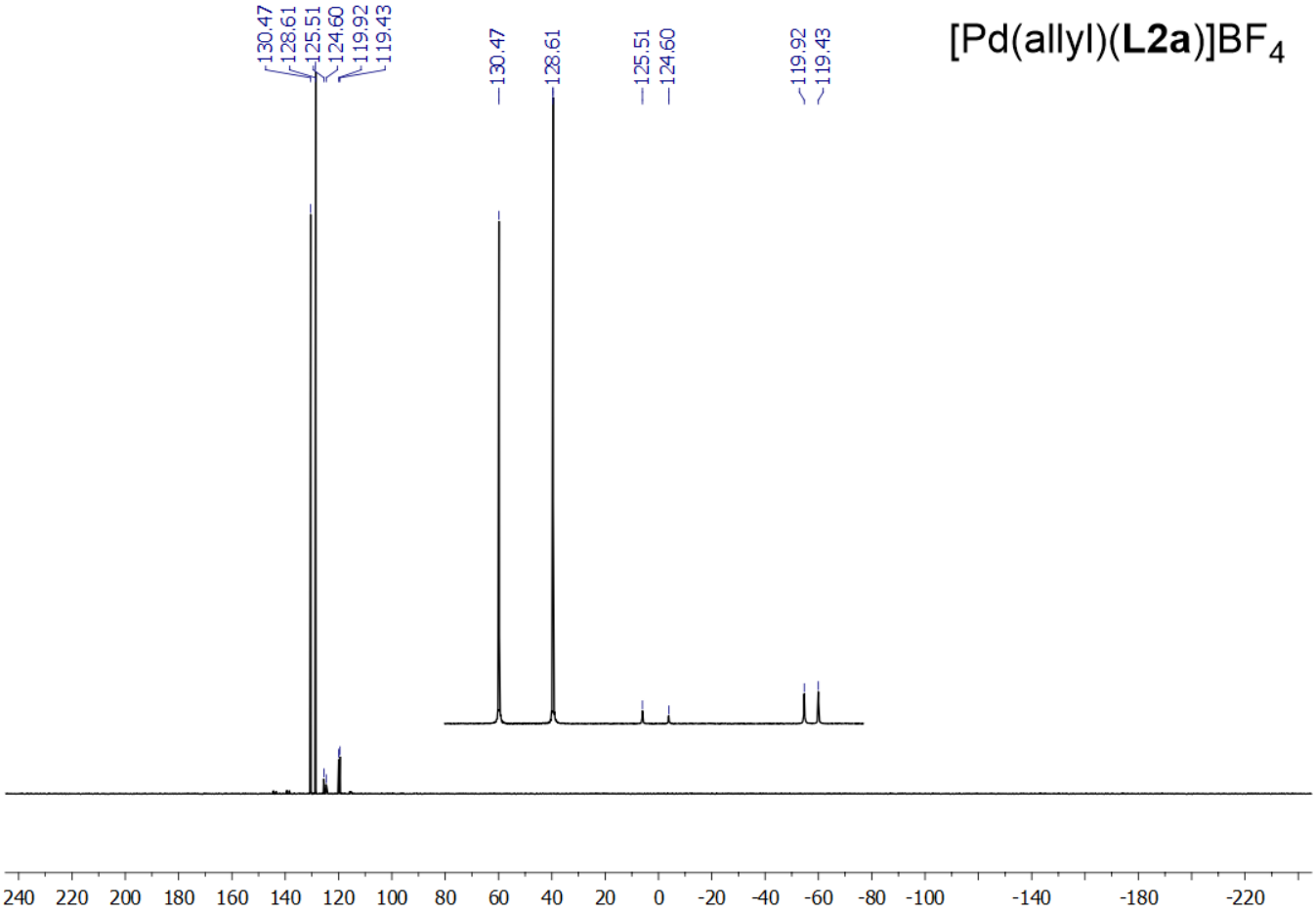


[Pd(allyl)(**L1b**)]BF_4, $^{13}C\{^1H\}$ DEPT spectrum.

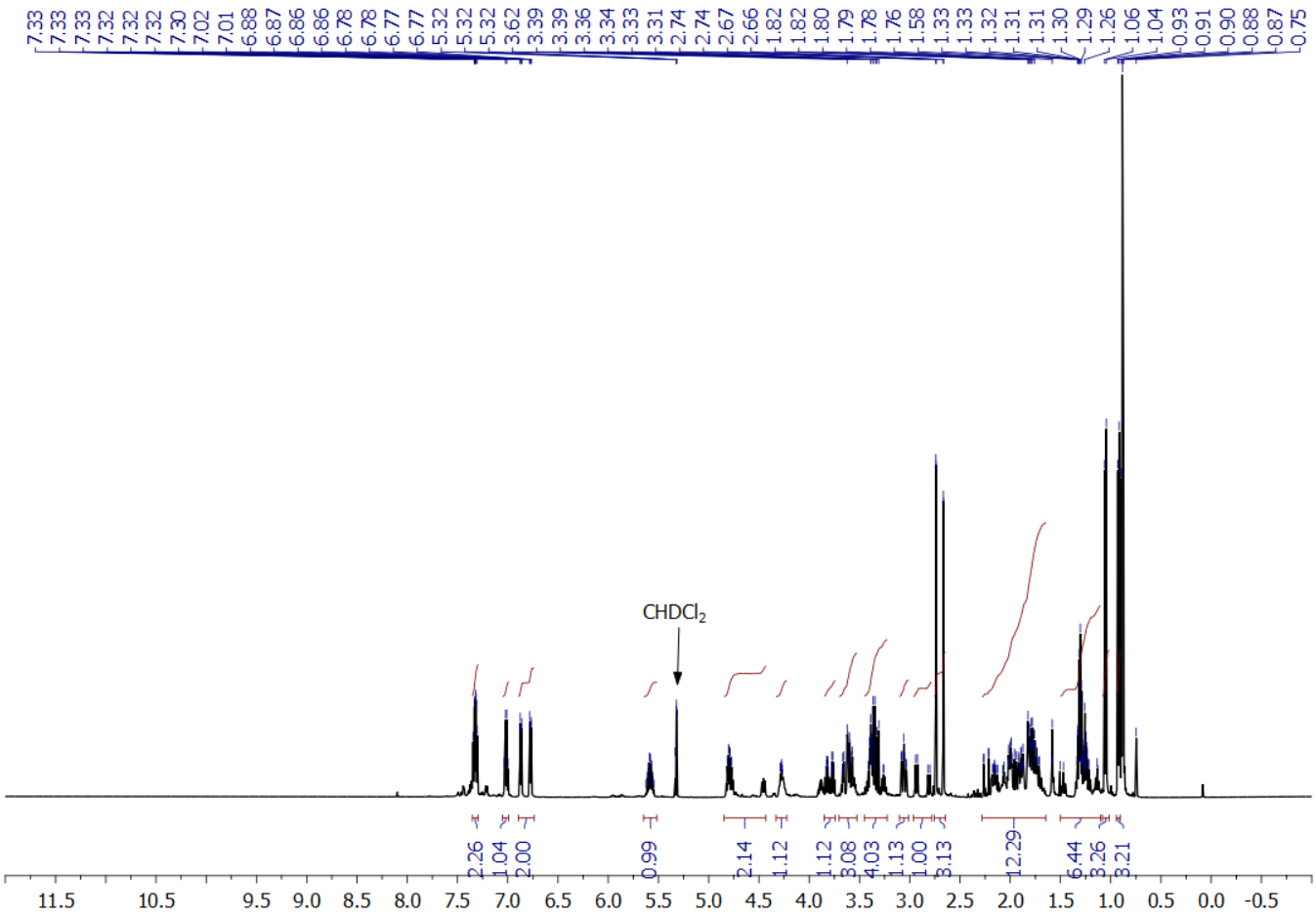


[Pd(allyl)(**L1b**)]BF_4, HRMS spectrum: [Pd(allyl)(**L1b**)]$^+$, experimental (top) and calculated (bottom) peaks.

NMR AND HRMS SPECTRA

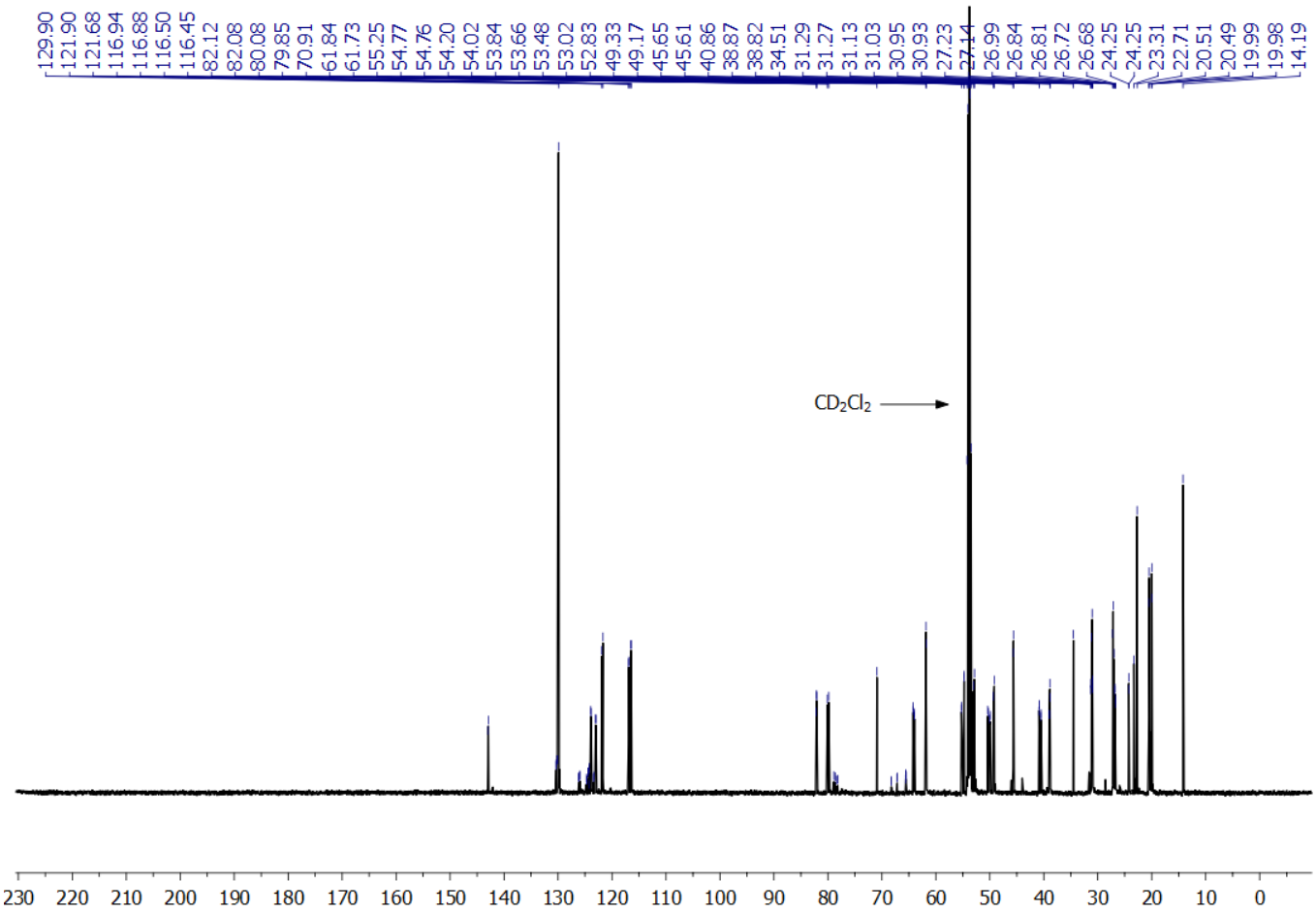


[Pd(allyl)(**L2a**)]BF_4, $^{31}P\{^1H\}$ spectrum.

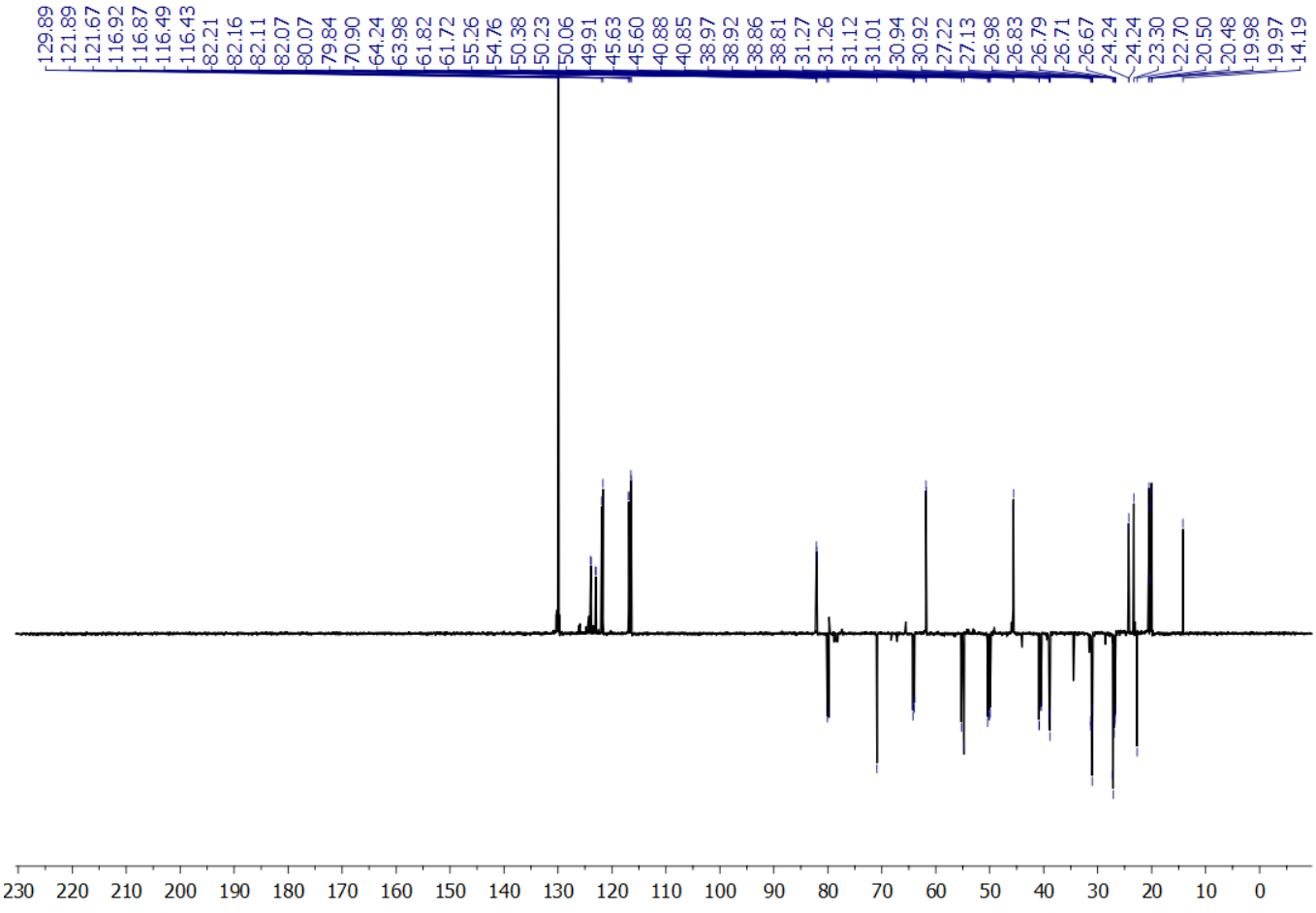


[Pd(allyl)(**L2a**)]BF_4, ^1H spectrum.

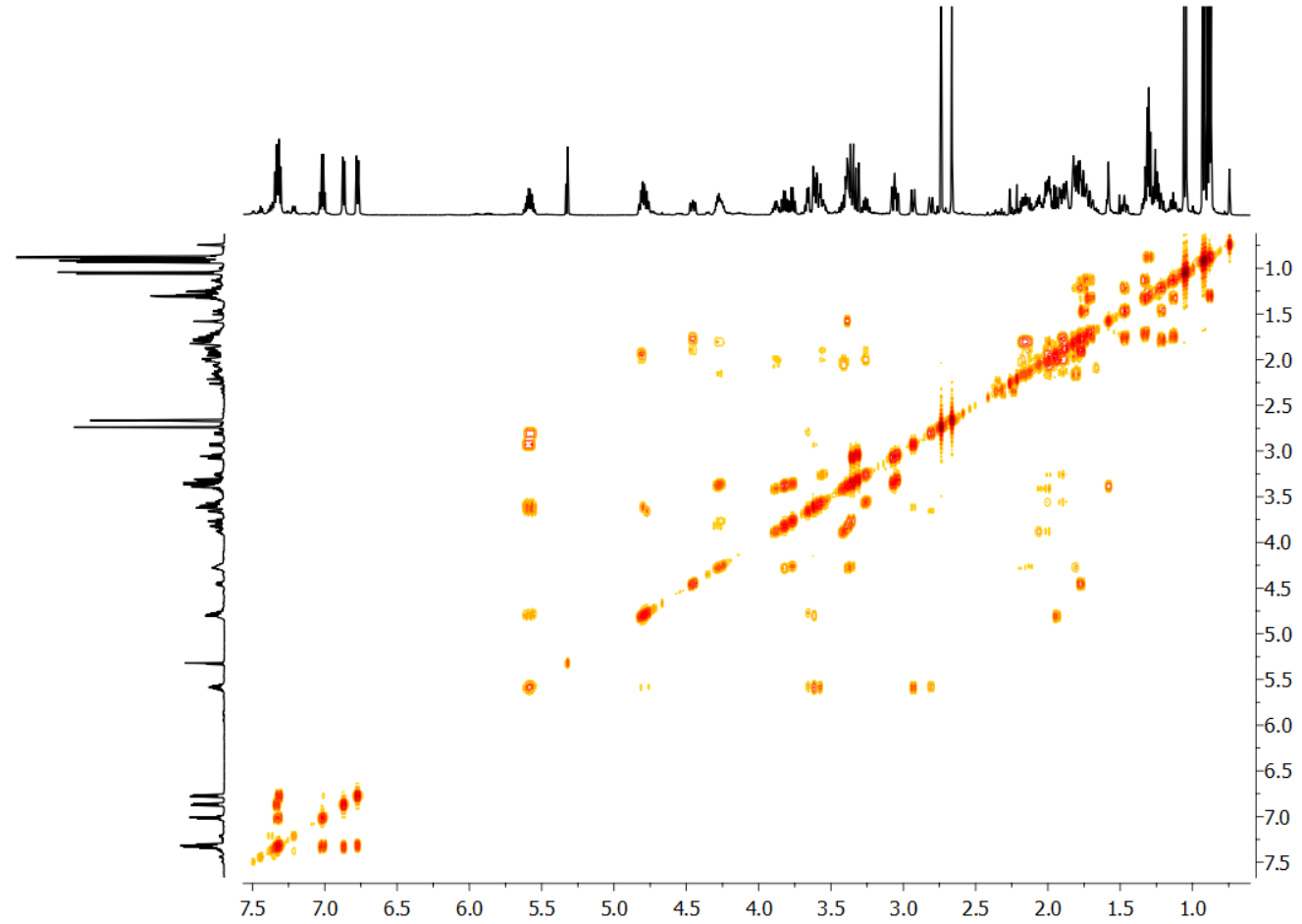
NMR AND HRMS SPECTRA



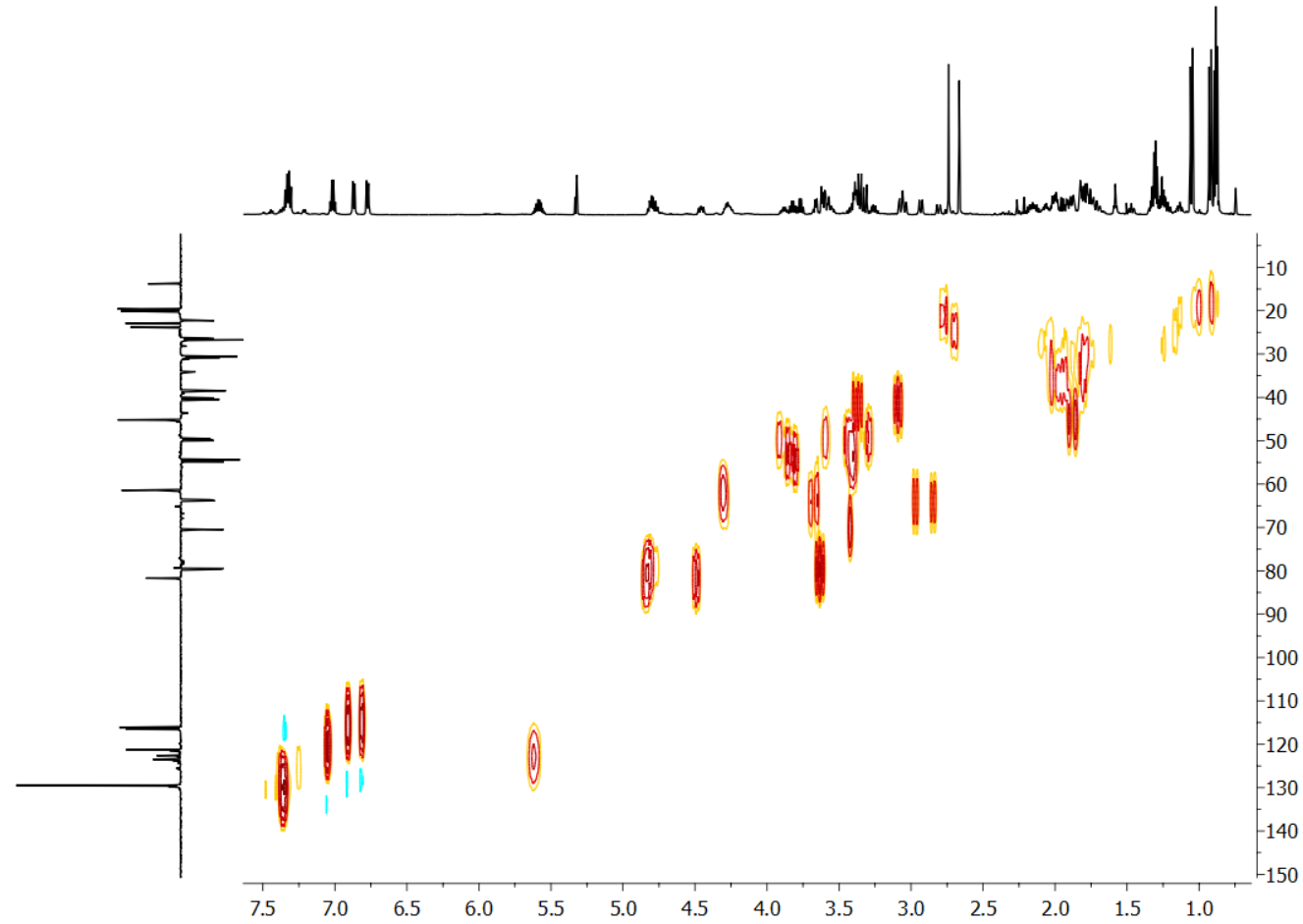
[Pd(allyl)(**L2a**)]BF_4, $^{13}C\{^1H\}$ spectrum.



[Pd(allyl)(**L2a**)]BF_4, $^{13}C\{^1H\}$ DEPT spectrum.

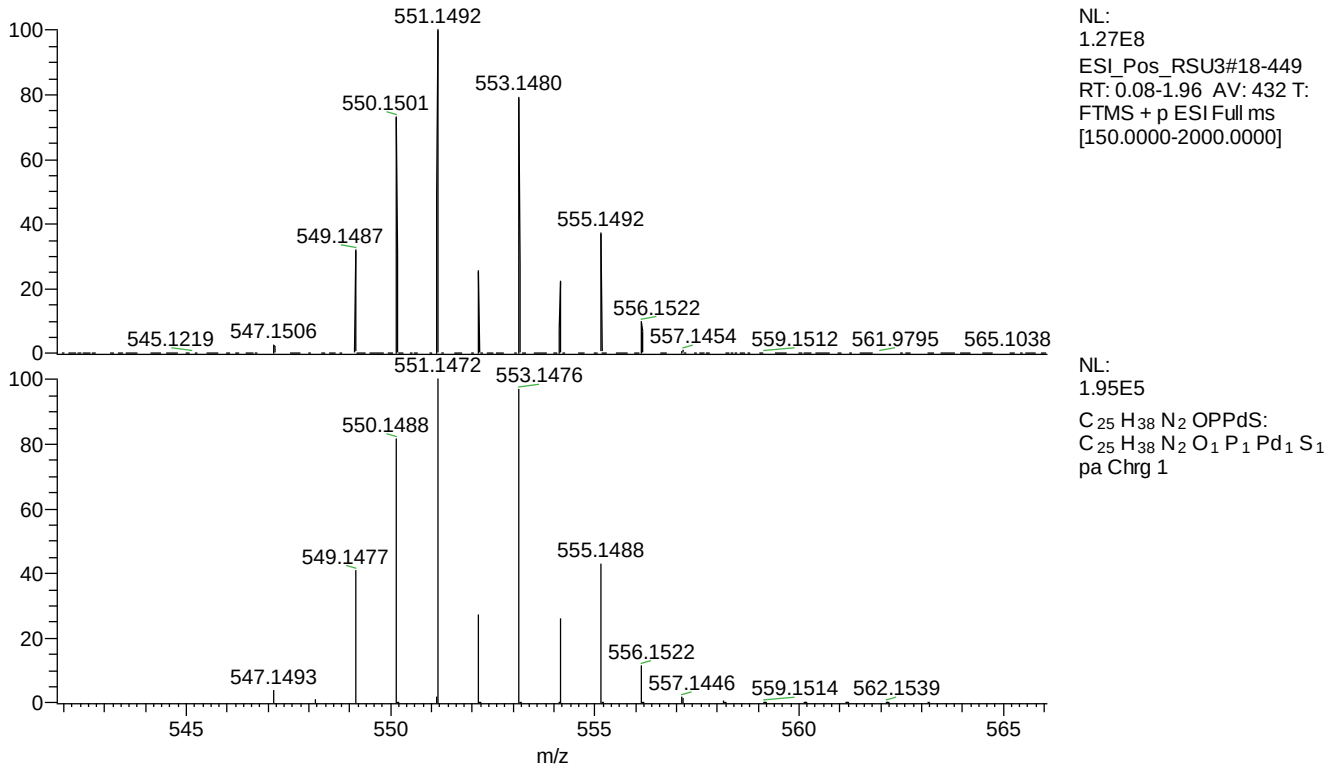


[Pd(allyl)(**L2a**)]BF_4, ^{1}H-^{1}H COSY spectrum.

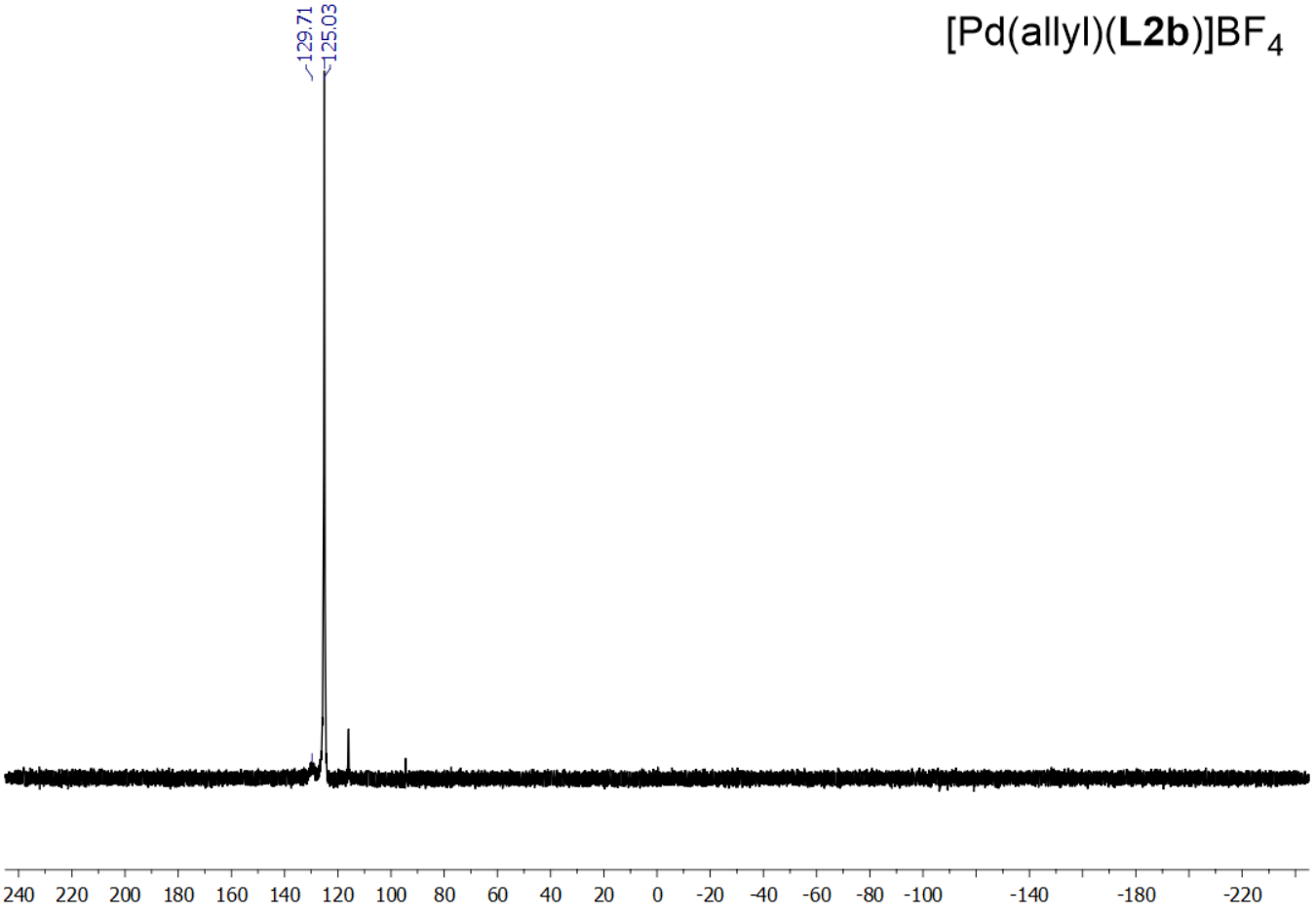


[Pd(allyl)(**L2a**)]BF_4, ^{1}H-^{13}C HSQC spectrum.

NMR AND HRMS SPECTRA

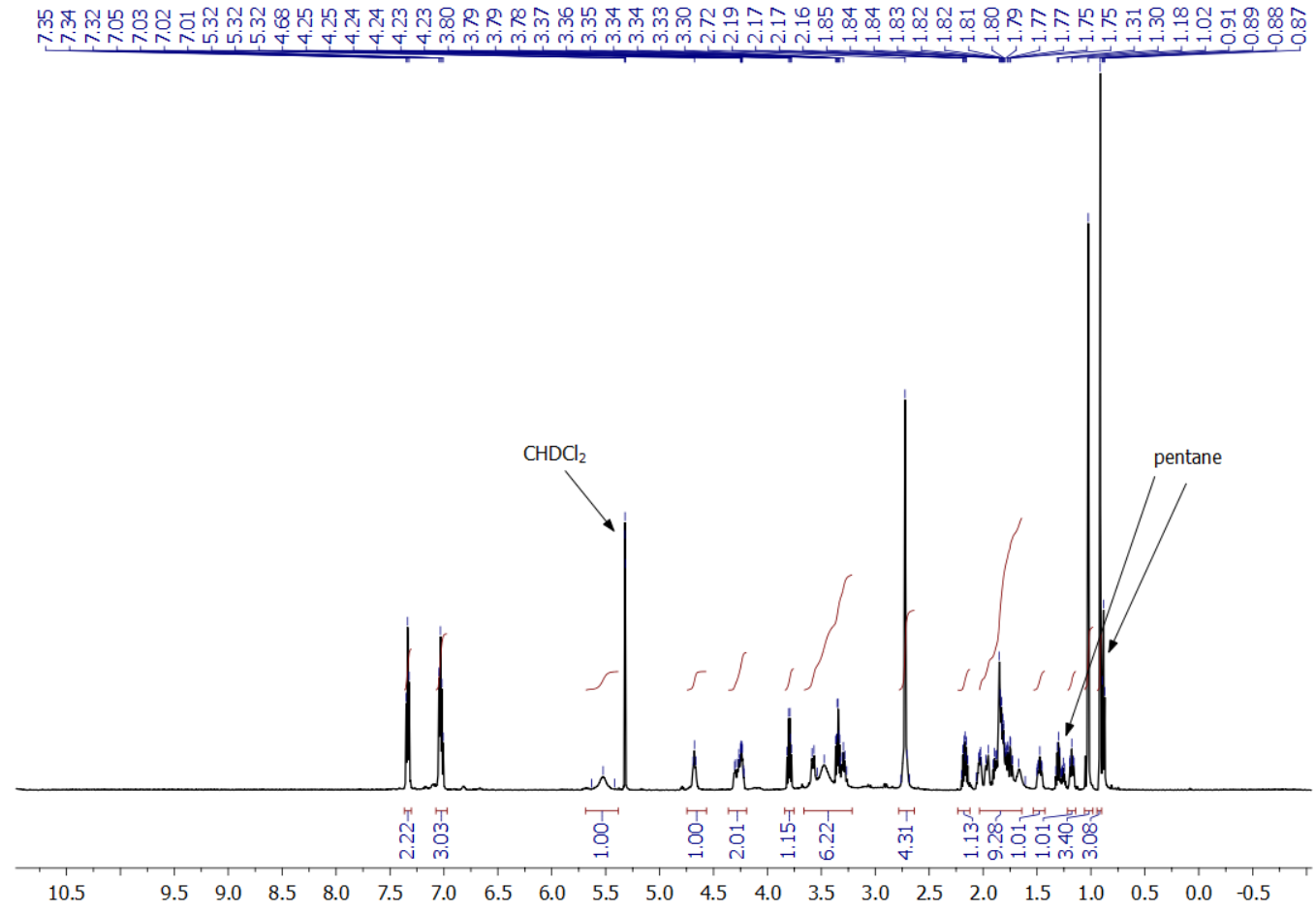


[Pd(allyl)(**L2a**)]BF_4, HRMS spectrum: [Pd(allyl)(**L2a**)]$^+$, experimental (top) and calculated (bottom) peaks.

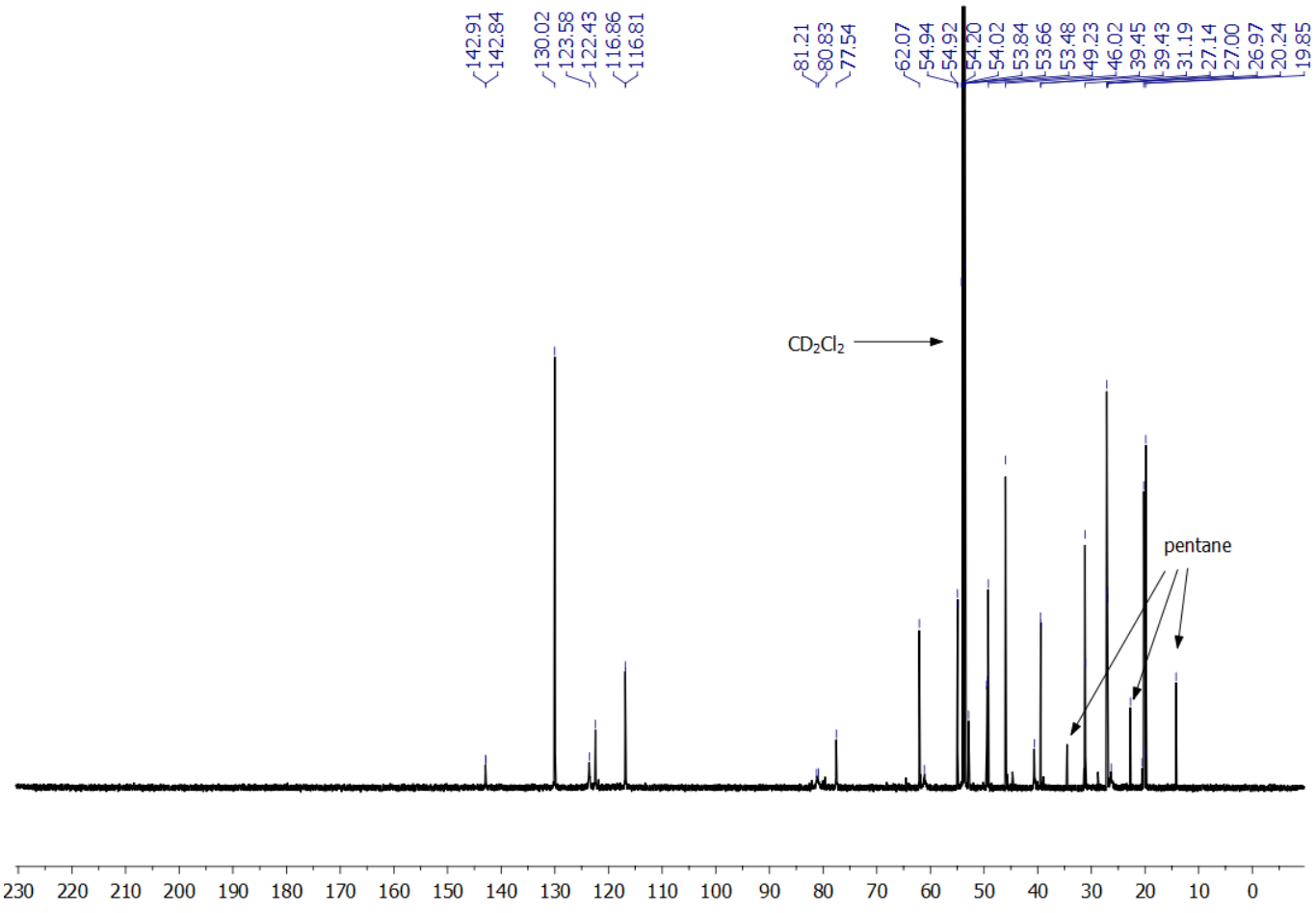


[Pd(allyl)(**L2b**)]BF_4, $^{31}P\{^1H\}$ spectrum.

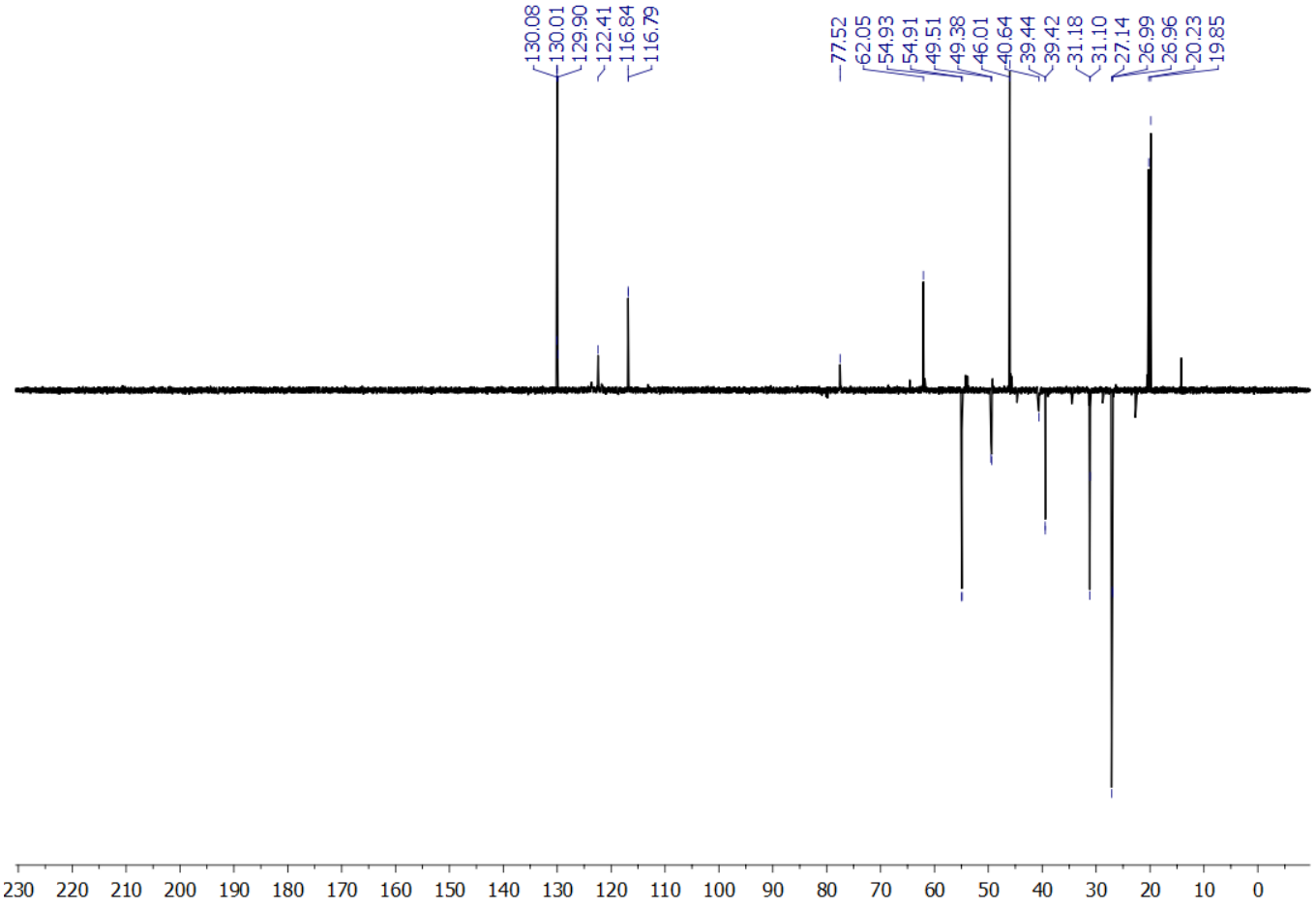
NMR AND HRMS SPECTRA



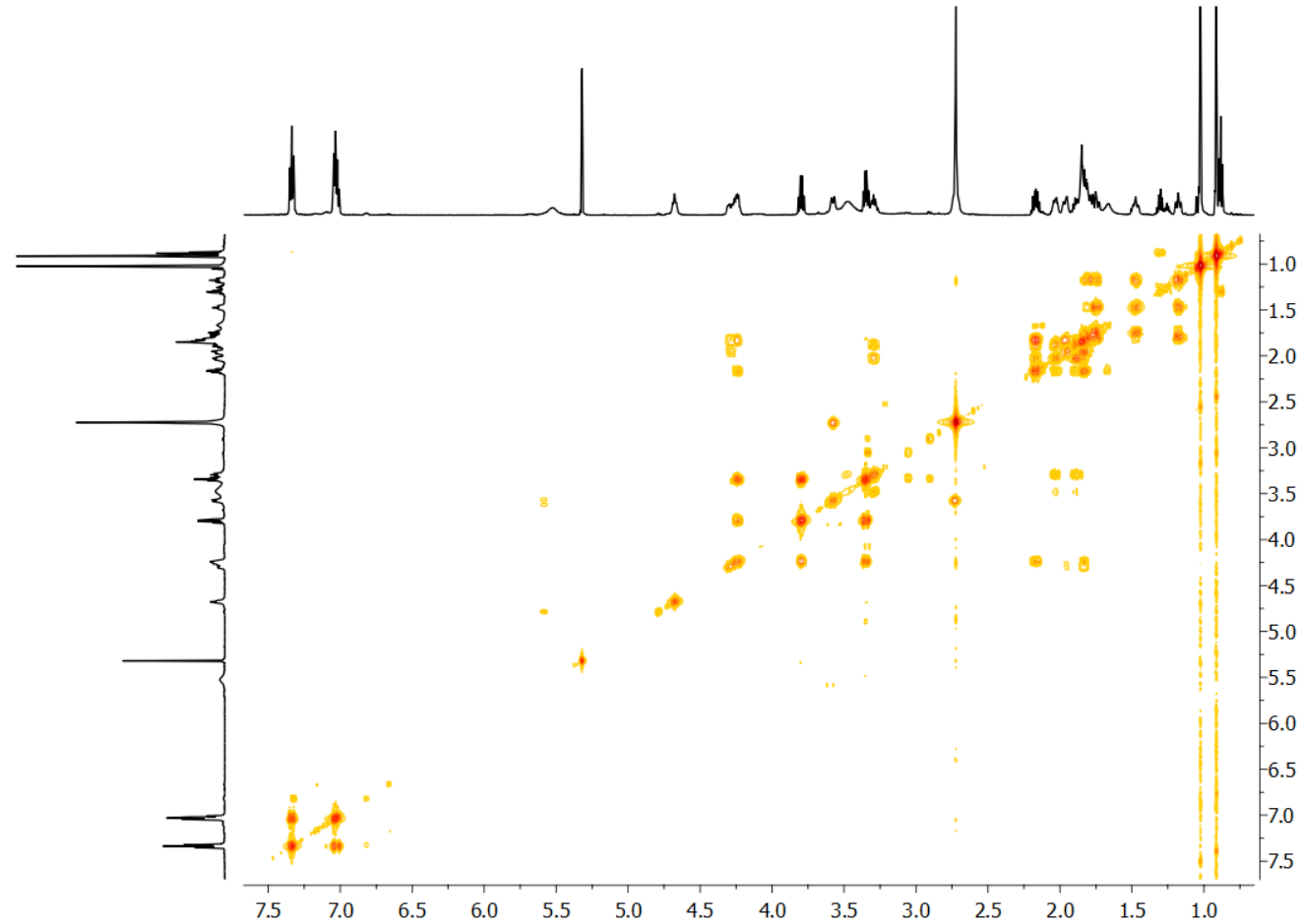
[Pd(allyl)(**L2b**)]BF_4, ^1H spectrum.



[Pd(allyl)(**L2b**)]BF_4, $^{13}C\{^1H\}$ spectrum.

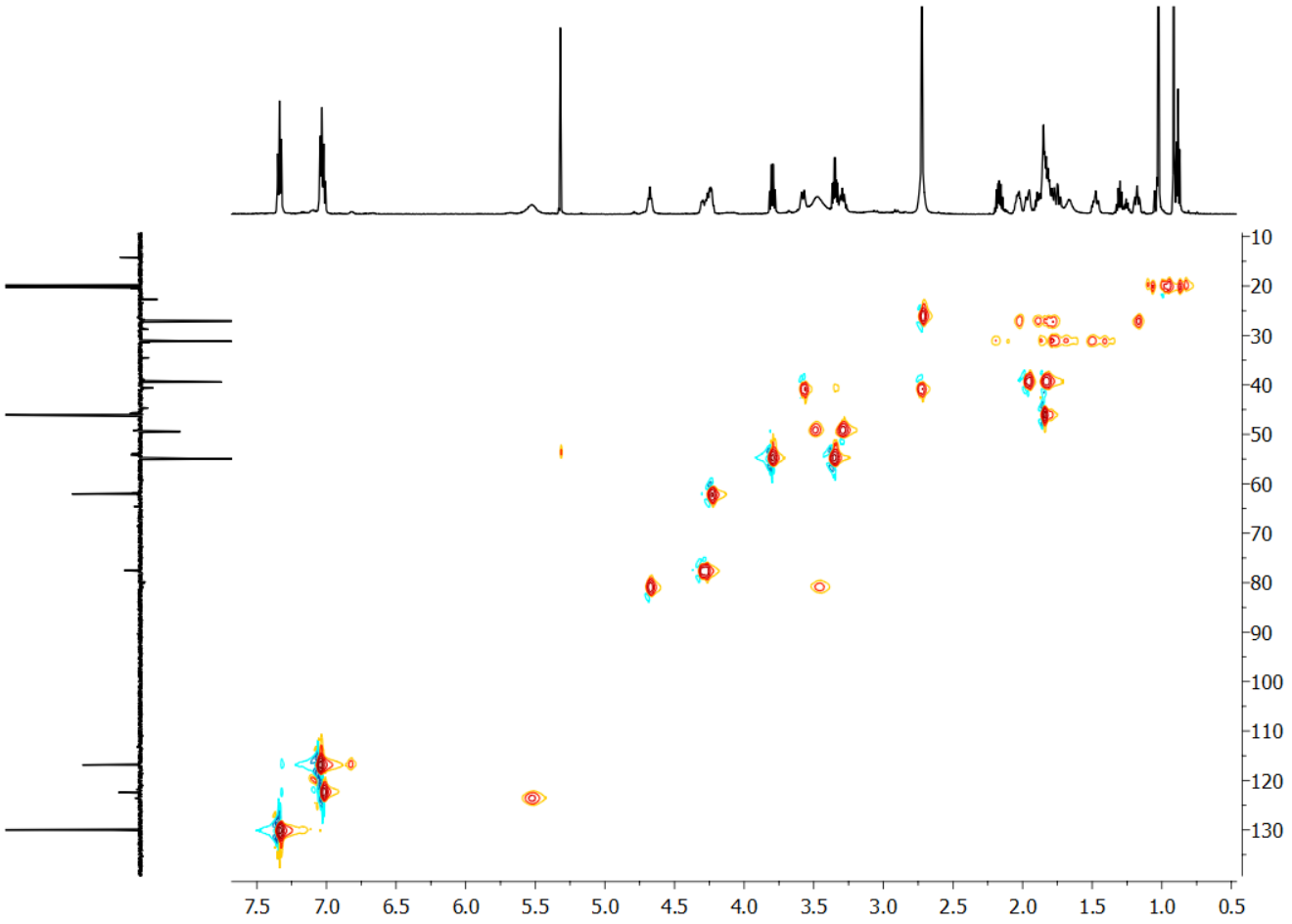


[Pd(allyl)(**L2b**)]BF_4, $^{13}C\{^1H\}$ DEPT spectrum.

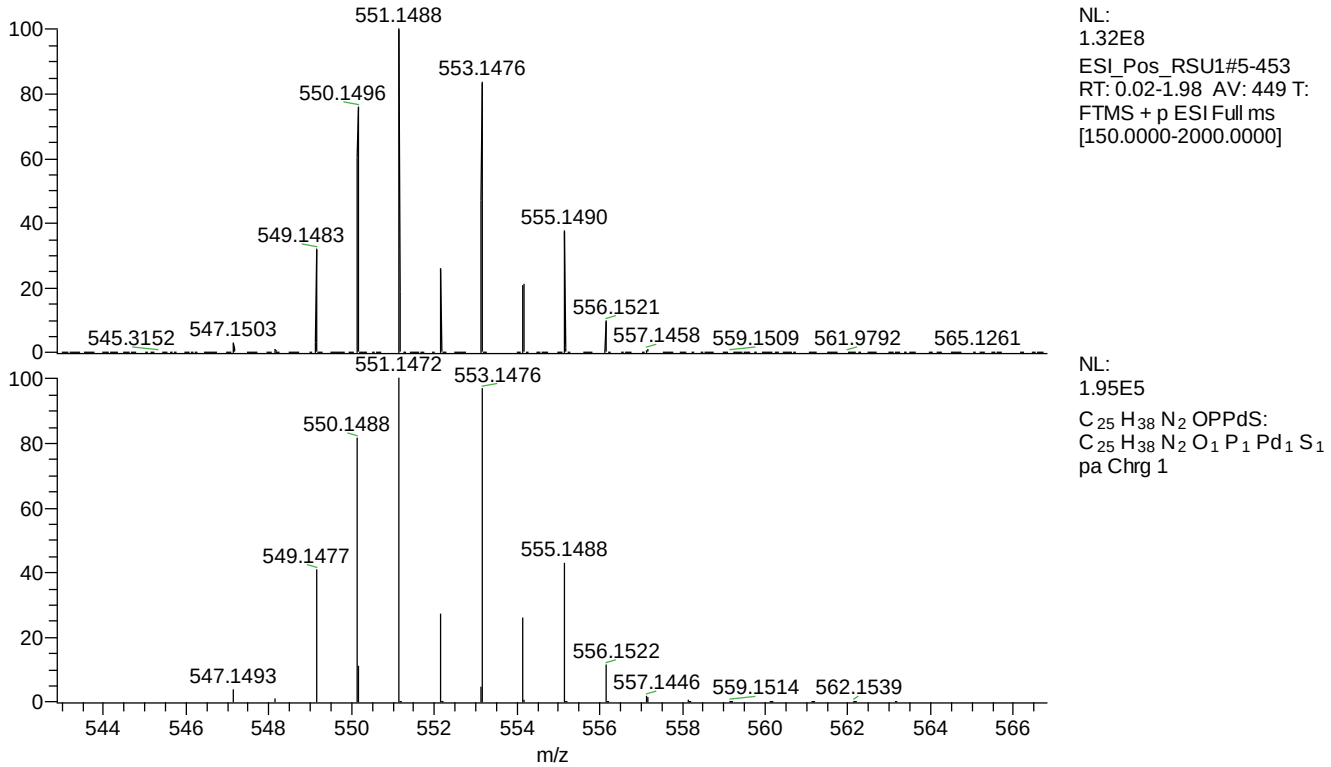


[Pd(allyl)(**L2b**)]BF_4, ^1H-^1H COSY spectrum.

NMR AND HRMS SPECTRA

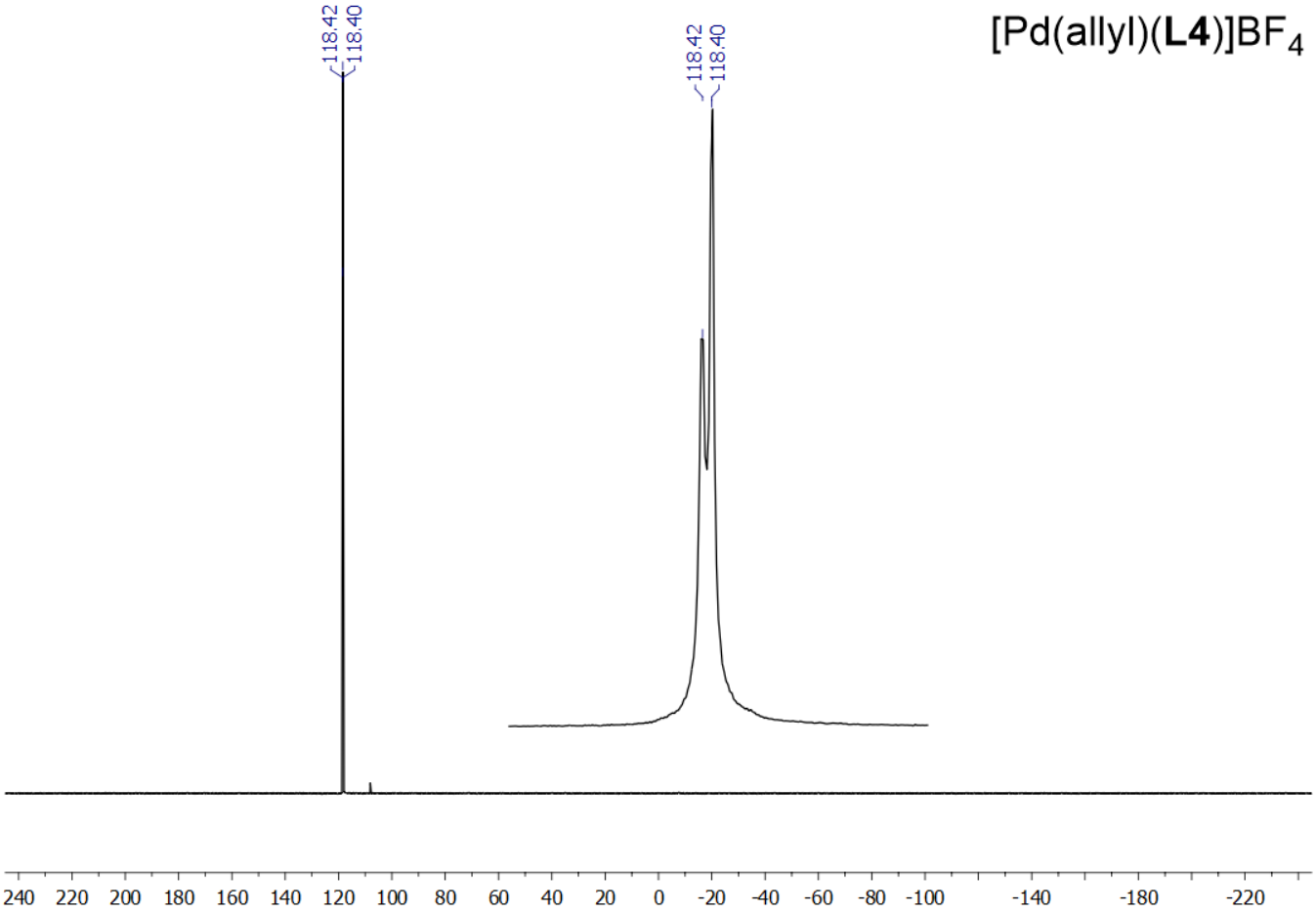


[Pd(allyl)(**L2b**)]BF_4, ^{1}H-^{13}C HSQC spectrum.

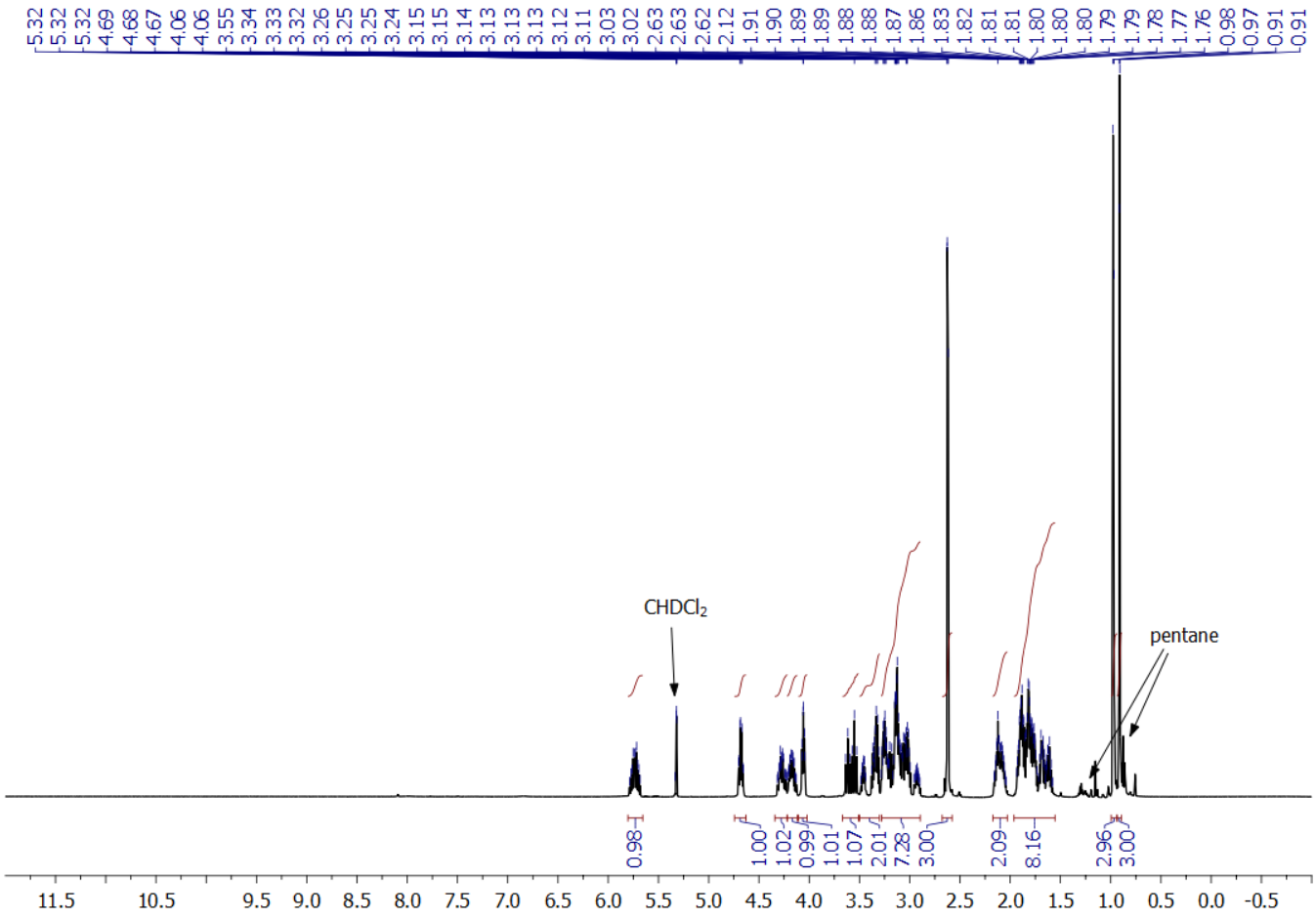


[Pd(allyl)(**L2b**)]BF_4, HRMS spectrum: [Pd(allyl)(**L2b**)]$^{+}$, experimental (top) and calculated (bottom) peaks.

NMR AND HRMS SPECTRA

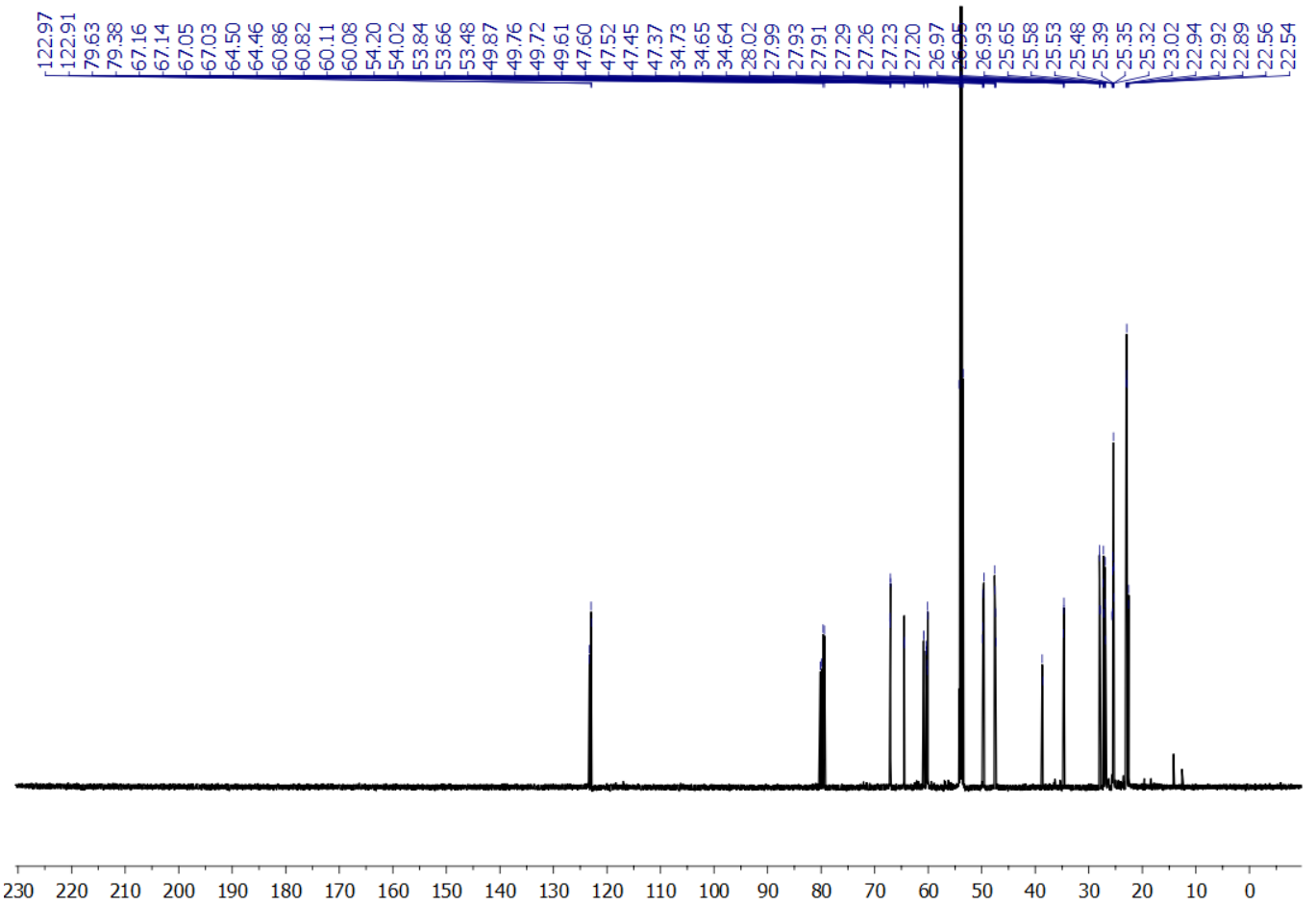


[Pd(allyl)(**L4**)]BF_4, $^{31}P\{^1H\}$ spectrum.

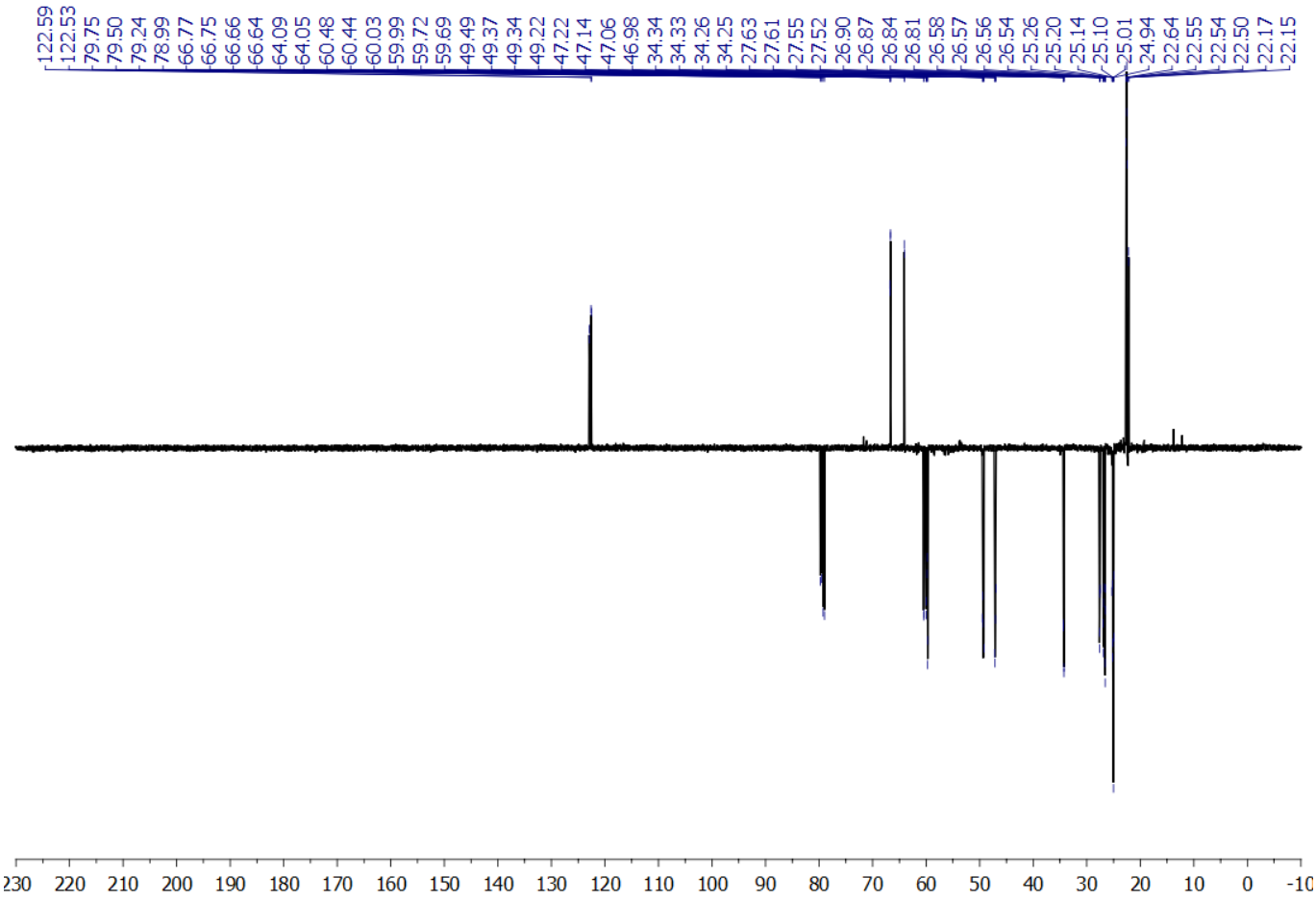


[Pd(allyl)(**L4**)]BF_4, ^1H spectrum.

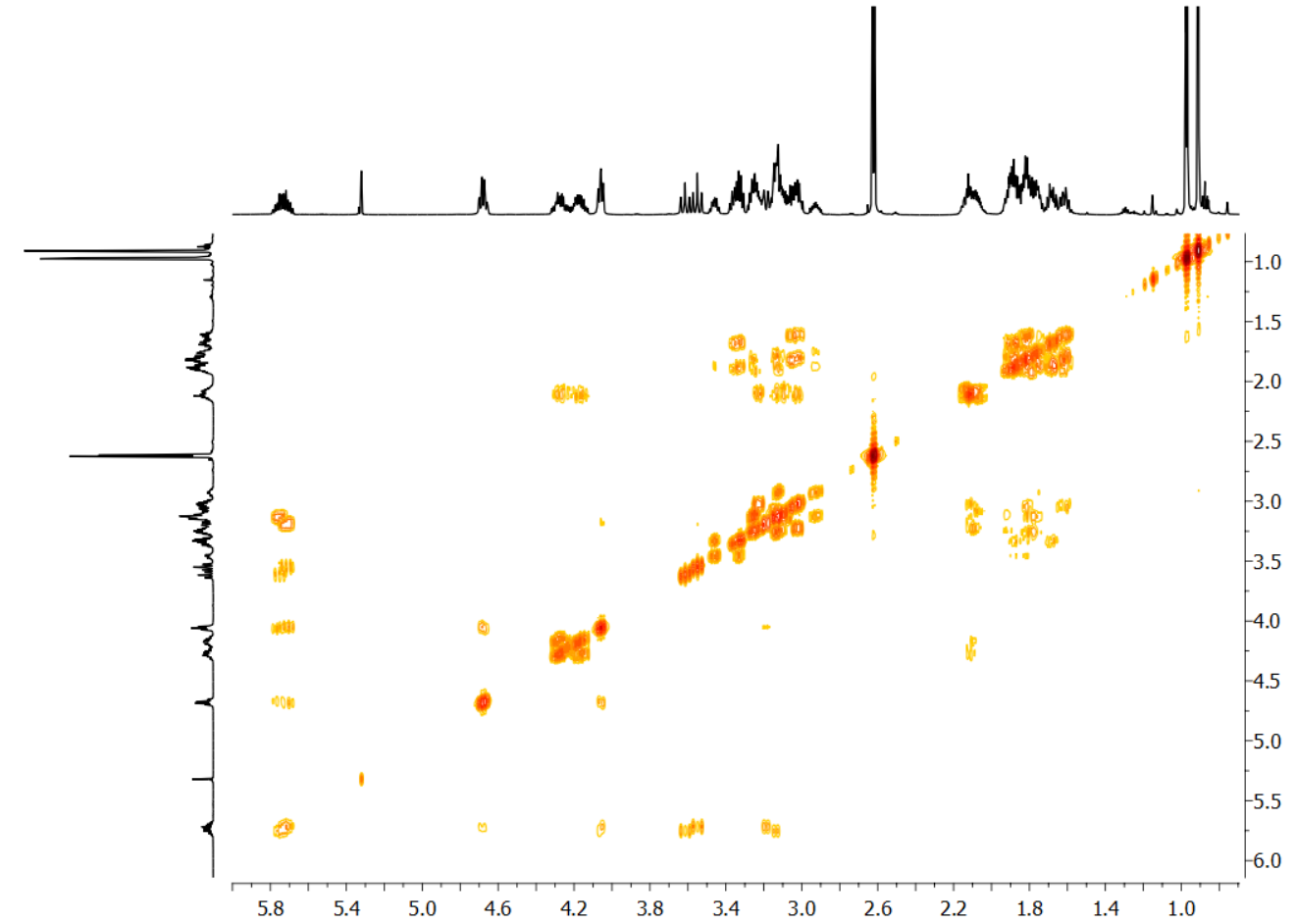
NMR AND HRMS SPECTRA



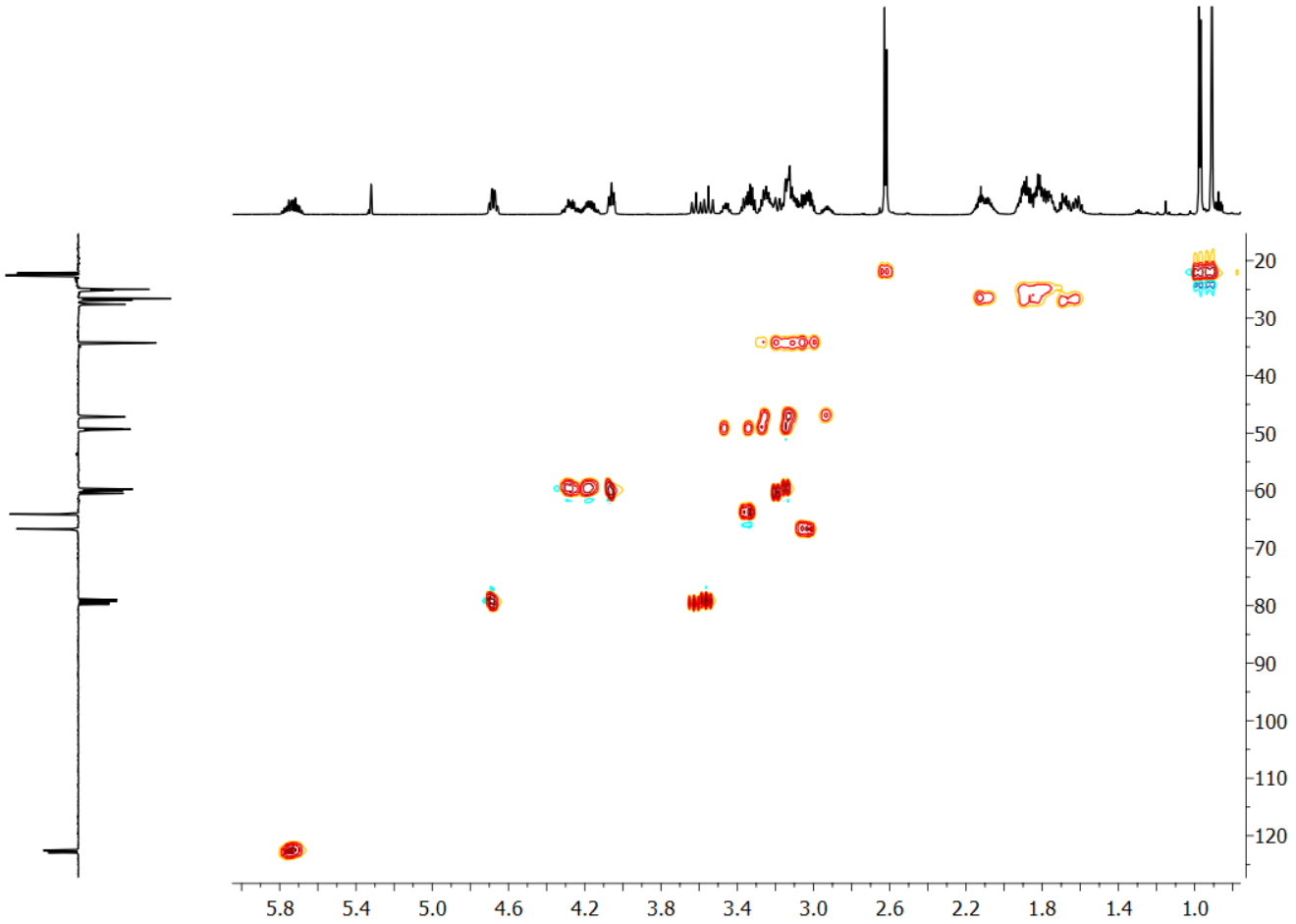
[Pd(allyl)(**L4**)]BF_4, $^{13}C\{^1H\}$ spectrum.



[Pd(allyl)(**L4**)]BF_4, $^{13}C\{^1H\}$ DEPT spectrum.

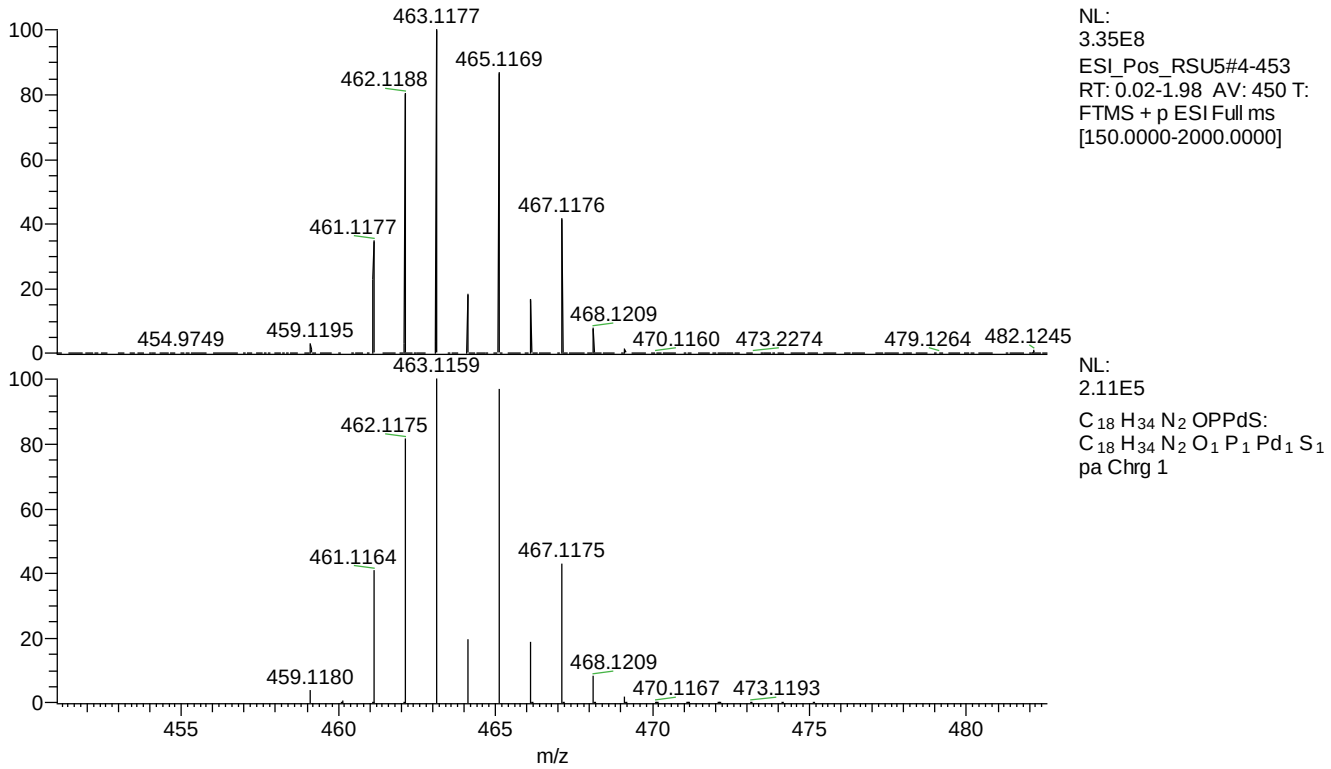


[Pd(allyl)(**L4**)]BF_4, ^{1}H-^{1}H COSY spectrum.

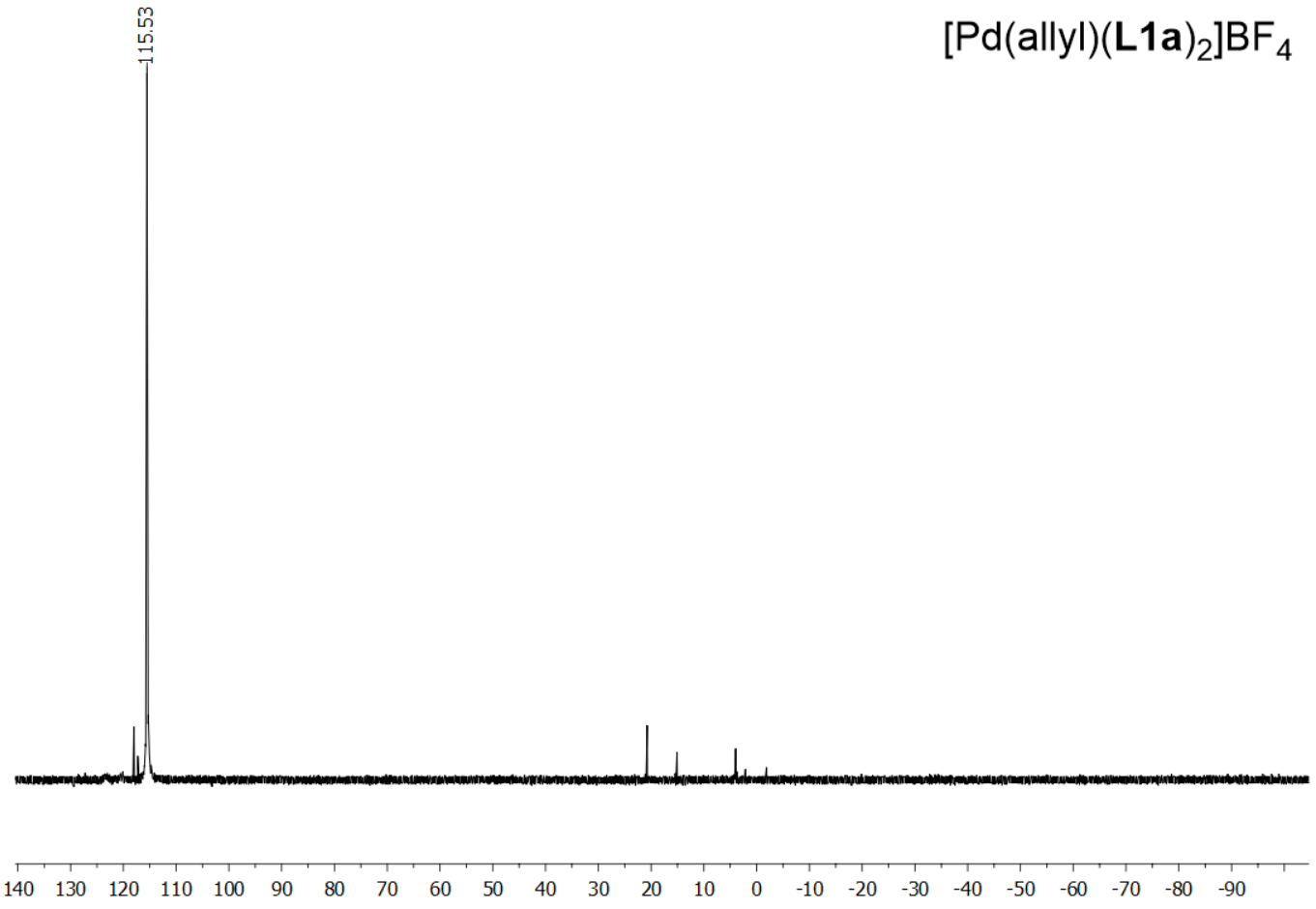


[Pd(allyl)(**L4**)]BF_4, ^{1}H-^{13}C HSQC spectrum.

NMR AND HRMS SPECTRA

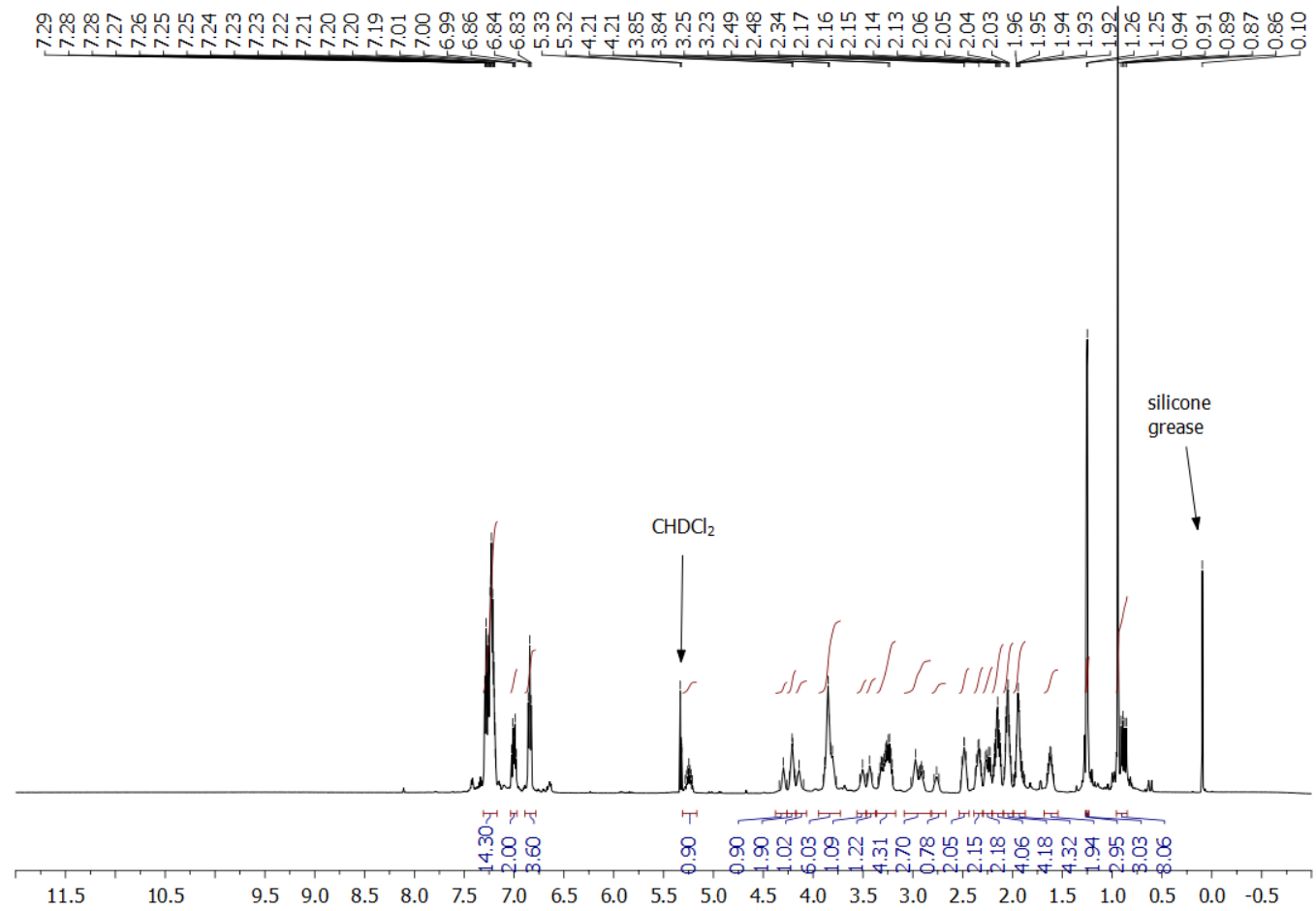


[Pd(allyl)(**L4**)]BF_4, HRMS spectrum: [Pd(allyl)(**L4**)]$^+$, experimental (top) and calculated (bottom) peaks.

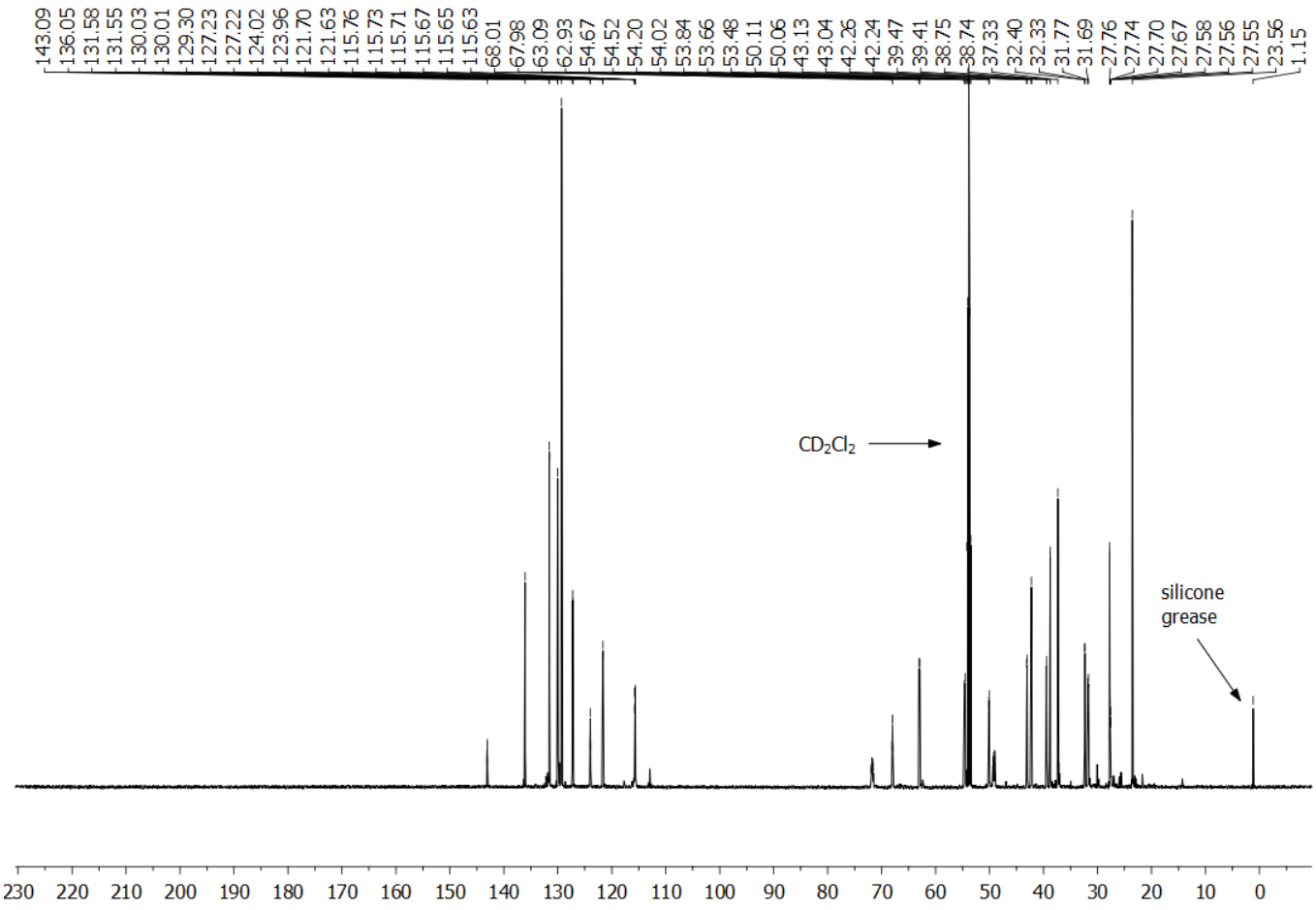


[Pd(allyl)(**L1a**)$_2$]BF_4, $^{31}P\{^1H\}$ spectrum.

NMR AND HRMS SPECTRA

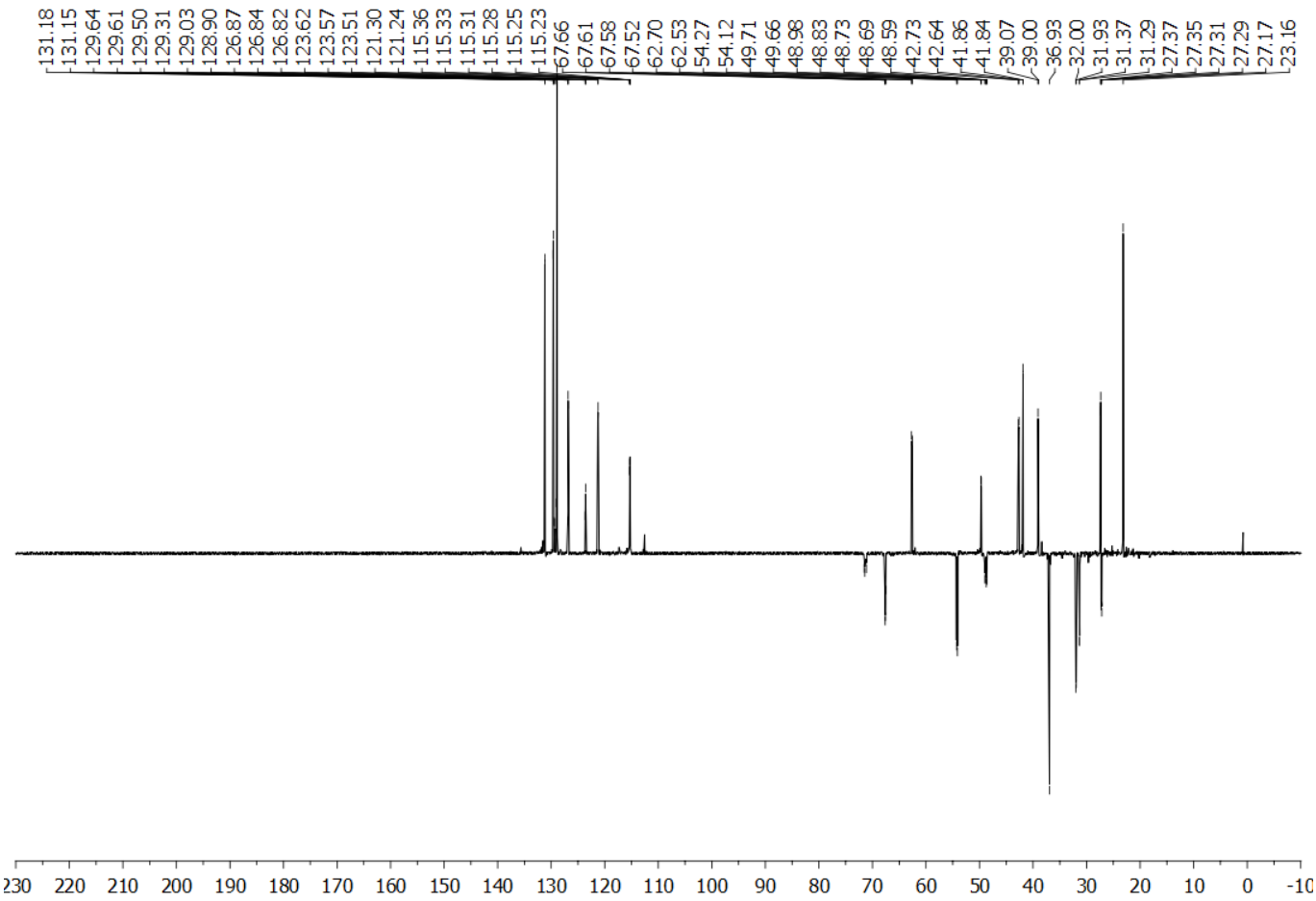


[Pd(allyl)(**L1a**)$_2$]BF$_4$, ^{1}H spectrum.

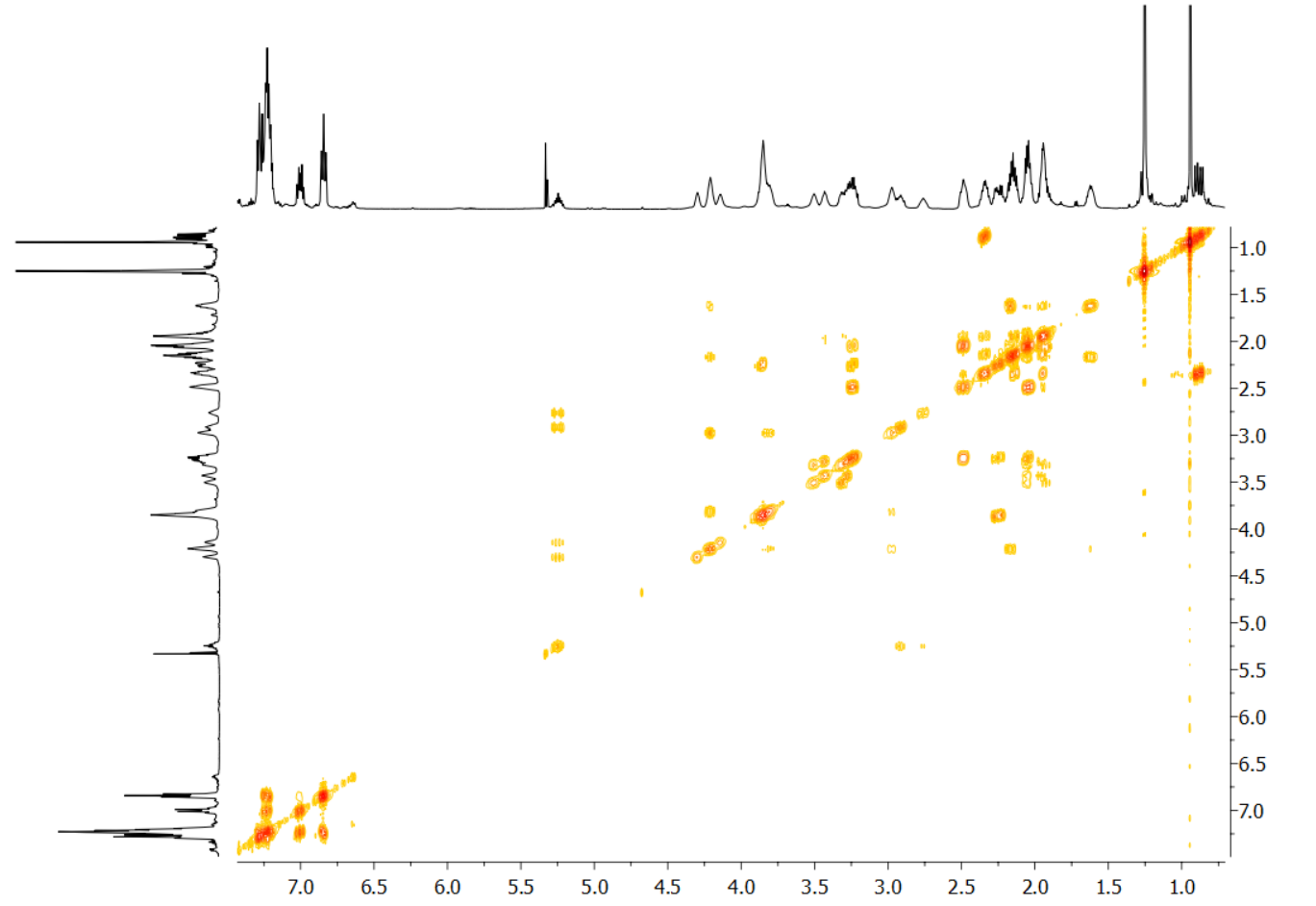


[Pd(allyl)(**L1a**)$_2$]BF$_4$, ^{13}C{^{1}H} spectrum.

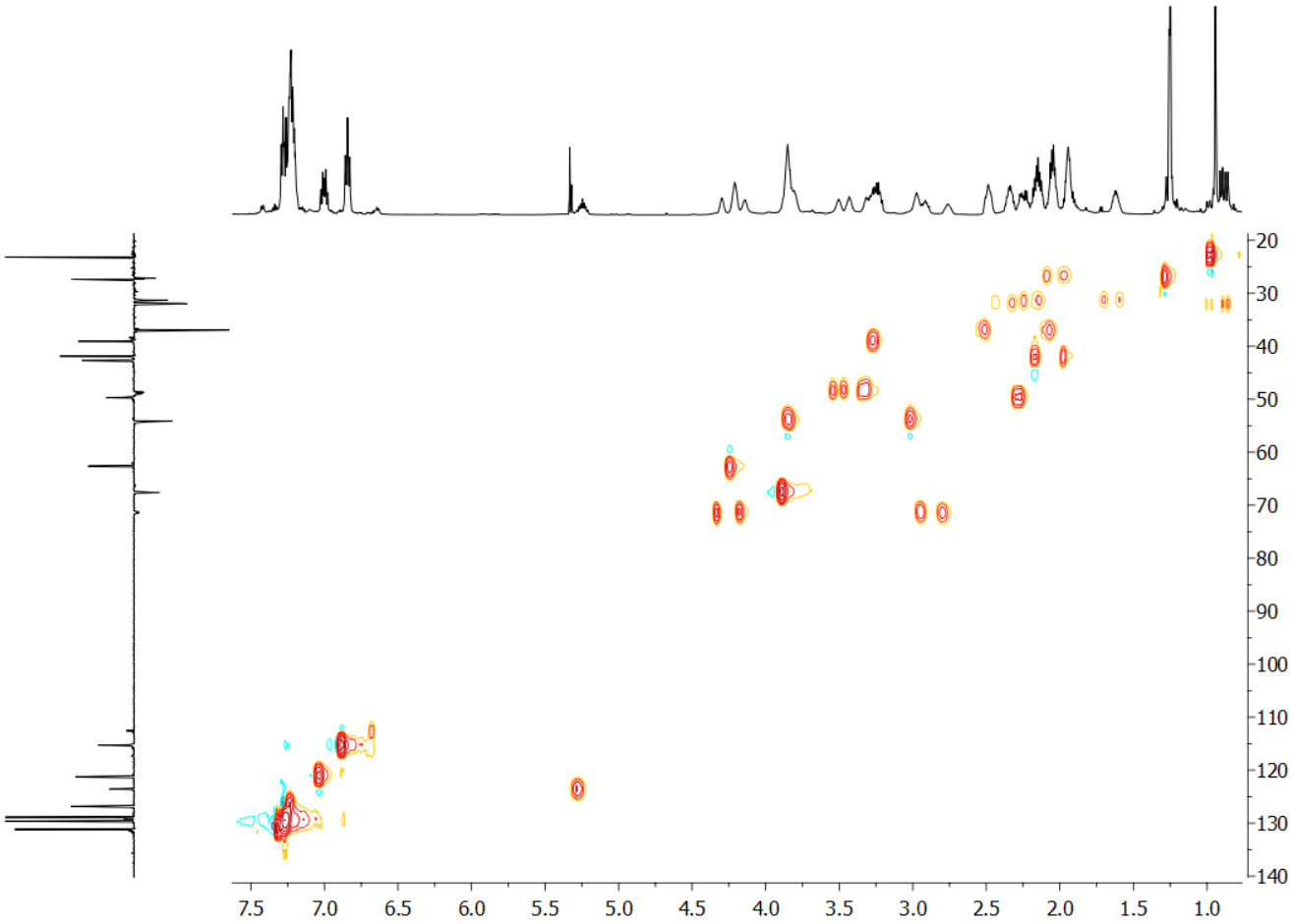
NMR AND HRMS SPECTRA



[Pd(allyl)(**L1a**)$_2$]BF$_4$, ^{13}C{^{1}H} DEPT spectrum.

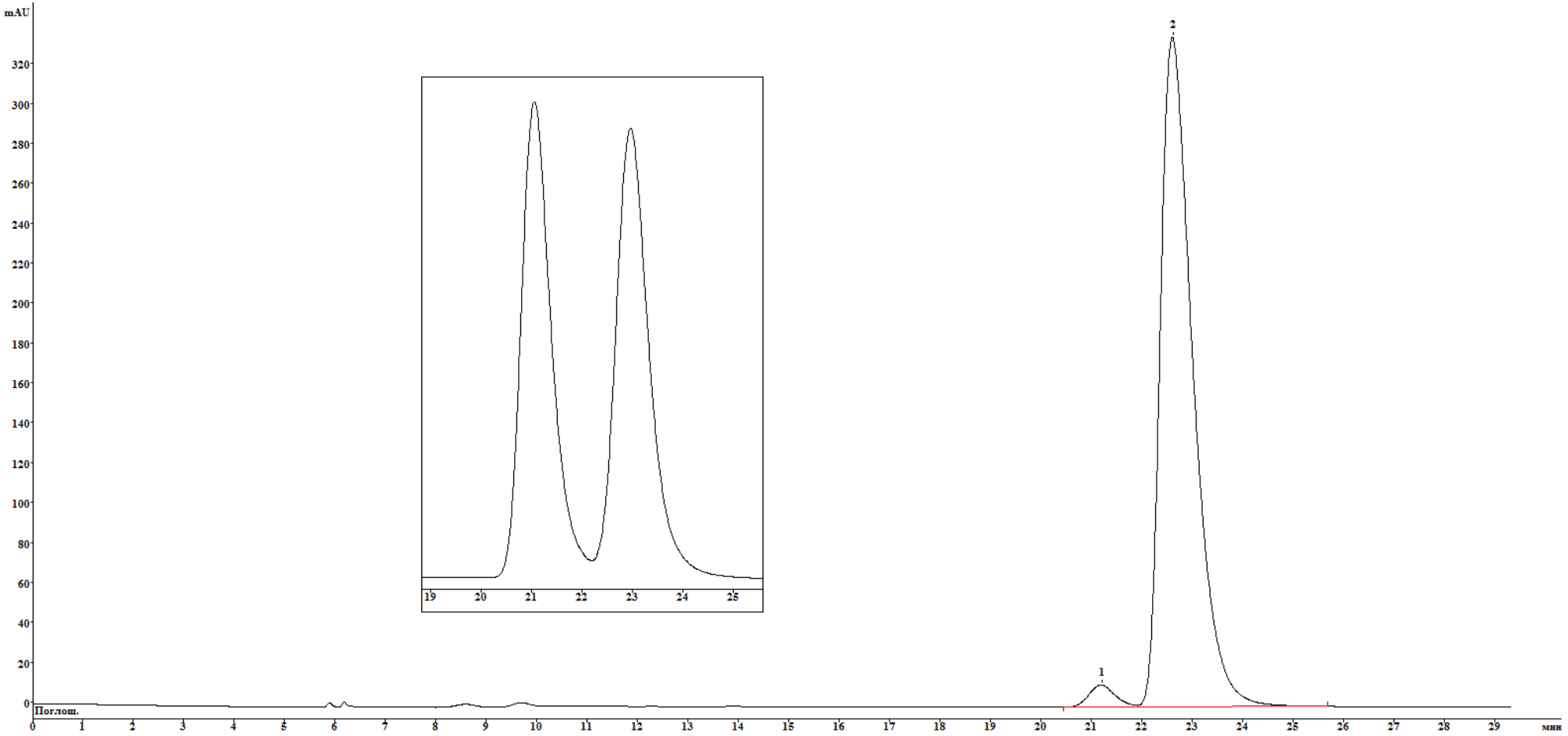


[Pd(allyl)(**L1a**)$_2$]BF$_4$, ^{1}H-^{1}H COSY spectrum.



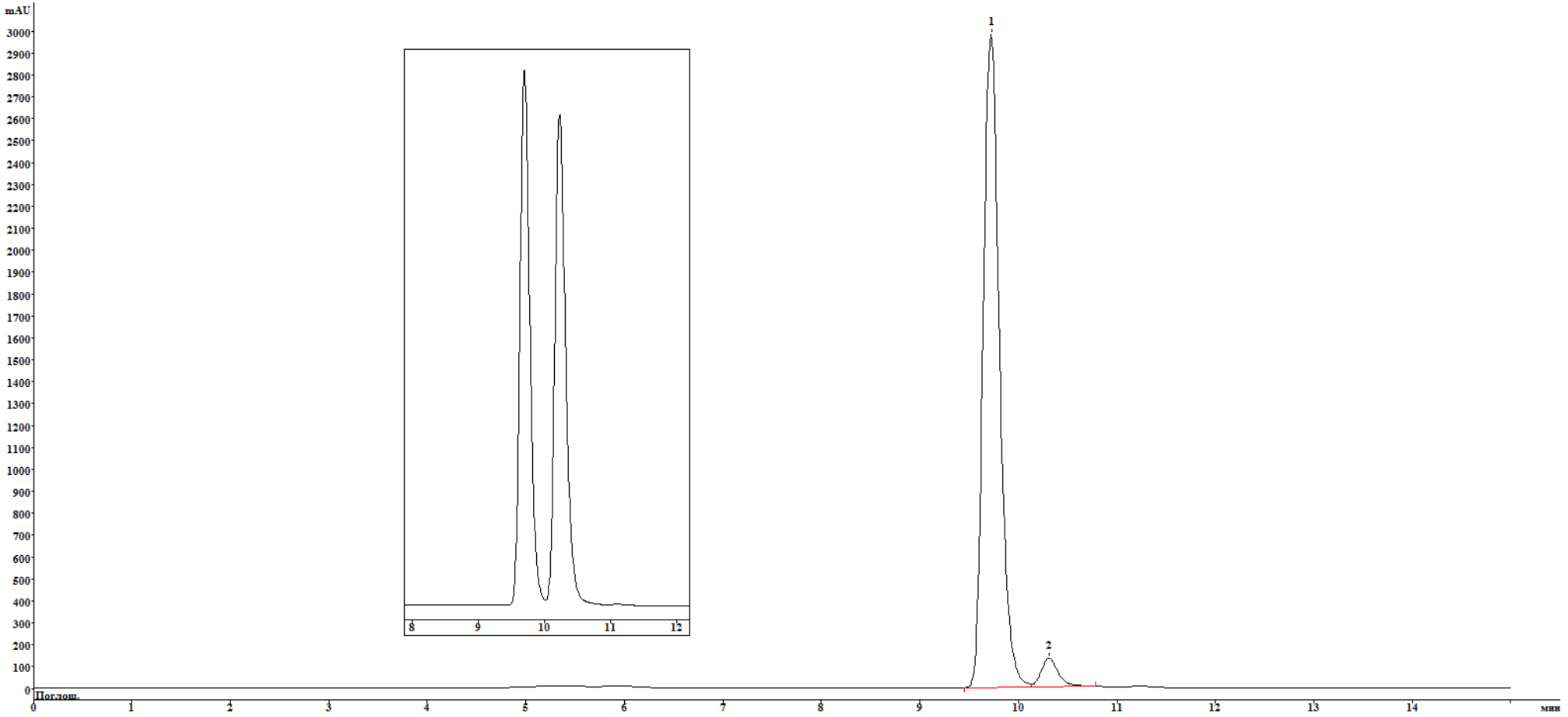
[Pd(allyl)(**L1a**)$_2$]BF_4, ^1H-^{13}C HSQC spectrum.

HPLC TRACES



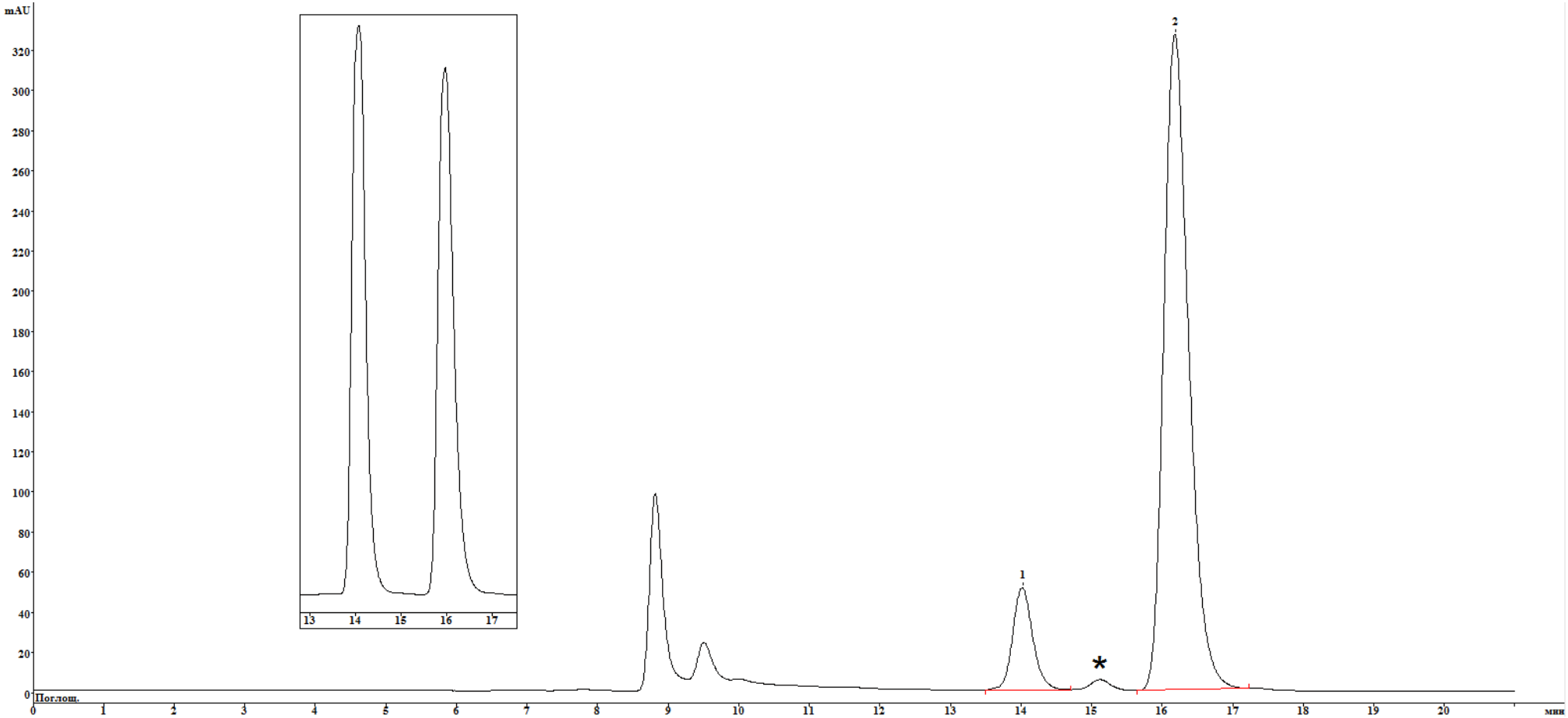
Chiral HPLC trace for the Pd-catalyzed asymmetric allylic alkylation of **4** with dimethyl malonate (entry 15 in Table 1) and for a racemic mixture of **5a** (in the frame). Kromasil 5-CelluCoat, C_6H_{14}/*i*PrOH = 99/1, 0.6 mL/min, 254 nm, t(*R*) = 21.2 min, t(*S*) = 22.8 min.

HPLC TRACES



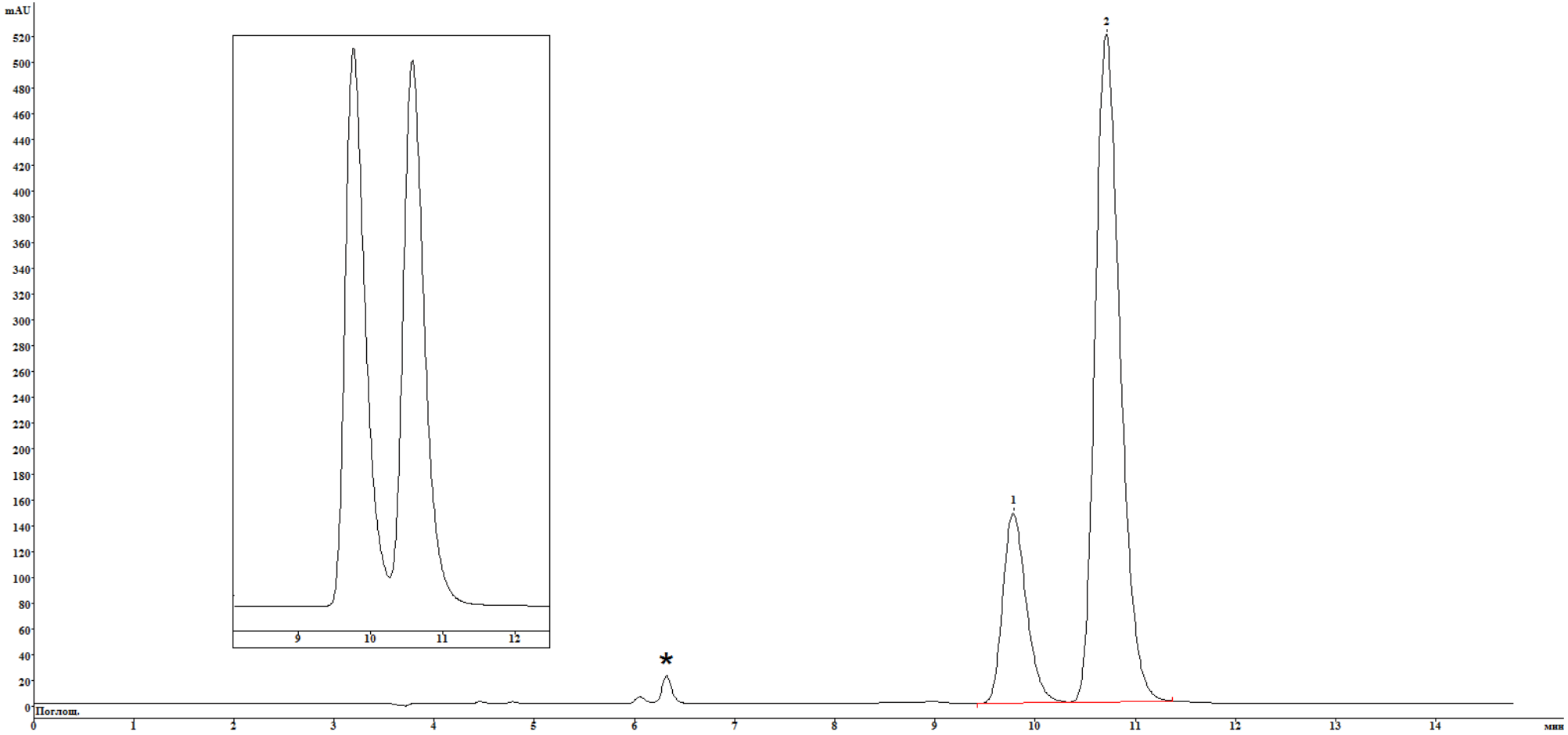
Chiral HPLC trace for the Pd-catalyzed asymmetric allylic amination of **4** with pyrrolidine (entry 14 in Table 2) and for a racemic mixture of **5b** (in the frame). Daicel Chiralcel OD-H, C_6H_{14}/*i*PrOH = 95/5, 0.4 mL/min, 254 nm, t(*R*) = 9.7 min, t(*S*) = 10.3 min.

HPLC TRACES



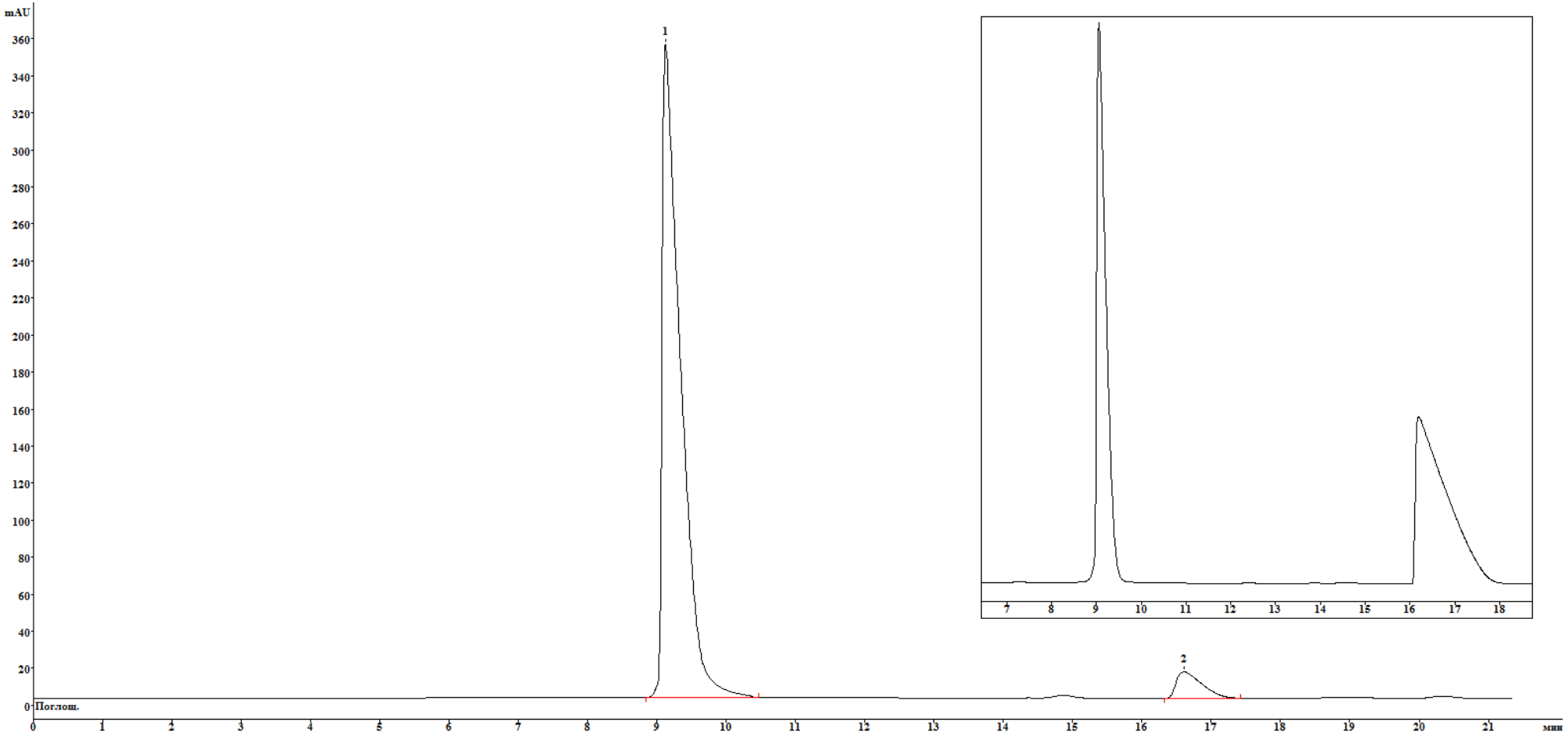
Chiral HPLC trace for the Pd-catalyzed asymmetric allylic alkylation of **6** with ethyl 2-oxocyclohexane-1-carboxylate (entry 2 in Table 3) and for a racemic mixture of **8** (in the frame). Kromasil 5-CelluCoat, C_6H_{14}/*i*PrOH = 95/5, 0.4 mL/min, 254 nm, t(*R*) = 14.0 min, t(*S*) = 16.2 min.
* starting substrate 5

HPLC TRACES



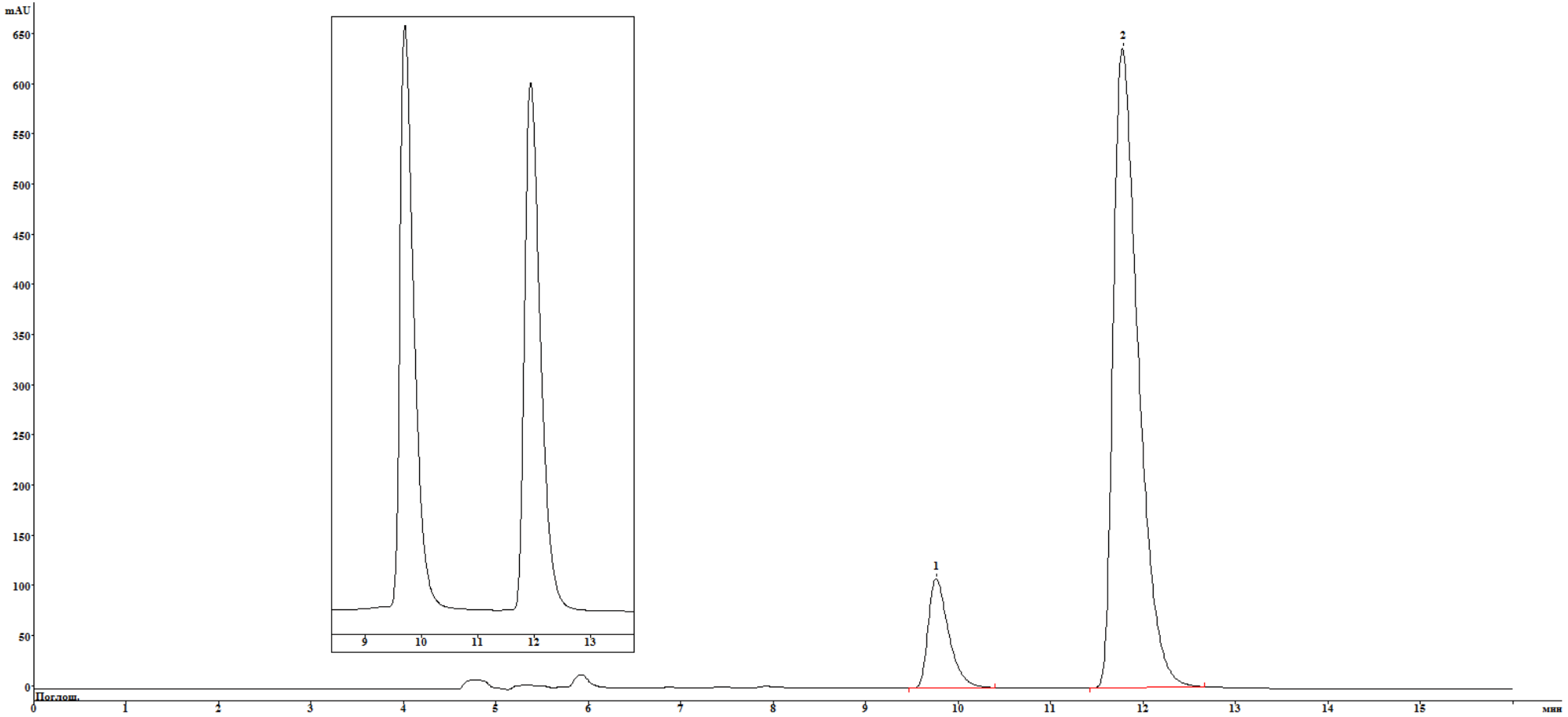
Chiral HPLC trace for the Pd-catalyzed asymmetric allylic alkylation of **6** with ethyl 2-acetamido-3-oxobutanoate (entry 14 in Table 4) and for a racemic mixture of **10** (in the frame). Daicel Chiralcel OD-H, C_6H_{14}/*i*PrOH = 85/15, 0.8 mL/min, 254 nm, *t*(*S*) = 9.8 min, *t*(*R*) = 10.7 min.
* starting substrate **5**

HPLC TRACES



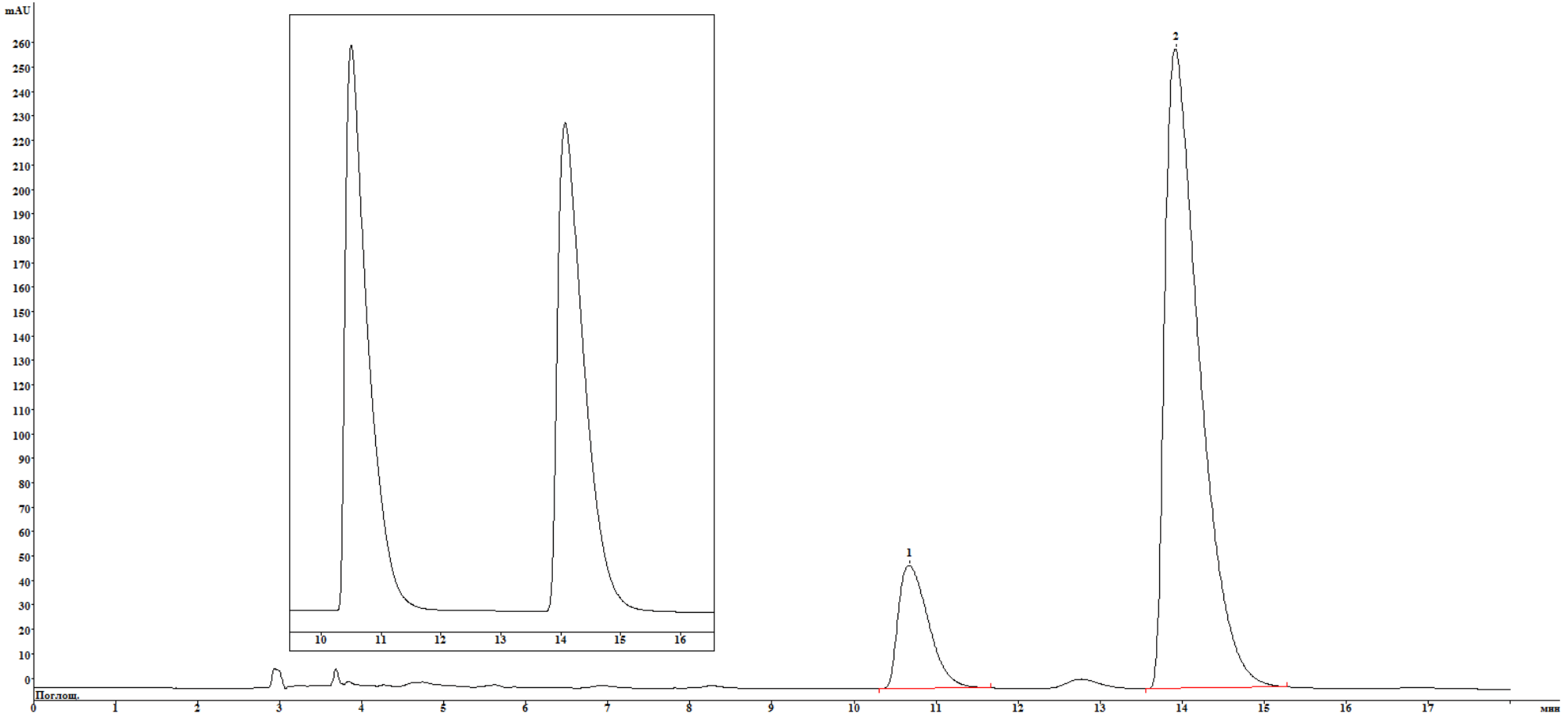
Chiral HPLC trace for the Rh-catalyzed asymmetric hydrogenation of **11a** (entry 10 in Table 5) and for a racemic mixture of **12a** (in the frame). Daicel Chiralcel OD-H, C_6H_{14}/*i*PrOH = 98/2, 0.8 mL/min, 215 nm, t(*R*) = 9.2 min, t(*S*) = 16.7 min.

HPLC TRACES



Chiral HPLC trace for the Rh-catalyzed asymmetric hydrogenation of **11b** (entry 11 in Table 5) and for a racemic mixture of **12b** (in the frame). Daicel Chiralcel OD-H, C_6H_{14}/*i*PrOH = 4/1, 0.6 mL/min, 215 nm, t(*R*) = 9.8 min, t(*S*) = 11.8 min.

HPLC TRACES



Chiral HPLC trace for the Rh-catalyzed asymmetric hydrogenation of **11c** (entry 12 in Table 5) and for a racemic mixture of **12c** (in the frame). Daicel Chiralcel OD-H, C_6H_{14}/*i*PrOH = 9/1, 1.0 mL/min, 219 nm, *t*(*R*) = 10.7 min, *t*(*S*) = 14.0 min.