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Supporting Information

Oxalamide-Based Bisdiamidophosphites: Synthesis, Coordination, and Application in Asymmetric Metallocatalysis

Konstantin N. Gavrilov,* Igor S. Mikhel, Sergey V. Zheglov, Vladislav K. Gavrilov, Ilya V. Chuchelkin, Ilya D. Firsin, Kirill P. Birin, Ivan S. Pytskii, Ksenia A. Paseshnichenko, Victor A. Tafeenko, Vladimir V. Chernyshev and Alexei A. Shiryaev

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EXPERIMENTAL SECTION

General: ^{31}P, ^{13}C and ^{1}H NMR spectra were recorded with a Bruker AMX 400 (162.0 MHz for ^{31}P, 100.6 MHz for ^{13}C and 400.1 MHz for ^{1}H) and a Bruker Avance III 600 (242.9 MHz for ^{31}P, 150.9 MHz for ^{13}C and 600.1 MHz for ^{1}H) instruments. Complete assignment of all the resonances in ^{1}H and ^{13}C NMR spectra was achieved by the use of APT, DEPT, COSY, ROESY, HSQC and HMBC techniques. The chemical shifts are referenced to residual solvent peaks (^{1}H, ^{13}C NMR) or H_3PO_4 85% as external standard (^{31}P NMR). ^{15}N-^{1}H HMBC NMR spectra were recorded with a Bruker Avance III 600 (60.8 MHz) spectrometer. All chemical shifts are reported with respect to liquid NH_3 at 0 ppm. Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, m = multiplet); coupling constants ^{n}J in Hertz (Hz), «n» values are reported in the case of their unambiguous determination. DOSY diffusion experiments were performed with double-stimulated echo dstegp3s pulse sequence from TopSpin 3.2 program package. The molecular structures of **L1a** and **L1c** were confirmed by X-ray structure determination from powder data measured at room temperature on the laboratory diffractometers. The X-ray powder diffraction data for **L1a** were collected using a Huber G670 Guinier camera (Cu $K_{\alpha 1}$ radiation, λ = 1.54059 Å) equipped with an imaging-plate detector. The X-ray powder diffraction data for **L1c** were collected using a Panalytical EMPYREAN instrument with a linear Xcelerator detector using nonmonochromated Cu K_α radiation. The powder patterns were indexed, and the crystal structures were 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 crystal data, data collection and refinement parameters are given in Table S1. The diffraction profiles after the final bond-restrained Rietveld refinement are shown in Fig. S1. The structures of **L2** and **L5** were determined from X-ray single crystal diffraction data. Both intensity data sets were collected at room temperature using a CAD4 (for **L2**) and STADIVARI Pilatus100K (for **L5**) diffractometers, Cu K_α radiation in both cases (λ = 1.54186 Å). The crystal structures were solved by direct methods. Crystallographic programs used for structure solution and refinement, respectively, were *SHELXS* and *SHELXL*.[4] The structures were refined by full-matrix least-squares on F^2. The diffraction data set for **L5** was obtained from a very small crystal, that is why the isotropic displacement parameters were refined for non-H atoms. Hydrogen atoms were placed geometrically and refined using a riding model with U_{iso} constrained at 1.2-1.5 times U_{eq} of the carrier C or N atoms. The crystal data, data

collection and refinement parameters are given in Table S2. The molecular structures of **L1a**, **L1c**, **L2** and **L5** are shown on Fig. 1 prepared with Mercury.[5] High resolution electrospray ionization (HR ESI) mass spectra were recorded on a Bruker MAXIS Impact instrument. HPLC analyses were performed on a Stayer instrument using Kromasil®, Chiralcel® and Knauer® columns. Optical rotations were measured with an Atago AP-300 polarimeter. Elemental analyses were performed on a CHN-microanalyzer Carlo Erba EA1108 CHNS-O. Density functional theory (DFT) calculations have been performed using the B3LYP exchange correlation functional[6] with the 6-31G(d) (for H, C, N, O, P, Cl) and the LANL2DZ (for Pd) basis sets, as implemented in the Spartan'14 program package.

All reactions were carried out under a dry argon atmosphere in flame-dried glassware and in freshly dried and distilled solvents. For example, toluene and tetrahydrofuran were freshly distilled from sodium benzophenone ketyl before use; dichloromethane was distilled from NaH. 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.

The following compounds were synthesized according to literature procedures: N^1,N^2-bis(1-hydroxy-2-methylpropan-2-yl)oxalamide (**1a**),[7] N^1-((*S*)-1-hydroxy-3-methylbutan-2-yl)-N^2-((2*S*,3*S*)-1-hydroxy-3- methylpentan-2-yl)oxalamide (**1b**),[8] N^1,N^2-bis((1*R*,2*S*)-2-hydroxy-2,3-dihydro-1*H*-inden-1-yl)oxalamide (**2**),[9] (*S*)-3-(anilinomethyl)-1,2,3,4-tetrahydroisoquinoline,[10] (5*S*)-2-chloro-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (**3**),[11] 2-chloro-1,3-diphenyl-1,3,2-diazaphospholidine (**5**),[12] $[Pd(allyl)Cl]_2$, (*E*)-1,3-diphenylallyl acetate (**8**),[13] diethyl aminomethylphosphonate,[14] cyclohex-2-en-1-yl ethyl carbonate (**15**),[15] $[Pd_2(dba)_3]\cdot CHCl_3$,[16] $[Pd(Cod)Cl_2]$,[17] methyl (*Z*)-2-acetamido-3-phenylacrylate (**20b**),[18] methyl (*Z*)-2-acetamido-3-(4-fluorophenyl)acrylate (**20c**),[19] methyl (*Z*)-2-acetamido-3-(naphthalen-2-yl)acrylate (**20d**)[20] and $[Rh(Cod)_2]BF_4$.[21] Pd-catalyzed allylic sulfonylation of **8** with sodium *para*-toluene sulfinate, alkylation with dimethyl malonate and 1-cyclohexenylpyrrolidine (**10**), amination with pyrrolidine and diethyl aminomethylphosphonate, allylic alkylation of cinnamyl acetate (**12**) witn ethyl 2-oxocyclohexane-1-carboxylate (**13**), allylic amination of cyclohex-2-en-1-yl ethyl carbonate

(**15**) with dibenzylamine, desymmetrization of **18** and Rh-catalyzed hydrogenation of substrates **20a-d** were performed according to the appropriate procedures.[3b,11,22,3c,23-28] Octane-1,8-diol, sodium *para*-toluene sulfinate, dimethyl malonate, BSA (*N*,*O*-bis(trimethylsilyl) acetamide), 1-cyclohexenylpyrrolidine (**10**), cinnamyl acetate (**12**), ethyl 2-oxocyclohexane-1-carboxylate (**13**), dibenzylamine, *meso*-cyclopent-4-ene-1,3-diol (**17**), tosyl isocyanate and dimethyl itaconate (**20a**) were purchased from Aldrich and Acros Organics.

Procedure for the Preparation of Phosphorylating Reagent 4: A solution of (*S*)-3-(anilinomethyl)-1,2,3,4-tetrahydroisoquinoline (0.98 g, 4.1 mmol) in benzene (20 mL) was added dropwise at 0 °C over 15 min to a vigorously stirred solution of PCl_3 (0.36 mL, 4.1 mmol) and Et_3N (1.14 mL, 8.2 mmol) in benzene (40 mL). The mixture was then briefly heated to boiling point and cooled down to 20 °C. Solid $Et_3N{\cdot}HCl$ was filtered off, and the filtrate was concentrated in vacuum (40 Torr). The residue was dried for 30 min at 10 Torr and distilled in vacuum (1 Torr). The product was obtained as a light yellow solid, yield 1.08 g (87 %).

(3a*S*)-1-Chloro-2-phenyl-1,2,3,3a,4,9-hexahydro-[1,3,2]diazaphospholo[1,5-*b*]isoquinoline (4): ^{1}H NMR (400.1 MHz, $CDCl_3$, 26 °C): δ = 7.33-7.28 (m, 2 H), 7.23-7.07 (m, 6 H), 7.00-6.95 (m, 1 H), 4.52-4.45 (m, 1 H), 4.42-4.33 (m, 1 H), 4.01-3.90 (m, 2 H), 3.53-3.46 (m, 1 H), 3.09-3.01 (m, 2 H) ppm. $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$, 26 °C): δ = 142.8 (d, ^{2}J(C,P) = 16.2 Hz, C_{Ph}), 132.5 (br. d, J(C,P) = 12.7 Hz, C_{Ar}), 132.3 (br. d, J(C,P) = 13.9 Hz, C_{Ar}), 129.4 (CH_{Ph}), 129.2 (CH_{Ar}), 126.7 (CH_{Ar}), 126.6 (CH_{Ar}), 126.3 (CH_{Ar}), 121.6 (CH_{Ph}), 116.4 (d, ^{3}J(C,P) = 15.0 Hz, CH_{Ph}), 56.8 (d, ^{2}J(C,P) = 10.4 Hz, NCH), 54.3 (d, ^{2}J(C,P) = 10.4 Hz, N$\underline{C}H_2$CH), 45.4 (d, ^{2}J(C,P) = 15.0 Hz, NCH_2), 34.6 (d, ^{3}J(C,P) = 4.6 Hz, CH_2) ppm. $^{31}P\{^{1}H\}$ NMR (162.0 MHz, $CDCl_3$, 26 °C): δ = 148.8 ppm.

General Procedure for the Preparation of Ligands: The relevant oxalamide **1a,b, 2** or octane-1,8-diol (1 mmol) was added in one portion to a vigorously stirred solution of the appropriate phosphorylating reagent **3**, **4** or **5** (2 mmol) and Et_3N (0.56 mL, 4 mmol) in toluene (20 mL). The mixture that obtained was stirred for 24 h at 20 °C, then heated to 45 °C, stirred at this temperature for 1 h, and cooled to 20 °C. The resulting suspension was

filtered through a short plug of SiO_2/Al_2O_3, the column was washed twice with toluene (5 mL), and the solvent was evaporated under reduced pressure (40 Torr). Products **L1a,b**, **L2**, **L4** and **L5** were additionally purified by flash chromatography on SiO_2 (toluene) followed by crystallization from heptane, product **L3** – by flash chromatography on Al_2O_3 (toluene). The obtained ligands were dried in vacuum (1 Torr) for 1 h (16 h of further high vacuum (10^{-3} Torr) drying is necessary for the preparation of analytically pure samples).

***N*^{1},*N*^{2}-Bis[1-((2*R*,5*S*)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octyloxy)-2-methylpropan-2-yl]oxalamide (L1a):** White solid, yield 0.51 g (80 %). ^{1}H NMR (600.1 MHz, $CDCl_3$, 26 °C): δ = 7.64 (br. s, 2H; NH), 7.26 (t, ^3J(H,H) = 7.8 Hz, 4H; CH_{meta}), 7.04 (d, ^3J(H,H) = 7.8 Hz, 4H; CH_{ortho}), 6.86 (t, ^3J(H,H) = 7.8 Hz, 2H; CH_{para}), 4.22-4.16 (m, 2H; NCH), 3.83-3.77 (m, 2H; $POCH_2$), 3.82-3.77 (m, 2H; $NC\underline{H}_2CH$), 3.61-3.53 (m, 2H; $NC\underline{H}_2CH_2$), 3.43 (dd, ^2J(H,H) = 10.2 Hz, ^3J(H,P) = 4.8 Hz, 2H; $POCH_2$), 3.26-3.18 (m, 2H; $NC\underline{H}_2CH_2$), 3.23-3.17 (m, 2H; $NC\underline{H}_2CH$), 2.12-2.04 (m, 2H; $NCHC\underline{H}_2$), 1.92-1.84 (m, 2H; $NCH_2C\underline{H}_2$), 1.81-1.72 (m, 2H; $NCH_2C\underline{H}_2$), 1.69-1.62 (m, 2H; $NCHC\underline{H}_2$), 1.35 (s, 6H; CH_3), 1.33 (s, 6H; CH_3) ppm. ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$, 27 °C): δ = 159.71 (CO), 145.57 (d, ^2J(C,P) = 16.1 Hz; PNC), 129.15 (CH_{meta}), 119.01 (CH_{para}), 114.75 (d, ^3J(C,P) = 11.6 Hz; CH_{ortho}), 67.81 (d, ^2J(C,P) = 5.9 Hz; $POCH_2$), 63.21 (d, ^2J(C,P) = 8.8 Hz; NCH), 55.11 (d, ^2J(C,P) = 7.1 Hz; $NC\underline{H}_2CH$), 53.95 (d, ^3J(C,P) = 2.0 Hz; $\underline{C}(CH_3)_2$), 48.68 (d, ^2J(C,P) = 38.3 Hz; $NC\underline{H}_2CH_2$), 32.12 ($NCHC\underline{H}_2$), 26.21 (d, ^3J(C,P) = 3.6 Hz; $NCH_2C\underline{H}_2$), 23.26 (CH_3), 23.19 (CH_3) ppm. ^{31}P{^{1}H} NMR (242.9 MHz, $CDCl_3$, 26 °C): δ = 122.68 ppm. ^{15}N-^{1}H HMBC NMR (60.8 MHz, $CDCl_3$, 27 °C): δ = 122.6 (d, ^1J(N,H) ≈ 91 Hz; NH), 92.5 (PNPh), 79.0 (PN). HR MS (ESI): Calcd. for $[C_{32}H_{47}N_6O_4P_2]^+$ 641.3129, Found 641.3151 $[M+H]^+$. $C_{32}H_{46}N_6O_4P_2$ (640.71): calcd. C 59.99, H 7.24, N 13.12; found C 60.21, H 7.28, N 13.04.

***N*^{1},*N*^{2}-Bis[(2*S*,3*S*)-1-((2*R*,5*S*)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octyloxy)-3-methylpentan-2-yl]oxalamide (L1b):** White solid, yield 0.52 g (75 %). ^{1}H NMR (600.1 MHz, $CDCl_3$, 30 °C): δ = 7.54 (d, ^3J(H,H) = 9.6 Hz, 2H; NH), 7.23 (t, ^3J(H,H) = 7.8 Hz, 4H; CH_{meta}), 7.00 (d, ^3J(H,H) = 8.4 Hz, 4H; CH_{ortho}), 6.83 (t, ^3J(H,H) = 7.8 Hz, 2H; CH_{para}), 4.19-4.13 (m, 2H; NCH), 3.86-3.80 (m, 2H; $POCH_2$), 3.83-3.78 (m, 2H; $NHC\underline{H}$), 3.75 (t, J(H,H) = 8.1 Hz, 2H; $NC\underline{H}_2CH$), 3.58-3.52 (m, 2H; $NC\underline{H}_2CH_2$), 3.56-3.50 (m, 2H; $POCH_2$), 3.24-3.18 (m, 2H; $NC\underline{H}_2CH$), 3.23-3.17 (m, 2H; $NC\underline{H}_2CH_2$), 2.11-2.04 (m, 2H; $NCHC\underline{H}_2$), 1.91-1.83 (m, 2H; $NCH_2C\underline{H}_2$), 1.81-1.73 (m, 2H; $NCH_2C\underline{H}_2$), 1.78-1.71 (m, 2H; $C\underline{H}CH_3$), 1.68-1.61 (m, 2H; $NCHC\underline{H}_2$), 1.47-1.39 (m, 2H; $C\underline{H}_2CH_3$),

1.10-1.00 (m, 2H; C$\underline{H}_2$CH$_3$), 0.91 (d, ^3J(H,H) = 7.2 Hz, 6H; CHC$\underline{H}_3$), 0.85 (t, ^3J(H,H) = 7.5 Hz, 6H; CH$_2$C$\underline{H}_3$) ppm. ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$, 30 °C): δ = 159.51 (CO), 145.49 (d, ^2J(C,P) = 15.8 Hz; PNC), 129.16 (CH_{meta}), 119.08 (CH_{para}), 114.83 (d, ^3J(C,P) = 11.8 Hz; CH_{ortho}), 63.31 (d, ^2J(C,P) = 8.6 Hz; NCH), 61.14 (d, ^2J(C,P) = 3.8 Hz; $POCH_2$), 54.93 (d, ^2J(C,P) = 6.9 Hz; N$\underline{C}$H$_2$CH), 54.35 (d, ^3J(C,P) = 2.9 Hz; NHCH), 48.63 (d, ^2J(C,P) = 38.2 Hz; N$\underline{C}$H$_2$CH$_2$), 35.19 ($\underline{C}$HCH$_3$), 32.13 (NCH$\underline{C}$H$_2$), 26.21 (d, ^3J(C,P) = 3.8 Hz; NCH$_2\underline{C}$H$_2$), 24.88 ($\underline{C}$H$_2$CH$_3$), 15.30 (CH$\underline{C}$H$_3$), 11.36 (CH$_2\underline{C}$H$_3$) ppm. ^{31}P{^{1}H} NMR (242.9 MHz, $CDCl_3$, 30 °C): δ = 123.82 ppm. HR MS (ESI): Calcd. for $[C_{36}H_{55}N_6O_4P_2]^+$ 697.3755, Found 697.3760 $[M+H]^+$. $C_{36}H_{54}N_6O_4P_2$ (696.81): calcd. C 62.05, H 7.81, N 12.06; found C 62.36, H 7.88, N 12.11.

***N*^{1},*N*^{2}-Bis[(1*R*,2*S*)-2-((2*R*,5*S*)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octyloxy)-2,3-dihydro-1*H*-inden-1-yl]oxalamide (L2):** White solid, yield 0.46 g (60 %). ^{1}H NMR (400.1 MHz, $CDCl_3$, 27 °C): δ = 8.31 (d, ^3J(H,H) = 8.8 Hz, 2H; NH), 7.33-7.19 (m, 12H; CH_{arom}), 7.01-6.96 (m, 4H; CH_{ortho}), 6.88 (t, ^3J(H,H) = 7.2 Hz, 2H; CH_{para}), 5.42 (dd, *J* = 8.8 Hz, *J* = 5.6 Hz, 2H; NHC$\underline{H}$), 5.00-4.92 (m, 2H), 4.23 (ddd, *J* = 4.8 Hz, *J* = 7.2 Hz, *J* = 12.0 Hz, 2H), 3.74 (t, *J* = 8.0 Hz, 2H), 3.48-3.37 (m, 2H), 3.24-3.07 (m, 8H), 2.14-2.043 (m, 2H; CH_2), 1.91-1.59 (m, 6H; CH_2) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 27 °C): δ = 159.74 (CO), 145.22 (d, ^2J(C,P) = 15.4 Hz; PNC), 140.46 (C_q, arom.), 139.69 (C_q, arom.), 129.08 (CH_{meta}), 127.91 (CH, arom.), 126.85 (CH, arom.), 124.88 (CH, arom.), 124.35 (CH, arom.), 118.99 (CH_{para}), 114.85 (d, ^3J(C,P) = 12.7 Hz; CH_{ortho}), 74.93 (d, ^2J(C,P) = 9.3 Hz; POCH), 62.48 (d, ^2J(C,P) = 8.3 Hz; NCH), 57.10 (NHCH), 54.01 (d, ^2J(C,P) = 6.5 Hz; N$\underline{C}$H$_2$CH), 48.14 (d, ^2J(C,P) = 35.6 Hz; N$\underline{C}$H$_2$CH$_2$), 39.52 (d, ^3J(C,P) = 2.7 Hz; OCH$\underline{C}$H$_2$), 31.66 (NCH$\underline{C}$H$_2$), 26.10 (d, ^3J(C,P) = 3.8 Hz; NCH$_2\underline{C}$H$_2$) ppm. ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$, 27 °C): δ = 132.00 ppm. HR MS (ESI): Calcd. for $[C_{42}H_{47}N_6O_4P_2]^+$ 761.3129, Found 761.3134 $[M+H]^+$; Calcd. for $[C_{42}H_{46}N_6O_4P_2Na]^+$ 783.2953, Found 783.2951 $[M+Na]^+$. $C_{42}H_{46}N_6O_4P_2$ (760.82): calcd. C 66.31, H 6.09, N 11.05; found C 66.57, H 6.04, N 10.94.

1,8-Bis((2*R*,5*S*)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octyloxy)octane (L3): Colorless viscous oil that solidified on standing, yield 0.47 g (85 %). ^{1}H NMR (400.1 MHz, $CDCl_3$, 27 °C): δ = 7.24 (t, ^3J(H,H) = 8.0 Hz, 4H; CH_{meta}), 7.03 (d, ^3J(H,H) = 8.0 Hz, 4H; CH_{ortho}), 6.83 (t, ^3J(H,H) = 7.2 Hz, 2H; CH_{para}), 4.21-4.09 (m, 2H; NCH), 3.82-3.46 (m, 8H; CH_2), 3.25-3.13 (m, 4H; CH_2), 2.11-1.98 (m, 2H; CH_2), 1.91-1.70 (m, 4H; CH_2), 1.70-1.58 (m, 2H; CH_2), 1.54-1.42 (m, 4H; CH_2), 1.31-1.09 (m, 8H; CH_2) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 27 °C): δ = 145.73 (d, ^2J(C,P) =

15.7 Hz; PNC), 128.92 (CH_{meta}), 118.62 (CH_{para}), 114.68 (d, ^3J(C,P) = 11.6 Hz; CH_{ortho}), 63.18 (d, ^2J(C,P) = 8.5 Hz; NCH), 62.19 (d, ^2J(C,P) = 2.7 Hz; $POCH_2$), 54.77 (d, ^2J(C,P) = 7.2 Hz; $N\underline{C}H_2CH$), 48.63 (d, ^2J(C,P) = 38.3 Hz; $N\underline{C}H_2CH_2$), 32.00 (CH_2), 30.73 (d, J(C,P) = 2.6 Hz; CH_2), 29.05 (CH_2), 26.05 (d, ^3J(C,P) = 3.8 Hz; $NCH_2\underline{C}H_2$), 25.81 (CH_2) ppm. $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 27 °C): δ = 122.60 ppm. $C_{30}H_{44}N_4O_2P_2$ (554.66): calcd. C 64.96, H 8.00, N 10.10; found C 65.16, H 7.95, N 10.00.

***N*^{1},*N*^{2}-Bis[1-(((3a*S*)-2-phenyl-3,3a,4,9-tetrahydro-[1,3,2]diazaphospholo[1,5-*b*]isoquinolin-1(2*H*)-yl)oxy)-2-methylpropan-2-yl]oxalamide (L4):** White solid, yield 0.54 g (70 %). ^1H NMR (600.1 MHz, $CDCl_3$, 26 °C): δ = 7.48 (br. s, 2H; NH), 7.43 (br. s, 2H; NH), 7.32-7.27 (m, 18H; NH + CH_{arom}), 7.25 (br. s, 2H; NH), 7.22-7.08 (m, 48H; CH_{arom}), 6.92-6.87 (m, 8H; CH_{arom}), 4.60 (dd, *J* = 16.2 Hz, *J* = 3.0 Hz, 4H), 4.52 (dd, *J* = 16.2 Hz, *J* = 8.4 Hz, 4H), 4.45 (dd, *J* = 16.2 Hz, *J* = 11.4 Hz, 4H), 4.34-4.28 (m, 4H), 4.05-3.96 (m, 8H), 3.96-3.90 (m, 4H), 3.79-3.72 (m, 8H), 3.71-3.62 (m, 8H), 3.56-3.47 (m, 8H), 3.41-3.34 (m, 4H), 3.16-3.08 (m, 4H), 3.02-2.94 (m, 8H), 2.81-2.72 (m, 4H), 1.35 (s, 6H; CH_3), 1.34 (s, 6H; CH_3), 1.33 (s, 6H; CH_3), 1.325 (s, 6H; CH_3), 1.122 (s, 6H; CH_3), 1.118 (s, 6H; CH_3), 1.03 (s, 6H; CH_3), 1.00 (s, 6H; CH_3) ppm. $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$, 30 °C): δ = 159.48 (CO), 159.47 (CO), 159.29 (CO), 159.27 (CO), 145.44 (d, ^2J(C,P) = 17.2 Hz; PNC), 145.35 (d, ^2J(C,P) = 15.4 Hz; PNC),145.30 (d, ^2J(C,P) = 15.4 Hz; PNC), 134.74 (d, J(C,P) = 6.6 Hz; C_q), 134.69 (d, J(C,P) = 6.9 Hz; C_q), 134.13 (d, J(C,P) = 4.4 Hz; C_q), 134.08 (d, J(C,P) = 1.4 Hz; C_q), 134.00 (d, J(C,P) = 1.4 Hz; C_q), 133.46 (d, J(C,P) = 0.8 Hz; C_q), 133.44 (d, J(C,P) = 0.8 Hz; C_q), 129.40 (CH_{arom}), 129.39 (CH_{arom}), 129.30 (CH_{arom}), 129.26 (CH_{arom}), 129.24 (CH_{arom}), 126.35 (CH_{arom}), 126.34 (CH_{arom}), 126.29 (CH_{arom}), 126.28 (CH_{arom}), 126.27 (CH_{arom}), 126.24 (CH_{arom}), 126.18 (CH_{arom}), 126.16 (CH_{arom}), 119.47 (CH_{para}), 119.44 (CH_{para}), 119.43 (CH_{para}), 115.04 (d, ^3J(C,P) = 13.7 Hz; CH_{ortho}), 115.03 (d, ^3J(C,P) = 13.7 Hz; CH_{ortho}), 114.90 (d, ^3J(C,P) = 14.0 Hz; CH_{ortho}), 114.88 (d, ^3J(C,P) = 13.9 Hz; CH_{ortho}), 68.88 ($POCH_2$), 68.77 ($POCH_2$), 68.03 (d, ^2J(C,P) = 3.8 Hz; $POCH_2$), 68.01 (d, ^2J(C,P) = 4.7 Hz; $POCH_2$), 56.29 (d, ^2J(C,P) = 9.7 Hz; NCH), 56.28 (d, ^2J(C,P) = 10.0 Hz; NCH), 55.74 (d, ^2J(C,P) = 10.6 Hz; NCH), 54.50 (d, J(C,P) = 9.4 Hz; NCH_2), 54.30 (d, ^3J(C,P) = 2.6 Hz; $\underline{C}(CH_3)_2$), 54.26 (d, ^3J(C,P) = 2.6 Hz; $\underline{C}(CH_3)_2$), 54.09 (d, ^3J(C,P) = 1.7 Hz; $\underline{C}(CH_3)_2$), 54.07 (d, ^3J(C,P) = 1.8 Hz; $\underline{C}(CH_3)_2$), 53.95 (d, J(C,P) = 9.5 Hz; NCH_2), 46.28 (d, ^2J(C,P) = 28.8 Hz; NCH_2), 45.32 (d, ^2J(C,P) = 22.0 Hz; NCH_2), 45.27 (d, ^2J(C,P) = 22.1 Hz; NCH_2), 35.54 (d, ^3J(C,P) = 2.9 Hz; CH_2), 35.51 (d, ^3J(C,P) = 2.9 Hz; CH_2), 34.41 (CH_2), 23.50 (CH_3), 23.49 (CH_3), 23.41 (CH_3), 23.34 (CH_3), 23.09 (CH_3), 22.94 (CH_3), 22.90 (CH_3) ppm. $^{31}P\{^1H\}$

NMR (242.9 MHz, $CDCl_3$, 30 °C): δ = 120.61 (23%), 120.37 (25%), 112.21 (26%), 111.75 (26%) ppm. HR MS (ESI): Calcd. for $[C_{42}H_{51}N_6O_4P_2]^+$ 765.3442, Found 765.3472 $[M+H]^+$. $C_{42}H_{50}N_6O_4P_2$ (764.85): calcd. C 65.96, H 6.59, N 10.99; found C 66.30, H 6.50, N 11.11.

***N*^{1},*N*^{2}-Bis((2*S*,3*S*)-1-((1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)oxy)-3-methylpentan-2 yl)oxalamide (L5):** White solid, yield 0.65 g (84 %). ^{1}H NMR (600.1 MHz, $CDCl_3$, 30 °C): δ = 7.32 (d, ^3J(H,H) ~ 9.6 Hz, 2H; NHCH), 7.32 (t, ^3J(H,H) = 7.8 Hz, 4H; CH_{meta}), 7.26 (t, ^3J(H,H) = 7.8 Hz, 4H; CH_{meta}), 7.18 (d, ^3J(H,H) = 7.8 Hz, 4H; CH_{ortho}), 7.13 (d, ^3J(H,H) = 7.8 Hz, 4H; CH_{ortho}), 6.94 (t, ^3J(H,H) = 7.5 Hz, 2H; CH_{para}), 6.87 (t, ^3J(H,H) = 7.2 Hz, 2H; CH_{para}), 3.95-3.77 (m, 8H; $PNCH_2$), 3.71-3.62 (m, 4H; $POCH_2$ + NHCH), 3.55-3.50 (m, 2H; $POCH_2$), 1.64-1.56 (m, 2H; $CHCH_3$), 1.36-1.27 (m, 2H; CH_2CH_3), 1.00-0.85 (m, 2H; CH_2CH_3), 0.76 (t, ^3J(H,H) = 7.5 Hz, 6H; CH_2CH_3), 0.67 (d, ^3J(H,H) = 6.6 Hz, 6H; $CHCH_3$) ppm. ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$, 30 °C): δ = 159.16 (CO), 144.91 (d, ^2J(C,P) = 5.7 Hz; PNC), 144.79 (d, ^2J(C,P) = 6.5 Hz; PNC), 129.38 (CH_{meta}), 129.37 (CH_{meta}), 120.27 (br. s, CH_{para}), 115.43 (d, ^3J(C,P) = 2.7 Hz; CH_{ortho}), 115.34 (d, ^3J(C,P) = 3.0 Hz; CH_{ortho}), 62.21 (d, ^2J(C,P) = 2.0 Hz; $POCH_2$), 54.19 (d, ^3J(C,P) = 2.9 Hz; NHCH), 47.53 (d, ^2J(C,P) = 10.1 Hz; $PNCH_2$), 47.38 (d, ^2J(C,P) = 10.1 Hz; $PNCH_2$), 34.68 ($CHCH_3$), 24.55 (CH_2CH_3), 15.23 ($CHCH_3$), 11.15 (CH_2CH_3) ppm. ^{31}P{^{1}H} NMR (242.9 MHz, $CDCl_3$, 30 °C): δ = 104.13 ppm. HR MS (ESI): Calcd. for $[C_{42}H_{55}N_6O_4P_2]^+$ 769.3755, Found 769.3742 $[M+H]^+$; Calcd. for $[C_{42}H_{54}N_6O_4P_2Na]^+$ 791.3579, Found 791.3564 $[M+Na]^+$. $C_{42}H_{54}N_6O_4P_2$ (768.88): calcd. C 65.61, H 7.08, N 10.93; found C 65.78, H 7.12, N 10.99.

General Procedure for the NMR Investigations of the Reactions L1a with [Pd(Cod)Cl_2] at 1:1 and 1:2 Molar Ratio.

An argon-flushed Schlenk tube equipped with magnetic stirring bar and septum was charged with 2 (or 1) equiv of **L1a** (0.0128 g (0.02 mmol) or 0.0064 g (0.01 mmol)) and 2 equiv of [Pd(Cod)Cl_2] (0.0057 g, 0.02 mmol), freshly distilled solvent $CDCl_3$ (1 mL) was added, and the mixture was stirred for 30 min at room temperature. Subsequently the samples were transferred to an argon-flushed NMR tubes and spectroscopic experiments were carried out.

***Trans*-[Pd(μ-L1a)Cl_2]$_2$ (6):** ^{1}H NMR (600.1 MHz, $CDCl_3$, 27 °C): δ = 7.45 (d, ^3J(H,H) = 7.8 Hz, 4H; CH_{ortho}), 7.31 (t, ^3J(H,H) = 7.8 Hz, 4H; CH_{meta}), 7.23 (br. s, 2H; NH), 7.01 (t, ^3J(H,H) = 7.8 Hz, 2H; CH_{para}), 4.57-4.49 (m, 2H; NCH_2CH_2), 4.16-4.08 (m, 2H; NCH), 4.00-3.94 (m, 2H; NCH_2CH),

3.97-3.92 (m, 2H; $POCH_2$), 3.76 (d, ^2J(H,H) = 9.6 Hz, 2H; $POCH_2$), 3.66 (t, J(H,H) = 9.9 Hz, 2H; NCH_2CH), 3.31-3.23 (m, 2H; NCH_2CH_2), 2.36-2.27 (m, 2H; NCH_2CH_2), 2.14-2.05 (m, 2H; $NCHCH_2$), 2.05-1.97 (m, 2H; NCH_2CH_2), 2.00-1.93 (m, 2H; $NCHCH_2$), 1.23 (s, 6H; CH_3), 1.04 (s, 6H; CH_3) ppm. $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$, 27 °C): δ = 159.22 (CO), 141.37 (vt, J(C,P) = 4.2 Hz; PNC), 129.18 (CH_{meta}), 122.44 (CH_{para}), 118.96 (vt, J(C,P) = 2.7 Hz; CH_{ortho}), 69.37 (vt, J(C,P) = 4.5 Hz; $POCH_2$), 61.47 (br. s; NCH), 56.41 (br. s; NCH_2CH), 53.86 (vt, J(C,P) = 3.9 Hz; $C(CH_3)_2$), 51.59 (vt, J(C,P) = 10.3 Hz; NCH_2CH_2), 30.53 (br. s; $NCHCH_2$), 26.17 (br. s; NCH_2CH_2), 25.13 (CH_3), 22.43 (CH_3) ppm. $^{31}P\{^1H\}$ NMR (242.9 MHz, $CDCl_3$, 27 °C): δ = 103.46 ppm. ^{15}N-^1H HMBC NMR (60.8 MHz, $CDCl_3$, 27 °C): δ = 122.1 (^1J(N,H) ≈ 91 Hz; NH). DOSY NMR (600.1 MHz, $CDCl_3$, 26 °C): D = 4.188x10^{-10} m^2/s, r_h = 10.17 Å.

[(PdCl(μ-Cl))$_2$(L1a)] (7): ^1H NMR (600.1 MHz, $CDCl_3$, 27 °C): δ = 7.41 (t, ^3J(H,H) = 7.8 Hz, 4H; CH_{meta}), 7.34 (d, ^3J(H,H) = 7.8 Hz, 4H; CH_{ortho}), 7.15 (br. s, 2H; NH), 7.10 (t, ^3J(H,H) = 7.2 Hz, 2H; CH_{para}), 4.72-4.65 (m, 2H; $POCH_2$), 4.66-4.58 (m, 2H; NCH_2CH_2), 4.12-4.04 (m, 2H; NCH), 3.87-3.79 (m, 2H; NCH_2CH), 3.69-3.62 (m, 2H; $POCH_2$), 3.55 (t, J(H,H) = 9.3 Hz, 2H; NCH_2CH), 3.43-3.35 (m, 2H; NCH_2CH_2), 2.40-2.33 (m, 2H; NCH_2CH_2), 2.16-2.09 (m, 1H; $NCHCH_2$), 2.13-2.06 (m, 2H; NCH_2CH_2), 1.89-1.82 (m, 2H; $NCHCH_2$), 1.29 (s, 6H; CH_3), 1.21 (s, 6H; CH_3) ppm. $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$, 28 °C): δ = 159.20 (CO), 141.68 (br. d, ^2J(C,P) = 8.9 Hz; PNC), 129.45 (CH_{meta}), 122.24 (br. s; CH_{para}), 116.68 (br. s; CH_{ortho}), 67.43 (br. d, ^2J(C,P) = 14.0 Hz; $POCH_2$), 61.81 (br. s; NCH), 55.04 (br. s; NCH_2CH), 53.06 (br. s; $C(CH_3)_2$), 48.65 (br. d, ^2J(C,P) = 15.2 Hz; NCH_2CH_2), 31.02 (br. s; $NCHCH_2$), 27.58 (br. d, ^3J(C,P) = 5.3 Hz; NCH_2CH_2), 25.96 (br. s; CH_3), 23.63 (br. s; CH_3) ppm. $^{31}P\{^1H\}$ NMR (242.9 MHz, $CDCl_3$, 27 °C): δ = 72.74 ppm. ^{15}N-^1H HMBC NMR (60.8 MHz, $CDCl_3$, 27 °C): δ = 119.8 (^1J(N,H) ≈ 92 Hz; NH), 88.6 (PNPh), 73.2 (PN). DOSY NMR (600.1 MHz, $CDCl_3$, 28 °C): D = 6.011x10^{-10} m^2/s, r_h = 7.13 Å.

Catalytic Experiments

Palladium-Catalyzed Asymmetric Allylic Sulfonylation of (*E*)-1,3-Diphenylallyl Acetate with Sodium *para*-Toluene Sulfinate: A solution of $[Pd(allyl)Cl]_2$ (0.0019 g, 0.005 mmol) and the appropriate ligand (0.01 mmol or 0.02 mmol) in THF (1.5 mL) was stirred for 40 min. In the case of the formation of complex **6**, a solution of $[Pd(Cod)Cl_2]$ (0.0029 g, 0.01 mmol) and the ligand **L1a** (0.0064 g, 0.01 mmol) in THF (1.5 mL) was stirred for 24 h. (*E*)-1,3-Diphenylallyl acetate (**8**) (0.05 mL, 0.25 mmol) was added and the solution stirred for 15 min, then sodium

para-toluene sulfinate (0.089 g, 0.5 mmol) was added and the reaction mixture stirred for a further 48 h, quenched with brine (3 mL) and extracted with THF (3 x 2 mL). The combined organic extracts were washed brine (2 x 2 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure (40 Torr) after filtration. Crystallization of the residue from EtOH, followed by desiccation in vacuum (10 Torr, 12 h), gave (*E*)-1,3-diphenyl-3-tosylprop-1-ene (**9a**) as white crystals.[29] Enantiomeric excess of **9a** was determined by HPLC.

Palladium-Catalyzed Asymmetric Allylic Alkylation of (*E*)-1,3-Diphenylallyl Acetate with Dimethyl Malonate: A solution of $[Pd(allyl)Cl]_2$ (0.0019 g, 0.005 mmol) and the appropriate ligand (0.01 mmol or 0.02 mmol) in the appropriate solvent (1.5 mL) was stirred for 40 min. In the case of the formation of complex **6**, a solution of $[Pd(Cod)Cl_2]$ (0.0029 g, 0.01 mmol) and the ligand **L1a** (0.0064 g, 0.01 mmol) in the appropriate solvent (1.5 mL) was stirred for 24 h. (*E*)-1,3-Diphenylallyl acetate (**8**) (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 potassium acetate (0.002 g) were added. The reaction mixture was stirred for 48 h, diluted with CH_2Cl_2 or THF (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 (*E*)-dimethyl 2-(1,3-diphenylallyl)malonate (**9b**).[30] 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.

Palladium-Catalyzed Asymmetric Allylic Amination of (*E*)-1,3-Diphenylallyl Acetate with Pyrrolidine: A solution of $[Pd(allyl)Cl]_2$ (0.0019 g, 0.005 mmol) and the appropriate ligand (0.01 mmol or 0.02 mmol) in the appropriate solvent (1.5 mL) was stirred for 40 min. In the case of the formation of complex **6**, a solution of $[Pd(Cod)Cl_2]$ (0.0029 g, 0.01 mmol) and the ligand **L1a** (0.0064 g, 0.01 mmol) in the appropriate solvent (1.5 mL) was stirred for 24 h. (*E*)-1,3-Diphenylallyl acetate (**8**) (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 48 h, diluted with CH_2Cl_2 or THF (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 (*E*)-1-(1,3-diphenylallyl)pyrrolidine (**9c**).[31] 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.

Palladium-Catalyzed Asymmetric Allylic Amination of (*E*)-1,3-Diphenylallyl Acetate with Diethyl Aminomethylphosphonate: A solution of $[Pd(allyl)Cl]_2$ (0.0019 g, 0.005 mmol) and the appropriate ligand (0.01 mmol or 0.02 mmol) in the appropriate solvent (1.5 mL) was stirred for 40 min. (*E*)-1,3-Diphenylallyl acetate (**8**) (0.05 mL, 0.25 mmol) was added and the solution stirred for 15 min, then diethyl aminomethylphosphonate (0.05 g, 0.3 mmol) was added. The reaction mixture was stirred for 48 h, diluted with CH_2Cl_2 or THF (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 diethyl (*E*)-(((1,3-diphenylallyl)amino)methyl)phosphonate (**9d**).[3c] 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.

Palladium-Catalyzed Asymmetric Allylic Alkylation of (*E*)-1,3-Diphenylallyl Acetate with 1-Cyclohexenylpyrrolidine: A solution of $[Pd(allyl)Cl]_2$ (0.0019 g, 0.005 mmol) and the appropriate ligand (0.01 mmol or 0.02 mmol) in the appropriate solvent (1.5 mL) was stirred for 40 min. (*E*)-1,3-Diphenylallyl acetate (**8**) (0.05 mL, 0.25 mmol) was added and the solution stirred for 15 min, then freshly distilled 1-cyclohexenylpyrrolidine (**10**) (0.115 g, 0.75 mmol) was added and the reaction mixture was stirred for further 48 h, quenched with saturated NH_4Cl solution (5 mL) for 2 h and extracted with CH_2Cl_2 (3 x 3 mL). The combined organic extracts were washed with water (3 mL), brine (3 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure (40 Torr) after filtration. The residue was dissolved in EtOAc/hexane (1:10) 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 (*E*)-2-(1,3-diphenylallyl)cyclohexanone of *anti*-configuration (**11a**) and *syn*-configuration (**11b**).[22] The ratio of *anti*- and *syn*-configuration was determined by ^1H NMR. 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 ^1H NMR and HPLC analysis.

Pd-Catalyzed Asymmetric Allylic Alkylation of Cinnamyl Acetate with Ethyl 2-Oxocyclohexane-1-carboxylate: A solution of $[Pd(allyl)Cl]_2$ (0.0019 g, 0.005 mmol) and the appropriate ligand (0.01 mmol or 0.02 mmol) in toluene (1.5 mL) was stirred for 40 min. Cinnamyl acetate (**12**) (0.04 mL, 0.25 mmol) was added and the solution stirred for 15 min. Ethyl 2-oxocyclohexane-1-carboxylate (**13**) (0.06 mL, 0.375 mmol), BSA (0.25 mL, 1 mmol) and $Zn(OAc)_2$ (0.005 g) were added. The reaction mixture was stirred for 48 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 Torr, 12 h) affording a residue containing ethyl 1-cinnamyl-2-oxocyclohexane-1-carboxylate (**14**).[23] 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.

Palladium-Catalyzed Asymmetric Allylic Amination of Cyclohex-2-en-1-yl Ethyl Carbonate with Dibenzylamine: A solution of $[Pd(allyl)Cl]_2$ (0.0019 g, 0.005 mmol) and the appropriate ligand (0.01 mmol or 0.02 mmol) in the appropriate solvent (1.5 mL) was stirred for 40 min. Cyclohex-2-en-1-yl ethyl carbonate (**15**) (0.043 g, 0.25 mmol) was added and the solution stirred for 15 min, then dibenzylamine (0.06 mL, 0.3 mmol) was added. The reaction mixture was stirred for 48 h, quenched with saturated NH_4Cl solution (5 mL) for 30 min and extracted with CH_2Cl_2 (3 x 3 mL). The combined organic extracts were washed with saturated NH_4Cl solution (2 x 2 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure (40 Torr) after filtration. The residue was purified by column chromatography on SiO_2 (EtOAc/hexane 1:20) affording *N*,*N*-dibenzylcyclohex-2-en-1-amine (**16**) as yellowish oil.[24,32] Enantiomeric excess of **16** was determined by HPLC.

Palladium-Catalyzed Desymmetrization of *N,N*'-Ditosyl-*meso*-cyclopent-4-ene-1,3-diol Biscarbamate: A solution of $[Pd_2(dba)_3]\cdot CHCl_3$ (0.005 g, 0.005 mmol) and the appropriate ligand (0.01 mmol or 0.02 mmol) in THF (1 mL) was stirred for 40 min. A solution of *N,N'*-ditosyl-*meso*-cyclopent-4-ene-1,3-diol biscarbamate (**18**) and Et_3N (14 µL, 0.099 mmol) in THF (0.5 mL) was added dropwise with vigorous stirring at -15 °C (compound **18** was prepared *in situ* as follows: to a solution of the *meso*-cyclopent-4-ene-1,3-diol **17** (0.01 g, 0.099 mmol) in THF (0.5 mL), tosyl isocyanate (35 µL, 0.232 mmol) was added; the mixture was stirred at 20 °C for 15 min, heated to 55 °C for 1 h, and cooled down to 20 °C). The

reaction mixture was stirred for 24 h at -15 °C and then warmed to room temperature. The solvent was removed under reduced pressure (40 Torr) and the residue was purified by flash chromatography on a short pad of SiO_2 (toluene). The solvent was evaporated at reduced pressure (40 Torr) and the residue was dried in vacuum (1 Torr, 2 h) gave the desired 3-tosyl-3,3a,6,6a-tetrahydro-2*H*-cyclopenta[*d*]oxazol-2-one (**19**) as a slightly yellow oil that solidified on standing.[26c,33] Enantiomeric excess of **19** was determined by HPLC.

Rhodium-Catalyzed Asymmetric Hydrogenation of Dimethyl Itaconate, Methyl (*Z*)-2-Acetamido-3-phenylacrylate, Methyl (*Z*)-2-Acetamido-3-(4-fluorophenyl)acrylate or Methyl (*Z*)-2-Acetamido-3-(naphthalen-2-yl)acrylate: A solution of $[Rh(Cod)_2]BF_4$ (0.001 g, 0.0025 mmol) and the appropriate ligand (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 1.5 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 (**21a**), methyl 2-acetamido-3-phenylpropanoate (**21b**), methyl 2-acetamido-3-(4-fluorophenyl)propanoate (**21c**) or methyl 2-acetamido-3-(naphthalen-2-yl)propanoate (**21d**).[34] 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 chiral HPLC analysis.

Crystallographic data for **L2**, **L5**, **L1c** and **L1a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1818463, 1818465, 1818468 and 1818470, respectively. Copies of data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[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, V. V. Chernyshev, *J. Appl. Crystallogr.* **1992**, *25*, 447–451.

[3] a) K. N. Gavrilov, S. V. Zheglov, I. V. Chuchelkin, M. G. Maksimova, I. D. Firsin, A. N. Fitch, V. V. Chernyshev, A. V. Maximychev, A. M. Perepukhov, *Tetrahedron: Asymmetry* **2017**, *28*, 1633–1643; b) K. N. Gavrilov, S. V. Zheglov, V. K. Gavrilov, M. G. Maksimova, V. A. Tafeenko, V. V. Chernyshev, K. P. Birin, I. S. Mikhel, *Tetrahedron* **2017**, *73*, 461–471; c)) K. N. Gavrilov, I. S. Mikhel, I. V. Chuchelkin, S. V. Zheglov, V. K. Gavrilov, K. P. Birin, V. A. Tafeenko, V. V. Chernyshev, N. S. Goulioukina, I. P. Beletskaya, *Chemistry Select* **2016**, *1*, 4173–4186.

[4] G. M. Sheldrick, *Acta Cryst.* **2015**, *C71*, 3–8.

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

[6] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.

[7] G. Altenhoff, R. Goddard, C. W. Lehmann, F. Glorius, *J. Am. Chem. Soc.* **2004,** *126*, 15195–15201.

[8] K. N. Gavrilov, A. I. Polosukhin, O. G. Bondarev, S. E. Lyubimov, K. A. Lyssenko, P. V. Petrovskii, V. A. Davankov, *J. Mol. Catal. A: Chemical* **2003**, *196*, 39–53.

[9] J.-N. Levy, C. M. Latham, L. Roisin, N. Kandziora, P. D. Fruscia, A. J. P. White, S. Woodward, M. J. Fuchter, *Org. Biomol. Chem*. **2012**, *10*, 512–515.

[10] N. Toselli, R. Fortrie, D. Martin, G. Buono, *Tetrahedron: Asymmetry* **2010**, *21*, 1238–1245.

[11] 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.

[12] M. R. Marre, M. Sanchez, J. F. Brazier, R. Wolf, J. Bellan, *Can. J. Chem*. **1982**, *60*, 456–468.

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

[14] F. K. Kalman, M. Woods, P. Caravan, P. Jurek, M. Spiller, G. Tircso, R. Kiraly, E. Brucher, A. D. Sherry, *Inorg. Chem*. **2007**, *46*, 5260–5270.

[15] J.-P. Genet, S. Juge, S. Achi, S. Mallart, J. R. Montes, G. Levif, *Tetrahedron* **1988**, *44*, 5263–5275.

[16] T. Ukai, H. Kawazura, Y. Ishii, J. J. Bonnet, J. A. Ibers, J*. Organomet. Chem*. **1974**, *65*, 253–266.

[17] D. Drew, J. R. Doyle, *Inorg. Synth*. **1972**, *13*, 47–55.

[18] S. Gladiali, L. Pinna, *Tetrahedron: Asymmetry* **1991**, *2*, 623–632.

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

[20] N. W. Boaz, S. E. Large, J. A. Ponasik, J. M. K. Moore, T. Barnette, W. D. Nottingham, *Org. Proc. Res. Dev*. **2005**, *9*, 472–478.

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

[22] a) X. Zhao, D. Liu, F. Xie, Y. Liu, W. Zhang, *Org. Biomol. Chem*. **2011**, *9*, 1871–1875; b) X. Zhao, D. Liu, F. Xie, W. Zhang, *Tetrahedron* **2009**, *65*, 512–517.

[23] 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.

[24] Y. Uozumi, H. Tanaka, K. Shibatomi, *Org. Lett*. **2004**, *6*, 281–283.

[25] K. N. Gavrilov, S. V. Zheglov, V. K. Gavrilov, M. G. Maksimova, I. A. Zamilatskov, *Russ. Chem. Bull., Int. Ed.* **2015**, *64*, 967–969.

[26] a) N. Buschmann, A. Rückert, S. Blechert, *J. Org. Chem*. **2002**, *67*, 4325–4329; b) B. M. Trost, D. E. Patterson, *J. Org. Chem*. **1998**, *63*, 1339–1341; c) V. Benessere, A. De Roma, R. Del Litto, M. Lega, F. Ruffo, *Eur. J. Org. Chem*. **2011**, 5779−5782; d) M. Lega, J. Margalef, F. Ruffo, O. Pàmies, M. Dieguez, *Tetrahedron: Asymmetry* **2013**, *24*, 995−1000.

[27] K. N. Gavrilov, S. V. Zheglov, E. A. Rastorguev, N. N. Groshkin, M. G. Maksimova, E. B. Benetsky, V. A. Davankov, M. T. Reetz, *Adv. Synth. Catal*. **2010**, *352*, 2599–2610.

[28] K. N. Gavrilov, A. A. Shiryaev, I. V. Chuchelkin, S. V. Zheglov, E. A. Rastorguev, V. A. Davankov, A. Börner, *Tetrahedron: Asymmetry*, **2012**, *23*, 1052−1057.

[29] a) D. Seebach, E. Devaquet, A. Ernst, M. Hayakawa, F. N. M. Kuhnle, W. B. Schweizer, B. Weber, *Helv. Chim. Acta* **1995**, *78*, 1636−1650; b) J. A. Wolfe, S. R. Hitchcock, Tetrahedron: Asymmetry **2010**, *21*, 2690−2695.

[30] 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.

[31] 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.

[32] H. Wu, F. Xie, Y. Wang, X. Zhao, D. Liu, W. Zhang, *Org. Biomol. Chem*. **2015**, *13*, 4248−4254.

[33] D. Zhao, Z. Wang, K. Ding, *Synlett* **2005**, 2067–2071.

[34] 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.

POWDER X-RAY AND SINGLE-CRYSTAL X-RAY STRUCTURE DETERMINATIONS

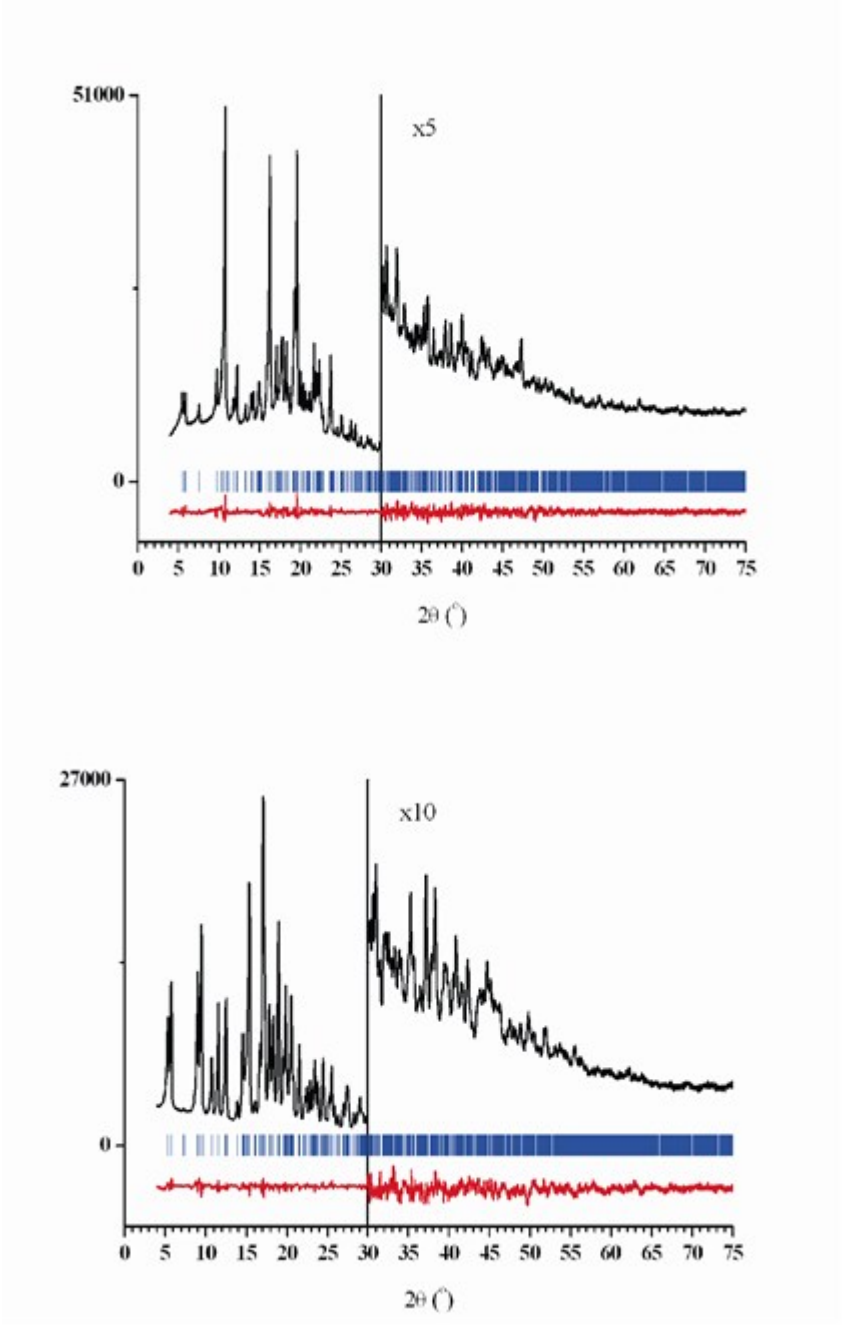


Figure S1. The final Rietveld plots for **L1a** (top) and **L1c** (bottom). The experimental and difference (experimental minus calculated) diffraction profiles are shown as the black and red lines, respectively. The vertical blue bars correspond to the calculated positions of the Bragg peaks.

Table S1. Crystal data for **L1a** and **L1c**.

	L1a	**L1c**
empirical formula	$C_{32}H_{46}N_6O_4P_2$	$C_{36}H_{54}N_6O_4P_2$
M_r	640.69	696.79
crystal system	Orthorhombic	Orthorhombic
space group	*P2₁2₁2*	*P2₁2₁2₁*
diffractometer	Huber G670	EMPYREAN
wavelength, Å	1.54059	1.5418
unit cell dimensions		
a, Å	32.0633(18)	30.7745(19)
b, Å	17.0210(13)	19.6066(15)
c, Å	6.3381(7)	6.2335(7)
volume, Å^3	3459.0(5)	3761.2(6)
Z	4	4
D_x (Mg m^{-3})	1.230	1.231
μ, mm^{-1}	1.494	1.413
$2\theta_{min}$ - $2\theta_{max}$, $\Delta 2\theta$ (°)	4.00 – 75.00, 0.01	4.006 – 75.015, 0.017
no. params/restraints	327/402	225/157
R_p, R_{wp}, R_{exp}	0.0175, 0.0219, 0.0135	0.0264, 0.0345, 0.0211

Table S2. Crystal data for **L2** and **L5**.

	L2	**L5**
empirical formula	$C_{42}H_{46}N_6O_4P_2$	$C_{42}H_{54}N_6O_4P_2$
M_r	760.79	764.82
crystal size, mm^3	0.26 x 0.17 x 0.16	0.08 x 0.06 x 0.04
crystal form, color	prism, colorless	irregular, colorless
crystal system	Orthorhombic	Monoclinic
space group	$P2_12_12_1$	$P2_1$
unit cell dimensions:		
a, Å	10.0150(4)	5.3423(7)
b, Å	15.4660(7)	23.445(5)
c, Å	25.1897(8)	16.708(3)
β, º	90	95.088(2)
volume, $Å^3$	3901.7(3)	2084.4(6)
Z	4	2
μ, mm^{-1}	1.417	1.326
Flack parameter	-0.04(4)	0.29(19)
no. reflections	7318/3898	4579/2895
collected/independent	[*R(int)* = 0.1358]	[*R(int)* = 0.13770]
no. parameters	487	174
GOF	0.840	0.742
final *R* indices [$I>2\sigma(I)$]	*R* = 0.0627, *wR* = 0.1489	*R* = 0.1181, *wR* = 0.3797

NMR SIGNAL ASSIGNMENT

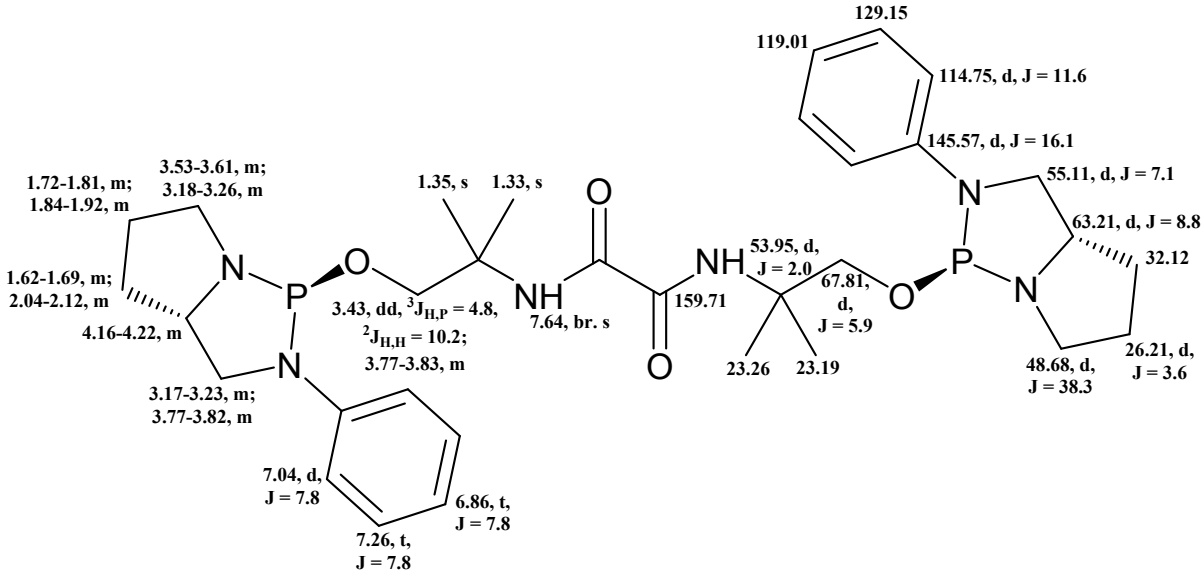


Figure S2. NMR Signal Assignment for **L1a**.

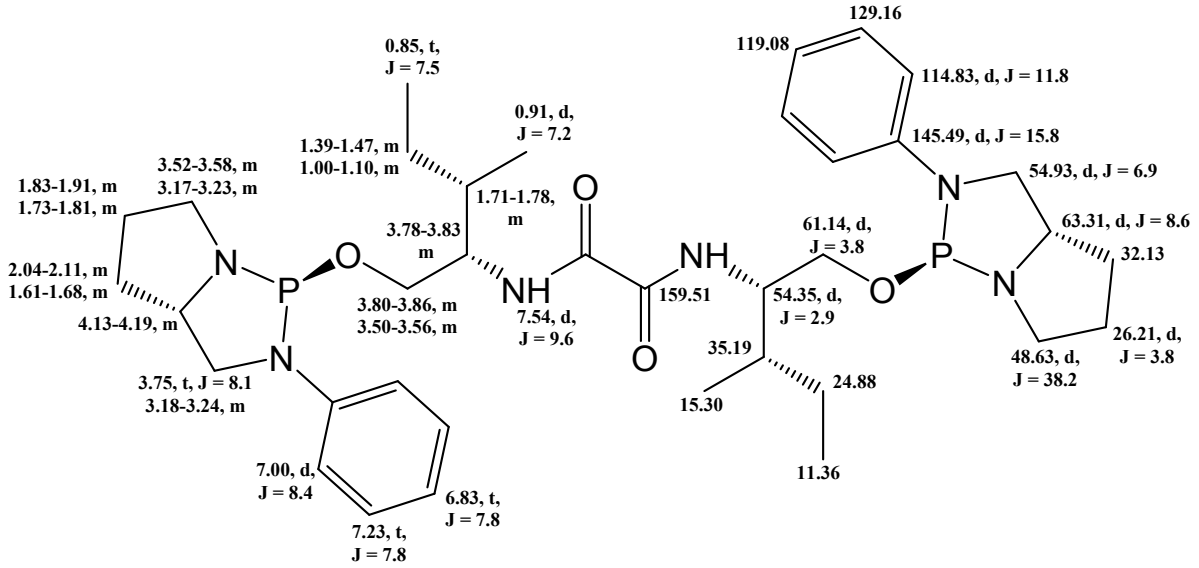


Figure S3. NMR Signal Assignment for **L1b**.

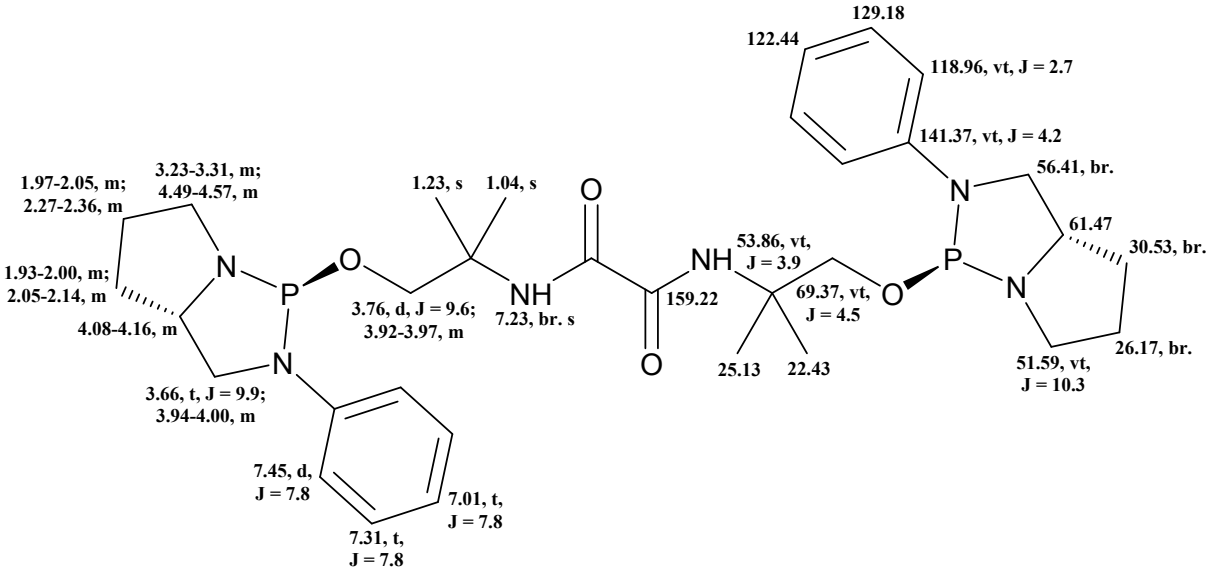


Figure S4. Full assignment of all ^{13}C and ^{1}H resonances for complex **6**.

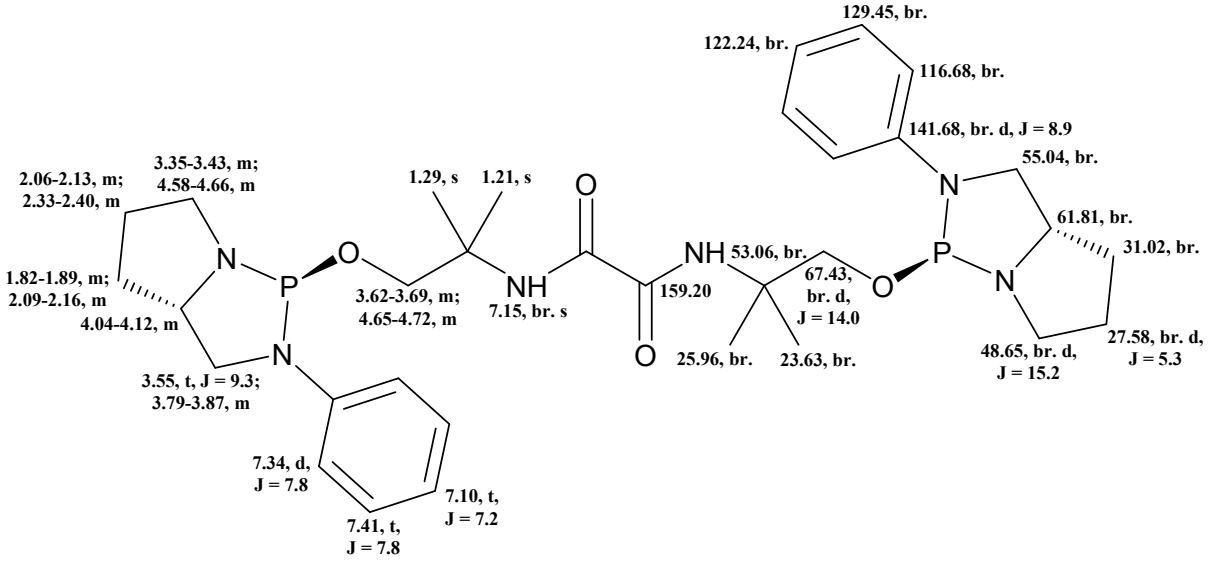
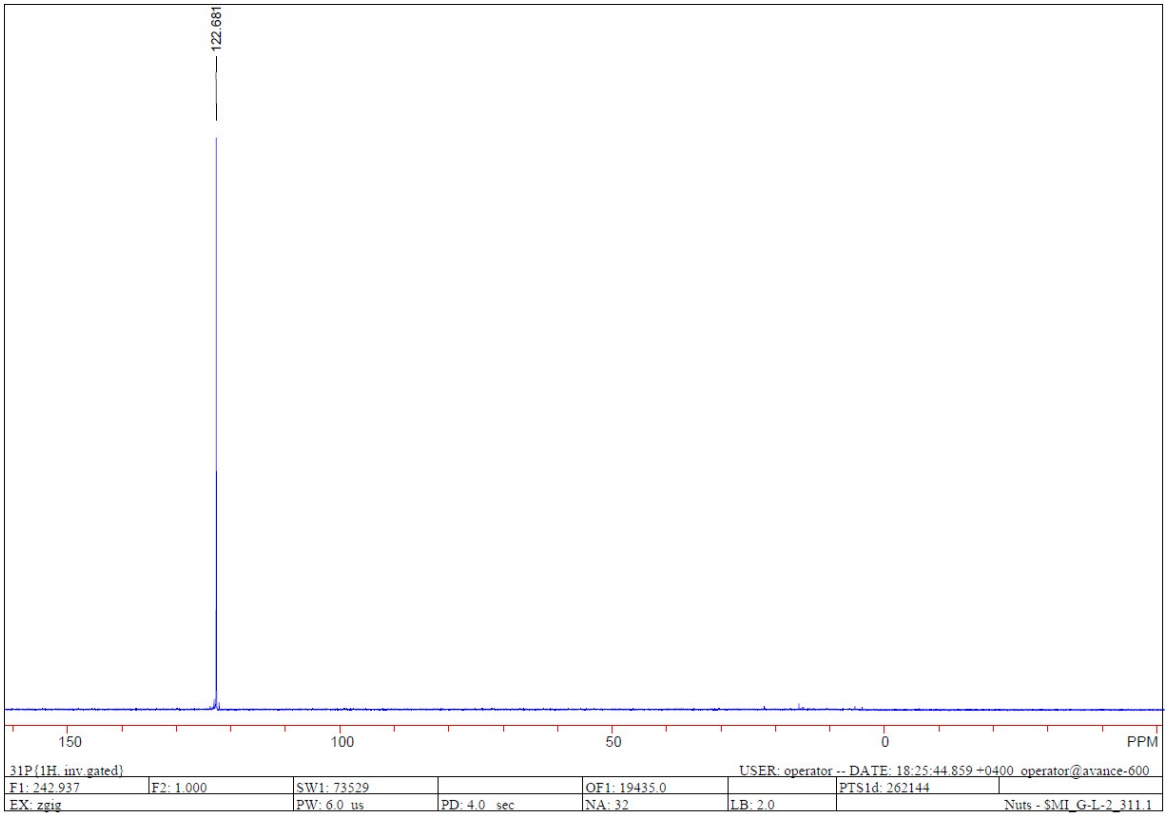


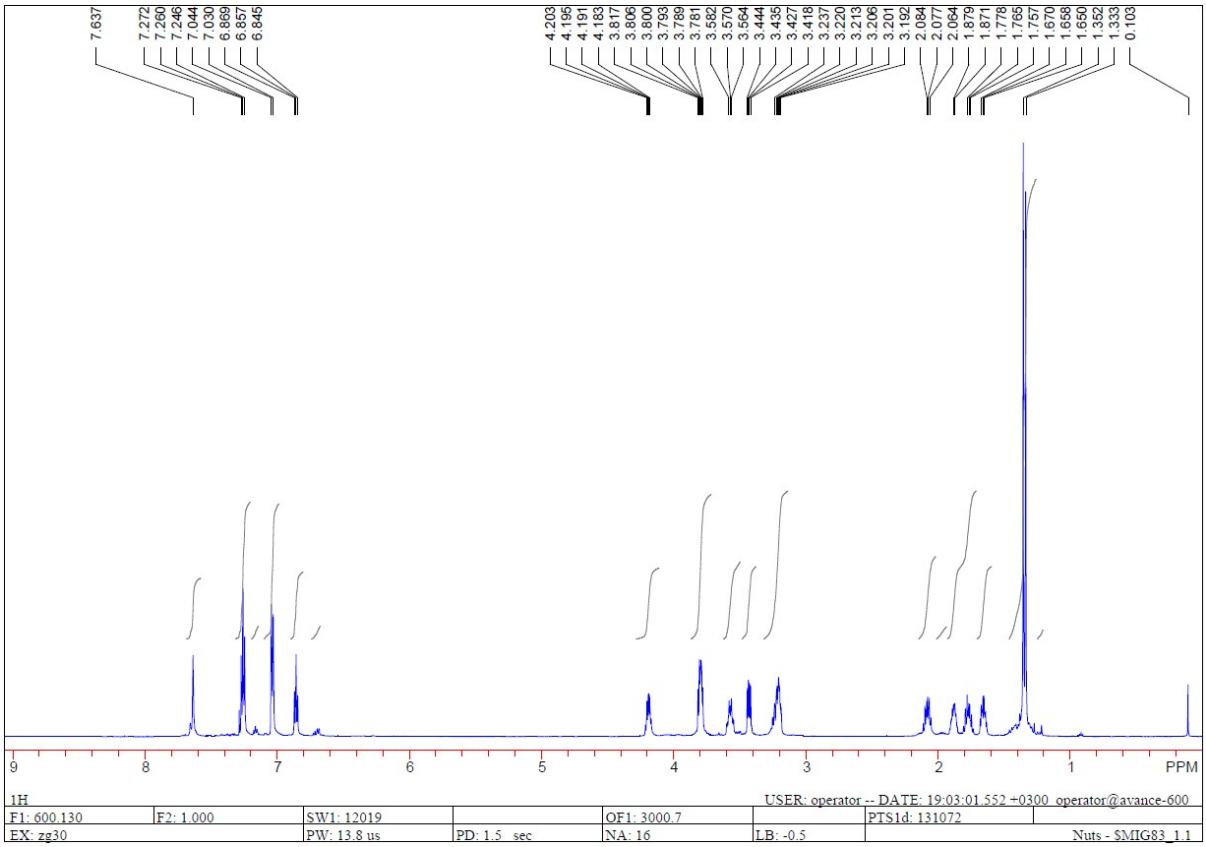
Figure S5. Full assignment of all ^{13}C and ^{1}H resonances for complex **7**.

NMR SPECTRA OF NEW COMPOUNDS

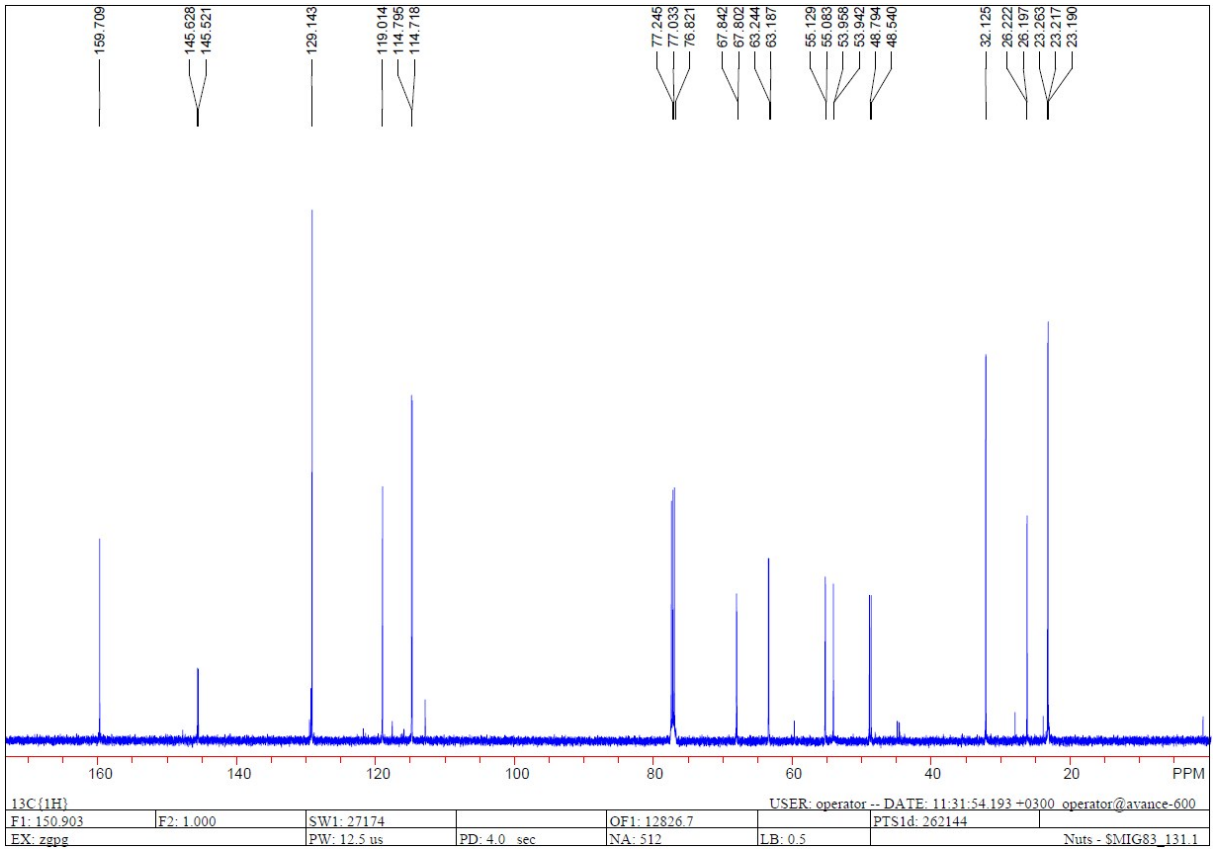
L1a, $^{31}P\{^{1}H\}$



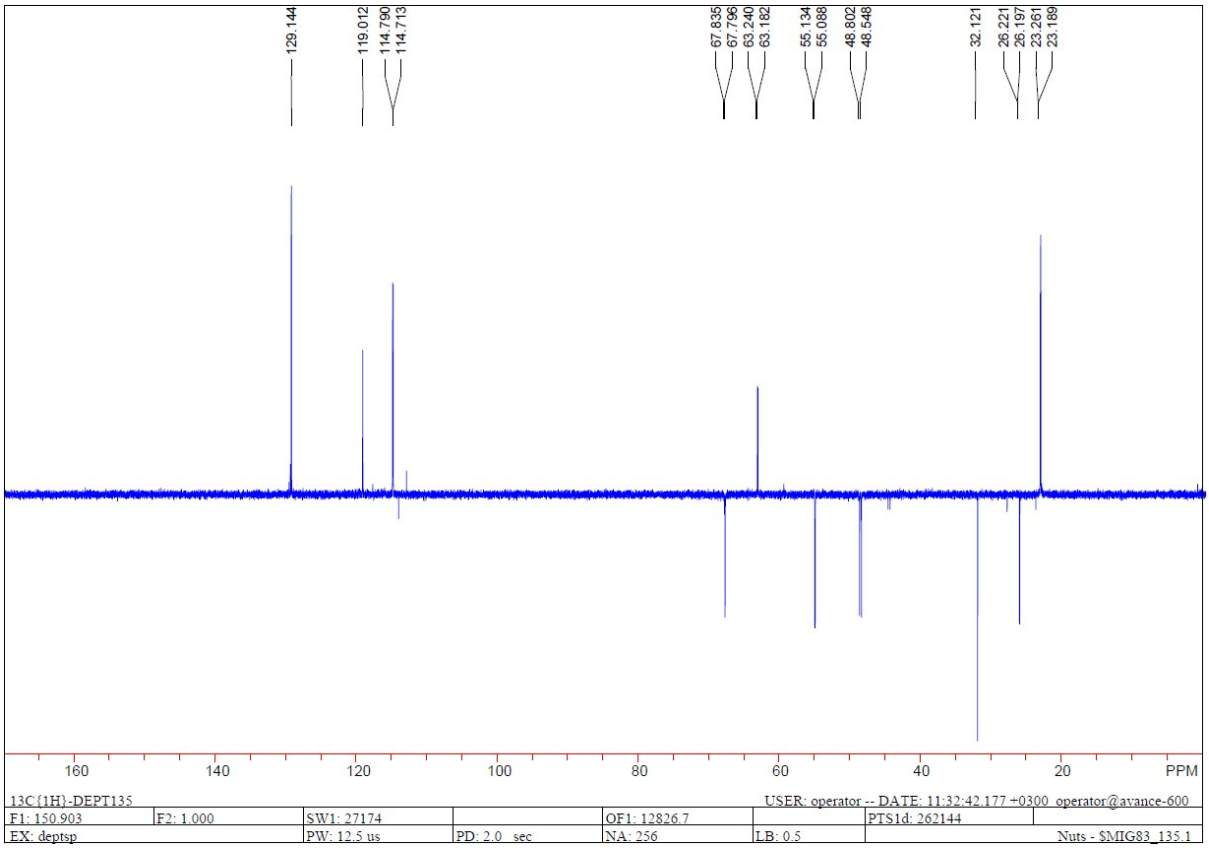
L1a, ^{1}H



L1a, $^{13}C\{^{1}H\}$



L1a, ^{13}C DEPT



L1a, ^{1}H-^{1}H COSY

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Spectrum Type	COSY	*Sweep Width (Hz)*	(4794.23, 4798.38)	*Temperature (degree C)*	26.900	*Title*	1H,1H-COSY

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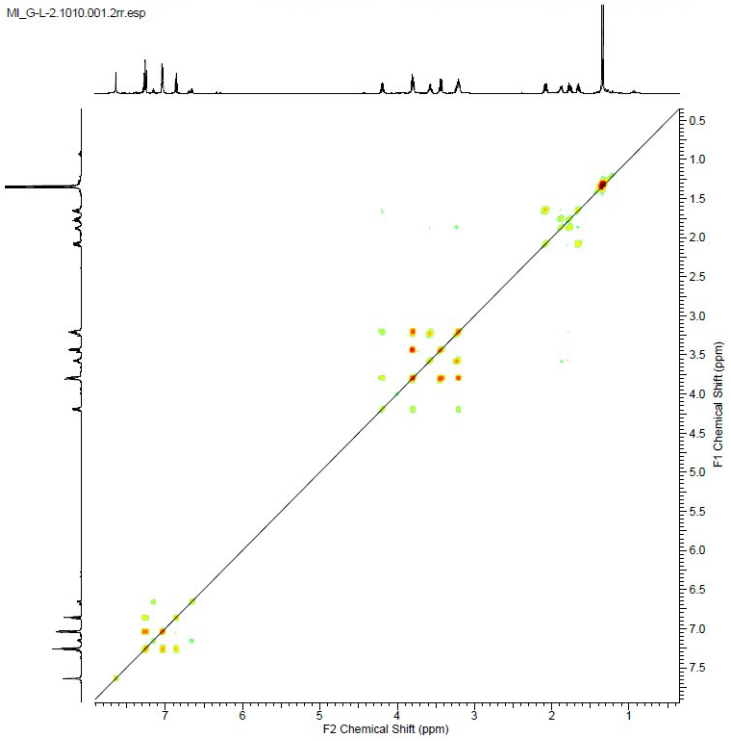

L1a, ^{1}H-^{1}H ROESY

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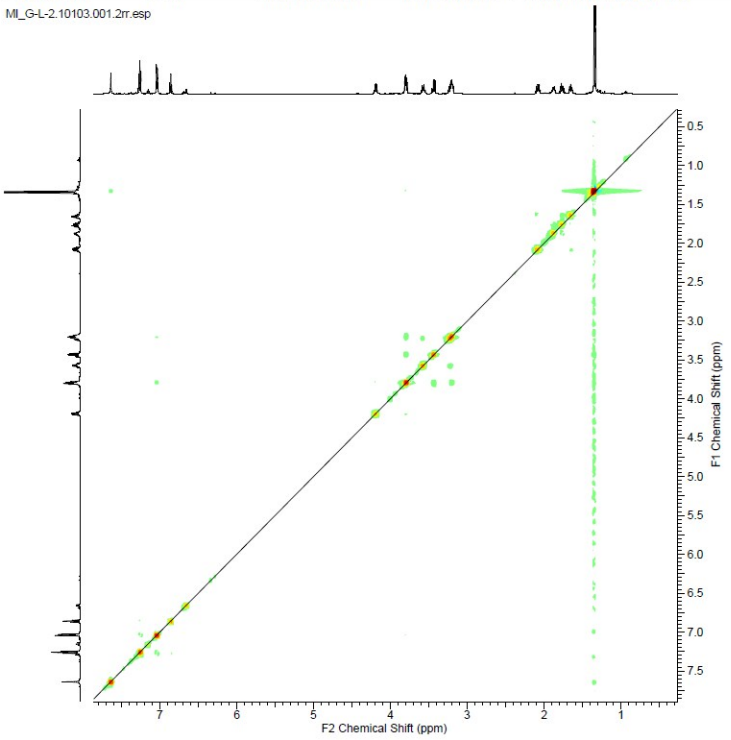

L1a, ^{1}H-^{13}C HSQC

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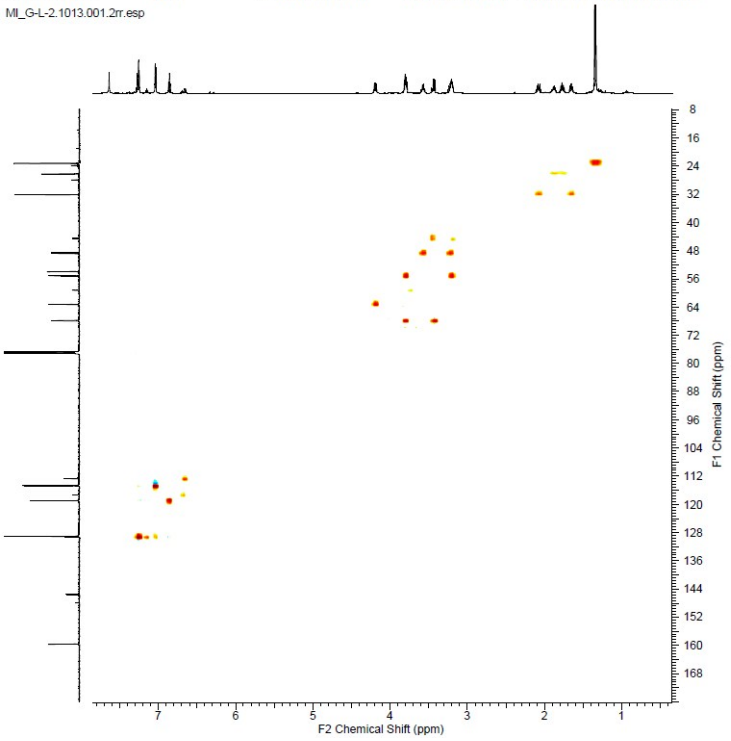

L1a, ^{1}H-^{13}C HMBC

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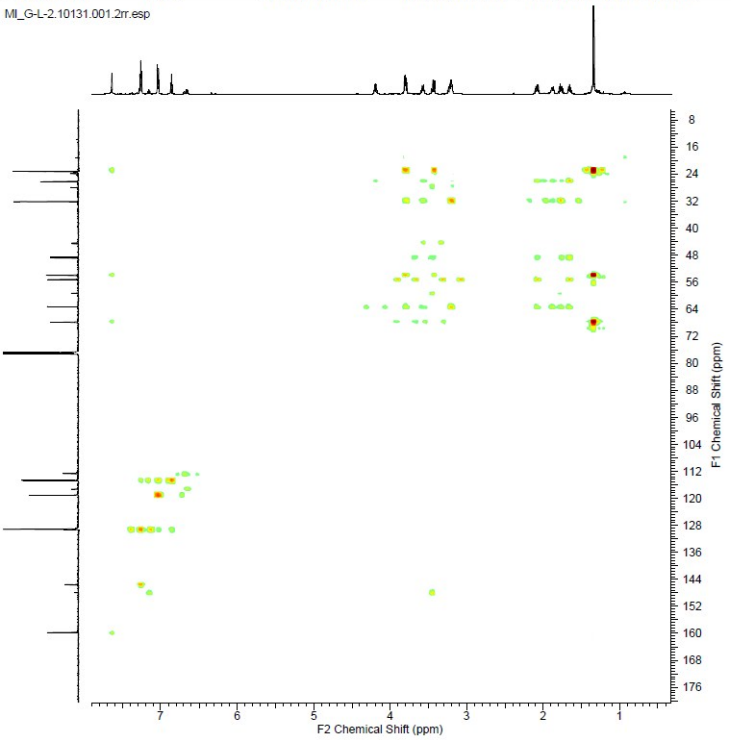

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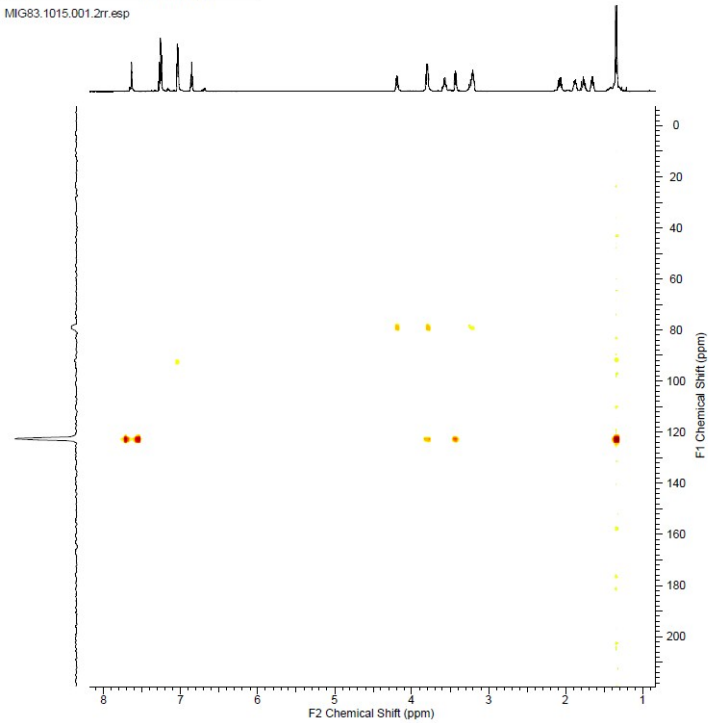
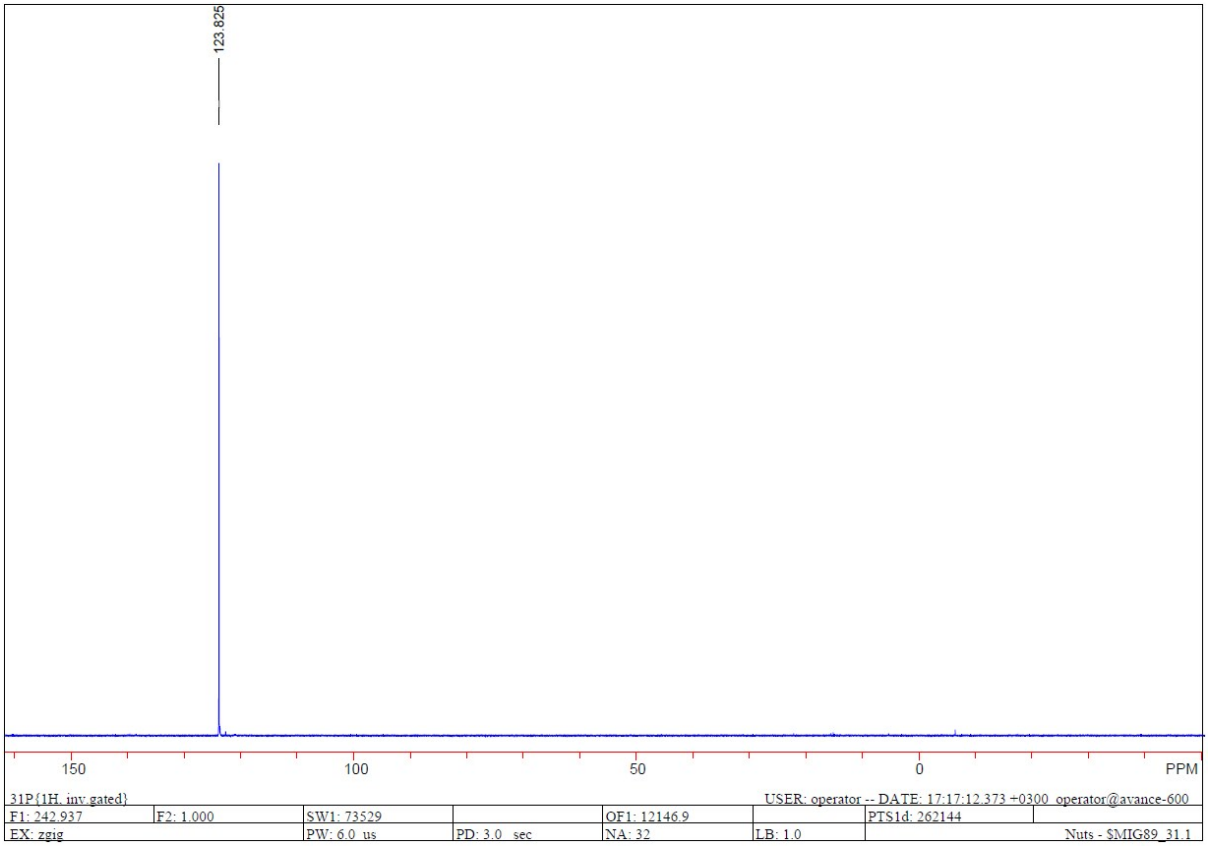
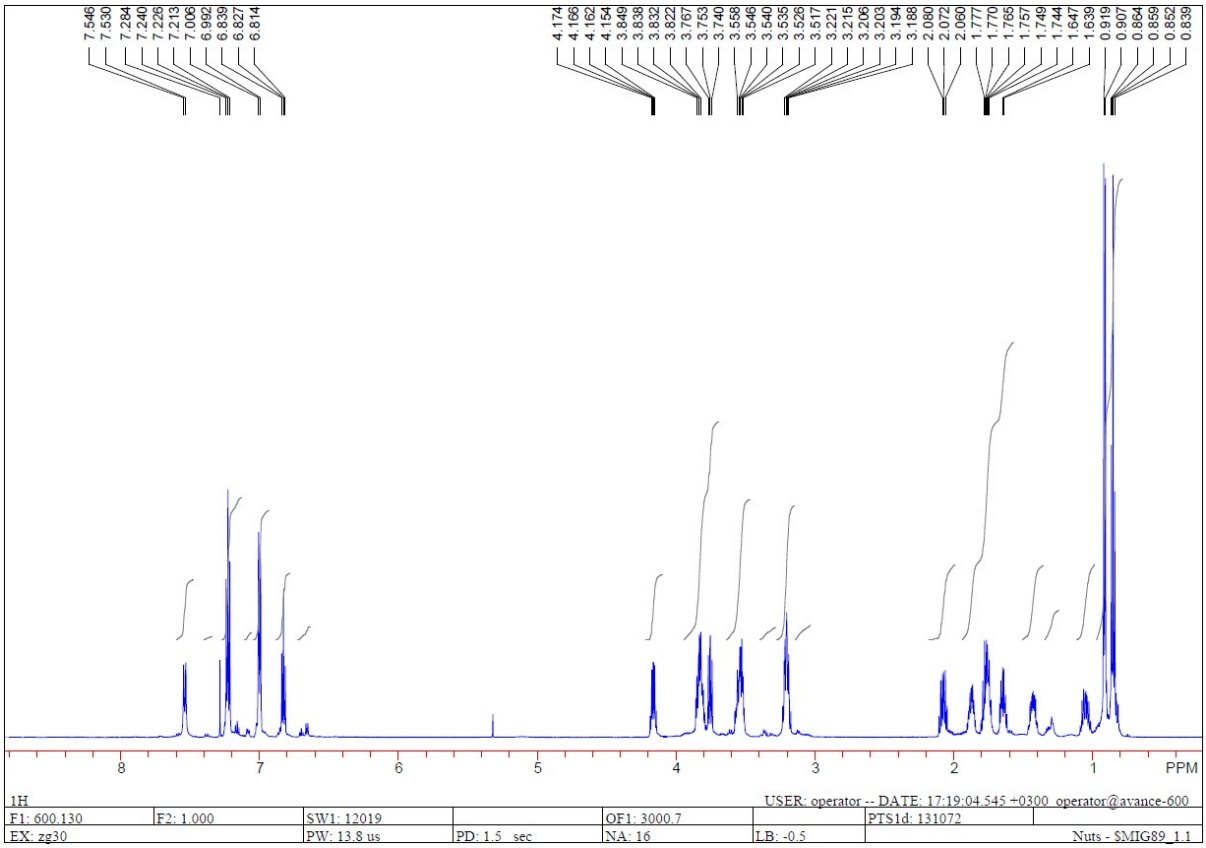


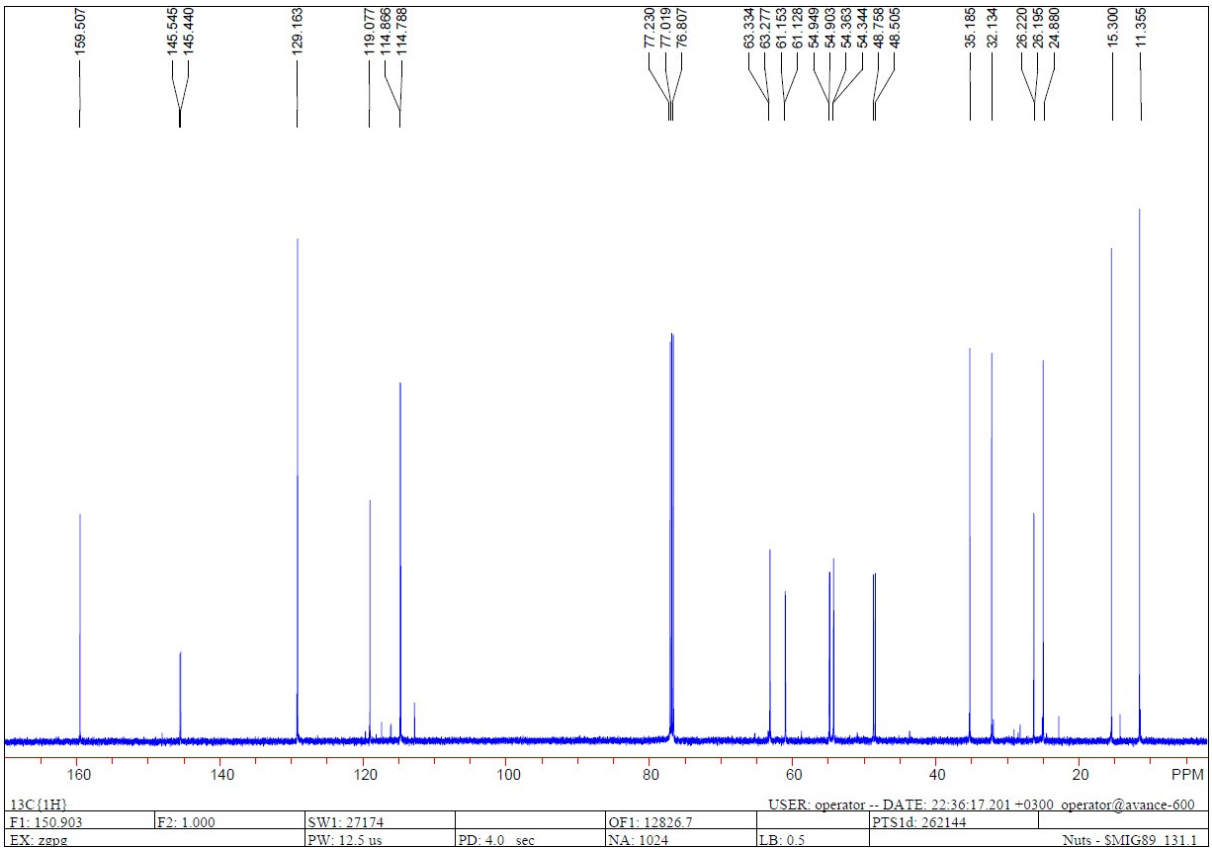
L1b, $^{31}P\{^{1}H\}$



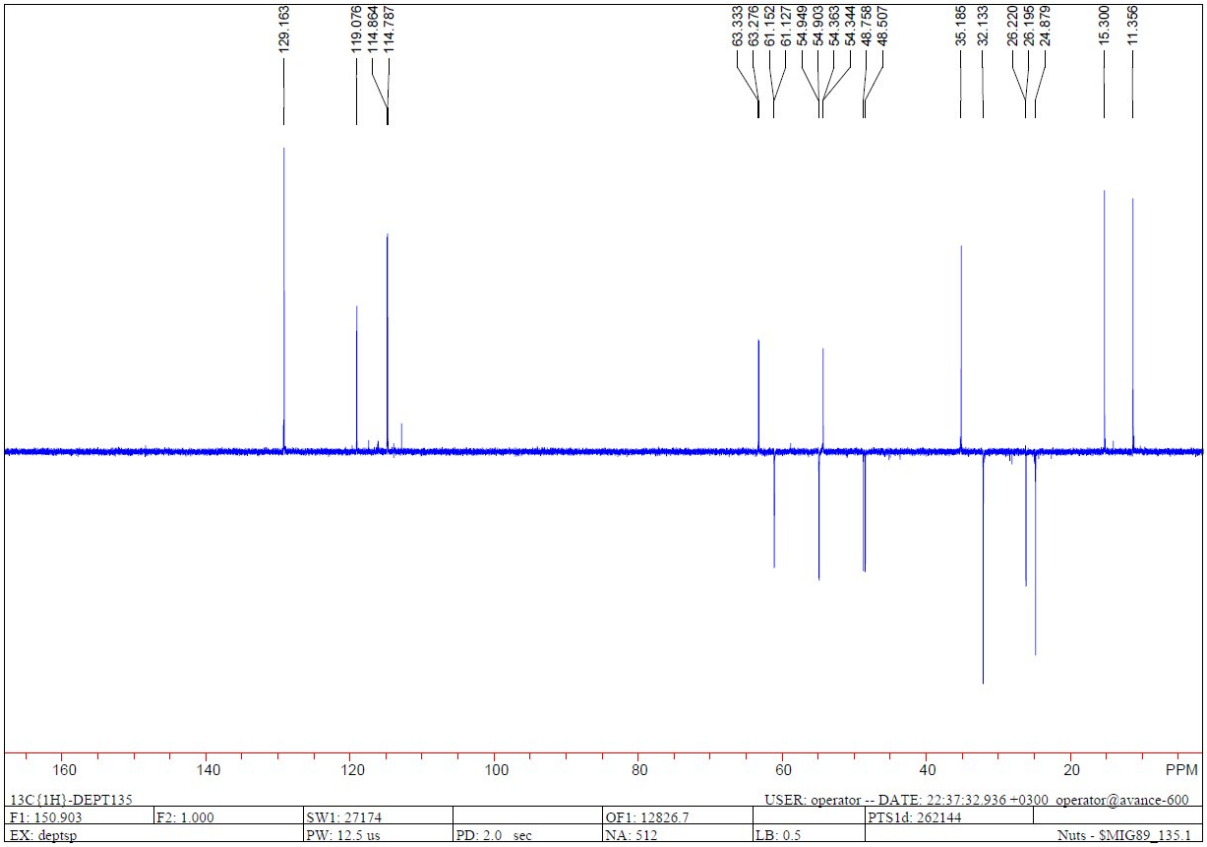
L1b, ^{1}H



L1b, $^{13}C\{^{1}H\}$

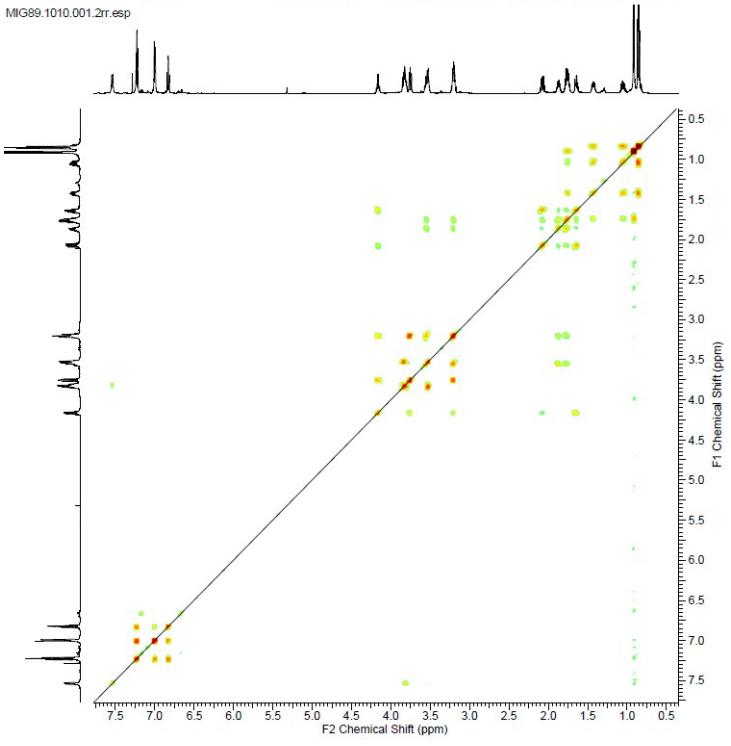


L1b, ^{13}C DEPT



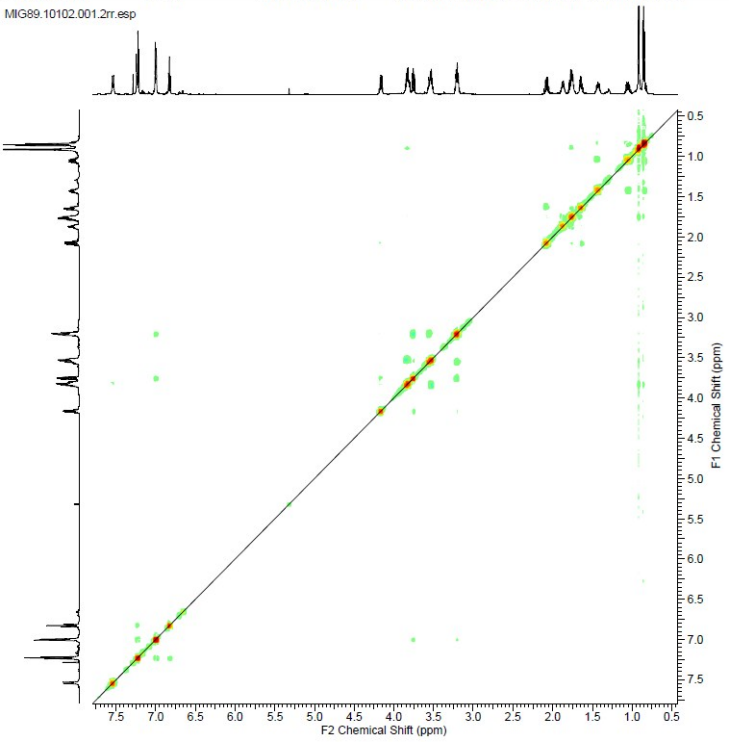
L1b, ^{1}H-^{1}H COSY

Acquisition Time (sec)	(0.4271, 0.4264)	*Comment*	5 mm PABBO BB-1H/D Z-GRD Z856701/0030			*Date*	17 May 2017 22:38:10
File Name	C:\Users\MIG\Documents\NMR_FILES_IPCE\MIG89\1010\pdata\1\2rr					*Frequency (MHz)*	(600.13, 600.13)
Nucleus	(1H, 1H)	*Number of Transients*	3	*Origin*	spect	*Original Points Count*	(2048, 2048)
Owner	operator	*Points Count*	(4096, 1024)	*Pulse Sequence*	cosygpqf	*Solvent*	CDCl3
Spectrum Type	COSY	*Sweep Width (Hz)*	(4794.23, 4798.38)	*Temperature (degree C)*	29.754	*Title*	1H,1H-COSY



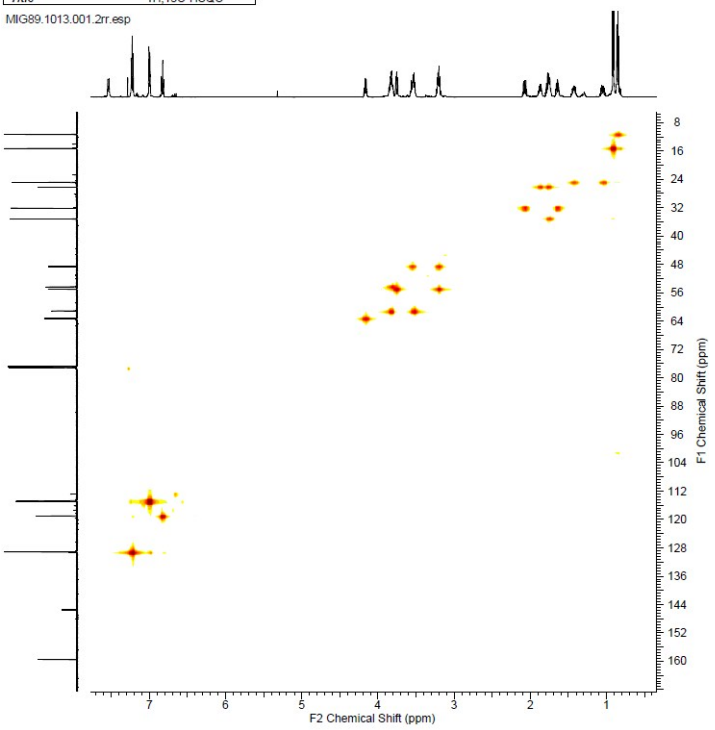
L1b, ^{1}H-^{1}H ROESY

Acquisition Time (sec)	(0.4271, 0.1066)	*Comment*	5 mm PABBO BB-1H/D Z-GRD Z856701/0030			*Date*	18 May 2017 11:17:00
File Name	C:\Users\MIG\Documents\NMR_FILES_IPCE\MIG89\10102\pdata\1\2rr					*Frequency (MHz)*	(600.13, 600.13)
Nucleus	(1H, 1H)	*Number of Transients*	16	*Origin*	spect	*Original Points Count*	(2048, 512)
Owner	operator	*Points Count*	(4096, 1024)	*Pulse Sequence*	roesyph.2	*Solvent*	CDCl3
Spectrum Type	ROESY	*Sweep Width (Hz)*	(4794.23, 4798.38)	*Temperature (degree C)*	30.124	*Title*	1H,1H-ROESY



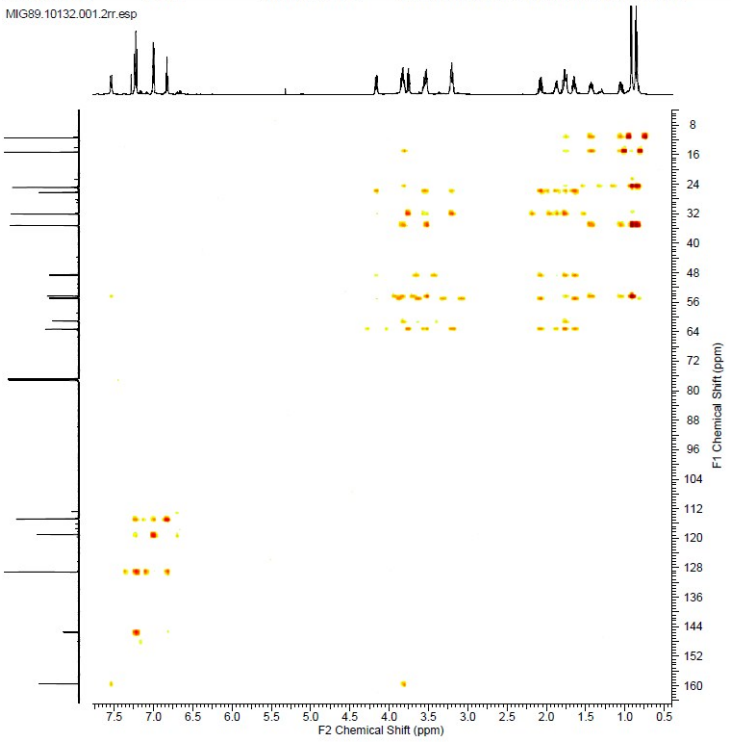
L1b, ^{1}H-^{13}C HSQC

Acquisition Time (sec)	(0.4271, 0.0754)	*Comment*	5 mm PABBO BB-1H/D Z-GRD Z856701/0030			*Date*	18 May 2017 01:10:08
File Name	C:\Users\MIG\Documents\NMR_FILES_IPCE\MIG89\1013\pdata\1\2rr					*Frequency (MHz)*	(600.13, 150.92)
Nucleus	(1H, 13C)	*Number of Transients*	2	*Origin*	spect	*Original Points Count*	(2048, 2048)
Owner	operator	*Points Count*	(2048, 1024)	*Pulse Sequence*	hsqcetgp	*Solvent*	CDCl3
Spectrum Type	HSQC	*Sweep Width (Hz)*	(4793.06, 27147.38)			*Temperature (degree C)*	30.046
Title	1H,13C-HSQC						

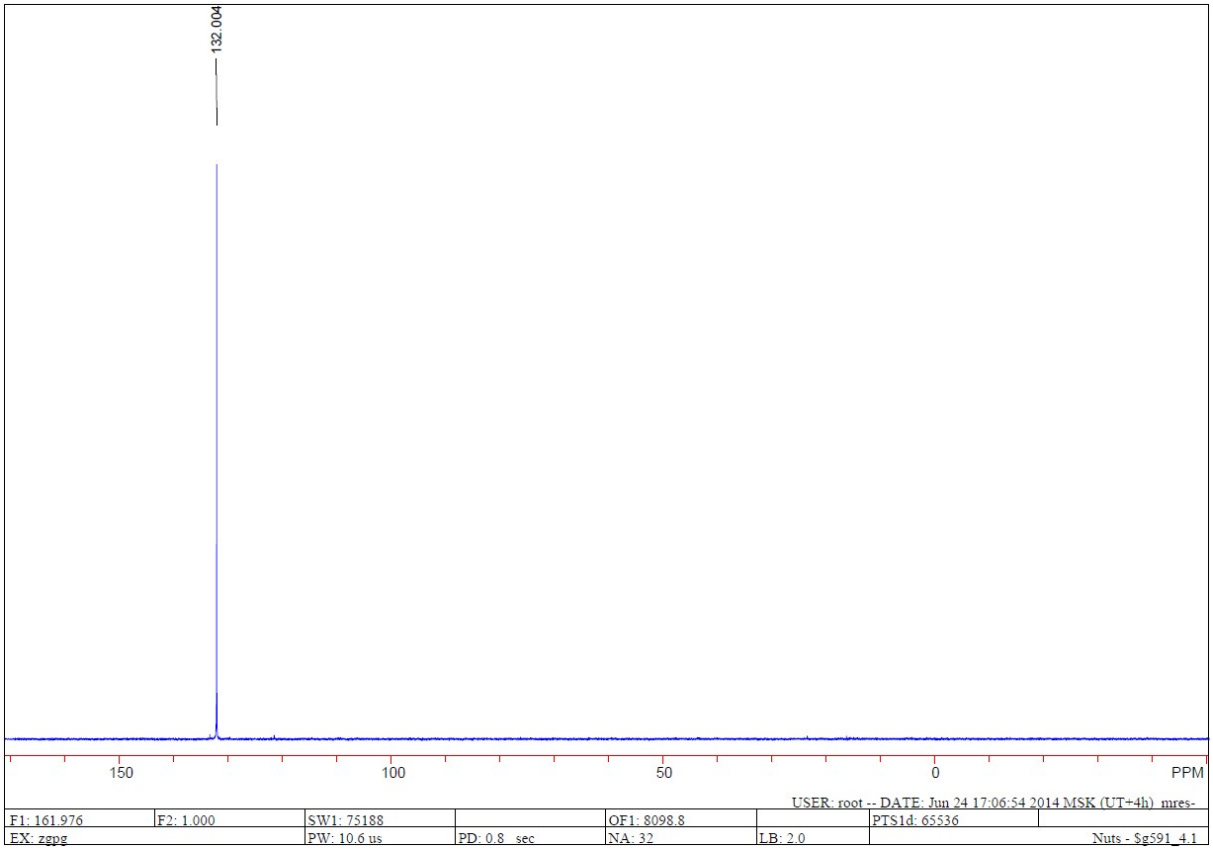


L1b, ^{1}H-^{13}C HMBC

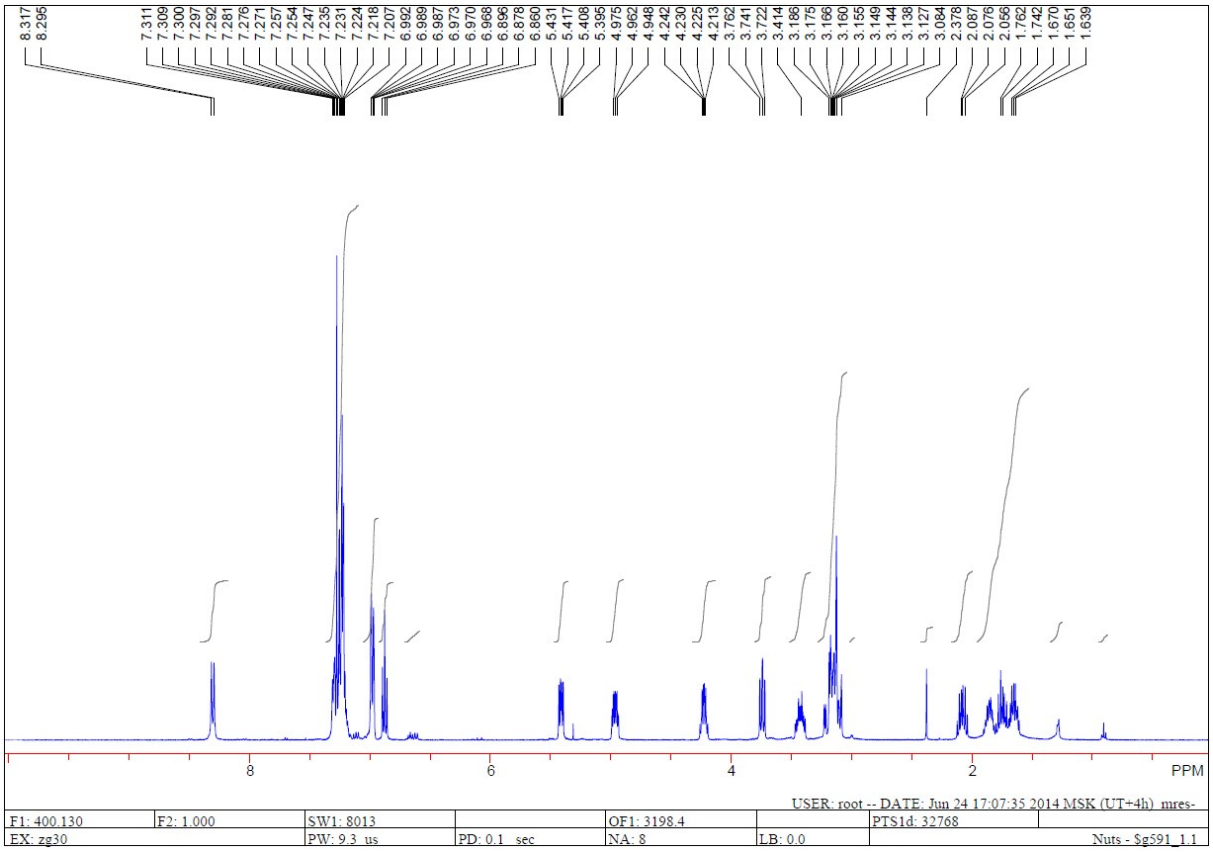
Acquisition Time (sec)	(0.4271, 0.0754)	*Comment*	5 mm PABBO BB-1H/D Z-GRD Z856701/0030			*Date*	18 May 2017 10:38:10
File Name	C:\Users\MIG\Documents\NMR_FILES_IPCE\MIG89\10132\pdata\1\2rr					*Frequency (MHz)*	(600.13, 150.92)
Nucleus	(1H, 13C)	*Number of Transients*	4	*Origin*	spect	*Original Points Count*	(2048, 2048)
Owner	operator	*Points Count*	(2048, 1024)	*Pulse Sequence*	hmbcgpndqf	*Solvent*	CDCl3
Spectrum Type	HMBC	*Sweep Width (Hz)*	(4793.06, 27147.38)	*Temperature (degree C)*	29.817	*Title*	1H,13C-HMBC



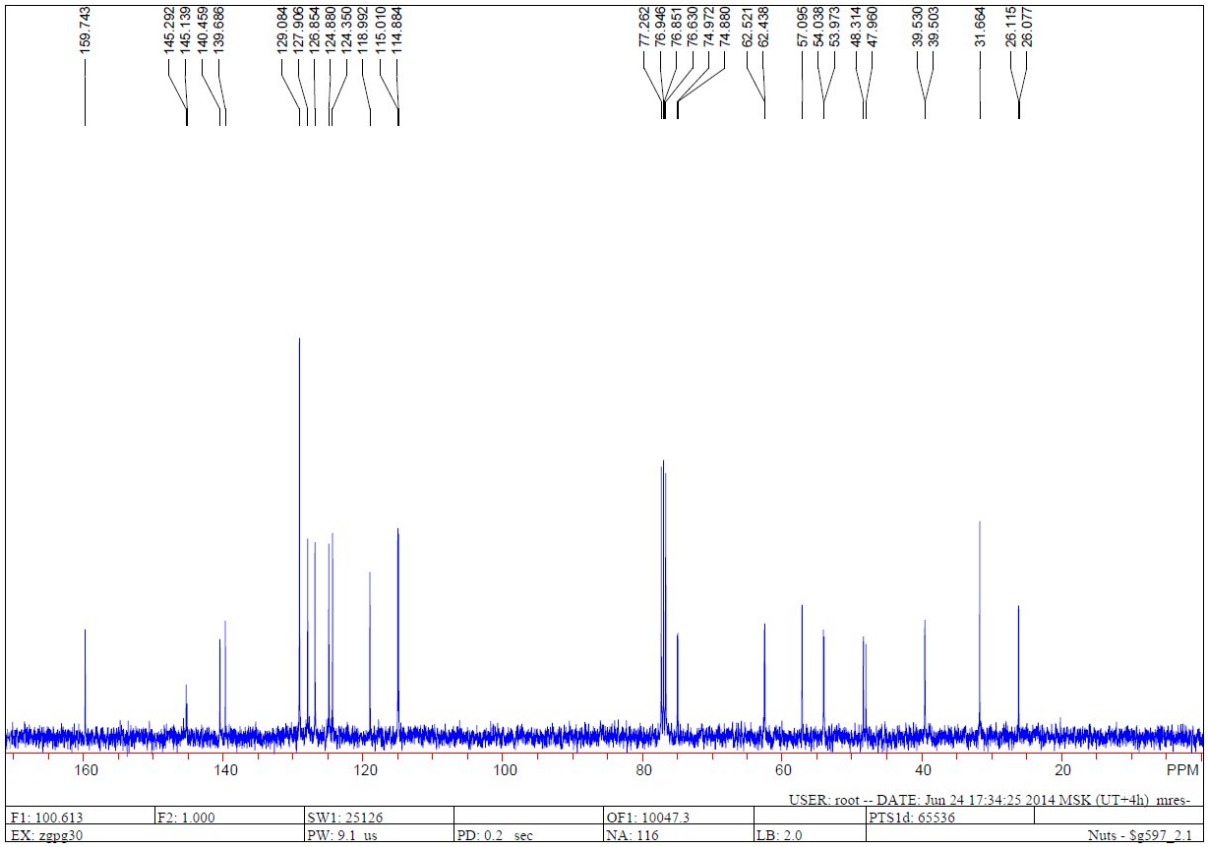
L2, $^{31}P\{^{1}H\}$



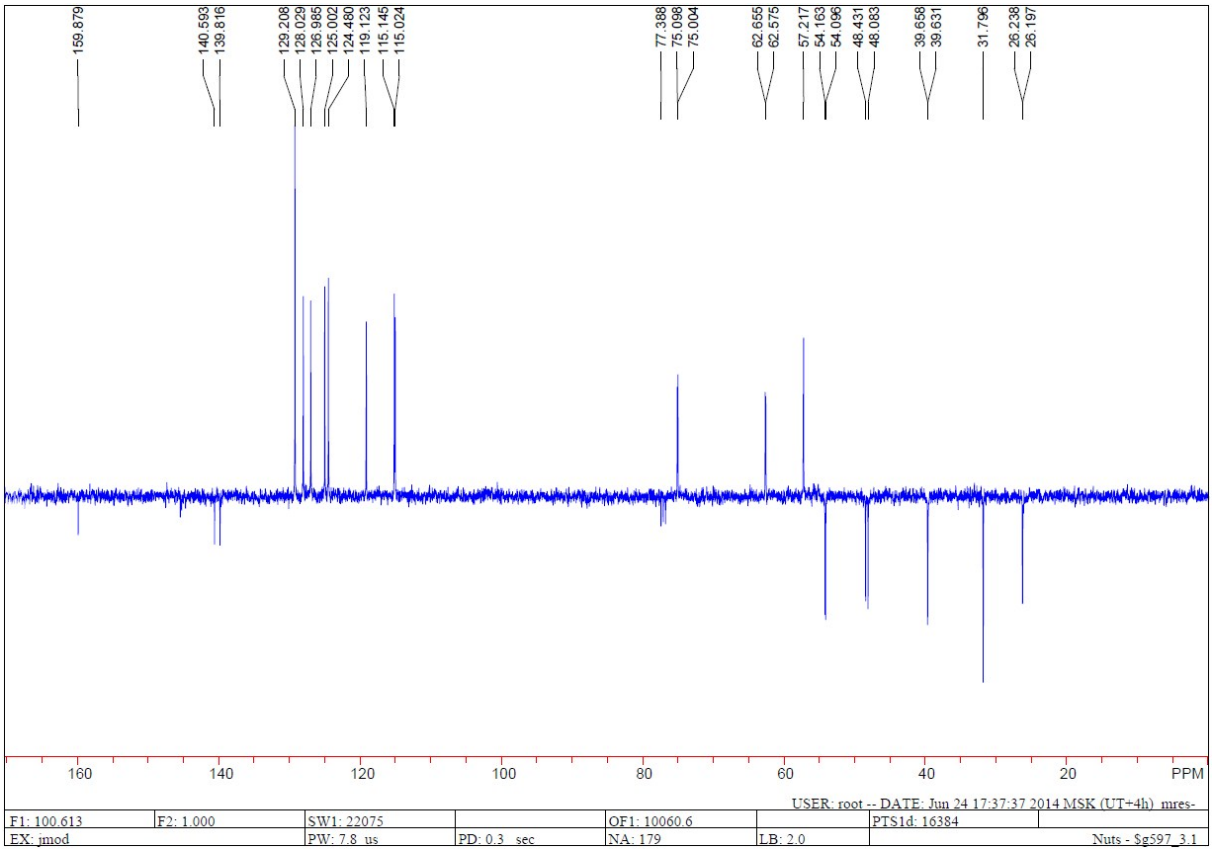
L2, ^{1}H



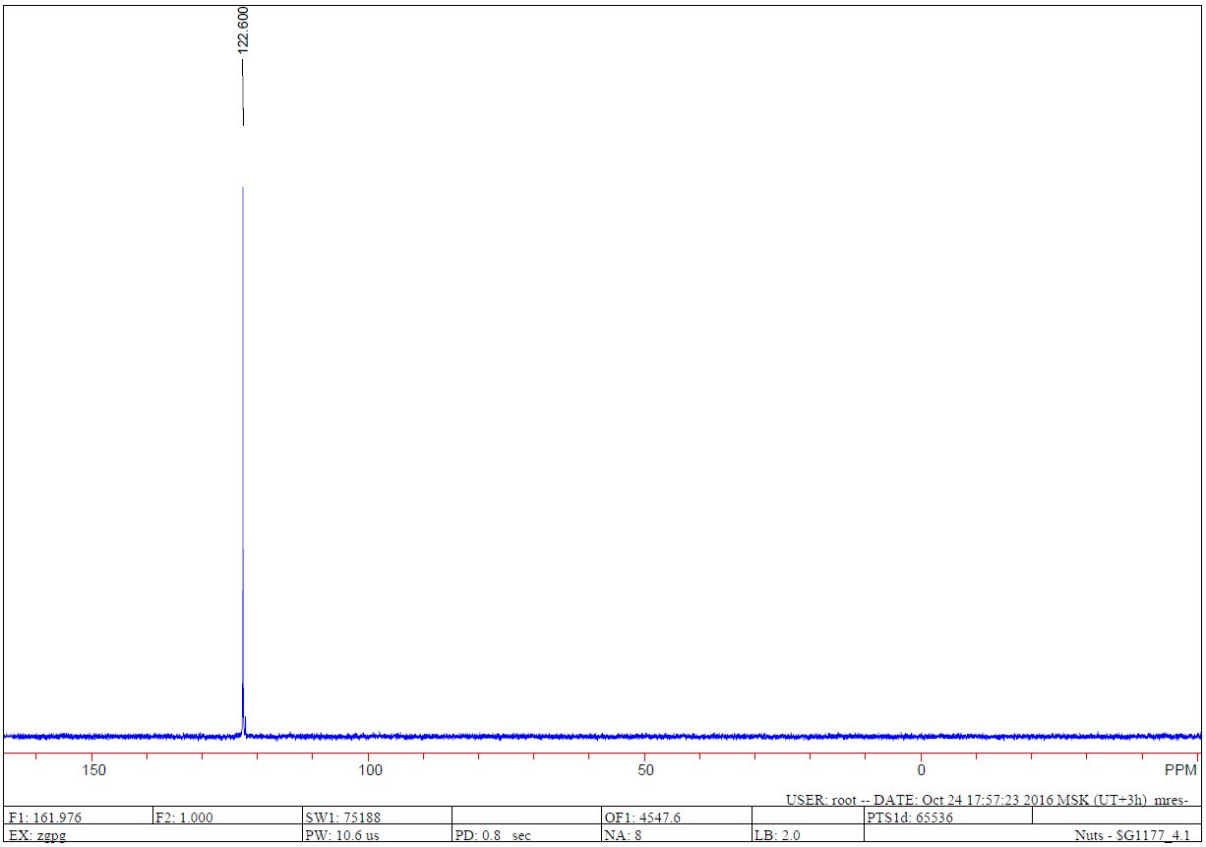
L2, $^{13}C\{^{1}H\}$



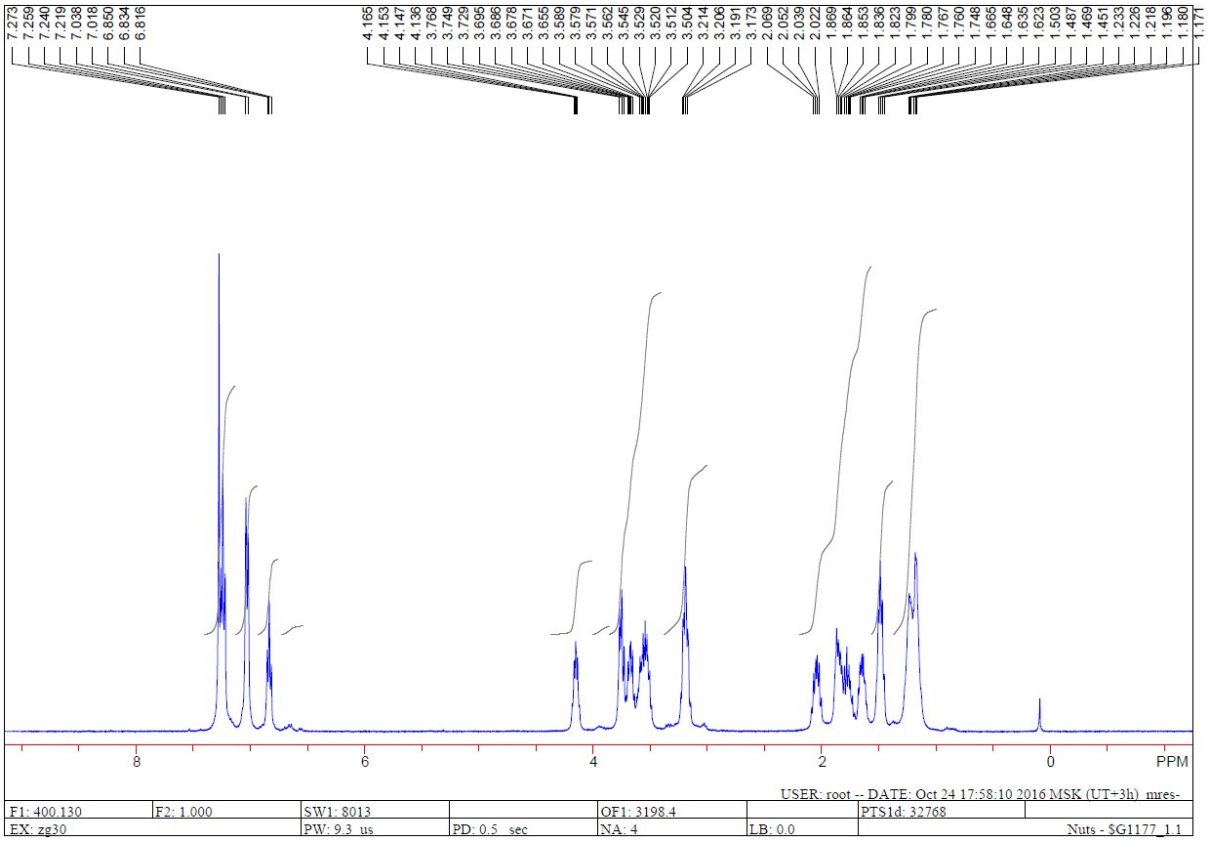
L2, ^{13}C APT



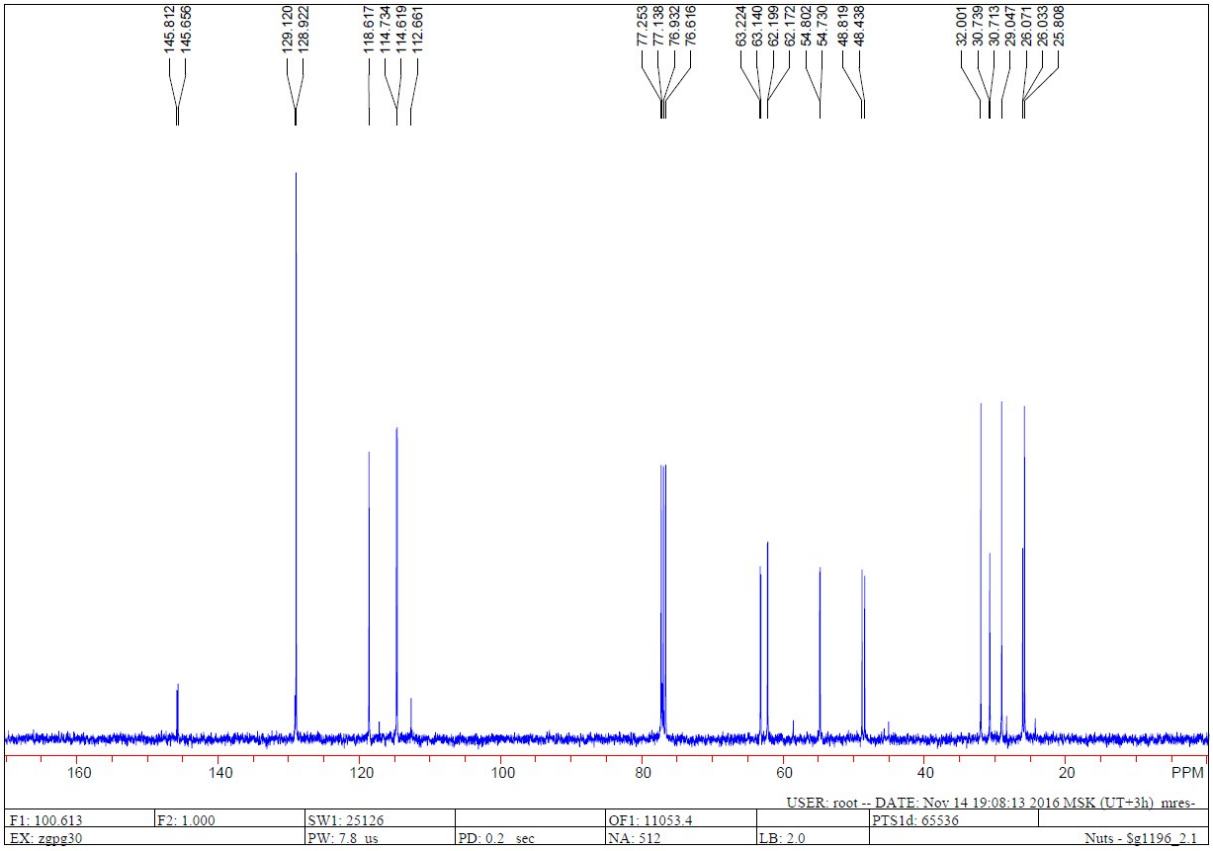
L3, $^{31}P\{^{1}H\}$



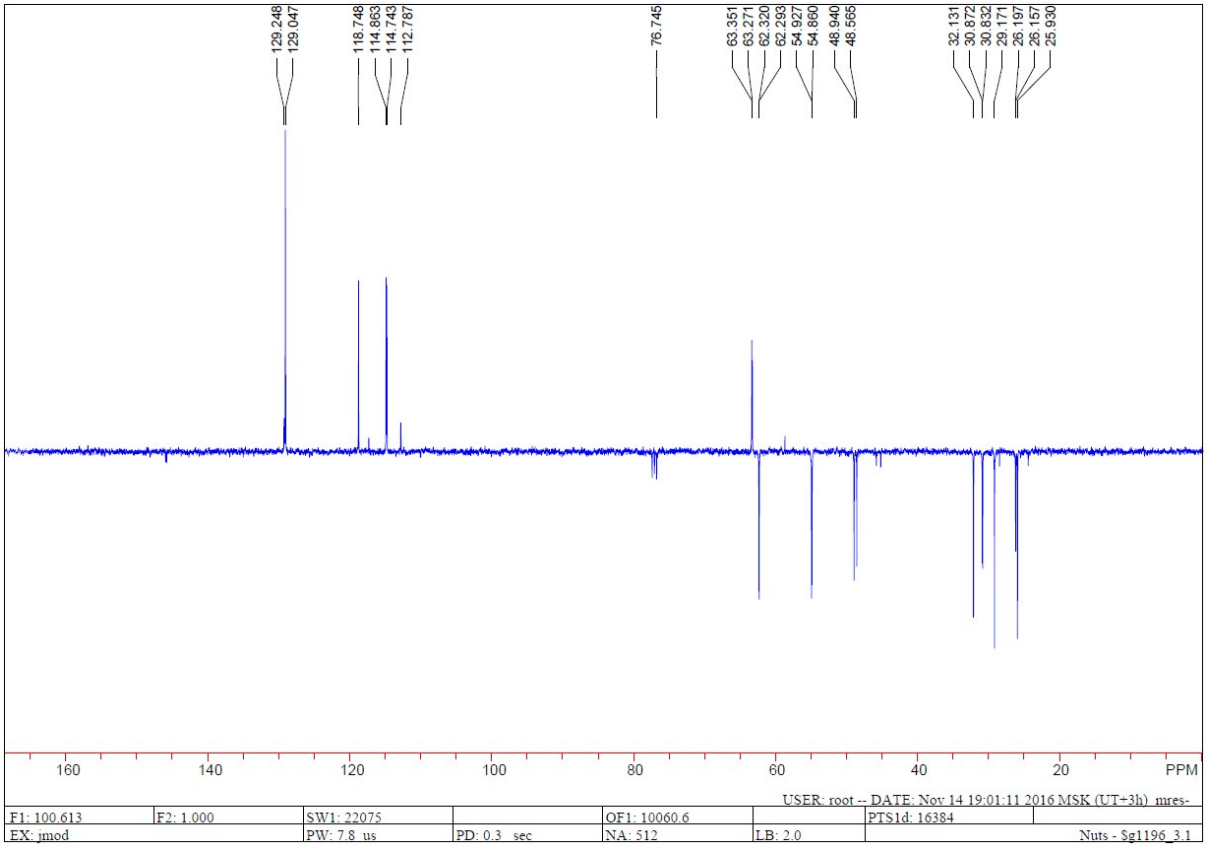
L3, ^{1}H



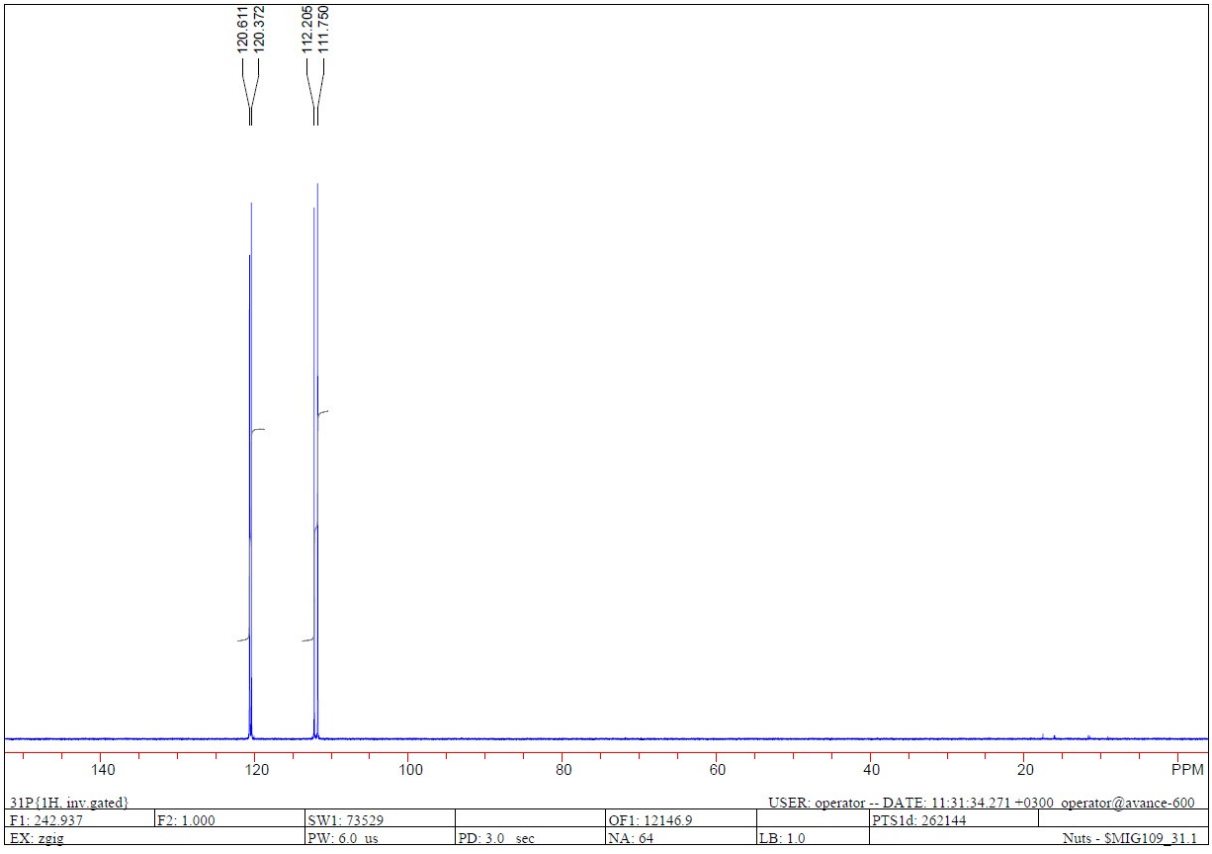
L3, $^{13}C\{^{1}H\}$



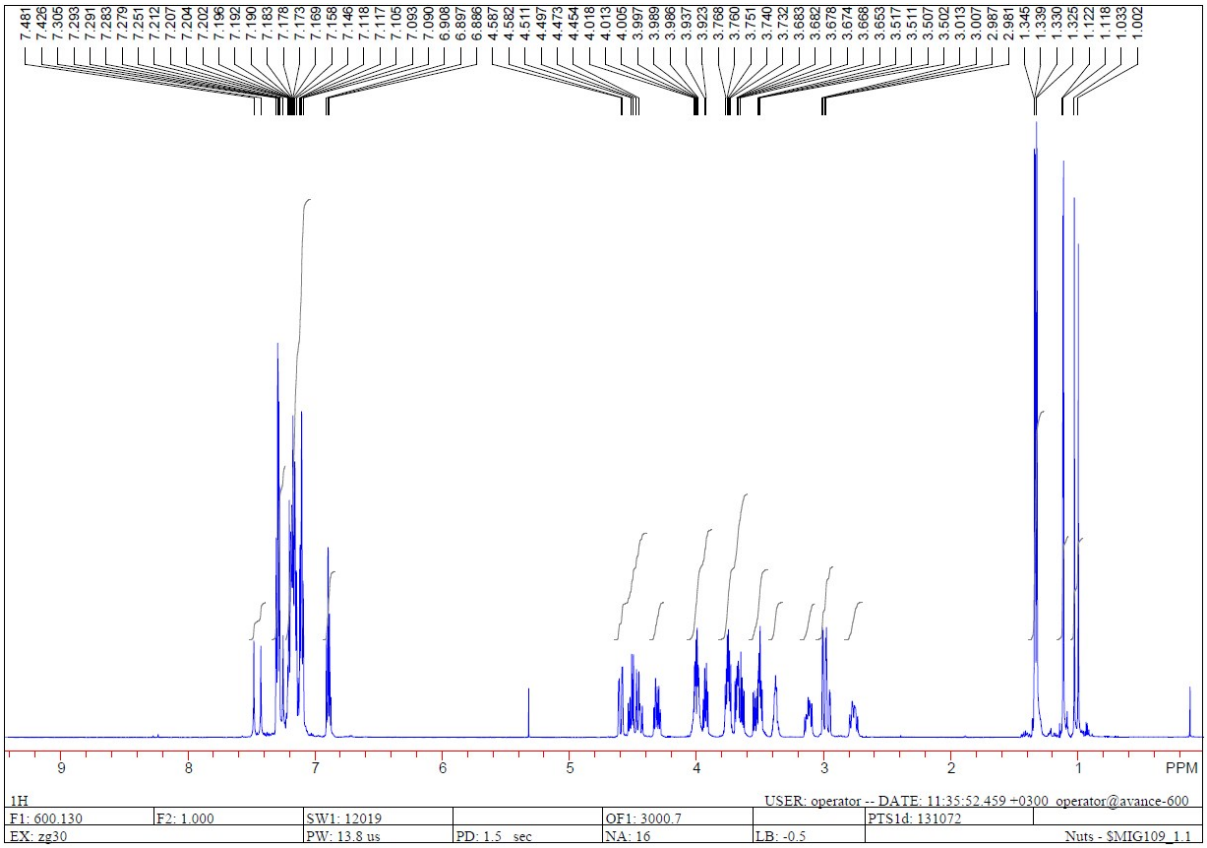
L3, ^{13}C APT



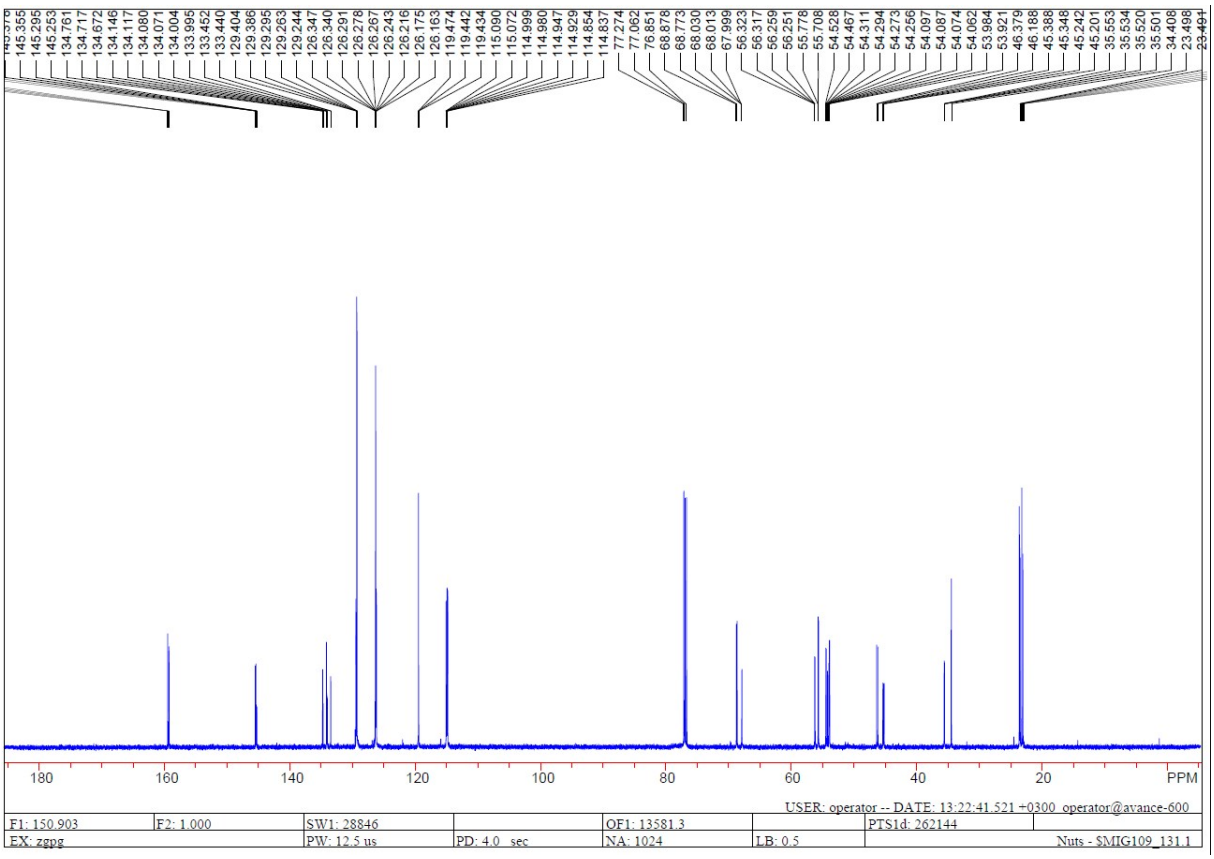
L4, $^{31}P\{^{1}H\}$



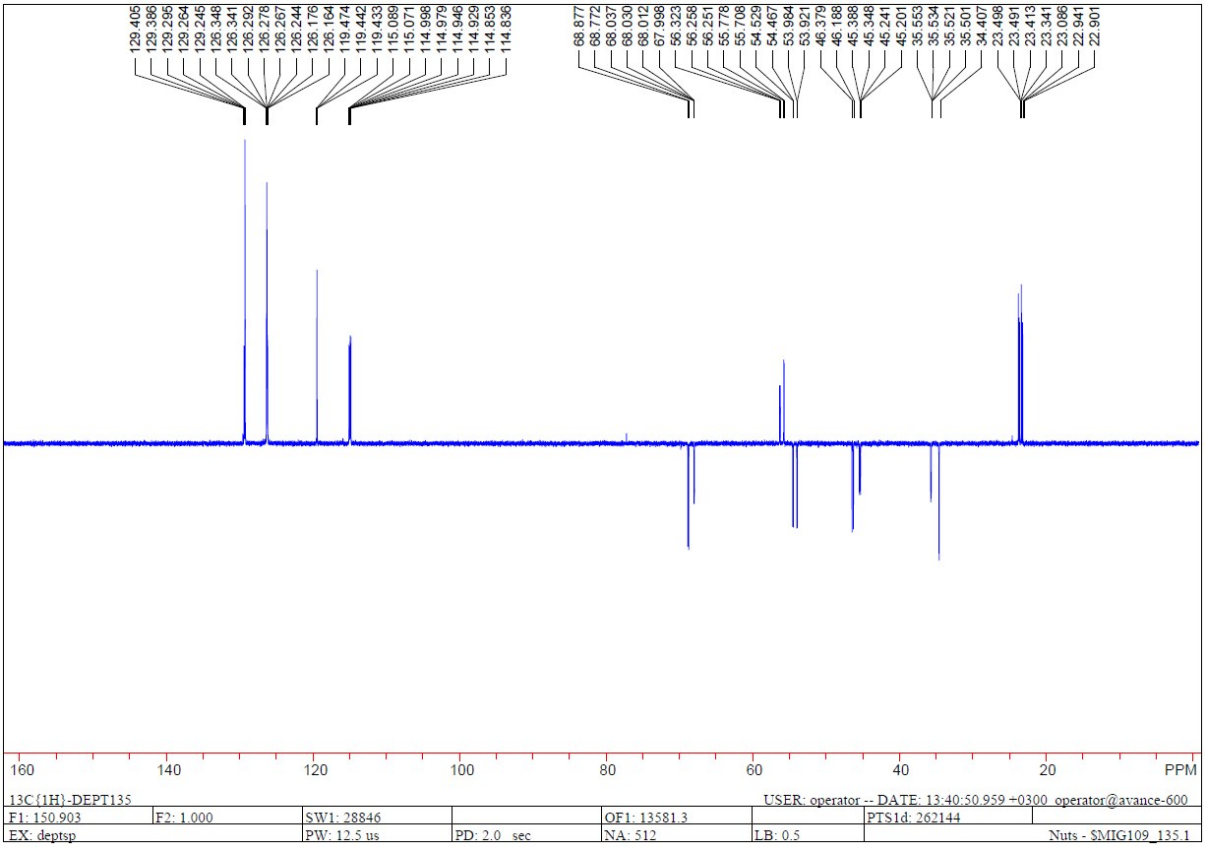
L4, ^{1}H



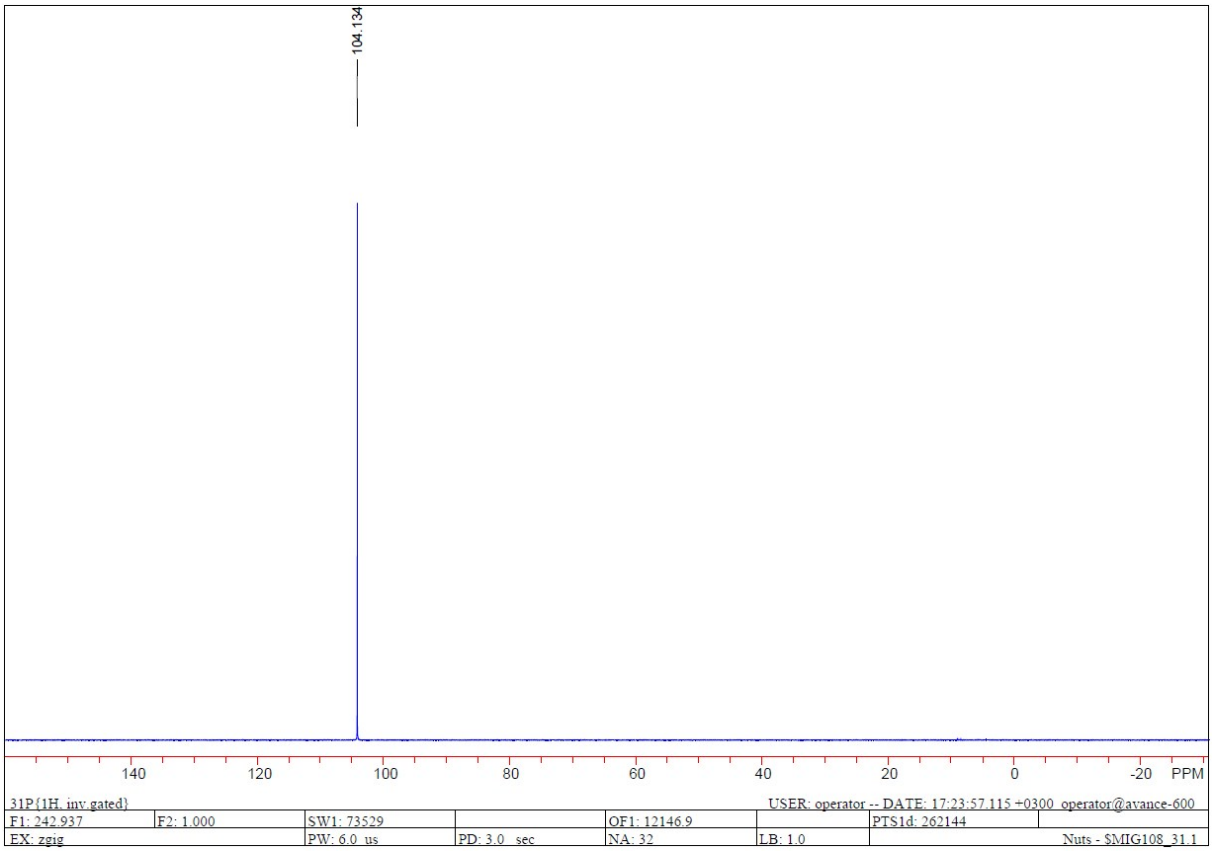
L4, $^{13}C\{^{1}H\}$



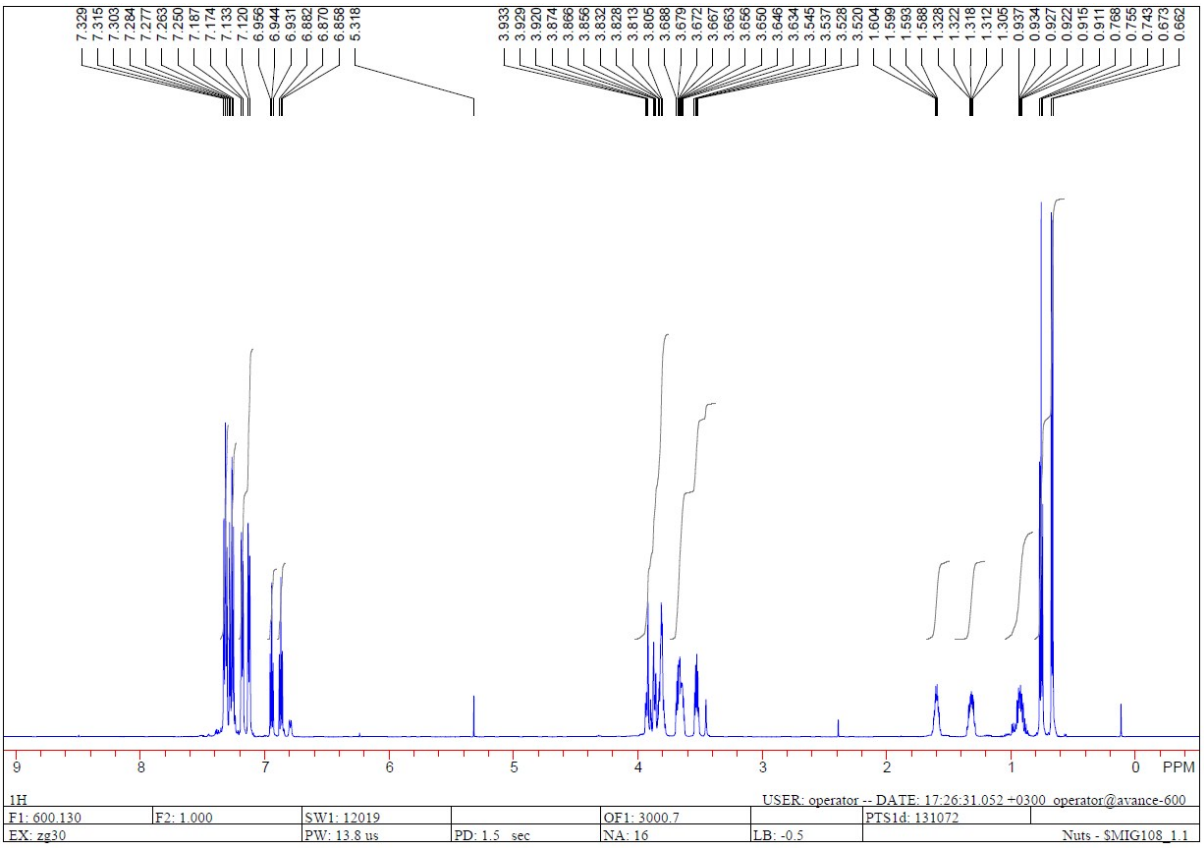
L4, ^{13}C DEPT



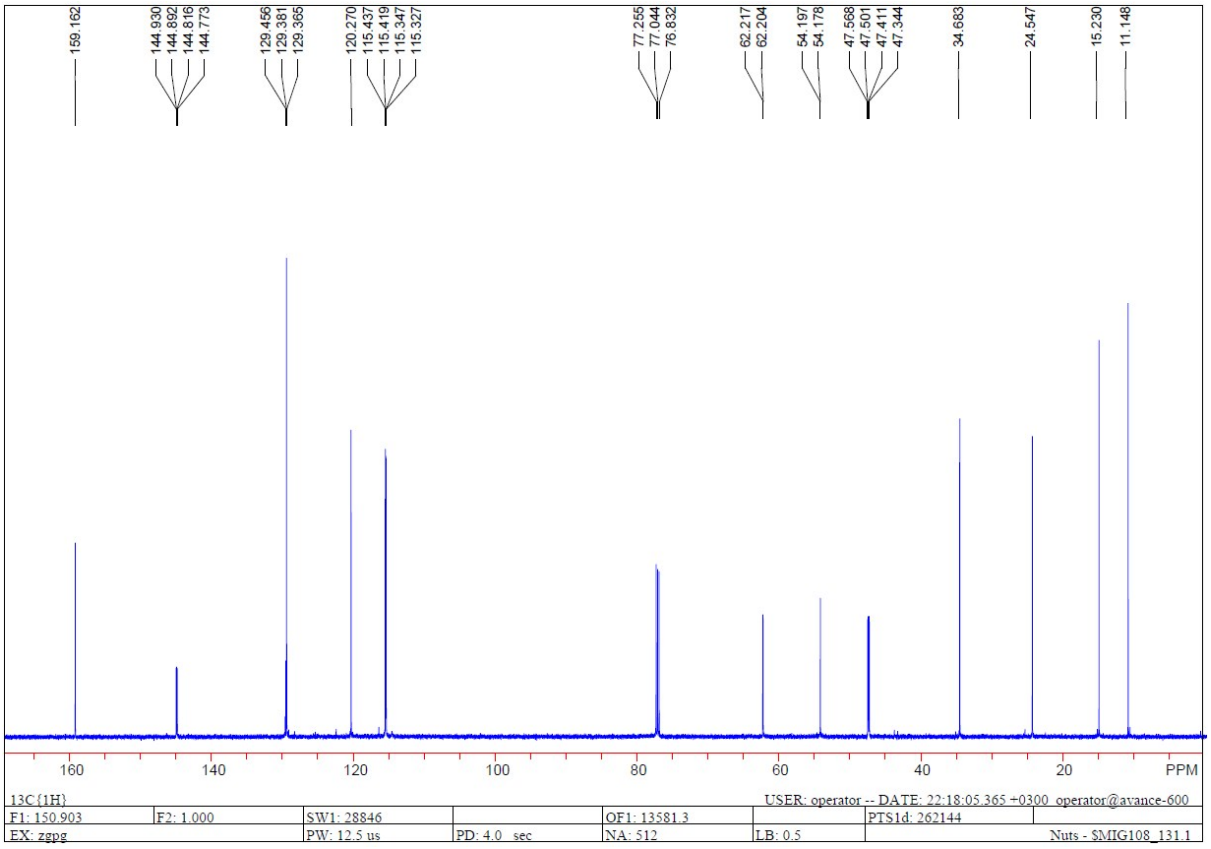
L5, ^{31}P{^{1}H}



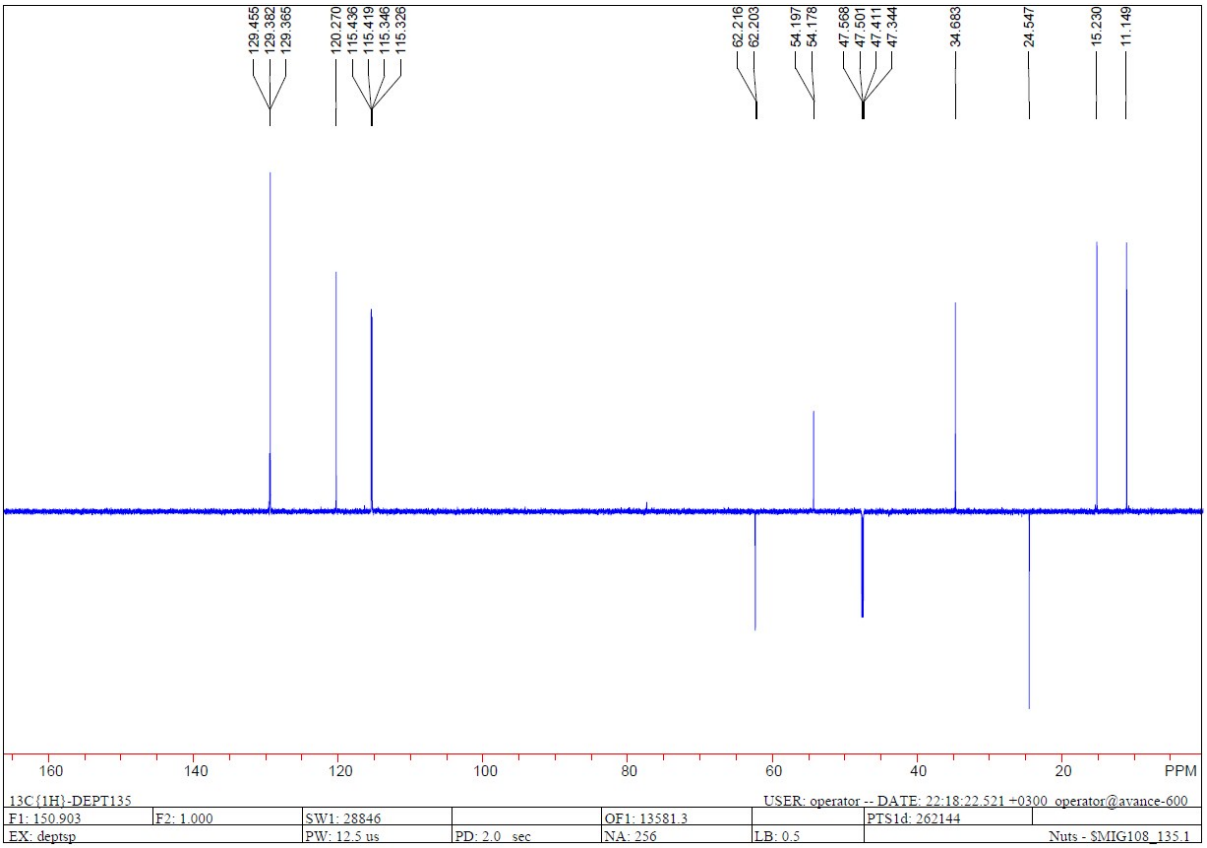
L5, ^{1}H



L5, ^{13}C{^{1}H}

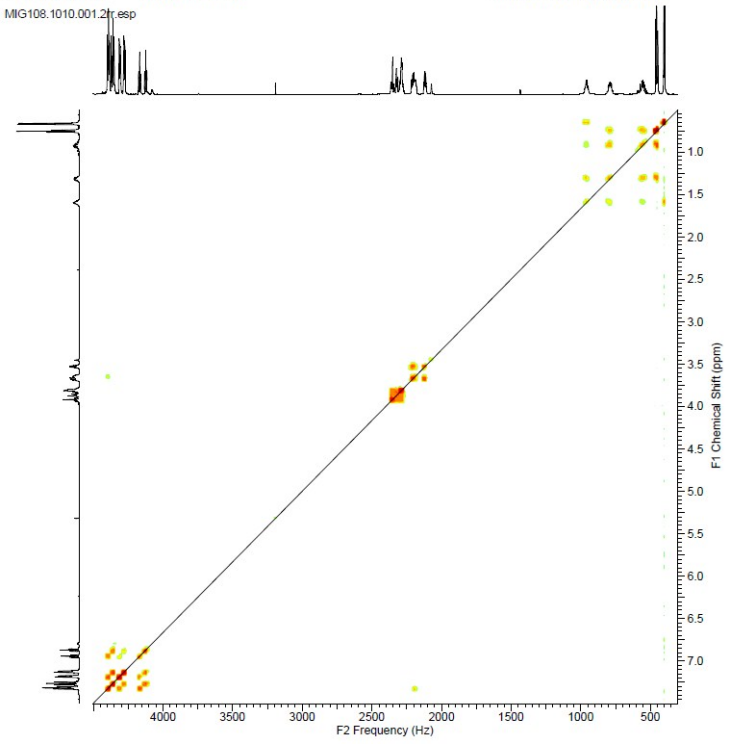


L5, ^{13}C DEPT



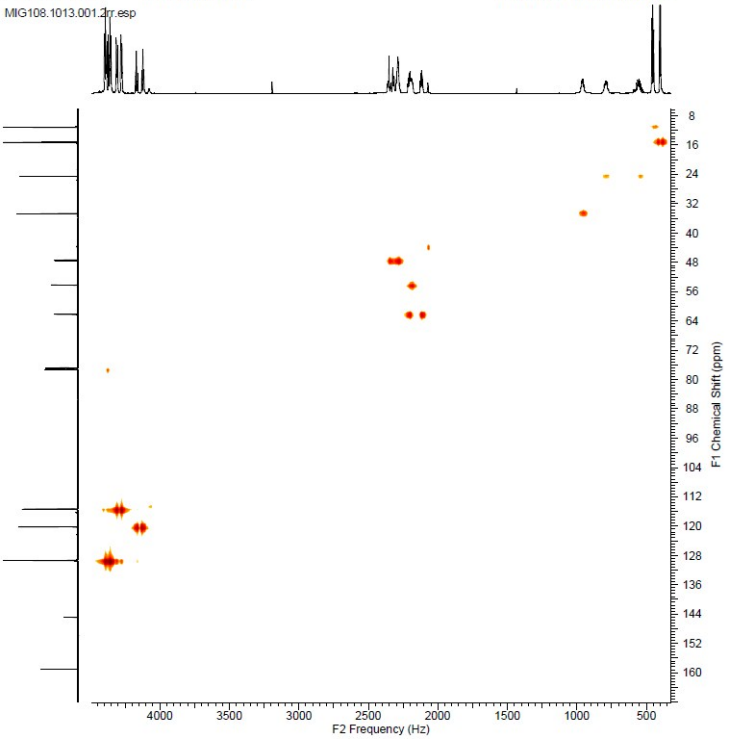
L5, ^{1}H-^{1}H COSY

Acquisition Time (sec)	(0.4874, 0.3656)	*Comment*	5 mm PABBO BB-1H/D Z-GRD Z856701/0030			*Date*	15 Mar 2018 22:19:00
File Name	C:\Users\MIG\Documents\MIG108\1010\pdata\1\2rr			*Frequency (MHz)*	(600.13, 600.13)	*Nucleus*	(1H, 1H)
Number of Transients	1	*Origin*	spect	*Original Points Count*	(2048, 1536)	*Owner*	operator
Points Count	(4096, 1024)	*Pulse Sequence*	cosygpqf	*Solvent*	CDCl3	*Spectrum Type*	COSY
Sweep Width (Hz)	(4200.65, 4197.58)			*Temperature (degree C)*	29.834	*Title*	1H,1H-COSY

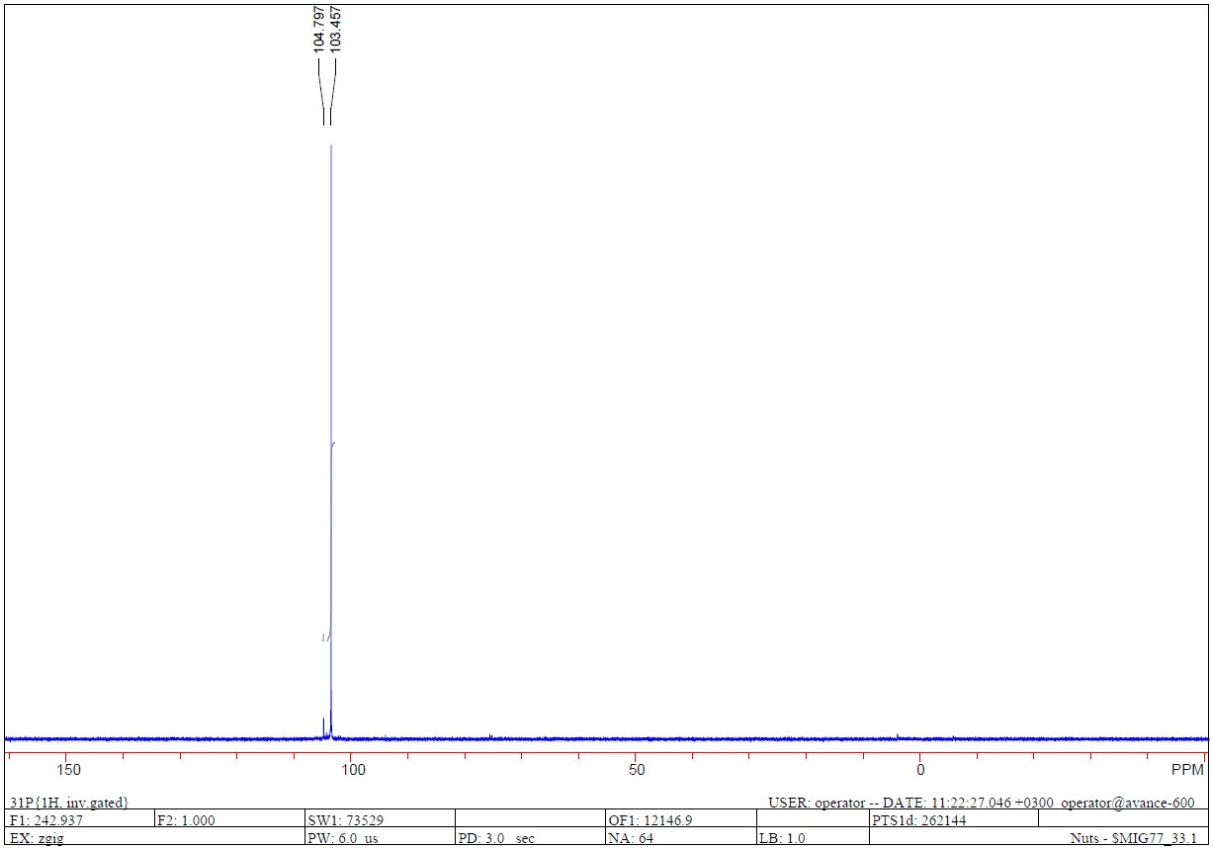


L5, ^{1}H-^{13}C HSQC

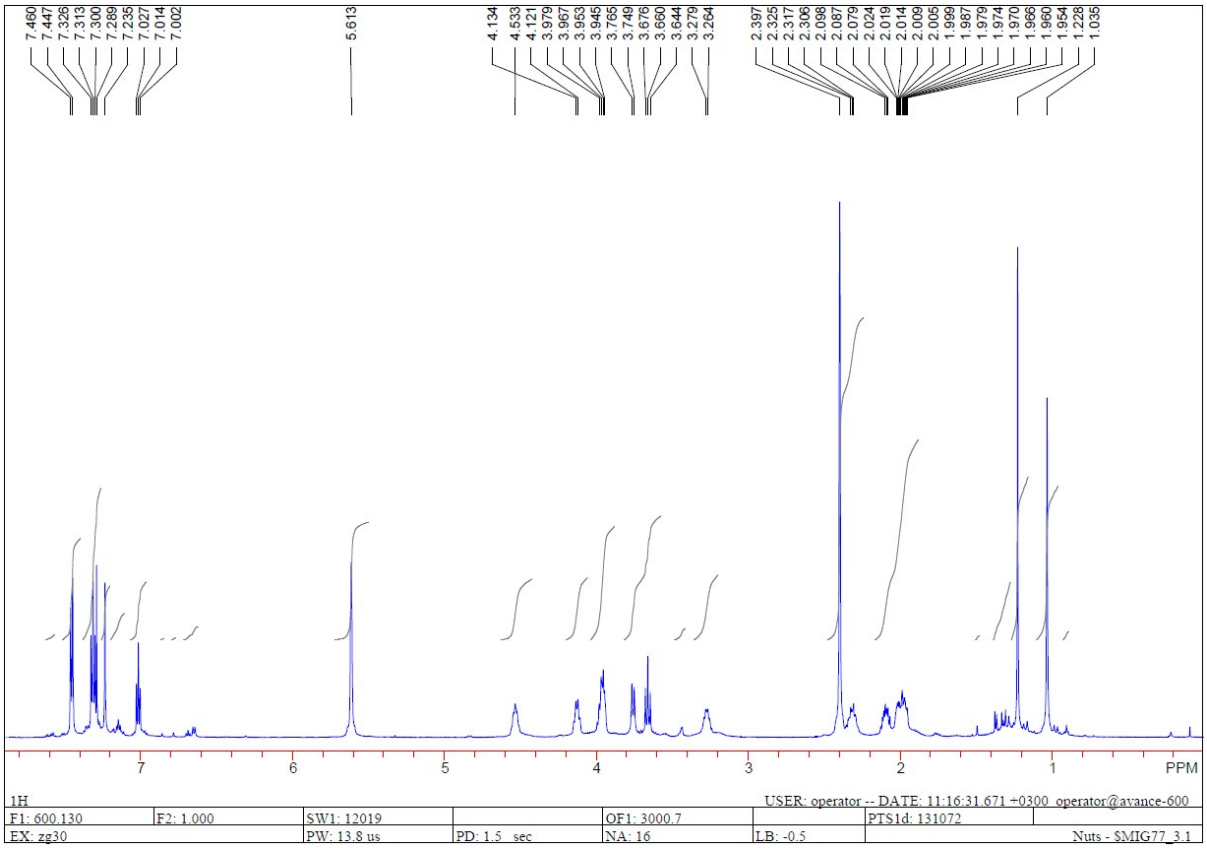
Acquisition Time (sec)	(0.4874, 0.0356)	*Comment*	5 mm PABBO BB-1H/D Z-GRD Z856701/0030			*Date*	15 Mar 2018 22:20:54
File Name	C:\Users\MIG\Documents\MIG108\1013\pdata\1\2rr			*Frequency (MHz)*	(600.13, 150.92)	*Nucleus*	(1H, 13C)
Number of Transients	1	*Origin*	spect	*Original Points Count*	(2048, 1024)	*Owner*	operator
Points Count	(2048, 1024)	*Pulse Sequence*	hsqcetgp	*Solvent*	CDCl3	*Spectrum Type*	HSQC
Sweep Width (Hz)	(4199.63, 28707.57)			*Temperature (degree C)*	30.015	*Title*	1H,13C-HSQC



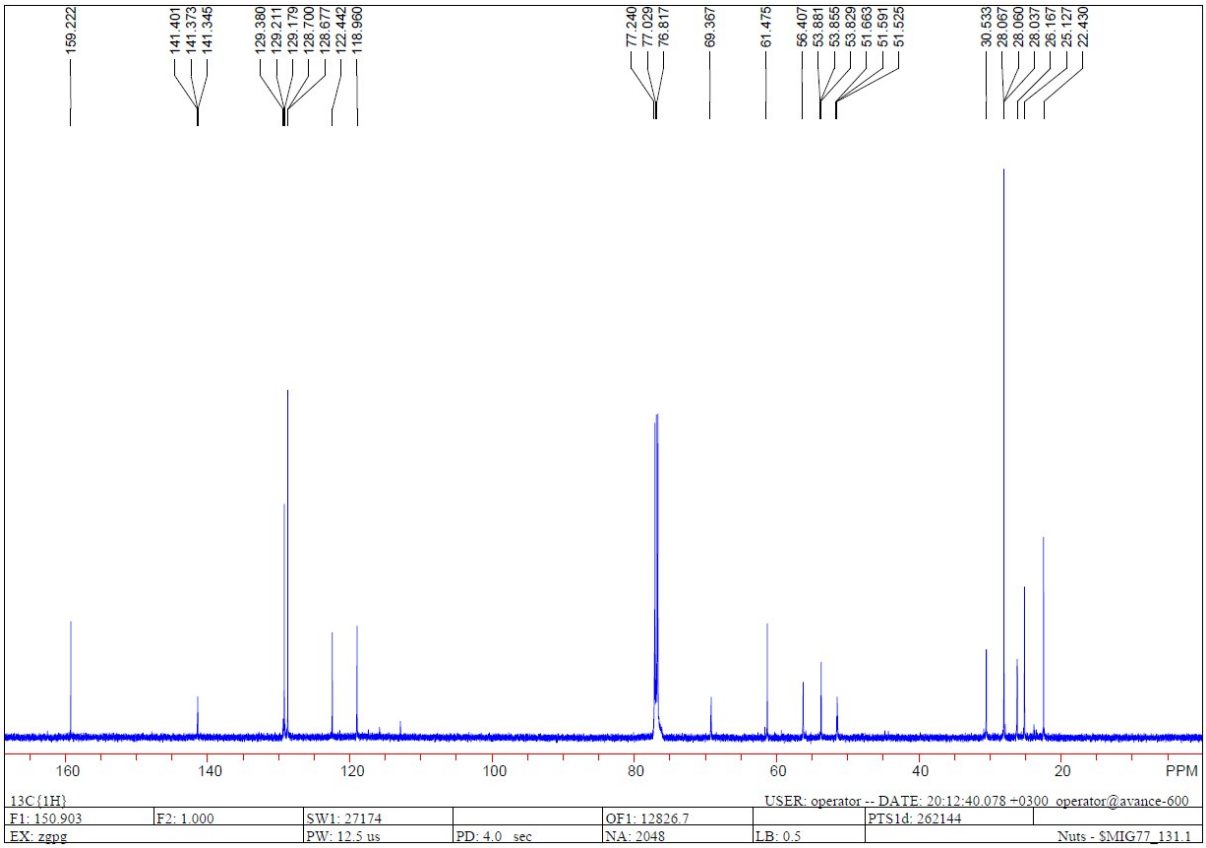
trans-[Pd(μ-**L1a**)Cl_2]$_2$ (**6**), $^{31}P\{^{1}H\}$



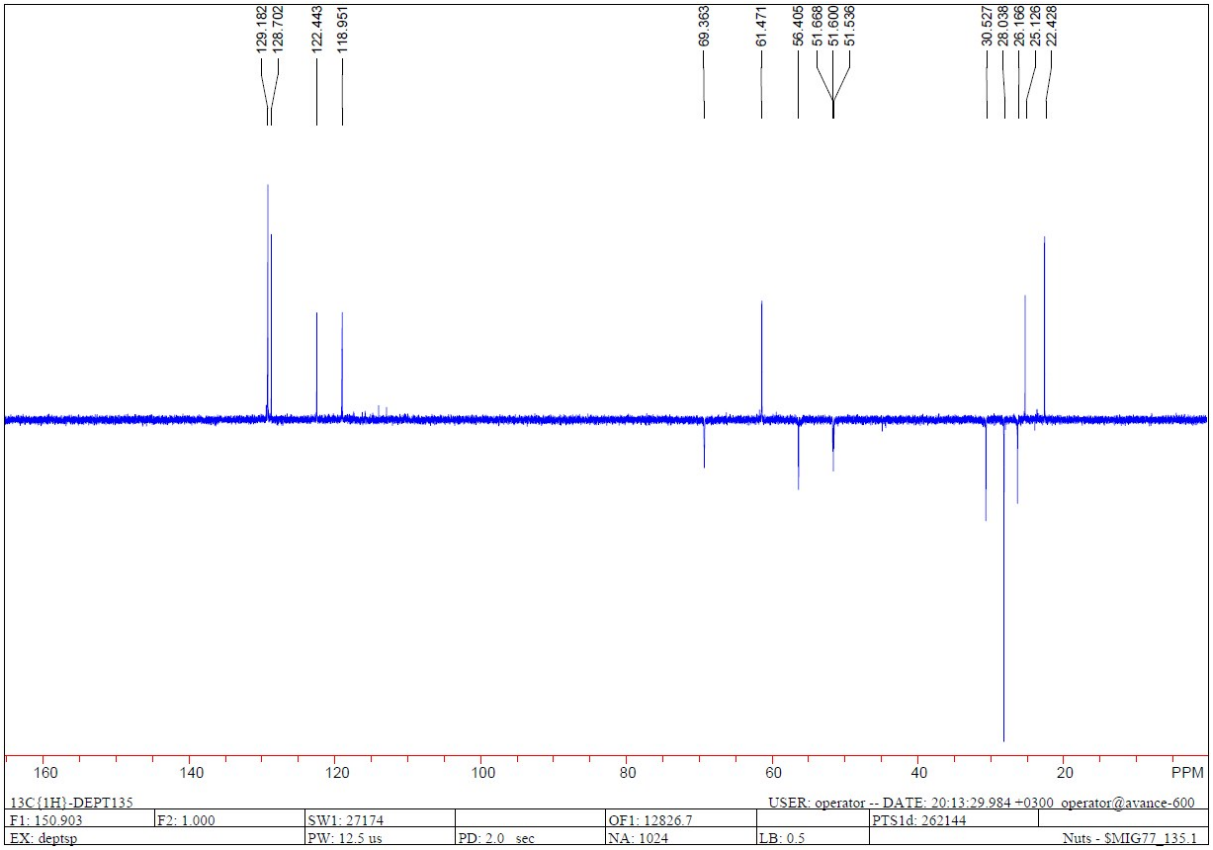
trans-[Pd(μ-**L1a**)Cl_2]$_2$ (**6**), ^{1}H



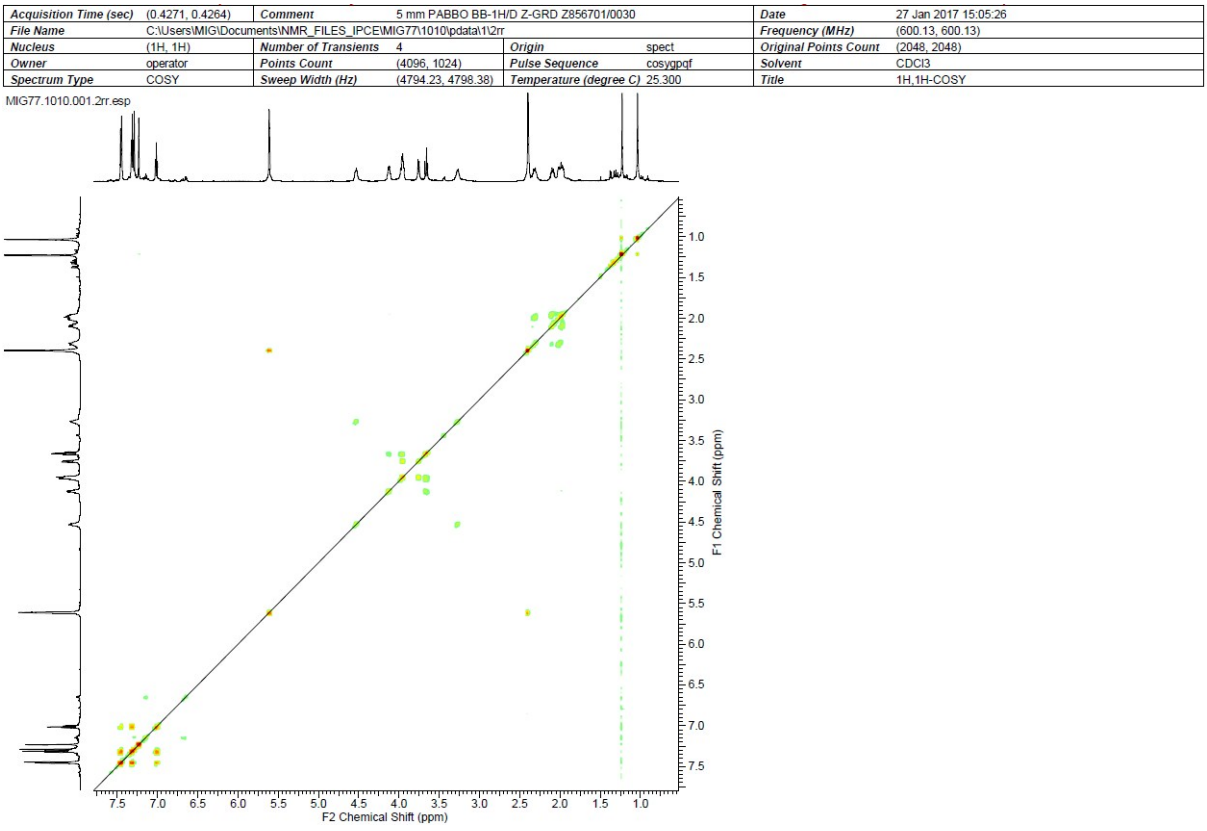
trans-[Pd(μ-**L1a**)Cl_2]$_2$ (**6**), ^{13}C{^{1}H}



trans-[Pd(μ-**L1a**)Cl_2]$_2$ (**6**), ^{13}C DEPT

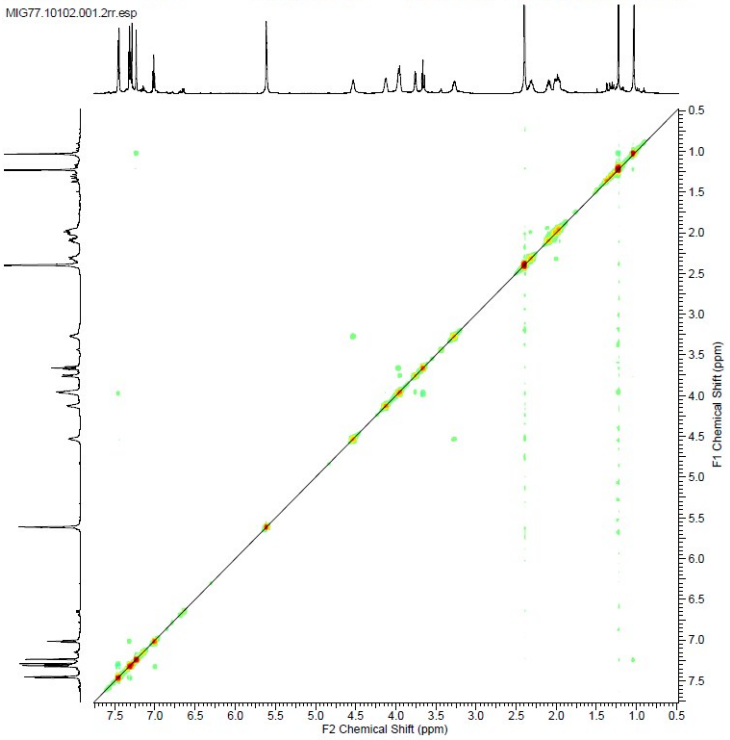


trans-[Pd(μ-**L1a**)Cl_2]$_2$ (**6**), ^{1}H-^{1}H COSY



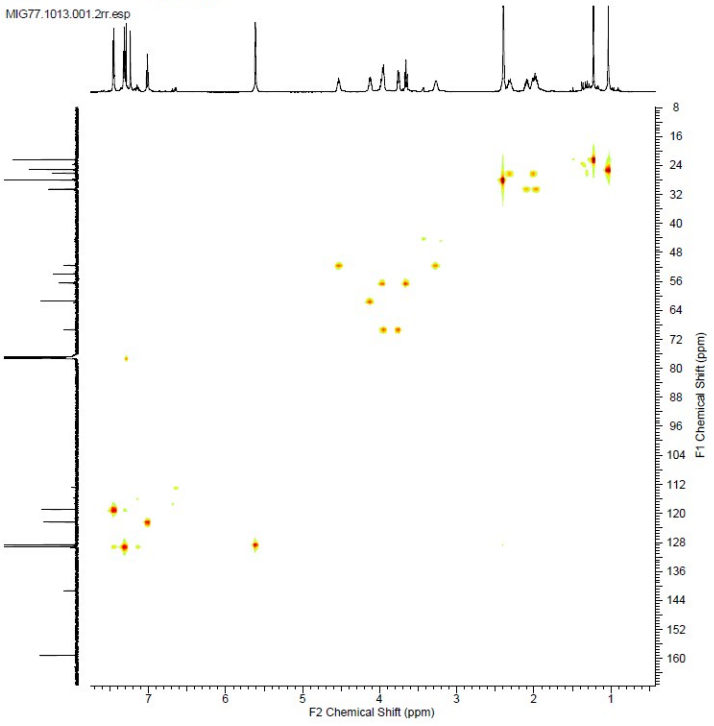
trans-[Pd(μ-**L1a**)Cl_2]$_2$ (**6**), ^{1}H-^{1}H ROESY

Acquisition Time (sec)	(0.4271, 0.1066)	*Comment*	5 mm PABBO BB-1H/D Z-GRD Z856701/0030			*Date*	01 Feb 2017 17:13:46
File Name	C:\Users\MIG\Documents\NMR_FILES_IPCE\MIG77\10102\pdata\1\2rr					*Frequency (MHz)*	(600.13, 600.13)
Nucleus	(1H, 1H)	*Number of Transients*	8	*Origin*	spect	*Original Points Count*	(2048, 512)
Owner	operator	*Points Count*	(4096, 1024)	*Pulse Sequence*	roesyph.2	*Solvent*	CDCl3
Spectrum Type	ROESY	*Sweep Width (Hz)*	(4794.23, 4798.38)	*Temperature (degree C)*	26.600	*Title*	1H,1H-ROESY



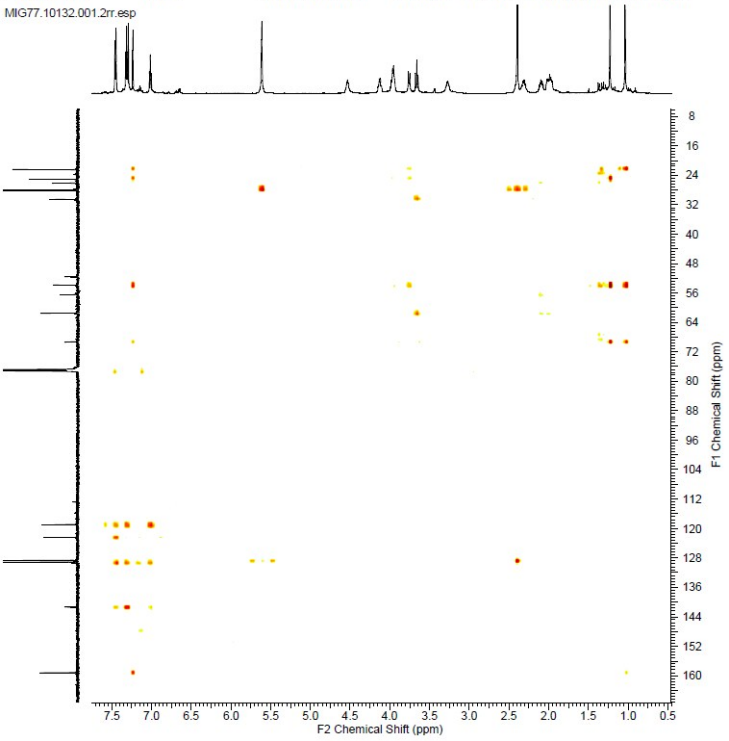
trans-[Pd(μ-**L1a**)Cl_2]$_2$ (**6**), ^{1}H-^{13}C HSQC

Acquisition Time (sec)	(0.4271, 0.0754)	*Comment*	5 mm PABBO BB-1H/D Z-GRD Z856701/0030			*Date*	01 Feb 2017 21:36:10
File Name	C:\Users\MIG\Documents\NMR_FILES_IPCE\MIG77\1013\pdata\1\2rr					*Frequency (MHz)*	(600.13, 150.92)
Nucleus	(1H, 13C)	*Number of Transients*	4	*Origin*	spect	*Original Points Count*	(2048, 2048)
Owner	operator	*Points Count*	(2048, 1024)	*Pulse Sequence*	hsqcetgp	*Solvent*	CDCl3
Spectrum Type	HSQC	*Sweep Width (Hz)*	(4793.06, 27147.38)			*Temperature (degree C)*	27.100
Title	1H,13C-HSQC						



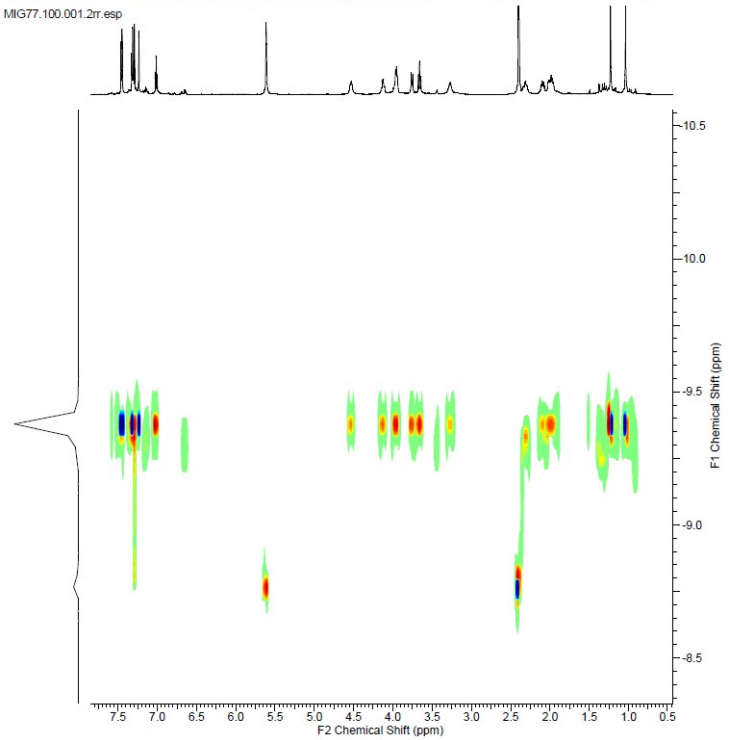
trans-[Pd(μ-**L1a**)Cl_2]$_2$ (**6**), ^{1}H-^{13}C HMBC

Acquisition Time (sec)	(0.4271, 0.0754)	*Comment*	5 mm PABBO BB-1H/D Z-GRD Z856701/0030			*Date*	02 Feb 2017 10:32:22
File Name	C:\Users\MIG\Documents\NMR_FILES_IPCE\MIG77\10132\pdata\1\2rr					*Frequency (MHz)*	(600.13, 150.92)
Nucleus	(1H, 13C)	*Number of Transients*	8	*Origin*	spect	*Original Points Count*	(2048, 2048)
Owner	operator	*Points Count*	(2048, 1024)	*Pulse Sequence*	hmbcgpndqf	*Solvent*	CDCl3
Spectrum Type	HMBC	*Sweep Width (Hz)*	(4793.06, 27147.38)	*Temperature (degree C)*	26.600	*Title*	1H,13C-HMBC

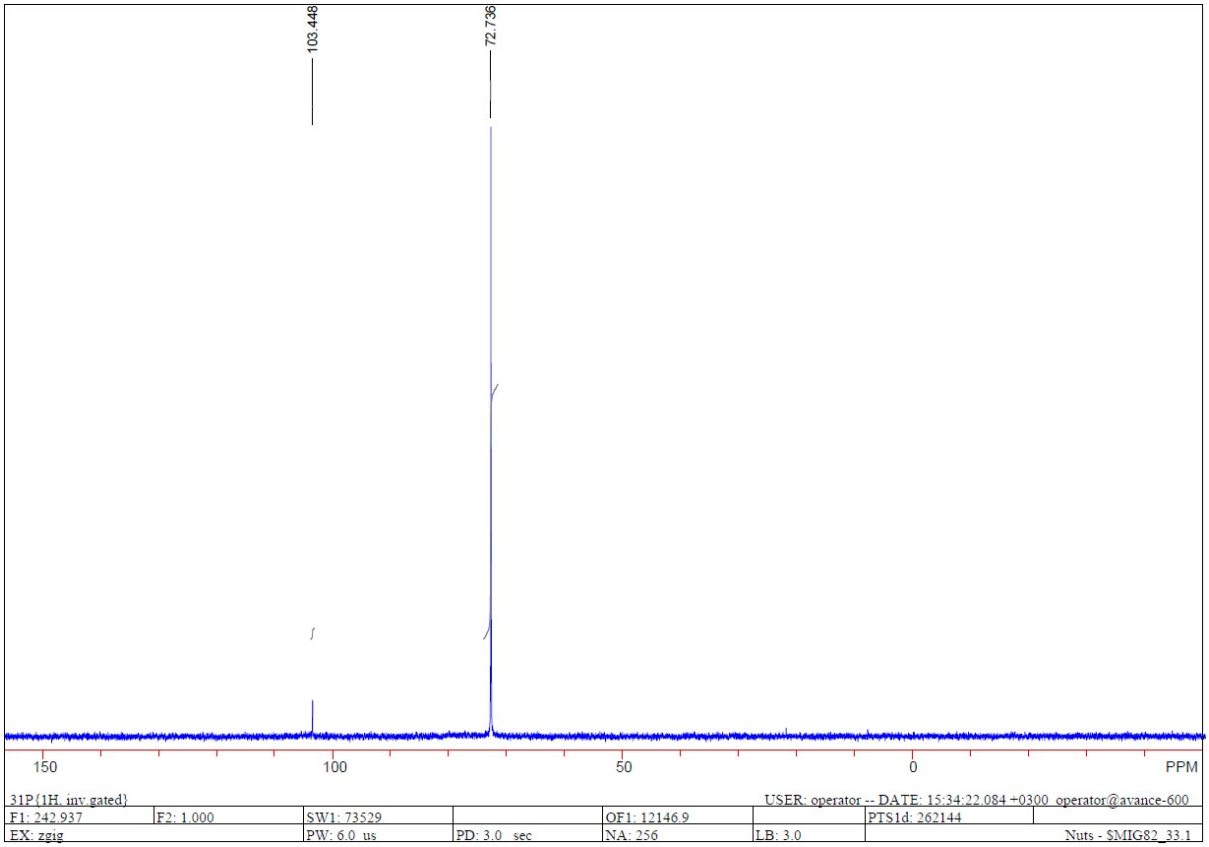


trans-[Pd(μ-**L1a**)Cl_2]$_2$ (**6**), DOSY

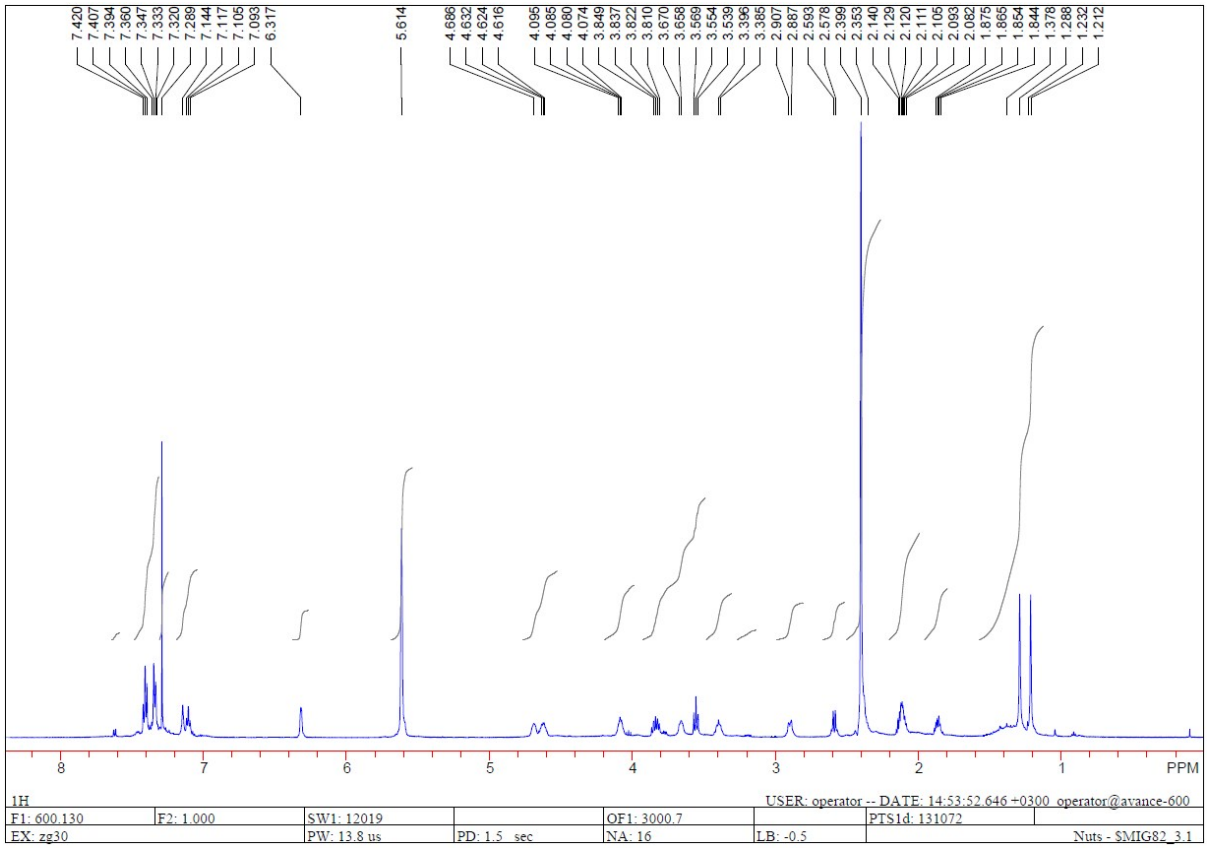
Acquisition Time (sec)	(1.7061, 0.0381)	*Comment*	5 mm PABBO BB-1H/D Z-GRD Z856701/0030			*Date*	02 Feb 2017 13:00:52
File Name	C:\Users\MIG\Documents\NMR_FILES_IPCE\MIG77\100\pdata\1\2rr					*Frequency (MHz)*	(600.13, 600.13)
Nucleus	(1H, 1H)	*Number of Transients*	16	*Origin*	spect	*Original Points Count*	(8192, 64)
Owner	operator	*Points Count*	(16384, 64)	*Pulse Sequence*	dstegp3s	*Solvent*	CDCl3
Sweep Width (Hz)	(4801.24, 1654.11)	*Temperature (degree C)*	26.100	*Title*	1H		



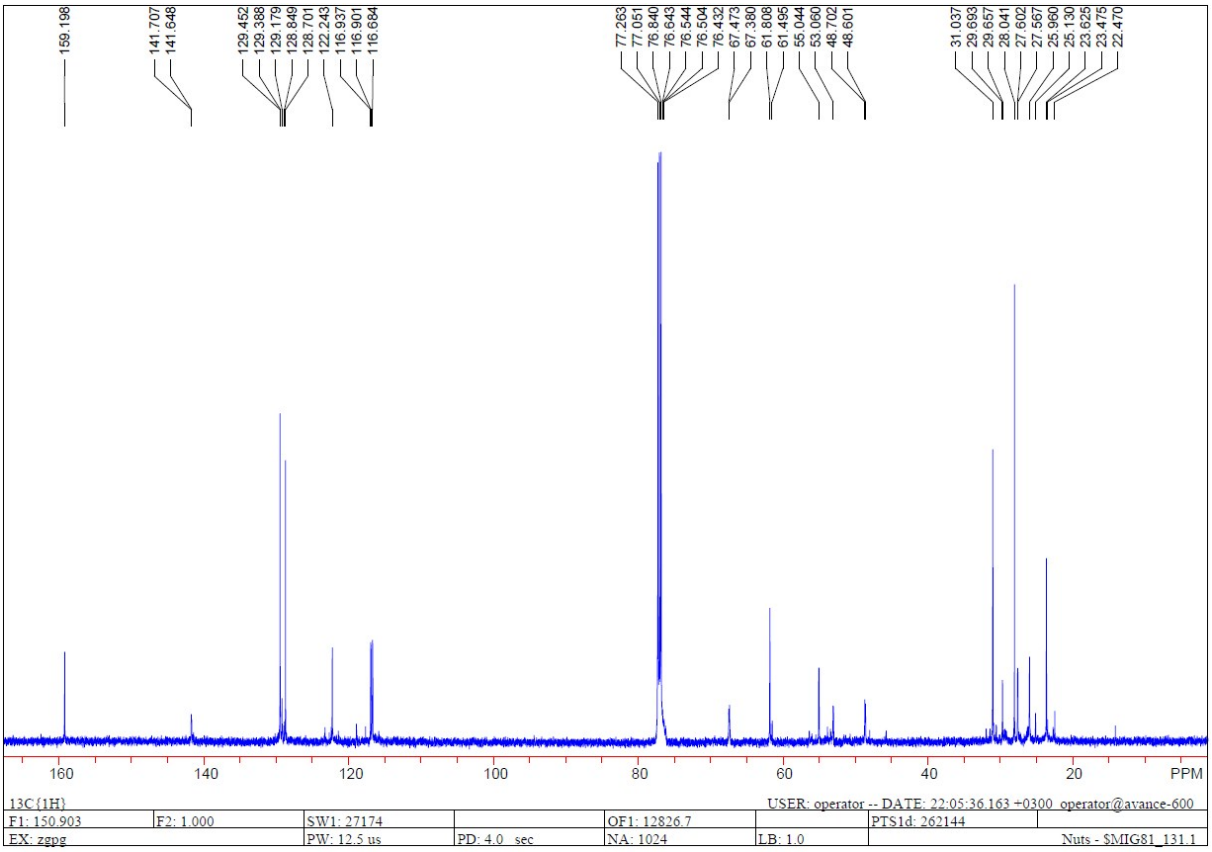
[(PdCl(μ-Cl))$_2$(**L1a**)] (**7**), $^{31}P\{^1H\}$



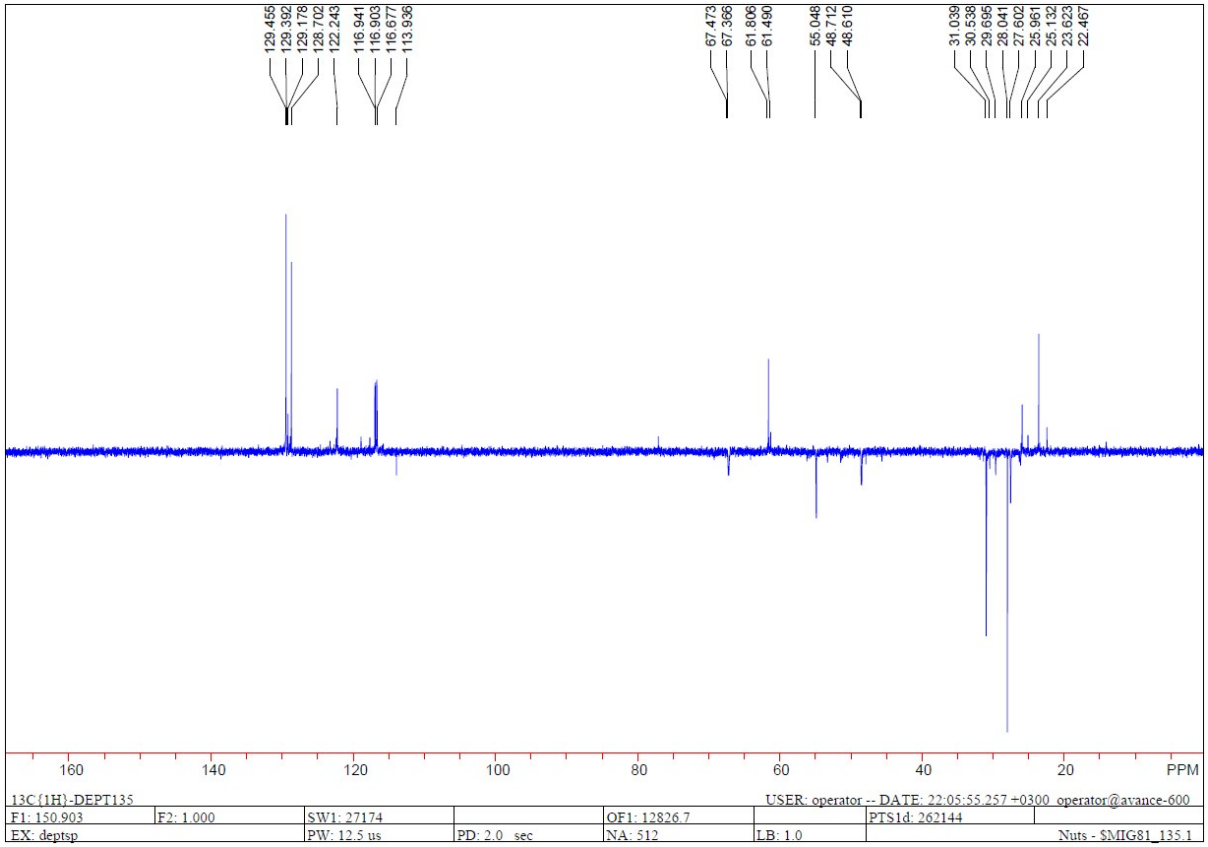
[(PdCl(μ-Cl))$_2$(**L1a**)] (**7**), ^1H



[(PdCl(μ-Cl))$_2$(**L1a**)] (**7**), ^{13}C{^{1}H}

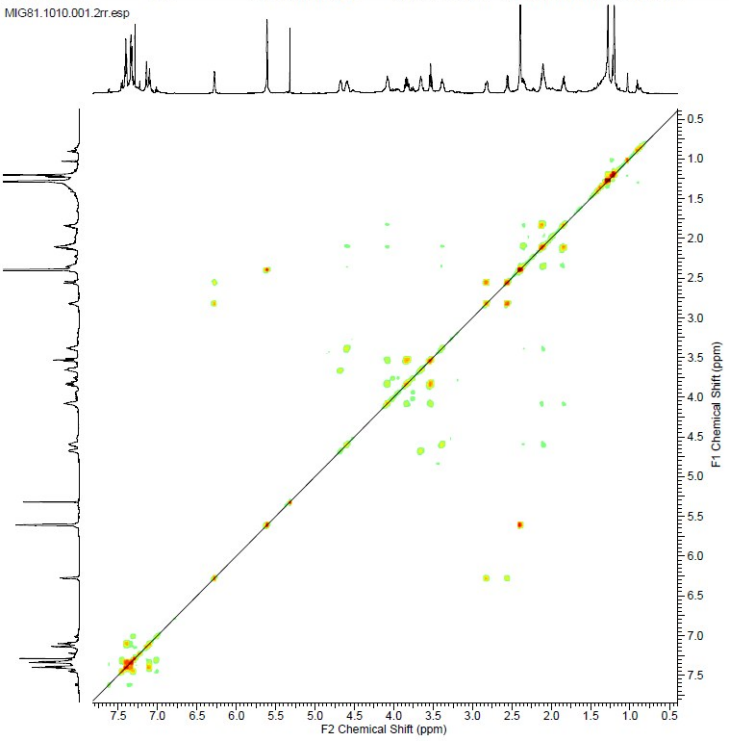


[(PdCl(μ-Cl))$_2$(**L1a**)] (**7**), ^{13}C DEPT



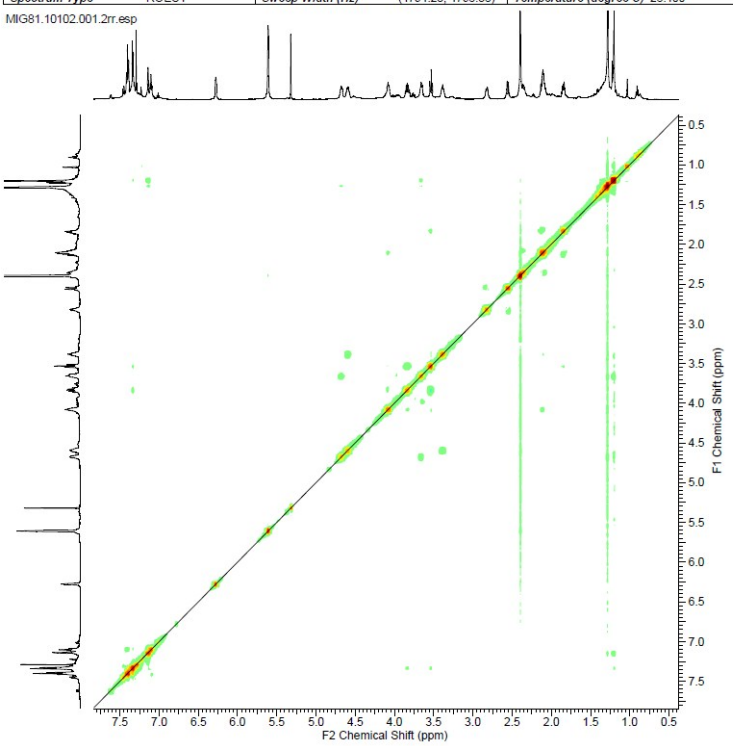
[(PdCl(μ-Cl))$_2$(**L1a**)] (**7**), ^{1}H-^{1}H COSY

Acquisition Time (sec)	(0.4271, 0.1549)	*Comment*	5 mm PABBO BB-1H/D Z-GRD Z856701/0030			*Date*	03 Mar 2017 01:19:06
File Name	C:\Users\MIG\Documents\NMR_FILES_IPCE\MIG81\1010\pdata\1\2rr					*Frequency (MHz)*	(600.13, 600.13)
Nucleus	(1H, 1H)	*Number of Transients*	6	*Origin*	spect	*Original Points Count*	(2048, 744)
Owner	operator	*Points Count*	(4096, 1024)	*Pulse Sequence*	cosygpqf	*Solvent*	CDCl3
Spectrum Type	COSY	*Sweep Width (Hz)*	(4794.23, 4798.38)	*Temperature (degree C)*	28.100	*Title*	1H,1H-COSY



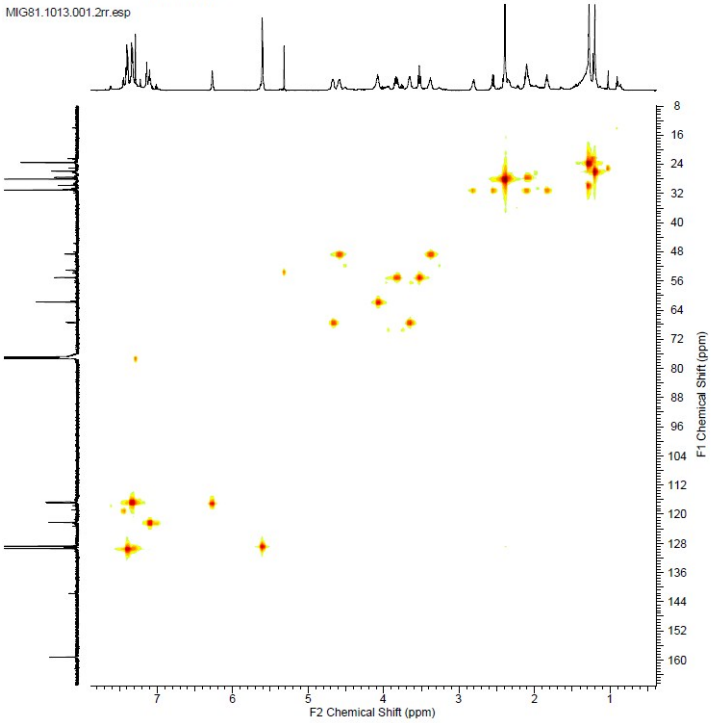
[(PdCl(μ-Cl))$_2$(**L1a**)] (**7**), ^{1}H-^{1}H ROESY

Acquisition Time (sec)	(0.4271, 0.1066)	*Comment*	5 mm PABBO BB-1H/D Z-GRD Z856701/0030			*Date*	03 Mar 2017 12:29:06
File Name	C:\Users\MIG\Documents\NMR_FILES_IPCE\MIG81\10102\pdata\1\2rr					*Frequency (MHz)*	(600.13, 600.13)
Nucleus	(1H, 1H)	*Number of Transients*	16	*Origin*	spect	*Original Points Count*	(2048, 512)
Owner	operator	*Points Count*	(4096, 1024)	*Pulse Sequence*	roesyph.2	*Solvent*	CDCl3
Spectrum Type	ROESY	*Sweep Width (Hz)*	(4794.23, 4798.38)	*Temperature (degree C)*	28.400	*Title*	1H,1H-ROESY



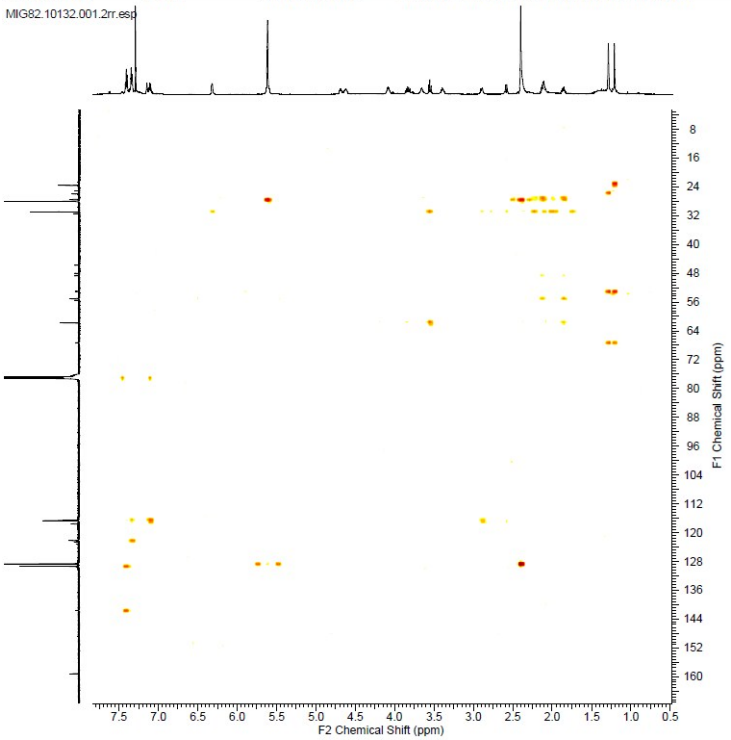
[(PdCl(μ-Cl))$_2$(**L1a**)] (**7**), ^{1}H-^{13}C HSQC

Acquisition Time (sec)	(0.2135, 0.0377)	*Comment*	5 mm PABBO BB-1H/D Z-GRD Z856701/0030			*Date*	03 Mar 2017 12:02:34
File Name	C:\Users\MIG\Documents\NMR_FILES_IPCE\MIG81\1013\pdata\1\2rr					*Frequency (MHz)*	(600.13, 150.92)
Nucleus	(1H, 13C)	*Number of Transients*	2	*Origin*	spect	*Original Points Count*	(1024, 1024)
Owner	operator	*Points Count*	(2048, 1024)	*Pulse Sequence*	hsqcetgp	*Solvent*	CDCl3
Spectrum Type	HSQC	*Sweep Width (Hz)*	(4793.06, 27147.38)			*Temperature (degree C)*	28.100
Title	1H,13C-HSQC						



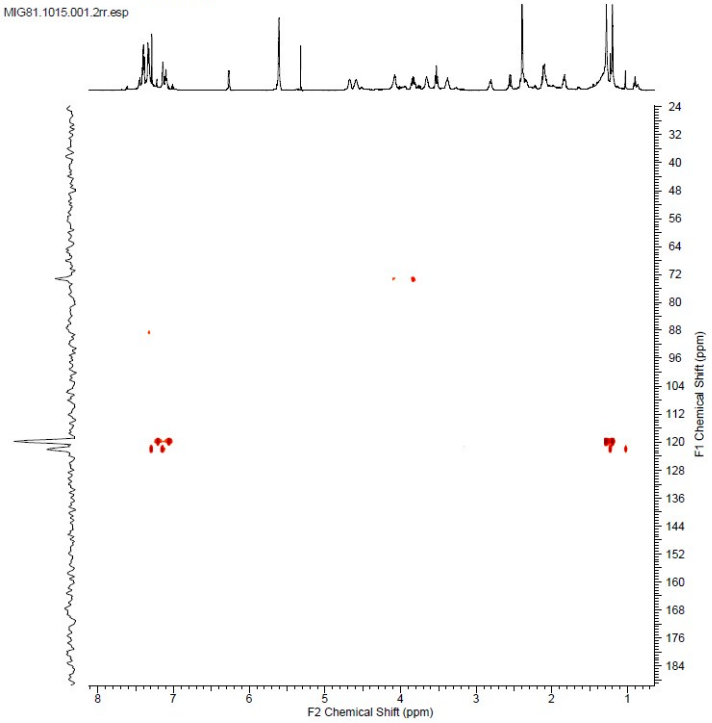
[(PdCl(μ-Cl))$_2$(**L1a**)] (**7**), ^{1}H-^{13}C HMBC

Acquisition Time (sec)	(0.2135, 0.0377)	*Comment*	5 mm PABBO BB-1H/D Z-GRD Z856701/0030			*Date*	30 Mar 2017 14:19:18
File Name	C:\Users\MIG\Documents\NMR_FILES_IPCE\MIG82\10132\pdata\1\2rr					*Frequency (MHz)*	(600.13, 150.92)
Nucleus	(1H, 13C)	*Number of Transients*	10	*Origin*	spect	*Original Points Count*	(1024, 1024)
Owner	operator	*Points Count*	(2048, 1024)	*Pulse Sequence*	hmbcgpndqf	*Solvent*	CDCl3
Spectrum Type	HMBC	*Sweep Width (Hz)*	(4793.06, 27147.38)	*Temperature (degree C)*	28.600	*Title*	1H,13C-HMBC



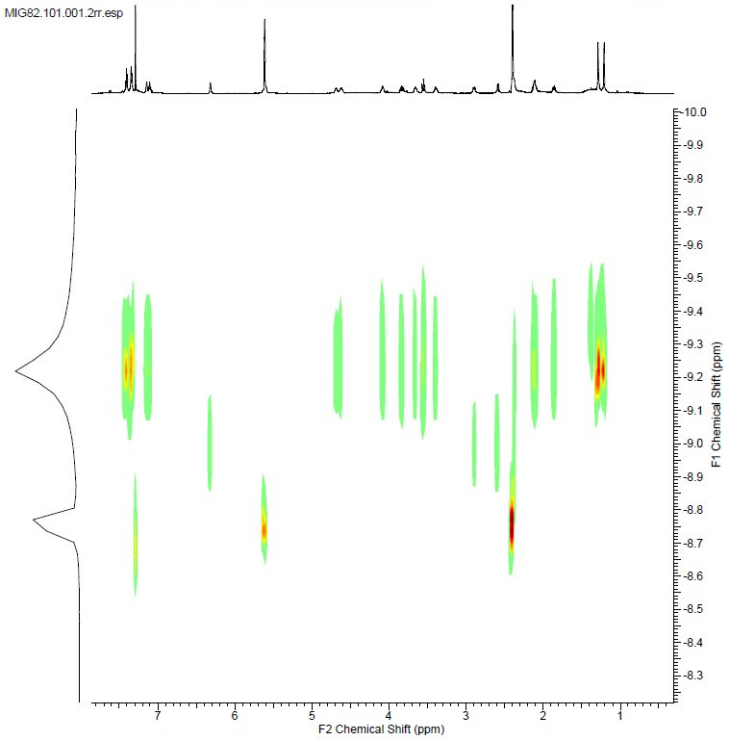
[(PdCl(μ-Cl))$_2$(**L1a**)] (**7**), ^{1}H-^{15}N HMBC

Acquisition Time (sec)	(0.4538, 0.0281)	*Comment*	5 mm PABBO BB-1H/D Z-GRD Z856701/0030			*Date*	10 Mar 2017 10:28:20
File Name	C:\Users\MIG\Documents\NMR_FILES_IPCE\MIG81\1015\pdata\1\2rr					*Frequency (MHz)*	(600.13, 60.82)
Nucleus	(1H, 15N)	*Number of Transients*	52	*Origin*	spect	*Original Points Count*	(2176, 512)
Owner	operator	*Points Count*	(2048, 1024)	*Pulse Sequence*	hmbcgpndqf	*Solvent*	CDCl3
Spectrum Type	HMBC	*Sweep Width (Hz)*	(4793.06, 18230.36)			*Temperature (degree C)*	27.200
Title	hmbc 1H 15N						



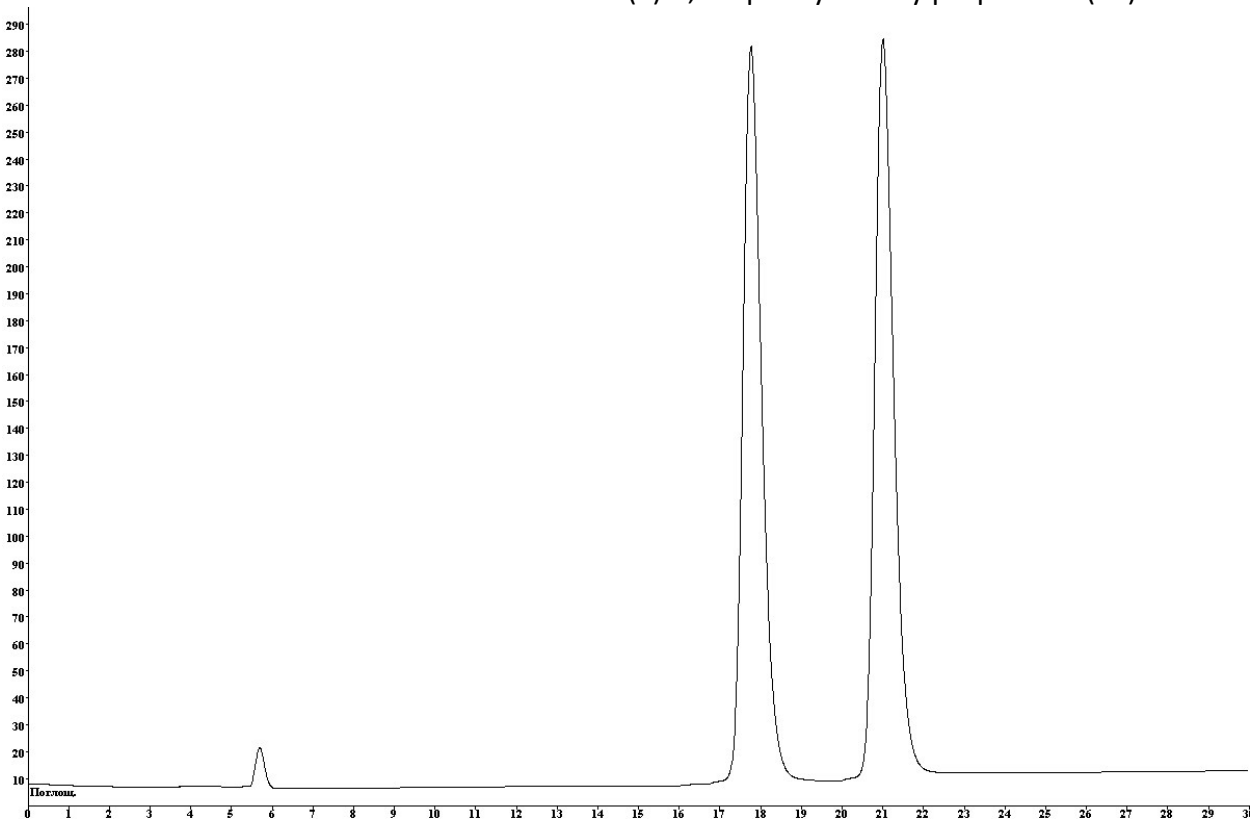
[(PdCl(μ-Cl))$_2$(**L1a**)] (**7**), DOSY

Acquisition Time (sec)	(1.7061, 0.0485)	*Comment*	5 mm PABBO BB-1H/D Z-GRD Z856701/0030			*Date*	24 Mar 2017 16:23:34
File Name	C:\Users\MIG\Documents\NMR_FILES_IPCE\MIG82\101\pdata\1\2rr					*Frequency (MHz)*	(600.13, 600.13)
Nucleus	(1H, 1H)	*Number of Transients*	16	*Origin*	spect	*Original Points Count*	(8192, 64)
Owner	operator	*Points Count*	(16384, 64)	*Pulse Sequence*	dstegp3s	*Solvent*	CDCl3
Sweep Width (Hz)	(4801.24, 1299.66)	*Temperature (degree C)*	27.800	*Title*	1H		

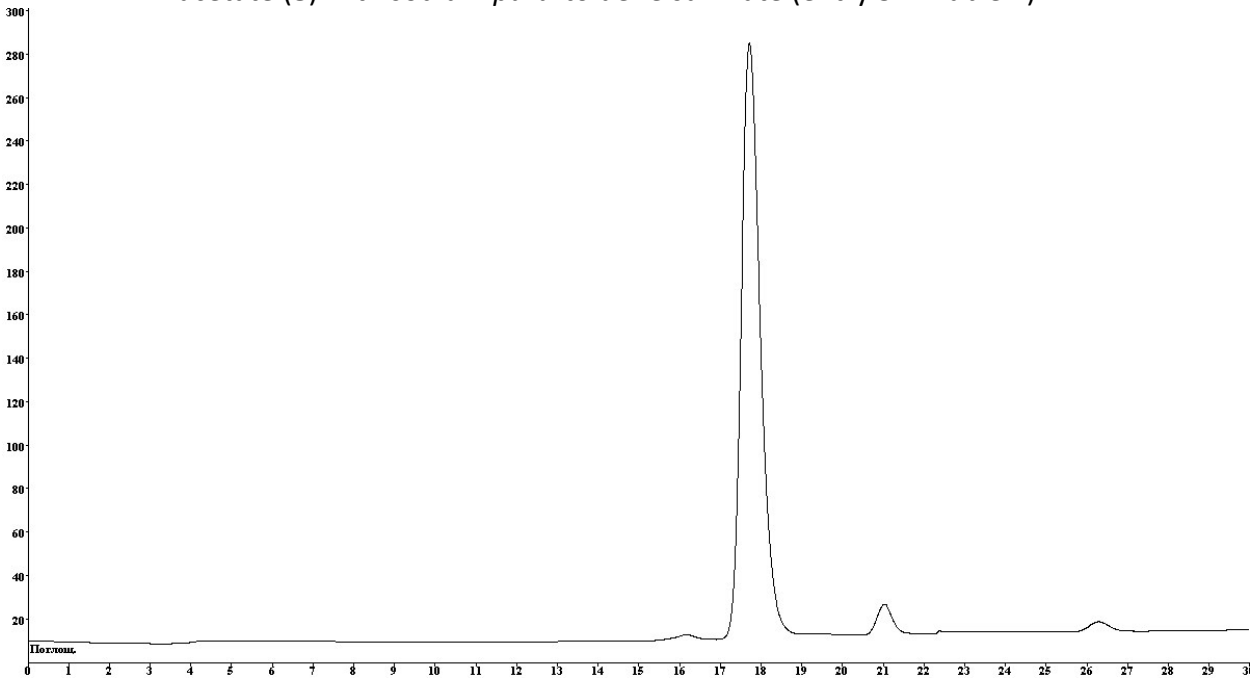


HPLC TRACES FOR THE Pd-CATALYZED ALLYLIC SUBSTITUTION AND Rh-CATALYZED HYDROGENATION

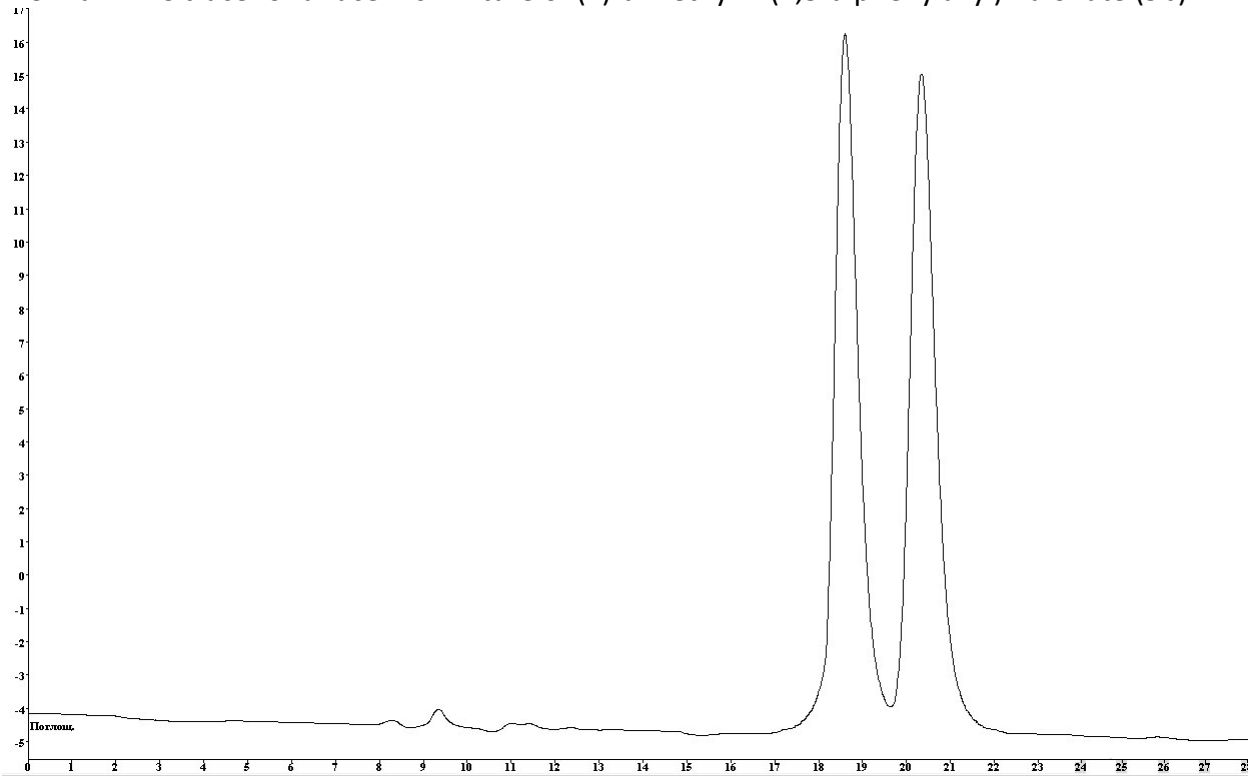
Chiral HPLC trace for a racemic mixture of (*E*)-1,3-diphenyl-3-tosylprop-1-ene (**9a**)



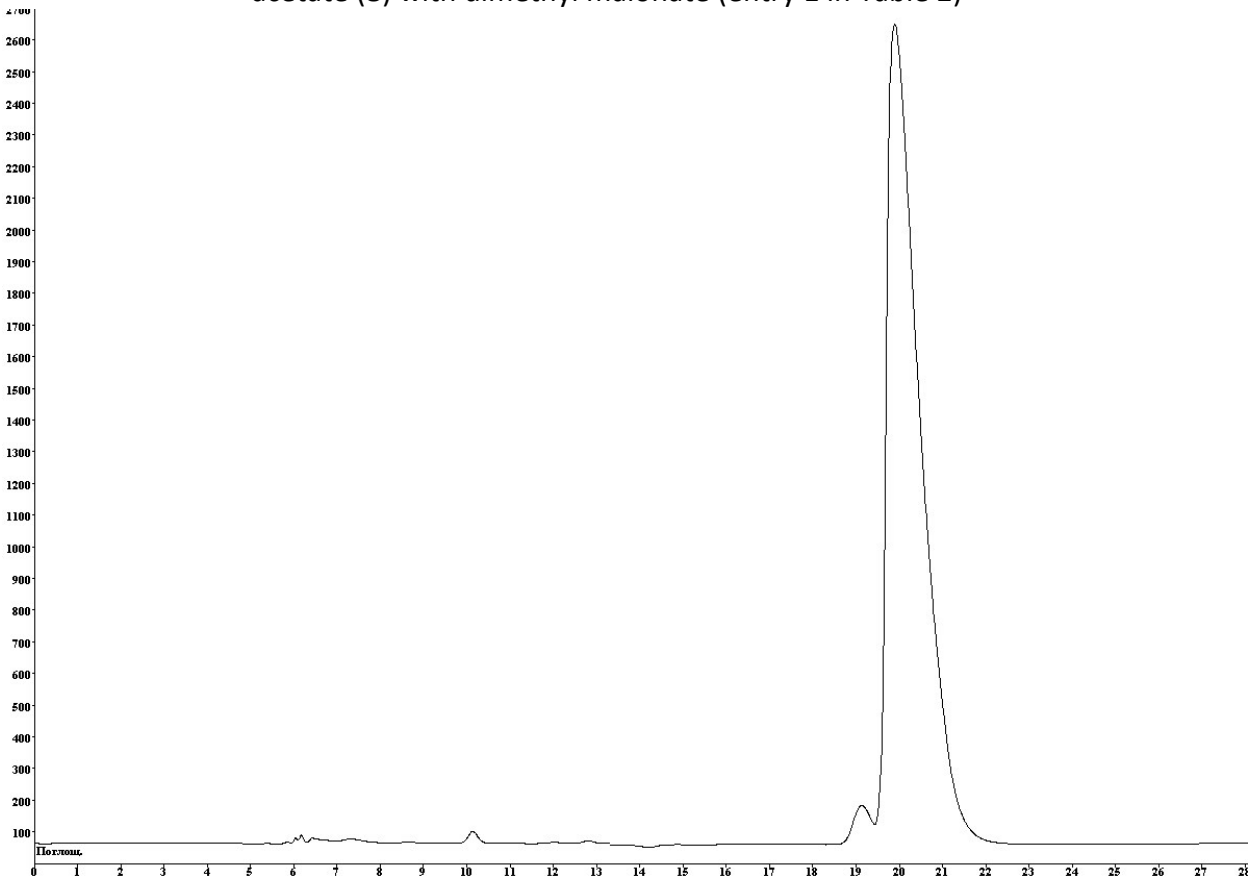
Chiral HPLC trace for the Pd-catalyzed asymmetric allylic sulfonylation of (*E*)-1,3-diphenylallyl acetate (**8**) with sodium *para*-toluene sulfinate (entry 3 in Table 1)



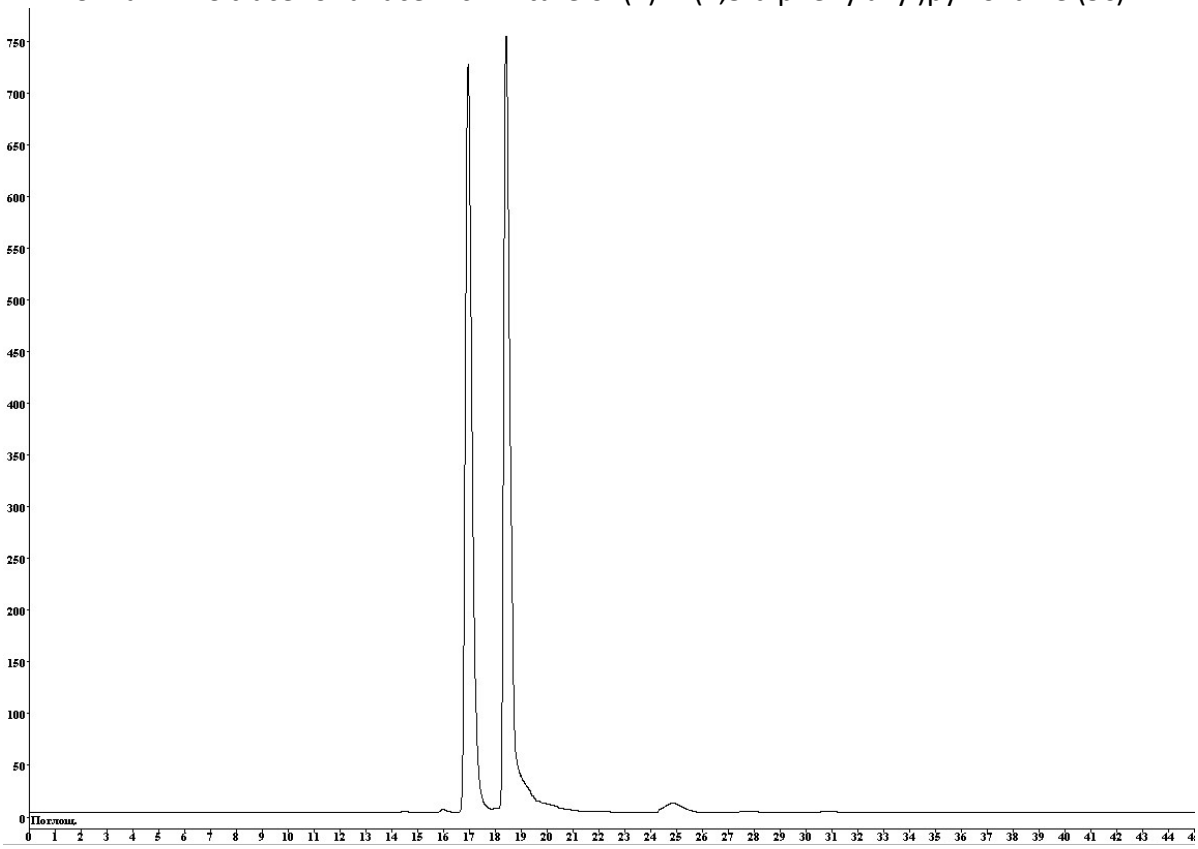
Chiral HPLC trace for a racemic mixture of (*E*)-dimethyl 2-(1,3-diphenylallyl)malonate (**9b**)



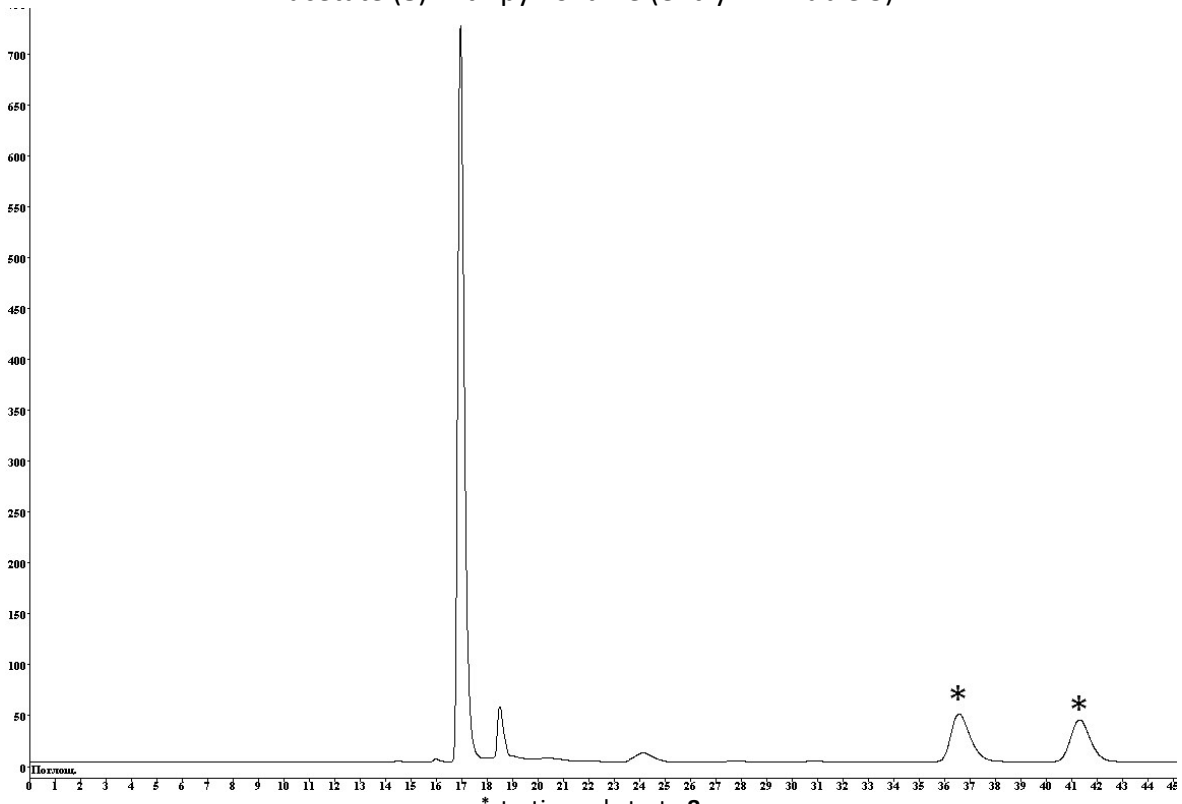
Chiral HPLC trace for the Pd-catalyzed asymmetric allylic alkylation of (*E*)-1,3-diphenylallyl acetate (**8**) with dimethyl malonate (entry 1 in Table 2)



Chiral HPLC trace for a racemic mixture of (*E*)-1-(1,3-diphenylallyl)pyrrolidine (**9c**)

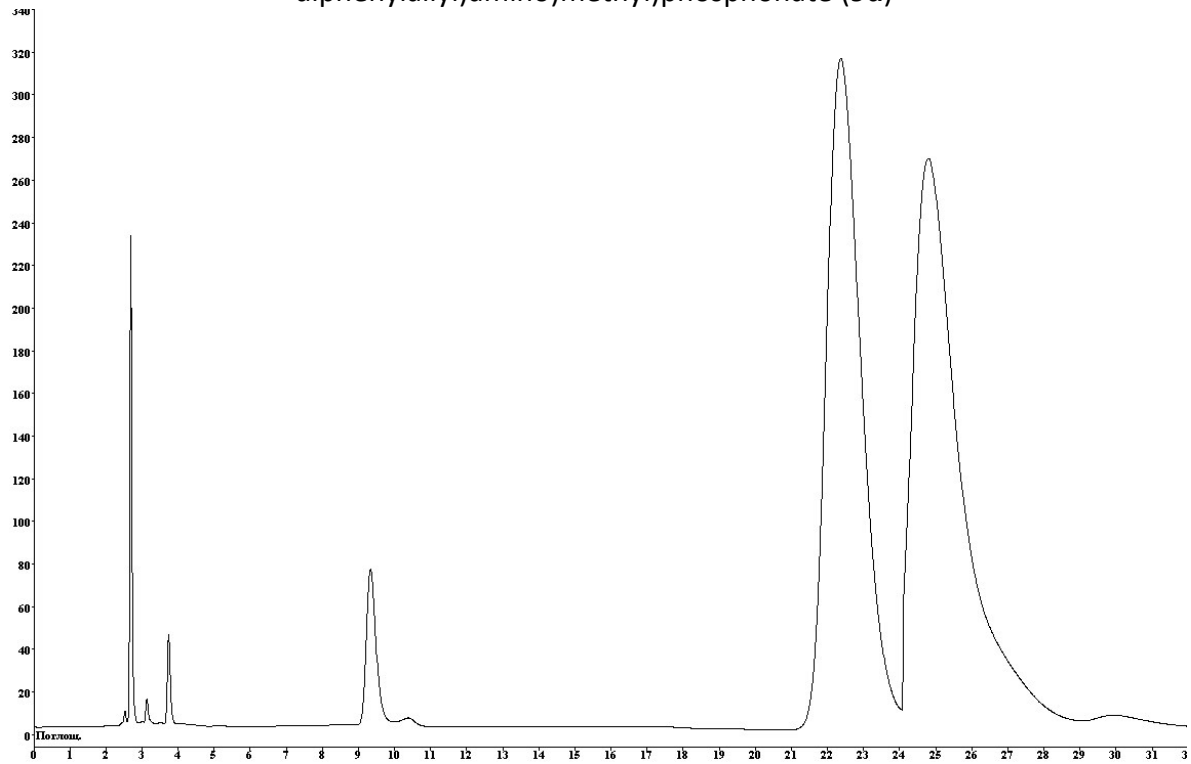


Chiral HPLC trace for the Pd-catalyzed asymmetric allylic amination of (*E*)-1,3-diphenylallyl acetate (**8**) with pyrrolidine (entry 7 in Table 3)

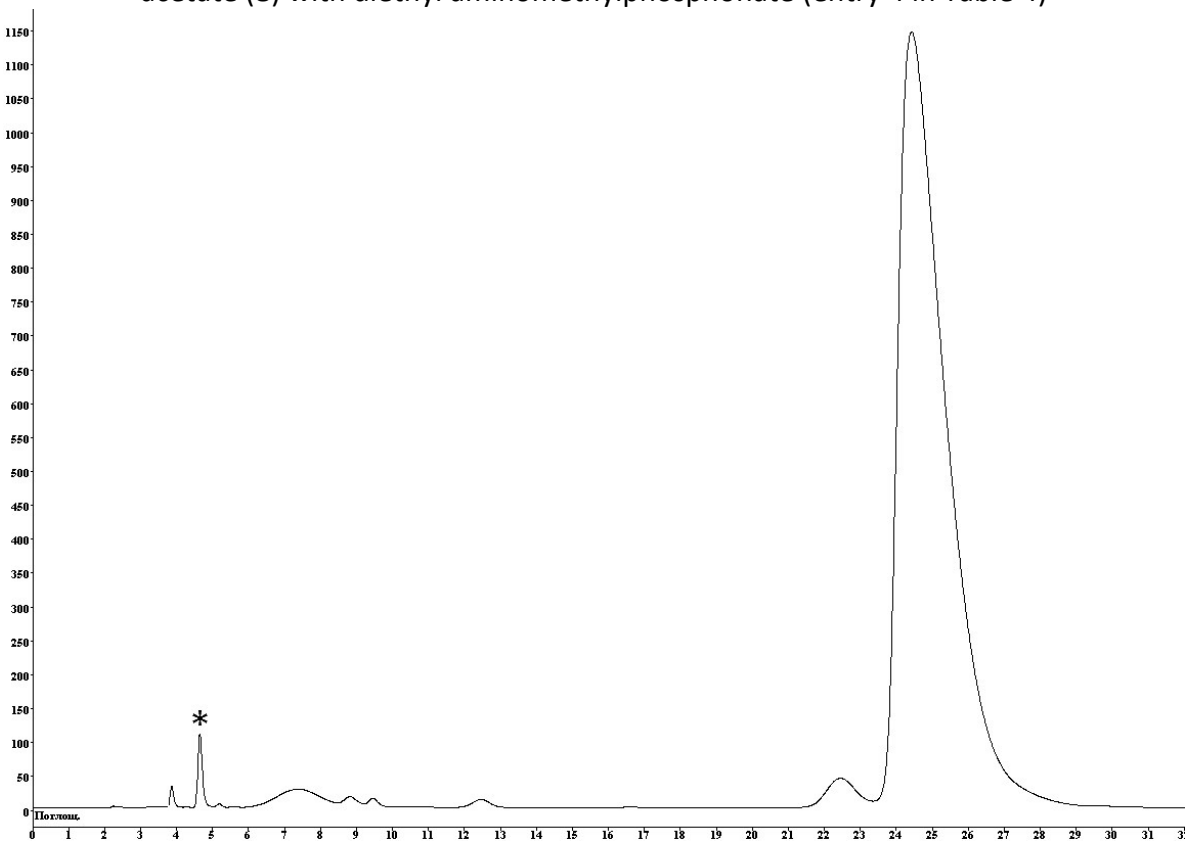


*starting substrate **8**

Chiral HPLC trace for a racemic mixture of diethyl (*E*)-(((1,3-diphenylallyl)amino)methyl)phosphonate (**9d**)

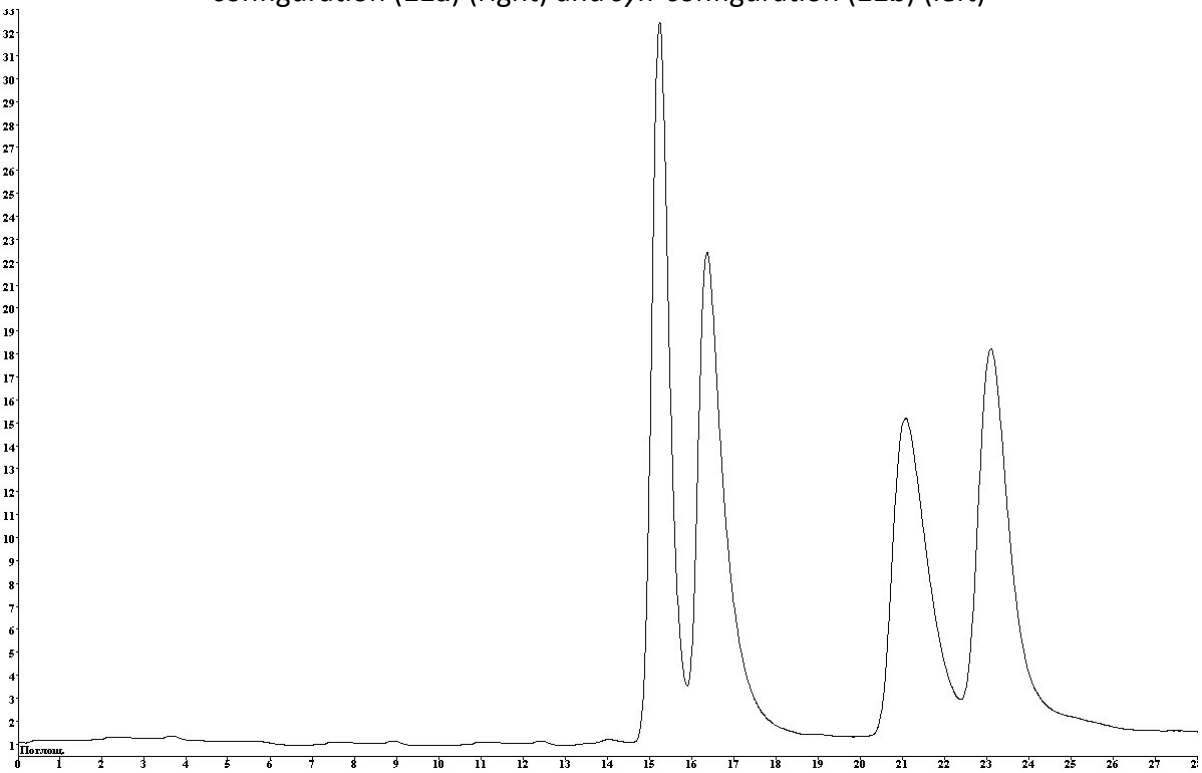


Chiral HPLC trace for the Pd-catalyzed asymmetric allylic amination of (*E*)-1,3-diphenylallyl acetate (**8**) with diethyl aminomethylphosphonate (entry 4 in Table 4)

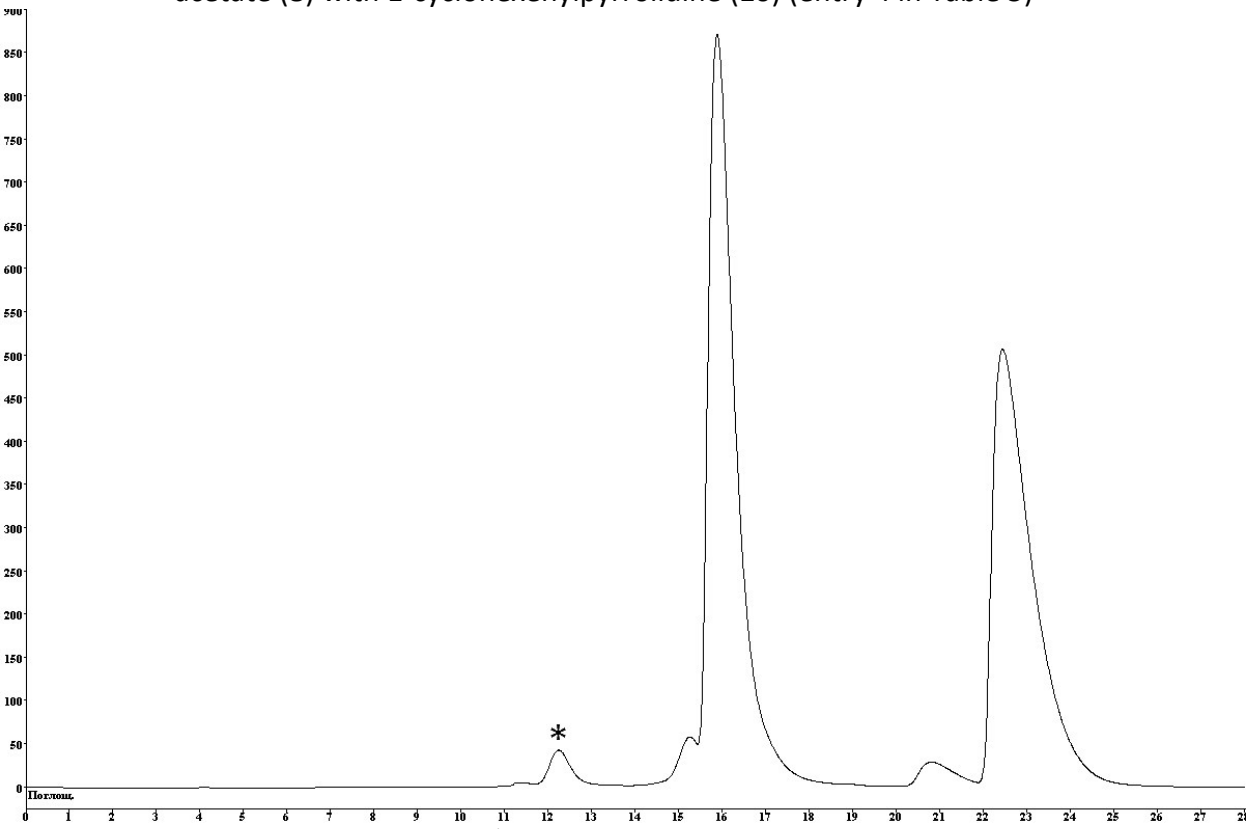


*starting substrate **8**

Chiral HPLC trace for a racemic mixture of (*E*)-2-(1,3-diphenylallyl)cyclohexanone of *anti*-configuration (**11a**) (right) and *syn*-configuration (**11b**) (left)

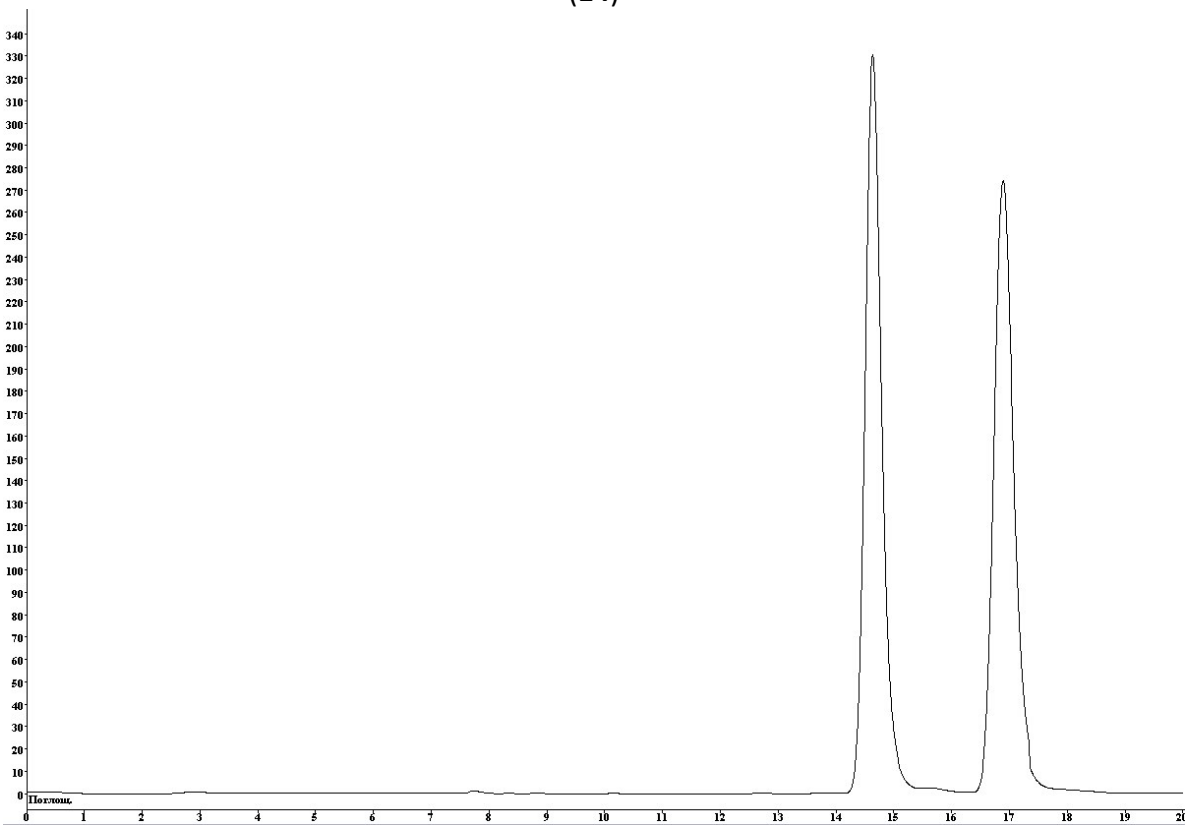


Chiral HPLC trace for the Pd-catalyzed asymmetric allylic alkylation of (*E*)-1,3-diphenylallyl acetate (**8**) with 1-cyclohexenylpyrrolidine (**10**) (entry 4 in Table 5)

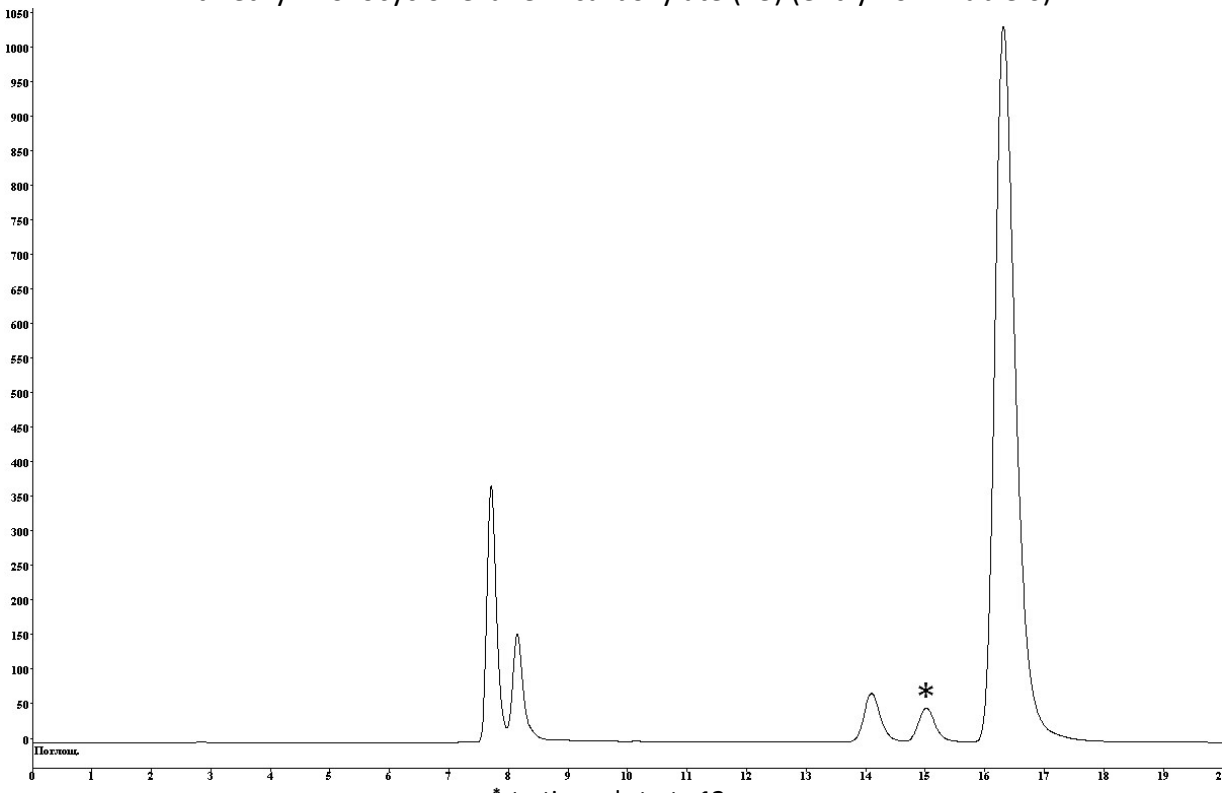


*starting substrate **8**

Chiral HPLC trace for a racemic mixture of ethyl 1-cinnamyl-2-oxocyclohexanecarboxylate (**14**)

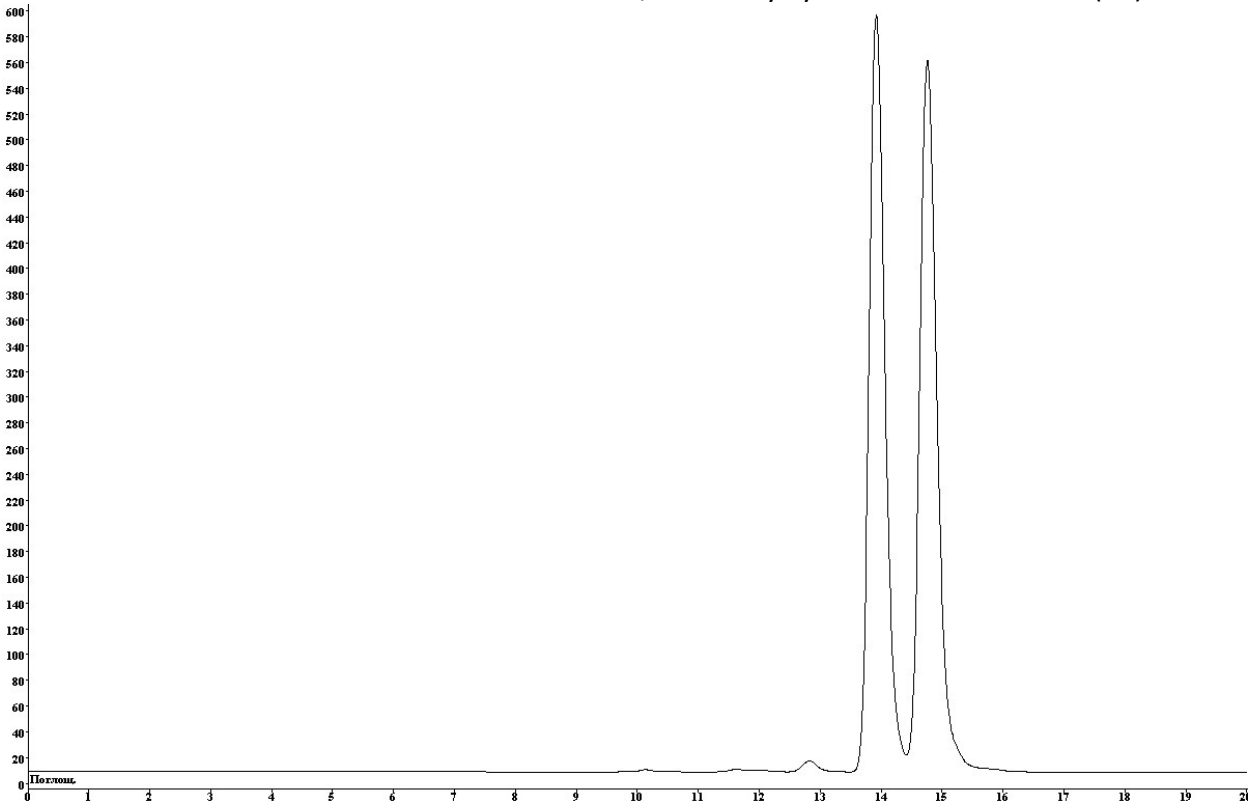


Chiral HPLC trace for the Pd-catalyzed asymmetric allylic alkylation of cinnamyl acetate (**12**) with ethyl 2-oxocyclohexane-1-carboxylate (**13**) (entry 10 in Table 6)

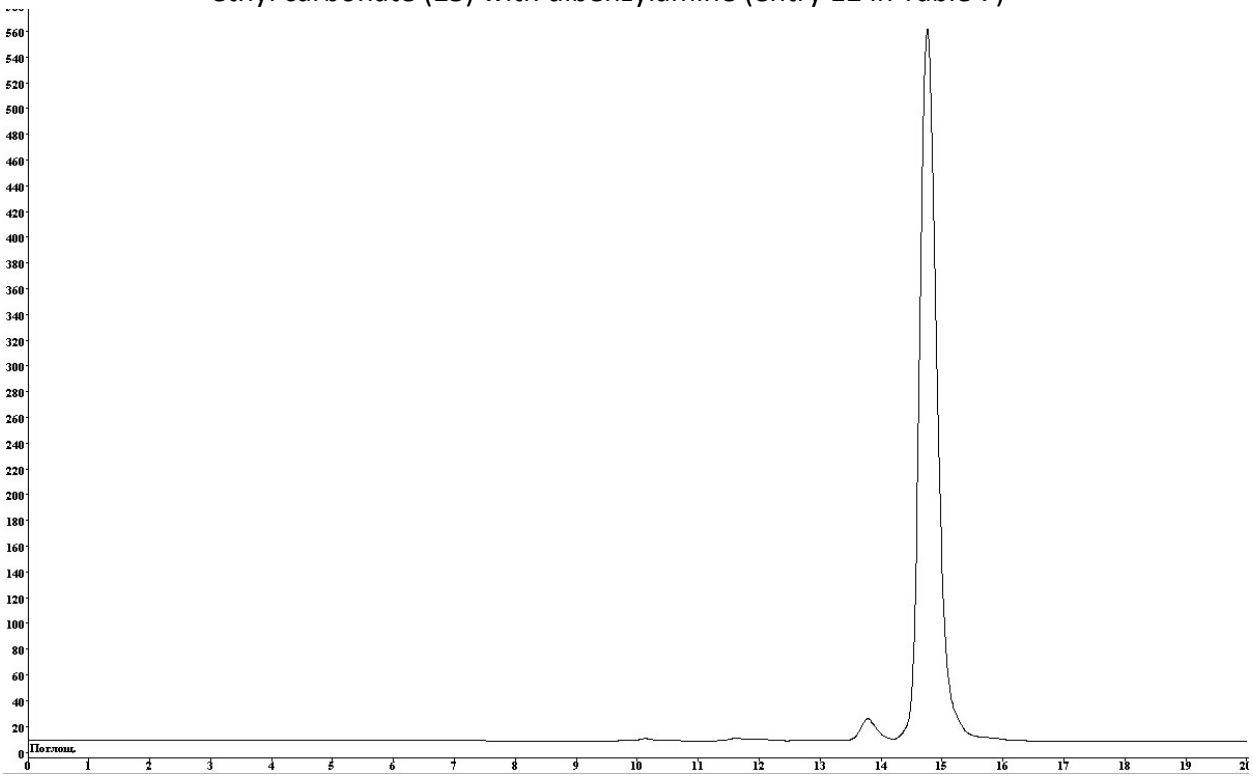


*starting substrate **12**

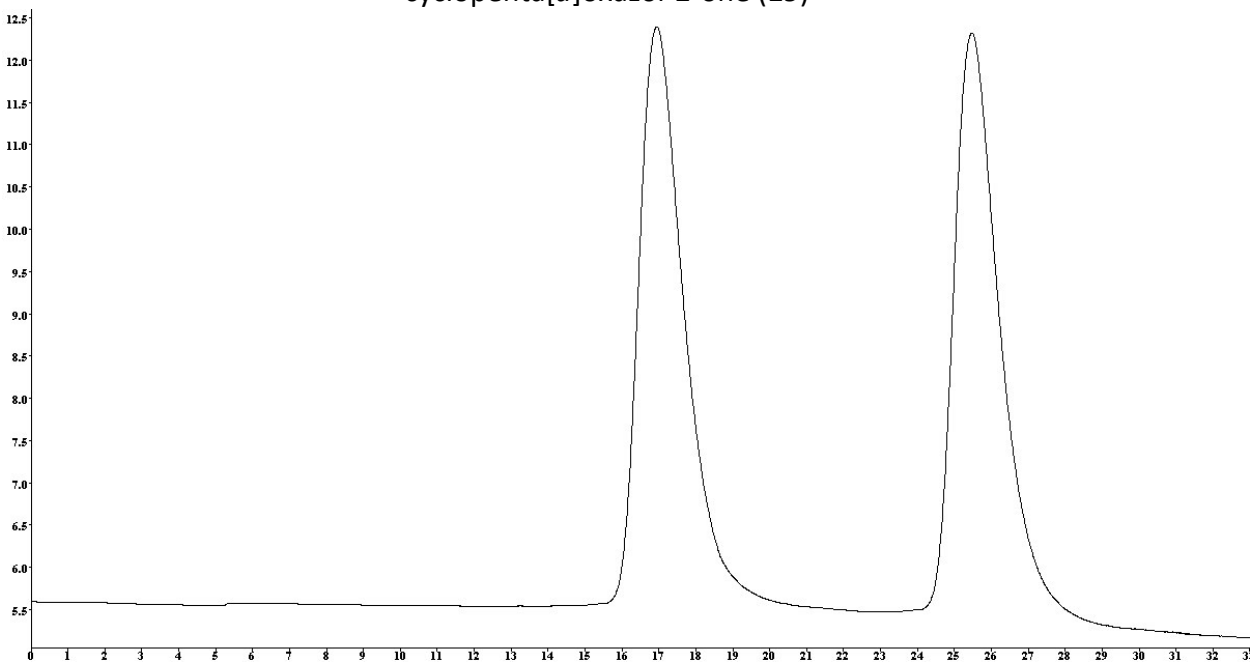
Chiral HPLC trace for a racemic mixture of *N*,*N*-dibenzylcyclohex-2-en-1-amine (**16**)



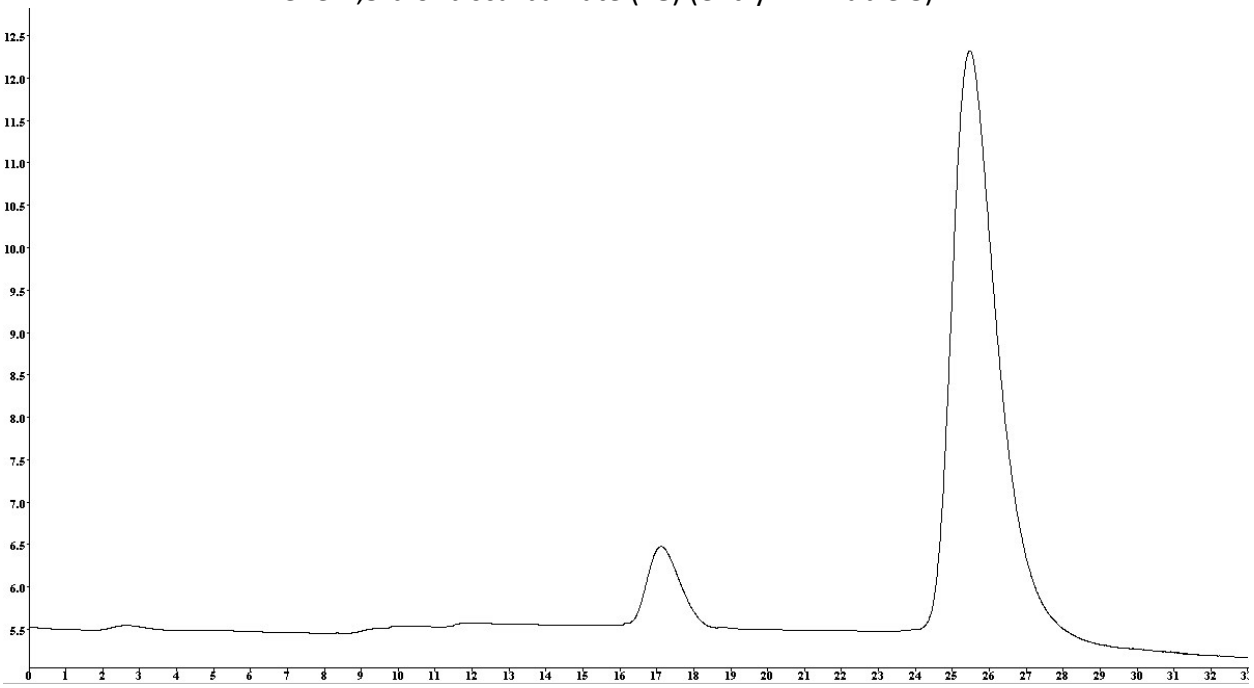
Chiral HPLC trace for the Pd-catalyzed asymmetric allylic amination of cyclohex-2-en-1-yl ethyl carbonate (**15**) with dibenzylamine (entry 12 in Table 7)



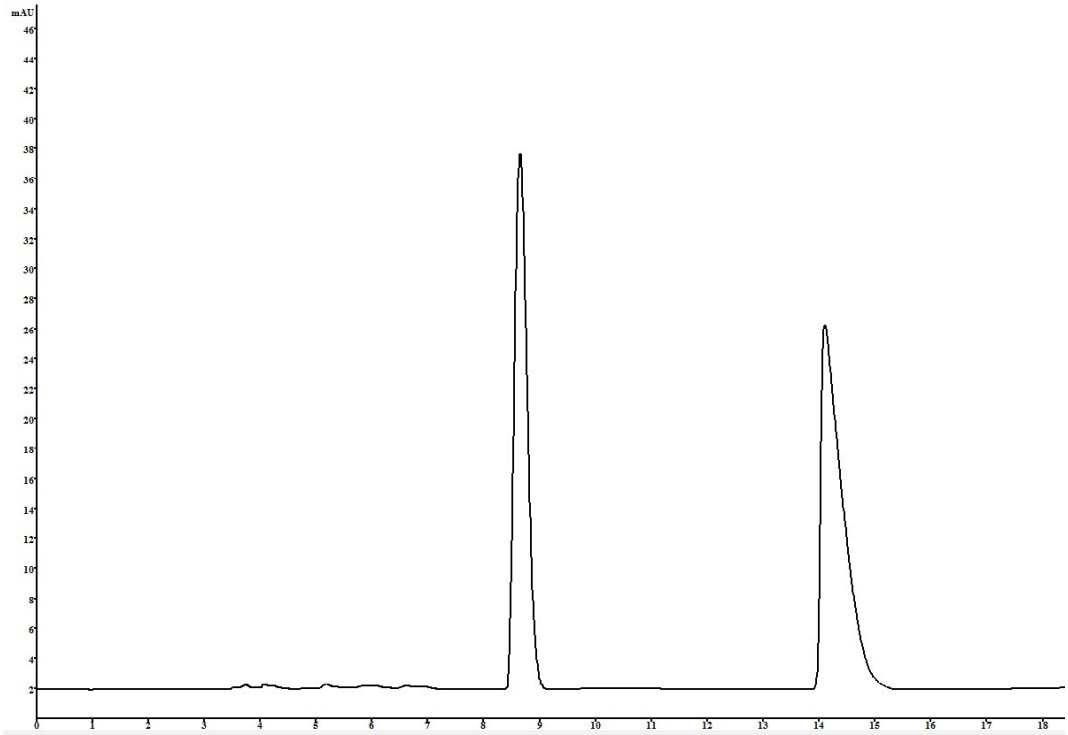
Chiral HPLC trace for a racemic mixture of 3-tosyl-3,3a,6,6a-tetrahydro-2*H*-cyclopenta[*d*]oxazol-2-one (**19**)



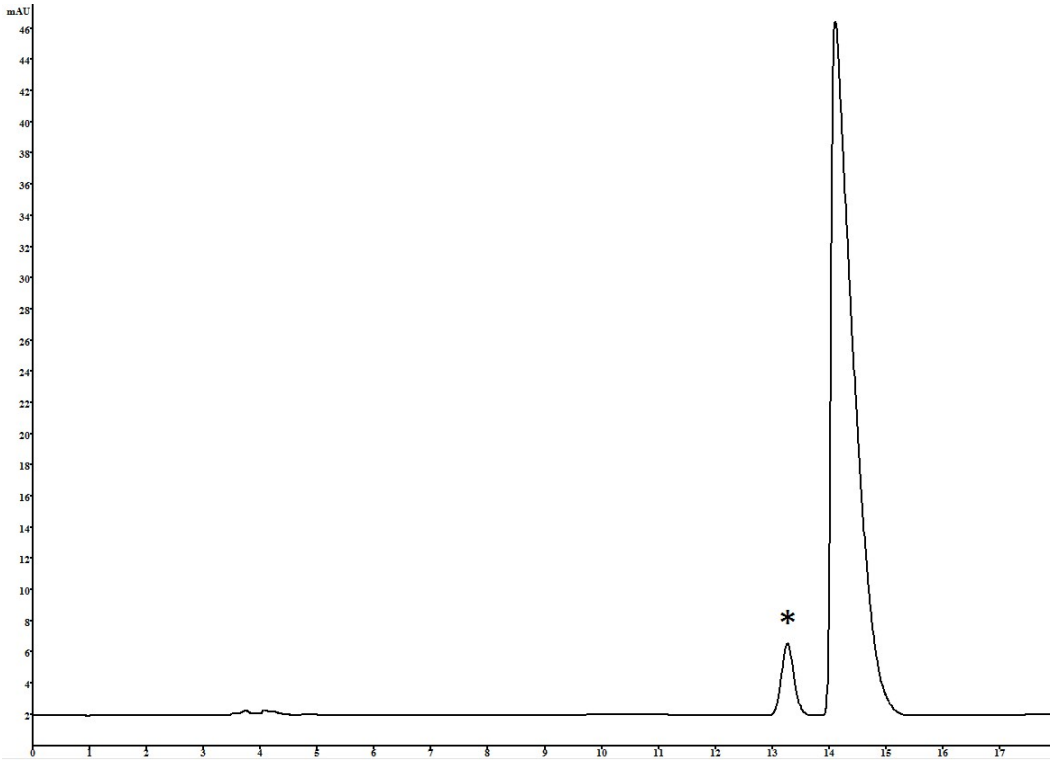
Chiral HPLC trace for the Pd-catalyzed desymmetrization of *N*,*N*′-ditosyl-*meso*-cyclopent-4-ene-1,3-diol biscarbamate (**18**) (entry 4 in Table 8)



Chiral HPLC trace for a racemic mixture of dimethyl 2-methylsuccinate (**21a**)

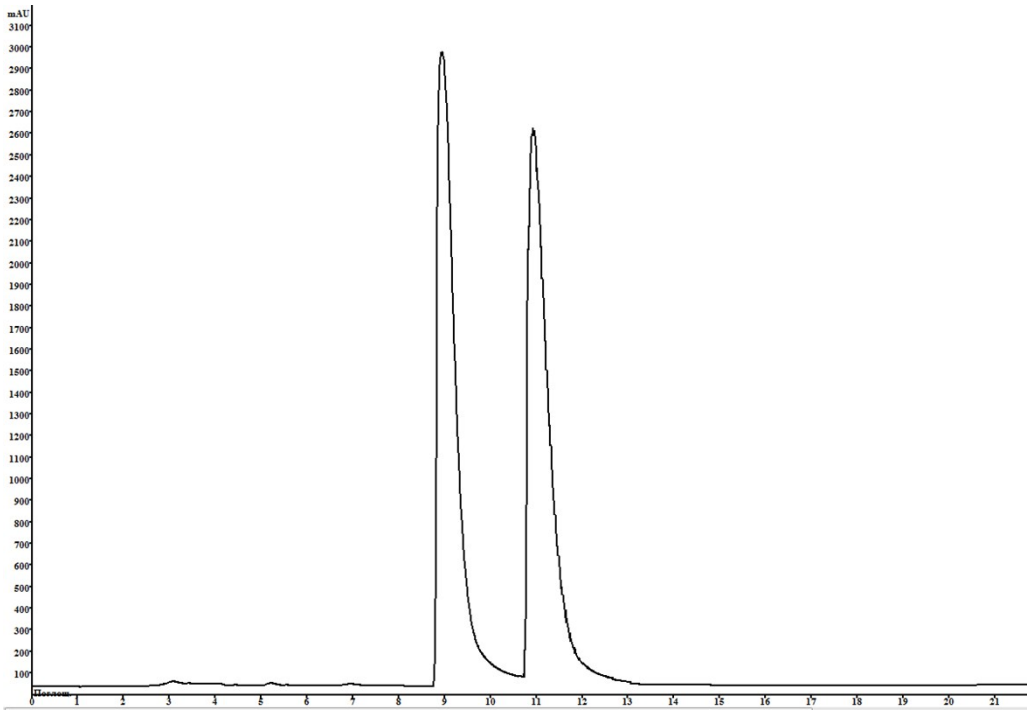


Chiral HPLC trace for the Rh-catalyzed asymmetric hydrogenation of dimethyl itaconate (**20a**) (entry 1 in Table 9).

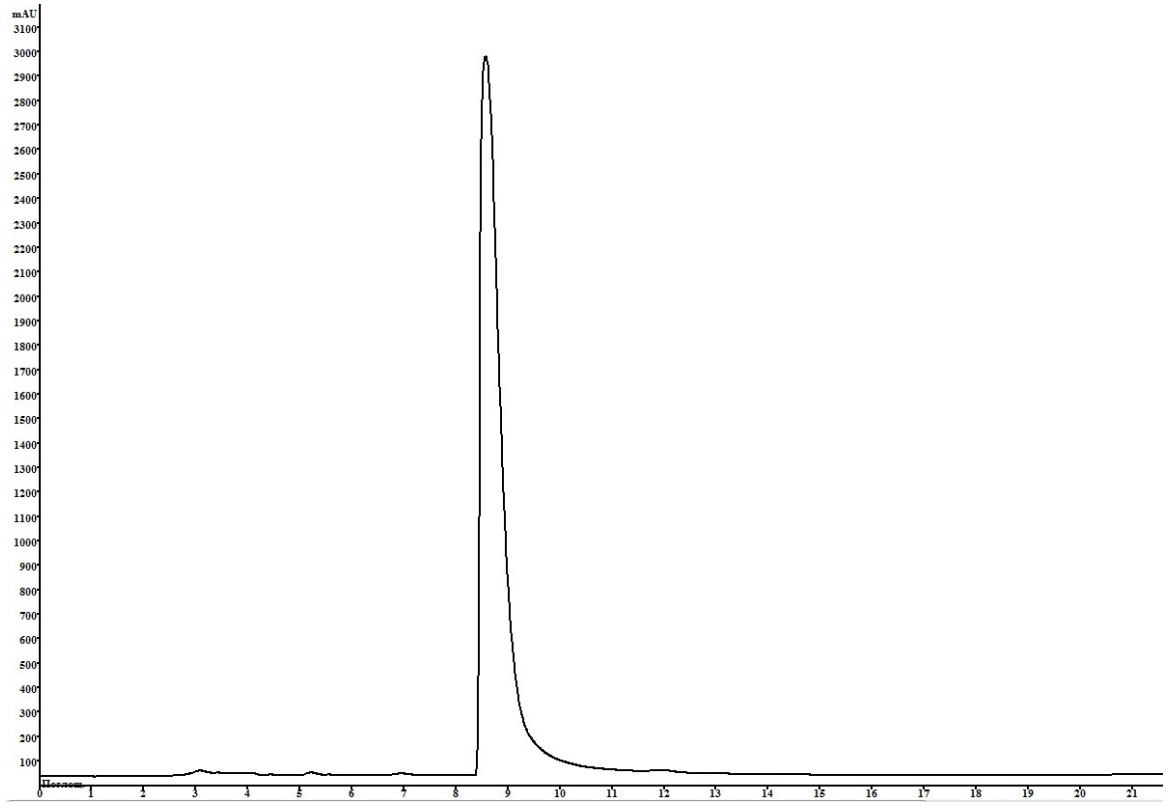


*starting substrate **20a**

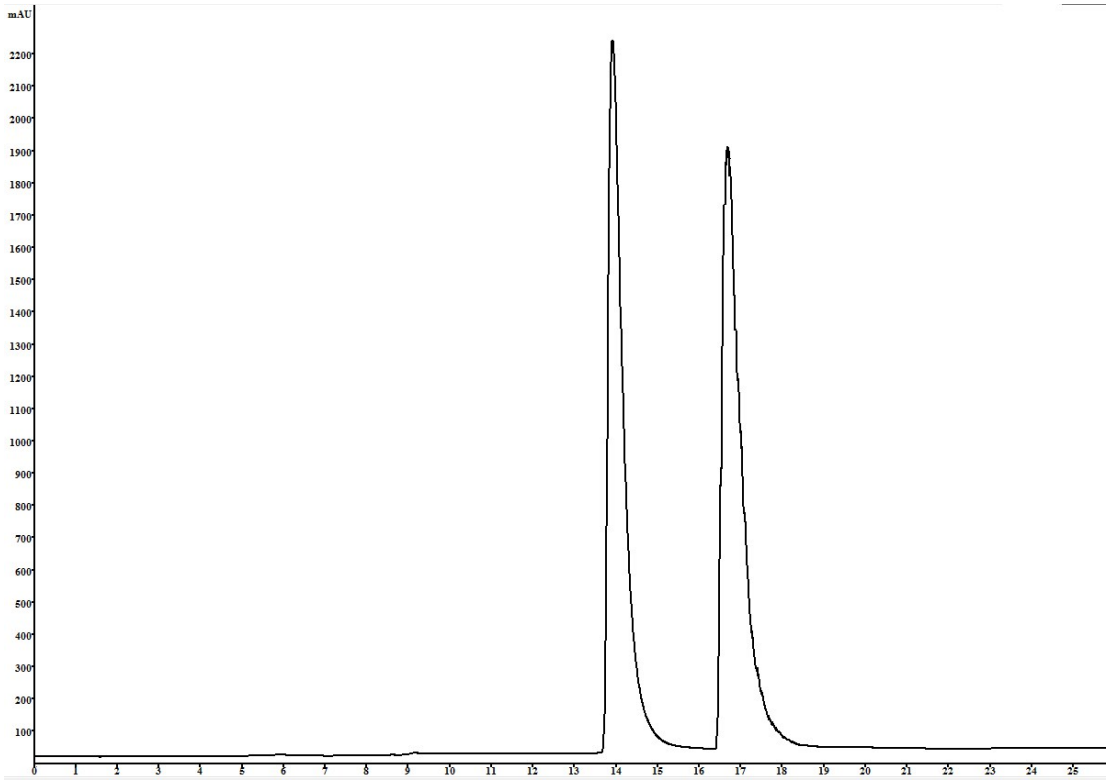
Chiral HPLC trace for a racemic mixture of methyl 2-acetamido-3-phenylpropanoate (**21b**)



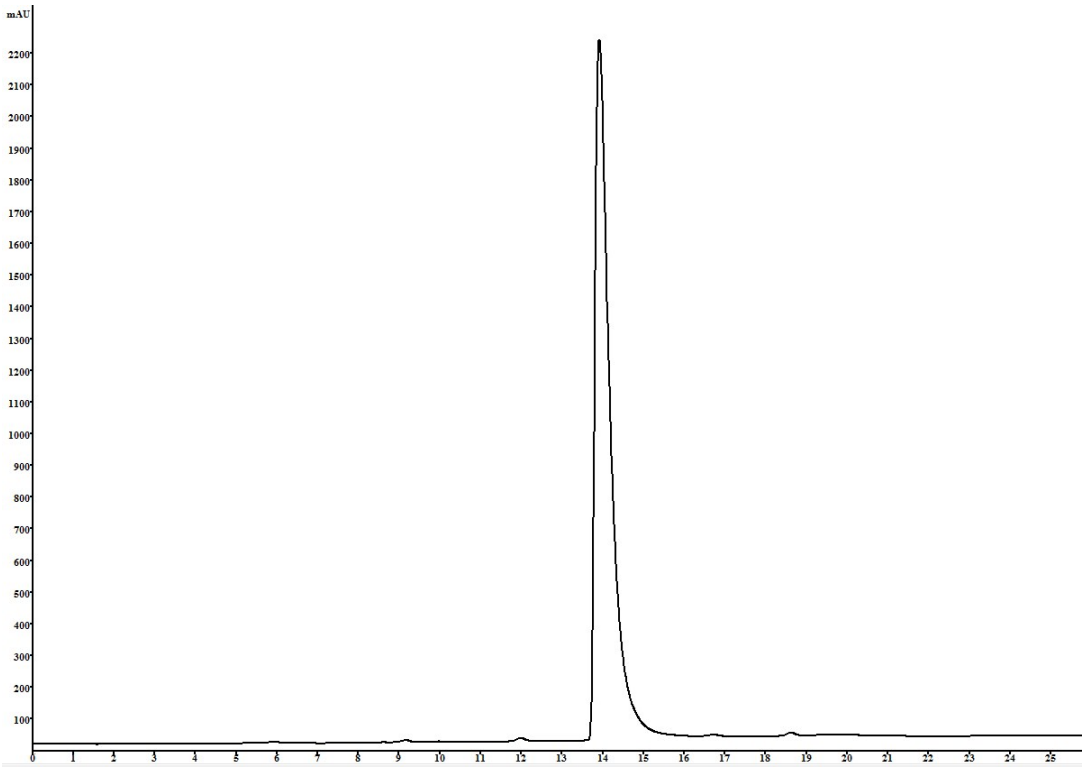
Chiral HPLC trace for the Rh-catalyzed asymmetric hydrogenation of methyl (*Z*)-2-acetamido-3-phenylacrylate (**20b**) (entry 6 in Table 9).



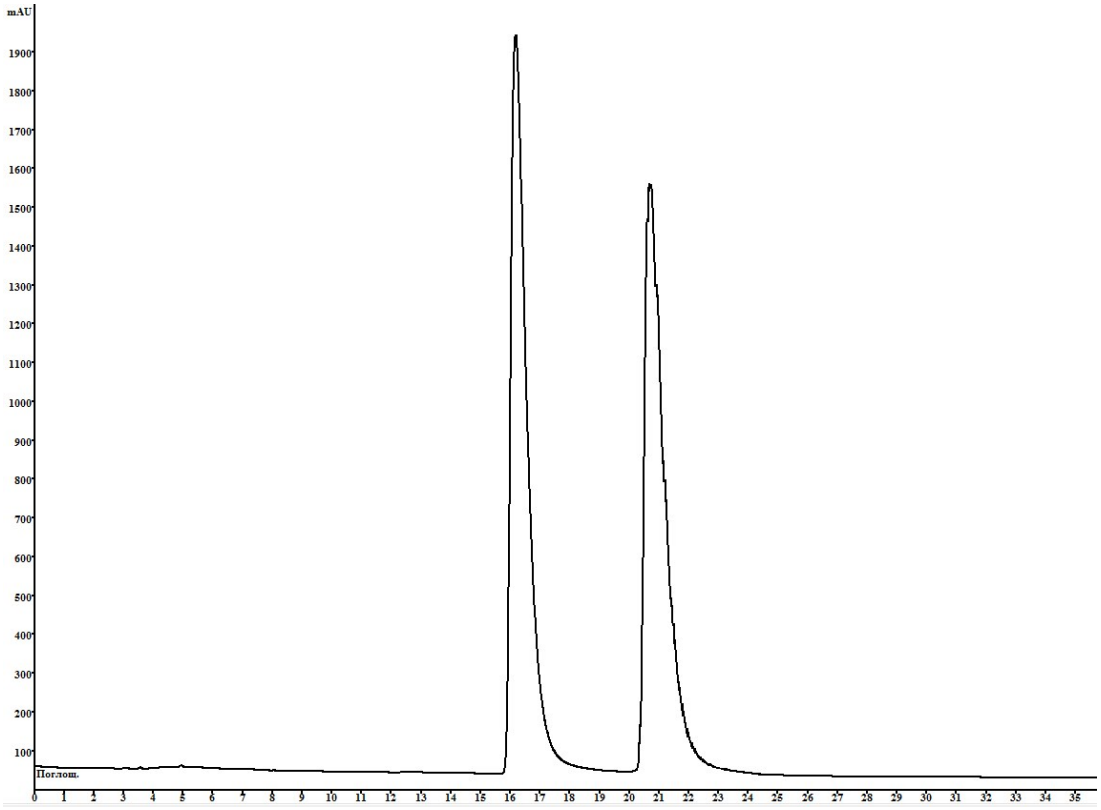
Chiral HPLC trace for a racemic mixture of methyl 2-acetamido-3-(4-fluorophenyl)propanoate (**21c**)



Chiral HPLC trace for the Rh-catalyzed asymmetric hydrogenation of methyl (*Z*)-2-acetamido-3-(4-fluorophenyl)acrylate (**20c**) (entry 11 in Table 9).



Chiral HPLC trace for a racemic mixture of methyl 2-acetamido-3-(naphthalen-2-yl)propanoate (**21d**)



Chiral HPLC trace for the Rh-catalyzed asymmetric hydrogenation of methyl (*Z*)-2-acetamido-3-(naphthalen-2-yl)acrylate (**20d**) (entry 16 in Table 9).