SUPPORTING INFORMATION

Diastereomeric *P,P**-mixed-donor phosphine-diamidophosphites with an oxalamide backbone as bridging ligands

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GENERAL

$^{31}P\{^1H\}$, $^{13}C\{^1H\}$ and ^1H NMR spectra were recorded with Bruker Avance 600 (242.9 MHz for $^{31}P\{^1H\}$, 150.9 MHz for $^{13}C\{^1H\}$ and 600.1 MHz for ^1H) instrument. ^1H and $^{13}C\{^1H\}$ NMR signals were attributed using DEPT, $^1H,^1H$ – COSY, $^{13}C,^1H$ – HSQC techniques. The chemical shifts are referenced to residual solvent peaks (^1H, $^{13}C\{^1H\}$ NMR) or H_3PO_4 85% as external standard ($^{31}P\{^1H\}$ NMR). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), All coupling constants (*J* values) were reported in Hertz (Hz). HPLC analyses were performed on a Stayer instrument using Kromasil 5-CelluCoat and Daicel Chiralcel OD-H columns. Optical rotations were measured with an Atago AP-300 polarimeter. Elemental analyses were performed on a CHN-microanalyzer Carlo Erba EA1108 CHNS-O. High-resolution mass spectra were recorded on a LCMS-9030 device (Shimadzu, Japan) by electrospray ionization mass spectrometry (ESI-MS). Measurements were carried out in positive ion mode; samples were dissolved in CH_2Cl_2 and injected into the mass-spectrometer chamber from an HPLC system LC-40 Nexera (Shimadzu, Japan). The following parameters were used: capillary voltage 4.0 kV; mass scanning range: m/z 100–1000; external calibration with solution NaI in $MeOH/H_2O$; drying and heating gases (nitrogen) (each 10 L/min); nebulizing gas (nitrogen) (3 L/min); interface temperature: 250C; flow rate 100% MeOH or AcN 0.4 mL/min. Molecular ions in the spectra were analyzed and matched with the appropriately calculated *m*/*z* and isotopic profiles in the LabSolutions v.5.114 program. The geometric structures of the complexes were optimized using the DFT method with the B3LYP functional and 3-21G* basis set, while the electrons of the rhodium atom were rendered by the LaNL2DZ basis set. Calculations of the structures for both mononuclear and dinuclear complexes were carried out in the solution of dichloromethane. The energies of the mononuclear and binuclear forms of the ligands were calculated using the B3LYP functional with a larger 6-31G(d,p) basis set, in solution of dichloromethane.

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. 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: (5*S*)-2-chloro-3-phenyl-1,3-diaza-2 phosphabicyclo[3.3.0]octane and (5*R*)-2-chloro-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane ((S_C)-**4** and (R_C)-**4**),[1] $[Pd(allyl)Cl]_2$ and (*E*)-1,3-diphenylallyl acetate (**5**),[2] ethyl 2-acetamido-3-oxobutanoate,[3] $[Rh(Cod)_2]BF_4$,[4] methyl (*Z*)-2-acetamido-3-phenylacrylate (**12b**)[5] and methyl (*Z*)-2-acetamido-3-(4-fluorophenyl)acrylate (**12c**).[6]

Pd-catalyzed allylic sulfonylation of (*E*)-1,3-diphenylallyl acetate (**5**) with sodium *para*-toluenesulfinate, its amination with pyrrolidine and alkylation with dimethyl malonate, allylic alkylation of cinnamyl acetate (**7**) with ethyl 2-oxocyclohexane-1-carboxylate (**8**) and ethyl 2-acetamido-3-oxobutanoate (**10**) as well as Rh-catalyzed hydrogenation of **12a-c** were performed according to the appropriate procedures.[7]

2-(Diphenylphosphaneyl)ethan-1-amine (**1**), ethyl 2-chloro-2-oxoacetate, (*S*)-tert-leucinol, sodium *para*-toluenesulfinate, dimethyl malonate, BSA (*N*,*O*-bis(trimethylsilyl)acetamide), cinnamyl acetate (**7**), ethyl 2-oxocyclohexane-1-carboxylate (**8**) and dimethyl itaconate (**12a**) were purchased from Aldrich and Acros Organics.

EXPERIMENTAL SECTION

Procedure for the preparation of amidophosphine 2: A solution of ethyl 2-chloro-2-oxoacetate (1.40 mL, 12.5 mmol) in CH_2Cl_2 (10 mL) was added dropwise at - 30 °C over 10 min to a vigorously stirred solution of 2-(diphenylphosphaneyl)ethan-1-amine (**1**) (2.29 g, 10.0 mmol) and Et_3N (1.81 mL, 13.0 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was brought to 20°C, allowed to stir overnight, diluted with CH_2Cl_2 (80 mL), washed with a saturated aqueous $NaHCO_3$ solution (2 x 30 mL) and brine (30 mL). The organic phase was dried over Na_2SO_4, filtered and concentrated under reduced pressure (40 Torr). The obtained residue was dried in vacuum (1 Torr, 12 h).

Ethyl 2-((2-(diphenylphosphaneyl)ethyl)amino)-2-oxoacetate (**2**): Yellowish oil, solidifying upon standing, yield 3.19 g (97 %). ^{1}H NMR (600.1 MHz, $CDCl_3$, 25^{o}C): 1.36 (t, ^3J(H,H) = 7.1, 3H; C$\underline{H}_3$CH$_2$), 2.34-2.37 (m, 2H; CH$_2$P), 3.44-3.52 (m, 2H; C$\underline{H}_2$NH), 4.31 (q, ^3J(H,H) = 7.2, 2H; CH$_3$C$\underline{H}_2$), 7.22-7.46 (m, 11H; CH(Ph) and CH$_2$N$\underline{H}$) ppm. ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$, 25^{o}C): 14.04 (s; $\underline{C}$H$_3$CH$_2$), 28.03 (d, ^1J(C,P) = 14.1; CH$_2$P), 37.38 (d, ^2J(C,P) = 21.7; CH$_2$NH), 63.17 (s; CH$_3\underline{C}$H$_2$), 128.71 (d, ^3J(C,P) = 6.9; CH(Ph)), 129.01 (s; CH(Ph)), 132.75 (d, ^2J(C,P) = 19.0; CH(Ph)), 137.39 (d, ^1J(C,P) = 11.9; C(Ph)), 156.58 (s; CO), 160.54 (s; CO) ppm. ^{31}P{^{1}H} NMR (242.9 MHz, $CDCl_3$, 25^{o}C): -21.39 (s) ppm. $C_{18}H_{20}NO_3P$ (329.12): calcd. C, 65.65; H, 6.12; N, 4.25; found C, 65.85; H, 6.19; N, 4.18.

Procedure for the preparation of hydroxyphosphine 3: To an intensively stirred solution of reagent **2** (2.96 g, 9 mmol) in toluene (15 mL), (*S*)-tert-leucinol was added in one portion (1.06 g, 9 mmol) at 20°C. The resulting mixture was heated to reflux, refluxed for 12 h, and cooled to 20°C. The solvent was removed under reduced pressure (40 Torr), the resulting product **3** was purified by column chromatography on SiO_2 (toluene/Et_3N 9/1).

(*S*)-N^1-(2-(diphenylphosphaneyl)ethyl)-N^2-(1-hydroxy-3,3-dimethylbutan-2-yl)oxalamide (**3**): White powder, yield 1.95 g (54 %). ^1H NMR (600.1 MHz, $CDCl_3$, 25°C): 0.96 (s, 9H; $CH_3(^tBu)$), 2.31 (br, 1H; $CH_2O\underline{H}$), 2.32-2.36 (m, 2H; CH_2P), 3.39-3.47 (m, 2H; $C\underline{H}_2NH$), 3.60 (dd, $^2J(H,H)$ = 11.3, $^3J(H,H)$ = 8.1, 1H; $C\underline{H}_2OH$), 3.75 (ddd, $^3J(H,H)$ = 10.0, $^3J(H,H)$ = 8.1, $^3J(H,H)$ = 3.3, 1H; $C\underline{H}NH$), 3.86 (dd, $^2J(H,H)$ = 11.3, $^3J(H,H)$ = 3.3, 1H; $C\underline{H}_2OH$), 7.32-7.37 (m, 6H; CH(Ph)), 7.41-7.45 (m, 4H; CH(Ph)), 7.58 (d, $^3J(H,H)$ = 9.9, 1H; $CHN\underline{H}$), 7.74 (br, 1H; $CH_2N\underline{H}$) ppm. $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$, 25°C): 26.95 (s; $CH_3(^tBu)$), 28.28 (d, $^1J(C,P)$ = 14.0; CH_2P), 33.85 (s; $C(^tBu)$), 37.29 (d, $^2J(C,P)$ = 23.2; CH_2NH), 60.76 (s; CHNH), 62.58 (s; CH_2OH), 128.77 (d, $^3J(C,P)$ = 6.9; CH(Ph)), 129.08 (s; CH(Ph)), 132.81 (d, $^2J(C,P)$ = 19.0; CH(Ph)), 137.48 (d, $^1J(C,P)$ = 13.7; C(Ph)), 159.83 (s; CO), 160.68 (s; CO) ppm. $^{31}P\{^1H\}$ NMR (242.9 MHz, $CDCl_3$, 25°C): -21.39 (s) ppm. $C_{22}H_{29}N_2O_3P$ (400.19): calcd. C, 65.98; H, 7.30; N, 7.00; found C, 66.11; H, 7.34; N, 7.05.

General procedure for the preparation of ligands: The reagent **3** (0.80 g, 2 mmol) was added at −70 °C in one portion to a vigorously stirred solution of the appropriate phosphorylating reagent **4a** or **4b** (0.48 g, 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).

N^1-((*S*)-3,3-dimethyl-1-(((1*R*,3a*S*)-2-phenylhexahydro-1*H*-pyrrolo[1,2-*c*][1,3,2]diazaphosphol-1-yl)oxy)butan-2-yl)-N^2-(2-(diphenylphosphaneyl)ethyl)oxalamide (**5a**): Colorless oil, solidifying upon standing, yield 0.79 g (65 %). ^1H NMR (600.1 MHz, $CDCl_3$, 25°C): 0.92 (s, 9H; $CH_3(^tBu)$), 1.57-1.66 (m, 1H; $C(6)H_2$)[a], 1.68-1.77 (m, 1H; $C(7)H_2$), 1.79-1.89 (m, 1H; $C(7)H_2$), 2.01-2.09 (m, 1H; $C(6)H_2$), 2.32-2.35 (m, 2H; CH_2P), 3.14-3.22 (m, 2H; $C(4)H_2$ and $C(8)H_2$), 3.42 (dtd, $^3J(H,P)$ = 10.0, $^3J(H,H)$ = 7.9, $^3J(H,H)$ = 6.0, 2H; $C\underline{H}_2NH$), 3.48-3.56 (m, 1H;

C(8)H_2), 3.60-3.65 (m, 1H; CH_2O), 3.69-3.74 (m, 1H; C(4)H_2), 3.71-3.77 (m, 1H; C<u>H</u>NH), 3.80 (dt, ^2J(H,H) = 10.1, ^3J(H,H) = ^3J(H,P*) = 5.8, 1H; CH_2O), 4.08-4.15 (m, 1H; C(5)H), 6.77 (tt, ^3J(H,H) = 7.3, ^4J(H,H) = 1.1, 1H; C(12)H), 6.96-6.99 (m, 2H; C(10)H and C(14)H), 7.17-7.22 (m, 2H; C(11)H and C(13)H), 7.33-7.38 (m, 6H; CH(Ph)), 7.42-7.47 (m, 4H; CH(Ph)), 7.53 (t, ^3J(H,H) = 6.0, 1H; CH_2N<u>H</u>), 7.59 (d, ^3J(H,H) = 10.0, 1H; CHN<u>H</u>) ppm. $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$, 25°C): 26.27 (d, ^3J(C,P*) = 3.8; C(7)H_2), 27.08 (s; CH_3(^{t}Bu)), 28.31 (d, ^1J(C,P) = 14.2; CH_2P), 32.21 (s; C(6)H_2), 34.45 (s; C(^{t}Bu)), 37.17 (d, ^2J(C,P) = 23.7; CH_2NH), 48.77 (d, ^2J(C,P*) = 38.2; C(8)H_2), 55.11 (d, ^2J(C,P*) = 6.8; C(4)H_2), 57.76 (d, ^3J(C,P*) = 2.9; CHNH), 60.94 (d, ^2J(C,P*) = 4.3; CH_2O), 63.43 (d, ^2J(C,P*) = 8.6; C(5)H), 114.90 (d, ^3J(C,P*) = 11.5; C(10)H and C(14)H), 119.10 (s; C(12)H), 128.72 (d, ^3J(C,P) = 6.9; CH(Ph)), 129.00 (s; CH(Ph)), 129.24 (s; C(11)H and C(13)H), 132.78 (d, ^2J(C,P) = 19.0; CH(Ph)), 137.56 (d, ^1J(C,P) = 12.3; C(Ph)), 137.59 (d, ^1J(C,P) = 12.3; C(Ph)), 145.56 (d, ^2J(C,P*) = 16.1; C(9)), 159.67 (s; CO), 159.80 (s; CO) ppm. $^{31}P\{^1H\}$ NMR (242.9 MHz, $CDCl_3$, 25°C): -21.33 (s; P), 123.46 (s; P*) ppm. $C_{33}H_{42}N_4O_3P_2$ (604.27): calcd. C, 65.55; H, 7.00; N, 9.27; found C, 65.71; H, 6.94; N, 9.15.

[a] See Figure S1 for the carbon-numbering scheme.

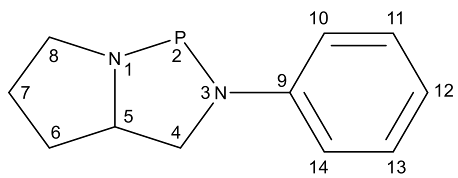

Figure S1 Carbon-numbering scheme for the phenylhexahydropyrrolo[1,2-c][1,3,2]diazaphospholidine core.

N[1]-((*S*)-3,3-dimethyl-1-(((1*S*,3a*R*)-2-phenylhexahydro-1*H*-pyrrolo[1,2-*c*][1,3,2]diazaphosphol-1-yl)oxy)butan-2-yl)-*N*[2]-(2-(diphenylphosphaneyl)ethyl)oxalamide (**5b**): Colorless oil, solidifying upon standing, yield 0.83 g (69 %). ^1H NMR (600.1 MHz, $CDCl_3$, 25°C): 0.90 (s, 9H; CH_3(^{t}Bu)), 1.57-1.62 (m, 1H; C(6)H_2)[a], 1.69-1.76 (m, 1H; C(7)H_2), 1.78-1.84 (m, 1H; C(7)H_2), 1.97-2.03 (m, 1H; C(6)H_2), 2.32-2.40 (m, 2H; CH_2P), 3.15-3.21 (m, 2H; C(4)H_2 and C(8)H_2), 3.41-3.48 (m, 2H; C<u>H</u>$_2$NH), 3.52-3.57 (m, 1H; C(8)H_2), 3.60 (dt, ^2J(H,H) = 10.7, ^3J(H,H) = ^3J(H,P*) = 5.3, 1H; CH_2O), 3.72-3.75 (m, 1H; C(4)H_2), 3.75-3.78 (m, 1H; C<u>H</u>NH), 3.81-3.85 (m, 1H; CH_2O), 4.03-4.08 (m, 1H; C(5)H), 6.82 (t, ^3J(H,H) = 7.2, 1H; C(12)H), 6.98-7.00 (m, 2H; C(10)H and C(14)H), 7.22-7.24 (m, 2H; C(11)H and C(13)H), 7.34-7.38 (m, 6H; CH(Ph)), 7.44-7.47 (m, 4H; CH(Ph)), 7.62-7.64 (m, 1H; CH_2N<u>H</u>), 7.63-7.65 (m, 1H; CHN<u>H</u>) ppm. $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$, 25°C): 26.30 (d, ^3J(C,P*) = 3.7; C(7)H_2), 27.16 (s; CH_3(^{t}Bu)), 28.41 (d, ^1J(C,P) = 14.0; CH_2P), 32.29 (s; C(6)H_2), 34.54 (s; C(^{t}Bu)), 37.20 (d, ^2J(C,P) = 23.2; CH_2NH), 48.78 (d, ^2J(C,P*) = 38.5;

$C(8)H_2$), 55.08 (d, ^2J(C,P*) = 7.2; $C(4)H_2$), 57.82 (d, ^3J(C,P*) = 2.7; CHNH), 61.42 (d, ^2J(C,P*) = 5.6; CH_2O), 63.43 (d, ^2J(C,P*) = 8.8; C(5)H), 114.94 (d, ^3J(C,P*) = 12.0; C(10)H and C(14)H), 119.18 (s; C(12)H), 128.76 (d, ^3J(C,P) = 6.7; CH(Ph)), 129.04 (s; CH(Ph)), 129.06 (s; CH(Ph)), 129.28 (s; C(11)H and C(13)H), 132.81 (d, ^2J(C,P) = 18.9; CH(Ph)), 132.83 (d, ^2J(C,P) = 18.9; CH(Ph)), 137.67 (d, ^1J(C,P) = 12.3; C(Ph)), 145.65 (d, ^2J(C,P*) = 16.0; C(9)), 159.75 (s; CO), 159.87 (s; CO) ppm. $^{31}P\{^1H\}$ NMR (242.9 MHz, $CDCl_3$, 25°C): -21.43 (s; P), 122.64 (s; P*) ppm. $C_{33}H_{42}N_4O_3P_2$ (604.27): calcd. C, 65.55; H, 7.00; N, 9.27; found C, 65.81; H, 7.09; N, 9.42.

[a] See Figure S1 for the carbon-numbering scheme.

Procedure for the preparation of $Pd_2(allyl)_2Cl_2$(5b): A solution of **5b** (36.3 mg, 0.06 mmol) in THF (2.5 mL) was added dropwise to a vigorously stirred solution of $[Pd(allyl)Cl]_2$ (22.0 mg, 0.06 mmol) in THF (2.5 mL). The solution was stirred for 1 hour at r. t., then concentrated and dried in vacuo (10^{-3} Torr). The product was dissolved in CD_2Cl_2 (0.5 mL) and transferred to a NMR tube.

$Pd_2(allyl)_2Cl_2$(**5b**): ^1H NMR (600.1 MHz, CD_2Cl_2, 25°C): 0.95 (s, 9H; $CH_3(^tBu)$), 1.74-2.19 (br.m, 4H; $C(6)H_2$ and $C(7)H_2$)[a], 2.63-3.63 (br.m, 4H; CH_2(allyl))[b], 2.78-2.82 (m, 2H; CH_2P), 3.02-3.22 (br.m, 1H; $C(8)H_2$), 3.32-3.45 (m, 1H; $C(4)H_2$), 3.41-3.45 (m, 1H; CH_2(allyl)), 3.57-3.64 (m, 2H; C<u>H</u>$_2$NH), 3.64-3.71 (m, 1H; CH_2(allyl)), 3.75-4.15 (br.m, 1H; $C(8)H_2$), 3.77-3.81 (m, 1H; $C(4)H_2$), 3.81-3.86 (m, 1H; CH_2O), 3.83-3.88 (m, 1H; C<u>H</u>NH), 3.93-4.07 (br.m, 1H; CH_2O), 4.09-4.14 (m, 1H; C(5)H), 4.46 (dd, J = 10.3, J = 8.1, 1H; CH_2(allyl)), 4.68 (br.s, 1H; CH_2(allyl)), 5.43-5.48 (m, 1H; CH(allyl)), 5.54-5.61 (m, 1H; CH(allyl)), 6.88 (t, ^3J(H,H) = 7.3, 1H; C(12)H), 6.93-7.11 (br.m, 2H; C(10)H and C(14)H), 7.21-7.23 (m, 2H; C(11)H and C(13)H), 7.43-7.49 (m, 6H; CH(Ph)), 7.52 (d, ^3J(H,H) = 10.2, 1H; CHN<u>H</u>), 7.58-7.63 (m, 4H; CH(Ph)), 8.99 (t, ^3J(H,H) = 10.2, 1H; CH_2N<u>H</u>) ppm. $^{13}C\{^1H\}$ NMR (150.9 MHz, CD_2Cl_2, 25°C): 26.84 (br; $C(7)H_2$), 26.96 (s; $CH_3(^tBu)$), 27.58 (d, ^1J(C,P) = 23.3; CH_2P), 31.21 (d, ^3J(C,P*) = 2.4; $C(6)H_2$), 34.26 (s; $C(^tBu)$), 36.14 (d, ^2J(C,P) = 7.2; CH_2NH), 49.50 (d, ^2J(C,P*) = 23.1; $C(8)H_2$), 55.89 (s; $C(4)H_2$), 56.08 (br; CH_2(allyl)), 57.58 (d, ^3J(C,P*) = 6.1; CHNH), 59.09 (br; CH_2(allyl)), 62.26 (s; C(5)H), 62.90 (d, ^2J(C,P*) = 13.2; CH_2O), 79.24 (d, ^2J(C,P*) = 44.8; CH_2(allyl)), 79.78 (d, ^2J(C,P) = 32.3; CH_2(allyl)), 115.98 (d, ^3J(C,P*) = 7.5; C(10)H and C(14)H), 118.32 (d, ^2J(C,P) = 5.5; CH(allyl)), 119.14 (d, ^2J(C,P*) = 9.2; CH(allyl)), 120.87 (s; C(12)H), 129.13 (s; CH(Ph)), 129.20 (s; CH(Ph)), 129.45 (s; C(11)H and C(13)H), 130.98 (s; CH(Ph)), 131.03 (s; CH(Ph)), 132.70 (br; C(Ph)), 133.04 (br; CH(Ph)), 144.04 (d, ^2J(C,P*) = 12.6; C(9)), 159.74 (s; CO), 160.21 (s; CO) ppm. $^{31}P\{^1H\}$ NMR (242.9 MHz, CD_2Cl_2, 25°C): 18.45 (s; P), 127.86 and 128.09 (br.s and br.s; P*) ppm.

[a] See Figure S1 for the carbon-numbering scheme.

[b] See Figure S2 for the NMR signal assignments for the η^3-allyl ligands.

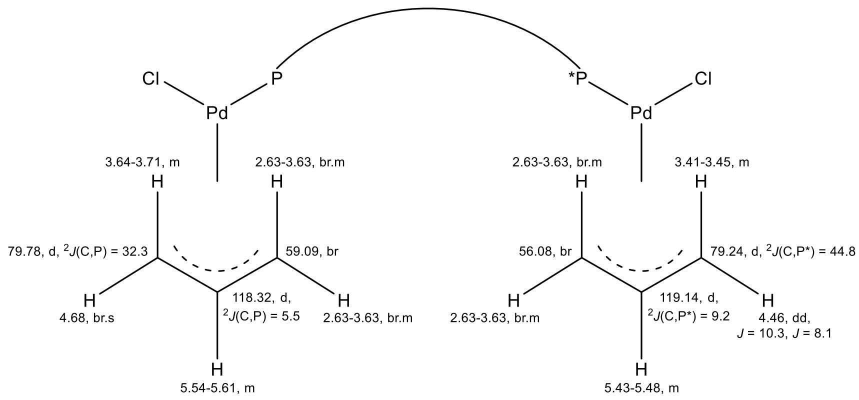

Figure S2 NMR signal assignments for the η^3-allyl ligands.

Procedure for the preparation of [Pd(allyl)(5b)]$_2$Cl$_2$: A solution of **5b** (72.6 mg, 0.12 mmol) in THF (3.0 mL) was added dropwise to a vigorously stirred solution of [Pd(allyl)Cl]$_2$ (22.0 mg, 0.06 mmol) in THF (2.5 mL). The solution was stirred for 1 hour at r. t., then concentrated and dried in vacuo (15 Torr). The product was dissolved in CH_2Cl_2 (0.5 mL) and added dropwise to pentane (15 mL) with vigorous stirring. The precipitated complex was separated by centrifugation and dried in vacuum (10^{-3} Torr).

[Pd(allyl)(**5b**)]$_2$Cl$_2$: White powder, yield 89 mg (89 %). ^{1}H NMR (600.1 MHz, CD_2Cl_2, 25^{o}C): 0.86 (s, 18H; CH$_3$(^{t}Bu)), 1.70-2.17 (m, 8H), 2.81-4.91 (m, 34H), 6.40-7.82 (m, 32H; CH(Ph) and NH), 9.32-9.34 (m, 2H; NH) ppm. ^{13}C{^{1}H} NMR (150.9 MHz, CD_2Cl_2, 25^{o}C): 26.70 (s; CH$_3$(^{t}Bu)), 27.20 (s; C(7)H$_2$)[a], 31.94 (s; C(6)H$_2$), 34.10 (s; C(^{t}Bu)), 36.76 (br; CH$_2$NH), 49.54 (d, ^2J(C,P*) = 24.3; C(8)H$_2$), 55.04 (s; C(4)H$_2$), 59.19 (s; CHNH), 62.89 (s; C(5)H), 65.86 (br; CH$_2$O), 115.80 (s; CH), 120.68 (br; CH), 121.50 (s; CH), 129.12 (s; CH), 129.20 (s; CH), 129.36 (s; CH), 129.44 (s; CH), 129.69 (s; CH),131.13 (s; CH), 131.27 (s; CH), 133.01-133.31 (m; CH), 143.29 (br; C(9)), 159.25 (s; CO), 161.41 (s; CO) ppm. ^{31}P{^{1}H} NMR (242.9 MHz, CD_2Cl_2, 25^{o}C): 13.00 (d; ^2J(P,P*) = 67.3; P), 120.47 (d; ^2J(P,P*) = 67.3; P*) ppm. $C_{72}H_{94}Cl_2N_8O_6P_4Pd_2$: calcd. C, 54.90; H, 6.02; N, 7.11; found C, 55.16; H, 6.12; N, 6.95. M/z = 752.2180 (calcld. 752.2212 for [Pd(allyl)(**5b**)]$_2^{2+}$), 92%.

[a] See Figure S1 for the carbon-numbering scheme.

Procedure for the preparation of [Pd(allyl)(5b)]$_2$(BF$_4$)$_2$: A solution of **5b** (72.6 mg, 0.12 mmol) in THF (3.0 mL) was added dropwise to a vigorously stirred solution of [Pd(allyl)Cl]$_2$ (22.0 mg, 0.06 mmol) in THF (2.5 mL). The solution was stirred for 1 hour at r. t., then covered with foil and AgBF$_4$ (23.4 mg, 0.12 mmol)was added. The suspension was stirred for 1 hour at r. t., then the precipitate was removed by centrifugation, and the solution was concentrated and dried in vacuo (15 Torr). The product was dissolved in CH_2Cl_2 (0.5 mL) and added dropwise to pentane (15 mL) with vigorous stirring. The precipitated complex was separated by centrifugation and dried in vacuum (10^{-3} Torr).

$[Pd(allyl)(\mathbf{5b})]_2(BF_4)_2$: White powder, yield 85 mg (84 %). ^1H NMR (600.1 MHz, CD_2Cl_2, 25°C): 0.89, 0.90, 0.91 (s, s, s, 18H; $CH_3(^tBu)$), 1.72-2.18 (m, 8H, including CH_2(allyl))[a], 2.77-3.58 (m, 18H, including CH_2(allyl)), 3.72-4.09 (m, 12H, including CH_2(allyl)), 4.21-4.29 (m, 2H), 4.85-4.93, 5.82-5.89 (m, 2H; CH(allyl)), 6.38-6.40, 6.49-6.51 (m, m, 4H; C(10)H and C(14)H)[b], 6.90-6.93 (m, 2H; C(12)H), 7.08-7.13 (m, 4H; C(11)H and C(13)H), 7.49-7.56 (m, 10H; CH(Ph)), 7.62-7.76 (m, 12H; CH(Ph) and NH), 9.32-9.37 (m, 2H; NH) ppm. $^{13}C\{^1H\}$ NMR (150.9 MHz, CD_2Cl_2, 25°C): 26.50, 26.66 (s, br; $CH_3(^tBu)$), 26.64 (br; CH_2P), 27.02-27.11 (m; $C(7)H_2$), 31.81-31.89 (m; $C(6)H_2$), 34.07, 34.08 (s, s; $C(^tBu)$), 35.53, 35.56, 35.71 (s, s, s; CH_2NH), 49.38-49.83 (m; $C(8)H_2$), 54.70-54.72, 54.99-55.01 (m, m; $C(4)H_2$), 58.89-58.91 (m; CHNH), 62.83, 63.02 (s, s; C(5)H), 65.26, 65.34, 65.52, 65.58 (d, $^2J(C,P^*)$ = 15.3, d, $^2J(C,P^*)$ = 15.5, d, $^2J(C,P^*)$ = 14.9, d, $^2J(C,P^*)$ = 15.6; CH_2O), 66.51, 66.59, 69.38, 69.49 (dd, $^2J(C,P)$ = 28.2, $^2J(C,P^*)$ = 3.1, dd, $^2J(C,P)$ = 28.5, $^2J(C,P^*)$ = 3.3, dd, $^2J(C,P)$ = 27.8, $^2J(C,P^*)$ = 3.1, dd, $^2J(C,P)$ = 27.6, $^2J(C,P^*)$ = 3.0; $CH_2(allyl)^{cis\ to\ P^*}$), 76.13-76.39, 78.62-78.90 (m, m; $CH_2(allyl)^{cis\ to\ P}$), 115.16-115.26 (m; C(10)H and C(14)H), 121.63-121.78 (m; C(12)H), 123.84-123.99, 124.66-124.81 (m, m; CH(allyl)), 128.30-128.37, 128.61-128.68, 132.25-132.55 (m, m, m; C(Ph)), 129.28-129.45 (m, CH(Ph)), 129.52 (s, CH(Ph)), 129.59 (s, CH(Ph)), 129.78, 129.93 (s, s; C(11)H and C(13)H), 131.27-131.32 (m, CH(Ph)), 131.43-131.47 (m, CH(Ph)), 131.66-131.71 (m, CH(Ph)), 131.81-131.86 (m, CH(Ph)), 131.99 (s, CH(Ph)), 132.07 (s, CH(Ph)), 132.32-132.41 (m, CH(Ph)), 133.05, 133.10, 133.22, 133.26 (d, $^2J(C,P)$ = 11.7, d, $^2J(C,P)$ = 11.6, d, $^2J(C,P)$ = 11.6, d, $^2J(C,P)$ = 11.7; CH(Ph)), 142.54-142.70 (m; C(9)), 158.67, 158.71, 158.73, 158.75 (s, s, s, s; CO), 161.12, 161.15, 161.17 (s, s, s; CO) ppm. $^{31}P\{^1H\}$ NMR (242.9 MHz, CD_2Cl_2, 25°C): 17.33 (23%), 17.56 (42%), 17.80 (12%), 18.02 (23%) (d; $^2J(P,P^*)$ = 66.9, d; $^2J(P,P^*)$ = 66.9, d; $^2J(P,P^*)$ = 67.8, d; $^2J(P,P^*)$ = 67.8; P), 123.32 (12%), 123.40 (23%), 124.15 (23%), 124.17 (42%) (d; $^2J(P,P^*)$ = 67.3, d; $^2J(P,P^*)$ = 67.9, d; $^2J(P,P^*)$ = 67.1, d; $^2J(P,P^*)$ = 67.1; P*) ppm. $C_{72}H_{94}B_2F_8N_8O_6P_4Pd_2$: calcd. C, 51.54; H, 5.65; N, 6.68; found C, 51.75; H, 5.58; N, 6.75. M/z = 752.2177 (calcld. 752.2212 for $[Pd(allyl)(\mathbf{5b})]_2^{2+}$), 100%.

[a] See Figure S3 for the NMR signal assignments for the η^3-allyl ligand.

[b] See Figure S1 for the carbon-numbering scheme.

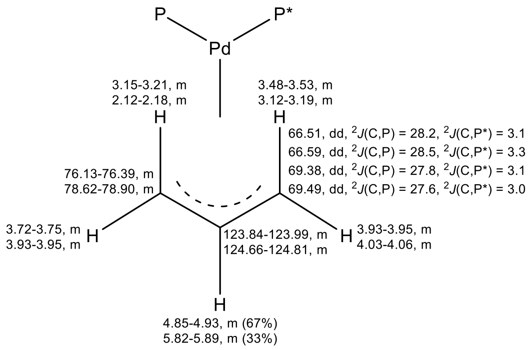

Figure S3 NMR signal assignments for the η^3-allyl ligand.

Procedure for the preparation of [Rh(COD)(5b)]$_2$(BF$_4$)$_2$: A solution of **5b** (60.5 mg, 0.1 mmol) in THF (3.0 mL) was added dropwise to a vigorously stirred solution of [Rh(COD)$_2$]BF$_4$ (40.6 mg, 0.1 mmol) in THF (2.5 mL). The solution was stirred owernight at r. t., then was concentrated to 2 mL and added dropwise to cold pentane (15 mL, -45°C) with vigorous stirring. The precipitated complex was washed with cold pentane (5 mL, , -45°C) and dried in vacuum (10^{-3} Torr).

[Rh(COD)(**5b**)]$_2$(BF$_4$)$_2$**:** White powder, yield 73 mg (81 %). ^{1}H NMR (600.1 MHz, CD$_2$Cl$_2$, 25^{o}C): 0.80 (s, 18H; CH$_3$(^{t}Bu)), 1.95-2.05 (m, 6H; CH$_2$), 2.22-2.32 (m, 12H; CH$_2$), 2.39-2.48 (m, 6H; CH$_2$), 3.24 (t, *J* = 9.7 2H; C(4)H$_2$)[a], 3.27-3.33 (m, 4H; CH$_2$), 3.41-3.54 (m, 6H; CH$_2$), 3.72 (t, ^3J(H,H) =10.2, 2H; C<u>H</u>NH), 3.93-3.97 (m, 2H; C(4)H$_2$), 4.11-4.16 (m, 2H; C(5)H), 4.17-4.22 (m, 4H; C<u>H$_2$</u>NH), 4.46-4.50 (m, 2H; CH$_2$), 4.53-4.59 (m, 2H; CH(COD)), 4.61-4.66 (m, 2H; CH(COD)), 4.67-4.72 (m, 2H; CH(COD)), 4.99-5.05 (m, 2H; CH(COD)), 6.86 (t, ^3J(H,H) = 7.4, 2H; C(12)H), 7.06-7.08 (m, 4H; C(10)H and C(14)H), 7.27-7.29 (m, 4H; C(11)H and C(13)H), 7.38-7.43 (m, 10H; CH(Ph)), 7.44 (d, ^3J(H,H) =11.0, 2H; CHN<u>H</u>), 7.58-7.65 (m, 6H; CH(Ph)), 7.86-7.89 (m, 4H; CH(Ph)), 9.57 (t, ^3J(H,H) =5.6, 2H; CH$_2$N<u>H</u>) ppm. ^{13}C{^{1}H} NMR (150.9 MHz, CD$_2$Cl$_2$, 25^{o}C): 26.44 (d, ^1J(C,P) = 25.8; CH$_2$P), 26.68 (s; CH$_3$(^{t}Bu)), 27.11 (d, ^3J(C,P*) = 4.7; C(7)H$_2$), 29.73-29.76 (m; CH$_2$), 30.23 (s; CH$_2$) 30.57 (d, *J* = 2.5; CH$_2$), 31.20 (d, *J* = 2.7; CH$_2$), 31.37(d, *J* = 3.5; CH$_2$), 34.52 (s; C(^{t}Bu)), 38.13 (d, ^2J(C,P) = 8.5; CH$_2$NH), 51.89 (d, ^2J(C,P*) = 18.6; C(8)H$_2$), 56.86 (s; C(4)H$_2$), 58.74 (d, ^3J(C,P*) = 6.6; CHNH), 62.67 (s; C(5)H), 65.34 (d, ^2J(C,P*) = 13.1; CH$_2$O), 97.39 (dd, *J* = 9.8, *J* = 7.4; CH(COD)), 101.79 (t, *J* = 7.4; CH(COD)), 102.58 (dd, *J* = 14.6, *J* = 5.7; CH(COD)), 107.45 (dd, *J* = 9.7, *J* = 6.5; CH(COD)), 115.97 (d, ^3J(C,P*) = 6.6; C(10)H and C(14)H), 121.06 (s; C(12)H), 129.54 (d, ^2J(C,P) = 9.2; CH(Ph)), 129.66 (d, ^2J(C,P) = 10.5; CH(Ph)), 129.94 (s; C(11)H and C(13)H), 130.38 (d, ^1J(C,P) = 40.2; C(Ph)), 131.13 (d, ^4J(C,P) = 2.4; CH(Ph)), 131.31 (d, ^3J(C,P) = 8.7; CH(Ph)), 131.87 (d, ^4J(C,P) = 2.3; CH(Ph)), 132.74 (d, ^3J(C,P) = 11.8; CH(Ph)), 133.43 (dd, ^1J(C,P) = 49.3, ^2J(C,Rh) = 2.8;

C(Ph)), 143.56 (d, ^{2}J(C,P*) = 10.5; C(9)), 158.83 (s; CO), 161.25 (s; CO) ppm. ^{31}P{^{1}H} NMR (242.9 MHz, CD_2Cl_2, 25°C): 18.44 (dd, ^{1}J(P,Rh) = 144.4, ^{2}J(P,P*) = 36.3; P), 111.07 (dd, ^{1}J(P,Rh) = 217.5, ^{2}J(P,P*) = 36.4; P*) ppm. $C_{82}H_{108}B_2F_8N_8O_6P_4Rh_2$: calcd. C, 54.56; H, 6.03; N, 6.21; found C, 54.85; H, 5.94; N, 6.02. M/z = 815.2748 (calcld. 815.2752 for [Rh(COD)(**5b**)]$_2^{2+}$), 100%.

[a] See Figure S1 for the carbon-numbering scheme.

Procedure for the reaction of 5b with [Pd(allyl)Cl]$_2$ (ligand-to metal molar ratio = 2/1): A solution of **5b** (72.6 mg, 0.12 mmol) in THF (2.5 mL) was added dropwise to a vigorously stirred solution of [Pd(allyl)Cl]$_2$ (11.0 mg, 0.03 mmol) in THF (2.5 mL). The solution was stirred for 1 hour at r. t., then concentrated and dried in vacuo (10^{-3} Torr). The product was dissolved in CD_2Cl_2 (1.0 mL) and 0.5 mL of solution was transferred to a NMR tube.

Procedure for the reaction of 5b with [Rh(COD)Cl]$_2$ (ligand-to metal molar ratio = 2/1): A solution of **5b** (60.5 mg, 0.10 mmol) in THF (2.5 mL) was added dropwise to a vigorously stirred solution of [Rh(COD)$_2$]BF_4 (20.0 mg, 0.05 mmol) in THF (2.5 mL). The solution was stirred for 1 hour at r. t., then concentrated and dried in vacuo (10^{-3} Torr). The product was dissolved in CD_2Cl_2 (1.0 mL) and 0.5 mL of solution was transferred to a NMR tube.

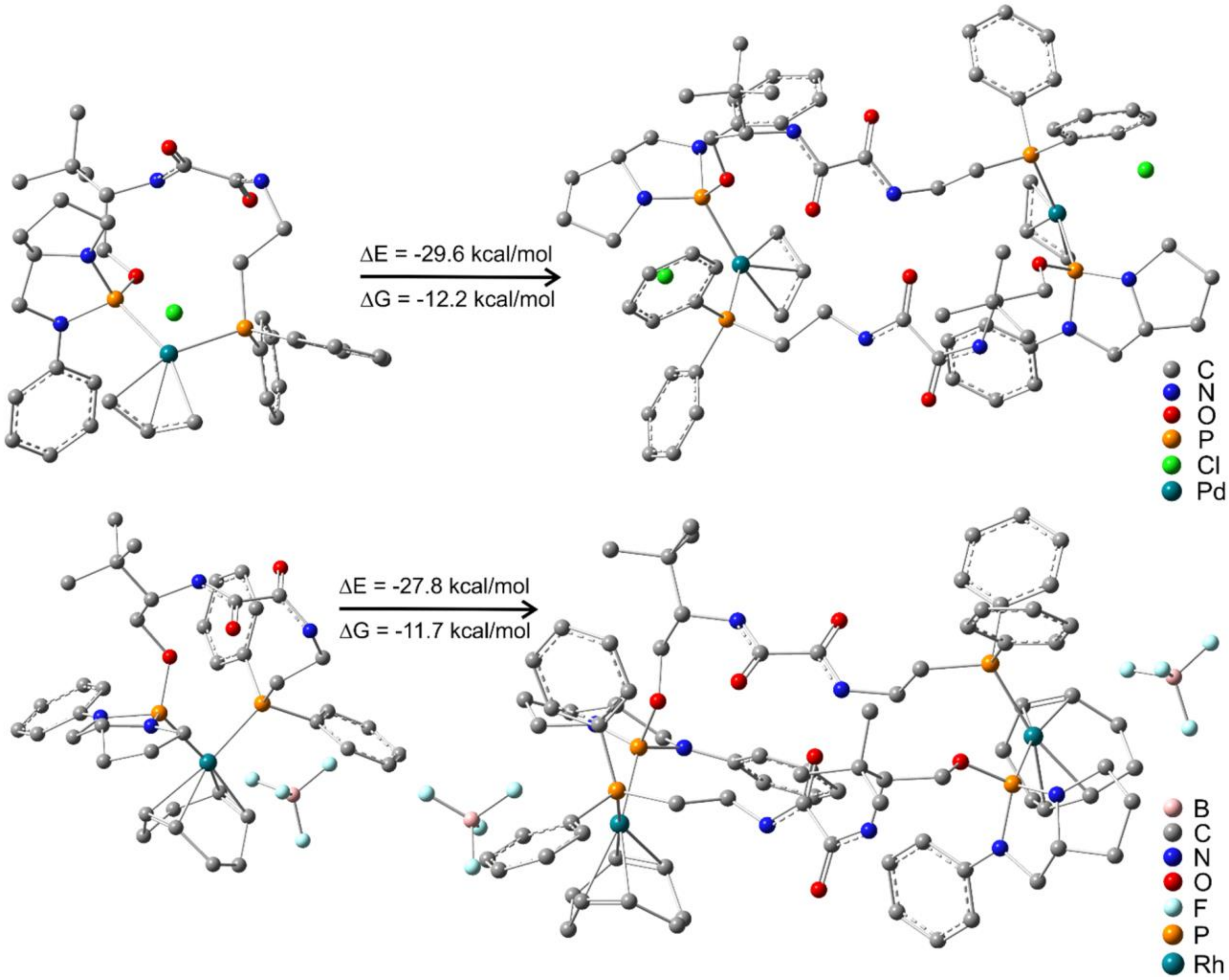

Figure S4 The structures of [Pd(allyl)(**5b**)]$_2$Cl$_2$ (top) and [Rh(COD)(**5b**)]$_2$(BF$_4$)$_2$ (bottom) in their mononuclear and dinuclear forms. Hydrogen atoms are omitted for clarity

Palladium-catalyzed asymmetric allylic sulfonylation of (*E*)-1,3-diphenylallyl acetate with sodium *para*-toluenesulfinate: A solution of [Pd(allyl)Cl]$_2$ (0.001 g, 0.0025 mmol) and the appropriate ligand (0.0015 g, 0.0025 mmol, 0.003 g, 0.005 mmol or 0.006 g, 0.01 mmol) in THF (1.5 mL) was stirred for 40 min. (*E*)-1,3-Diphenylallyl acetate (**5**) (0.05 mL, 0.25 mmol) was added and the solution stirred for 15 min, then sodium *para*-toluenesulfinate (0.089 g, 0.5 mmol) was added and the reaction mixture stirred for a further 24 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 (**6a**) as white crystals.[8] Enantiomeric excess of **6a** was determined by HPLC analysis.

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

(0.0015 g, 0.0025 mmol, 0.003 g, 0.005 mmol or 0.006 g, 0.01 mmol) in the appropriate solvent (1.5 mL) was stirred for 40 min. (*E*)-1,3-Diphenylallyl acetate (**5**) (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 (**6b**).[9] 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 dimethyl malonate: A solution of $[Pd(allyl)Cl]_2$ (0.001 g, 0.0025 mmol) and the appropriate ligand (0.0015 g, 0.0025 mmol, 0.003 g, 0.005 mmol or 0.006 g, 0.01 mmol) in the appropriate solvent (1.5 mL) was stirred for 40 min. (*E*)-1,3-Diphenylallyl acetate (**5**) (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 (**6c**).[10] 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 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 (0.0015 g, 0.0025 mmol, 0.003 g, 0.005 mmol or 0.006 g, 0.01 mmol) in toluene (1.5 mL) was stirred for 40 min. Cinnamyl acetate (**7**) (0.04 mL, 0.25 mmol) was added and the solution stirred for 15 min. β-Ketoether **8** (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 (**9**).[11] 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 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 (0.0015 g, 0.0025 mmol, 0.003 g, 0.005 mmol or 0.006 g, 0.01 mmol) in toluene (1.5 mL) was stirred for 40 min. Cinnamyl acetate (**7**) (0.04 mL, 0.25 mmol) was added and the solution stirred for 15 min. α-Acetamido-β-Ketoether **10** (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 (**11**).[12] 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.

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 $[Rh(Cod)_2]BF_4$ (0.001 g, 0.0025 mmol) and the appropriate ligand (0.0015 g, 0.0025 mmol or 0.003 g, 0.005 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 (**14a**), methyl 2-acetamido-3-phenylpropanoate (**14b**) or methyl 2-acetamido-3-(4-fluorophenyl)propanoate (**14c**).[13] 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.

Table S1. Pd-catalyzed allylic sulfonylation of *rac*-**6** with sodium *para*-toluenesulfinate. [a]

Entry	Compound	L/Pd	Yield [%]	*Ee* [%] [b,c]
1	**5a**	0.5	83	68(*S*)
2	**5a**	1	78	55 (*S*)
3	**5a**	2	87	82 (*S*)
4	**5b**	1	55	47 (*R*)
5	**5b**	2	32	23 (*R*)

[a] All reactions were carried out with 1 mol% of $[Pd(allyl)Cl]_2$ in THF at RT for 24 h. [b] The conversion of substrate *rac*-**6** and enantiomeric excess of **7a** were determined by HPLC (Kromasil 5-CelluCoat, C_6H_{14}/*i*PrOH = 4/1, 0.5 mL/min, 254 nm, *t*(*R*) = 17.8 min, *t*(*S*) = 20.7 min). [c] The absolute configurations were assigned by comparison of the HPLC retention times reported in the literature.[7a]

Table S2. Pd-catalyzed allylic amination of *rac*-**6** with pyrrolidine. [a]

Entry	Compound	L/Pd	Solvent	Conversion [%]	*Ee* [%] [b,c]
1	**5a**	0.5	THF	100	83 (*R*)
2	**5a**	1	THF	100	55 (*R*)
3	**5a**	2	THF	94	70 (*R*)
4	**5a**	0.5	CH_2Cl_2	100	72 (*R*)
5	**5a**	1	CH_2Cl_2	100	67 (*R*)
6	**5a**	2	CH_2Cl_2	100	75 (*R*)
7	**5b**	1	THF	100	73 (*S*)
8	**5b**	2	THF	100	70 (*S*)
9	**5b**	1	CH_2Cl_2	100	57 (*S*)
10	**5b**	2	CH_2Cl_2	100	65 (*S*)

[a] All reactions were carried out with 1 mol% of $[Pd(allyl)Cl]_2$ at RT for 24 h. [b] The conversion of substrate *rac*-**6** and enantiomeric excess of **7b** were determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}/*i*PrOH = 95/5, 0.4 mL/min, 254 nm, *t*(*R*) = 10.3 min, *t*(*S*) = 10.9 min). [c] The absolute configurations was assigned by comparison of the HPLC retention times reported in the literature.[7a,b,9b]

Table S3. Pd-catalyzed allylic alkylation of *rac*-**6** with dimethyl malonate. [a]

Entry	Compound	L/Pd	Solvent	Conversion [%]	*Ee* [%] [b,c]
1	**5a**	0.5	THF	98	82(*S*)
2	**5a**	1	THF	75	80 (*S*)
3	**5a**	2	THF	45	92 (*S*)
4	**5a**	0.5	CH_2Cl_2	100	87 (*S*)
5	**5a**	1	CH_2Cl_2	100	82 (*S*)
6	**5a**	2	CH_2Cl_2	100	80 (*S*)
7	**5b**	1	THF	96	60 (*R*)
8	**5b**	2	THF	93	57 (*R*)
9	**5b**	1	CH_2Cl_2	100	66 (*R*)
10	**5b**	2	CH_2Cl_2	100	64 (*R*)

[a] All reactions were carried out with 1 mol% of $[Pd(allyl)Cl]_2$ at RT for 24 h (BSA, KOAc). [b] The conversion of substrate *rac*-**6** and enantiomeric excess of **7c** were determined by HPLC (Kromasil 5-CelluCoat, C_6H_{14}/*i*PrOH = 99/1, 0.6 mL/min, 254 nm, *t*(*R*) = 19.7 min, *t*(*S*) = 21.0 min). [c] The absolute configurations were assigned by comparison of the HPLC retention times reported in the literature.[7b,13,]

Table S4. Pd-catalyzed allylic alkylation of **8** with ethyl 2-oxocyclohexane-1-carboxylate (**9**) and ethyl 2-acetamido-3-oxobutanoate (**11**). [a]

Entry	Compound	L/Pd	Conversion [%]	Product	*Ee* [%] [b,c]
1	**5a**	0.5	52	**10**	61 (*S*)
2	**5a**	1	61	**10**	48 (*S*)
3	**5a**	2	36	**10**	34 (*S*)
4	**5b**	1	55	**10**	38 (*R*)
5	**5b**	2	79	**10**	38 (*R*)
6	**5a**	0.5	100	**12**	31 (*R*)
7	**5a**	1	100	**12**	54 (*R*)
8	**5a**	2	100	**12**	58 (*R*)
9	**5b**	1	22	**12**	34 (*S*)
10	**5b**	2	94	**12**	41 (*S*)

[a] All reactions were carried out with 1 mol% of $[Pd(allyl)Cl]_2$ in toluene at RT for 24 h (BSA, $Zn(OAc)_2$ or BSA, KOAc, respectively). [b] The conversion of substrate **8** and enantiomeric excesses of **10** and **12** were determined by HPLC (**10**, Kromasil 5-CelluCoat, C_6H_{14}/*i*PrOH = 95/5, 0.4 mL/min, 254 nm, *t*(*R*) = 14.2 min, *t*(*S*) = 16.4 min; **12**, Daicel Chiralcel OD-H, C_6H_{14}/*i*PrOH = 85/15, 0.8 mL/min, 254 nm, *t*(*S*) = 9.7 min, *t*(*R*) = 10.6 min). [c] The absolute configurations were assigned by comparison of the HPLC retention times reported in the literature.[7b,11]

Table S5. Rh-catalyzed hydrogenation of **13a-c**. [a]n

Entry	Compound	L/Rh	Product	Conversion [%]	*Ee* [%] [b,c]
1	**5a**	1	**14a**	43	78 (*S*)
2	**5a**	2	**14a**	14	77 (*S*)
3	**5a**	1	**14b**	100	63 (*R*)
4	**5a**	2	**14b**	71	86 (*R*)
5	**5a**	1	**14c**	54	74 (*R*)
6	**5a**	2	**14c**	10	82 (*R*)
7	**5b**	1	**14a**	21	19 (*R*)
8	**5b**	1	**14b**	100	48 (*S*)
9	**5b**	1	**14c**	28	50 (*S*)

[a] All reactions were carried out with 1 mol% of $[Rh(COD)_2]BF_4$ in CH_2Cl_2 at RT for 24 h (6 atm. H_2). [b] The conversion of substrates **13a-c** and enantiomeric excesses of **14a-c** were determined by HPLC (**14a**, Daicel Chiralcel OD-H, C_6H_{14}/*i*PrOH = 98/2, 0.8 mL/min, 215 nm, *t*(*R*) = 9.9 min, *t*(*S*) = 16.9 min; **14b**, Daicel Chiralcel OD-H, C_6H_{14}/*i*PrOH = 4/1, 0.6 mL/min, 215 nm, *t*(*R*) = 9.4 min, *t*(*S*) = 11.3 min; **14c**, Daicel Chiralcel OD-H, C_6H_{14}/*i*PrOH = 9/1, 1.0 mL/min, 219 nm, *t*(*R*) = 10.8 min, *t*(*S*) = 13.5 min). [c] The absolute configurations were assigned by comparison of the HPLC retention times reported in the literature.[13a,b,14]

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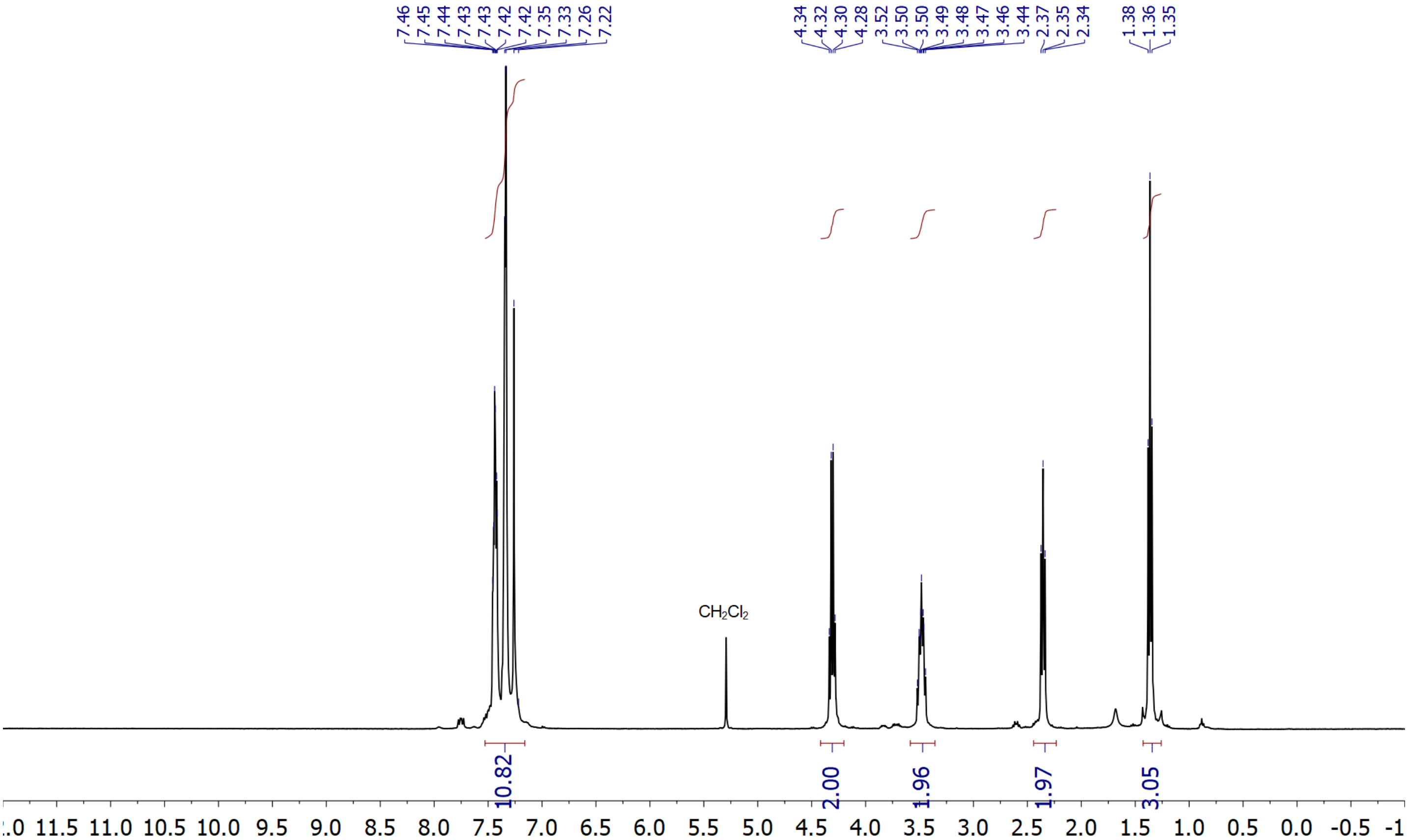


Figure S5a ^{1}H spectrum for **2**

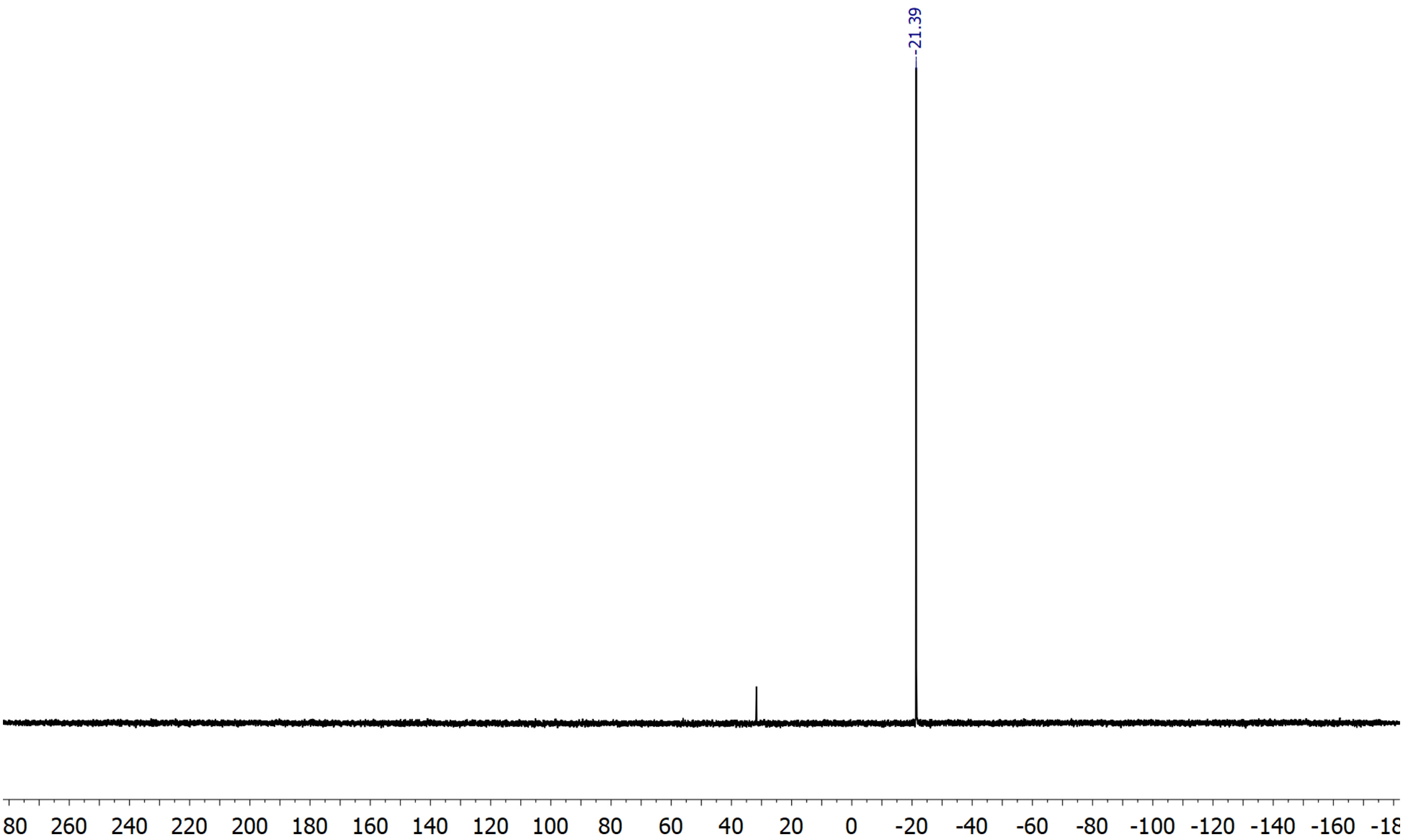


Figure S5b ^{31}P{^{1}H} spectrum for **2**

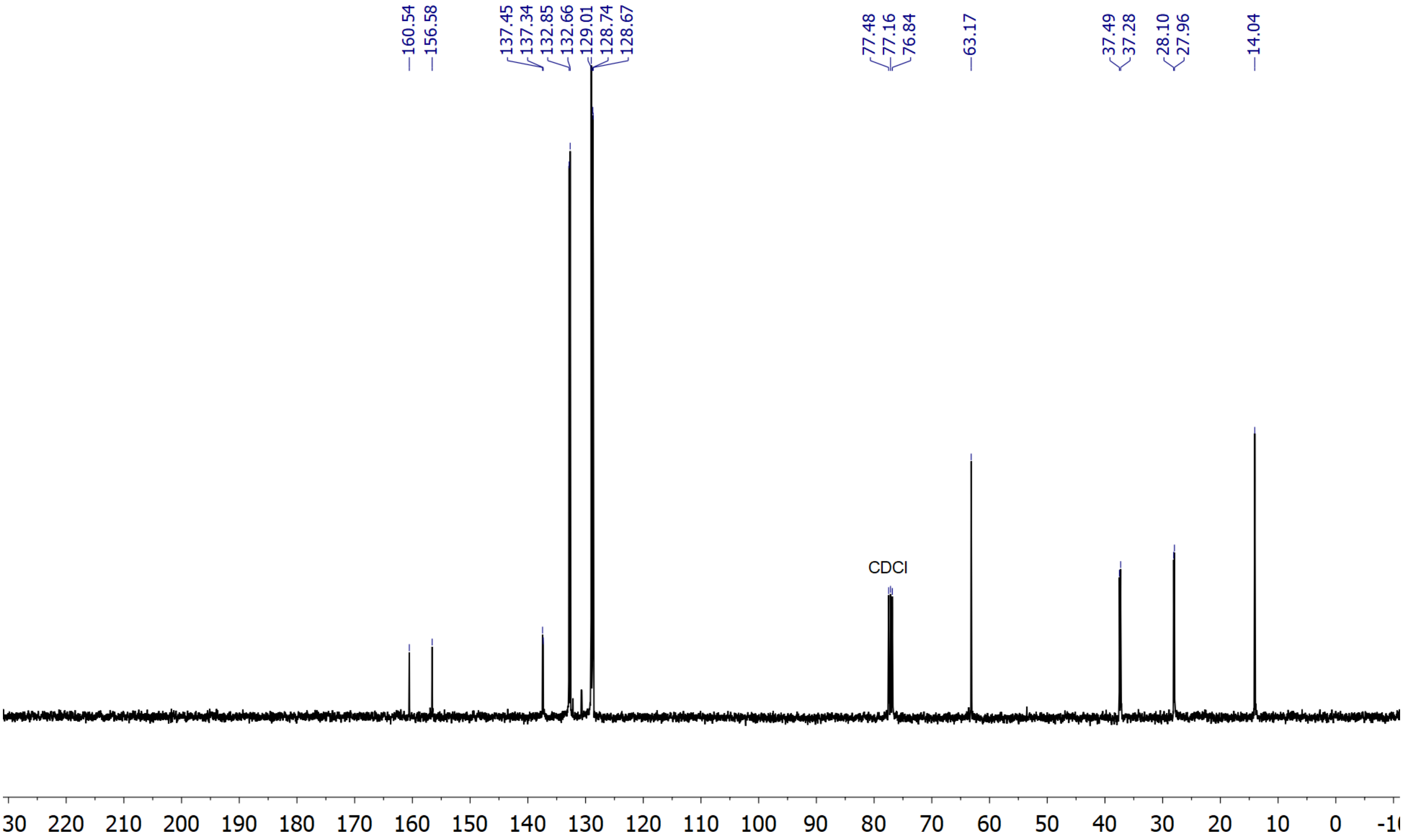


Figure S5c $^{13}C\{^{1}H\}$ spectrum for **2**

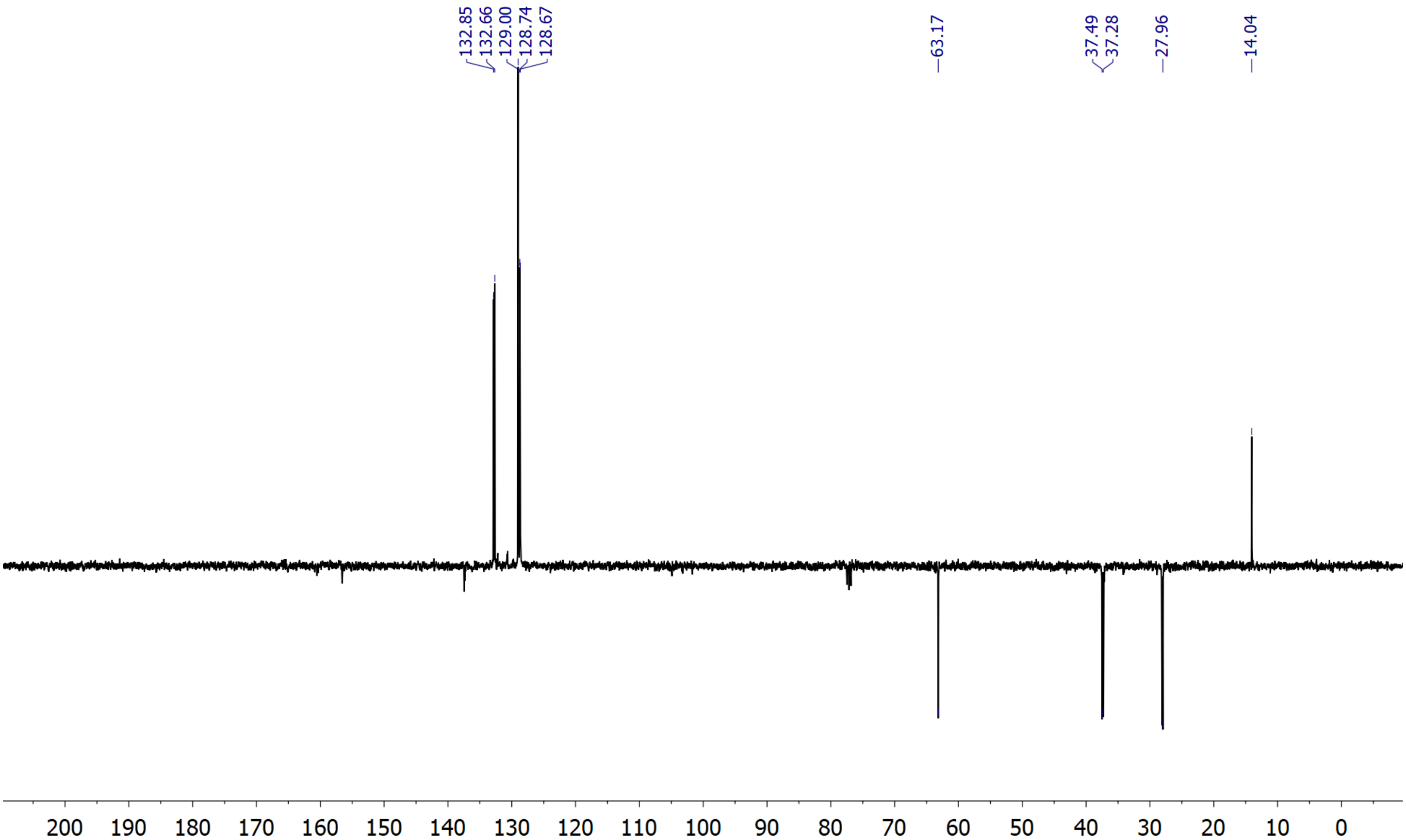


Figure S5d $^{13}C\{^{1}H\}$ DEPT spectrum for **2**

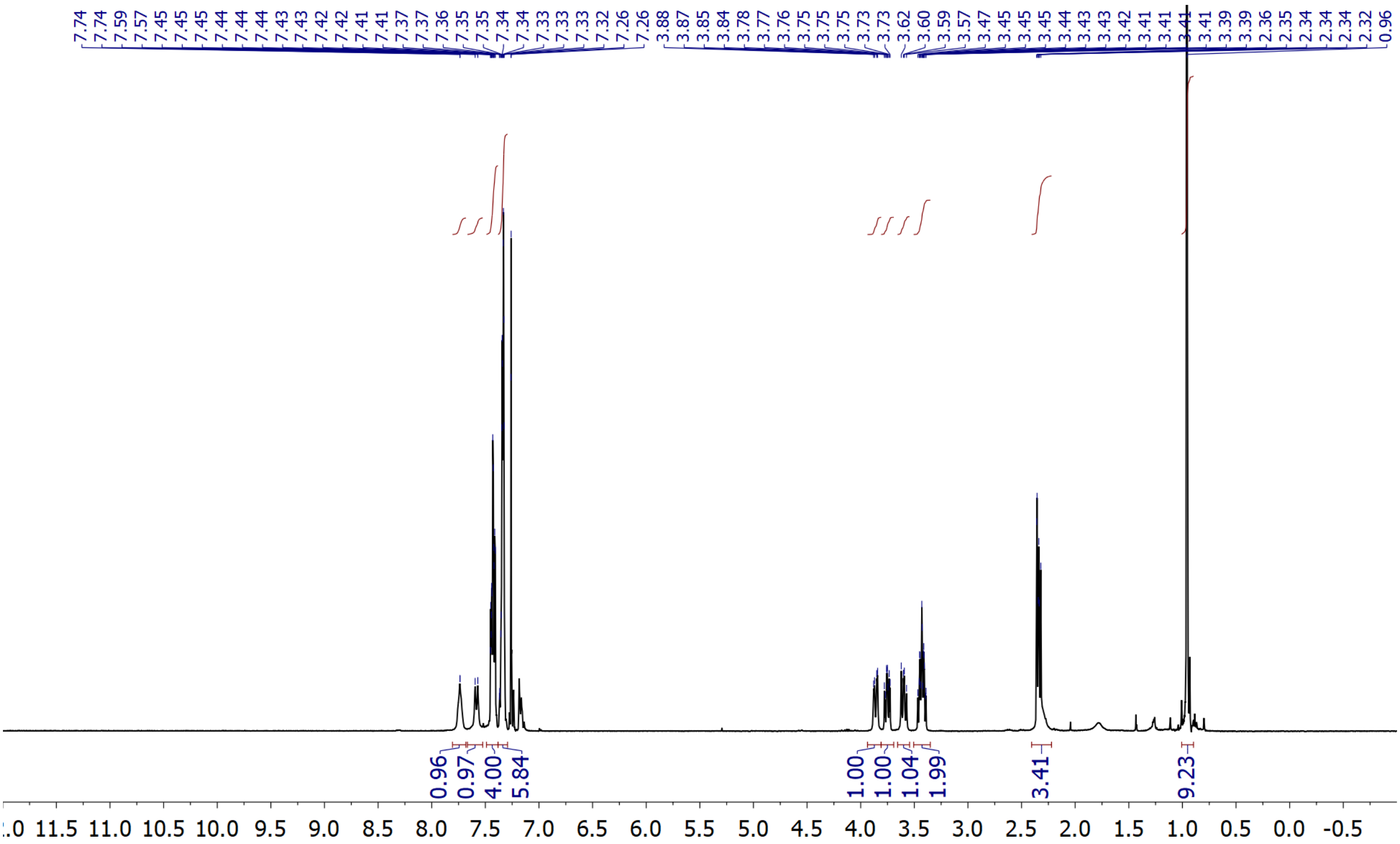
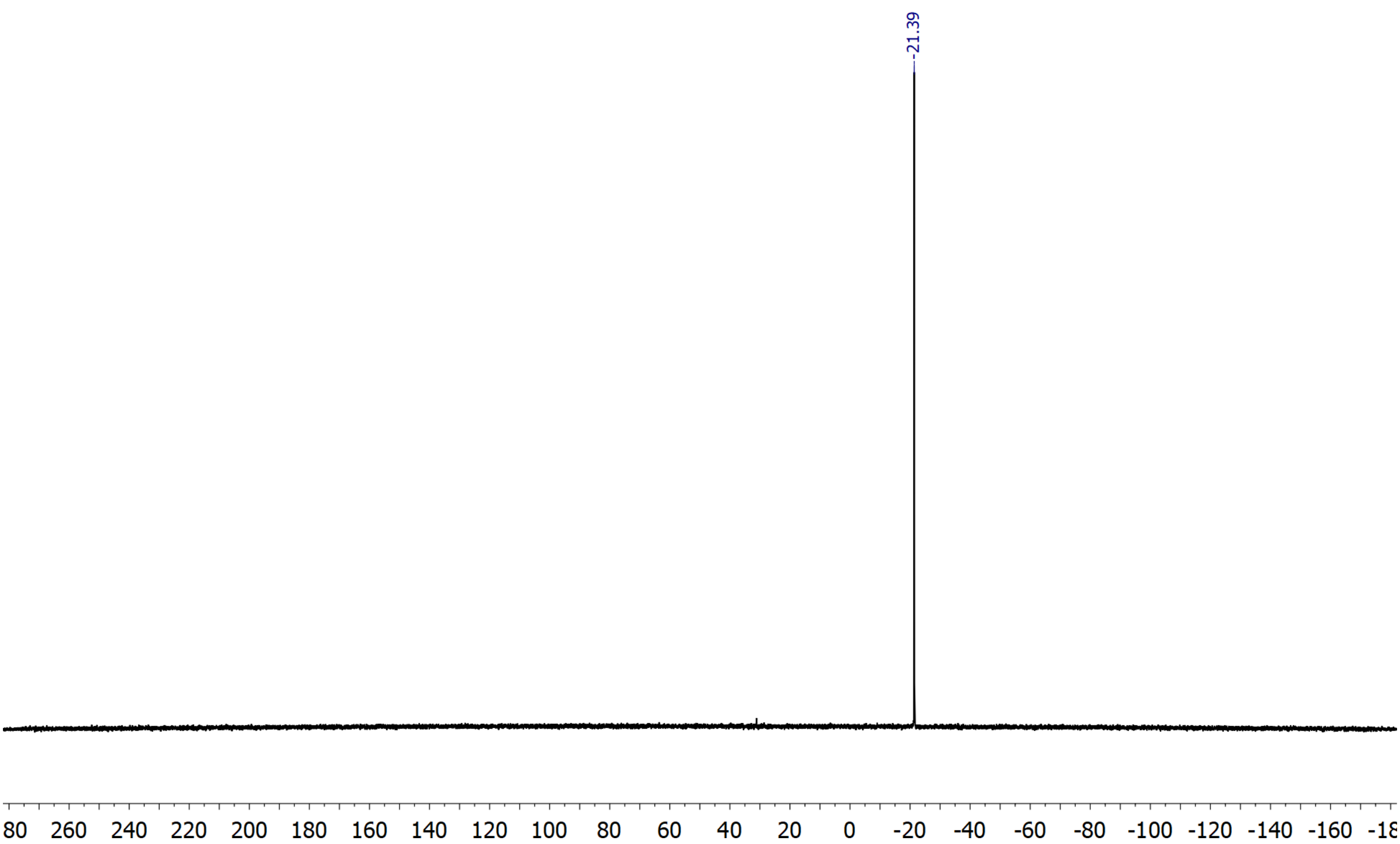


Figure S6a ^{1}H spectrum for **3**



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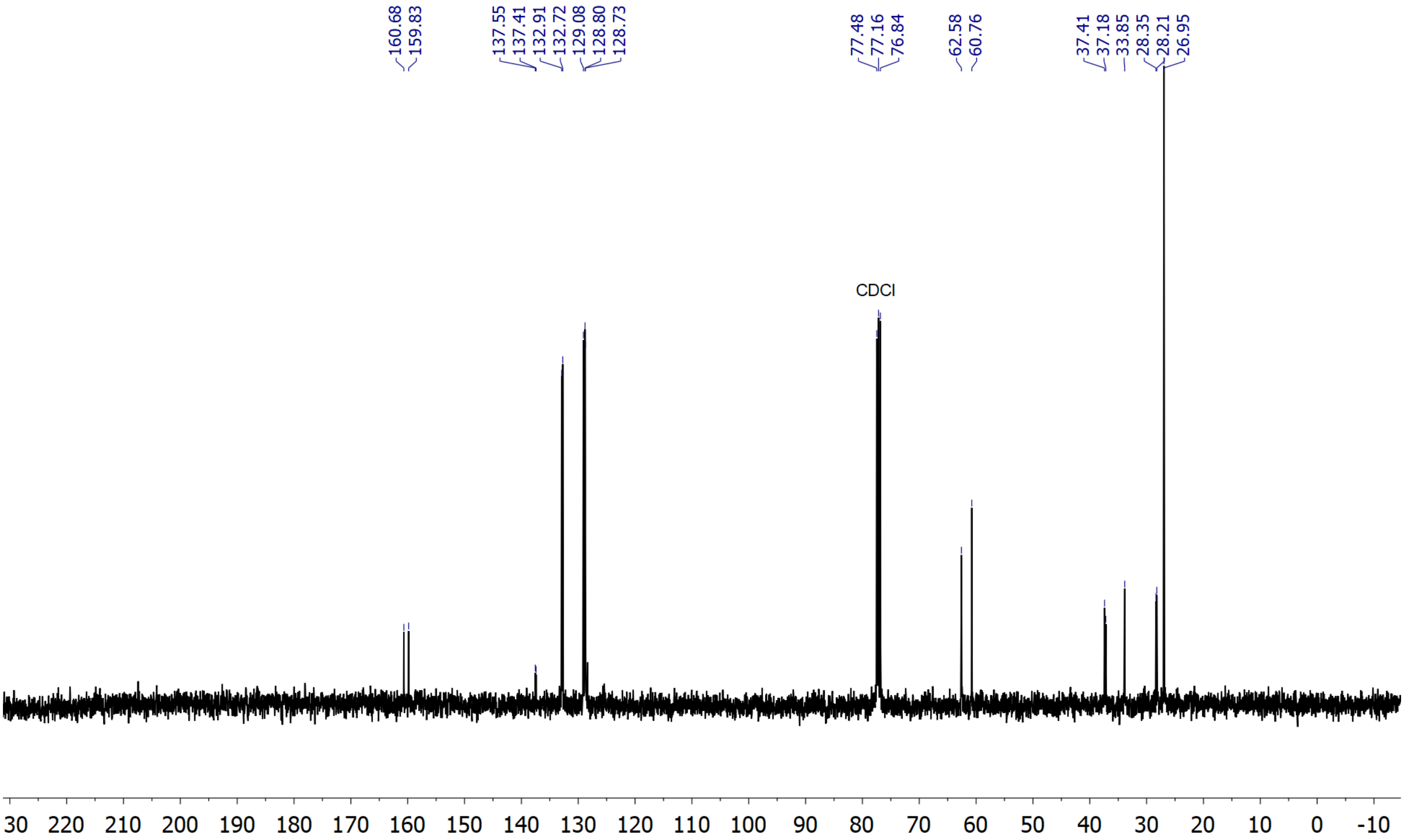


Figure S6c $^{13}C\{^1H\}$ spectrum for **3**

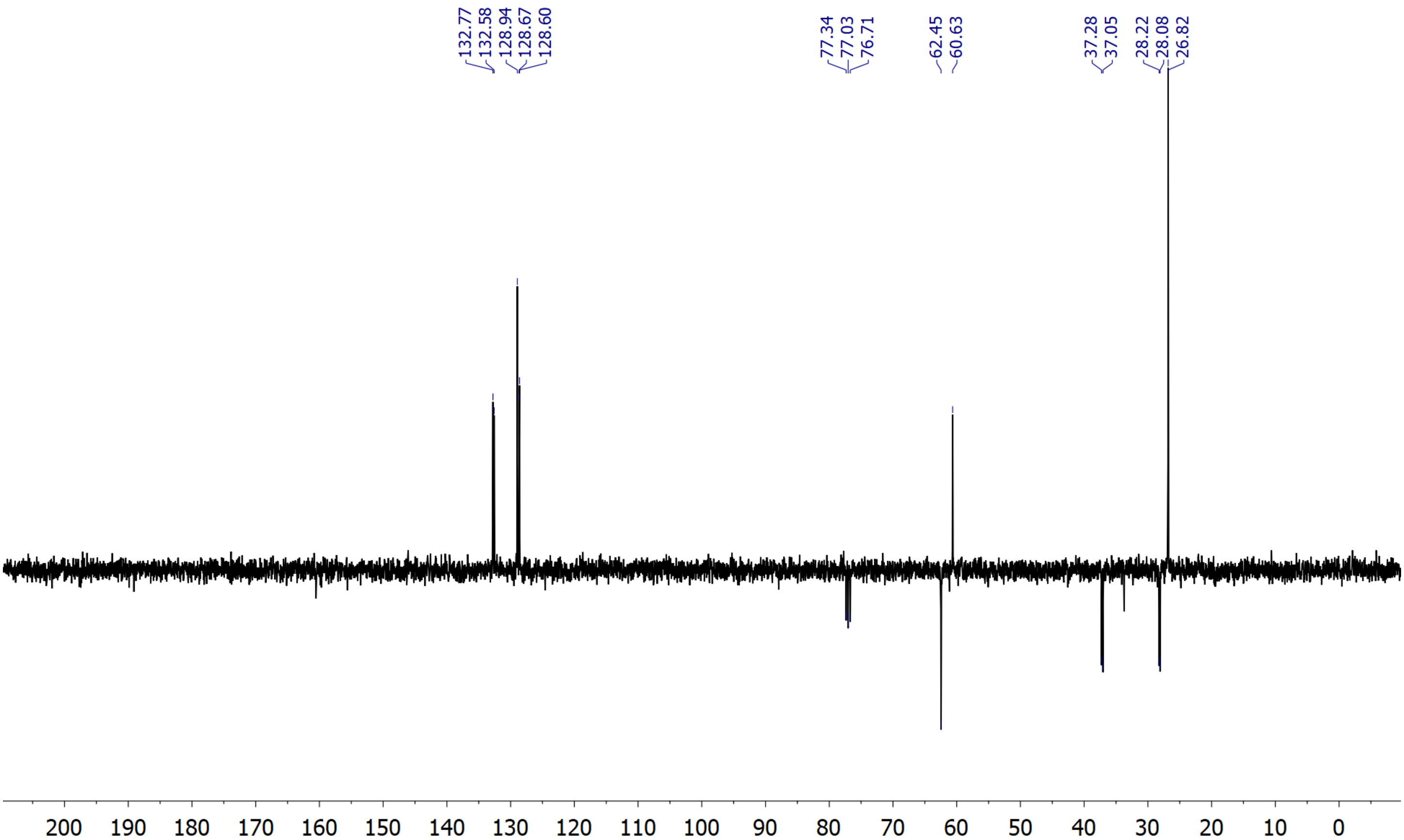


Figure S6d $^{13}C\{^1H\}$ DEPT spectrum for **3**

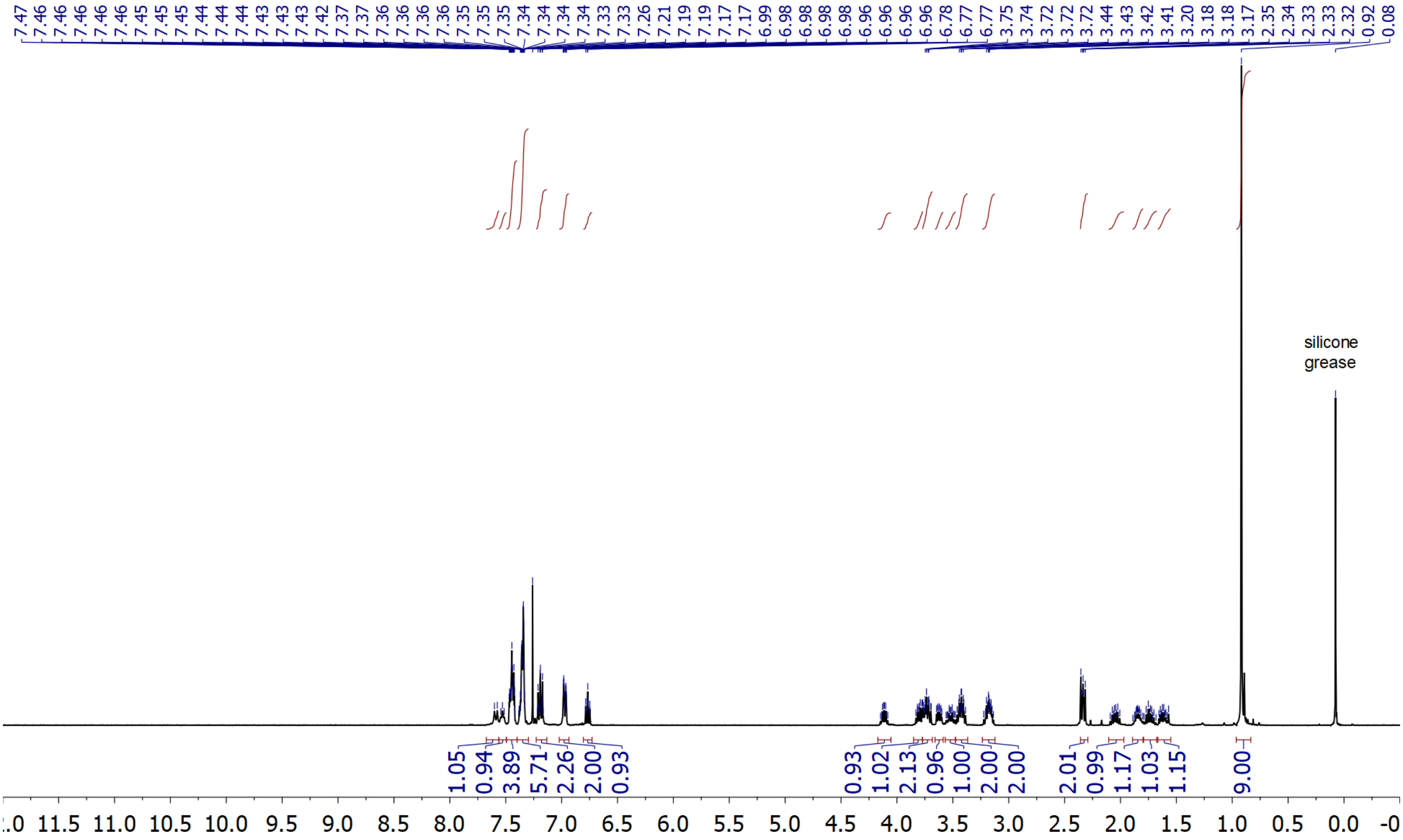


Figure S7a ^{1}H spectrum for **5a**

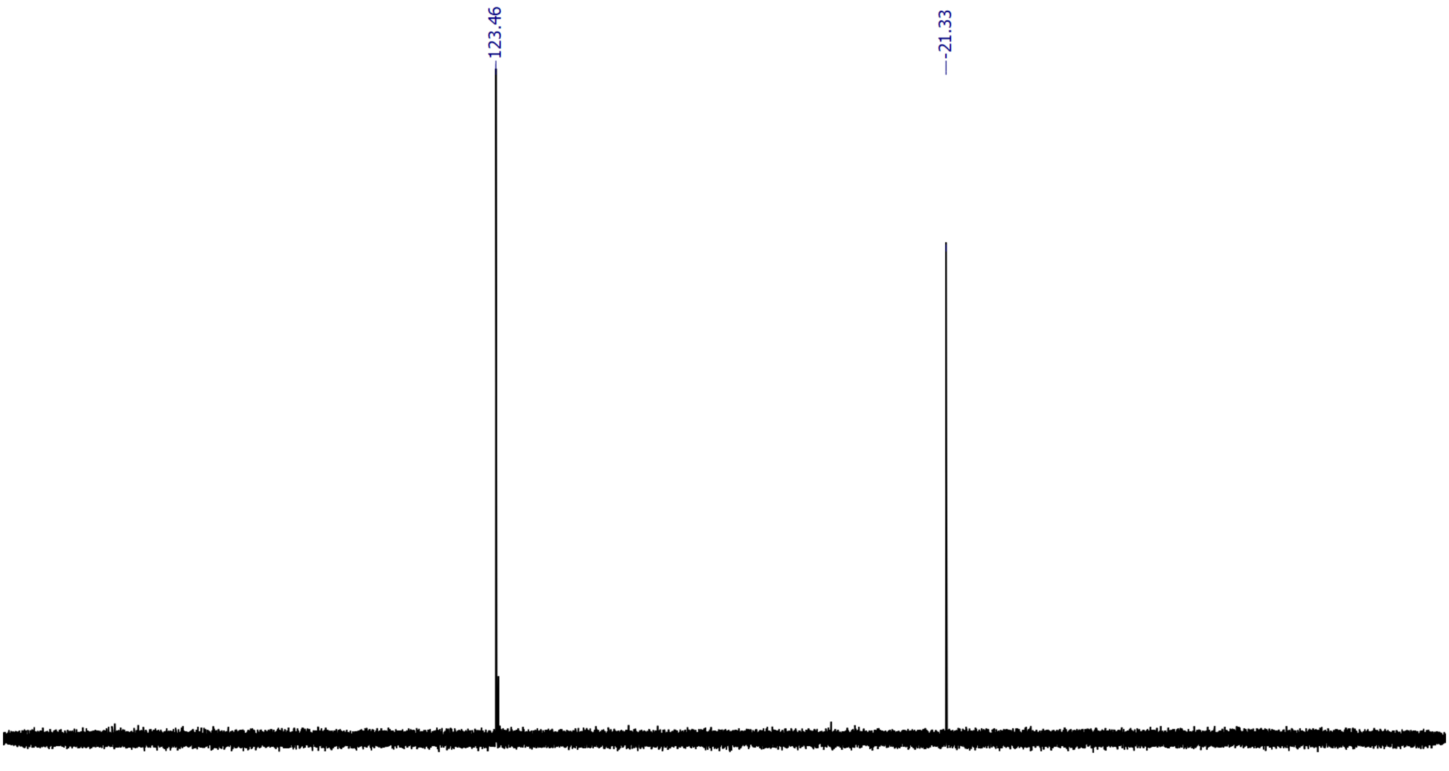
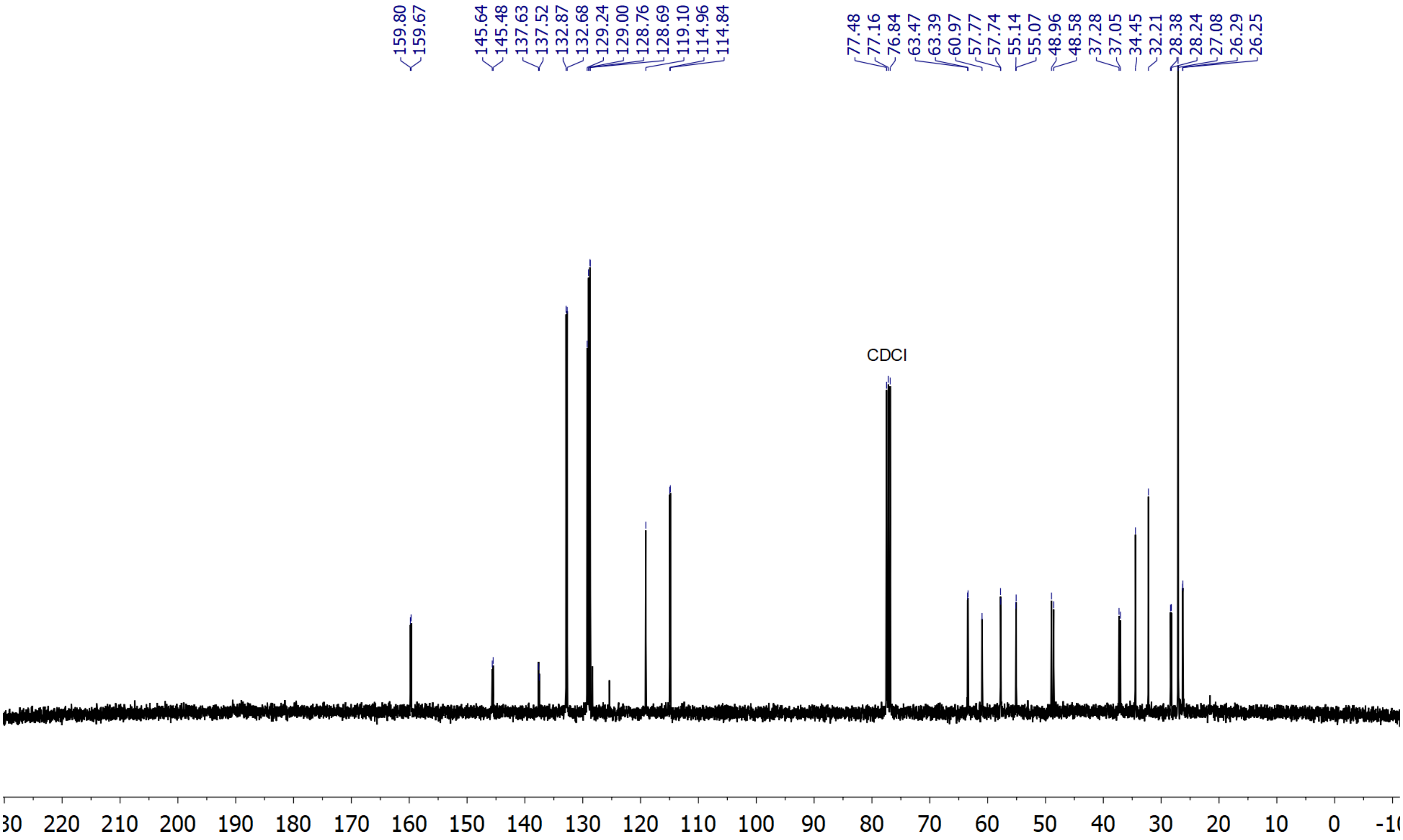


Figure S7b $^{31}P\{^{1}H\}$ spectrum for **5a**



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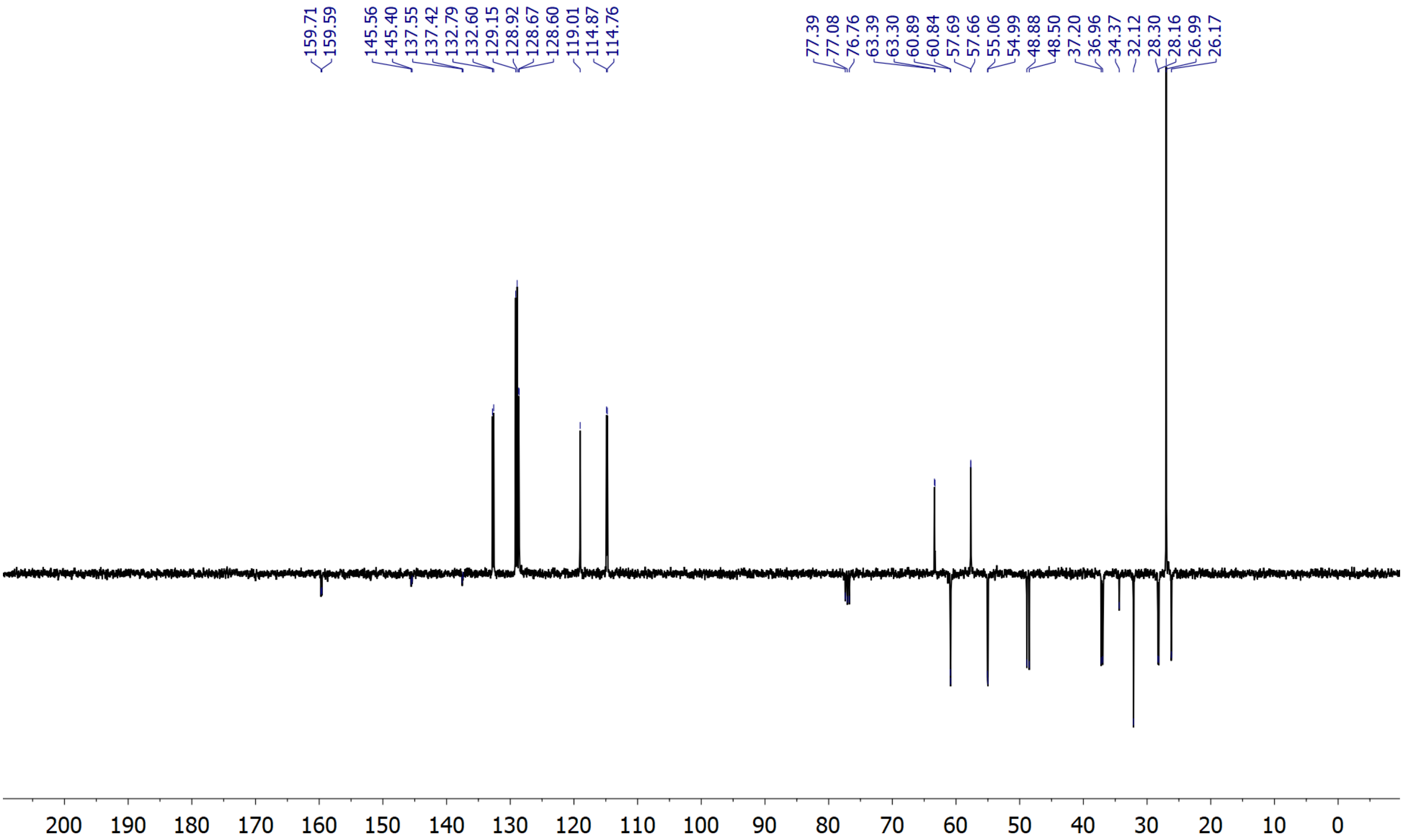


Figure S7d $^{13}C\{^1H\}$ DEPT spectrum for **5a**

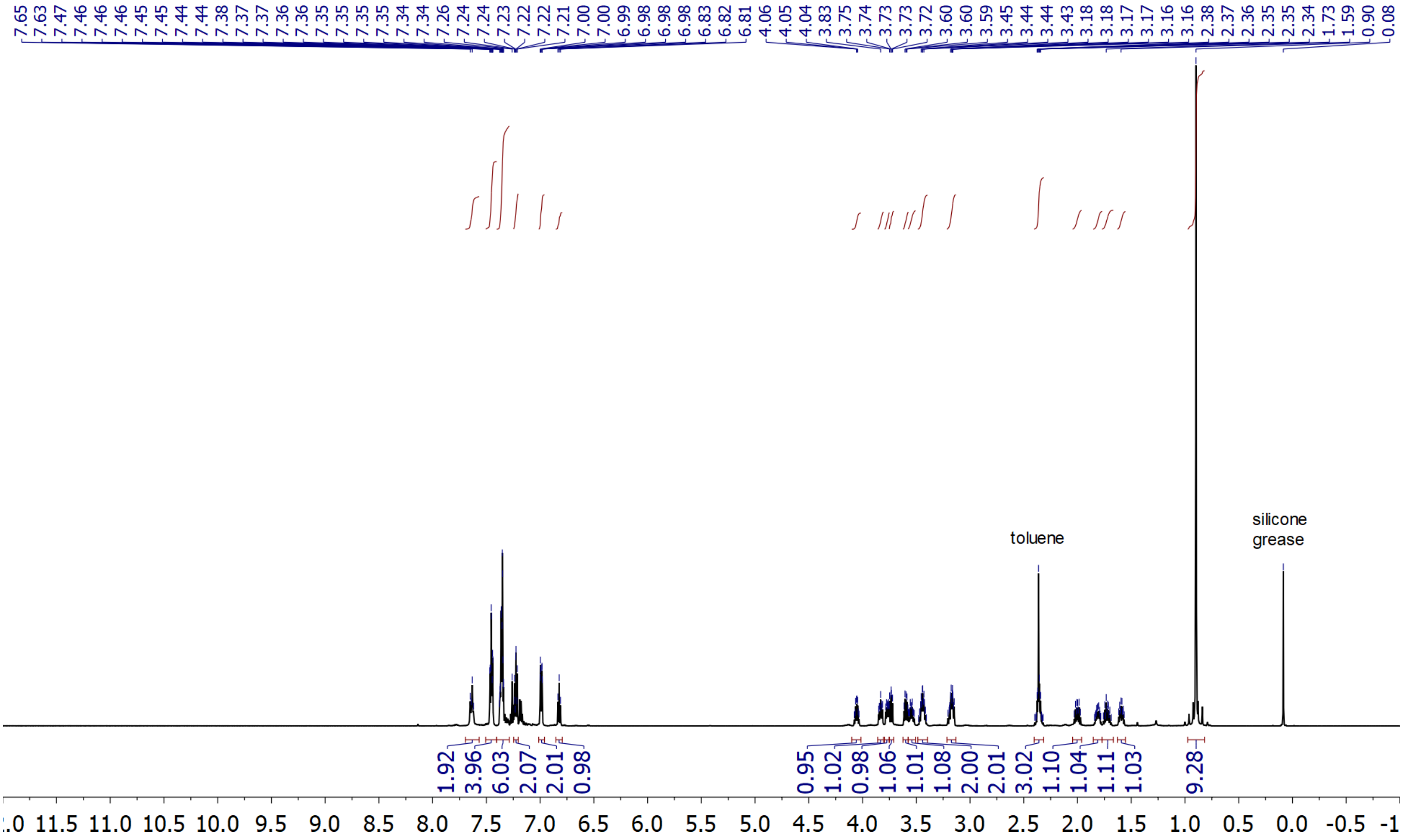


Figure S8a ^{1}H spectrum for **5b**

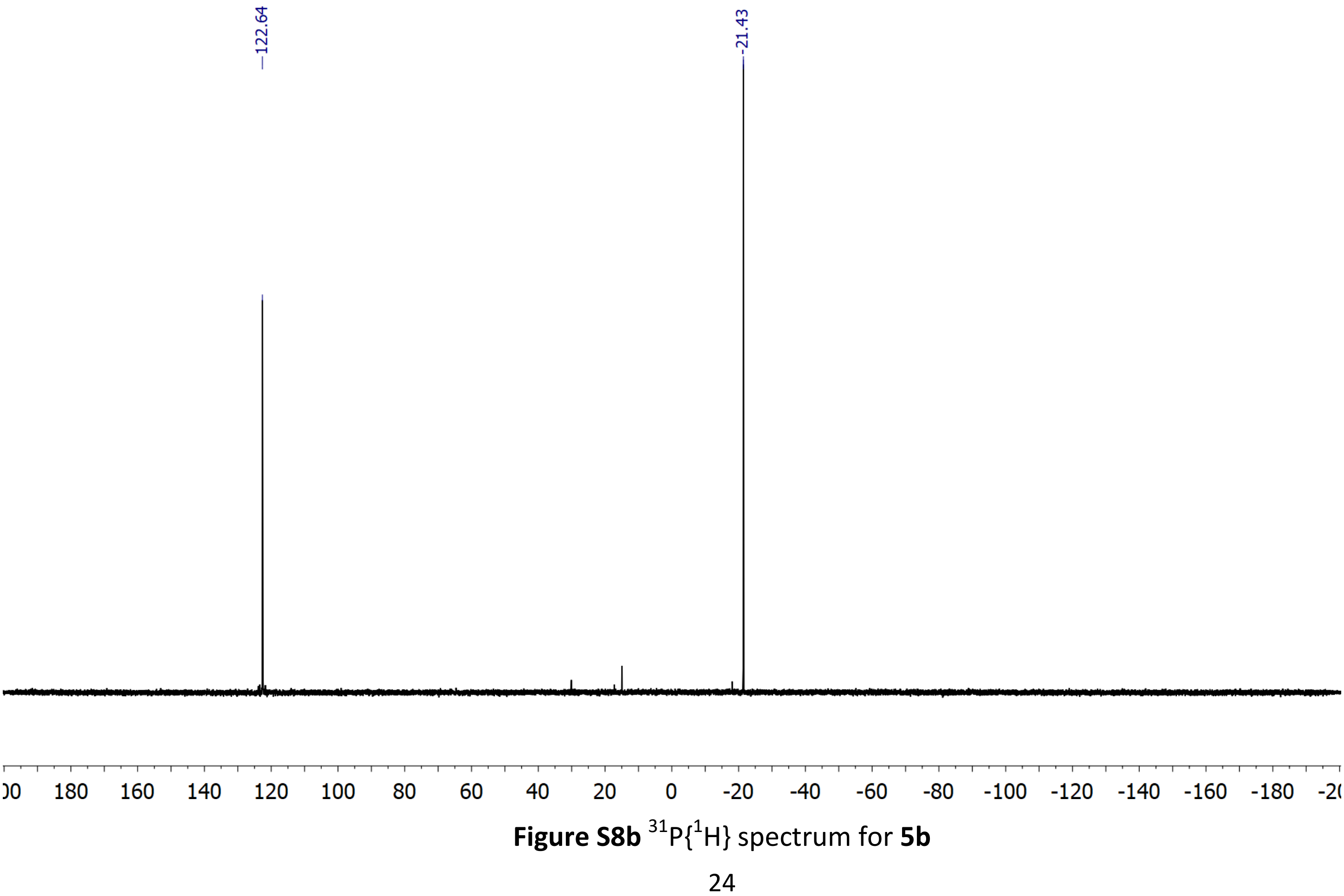
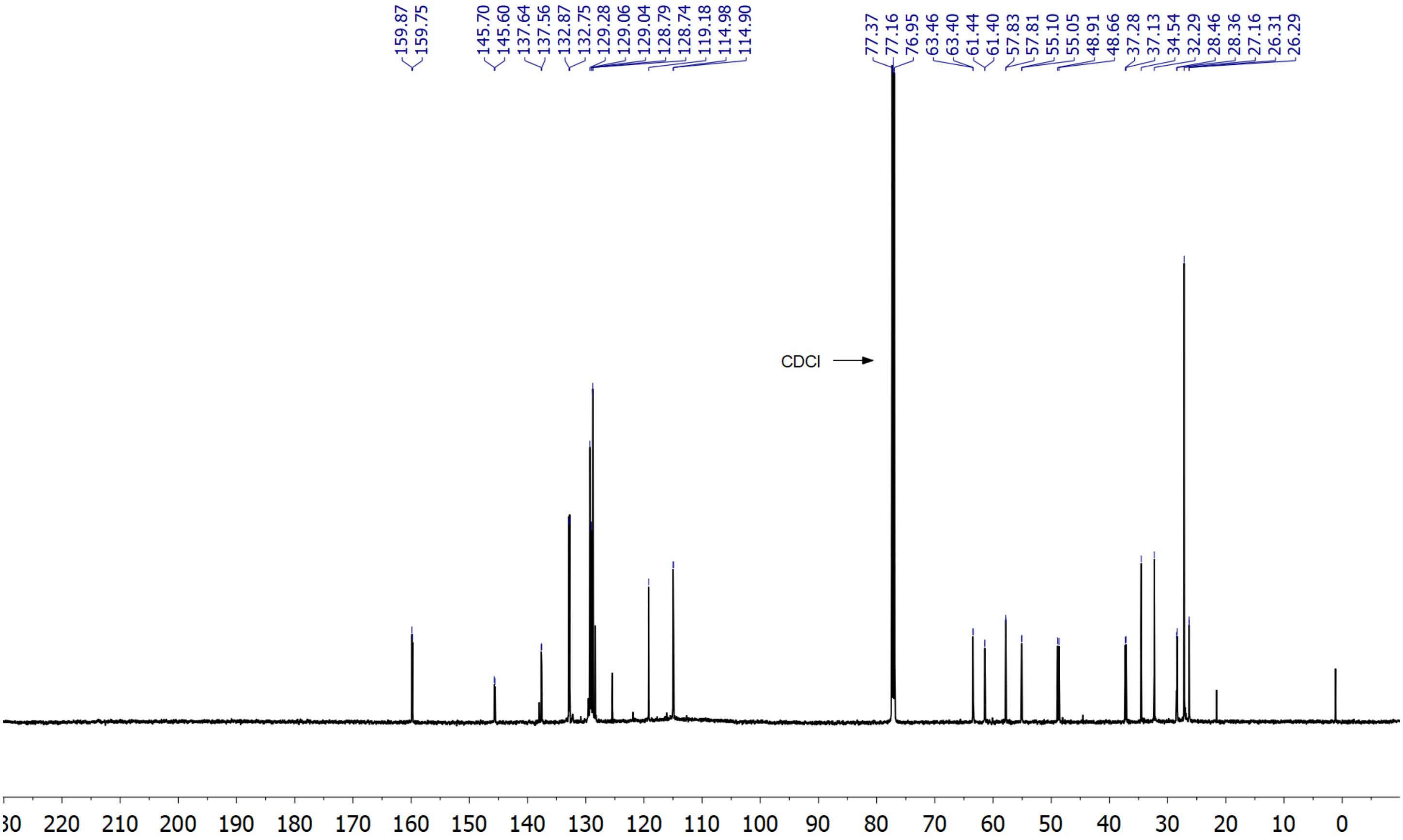


Figure S8b $^{31}P\{^{1}H\}$ spectrum for **5b**



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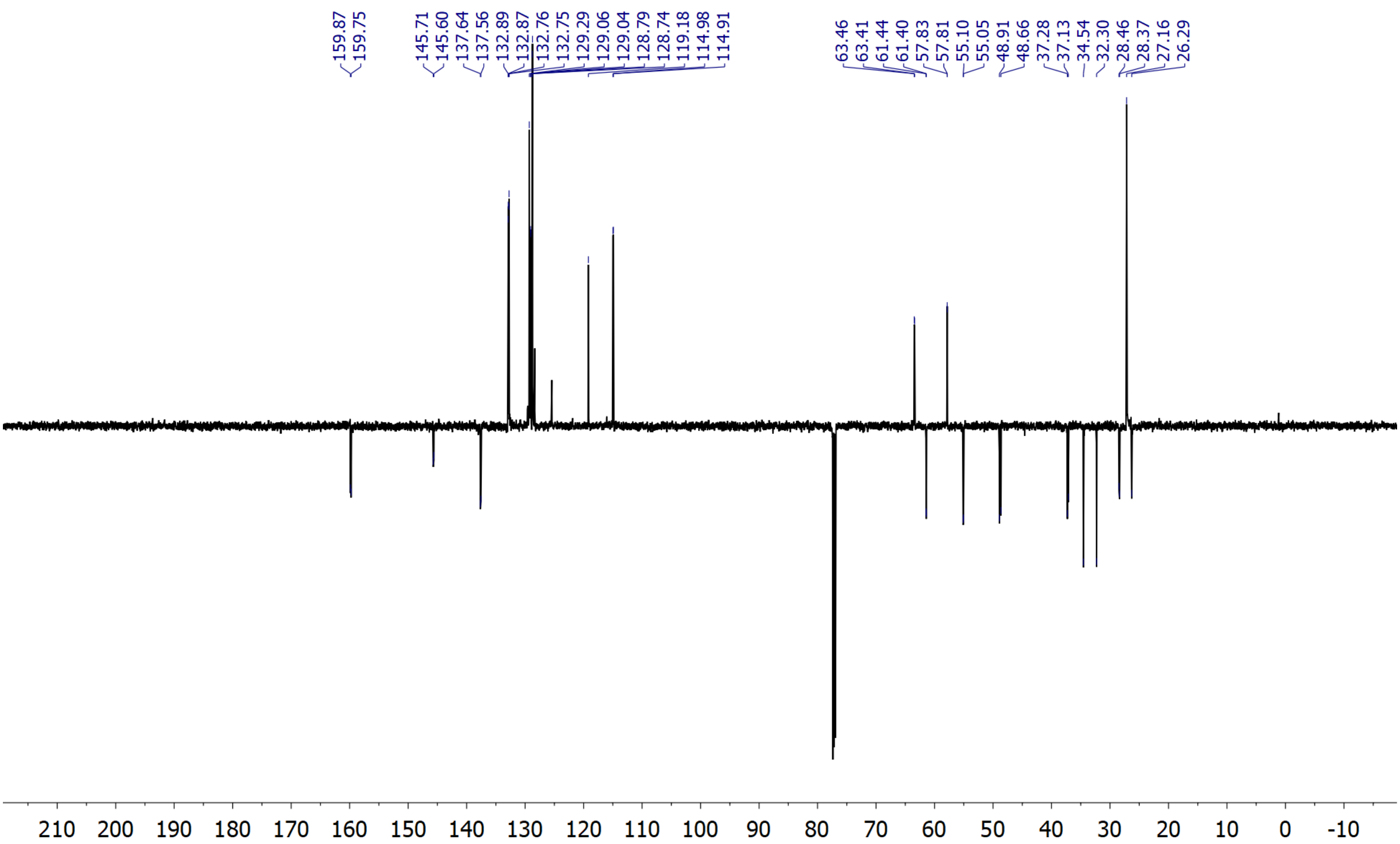


Figure S8d $^{13}C\{^{1}H\}$ DEPT spectrum for **5b**

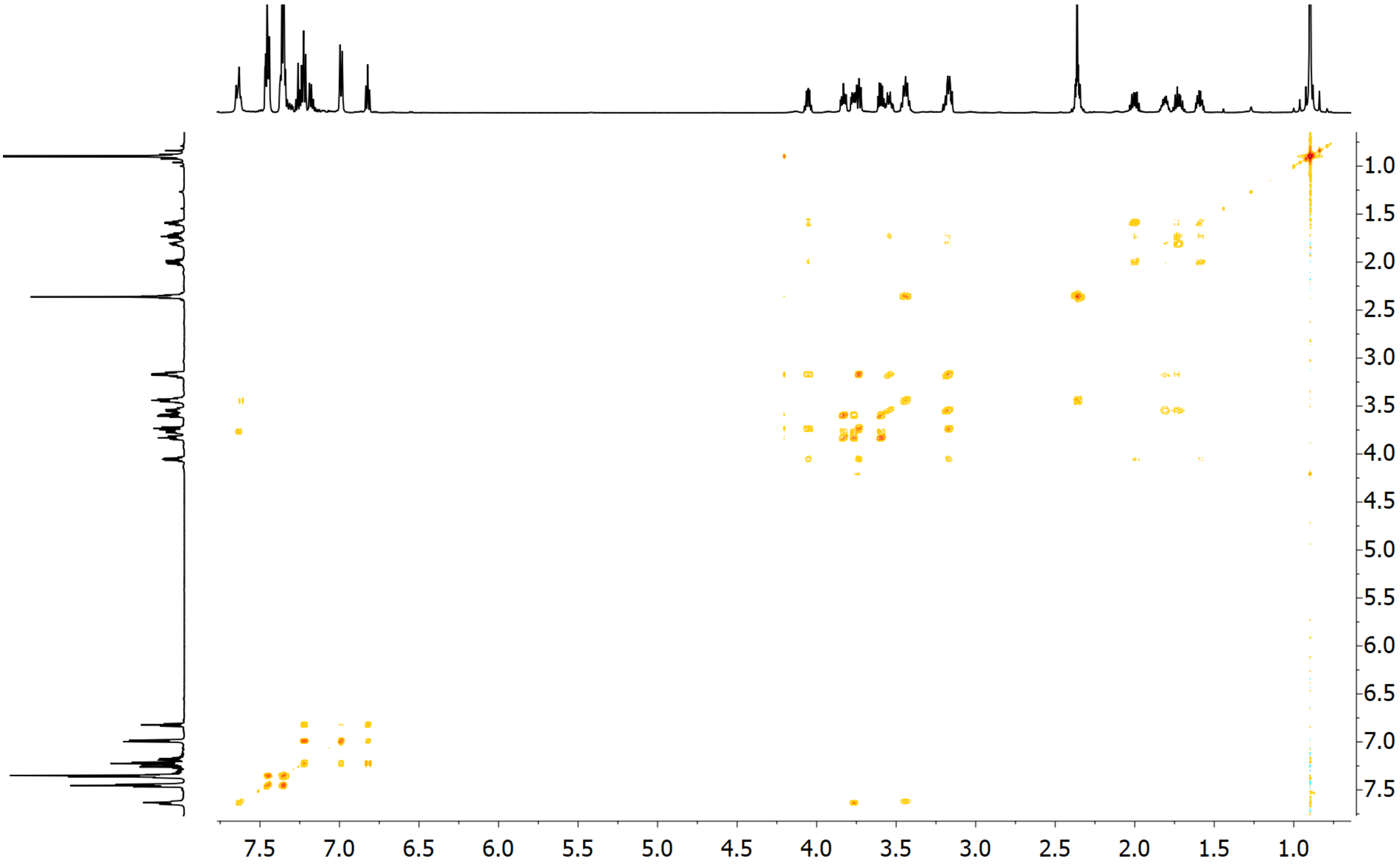


Figure S8e ¹H-¹H-COSY spectrum for **5b**

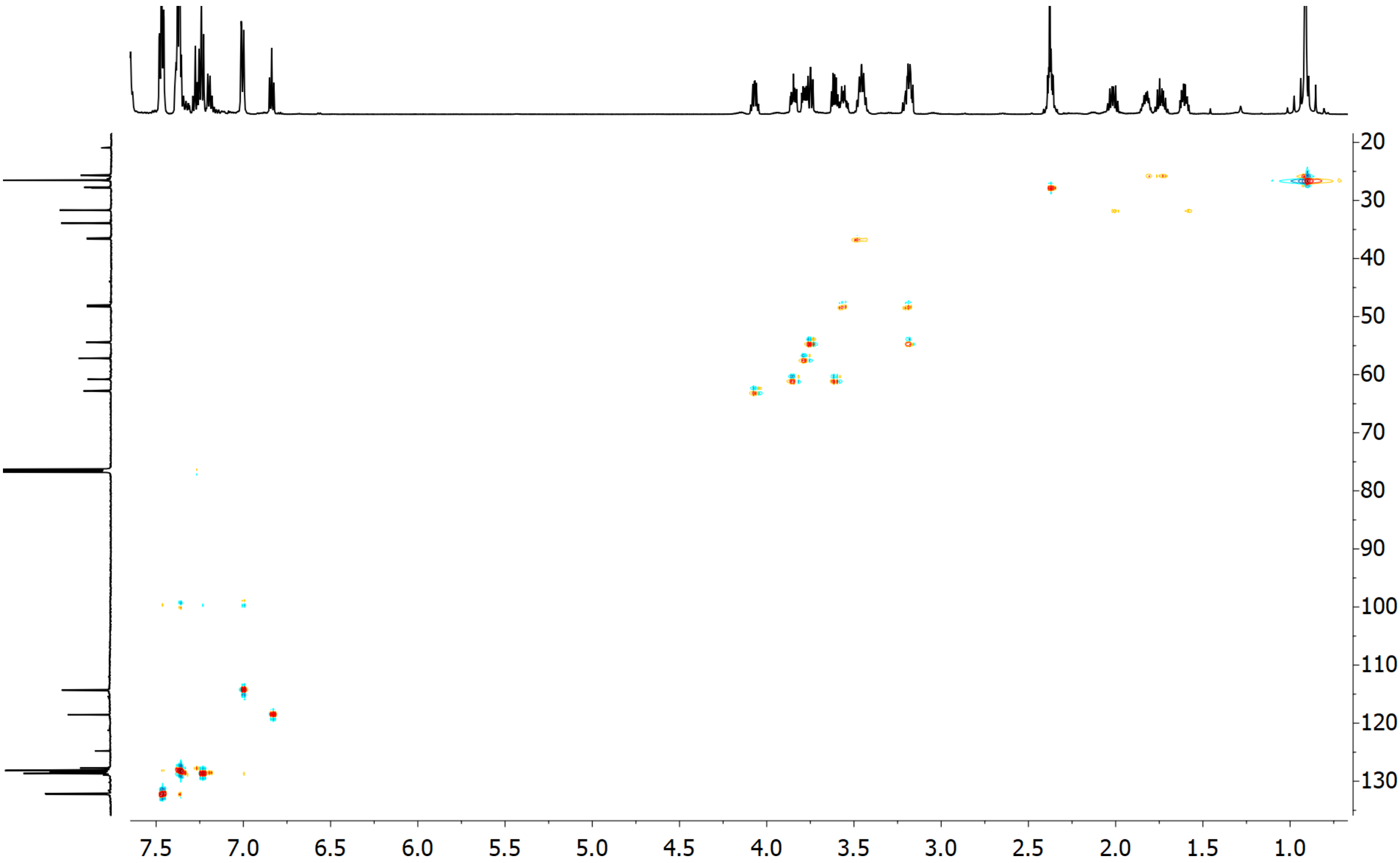


Figure S8f ¹H-¹³C-HSQC spectrum for **5b**

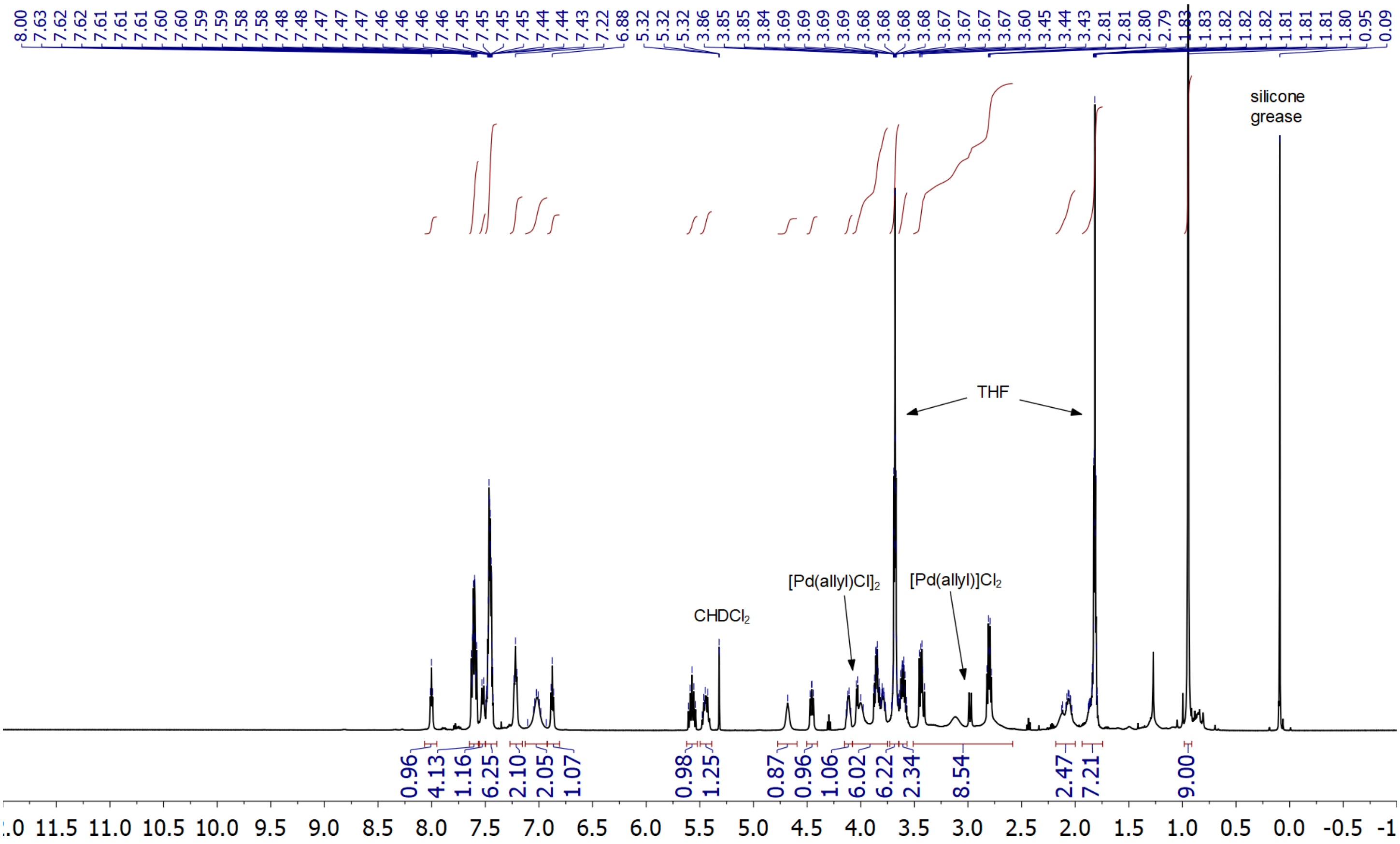


Figure S9a ^{1}H spectrum for $Pd_2(allyl)_2Cl_2$(**5b**)

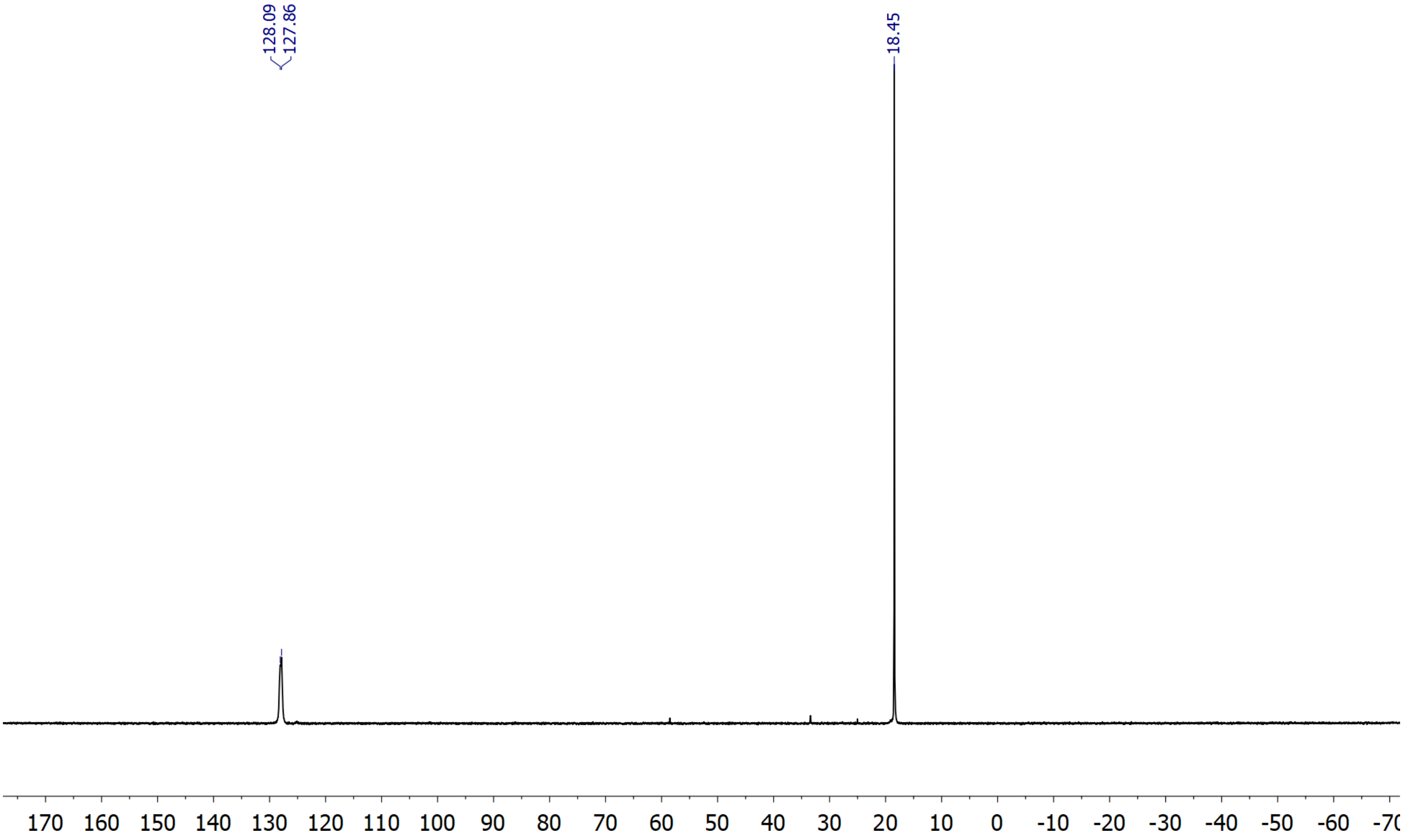


Figure S9b $^{31}P\{^{1}H\}$ spectrum for $Pd_2(allyl)_2Cl_2$(**5b**)

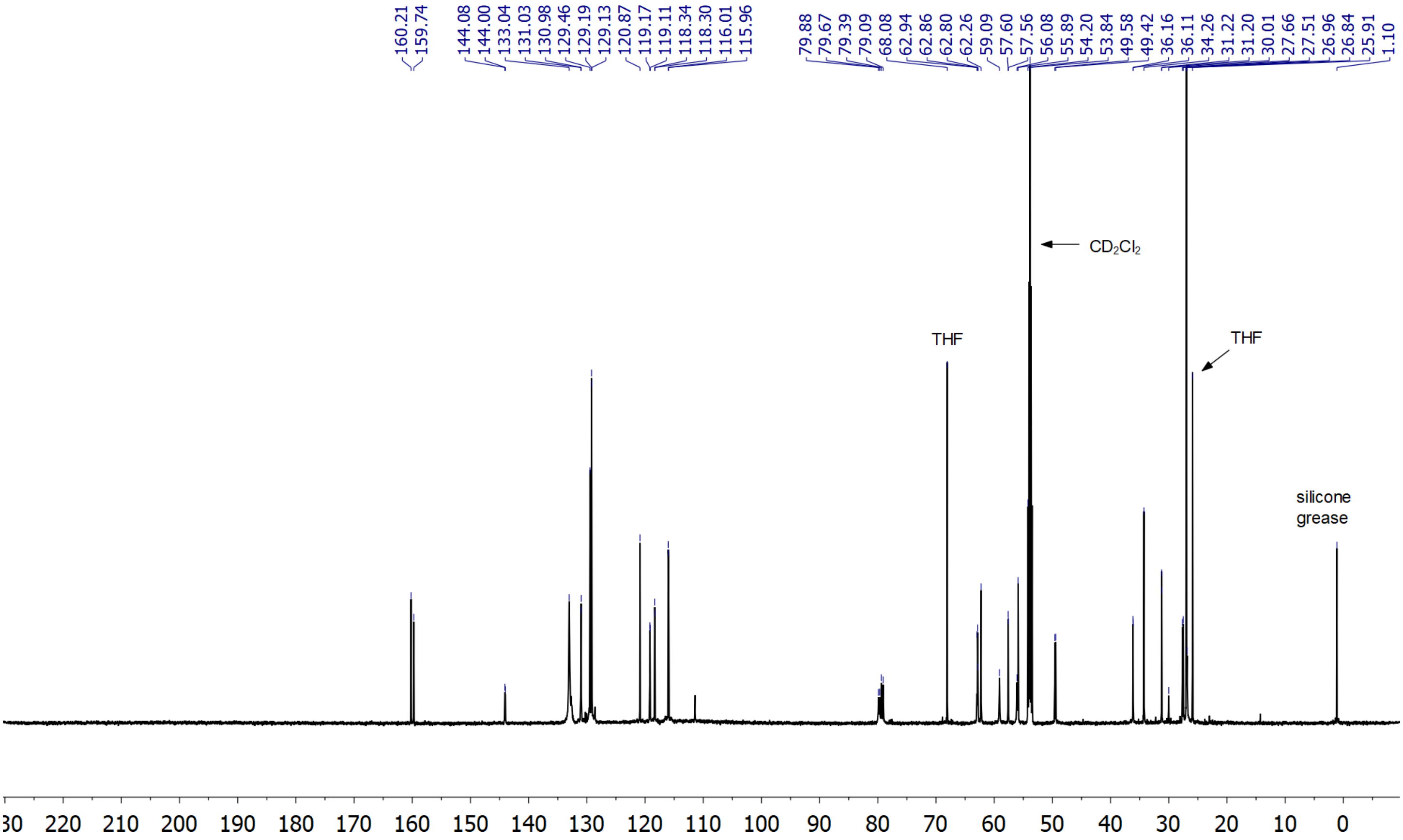


Figure S9c $^{13}C\{^1H\}$ spectrum for $Pd_2(allyl)_2Cl_2$(**5b**)

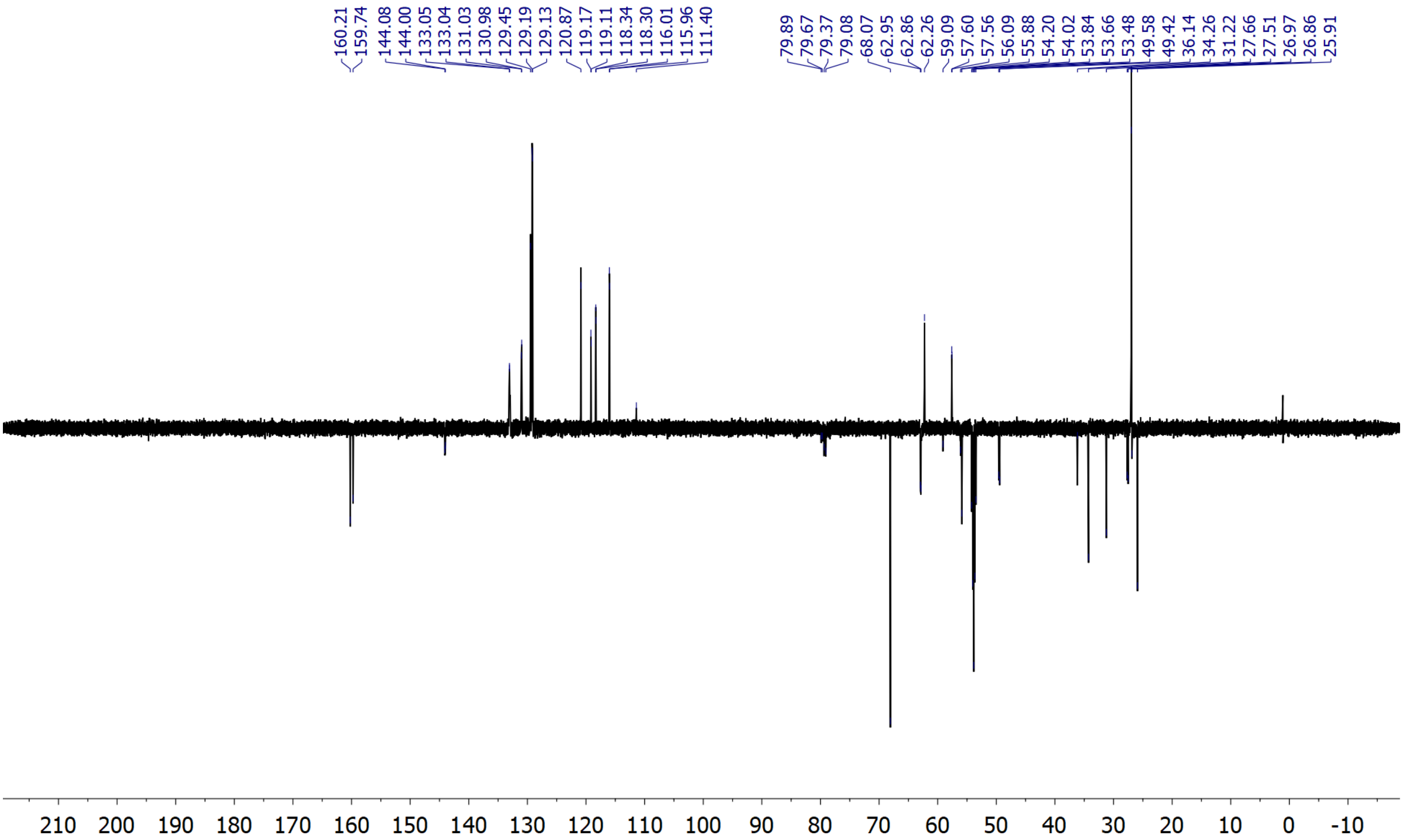


Figure S9d $^{13}C\{^1H\}$ DEPT spectrum for $Pd_2(allyl)_2Cl_2$(**5b**)

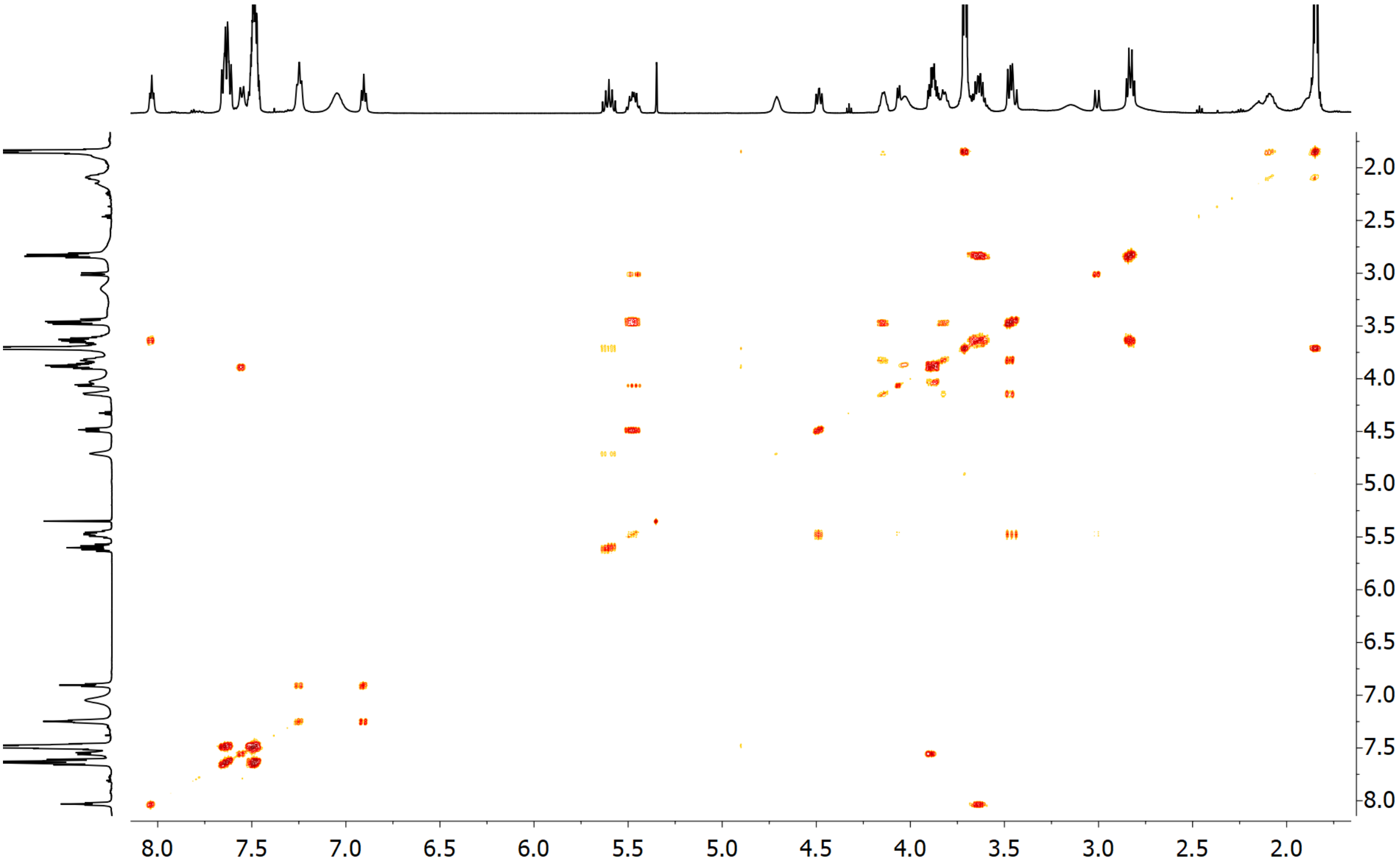


Figure S9e ^{1}H-^{1}H-COSY spectrum for $Pd_2(allyl)_2Cl_2$(**5b**)

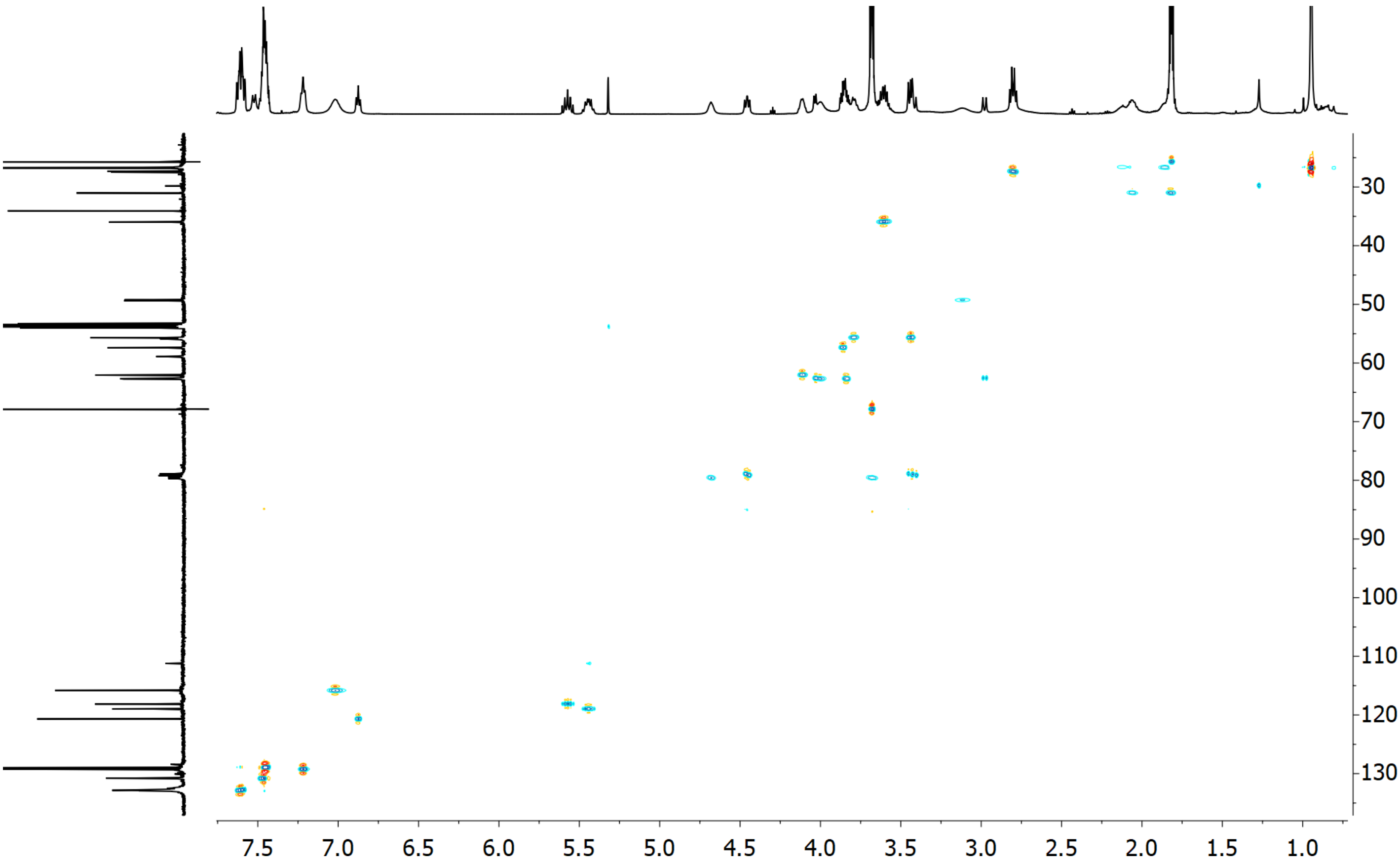


Figure S9f ^{1}H-^{13}C-HSQC spectrum for $Pd_2(allyl)_2Cl_2$(**5b**)

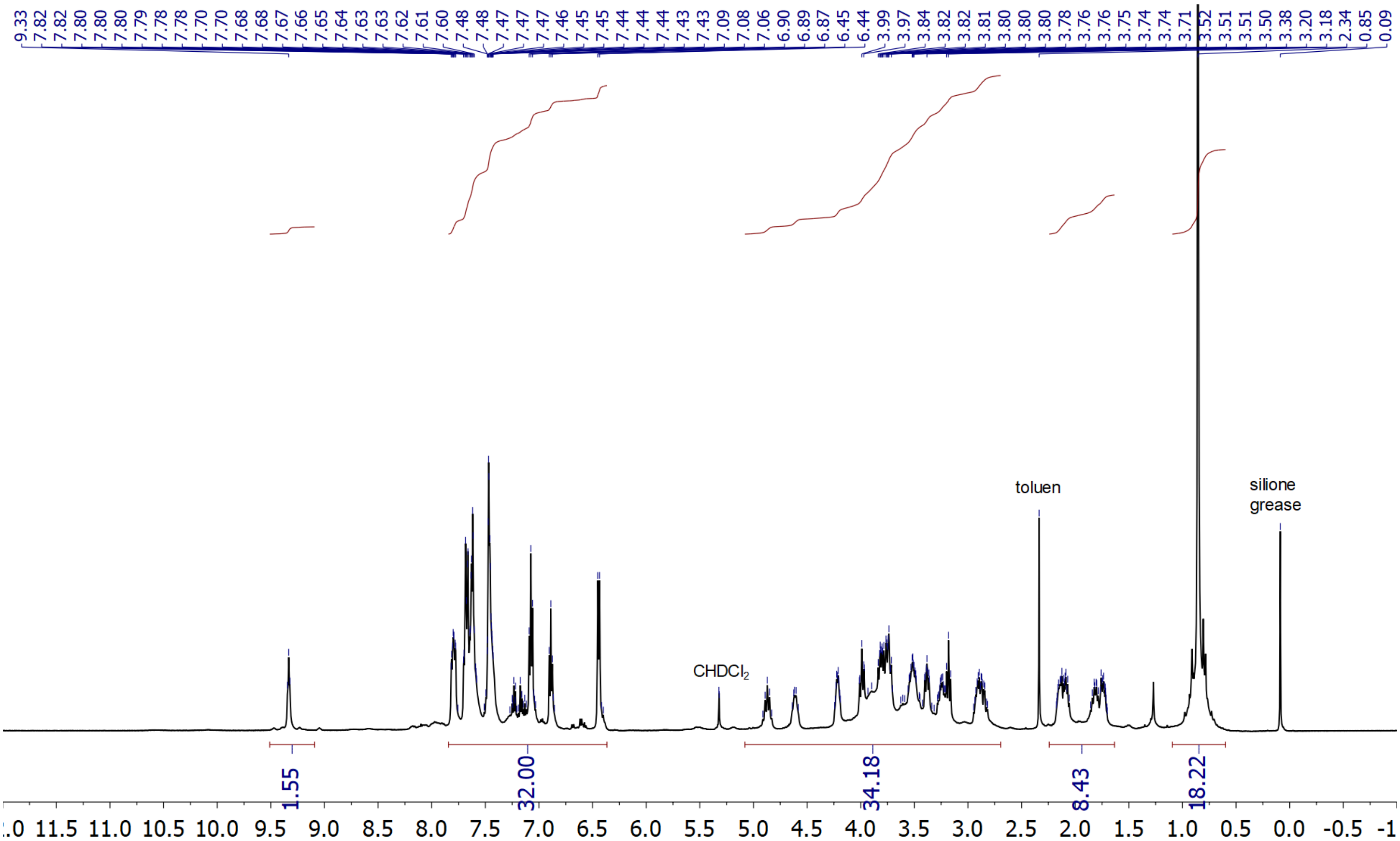


Figure S10a ^{1}H spectrum for $[Pd(allyl)(\mathbf{5b})]_2Cl_2$

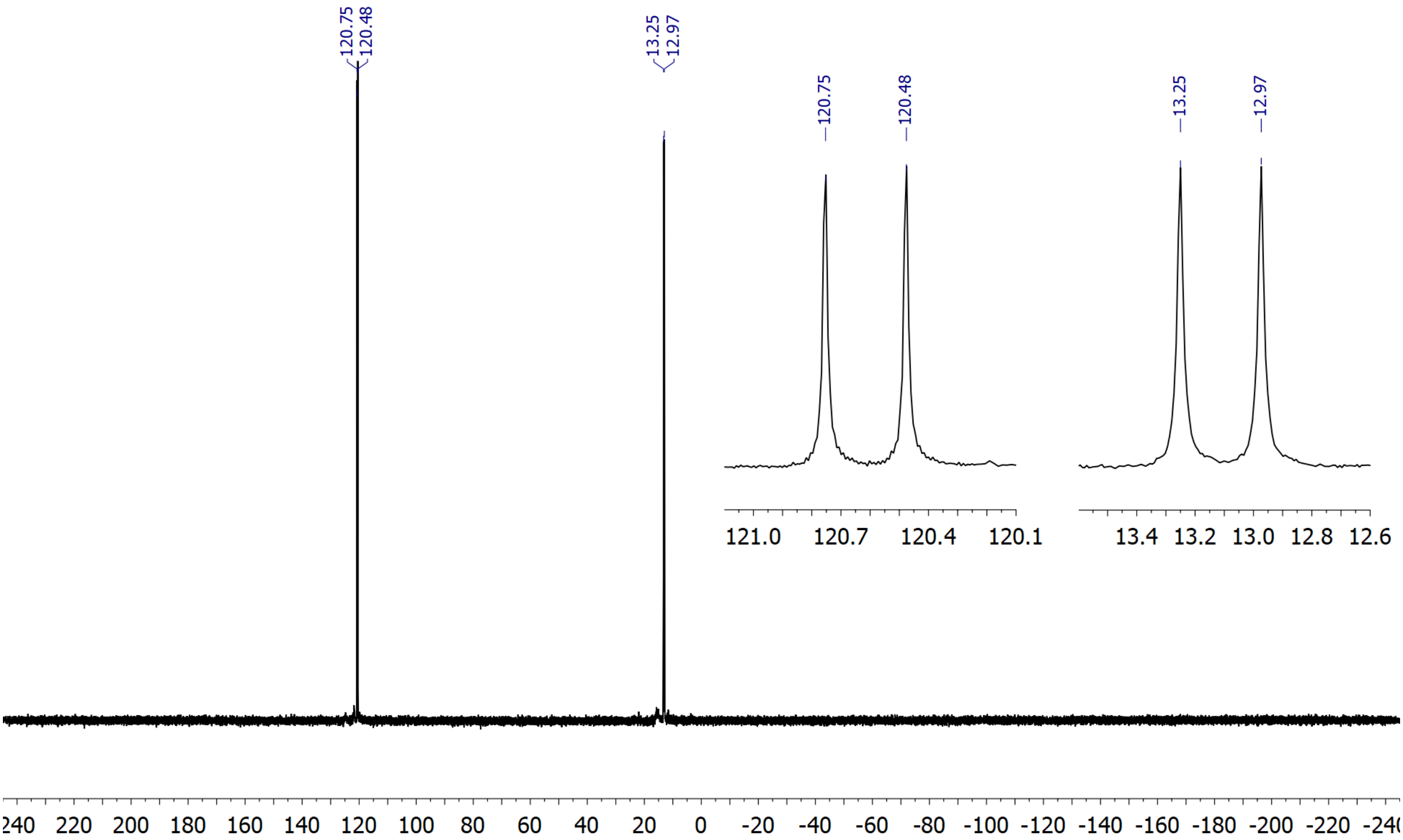


Figure S10b $^{31}P\{^{1}H\}$ spectrum for $[Pd(allyl)(\mathbf{5b})]_2Cl_2$

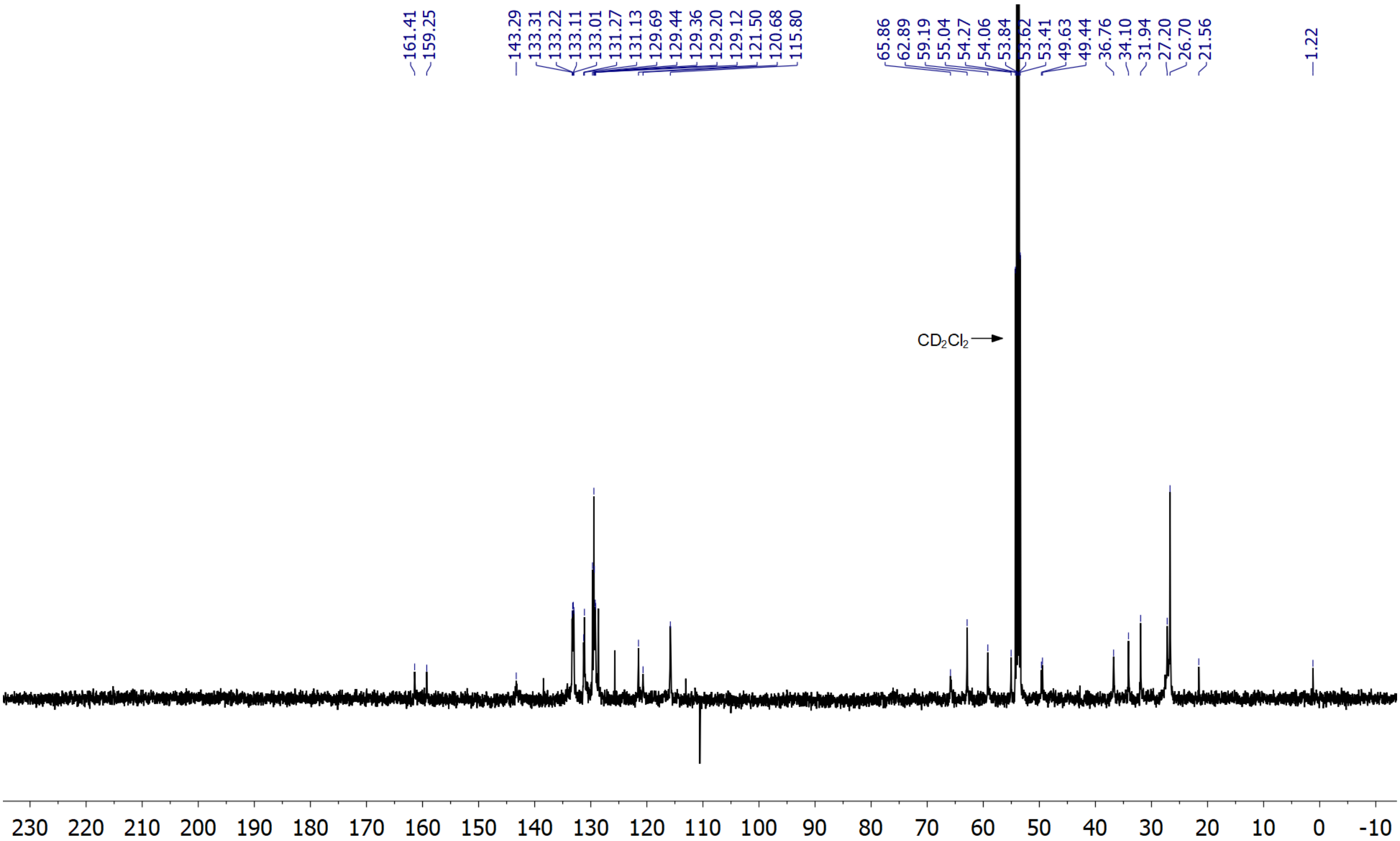


Figure S10c $^{13}C\{^{1}H\}$ spectrum for [Pd(allyl)(**5b**)]$_2$Cl$_2$

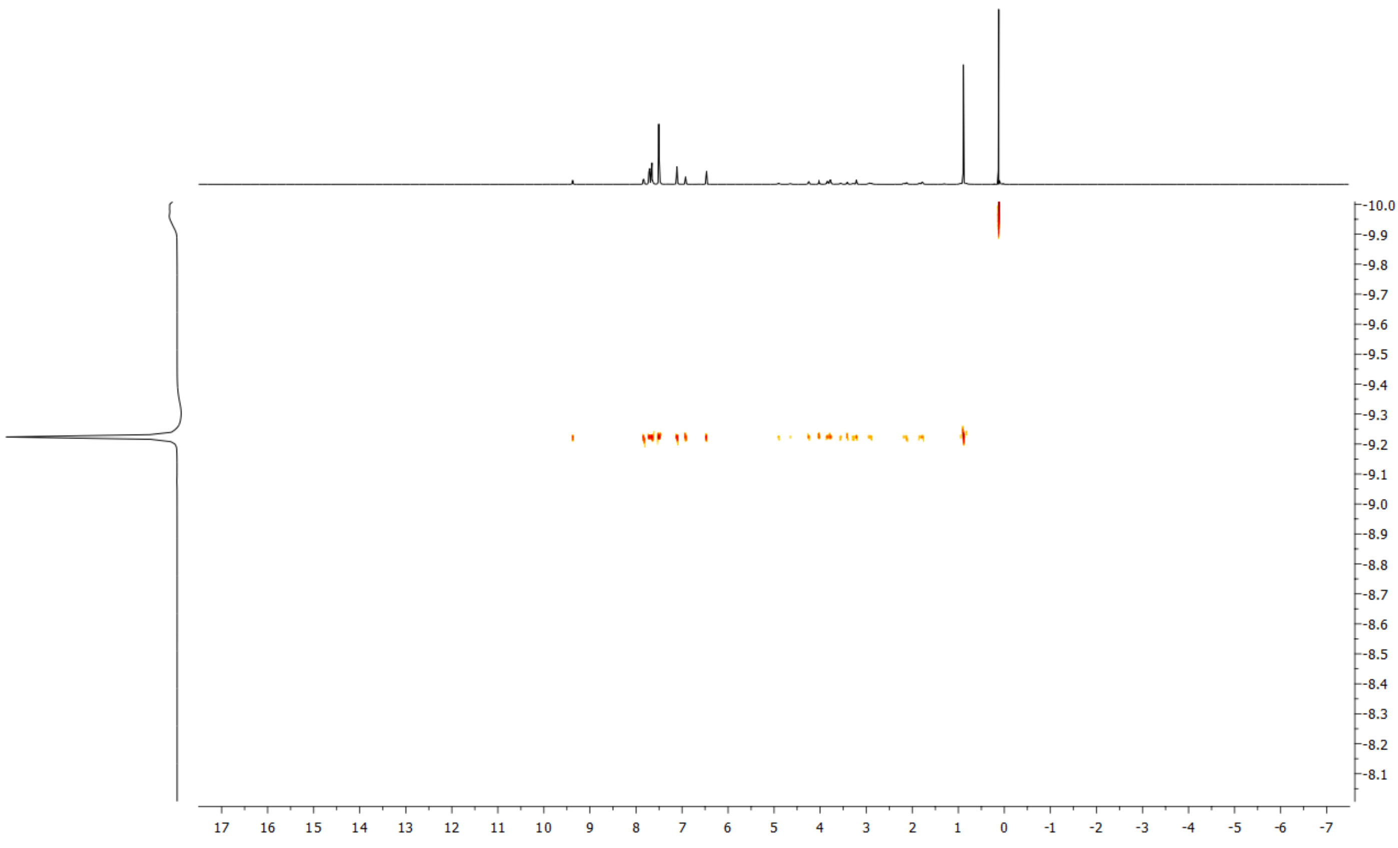


Figure S10d 2D DOSY spectrum for [Pd(allyl)(**5b**)]$_2$Cl$_2$

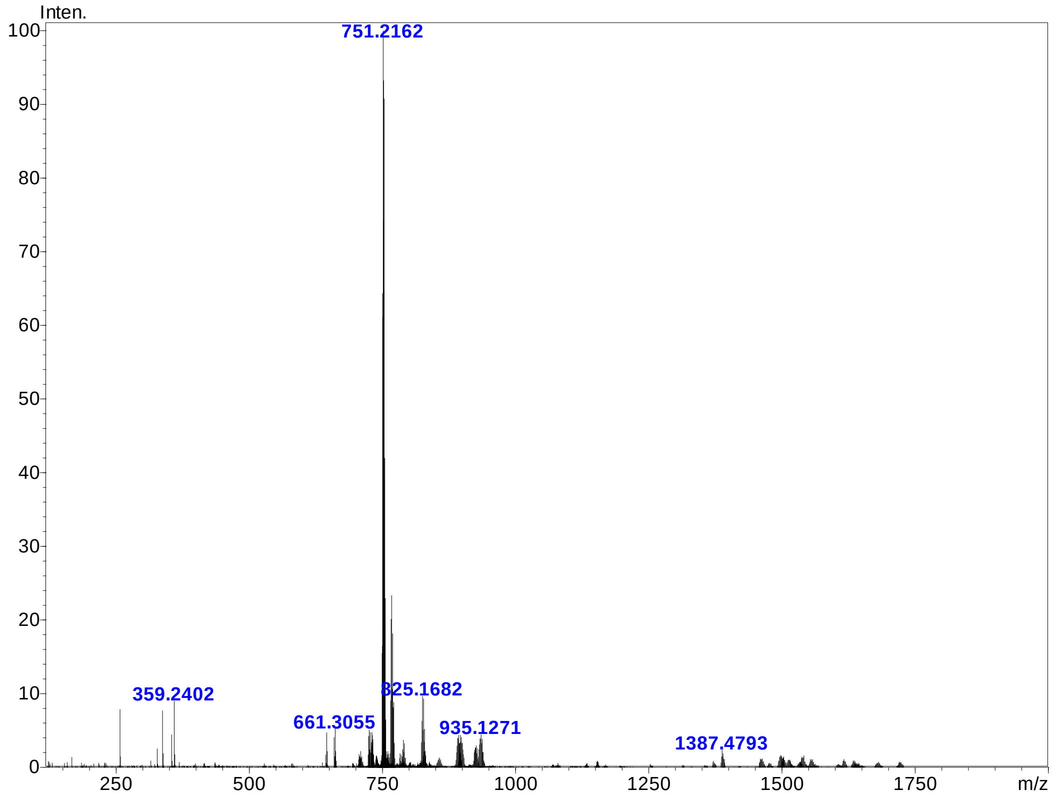


Figure S10e HRMS spectrum for [Pd(allyl)(**5b**)]$_2$Cl$_2$

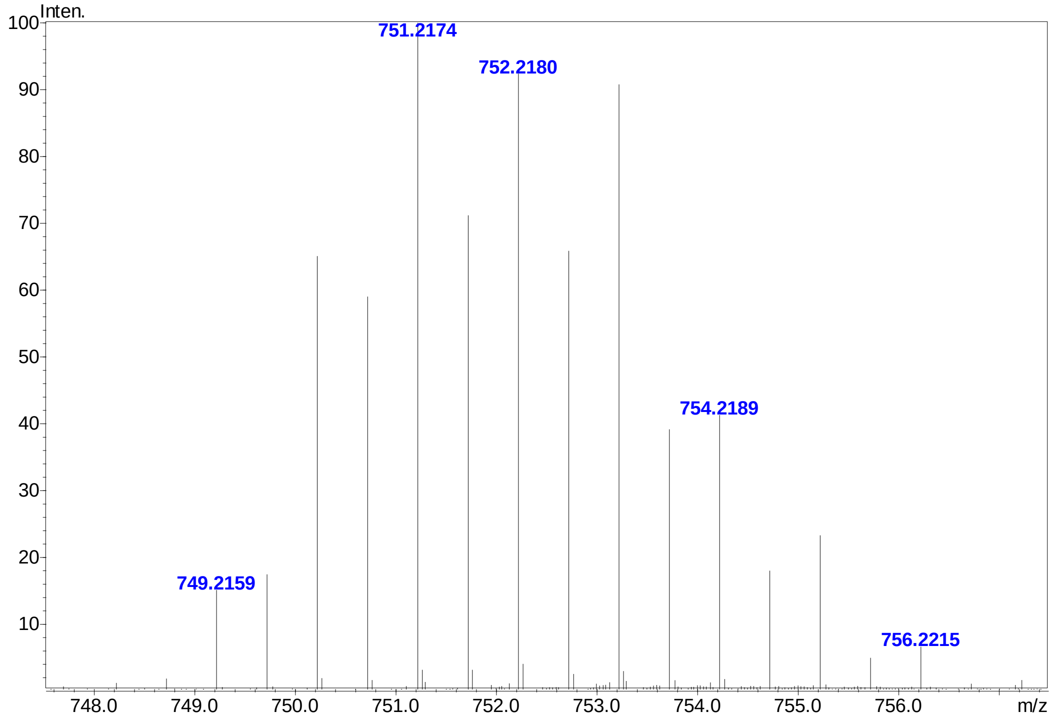


Figure S10f HRMS spectrum for [Pd(allyl)(**5b**)]$_2$Cl$_2$ ([Pd(allyl)(**5b**)]$_2^{2+}$ region)

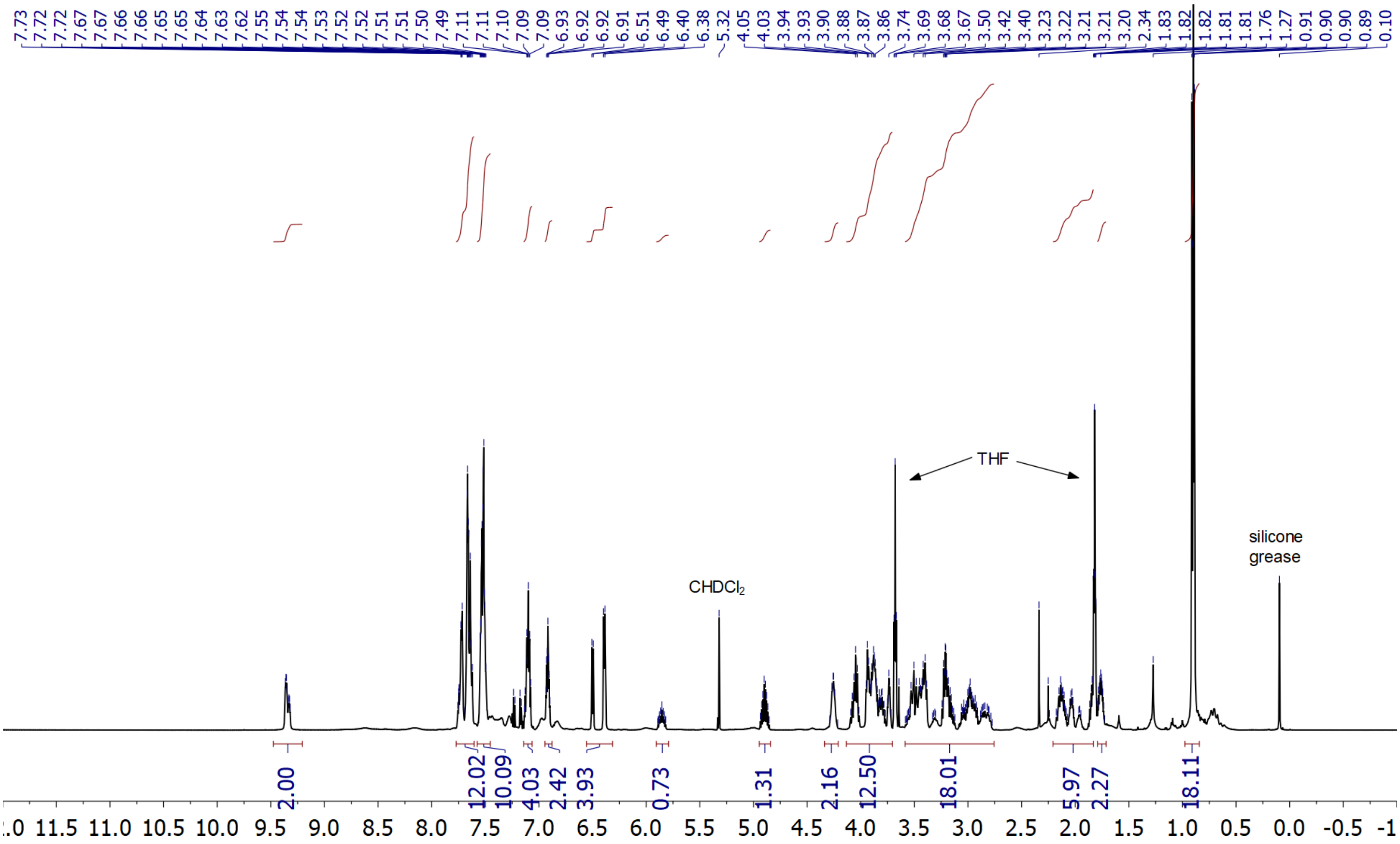


Figure S11a ^{1}H spectrum for $[Pd(allyl)(\mathbf{5b})]_2(BF_4)_2$

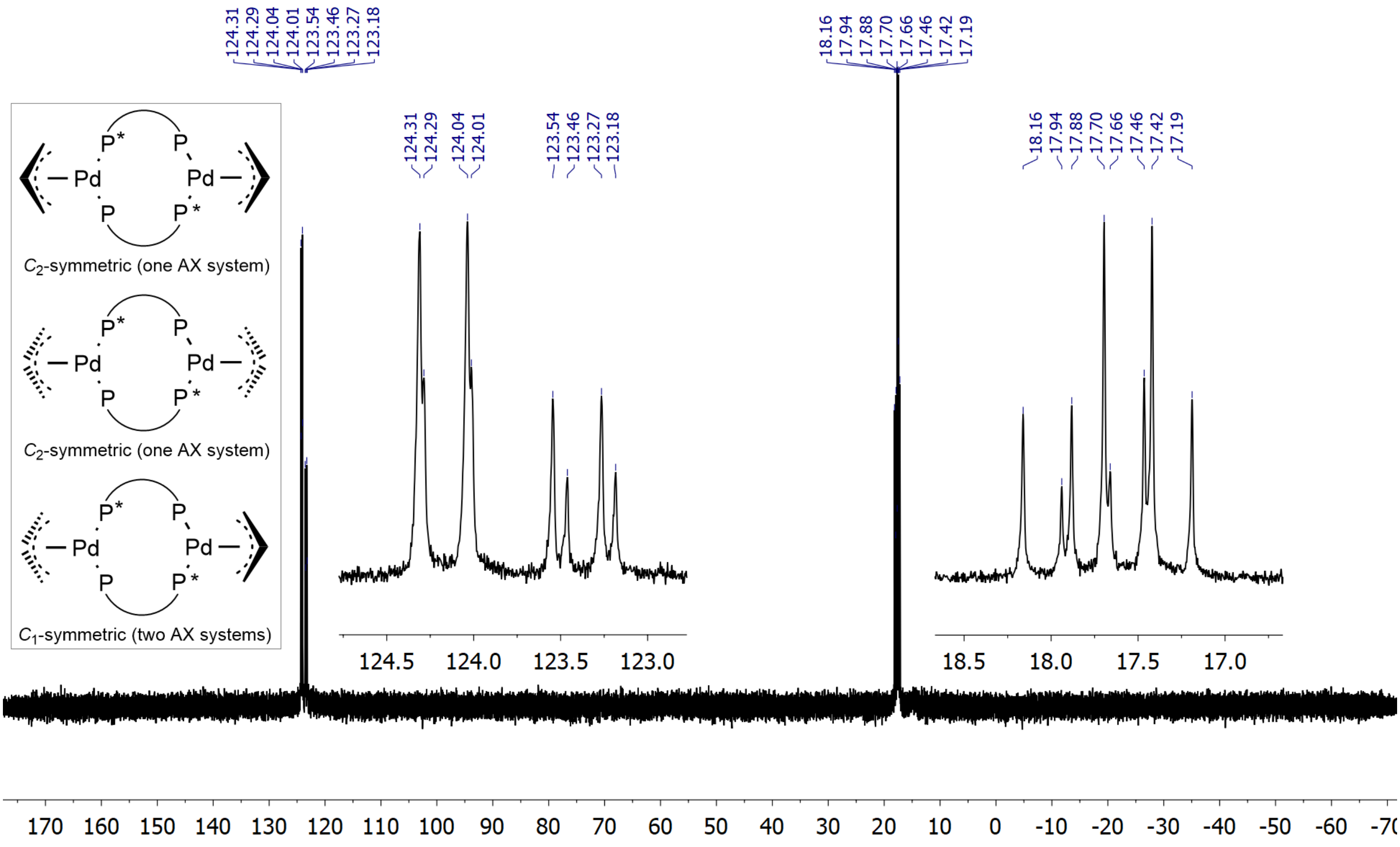


Figure S11b $^{31}P\{^{1}H\}$ spectrum for $[Pd(allyl)(\mathbf{5b})]_2(BF_4)_2$

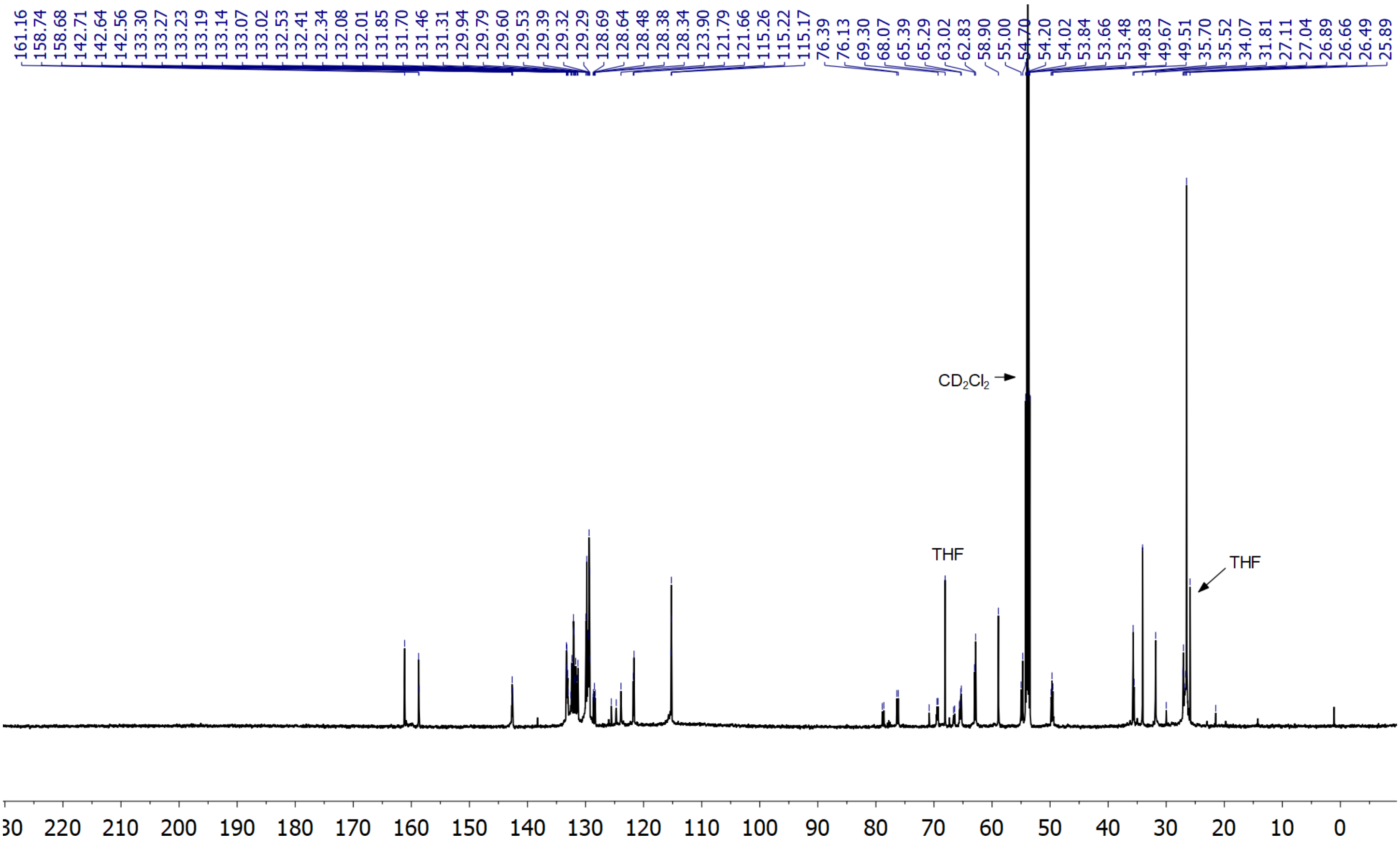


Figure S11c $^{13}C\{^1H\}$ spectrum for $[Pd(allyl)(\mathbf{5b})]_2(BF_4)_2$

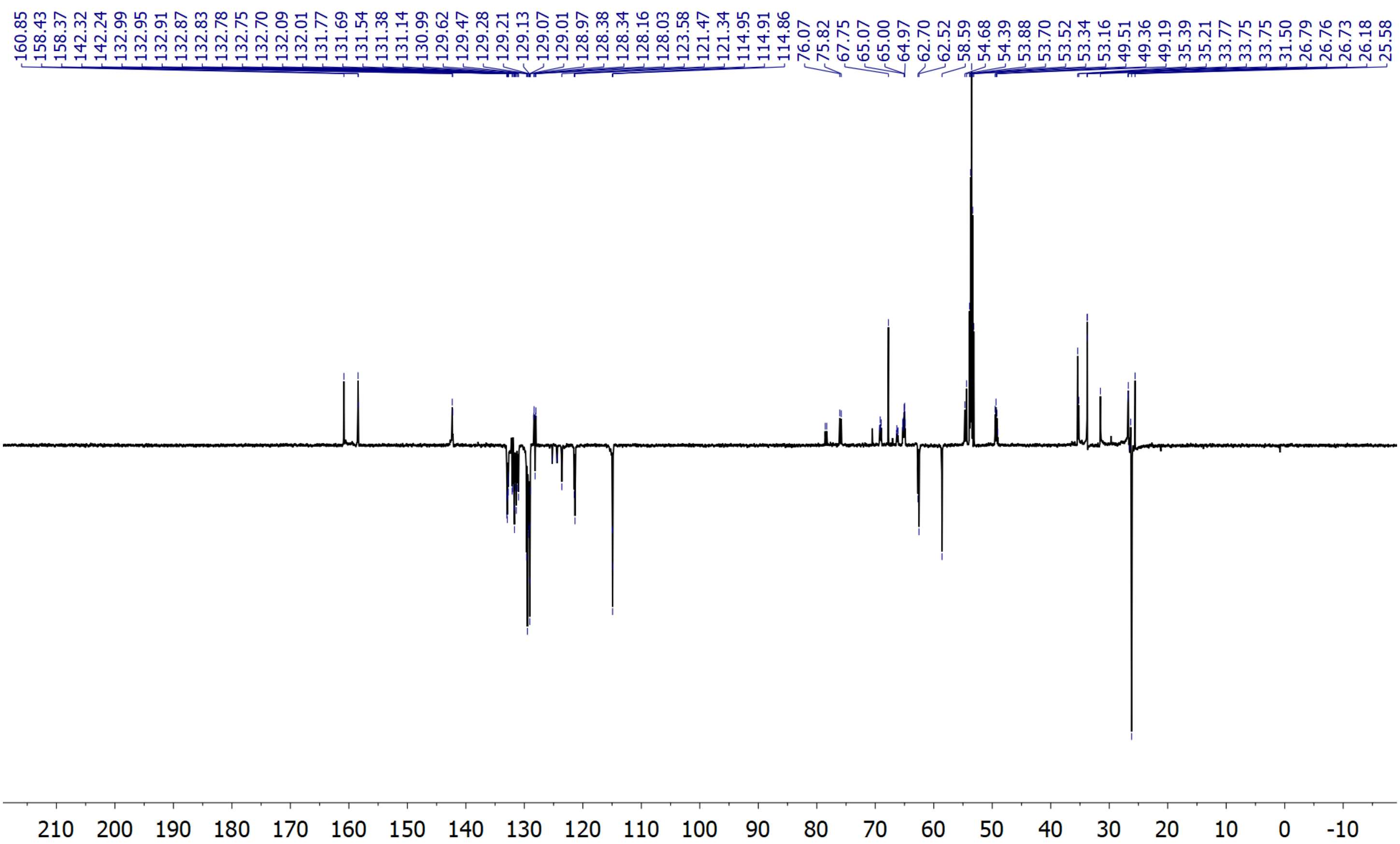


Figure S11d $^{13}C\{^1H\}$ DEPT spectrum for $[Pd(allyl)(\mathbf{5b})]_2(BF_4)_2$

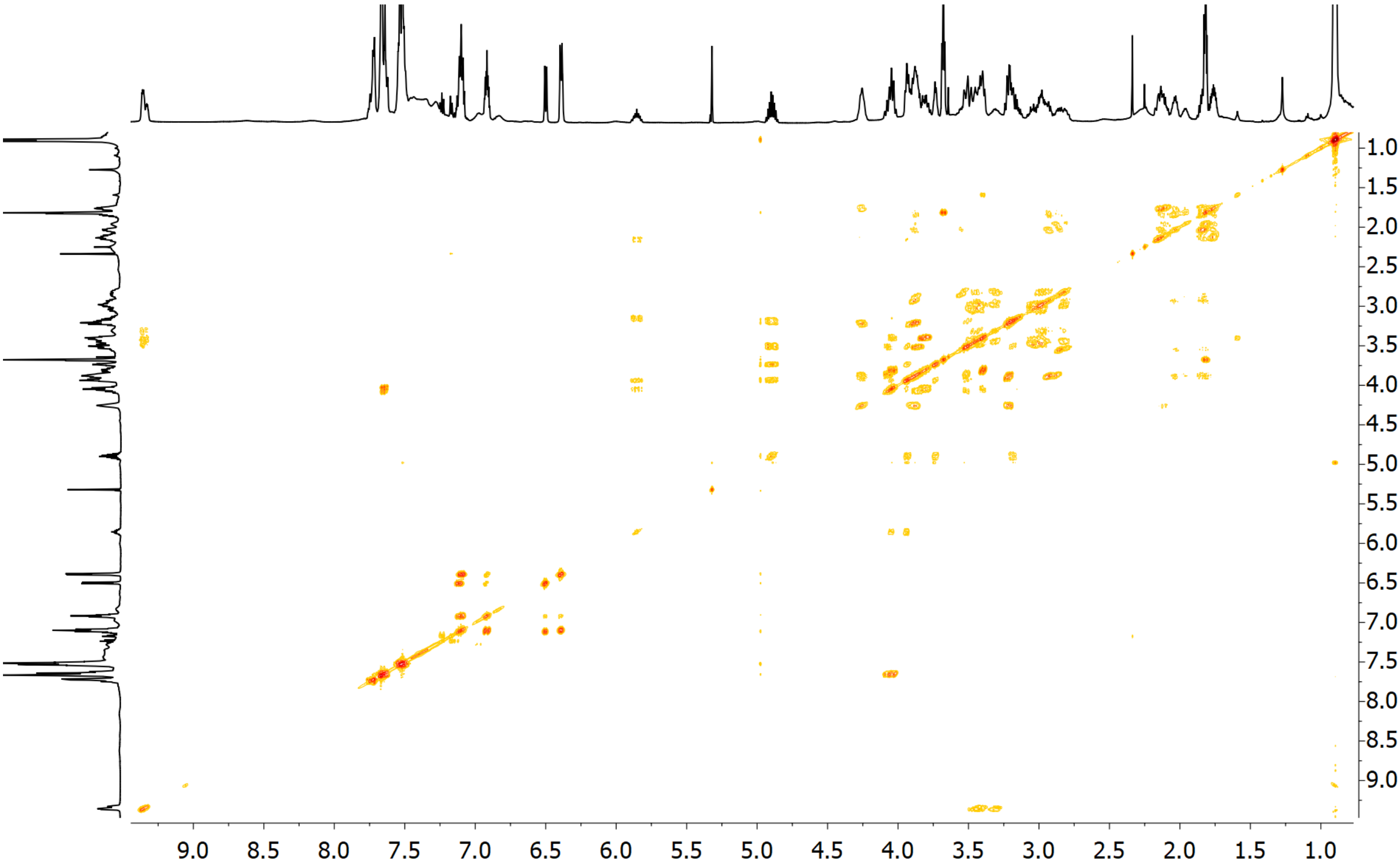


Figure S11e ¹H-¹H-COSY spectrum for [Pd(allyl)(**5b**)]$_2$(BF$_4$)$_2$

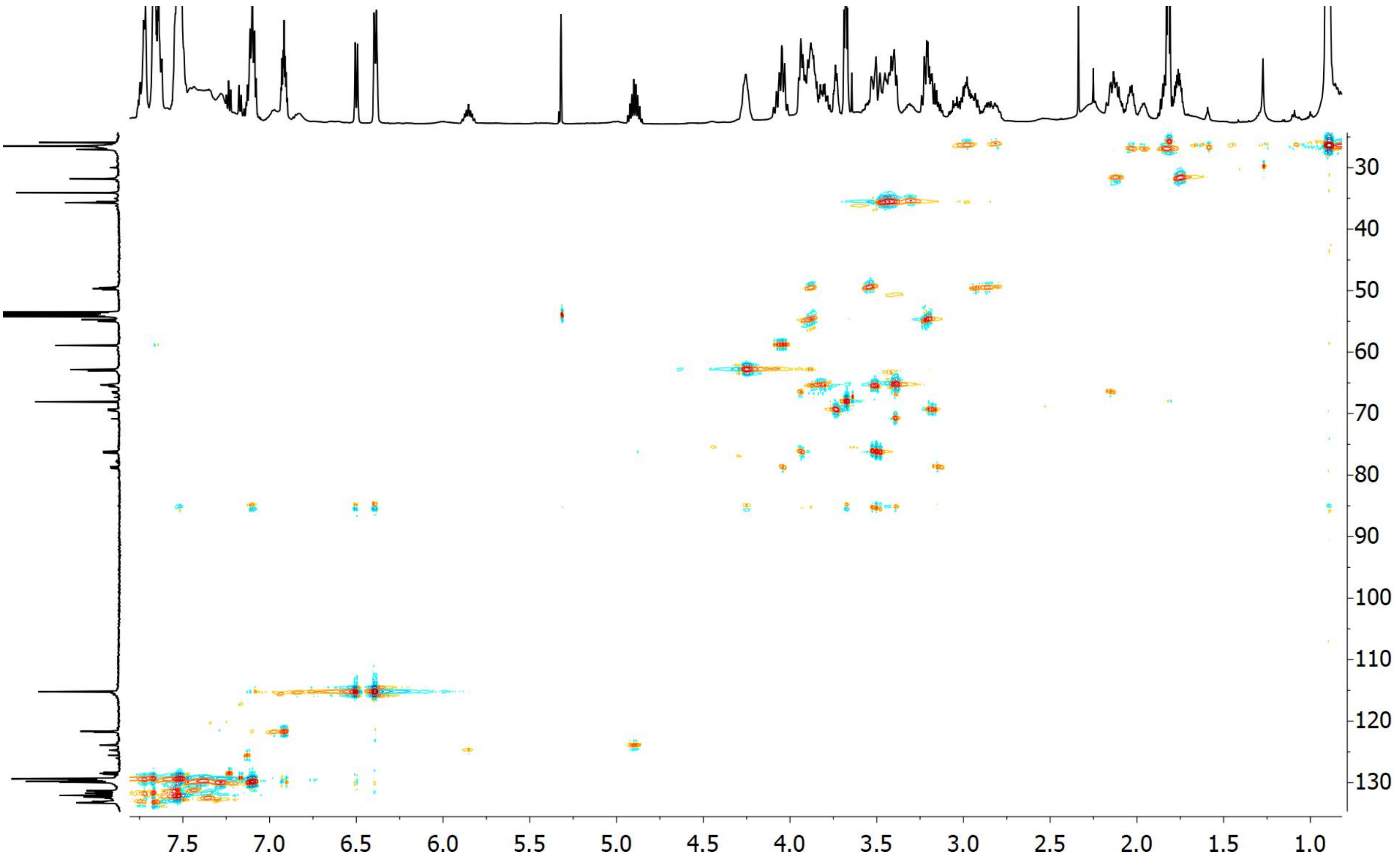


Figure S11f ¹H-¹³C-HSQC spectrum for [Pd(allyl)(**5b**)]$_2$(BF$_4$)$_2$

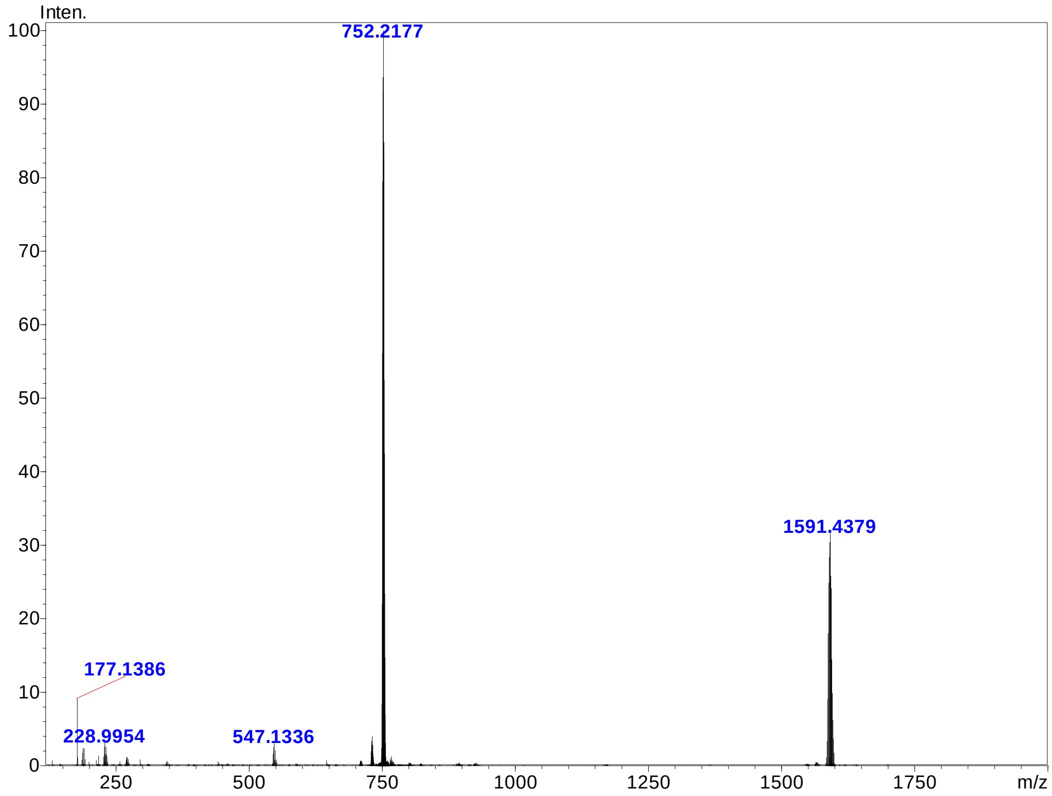


Figure S11g HRMS spectrum for [Pd(allyl)(**5b**)]$_2$(BF$_4$)$_2$

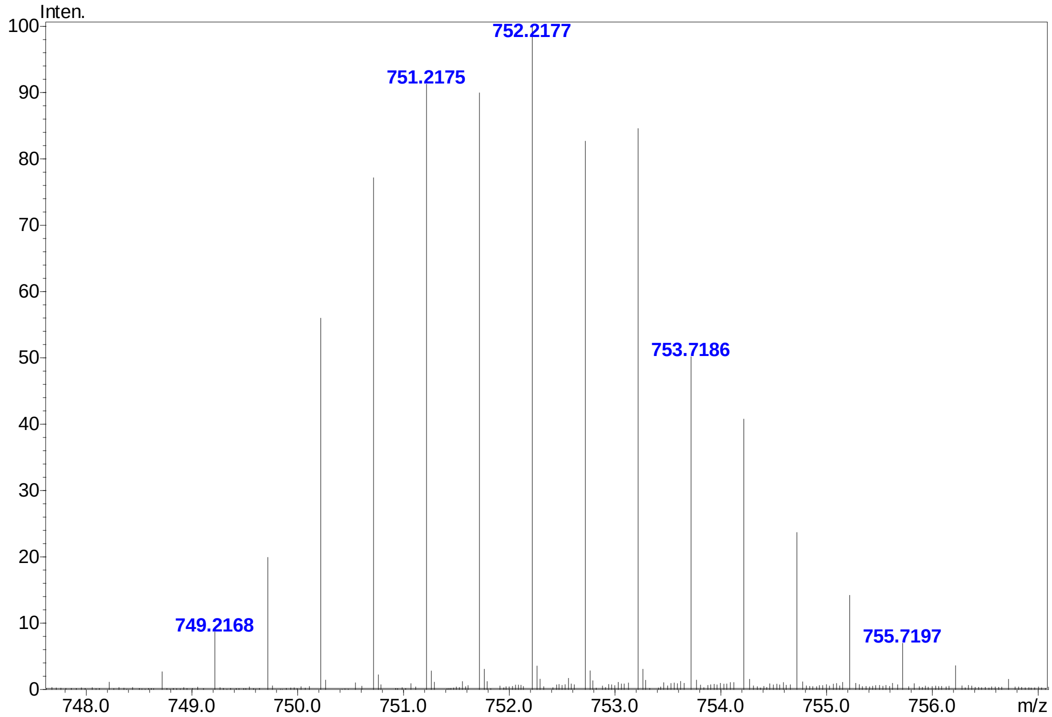


Figure S11h HRMS spectrum for [Pd(allyl)(**5b**)]$_2$(BF$_4$)$_2$ ([Pd(allyl)(**5b**)]$_2^{2+}$ region)

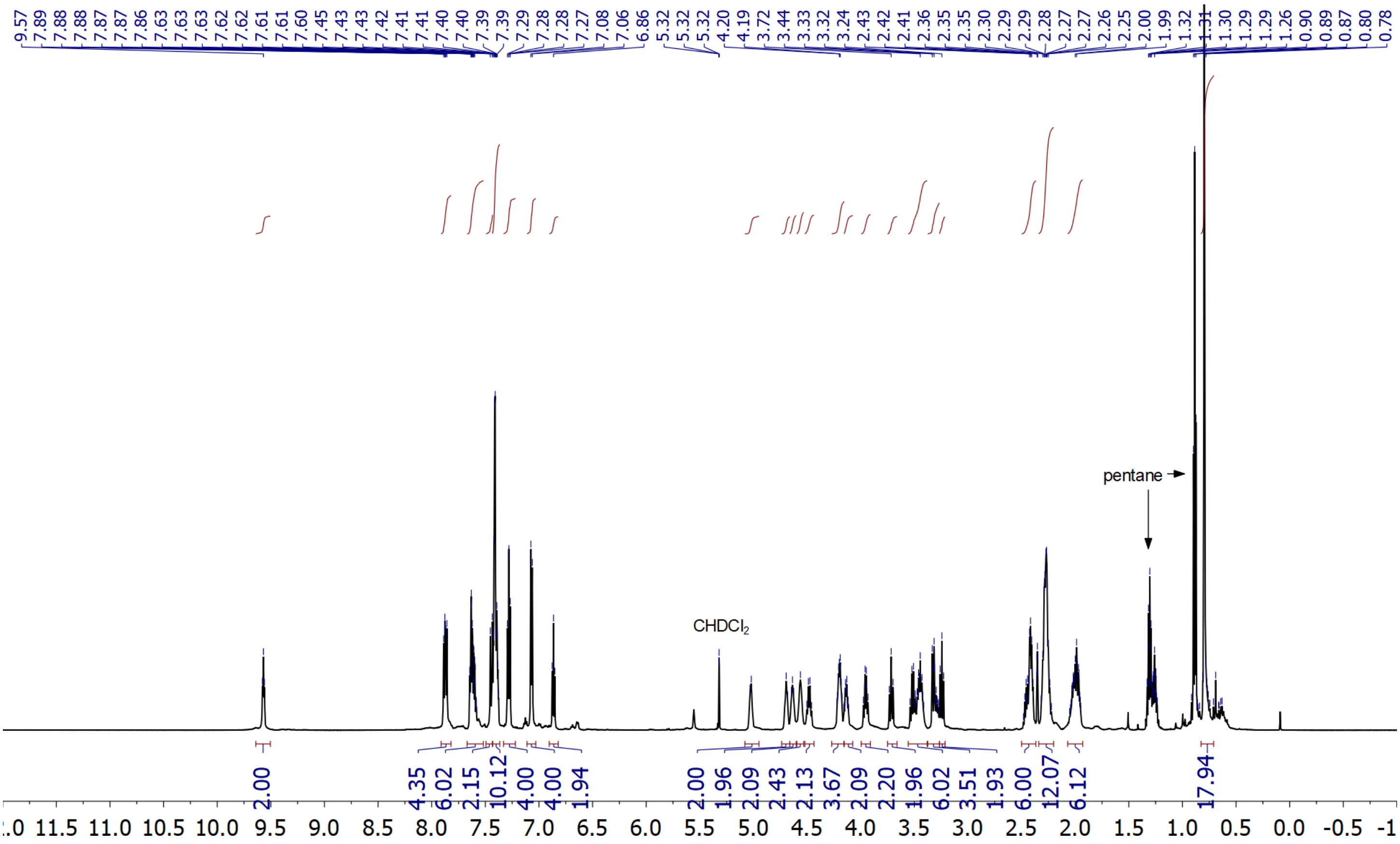


Figure S12a ^{1}H spectrum for $[Rh(COD)(\mathbf{5b})]_2(BF_4)_2$

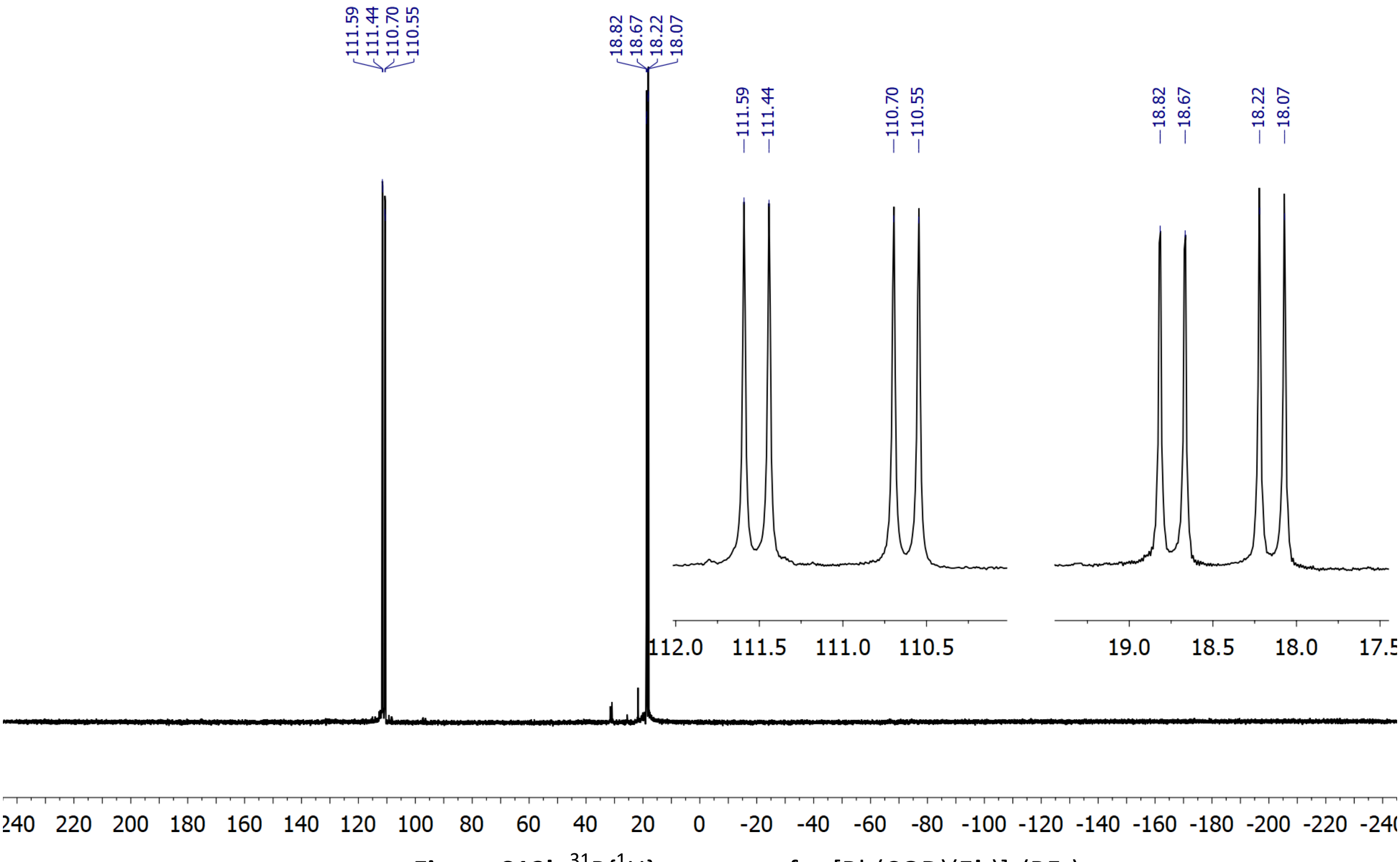


Figure S12b $^{31}P\{^{1}H\}$ spectrum for $[Rh(COD)(\mathbf{5b})]_2(BF_4)_2$

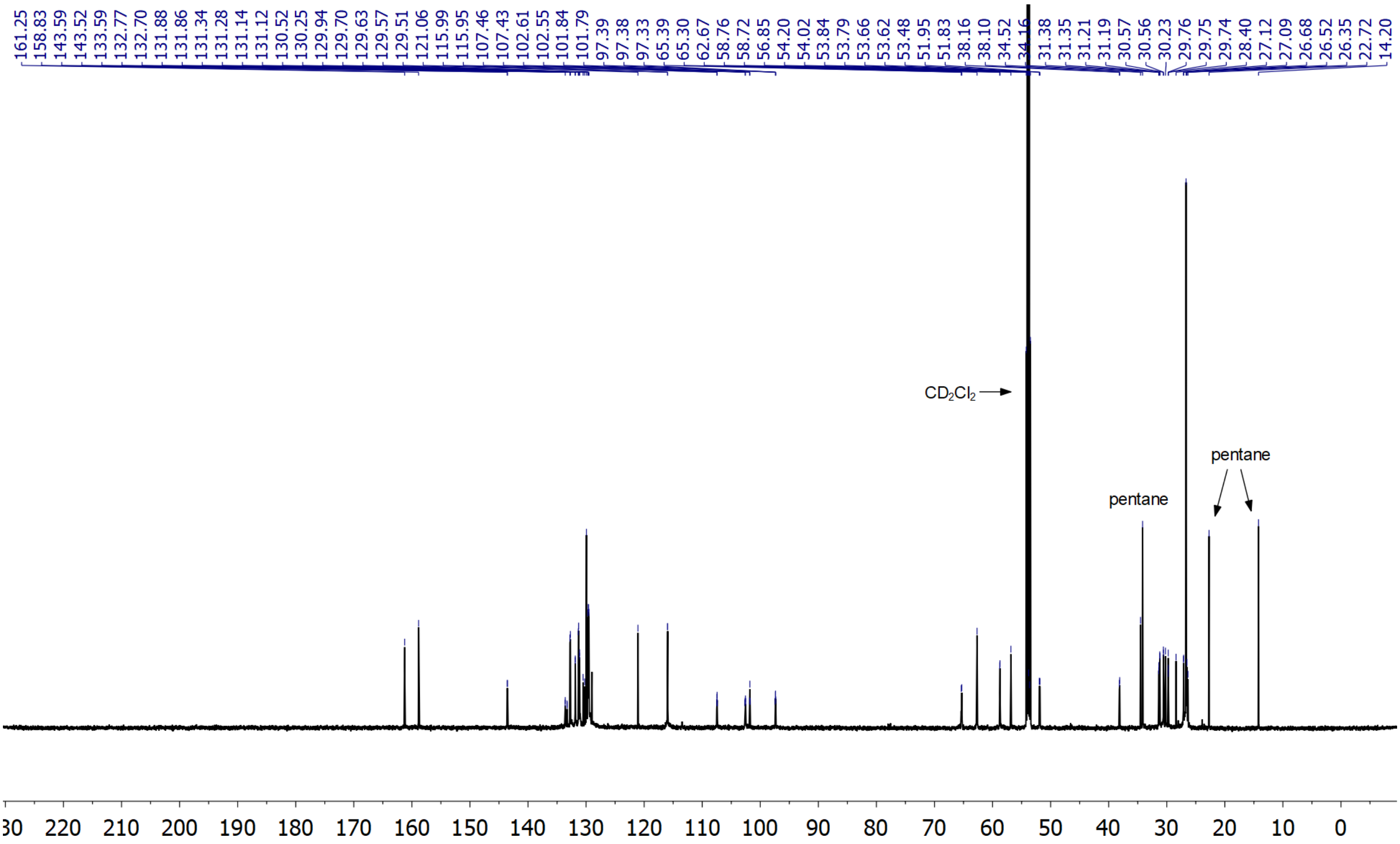


Figure S12c $^{13}C\{^1H\}$ spectrum for [Rh(COD)(**5b**)]$_2$(BF$_4$)$_2$

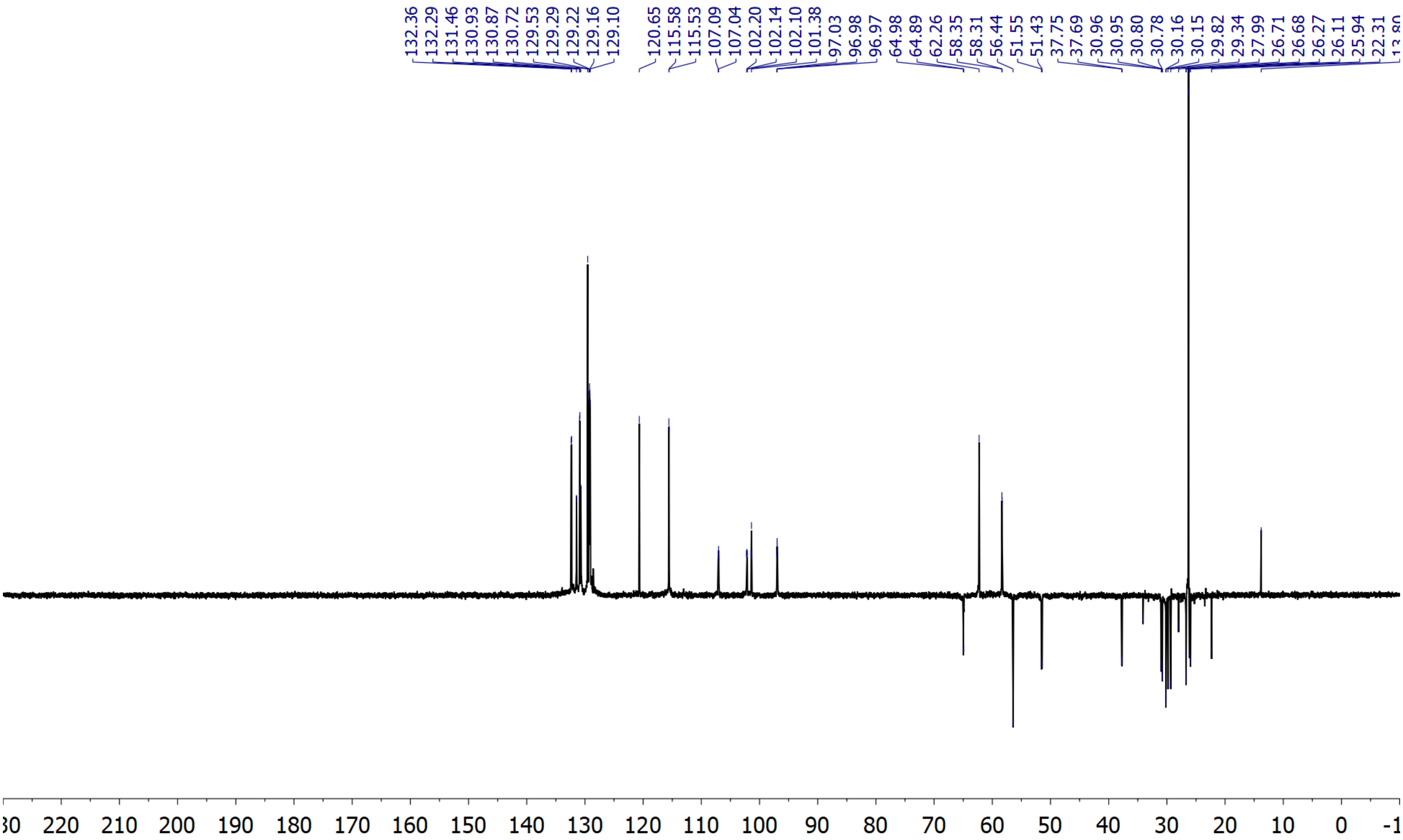


Figure S12d $^{13}C\{^1H\}$ DEPT spectrum for [Rh(COD)(**5b**)]$_2$(BF$_4$)$_2$

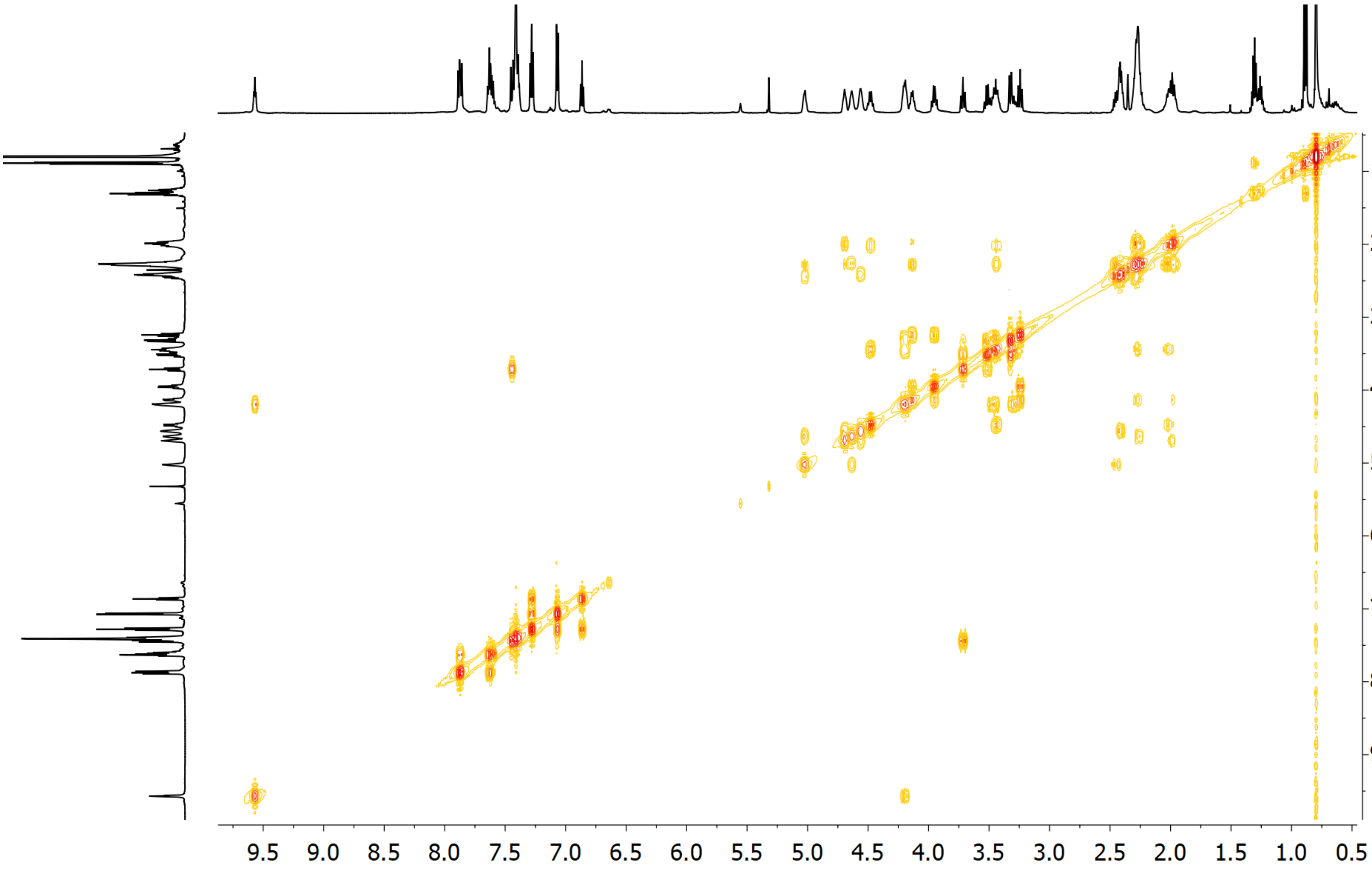


Figure S12e ^{1}H-^{1}H-COSY spectrum for $[Rh(COD)(\mathbf{5b})]_2(BF_4)_2$

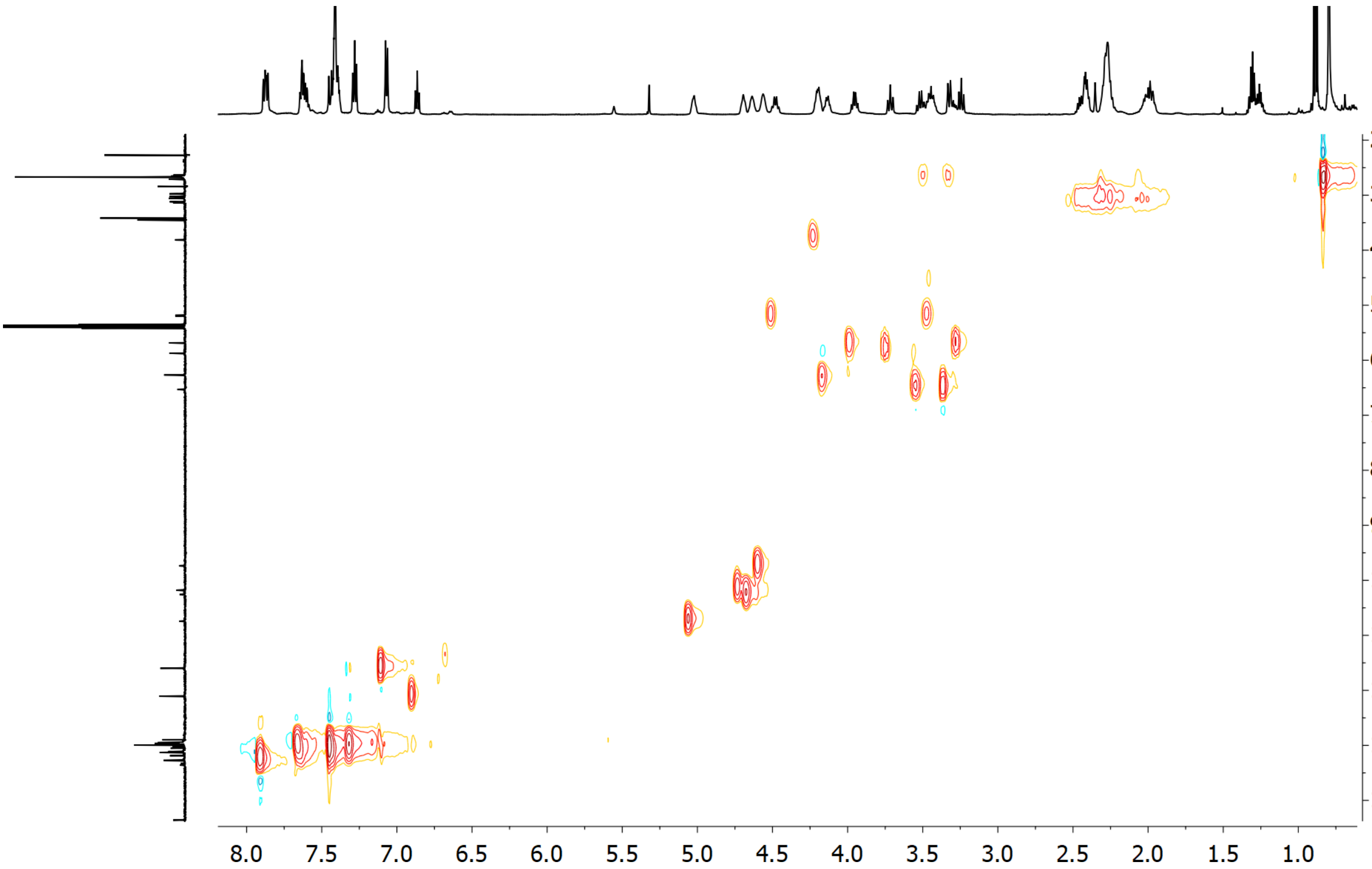


Figure S12f ^{1}H-^{13}C-HSQC spectrum for $[Rh(COD)(\mathbf{5b})]_2(BF_4)_2$

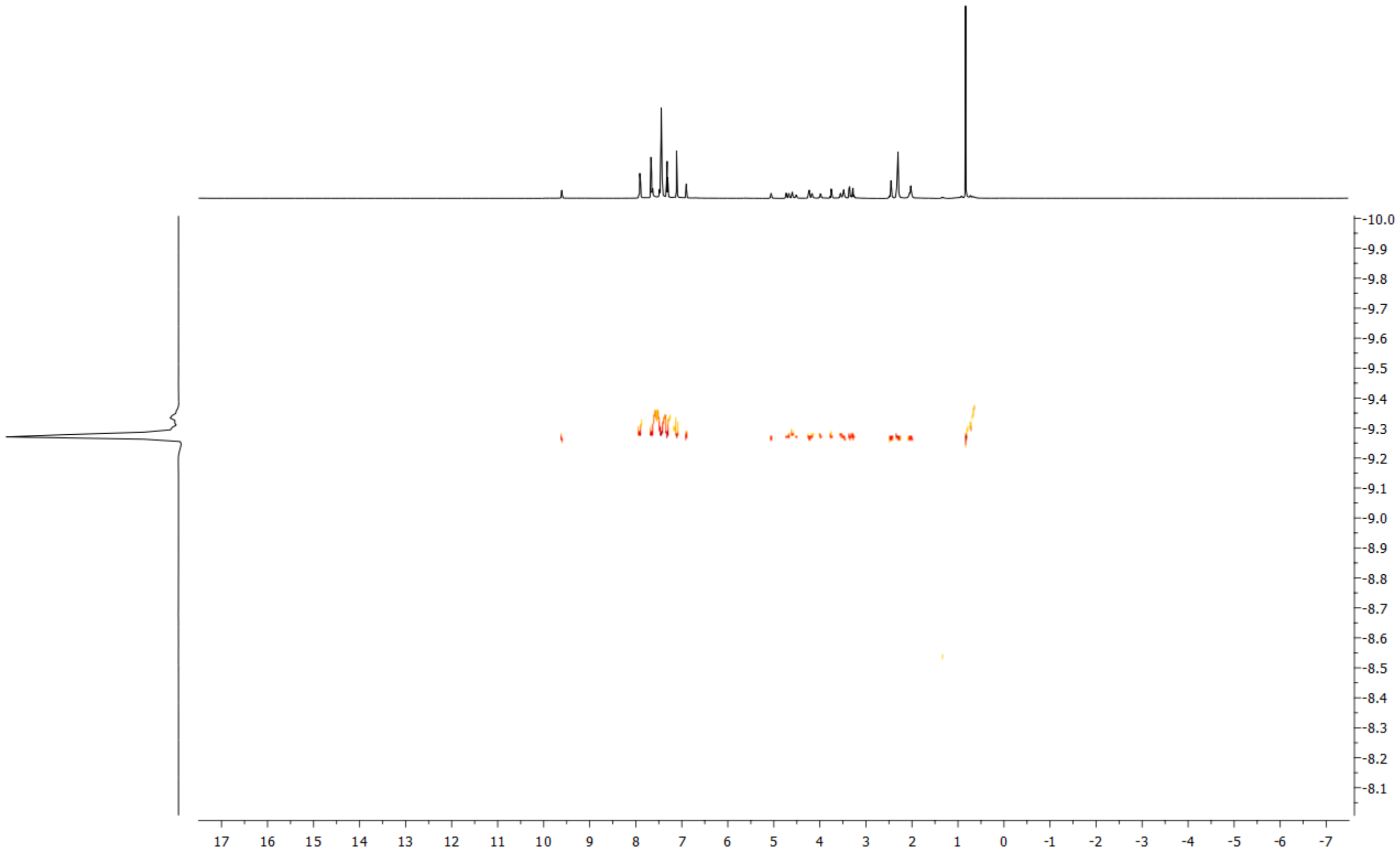


Figure S12g 2D DOSY spectrum for [Rh(COD)(**5b**)]$_2$(BF$_4$)$_2$

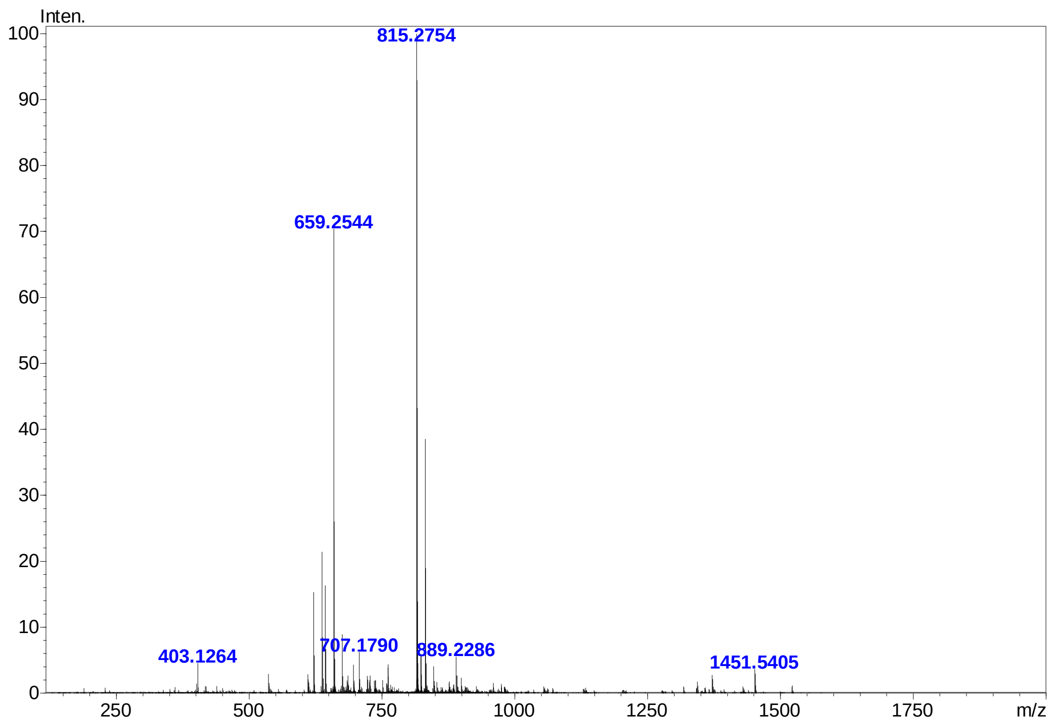


Figure S12h HRMS spectrum for [Rh(COD)(**5b**)]$_2$(BF$_4$)$_2$

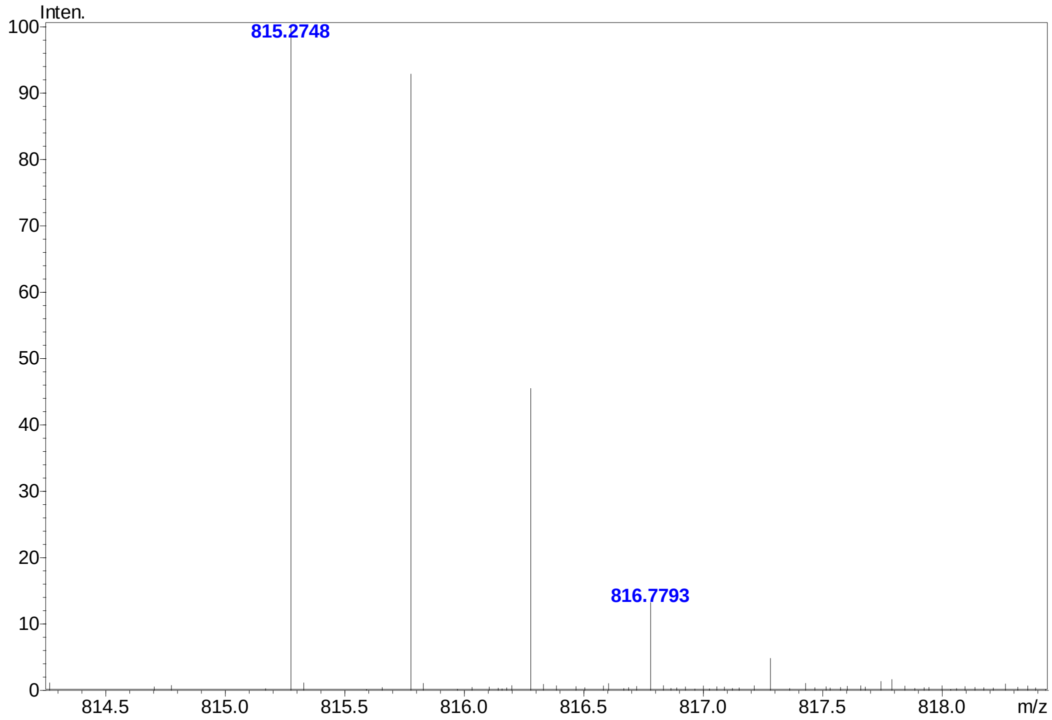


Figure S12i HRMS spectrum for $[Rh(COD)(\mathbf{5b})]_2(BF_4)_2$ ($[Rh(COD)(\mathbf{5b})]_2^{2+}$ region)

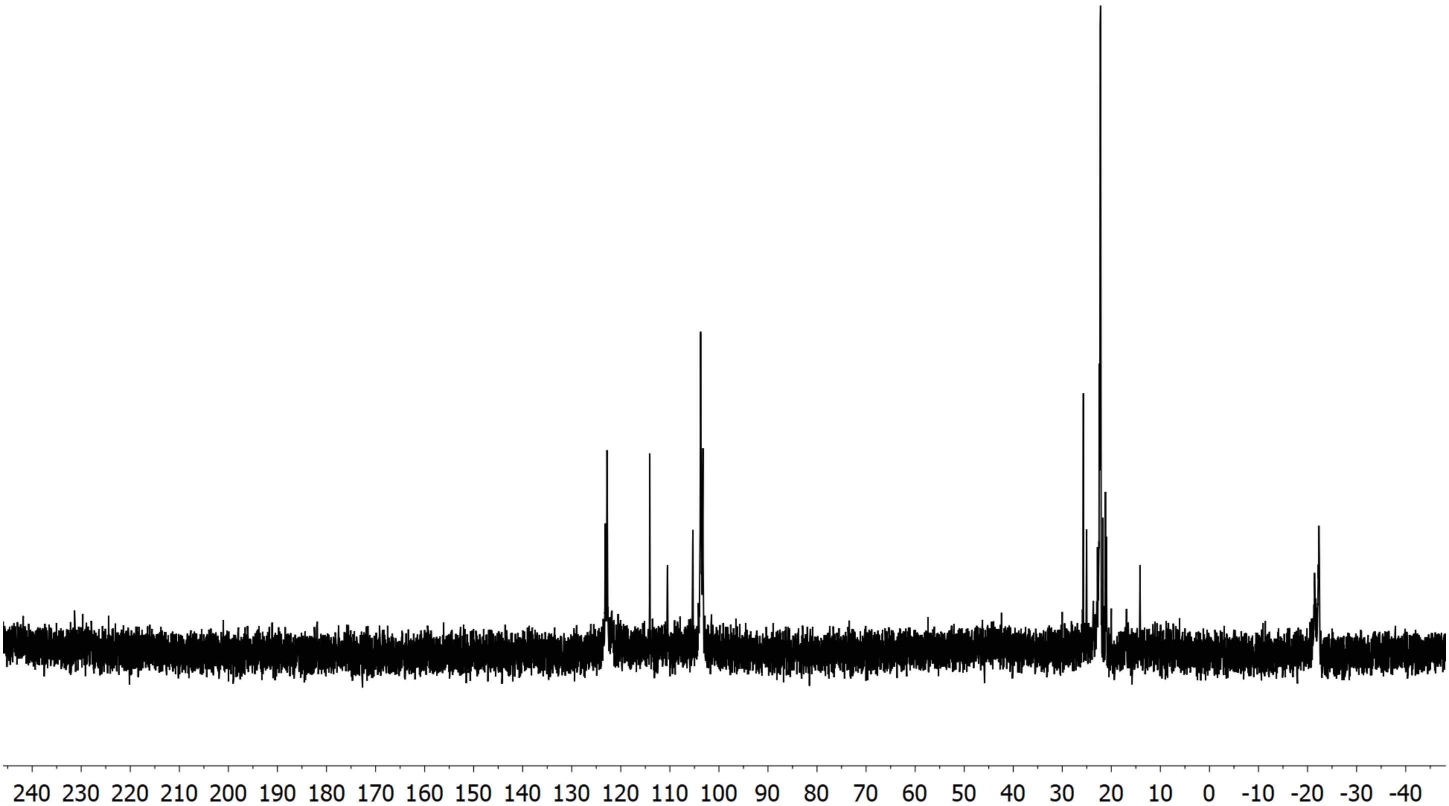


Figure S13a $^{31}P\{^1H\}$ spectrum for the reaction of **5b** with $[Pd(allyl)Cl]_2$ (L/M molar ratio = 2/1)

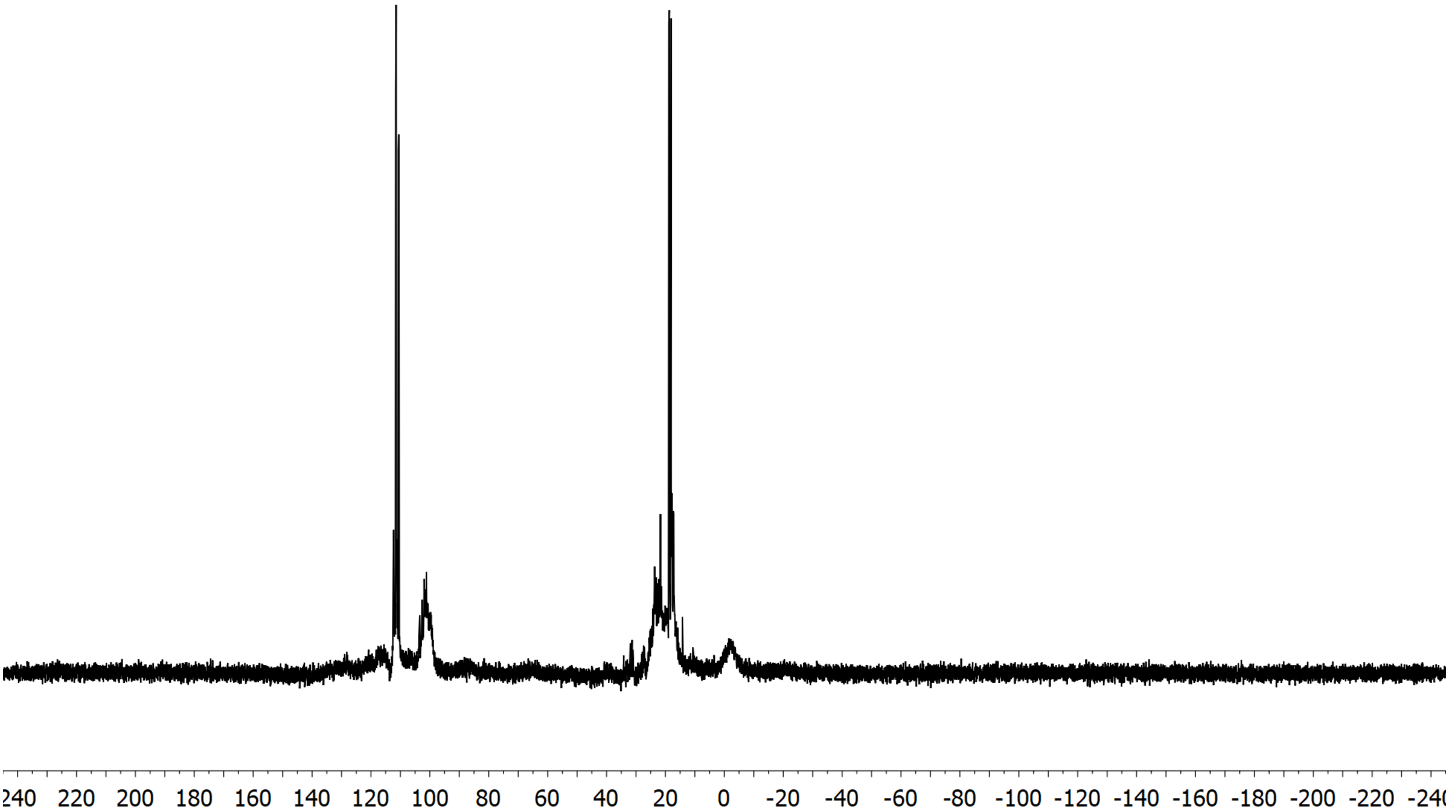


Figure S13b $^{31}P\{^1H\}$ spectrum for the reaction of **5b** with $[Rh(COD)_2]BF_4$ (L/M molar ratio = 2/1)

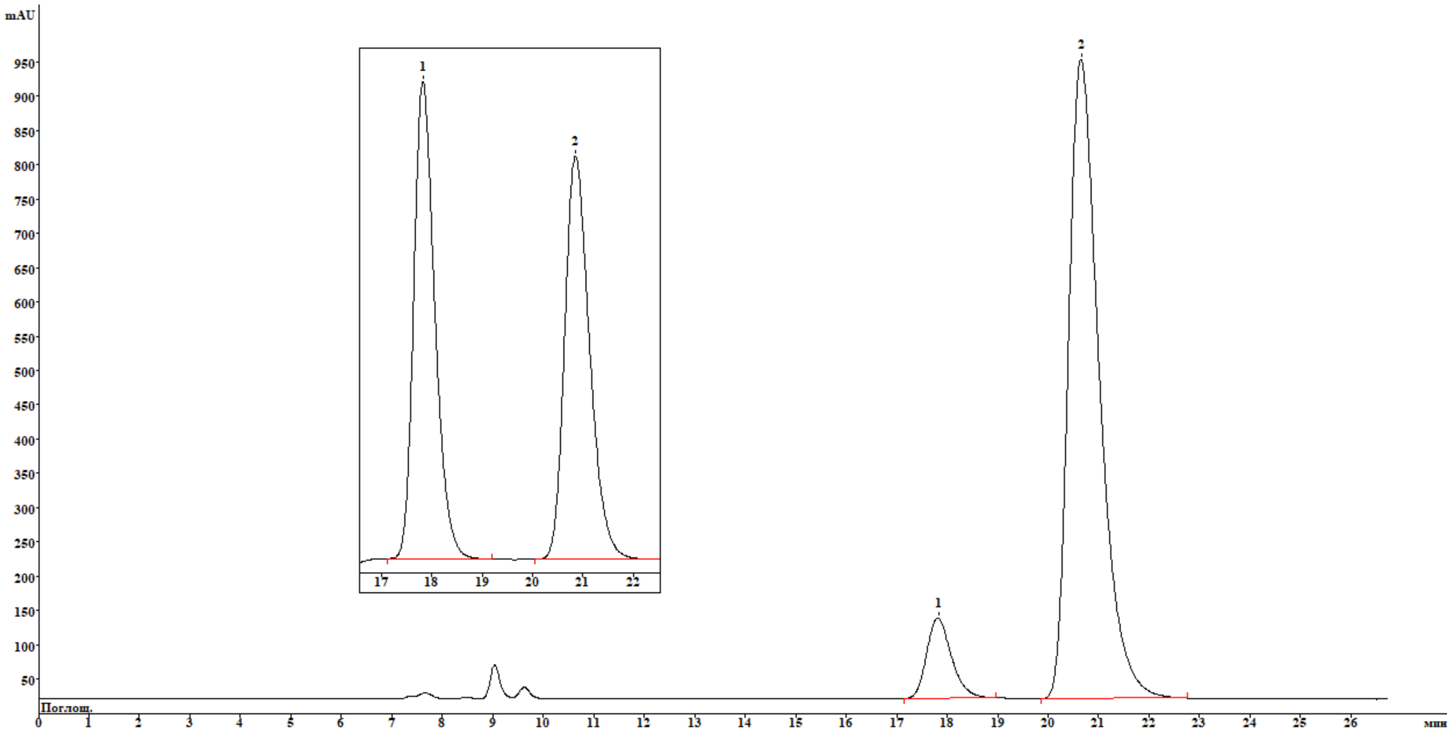


Figure S14 Chiral HPLC trace for the Pd-catalyzed allylic sulfonylation of *rac*-**6** with sodium *para*-toluenesulfinate (entry 3 in Table S1) and for a racemic mixture of **7a** (in the frame).

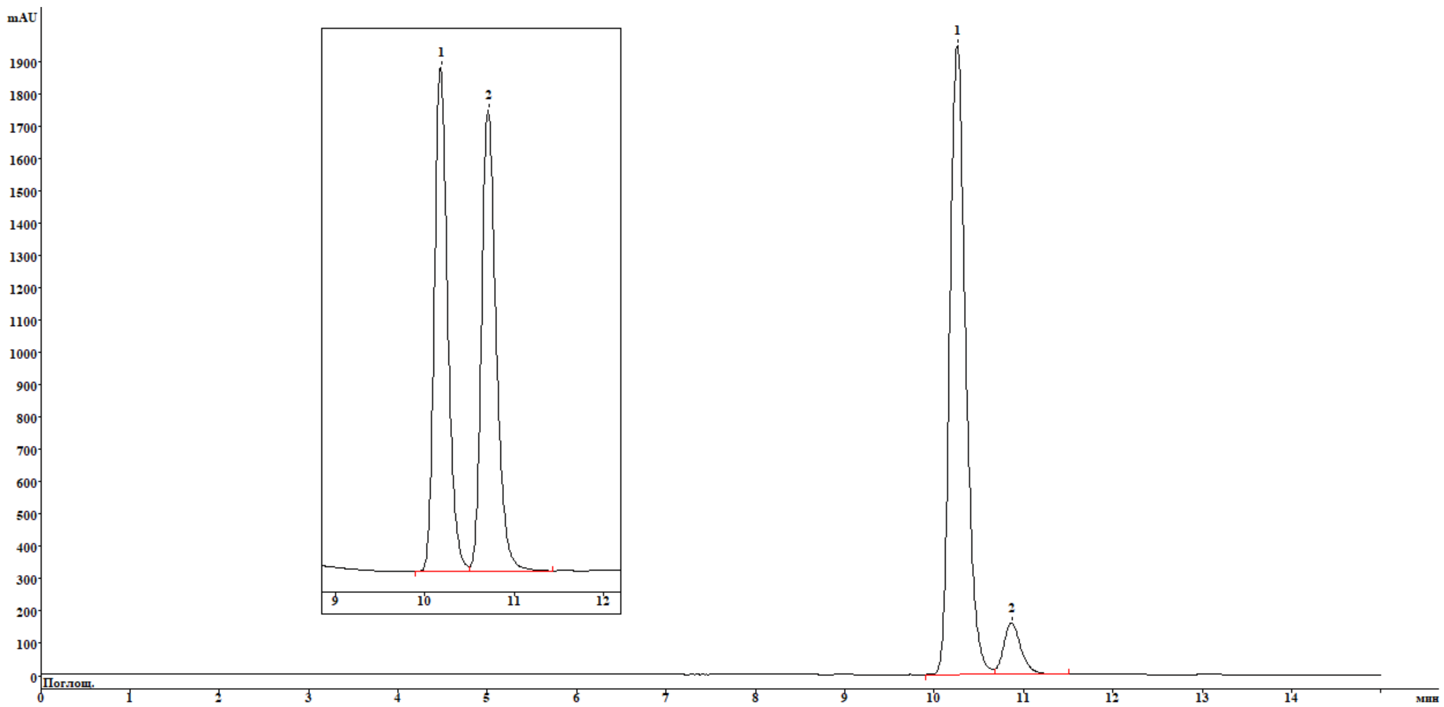
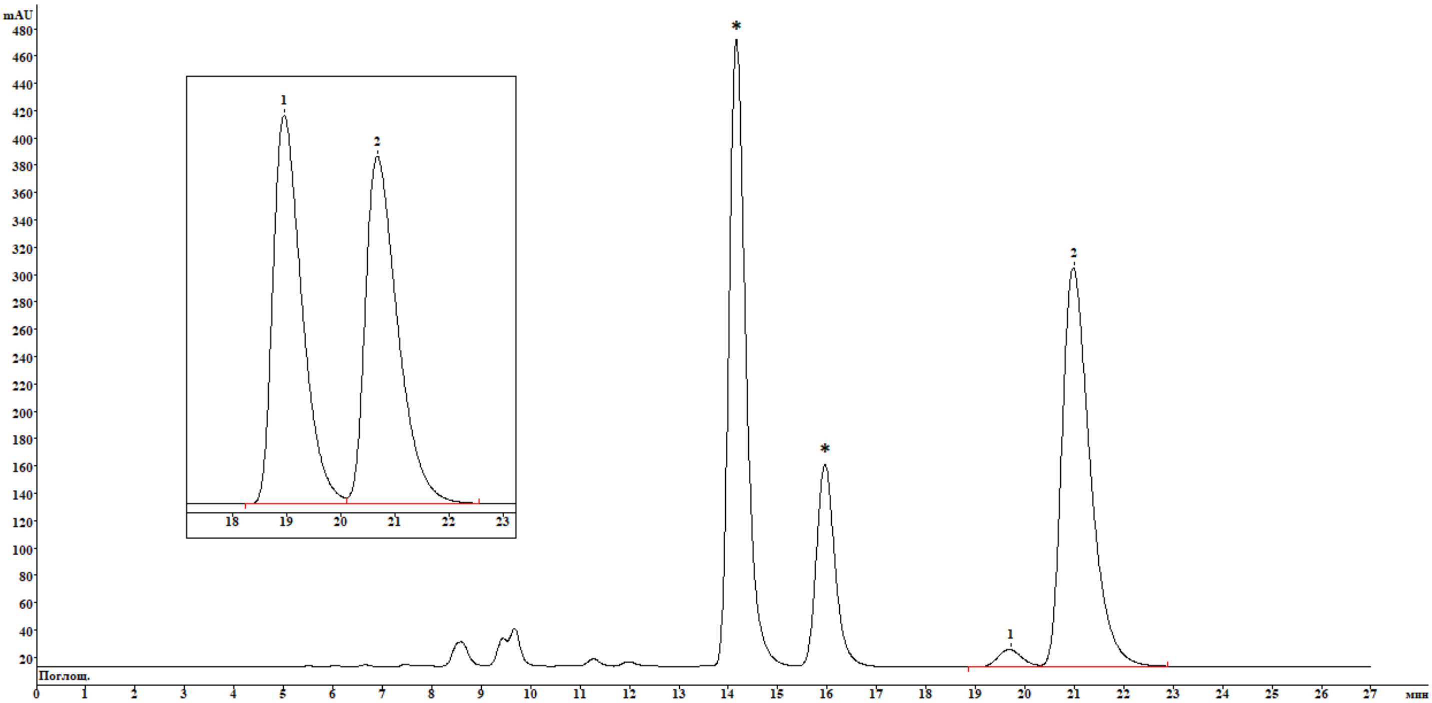
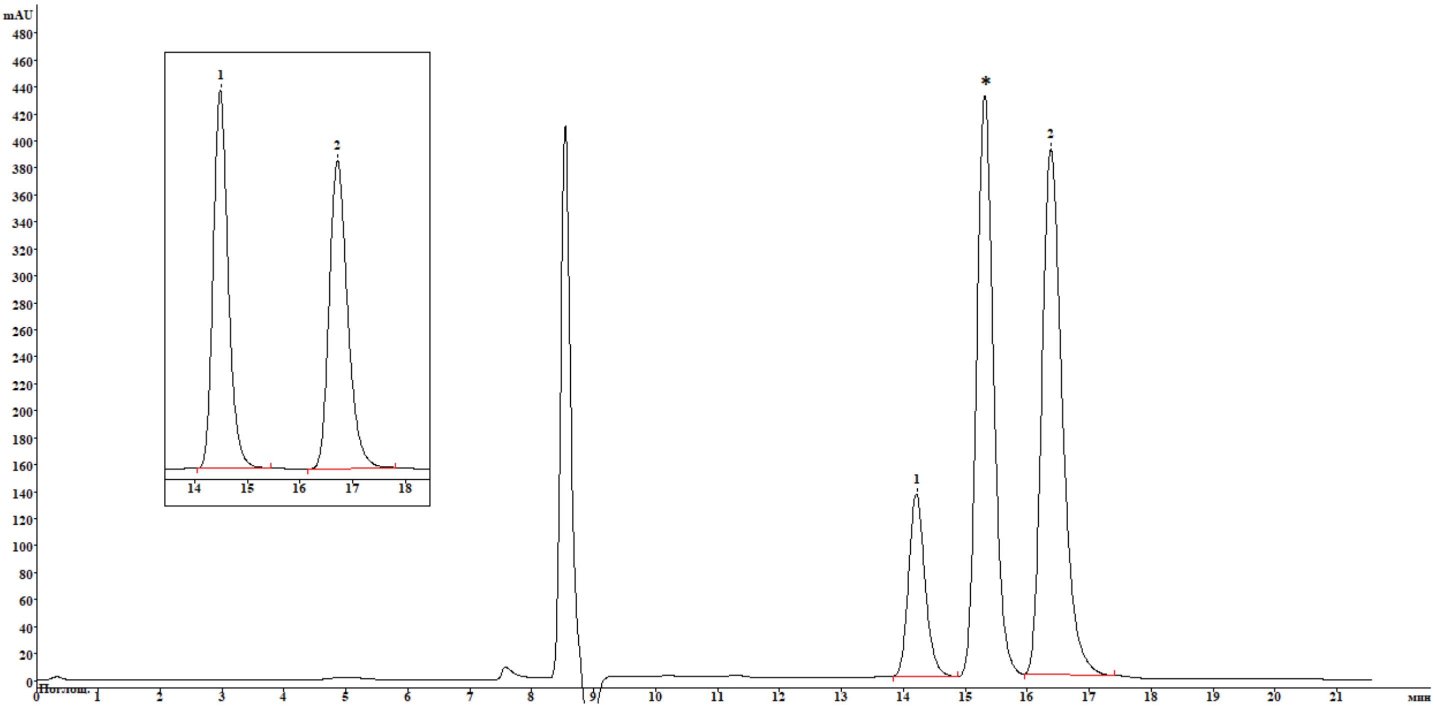


Figure S15 Chiral HPLC trace for the Pd-catalyzed allylic amination of *rac*-**6** with pyrrolidine (entry 1 in Table S2) and for a racemic mixture of **7b** (in the frame).



* starting substrate **6**

Figure S16 Chiral HPLC trace for the Pd-catalyzed allylic alkylation of *rac*-**6** with dimethyl malonate (entry 3 in Table S3) and for a racemic mixture of **7c** (in the frame).



* starting substrate **8**

Figure S17 Chiral HPLC trace for the Pd-catalyzed allylic alkylation of **8** with ethyl 2-oxocyclohexane-1-carboxylate (**9**) (entry 1 in Table S4) and for a racemic mixture of **10** (in the frame).

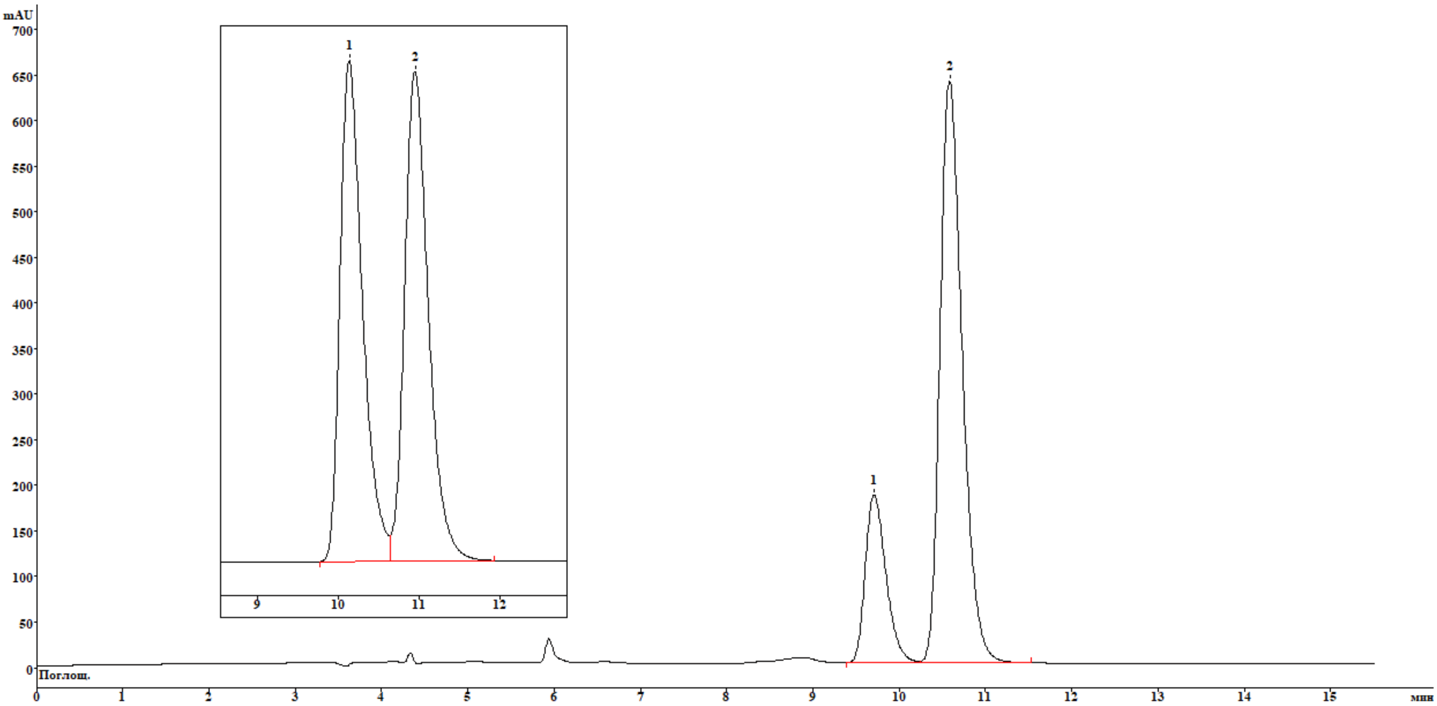
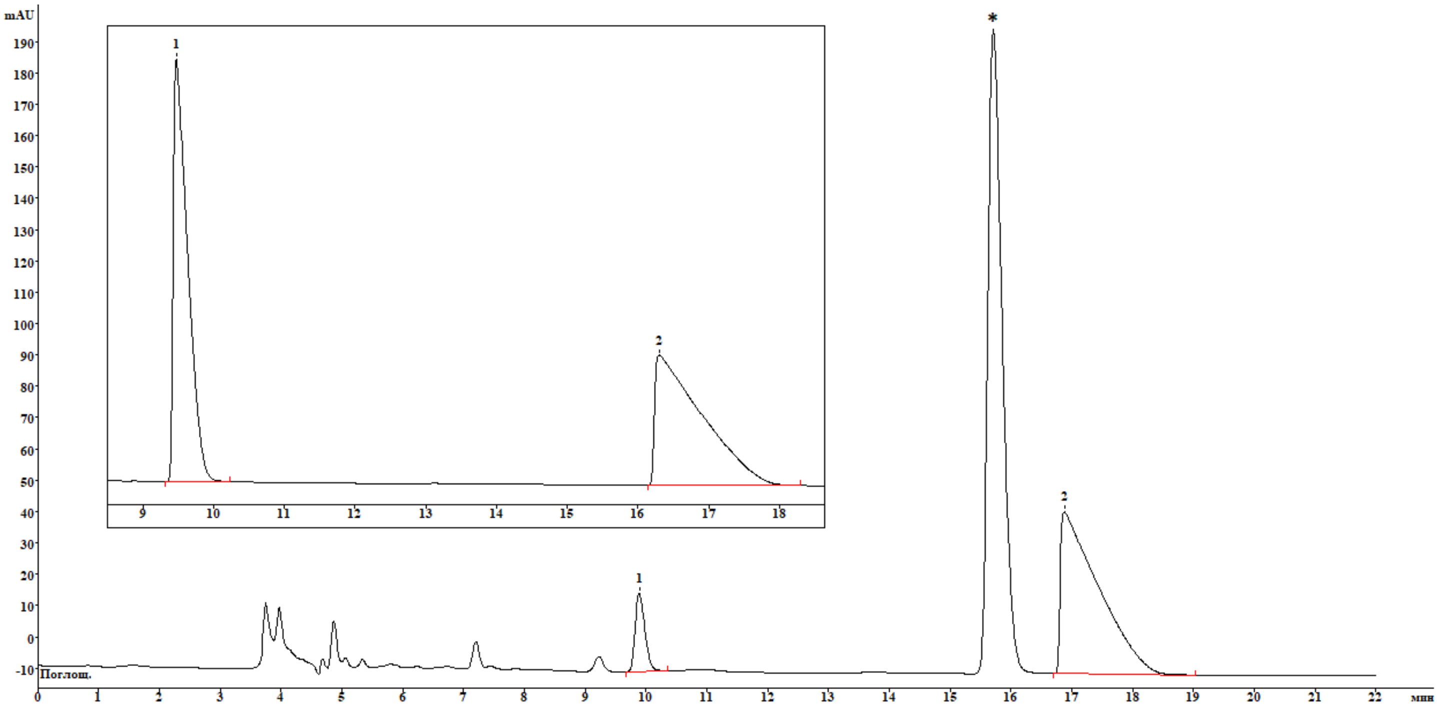
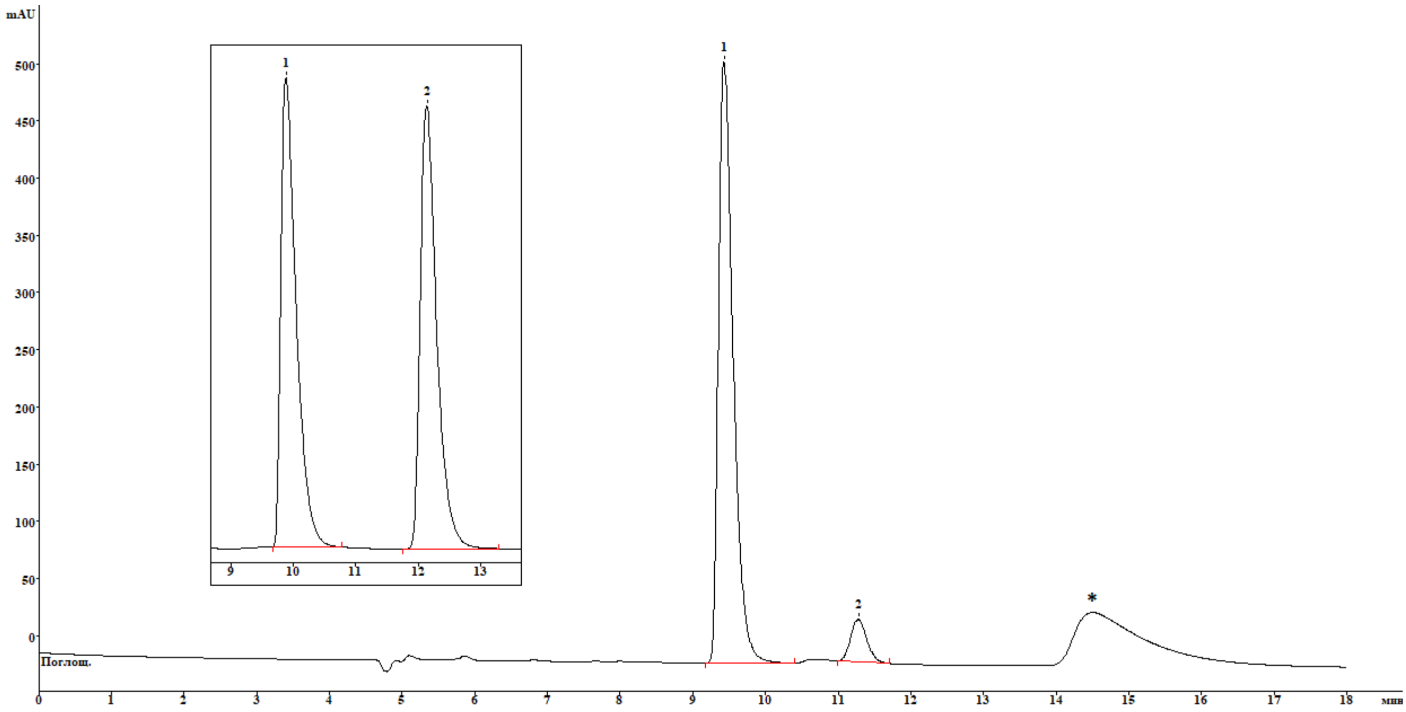


Figure S18 Chiral HPLC trace for the Pd-catalyzed allylic alkylation of **8** with ethyl 2-acetamido-3-oxobutanoate (**11**) (entry 8 in Table S4) and for a racemic mixture of **12** (in the frame).



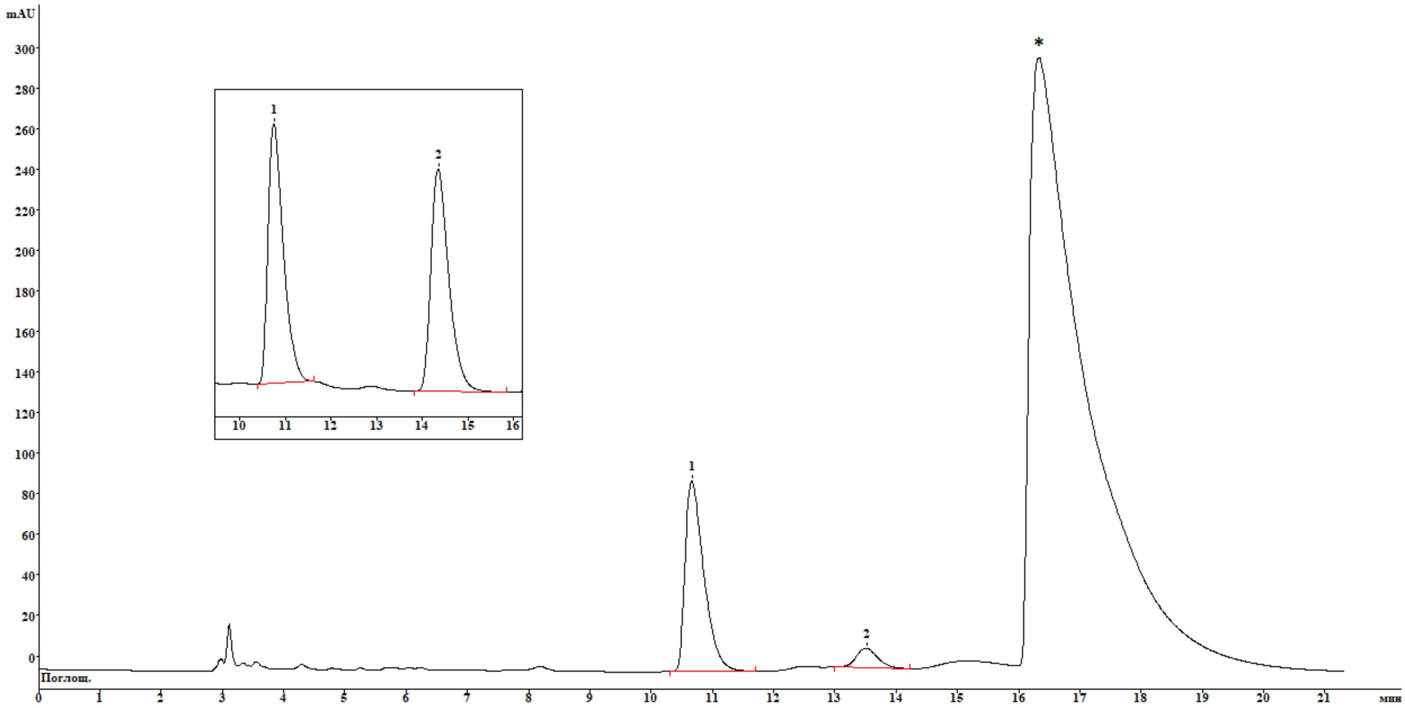
***** starting substrate **13a**

Figure S19 Chiral HPLC trace for the Rh-catalyzed hydrogenation of **13a** (entry 1 in Table S5) and for a racemic mixture of **14a** (in the frame).



* starting substrate **13b**

Figure S20 Chiral HPLC trace for the Rh-catalyzed hydrogenation of **13b** (entry 4 in Table S5) and for a racemic mixture of **14b** (in the frame).



* starting substrate **13c**

Figure S21 Chiral HPLC trace for the Rh-catalyzed hydrogenation of **13c** (entry 6 in Table S5) and for a racemic mixture of **14c** (in the frame).