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SUPPLEMENTARY INFORMATION

Diamidophosphites from β-Hydroxyamides: Readily Assembled Ligands for Pd-Catalyzed Asymmetric Allylic Substitution

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TABLE OF CONTENTS

GENERAL

^{31}P, ^{13}C and ^{1}H NMR spectra were recorded with Bruker AMX 400 (162.0 MHz for ^{31}P, 100.6 MHz for ^{13}C and 400.1 MHz for ^{1}H), Avance 600 (242.9 MHz for ^{31}P, 150.9 MHz for ^{13}C and 600.1 MHz for ^{1}H) and Varian Inova 500 (202.3 MHz for ^{31}P, 125.7 MHz for ^{13}C and 499.8 MHz for ^{1}H) instruments. ^{1}H and ^{13}C NMR signals were attributed using APT, DEPT, COSY, NOESY, 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). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, m = multiplet, vt = virtual triplet). The X-ray data of **4**, **L3d** and [Pd(allyl)(**L3d**)$_2$]BF_4 were collected by using STOE diffractometer Pilatus100K detector, focusing mirror collimation Cu Kα (1.54086 Å) radiation, rotation method mode. STOE X-AREA software was used for cells refinement and data reduction. Data collection and image processing was performed with X-Area 1.67 (STOE & Cie GmbH, Darmstadt, Germany, 2013). Intensity data were scaled with LANA (part of X-Area) in order to minimize differences of intensities of symmetry-equivalent reflections (multi-scan method). The structures were solved and refined with SHELX[1] program. The non-hydrogen atoms were refined by using the anisotropic full matrix least-square procedure. Hydrogen atoms were placed in the calculated positions and allowed to ride on their parent atoms [C-H 0.93-0.98; Uiso 1.2 Ueq (parent atom)]. Molecular geometry calculations were performed with the SHELX program, and the molecular graphics were prepared by using DIAMOND[2] software. The molecular structure of **L1d** was confirmed by X-ray structure determination from powder data measured at room temperature on the laboratory diffractometer Stoe Stadi-P equipped with curved germanium monochromator (Cu $K_{\alpha 1}$ radiation, λ = 1.54059 Å) and linear detector. The powder pattern was indexed in triclinic unit cell, and the crystal structure was solved with the use of simulated annealing technique[3] and refined with the program MRIA[4] following the known procedures described by us earlier.[5-8] The molecular structure and portion of the crystal packing of **L1d** prepared with Mercury.[9] CCDC 1966050, 1908962, 1908958, 1908963 of **L1d**, **L3d**, [Pd(allyl)(**L3d**)$_2$]BF_4 and **4** respectively, contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. HPLC analyses were performed on a Stayer instrument using Kromasil 5-CelluCoat, 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.

All calculations were performed using the resources of the Joint Supercomputer Center (JSC) supercomputer MVS-1000M (www.jscc.ru). The gradient-corrected exchange-correlation Perdew, Burke, and Ernzerhof (PBE) functional[10, 11] was used for calculations. The efficient resolution of identity

GENERAL

(RI) and parallel implementation of evaluating both Coulomb and exchange-correlation integrals with optimized fitting Gaussian basis sets in the PRIRODA code permits the performance of calculations of the molecular systems with a large number of basis functions.[12] A large integration grid (which comprises about 800 000 points over calculated molecules) with a 5 x 10^{-8} accuracy parameter of the adaptively generated grid was used. This parameter is responsible for the precision of the exchange-correlation energy per atom. The 10^{-6} threshold on the orbital gradients at the energy calculation stage and 10^{-5} threshold on the molecular gradient at the geometry optimization procedure were employed. In all calculations the spin-restricted formalism was chosen. For all atoms TZ2P valence basis set and triple-f effective core potentials for C, N, O, P atoms.[13] All geometries for the reaction species and transition states were completely optimized without any symmetry constraints. Systematic vibrational analysis was performed to confirm whether an optimized geometry corresponds to a transition state with only one imaginary frequency or to a local minimum without an imaginary frequency. Zero-point-vibrational-energy (ZPVE) corrections were taken into account in calculating the energies of the stable rotamers. A rigid rotor and harmonic oscillator models were used for evaluation of the temperature (at 298 K) and entropy corrections for subsequent calculation of the Gibbs energies of the whole processes under discussion.

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: *tert*-butyl (1-hydroxy-2-methylpropan-2-yl)carbamate (**1a**),[14] *tert*-butyl (*S*)-(1-hydroxy-3,3-dimethylbutan-2-yl)carbamate (**1b**),[15] *tert*-butyl ((2*S*,3*S*)-1-hydroxy-3-methylpentan-2-yl)carbamate (**1c**),[16] *tert*-butyl (*S*)-(1-hydroxy-4-(methylthio)butan-2-yl)carbamate (**1d**),[16, 17] *tert*-butyl (*S*)-2-(hydroxymethyl)pyrrolidine-1-carboxylate (**2**),[18] (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 ((5*S*)- and (5*R*)-**5**),[19] 2-chloro-1,3-diphenyl-1,3,2-diazaphospholidine (**6**),[20] $[Pd(allyl)Cl]_2$[21] and (*E*)-1,3-diphenylallyl ethyl carbonate (**7**).[22] Pseudodipeptides **3a-c**, **3e, 3f** and **4** were synthesized according to reported procedure[23] and have been successfully characterized. Pd-catalyzed allylic alkylation of **7** with dimethyl malonate, its amination with pyrrolidine, allylic alkylation of cinnamyl acetate (**9**) with ethyl 2-oxocyclohexane-1-carboxylate (**10**) or ethyl 2-oxocyclopentane-1-carboxylate (**12**) were performed according to the appropriate procedures.[19, 6, 24]

Dimethyl malonate, BSA (*N*,*O*-bis(trimethylsilyl) acetamide), cinnamyl acetate (**9**), ethyl 2-oxocyclohexane-1-carboxylate (**10**) and ethyl 2-oxocyclopentane-1-carboxylate (**12**) were purchased from Aldrich and Acros Organics.

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EXPERIMENTAL SECTION

tert-butyl (2-((1-hydroxy-2-methylpropan-2-yl)amino)-2-oxoethyl)carbamate (**3a**): White solid, yield 2.586 g (70 %). ^{1}H NMR (600.1 MHz, $CDCl_3$, 19.7 °C): δ = 1.29 (s, 6H), 1.44 (s, 9H), 3.58 (br.s, 2H), 3.71 (br.s, 2H), 5.42 (br.s, 1H), 6.40 (br.s, 1H), ppm. ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$, 23.10 °C): δ = 24.43, 28.22, 44.92, 56.02, 69.73, 155.59, 170.15 ppm. $C_{11}H_{22}N_2O_4$ (246.31): calcd. C 53.64, H 9.00, N 11.37; found C 53.72, H 8.97, N 11.41.

tert-butyl (2-((2-hydroxy-1,1-diphenylethyl)amino)-2-oxoethyl)carbamate (**3b**): White solid, yield 4.056 g (73 %). ^{1}H NMR (499.9 MHz, $CDCl_3$, ambient temperature): δ = 1.44 (s, 9H), 3.83 (d, ^{3}J(H,H) = 5.9 Hz, 1H), 4.40 (s, 1H), 5.26 (br.s, 1H), 7.15 (br.s, 1H), 7.27-7.36 (m, 10H) ppm. ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, ambient temperature): δ = 28.25, 45.62, 68.73, 69.13, 80.81, 127.24, 127.66, 128.53, 142.19, 156.28 (br), 170.43 ppm. $C_{21}H_{26}N_2O_4$ (370.45): calcd. C 68.09, H 7.07, N 7.56; found C 68.17, H 7.02, N 7.61.

tert-butyl (*R*)-(2-((1-hydroxybutan-2-yl)amino)-2-oxoethyl)carbamate (**3c**): White solid, yield 2.882 g (78 %). ^{1}H NMR (499.9 MHz, $CDCl_3$, ambient temperature): δ = 0.95 (t, ^{3}J(H,H) = 7.6 Hz, 3H), 1.46 (s, 9H), 1.49-1.55 (m, 1H), 1.58-1.66 (m, 1H), 2.84 (br.s, 1H), 3.57 (dd, ^{2}J(H,H) = 11.2 Hz, ^{3}J(H,H) = 5.6 Hz, 1H), 3.70 (dd, ^{2}J(H,H) = 11.2 Hz, ^{3}J(H,H) = 3.7 Hz, 1H), 3.74-3.84 (m, 2H), 3.84-3.90 (m, 1H), 5.22-5.37 (br.m, 1H), 6.26-56.43, (br.m, 1H) ppm. ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, ambient temperature): δ = 10.38, 24.12, 28.29, 44.70 (br), 53.40, 64.67, 80.41 (br), 156.29 (br), 170.27 ppm. $C_{11}H_{22}N_2O_4$ (246.31): calcd. C 53.64, H 9.00, N 11.37; found C 53.79, H 8.95, N 11.22.

tert-butyl ((2*S*,3*S*)-1-(((2*S*,3*S*)-1-hydroxy-3-methylpentan-2-yl)amino)-3-methyl-1-oxopentan-2-yl)carbamate (**3e**): White solid, yield 3.319 g (67 %). ^{1}H NMR (400.1 MHz, $CDCl_3$, 27.0 °C): δ = 0.88-0.97 (m, 12H), 1.10-1.21 (m, 2H), 1.45 (s, 9H), 1.47-1.58 (m, 2H), 1.60-1.71 (m, 1H), 1.86-1.96 (m, 1H), 2.52 (br.s, 1H), 3.65 (dd, ^{2}J(H,H) = 11.4 Hz, ^{3}J(H,H) = 6.1 Hz, 1H), 3.73 (dd, ^{2}J(H,H) = 11.4 Hz, ^{3}J(H,H) = 3.5 Hz, 1H), 3.77-3.83 (m, 1H), 3.88 (t, ^{3}J(H,H) = 7.0 Hz, 1H), 4.96-5.13 (br.m, 1H), 6.18-6.32 (br.m, 1H) ppm. ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, ambient temperature): δ = 11.17, 15.50, 15.61, 24.89, 25.41, 28.27, 35.39, 36.52, 56.08, 59.94 (br), 63.40, 80.09 (br), 156.05, 172.31 ppm. $C_{17}H_{34}N_2O_4$ (330.25): calcd. C 61.79, H 10.37, N 8.48; found C 61.70, H 10.43, N 8.52.

tert-butyl (*S*)-(2-((1-hydroxy-4-(methylthio)butan-2-yl)amino)-2-oxoethyl)carbamate (**3f**): White solid, yield 2.982 g (68 %). ^{1}H NMR (499.9 MHz, $CDCl_3$, ambient temperature): δ = 1.45 (s, 9H), 1.76-1.83 (m, 1H), 1.83-1.90 (m, 1H), 2.09 (s, 3H), 2.49-2.58 (m, 2H), 3.43 (br.s, 1H), 3.59 (br.dd, ^{2}J(H,H) = 11.2 Hz, ^{3}J(H,H) = 5.2 Hz, 1H), 3.68 (dd, ^{2}J(H,H) = 11.2 Hz, ^{3}J(H,H) = 3.7 Hz, 1H), 3.74 (br.dd, ^{2}J(H,H) = 16.6 Hz,

^3J(H,H) = 5.2 Hz, 1H), 3.81 (dd, ^2J(H,H) = 16.6 Hz, ^3J(H,H) = 6.0 Hz, 1H), 4.02-4.13 (br.m, 1H), 5.51 (br.s, 1H), 6.72 (d, ^3J(H,H) = 8.3 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, ambient temperature): δ = 15.49, 28.32, 30.61, 30.71, 44.71 (br), 51.20, 64.54, 80.47 (br), 156.28 (br), 170.17 ppm. $C_{12}H_{24}N_2O_4S$ (292.39): calcd. C 49.29, H 8.27, N 9.58; found C 49.25, H 8.31, N 9.67.

tert-butyl (*S*)-2-((1-hydroxy-2-methylpropan-2-yl)carbamoyl)pyrrolidine-1-carboxylate (**4**): White solid, yield 3.170 g (64 %). ^1H NMR (499.9 MHz, CD_3OD, ambient temperature): δ = 1.29 (s, 6H), 1.45 (s, 9H), 1.80-1.87 (m, 1H), 1.90-1.98 (m, 2H), 2.07-2.27 (br.m, 1H), 3.38-3.43 (m, 1H), 3.42-3.53 (br.m, 2H), 3.56-3.72 (br.m, 1H), 4.11-4.13 (m, 1H) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, ambient temperature): δ = 24.43, 24.63, 28.28, 47.05, 55.74, 60.95 (br), 69.64 (br), 80.53, 155.45 (br), 172.81 (br) ppm. $C_{14}H_{26}N_2O_4$ (286.37): calcd. C 58.72, H 9.15, N 9.78; found C 58.95, H 9.12, N 9.75.

General Procedure for the Preparation of Ligands: The relevant *N*-Boc-amino alcohol **1a-d**, **2** or pseudodipeptides **3b**, **3c**, **3e**, **3f**, **4** (2 mmol) was added in one portion to a vigorously stirred solution of the appropriate phosphorylating reagent (5*S*)-**5**, (5*R*)-**5** or **6** (2 mmol) and Et_3N (0.56 mL, 4 mmol) in toluene (15 mL) at 20 °C. The mixture that obtained was stirred for 24 h at 20 °C. The resulting suspension was filtered through a short plug of SiO_2/Al_2O_3, the column was washed with toluene (2 x 15 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 (1 Torr) for 1 h (16 h of further high vacuum (10^{-3} Torr) drying is necessary for the preparation of analytically pure samples).

(2*R*,5*S*)-2-[2-((*tert*-butoxycarbonyl)amino)-2-methylpropoxy]-3-phenyl-1,3-diaza-2-phosphabi-cyclo[3.3.0]octane (**L1a**): Colorless oil, yield 0.724 g (92 %). ^1H NMR (400.1 MHz, $CDCl_3$, 26 °C): δ = 1.27 (s, 3H; CH_3), 1.29 (s, 3H; CH_3), 1.44 (s, 9H; $(CH_3)_3C$), 1.65-1.70 (m, 1H; $C\underline{H}_2$), 1.75-1.82 (m, 1H; $NCH_2C\underline{H}_2$), 1.85-1.92 (m, 1H; $NCH_2C\underline{H}_2$), 2.04-2.11 (m, 1H; $C\underline{H}_2$), 3.19-3.24 (m, 1H; $NC\underline{H}_2CH$), 3.21-3.27 (m, 1H; $NC\underline{H}_2CH_2$), 3.34 (dd, ^2J(H,H) = 10.2 Hz, ^3J(H,P) = 5.4 Hz, 1H; $POCH_2$), 3.56-3.62 (m, 1H; $NC\underline{H}_2CH_2$), 3.69 (br.t, ^2J(H,H) ~ ^3J(H,P) = 9.0 Hz, 1H; $POCH_2$), 3.80 (t, ^2J(H,H) ~ ^3J(H,H) = 8.1 Hz, 1H; $NC\underline{H}_2CH$), 4.17-4.21 (m, 1H; $NCH_2C\underline{H}$), 5.33 (br.s, 1H; NH), 6.87 (t, ^3J(H,H) = 7.8 Hz, 1H; CH_{para}), 7.04 (d, ^3J(H,H) = 7.8 Hz, 2H; CH_{ortho}), 7.25-7.28 (m, 2H; CH_{meta}) ppm. $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$, 27 °C): δ = 23.66 (s, CH_3), 23.75 (s; CH_3), 26.19 (d, ^3J(C,P) = 3.5 Hz; $NCH_2\underline{C}H_2$), 28.50 (s; $(\underline{C}H_3)_3C$), 32.07 (s; $\underline{C}H_2$), 48.66 (d, ^2J(C,P) = 37.9 Hz; $N\underline{C}H_2CH_2$), 52.47 (d, ^3J(C,P) = 2.1 Hz; $\underline{C}(CH_3)_2$), 55.09 (d, ^2J(C,P) = 6.7 Hz; $N\underline{C}H_2CH$), 63.08 (d, ^2J(C,P) = 8.5 Hz; $NCH_2\underline{C}H$), 69.42 (d, ^2J(C,P) = 5.1 Hz; $POCH_2$), 78.47 (s; $(CH_3)_3\underline{C}$), 114.79 (d, ^3J(C,P) = 11.5 Hz; CH_{ortho}), 119.10 (s; CH_{para}), 129.17 (s; CH_{meta}), 145.51 (d, ^2J(C,P) = 16.0 Hz; CNP), 154.85 (s; CO) ppm. $^{31}P\{^1H\}$ NMR

EXPERIMENTAL SECTION

(202.4 MHz, $CDCl_3$, ambient temperature): δ = 123.59 (s) ppm. $C_{20}H_{32}N_3O_3P$ (393.47): calcd. C 61.05, H 8.20, N 10.68; found C 61.26, H 8.28, N 10.54.

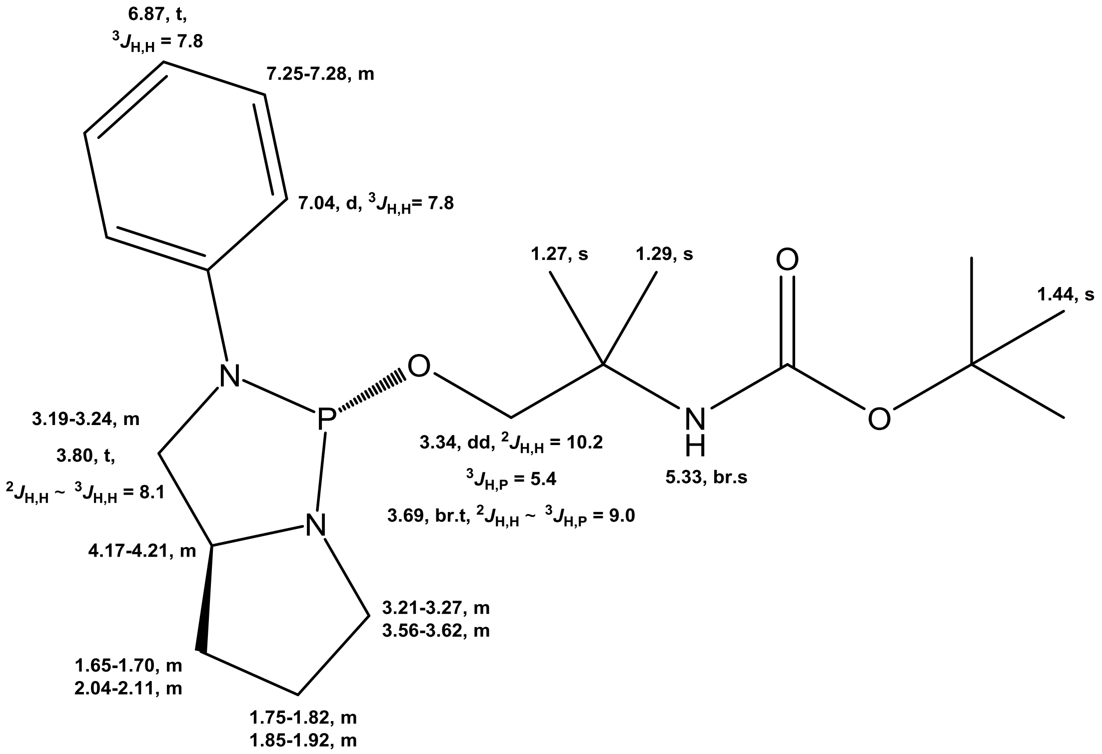

Figure S1a. [1]H NMR Signal Assignment for **L1a**.

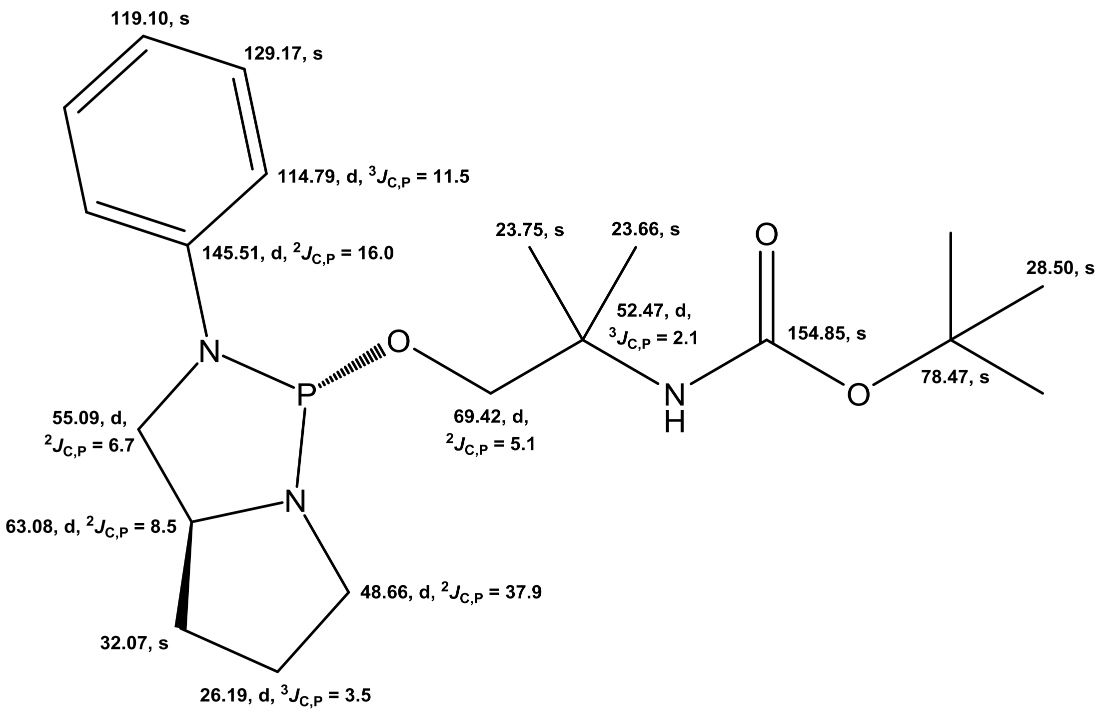

Figure S1b. [13]C NMR Signal Assignment for **L1a**.

EXPERIMENTAL SECTION

(2*R*,5*S*)-2-[(*S*)-2-((*tert*-butoxycarbonyl)amino)-3,3-dimethylbutoxy]-3-phenyl-1,3-diaza-2-phospha-bicyclo[3.3.0]octane (**L1b**): Colorless oil, yield 0.784 g (93 %). ^{1}H NMR (499.9 MHz, $CDCl_3$, ambient temperature): δ = 0.94 (s, 9H; $(C\underline{H}_3)_3CCH$), 1.41 (s, 9H; $(C\underline{H}_3)_3C$), 1.62-1.68 (m, 1H; $C\underline{H}_2$), 1.73-1.82 (m, 1H; $NCH_2C\underline{H}_2$), 1.83-1.90 (m, 1H; $NCH_2C\underline{H}_2$), 2.03-2.10 (m, 1H; $C\underline{H}_2$), 3.18-3.22 (m, 1H; $NC\underline{H}_2CH$), 3.22-3.29 (m, 1H; $NC\underline{H}_2CH_2$), 3.44-3.48 (m, 1H; $(CH_3)_3CC\underline{H}$), 3.53-3.59 (m, 1H; $NC\underline{H}_2CH_2$), 3.64-3.68 (m, 1H; $POCH_2$), 3.75 (t, ^{2}J(H,H) ~ ^{3}J(H,H) = 8.0 Hz, 1H; $NC\underline{H}_2CH$), 3.85-3.89 (m, 1H; $POCH_2$), 4.11-4.16 (m, 1H; $NCH_2C\underline{H}$), 5.08 (br.d, ^{3}J(H,H) = 9.5 Hz, 1H; NH), 6.85 (t, ^{3}J(H,H) = 7.2 Hz, 1H; CH_{para}), 7.01 (d, ^{3}J(H,H) = 7.8 Hz, 2H; CH_{ortho}), 7.25 (t, ^{3}J(H,H) = 7.8 Hz, 2H; CH_{meta}) ppm. $^{13}C\{^{1}H\}$ NMR (125.7 MHz, $CDCl_3$, ambient temperature): δ = 26.16 (d, ^{3}J(C,P) = 4.8 Hz; $NCH_2\underline{C}H_2$), 27.10 (s; $(\underline{C}H_3)_3CCH$), 28.36 (s; $(\underline{C}H_3)_3C$), 32.17 (s; $\underline{C}H_2$), 34.46 (br.s; $(CH_3)_3\underline{C}CH$), 48.62 (d, ^{2}J(C,P) = 38.1 Hz; $N\underline{C}H_2CH_2$), 54.79 (d, ^{2}J(C,P) = 6.7 Hz; $N\underline{C}H_2CH$), 58.00 (br.s; $(CH_3)_3C\underline{C}H$), 62.30 (br.s; $POCH_2$), 63.28 (d, ^{2}J(C,P) = 8.6 Hz; $NCH_2\underline{C}H$), 78.63 (br.s; $(CH_3)_3\underline{C}$), 114.86 (d, ^{3}J(C,P) = 12.4 Hz; CH_{ortho}), 118.99 (s; CH_{para}), 129.06 (s; CH_{meta}), 145.50 (d, ^{2}J(C,P) = 15.3 Hz; CNP), 156.09 (s; CO) ppm. $^{31}P\{^{1}H\}$ NMR (162.0 MHz, $CDCl_3$, 27 °C): δ = 125.59 (s) ppm. $C_{22}H_{36}N_3O_3P$ (421.52): calcd. C 62.69, H 8.61, N 9.97; found C 62.93, H 8.70, N 9.76.

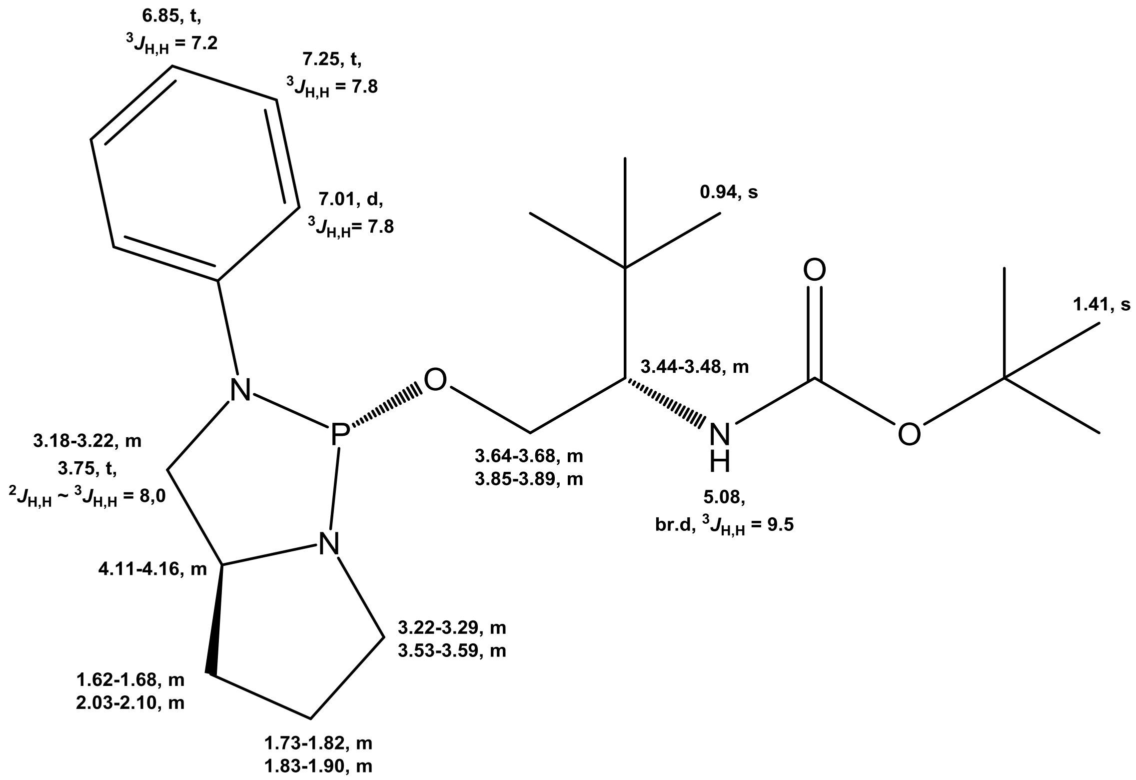

Figure S2a. ^{1}H NMR Signal Assignment for **L1b**.

EXPERIMENTAL SECTION

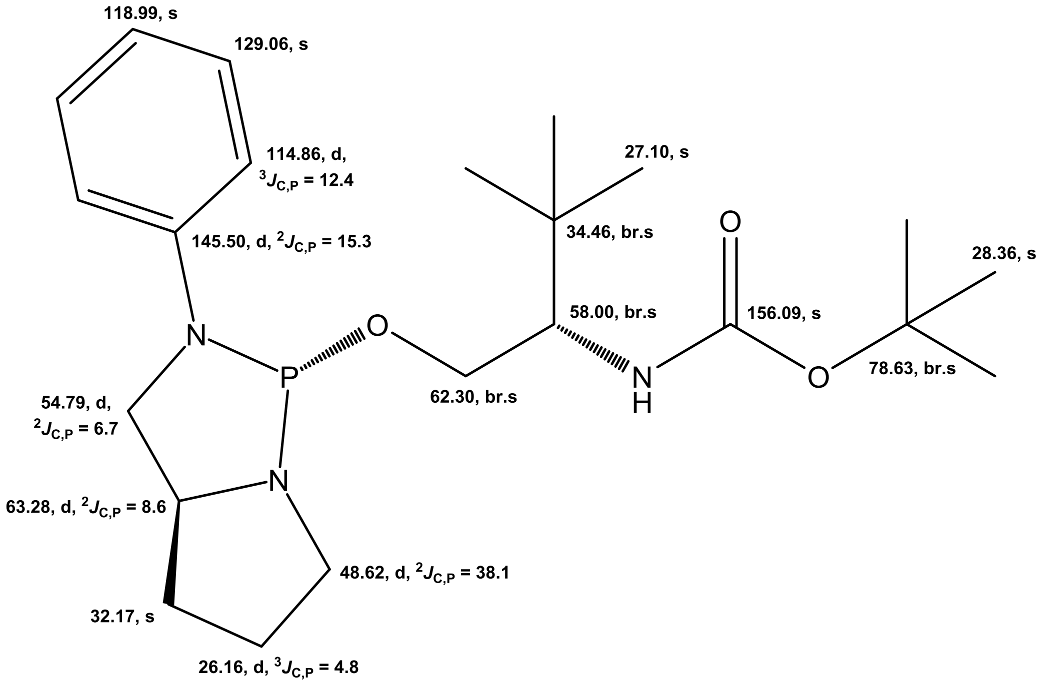

Figure S2b. ^{13}C NMR Signal Assignment for **L1b**.

(2*R*,5*S*)-2-[(2*S*,3*S*)-2-((*tert*-butoxycarbonyl)amino)-3-methylpentyloxy]-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (**L1c**): Colorless oil, yield 0.759 g (90 %). ^{1}H NMR (600.1 MHz, $CDCl_3$, 16 °C): δ = 0.86 (t, ^3J(H,H) = 7.4 Hz, 3H; $C\underline{H}_3CH_2$), 0.89 (d, ^3J(H,H) = 6.7 Hz, 3H; $C\underline{H}_3CH$), 1.01-1.09 (m, 1H; $CH_3C\underline{H}_2$), 1.45-1.53 (m, 1H; $CH_3C\underline{H}_2$), 1.58-1.67 (br.m, 1H; $CH_3C\underline{H}$) 1.37 (s, 9H; $(C\underline{H}_3)_3C$), 1.61-1.67 (m, 1H; $C\underline{H}_2$), 1.72-1.80 (m, 1H; $NCH_2C\underline{H}_2$), 1.83-1.89 (m, 1H; $NCH_2C\underline{H}_2$), 2.03-2.08 (m, 1H; $C\underline{H}_2$), 3.16-3.21 (m, 1H; $NC\underline{H}_2CH$), 3.18-3.24 (m, 1H; $NC\underline{H}_2CH_2$), 3.43-3.47 (m, 1H; $NHC\underline{H}$), 3.53-3.57 (m, 1H; $NC\underline{H}_2CH_2$), 3.55-3.58 (m, 1H; $POCH_2$), 3.75 (t, ^2J(H,H) ~ ^3J(H,H) = 8,0 Hz, 1H; $NC\underline{H}_2CH$), 3.80-3.84 (m, 1H; $POCH_2$), 4.12-4.17 (m, 1H; $NCH_2C\underline{H}$), 4.95 (br.d, ^3J(H,H) = 9.0 Hz, 1H; $N\underline{H}CH$), 6.84 (t, ^3J(H,H) = 7.4 Hz, 1H; CH_{para}), 7.00 (d, ^3J(H,H) = 7.7 Hz, 2H; CH_{ortho}), 7.24 (t, ^3J(H,H) = 7.9 Hz, 2H; CH_{meta}) ppm. $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$, 15 °C): δ = 11.44 (s; $\underline{C}H_3CH_2$), 15.27 (s; $\underline{C}H_3CH$), 25.22 (s; $CH_3\underline{C}H_2$), 26.11 (d, ^3J(C,P) = 3.4 Hz; $NCH_2\underline{C}H_2$), 28.27 (s; $(\underline{C}H_3)_3C$), 32.00 (s; $\underline{C}H_2$), 35.55 (s; $CH_3\underline{C}H$), 48.66 (d, ^2J(C,P) = 37.9 Hz; $N\underline{C}H_2CH_2$), 54.70 (br.s; $NH\underline{C}H$), 54.90 (d, ^2J(C,P) = 6.9 Hz; $N\underline{C}H_2CH$), 62.13 (d, ^2J(C,P) = 3.4 Hz; $POCH_2$), 63.10 (d, ^2J(C,P) = 9.2 Hz; $NCH_2\underline{C}H$), 78.72 (br.s; $(CH_3)_3\underline{C}$), 114.63 (d, ^3J(C,P) = 11.5 Hz; CH_{ortho}), 118.91 (s; CH_{para}), 129.07 (s; CH_{meta}), 145.40 (d, ^2J(C,P) = 16.1 Hz; CNP), 155.74 (s; CO) ppm. $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 27 °C): δ = 124.46 (s) ppm. $C_{22}H_{36}N_3O_3P$ (421.52): calcd. C 62.69, H 8.61, N 9.97; found C 62.98, H 8.55, N 10.11.

EXPERIMENTAL SECTION

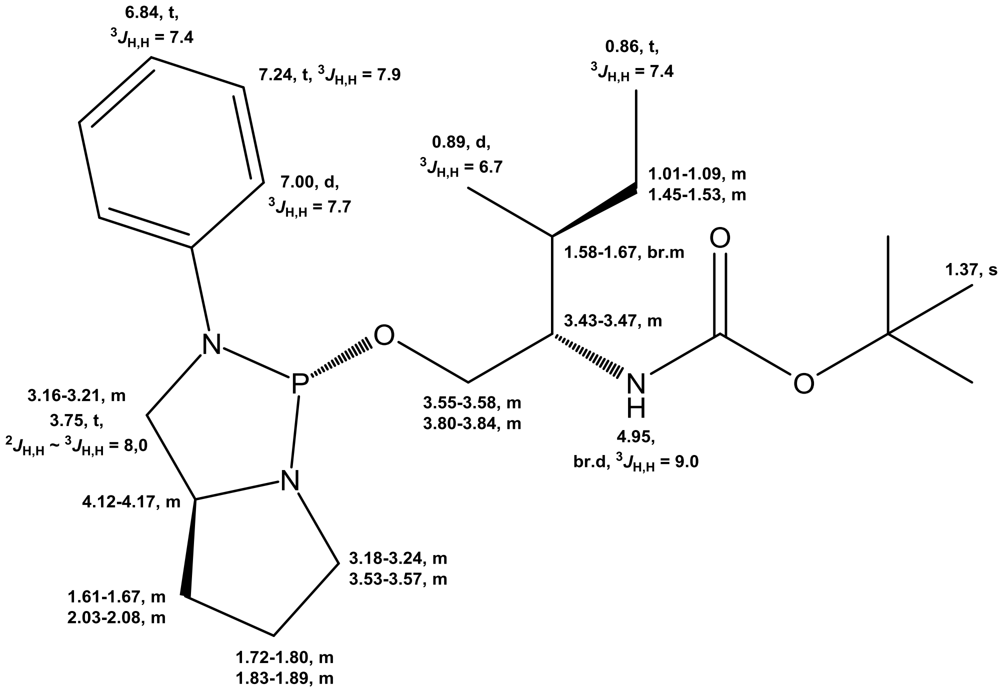

Figure S3a. ^{1}H NMR Signal Assignment for **L1c**.

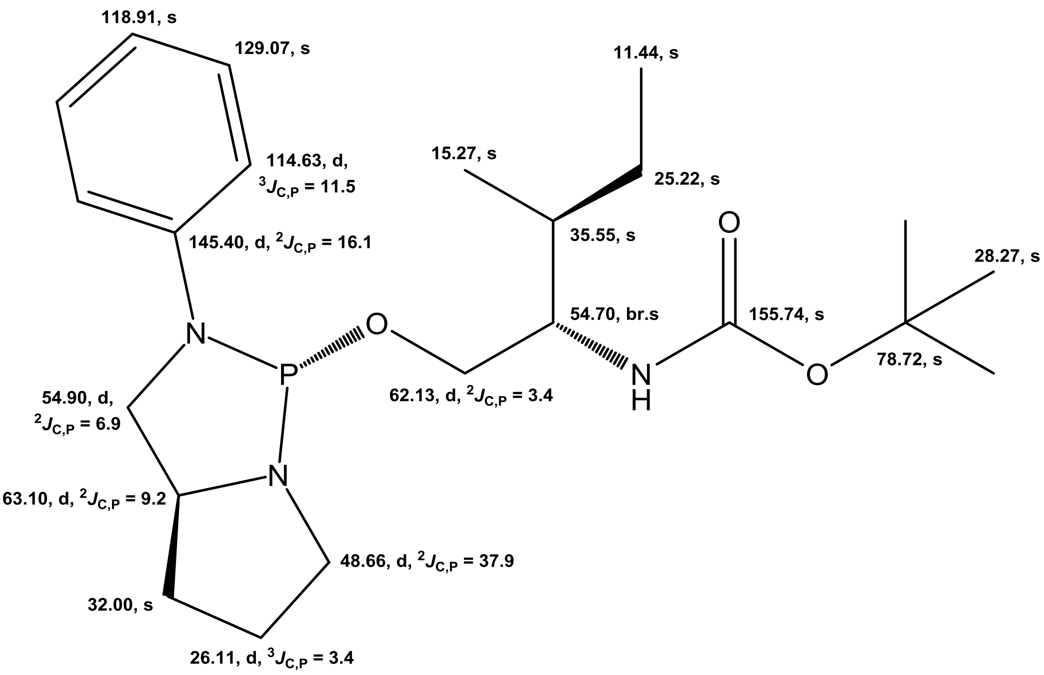

Figure S3b. ^{13}C NMR Signal Assignment for **L1c**.

EXPERIMENTAL SECTION

(2*R*,5*S*)-2-[(*S*)-2-((*tert*-butoxycarbonyl)amino)-4-(methylthio)butoxy]-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (**L1d**): White solid, yield 0.791 g (90 %). ^{1}H NMR (499.9 MHz, $CDCl_3$, ambient temperature): δ = 1.38 (s, 9H; $(C\underline{H}_3)_3C$), 1.61-1.67 (m, 1H; $C\underline{H}_2$), 1.75-1.82 (m, 1H; $NCH_2C\underline{H}_2$), 1.75-1.86 (m, 2H; $SCH_2C\underline{H}_2$), 1.82-1.90 (m, 1H; $NCH_2C\underline{H}_2$), 2.02-2.07 (m, 1H; $C\underline{H}_2$), 2.09 (s, 3H; CH_3), 2.50 (t, ^{3}J(H,H) = 7.6 Hz, 2H; $SC\underline{H}_2CH_2$), 3.18-3.25 (m, 1H; $NC\underline{H}_2CH$), 3.18-3.25 (m, 1H; $NC\underline{H}_2CH_2$), 3.52-3.58 (m, 1H; $NC\underline{H}_2CH_2$), 3.58-3.64 (br.m, 1H; $POCH_2$), 3.72-3.77 (m, 1H; $POCH_2$), 3.73-3.78 (m, 1H; $NHC\underline{H}$), 3.75-3.78 (m, 1H; $NC\underline{H}_2CH$), 4.12-4.18 (m, 1H; $NCH_2C\underline{H}$), 4.91-5.05 (br.m, 1H; $N\underline{H}CH$), 6.85 (t, ^{3}J(H,H) = 7.3 Hz, 1H; CH_{para}), 7.01 (d, ^{3}J(H,H) = 7.8 Hz, 2H; CH_{ortho}), 7.24 (t, ^{3}J(H,H) = 8.0 Hz, 2H; CH_{meta}) ppm. ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, ambient temperature): δ = 15.42 (s; $\underline{C}H_3$), 26.20 (d, ^{3}J(C,P) = 3.9 Hz; $NCH_2\underline{C}H_2$), 28.33 (s; $(\underline{C}H_3)_3C$), 30.70 (s; $S\underline{C}H_2CH_2$), 31.76 (s; $SCH_2\underline{C}H_2$), 32.18 (s; $\underline{C}H_2$), 48.51 (d, ^{2}J(C,P) = 37.4 Hz; $N\underline{C}H_2CH_2$), 50.24 (br.s; $NH\underline{C}H$), 54.76 (d, ^{2}J(C,P) = 7.1 Hz; $N\underline{C}H_2CH$), 63.28 (d, ^{2}J(C,P) = 8.5 Hz; $NCH_2\underline{C}H$), 64.16 (s; $POCH_2$), 79.04 (br.s; $(CH_3)_3\underline{C}$), 114.90 (d, ^{3}J(C,P) = 12.1 Hz; CH_{ortho}), 119.43 (s; CH_{para}), 129.12 (s; CH_{meta}), 145.45 (d, ^{2}J(C,P) = 15.5 Hz; CNP), 155.43 (s; CO) ppm. ^{31}P{^{1}H} NMR (202.4 MHz, $CDCl_3$, ambient temperature): δ = 125.22 (s) ppm. $C_{21}H_{34}N_3O_3PS$ (439.55): calcd. C 57.38, H 7.80, N 9.56; found C 57.56, H 7.88, N 9.59.

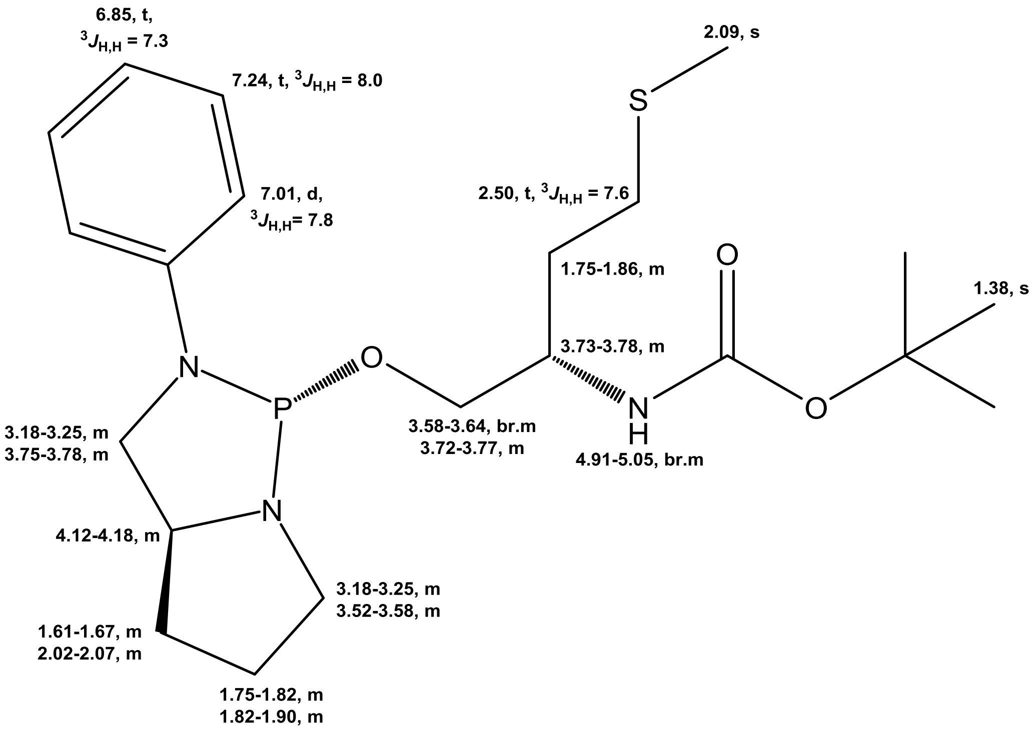

Figure S4a. ^{1}H NMR Signal Assignment for **L1d**.

EXPERIMENTAL SECTION

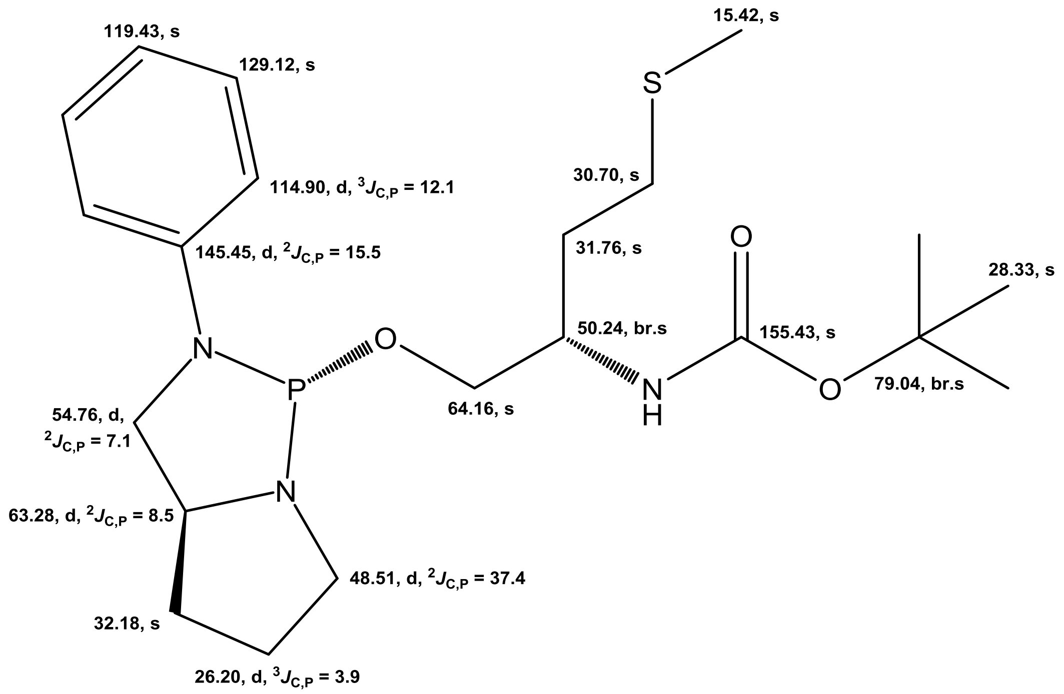

Figure S4b. ^{13}C NMR Signal Assignment for **L1d**.

(2*R*,5*S*)-2-[((*S*)-1-(*tert*-butoxycarbonyl)pyrrolidin-2-yl)methoxy]-3-phenyl-1,3-diaza-2-phospha-bicyclo[3.3.0]octane (**L2**): Colorless oil, yield 0.762 g (94 %). ^{1}H NMR (600.1 MHz, $CD_3C_6D_5$, -20 °C): δ = 1.06-1.11 (m, 1H; $C\underline{H}_2$), 1.17-1.27 (m, 1H; $NCH_2C\underline{H}_2$), 1.21-1.27 (m, 1H; $C\underline{H}_2CH_2NBoc$), 1.28-1.38 (m, 1H; $NCH_2C\underline{H}_2$), 1.45 (s, 9H; $(C\underline{H}_3)_3C$), 1.45-1.56 (br.m, 1H; $C\underline{H}_2CHNBoc$), 1.46-1.51 (m, 1H; $C\underline{H}_2CH_2NBoc$), 1.46-1.53 (m, 1H; $C\underline{H}_2$), 1.84-1.92 (br.m, 1H; $C\underline{H}_2CHNBoc$), 2.62 (br.t, 1H; $NC\underline{H}_2CH$), 2.86-2.92 (m, 1H; $NC\underline{H}_2CH_2$), 2.99-3.03 (m, 1H; $CH_2C\underline{H}_2NBoc$), 3,08-3.11 (m, 1H; $CH_2C\underline{H}_2NBoc$), 3.25-3.31 (m, 1H; $NC\underline{H}_2CH$), 3.32-3.40 (m, 1H; $NC\underline{H}_2CH_2$), 3.35-3.41 (m, 1H; $POCH_2$), 3.96-4.00 (m, 1H; $NCH_2C\underline{H}$), 4.12-4.17 (br.m, 1H; $POCH_2$), 4.13-4.19 (m, 1H; $CH_2C\underline{H}NBoc$), 6.85 (t, ^{3}J(H,H) = 7.0 Hz, 1H; CH_{para}), 7.07 (d, ^{3}J(H,H) = 8.1 Hz, 2H; CH_{ortho}), 7.21 (t, ^{3}J(H,H) = 7.7 Hz, 2H; CH_{meta}) (major rotamer), 1.12-1.16 (m, 1H; $C\underline{H}_2$), 1.16-1.21 (m, 1H; $C\underline{H}_2CH_2NBoc$), 1.17-1.27 (m, 1H; $NCH_2C\underline{H}_2$), 1.28-1.38 (m, 1H; $NCH_2C\underline{H}_2$), 1.35-1.39 (m, 1H; $C\underline{H}_2CH_2NBoc$), 1.45-1.56 (br.m, 1H; $C\underline{H}_2CHNBoc$), 1.47 (s, 9H; $(C\underline{H}_3)_3C$), 1.50-1.57 (m, 1H; $C\underline{H}_2$), 1.79-1.82 (m, 1H; $C\underline{H}_2CHNBoc$), 2.67 (br.t, 1H; $NC\underline{H}_2CH$), 2.93-2.97 (m, 1H; $NC\underline{H}_2CH_2$), 3.22-3.28 (m, 2H; $CH_2C\underline{H}_2NBoc$), 3.25-3.31 (m, 1H; $NC\underline{H}_2CH$), 3.32-3.40 (m, 1H; $NC\underline{H}_2CH_2$), 3.35-3.41 (m, 1H; $POCH_2$), 3.81-3.85 (m, 1H; $NCH_2C\underline{H}$), 3.85-3.90 (m, 1H; $CH_2C\underline{H}NBoc$), 3.90-3.95 (br.m, 1H; $POCH_2$), 6.85 (t, ^{3}J(H,H) = 7.0 Hz, 1H; CH_{para}), 7.07 (d, ^{3}J(H,H) = 8.1 Hz, 2H; CH_{ortho}), 7.21 (t, ^{3}J(H,H) = 7.7 Hz, 2H; CH_{meta}) (minor rotamer) ppm. $^{13}C\{^{1}H\}$ NMR (150.9 MHz, $CD_3C_6D_5$, -20 °C): δ = 23.47 (s; $\underline{C}H_2CH_2NBoc$), 25.91 (d, ^{3}J(C,P) = 3.1 Hz; $NCH_2\underline{C}H_2$), 27.74 (s; $\underline{C}H_2CHNBoc$), 28.34 (s; $(\underline{C}H_3)_3C$), 31.56 (s; $\underline{C}H_2$), 46.84 (s; $CH_2\underline{C}H_2NBoc$), 48.80 (d, ^{2}J(C,P) = 39.8 Hz; $N\underline{C}H_2CH_2$), 55.25 (d, ^{2}J(C,P) = 6.6 Hz; $N\underline{C}H_2CH$), 57.49 (d, ^{3}J(C,P) = 2.0 Hz; $CH_2\underline{C}HNBoc$), 61.81 (d, ^2J(C,P) = 6.6 Hz; $POCH_2$), 62.69 (d, ^2J(C,P) = 8.6 Hz; $NCH_2\underline{C}H$), 78.33 (s; $(CH_3)_3\underline{C}$), 114.92 (d, ^3J(C,P) = 11,2 Hz; CH_{ortho}), 118.77 (s; CH_{para}), 129.17 (s; CH_{meta}), 146.19 (d, ^2J(C,P) = 15.8 Hz; CNP), 154.15 (s; CO) (major rotamer), 22.58 (s; $\underline{C}H_2CH_2NBoc$), 25.98 (d, ^3J(C,P) = 3.6 Hz; $NCH_2\underline{C}H_2$), 28.36 (s; $(\underline{C}H_3)_3C$), 28.82 (s; $\underline{C}H_2CHNBoc$), 31.67 (s; $\underline{C}H_2$), 46.72 (s; $CH_2\underline{C}H_2NBoc$), 48.95 (d, ^2J(C,P) = 39.8 Hz; $N\underline{C}H_2CH_2$), 55.01 (d, ^2J(C,P) = 7.1 Hz; $N\underline{C}H_2CH$), 57.32 (d, ^3J(C,P) = 2.5 Hz; $CH_2\underline{C}HNBoc$), 62.58 (d, ^2J(C,P) = 5.1 Hz; $POCH_2$), 63.27 (d, ^2J(C,P) = 8.6 Hz; $NCH_2\underline{C}H$), 78.34 (s; $(CH_3)_3\underline{C}$), 114.91 (d, ^3J(C,P) = 11,7 Hz; CH_{ortho}), 119.10 (s; CH_{para}), 129.32 (s; CH_{meta}), 145.99 (d, ^2J(C,P) = 16.3 Hz; CNP), 153.75 (s; CO) (minor rotamer) ppm. $^{31}P\{^1H\}$ NMR (242.9 MHz, $CD_3C_6D_5$, -20 °C): δ = 122.80 (s) (major rotamer), 125.09 (s) (minor rotamer) ppm. $C_{21}H_{32}N_3O_3P$ (405.48): calcd. C 62.21, H 7.96, N 10.36; found C 62.47, H 8.01, N 10.25.

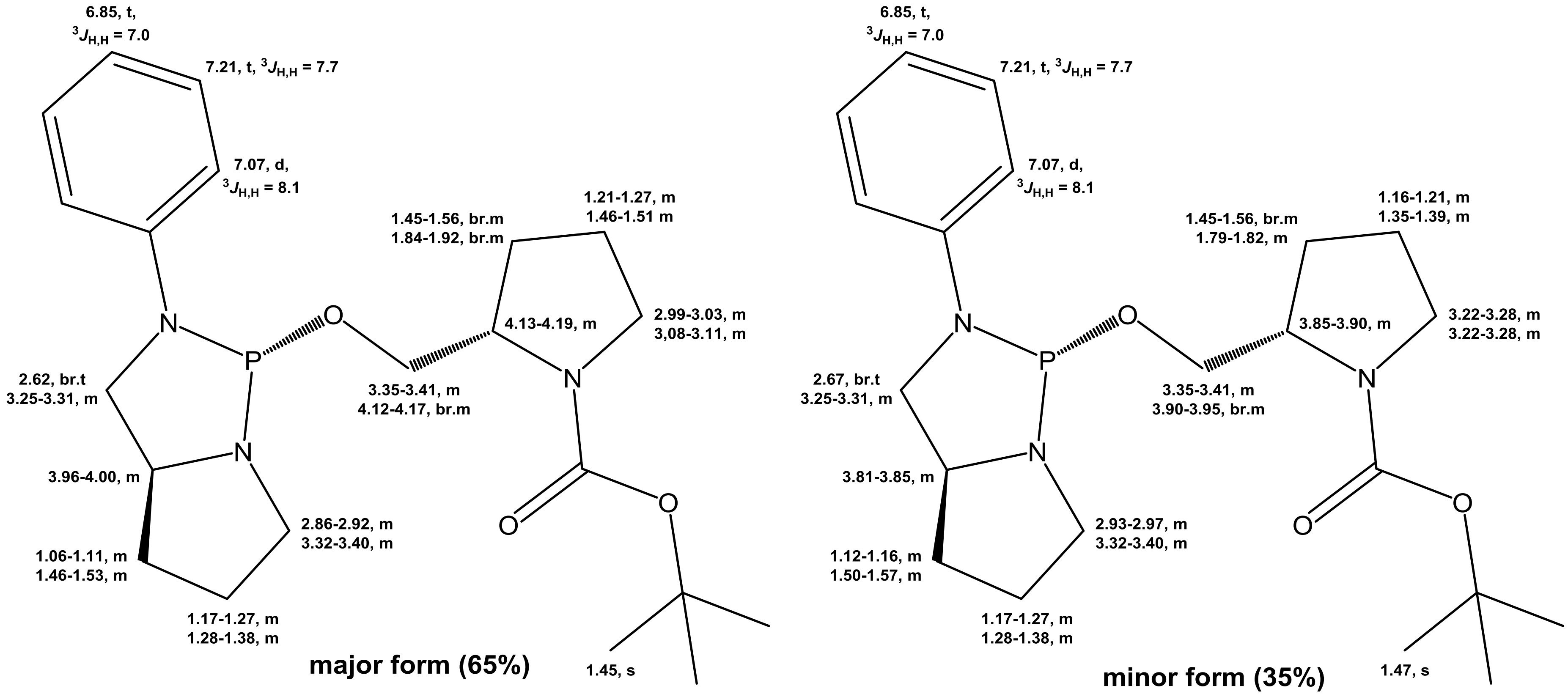

Figure S5a. ^{1}H NMR Signal Assignment for **L2**.

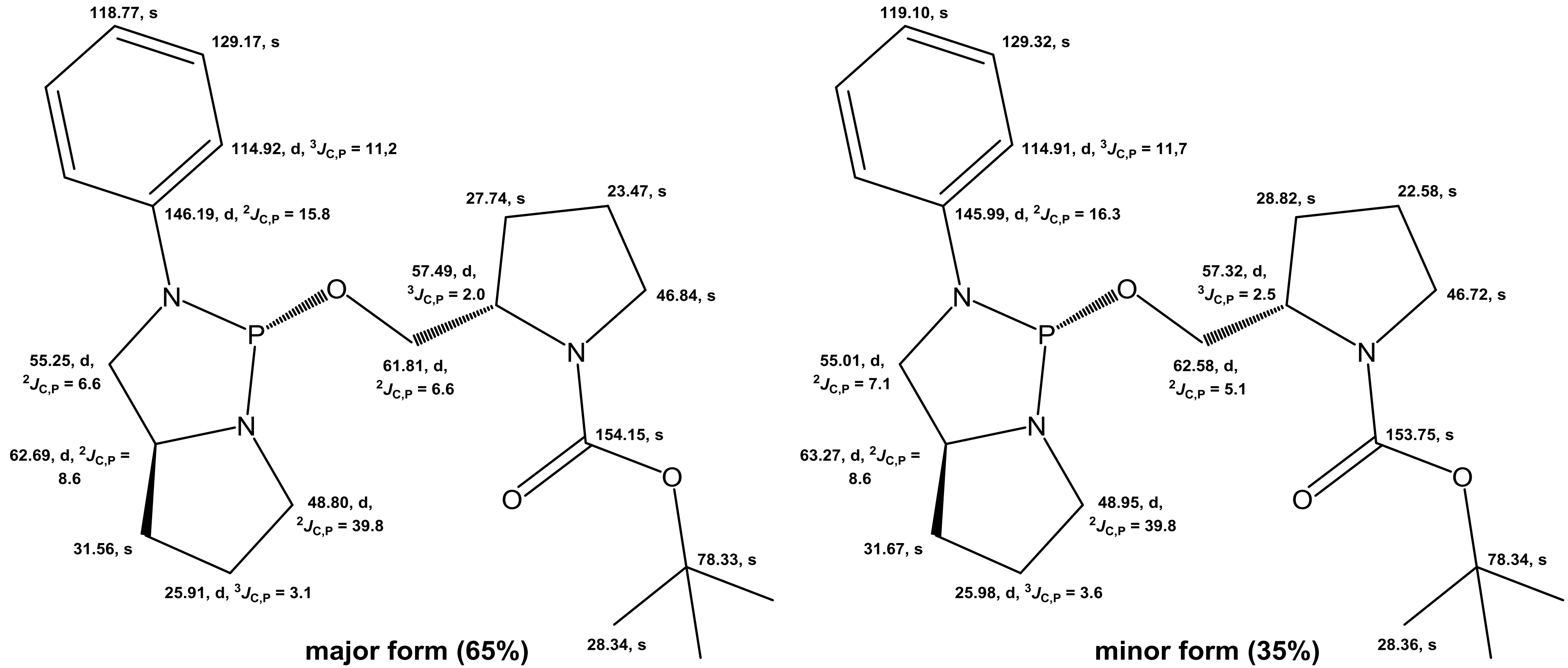

Figure S5b. ^{13}C NMR Signal Assignment for **L2**.

EXPERIMENTAL SECTION

(2*R*,5*S*)-2-[2-(2-((*tert*-butoxycarbonyl)amino)acetamido)-2-methylpropoxy]-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (**L3a**): White solid, yield 0.883 g (98 %). ^{1}H NMR (499.9 MHz, $CDCl_3$, ambient temperature): δ = 1.31 (s, 3H; CH_3), 1.32 (s, 3H; CH_3), 1.46 (s, 9H; $(CH_3)_3C$), 1.62-1.68 (m, 1H; $C\underline{H}_2$), 1.72-1.81 (m, 1H; $NCH_2C\underline{H}_2$), 1.84-1.91 (m, 1H; $NCH_2C\underline{H}_2$), 2.03-2.10 (m, 1H; $C\underline{H}_2$), 3.15-3.22 (m, 1H; $NC\underline{H}_2CH$), 3.15-3.22 (m, 1H; $NC\underline{H}_2CH_2$), 3.43-3.56 (br.m, 2H; $C\underline{H}_2NHBoc$), 3.51 (br.dd, ^{2}J(H,H) = 10.1 Hz, ^{3}J(H,P) = 6.4 Hz, 1H; $POCH_2$), 3.55-3.60 (m, 1H; $NC\underline{H}_2CH_2$), 3.63 (dd, ^{2}J(H,H) = 10.1 Hz, ^{3}J(H,P) = 6.4 Hz, 1H; $POCH_2$), 3.80 (t, ^{2}J(H,H) ~ ^{3}J(H,H) = 8,1 Hz, 1H; $NC\underline{H}_2CH$), 4.15-4.20 (m, 1H; $NCH_2C\underline{H}$), 4.92 (br.s, 1H; $CH_2N\underline{H}Boc$), 6.1 (br.s, 1H; CNH), 6.86 (t, ^{3}J(H,H) = 7.3 Hz, 1H; CH_{para}), 7.03 (d, ^{3}J(H,H) = 7.8 Hz, 2H; CH_{ortho}), 7.26 (t, ^{3}J(H,H) = 7.3 Hz, 2H; CH_{meta}) ppm. $^{13}C\{^{1}H\}$ NMR (150.9 MHz, $CDCl_3$, 24 °C): δ = 23.36 (s, CH_3), 23.68 (s; CH_3), 26.07 (d, ^{3}J(C,P) = 4.0 Hz; $NCH_2\underline{C}H_2$), 28.24 (s; $(\underline{C}H_3)_3C$), 32.08 (s; $\underline{C}H_2$), 44.38 (br.s; $\underline{C}H_2NHBoc$), 48.80 (d, ^{2}J(C,P) = 38.4 Hz; $N\underline{C}H_2CH_2$), 53.70 (s; CNH), 55.00 (d, ^{2}J(C,P) = 6.9 Hz; $N\underline{C}H_2CH$), 63.19 (d, ^{2}J(C,P) = 9.2 Hz; $NCH_2\underline{C}H$), 68.36 (d, ^{2}J(C,P) = 6.3 Hz; $POCH_2$), 79.64 (s; $(CH_3)_3\underline{C}$), 114.64 (d, ^{3}J(C,P) = 12.1 Hz; CH_{ortho}), 118.98 (s; CH_{para}), 129.08 (s; CH_{meta}), 145.36 (d, ^{2}J(C,P) = 15.5 Hz; CNP), 155.73 (br.s; C(O)O), 168.33 (s; CO) ppm. $^{31}P\{^{1}H\}$ NMR (202.4 MHz, $CDCl_3$, ambient temperature): δ = 123.10 (s) ppm. $C_{22}H_{35}N_4O_4P$ (450.52): calcd. C 58.65, H 7.83, N 12.44; found C 58.87, H 7.93, N 12.56.

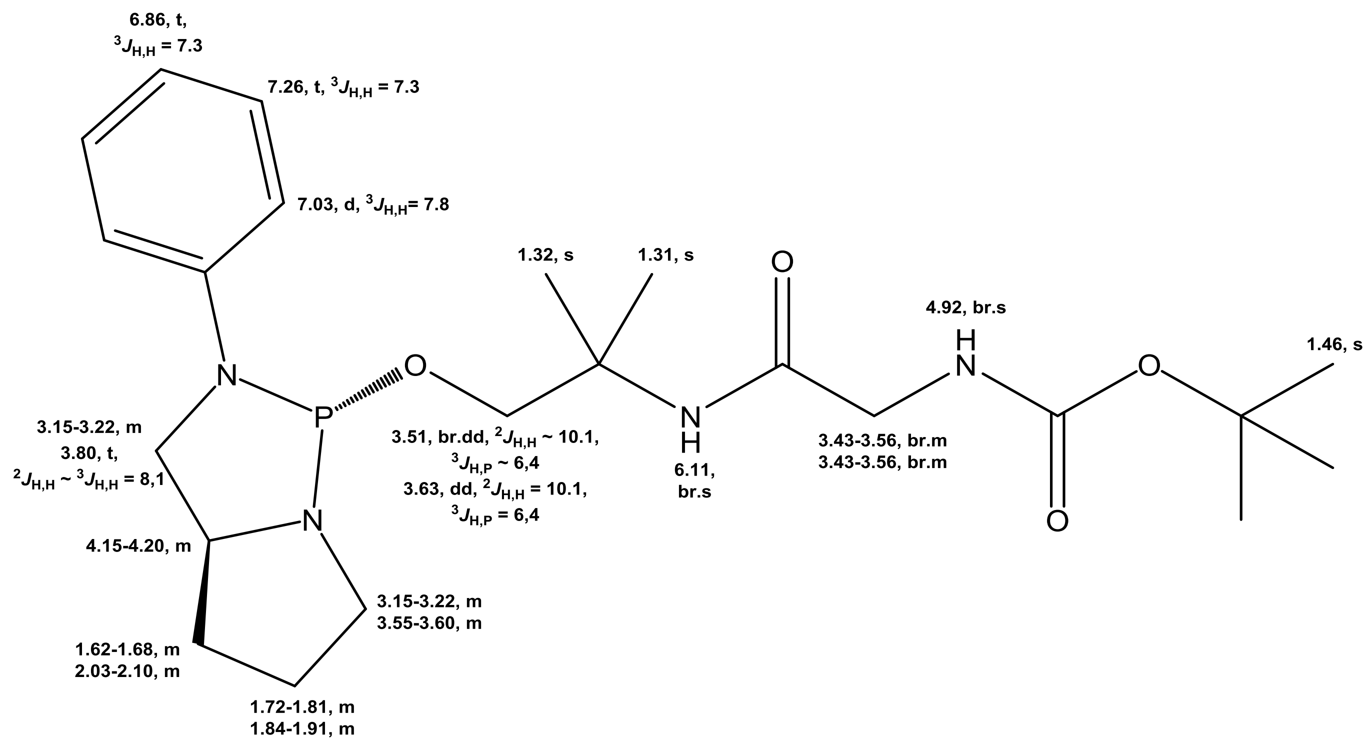

Figure S6a. ^{1}H NMR Signal Assignment for **L3a**.

EXPERIMENTAL SECTION

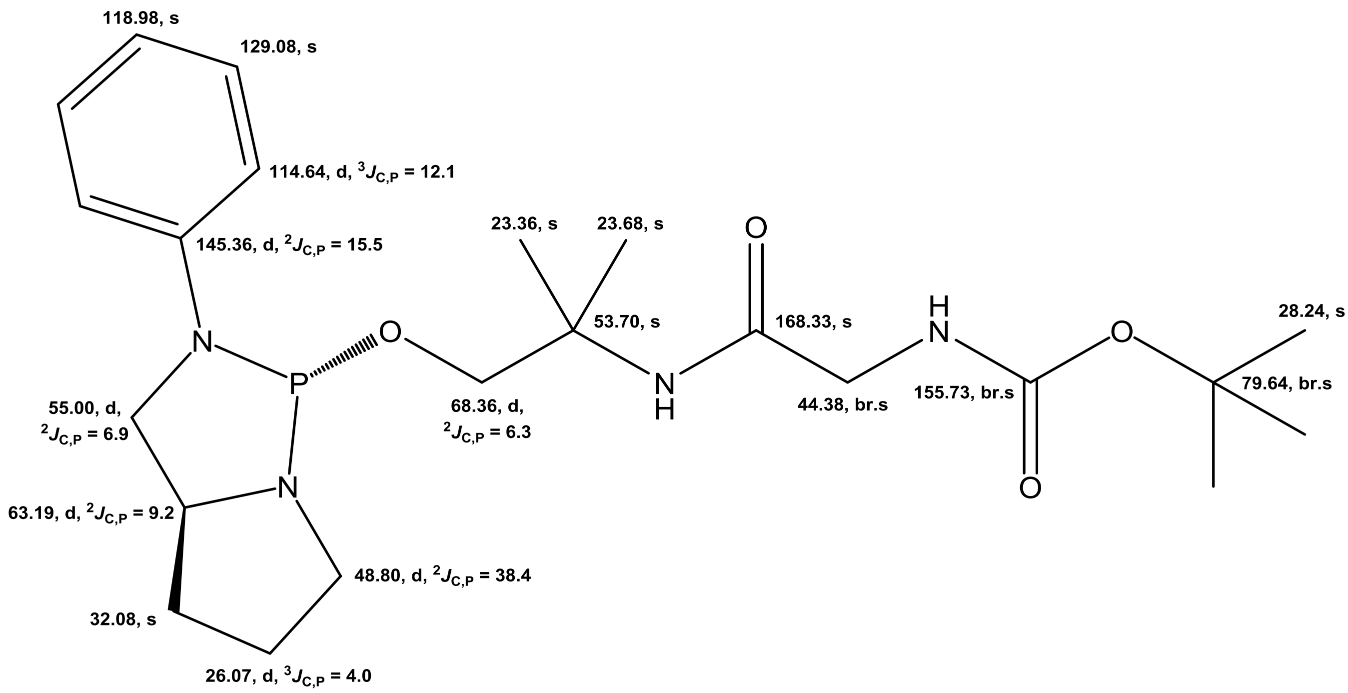

Figure S6b. ^{13}C NMR Signal Assignment for **L3a**.

(2*R*,5*S*)-2-[2-(2-((*tert*-butoxycarbonyl)amino)acetamido)-2,2-diphenylethoxy]-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (**L3b**): White solid, yield 1.057 g (92 %). ^{1}H NMR (600.1 MHz, $CDCl_3$, 22 °C): 1.46 (s, 9H; $(CH_3)_3C$), 1.60-1.65 (m, 1H; $C\underline{H}_2$), 1.71-1.78 (m, 1H; $NCH_2C\underline{H}_2$), 1.83-1.89 (m, 1H; $NCH_2C\underline{H}_2$), 2.02-2.08 (m, 1H; $C\underline{H}_2$), 3.14-3.19 (m, 1H; $NC\underline{H}_2CH$), 3.15-3.21 (m, 1H; $NC\underline{H}_2CH_2$), 3.54-3.60 (br.m, 1H; $C\underline{H}_2NHBoc$), 3.63-3.69 (br.m, 1H; $C\underline{H}_2NHBoc$), 3.52-3.57 (m, 1H; $NC\underline{H}_2CH_2$), 3.78 (t, ^{2}J(H,H) ~ ^{3}J(H,H) = 8,1 Hz, 1H; $NC\underline{H}_2CH$), 4.17-4.21 (m, 1H; $NCH_2C\underline{H}$), 4.30 (dd, ^{2}J(H,H) = 10.3 Hz, ^{3}J(H,P) = 5,1 Hz, 1H; $POCH_2$), 4.53 (dd, ^{2}J(H,H) = 10.5 Hz, ^{3}J(H,P) = 5,3 Hz, 1H; $POCH_2$), 5.03 (br.s, 1H; $CH_2N\underline{H}Boc$), 6.87 (t, ^{3}J(H,H) = 7.3 Hz, 1H; CH_{para}), 6.95 (d, ^{3}J(H,H) = 7.7 Hz, 2H; CH_{ortho}), 7.08 (br.s, 1H; CNH), 7.20-7.24' (m, 4H; CH_{para}), 7.23 (t, ^{3}J(H,H) = 7.3 Hz, 2H; CH_{meta}), 7.26-7.30' (m, 6H; CH_{ortho} + CH_{meta}) ppm. ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$, 22 °C): δ = 26.11 (d, ^{3}J(C,P) = 4.0 Hz; $NCH_2\underline{C}H_2$), 28.21 (s; $(\underline{C}H_3)_3C$), 32.09 (s; $\underline{C}H_2$), 44.69 (br.s; $\underline{C}H_2NHBoc$), 48.78 (d, ^{2}J(C,P) = 37.3 Hz; $N\underline{C}H_2CH_2$), 54.96 (d, ^{2}J(C,P) = 7.5 Hz; $N\underline{C}H_2CH$), 63.42 (d, ^{2}J(C,P) = 8.6 Hz; $NCH_2\underline{C}H$), 65.23 (s; $(Ph_2)CNH$), 66.39 (d, ^{2}J(C,P) = 6.9 Hz; $POCH_2$), 79.78 (br.s; $(CH_3)_3\underline{C}$), 114.79 (d, ^{3}J(C,P) = 12.1 Hz; CH_{ortho}), 119.02 (s; CH_{para}), 127.02' (s; CH_{para}), 127.08'' (s; CH_{para}), 127.18' (s; CH_{meta}), 127.34'' (s; CH_{meta}), 128.00' (s; CH_{ortho}), 128.04'' (s; CH_{ortho}), 129.07 (s; CH_{meta}), 141.68' (s; C_{ipso}), 141.84'' (s; C_{ipso}), 145.32 (d, ^{2}J(C,P) = 17.7 Hz; CNP), 155.86 (br.s; C(O)O), 168.06 (s; CO) ppm. ^{31}P{^{1}H} NMR (202.4 MHz, $CDCl_3$, ambient temperature): δ = 123.29 (s) ppm. $C_{32}H_{39}N_4O_4P$ (574.66): calcd. C 66.88, H 6.84, N 9.75; found C 67.23, H 6.94, N 9.56.

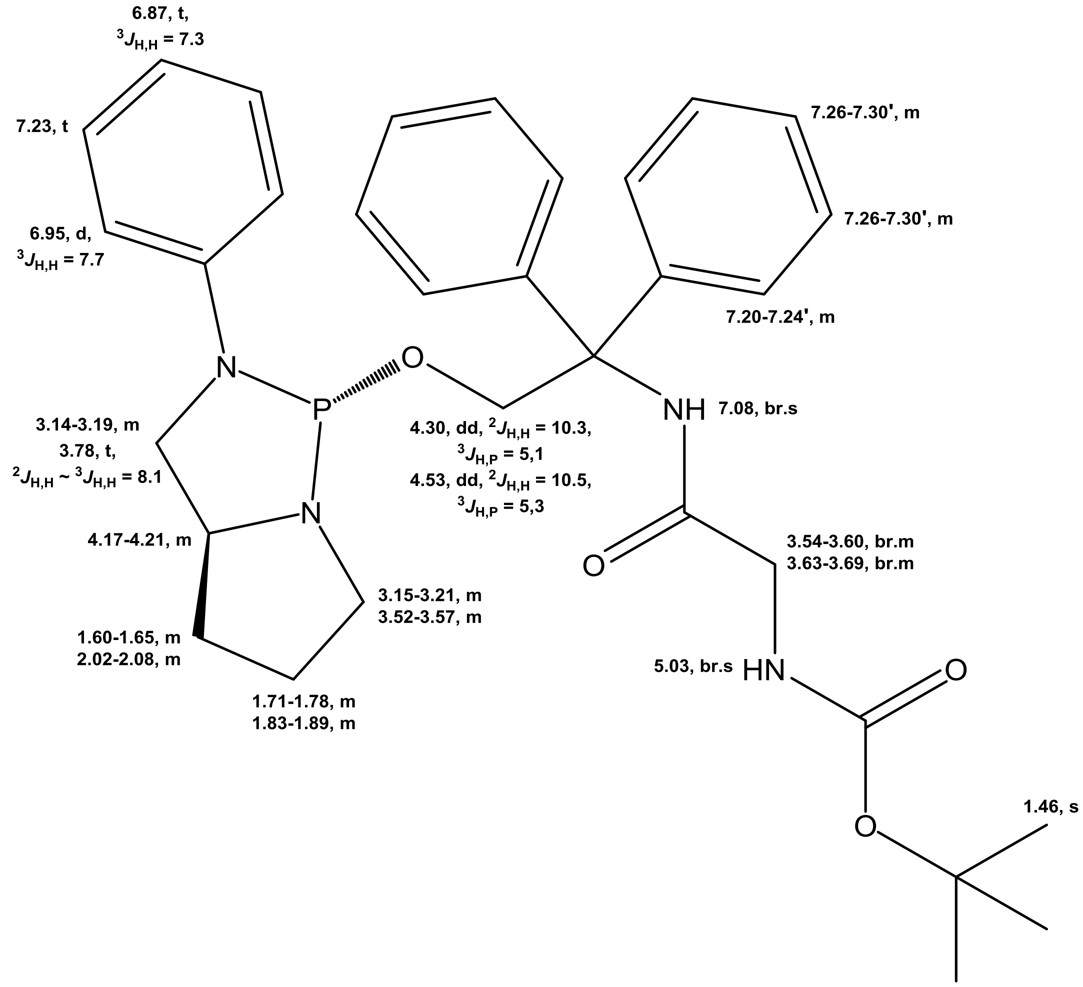

Figure S7a. ^{1}H NMR Signal Assignment for **L3b**.

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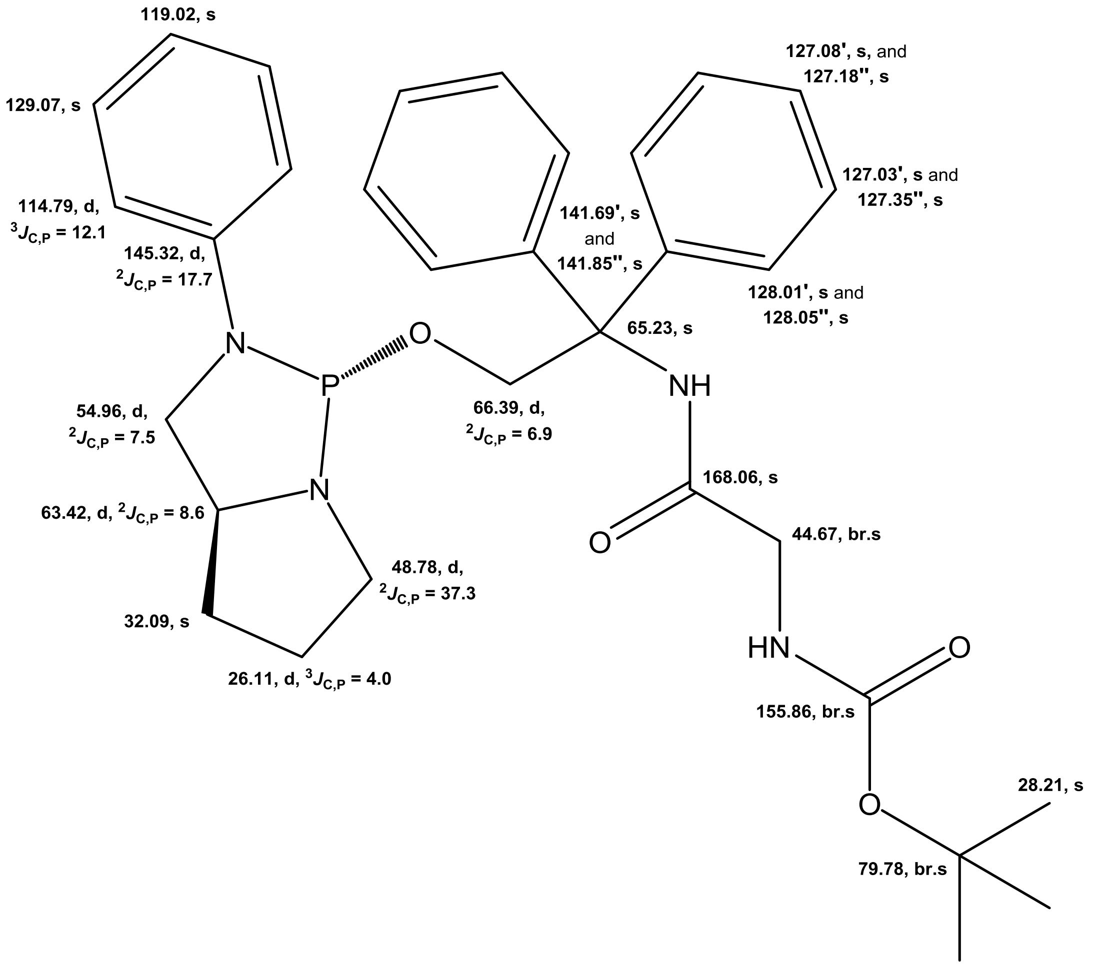


Figure S7b. ^{13}C NMR Signal Assignment for **L3b**.

(2*R*,5*S*)-2-[(*R*)-2-(2-((*tert*-butoxycarbonyl)amino)acetamido)butoxy]-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (**L3c**): White solid, yield 0.883 g (98 %). ^{1}H NMR (499.9 MHz, $CDCl_3$, ambient temperature): δ = 0.76 (t, ^3J(H,H) = 7.5 Hz, 3H; C$\underline{H}_3$CH$_2$), 1.42-1.53 (m, 2H; CH$_3$C$\underline{H}_2$), 1.46 (s, 9H; $(CH_3)_3C$), 1.59-1.66 (m, 1H; C$\underline{H}_2$), 1.71-1.80 (m, 1H; NCH$_2$C$\underline{H}_2$), 1.82-1.89 (m, 1H; NCH$_2$C$\underline{H}_2$), 2.01-2.08 (m, 1H; C$\underline{H}_2$), 3.14-3.19 (m, 1H; NC$\underline{H}_2$CH$_2$), 3.15-3.20 (m, 1H; NC$\underline{H}_2$CH), 3.54-3.59 (m, 1H; POCH$_2$), 3.65-3.79 (br.m, 2H; C$\underline{H}_2$NHBoc), 3.69-3.73 (m, 1H; POCH$_2$), 3.53-3.60 (m, 1H; NC$\underline{H}_2$CH$_2$), 3.84-3.90 (m, 1H; C$\underline{H}$NH), 3.78 (dd, ^2J(H,H) = 8.4 Hz, ^3J(H,H) = 7,8 Hz, 1H; NC$\underline{H}_2$CH), 4.09-4.14 (m, 1H; NCH$_2$C$\underline{H}$), 5.10 (br.s, 1H; CH$_2$N$\underline{H}$Boc), 6.19 (br.d, ^3J(H,H) = 7.6 Hz, 1H; CHN$\underline{H}$), 6.84 (t, ^3J(H,H) = 7.3 Hz, 1H; CH$_{para}$), 7.01 (d, ^3J(H,H) = 7.6 Hz, 2H; CH$_{ortho}$), 7.24 (t, ^3J(H,H) = 8.0 Hz, 2H; CH$_{meta}$) ppm. ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, ambient temperature): δ = 10.22 (s; $\underline{C}$H$_3$CH$_2$), 24.51 (s; CH$_3\underline{C}$H$_2$), 26.15 (d, ^3J(C,P) = 3.8 Hz; NCH$_2\underline{C}$H$_2$), 28.30 (s; ($\underline{C}$H$_3$)$_3$C), 32.17 (s; $\underline{C}$H$_2$), 44.38 (br.s; $\underline{C}$H$_2$NHBoc), 48.73 (d, ^2J(C,P) = 38.2 Hz; N$\underline{C}$H$_2$CH$_2$), 50.94 (d, ^3J(C,P) = 2.9 Hz; CHNH), 54.95 (d, ^2J(C,P) = 6.7 Hz; N$\underline{C}$H$_2$CH), 62.95 (d, ^2J(C,P) = 4.8 Hz; POCH$_2$), 63.30 (d, ^2J(C,P) = 8.6 Hz; NCH$_2\underline{C}$H), 79.94 (s; (CH$_3$)$_3\underline{C}$), 114.80 (d, ^3J(C,P) = 12.4 Hz; CH$_{ortho}$), 119.07 (s; CH$_{para}$), 129.08 (s;

CH_{meta}), 145.48 (d, ^2J(C,P) = 16.2 Hz; CNP), 155.77 (br.s; C(O)O), 168.64 (s; CO) ppm. $^{31}P\{^1H\}$ NMR (202.4 MHz, $CDCl_3$, ambient temperature): δ = 122.95 (s) ppm. $C_{22}H_{35}N_4O_4P$ (450.52): calcd. C 58.65, H 7.83, N 12.44; found C 58.86, H 7.80, N 12.38.

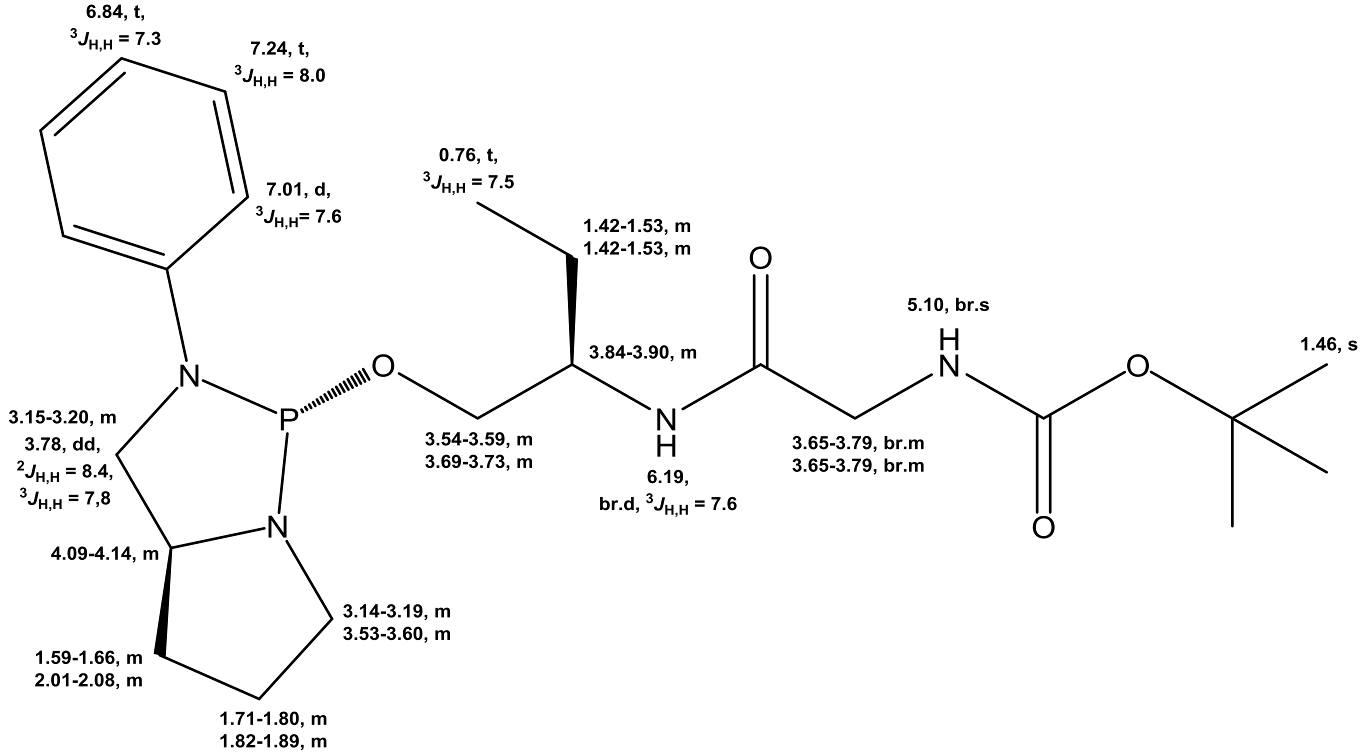


Figure S8a. ^{1}H NMR Signal Assignment for **L3c**.

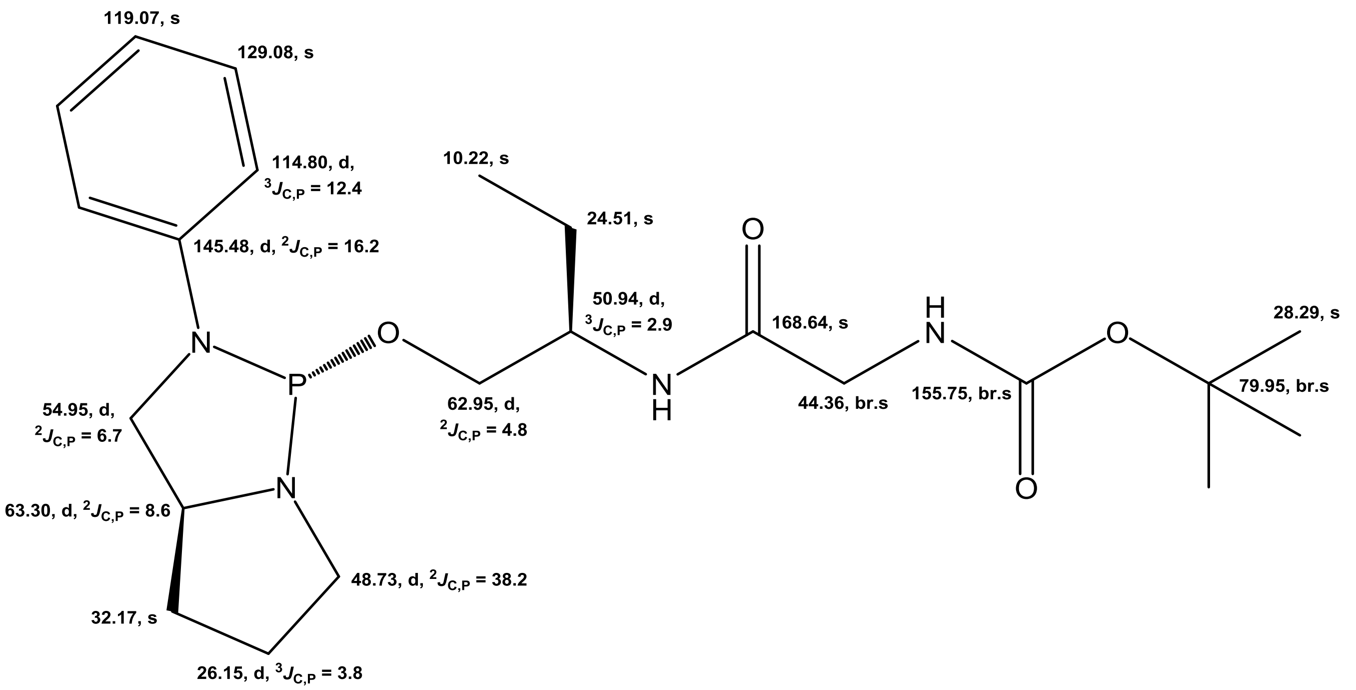


Figure S8b. ^{13}C NMR Signal Assignment for **L3c**.

EXPERIMENTAL SECTION

(2*R*,5*S*)-2-[(2*S*,3*S*)-2-((2*S*,3*S*)-2-((*tert*-butoxycarbonyl)amino)-3-methylpentanamido)-3-methylpentyloxy]-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (**L3e**): White solid, yield 1.037 g (97 %). ^{1}H NMR (499.9 MHz, $CDCl_3$, ambient temperature): δ = 0.72 (d, ^3J(H,H) = 6.9 Hz, 3H; $C\underline{H}_3CH$), 0.83 (t, ^3J(H,H) = 7.5 Hz, 3H; $C\underline{H}_3CH_2$), 0.84' (t, ^3J(H,H) = 7.5 Hz, 3H; $C\underline{H}_3CH_2$), 0.89' (d, ^3J(H,H) = 6.9 Hz, 3H; $C\underline{H}_3CH$), 1.01-1.10 (m, 1H; $CH_3C\underline{H}_2$), 1.01-1.10' (m, 1H; $CH_3C\underline{H}_2$), 1.41-1.48 (m, 1H; $CH_3C\underline{H}_2$), 1.42-1.49' (m, 1H; $CH_3C\underline{H}_2$), 1.43 (s, 9H; $(CH_3)_3C$), 1.59-1.65 (m, 1H; $C\underline{H}_2$), 1.64-1.73' (m, 1H; $CH_3C\underline{H}$), 1.65-1.73 (m, 1H; $CH_3C\underline{H}$), 1.74-1.81 (m, 1H; $NCH_2C\underline{H}_2$), 1.82-1.89 (m, 1H; $NCH_2C\underline{H}_2$), 2.02-2.09 (m, 1H; $C\underline{H}_2$), 3.14-3.20 (m, 1H; $NC\underline{H}_2CH_2$), 3.16-3.21 (m, 1H; $NC\underline{H}_2CH$), 3.41-3.45 (m, 1H; $POCH_2$), 3.54-3.60 (m, 1H; $NC\underline{H}_2CH_2$), 3.70-3.73 (m, 1H; $C\underline{H}NHBoc$), 3.85-3.88 (m, 1H; $POCH_2$), 3.71-3.74 (m, 1H; $NC\underline{H}_2CH$), 3.80-3.85 (m, 1H $C\underline{H}NH$), 4.10-4.15 (m, 1H; $NCH_2C\underline{H}$), 5.04 (br.d, ^3J(H,H) ~ 7.5 Hz, 1H; $CH_2N\underline{H}Boc$), 6.03 (br.d, ^3J(H,H) ~ 7.51 Hz, 1H; $CHN\underline{H}$), 6.83 (t, ^3J(H,H) = 7.3 Hz, 1H; CH_{para}), 6.99 (d, ^3J(H,H) = 7.8 Hz, 2H; CH_{ortho}), 7.22 (t, ^3J(H,H) = 8.1Hz, 2H; CH_{meta}) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, ambient temperature): δ = 11.13 (s; $\underline{C}H_3CH_2$), 11.16' (s; $\underline{C}H_3CH_2$), 15.17 (s; $\underline{C}H_3CH$), 15.38' (s; $\underline{C}H_3CH$), 24.77' (s; $CH_3\underline{C}H_2$), 25.13 (s; $CH_3\underline{C}H_2$), 26.20 (d, ^3J(C,P) = 4.8 Hz; $NCH_2\underline{C}H_2$), 28.31 (s; $(\underline{C}H_3)_3C$), 32.26 (s; $\underline{C}H_2$), 35.30 (s; $CH_3\underline{C}H$), 36.95' (br.s; $CH_3\underline{C}H$), 48.59 (d, ^2J(C,P) = 38.1 Hz; $N\underline{C}H_2CH_2$), 53.36 (d; ^3J(C,P) = 3.8 Hz; CHNH), 54.86 (d, ^2J(C,P) = 7.6 Hz; $N\underline{C}H_2CH$), 59.53 (br.s; CHNHBoc), 61.93 (d, ^2J(C,P) = 4.8 Hz; $POCH_2$), 63.52 (d, ^2J(C,P) = 8.6 Hz; $NCH_2\underline{C}H$), 79.51 (br.s; $(CH_3)_3\underline{C}$), 114.76 (d, ^3J(C,P) = 12.4 Hz; CH_{ortho}), 119.10 (s; CH_{para}), 129.13 (s; CH_{meta}), 145.55 (d, ^2J(C,P) = 16.2 Hz; CNP), 155.67 (br.s; C(O)O), 171.08 (s; CO) ppm. $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 26 °C): δ = 122.47 (s) ppm. $C_{28}H_{47}N_4O_4P$ (534.68): calcd. C 62.90, H 8.86, N 10.48; found C 63.06, H 8.92, N 10.40.

EXPERIMENTAL SECTION

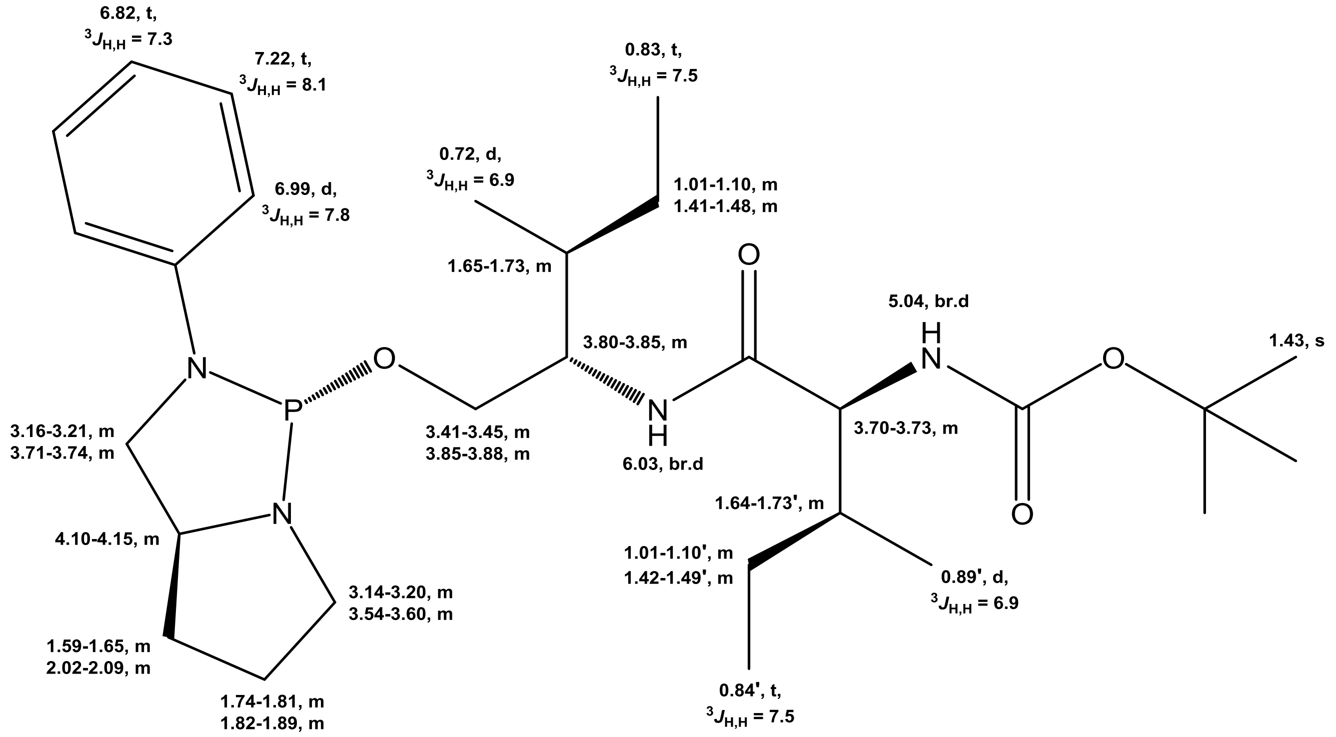


Figure S9a. ^{1}H NMR Signal Assignment for **L3e**.

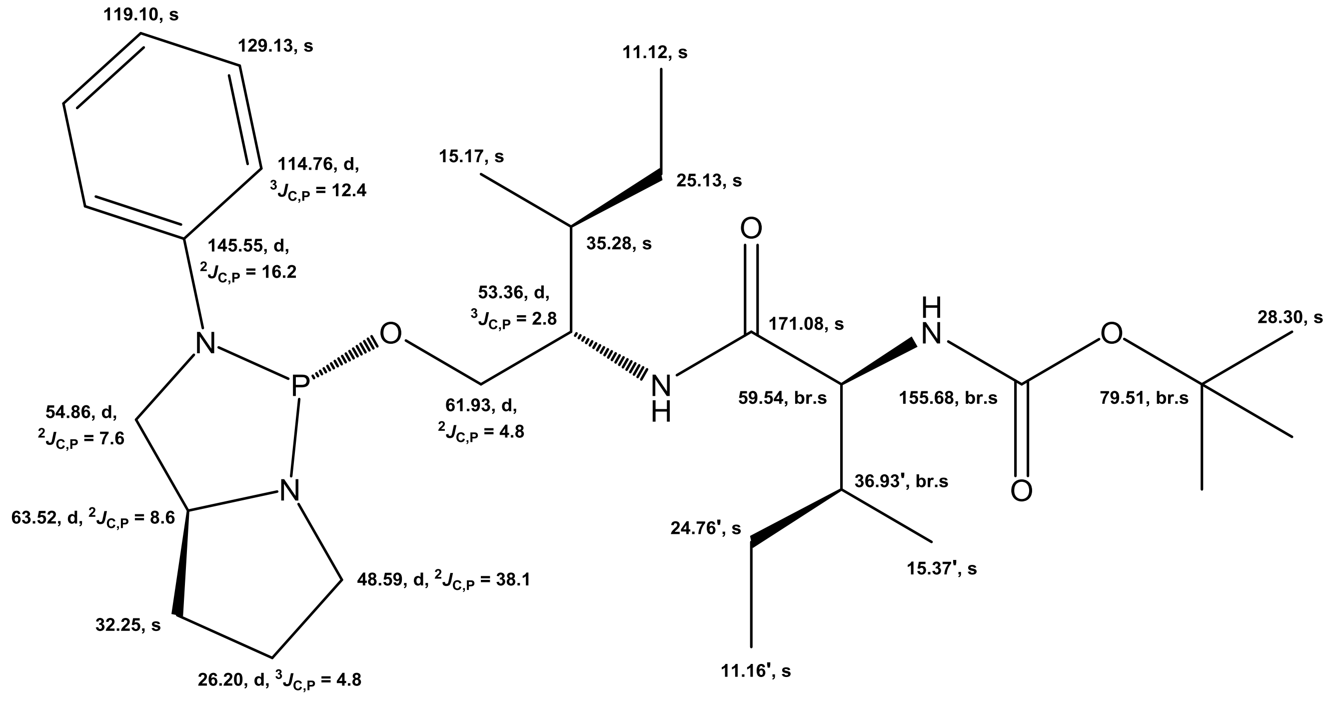


Figure S9b. ^{13}C NMR Signal Assignment for **L3e**.

(2*R*,5*S*)-2-[(*S*)-2-(2-((*tert*-butoxycarbonyl)amino)acetamido)-4-(methylthio)butoxy]-3-phenyl-1,3-diaza-2-phospha-bicyclo[3.3.0]octane (**L3f**): White solid, yield 0.705 g (71 %). ^{1}H NMR (499.9 MHz, $CDCl_3$, ambient temperature): δ = 1.47 (s, 9H; $(CH_3)_3C$), 1.59-1.65 (m, 1H; C$\underline{H}_2$), 1.75-1.82 (m, 1H; $NCH_2C\underline{H}_2$),

EXPERIMENTAL SECTION

1.82-1.87 (m, 2H; $SCH_2C\underline{H}_2$), 1.82-1.90 (m, 1H; $NCH_2C\underline{H}_2$), 2.03-2.10 (m, 1H; $C\underline{H}_2$), 2.08 (s, 3H; CH_3), 2.48 (t, ^3J(H,H) = 7.5 Hz, 2H; $SC\underline{H}_2CH_2$), 3.15-3.21 (m, 1H; $NC\underline{H}_2CH_2$), 3.17-3.22 (m, 1H; $NC\underline{H}_2CH$), 3.32-3.45 (br.m, 1H; $C\underline{H}_2NHBoc$), 3.50-3.54 (m, 1H; $C\underline{H}_2NHBoc$), 3.53-3.61 (m, 1H; $NC\underline{H}_2CH_2$), 3.53-3.61 (m, 1H; $POCH_2$), 3.72-3.76 (m, 1H; $POCH_2$), 3.79 (dd, ^2J(H,H) = 8.9 Hz, ^3J(H,H) = 7,4 Hz, 1H; $NC\underline{H}_2CH$), 4.07-4.16 (m, 1H; $C\underline{H}NH$), 4.10-4.17 (m, 1H; $NCH_2C\underline{H}$), 4.76 (br.s, 1H; $CH_2N\underline{H}Boc$), 6.08 (br.d, ^3J(H,H) = 8.6 Hz, 1H; $CHN\underline{H}$), 6.87 (t, ^3J(H,H) = 7.3 Hz, 1H; CH_{para}), 7.03 (d, ^3J(H,H) = 7.6 Hz, 2H; CH_{ortho}), 7.26-7.29 (m, 2H; CH_{meta}) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, ambient temperature): δ = 15.46 (s; CH_3), 26.26 (d, ^3J(C,P) = 3.9 Hz; $NCH_2\underline{C}H_2$), 28.35 (s; $(\underline{C}H_3)_3C$), 30.63 (s; $S\underline{C}H_2CH_2$), 31.00 (s; $SCH_2\underline{C}H_2$), 32.44 (s; $\underline{C}H_2$), 44.26 (br.s; $\underline{C}H_2NHBoc$), 48.69 (d, ^2J(C,P) = 38.0 Hz; $N\underline{C}H_2CH_2$), 48.82 (s; CHNH), 54.95 (d, ^2J(C,P) = 7.4 Hz; $N\underline{C}H_2CH$), 63.38 (d, ^2J(C,P) = 5.1 Hz; $POCH_2$), 63.53 (d, ^2J(C,P) = 8.8 Hz; $NCH_2\underline{C}H$), 80.09 (br.s; $(CH_3)_3\underline{C}$), 114.90 (d, ^3J(C,P) = 12.5 Hz; CH_{ortho}), 119.19 (s; CH_{para}), 129.32 (s; CH_{meta}), 145.59 (d, ^2J(C,P) = 15.6 Hz; CNP), 155.69 (br.s; C(O)O), 168.76 (s; CO) ppm. $^{31}P\{^1H\}$ NMR (202.4 MHz, $CDCl_3$, ambient temperature): δ = 122.26 (s) ppm. $C_{23}H_{37}N_4O_4PS$ (496.61): calcd. C 55.63, H7.51, N 11.28; found C 55.47, H 7.60, N 11.43.

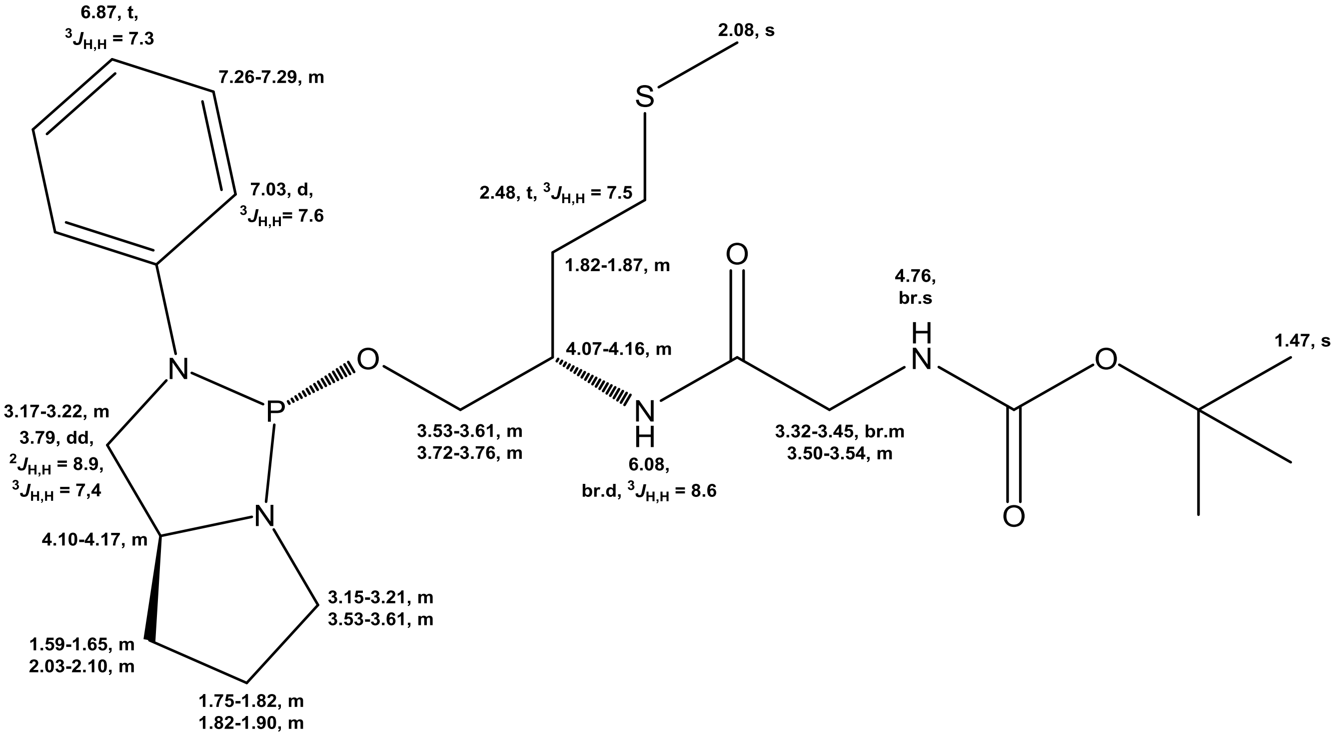


Figure S10a. ^{1}H NMR Signal Assignment for **L3f**.

EXPERIMENTAL SECTION

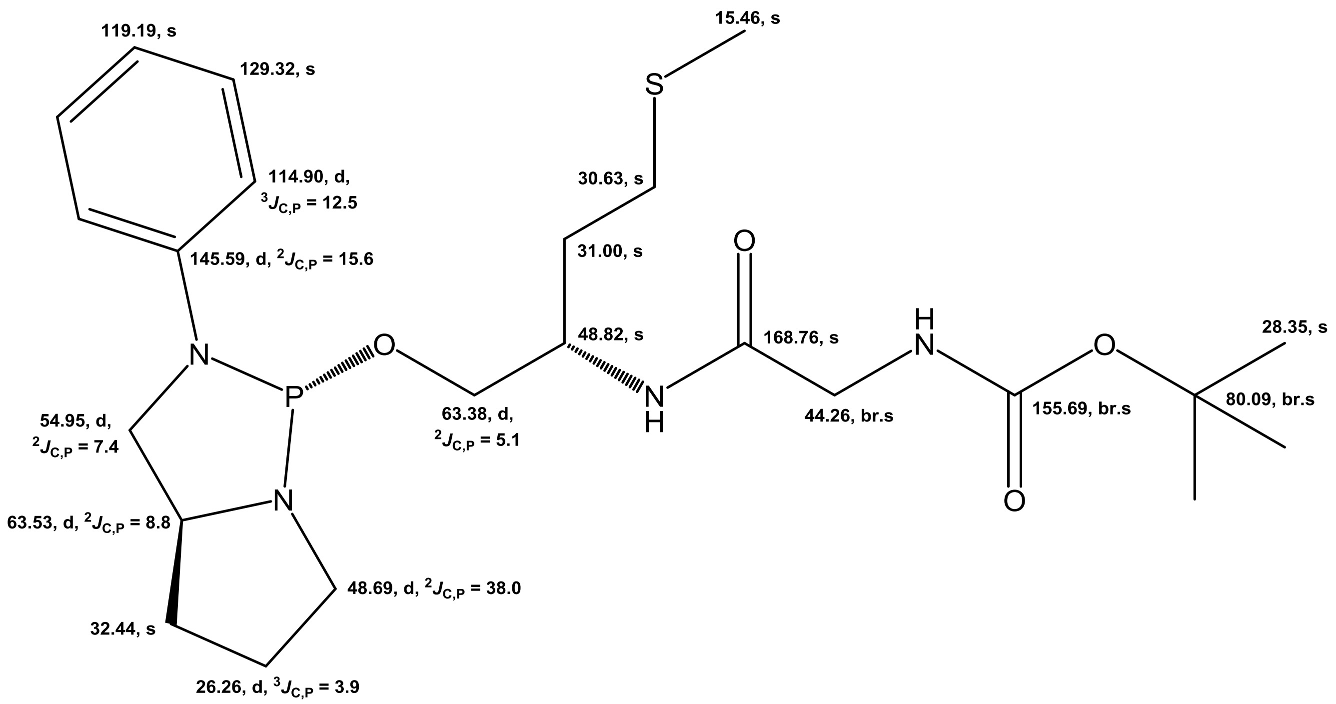


Figure S10b. ^{13}C NMR Signal Assignment for **L3f**.

(2*S*,5*R*)-2-[(2*S*,3*S*)-2-((2*S*,3*S*)-2-((*tert*-butoxycarbonyl)amino)-3-methylpentanamido)-3-methylpentyloxy]-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (**L3g**): White solid, yield 0.952 g (89 %). ^{1}H NMR (499.9 MHz, $CDCl_3$, ambient temperature): δ = 0.68 (d, ^3J(H,H) = 6.9Hz, 3H; $C\underline{H}_3CH$), 0.81 (t, ^3J(H,H) = 7.6 Hz, 3H; $C\underline{H}_3CH_2$), 0.93' (t, ^3J(H,H) = 7.3 Hz, 3H; $C\underline{H}_3CH_2$), 0.94' (d, ^3J(H,H) = 6.4 Hz, 3H; $C\underline{H}_3CH$), 0.99-1.08 (m, 1H; $CH_3C\underline{H}_2$), 1.13-1.21' (m, 1H; $CH_3C\underline{H}_2$), 1.40-1.49 (m, 1H; $CH_3C\underline{H}_2$), 1.44 (s, 9H; $(CH_3)_3C$), 1.51-1.60' (br.m, 1H; $CH_3C\underline{H}_2$), 1.55-1.66 (m, 1H; $C\underline{H}_2$), 1.56-1.66 (m, 1H; $CH_3C\underline{H}$), 1.71-1.81 (m, 1H; $NCH_2C\underline{H}_2$), 1.78-1.88 (m, 1H; $NCH_2C\underline{H}_2$), 1.80-1.89' (m, 1H; $CH_3C\underline{H}$), 1.98-2.05 (m, 1H; $C\underline{H}_2$), 3.09-3.16 (m, 1H; $NC\underline{H}_2CH_2$), 3.16-3.21 (m, 1H; $NC\underline{H}_2CH$), 3.52-3.59 (m, 1H; $NC\underline{H}_2CH_2$), 3.56-3.62 (m, 1H; $POCH_2$), 3.66-3.70 (m, 1H; $POCH_2$), 3.73-3.78 (m, 1H; $NC\underline{H}_2CH$), 3.75-3.81 (m, 1H; $C\underline{H}NH$), 3.87 (br.t, ^3J(H,H) ~ ^3J(H,H) = 7,8 Hz, 1H; $C\underline{H}NHBoc$), 4.06-4.11 (m, 1H; $NCH_2C\underline{H}$), 5.10 (br.d, ^3J(H,H) = 8.3 Hz, 1H; $CH_2N\underline{H}Boc$), 6.01 (br.d, ^3J(H,H) = 9.8 Hz, 1H; $CHN\underline{H}$), 6.84 (t, ^3J(H,H) = 7.3 Hz, 1H; CH_{para}), 7.01 (d, ^3J(H,H) = 7.8 Hz, 2H; CH_{ortho}), 7.23 (t, ^3J(H,H) = 7.8 Hz, 2H; CH_{meta}) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, ambient temperature): δ = 11.00 (s; $\underline{C}H_3CH_2$), 11.34' (s; $\underline{C}H_3CH_2$), 15.21 (s; $\underline{C}H_3CH$), 15.45' (s; $\underline{C}H_3CH$), 24.95' (s; $CH_3\underline{C}H_2$), 25.30 (s; $CH_3\underline{C}H_2$), 26.21 (d, ^3J(C,P) = 3.8Hz; $NCH_2\underline{C}H_2$), 28.32 (s; $(\underline{C}H_3)_3C$), 32.29 (s; $\underline{C}H_2$), 35.19 (s; $CH_3\underline{C}H$), 37.26' (s; $CH_3\underline{C}H$), 48.59 (d, ^2J(C,P) = 38.2 Hz; $N\underline{C}H_2CH_2$), 53.35 (d, ^3J(C,P) = 2.9 Hz; CHNH), 54.94 (d, ^2J(C,P) = 6.7 Hz; $N\underline{C}H_2CH$), 59.52 (br.s; CHNHBoc), 61.55 (d, ^2J(C,P) = 5.7 Hz; $POCH_2$), 63.56 (d, ^2J(C,P) = 8.6 Hz; $NCH_2\underline{C}H$), 79.59 (br.s; $(CH_3)_3\underline{C}$), 114.81 (d, ^3J(C,P) = 12.4 Hz; CH_{ortho}), 119.05 (s; CH_{para}), 129.04 (s; CH_{meta}), 145.56 (d,

EXPERIMENTAL SECTION

${}^{2}J$(C,P) = 15.3 Hz; CNP), 155.64 (br.s; C(O)O), 170.93 (s; CO) ppm. ${}^{31}P\{{}^{1}H\}$ NMR (202.4 MHz, $CDCl_3$, ambient temperature): δ = 121.46 (s) ppm. $C_{28}H_{47}N_4O_4P$ (534.68): calcd. C 62.90, H 8.86, N 10.48; found C 63.04, H 8.90, N 10.45.

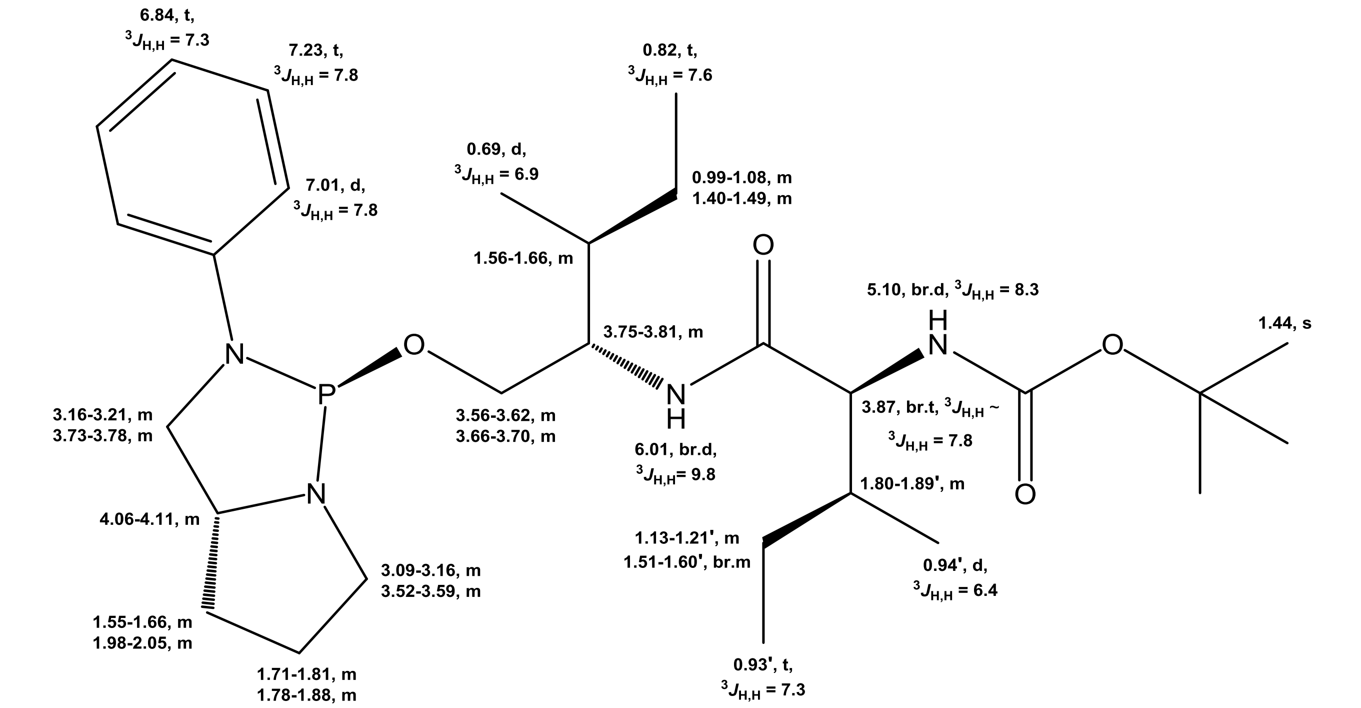


Figure S11a. ^{1}H NMR Signal Assignment for **L3g**.

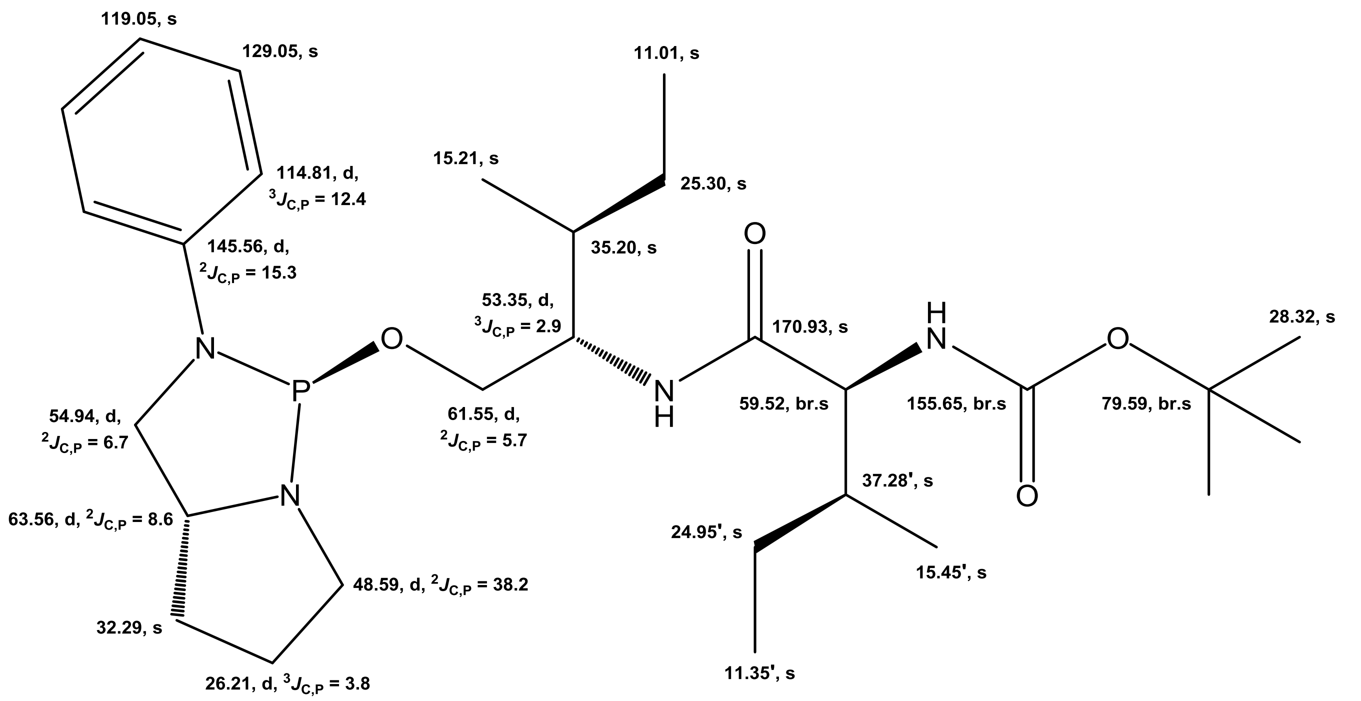
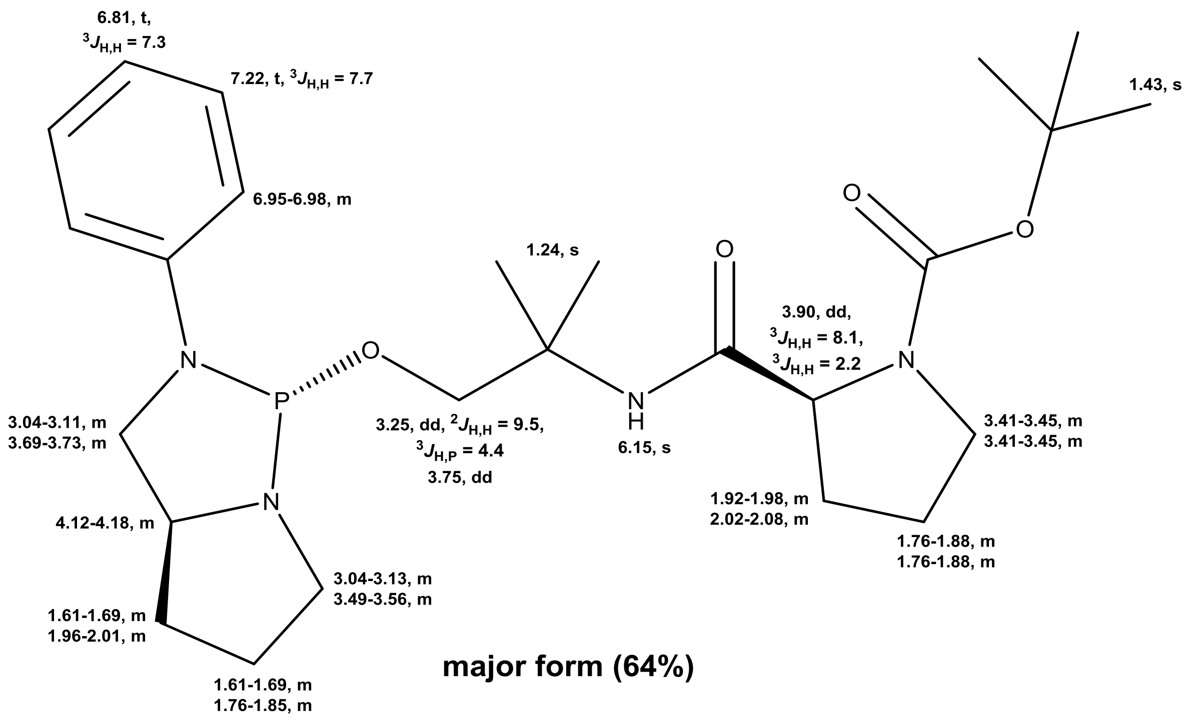


Figure S11b. ^{13}C NMR Signal Assignment for **L3g**.

EXPERIMENTAL SECTION

(2*R*,5*S*)-2-[2-((*S*)-1-(*tert*-butoxycarbonyl)pyrrolidine-2-carboxamido)-2-methylpropoxy]-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (**L4**): White solid, yield 0.932 g (95 %). ^{1}H NMR (600.1 MHz, $CDCl_3$, -20 °C): δ = 1.24 (s, 6H; $(CH_3)_2$), 1.43 (s, 9H; $(C\underline{H}_3)_3C$), 1.61-1.69 (m, 1H; $C\underline{H}_2$), 1.61-1.69 (m, 1H; $NCH_2C\underline{H}_2$), 1.76-1.85 (m, 1H; $NCH_2C\underline{H}_2$), 1.76-1.88 (m, 2H; $C\underline{H}_2CH_2NBoc$), 1.92-1.98 (m, 1H; $C\underline{H}_2CHNBoc$), 1.96-2.01 (m, 1H; $C\underline{H}_2$), 2.02-2.08 (m, 1H; $C\underline{H}_2CHNBoc$), 3.04-3.11 (m, 1H; $NC\underline{H}_2CH$), 3.04-3.13 (m, 1H; $NC\underline{H}_2CH_2$), 3.25 (dd, ^2J(H,H) = 9.5 Hz, ^3J(H,P) = 4.4 Hz, 1H; $POCH_2$), 3.41-3.45 (m, 2H; $CH_2C\underline{H}_2NBoc$), 3.49-3.56 (m, 1H; $NC\underline{H}_2CH_2$), 3.69-3.73 (m, 1H; $NC\underline{H}_2CH$), 3.75 (dd, 1H; $POCH_2$), 3.90 (dd, ^3J(H,H) = 8.1 Hz, ^3J(H,H) = 2.2 Hz, 1H; $CH_2C\underline{H}NBoc$), 4.12-4.18 (m, 1H; $NCH_2C\underline{H}$), 6.15 (s, 1H; NH), 6.81 (t, ^3J(H,H) = 7.3 Hz, 1H; CH_{para}), 6.95-6.98 (m, 2H; CH_{ortho}), 7.22 (t, ^3J(H,H) = 7.7 Hz, 2H; CH_{meta}) (major rotamer), 1.29 (s, 6H; $(CH_3)_2$), 1.45 (s, 9H; $(C\underline{H}_3)_3C$), 1.61-1.69 (m, 1H; $C\underline{H}_2$), 1.61-1.69 (m, 1H; $NCH_2C\underline{H}_2$), 1.71-1.75 (m, 1H; $C\underline{H}_2CHNBoc$), 1.76-1.85 (m, 1H; $NCH_2C\underline{H}_2$), 1.76-1.88 (m, 2H; $C\underline{H}_2CH_2NBoc$), 1.96-2.01, (m, 1H; $C\underline{H}_2$), 2.07-2.11 (m, 1H; $C\underline{H}_2CHNBoc$), 3.02-3.10 (m, 1H; $NC\underline{H}_2CH$), 3.04-3.13 (m, 1H; $NC\underline{H}_2CH_2$), 3.21-3.25 (m, 1H; $CH_2C\underline{H}_2NBoc$), 3.36-3.39 (m, 1H; $CH_2C\underline{H}_2NBoc$), 3.37-3.39 (m, 1H; $POCH_2$), 3.49-3.56 (m, 1H; $NC\underline{H}_2CH_2$), 3.69-3.73 (m, 1H; $NC\underline{H}_2CH$), 3.72-3.74 (m, 1H; $POCH_2$), 4.02 (d, ^3J(H,H) = 8.1 Hz, 1H; $CH_2C\underline{H}NBoc$), 4.12-4.18 (m, 1H; $NCH_2C\underline{H}$), 6.78-6.80 (m, 1H; CH_{para}), 6.90 (s, 1H; NH), 6.95-6.98 (m, 2H; CH_{ortho}), 7.19-7.21 (m, 2H; CH_{meta}) (minor rotamer) ppm. $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$, -20 °C): δ = 23.09 (s; CH_3), 23.34 (s; CH_3), 23.34 (s; $\underline{C}H_2CH_2NBoc$), 25.73 (d, ^3J(C,P) = 3.1 Hz; $NCH_2\underline{C}H_2$), 28.03 (s; $(\underline{C}H_3)_3C$), 30.85 (s; $\underline{C}H_2CHNBoc$), 31.45 (s; $\underline{C}H_2$), 46.60 (s; $CH_2\underline{C}H_2NBoc$), 48.77 (d, ^2J(C,P) = 38.7 Hz; $N\underline{C}H_2CH_2$), 53.02 (d, ^3J(C,P) = 2.0 Hz; C), 54.88 (d, ^2J(C,P) = 6.1 Hz; $N\underline{C}H_2CH$), 61.13 (s; $CH_2\underline{C}HNBoc$), 62.69 (d, ^2J(C,P) = 9.2 Hz; $NCH_2\underline{C}H$), 67.52 (d, ^2J(C,P) = 8.1 Hz; $POCH_2$), 79.99 (s; $(CH_3)_3\underline{C}$), 114.06 (d, ^3J(C,P) = 11.7 Hz; CH_{ortho}), 118.54 (s; CH_{para}), 128.88 (s; CH_{meta}), 145.04 (d, ^2J(C,P) = 16.8 Hz; CNP), 154,26 (s; C(O)O), 171.93 (s; CO) (major rotamer), 23.29 (s; CH_3), 23.54 (s; CH_3), 24.15 (s; $\underline{C}H_2CH_2NBoc$), 25.73 (d, ^3J(C,P) = 3.1 Hz; $NCH_2\underline{C}H_2$), 28.03 (s; $(\underline{C}H_3)_3C$), 27.86 (s; $\underline{C}H_2CHNBoc$), 31.34 (s; $\underline{C}H_2$), 46.63 (s; $CH_2\underline{C}H_2NBoc$), 48.79 (d, ^2J(C,P) = 39.2 Hz; $N\underline{C}H_2CH_2$), 53.06 (d, ^3J(C,P) = 2.5 Hz; C), 55.01 (d, ^2J(C,P) = 6.1 Hz; $N\underline{C}H_2CH$), 59.94 (s; $CH_2\underline{C}HNBoc$), 62.59 (d, ^2J(C,P) = 9.2 Hz; $NCH_2\underline{C}H$), 66.86 (d, ^2J(C,P) = 9.2 Hz; $POCH_2$), 79.72 (s; $(CH_3)_3\underline{C}$), 114.08 (d, ^3J(C,P) = 11.7 Hz; CH_{ortho}), 118.35 (s; CH_{para}), 128.76 (s; CH_{meta}), 145.20 (d, ^2J(C,P) = 16.8 Hz; CNP), 155.16 (s; C(O)O), 171.23 (s; CO) (minor rotamer) ppm. $^{31}P\{^1H\}$ NMR (242.9 MHz, $CDCl_3$, -20 °C): δ = 124.11 (s) (minor rotamer), 124.96 (s) (major rotamer) ppm. $C_{25}H_{39}N_4O_4P$ (490.58): calcd. C 61.21, H 8.01, N 11.42; found C 61.34, H 8.07, N 11.37.



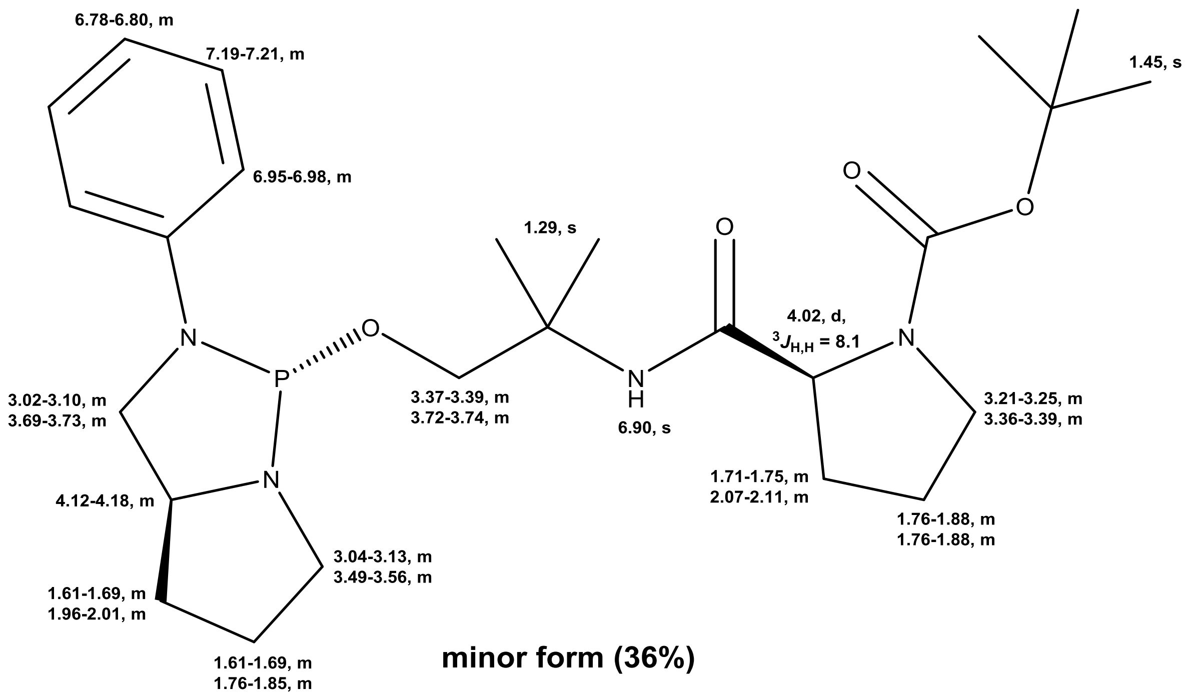
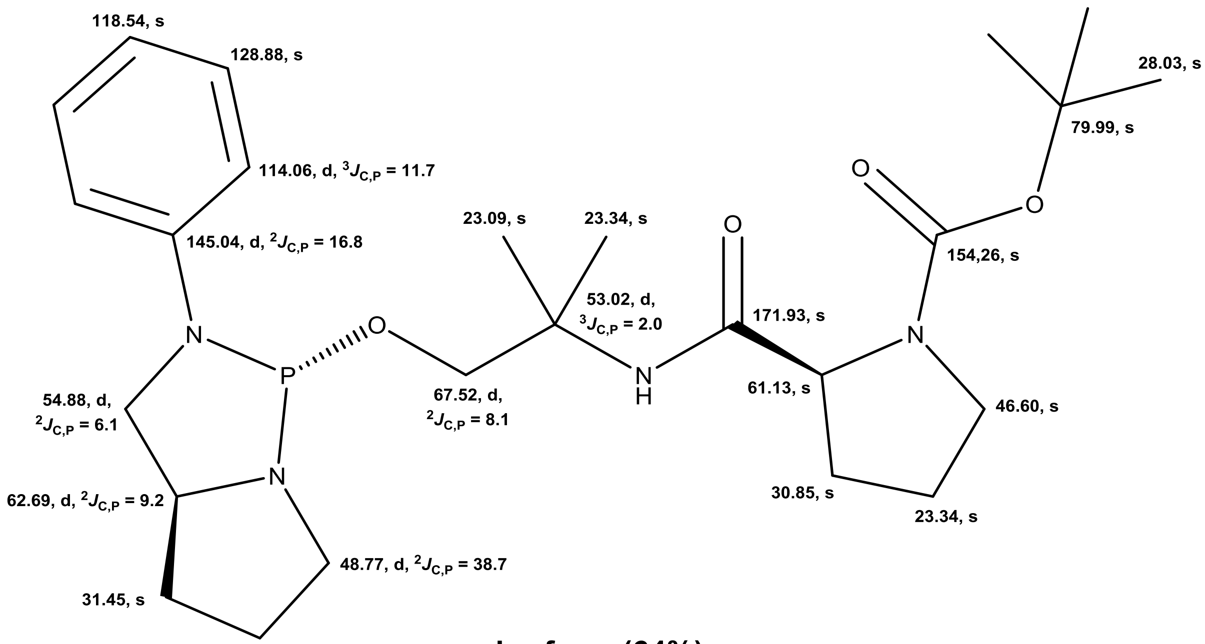
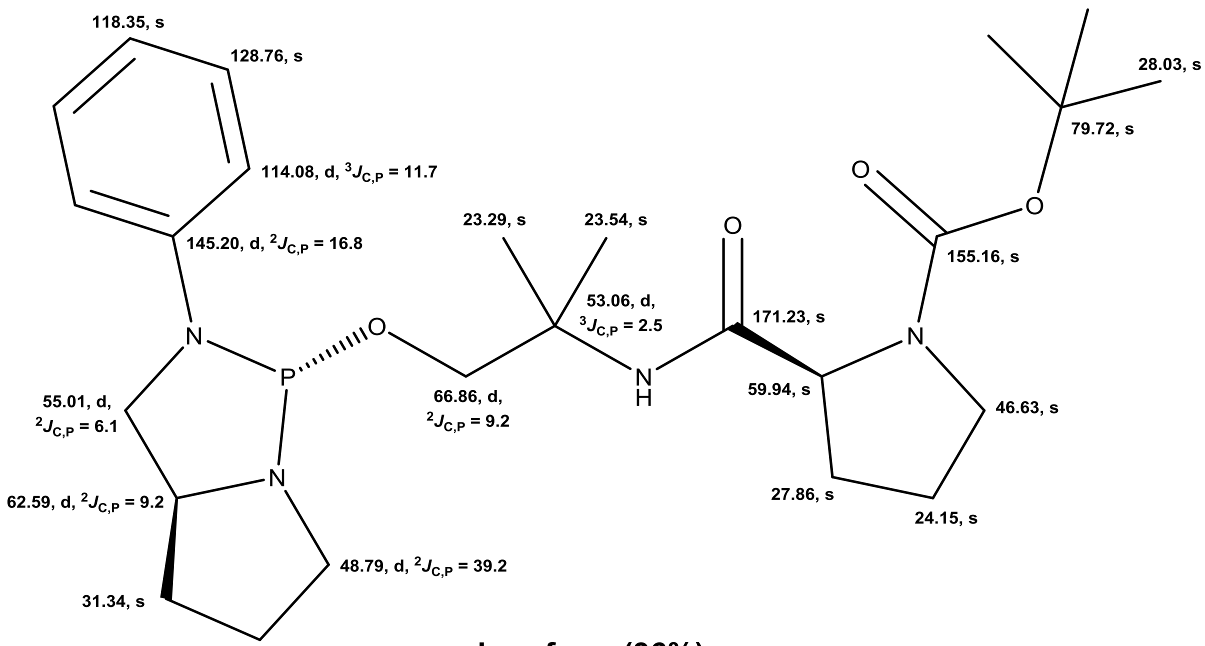


Figure S12a. ^{1}H NMR Signal Assignment for **L4**.

EXPERIMENTAL SECTION



major form (64%)



minor form (36%)

Figure S12b. ^{13}C NMR Signal Assignment for **L4**.

EXPERIMENTAL SECTION

2-[(*R*)-2-(2-((*tert*-butoxycarbonyl)amino)acetamido)butoxy]-1,3-diphenyl-1,3,2-diazaphospholidine (**L5**): White solid, yield 0.798 g (82 %). ^{1}H NMR (600.1 MHz, $CDCl_3$, 25 °C): δ = 0.74 (t, ^3J(H,H) = 7.3 Hz, 3H; C<u>H</u>$_3$CH$_2$), 1.36-1.46 (m, 1H; CH$_3$C<u>H</u>$_2$), 1.44-1.52 (m, 1H; CH$_3$C<u>H</u>$_2$), 1.46 (s, 9H; $(CH_3)_3C$), 3.28-3.38 (br.m, 2H; C<u>H</u>$_2$NHBoc), 3.48 (dd, ^2J(H,H) = 17.0 Hz, ^3J(H,H) = 6,0 Hz, 1H; C<u>H</u>$_2$NHBoc), 3.54-3.61 (m, 2H; POCH$_2$), 3.74-3.81 (m, 1H; C<u>H</u>NH), 3.74-3.81 (m, 2H; CH$_2$), 3.87-3.93 (m, 2H; CH$_2$), 4.66 (br.s, 1H; CH$_2$N<u>H</u>Boc), 5.81 (br.s, 1H; CHN<u>H</u>), 6.93-6.96 (m, 2H; CH_{para}), 7.16 (d, ^3J(H,H) = 7.4 Hz, 4H; CH_{ortho}), 7.30-7.35 (m, 4H; CH_{meta}) ppm. ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$, 25 °C): δ = 10.16 (s; <u>C</u>H$_3$CH$_2$), 23.87 (s; CH$_3$<u>C</u>H$_2$), 28.17 (s; (<u>C</u>H$_3$)$_3$C), 43.93 (br.s; <u>C</u>H$_2$NHBoc), 47.25 (d, ^2J(C,P) = 10.3 Hz; CH$_2$), 47.37 (d, ^2J(C,P) = 10.3 Hz; CH$_2$), 50.67 (d, ^3J(C,P) = 2.3 Hz; CHNH), 63.94 (s; POCH$_2$), 79.79 (br.s; (CH$_3$)$_3$<u>C</u>), 115.08 (d, ^3J(C,P) = 13.8 Hz; CH_{ortho}), 115.13 (d, ^3J(C,P) = 13.8 Hz; CH_{ortho}), 119.98 (s; CH_{para}), 120.09 (s; CH_{para}), 129.24 (s; CH_{meta}), 129.31 (s; CH_{meta}), 144.74 (d, ^2J(C,P) = 17.2 Hz; CNP), 144.89 (d, ^2J(C,P) = 18.4 Hz; CNP), 155.64 (br.s; C(O)O), 168.76 (s; CO) ppm. ^{31}P{^{1}H} NMR (202.4 MHz, $CDCl_3$, ambient temperature): δ = 102.78 (s) ppm. $C_{25}H_{35}N_4O_4P$ (486.55): calcd. C 61.71, H 7.25, N 11.52; found C 61.87, H 7.32, N 11.63.

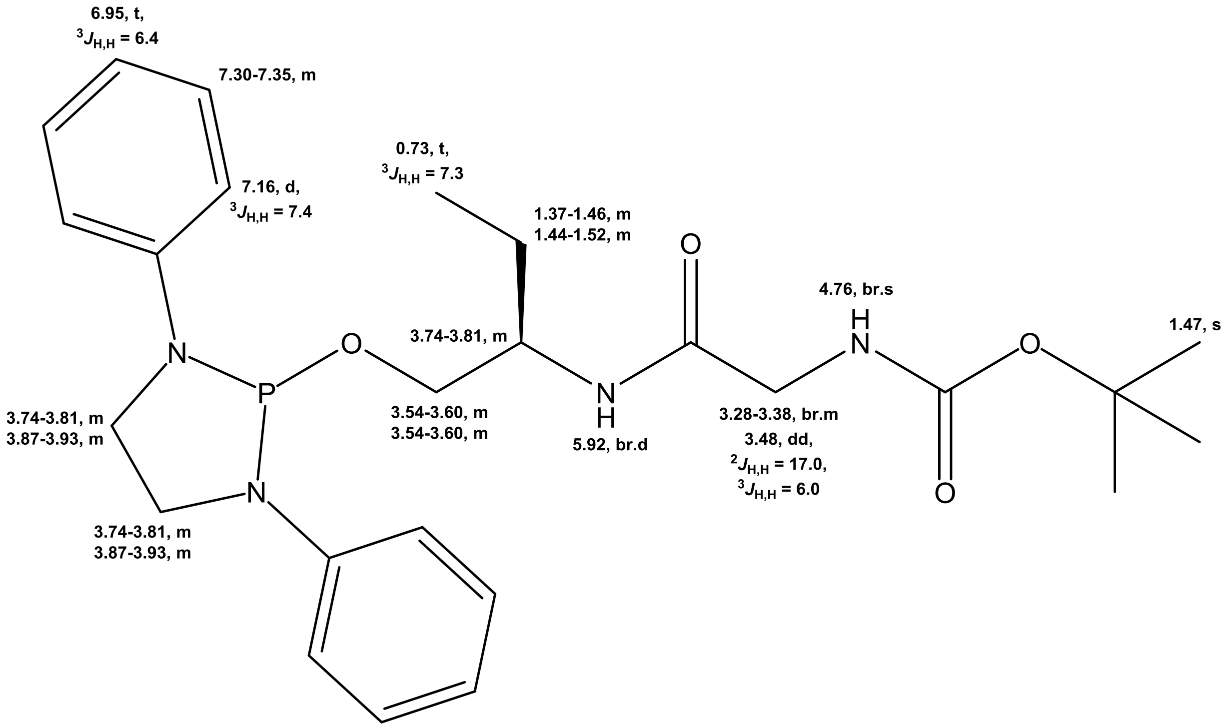


Figure S13a. ^{1}H NMR Signal Assignment for **L5**.

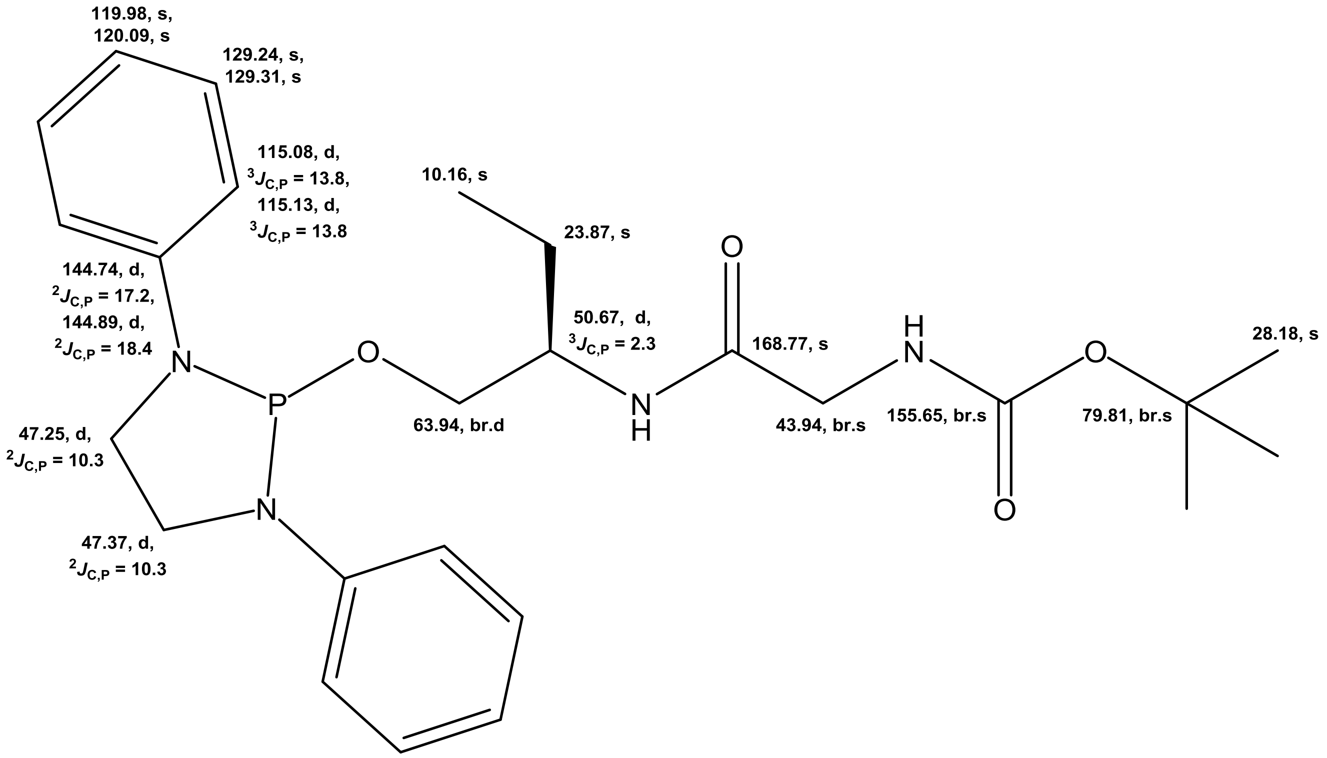


Figure S13b. ^{13}C NMR Signal Assignment for **L5**.

General Procedure for the Preparation of Cationic Palladium Complexes of the General Formula [Pd(allyl)(L)$_2$]BF$_4$: A solution of the relevant ligand **L1d**, **L3a-g**, **L4** (0.4 mmol) in CH_2Cl_2 (2 mL) was added dropwise over 30 min to a stirred solution of $[Pd(allyl)Cl]_2$ (0.037 g, 0.1 mmol) in CH_2Cl_2 (1 mL) at 20 °C. The reaction mixture was stirred for a further 1 h at 20 °C. A solution of $AgBF_4$ (0.039 g, 0.2 mmol) in THF (2 mL) was added dropwise over 30 min to the resulting solution, and the reaction mixture was stirred for 1.5 h at 20 °C. The precipitate of AgCl formed was separated by centrifugation. Solution was filtered through SiO_2, solvent was removed in vacuum (40 Torr) and the product was dried in air and in vacuum (1 Torr).

[Pd(allyl)(**L1d**)$_2$]BF$_4$: Gray solid, yield 0.218 g (98 %). ^{1}H NMR[a] (499.9 MHz, CD_2Cl_2, ambient temperature): δ = 1.41 and 1.42 (s, 18H; (C<u>H</u>$_3$)$_3$C), 1.60-1.71 (br.m, 2H; C<u>H</u>$_2$), 1.63-1.82 (br.m, 4H; SCH$_2$C<u>H</u>$_2$), 1.84-1.92 (m, 2H; NCH$_2$C<u>H</u>$_2$), 2.00-2.10 (m, 2H; NCH$_2$C<u>H</u>$_2$), 2.04 and 2.06 (s, 6H; CH$_3$), 2.11-2.19 (m, 2H; C<u>H</u>$_2$), 2.43-2.55 (m, 4H; SC<u>H</u>$_2$CH$_2$), 2.58-2.72 (br.m, 1H; CH$_{2allyl}$ (*anti*)), 2.75-2.87' (br.m, 1H; CH$_{2allyl}$ (*anti*)), 2.89-3.04 (br.m, 2H; NC<u>H</u>$_2$CH), 3.29-3.38 and 3.38-3.45 (br.m, 2H; NC<u>H</u>$_2$CH$_2$), 3.40-3.48 and 3.49-3.60 (br.m, 2H; NC<u>H</u>$_2$CH$_2$), 3.64-3.77 (br.m, 2H; POCH$_2$), 3.77-3.90 (br.m, 2H; NHC<u>H</u>), 3.77-3.91 (br.m, 2H; NC<u>H</u>$_2$CH), 3.87-4.00 (br.m, 2H; POCH$_2$), 4.00-4.08' (br.m, 1H; CH$_{2allyl}$ (*syn*)), 4.13-4.19 (br.m, 1H; CH$_{2allyl}$ (*syn*)), 4.19-4.30 (br.m, 2H; NCH$_2$C<u>H</u>), 5.03-5.18 (br.m, 2H; N<u>H</u>CH), 5.18-5.26 (m, 1H; CH$_{allyl}$), 6.89 and

6.93 (d, ^3J(H,H) = 7.9 and 7.8 Hz, 4H; CH_{ortho}), 6.99-7.03 (m, 2H; CH_{para}), 7.27-7.31 (m, 4H; CH_{meta}) ppm. $^{13}C\{^1H\}$ NMR[a] (125.7 MHz, CD_2Cl_2, ambient temperature): δ = 16.05 (s; $\underline{C}H_3$), 27.68-27.76 (m; $NCH_2\underline{C}H_2$), 28.88 (s; $(\underline{C}H_3)_3C$), 31.08 (s; $S\underline{C}H_2CH_2$), 31.85 and 31.99 (br.s; $\underline{C}H_2$), 32.48 and 32.56 (br.s; $SCH_2\underline{C}H_2$), 49.43 and 49.71 (vt, J(C,P) = 10.9 and 11.8 Hz; $N\underline{C}H_2CH_2$), 50.97 (br.s; $NH\underline{C}H$), 54.86 and 55.02 (s; $N\underline{C}H_2CH$), 63.07 and 63.22 (s; $NCH_2\underline{C}H$), 66.81-67.00 (br.m; $POCH_2$), 70.95-71.23' (br.m; CH_{2allyl}), 71.09-71.41 (br.m; CH_{2allyl}), 80.12 (br.s; $(CH_3)_3\underline{C}$), 115.99 and 116.12 (s; CH_{ortho}), 122.11 and 122.20 (s; CH_{para}), 124.16 (t, ^2J(C,P) = 8.5 Hz; CH_{allyl}), 130.36 (s; CH_{meta}), 143.28-143.45 (br.m; CNP), 156.23 (s; C(O)O) ppm. $^{31}P\{^1H\}$ NMR (202.4 MHz, CD_2Cl_2, ambient temperature): δ = 117.20 (br.s) ppm. $C_{45}H_{73}BF_4N_6O_6P_2PdS_2$ (1113.41): calcd. C 48.54, H 6.61, N 7.55; found C 48.78, H 6.69, N 7.71.

[a] The nonequivalent signals of two *P*-ligands are listed in order of increasing chemical shifts using the conjunction "and".

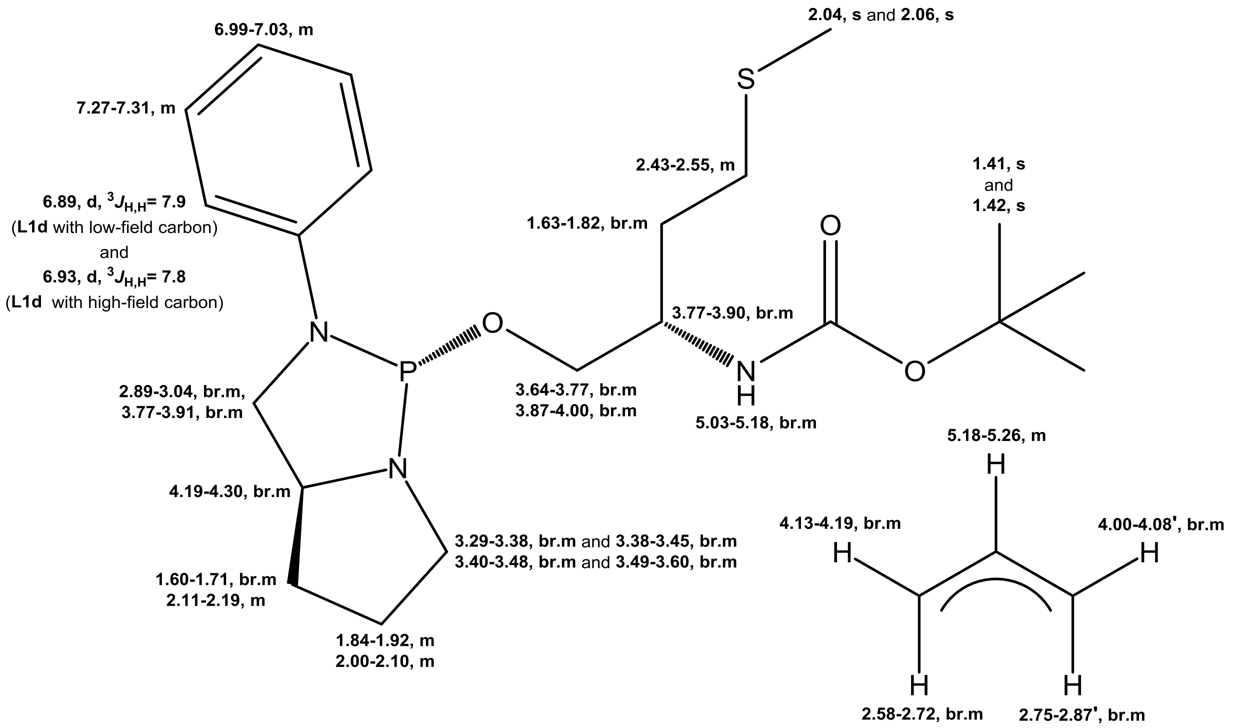


Figure S14a. ^{1}H NMR Signal Assignment for [Pd(allyl)(**L1d**)$_2$]BF_4.

EXPERIMENTAL SECTION

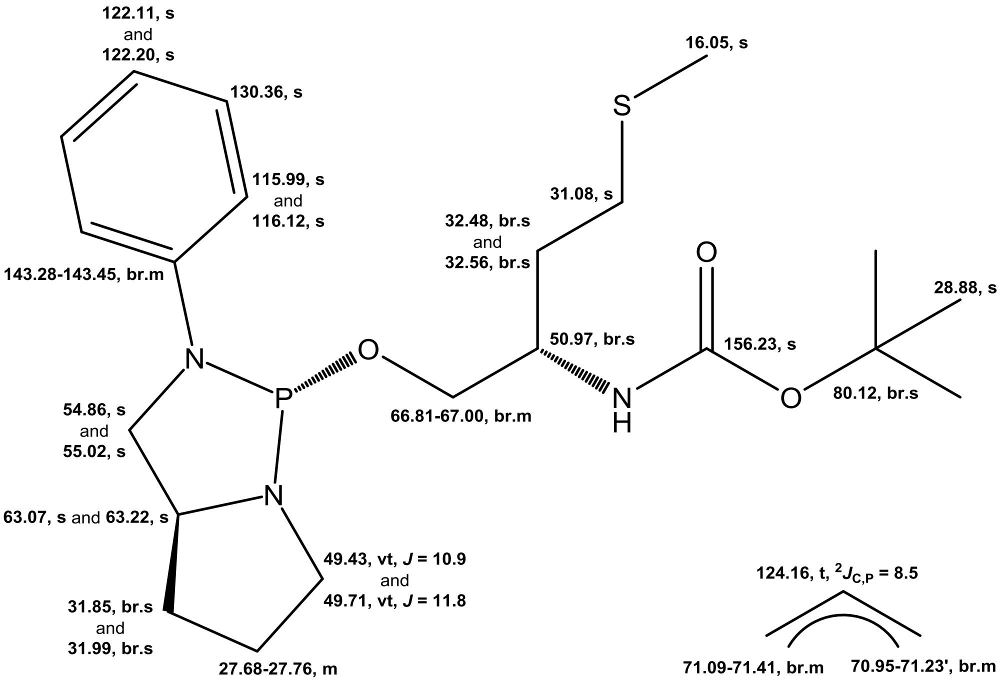


Figure S14b. ^{13}C NMR Signal Assignment for [Pd(allyl)(**L1d**)$_2$]BF_4.

[Pd(allyl)(**L3a**)$_2$]BF_4: White solid, yield 0.209 g (92 %). ^1H NMR[a] (499.9 MHz, CD_2Cl_2, ambient temperature): δ = 1.24 and 1.26 (s; 6H; CH_3), 1.27 and 1.28 (s; 6H; CH_3), 1.32-1.39 (br.m, 2H; $C\underline{H}_2$), 1.43 (s, 18H; $(CH_3)_3C$), 1.87-1.98 (m, 2H; $NCH_2C\underline{H}_2$), 1.99-2.07 (m, 2H; $NCH_2C\underline{H}_2$), 2.01-2.09 (m, 2H; $C\underline{H}_2$), 2.31-2.46 (br.m, 2H; $NC\underline{H}_2CH$), 2.98-3.07 (br.m, 1H; CH_{2allyl} (*anti*)), 3.06-3.16' (br.m, 1H; CH_{2allyl} (*anti*)), 3.28-3.36 (br.m, 2H; $NC\underline{H}_2CH_2$), 3.49-3.58 (br.m, 4H; $C\underline{H}_2NHBoc$), 3.37-3.44 and 3.42-3.48 (br.m, 2H; $NC\underline{H}_2CH_2$), 3.58-3.67 (br.m, 2H; $NC\underline{H}_2CH$), 3.71-3.78 (m, 2H; $POCH_2$), 4.02-4.11 (br.m, 2H; $POCH_2$), 4.12-4.22 (br.m, 2H; $NCH_2C\underline{H}$), 4.41-4.54 (br.m, 1H; CH_{2allyl} (*syn*)), 4.41-4.54' (br.m, 1H; CH_{2allyl} (*syn*)), 5.14 (br.s, 2H; $CH_2N\underline{H}Boc$), 5.38-5.49 (m, 1H; CH_{allyl}), 6.16 and 6.18 (br.s, 2H; CNH), 6.84 and 6.85 (d, ^3J(H,H) = 6.8 and 7.3 Hz, 4H; CH_{ortho}), 6.97 and 6.99 (t, ^3J(H,H) = 7.8 and 7.3 Hz, 2H; CH_{para}), 7.28 and 7.30 (t, ^3J(H,H) = 7.8 and 7.8 Hz, 4H; CH_{meta}) ppm. $^{13}C\{^1H\}$ NMR[a] (125.7 MHz, CD_2Cl_2, ambient temperature): δ = 24.73 (s; CH_3), 24.94 (s; CH_3), 27.99 and 28.10 (br.s; $NCH_2\underline{C}H_2$), 28.73 (s; $(\underline{C}H_3)_3C$), 31.67 and 31.73 (s; $\underline{C}H_2$), 45.32 (br.s; $\underline{C}H_2NHBoc$), 48.66-48.88 and 48.88-49.08 (br.m; $N\underline{C}H_2CH_2$), 54.14 (s; CNH), 54.50 (br.s; $N\underline{C}H_2CH$), 63.00 and 63.22 (s; $NCH_2\underline{C}H$), 69.54-69.63 and 69.63-69.72 (br.m; $POCH_2$), 72.44-72.69 (br.m; CH_{2allyl}), 72.62-72.92' (br.m; CH_{2allyl}), 80.22 (s; $(CH_3)_3\underline{C}$), 115.88 (s; CH_{ortho}), 121.66 (s; CH_{para}), 123.80 (br.s; CH_{allyl}), 130.23 (s; CH_{meta}), 143.38 (br.s; CNP), 156.55 (br.s; C(O)O), 169.72 (s; CO) ppm. $^{31}P\{^1H\}$ NMR (242.9 MHz, CD_2Cl_2, 19 °C): δ = 113.51 (br.s) ppm. $C_{47}H_{75}BF_4N_8O_8P_2Pd$ (1135.34): calcd. C 49.72, H 6.66, N 9.87; found C 49.98, H 6.76, N 9.61.

[a] The nonequivalent signals of two *P*-ligands are listed in order of increasing chemical shifts using the conjunction "and".

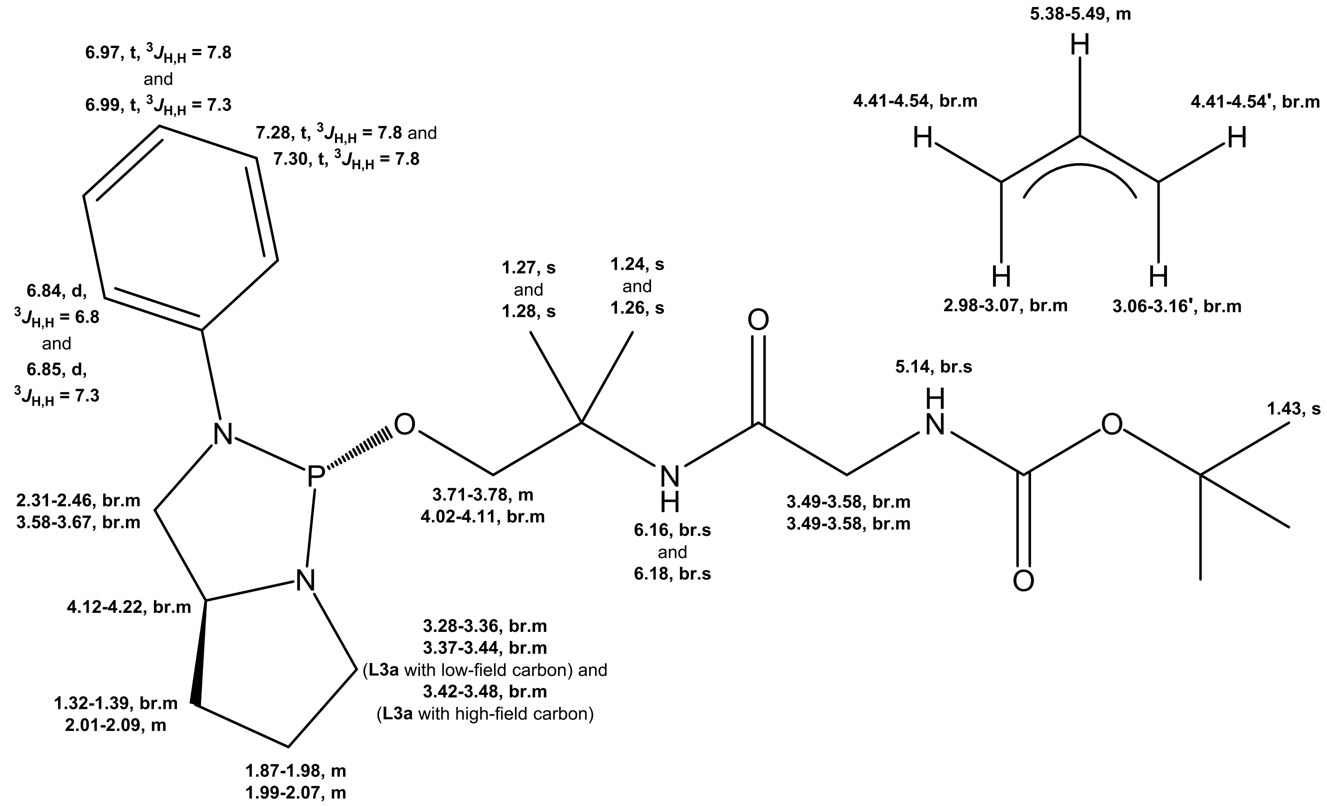


Figure S15a. ^{1}H NMR Signal Assignment for [Pd(allyl)(**L3a**)$_2$]BF_4.

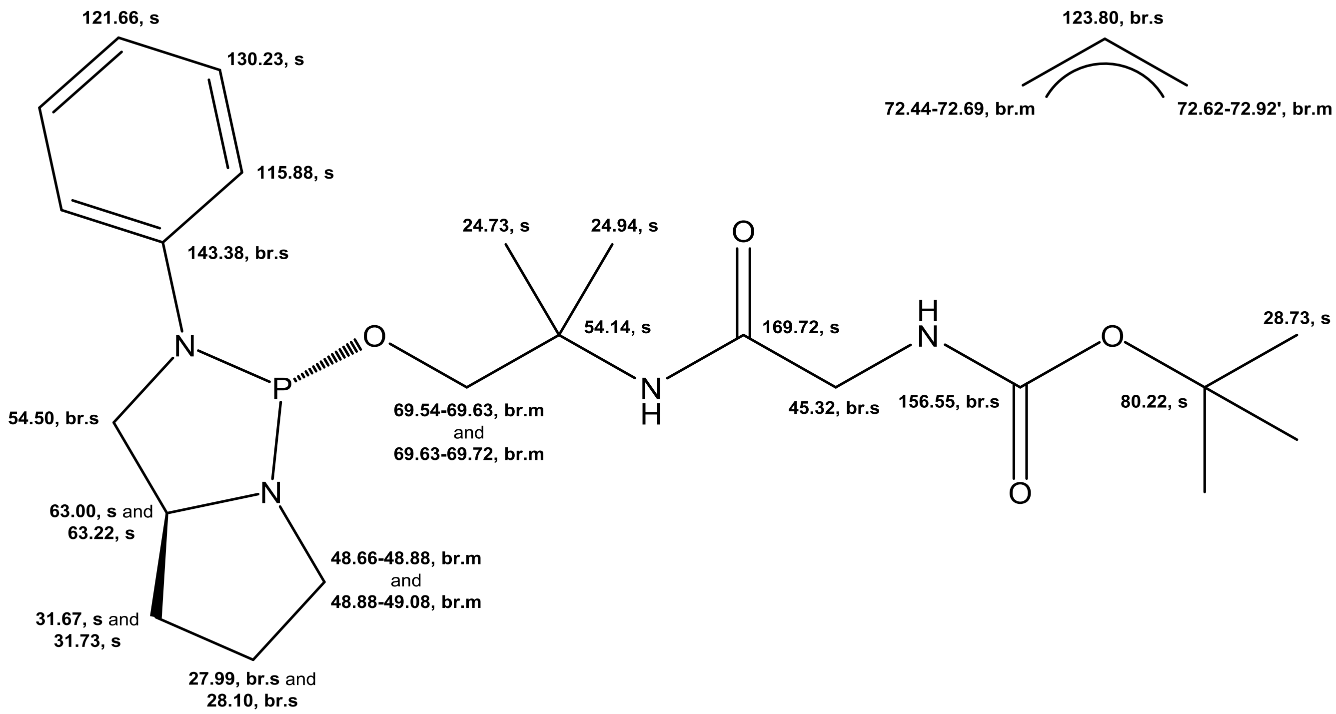


Figure S15b. ^{13}C NMR Signal Assignment for [Pd(allyl)(**L3a**)$_2$]BF_4.

EXPERIMENTAL SECTION

[Pd(allyl)(**L3b**)$_2$]BF$_4$: White solid, yield 0.219 g (79 %). ^{1}H NMR[a] (499.9 MHz, CD_2Cl_2, ambient temperature): δ = 0.95-1.01 and 1.02-1.08 (m, 2H; $C\underline{H}_2$), 1.40-1.48 (br.m, 2H; $NCH_2C\underline{H}_2$), 1.44 (s, 18H; $(CH_3)_3C$), 1.55-1.63 and 1.62-1.70 (br.m, 2H; $NC\underline{H}_2CH$), 1.87-1.99 (br.m, 2H; $C\underline{H}_2$), 2.00-2.11 (br.m, 2H; $NCH_2C\underline{H}_2$), 2.77-2.87 (br.m, 1H; CH_{2allyl} (*anti*)), 2.94-3.03 and 3.09-3.16 (br.m, 2H; $NC\underline{H}_2CH_2$), 2.95-3.06 and 3.25-3.35 (br.m, 2H; $NC\underline{H}_2CH_2$), 3.25-3.36' (br.m, 1H; CH_{2allyl} (*anti*)), 3.33-3.42 (br.m, 2H; $NC\underline{H}_2CH$), 3.59 (br.dd, ^2J(H,H) ~ 5.1 Hz, ^3J(H,H) ~ 3.9 Hz, 2H; $C\underline{H}_2NHBoc$), 3.64 (br.m, 2H; $C\underline{H}_2NHBoc$), 3.97-4.05 (m, 2H; $NCH_2C\underline{H}$), 4.19-4.24' (br.m, 1H; CH_{2allyl} (*syn*)), 4.20-4.27 and 4.26-4.34 (br.m, 2H; $POCH_2$), 4.32-4.41 (br.m, 1H; CH_{2allyl} (*syn*)), 4.83-4.92 (br.m, 2H; $POCH_2$), 5.29-5.44 (br.m, 1H; CH_{allyl}), 5.50 (br.s, 2H; $CH_2N\underline{H}Boc$), 6.49 and 6.65 (d, ^3J(H,H) = 8.1 and 8.1 Hz, 4H; CH_{ortho}), 6.93 and 6.97 (t, ^3J(H,H) = 7.3 and 7.5 Hz, 2H; CH_{para}), 7.14-7.23' (m, 8H; CH_{para}), 7.16-7.22 and 7.22-7.28 (m, 4H; CH_{meta}), 7.20 (br.s, 2H; CNH), 7.21-7.32' (m, 8H; CH_{meta}), 7.23-7.35' (m, 8H; CH_{para}) ppm. ^{13}C{^{1}H} NMR[a] (125.7 MHz, CD_2Cl_2, ambient temperature): δ = 28.33 and 28.38 (br.s; $NCH_2\underline{C}H_2$), 28.68 (s; $(\underline{C}H_3)_3C$), 31.31 (s; $\underline{C}H_2$), 45.94 (br.s; $\underline{C}H_2NHBoc$), 47.27-47-56 (br.m; $N\underline{C}H_2CH_2$), 53.79 (br.s; $N\underline{C}H_2CH$), 63.23 and 63.52 (br.s; $NCH_2\underline{C}H$), 65.13 (br.s; CNH), 68.35 and 68.35, (s and br.s; $POCH_2$), 74.01 (br.d, $^2J(C,P_{trans})$ ~ 35.3 Hz; CH_{2allyl}), 75.48' (br.d, $^2J(C,P_{trans})$ ~ 39.1 Hz; CH_{2allyl}), 80.41 and 80.54 (br.s; $(CH_3)_3\underline{C}$), 115.50-115.57 and 115.63-115.71 (br.m; CH_{ortho}), 121.31 and 121.40 (s; CH_{para}), 127.37-127.53' (m; CH_{para}), 127.94-128.10' (m; CH_{meta}), 128.82-128.92' (m; CH_{ortho}), 130.21 and 130.29 (s; CH_{meta}), 123.16 (br.s; CH_{allyl}), 142.50-142.77' (br.m; C_{ipso}), 142.79-142.94 and 143.00-143.12 (br.m; CNP), 155.96 (br.s; C(O)O), 169.75 and 169.87 (s; CO) ppm. ^{31}P{^{1}H} NMR[a] (202.4 MHz, CD_2Cl_2, ambient temperature): δ = 113.34 (br.d, ^2J(P,P) = 82.4 Hz) and 112.85 (br.d, ^2J(P,P) = 82.4 Hz) ppm. $C_{67}H_{83}BF_4N_8O_8P_2Pd$ (1383.62): calcd. C 58.16, H 6.05, N 8.10; found C 58.45, H 6.12, N 7.85.

[a] The nonequivalent signals of two *P*-ligands are listed in order of increasing chemical shifts using the conjunction "and".

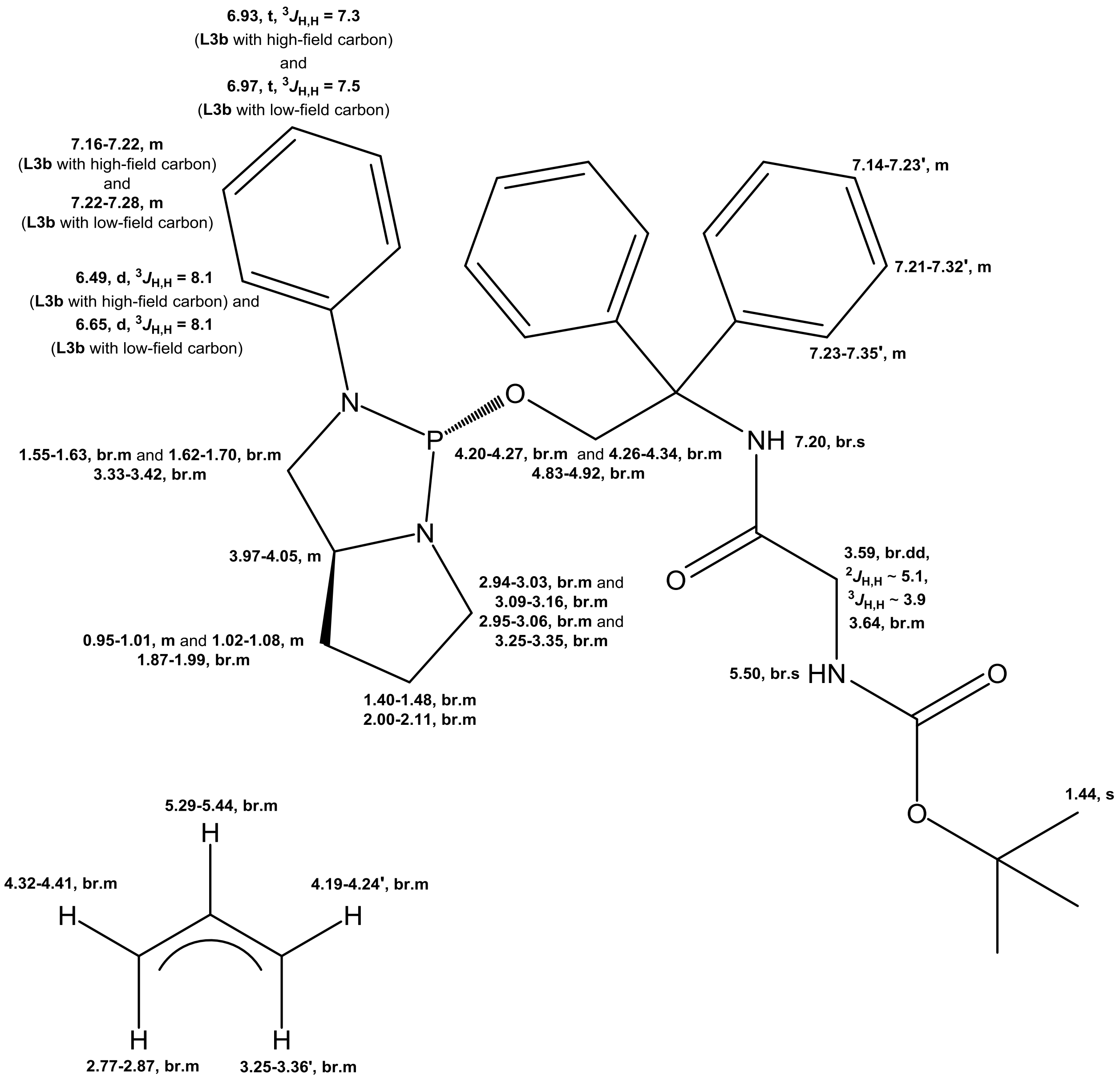


Figure S16a. ^{1}H NMR Signal Assignment for [Pd(allyl)(**L3b**)$_2$]BF$_4$.

EXPERIMENTAL SECTION

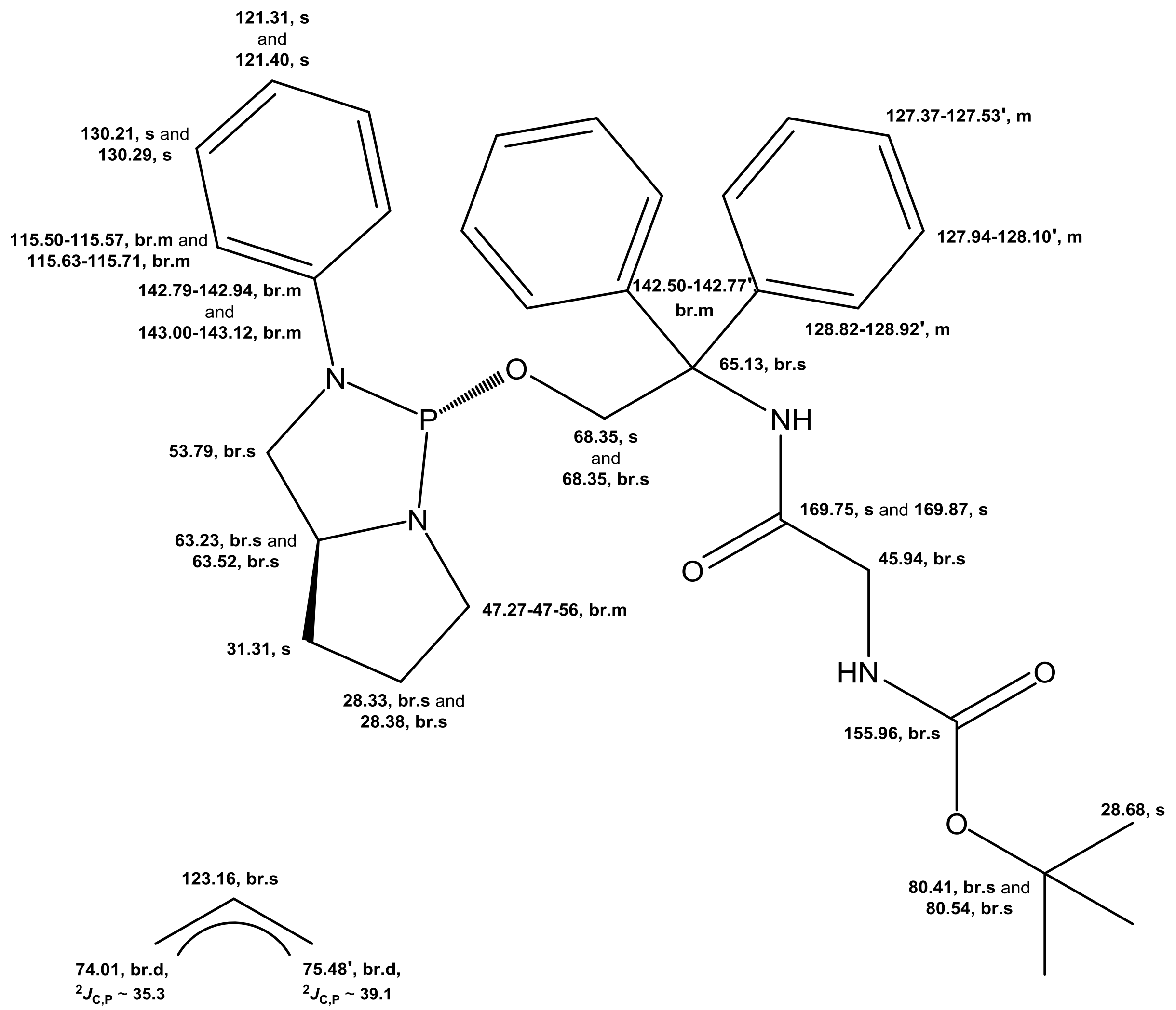


Figure S16b. ^{13}C NMR Signal Assignment for [Pd(allyl)(**L3b**)$_2$]BF$_4$.

[Pd(allyl)(**L3c**)$_2$]BF$_4$: White solid, yield 0.191 g (84 %). ^{1}H NMR[*a*] (499.9 MHz, CD$_2$Cl$_2$, ambient temperature): δ = 0.79 and 0.81 (t, ^3J(H,H) = 7.3 and 7.3 Hz, 6H; C$\underline{H}_3$CH$_2$), 1.35-1.48 (m, 2H; CH$_3$C$\underline{H}_2$), 1.42 (s, 18H; (CH$_3$)$_3$C), 1.51-1.62 (m, 2H; CH$_3$C$\underline{H}_2$), 1.56-1.66 (br.m, 2H; C$\underline{H}_2$), 1.84-1.93 (m, 2H; NCH$_2$C$\underline{H}_2$), 2.01-2.08 (m, 2H; NCH$_2$C$\underline{H}_2$), 2.11-2.19 (m, 2H; C$\underline{H}_2$), 2.77-2.90' (br.m, 1H; CH$_{2allyl}$ (*anti*)), 2.88-3.00 (br.m, 1H; CH$_{2allyl}$ (*anti*)), 2.90-3.02 (br.m, 2H; NC$\underline{H}_2$CH), 3.27-3.34 and 3.31-3.37 (br.m, 2H; NC$\underline{H}_2$CH$_2$), 3.41-3.49 and 3.49-3.57 (br.m, 2H; NC$\underline{H}_2$CH$_2$), 3.62-3.70 (m, 4H; C$\underline{H}_2$NHBoc), 3.74-3.81 (br.m, 2H; POCH$_2$), 3.81-3.89 (br.m, 2H; POCH$_2$), 3.82-3.92 (br.m, 2H; NC$\underline{H}_2$CH), 3.83-3.95 (br.m, 2H; C$\underline{H}$NH), 4.10-4.20 (br.m, 1H; CH$_{2allyl}$ (*syn*)), 4.21-4.31 (m, 2H; NCH$_2$C$\underline{H}$), 4.21-4.31' (br.m, 1H; CH$_{2allyl}$ (*syn*)), 5.26-5.34 (m, 1H; CH$_{allyl}$), 5.39 (br.s, 2H; CH$_2$N$\underline{H}$Boc), 6.41 and 6.43 (br.d, ^3J(H,H) ~ 8.6 and 8.8 Hz, 2H; CHN$\underline{H}$), 6.83 and 6.87 (d, ^3J(H,H) = 8.1 and 8.1 Hz, 4H; CH$_{ortho}$), 6.96 and 6.97 (t, ^3J(H,H) = 7.3 and 7.3 Hz, 2H; CH$_{para}$), 7.24 and 7.24 (t, ^3J(H,H) = 7.7 and 7.7 Hz, 4H; CH$_{meta}$) ppm. ^{13}C{^{1}H} NMR[*a*] (125.7 MHz, CD$_2$Cl$_2$, ambient temperature): δ = 10.60 and 10.63 (s; $\underline{C}$H$_3$CH$_2$), 24.92 and 24.96 (s; CH$_3\underline{C}$H$_2$), 27.68 and 27.79 (br.s; NCH$_2\underline{C}$H$_2$), 28.70 (s;

$(\underline{C}H_3)_3C$), 31.92 and 32.02 (s; $\underline{C}H_2$), 44.98 (br.s; $\underline{C}H_2NHBoc$), 49.22 and 49.50 (br.d, $^2J(C,P)$ ~ 22.9 and 21.9 Hz; $N\underline{C}H_2CH_2$), 51.53 (s; CHNH), 54.86 and 55.02 (s; $N\underline{C}H_2CH$), 63.09 and 63.24 (s; $NCH_2\underline{C}H$), 143.25-143.40 (br.m; $POCH_2$), 71.76 (br.d, $^2J(C,P_{trans})$ ~ 39.1 Hz; CH_{2allyl}), 72.15' (br.d, $^2J(C,P_{trans})$ ~ 40.1 Hz; CH_{2allyl}), 80.17 (br.s; $(CH_3)_3\underline{C}$), 115.89 and 115.99 (br.s; CH_{ortho}), 121.78 and 121.87 (s; CH_{para}), 124.38 (t, $^2J(C,P)$ = 8.6 Hz; CH_{allyl}), 130.18 and 130.20 (s; CH_{meta}), 143.25-143.40 (br.m; CNP), 156.59 (br.s; C(O)O), 170.36 and 170.39 (s; CO) ppm. $^{31}P\{^1H\}$ NMR[a] (202.4 MHz, CD_2Cl_2, ambient temperature): δ = 115.91 (br.d, $^2J(P,P)$ = 90.0 Hz) and 116.45 (br.d, $^2J(P,P)$ = 90.0 Hz) ppm. $C_{47}H_{75}BF_4N_8O_8P_2Pd$ (1135.34): calcd. C 49.72, H 6.66, N 9.87; found C 50.00, H 6.75, N 10.02.

[a] The nonequivalent signals of two *P*-ligands are listed in order of increasing chemical shifts using the conjunction "and".

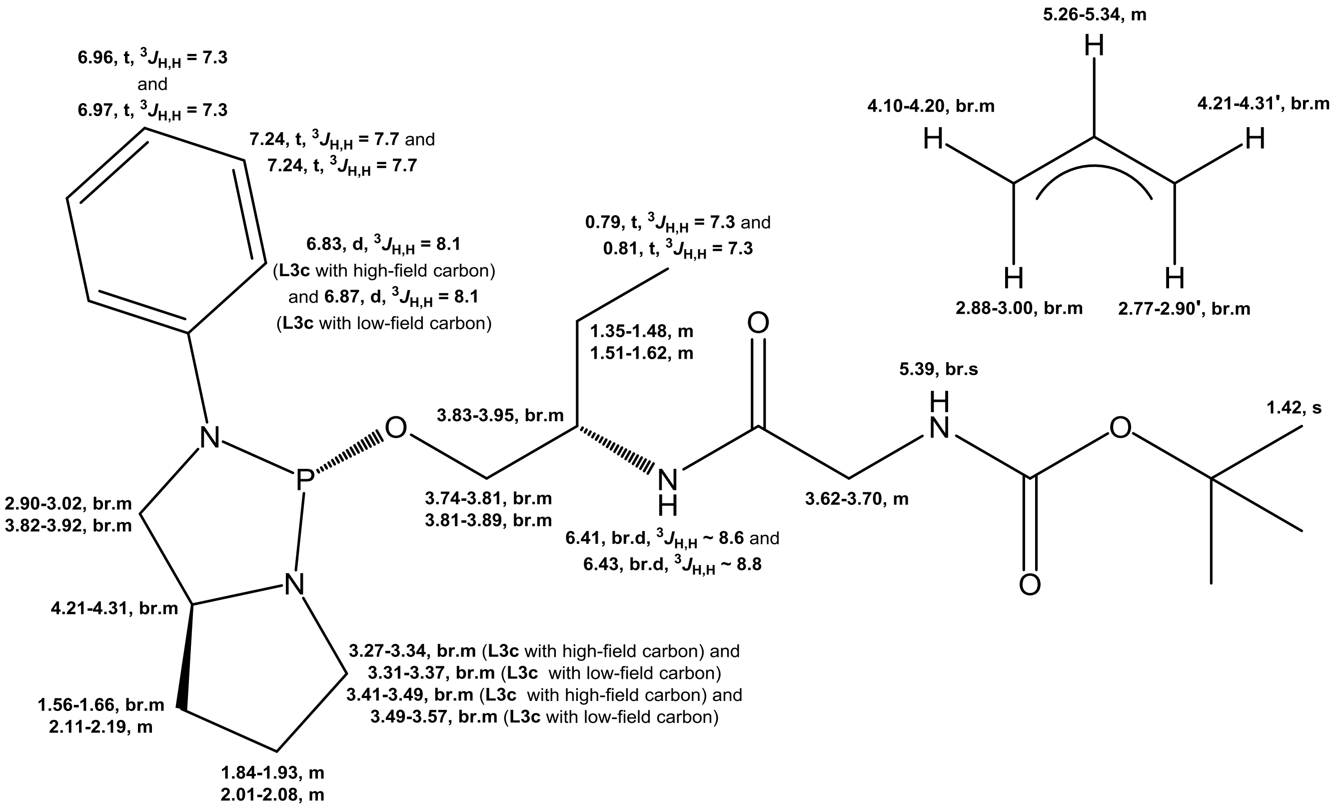


Figure S17a. ^1H NMR Signal Assignment for $[Pd(allyl)(\mathbf{L3c})_2]BF_4$.

EXPERIMENTAL SECTION

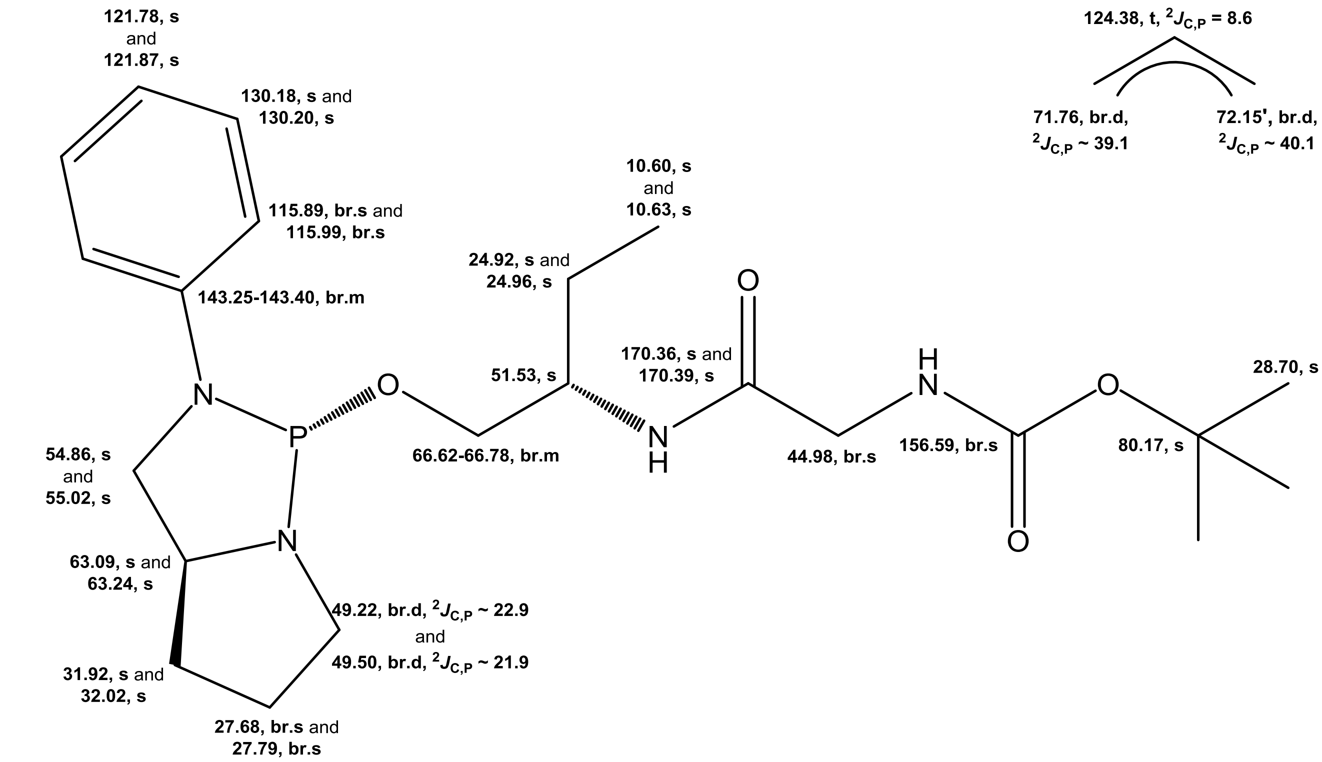


Figure S17b. ^{13}C NMR Signal Assignment for [Pd(allyl)(**L3c**)$_2$]BF_4.

[Pd(allyl)(**L3d**)$_2$]BF_4: White solid, yield 0.243 g (93 %). ^{1}H NMR (600.1[a] MHz, CD_2Cl_2, 22.6 °C): δ = 0.77' (s, 9H; $(C\underline{H}_3)_3C$), 0.98'' (s, 9H; $(C\underline{H}_3)_3C$), 1.14-1.30 (br.m, 1H; $C\underline{H}_2$), 1.40 (s, 9H; $(CH_3)_3C$), 1.88-1.96 (m, 2H; $NCH_2C\underline{H}_2$), 1.91-2.00 (m, 1H; $C\underline{H}_2$), 2.04-2.10 (m, 1H; $NC\underline{H}_2CH$), 3.12-3.19 (br.m, 1H; $NC\underline{H}_2CH_2$), 3.20-3.25 (br.m, 1H; $NC\underline{H}_2CH_2$), 3.45-3.52 (br.m, 1H; $NC\underline{H}_2CH$), 3.60-3.65 (br.m, 1H; $POCH_2$), 3.72-3.78 (br.m, 1H; $POCH_2$), 3.80-3.82 (m, 1H; C$\underline{H}$NHBoc), 3.81-3.88 (br.m, 1H; C$\underline{H}$NH), 3.99-4.06 (m, 1H; $NCH_2C\underline{H}$), 5.25 (br.d, ^3J(H,H) ~ 9.5, 1H; CHN$\underline{H}$Boc), 6.22 (br.d, ^3J(H,H) ~ 8.1, 1H; CHN$\underline{H}$), 6.81 (d, ^3J(H,H) = 7.3 Hz, 2H; CH_{ortho}), 6.99 (t, ^3J(H,H) = 7.3 Hz, 1H; CH_{para}), 7.30 (t, ^3J(H,H) = 7.7 Hz, 2H; CH_{meta}) (**L**), 0.76' (s, 9H; $(C\underline{H}_3)_3C$), 0.99'' (s, 9H; $(C\underline{H}_3)_3C$), 1.14-1.30 (br.m, 1H; $C\underline{H}_2$), 1.40 (s, 9H; $(CH_3)_3C$), 1.96-2.06 (m, 2H; $NCH_2C\underline{H}_2$), 1.91-2.00 (m, 1H; $C\underline{H}_2$), 2.04-2.10, (m, 1H; $NC\underline{H}_2CH$), 3.25-3.30 (br.m, 1H; $NC\underline{H}_2CH_2$), 3.31-3.38 (br.m, 1H; $NC\underline{H}_2CH_2$), 3.45-3.52 (br.m, 1H; $NC\underline{H}_2CH$), 3.59-3.63 (br.m, 1H; $POCH_2$), 3.68-3.72 (br.m, 1H; $POCH_2$), 3.79-3.80 (m, 1H; C$\underline{H}$NHBoc), 3.81-3.88 (br.m, 1H; C$\underline{H}$NH), 4.01-4.09 (m, 1H; $NCH_2C\underline{H}$), 5.23 (br.d, ^3J(H,H) ~ 9.5, 1H; CHN$\underline{H}$Boc), 6.16 (br.d, ^3J(H,H) ~ 8.8, 1H; CHN$\underline{H}$), 6.72 (d, ^3J(H,H) = 8.1 Hz, 2H; CH_{ortho}), 6.95 (t, ^3J(H,H) = 7.0 Hz, 1H; CH_{para}), 7.26 (t, ^3J(H,H) = 7.3 Hz, 2H; CH_{meta}) (**L'**), 3.08-3.13' (br.m, 1H; CH_2 (*anti*)), 3.30-3.36 (br.m, 1H; CH_2 (*anti*)), 4.77-4.84 (br.m, 1H; CH_2 (*syn*)), 4.81-4.88' (br.m, 1H; CH_2 (*syn*)), 5.46-5.55 (br.m, 1H; CH) (**allylic ligand**) ppm. $^{13}C\{^1H\}$ NMR (150.9[b] MHz, CD_2Cl_2, 22.6 °C): δ = 26.87'' (s; $(\underline{C}H_3)_3C$), 26.97' (s; $(\underline{C}H_3)_3C$), 28.04 (vt, J = 3.8 Hz; $NCH_2\underline{C}H_2$), 28.59 (s; $(\underline{C}H_3)_3C$), 31.38 (br.s; $\underline{C}H_2$), 34.35'' (br.s; $(CH_3)_3\underline{C}$), 34.55' (s; $(CH_3)_3\underline{C}$), 47.92-48.06 (m; $N\underline{C}H_2CH_2$), 54.09 (s; $N\underline{C}H_2CH$), 57.39 (br.s;

CHNH), 62.95 (s; $NCH_2\underline{C}H$), 63.34 (br.s; $\underline{C}HNHBoc$), 65.80 (vt, J = 6.6 Hz; $POCH_2$), 80.08 (s; $(CH_3)_3\underline{C}$), 115.60 (vt, J ~ 4.4 Hz; CH_{ortho}), 121.49 (s; CH_{para}), 130.30 (s; CH_{meta}), 143.09 (vt, J ~ 5.3 Hz; CNP), 156.52 (br.s; C(O)O), 171.47 (s; CO) (**L**), 26.94'' (s; $(\underline{C}H_3)_3C$), 27.03' (s; $(\underline{C}H_3)_3C$), 28.27 (vt, J = 3.8 Hz; $NCH_2\underline{C}H_2$), 28.59 (s; $(\underline{C}H_3)_3C$), 31.38 (br.s; $\underline{C}H_2$), 34.40'' (br.s; $(CH_3)_3\underline{C}$), 34.55' (s; $(CH_3)_3\underline{C}$), 47.85-47.99 (m; $N\underline{C}H_2CH_2$), 54.09 (s; $N\underline{C}H_2CH$), 57.47 (br.s; CHNH), 63.25 (s; $NCH_2\underline{C}H$), 63.25 (br.s; $\underline{C}HNHBoc$), 66.06 (vt, J = 6.6 Hz; $POCH_2$), 80.08 (s; $(CH_3)_3\underline{C}$), 115.52 (vt, J ~ 4.4 Hz; CH_{ortho}), 121.45 (s; CH_{para}), 130.22 (s; CH_{meta}), 143.00 (vt, J ~ 5.3 Hz; CNP), 156.52 (br.s; C(O)O), 171.52 (s; CO) (**L'**), 73.96' (vt, J = 21.0 Hz; CH_2), 74.77 (vt, J = 22.1 Hz; CH_2), 123.26 (t, ^2J(C,P) = 8.6 Hz; CH) (**allylic ligand**) ppm. $^{31}P\{^1H\}$ NMR (242.4 MHz, CD_2Cl_2, 26 °C): δ = 116.58 (br.s) ppm. $C_{59}H_{99}BF_4N_8O_8P_2Pd$ (1303.66): calcd. C 54.36, H 7.65, N 8.60; found C 54.89, H 7.60, N 8.67.

[a] The value of some coupling constants was determined in the following conditions: 499.9 MHz, CD_2Cl_2, ambient temperature.
[b] The value of some coupling constants was determined in the following conditions: 125.7 MHz, CD_2Cl_2, ambient temperature.

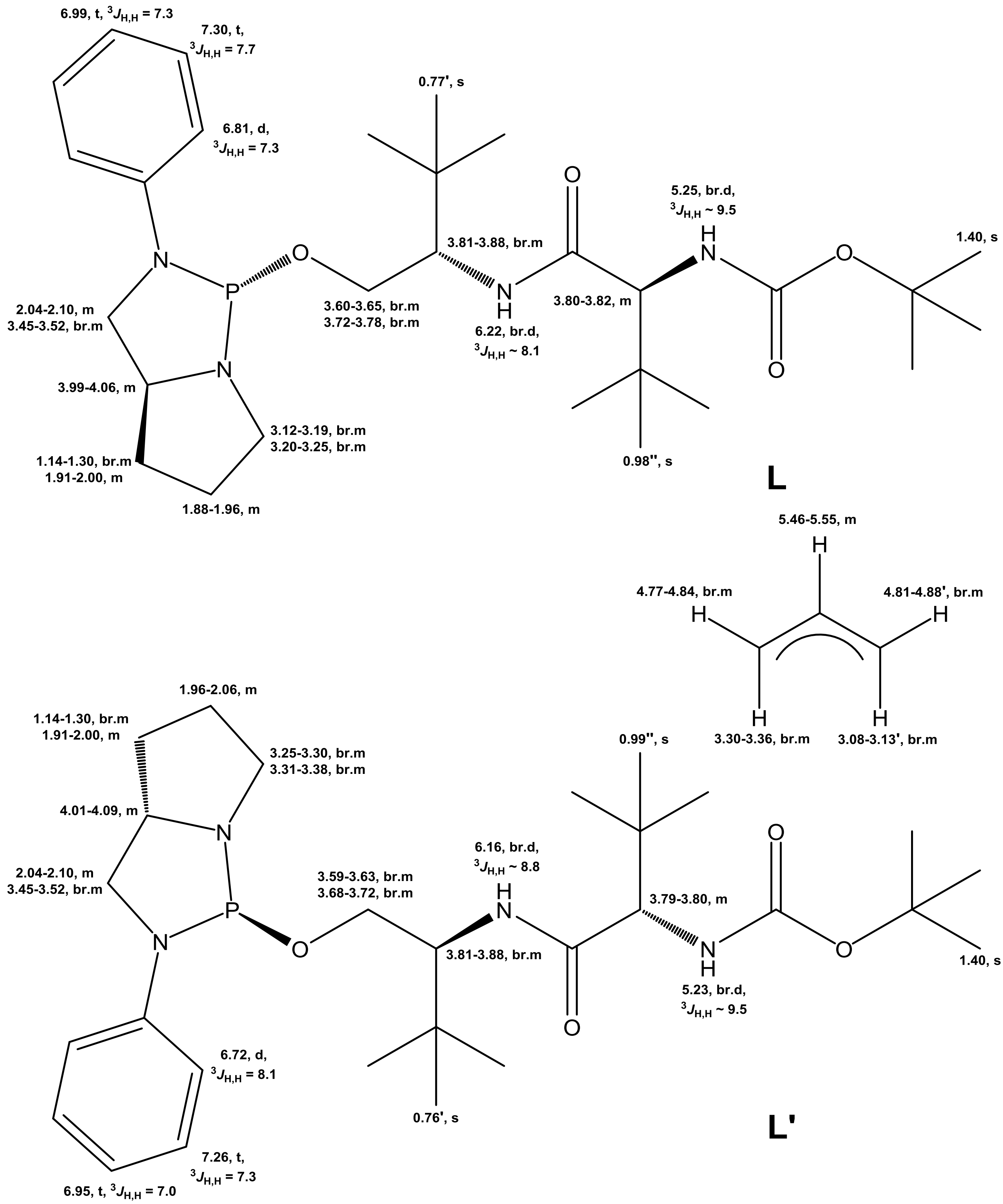


Figure S18a. Full ^{1}H NMR Signal Assignment for [Pd(allyl)(**L3d**)$_2$]BF_4.

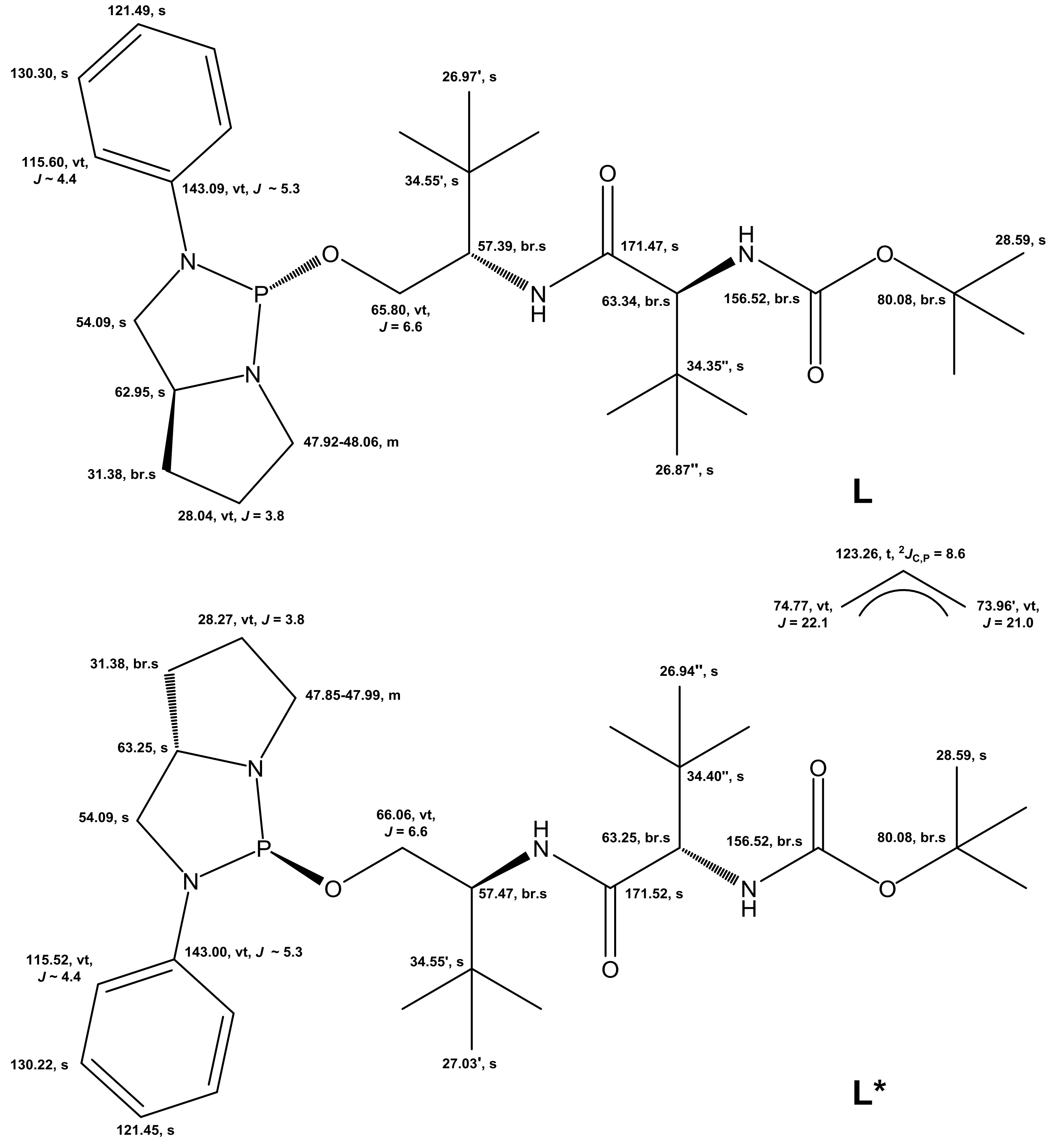


Figure S18b. Full ^{13}C NMR Signal Assignment for [Pd(allyl)(**L3d**)$_2$]BF_4.

[Pd(allyl)(**L3e**)$_2$]BF_4: White solid, yield 0.229 g (88 %). ^1H NMR[a] (499.9 MHz, CD_2Cl_2, ambient temperature): δ = 0.72 and 0.73 (t, ^3J(H,H) = 7.1 and 7.3 Hz, 6H; C<u>H</u>$_3$CH$_2$), 0.78-0.81' (m, 6H; C<u>H</u>$_3$CH), 0.81-0.84' (m, 6H; C<u>H</u>$_3$CH$_2$), 0.86 and 0.86 (d, ^3J(H,H) = 6.6 and 6.8 Hz, 6H; C<u>H</u>$_3$CH), 0.95-1.04 (m, 4H; CH$_3$C<u>H</u>$_2$), 1.06-1.09' (m, 4H; CH$_3$C<u>H</u>$_2$), 1.27-1.35 (br.m, 4H; CH$_3$C<u>H</u>$_2$), 1.37-1.51' (br.m, 4H; CH$_3$C<u>H</u>$_2$), 1.41 (s, 18H; (CH$_3$)$_3$C), 1.41-1.50 (br.m, 2H; C<u>H</u>$_2$), 1.54-1.64 (br.m, 2H; CH$_3$C<u>H</u>), 1.74-1.84' (br.m, 2H; CH$_3$C<u>H</u>), 1.88-1.95 (m, 2H; $NCH_2C\underline{H}_2$), 1.97-2.05 (m, 2H; $NCH_2C\underline{H}_2$), 2.02-2.11 (br.m, 2H; $C\underline{H}_2$), 2.37-2.56 (br.m, 2H; $NC\underline{H}_2CH$), 3.02-3.12 (br.m, 1H; CH_{2allyl} (*anti*)), 3.06-3.17' (br.m, 1H; CH_{2allyl} (*anti*)), 3.23-3.31 (br.m, 2H; $NC\underline{H}_2CH_2$), 3.34-3.41 and 3.41-3.49 (br.m, 2H; $NC\underline{H}_2CH_2$), 3.52-3.61 (br.m, 2H; $POCH_2$), 3.58-3.68 (br.m, 2H; $NC\underline{H}_2CH$), 3.73-3.82 (m, 2H; $C\underline{H}NHBoc$), 3.83-3.90 (br.m, 2H; $C\underline{H}NH$), 3.84-3.95 (br.m, 2H; $POCH_2$), 4.07-4.17 (br.m, 2H; $NCH_2C\underline{H}$), 4.43-4.53 (br.m, 1H; CH_{2allyl} (*syn*)), 4.49-4.62' (br.m, 1H; CH_{2allyl} (*syn*)), 5.08-5.15 and 5.11-5.20 (br.m, 2H; $CHN\underline{H}Boc$), 5.39-5.52 (m, 1H; CH_{allyl}), 6.43 and 6.47 (br.s; $CHN\underline{H}$), 6,78 and 6.83 (d, ^3J(H,H) = 8.1 and 7.8 Hz, 4H; CH_{ortho}), 6.96 and 6.98 (t, ^3J(H,H) = 7.1 and 7.1 Hz, 2H; CH_{para}), 7.24 and 7.28 (t, ^3J(H,H) = 7.9 and 7.9 Hz, 4H; CH_{meta}) ppm. $^{13}C\{^1H\}$ NMR[a] (125.7 MHz, CD_2Cl_2, ambient temperature): δ = 11.39 (s; $\underline{C}H_3CH_2$), 11.58' (s; $\underline{C}H_3CH_2$), 15.87 (s; $\underline{C}H_3CH$), 16.24' (s; $\underline{C}H_3CH$), 24.99 (s; $CH_3\underline{C}H_2$), 25.17' (s; $CH_3\underline{C}H_2$), 27.93 and 28.07 (br.s; $NCH_2\underline{C}H_2$), 28.69 (s; $(\underline{C}H_3)_3C$), 31.71 (br.s; $\underline{C}H_2$), 35.66 and 35.76 (s; $CH_3\underline{C}H$), 36.78' (br.s; $CH_3\underline{C}H$), 48.64-49.00 (br.m; $N\underline{C}H_2CH_2$), 54.00 (br.s; CHNH), 54.52 and 54.60 (br.s; $N\underline{C}H_2CH$), 60.34 (br.s; $\underline{C}HNHBoc$), 63.17 and 63.39 (br.s; $NCH_2\underline{C}H$), 65.47 (br.s; $POCH_2$), 72.71 (br.vt, *J* ~ 20.0 Hz; CH_{2allyl}), 73.19' (br.vt, *J* ~ 21.0 Hz; CH_{2allyl}), 80.27 (s; $(CH_3)_3\underline{C}$), 115.71 (s; CH_{ortho}), 121.79 (s; CH_{para}), 124.02 (br.s; CH_{allyl}), 130.31 and 130.38 (s; CH_{meta}), 143.21 (s; CNP), 156.60 (br.s; C(O)O), 172.33 (s; CO) ppm. $^{31}P\{^1H\}$ NMR (202.4 MHz, CD_2Cl_2, ambient temperature): δ = 115.07 (br.s) ppm. $C_{59}H_{99}BF_4N_8O_8P_2Pd$ (1303.66): calcd. C 54.36, H 7.65, N 8.60; found C 54.60, H 7.75, N 8.47.

[a] The nonequivalent signals of two *P*-ligands are listed in order of increasing chemical shifts using the conjunction "and".

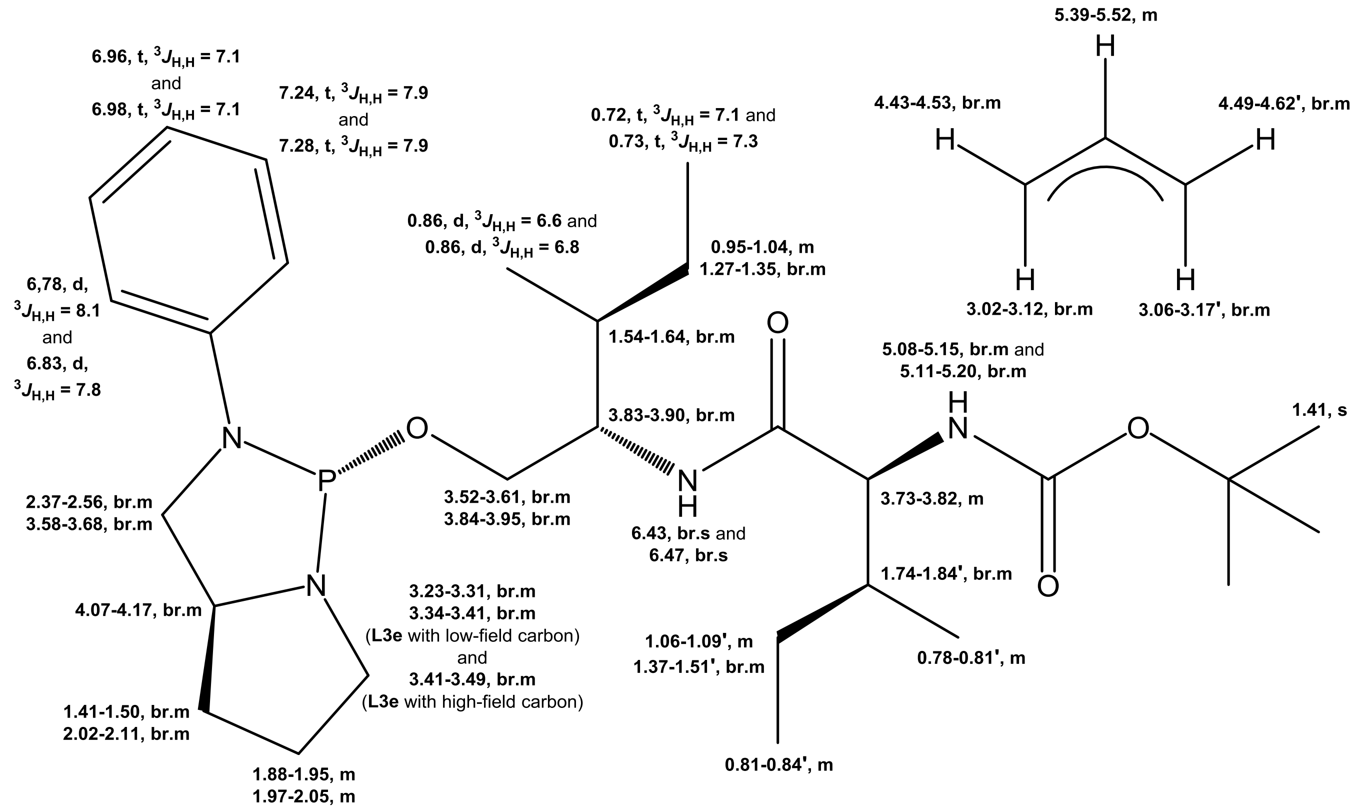


Figure S19a. ^1H NMR Signal Assignment for $[Pd(allyl)(\mathbf{L3e})_2]BF_4$.

EXPERIMENTAL SECTION

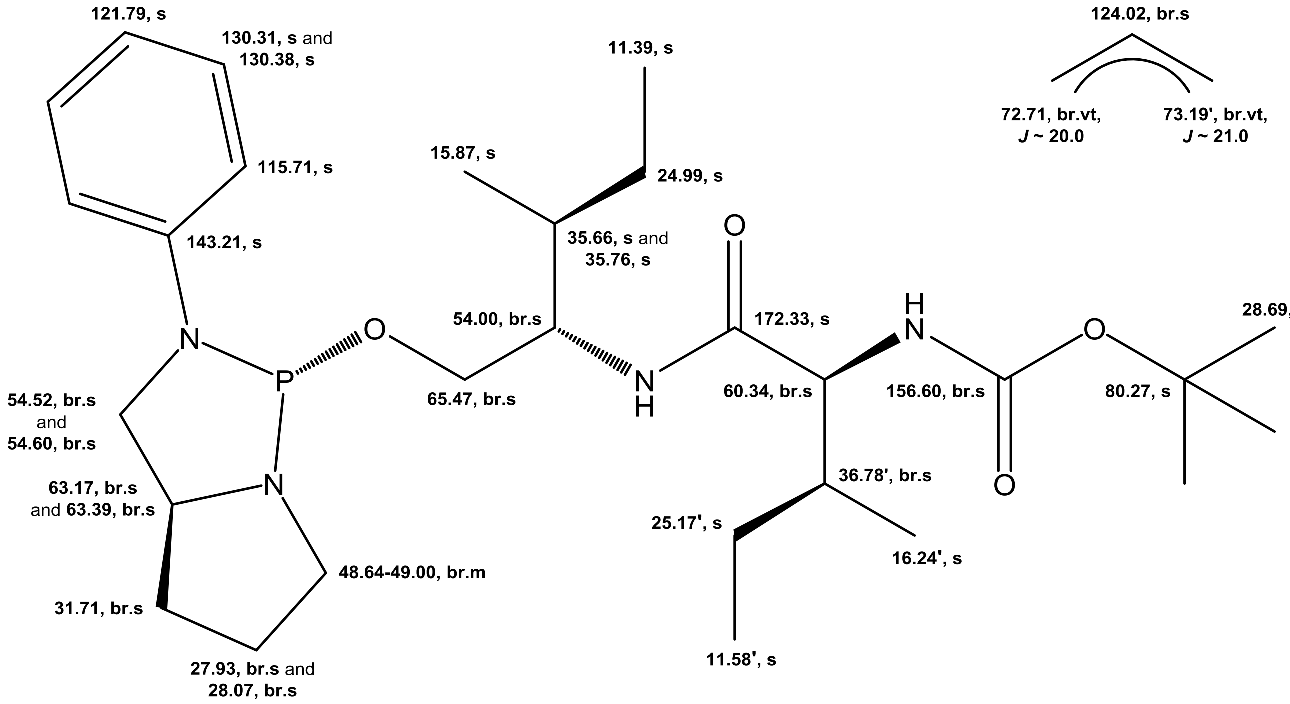


Figure S19b. ^{13}C NMR Signal Assignment for [Pd(allyl)(**L3e**)$_2$]BF_4.

[Pd(allyl)(**L3f**)$_2$]BF_4: yellowish solid, yield 0.238 g (97 %). ^{1}H NMR[a] (499.9 MHz, CD_2Cl_2, ambient temperature): δ = 1.43 (s, 18H; (C<u>H</u>$_3$)$_3$C), 1.52-1.65 (m, 2H; C<u>H</u>$_2$), 1.67-1.83 (br.m, 4H; SCH$_2$C<u>H</u>$_2$), 1.82-1.94 (br.m, 2H; NCH$_2$C<u>H</u>$_2$), 1.98-2.10 (br.m, 2H; NCH$_2$C<u>H</u>$_2$), 2.04 (br.s, 6H; CH$_3$), 2.08-2.21 (m, 2H; C<u>H</u>$_2$), 2.37-2.47 (br.m, 2H; SC<u>H</u>$_2$CH$_2$), 2.47-2.57 (br.m, 2H; SC<u>H</u>$_2$CH$_2$), 2.68-2.84' (br.m, 1H; CH$_{2\text{allyl}}$ (*anti*)), 2.71-2.96 (br.m, 2H; NC<u>H</u>$_2$CH), 2.76-2.94 (br.m, 1H; CH$_{2\text{allyl}}$ (*anti*)), 3.25-3.35 and 3.35-3.41 (br.m, 2H; NC<u>H</u>$_2$CH$_2$), 3.40-3.45 and 3.44-3.52 (br.m, 2H; NC<u>H</u>$_2$CH$_2$), 3.70.-3.77 (br.m, 2H; POCH$_2$), 3.69-3.70 (m, 4H; C<u>H</u>$_2$NHBoc), 3.72-3.81 (br.m, 2H; NC<u>H</u>$_2$CH), 3.90-3.99 (br.m, 2H; POCH$_2$), 4.05-4.21 (br.m, 1H; CH$_{2\text{allyl}}$ (*syn*)), 4.10-4.22 (br.m, 2H; NHC<u>H</u>), 4.20-4.30 (m, 2H; NCH$_2$C<u>H</u>), 4.20-4.36' (br.m, 1H; CH$_{2\text{allyl}}$ (*syn*)), 5.40-5.54 (br.m, 2H; CHN<u>H</u>Boc), 5.17-5.32 (br.m, 1H; CH$_{\text{allyl}}$), 6.80-6.95 (br.m, 2H; N<u>H</u>CH), 6.88-6.92 (br.m, 4H; CH$_{\text{ortho}}$), 6.99 (t, ^3J(H,H) = 7.1 Hz, 2H; CH$_{\text{para}}$), 7.29 (t, ^3J(H,H) = 7.7 Hz, 4H; CH$_{\text{meta}}$) ppm. ^{13}C{^{1}H} NMR[a] (125.7 MHz, CD_2Cl_2, ambient temperature): δ = 16.05 (s; <u>C</u>H$_3$), 27.79 (br.s; NCH$_2$<u>C</u>H$_2$), 28.77 (s; (<u>C</u>H$_3$)$_3$C), 30.99 (s; S<u>C</u>H$_2$CH$_2$), 31.81 (br.s; SCH$_2$<u>C</u>H$_2$), 31.87 (br.s; <u>C</u>H$_2$), 44.99 (br.s; <u>C</u>H$_2$NHBoc), 49.03-49.89 (br.m; N<u>C</u>H$_2$CH$_2$), 49.56 (s; NH<u>C</u>H), 54.87 (br.s; N<u>C</u>H$_2$CH), 62.88-63.19 (br.m; NCH$_2$<u>C</u>H), 66.47 (s; POCH$_2$), 70.59-71.20 (br.m; CH$_{2\text{allyl}}$), 71.20-71.67' (br.m; CH$_{2\text{allyl}}$), 80.27 (s; (CH$_3$)$_3$<u>C</u>), 116.06 (br.s; CH$_{\text{ortho}}$), 122.01 (s; CH$_{\text{para}}$), 124.03 (t, ^2J(C,P) = 8.6 Hz; CH$_{\text{allyl}}$), 130.30 (s; CH$_{\text{meta}}$), 143.28-143.49 (m; CNP), 156.64 (br.s; C(O)O), 170.68 (s; CO), ppm. ^{31}P{^{1}H} NMR (202.4 MHz, CD_2Cl_2, ambient temperature): δ = 116.85 (br.s) ppm. $C_{49}H_{79}BF_4N_8O_8P_2PdS_2$ (1227.51): calcd. C 47.95, H 6.49, N 9.13; found C 48.27, H 6.60, N 9.20.

[a] The nonequivalent signals of two *P*-ligands are listed in order of increasing chemical shifts using the conjunction "and".

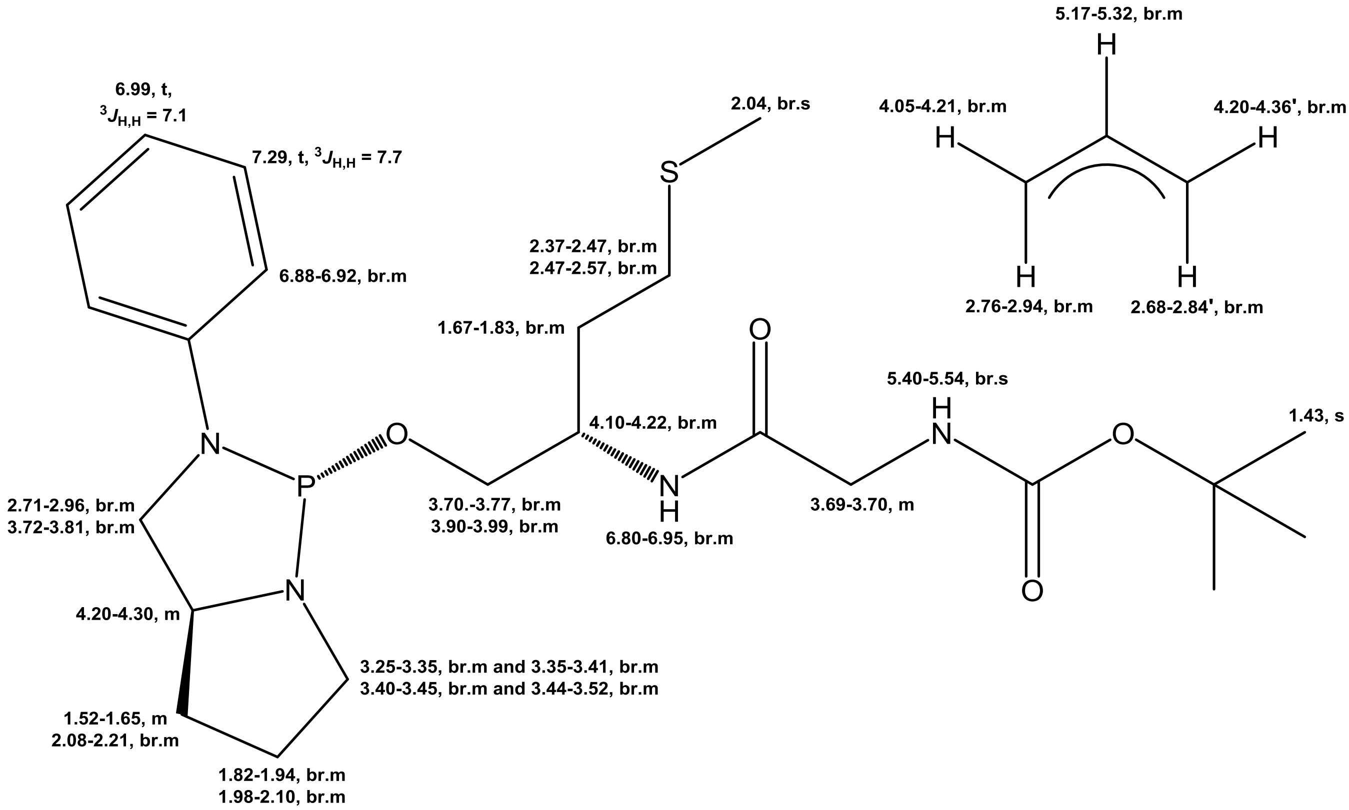


Figure S20a. ^{1}H NMR Signal Assignment for [Pd(allyl)(**L3f**)$_2$]BF_4.

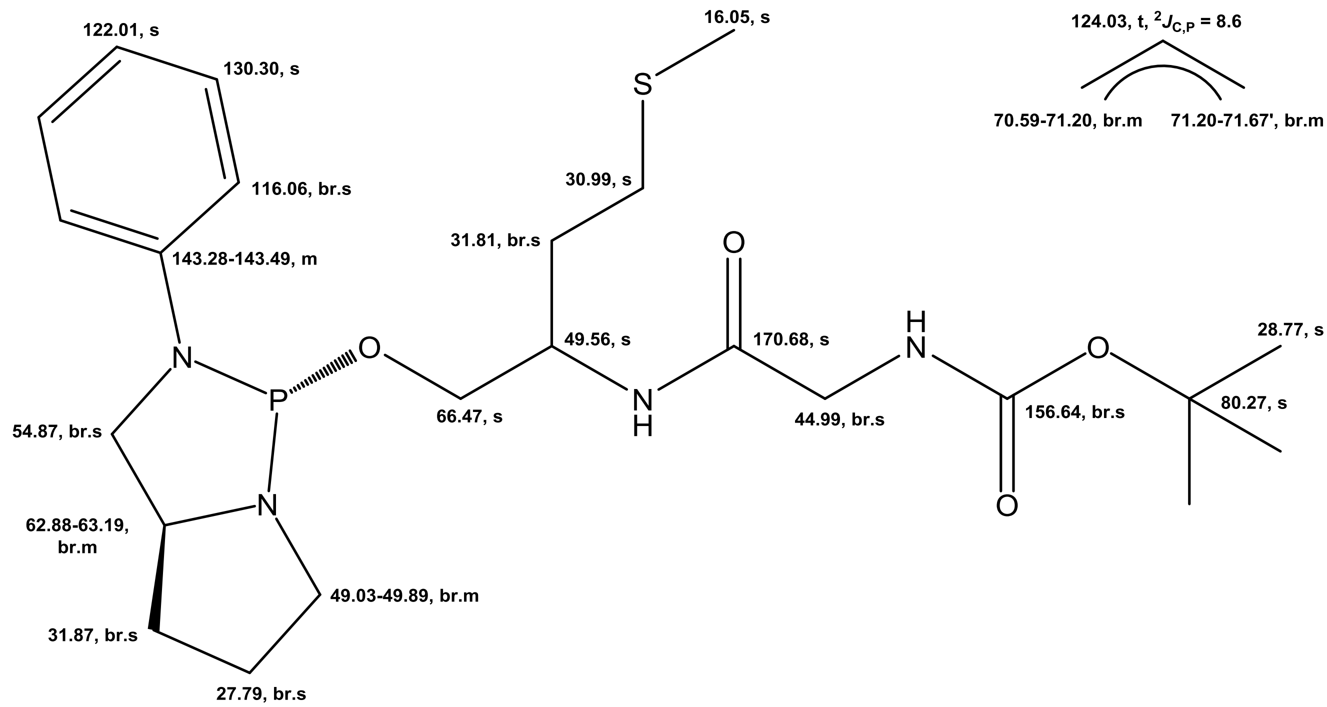


Figure S20b. ^{13}C NMR Signal Assignment for [Pd(allyl)(**L3f**)$_2$]BF_4.

EXPERIMENTAL SECTION

[Pd(allyl)(**L3g**)$_2$]BF_4: White solid, yield 0.193 g (74 %). ^{1}H NMR[*a*] (499.9 MHz, CD_2Cl_2, ambient temperature): δ = 0.72-0.75 (m, 6H; $C\underline{H}_3CH$), 0.84 (br.t, ^3J(H,H) ~ 6.8 Hz, 6H; $C\underline{H}_3CH_2$), 0.86-0.89' (br.m, 6H; $C\underline{H}_3CH_2$), 0.89-0.91' (m, 6H; $C\underline{H}_3CH$), 1.02-1.13 (br.m, 4H; $CH_3C\underline{H}_2$), 1.05-1.17' (m, 4H; $CH_3C\underline{H}_2$), 1.31-1.42 (br.m, 2H; $C\underline{H}_2$), 1.38-1.47 (br.m, 4H; $CH_3C\underline{H}_2$), 1.41 (s, 18H; $(CH_3)_3C$), 1.47-1.55' (br.m, 4H; $CH_3C\underline{H}_2$), 1.54-1.65 (br.m, 2H; $CH_3C\underline{H}$), 1.84-1.91' (br.m, 2H; $CH_3C\underline{H}$), 1.88-1.95 (m, 2H; $NCH_2C\underline{H}_2$), 1.98-2.05 (m, 2H; $NCH_2C\underline{H}_2$), 1.99-2.10 (br.m, 2H; $C\underline{H}_2$), 2.21-2.40 (br.m, 2H; $NC\underline{H}_2CH$), 3.06-3.17 (br.m, 1H; CH_{2allyl} (*anti*)), 3.16-3.25' (br.m, 1H; CH_{2allyl} (*anti*)), 3.25-3.32 and 3.30-3.35 (br.m, 2H; $NC\underline{H}_2CH_2$), 3.30-3.35 and 3.36-3.45 (br.m, 2H; $NC\underline{H}_2CH_2$), 3.49-3.56 and 3.54-3.60 (br.m, 2H; $POCH_2$), 3.55-3.65 (br.m, 2H; $NC\underline{H}_2CH$), 3.80-3.87 (br.m, 2H; $C\underline{H}NHBoc$), 3.84-3.88 (m, 2H; $POCH_2$), 3.90-3.99 (br.m, 2H; $C\underline{H}NH$), 4.01-4.12 (br.m, 2H; $NCH_2C\underline{H}$), 4.56-4.67 (br.m, 1H; CH_{2allyl} (*syn*)), 4.67-4.78' (br.m, 1H; CH_{2allyl} (*syn*)), 5.15-5.29 (br.m, 2H; $CHN\underline{H}Boc$), 5.42-5.54 (m, 1H; CH_{allyl}), 6.35-6.39 (m; $CHN\underline{H}$), 6,76 and 6.81 (d, ^3J(H,H) = 7.3 and 7.8 Hz, 4H; CH_{ortho}), 6.96 and 6.98 (t, ^3J(H,H) = 6.8 and 6.8 Hz, 2H; CH_{para}), 7.24 and 7.28 (t, ^3J(H,H) = 7.8 and 8.0 Hz, 4H; CH_{meta}) ppm. $^{13}C\{^1H\}$ NMR[*a*] (125.7 MHz, CD_2Cl_2, ambient temperature): δ = 11.42 (s; $\underline{C}H_3CH_2$), 11.60' (s; $\underline{C}H_3CH_2$), 16.03' and 16.05' (s; $\underline{C}H_3CH$), 16.27 and 16.33 (s; $\underline{C}H_3CH$), 25.03 (s; $CH_3\underline{C}H_2$), 25.24' and 25.30' (s; $CH_3\underline{C}H_2$), 28.05 and 28.25 (br.s; $NCH_2\underline{C}H_2$), 28.69 (s; $(\underline{C}H_3)_3C$), 31.73 (br.s; $\underline{C}H_2$), 35.81 and 35.89 (s; $CH_3\underline{C}H$), 36.81' (br.s; $CH_3\underline{C}H$), 48.38 and 48.57 (br.d, ^2J(C,P) ~ 21.9 and 22.9 Hz; $N\underline{C}H_2CH_2$), 53.92 (br.s; CHNH), 54.42 (br.s; $N\underline{C}H_2CH$), 60.42 (br.s; $\underline{C}HNHBoc$), 63.15 and 63.42 (s; $NCH_2\underline{C}H$), 65.69-65.82 and 65.82-65.94 (br.m; $POCH_2$), 73.30 (br.d, $^2J(C,P_{trans})$ ~ 40.1; CH_{2allyl}), 74.33' (br.d, $^2J(C,P_{trans})$ ~ 40.1; CH_{2allyl}), 80.28 (s; $(CH_3)_3\underline{C}$), 115.79 (s; CH_{ortho}), 121.72 (s; CH_{para}), 123.96 (t, $^2J(C,P_{trans})$ = 8.1; CH_{allyl}), 130.24 and 130.29 (s; CH_{meta}), 143.21 (br.s; CNP), 156.57 (br.s; C(O)O), 172.23 and 172.31 (s; CO) ppm. $^{31}P\{^1H\}$ NMR[*a*] (202.4 MHz, CD_2Cl_2, ambient temperature): δ = 114.86 (br.d, ^2J(P,P) = 82.7 Hz) and 115.40 (br.d, ^2J(P,P) = 82.7 Hz) ppm. $C_{59}H_{99}BF_4N_8O_8P_2Pd$ (1303.66): calcd. C 54.36, H 7.65, N 8.60; found C 54.62, H 7.67, N 8.70

[*a*] The nonequivalent signals of two *P*-ligands are listed in order of increasing chemical shifts using the conjunction "and".

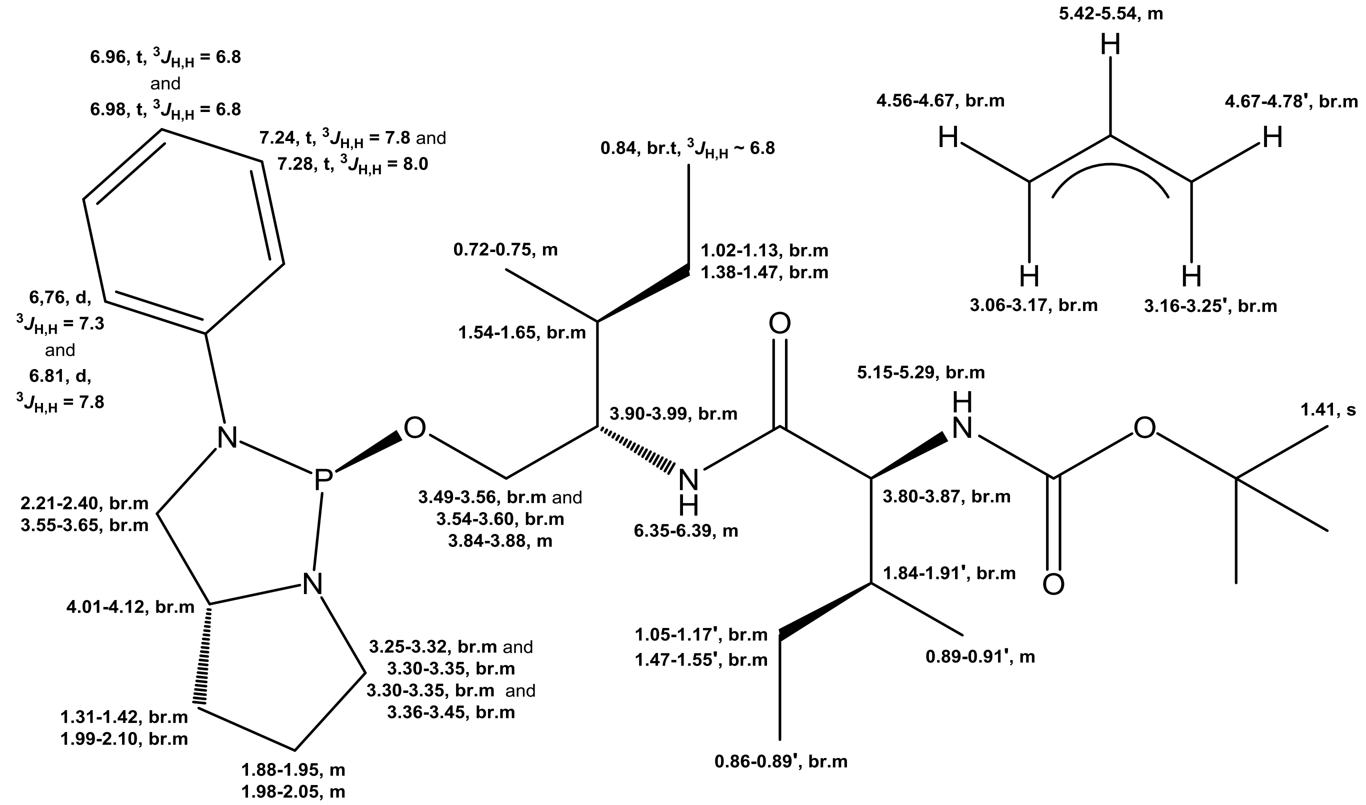


Figure S21a. ^{1}H NMR Signal Assignment for [Pd(allyl)(**L3g**)$_2$]BF$_4$.

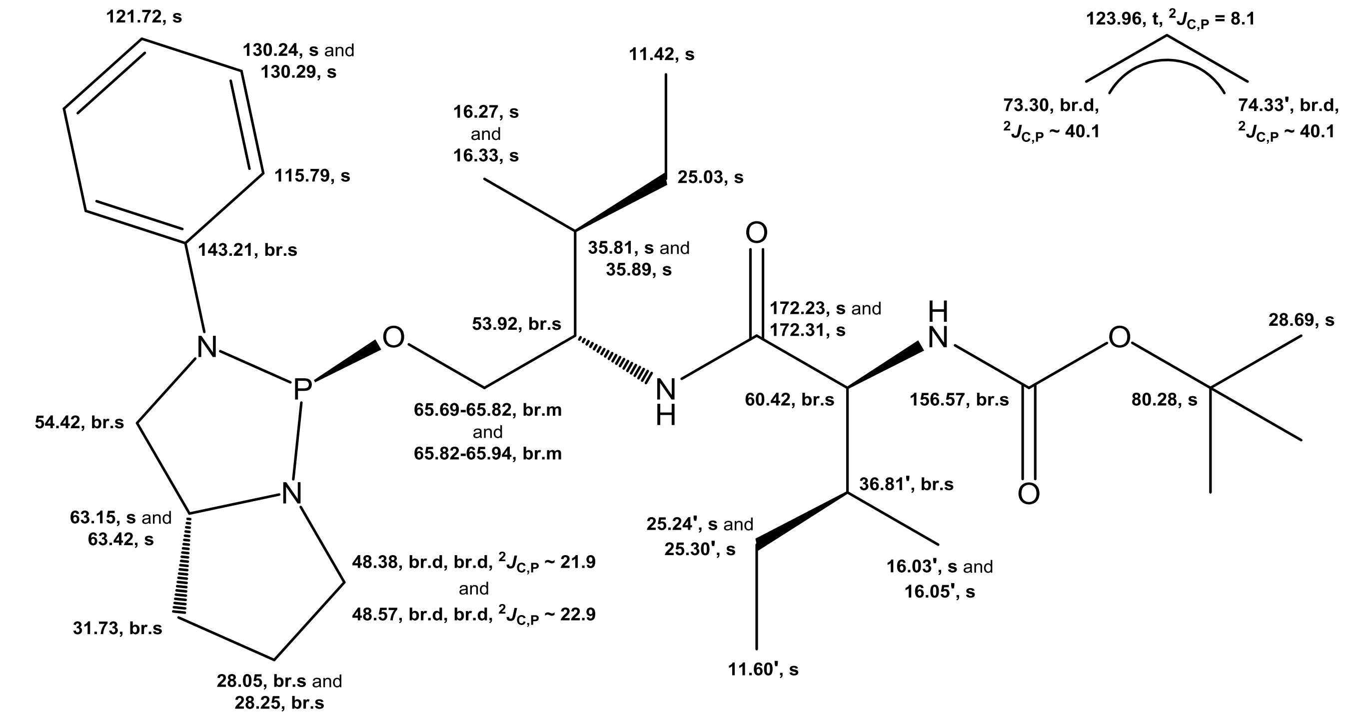


Figure S21b. ^{13}C NMR Signal Assignment for [Pd(allyl)(**L3g**)$_2$]BF$_4$.

EXPERIMENTAL SECTION

[Pd(allyl)(**L4**)$_2$]BF_4: White solid, yield 0.175 g (72 %). ^{1}H NMR[a] (499.9 MHz, CD_2Cl_2, ambient temperature): δ = 1.21-1.30 (br.m, 12H; CH_3), 1.33-1.52 (br.m, 2H; CH_2), 1.43 (br.s, 18H; $(C\underline{H}_3)_3C$), 1.71-1.80 (br.m, 8H; CH_2), 1.86-2.00 (br.m, 2H; CH_2), 1.99-2.12 (br.m, 2H; CH_2), 2.00-2.11 (br.m, 2H; CH_2), 2.34-2.59 (br.m, 2H; CH_2), 2.85-3.15 (br.m, 2H; CH_{2allyl} (*anti*)), 3.19-3.42 (br.m, 4H; CH_2), 3.32-3.41 (br.m, 2H; CH_2), 3.41-3.53 (br.m, 1H; CH_2), 3.56-3.74 (br.m, 2H; CH_2), 3.80-4.10 (br.m, 4H; CH_2), 3.89-3.94 (m, 2H; CH), 4.10-4.23 (br.m, 2H; CH), 4.33-4.67 (br.m, 2H; CH_{2allyl} (*syn*)), 5.26-5.57 (m, 1H; CH_{allyl}), 5.95 (br.s, 2H; NH), 6.85 (t, ^3J(H,H) = 7.3 Hz, 4H; CH_{ortho}), 6.95-7.00 (m, 2H; CH_{para}), 7.27 and 7.29 (t, ^3J(H,H) = 7.6 and 7.6 Hz, 4H; CH_{meta}) ppm. $^{13}C\{^1H\}$ NMR[a] (125.7 MHz, CD_2Cl_2, ambient temperature): δ = 24.20 and 25.43 (br.s; $(\underline{C}H_3)_2C$), 24,61-25.26 (br.m; CH_2), 27.91 and 28.04 (br.s; CH_2), 28.73 (s; $(\underline{C}H_3)_3C$), 31.59 and 31.68 (s; CH_2), 47.70 (s; CH_2), 48.57-49.23 and 48.57-49.23 (br.m; CH_2), 53.79 (br.s; $(CH_3)_2\underline{C}$), 54.49 and 54.55 (br.s; CH_2), 60.98 (br.s; CH), 63.02 and 63.23 (s; CH), 69.22-70.10 (br.m; CH_2), 71.91-73.12 (br.m; CH_{2allyl}), 80.47 (s; $(CH_3)_3\underline{C}$), 115.87 and 115.88 (s; CH_{ortho}), 121.63 and 121.66 (s; CH_{para}), 123.70 (t, ^2J(C,P) = 8.1 Hz; CH_{allyl}), 130.13 and 130.17 (s; CH_{meta}), 143.30 (br.s; CNP), 156.44 (br.s; C(O)O), 172.02 (br.s; CO) ppm. $^{31}P\{^1H\}$ NMR (202.4 MHz, CD_2Cl_2, ambient temperature): δ = 102.61-103.37 (br.m) (minor signal), 114.69-115.46 (br.m) (major signal) ppm. $C_{53}H_{83}BF_4N_8O_8P_2Pd$ (1215.47): calcd. C 52.37, H 6.88, N 9.22; found C 52.65, H 7.01, N 9.02.

[a] The nonequivalent signals of two *P*-ligands are listed in order of increasing chemical shifts using the conjunction "and".

General Procedure for the Preparation of Cationic Palladium Chelate Complexes of the General Formula [Pd(allyl)(L)]BF$_4$: A solution of the relevant ligand **L1d**, **L3f** (0.2 mmol) in CH_2Cl_2 (2 mL) was added dropwise over 30 min to a stirred solution of [Pd(allyl)Cl]$_2$ (0.037 g, 0.1 mmol) in CH_2Cl_2 (1 mL) at 20 °C. The reaction mixture was stirred for a further 1 h at 20 °C. A solution of $AgBF_4$ (0.039 g, 0.2 mmol) in THF (2 mL) was added to the resulting solution, and the reaction mixture was stirred for 1.5 h at 20 °C. The precipitate of AgCl formed was separated by centrifugation. Solution was filtered through SiO_2, solvent was removed in vacuum (40 Torr) and the product was dried in air and in vacuum (1 Torr).

[Pd(allyl)(**L1d**)]BF_4: yellowish solid, yield 0.125 g (93 %). ^{1}H NMR[a] (499.9 MHz, CD_2Cl_2, ambient temperature): δ = 1.35-1.41 (m, 9H), 1.50-1.63 (br.m, 1H), 1.65-1.80 (br.m, 2H), 1.84-1.96 (br.m, 1H), 1.96-2.21 (m, 2H), 2.31 and 2.43 (br.s, 3H; CH_3S), 2.62-3.93 (br.m, 3H), 3.19-3.40 (br.m, 2H), 3.41-3.65 (br.m, 2H), 3.71-4.02 (br.m, 4H), 4.15-4.38 (br.m, 2H), 4.55-4.69 (br.m, 1H), 5.26-5.39 (br.m, 1H), 5.62-5.79 (br.m, 1H), 6.87-7.06 (m, 3H), 7.26.-7.31 (m, 2H) ppm. $^{13}C\{^1H\}$ NMR[a] (125.7 MHz, CD_2Cl_2, ambient temperature): δ = 20.65 and 21.35 (br.s; CH_3S), 27.69 (br.s), 27.89 and 27.97 (br.s), 28.91 and 28.99 (s), 31.62 (br.s), 31.83-32.04 (br.m), 32.37 (br.s), 49.13-49.47 (br.m), 50.89-51.30 (br.m), 54.88 and 55.02 (br.s), 55.64 (br.s), 63.06 (br.s), 66.68-67.03 (br.m), 69.37-69.77 and 71.84-72.35 (br.m; CH_{2allyl} (*cis* position to P atom)), 80.08 (s), 81.25-82-10 (br.m; CH_{2allyl} (*trans* to P atom)), 116.19 and 116.36 (br.s), 121.94-122.00 and 122.33 (br.m and br.s), 124.03 and 124.23 (br.s; CH_{allyl}), 130.47 (s), 143.39-143.60 (br.m), 156.33 and 156.47 (br.s), ppm. $^{31}P\{^1H\}$ NMR[a] (202.4 MHz, CD_2Cl_2, ambient temperature): δ = 116.16 and 117.65 (br.s) ppm. $C_{24}H_{39}BF_4N_3O_3PPdS$ (673.85): calcd. C 42.78, H 5.83, N 6.24; found C 42.89, H 5.91, N 6.36.

[a] The separate signals of *exo*- and *endo*- forms are listed in order of increasing chemical shifts using the conjunction "and".

[Pd(allyl)(**L3f**)]BF_4: yellowish solid, yield 0.139 g (95 %). ^1H NMR[a] (499.9 MHz, CD_2Cl_2, ambient temperature): δ = 1.42 and 1.43 (br.s, 9H), 1.66-1.77 (br.m, 1H), 1.87-2.28 (br.m, 5H), 2.30-2.55 (br.m, 3H; CH_3S), 2.59-3.65 (br.m, 8H), 3.72-4.46 (br.m, 7H), 4.58-4.79 (br.m, 1H), 5.38-5.88 (br.m, 2H), 6.69-7.42 (br.m, 6H) ppm. $^{13}C\{^1H\}$ NMR[a] (125.7 MHz, CD_2Cl_2, ambient temperature): δ = 21.14 and 22.06 (br.s; CH_3S), 27.63 (s), 28.91 (s), 31.32 (s), 32.37 (s), 36.07-37.16 (br.m), 44.92 (br.s), 49.32-49.59 (m), 55.54 (br.s), 63.07 (s), 66.32-66.95 (br.m), 71.51-72.51 (br.m; CH_{2allyl} (*cis* position to P atom)), 80.15 (s), 81.35-82.16 (br.m; CH_{2allyl} (*trans* to P atom)), 116.19-116.37 (m), 122.46 (s), 124.31 (br.s; CH_{allyl}), 130.50 (s), 143.26-143.56 (br.m), 156.74 (s), 170.91-171.21 (m) (major signals); 24.26 (s), 26.32 (s), 27.09 (br.s), 27.91-28.01 (m), 28.51 (s), 30.38 (s), 31.91-32.07 (m), 47.12 (s), 51.83 (br.s), 54.85-54.97 (m), 58.81 (s), 61.34 (s), 61.69 (s), 62.39 (br.s), 63.25 (s) 68.46 (s), 114.16 (br.s), 121.00 (s), 121.93 (br,s), 130.50 (s), 126.19 (br.s), 130.06 (s), 130.16 (s) (minor signals) ppm. $^{31}P\{^1H\}$ NMR[a] (202.4 MHz, CD_2Cl_2, ambient temperature): δ = 116.07 and 116.72 (s), 117.38 and 117.80 (br.s) ppm. $C_{26}H_{42}BF_4N_4O_4PPdS$ (730.90): calcd. C 42.73, H 5.79, N 7.67; found C 42.45, H 5.85, N 7.81.

[a] The separate signals of *exo*- and *endo*- forms are listed in order of increasing chemical shifts using the conjunction "and".

Palladium-Catalyzed Asymmetric Allylic Alkylation of (*E*)-1,3-Diphenylallyl Ethyl Carbonate 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 CH_2Cl_2 (1.5 mL) was stirred for 40 min or the appropriate complex (0.01 mmol) was dissolved in CH_2Cl_2 (1.5 mL). (*E*)-1,3-diphenylallyl ethyl carbonate (**7**) (0.056 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 (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 (**8a**).[1] 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.

EXPERIMENTAL SECTION

Palladium-Catalyzed Asymmetric Allylic Amination of (*E*)-1,3-Diphenylallyl Ethyl Carbonate 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 CH_2Cl_2 (1.5 mL) was stirred for 40 min or the appropriate complex (0.01 mmol) was dissolved in CH_2Cl_2 (1.5 mL). (*E*)-1,3-diphenylallyl ethyl carbonate (**7**) (0.056 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 (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 (**8b**).[2] 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 or Ethyl 2-Oxocyclopentane-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 or the appropriate complex (0.01 mmol) was dissolved in toluene (1.5 mL). Cinnamyl acetate (**9**) (0.04 mL, 0.25 mmol) was added and the solution stirred for 15 min. β-Keto ether **10** or **12** (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 (**11**) or ethyl 1-cinnamyl-2-oxocyclopentane-1-carboxylate (**13**).[3] 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.

1. 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.
2. a) D. Smyth, H. Tye, C. Eldred, N. W. Alcock, M. Wills, *J. Chem. Soc., Perkin Trans. 1*, **2001**, 2840; b) J. Chen, F. Lang, D. Li, L. Cun, J. Zhu, J. Deng, J. Liao, *Tetrahedron: Asymmetry*, **2009**, *20*, 1953.
3. a) T. Nemoto, T. Matsumoto, T. Masuda, T. Hitomi, K. Hatano, Y. Hamada, *J. Am. Chem. Soc.*, **2004**, *126*, 3690; b) T. Nemoto, T. Masuda, T. Matsumoto, Y. Hamada, *J. Org. Chem.*, **2005**, *70*, 7172; c) Y. Kita, R. D. Kavthe, H. Oda, K. Mashima, *Angew. Chem. Int. Ed.*, **2016**, *55*, 1098.

NMR SPECTRA OF NEW COMPOUNDS

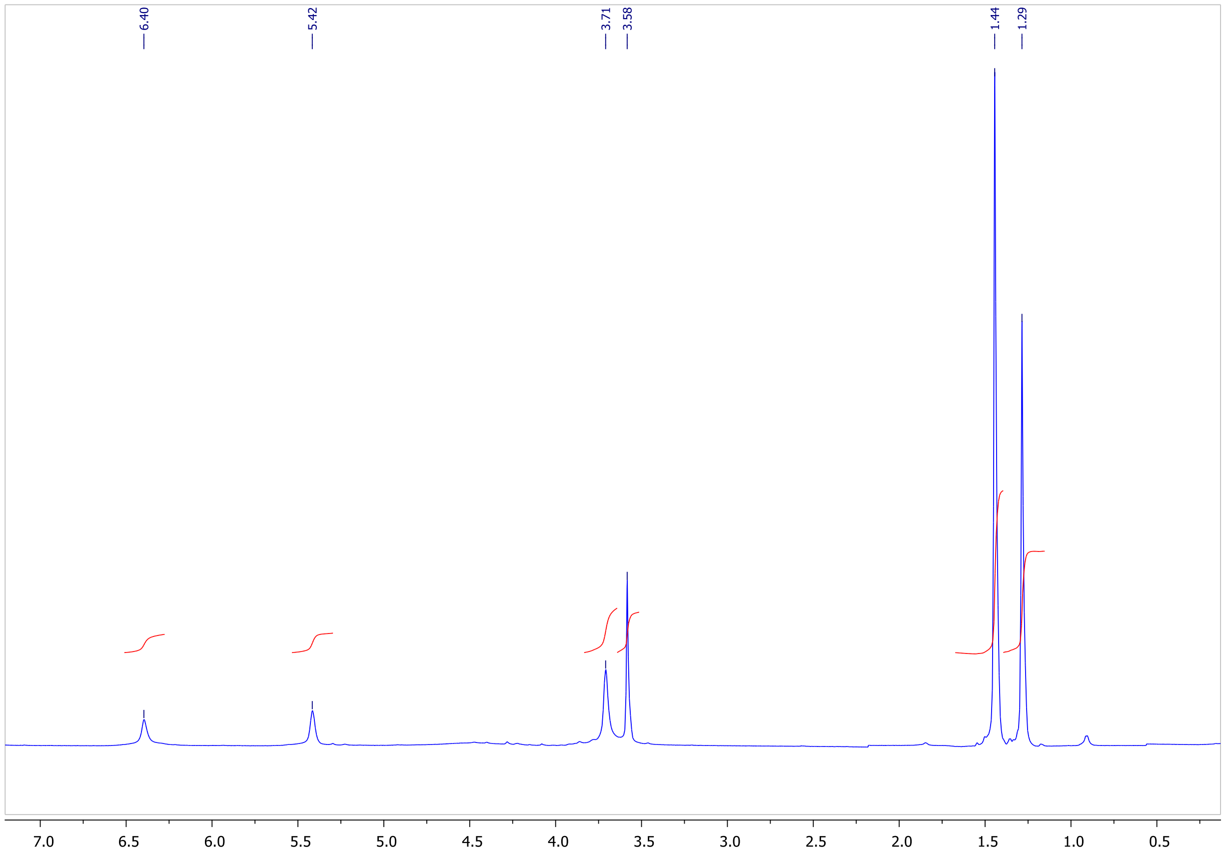


Figure S22a. **3a**, ^{1}H (600.1 MHz, $CDCl_3$, 19.7 °C).

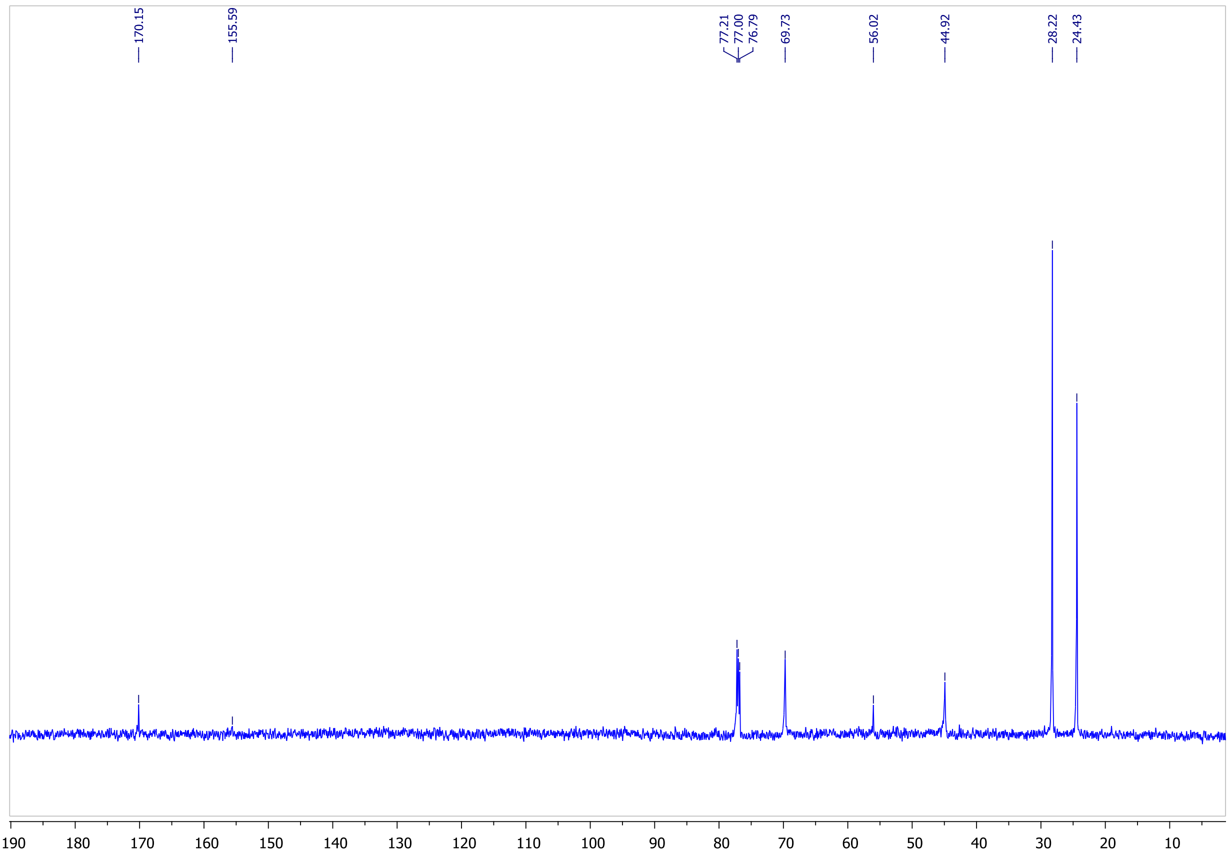


Figure S22b. **3a**, ^{13}C{^{1}H} (150.9 MHz, $CDCl_3$, 23.10 °C).

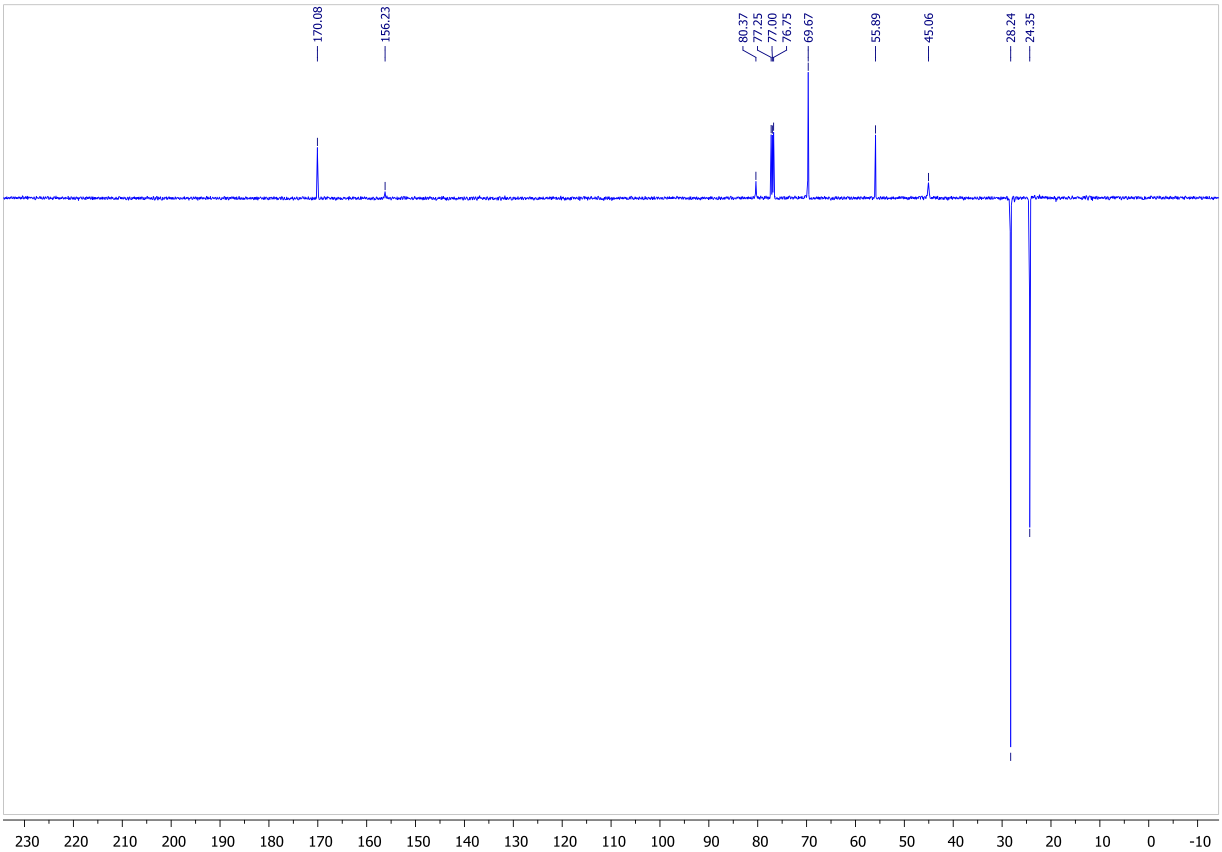


Figure S22c. **3a**, $^{13}C\{^{1}H\}$ APT (125.7 MHz, $CDCl_3$, ambient temperature).

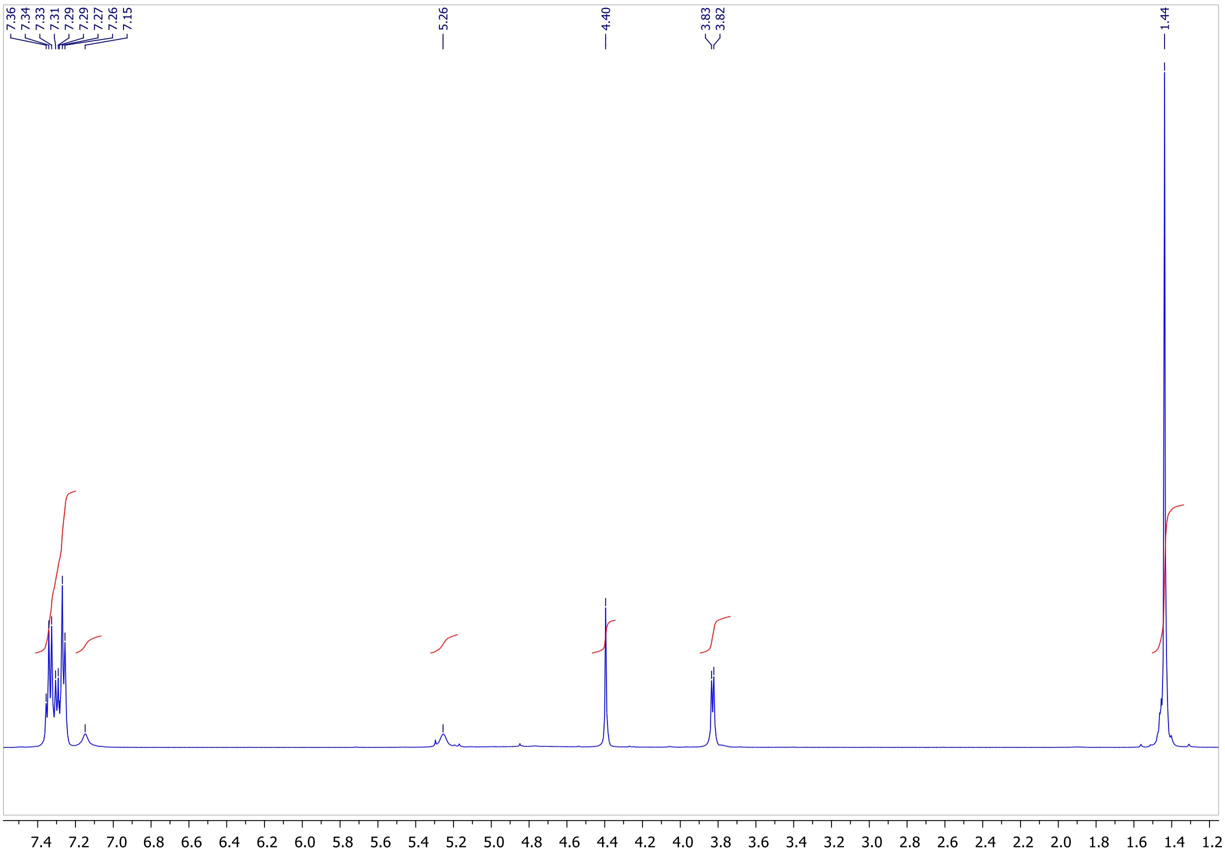


Figure S23a. **3b**, ^{1}H (499.9 MHz, $CDCl_3$, ambient temperature).

NMR SPECTRA OF NEW COMPOUNDS

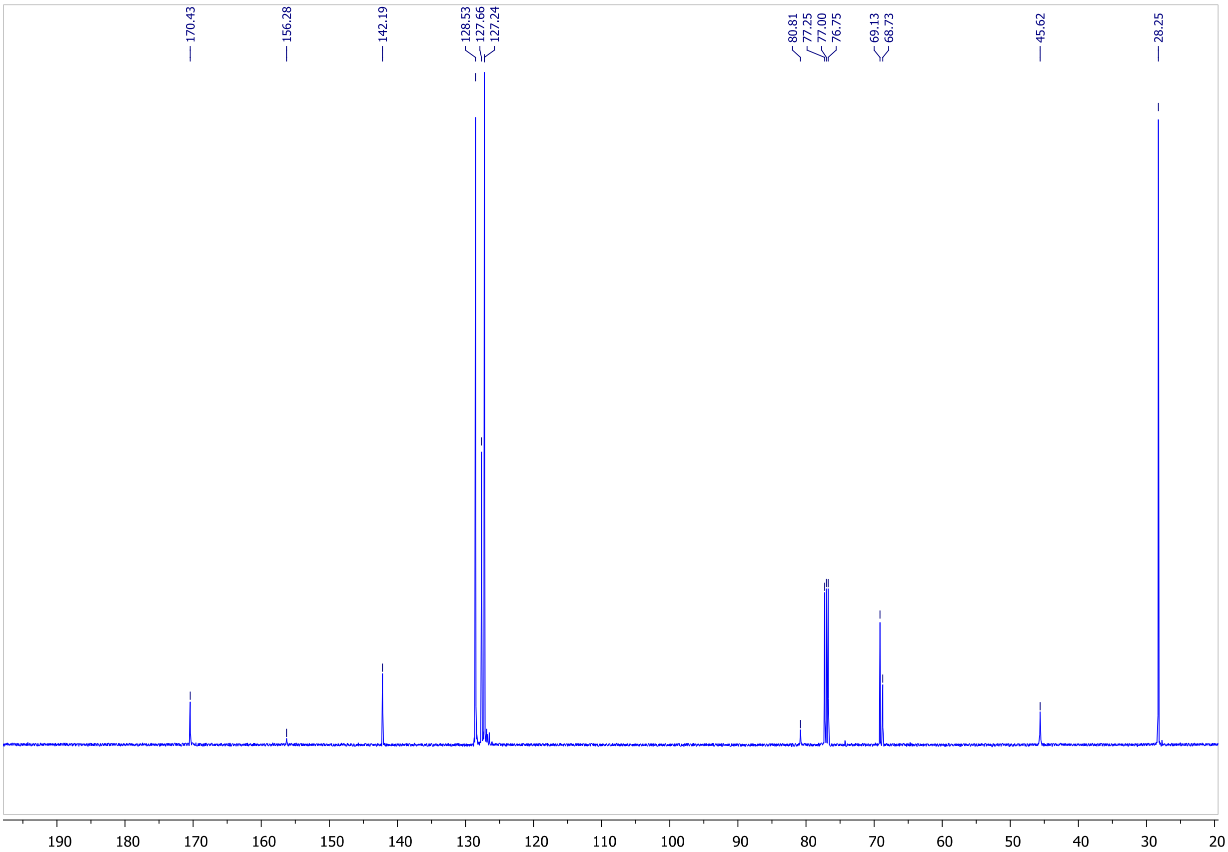


Figure S23b. **3b**, $^{13}C\{^{1}H\}$ (125.7 MHz, $CDCl_3$, ambient temperature).

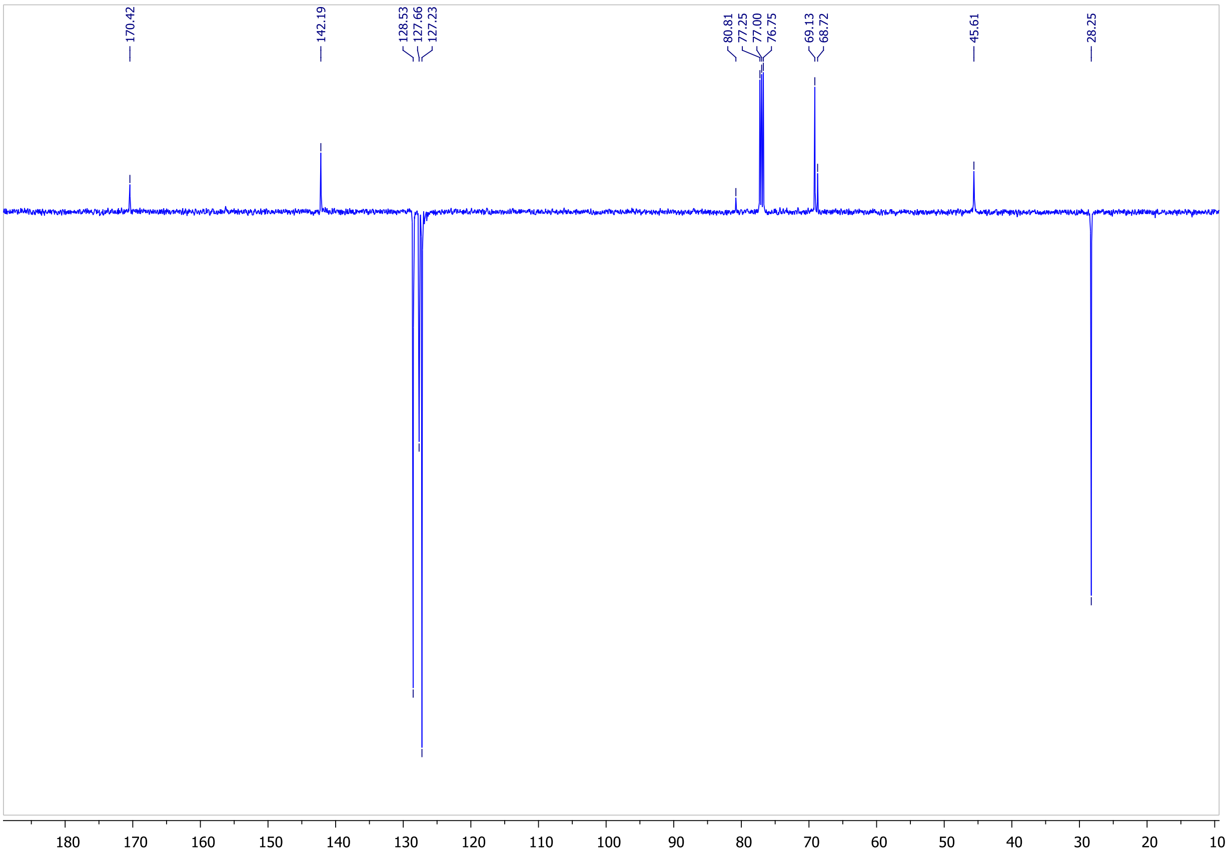


Figure S23c. **3b**, $^{13}C\{^{1}H\}$ APT (125.7 MHz, $CDCl_3$, ambient temperature).

NMR SPECTRA OF NEW COMPOUNDS

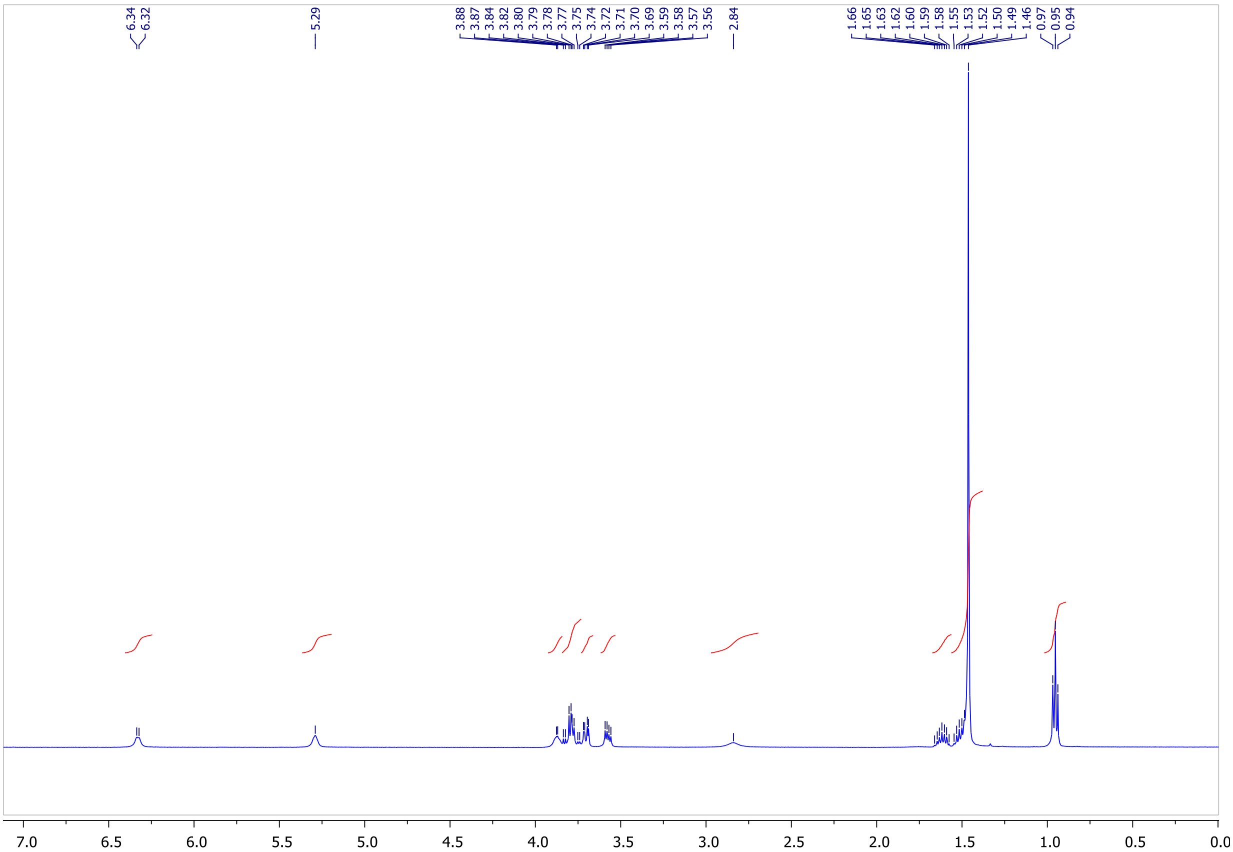


Figure S24a. **3c**, ^{1}H (499.9 MHz, $CDCl_3$, ambient temperature).

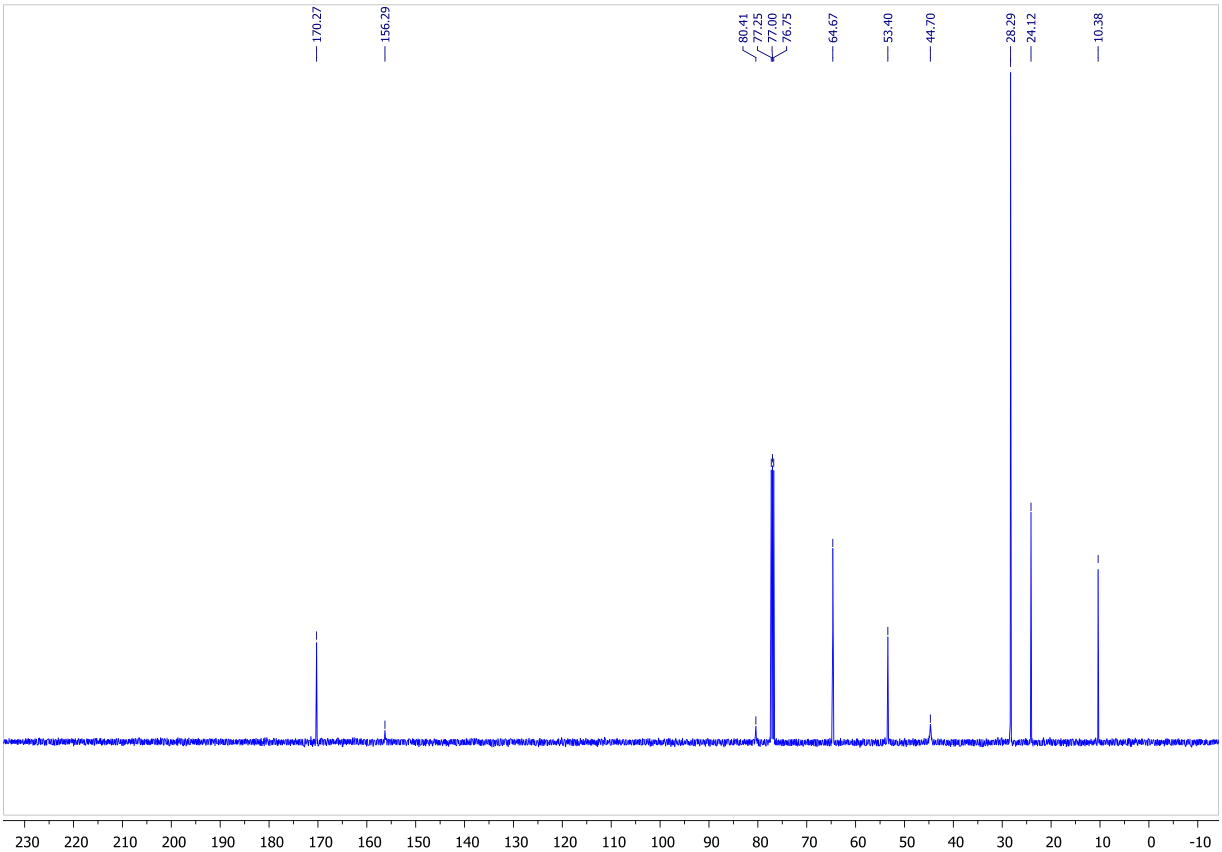


Figure S24b. **3c**, $^{13}C\{^{1}H\}$ (125.7 MHz, $CDCl_3$, ambient temperature).

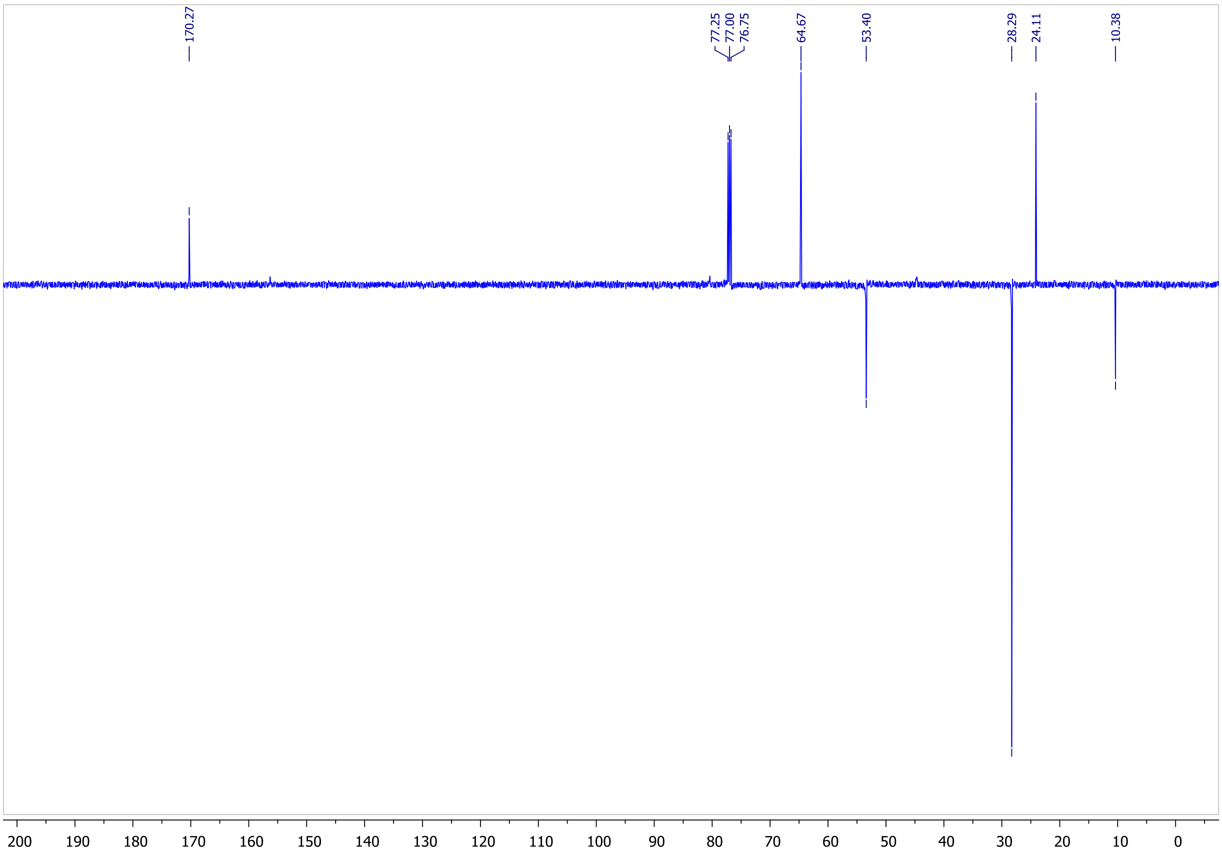


Figure S24c. **3c**, $^{13}C\{^{1}H\}$ APT (125.7 MHz, $CDCl_3$, ambient temperature).

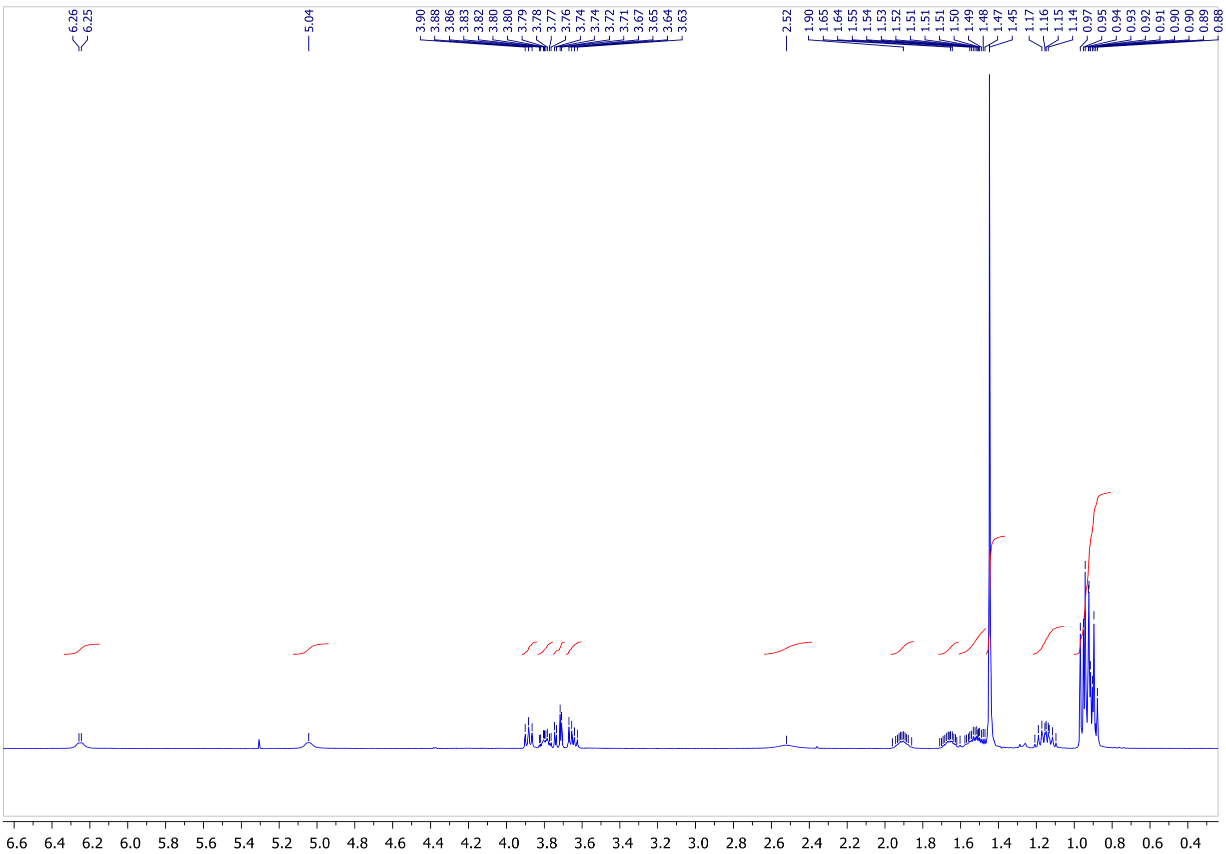


Figure S25a. **3e**, ^{1}H (400.1 MHz, $CDCl_3$, 27.0 °C).

NMR SPECTRA OF NEW COMPOUNDS

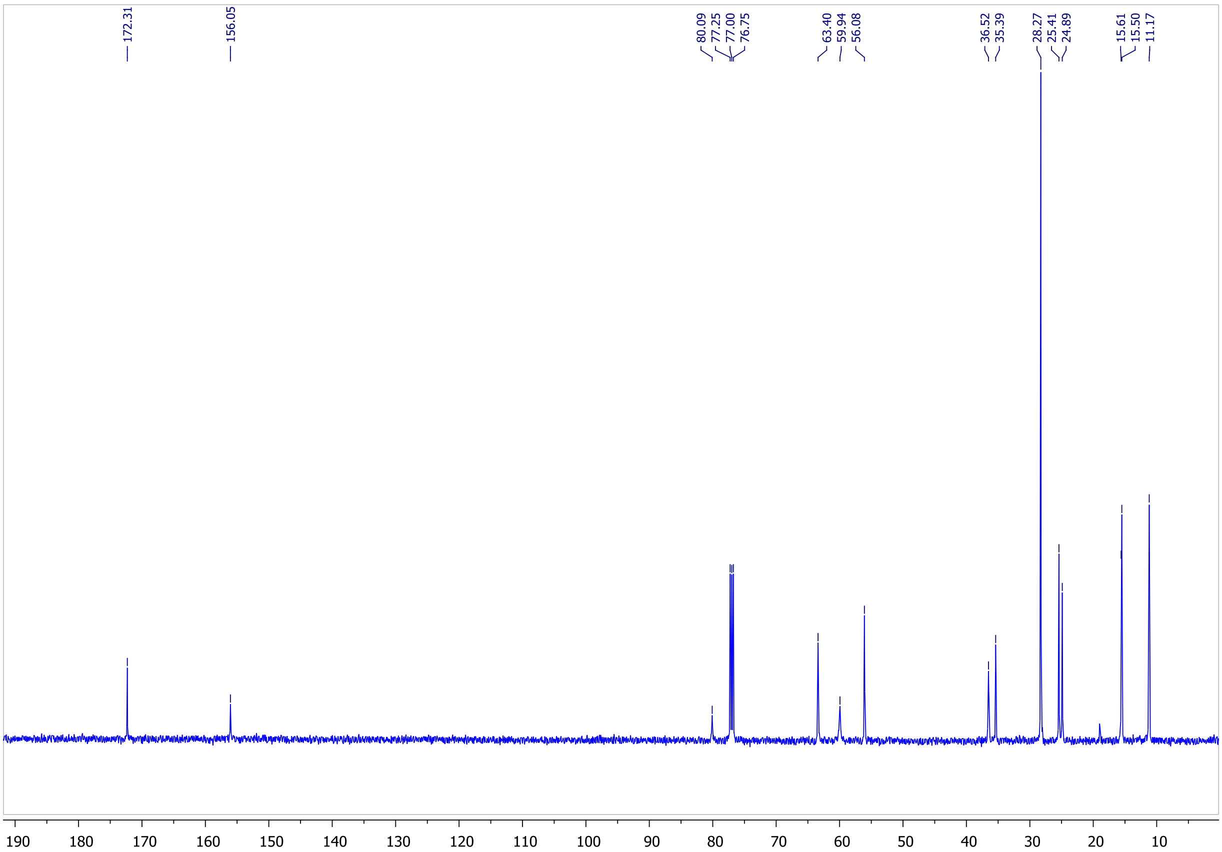


Figure S25b. **3e**, $^{13}C\{^1H\}$ (125.7 MHz, $CDCl_3$, ambient temperature).

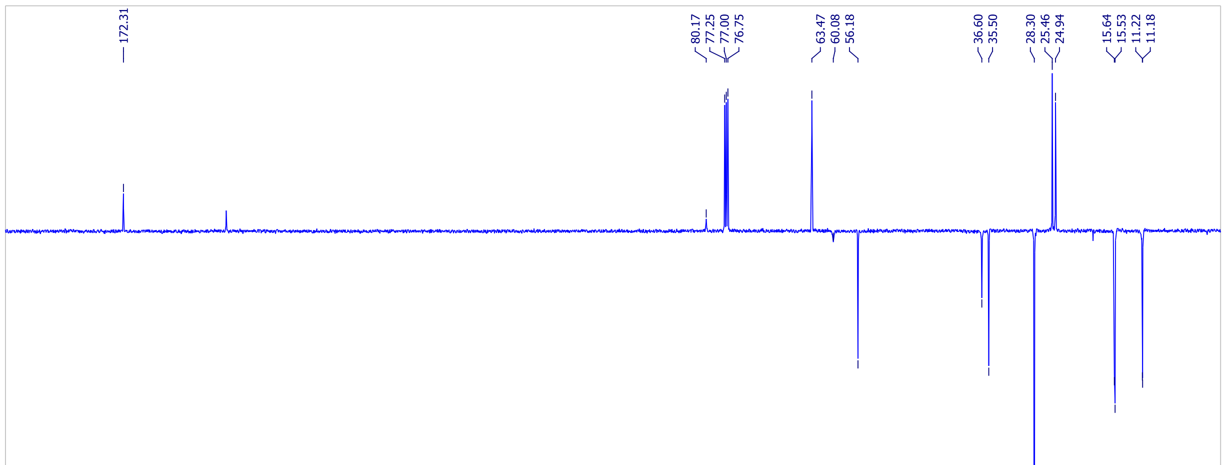


Figure S25c. **3e**, $^{13}C\{^1H\}$ APT (125.7 MHz, $CDCl_3$, ambient temperature).

NMR SPECTRA OF NEW COMPOUNDS

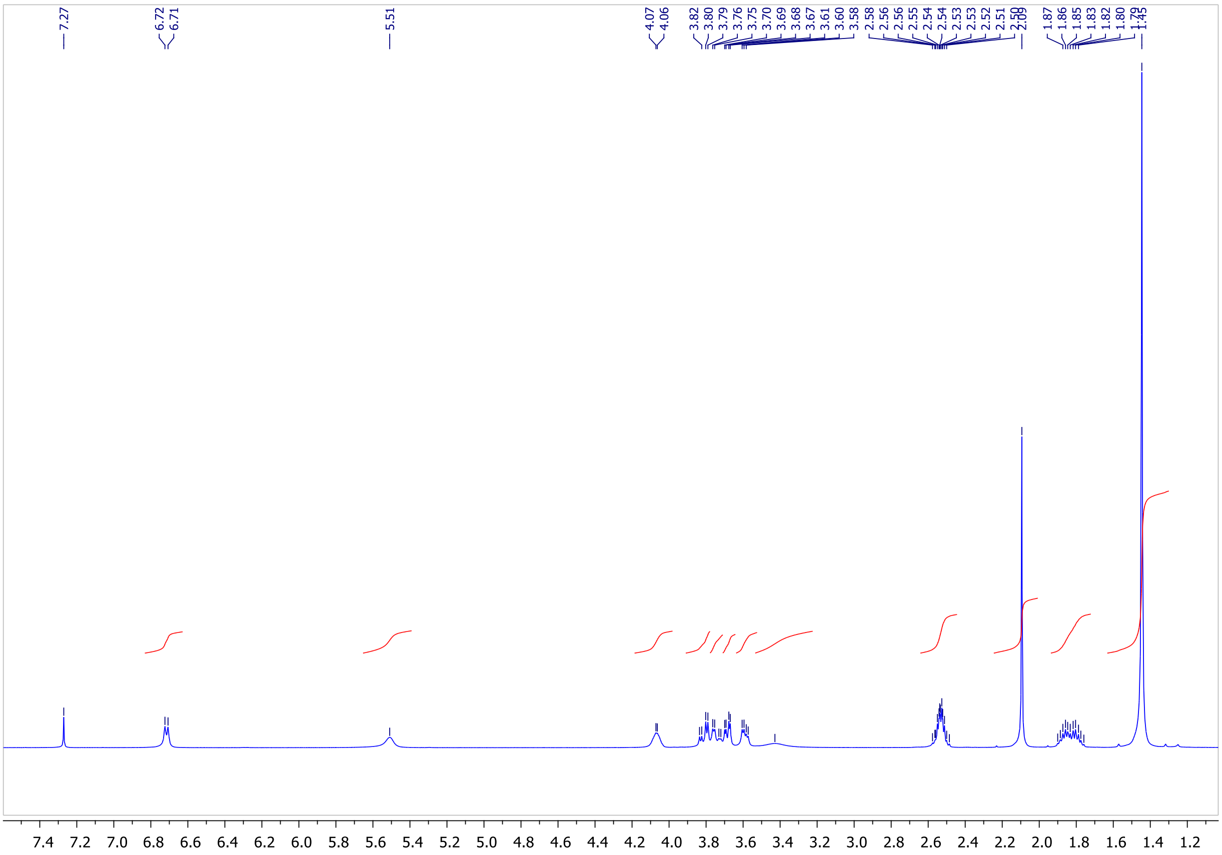


Figure S26a. **3f**, ^{1}H (499.9 MHz, $CDCl_3$, ambient temperature).

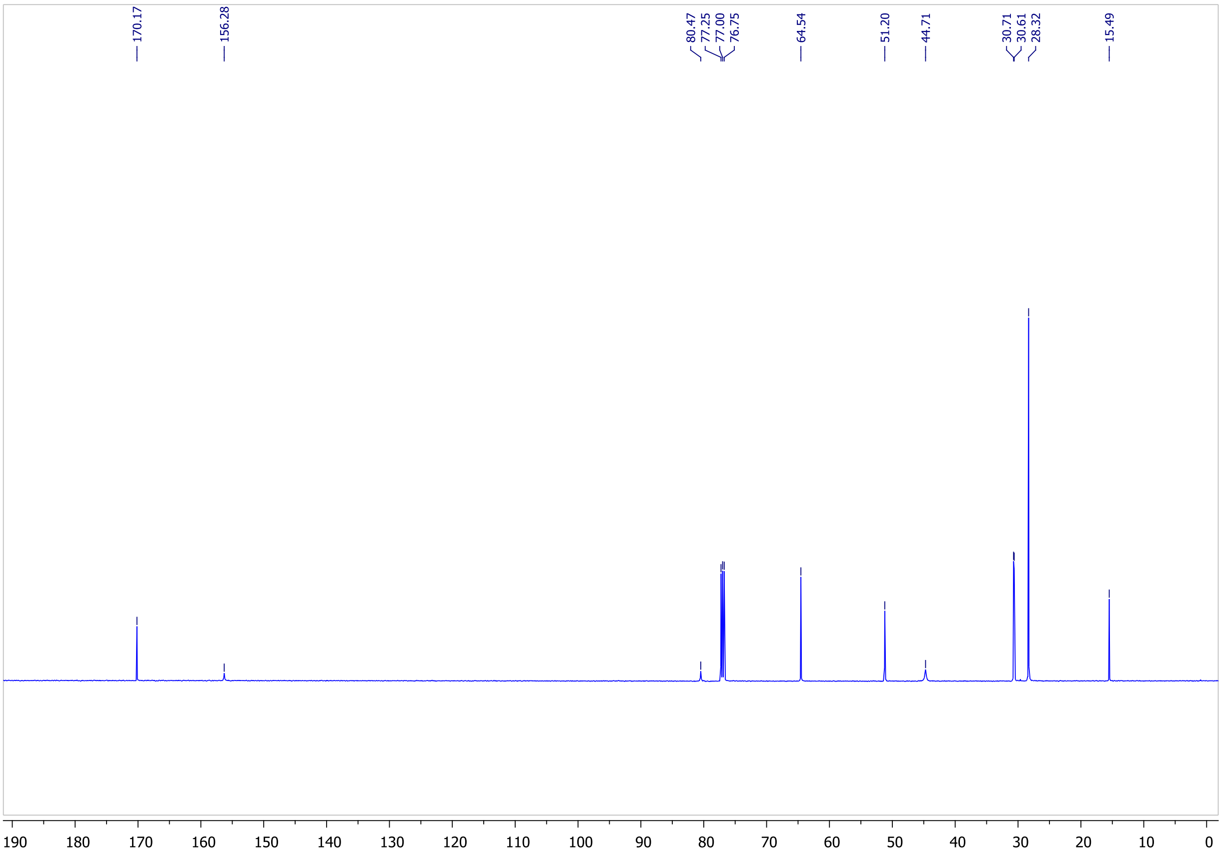


Figure S26b. **3f**, $^{13}C\{^{1}H\}$ (125.7 MHz, $CDCl_3$, ambient temperature).

NMR SPECTRA OF NEW COMPOUNDS

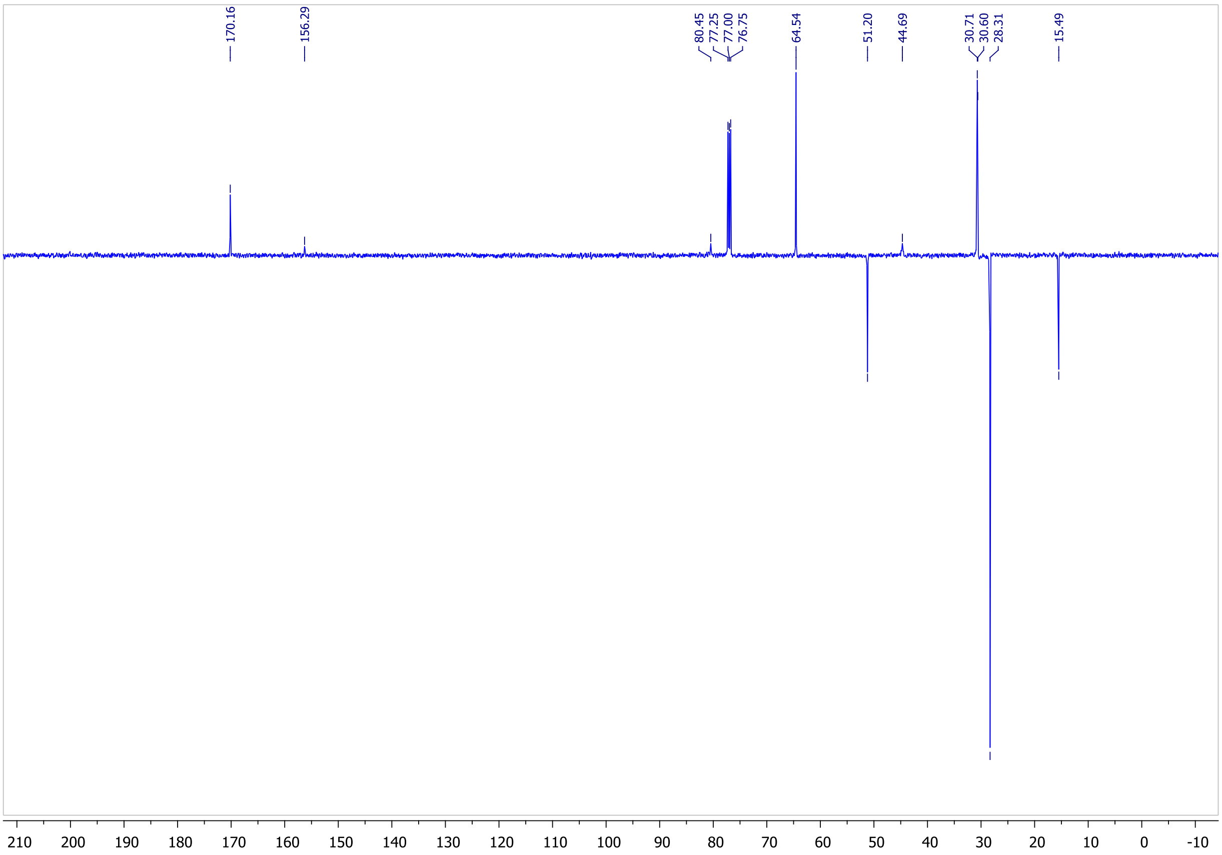


Figure S26c. **3f**, $^{13}C\{^1H\}$ APT (125.7 MHz, $CDCl_3$, ambient temperature).

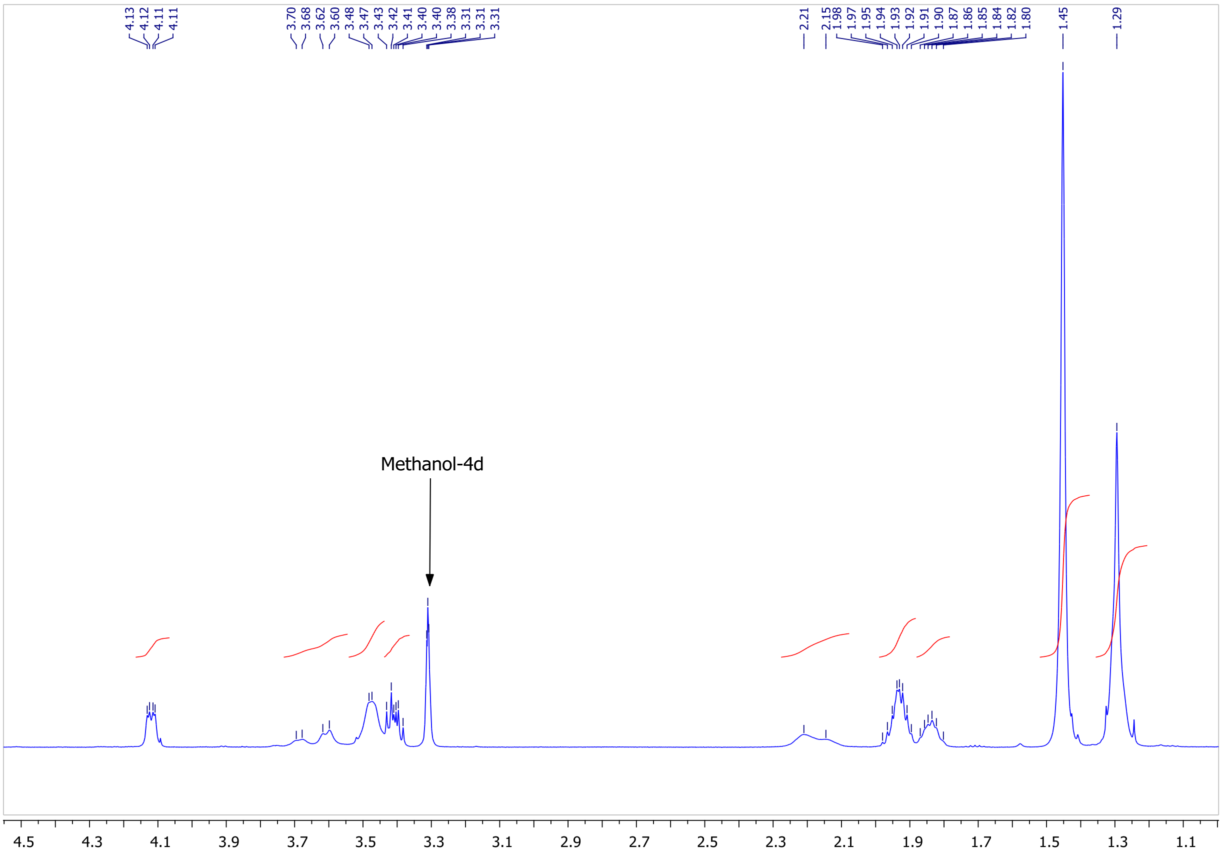


Figure S27a. **4**, ^1H (499.9 MHz, CD_3OD, ambient temperature).

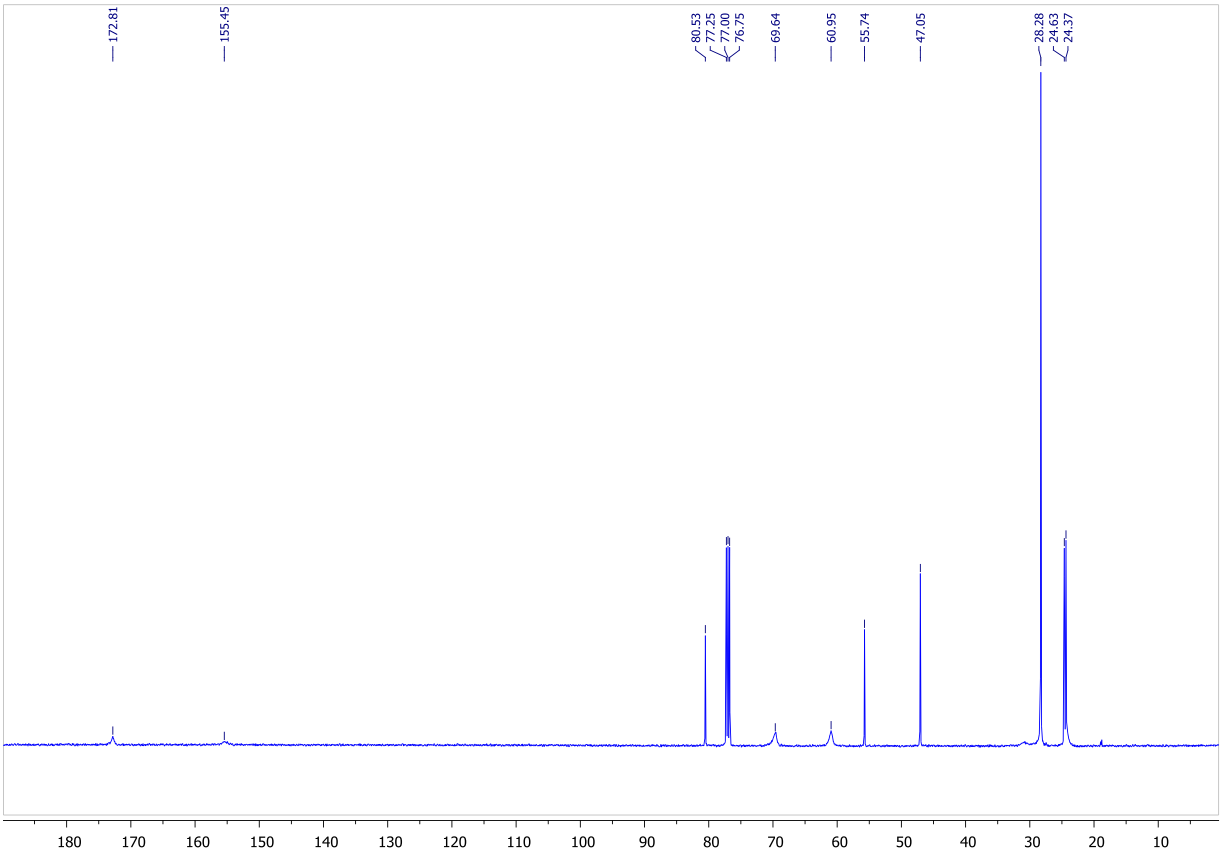


Figure S27b. **4**, $^{13}C\{^{1}H\}$ (125.7 MHz, $CDCl_3$, ambient temperature).

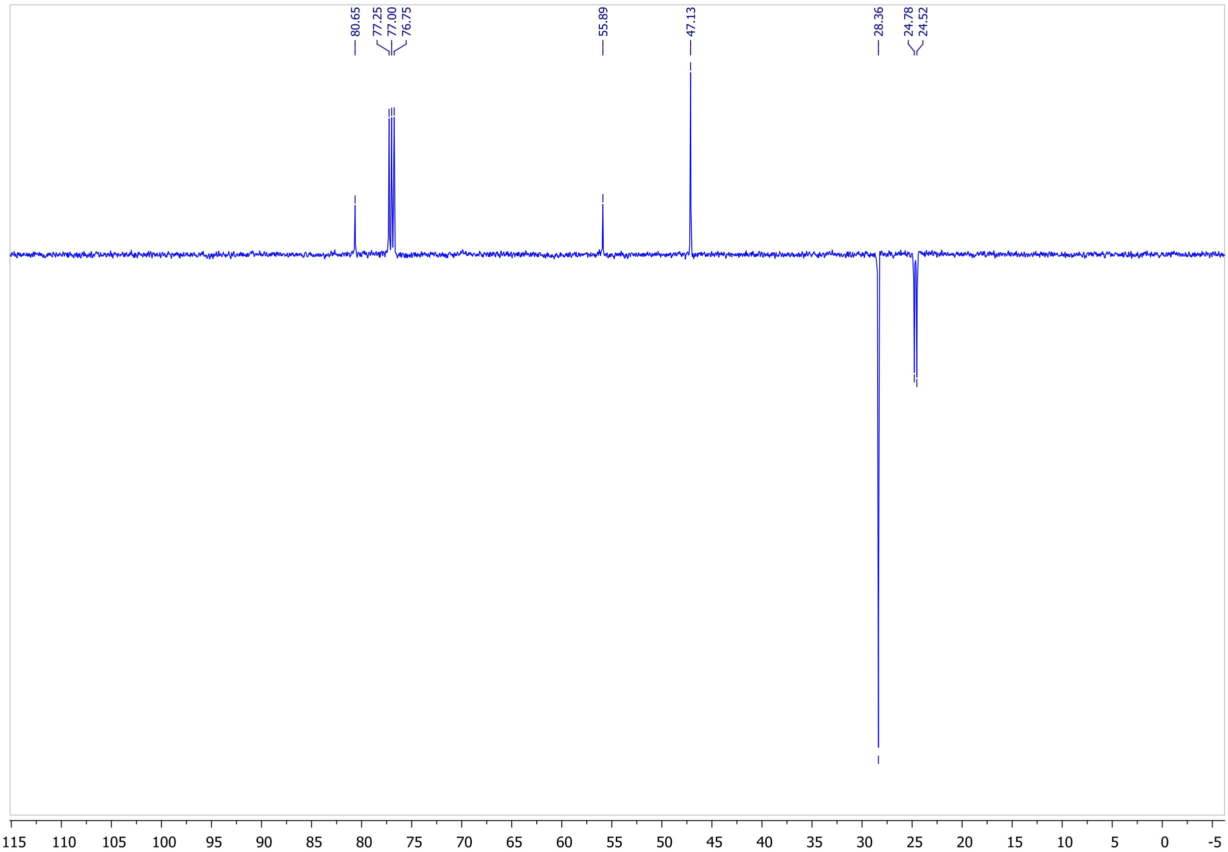


Figure S27c. **4**, $^{13}C\{^{1}H\}$ APT (125.7 MHz, $CDCl_3$, ambient temperature).

NMR SPECTRA OF NEW COMPOUNDS

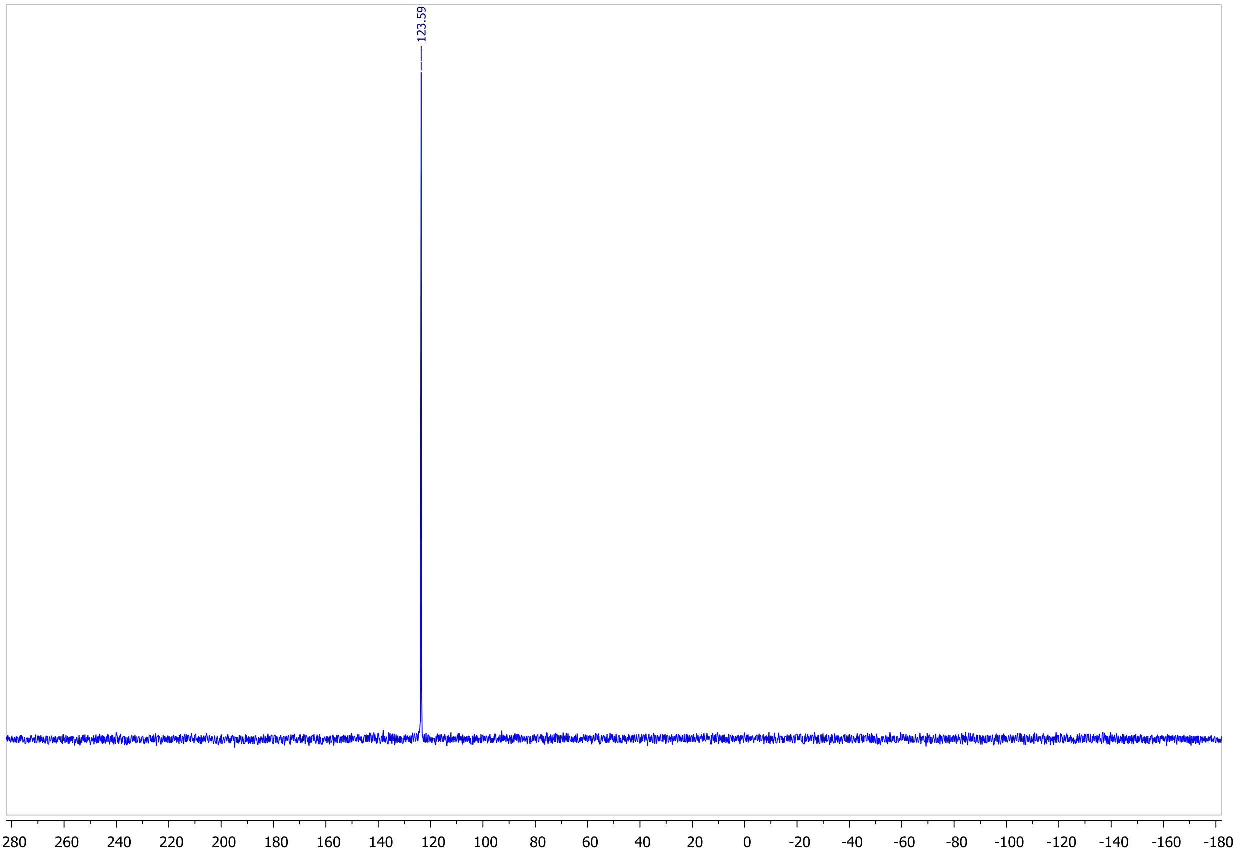


Figure S28a. **L1a**, $^{31}P\{^{1}H\}$ (202.4 MHz, $CDCl_3$, ambient temperature).

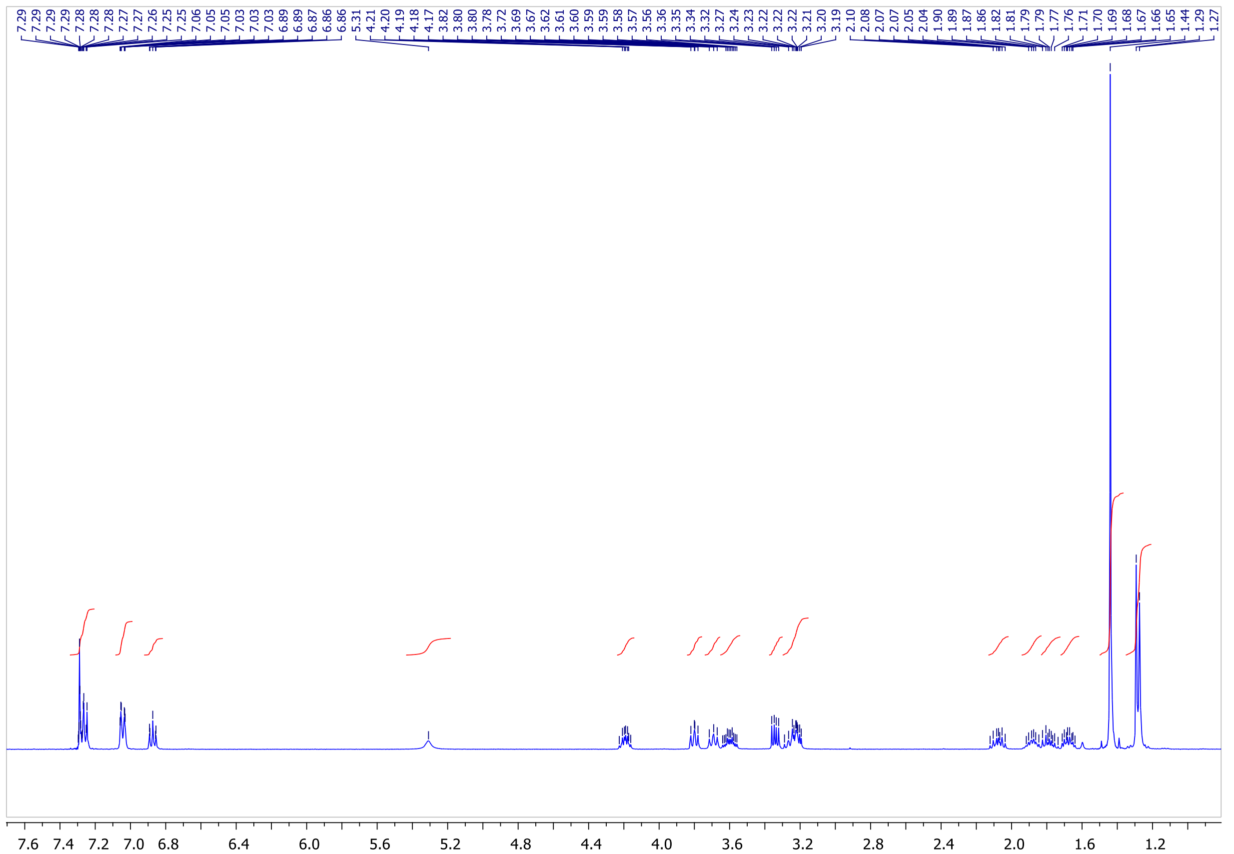


Figure S28b. **L1a**, ^{1}H (400.1 MHz, $CDCl_3$, 26 °C).

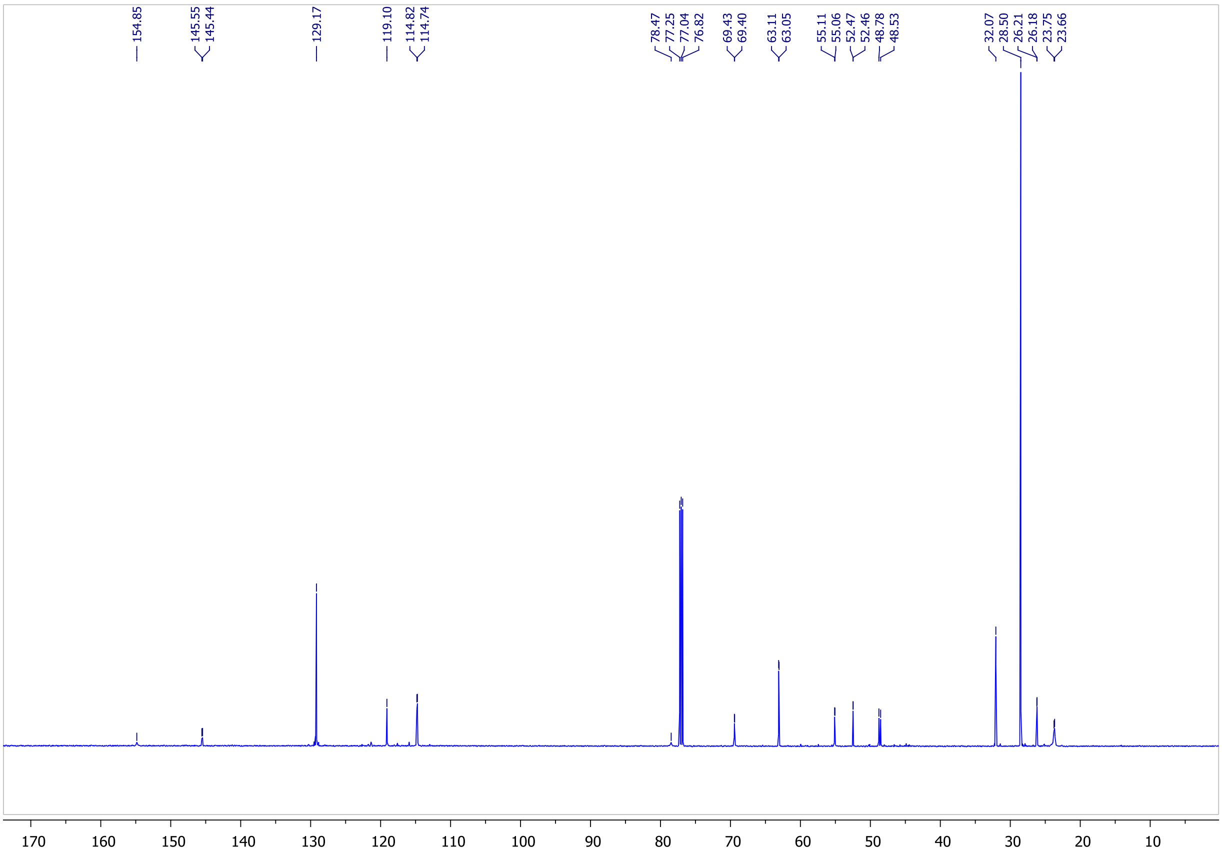


Figure S28c. **L1a**, $^{13}C\{^{1}H\}$ (150.9 MHz, $CDCl_3$, 27 °C).

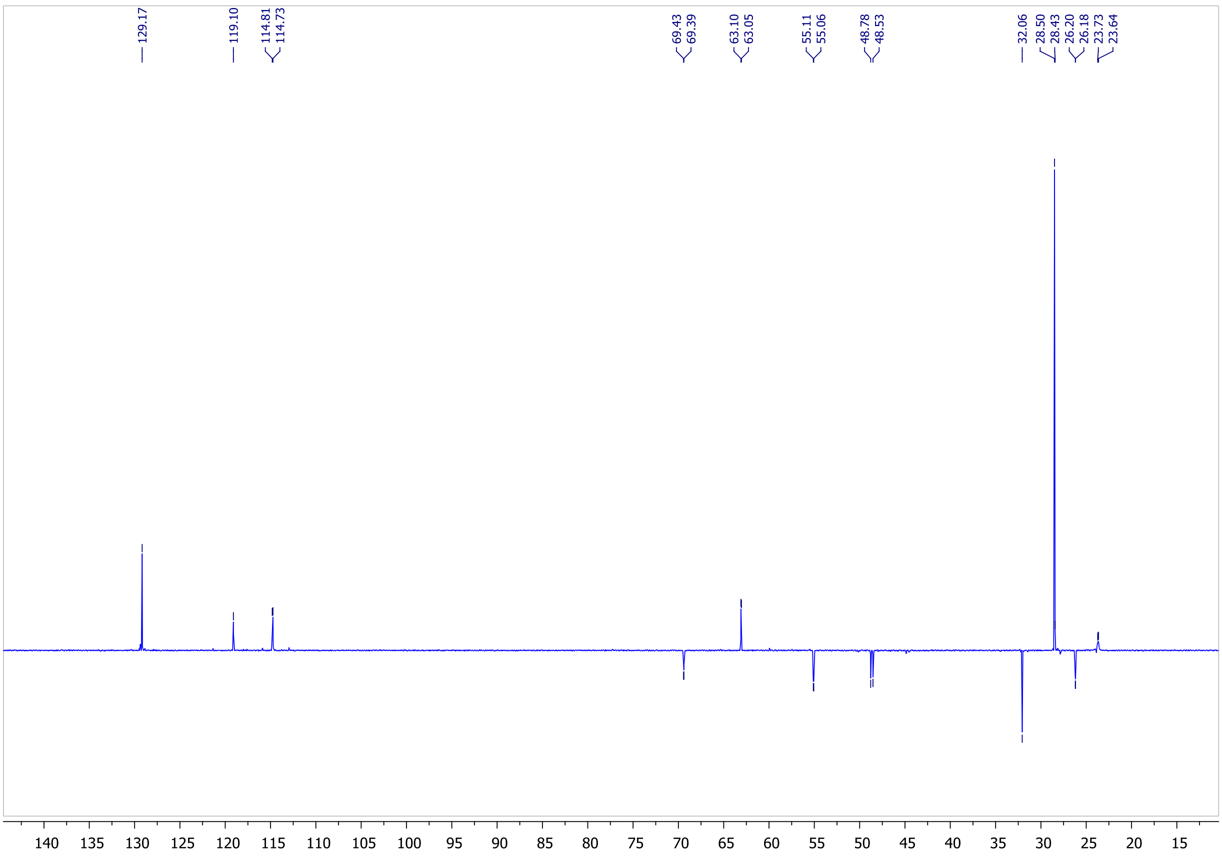


Figure S28d. **L1a**, $^{13}C\{^{1}H\}$ DEPT (150.9 MHz, $CDCl_3$, 27 °C).

NMR SPECTRA OF NEW COMPOUNDS

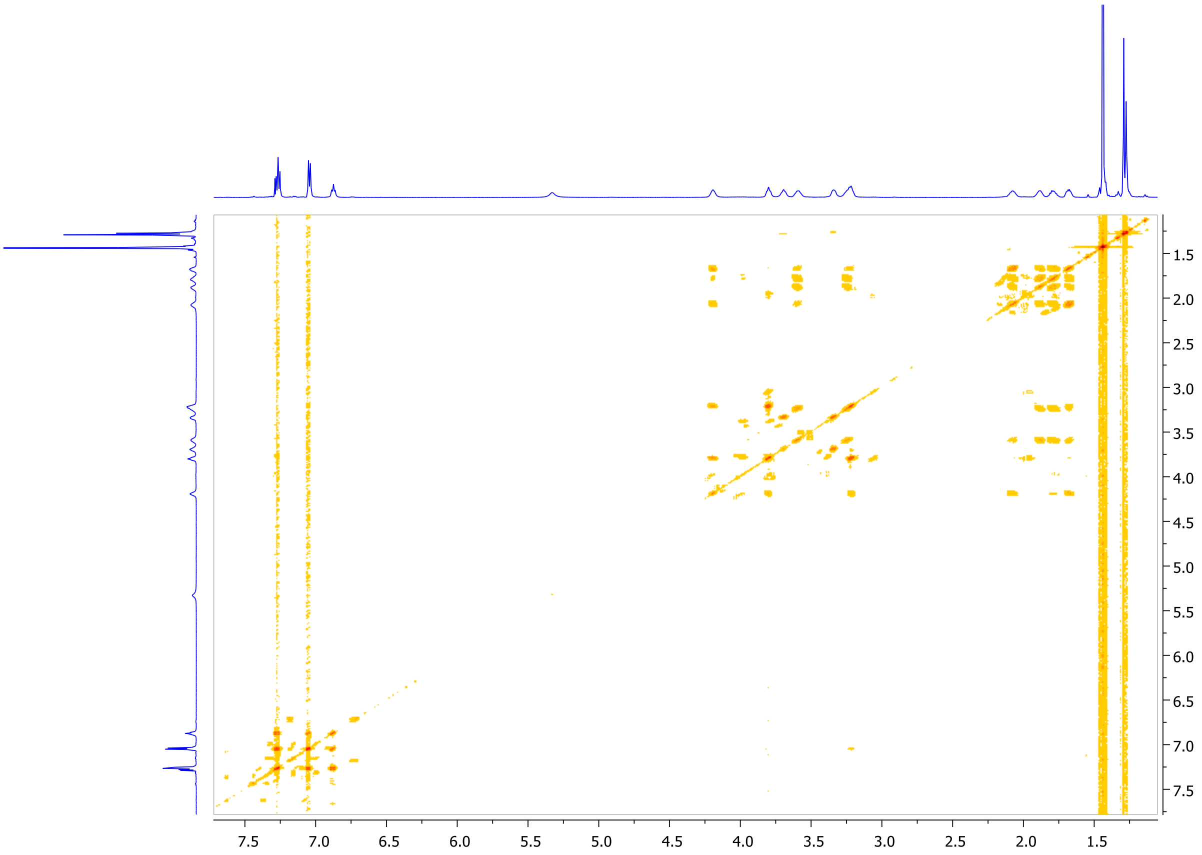


Figure S28e. **L1a**, ^{1}H-^{1}H COSY.

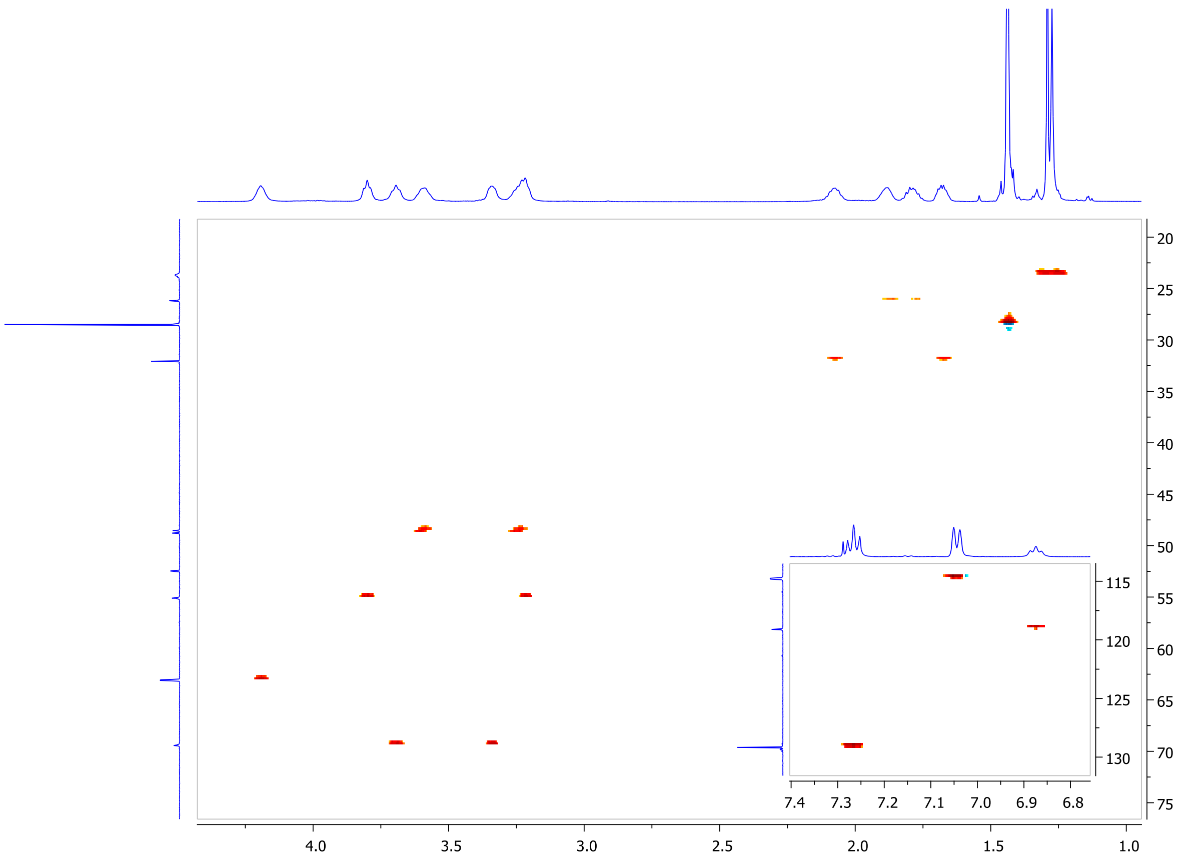


Figure S28f. **L1a**, ^{1}H-^{13}C HSQC.

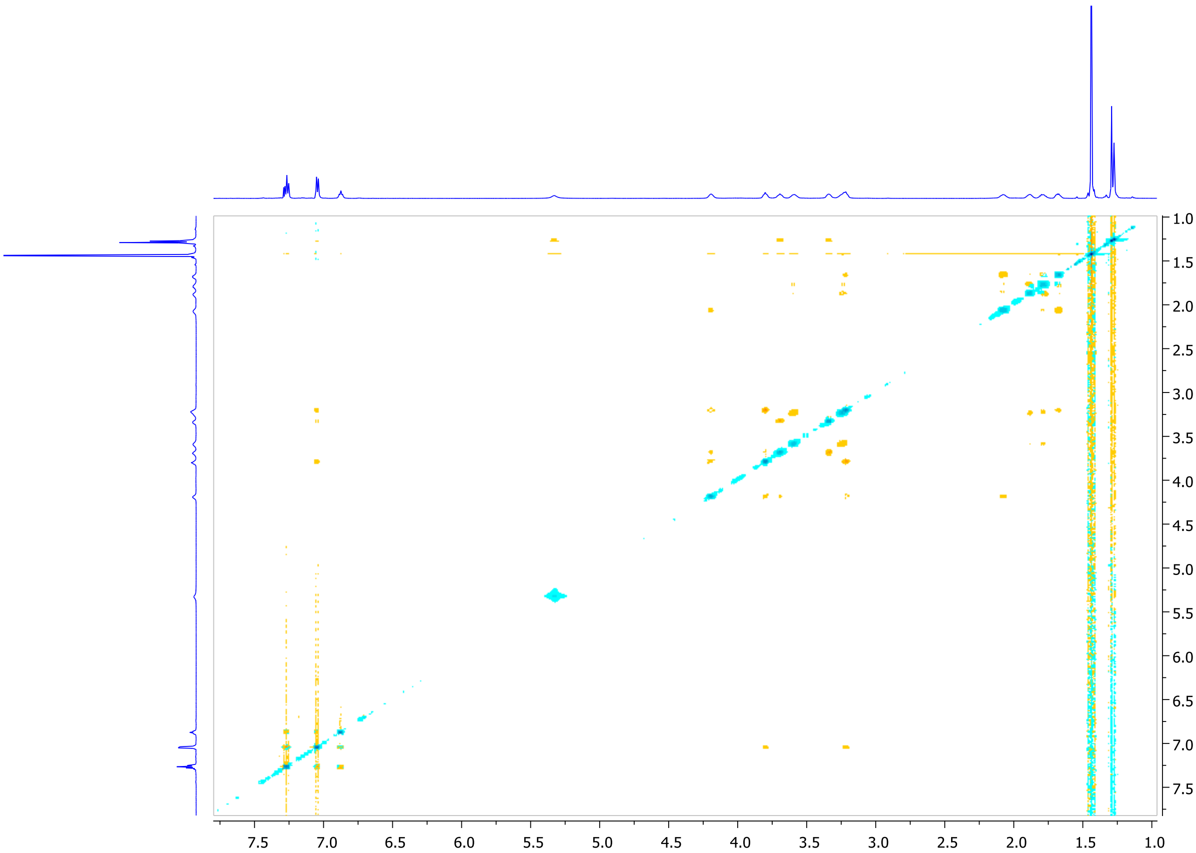


Figure S28g. **L1a**, ^{1}H-^{1}H NOESY.

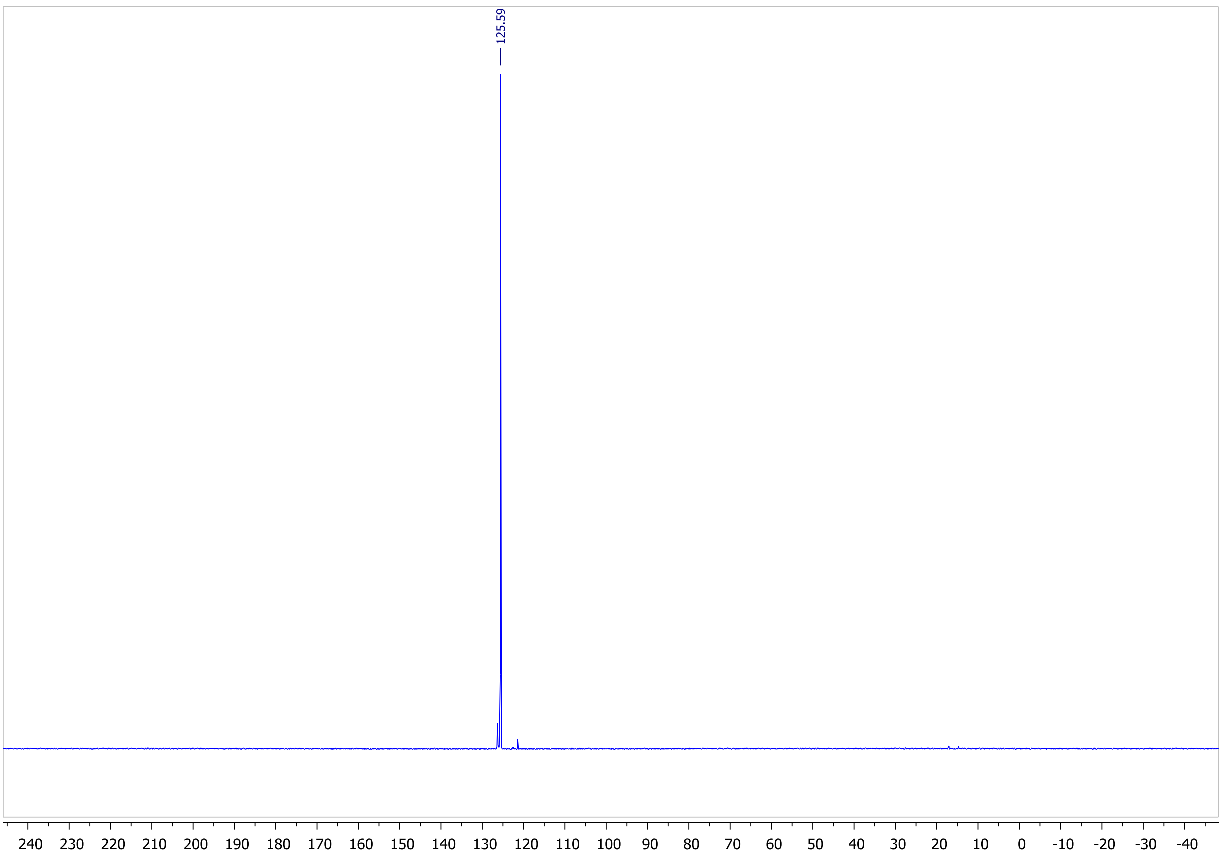


Figure S29a. **L1b**, $^{31}P\{^{1}H\}$ (162.0 MHz, $CDCl_3$, 27 °C).

NMR SPECTRA OF NEW COMPOUNDS

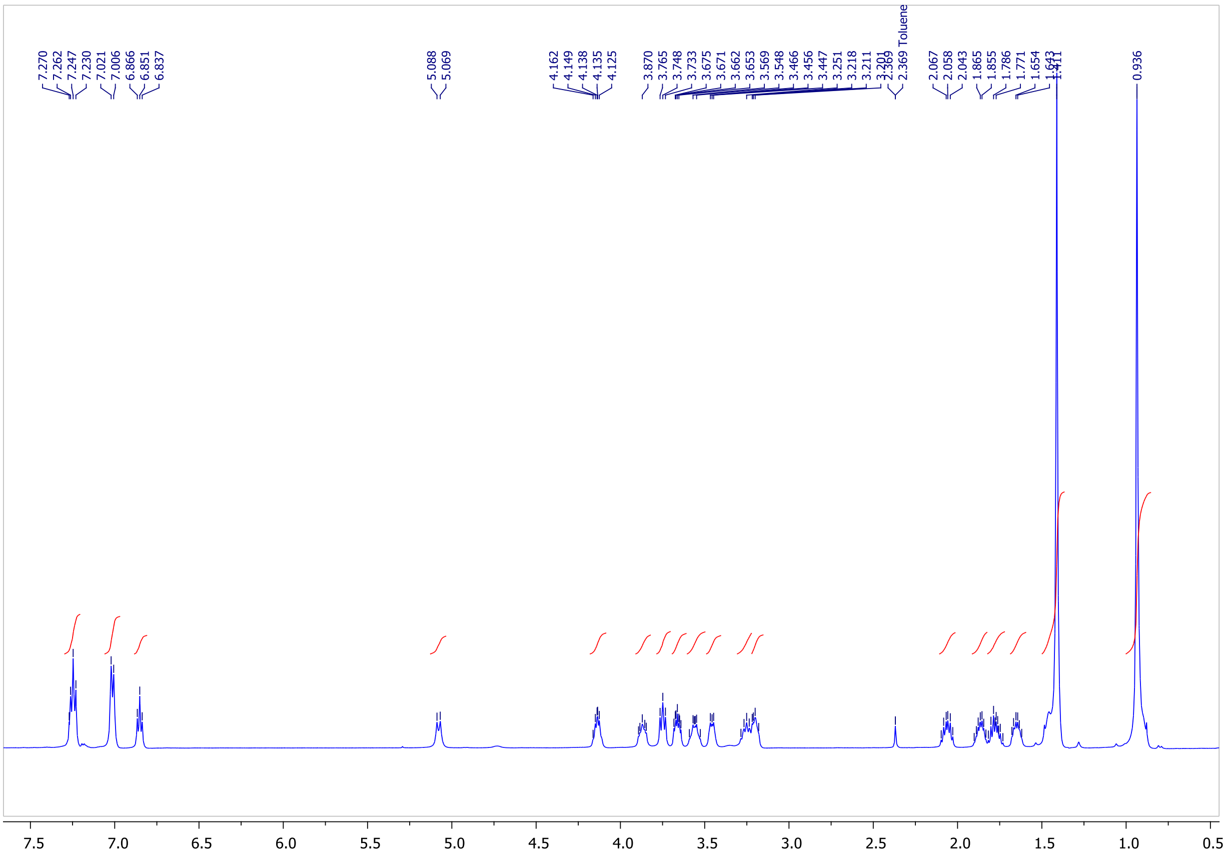


Figure S29b. **L1b**, ^{1}H (499.9 MHz, $CDCl_3$, ambient temperature).

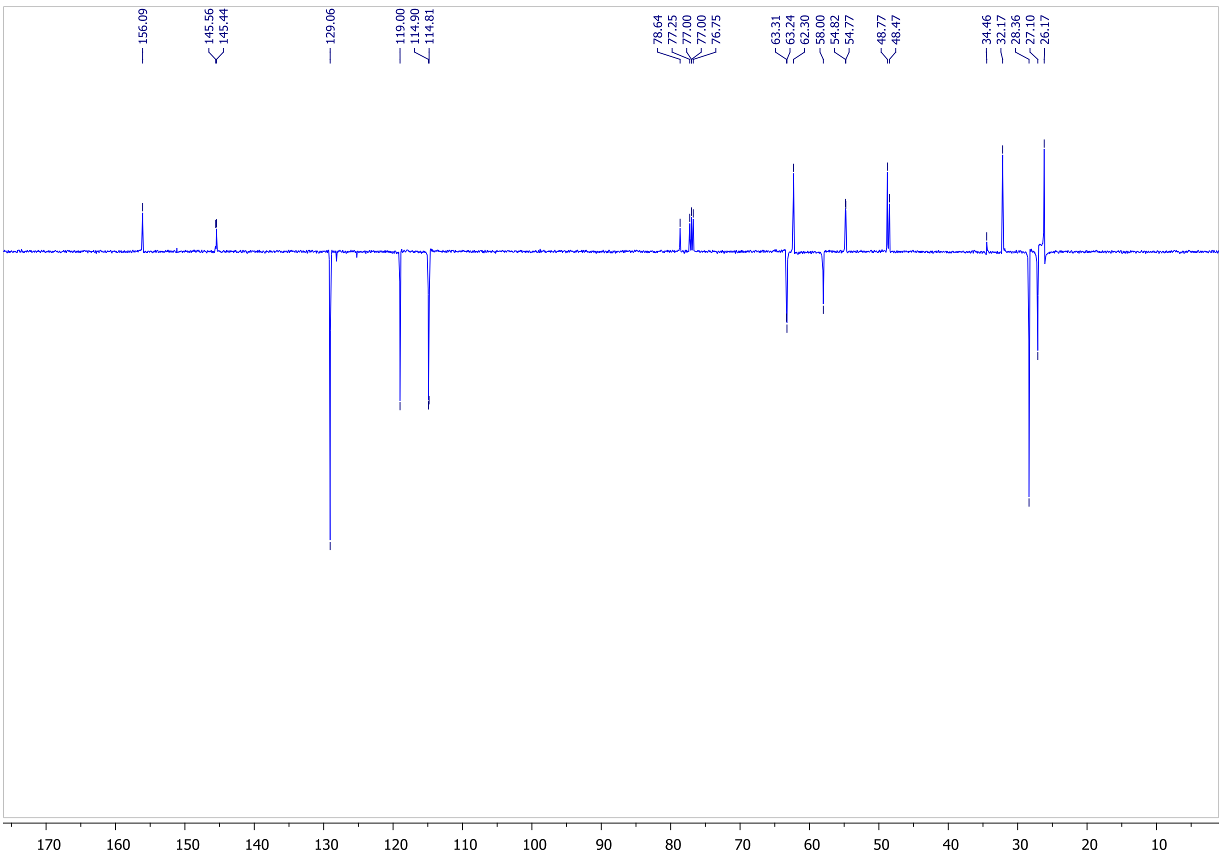


Figure S29c. **L1b**, $^{13}C\{^{1}H\}$ DEPT (125.7 MHz, $CDCl_3$, ambient temperature).

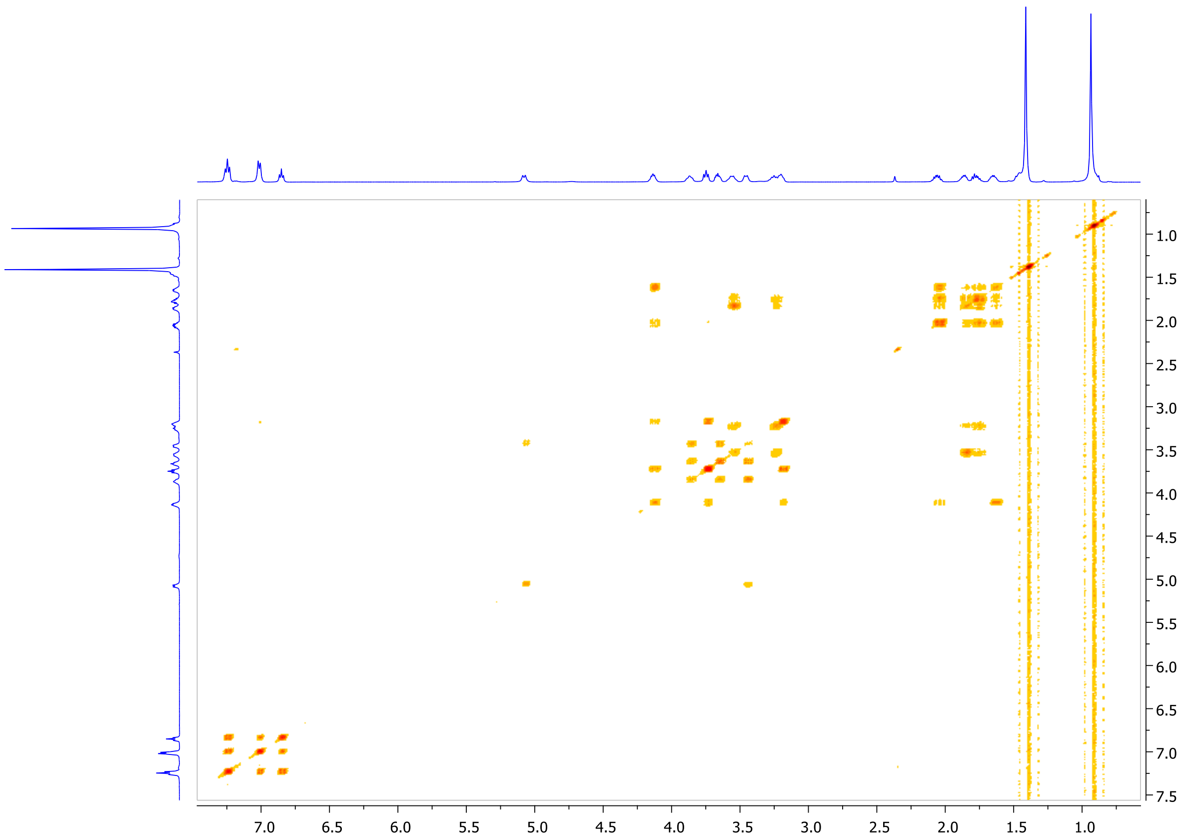


Figure S29d. **L1b**, ^{1}H-^{1}H COSY.

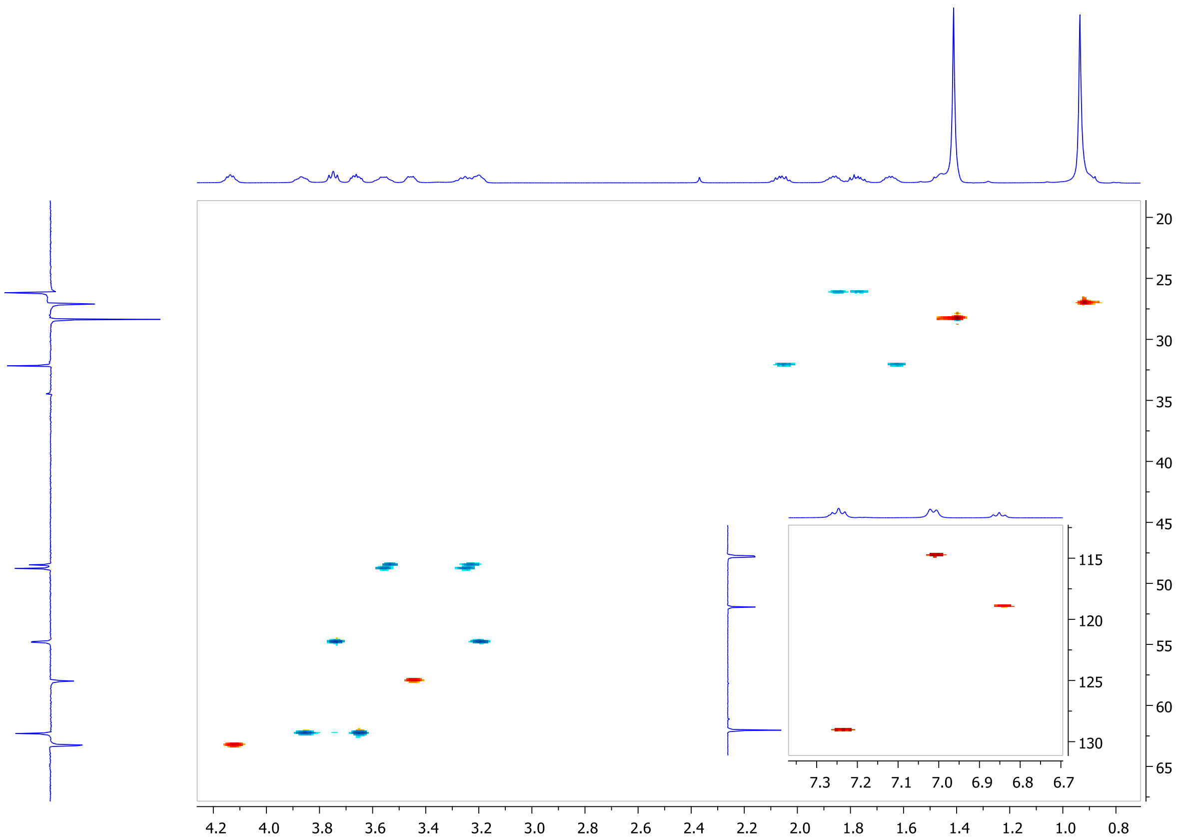


Figure S29e. **L1b**, ^{1}H-^{13}C HSQC.

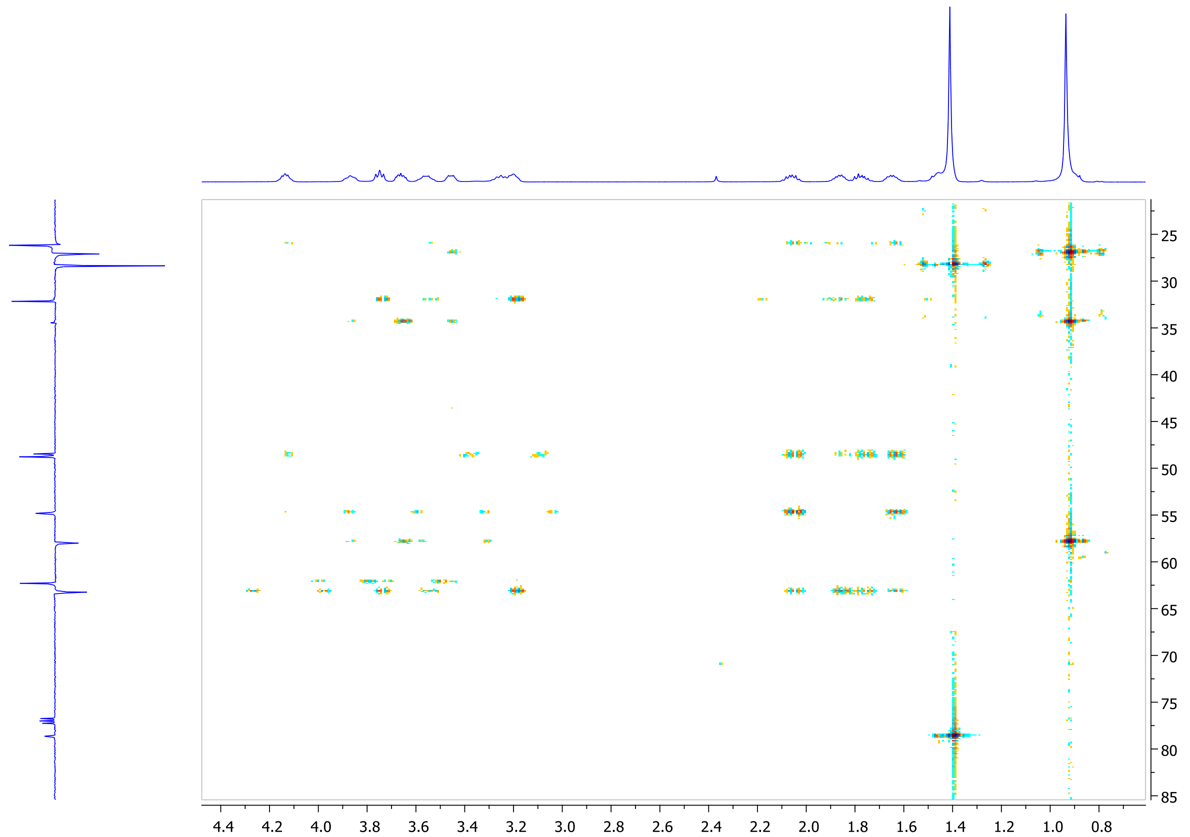


Figure S29f. **L1b**, ^{1}H-^{13}C HMBC (fragment of the spectrum).

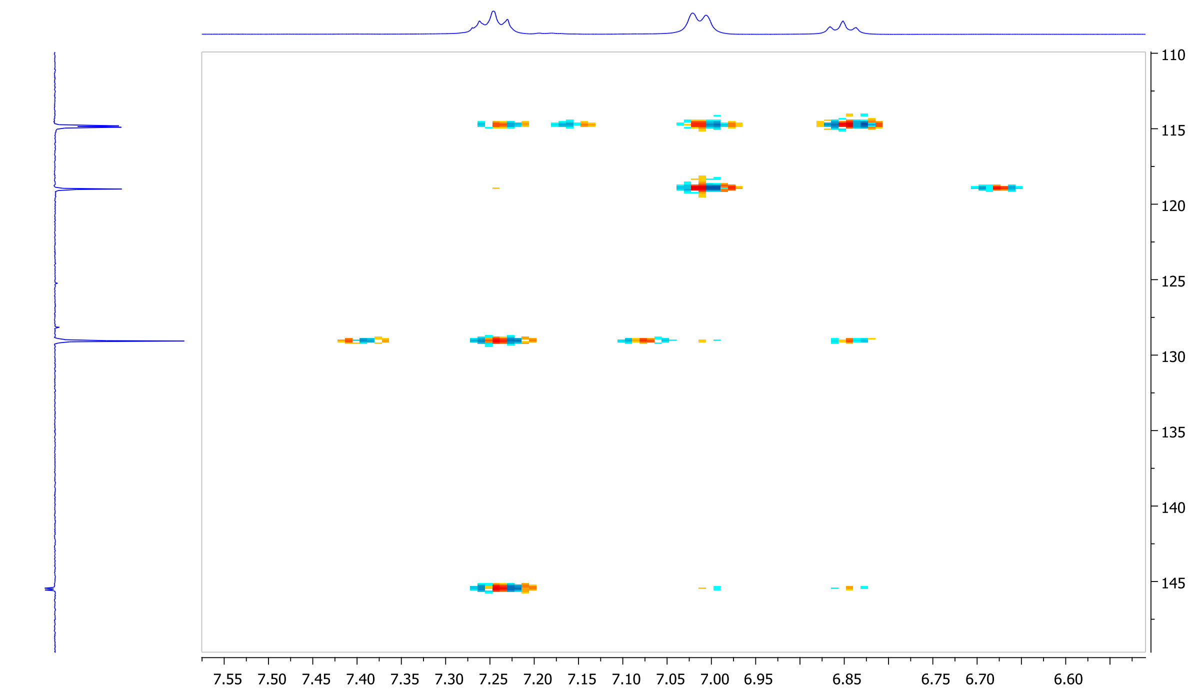


Figure S29g. **L1b**, ^{1}H-^{13}C HMBC (fragment of the spectrum).

NMR SPECTRA OF NEW COMPOUNDS

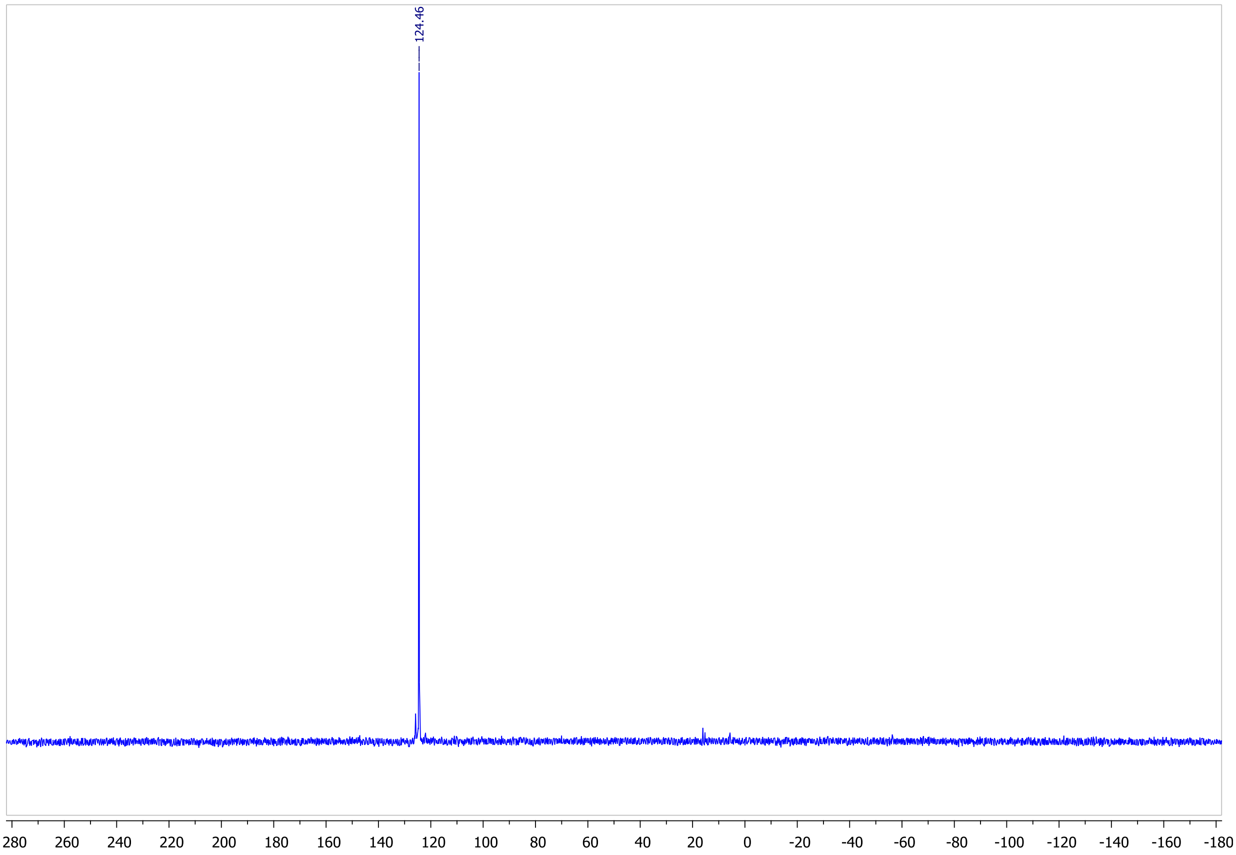


Figure S30a. **L1c**, $^{31}P\{^{1}H\}$ (162.0 MHz, $CDCl_3$, 27 °C).

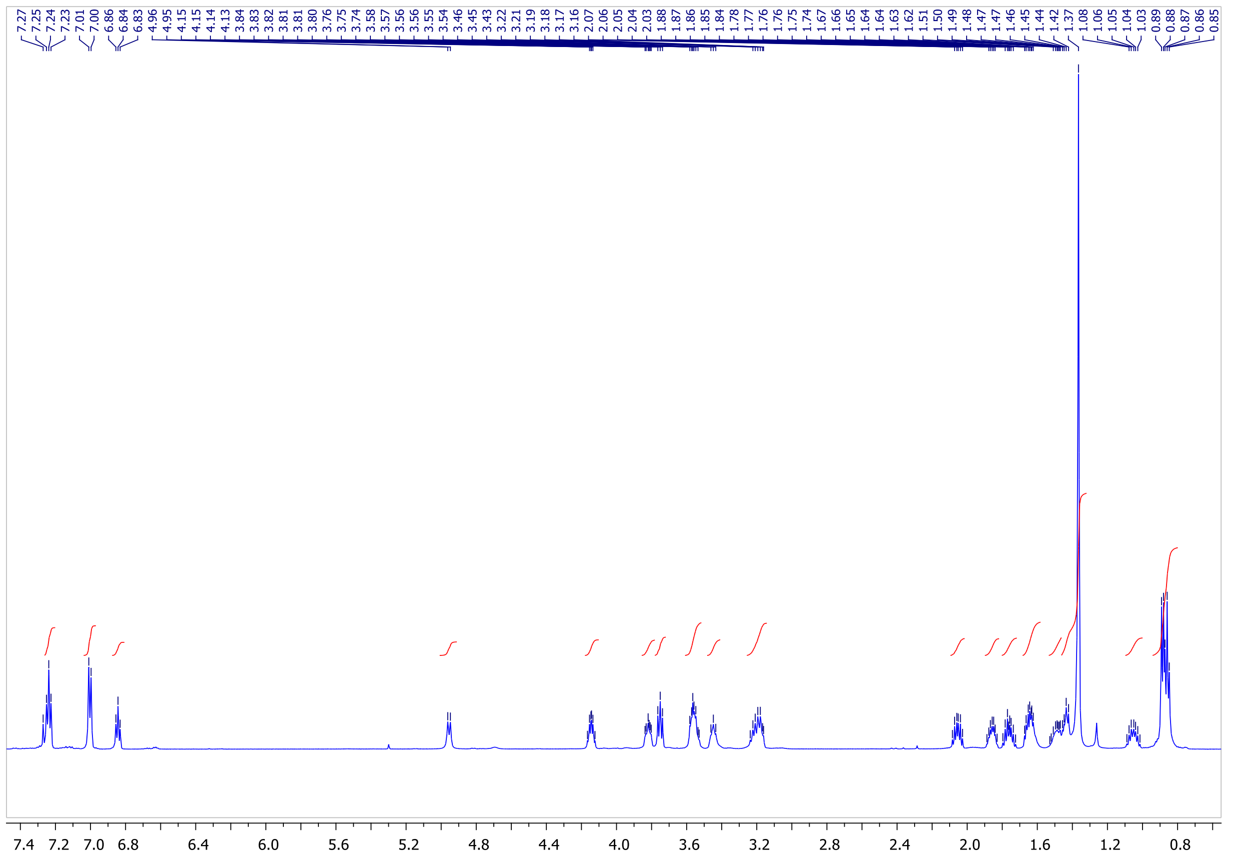


Figure S30b. **L1c**, ^{1}H (600.1 MHz, $CDCl_3$, 16 °C).

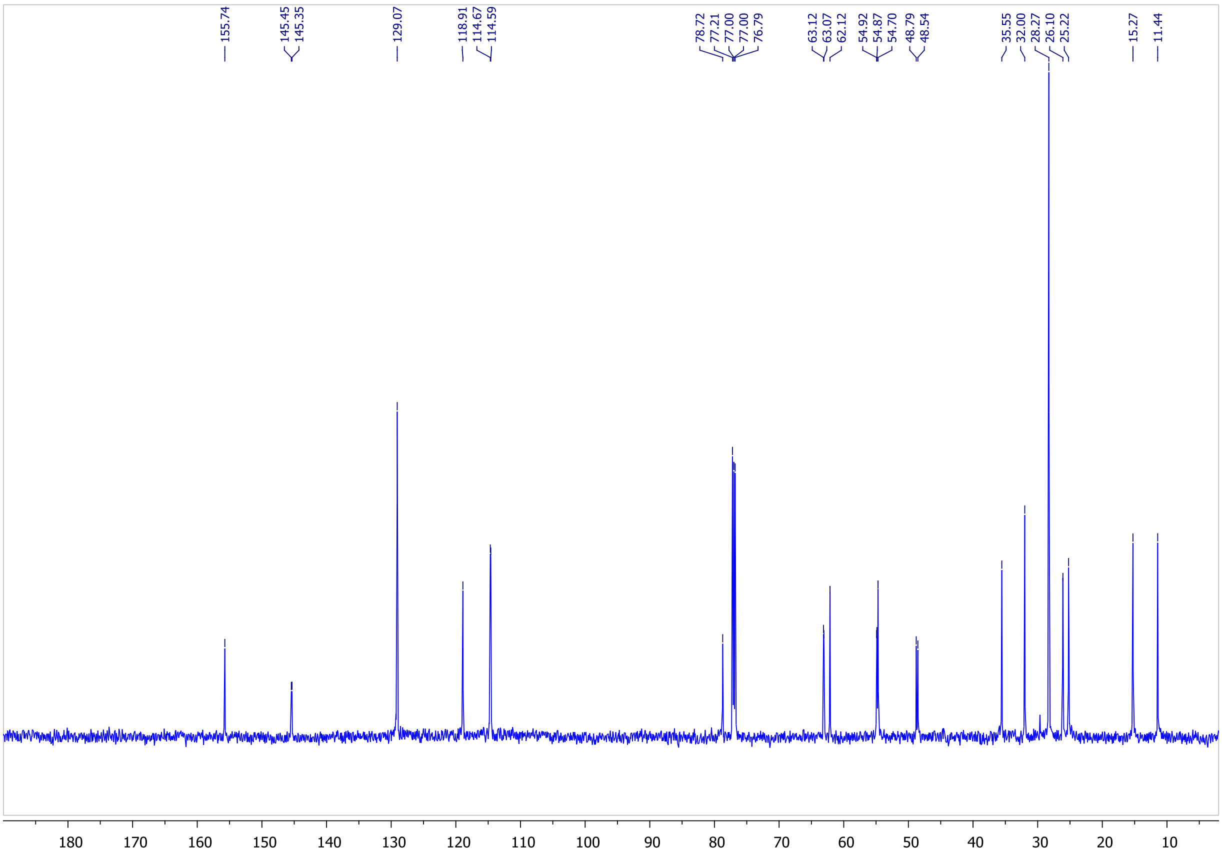


Figure S30c. **L1c**, $^{13}C\{^{1}H\}$ (150.9 MHz, $CDCl_3$, 15 °C).

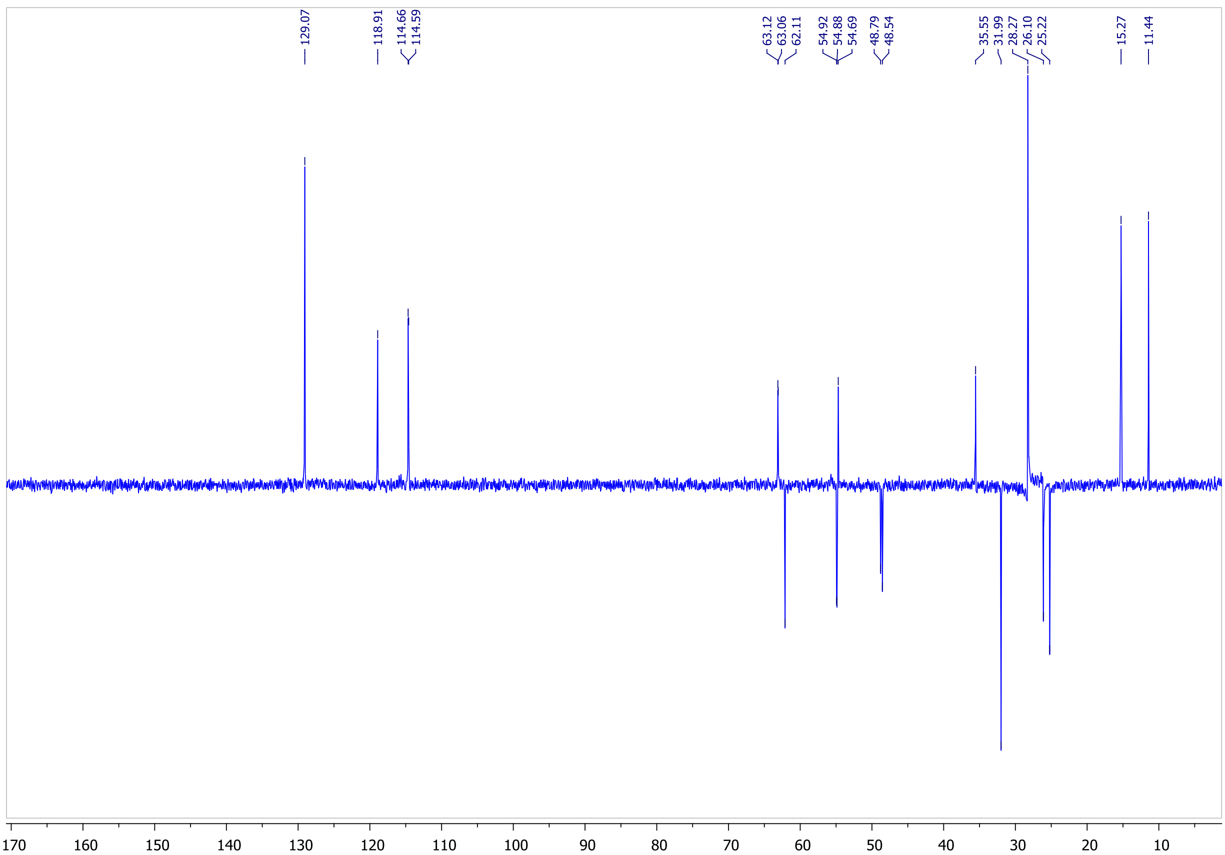


Figure S30d. **L1c**, $^{13}C\{^{1}H\}$ DEPT (150.9 MHz, $CDCl_3$, 15 °C).

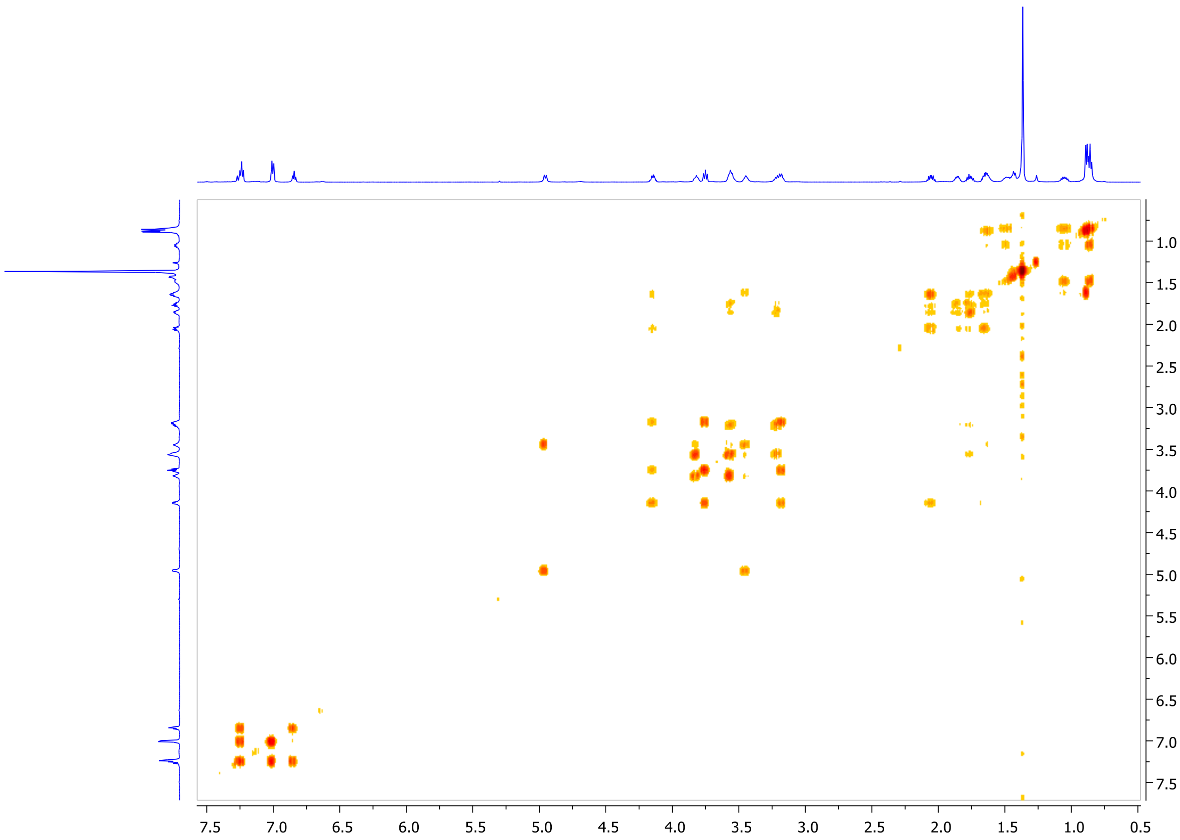


Figure S30e. **L1c**, ^{1}H-^{1}H COSY.

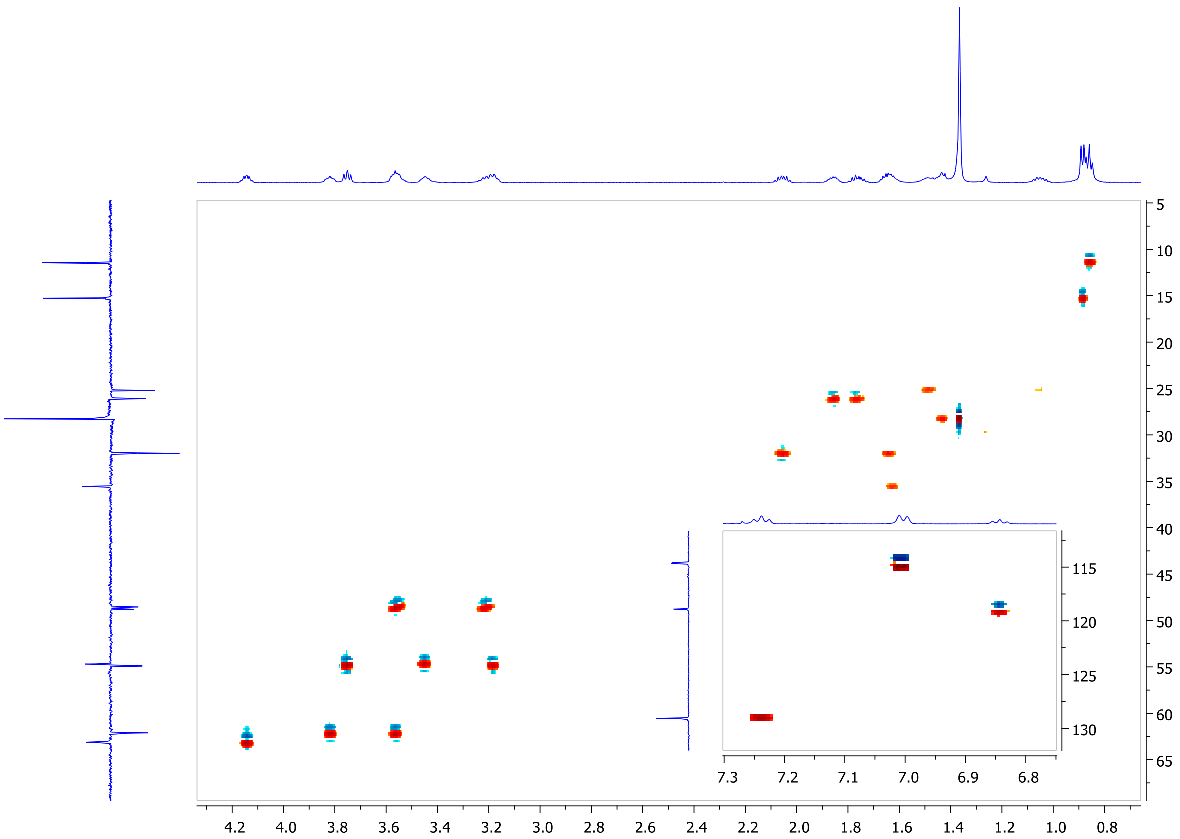


Figure S30f. **L1c**, ^{1}H-^{13}C HSQC.

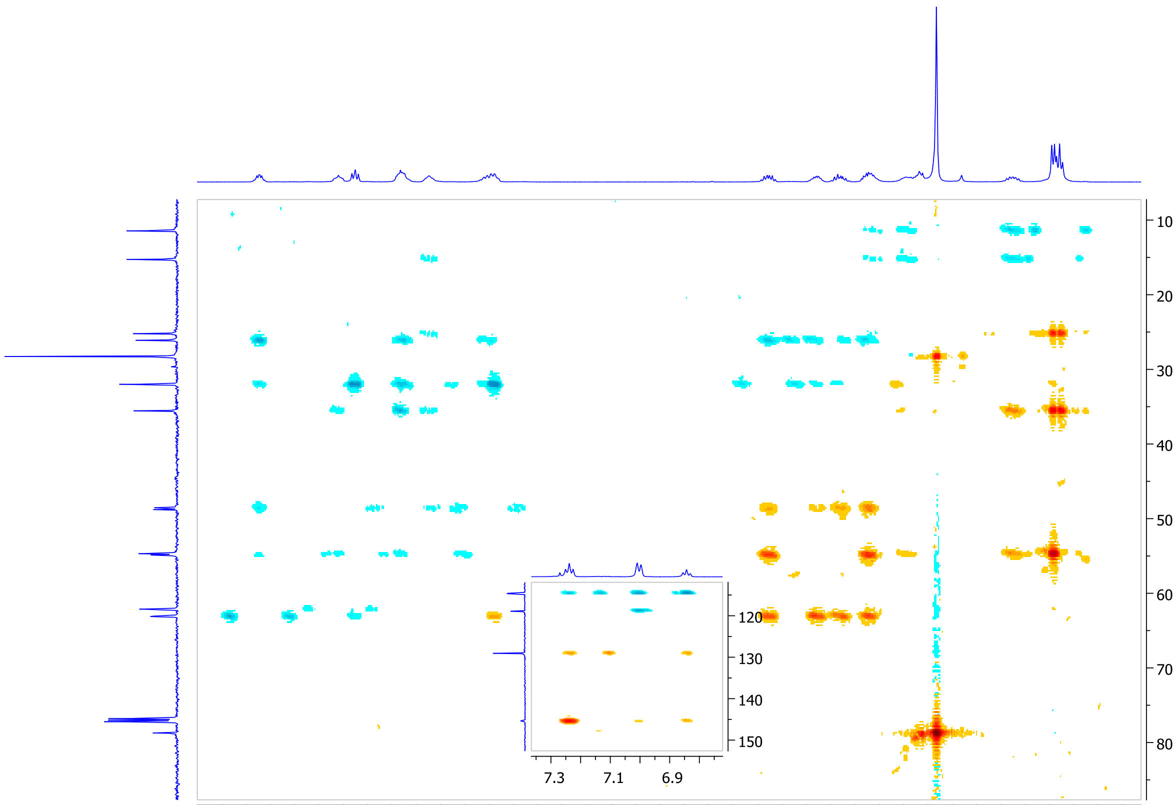


Figure S30g. **L1c**, ^{1}H-^{13}C HMBC

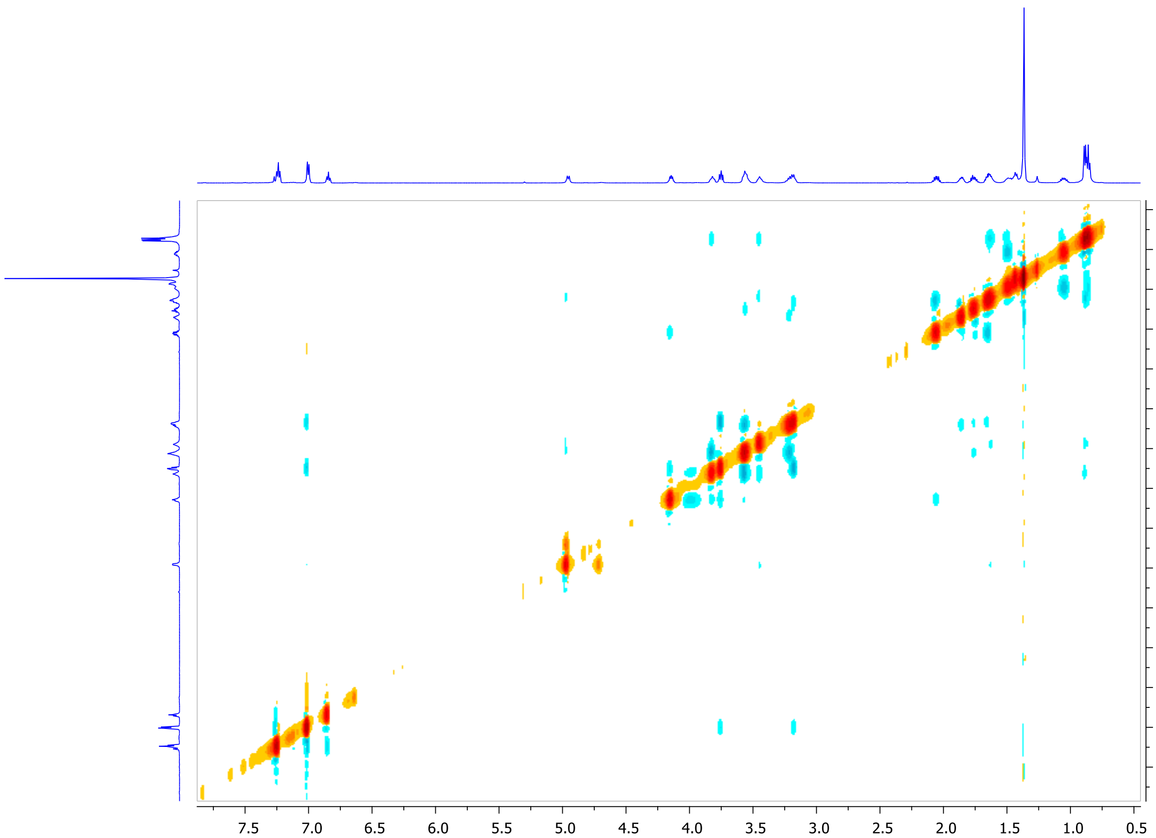


Figure S30h. **L1c**, ^{1}H-^{1}H NOESY.

NMR SPECTRA OF NEW COMPOUNDS

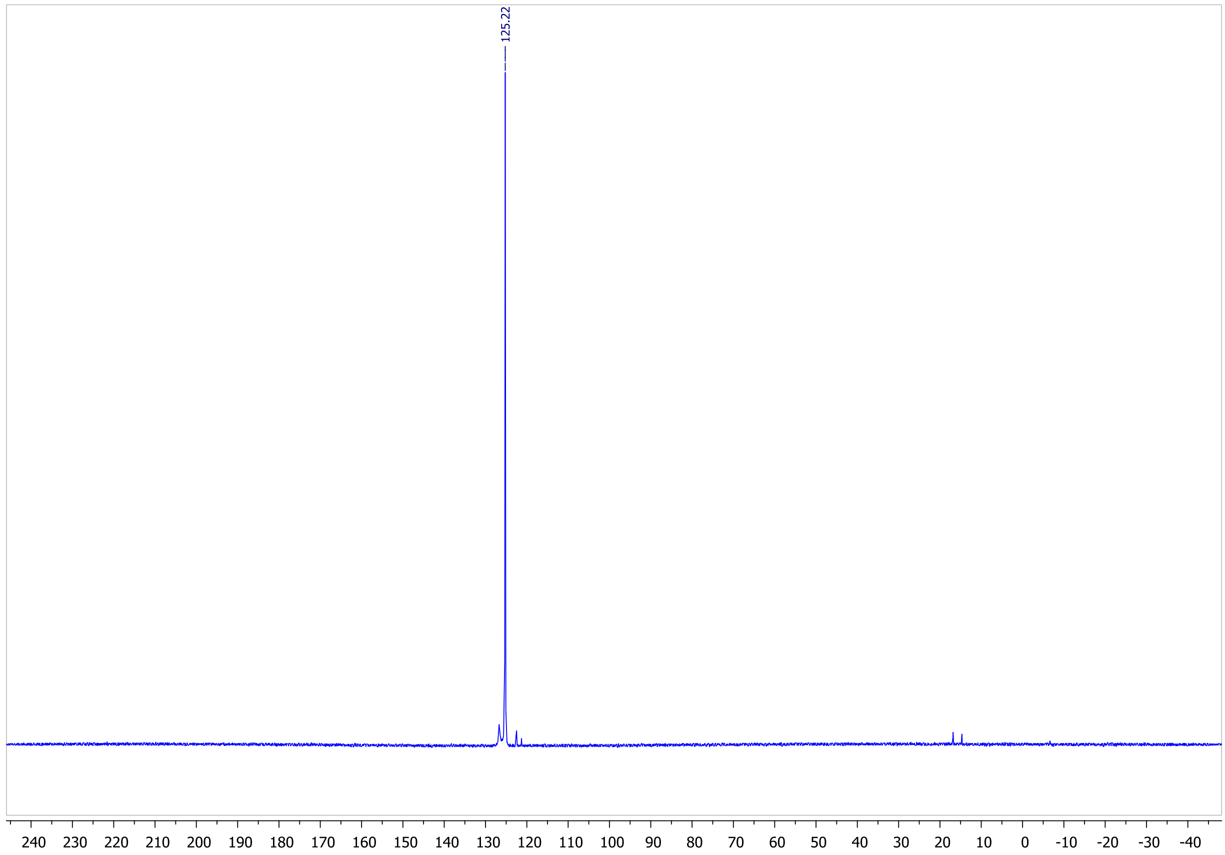


Figure S31a. **L1d**, $^{31}P\{^{1}H\}$ (202.4 MHz, $CDCl_3$, ambient temperature).

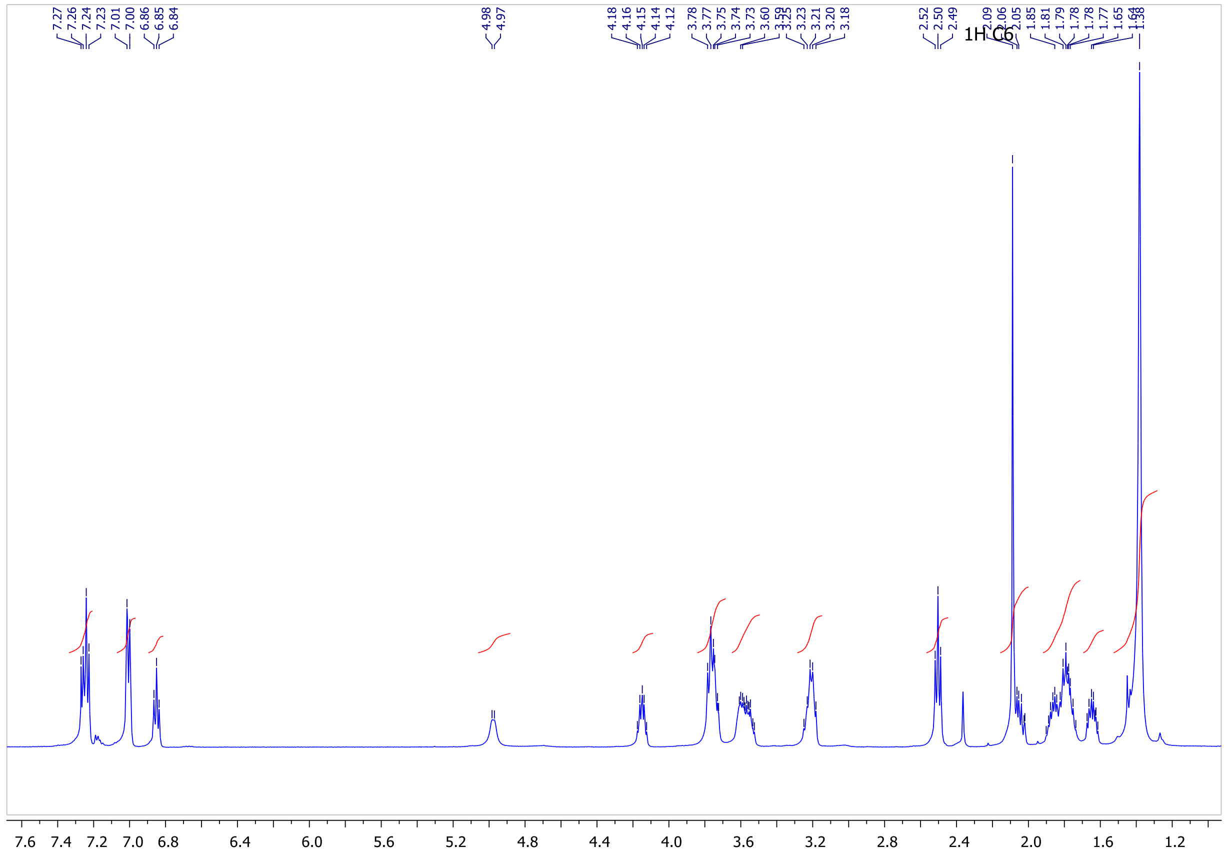


Figure S31b. **L1d**, ^{1}H (499.9 MHz, $CDCl_3$, ambient temperature).

NMR SPECTRA OF NEW COMPOUNDS

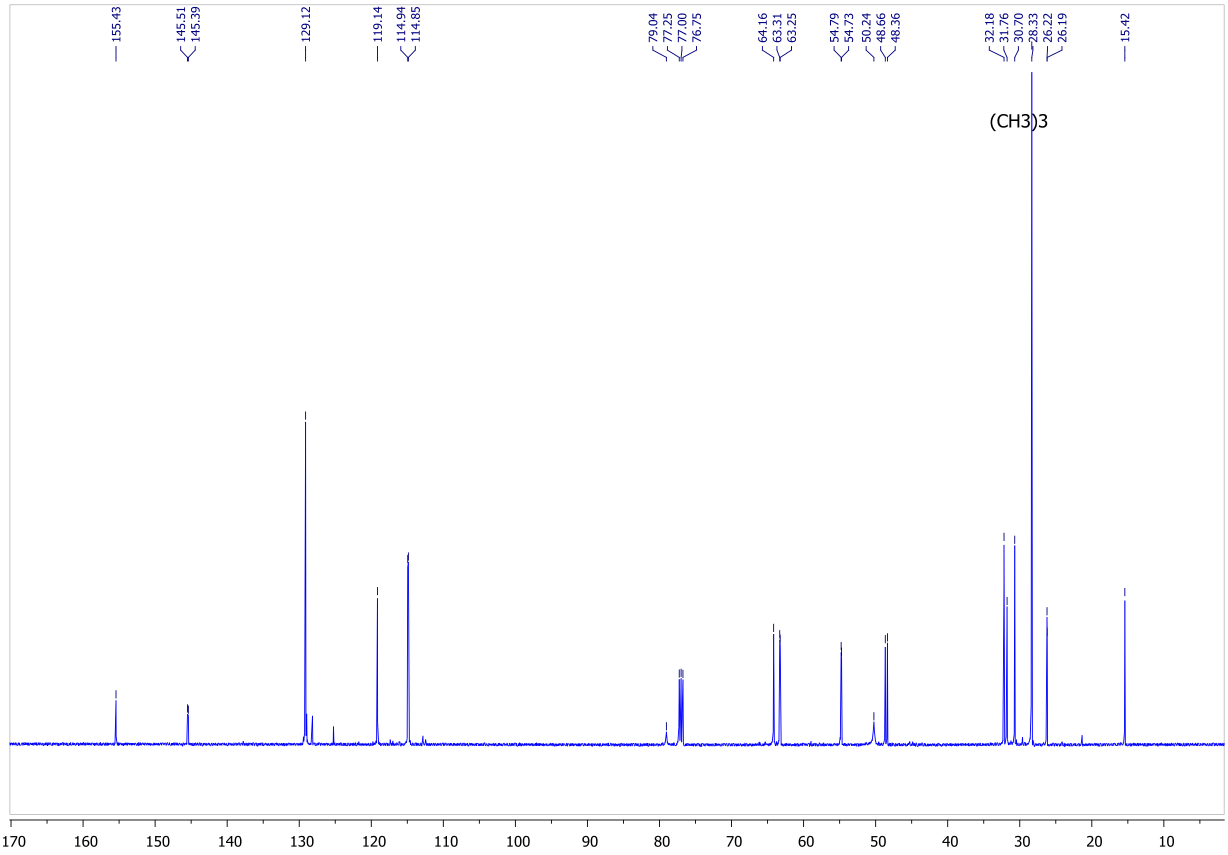


Figure S31c. **L1d**, $^{13}C\{^{1}H\}$ (125.7 MHz, $CDCl_3$, ambient temperature).

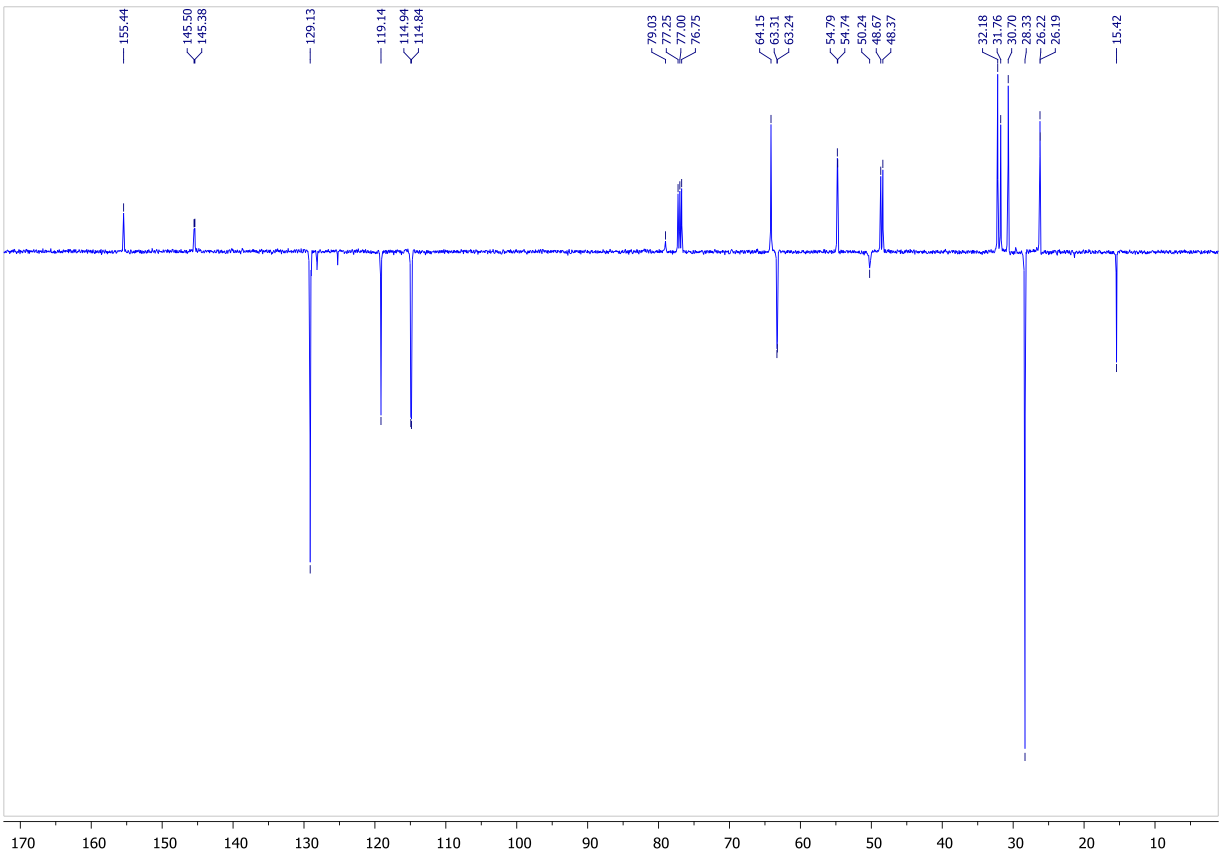


Figure S31d. **L1d**, $^{13}C\{^{1}H\}$ APT (125.7 MHz, $CDCl_3$, ambient temperature).

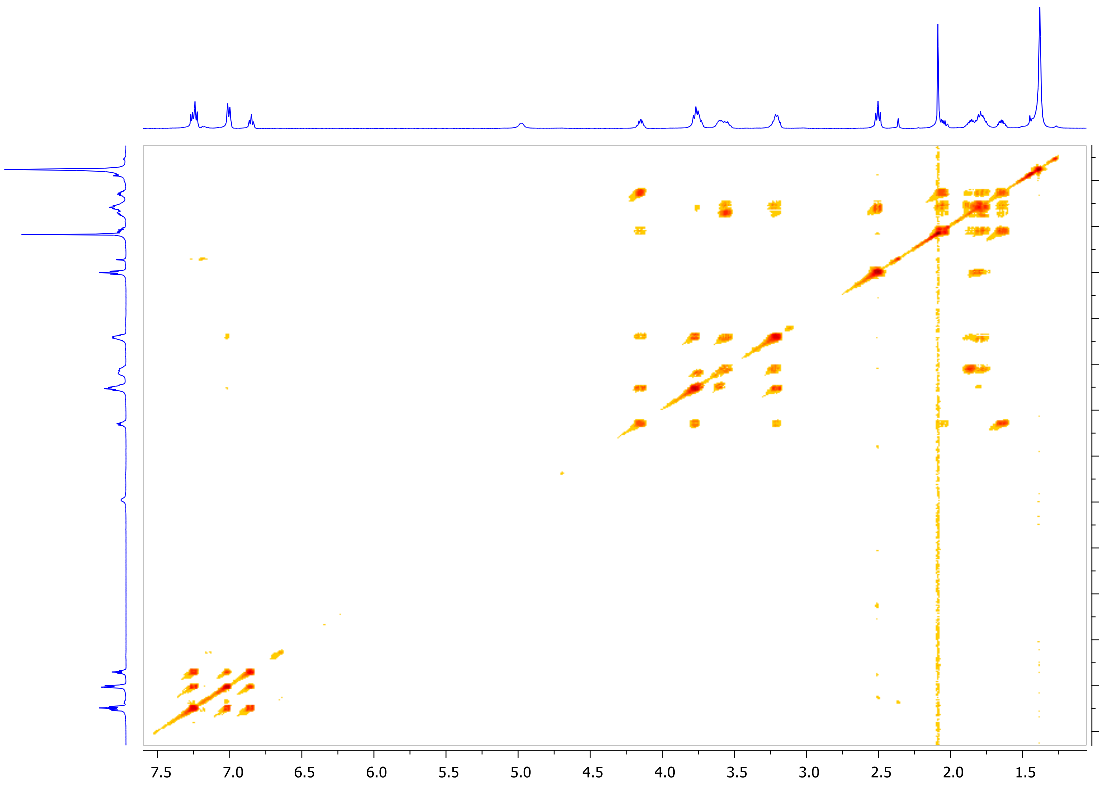


Figure S31e. **L1d**, ^{1}H-^{1}H COSY.

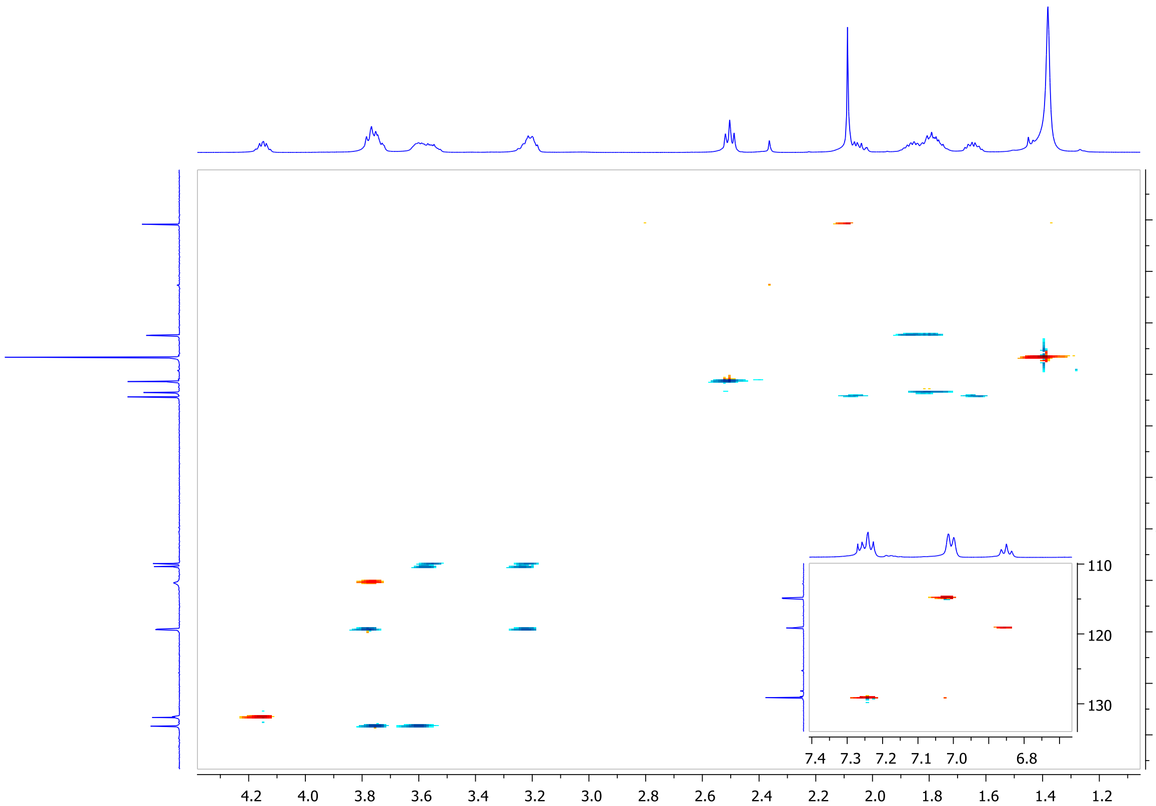


Figure S31f. **L1d**, ^{1}H-^{13}C HSQC.

NMR SPECTRA OF NEW COMPOUNDS

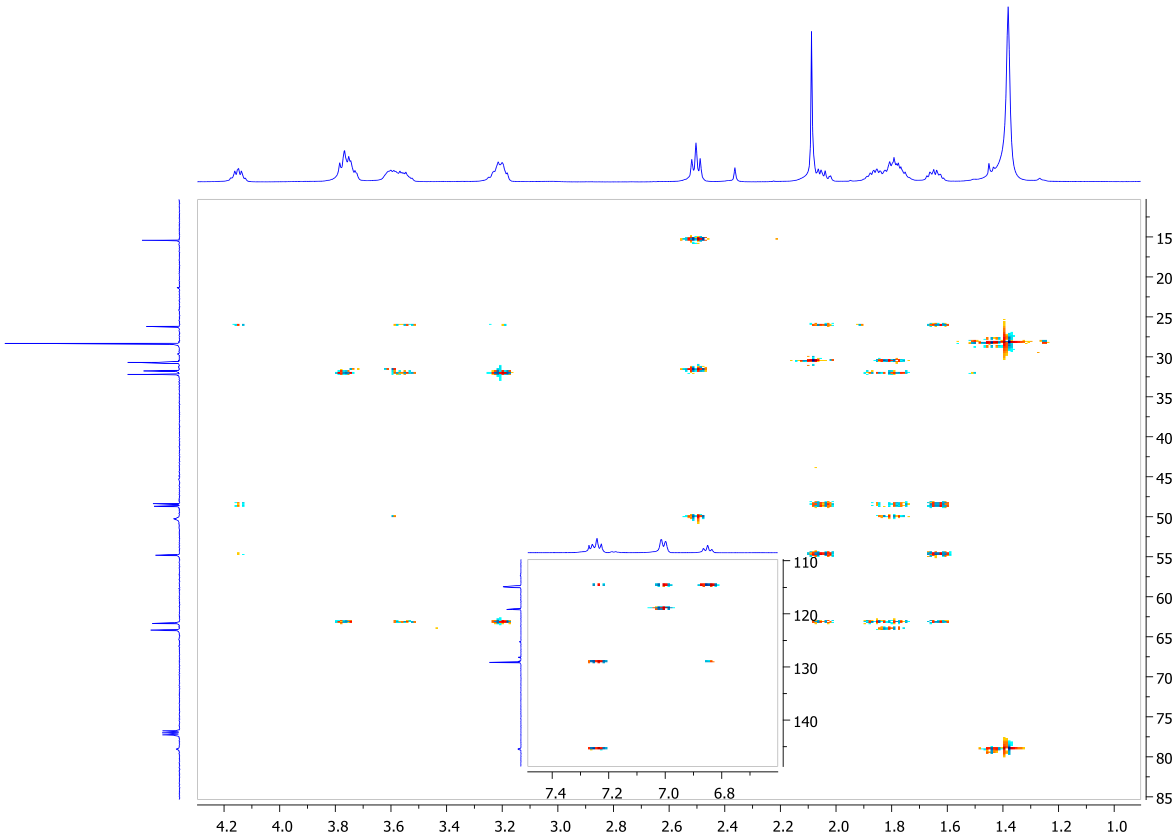


Figure S31g. **L1d**, ^{1}H-^{13}C HMBC.

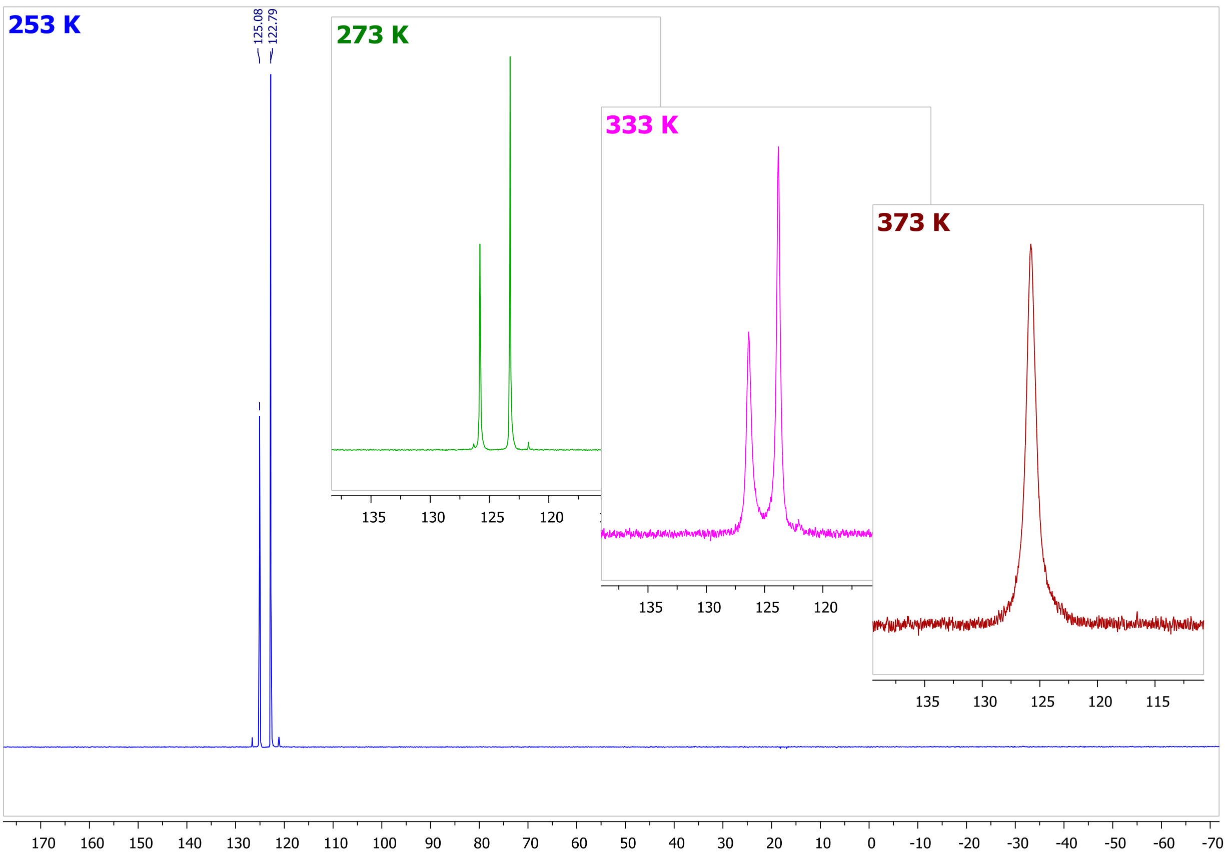


Figure S32a. **L2**, $^{31}P\{^{1}H\}$, (242.9 MHz, $CD_3C_6D_5$).

NMR SPECTRA OF NEW COMPOUNDS

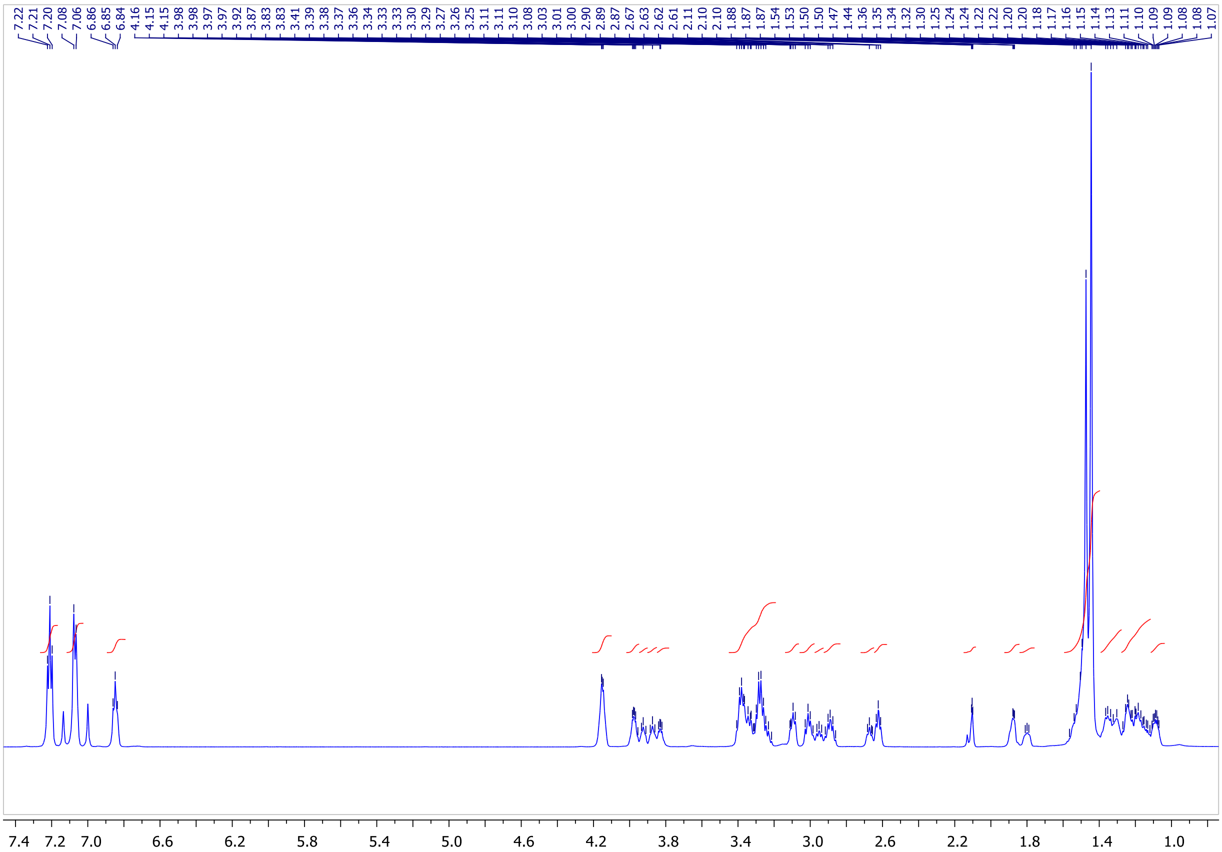


Figure S32b. **L2**, ^{1}H (600.1 MHz, $CD_3C_6D_5$, -20 °C).

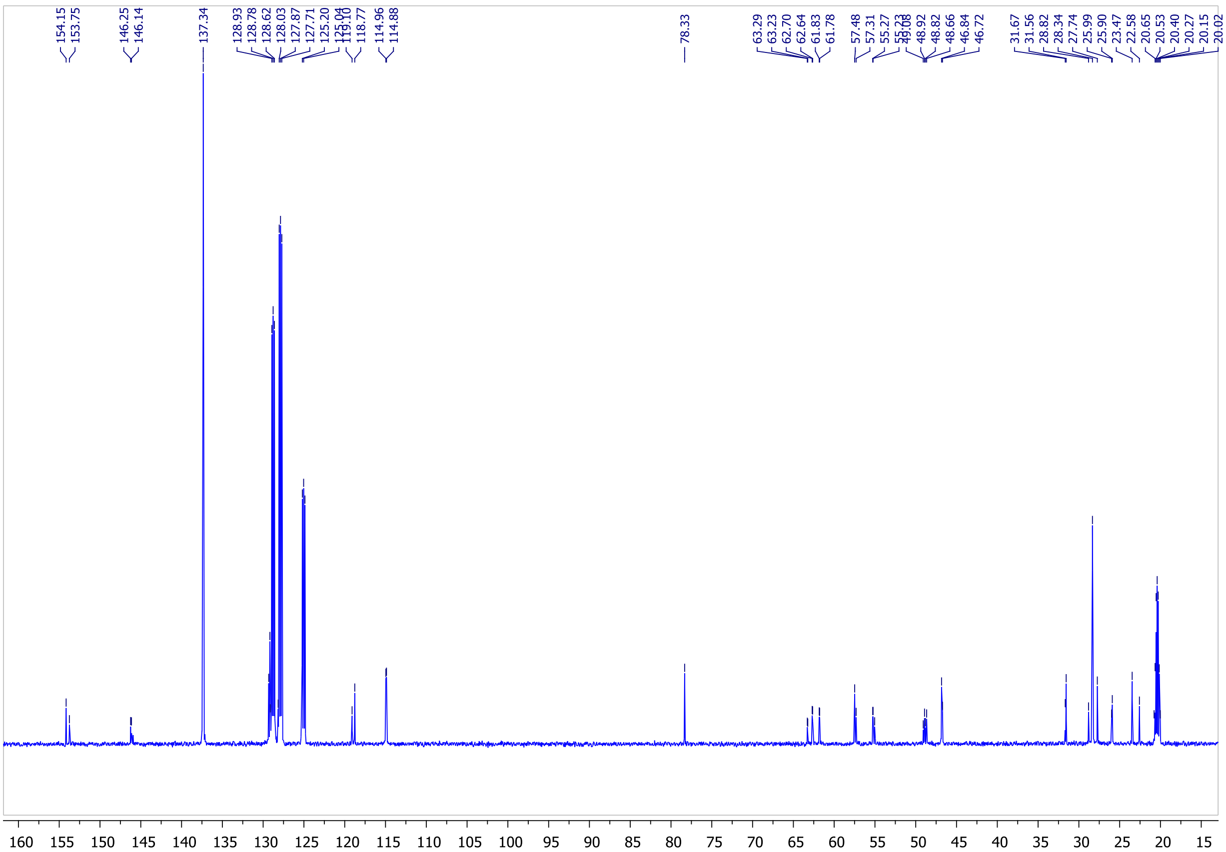


Figure S32c. **L2**, $^{13}C\{^{1}H\}$ (150.9 MHz, $CD_3C_6D_5$, -20 °C).

NMR SPECTRA OF NEW COMPOUNDS

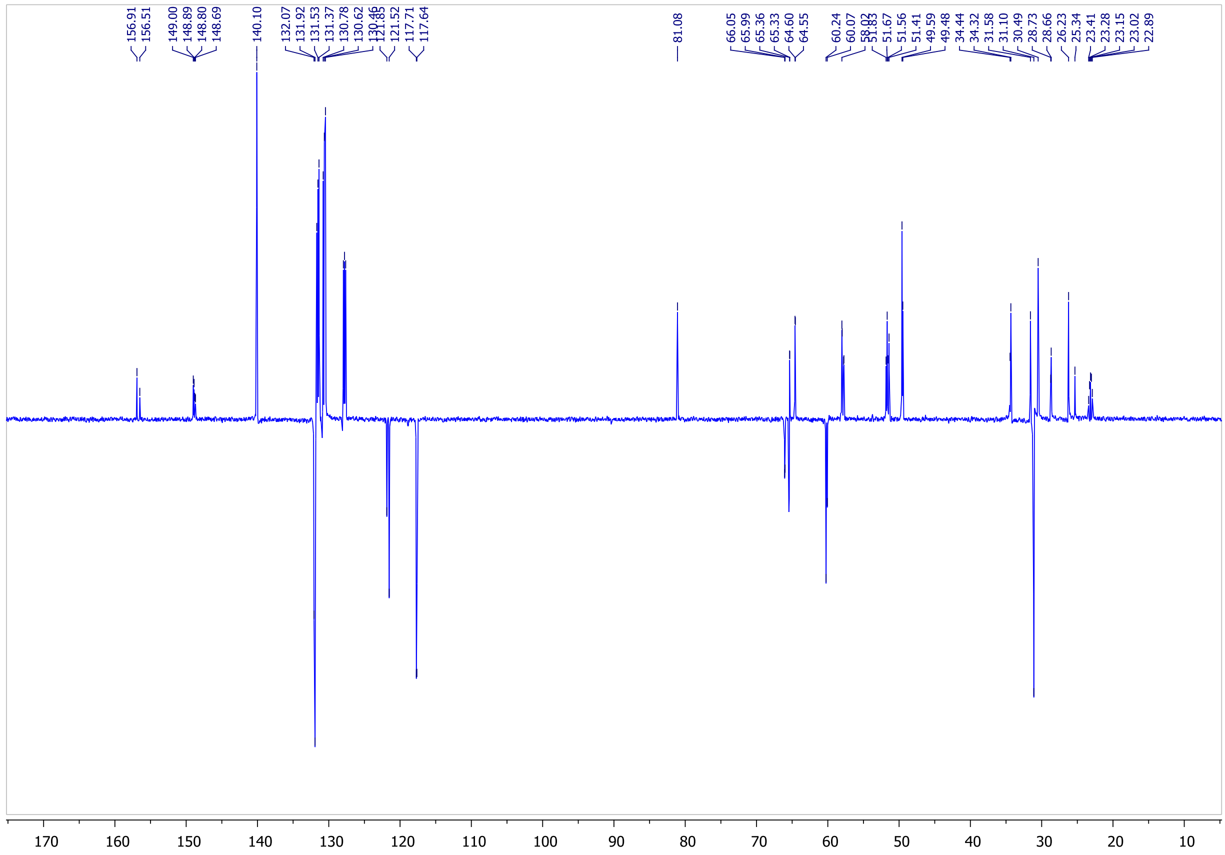


Figure S32d. **L2**, $^{13}C\{^{1}H\}$ APT (150.9 MHz, $CD_3C_6D_5$, -20 °C).

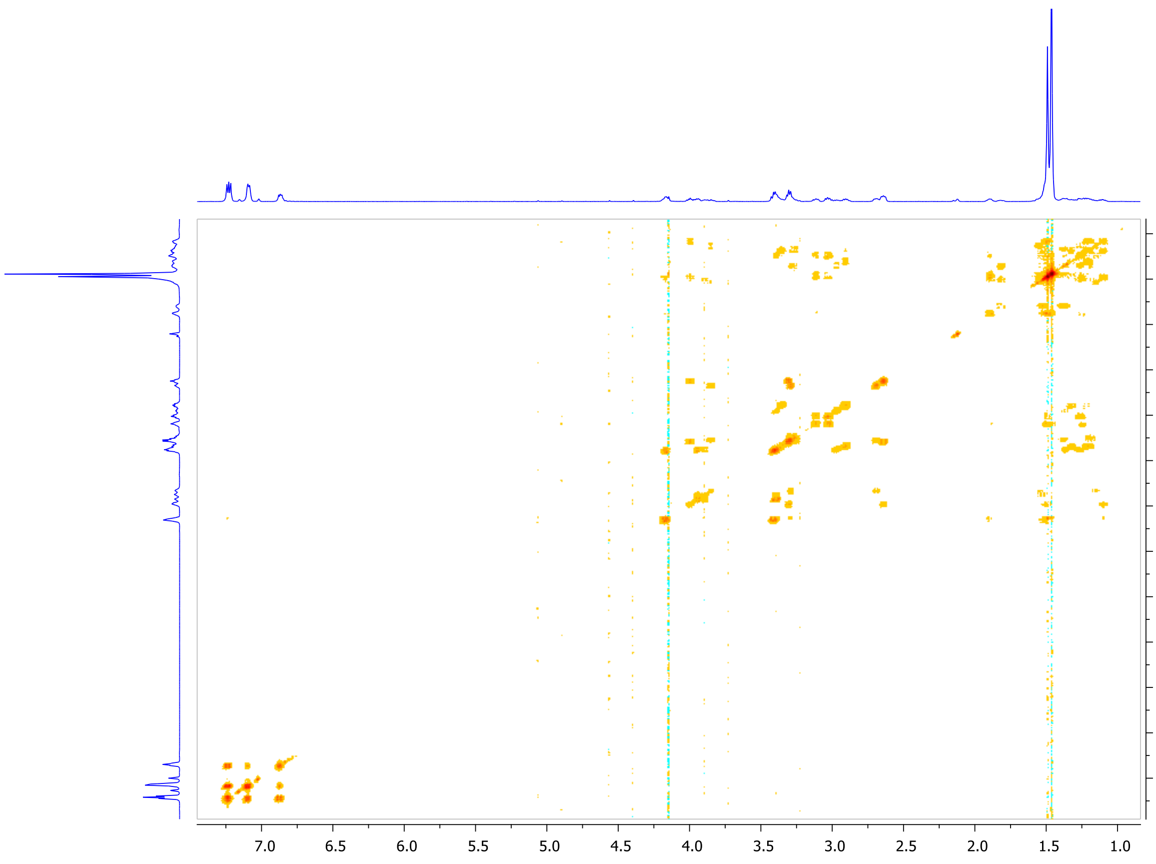


Figure S32e. **L2**, ^{1}H-^{1}H COSY.

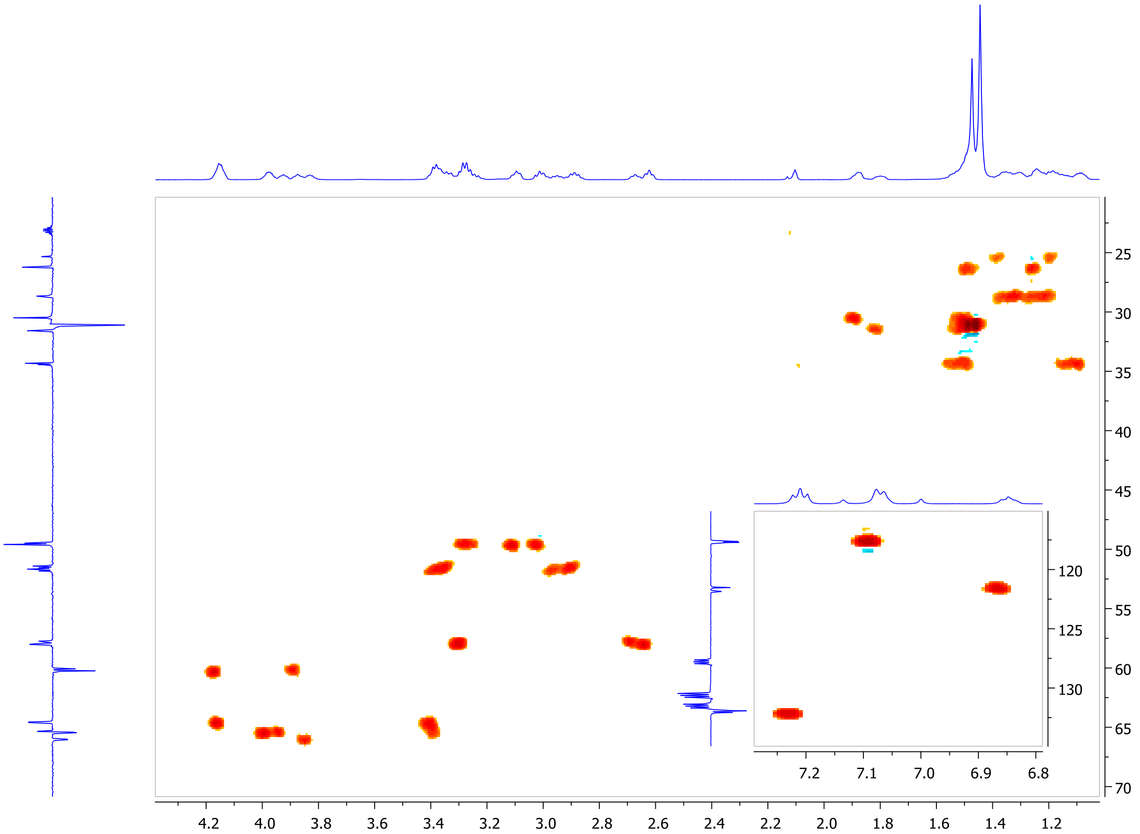


Figure S32f. **L2**, ^{1}H-^{13}C HSQC.

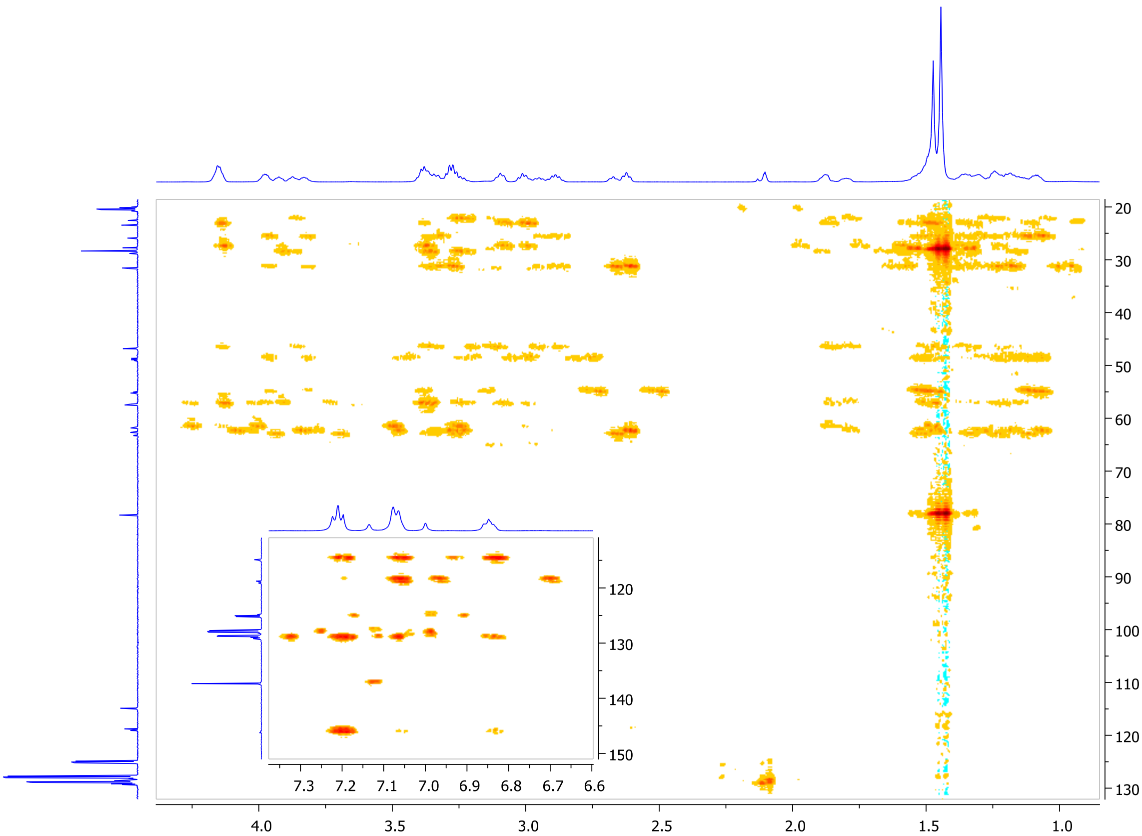


Figure S32g. **L2**, ^{1}H-^{13}C HMBC.

NMR SPECTRA OF NEW COMPOUNDS

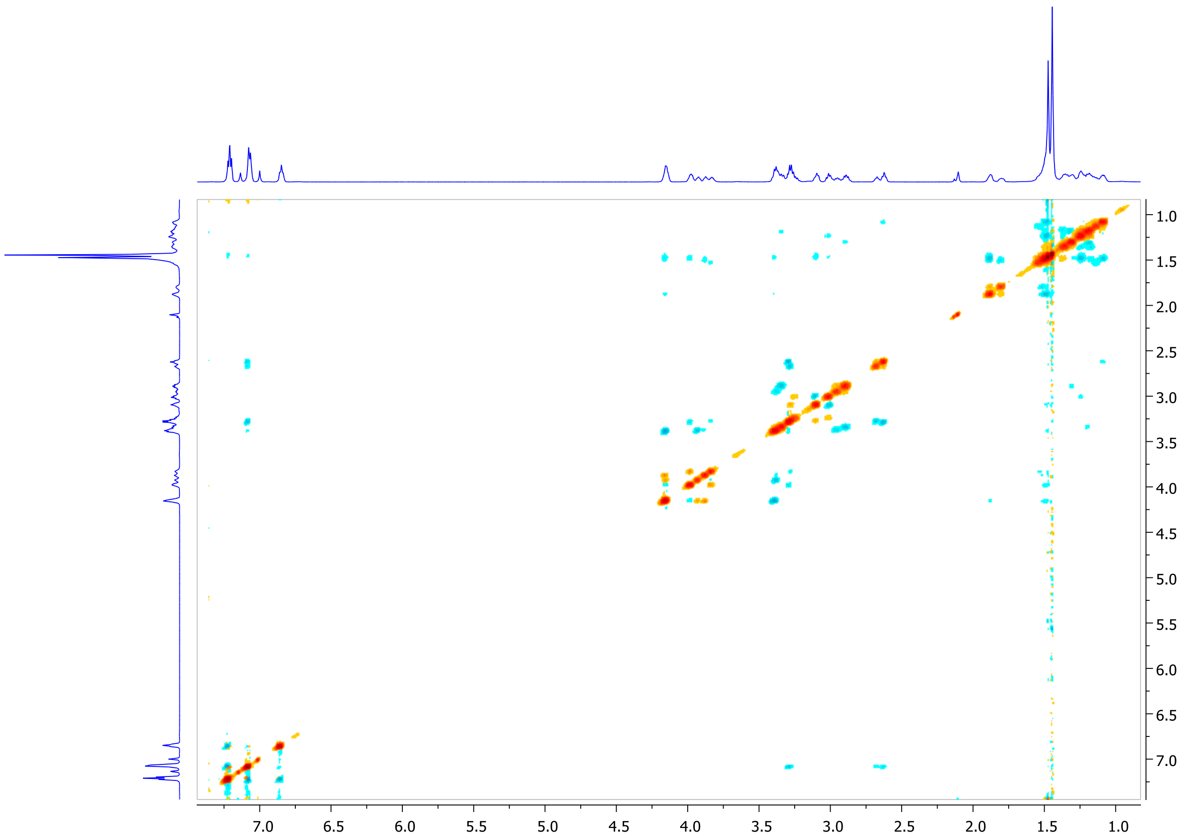


Figure S32h. **L2**, ^{1}H-^{1}H NOESY.

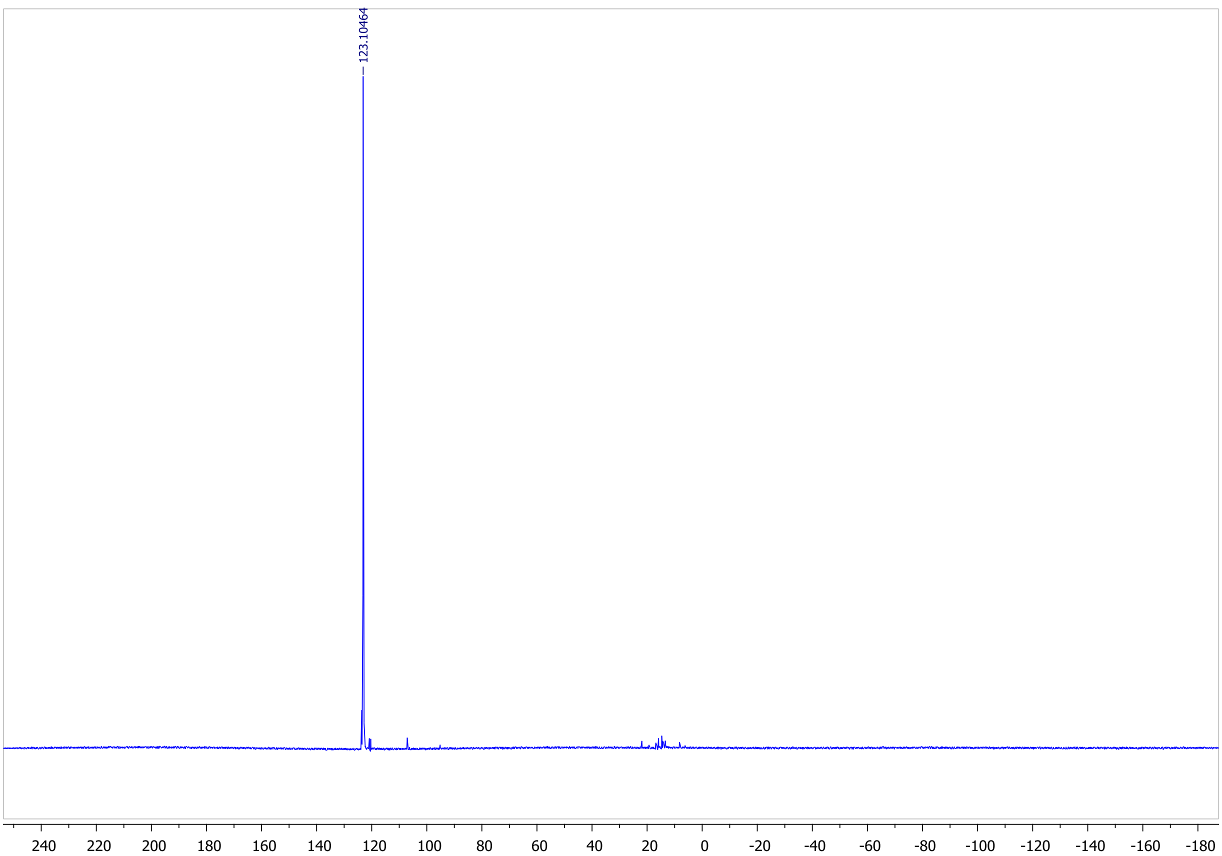


Figure S33a. **L3a**, $^{31}P\{^{1}H\}$ (202.4 MHz, $CDCl_3$, ambient temperature).

NMR SPECTRA OF NEW COMPOUNDS

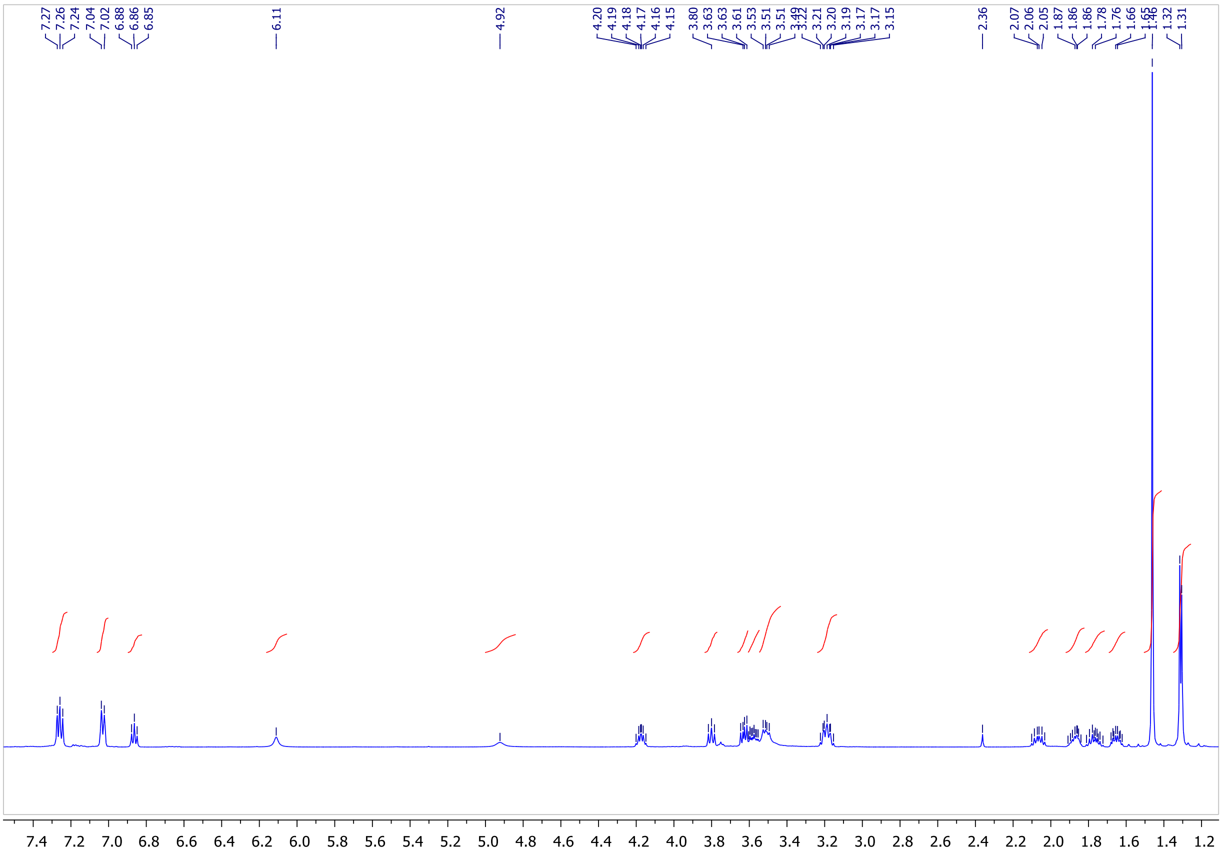


Figure S33b. **L3a**, ^{1}H (499.9 MHz, $CDCl_3$, ambient temperature).

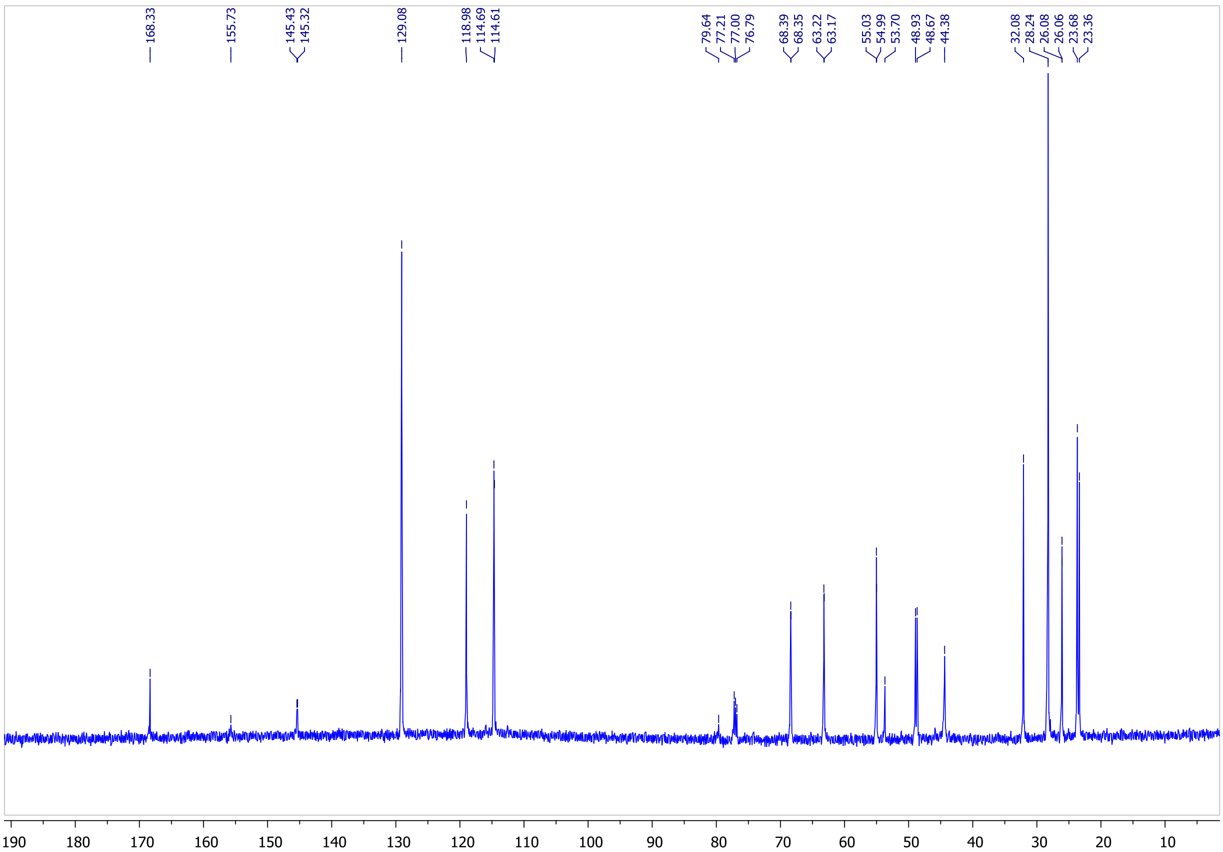


Figure S33c. **L3a**, $^{13}C\{^{1}H\}$ (150.9 MHz, $CDCl_3$, 24 °C).

NMR SPECTRA OF NEW COMPOUNDS

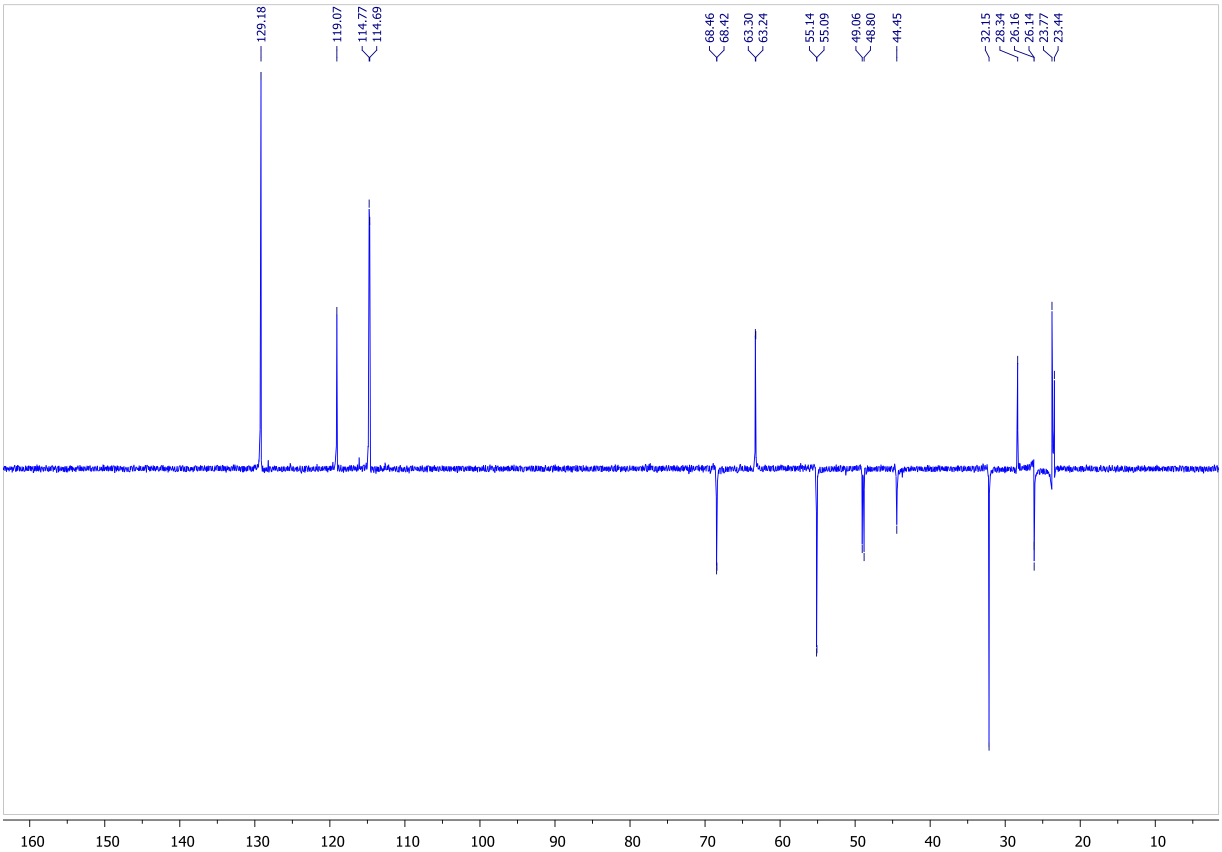


Figure S33d. **L3a**, $^{13}C\{^{1}H\}$ DEPT (150.9 MHz, $CDCl_3$, 24 °C).

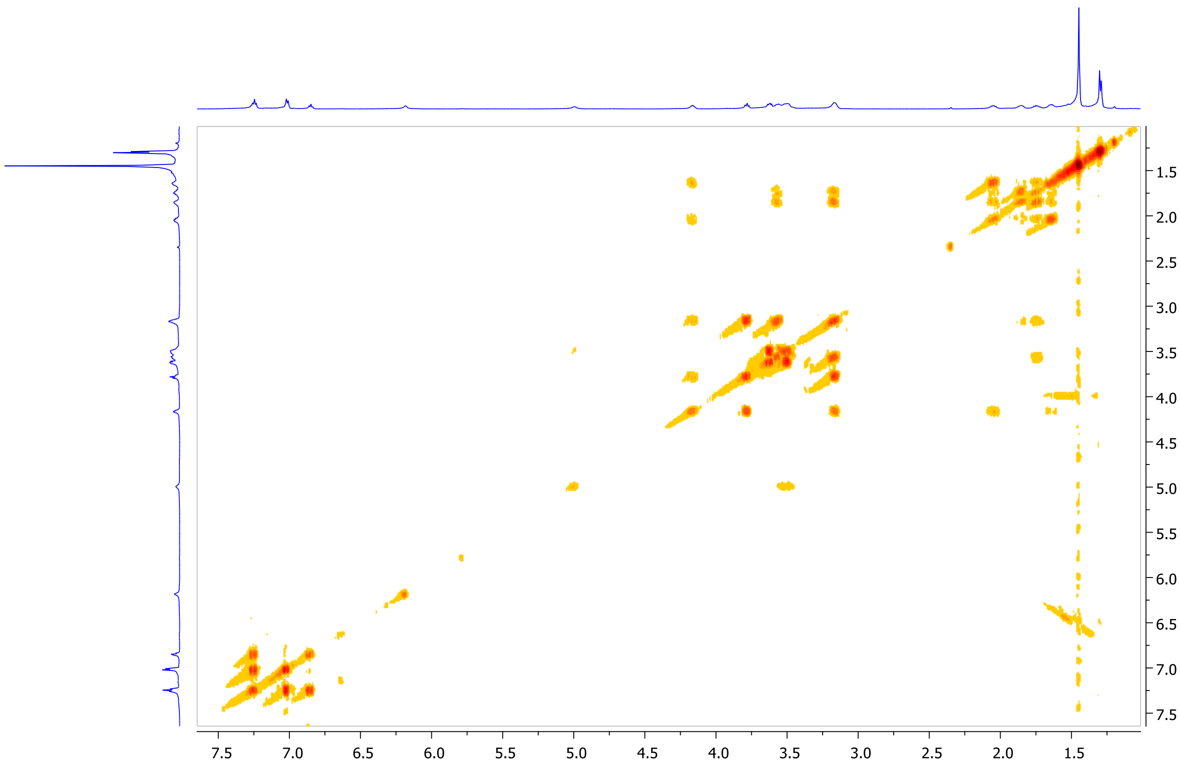


Figure S33e. **L3a**, ^{1}H-^{1}H COSY.

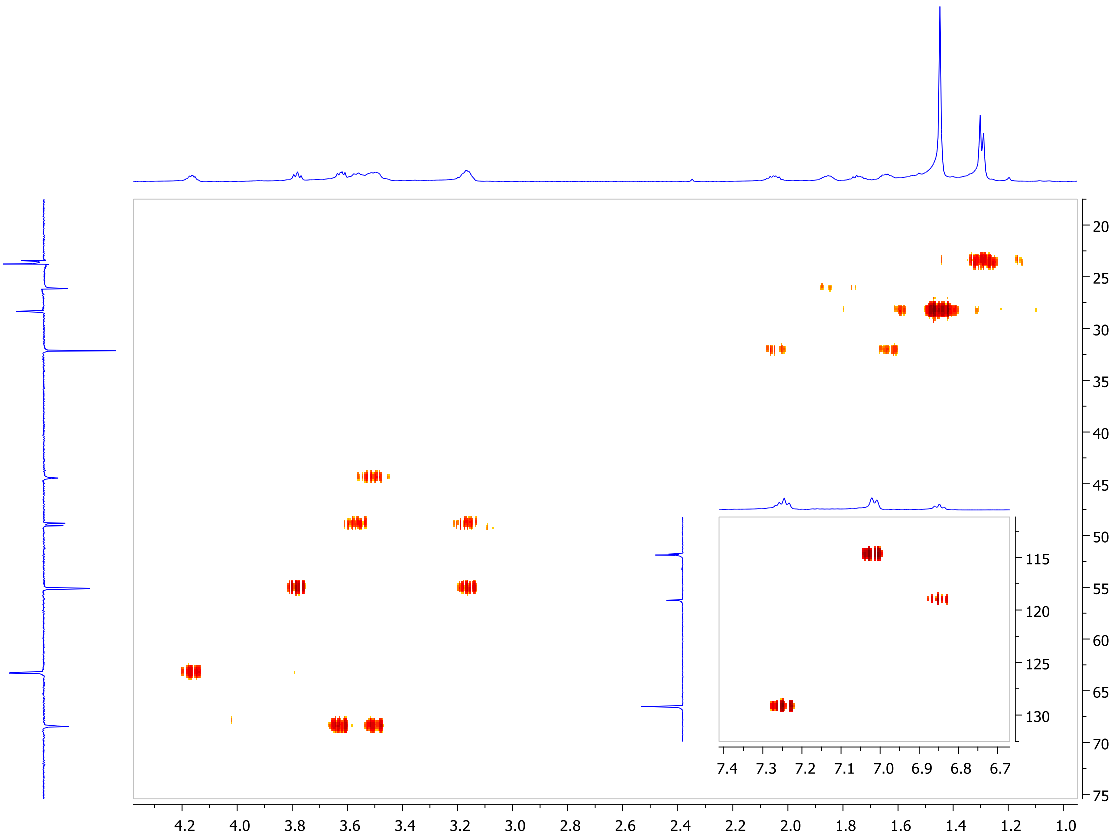


Figure S33f. **L3a**, ^{1}H-^{13}C HSQC.

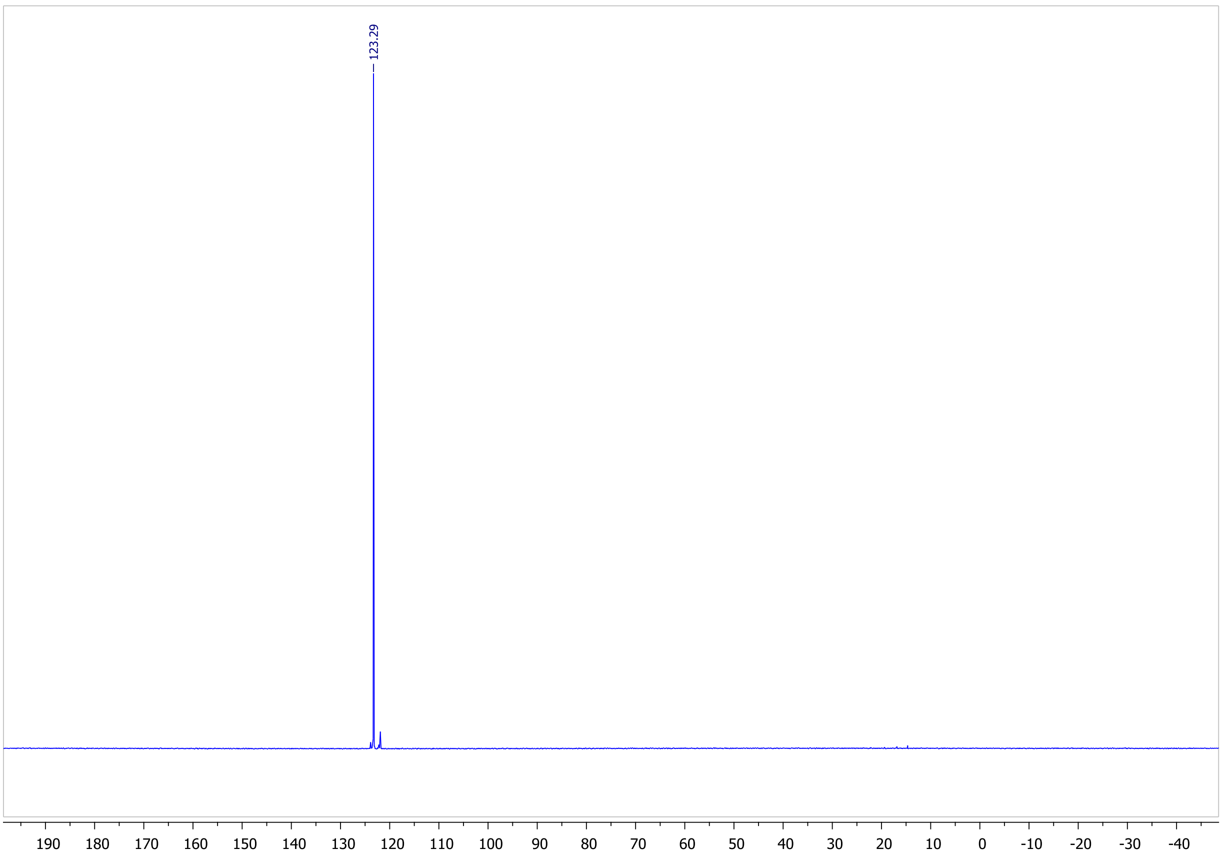


Figure S34a. **L3b**, $^{31}P\{^{1}H\}$ (202.4 MHz, $CDCl_3$, ambient temperature).

NMR SPECTRA OF NEW COMPOUNDS

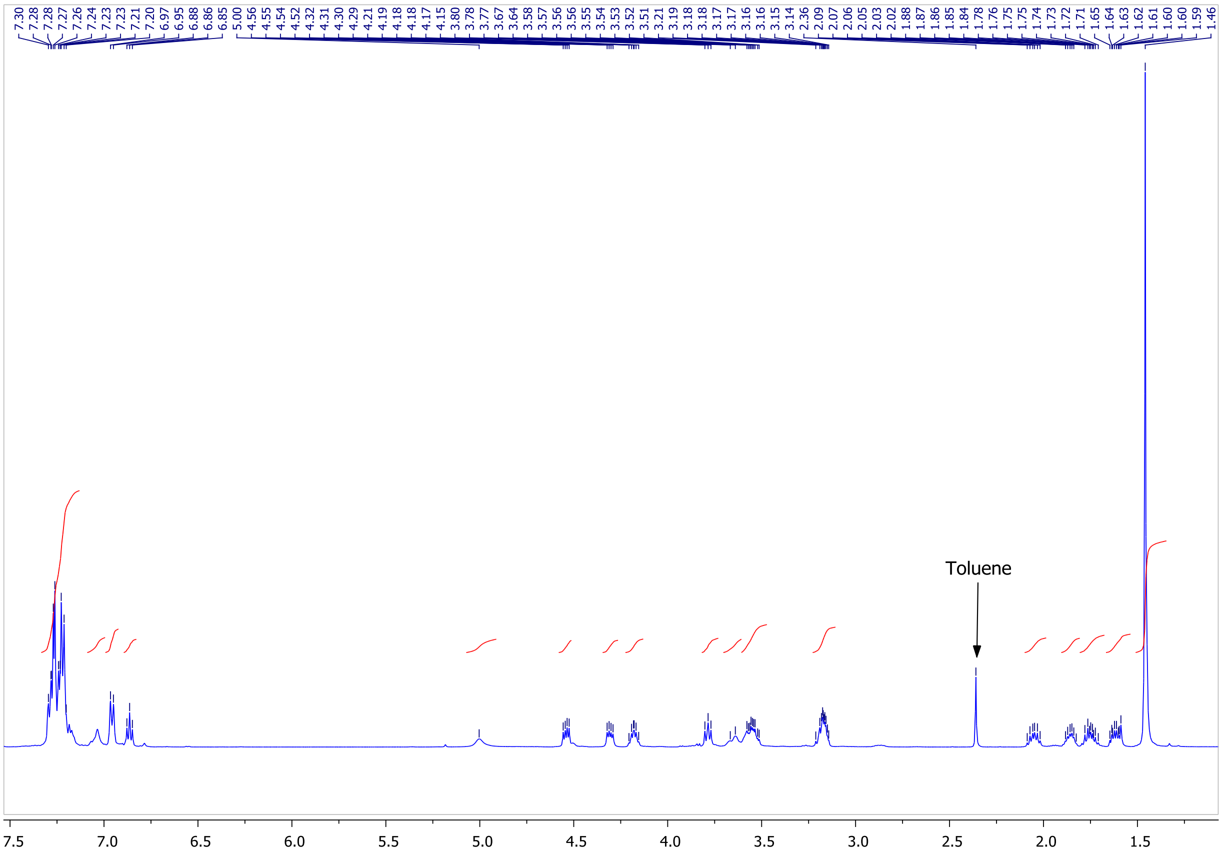


Figure S34b. **L3b**, ^{1}H (600.1 MHz, $CDCl_3$, 22 °C).

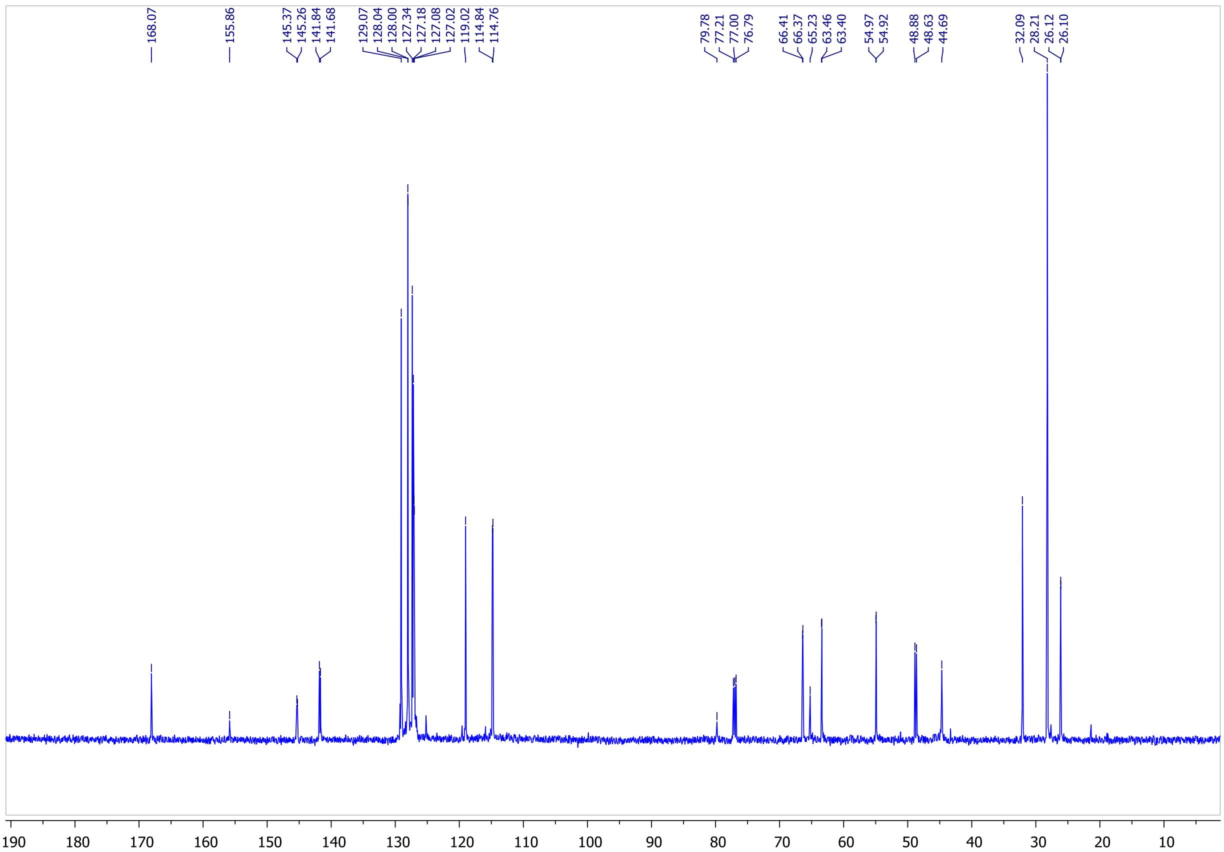


Figure S34c. **L3b**, $^{13}C\{^{1}H\}$ (150.9 MHz, $CDCl_3$, 22 °C).

NMR SPECTRA OF NEW COMPOUNDS

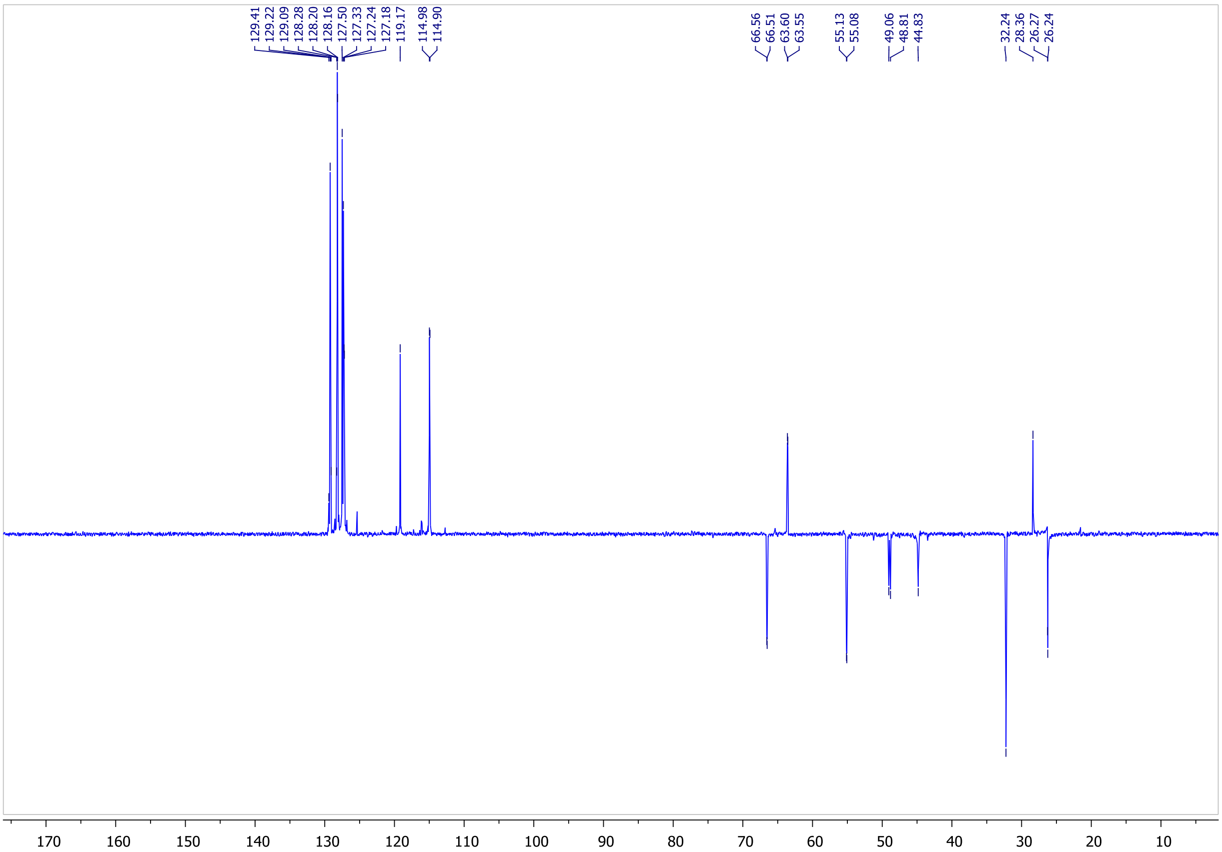


Figure S34d. **L3b**, $^{13}C\{^1H\}$ DEPT (150.9 MHz, $CDCl_3$, 22 °C).

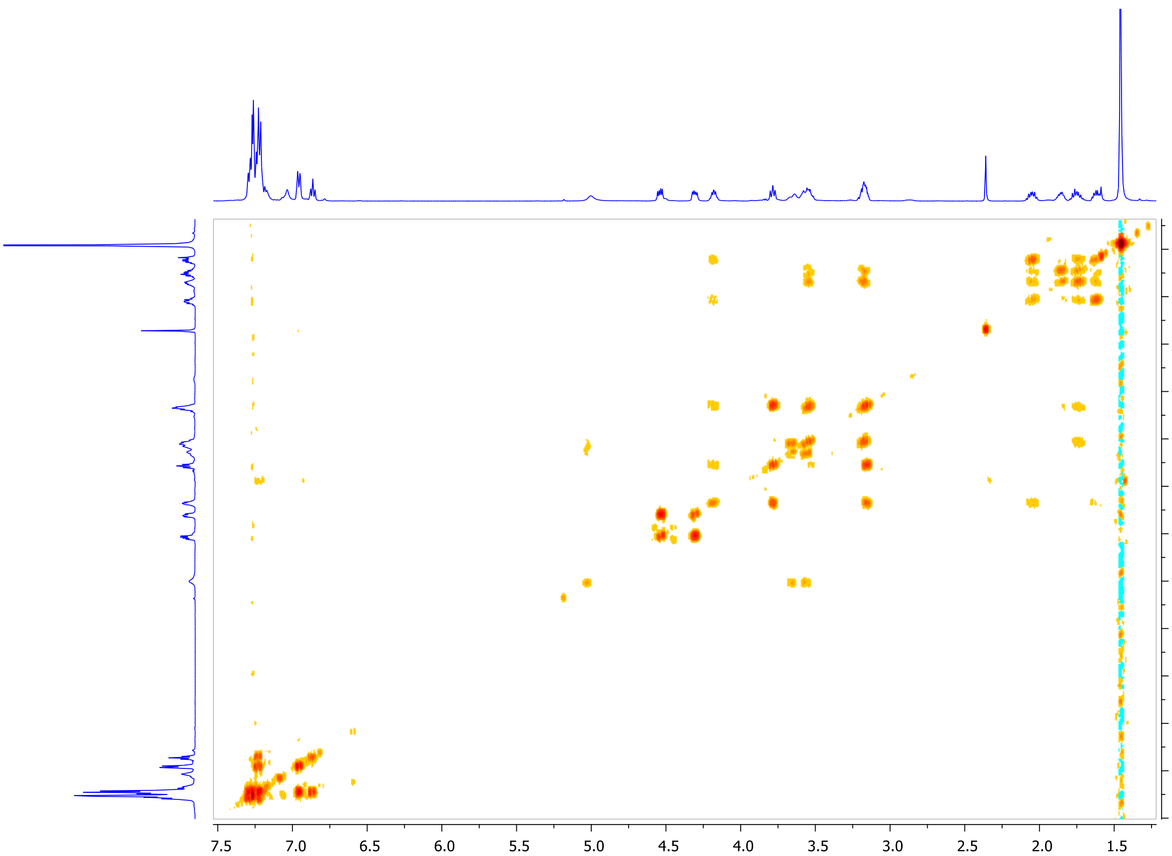


Figure S34e. **L3b**, ^1H-^1H COSY.

NMR SPECTRA OF NEW COMPOUNDS

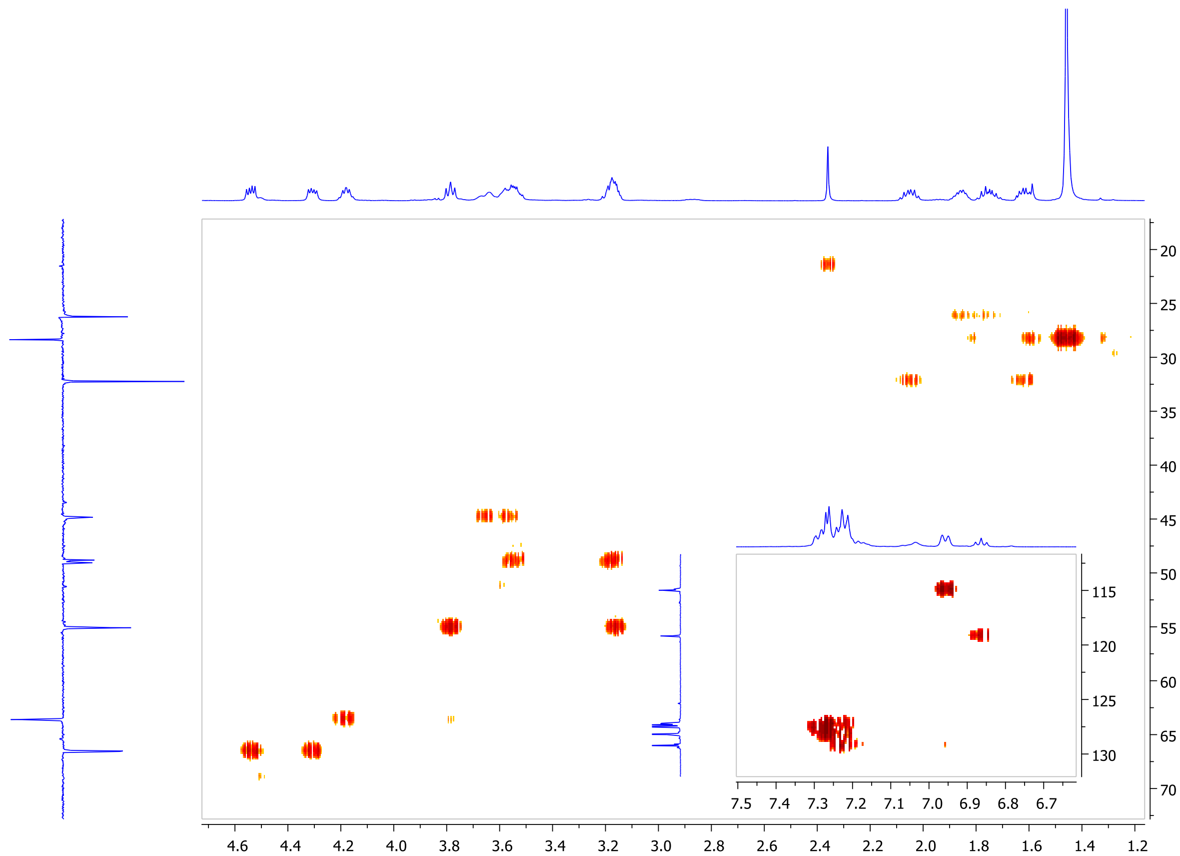


Figure S34f. **L3b**, ^{1}H-^{13}C HSQC.

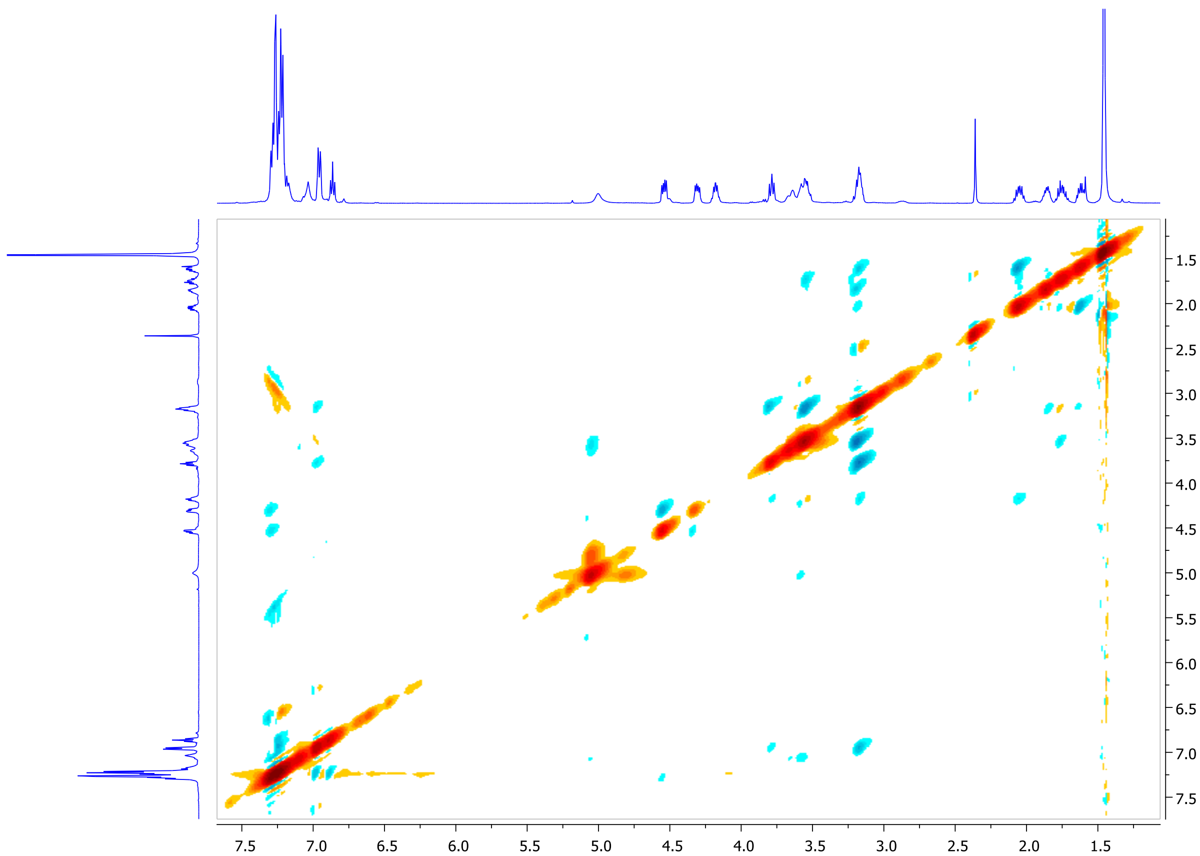


Figure S34g. **L3b**, ^{1}H-^{1}H NOESY.

NMR SPECTRA OF NEW COMPOUNDS

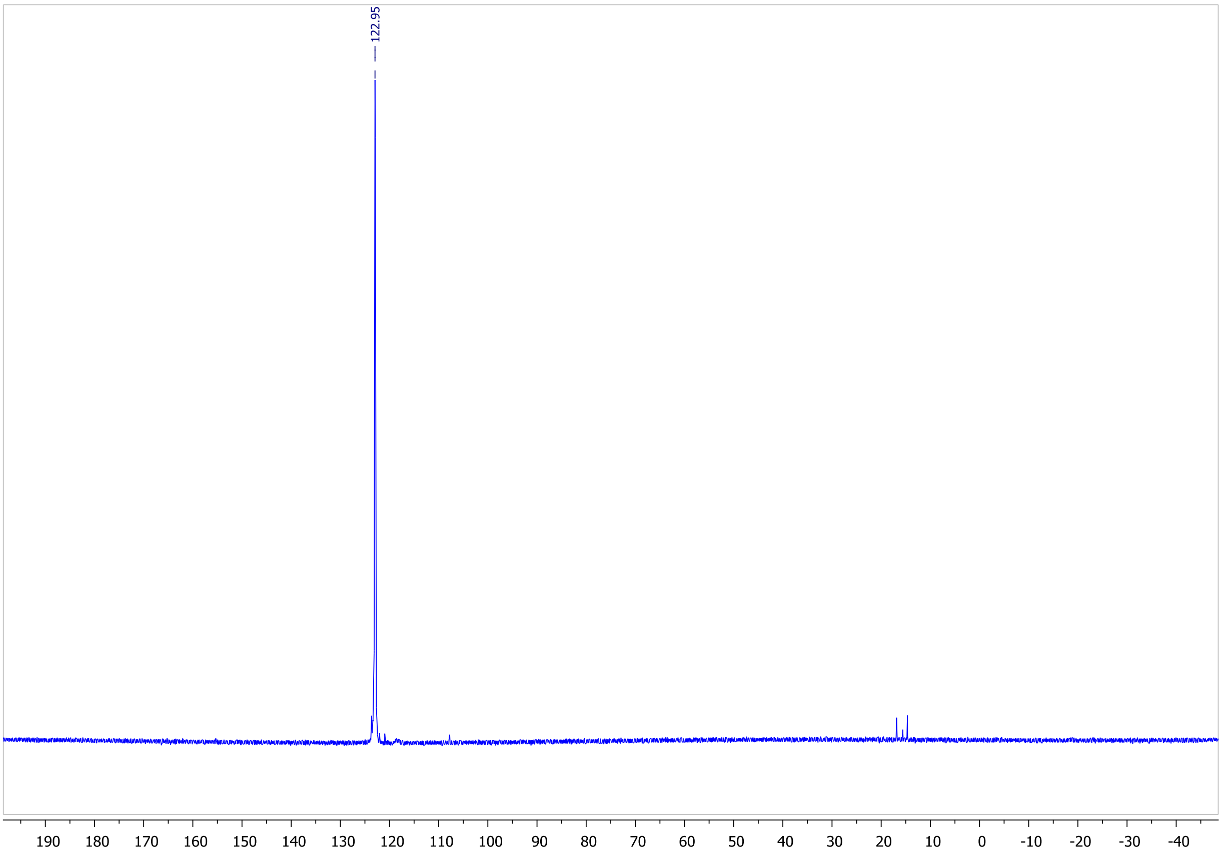


Figure S35a. **L3c**, $^{31}P\{^{1}H\}$ (202.4 MHz, $CDCl_3$, ambient temperature).

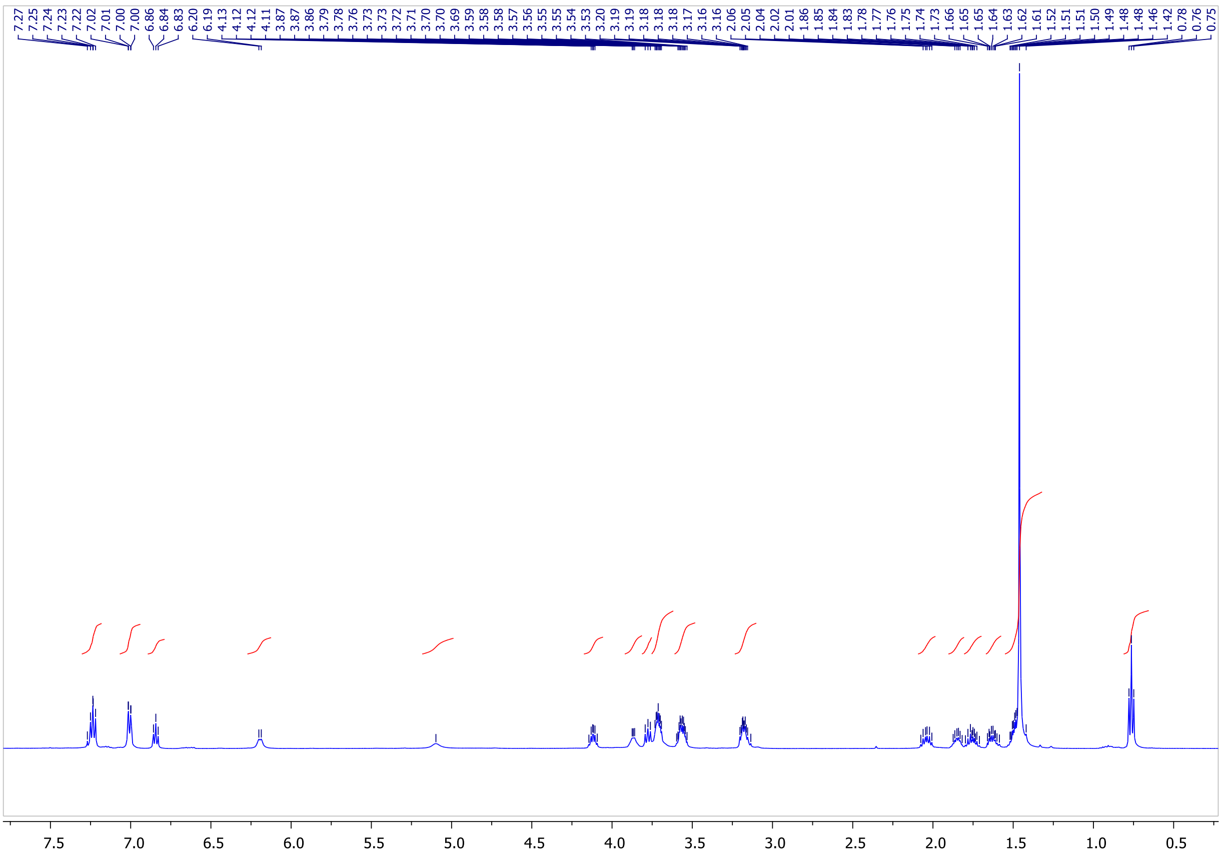


Figure S35b. **L3c**, ^{1}H (499.9 MHz, $CDCl_3$, ambient temperature).

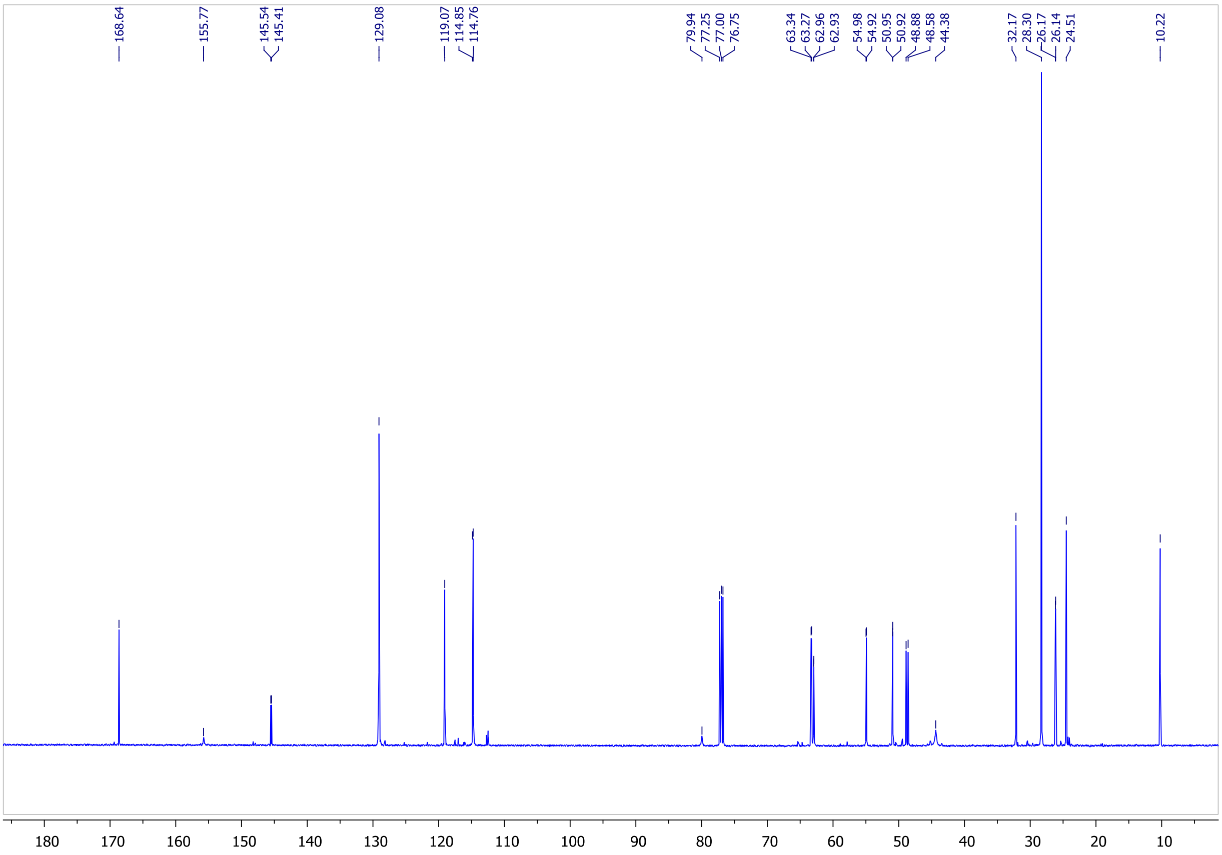


Figure S35c. **L3c**, $^{13}C\{^{1}H\}$ (125.7 MHz, $CDCl_3$, ambient temperature).

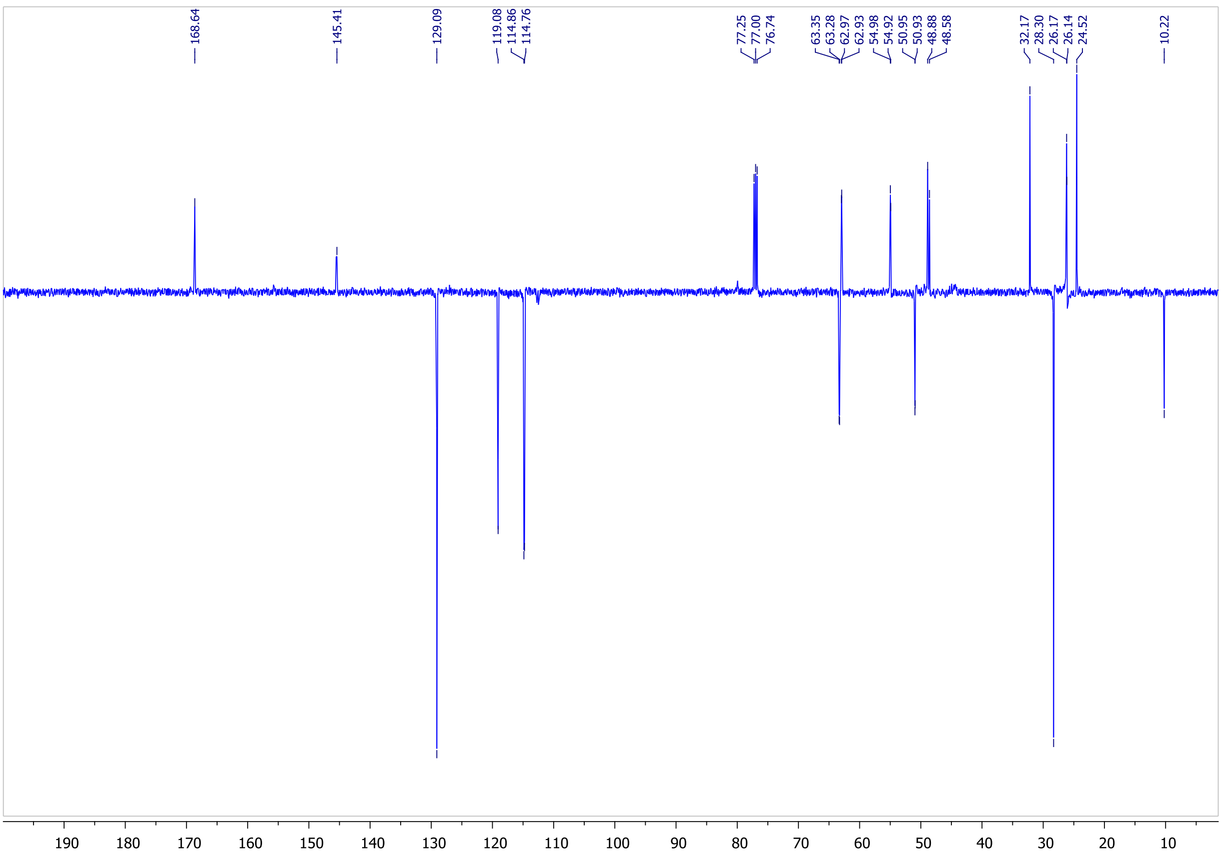


Figure S35d. **L3c**, $^{13}C\{^{1}H\}$ APT (125.7 MHz, $CDCl_3$, ambient temperature).

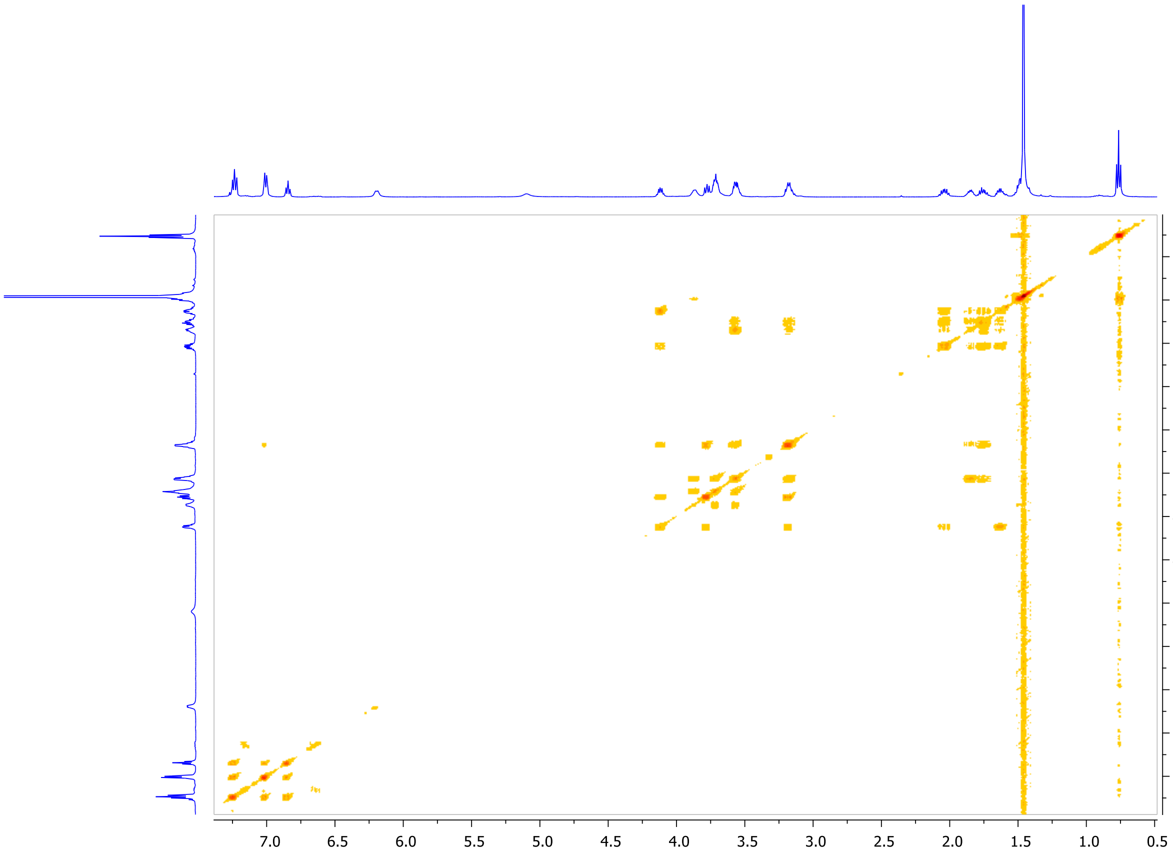


Figure S35e. **L3c**, ^{1}H-^{1}H COSY.

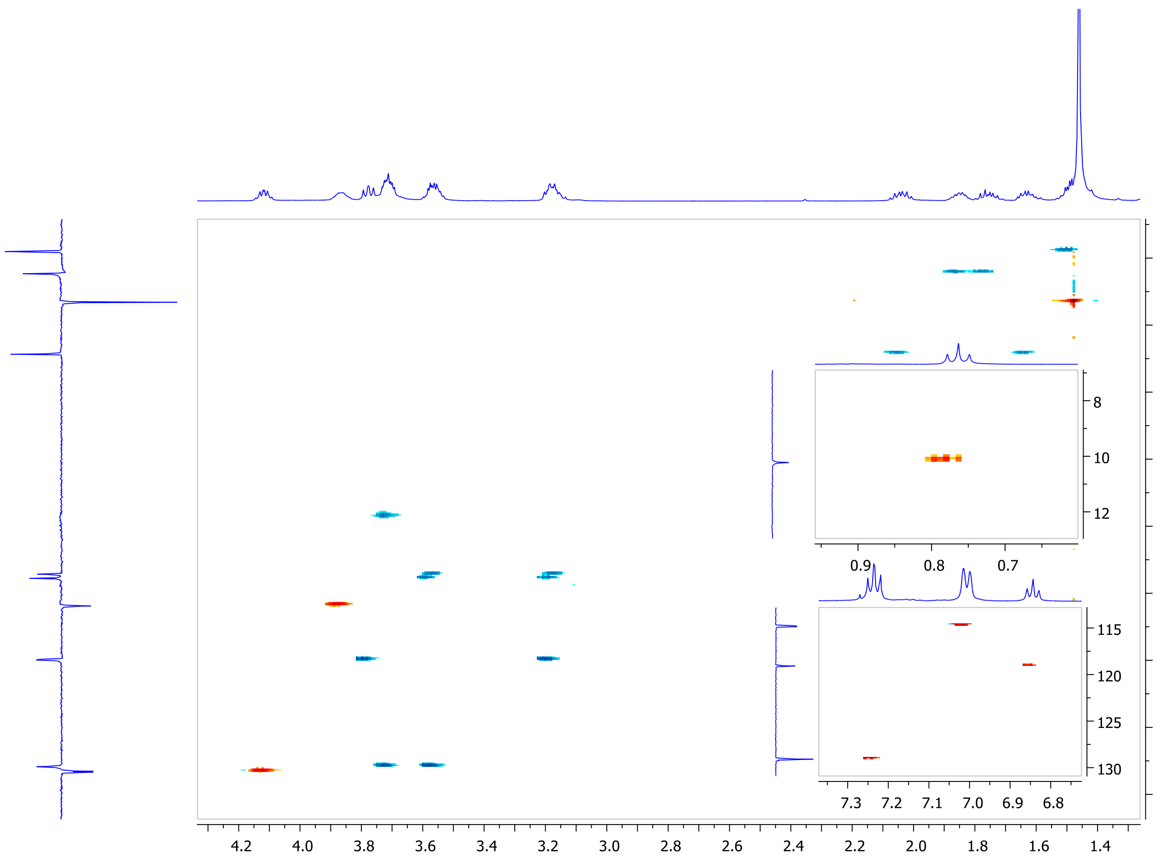


Figure S35f. **L3c**, ^{1}H-^{13}C HSQC.

NMR SPECTRA OF NEW COMPOUNDS

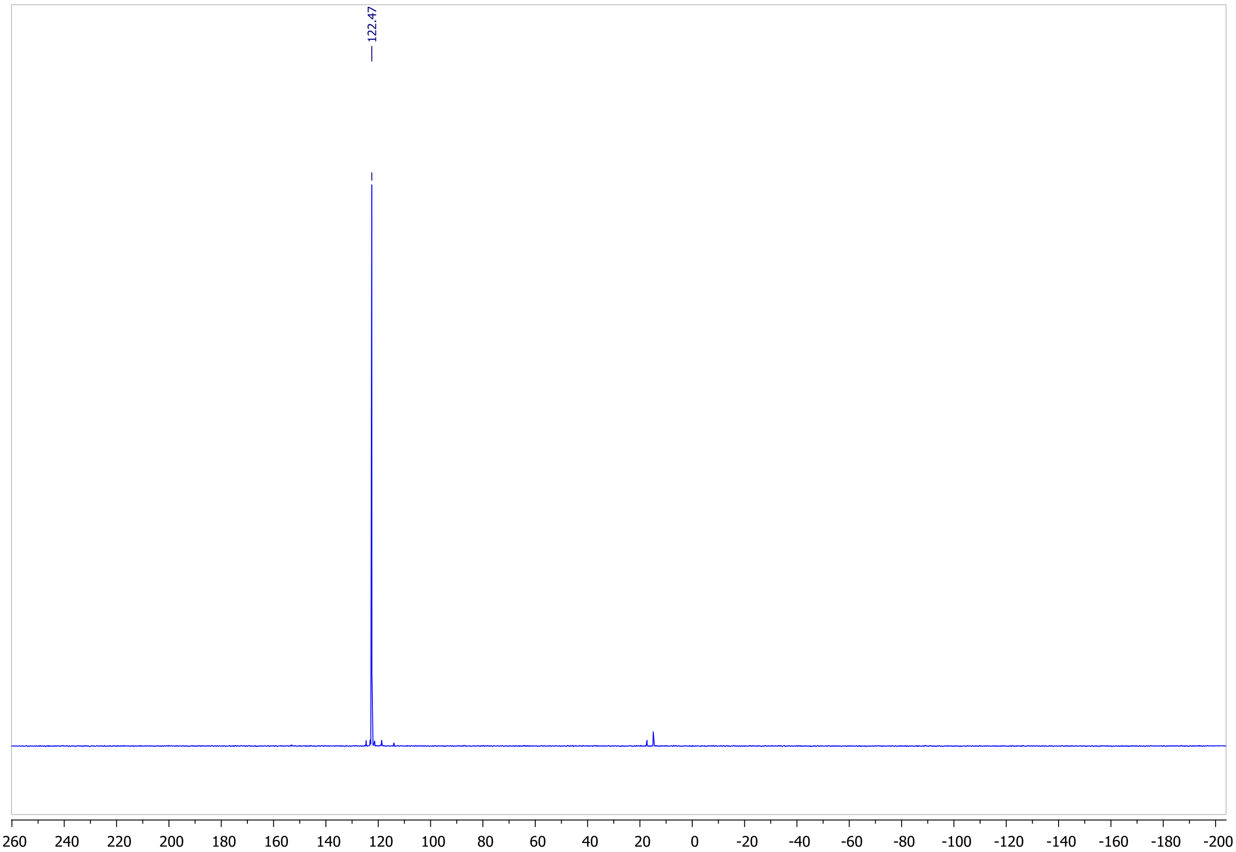


Figure S36a. **L3e**, $^{31}P\{^1H\}$ (162.0 MHz, $CDCl_3$, 26 °C).

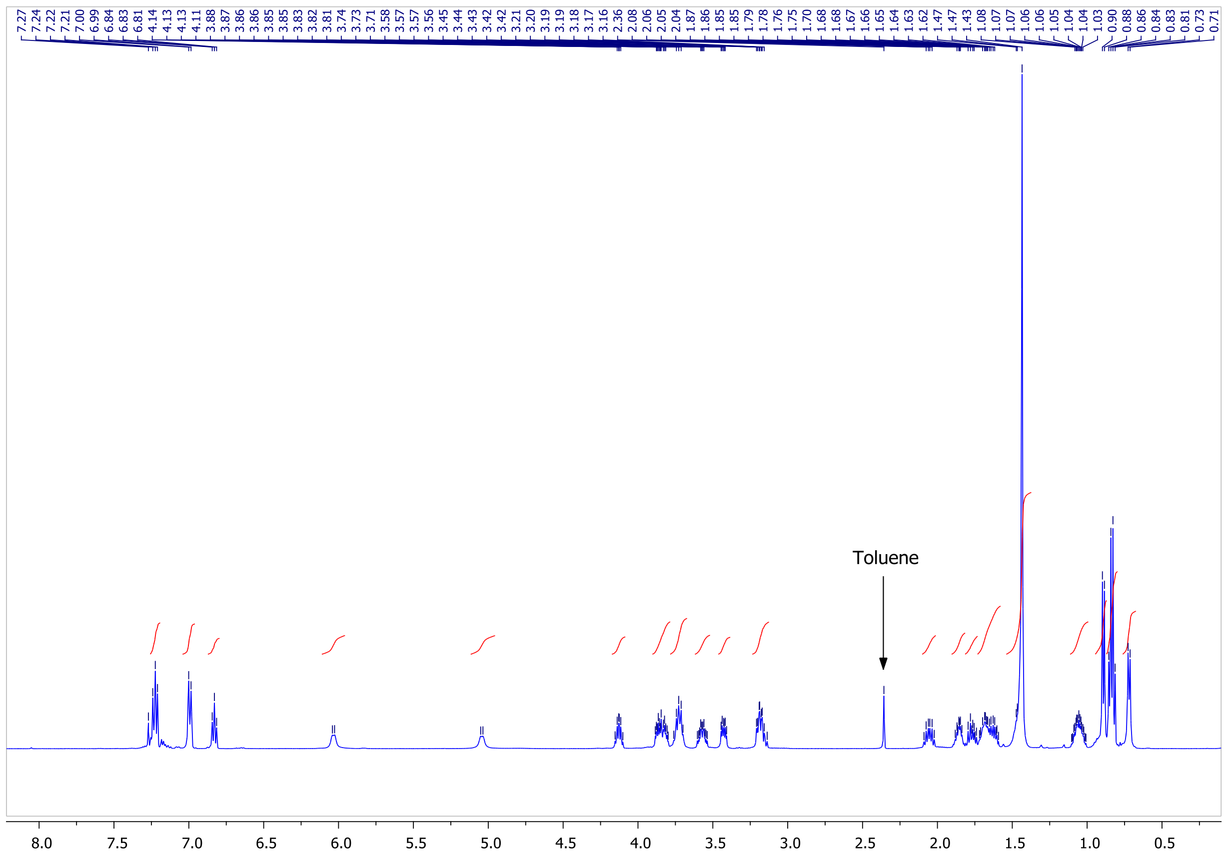


Figure S36b. **L3e**, ^1H (499.9 MHz, $CDCl_3$, ambient temperature).

NMR SPECTRA OF NEW COMPOUNDS

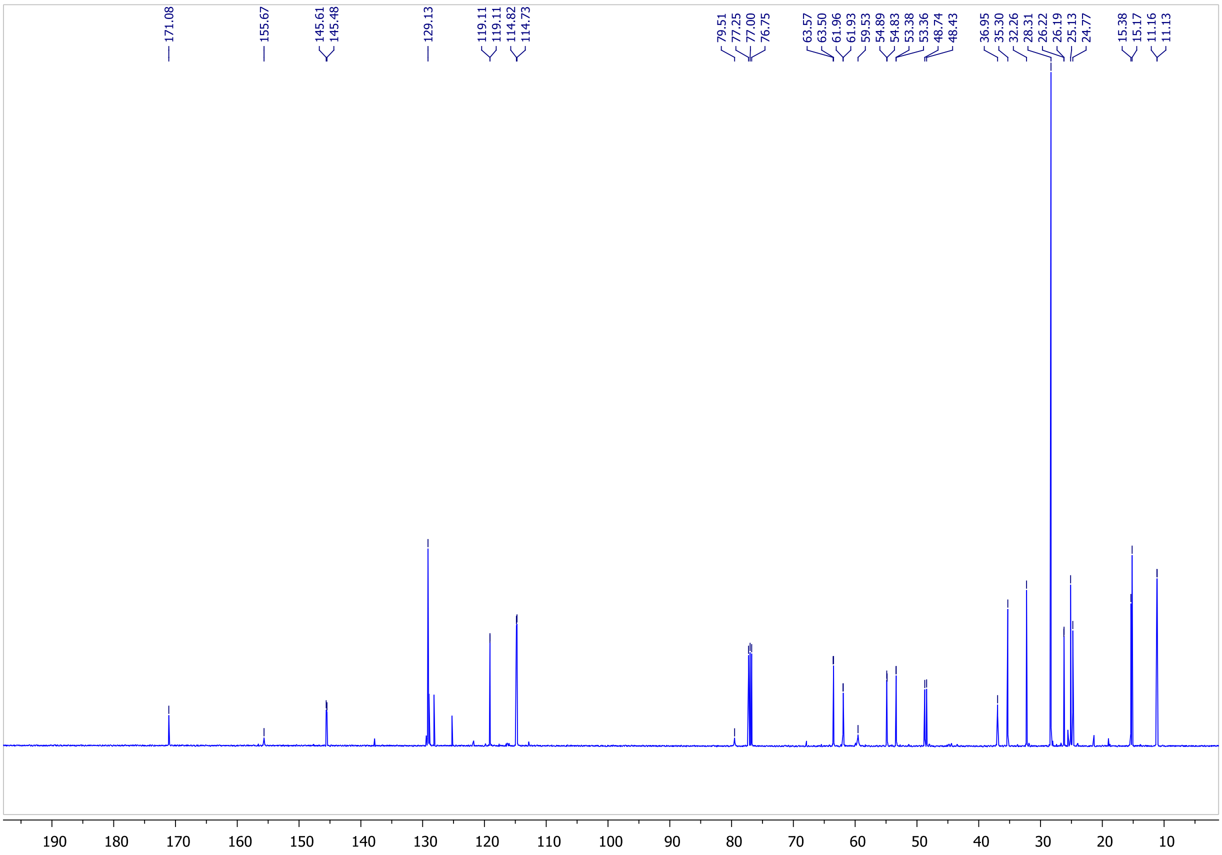


Figure S36c. **L3e**, $^{13}C\{^{1}H\}$ (125.7 MHz, $CDCl_3$, ambient temperature).

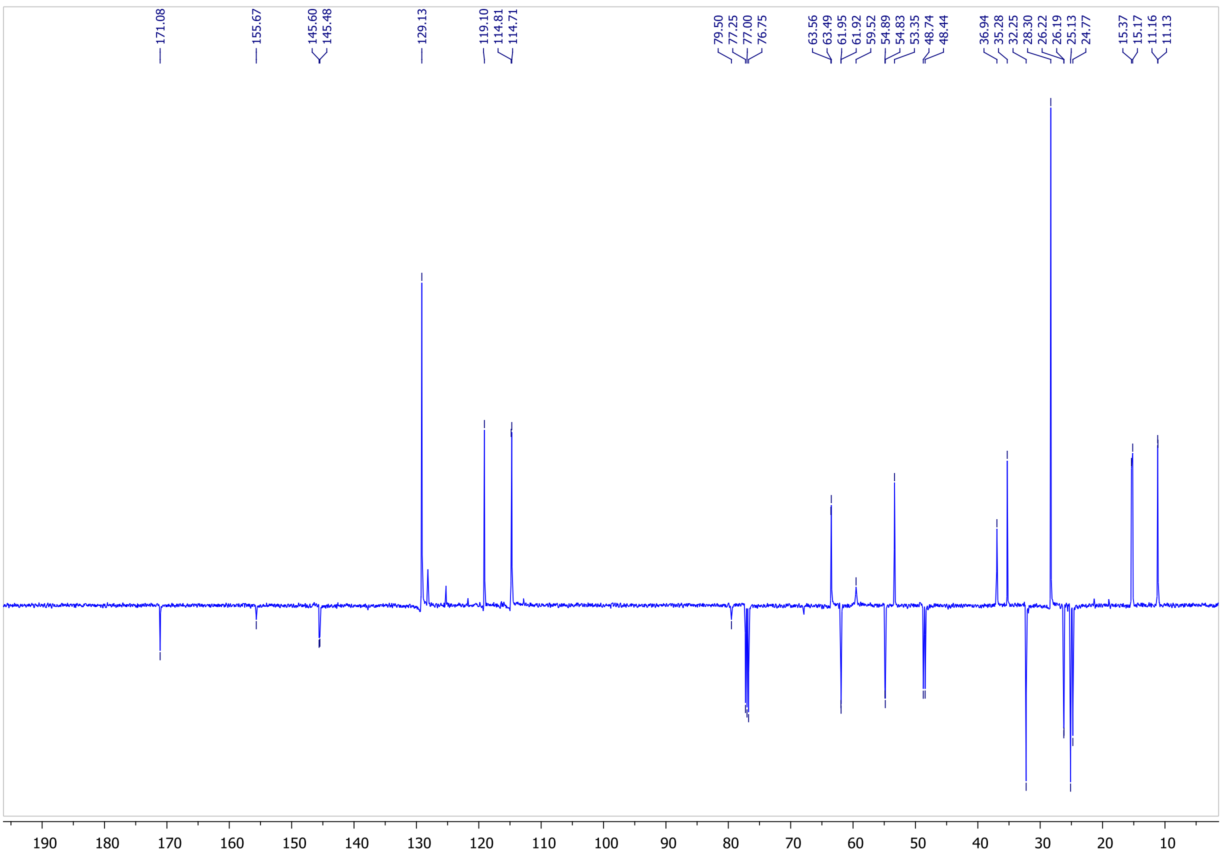


Figure S36d. **L3e**, $^{13}C\{^{1}H\}$ APT (125.7 MHz, $CDCl_3$, ambient temperature).

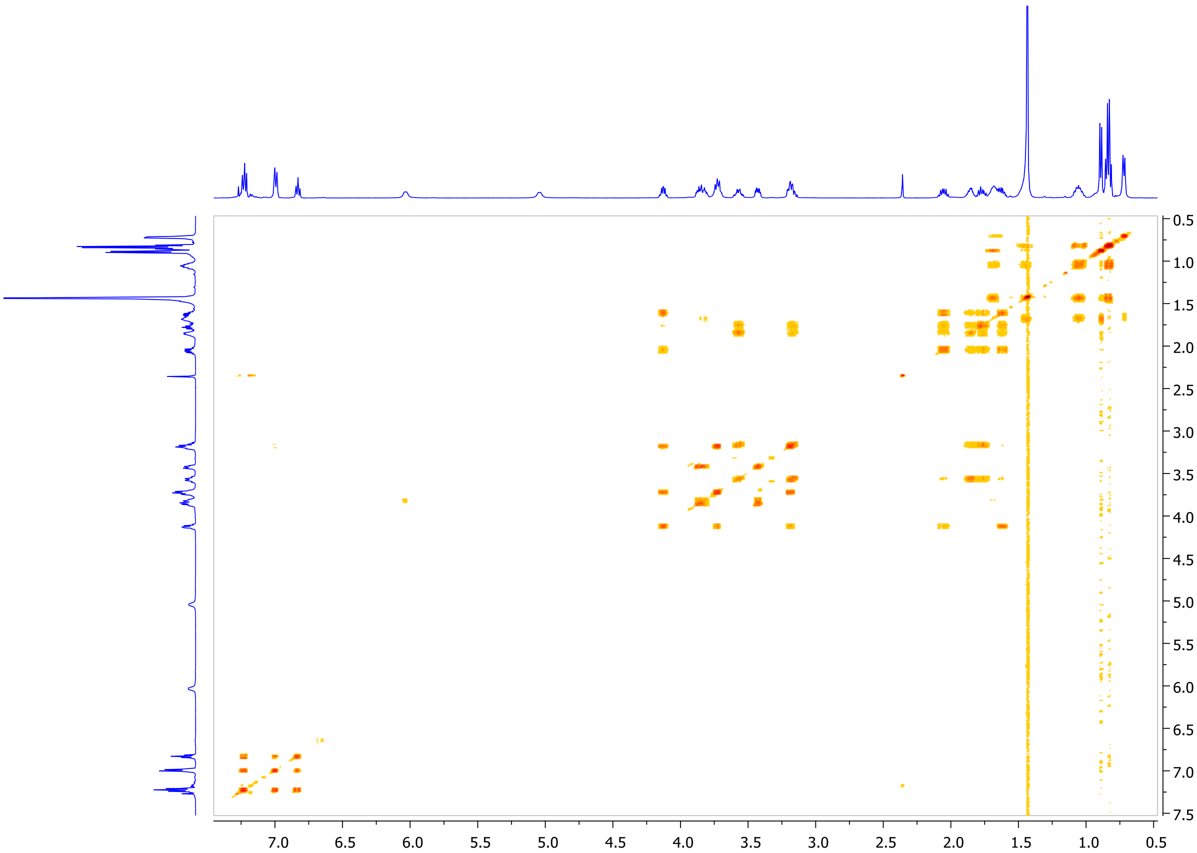


Figure S36e. **L3e**, ^{1}H-^{1}H COSY.

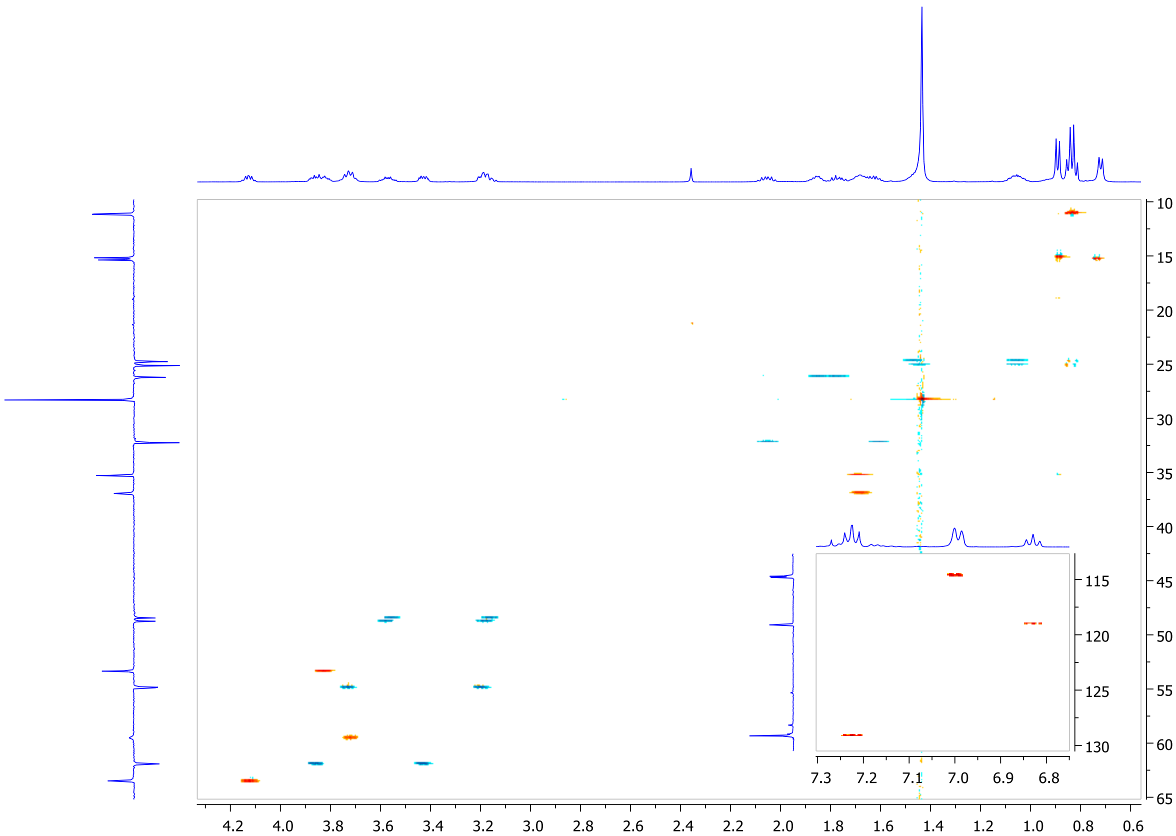


Figure S36f. **L3e**, ^{1}H-^{13}C HSQC.

NMR SPECTRA OF NEW COMPOUNDS

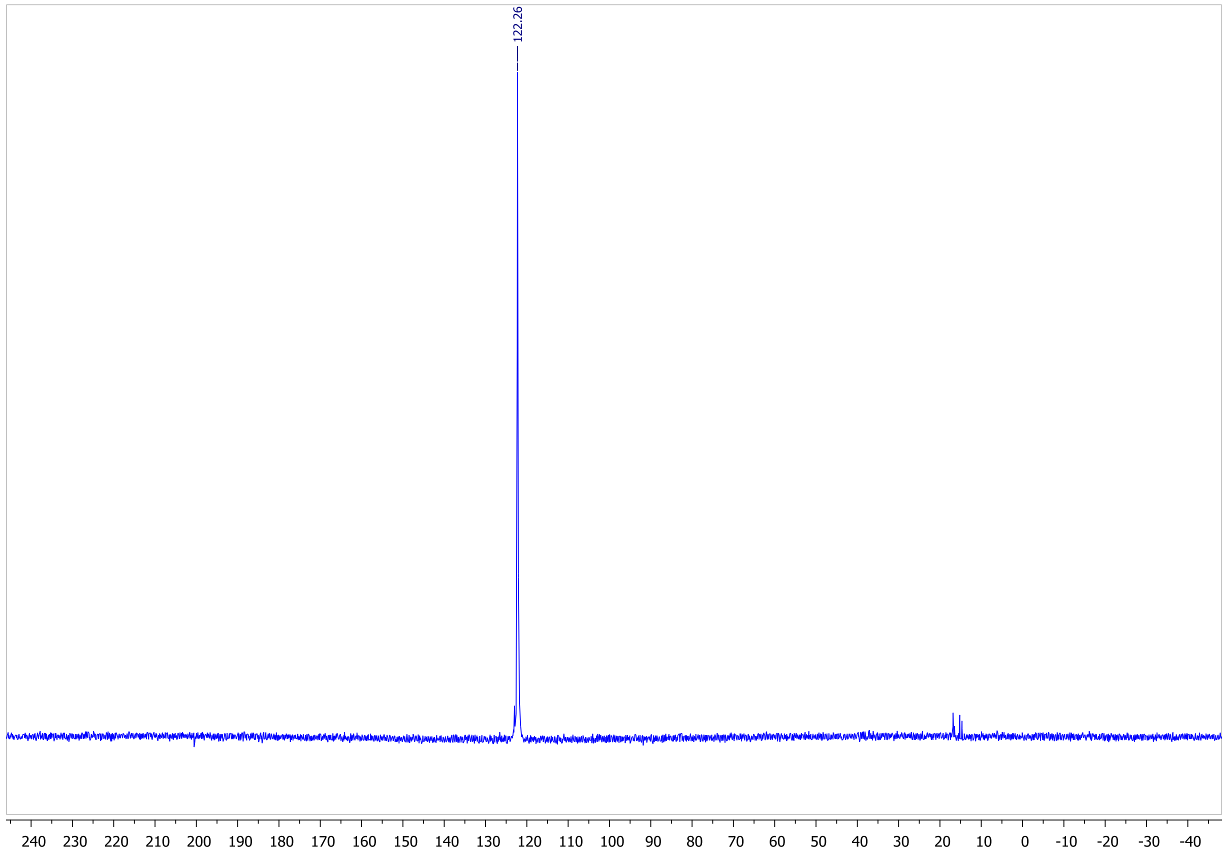


Figure S37a. **L3f**, $^{31}P\{^{1}H\}$ (202.4 MHz, $CDCl_3$, ambient temperature).

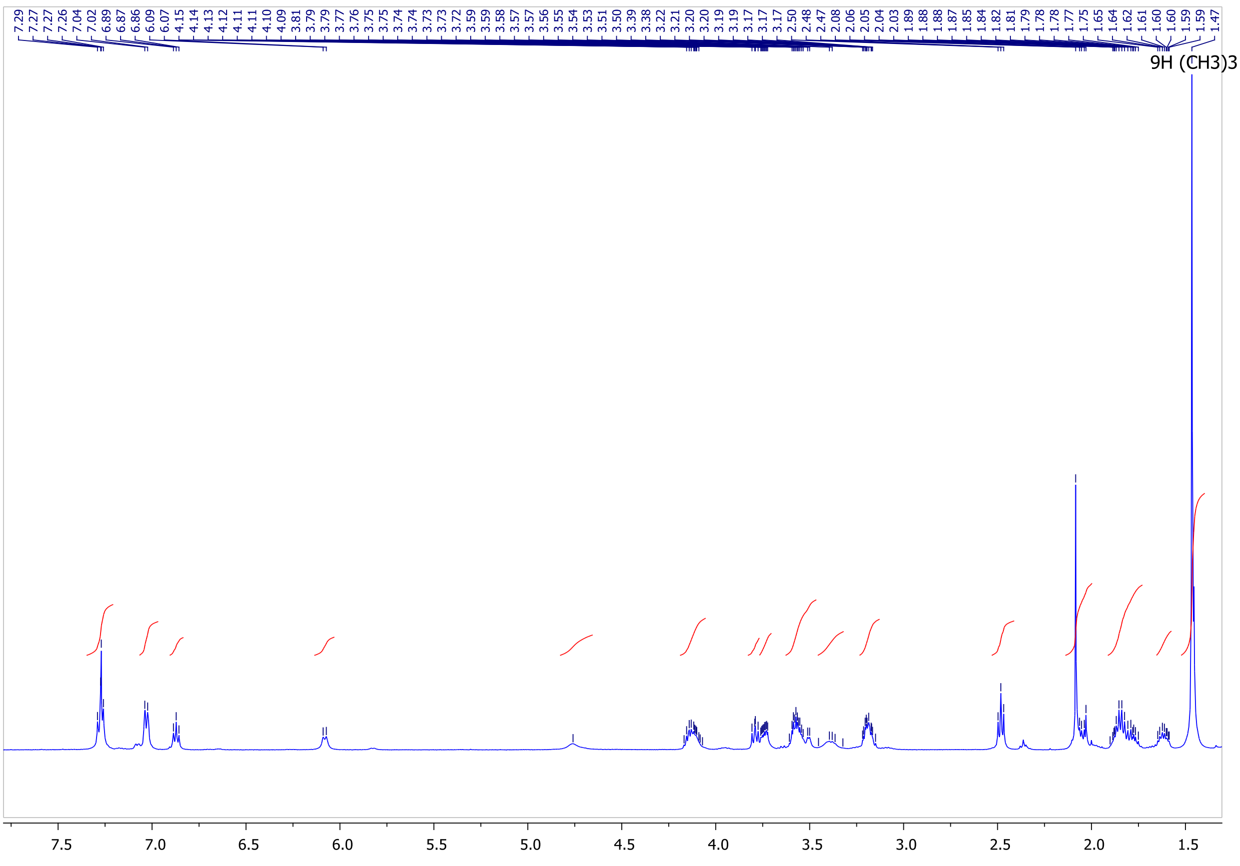


Figure S37b. **L3f**, ^{1}H (499.9 MHz, $CDCl_3$, ambient temperature).

NMR SPECTRA OF NEW COMPOUNDS

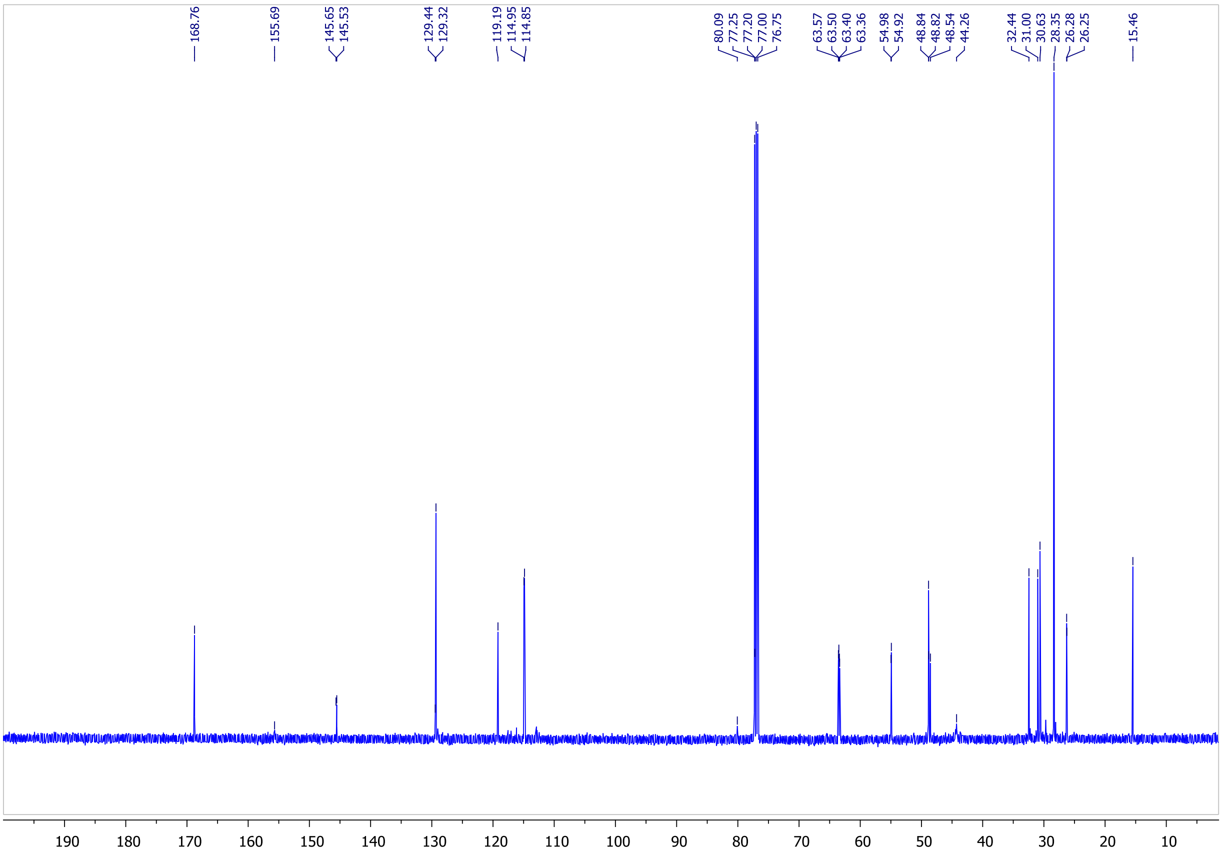


Figure S37c. **L3f**, $^{13}C\{^{1}H\}$ (125.7 MHz, $CDCl_3$, ambient temperature).

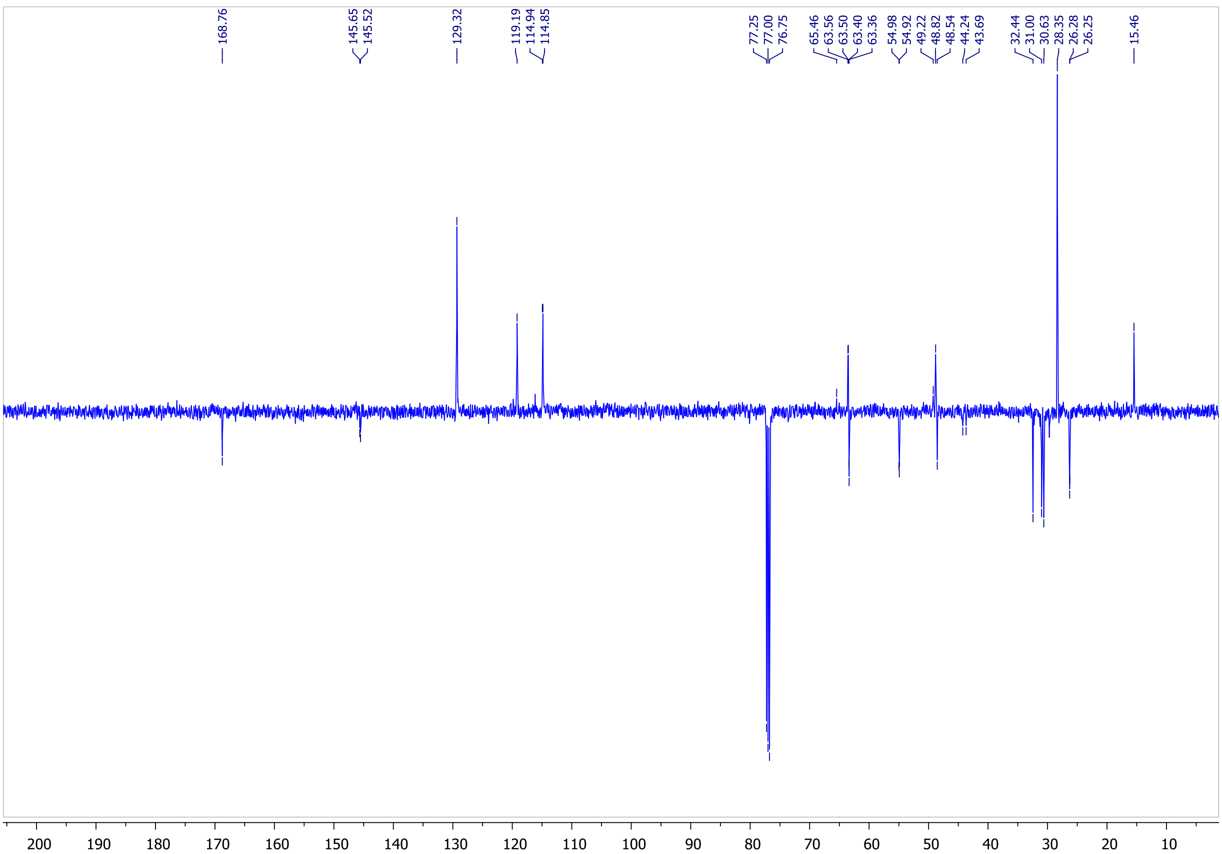


Figure S37d. **L3f**, $^{13}C\{^{1}H\}$ APT (125.7 MHz, $CDCl_3$, ambient temperature).

NMR SPECTRA OF NEW COMPOUNDS

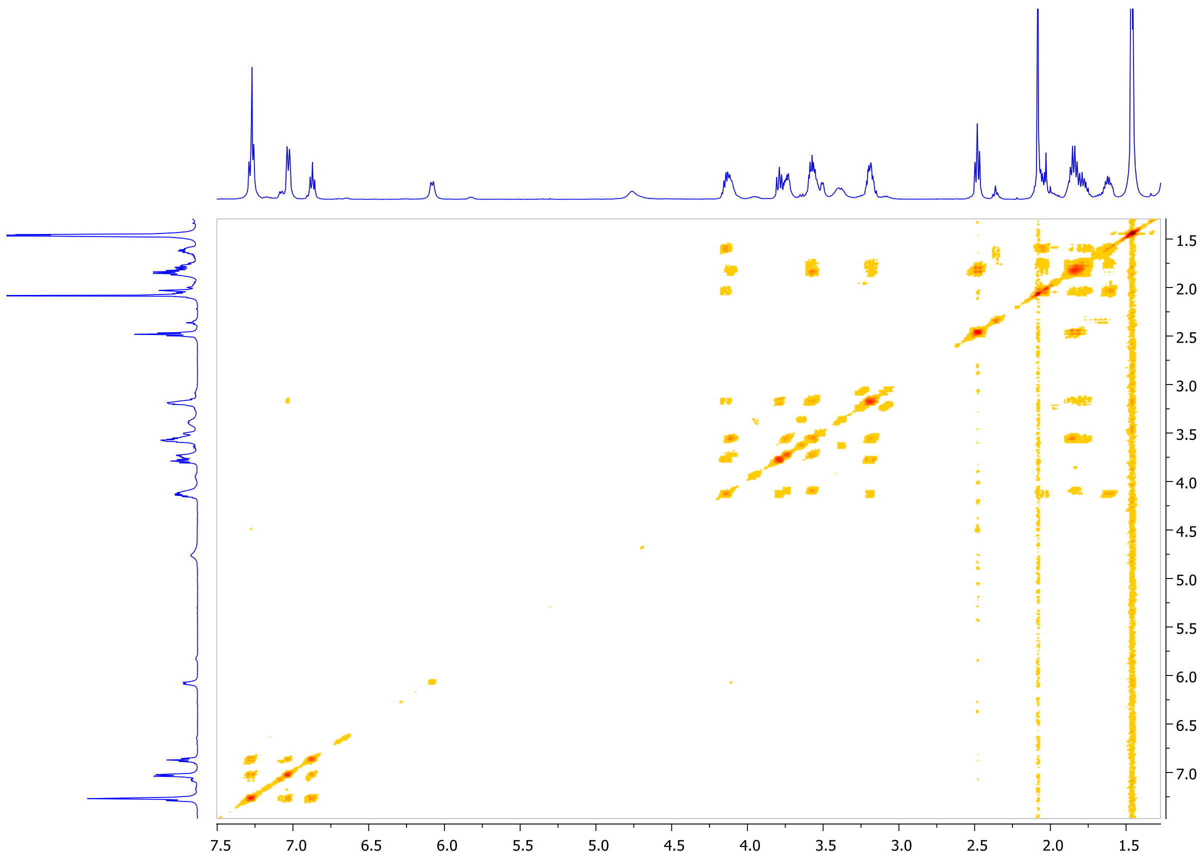


Figure S37e. **L3f**, ^{1}H-^{1}H COSY.

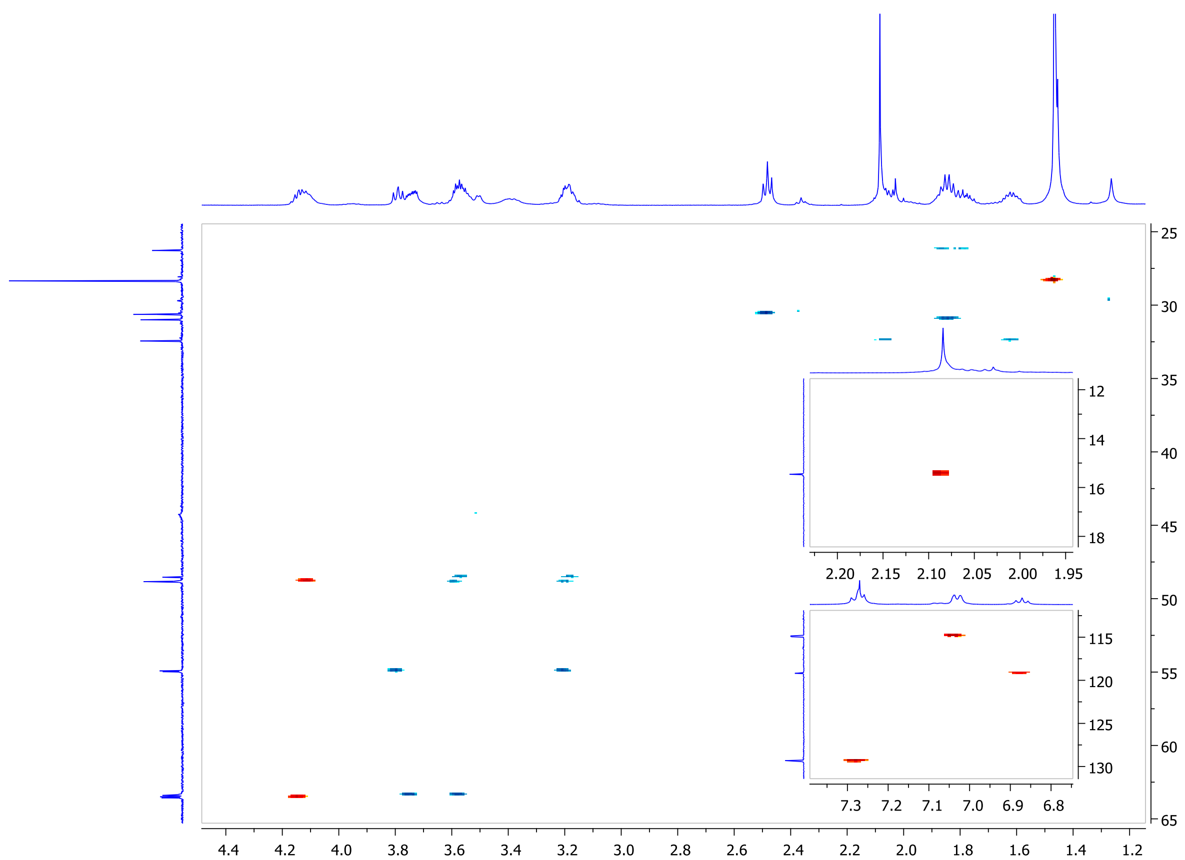


Figure S37f. **L3f**, ^{1}H-^{13}C HSQC.

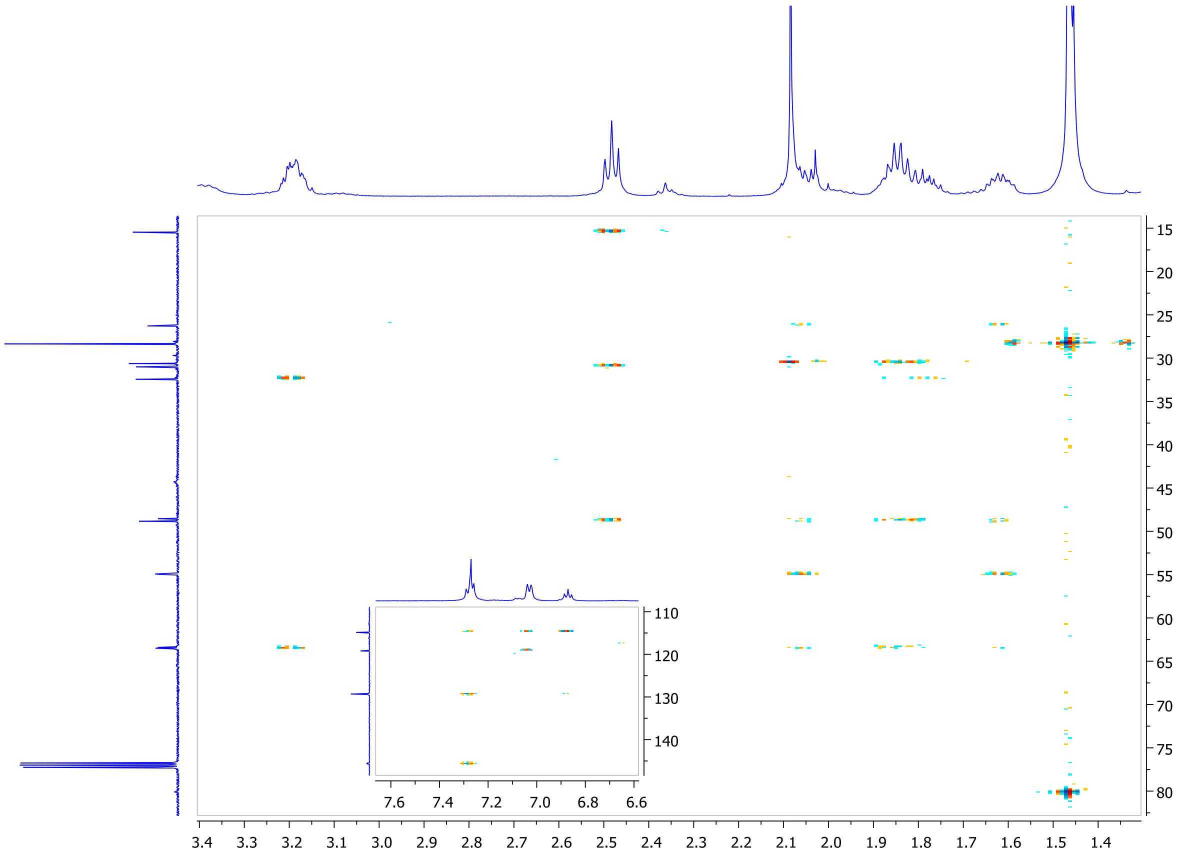


Figure S37g. **L3f**, ^{1}H-^{13}C HMBC.

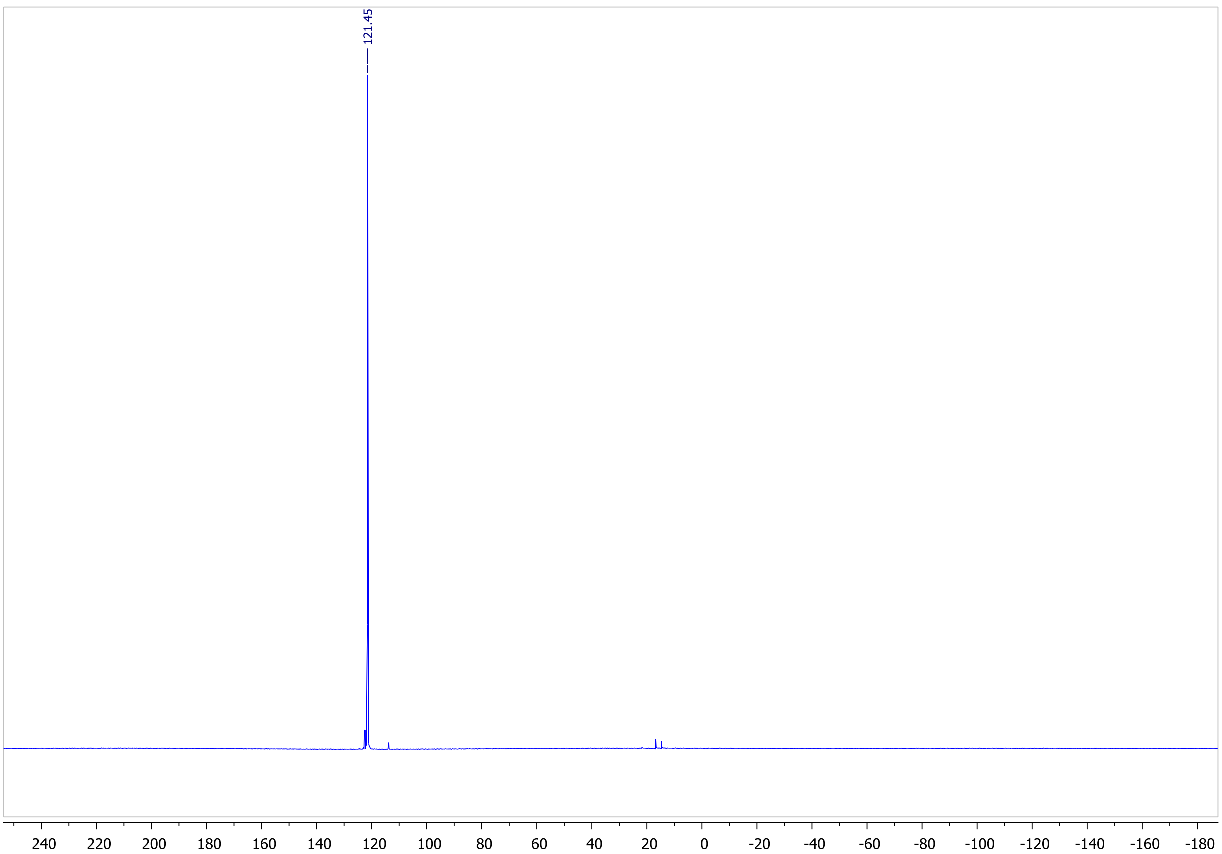


Figure S38a. **L3g**, ^{31}P{^{1}H} (202.4 MHz, $CDCl_3$, ambient temperature).

NMR SPECTRA OF NEW COMPOUNDS

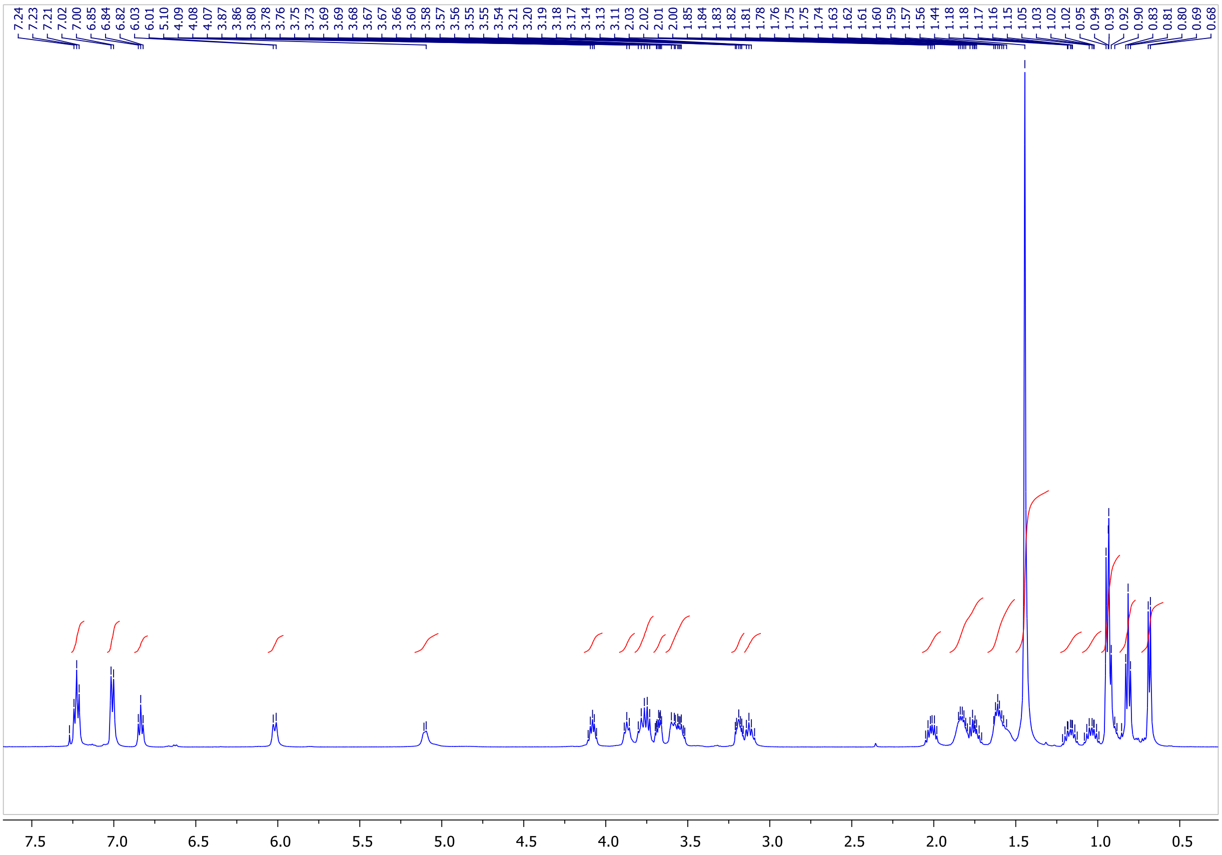


Figure S38b. **L3g**, ^{1}H (499.9 MHz, $CDCl_3$, ambient temperature).

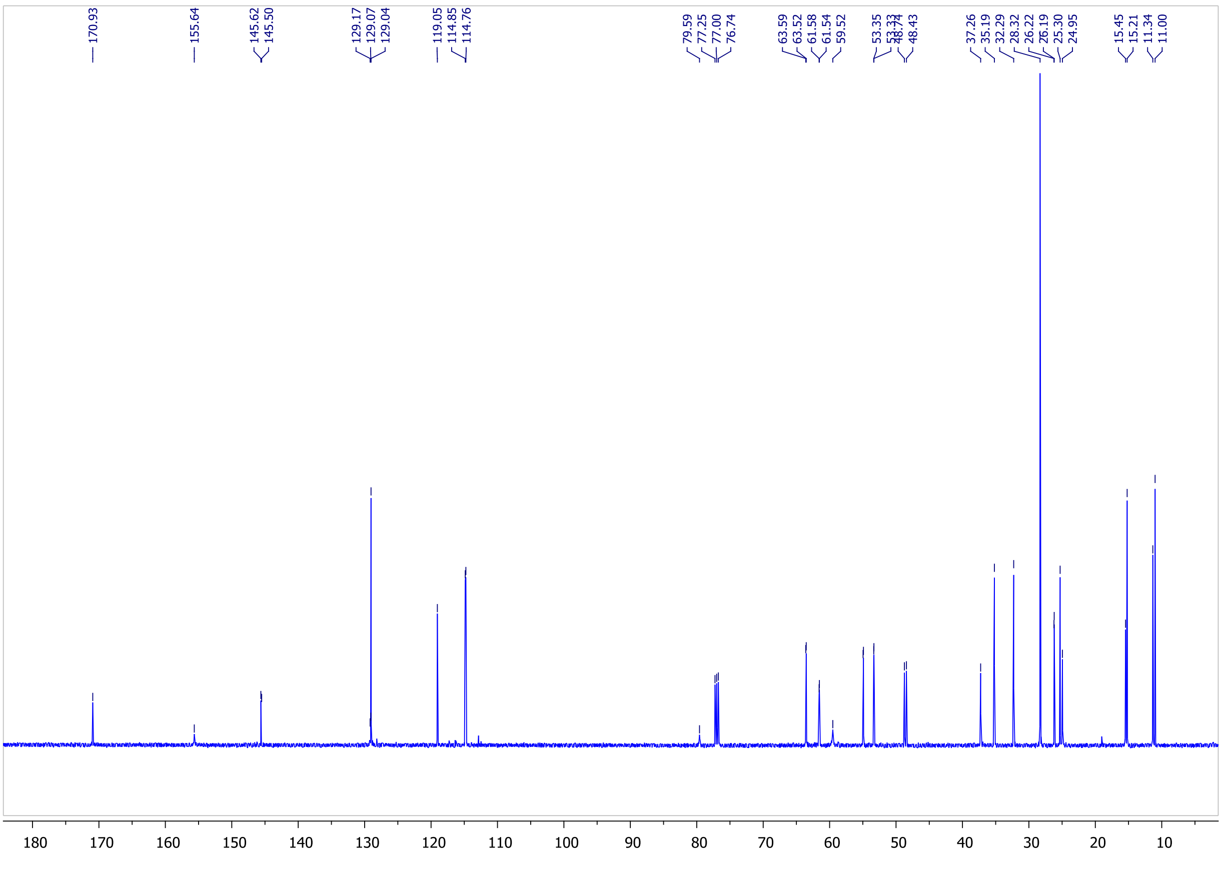


Figure S38c. **L3g**, $^{13}C\{^{1}H\}$ (125.7 MHz, $CDCl_3$, ambient temperature).

NMR SPECTRA OF NEW COMPOUNDS

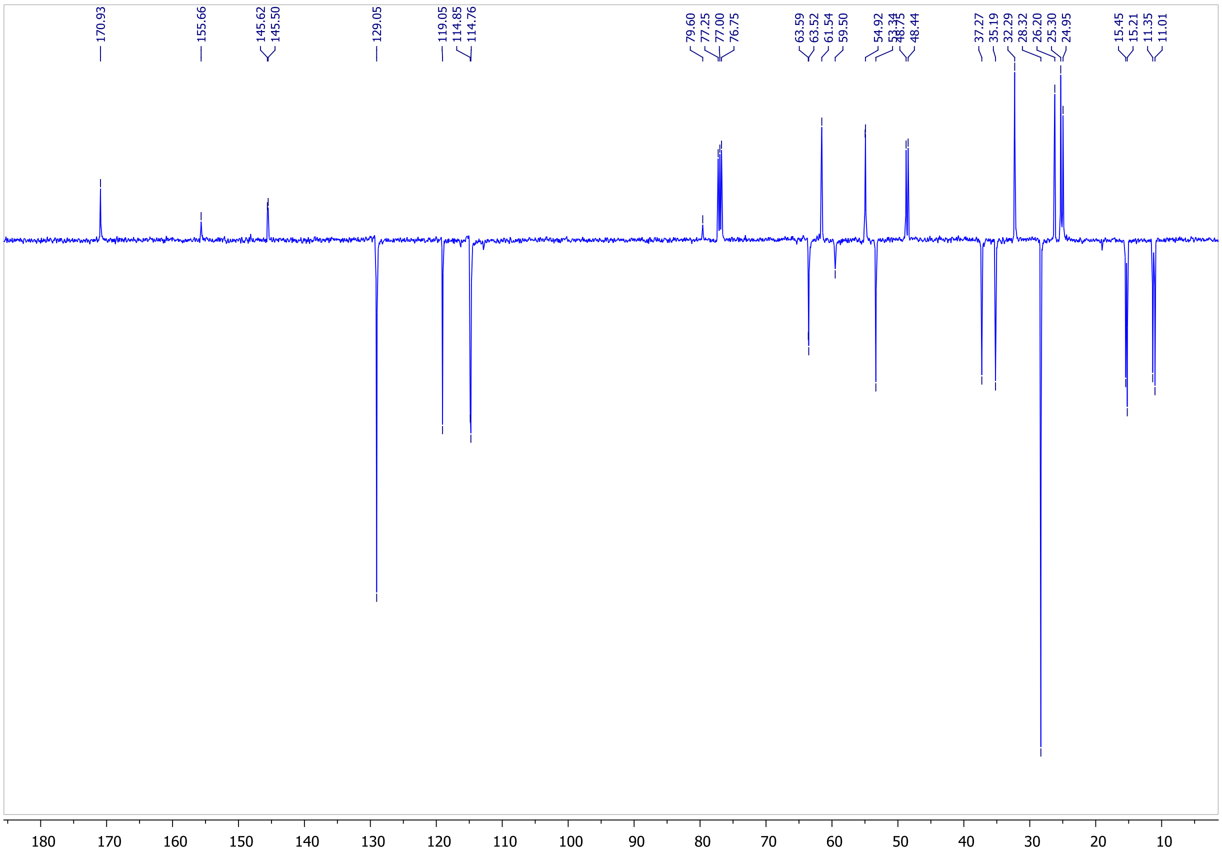


Figure S38d. **L3g**, $^{13}C\{^1H\}$ APT (125.7 MHz, $CDCl_3$, ambient temperature).

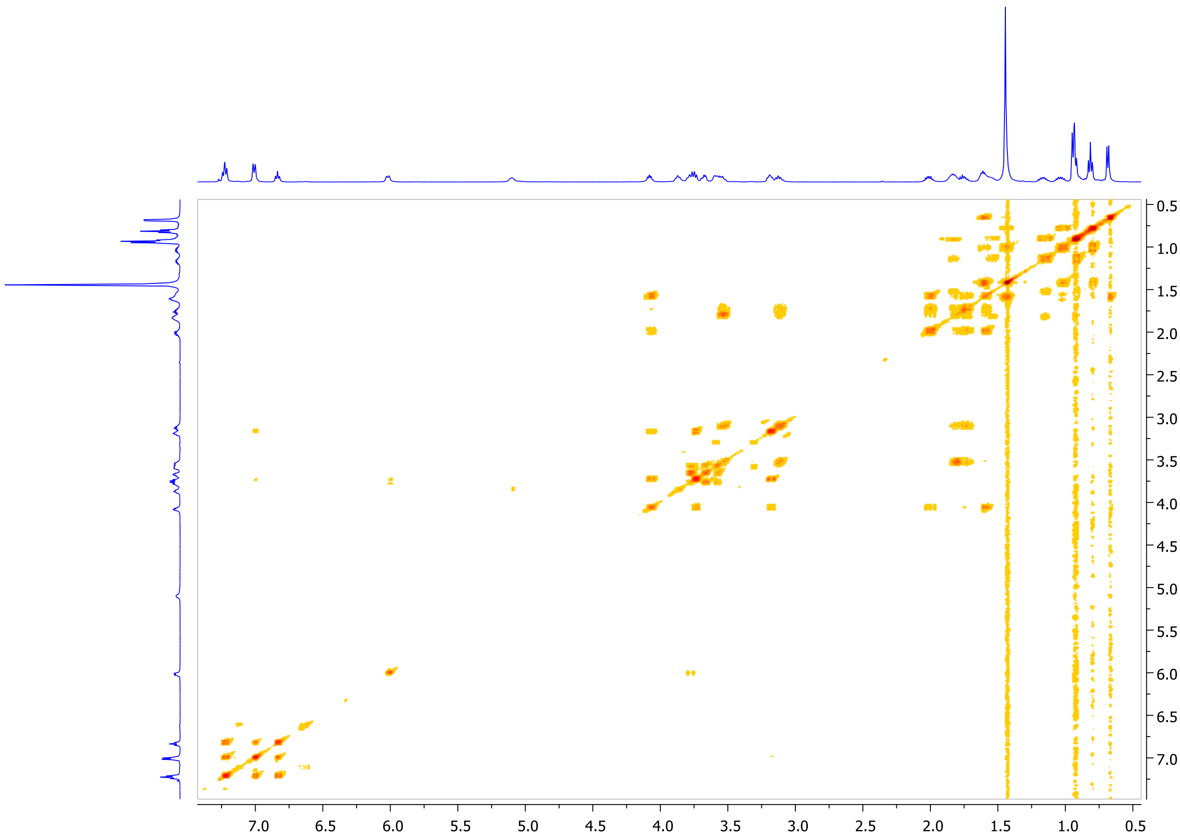


Figure S38e. **L3g**, ^1H-^1H COSY.

NMR SPECTRA OF NEW COMPOUNDS

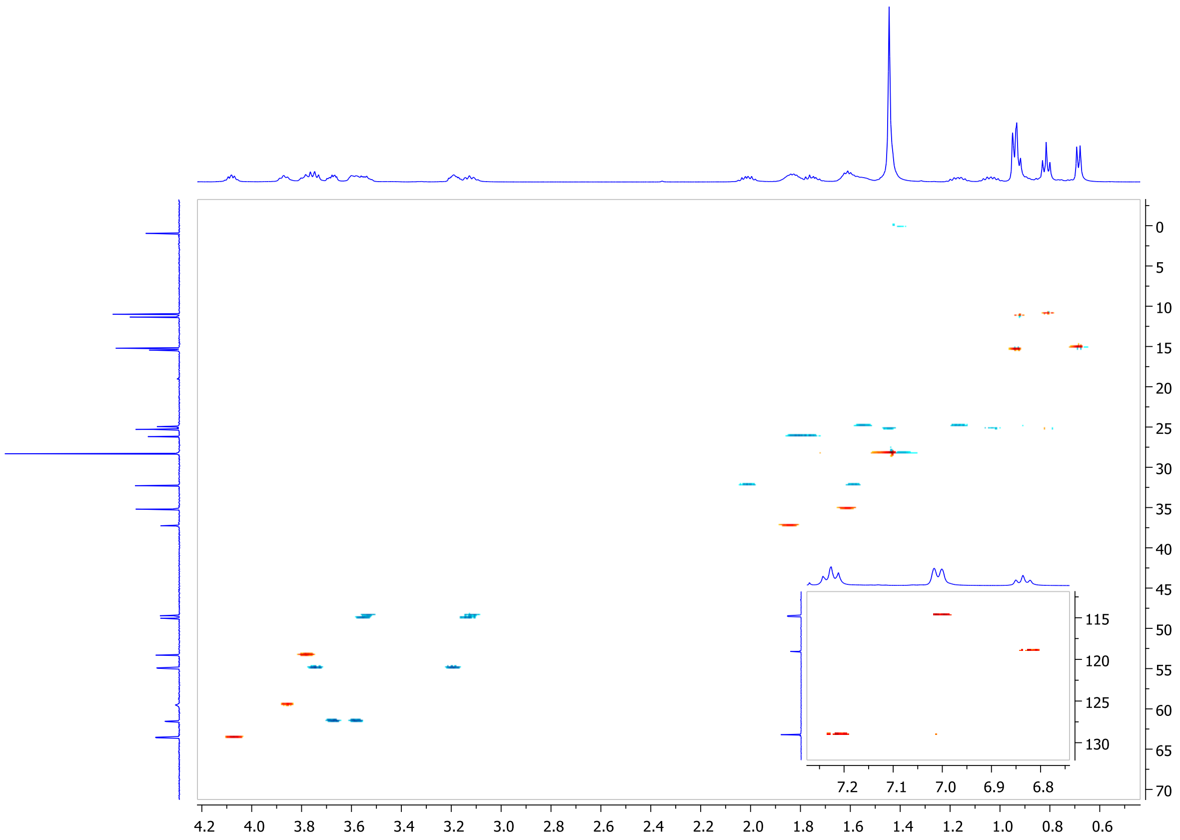


Figure S38f. **L3g**, ¹H-¹³C HSQC.

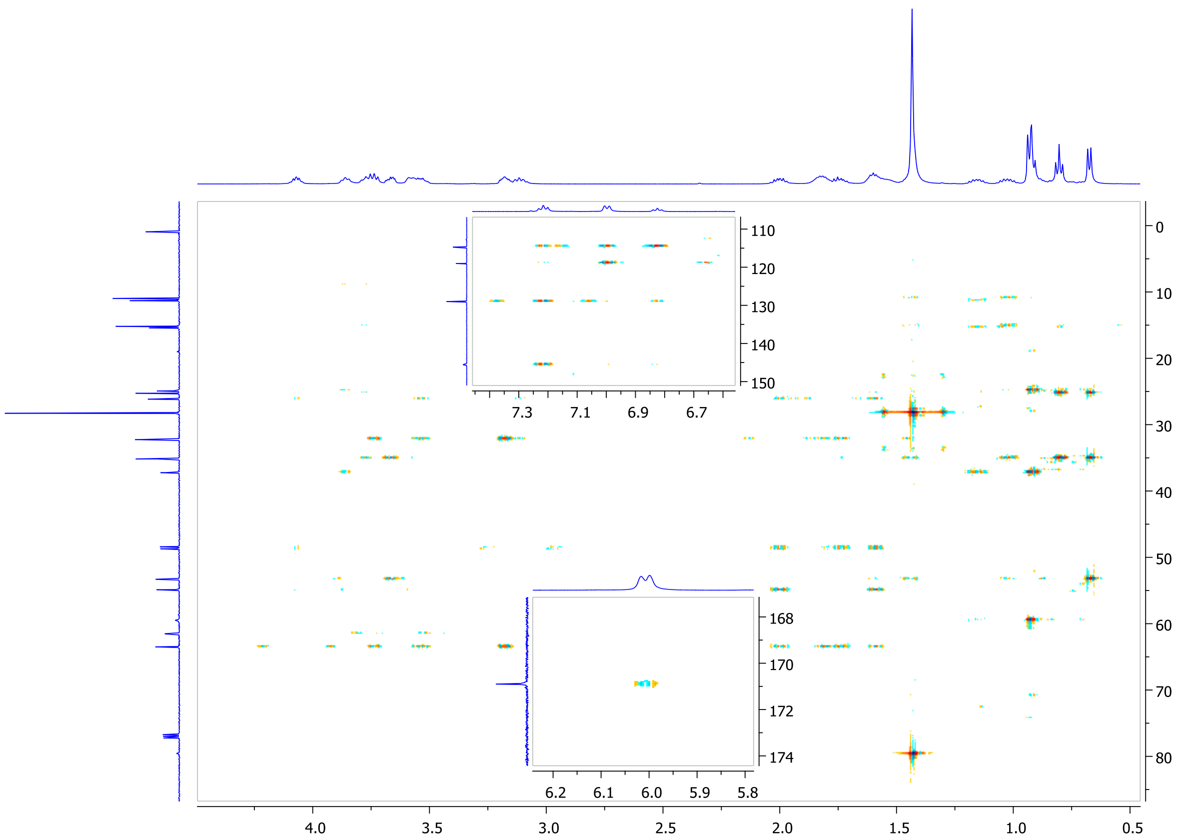


Figure S38g. **L3g**, ¹H-¹³C HMBC.

NMR SPECTRA OF NEW COMPOUNDS

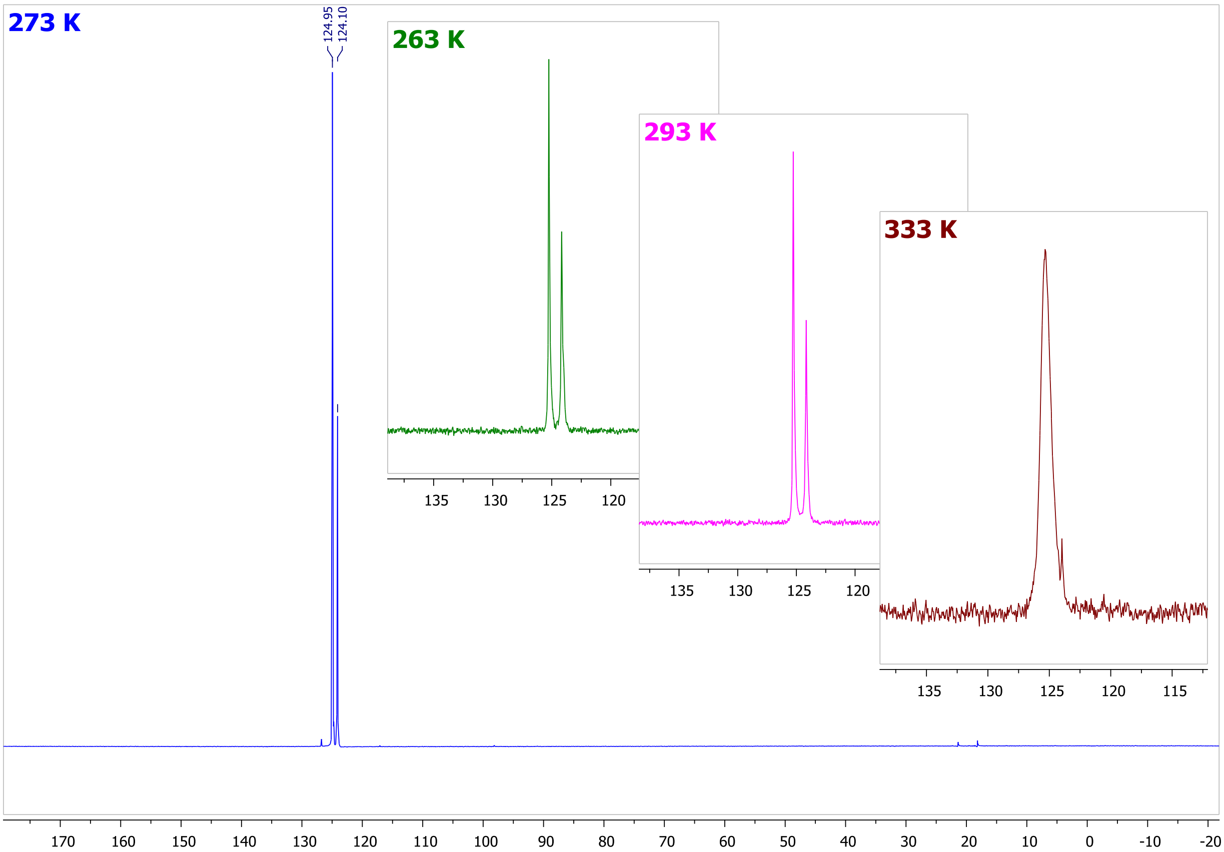


Figure S39a. **L4**, $^{31}P\{^1H\}$ (242.9 MHz, $CDCl_3$).

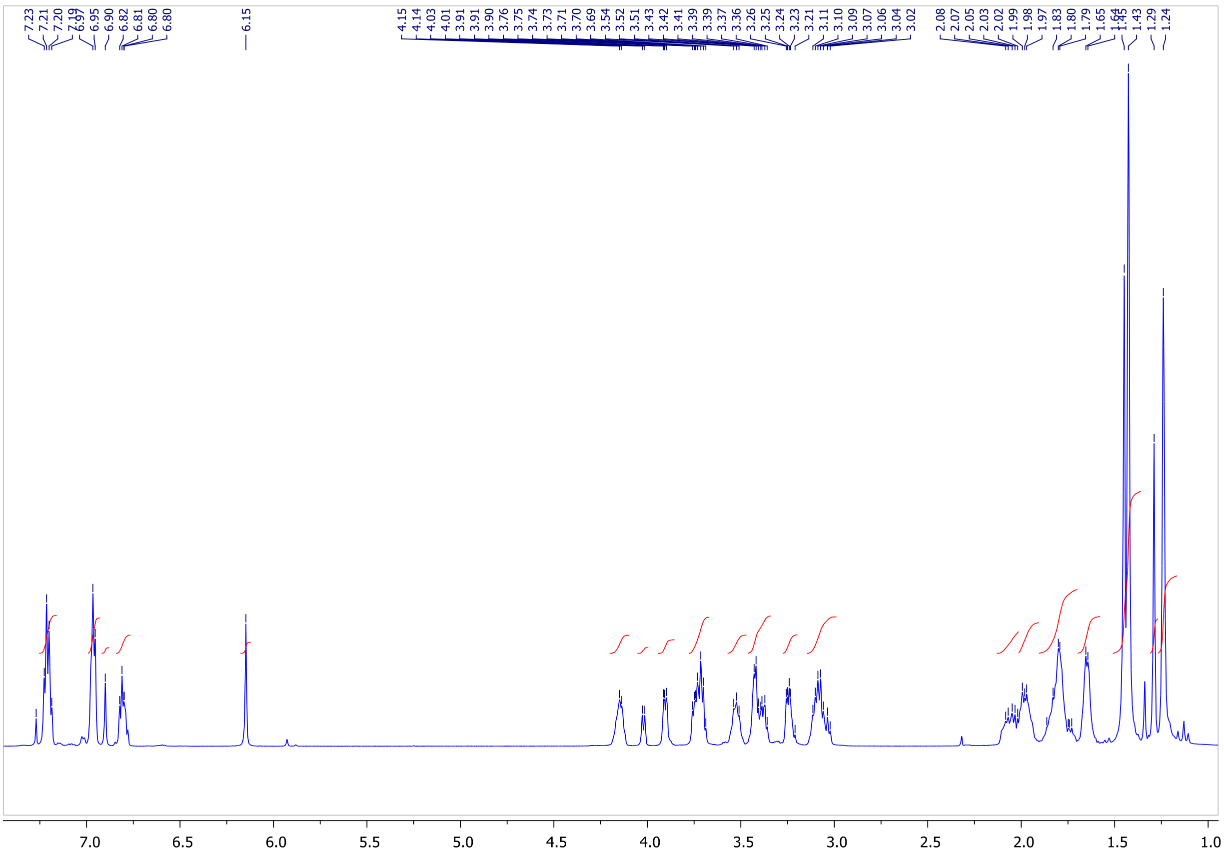


Figure S39b. **L4**, ^1H (600.1 MHz, $CDCl_3$, -20 °C).

NMR SPECTRA OF NEW COMPOUNDS

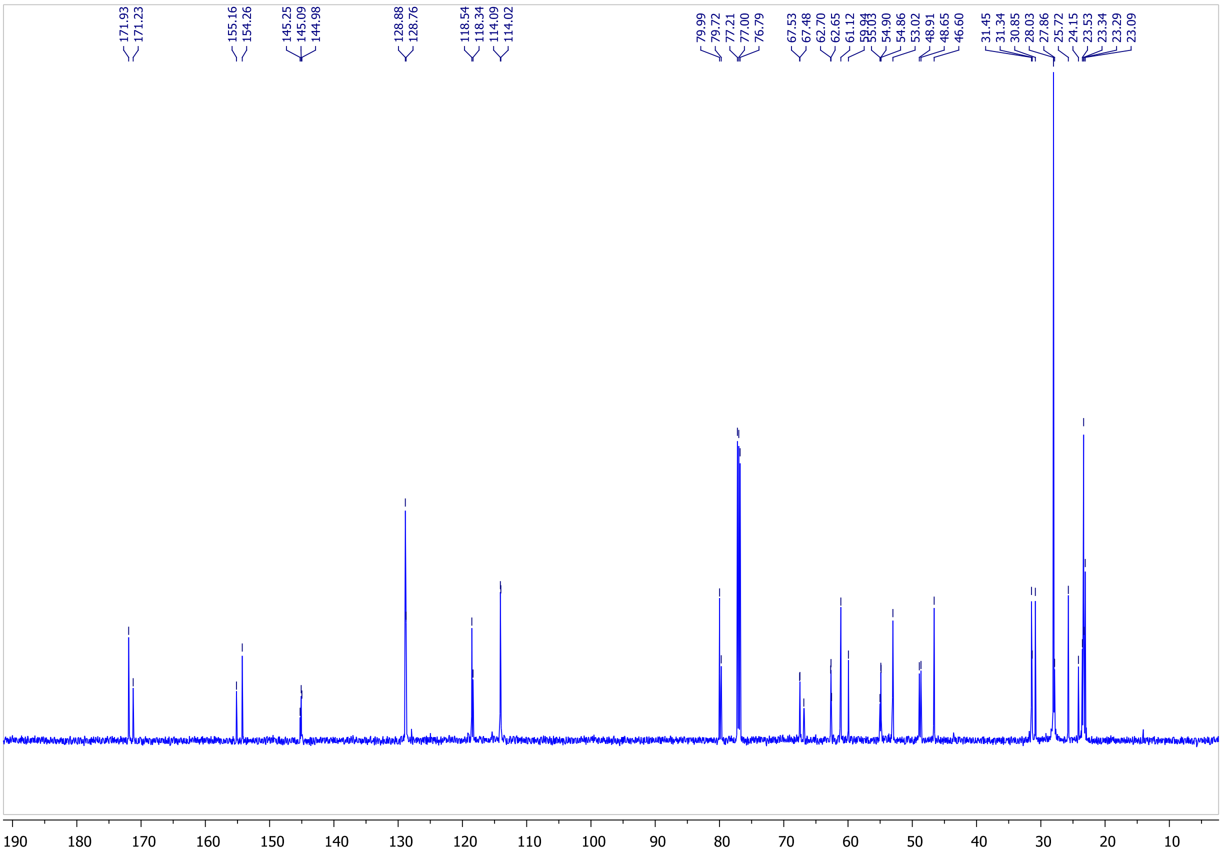


Figure S39c. **L4**, $^{13}C\{^{1}H\}$ (150.9 MHz, $CDCl_3$, -20 °C).

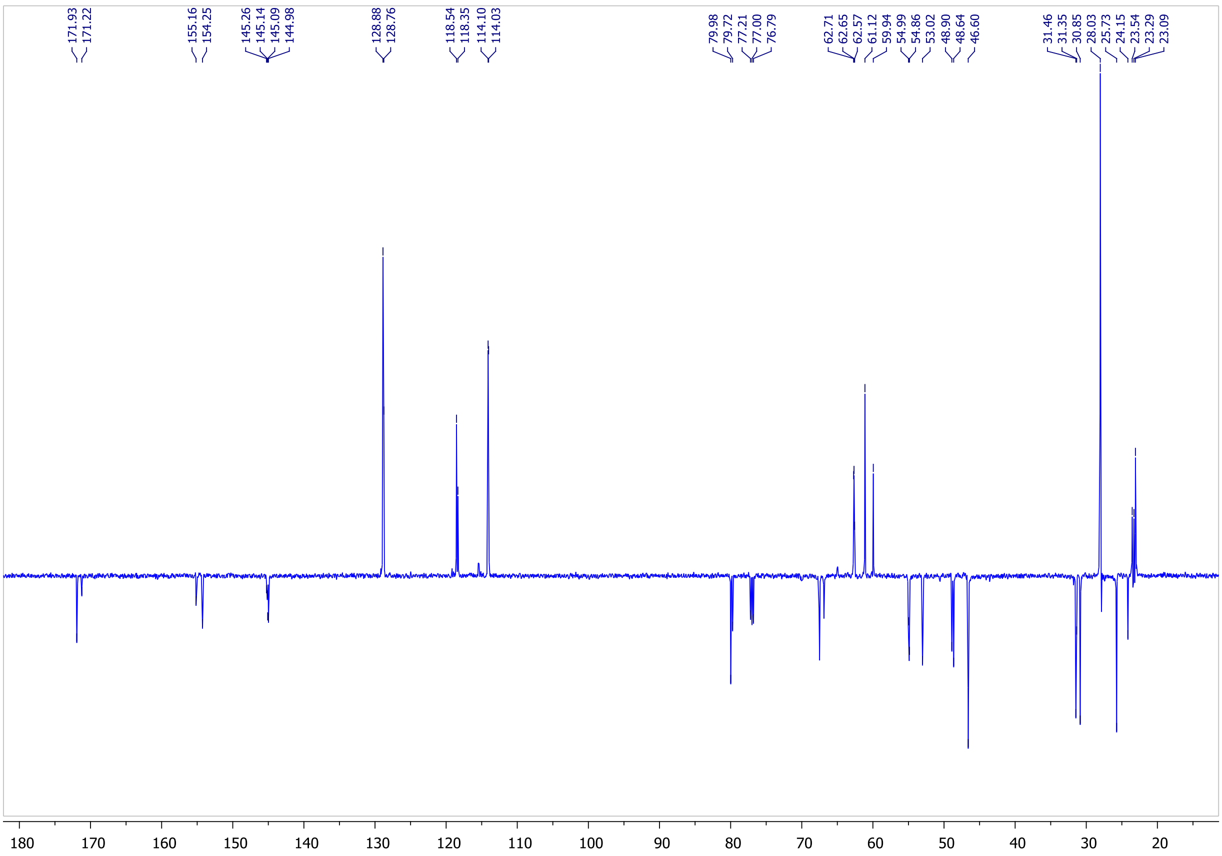


Figure S39d. **L4**, $^{13}C\{^{1}H\}$ APT (150.9 MHz, $CDCl_3$, -20 °C).

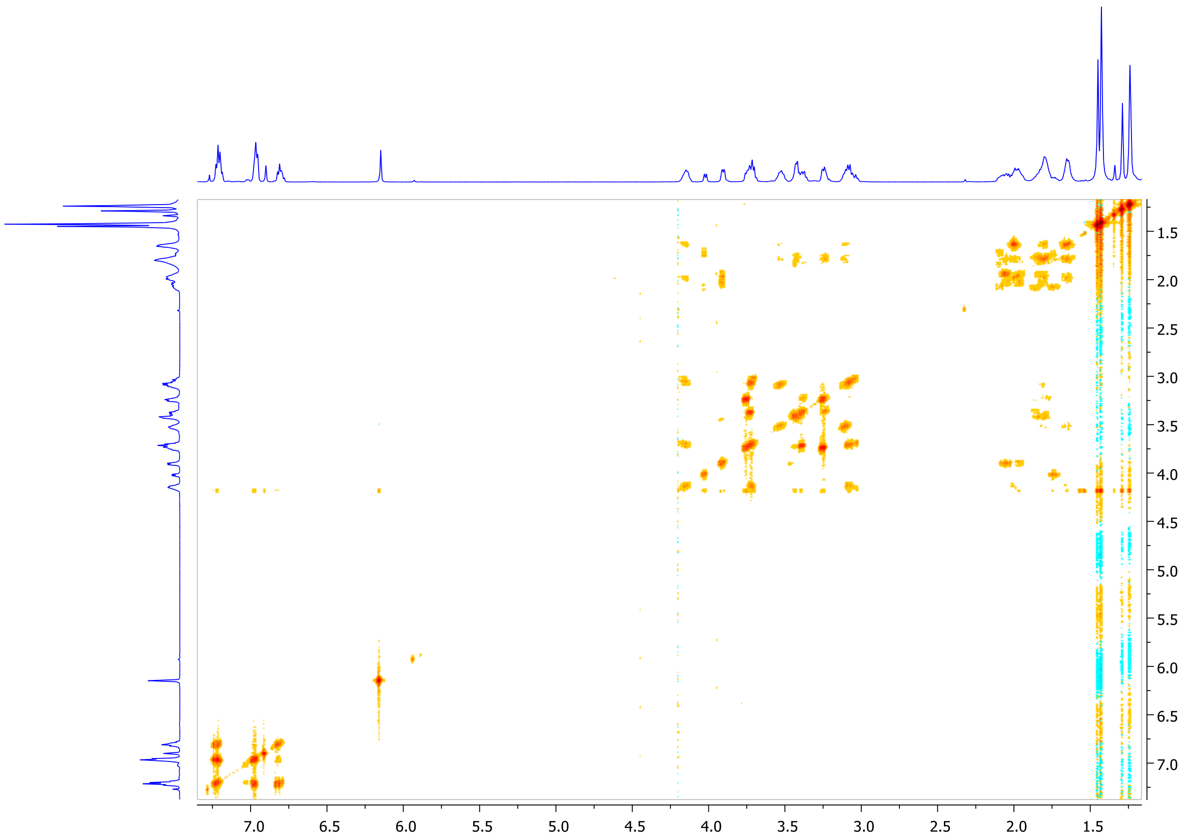


Figure S39e. **L4**, ^{1}H-^{1}H COSY.

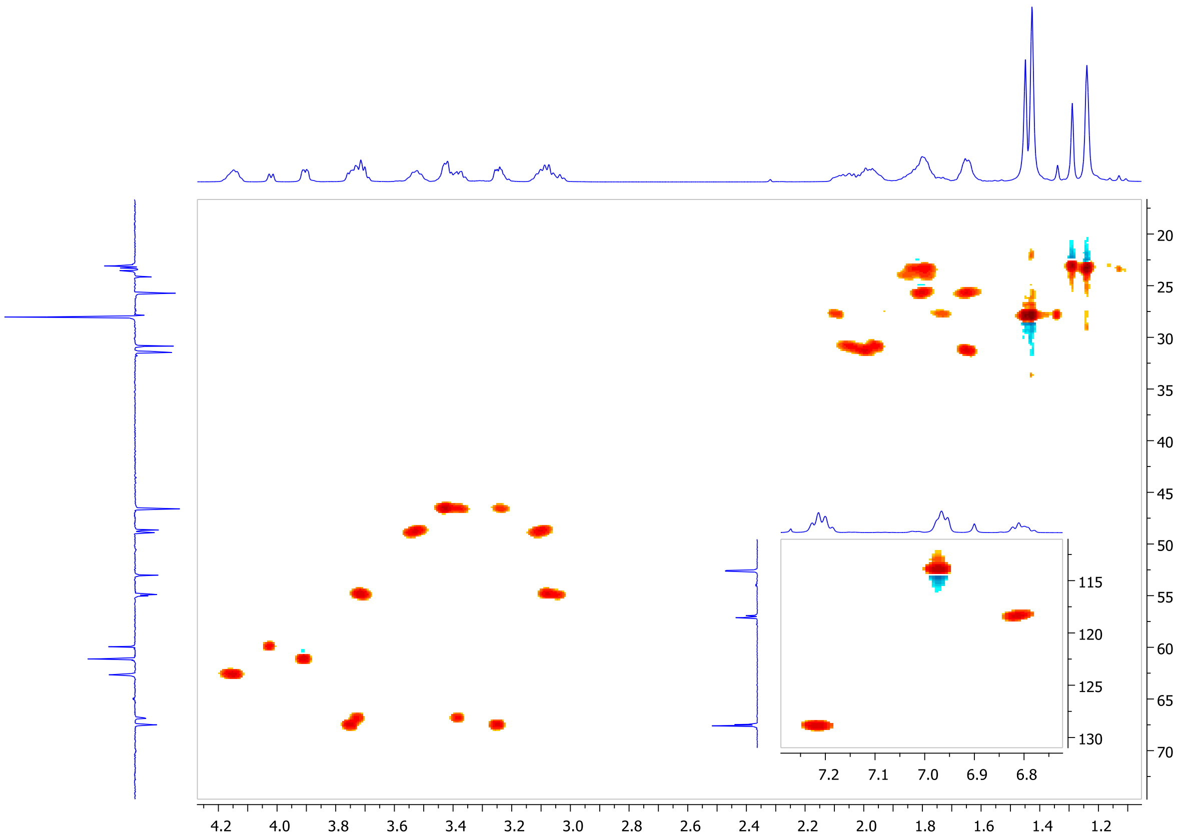


Figure S39f. **L4**, ^{1}H-^{13}C HSQC.

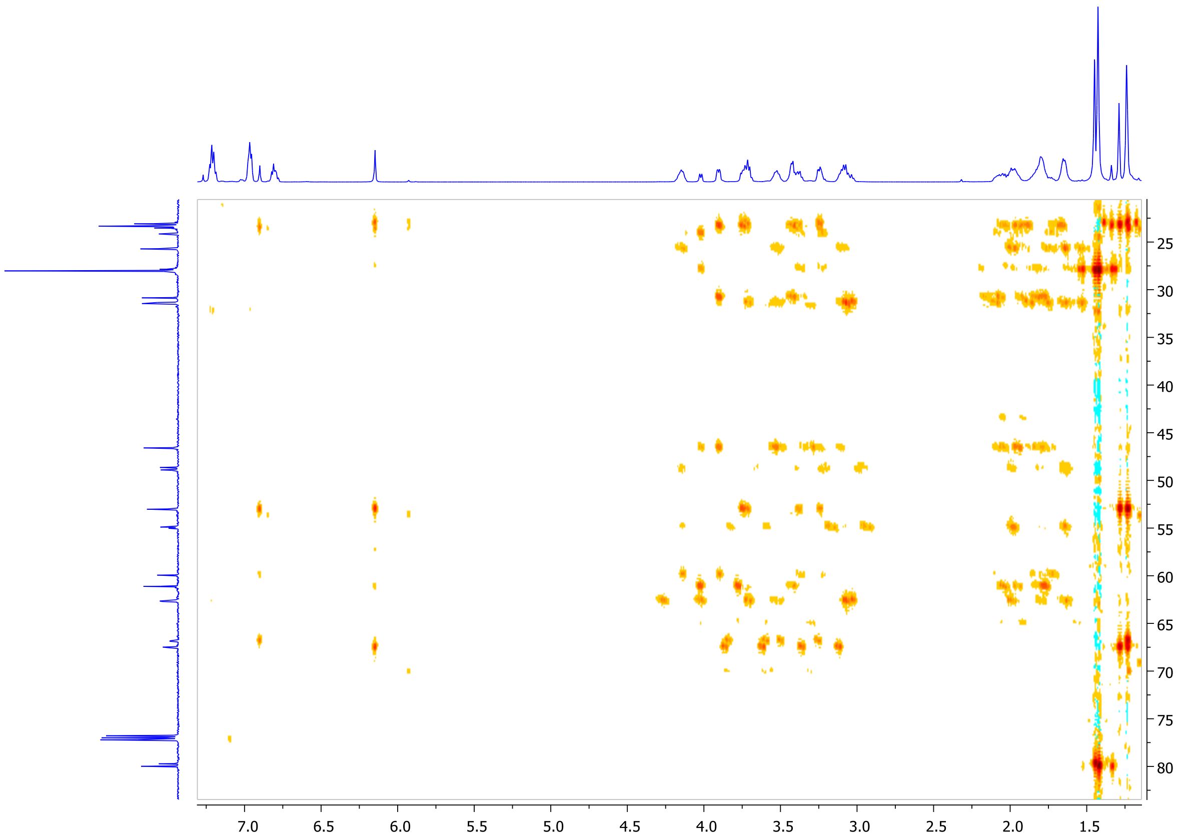


Figure S39g. **L4**, ^{1}H-^{13}C HMBC (fragment of the spectrum).

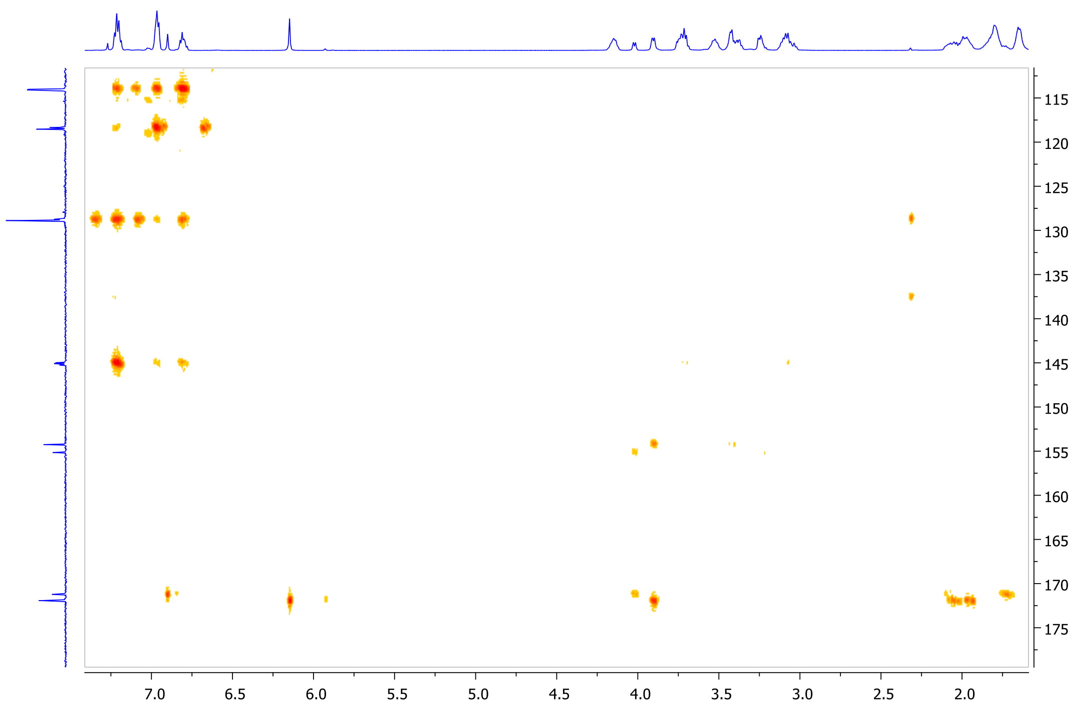


Figure S39h. **L4**, ^{1}H-^{13}C HMBC (fragment of the spectrum).

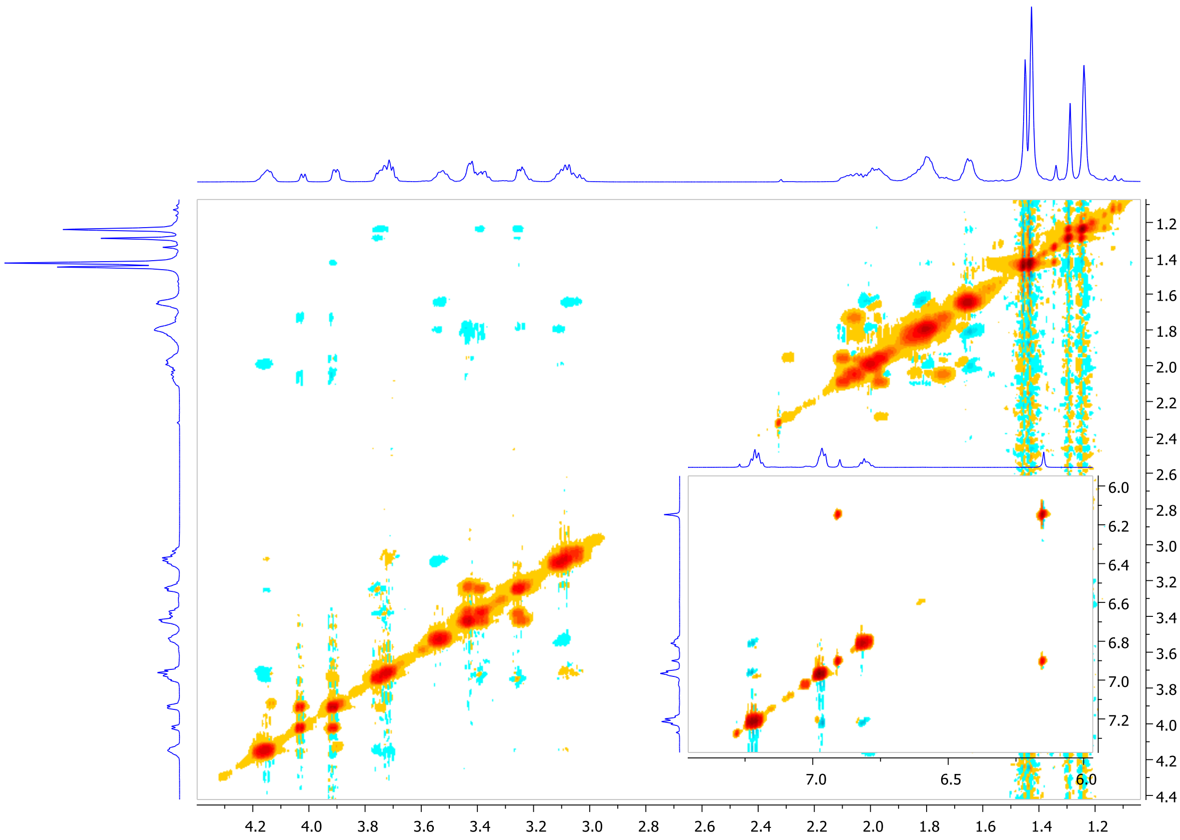


Figure S39i. **L4**, ^{1}H-^{1}H NOESY.

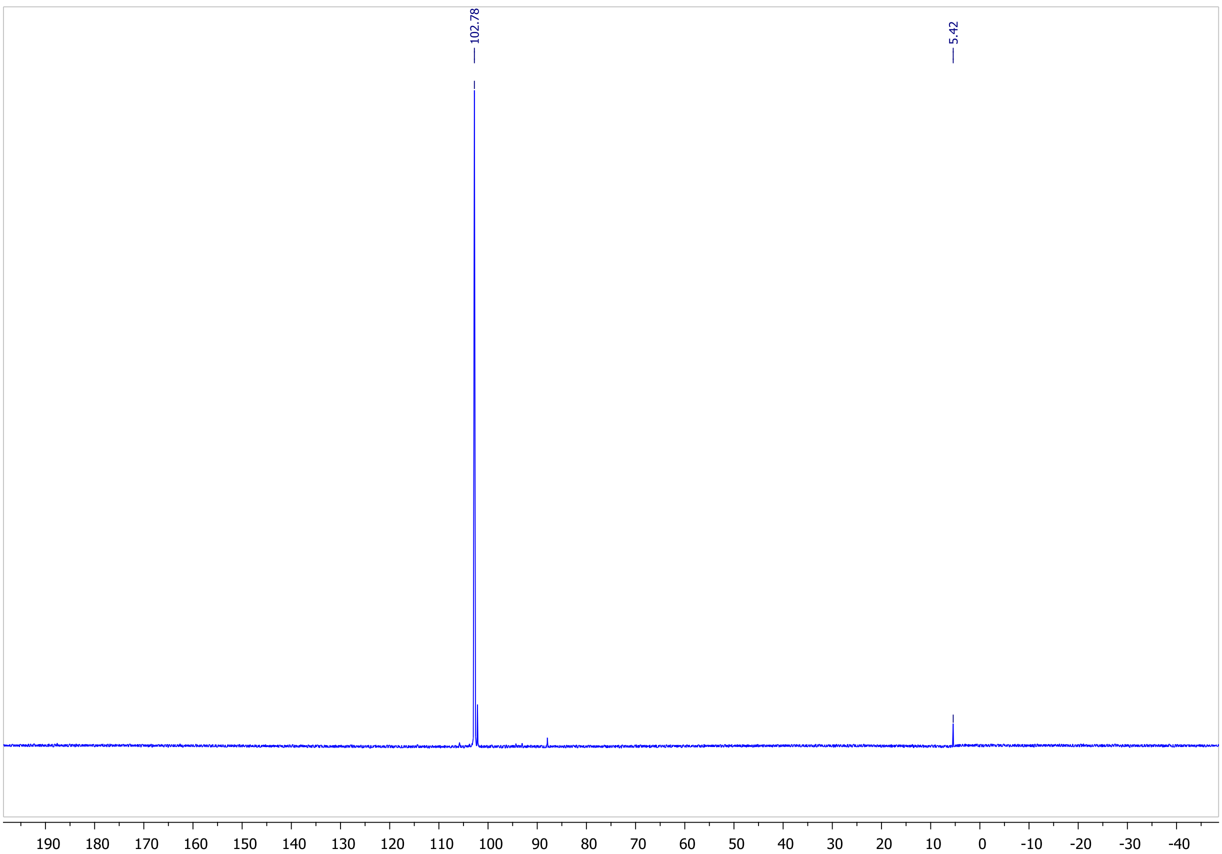


Figure S40a. **L5**, ^{31}P{^{1}H} (202.4 MHz, $CDCl_3$, ambient temperature).

NMR SPECTRA OF NEW COMPOUNDS

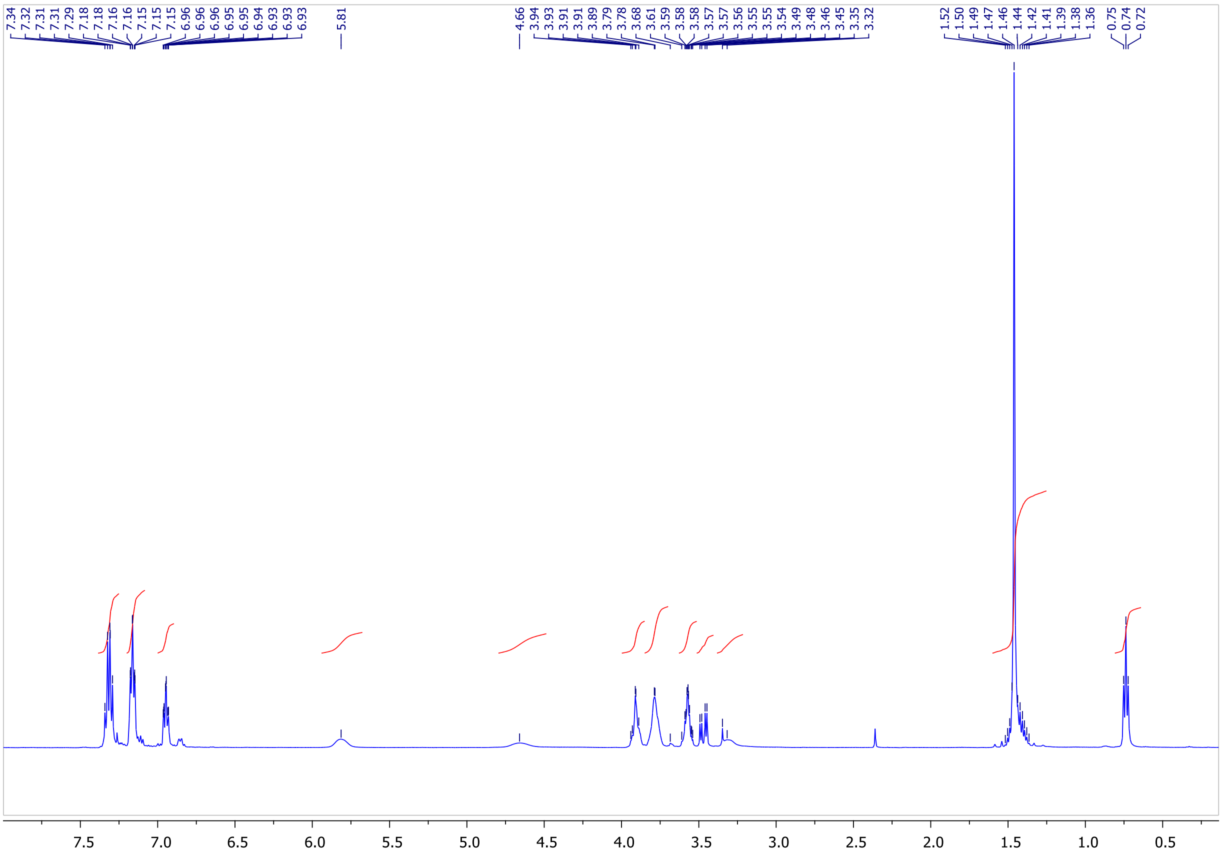


Figure S40b. **L5**, ^{1}H (600.1 MHz, $CDCl_3$, 25 °C).

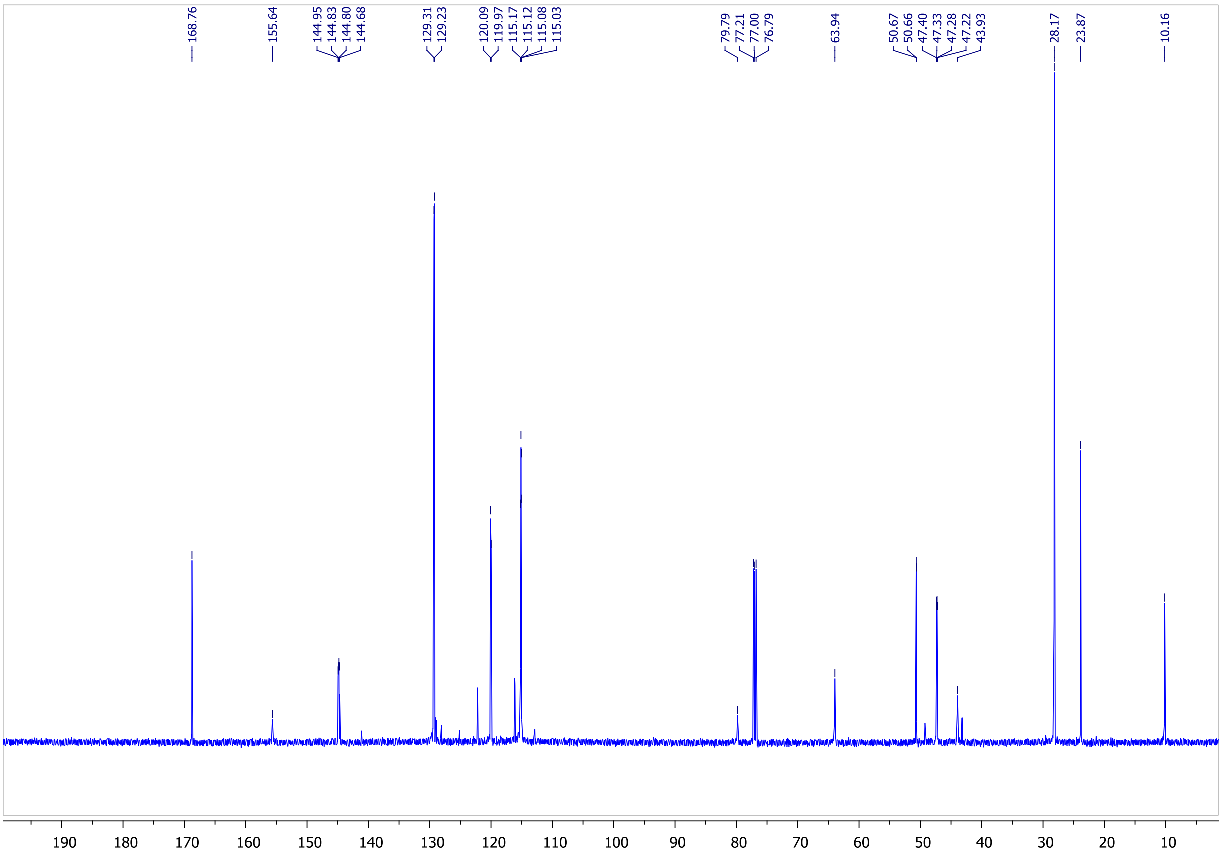


Figure S40c. **L5**, $^{13}C\{^{1}H\}$ (150.9 MHz, $CDCl_3$, 25 °C).

NMR SPECTRA OF NEW COMPOUNDS

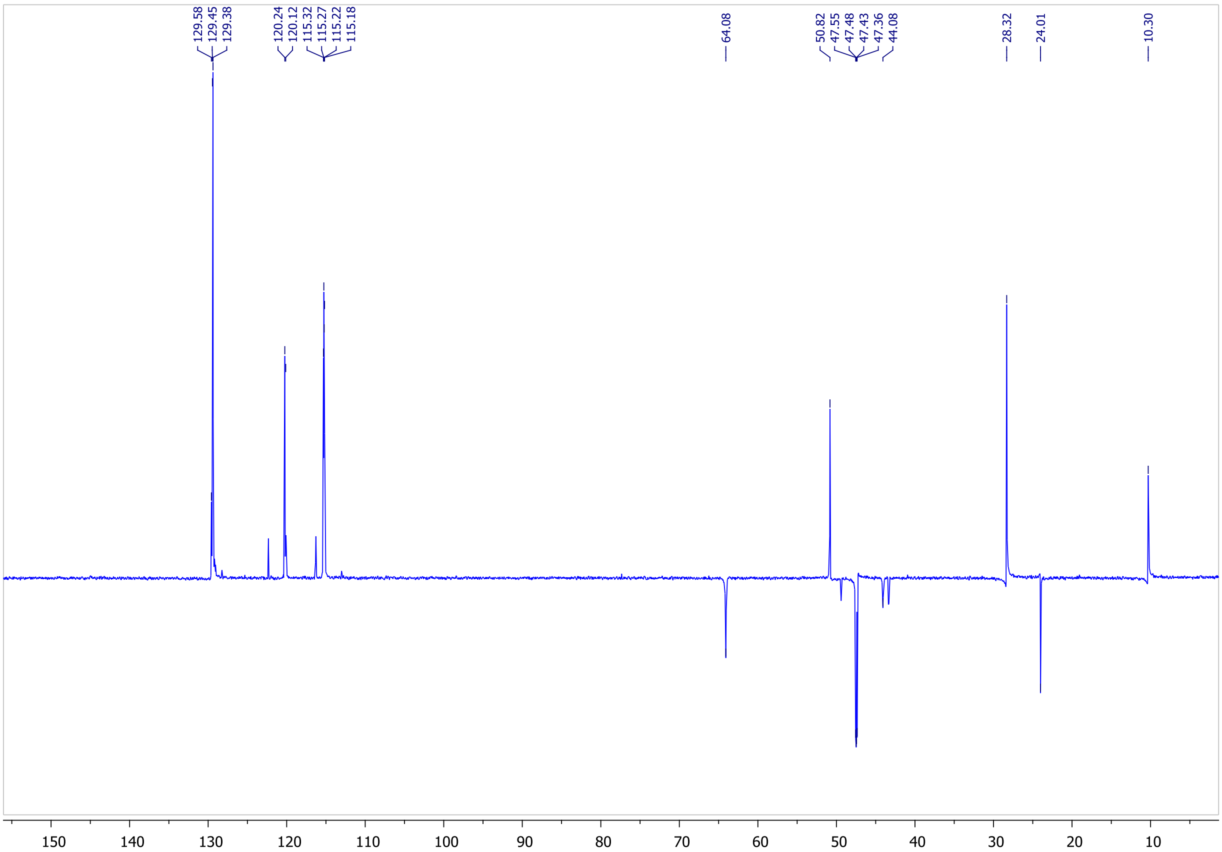


Figure S40d. **L5**, $^{13}C\{^{1}H\}$ DEPT (150.9 MHz, $CDCl_3$, 25 °C).

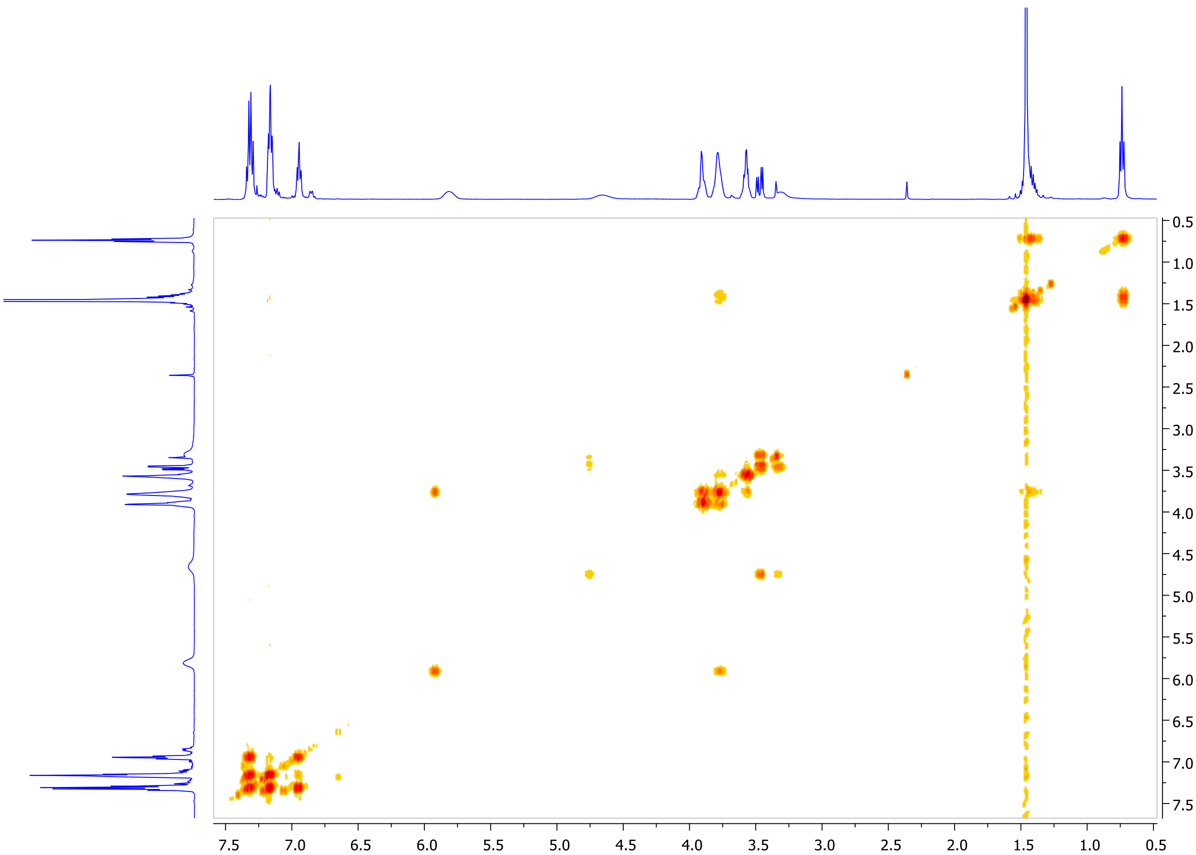


Figure S40e. **L5**, ^{1}H-^{1}H COSY.

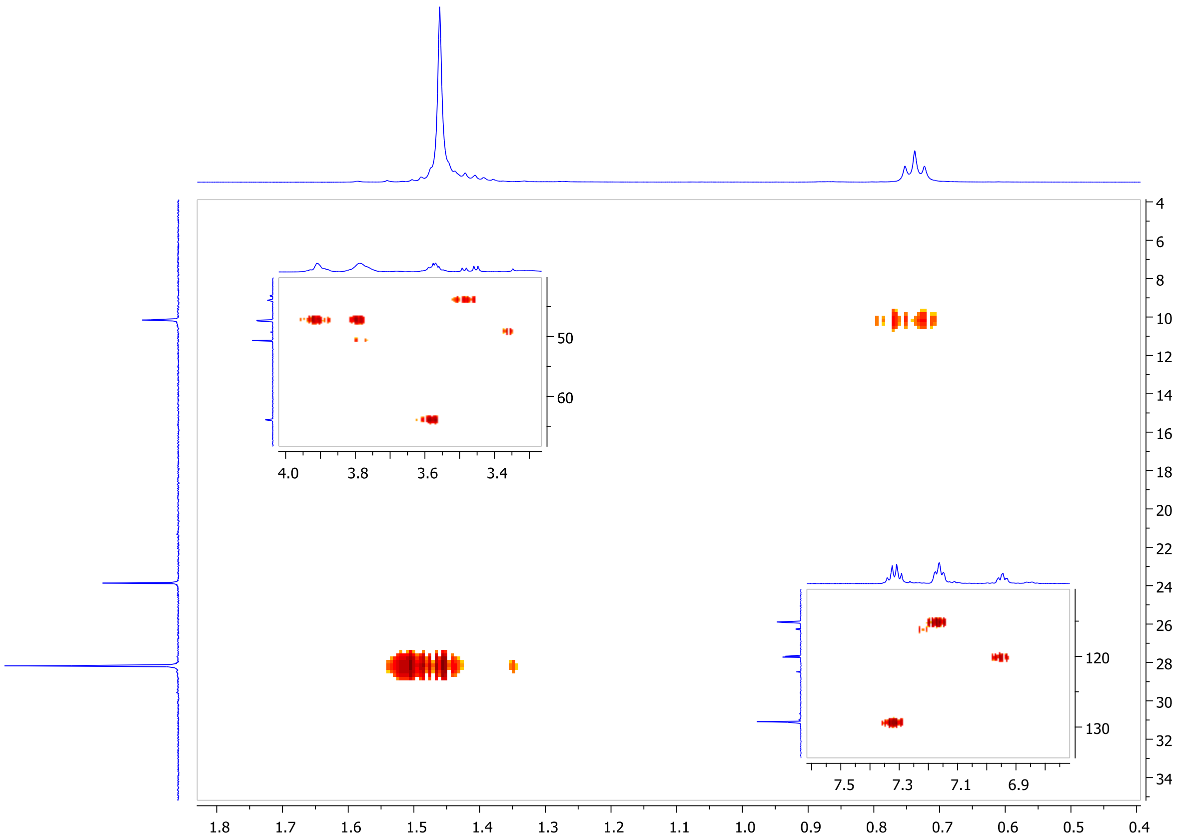


Figure S40f. **L5**, ^{1}H-^{13}C HSQC.

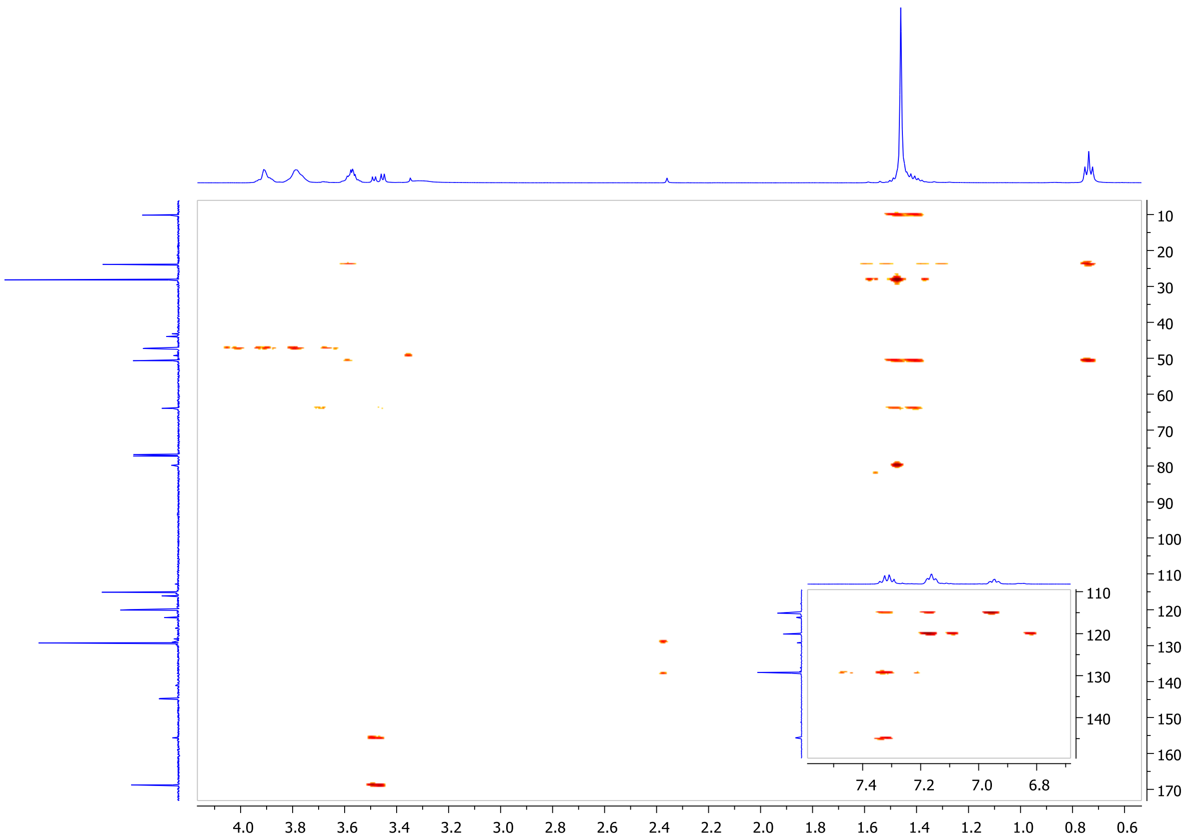


Figure S40g. **L5**, ^{1}H-^{13}C HMBC.

NMR SPECTRA OF NEW COMPOUNDS

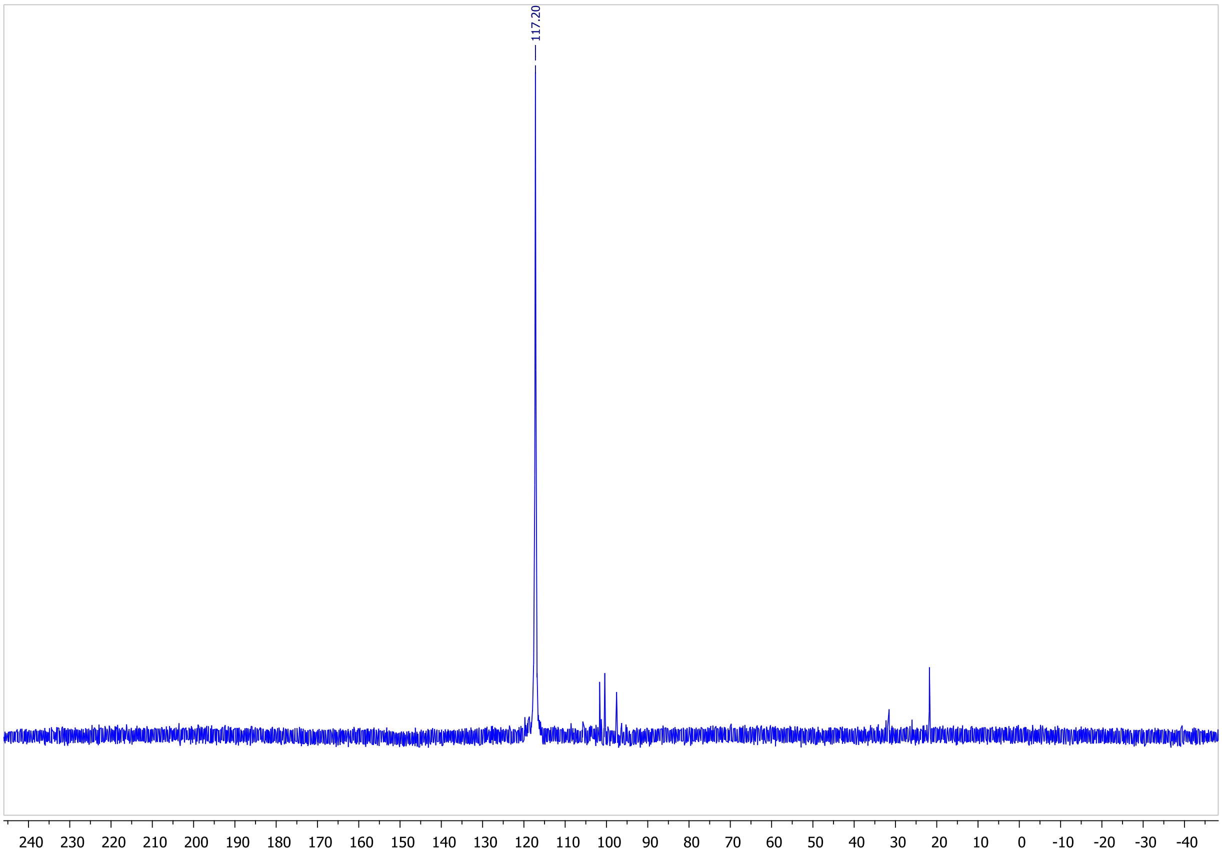


Figure S41a. [Pd(allyl)(**L1d**)$_2$]BF_4, $^{31}P\{^1H\}$ (202.4 MHz, CD_2Cl_2, ambient temperature).

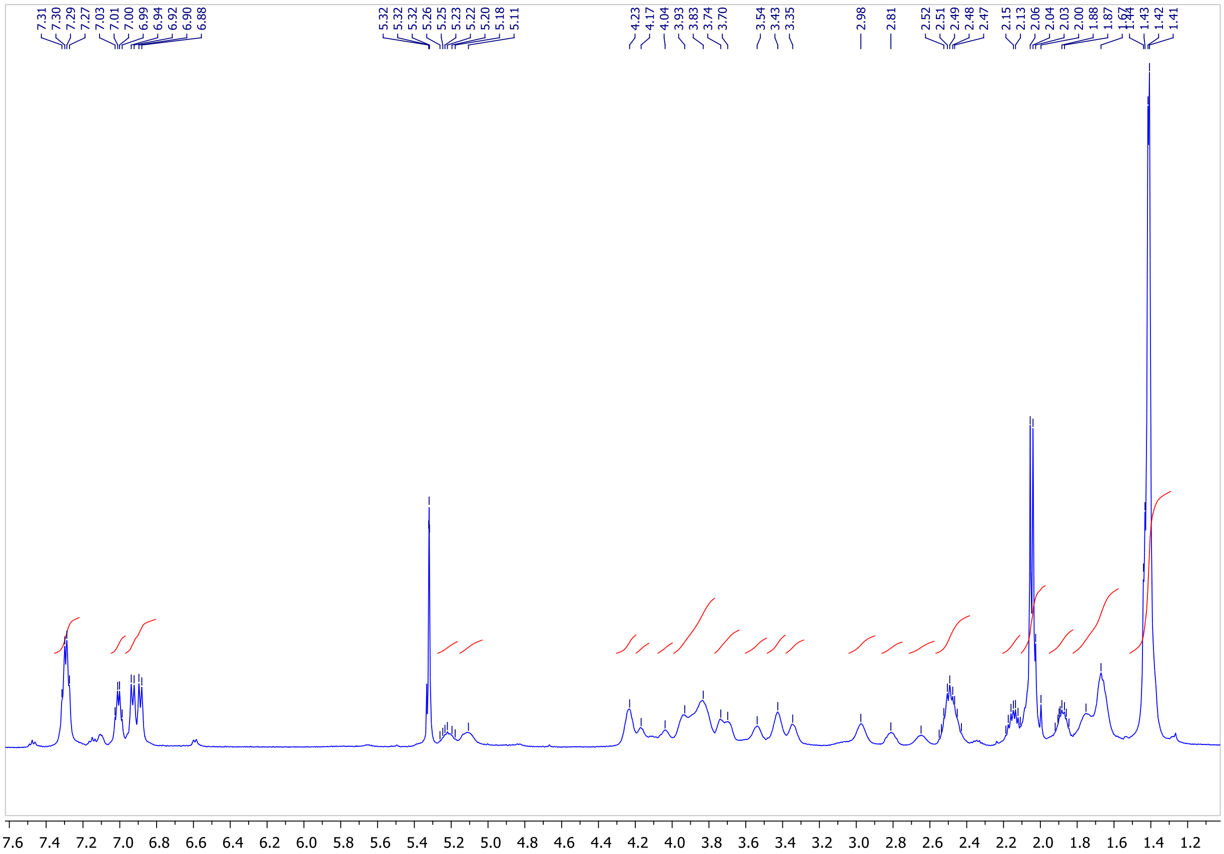


Figure S41b. [Pd(allyl)(**L1d**)$_2$]BF_4, ^1H (499.9 MHz, CD_2Cl_2, ambient temperature).

NMR SPECTRA OF NEW COMPOUNDS

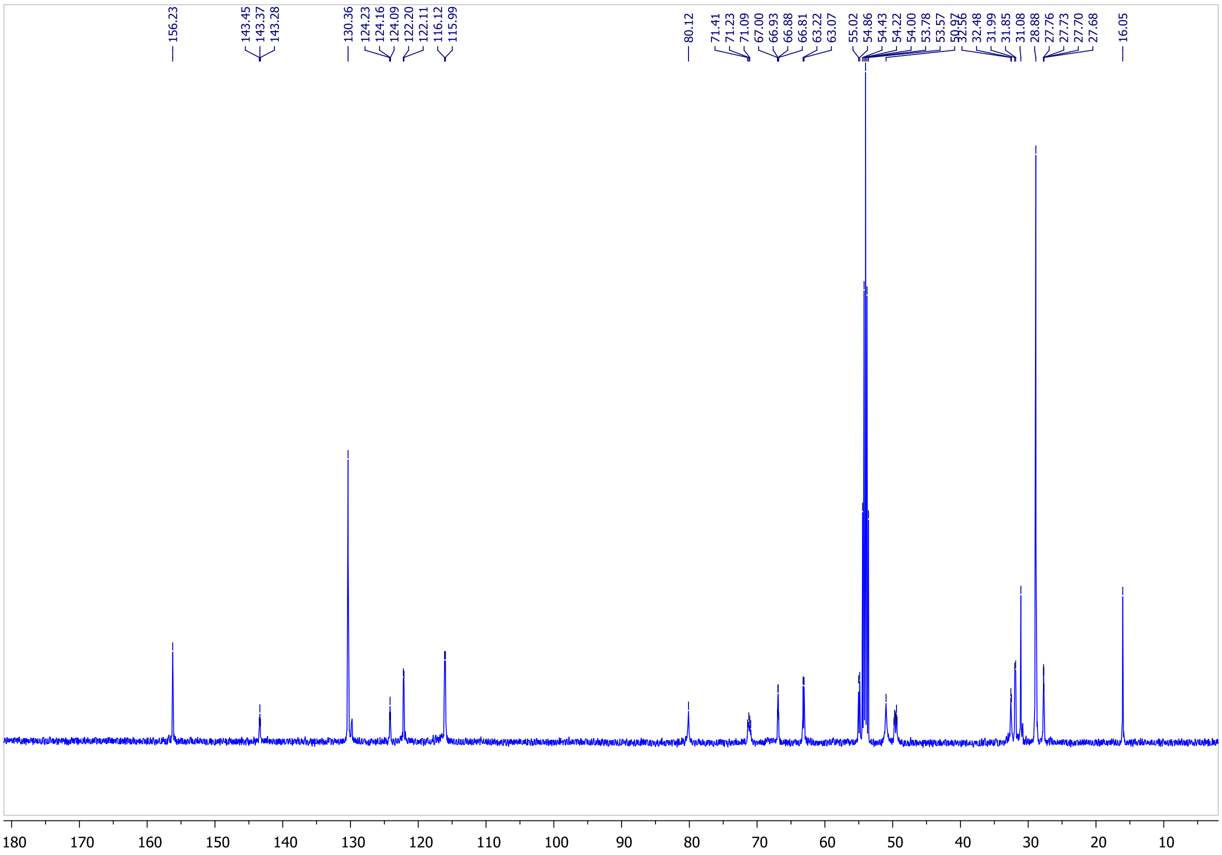


Figure S41c. [Pd(allyl)(**L1d**)$_2$]BF$_4$, ^{13}C{^{1}H} (125.7 MHz, CD$_2$Cl$_2$, ambient temperature).

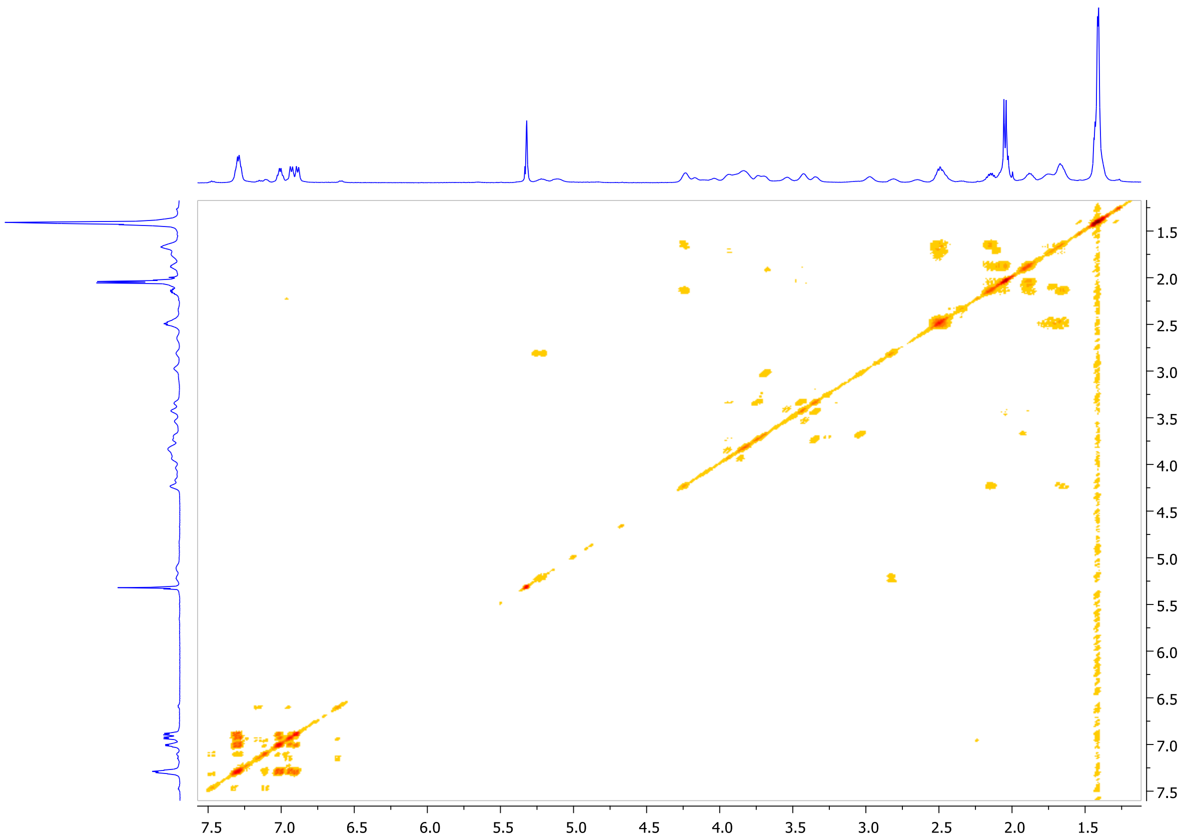


Figure S41d. [Pd(allyl)(**L1d**)$_2$]BF$_4$, ^{1}H-^{1}H COSY.

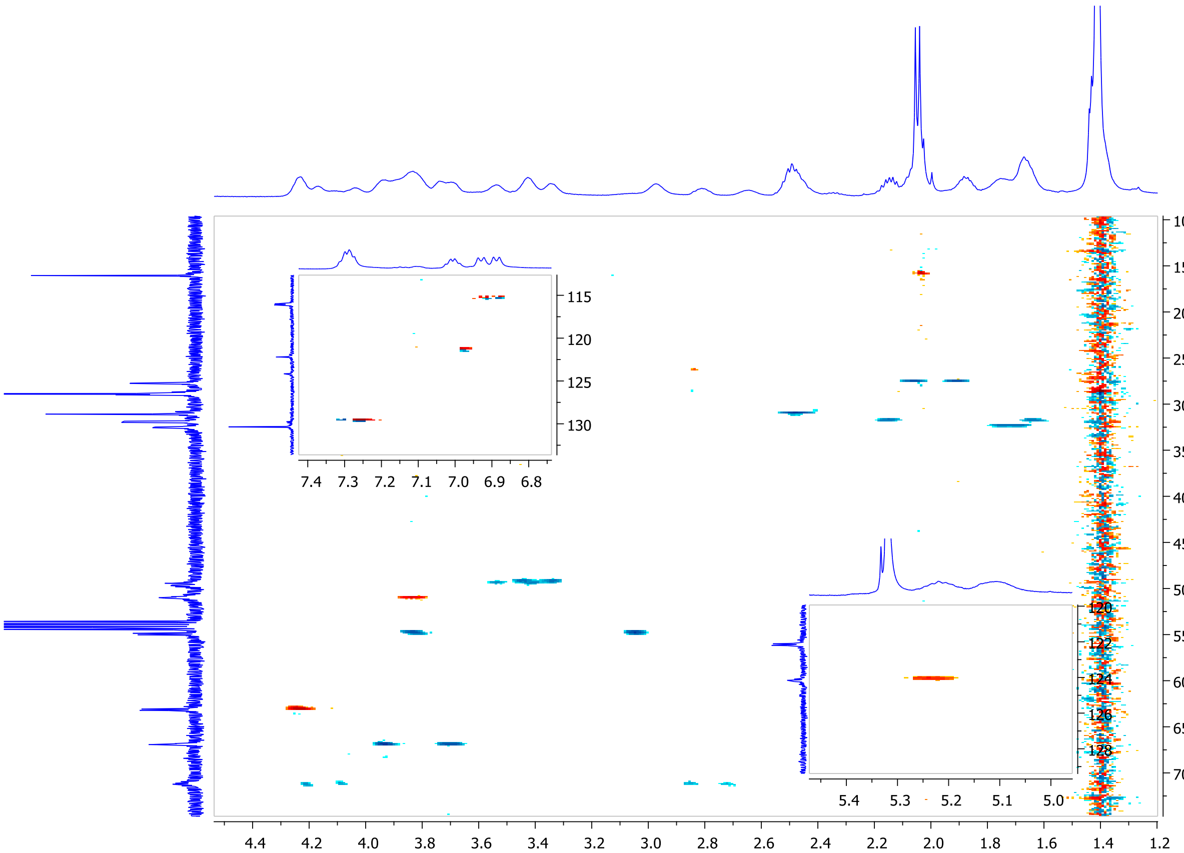


Figure S41e. [Pd(allyl)(**L1d**)$_2$]BF_4, ^1H-^{13}C HSQC.

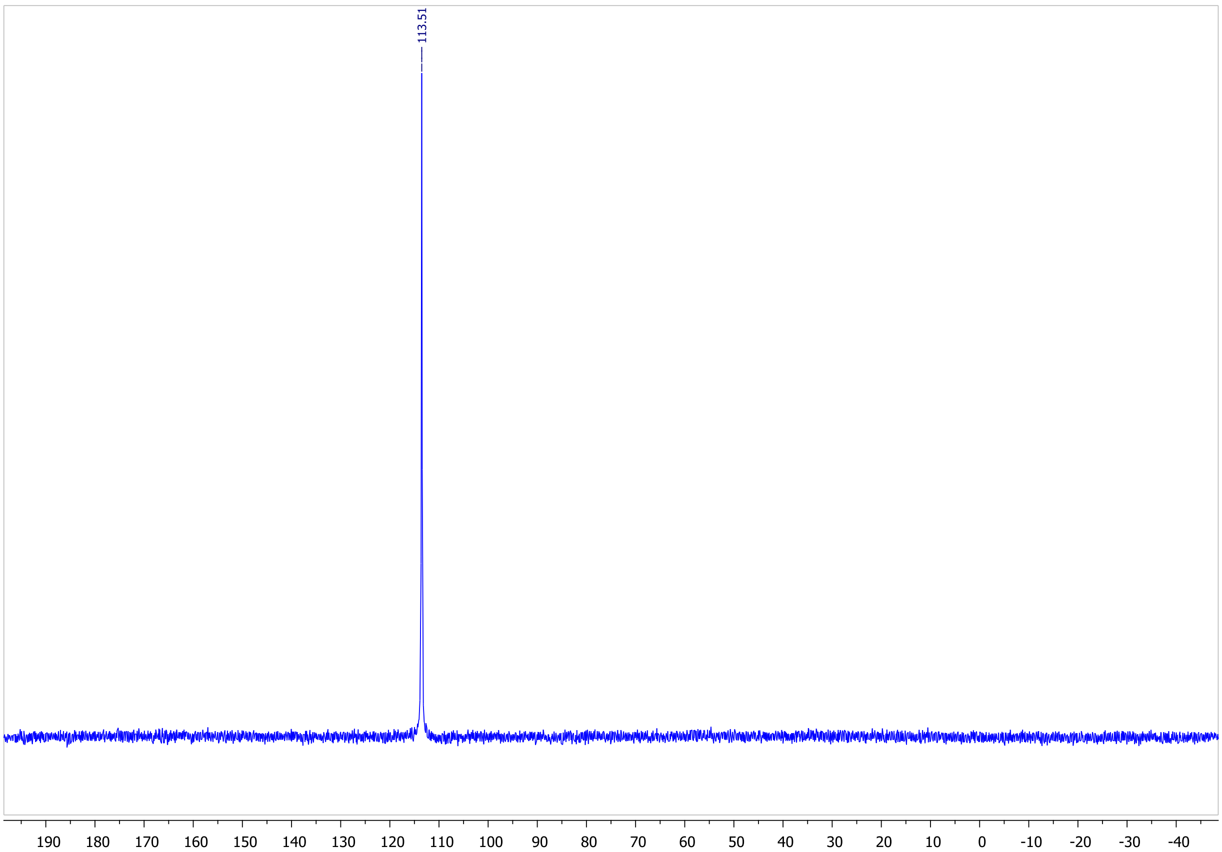


Figure S42a. [Pd(allyl)(**L3a**)$_2$]BF_4, $^{31}P\{^1H\}$ (242.9 MHz, CD_2Cl_2, 19 °C).

NMR SPECTRA OF NEW COMPOUNDS

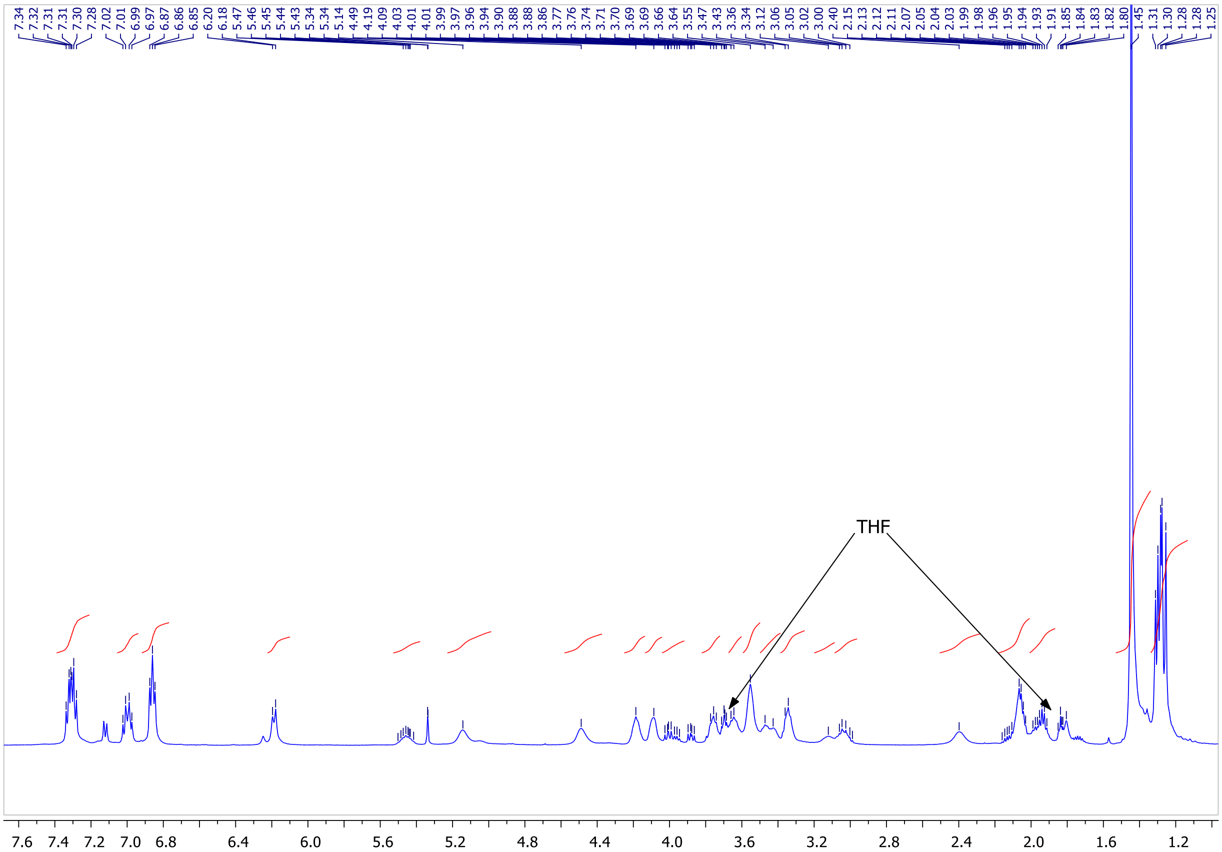


Figure S42b. [Pd(allyl)(**L3a**)$_2$]BF_4, ^{1}H (499.9 MHz, CD_2Cl_2, ambient temperature).

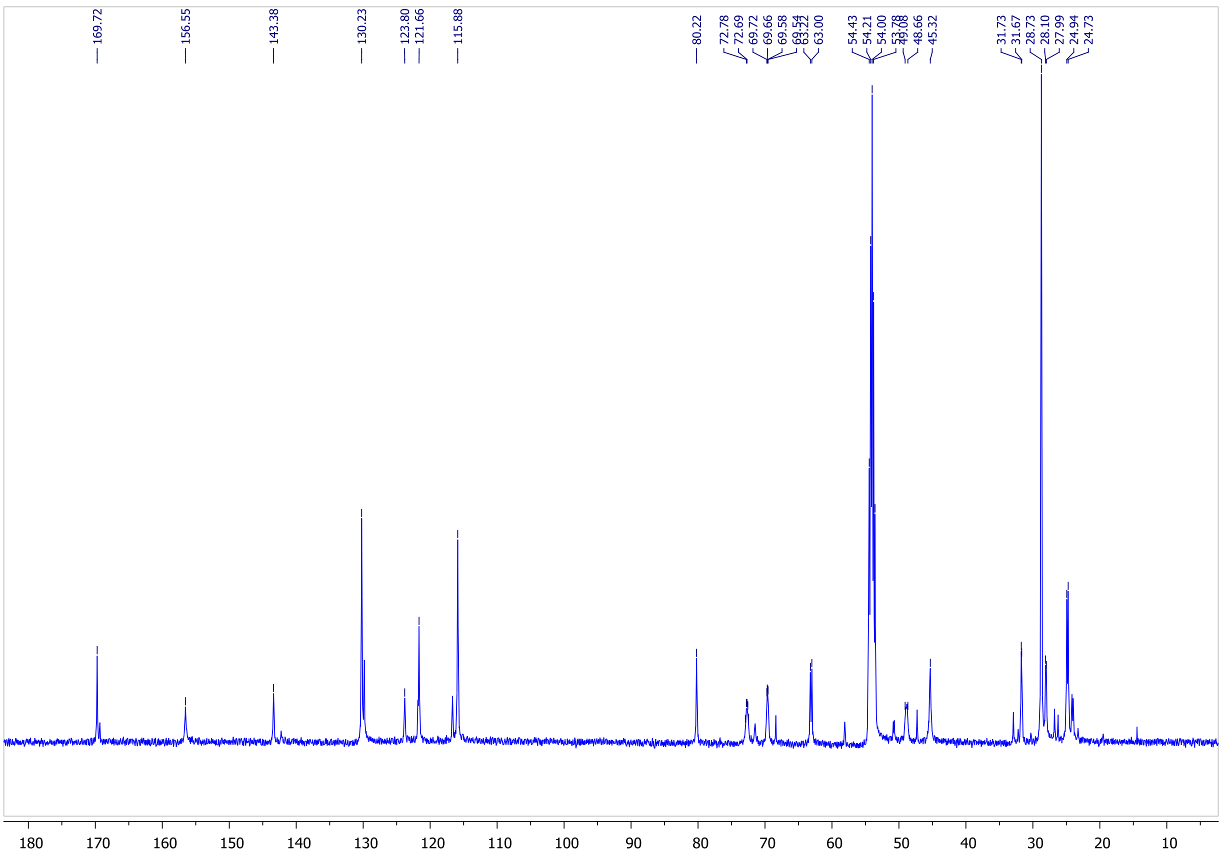


Figure S42c. [Pd(allyl)(**L3a**)$_2$]BF_4, $^{13}C\{^{1}H\}$ (125.7 MHz, CD_2Cl_2, ambient temperature).

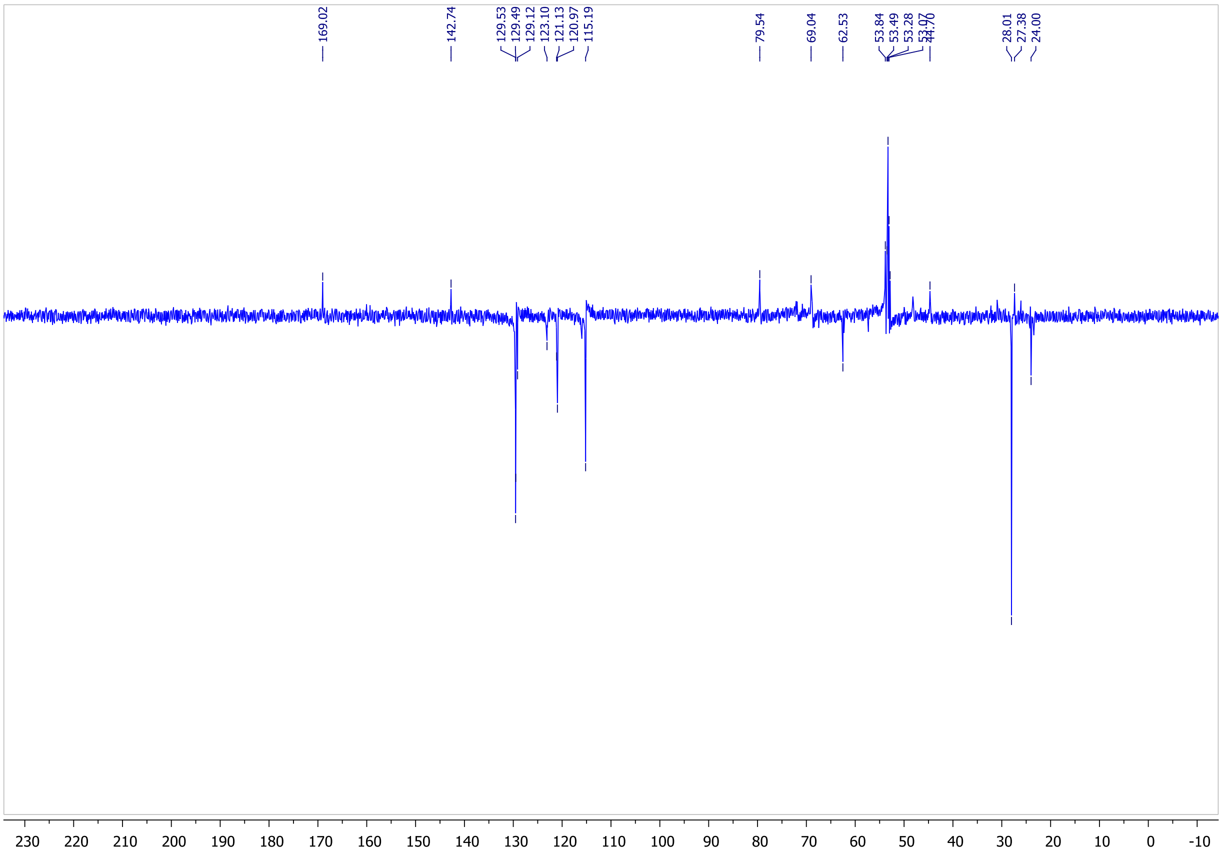


Figure S42d. [Pd(allyl)(**L3a**)$_2$]BF_4, $^{13}C\{^1H\}$ APT (125.7 MHz, CD_2Cl_2, ambient temperature).

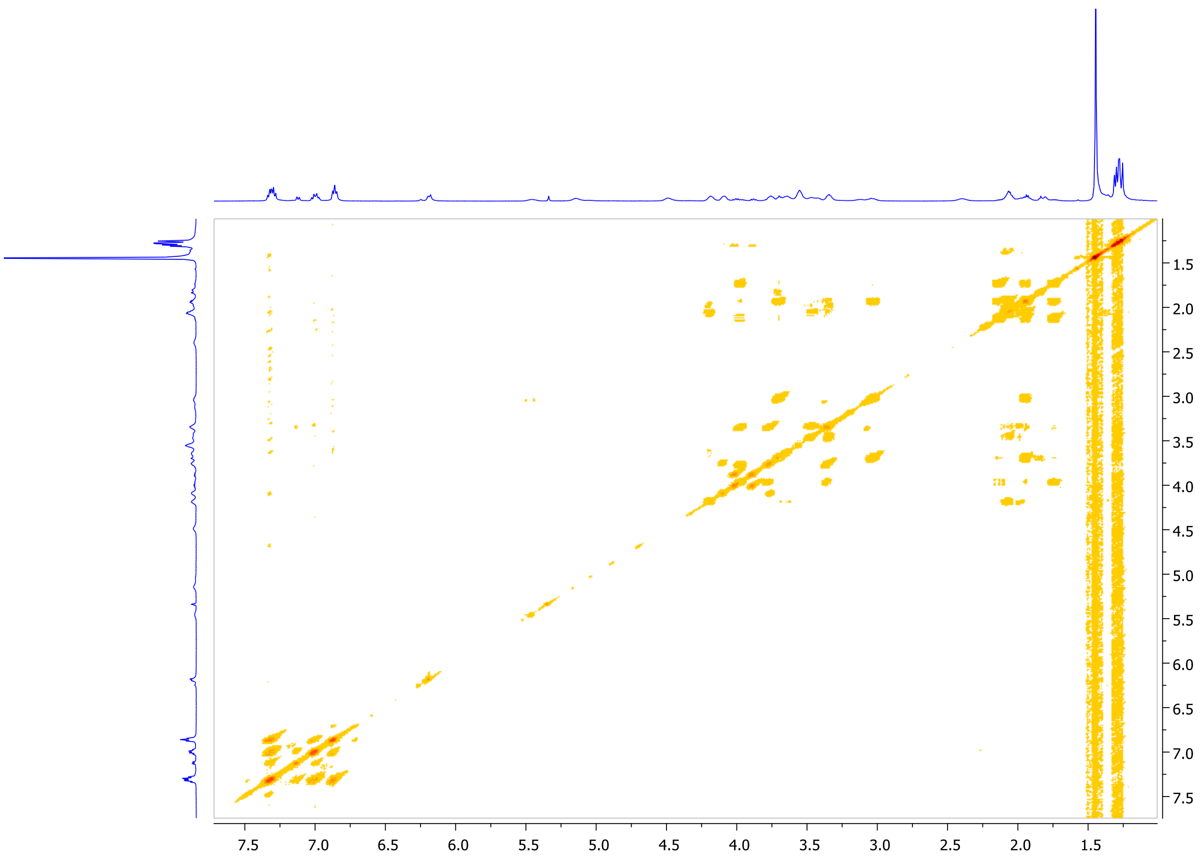


Figure S42e. [Pd(allyl)(**L3a**)$_2$]BF_4, ^1H-^1H COSY.

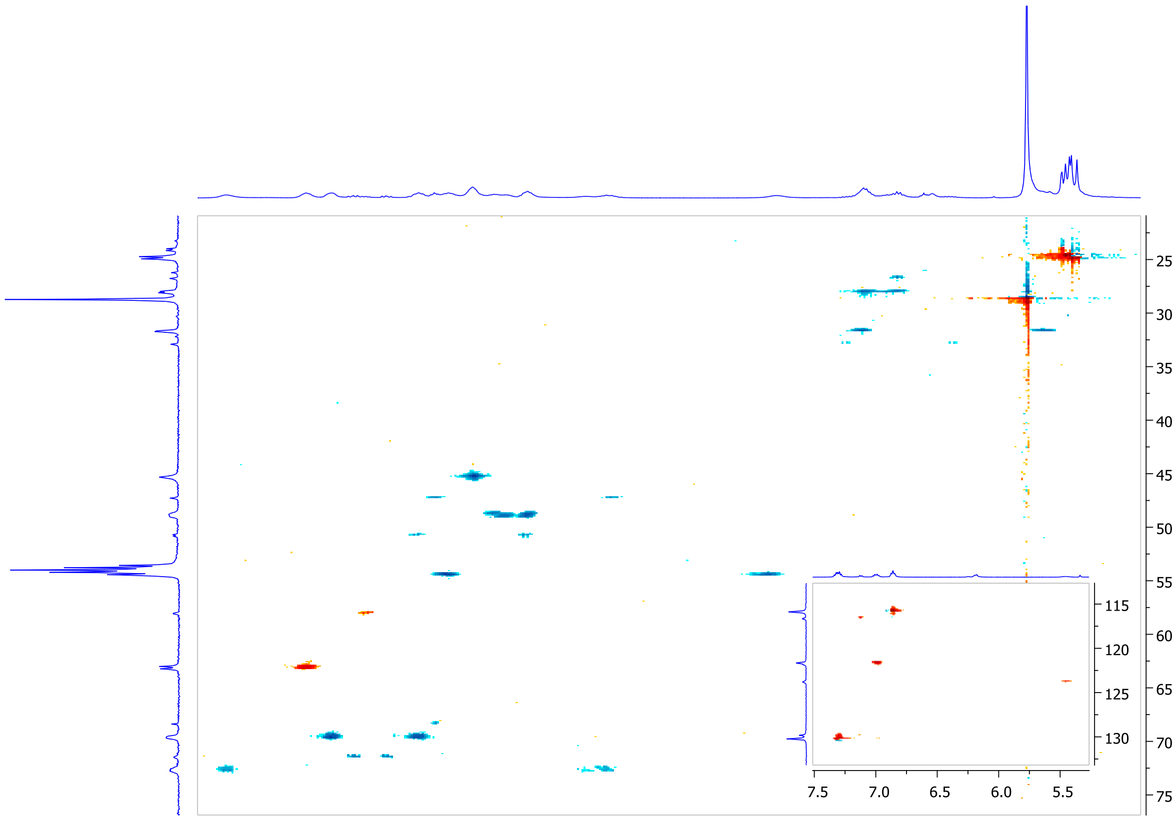


Figure S42f. [Pd(allyl)(**L3a**)$_2$]BF_4, ^{1}H-^{13}C HSQC.

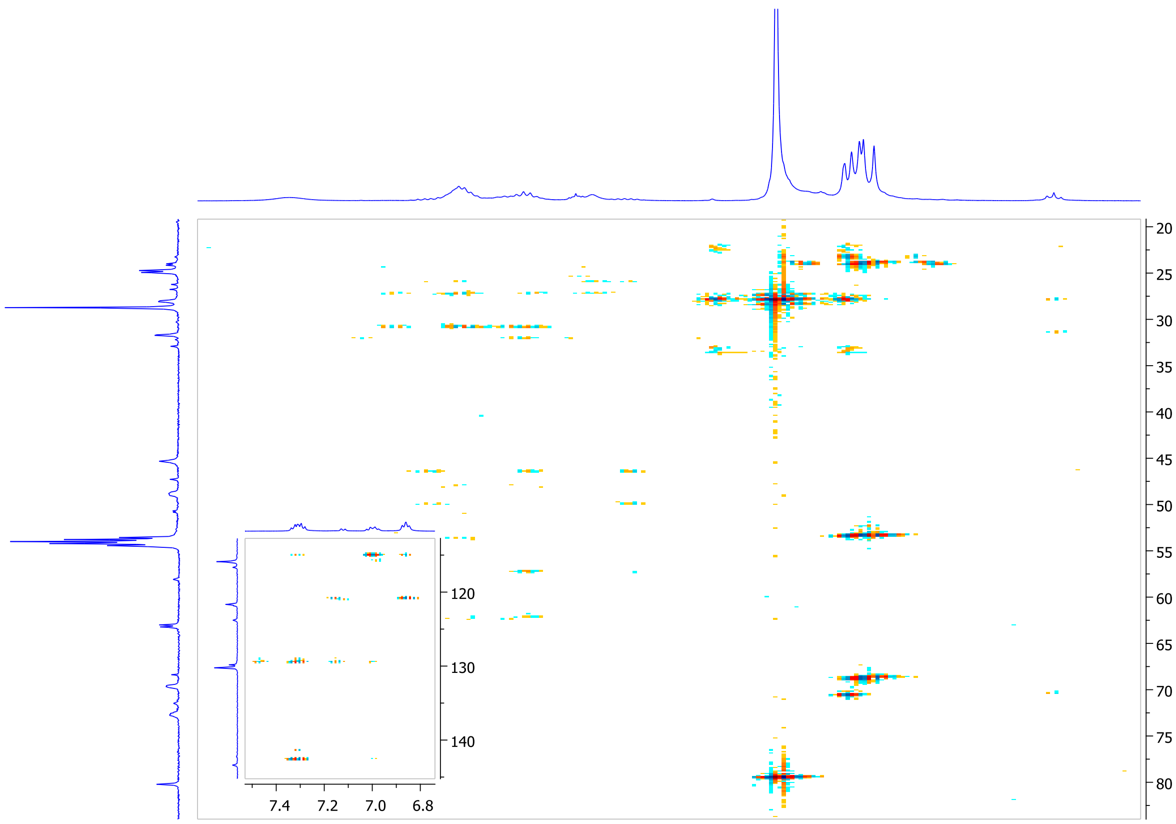


Figure S42g. [Pd(allyl)(**L3a**)$_2$]BF_4, ^{1}H-^{13}C HMBC.

NMR SPECTRA OF NEW COMPOUNDS

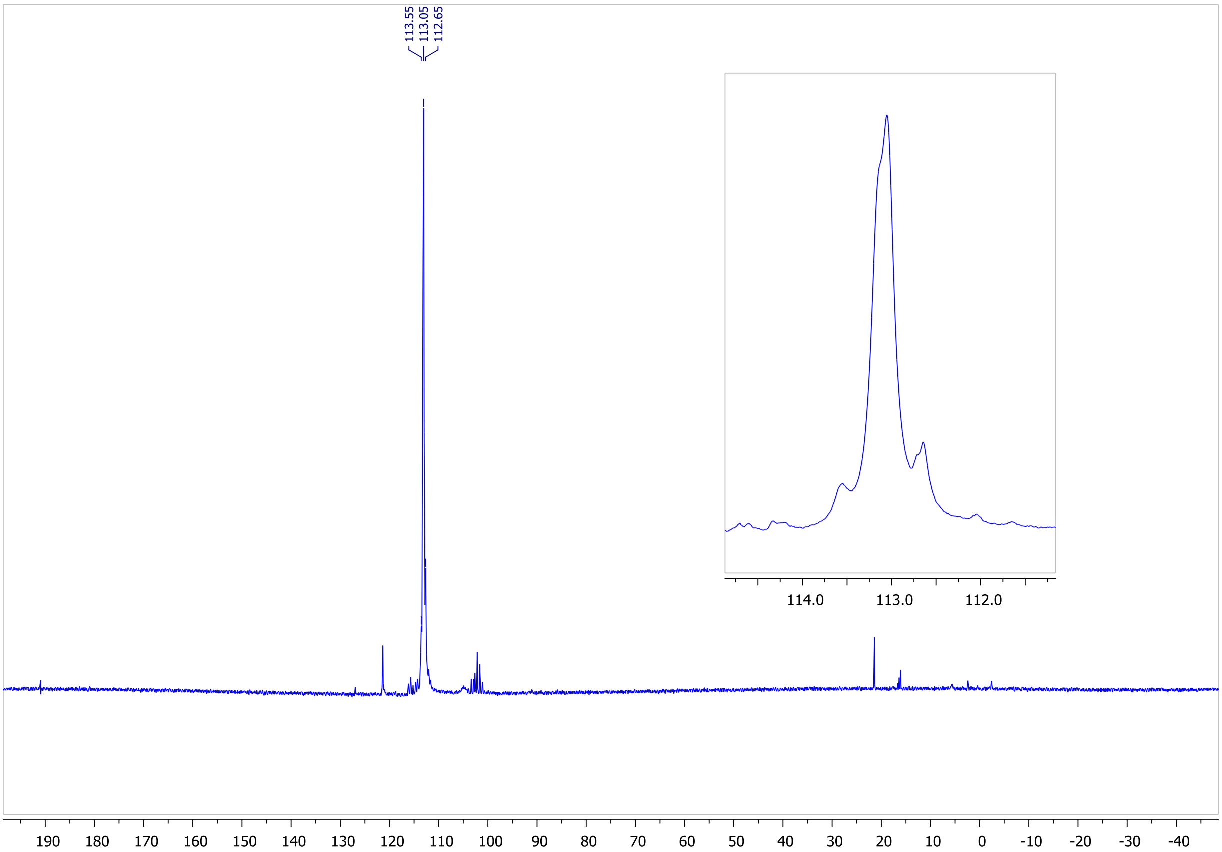


Figure S43a. [Pd(allyl)(**L3b**)$_2$]BF_4, $^{31}P\{^1H\}$ (202.4 MHz, CD_2Cl_2, ambient temperature).

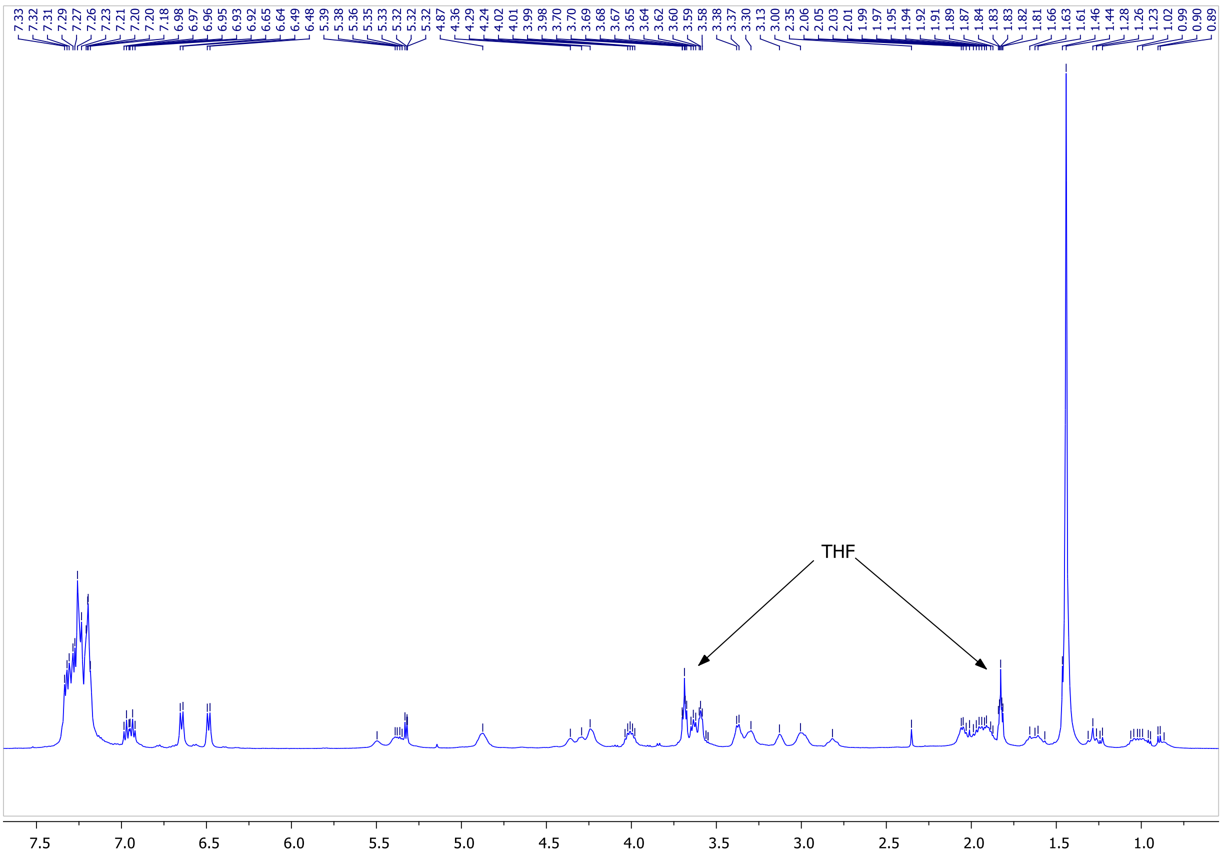


Figure S43b. [Pd(allyl)(**L3b**)$_2$]BF_4, ^1H (499.9 MHz, CD_2Cl_2, ambient temperature).

NMR SPECTRA OF NEW COMPOUNDS

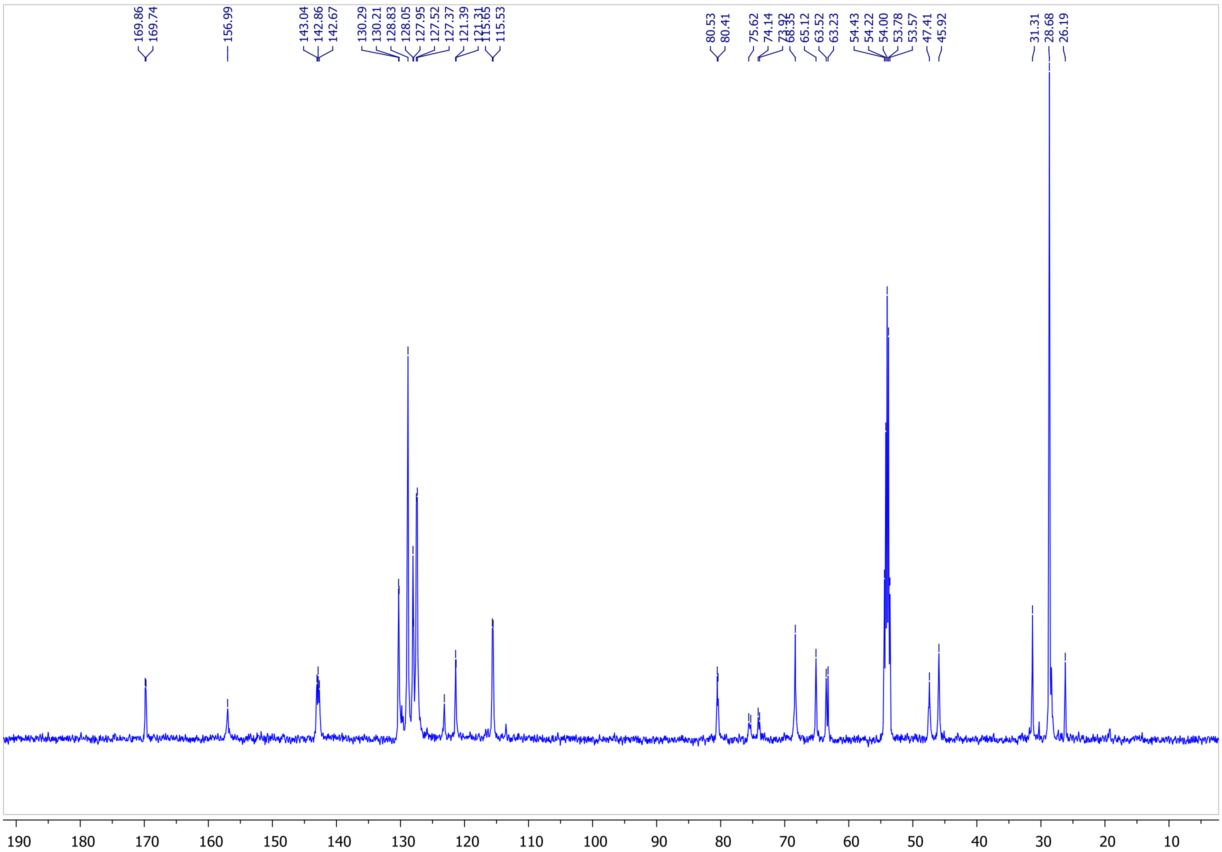


Figure S43c. [Pd(allyl)(**L3b**)$_2$]BF_4, $^{13}C\{^1H\}$ (125.7 MHz, CD_2Cl_2, ambient temperature).

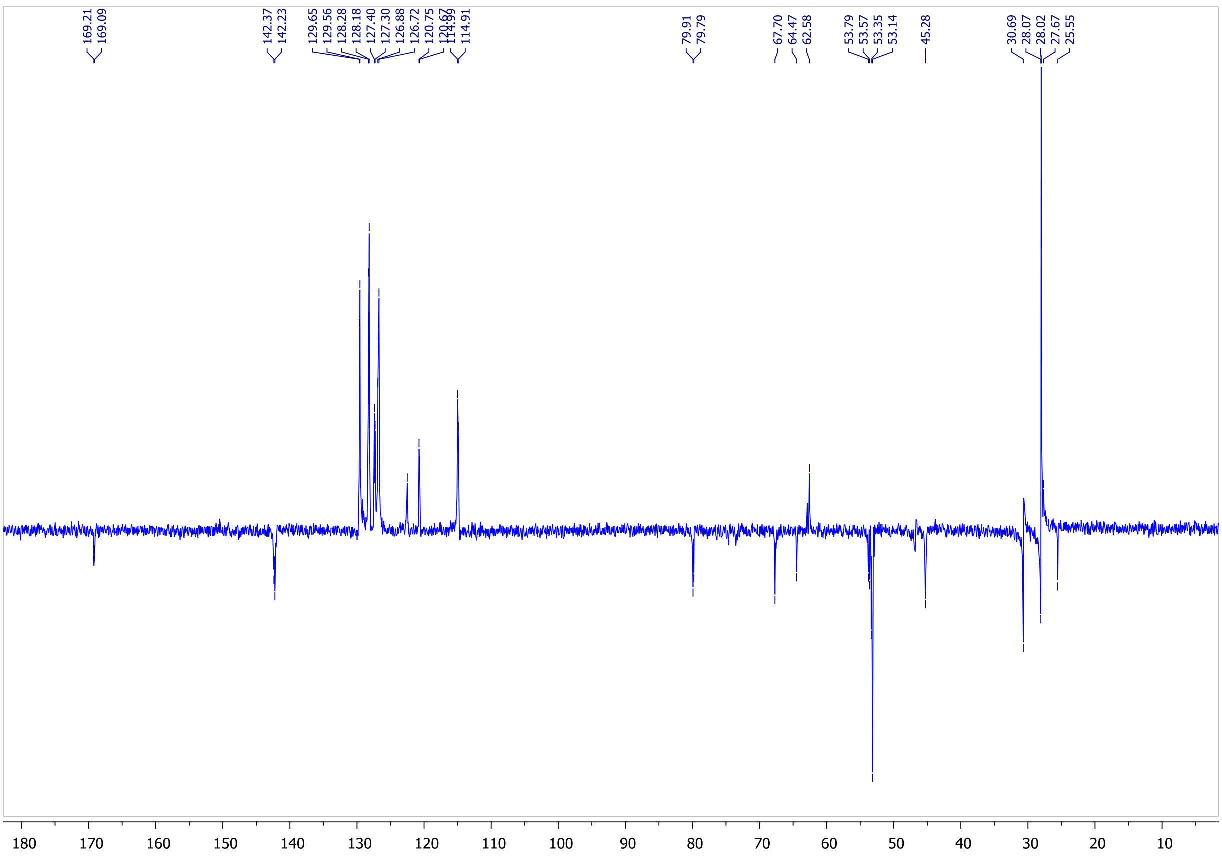


Figure S43d. [Pd(allyl)(**L3b**)$_2$]BF_4, $^{13}C\{^1H\}$ APT (125.7 MHz, CD_2Cl_2, ambient temperature).

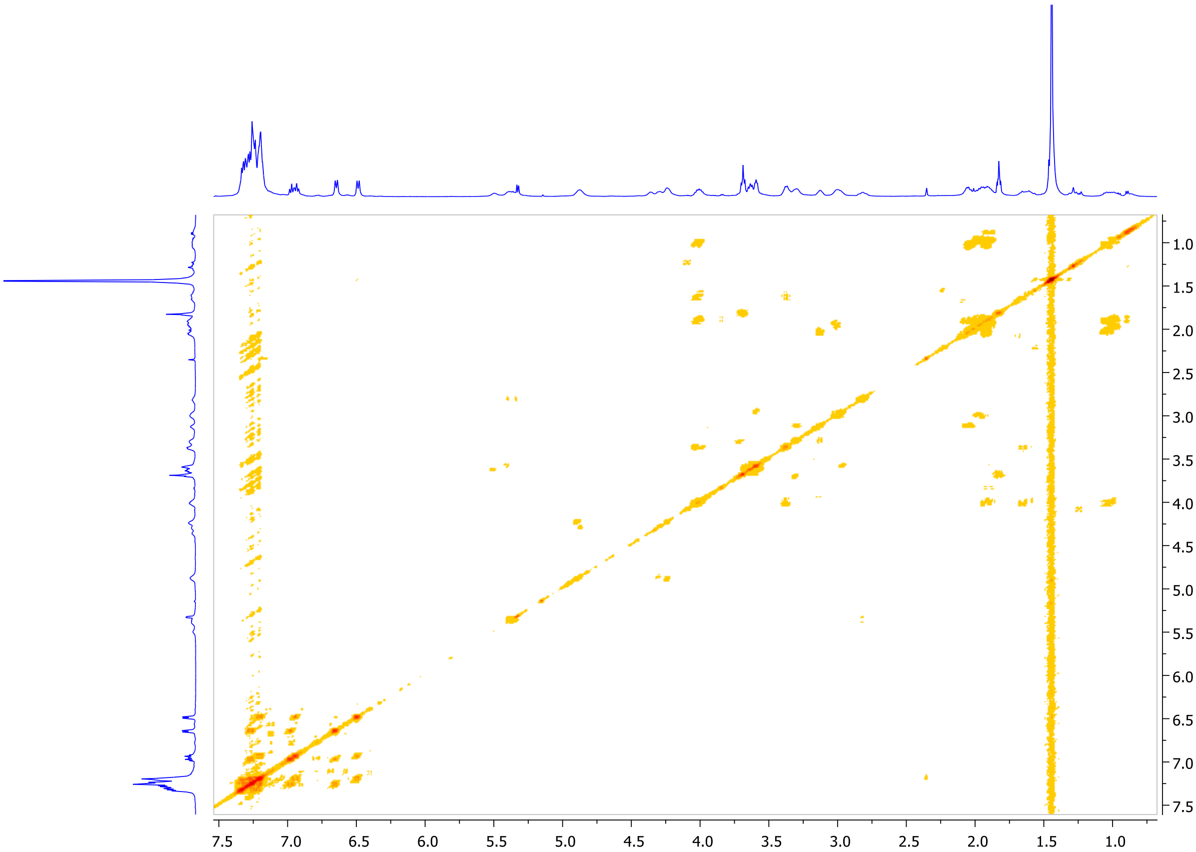


Figure S43e. [Pd(allyl)(**L3b**)$_2$]BF_4, ^{1}H-^{1}H COSY.

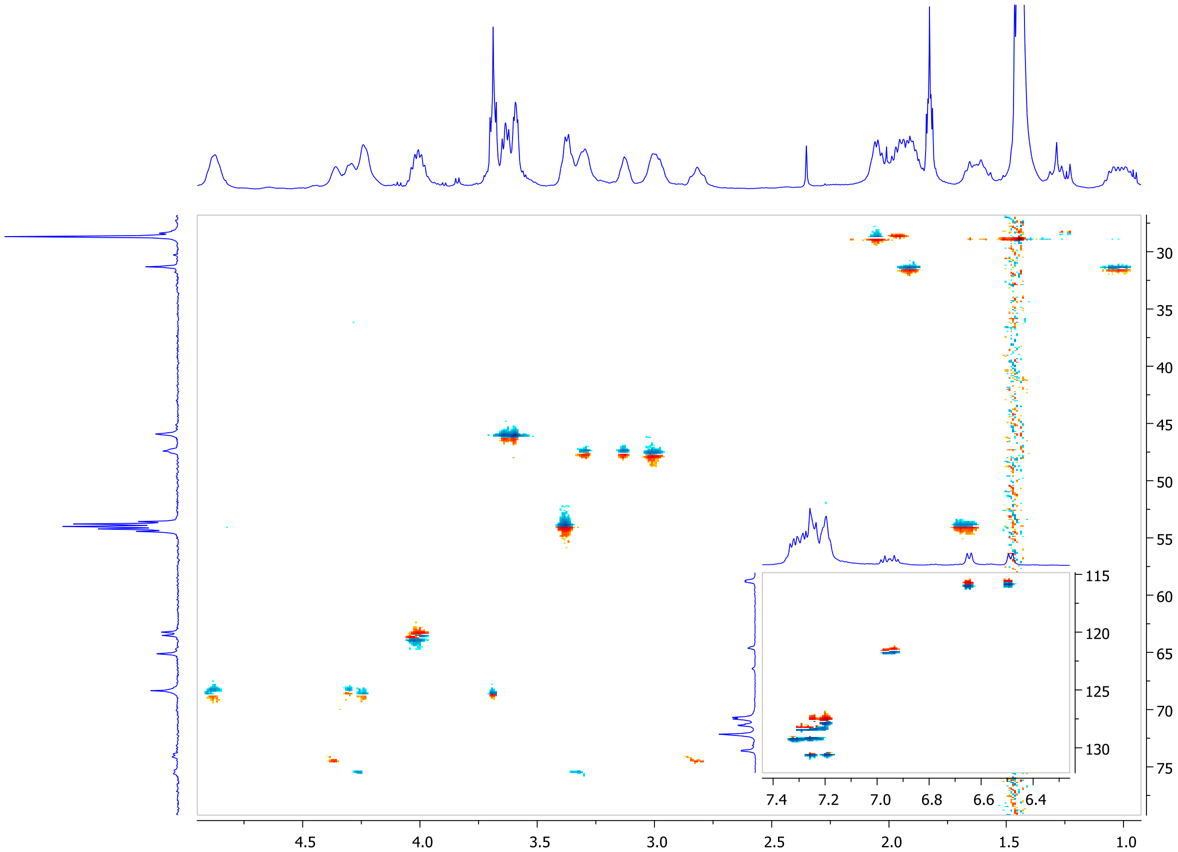


Figure S43f. [Pd(allyl)(**L3b**)$_2$]BF_4, ^{1}H-^{13}C HSQC.

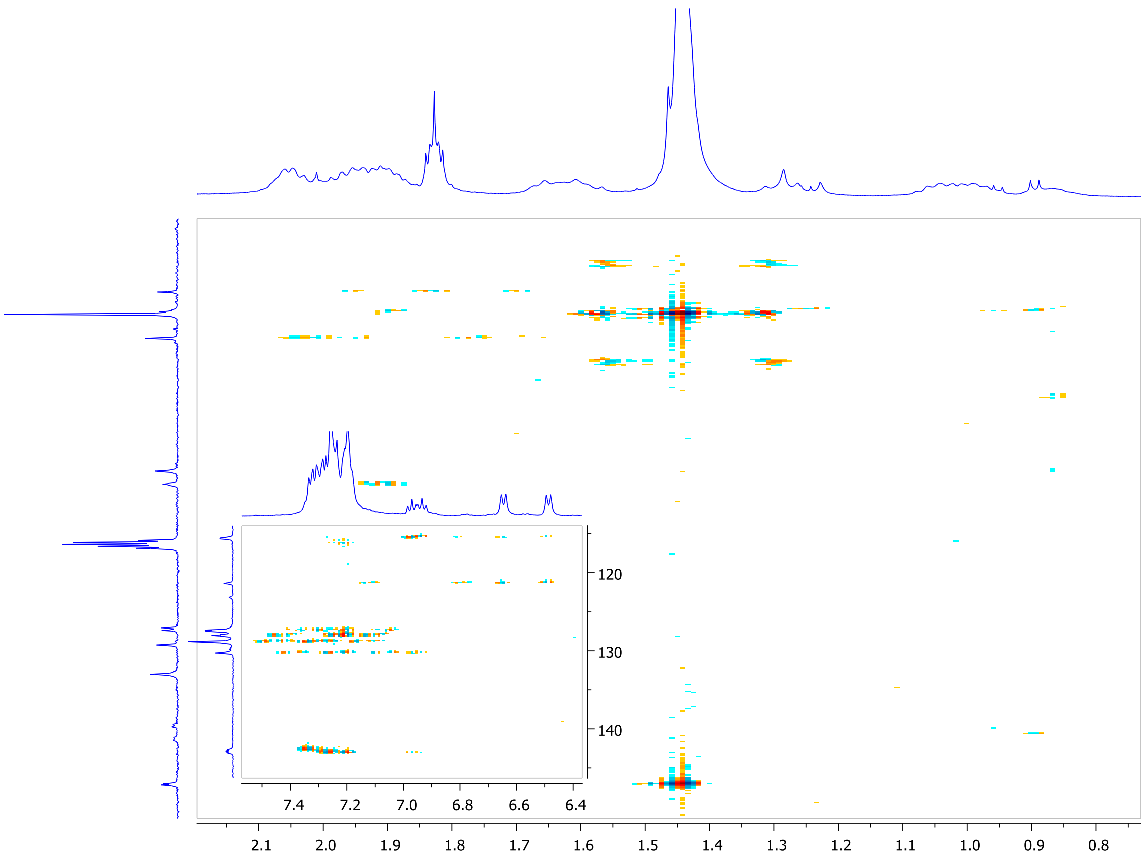


Figure S43g. [Pd(allyl)(**L3b**)$_2$]BF$_4$, ^{1}H-^{13}C HMBC.

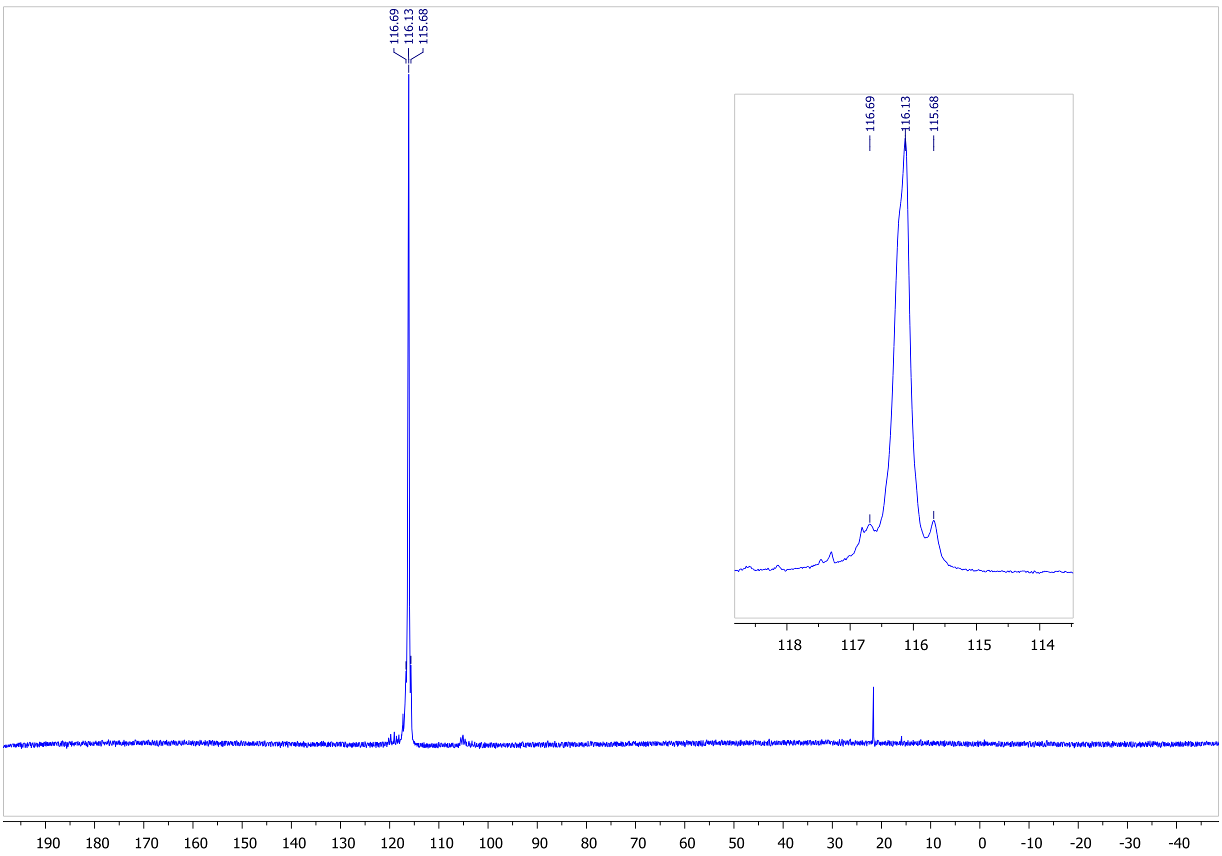


Figure S44a. [Pd(allyl)(**L3c**)$_2$]BF$_4$, ^{31}P{^{1}H} (202.4 MHz, CD$_2$Cl$_2$, ambient temperature).

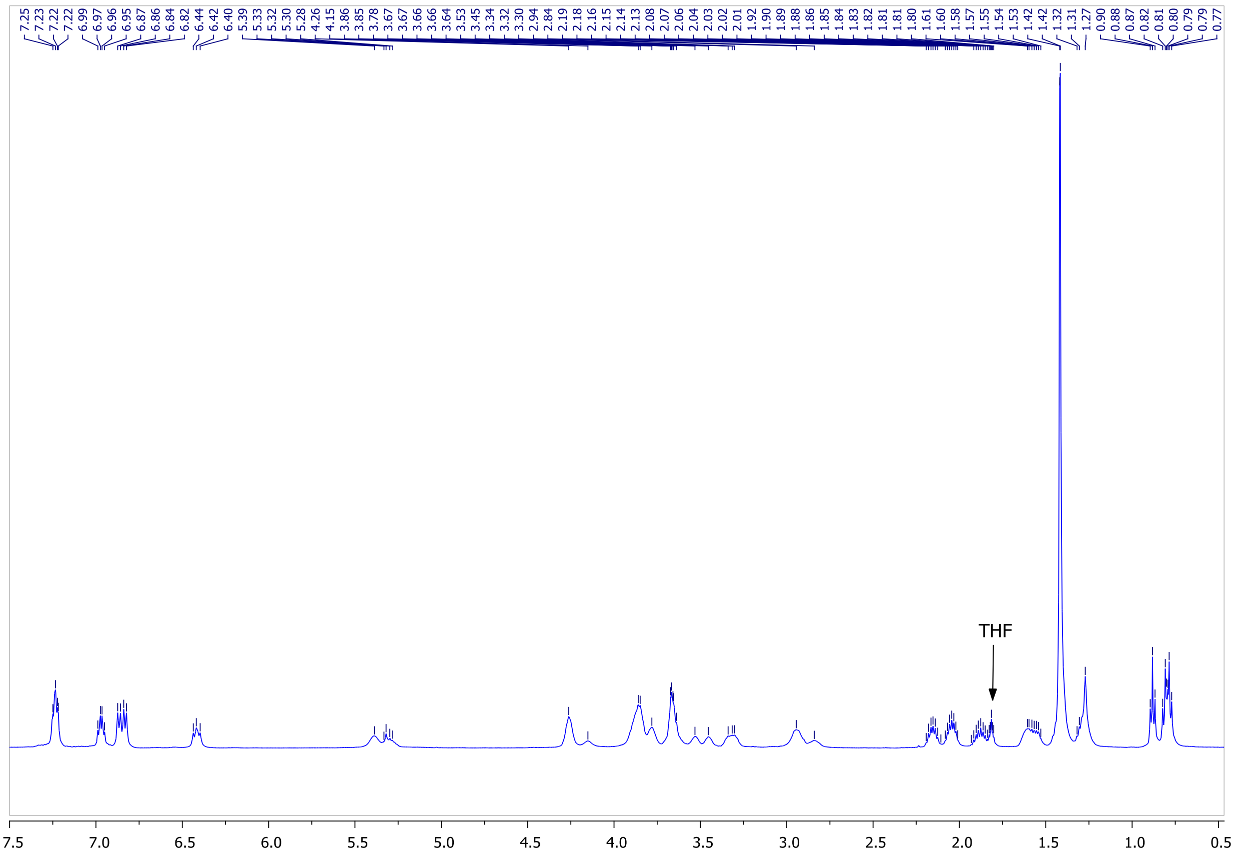


Figure S44b. [Pd(allyl)(**L3c**)$_2$]BF_4, ^1H (499.9 MHz, CD_2Cl_2, ambient temperature).

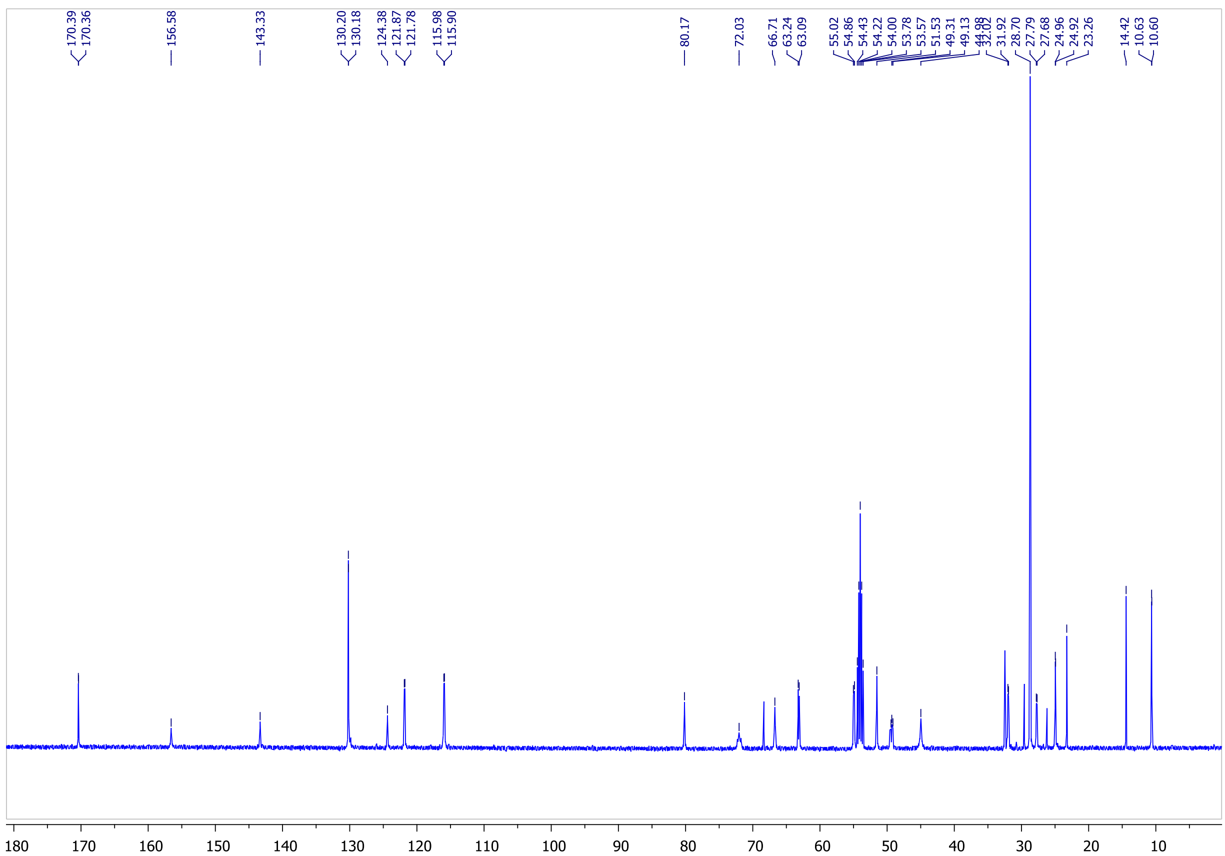


Figure S44c. [Pd(allyl)(**L3c**)$_2$]BF_4, $^{13}C\{^1H\}$ (125.7 MHz, CD_2Cl_2, ambient temperature).

NMR SPECTRA OF NEW COMPOUNDS

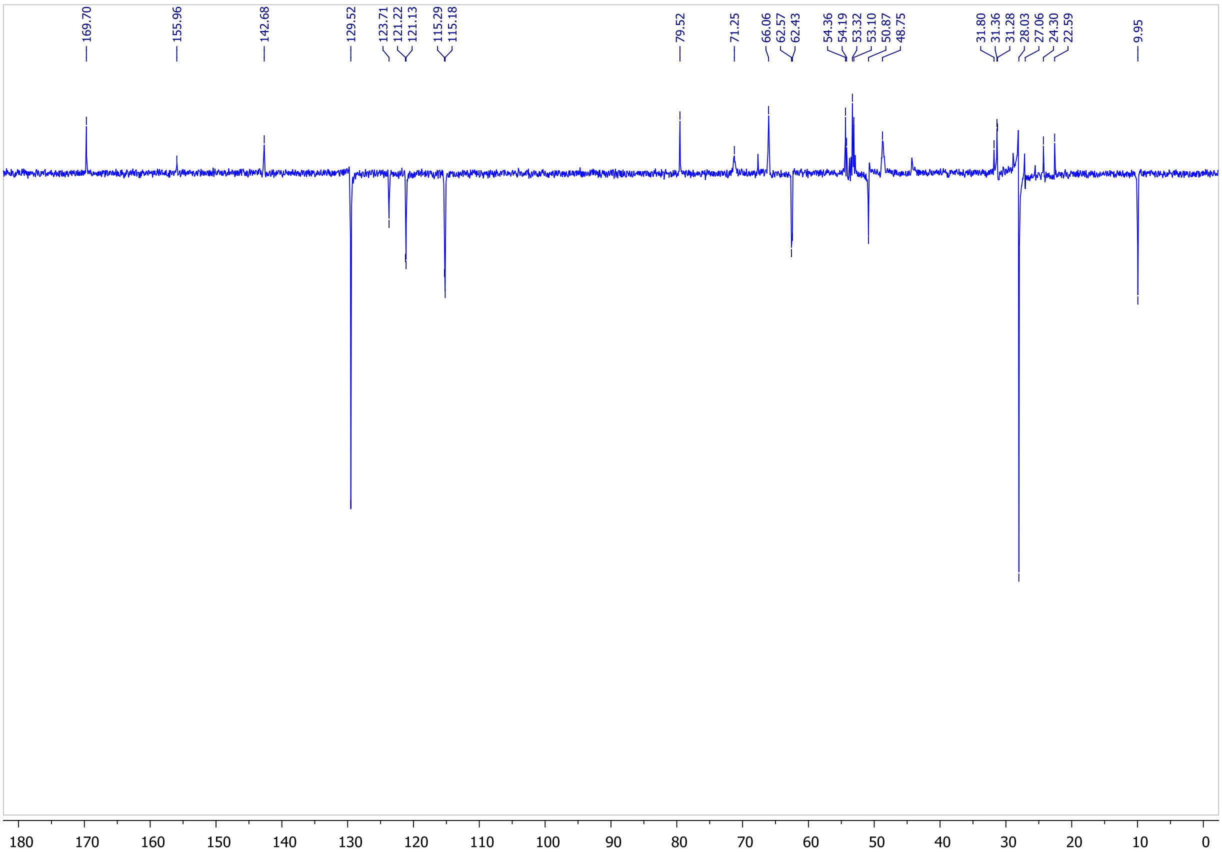


Figure S44d. [Pd(allyl)(**L3c**)$_2$]BF_4, $^{13}C\{^1H\}$ APT (125.7 MHz, CD_2Cl_2, ambient temperature).

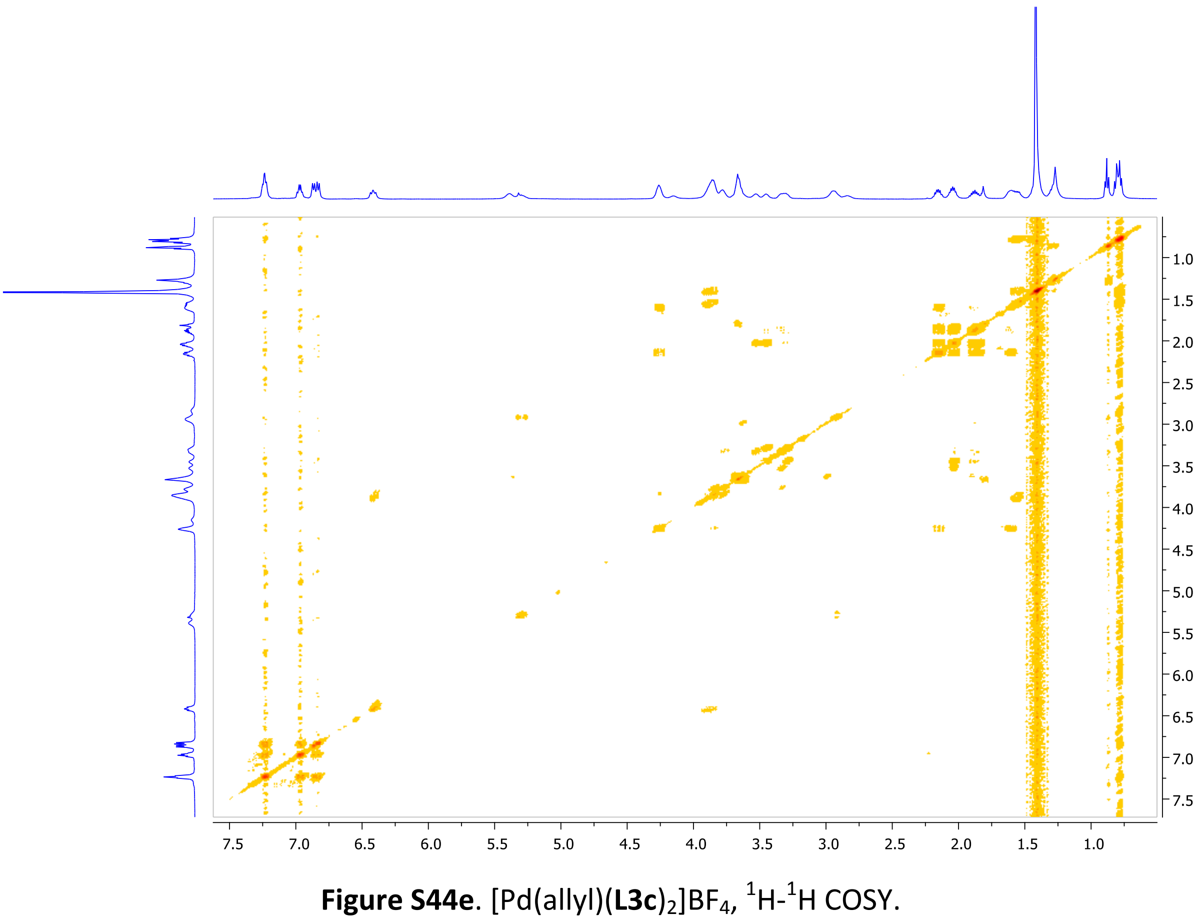


Figure S44e. [Pd(allyl)(**L3c**)$_2$]BF_4, ^1H-^1H COSY.

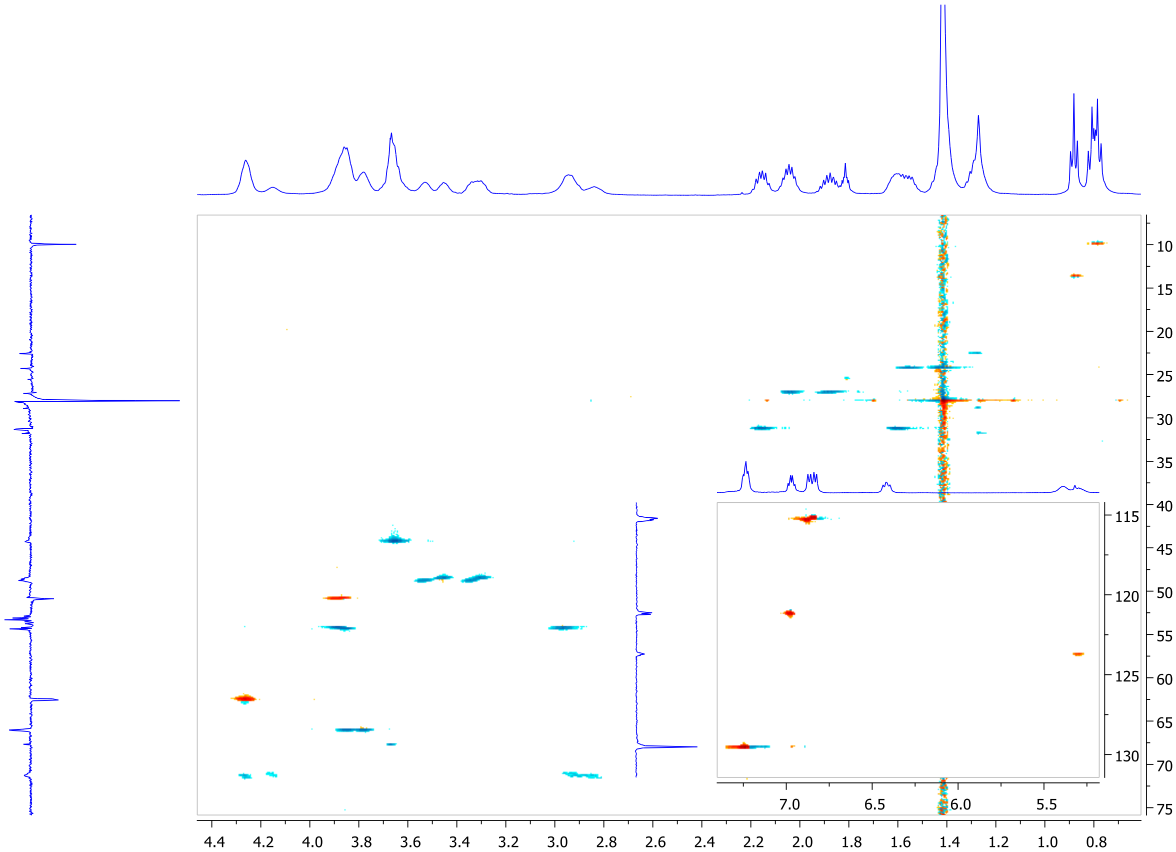


Figure S44f. [Pd(allyl)(**L3c**)$_2$]BF_4, ^{1}H-^{13}C HSQC.

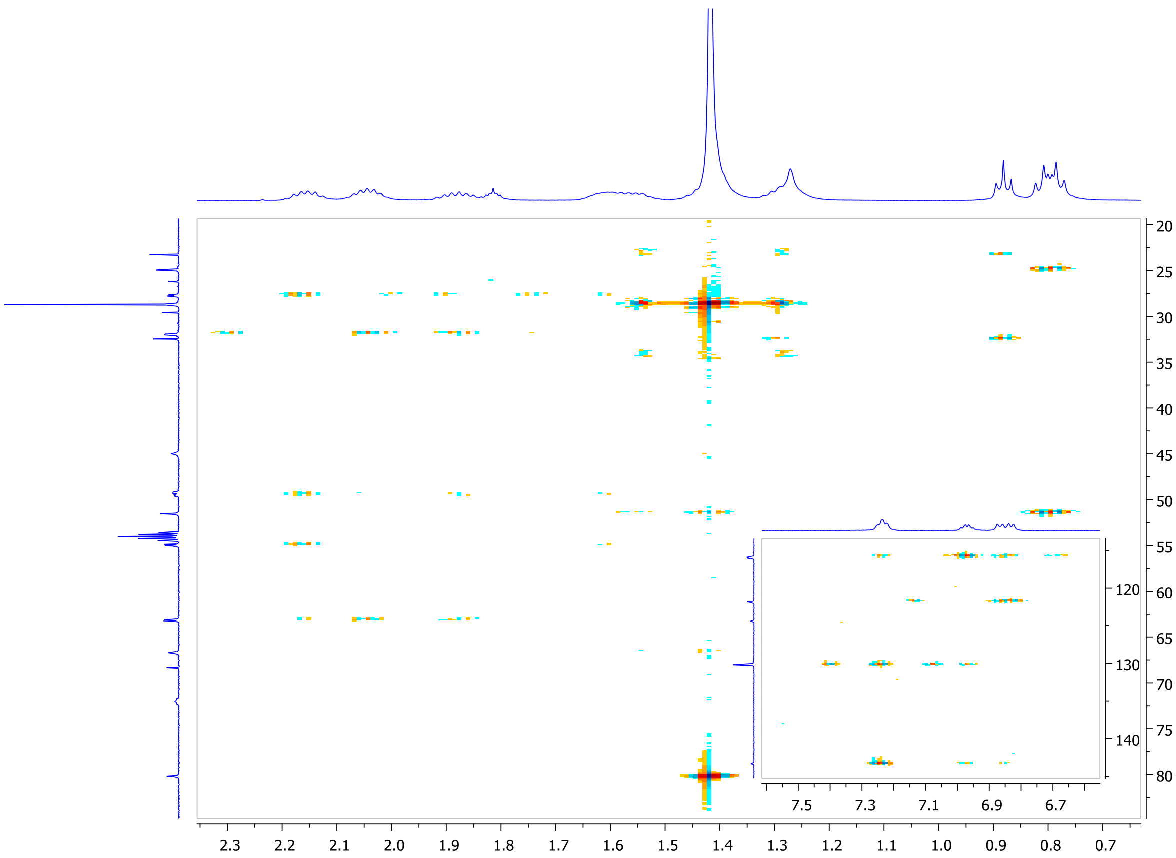


Figure S44g. [Pd(allyl)(**L3c**)$_2$]BF_4, ^{1}H-^{13}C HMBC.

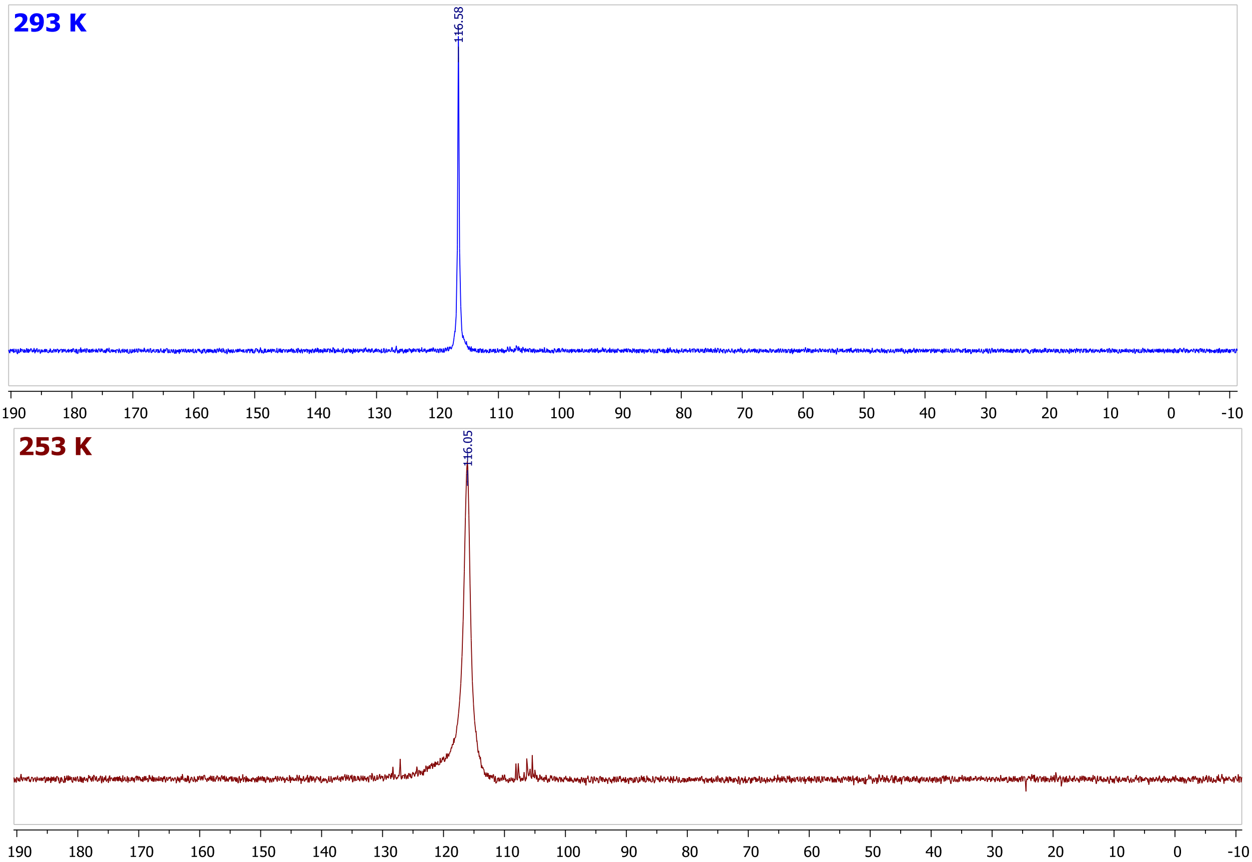


Figure S45a. [Pd(allyl)(**L3d**)$_2$]BF$_4$, ^{31}P{^{1}H} (202.4 MHz, CD$_2$Cl$_2$).

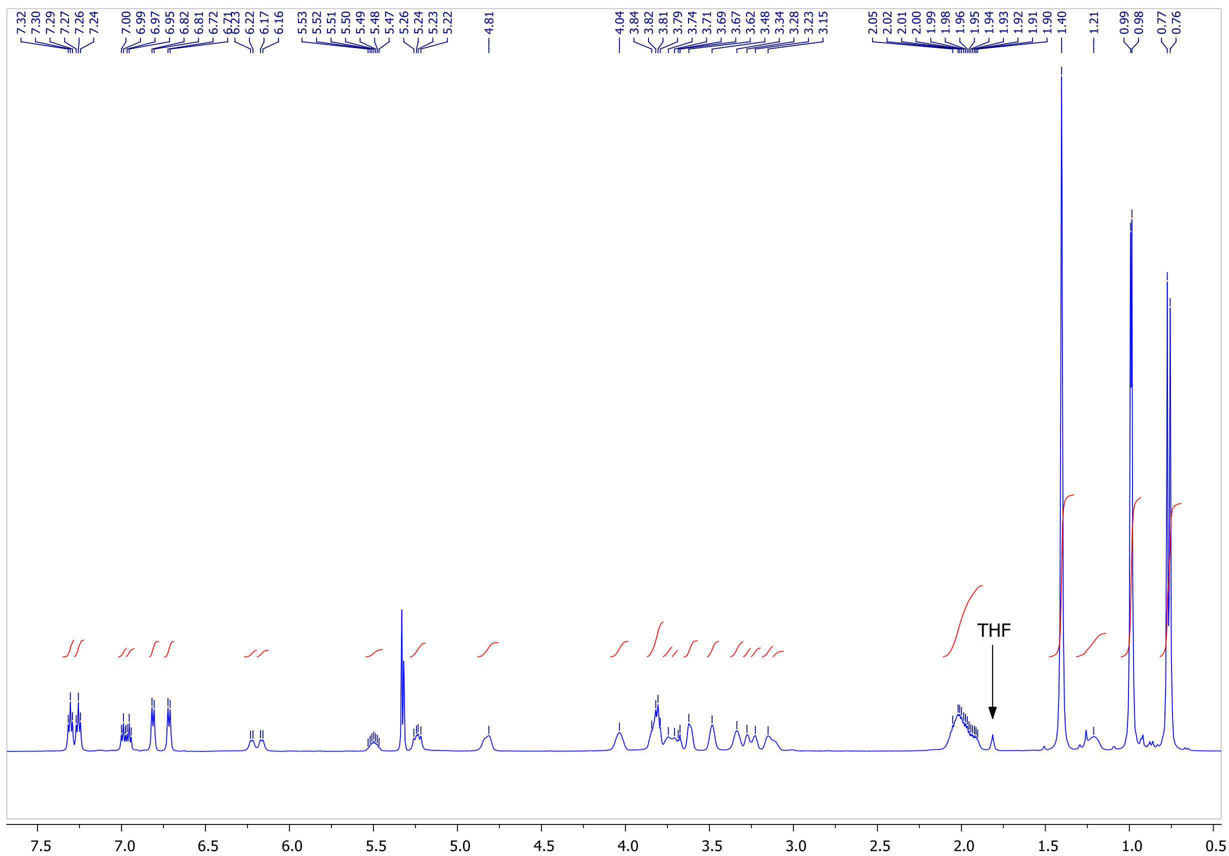


Figure S45b. [Pd(allyl)(**L3d**)$_2$]BF$_4$, ^{1}H (600.13 MHz, CD$_2$Cl$_2$, 20 °C).

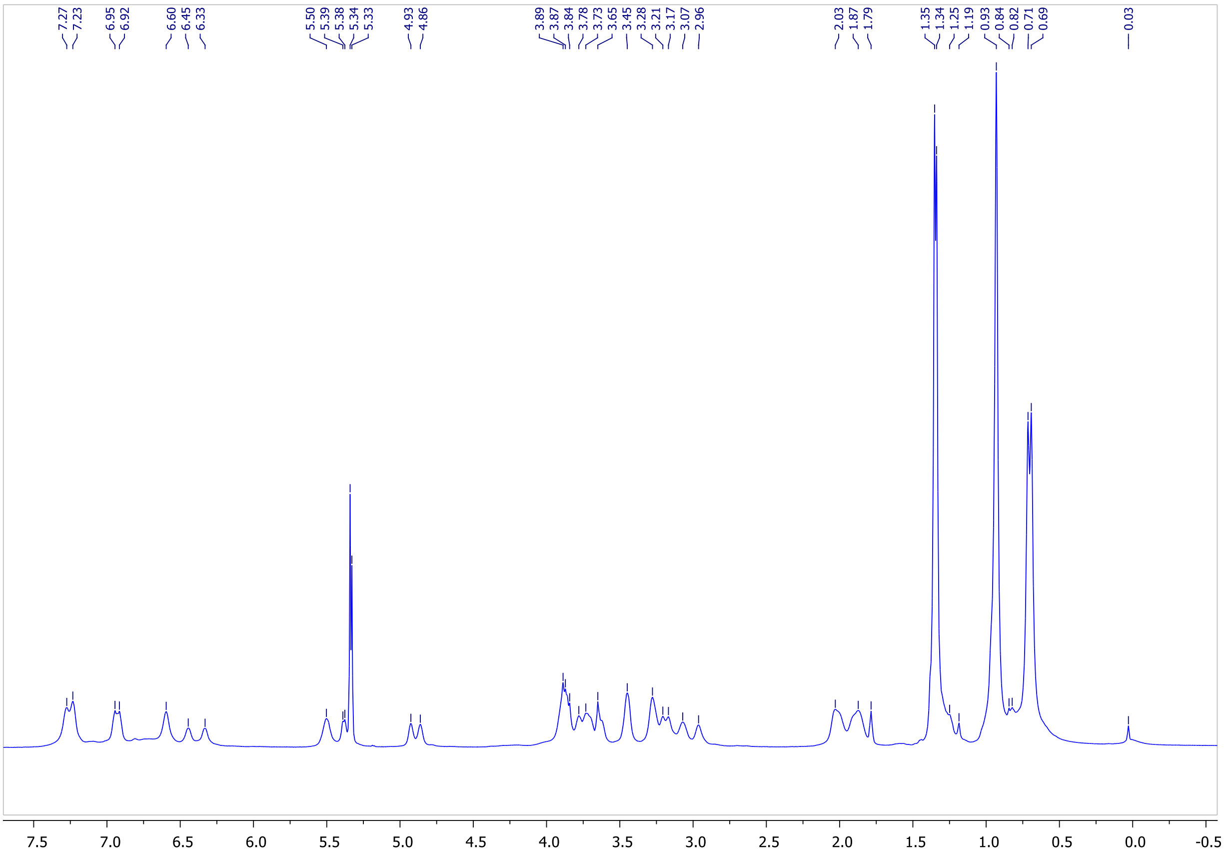


Figure S45c. [Pd(allyl)(**L3d**)$_2$]BF_4, ^1H (600.13 MHz, CD_2Cl_2, -50 °C).

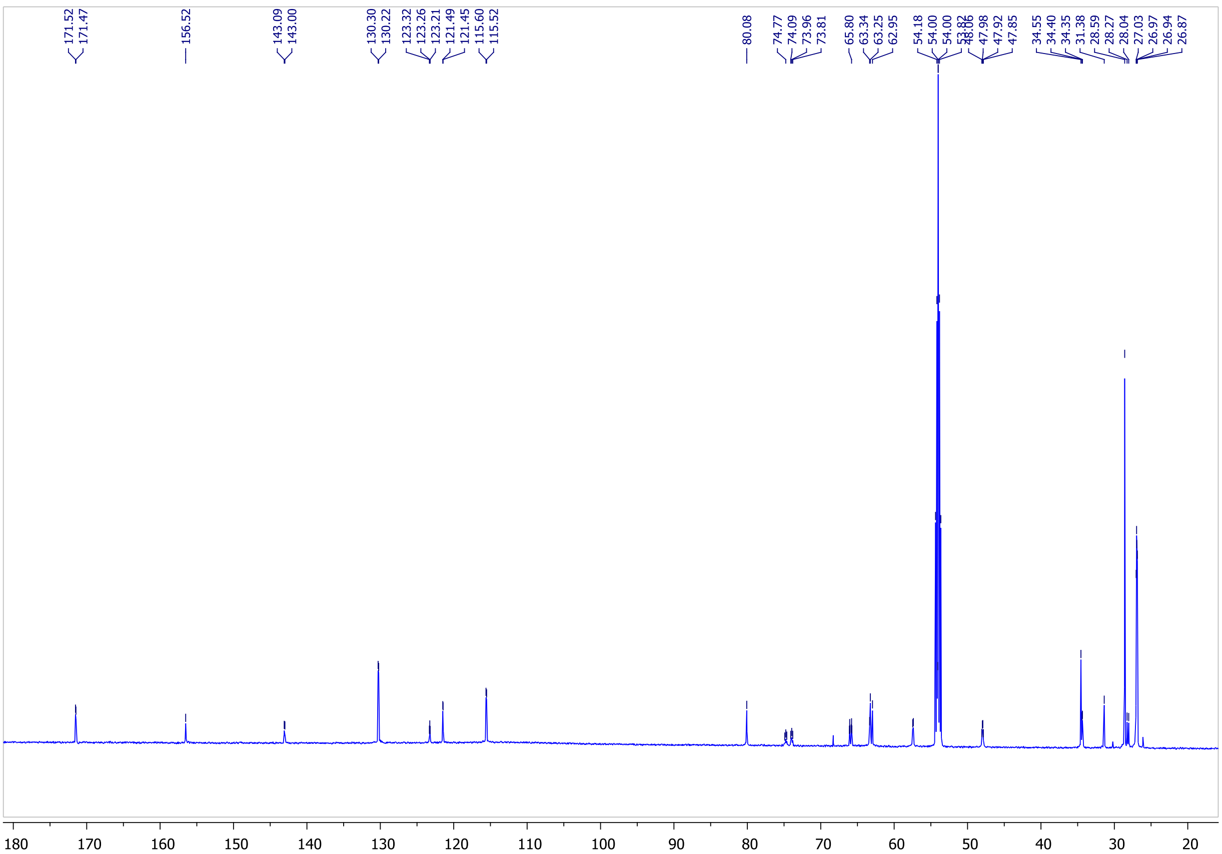


Figure S45d. [Pd(allyl)(**L3d**)$_2$]BF_4, $^{13}C\{^1H\}$ (150.9 MHz, CD_2Cl_2, 20 °C).

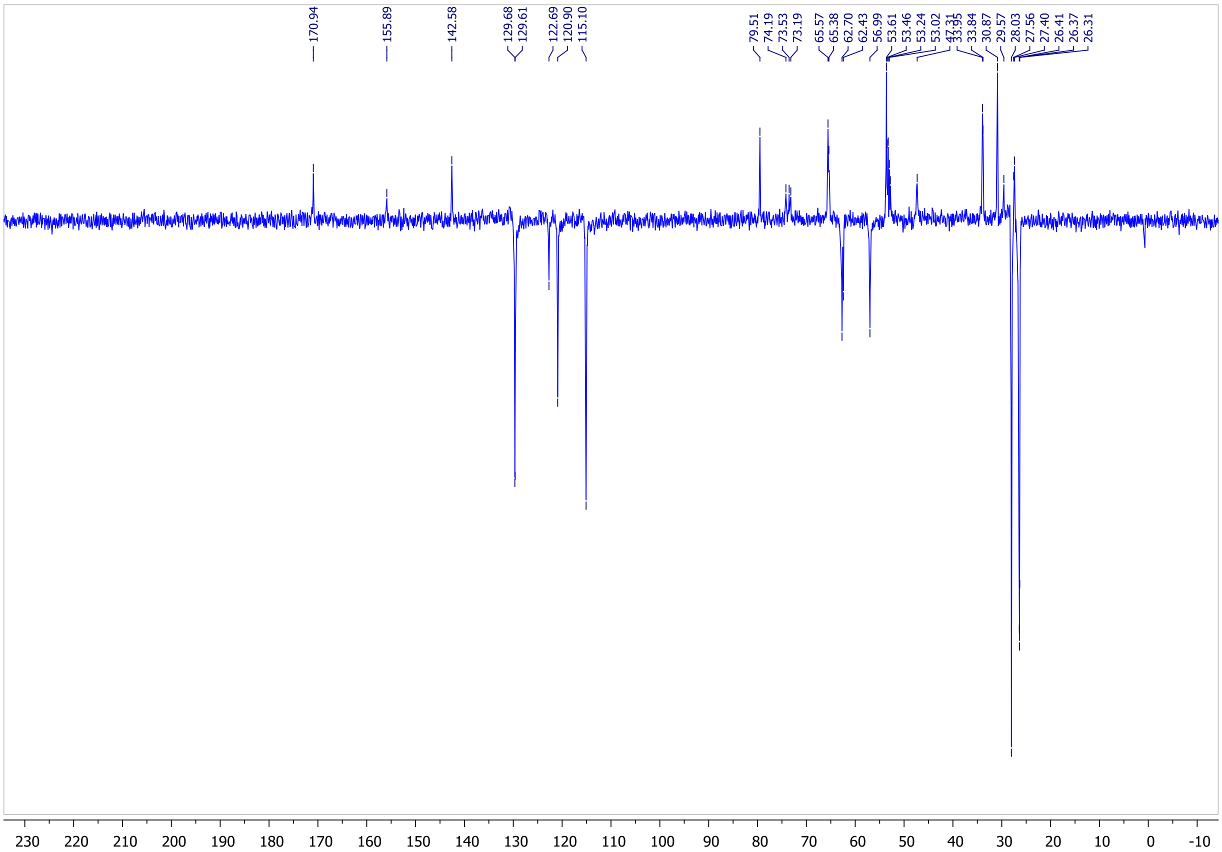


Figure S45e. [Pd(allyl)(**L3d**)$_2$]BF_4, $^{13}C\{^1H\}$ APT (150.9 MHz, CD_2Cl_2, 20 °C).

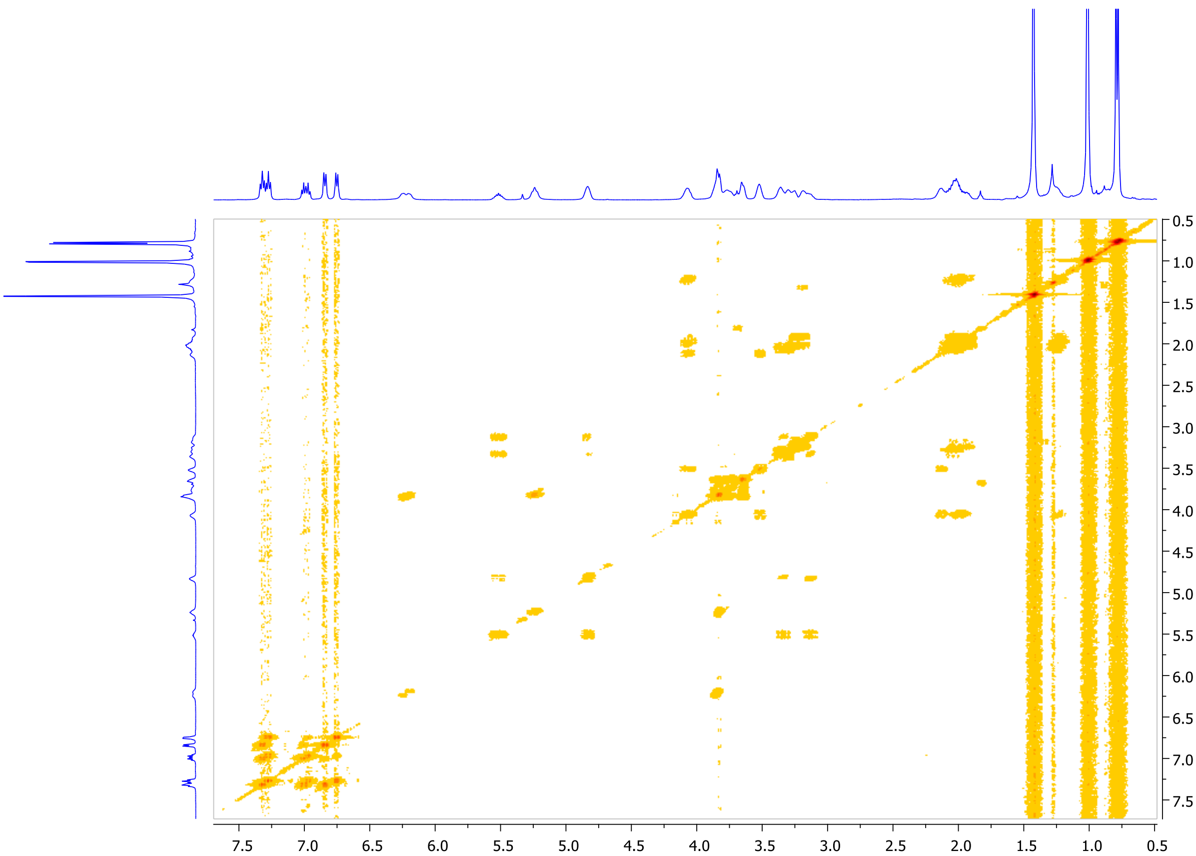


Figure S45f. [Pd(allyl)(**L3d**)$_2$]BF_4, ^1H-^1H COSY.

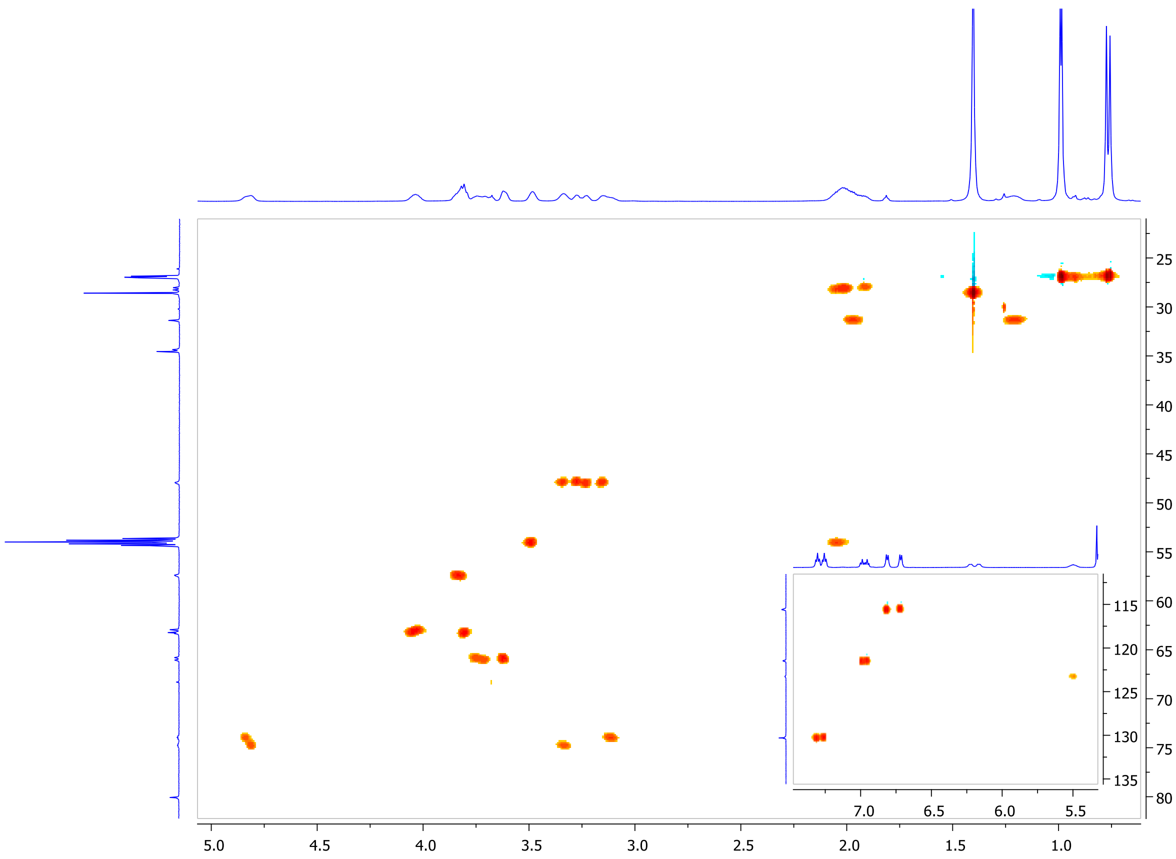


Figure S45g. [Pd(allyl)(**L3d**)$_2$]BF_4, ^{1}H-^{13}C HSQC.

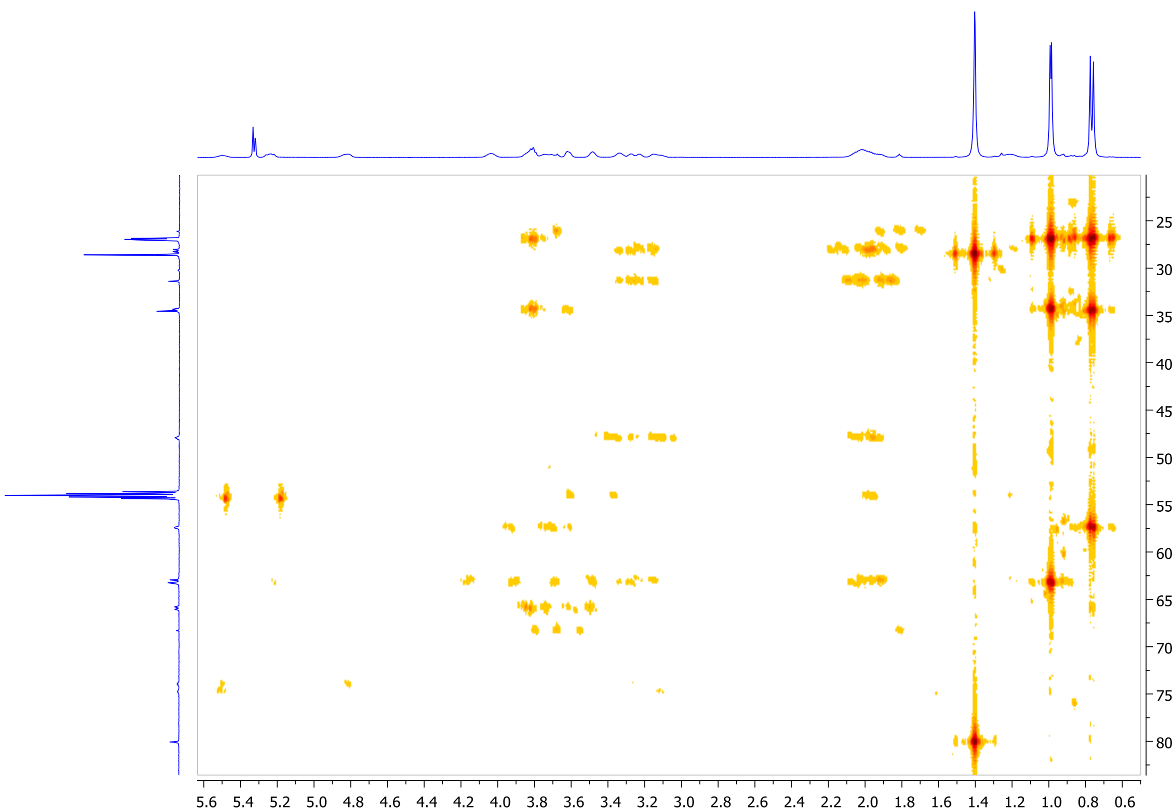


Figure S45h. [Pd(allyl)(**L3d**)$_2$]BF_4, ^{1}H-^{13}C HMBC (fragment of the spectrum).

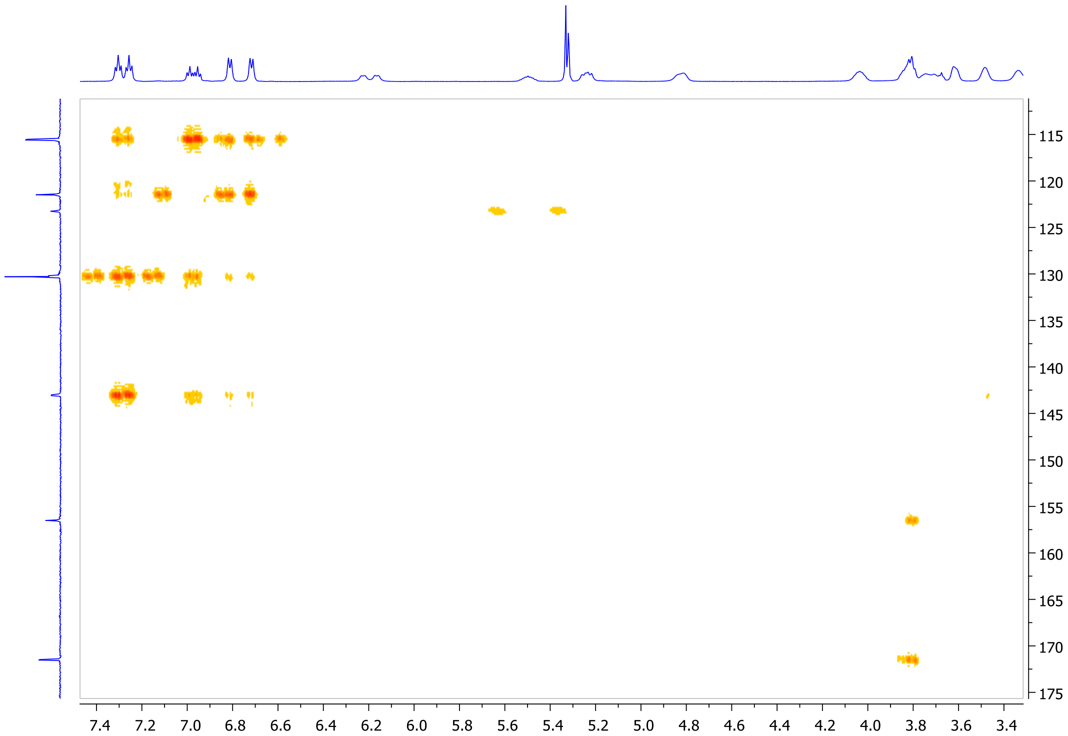


Figure S45i. [Pd(allyl)(**L3d**)$_2$]BF$_4$, ^{1}H-^{13}C HMBC (fragment of the spectrum).

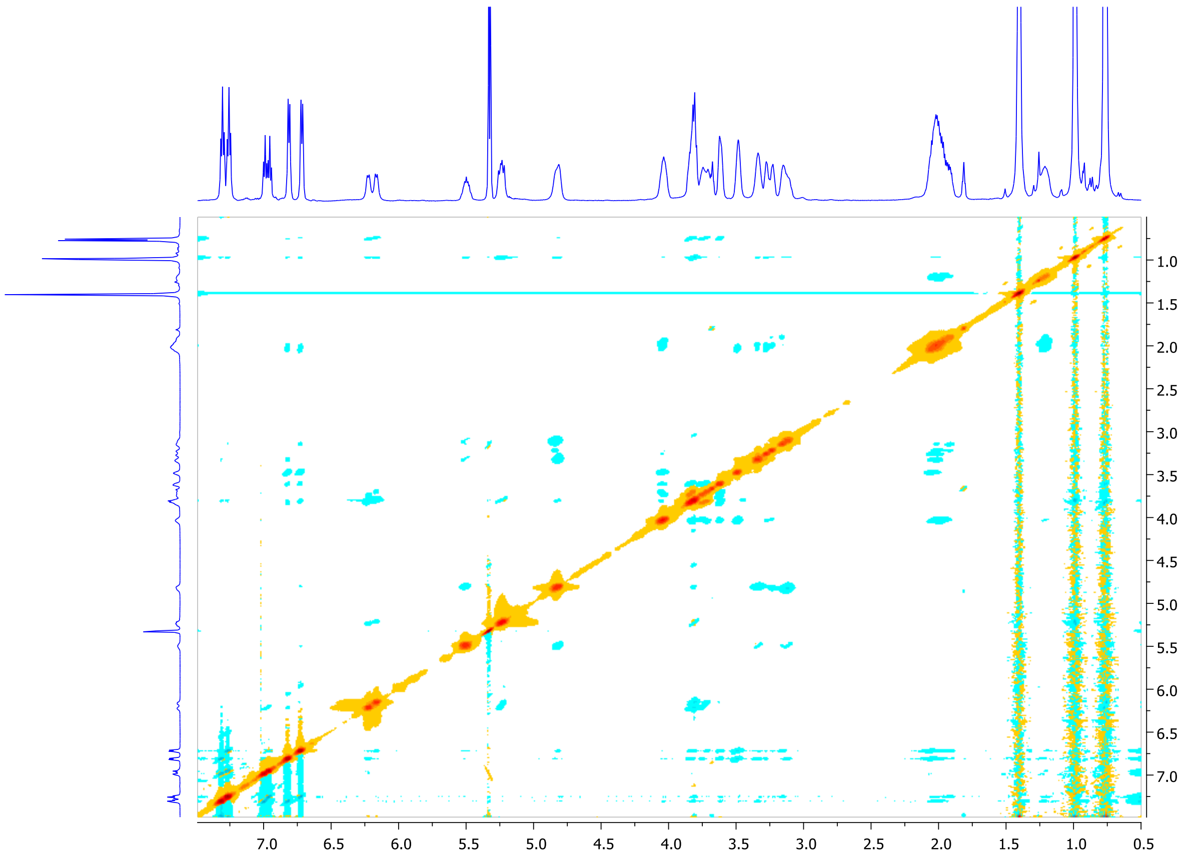


Figure S45j. [Pd(allyl)(**L3d**)$_2$]BF$_4$, ^{1}H-^{1}H NOESY.

NMR SPECTRA OF NEW COMPOUNDS

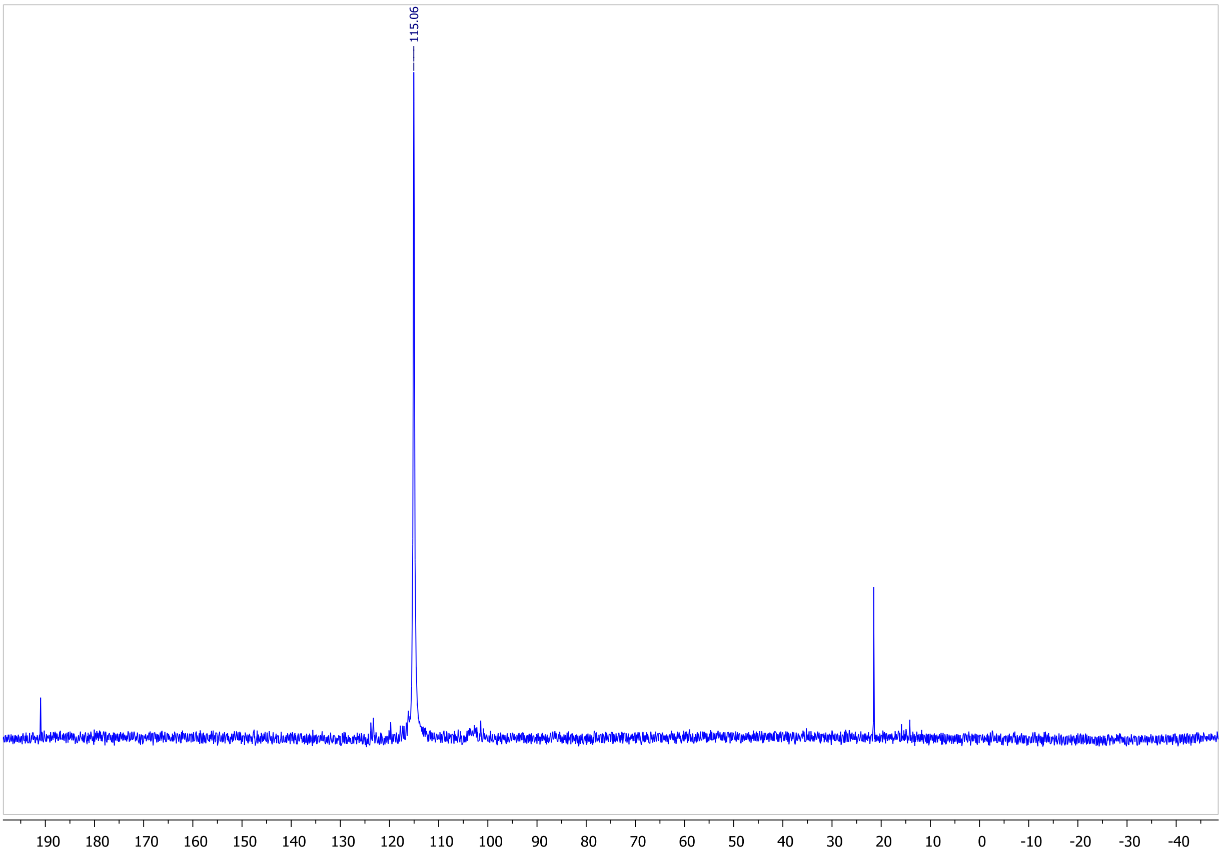


Figure S46a. [Pd(allyl)(**L3e**)$_2$]BF_4, $^{31}P\{^1H\}$ (202.4 MHz, CD_2Cl_2, ambient temperature).

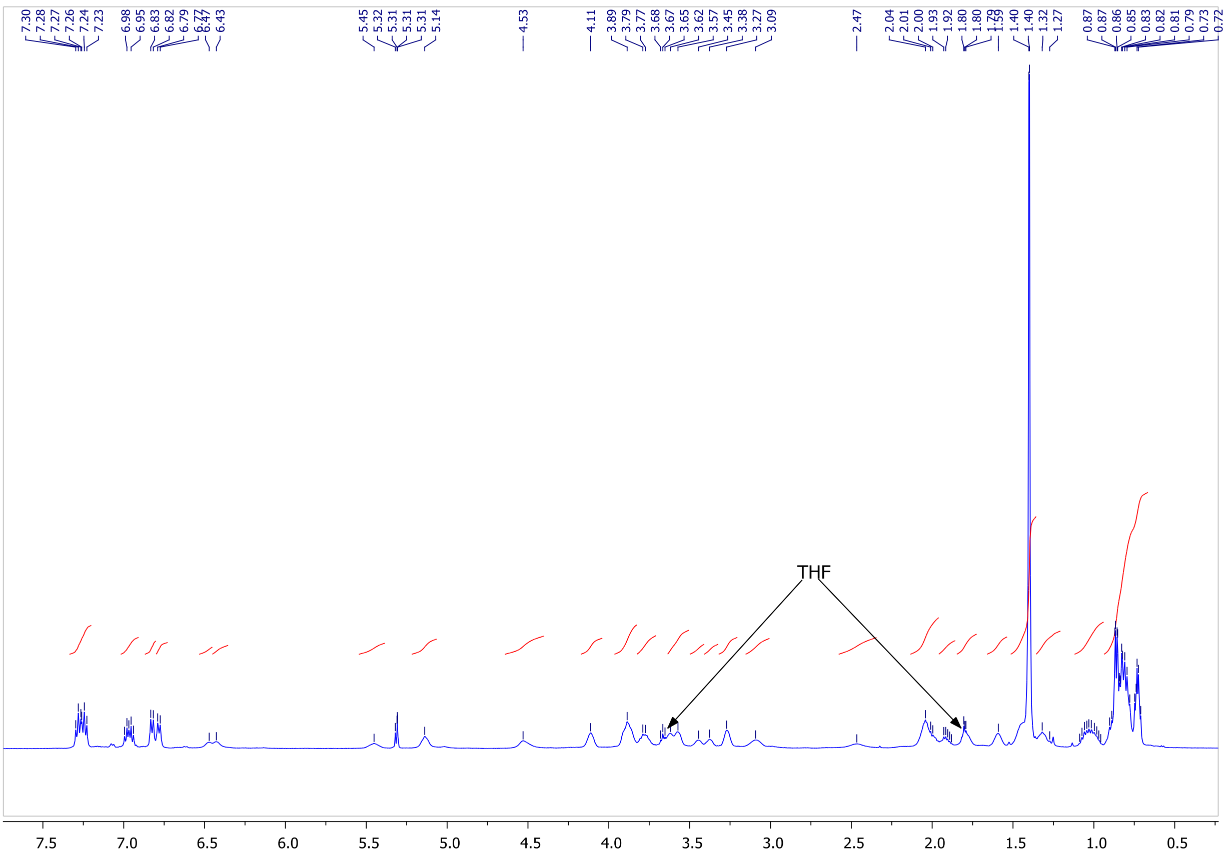


Figure S46b. [Pd(allyl)(**L3e**)$_2$]BF_4, ^1H (499.9 MHz, CD_2Cl_2, ambient temperature).

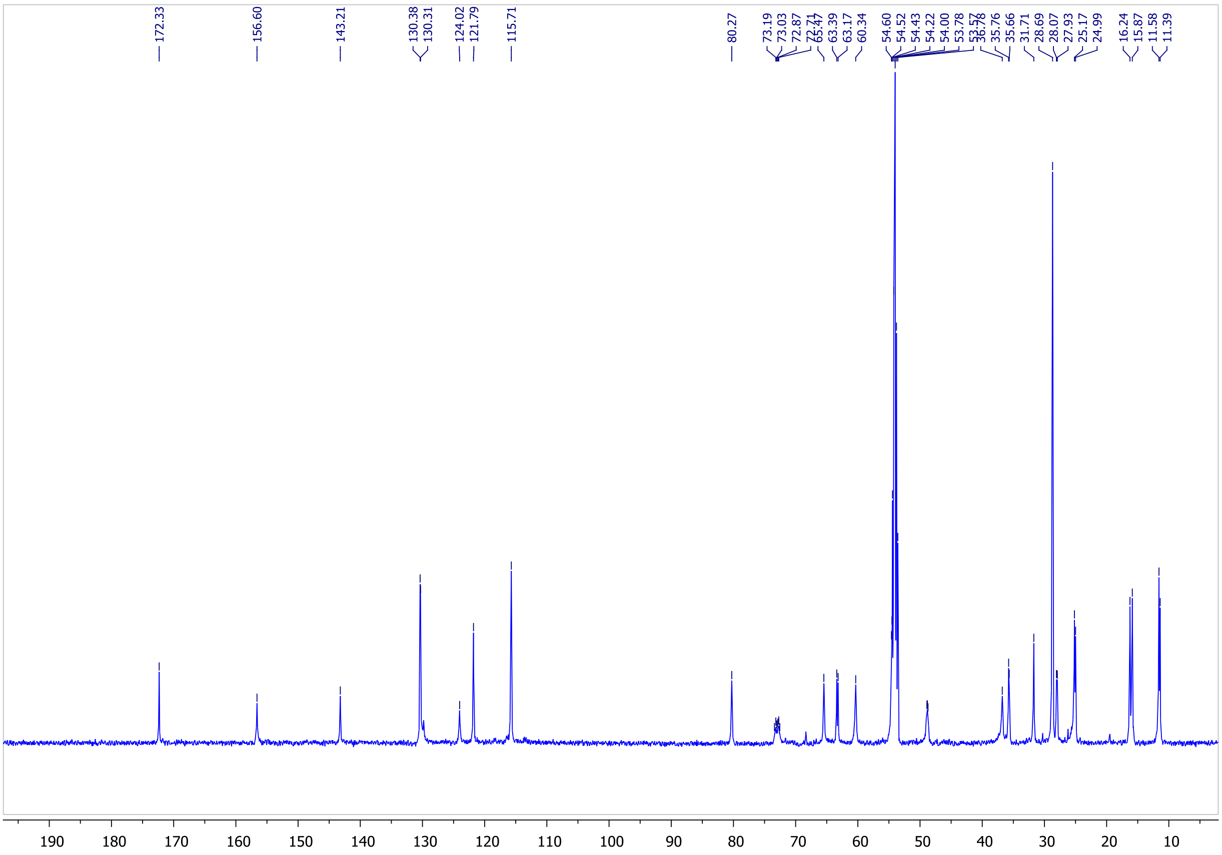


Figure S46c. [Pd(allyl)(**L3e**)$_2$]BF_4, $^{13}C\{^1H\}$ (125.7 MHz, CD_2Cl_2, ambient temperature).

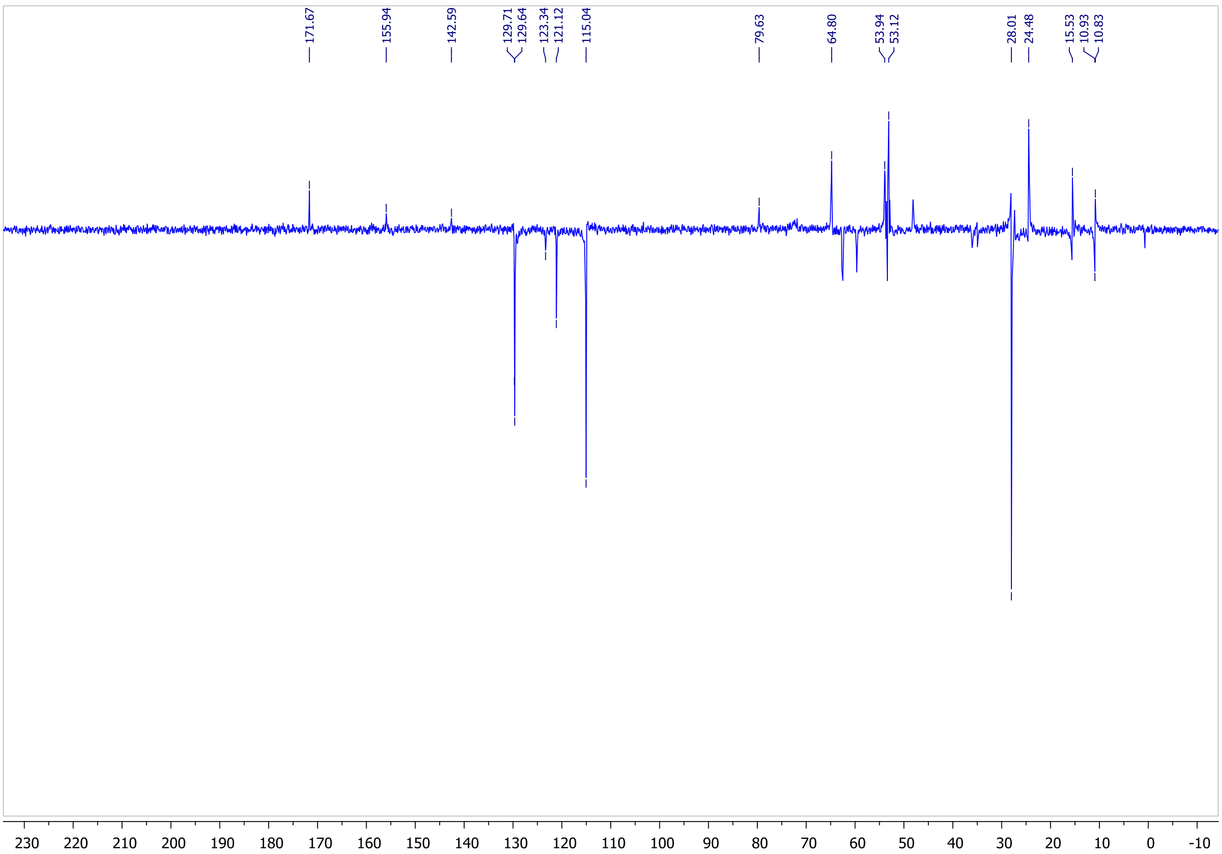


Figure S46d. [Pd(allyl)(**L3e**)$_2$]BF_4, $^{13}C\{^1H\}$ APT (125.7 MHz, CD_2Cl_2, ambient temperature).

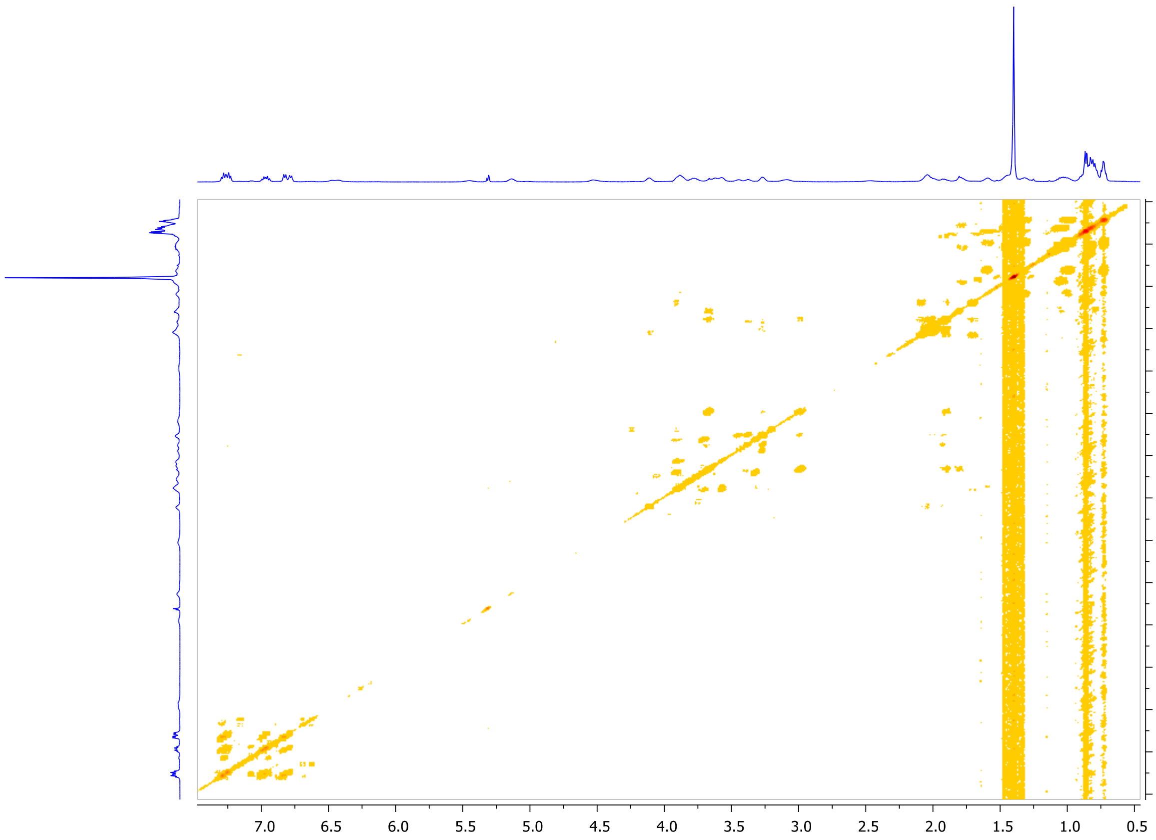


Figure S46e. [Pd(allyl)(**L3e**)$_2$]BF_4, ^1H-^1H COSY.

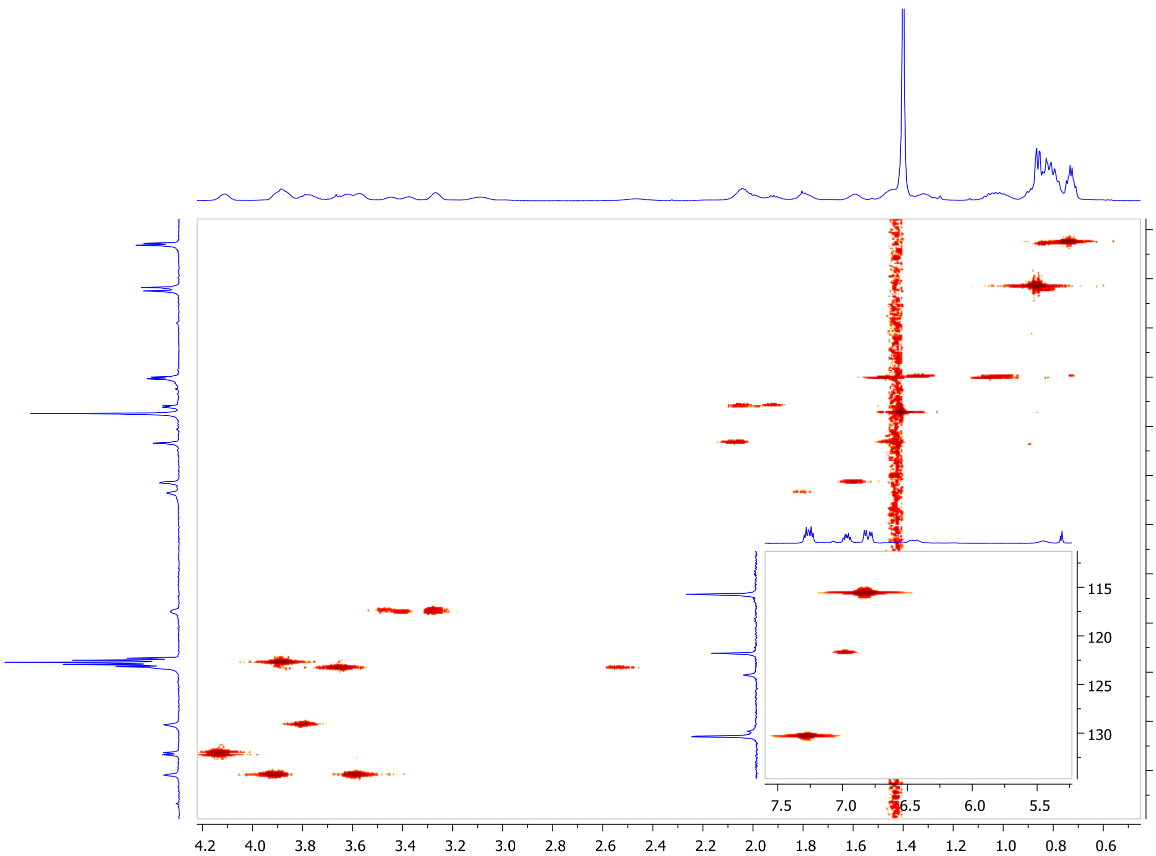


Figure S46f. [Pd(allyl)(**L3e**)$_2$]BF_4, ^1H-^{13}C HSQC.

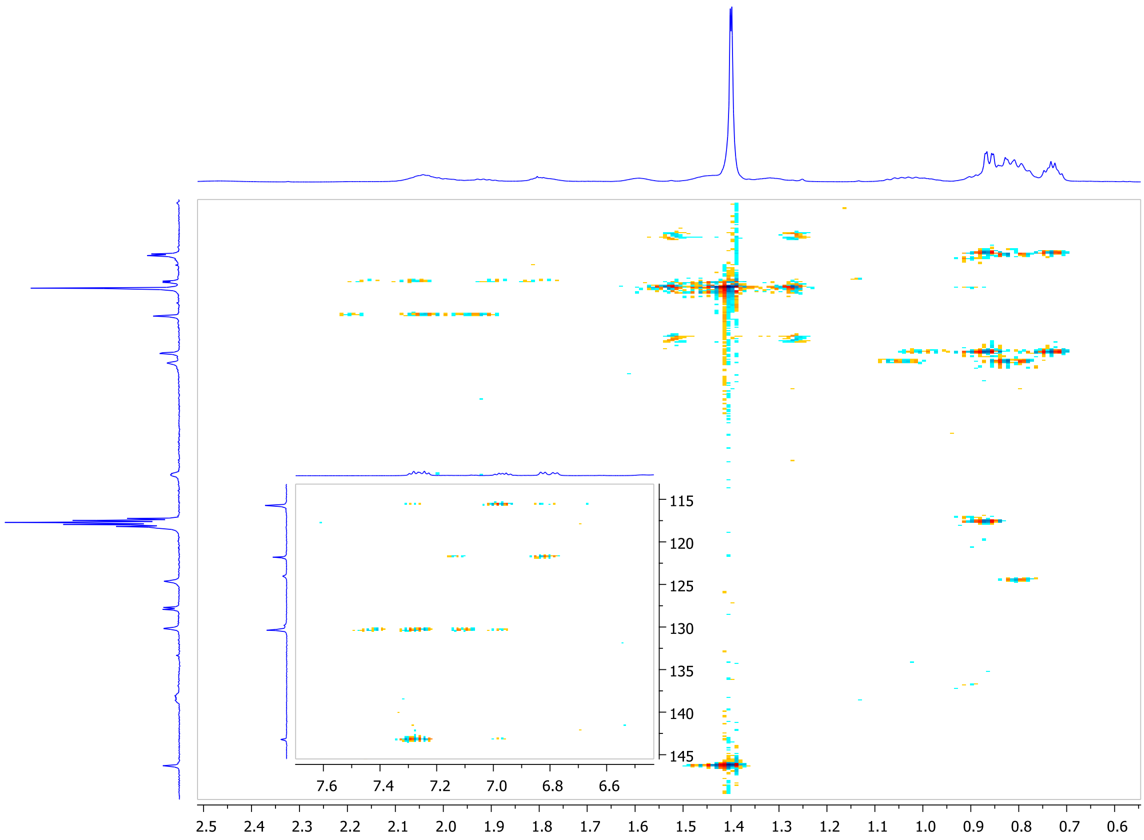


Figure S56g. [Pd(allyl)(**L3e**)$_2$]BF_4, ^{1}H-^{13}C HMBC.

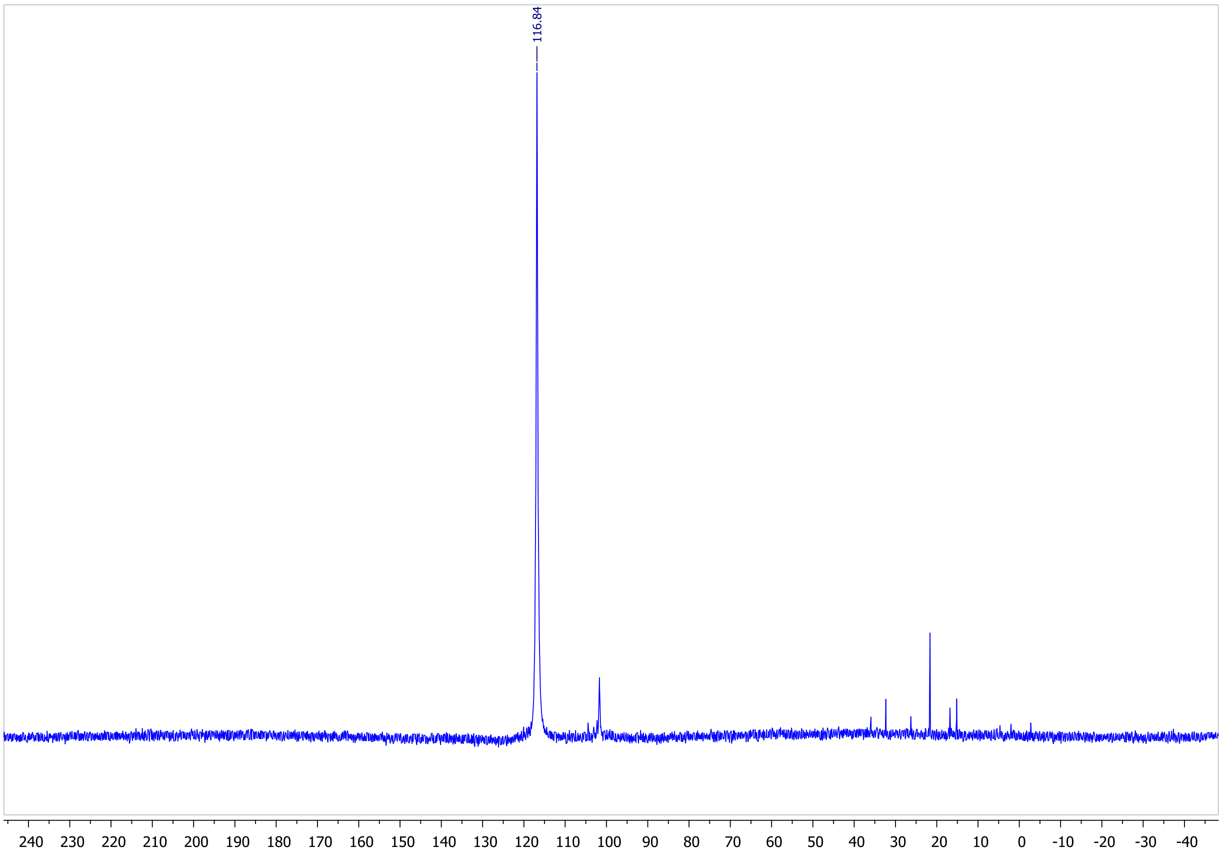


Figure S47a. [Pd(allyl)(**L3f**)$_2$]BF_4, $^{31}P\{^{1}H\}$ (202.4 MHz, CD_2Cl_2, ambient temperature).

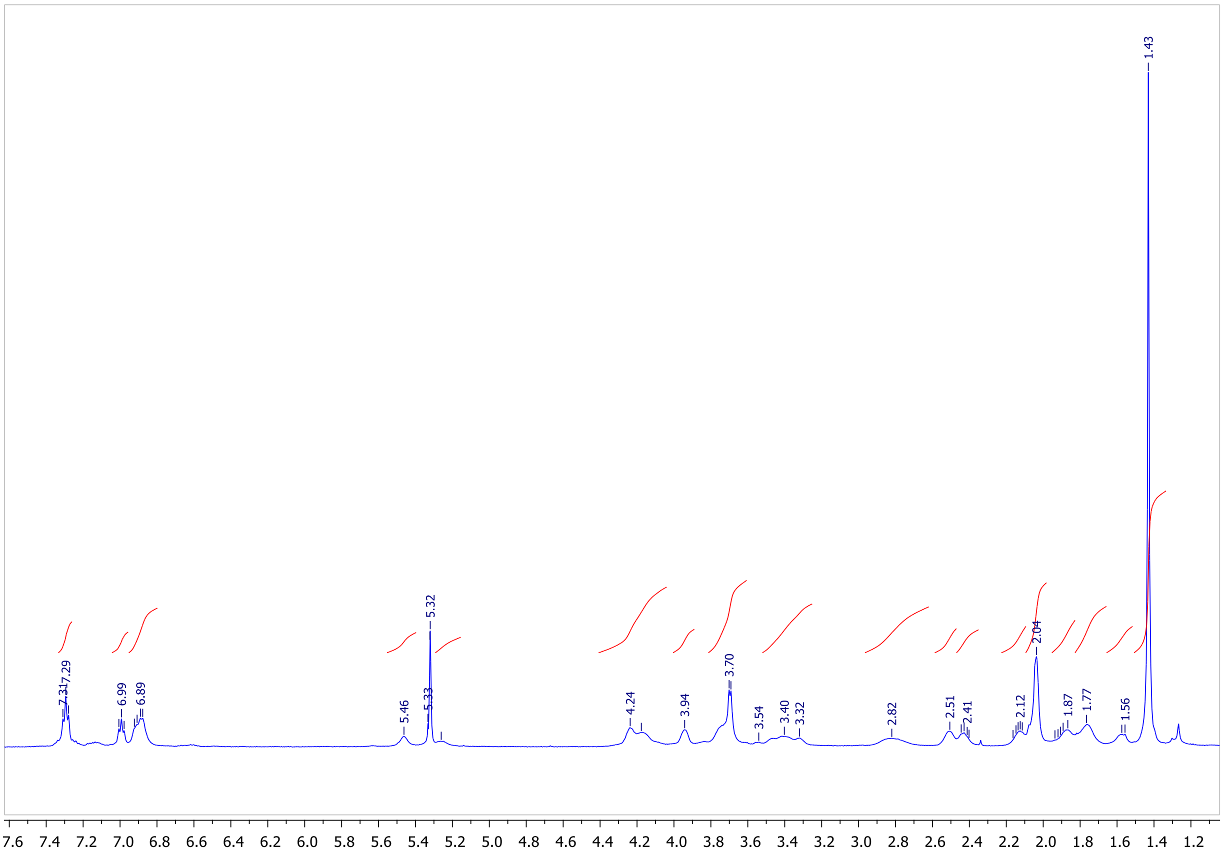


Figure S47b. [Pd(allyl)(**L3f**)$_2$]BF_4, ^{1}H (499.9 MHz, CD_2Cl_2, ambient temperature).

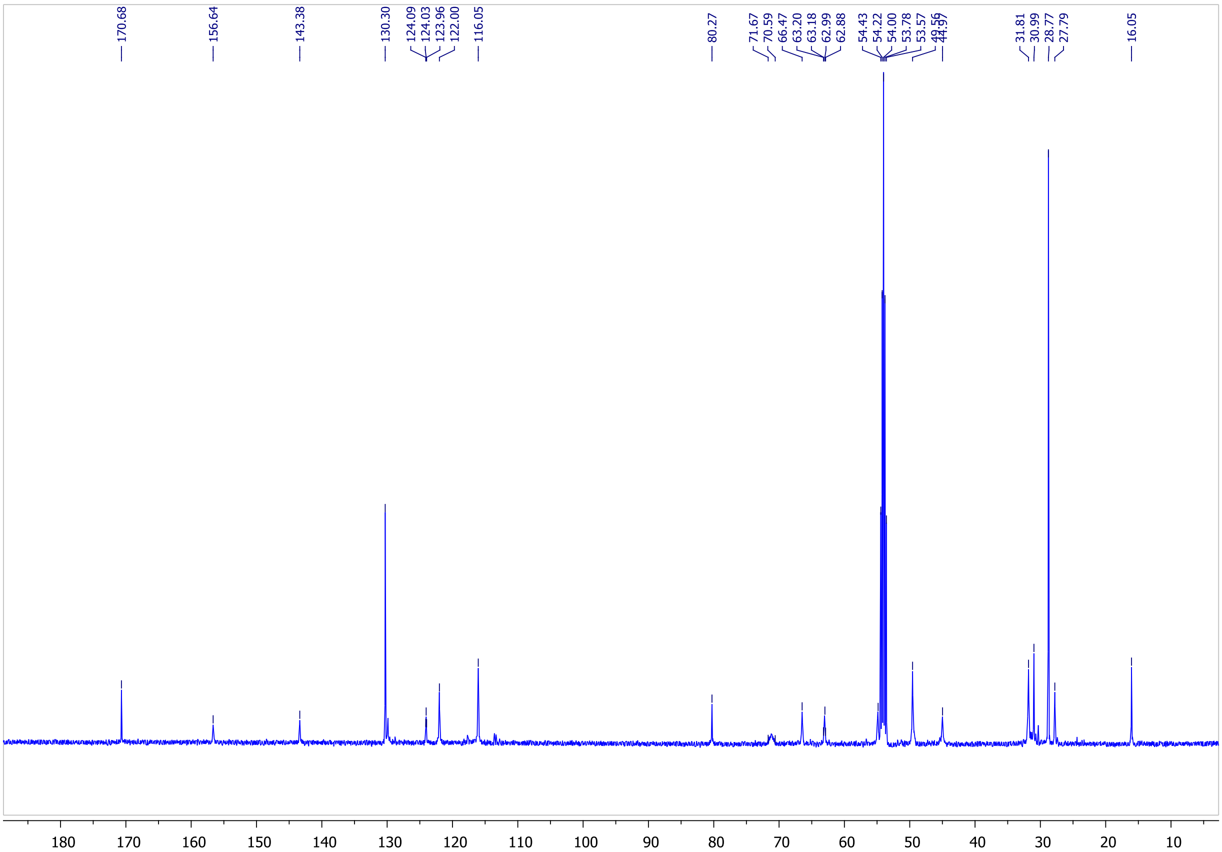


Figure S47c. [Pd(allyl)(**L3f**)$_2$]BF_4, $^{13}C\{^1H\}$ (125.7 MHz, CD_2Cl_2, ambient temperature).

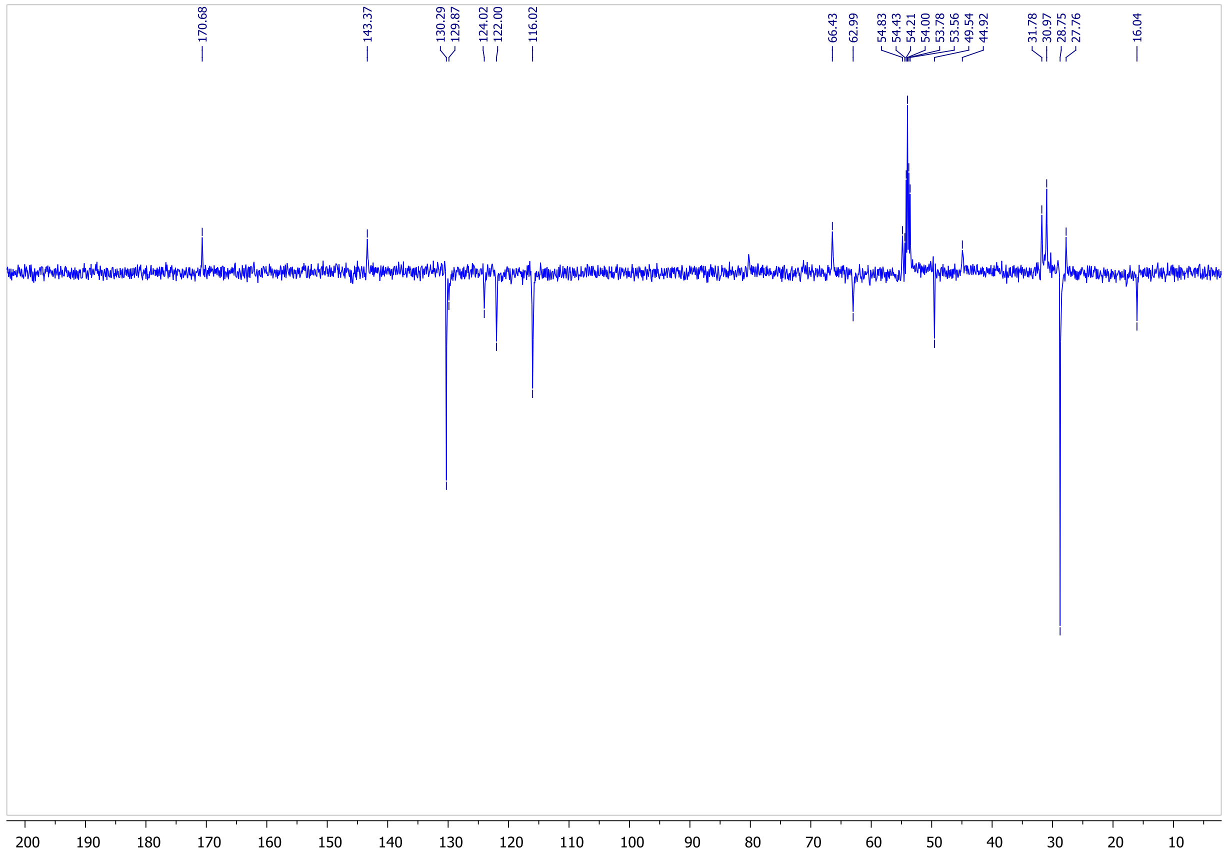


Figure S47d. [Pd(allyl)(**L3f**)$_2$]BF_4, $^{13}C\{^1H\}$ APT (125.7 MHz, CD_2Cl_2, ambient temperature).

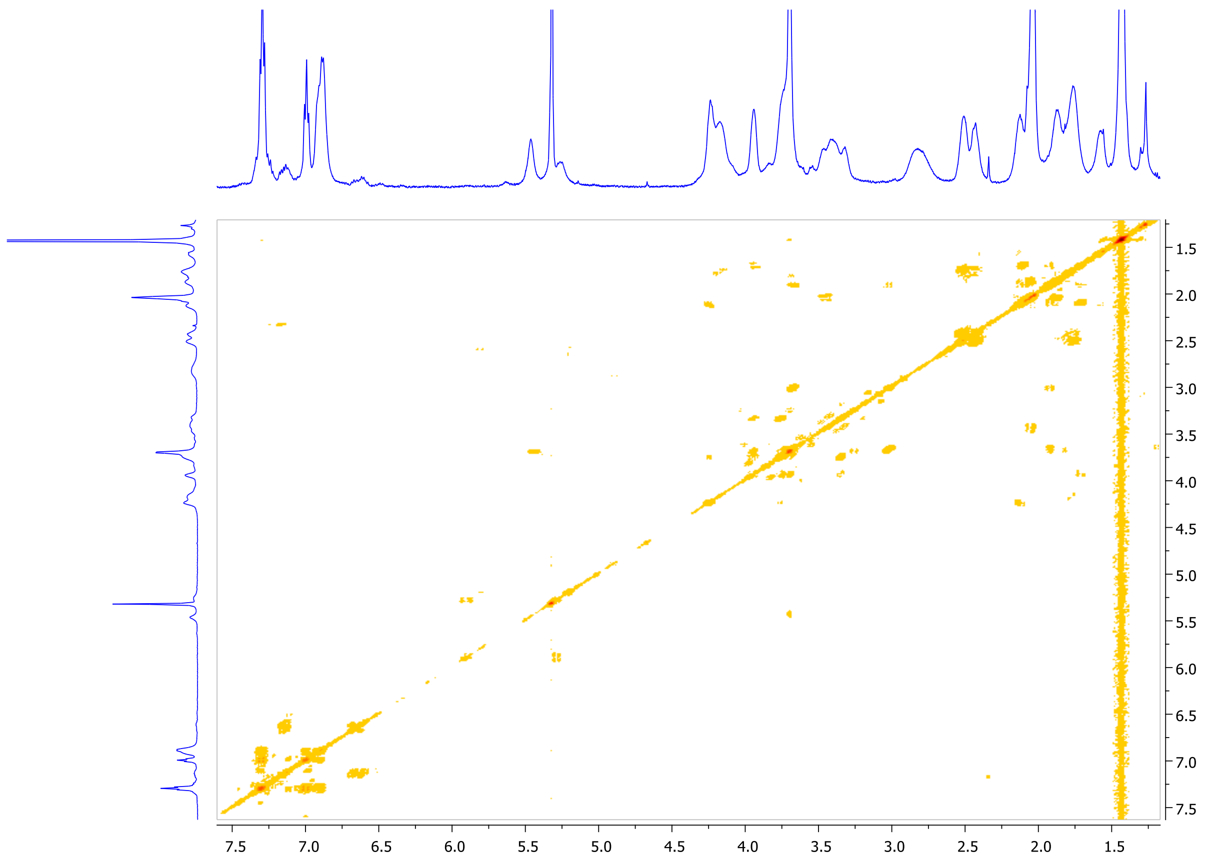


Figure S47e. [Pd(allyl)(**L3f**)$_2$]BF_4, ^1H-^1H COSY.

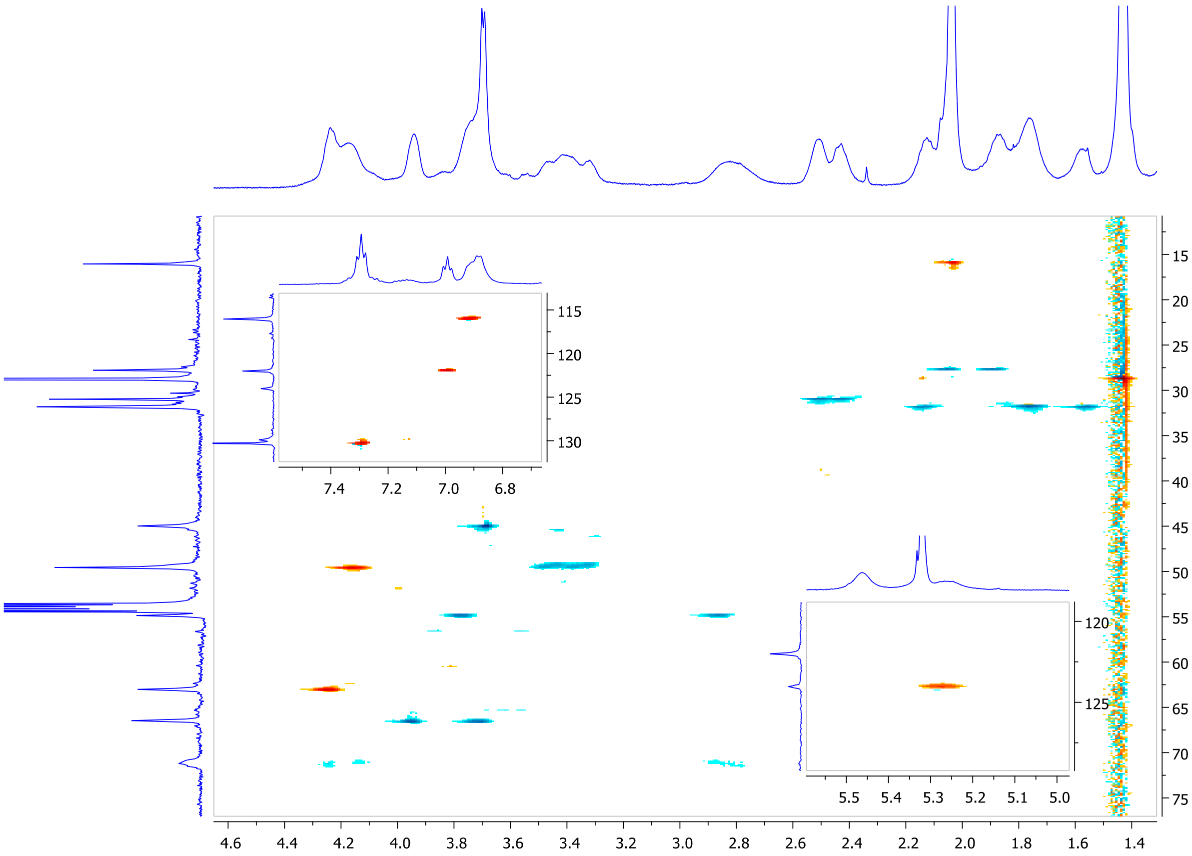


Figure S47f. [Pd(allyl)(**L3f**)$_2$]BF$_4$, ^{1}H-^{13}C HSQC.

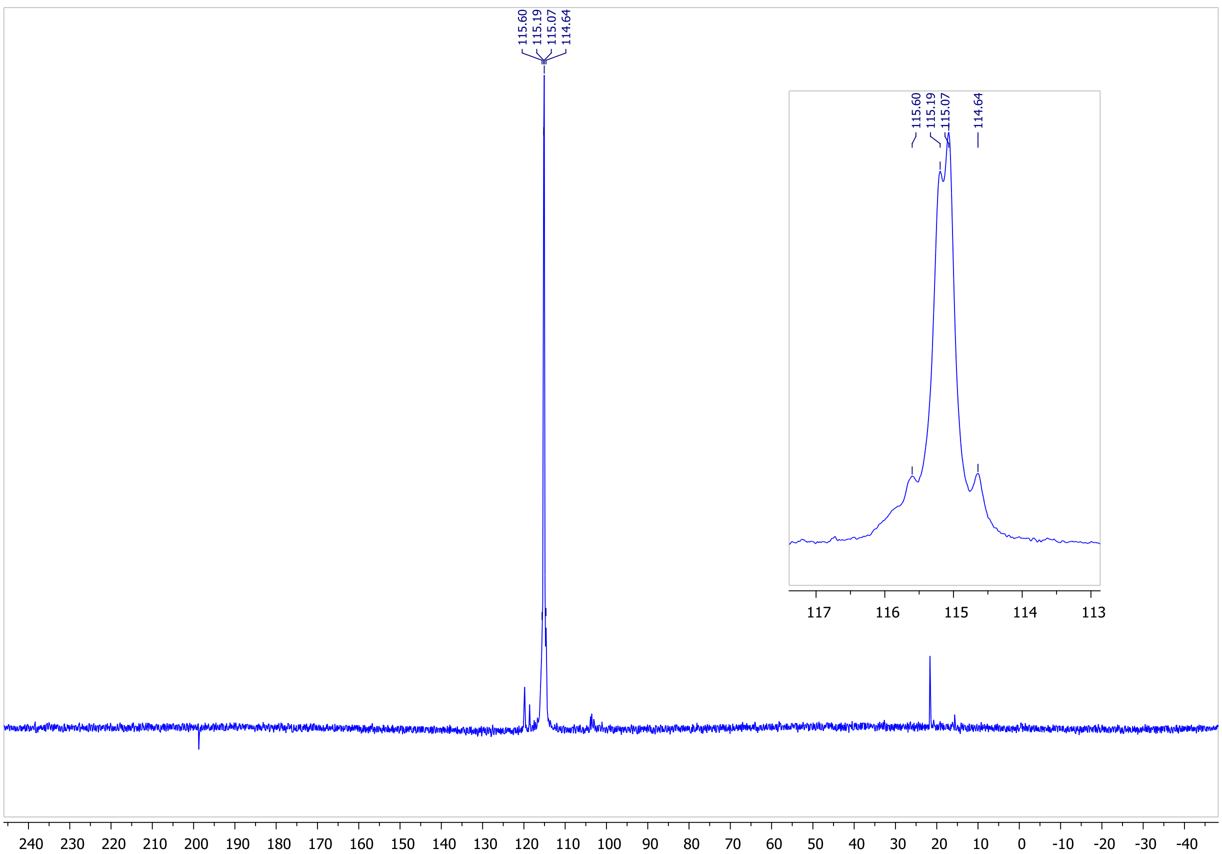


Figure S48a. [Pd(allyl)(**L3g**)$_2$]BF$_4$, ^{31}P{^{1}H} (202.4 MHz, CD$_2$Cl$_2$, ambient temperature).

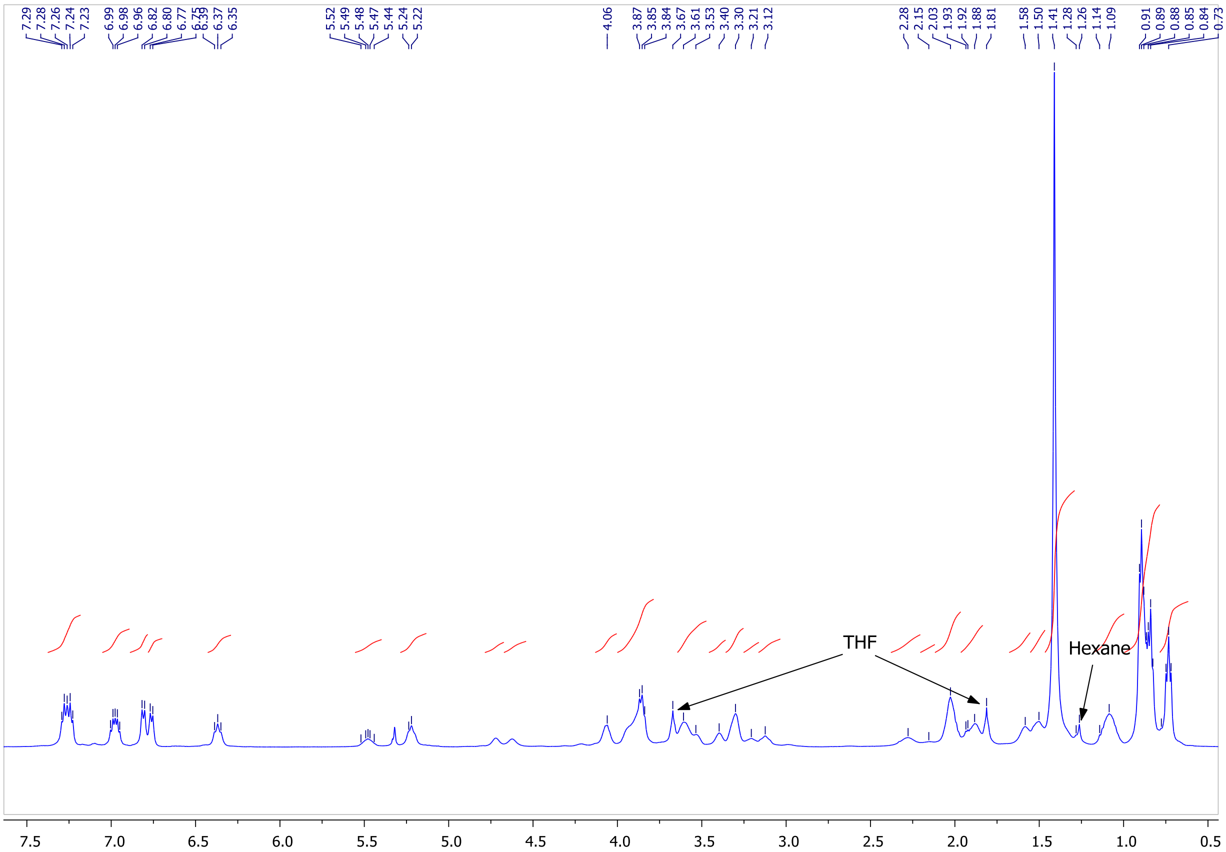


Figure S48b. [Pd(allyl)(**L3g**)$_2$]BF_4, ^{1}H (499.9 MHz, CD_2Cl_2, ambient temperature).

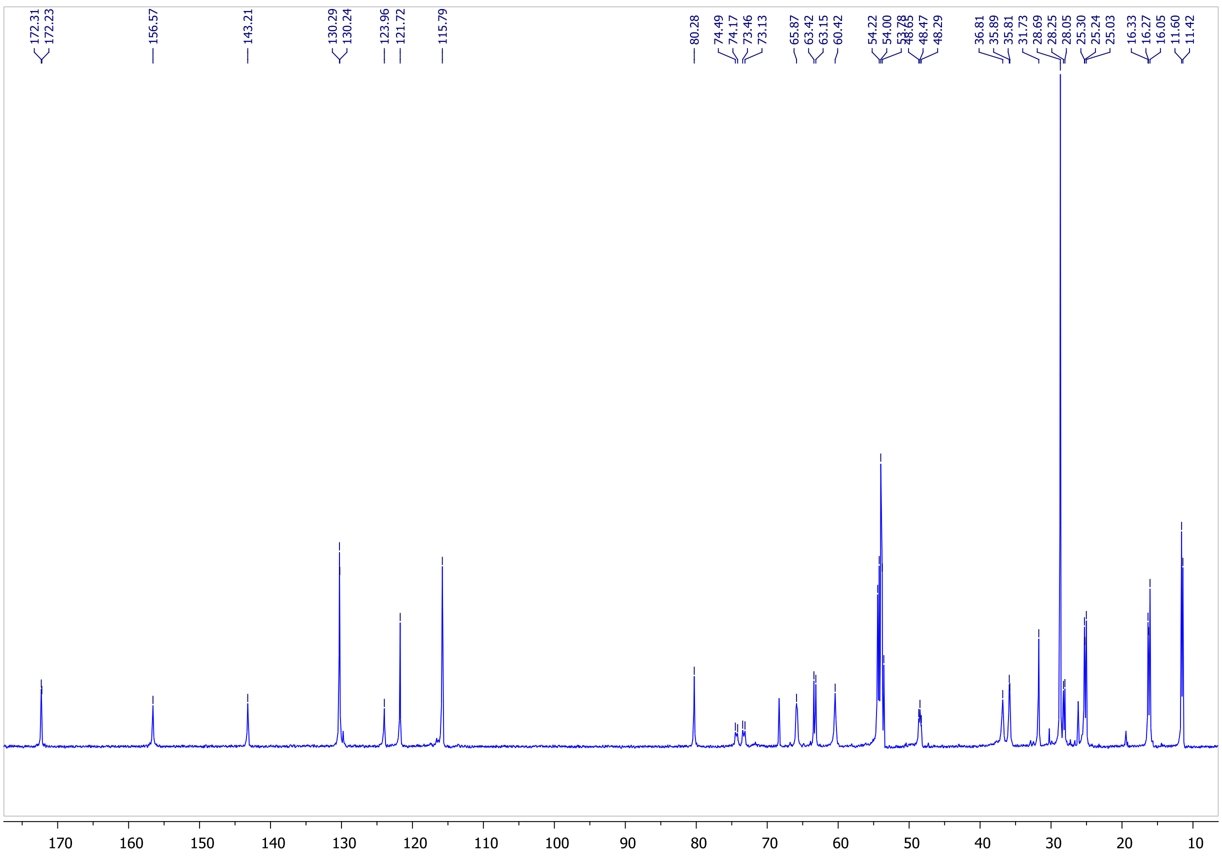


Figure S48c. [Pd(allyl)(**L3g**)$_2$]BF_4, ^{13}C{^{1}H} (125.7 MHz, CD_2Cl_2, ambient temperature).

NMR SPECTRA OF NEW COMPOUNDS

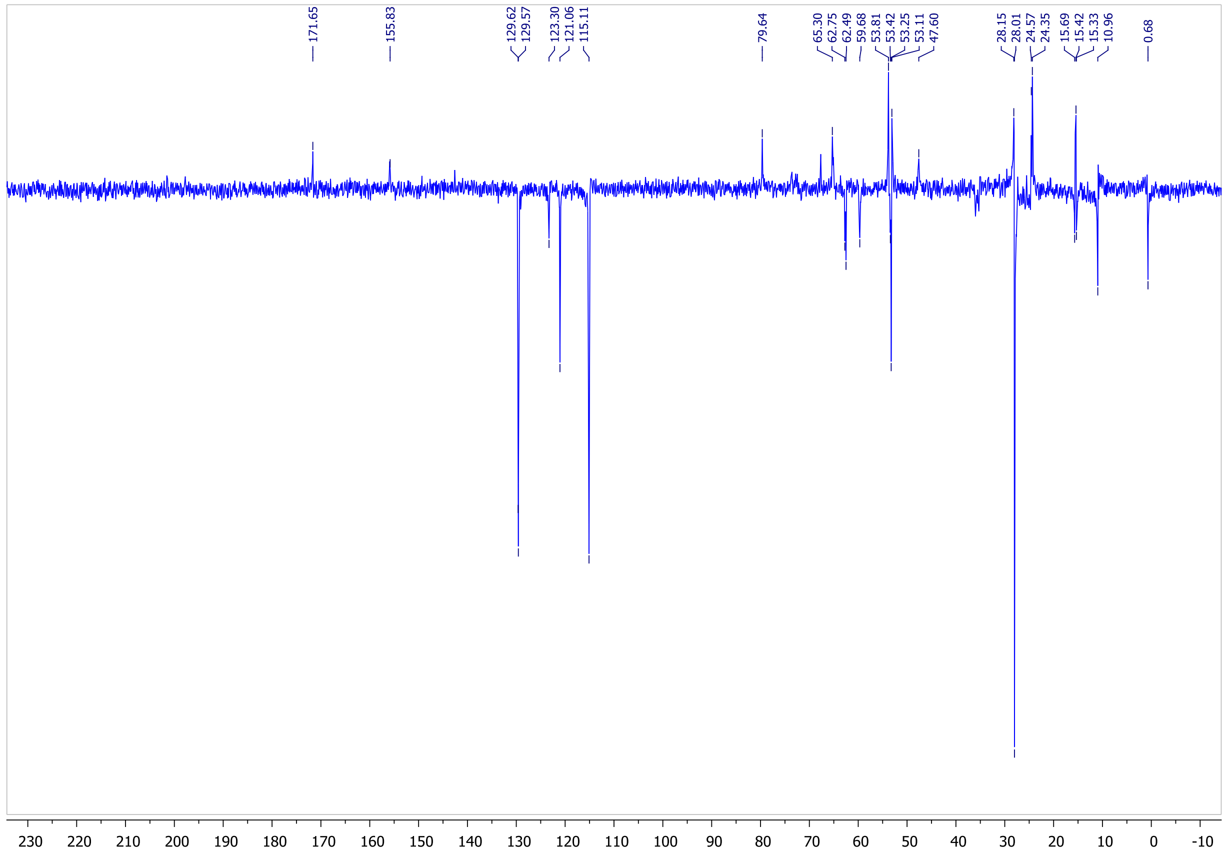


Figure S48d. [Pd(allyl)(**L3g**)$_2$]BF_4, $^{13}C\{^1H\}$ APT (125.7 MHz, CD_2Cl_2, ambient temperature).

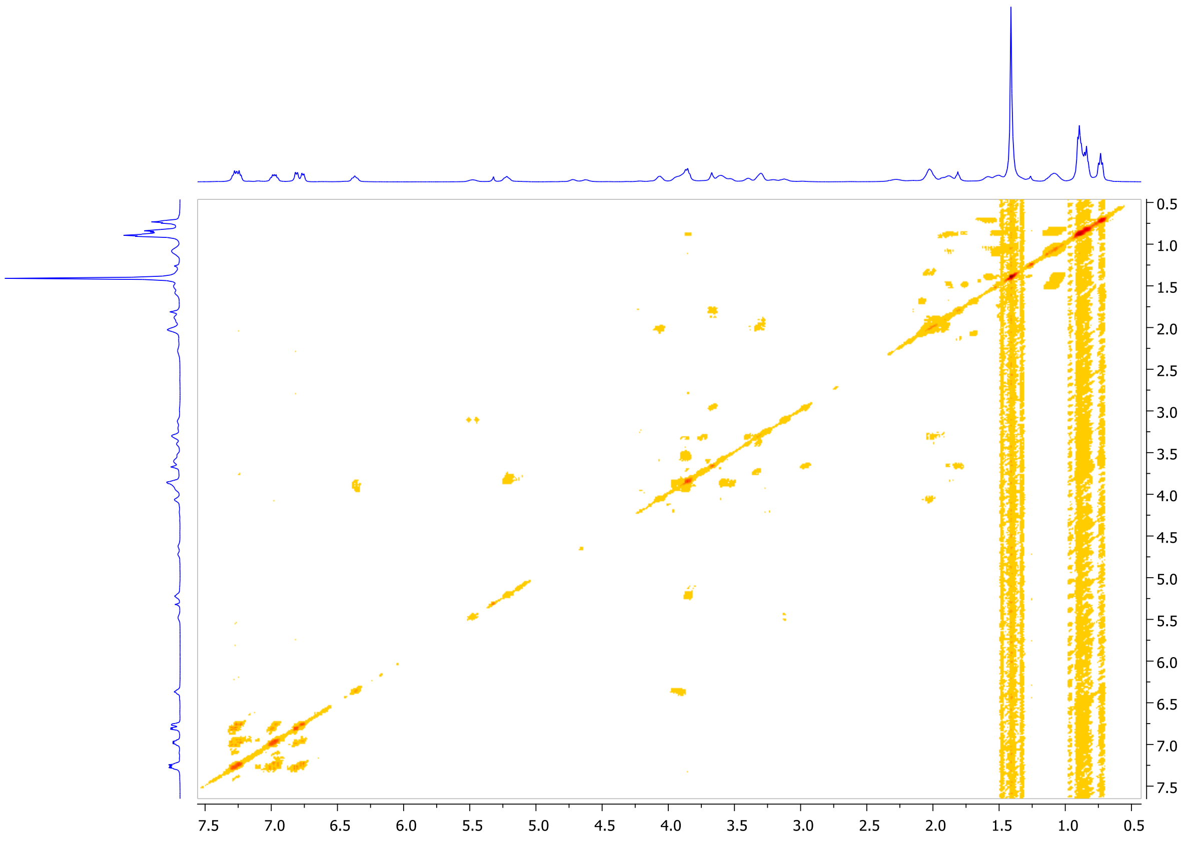


Figure S48e. [Pd(allyl)(**L3g**)$_2$]BF_4, ^1H-^1H COSY.

NMR SPECTRA OF NEW COMPOUNDS

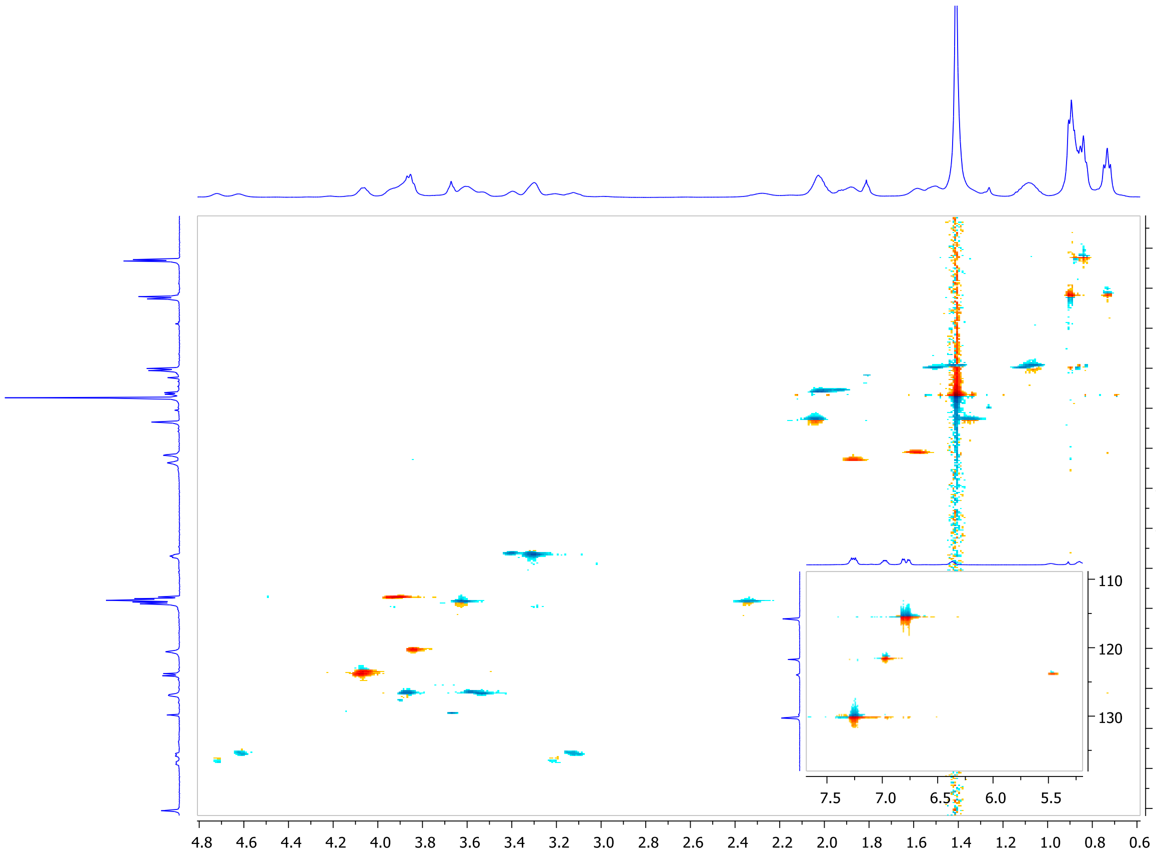


Figure S48f. [Pd(allyl)(**L3g**)$_2$]BF_4, ^{1}H-^{13}C HSQC.

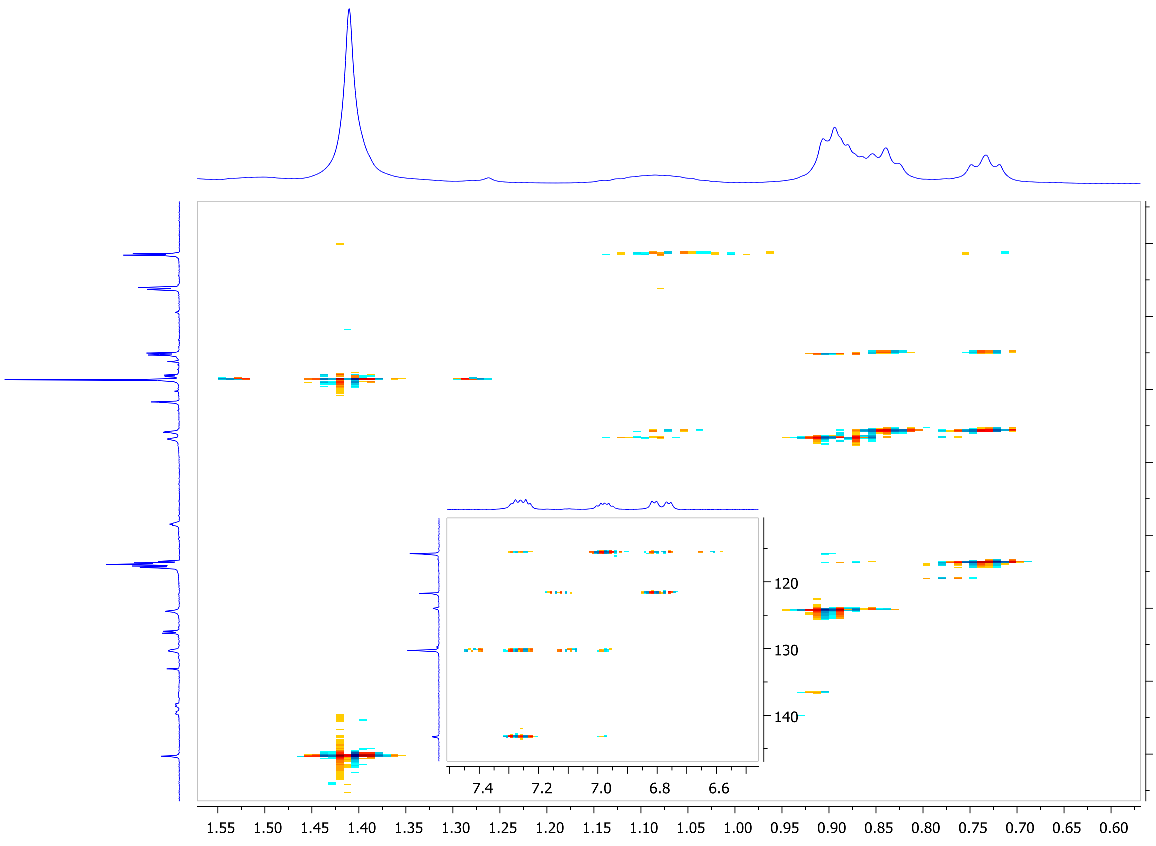


Figure S48g. [Pd(allyl)(**L3g**)$_2$]BF_4, ^{1}H-^{13}C HMBC.

NMR SPECTRA OF NEW COMPOUNDS

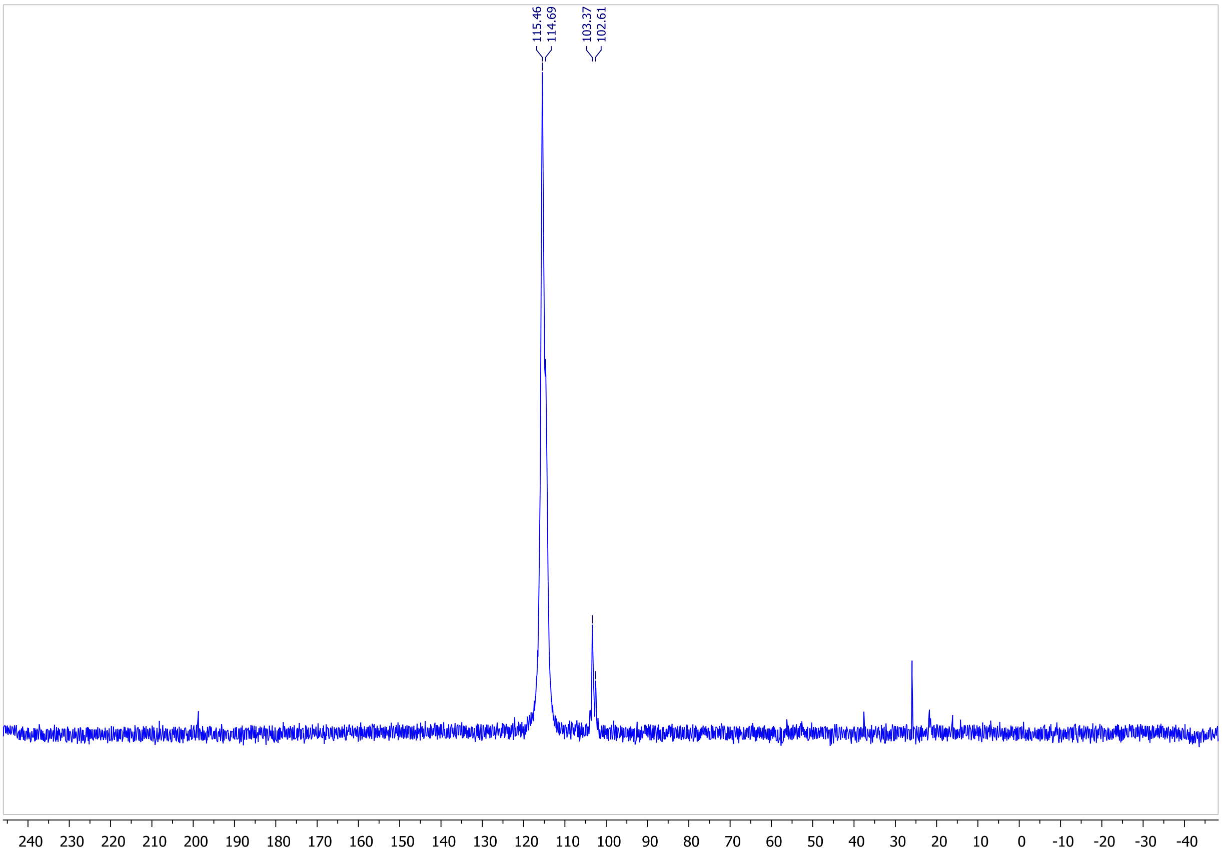


Figure S49a. [Pd(allyl)(**L4**)$_2$]BF_4, $^{31}P\{^1H\}$ (202.4 MHz, CD_2Cl_2, ambient temperature).

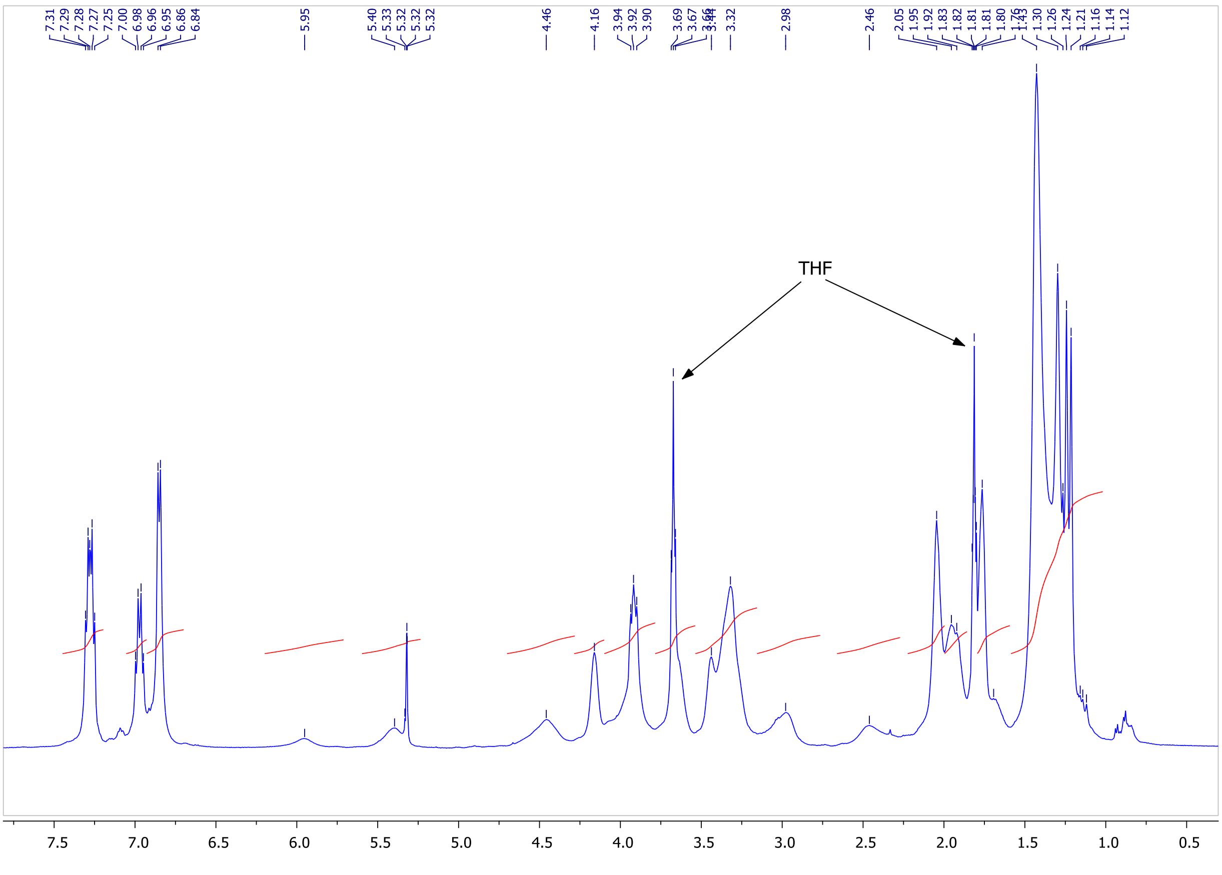


Figure S49b. [Pd(allyl)(**L4**)$_2$]BF_4, ^1H (499.9 MHz, CD_2Cl_2, ambient temperature).

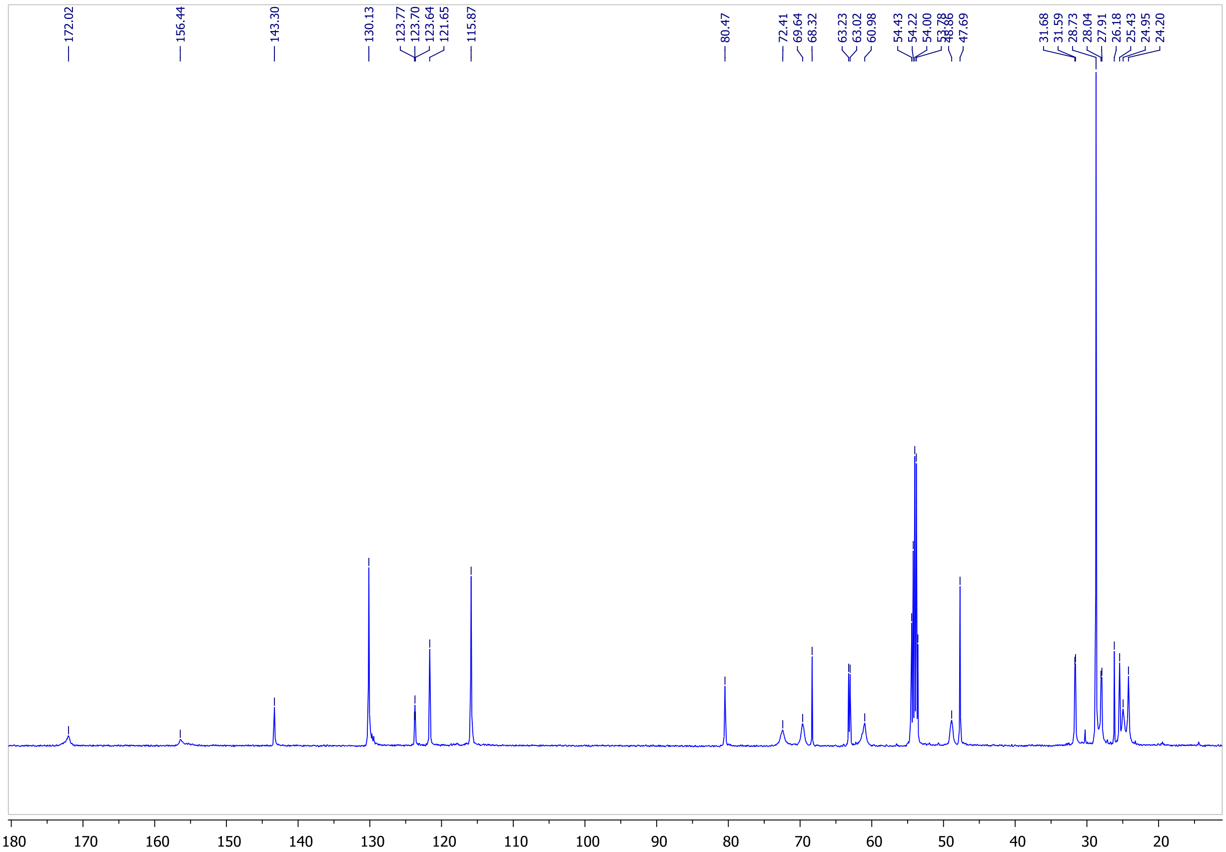


Figure S49c. [Pd(allyl)(**L4**)$_2$]BF_4, $^{13}C\{^1H\}$ (125.7 MHz, CD_2Cl_2, ambient temperature).

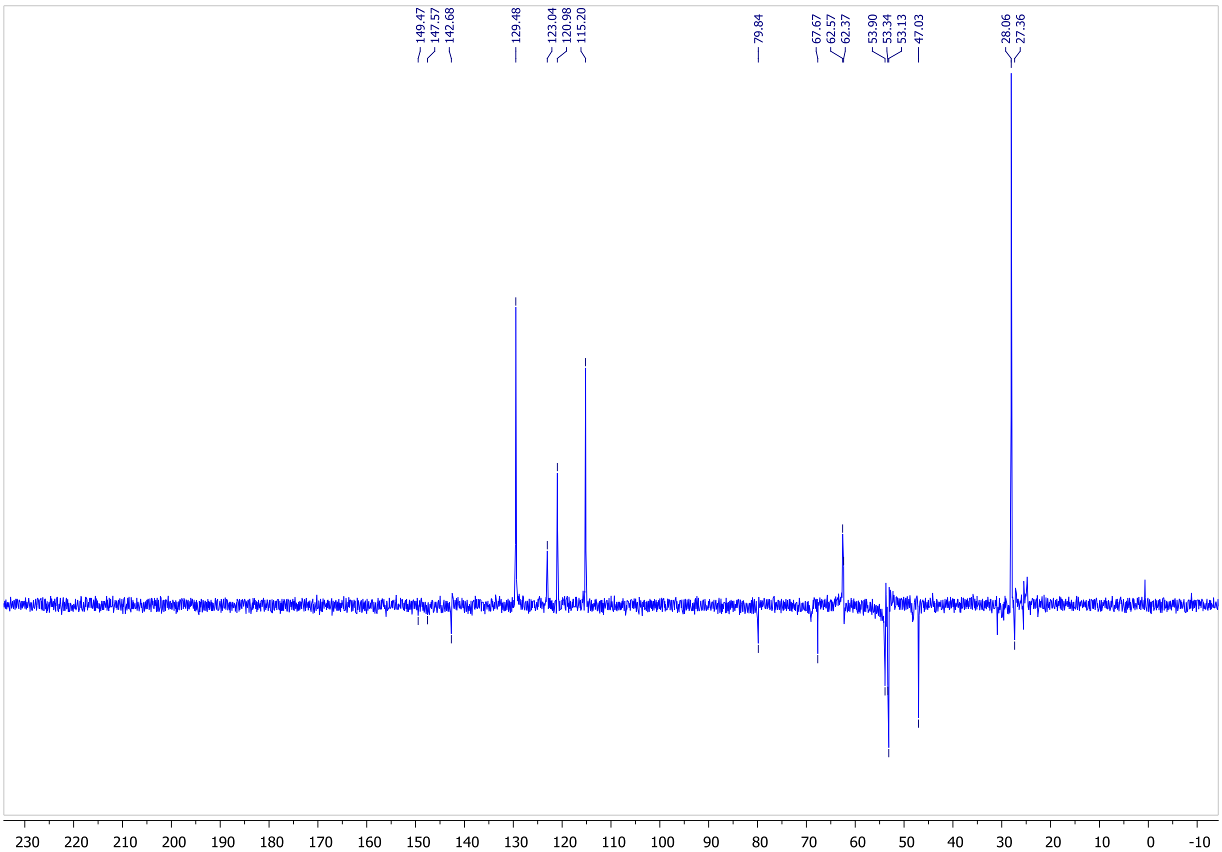


Figure S49d. [Pd(allyl)(**L4**)$_2$]BF_4, $^{13}C\{^1H\}$ APT (125.7 MHz, CD_2Cl_2, ambient temperature).

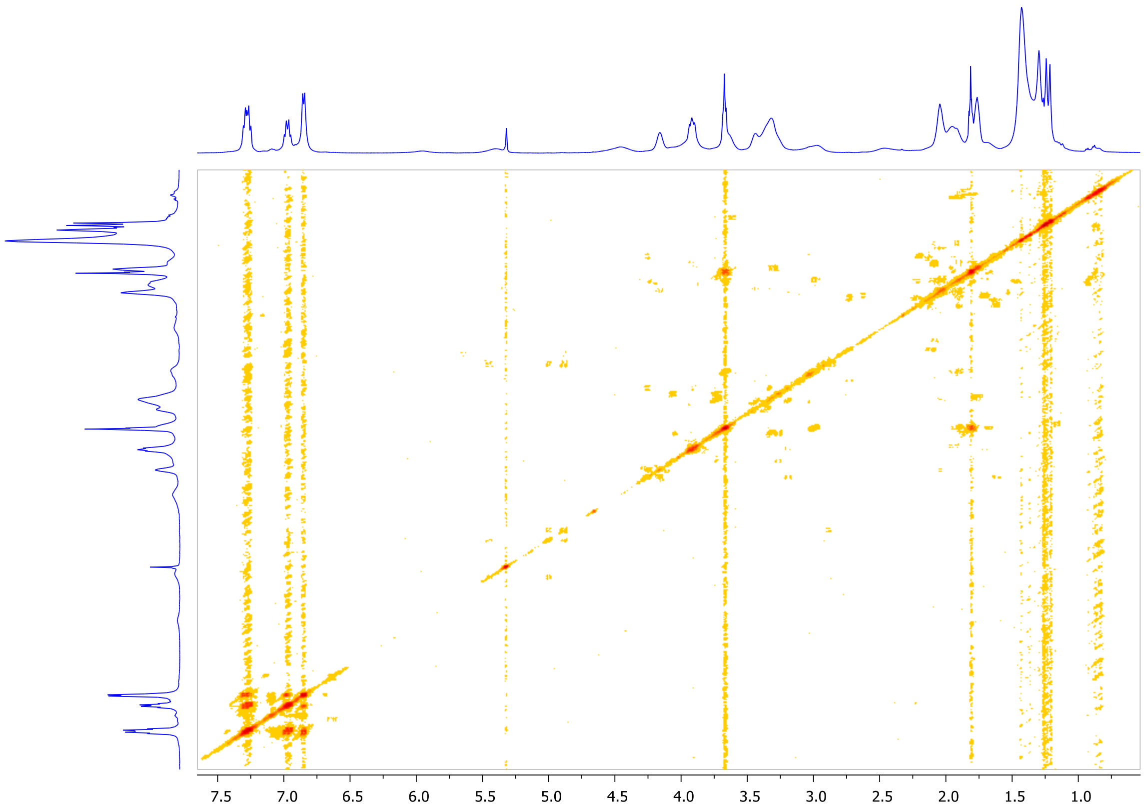


Figure S49e. [Pd(allyl)(**L4**)$_2$]BF_4, ^{1}H-^{1}H COSY.

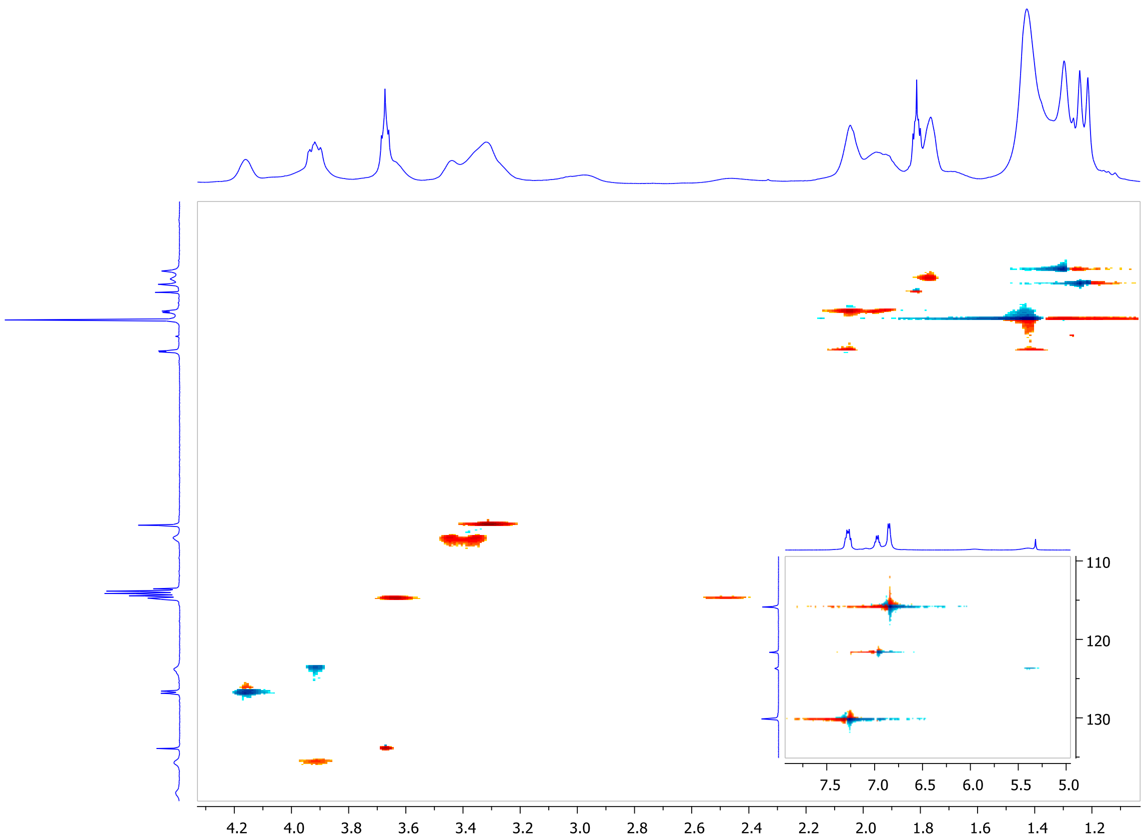


Figure S49f. [Pd(allyl)(**L4**)$_2$]BF_4, ^{1}H-^{13}C HSQC.

NMR SPECTRA OF NEW COMPOUNDS

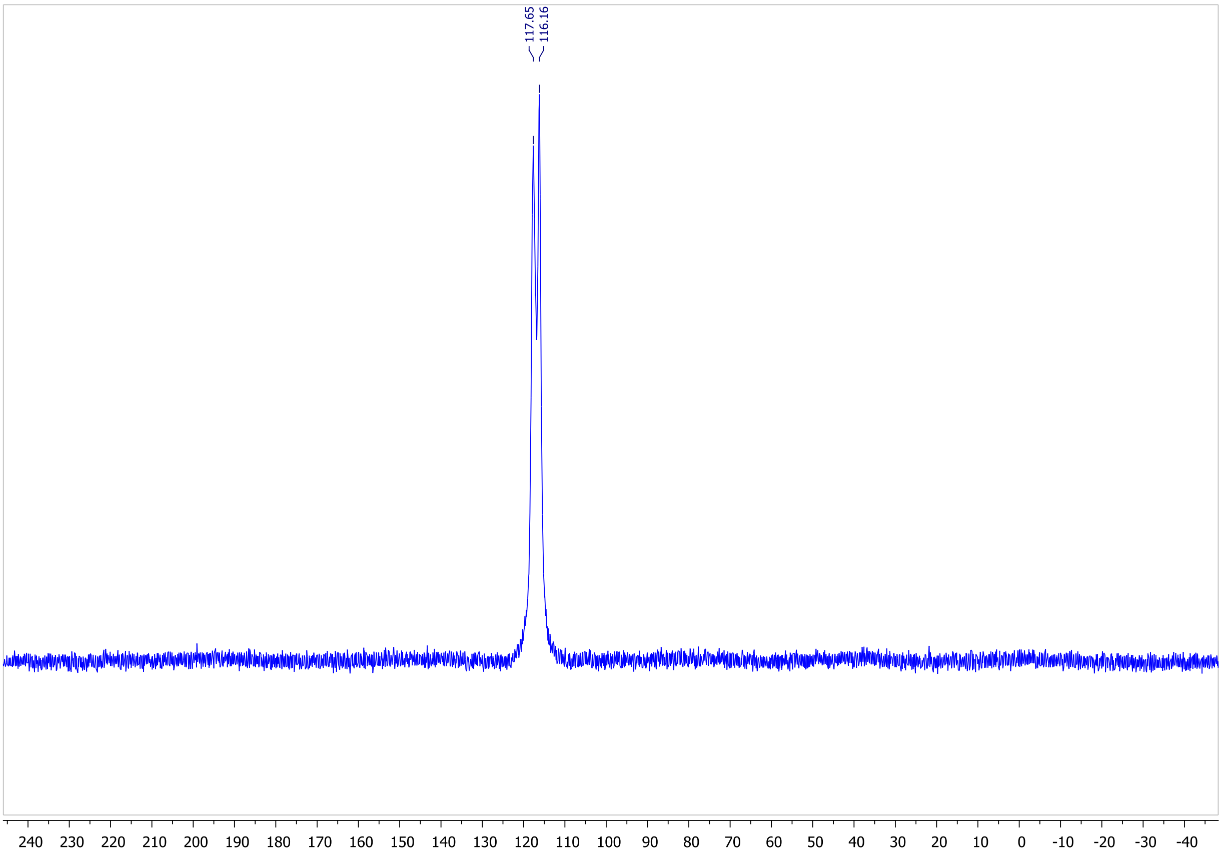


Figure S50a. [Pd(allyl)(**L1d**)]BF_4, $^{31}P\{^1H\}$ (202.4 MHz, CD_2Cl_2, ambient temperature).

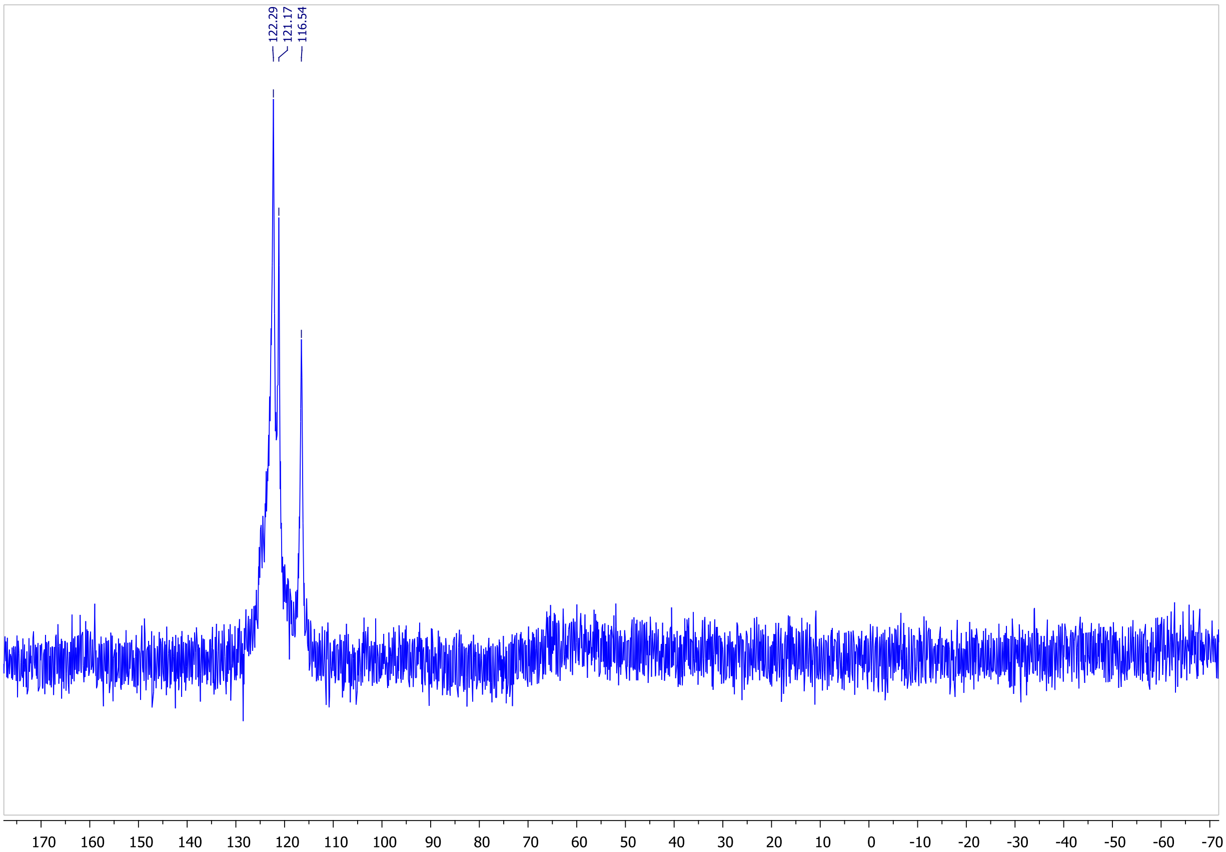


Figure S50b. [Pd(allyl)(**L1d**)]BF_4, $^{31}P\{^1H\}$ (242.9 MHz, CD_2Cl_2, -40 °C).

NMR SPECTRA OF NEW COMPOUNDS

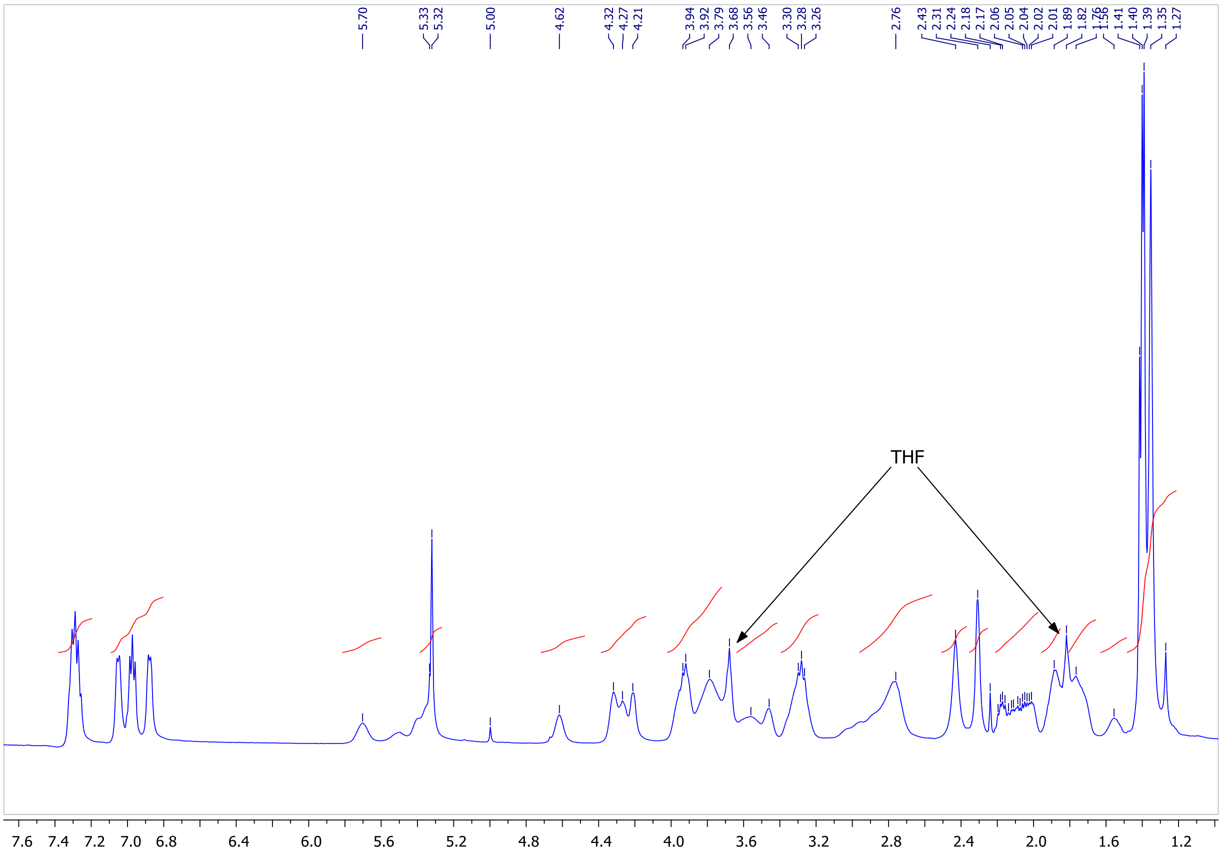


Figure S50c. [Pd(allyl)(**L1d**)]BF_4, ^{1}H (499.9 MHz, CD_2Cl_2, ambient temperature).

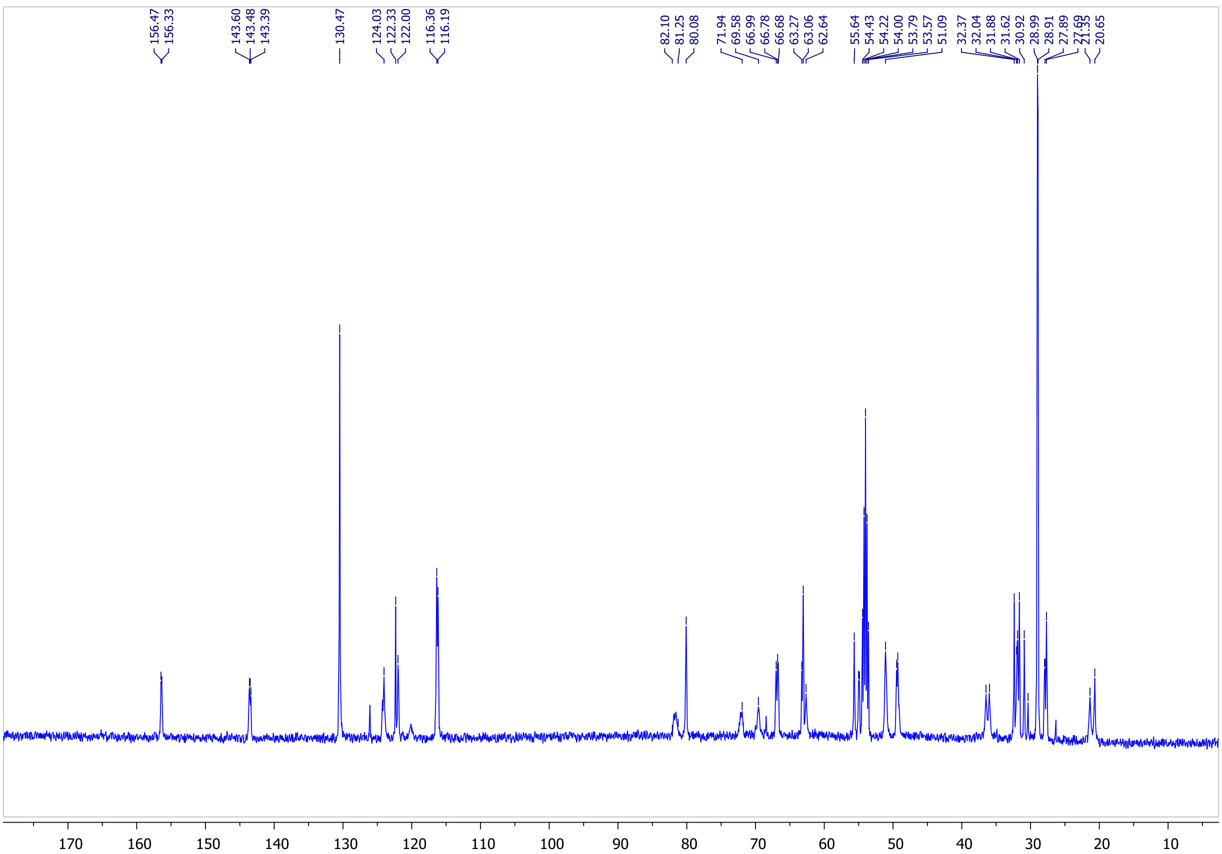


Figure S50d. [Pd(allyl)(**L1d**)]BF_4, $^{13}C\{^{1}H\}$ (125.7 MHz, CD_2Cl_2, ambient temperature).

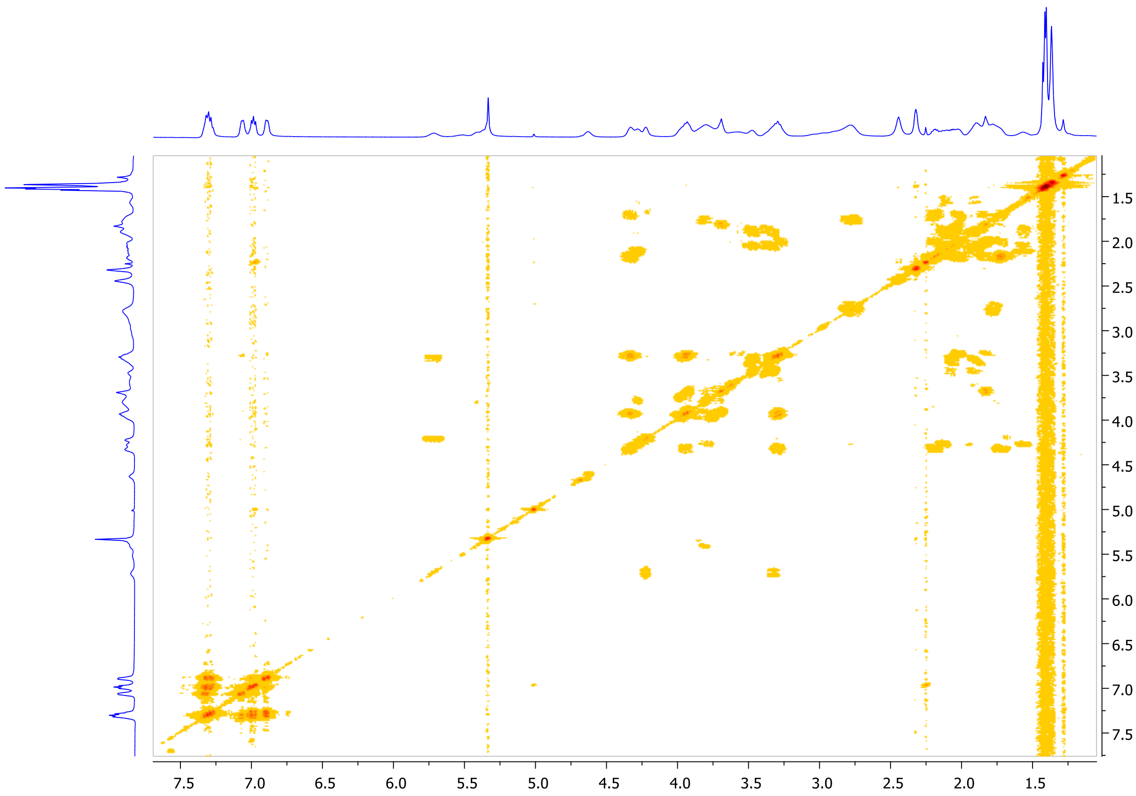


Figure S50e. [Pd(allyl)(**L1d**)]BF_4, ^1H-^1H COSY.

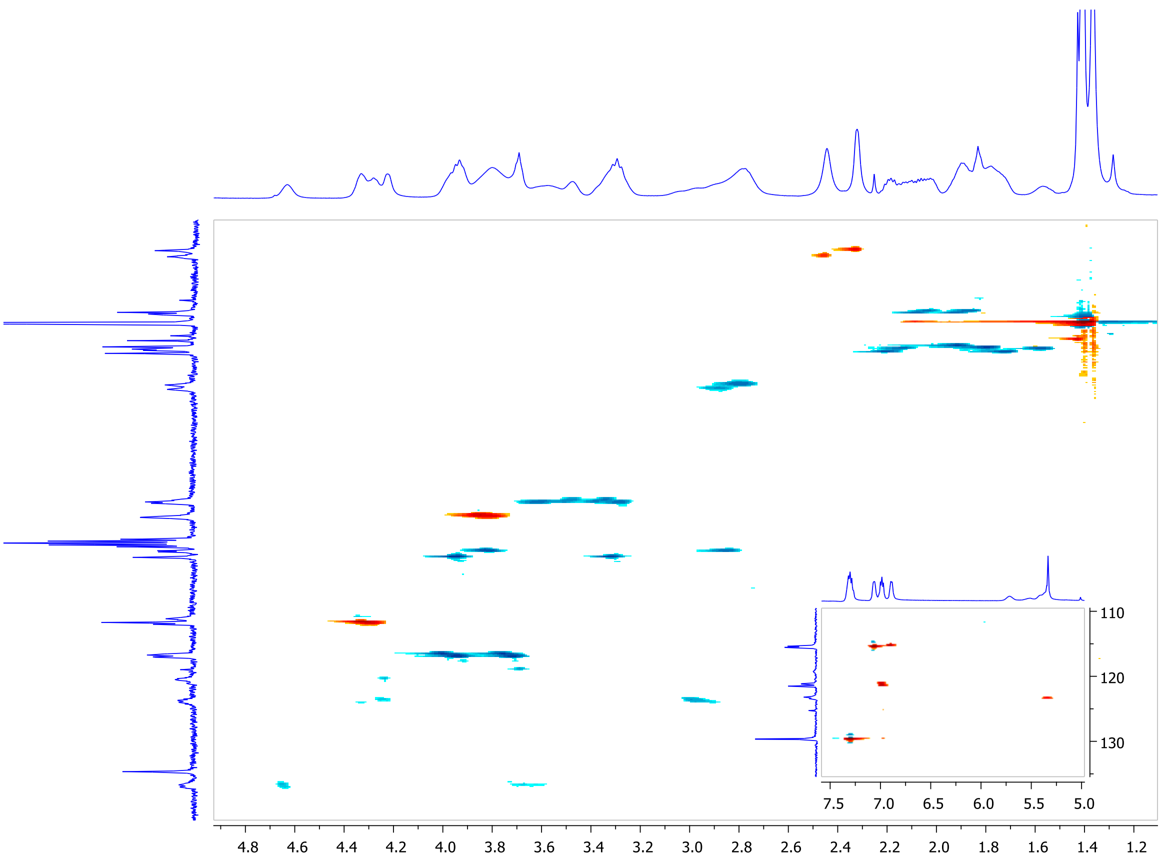


Figure S50f. [Pd(allyl)(**L1d**)]BF_4, ^1H-^{13}C HSQC.

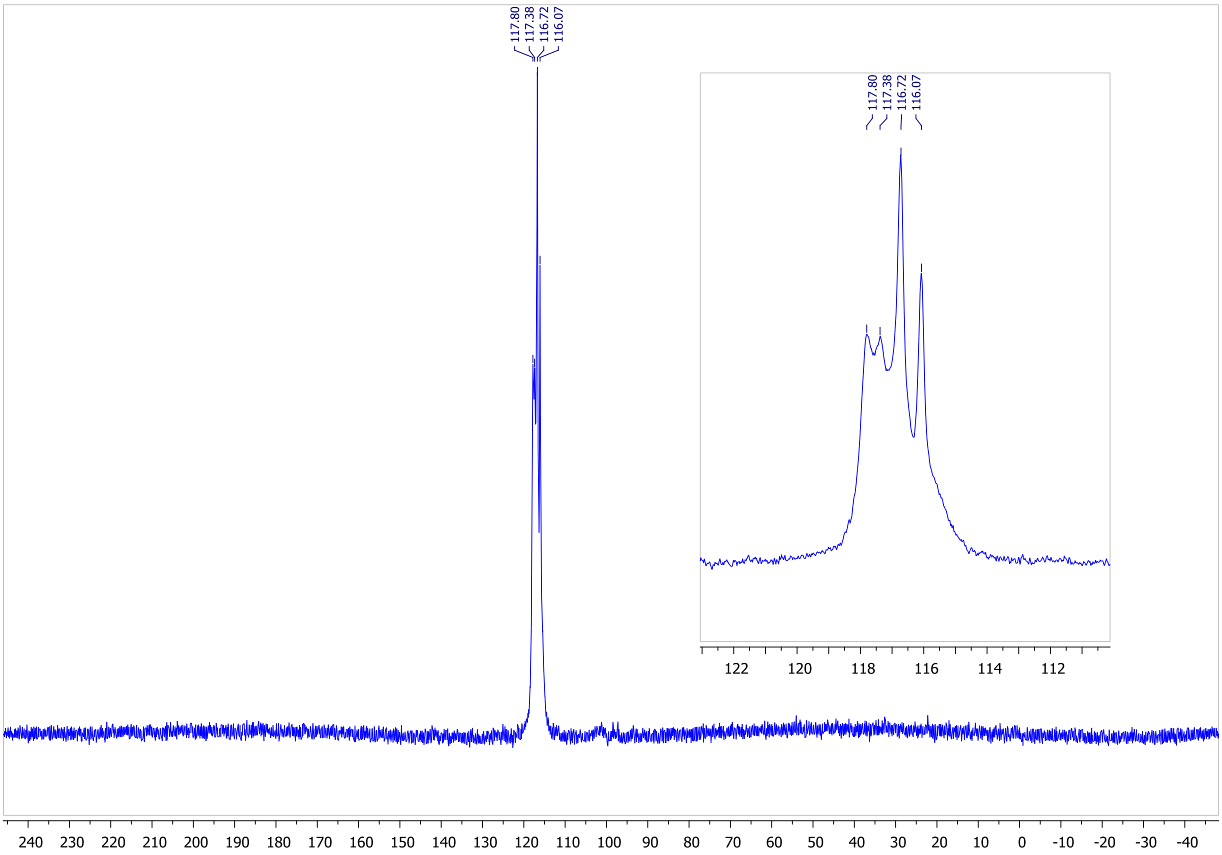


Figure S51a. [Pd(allyl)(**L3f**)]BF_4, $^{31}P\{^1H\}$ (202.4 MHz, CD_2Cl_2, ambient temperature).

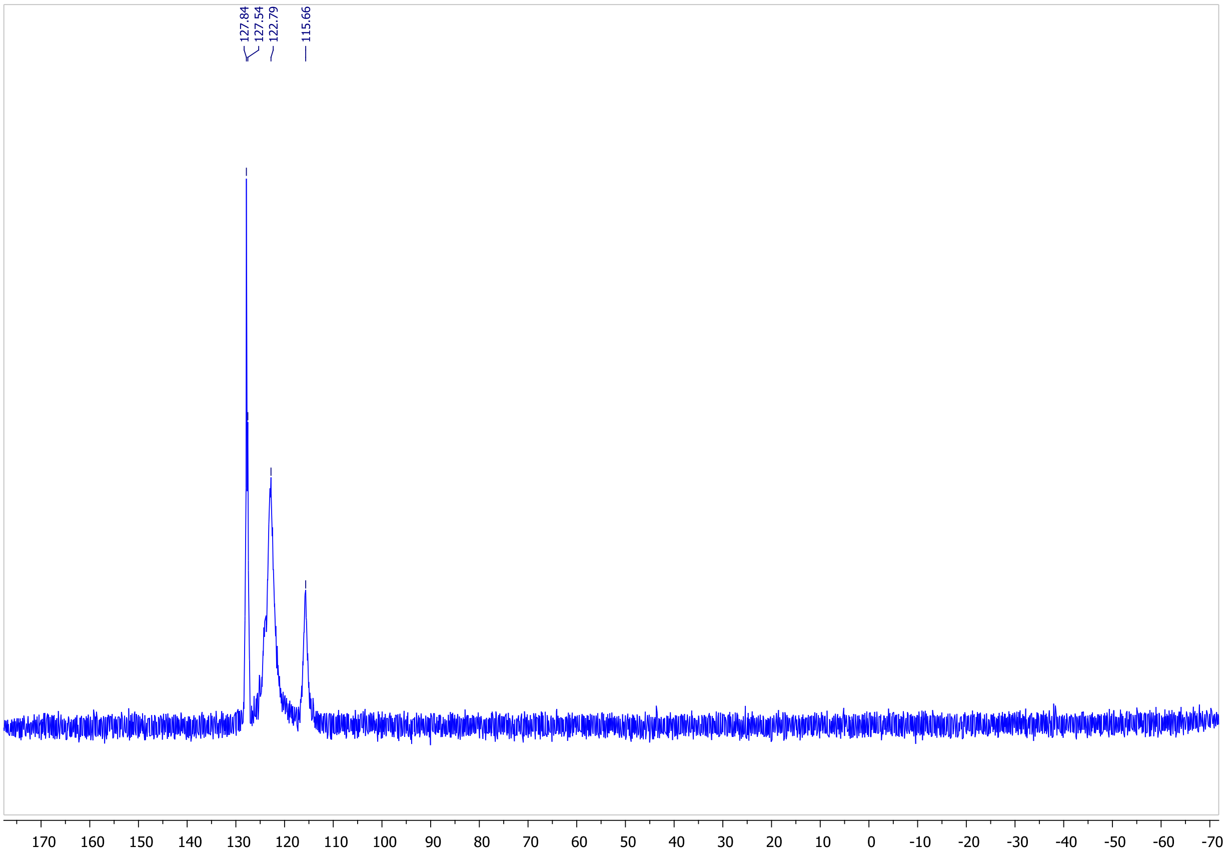


Figure S51b. [Pd(allyl)(**L3f**)]BF_4, $^{31}P\{^1H\}$ (242.9 MHz, CD_2Cl_2, -40 °C).

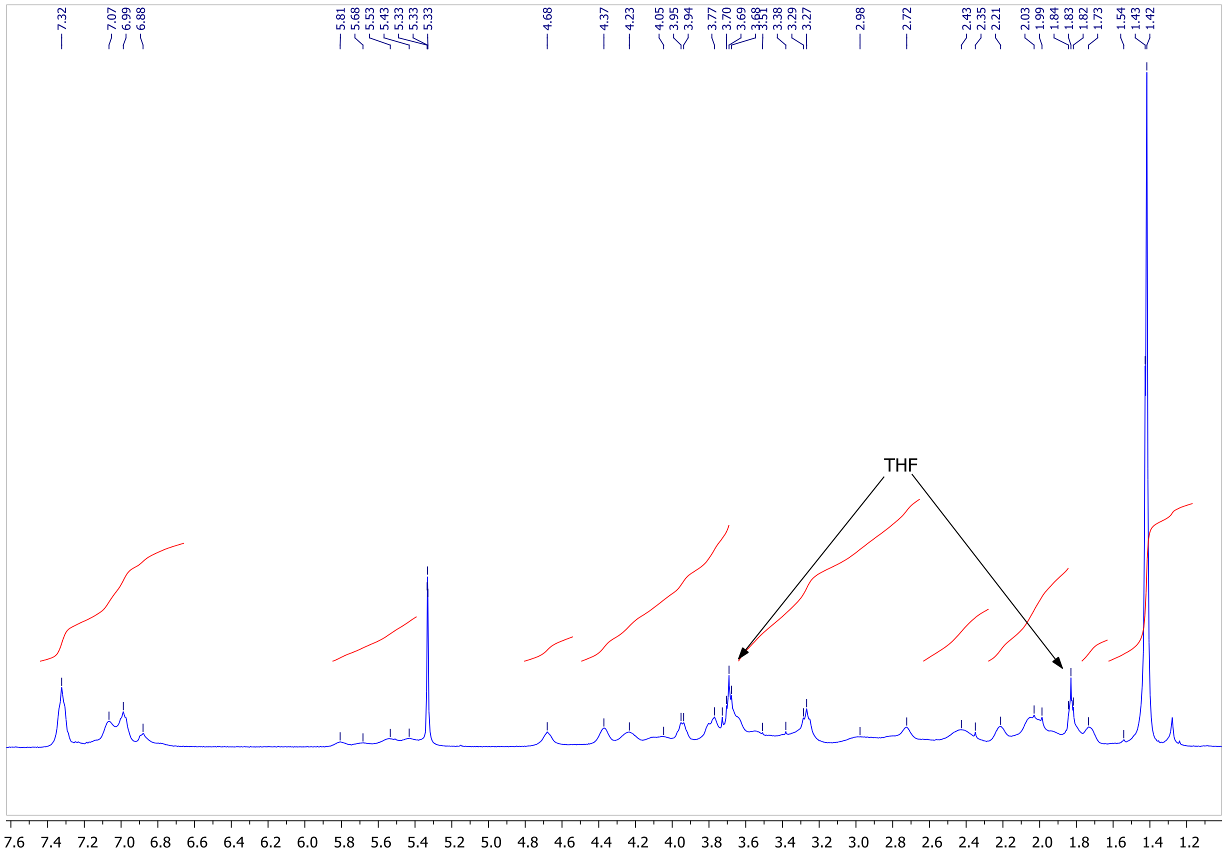


Figure S51c. [Pd(allyl)(**L3f**)]BF_4, ^{1}H (499.9 MHz, CD_2Cl_2, ambient temperature).

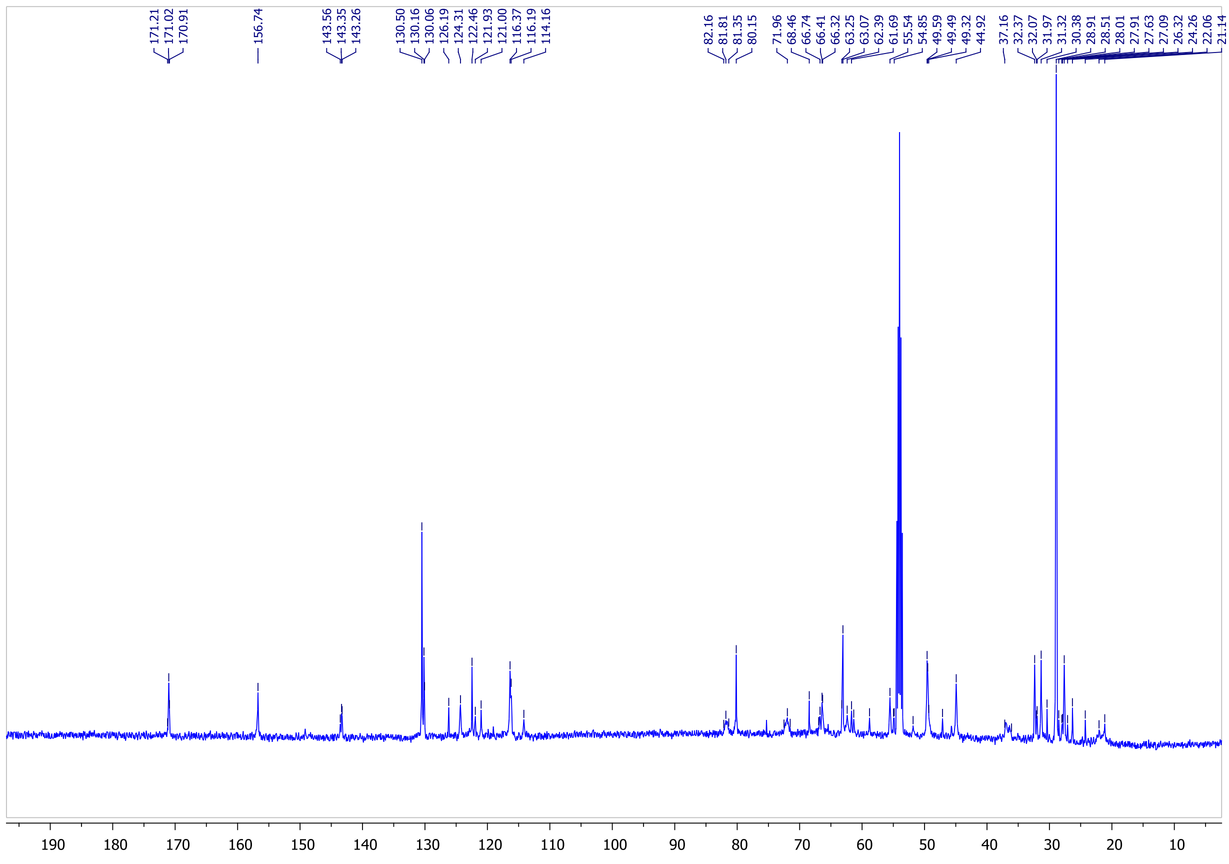


Figure S51d. [Pd(allyl)(**L3f**)]BF_4, $^{13}C\{^{1}H\}$ (125.7 MHz, CD_2Cl_2, ambient temperature).

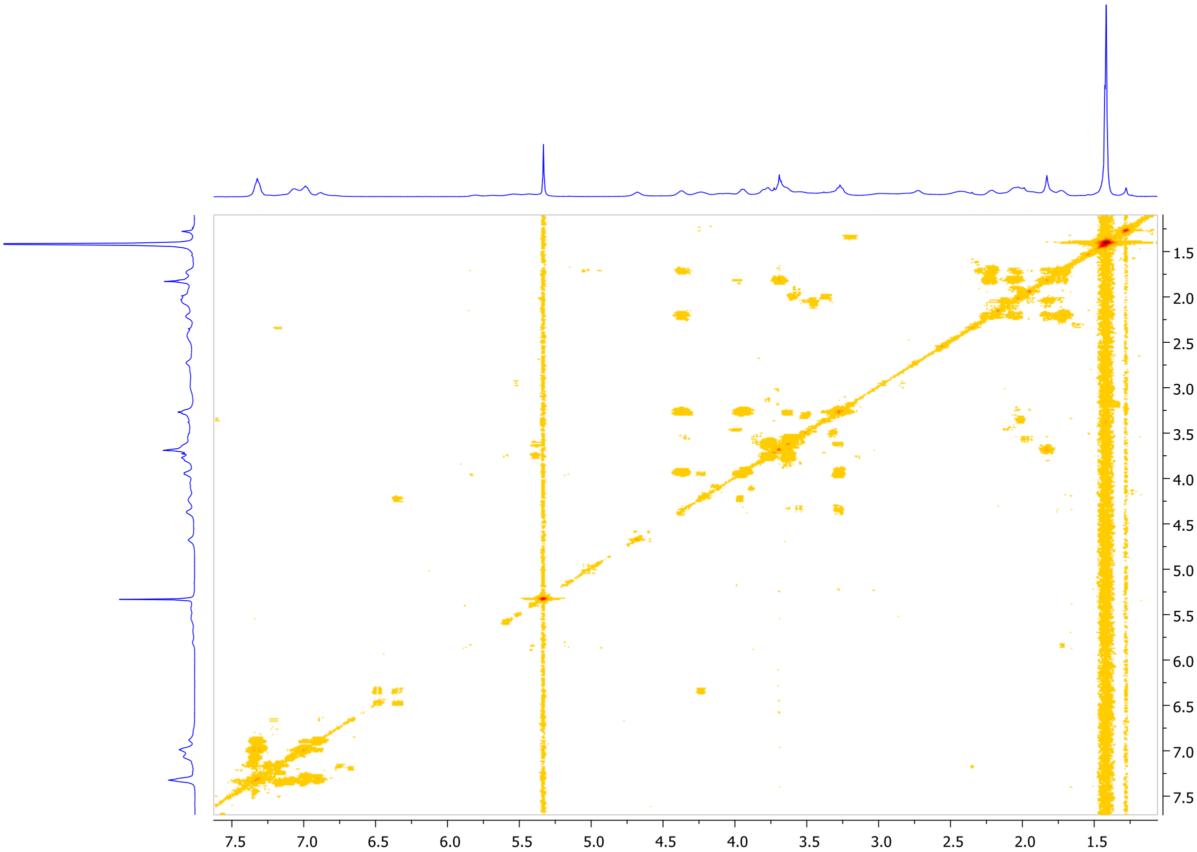


Figure S51e. [Pd(allyl)(**L3f**)]BF_4, ^1H-^1H COSY.

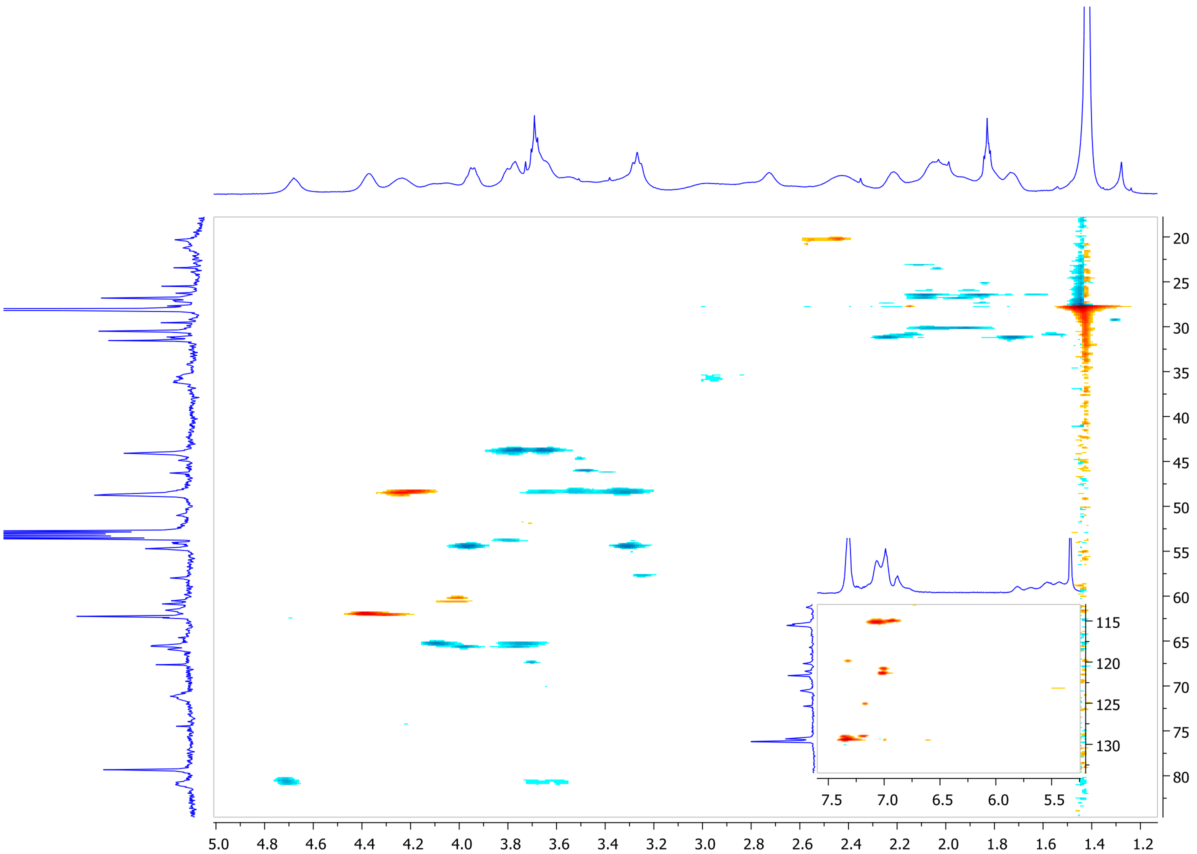


Figure S51f. [Pd(allyl)(**L3f**)]BF_4, ^1H-^{13}C HSQC.

X-RAY STRUCTURE DETERMINATIONS

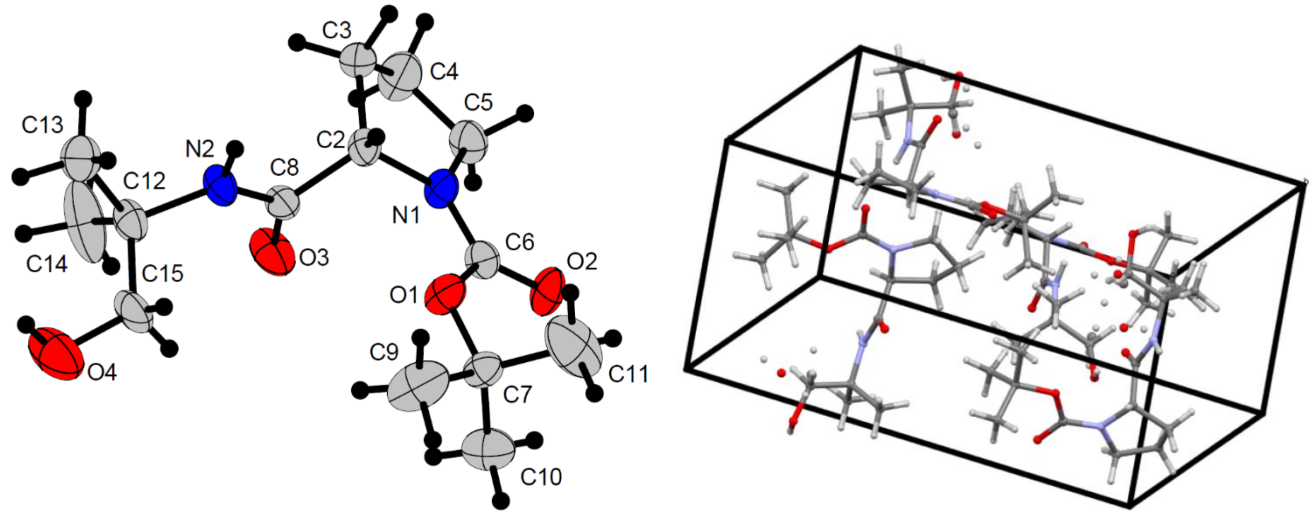


Figure S52. The molecular structure (left) and unit cell (right) of **4**.

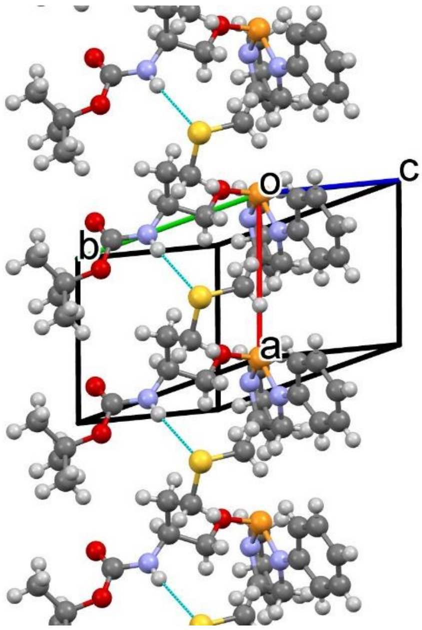


Figure S53. The N---H…S hydrogen-bonded (blue lines) chain of the molecules in the crystal structure of **L1d**

X-RAY STRUCTURE DETERMINATIONS

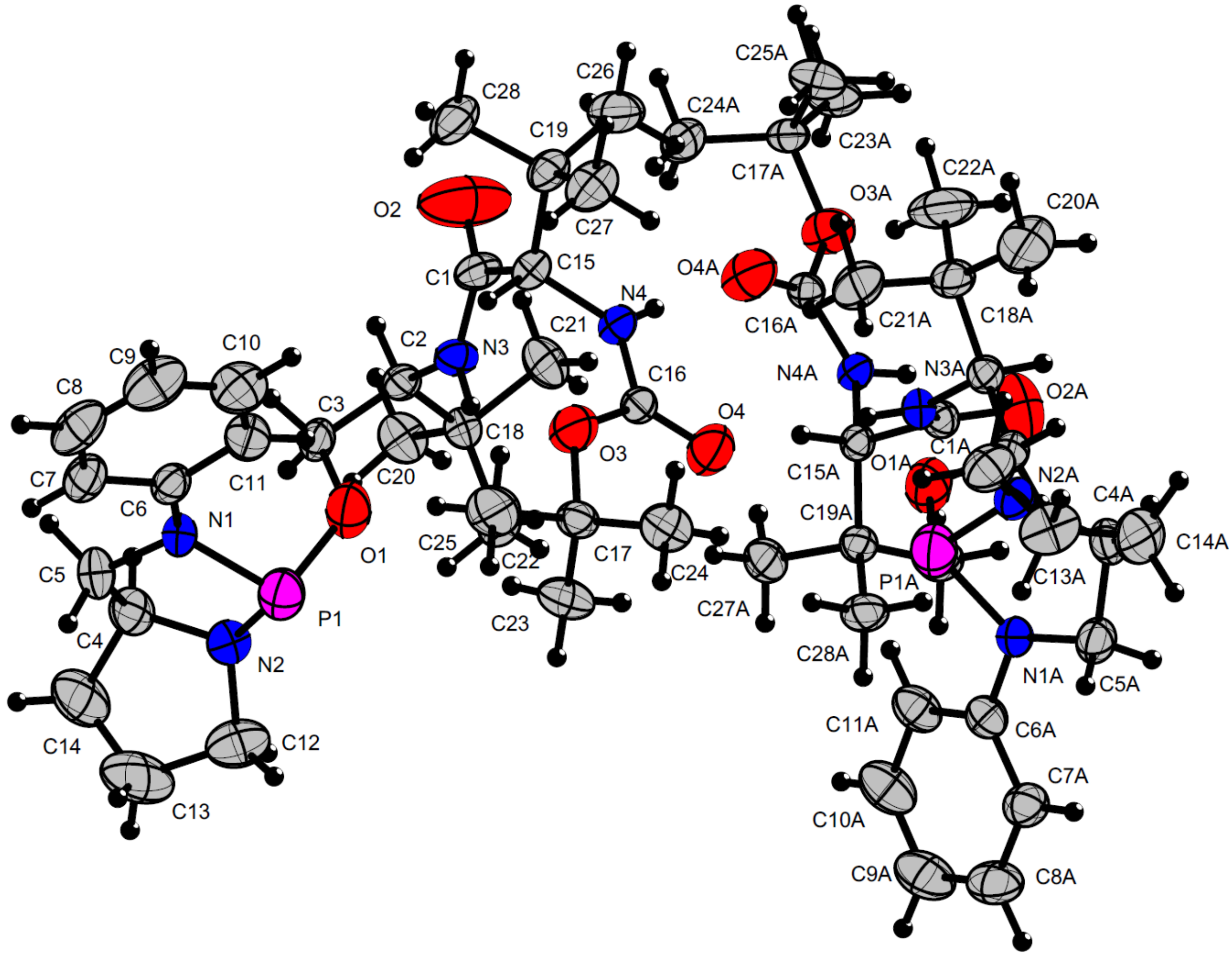


Figure S54. The structure of the supramolecular assembly consisting of two molecules of **L3d** with atomic numbering scheme.

X-RAY STRUCTURE DETERMINATIONS

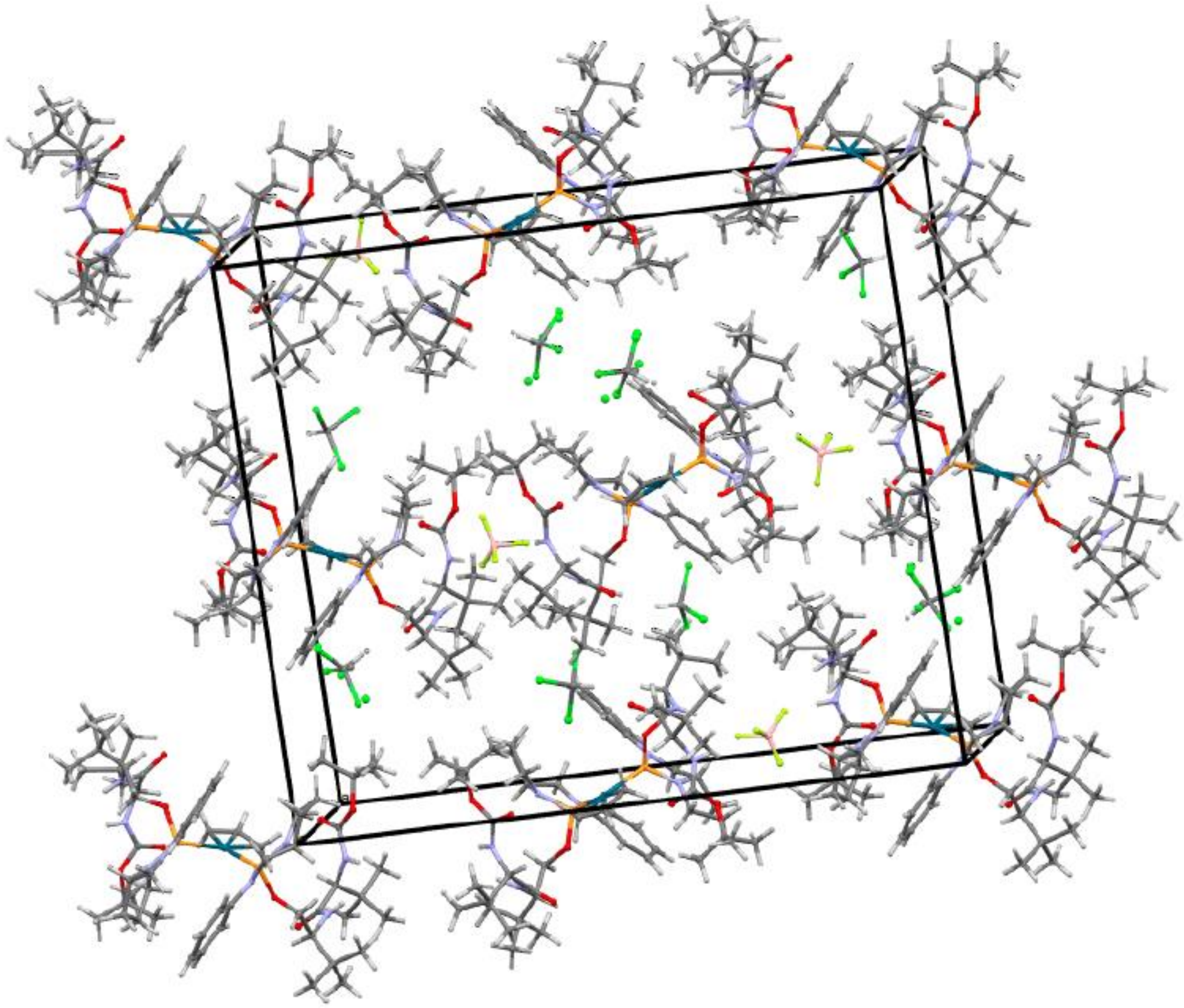


Figure S55. The unit cell of [Pd(allyl)(**L3d**)$_2$]BF_4.

X-RAY STRUCTURE DETERMINATIONS

Table S1. Crystal data and structure refinement for **4**.

Empirical formula	C14 H26 N2 O4	
Formula weight	286.37	
Temperature	293(2) K	
Wavelength	1.54186 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 8.4766(3) Å	α = 90°.
	b = 11.7814(4) Å	β = 90°.
	c = 16.6402(7) Å	γ = 90°.
Volume	1661.79(11) Å^3	
Z	4	
Density (calculated)	1.145 Mg/m^3	
Absorption coefficient	0.683 mm^{-1}	
F(000)	624	
Crystal size	.17 x .14 x .12 mm^3	
Theta range for data collection	4.599 to 66.727°.	
Index ranges	-9<=h<=10, -13<=k<=9, -18<=l<=19	
Reflections collected	10760	
Independent reflections	2902 [R(int) = 0.1237]	
Completeness to theta = 66.727°	99.5 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2902 / 4 / 195	
Goodness-of-fit on F^2	0.819	
Final R indices [I>2sigma(I)]	R1 = 0.0609, wR2 = 0.1269	
R indices (all data)	R1 = 0.1435, wR2 = 0.1479	
Absolute structure parameter	-0.5(5)	
Extinction coefficient	0.0083(9)	
Largest diff. peak and hole	0.247 and -0.318 e.Å^{-3}	

X-RAY STRUCTURE DETERMINATIONS

Table S2. Bond lengths [Å] and angles [°] for **4**.

O(1)-C(6)	1.336(6)	C(11)-H(11B)	0.9600
O(1)-C(7)	1.459(6)	C(11)-H(11C)	0.9600
O(2)-C(6)	1.233(6)	C(13)-C(121)	1.540(8)
O(3)-C(8)	1.223(6)	C(13)-C(12)	1.540(8)
N(1)-C(6)	1.317(6)	C(13)-H(13A)	0.9600
N(1)-C(5)	1.459(6)	C(13)-H(13B)	0.9600
N(1)-C(2)	1.477(6)	C(13)-H(13C)	0.9600
N(2)-C(8)	1.344(6)	C(14)-C(121)	1.515(10)
N(2)-C(121)	1.471(8)	C(14)-C(12)	1.515(10)
N(2)-C(12)	1.471(8)	C(14)-H(14A)	0.9600
N(2)-H(2)	0.8600	C(14)-H(14B)	0.9600
C(2)-C(8)	1.517(8)	C(14)-H(14C)	0.9600
C(2)-C(3)	1.517(8)	C(12)-C(15)	1.511(10)
C(2)-H(2A)	0.9800	C(15)-O(4)	1.358(16)
C(3)-C(4)	1.515(8)	C(15)-H(15A)	0.9700
C(3)-H(3A)	0.9700	C(15)-H(15B)	0.9700
C(3)-H(3B)	0.9700	O(4)-H(4)	0.8200
C(4)-C(5)	1.461(8)	C(121)-C(151)	1.52(3)
C(4)-H(4A)	0.9700	C(151)-O(41)	1.37(3)
C(4)-H(4B)	0.9700	C(151)-H(15C)	0.9700
C(5)-H(5A)	0.9700	C(151)-H(15D)	0.9700
C(5)-H(5B)	0.9700	O(41)-H(41)	0.8200
C(7)-C(9)	1.501(9)	C(6)-O(1)-C(7)	122.1(4)
C(7)-C(10)	1.509(8)	C(6)-N(1)-C(5)	122.1(4)
C(7)-C(11)	1.511(10)	C(6)-N(1)-C(2)	125.5(4)
C(9)-H(9A)	0.9600	C(5)-N(1)-C(2)	112.4(4)
C(9)-H(9B)	0.9600	C(8)-N(2)-C(121)	128.7(5)
C(9)-H(9C)	0.9600	C(8)-N(2)-C(12)	128.7(5)
C(10)-H(10A)	0.9600	C(8)-N(2)-H(2)	115.7
C(10)-H(10B)	0.9600	C(12)-N(2)-H(2)	115.7
C(10)-H(10C)	0.9600	N(1)-C(2)-C(8)	111.6(4)
C(11)-H(11A)	0.9600	N(1)-C(2)-C(3)	101.9(4)

C(8)-C(2)-C(3)	111.7(5)	N(2)-C(8)-C(2)	113.3(5)
N(1)-C(2)-H(2A)	110.4	C(7)-C(9)-H(9A)	109.5
C(8)-C(2)-H(2A)	110.4	C(7)-C(9)-H(9B)	109.5
C(3)-C(2)-H(2A)	110.4	H(9A)-C(9)-H(9B)	109.5
C(4)-C(3)-C(2)	105.6(4)	C(7)-C(9)-H(9C)	109.5
C(4)-C(3)-H(3A)	110.6	H(9A)-C(9)-H(9C)	109.5
C(2)-C(3)-H(3A)	110.6	H(9B)-C(9)-H(9C)	109.5
C(4)-C(3)-H(3B)	110.6	C(7)-C(10)-H(10A)	109.5
C(2)-C(3)-H(3B)	110.6	C(7)-C(10)-H(10B)	109.5
H(3A)-C(3)-H(3B)	108.7	H(10A)-C(10)-H(10B)	109.5
C(5)-C(4)-C(3)	105.3(5)	C(7)-C(10)-H(10C)	109.5
C(5)-C(4)-H(4A)	110.7	H(10A)-C(10)-H(10C)	109.5
C(3)-C(4)-H(4A)	110.7	H(10B)-C(10)-H(10C)	109.5
C(5)-C(4)-H(4B)	110.7	C(7)-C(11)-H(11A)	109.5
C(3)-C(4)-H(4B)	110.7	C(7)-C(11)-H(11B)	109.5
H(4A)-C(4)-H(4B)	108.8	H(11A)-C(11)-H(11B)	109.5
N(1)-C(5)-C(4)	105.3(4)	C(7)-C(11)-H(11C)	109.5
N(1)-C(5)-H(5A)	110.7	H(11A)-C(11)-H(11C)	109.5
C(4)-C(5)-H(5A)	110.7	H(11B)-C(11)-H(11C)	109.5
N(1)-C(5)-H(5B)	110.7	C(12)-C(13)-H(13A)	109.5
C(4)-C(5)-H(5B)	110.7	C(12)-C(13)-H(13B)	109.5
H(5A)-C(5)-H(5B)	108.8	H(13A)-C(13)-H(13B)	109.5
O(2)-C(6)-N(1)	123.7(5)	C(12)-C(13)-H(13C)	109.5
O(2)-C(6)-O(1)	123.7(5)	H(13A)-C(13)-H(13C)	109.5
N(1)-C(6)-O(1)	112.6(5)	H(13B)-C(13)-H(13C)	109.5
O(1)-C(7)-C(9)	102.8(5)	C(12)-C(14)-H(14A)	109.5
O(1)-C(7)-C(10)	110.8(5)	C(12)-C(14)-H(14B)	109.5
C(9)-C(7)-C(10)	110.4(6)	H(14A)-C(14)-H(14B)	109.5
O(1)-C(7)-C(11)	110.0(5)	C(12)-C(14)-H(14C)	109.5
C(9)-C(7)-C(11)	112.4(7)	H(14A)-C(14)-H(14C)	109.5
C(10)-C(7)-C(11)	110.2(6)	H(14B)-C(14)-H(14C)	109.5
O(3)-C(8)-N(2)	124.5(5)	N(2)-C(12)-C(15)	108.8(7)
O(3)-C(8)-C(2)	121.9(5)	N(2)-C(12)-C(14)	111.8(5)

C(15)-C(12)-C(14)	111.7(8)
N(2)-C(12)-C(13)	105.7(5)
C(15)-C(12)-C(13)	108.7(6)
C(14)-C(12)-C(13)	109.8(6)
O(4)-C(15)-C(12)	117.6(9)
O(4)-C(15)-H(15A)	107.9
C(12)-C(15)-H(15A)	107.9
O(4)-C(15)-H(15B)	107.9
C(12)-C(15)-H(15B)	107.9
H(15A)-C(15)-H(15B)	107.2
C(15)-O(4)-H(4)	109.5
N(2)-C(121)-C(14)	111.8(5)
N(2)-C(121)-C(151)	95(4)
C(14)-C(121)-C(151)	118(3)
N(2)-C(121)-C(13)	105.7(5)
C(14)-C(121)-C(13)	109.8(6)
C(151)-C(121)-C(13)	114.2(18)
O(41)-C(151)-C(121)	113(3)
O(41)-C(151)-H(15C)	109.0
C(121)-C(151)-H(15C)	109.0
O(41)-C(151)-H(15D)	109.0
C(121)-C(151)-H(15D)	109.0
H(15C)-C(151)-H(15D)	107.8
C(151)-O(41)-H(41)	109.5

Table S3. Torsion angles [°] for **4**.

C(6)-N(1)-C(2)-C(8)	-71.6(7)
C(5)-N(1)-C(2)-C(8)	108.1(6)
C(6)-N(1)-C(2)-C(3)	169.0(5)
C(5)-N(1)-C(2)-C(3)	-11.3(6)
N(1)-C(2)-C(3)-C(4)	25.7(7)
C(8)-C(2)-C(3)-C(4)	-93.6(6)
C(2)-C(3)-C(4)-C(5)	-31.8(8)
C(6)-N(1)-C(5)-C(4)	171.6(6)
C(2)-N(1)-C(5)-C(4)	-8.1(7)
C(3)-C(4)-C(5)-N(1)	24.2(7)
C(5)-N(1)-C(6)-O(2)	2.0(9)
C(2)-N(1)-C(6)-O(2)	-178.3(5)
C(5)-N(1)-C(6)-O(1)	-177.7(5)
C(2)-N(1)-C(6)-O(1)	2.0(8)
C(7)-O(1)-C(6)-O(2)	4.7(9)
C(7)-O(1)-C(6)-N(1)	-175.7(5)
C(6)-O(1)-C(7)-C(9)	-178.3(6)
C(6)-O(1)-C(7)-C(10)	-60.3(7)
C(6)-O(1)-C(7)-C(11)	61.9(8)
C(121)-N(2)-C(8)-O(3)	0.5(9)
C(12)-N(2)-C(8)-O(3)	0.5(9)
C(121)-N(2)-C(8)-C(2)	174.8(5)
C(12)-N(2)-C(8)-C(2)	174.8(5)
N(1)-C(2)-C(8)-O(3)	-27.3(8)

C(3)-C(2)-C(8)-O(3)	86.1(7)
N(1)-C(2)-C(8)-N(2)	158.3(4)
C(3)-C(2)-C(8)-N(2)	-88.4(6)
C(8)-N(2)-C(12)-C(15)	80.4(8)
C(8)-N(2)-C(12)-C(14)	-43.4(9)
C(8)-N(2)-C(12)-C(13)	-163.0(6)
N(2)-C(12)-C(15)-O(4)	177.3(8)
C(14)-C(12)-C(15)-O(4)	-58.7(11)
C(13)-C(12)-C(15)-O(4)	62.6(11)
C(8)-N(2)-C(121)-C(14)	-43.4(9)
C(8)-N(2)-C(121)-C(151)	80.1(19)
C(8)-N(2)-C(121)-C(13)	-163.0(6)
N(2)-C(121)-C(151)-O(41)	94(7)
C(14)-C(121)-C(151)-O(41)	-147(5)
C(13)-C(121)-C(151)-O(41)	-15(9)

X-RAY STRUCTURE DETERMINATIONS

Table S4. Hydrogen bonds for **4** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2)...O(2)#1	0.86	2.04	2.892(6)	173.7
C(2)-H(2A)...O(2)#1	0.98	2.65	3.329(6)	126.8
C(10)-H(10C)...O(2)	0.96	2.40	2.927(8)	114.3
C(11)-H(11A)...O(2)	0.96	2.45	3.009(9)	116.8
C(14)-H(14C)...O(3)	0.96	2.46	2.950(10)	111.1
O(4)-H(4)...O(3)#2	0.82	2.04	2.808(6)	155.5

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,y+1/2,-z+1/2 #2 -x+1,y+1/2,-z+1/2

X-RAY STRUCTURE DETERMINATIONS

Table S5. Crystal data and structure refinement for **L3d**.

Empirical formula	C28 H47 N4 O4 P	
Formula weight	534.66	
Temperature	295(2) K	
Wavelength	1.54186 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 11.6047(3) Å	α = 90°.
	b = 17.8713(4) Å	β = 90°.
	c = 29.6253(6) Å	γ = 90°.
Volume	6144.0(2) $Å^3$	
Z	8	
Density (calculated)	1.156 Mg/m^3	
Absorption coefficient	1.085 mm^{-1}	
F(000)	2320	
Crystal size	.23 x .18 x .16 mm^3	
Theta range for data collection	3.876 to 74.045°.	
Index ranges	-13<=h<=14, -17<=k<=22, -36<=l<=31	
Reflections collected	108123	
Independent reflections	12078 [R(int) = 0.0404]	
Completeness to theta = 67.686°	100.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12078 / 0 / 692	
Goodness-of-fit on F^2	0.945	
Final R indices [I>2sigma(I)]	R1 = 0.0388, wR2 = 0.0932	
R indices (all data)	R1 = 0.0497, wR2 = 0.0976	
Absolute structure parameter	-0.002(5)	
Extinction coefficient	0.00050(7)	
Largest diff. peak and hole	0.418 and -0.249 e.$Å^{-3}$	

X-RAY STRUCTURE DETERMINATIONS

Table S6. Bond lengths [Å] and angles [°] for **L3d**.

P(1)-O(1)	1.618(2)	C(7)-H(7)	0.9300
P(1)-N(2)	1.662(3)	C(8)-C(9)	1.345(7)
P(1)-N(1)	1.715(2)	C(8)-H(8)	0.9300
O(1)-C(3)	1.431(3)	C(9)-C(10)	1.350(6)
O(3)-C(16)	1.325(3)	C(9)-H(9)	0.9300
O(3)-C(17)	1.466(3)	C(10)-C(11)	1.378(5)
O(4)-C(16)	1.210(3)	C(10)-H(10)	0.9300
N(1)-C(6)	1.398(4)	C(11)-H(11)	0.9300
N(1)-C(5)	1.450(4)	C(12)-C(13)	1.491(7)
N(2)-C(4)	1.457(4)	C(12)-H(12A)	0.9700
N(2)-C(12)	1.465(5)	C(12)-H(12B)	0.9700
N(30)-C(1)	1.313(4)	C(13)-C(14)	1.440(7)
N(30)-C(2)	1.452(3)	C(13)-H(13A)	0.9700
N(30)-H(30)	0.8600	C(13)-H(13B)	0.9700
N(40)-C(16)	1.334(3)	C(14)-H(14A)	0.9700
N(40)-C(15)	1.451(3)	C(14)-H(14B)	0.9700
N(40)-H(40)	0.8600	C(15)-C(19)	1.540(4)
C(1)-O(2)	1.218(4)	C(15)-H(15)	1.01(3)
C(1)-C(15)	1.536(4)	C(17)-C(24)	1.490(4)
C(2)-C(3)	1.512(4)	C(17)-C(23)	1.495(5)
C(2)-C(18)	1.540(4)	C(17)-C(25)	1.507(5)
C(2)-H(2)	0.94(3)	C(18)-C(22)	1.508(4)
C(3)-H(3A)	0.9700	C(18)-C(21)	1.521(4)
C(3)-H(3B)	0.9700	C(18)-C(20)	1.531(4)
C(4)-C(5)	1.509(5)	C(19)-C(27)	1.515(5)
C(4)-C(14)	1.513(5)	C(19)-C(26)	1.519(5)
C(4)-H(4)	0.94(4)	C(19)-C(28)	1.519(4)
C(5)-H(5A)	0.9700	C(20)-H(20A)	0.9600
C(5)-H(5B)	0.9700	C(20)-H(20B)	0.9600
C(6)-C(11)	1.374(5)	C(20)-H(20C)	0.9600
C(6)-C(7)	1.383(4)	C(21)-H(21A)	0.9600
C(7)-C(8)	1.386(6)	C(21)-H(21B)	0.9600

C(21)-H(21C)	0.9600	N(2A)-C(12A)	1.469(4)
C(22)-H(22A)	0.9600	N(30A)-C(1A)	1.330(3)
C(22)-H(22B)	0.9600	N(30A)-C(2A)	1.448(3)
C(22)-H(22C)	0.9600	N(30A)-H(30A)	0.8600
C(23)-H(23A)	0.9600	N(40A)-C(16A)	1.346(3)
C(23)-H(23B)	0.9600	N(40A)-C(15A)	1.448(3)
C(23)-H(23C)	0.9600	N(40A)-H(40A)	0.8600
C(24)-H(24A)	0.9600	C(1A)-C(15A)	1.527(3)
C(24)-H(24B)	0.9600	C(2A)-C(3A)	1.503(4)
C(24)-H(24C)	0.9600	C(2A)-C(18A)	1.545(4)
C(25)-H(25A)	0.9600	C(2A)-H(2A)	0.94(3)
C(25)-H(25B)	0.9600	C(3A)-H(3A1)	0.9700
C(25)-H(25C)	0.9600	C(3A)-H(3A2)	0.9700
C(26)-H(26A)	0.9600	C(4A)-C(5A)	1.511(5)
C(26)-H(26B)	0.9600	C(4A)-C(14A)	1.522(5)
C(26)-H(26C)	0.9600	C(4A)-H(4A)	1.00(3)
C(27)-H(27A)	0.9600	C(5A)-H(5A1)	0.9700
C(27)-H(27B)	0.9600	C(5A)-H(5A2)	0.9700
C(27)-H(27C)	0.9600	C(6A)-C(7A)	1.378(4)
C(28)-H(28A)	0.9600	C(6A)-C(11A)	1.384(4)
C(28)-H(28B)	0.9600	C(7A)-C(8A)	1.364(5)
C(28)-H(28C)	0.9600	C(7A)-H(7A)	0.9300
P(1A)-O(1A)	1.620(2)	C(8A)-C(9A)	1.363(6)
P(1A)-N(2A)	1.662(3)	C(8A)-H(8A)	0.9300
P(1A)-N(1A)	1.724(2)	C(9A)-C(10A)	1.359(6)
O(1A)-C(3A)	1.422(3)	C(9A)-H(9A)	0.9300
O(2A)-C(1A)	1.210(3)	C(10A)-C(11A)	1.371(5)
O(3A)-C(16A)	1.332(3)	C(10A)-H(10A)	0.9300
O(3A)-C(17A)	1.462(3)	C(11A)-H(11A)	0.9300
O(4A)-C(16A)	1.200(3)	C(12A)-C(13A)	1.503(5)
N(1A)-C(6A)	1.403(4)	C(12A)-H(12C)	0.9700
N(1A)-C(5A)	1.438(4)	C(12A)-H(12D)	0.9700
N(2A)-C(4A)	1.468(4)	C(13A)-C(14A)	1.487(6)

C(13A)-H(13C)	0.9700	C(26A)-H(26D)	0.9600
C(13A)-H(13D)	0.9700	C(26A)-H(26E)	0.9600
C(14A)-H(14C)	0.9700	C(26A)-H(26F)	0.9600
C(14A)-H(14D)	0.9700	C(27A)-H(27D)	0.9600
C(15A)-C(19A)	1.534(4)	C(27A)-H(27E)	0.9600
C(15A)-H(15A)	0.93(3)	C(27A)-H(27F)	0.9600
C(17A)-C(24A)	1.491(4)	C(28A)-H(28D)	0.9600
C(17A)-C(23A)	1.494(4)	C(28A)-H(28E)	0.9600
C(17A)-C(25A)	1.509(4)	C(28A)-H(28F)	0.9600
C(18A)-C(21A)	1.506(5)	O(1)-P(1)-N(2)	106.02(12)
C(18A)-C(22A)	1.510(6)	O(1)-P(1)-N(1)	102.67(11)
C(18A)-C(20A)	1.513(5)	N(2)-P(1)-N(1)	90.81(12)
C(19A)-C(27A)	1.516(4)	C(3)-O(1)-P(1)	123.85(16)
C(19A)-C(26A)	1.520(4)	C(16)-O(3)-C(17)	121.42(19)
C(19A)-C(28A)	1.527(4)	C(6)-N(1)-C(5)	120.9(2)
C(20A)-H(20D)	0.9600	C(6)-N(1)-P(1)	121.71(18)
C(20A)-H(20E)	0.9600	C(5)-N(1)-P(1)	112.8(2)
C(20A)-H(20F)	0.9600	C(4)-N(2)-C(12)	109.4(3)
C(21A)-H(21D)	0.9600	C(4)-N(2)-P(1)	115.6(2)
C(21A)-H(21E)	0.9600	C(12)-N(2)-P(1)	122.0(2)
C(21A)-H(21F)	0.9600	C(1)-N(30)-C(2)	127.1(2)
C(22A)-H(22D)	0.9600	C(1)-N(30)-H(30)	116.5
C(22A)-H(22E)	0.9600	C(2)-N(30)-H(30)	116.5
C(22A)-H(22F)	0.9600	C(16)-N(40)-C(15)	126.5(2)
C(23A)-H(23D)	0.9600	C(16)-N(40)-H(40)	116.7
C(23A)-H(23E)	0.9600	C(15)-N(40)-H(40)	116.7
C(23A)-H(23F)	0.9600	O(2)-C(1)-N(30)	121.6(3)
C(24A)-H(24D)	0.9600	O(2)-C(1)-C(15)	124.2(3)
C(24A)-H(24E)	0.9600	N(30)-C(1)-C(15)	113.8(2)
C(24A)-H(24F)	0.9600	N(30)-C(2)-C(3)	107.5(2)
C(25A)-H(25D)	0.9600	N(30)-C(2)-C(18)	112.8(2)
C(25A)-H(25E)	0.9600	C(3)-C(2)-C(18)	115.4(2)
C(25A)-H(25F)	0.9600	N(30)-C(2)-H(2)	106.9

C(3)-C(2)-H(2)	106.9	C(9)-C(10)-H(10)	119.7
C(18)-C(2)-H(2)	106.9	C(11)-C(10)-H(10)	119.7
O(1)-C(3)-C(2)	108.98(19)	C(6)-C(11)-C(10)	120.4(4)
O(1)-C(3)-H(3A)	109.9	C(6)-C(11)-H(11)	119.8
C(2)-C(3)-H(3A)	109.9	C(10)-C(11)-H(11)	119.8
O(1)-C(3)-H(3B)	109.9	N(2)-C(12)-C(13)	103.6(4)
C(2)-C(3)-H(3B)	109.9	N(2)-C(12)-H(12A)	111.0
H(3A)-C(3)-H(3B)	108.3	C(13)-C(12)-H(12A)	111.0
N(2)-C(4)-C(5)	105.7(3)	N(2)-C(12)-H(12B)	111.0
N(2)-C(4)-C(14)	105.4(3)	C(13)-C(12)-H(12B)	111.0
C(5)-C(4)-C(14)	115.5(3)	H(12A)-C(12)-H(12B)	109.0
N(2)-C(4)-H(4)	110.0	C(14)-C(13)-C(12)	106.4(4)
C(5)-C(4)-H(4)	110.0	C(14)-C(13)-H(13A)	110.5
C(14)-C(4)-H(4)	110.0	C(12)-C(13)-H(13A)	110.5
N(1)-C(5)-C(4)	105.2(2)	C(14)-C(13)-H(13B)	110.5
N(1)-C(5)-H(5A)	110.7	C(12)-C(13)-H(13B)	110.5
C(4)-C(5)-H(5A)	110.7	H(13A)-C(13)-H(13B)	108.6
N(1)-C(5)-H(5B)	110.7	C(13)-C(14)-C(4)	104.8(3)
C(4)-C(5)-H(5B)	110.7	C(13)-C(14)-H(14A)	110.8
H(5A)-C(5)-H(5B)	108.8	C(4)-C(14)-H(14A)	110.8
C(11)-C(6)-C(7)	118.4(3)	C(13)-C(14)-H(14B)	110.8
C(11)-C(6)-N(1)	120.6(3)	C(4)-C(14)-H(14B)	110.8
C(7)-C(6)-N(1)	120.9(3)	H(14A)-C(14)-H(14B)	108.9
C(6)-C(7)-C(8)	119.8(4)	N(40)-C(15)-C(1)	108.5(2)
C(6)-C(7)-H(7)	120.1	N(40)-C(15)-C(19)	112.8(2)
C(8)-C(7)-H(7)	120.1	C(1)-C(15)-C(19)	115.8(2)
C(9)-C(8)-C(7)	120.7(4)	N(40)-C(15)-H(15)	106.3
C(9)-C(8)-H(8)	119.6	C(1)-C(15)-H(15)	106.3
C(7)-C(8)-H(8)	119.6	C(19)-C(15)-H(15)	106.3
C(8)-C(9)-C(10)	120.1(4)	O(4)-C(16)-O(3)	124.6(2)
C(8)-C(9)-H(9)	120.0	O(4)-C(16)-N(40)	123.0(2)
C(10)-C(9)-H(9)	120.0	O(3)-C(16)-N(40)	112.3(2)
C(9)-C(10)-C(11)	120.6(4)	O(3)-C(17)-C(24)	111.3(2)

O(3)-C(17)-C(23)	108.5(3)	H(22A)-C(22)-H(22C)	109.5
C(24)-C(17)-C(23)	113.0(3)	H(22B)-C(22)-H(22C)	109.5
O(3)-C(17)-C(25)	101.3(2)	C(17)-C(23)-H(23A)	109.5
C(24)-C(17)-C(25)	110.2(3)	C(17)-C(23)-H(23B)	109.5
C(23)-C(17)-C(25)	111.9(3)	H(23A)-C(23)-H(23B)	109.5
C(22)-C(18)-C(21)	109.7(3)	C(17)-C(23)-H(23C)	109.5
C(22)-C(18)-C(20)	109.1(3)	H(23A)-C(23)-H(23C)	109.5
C(21)-C(18)-C(20)	108.4(3)	H(23B)-C(23)-H(23C)	109.5
C(22)-C(18)-C(2)	112.5(3)	C(17)-C(24)-H(24A)	109.5
C(21)-C(18)-C(2)	108.4(3)	C(17)-C(24)-H(24B)	109.5
C(20)-C(18)-C(2)	108.6(2)	H(24A)-C(24)-H(24B)	109.5
C(27)-C(19)-C(26)	109.1(3)	C(17)-C(24)-H(24C)	109.5
C(27)-C(19)-C(28)	108.3(3)	H(24A)-C(24)-H(24C)	109.5
C(26)-C(19)-C(28)	111.0(3)	H(24B)-C(24)-H(24C)	109.5
C(27)-C(19)-C(15)	107.2(3)	C(17)-C(25)-H(25A)	109.5
C(26)-C(19)-C(15)	111.8(3)	C(17)-C(25)-H(25B)	109.5
C(28)-C(19)-C(15)	109.4(3)	H(25A)-C(25)-H(25B)	109.5
C(18)-C(20)-H(20A)	109.5	C(17)-C(25)-H(25C)	109.5
C(18)-C(20)-H(20B)	109.5	H(25A)-C(25)-H(25C)	109.5
H(20A)-C(20)-H(20B)	109.5	H(25B)-C(25)-H(25C)	109.5
C(18)-C(20)-H(20C)	109.5	C(19)-C(26)-H(26A)	109.5
H(20A)-C(20)-H(20C)	109.5	C(19)-C(26)-H(26B)	109.5
H(20B)-C(20)-H(20C)	109.5	H(26A)-C(26)-H(26B)	109.5
C(18)-C(21)-H(21A)	109.5	C(19)-C(26)-H(26C)	109.5
C(18)-C(21)-H(21B)	109.5	H(26A)-C(26)-H(26C)	109.5
H(21A)-C(21)-H(21B)	109.5	H(26B)-C(26)-H(26C)	109.5
C(18)-C(21)-H(21C)	109.5	C(19)-C(27)-H(27A)	109.5
H(21A)-C(21)-H(21C)	109.5	C(19)-C(27)-H(27B)	109.5
H(21B)-C(21)-H(21C)	109.5	H(27A)-C(27)-H(27B)	109.5
C(18)-C(22)-H(22A)	109.5	C(19)-C(27)-H(27C)	109.5
C(18)-C(22)-H(22B)	109.5	H(27A)-C(27)-H(27C)	109.5
H(22A)-C(22)-H(22B)	109.5	H(27B)-C(27)-H(27C)	109.5
C(18)-C(22)-H(22C)	109.5	C(19)-C(28)-H(28A)	109.5

C(19)-C(28)-H(28B)	109.5	C(2A)-C(3A)-H(3A1)	109.5
H(28A)-C(28)-H(28B)	109.5	O(1A)-C(3A)-H(3A2)	109.5
C(19)-C(28)-H(28C)	109.5	C(2A)-C(3A)-H(3A2)	109.5
H(28A)-C(28)-H(28C)	109.5	H(3A1)-C(3A)-H(3A2)	108.1
H(28B)-C(28)-H(28C)	109.5	N(2A)-C(4A)-C(5A)	105.6(2)
O(1A)-P(1A)-N(2A)	105.67(12)	N(2A)-C(4A)-C(14A)	103.9(3)
O(1A)-P(1A)-N(1A)	102.73(12)	C(5A)-C(4A)-C(14A)	115.7(3)
N(2A)-P(1A)-N(1A)	90.47(12)	N(2A)-C(4A)-H(4A)	110.4
C(3A)-O(1A)-P(1A)	122.84(16)	C(5A)-C(4A)-H(4A)	110.4
C(16A)-O(3A)-C(17A)	121.57(19)	C(14A)-C(4A)-H(4A)	110.4
C(6A)-N(1A)-C(5A)	120.6(2)	N(1A)-C(5A)-C(4A)	106.3(2)
C(6A)-N(1A)-P(1A)	120.6(2)	N(1A)-C(5A)-H(5A1)	110.5
C(5A)-N(1A)-P(1A)	113.71(19)	C(4A)-C(5A)-H(5A1)	110.5
C(4A)-N(2A)-C(12A)	109.6(3)	N(1A)-C(5A)-H(5A2)	110.5
C(4A)-N(2A)-P(1A)	116.2(2)	C(4A)-C(5A)-H(5A2)	110.5
C(12A)-N(2A)-P(1A)	120.9(2)	H(5A1)-C(5A)-H(5A2)	108.7
C(1A)-N(30A)-C(2A)	122.9(2)	C(7A)-C(6A)-C(11A)	118.5(3)
C(1A)-N(30A)-H(30A)	118.6	C(7A)-C(6A)-N(1A)	121.6(3)
C(2A)-N(30A)-H(30A)	118.6	C(11A)-C(6A)-N(1A)	119.8(3)
C(16A)-N(40A)-C(15A)	121.4(2)	C(8A)-C(7A)-C(6A)	120.3(4)
C(16A)-N(40A)-H(40A)	119.3	C(8A)-C(7A)-H(7A)	119.8
C(15A)-N(40A)-H(40A)	119.3	C(6A)-C(7A)-H(7A)	119.8
O(2A)-C(1A)-N(30A)	123.8(2)	C(9A)-C(8A)-C(7A)	121.3(4)
O(2A)-C(1A)-C(15A)	121.3(2)	C(9A)-C(8A)-H(8A)	119.4
N(30A)-C(1A)-C(15A)	114.9(2)	C(7A)-C(8A)-H(8A)	119.4
N(30A)-C(2A)-C(3A)	110.4(2)	C(10A)-C(9A)-C(8A)	118.6(4)
N(30A)-C(2A)-C(18A)	111.3(2)	C(10A)-C(9A)-H(9A)	120.7
C(3A)-C(2A)-C(18A)	117.0(2)	C(8A)-C(9A)-H(9A)	120.7
N(30A)-C(2A)-H(2A)	105.7	C(9A)-C(10A)-C(11A)	121.5(4)
C(3A)-C(2A)-H(2A)	105.7	C(9A)-C(10A)-H(10A)	119.2
C(18A)-C(2A)-H(2A)	105.7	C(11A)-C(10A)-H(10A)	119.2
O(1A)-C(3A)-C(2A)	110.8(2)	C(10A)-C(11A)-C(6A)	119.8(4)
O(1A)-C(3A)-H(3A1)	109.5	C(10A)-C(11A)-H(11A)	120.1

C(6A)-C(11A)-H(11A)	120.1
N(2A)-C(12A)-C(13A)	103.9(3)
N(2A)-C(12A)-H(12C)	111.0
C(13A)-C(12A)-H(12C)	111.0
N(2A)-C(12A)-H(12D)	111.0
C(13A)-C(12A)-H(12D)	111.0
H(12C)-C(12A)-H(12D)	109.0
C(14A)-C(13A)-C(12A)	102.4(3)
C(14A)-C(13A)-H(13C)	111.3
C(12A)-C(13A)-H(13C)	111.3
C(14A)-C(13A)-H(13D)	111.3
C(12A)-C(13A)-H(13D)	111.3
H(13C)-C(13A)-H(13D)	109.2
C(13A)-C(14A)-C(4A)	105.5(3)
C(13A)-C(14A)-H(14C)	110.6
C(4A)-C(14A)-H(14C)	110.6
C(13A)-C(14A)-H(14D)	110.6
C(4A)-C(14A)-H(14D)	110.6
H(14C)-C(14A)-H(14D)	108.8
N(40A)-C(15A)-C(1A)	107.4(2)
N(40A)-C(15A)-C(19A)	112.3(2)
C(1A)-C(15A)-C(19A)	114.2(2)
N(40A)-C(15A)-H(15A)	107.5
C(1A)-C(15A)-H(15A)	107.5
C(19A)-C(15A)-H(15A)	107.5
O(4A)-C(16A)-O(3A)	125.3(2)
O(4A)-C(16A)-N(40A)	125.0(2)
O(3A)-C(16A)-N(40A)	109.7(2)
O(3A)-C(17A)-C(24A)	110.4(2)
O(3A)-C(17A)-C(23A)	101.9(2)
C(24A)-C(17A)-C(23A)	110.6(3)
O(3A)-C(17A)-C(25A)	109.6(2)
C(24A)-C(17A)-C(25A)	113.4(3)
C(23A)-C(17A)-C(25A)	110.3(3)
C(21A)-C(18A)-C(22A)	108.0(3)
C(21A)-C(18A)-C(20A)	108.6(4)
C(22A)-C(18A)-C(20A)	110.3(4)
C(21A)-C(18A)-C(2A)	112.9(3)
C(22A)-C(18A)-C(2A)	108.0(3)
C(20A)-C(18A)-C(2A)	109.0(3)
C(27A)-C(19A)-C(26A)	110.0(2)
C(27A)-C(19A)-C(28A)	108.6(2)
C(26A)-C(19A)-C(28A)	109.8(2)
C(27A)-C(19A)-C(15A)	107.8(2)
C(26A)-C(19A)-C(15A)	112.4(2)
C(28A)-C(19A)-C(15A)	108.2(2)
C(18A)-C(20A)-H(20D)	109.5
C(18A)-C(20A)-H(20E)	109.5
H(20D)-C(20A)-H(20E)	109.5
C(18A)-C(20A)-H(20F)	109.5
H(20D)-C(20A)-H(20F)	109.5
H(20E)-C(20A)-H(20F)	109.5
C(18A)-C(21A)-H(21D)	109.5
C(18A)-C(21A)-H(21E)	109.5
H(21D)-C(21A)-H(21E)	109.5
C(18A)-C(21A)-H(21F)	109.5
H(21D)-C(21A)-H(21F)	109.5
H(21E)-C(21A)-H(21F)	109.5
C(18A)-C(22A)-H(22D)	109.5
C(18A)-C(22A)-H(22E)	109.5
H(22D)-C(22A)-H(22E)	109.5
C(18A)-C(22A)-H(22F)	109.5
H(22D)-C(22A)-H(22F)	109.5
H(22E)-C(22A)-H(22F)	109.5
C(17A)-C(23A)-H(23D)	109.5
C(17A)-C(23A)-H(23E)	109.5

H(23D)-C(23A)-H(23E)	109.5
C(17A)-C(23A)-H(23F)	109.5
H(23D)-C(23A)-H(23F)	109.5
H(23E)-C(23A)-H(23F)	109.5
C(17A)-C(24A)-H(24D)	109.5
C(17A)-C(24A)-H(24E)	109.5
H(24D)-C(24A)-H(24E)	109.5
C(17A)-C(24A)-H(24F)	109.5
H(24D)-C(24A)-H(24F)	109.5
H(24E)-C(24A)-H(24F)	109.5
C(17A)-C(25A)-H(25D)	109.5
C(17A)-C(25A)-H(25E)	109.5
H(25D)-C(25A)-H(25E)	109.5
C(17A)-C(25A)-H(25F)	109.5
H(25D)-C(25A)-H(25F)	109.5
H(25E)-C(25A)-H(25F)	109.5
C(19A)-C(26A)-H(26D)	109.5
C(19A)-C(26A)-H(26E)	109.5
H(26D)-C(26A)-H(26E)	109.5
C(19A)-C(26A)-H(26F)	109.5
H(26D)-C(26A)-H(26F)	109.5
H(26E)-C(26A)-H(26F)	109.5
C(19A)-C(27A)-H(27D)	109.5
C(19A)-C(27A)-H(27E)	109.5
H(27D)-C(27A)-H(27E)	109.5
C(19A)-C(27A)-H(27F)	109.5
H(27D)-C(27A)-H(27F)	109.5
H(27E)-C(27A)-H(27F)	109.5
C(19A)-C(28A)-H(28D)	109.5
C(19A)-C(28A)-H(28E)	109.5
H(28D)-C(28A)-H(28E)	109.5
C(19A)-C(28A)-H(28F)	109.5
H(28D)-C(28A)-H(28F)	109.5
H(28E)-C(28A)-H(28F)	109.5

X-RAY STRUCTURE DETERMINATIONS

Table S7. Torsion angles [°] for **L3d**.

N(2)-P(1)-O(1)-C(3)	48.5(2)	C(7)-C(8)-C(9)-C(10)	0.1(7)
N(1)-P(1)-O(1)-C(3)	-46.0(2)	C(8)-C(9)-C(10)-C(11)	-0.1(7)
O(1)-P(1)-N(1)-C(6)	-80.3(2)	C(7)-C(6)-C(11)-C(10)	1.3(5)
N(2)-P(1)-N(1)-C(6)	173.1(2)	N(1)-C(6)-C(11)-C(10)	-179.6(3)
O(1)-P(1)-N(1)-C(5)	123.6(2)	C(9)-C(10)-C(11)-C(6)	-0.6(6)
N(2)-P(1)-N(1)-C(5)	17.0(2)	C(4)-N(2)-C(12)-C(13)	-17.3(4)
O(1)-P(1)-N(2)-C(4)	-100.1(2)	P(1)-N(2)-C(12)-C(13)	122.2(3)
N(1)-P(1)-N(2)-C(4)	3.4(2)	N(2)-C(12)-C(13)-C(14)	30.7(5)
O(1)-P(1)-N(2)-C(12)	122.7(3)	C(12)-C(13)-C(14)-C(4)	-32.0(6)
N(1)-P(1)-N(2)-C(12)	-133.8(3)	N(2)-C(4)-C(14)-C(13)	20.8(5)
C(2)-N(30)-C(1)-O(2)	-9.6(6)	C(5)-C(4)-C(14)-C(13)	-95.6(5)
C(2)-N(30)-C(1)-C(15)	176.5(3)	C(16)-N(40)-C(15)-C(1)	-115.4(3)
C(1)-N(30)-C(2)-C(3)	-122.1(3)	C(16)-N(40)-C(15)-C(19)	114.8(3)
C(1)-N(30)-C(2)-C(18)	109.5(3)	O(2)-C(1)-C(15)-N(40)	-115.0(4)
P(1)-O(1)-C(3)-C(2)	-171.95(19)	N(30)-C(1)-C(15)-N(40)	58.7(4)
N(30)-C(2)-C(3)-O(1)	-46.3(3)	O(2)-C(1)-C(15)-C(19)	13.1(5)
C(18)-C(2)-C(3)-O(1)	80.6(3)	N(30)-C(1)-C(15)-C(19)	-173.2(3)
C(12)-N(2)-C(4)-C(5)	121.2(3)	C(17)-O(3)-C(16)-O(4)	-6.7(4)
P(1)-N(2)-C(4)-C(5)	-21.2(3)	C(17)-O(3)-C(16)-N(40)	173.7(2)
C(12)-N(2)-C(4)-C(14)	-1.6(4)	C(15)-N(40)-C(16)-O(4)	176.4(3)
P(1)-N(2)-C(4)-C(14)	-144.0(3)	C(15)-N(40)-C(16)-O(3)	-3.9(4)
C(6)-N(1)-C(5)-C(4)	172.7(3)	C(16)-O(3)-C(17)-C(24)	59.9(3)
P(1)-N(1)-C(5)-C(4)	-30.9(3)	C(16)-O(3)-C(17)-C(23)	-65.1(3)
N(2)-C(4)-C(5)-N(1)	31.1(4)	C(16)-O(3)-C(17)-C(25)	177.0(3)
C(14)-C(4)-C(5)-N(1)	147.2(3)	N(30)-C(2)-C(18)-C(22)	67.4(3)
C(5)-N(1)-C(6)-C(11)	-171.4(3)	C(3)-C(2)-C(18)-C(22)	-56.7(3)
P(1)-N(1)-C(6)-C(11)	34.3(4)	N(30)-C(2)-C(18)-C(21)	-54.0(3)
C(5)-N(1)-C(6)-C(7)	7.7(4)	C(3)-C(2)-C(18)-C(21)	-178.1(3)
P(1)-N(1)-C(6)-C(7)	-146.5(2)	N(30)-C(2)-C(18)-C(20)	-171.6(2)
C(11)-C(6)-C(7)-C(8)	-1.3(5)	C(3)-C(2)-C(18)-C(20)	64.3(3)
N(1)-C(6)-C(7)-C(8)	179.5(3)	N(40)-C(15)-C(19)-C(27)	-59.9(3)
C(6)-C(7)-C(8)-C(9)	0.6(6)	C(1)-C(15)-C(19)-C(27)	174.1(3)

N(40)-C(15)-C(19)-C(26)	59.6(3)	C(11A)-C(6A)-C(7A)-C(8A)	-1.8(5)
C(1)-C(15)-C(19)-C(26)	-66.4(4)	N(1A)-C(6A)-C(7A)-C(8A)	178.1(3)
N(40)-C(15)-C(19)-C(28)	-177.1(3)	C(6A)-C(7A)-C(8A)-C(9A)	0.3(6)
C(1)-C(15)-C(19)-C(28)	56.9(4)	C(7A)-C(8A)-C(9A)-C(10A)	1.6(6)
N(2A)-P(1A)-O(1A)-C(3A)	46.0(2)	C(8A)-C(9A)-C(10A)-C(11A)	-2.0(7)
N(1A)-P(1A)-O(1A)-C(3A)	-48.2(2)	C(9A)-C(10A)-C(11A)-C(6A)	0.5(6)
O(1A)-P(1A)-N(1A)-C(6A)	-83.5(2)	C(7A)-C(6A)-C(11A)-C(10A)	1.4(5)
N(2A)-P(1A)-N(1A)-C(6A)	170.3(2)	N(1A)-C(6A)-C(11A)-C(10A)	-178.5(3)
O(1A)-P(1A)-N(1A)-C(5A)	121.4(2)	C(4A)-N(2A)-C(12A)-C(13A)	-23.5(4)
N(2A)-P(1A)-N(1A)-C(5A)	15.2(2)	P(1A)-N(2A)-C(12A)-C(13A)	115.9(3)
O(1A)-P(1A)-N(2A)-C(4A)	-100.5(2)	N(2A)-C(12A)-C(13A)-C(14A)	36.6(4)
N(1A)-P(1A)-N(2A)-C(4A)	2.9(2)	C(12A)-C(13A)-C(14A)-C(4A)	-36.7(4)
O(1A)-P(1A)-N(2A)-C(12A)	122.6(2)	N(2A)-C(4A)-C(14A)-C(13A)	22.6(4)
N(1A)-P(1A)-N(2A)-C(12A)	-134.0(3)	C(5A)-C(4A)-C(14A)-C(13A)	-92.7(4)
C(2A)-N(30A)-C(1A)-O(2A)	6.4(4)	C(16A)-N(40A)-C(15A)-C(1A)	-90.4(3)
C(2A)-N(30A)-C(1A)-C(15A)	-171.5(2)	C(16A)-N(40A)-C(15A)-C(19A)	143.3(2)
C(1A)-N(30A)-C(2A)-C(3A)	-112.2(3)	O(2A)-C(1A)-C(15A)-N(40A)	-53.1(3)
C(1A)-N(30A)-C(2A)-C(18A)	116.1(3)	N(30A)-C(1A)-C(15A)-N(40A)	124.8(2)
P(1A)-O(1A)-C(3A)-C(2A)	-165.48(19)	O(2A)-C(1A)-C(15A)-C(19A)	72.2(3)
N(30A)-C(2A)-C(3A)-O(1A)	-59.9(3)	N(30A)-C(1A)-C(15A)-C(19A)	-110.0(3)
C(18A)-C(2A)-C(3A)-O(1A)	68.8(3)	C(17A)-O(3A)-C(16A)-O(4A)	3.6(4)
C(12A)-N(2A)-C(4A)-C(5A)	123.0(3)	C(17A)-O(3A)-C(16A)-N(40A)	-177.2(2)
P(1A)-N(2A)-C(4A)-C(5A)	-18.5(3)	C(15A)-N(40A)-C(16A)-O(4A)	-11.3(4)
C(12A)-N(2A)-C(4A)-C(14A)	0.8(4)	C(15A)-N(40A)-C(16A)-O(3A)	169.6(2)
P(1A)-N(2A)-C(4A)-C(14A)	-140.7(2)	C(16A)-O(3A)-C(17A)-C(24A)	-63.4(3)
C(6A)-N(1A)-C(5A)-C(4A)	177.2(3)	C(16A)-O(3A)-C(17A)-C(23A)	179.1(3)
P(1A)-N(1A)-C(5A)-C(4A)	-27.7(3)	C(16A)-O(3A)-C(17A)-C(25A)	62.2(3)
N(2A)-C(4A)-C(5A)-N(1A)	27.5(3)	N(30A)-C(2A)-C(18A)-C(21A)	60.7(4)
C(14A)-C(4A)-C(5A)-N(1A)	141.8(3)	C(3A)-C(2A)-C(18A)-C(21A)	-67.6(4)
C(5A)-N(1A)-C(6A)-C(7A)	9.4(4)	N(30A)-C(2A)-C(18A)-C(22A)	-58.7(4)
P(1A)-N(1A)-C(6A)-C(7A)	-144.0(3)	C(3A)-C(2A)-C(18A)-C(22A)	173.1(3)
C(5A)-N(1A)-C(6A)-C(11A)	-170.7(3)	N(30A)-C(2A)-C(18A)-C(20A)	-178.5(4)
P(1A)-N(1A)-C(6A)-C(11A)	35.9(4)	C(3A)-C(2A)-C(18A)-C(20A)	53.2(4)

N(40A)-C(15A)-C(19A)-C(27A)	-65.3(3)
C(1A)-C(15A)-C(19A)-C(27A)	172.1(2)
N(40A)-C(15A)-C(19A)-C(26A)	56.1(3)
C(1A)-C(15A)-C(19A)-C(26A)	-66.5(3)
N(40A)-C(15A)-C(19A)-C(28A)	177.5(2)
C(1A)-C(15A)-C(19A)-C(28A)	54.9(3)

Table S8. Hydrogen bonds for **L3d** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(40)-H(40)...O(4A)	0.86	2.06	2.908(3)	168.1
C(11)-H(11)...O(1)	0.93	2.55	3.225(4)	129.8
C(13)-H(13B)...O(2A)#1	0.97	2.48	3.300(6)	142.5
C(23)-H(23C)...O(4)	0.96	2.51	3.041(4)	115.1
C(24)-H(24A)...O(4)	0.96	2.37	2.903(4)	114.9
N(30A)-H(30A)...O(4)	0.86	2.18	3.010(3)	163.5
C(11A)-H(11A)...O(1A)	0.93	2.57	3.250(4)	129.9
C(15A)-H(15A)...O(4)	0.93	2.39	3.253(3)	153.2
C(24A)-H(24F)...O(4A)	0.96	2.42	2.980(4)	117.2
C(25A)-H(25D)...O(4A)	0.96	2.45	3.007(4)	116.7

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y+1/2,-z+3/2

X-RAY STRUCTURE DETERMINATIONS

Table S9. Crystal data and structure refinement for [Pd(allyl)(**L3d**)$_2$]BF_4.

Identification code	gavr35	
Empirical formula	C61 H101 B Cl6 F4 N8 O8 P2 Pd	
Formula weight	1542.34	
Temperature	293(2) K	
Wavelength	1.54186 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 10.8737(6) Å	α = 90°.
	b = 24.9640(10) Å	β = 90°.
	c = 29.062(2) Å	γ = 90°.
Volume	7888.9(8) Å^3	
Z	4	
Density (calculated)	1.299 Mg/m^3	
Absorption coefficient	4.655 mm^{-1}	
F(000)	3224	
Crystal size	.17 x .15 x .09mm^3	
Theta range for data collection	3.519 to 56.462°.	
Index ranges	-6<=h<=11, -26<=k<=22, -30<=l<=30	
Reflections collected	37788	
Independent reflections	8871 [R(int) = 0.1042]	
Completeness to theta = 56.462°	91.3 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8871 / 910 / 841	
Goodness-of-fit on F^2	0.916	
Final R indices [I>2sigma(I)]	R1 = 0.0902, wR2 = 0.2319	
R indices (all data)	R1 = 0.1806, wR2 = 0.2625	
Absolute structure parameter	-0.036(11)	
Extinction coefficient	0.00152(18)	
Largest diff. peak and hole	1.035 and -0.541 e.Å^{-3}	

X-RAY STRUCTURE DETERMINATIONS

Table S10. Bond lengths [Å] and angles [°] for [Pd(allyl)(**L3d**)$_2$]BF_4.

Pd(1)-C(82)	2.06(3)	O(1)-C(12)	1.46(2)
Pd(1)-C(81)	2.11(2)	O(2)-C(18)	1.20(3)
Pd(1)-C(83)	2.19(2)	O(3)-C(24)	1.20(3)
Pd(1)-P(1A)	2.265(6)	O(4)-C(24)	1.33(3)
Pd(1)-P(1)	2.283(6)	O(4)-C(25)	1.46(3)
Cl(1)-C(90)	1.75(3)	N(1)-C(1)	1.40(3)
Cl(2)-C(90)	1.71(3)	N(1)-C(7)	1.51(3)
Cl(3)-C(90)	1.71(3)	N(2)-C(8)	1.49(3)
C(90)-H(90)	0.9800	N(2)-C(11)	1.54(3)
B(1)-F(1)	1.323(13)	N(3)-C(18)	1.39(3)
B(1)-F(2)	1.326(13)	N(3)-C(13)	1.40(3)
B(1)-F(4)	1.334(13)	N(3)-H(33)	0.8600
B(1)-F(3)	1.334(13)	N(4)-C(24)	1.34(3)
C(81)-C(82)	1.24(3)	N(4)-C(19)	1.47(3)
C(81)-H(81A)	0.9700	N(4)-H(44)	0.8600
C(81)-H(81B)	0.9700	C(1)-C(6)	1.378(13)
C(82)-C(83)	1.19(4)	C(1)-C(2)	1.385(13)
C(82)-H(82)	0.9300	C(2)-C(3)	1.387(13)
C(83)-H(83A)	0.9700	C(2)-H(2)	0.9300
C(83)-H(83B)	0.9700	C(3)-C(4)	1.397(13)
C(70)-Cl(5)	1.684(13)	C(3)-H(3)	0.9300
C(70)-Cl(6)	1.688(12)	C(4)-C(5)	1.378(13)
C(70)-Cl(4)	1.729(12)	C(4)-H(4)	0.9300
C(70)-H(70)	0.9800	C(5)-C(6)	1.375(13)
C(71)-Cl(61)	1.69(3)	C(5)-H(5)	0.9300
C(71)-Cl(51)	1.69(3)	C(6)-H(6)	0.9300
C(71)-Cl(41)	1.710(13)	C(7)-C(8)	1.49(3)
C(71)-H(71)	0.9800	C(7)-H(7A)	0.9700
P(1)-N(2)	1.618(19)	C(7)-H(7B)	0.9700
P(1)-O(1)	1.621(17)	C(8)-C(9)	1.53(4)
P(1)-N(1)	1.719(18)	C(8)-H(8)	0.9800

C(9)-C(10)	1.60(4)	C(21)-H(21C)	0.9600
C(9)-H(9A)	0.9700	C(22)-H(22A)	0.9600
C(9)-H(9B)	0.9700	C(22)-H(22B)	0.9600
C(10)-C(11)	1.56(3)	C(22)-H(22C)	0.9600
C(10)-H(10A)	0.9700	C(23)-H(23A)	0.9600
C(10)-H(10B)	0.9700	C(23)-H(23B)	0.9600
C(11)-H(11A)	0.9700	C(23)-H(23C)	0.9600
C(11)-H(11B)	0.9700	C(25)-C(26)	1.47(4)
C(12)-C(13)	1.62(3)	C(25)-C(27)	1.56(4)
C(12)-H(12A)	0.9700	C(25)-C(28)	1.63(4)
C(12)-H(12B)	0.9700	C(26)-H(26A)	0.9600
C(13)-C(14)	1.57(3)	C(26)-H(26B)	0.9600
C(13)-H(13)	0.9800	C(26)-H(26C)	0.9600
C(14)-C(15)	1.54(3)	C(27)-H(27A)	0.9600
C(14)-C(16)	1.56(3)	C(27)-H(27B)	0.9600
C(14)-C(17)	1.56(3)	C(27)-H(27C)	0.9600
C(15)-H(15A)	0.9600	C(28)-H(28A)	0.9600
C(15)-H(15B)	0.9600	C(28)-H(28B)	0.9600
C(15)-H(15C)	0.9600	C(28)-H(28C)	0.9600
C(16)-H(16A)	0.9600	P(1A)-O(1A)	1.609(17)
C(16)-H(16B)	0.9600	P(1A)-N(2A)	1.64(2)
C(16)-H(16C)	0.9600	P(1A)-N(1A)	1.703(18)
C(17)-H(17A)	0.9600	O(1A)-C(12A)	1.46(2)
C(17)-H(17B)	0.9600	O(2A)-C(18A)	1.25(3)
C(17)-H(17C)	0.9600	O(3A)-C(24A)	1.22(3)
C(18)-C(19)	1.53(3)	O(4A)-C(24A)	1.32(3)
C(19)-C(20)	1.55(3)	O(4A)-C(25A)	1.48(3)
C(19)-H(19)	0.9800	N(1A)-C(1A)	1.39(3)
C(20)-C(23)	1.53(3)	N(1A)-C(7A)	1.46(3)
C(20)-C(21)	1.54(3)	N(2A)-C(11A)	1.40(3)
C(20)-C(22)	1.54(3)	N(2A)-C(8A)	1.53(3)
C(21)-H(21A)	0.9600	N(3A)-C(18A)	1.33(3)
C(21)-H(21B)	0.9600	N(3A)-C(13A)	1.52(3)

N(3A)-H(33A)	0.8600	C(14A)-C(17A)	1.50(4)
N(4A)-C(24A)	1.27(3)	C(14A)-C(15A)	1.54(3)
N(4A)-C(19A)	1.45(3)	C(14A)-C(16A)	1.56(3)
N(4A)-H(44A)	0.8600	C(15A)-H(15D)	0.9600
C(1A)-C(6A)	1.387(13)	C(15A)-H(15E)	0.9600
C(1A)-C(2A)	1.394(13)	C(15A)-H(15F)	0.9600
C(2A)-C(3A)	1.378(13)	C(16A)-H(16D)	0.9600
C(2A)-H(2A)	0.9300	C(16A)-H(16E)	0.9600
C(3A)-C(4A)	1.376(13)	C(16A)-H(16F)	0.9600
C(3A)-H(3A)	0.9300	C(17A)-H(17D)	0.9600
C(4A)-C(5A)	1.371(13)	C(17A)-H(17E)	0.9600
C(4A)-H(4A)	0.9300	C(17A)-H(17F)	0.9600
C(5A)-C(6A)	1.387(13)	C(18A)-C(19A)	1.53(3)
C(5A)-H(5A)	0.9300	C(19A)-C(20A)	1.55(3)
C(6A)-H(6A)	0.9300	C(19A)-H(19A)	0.9800
C(7A)-C(8A)	1.51(3)	C(20A)-C(21A)	1.49(4)
C(7A)-H(7A1)	0.9700	C(20A)-C(22A)	1.52(3)
C(7A)-H(7A2)	0.9700	C(20A)-C(23A)	1.61(3)
C(8A)-C(9A)	1.56(4)	C(21A)-H(21D)	0.9600
C(8A)-H(8A)	0.9800	C(21A)-H(21E)	0.9600
C(9A)-C(10A)	1.43(3)	C(21A)-H(21F)	0.9600
C(9A)-H(9A1)	0.9700	C(22A)-H(22D)	0.9600
C(9A)-H(9A2)	0.9700	C(22A)-H(22E)	0.9600
C(10A)-C(11A)	1.50(3)	C(22A)-H(22F)	0.9600
C(10A)-H(10C)	0.9700	C(23A)-H(23D)	0.9600
C(10A)-H(10D)	0.9700	C(23A)-H(23E)	0.9600
C(11A)-H(11C)	0.9700	C(23A)-H(23F)	0.9600
C(11A)-H(11D)	0.9700	C(25A)-C(27A)	1.42(3)
C(12A)-C(13A)	1.53(3)	C(25A)-C(26A)	1.52(4)
C(12A)-H(12C)	0.9700	C(25A)-C(28A)	1.60(3)
C(12A)-H(12D)	0.9700	C(26A)-H(26D)	0.9600
C(13A)-C(14A)	1.46(3)	C(26A)-H(26E)	0.9600
C(13A)-H(13A)	0.9800	C(26A)-H(26F)	0.9600

C(27A)-H(27D)	0.9600	H(81A)-C(81)-H(81B)	113.6
C(27A)-H(27E)	0.9600	C(83)-C(82)-C(81)	147(5)
C(27A)-H(27F)	0.9600	C(83)-C(82)-Pd(1)	80(2)
C(28A)-H(28D)	0.9600	C(81)-C(82)-Pd(1)	74.9(17)
C(28A)-H(28E)	0.9600	C(83)-C(82)-H(82)	106.6
C(28A)-H(28F)	0.9600	C(81)-C(82)-H(82)	106.6
C(82)-Pd(1)-C(81)	34.6(9)	Pd(1)-C(82)-H(82)	139.6
C(82)-Pd(1)-C(83)	32.3(11)	C(82)-C(83)-Pd(1)	67.7(18)
C(81)-Pd(1)-C(83)	65.5(10)	C(82)-C(83)-H(83A)	116.9
C(82)-Pd(1)-P(1A)	129.9(10)	Pd(1)-C(83)-H(83A)	116.9
C(81)-Pd(1)-P(1A)	96.5(8)	C(82)-C(83)-H(83B)	116.9
C(83)-Pd(1)-P(1A)	161.9(8)	Pd(1)-C(83)-H(83B)	116.9
C(82)-Pd(1)-P(1)	121.9(9)	H(83A)-C(83)-H(83B)	113.9
C(81)-Pd(1)-P(1)	156.1(8)	Cl(5)-C(70)-Cl(6)	118.9(18)
C(83)-Pd(1)-P(1)	90.6(8)	Cl(5)-C(70)-Cl(4)	104.7(17)
P(1A)-Pd(1)-P(1)	107.4(2)	Cl(6)-C(70)-Cl(4)	112.6(18)
Cl(3)-C(90)-Cl(2)	111.0(16)	Cl(5)-C(70)-H(70)	106.6
Cl(3)-C(90)-Cl(1)	109.6(16)	Cl(6)-C(70)-H(70)	106.6
Cl(2)-C(90)-Cl(1)	108.7(13)	Cl(4)-C(70)-H(70)	106.6
Cl(3)-C(90)-H(90)	109.1	Cl(61)-C(71)-Cl(51)	109(2)
Cl(2)-C(90)-H(90)	109.1	Cl(61)-C(71)-Cl(41)	126(3)
Cl(1)-C(90)-H(90)	109.1	Cl(51)-C(71)-Cl(41)	105(2)
F(1)-B(1)-F(2)	116.0(19)	Cl(61)-C(71)-H(71)	105.2
F(1)-B(1)-F(4)	114(2)	Cl(51)-C(71)-H(71)	105.2
F(2)-B(1)-F(4)	109.0(19)	Cl(41)-C(71)-H(71)	105.2
F(1)-B(1)-F(3)	108.4(18)	N(2)-P(1)-O(1)	109.9(9)
F(2)-B(1)-F(3)	114.8(19)	N(2)-P(1)-N(1)	91.9(9)
F(4)-B(1)-F(3)	92(2)	O(1)-P(1)-N(1)	105.3(10)
C(82)-C(81)-Pd(1)	70.5(17)	N(2)-P(1)-Pd(1)	116.4(8)
C(82)-C(81)-H(81A)	116.6	O(1)-P(1)-Pd(1)	103.3(6)
Pd(1)-C(81)-H(81A)	116.6	N(1)-P(1)-Pd(1)	129.1(6)
C(82)-C(81)-H(81B)	116.6	C(12)-O(1)-P(1)	117.7(14)
Pd(1)-C(81)-H(81B)	116.6	C(24)-O(4)-C(25)	120(2)

C(1)-N(1)-C(7)	122.6(17)	C(8)-C(7)-H(7B)	111.5
C(1)-N(1)-P(1)	123.9(14)	N(1)-C(7)-H(7B)	111.5
C(7)-N(1)-P(1)	112.3(15)	H(7A)-C(7)-H(7B)	109.3
C(8)-N(2)-C(11)	114.4(19)	N(2)-C(8)-C(7)	107.7(16)
C(8)-N(2)-P(1)	114.4(16)	N(2)-C(8)-C(9)	104(2)
C(11)-N(2)-P(1)	128.5(14)	C(7)-C(8)-C(9)	112(2)
C(18)-N(3)-C(13)	123.1(18)	N(2)-C(8)-H(8)	110.8
C(18)-N(3)-H(33)	118.4	C(7)-C(8)-H(8)	110.8
C(13)-N(3)-H(33)	118.4	C(9)-C(8)-H(8)	110.8
C(24)-N(4)-C(19)	124(2)	C(8)-C(9)-C(10)	102(2)
C(24)-N(4)-H(44)	118.0	C(8)-C(9)-H(9A)	111.4
C(19)-N(4)-H(44)	118.0	C(10)-C(9)-H(9A)	111.4
C(6)-C(1)-C(2)	114(2)	C(8)-C(9)-H(9B)	111.4
C(6)-C(1)-N(1)	122(2)	C(10)-C(9)-H(9B)	111.4
C(2)-C(1)-N(1)	123.9(17)	H(9A)-C(9)-H(9B)	109.3
C(1)-C(2)-C(3)	124(2)	C(11)-C(10)-C(9)	106(2)
C(1)-C(2)-H(2)	117.8	C(11)-C(10)-H(10A)	110.5
C(3)-C(2)-H(2)	117.8	C(9)-C(10)-H(10A)	110.5
C(2)-C(3)-C(4)	120(2)	C(11)-C(10)-H(10B)	110.5
C(2)-C(3)-H(3)	120.2	C(9)-C(10)-H(10B)	110.5
C(4)-C(3)-H(3)	120.2	H(10A)-C(10)-H(10B)	108.7
C(5)-C(4)-C(3)	116(2)	N(2)-C(11)-C(10)	99.7(19)
C(5)-C(4)-H(4)	121.9	N(2)-C(11)-H(11A)	111.8
C(3)-C(4)-H(4)	121.9	C(10)-C(11)-H(11A)	111.8
C(6)-C(5)-C(4)	122(2)	N(2)-C(11)-H(11B)	111.8
C(6)-C(5)-H(5)	118.8	C(10)-C(11)-H(11B)	111.8
C(4)-C(5)-H(5)	118.8	H(11A)-C(11)-H(11B)	109.6
C(5)-C(6)-C(1)	123(2)	O(1)-C(12)-C(13)	99.1(16)
C(5)-C(6)-H(6)	118.6	O(1)-C(12)-H(12A)	111.9
C(1)-C(6)-H(6)	118.6	C(13)-C(12)-H(12A)	111.9
C(8)-C(7)-N(1)	101.6(18)	O(1)-C(12)-H(12B)	111.9
C(8)-C(7)-H(7A)	111.5	C(13)-C(12)-H(12B)	111.9
N(1)-C(7)-H(7A)	111.5	H(12A)-C(12)-H(12B)	109.6

N(3)-C(13)-C(14)	114.5(17)	N(4)-C(19)-C(18)	114.8(18)
N(3)-C(13)-C(12)	105.7(19)	N(4)-C(19)-C(20)	112.6(19)
C(14)-C(13)-C(12)	112.0(19)	C(18)-C(19)-C(20)	115(2)
N(3)-C(13)-H(13)	108.2	N(4)-C(19)-H(19)	104.3
C(14)-C(13)-H(13)	108.2	C(18)-C(19)-H(19)	104.3
C(12)-C(13)-H(13)	108.2	C(20)-C(19)-H(19)	104.3
C(15)-C(14)-C(16)	109(2)	C(23)-C(20)-C(21)	109.3(19)
C(15)-C(14)-C(17)	112(2)	C(23)-C(20)-C(22)	109(2)
C(16)-C(14)-C(17)	109(2)	C(21)-C(20)-C(22)	110.5(19)
C(15)-C(14)-C(13)	108(2)	C(23)-C(20)-C(19)	109.7(18)
C(16)-C(14)-C(13)	109(2)	C(21)-C(20)-C(19)	111(2)
C(17)-C(14)-C(13)	110(2)	C(22)-C(20)-C(19)	107.1(19)
C(14)-C(15)-H(15A)	109.5	C(20)-C(21)-H(21A)	109.5
C(14)-C(15)-H(15B)	109.5	C(20)-C(21)-H(21B)	109.5
H(15A)-C(15)-H(15B)	109.5	H(21A)-C(21)-H(21B)	109.5
C(14)-C(15)-H(15C)	109.5	C(20)-C(21)-H(21C)	109.5
H(15A)-C(15)-H(15C)	109.5	H(21A)-C(21)-H(21C)	109.5
H(15B)-C(15)-H(15C)	109.5	H(21B)-C(21)-H(21C)	109.5
C(14)-C(16)-H(16A)	109.5	C(20)-C(22)-H(22A)	109.5
C(14)-C(16)-H(16B)	109.5	C(20)-C(22)-H(22B)	109.5
H(16A)-C(16)-H(16B)	109.5	H(22A)-C(22)-H(22B)	109.5
C(14)-C(16)-H(16C)	109.5	C(20)-C(22)-H(22C)	109.5
H(16A)-C(16)-H(16C)	109.5	H(22A)-C(22)-H(22C)	109.5
H(16B)-C(16)-H(16C)	109.5	H(22B)-C(22)-H(22C)	109.5
C(14)-C(17)-H(17A)	109.5	C(20)-C(23)-H(23A)	109.5
C(14)-C(17)-H(17B)	109.5	C(20)-C(23)-H(23B)	109.5
H(17A)-C(17)-H(17B)	109.5	H(23A)-C(23)-H(23B)	109.5
C(14)-C(17)-H(17C)	109.5	C(20)-C(23)-H(23C)	109.5
H(17A)-C(17)-H(17C)	109.5	H(23A)-C(23)-H(23C)	109.5
H(17B)-C(17)-H(17C)	109.5	H(23B)-C(23)-H(23C)	109.5
O(2)-C(18)-N(3)	124(2)	O(3)-C(24)-O(4)	126(3)
O(2)-C(18)-C(19)	119(2)	O(3)-C(24)-N(4)	125(3)
N(3)-C(18)-C(19)	116(2)	O(4)-C(24)-N(4)	108(3)

O(4)-C(25)-C(26)	115(2)	C(1A)-N(1A)-P(1A)	123.7(15)
O(4)-C(25)-C(27)	102(3)	C(7A)-N(1A)-P(1A)	111.7(14)
C(26)-C(25)-C(27)	113(3)	C(11A)-N(2A)-C(8A)	110.4(19)
O(4)-C(25)-C(28)	106(2)	C(11A)-N(2A)-P(1A)	128.0(16)
C(26)-C(25)-C(28)	107(3)	C(8A)-N(2A)-P(1A)	114.4(15)
C(27)-C(25)-C(28)	112(2)	C(18A)-N(3A)-C(13A)	124(2)
C(25)-C(26)-H(26A)	109.5	C(18A)-N(3A)-H(33A)	117.9
C(25)-C(26)-H(26B)	109.5	C(13A)-N(3A)-H(33A)	117.9
H(26A)-C(26)-H(26B)	109.5	C(24A)-N(4A)-C(19A)	123(2)
C(25)-C(26)-H(26C)	109.5	C(24A)-N(4A)-H(44A)	118.6
H(26A)-C(26)-H(26C)	109.5	C(19A)-N(4A)-H(44A)	118.6
H(26B)-C(26)-H(26C)	109.5	N(1A)-C(1A)-C(6A)	121.5(18)
C(25)-C(27)-H(27A)	109.5	N(1A)-C(1A)-C(2A)	119(2)
C(25)-C(27)-H(27B)	109.5	C(6A)-C(1A)-C(2A)	120(2)
H(27A)-C(27)-H(27B)	109.5	C(3A)-C(2A)-C(1A)	116(2)
C(25)-C(27)-H(27C)	109.5	C(3A)-C(2A)-H(2A)	121.8
H(27A)-C(27)-H(27C)	109.5	C(1A)-C(2A)-H(2A)	121.8
H(27B)-C(27)-H(27C)	109.5	C(4A)-C(3A)-C(2A)	125(2)
C(25)-C(28)-H(28A)	109.5	C(4A)-C(3A)-H(3A)	117.4
C(25)-C(28)-H(28B)	109.5	C(2A)-C(3A)-H(3A)	117.4
H(28A)-C(28)-H(28B)	109.5	C(5A)-C(4A)-C(3A)	118(3)
C(25)-C(28)-H(28C)	109.5	C(5A)-C(4A)-H(4A)	121.2
H(28A)-C(28)-H(28C)	109.5	C(3A)-C(4A)-H(4A)	121.2
H(28B)-C(28)-H(28C)	109.5	C(4A)-C(5A)-C(6A)	120(3)
O(1A)-P(1A)-N(2A)	109.6(9)	C(4A)-C(5A)-H(5A)	120.2
O(1A)-P(1A)-N(1A)	105.2(10)	C(6A)-C(5A)-H(5A)	120.2
N(2A)-P(1A)-N(1A)	94.1(9)	C(1A)-C(6A)-C(5A)	122(2)
O(1A)-P(1A)-Pd(1)	105.0(5)	C(1A)-C(6A)-H(6A)	119.2
N(2A)-P(1A)-Pd(1)	117.1(8)	C(5A)-C(6A)-H(6A)	119.2
N(1A)-P(1A)-Pd(1)	124.9(6)	N(1A)-C(7A)-C(8A)	109.5(18)
C(12A)-O(1A)-P(1A)	121.0(13)	N(1A)-C(7A)-H(7A1)	109.8
C(24A)-O(4A)-C(25A)	125(2)	C(8A)-C(7A)-H(7A1)	109.8
C(1A)-N(1A)-C(7A)	124.6(17)	N(1A)-C(7A)-H(7A2)	109.8

C(8A)-C(7A)-H(7A2)	109.8
H(7A1)-C(7A)-H(7A2)	108.2
C(7A)-C(8A)-N(2A)	104.0(16)
C(7A)-C(8A)-C(9A)	117(2)
N(2A)-C(8A)-C(9A)	104(2)
C(7A)-C(8A)-H(8A)	110.5
N(2A)-C(8A)-H(8A)	110.5
C(9A)-C(8A)-H(8A)	110.5
C(10A)-C(9A)-C(8A)	106(2)
C(10A)-C(9A)-H(9A1)	110.5
C(8A)-C(9A)-H(9A1)	110.5
C(10A)-C(9A)-H(9A2)	110.5
C(8A)-C(9A)-H(9A2)	110.5
H(9A1)-C(9A)-H(9A2)	108.7
C(9A)-C(10A)-C(11A)	111(3)
C(9A)-C(10A)-H(10C)	109.5
C(11A)-C(10A)-H(10C)	109.5
C(9A)-C(10A)-H(10D)	109.5
C(11A)-C(10A)-H(10D)	109.5
H(10C)-C(10A)-H(10D)	108.0
N(2A)-C(11A)-C(10A)	106(2)
N(2A)-C(11A)-H(11C)	110.5
C(10A)-C(11A)-H(11C)	110.5
N(2A)-C(11A)-H(11D)	110.5
C(10A)-C(11A)-H(11D)	110.5
H(11C)-C(11A)-H(11D)	108.6
O(1A)-C(12A)-C(13A)	109.8(17)
O(1A)-C(12A)-H(12C)	109.7
C(13A)-C(12A)-H(12C)	109.7
O(1A)-C(12A)-H(12D)	109.7
C(13A)-C(12A)-H(12D)	109.7
H(12C)-C(12A)-H(12D)	108.2
C(14A)-C(13A)-N(3A)	112.4(18)
C(14A)-C(13A)-C(12A)	118(2)
N(3A)-C(13A)-C(12A)	105(2)
C(14A)-C(13A)-H(13A)	106.9
N(3A)-C(13A)-H(13A)	106.9
C(12A)-C(13A)-H(13A)	106.9
C(13A)-C(14A)-C(17A)	111(2)
C(13A)-C(14A)-C(15A)	110(2)
C(17A)-C(14A)-C(15A)	106(2)
C(13A)-C(14A)-C(16A)	112(3)
C(17A)-C(14A)-C(16A)	111(2)
C(15A)-C(14A)-C(16A)	106(2)
C(14A)-C(15A)-H(15D)	109.5
C(14A)-C(15A)-H(15E)	109.5
H(15D)-C(15A)-H(15E)	109.5
C(14A)-C(15A)-H(15F)	109.5
H(15D)-C(15A)-H(15F)	109.5
H(15E)-C(15A)-H(15F)	109.5
C(14A)-C(16A)-H(16D)	109.5
C(14A)-C(16A)-H(16E)	109.5
H(16D)-C(16A)-H(16E)	109.5
C(14A)-C(16A)-H(16F)	109.5
H(16D)-C(16A)-H(16F)	109.5
H(16E)-C(16A)-H(16F)	109.5
C(14A)-C(17A)-H(17D)	109.5
C(14A)-C(17A)-H(17E)	109.5
H(17D)-C(17A)-H(17E)	109.5
C(14A)-C(17A)-H(17F)	109.5
H(17D)-C(17A)-H(17F)	109.5
H(17E)-C(17A)-H(17F)	109.5
O(2A)-C(18A)-N(3A)	122(3)
O(2A)-C(18A)-C(19A)	119(2)
N(3A)-C(18A)-C(19A)	119(2)
N(4A)-C(19A)-C(18A)	111(2)

N(4A)-C(19A)-C(20A)	116(2)
C(18A)-C(19A)-C(20A)	114(2)
N(4A)-C(19A)-H(19A)	104.5
C(18A)-C(19A)-H(19A)	104.5
C(20A)-C(19A)-H(19A)	104.5
C(21A)-C(20A)-C(22A)	114(3)
C(21A)-C(20A)-C(19A)	111(2)
C(22A)-C(20A)-C(19A)	107(2)
C(21A)-C(20A)-C(23A)	111(3)
C(22A)-C(20A)-C(23A)	107(2)
C(19A)-C(20A)-C(23A)	107(2)
C(20A)-C(21A)-H(21D)	109.5
C(20A)-C(21A)-H(21E)	109.5
H(21D)-C(21A)-H(21E)	109.5
C(20A)-C(21A)-H(21F)	109.5
H(21D)-C(21A)-H(21F)	109.5
H(21E)-C(21A)-H(21F)	109.5
C(20A)-C(22A)-H(22D)	109.5
C(20A)-C(22A)-H(22E)	109.5
H(22D)-C(22A)-H(22E)	109.5
C(20A)-C(22A)-H(22F)	109.5
H(22D)-C(22A)-H(22F)	109.5
H(22E)-C(22A)-H(22F)	109.5
C(20A)-C(23A)-H(23D)	109.5
C(20A)-C(23A)-H(23E)	109.5
H(23D)-C(23A)-H(23E)	109.5
C(20A)-C(23A)-H(23F)	109.5
H(23D)-C(23A)-H(23F)	109.5
H(23E)-C(23A)-H(23F)	109.5
O(3A)-C(24A)-N(4A)	128(3)
O(3A)-C(24A)-O(4A)	120(3)
N(4A)-C(24A)-O(4A)	112(3)
C(27A)-C(25A)-O(4A)	104(2)
C(27A)-C(25A)-C(26A)	112(3)
O(4A)-C(25A)-C(26A)	108(2)
C(27A)-C(25A)-C(28A)	112(3)
O(4A)-C(25A)-C(28A)	109(3)
C(26A)-C(25A)-C(28A)	111(2)
C(25A)-C(26A)-H(26D)	109.5
C(25A)-C(26A)-H(26E)	109.5
H(26D)-C(26A)-H(26E)	109.5
C(25A)-C(26A)-H(26F)	109.5
H(26D)-C(26A)-H(26F)	109.5
H(26E)-C(26A)-H(26F)	109.5
C(25A)-C(27A)-H(27D)	109.5
C(25A)-C(27A)-H(27E)	109.5
H(27D)-C(27A)-H(27E)	109.5
C(25A)-C(27A)-H(27F)	109.5
H(27D)-C(27A)-H(27F)	109.5
H(27E)-C(27A)-H(27F)	109.5
C(25A)-C(28A)-H(28D)	109.5
C(25A)-C(28A)-H(28E)	109.5
H(28D)-C(28A)-H(28E)	109.5
C(25A)-C(28A)-H(28F)	109.5
H(28D)-C(28A)-H(28F)	109.5
H(28E)-C(28A)-H(28F)	109.5

X-RAY STRUCTURE DETERMINATIONS

Table S11. Torsion angles [°] for [Pd(allyl)(**L3d**)$_2$]BF_4.

Pd(1)-C(81)-C(82)-C(83)	42(7)	P(1)-N(2)-C(8)-C(7)	-26(3)
C(81)-C(82)-C(83)-Pd(1)	-41(7)	C(11)-N(2)-C(8)-C(9)	17(3)
N(2)-P(1)-O(1)-C(12)	50.9(17)	P(1)-N(2)-C(8)-C(9)	-145.6(18)
N(1)-P(1)-O(1)-C(12)	-46.9(16)	N(1)-C(7)-C(8)-N(2)	34(3)
Pd(1)-P(1)-O(1)-C(12)	175.7(13)	N(1)-C(7)-C(8)-C(9)	148(2)
N(2)-P(1)-N(1)-C(1)	-175.4(19)	N(2)-C(8)-C(9)-C(10)	-32(3)
O(1)-P(1)-N(1)-C(1)	-64.2(19)	C(7)-C(8)-C(9)-C(10)	-149(2)
Pd(1)-P(1)-N(1)-C(1)	58(2)	C(8)-C(9)-C(10)-C(11)	38(3)
N(2)-P(1)-N(1)-C(7)	16.8(17)	C(8)-N(2)-C(11)-C(10)	6(3)
O(1)-P(1)-N(1)-C(7)	128.1(15)	P(1)-N(2)-C(11)-C(10)	166(2)
Pd(1)-P(1)-N(1)-C(7)	-110.1(14)	C(9)-C(10)-C(11)-N(2)	-26(3)
O(1)-P(1)-N(2)-C(8)	-101.7(18)	P(1)-O(1)-C(12)-C(13)	-169.0(12)
N(1)-P(1)-N(2)-C(8)	5.4(19)	C(18)-N(3)-C(13)-C(14)	113(2)
Pd(1)-P(1)-N(2)-C(8)	141.5(16)	C(18)-N(3)-C(13)-C(12)	-124(2)
O(1)-P(1)-N(2)-C(11)	98(2)	O(1)-C(12)-C(13)-N(3)	72.2(18)
N(1)-P(1)-N(2)-C(11)	-155(2)	O(1)-C(12)-C(13)-C(14)	-162.6(16)
Pd(1)-P(1)-N(2)-C(11)	-19(2)	N(3)-C(13)-C(14)-C(15)	-59(3)
C(7)-N(1)-C(1)-C(6)	2(3)	C(12)-C(13)-C(14)-C(15)	-179.0(19)
P(1)-N(1)-C(1)-C(6)	-165.0(19)	N(3)-C(13)-C(14)-C(16)	59(3)
C(7)-N(1)-C(1)-C(2)	-173(2)	C(12)-C(13)-C(14)-C(16)	-61(3)
P(1)-N(1)-C(1)-C(2)	21(3)	N(3)-C(13)-C(14)-C(17)	179(2)
C(6)-C(1)-C(2)-C(3)	2(4)	C(12)-C(13)-C(14)-C(17)	59(2)
N(1)-C(1)-C(2)-C(3)	177(2)	C(13)-N(3)-C(18)-O(2)	-3(4)
C(1)-C(2)-C(3)-C(4)	-5(4)	C(13)-N(3)-C(18)-C(19)	174(2)
C(2)-C(3)-C(4)-C(5)	6(4)	C(24)-N(4)-C(19)-C(18)	-127(2)
C(3)-C(4)-C(5)-C(6)	-5(4)	C(24)-N(4)-C(19)-C(20)	99(3)
C(4)-C(5)-C(6)-C(1)	2(4)	O(2)-C(18)-C(19)-N(4)	148(2)
C(2)-C(1)-C(6)-C(5)	0(4)	N(3)-C(18)-C(19)-N(4)	-29(3)
N(1)-C(1)-C(6)-C(5)	-175(2)	O(2)-C(18)-C(19)-C(20)	-79(3)
C(1)-N(1)-C(7)-C(8)	160(2)	N(3)-C(18)-C(19)-C(20)	104(2)
P(1)-N(1)-C(7)-C(8)	-32(2)	N(4)-C(19)-C(20)-C(23)	81(3)
C(11)-N(2)-C(8)-C(7)	137(2)	C(18)-C(19)-C(20)-C(23)	-54(3)

N(4)-C(19)-C(20)-C(21)	-40(3)	C(2A)-C(3A)-C(4A)-C(5A)	-1(5)
C(18)-C(19)-C(20)-C(21)	-174.2(19)	C(3A)-C(4A)-C(5A)-C(6A)	-1(5)
N(4)-C(19)-C(20)-C(22)	-161(2)	N(1A)-C(1A)-C(6A)-C(5A)	-179(2)
C(18)-C(19)-C(20)-C(22)	65(3)	C(2A)-C(1A)-C(6A)-C(5A)	-3(4)
C(25)-O(4)-C(24)-O(3)	-15(4)	C(4A)-C(5A)-C(6A)-C(1A)	3(5)
C(25)-O(4)-C(24)-N(4)	170(2)	C(1A)-N(1A)-C(7A)-C(8A)	154(2)
C(19)-N(4)-C(24)-O(3)	7(4)	P(1A)-N(1A)-C(7A)-C(8A)	-24(2)
C(19)-N(4)-C(24)-O(4)	-178.6(18)	N(1A)-C(7A)-C(8A)-N(2A)	25(3)
C(24)-O(4)-C(25)-C(26)	60(3)	N(1A)-C(7A)-C(8A)-C(9A)	139(2)
C(24)-O(4)-C(25)-C(27)	-176(2)	C(11A)-N(2A)-C(8A)-C(7A)	134(2)
C(24)-O(4)-C(25)-C(28)	-59(3)	P(1A)-N(2A)-C(8A)-C(7A)	-18(2)
N(2A)-P(1A)-O(1A)-C(12A)	44.3(19)	C(11A)-N(2A)-C(8A)-C(9A)	11(2)
N(1A)-P(1A)-O(1A)-C(12A)	-55.9(18)	P(1A)-N(2A)-C(8A)-C(9A)	-141.2(17)
Pd(1)-P(1A)-O(1A)-C(12A)	170.8(15)	C(7A)-C(8A)-C(9A)-C(10A)	-116(2)
O(1A)-P(1A)-N(1A)-C(1A)	-56(2)	N(2A)-C(8A)-C(9A)-C(10A)	-2(3)
N(2A)-P(1A)-N(1A)-C(1A)	-167.2(19)	C(8A)-C(9A)-C(10A)-C(11A)	-8(3)
Pd(1)-P(1A)-N(1A)-C(1A)	65(2)	C(8A)-N(2A)-C(11A)-C(10A)	-16(3)
O(1A)-P(1A)-N(1A)-C(7A)	122.7(16)	P(1A)-N(2A)-C(11A)-C(10A)	132(2)
N(2A)-P(1A)-N(1A)-C(7A)	11.1(17)	C(9A)-C(10A)-C(11A)-N(2A)	15(3)
Pd(1)-P(1A)-N(1A)-C(7A)	-116.2(14)	P(1A)-O(1A)-C(12A)-C(13A)	-159.3(16)
O(1A)-P(1A)-N(2A)-C(11A)	110(2)	C(18A)-N(3A)-C(13A)-C(14A)	123(3)
N(1A)-P(1A)-N(2A)-C(11A)	-142(2)	C(18A)-N(3A)-C(13A)-C(12A)	-107(2)
Pd(1)-P(1A)-N(2A)-C(11A)	-9(2)	O(1A)-C(12A)-C(13A)-C(14A)	-164(2)
O(1A)-P(1A)-N(2A)-C(8A)	-102.8(17)	O(1A)-C(12A)-C(13A)-N(3A)	69(2)
N(1A)-P(1A)-N(2A)-C(8A)	5.0(18)	N(3A)-C(13A)-C(14A)-C(17A)	-55(3)
Pd(1)-P(1A)-N(2A)-C(8A)	137.9(14)	C(12A)-C(13A)-C(14A)-C(17A)	-178(2)
C(7A)-N(1A)-C(1A)-C(6A)	-175(2)	N(3A)-C(13A)-C(14A)-C(15A)	-172(2)
P(1A)-N(1A)-C(1A)-C(6A)	3(3)	C(12A)-C(13A)-C(14A)-C(15A)	65(3)
C(7A)-N(1A)-C(1A)-C(2A)	9(3)	N(3A)-C(13A)-C(14A)-C(16A)	70(3)
P(1A)-N(1A)-C(1A)-C(2A)	-172.7(18)	C(12A)-C(13A)-C(14A)-C(16A)	-53(3)
N(1A)-C(1A)-C(2A)-C(3A)	177(2)	C(13A)-N(3A)-C(18A)-O(2A)	-12(4)
C(6A)-C(1A)-C(2A)-C(3A)	1(4)	C(13A)-N(3A)-C(18A)-C(19A)	176(2)
C(1A)-C(2A)-C(3A)-C(4A)	1(4)	C(24A)-N(4A)-C(19A)-C(18A)	-127(3)

C(24A)-N(4A)-C(19A)-C(20A)	100(3)
O(2A)-C(18A)-C(19A)-N(4A)	149(2)
N(3A)-C(18A)-C(19A)-N(4A)	-39(3)
O(2A)-C(18A)-C(19A)-C(20A)	-77(3)
N(3A)-C(18A)-C(19A)-C(20A)	96(3)
N(4A)-C(19A)-C(20A)-C(21A)	175(3)
C(18A)-C(19A)-C(20A)-C(21A)	43(3)
N(4A)-C(19A)-C(20A)-C(22A)	-60(3)
C(18A)-C(19A)-C(20A)-C(22A)	168(2)
N(4A)-C(19A)-C(20A)-C(23A)	54(3)
C(18A)-C(19A)-C(20A)-C(23A)	-78(3)
C(19A)-N(4A)-C(24A)-O(3A)	11(4)
C(19A)-N(4A)-C(24A)-O(4A)	-170.5(19)
C(25A)-O(4A)-C(24A)-O(3A)	-11(4)
C(25A)-O(4A)-C(24A)-N(4A)	170(2)
C(24A)-O(4A)-C(25A)-C(27A)	-168(3)
C(24A)-O(4A)-C(25A)-C(26A)	73(3)
C(24A)-O(4A)-C(25A)-C(28A)	-48(3)

X-RAY STRUCTURE DETERMINATIONS

Table S12. Crystal data for **L1d**.

empirical formula	$C_{21}H_{34}N_3O_3PS$
M_r	439.54
crystal system	Triclinic
space group	*P 1*
diffractometer	Stoe Stadi-P
wavelength, Å	1.54059
unit cell dimensions	
a, Å	6.2154(9)
b, Å	9.2338(12)
c, Å	11.1198(15)
α, °	79.356(14)
β, °	86.919(17)
γ, °	70.801(12)
volume, Å^3	592.30(14)
Z	1
D_x (Mg m^{-3})	1.232
μ, mm^{-1}	2.058
$2\theta_{min}$ - $2\theta_{max}$, $\Delta 2\theta$ (°)	7.00 – 70.09, 0.01
no. params/restraints	141/119
R_p, R_{wp}, R_{exp}	0.0315, 0.0415, 0.0275

X-RAY STRUCTURE DETERMINATIONS

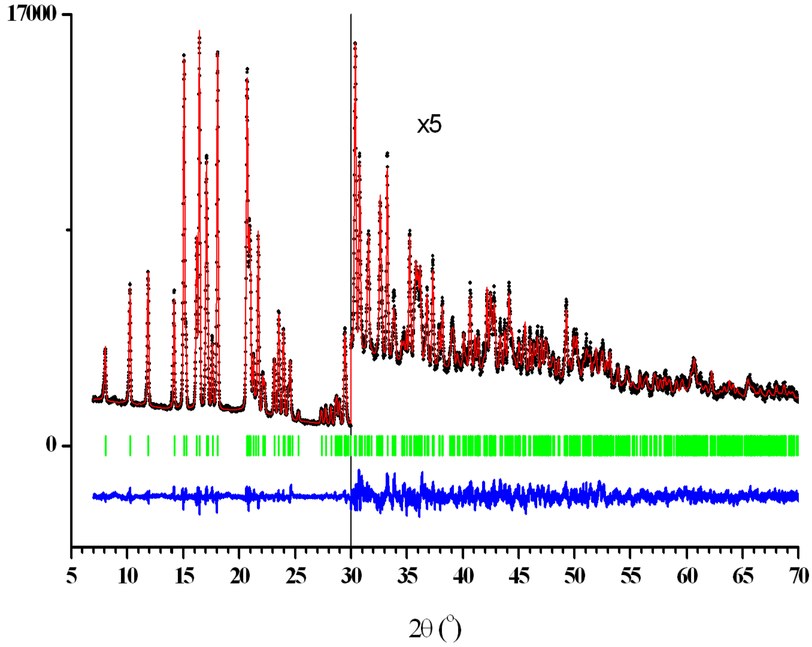


Figure S56. The final Rietveld plot for **L1d**. The experimental diffraction profile is indicated by black dots. The calculated diffraction profile is shown as the upper red line, the difference profile is shown as the bottom blue line, and the vertical green bars correspond to the calculated positions of the Bragg peaks.

HPLC TRACES FOR THE Pd-CATALYZED ALLYLIC SUBSTITUTION

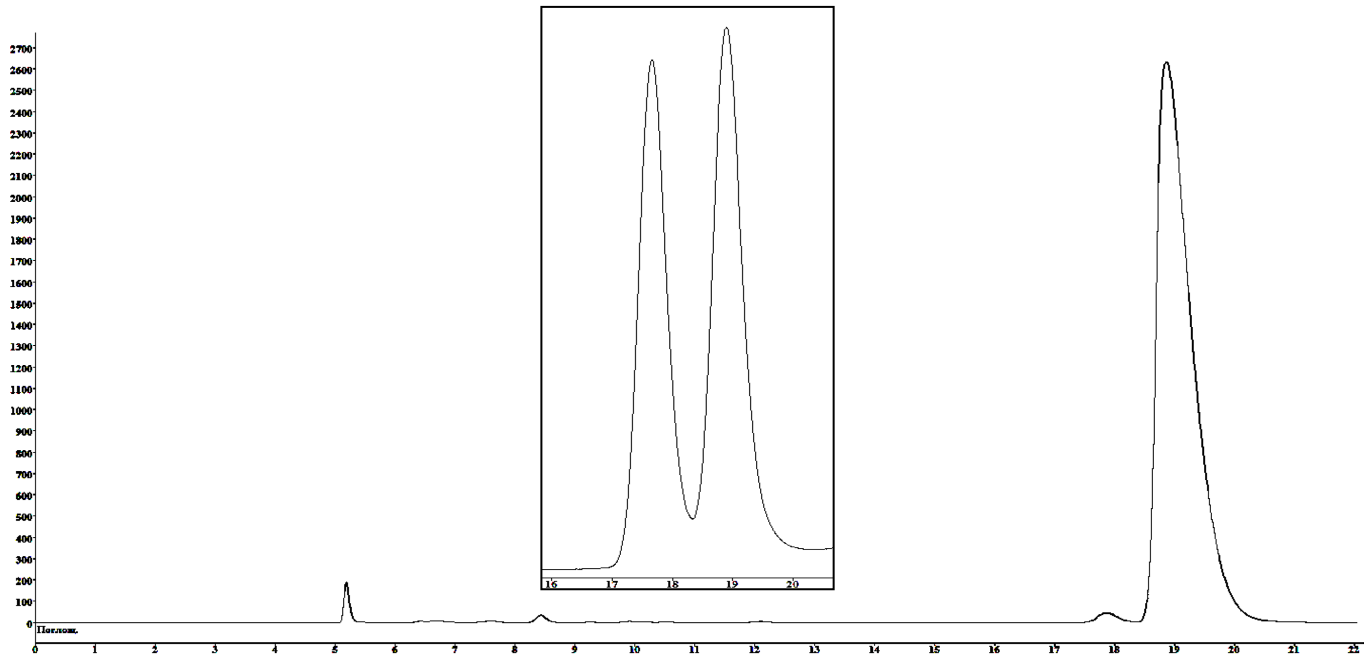


Figure S57. Chiral HPLC trace for the Pd-catalyzed asymmetric allylic alkylation of (*E*)-1,3-diphenylallyl ethyl carbonate (**7**) with dimethyl malonate (entry 2 in Table 1) and for a racemic mixture of (*E*)-dimethyl 2-(1,3-diphenylallyl)malonate (**8a**) (in the frame).

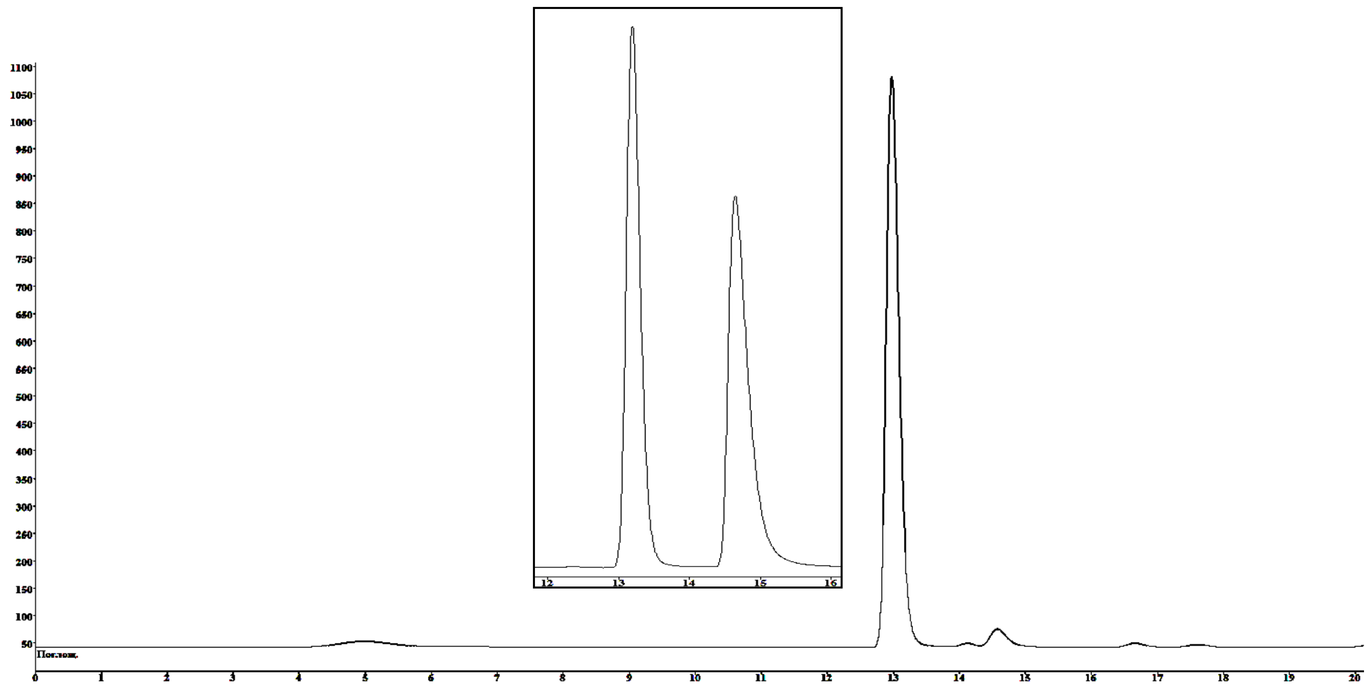


Figure S58. Chiral HPLC trace for the Pd-catalyzed asymmetric allylic amination of (*E*)-1,3-diphenylallyl ethyl carbonate (**7**) with pyrrolidine (entry 2 in Table 2) and for a racemic mixture of (*E*)-1-(1,3-diphenylallyl)pyrrolidine (**8b**) (in the frame).

HPLC TRACES FOR THE Pd-CATALYZED ALLYLIC SUBSTITUTION

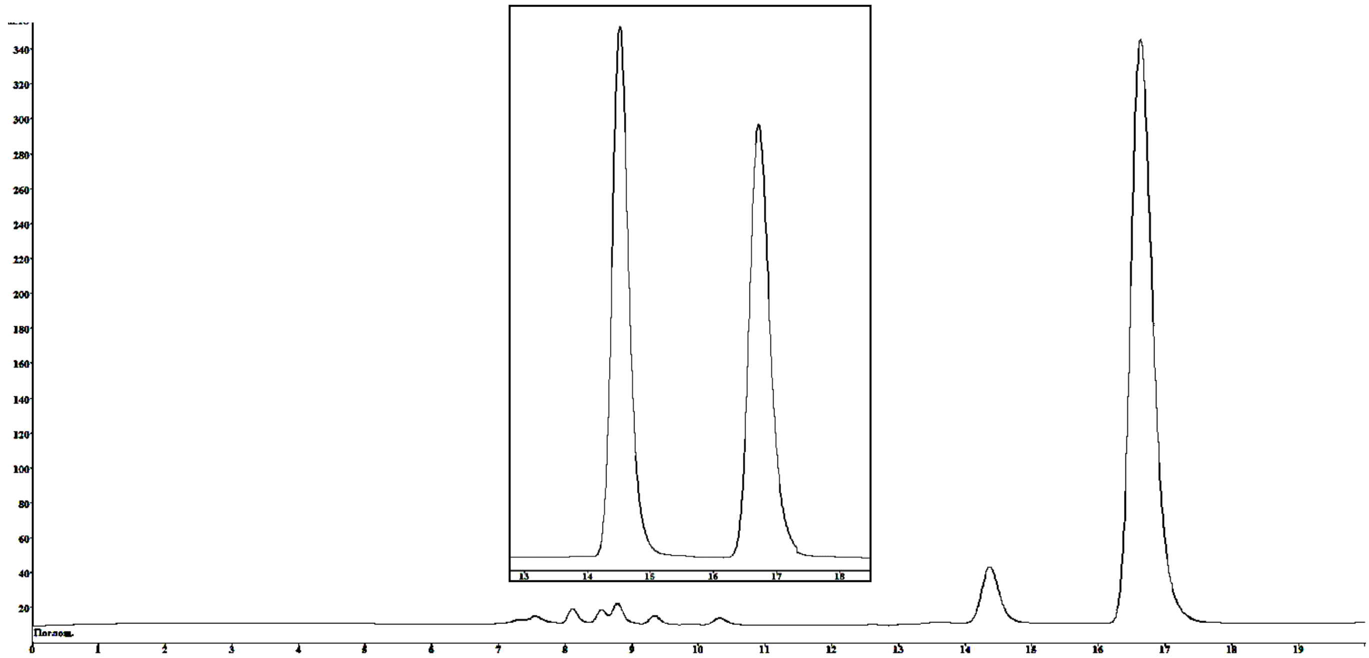


Figure S59. Chiral HPLC trace for the Pd-catalyzed asymmetric allylic alkylation of cinnamyl acetate (**9**) with ethyl 2-oxocyclohexane-1-carboxylate (**10**) (entry 9 in Table 3) and for a racemic mixture of ethyl 1-cinnamyl-2-oxocyclohexanecarboxylate (**11**) (in the frame).

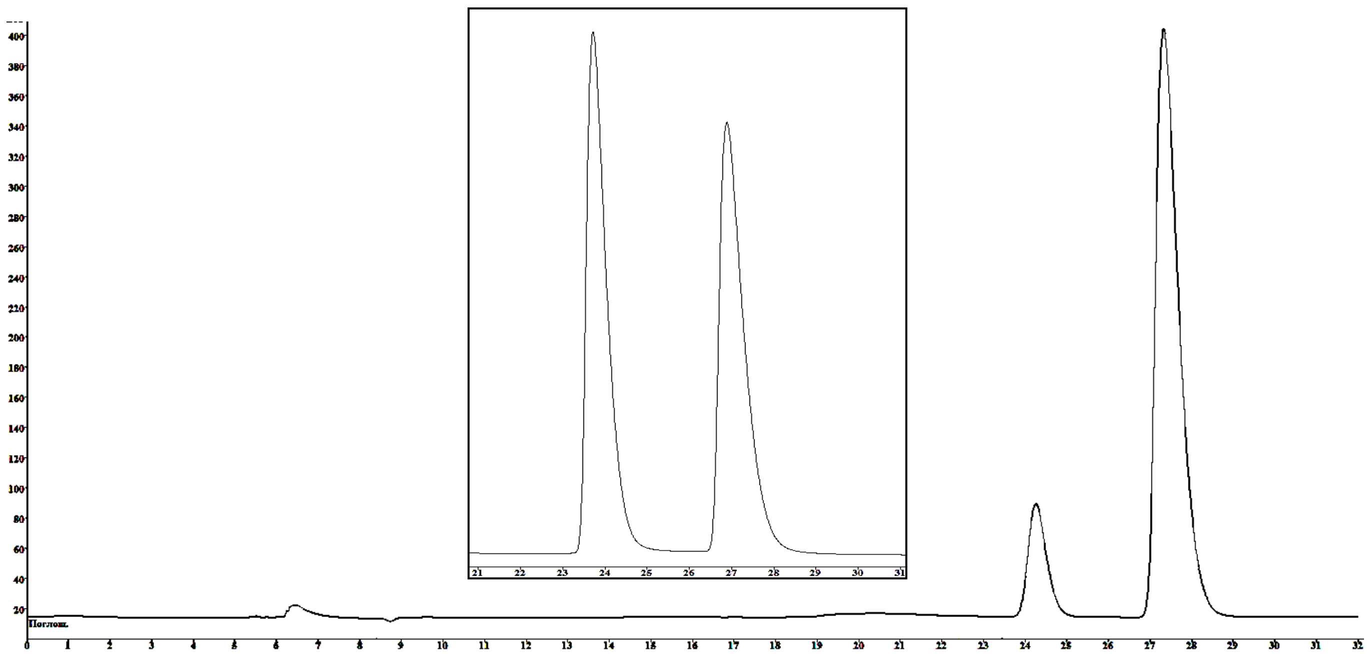


Figure S60. Chiral HPLC trace for the Pd-catalyzed asymmetric allylic alkylation of cinnamyl acetate (**9**) with ethyl 2-oxocyclopentane-1-carboxylate (**12**) (entry 8 in Table 4) and for a racemic mixture of ethyl 1-cinnamyl-2-oxocyclopentanecarboxylate (**13**) (in the frame).

STUDIES OF INTRAMOLECULAR ROTATION IN N-BOC-PROLINE DERIVATIVES

Due to the hindered rotations at room temperature about the C–N bonds of the carboxamides, two groups of signals corresponding to the *cis* and *trans* orientations of the two t-butoxycarbonyl-groups with respect to the pyrrolydine ring of proline are observed for precursor **4** and both ligands **L2** and **L4** (**Figure S61**). (*Cis* and *trans* orientations correspond to the *Z* and *E* isomers respectively, when we consider the double bonds between nitrogen and carbon atoms of the Boc-amide-group.) Heating or freezing of the solutions in toluene-d8 (or $CDCl_3$) allows determining the coalescence temperature for the signals of the *tert*-butyl groups protons for precursor **4** or ^{31}P signals for both ligands **L2** and **L4**. The coalescence temperatures are represented in **Table S13**. It is possible to calculate $\Delta G\#$ at coalescence temperature for the intramolecular rotation using Eiring equation. The calculated values are represented in **Table S13**. We can find both salvation and substitution contributes the intermolecular rotation barriers, as the attachment of the phosphorous group to the precursor **4** led to increase the rotation barrier and the changing the solvent from $CDCl_3$ to toluene-d8 also lead to obstruction of the rotation.

To test the assumption of the restricted intramolecular rotation in Boc-proline moiety we decided as a first step to perform DFT calculations of potential energy surface (PES) along the O=C-N-C(H) torsion angle using first-principles DFT (GGA PBE).[1, 2] The intercept curve (**Figure S61**) shows two minima corresponding two rotamers of **4** and **L4** and two maxima between them. The relaxed geometries of **4** and **L4** were completely optimized for the gas phase conditions.[3] The precision analysis of PES specifies the relative energies of minima and transition states at the tops of the intercept curve (**Table S13**).

Table S13. Calculated and experimental parameters of intramolecular rotation around the Boc-Pro amide bond in **4**, **L2** and **L4**

	4		**L4**		**L2**	
	deg	ΔE, kcal/mol	deg	ΔE, kcal/mol	deg	ΔE, kcal/mol
Minima	11.27 196.86	0 3.38	11.35 197.12	0 3.24	8.43 189.46	0 0.13
Transition states	115.03 298.92	16.42 15.91	114.94 298.31	16.44 15.71	115.06 298.21	15.70 16.60
Energy of intermolecular rotation barrier from NMR, kcal/mol	13.0		15.6		18.4	
Coalescence temperatures	286		341		403	

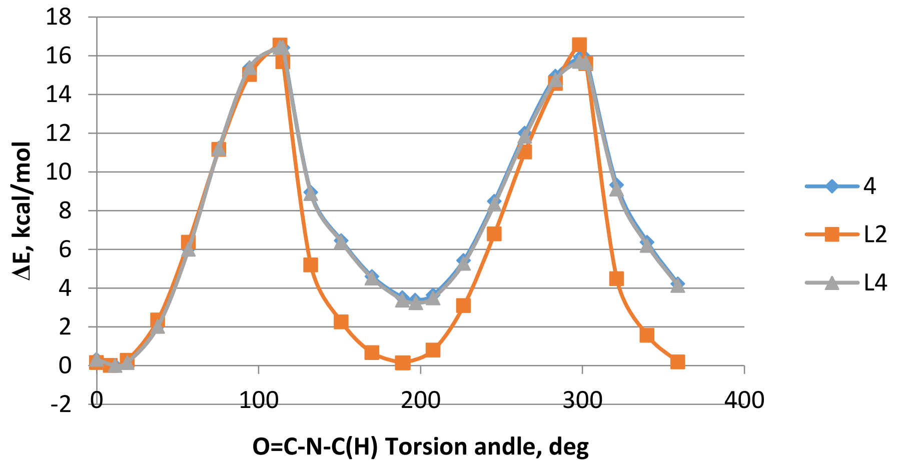


Figure S61. Intramolecular rotation around the Boc-Pro amide bond in in **4**, **L2** and **L4**.

1. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
2. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1997, **78**, 1396.
3. D. N. Laikov, *Chem. Phys. Lett.*, 2005, **416**, 116.