SUPPLEMENTARY INFORMATION

Diverse “roof shape” chiral diamidophosphites: Palladium coordination and catalytic application

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TABLE OF CONTENTS

GENERAL

$^{31}P\{^{1}H\}$, $^{13}C\{^{1}H\}$ and ^{1}H NMR spectra were recorded with Bruker Avance 600 (242.9 MHz for $^{31}P\{^{1}H\}$, 150.9 MHz for $^{13}C\{^{1}H\}$ and 600.1 MHz for ^{1}H) and Varian Inova 500 (202.3 MHz for $^{31}P\{^{1}H\}$, 125.7 MHz for $^{13}C\{^{1}H\}$ and 499.8 MHz for ^{1}H) instruments. ^{1}H and $^{13}C\{^{1}H\}$ NMR signals were attributed using APT, DEPT, $^{1}H,^{1}H$ – COSY, $^{1}H,^{1}H$ – TOCSY, $^{1}H,^{1}H$ – NOESY, $^{13}C,^{1}H$ – HSQC and $^{13}C,^{1}H$ – HMBC techniques. The chemical shifts are referenced to residual solvent peaks (^{1}H, $^{13}C\{^{1}H\}$ 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, q = quartet). Diffusion-ordered NMR spectroscopy (DOSY) was performed on a Bruker Avance 600 spectrometer equipped with a direct Quattro Nucleus Probe (QNP) and a z-gradient coil controlled by a Great 1/10 gradient unit, by using the double-stimulated echo pulse sequence dstegp3s from the Bruker TopSpin 4.0.7 program package without spinning in CD_2Cl_2 at 303K. The residual resonance of $CHDCl_2$ was used as internal standard. Hydrodynamic radii were calculated from diffusion coefficients using the Stokes-Einstein equation with correction factor 1 (assuming the spherical particle). The structures of molecules were calculated using the Gaussian 09W[1] software package with density functional theory (DFT) method implementing the hybrid correlation-exchange functional B3LYP.[2] For mononuclear complex [Pd(allyl)(**L1a**)]BF_4 the 3-21G basis set was used for geometry optimizations and the 6-31G(d) basis set was used for volume and energy calculations, electrons of palladium atom were rendered by the LaNL2DZ basis set with an effective potential for internal electrons. The solvent effects were accounted by the polarizable continuum model (PCM). Geometries of dinuclear complex [Pd(allyl)(**L5a**)]$_2$(BF_4)$_2$ were optimized using the semi-empirical PM6 method and molecular volumes were computed by the DFT method with the 3-21G basis set. Mass spectra were recorded on a Bruker FT-ICR-MS solariX XR 15T spectrometer (ESI-TOF). HPLC analyses were performed on a Stayer instrument using Kromasil 5-CelluCoat and Daicel Chiralcel OD-H columns. Optical rotations were measured with an Atago AP-300 polarimeter. Elemental analyses were performed on a CHN-microanalyzer Carlo Erba EA1108 CHNS-O.

The molecular structures of **L1a** and **L1b** were confirmed by single-crystal X-ray structure determinations. The diffraction intensities of **L1a** and **L1b** were collected on STOE diffractometer equipped with Pilatus100K detector and focusing mirror collimation (Cu $K\alpha_1$ radiation, l = 1.54086 Å) in a rotation 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.[3] 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[4] programs. The non-hydrogen atoms were refined by using the anisotropic full matrix least-square procedure. H-atoms were placed in calculated positions and refined in a riding mode. The crystal data, data collection and refinement parameters for **L1a** and **L1b** are given in Table S2. The molecular structures of **L1a** and **L1b** are shown in Figure 2, prepared with DIAMOND[5] software.

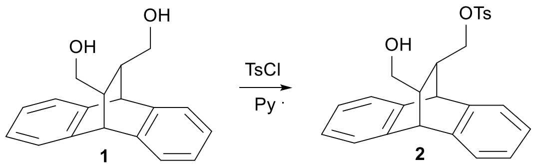
The crystal structures of **L4** and **L5a** were determined from powder data measured at room temperature on the beamline ID22 of the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The instrument is equipped with a cryogenically cooled double-crystal Si 111 monochromator and Si 111 analyzers. Each powder sample was loaded into a 1 mm diameter borosilicate thin-walled glass capillary which was rotated during measurements at a rate of 1200 rpm to improve the powder averaging. The powder patterns of **L4** and **L5a** were indexed in orthorhombic and monoclinic unit cells, respectively, and based on the systematic extinction rules the chiral space groups $P2_12_12_1$ and $P2_1$ were selected for the structure determination. The crystal structures were solved with the use of simulated annealing technique[6] and refined with the program MRIA[7] following the known procedures described by us earlier.[8-11] In the refinement, geometrical parameters of the rigid ferrocene fragment were kept close to the reported values (see, for example[12-14]). All non-H atoms were isotropically refined. H atoms were placed in calculated positions and not refined. The experimental and calculated diffraction profiles after the final bond-restrained Rietveld refinement are shown in Figures S1 and S2. The crystal data, data collection and refinement parameters for **L4** and **L5a** are given in Table S3. The molecular structures of **L4** and **L5a** are shown on Figure 3, prepared with *Mercury*.[15]

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. For the preparation of analytically pure samples, the obtained compounds were additionally dried in high vacuum (10^{-3} Torr) for 16 h.

The following compounds were synthesized according to literature procedures: (11*S*,12*S*)-bis(hydroxymethyl)-9,10-dihydro-9,10-ethanoanthracene (**1**),[16] (5*S*)-2-chloro-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane and (5*R*)-2-chloro-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane ((S_C)-**7** and (R_C)-**7**),[17] (1*S*,2*S*)-N^1,N^2-diphenylcyclohexane-1,2-diamine and (1*R*,2*R*)-N^1,N^2-diphenylcyclohexane-1,2-diamine ((*S*,*S*)-**S1** and (*R*,*R*)-**S1**),[18] $[Pd(allyl)Cl]_2$ and (*E*)-1,3-diphenylallyl acetate (**9**),[19] ethyl 2-acetamido-3-oxobutanoate (**14**),[20] 2-(diethoxyphosphoryl)-1-phenylallyl acetate (**18**).[21] (1*S*,2*S*)- and (1*R*,2*R*)-Cyclohexane-1,2-diamine (starting compound for the preparation of **S1**) was resolved from the racemic mixture using (*S*,*S*)- and (*R*,*R*)-tartaric acid, respectively, following the known procedure.[22] Pd-catalyzed allylic alkylation of **9** with dimethyl malonate, its amination with pyrrolidine or phthalimide, allylic alkylation of cinnamyl acetate (**11**) with ethyl 2-oxocyclohexane-1-carboxylate (**12**), ethyl 2-acetamido-3-oxobutanoate (**14**) or 2-acetyl-3,4-dihydronaphthalen-1(2*H*)-one (**16**), allylic amination of **18** with aniline were performed according to the appropriate procedures.[9,17,21,23-25]

p-Toluenesulfonyl chloride, thiophenol, ferrocenecarboxaldehyde, racemic cyclohexane-1,2-diamine, dimethyl malonate, BSA (*N*,*O*-bis(trimethylsilyl)acetamide), cinnamyl acetate (**11**), ethyl 2-oxocyclohexane-1-carboxylate (**12**) and 2-acetyl-3,4-dihydronaphthalen-1(2*H*)-one (**16**) were purchased from Aldrich and Acros Organics.

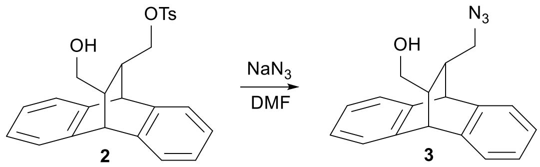
EXPERIMENTAL SECTION



Procedure for the Preparation of Monotosylate 2: A solution of *p*-toluenesulfonyl chloride (4.39 g, 23 mmol) in pyridine (10 mL) was added at 0 °C to a stirred solution of diol **1** (5.86 g, 22 mmol) in pyridine (15 mL) over 5 min. The reaction mixture was stirred for 16 h at 0 °C. CH_2Cl_2 (60 mL) and ice (4.0 g) were then added. The organic layer was washed in turn with 4 M HCl (25 mL), saturated $NaHCO_3$ (20 mL) and brine (20 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuum (40 Torr). The residue was dried for 30 min at 10 Torr and chromatographed on Al_2O_3 (hexane/EtOAc = 2/1).

((11*S*,12*S*)-12-((Tosyloxy)methyl)-9,10-dihydro-9,10-ethanoanthracen-11-yl)methanol (**2**): White viscous foam that solidified on standing, yield 4.26 g (46 %). ^{1}H NMR (600.1 MHz, $CDCl_3$, 30 ^{o}C): δ = 1.42-1.45 (m, 1H; $CHC\underline{H}CH_2OH$), 1.58 (br.s, 1H; $CHCHCH_2O\underline{H}$), 1.72-1.76 (m, 1H; $CHC\underline{H}CH_2OTs$), 2.47 (s, 3H; CH_3), 3.11-3.14 (dd, ^2J(H,H) = 10.4 Hz, ^3J(H,H) = 8.7 Hz, 1H; $CHCHC\underline{H}_2OH$), 3.28-3.30 (dd, ^2J(H,H) = 10.4 Hz, ^3J(H,H) = 6.3 Hz, 1H; $CHCHC\underline{H}_2OH$), 3.38 (t, ^2J(H,H) ~ ^3J(H,H) = 9.8 Hz, 1H; $CHCHC\underline{H}_2OTs$), 3.81-3.84 (dd, ^2J(H,H) = 9.6 Hz, ^3J(H,H) = 5.3 Hz, 1H; $CHCHC\underline{H}_2OTs$), 4.27 (d, ^3J(H,H) = 2.2 Hz, 1H; $C\underline{H}CHCH_2OTs$), 4.29 (d, ^3J(H,H) = 2.3 Hz, 1H; $C\underline{H}CHCH_2OH$), 6.97-7.01 (m, 2H; CH(Ar)), 7.07-7.10 (m, 1H; CH(Ar)), 7.10-7.14 (m, 2H; CH(Ar)), 7.22-7.27 (m, 3H; CH(Ar)), 7.35 (br.d, ^3J(H,H) ~ 8.0 Hz, 2H; CH(Ts)), 7.77 (br.d, ^3J(H,H) ~ 8.3 Hz, 2H; CH(Ts)) ppm. ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$, 30 ^{o}C): δ = 21.59 (CH_3), 42.29 ($CH\underline{C}HCH_2OTs$), 45.04 ($\underline{C}HCHCH_2OTs$), 45.15 ($CH\underline{C}HCH_2OH$), 45.30 ($\underline{C}HCHCH_2OH$), 65.23 ($CHCH\underline{C}H_2OH$), 72.16 ($CHCH\underline{C}H_2OTs$), 123.34 (CH(Ar)), 123.64 (CH(Ar)), 125.23 (CH(Ar)), 125.50 (CH(Ar)), 125.76 (CH(Ar)), 125.98 (CH(Ar)), 126.24 (CH(Ar)), 126.26 (CH(Ar)), 127.91 (CH(Ts)), 129.87 (CH(Ts)), 132.90 (C(Ts)), 139.62 (C(Ar)), 140.40 (C(Ar)), 142.44 (C(Ar)), 143.16 (C(Ar)), 144.82 (C(Ts)) ppm. $C_{25}H_{24}O_4S$ (420.14): calcd. C, 71.41; H, 5.75; found C 71.56, H 5.70.

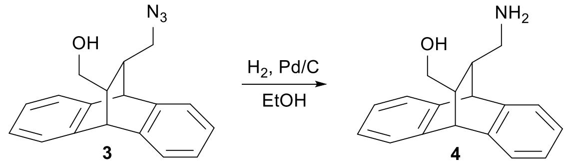
EXPERIMENTAL SECTION



Procedure for the Preparation of Azido Alcohol 3: Monotosylate **2** (3.28 g, 7.8 mmol) was dissolved in DMF (30 mL) and NaN_3 (1.01 g, 15.6 mmol) was added. The reaction mixture was stirred for 12 h at 100 °C. The DMF was removed under reduced pressure (1 Torr) and EtOAc (30 mL) and water (15 mL) were added to the residue. The aqueous phase was further extracted with EtOAc (2 x 30 mL). The combined organic phases was dried over anhydrous Na_2SO_4 and concentrated in vacuum (40 Torr). The residue was dried for 30 min at 10 Torr and chromatographed on SiO_2 (hexane/EtOAc = 2/1).

((11*S*,12*S*)-12-(Azidomethyl)-9,10-dihydro-9,10-ethanoanthracen-11-yl)methanol (**3**): White solid, yield 1.95 g (86 %). ^{1}H NMR (600.1 MHz, $CDCl_3$, 27 °C): δ = 1.56-1.64 (m, 2H; $CH_2C\underline{H}$), 1.70 (br.s, 1H; OH), 2.87-2.93 (dd, ^2J(H,H) = 12.0 Hz, ^3J(H,H) = 9.0 Hz, 1H; $C\underline{H}_2CH$), 3.06-3.10 (dd, ^2J(H,H) = 12.0 Hz, ^3J(H,H) = 6.3 Hz, 1H; $C\underline{H}_2CH$), 3.14-3.19 (dd, ^2J(H,H) = 10.3 Hz, ^3J(H,H) = 8.3 Hz, 1H; $C\underline{H}_2CH$), 3.31-3.35 (dd, ^2J(H,H) = 10.3 Hz, ^3J(H,H) = 6.0 Hz, 1H; $C\underline{H}_2CH$), 4.28 (d, ^3J(H,H) = 2.1 Hz, 1H; CH), 4.35 (d, ^3J(H,H) = 2.1 Hz, 1H; CH), 7.11-7.19 (m, 4H; CH(Ar)), 7.29-7.33 (m, 4H; CH(Ar)) ppm. $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$, 27 °C): δ = 42.95 (CH), 45.66 (CH), 46.30(CH), 46.52 (CH), 55.41 (CH_2), 65.49 (CH_2), 123.54 (CH(Ar)), 123.56 (CH(Ar)), 125.21 (CH(Ar)), 125.40 (CH(Ar)), 125.89 (CH(Ar)), 125.94 (CH(Ar)), 126.19 (CH(Ar)), 126.32 (CH(Ar)), 140.06 (C(Ar)), 140.45 (C(Ar)), 142.77 (C(Ar)), 143.19 (C(Ar)) ppm. All spectroscopic data for compound **3** were in good agreement with the literature.[26]

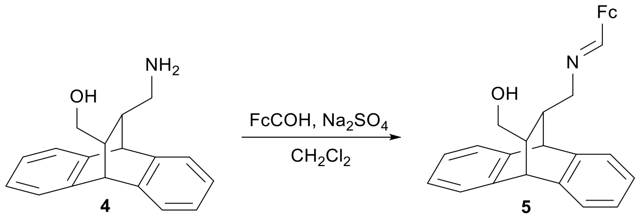
EXPERIMENTAL SECTION



Procedure for the Preparation of Amino Alcohol 4: Azido alcohol **3** (1.46 g, 5.02 mmol) was dissolved in ethanol (30 mL) and hydrogenated with 10% Pd/C (0.17 g) at room temperature in a hydrogen atmosphere for 5 h. The reaction mixture was filtered through a thin layer of Celite and concentrated in vacuum (40 Torr). The residue was dried for 30 min at 10 Torr and then for 12 h at 10^{-3} Torr.

((11*S*,12*S*)-12-(Aminomethyl)-9,10-dihydro-9,10-ethanoanthracen-11-yl)methanol (**4**): White solid, yield 1.29 g (97 %). (499.9 MHz, $CDCl_3$, ambient temperature): δ = 1.56-1.61 (m, 1H; $CHC\underline{H}CH_2NH_2$), 1.70-1.74 (m, 1H; $CHC\underline{H}CH_2OH$), 1.89-1.93 (dd, ^2J(H,H) = 12.4 Hz, ^3J(H,H) = 10.9 Hz, 1H; $CHCH\underline{CH_2}NH_2$), 2.39 (br.s, 3H; $CHCHCH_2O\underline{H}$ and $CHCHCH_2NH_2$), 2.87 (t, ^2J(H,H) = ^3J(H,H) = 9.8 Hz, 1H; $CHCH\underline{CH_2}OH$), 2.90-2.93 (dd, ^2J(H,H) = 12.4 Hz, ^3J(H,H) = 4.3 Hz, 1H; $CHCH\underline{CH_2}NH_2$), 3.62-3.65 (dd, ^2J(H,H) = 9.8 Hz, ^3J(H,H) = 4.8 Hz, 1H; $CHCH\underline{CH_2}OH$), 4.12 (d, ^3J(H,H) = 1.6 Hz, 1H; $C\underline{H}CHCH_2NH_2$), 4.15 (d, ^3J(H,H) = 1.6 Hz, 1H; $C\underline{H}CHCH_2OH$), 7.08-7.14 (m, 4H; CH(Ar)), 7.23-7.28 (m, 4H; CH(Ar)) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, ambient temperature): δ = 46.10 ($CHCH\underline{C}H_2NH_2$), 47.34 ($\underline{C}HCHCH_2OH$), 47.85 ($CH\underline{C}HCH_2NH_2$), 48.07 ($\underline{C}HCHCH_2NH_2$), 48.18 ($CH\underline{C}HCH_2OH$), 66.44 ($CHCH\underline{C}H_2OH$), 123.03 (CH(Ar)), 123.12 (CH(Ar)), 124.88 (CH(Ar)), 125.56 (CH(Ar)), 125.68 (CH(Ar)), 125.95 (CH(Ar)), 126.00 (CH(Ar)), 140.62 (C(Ar)), 140.66 (C(Ar)), 143.75 (C(Ar)), 143.97 (C(Ar)) ppm. $C_{18}H_{19}NO$ (265.15): calcd. C, 81.47; H, 7.22; N, 5.28; found C, 81.75; H, 7.30; N, 5.17.

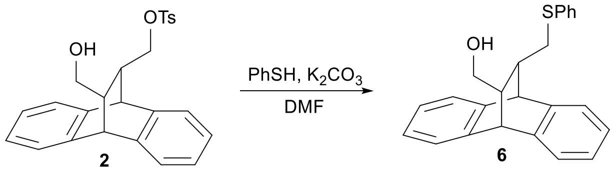
EXPERIMENTAL SECTION



Procedure for the Preparation of Imino Alcohol 5: Amino alcohol **4** (1.33 g, 5 mmol) was dissolved in CH_2Cl_2 (10 mL). Ferrocenecarboxaldehyde (1.07 g, 5 mmol) and Na_2SO_4 (1.42 g, 10 mmol) were added to this solution with stirring, and the reaction mixture was heated under reflux for 4 h. After the mixture had cooled to room temperature, the Na_2SO_4 was filtered off and washed with CH_2Cl_2. The filtrate was passed through a short plug of SiO_2 and concentrated in vacuum (40 Torr). The residue was dried for 30 min at 10 Torr and crystallized from toluene.

((11*S*,12*S*)-12-((((*E*)-Ferrocenylidene)amino)methyl)-9,10-dihydro-9,10-ethanoanthracen-11-yl)methanol (**5**): Orange-red solid, yield 1.89 g (82 %). ^{1}H NMR (600.1 MHz, Toluene-d8, 30 °C): δ = 1.89-1.94 (m, 1H; CHC<u>H</u>CH_2N), 1.91-1.96 (m, 1H; CHC<u>H</u>CH_2OH), 2.67-2.71 (m, 1H; CHCHC<u>H</u>$_2$N), 3.07 (t, ^2J(H,H) = ^3J(H,H) = 9.7 Hz, 1H; CHCHC<u>H</u>$_2$OH), 3.18-3.21 (dd, ^2J(H,H) = 12.8 Hz, ^3J(H,H) = 4.3 Hz, 1H; CHCHC<u>H</u>$_2$N), 3.71-3.73 (dd, ^2J(H,H) = 9.7 Hz, ^3J(H,H) = 4.7 Hz, 1H; CHCHC<u>H</u>$_2$OH), 3.95-3.96 (m, 1H; C<u>H</u>CHCH_2OH), 3.98 (s, 5H; C_5H_5(Fc)), 4.00 (d, ^3J(H,H) = 1.4 Hz, 1H; C<u>H</u>CHCH_2N), 4.04-4.06 (m, 2H; CH(Fc)), 4.12 (br.s, 1H; CHCHCH_2O<u>H</u>), 4.47 (br.s, 1H; CH(Fc)), 4.54 (br.s, 1H; CH(Fc)), 6.95-7.05 (m, 4H; CH(Ar)), 7.08-7.14 (m, 4H; CH(Ar)), 7.65 (s, 1H; FcCH) ppm. ^{13}C{^{1}H} NMR (150.9 MHz, Toluene-d8, 30 °C): δ = 46.36 (CH<u>C</u>HCH_2N), 47.85 (<u>C</u>HCHCH_2OH), 48.14 (CH<u>C</u>HCH_2OH), 48.71 (<u>C</u>HCHCH_2N), 65.57 (CHCH<u>C</u>H$_2$N), 67.25 (CHCH<u>C</u>H$_2$OH), 68.79 (CH(Fc)), 69.08 (CH(Fc)), 69.53 (C_5H_5(Fc)), 70.68 (CH(Fc)), 70.79 (CH(Fc)), 80.27 (C(Fc)), 123.37 (CH(Ar)), 123.54 (CH(Ar)), 125.18 (CH(Ar)), 125.19 (CH(Ar)), 125.74 (CH(Ar)), 125.94 (CH(Ar)), 126.15 (CH(Ar)), 126.29 (CH(Ar)), 141.16 (C(Ar)), 141.30 (C(Ar)), 144.04 (C(Ar)), 144.61 (C(Ar)), 162.17 (FcCH) ppm. $C_{29}H_{27}FeNO$ (461.14): calcd. C, 75.49; H, 5.90; N, 3.04; found C, 75.69; H, 5.94; N, 3.12.

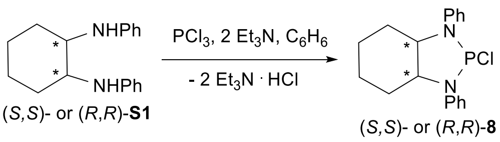
EXPERIMENTAL SECTION



Procedure for the Preparation of Thioether Alcohol 6: Monotosylate **2** (3.49 g, 8.3 mmol) was dissolved in DMF (25 mL), thiophenol (1.7 mL, 16.6 mmol) and K_2CO_3 (2.29 g, 16.6 mmol) were added. The reaction mixture was stirred for 12 h at room temperature, diluted with water (50 mL), and then extracted with hexane/EtOAc = 2/1 (2 x 50 mL). The combined organic extracts was washed with brine (50 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuum (40 Torr). The residue was dried for 30 min at 10 Torr and chromatographed on SiO_2 (hexane/AcOEt = 3/1).

((11*S*,12*S*)-12-((Phenylthio)methyl)-9,10-dihydro-9,10-ethanoanthracen-11-yl)methanol (**6**): White foam, yield 2.41 g (81 %). ^{1}H NMR (600.1 MHz, $CDCl_3$, 30 ^{o}C): δ = 1.56-1.60 (br.m, 2H; $CHCHCH_2O\underline{H}$ and $CHC\underline{H}CH_2S$), 1.70-1.74 (m, 1H; $CHC\underline{H}CH_2OH$), 2.59-2.62 (dd, ^2J(H,H) = 13.0 Hz, ^3J(H,H) = 8.4 Hz, 1H; $CHCH\underline{C}\underline{H}_2S$), 2.66-2.69 (dd, ^2J(H,H) = 13.0 Hz, ^3J(H,H) = 6.8 Hz, 1H; $CHCHC\underline{H_2}S$), 3.02-3.06 (dd, ^2J(H,H) = 10.3 Hz, ^3J(H,H) = 9.2 Hz, 1H; $CHCHC\underline{H_2}OH$), 3.37-3.40 (dd, ^2J(H,H) = 10.4 Hz, ^3J(H,H) = 5.9 Hz, 1H; $CHCHC\underline{H_2}OH$), 4.36 (d, ^3J(H,H) = 2.3 Hz, 1H; $C\underline{H}CHCH_2OH$), 4.37 (d, ^3J(H,H) = 2.2 Hz, 1H; $C\underline{H}CHCH_2S$), 7.08-7.17 (m, 5H; CH(Ar) and CH(Ph)), 7.24-7.32 (m, 8H; CH(Ar) and CH(Ph)) ppm. $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$, 30 ^{o}C): δ = 39.22 ($CHCH\underline{C}H_2S$), 42.24 ($CH\underline{C}HCH_2S$), 45.87 ($\underline{C}HCHCH_2OH$), 47.84 ($\underline{C}HCHCH_2S$), 49.07 ($CH\underline{C}HCH_2OH$), 65.64 ($CHCH\underline{C}H_2OH$), 123.49 (CH(Ar)), 123.53 (CH(Ar)), 125.18 (CH(Ar)), 125.51 (CH(Ar)), 125.72 (CH(Ar)), 125.80 (CH(Ar)), 126.03 (CH(Ar)), 126.19 (*p*-CH(Ph)), 128.94 (*o*-CH(Ph)), 129.16 (*m*-CH(Ph)), 136.16 (*p*-C(Ph)), 140.51 (C(Ar)), 140.61 (C(Ar)), 143.19 (C(Ar)), 143.28 (C(Ar)) ppm. $C_{24}H_{22}OS$ (358.14): calcd. C, 80.41; H, 6.19; found C, 80.58; H, 6.13.

EXPERIMENTAL SECTION



General Procedure for the Preparation of Phosphorylating Reagent (*S*,*S*)-8 and (*R*,*R*)-8: A solution of the 1,2-diamine (*S*,*S*)-**S1** or (*R*,*R*)-**S1** (1.09 g, 4.1 mmol) in benzene (20 mL) was added dropwise at 0 °C over 15 min to a vigorously stirred solution of PCl_3 (0.36 mL, 4.1 mmol) and Et_3N (1.14 mL, 8.2 mmol) in benzene (40 mL). The mixture was then briefly heated to boiling point and cooled down to 20 °C. Solid $Et_3N{\cdot}HCl$ was filtered off, and the filtrate was concentrated in vacuum (40 Torr). The residue was dried in vacuum (10^{-3} Torr) for 8 h.

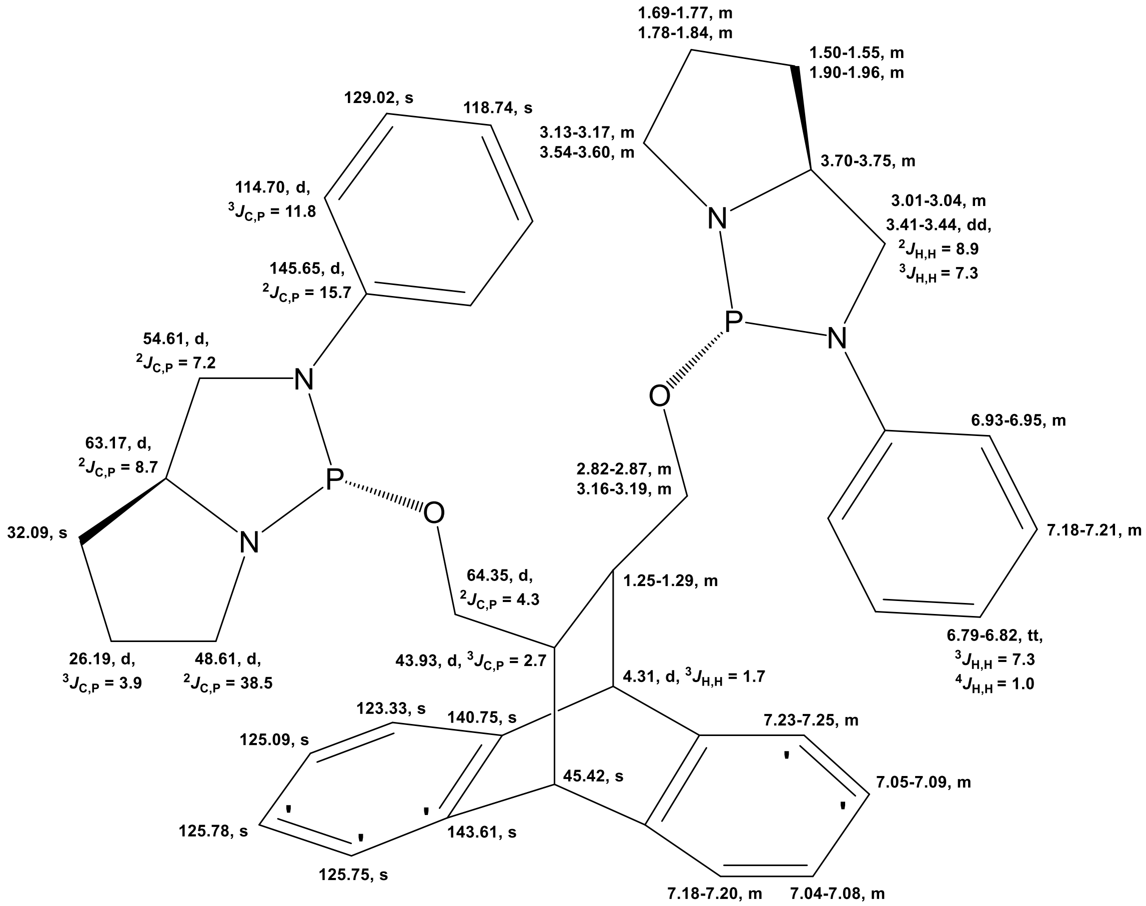
(1*R*,5*R*)-3-chloro-2,4-diphenyl-2,4-diaza-3-phosphabicyclo[3.4.0]nonane ((*R*,*R*)-**8**): Yellowish solid, yield 1.30 g (96 %). ^1H NMR (499.9 MHz, $CDCl_3$, ambient temperature): δ = 1.25-1.45 (br.m, 2H; $C\underline{H}_2CH$), 1.33-1.53 (br.m, 2H; CH_2), 1.91-1.92 (br.m, 2H; CH_2), 2.33 (br.s, 1H; $C\underline{H}_2CH$), 2.46 (br.s, 1H; $C\underline{H}_2CH$), 3.65 (br.s, 1H; $CH_2C\underline{H}$), 3.94 (br.s, 1H; $CH_2C\underline{H}$), 7.03-7.16 (br.m, 2H; *p*-CH(Ph)), 7.16-7.28 (br.m, 4H; *o*-CH(Ph)), 7.31-7.46 (br.m, 4H; *m*-CH(Ph)) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, ambient temperature): δ = 24.32 (s; CH_2), 28.57 (s; $\underline{C}H_2CH$), 28.99 (s; $\underline{C}H_2CH$), 65.77 (br.s; $CH_2\underline{C}H$), 66.08 (br.s; $CH_2\underline{C}H$), 119.69 (br.s; *o*-CH(Ph)), 124.76 (br.s; *o*-CH(Ph)), 123.00 (br.s; *p*-CH(Ph)), 125.38 (br.s; *p*-CH(Ph)), 129.22 (s; *m*-CH(Ph)), 139.37 (br.s; *i*-C(Ph)), 141.81 (br.s; *i*-C(Ph)) ppm. $^{31}P\{^1H\}$ NMR (202.4 MHz, $CDCl_3$, ambient temperature): δ = 156.19 (s) ppm.

(1*S*,5*S*)-3-chloro-2,4-diphenyl-2,4-diaza-3-phosphabicyclo[3.4.0]nonane ((*S*,*S*)-**8**): Yellowish solid, yield 1.22 g (90 %). The ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR signals match the corresponding signals for (*R*,*R*)-**8**.

General Procedure for the Preparation of Ligands: The relevant compound **1** (1 mmol) or **2**,**5**,**6** (2 mmol) was added in one portion to a vigorously stirred solution of the appropriate phosphorylating reagent (S_C)-**7**, (R_C)-**7**), (*S*,*S*)-**8** or (*R*,*R*)-**8** (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 (10^{-3} Torr).

(11*S*,12*S*)-Bis[((2*R*,5*S*)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octyloxy)methyl]-9,10-dihydro-9,10-ethanoanthracene (**L1a**): White solid, yield 0.63 g (94 %). ^1H NMR (600.1 MHz, $CDCl_3$, 30 °C): δ = 1.25-1.29 (m, 2H; $CHC\underline{H}CH_2O$), 1.50-1.55 (m, 2H; CH_2), 1.69-1.77 (m, 2H; $C\underline{H}_2CH_2N$), 1.78-1.84 (m, 2H; $C\underline{H}_2CH_2N$), 1.90-1.96 (m, 2H; CH_2), 2.82-2.87 (m, 2H; $CHCHC\underline{H}_2O$), 3.01-3.04 (m, 2H; $C\underline{H}_2CHN$), 3.13-3.17

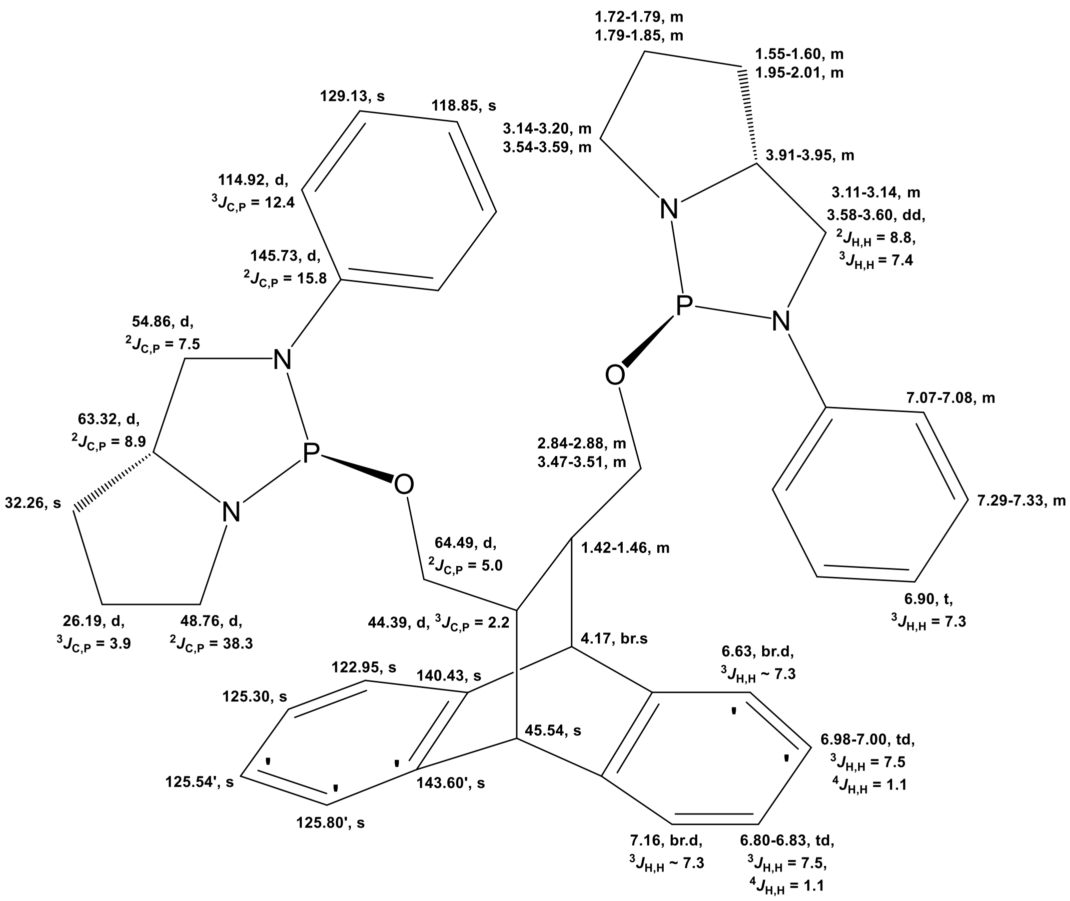
(m, 2H; $CH_2C\underline{H}_2N$), 3.16-3.19 (m, 2H; $CHCHC\underline{H}_2O$), 3.41-3.44 (dd, $^2J(H,H)$ = 8.9 Hz, $^3J(H,H)$ = 7.3 Hz, 2H; $C\underline{H}_2CHN$), 3.54-3.60 (m, 2H; $CH_2C\underline{H}_2N$), 3.70-3.75 (m, 2H; $CH_2C\underline{H}N$), 4.31 (d, $^3J(H,H)$ = 1.7 Hz, 2H; $C\underline{H}CHCH_2O$), 6.79-6.82 (tt, $^3J(H,H)$ = 7.3 Hz, $^4J(H,H)$ = 1.0 Hz, 2H; *p*-CH(Ph)), 6.93-6.95 (m, 4H; *o*-CH(Ph)), 7.04-7.08 (m, 2H; $C\underline{H}CHC(Ar)$), 7.05-7.09 (m, 2H; $C\underline{H}'CH'C'(Ar)$), 7.18-7.20 (m, 2H; $CHC\underline{H}C(Ar)$), 7.18-7.21 (m, 4H; *m*-CH(Ph)), 7.23-7.25 (m, 2H; $CH'C\underline{H}'C'(Ar)$) ppm. $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$, 30 °C): δ = 26.19 (d, $^3J(C,P)$ = 3.9 Hz; $\underline{C}H_2CH_2N$), 32.09 (s; CH_2), 43.93 (d, $^3J(C,P)$ = 2.7 Hz; $CH\underline{C}HCH_2O$), 45.42 (s; $\underline{C}HCHCH_2O$), 48.61 (d, $^2J(C,P)$ = 38.5 Hz; $CH_2\underline{C}H_2N$), 54.61 (d, $^2J(C,P)$ = 7.2 Hz; $\underline{C}H_2CHN$), 63.17 (d, $^2J(C,P)$ = 8.7 Hz; $CH_2\underline{C}HN$), 64.35 (d, $^2J(C,P)$ = 4.3 Hz; $CHCH\underline{C}H_2O$), 114.70 (d, $^3J(C,P)$ = 11.8 Hz; *o*-CH(Ph)), 118.74 (s; *p*-CH(Ph)), 123.33 (s; $CH\underline{C}HC(Ar)$), 125.09 (s; $\underline{C}HCHC(Ar)$), 125.75 (s; $CH'\underline{C}H'C'(Ar)$), 125.78 (s; $\underline{C}H'CH'C'(Ar)$), 129.02 (s; *m*-CH(Ph)), 140.75 (s; $CHCH\underline{C}(Ar)$), 143.61 (s; $CH'CH'\underline{C}'(Ar)$), 145.65 (d, $^2J(C,P)$ = 15.7 Hz; C(Ph)) ppm. $^{31}P\{^1H\}$ NMR (242.9 MHz, $CDCl_3$, 30 °C): δ = 121.26 (s) ppm. $C_{40}H_{44}N_4O_2P_2$ (674.29): calcd. C 71.20, H 6.57, N 8.30; found C 71.34, H 6.63, N 8.24.



$^{13}C\{^1H\}$ (left part of the picture) and ^1H (right part of the picture) NMR Signals Assignment for **L1a**.

EXPERIMENTAL SECTION

(11*S*,12*S*)-Bis[((2*S*,5*R*)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octyloxy)methyl]-9,10-dihydro-9,10-ethanoanthracene (**L1b**): White solid, yield 0.57 g (85 %). ^{1}H NMR (600.1 MHz, $CDCl_3$, 30 °C): δ = 1.42-1.46 (m, 2H; $CHC\underline{H}CH_2O$), 1.55-1.60 (m, 2H; CH_2), 1.72-1.79 (m, 2H; $C\underline{H}_2CH_2N$), 1.79-1.85 (m, 2H; $C\underline{H}_2CH_2N$), 1.95-2.01 (m, 2H; CH_2), 2.84-2.88 (m, 2H; $CHCHC\underline{H}_2O$), 3.11-3.14 (m, 2H; $C\underline{H}_2CHN$), 3.14-3.20 (m, 2H; $CH_2C\underline{H}_2N$), 3.47-3.51 (m, 2H; $CHCHC\underline{H}_2O$), 3.54-3.59 (m, 2H; $CH_2C\underline{H}_2N$), 3.58-3.60 (dd, ^2J(H,H) = 8.8 Hz, ^3J(H,H) = 7.4 Hz, 2H; $C\underline{H}_2CHN$), 3.91-3.95 (m, 2H; $CH_2C\underline{H}N$), 4.17 (br.s, 2H; $C\underline{H}CHCH_2O$), 6.63 (br.d, ^3J(H,H) ~ 7.3 Hz, 2H; $CH'C\underline{H'}C'$(Ar)), 6.80-6.83 (td, ^3J(H,H) = 7.5 Hz, ^4J(H,H) = 1.1 Hz, 2H; $C\underline{H}CHC$(Ar)), 6.90 (t, ^3J(H,H) = 7.3 Hz, 2H; *p*-CH(Ph)), 6.98-7.00 (td, ^3J(H,H) = 7.5 Hz, ^4J(H,H) = 1.1 Hz, 2H; $C\underline{H'}CH'C'$(Ar)), 7.07-7.08 (m, 4H; *o*-CH(Ph)), 7.16 (br.d, ^3J(H,H) ~ 7.3 Hz, 2H; $CHC\underline{H}C$(Ar)), 7.29-7.33 (m, 4H; *m*-CH(Ph)) ppm. ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$, 30 °C): δ = 26.19 (d, ^3J(C,P) = 3.9 Hz; $\underline{C}H_2CH_2N$), 32.26 (s; CH_2), 44.39 (d, ^3J(C,P) = 2.2 Hz; $CH\underline{C}HCH_2O$), 45.54 (s; $\underline{C}HCHCH_2O$), 48.76 (d, ^2J(C,P) = 38.3 Hz; $CH_2\underline{C}H_2N$), 54.86 (d, ^2J(C,P) = 7.5 Hz; $\underline{C}H_2CHN$), 63.32 (d, ^2J(C,P) = 8.9 Hz; $CH_2\underline{C}HN$), 64.49 (d, ^2J(C,P) = 5.0 Hz; $CHCH\underline{C}H_2O$), 114.92 (d, ^3J(C,P) = 12.4 Hz; *o*-CH(Ph)), 118.85 (s; *p*-CH(Ph)), 122.95 (s; $CH\underline{C}HC$(Ar)), 125.30 (s; $\underline{C}HCHC$(Ar)), 125.54 (s; $\underline{C}H'CH'C'$(Ar)), 125.80 (s; $CH'\underline{C}H'C'$(Ar)) 129.13 (s; *m*-CH(Ph)), 140.43 (s; $CHCH\underline{C}$(Ar)), 143.60 (s; $CH'CH'\underline{C}'$(Ar)), 145.73 (d, ^2J(C,P) = 15.8 Hz; C(Ph)) ppm. ^{31}P{^{1}H} NMR (242.9 MHz, $CDCl_3$, 30 °C): δ = 120.58 (s) ppm. $C_{40}H_{44}N_4O_2P_2$ (674.29): calcd. C 71.20, H 6.57, N 8.30; found C 71.44, H 6.64, N 8.17.



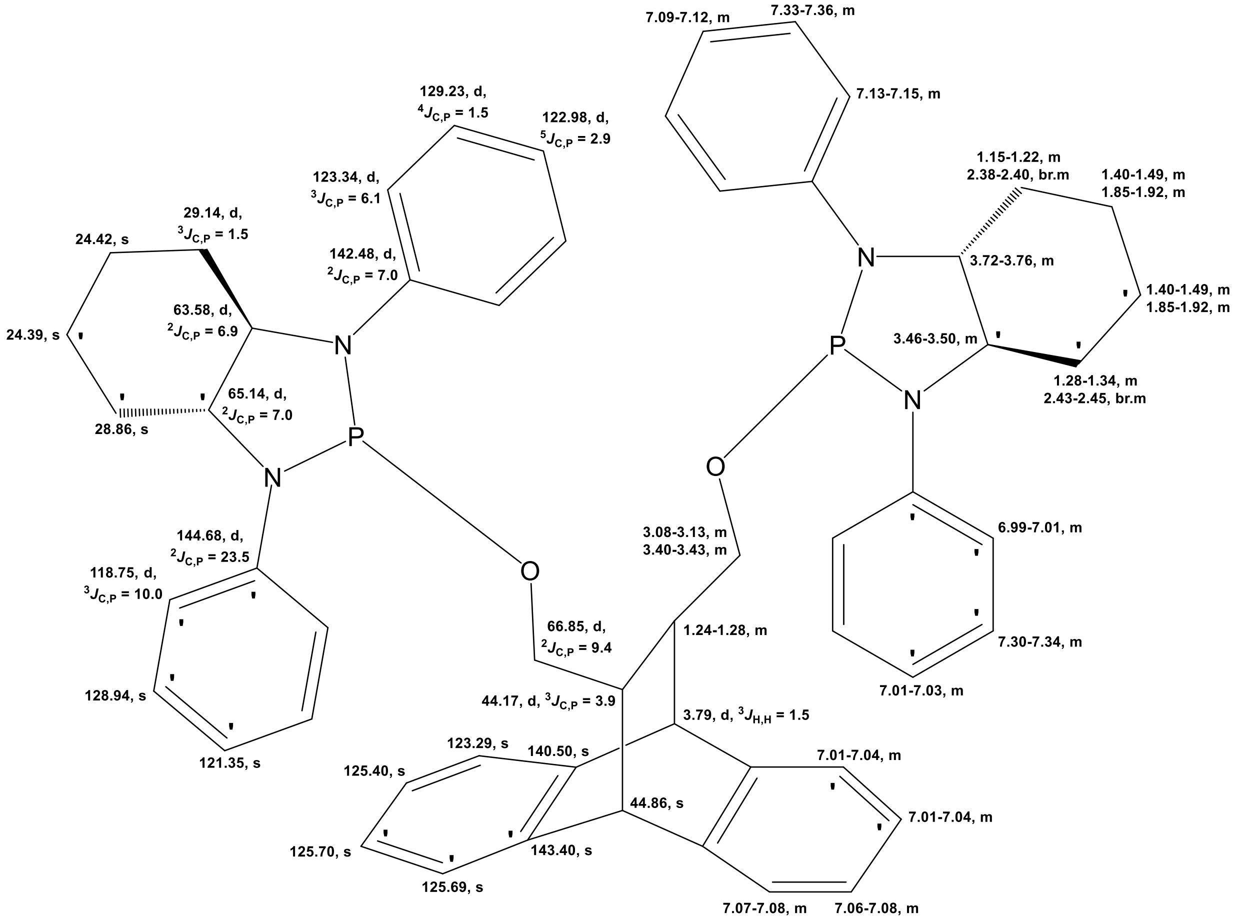
^{13}C{^{1}H} (left part of the picture) and ^{1}H (right part of the picture) NMR Signals Assignment for **L1b**.

EXPERIMENTAL SECTION

(11*S*,12*S*)-Bis[((1*S*,5*S*)-2,4-diphenyl-2,4-diaza-3-phosphabicyclo[3.4.0]nonan-3-yloxy)methyl]-9,10-dihydro-9,10-ethanoanthracene (**L2a**): White solid, yield 0.81 g (95 %). ^{1}H NMR (600.1 MHz, $CDCl_3$, 30 °C): δ = 0.92-0.98 (m, 2H; C$\underline{H}_2$CHN), 1.01-1.06 (br.m, 2H; CHC$\underline{H}$CH$_2$O), 1.08-1.14 (m, 2H; C$\underline{H}_2$CHN), 1.27-1.36 (m, 4H; CH$_2$), 1.64-1.67 (m, 2H; CH$_2$), 1.80-1.84 (m, 2H; CH$_2$), 2.21-2.23 (br.m, 2H; C$\underline{H}_2$CHN), 2.31-2.33 (br.m, 2H; C$\underline{H}_2$CHN), 2.69-2.78 (br.m, 2H; CHCHC$\underline{H}_2$O), 3.38-3.42 (m, 2H; CH$_2$C$\underline{H}$N), 3.45-3.50 (br.m, 2H; CHCHC$\underline{H}_2$O), 3.51-3.55 (m, 2H; CH$_2$C$\underline{H}$N), 4.22 (d, ^3J(H,H) = 3.3 Hz, 2H; C$\underline{H}$CHCH$_2$O), 6.94-6.96 (m, 2H; CH(Ar)), 6.97-7.01 (m, 4H; CH(Ar)), 6.98-7.02 (m, 2H; CH(Ar)), 7.02-7.08 (m, 10H; CH(Ar)), 7.09-7.13 (m, 2H; CH(Ar)), 7.23-7.26 (m, 4H; CH(Ar)), 7.27-7.31 (m, 4H; CH(Ar)) ppm. ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$, 30 °C): δ = 24.25 (s; CH$_2$), 24.31 (s; CH$_2$), 28.41 (s; $\underline{C}$H$_2$CHN), 29.11 (s; $\underline{C}$H$_2$CHN), 44.54 (br.s; CH$\underline{C}$HCH$_2$O), 45.20 (s; $\underline{C}$HCHCH$_2$O), 63.47 (d, ^2J(C,P) = 7.2 Hz; CH$_2\underline{C}$HN), 64.89 (d, ^2J(C,P) = 6.9 Hz; CH$_2\underline{C}$HN), 65.97 (d, ^2J(C,P) = 4.4 Hz; CHCH$\underline{C}$H$_2$O), 118.88 (d, ^3J(C,P) = 9.4 Hz; *o*-CH(Ph)), 121.44 (s; *p*-CH(Ph)), 122.63 (br.s; *p*-CH(Ph)), 122.72 (d, ^3J(C,P) = 6.6 Hz; *o*-CH(Ph)), 123.20 (s; CH(Ar)), 125.61 (s; CH(Ar)), 125.90 (s; CH(Ar)), 128.89 (s; *m*-CH(Ph)), 129.16 (s; *m*-CH(Ph)), 140.30 (s; C(Ar)), 142.26 (d, ^2J(C,P) = 7.1 Hz; C(Ph)), 143.62 (s; C(Ar)), 144.69 (d, ^2J(C,P) = 23.5 Hz; C(Ph)) ppm. ^{31}P{^{1}H} NMR (242.9 MHz, $CDCl_3$, 30 °C): δ = 125.44 (s) ppm. $C_{54}H_{56}N_4O_2P_2$ (854.39): calcd. C 75.86, H 6.60, N 6.55; found C 76.07, H 6.69, N 6.70.

(11*S*,12*S*)-Bis[((1*R*,5*R*)-2,4-diphenyl-2,4-diaza-3-phosphabicyclo[3.4.0]nonan-3-yloxy)methyl]-9,10-dihydro-9,10-ethanoanthracene (**L2b**): White solid, yield 0.82 g (96 %). ^{1}H NMR (600.1 MHz, $CDCl_3$, 30 °C): δ = 1.15-1.22 (m, 2H; C$\underline{H}_2$CHN), 1.24-1.28 (m, 2H; CHC$\underline{H}$CH$_2$O), 1.28-1.34 (m, 2H; C$\underline{H}_2$’CH’N), 1.40-1.49 (m, 4H; CH$_2$ and CH$_2$’), 1.85-1.92 (m, 4H; CH$_2$ and CH$_2$’), 2.38-2.40 (br.m, 2H; C$\underline{H}_2$CHN), 2.43-2.45 (br.m, 2H; C$\underline{H}_2$’CH’N), 3.08-3.13 (m, 2H; CHCHC$\underline{H}_2$O), 3.40-3.43 (m, 2H; CHCHC$\underline{H}_2$O), 3.46-3.50 (m, 2H; CH$_2$’C$\underline{H’}$N), 3.72-3.76 (m, 2H; CH$_2$C$\underline{H}$N), 3.79 (d, ^3J(H,H) = 1.5 Hz, 2H; C$\underline{H}$CHCH$_2$O), 6.99-7.01 (m, 4H; *o*-CH’(Ph)), 7.01-7.03 (m, 2H; *p*-CH’(Ph)), 7.01-7.04 (m, 4H; C$\underline{H’}$CH’C’(Ar) and CH’C$\underline{H’}$C’(Ar)), 7.06-7.08 (m, 2H; C$\underline{H}$CHC(Ar)), 7.07-7.08 (m, 2H; CHC$\underline{H}$C(Ar)), 7.09-7.12 (m, 2H; *p*-CH(Ph)), 7.13-7.15 (m, 4H; *o*-CH(Ph)), 7.30-7.34 (m, 4H; *m*-CH’(Ph)), 7.33-7.36 (m, 4H; *m*-CH(Ph)) ppm. ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$, 30 °C): δ = 24.39 (s; CH$_2$’), 24.42 (s; CH$_2$), 28.86 (s; $\underline{C}$H$_2$’CH’N), 29.14 (d, ^3J(C,P) = 1.5 Hz; $\underline{C}$H$_2$CHN), 44.17 (d, ^3J(C,P) = 3.9 Hz; CH$\underline{C}$HCH$_2$O), 44.86 (s; $\underline{C}$HCHCH$_2$O), 63.58 (d, ^2J(C,P) = 6.9 Hz; CH$_2\underline{C}$HN), 65.14 (d, ^2J(C,P) = 7.0 Hz; CH$_2$’$\underline{C}$H’N), 66.85 (d, ^2J(C,P) = 9.4 Hz; CHCH$\underline{C}$H$_2$O), 118.75 (d, ^3J(C,P) = 10.0 Hz; *o*-CH’(Ph)), 121.35 (s; *p*-CH’(Ph)), 122.98 (d, ^5J(C,P) = 2.9 Hz; *p*-CH(Ph)), 123.29 (s; CH$\underline{C}$HC(Ar)), 123.34 (d, ^3J(C,P) = 6.1 Hz; *o*-CH(Ph)), 125.40 (s; $\underline{C}$HCHC(Ar)), 125.69 (s; CH’$\underline{C}$H’C’(Ar)), 125.70 (s; $\underline{C}$H’CH’C’(Ar)), 128.94 (s; *m*-CH’(Ph)), 129.23 (d, ^4J(C,P) = 1.5 Hz; *m*-CH(Ph)), 140.50 (s; CHCH$\underline{C}$(Ar)), 142.48 (d, ^2J(C,P) = 7.0 Hz; C(Ph)), 143.40 (s; CH’CH’$\underline{C’}$(Ar)), 144.68 (d, ^2J(C,P) = 23.5 Hz; C’(Ph)) ppm. ^{31}P{^{1}H} NMR (242.9 MHz, $CDCl_3$, 30 °C): δ = 129.80 (s) ppm. $C_{54}H_{56}N_4O_2P_2$ (854.39): calcd. C 75.86, H 6.60, N 6.55; found C 76.16, H 6.72, N 6.34.

EXPERIMENTAL SECTION



$^{13}C\{^1H\}$ (left part of the picture) and ^1H (right part of the picture) NMR Signals Assignment for **L2b**.

(11*S*,12*S*)-11-[((2*R*,5*S*)-3-Phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octyloxy)methyl]-12-((tosyloxy)methyl)-9,10-dihydro-9,10-ethanoanthracene (**L3a**): White solid, yield 1.10 g (88 %). ^1H NMR (600.1 MHz, $CDCl_3$, 30 °C): δ = 1.35-1.39 (m, 1H; $CHC\underline{H}CH_2OP$), 1.57-1.61 (m, 1H; $CHC\underline{H}CH_2OTs$), 1.57-1.62 (m, 1H; CH_2), 1.74-1.81 (m, 1H; $C\underline{H}_2CH_2N$), 1.83-1.89 (m, 1H; $C\underline{H}_2CH_2N$), 1.97-2.03 (m, 1H; CH_2), 2.48 (s, 3H; $C\underline{H}_3CCH(Ts)$), 3.07-3.12 (m, 1H; $CHCHC\underline{H}_2OP$), 3.12-3.15 (m, 1H; $C\underline{H}_2CHN$), 3.17-3.21 (m, 2H; $CHCHC\underline{H}_2OP$ and $CH_2C\underline{H}_2N$), 3.23 (br.t, $^2J(H,H) \sim {}^3J(H,H) \sim 10.0$ Hz, 1H; $CHCHC\underline{H}_2OTs$), 3.58-3.64 (m, 1H; $CH_2C\underline{H}_2N$), 3.60-3.63 (m, 1H; $C\underline{H}_2CHN$), 3.72-3.75 (dd, $^2J(H,H)$ = 9.5 Hz, $^3J(H,H)$ = 4.9 Hz, 1H; $CHCHC\underline{H}_2OTs$), 3.88-3.92 (m, 1H; $CH_2C\underline{H}N$), 4.23 (d, $^3J(H,H)$ = 2.1 Hz, 1H; $C\underline{H}CHCH_2OTs$), 4.31 (d, $^3J(H,H)$ = 2.1 Hz, 1H; $C\underline{H}CHCH_2OP$), 6.87 (t, $^3J(H,H)$ = 7.3 Hz, 1H; *p*-CH(Ph)), 6.94-6.97 (m, 1H; $C\underline{H}CHC(Ar)$), 6.96-6.97 (m, 1H; $CHC\underline{H}C(Ar)$), 6.97-7.00 (m, 2H; *o*-CH(Ph)), 7.06-7.08 (td, $^3J(H,H)$ = 7.1 Hz, $^4J(H,H)$ = 1.9 Hz, 1H; $C\underline{H}CHC(Ar)$), 7.10-7.12 (td, $^3J(H,H)$ = 7.1 Hz, $^4J(H,H)$ = 1.8 Hz, 1H; $C\underline{H}CHC(Ar)$), 7.11-7.14 (td, $^3J(H,H)$ = 7.2 Hz, $^4J(H,H)$ = 1.9 Hz, 1H; $C\underline{H}CHC(Ar)$), 7.18 (d, $^3J(H,H)$ = 7.4 Hz, 1H; $CHC\underline{H}C(Ar)$) 7.22-7.24 (m, 1H; $CHC\underline{H}C(Ar)$), 7.24-7.27 (m, 2H; *m*-CH(Ph)), 7.26-7.27 (m, 1H; $CHC\underline{H}C(Ar)$), 7.33 (d, $^3J(H,H)$ = 8.1 Hz, 2H; $CH_3CC\underline{H}(Ts)$), 7.74 (d, $^3J(H,H)$ = 8.2 Hz, 2H; SCCH(Ts)) ppm. $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$, 30 °C): δ = 21.59 (s; $\underline{C}H_3CCH(Ts)$), 26.19 (d, $^3J(C,P)$ = 3.8 Hz; $\underline{C}H_2CH_2N$), 32.12 (s; CH_2), 42.37 (s; $CH\underline{C}HCH_2OTs$), 43.53 (d, $^3J(C,P)$ = 2.6 Hz; $CH\underline{C}HCH_2OP$), 44.88 (s; $\underline{C}HCHCH_2OTs$), 45.28 (s; $\underline{C}HCHCH_2OP$), 48.64 (d, $^2J(C,P)$ = 38.4

Hz; $CH_2\underline{C}H_2N$), 54.62 (d, ^2J(C,P) = 7.2 Hz; $\underline{C}H_2CHN$), 63.30 (d, ^2J(C,P) = 8.7 Hz; $CH_2\underline{C}HN$), 64.40 (d, ^2J(C,P) = 3.8 Hz; $CHCH\underline{C}H_2OP$), 71.77 (s; $CHCH\underline{C}H_2OTs$), 114.76 (d, ^3J(C,P) = 12.0 Hz; *o*-CH(Ph)), 118.96 (s; *p*-CH(Ph)), 123.40 (s; $CH\underline{C}HC(Ar)$), 123.52 (s; $CH\underline{C}HC(Ar)$), 125.45 (s; $CH\underline{C}HC(Ar)$), 125.57 (s; $CH\underline{C}HC(Ar)$), 125.63 (s; $\underline{C}HCHC(Ar)$), 125.67 (s; $\underline{C}HCHC(Ar)$), 126.10 (s; $\underline{C}HCHC(Ar)$), 126.15 (s; $\underline{C}HCHC(Ar)$), 127.91 (s; $SC\underline{C}H(Ts)$), 129.12 (s; *m*-CH(Ph)), 129.83 (s; $CH_3C\underline{C}H(Ts)$), 132.89 (s; $CH_3\underline{C}CH(Ts)$), 139.54 (s; $CHCH\underline{C}(Ar)$), 140.34 (s; $CHCH\underline{C}(Ar)$), 142.44 (s; $CHCH\underline{C}(Ar)$), 143.12 (s; $CHCH\underline{C}(Ar)$), 144.69 (s; $S\underline{C}CH(Ts)$), 145.49 (d, ^2J(C,P) = 15.6 Hz; C(Ph)) ppm. $^{31}P\{^1H\}$ NMR (242.9 MHz, $CDCl_3$, 30 °C) δ = 122.29 (s) ppm. $C_{36}H_{37}N_2O_4PS$ (624.22): calcd. C 69.21, H 5.97, N 4.48; found C 69.33, H 6.01, N 4.42.

(11*S*,12*S*)-11-[((2*S*,5*R*)-3-Phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octyloxy)methyl]-12-((tosyloxy)methyl)-9,10-dihydro-9,10-ethanoanthracene (**L3b**): White solid, yield 1.07 g (86 %). ^1H NMR (600.1 MHz, $CDCl_3$, 30 °C): δ = 1.36-1.39 (m, 1H; $CH\underline{H}CH_2OP$), 1.53-1.58 (m, 1H; CH_2), 1.67-1.71 (m, 1H; $CH\underline{H}CH_2OTs$), 1.71-1.77 (m, 1H; $C\underline{H_2}CH_2N$), 1.78-1.84 (m, 1H; $C\underline{H_2}CH_2N$), 1.94-1.99 (m, 1H; CH_2), 2.48 (s, 3H; $C\underline{H_3}CCH(Ts)$), 2.93-2.97 (m, 1H; $CHCHC\underline{H_2}OP$), 3.09-3.14 (m, 1H; $C\underline{H_2}CHN$), 3.11-3.15 (m, 1H; $CH_2C\underline{H_2}N$), 3.24-3.27 (dd, ^2J(H,H) = 10.3 Hz, ^3J(H,H) = 9.7 Hz, 1H; $CHCHC\underline{H_2}OTs$), 3.32-3.35 (m, 1H; $CHCHC\underline{H_2}OP$), 3.50-3.55 (m, 1H; $CH_2C\underline{H_2}N$), 3.56-3.58 (m, 1H; $C\underline{H_2}CHN$), 3.80-3.85 (m, 1H; $CH_2C\underline{H}N$), 3.87-3.89 (dd, ^2J(H,H) = 9.5 Hz, ^3J(H,H) = 4.8 Hz, 1H; $CHCHC\underline{H_2}OTs$), 4.15 (d, ^3J(H,H) = 2.2 Hz, 1H; $C\underline{H}CHCH_2OP$), 4.22 (d, ^3J(H,H) = 2.1 Hz, 1H; $C\underline{H}CHCH_2OTs$), 6.76 (br.d, ^3J(H,H) ~ 7.3 Hz, 1H; CH(Ar)), 6.87-6.96 (m, 3H; CH(Ar)), 6.88-6.90 (m, 1H; *p*-CH(Ph)), 7.02-7.03 (m, 2H; *o*-CH(Ph)), 7.02-7.07 (m, 2H; CH(Ar)), 7.17-7.20 (m, 2H; CH(Ar)), 7.27-7.30 (m, 2H; *m*-CH(Ph)), 7.35-7.37 (m, 2H; $CH_3CC\underline{H}(Ts)$), 7.78-7.80 (m, 2H; SCCH(Ts)) ppm. $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$, 30 °C): δ = 21.62 (s; $\underline{C}H_3CCH(Ts)$), 26.16 (d, ^3J(C,P) = 3.9 Hz; $\underline{C}H_2CH_2N$), 32.21 (s; CH_2), 42.54 (s; $CH\underline{C}HCH_2OTs$), 43.73 (d, ^3J(C,P) = 2.1 Hz; $CH\underline{C}HCH_2OP$), 44.90 (s; $\underline{C}HCHCH_2OTs$), 45.35 (s; $\underline{C}HCHCH_2OP$), 48.65 (d, ^2J(C,P) = 38.3 Hz; $CH_2\underline{C}H_2N$), 54.76 (d, ^2J(C,P) = 7.4 Hz; $\underline{C}H_2CHN$), 63.29 (d, ^2J(C,P) = 8.8 Hz; $CH_2\underline{C}HN$), 64.21 (d, ^2J(C,P) = 4.7 Hz; $CHCH\underline{C}H_2OP$), 71.94 (s; $CHCH\underline{C}H_2OTs$), 114.88 (d, ^3J(C,P) = 12.3 Hz; *o*-CH(Ph)), 118.95 (d, ^5J(C,P) = 0.8 Hz; *p*-CH(Ph)), 123.23 (s; CH(Ar)), 123.37 (s; CH(Ar)), 125.49 (s; CH(Ar)), 125.62 (s; CH(Ar)), 125.74 (s; CH(Ar)), 125.79 (s; CH(Ar)), 125.92 (s; CH(Ar)), 126.15 (s; CH(Ar)), 127.98 (s; $SC\underline{C}H(Ts)$), 129.15 (s; *m*-CH(Ph)), 129.88 (s; $CH_3C\underline{C}H(Ts)$), 132.96 (s; $CH_3\underline{C}CH(Ts)$), 139.51 (s; C(Ar)), 140.10 (s; C(Ar)), 142.42 (s; C(Ar)), 143.28 (s; C(Ar)), 144.76 (s; $S\underline{C}CH(Ts)$), 145.60 (d, ^2J(C,P) = 15.8 Hz; C(Ph)) ppm. $^{31}P\{^1H\}$ NMR (242.9 MHz, $CDCl_3$, 30 °C) δ = 121.22 (s) ppm. $C_{36}H_{37}N_2O_4PS$ (624.22): calcd. C 69.21, H 5.97, N 4.48; found C 69.41, H 6.05, N 4.61.

(11*S*,12*S*)-11-[((2*R*,5*S*)-3-Phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octyloxy)methyl]-12-((((*E*)-ferrocenylidene)amino)methyl)-9,10-dihydro-9,10-ethanoanthracene (**L4**): Orange solid, yield 1.06 g (80 %). ^1H NMR (600.1 MHz, $CDCl_3$, 30 °C): δ = 1.47-1.51 (m, 1H; $CH\underline{H}CH_2N$), 1.52-1.57 (m, 1H; CH_2), 1.64-

1.67 (m, 1H; $CHC\underline{H}CH_2OP$), 1.72-1.79 (m, 1H; $C\underline{H}_2CH_2N$), 1.80-1.86 (m, 1H; $C\underline{H}_2CH_2N$), 1.92-1.98 (m, 1H; CH_2), 2.83-2.86 (dd, ^2J(H,H) = 11.6 Hz, ^3J(H,H) = 9.1 Hz, 1H; $CHCHC\underline{H}_2N$), 2.90-2.95 (m, 1H; $CHCHC\underline{H}_2OP$), 3.08-3.11 (ddd, ^2J(H,H) = 9.1 Hz, ^3J(H,H) = 7.3 Hz, ^3J(H,P) = 3.7 Hz, 1H; $C\underline{H}_2CHN$), 3.18-3.21 (m, 1H; $CHCHC\underline{H}_2N$), 3.21-3.26 (m, 1H; $CH_2C\underline{H}_2N$), 3.46-3.49 (m, 1H; $CHCHC\underline{H}_2OP$), 3.57-3.60 (m, 1H; $C\underline{H}_2CHN$), 3.61-3.66 (m, 1H; $CH_2C\underline{H}_2N$), 3.82-3.86 (m, 1H; $CH_2C\underline{H}N$), 4.11 (d, ^3J(H,H) = 2.0 Hz, 1H; $C\underline{H}CHCH_2N$), 4.16 (s, 5H; C_5H_5(Fc)), 4.33-4.34 (m, 1H; CH(Fc)), 4.35-4.36 (m, 1H; CH(Fc)), 4.44 (d, ^3J(H,H) = 2.0 Hz, 1H; $C\underline{H}CHCH_2OP$), 4.57-4.58 (m, 1H; CH(Fc)), 4.58-4.59 (m, 1H; CH(Fc)), 6.84 (t, ^3J(H,H) = 7.3 Hz, 1H; *p*-CH(Ph)), 7.01-7.03 (m, 2H; *o*-CH(Ph)), 7.07-7.09 (m, 2H; CH(Ar)), 7.10-7.12 (m, 2H; CH(Ar)), 7.18-7.22 (m, 2H; CH(Ar)), 7.22-7.24 (m, 2H; *m*-CH(Ph)), 7.23-7.26 (m, 1H; CH(Ar)), 7.29-7.31 (m, 1H; CH(Ar)), 7.99 (s, 1H; FcCH) ppm. $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$, 30 °C): δ = 26.22 (d, ^3J(C,P) = 3.9 Hz; $\underline{C}H_2CH_2N$), 32.10 (s; CH_2), 43.76 (s; $CH\underline{C}HCH_2N$), 45.35 (d, ^3J(C,P) = 2.8 Hz; $CH\underline{C}HCH_2OP$), 45.51 (s; $\underline{C}HCHCH_2OP$), 46.38 (s; $\underline{C}HCHCH_2N$), 48.67 (d, ^2J(C,P) = 38.7 Hz; $CH_2\underline{C}H_2N$), 54.72 (d, ^2J(C,P) = 7.2 Hz; $\underline{C}H_2CHN$), 63.28 (d, ^2J(C,P) = 8.8 Hz; $CH_2\underline{C}HN$), 64.42 (d, ^2J(C,P) = 5.1 Hz; $CHCH\underline{C}H_2OP$), 65.65 (s; $CHCH\underline{C}H_2N$), 68.25 (s; CH(Fc)), 68.53 (s; CH(Fc)), 69.01 (s; C_5H_5(Fc)), 70.31 (s; CH(Fc)), 80.71 (s; C(Fc)), 114.74 (d, ^3J(C,P) = 11.7 Hz; *o*-CH(Ph)), 118.78 (s; *p*-CH(Ph)), 123.11 (s; CH(Ar)), 123.68 (s; CH(Ar)), 125.11 (s; CH(Ar)), 125.12 (s; CH(Ar)), 125.34 (s; CH(Ar)), 125.76 (s; CH(Ar)), 125.87 (s; CH(Ar)), 125.90 (s; CH(Ar)), 129.06 (s; *m*-CH(Ph)), 140.87 (s; C(Ar)), 140.89 (s; C(Ar)), 143.71 (s; C(Ar)), 143.88 (s; C(Ar)), 145.71 (d, ^2J(C,P) = 15.8 Hz; C(Ph)), 161.39 (s; FcCH) ppm. $^{31}P\{^1H\}$ NMR (242.9 MHz, $CDCl_3$, 30 °C) δ = 120.86 (s) ppm. $C_{40}H_{40}FeN_3OP$ (665.23): calcd. C 72.18, H 6.06, N 6.31; found C 72.31, H 6.11, N 6.41.

(11*S*,12*S*)-11-[((2*R*,5*S*)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octyloxy)methyl]-12-((phenylthio)methyl)-9,10-dihydro-9,10-ethanoanthracene (**L5a**): White solid, yield 1.02 g (91 %). ^1H NMR (600.1 MHz, $CDCl_3$, 30 °C): δ = 1.41-1.44 (m, 1H; $CHC\underline{H}CH_2S$), 1.57-1.62 (m, 1H; CH_2), 1.70-1.74 (m, 1H; $CHC\underline{H}CH_2OP$), 1.75-1.81 (m, 1H; $C\underline{H}_2CH_2N$), 1.83-1.89 (m, 1H; $C\underline{H}_2CH_2N$), 1.96-2.02 (m, 1H; CH_2), 2.48-2.52 (dd, ^2J(H,H) = 13.0 Hz, ^3J(H,H) = 9.0 Hz, 1H; $CHCHC\underline{H}_2S$), 2.61-2.64 (dd, ^2J(H,H) = 13.0 Hz, ^3J(H,H) = 6.2 Hz, 1H; $CHCHC\underline{H}_2S$), 2.94-2.99 (m, 1H; $CHCHC\underline{H}_2OP$), 3.14-3.17 (ddd, ^2J(H,H) = 9.0 Hz, ^3J(H,H) = 7.1 Hz, ^3J(H,P) = 3.9 Hz, 1H; $C\underline{H}_2CHN$), 3.21-3.26 (m, 1H; $CH_2C\underline{H}_2N$), 3.34-3.37 (m, 1H; $CHCHC\underline{H}_2OP$), 3.61-3.64 (m, 1H; $C\underline{H}_2CHN$), 3.63-3.68 (m, 1H; $CH_2C\underline{H}_2N$), 3.86-3.90 (m, 1H; $CH_2C\underline{H}N$), 4.34 (d, ^3J(H,H) = 2.0 Hz, 1H; $C\underline{H}CHCH_2S$), 4.41 (d, ^3J(H,H) = 1.9 Hz, 1H; $C\underline{H}CHCH_2OP$), 6.86-6.89 (m, 1H; CH(Ar)), 7.03-7.05 (m, 2H; CH(Ar)), 7.10-7.18 (m, 5H; CH(Ar)), 7.20-7.31 (m, 10H; CH(Ar)) ppm. $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$, 30 °C): δ = 26.21 (d, ^3J(C,P) = 3.8 Hz; $\underline{C}H_2CH_2N$), 32.14 (s; CH_2), 38.66 (s; $CHCH\underline{C}H_2S$), 42.36 (s; $CH\underline{C}HCH_2S$), 45.76 (s; $\underline{C}HCHCH_2OP$), 47.51 (s; $\underline{C}HCHCH_2S$), 47.52 (d, ^3J(C,P) = 3.7 Hz; $CH\underline{C}HCH_2OP$), 48.64 (d, ^2J(C,P) = 38.5 Hz; $CH_2\underline{C}H_2N$), 54.70 (d, ^2J(C,P) = 7.2 Hz; $\underline{C}H_2CHN$), 63.23 (d, ^2J(C,P) = 8.8 Hz; $CH_2\underline{C}HN$), 64.53 (d, ^2J(C,P) = 4.6 Hz; $CHCH\underline{C}H_2OP$), 114.75 (d, ^3J(C,P) = 11.8 Hz; *o*-CH(Ph)), 118.87 (s; *p*-CH(Ph)), 123.32 (s;

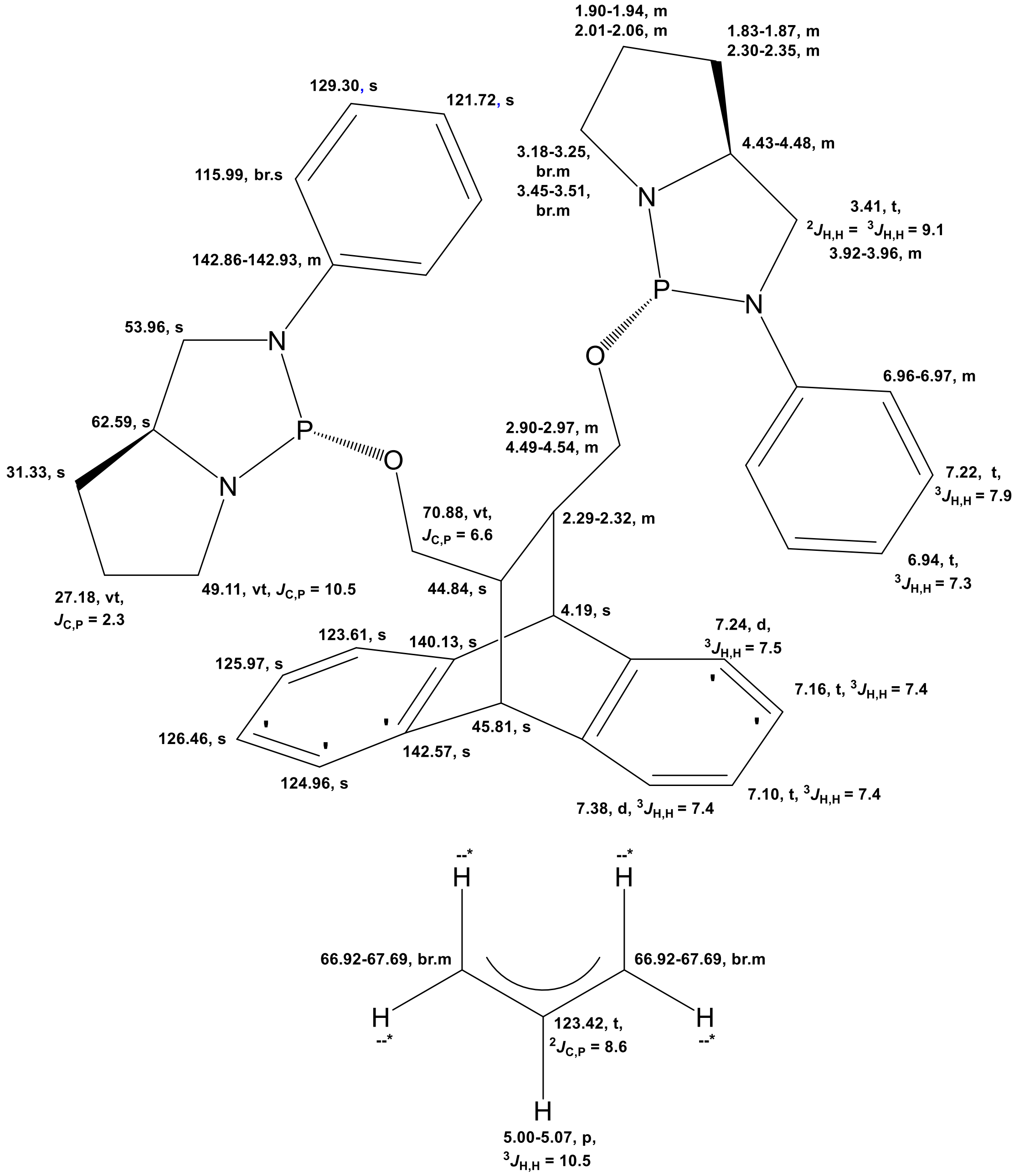
CH(Ar)), 123.59 (s; CH(Ar)), 125.35 (s; CH(Ar)), 125.42 (s; CH(Ar)), 125.57 (s; CH(Ar)), 125.73 (s; CH(Ar)), 125.78 (s; *p*-CH(Ph)), 125.83 (s; CH(Ar)), 126.09 (s; CH(Ar)), 128.82 (s; *m*-CH(Ph)), 129.08 (s; *m*-CH(Ph) and *o*-CH(Ph)), 136.28 (s; C(Ph)), 140.42 (s; C(Ar)), 140.64 (s; C(Ar)), 143.28 (s; C(Ar)), 143.37 (s; C(Ar)), 145.62 (d, ^2J(C,P) = 15.5 Hz; C(Ph)) ppm. $^{31}P\{^1H\}$ NMR (242.9 MHz, $CDCl_3$, 30 °C) δ = 121.27 (s) ppm. $C_{35}H_{35}N_2OPS$ (562.22): calcd. C 74.71, H 6.27, N 4.98; found C 74.82, H 6.24, N 4.93.

(11*S*,12*S*)-11-[((2*R*,5*S*)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octyloxy)methyl]-12-((phenylthio)methyl)-9,10-dihydro-9,10-ethanoanthracene (**L5b**): White solid, yield 1.09 g (97 %). ^1H NMR (600.1 MHz, $CDCl_3$, 30 °C): δ = 1.50-1.54 (m, 2H; $CHC\underline{H}CH_2S$ and CH_2), 1.67-1.73 (m, 1H; $C\underline{H_2}CH_2N$), 1.69-1.73 (m, 1H; $CHC\underline{H}CH_2OP$), 1.74-1.80 (m, 1H; $C\underline{H_2}CH_2N$), 1.89-1.95 (m, 1H; CH_2), 2.45-2.49 (dd, ^2J(H,H) = 13.0 Hz, ^3J(H,H) = 9.5 Hz, 1H; $CHCHC\underline{H_2}S$), 2.78-2.81 (dd, ^2J(H,H) = 13.0 Hz, ^3J(H,H) = 5.7 Hz, 1H; $CHCHC\underline{H_2}S$), 2.85-2.89 (m, 1H; $CHCHC\underline{H_2}OP$), 3.07-3.11 (m; 1H; $C\underline{H_2}CHN$), 3.07-3.12 (m, 1H; $CH_2C\underline{H_2}N$), 3.41-3.45 (m, 1H; $CHCHC\underline{H_2}OP$), 3.49-3.53 (m, 1H; $CH_2C\underline{H_2}N$), 3.53-3.55 (m, 1H; $C\underline{H_2}CHN$), 3.78-3.82 (m, 1H; $CH_2C\underline{H}N$), 4.22 (d, ^3J(H,H) = 1.8 Hz, 1H; $C\underline{H}CHCH_2OP$), 4.34 (d, ^3J(H,H) = 1.8 Hz, 1H; $C\underline{H}CHCH_2S$), 6.76 (d, ^3J(H,H) = 7.3 Hz, 1H; CH(Ar)), 6.85 (t, ^3J(H,H) = 7.4 Hz, 1H; CH(Ar)), 6.88 (t, ^3J(H,H) = 7.3 Hz, 1H; CH(Ar)), 6.99 (t, ^3J(H,H) = 7.4 Hz, 1H; CH(Ar)), 7.04-7.05 (m, 2H; CH(Ar)), 7.07-7.11 (m, 2H; CH(Ar)), 7.13-7.19 (m, 2H; CH(Ar)), 7.17-7.18 (m, 1H; CH(Ar)), 7.20-7.22 (m, 1H; CH(Ar)), 7.23-7.26 (m, 2H; CH(Ar)), 7.27-7.29 (m, 2H; CH(Ar)), 7.31-7.33 (m, 2H; CH(Ar)) ppm. $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$, 30 °C): δ = 26.18 (d, ^3J(C,P) = 3.9 Hz; $\underline{C}H_2CH_2N$), 32.19 (s; CH_2), 38.63 (s; $CHCH\underline{C}H_2S$), 42.65 (s; $CH\underline{C}HCH_2S$), 45.86 (s; $\underline{C}HCHCH_2OP$), 47.34 (s; $\underline{C}HCHCH_2S$), 47.77 (d, ^3J(C,P) = 2.1 Hz; $CH\underline{C}HCH_2OP$), 48.61 (d, ^2J(C,P) = 38.2 Hz; $CH_2\underline{C}H_2N$), 54.76 (d, ^2J(C,P) = 7.4 Hz; $\underline{C}H_2CHN$), 63.27 (d, ^2J(C,P) = 8.8 Hz; $CH_2\underline{C}HN$), 64.49 (d, ^2J(C,P) = 4.7 Hz; $CHCH\underline{C}H_2OP$), 114.88 (d, ^3J(C,P) = 12.3 Hz; *o*-CH(Ph)), 118.85 (s; *p*-CH(Ph)), 123.07 (s; CH(Ar)), 123.49 (s; CH(Ar)), 125.48 (s; CH(Ar)), 125.57 (s; CH(Ar)), 125.64 (s; CH(Ar)), 125.70 (s; CH(Ar)), 125.74 (s; CH(Ar)), 126.06 (s; CH(Ar)), 128.86 (s; CH(Ar)), 128.91 (s; CH(Ar)), 129.10 (br.s *m*-CH(Ph)), 136.52 (s; C(Ph)), 140.35 (s; C(Ar)), 140.39 (s; C(Ar)), 143.19 (s; C(Ar)), 143.51 (s; C(Ar)), 145.68 (d, ^2J(C,P) = 15.8 Hz; C(Ph)) ppm. $^{31}P\{^1H\}$ NMR (242.9 MHz, $CDCl_3$, 30 °C) δ = 120.64 (s) ppm. $C_{35}H_{35}N_2OPS$ (562.22): calcd. C 74.71, H 6.27, N 4.98; found C 74.94, H 6.34, N 5.10.

EXPERIMENTAL SECTION

Preparation of [Pd(allyl)(L1a)]BF_4 complex. A solution of **L1a** (135 mg, 0.2 mmol) in THF (3 mL) was added dropwise over 30 min to a stirred solution of $[Pd(allyl)Cl]_2$ (37 mg, 0.1 mmol) in THF (2 mL) at 20 °C. The reaction mixture was stirred for a further 1 h at 20 °C. $AgBF_4$ (39 mg, 0.2 mmol) was added to the resulting solution, and the reaction mixture was stirred for 1.5 h at 20 °C. The precipitate of AgCl formed was separated by centrifugation, solvent was removed in vacuum (40 Torr) and the crude product was dried in air and in vacuum (10^{-3} Torr). The product was dissolved in CH_2Cl_2 (0.3 mL) and reprecipitated from petroleum ether (10 mL). The precipitate of the product was separated by centrifugation and dried in air and in vacuum (10^{-3} Torr).

[Pd(allyl)(**L1a**)]BF_4: White solid, yield 0.17 g (91 %). ^{1}H NMR (600.1 MHz, $CDCl_3$, 25 °C): δ = 1.83-1.87 (m, 2H; CH_2), 1.90-1.94 (m, 2H; $C\underline{H}_2CH_2N$), 2.01-2.06 (m, 2H; $C\underline{H}_2CH_2N$), 2.29-2.32 (m, 2H; $CHC\underline{H}CH_2O$), 2.30-2.35 (m, 2H; CH_2), 2.90-2.97 (m, 2H; $CHCHC\underline{H}_2O$), 3.18-3.25 (br.m, 2H; $CH_2C\underline{H}_2N$), 3.41 (t, ^2J(H,H) = ^3J(H,H) = 9.1 Hz, 2H; $C\underline{H}_2CHN$), 3.45-3.51 (br.m, 2H; $CH_2C\underline{H}_2N$), 3.92-3.96 (m, 2H; $C\underline{H}_2CHN$), 4.19 (s, 2H; $C\underline{H}CHCH_2O$), 4.43-4.48 (m, 2H; $CH_2C\underline{H}N$), 4.49-4.54 (m, 2H; $CHCHC\underline{H}_2O$), 5.00-5.07 (p, ^3J(H,H) = 10.5 Hz, CH(allyl)), 6.94 (t, ^3J(H,H) = 7.3 Hz, 2H; *p*-CH(Ph)), 6.96-6.97 (m, 4H; *o*-CH(Ph)), 7.10 (t, ^3J(H,H) = 7.4 Hz, 2H; $C\underline{H}CHC$(Ar)), 7.16 (t, ^3J(H,H) = 7.4 Hz, 2H; $C\underline{H'}CH'C'$(Ar)), 7.22 (t, ^3J(H,H) = 7.9 Hz, 4H; *m*-CH(Ph)), 7.24 (d, ^3J(H,H) = 7.4 Hz, 2H; $CH'C\underline{H'}C'$(Ar)), 7.38 (d, ^3J(H,H) = 7.4 Hz, 2H; $CHC\underline{H}C$(Ar)) ppm. $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$, 25 °C): δ = 27.18 (vt, *J*(C,P) = 2.3 Hz; $\underline{C}H_2CH_2N$), 31.33 (s; CH_2), 44.84 (s; $CH\underline{C}HCH_2O$), 45.81 (s; $\underline{C}HCHCH_2O$), 49.11 (vt, *J*(C,P) = 10.5 Hz; $CH_2\underline{C}H_2N$), 53.96 (s; $\underline{C}H_2CHN$), 62.59 (s; $CH_2\underline{C}HN$), 66.92-67.69 (br.m, CH_2(allyl)), 70.88 (vt, *J*(C,P) = 6.6 Hz; $CHCH\underline{C}H_2O$), 115.99 (br.s; *o*-CH(Ph)), 121.72 (s; *p*-CH(Ph)), 123.42 (t, ^2J(C,P) = 8.6 Hz; CH(allyl)), 123.61 (s; $CH\underline{C}HC$(Ar)), 124.96 (s; $CH'\underline{C}H'C'$(Ar)), 125.97 (s; $\underline{C}HCHC$(Ar)), 126.46 (s; $\underline{C}H'CH'C'$(Ar)), 129.30 (s; *m*-CH(Ph)), 140.13 (s; $CHCH\underline{C}$(Ar)), 142.57 (s; $CH'CH'\underline{C'}$(Ar)), 142.86-142.93 (m; C(Ph)) ppm. $^{31}P\{^1H\}$ NMR (242.9 MHz, $CDCl_3$, 25 °C): δ = 117.80 (s) ppm. $C_{43}H_{49}BF_4N_4O_2P_2Pd$ (908.24): calcd. C 56.81, H 5.43, N 6.16; found C 57.06, H 5.50, N 6.28.



* too broad to detect a chemical shift

$^{13}C\{^{1}H\}$ and ^{1}H NMR Signals Assignment for [Pd(allyl)(**L1a**)]BF_4.

EXPERIMENTAL SECTION

Preparation of [Pd(allyl)(L5a)]$_2$(BF$_4$)$_2$. A solution of **L5a** (112.5 mg, 0.2 mmol) in THF (2 mL) was added dropwise over 30 min to a stirred solution of [Pd(allyl)Cl]$_2$ (37 mg, 0.1 mmol) in THF (1 mL) at 20 °C. The reaction mixture was stirred for a further 1 h at 20 °C. $AgBF_4$ (39 mg, 0.2 mmol) was added to the resulting solution, and the reaction mixture was stirred for 1.5 h at 20 °C. The precipitate of [Pd(allyl)(**L5a**)]$_2$(BF$_4$)$_2$ and AgCl was separated by centrifugation and washed with THF (2 x 10 mL). The crude product was dissolved in CH_2Cl_2 than the precipitate of AgCl was separated by centrifugation. Solvent was removed in vacuum (40 Torr) and the product was dried in air and in vacuum (10^{-3} Torr). The product was washed with boiling THF (2 x 15 mL) then dried in air and in vacuum (10^{-3} Torr).

Pd(allyl)(**L5a**)]$_2$(BF$_4$)$_2$: White solid, yield 45 mg (28 %). ^{1}H NMR (600.1 MHz, CD_2Cl_2, 30 °C): δ = 1.45-1.80 (m, 7H), 1.83-2.27 (m, 7H), 2.37-3.66 (m, 17H), 3.71-4.73 (m, 11H), 5.18-5.97 (m, 2H; CH(allyl)), 6.35-7.93 (m, 36H; CH(Ar)), ppm. ^{13}C{^{1}H} NMR (150.9 MHz, CD_2Cl_2, 30 °C): δ = 27.12-27.43 (m; $\underline{C}H_2CH_2N$), 32.55 (s; CH_2), 32.79 (s; CH_2), 41.06 (s; $\underline{C}HCH_2S$), 41.70 (s; $\underline{C}HCH_2S$), 41.96 (s; $\underline{C}HCH_2S$), 42.59 (s; $\underline{C}HCH_2S$), 45.60 (br.s; $CH\underline{C}H_2S$), 46.53 (s; CH), 46.97 (s; CH), 47.09 (s; CH), 47.20 (s; CH), 47.36 (s; CH), 47.44 (s; CH), 47.47 (s; CH), 47.51 (br.s; $CH\underline{C}H_2S$), 47.85 (s; CH), 48.09 (s; CH), 48.29 (br.s; $CH\underline{C}H_2S$), 49.26-49.96 (m; $CH_2\underline{C}H_2N$), 54.31 (s; $\underline{C}H_2CHN$), 54.45 (s; $\underline{C}H_2CHN$), 54.61 (s; $\underline{C}H_2CHN$), 54.75 (s; $\underline{C}H_2CHN$), 63.13 (br.s; CH_2(allyl)^c), 63.25 (br.s; CH_2(allyl)^c), 63.29 (s; $CH_2\underline{C}HN$), 63.35 (s; $CH_2\underline{C}HN$), 64.71 (br.s; CH_2(allyl)^c), 64.97 (br.s; CH_2(allyl)^c), 67.94 (d, ^2J(C,P) = 12.6 Hz; CH_2OP), 68.19 (d, ^2J(C,P) = 12.8 Hz; CH_2OP), 68.64 (d, ^2J(C,P) = 14.3 Hz; CH_2OP), 85.06 (d, ^2J(C,P) = 39.0 Hz; CH_2(allyl)^t), 85.42 (d, ^2J(C,P) = 39.8 Hz; CH_2(allyl)^t), 85.51 (d, ^2J(C,P) = 36.1 Hz; CH_2(allyl)^t), 85.75 (d, ^2J(C,P) = 36.3 Hz; CH_2(allyl)^t), 115.11-115.19 (m; CH(Ar)), 115.39-115.47 (m; CH(Ar)), 121.70 (s; CH(Ar)), 121.85 (s; CH(Ar)), 121.95 (s; CH(Ar)), 122.08 (s; CH(Ar)), 123.85 (d, ^2J(C,P) = 8.0 Hz; CH(allyl)), 123.96 (d, ^2J(C,P) = 9.2 Hz; CH(allyl)), 124.22 (s; CH(Ar)), 124.33 (s; CH(Ar)), 124.38 (s; CH(Ar)), 124.49 (s; CH(Ar)), 124.83 (s; CH(Ar)), 124.87 (s; CH(Ar)), 124.93-125.00 (m; CH(allyl)), 125.28 (s; CH(Ar)), 125.55 (s; CH(Ar)), 126.46 (s; CH(Ar)), 126.56 (s; CH(Ar)), 126.69 (s; CH(Ar)), 126.78 (s; CH(Ar)), 126.90 (s; CH(Ar)), 127.11 (s; CH(Ar)), 127.33 (s; CH(Ar)), 127.42 (s; CH(Ar)), 129.80 (s; CH(Ar)), 129.93 (s; CH(Ar)), 129.99 (s; CH(Ar)), 130.11 (s; CH(Ar)), 130.47 (s; CH(Ar)), 130.59 (s; CH(Ar)), 130.78 (s; CH(Ar)), 130.82 (s; CH(Ar)), 130.88 (s; CH(Ar)), 130.95 (s; CH(Ar)), 131.06 (s; CH(Ar)), 131.09 (s; CH(Ar)), 131.56 (s; CH(Ar)), 140.11-143.10 (m; C(Ar)) ppm. ^{31}P{^{1}H} NMR (242.9 MHz, CD_2Cl_2, 30 °C) δ = 117.29 (s (9%)), 117.65 (s (23%)), 117.71 (s (23%)), 118.10 (s (44%)) ppm. $C_{76}H_{80}B_2F_8N_4O_2P_2Pd_2S_2$ (1592.33): calcd. C 57.27, H 5.06, N 3.51; found C 57.40, H 5.02, N 3.57.

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 **L3a, L4**, **L5b** (0.4 mmol) in THF (3 mL) was added dropwise over 30 min to a stirred solution of [Pd(allyl)Cl]$_2$ (37 mg, 0.1 mmol) in THF (2 mL) at 20 °C. The reaction mixture was stirred for a further 1 h at 20 °C. $AgBF_4$ (39 mg, 0.2 mmol) was added to the resulting solution, and the reaction mixture was stirred for 1.5 h at 20 °C. The precipitate of AgCl formed was separated by centrifugation, solvent was removed in vacuum (40 Torr) and the crude product was dried in air and in vacuum (10^{-3} Torr). The product was dissolved in CH_2Cl_2 (0.3 mL) and reprecipitated from hexane (10 mL). The precipitate of the product was separated by centrifugation and dried in air and in vacuum (10^{-3} Torr).

Pd(allyl)(**L3a**)$_2$]BF_4: White solid, yield 0.21 g (71 %). ^{1}H NMR (600.1 MHz, $CDCl_3$, 30 °C): δ = 1.42-1.55 (br.m, 2H; CH_2), 1.47-1.51 (m, 2H; $CHC\underline{H}CH_2OP$), 1.58-1.64 (m, 2H; $CHC\underline{H}CH_2OTs$), 1.99-2.13 (m, 2H; CH_2), 2.00-2.12 (m, 4H; $C\underline{H}_2CH_2N$), 2.38-2.61 (br.m, 2H; $C\underline{H}_2CHN$), 2.45 and 2.46 (s, 3H and s, 3H; $C\underline{H}_3CCH$(Ts)), 3.08-3.13 (m, 1H; CH_2'(allyl$_{anti}$)), 3.16-3.23 (br.m, 1H; CH_2(allyl$_{anti}$)), 3.16-3.29 (br.m, 2H; $CHCH\underline{H}_2OP$), 3.27 and 3.30 (t, ^2J(H,H) = ^3J(H,H) = 9.4 Hz, 1H and t, ^2J(H,H) = ^3J(H,H) = 9.2 Hz, 1H; $CHCH\underline{H}_2OTs$), 3.33-3.38 (m, 2H; $CHCH\underline{H}_2OP$), 3.39-3.45 (m, 2H; $CH_2C\underline{H}_2N$), 3.46-3.53 (m, 2H; $C\underline{H}_2CHN$), 3.54-3.56 and 3.59-3.61 (dd, ^2J(H,H) = 9.6 Hz, ^3J(H,H) = 6.0 Hz, 1H and dd, ^2J(H,H) = 9.6 Hz, ^3J(H,H) = 5.7 Hz, 1H; $CHCH\underline{H}_2OTs$), 3.64-3.67 (m, 2H; $CH_2C\underline{H}_2N$), 3.87-3.94 and 3.94-3.99 (m, 1H and m, 1H; $CH_2C\underline{H}N$), 4.11 and 4.12 (d, ^3J(H,H) = 1.8 Hz, 1H and d, ^3J(H,H) = 1.8 Hz, 1H; $C\underline{H}CHCH_2OTs$), 4.19 (d, ^3J(H,H) = 1.7 Hz, 2H; $C\underline{H}CHCH_2OP$), 4.54 (br.s, 2H; CH_2(allyl$_{syn}$)), CH_2'(allyl$_{syn}$)), 5.53-5.64 (br.m, 1H; CH (allyl), 6.74 and 6.76 (d, ^3J(H,H) = 8.0 Hz, 2H and d, ^3J(H,H) = 8.1 Hz, 2H; *o*-CH(Ph)), 6.85 and 6.88 (d, ^3J(H,H) = 7.2 Hz, 1H and d, ^3J(H,H) = 7.3 Hz, 1H; CH(Ar)), 6.92-6.95 (m, 2H; CH(Ar)), 6.93-6.96 (m, 2H; *p*-CH(Ph)), 7.02-7.08 (m, 6H; CH(Ar)), 7.10-7.19 (m, 6H; CH(Ar)), 7.23-7.28 (m, 4H; *m*-CH(Ph)), 7.31 and 7.32 (d, ^3J(H,H) = 7.9 Hz, 2H and d, ^3J(H,H) = 7.9 Hz, 2H; $CH_3CC\underline{H}$(Ts)), 7.64-7.67 (m, 4H; SCCH(Ts)) ppm. $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$, 30 °C): δ = 21.57 (s; $\underline{C}H_3CCH$(Ts)), 27.25-27.29 and 27.45-27.39 (m and m; $\underline{C}H_2CH_2N$), 31.09 and 31.20 (s and s; CH_2), 42.23 and 42.26 (s and s; $CH\underline{C}HCH_2OTs$), 43.04 (br.s; $CH\underline{C}HCH_2OP$), 44.78 and 44.83 (s and s; $\underline{C}HCHCH_2OTs$), 45.40 (s; $\underline{C}HCHCH_2OP$), 48.19-48.43 and 48.43-48.64 (br.m and br.m; $CH_2\underline{C}H_2N$), 53.54 and 53.68 (s and s; $\underline{C}H_2CHN$), 62.44 and 62.68 (s and s; $CH_2\underline{C}HN$), 66.90-67.04 (m; $CHCH\underline{C}H_2OP$), 71.82 and 72.03 (s and s; $CHCH\underline{C}H_2OTs$), 72.34 (vt, J(C,P) = 20.6 Hz; CH_2(allyl)), 72.70 (vt, J(C,P) = 20.9 Hz; CH_2'(allyl)), 114.94 (s; *o*-CH(Ph)), 121.00 and 121.03 (s and s; *p*-CH(Ph)), 123.49 and 123.53 (s and s; $CH\underline{C}HC$(Ar)), 123.63 (s; $CH\underline{C}HC$(Ar)), 123.78 (t, ^2J(C,P) = 8.3 Hz; CH(allyl)), 125.19 (s; $CH\underline{C}HC$(Ar)), 125.21 and 125.27 (s and s; $CH\underline{C}HC$(Ar)), 125.79 and 125.80 (s and s; $\underline{C}HCHC$(Ar)), 125.87 and 125.90 (s and s; $\underline{C}HCHC$(Ar)), 126.39 and 126.44 (s and s; $\underline{C}HCHC$(Ar)), 126.47 and 126.48 (s and s; $\underline{C}HCHC$(Ar)), 127.68 and 127.71 (s and s; $SC\underline{C}H$(Ts)), 129.58 and 129.63 (s and s; *m*-CH(Ph)), 129.96 (s; $CH_3C\underline{C}H$(Ts)), 132.51 (s; $CH_3\underline{C}CH$(Ts)), 139.04 (s; $CHCH\underline{C}$(Ar)), 139.66 and 139.79 (s and s; $CHCH\underline{C}$(Ar)), 142.21 and 142.24 (s and s; $CHCH\underline{C}$(Ar)), 142.35 and 142.37 (s and s; $CHCH\underline{C}$(Ar)), 142.21-142.37 (m; C(Ph)), 145.10 (s; $S\underline{C}CH$(Ts)) ppm. $^{31}P\{^1H\}$ NMR (242.9 MHz, $CDCl_3$, 30 °C) δ = 116.23 (s) ppm. $C_{75}H_{79}BF_4N_4O_8P_2PdS_2$ (1482.39): calcd. C 60.71, H 5.37, N 3.78; found C 61.00, H 5.47, N 3.62.

Pd(allyl)(**L4**)$_2$]BF_4: Orange solid, yield 0.16 g (50 %). ^1H NMR (600.1 MHz, $CDCl_3$, 30 °C): δ = 1.42-2.18 (br.m, 12H), 2.56-3.28 (br.m, 10H), 3.43-3.93 (br.m, 10H), 4.05-4.75 (br.m, 24H), 5.52-5.66 (br.m, 1H; CH(allyl)), 6.76-7.31 (br.m, 26H; CH(Ar)), 8.01 (br.s, 2H; $CH_2N=C\underline{H}$) ppm. $^{13}C\{^1H\}$ NMR (150.9 MHz, CD_2Cl_2, 30 °C): δ = 27.86 and 28.00 (s and s; $\underline{C}H_2CH_2N$), 31.73 (s; CH_2), 44.40 (br.s; CH), 45.75 (br.s; CH), 46.55 (s; CH), 47.39 (s; CH), 49.34-49.80 (br.m; $CH_2\underline{C}H_2N$), 54.28 (br.s; $\underline{C}H_2CHN$), 63.08 and 63.29 (s and s; $CH_2\underline{C}HN$), 65.47-66.21 (br.m; CH_2OP, $\underline{C}H_2N=CH$), 68.22 (br.s; CH(Fc)), 69.01 (br.s; CH(Fc)), 69.85 (br.s; C_5H_5(Fc)), 71.26-72.42 (br.m; CH(Fc), CH_2(allyl)), 80.52 (br.s; C(Fc)), 115.70 (s; *o*-CH(Ph)), 121.83 (s; *p*-CH(Ph)), 123.83-123.97 (m; CH(allyl), 123.89 (s; CH(Ar)), 124.17 (s; CH(Ar)), 125.79 (s; CH(Ar)), 125.95 (s; CH(Ar)), 126.09 (s; CH(Ar)), 126.46 (s; CH(Ar)), 126.74 (s; CH(Ar)), 126.99 (s; CH(Ar)), 130.30 (s; *m*-CH(Ph)), 140.74 and 140.78 (s and s; C(Ar)), 141.24 (s; C(Ar)), 143.18 (m; C(Ph)), 143.53 (s; C(Ar)), 144.45 (s; C(Ar)), 162.81 (br.s; $CH_2N=\underline{C}H$) ppm. $^{31}P\{^1H\}$ NMR (242.9 MHz, CD_2Cl_2, 30 °C) δ = 115.90 (br.s) ppm. $C_{83}H_{85}BF_4Fe_2N_6O_2P_2Pd$ (1564.40): calcd. C 63.68, H 5.47, N 5.37; found C 64.02, H 5.58, N 5.58.

Pd(allyl)(**L5b**)$_2$]BF_4: White solid, yield 0.22 g (81 %). ^1H NMR (600.1 MHz, CD_2Cl_2, 30 °C): δ = 1.40-1.45 (m, 2H; $CHC\underline{H}CH_2S$), 1.67-1.74 (m, 2H; CH_2), 1.94-2.00 (m, 2H; $CHC\underline{H}CH_2OP$), 2.01-2.08 (m, 2H; $C\underline{H}_2CH_2N$), 2.09-2.15 (m, 2H; $C\underline{H}_2CH_2N$), 2.09-2.17 (m, 2H; CH_2), 2.35 and 2.37 (br.t, ^2J(H,H) ~ ^3J(H,H) = 8.5 Hz, 1H and br.t, ^2J(H,H) ~ ^3J(H,H) = 8.5 Hz, 1H; $CHCHC\underline{H}_2S$), 2.73-2.77 and 2.78-2.81 (dd, ^2J(H,H) = 12.9 Hz, ^3J(H,H) = 7.1 Hz, 1H and dd, ^2J(H,H) = 12.9 Hz, ^3J(H,H) = 7.0 Hz, 1H; $CHCHC\underline{H}_2S$), 2.83-2.87 (br.m, 1H; CH_2(allyl$_{anti}$)), 2.93-3.01 (m, 2H; $CHCHC\underline{H}_2OP$), 3.00-3.05 (m, 1H; CH_2'(allyl$_{anti}$)), 3.06-3.15 (br.m; 2H; $C\underline{H}_2CHN$), 3.42-3.47 and 3.48-3.53 (m, 1H and m, 1H; $CH_2C\underline{H}_2N$), 3.61-3.66 and 3.72-3.78 (m, 1H and br.m, 1H; $CH_2C\underline{H}_2N$), 3.71-3.77 (br.m, 2H; $C\underline{H}_2CHN$), 3.84-3.88 (m, 2H; $CHCHC\underline{H}_2OP$), 3.93-4.01 (m, 2H; $CH_2C\underline{H}N$), 4.09-4.16 (br.m, 1H; CH_2'(allyl$_{syn}$)), 4.22 and 4.27 (s, 1H and d, ^3J(H,H) = 1.2 Hz, 1H; $C\underline{H}CHCH_2OP$), 4.22 (s, 2H; $C\underline{H}CHCH_2S$), 4.23-4.28 (br.m, 1H; CH_2(allyl$_{syn}$)), 5.35-5.42 (tt, ^3J(H,H) = 13.9 Hz, ^3J(H,H) = 7.0 Hz, 1H; CH(allyl)), 6.69 and 6.79 (br.d, ^3J(H,H) ~ 7.3 Hz, 1H and br.d, ^3J(H,H) ~ 7.2 Hz, 1H; CH(Ar)), 6.82 and 6.85 (td, ^3J(H,H) = 7.5 Hz, ^4J(H,H) = 0.8 Hz, 1H and td, ^3J(H,H) = 7.5 Hz, ^4J(H,H) = 0.9 Hz, 1H; CH(Ar)), 6.95 and 6.99-7.00 (d, ^3J(H,H) = 8.1 Hz, 2H and m, 2H; *o*-CH(Ph)), 6.99-7.03 (m, 2H; *p*-CH(Ph)), 7.04-7.05 (m, 4H; *o*-CH(Ph)), 7.10-7.21 (m, 12H; CH(Ar)), 7.11-7.13 (m, 2H; *p*-CH(Ph)), 7.16-7.19 (m, 4H; *m*-CH(Ph)), 7.38-7.41 and 7.39-7.42 (m, 2H and m, 2H; *m*-CH(Ph)) ppm. $^{13}C\{^1H\}$ NMR (150.9 MHz, CD_2Cl_2, 30 °C): δ = 27.83 and 27.96 (d, ^3J(C,P) = 4.9 Hz and d, ^3J(C,P) = 5.7 Hz; $\underline{C}H_2CH_2N$), 31.91 and 32.08 (s and s; CH_2), 39.35 and 39.39 (s and s; $CHCH\underline{C}H_2S$), 42.66 and 42.69 (s and s; $CH\underline{C}HCH_2S$), 46.27 (s; $\underline{C}HCHCH_2OP$), 47.55-47.60 (m; $CH\underline{C}HCH_2OP$), 48.59 and 48.69 (s and s; $\underline{C}HCHCH_2S$), 49.51 and 49.86 (d,

^2J(C,P) = 22.1 Hz and d, ^2J(C,P) = 23.2 Hz; CH$_2$C̲H$_2$N), 54.64 and 54.80 (s and s; C̲H$_2$CHN), 63.04 and 63.17 (s and s; CH$_2$C̲HN), 67.17 and 67.37 (d, ^2J(C,P) = 11.9 Hz and d, ^2J(C,P) = 12.2 Hz; CHCHC̲H$_2$OP), 71.59-71.87 (dd, $^2J(C,P)_{trans}$ = 32.1 Hz, $^2J(C,P)_{cis}$ = 10.4 Hz; CH$_2$(allyl)), 72.04-72.33 (dd, $^2J(C,P)_{trans}$ = 32.7 Hz, $^2J(C,P)_{cis}$ = 10.7 Hz; CH$_2$(allyl)), 115.89 and 116.02 (d, ^3J(C,P) = 7.4 Hz and d, ^3J(C,P) = 7.1 Hz; *o*-CH(Ph)), 122.03 and 122.12 (s and s; *p*-CH(Ph)), 123.78 and 123.81 (s and s; CH(Ar)), 123.92 and 123.98 (s and s; CH(Ar)), 124.55 (t, ^2J(C,P) = 8.4 Hz; CH(allyl)), 126.20 (s; CH(Ar)), 126.23 and 126.24 (s and s; CH(Ar)), 126.33 (s; CH(Ar)), 126.65 (s; CH(Ar)), 126.70 and 126.72 (s and s; *p*-CH(Ph)), 126.76 and 126.81 (s and s; CH(Ar)), 127.01 (s; CH(Ar)), 129.34 and 129.38 (s and s; *o*-CH(Ph)), 129.54 and 129.56 (s and s; *m*-CH(Ph)), 130.39 and 130.43 (s and s; *m*-CH(Ph)), 136.29 and 136.31 (s and s; C(Ph)), 139.96 and 140.03 (s and s; C(Ar)), 140.80 and 140.83 (s and s; C(Ar)), 143.14-143.31 (m; C(Ph)), 143.22 and 143.24 (s and s; C(Ar)), 143.91 and 143.94 (s and s; C(Ar)) ppm. ^{31}P{^{1}H} NMR (242.9 MHz, CD$_2$Cl$_2$, 30 °C) δ = 115.70 and 115.98 (AB, ^2J(P,P) = 92.0 Hz) ppm. $C_{73}H_{75}BF_4N_4O_2P_2PdS_2$ (1358.39): calcd. C 64.48, H 5.56, N 4.12; found C 64.60, H 5.61, N 4.06.

Table S1. ^{31}P{^{1}H]}NMR chemical shifts of novel diamidophosphites and Pd(II) complexes.

Compound	δ_P
L1a	121.26 (s)
L1b	120.58 (s)
L2a	125.44 (s)
L2b	129.80 (s)
L3a	122.29 (s)
L3b	121.22 (s)
L4	120.86 (s)
L5a	121.27 (s)
L5b	120.64 (s)
[Pd(allyl)(**L1a**)]BF$_4$	117.80 (s)
Pd(allyl)(**L5a**)]$_2$(BF$_4$)$_2$	117.29 (s (9%)), 117.65 (s (23%)), 117.71 (s (23%)), 118.10 (s (44%))
Pd(allyl)(**L3a**)$_2$]BF$_4$	116.23 (s)
Pd(allyl)(**L4**)$_2$]BF$_4$	115.90 (br.s)
Pd(allyl)(**L5b**)$_2$]BF$_4$	115.70, 115.98 (AB, ^2J(P,P) = 92.0 Hz)

EXPERIMENTAL SECTION

Palladium-Catalyzed Asymmetric Allylic Alkylation of (*E*)-1,3-Diphenylallyl Acetate with Dimethyl Malonate: A solution of $[Pd(allyl)Cl]_2$ (0.001 g, 0.0025 mmol) and the appropriate ligand (0.005 mmol or 0.01 mmol) in the appropriate solvent (1.5 mL) was stirred for 40 min or the appropriate cationic complex (0.005 mmol) was dissolved in the appropriate solvent (1.5 mL). (*E*)-1,3-diphenylallyl acetate (**9**) (0.05 mL, 0.25 mmol) was added and the solution stirred for 15 min. Dimethyl malonate (0.05 ml, 0.44 mmol), BSA (0.11 mL, 0.44 mmol) and KOAc (0.002 g) were added. The reaction mixture was stirred for 24 h, diluted with CH_2Cl_2 (2 mL) and filtered through a thin layer of SiO_2. The filtrate was evaporated at reduced pressure (40 Torr) and dried in vacuum (10^{-3} Torr) affording a residue containing dimethyl (*E*)-2-(1,3-diphenylallyl)malonate (**10a**).[27] In order to evaluate *ee* and conversion, the obtained residue was dissolved in an appropriate eluent mixture (8 mL) and a sample was taken for HPLC analysis.

Palladium-Catalyzed Asymmetric Allylic Amination of (*E*)-1,3-Diphenylallyl Acetate with Pyrrolidine and Phthalimide: A solution of $[Pd(allyl)Cl]_2$ (0.001 g, 0.0025 mmol) and the appropriate ligand (0.005 mmol or 0.01 mmol) in the appropriate solvent (1.5 mL) was stirred for 40 min or the appropriate cationic complex (0.005 mmol) was dissolved in the appropriate solvent (1.5 mL). (*E*)-1,3-diphenylallyl acetate (**9**) (0.05 mL, 0.25 mmol) was added and the solution stirred for 15 min, then freshly distilled pyrrolidine (0.06 mL, 0.75 mmol) or phthalimide (0.045 g, 0.3 mmol) and K_2CO_3 (0.083 g, 0.6 mmol) were added. The reaction mixture was stirred for 24 h, diluted with CH_2Cl_2 (2 mL) and filtered through a thin layer of SiO_2. The filtrate was evaporated at reduced pressure (40 Torr) and dried in vacuum (10^{-3} Torr) affording a residue containing (*E*)-1-(1,3-diphenylallyl)pyrrolidine (**10b**)[28] or (*E*)-2-(1,3-diphenylallyl)isoindoline-1,3-dione (**10c**).[23,29] In order to evaluate *ee* and conversion, the obtained residue was dissolved in an appropriate eluent mixture (8 mL) and a sample was taken for HPLC analysis.

Palladium-Catalyzed Asymmetric Allylic Alkylation of Cinnamyl Acetate with Ethyl 2-Oxocyclohexane-1-Carboxylate: A solution of $[Pd(allyl)Cl]_2$ (0.001 g, 0.0025 mmol) and the appropriate ligand (0.005 mmol or 0.01 mmol) in toluene (1.5 mL) was stirred for 40 min or the appropriate cationic complex (0.005 mmol) was dissolved in toluene (1.5 mL). Cinnamyl acetate (**11**) (0.04 mL, 0.25 mmol) was added and the solution stirred for 15 min. β-Ketoether **12** (0.06 mL, 0.375 mmol), BSA (0.125 mL, 0.5 mmol) and $Zn(OAc)_2$ (0.005 g) were added. The reaction mixture was stirred for 24 h, diluted with toluene (2 mL) and filtered through a thin layer of SiO_2. The filtrate was evaporated at reduced pressure (40 Torr) and dried in vacuum (10^{-3} Torr) affording a residue containing ethyl 1-cinnamyl-2-oxocyclohexane-1-carboxylate (**13**).[24a,b] 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 Alkylation of Cinnamyl Acetate with Ethyl 2-Acetamido-3-Oxobutanoate: A solution of $[Pd(allyl)Cl]_2$ (0.001 g, 0.0025 mmol) and the appropriate ligand (0.005 mmol or 0.01 mmol) in toluene (1.5 mL) was stirred for 40 min or the appropriate cationic complex (0.005 mmol) was dissolved in toluene (1.5 mL). Cinnamyl acetate (**11**) (0.04 mL, 0.25 mmol) was added and the solution stirred for 15 min. α-Acetamido-β-Ketoether **14** (0.07 g, 0.375 mmol), BSA (0.125 mL, 0.5 mmol) and KOAc (0.003 g) were added. The reaction mixture was stirred for 24 h, diluted with toluene (2 mL) and filtered through a thin layer of SiO_2. The filtrate was evaporated at reduced pressure (40 Torr) and dried in vacuum (10^{-3} Torr) affording a residue containing ethyl (*E*)-2-acetamido-2-acetyl-5-phenylpent-4-enoate (**15**).[25a] 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 2-Acetyl-3,4-Dihydronaphthalen-1(2*H*)-one: A solution of $[Pd(allyl)Cl]_2$ (0.001 g, 0.0025 mmol) and the appropriate ligand (0.005 mmol or 0.01 mmol) in toluene (1.5 mL) was stirred for 40 min or the appropriate cationic complex (0.005 mmol) was dissolved in toluene (1.5 mL). Cinnamyl acetate (**11**) (0.04 mL, 0.25 mmol) was added and the solution stirred for 15 min. 1,3-Diketone **16** (0.047 g, 0.25 mmol), BSA (0.125 mL, 0.5 mmol) and $Zn(OAc)_2$ (0.005 g) were added. The reaction mixture was stirred for 24 h, diluted with toluene (2 mL) and filtered through a thin layer of SiO_2. The filtrate was evaporated at reduced pressure (40 Torr) and dried in vacuum (10^{-3} Torr) affording a residue containing 2-acetyl-2-cinnamyl-3,4-dihydronaphthalen-1(2*H*)-one (**17**).[30] In order to evaluate *ee* and conversion, the obtained residue was dissolved in an appropriate eluent mixture (8 mL) and a sample was taken for HPLC analysis.

Palladium-Catalyzed Asymmetric Allylic Amination of 2-(Diethoxyphosphoryl)-1-Phenylallyl Acetate with Aniline: A solution of $[Pd(allyl)Cl]_2$ (0.001 g, 0.0025 mmol) and the appropriate ligand (0.005 mmol or 0.01 mmol) in CH_2Cl_2 (1.5 mL) was stirred for 40 min or the appropriate cationic complex (0.005 mmol) was dissolved in CH_2Cl_2 (1.5 mL). 2-(Diethoxyphosphoryl)-1-phenylallyl acetate (**18**) (0.08 g, 0.25 mmol) was added and the solution stirred for 15 min, then freshly distilled aniline (0.05 mL, 0.5 mmol) and K_2CO_3 (0.069 g, 0.5 mmol) were added. The reaction mixture was stirred for 24 h, diluted with CH_2Cl_2 (2 mL) and filtered through a thin layer of SiO_2. The filtrate was evaporated at reduced pressure (40 Torr) and dried in vacuum (10^{-3} Torr) affording a residue containing mixture of diethyl (3-phenyl-3-(phenylamino)prop-1-en-2-yl)phosphonate (**19**), (*E*)-diethyl (1-phenyl-3-(phenylamino)prop-1-en-2-yl)phosphonate (**20**) and (*E*)-2-(diethoxyphosphoryl)-3-phenylallyl acetate (**21**).[21] Conversion of **18** and the ratio of **19**/**20**/**21** were determined by ^{31}P NMR spectroscopy in $CHCl_3$. In order to evaluate *ee*, the obtained residue was dissolved in an appropriate eluent mixture (8 mL) and a sample was taken for HPLC analysis.

CRYSTAL DATA FOR NEW LIGANDS

Table S2. Crystal data for **L1a** and **L1b** (single-crystals).

	L1a	**L1b**
CCDC number	2055283	2055284
empirical formula	$C_{40}H_{44}N_4O_2P_2$	$C_{40}H_{44}N_4O_2P_2$
formula weight	674.73	674.73
T, K	293(2)	293(2)
wavelength, Å	1.54086	1.54086
crystal system	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$P2_12_12_1$
a, Å	9.4156(4)	9.0658(2)
b, Å	17.1568(7)	17.9593(6)
c, Å	22.3751(7)	22.1974(8)
volume, $Å^3$	3614.5(2)	3614.08(19)
Z	4	4
D_x, g cm^{-3}	1.240	1.240
μ, mm^{-1}	1.404	1.404
crystal size, mm^3	0.22 x 0.15 x 0.13	0.12 x 0.11 x 0.10
$\theta_{min} – \theta_{max}$, °	3.95 – 70.95	3.98 – 68.37
hkl range	$-11 \le h \le 5$, $-21 \le k \le 19$, $-26 \le l \le 27$	$-7 \le h \le 10$, $-21 \le k \le 20$, $-26 \le l \le 26$
reflections collected	20930	25176
independent reflections	6402 [R_{int} = 0.143]	6534 [R_{int} = 0.044]
goodness-of-fit	0.614	1.107
data/restraints/parameters	6402 / 0 / 434	6534 / 0 / 434
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0433, wR_2 = 0.0656	R_1 = 0.0445, wR_2 = 0.1197
Absolute structure parameter	-0.01(3)	-0.002(8)
Largest diff. peak/hole, e·$Å^{-3}$	0.191 / -0.234	0.316 / -0.235

CRYSTAL DATA FOR NEW LIGANDS

Table S3. Crystal data for **L4** and **L5a** (powders)**.**

	L5a	**L4**
CCDC number	2056573	2056574
empirical formula	$C_{35}H_{35}N_2OPS$	$C_{40}H_{40}FeN_3OP$
T, K	293(2)	293(2)
formula weight	562.68	665.57
particle morphology, color	needle, colorless	prism, brown
wavelength, Å	0.354345(4)	0.354345(4)
crystal system	monoclinic	orthorhombic
space group	$P2_1$	$P2_12_12_1$
a, Å	16.6231(12)	22.3219(13)
b, Å	11.4030(10)	18.9753(12)
c, Å	10.4537(9)	8.0785(8)
β, °	95.968(12)	90
volume, Å^3	1496.6(2)	3421.8(5)
Z	2	4
M_{20}[a]	94	110
F_{30}[b]	152 (0.003, 43)	233 (0.002, 34)
D_x, g cm^{-3}	1.249	1.292
$2\theta_{min} – 2\theta_{max}$, increment, °	1.300 – 20.000, 0.002	1.300 – 20.000, 0.002
no. params/restraints	191/135	211/175
$R_p/R_{wp}/R_{exp}$[c]	0.0313/0.0409/0.0166	0.0327/0.0461/0.0165
goodness-of-fit	2.455	2.798

[a] M_{20} is defined according to[31]. [b] F_{30} is defined according to[32]. [c] R_p, R_{wp} and R_{exp} are defined according to[33].

CRYSTAL DATA FOR NEW LIGANDS

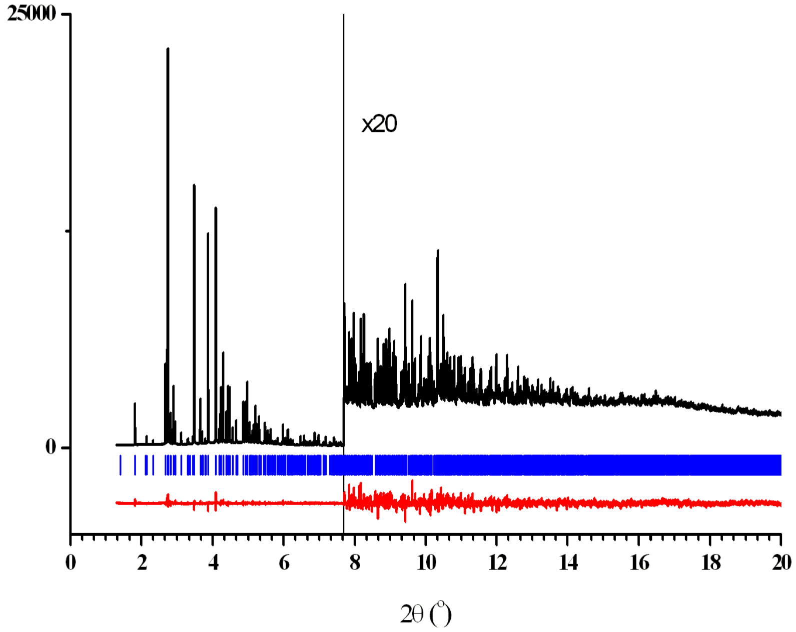


Figure S1. The final Rietveld plot for **L4**, showing the experimental and difference diffraction profiles as black (top) and red (bottom) curves, respectively. The vertical blue bars correspond to the calculated positions of the Bragg peaks.

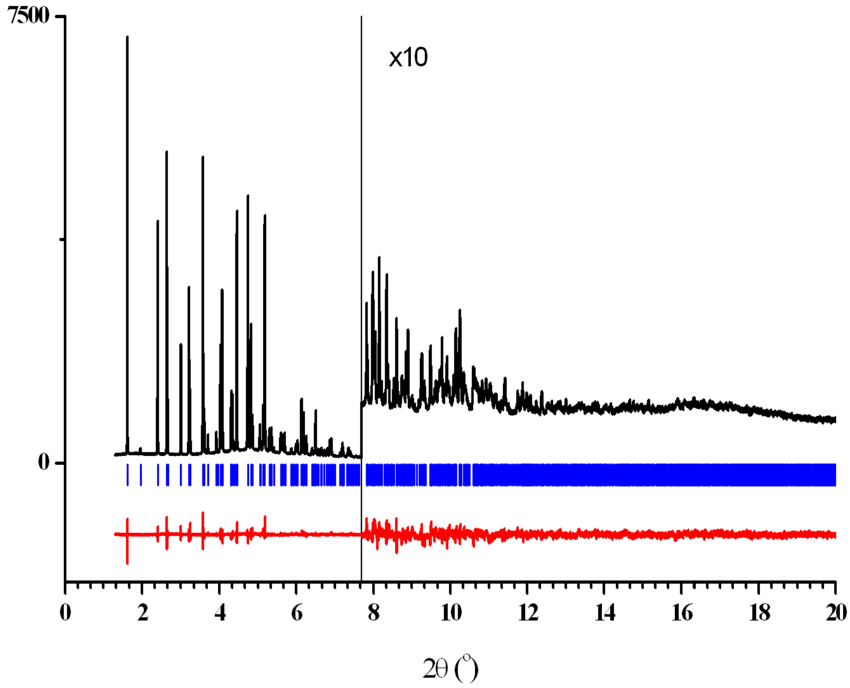


Figure S2. The final Rietveld plot for **L5a**, showing the experimental and difference diffraction profiles as black (top) and red (bottom) curves, respectively. The vertical blue bars correspond to the calculated positions of the Bragg peaks.

CRYSTAL DATA FOR NEW LIGANDS

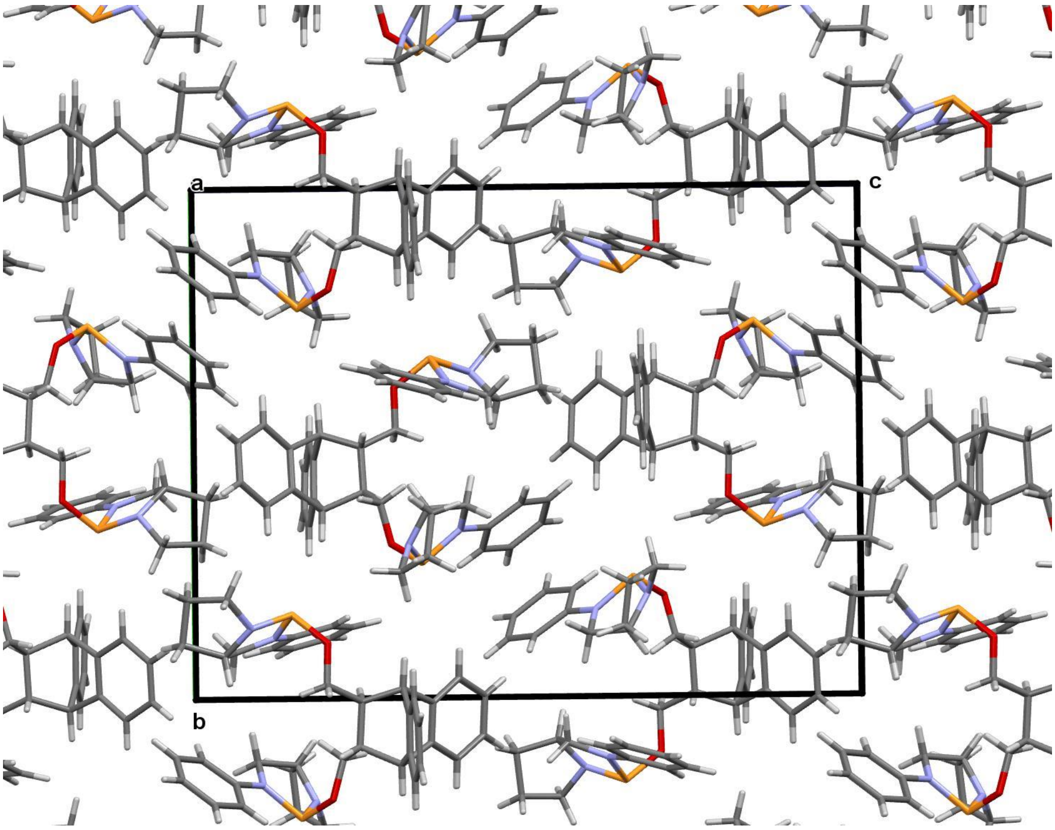


Figure S3. A portion of the crystal packing in **L1a** viewed down the axis *a*.

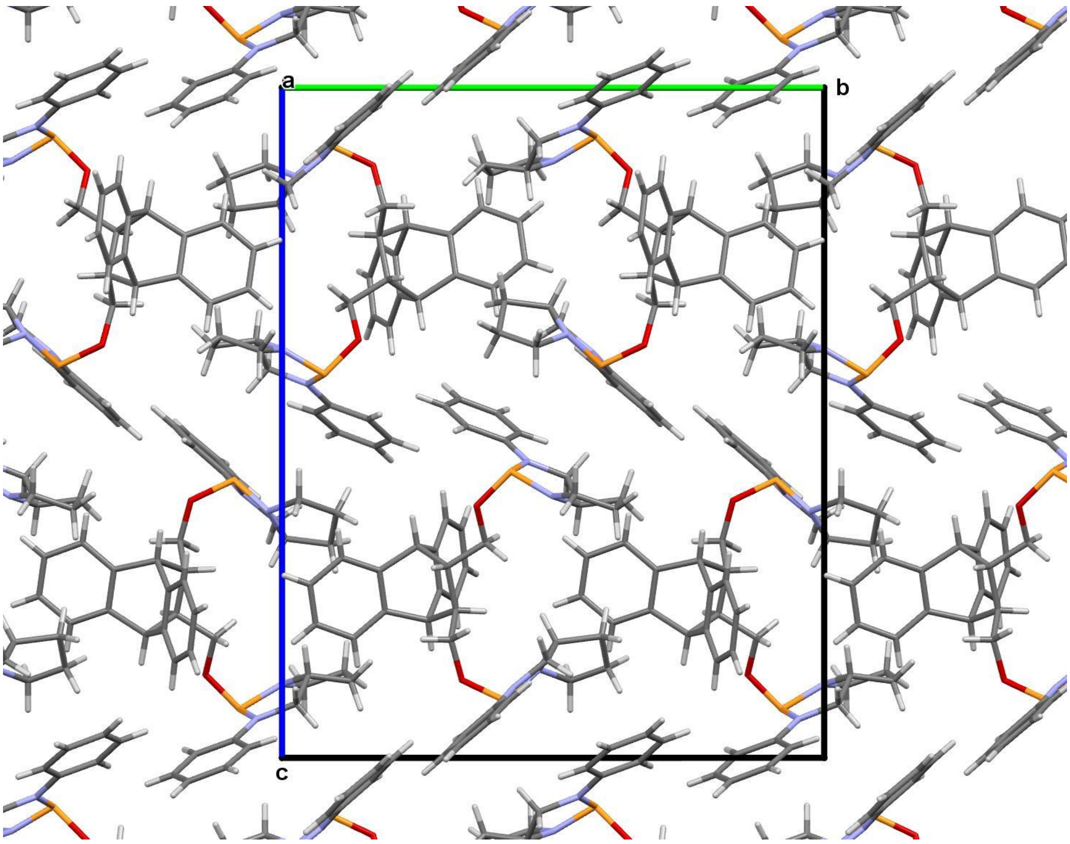


Figure S4. A portion of the crystal packing in **L1b** viewed down the axis *a*.

CRYSTAL DATA FOR NEW LIGANDS

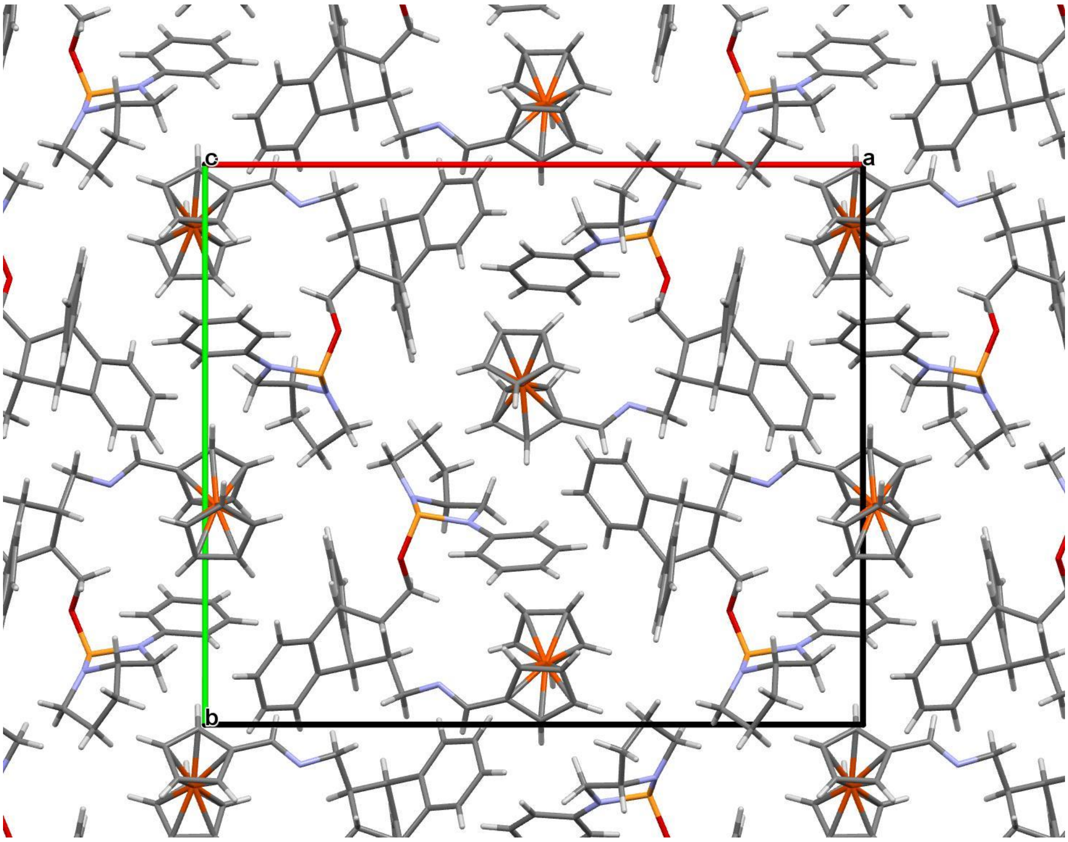


Figure S5. A portion of the crystal packing in **L4** viewed along the axis *c*.

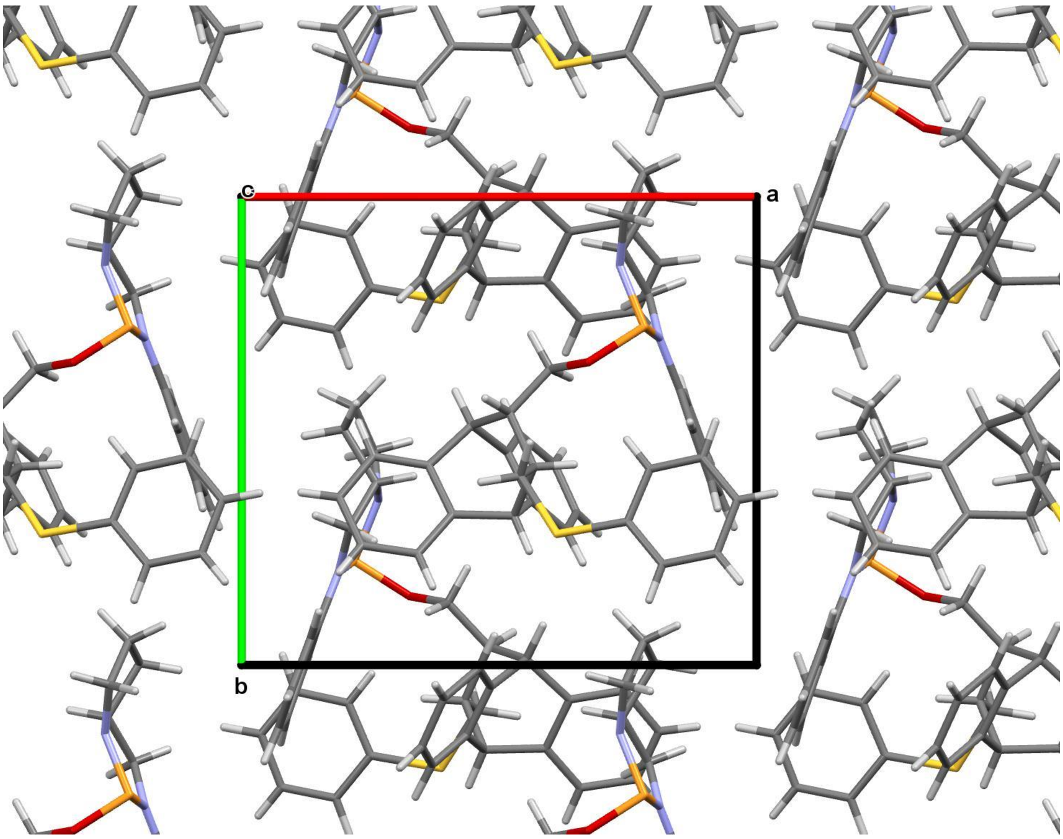


Figure S6. A portion of the crystal packing in **L5a** viewed along the axis *c*.

CALCULATED STRUCTURES OF PALLADIUM(II) COMPLEXES

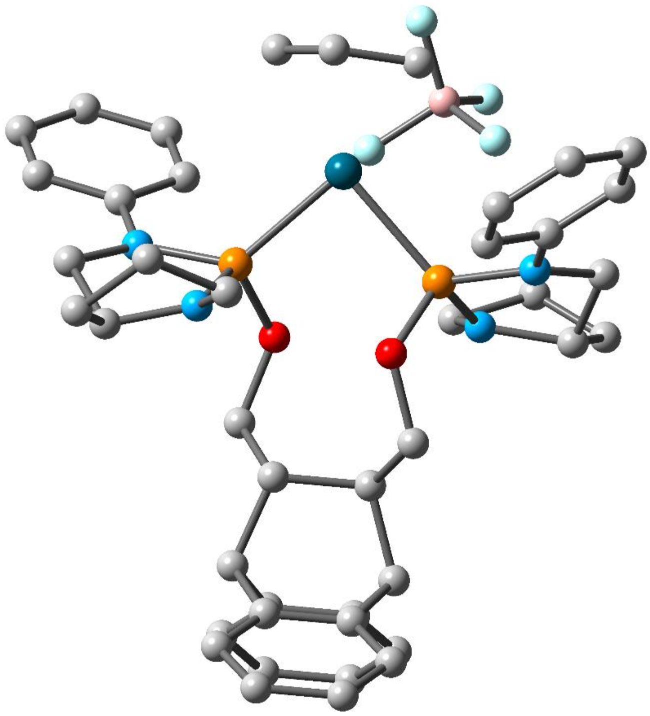


Figure S7. Calculated structure of [Pd(allyl)(**L1a**)]BF_4.

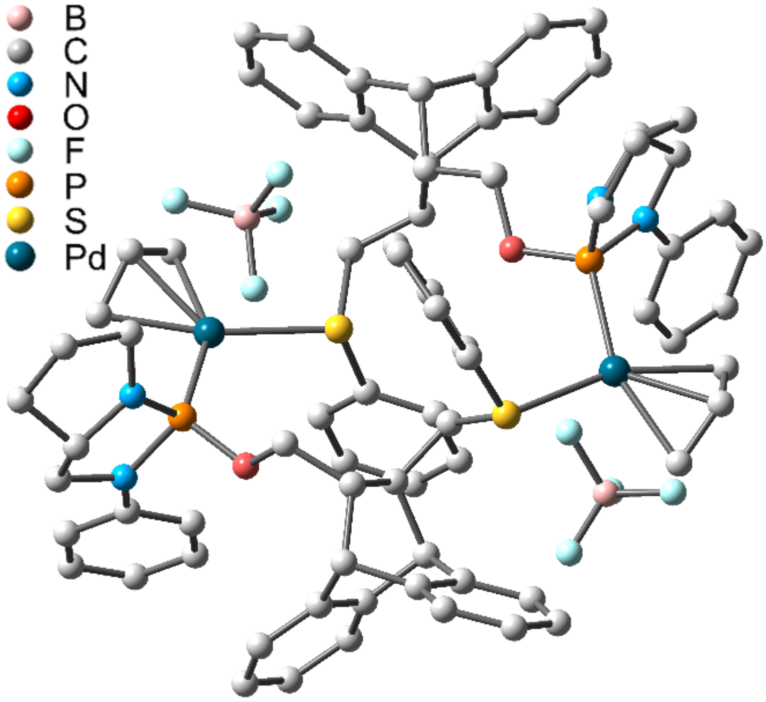
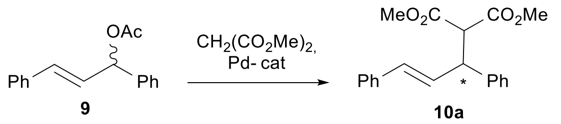


Figure S8. Calculated structure of [Pd(allyl)(**L5a**)]$_2$(BF_4)$_2$.

CATALYTIC RESULTS

Table S4. Pd-catalyzed allylic alkylation of **9** with dimethyl malonate. [a]

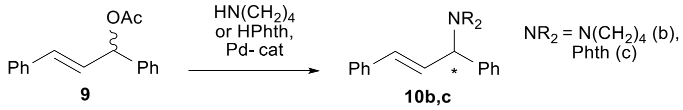


Entry	Compound	L/Pd	Solvent	Conversion [%]	Ee [%] [b,c]
1	**L1a**	1	THF	100	98 (*S*)
2	**L1a**	2	THF	100	96 (*S*)
3	**L1a**	1	CH_2Cl_2	100	98 (*S*)
4	**L1a**	2	CH_2Cl_2	100	98 (*S*)
5	[Pd(allyl)(**L1a**)]BF_4	1	THF	100	98 (*S*)
6	[Pd(allyl)(**L1a**)]BF_4	1	CH_2Cl_2	100	97 (*S*)
7	**L1b**	1	THF	97	89 (*R*)
8	**L1b**	2	THF	58	92 (*R*)
9	**L1b**	1	CH_2Cl_2	100	95 (*R*)
10	**L1b**	2	CH_2Cl_2	100	92 (*R*)
11	**L2a**	1	THF	100	78 (*S*)
12	**L2a**	2	THF	100	78 (*S*)
13	**L2a**	1	CH_2Cl_2	100	85 (*S*)
14	**L2a**	2	CH_2Cl_2	100	85 (*S*)
15	**L2b**	1	THF	100	19 (*R*)
16	**L2b**	2	THF	100	20 (*R*)
17	**L2b**	1	CH_2Cl_2	100	8 (*R*)
18	**L2b**	2	CH_2Cl_2	100	8 (*R*)
19	**L3a**	1	THF	91	86 (*S*)
20	**L3a**	2	THF	93	87 (*S*)
21	**L3a**	1	CH_2Cl_2	100	92 (*S*)
22	**L3a**	2	CH_2Cl_2	100	94 (*S*)
23	[Pd(allyl)(**L3a**)$_2$]BF_4	2	CH_2Cl_2	100	93 (*S*)
24	**L3b**	1	CH_2Cl_2	100	85 (*R*)
25	**L3b**	2	CH_2Cl_2	100	92 (*R*)
26	**L4**	1	THF	100	88 (*S*)
27	**L4**	2	THF	100	90 (*S*)
28	**L4**	1	CH_2Cl_2	100	91 (*S*)
29	**L4**	2	CH_2Cl_2	100	93 (*S*)
30	[Pd(allyl)(**L4**)$_2$]BF_4	2	CH_2Cl_2	100	90 (*S*)

31	**L5a**	1	THF	93	87 (*S*)
32	**L5a**	2	THF	91	87 (*S*)
33	**L5a**	1	CH_2Cl_2	100	83 (*S*)
34	**L5a**	2	CH_2Cl_2	100	92 (*S*)
35	[Pd(allyl)(**L5a**)]$_2$(BF$_4$)$_2$	1	CH_2Cl_2	100	91 (*S*)
36	**L5b**	1	THF	100	91 (*R*)
37	**L5b**	2	THF	100	90 (*R*)
38	**L5b**	1	CH_2Cl_2	100	93 (*R*)
39	**L5b**	2	CH_2Cl_2	100	94 (*R*)
40	[Pd(allyl)(**L5b**)$_2$]BF$_4$	2	CH_2Cl_2	100	94 (*R*)

[a] All reactions were carried out with 1 mol% of [Pd(allyl)Cl]$_2$ at room temperature for 24 h (BSA, KOAc). [b] The conversion of substrate **9** and enantiomeric excess of **10a** were determined by HPLC (Kromasil 5-CelluCoat, C_6H_{14}/*i*PrOH = 99/1, 0.6 mL/min, 254 nm, *t*(*R*) = 19.4 min, *t*(*S*) = 20.8 min). [c] The absolute configurations were assigned by comparison of the HPLC retention times reported in the literature.[9,34]

Table S5. Pd-catalyzed allylic amination of **9** with pyrrolidine and phthalimide. [a]



Entry	Compound	L/Pd	Solvent	Product	Conversion [%]	*Ee* [%] [b,c]
1	**L1a**	1	THF	**10b**	100	96 (*R*)
2	**L1a**	2	THF	**10b**	100	94 (*R*)
3	**L1a**	1	CH_2Cl_2	**10b**	100	45 (*R*)
4	**L1a**	2	CH_2Cl_2	**10b**	100	67 (*R*)
5	**L1a**	1	CH_2Cl_2	**10c**	100	98 (*R*)
6	[Pd(allyl)(**L1a**)]BF$_4$	1	THF	**10b**	100	97 (*R*)
7	[Pd(allyl)(**L1a**)]BF$_4$	1	CH_2Cl_2	**10b**	100	59 (*R*)
8	[Pd(allyl)(**L1a**)]BF$_4$	1	CH_2Cl_2	**10c**	100	98 (*R*)
9	**L1b**	1	THF	**10b**	99	94 (*S*)
10	**L1b**	2	THF	**10b**	97	93 (*S*)
11	**L1b**	1	CH_2Cl_2	**10b**	100	93 (*S*)
12	**L1b**	2	CH_2Cl_2	**10b**	100	87 (*S*)
13	**L1b**	1	CH_2Cl_2	**10c**	100	97 (*S*)
14	**L2a**	1	THF	**10b**	100	46 (*R*)
15	**L2a**	2	THF	**10b**	100	50 (*R*)
16	**L2a**	1	CH_2Cl_2	**10b**	100	55 (*R*)

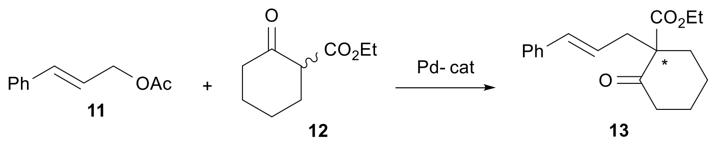
CATALYTIC RESULTS

17	**L2a**	2	CH_2Cl_2	**10b**	100	29 (*R*)
18	**L2a**	1	CH_2Cl_2	**10c**	18	63 (*R*)
19	**L2b**	1	THF	**10b**	100	48 (*S*)
20	**L2b**	2	THF	**10b**	100	34 (*S*)
21	**L2b**	1	CH_2Cl_2	**10b**	100	42 (*S*)
22	**L2b**	2	CH_2Cl_2	**10b**	100	29 (*S*)
23	**L2b**	1	CH_2Cl_2	**10c**	17	18 (*S*)
24	**L3a**	1	THF	**10b**	88	90 (*R*)
25	**L3a**	2	THF	**10b**	100	93 (*R*)
26	**L3a**	1	CH_2Cl_2	**10b**	100	79 (*R*)
27	**L3a**	2	CH_2Cl_2	**10b**	100	83 (*R*)
28	**L3a**	1	CH_2Cl_2	**10c**	0	-
29	**L3a**	2	CH_2Cl_2	**10c**	94	95 (*R*)
30	[Pd(allyl)(**L3a**)$_2$]BF_4	2	THF	**10b**	100	75 (*R*)
31	[Pd(allyl)(**L3a**)$_2$]BF_4	2	CH_2Cl_2	**10c**	18	95 (*R*)
32	**L3b**	1	THF	**10b**	36	91 (*S*)
33	**L3b**	2	THF	**10b**	100	91 (*S*)
34	**L3b**	1	CH_2Cl_2	**10c**	0	-
35	**L3b**	2	CH_2Cl_2	**10c**	32	94 (*S*)
36	**L4**	1	THF	**10b**	100	91 (*R*)
37	**L4**	2	THF	**10b**	100	92 (*R*)
38	**L4**	1	CH_2Cl_2	**10b**	100	76 (*R*)
39	**L4**	2	CH_2Cl_2	**10b**	100	68 (*R*)
40	**L4**	1	CH_2Cl_2	**10c**	0	-
41	**L4**	2	CH_2Cl_2	**10c**	93	95 (*R*)
42	[Pd(allyl)(**L4**)$_2$]BF_4	2	THF	**10b**	81	90 (*R*)
43	[Pd(allyl)(**L4**)$_2$]BF_4	2	CH_2Cl_2	**10c**	17	95 (*R*)
44	**L5a**	1	THF	**10b**	83	91 (*R*)
45	**L5a**	2	THF	**10b**	99	92 (*R*)
46	**L5a**	1	CH_2Cl_2	**10b**	100	82 (*R*)
47	**L5a**	2	CH_2Cl_2	**10b**	100	83 (*R*)
48	**L5a**	1	CH_2Cl_2	**10c**	0	-
49	**L5a**	2	CH_2Cl_2	**10c**	58	94 (*R*)
50	[Pd(allyl)(**L5a**)]$_2$(BF_4)$_2$	1	THF	**10b**	100	88 (*R*)
51	[Pd(allyl)(**L5a**)]$_2$(BF_4)$_2$	1	CH_2Cl_2	**10c**	0	-

52	**L5b**	1	THF	**10b**	100	93 (*S*)
53	**L5b**	2	THF	**10b**	100	92 (*S*)
54	**L5b**	1	CH_2Cl_2	**10b**	100	83 (*S*)
55	**L5b**	2	CH_2Cl_2	**10b**	100	78 (*S*)
56	**L5b**	1	CH_2Cl_2	**10c**	0	-
57	**L5b**	2	CH_2Cl_2	**10c**	100	95 (*S*)
58	[Pd(allyl)(**L5b**)$_2$]BF_4	2	THF	**10b**	100	75 (*S*)
59	[Pd(allyl)(**L5b**)$_2$]BF_4	2	CH_2Cl_2	**10c**	42	95 (*S*)

[a] All reactions were carried out with 1 mol% of [Pd(allyl)Cl]$_2$ at room temperature for 24 h. [b] The conversion of substrate **9** and enantiomeric excess of **10b** were determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}/*i*PrOH/Et_2NH = 200/1/0.1, 0.4 mL/min, 254 nm, *t*(*R*) = 13.7 min, *t*(*S*) = 15.5 min); **10c** – (Daicel Chiralcel OD-H, C_6H_{14}/*i*PrOH = 9/1, 1.0 mL/min, 254 nm, *t*(*S*) = 7.3 min, *t*(*R*) = 8.4 min). [c] The absolute configurations was assigned by comparison of the HPLC retention times reported in the literature.[9,28b,34a,35]

Table S6. Pd-catalyzed allylic alkylation of **11** with **12**. [a]

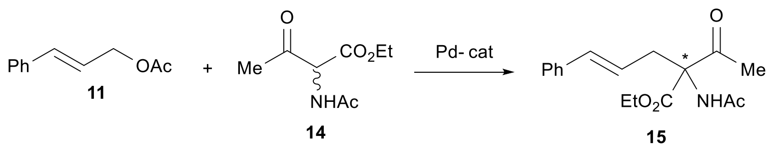


Entry	Compound	L/Pd	Conversion [%]	*Ee* [%] [b,c]
1	**L1a**	1	100	59 (*S*)
2	**L1a**	2	83	62 (*S*)
3	[Pd(allyl)(**L1a**)]BF_4	1	59	57 (*S*)
4	**L1b**	1	100	84 (*R*)
5	**L1b**	2	100	81 (*R*)
6	**L2a**	1	100	65 (*R*)
7	**L2a**	2	100	64 (*R*)
8	**L2b**	1	97	36 (*S*)
9	**L2b**	2	96	38 (*S*)
10	**L3a**	1	31	85 (*S*)
11	**L3a**	2	100	88 (*S*)
12	[Pd(allyl)(**L3a**)$_2$]BF_4	2	100	74 (*S*)
13	**L3b**	1	39	80 (*R*)
14	**L3b**	2	100	88 (*R*)
15	**L4**	1	27	85 (*S*)
16	**L4**	2	100	87 (*S*)
17	[Pd(allyl)(**L4**)$_2$]BF_4	2	100	80 (*S*)

18	**L5a**	1	15	69 (*S*)
19	**L5a**	2	99	86 (*S*)
20	[Pd(allyl)(**L5a**)]$_2$(BF$_4$)$_2$	1	22	77 (*S*)
21	**L5b**	1	10	89 (*R*)
22	**L5b**	2	81	90 (*R*)
23	[Pd(allyl)(**L5b**)$_2$]BF$_4$	2	82	66 (*R*)

[a] All reactions were carried out with 1 mol% of [Pd(allyl)Cl]$_2$ in toluene at room temperature for 24 h (BSA, Zn(OAc)$_2$). [b] The conversion of substrate **11** and enantiomeric excess of **13** were determined by HPLC (Kromasil 5-CelluCoat, C_6H_{14}/*i*PrOH = 95/5, 0.4 mL/min, 254 nm, *t*(*R*) = 14.3 min, *t*(*S*) = 16.7 min). [c] The absolute configuration was assigned by comparison of the HPLC retention times reported in the literature.[24]

Table S7. Pd-catalyzed allylic alkylation of **11** with **14**. [a]



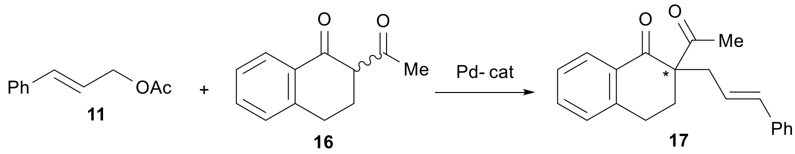
Entry	Compound	L/Pd	Conversion [%]	*Ee* [%] [b,c]
1	**L1a**	1	100	76 (*R*)
2	**L1a**	2	100	72 (*R*)
3	[Pd(allyl)(**L1a**)]BF$_4$	1	100	76 (*R*)
4	**L1b**	1	100	73 (*S*)
5	**L1b**	2	100	67 (*S*)
6	**L2a**	1	100	27 (*S*)
7	**L2a**	2	100	27 (*S*)
8	**L2b**	1	100	22 (*R*)
9	**L2b**	2	100	22 (*R*)
10	**L3a**	1	100	64 (*R*)
11	**L3a**	2	100	61 (*R*)
12	[Pd(allyl)(**L3a**)$_2$]BF$_4$	2	100	60 (*R*)
13	**L3b**	1	100	72 (*S*)
14	**L3b**	2	100	69 (*S*)
15	**L4**	1	100	62 (*R*)
16	**L4**	2	100	54 (*R*)
17	[Pd(allyl)(**L4**)$_2$]BF$_4$	2	100	68 (*R*)
18	**L5a**	1	95	51 (*R*)
19	**L5a**	2	100	60 (*R*)

CATALYTIC RESULTS

20	[Pd(allyl)(**L5a**)]$_2$(BF$_4$)$_2$	1	100	58 (*R*)
21	**L5b**	1	100	64 (*S*)
22	**L5b**	2	100	55 (*S*)
23	[Pd(allyl)(**L5b**)$_2$]BF$_4$	2	100	66 (*S*)

[a] All reactions were carried out with 1 mol% of [Pd(allyl)Cl]$_2$ in toluene at room temperature for 24 h (BSA, KOAc). [b] The conversion of substrate **11** and enantiomeric excess of **15** were determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}/*i*PrOH = 85/15, 0.8 mL/min, 254 nm, *t*(*S*) = 9.8 min, *t*(*R*) = 10.7 min). [c] The absolute configuration was assigned by comparison of the HPLC retention times reported in the literature.[36]

Table S8. Pd-catalyzed allylic alkylation of **11** with **16**. [a]

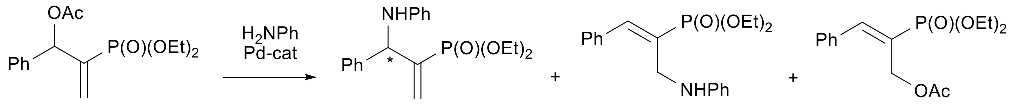


Entry	Compound	L/Pd	Conversion [%]	Ee [%] [b,c]
1	**L1a**	1	100	5 (*S*)
2	**L1a**	2	100	6 (*S*)
3	[Pd(allyl)(**L1a**)]BF$_4$	1	100	7 (*S*)
4	**L1b**	1	46	42 (*R*)
5	**L1b**	2	100	13 (*R*)
6	**L2a**	1	100	11 (*S*)
7	**L2a**	2	100	12 (*S*)
8	**L2b**	1	100	24 (*R*)
9	**L2b**	2	100	22 (*R*)
10	**L3a**	1	70	66 (*S*)
11	**L3a**	2	100	61 (*S*)
12	**L3b**	1	34	3 (*R*)
13	**L3b**	2	100	27 (*R*)
14	**L4**	1	87	46 (S)
15	**L4**	2	100	30 (*S*)
16	**L5a**	1	66	49 (*S*)
17	**L5a**	2	100	45 (*S*)
18	**L5b**	1	60	40 (*R*)
19	**L5b**	2	100	32 (*R*)

CATALYTIC RESULTS

[a] All reactions were carried out with 1 mol% of $[Pd(allyl)Cl]_2$ in toluene at room temperature for 24 h (BSA, $Zn(OAc)_2$). [b] The conversion of substrate **11** and enantiomeric excess of **17** were determined by HPLC (Kromasil 5-CelluCoat, C_6H_{14}/*i*PrOH = 95/5, 0.8 mL/min, 254 nm, *t*(*S*) = 11.2 min, *t*(*R*) = 13.3 min). [c] The absolute configuration was assigned by comparison of the HPLC retention times reported in the literature.[37]

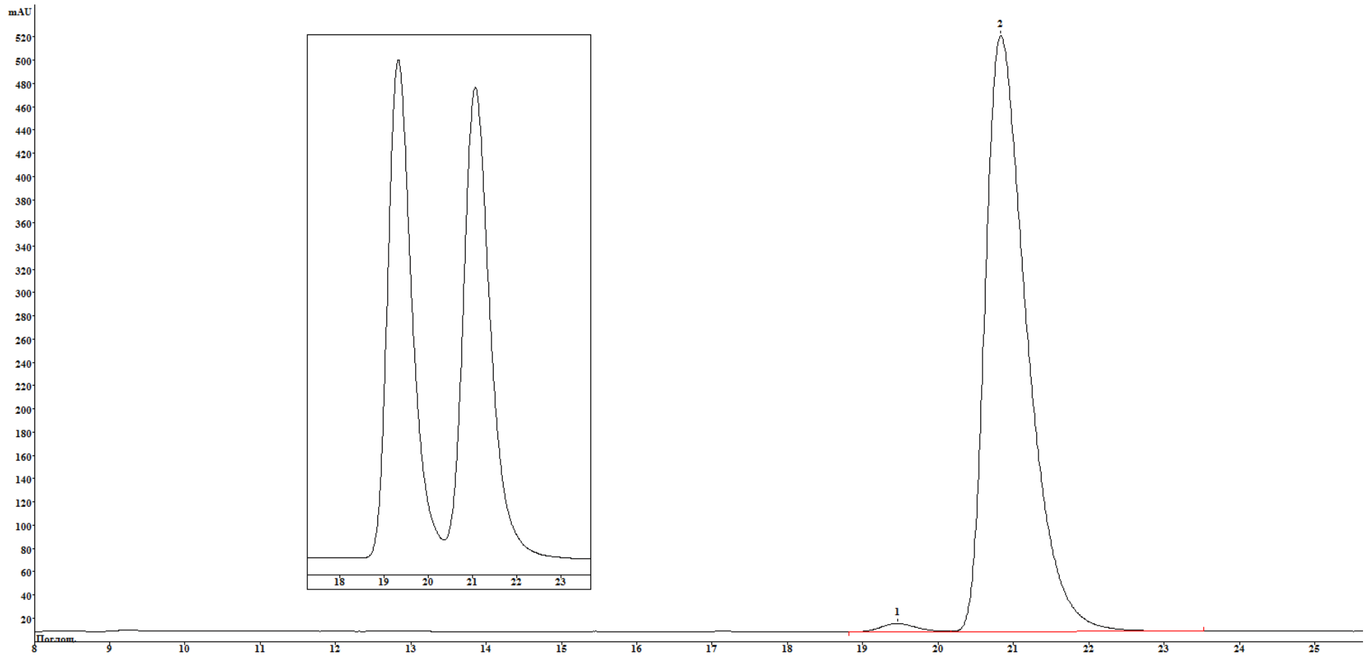
Table S9. Pd-catalyzed allylic amination of **18** with aniline. [a]



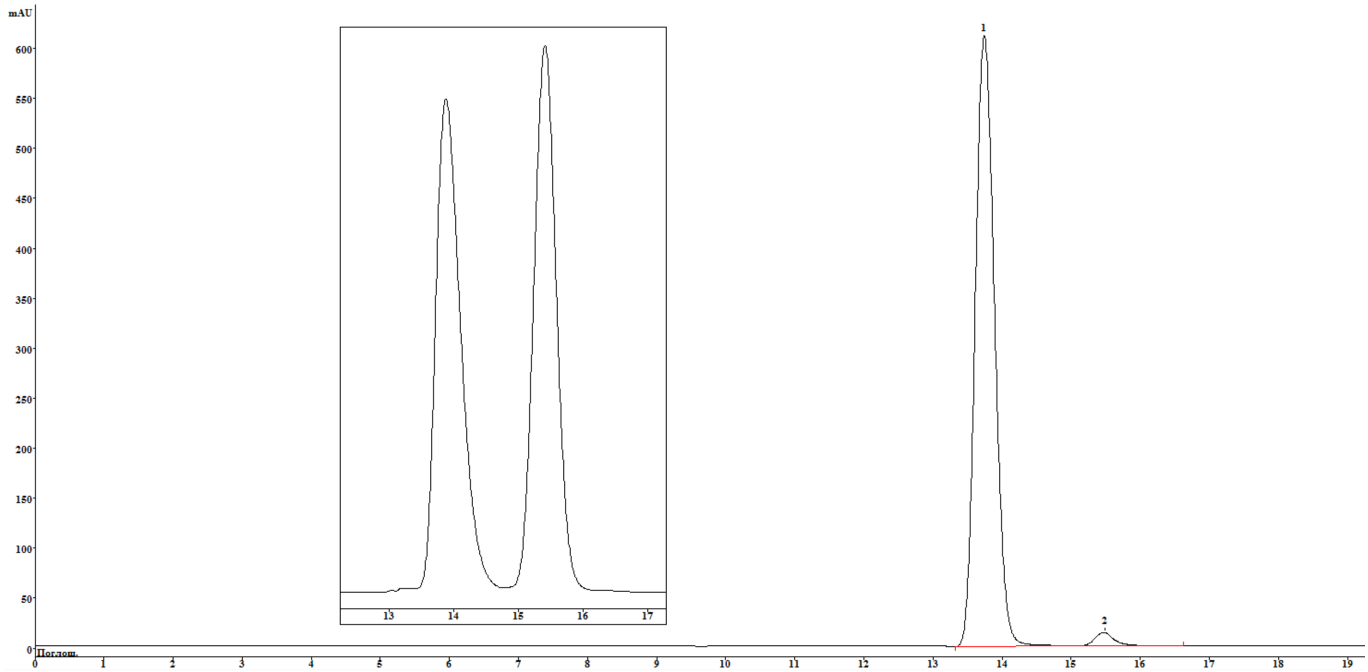
Entry	Compound	L/Pd	Conversion [%]	19/20/21 [b]	*Ee* [%] [c,d]
1	**L1a**	1	100	15/85/0	22 (*R*)
2	[Pd(allyl)(**L1a**)]BF_4	1	100	17/83/0	18 (*R*)
3	**L1b**	1	100	11/89/0	2 (*S*)
4	**L2a**	1	100	5/95/0	n. d.
5	**L2b**	1	100	0/100/0	-
6	**L3a**	1	100	8/92/0	25 (*R*)
7	**L3a**	2	100	57/43/0	71 (*R*)
8	[Pd(allyl)(**L3a**)$_2$]BF_4	2	100	51/49/0	66 (*R*)
9	**L3b**	1	100	6/94/0	n. d.
10	**L3b**	2	100	65/35/0	38 (*S*)
11	**L4**	1	95	18/65/17	10 (*R*)
12	**L4**	2	100	70/30/0	64 (*R*)
13	[Pd(allyl)(**L4**)$_2$]BF_4	2	100	32/34/34	63 (*R*)
14	**L5a**	1	100	6/94/0	28 (*R*)
15	**L5a**		100	62/38/0	66 (*R*)
16	[Pd(allyl)(**L5a**)]$_2$(BF_4)$_2$		100	28/72/0	47 (*R*)
17	**L5b**		100	6/94/0	6 (*S*)
18	**L5b**		100	50/50/0	3 (*S*)
19	[Pd(allyl)(**L5b**)$_2$]BF_4		100	45/40/15	2 (*S*)

[a] All reactions were carried out with 1 mol% of $[Pd(allyl)Cl]_2$ in CH_2Cl_2 at room temperature for 24 h (K_2CO_3). [b] The conversion of substrate **18** and the ratio of **19/20/21** were determined by ^{31}P NMR spectroscopy. [c] The enantiomeric excess of **19** were determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}/*i*PrOH = 9/1, 1.0 mL/min, 254 nm, *t*(*S*) = 5.9 min, *t*(*R*) = 6.9 min). [d] The absolute configuration was assigned by comparison of the HPLC retention times reported in the literature.[21]

HPLC TRACES FOR THE PD-CATALYZED ALLYLIC SUBSTITUTION

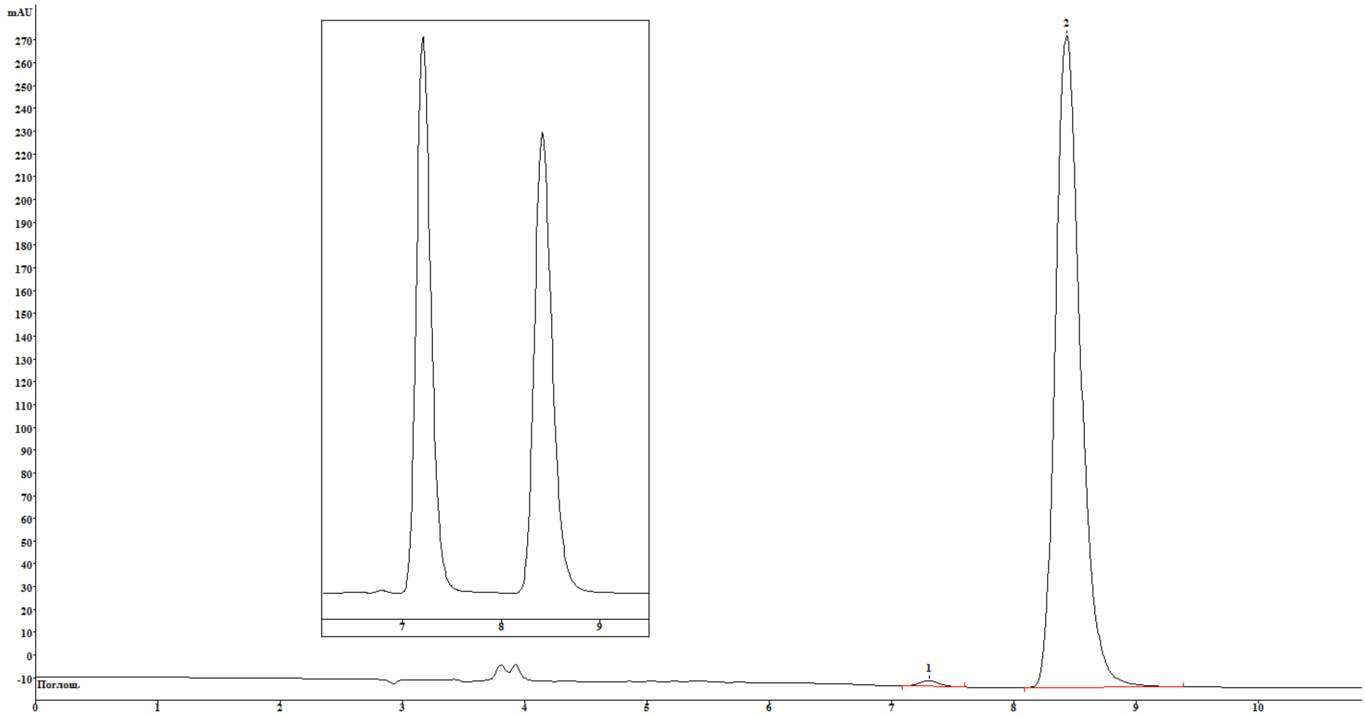


Chiral HPLC trace for the Pd-catalyzed asymmetric allylic alkylation of **9** with dimethyl malonate (entry 1 in Table 1) and for a racemic mixture of **10a** (in the frame).

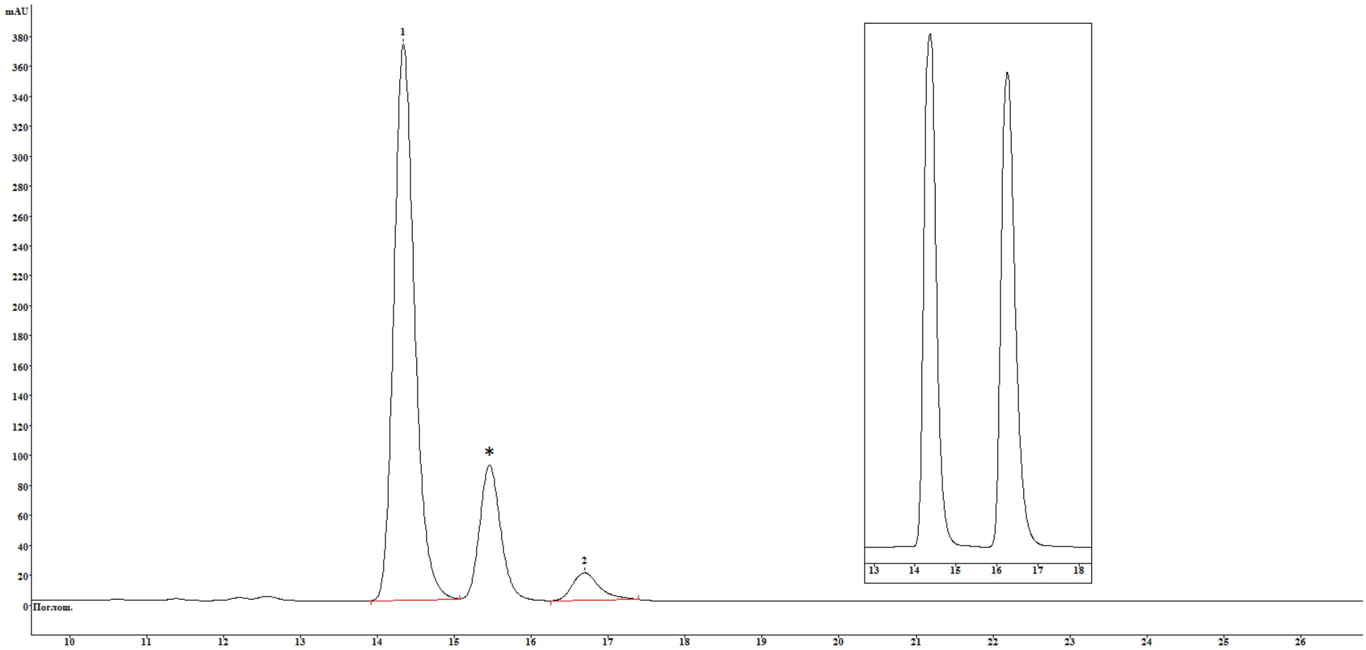


Chiral HPLC trace for the Pd-catalyzed asymmetric allylic amination of **9** with pyrrolidine (entry 6 in Table 2) and for a racemic mixture of **10b** (in the frame).

HPLC TRACES FOR THE PD-CATALYZED ALLYLIC SUBSTITUTION



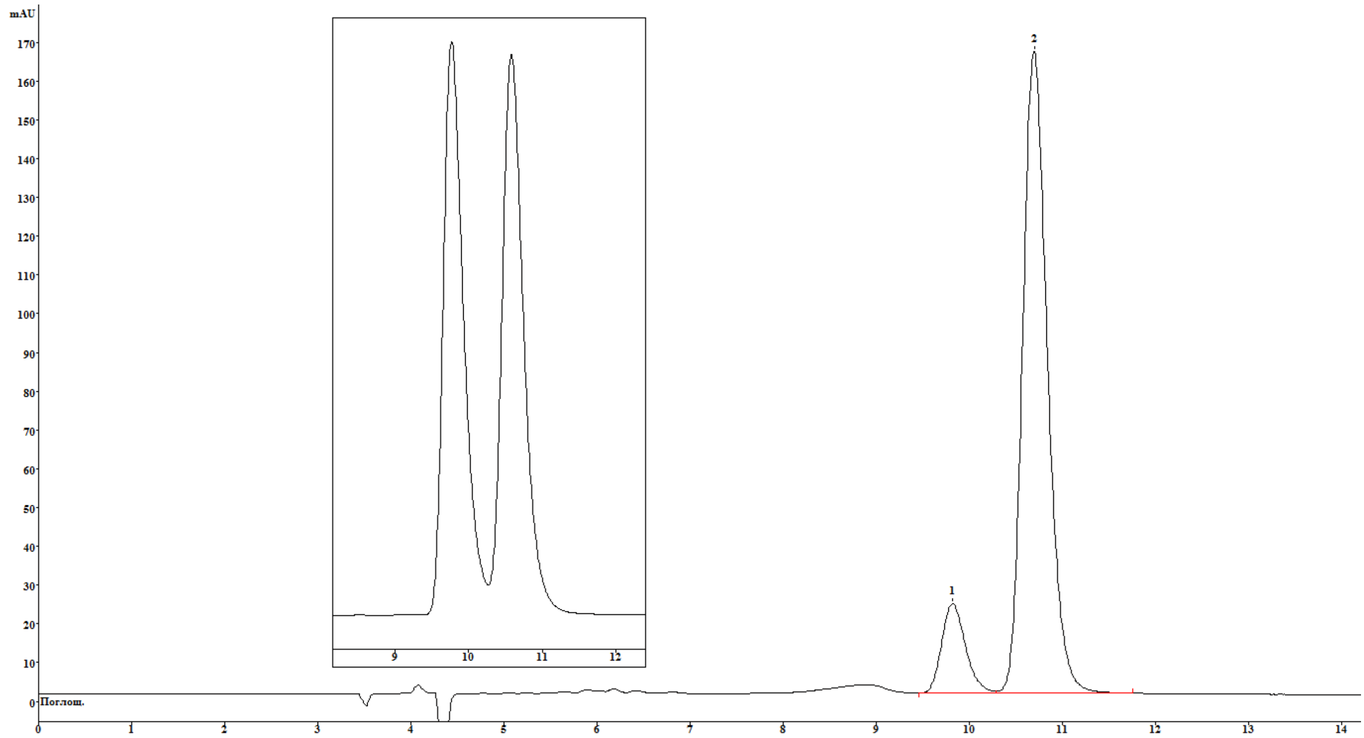
Chiral HPLC trace for the Pd-catalyzed asymmetric allylic amination of **9** with phthalimide (entry 5 in Table 2) and for a racemic mixture of **10c** (in the frame).



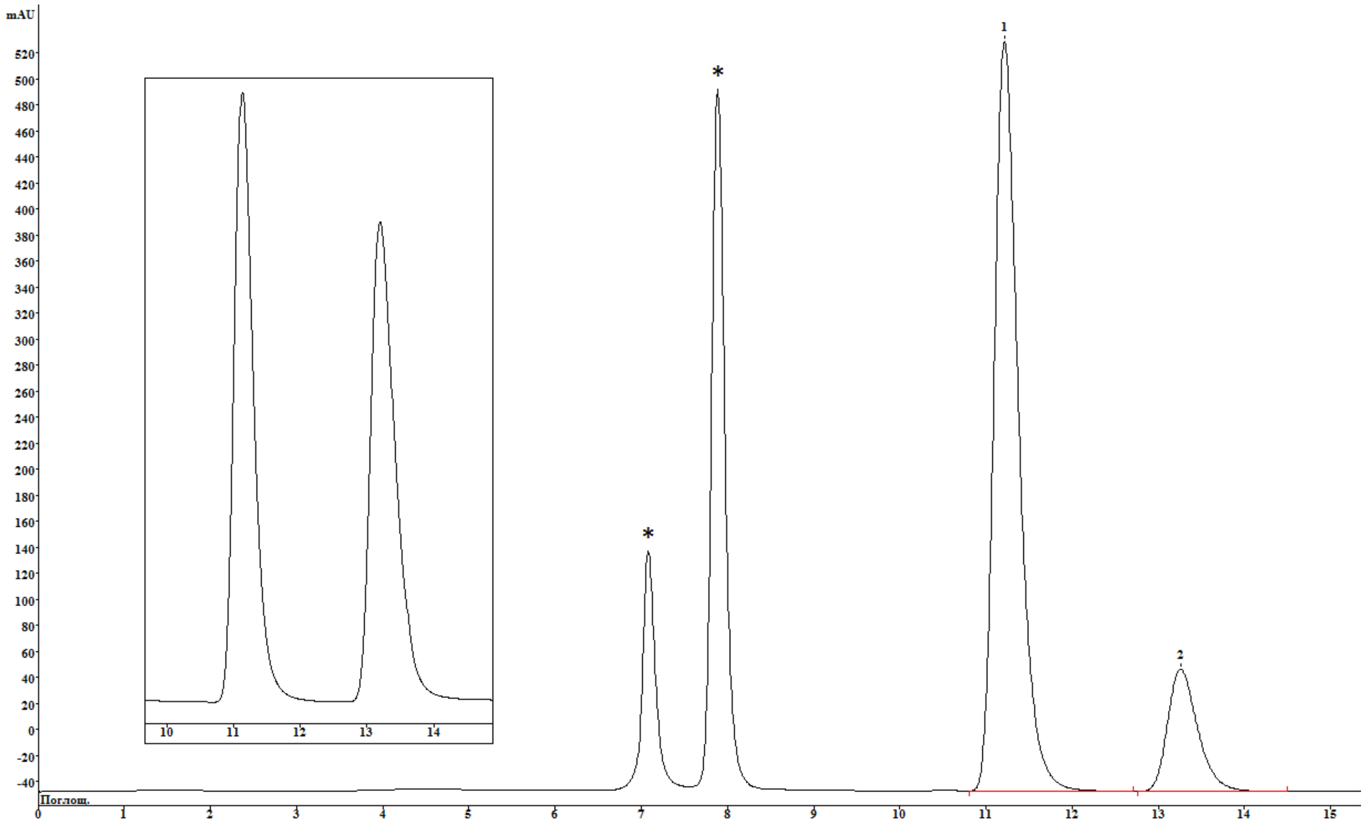
* cinnamyl acetate **11**

Chiral HPLC trace for the Pd-catalyzed asymmetric allylic alkylation of cinnamyl acetate **11** with ethyl 2-oxocyclohexane-1-carboxylate **12** (entry 22 in Table 3) and for a racemic mixture of **13** (in the frame).

HPLC TRACES FOR THE PD-CATALYZED ALLYLIC SUBSTITUTION



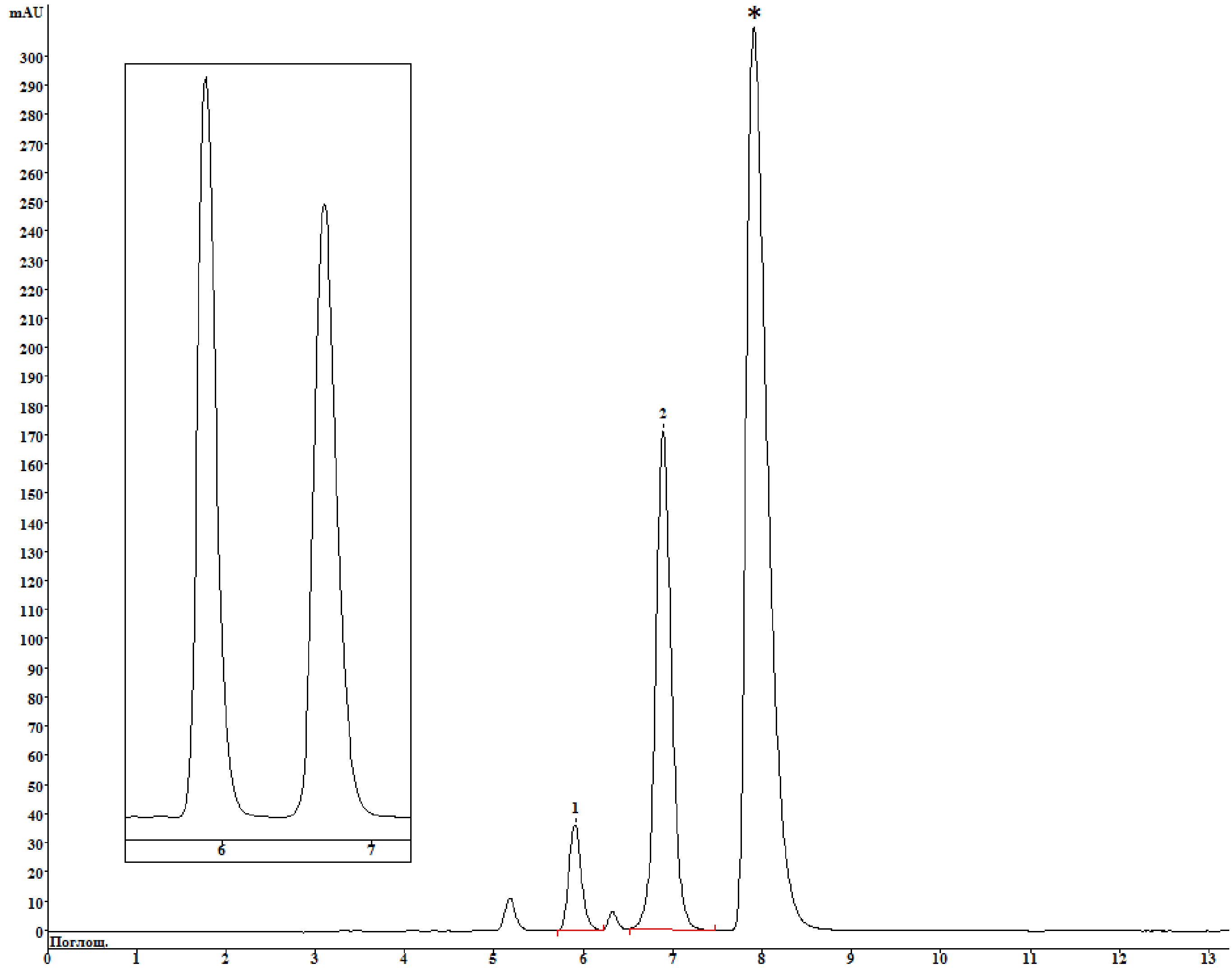
Chiral HPLC trace for the Pd-catalyzed asymmetric allylic alkylation of cinnamyl acetate **11** with ethyl 2-acetamido-3-oxobutanoate **14** (entry 1 in Table 4) and for a racemic mixture of **15** (in the frame).



* cinnamyl acetate **11**

Chiral HPLC trace for the Pd-catalyzed asymmetric allylic alkylation of cinnamyl acetate **11** with 2-acetyl-1-tetralone **16** (entry 10 in Table 5) and for a racemic mixture of **17** (in the frame).

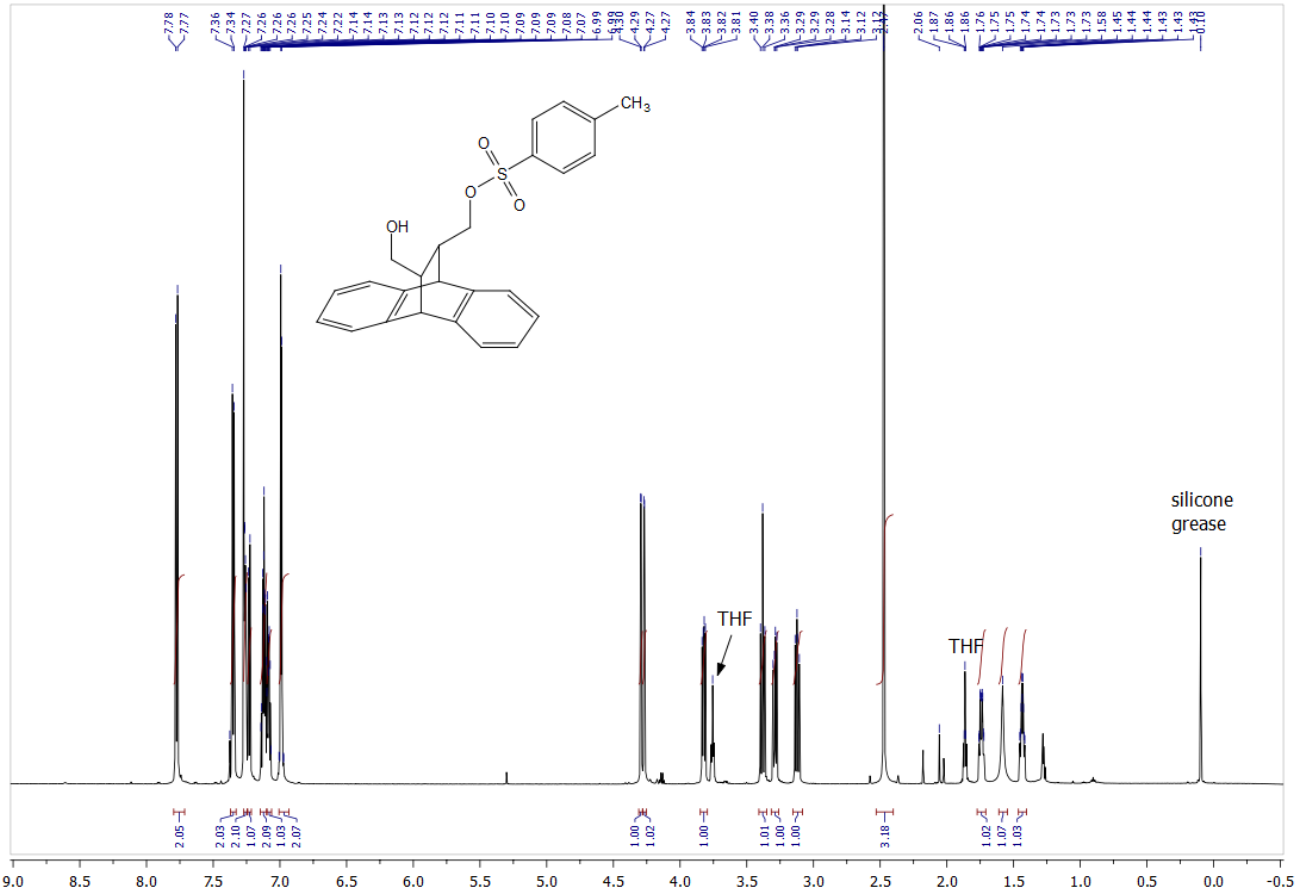
HPLC TRACES FOR THE PD-CATALYZED ALLYLIC SUBSTITUTION



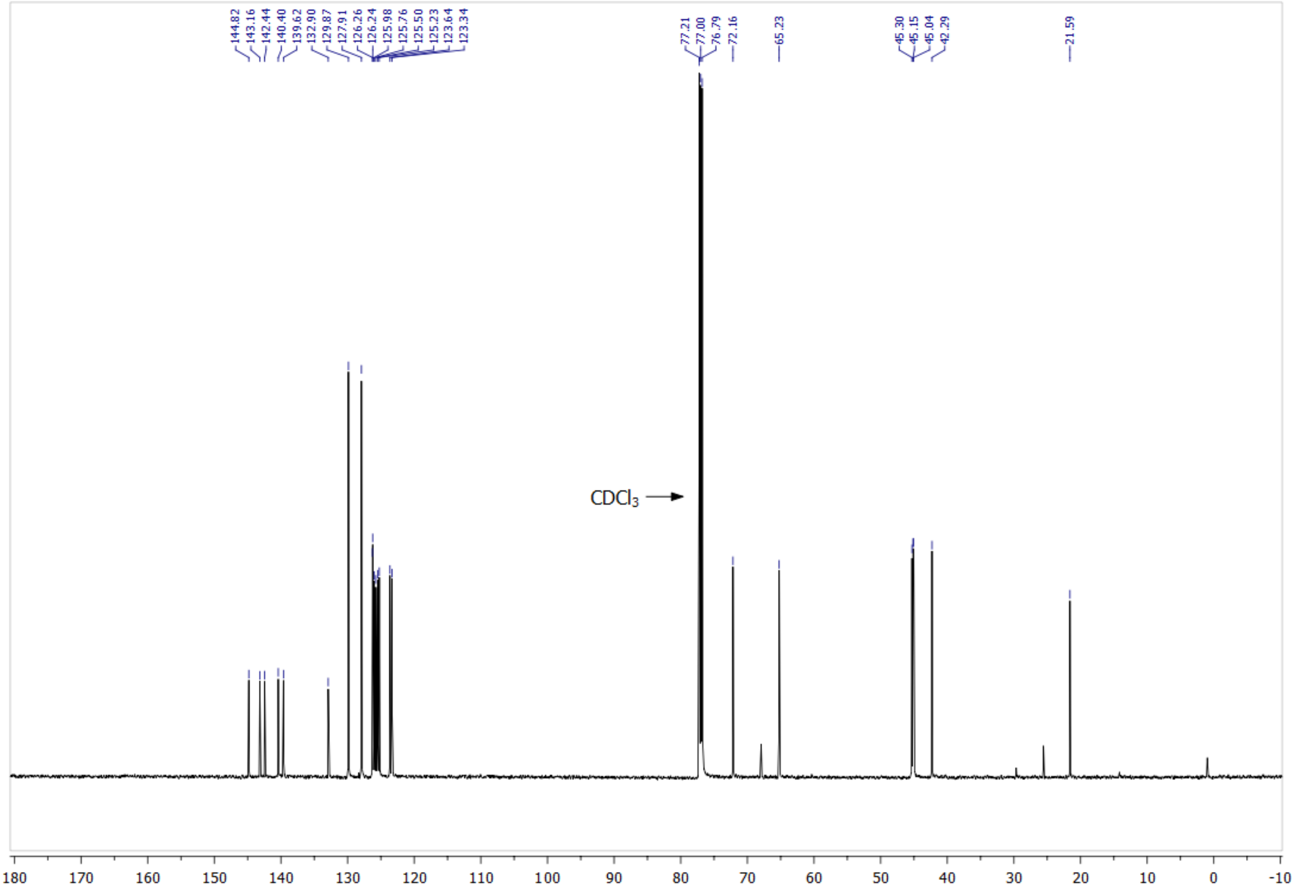
* product **20**

Chiral HPLC trace for the Pd-catalyzed allylic amination of **18** with aniline (entry 7 in Table 6) and for a racemic mixture of **19** (in the frame).

NMR AND MASS SPECTRA

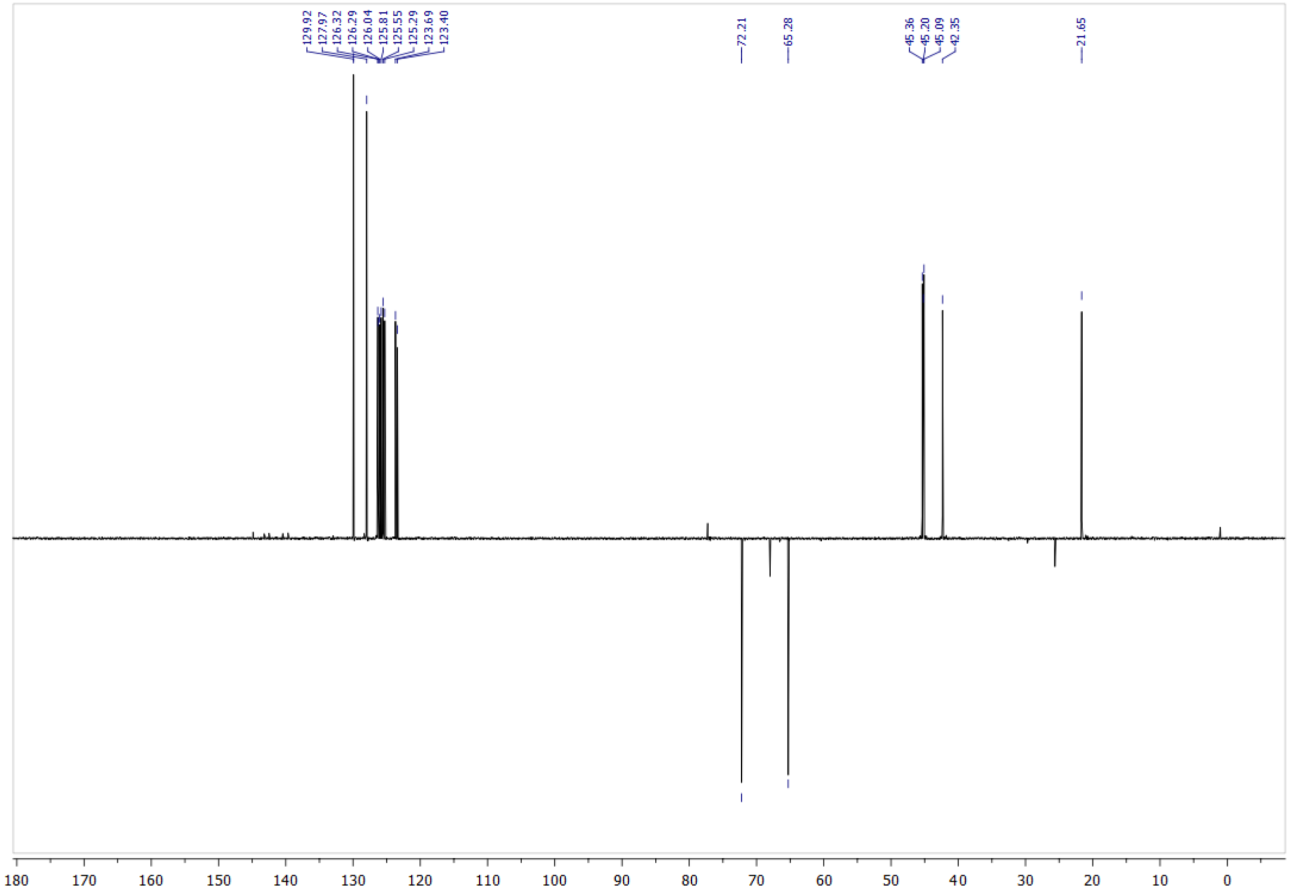


2, ^{1}H (600.1 MHz, $CDCl_3$, 30 °C).

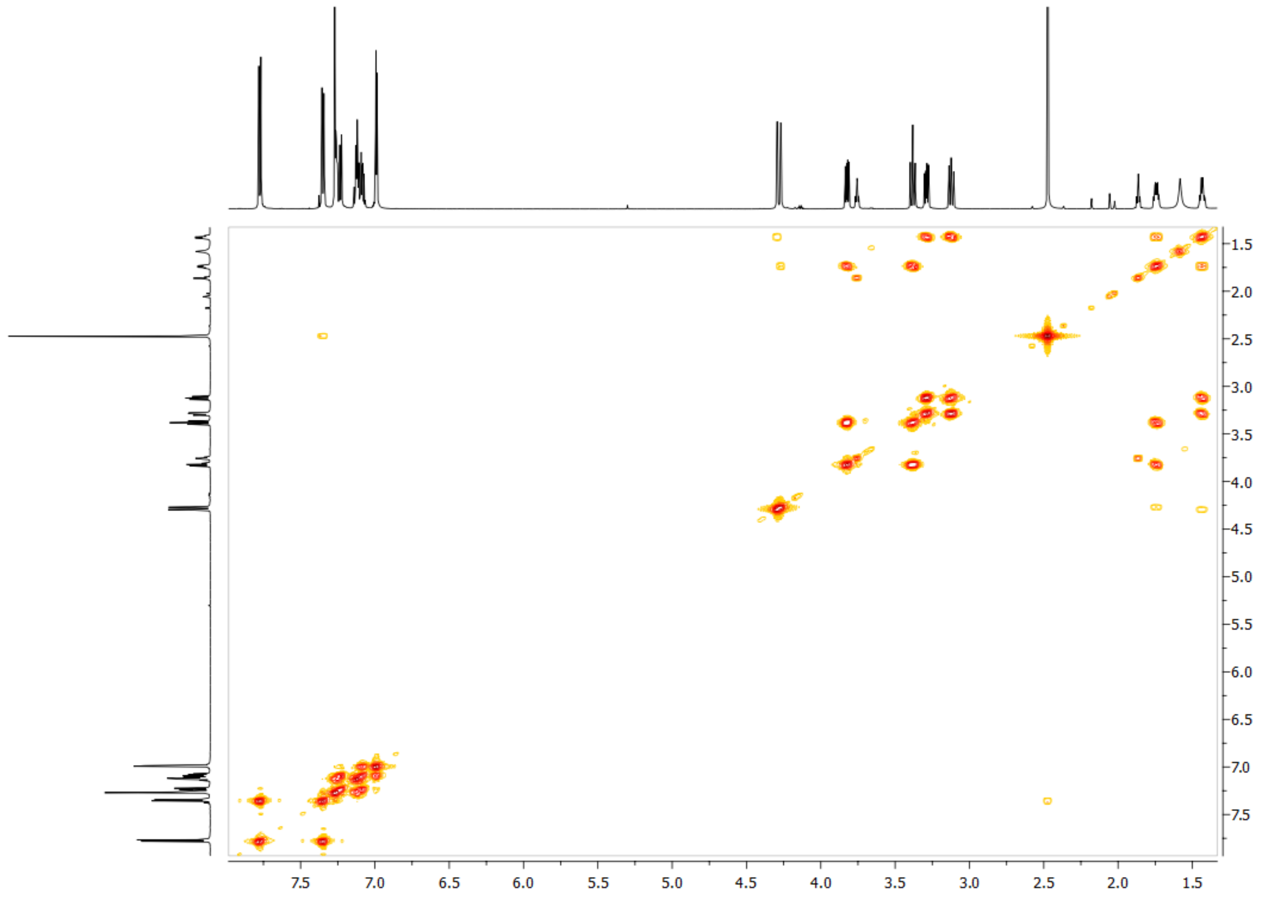


2, $^{13}C\{^{1}H\}$ (150.9 MHz, $CDCl_3$, 30 °C).

NMR AND MASS SPECTRA

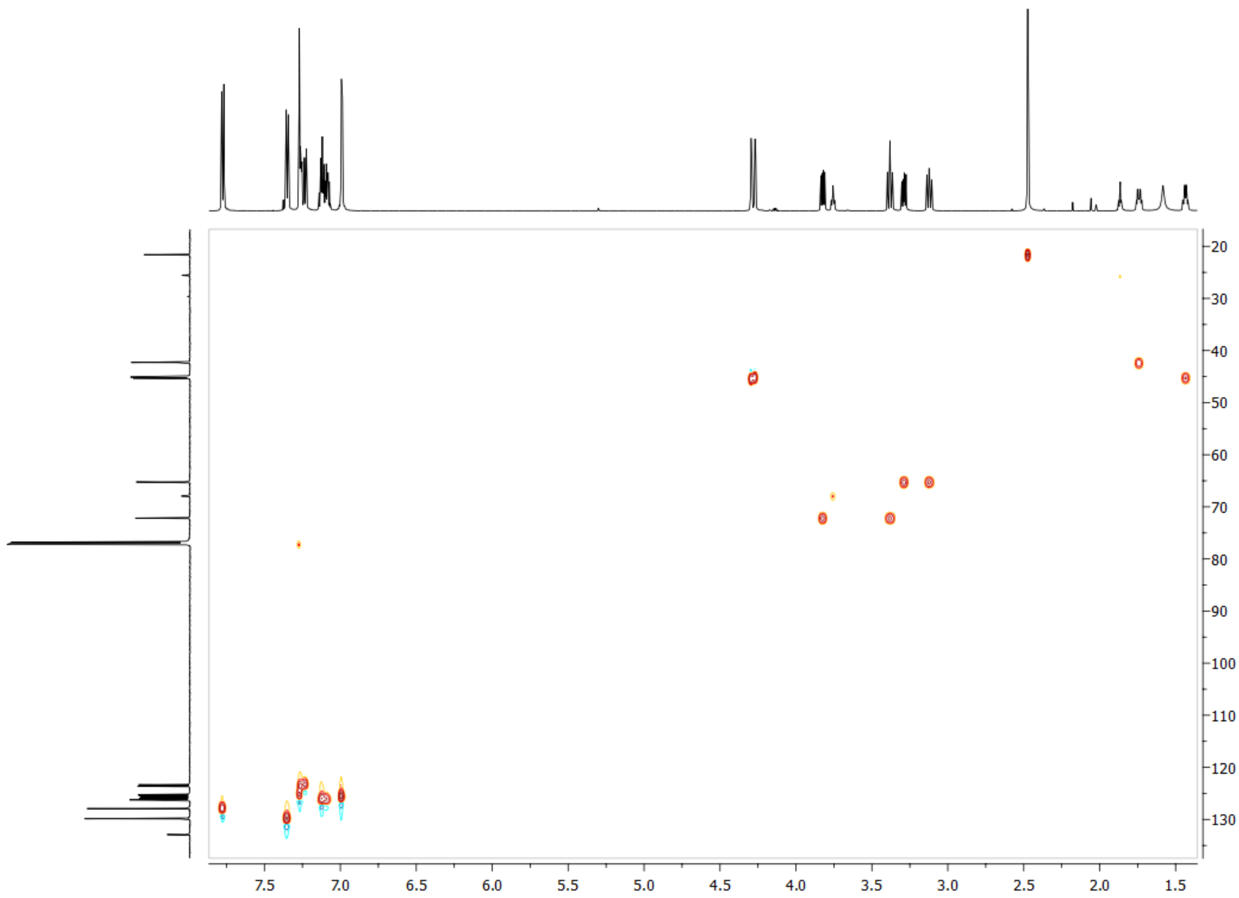


2, $^{13}C\{^{1}H\}$ DEPT (150.9 MHz, $CDCl_3$, 30 °C).

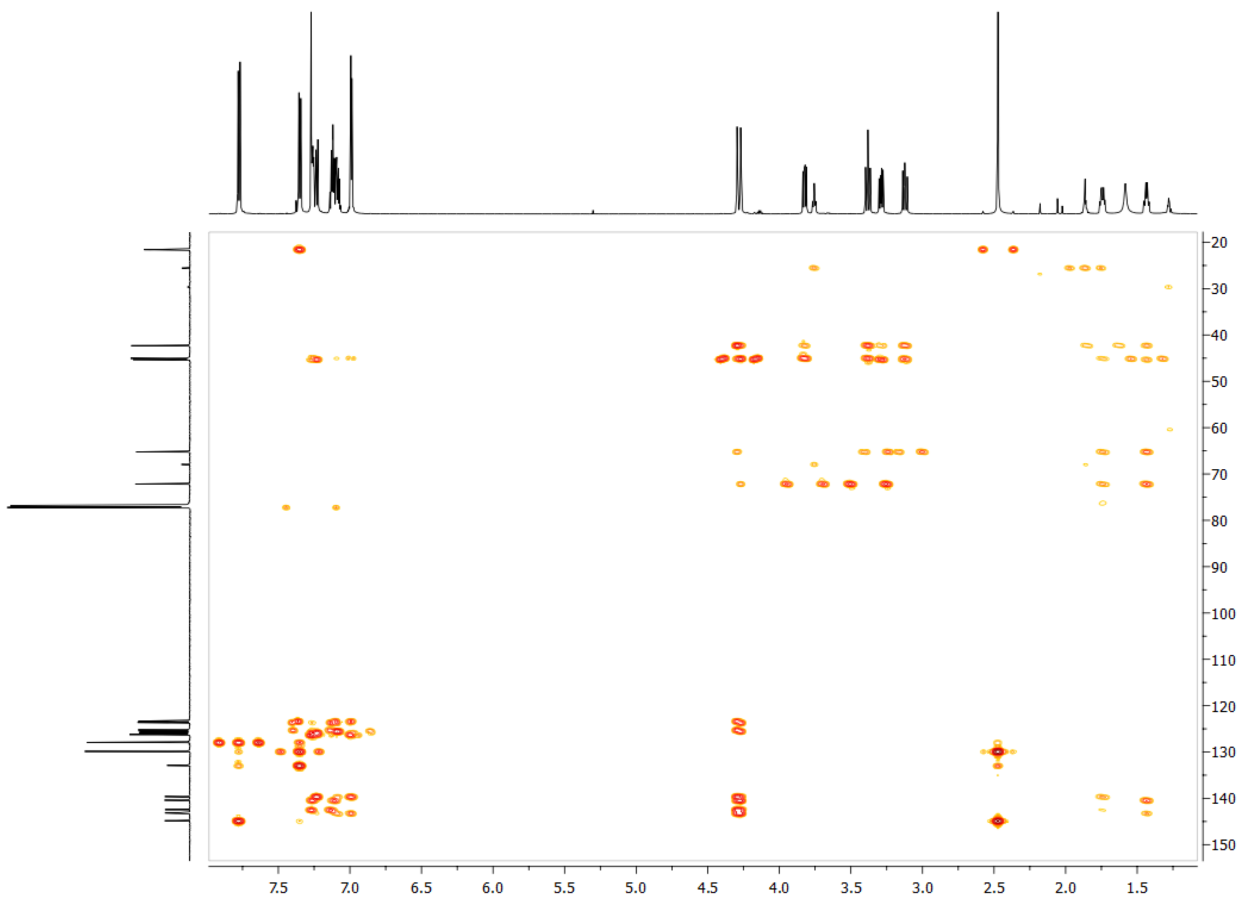


2, ^{1}H-^{1}H COSY.

NMR AND MASS SPECTRA

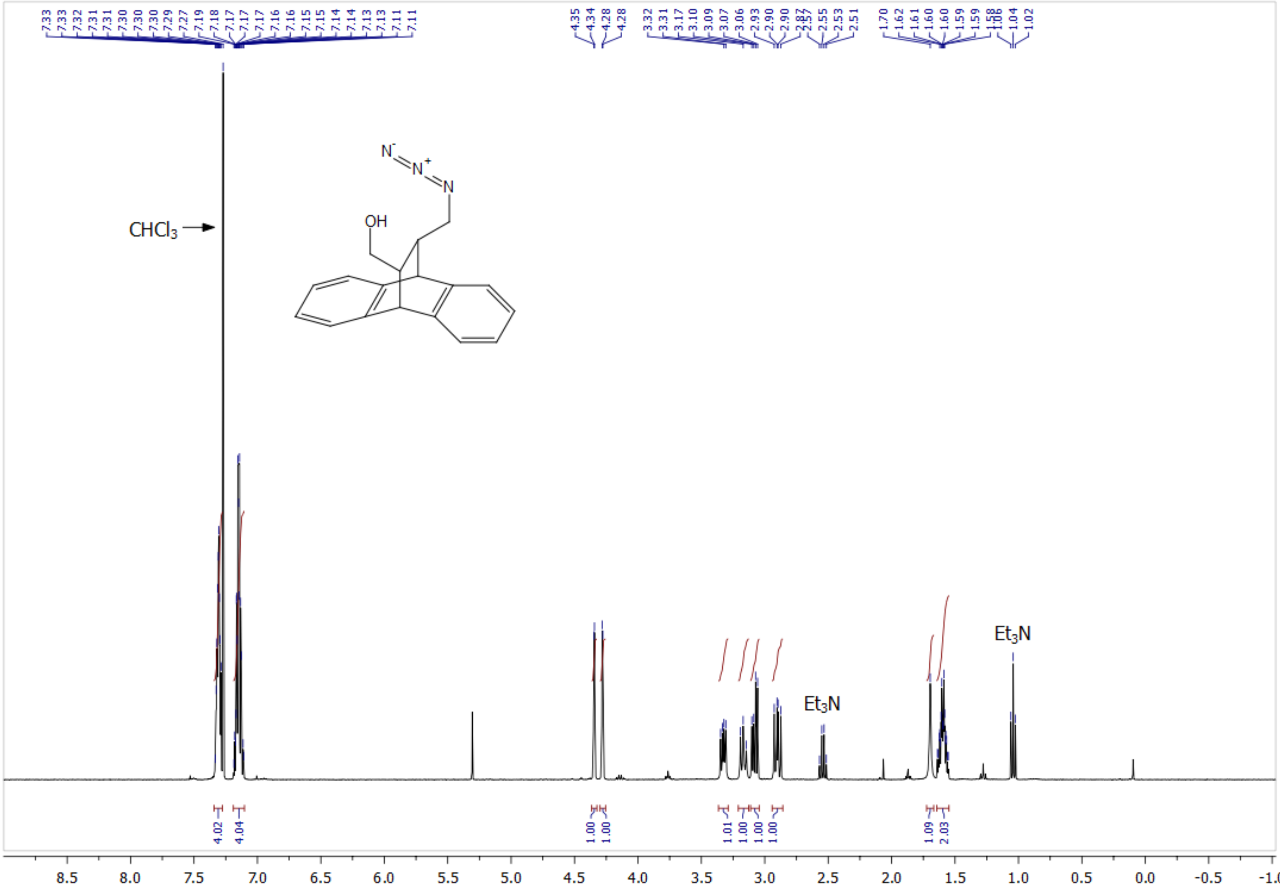


2, ^{1}H-^{13}C HSQC.

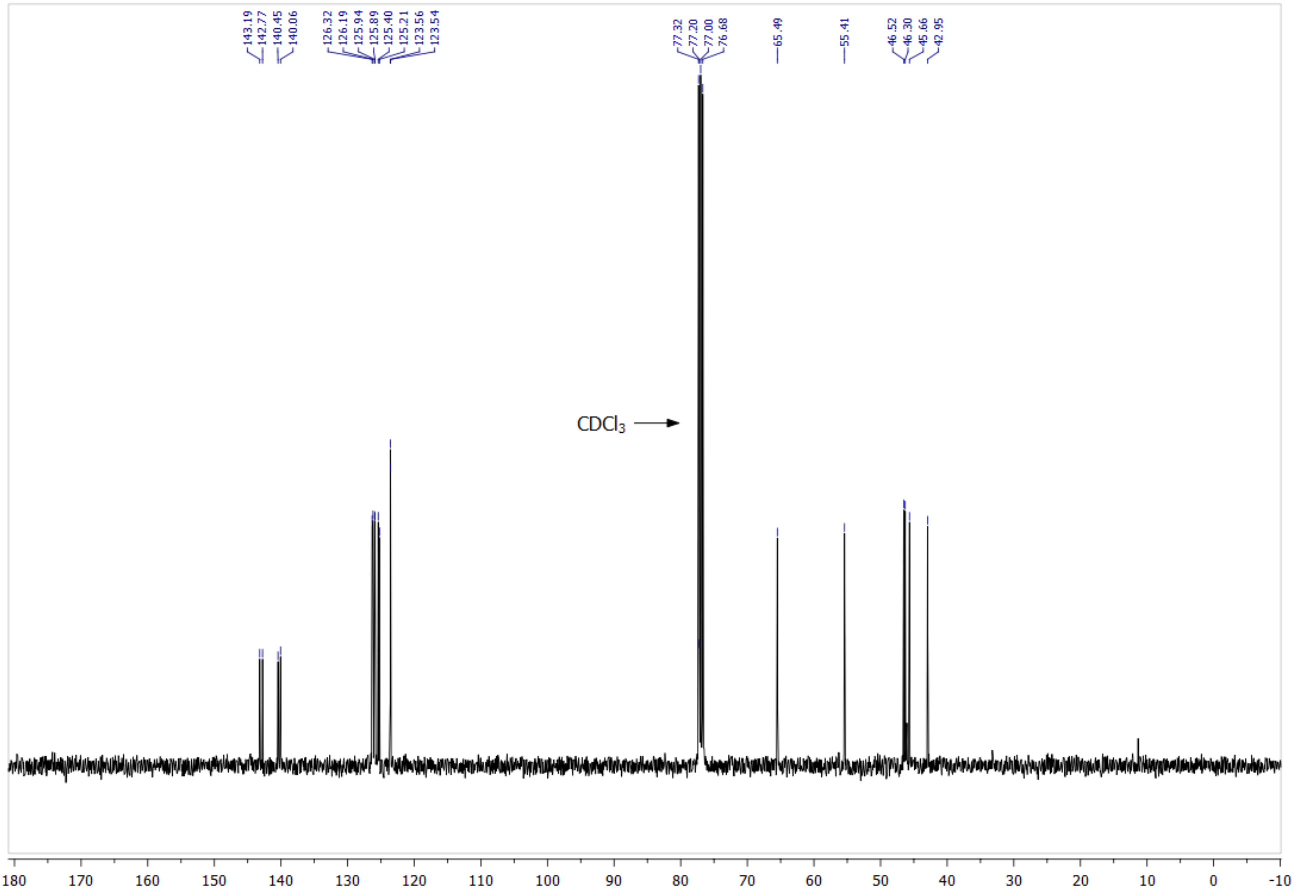


2, ^{1}H-^{13}C HMBC.

NMR AND MASS SPECTRA

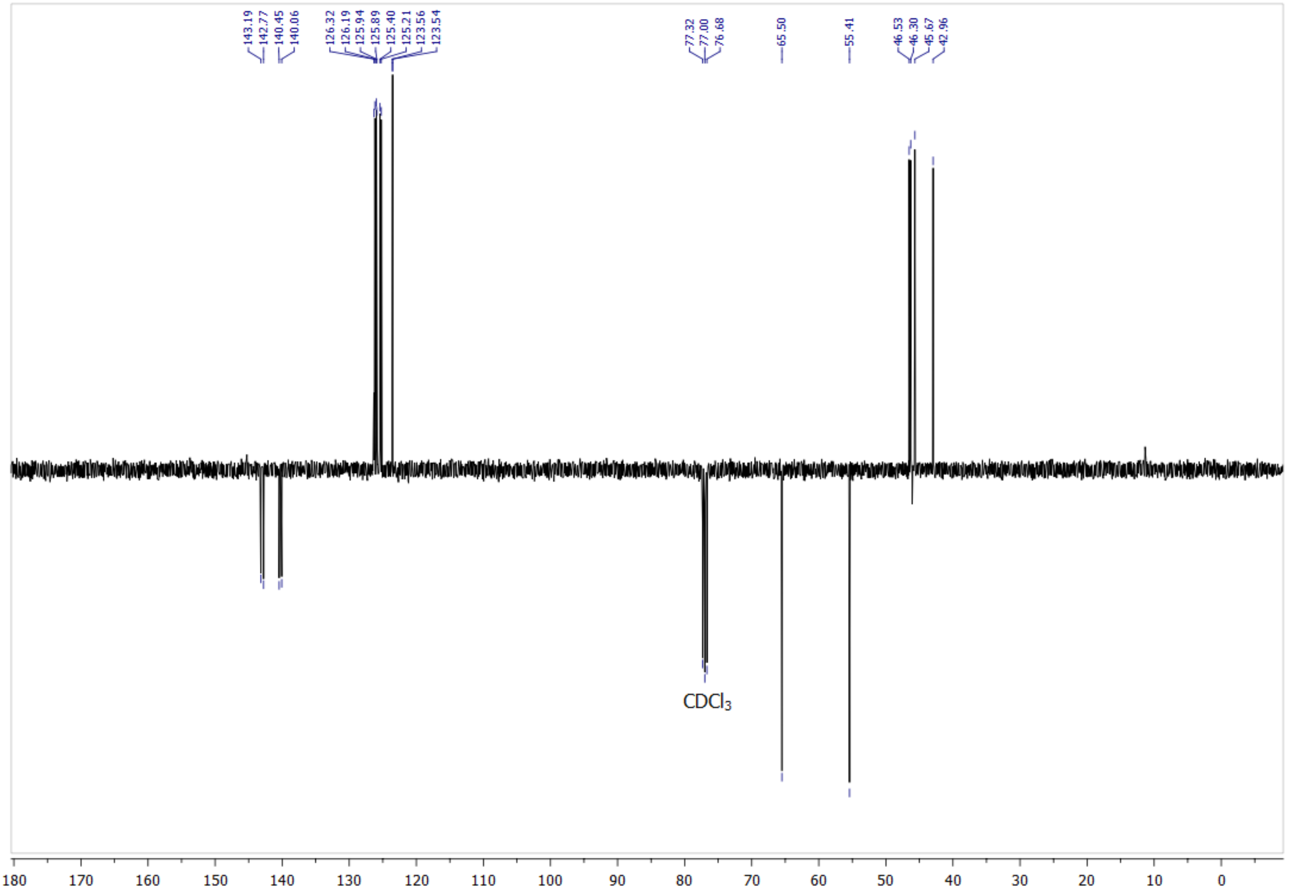


3, ^{1}H (600.1 MHz, $CDCl_3$, 30 °C).

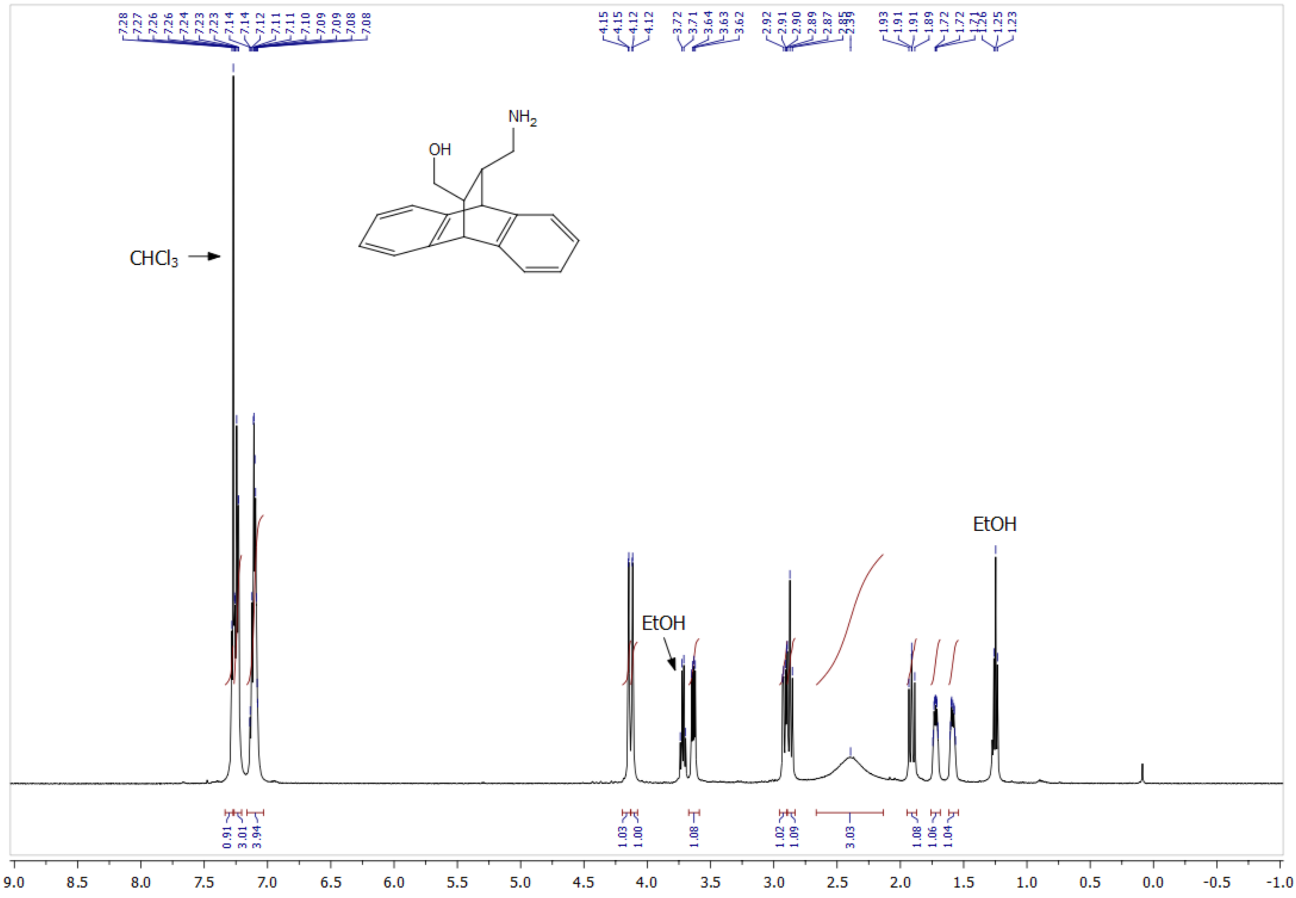


3, $^{13}C\{^{1}H\}$ (150.9 MHz, $CDCl_3$, 30 °C).

NMR AND MASS SPECTRA

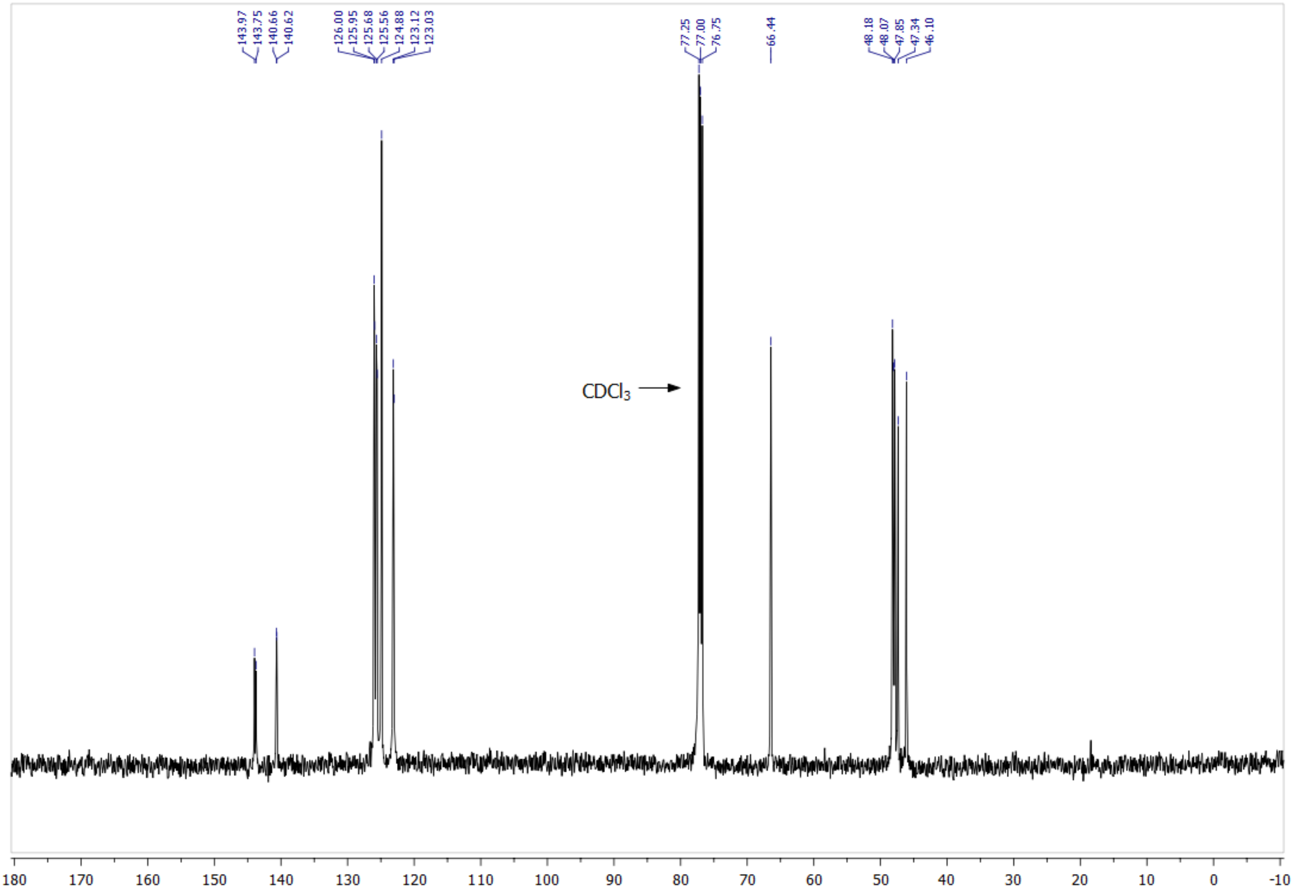


3, $^{13}C\{^{1}H\}$ DEPT (150.9 MHz, $CDCl_3$, 30 °C).

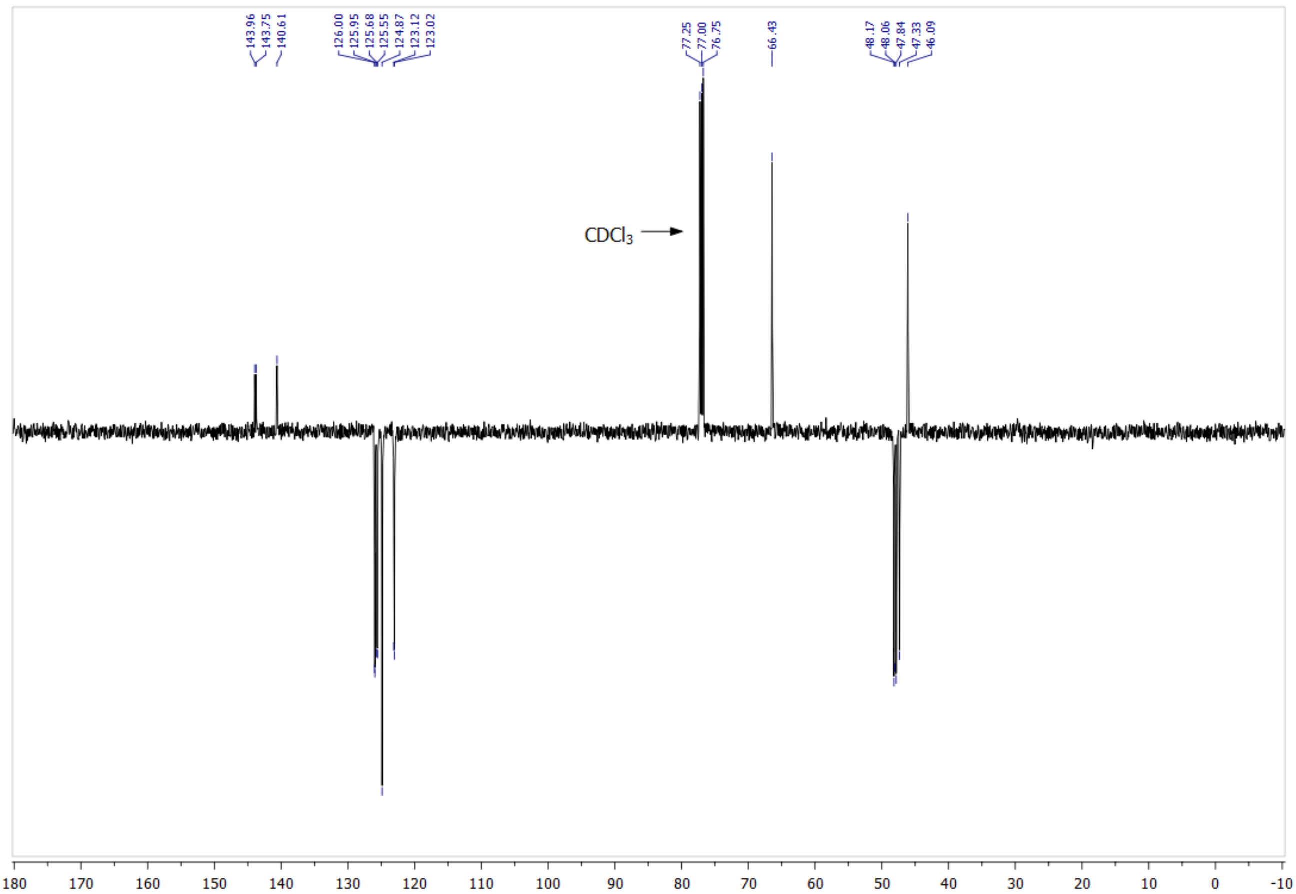


4, ^{1}H (499.9 MHz, $CDCl_3$, ambient temperature).

NMR AND MASS SPECTRA

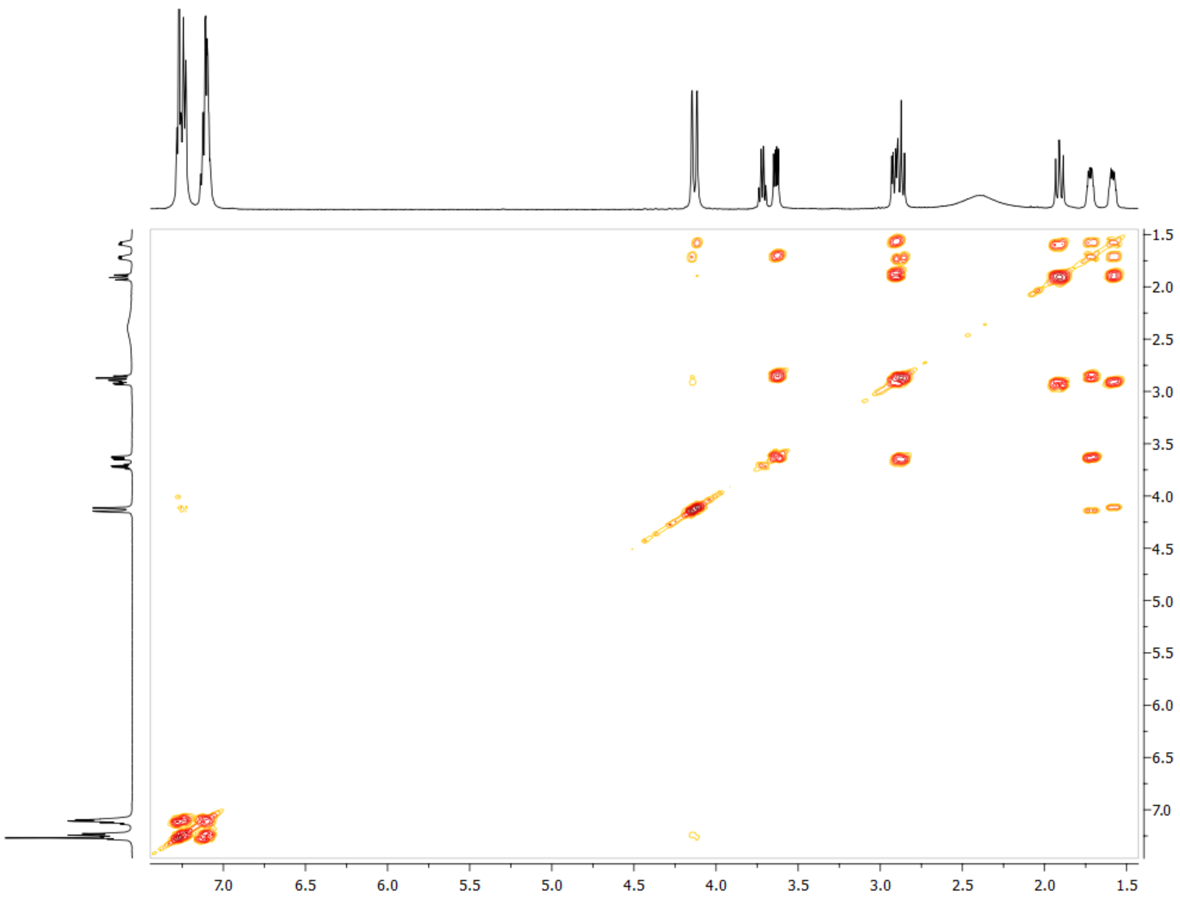


4, $^{13}C\{^{1}H\}$ (125.7 MHz, $CDCl_3$, ambient temperature).

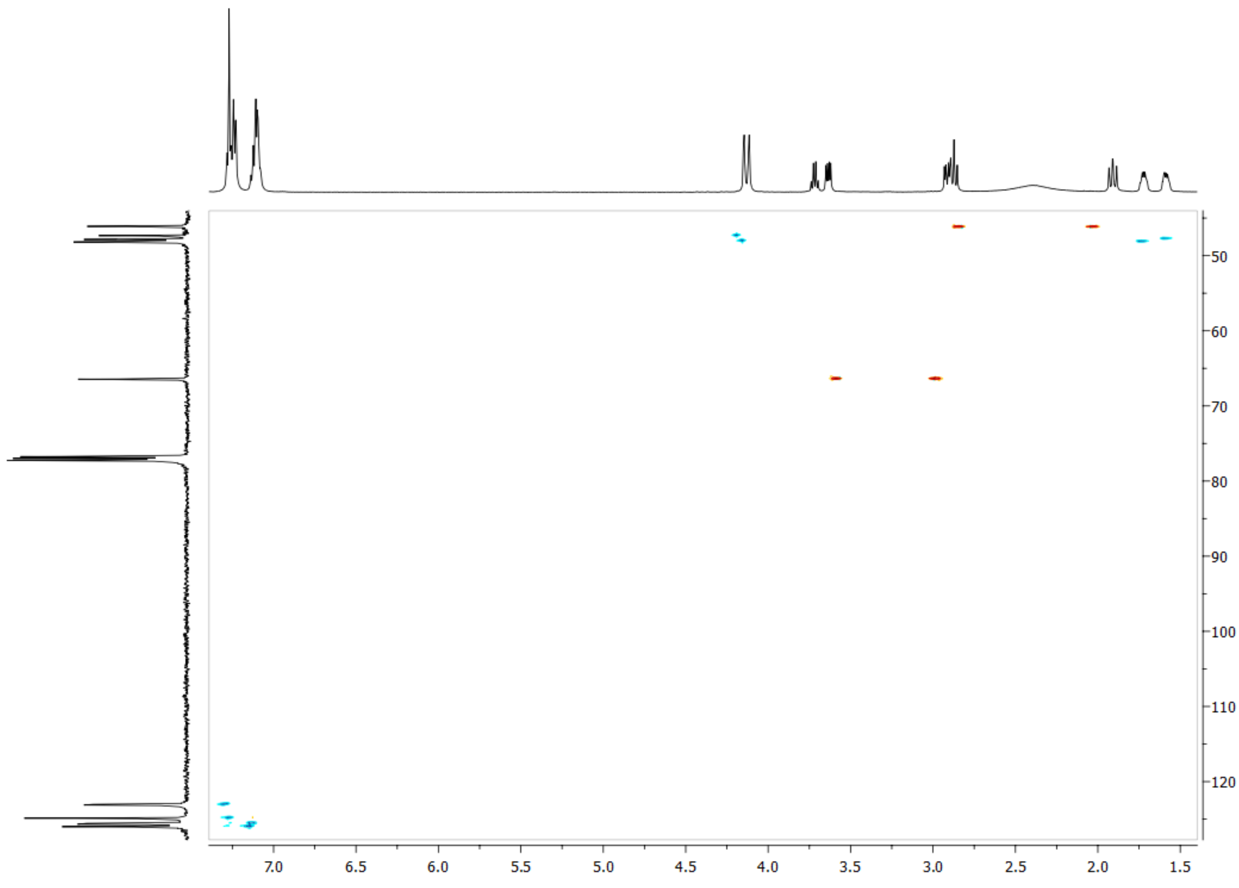


4, $^{13}C\{^{1}H\}$ APT (125.7 MHz, $CDCl_3$, ambient temperature).

NMR AND MASS SPECTRA

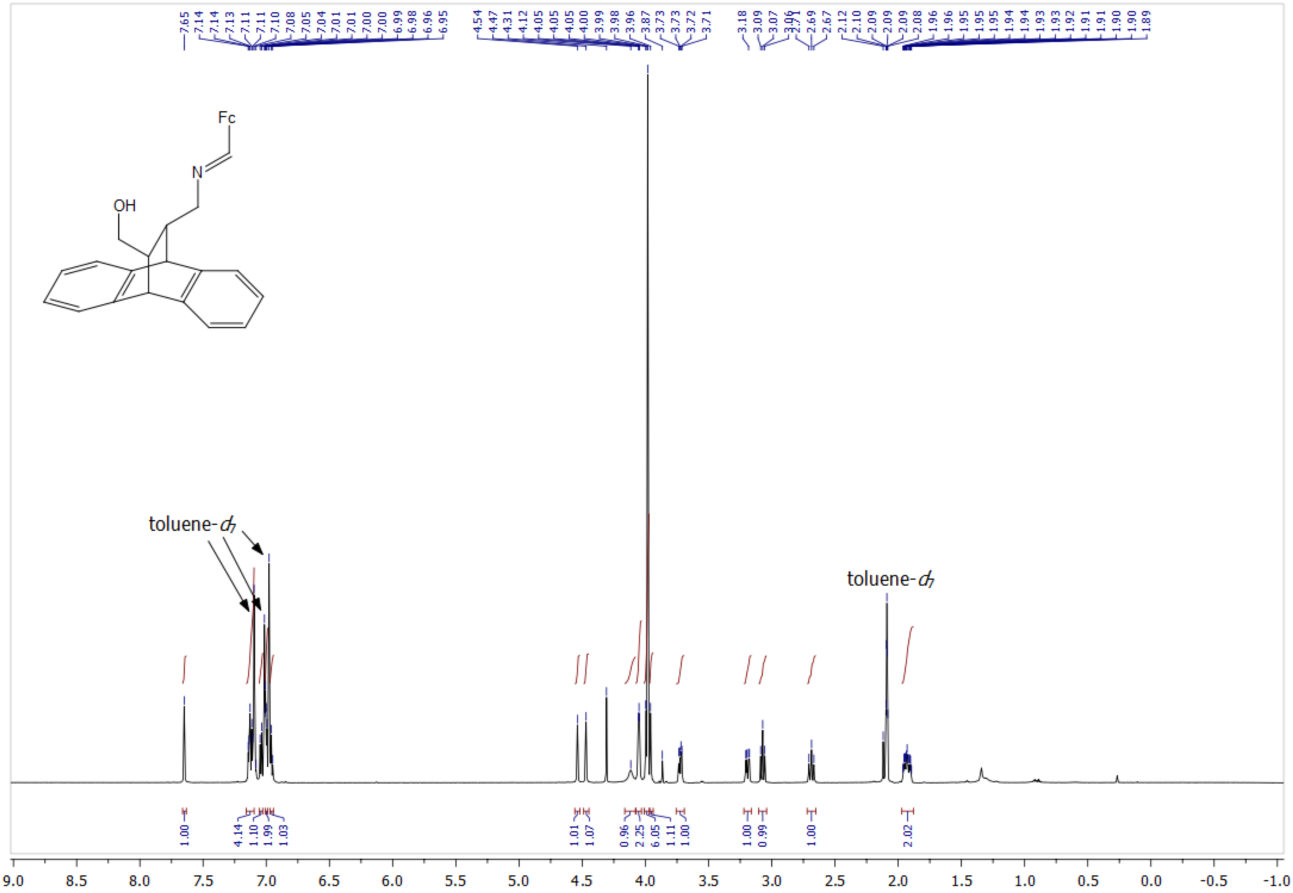


4, ^{1}H-^{1}H COSY.

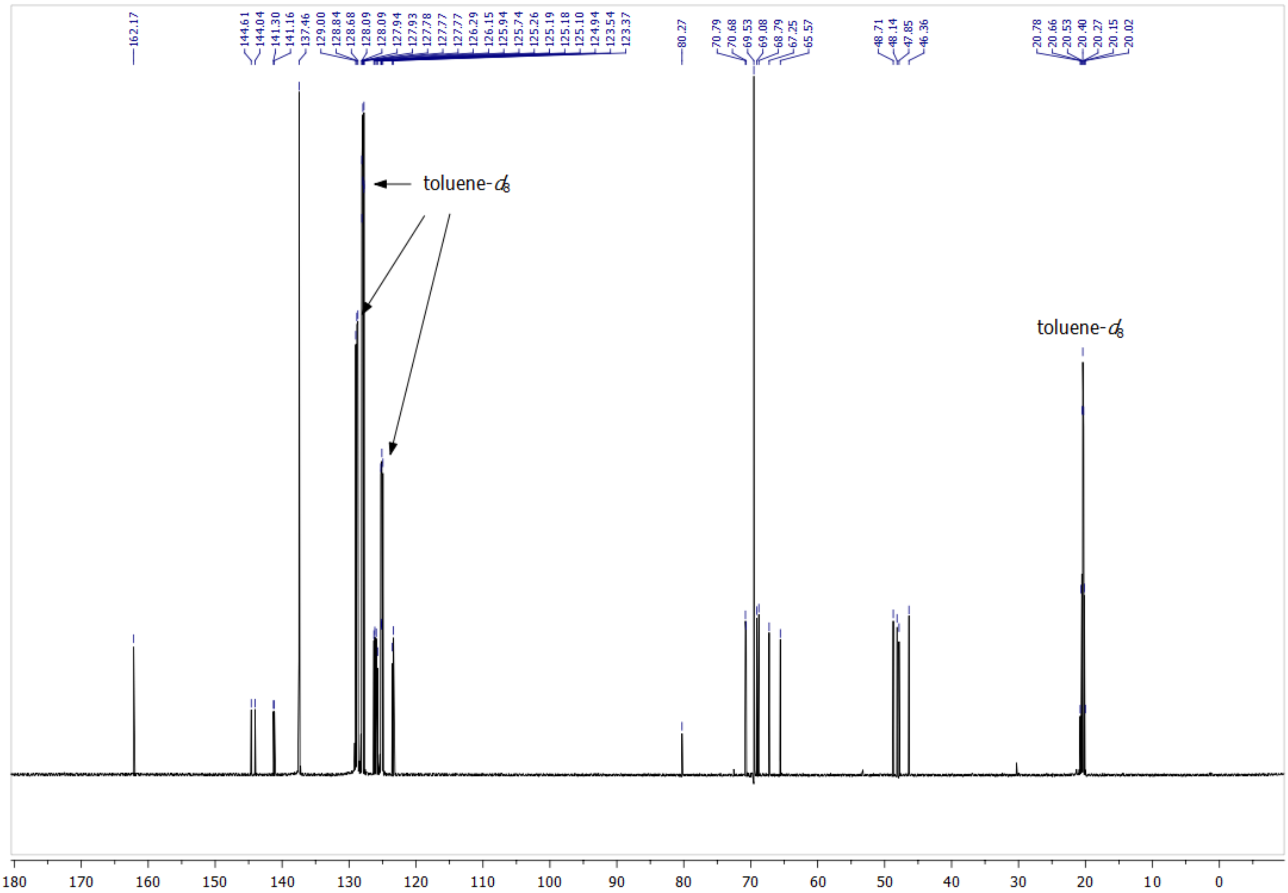


4, ^{1}H-^{13}C HSQC.

NMR AND MASS SPECTRA

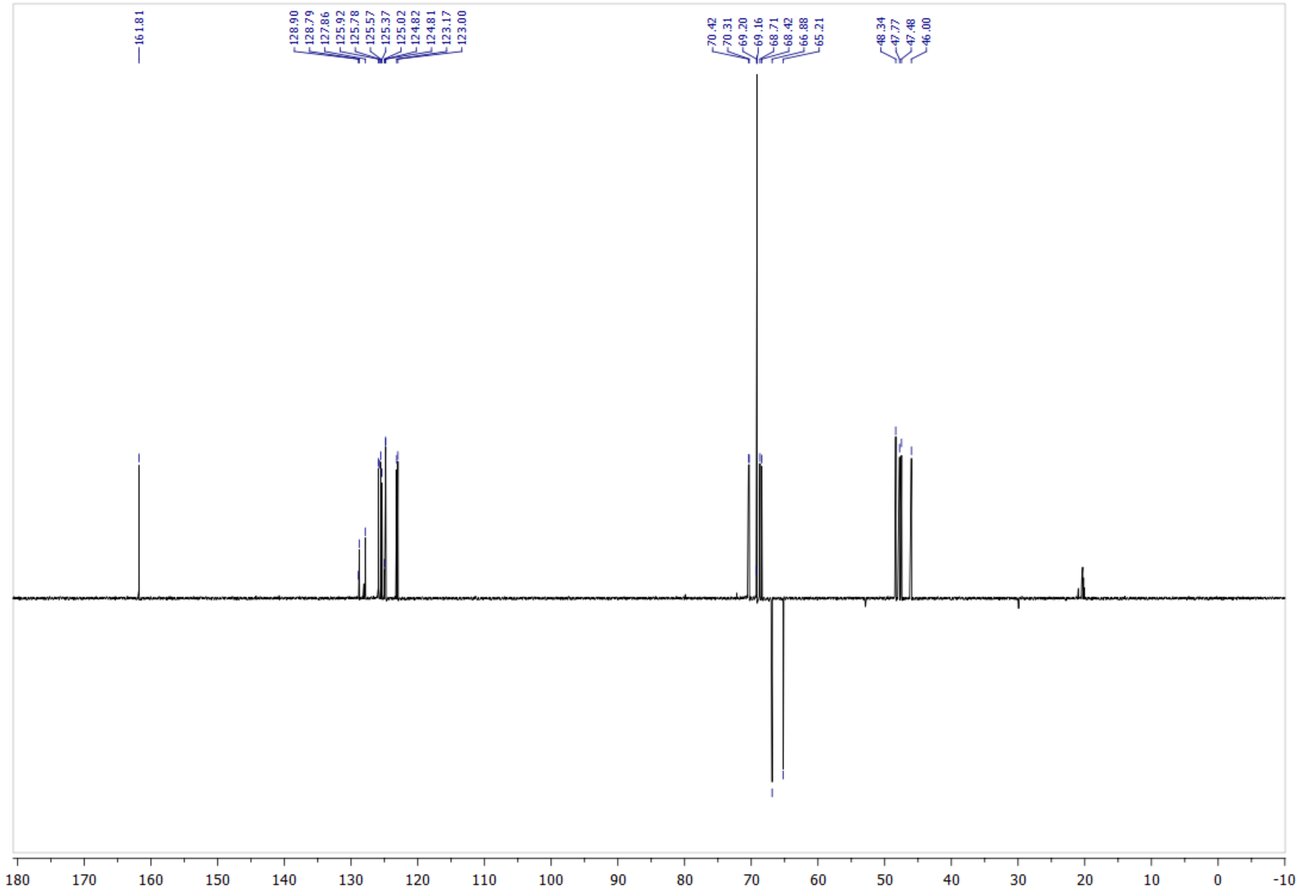


5, ^{1}H (600.1 MHz, $CDCl_3$, 30 °C).

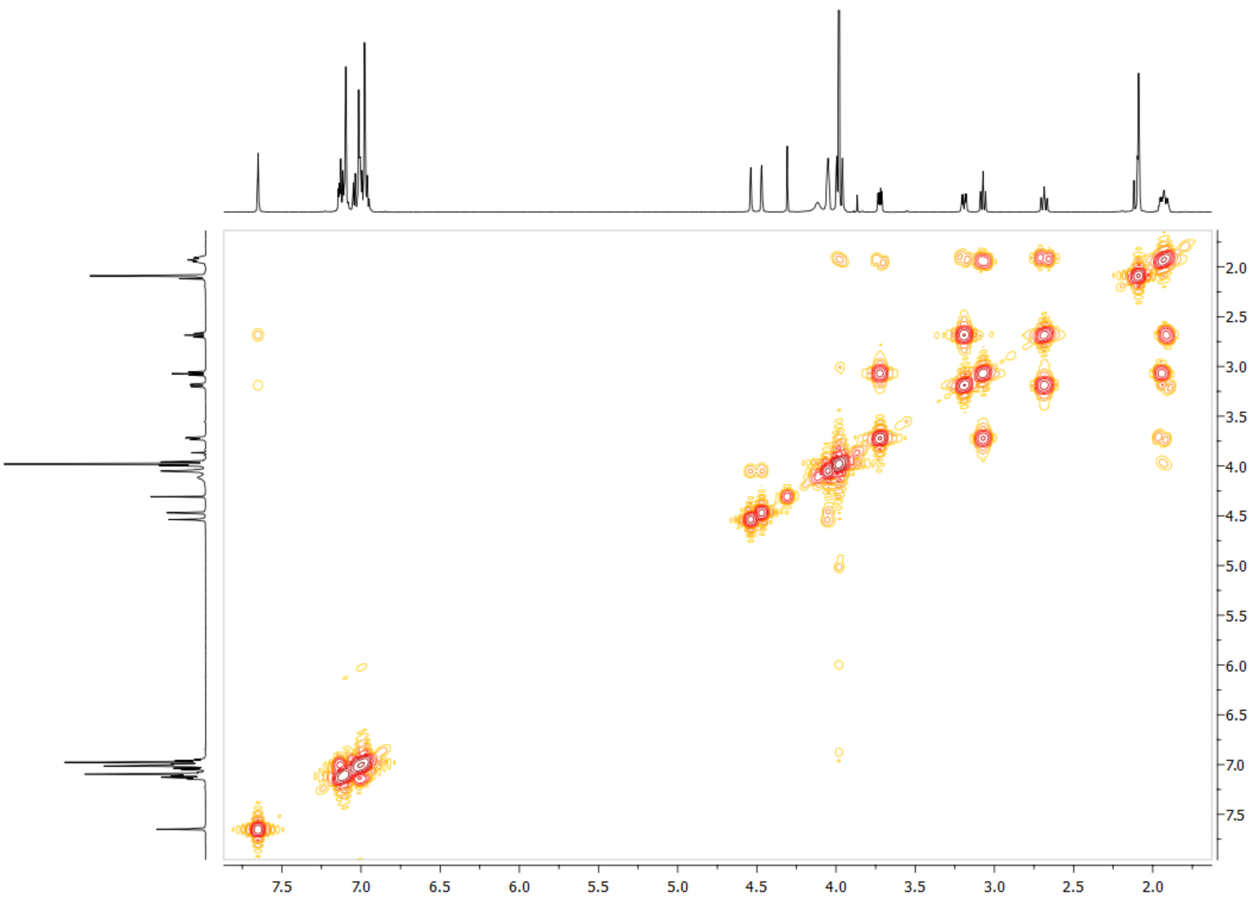


5, $^{13}C\{^{1}H\}$ (150.9 MHz, $CDCl_3$, 30 °C).

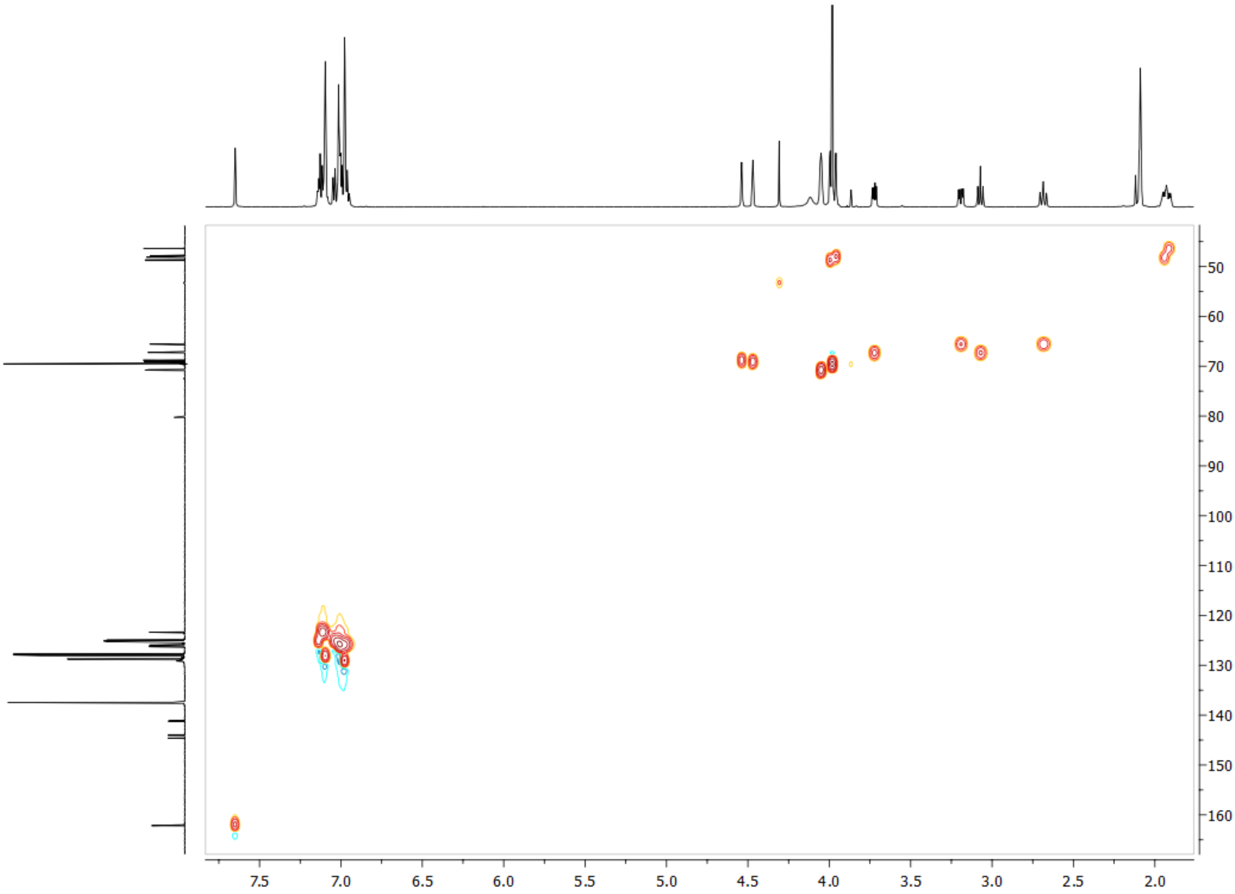
NMR AND MASS SPECTRA



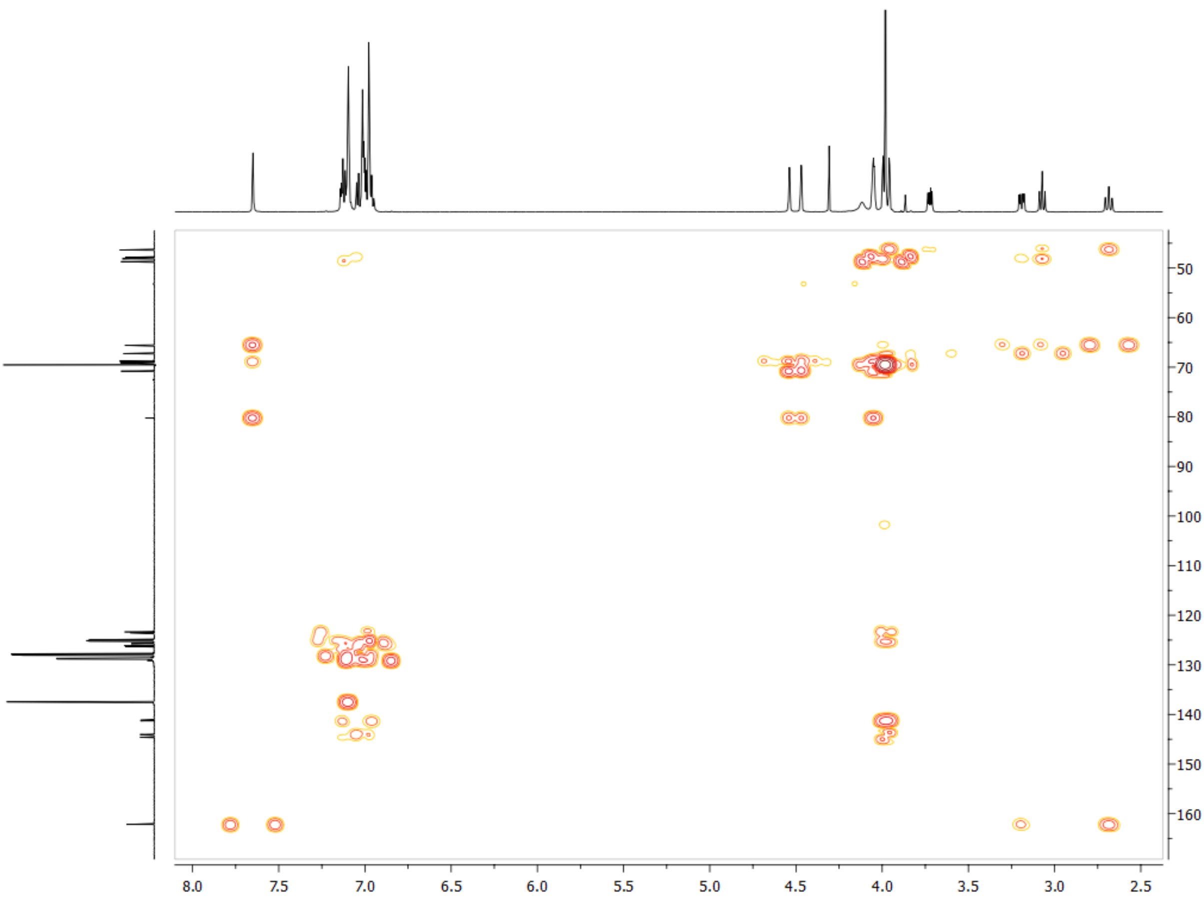
5, $^{13}C\{^{1}H\}$ DEPT (150.9 MHz, $CDCl_3$, 30 °C).



5, ^{1}H-^{1}H COSY.

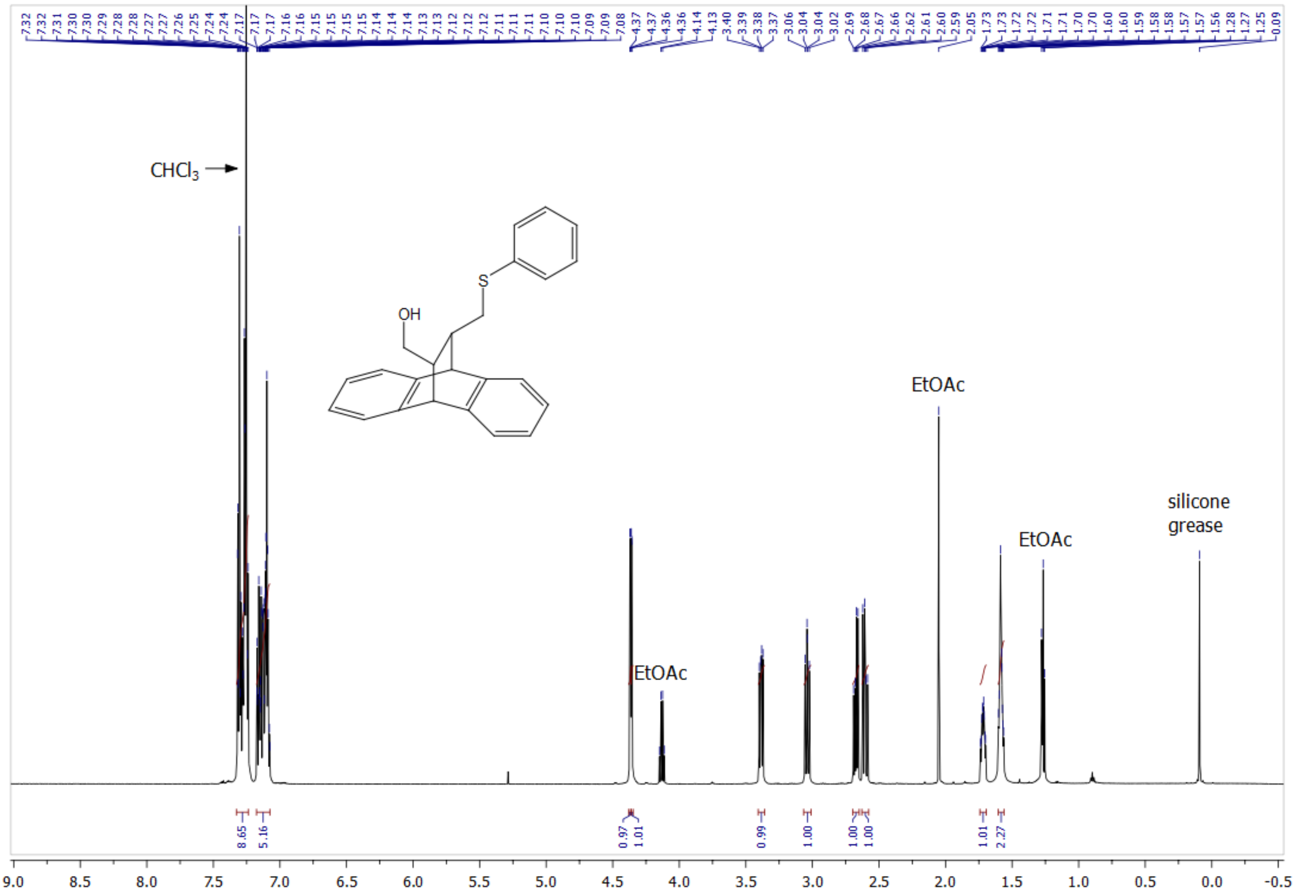


5, ^{1}H-^{13}C HSQC.

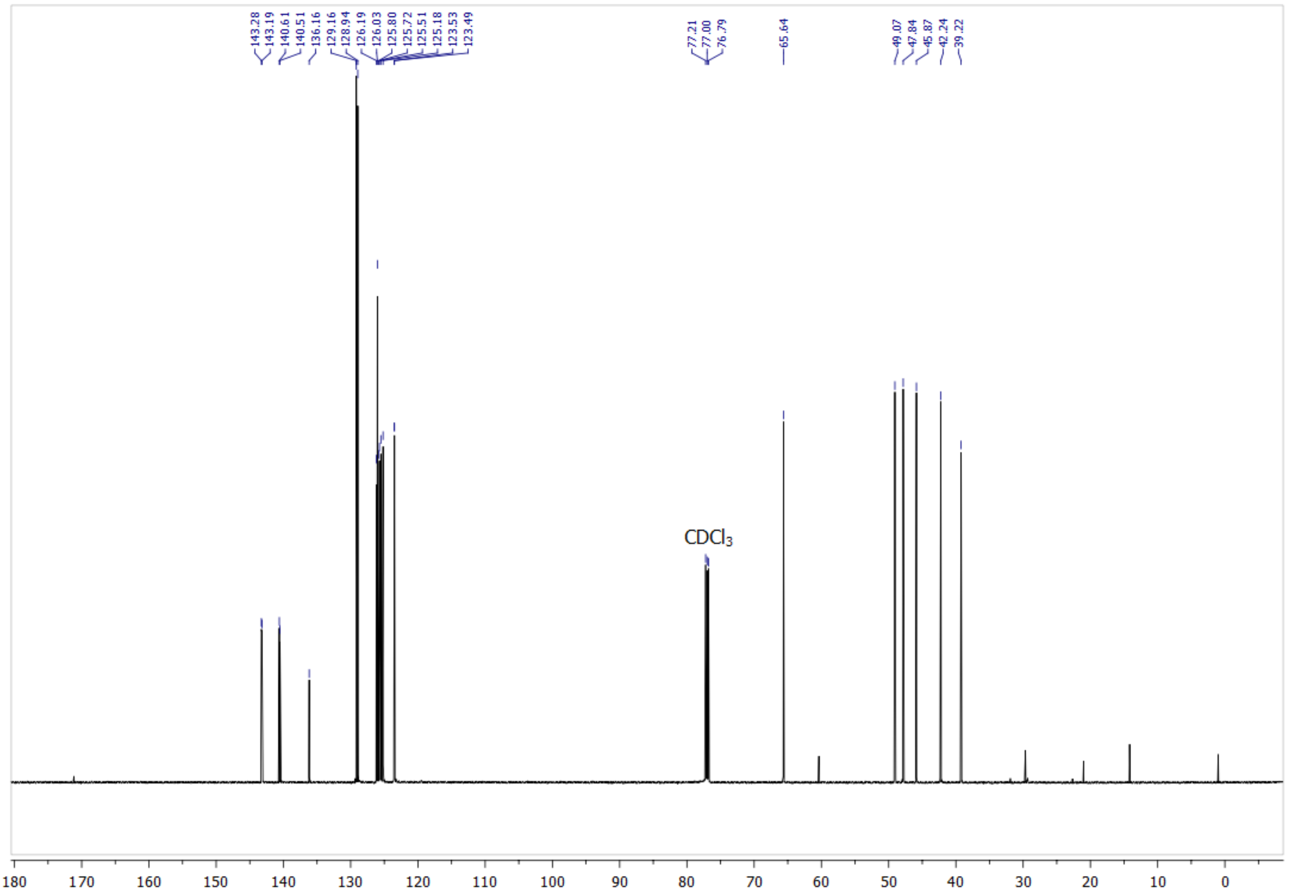


5, ^{1}H-^{13}C HMBC.

NMR AND MASS SPECTRA

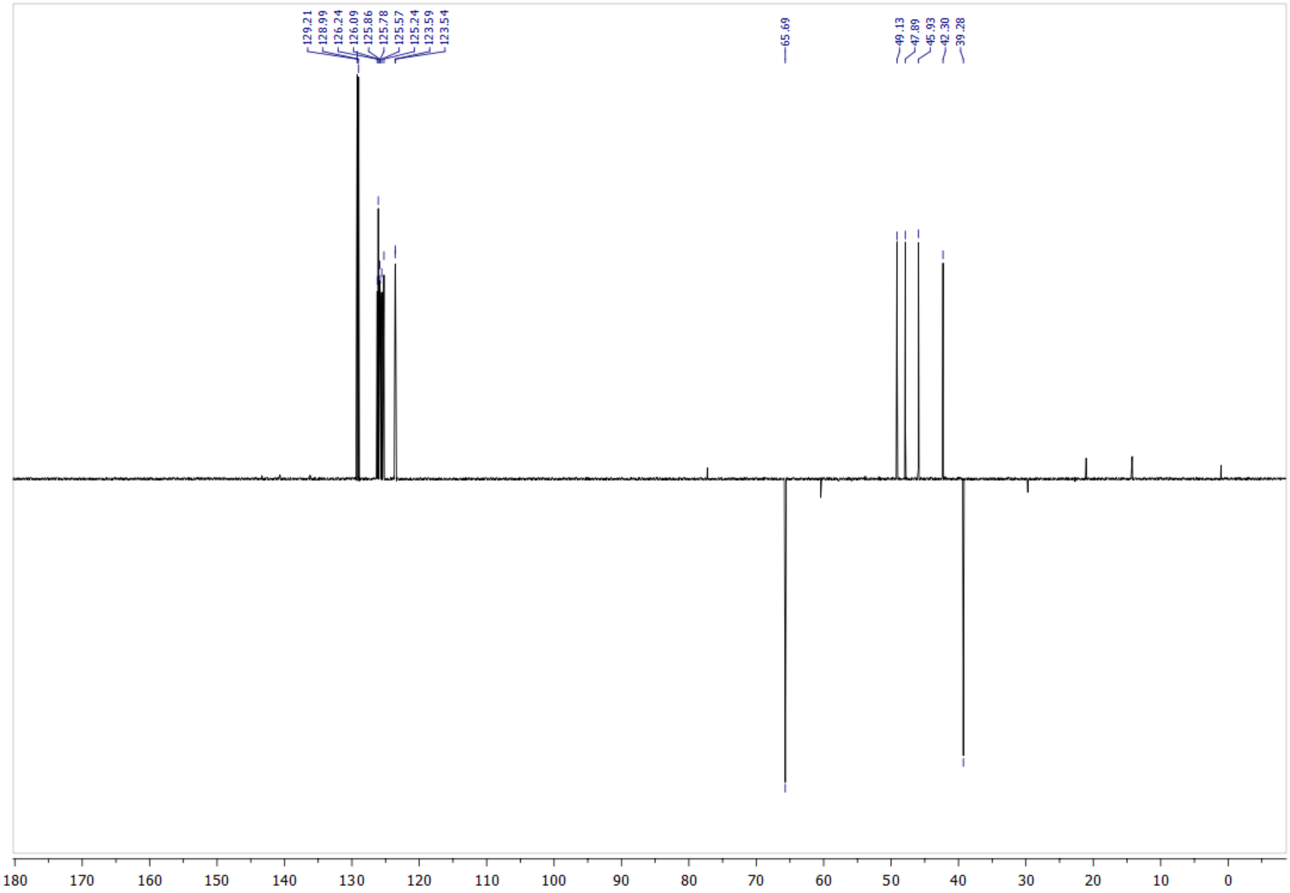


6, ^{1}H (600.1 MHz, $CDCl_3$, 30 °C).

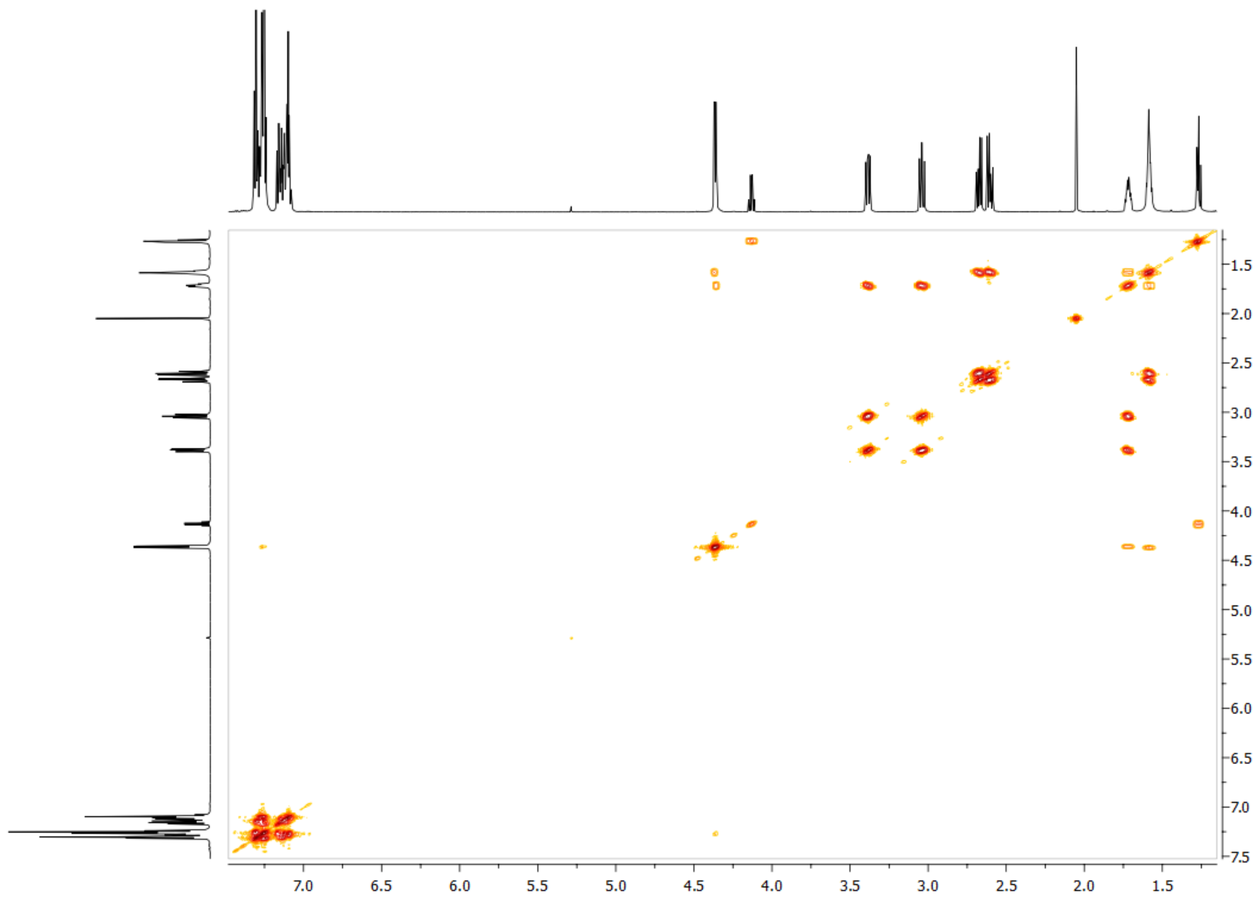


6, $^{13}C\{^{1}H\}$ (150.9 MHz, $CDCl_3$, 30 °C).

NMR AND MASS SPECTRA

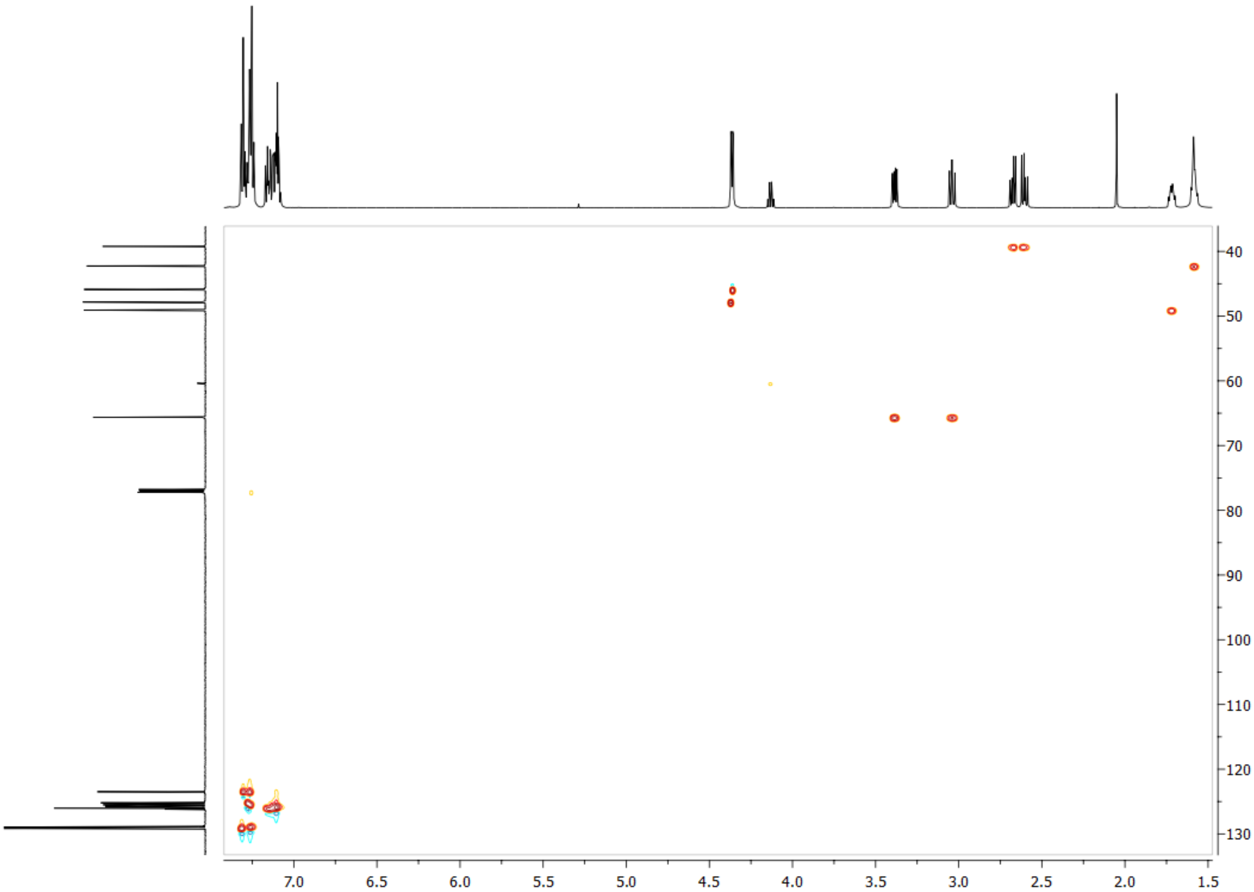


6, $^{13}C\{^{1}H\}$ DEPT (150.9 MHz, $CDCl_3$, 30 °C).

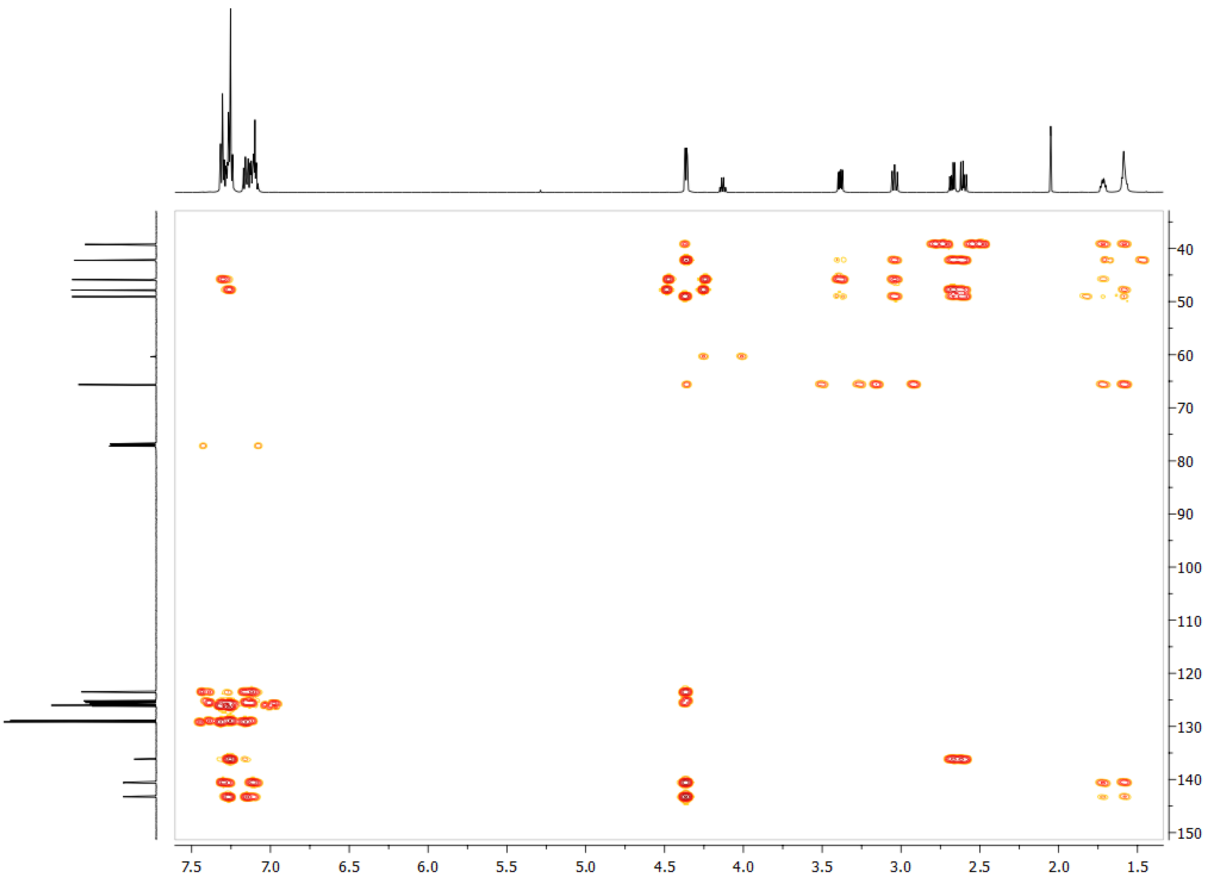


6, ^{1}H-^{1}H COSY.

NMR AND MASS SPECTRA

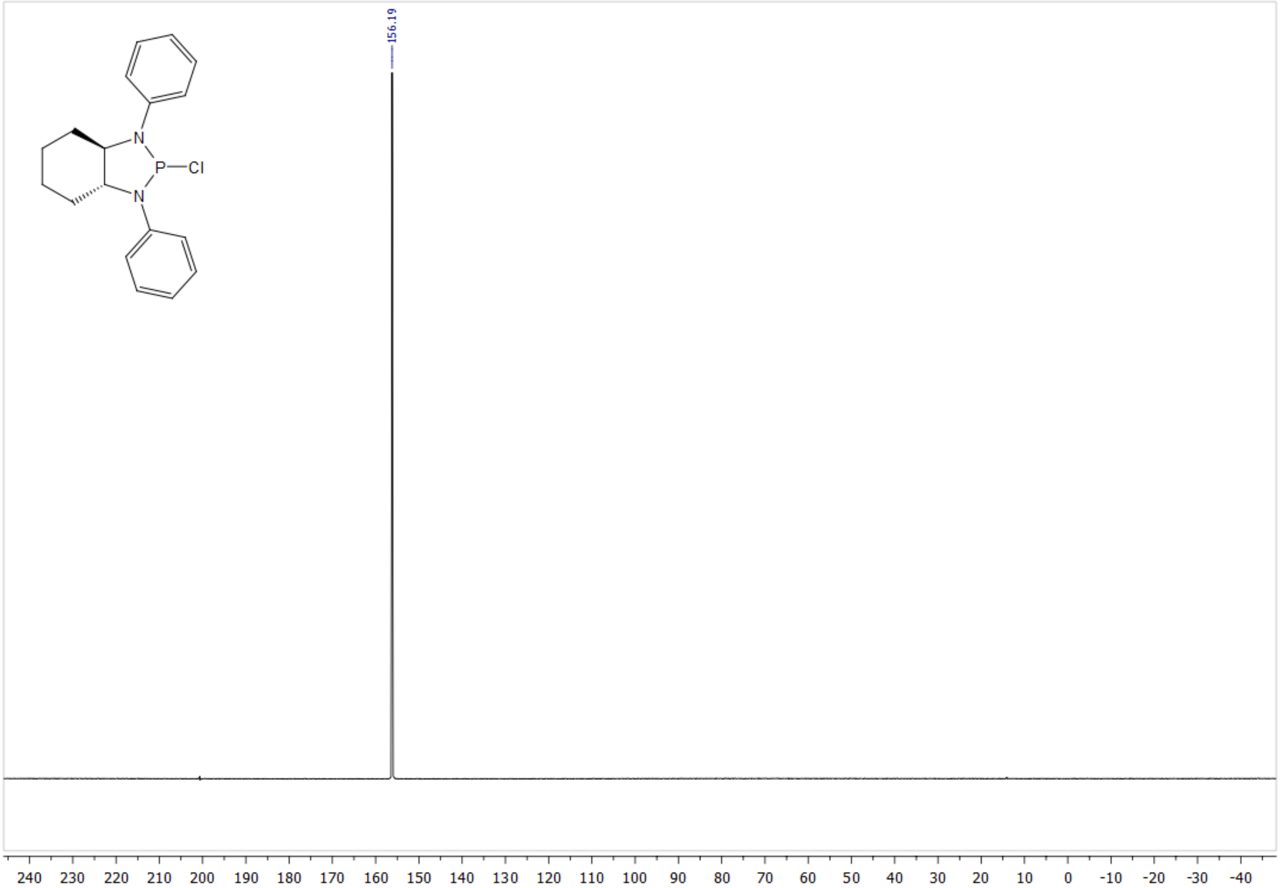


6, ^{1}H-^{13}C HSQC.

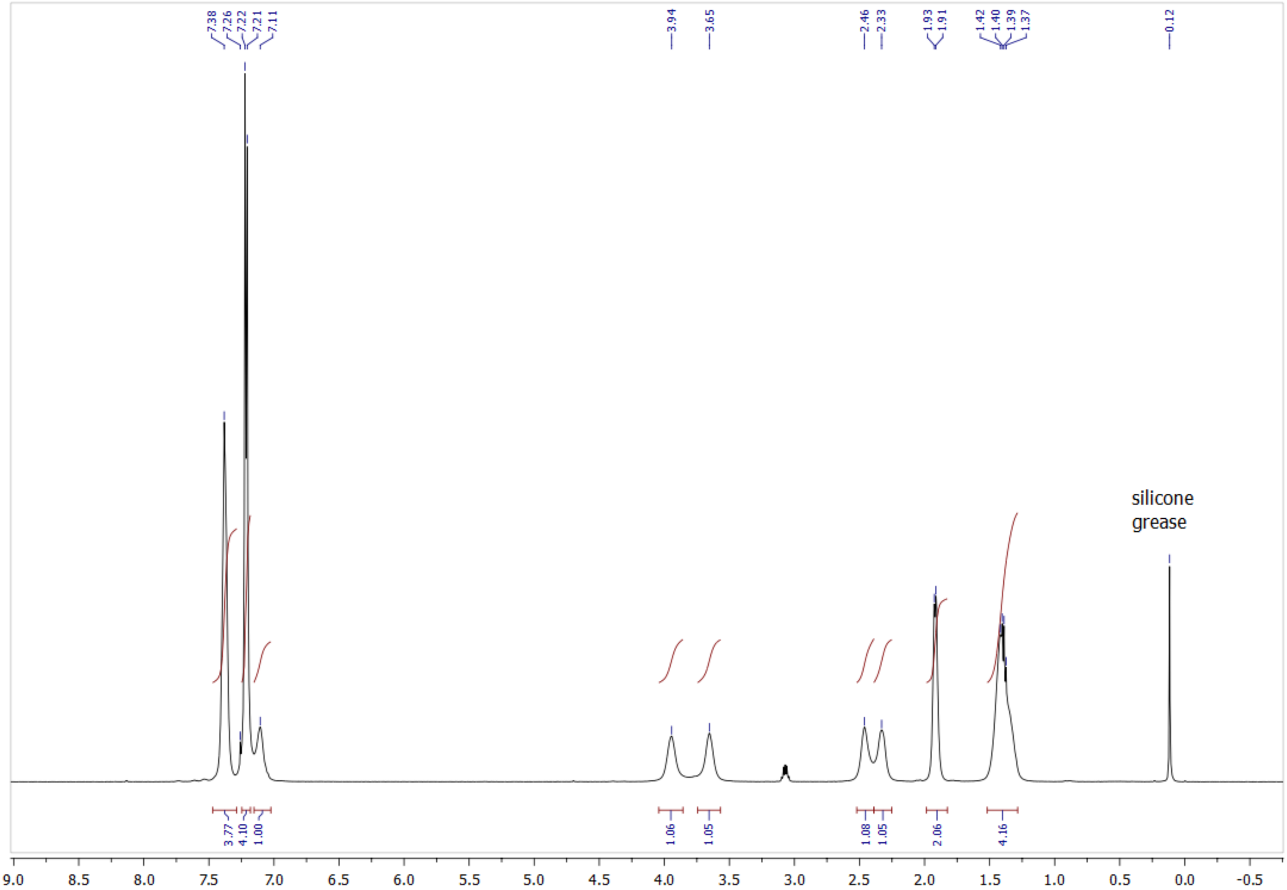


6, ^{1}H-^{13}C HMBC.

NMR AND MASS SPECTRA

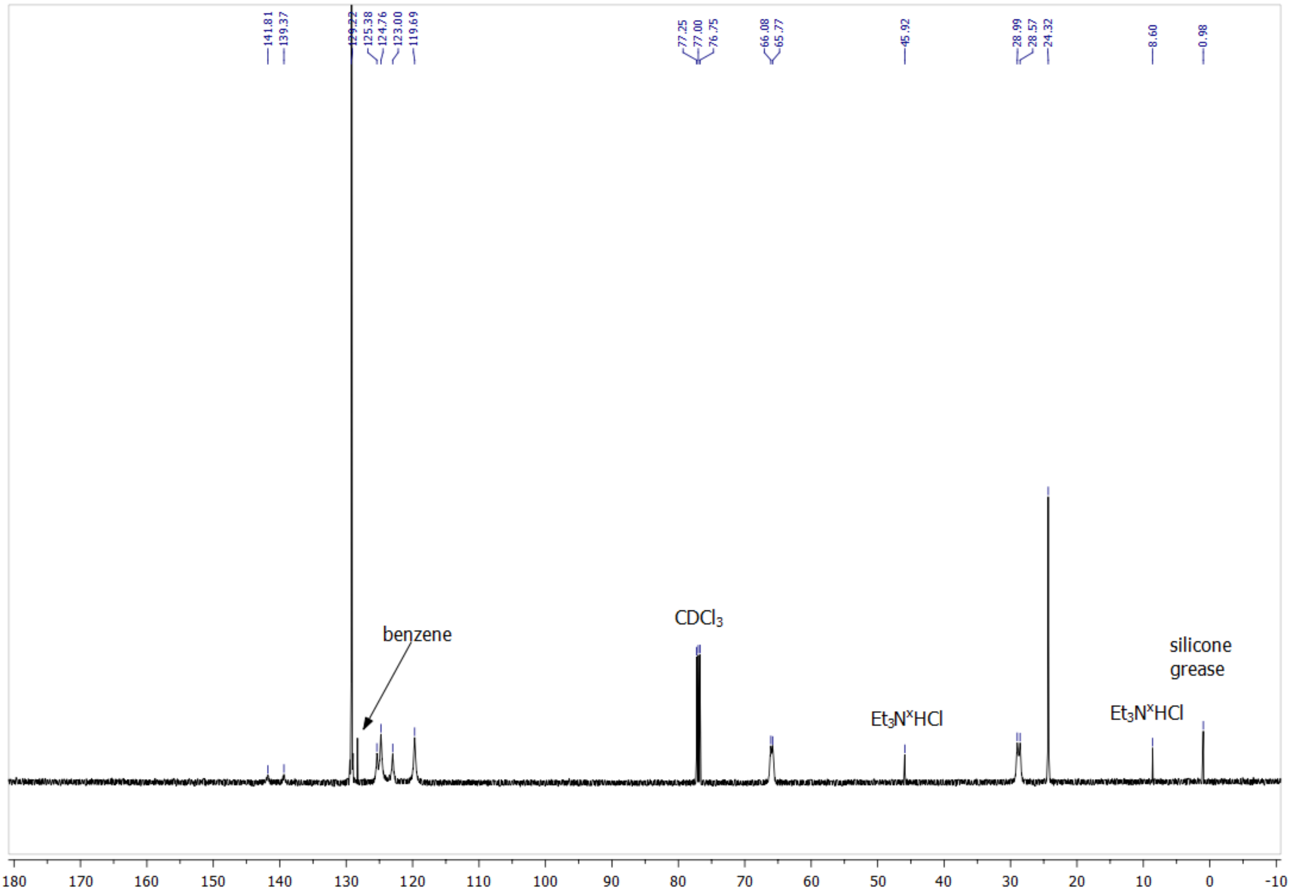


8, $^{31}P\{^1H\}$ (202.4 MHz, $CDCl_3$, ambient temperature).

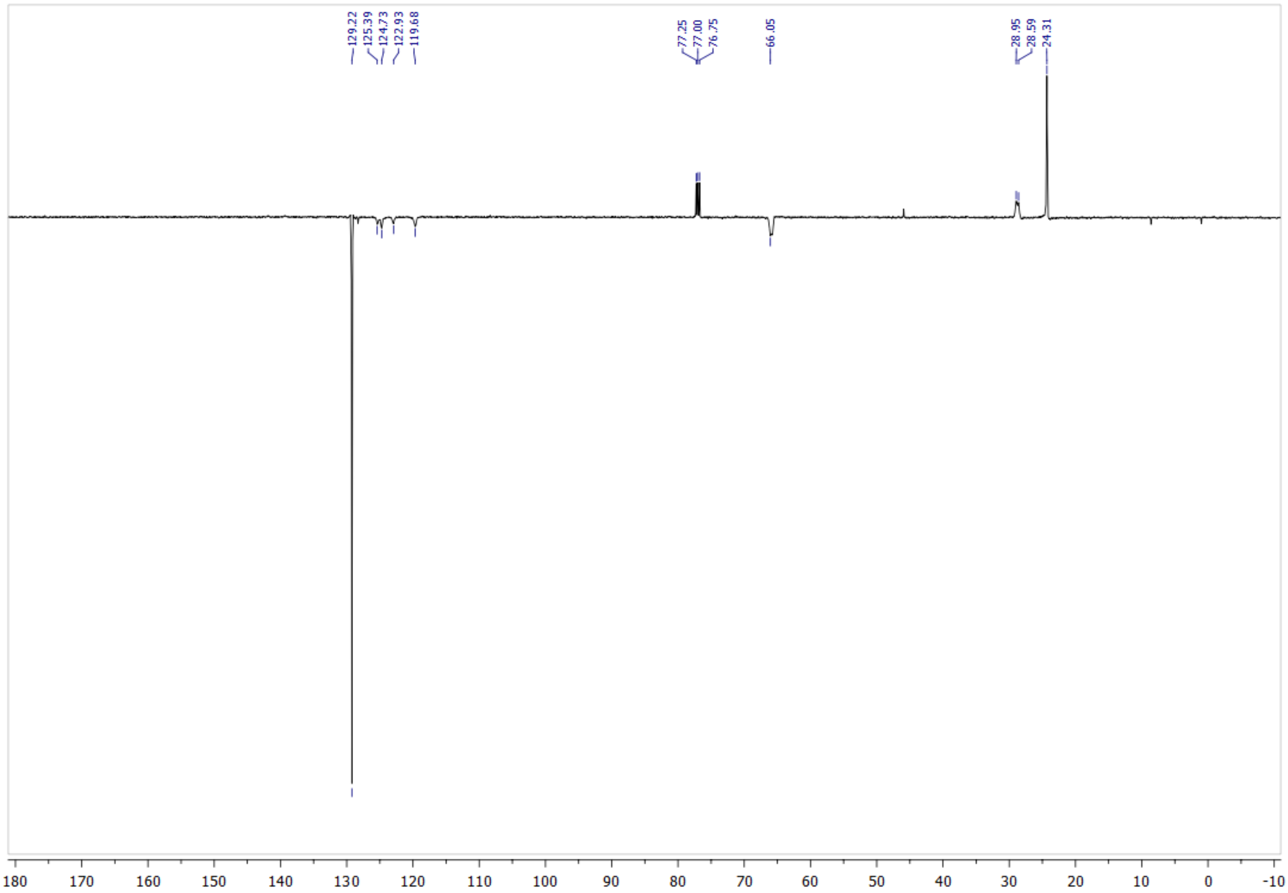


8, ^1H (499.9 MHz, $CDCl_3$, ambient temperature).

NMR AND MASS SPECTRA

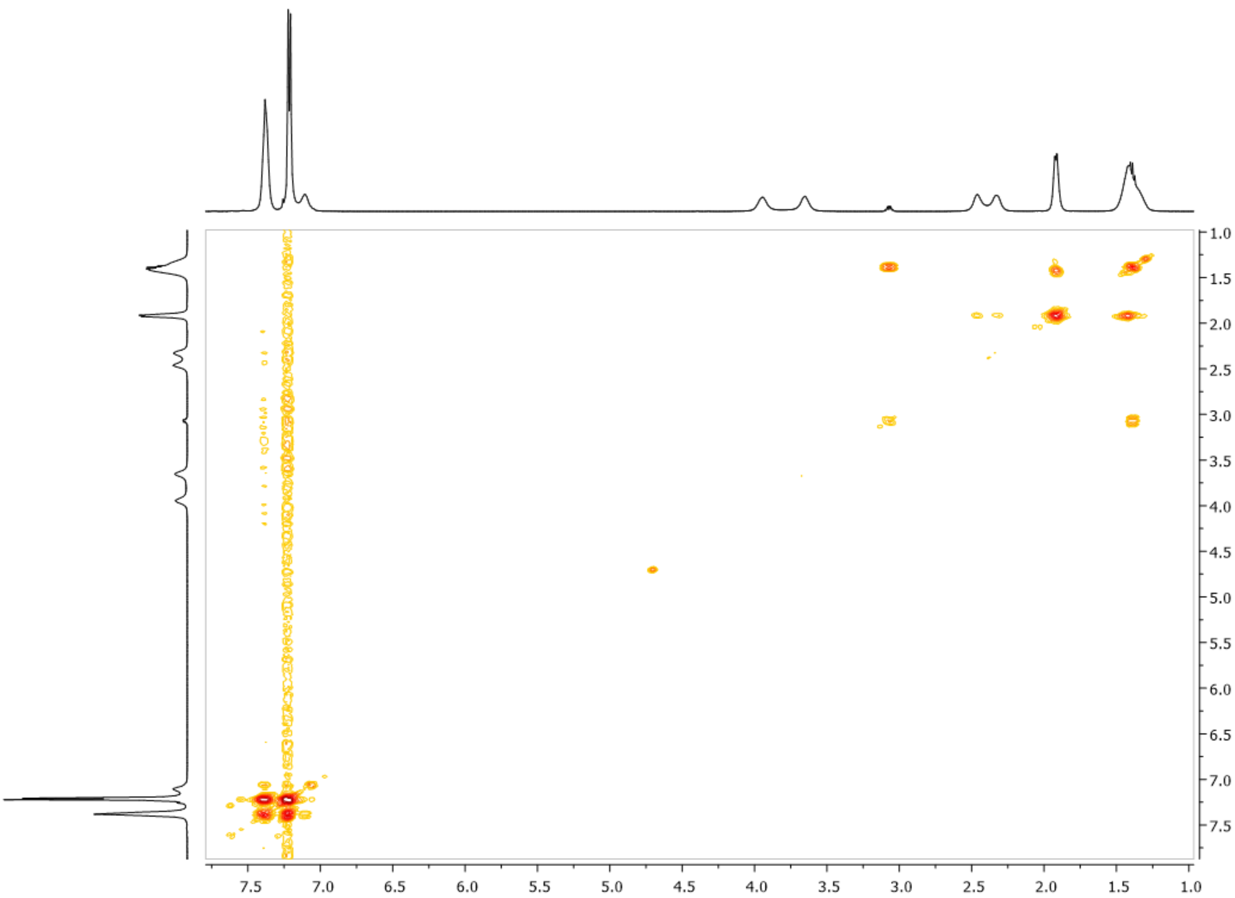


8, $^{13}C\{^{1}H\}$ (125.7 MHz, $CDCl_3$, ambient temperature).

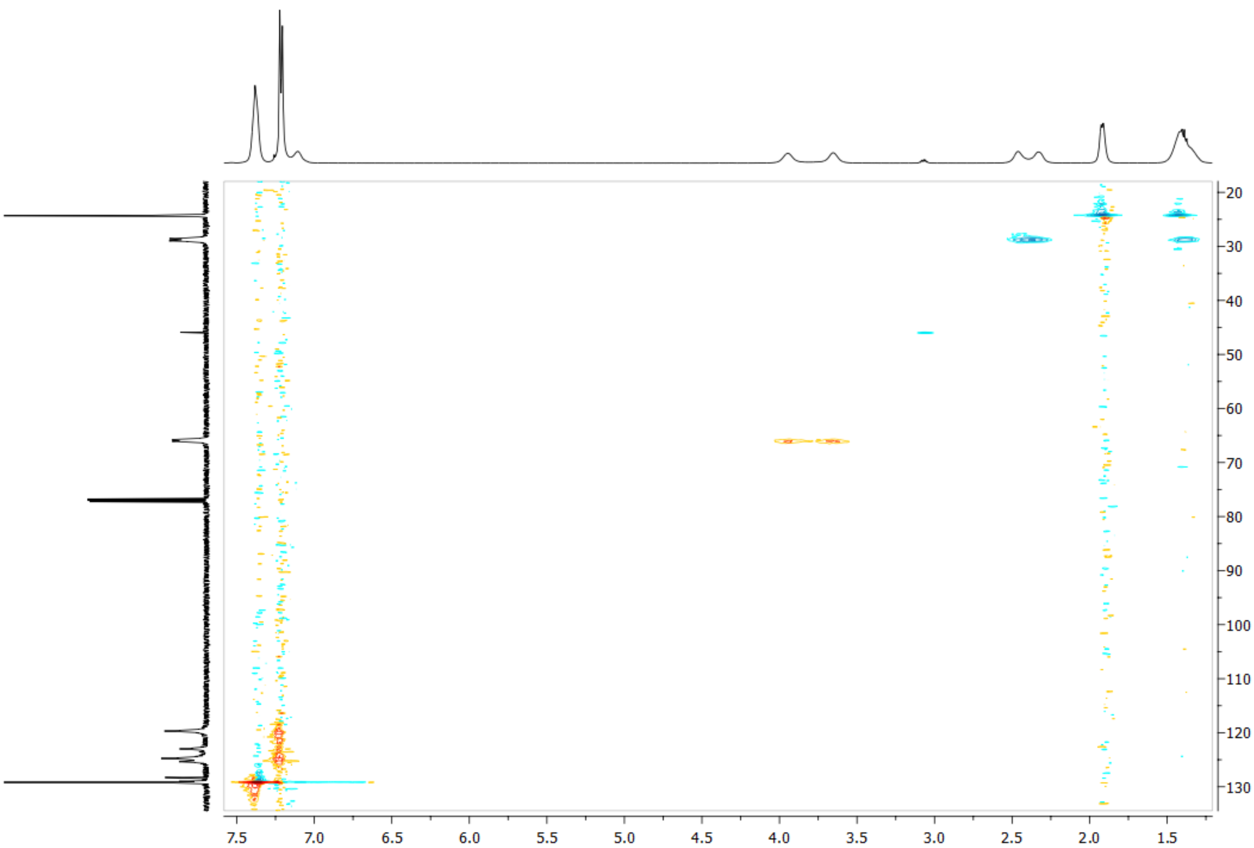


8, $^{13}C\{^{1}H\}$ APT (125.7 MHz, $CDCl_3$, ambient temperature).

NMR AND MASS SPECTRA

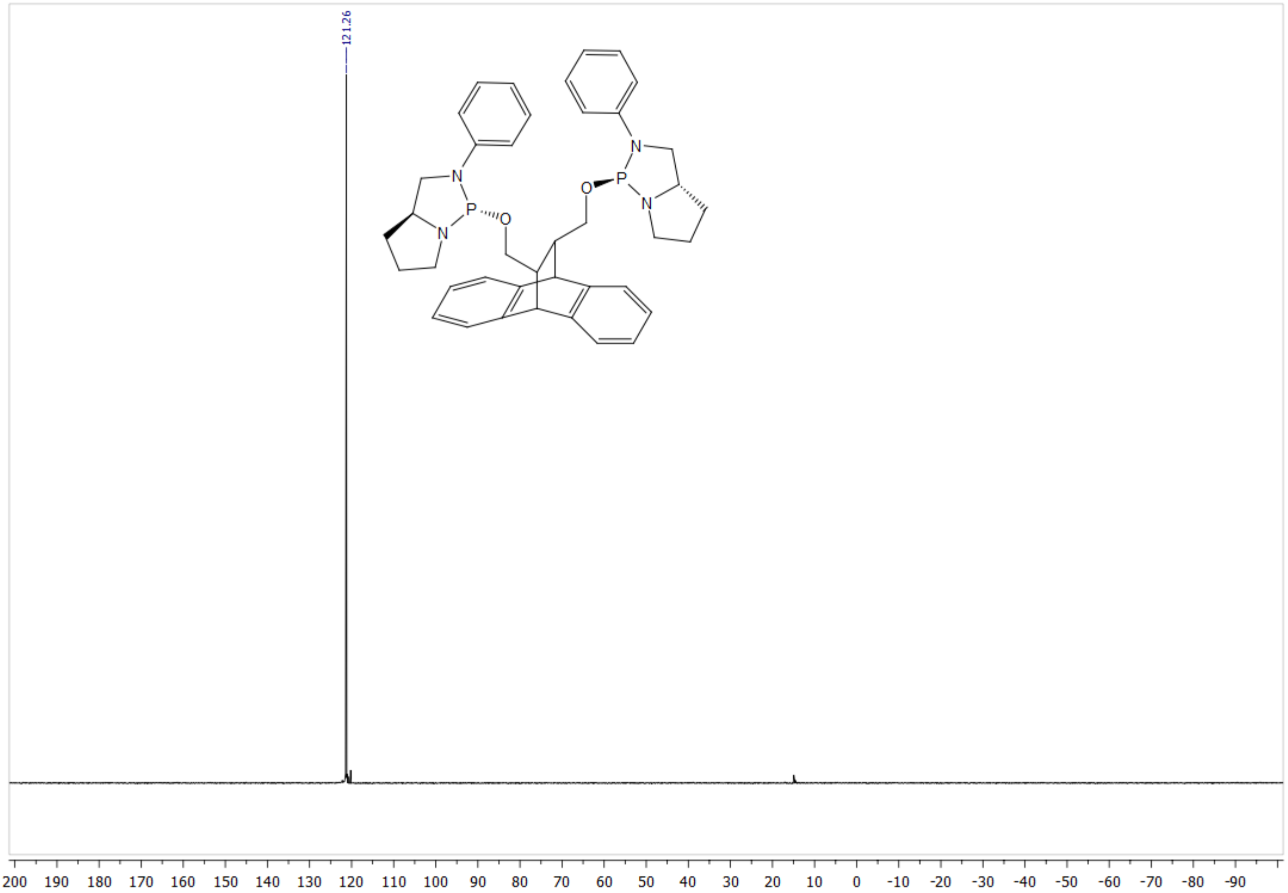


8, ^{1}H-^{1}H COSY.

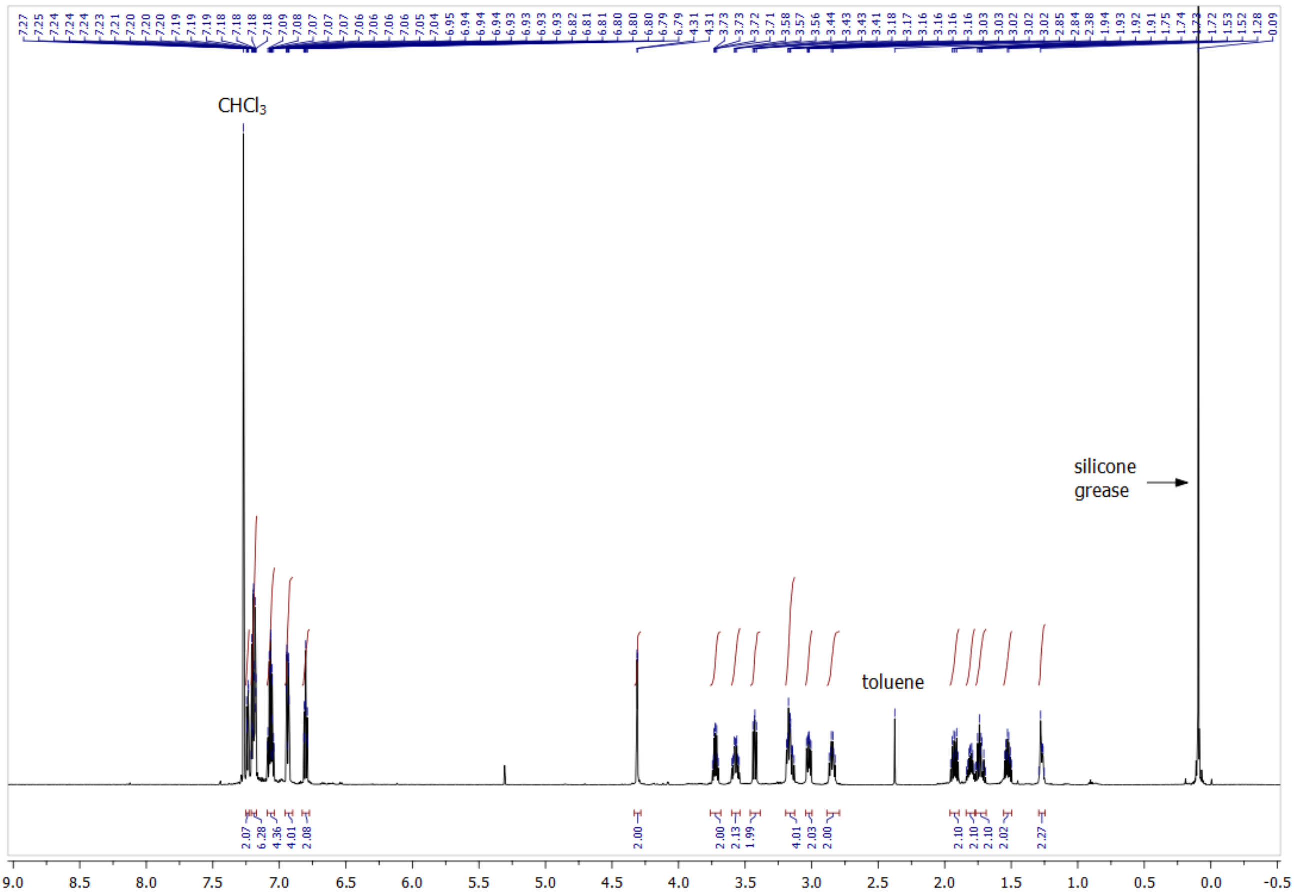


8, ^{1}H-^{13}C HSQC.

NMR AND MASS SPECTRA

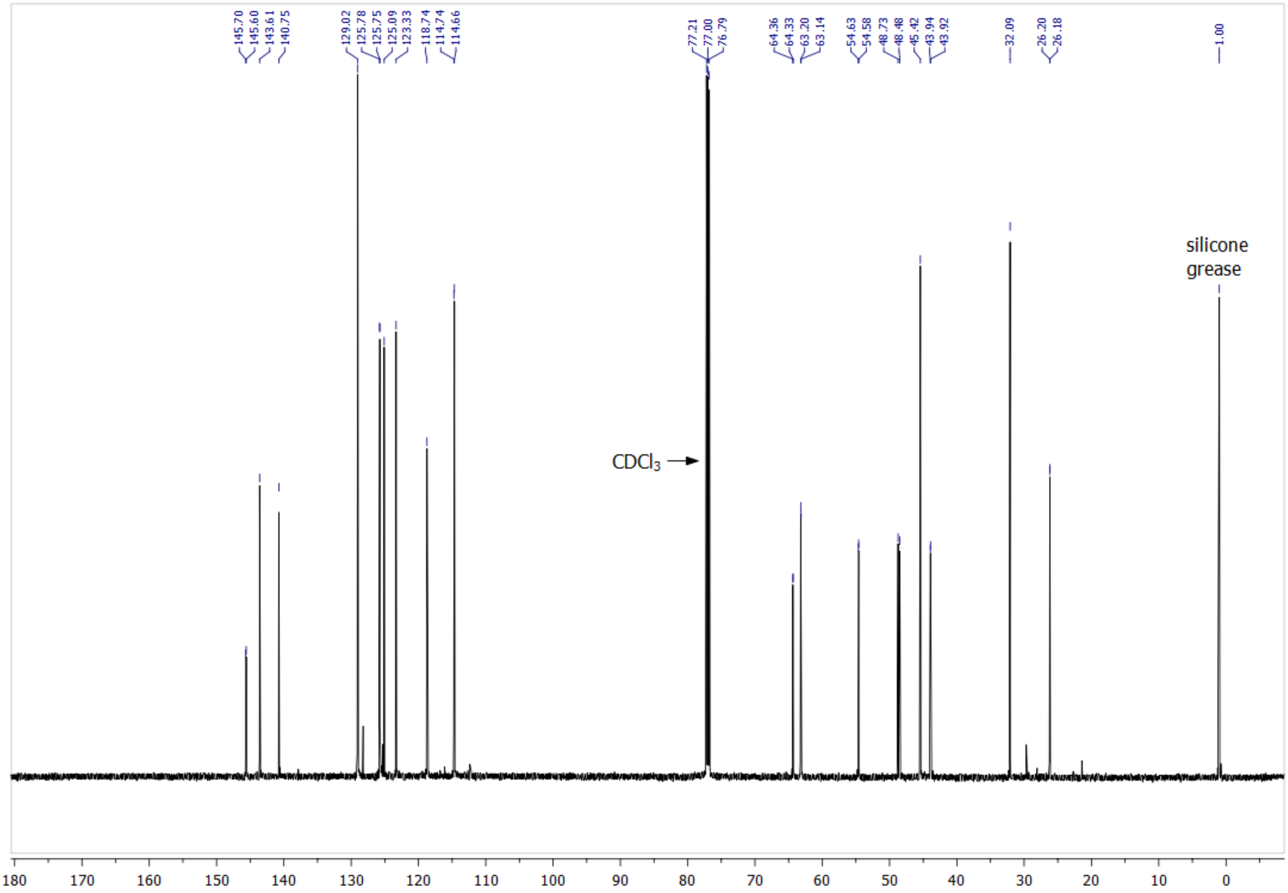


L1a, $^{31}P\{^{1}H\}$ (242.9 MHz, $CDCl_3$, 30 °C).

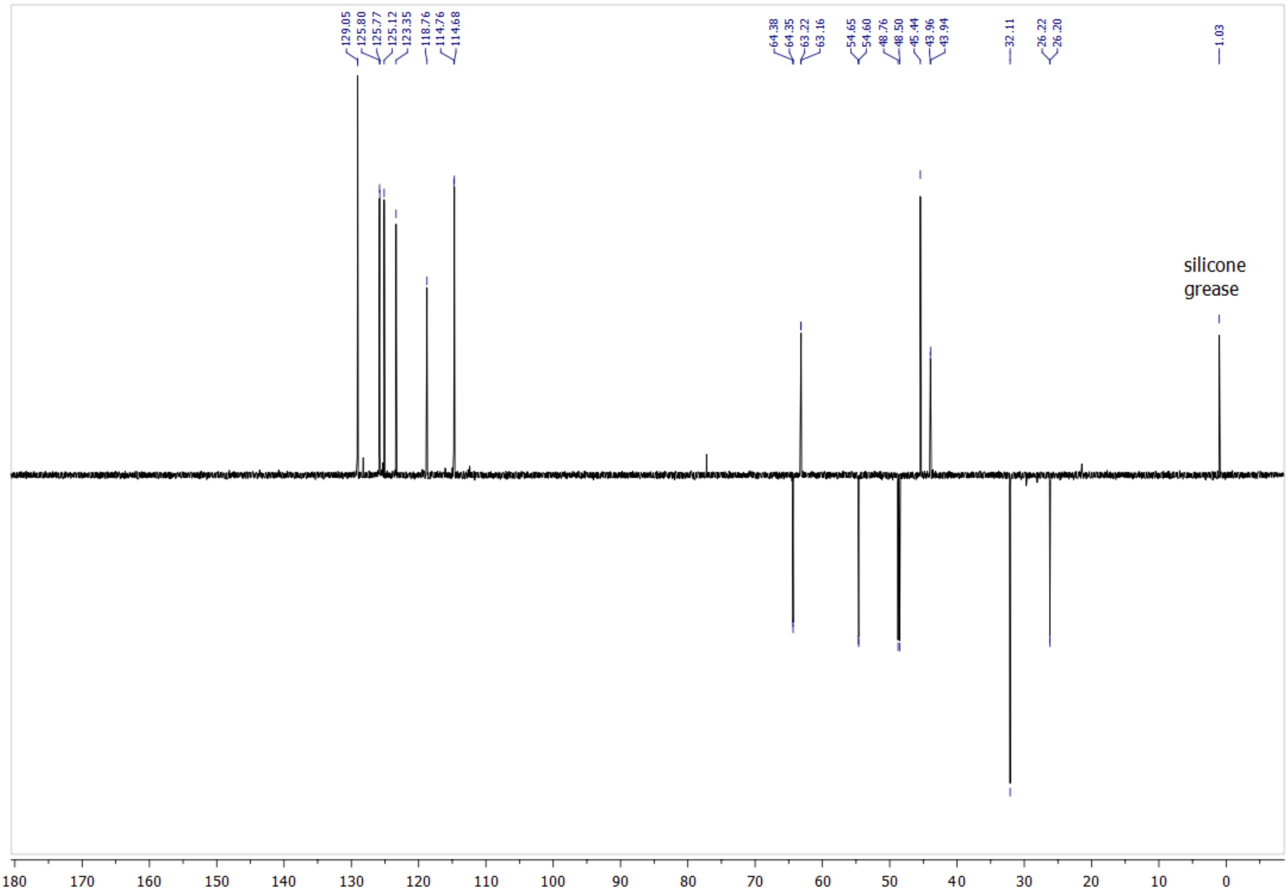


L1a, ^{1}H (600.1 MHz, $CDCl_3$, 30 °C).

NMR AND MASS SPECTRA

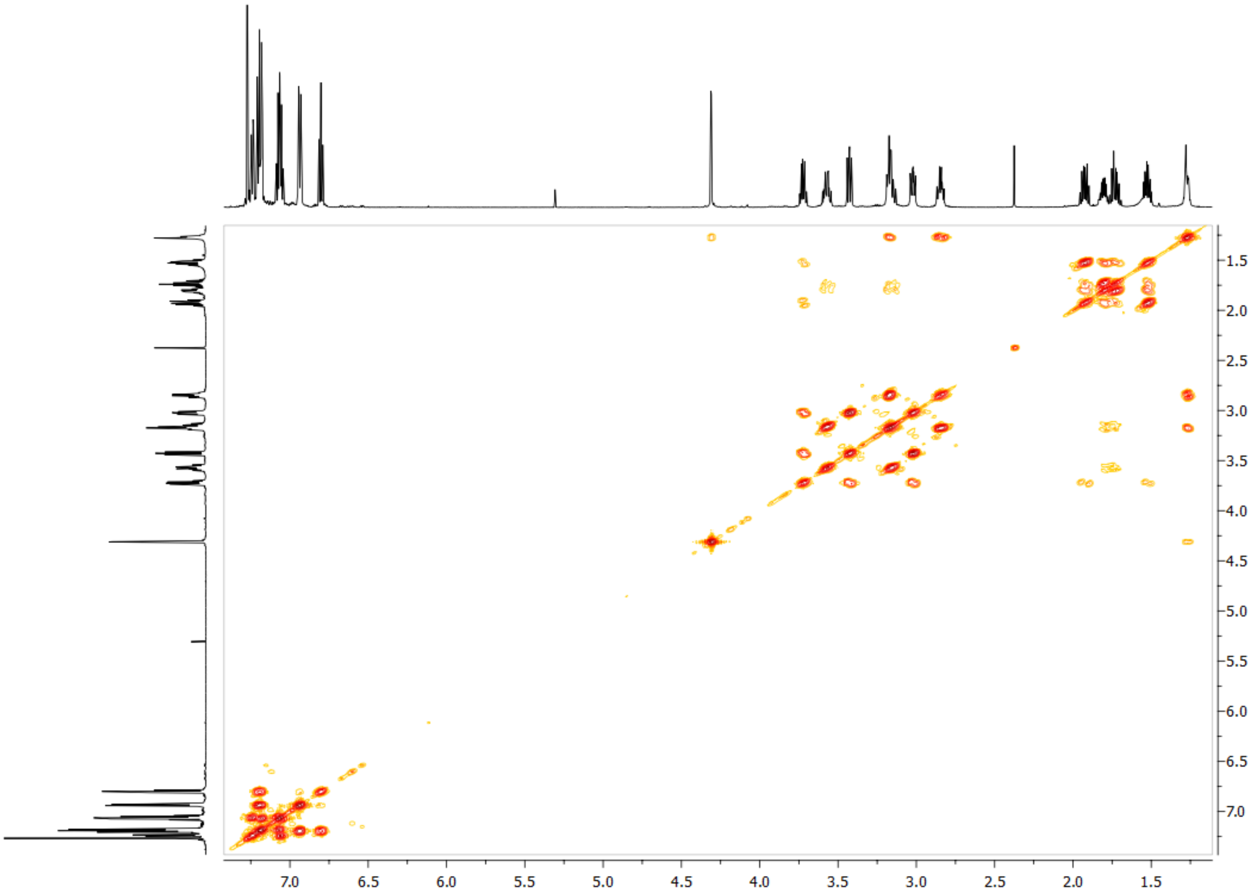


L1a, $^{13}C\{^{1}H\}$ (150.9 MHz, $CDCl_3$, 30 °C).

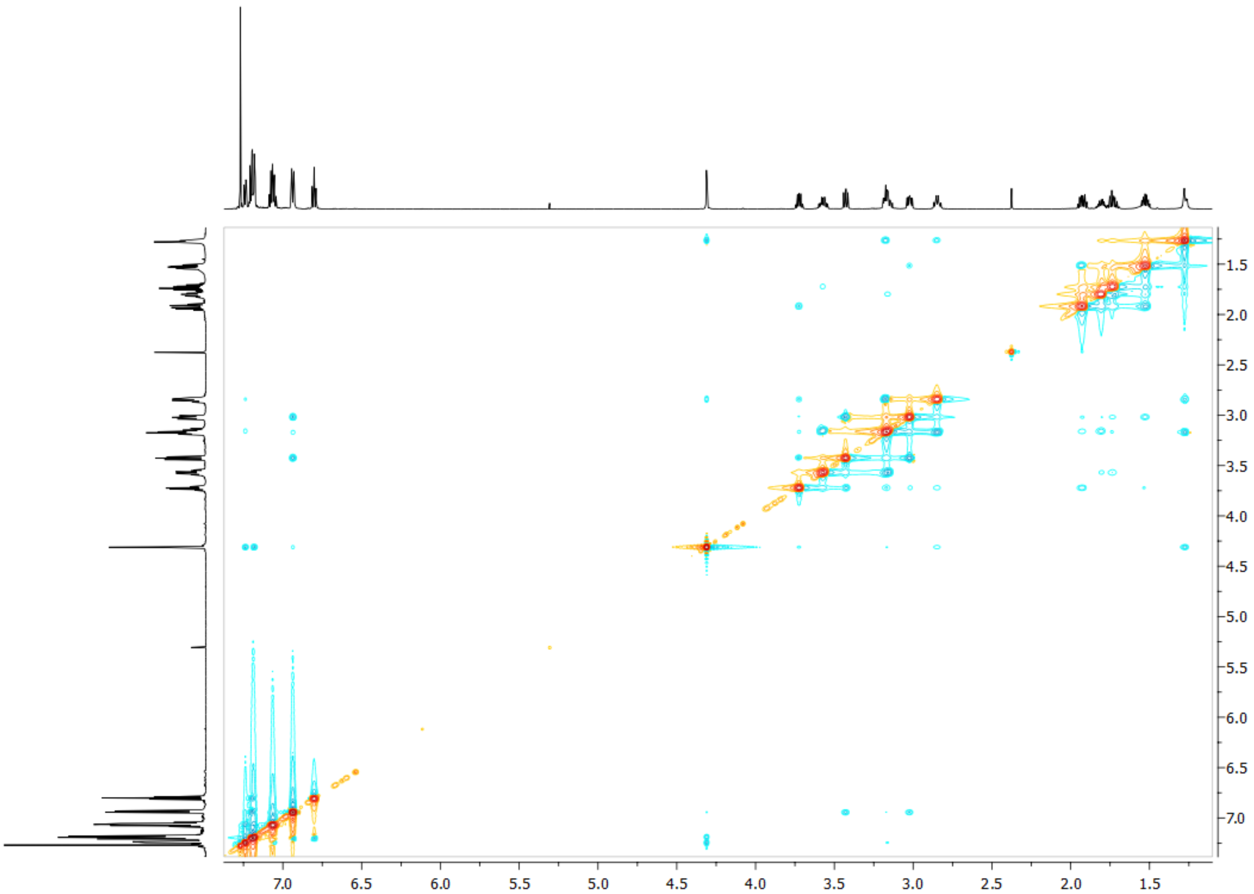


L1a, $^{13}C\{^{1}H\}$ DEPT (150.9 MHz, $CDCl_3$, 30 °C).

NMR AND MASS SPECTRA

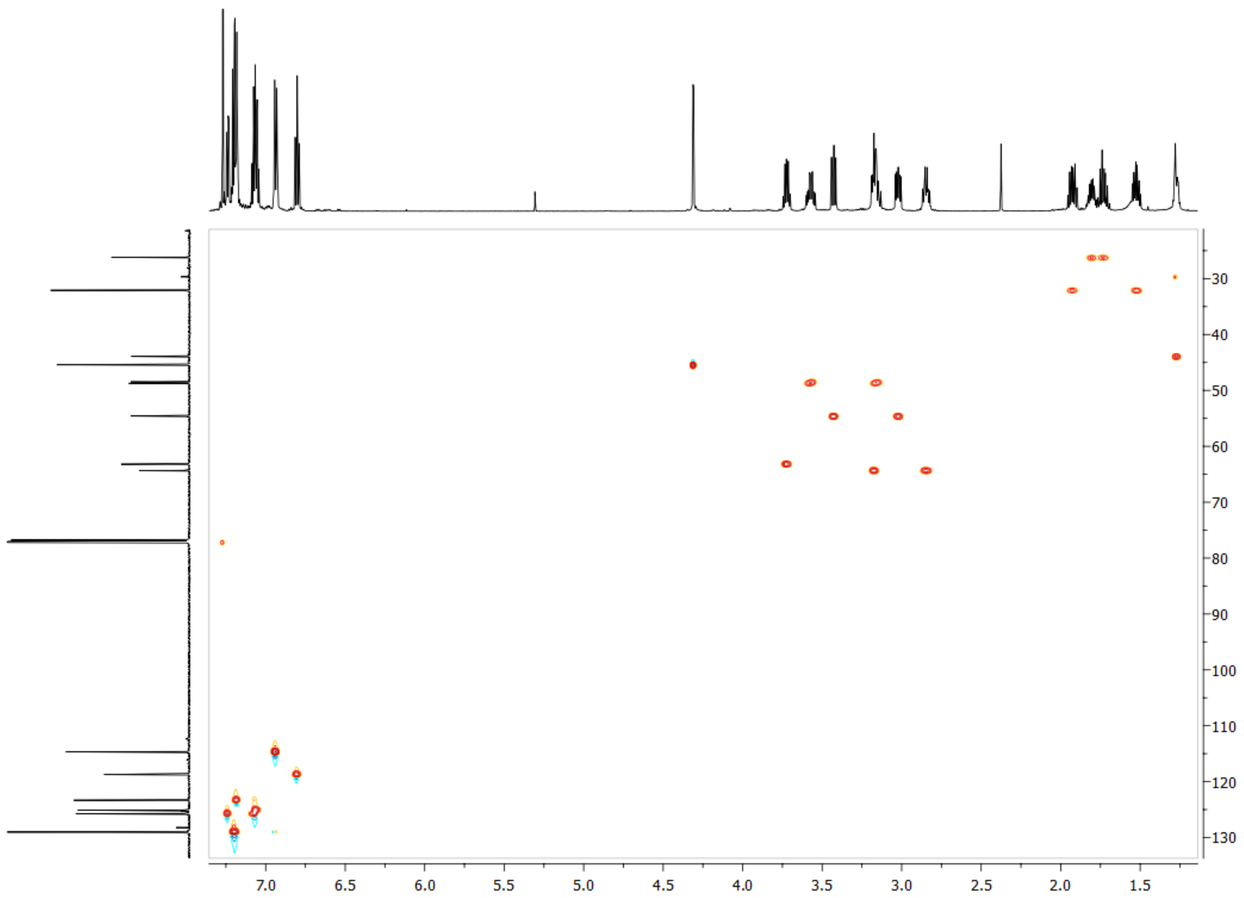


L1a, ^{1}H-^{1}H COSY.

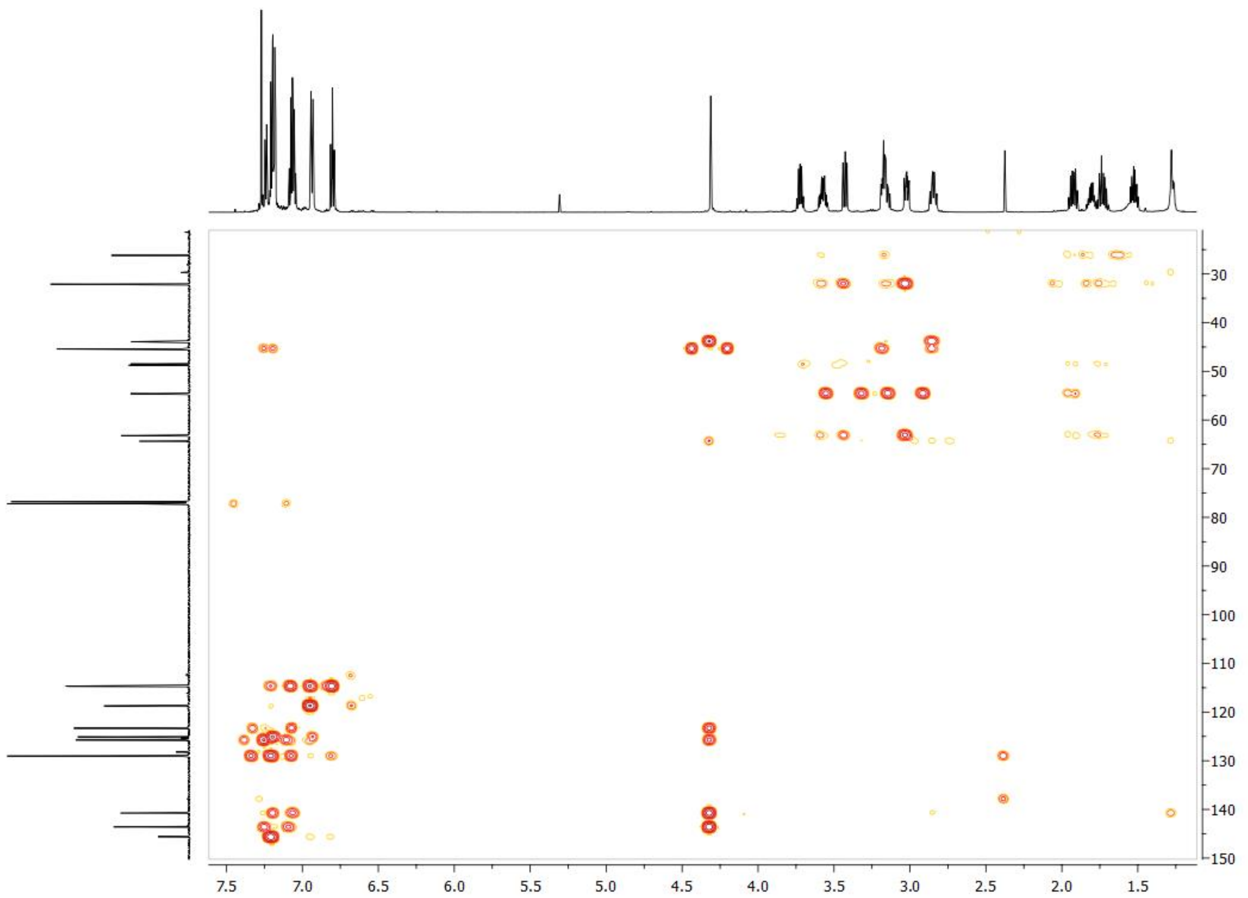


L1a, ^{1}H-^{1}H NOESY.

NMR AND MASS SPECTRA

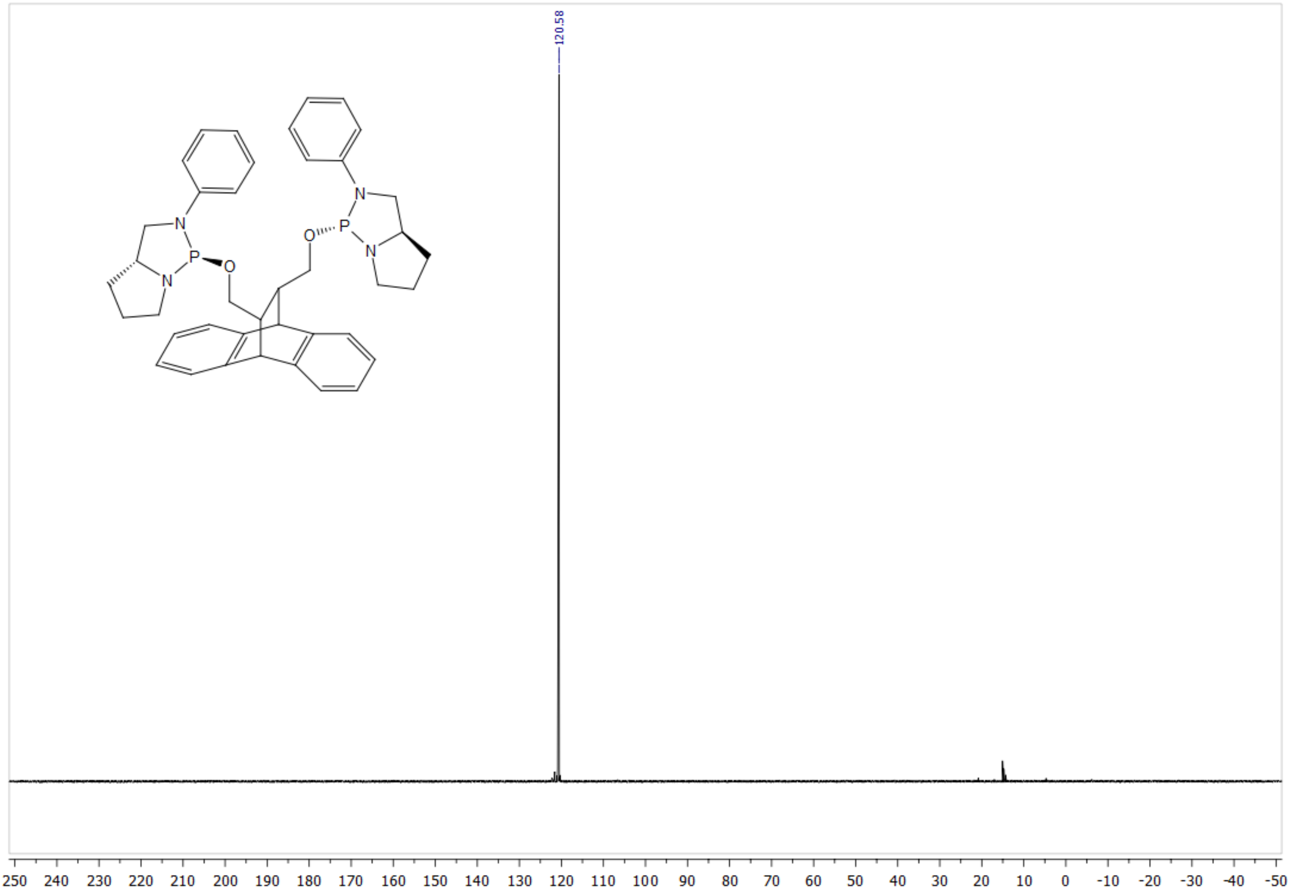


L1a, ^{1}H-^{13}C HSQC.

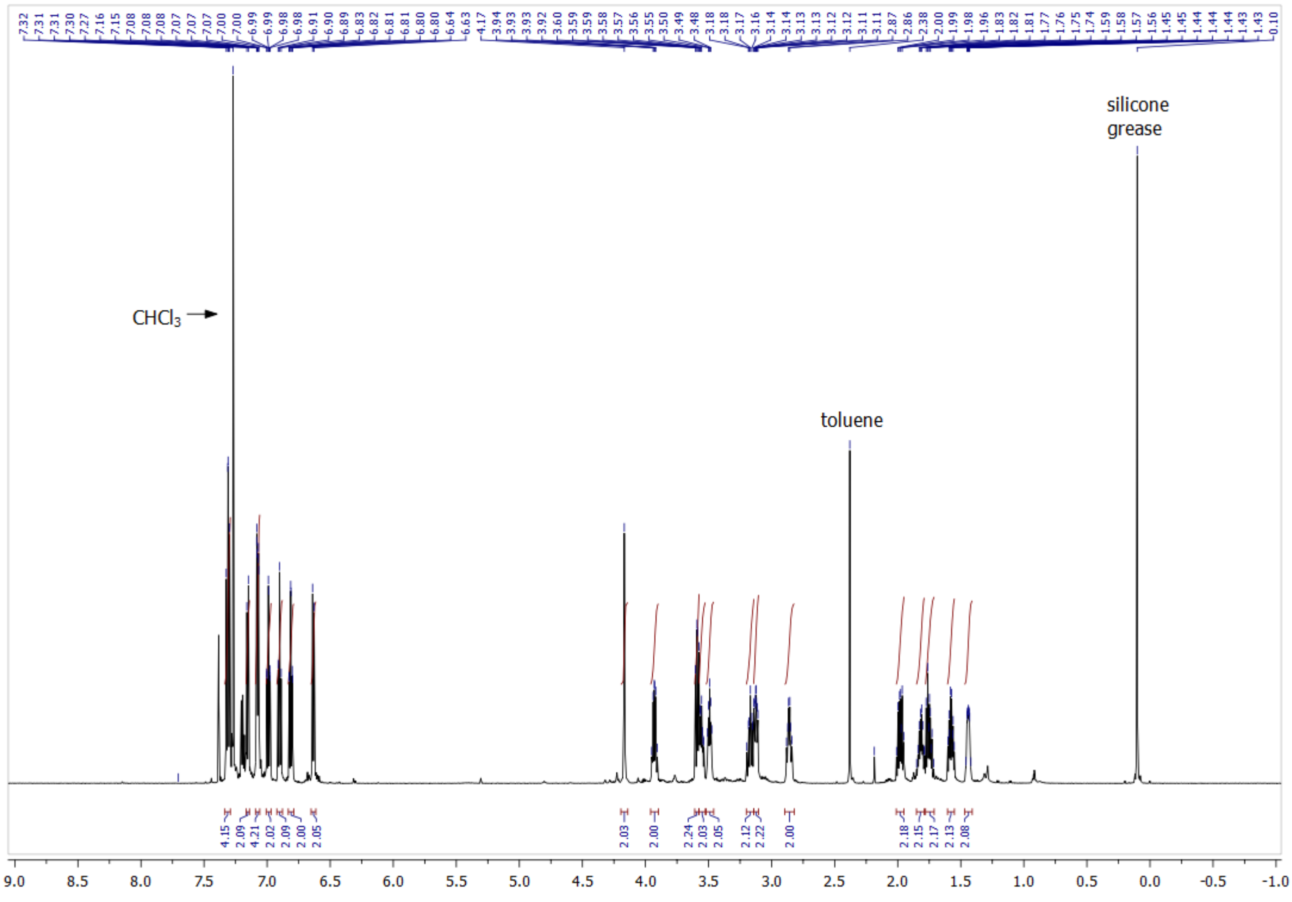


L1a, ^{1}H-^{13}C HMBC.

NMR AND MASS SPECTRA

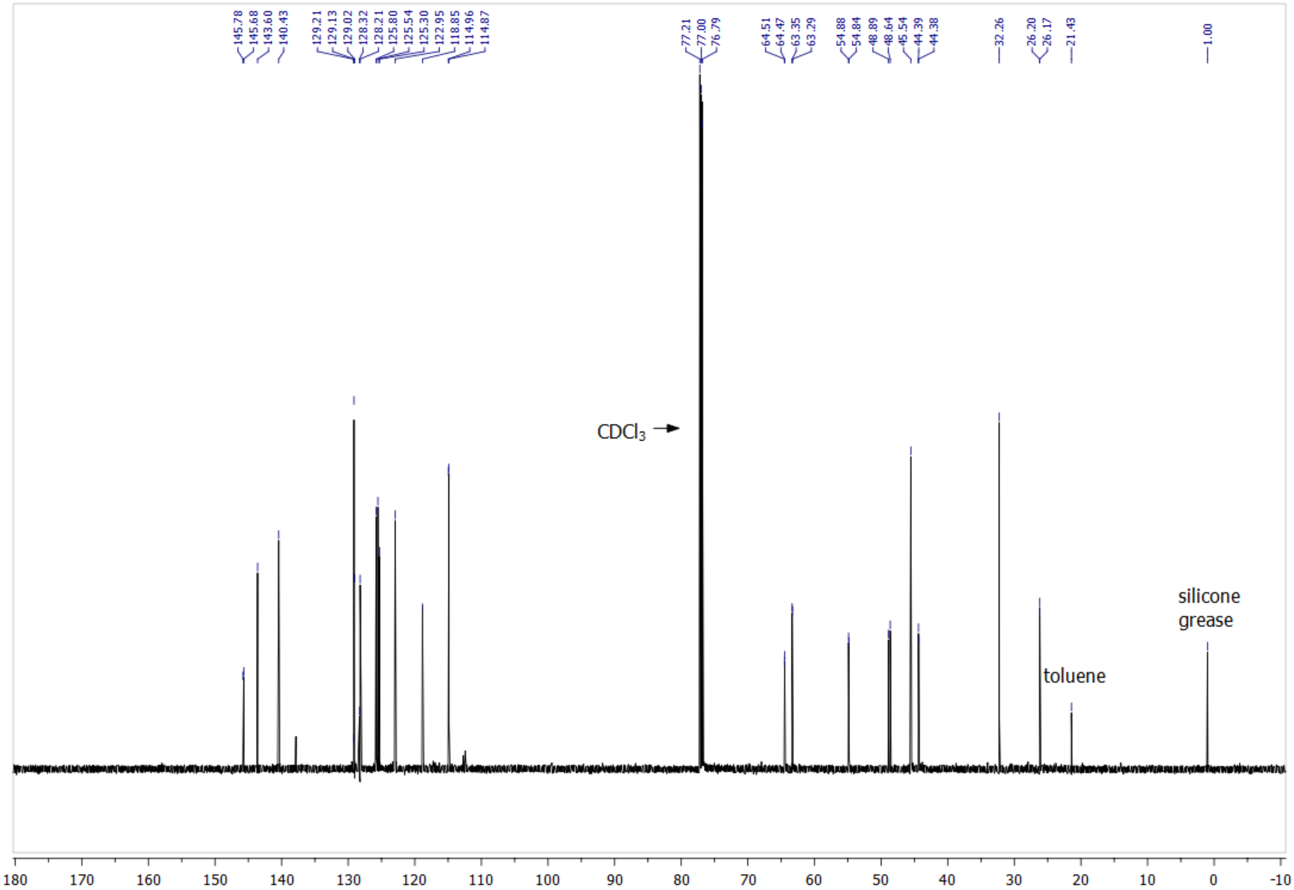


L1b, $^{31}P\{^{1}H\}$ (242.9 MHz, $CDCl_3$, 30 °C).

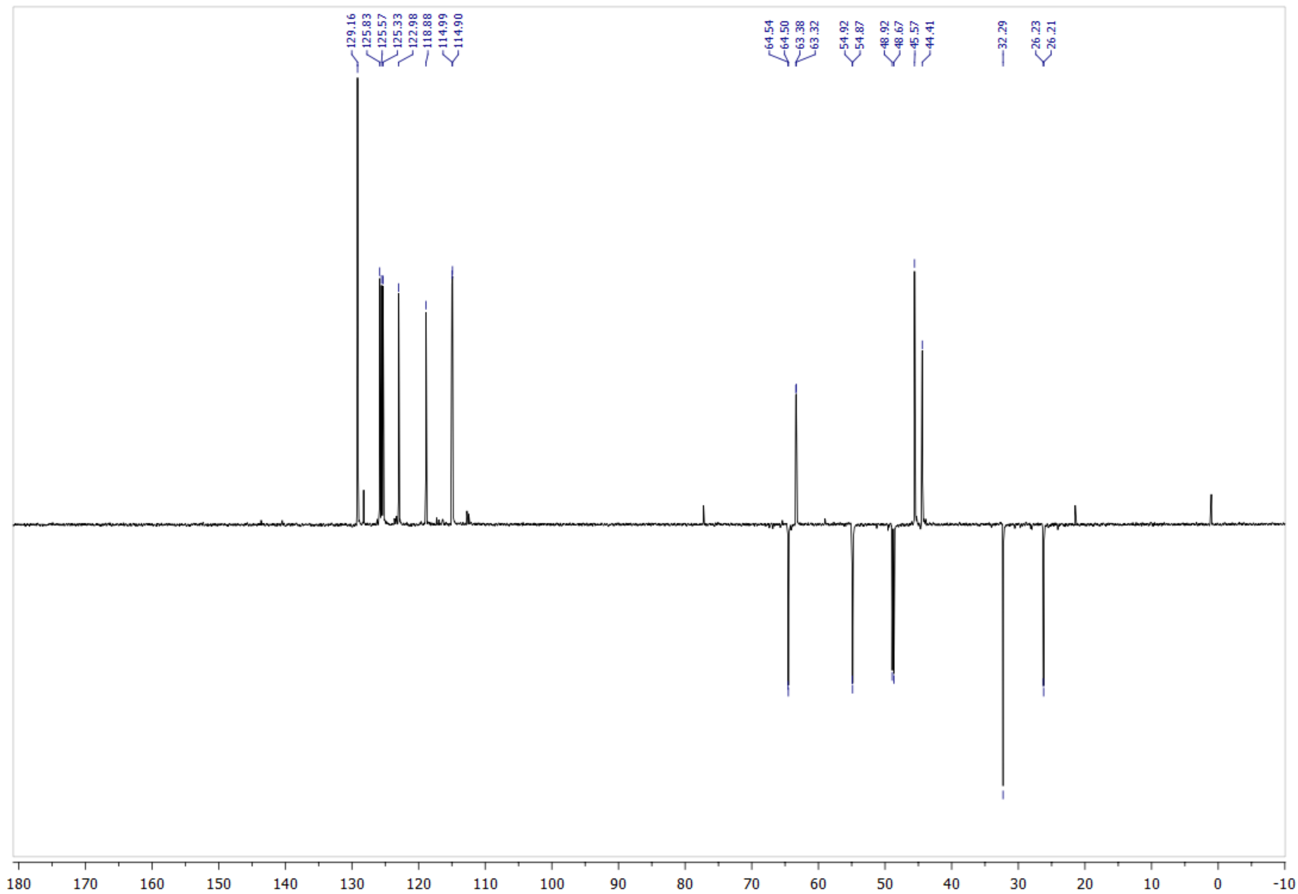


L1b, ^{1}H (600.1 MHz, $CDCl_3$, 30 °C).

NMR AND MASS SPECTRA

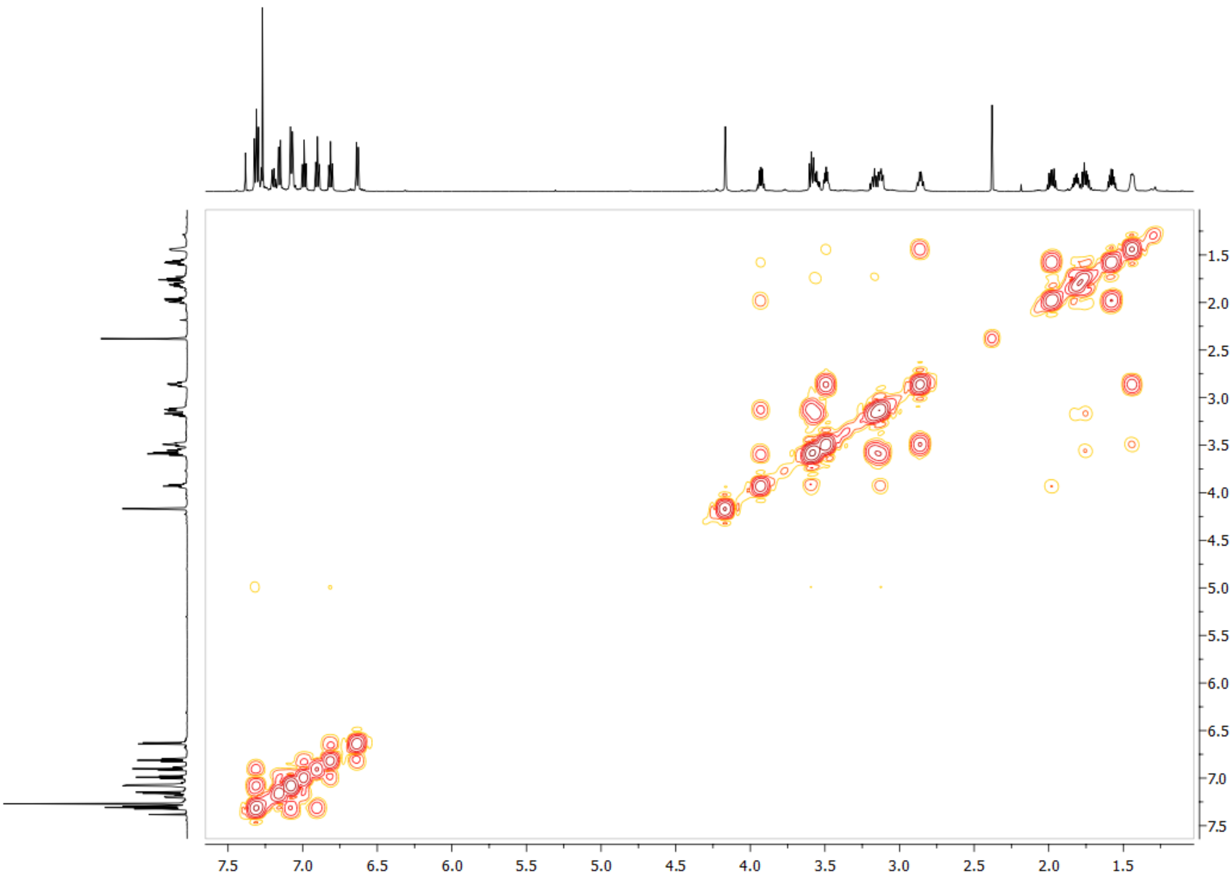


L1b, $^{13}C\{^{1}H\}$ (150.9 MHz, $CDCl_3$, 30 °C).

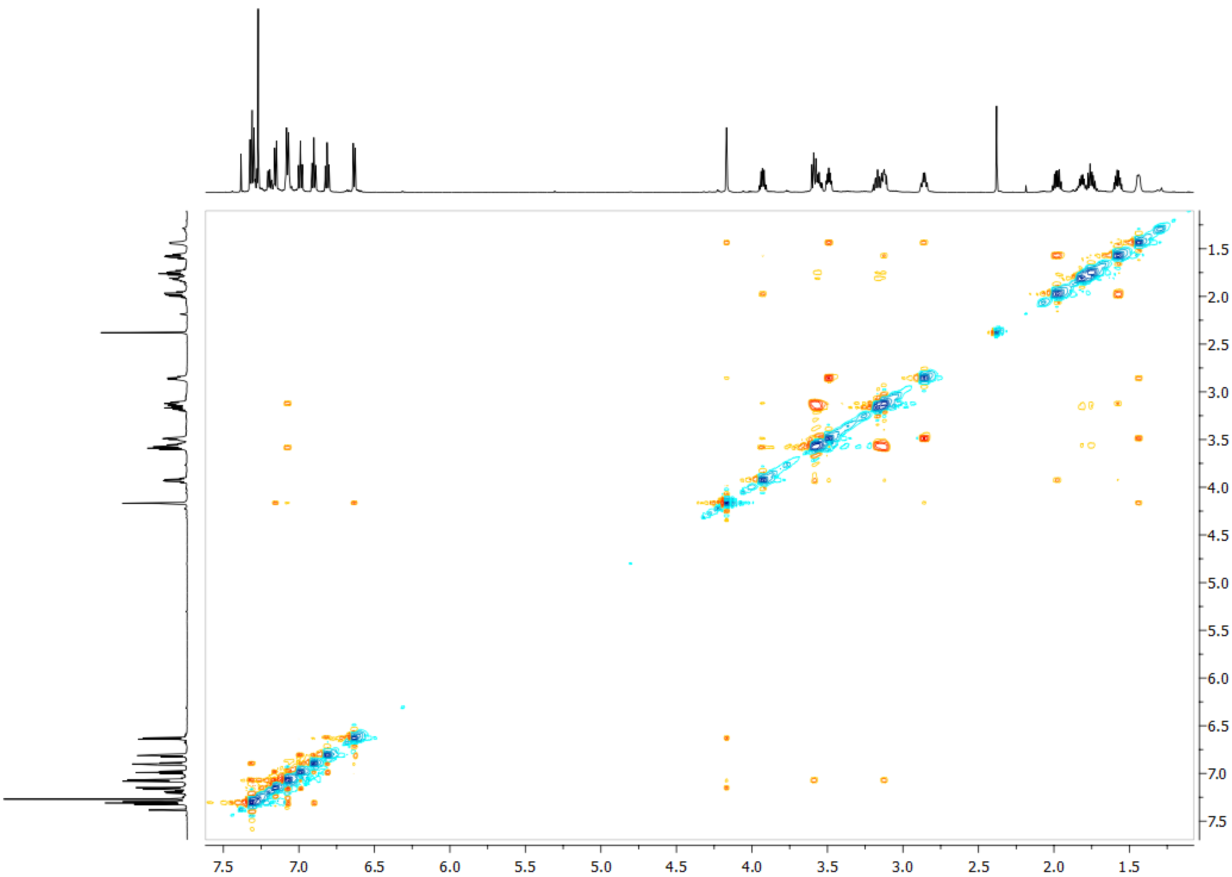


L1b, $^{13}C\{^{1}H\}$ DEPT (150.9 MHz, $CDCl_3$, 30 °C).

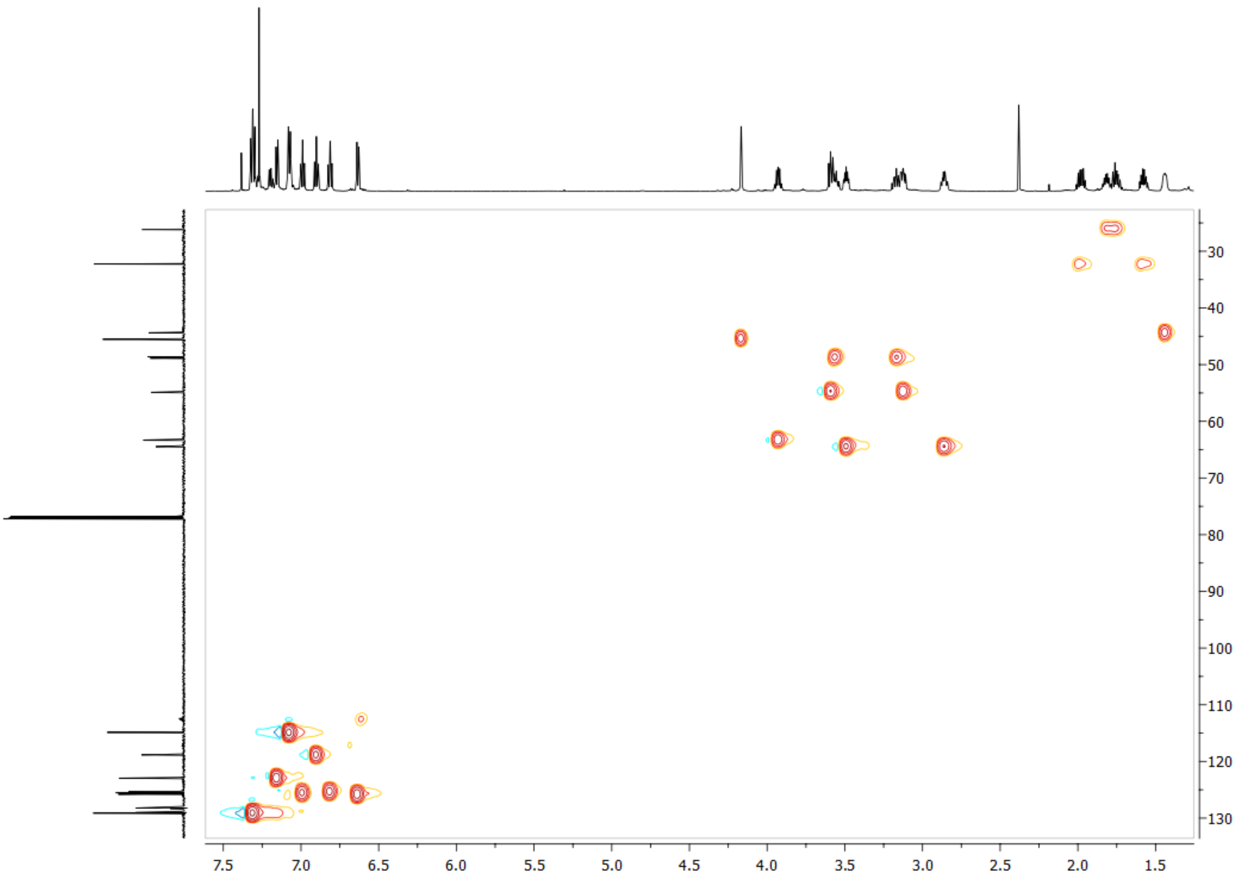
NMR AND MASS SPECTRA



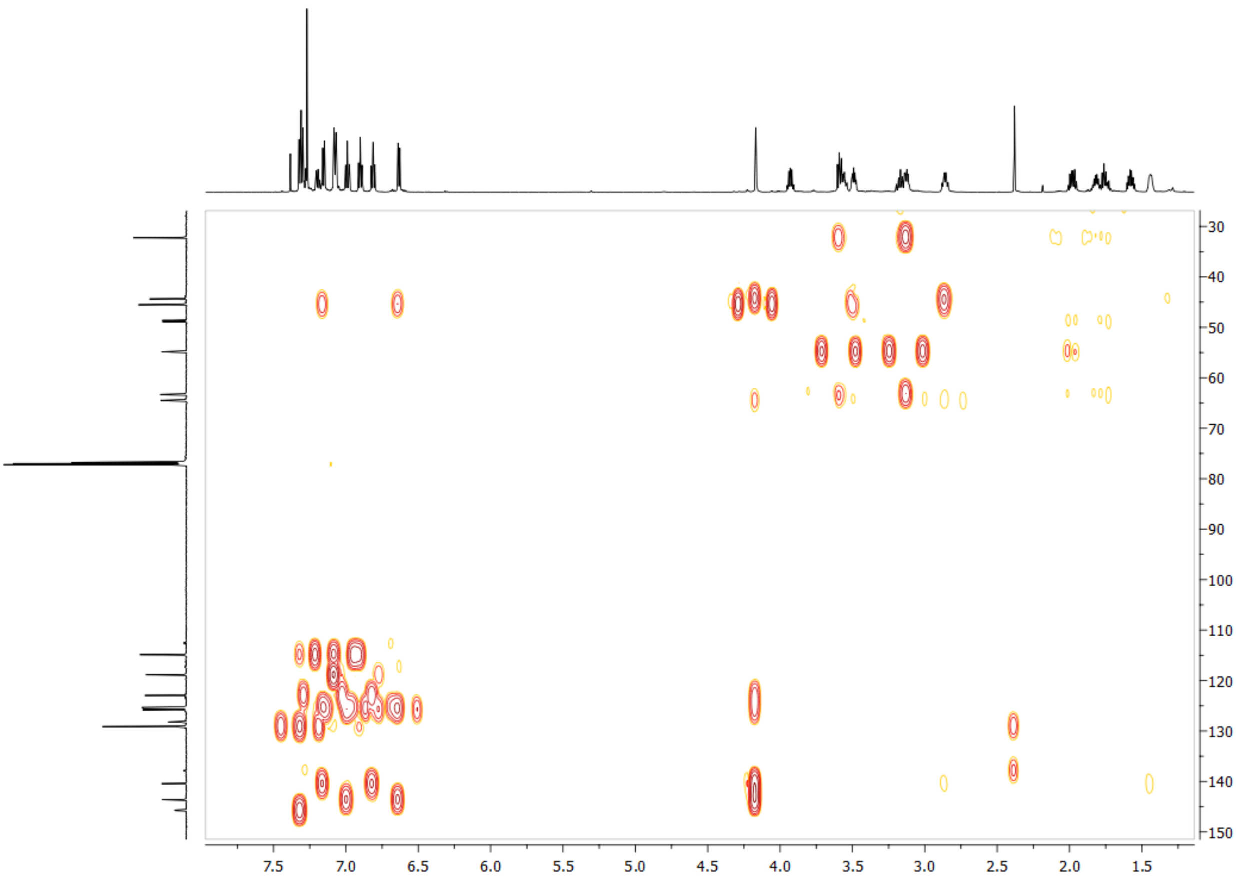
L1b, ^{1}H-^{1}H COSY.



L1b, ^{1}H-^{1}H NOESY.

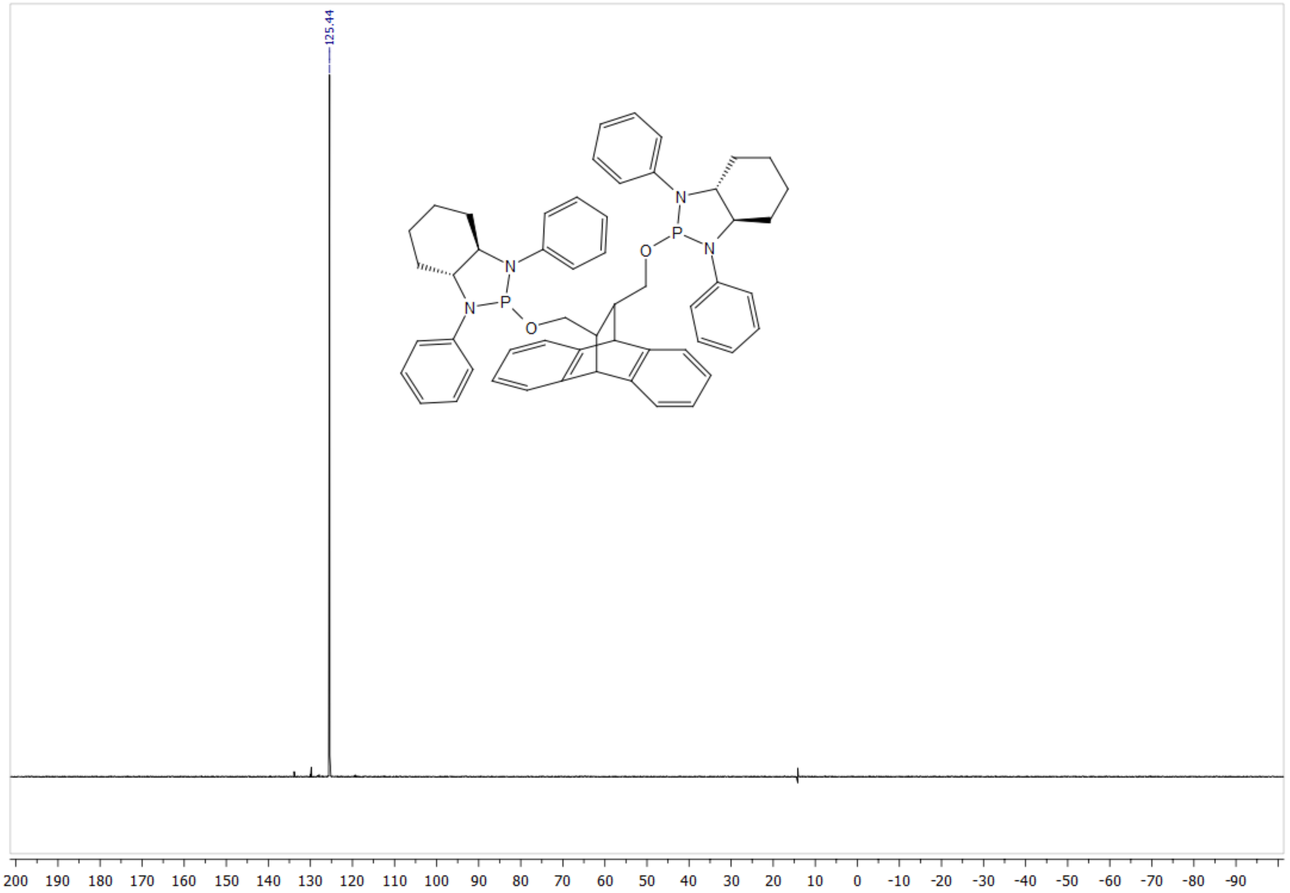


L1b, ^{1}H-^{13}C HSQC.

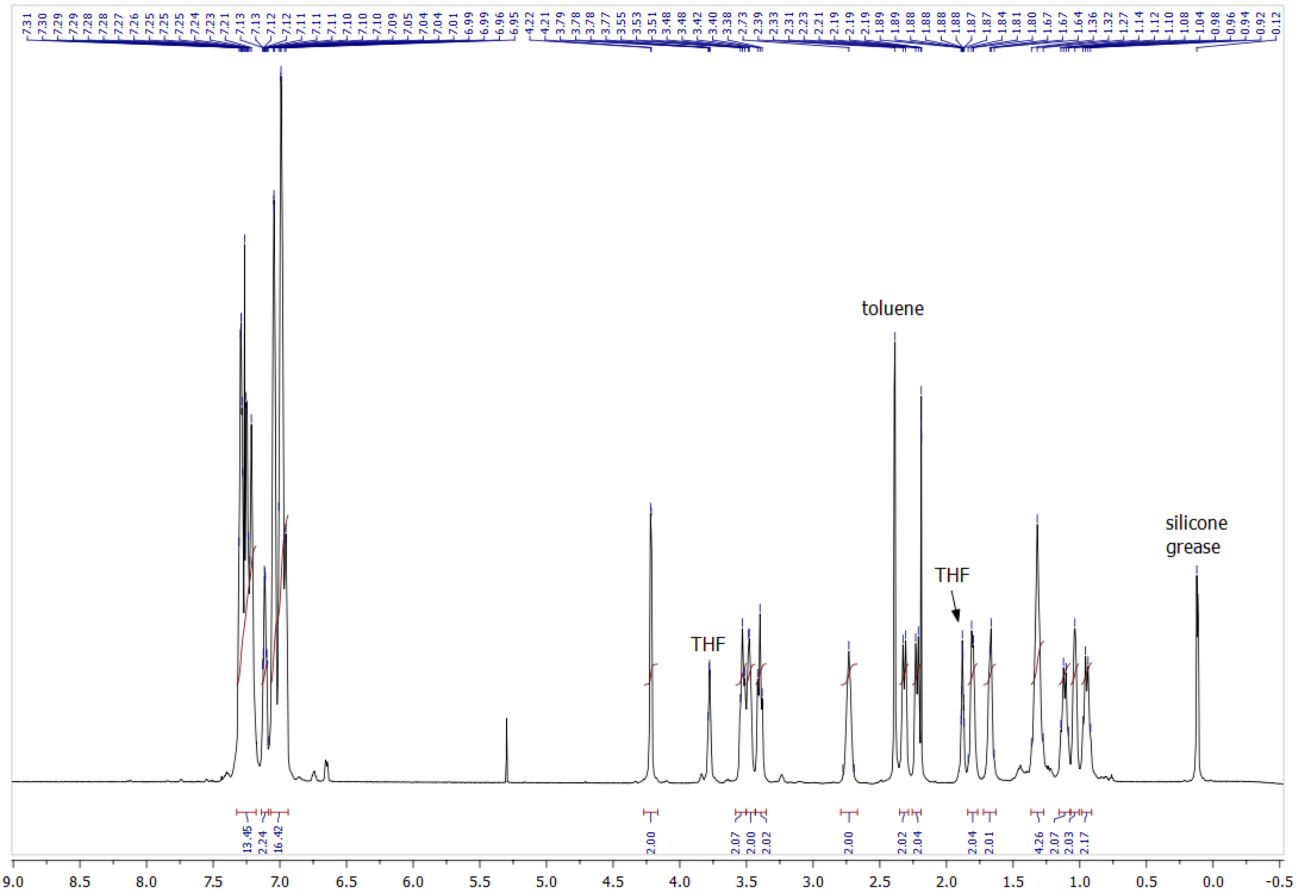


L1b, ^{1}H-^{13}C HMBC.

NMR AND MASS SPECTRA

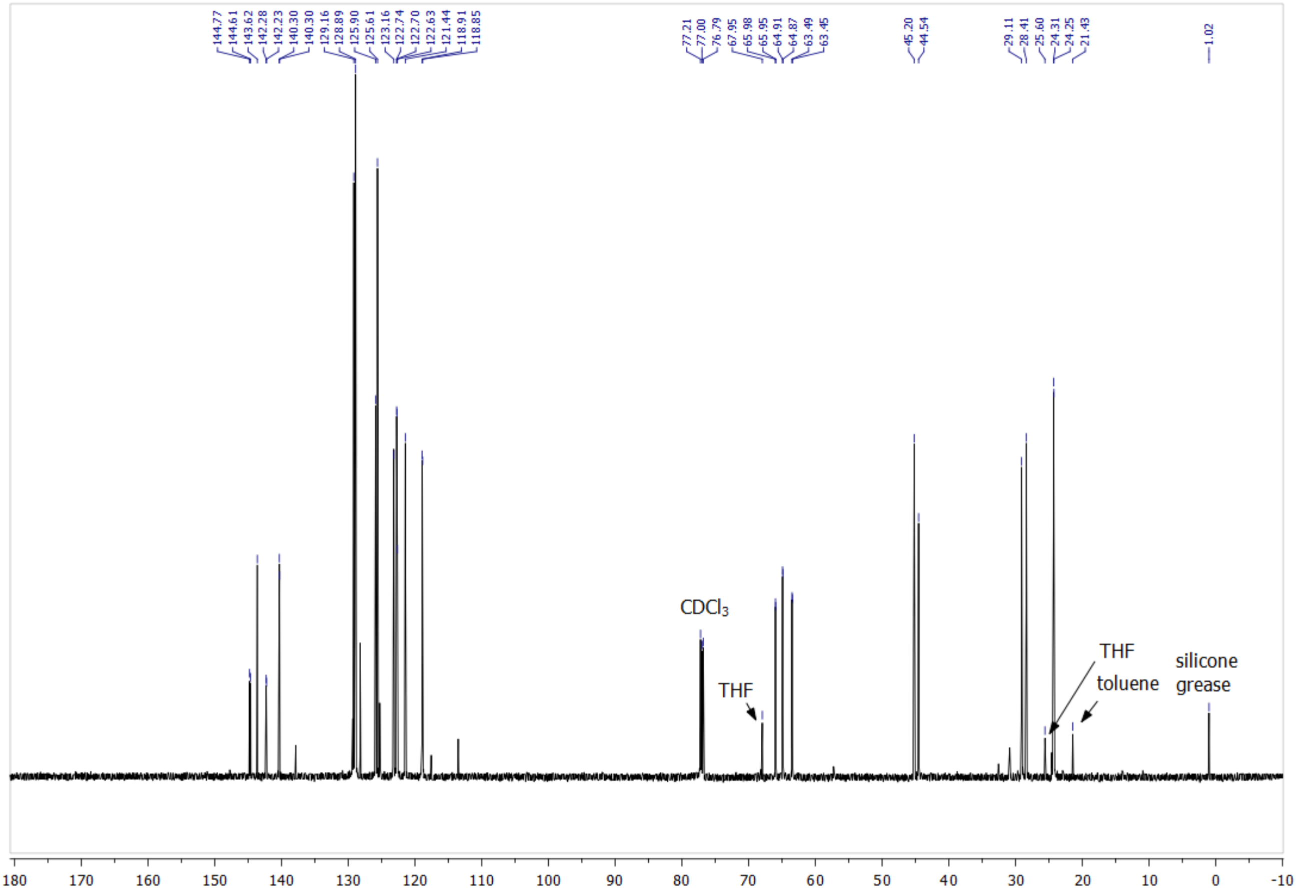


L2a, $^{31}P\{^{1}H\}$ (242.9 MHz, $CDCl_3$, 30 °C).

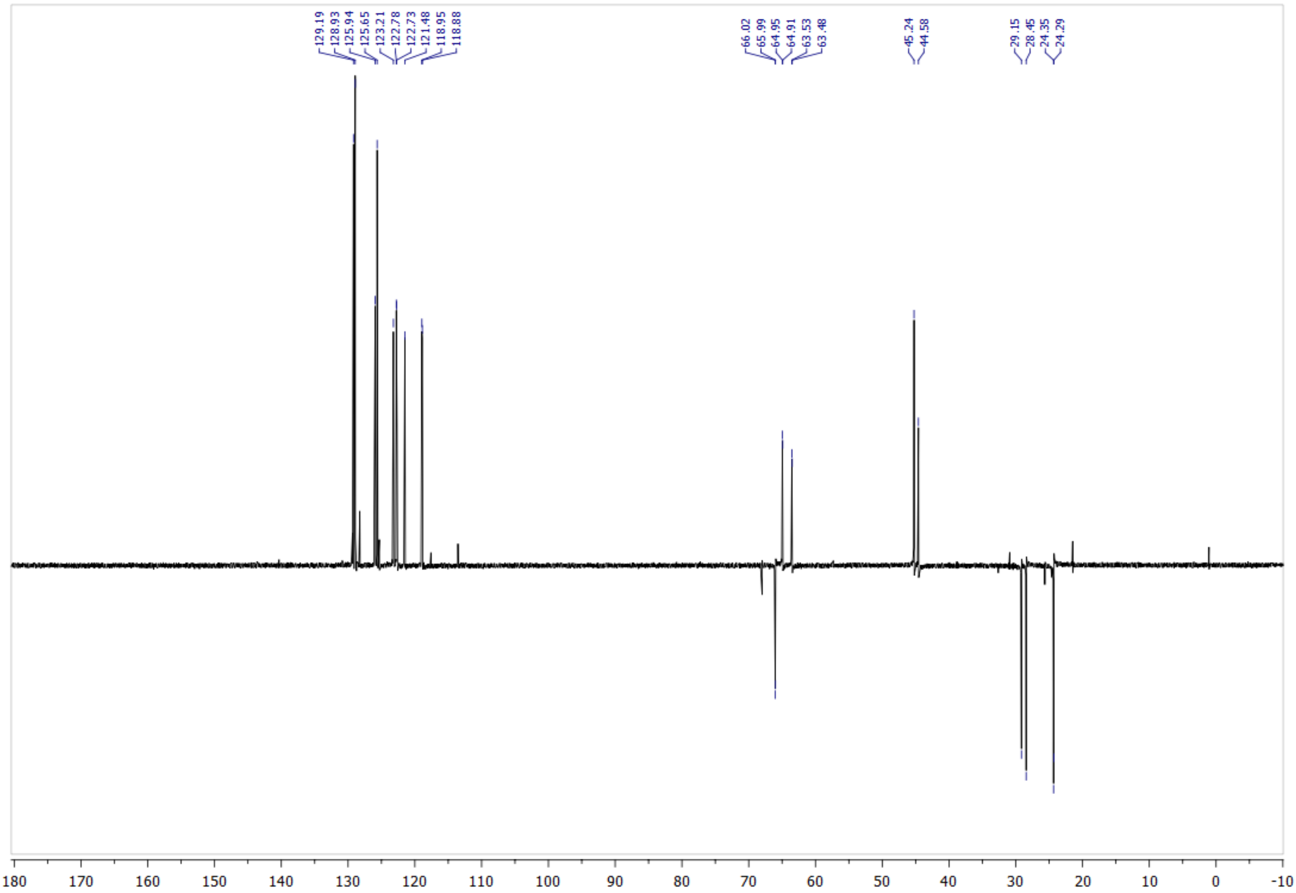


L2a, ^{1}H (600.1 MHz, $CDCl_3$, 30 °C).

NMR AND MASS SPECTRA

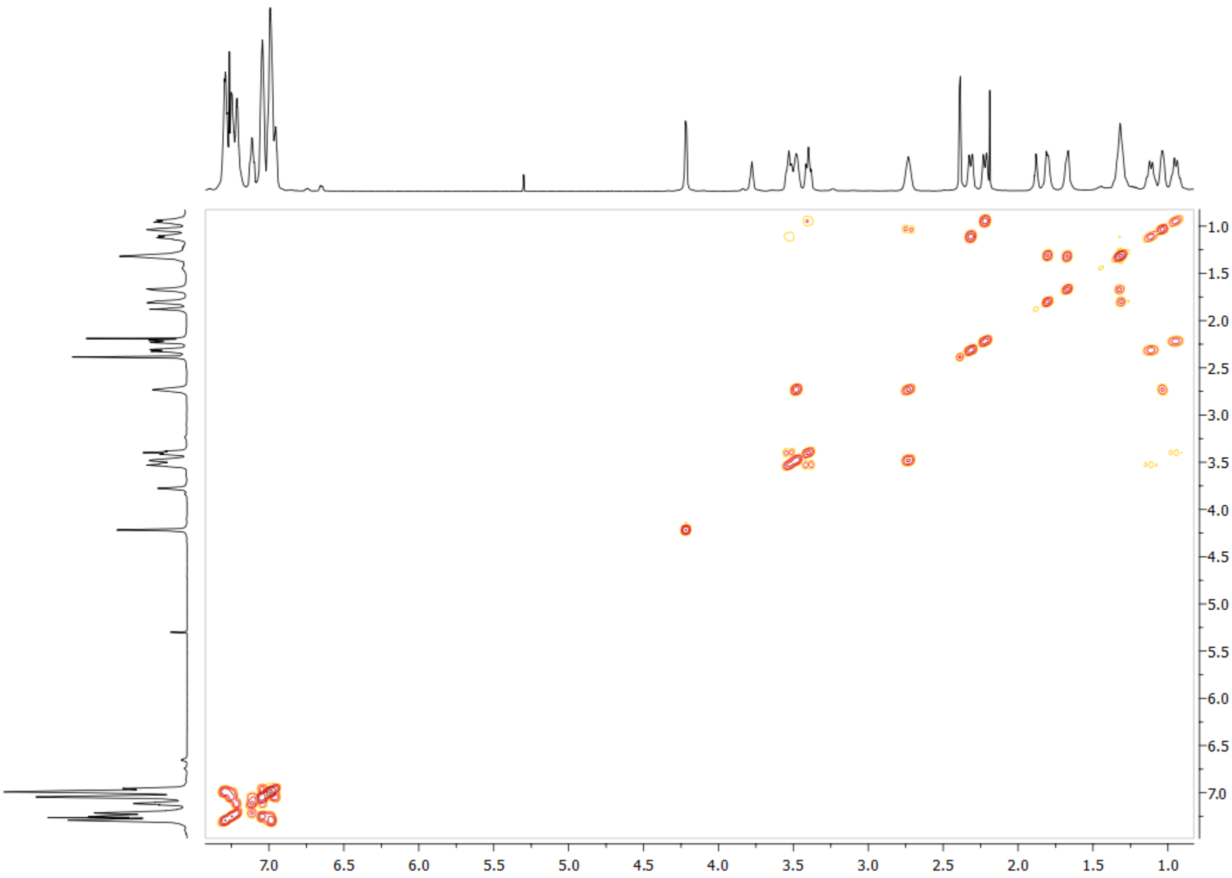


L2a, $^{13}C\{^{1}H\}$ (150.9 MHz, $CDCl_3$, 30 °C).

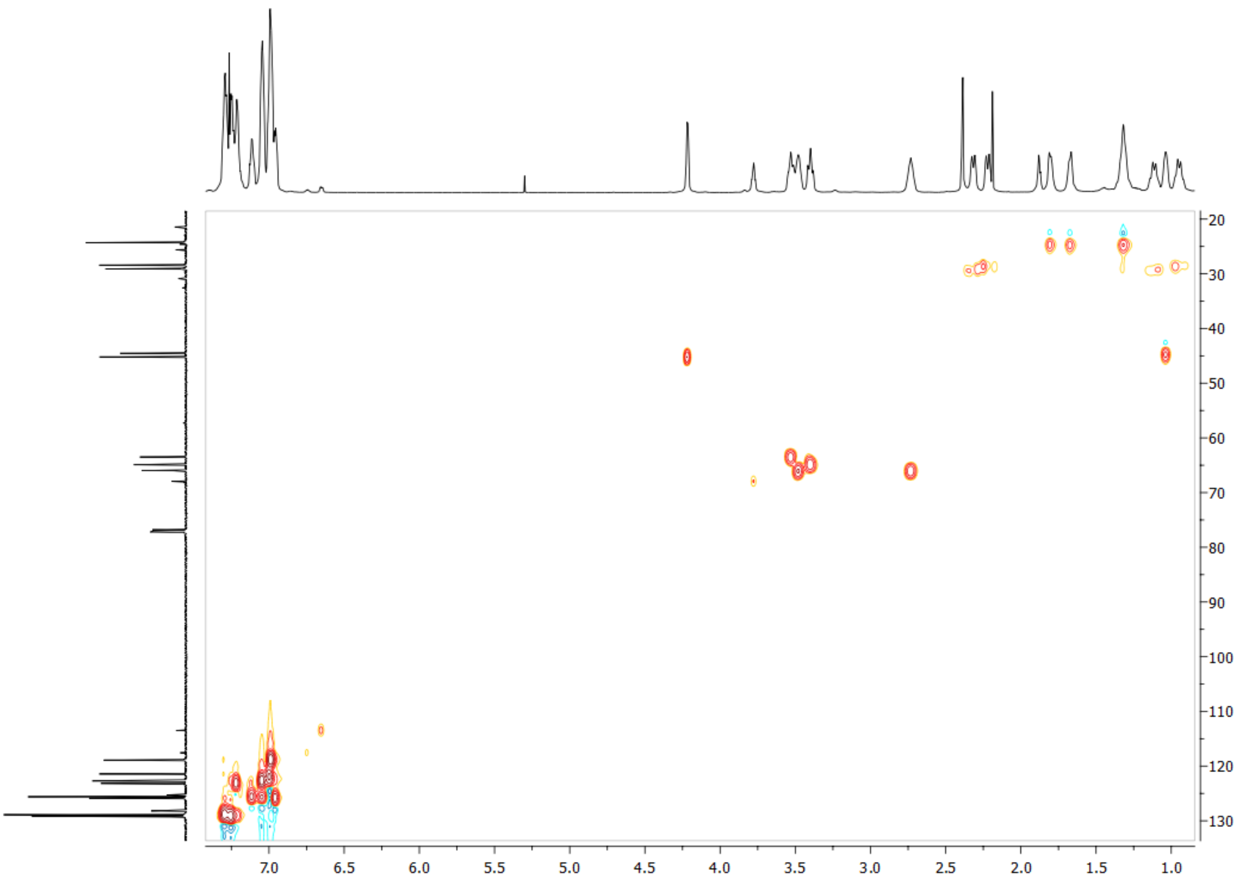


L2a, $^{13}C\{^{1}H\}$ DEPT (150.9 MHz, $CDCl_3$, 30 °C).

NMR AND MASS SPECTRA



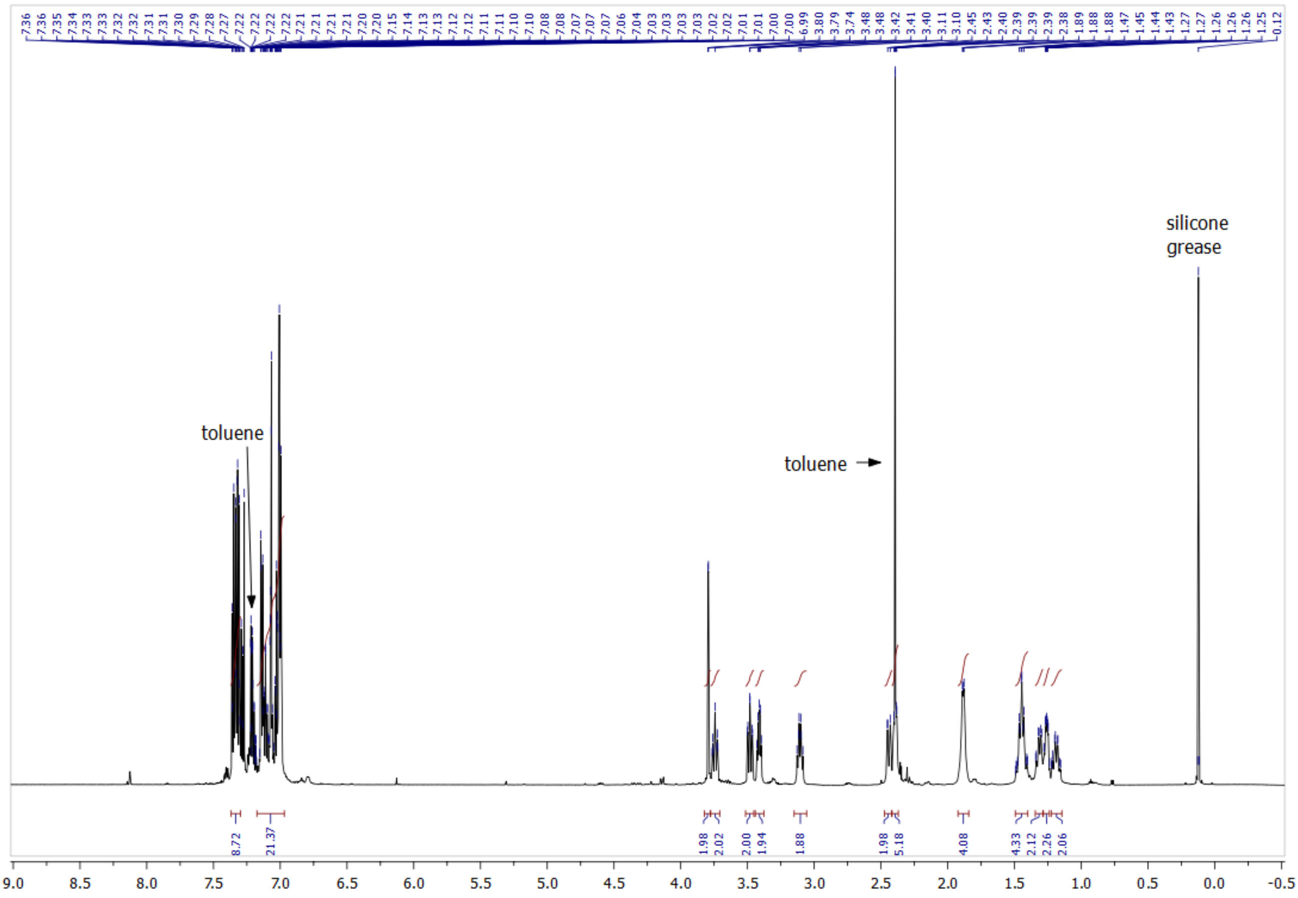
L2a, ^1H-^1H COSY.



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

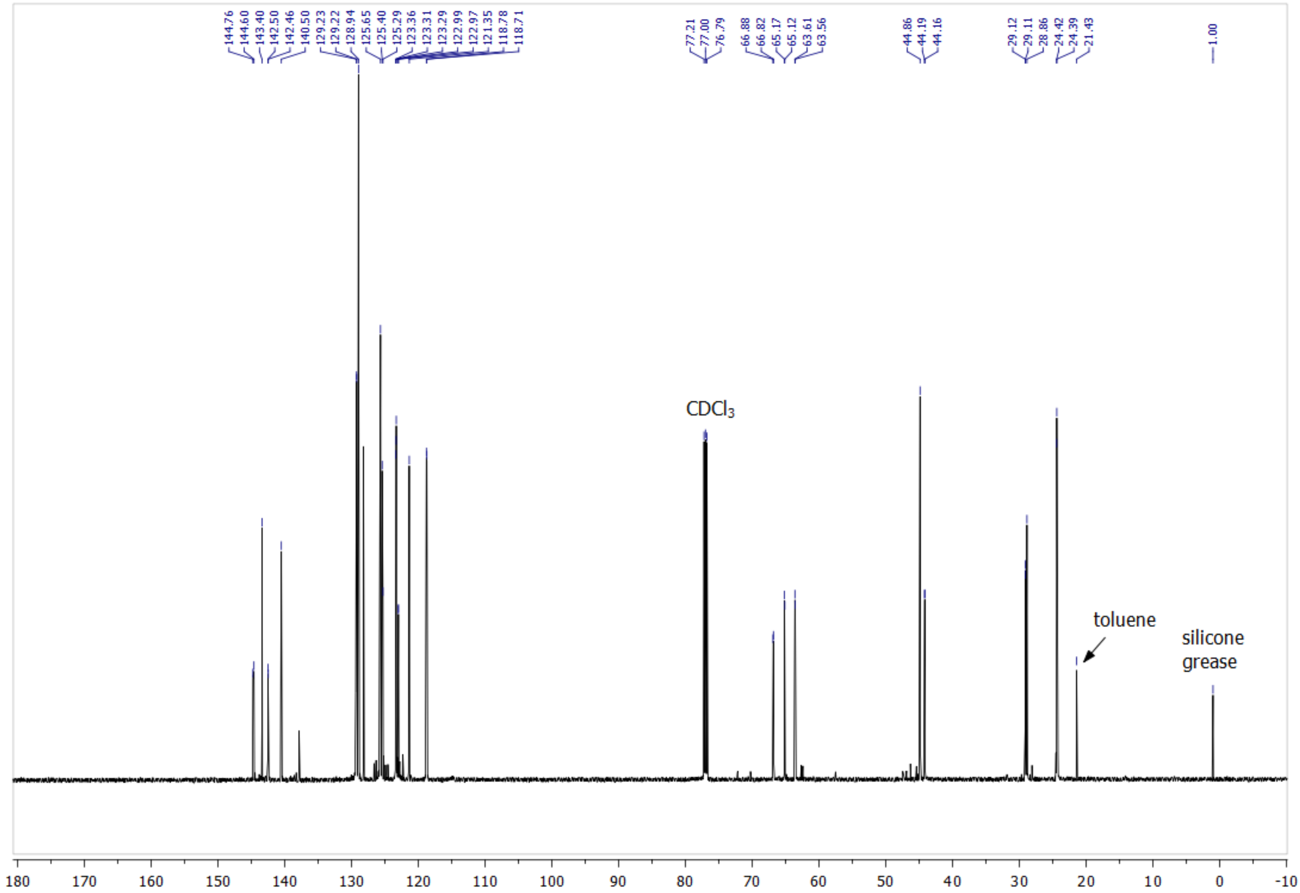
NMR AND MASS SPECTRA

L2b, $^{31}P\{^1H\}$ (242.9 MHz, $CDCl_3$, 30 °C).

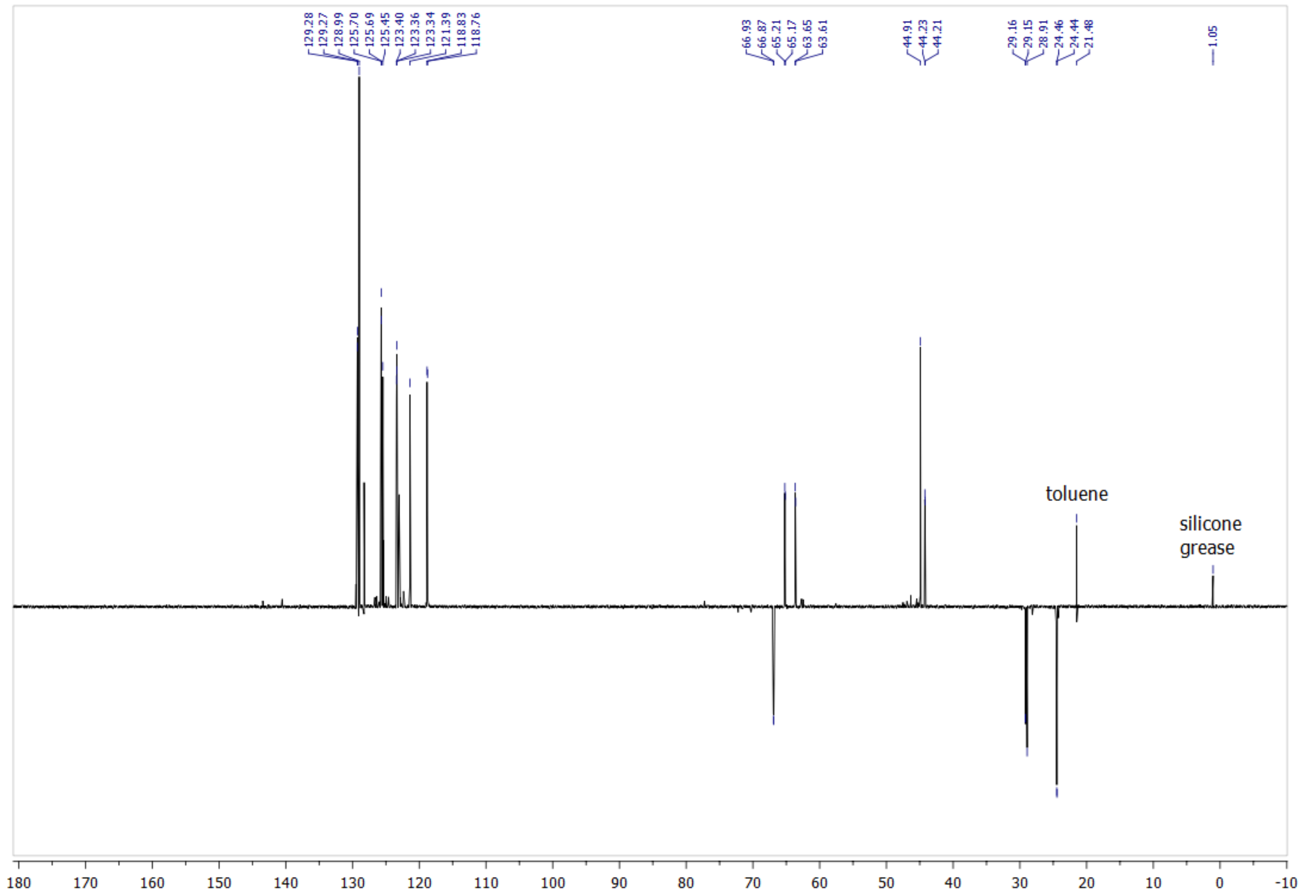


L2b, ^1H (600.1 MHz, $CDCl_3$, 30 °C).

NMR AND MASS SPECTRA

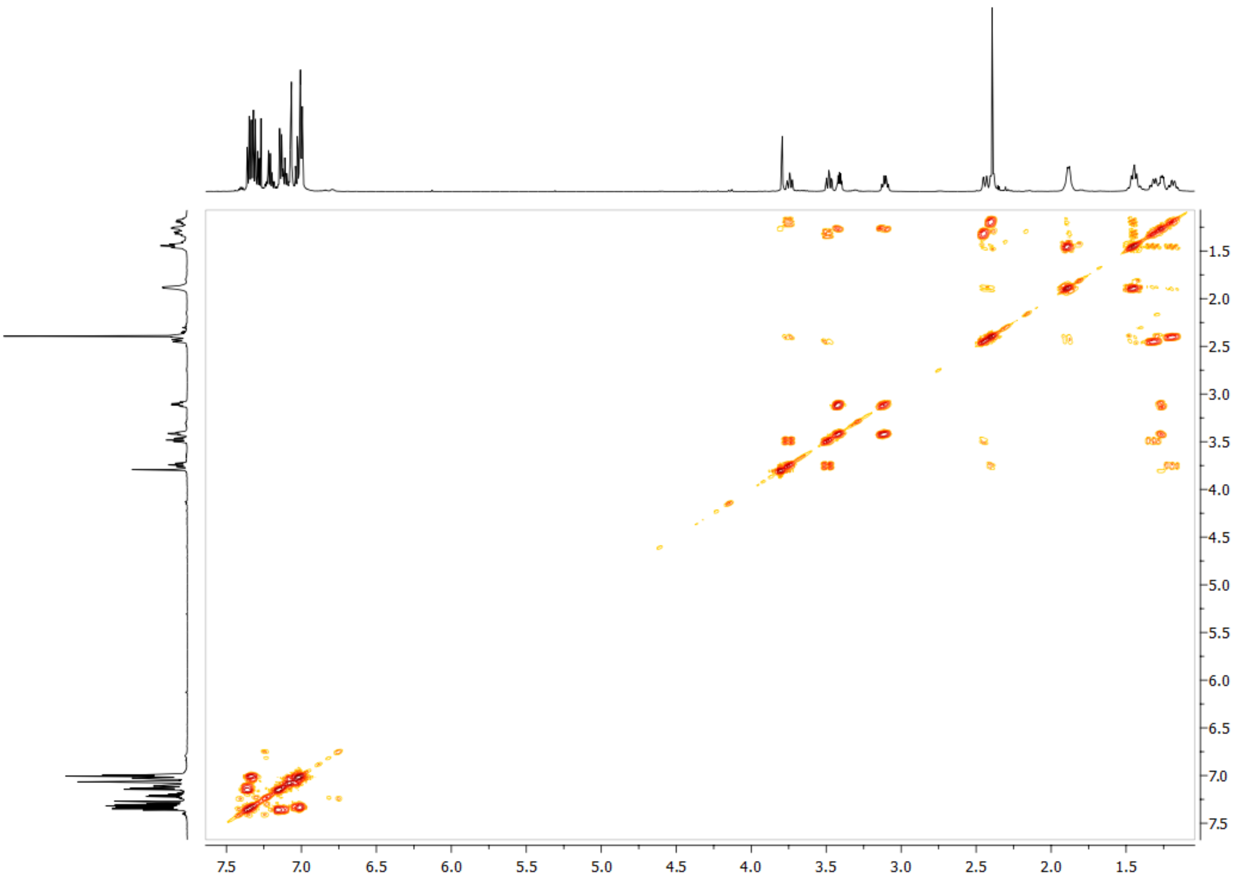


L2b, $^{13}C\{^{1}H\}$ (150.9 MHz, $CDCl_3$, 30 °C).

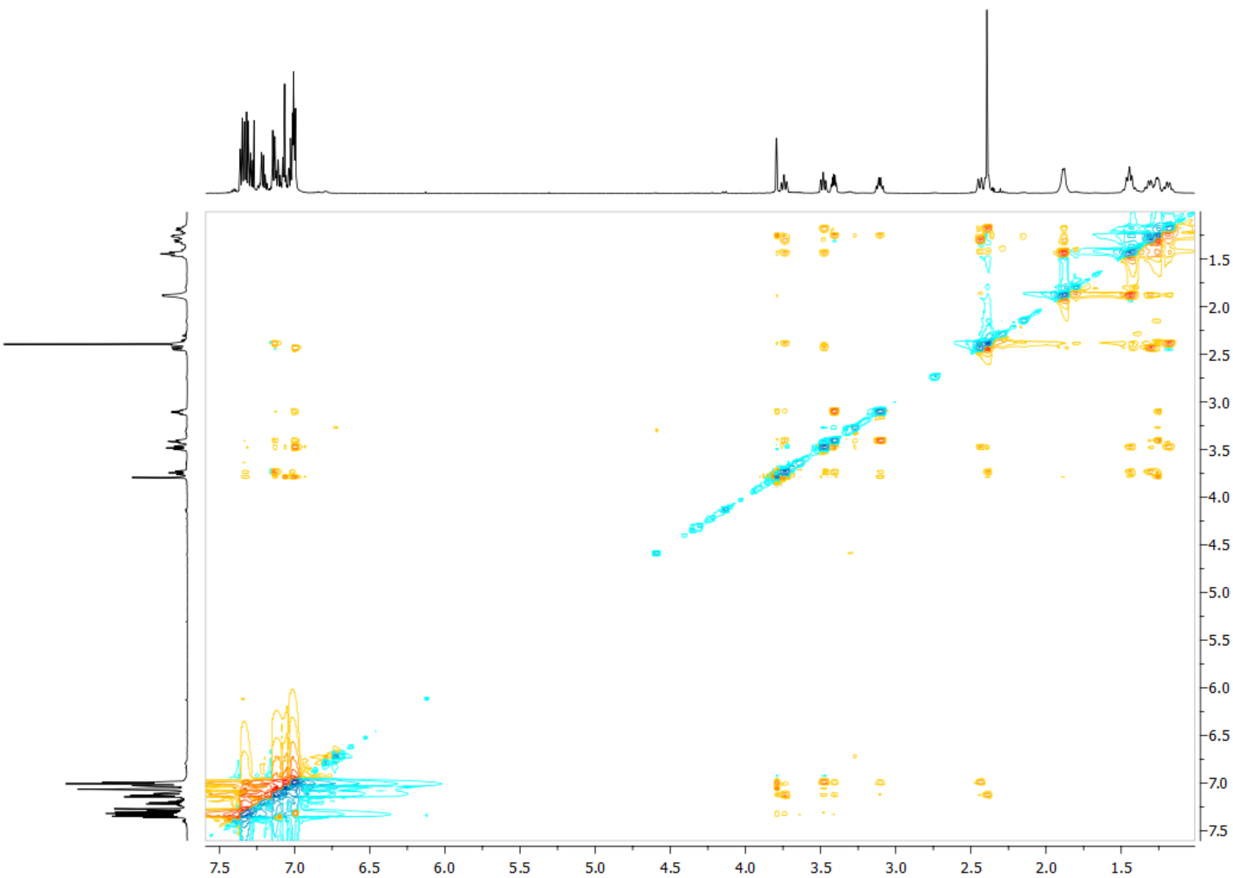


L2b, $^{13}C\{^{1}H\}$ DEPT (150.9 MHz, $CDCl_3$, 30 °C).

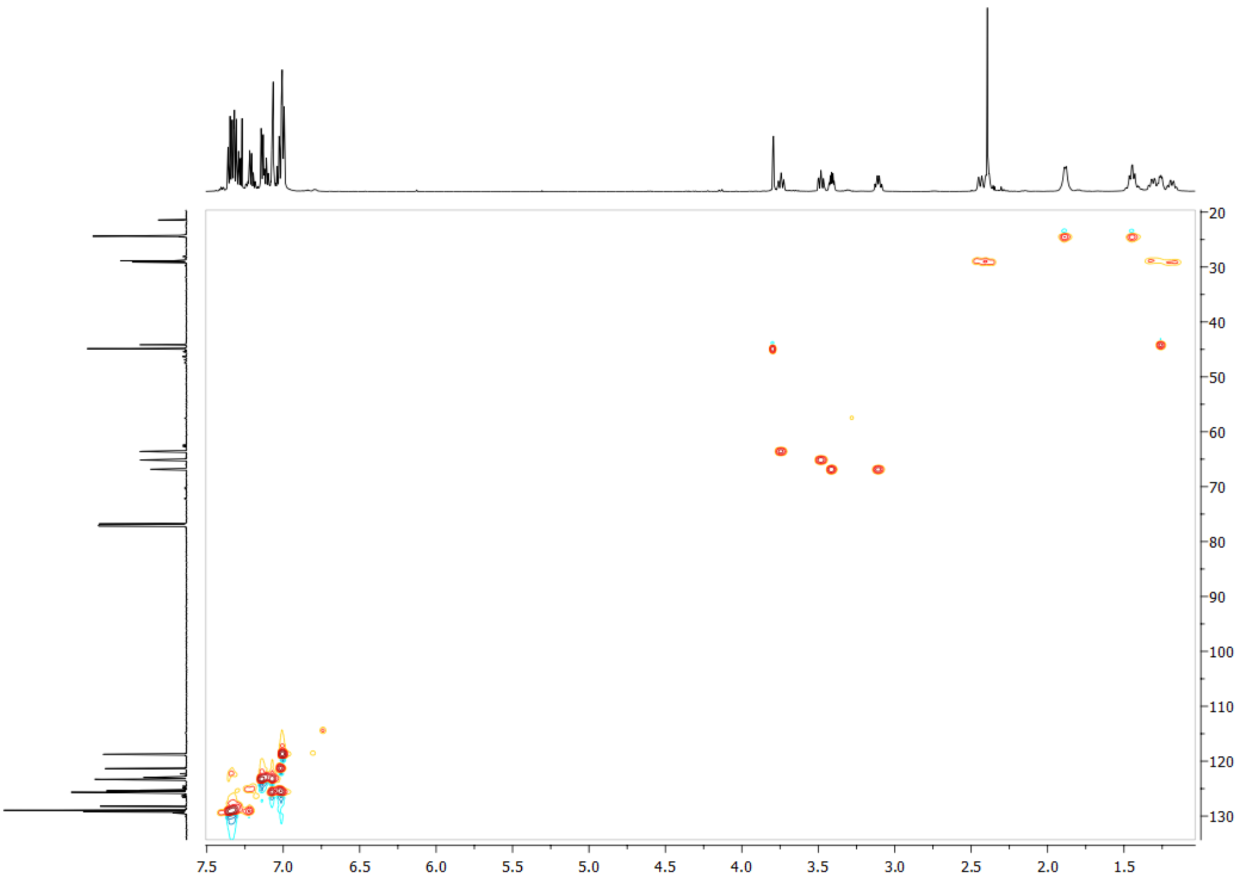
NMR AND MASS SPECTRA



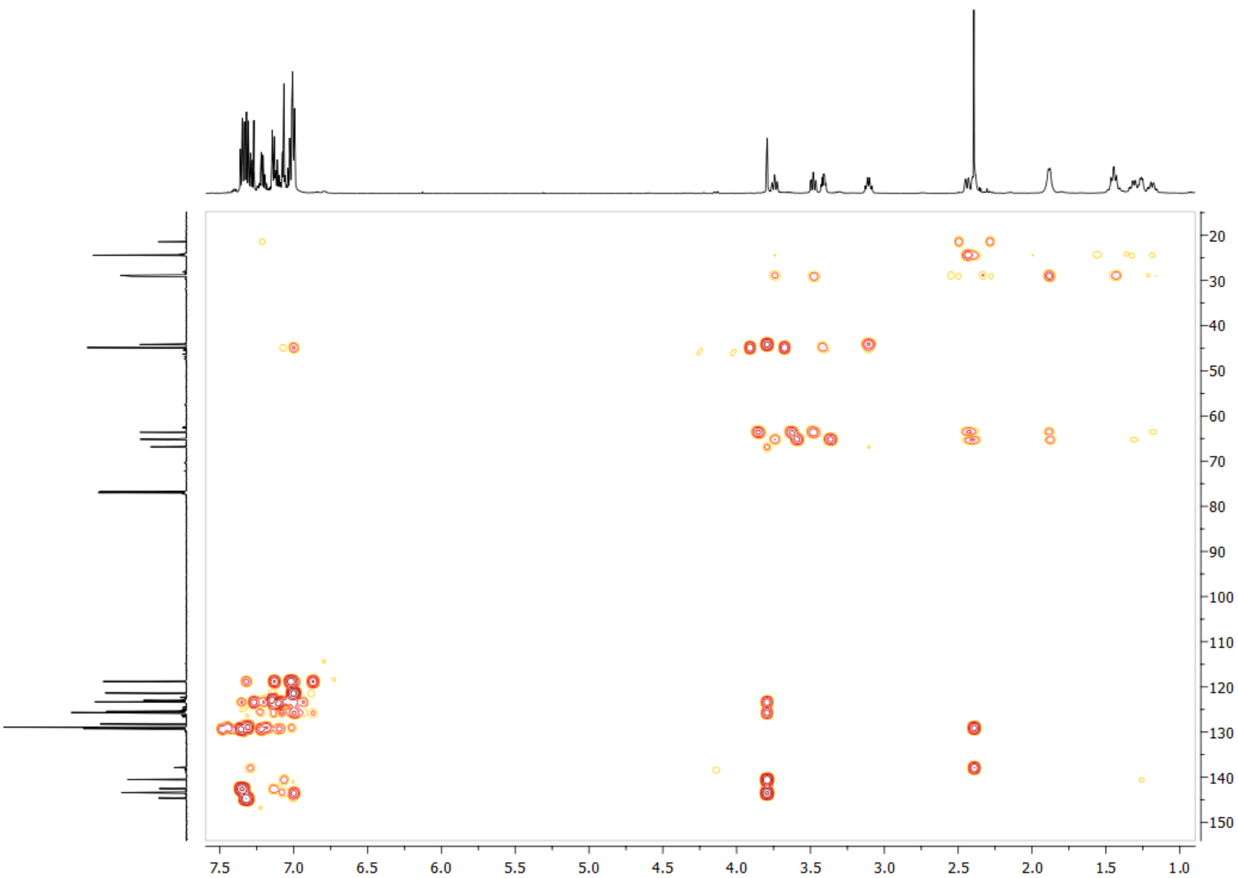
L2b, ^{1}H-^{1}H COSY.



L2b, ^{1}H-^{1}H NOESY.

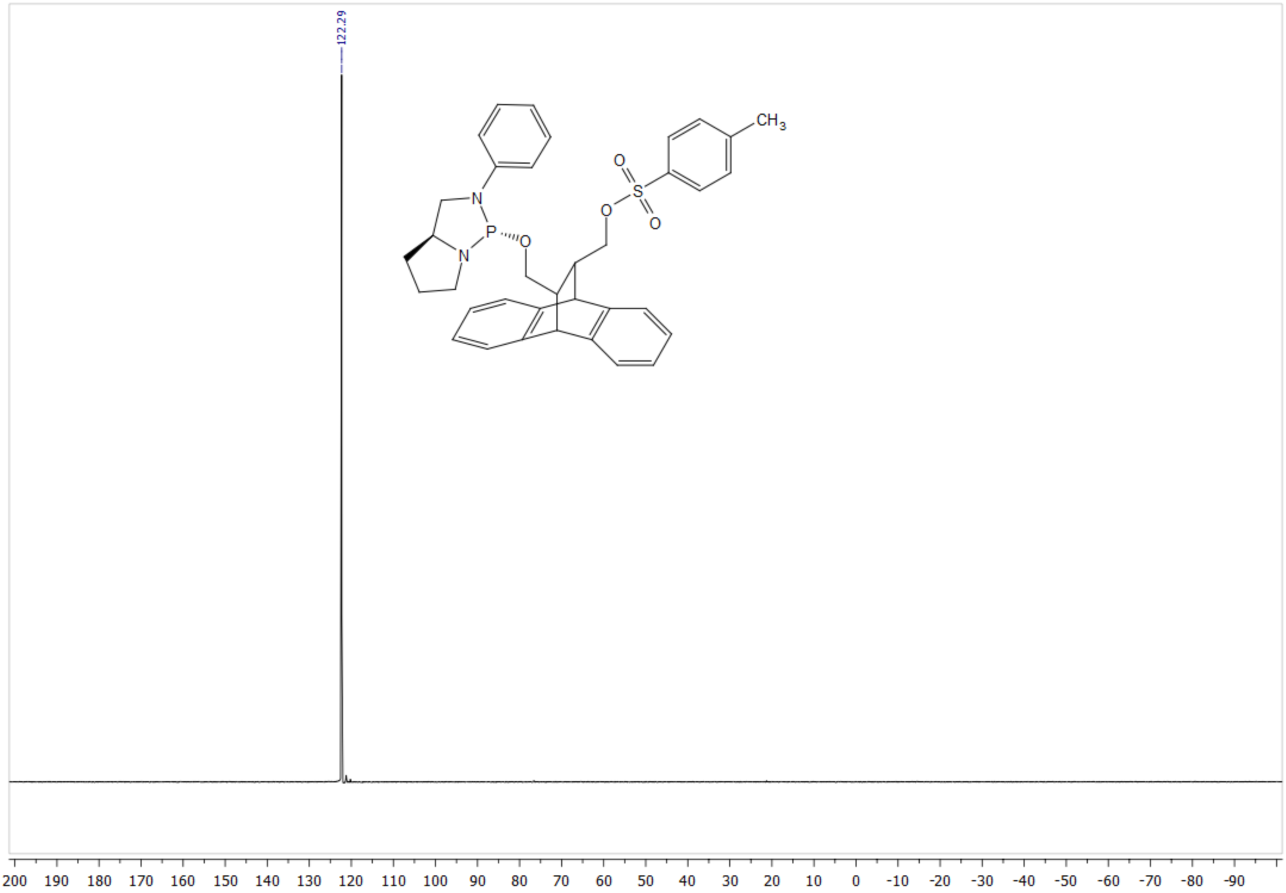


L2b, ^{1}H-^{13}C HSQC.

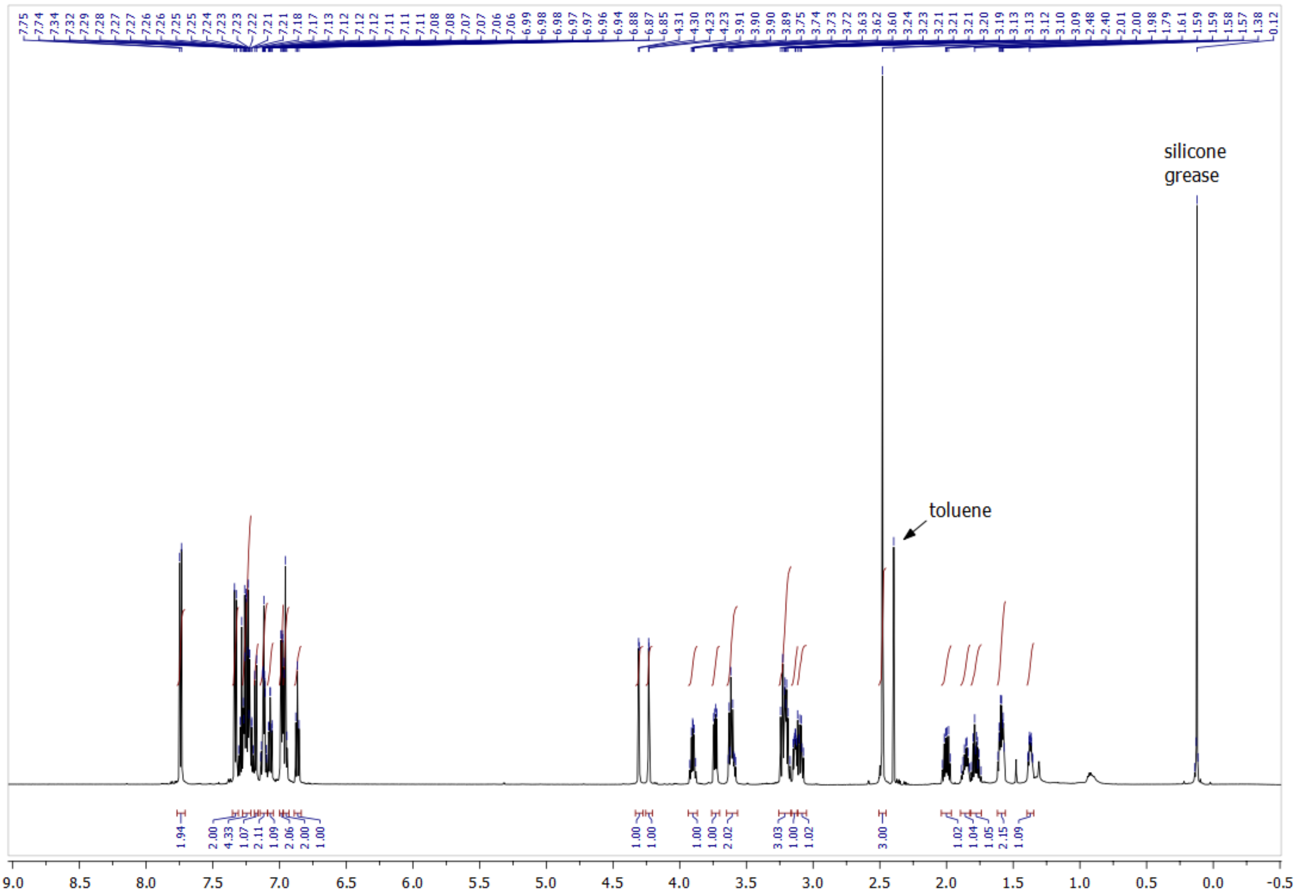


L2b, ^{1}H-^{13}C HMBC.

NMR AND MASS SPECTRA

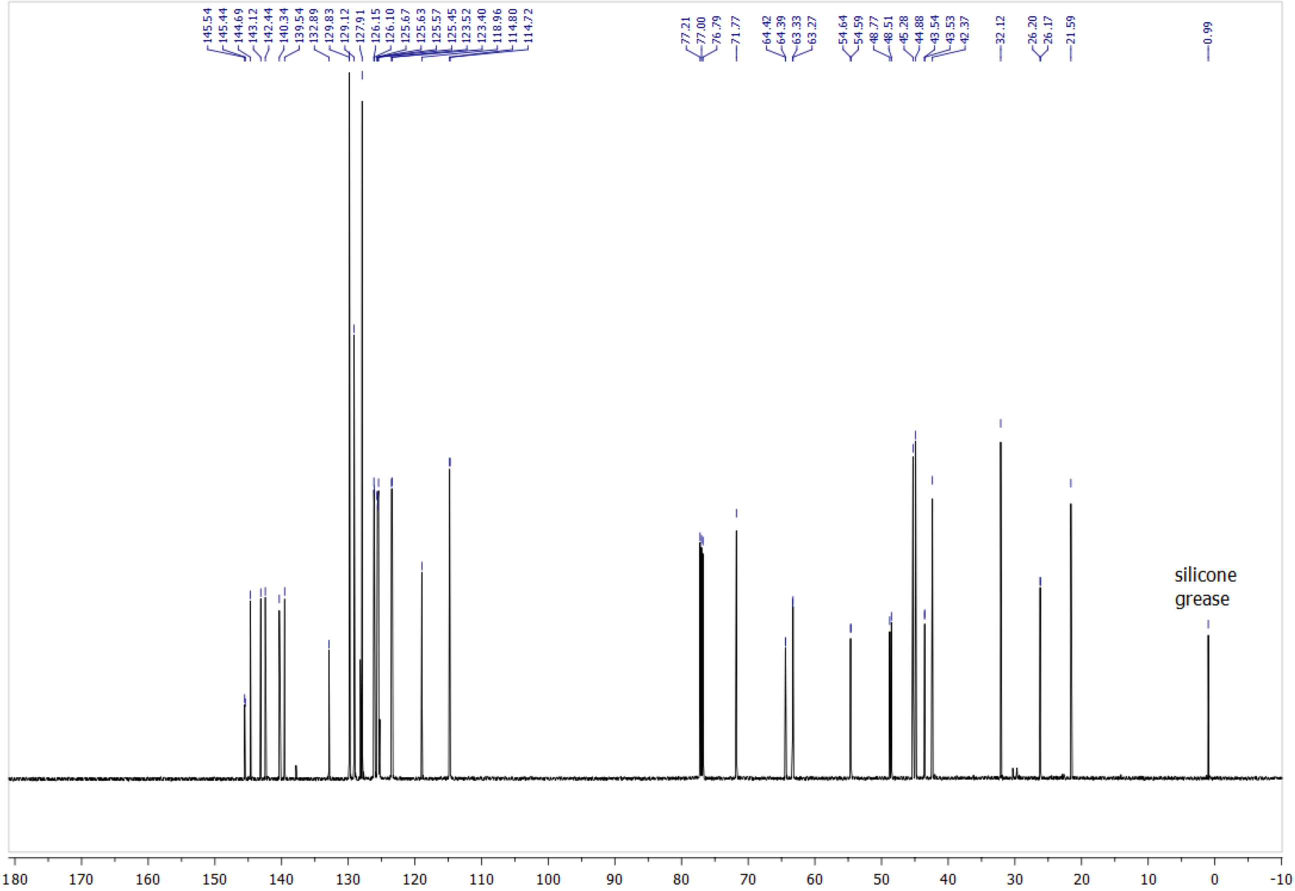


L3a, $^{31}P\{^{1}H\}$ (242.9 MHz, $CDCl_3$, 30 °C).

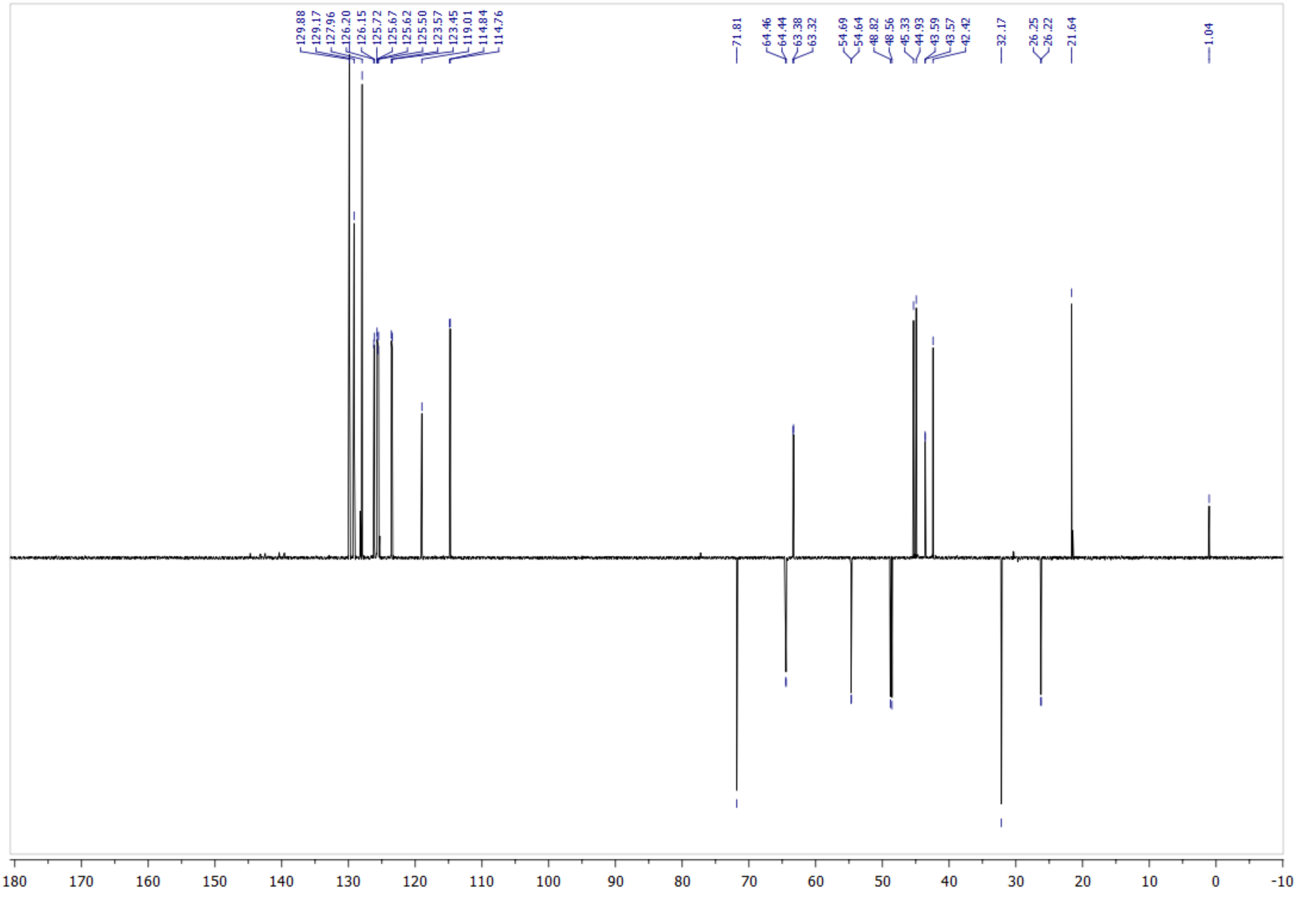


L3a, ^{1}H (600.1 MHz, $CDCl_3$, 30 °C).

NMR AND MASS SPECTRA

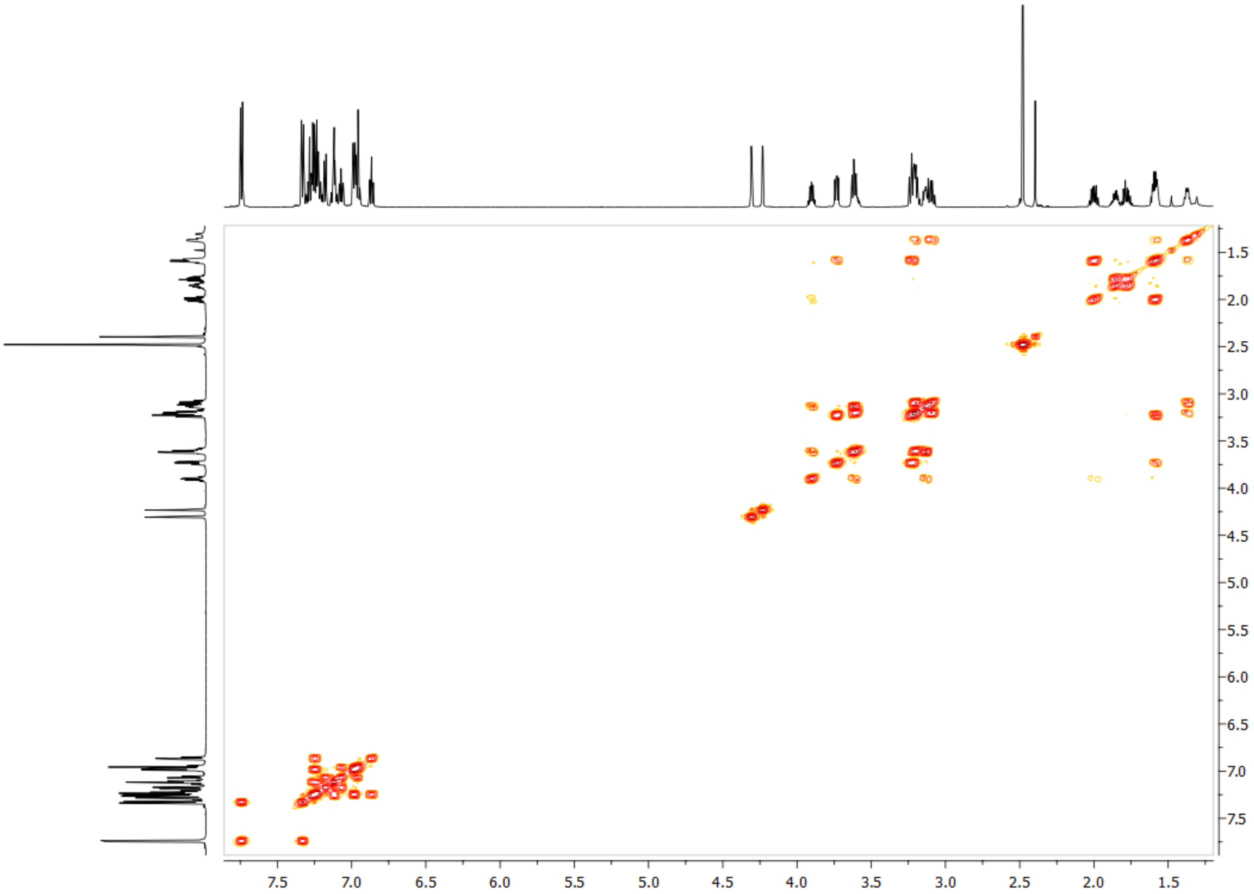


L3a, $^{13}C\{^{1}H\}$ (150.9 MHz, $CDCl_3$, 30 °C).

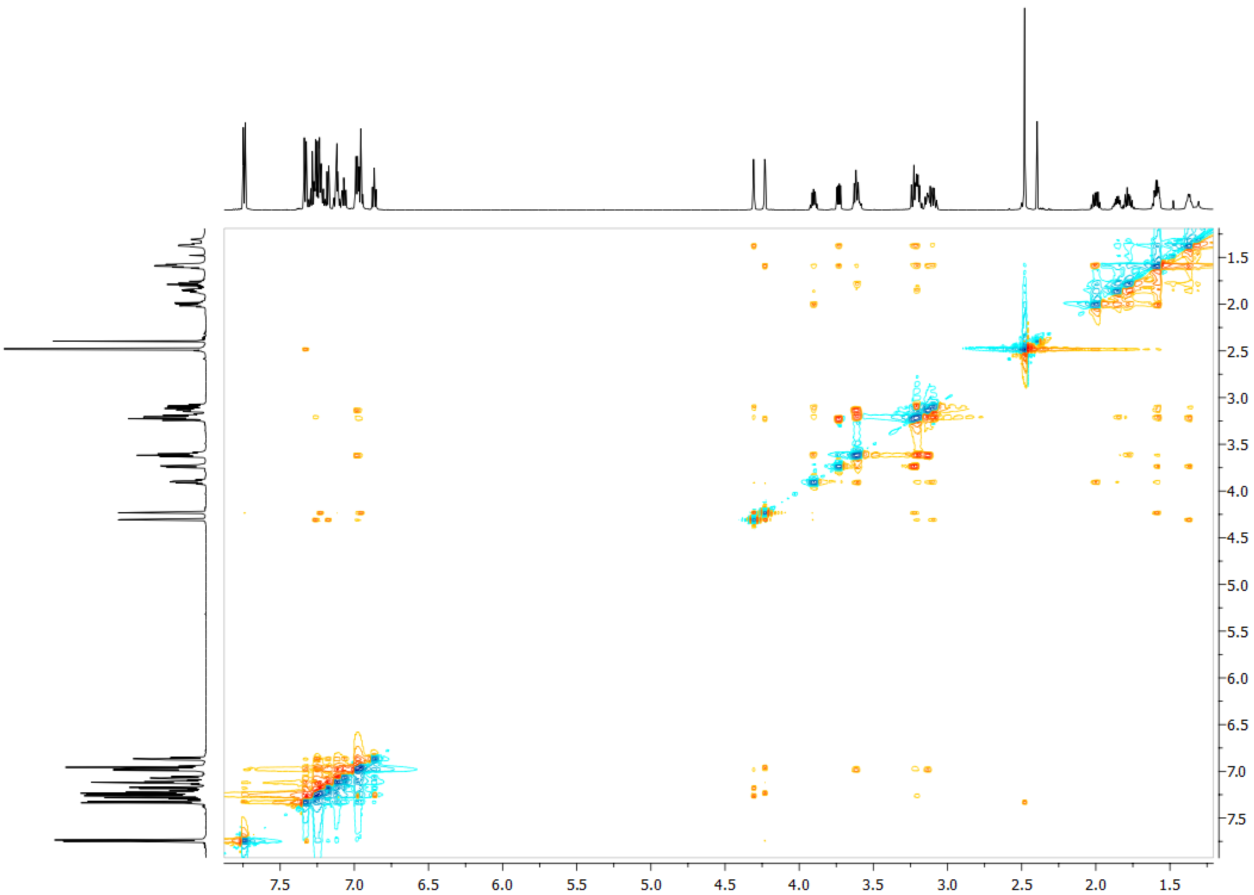


L3a, $^{13}C\{^{1}H\}$ DEPT (150.9 MHz, $CDCl_3$, 30 °C).

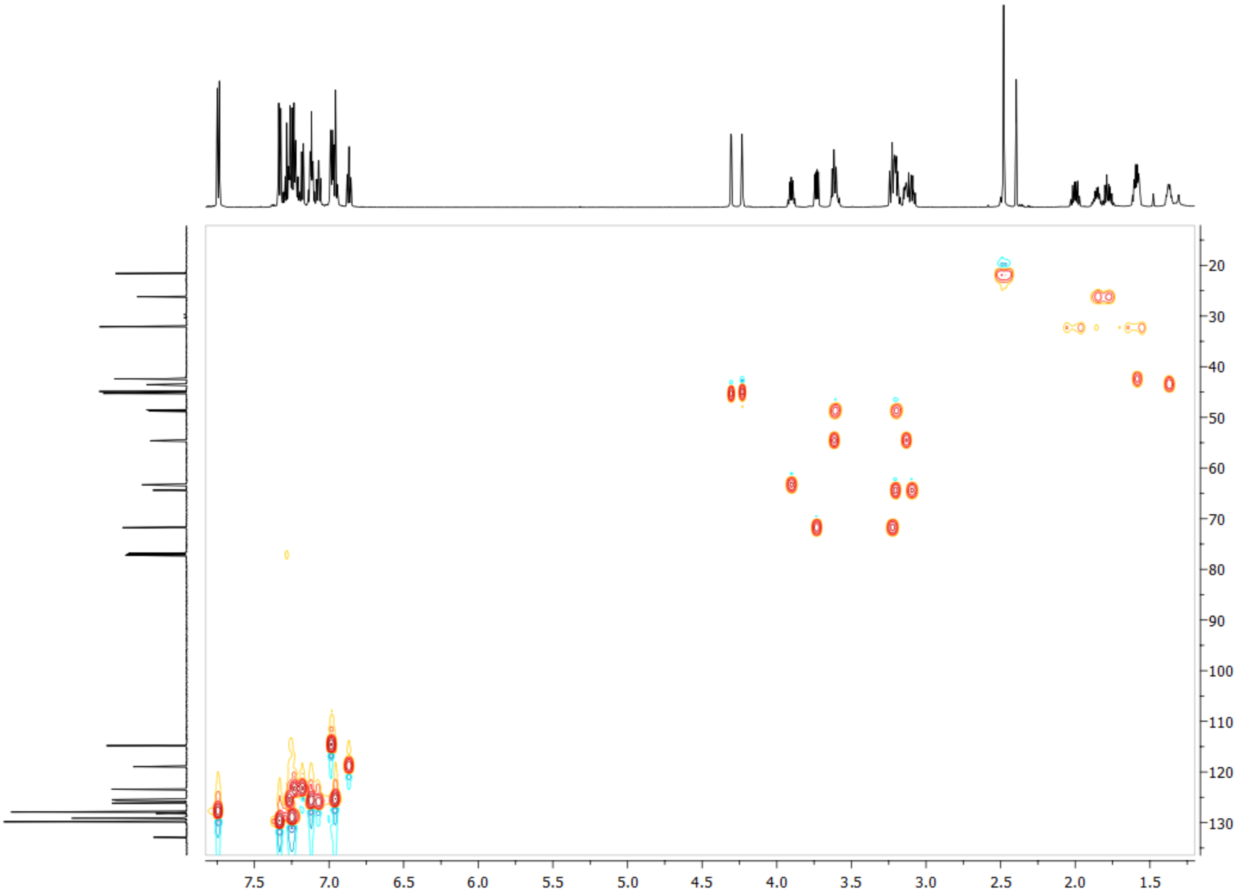
NMR AND MASS SPECTRA



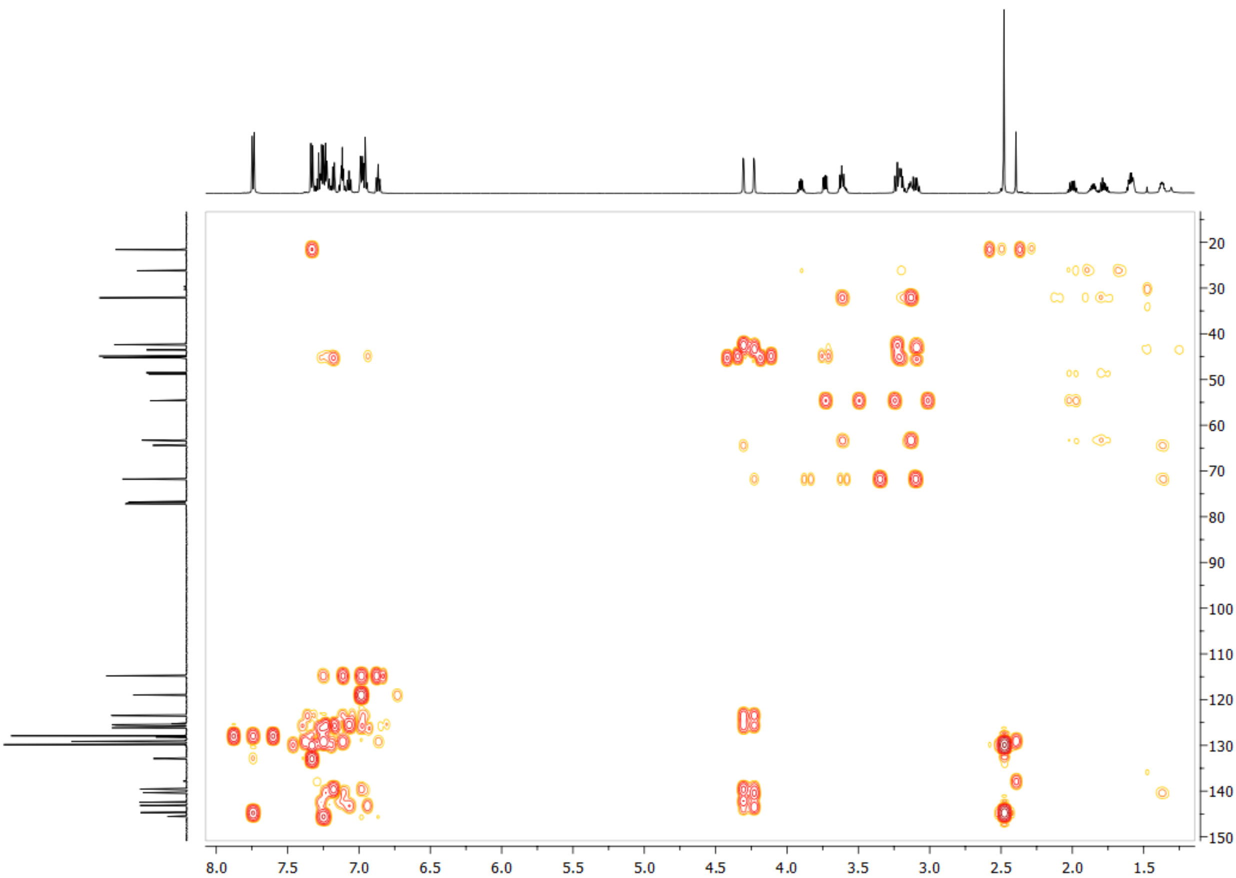
L3a, ¹H-¹H COSY.



L3a, ¹H-¹H NOESY.

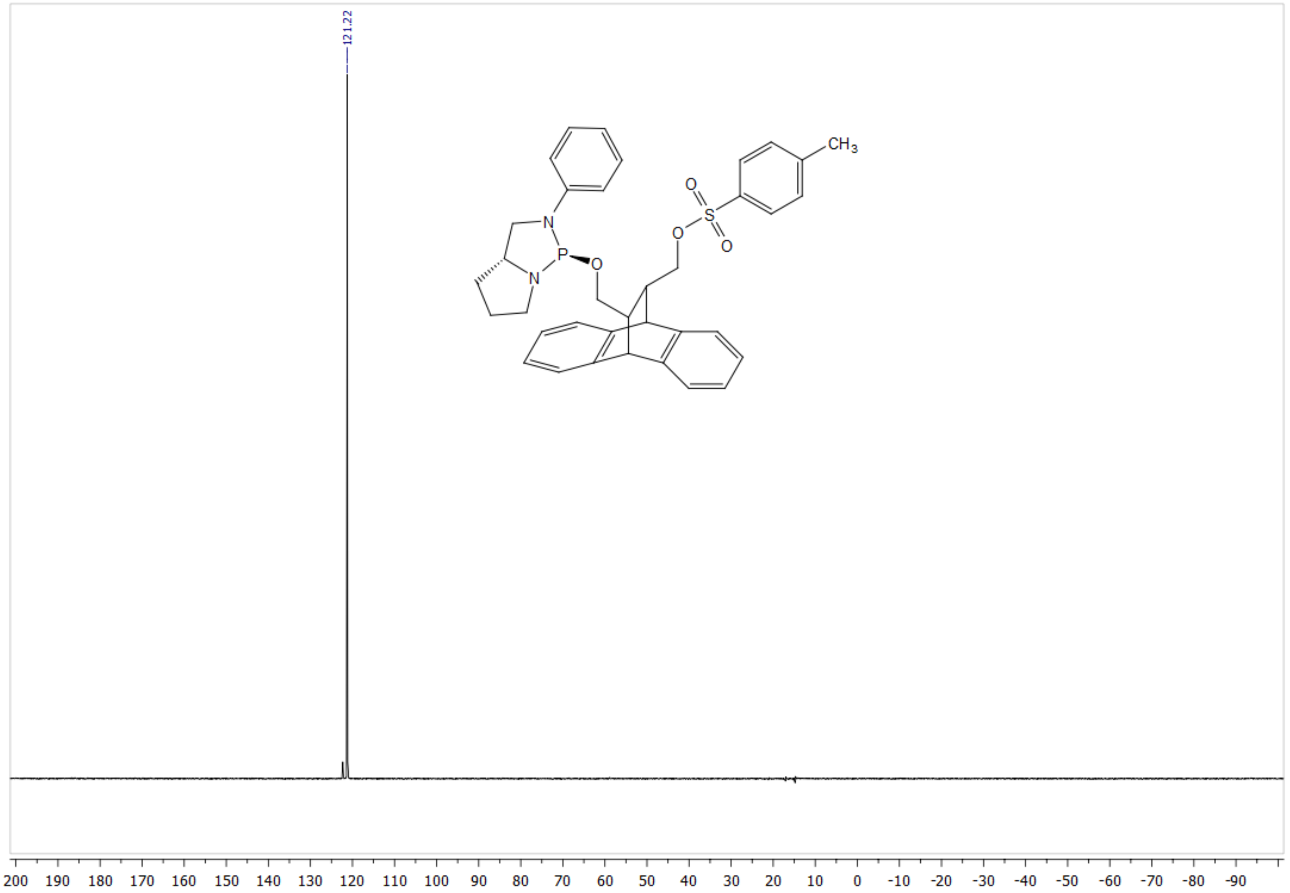


L3a, ^{1}H-^{13}C HSQC.

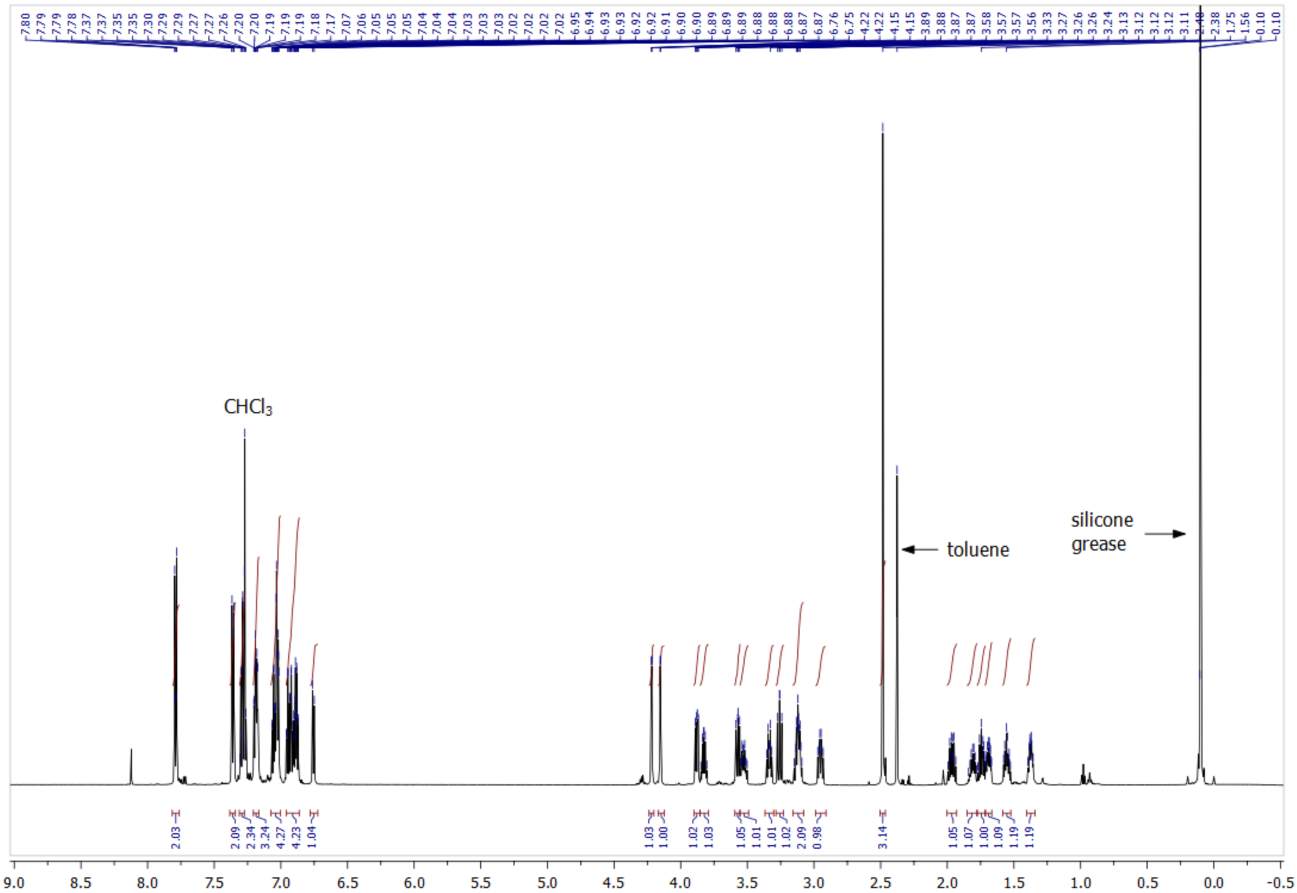


L3a, ^{1}H-^{13}C HMBC.

NMR AND MASS SPECTRA

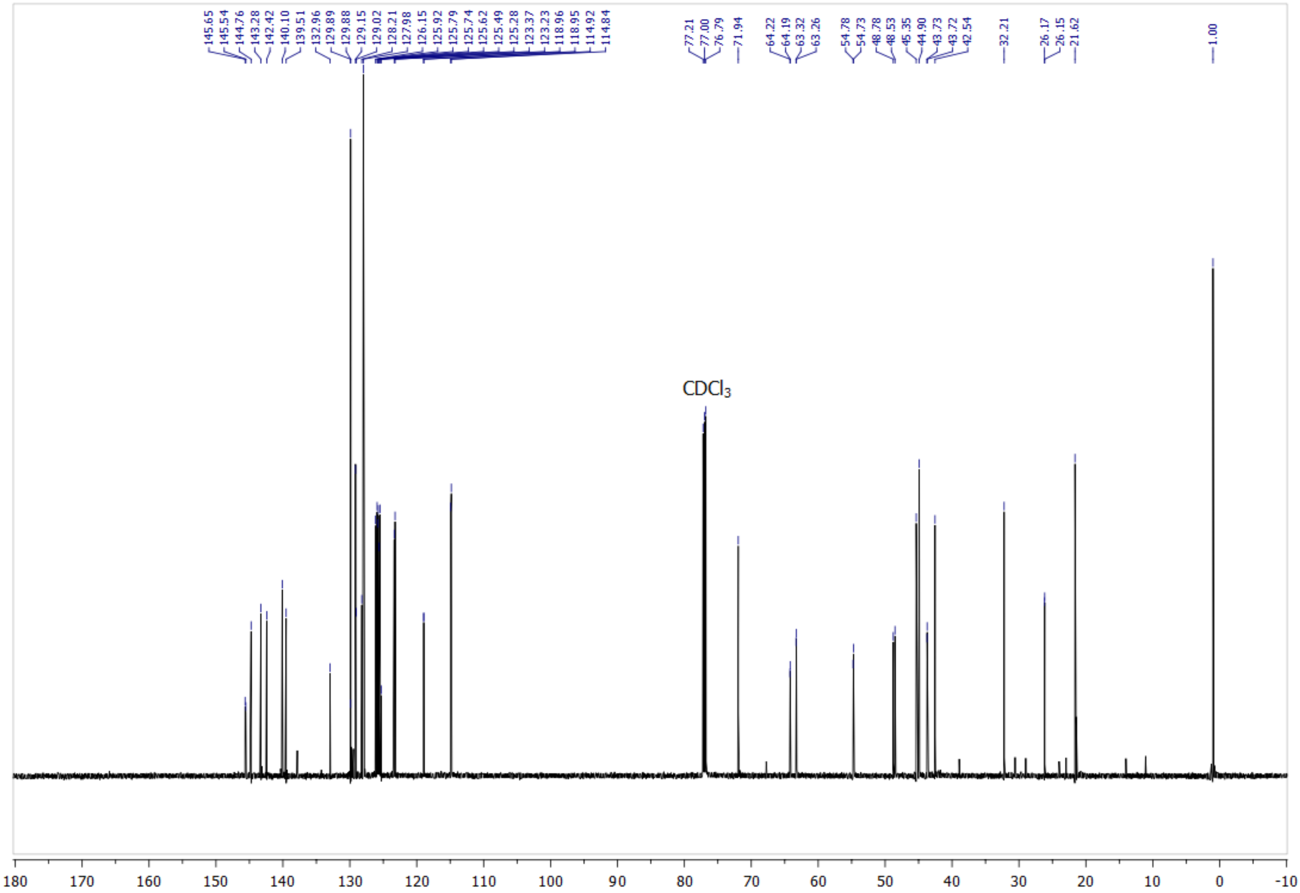


L3b, $^{31}P\{^{1}H\}$ (242.9 MHz, $CDCl_3$, 30 °C).

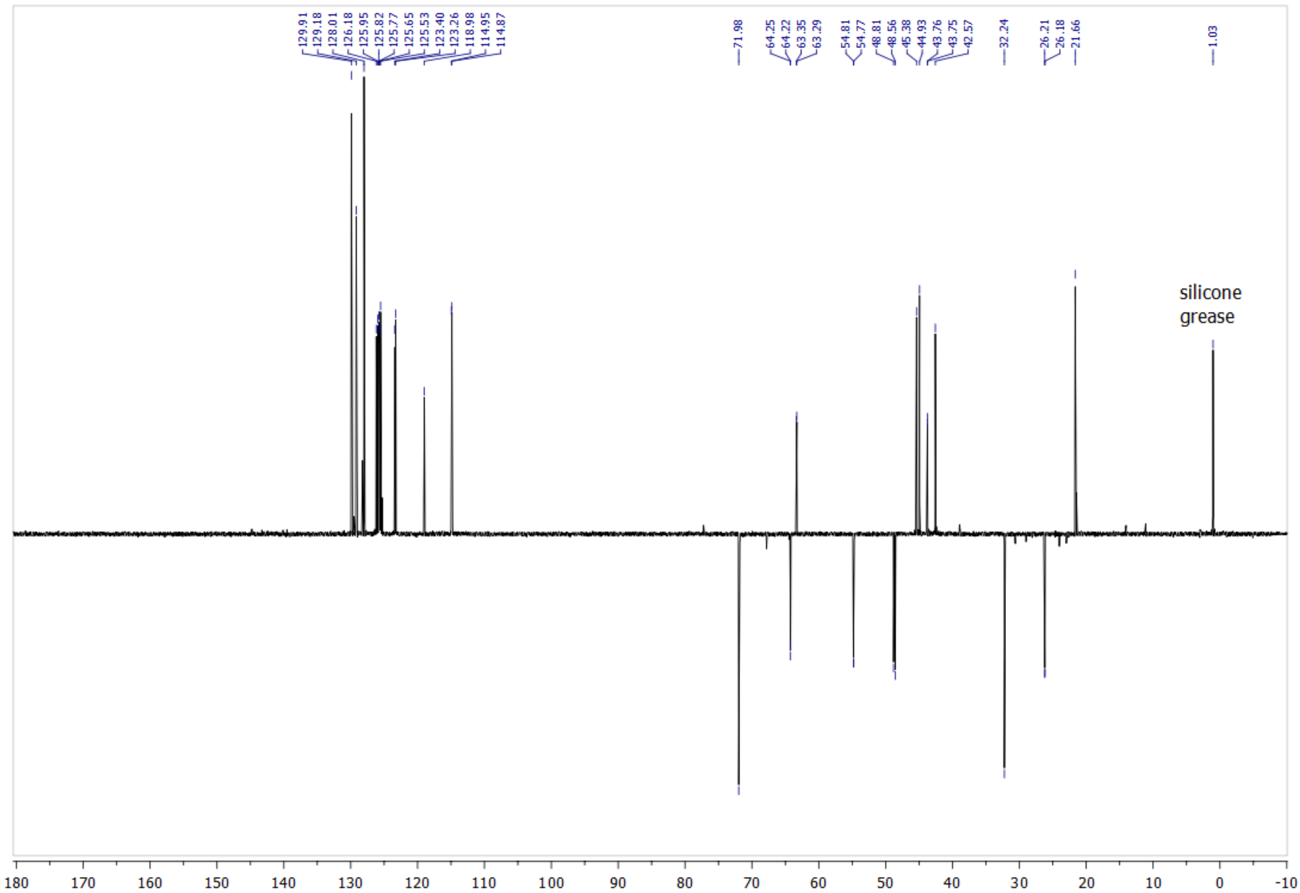


L3b, ^{1}H (600.1 MHz, $CDCl_3$, 30 °C).

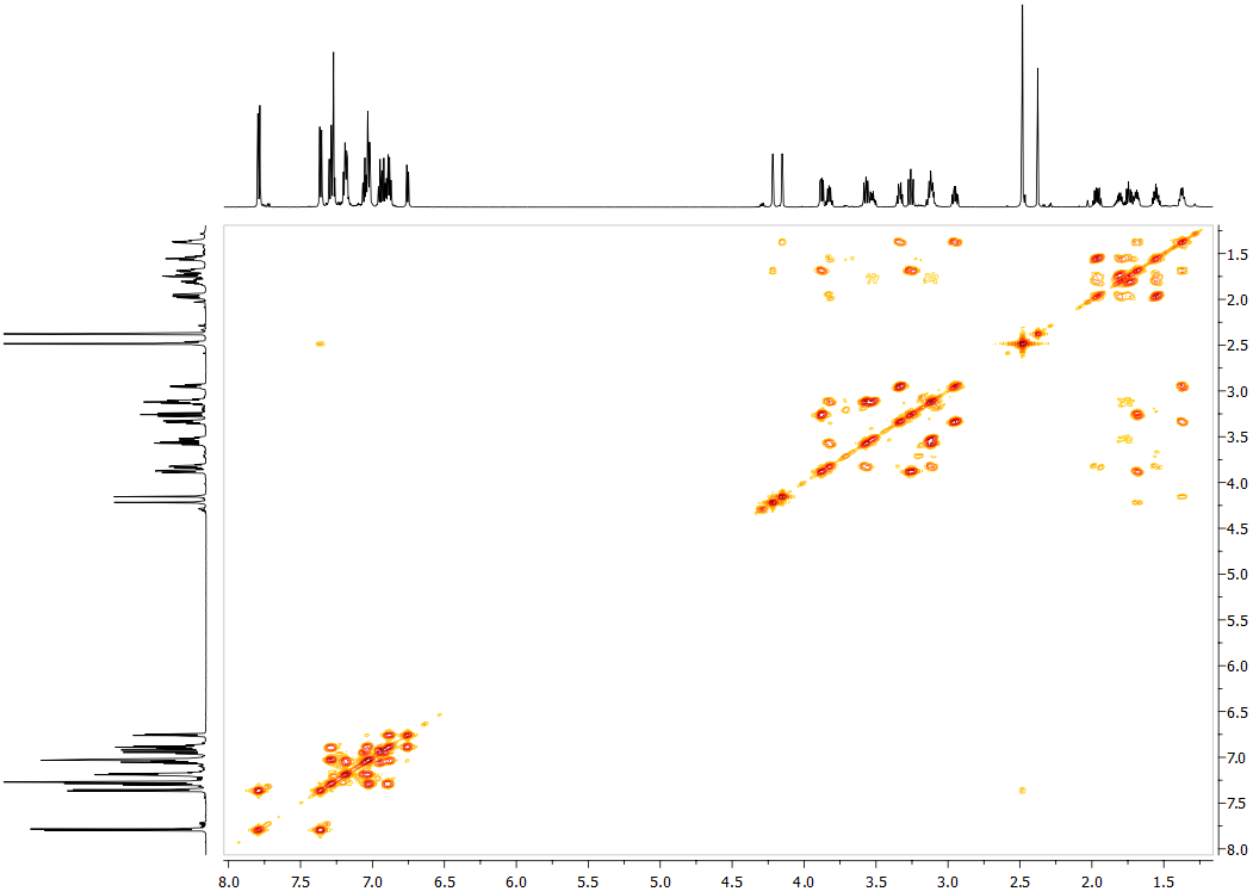
NMR AND MASS SPECTRA



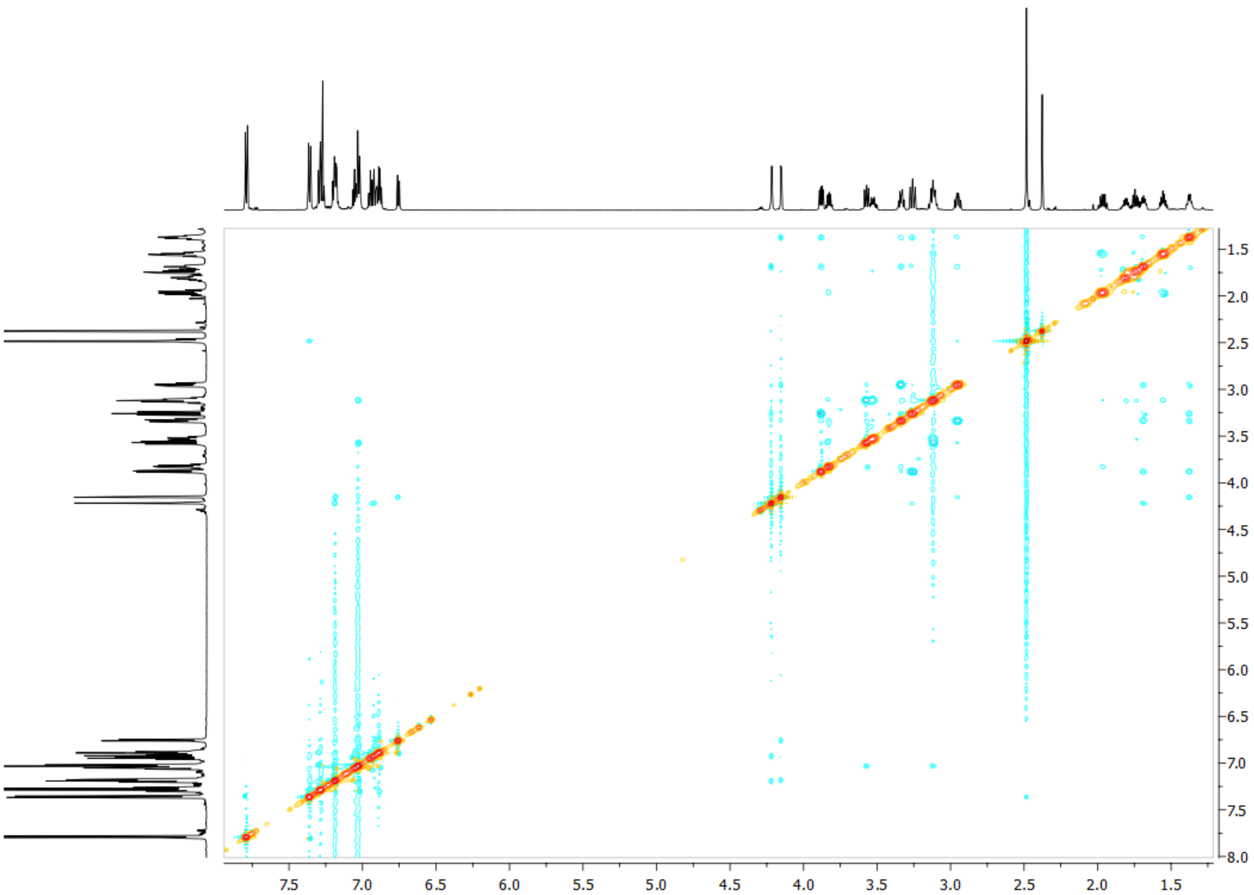
L3b, $^{13}C\{^{1}H\}$ (150.9 MHz, $CDCl_3$, 30 °C).



L3b, $^{13}C\{^{1}H\}$ DEPT (150.9 MHz, $CDCl_3$, 30 °C).

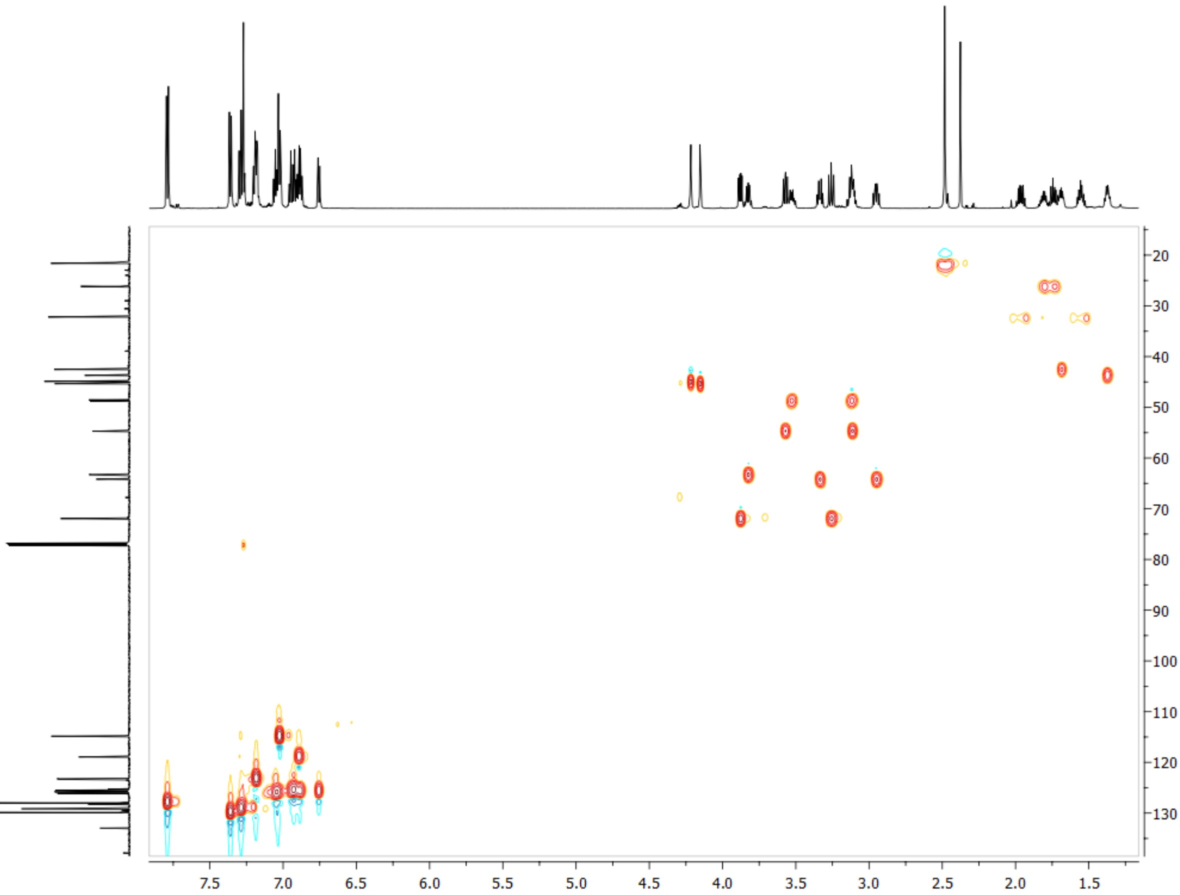


L3b, ^{1}H-^{1}H COSY.

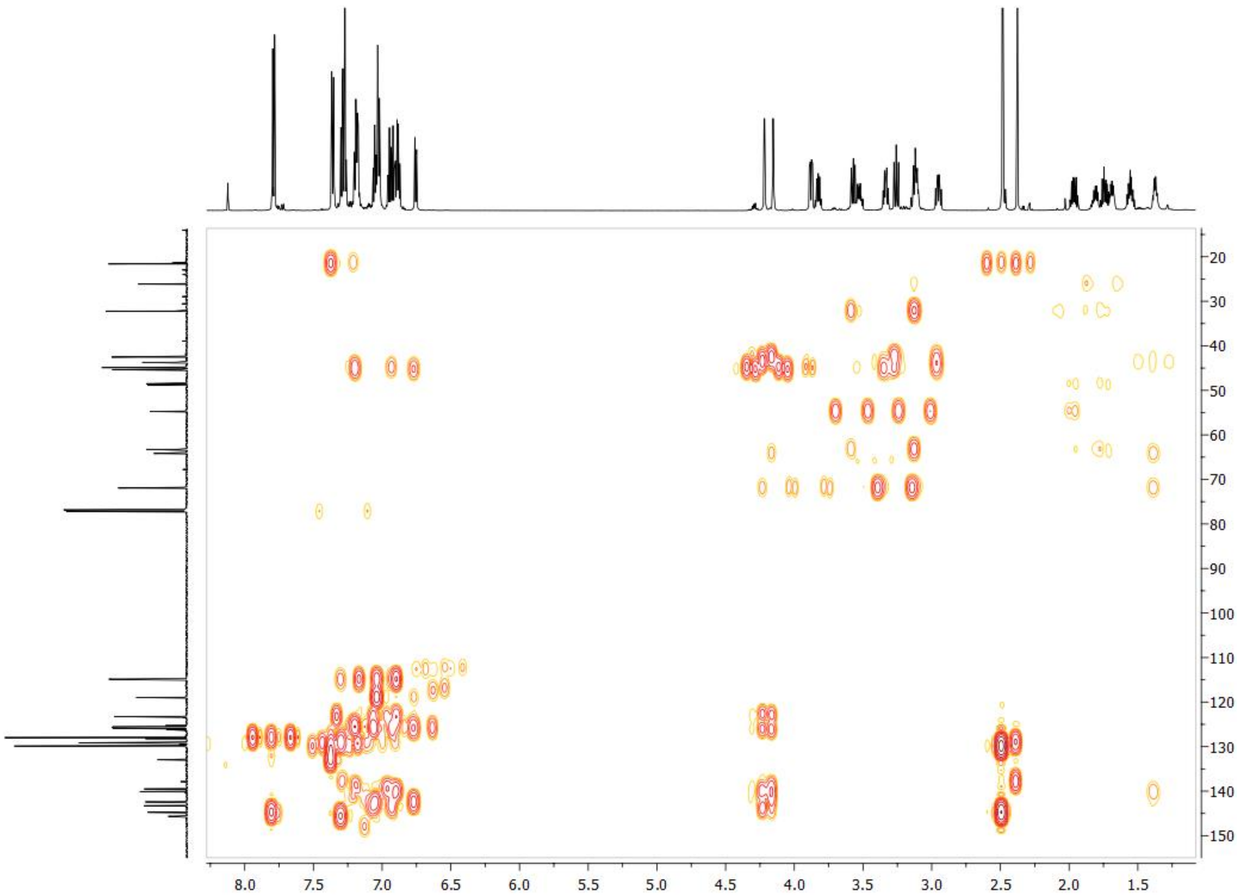


L3b, ^{1}H-^{1}H NOESY.

NMR AND MASS SPECTRA

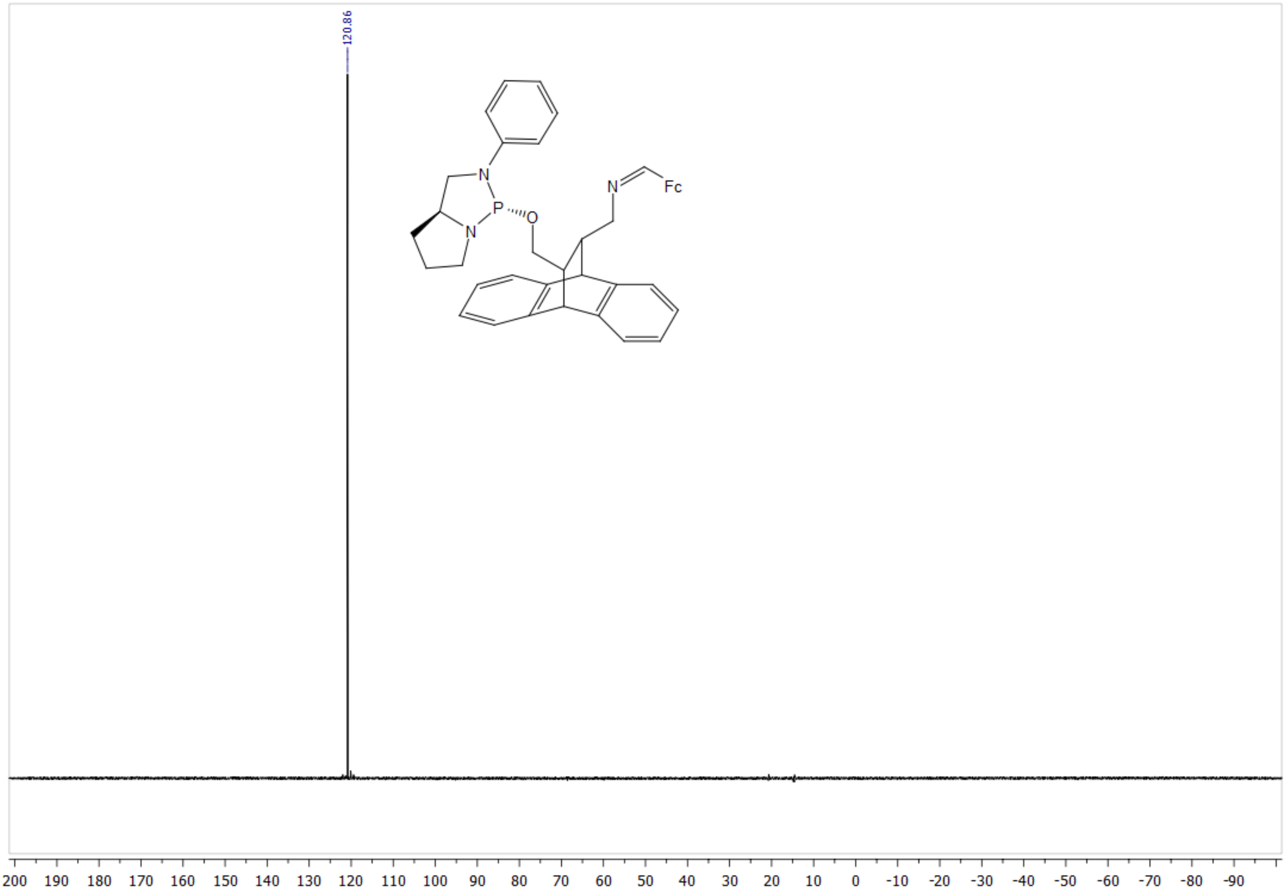


L3b, ^{1}H-^{13}C HSQC.

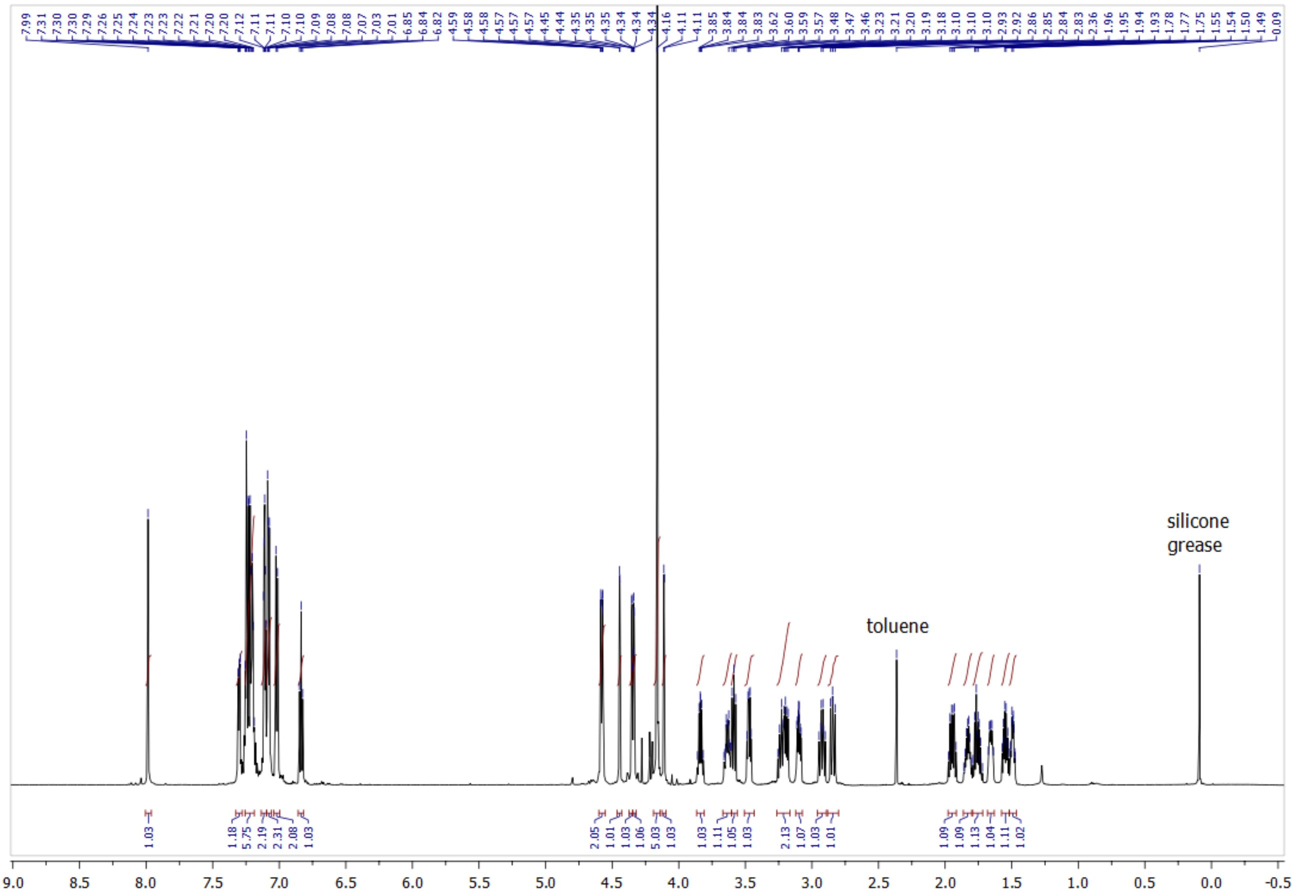


L3b, ^{1}H-^{13}C HMBC.

NMR AND MASS SPECTRA

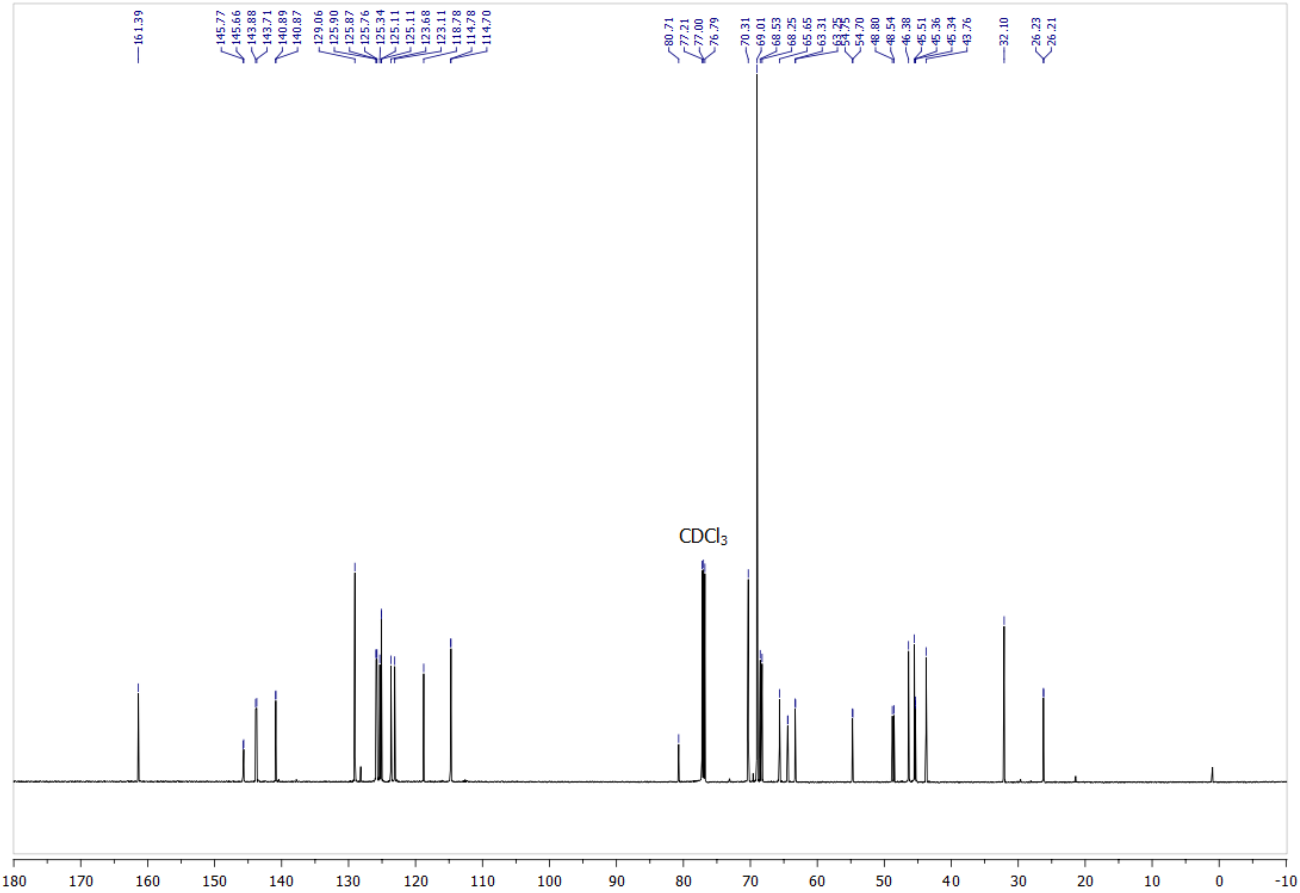


L4, $^{31}P\{^1H\}$ (242.9 MHz, $CDCl_3$, 30 °C).

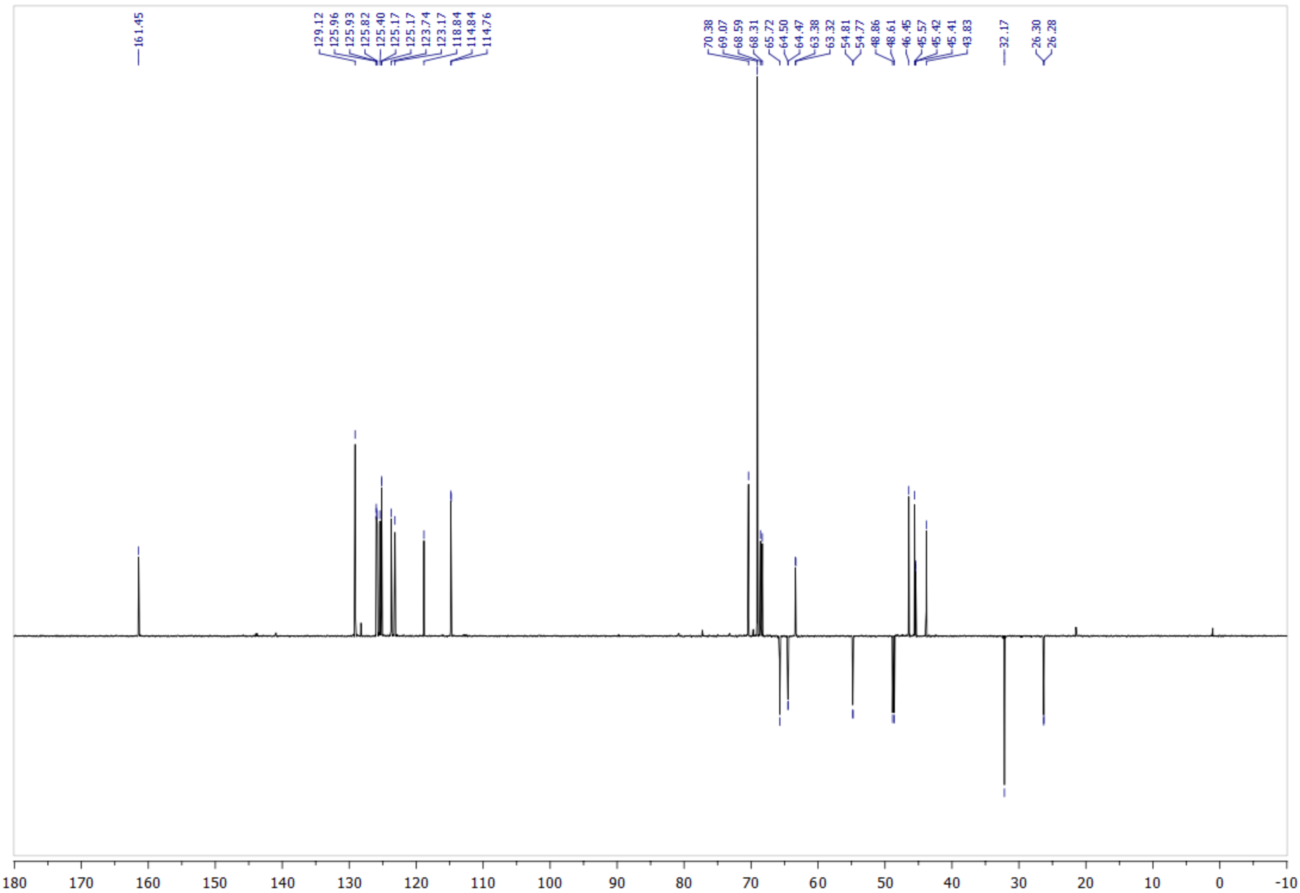


L4, ^{1}H (600.1 MHz, $CDCl_3$, 30 °C).

NMR AND MASS SPECTRA

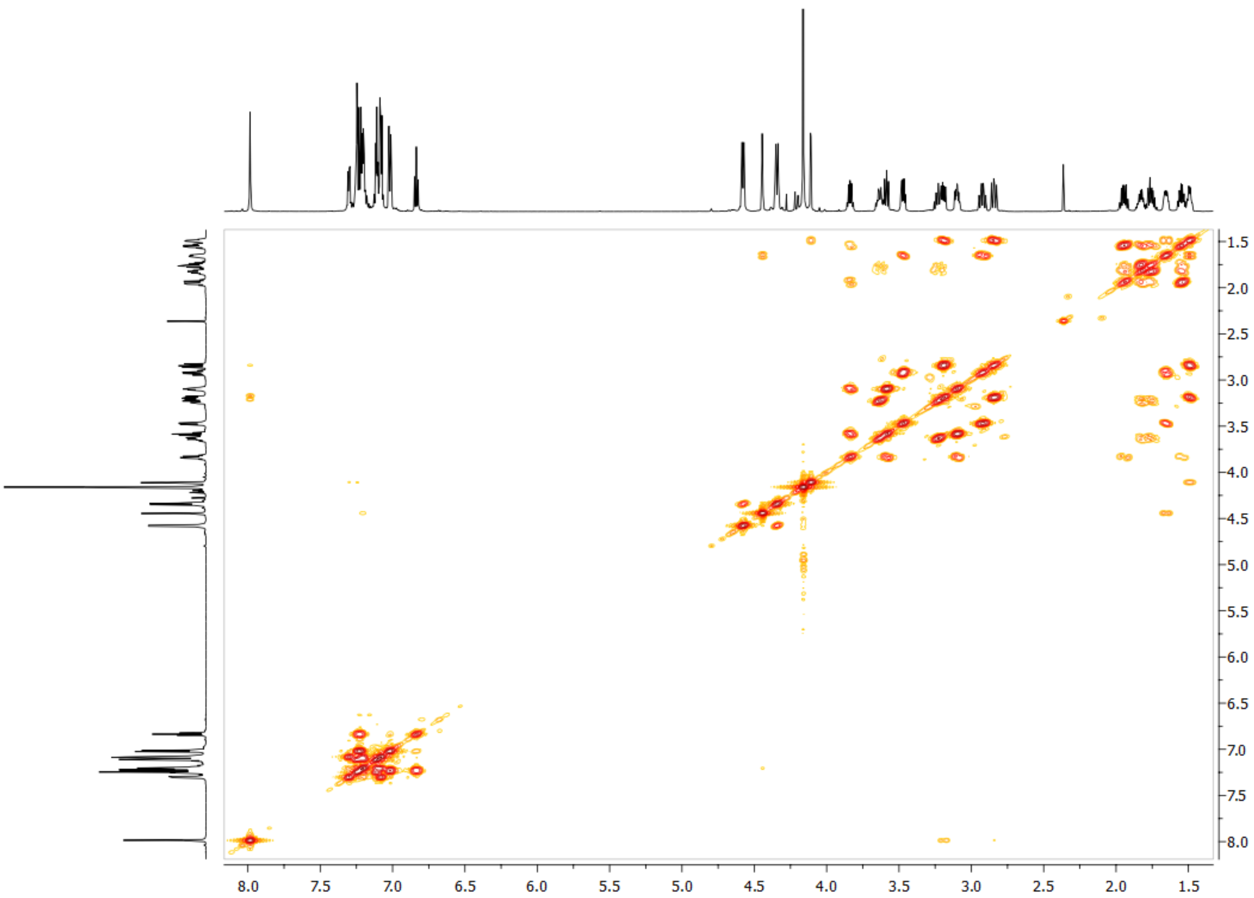


L4, $^{13}C\{^{1}H\}$ (150.9 MHz, $CDCl_3$, 30 ^{o}C).

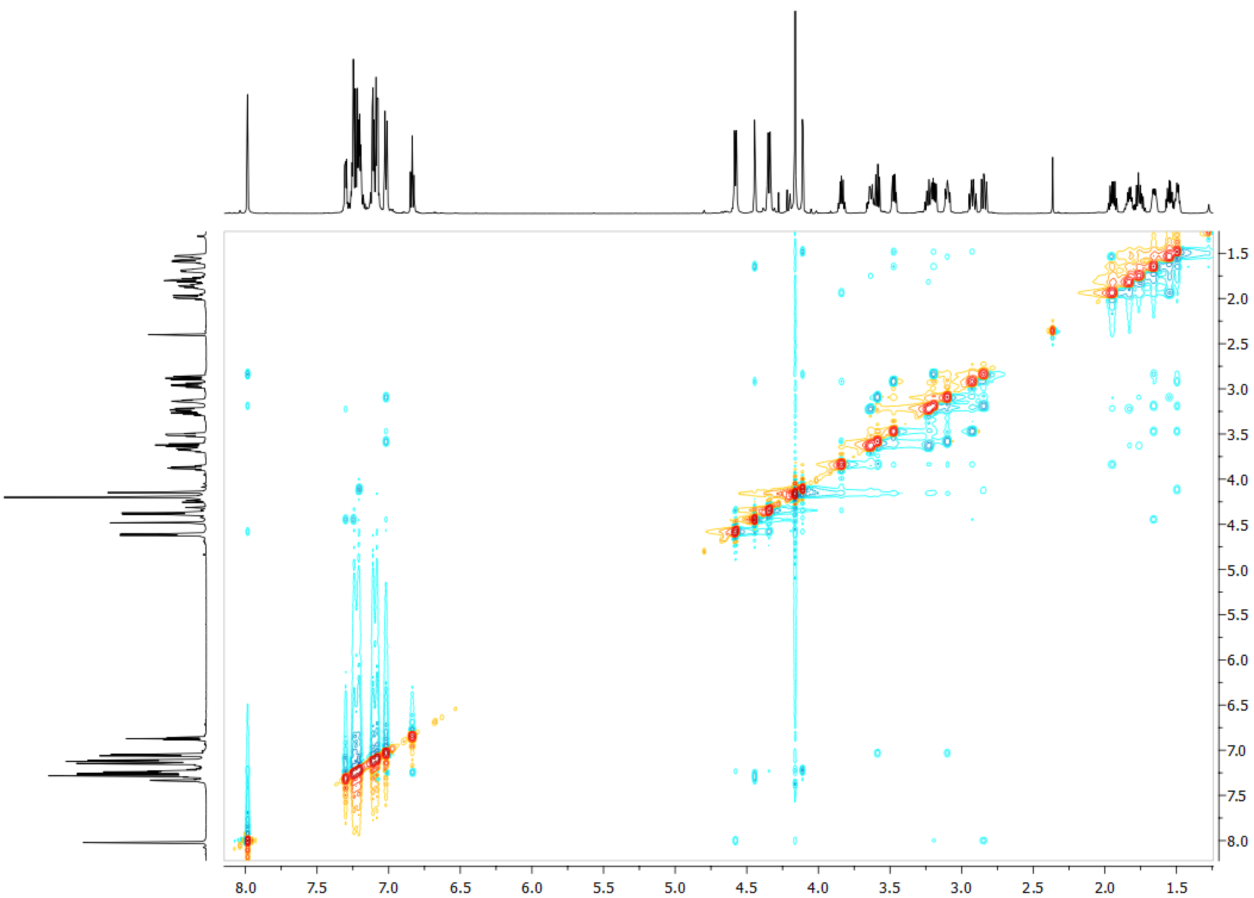


L4, $^{13}C\{^{1}H\}$ DEPT (150.9 MHz, $CDCl_3$, 30 ^{o}C).

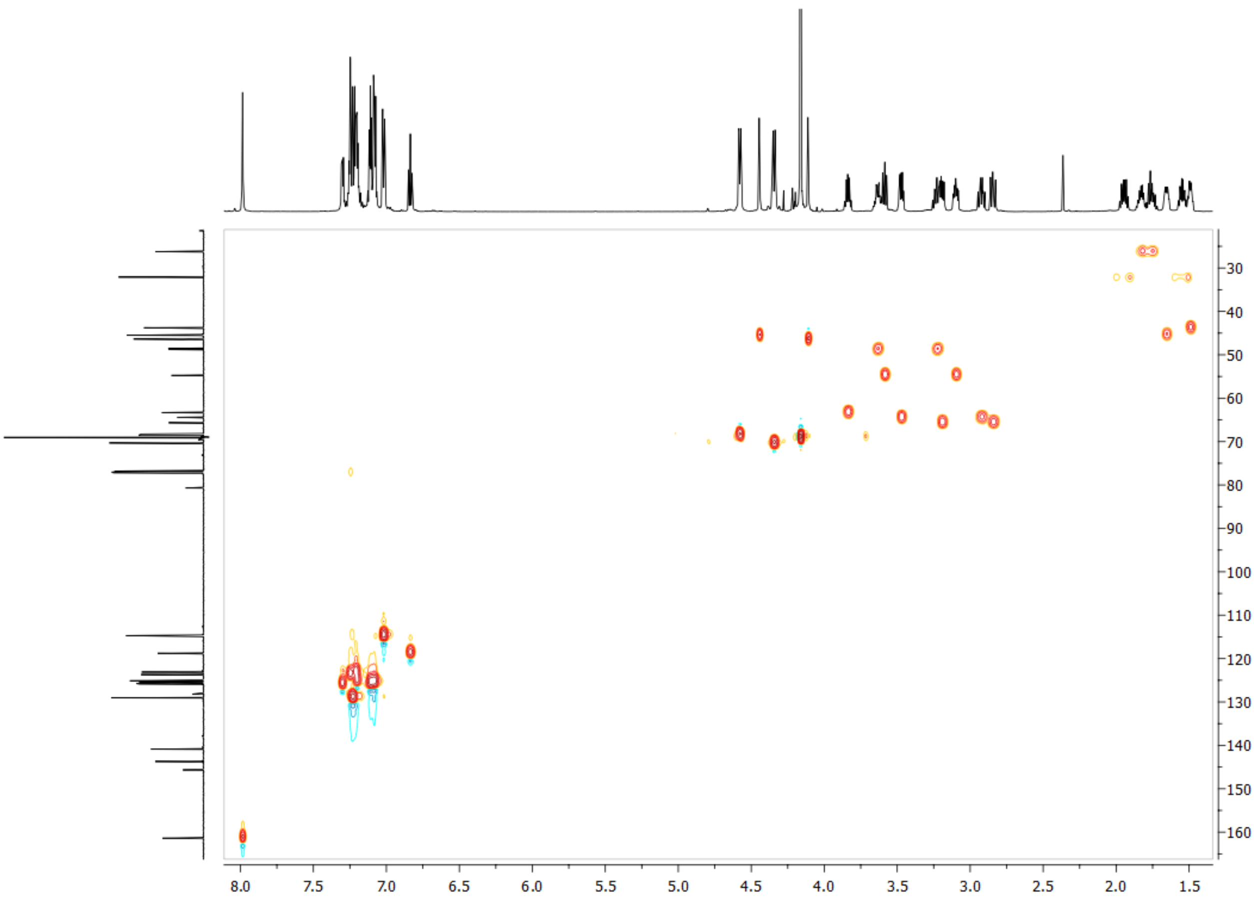
NMR AND MASS SPECTRA



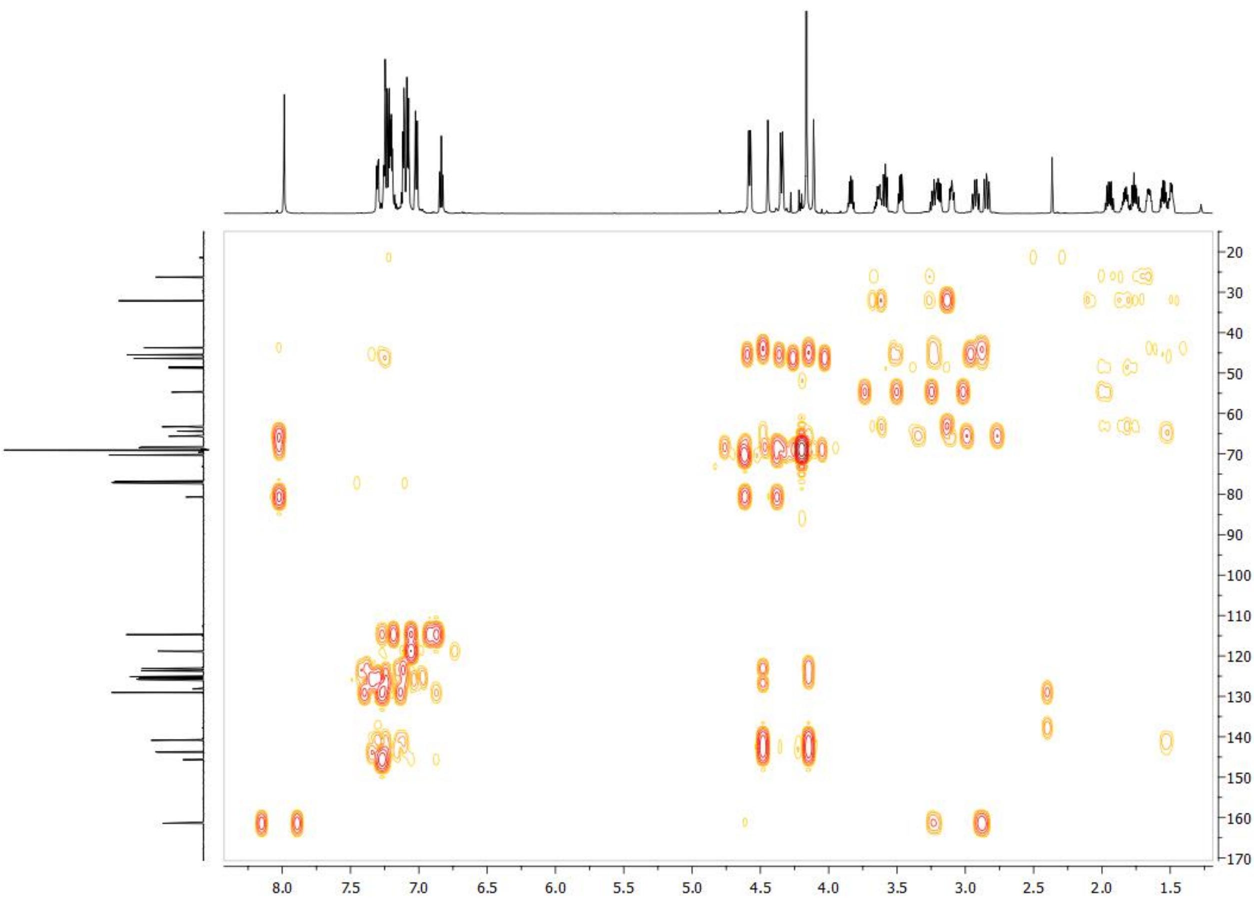
L4, ^{1}H-^{1}H COSY.



L4, ^{1}H-^{1}H NOESY.

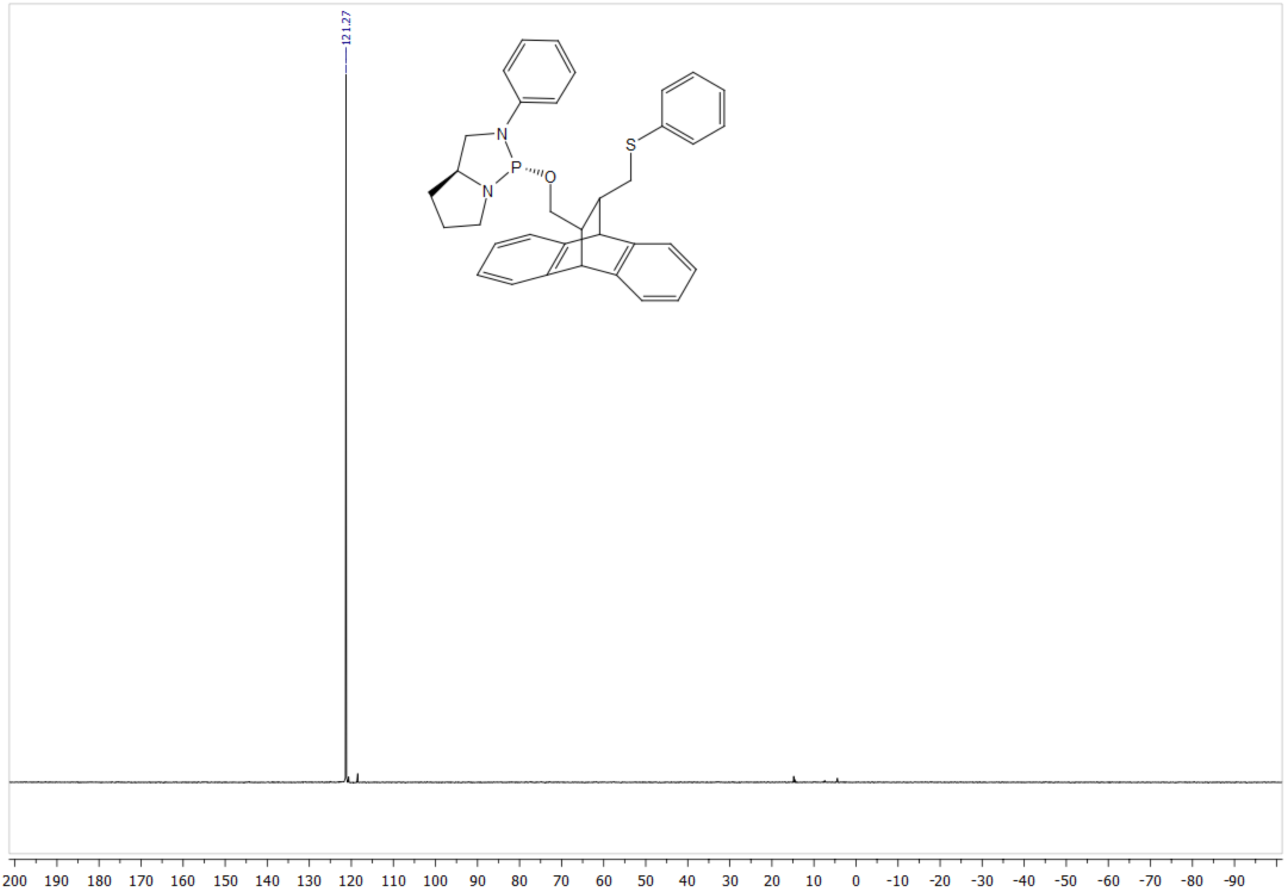


L4, ^{1}H-^{13}C HSQC.

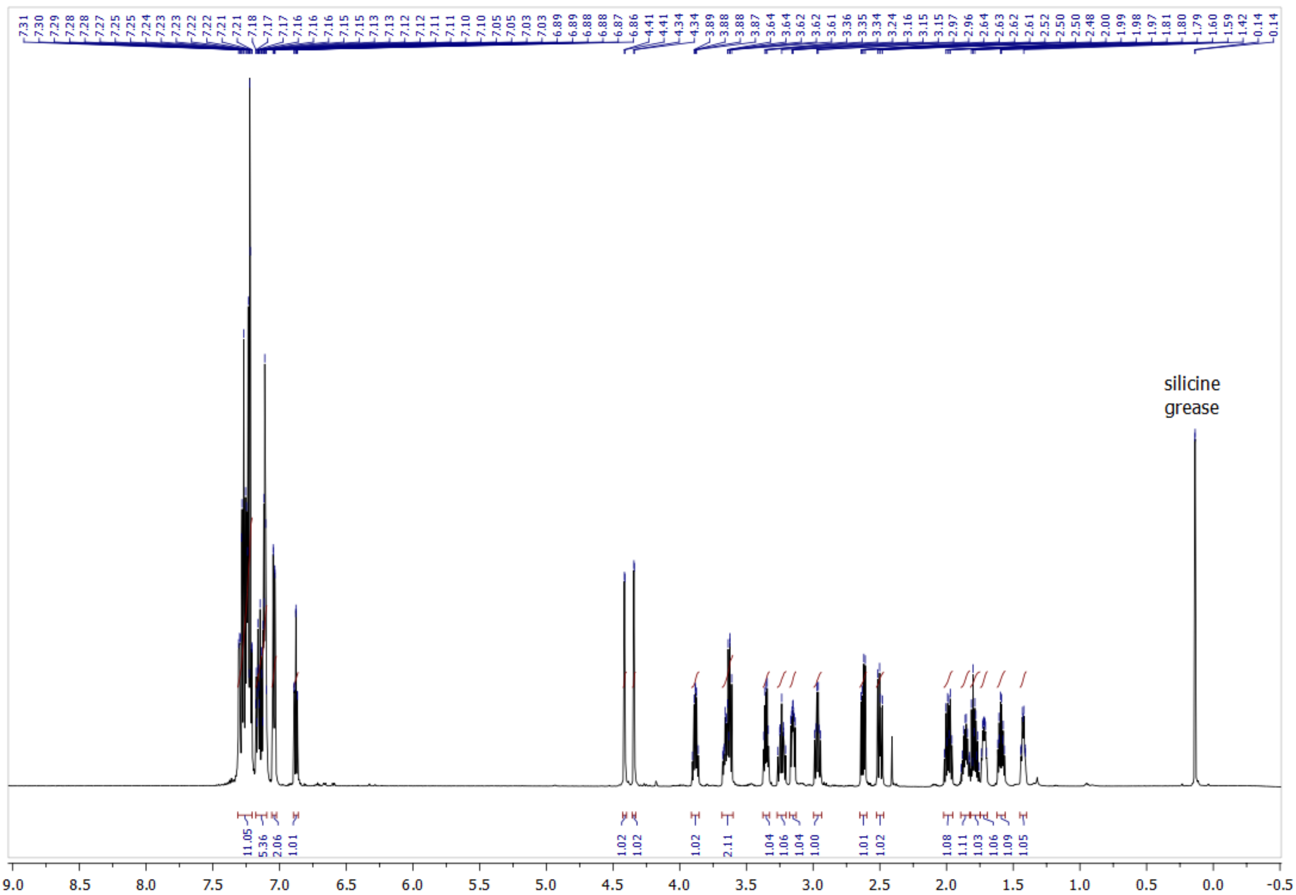


L4, ^{1}H-^{13}C HMBC.

NMR AND MASS SPECTRA

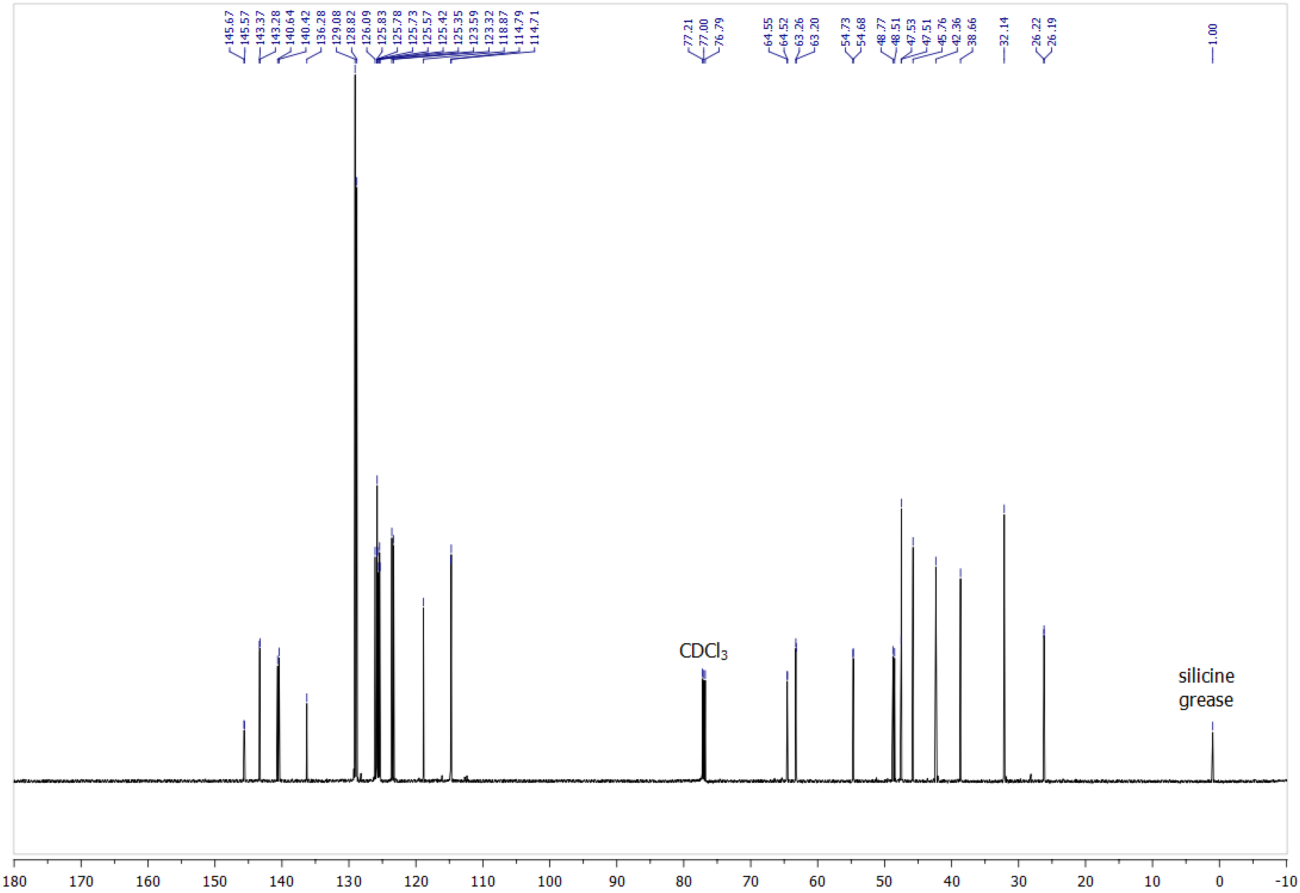


L5a, $^{31}P\{^{1}H\}$ (242.9 MHz, $CDCl_3$, 30 °C).

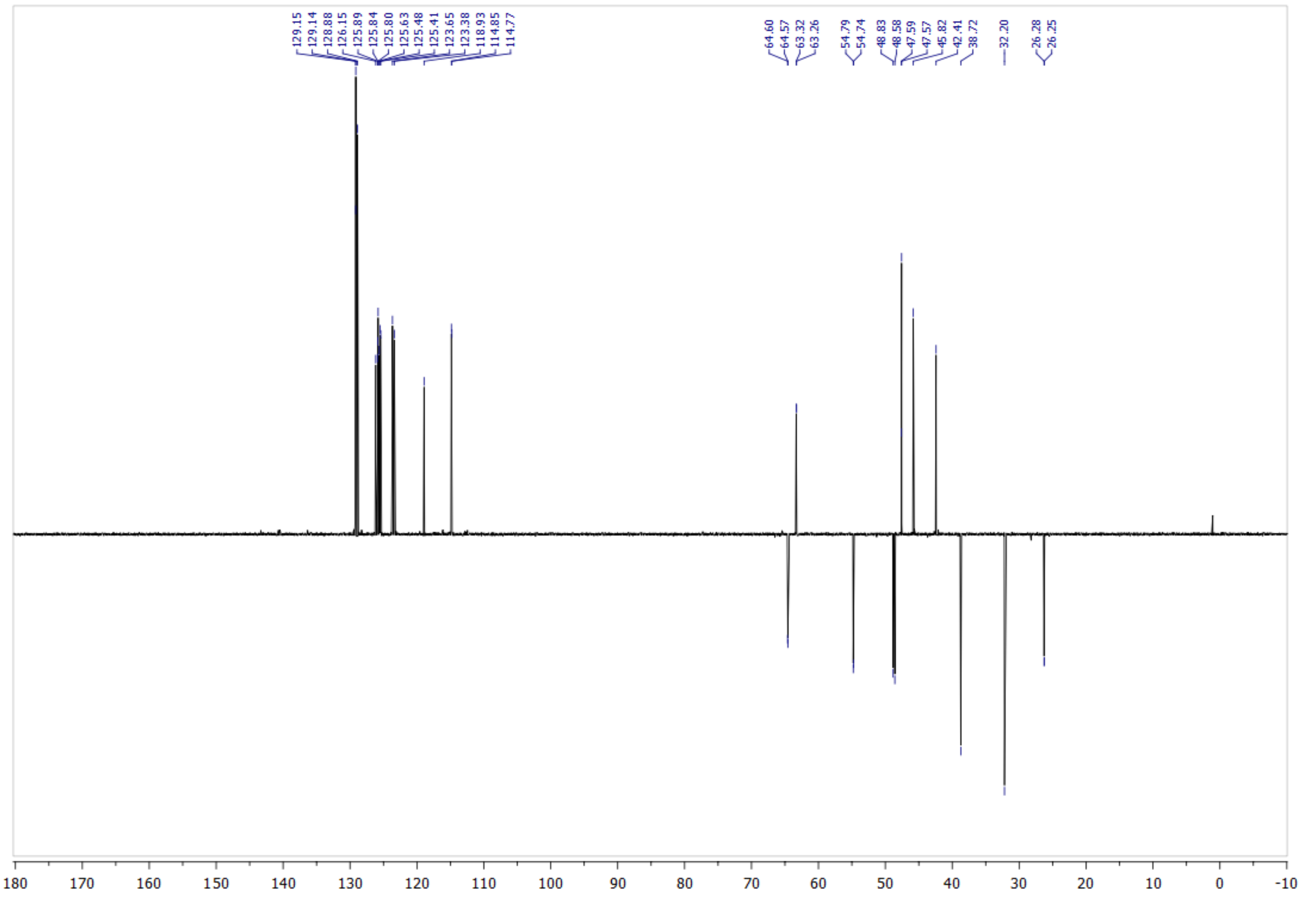


L5a, ^{1}H (600.1 MHz, $CDCl_3$, 30 °C).

NMR AND MASS SPECTRA

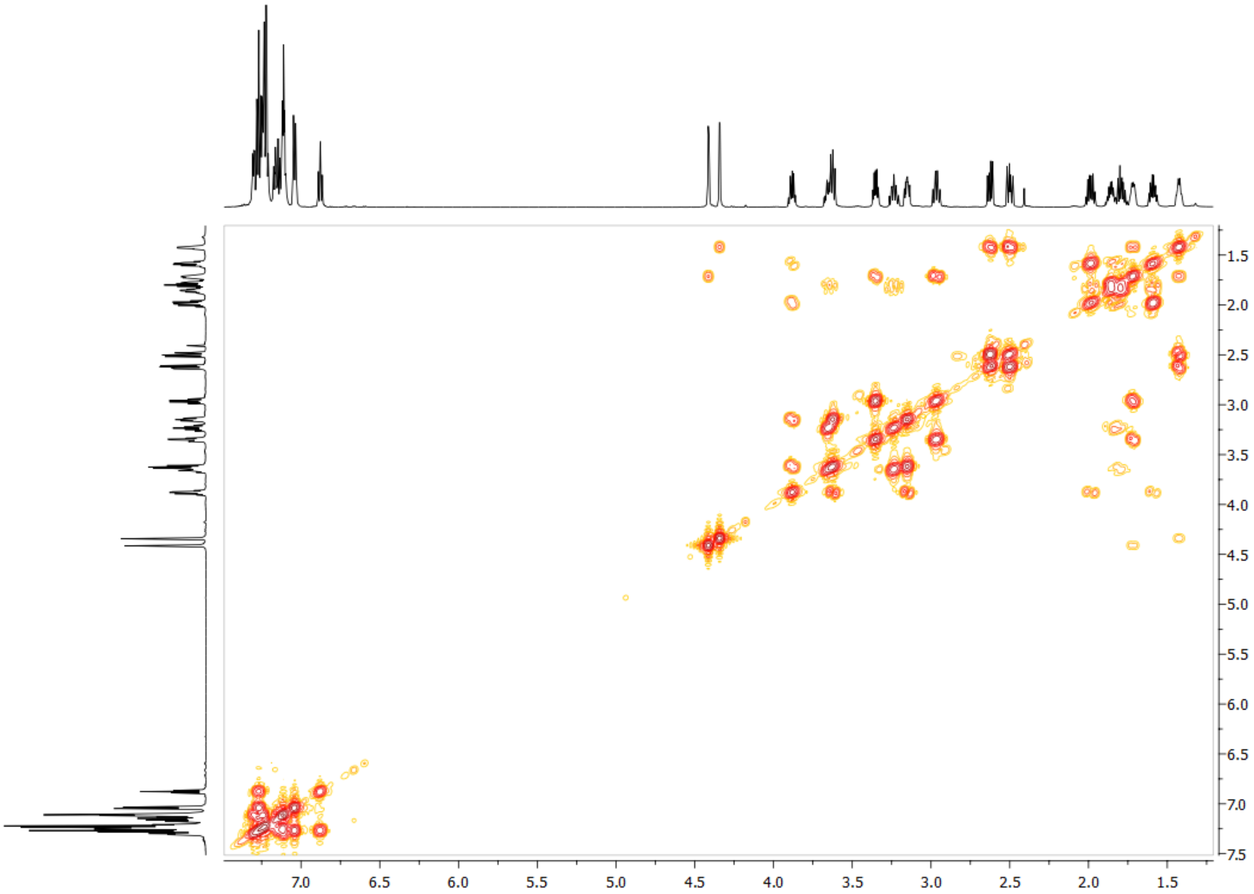


L5a, $^{13}C\{^{1}H\}$ (150.9 MHz, $CDCl_3$, 30 °C).

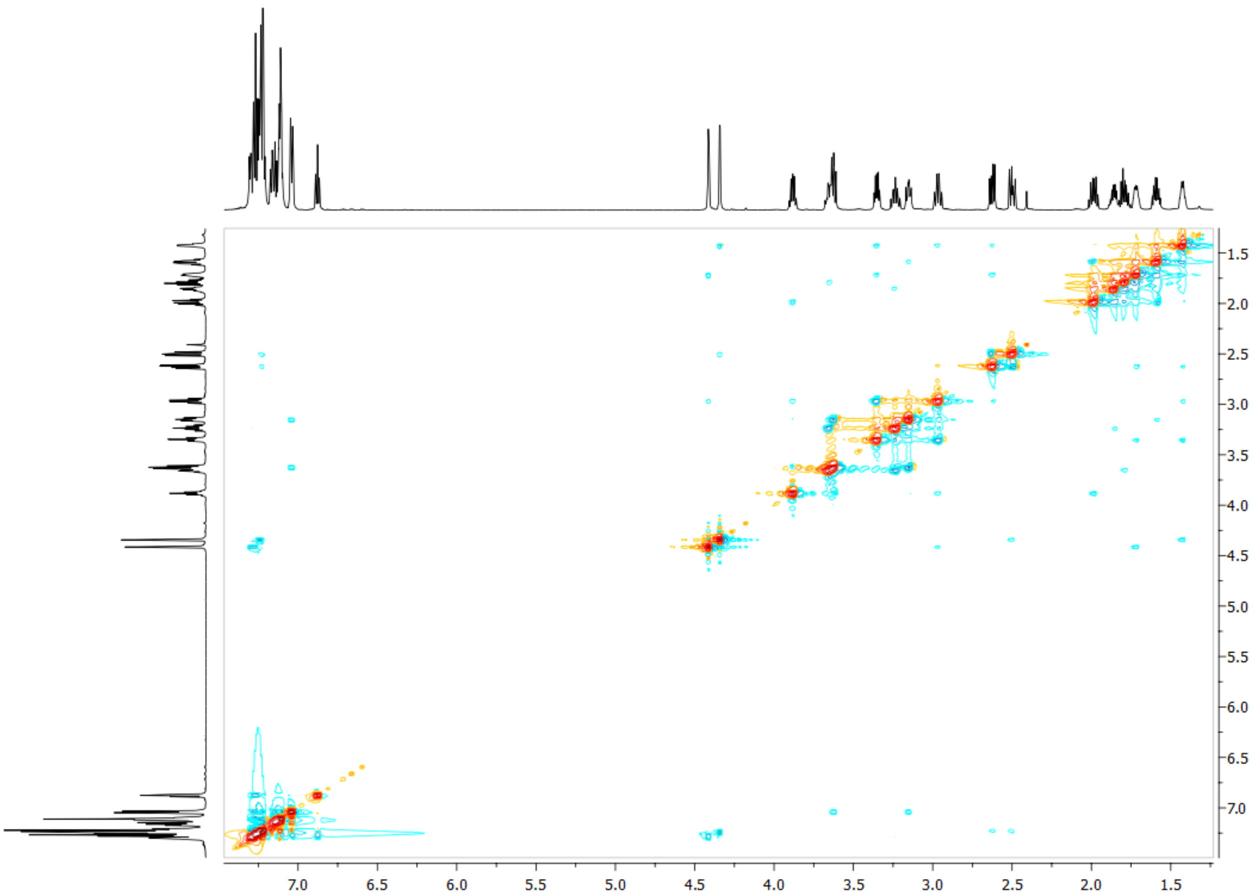


L5a, $^{13}C\{^{1}H\}$ DEPT (150.9 MHz, $CDCl_3$, 30 °C).

NMR AND MASS SPECTRA

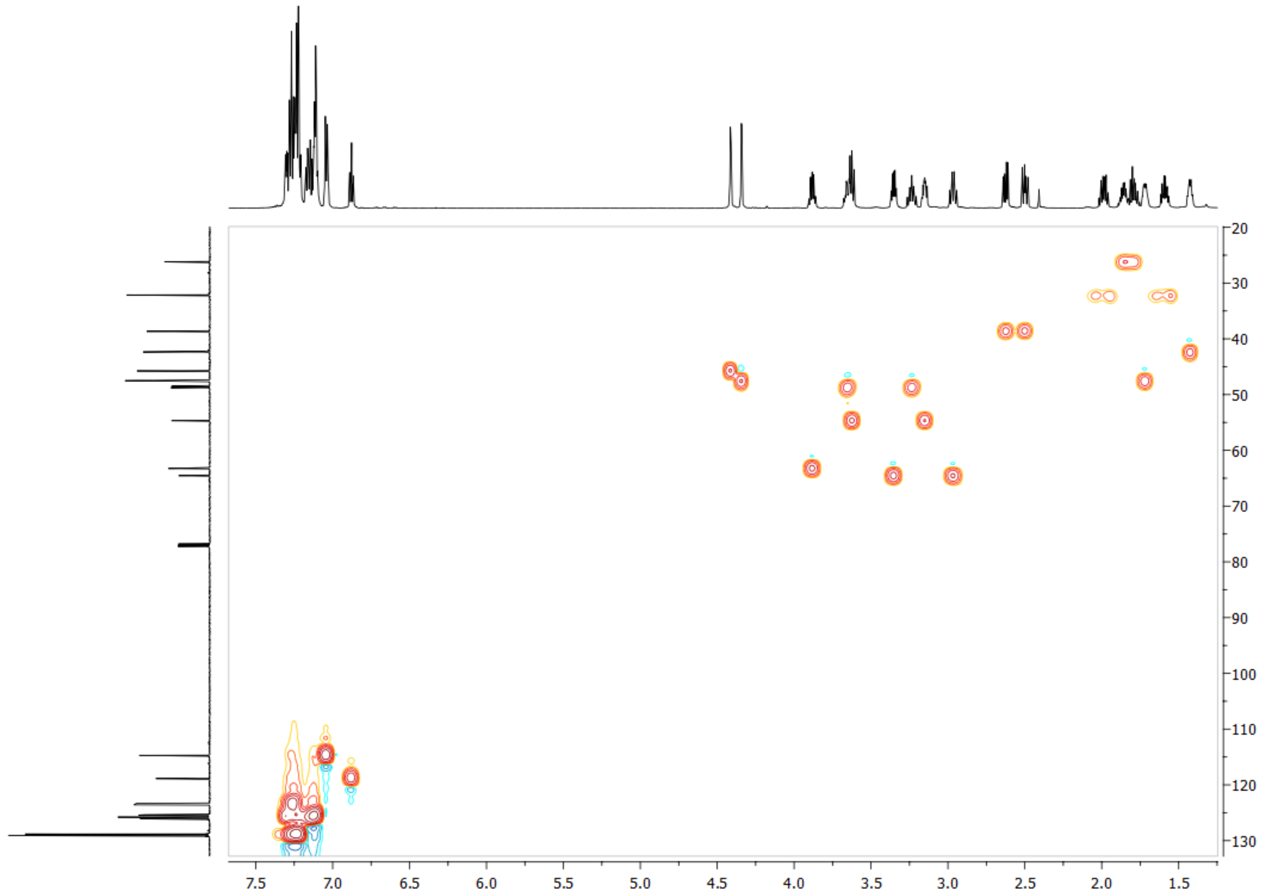


L5a, ^{1}H-^{1}H COSY.

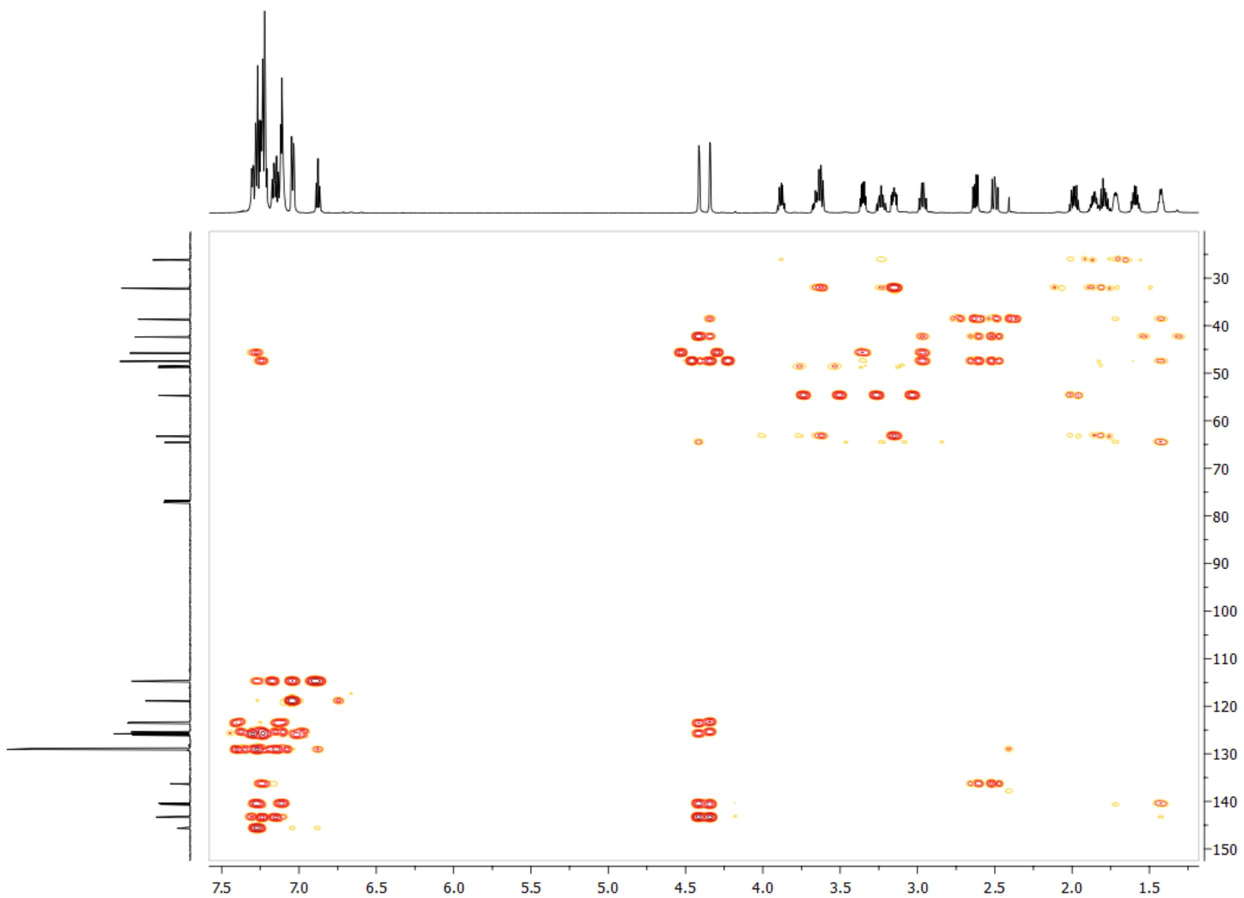


L5a, ^{1}H-^{1}H NOESY.

NMR AND MASS SPECTRA

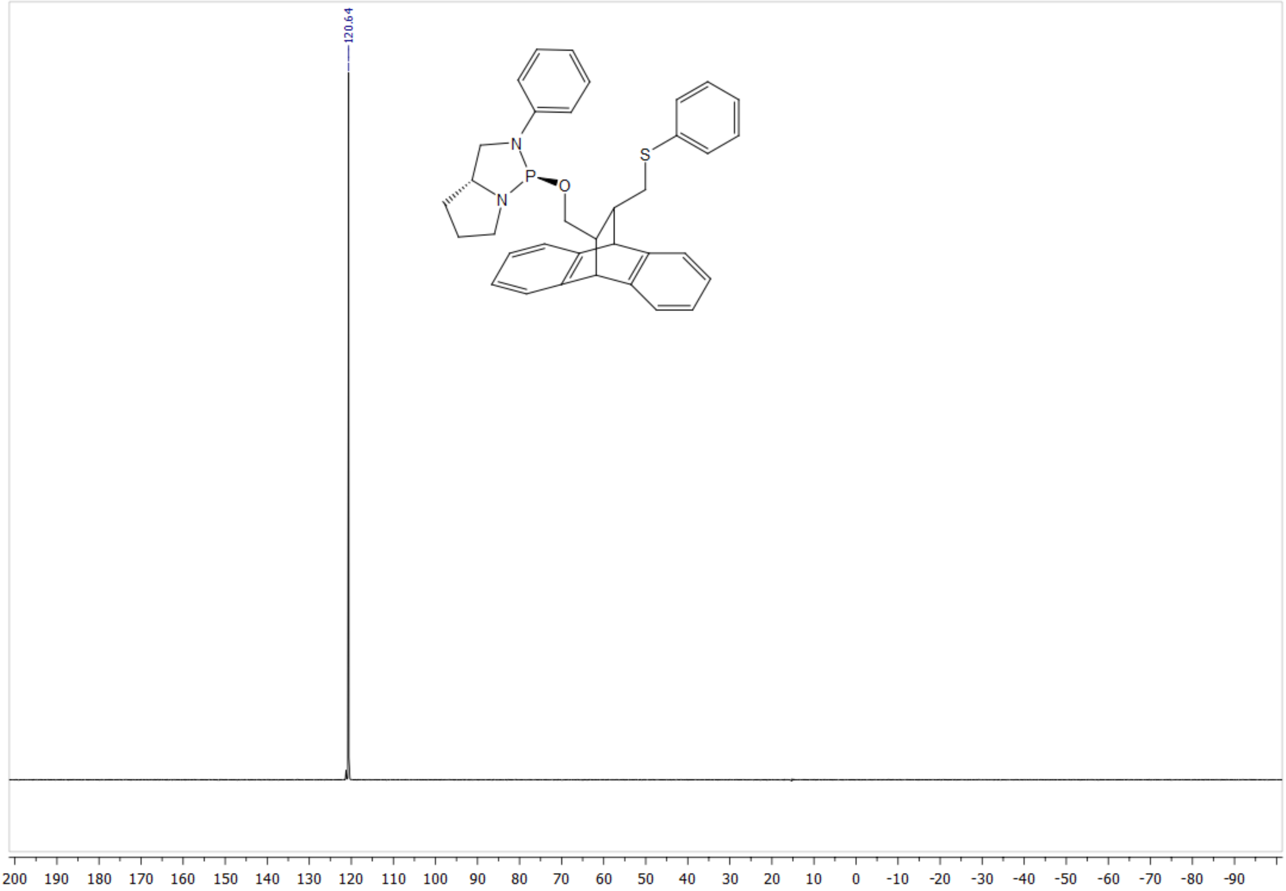


L5a, ^{1}H-^{13}C HSQC.

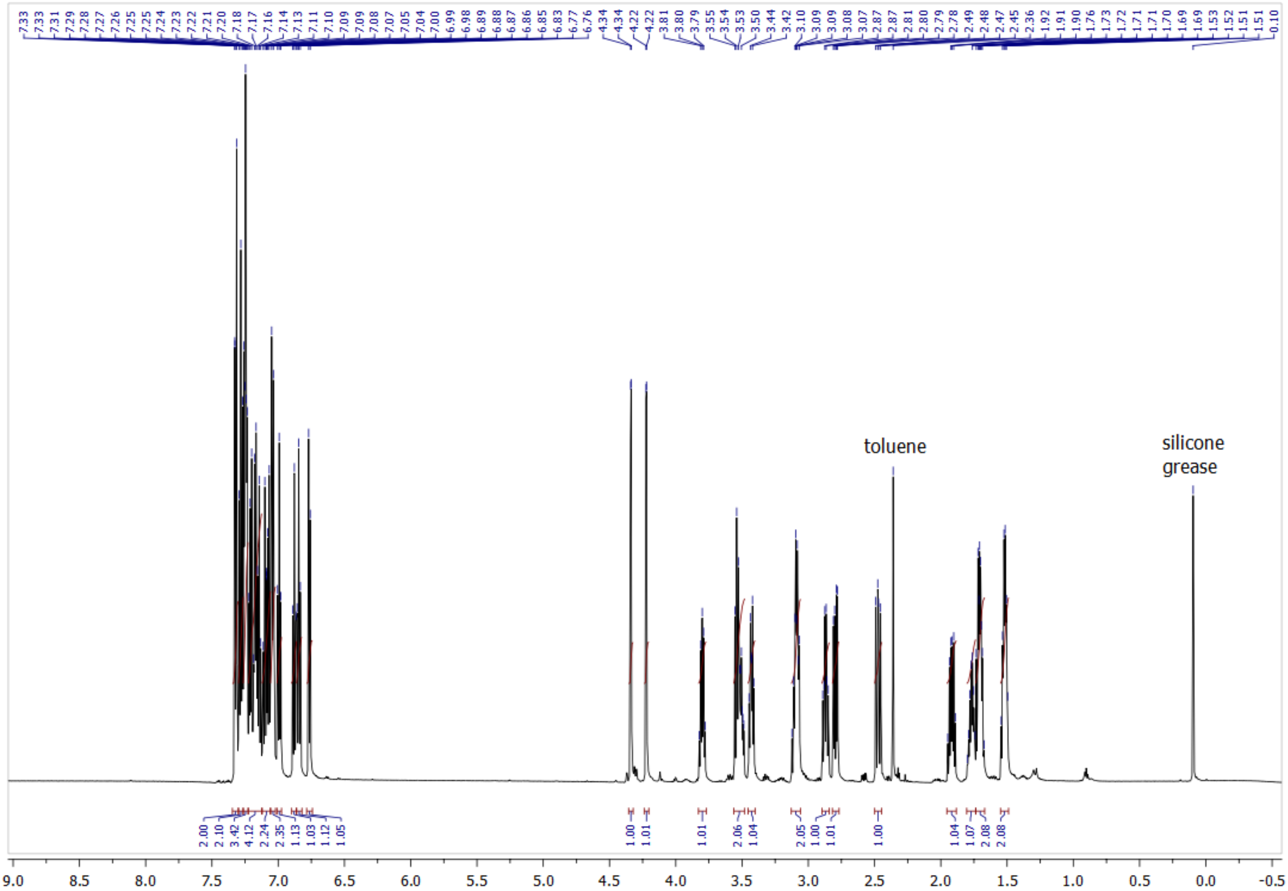


L5a, ^{1}H-^{13}C HMBC.

NMR AND MASS SPECTRA

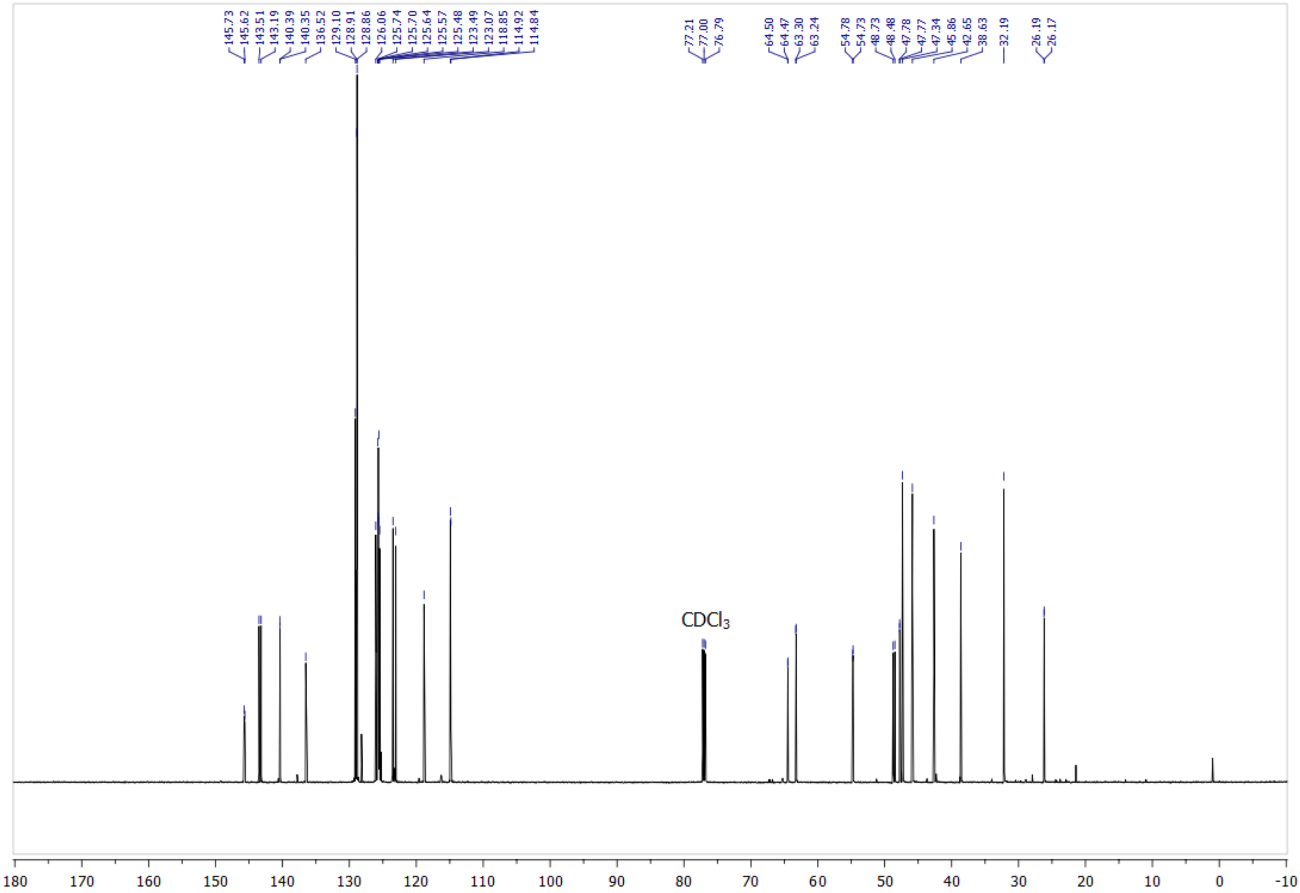


L5b, $^{31}P\{^{1}H\}$ (242.9 MHz, $CDCl_3$, 30 °C).

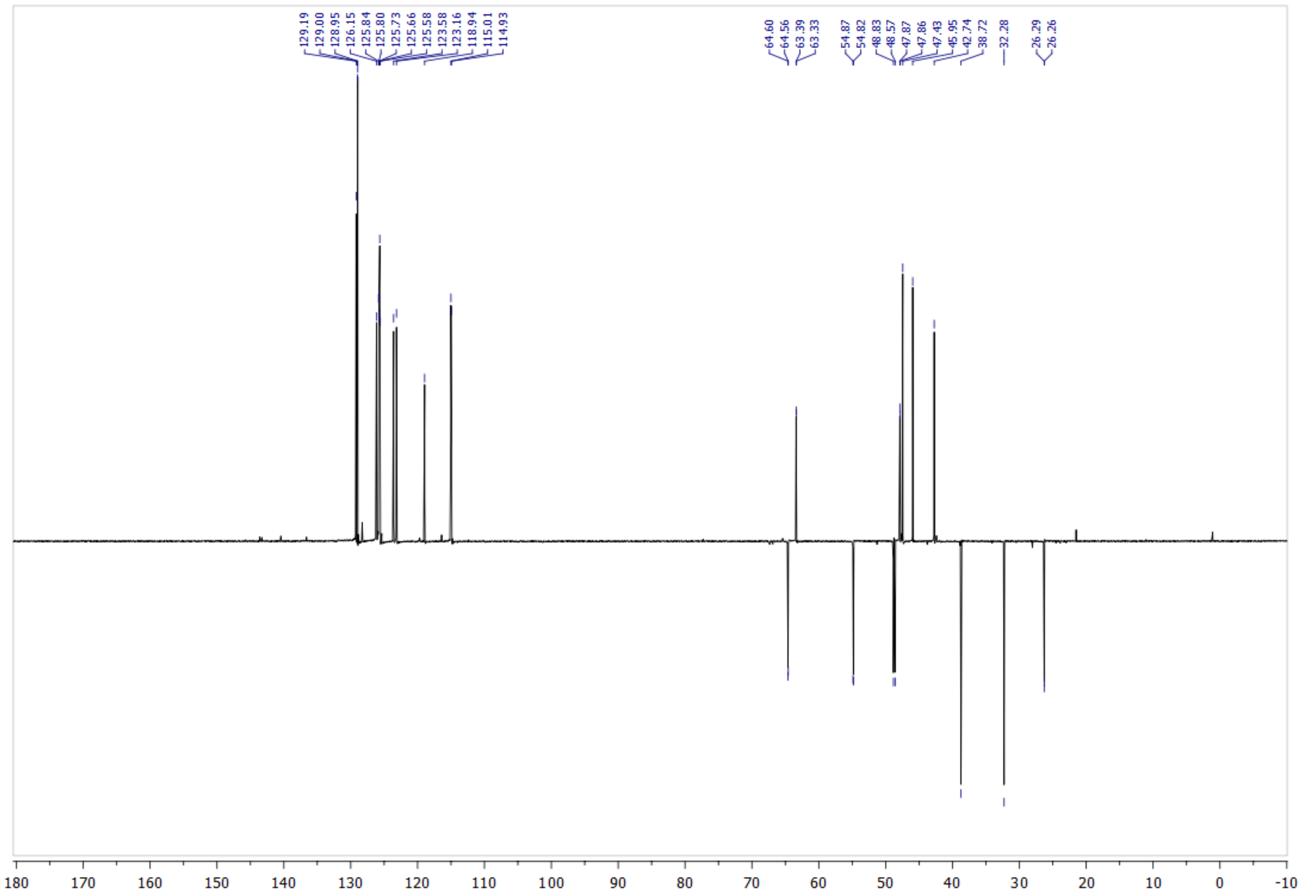


L5b, ^{1}H (600.1 MHz, $CDCl_3$, 30 °C).

NMR AND MASS SPECTRA

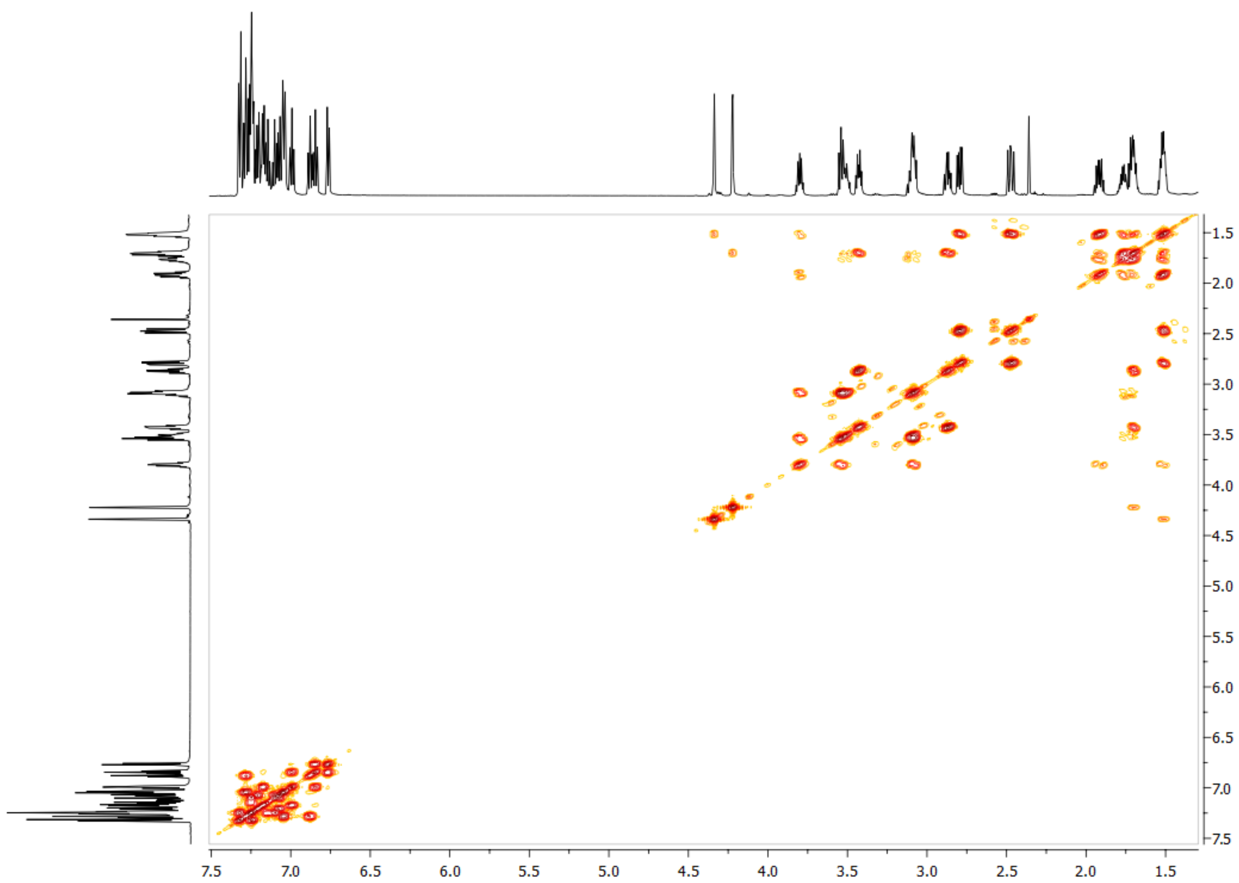


L5b, $^{13}C\{^{1}H\}$ (150.9 MHz, $CDCl_3$, 30 °C).

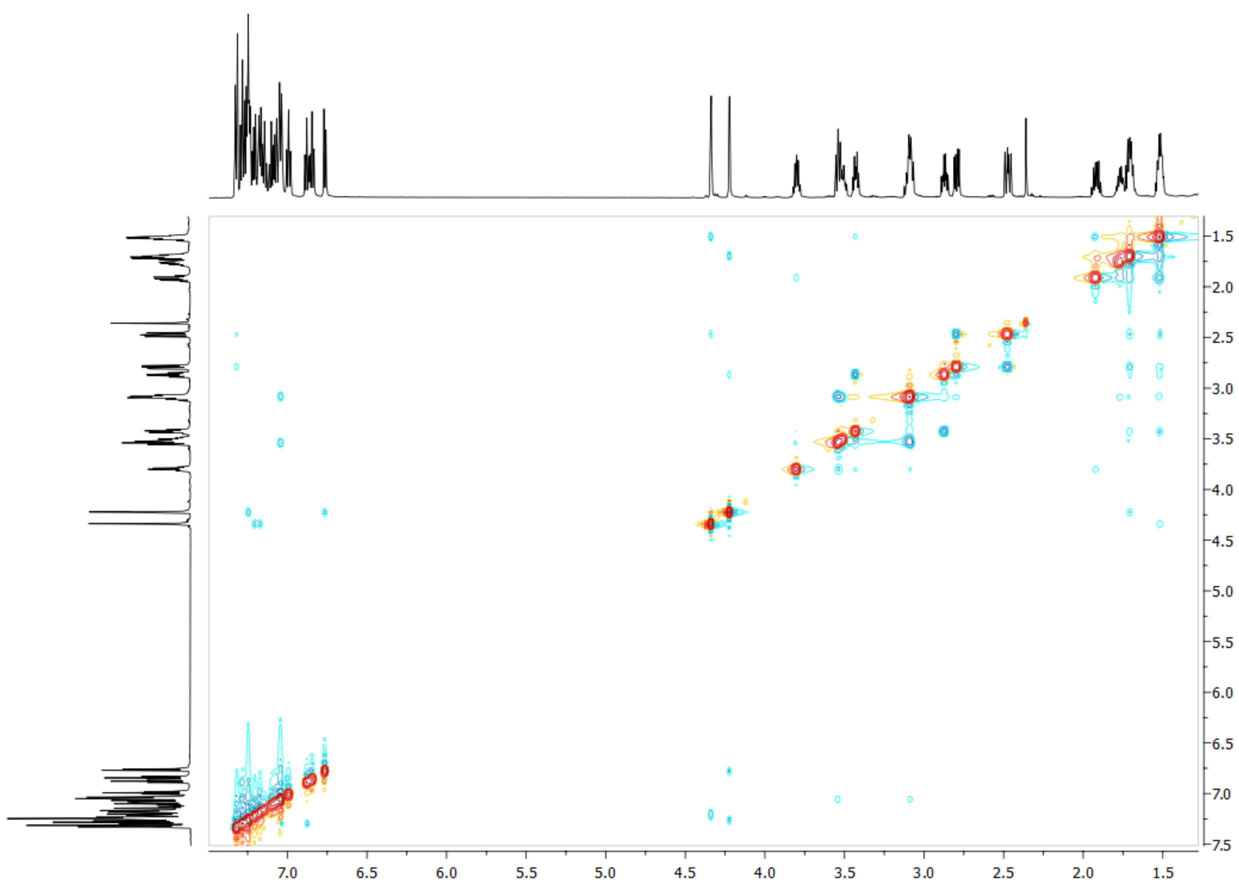


L5b, $^{13}C\{^{1}H\}$ DEPT (150.9 MHz, $CDCl_3$, 30 °C).

NMR AND MASS SPECTRA

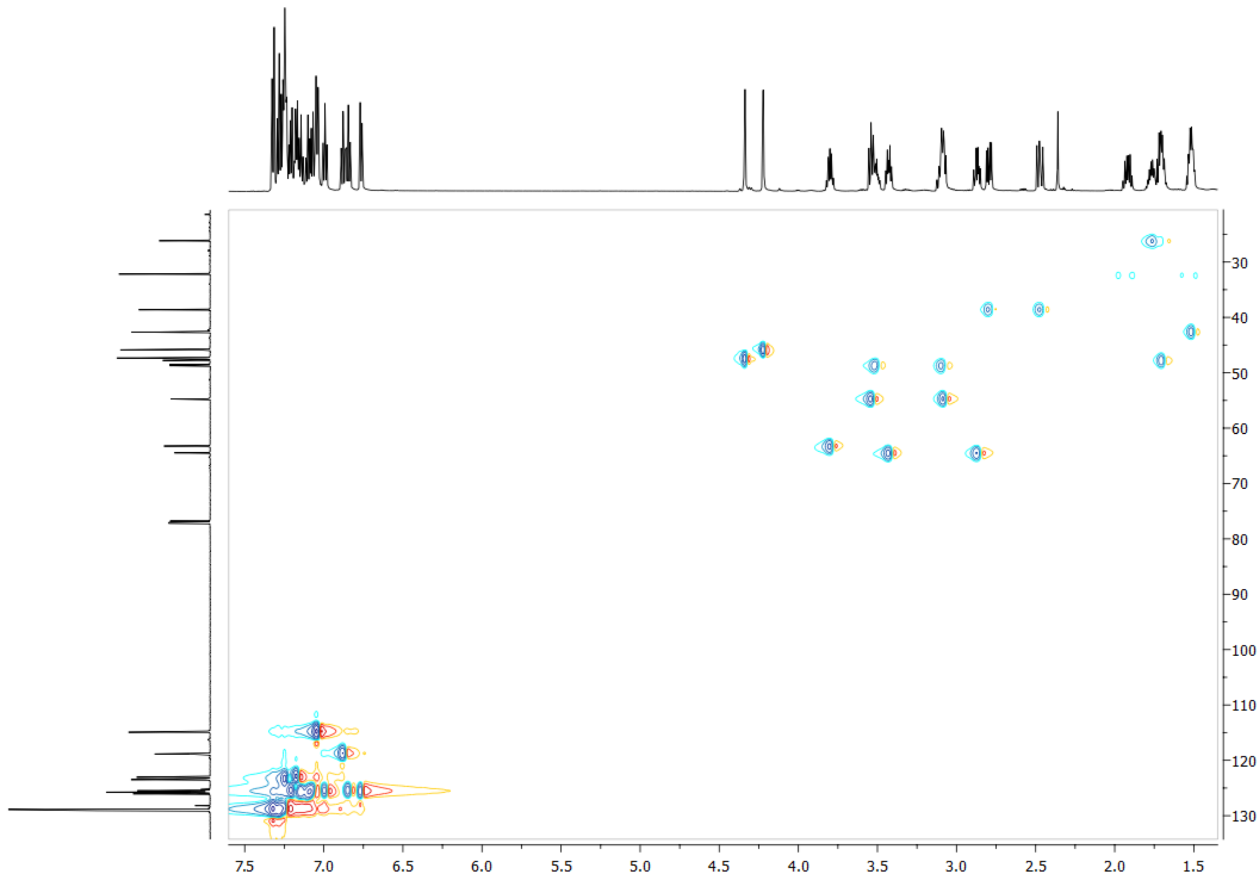


L5b, ^{1}H-^{1}H COSY.

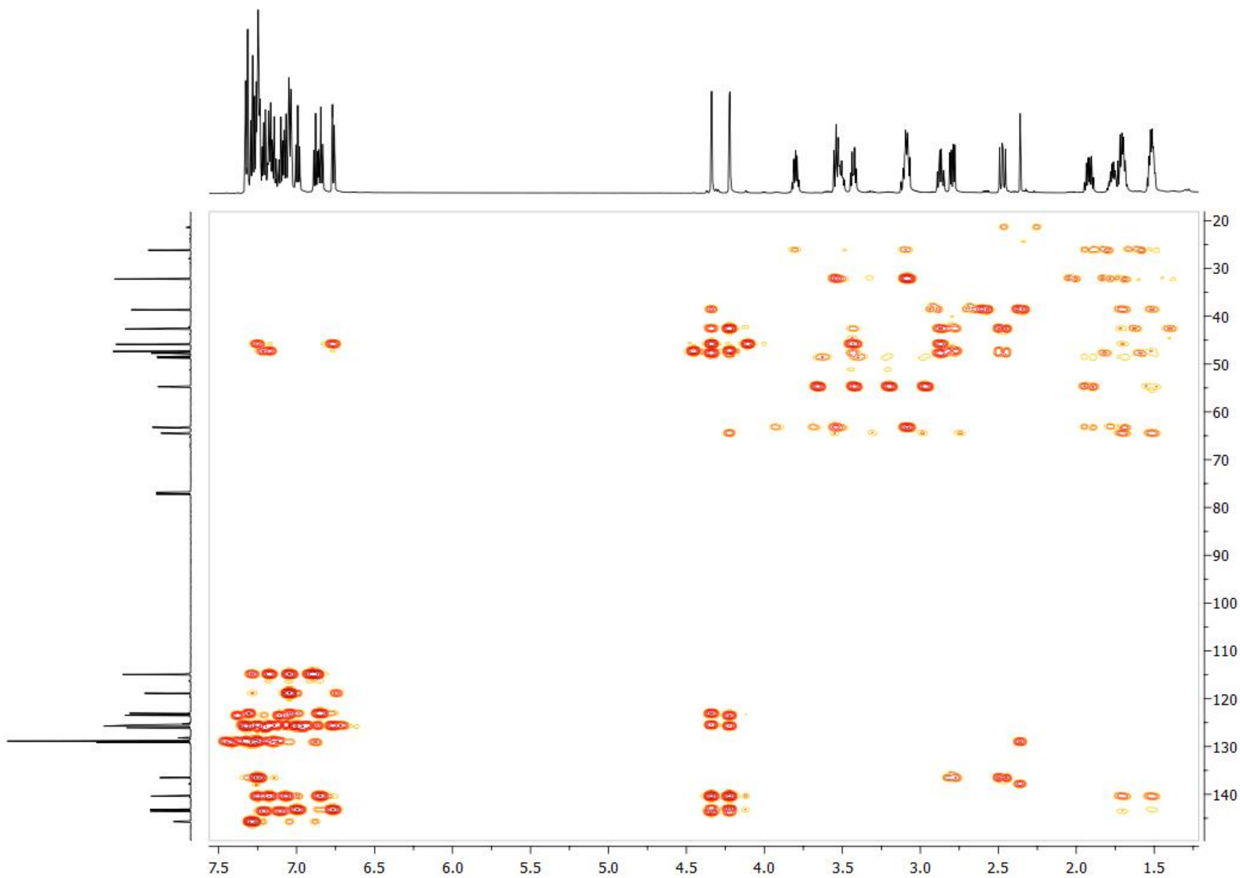


L5b, ^{1}H-^{1}H NOESY.

NMR AND MASS SPECTRA

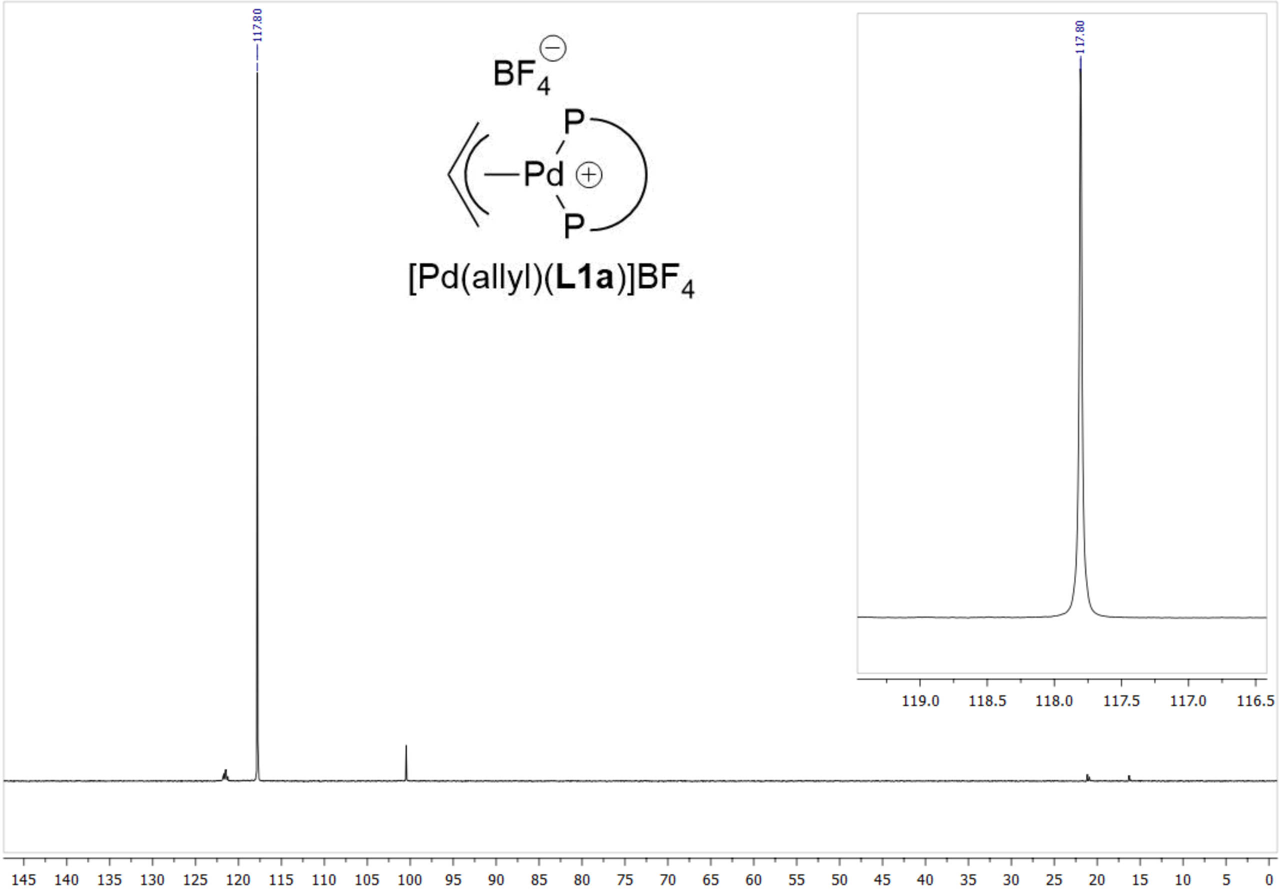


L5b, ^{1}H-^{13}C HSQC.

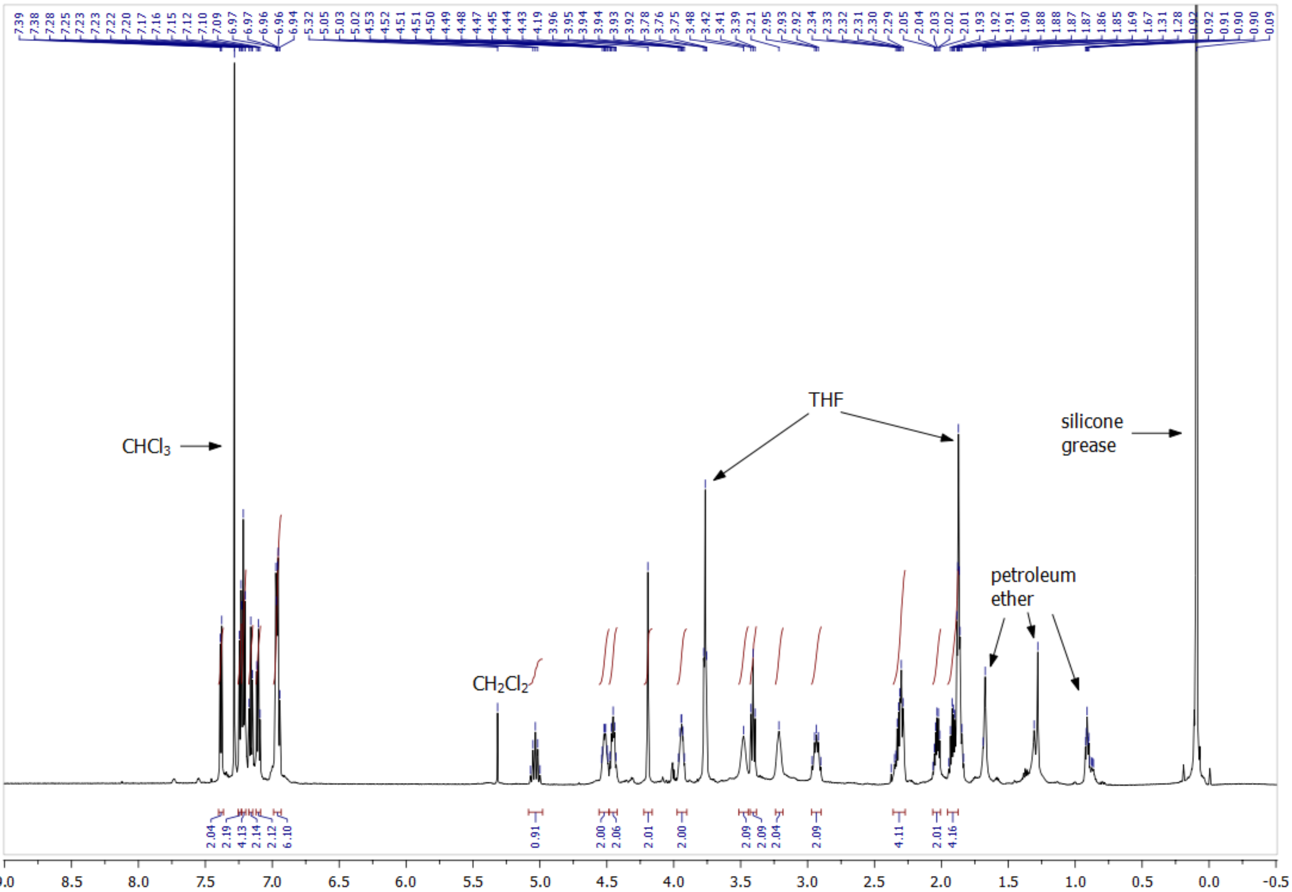


L5b, ^{1}H-^{13}C HMBC.

NMR AND MASS SPECTRA

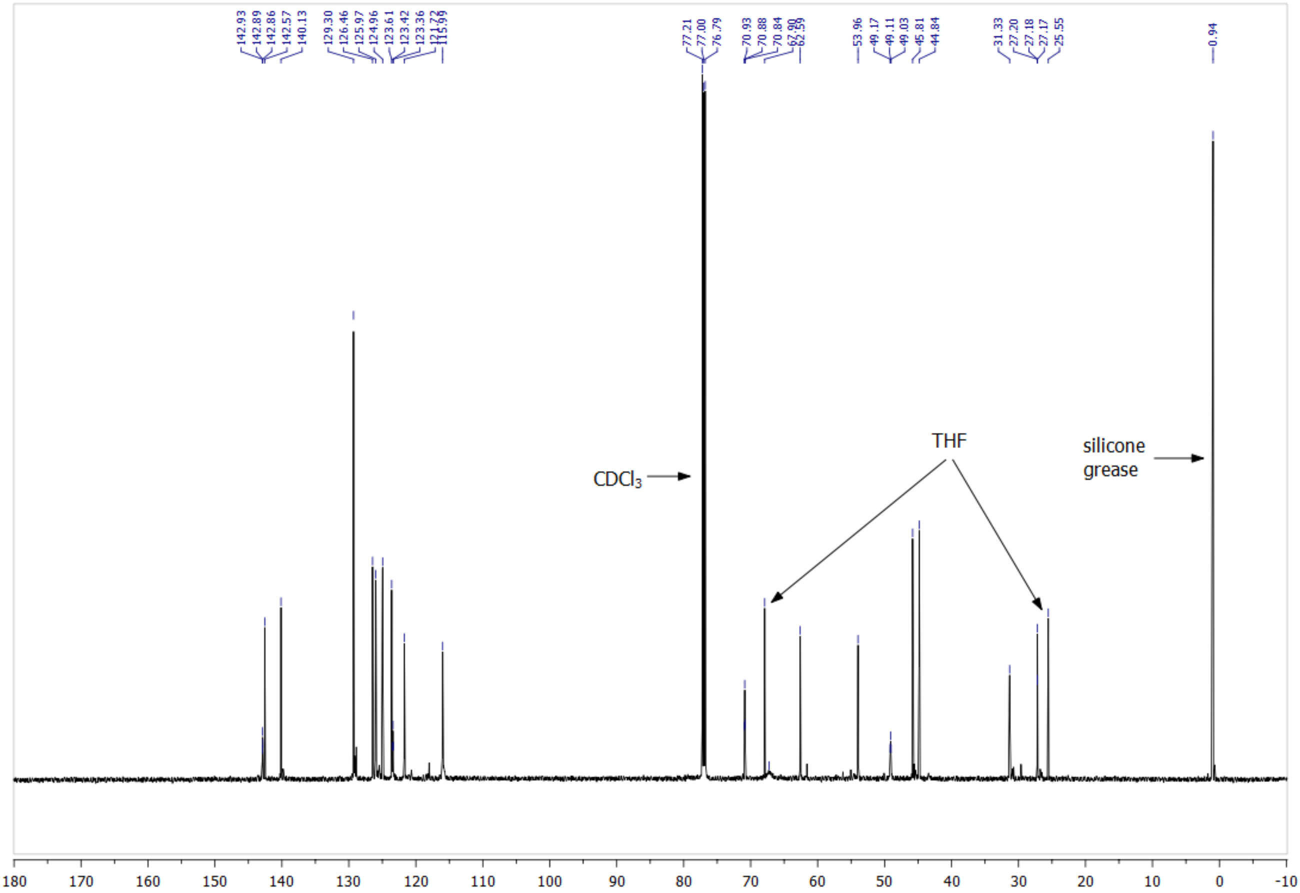


[Pd(allyl)(**L1a**)]BF_4, $^{31}P\{^1H\}$ (242.9 MHz, $CDCl_3$, 30 °C).

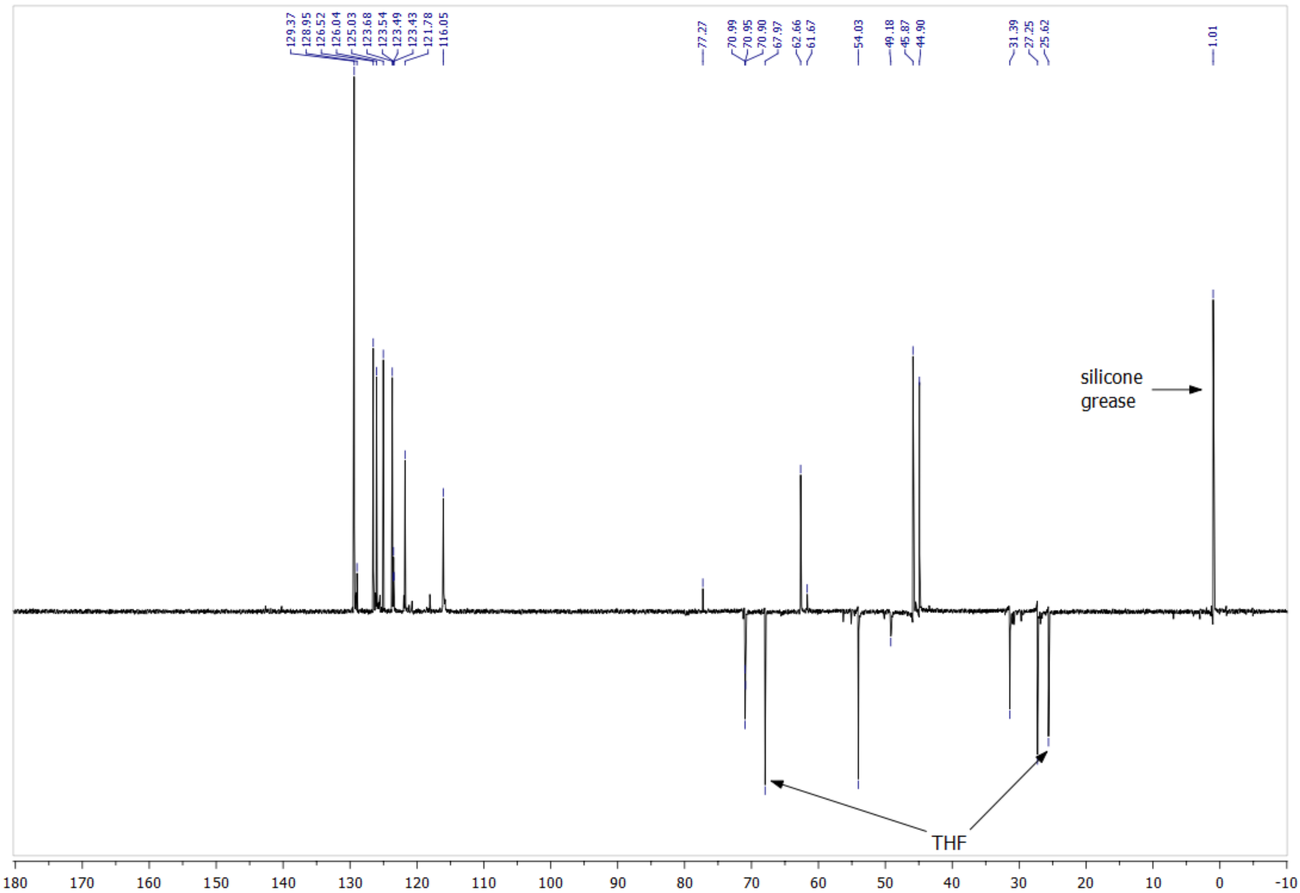


[Pd(allyl)(**L1a**)]BF_4, ^1H (600.1 MHz, $CDCl_3$, 30 °C).

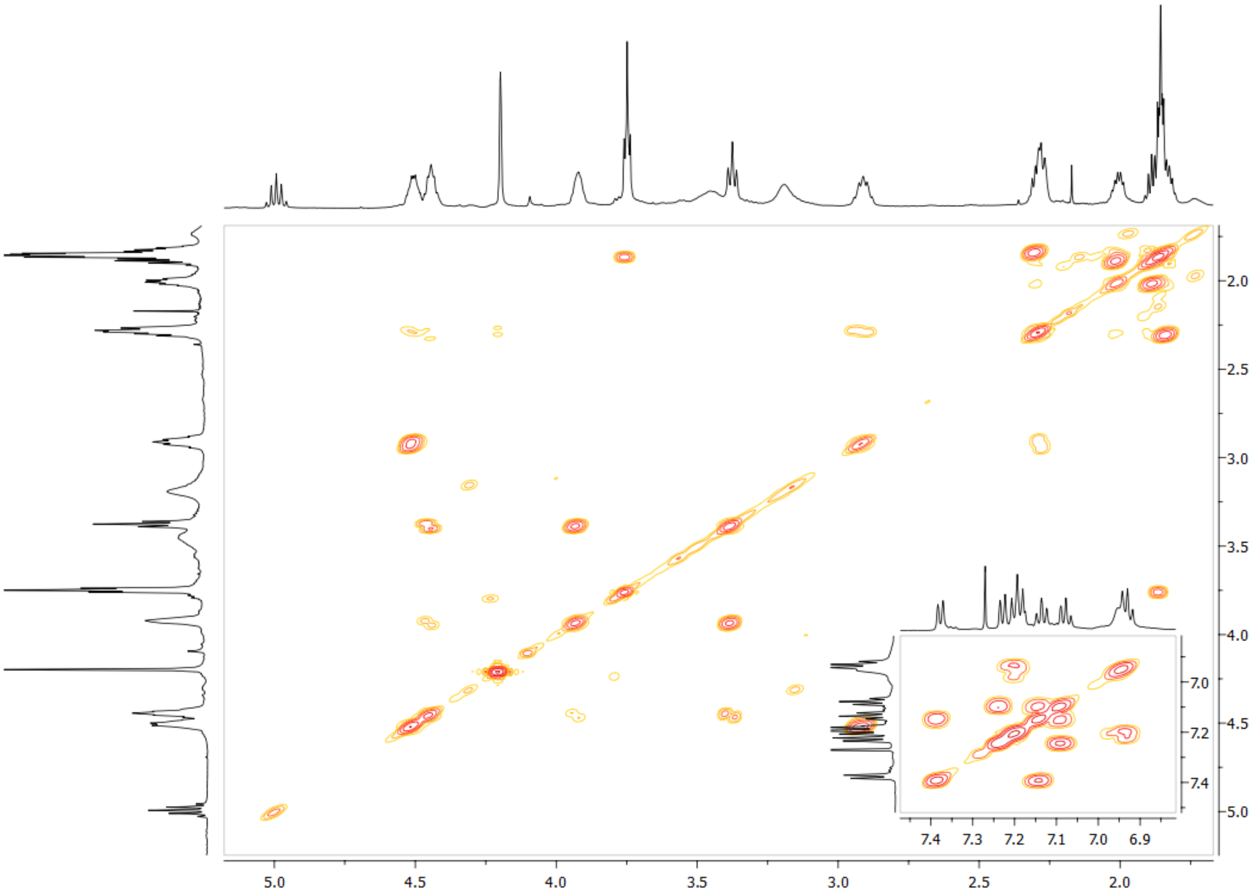
NMR AND MASS SPECTRA



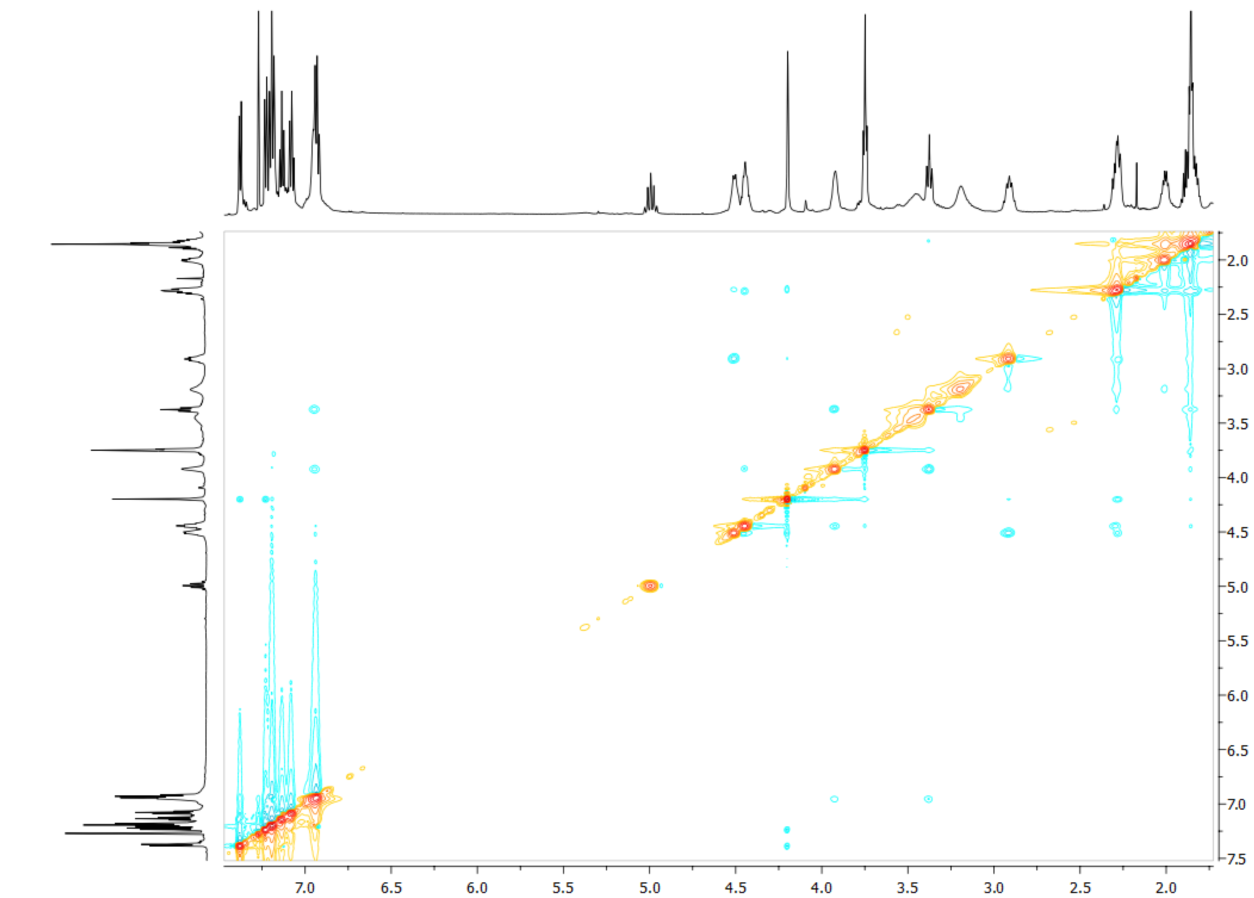
[Pd(allyl)(**L1a**)]BF_4, $^{13}C\{^1H\}$ (150.9 MHz, $CDCl_3$, 30 °C).



[Pd(allyl)(**L1a**)]BF_4, $^{13}C\{^1H\}$ DEPT (150.9 MHz, $CDCl_3$, 30 °C).

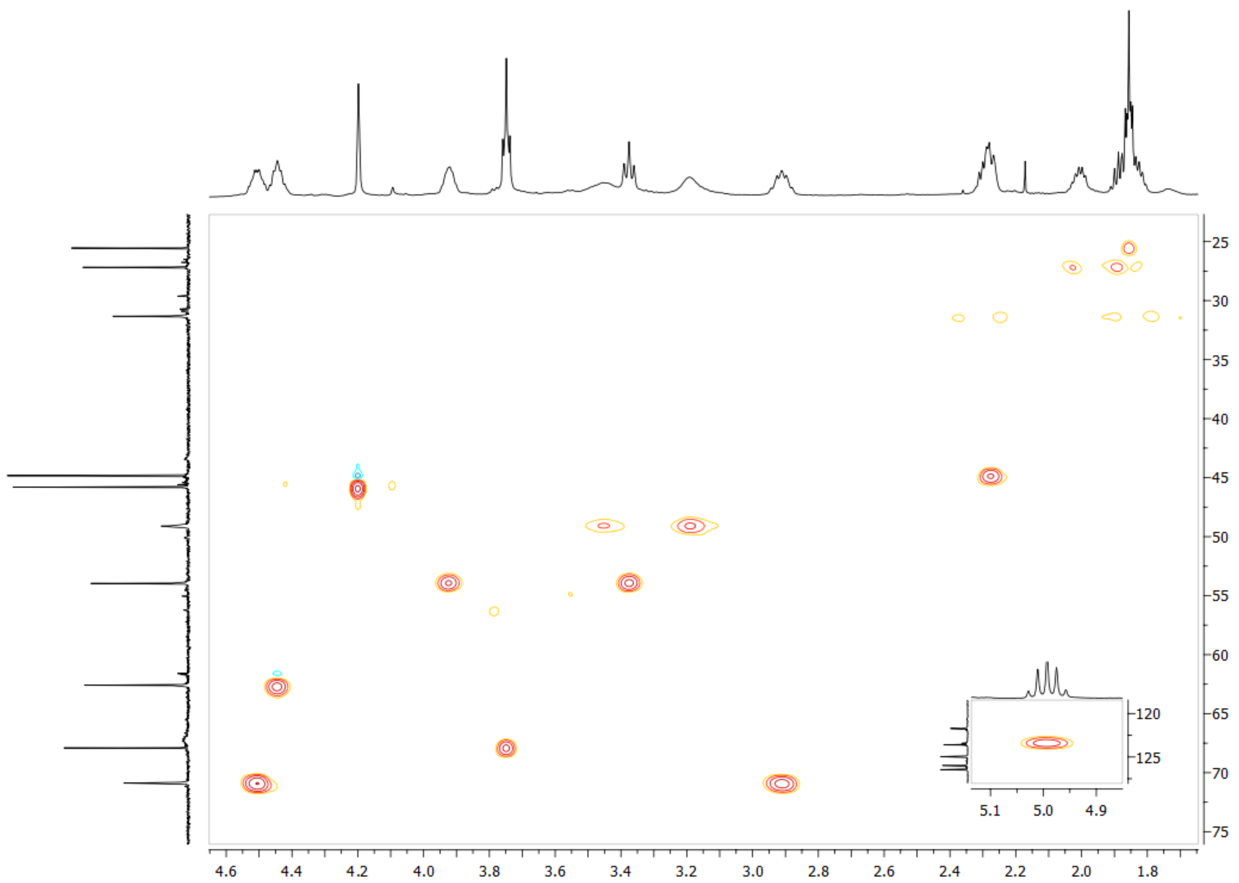


[Pd(allyl)(**L1a**)]BF_4, ^1H-^1H COSY.

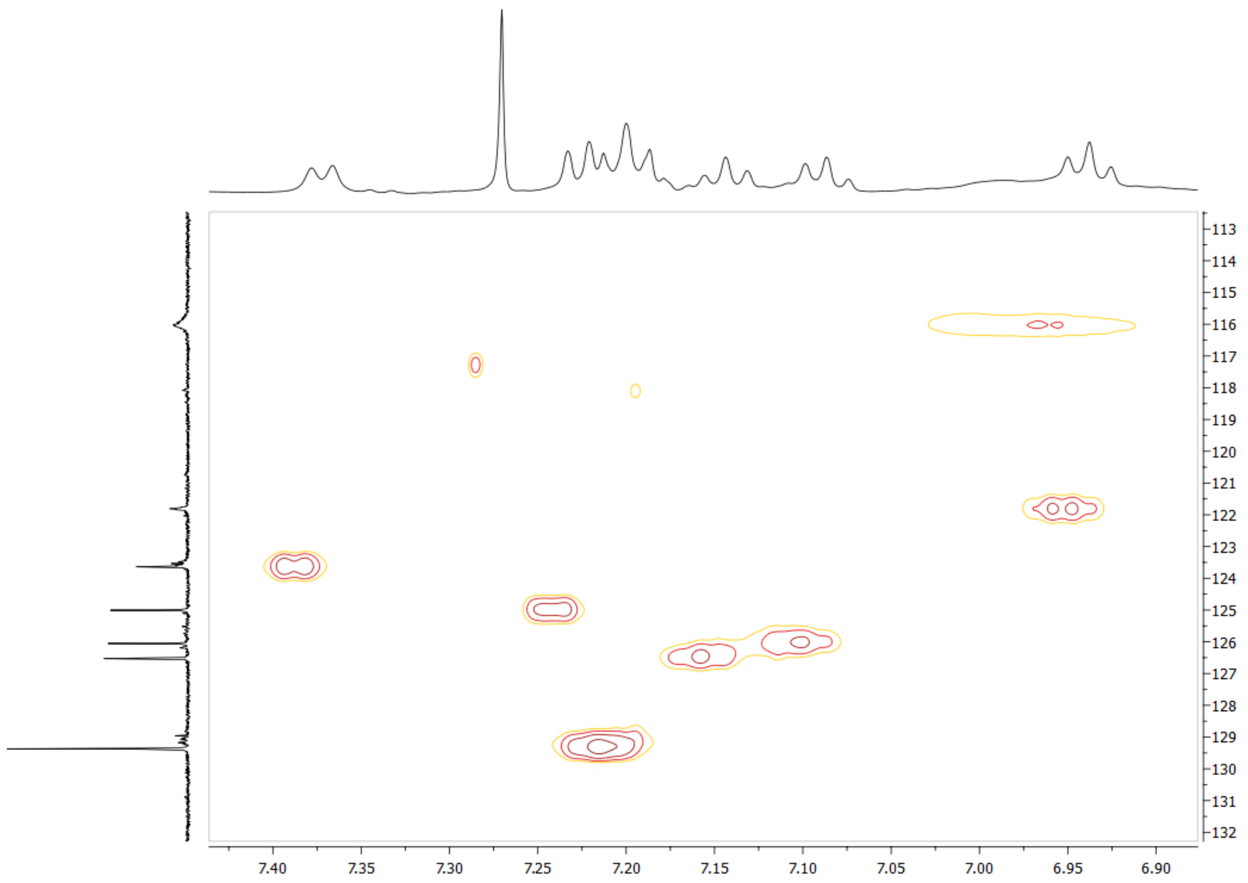


[Pd(allyl)(**L1a**)]BF_4, ^1H-^1H NOESY.

NMR AND MASS SPECTRA

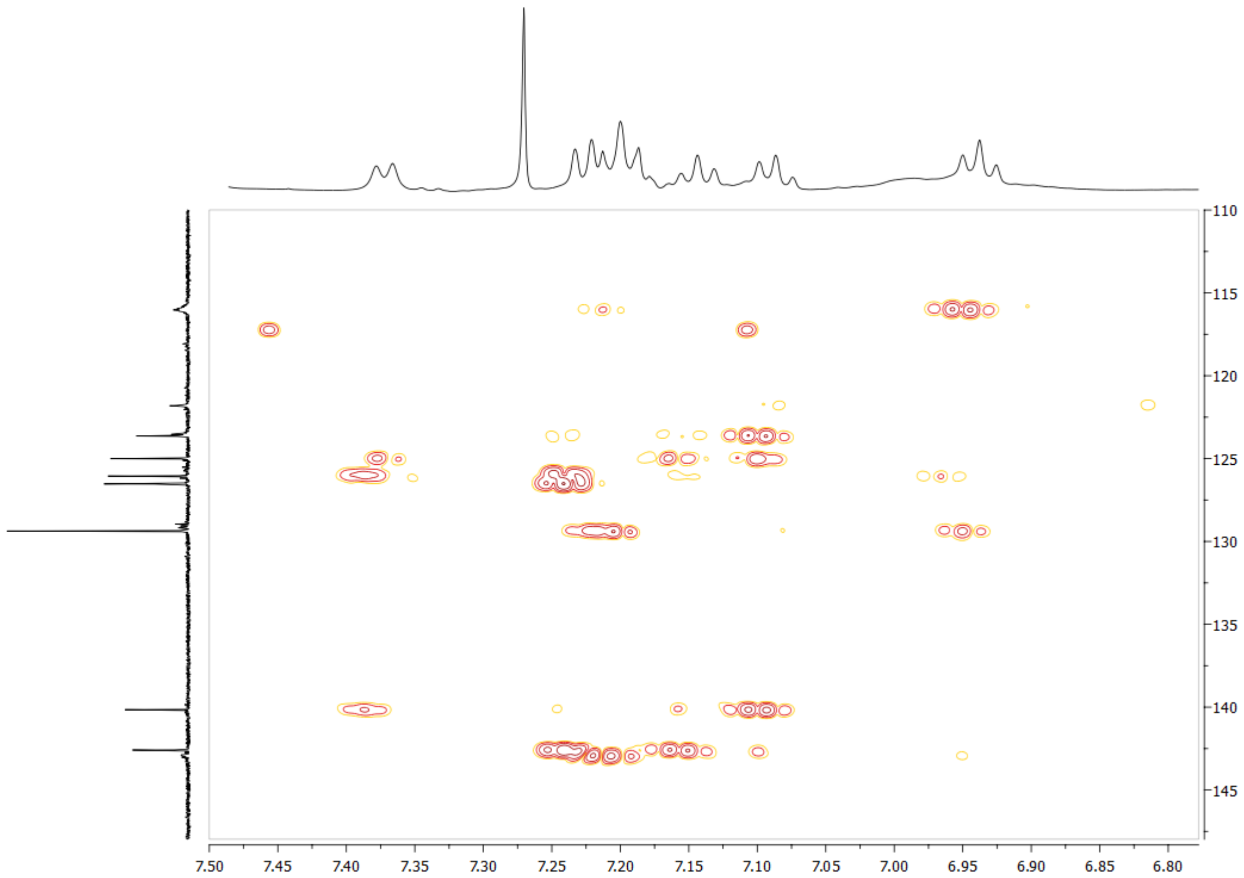


[Pd(allyl)(**L1a**)]BF_4, ^{1}H-^{13}C HSQC (fragment of the spectrum).

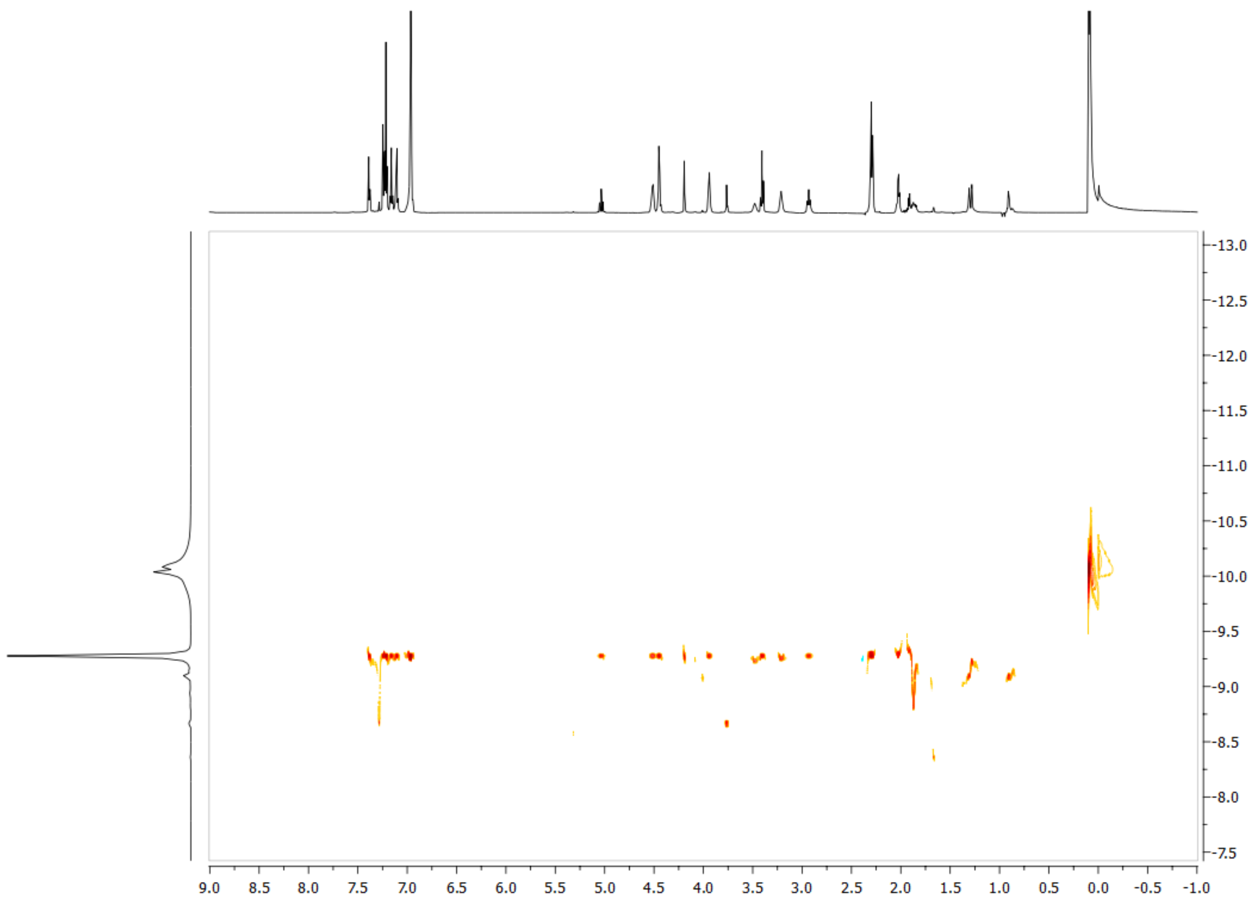


[Pd(allyl)(**L1a**)]BF_4, ^{1}H-^{13}C HSQC (fragment of the spectrum).

NMR AND MASS SPECTRA

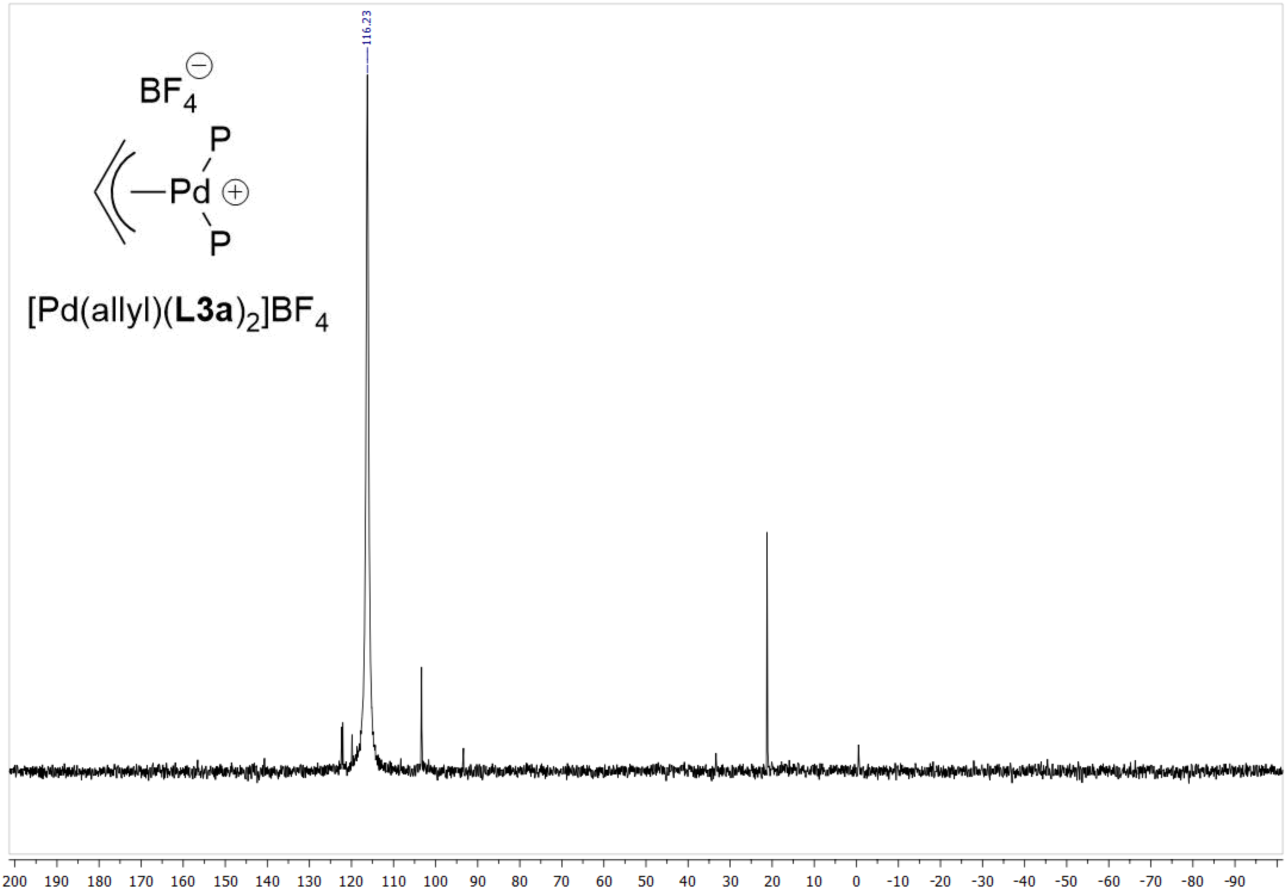


[Pd(allyl)(**L1a**)]BF_4, ^1H-^{13}C HMBC (fragment of the spectrum).

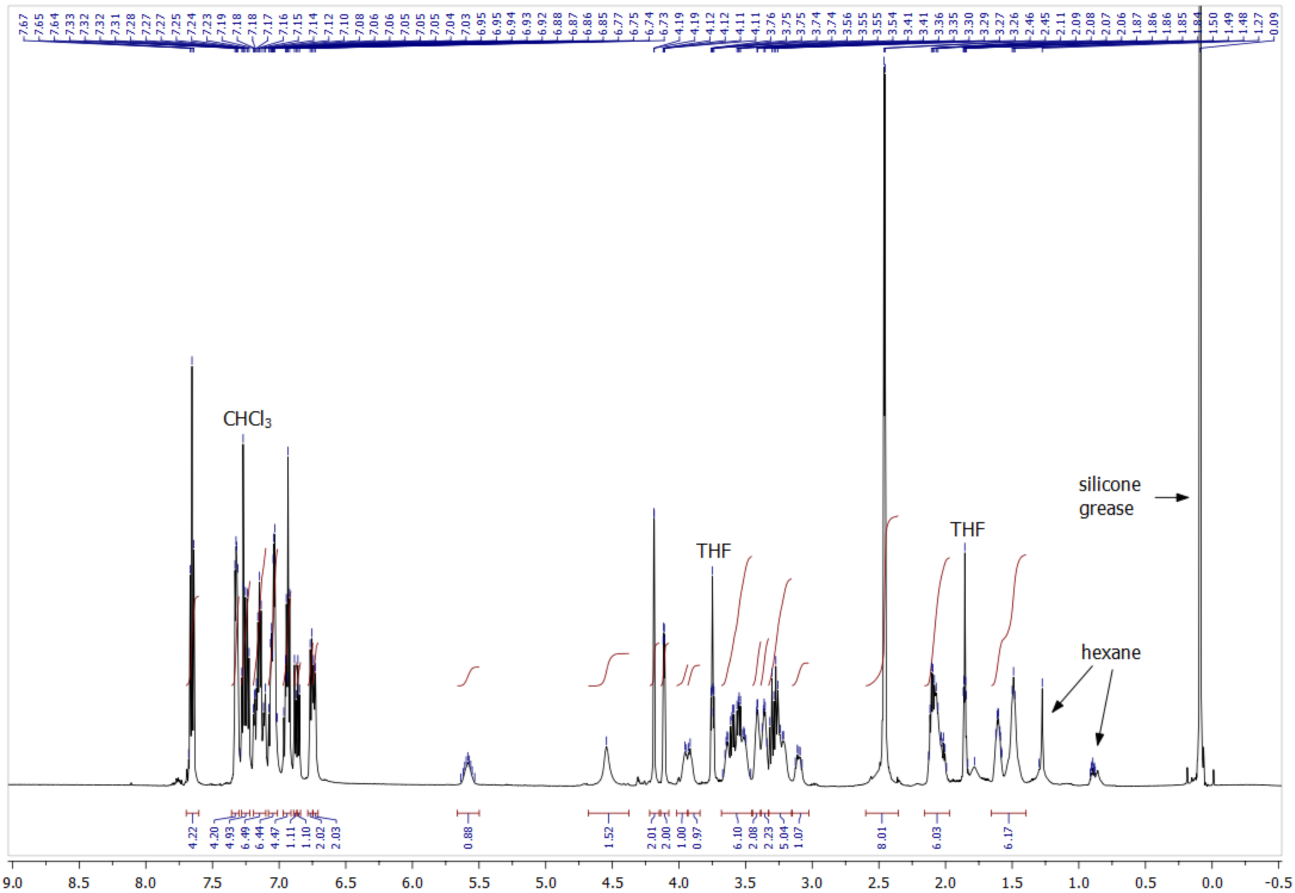


[Pd(allyl)(**L1a**)]BF_4, DOSY.

NMR AND MASS SPECTRA

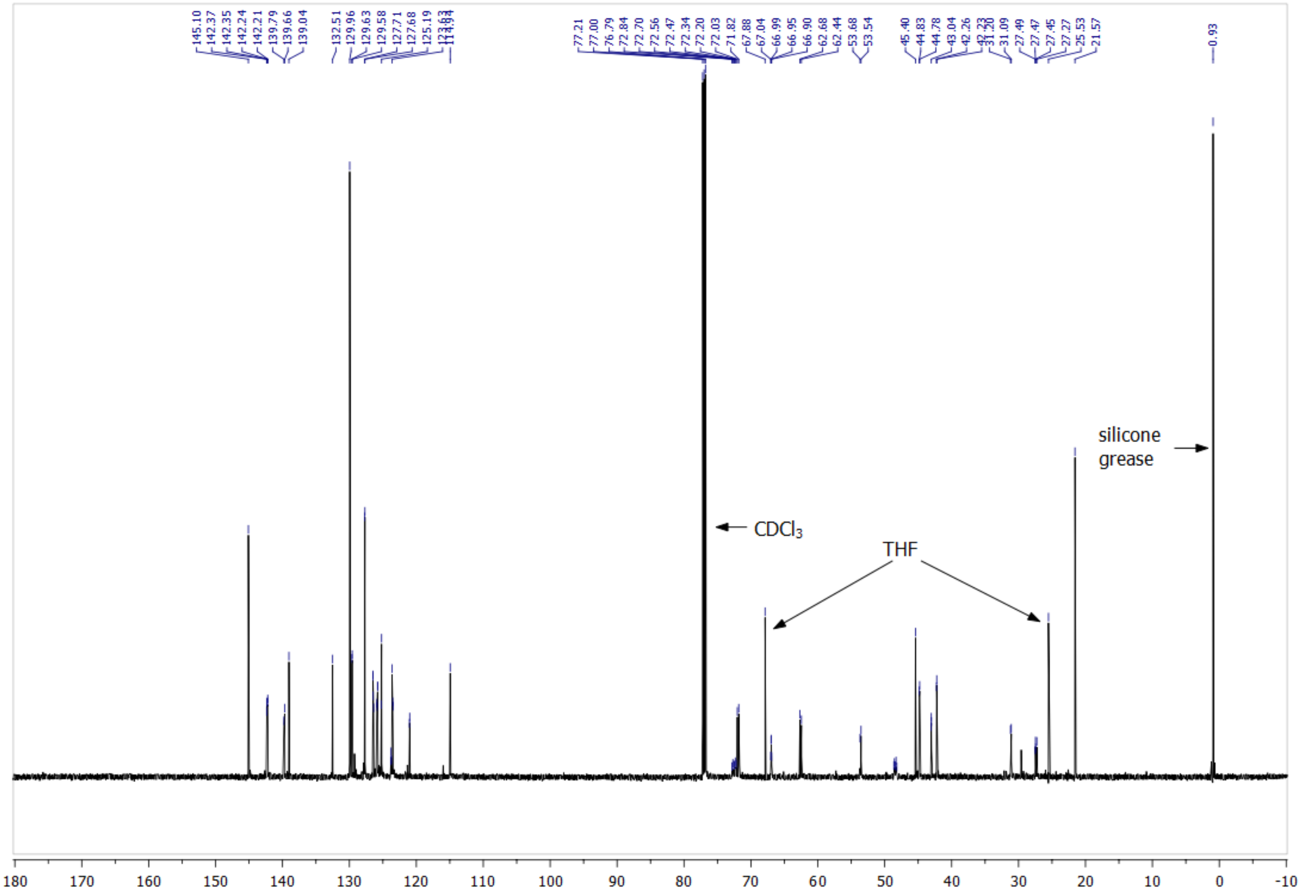


[Pd(allyl)(**L3a**)$_2$]BF$_4$, ^{31}P{^{1}H} (242.9 MHz, CDCl$_3$, 30 °C).

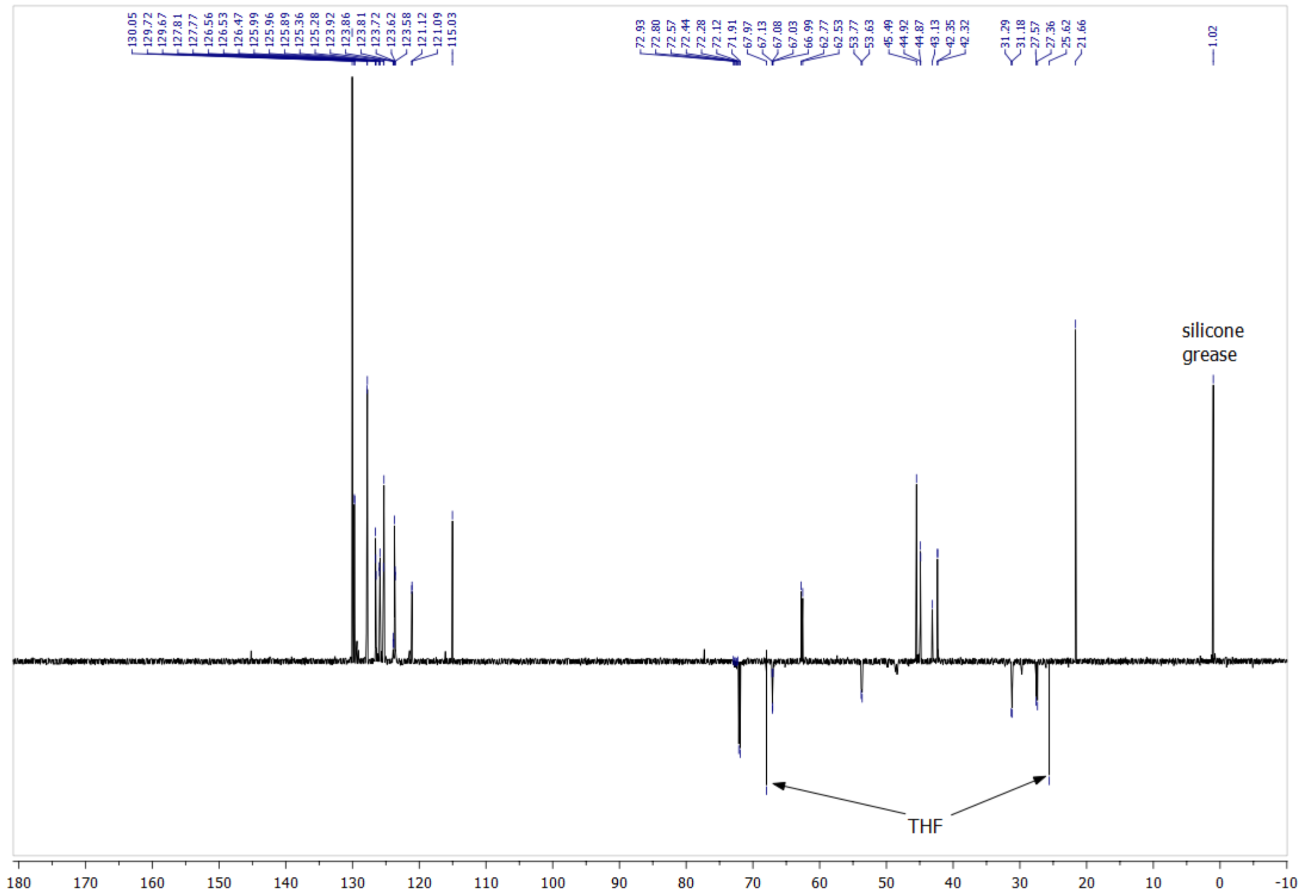


[Pd(allyl)(**L3a**)$_2$]BF$_4$, ^{1}H (600.1 MHz, CDCl$_3$, 30 °C).

NMR AND MASS SPECTRA

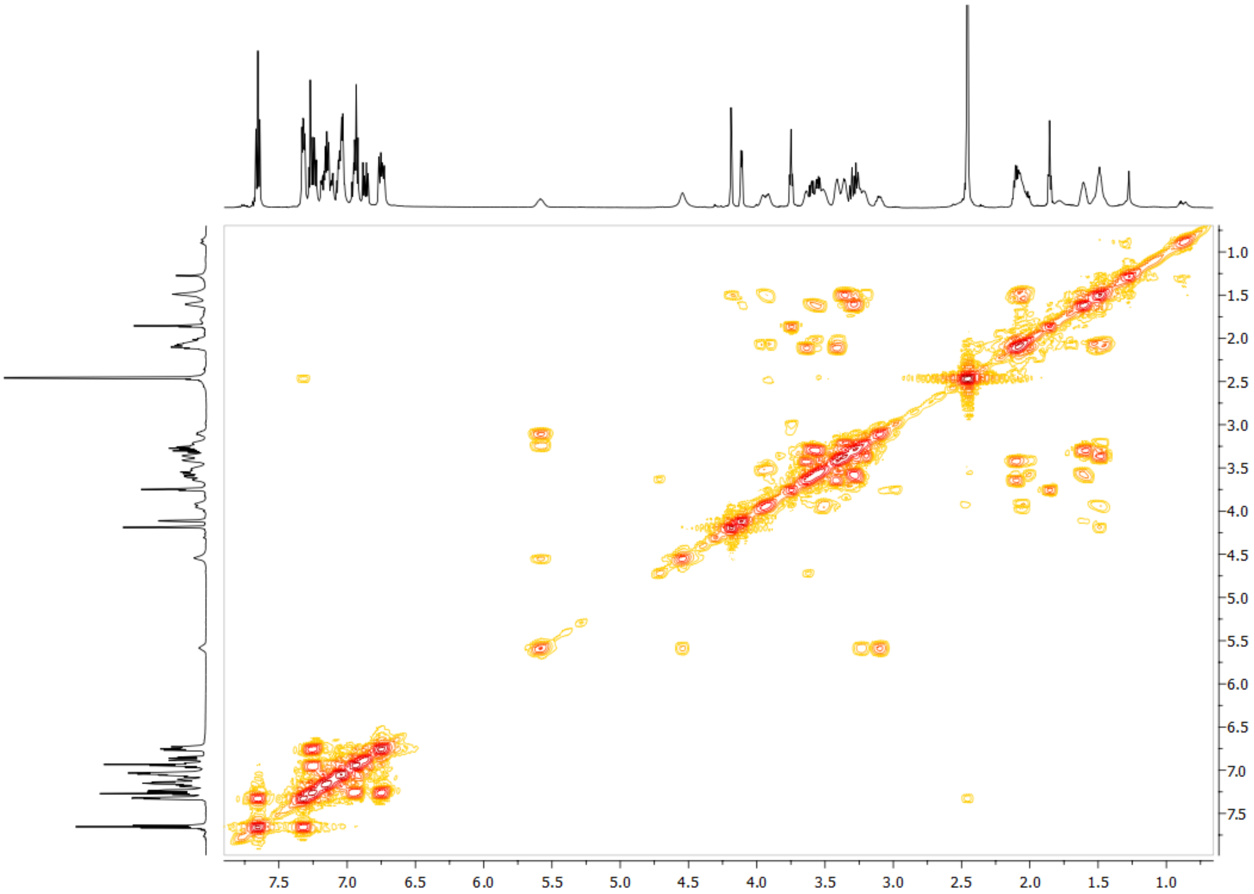


[Pd(allyl)(**L3a**)$_2$]BF_4, $^{13}C\{^1H\}$ (150.9 MHz, $CDCl_3$, 30 °C).

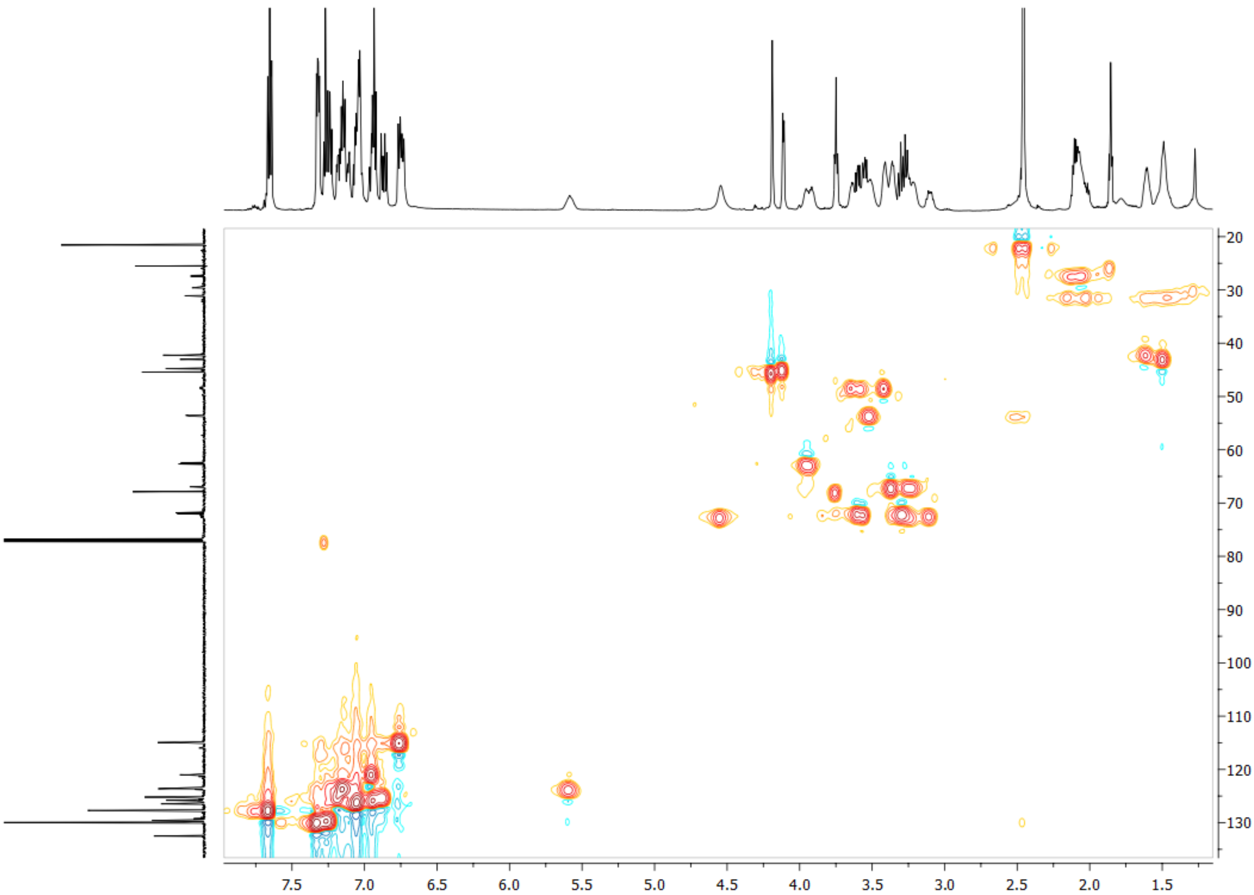


[Pd(allyl)(**L3a**)$_2$]BF_4, $^{13}C\{^1H\}$ DEPT (150.9 MHz, $CDCl_3$, 30 °C).

NMR AND MASS SPECTRA

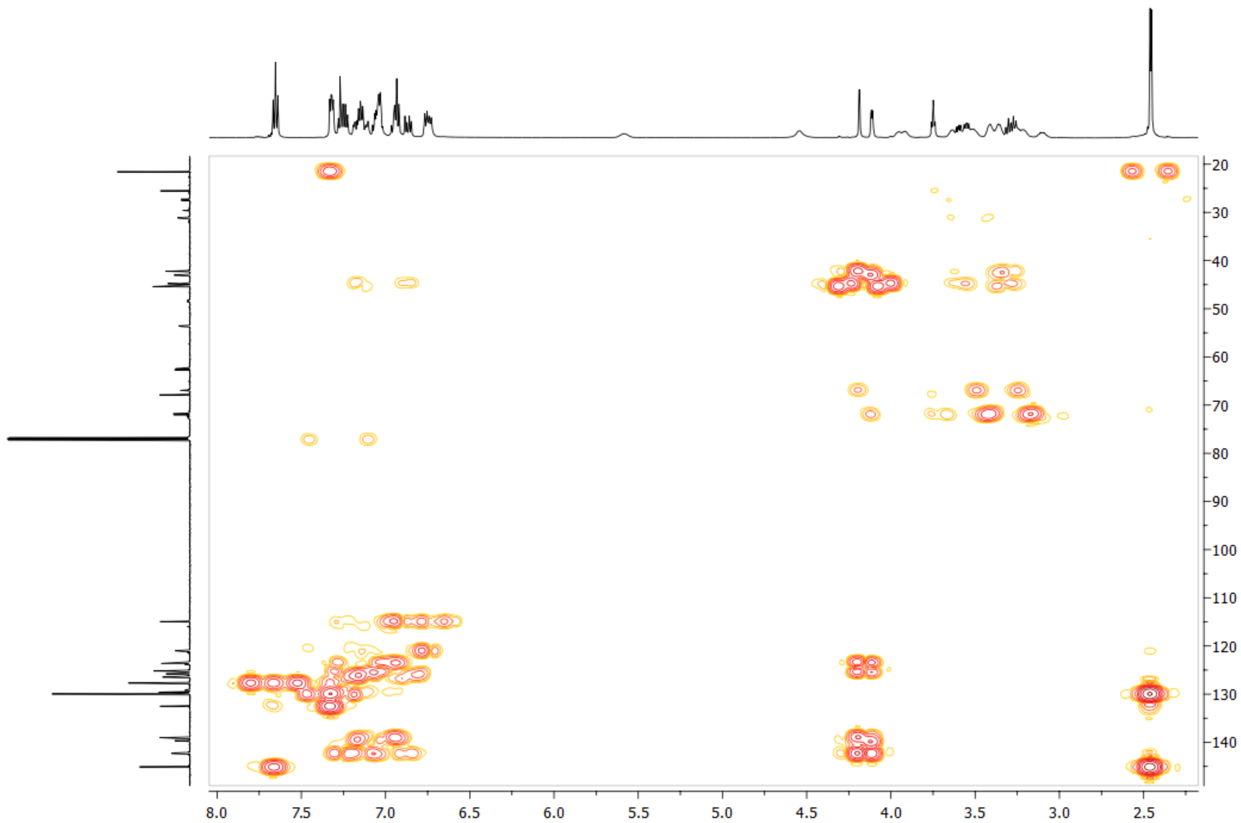


[Pd(allyl)(**L3a**)$_2$]BF_4, ^{1}H-^{1}H COSY.

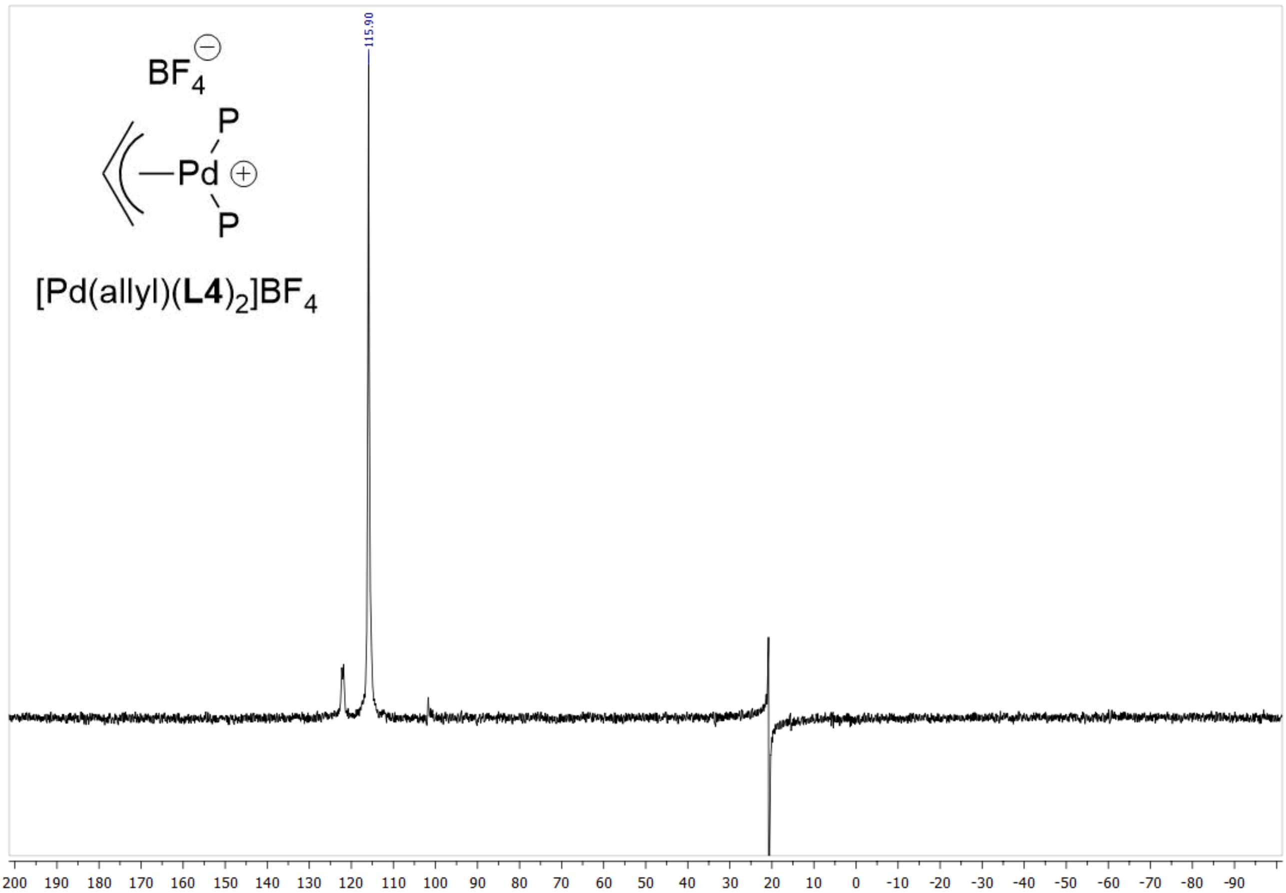


[Pd(allyl)(**L3a**)$_2$]BF_4, ^{1}H-^{13}C HSQC.

NMR AND MASS SPECTRA

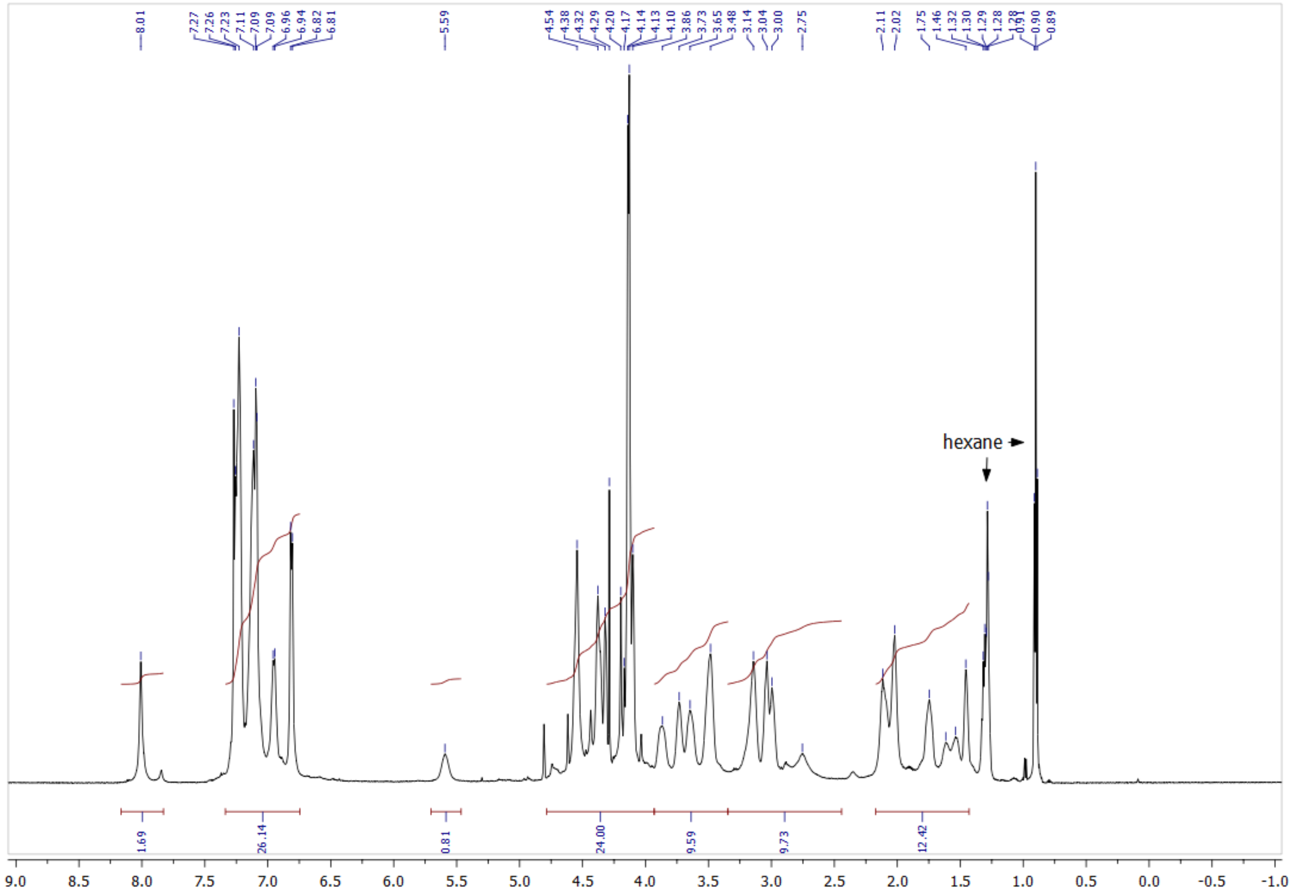


[Pd(allyl)(**L3a**)$_2$]BF_4, ^{1}H-^{13}C HMBC.

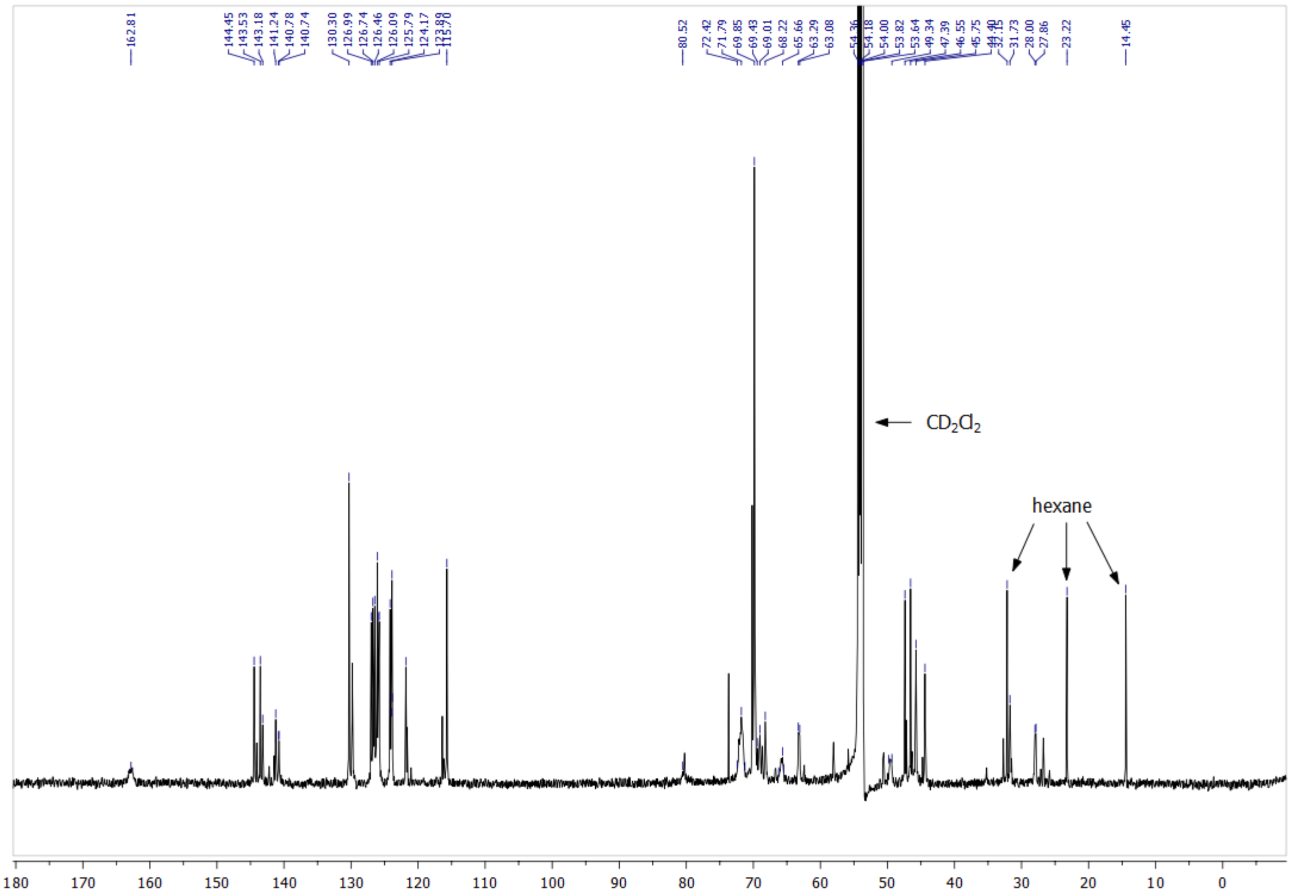


[Pd(allyl)(**L4**)$_2$]BF_4, ^{31}P{^{1}H} (242.9 MHz, $CDCl_3$, 30 °C).

NMR AND MASS SPECTRA

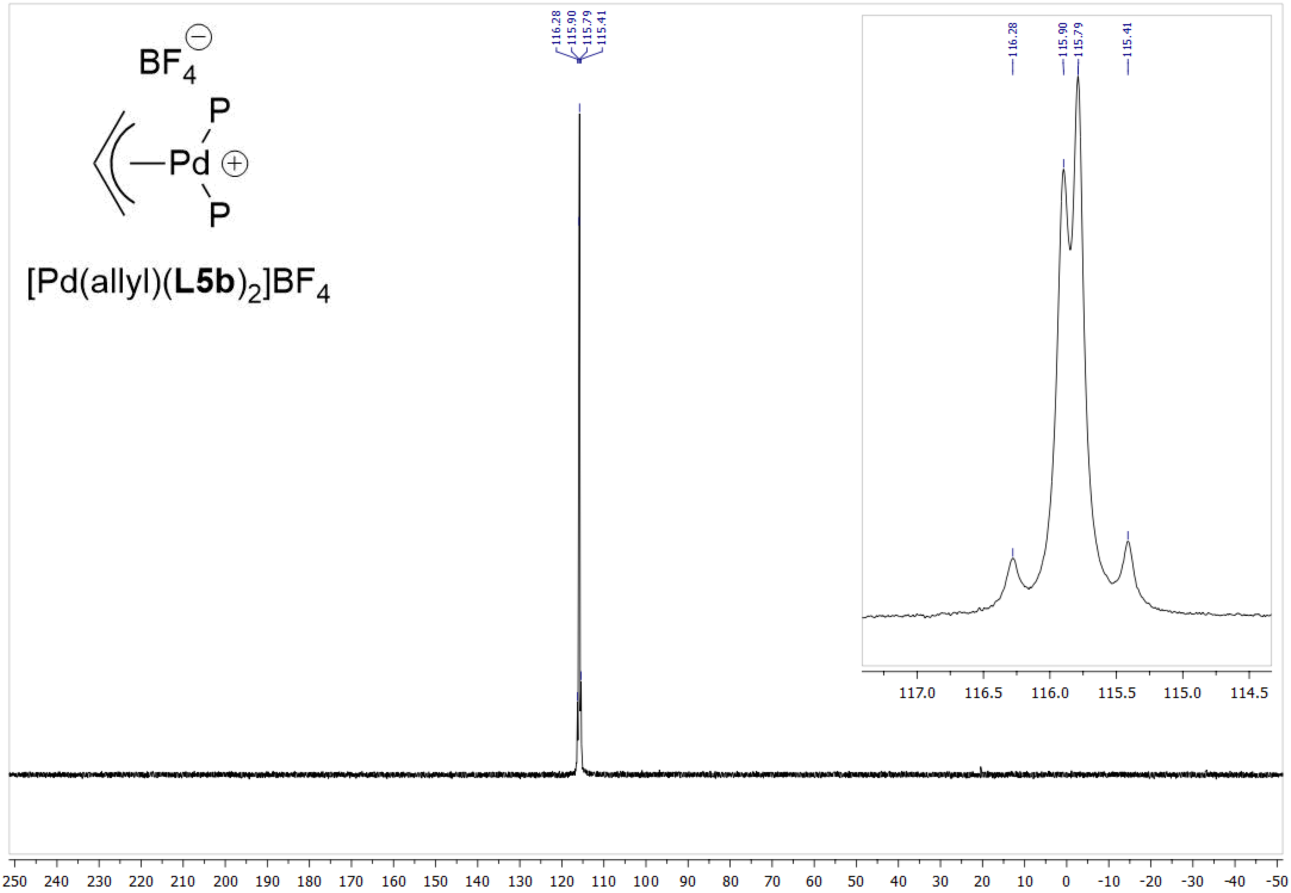


[Pd(allyl)(**L4**)$_2$]BF$_4$, ^{1}H (600.1 MHz, $CDCl_3$, 30 °C).

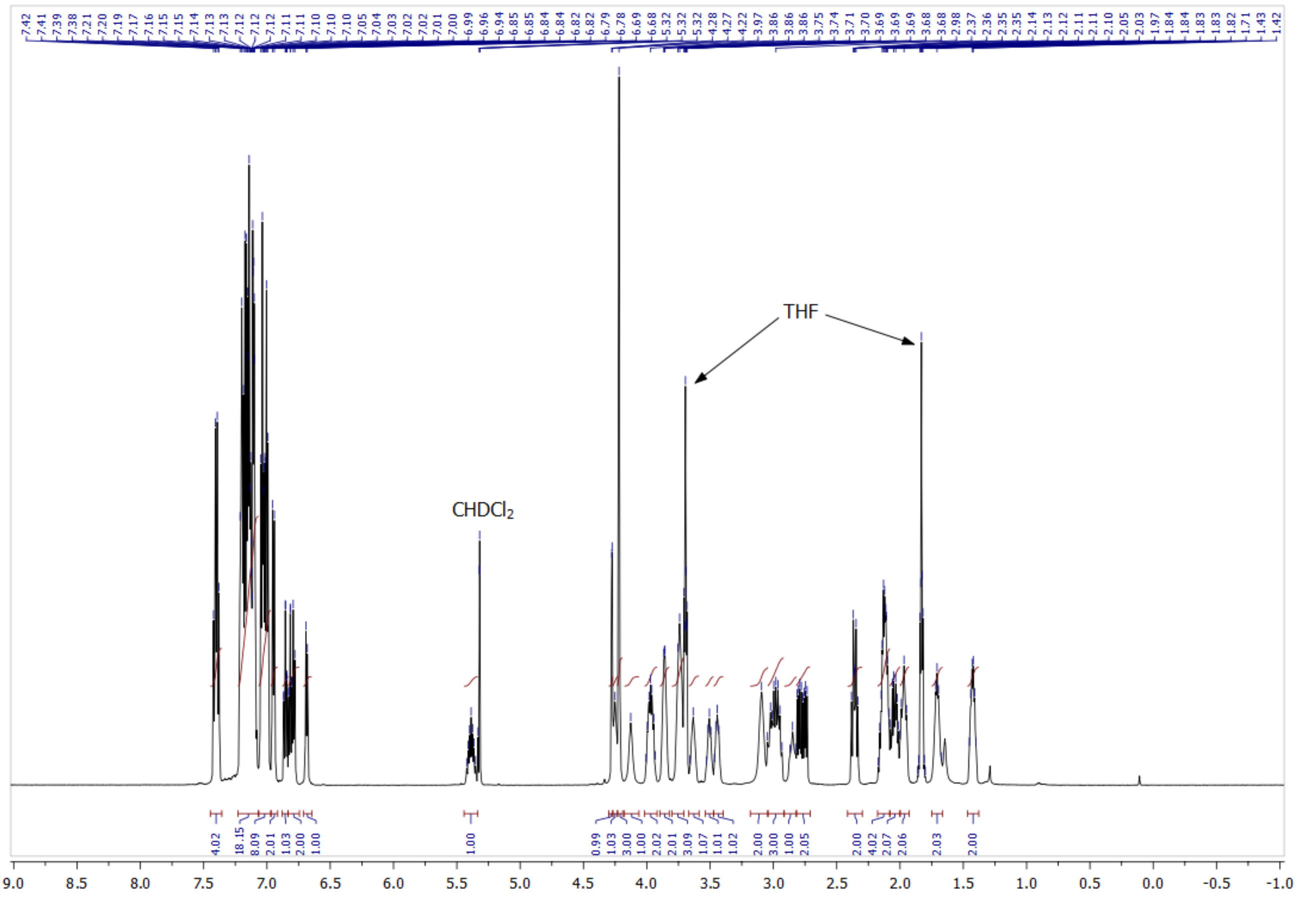


[Pd(allyl)(**L4**)$_2$]BF$_4$, ^{13}C{^{1}H} (150.9 MHz, $CDCl_3$, 30 °C).

NMR AND MASS SPECTRA

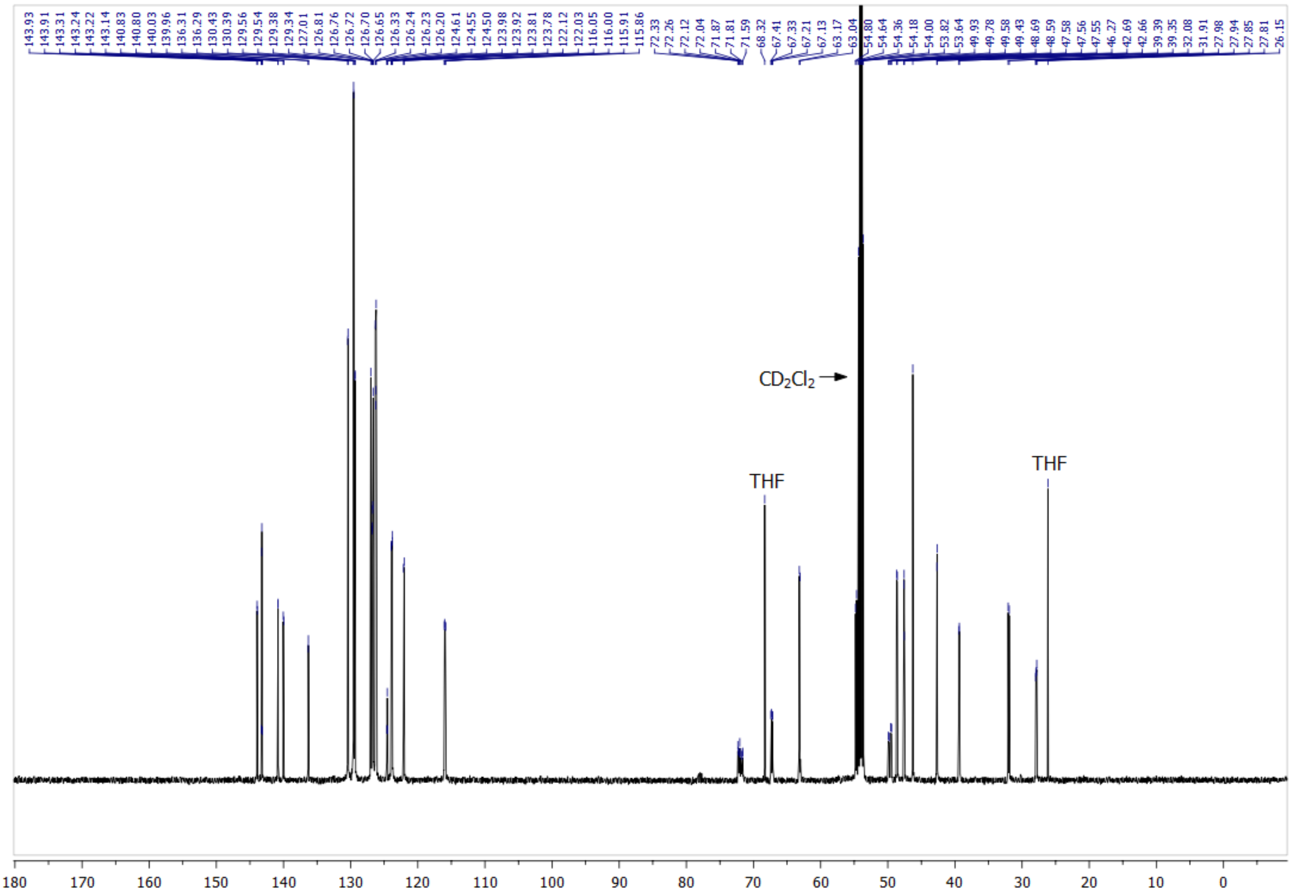


[Pd(allyl)(**L5b**)$_2$]BF_4, $^{31}P\{^1H\}$ (242.9 MHz, $CDCl_3$, 30 °C).

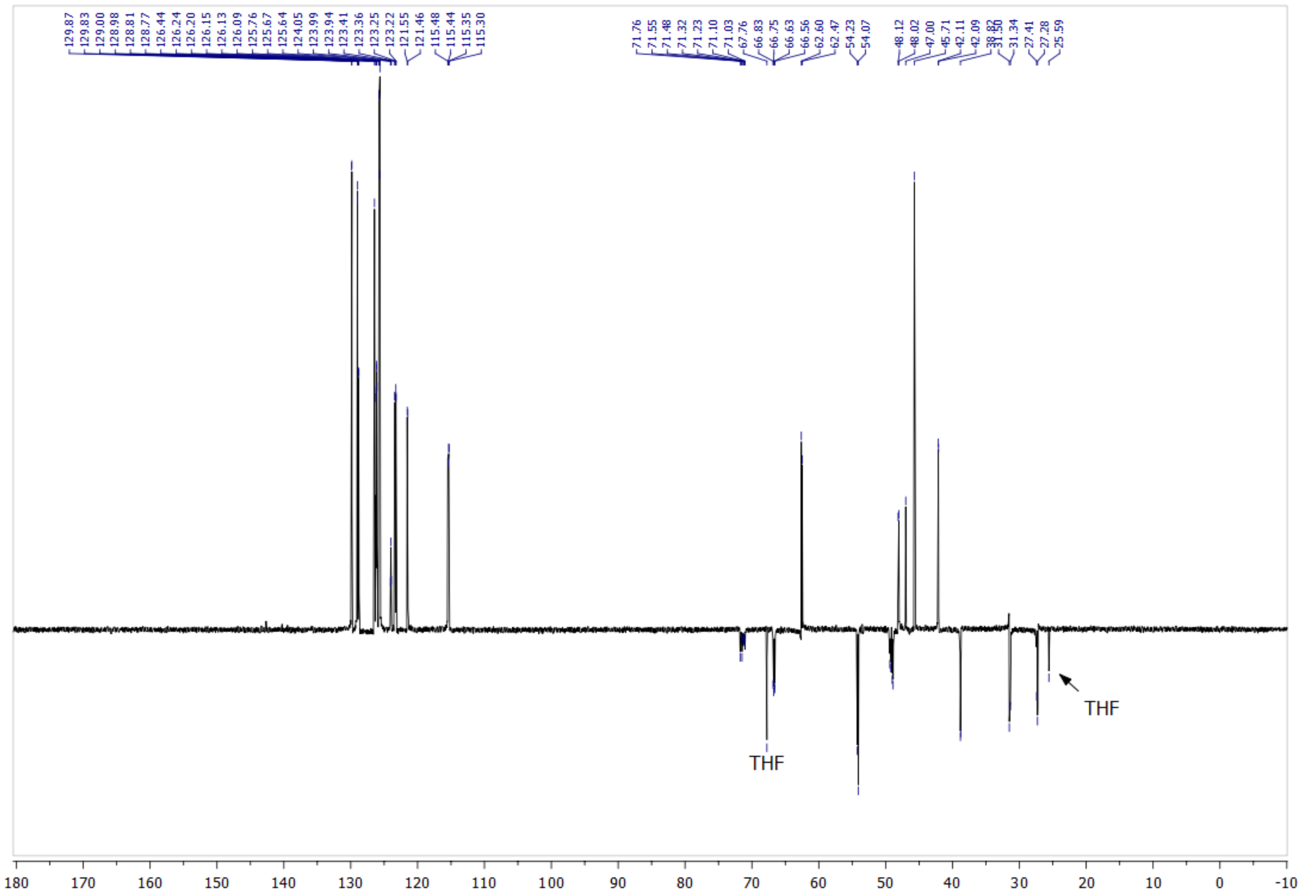


[Pd(allyl)(**L5b**)$_2$]BF_4, ^1H (600.1 MHz, $CDCl_3$, 30 °C).

NMR AND MASS SPECTRA

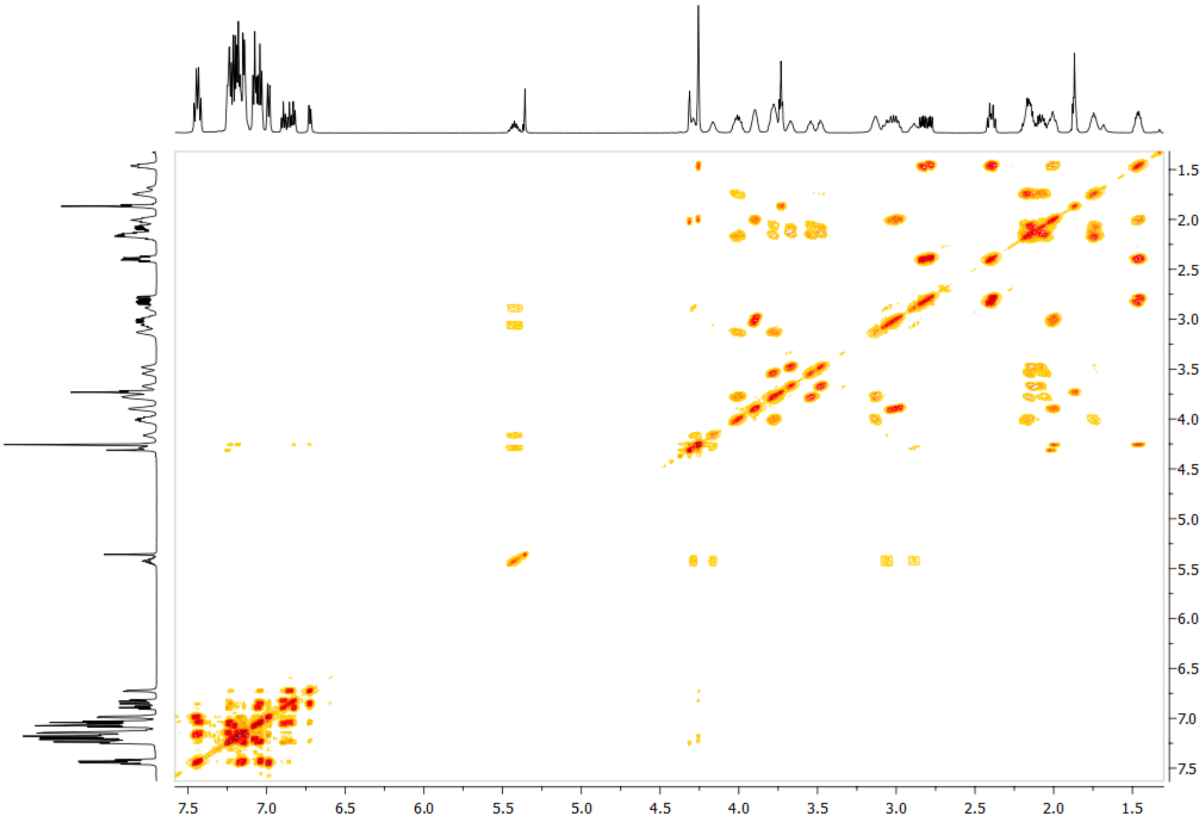


[Pd(allyl)(**L5b**)$_2$]BF_4, $^{13}C\{^1H\}$ (150.9 MHz, $CDCl_3$, 30 °C).

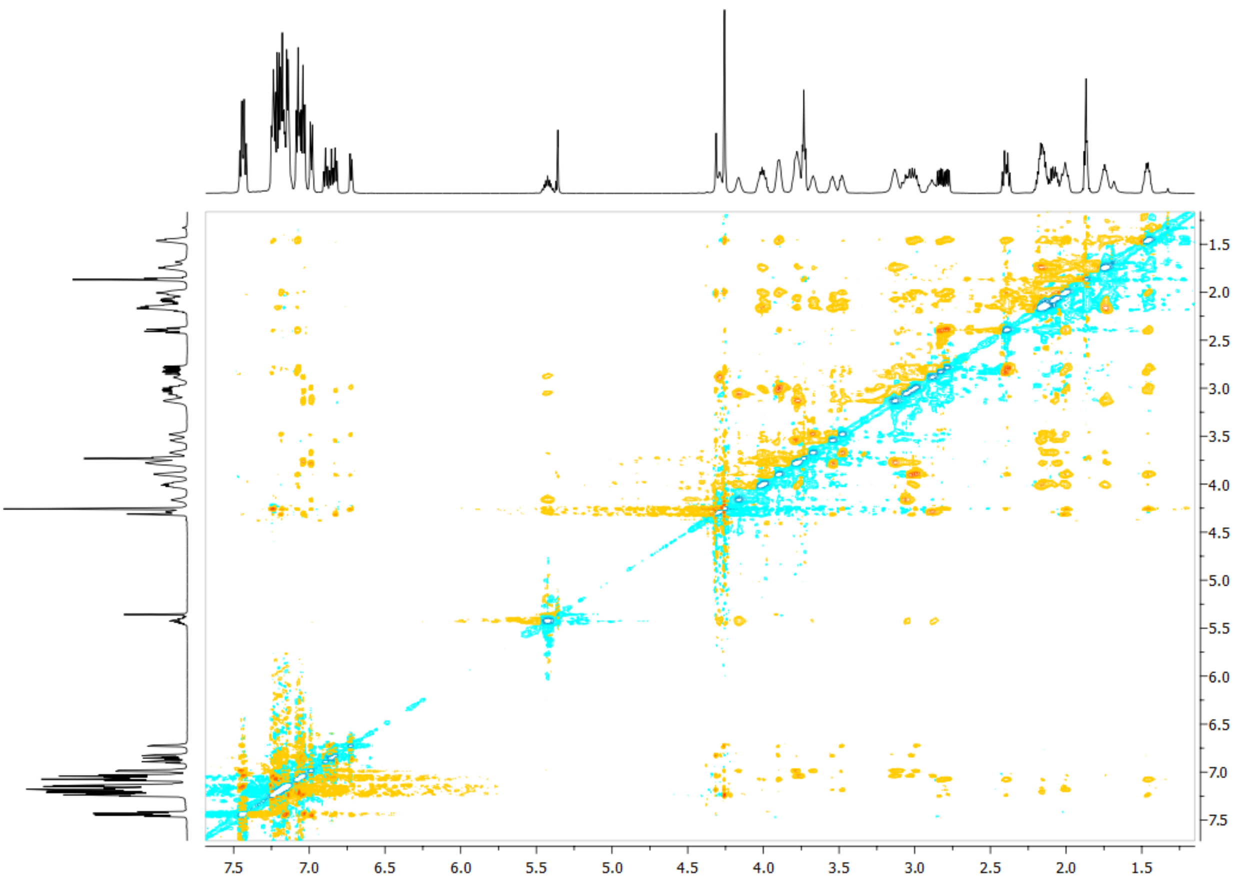


[Pd(allyl)(**L5b**)$_2$]BF_4, $^{13}C\{^1H\}$ DEPT (150.9 MHz, $CDCl_3$, 30 °C).

NMR AND MASS SPECTRA

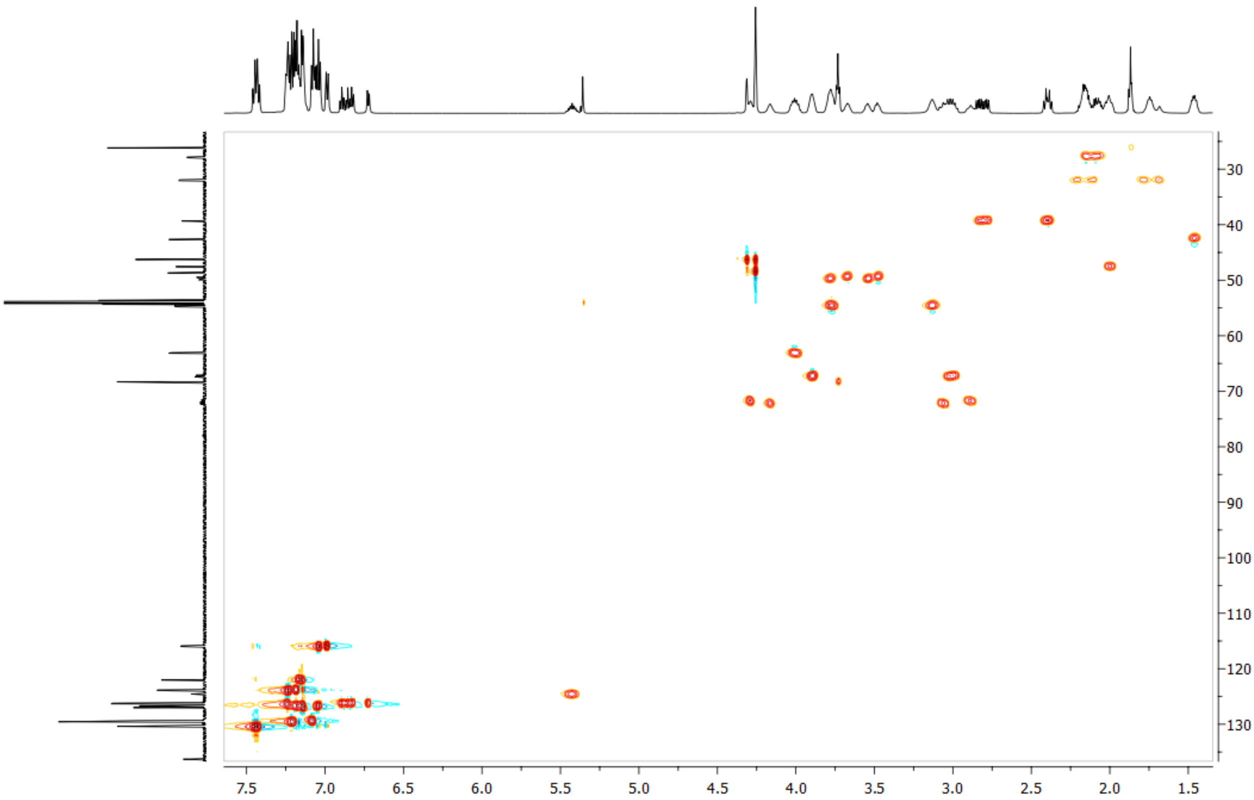


[Pd(allyl)(**L5b**)$_2$]BF$_4$, ^{1}H-^{1}H COSY.

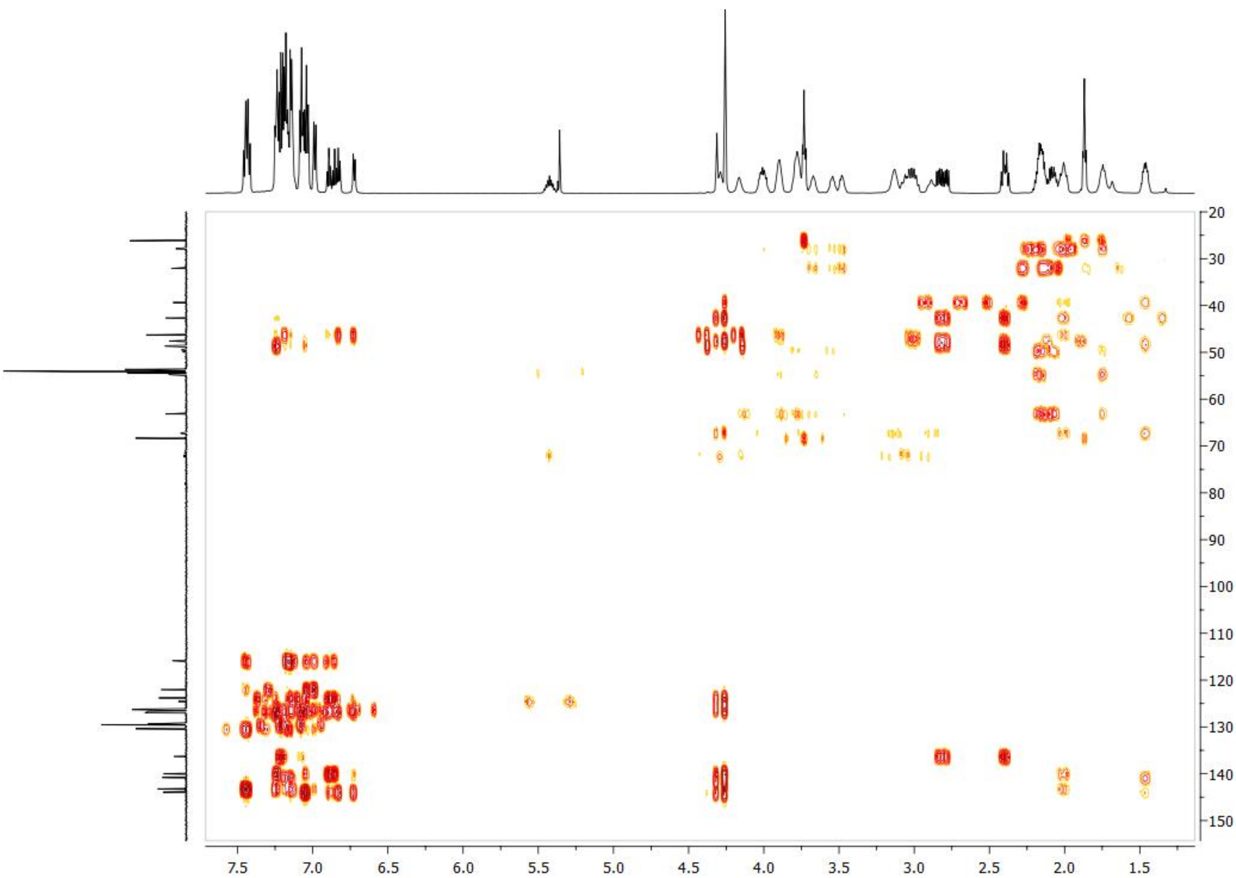


[Pd(allyl)(**L5b**)$_2$]BF$_4$, ^{1}H-^{1}H NOESY.

NMR AND MASS SPECTRA

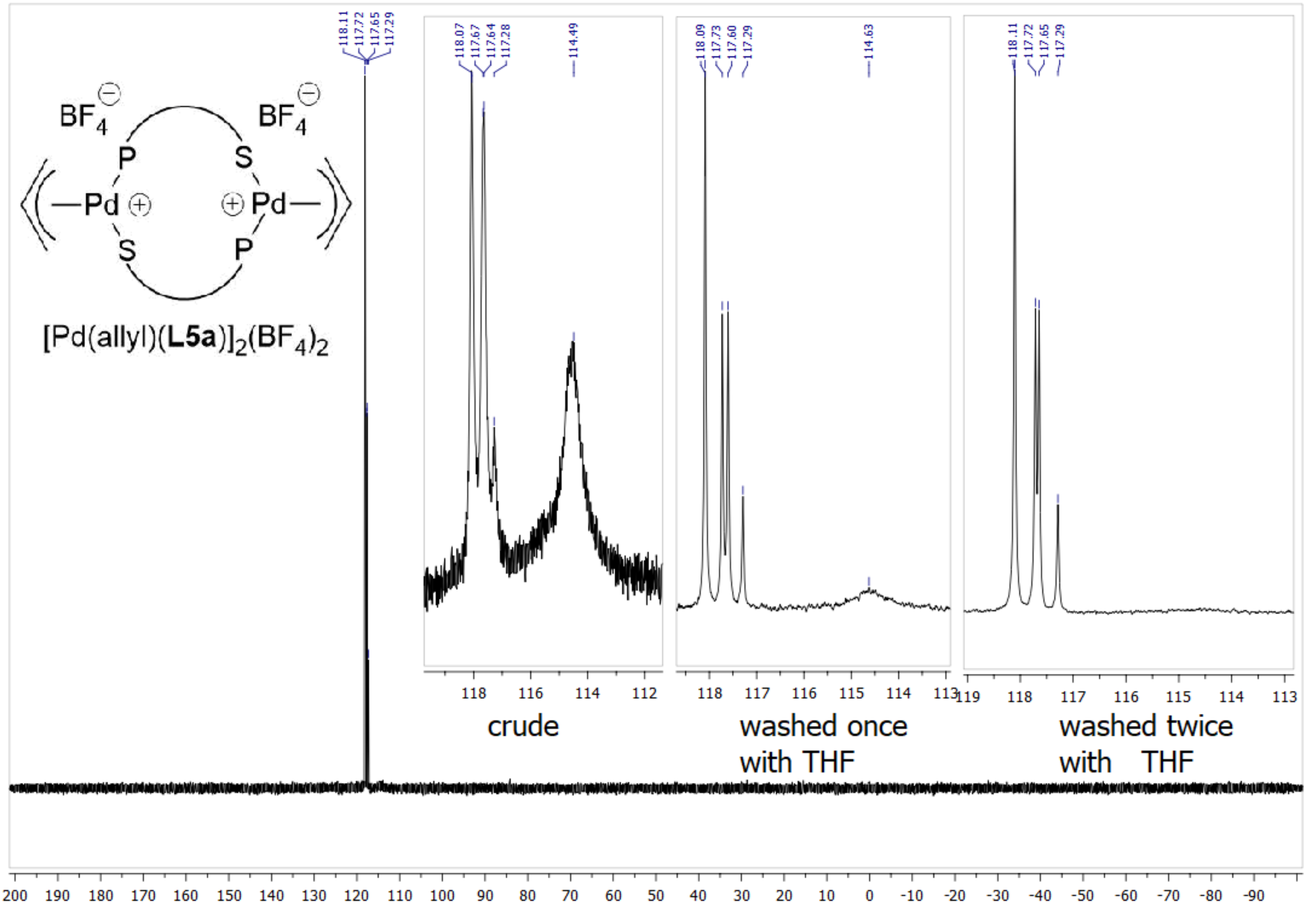


[Pd(allyl)(**L5b**)$_2$]BF_4, ^{1}H-^{13}C HSQC.

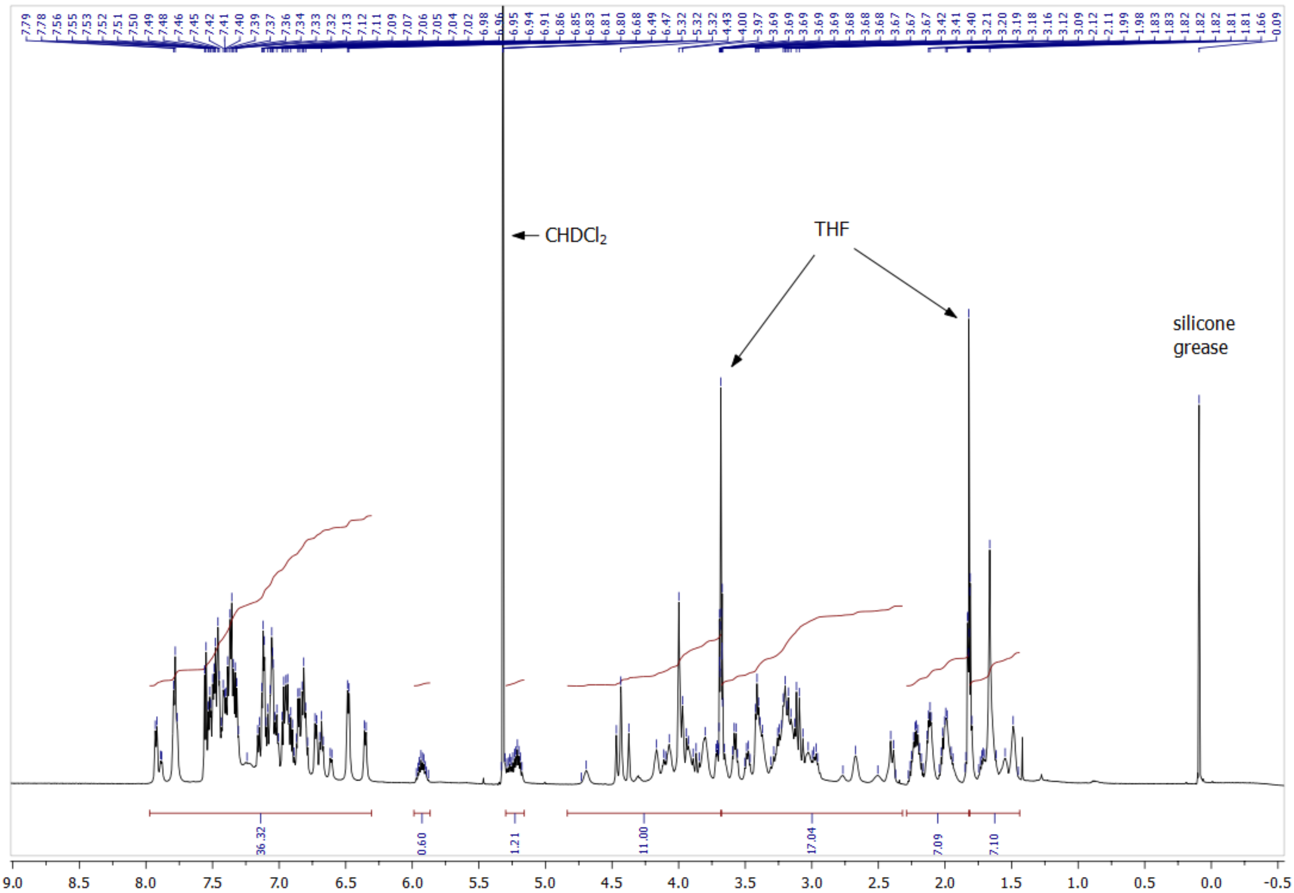


[Pd(allyl)(**L5b**)$_2$]BF_4, ^{1}H-^{13}C HMBC.

NMR AND MASS SPECTRA

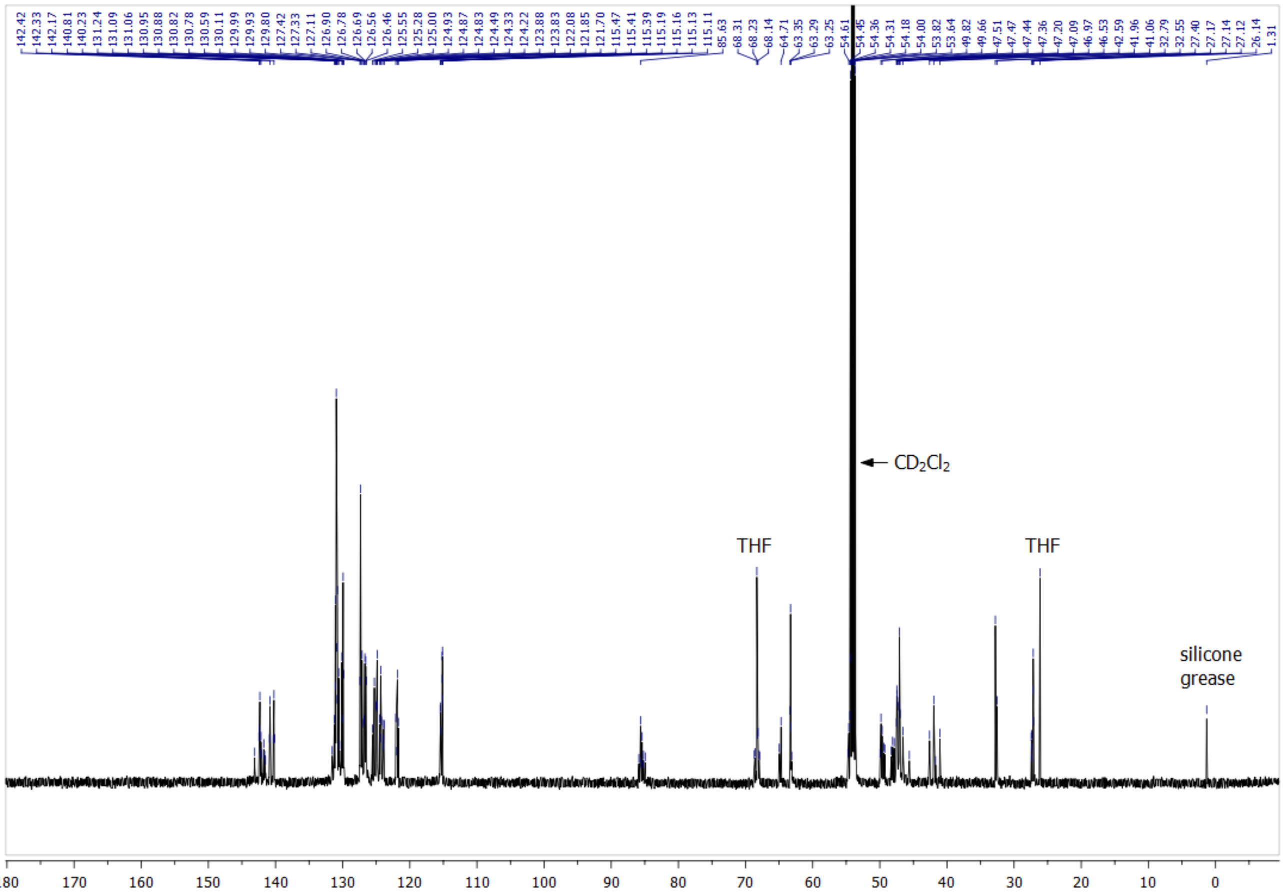


[Pd(allyl)(**L5a**)]$_2$(BF$_4$)$_2$, ^{31}P{^{1}H} (242.9 MHz, CDCl$_3$, 30 °C).

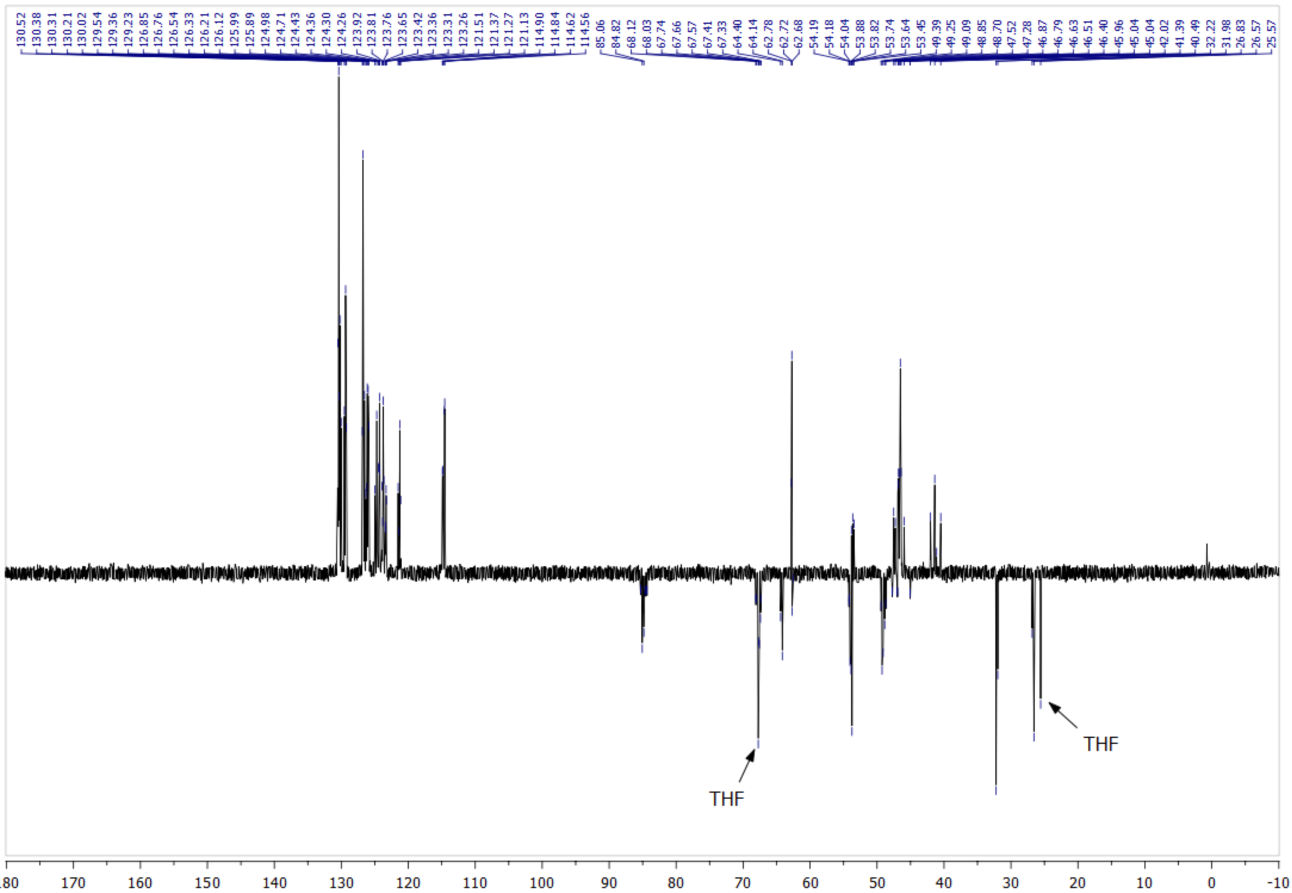


[Pd(allyl)(**L5a**)]$_2$(BF$_4$)$_2$, ^{1}H (600.1 MHz, CDCl$_3$, 30 °C).

NMR AND MASS SPECTRA

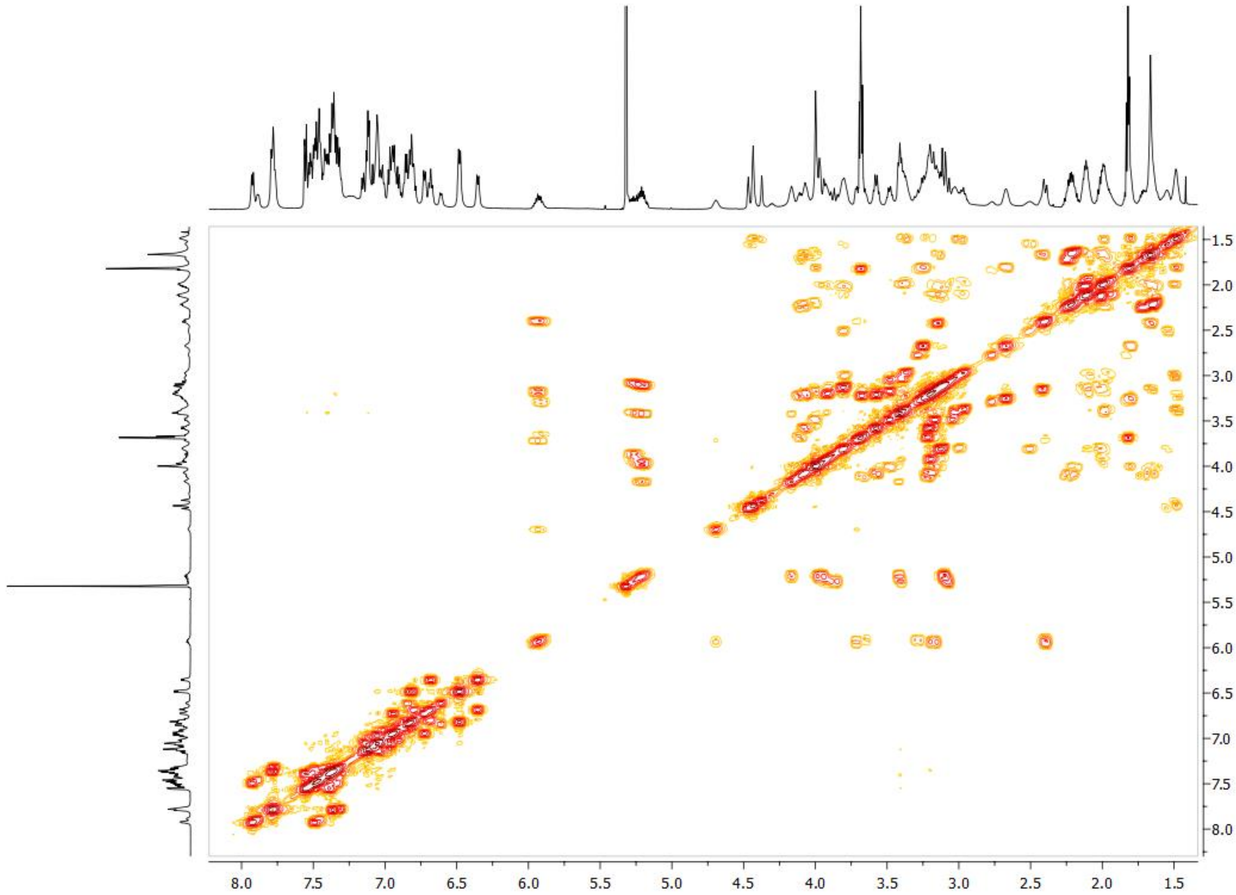


[Pd(allyl)(**L5a**)]$_2$(BF$_4$)$_2$, ^{13}C{^{1}H} (150.9 MHz, CDCl$_3$, 30 °C).

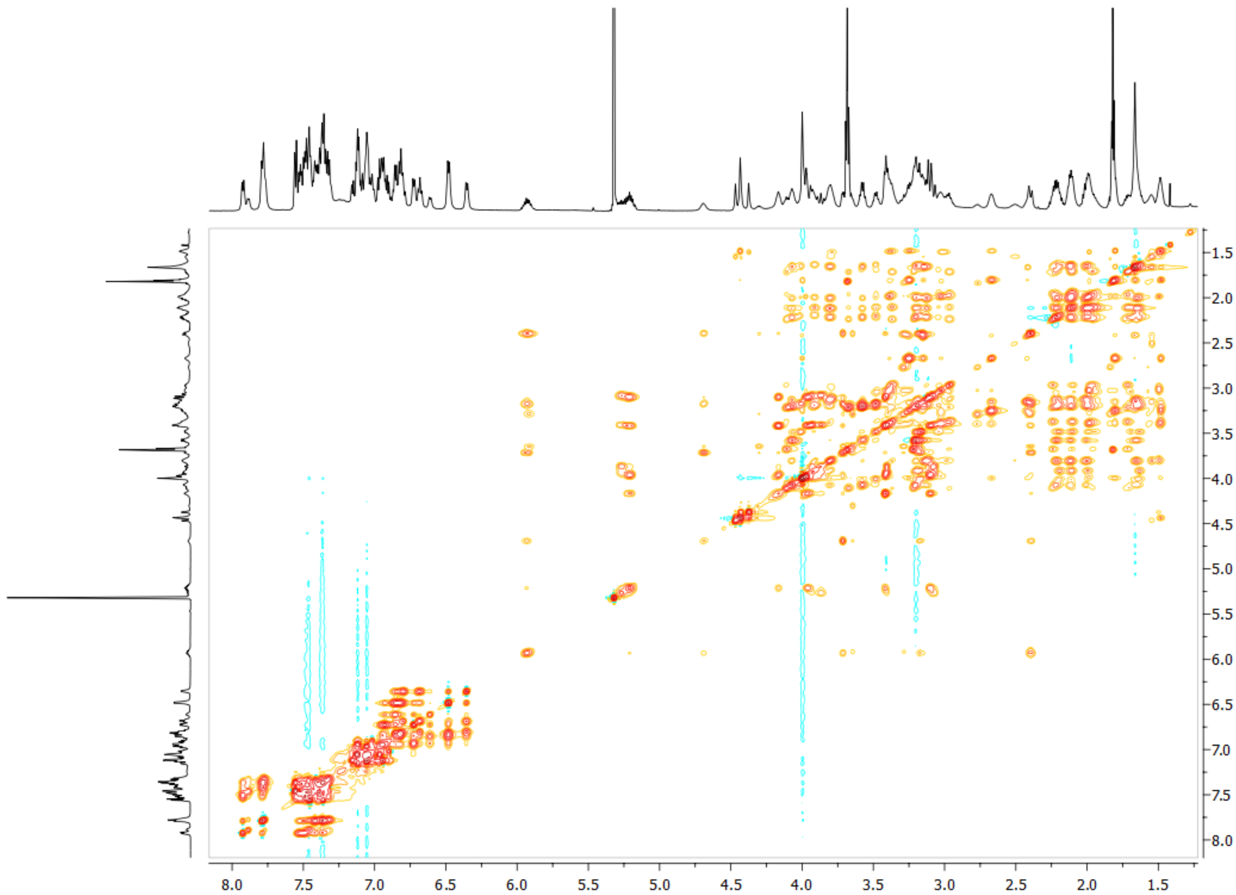


[Pd(allyl)(**L5a**)]$_2$(BF$_4$)$_2$, ^{13}C{^{1}H} DEPT (150.9 MHz, CDCl$_3$, 30 °C).

NMR AND MASS SPECTRA

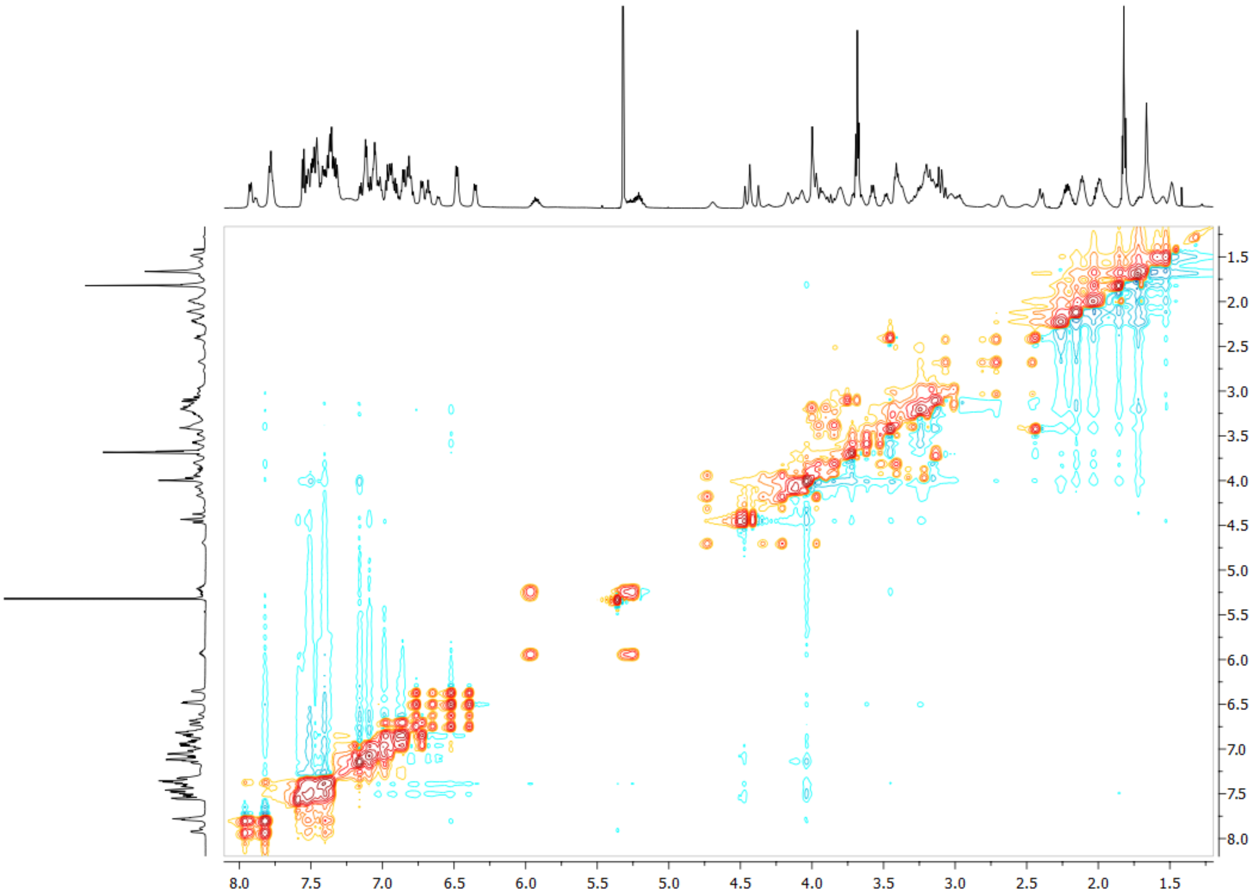


[Pd(allyl)(**L5a**)]$_2$(BF$_4$)$_2$, ^{1}H-^{1}H COSY.

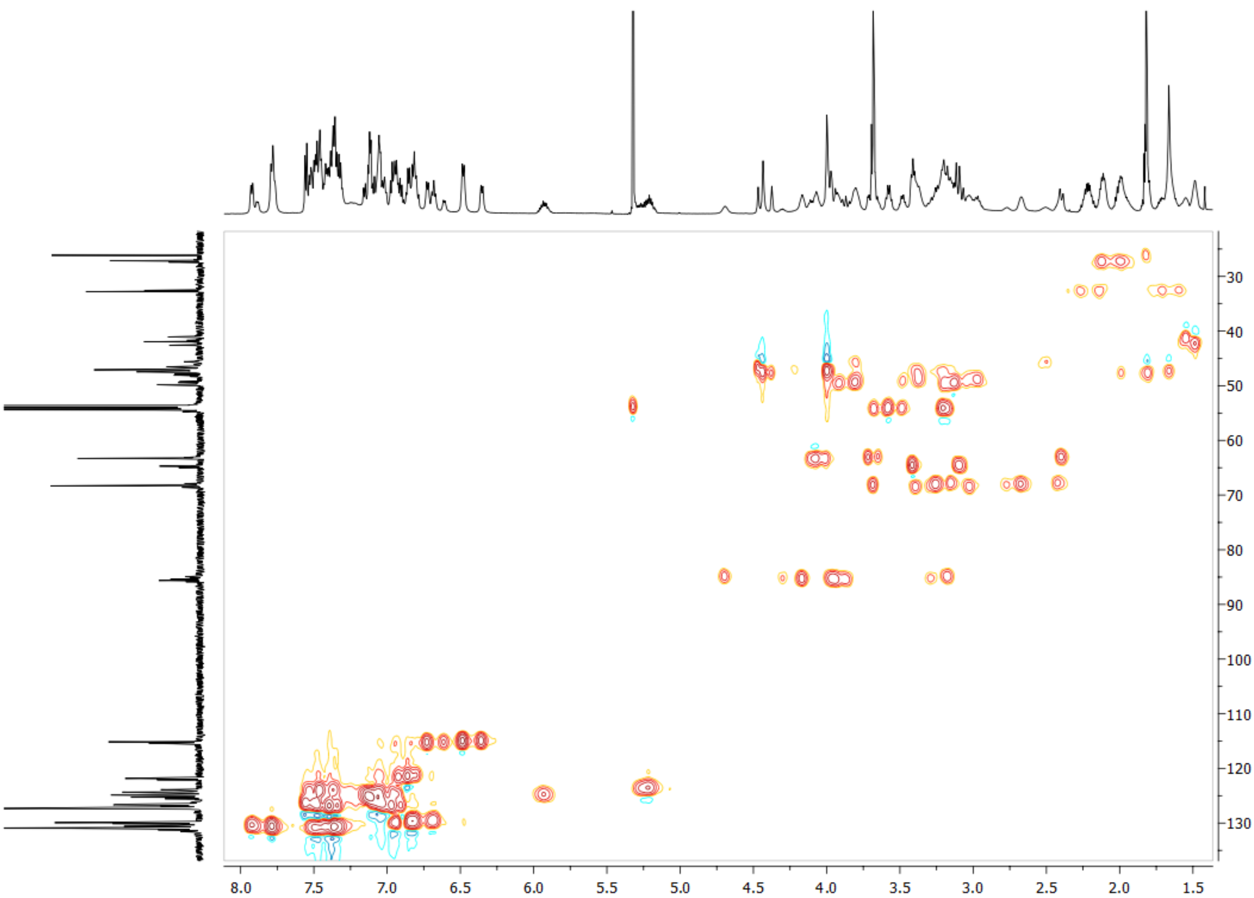


[Pd(allyl)(**L5a**)]$_2$(BF$_4$)$_2$, ^{1}H-^{1}H TOCSY.

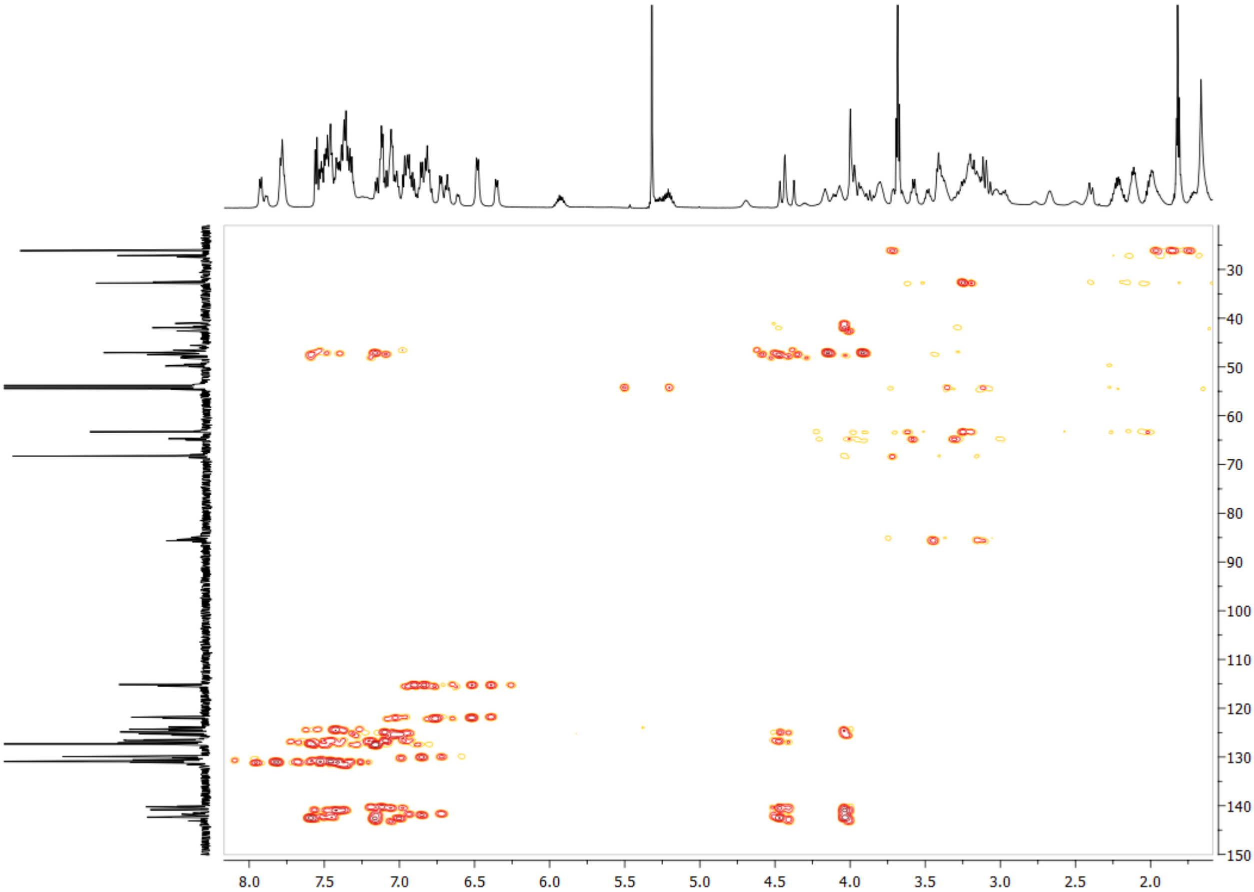
NMR AND MASS SPECTRA



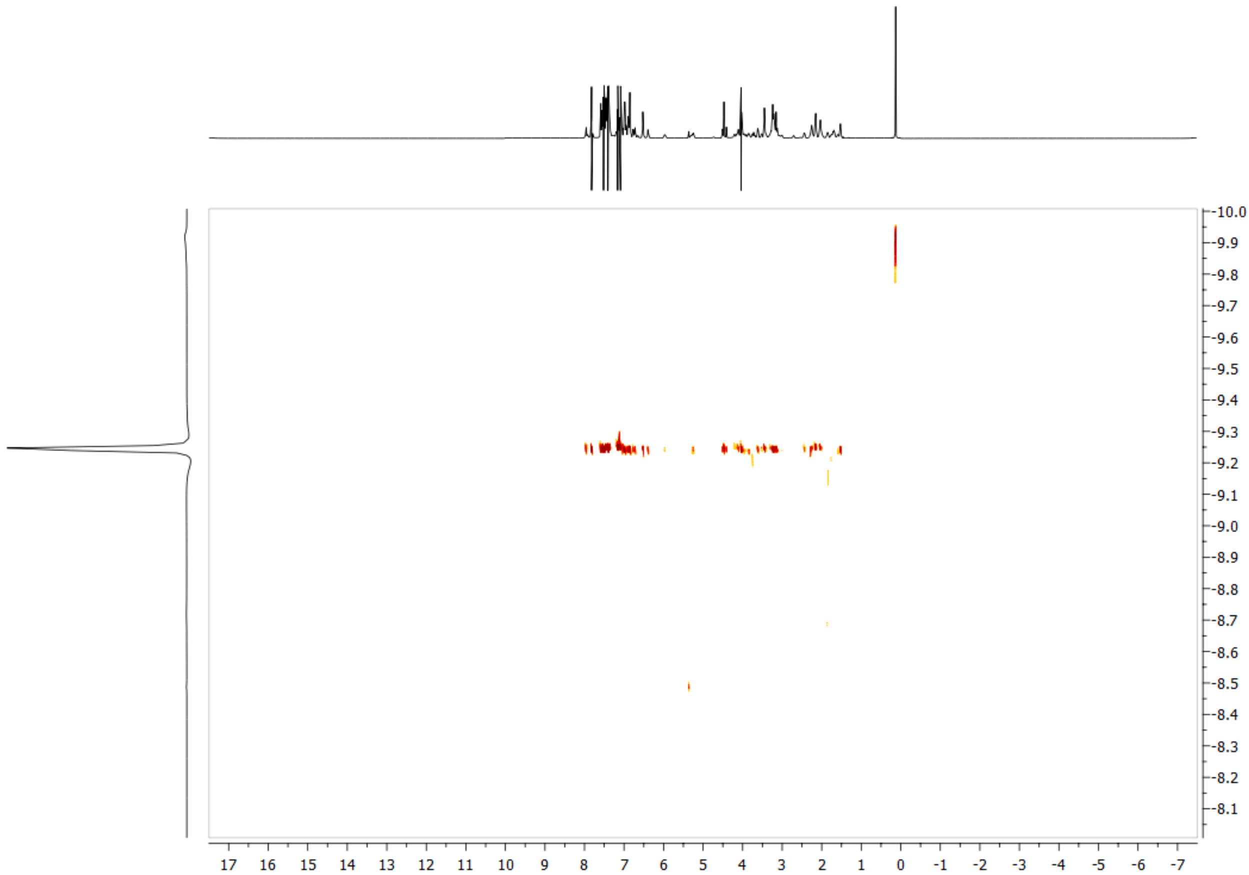
[Pd(allyl)(**L5a**)]$_2$(BF$_4$)$_2$, ^{1}H-^{1}H NOESY.



[Pd(allyl)(**L5a**)]$_2$(BF$_4$)$_2$, ^{1}H-^{13}C HSQC.

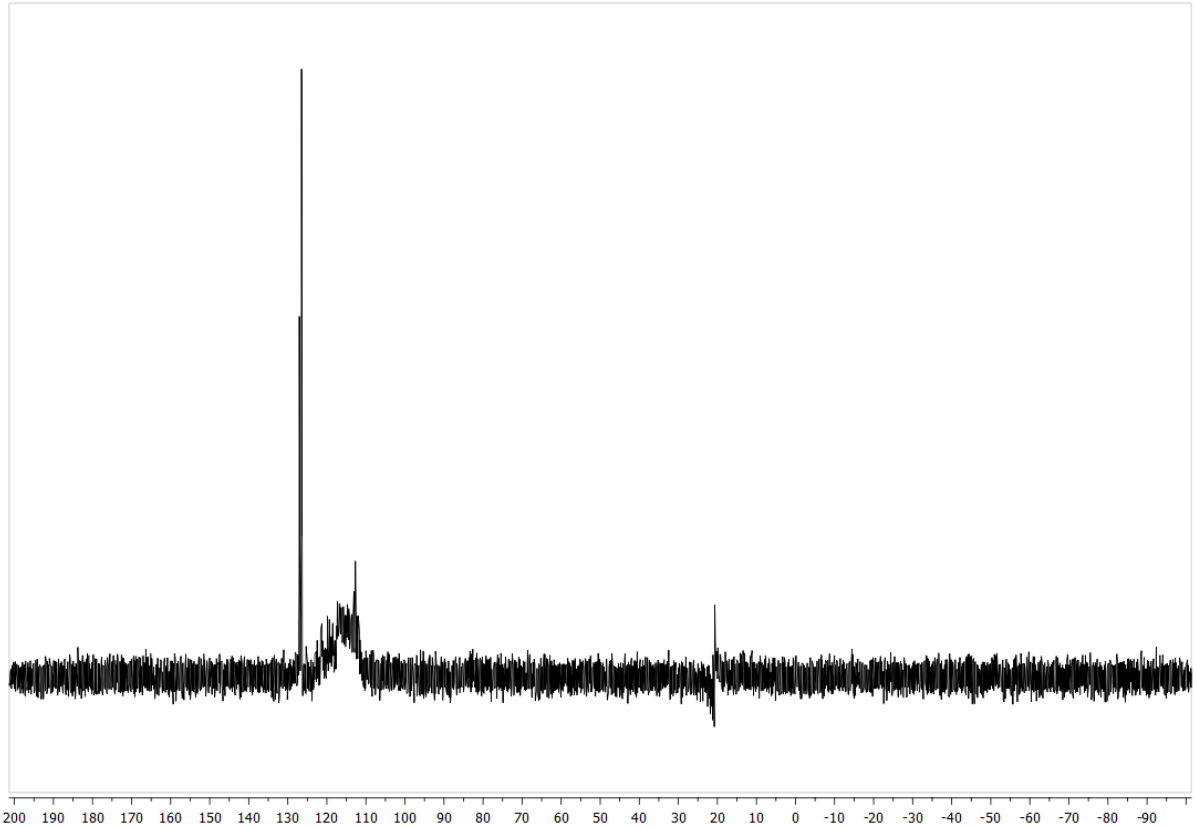


[Pd(allyl)(**L5a**)]$_2$(BF$_4$)$_2$, ^{1}H-^{13}C HMBC.

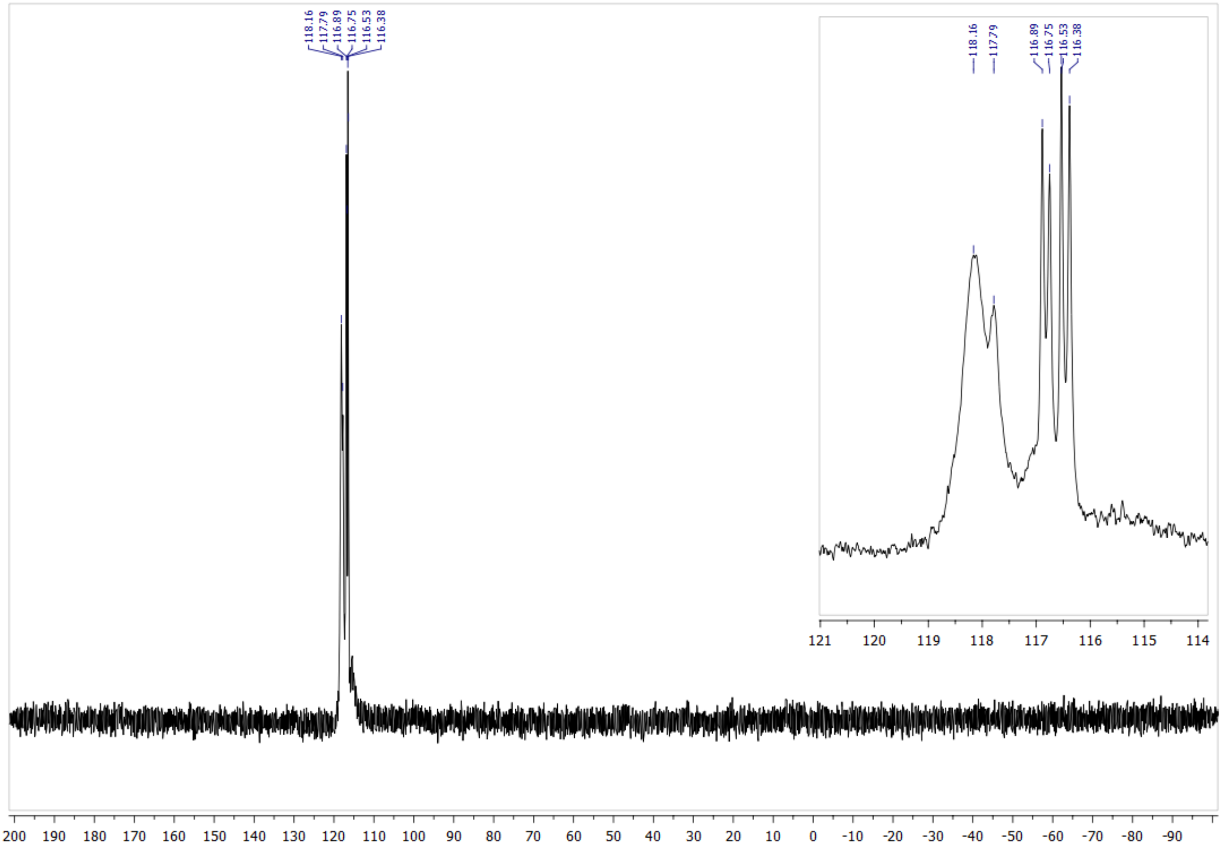


[Pd(allyl)(**L5a**)]$_2$(BF$_4$)$_2$, DOSY.

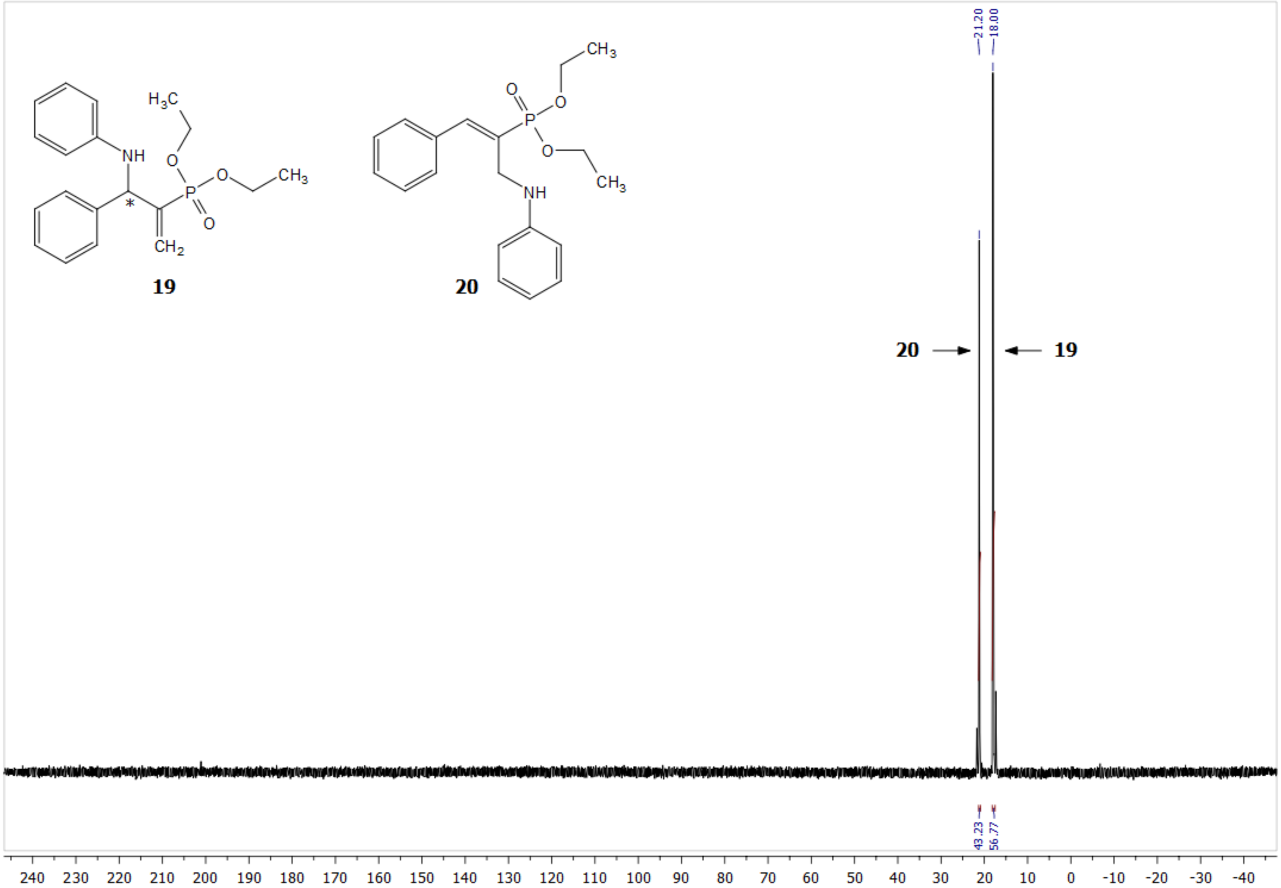
NMR AND MASS SPECTRA



Products of the complexation of **L4** with $[Pd(allyl)Cl]_2$ in the presence of $AgBF_4$ (the molar ratio of L/Pd = 1) $^{31}P\{^1H\}$ (242.9 MHz, $CDCl_3$, 30 °C).



Products of the complexation of **L5b** with $[Pd(allyl)Cl]_2$ in the presence of $AgBF_4$ (the molar ratio of L/Pd = 1) $^{31}P\{^1H\}$ (242.9 MHz, $CDCl_3$, 30 °C).



Pd-catalyzed allylic amination of **18** with aniline (entry 7 in Table 6). $^{31}P\{^{1}H\}$ (202.3 MHz, $CHCl_3$, ambient temp.).

Display Report

Analysis Info

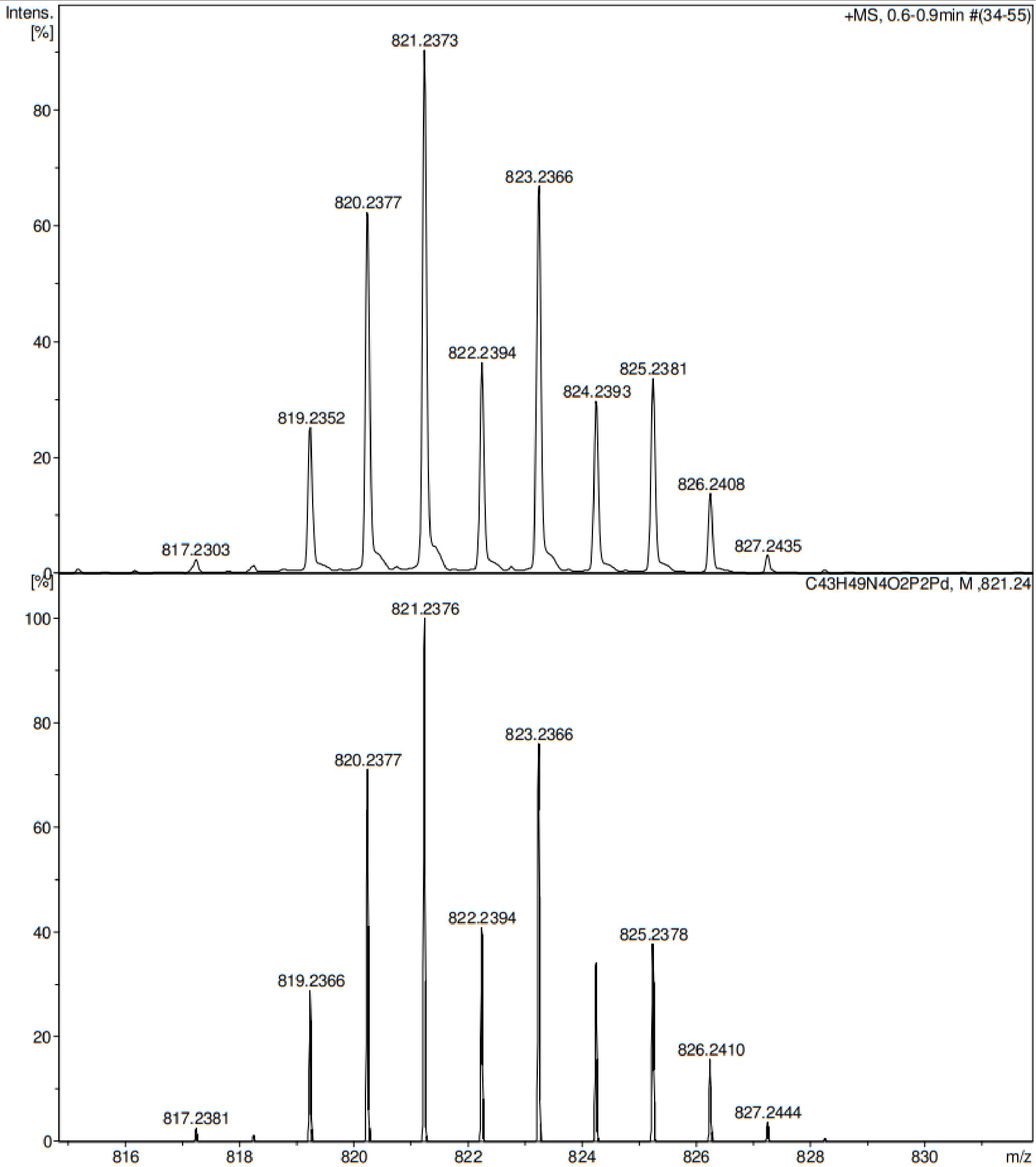
Analysis Name D:\Data\Kolotyrkina\2020\Kostenko\0318025.d
Method tune_50-1600.m
Sample Name /ZSGN RSU1
Comment C43H49N4O2P2Pd mH 822.2453 calibrant added CH3CN

Acquisition Date 18.03.2020 16:00:39

Operator BDAL@DE
Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Bruker Compass DataAnalysis 4.0 printed: 18.03.2020 16:07:11 Page 1 of 1

[Pd(allyl)(**L1a**)]BF_4, ESI-TOF MS.

Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2020\Kostenko\0318027.d	Acquisition Date	18.03.2020 16:17:22
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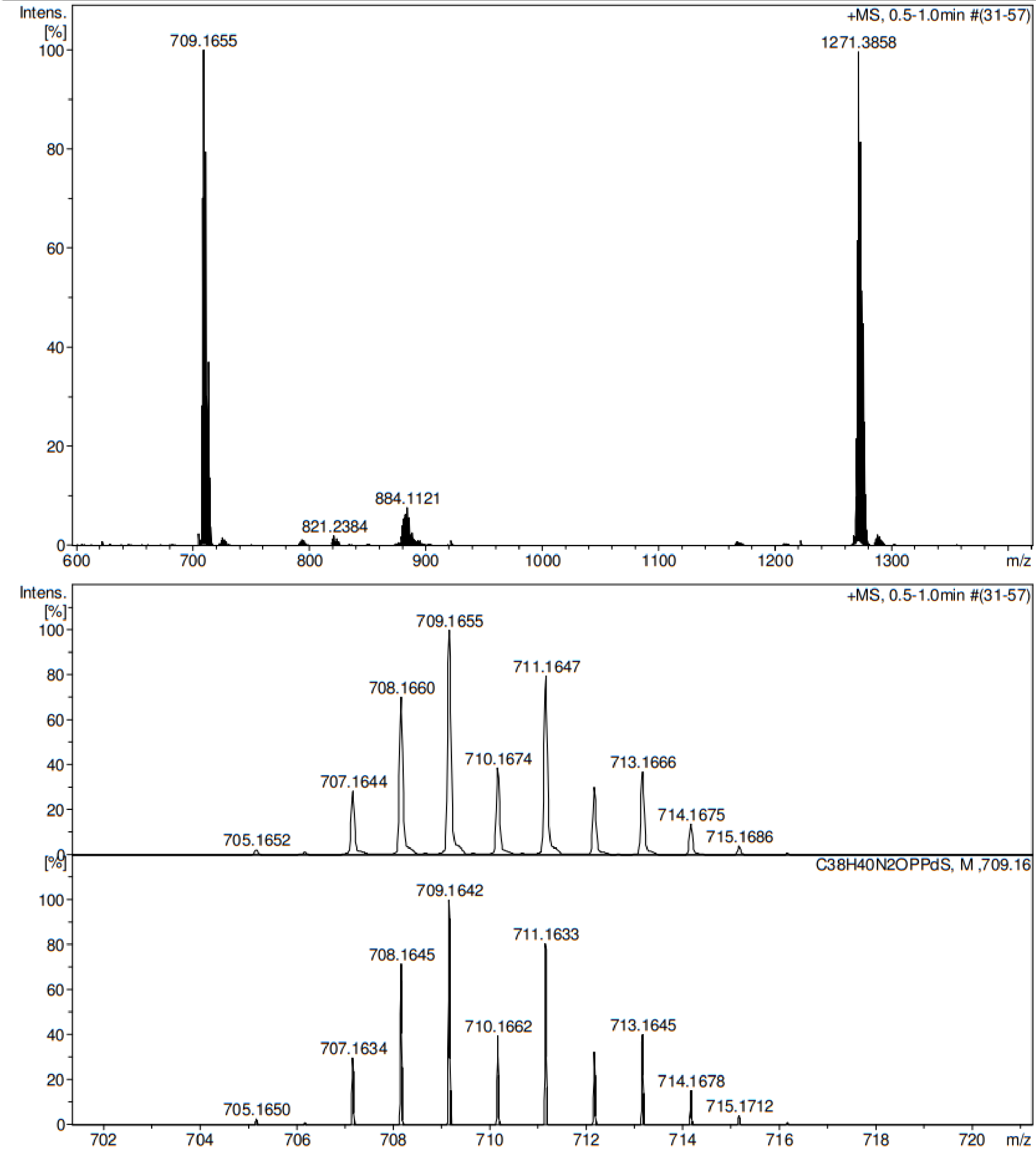
Sample Name	/ZSGN RSU3	Instrument / Ser#	micrOTOF 10248
Comment	C38H40N2OPPdS m 709.1641 calibrant added CH3CN		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Bruker Compass DataAnalysis 4.0 printed: 18.03.2020 16:20:53 Page 1 of 1

$[Pd(allyl)($**L5a**$)]_2(BF_4)_2$, ESI-TOF MS.

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